SOLUTIONS MANUAL

Jan William Simek

SIXTH EDITION

ORGANIC CHEMISTRY

L. G. Wade, Jr.

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California Polytechnic State University

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PREFACE
Hints for Passing Organic Chemistry

Do you want to pass your course in organic chemistry? Here is my best advice, based on over thirty years of observing students learning organic chemistry:

Hint #1: *Do the problems.* It seems straightforward, but humans, including students, try to take the easy way out until they discover there is no short-cut. Unless you have a measured IQ above 200 and comfortably cruise in the top 1% of your class, *do the problems.* Usually your teacher (professor or teaching assistant) will recommend certain ones; try to do all those recommended. If you do half of them, you will be half-prepared at test time. (Do you want your surgeon coming to your appendectomy having practiced only *half* the procedure?) And when you do the problems, keep this Solutions Manual CLOSED. Avoid looking at *my* answer before you write *your* answer—your trying and struggling with the problem is the most valuable part of the problem. Discovery is a major part of learning. Remember that the primary goal of doing these problems is *not* just getting the right answer, but understanding the material well enough to get right answers to the questions you haven't seen yet.

Hint #2: *Keep up.* Getting behind in your work in a course that moves as quickly as this one is the Kiss of Death. For most students, organic chemistry is the most rigorous intellectual challenge they have faced so far in their studies. Some are taken by surprise at the diligence it requires. Don't think that you can study all of the material the couple of days before the exam—well, you can, but you won't pass. Study organic chemistry like a foreign language: try to do some every day so that the freshly-trained neurons stay sharp.

Hint #3: *Get help when you need it.* Use your teacher's office hours when you have difficulty. Many schools have tutoring centers (in which organic chemistry is a popular offering). Here's a secret: absolutely the best way to cement this material in your brain is to get together with a few of your fellow students and make up problems for each other, then correct and discuss them. When *you* write the problems, you will gain great insight into what this is all about.

Purpose of this Solutions Manual

So what is the point of this Solutions Manual? First, I can't do your studying for you. Second, since I am not leaning over your shoulder as you write your answers, I can't give you direct feedback on what you write and think—the print medium is limited in its usefulness. What I *can* do for you is: 1) provide correct answers; the publishers, Professor Wade, Professor Kantorowski (my reviewer), and I have gone to great lengths to assure that what I have written is correct, for we all understand how it can shake a student's confidence to discover that the answer book flubbed up; 2) provide a considerable degree of rigor; beyond the fundamental requirement of correctness, I have tried to flesh out these answers, being complete but succinct; 3) provide insight into how to solve a problem and into where the sticky intellectual points are. Insight is the toughest to accomplish, but over the years, I have come to understand where students have trouble, so I have tried to anticipate your questions and to add enough detail so that the concept, as well as the answer, is clear.

It is difficult for students to understand or acknowledge that their teachers are human (some are more human than others). Since I am human (despite what my students might report), I can and do make mistakes. If there are mistakes in this book, they are my sole responsibility, and I am sorry. If you find one, PLEASE let me know so that it can be corrected in future printings. Nip it in the bud.

What's New in this edition?

Better answers! Part of my goal in this edition has been to add more explanatory material to clarify how to arrive at the answer. The possibility of more than one answer to a problem has been noted. The IUPAC Nomenclature appendix has been expanded to include bicyclics, heteroatom replacements, and the Cahn-Ingold-Prelog system of stereochemical designation.

Better graphics! The print medium is very limited in its ability to convey three-dimensional structural information, a problem that has plagued organic chemists for over a century. I have added some graphics created in the software, Chem3D®, to try to show atoms in space where that information is a key part of the solution. In drawing NMR spectra, representational line drawings have replaced rudimentary attempts at drawing peaks from previous editions.

Better jokes? Too much to hope for.

Some Web Stuff

Prentice-Hall maintains a web site dedicated to the Wade text: try **www.prenhall.com/wade**. Two essential web sites providing spectra are listed on the bottom of p. 270.

Acknowledgments

No project of this scope is ever done alone. These are team efforts, and there are several people who have assisted and facilitated in one fashion or another who deserve my thanks.

Professor L. G. Wade, Jr., your textbook author, is a remarkable person. He has gone to extraordinary lengths to make the textbook as clear, organized, informative and insightful as possible. He has solicited and followed my suggestions on his text, and his comments on my solutions have been perceptive and valuable. We agreed early on that our primary goal is to help the students learn a fascinating and challenging subject, and all of our efforts have been directed toward that goal. I have appreciated our collaboration.

My new colleague, Dr. Eric Kantorowski, has reviewed the entire manuscript for accuracy and style. His diligence, attention to detail and chemical wisdom have made this a better manual. Eric stands on the shoulders of previous reviewers who scoured earlier editions for errors: Jessica Gilman, Dr. Kristen Meisenheimer, and Dr. Dan Mattern. Mr. Richard King has offered numerous suggestions on how to clarify murky explanations. I am grateful to them all.

The people at Prentice-Hall have made this project possible. Good books would not exist without their dedication, professionalism, and experience. Among the many people who contributed are: Lee Englander, who connected me with this project; Nicole Folchetti, Advanced Chemistry Editor; and Kristen Kaiser and Carole Snyder, Project Managers.

The entire manuscript was produced using *ChemDraw®*, the remarkable software for drawing chemical structures developed by CambridgeSoft Corp., Cambridge, MA. We, the users of sophisticated software like ChemDraw, are the beneficiaries of the intelligence and creativity of the people in the computer industry. We are fortunate that they are so smart.

Finally, I appreciate my friends who supported me throughout this project, most notably my good friend of almost forty years, Judy Lang. The students are too numerous to list, but it is for them that all this happens.

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DEDICATION

To my inspirational chemistry teachers:

Joe Plaskas, who made the batter;

Kurt Kaufman, who baked the cake;

Carl Djerassi, who put on the icing;

and to my parents:

Ervin J. and Imilda B. Simek,

who had the original concept.

SYMBOLS AND ABBREVIATIONS

Below is a list of symbols and abbreviations used in this Solutions Manual, consistent with those used in the textbook by Wade. (Do not expect all of these to make sense to you now. You will learn them throughout your study of organic chemistry.)

BONDS

——— a single bond

═══ a double bond

≡≡≡ a triple bond

——◣ a bond in three dimensions, coming out of the paper toward the reader

▥▥▥▥ a bond in three dimensions, going behind the paper away from the reader

- - - - - - a stretched bond, in the process of forming or breaking

ARROWS

——→ in a reaction, shows direction from reactants to products

⇌ signifies equilibrium (not to be confused with resonance)

←——→ signifies resonance (not to be confused with equilibrium)

⌒⌒ shows direction of electron movement:
the arrowhead with one barb shows movement of one electron;
the arrowhead with two barbs shows movement of a pair of electrons

+——→ shows polarity of a bond or molecule, the arrowhead signifying the more negative end of the dipole

SUBSTITUENT GROUPS

Me   a methyl group, CH_3

Et   an ethyl group, CH_2CH_3

Pr   a propyl group, a three carbon group (two possible arrangements)

Bu   a butyl group, a four carbon group (four possible arrangements)

R   the general abbreviation for an alkyl group (or any substituent group not under scrutiny)

Ph   a phenyl group, the name of a benzene ring as a substituent, represented:
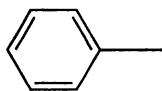
       or
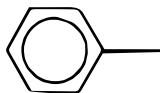
Ar   the general name for an aromatic group

Symbols and Abbreviations, continued
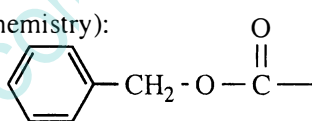
SUBSTITUENT GROUPS, continued

Ac an acetyl group: $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$

Cy a cyclohexyl group:
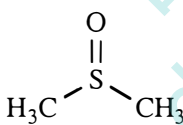
Ts tosyl, or *p*-toluenesulfonyl group: CH_3-⟨benzene⟩$-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-$

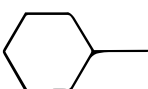Boc a *t*-butoxycarbonyl group (amino acid and peptide chemistry): $(CH_3)_3C-O-\overset{\overset{\displaystyle O}{\|}}{C}-$
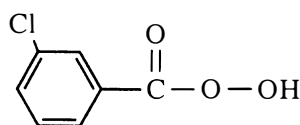
Z, or Cbz a carbobenzoxy (benzyloxycarbonyl) group (amino acid and peptide chemistry): ⟨benzene⟩$-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-$

REAGENTS AND SOLVENTS
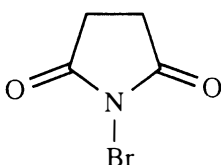
DCC **di**cyclohexyl**c**arbodiimide ⟨cyclohexyl⟩$-N=C=N-$⟨cyclohexyl⟩

DMSO **d**i**m**ethyl**s**ulf**o**xide $H_3C\overset{\overset{\displaystyle O}{\|}}{\underset{\displaystyle S}{}}CH_3$

ether diethyl ether, $CH_3CH_2OCH_2CH_3$

MCPBA *m*eta-**c**hloro**p**eroxy**b**enzoic acid ⟨Cl-benzene⟩$-\overset{\overset{\displaystyle O}{\|}}{C}-O-OH$

MVK **m**ethyl **v**inyl **k**etone $H_3C-\overset{\overset{\displaystyle O}{\|}}{C}\diagup\diagdown$

NBS *N*-**b**romo**s**uccinimide $O=$⟨pyrrolidinedione ring⟩$=O$, $N-Br$

continued on next page

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Symbols and Abbreviations, continued

REAGENTS AND SOLVENTS, continued

PCC   **p**yridinium **c**hloro**c**hromate, $CrO_3 \cdot HCl \cdot N$

Sia$_2$BH   disiamylborane

THF   **t**etra**h**ydro**f**uran

SPECTROSCOPY

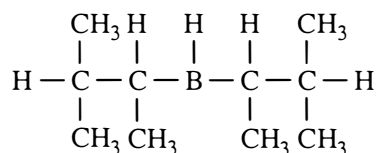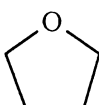|	
IR	**i**nf**r**a**r**ed spectroscopy
NMR	**n**uclear **m**agnetic **r**esonance spectroscopy
MS	**m**ass **s**pectrometry
UV	**u**ltra**v**iolet spectroscopy
ppm	**p**arts **p**er **m**illion, a unit used in NMR
Hz	hertz, cycles per second, a unit of frequency
MHz	megahertz, millions of cycles per second
TMS	**t**etra**m**ethyl**s**ilane, $(CH_3)_4Si$, the reference compound in NMR
s, d, t, q	**s**inglet, **d**oublet, **t**riplet, **q**uartet, referring to the number of peaks an NMR absorption gives
nm	nanometers, 10^{-9} meters (usually used as a unit of wavelength)
m/z	mass-to-charge ratio, in mass spectrometry
δ	in NMR, chemical shift value, measured in ppm
λ	wavelength
ν	frequency

OTHER

a, ax	axial (in chair forms of cyclohexane)
e, eq	equatorial (in chair forms of cyclohexane)
HOMO	**h**ighest **o**ccupied **m**olecular **o**rbital
LUMO	**l**owest **u**noccupied **m**olecular **o**rbital
NR	no reaction
o, m, p	*ortho, meta, para* (positions on an aromatic ring)
Δ	when written over an arrow: "heat"; when written before a letter: "change in"
δ^+, δ^-	partial positive charge, partial negative charge
$h\nu$	energy from electromagnetic radiation (light)
$[\alpha]_D$	specific rotation at the D line of sodium (589 nm)

CHAPTER 1—INTRODUCTION AND REVIEW

1-1   Na $1s^2 2s^2 2p^6 3s^1$ P $1s^2 2s^2 2p^6 3s^2 3p_x{}^1 3p_y{}^1 3p_z{}^1$

Mg $1s^2 2s^2 2p^6 3s^2$ S $1s^2 2s^2 2p^6 3s^2 3p_x{}^2 3p_y{}^1 3p_z{}^1$

Al $1s^2 2s^2 2p^6 3s^2 3p_x{}^1$ Cl $1s^2 2s^2 2p^6 3s^2 3p_x{}^2 3p_y{}^2 3p_z{}^1$

Si $1s^2 2s^2 2p^6 3s^2 3p_x{}^1 3p_y{}^1$ Ar $1s^2 2s^2 2p^6 3s^2 3p_x{}^2 3p_y{}^2 3p_z{}^2$

1-2   In this book, lines between atom symbols represent covalent bonds between those atoms. Nonbonding electrons are indicated with dots.

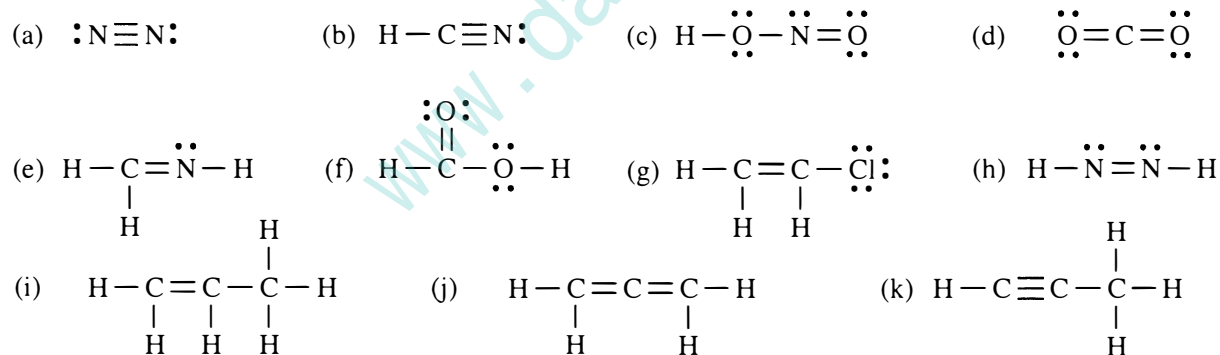(a) $H-\overset{\displaystyle ..}{\underset{\displaystyle H}{N}}-H$

(b) $H-\overset{\displaystyle ..}{\underset{\displaystyle ..}{O}}-H$

(c) $H-\overset{\displaystyle ..}{\underset{\displaystyle H}{O}}-H\;^{+}$

(d) H—C—C—C—H (propane, with three H on top and bottom)

(e) $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{..}{\underset{H}{N}}-H$

(f) $H-\overset{H}{\underset{H}{C}}-\overset{..}{\underset{..}{O}}-\overset{H}{\underset{H}{C}}-H$

(g) $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{..}{\underset{..}{F}}:$

(h) H—C—C—C—H (with :O: above center carbon, H substituents)

(i) $H-\overset{}{\underset{\displaystyle H}{B}}-H$

(j) $:\overset{..}{\underset{..}{F}}-\overset{\displaystyle :F:}{B}-\overset{..}{\underset{..}{F}}:$ with :F: below
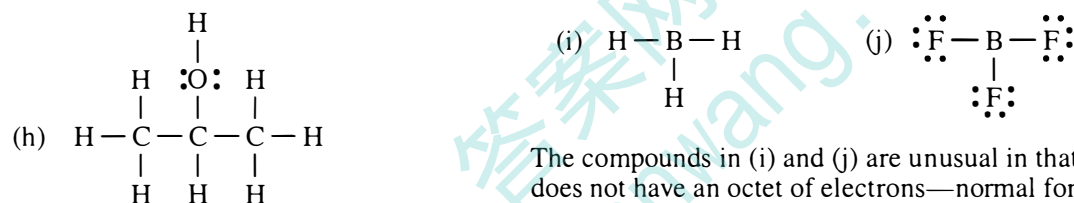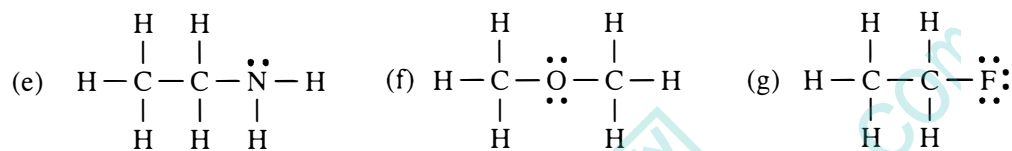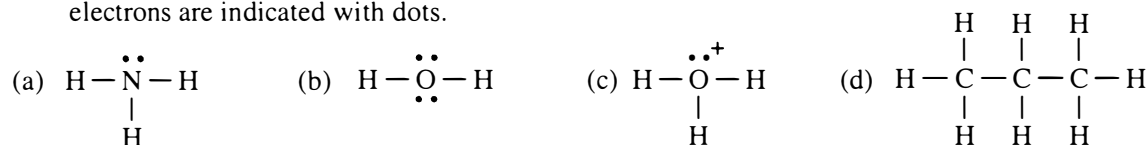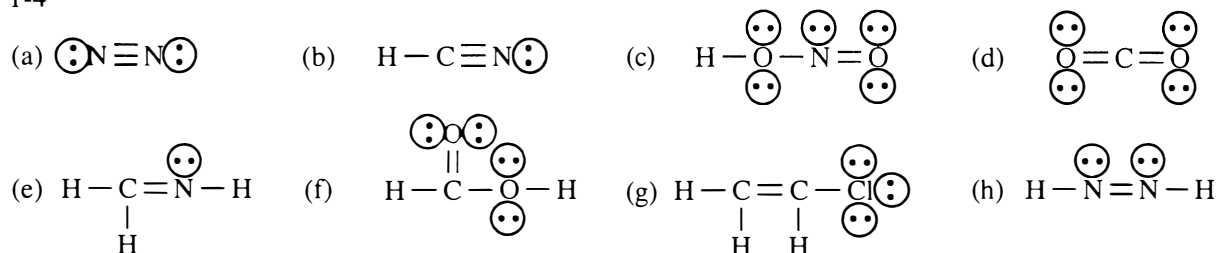
The compounds in (i) and (j) are unusual in that boron does not have an octet of electrons—normal for boron because it has only three valence electrons.
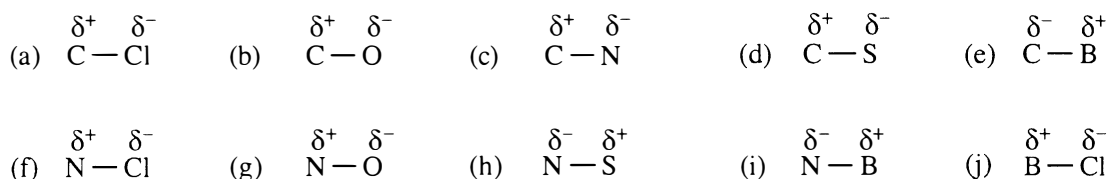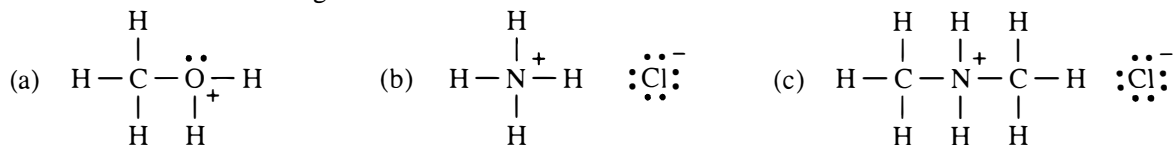
1-3

(a) $:N\equiv N:$

(b) $H-C\equiv N:$

(c) $H-\overset{..}{\underset{..}{O}}-\overset{..}{N}=\overset{..}{\underset{..}{O}}$

(d) $\overset{..}{\underset{..}{O}}=C=\overset{..}{\underset{..}{O}}$

(e) $H-\overset{..}{C}=\overset{}{\underset{\displaystyle H}{N}}-H$

(f) $H-\overset{\displaystyle :O:}{C}-\overset{..}{\underset{..}{O}}-H$

(g) $H-\overset{}{\underset{\displaystyle H}{C}}=\overset{}{\underset{\displaystyle H}{C}}-\overset{..}{\underset{..}{Cl}}:$

(h) $H-\overset{..}{N}=\overset{..}{N}-H$

(i) $H-\overset{}{\underset{\displaystyle H}{C}}=\overset{}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$

(j) $H-\overset{}{\underset{\displaystyle H}{C}}=C=\overset{}{\underset{\displaystyle H}{C}}-H$

(k) $H-C\equiv C-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$

1-4

(a) $:N\equiv N:$ (with circled electron pairs)

(b) $H-C\equiv N:$ (with circled electron pair)

(c) H—O—N=O (with circled electron pairs on O atoms)

(d) O=C=O (with circled electron pairs on O atoms)

(e) $H-C=\overset{..}{\underset{\displaystyle H}{N}}-H$ (with circled electron pair on N)

(f) H—C—O—H (with circled electron pairs, double bond region)

(g) H—C=C—Cl (with circled electron pairs on Cl, H substituents)

(h) H—N=N—H (with circled electron pairs on N atoms)

There are no unshared electron pairs in parts (i), (j), and (k).
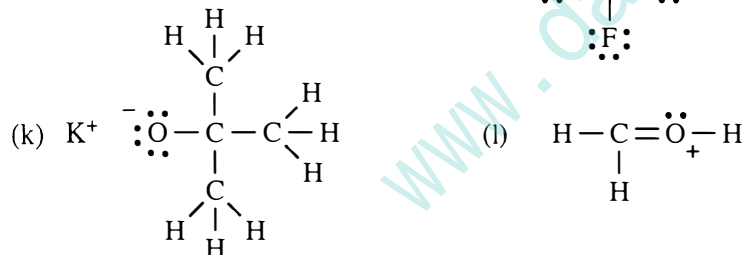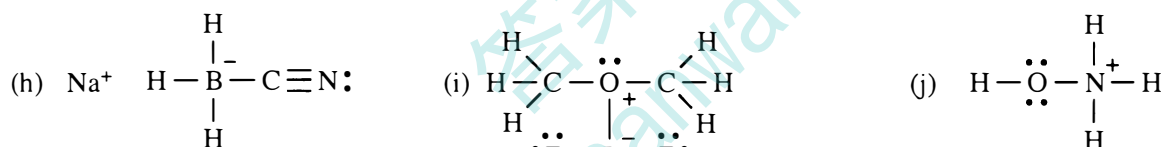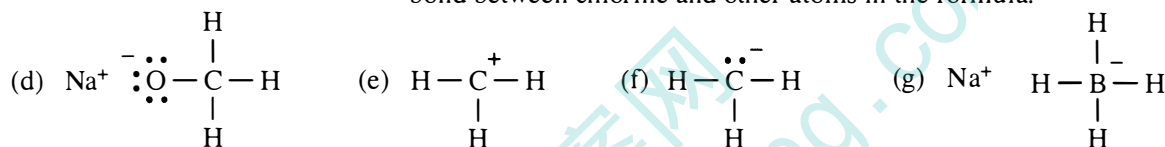
1-5 The symbols "δ⁺" and "δ⁻" indicate bond polarity by showing partial charge. (In the arrow symbolism, the arrow should point to the partial negative charge.)

(a) $\overset{\delta^+}{C}-\overset{\delta^-}{Cl}$　　(b) $\overset{\delta^+}{C}-\overset{\delta^-}{O}$　　(c) $\overset{\delta^+}{C}-\overset{\delta^-}{N}$　　(d) $\overset{\delta^+}{C}-\overset{\delta^-}{S}$　　(e) $\overset{\delta^-}{C}-\overset{\delta^+}{B}$

(f) $\overset{\delta^+}{N}-\overset{\delta^-}{Cl}$　　(g) $\overset{\delta^+}{N}-\overset{\delta^-}{O}$　　(h) $\overset{\delta^-}{N}-\overset{\delta^+}{S}$　　(i) $\overset{\delta^-}{N}-\overset{\delta^+}{B}$　　(j) $\overset{\delta^+}{B}-\overset{\delta^-}{Cl}$

1-6 Non-zero formal charges are shown beside the atoms.

(a) Lewis structure of $H-C-O-H$ with H's on C and + on O

(b) Lewis structure of $H-N-H$ with + on N, and $:\ddot{Cl}:^-$ chloride ion

(c) Lewis structure of $H-C-N-C-H$ with + on N, and $:\ddot{Cl}:^-$ chloride ion

In (b) and (c), the chlorine is present as chloride ion. There is no covalent bond between chlorine and other atoms in the formula.

(d) Na^+ $:\overset{-}{\ddot{O}}-C-H$

(e) $H-\overset{+}{C}-H$

(f) $H-\overset{-}{\ddot{C}}-H$

(g) Na^+ $H-\overset{-}{B}-H$

(h) Na^+ $H-\overset{-}{B}-C\equiv N:$

(i) $H-C-\overset{+}{\ddot{O}}-C-H$ with $:\overset{-}{F}-B-\overset{..}{F}:$ below and $:\overset{..}{F}:$

(j) $H-\overset{..}{\ddot{O}}-\overset{+}{N}-H$

(k) K^+ $:\overset{-}{\ddot{O}}-C-C-H$ (with CH₃ groups)
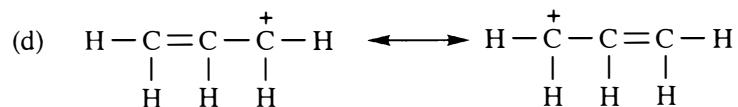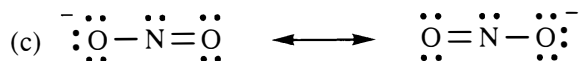
(l) $H-C=\overset{+}{\ddot{O}}-H$

As shown in (d), (g), (h), and (k), alkali metals like sodium and potassium form only ionic bonds, never covalent bonds.

1-7 Resonance forms in which all atoms have full octets are the most significant contributors. In resonance forms, ALL ATOMS KEEP THEIR POSITIONS—ONLY ELECTRONS ARE SHOWN IN DIFFERENT POSITIONS.
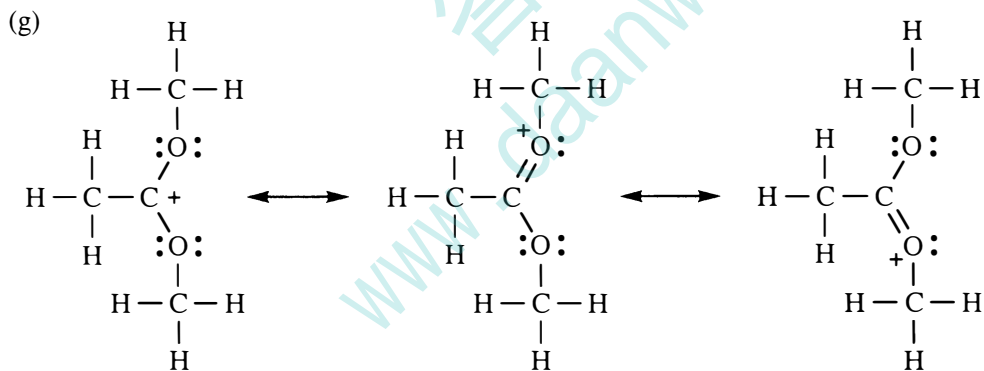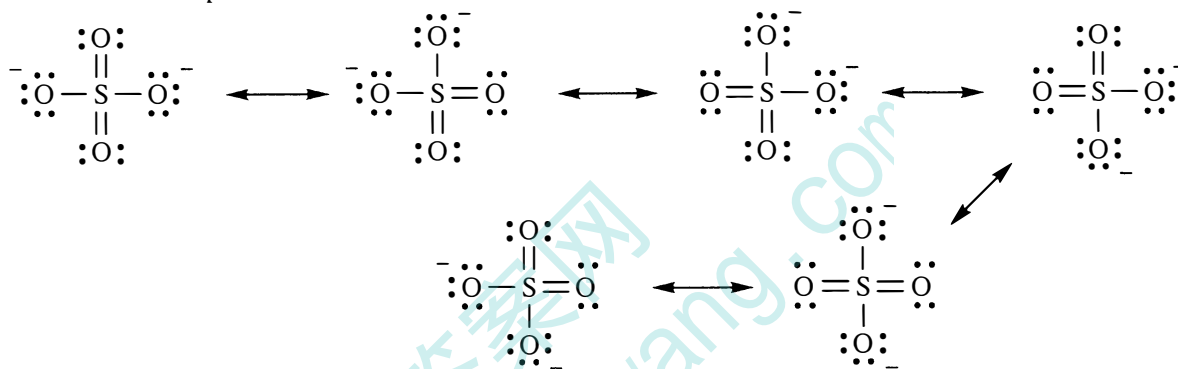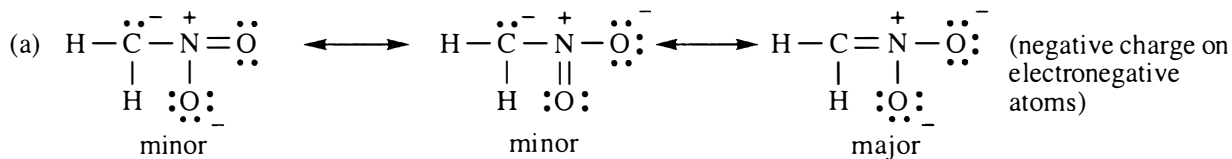
(a) $:\overset{-}{\ddot{O}}-C(=O)-\overset{-}{\ddot{O}}: \longleftrightarrow :\overset{-}{\ddot{O}}-C=O \longleftrightarrow O=C-\overset{-}{\ddot{O}}:$

(b) $:\overset{-}{\ddot{O}}-\overset{+}{N}(=O)-\overset{-}{\ddot{O}}: \longleftrightarrow :\overset{-}{\ddot{O}}-\overset{+}{N}=O \longleftrightarrow O=\overset{+}{N}-\overset{-}{\ddot{O}}:$

1-7 continued

(c) :Ö—N=Ö: ⟷ Ö=N—Ö:⁻

(d) H—C=C—C⁺—H ⟷ H—C⁺—C=C—H
        | | | | | |
        H   H   H   H   H   H

(e) H—C=C—C⁻—H ⟷ H—C⁻—C=C—H
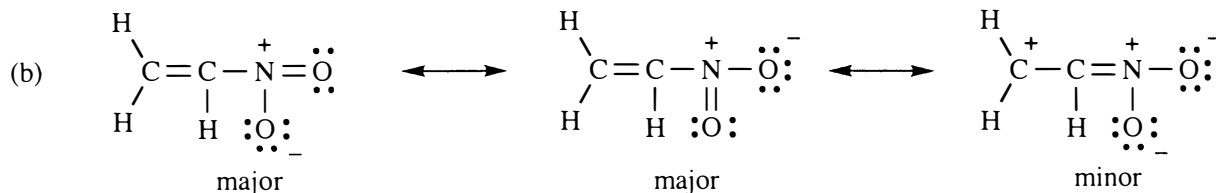 | | | | | |
        H   H   H   H   H   H
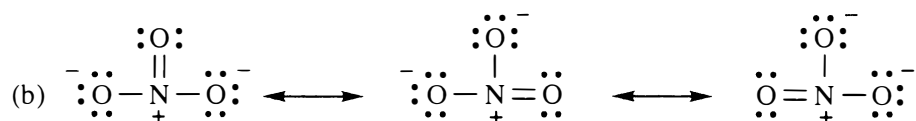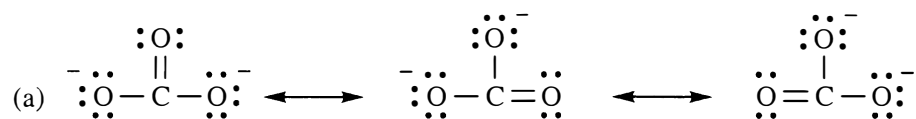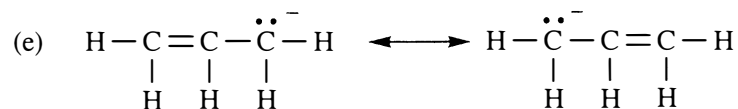
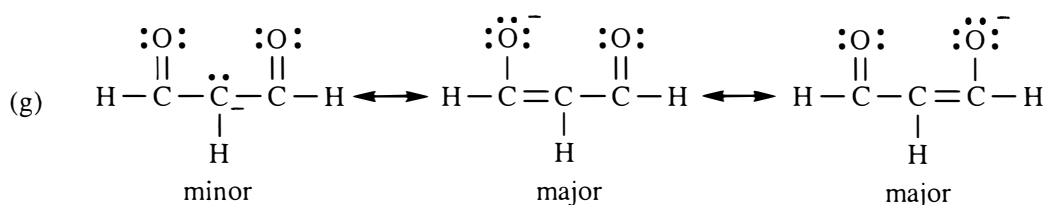(f) Sulfur can have up to 12 electrons around it because it has d orbitals accessible.
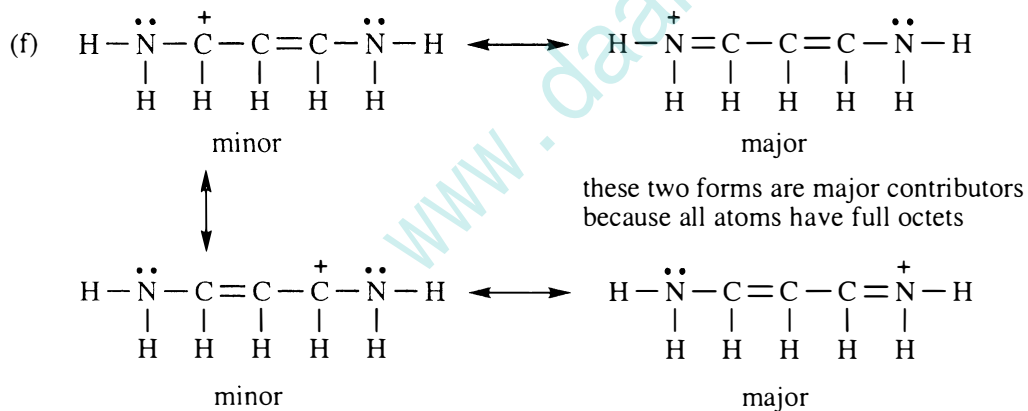
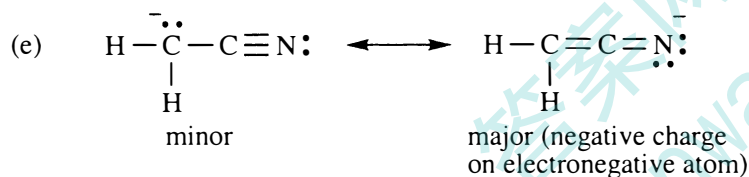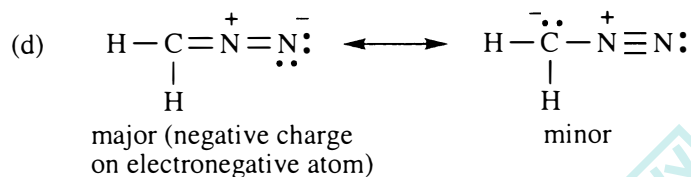:O: :Ö:⁻   :Ö:⁻   :O:
 ‖ | | ‖
⁻:Ö—S—Ö:⁻   ⟷   ⁻:Ö—S=Ö   ⟷   Ö=S—Ö:⁻   ⟷   Ö=S—Ö:⁻
 ‖   ‖   ‖ |
:O: :O: :O: :Ö:⁻

                    :O: :Ö:⁻
                     ‖ |
              ⁻:Ö—S=Ö: ⟷   Ö=S=Ö:
                     | |
                    :Ö:⁻   :Ö:⁻

(g)

        H   H   H
        | | |
    H—C—H   H—C—H   H—C—H
        | | |
    H :O: H   ⁺O: H :O:
    | / | ‖ | /
H—C—C⁺   ⟷   H—C—C   ⟷   H—C—C
    | \ | | | ‖
    H :O: H :O: H   ⁺O:
        | | |
    H—C—H   H—C—H   H—C—H
        | | |
        H   H   H

1-8 Major resonance contributors would have the lowest energy. The most important factors are: maximize full octets; maximize bonds; put negative charge on electronegative atoms; minimize charge separation.

(a) H—C⁻—N⁺=Ö: ⟷ H—C⁻—N⁺—Ö:⁻ ⟷ H—C=N⁺—Ö:⁻   (negative charge on
         | ‖ | | | | electronegative
         H :O: H :O: H :O:⁻   atoms)
       minor   minor   major

3

1-8 continued

(b)

$$\overset{H}{\underset{H}{\diagup}}C=C\overset{|}{\underset{\overset{|}{:O:^{-}}}{-}}\overset{+}{N}=\overset{..}{O}\quad\longleftrightarrow\quad \overset{H}{\underset{H}{\diagup}}C=C\overset{|}{\underset{\overset{||}{:O:}}{-}}\overset{+}{N}-\overset{..}{\underset{..}{O}}:^{-}\quad\longleftrightarrow\quad \overset{H}{\underset{H}{\diagup}}\overset{+}{C}-C\overset{|}{\underset{\overset{|}{:O:^{-}}}{-}}\overset{+}{N}=\overset{..}{\underset{..}{O}}:^{-}$$

major   major   minor

These two forms have equivalent energy and are major because they have full octets, more bonds, and less charge separation than the minor contributor.

(c)

$$H-C\overset{..}{=}\overset{}{O}-H \quad\longleftrightarrow\quad H-\overset{+}{C}-\overset{..}{\underset{..}{O}}-H$$
$$\underset{H}{|}\quad+\qquad\qquad\underset{H}{|}$$

major   minor
(octets, more bonds)

(d)

$$H-\overset{+}{C}=\overset{}{N}=\overset{..}{\underset{..}{N}}:^{-} \quad\longleftrightarrow\quad H-\overset{-}{\underset{..}{C}}\overset{..}{-}\overset{+}{N}\equiv N:$$
$$\underset{H}{|}\qquad\qquad\qquad\underset{H}{|}$$

major (negative charge   minor
on electronegative atom)

(e)

$$H-\overset{-}{\underset{..}{C}}-C\equiv N: \quad\longleftrightarrow\quad H-C=C=\overset{}{\underset{..}{N}}:^{-}$$
$$\underset{H}{|}\qquad\qquad\qquad\underset{H}{|}$$

minor   major (negative charge
on electronegative atom)

(f)

$$H-\overset{..}{N}-\overset{+}{C}-C=C-\overset{..}{N}-H \quad\longleftrightarrow\quad H-\overset{+}{N}=C-C=C-\overset{..}{N}-H$$
$$\quad\underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\qquad\qquad\underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}$$

minor   major

these two forms are major contributors
because all atoms have full octets

$$H-\overset{..}{N}-C=C-\overset{+}{C}-\overset{..}{N}-H \quad\longleftrightarrow\quad H-\overset{..}{N}-C=C-C=\overset{+}{N}-H$$
$$\quad\underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\qquad\qquad\underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}\ \underset{H}{|}$$

minor   major

(g)

$$\overset{:O:}{\underset{}{||}}\quad\overset{:O:}{\underset{}{||}}\qquad\qquad\overset{:\overset{..}{O}:^{-}}{\underset{}{|}}\quad\overset{:O:}{\underset{}{||}}\qquad\qquad\overset{:O:}{\underset{}{||}}\quad\overset{:\overset{..}{O}:^{-}}{\underset{}{|}}$$
$$H-C-\overset{..}{\underset{..}{C}}-C-H \longleftrightarrow H-C=C-C-H \longleftrightarrow H-C-C=C-H$$
$$\qquad\underset{H}{|}^{-}\qquad\qquad\qquad\underset{H}{|}\qquad\qquad\qquad\underset{H}{|}$$

minor   major   major

these two have equivalent energy and are major because the
negative charge is on the more electronegative oxygen atom

4

1-8 continued

(h)

$$\text{(major, no charge separation)} \quad H-\overset{\overset{:O:}{||}}{C}-\overset{..}{N}(H)-H \quad \longleftrightarrow \quad \text{(minor)} \quad H-\overset{\overset{:\overset{..}{O}:^{-}}{|}}{C}=\overset{+}{N}(H)-H$$

major (no charge separation) minor
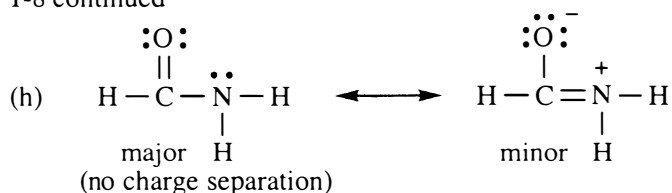
1-9 Your Lewis structures may *appear* different from these. As long as the atoms are connected in the same order and by the same type of bond, they are equivalent structures. For now, the exact placement of the atoms on the page is not significant. A Lewis structure is "complete" with unshared electron pairs shown.

(a) A six-carbon chain with one branch CH₃:

H₃C—CH₂—CH₂—CH₂—CH(CH₃)—CH₃ (fully drawn as Lewis structure with all H shown)

(b) H₃C—CH₂—CH(CH₃)—CH₂—Cl: (with three lone pairs on Cl)

(c) H₃C—CH₂—C(=O)—CH=CH₂ (drawn with :O: double bond)

(d) H₃C—CH₂—C(=O)—CH₃ (drawn with :O: double bond)
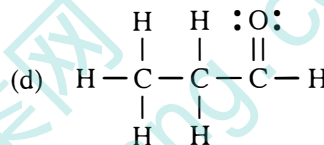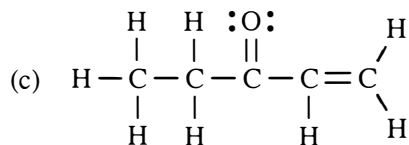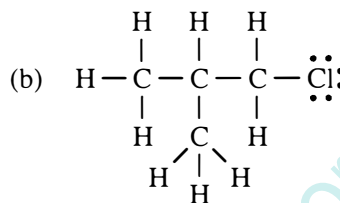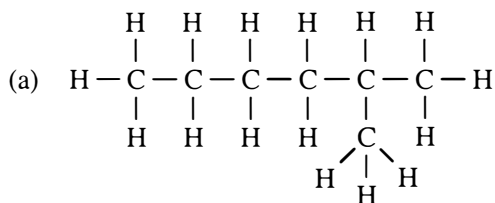
Always be alert for the implied double or triple bond. Remember that C has to have four bonds, nitrogen has three bonds, oxygen has two bonds, and hydrogen has one bond. The only exceptions to these valence rules are structures with formal charges.

(e) H₃C—CH₂—C≡N: (with :O: — drawn as CH₃—C(=O?)...)

$$H-\overset{H}{\underset{H}{\overset{|}{C}}}-\overset{:O:}{\overset{||}{C}}-C\equiv N:$$

(f) A branched structure:

$$(H_3C)\!-\!\overset{\overset{CH_3}{|}}{\underset{CH_3}{C}}\!-\!\overset{:O:}{\overset{||}{C}}\!-\!\overset{..}{O}\!-\!H$$

(g)

$$H-\overset{H}{\underset{H}{\overset{|}{C}}}-\overset{H}{\underset{H}{\overset{|}{C}}}-\overset{:O:}{\overset{||}{C}}-\overset{H}{\underset{H}{\overset{|}{C}}}-\overset{H}{\underset{H}{\overset{|}{C}}}-H$$
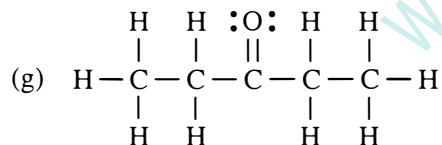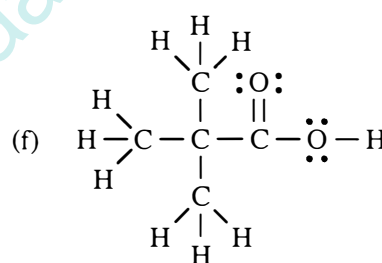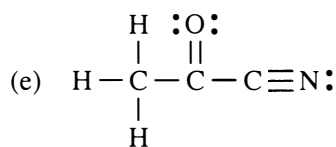
1-10 Complete Lewis structures show all atoms, bonds, and unshared electron pairs.

(a) A six-membered ring containing N (with lone pair on N), all carbons bearing H atoms, with an N—H.

(b) A fused/bicyclic structure containing O (with lone pairs on O).

(c) A five-membered ring: C=C double bond, two carbons attached to H, bridging to carbons and N (with N—H), :N: with lone pair shown.

1-10 continued

(d)

(e)

(f)

(g)

(h)
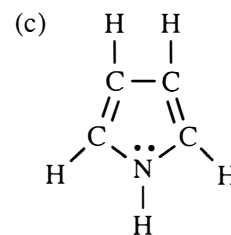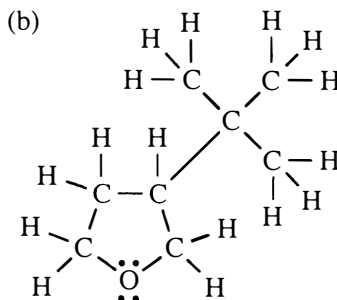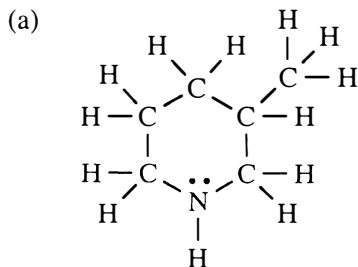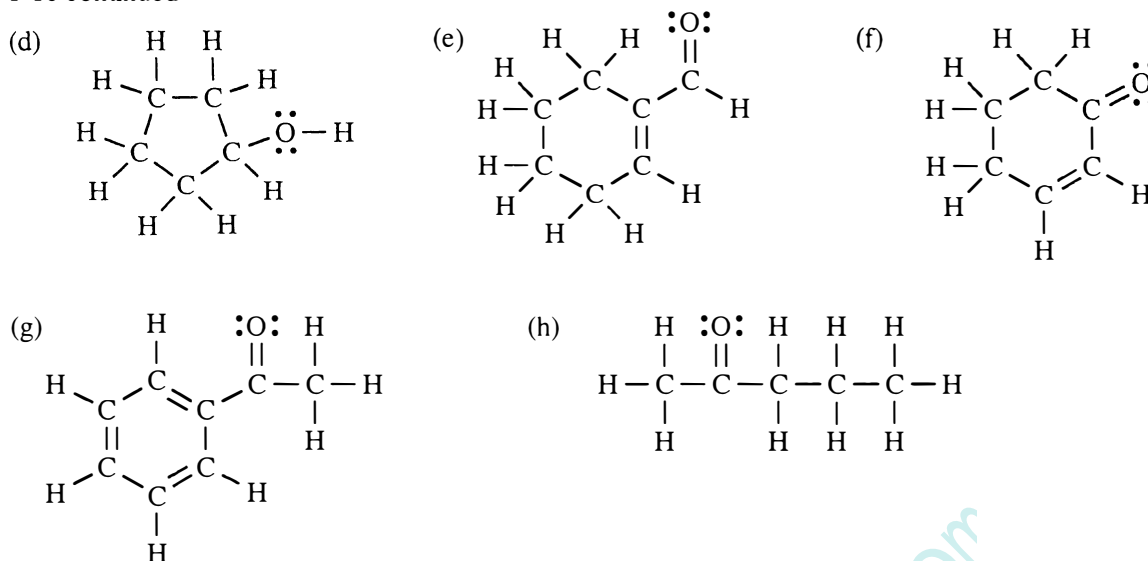
1-11 There is often more than one correct way to write condensed structural formulas. You must often make inferences about what a condensed formula means according to valence rules, especially in structures with C=O as shown in parts (a) and (d).

(a) $CH_3COCH_2CH_2CH_3$
(the O has a double bond to the carbon preceding it)

(b) $(CH_3)_2CHCH_2CH_2OH$

or $CH_3CH(CH_3)CH_2CH_2OH$

(c) $(CH_3)_2CHCH_2CH(OH)CH_3$

or $CH_3CH(CH_3)CH_2CH(OH)CH_3$

(d) $CH_3CH_2CH(CH_3)CH_2CHO$
(the O has a double bond to the carbon preceding it)
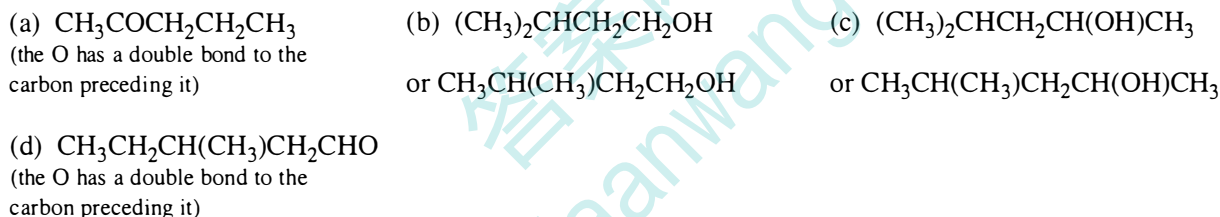
1-12 If the percent values do not sum to 100%, the remainder must be oxygen. Assume 100 g of sample; percents then translate directly to grams of each element.

There are usually many possible structures for a molecular formula. Yours may be different from the examples shown here.

(a) $\dfrac{40.0 \text{ g C}}{12.0 \text{ g/mole}}$ = 3.33 moles C ÷ 3.33 moles = 1 C

$\dfrac{6.67 \text{ g H}}{1.01 \text{ g/mole}}$ = 6.60 moles H ÷ 3.33 moles = 1.98 ≈ 2 H

$\dfrac{53.33 \text{ g O}}{16.0 \text{ g/mole}}$ = 3.33 moles O ÷ 3.33 moles = 1 O

empirical formula = $\boxed{CH_2O}$ ⟹ empirical weight = 30

molecular weight = 90, three times the empirical weight ⟹

three times the empirical formula = molecular formula = $\boxed{C_3H_6O_3}$

some possible structures:

MANY other structures possible.

6
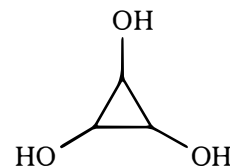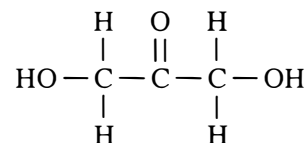
1-12 continued

(b) $\dfrac{32.0 \text{ g C}}{12.0 \text{ g/mole}}$ = 2.67 moles C ÷ 1.34 moles = 1.99 ≈ 2 C

$\dfrac{6.67 \text{ g H}}{1.01 \text{ g/mole}}$ = 6.60 moles H ÷ 1.34 moles = 4.93 ≈ 5 H

$\dfrac{18.7 \text{ g N}}{14.0 \text{ g/mole}}$ = 1.34 moles N ÷ 1.34 moles = 1 N

$\dfrac{42.6 \text{ g O}}{16.0 \text{ g/mole}}$ = 2.66 moles O ÷ 1.34 moles = 1.99 ≈ 2 O

empirical formula = $C_2H_5NO_2$ ⟹ empirical weight = 75

molecular weight = 75, same as the empirical weight ⟹

empirical formula = molecular formula = $C_2H_5NO_2$

some possible structures:
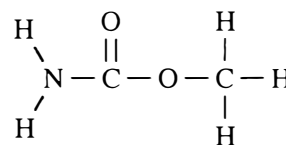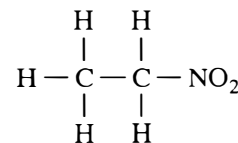
MANY other structures possible.

(c) $\dfrac{37.2 \text{ g C}}{12.0 \text{ g/mole}}$ = 3.10 moles C ÷ 1.55 moles = 2 C

$\dfrac{7.75 \text{ g H}}{1.01 \text{ g/mole}}$ = 7.67 moles H ÷ 1.55 moles = 4.95 ≈ 5 H

$\dfrac{55.0 \text{ g Cl}}{35.45 \text{ g/mole}}$ = 1.55 moles Cl ÷ 1.55 moles = 1 Cl

empirical formula = C_2H_5Cl ⟹ empirical weight = 64.46

molecular weight = 64, same as the empirical weight ⟹

empirical formula = molecular formula = C_2H_5Cl

There is only one structure possible with this molecular formula:
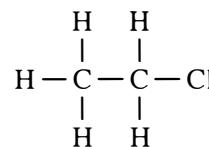
(d) $\dfrac{38.4 \text{ g C}}{12.0 \text{ g/mole}}$ = 3.20 moles C ÷ 1.60 moles = 2 C

$\dfrac{4.80 \text{ g H}}{1.01 \text{ g/mole}}$ = 4.75 moles H ÷ 1.60 moles = 2.97 ≈ 3 H

$\dfrac{56.8 \text{ g Cl}}{35.45 \text{ g/mole}}$ = 1.60 moles Cl ÷ 1.60 moles = 1 Cl

empirical formula = C_2H_3Cl ⟹ empirical weight = 62.45

molecular weight = 125, twice the empirical weight ⟹

twice the empirical formula = molecular formula = $C_4H_6Cl_2$

some possible structures:
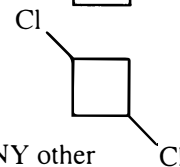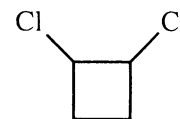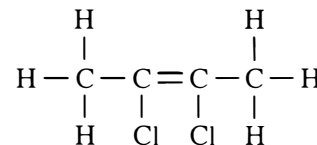
MANY other structures possible.

1-13

(a)   5.00 g HBr x $\dfrac{1 \text{ mole HBr}}{80.9 \text{ g HBr}}$ = 0.0618 moles HBr

0.0618 moles HBr $\Longrightarrow$ 0.0618 moles H_3O^+ (100% dissociated)
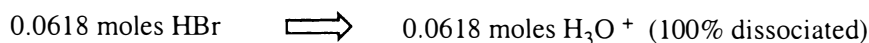
$\dfrac{0.0618 \text{ moles } H_3O^+}{100 \text{ mL}}$ x $\dfrac{1000 \text{ mL}}{1 \text{ L}}$ = $\dfrac{0.618 \text{ moles } H_3O^+}{1 \text{ L solution}}$

pH = $-\log_{10}[H_3O^+]$ = $-\log_{10}(0.618)$ = $\boxed{0.209}$

(b)   1.50 g NaOH x $\dfrac{1 \text{ mole NaOH}}{40.0 \text{ g NaOH}}$ = 0.0375 moles NaOH

0.0375 moles NaOH $\Longrightarrow$ 0.0375 moles $^-$OH (100% dissociated)
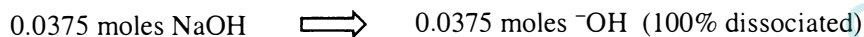
$\dfrac{0.0375 \text{ moles } ^-OH}{50. \text{ mL}}$ x $\dfrac{1000 \text{ mL}}{1 \text{ L}}$ = $\dfrac{0.75 \text{ moles } ^-OH}{1 \text{ L solution}}$ = 0.75 M

$[H_3O^+]$ = $\dfrac{1 \times 10^{-14}}{[^-OH]}$ = $\dfrac{1 \times 10^{-14}}{0.75}$ = 1.33×10^{-14}

pH = $-\log_{10}[H_3O^+]$ = $-\log_{10}(1.33 \times 10^{-14})$ = $\boxed{13.88}$

(the number of decimal places in a pH value is the number of significant figures)

1-14

(a) By definition, an acid is any species that can donate a proton. Ammonia has a proton bonded to nitrogen, so ammonia can be an acid (although a very weak one). A base is a proton acceptor, that is, it must have a pair of electrons to share with a proton; in theory, any atom with an unshared electron pair can be a base. The nitrogen in ammonia has an unshared electron pair so ammonia is basic. In water, ammonia is too weak an acid to give up its proton; instead, it acts as a base and pulls a proton from water to a small extent.

(b)   water as an acid: H_2O + NH_3 $\rightleftharpoons$ $^-$OH + NH_4^+

water as a base: H_2O + HCl $\rightleftharpoons$ H_3O^+ + Cl^-

(c)   methanol as an acid: CH_3OH + NH_3 $\rightleftharpoons$ CH_3O^- + NH_4^+

methanol as a base: CH_3OH + H_2SO_4 $\rightleftharpoons$ $CH_3OH_2^+$ + HSO_4^-
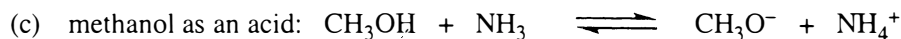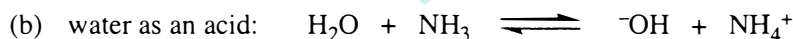
1-15

(a)
$$HCOOH + \ ^-CN \ \rightleftharpoons \ HCOO^- + HCN$$

HCOOH	$^-$CN		HCOO$^-$	HCN	FAVORS
stronger acid pK$_a$ 3.76	stronger base		weaker base	weaker acid pK$_a$ 9.22	**PRODUCTS**

(b)
$$CH_3COO^- + CH_3OH \rightleftharpoons CH_3COOH + CH_3O^-$$

CH$_3$COO$^-$	CH$_3$OH	CH$_3$COOH	CH$_3$O$^-$	FAVORS
weaker base	weaker acid pK$_a$ 15.5	stronger acid pK$_a$ 4.74	stronger base	**REACTANTS**

(c)
$$CH_3OH + NaNH_2 \rightleftharpoons CH_3O^- \ Na^+ + NH_3$$

CH$_3$OH	NaNH$_2$	CH$_3$O$^-$ Na$^+$	NH$_3$	FAVORS
stronger acid pK$_a$ 15.5	stronger base	weaker base	weaker acid pK$_a$ 33	**PRODUCTS**

(d)
$$Na^+ \ ^-OCH_3 + HCN \rightleftharpoons HOCH_3 + NaCN$$

Na$^+$ $^-$OCH$_3$	HCN	HOCH$_3$	NaCN	FAVORS
stronger base	stronger acid pK$_a$ 9.22	weaker acid pK$_a$ 15.5	weaker base	**PRODUCTS**

(e)
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

HCl	H$_2$O	H$_3$O$^+$	Cl$^-$	FAVORS
stronger acid	stronger base	weaker acid	weaker base	**PRODUCTS**

The first reaction in Table 1-5 shows the K_{eq} for this reaction is 160, favoring products.

(f)
$$H_3O^+ + CH_3O^- \rightleftharpoons H_2O + CH_3OH$$

H$_3$O$^+$	CH$_3$O$^-$	H$_2$O	CH$_3$OH	FAVORS
stronger acid pK$_a$ −1.7	stronger base	weaker base	weaker acid pK$_a$ 15.5	**PRODUCTS**

The seventh reaction in Table 1-5 shows the K_{eq} for the *reverse* of this reaction is 3.2 x 10^{-16}. Therefore, K_{eq} for this reaction as written must be the inverse, or 3.1 x 10^{15}, strongly favoring products.

1-16

$$CH_3-\overset{\overset{\displaystyle :O:}{||}}{C}-\overset{..}{\underset{..}{O}}-H \ + \ H^+ \ \rightleftharpoons \ CH_3-\overset{\overset{\displaystyle :O:}{||}}{C}-\overset{..}{\underset{\overset{+|}{H}}{O}}-H$$
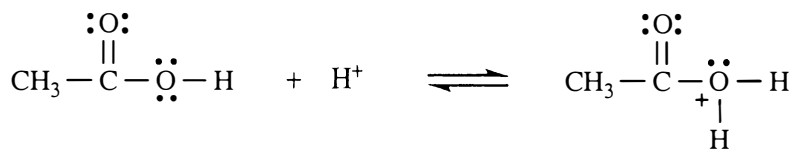
Protonation of the double-bonded oxygen gives three resonance forms (as shown in Solved Problem 1-5(c)); protonation of the single-bonded oxygen gives only one. In general, the more resonance forms a species has, the more stable it is, so the proton would bond to the oxygen that gives a more stable species, that is, the double-bonded oxygen.

1-17 In Solved Problem 1-4, the structures of ethanol and methylamine are shown to be similar to methanol and ammonia, respectively. We must infer that their acid-base properties are also similar.

(a) This problem can be viewed in two ways. 1) Quantitatively, the pK_a values determine the order of acidity. 2) Qualitatively, the stabilities of the conjugate bases determine the order of acidity (see Solved Problem 1-4 for structures): the conjugate base of acetic acid, acetate ion, is resonance-stabilized, so acetic acid is the most acidic; the conjugate base of ethanol has a negative charge on a very electronegative oxygen atom; the conjugate base of methylamine has a negative charge on a mildly electronegative nitrogen atom and is therefore the least stabilized, so methylamine is the least acidic.

<div align="center">

acetic acid   >   ethanol   >   methylamine

pK_a 4.74 $pK_a \approx 15.5$ $pK_a \approx 33$

strongest acid   weakest acid

</div>
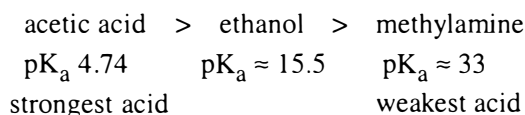
(b) Ethoxide ion is the conjugate base of ethanol, so it must be a stronger base than ethanol; Solved Problem 1-4 indicates ethoxide is analogous to hydroxide in base strength. Methylamine has pK_b 3.36. The basicity of methylamine is between the basicity of ethoxide ion and ethanol.

<div align="center">

ethoxide ion   >   methylamine   >   ethanol

strongest base   weakest base

</div>
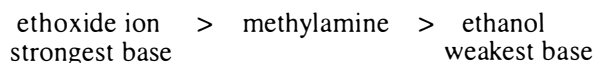
1-18 Curved arrows show electron movement, as described in text section 1-14.

(a) equilibrium favors PRODUCTS

(b) equilibrium favors PRODUCTS

(c) equilibrium favors PRODUCTS

conjugate base, weaker base

1-18 continued

(d)

Na⁺ :Ö—H   +   H—S—H   ⇌   H—Ö—H   +   Na⁺ :S—H

stronger base   stronger acid   conjugate acid   conjugate base
                                          weaker acid   weaker base

equilibrium favors PRODUCTS

(e)

          H
          |⁺
CH₃—N—H   +   CH₃—Ö:⁻   ⇌   CH₃—N—H   +   CH₃—Ö—H
          | |
          H   H

                  stronger base   conjugate base   conjugate acid
                                       weaker base   weaker acid
stronger acid

equilibrium favors PRODUCTS

(f)

      :O:
      ||
CH₃—C—Ö—H + CH₃—Ö:⁻ ⇌ CH₃—Ö—H + { :O: :Ö:⁻
                                        || |
stronger acid   stronger base   conjugate acid   CH₃—C—Ö:⁻ ↔ CH₃—C=Ö: }
                                  weaker acid
                                                   conjugate base
                                                   weaker base

equilibrium favors PRODUCTS

(g)

      :O: :O: :O: :O:⁻
      || || || |
CH₃—C—Ö—H + {⁻:Ö—S—CH₃ ↔ Ö=S—CH₃ ↔ Ö=S—CH₃ }
                         || | ||
weaker acid   :O: :O:⁻   :O:

                                         weaker base

equilibrium favors REACTANTS

⇌ { :O: :Ö:⁻ }   :O:
      || | ||
    CH₃—C—Ö: ↔ CH₃—C=Ö: } + H—Ö—S—CH₃
                                         ||
   conjugate base   :O:
   stronger base
                                  conjugate acid
                                  stronger acid

1-19 Solutions for (a) and (b) are presented in the Solved Problem in the text. Here, the newly formed bonds are shown in bold.

(c)

            H
            |⁻
H—B—H   +   CH₃—Ö—CH₃   ⇌   H—B—H
    | |⁺
acid H   base   CH₃—Ö—CH₃

(d)

      :O: :Ö:⁻
      || |
CH₃—C—H   +   ⁻:Ö—H   ⇌   CH₃—C—H
                                  |
acid   base   :O—H
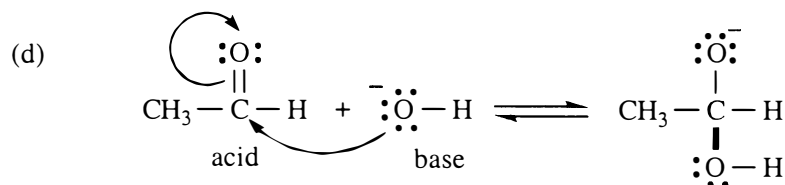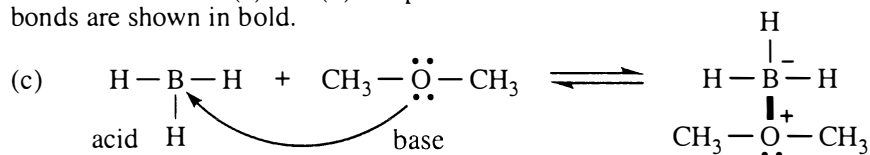
1-19 continued

(e) Bronsted-Lowry—proton transfer

(f)
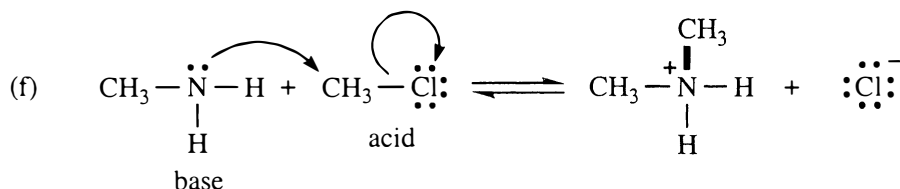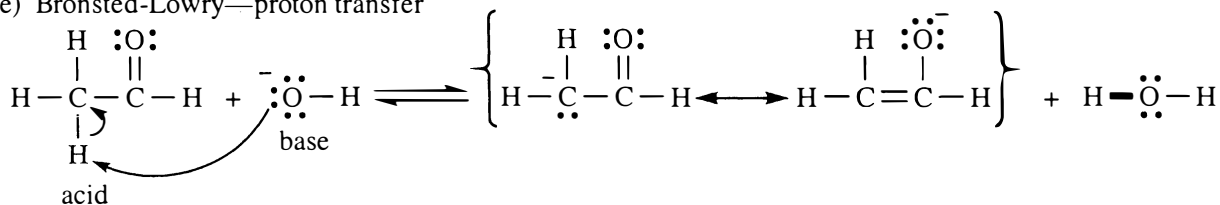
1-20

Learning organic chemistry is similar to learning a foreign language: new vocabulary, new grammar (the reactions), some new concepts, and even a new alphabet (the symbolism of chemistry). This type of definition question is intended to help you review the vocabulary and concepts in each chapter. All of the definitions and examples are presented in the Glossary and in the chapter, so this Solutions Manual will not repeat them. Use these questions to evaluate your comprehension and to guide your review of the important concepts in the chapter.

1-21 (a) CARBON!   (b) oxygen   (c) phosphorus   (d) chlorine

1-22

valence e⁻ →	1	2	3	4	5	6	7	8
	H							He (2e⁻)
	Li	Be	B	C	N	O	F	Ne
					P	S	Cl	
							Br	
							I	

1-23

(a) ionic only   (b) covalent (H—O⁻) and ionic (Na⁺ ⁻OH)

(c) covalent (H—C and C—Li), but the C—Li bond is strongly polarized

(d) covalent only   (e) covalent (H—C and C—O⁻) and ionic (Na⁺ ⁻OCH₃)

(f) covalent (H—C and C=O and C—O⁻) and ionic (HCO₂⁻ Na⁺)   (g) covalent only

1-24

(a)

(b)

CANNOT EXIST
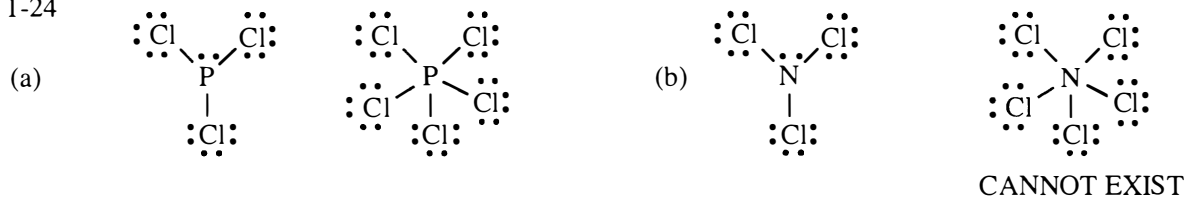
NCl_5 violates the octet rule; nitrogen can have no more than eight electrons (or four atoms) around it. Phosphorus, a third-row element, can have more than eight electrons because phosphorus can used orbitals in bonding, so PCl_5 is a stable, isolable compound.

1-25 Your Lewis structures may look different from these. As long as the atoms are connected in the same order and by the same type of bond, they are equivalent structures. For now, the exact placement of the atoms on the page is not significant.

(a) H—N—N—H (with H, H below and lone pairs on each N)

(b) H—N=N—H (with lone pairs on each N)

(c) methylammonium-type structure with N⁺ bonded to C groups and :Cl:⁻

(d) H—C—C≡N: (with H's on first C)

(e) H—C—C—H with :O: double bonded (with H's)

(f) H—C—S—C—H with :O: double bonded (with H's)

(g) H—O—S—O—H with :O: above (double bond) and :O: below

(h) H—C—N=C=O (with H's on C)

(i) H—C—O—S—O—C—H with :O: above and :O: below

(j) H—C—C—C—H with :N above (double bonded, with H's)

(k) structure with central C bonded to CH₃ groups, C, and N=O:

1-26

(a) H—C—C=C—C—C=C—C—O—H chain (with H's on each carbon and :O: double bonded)

(b) :N≡C—C—C—C—C—H chain (with H :O: H :O: groups)

1-26 continued

(c)
```
        H—Ö:  H  :O:
        |     |    ||
H—C=C—C—C—C—Ö—H
  |  |  |  |    ··
  H  H  H  H
```

(d)
```
              H  H
              \ /
               C
              /|\
            H C H
              |
        H  H  C  :O:
        |  |  |   ||
H—C—C—C—C—C—H
  |  |  |  |  ··
  H  H  C  C  H
       /|\ /|\
      H H H H | H
           C
          /|\
         H H H
```

1-27 In each set below, the second structure is a more correct line formula. Since chemists are human (surprise!), they will take shortcuts where possible; the first structure in each pair uses a common abbreviation, either COOH or CHO. Make sure you understand that COOH does not stand for C—O—O—H. Likewise for CHO.

(a) ⌇⌇⌇COOH

OR ⌇⌇⌇ —OH / O

(b) N≡C⌇⌇CHO (with O below)

OR N≡C⌇⌇—H (with two O below)

(c) ⌇⌇COOH / OH

OR ⌇⌇—OH / OH, O

(d) ⌇⌇CHO OR ⌇⌇—H / O

1-28

(a)
```
      H  H  H  H
      |  |  |  |
  H—C—C—C—C—H      and
      |  |  |  |
      H  H  H  H
```
```
      H  H  H
      |  |  |
  H—C—C—C—H
      |  |  |
      H  C  H
        /|\
      H  |  H
         H
```
these are the only two possibilities, but your structures may appear different—making models will help you visualize these structures

(b)
```
      H  H  H
      |  |  |
  H—C—C—N:
      |  |  |
      H  H  H
```
and
```
      H  H  H
      |  |  |
  H—C—N—C—H
      |  ··  |
      H      H
```
these are the only two possibilities, but your structures may appear different—making models will help you visualize these structures

14

1-28 continued

(c) There are several other possibilities as well. Your answer may be correct even if it does not appear here. Check with others in your study group.

(d)
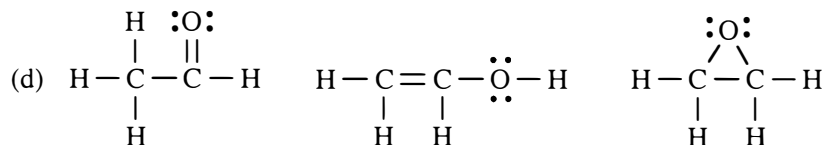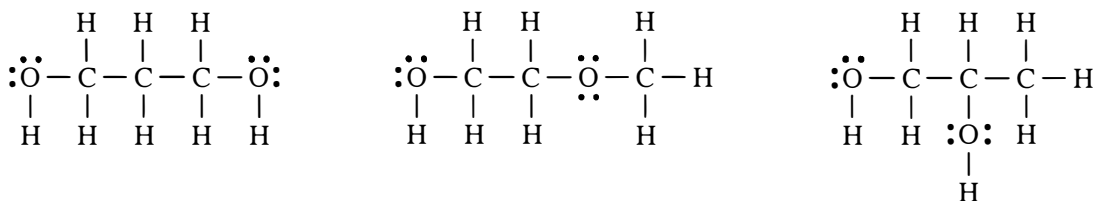
These are the only three structures with this molecular formula.

1-29

(a) only three possible structures

HOCH$_2$CH$_2$CH$_3$ CH$_3$CH$_2$OCH$_3$ CH$_3$CH(OH)CH$_3$

(b) There are several other possibilities as well.

CH$_3$CH$_2$CHO   CH$_3$COCH$_3$ H$_2$C $=$ CHCH$_2$OH   H$_2$C $=$ C(OH)CH$_3$

H$_2$C $=$ CHOCH$_3$
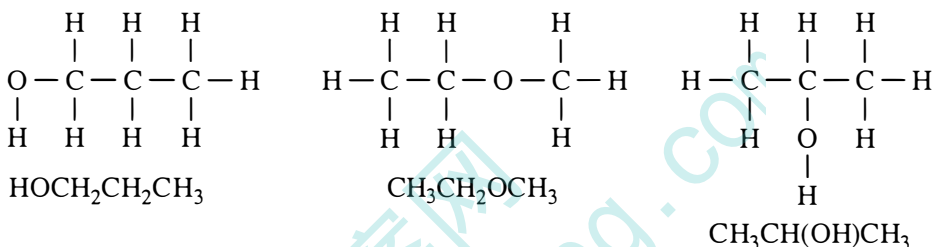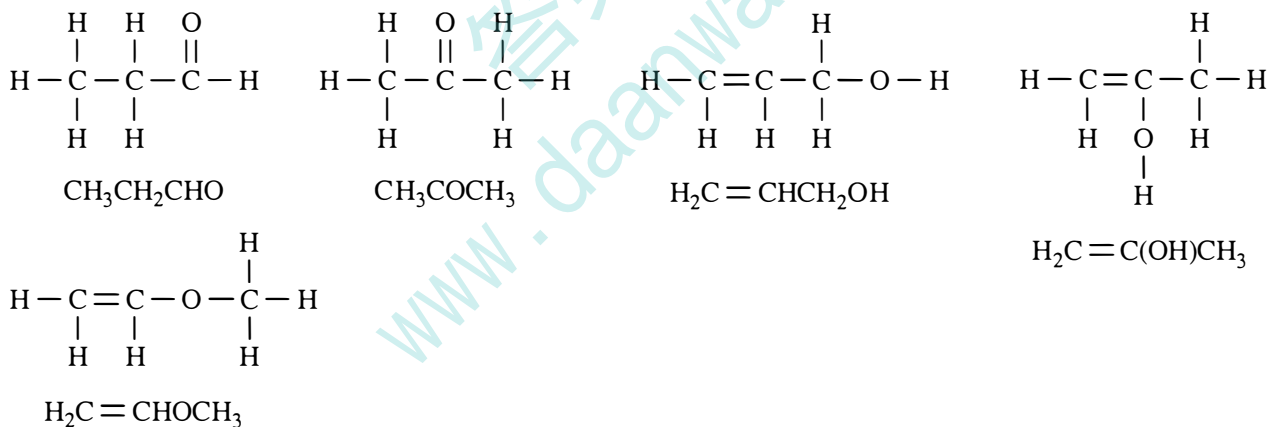
1-30 General rule: *molecular formulas of stable hydrocarbons must have an even number of hydrogens.* The formula CH$_2$ does not have enough atoms to bond with the four orbitals of carbon.

one carbon:
CH$_4$

two carbons: H$-$C$\equiv$C$-$H   C$_2$H$_2$ C$_2$H$_4$ C$_2$H$_6$

three carbons: H$-$C$\equiv$C$-$C$-$H   C$_3$H$_4$ C$_3$H$_6$ C$_3$H$_8$

15

1-31

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)
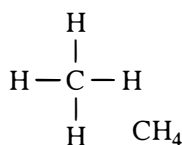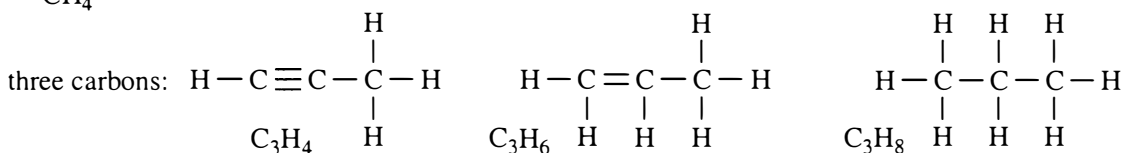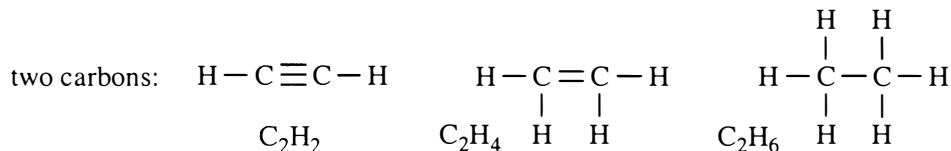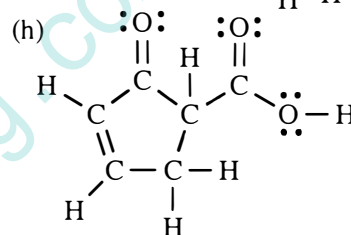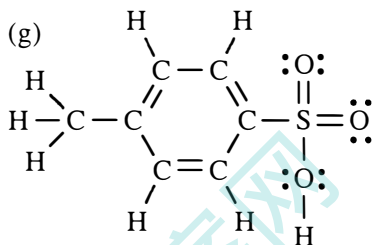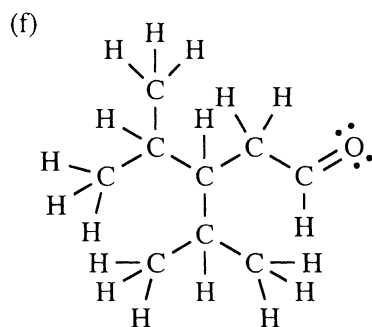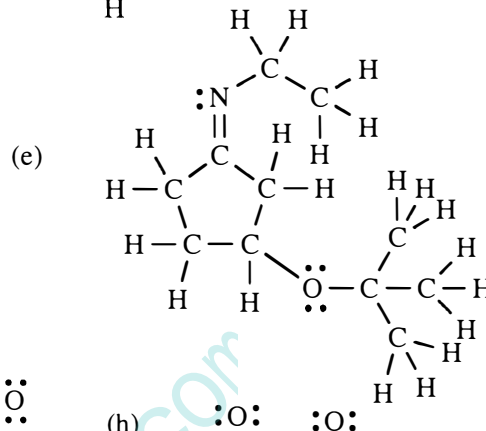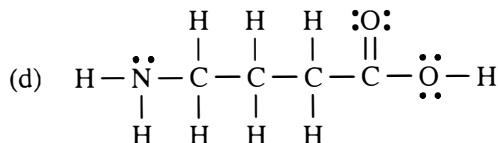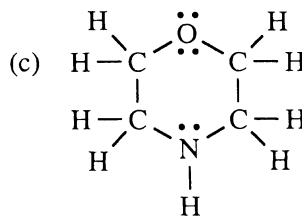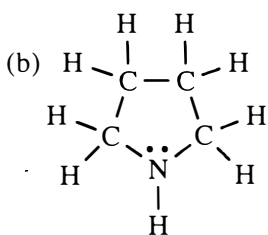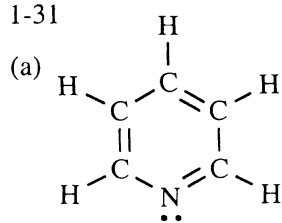
1-32 (a) C_5H_5N (b) C_4H_9N (c) C_4H_9NO (d) $C_4H_9NO_2$ (e) $C_{11}H_{21}NO$

(f) $C_9H_{18}O$ (g) $C_7H_8O_3S$ (h) $C_6H_6O_3$

1-33

(a) $100\% - 62.0\%\ C - 10.4\%\ H = 27.6\%$ oxygen

$$\frac{62.0\ g\ C}{12.0\ g/mole} = 5.17\ moles\ C \div 1.73\ moles = 2.99 \approx 3\ C$$

$$\frac{10.4\ g\ H}{1.01\ g/mole} = 10.3\ moles\ H \div 1.73\ moles = 5.95 \approx 6\ H$$

$$\frac{27.6\ g\ O}{16.0\ g/mole} = 1.73\ moles\ O \div 1.73\ moles = 1\ O$$

(b) empirical formula = $\boxed{C_3H_6O}$ $\Longrightarrow$ empirical weight = 58

molecular weight = 117, about double the empirical weight

$\Longrightarrow$ double the empirical formula = molecular formula = $\boxed{C_6H_{12}O_2}$
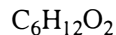
(c) some possible structures—MANY other structures possible:

16
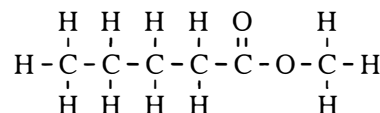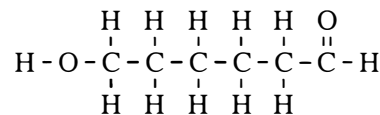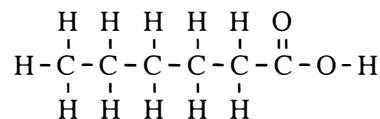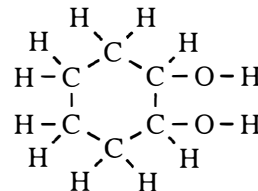
1-34 Non-zero formal charges are shown by the atoms.

(a)
$$H-\overset{|}{\underset{H}{C}}=\overset{+}{N}=\overset{-}{\ddot{N}} \longleftrightarrow H-\overset{|}{\underset{H}{C}}-\overset{+}{N}\equiv N$$

(b)
$$H_3C-\overset{+}{\underset{(CH_3)_2}{N}}-\overset{-}{\ddot{O}}$$
(tetramethyl with CH_3 groups around $\overset{+}{N}$ and $\ddot{O}^-$)

(c)
$$H-\overset{}{C}=\overset{}{C}-\overset{+}{\underset{H}{C}}-H$$
(with H, H, H below)

(d)
$$H-\overset{|}{\underset{H}{C}}-\overset{+}{N}=\ddot{O}$$
with $:\ddot{O}:^-$ below N

(e)
$$H-\overset{|}{\underset{H}{C}}-\overset{+}{\ddot{O}}-\overset{|}{\underset{H}{C}}-H$$
with CH_3 ($\overset{}{C}$ with H, H, H) below the $\overset{+}{O}$
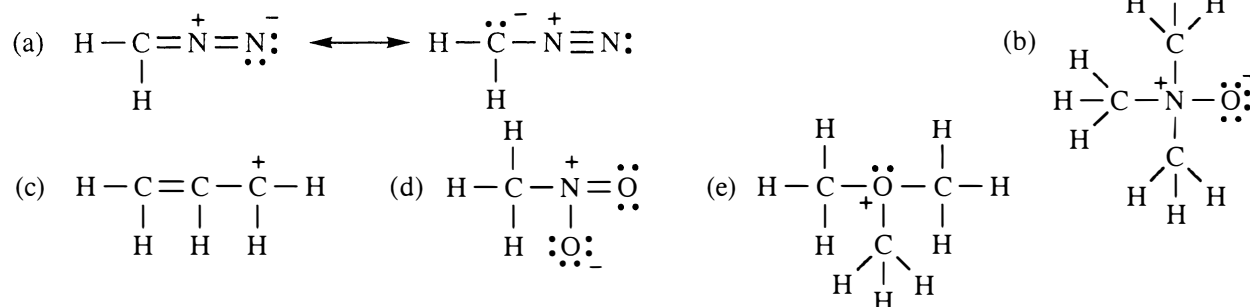
1-35 The symbols "δ^+" and "δ^-" indicate bond polarity by showing partial charge. Electronegativity differences greater than or equal to 0.5 are considered large.

(a) $\overset{\delta^+}{C}-\overset{\delta^-}{Cl}$ large

(b) $\overset{\delta^-}{C}-\overset{\delta^+}{H}$ small

(c) $\overset{\delta^-}{C}-\overset{\delta^+}{Li}$ large

(d) $\overset{\delta^+}{C}-\overset{\delta^-}{N}$ small

(e) $\overset{\delta^+}{C}-\overset{\delta^-}{O}$ large

(f) $\overset{\delta^-}{C}-\overset{\delta^+}{B}$ large

(g) $\overset{\delta^-}{C}-\overset{\delta^+}{Mg}$ large

(h) $\overset{\delta^-}{N}-\overset{\delta^+}{H}$ large

(i) $\overset{\delta^-}{O}-\overset{\delta^+}{H}$ large

(j) $\overset{\delta^+}{C}-\overset{\delta^-}{Br}$ small
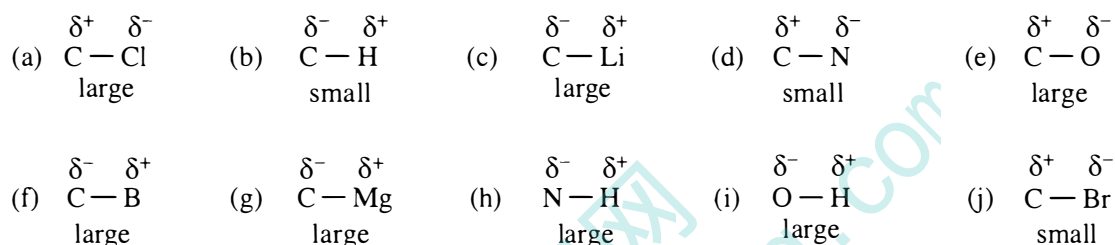
1-36 Resonance forms must have atoms in identical positions. If any atom moves position, it is a different structure.

(a) different compounds—a hydrogen atom has changed position
(b) resonance forms—only the position of electrons is different
(c) resonance forms—only the position of electrons is different
(d) resonance forms—only the position of electrons is different
(e) different compounds—a hydrogen atom has changed position
(f) resonance forms—only the position of electrons is different
(g) resonance forms—only the position of electrons is different
(h) different compounds—a hydrogen atom has changed position
(i) resonance forms—only the position of electrons is different
(j) resonance forms—only the position of electrons is different

1-37

(a)
$$H-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-\overset{||\,\ddot{O}}{C}-H \longleftrightarrow H-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}=\overset{:\ddot{O}:^-}{C}-H$$

(b)
$$H-\overset{||\,:O:}{C}-C=\overset{}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-H \longleftrightarrow H-\overset{||\,:O:}{C}-\overset{}{\underset{H}{C}}-\overset{}{\underset{H}{C}}=\overset{}{\underset{H}{C}}-H \longleftrightarrow H-\overset{:\ddot{O}:^-}{C}=\overset{}{\underset{H}{C}}-\overset{}{\underset{H}{C}}=\overset{}{\underset{H}{C}}-H$$

17

1-37 continued

(c)

(d)

(e)

(f)

(g)

(h)

(i) $CH_3-C=C-C=C-\overset{+}{C}-CH_3 \longleftrightarrow CH_3-C=C-\overset{+}{C}-C=C-CH_3$
with H substituents below each carbon

$CH_3-\overset{+}{C}-C=C-C=C-CH_3$
with H substituents below each carbon
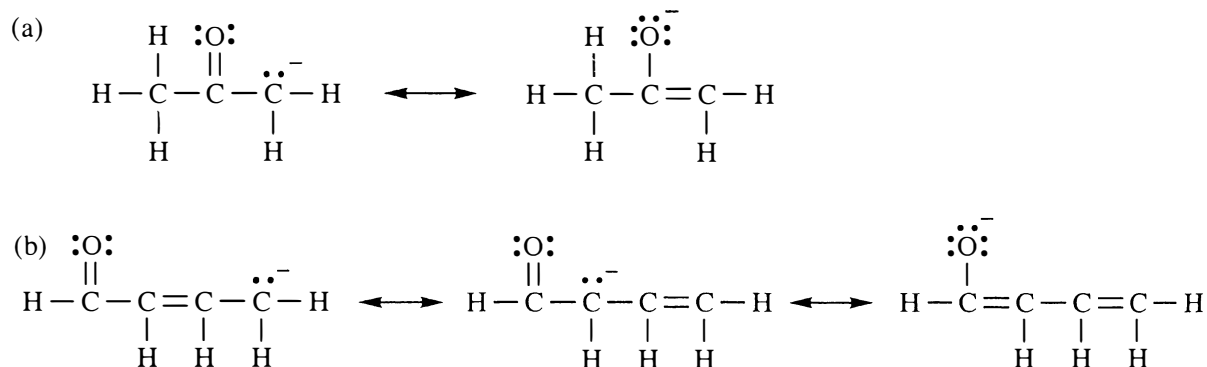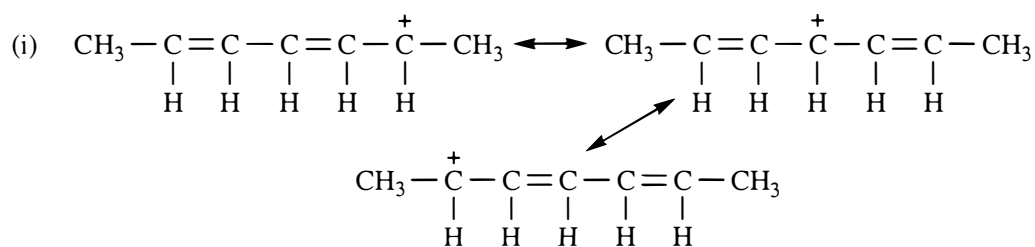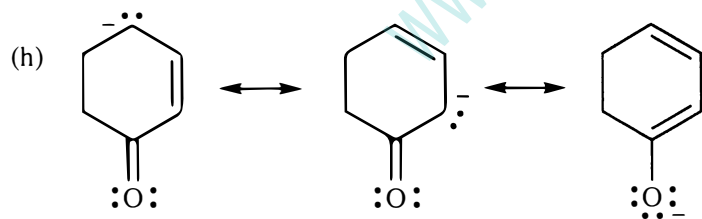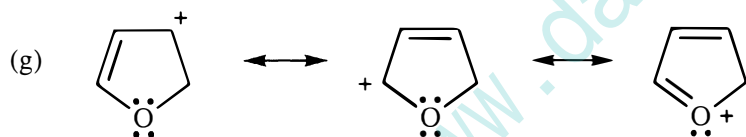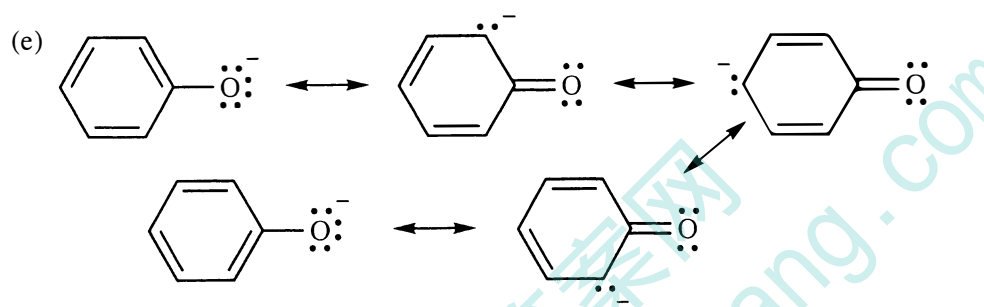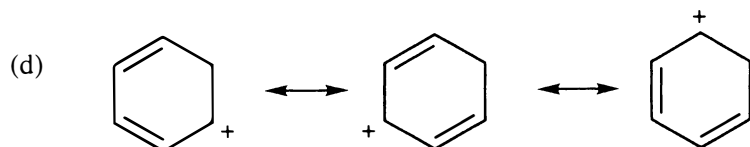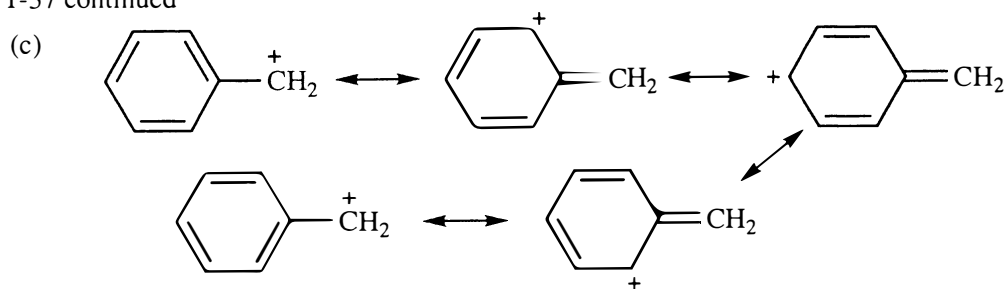
(j) no resonance forms—the charge must be on an atom next to a double or triple bond, or next to a non-bonded pair of electrons, in order for resonance to delocalize the charge

1-38

(a) $\overset{..}{\underset{..}{O}}=\overset{}{\underset{+}{S}}-\overset{..}{\underset{..}{O}}\overset{-}{:}$ ⟷ $:\overset{..}{\underset{..}{O}}-\overset{}{\underset{+}{S}}=\overset{..}{\underset{..}{O}}$ ⟷ $\overset{..}{\underset{..}{O}}=\overset{}{S}=\overset{..}{\underset{..}{O}}$

(b) $\overset{..}{\underset{..}{O}}=\overset{}{\underset{+}{O}}-\overset{..}{\underset{..}{O}}\overset{-}{:}$ ⟷ $:\overset{..}{\underset{..}{O}}\overset{-}{}-\overset{}{\underset{+}{O}}=\overset{..}{\underset{..}{O}}$
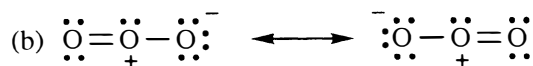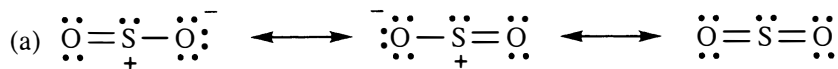
(c) The last resonance form of SO_2 has no equivalent form in O_3. Sulfur, a third row element, can have more than eight electrons around it because of d orbitals, whereas oxygen, a second row element, must adhere strictly to the octet rule.

1-39

(a)
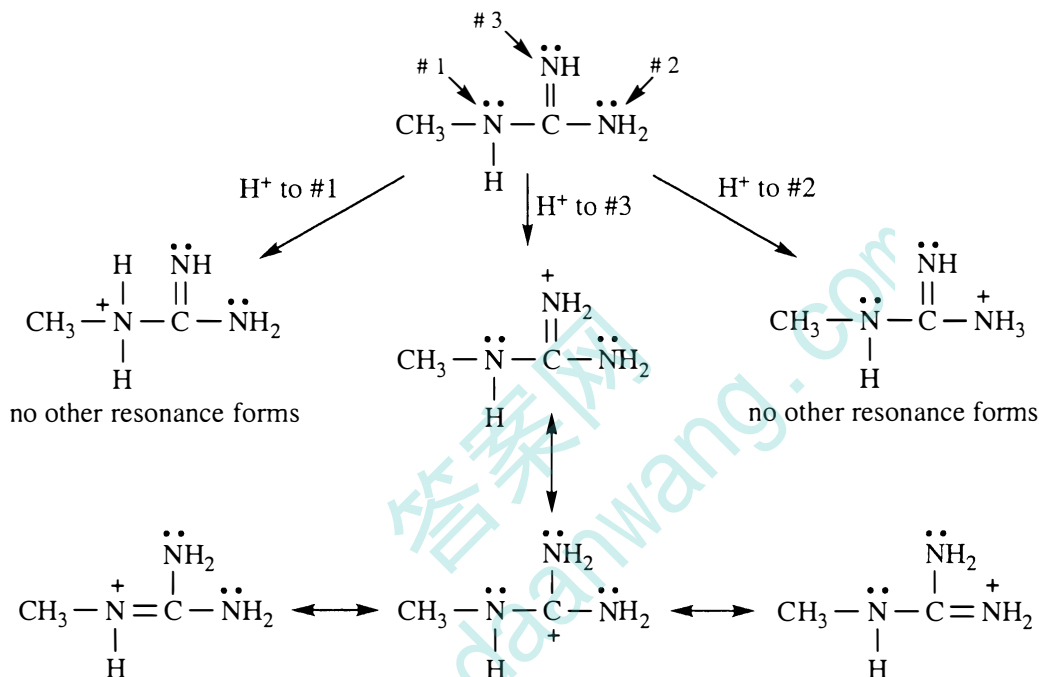
(b) Protonation at nitrogen #3 gives four resonance forms that delocalize the positive charge over all three nitrogens and a carbon—a very stable condition. Nitrogen #3 will be protonated preferentially, which we interpret as being more basic.

1-40

(a) $CH_3-\overset{\overset{..}{\overset{-}{}}}{\underset{\underset{H}{|}}{C}}-C\equiv N:$ ⟷ $CH_3-\overset{\underset{\underset{H}{|}}{}}{C}=C=\overset{..}{\underset{..}{N}}\overset{-}{}$

minor   major (negative charge on electronegative atom)

(b) $CH_3-\overset{\overset{:\overset{..}{O}:^-}{|}}{C}=\overset{\underset{H}{|}}{C}-\overset{\overset{+}{}}{\underset{\underset{H}{|}}{C}}-CH_3$ ⟷ $CH_3-\overset{\overset{:\overset{..}{O}:^-}{|}}{\underset{+}{C}}-\overset{\underset{H}{|}}{C}=\overset{\underset{H}{|}}{C}-CH_3$ ⟷ $CH_3-\overset{\overset{:\overset{..}{O}:}{||}}{C}-\overset{\underset{H}{|}}{C}=\overset{\underset{H}{|}}{C}-CH_3$

minor   minor   major—full octets, no charge separation

19

1-40 continued

(c)

negative charge on electronegative atoms—equal energy

(d)

minor   minor   major—negative charge on electronegative atoms
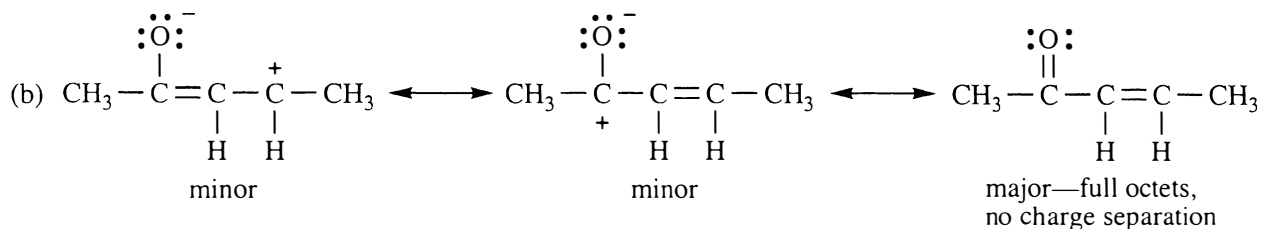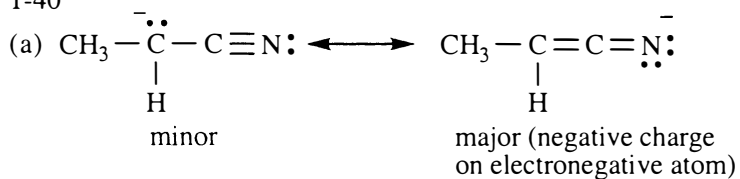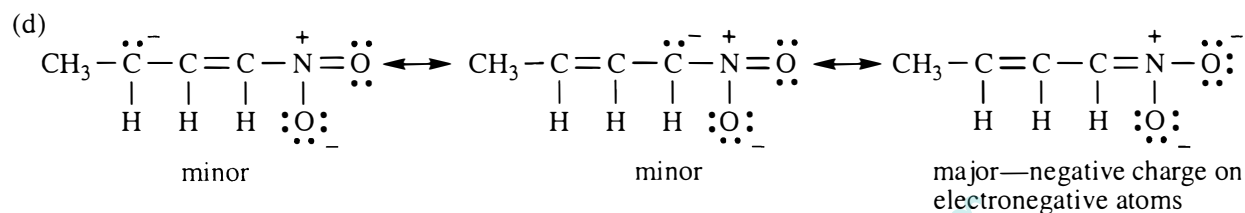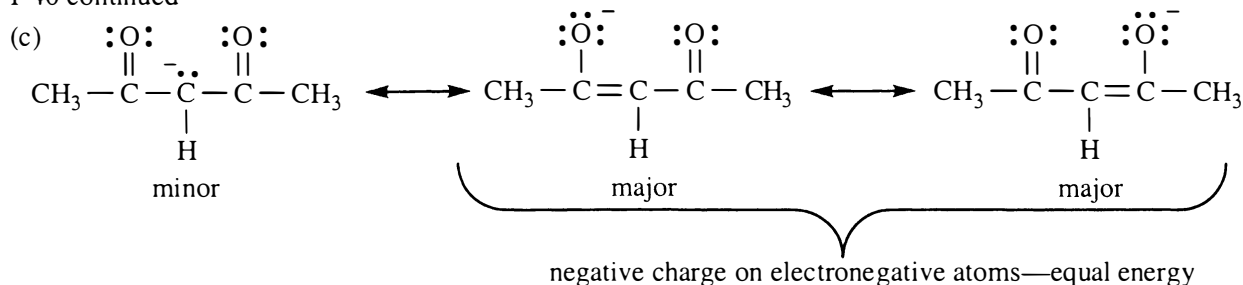
NOTE: The two structures below are resonance forms, varying from the first two structures in part (d) by the different positions of the double bonds in the NO₂. Usually, chemists omit drawing the second form of the NO₂ group although we all understand that its presence is implied. It is good idea to draw all the resonance forms until they become second nature. The importance of understanding resonance forms cannot be overemphasized.

(e)

minor   major—full octets   major—full octets

equal energy

1-41

(a)

no resonance stabilization   more stable—resonance stabilized

(b)

more stable—resonance stabilized   no resonance stabilization

1-41 continued

(c)

$$H-\overset{\underset{\displaystyle H}{|}}{\overset{..}{\underset{}{C}}}-CH_3$$

no resonance stabilization

$$H-\overset{\underset{\displaystyle H}{|}}{\overset{..}{\underset{}{C}}}-C\equiv N:\quad\longleftrightarrow\quad H-\overset{\underset{\displaystyle H}{|}}{C}=C=\overset{..}{N}:$$

more stable—resonance stabilized

(d)

more stable—resonance stabilized

no resonance stabilization

(e)

$$CH_3-\overset{..}{N}-CH_3$$
$$CH_3-\overset{}{\underset{+}{C}}-CH_3$$

$$\longleftrightarrow$$

$$CH_3-\overset{+}{\underset{||}{N}}-CH_3$$
$$CH_3-\overset{}{C}-CH_3$$

more stable—resonance stabilized

$$CH_3-\overset{\underset{\displaystyle |}{H}}{\underset{}{C}}-CH_3$$
$$CH_3-\overset{}{\underset{+}{C}}-CH_3$$

no resonance stabilization

1-42 These pK_a values from the text, Table 1-5, and Appendix 5 provide the answers. The lower the pK_a, the stronger the acid.

least acidic						most acidic
NH_3	<	CH_3OH	<	CH_3COOH	<	H_2SO_4
33		15.5		4.74		–5

1-43 Conjugate bases of the weakest acids will be the strongest bases. The pK_a values of the conjugate acids are listed here. (The relative order of the first two was determined from the pK_a values of sulfuric acid and protonated acedic acid in Appendix 5 of the textbook.)

least basic										most basic
CH_3COOH	<	HSO_4^-	<	CH_3COO^-	<	CH_3O^-	<	NaOH	<	$^-NH_2$
from –6.1		from –5		from 4.74		from 15.5		from 15.7		from 33
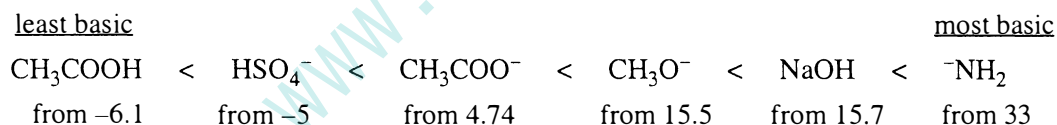
1-44
(a) $pK_a = -\log_{10} K_a = -\log_{10}(5.2 \times 10^{-5}) = \textbf{4.3}$ for phenylacetic acid

for propionic acid, pK_a 4.87: $K_a = 10^{-4.87} = \textbf{1.35} \times \textbf{10}^{-5}$

(b) phenylacetic acid is 3.9 times stronger than propionic acid

$$\frac{5.2 \times 10^{-5}}{1.35 \times 10^{-5}} = 3.9$$

(c)

$$\text{⬡}-CH_2COO^- + CH_3CH_2COOH \longleftrightarrow \text{⬡}-CH_2COOH + CH_3CH_2COO^-$$

weaker acid   stronger acid
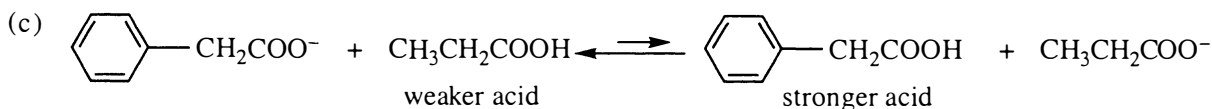
Equilibrium favors the weaker acid and base. In this reaction, **reactants** are favored.

1-45 The newly formed bond is shown in bold.

(a) $CH_3 - \ddot{O}:^- + CH_3 - \ddot{C}l: \longrightarrow CH_3 - \ddot{O} - CH_3 + :\ddot{C}l:^-$

      nucleophile   electrophile
      Lewis base   Lewis acid

(b) $CH_3 - \overset{+}{\underset{|}{\ddot{O}}} - CH_3 + H - \ddot{O} - H \longrightarrow CH_3 - \ddot{O} - CH_3 + H - \overset{+}{\underset{|}{\ddot{O}}} - H$
          H_3C CH_3

               nucleophile
  electrophile   Lewis base
  Lewis acid

(c)

$$H - \overset{\overset{\displaystyle :O:}{\|}}{C} - H + :\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{N}} - H \longrightarrow H - \overset{\overset{\displaystyle :\ddot{O}:^-}{|}}{C} - H$$

                                              $H - \overset{+}{N} - H$

  electrophile   nucleophile
  Lewis acid   Lewis base H

(d) $CH_3 - \ddot{N}H_2$ $CH_3CH_2 - \ddot{C}l: \longrightarrow CH_3 - \overset{\overset{\displaystyle H}{+|}}{N} - CH_2CH_3 + :\ddot{C}l:^-$

  nucleophile   electrophile $|$
  Lewis base   Lewis acid H

(e) $CH_3 - \overset{\overset{\displaystyle :O:}{\|}}{C} - CH_3 + H - \overset{\overset{\displaystyle :O:}{}}{\underset{\underset{\displaystyle :O:}{\|}}{\ddot{O} - S}} - \ddot{O}H \longrightarrow CH_3 - \overset{\overset{\displaystyle :\overset{+}{O} - H}{}}{C} - CH_3 + ^-:\ddot{O} - \overset{\overset{\displaystyle :O:}{\|}}{\underset{\underset{\displaystyle :O:}{\|}}{S}} - \ddot{O}H$

  nucleophile
  Lewis base

                   electrophile
                   Lewis acid

(f) $(CH_3)_3C - \ddot{C}l: + AlCl_3 \longrightarrow H_3C - \overset{\overset{\displaystyle CH_3}{+|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} + :\ddot{C}l - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{Al}} - Cl^-$

  nucleophile   electrophile
  Lewis base   Lewis acid

This may also be written in two steps: association of the Cl with Al, and a second step where the C—Cl bond breaks.

(g) $CH_3 - \overset{\overset{\displaystyle :O:}{\|}}{C} - \underset{\underset{\displaystyle H}{|}}{CH_2} + ^-:\ddot{O} - H \longrightarrow CH_3 - \overset{\overset{\displaystyle :\ddot{O}:^-}{|}}{C} = CH_2 + H - \ddot{O} - H$

                     nucleophile
  electrophile   Lewis base
  Lewis acid

1-45 continued

(h) F — B — F   CH₂ = CH₂ ⟶   F — B ▬ CH₂ — CH₂

electrophile   nucleophile
Lewis acid   Lewis base

(i) ⁻BF₃ — CH₂ — CH₂⁺ + CH₂ = CH₂ ⟶ ⁻BF₃ — CH₂ — CH₂ ▬ CH₂ — CH₂⁺

electrophile   nucleophile
Lewis acid   Lewis base

1-46

(a) H₂SO₄ + CH₃COO⁻ ⇌ HSO₄⁻ + CH₃COOH

(b) CH₃COOH + (CH₃)₃N: ⇌ CH₃COO⁻ + (CH₃)₃N⁺ — H

(c) C₆H₅ — C(=O) — O — H + ⁻OH ⇌ C₆H₅ — C(=O) — O⁻ + H₂O

(d) (CH₃)₃N⁺ — H + ⁻OH ⇌ (CH₃)₃N: + H₂O

(e) HO — C(=O) — OH + 2 ⁻OH ⇌ ⁻O — C(=O) — O⁻ + 2 H₂O

(f) H₂O + NH₃ ⇌ HO⁻ + ⁺NH₄

(g) HCOOH + CH₃O⁻ ⇌ HCOO⁻ + CH₃OH

1-47

(a) CH₃CH₂ — O — H + CH₃ — Li ⟶ CH₃CH₂ — O⁻ Li⁺ + CH₄

(b) The conjugate acid of CH₃Li is CH₄. Table 1-5 gives the pKₐ of CH₄ as > 40, one of the weakest acids known. The conjugate base of one of the weakest acids known must be one of the strongest bases known.

23

1-48

From the amounts of CO_2 and H_2O generated, the milligrams of C and H in the original sample can be determined, thus giving by difference the amount of oxygen in the 5.00 mg sample. From these values, the empirical formula and empirical weight can be calculated.

(a) how much carbon in 14.54 mg CO_2

$$14.54 \text{ mg } CO_2 \text{ x } \frac{1 \text{ mmole } CO_2}{44.01 \text{ mg } CO_2} \text{ x } \frac{1 \text{ mmole C}}{1 \text{ mmole } CO_2} \text{ x } \frac{12.01 \text{ mg C}}{1 \text{ mmole C}} = 3.968 \text{ mg C}$$

how much hydrogen in 3.97 mg H_2O

$$3.97 \text{ mg } H_2O \text{ x } \frac{1 \text{ mmole } H_2O}{18.016 \text{ mg } H_2O} \text{ x } \frac{2 \text{ mmoles H}}{1 \text{ mmole } H_2O} \text{ x } \frac{1.008 \text{ mg H}}{1 \text{ mmole H}} = 0.444 \text{ mg H}$$

how much oxygen in 5.00 mg estradiol

5.00 mg estradiol - 3.968 mg C - 0.444 mg H = 0.59 mg O

calculate empirical formula

$$\frac{3.968 \text{ mg C}}{12.01 \text{ mg/mole}} = 0.3304 \text{ mmoles C } \div 0.037 \text{ mmoles } = 8.93 \approx 9 \text{ C}$$

$$\frac{0.444 \text{ mg H}}{1.008 \text{ mg/mole}} = 0.440 \text{ mmoles H } \div 0.037 \text{ mmoles } = 11.9 \approx 12 \text{ H}$$

$$\frac{0.59 \text{ mg O}}{16.00 \text{ mg/mole}} = 0.037 \text{ mmoles O } \div 0.037 \text{ mmoles } = 1 \text{ O}$$

empirical formula = $\boxed{C_9H_{12}O}$ $\Longrightarrow$ empirical weight = 136

(b) molecular weight = 272, exactly twice the empirical weight

twice the empirical formula = molecular formula = $\boxed{C_{18}H_{24}O_2}$

CHAPTER 2—STRUCTURE AND PROPERTIES OF ORGANIC MOLECULES

2-1 The fundamental principle of organic chemistry is that a molecule's chemical and physical properties depend on the molecule's structure: the structure-function or structure-reactivity correlation. It is essential that you understand the three-dimensional nature of organic molecules, and there is no better device to assist you than a molecular model set. You are strongly encouraged to use models regularly when reading the text and working the problems.

(a) requires use of models

(b)

The wedge bonds represent bonds coming out of the plane of the paper toward you.
The dashed bonds represent bonds going behind the plane of the paper.
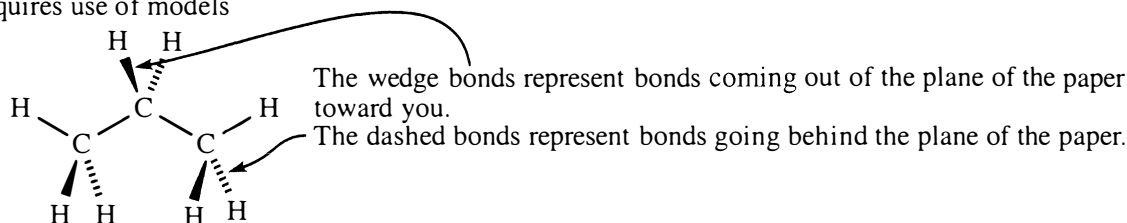
2-2 (a) The hybridization of oxygen is sp^3 since it has two sigma bonds and two pairs of nonbonding electrons. The reason that the bond angle of 104.5° is less than the perfect tetrahedral angle of 109.5° is that the lone pairs in the two sp^3 orbitals are repelling each other more strongly than the electron pairs in the sigma bonds, thereby compressing the bond angle.
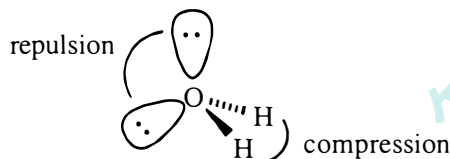
(b) The electrostatic potential map for water shows that the hydrogens have low electron potential (blue), and the area of the unshared electron pairs in sp^3 orbitals has high electron potential (red).
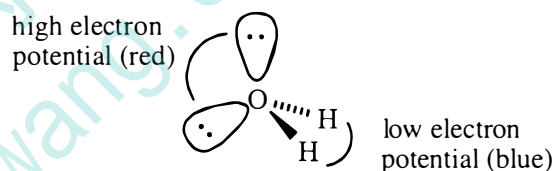
2-3 Each double-bonded atom is sp^2 hybridized with bond angles about 120°; geometry around sp^2 atoms is trigonal planar. In (a), all four carbons and the two hydrogens on the sp^2 carbons are all in one plane. Each carbon on the end is sp^3 hybridized with tetrahedral geometry and bond angles about 109°. In (b), the two carbons, the nitrogen, and the two hydrogens on the sp^2 carbon are all in one plane. The CH_3 carbon is sp^3 hybridized with tetrahedral geometry and bond angles about 109°.

(a)

(b)
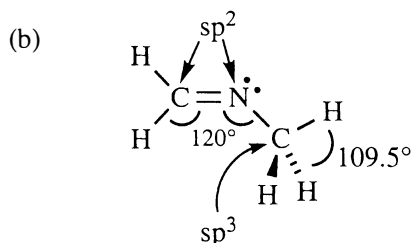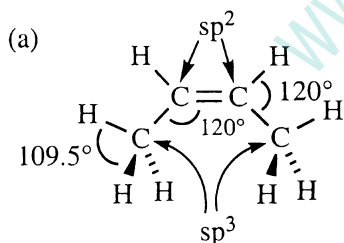
2-4 The hybridization of the nitrogen and the triple-bonded carbon are sp, giving linear geometry (C—C—N are linear) and a bond angle around the triple-bonded carbon of 180°. The CH_3 carbon is sp^3 hybridized, tetrahedral, with bond angles about 109°.

25
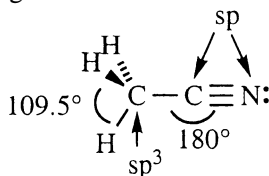
2-5

(a) linear, bond angle 180°

$$O = C = O$$

$$sp^2 \quad sp \quad sp^2$$
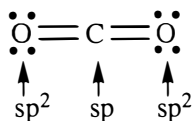
(b) all atoms are sp^3; tetrahedral geometry and bond angles of 109° around each atom
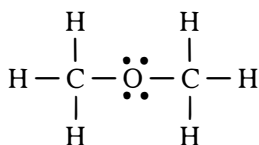
not a bond—shows lone pair coming out of paper
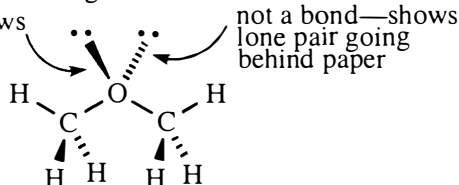
not a bond—shows lone pair going behind paper

(c) all atoms are sp^3; tetrahedral geometry and bond angles of 109° around each atom
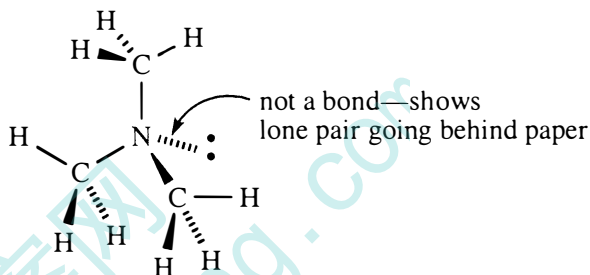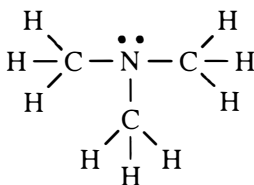
not a bond—shows lone pair going behind paper

(d) trigonal planar around the carbon, bond angles 120°; tetrahedral around the single-bonded oxygen, bond angle 109°
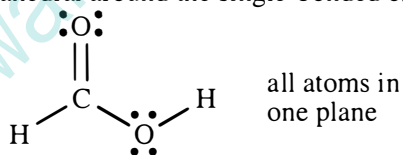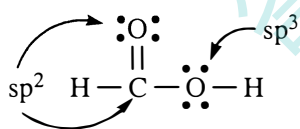
all atoms in one plane

(e) carbon and nitrogen both sp, linear, bond angle 180°

$$H — C \equiv N \colon$$

all three atoms in a line
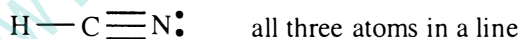
(f) trigonal planar around the sp^2 carbons, bond angles 120°; around the sp^3 carbon, tetrahedral geometry and 109° angles
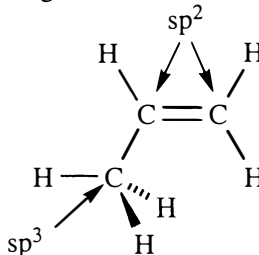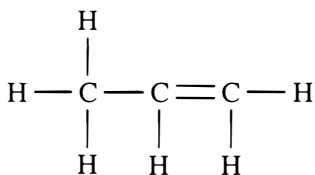
(g) trigonal planar, bond angle about 120°
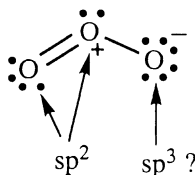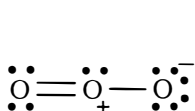
(the other resonance form of ozone shows that BOTH end oxygens must be sp^2— see Solved Problem 2-8)

$$sp^2 \quad sp^3 \, ?$$

26

2-6 Carbon-2 is sp hybridized. If the p orbitals making the pi bond between C-1 and C-2 are in the plane of the paper (putting the hydrogens in front of and behind the paper), then the other p orbital on C-2 must be perpendicular to the plane of the paper, making the pi bond between C-2 and C-3 perpendicular to the paper. This necessarily places the hydrogens on C-3 in the plane of the paper. (Models will surely help.)

model of *perpendicular* π bonds
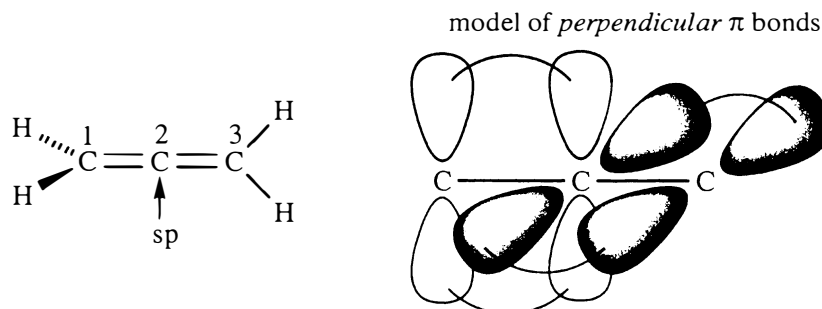
2-7 For clarity, electrons in sigma bonds are not shown.

(a) carbon and oxygen are both sp² hybridized

One pair of electrons on oxygen is always in an sp² orbital. The other pair of electrons is shown in a p orbital in the first resonance form, and in a pi bond in the second resonance form.

empty orbital
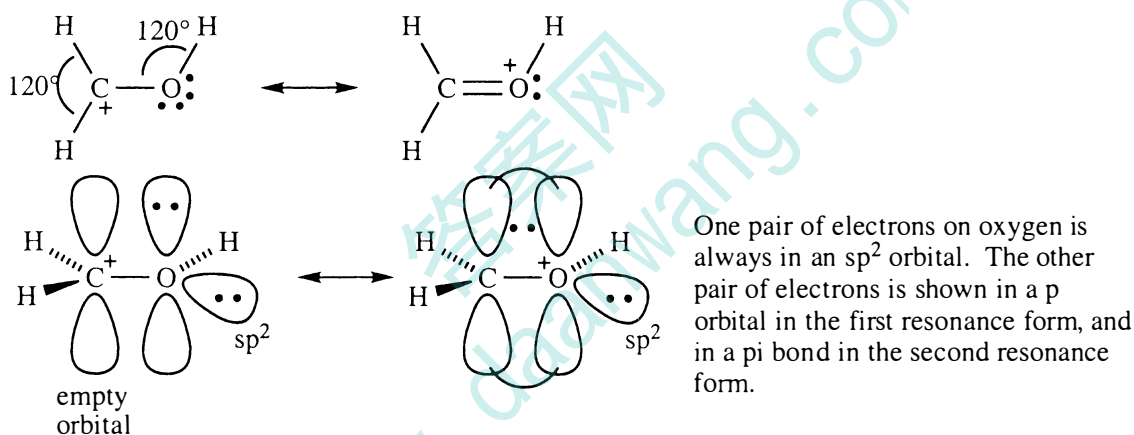
(b) oxygen and both carbons are sp² hybridized
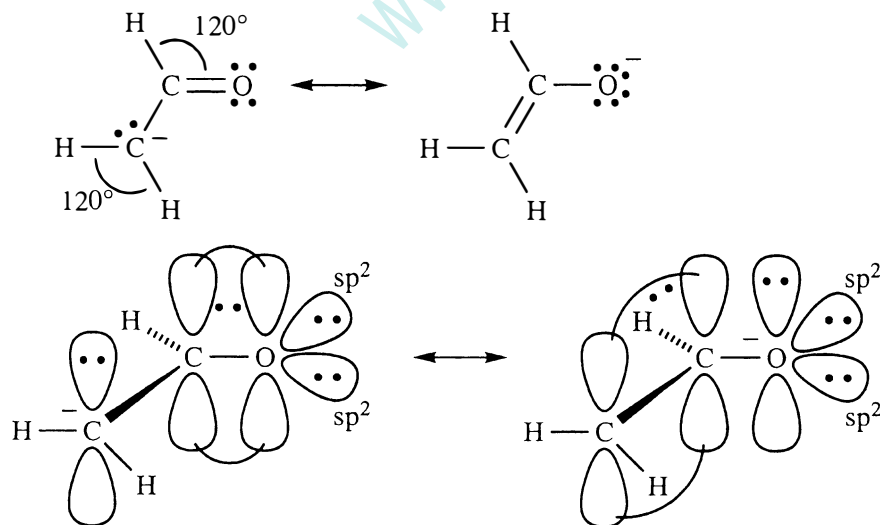
2-7 continued

(c) the nitrogen and the carbon bonded to it are sp hybridized; the left carbon is sp²
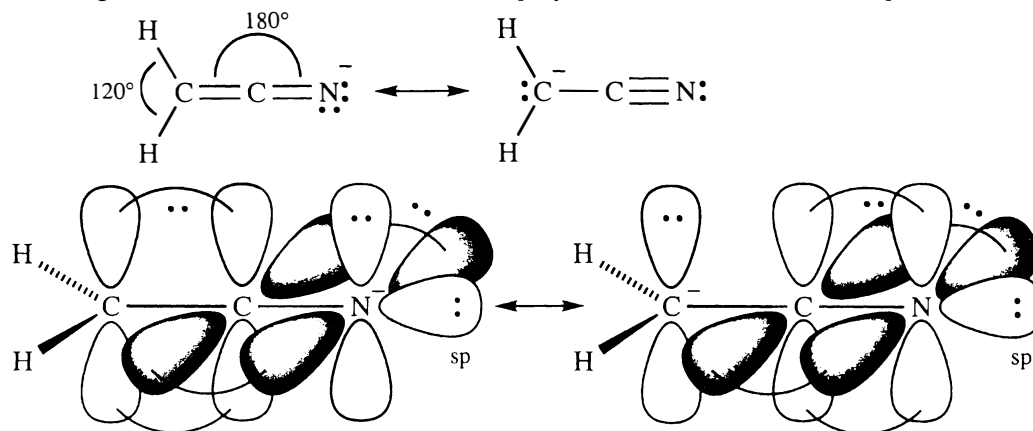
(d) the boron and the oxygens bonded to it are sp² hybridized
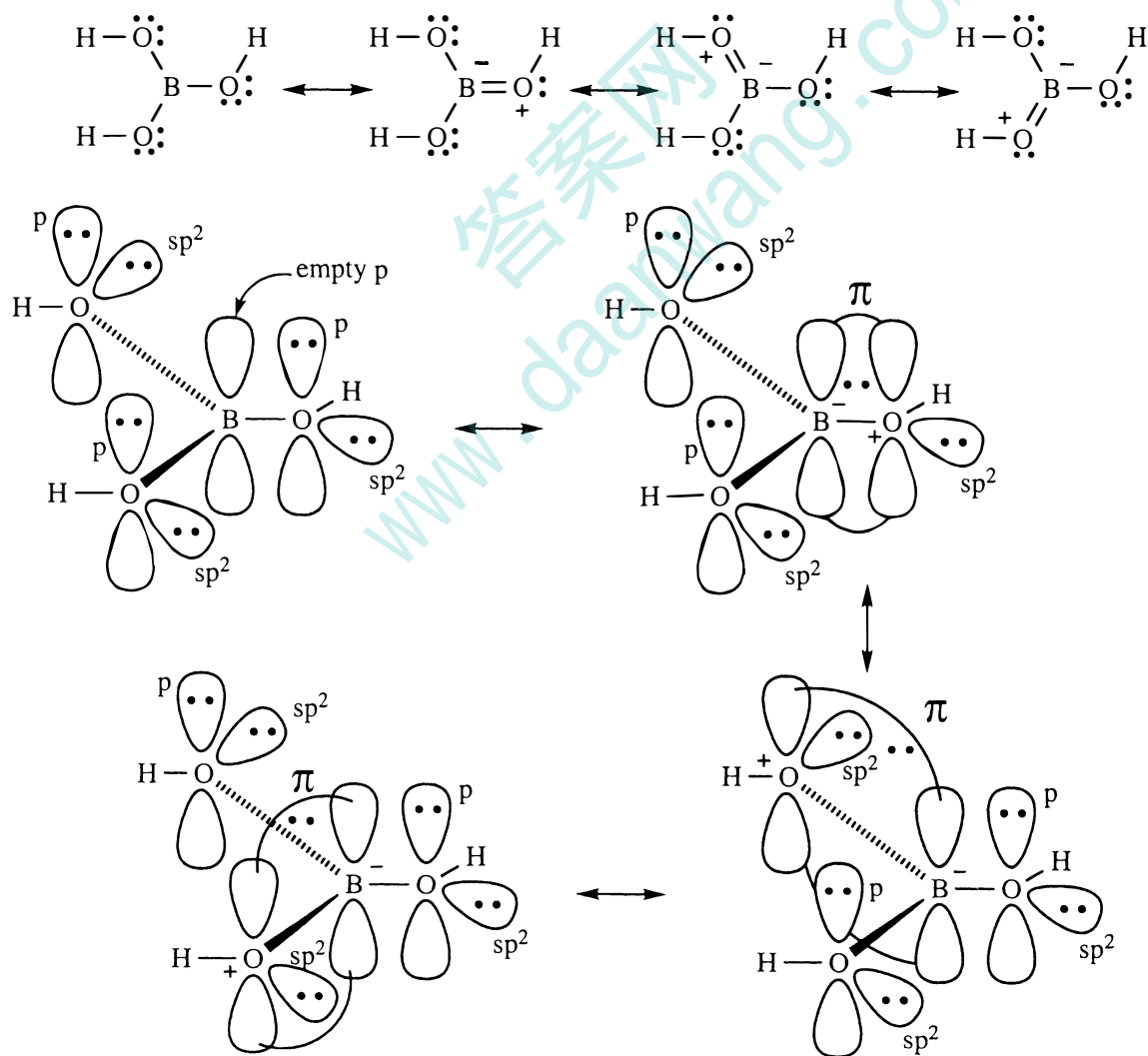
2-8 Very commonly in organic chemistry, we have to determine whether two structures are the same or different, and if they are different, what structural features are different. In order for two structures to be the same, all bonding connections have to be identical, and in the case of double bonds, the groups must be on the same side of the double bond in both structures. (A good exercise to do with your study group is to draw two structures and ask if they are the same; or draw one structure and ask how to draw a different compound.)

(a) different compounds; H and CH_3 on one carbon of the double bond, and CH_3 and CH_2CH_3 on the other carbon—same in both structures; drawing a plane through the p orbitals shows the H and CH_3 are on the same side of the double bond in the first structure, and the H and the CH_2CH_3 are on the same side in the second structure, so they are DIFFERENT compounds

these are DIFFERENT
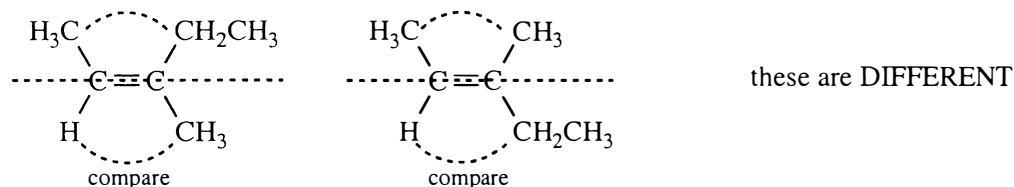
(b) same compound; in the structure on the right, the right carbon has been rotated, but the bonding is identical between the two structures

(c) different compounds; H and Br on one carbon, F and Cl on the other carbon in both structures; H and Cl on the same side of the plane through the C=C in the first structure, and H and F on the same side of the plane through the C=C in the second structure, so they are DIFFERENT compounds

(d) same compound: in the structure on the right, the right carbon has been rotated 120°

2-9

(a)

(b)

NOT INTER-CONVERTIBLE

two CH_3's on opposite sides of the C=N

two CH_3's on the same side of the C=N
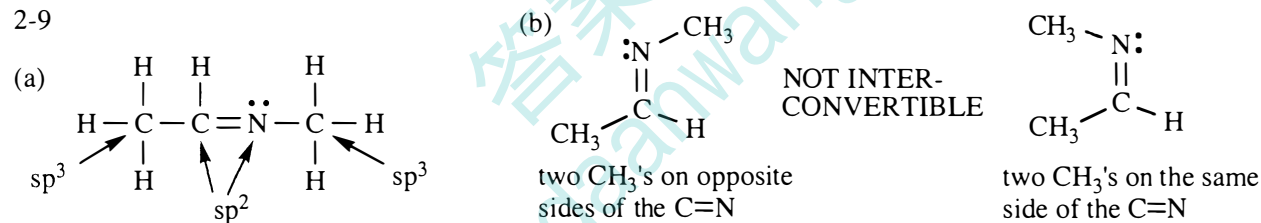
(c) the CH_3 on the N is on the same side as another CH_3 no matter how it is drawn—only one possible structure

2-10

(a)

and
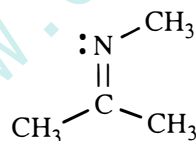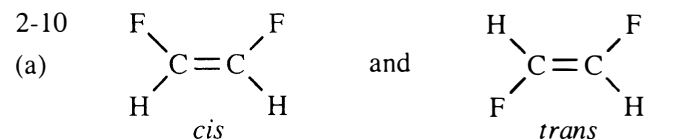
(b) no *cis-trans* isomerism
(c) no *cis-trans* isomerism   two identical groups on one
(d) no *cis-trans* isomerism   carbon of the double bond

(f)

and
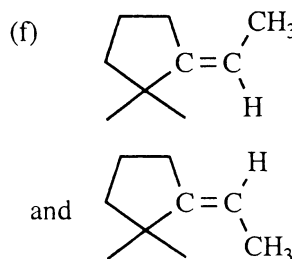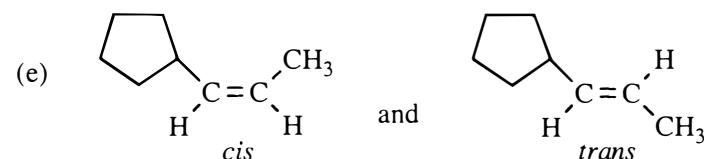
"cis" and *"trans"* not defined for this example

(e)

and

29

2-11 Models will be helpful here.
(a) cis-trans isomers—the first is trans, the second is cis
(b) constitutional isomers—the carbon skeleton is different
(c) constitutional isomers—the bromines are on different carbons in the first structure, on the same carbon in the second structure
(d) same compound—just flipped over
(e) same compound—just rotated
(f) same compound—just rotated
(g) not isomers—different molecular formulas
(h) constitutional isomers—the double bond has changed position
(i) same compound—just reversed
(j) constitutional isomers—the CH_3 groups are in different relative positions
(k) constitutional isomers—the double bond is in a different position relative to the CH_3

2-12
(a) $2.4\,D = 4.8 \times \delta \times 1.21\,\text{Å}$

   $\delta = 0.41$, or 41% of a positive charge on carbon and 41% of a negative charge on oxygen

(b)
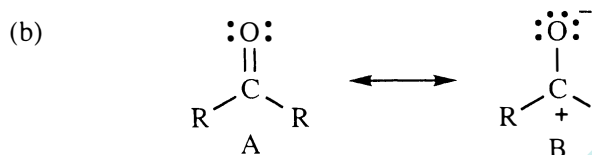
Resonance form A must be the major contributor. If B were the major contributor, the value of the charge separation would be between 0.5 and 1.0. Even though B is "minor", it is quite significant, explaining in part the high polarity of the C=O.

2-13

Both NH_3 and NF_3 have a pair of nonbonding electrons on the nitrogen. In NH_3, the *direction* of polarization of the N—H bonds is *toward* the nitrogen; thus, all three bond polarities and the lone pair polarity reinforce each other. In NF_3, on the other hand, the direction of polarization of the N—F bonds is *away* from the nitrogen; the three bond polarities cancel the lone pair polarity, so the net result is a very small *molecular* dipole moment.

polarities reinforce;
large dipole moment

polarities oppose;
small dipole moment

2-14 Some magnitudes of dipole moments are difficult to predict; however, the direction of the dipole should be straightforward, in most cases. Actual values of molecular dipole moments are given in parentheses. (Each halogen atom has three nonbonded electron pairs, not shown below.) The C—H is usually considered non-polar.

(a)

large dipole (1.54)

(b)

large dipole (1.81)

2-14 continued

(c)

F⠄⠄⠄⠄C (with F atoms around it)   net dipole = 0

(d)

large dipole (1.70)
net

(e)

each end oxygen has one-half negative charge as it is the composite of two resonance forms; see solution to 1-38(b)

small dipole (0.52)

net

(f)

H — C ≡ N (:)

net

large dipole (2.95)

(g)

large dipole (2.72)
net

(h)

large dipole
net

(i)

small dipole (0.67)
net

(j)

large dipole (1.45)
net

(k)

net dipole = 0

(l)

Cl — Be — Cl

net dipole = 0

(m)
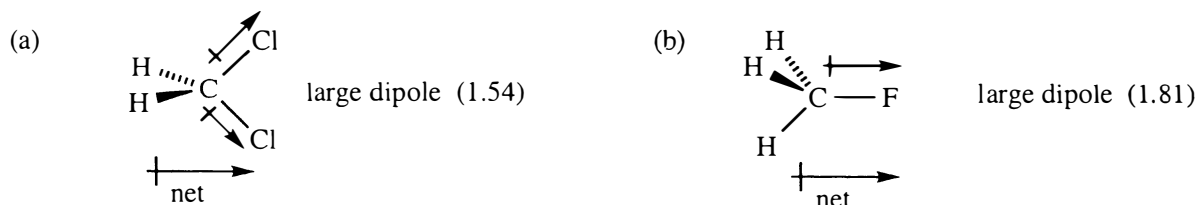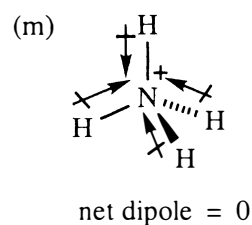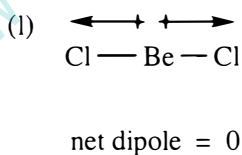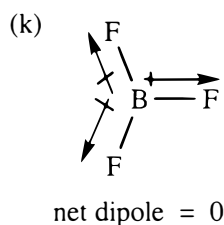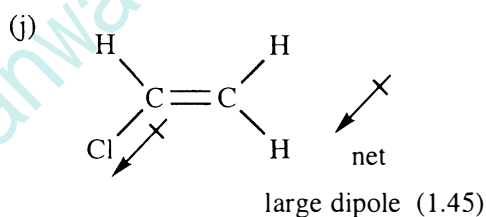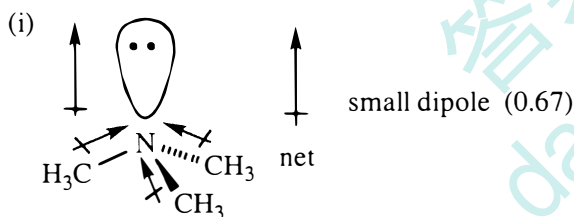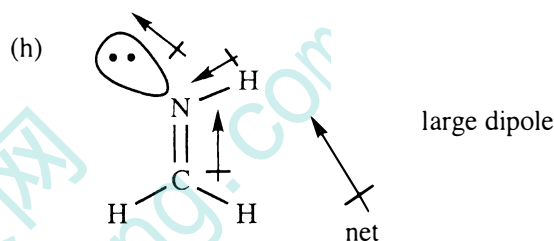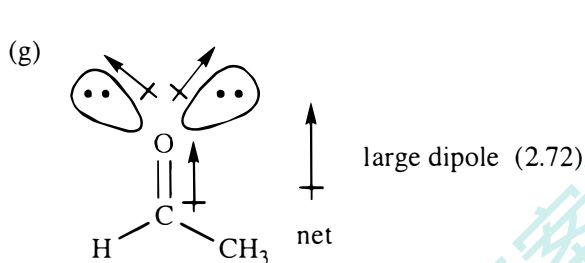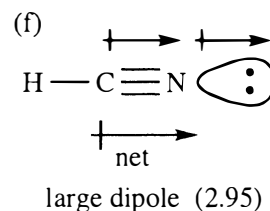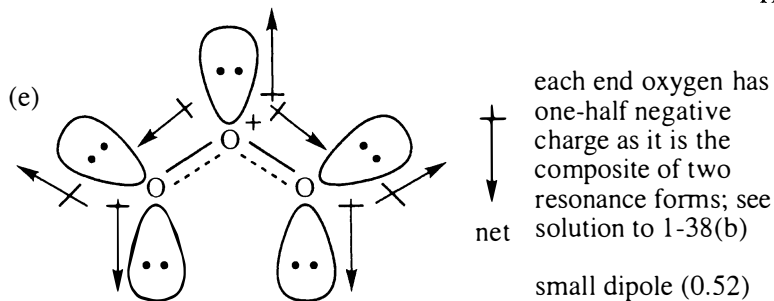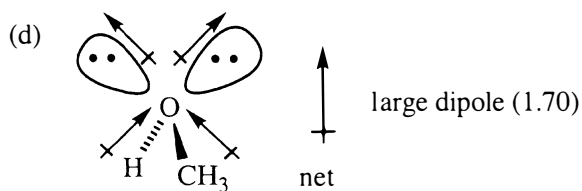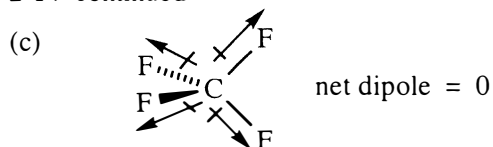
net dipole = 0

In (k) through (m), the symmetry of the molecule allows the individual bond dipoles to cancel.

2-15 With chlorines on the same side of the double bond, the bond dipole moments reinforce each other, resulting in a large net dipole. With chlorines on opposite sides of the double bond, the bond dipole moments exactly cancel each other, resulting in a zero net dipole.

large net dipole

net dipole = 0

2-16

(a)
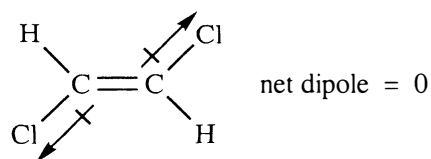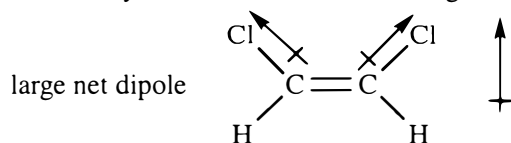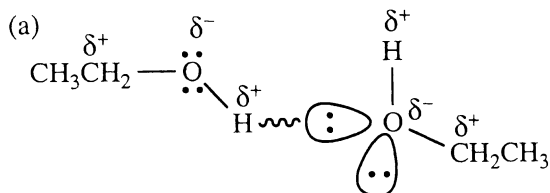
(hydrogen bonds shown as wavy bond)

(b)
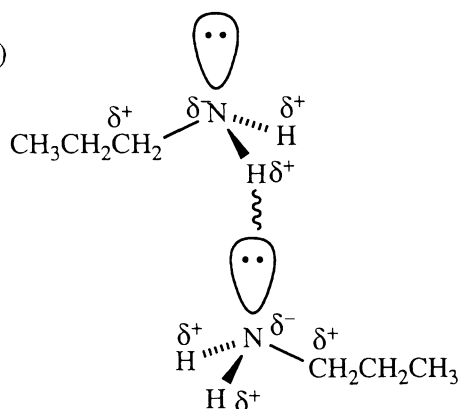
2-17

(a) $(CH_3)_2CHCH_2CH_2CH(CH_3)_2$ has less branching and boils at a higher temperature than $(CH_3)_3CC(CH_3)_3$.

(b) $CH_3(CH_2)_5CH_2OH$ can form hydrogen bonds and will boil at a much higher temperature than $CH_3(CH_2)_6CH_3$ which cannot form hydrogen bonds.

(c) $HOCH_2(CH_2)_4CH_2OH$ can form hydrogen bonds at both ends and has no branching; it will boil at a much higher temperature than $(CH_3)_3CCH(OH)CH_3$.

(d) $(CH_3CH_2CH_2)_2NH$ has an N—H bond and can form hydrogen bonds; it will boil at a higher temperature than $(CH_3CH_2)_3N$ which cannot form hydrogen bonds.

(e) The second compound shown (**B**) has the higher boiling point for two reasons: **B** has a higher molecular weight than **A**; and **B**, a primary amine with two N—H bonds, has more opportunity for forming hydrogen bonds than **A**, a secondary amine with only one N—H bond.

2-18

(a) $CH_3CH_2OCH_2CH_3$ can form hydrogen bonds with water and is more soluble than $CH_3CH_2CH_2CH_2CH_3$ which cannot form hydrogen bonds with water.

(b) $CH_3CH_2NHCH_3$ is more water soluble because it can form hydrogen bonds; $CH_3CH_2CH_2CH_3$ cannot form hydrogen bonds.

(c) CH_3CH_2OH is more soluble in water. The polar O—H group forms hydrogen bonds with water, overcoming the resistance of the non-polar CH_3CH_2 group toward entering the water. In $CH_3CH_2CH_2CH_2OH$, however, the hydrogen bonding from only one OH group cannot carry a four-carbon chain into the water; this substance is only slightly soluble in water.

(d) Both compounds form hydrogen bonds with water at the double-bonded oxygen, but only the smaller molecule (CH_3COCH_3) dissolves. The cyclic compound has too many non-polar CH_2 groups to dissolve.

2-19

(a) alkane

(Usually, we use the term "alkane" only when no other groups are present.)

(b) alkene

(c) alkyne

(d) cycloalkyne

(e) cycloalkane

(f) aromatic hydrocarbon and alkene

(g) cycloalkene

(h) alkyne, alkene, cycloalkane

(i) aromatic hydrocarbon and cycloalkene

2-20

(a) aldehyde

(b) alcohol

(c) ketone

(d) ether

(e) carboxylic acid

(f) ether

(g) ketone

(h) aldehyde

(i) alcohol

2-21

(a) amide

(b) amine

(c) ester

(d) acid chloride

(e) ether

(f) nitrile

(g) carboxylic acid

(h) cyclic ester

(i) ketone and ether

(j) amine

(k) cyclic amide

(l) amide

(m) ketone and amine

(n) cyclic ester

(o) nitrile

(p) ketone

2-22 When the identity of a functional group depends on several atoms, all of those atoms should be circled. For example, an ether is an oxygen between two carbons, so the oxygen and both carbons should be circled. A ketone is a carbonyl group between two other carbons, so all those atoms should be circled.

(a) $CH_2=CHOH_2CH_3$

alkene

(b) CH_3-O-CH_3

ether

(c) CH_3-C-H, O

aldehyde

2-22 continued

(d)

H—C—NH₂ (with O double-bonded to C)

amide

(this also looks like an aldehyde, but an amide has higher "priority" as you will see later)

(e) CH₃—N—CH₃ (with H below N)

amine

(f) R—C—O—H (with O double-bonded to C)
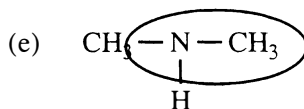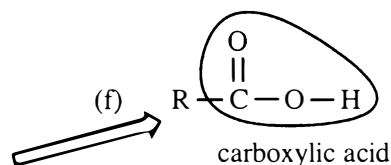
carboxylic acid

Suggested by student Richard King: R is the symbol that organic chemists use to represent alkyl and aryl groups. As you will see in the course of your study, there are quite a few ways that carbon and hydrogen atoms can go together to form alkyl and aryl groups. So when you see this symbol, you should know that it represents ONLY some combination of carbon and hydrogen atoms—except when it includes other atoms.

(g)

CH₂OH

alcohol

aromatic

(h)

C≡N

nitrile

alkene

(i)

(ring with O double bond)

ketone

(j)
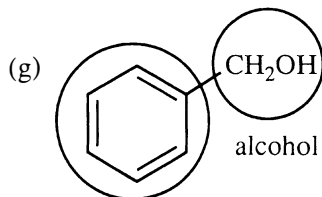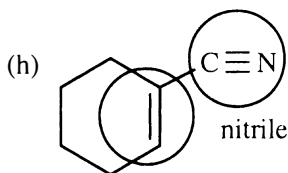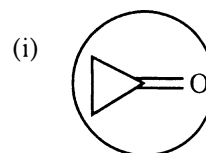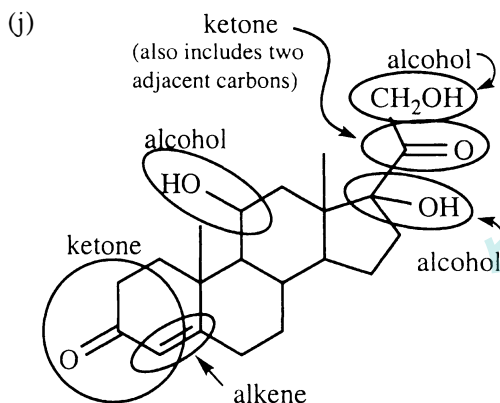
ketone
(also includes two adjacent carbons)

alcohol
CH₂OH

alcohol
HO

OH
alcohol

ketone
O

alkene

(k)

aromatic
CH₃

CH₃

ether
CH₃
O
R

HO

alcohol
CH₃

R = (CH₂CH₂CH₂CH(CH₃))₃CH₃
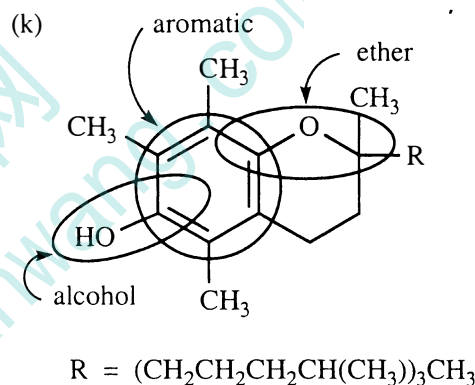
2-23 Please refer to solution 1-20, page 12 of this Solutions Manual.

2-24 The examples here are representative. Your examples may be different and still correct. What is important in this problem is to have the same functional group.

(a) alkane: hydrocarbon with all single bonds; can be acyclic (no ring) or cyclic

H—C—C—C—H (with H on each carbon)
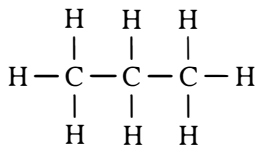
(b) alkene: contains a carbon-carbon double bond

H—C—C=C—H (with H)
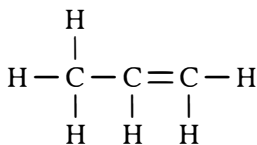
(c) alkyne: contains a carbon-carbon triple bond

H—C—C≡C—H (with H)
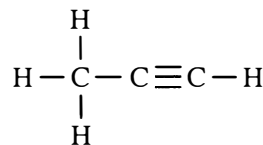
(d) alcohol: contains an OH group on a carbon

H—C—C—O—H (with H)
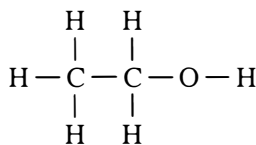
(e) ether: contains an oxygen between two carbons

H—C—O—C—H (with H)

(f) ketone: conatins a carbonyl group between two carbons

H—C—C—C—H (with O double bond on middle C)
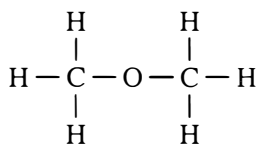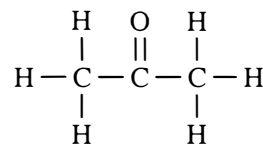
2-24 continued

(g) aldehyde: contains a carbonyl group with a hydrogen on one side
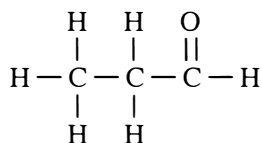
(h) aromatic hydrocarbon: a cyclic hydrocarbon with alternating double and single bonds
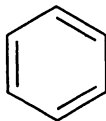
(i) carboxylic acid: contains a carbonyl group with an OH group on one side
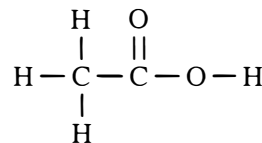
(j) ester: contains a carbonyl group with an O—C on one side
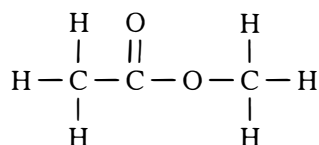
(k) amine: contains a nitrogen bonded to one, two, or three carbons
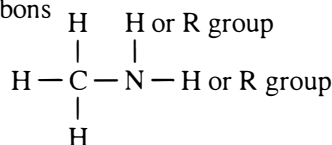
(l) amide: contains a carbonyl group with a nitrogen on one side
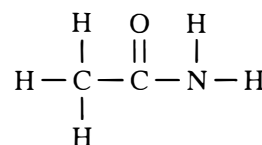
(m) nitrile: contains the carbon-nitrogen triple bond: $H_3C—C≡N$

2-25 Models show that the tetrahedral geometry of CH_2Cl_2 precludes stereoisomers.

2-26
(a)
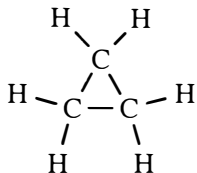
(b) Cyclopropane must have 60° bond angles compared with the usual sp^3 bond angle of 109.5° in an acyclic molecule.

(c) Like a bent spring, bonds that deviate from their normal angles or positions are highly strained. Cyclopropane is reactive because breaking the ring relieves the strain.

2-27

(a)
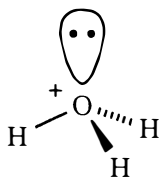
sp^3, ≈ 109°

(b)
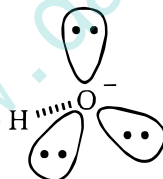
sp^3 , no bond angle because oxygen is bonded to only one atom

(c)
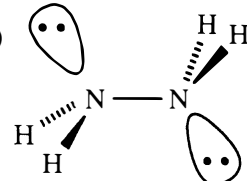
both sp^3, all ≈ 109°

(d)
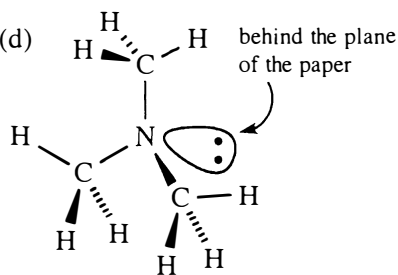
all sp^3, all ≈ 109°

(e)
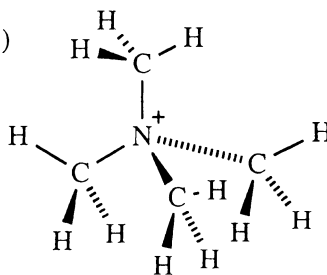
all sp^3, all ≈ 109°

(f)
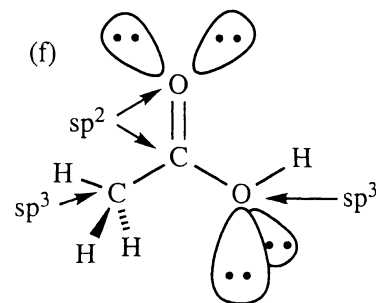
angles around sp^3 atoms ≈ 109°
angles around sp^2 carbon ≈ 120°

2-27 continued

(g)
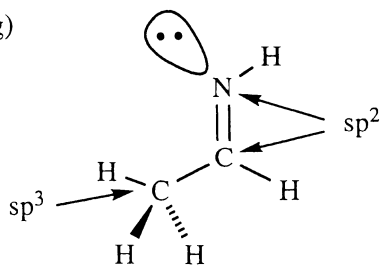
angles around sp^3 atom ≈ 109°
angles around sp^2 atoms ≈ 120°

(h) in front of the plane of the paper   behind the plane of the paper
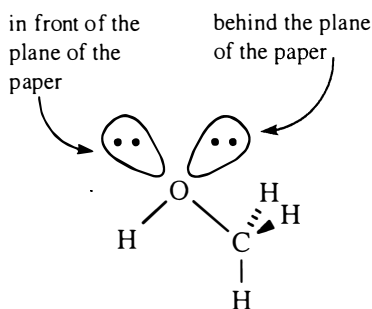
both sp^3, all ≈ 109°

(i)
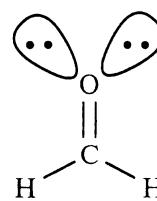
both sp^2, all ≈ 120°

2-28 For clarity in these pictures, bonds between hydrogen and an sp^3 atom are not labeled; these bonds are s-sp^3 overlap.

(a)

sp^3-sp^3

H — C — N — C — H

109°

(b)

sp^3-sp^3

H — C — C — O — H

109°

(c) 109° H sp^3-sp^2 sp^2-sp^3 120°   109°

H — C — C = N — C — H

sp^2-s sp^2-sp^2 + p-p   120°

(d) 109° H sp^3-sp^2 120°   109°

H — C — C = C

sp^2-s sp^2-sp^2 + p-p   109° sp^2-sp^3

(e) sp-sp + two p-p   120°

109°

H — C — C ≡ C — C — H

sp^3-sp   sp-sp^2 sp^2-s   180°

sp^2-sp^2 + p-p

(f) 109° H   180°

H — N — C — C ≡ N:

sp^3-sp^3 sp^3-sp   sp-sp + two p-p

(g) 120° sp^2-sp^2 + p-p

H — C — C — C — H

109° sp^3-sp^2 sp^2-sp^3 109°

37

2-28 continued

(h)

(i)
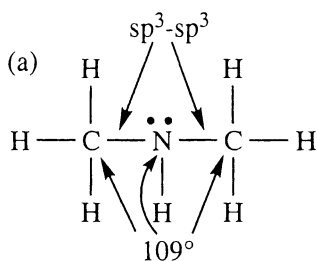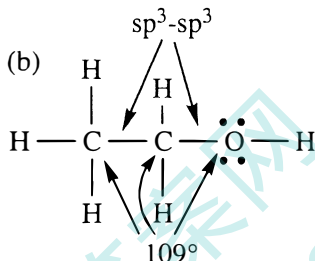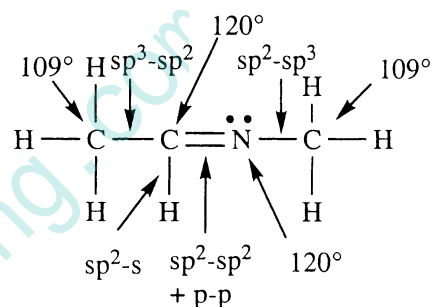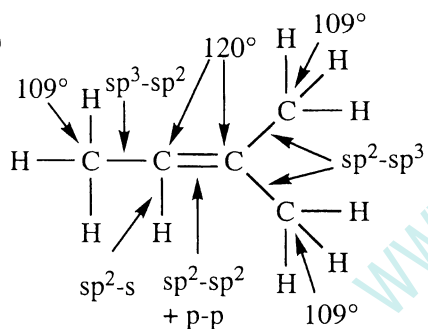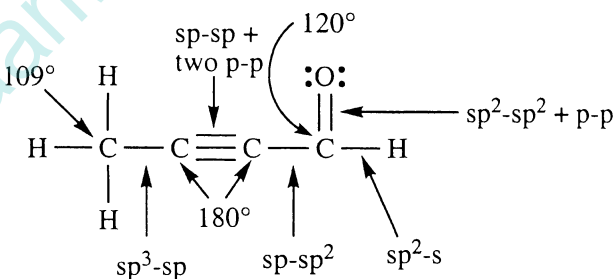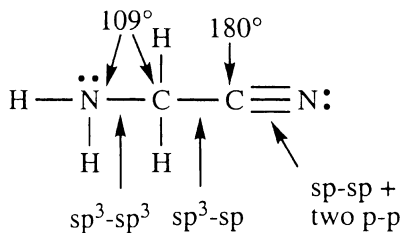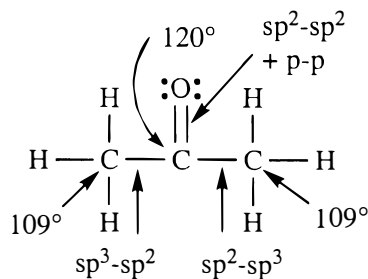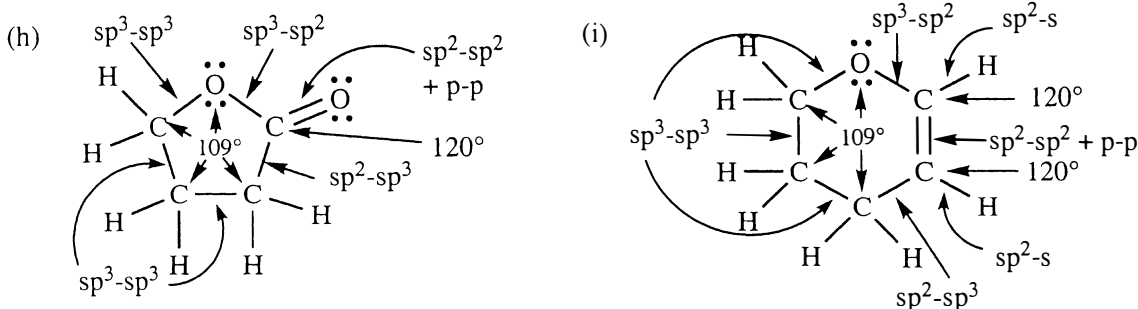
2-29 The second resonance form of formamide is a minor but significant resonance contributor. It shows that the nitrogen-carbon bond has some double bond character, requiring that the nitrogen be sp^2 hybridized with bond angles approaching 120°.
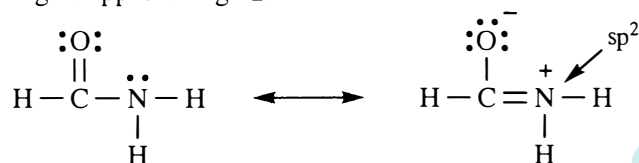
2-30

(a) The major resonance contributor shows a carbon-carbon double bond, suggesting that both carbons are sp^2 hybridized with trigonal planar geometry. The CH$_3$ carbon is sp^3 hybridized with tetrahedral geometry.

minor   major
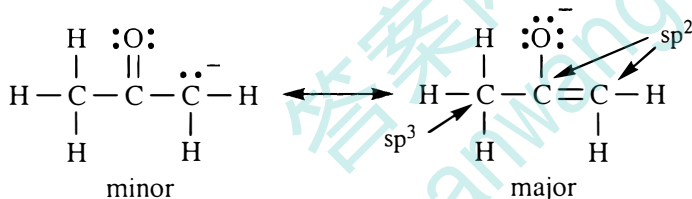
(b) The major resonance contributor shows a carbon-nitrogen double bond, suggesting that all three carbons and the nitrogen are sp^2 hybridized with trigonal planar geometry.

minor   minor   major
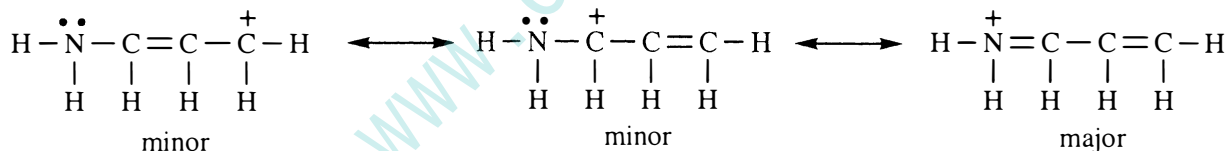
2-31 In (c) and (d), the unshadowed p orbitals are vertical and parallel. The shadowed p orbitals are perpendicular and horizontal.

(a)

(b)

(c)

(d)

38

2-32

(a)

cis
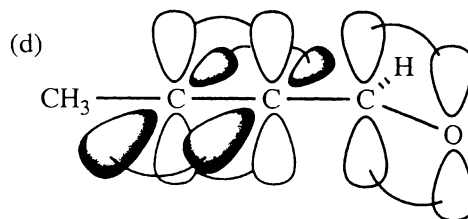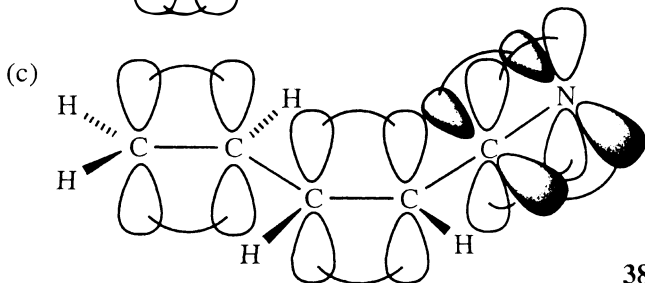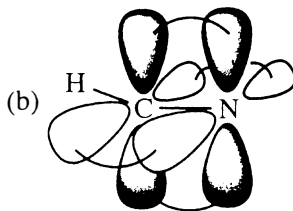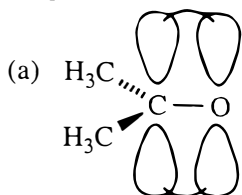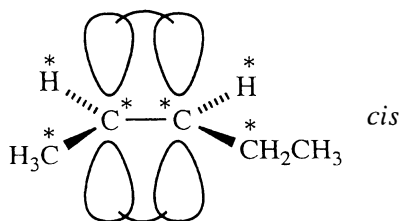
(b) The coplanar atoms in the structures to the left and below are marked with asterisks.

(c)

trans

There are still six coplanar atoms.
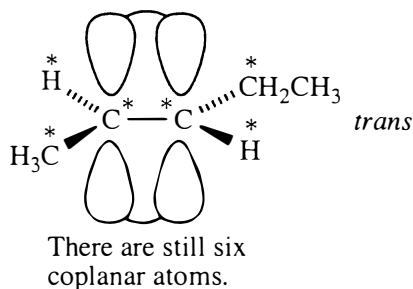
(d)
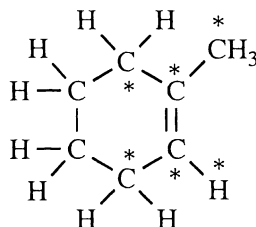
2-33 Collinear atoms are marked with asterisks.
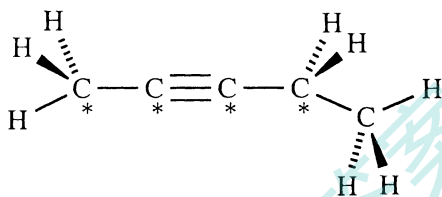
2-34

(a) no *cis-trans* isomerism

(b)

cis

and
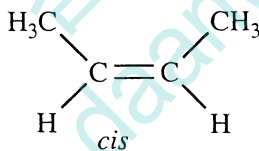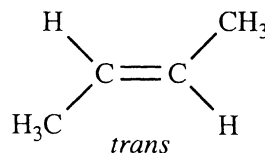
trans

(c) no *cis-trans* isomerism

(d) Theoretically, cyclopentene could show cis-trans isomerism. In reality, the *trans* form is too unstable to exist because of the necessity of stretched bonds and deformed bond angles. *trans*-Cyclopentene has never been detected.

cis
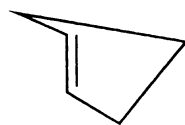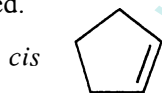
"trans"—not possible because of ring strain

(e)
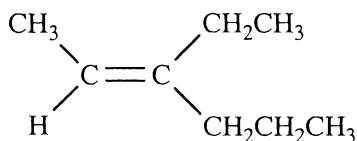
and
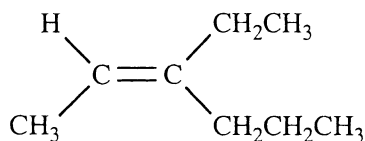
these are *cis-trans* isomers, but the designation of *cis* and *trans* to specific structures is not defined because of four different groups on the double bond

2-35

(a) constitutional isomers—the carbon skeletons are different
(b) constitutional isomers—the position of the chlorine atom has changed
(c) cis-trans isomers—the first is *cis,* the second is *trans*
(d) constitutional isomers—the carbon skeletons are different
(e) cis-trans isomers—the first is *trans,* the second is *cis*
(f) same compound—rotation of the first structure gives the second
(g) cis-trans isomers—the first is *cis,* the second is *trans*
(h) constitutional isomers—the position of the double bond relative to the ketone has changed (while it is true that the first double bond is *cis* and the second is *trans,* in order to have *cis-trans* isomers, the rest of the structure must be identical)

2-36 CO_2 is linear; its bond dipoles cancel, so it has no net dipole. SO_2 is bent, so its bond dipoles do not cancel.

net dipole moment = 0   net dipole moment
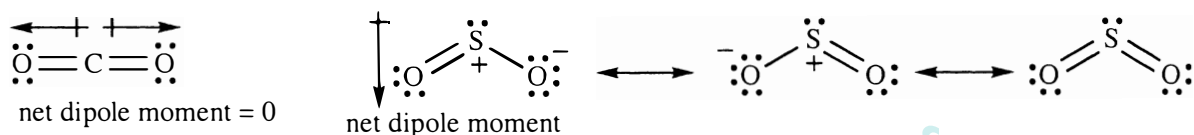
2-37 Some magnitudes of dipole moments are difficult to predict; however, the direction of the dipole should be straightforward in most cases. Actual values of molecular dipole moments are given in parentheses. (The C—H bond is usually considered non-polar.)

(a)

large dipole moment   or   large dipolemoment

(b)

large dipole moment (3.96)

(c)

net dipole moment = 0
electron pairs on bromines are not shown

(d)

large dipole moment (2.89)

(e)

net dipole moment = 0

(f)

moderate dipole moment

(g)

moderate dipole moment

electron pairs on chlorine are not shown

40
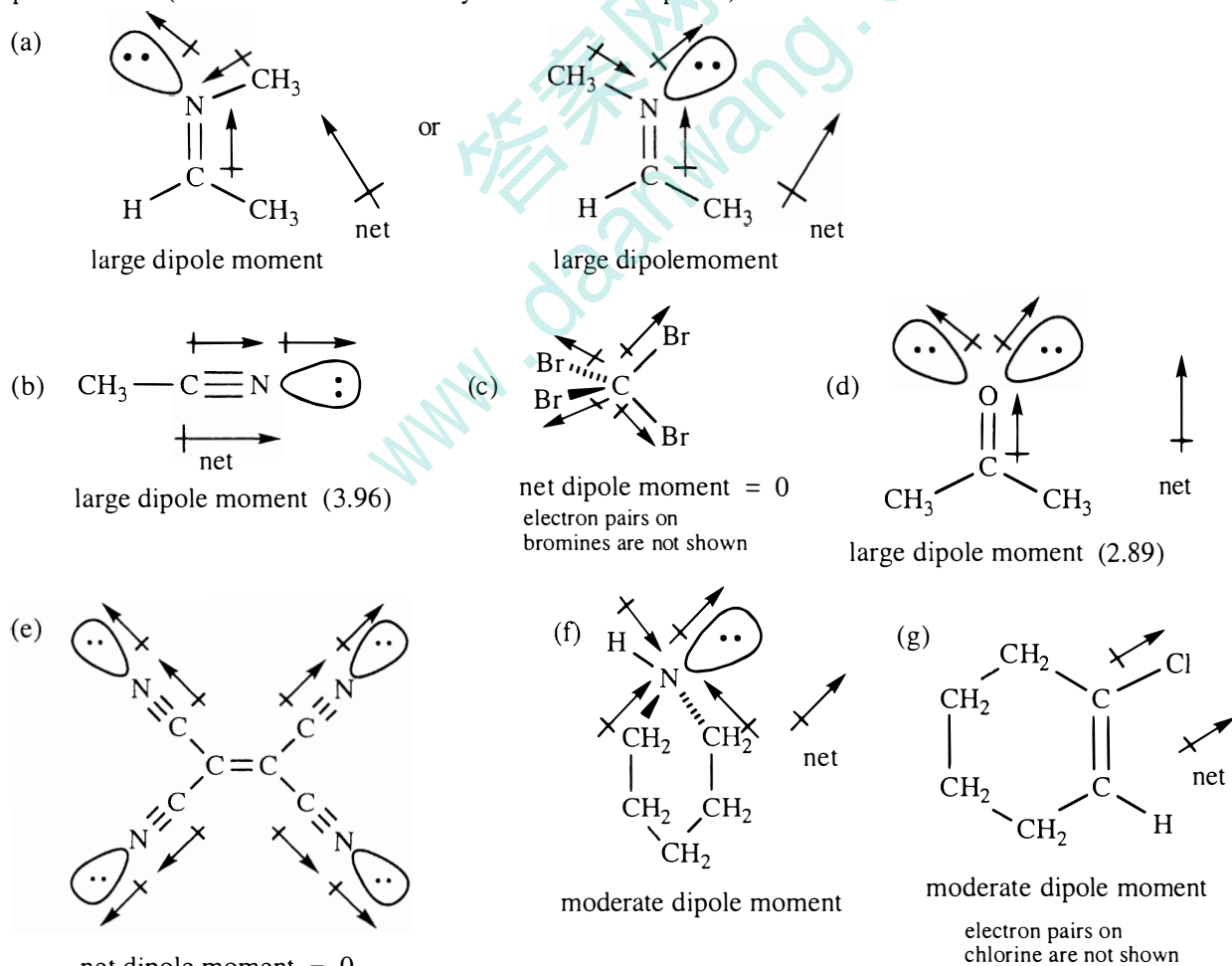
2-38 Diethyl ether and 1-butanol each have one oxygen, so each can form hydrogen bonds with water (water supplies the H for hydrogen bonding with diethyl ether); their water solubilities should be similar. The boiling point of 1-butanol is much higher because these molecules can hydrogen bond with each other, thus requiring more energy to separate one molecule from another. Diethyl ether molecules cannot hydrogen bond with each other, so it is relatively easy to separate them.

$$CH_3CH_2 — O — CH_2CH_3 \qquad\qquad CH_3CH_2CH_2CH_2 — OH$$
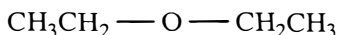
<table>
<tr><td align="center">diethyl ether</td><td align="center">1-butanol</td></tr>
<tr><td align="center">can hydrogen bond with water</td><td align="center">can hydrogen bond with water</td></tr>
<tr><td align="center">cannot hydrogen bond with itself</td><td align="center">can hydrogen bond with itself</td></tr>
</table>

2-39
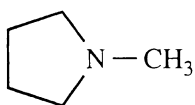
<table>
<tr><td align="center"><i>N</i>-methylpyrrolidine
b.p. 81°C</td><td align="center">piperidine
b.p. 106°C</td><td align="center">tetrahydropyran
b.p. 88°C</td><td align="center">cyclopentanol
b.p. 141°C</td></tr>
</table>
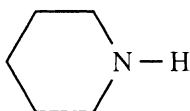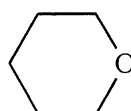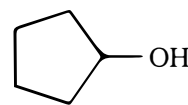
(a) Piperidine has an N—H bond, so it can hydrogen bond with other molecules of itself. *N*-Methylpyrrolidine has no N—H, so it cannot hydrogen bond and will require less energy (lower boiling point) to separate one molecule from another.

(b) Two effects need to be explained: 1) Why does cyclopentanol have a higher boiling point than tetrahydropyran? and 2) Why do the oxygen compounds have a greater difference in boiling points than the analogous nitrogen compounds?

The answer to the first question is the same as in (a): cyclopentanol can hydrogen bond with its neighbors while tetrahydropyran cannot.

The answer to the second question lies in the text, Table 2-1, that shows the bond dipole moments for C—O and H—O are much greater than C—N and H—N; bonds to oxygen are more polarized, with greater charge separation than bonds to nitrogen.

How is this reflected in the data? The boiling points of tetrahydropyran (88°C) and *N*-methylpyrrolidine (81°C) are close; tetrahydropyran molecules would have a slightly stronger dipole-dipole attraction, and tetrahydropyran is a little less "branched" than *N*-methylpyrrolidine, so it is reasonable that tetrahydropyran boils at a slightly higher temperature. The large difference comes when comparing the boiling points of cyclopentanol (141°C) and piperidine (106°C). The greater polarity of O—H versus N—H is reflected in a more negative oxygen (more electronegative than nitrogen) and a more positive hydrogen, resulting in a much stronger intermolecular attraction. The conclusion is that hydrogen bonding due to O—H is much stronger than that due to N—H.

2-40

(a) can hydrogen bond with itself and with water
(b) can hydrogen bond only with water
(c) can hydrogen bond with itself and with water
(d) can hydrogen bond only with water
(e) cannot hydrogen bond
(f) cannot hydrogen bond

(g) can hydrogen bond only with water
(h) can hydrogen bond with itself and with water
(i) can hydrogen bond only with water
(j) can hydrogen bond only with water
(k) can hydrogen bond only with water
(l) can hydrogen bond with itself and with water

2-41 Higher-boiling compounds are listed.

(a) $CH_3CH(OH)CH_3$ can form hydrogen bonds with other identical molecules
(b) $CH_3CH_2CH_2CH_2CH_3$ has a higher molecular weight than $CH_3CH_2CH_2CH_3$
(c) $CH_3CH_2CH_2CH_2CH_3$ has less branching than $(CH_3)_2CHCH_2CH_3$
(d) $CH_3CH_2CH_2CH_2CH_2Cl$ has a higher molecular weight AND dipole-dipole interaction compared with $CH_3CH_2CH_2CH_2CH_3$

2-42

(a)

O — ether

O — ether

(b)

$\overset{O}{\underset{}{\overset{\|}{C}}}$—OH — carboxylic acid

alkene

(c)

aldehyde

$\overset{O}{\underset{H}{\overset{\|}{C}}}$

alkene

(d)

$\overset{O}{\underset{}{\overset{\|}{}}}$ — ketone — CH$_3$

aromatic

(e)

$\overset{O}{\underset{}{\overset{\|}{C}}}$ — ester (cyclic)

O

alkene

(f)

O — amide (cyclic)

NH

(g)

CH$_2$OCH$_3$ — ether

aromatic

nitrile — C≡N

(h)

$\underset{CH_3 - CH - C - OCH_3}{\overset{NH_2 \quad\quad O}{\overset{|}{}\,\overset{\|}{}}}$

amine   ester

2-43

:O:
‖
CH$_3$—C—CH$_3$

sp^2—planar

:O:
‖
CH$_3$—S—CH$_3$ ⟷ CH$_3$—S$^+$—CH$_3$
       ‥   ‥

:Ö:$^-$
|
S$^+$

sp^3—tetrahedral
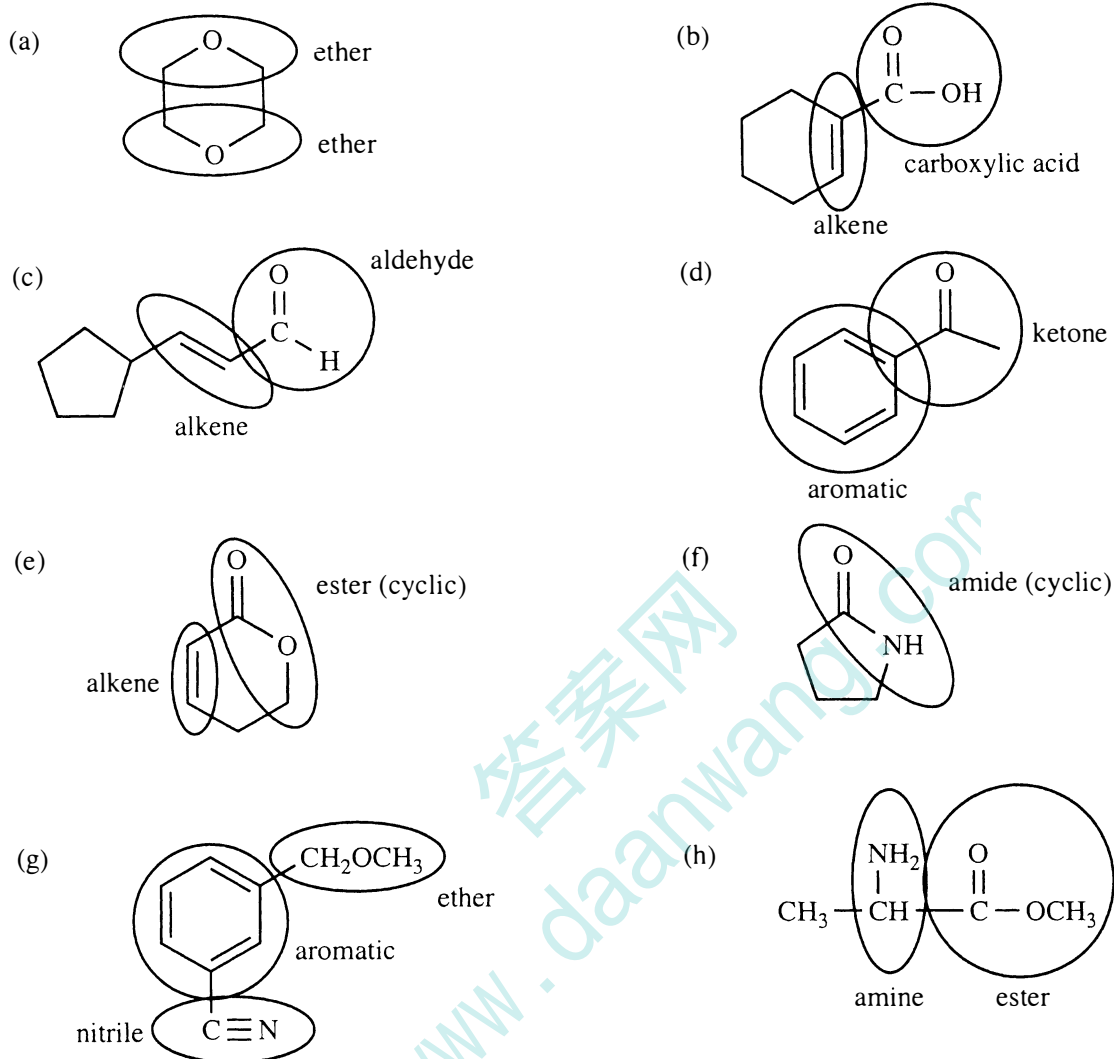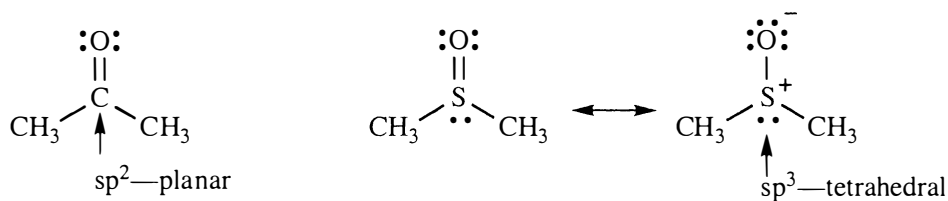
The key to this problem is understanding that sulfur has a *lone pair of electrons*. The second resonance form shows four pairs of electrons around the sulfur atom, an electronic configuration requiring sp^3 hybridization. Sulfur in DMSO cannot be sp^2 like carbon in acetone, so we would expect sulfur's geometry to be pyramidal (the four electron pairs around sulfur require tetrahedral geometry, but the three atoms around sulfur define its shape as pyramidal).

2-44

(a) penicillin G
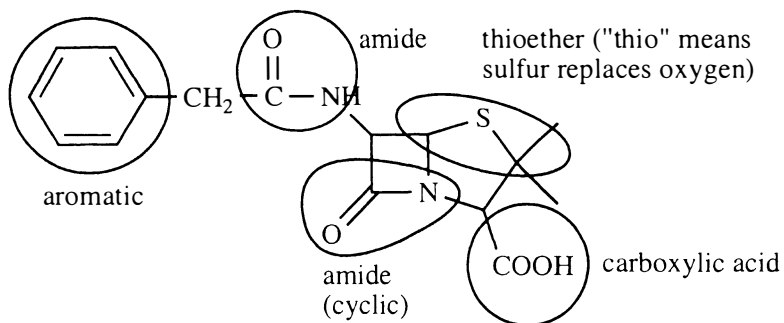
(b) dopamine
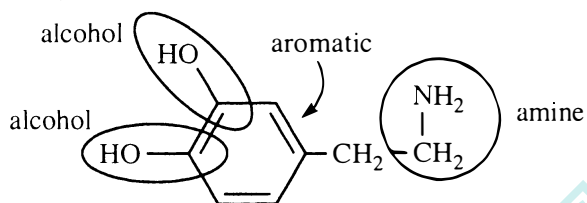
(In later chapters, you will learn that the OH group on a benzene ring is a special functional group called a "phenol". For now, it fits the broad definition of an alcohol.)

(c) thyroxine
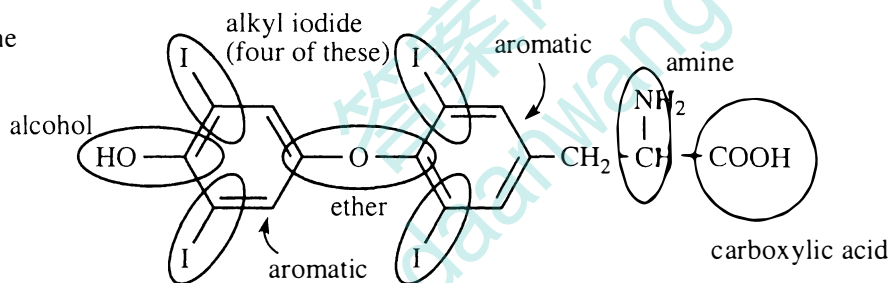
(d) testosterone
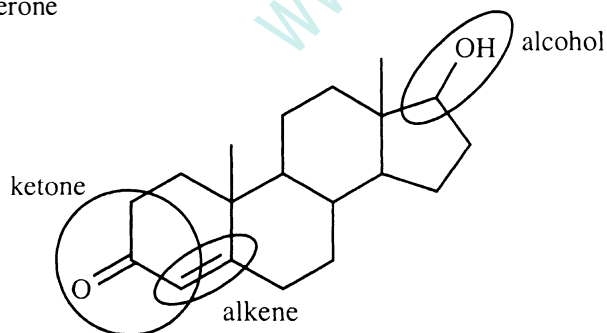
CHAPTER 3—STRUCTURE AND STEREOCHEMISTRY OF ALKANES

3-1

(a) C_nH_{2n+2} where n = 25 gives $C_{25}H_{52}$

(b) C_nH_{2n+2} where n = 44 gives $C_{44}H_{90}$

> Note to the student: The IUPAC system of nomenclature has a well defined set of rules determining how structures are named. You will find a summary of these rules as Appendix 1 in this Solutions Manual.

3-2 Use hyphens to separate letters from numbers. Longest chains may not always be written left to right.

(a) 3-methylpentane (always find the longest chain; it may not be written in a straight line)
(b) 2-bromo-3-methylpentane (always find the longest chain)
(c) 5-ethyl-2-methyl-4-propylheptane ("When there are two longest chains of equal length, use the chain with the greater number of substituents.")
(d) 4-isopropyl-2-methyldecane

3-3 This Solutions Manual will present line formulas where a question asks for an answer including a structure. If you use condensed structural formulas instead, be sure that you are able to "translate" one structure type into the other.

(a)   (b)   (c)

(d)
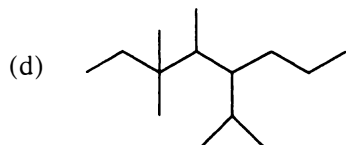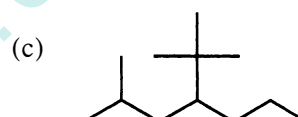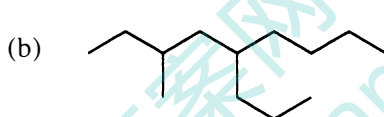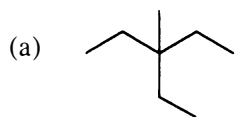
3-4 Separate numbers from numbers with commas.

(a) 2-methylbutane   (c) 3-ethyl-2-methylhexane   (e) 3-ethyl-2,2,4,5-tetramethylhexane
(b) 2,2-dimethylpropane   (d) 2,4-dimethylhexane   (f) 4-*t*-butyl-3-methylheptane

3-5 (Hints: *systematize* your approach to these problems. For the isomers of a six carbon formula, for example, start with the isomer containing all six carbons in a straight chain, then the isomers containing a five-carbon chain, then a four-carbon chain, *etc*. Carefully check your answers to AVOID DUPLICATE STRUCTURES.)

(a)
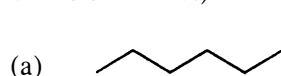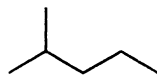
n-hexane   2-methylpentane   3-methylpentane
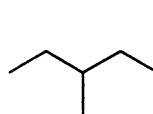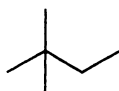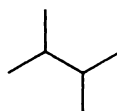
2,2-dimethylbutane   2,3-dimethylbutane

3-5 continued

(b)
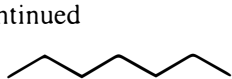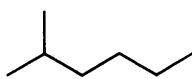
| *n*-heptane | 2-methylhexane | 3-methylhexane | 2,2-dimethylpentane |
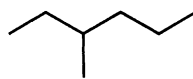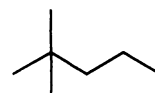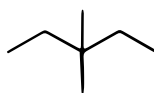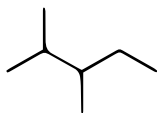
3,3-dimethylpentane   2,3-dimethylpentane   2,4-dimethylpentane   3-ethylpentane   2,2,3-trimethylbutane
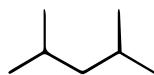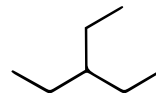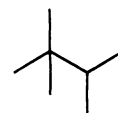
3-6 For this problem, the carbon numbers in the substituents are indicated in italics.

(a)
$$CH_3$$
$$-\overset{1}{C}H\overset{2}{C}H_3$$
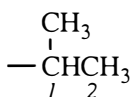
1-methylethyl
common name = isopropyl

(b)
$$CH_3$$
$$-\overset{1}{C}H_2\overset{2}{C}H\overset{3}{C}H_3$$
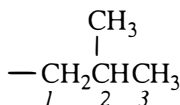
2-methylpropyl
common name = isobutyl

(c)
$$CH_3$$
$$-\overset{1}{C}H\overset{2}{C}H_2\overset{3}{C}H_3$$
$2°$
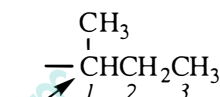
1-methylpropyl
common name = *sec*-butyl

(d)
$$CH_3$$
$$-\overset{1}{C}\overset{2}{-}CH_3$$
$$CH_3$$
$3°$
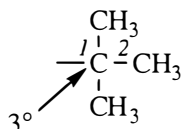
1,1-dimethylethyl
common name = *t*-butyl or *tert*-butyl

3-7

(a)
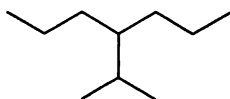
(b)
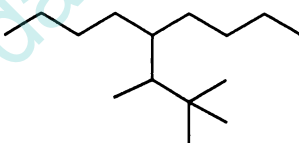
3-8 Once the number of carbons is determined, C_nH_{2n+2} gives the formula.
(a) $C_{10}H_{22}$ (b) $C_{15}H_{32}$

3-9

(a) (lowest b.p.) hexane < octane < decane (highest b.p.) —molecular weight

(b) $(CH_3)_3C-C(CH_3)_3$ < $CH_3CH_2C(CH_3)_2CH_2CH_2CH_3$ < octane —branching
       (lowest b.p.)   (highest b.p.)

3-10

(a) (lowest m.p.) hexane < octane < decane (highest m.p.) —molecular weight

(b) octane < $CH_3CH_2C(CH_3)_2CH_2CH_2CH_3$ < $(CH_3)_3C-C(CH_3)_3$ —branching
    (lowest m.p.)   (highest m.p.)

3-11

eclipsed   staggered   eclipsed

1 x 4.2 kJ/mole + 2 x 5.4 kJ/mole = 15.0 kJ/mole (3.6 kcal/mole)
     H - H   H - CH₃

3-12

All energy values are per mole.

(Note that the lowest energy conformers at 60° and 180° have at least one CH₃—CH₃ interaction = 3.8 kJ (0.9 kcal) higher than ethane.)
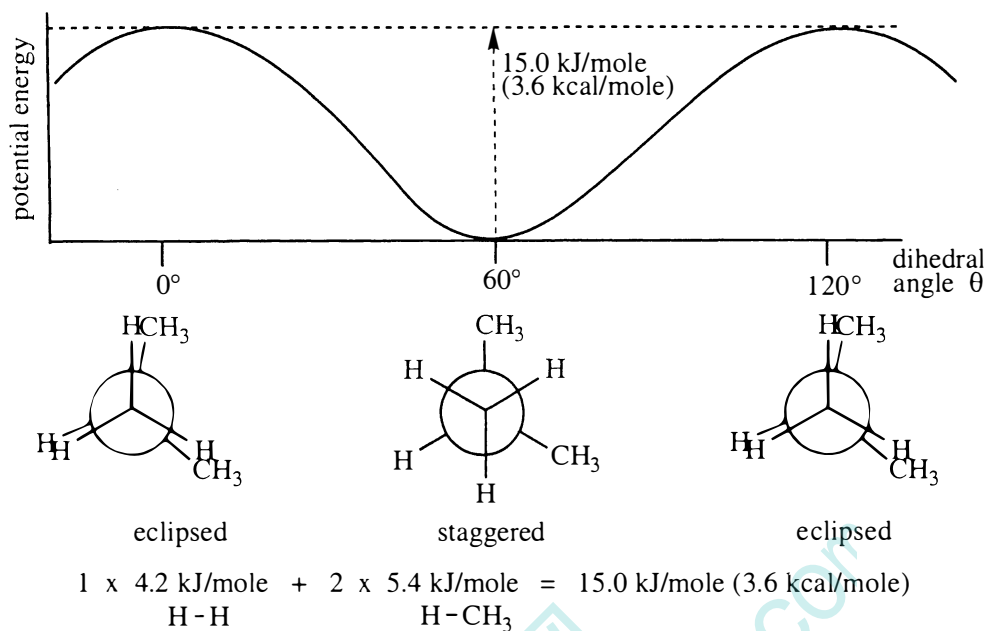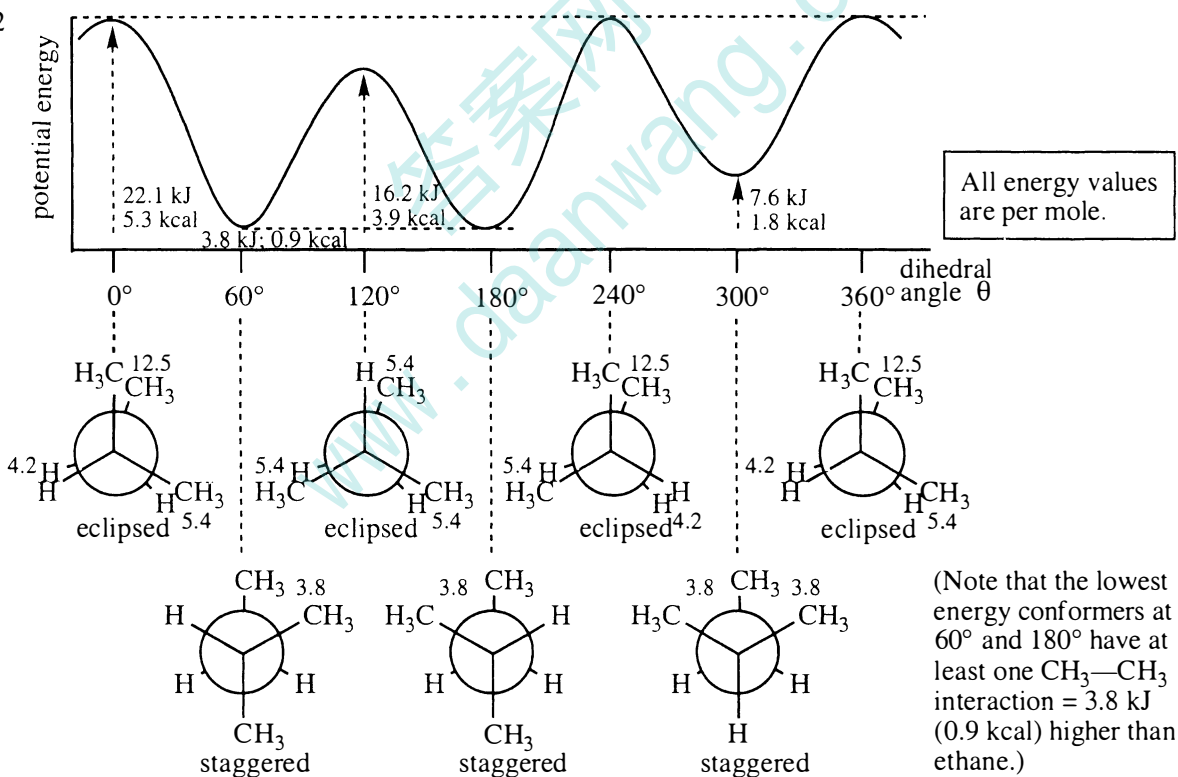
Relative energies on the graph above were calculated using these values from the text:
3.8 kJ/mole (0.9 kcal/mole) for a CH_3–CH_3 gauche (staggered) interaction; 4.2 kJ/mole (1.0 kcal/mole) for a H–H eclipsed interaction; 5.4 kJ/mole (1.3 kcal/mole) for a H–CH_3 eclipsed interaction; 12.5 kJ/mole (3.0 kcal/mole) for a CH_3–CH_3 eclipsed interaction. These values in kJ/mole are noted on each structure and are summed to give the energy value on the graph. Slight variation between this graph and the one in the text are due to rounding.

47

3-13
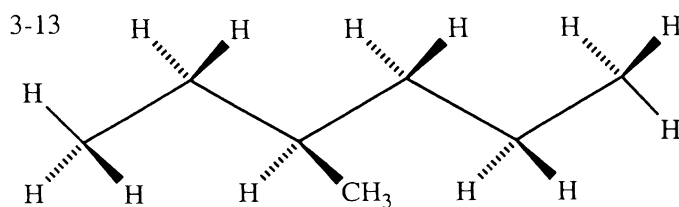
all bonds are staggered

▬◀	bold bonds are coming toward the reader from the plane of the paper
ⅲⅲⅲ	dashed bonds are coming toward the reader from the plane of the paper

3-14

(a) 3-*sec*-butyl-1,1-dimethylcyclopentane (the 5-membered ring gives the base name)
(b) 3-cyclopropyl-1,1-dimethylcyclohexane (the 6-membered ring gives the base name)
(c) 4-cyclobutylnonane (the chain is longer than the ring)

3-15 (a) $C_{12}H_{24}$ (b) C_9H_{18} (c) C_8H_{14} (d) $C_{10}H_{20}$

$CH_2CH_2CH_3$

CH_3
CH_3
CH_2CH_3
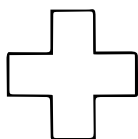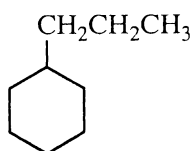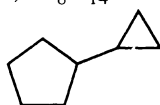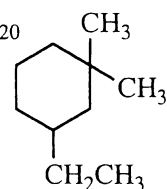
3-16

(a) no cis-trans isomerism possible

(b)

cis   trans

(c)

cis   trans

(d)

cis   trans
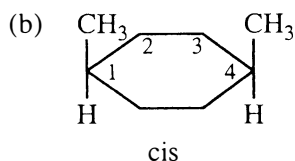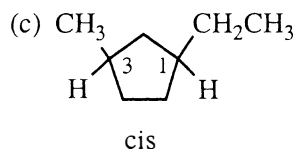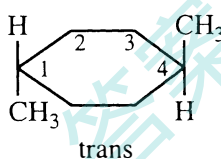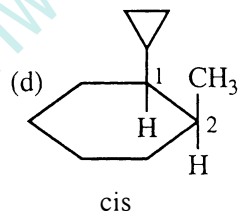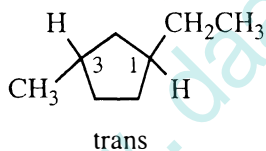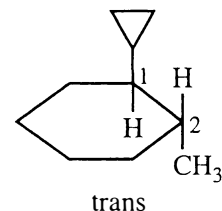
3-17 In (a) and (b), numbering of the ring is determined by the first group *alphabetically* being assigned to ring carbon 1.

(a) *cis*-1-methyl-3-propylcyclobutane ("m" comes before "p"—practice that alphabet!)
(b) *trans*-1-*t*-butyl-3-ethylcyclohexane (the prefixes *t*, *s*, and *n* are ignored in assigning alphabetical priority)
(c) *trans*-1,2-dimethylcyclopropane (either carbon with a CH_3 could be carbon-1; the same name results)

3-18 Combustion of the cis isomer gives off more energy, so *cis*-1,2-dimethylcyclopropane must start at a higher energy than the trans isomer. The Newman projection of the cis isomer shows the two methyls are eclipsed with each other; in the trans isomer, the methyls are still eclipsed, but with hydrogens, not each other—a lower energy.

more strain = higher energy

cis   trans

3-19 *trans*-1,2-Dimethylcyclobutane is more stable than *cis* because the two methyls can be farther apart when trans, as shown in the Newman projections.
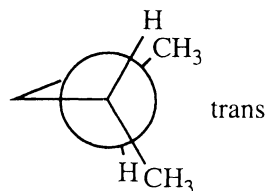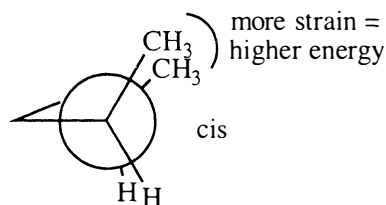
In the 1,3-dimethylcyclobutanes, however, the *cis* allows the methyls to be farther from other atoms and therefore more stable than the *trans*.

3-20

equatorial only

axial only

showing both axial
and equatorial

3-21 The abbreviation for a methyl group, CH_3, is "Me". Ethyl is "Et", propyl is "Pr", and butyl is "Bu".

(a)

all methyls axial
(all H's equatorial)

Note that axial groups alternate
up and down around the ring.

(b)

all methyls equatorial
(all H's axial)

3-22 Carbons 4 and 6 are behind the circles.
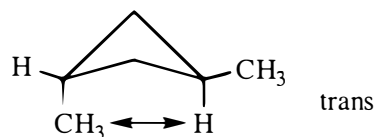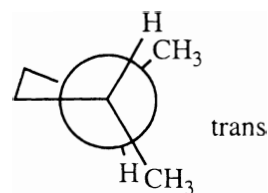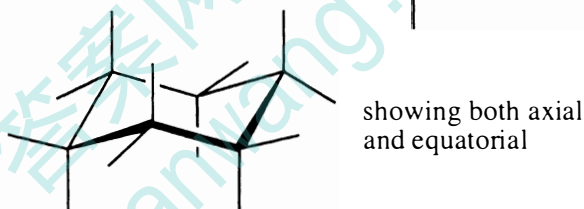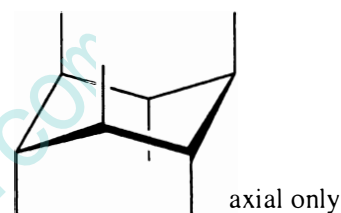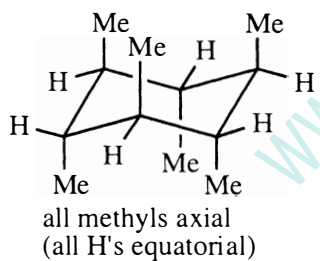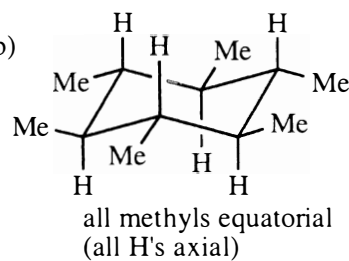
3-23 The isopropyl group can rotate so that its hydrogen is near the axial hydrogens on carbons 3 and 5, similar to a methyl group's hydrogen, and therefore similar to a methyl group in energy. The *t*-butyl group, however, must point a methyl group toward the hydrogens on carbons 3 and 5, giving severe diaxial interactions, causing the energy of this conformer to jump dramatically.

isopropylcyclohexane   *t*-butylcyclohexane
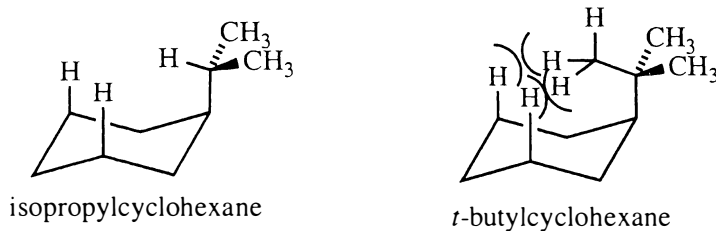
3-24 The most stable conformers have substituents equatorial.

(a)   (b)   (c)

3-25
(a) cis

equatorial, axial   EQUAL ENERGY   axial, equatorial

(b) trans

axial, axial
higher energy

equatorial, equatorial
lower energy
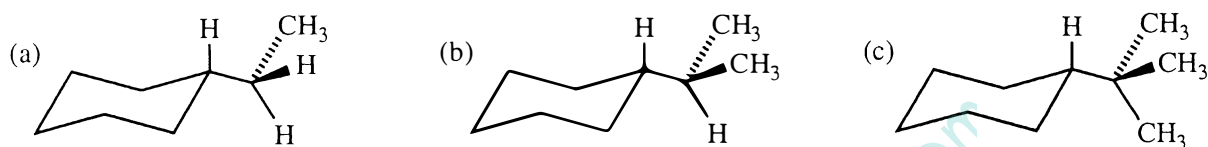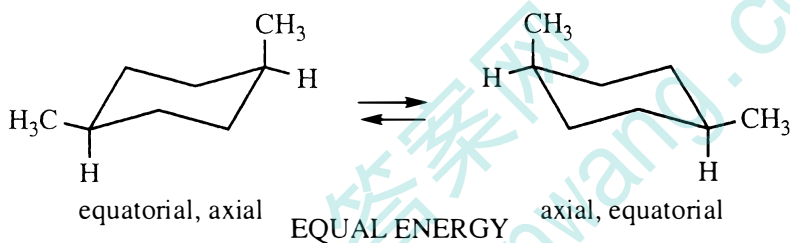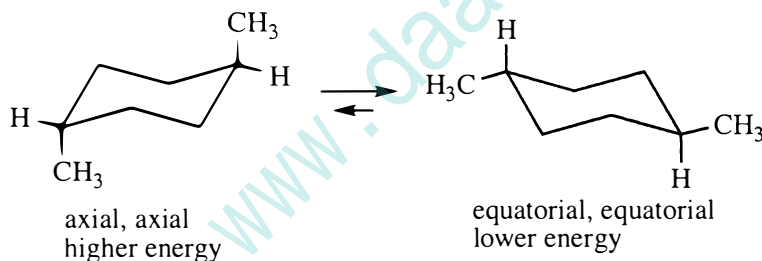
(c) The trans isomer is more stable because BOTH substituents can be in the preferred equatorial positions.

3-26

Positions	cis	trans
1,2	(e,a) or (a,e)	(e,e) or (a,a)
1,3	(e,e) or (a,a)	(e,a) or (a,e)
1,4	(e,a) or (a,e)	(e,e) or (a,a)

50

3-27 The more stable conformer places the larger group equatorial.

(a)

more stable

(b)

more stable

(c)

more stable

(d)

more stable
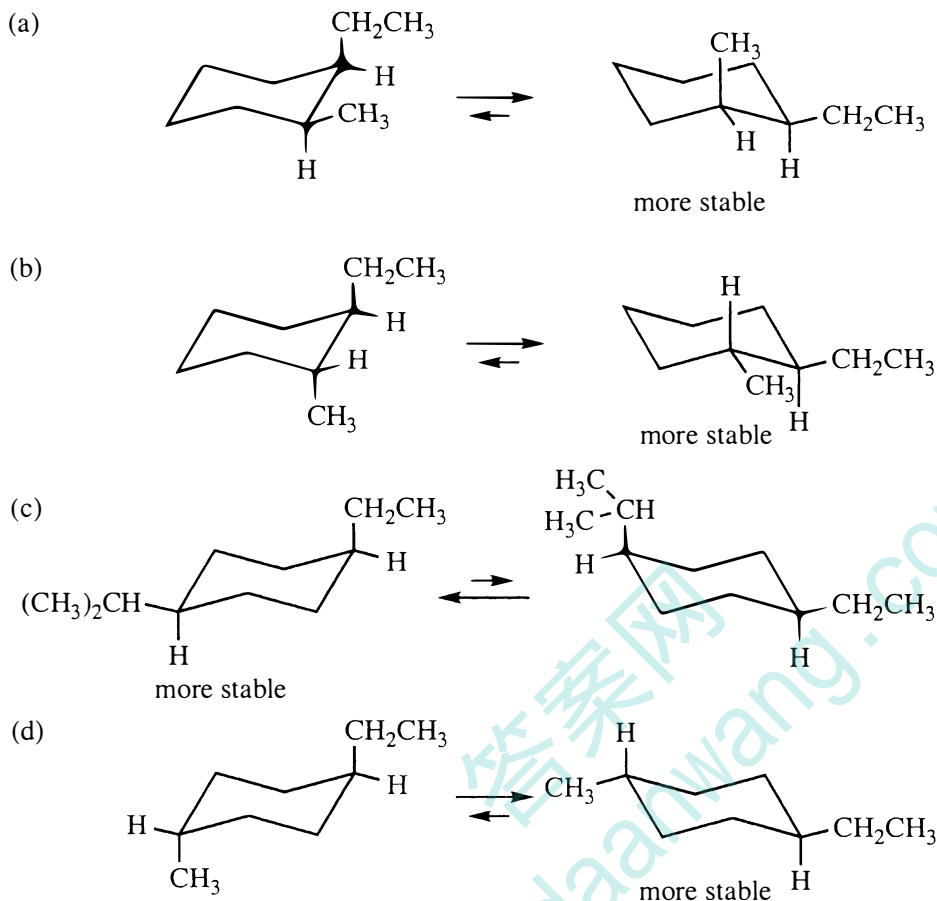
3-28 The key to determining cis and trans around a cyclohexane ring is to see whether a substituent group is "up" or "down" *relative to the H at the same carbon.* Two "up" groups or two "down" groups will be cis; one "up" and one "down" will be trans. This works independent of the conformation the molecule is in!

(a) *cis*-1,3-dimethylcyclohexane
(b) *cis*-1,4-dimethylcyclohexane
(c) *trans*-1,2-dimethylcyclohexane

(d) *cis*-1,3-dimethylcyclohexane
(e) *cis*-1,3-dimethylcyclohexane
(f) *trans*-1,4-dimethylcyclohexane

3-29

(a)

(b)
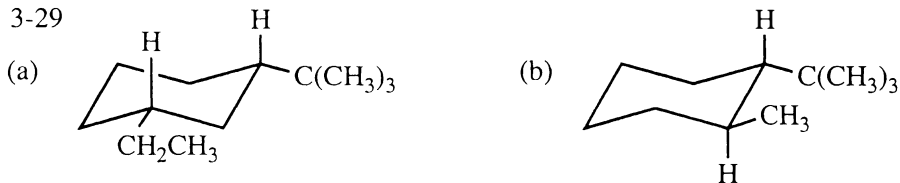
(c) Bulky substituents like *t*-butyl adopt equatorial rather than axial positions, even if that means altering the conformation of the ring. The twist boat conformation allows both bulky substituents to be "equatorial".

51
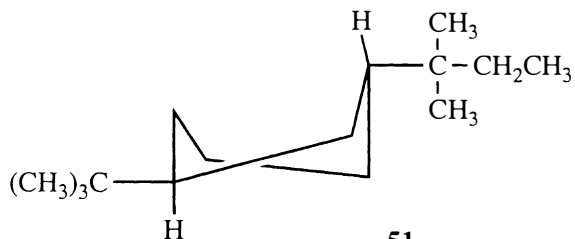
3-30 The nomenclature of bicyclic alkanes is summarized in Appendix 1.
(a) bicyclo[3.1.0]hexane   (b) bicyclo[3.3.1]nonane   (c) bicyclo[2.2.2]octane   (d) bicyclo[3.1.1]heptane

3-31 Using models is essential for this problem.
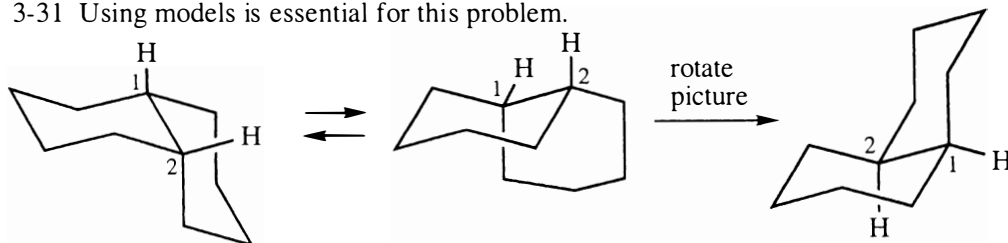
    from text Figure 3-29

3-32 Please refer to solution 1-20, page 12 of this Solutions Manual.

3-33
(a) The third structure is 2-methylpropane (isobutane). The other four structures are all *n*-butane. Remember that a compound's identity is determined by how the atoms are connected, not by the position of the atoms when a structure is drawn on a page.

(b) The two structures at the top-left and bottom-left are both *cis*-2-butene. The two structures at the top-center and bottom-center are both 1-butene. The unique structure at the upper right is *trans*-2-butene. The unique structure at the lower right is 2-methylpropene.

(c) The first two structures are both *cis*-1,2-dimethylcyclopentane. The next two structures are both *trans*-1,2-dimethylcyclopentane. The last structure is different from all the others, *cis*-1,3-dimethylcyclopentane.

(d)
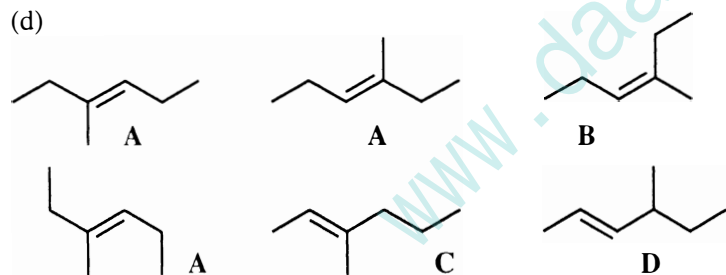
Analysis of the structures shows that some double bonds begin at carbon-2 and some at carbon-3 of the longest chain.
    The three structures labeled **A** are the same, with the double bond *trans*; **B** is a geometric isomer (*cis*) of **A**. **C** and **D** are constitutional isomers of the others.

(e) Naming the structures shows that three of the structures are *trans*-1,4-dimethylcyclohexane, two are the *cis* isomer, and one is *cis*-1,3-dimethylcyclohexane. Although a structure may be shown in two different conformations, it still represents only one compound.

cis-1,4-dimethyl   trans-1,4-dimethyl   cis-1,4-dimethyl

cis-1,3-dimethyl   trans-1,4-dimethyl   trans-1,4-dimethyl
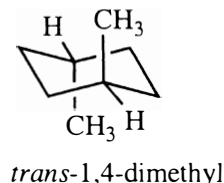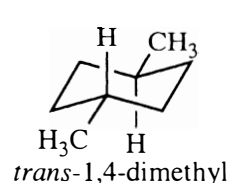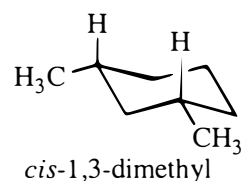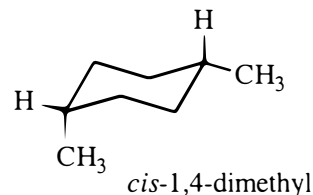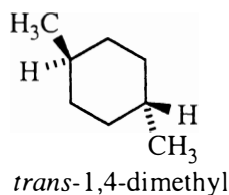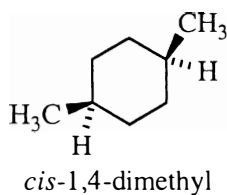
3-34 Line formulas are shown.

(a)

(b)

(c)

(d)

(e)

(f) CH_2CH_3 or CH_2CH_3

(g) H H

(h)

(i)

(j)

(k)

(l) Br Cl H H
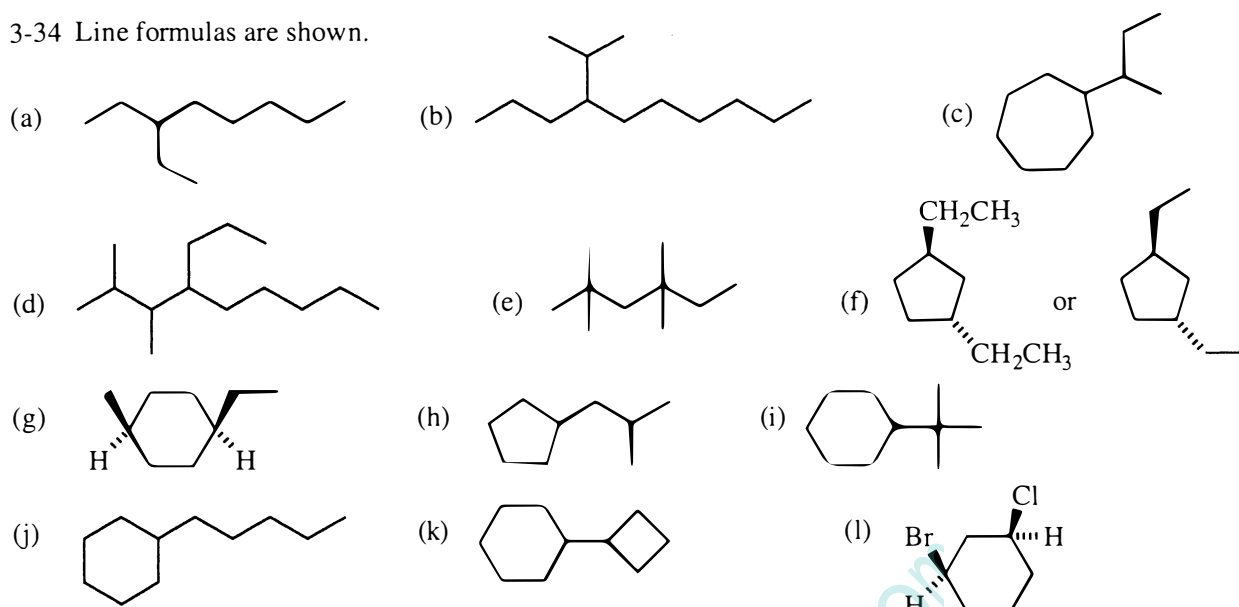
3-35 There are many possible answers to each of these problems. The ones shown here are examples of correct answers. Your answers may be different AND correct. Check your answers in your study group.

(a)

2-methylheptane

 or

3-methylheptane

4-methylheptane

(b)

4,5-diethyldecane

3,5-diethyldecane

(Any combination is correct except using position numbers 1 or 2 or 9 or 10. Why won't these work?)

(c) CH_2CH_3 CH_2CH_3

cis-1,2-diethylcycloheptane

CH_2CH_3 CH_2CH_3

cis-1,3-diethylcycloheptane

CH_2CH_3 CH_2CH_3

cis-1,4-diethylcycloheptane

NOT 1,5
NOT 1,6
NOT 1,7

(d) only two possible answers

CH_3 CH_3

trans-1,2-dimethylcyclopentane

CH_3 CH_3

trans-1,3-dimethylcyclopentane

53

3-35 continued

(e)

(2,3-dimethylpentyl)cycloheptane
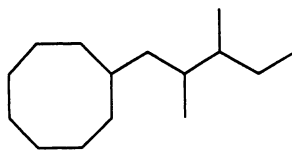
(2,3-dimethylpentyl)cyclooctane

Other ring sizes are possible, although they must have 6 or more carbons to be longer than the 5 carbons of the substituent chain.

(f)
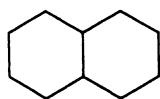
bicyclo[4.4.0]decane
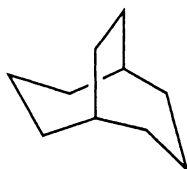
bicyclo[3.3.2]decane

Any combination where the number of carbons in the bridges sums to 8 will work. (Two carbons are the bridgehead carbons.)

3-36 $HO-CH_3$ $HO-CH_2CH_2CH_3$ $HO-CH_2CH_2CH_2CH_2CH_3$

$HO-CH_2CH_3$ $HO-CH_2CH_2CH_2CH_3$ $HO-CH_2CH_2CH_2CH_2CH_2CH_3$
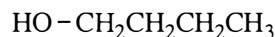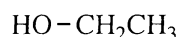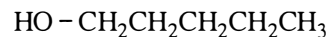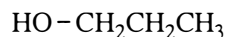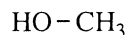
3-37

(a) 3-ethyl-2,2,6-trimethylheptane
(b) 3-ethyl-2,6,7-trimethyloctane
(c) 3,7-diethyl-2,2,8-trimethyldecane
(d) 2-ethyl-1,1-dimethylcyclobutane

(e) bicyclo[4.1.0]heptane
(f) cis-1-ethyl-3-propylcyclopentane
(g) (1,1-diethylpropyl)cyclohexane
(h) cis-1-ethyl-4-isopropylcyclodecane

3-38 There are eighteen isomers of C_8H_{18}. Here are eight of them. Yours may be different from the ones shown. An easy way to compare is to name yours and see if the names match.
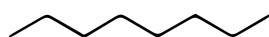
n-octane

2-methylheptane
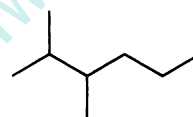
2,3-dimethylhexane
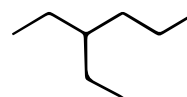
3-ethylhexane
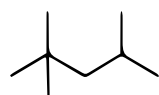
2,2,4-trimethylpentane
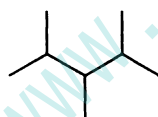
2,3,4-trimethylpentane
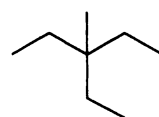
3-ethyl-3-methylpentane
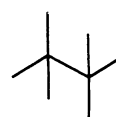
2,2,3,3-tetramethylbutane

3-39

(a)
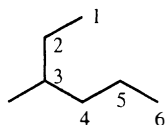
correct name: 3-methylhexane
(longer chain)

(b)
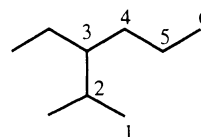
correct name: 3-ethyl-2-methylhexane
(more branching with this numbering)

(c)
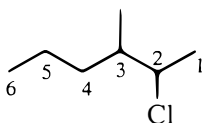
correct name: 2-chloro-3-methylhexane
(begin numbering at end closest to substituent)

(d)
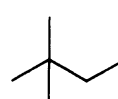
correct name: 2,2-dimethylbutane (include a position number for each substituent, regardless of redundancies)

54

3-39 continued

(e)
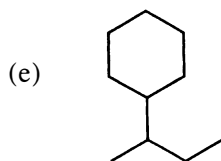
correct name: *sec*-butylcyclohexane or
(1-methylpropyl)cyclohexane
(the longer chain or ring is the base name)

(f)

CH$_2$CH$_3$

CH$_2$CH$_3$
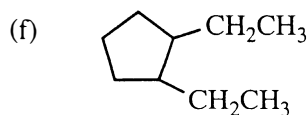
correct name: 1,2-diethylcyclopentane
(position numbers are the lowest possible)

3-40

(a) *n*-Octane has a higher boiling point than 2,2,3-trimethylpentane because linear molecules boil higher than branched molecules of the same molecular weight (increased van der Waals interaction).

(b) 2-Methylnonane has a higher boiling point than *n*-heptane because it has a significantly higher molecular weight than *n*-heptane.

(c) *n*-Nonane boils higher than 2,2,5-trimethylhexane for the same reason as in (a).

3-41 The point of attachment is shown by the bold bond at the left of each structure.

—CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$
1°   *n*-pentyl

—CHCH$_2$CH$_2$CH$_3$
2° CH$_3$ 1-methylbutyl

—CH$_2$CHCH$_2$CH$_3$
1°   CH$_3$ 2-methylbutyl

—CH$_2$CH$_2$CHCH$_3$
1°   CH$_3$ 3-methylbutyl
                    (isopentyl)

—CHCH$_2$CH$_3$
2° CH$_2$CH$_3$ 1-ethylpropyl

CH$_3$
—C$-$CH$_2$CH$_3$
3° CH$_3$ 1,1-dimethylpropyl
              (*t*-pentyl)

CH$_3$
—CHCHCH$_3$
2° CH$_3$ 1,2-dimethylpropyl
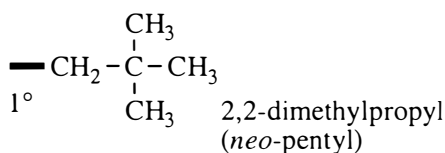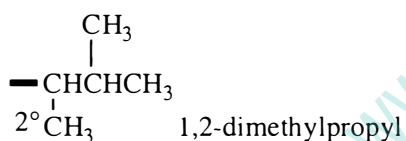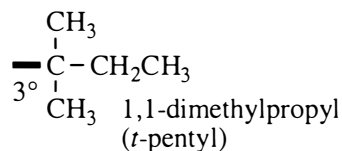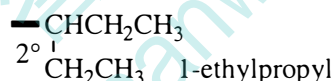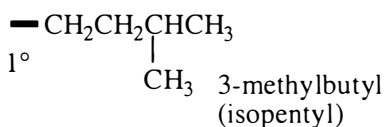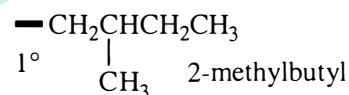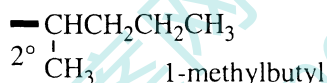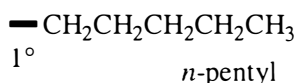
CH$_3$
—CH$_2$$-C-CH_3$
1°   CH$_3$ 2,2-dimethylpropyl
                  (*neo*-pentyl)

3-42 In each case, put the largest groups on adjacent carbons in anti positions to make the most stable conformations.

(a) 3-methylpentane

C-2 is the front carbon with H, H, and CH$_3$
C-3 is the back carbon with H, CH$_3$, and CH$_2$CH$_3$

4 5
CH$_2$CH$_3$

H   H

2

H   CH$_3$

1 CH$_3$

carbon-3 cannot be seen;
it is behind carbon-2

55

3-42 continued
(b) 3,3-dimethylhexane

C-3 is the front carbon with CH_3, CH_3, and CH_2CH_3
C-4 is the back carbon with H, H, and CH_2CH_3

carbon-4 cannot be seen;
it is behind carbon-3

3-43
(a)

(b)   more stable   less stable
             (lower energy)   (higher energy)

(c) From Section 3-14 of the text, each gauche interaction raises the energy 3.8 kJ/mole (0.9 kcal/mole), and each axial methyl has two gauche interactions, so the energy is:
2 methyls x 2 interactions per methyl x 3.8 kJ/mole per interaction = 15.2 kJ/mole (3.6 kcal/mole)

(d) The steric strain from the 1,3-diaxial interaction of the methyls must be the difference between the total energy and the energy due to gauche interactions:
           23 kJ/mole – 15.2 kJ/mole = 7.8 kJ/mole
           (5.4 kcal/mole – 3.6 kcal/mole = 1.8 kcal/mole)

3-44 The more stable conformer places the larger group equatorial.

(a)

more stable

(b)

more stable

(c)

more stable

56

3-44 continued

(d)

more stable

(e)

more stable

3-45 (Using models is essential to this problem.)

In both *cis*- and *trans*-decalin, the cyclohexane rings can be in chair conformations. The relative energies will depend on the number of axial substituents.

trans
no axial substituents
MORE STABLE

cis
one axial substituent

3-46 chair form of glucose—all substituents equatorial

(without ring H's shown)

4-4 continued

(b) The best conversion of cyclohexane to chlorocyclohexane would require the ratio of cyclohexane/ chlorine to be a large number. If the ratio were small, as the concentration of chlorocyclohexane increased during the reaction, chlorine would begin to substitute for a second hydrogen of chlorocyclohexane, generating unwanted products. The goal is to have chlorine attack a molecule of cyclohexane before it ever encounters a molecule of chlorocyclohexane, so the concentration of cyclohexane should be kept high.

4-5

(a) $K_{eq} = e^{-\Delta G°/RT}$ $\qquad -2.1\ kJ/mole = -2100\ J/mole$ $\qquad\qquad$ K = degrees kelvin

$\qquad = e^{-(-2100\ J/mole)/((8.314\ J/K\text{-mole}) \cdot (298\ K))}$

$\qquad = e^{2100/2478} = e^{0.847} =$ $\boxed{2.3}$

(b) $K_{eq} = 2.3 = \dfrac{[CH_3SH]\ [HBr]}{[CH_3Br]\ [H_2S]}$

	$[CH_3Br]$	$[H_2S]$	$[CH_3SH]$	$[HBr]$
initial concentrations:	1	1	0	0
final concentrations	1 – x	1 – x	x	x

$K_{eq} = 2.3 = \dfrac{x \cdot x}{(1-x)(1-x)} = \dfrac{x^2}{1 - 2x + x^2} \implies x^2 = 2.3\,x^2 - 4.6\,x + 2.3$

$0 = 1.3\,x^2 - 4.6\,x + 2.3 \implies x = 0.60,\ \ 1 - x = 0.40$

(using quadratic equation)

$\boxed{[CH_3SH] = [HBr] = 0.60\ M;\ \ [CH_3Br] = [H_2S] = 0.40\ M}$

4-6 2 acetone $\rightleftharpoons$ diacetone

Assume that the initial concentration of acetone is 1 molar, and 5% of the acetone is converted to diacetone. NOTE THE MOLE RATIO.

	[acetone]	[diacetone]
initial concentrations:	1 M	0
final concentrations:	0.95 M	0.025 M

$K_{eq} = \dfrac{[diacetone]}{[acetone]^2} = \dfrac{0.025}{(0.95)^2} = \boxed{0.028}$

$\Delta G° = -2.303\ RT \log_{10} K_{eq} = -2.303\ ((8.314\ J/K\text{-mole}) \cdot (298 K)) \cdot \log(0.028)$

$\qquad = \boxed{+8.9\ kJ/mole\qquad (+2.1\ kcal/mole)}$
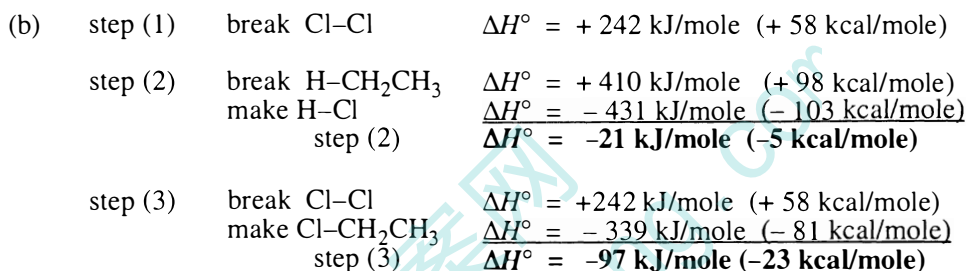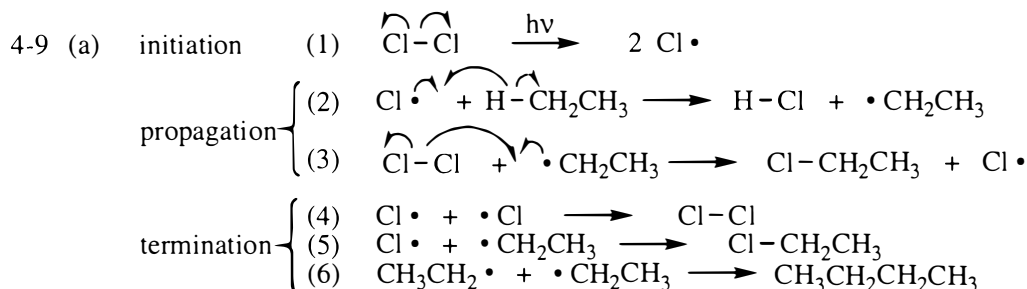
4-7 $\Delta S°$ will be negative since two molecules are combined into one, a loss of freedom of motion. Since $\Delta S°$ is negative, $-T\Delta S°$ is positive; but $\Delta G°$ is a large negative number since the reaction goes to completion. Therefore, $\Delta H°$ must also be a large negative number, necessarily larger in absolute value than $\Delta G°$. We can explain this by formation of two strong C–H bonds (410 kJ/mole each) after breaking a strong H–H bond (435 kJ/mole) and a WEAKER C=C pi bond.
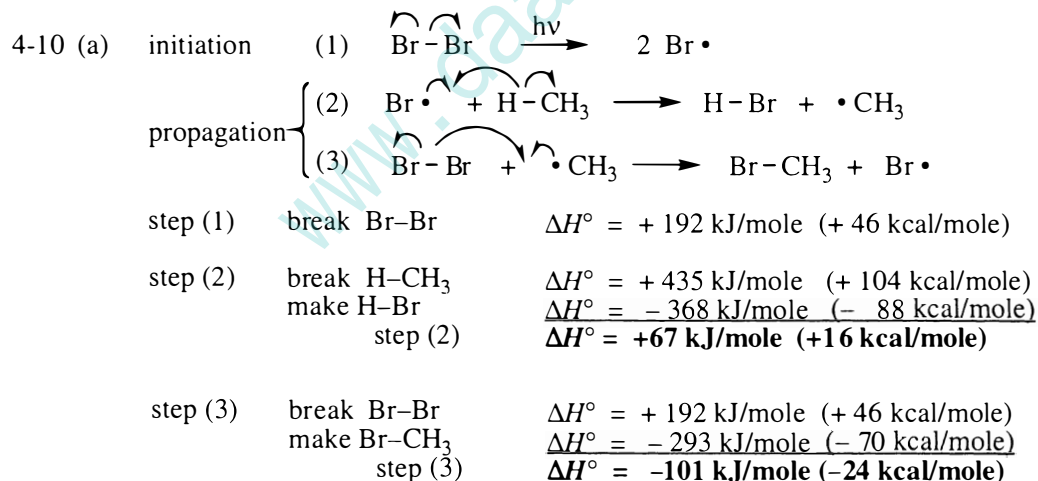
4-8

(a) $\Delta S°$ is positive—one molecule became two smaller molecules with greater freedom of motion

(b) $\Delta S°$ is negative—two smaller molecules combined into one larger molecule with less freedom of motion

(c) $\Delta S°$ cannot be predicted since the number of molecules in reactants and products is the same

4-9 (a) initiation (1) $Cl-Cl \xrightarrow{h\nu} 2\ Cl\cdot$

propagation
- (2) $Cl\cdot\ +\ H-CH_2CH_3 \longrightarrow H-Cl\ +\ \cdot CH_2CH_3$
- (3) $Cl-Cl\ +\ \cdot CH_2CH_3 \longrightarrow Cl-CH_2CH_3\ +\ Cl\cdot$

termination
- (4) $Cl\cdot\ +\ \cdot Cl \longrightarrow Cl-Cl$
- (5) $Cl\cdot\ +\ \cdot CH_2CH_3 \longrightarrow Cl-CH_2CH_3$
- (6) $CH_3CH_2\cdot\ +\ \cdot CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_3$

(b) step (1) break Cl–Cl $\Delta H° = +242$ kJ/mole (+ 58 kcal/mole)

step (2) break H–CH$_2$CH$_3$ $\Delta H° = +410$ kJ/mole (+98 kcal/mole)
make H–Cl $\Delta H° = -431$ kJ/mole (– 103 kcal/mole)
step (2) $\Delta H° =$ **–21 kJ/mole (–5 kcal/mole)**

step (3) break Cl–Cl $\Delta H° = +242$ kJ/mole (+ 58 kcal/mole)
make Cl–CH$_2$CH$_3$ $\Delta H° = -339$ kJ/mole (– 81 kcal/mole)
step (3) $\Delta H° =$ **–97 kJ/mole (–23 kcal/mole)**

(c) $\Delta H°$ for the reaction is the sum of the $\Delta H°$ values of the individual propagation steps:

– 21 kJ/mole + – 97 kJ/mole = **– 118 kJ/mole**
(– 5 kcal/mole + – 23 kcal/mole = **– 28 kcal/mole**)

4-10 (a) initiation (1) $Br-Br \xrightarrow{h\nu} 2\ Br\cdot$

propagation
- (2) $Br\cdot\ +\ H-CH_3 \longrightarrow H-Br\ +\ \cdot CH_3$
- (3) $Br-Br\ +\ \cdot CH_3 \longrightarrow Br-CH_3\ +\ Br\cdot$

step (1) break Br–Br $\Delta H° = +192$ kJ/mole (+ 46 kcal/mole)

step (2) break H–CH$_3$ $\Delta H° = +435$ kJ/mole (+ 104 kcal/mole)
make H–Br $\Delta H° = -368$ kJ/mole (– 88 kcal/mole)
step (2) $\Delta H° =$ **+67 kJ/mole (+16 kcal/mole)**

step (3) break Br–Br $\Delta H° = +192$ kJ/mole (+ 46 kcal/mole)
make Br–CH$_3$ $\Delta H° = -293$ kJ/mole (– 70 kcal/mole)
step (3) $\Delta H° =$ **–101 kJ/mole (–24 kcal/mole)**

(b) $\Delta H°$ for the reaction is the sum of the $\Delta H°$ values of the individual propagation steps:

+ 67 kJ/mole + – 101 kJ/mole = **– 34 kJ/mole**
(+ 16 kcal/mole + – 24 kcal/mole = **– 8 kcal/mole**)

61

4-11

(a) first order: the exponent of $[(CH_3)_3CCl]$ in the rate law = 1

(b) zeroth order: $[CH_3OH]$ does not appear in the rate law (its exponent is zero)

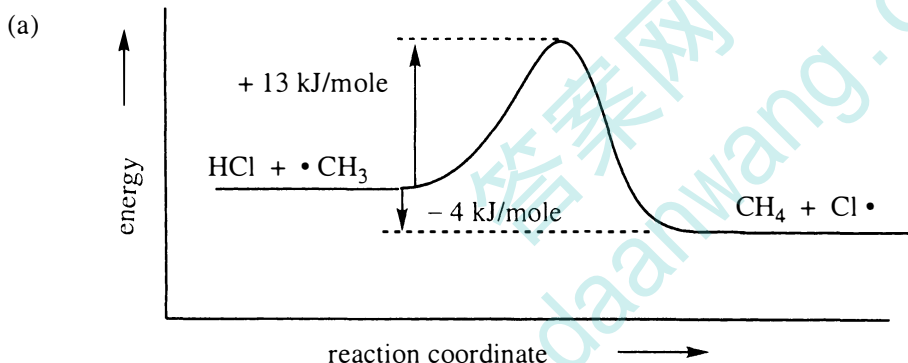(c) first order: the sum of the exponents in the rate law = 1 + 0 = **1**

4-12

(a) first order: the exponent of [cyclohexene] in the rate law = 1

(b) second order: the exponent of $[Br_2]$ in the rate law = 2

(c) third order: the sum of the exponents in the rate law = 1 + 2 = **3**

4-13

(a) the reaction rate depends on neither [ethylene] nor [hydrogen], so it is zeroth order in both species. The overall reaction must be zeroth order.

(b) rate = k_r

(c) The rate law does not depend on the concentration of the reactants. It must depend, therefore, on the only other chemical present, the catalyst. Apparently, whatever is happening on the surface of the catalyst determines the rate, regardless of the concentrations of the two gases. Increasing the surface area of the catalyst, or simply adding more catalyst, would accelerate the reaction.

4-14

(a)

(b) E_a = + 13 kJ/mole (+ 3 kcal/mole)

(c) $\Delta H°$ = – 4 kJ/mole (– 1 kcal/mole)

4-15

(a)

(b) reverse: $CH_3Cl + Cl • \longrightarrow Cl_2 + • CH_3$

(c) reverse: E_a = + 109 kJ/mole + + 4 kJ/mole = **+ 113 kJ/mole**

(+ 26 kcal/mole + + 1 kcal/mole = **+ 27 kcal/mole)**

62

4-16
(a)

numbers are kJ/mole

HBr + •CH$_3$ + Br$_2$

+ 75

+ 4

Br•
+ CH$_4$

+ 67

− 101

CH$_3$Br + Br•

+ 192

Br$_2$

energy →

reaction coordinate →

(b) The step leading to the highest energy transition state is rate-limiting. In this mechanism, the first propagation step is rate-limiting:

$$Br• + CH_4 \longrightarrow HBr + •CH_3$$

(c) (1) $\left[\begin{matrix} \delta• & \delta• \\ Br \text{------} Br \end{matrix} \right]^{\ddagger}$ ("δ•" means partial radical character on the atom)

(2) $\left[\begin{matrix} H \\ | \\ H-C\text{------}H\text{------}Br \\ | \\ H \end{matrix} \right]^{\ddagger}$ with δ• on C and δ• on Br

(3) $\left[\begin{matrix} H \\ | \\ H-C\text{------}Br\text{------}Br \\ | \\ H \end{matrix} \right]^{\ddagger}$ with δ• on C and δ• on Br

(d) $\Delta H°$ for the reaction is the sum of the $\Delta H°$ values of the individual propagation steps (refer to the solution to 4-10 (a) and (b)):

+ 67 kJ/mole + − 101 kJ/mole = **− 34 kJ/mole**
(+ 16 kcal/mole + − 24 kcal/mole = **− 8 kcal/mole**)

4-17

(a) initiation (1) I−I $\xrightarrow{h\nu}$ 2 I•

propagation { (2) I• + H−CH$_3$ $\longrightarrow$ H−I + •CH$_3$

(3) I−I + •CH$_3$ $\longrightarrow$ I−CH$_3$ + I•

step (1) break I–I $\Delta H° = +151$ kJ/mole (+ 36 kcal/mole)

step (2) break H–CH$_3$ $\Delta H° = +435$ kJ/mole (+ 104 kcal/mole)
make H–I $\Delta H° = -297$ kJ/mole (− 71 kcal/mole)
step (2) $\Delta H° = $ **+ 138 kJ/mole (+ 33 kcal/mole)**

step (3) break I–I $\Delta H° = +151$ kJ/mole (+ 36 kcal/mole)
make I–CH$_3$ $\Delta H° = -234$ kJ/mole (− 56 kcal/mole)
step (3) $\Delta H° = $ **−83 kJ/mole (−20 kcal/mole)**
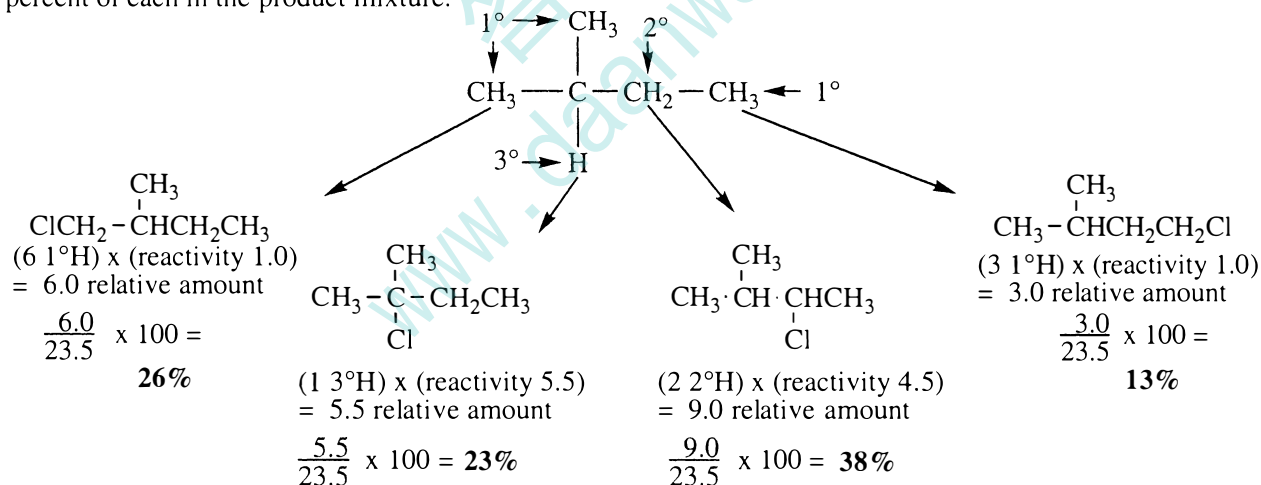
4-20 continued

Since $\Delta H°$ for forming the 3° radical is more negative than $\Delta H°$ for forming the 1° radical, it is reasonable to infer that the activation energy leading to the 3° radical is lower than the activation energy leading to the 1° radical.
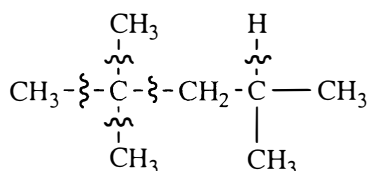
4-21

2-Methylbutane can produce four mono-chloro isomers. To calculate the relative amount of each in the product mixture, multiply the numbers of hydrogens which could lead to that product times the reactivity for that type of hydrogen. Each relative amount divided by the sum of all the amounts will provide the percent of each in the product mixture.
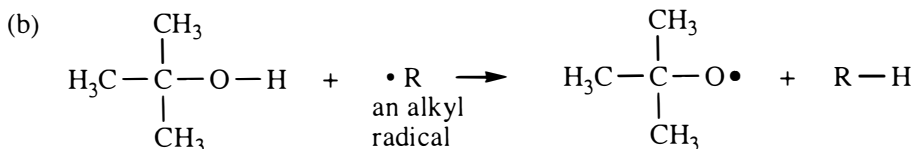

$$CH_3$$
$$ClCH_2 - CHCH_2CH_3$$
(6 1°H) x (reactivity 1.0)
= 6.0 relative amount

$\dfrac{6.0}{23.5}$ x 100 = **26%**

$$CH_3$$
$$CH_3 - C - CH_2CH_3$$
$$Cl$$
(1 3°H) x (reactivity 5.5)
= 5.5 relative amount

$\dfrac{5.5}{23.5}$ x 100 = **23%**

$$CH_3$$
$$CH_3 \cdot CH \cdot CHCH_3$$
$$Cl$$
(2 2°H) x (reactivity 4.5)
= 9.0 relative amount

$\dfrac{9.0}{23.5}$ x 100 = **38%**

$$CH_3$$
$$CH_3 - CHCH_2CH_2Cl$$
(3 1°H) x (reactivity 1.0)
= 3.0 relative amount

$\dfrac{3.0}{23.5}$ x 100 = **13%**

4-22

(a) When *n*-heptane is burned, only 1° and 2° radicals can be formed (from either C—H or C—C bond cleavage). These are high energy, unstable radicals which rapidly form other products. When isooctane (2,2,4-trimethylpentane, below) is burned, 3° radicals can be formed from either C—H or C—C bond cleavage. The 3° radicals are lower in energy than 1° or 2°, relatively stable, with lowered reactivity. Slower combustion translates to less "knocking."

isooctane (2,2,4-trimethylpentane)
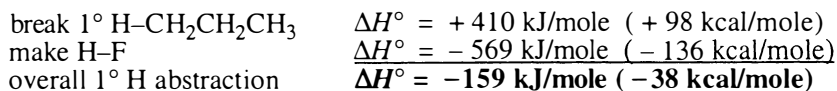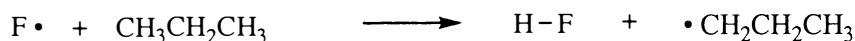
Any indicated bond cleavage will produce a 3° radical.
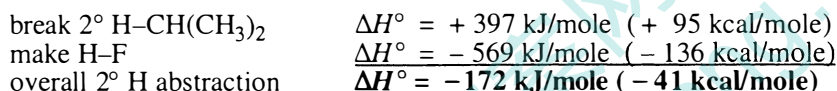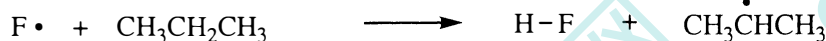
65

4-22 continued

(b)

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-H \quad + \quad \cdot R \quad \longrightarrow \quad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O\cdot \quad + \quad R-H$$

an alkyl radical

When the alcohol hydrogen is abstracted from *t*-butyl alcohol, a relatively stable *t*-butoxy radical ($(CH_3)_3C-O\cdot$) is produced. This low energy radical is slower to react than alkyl radicals, moderating the reaction and producing less "knocking."
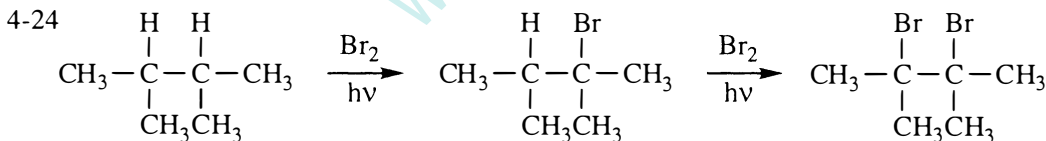
4-23

(a) 1° H abstraction

$$F\cdot \quad + \quad CH_3CH_2CH_3 \quad \longrightarrow \quad H-F \quad + \quad \cdot CH_2CH_2CH_3$$

break 1° H–CH$_2$CH$_2$CH$_3$	$\Delta H° = +410$ kJ/mole (+ 98 kcal/mole)
make H–F	$\Delta H° = -569$ kJ/mole (– 136 kcal/mole)
overall 1° H abstraction	$\Delta H° = -159$ kJ/mole (−38 kcal/mole)

2° H abstraction

$$F\cdot \quad + \quad CH_3CH_2CH_3 \quad \longrightarrow \quad H-F \quad + \quad CH_3\overset{\bullet}{C}HCH_3$$

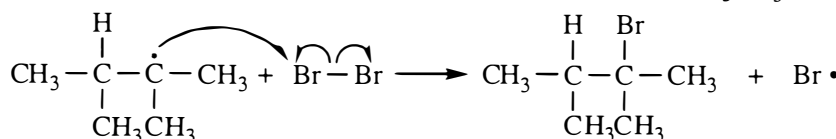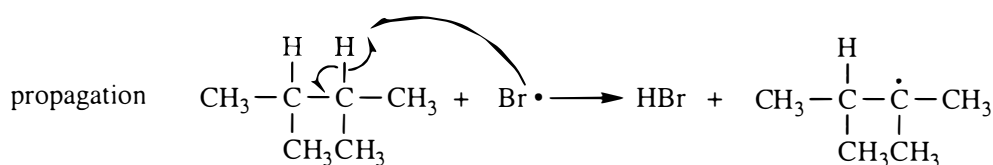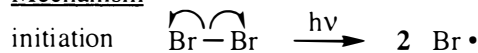|	
break 2° H–CH(CH$_3$)$_2$	$\Delta H° = +397$ kJ/mole (+ 95 kcal/mole)
make H–F	$\Delta H° = -569$ kJ/mole (– 136 kcal/mole)
overall 2° H abstraction	$\Delta H° = -172$ kJ/mole (−41 kcal/mole)

(b) Fluorination is extremely exothermic and is likely to be indiscriminate in which hydrogens are abstracted. (In fact, C—C bonds are also broken during fluorination.)

(c) Free radical fluorination is extremely exothermic. In exothermic reactions, the transition states resemble the starting materials more than the products, so while the 1° and 2° radicals differ by about 13 kJ/mole (3 kcal/mole), the transition states will differ by only a tiny amount. For fluorination, then, the rate of abstraction for 1° and 2° hydrogens will be virtually identical. Product ratios will depend on statistical factors only.
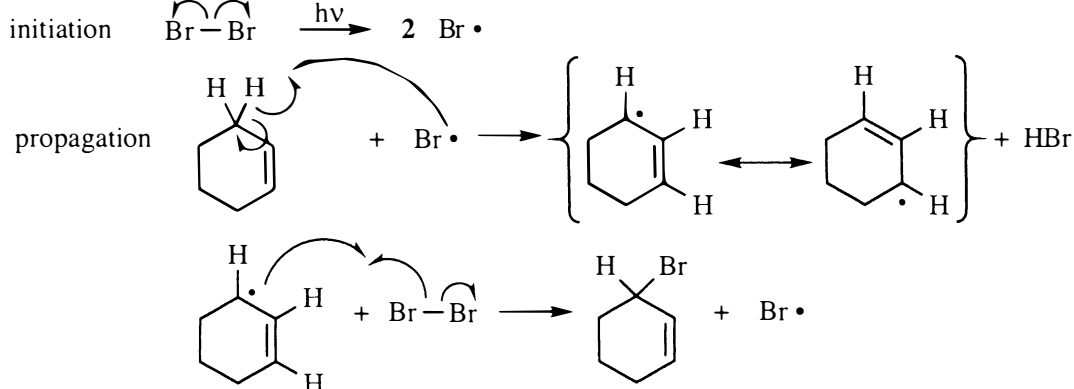
Fluorination is difficult to control, but if propane were monofluorinated, the product mixture would reflect the ratio of the types of hydrogens: six 1° H to two 2° H, or 3 : 1 ratio, giving 75% 1-fluoropropane and 25% 2-fluoropropane.
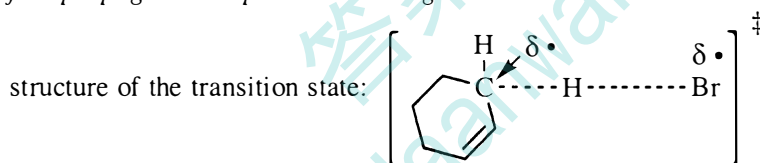
4-24

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 \xrightarrow[h\nu]{Br_2} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3 \xrightarrow[h\nu]{Br_2} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3$$

Mechanism

initiation $\quad Br-Br \xrightarrow{h\nu} 2\ Br\cdot$

propagation $\quad CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 + Br\cdot \longrightarrow HBr + CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{\bullet}{C}}{}}-CH_3$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{\bullet}{C}}{}}-CH_3 + Br-Br \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3 + Br\cdot$$

66

4-25 (a) <u>Mechanism</u>

initiation   Br—Br $\xrightarrow{h\nu}$ 2 Br•

propagation

(b) Energy calculation uses the value for the allylic C—H bond from Table 4-2.

First propagation step
break allylic H–CH[ring]	$\Delta H° = + 364$ kJ/mole	(+ 87 kcal/mole)
make H–Br	$\Delta H° = - 368$ kJ/mole	(– 88 kcal/mole)
overall allylic H abstraction	**$\Delta H° = -4$ kJ/mole**	**(−1 kcal/mole)**

Second propagation step
break Br–Br	$\Delta H° = + 192$ kJ/mole	(+ 46 kcal/mole)
make 2° C–Br	$\Delta H° = - 285$ kJ/mole	(– 68 kcal/mole)
overall C–Br formation	**$\Delta H° = -93$ kJ/mole**	**(−22 kcal/mole)**

The first propagation step is rate-limiting.

structure of the transition state:

(c) The Hammond postulate tells us that, in an exothermic reaction, the transition state is closer to the reactants in energy and in structure. Since the first propagation step is exothermic (although not by much), the transition state is closer to cyclohexene + bromine radical. This is indicated in the transition state structure by showing the H closer to the C than to the Br.

(d) A bromine radical will abstract the hydrogen with the lowest bond dissociation energy at the fastest rate. The allylic hydrogen of cyclohexene is more easily abstracted than a hydrogen of cyclohexane because the radical produced is stabilized by resonance. (Energy values below are per mole.)

aliphatic: 397 kJ (95 kcal) $\longrightarrow$ H H   H H $\longleftarrow$ 364 kJ (87 kcal): allylic
SLOWER   *FASTER*

4-26

BHA radical

67

4-27

Vitamin E

R–O–H + stabilized by resonance— less reactive than RO•

4-28   The triphenylmethyl cation is so stable because of the delocalization of the charge. The more resonance forms a species has, the more stable it will be.

(Note: these resonance forms do not include the simple benzene resonance forms as shown below; they are significant, but repetitive, so for simplicity, they are not drawn here.)
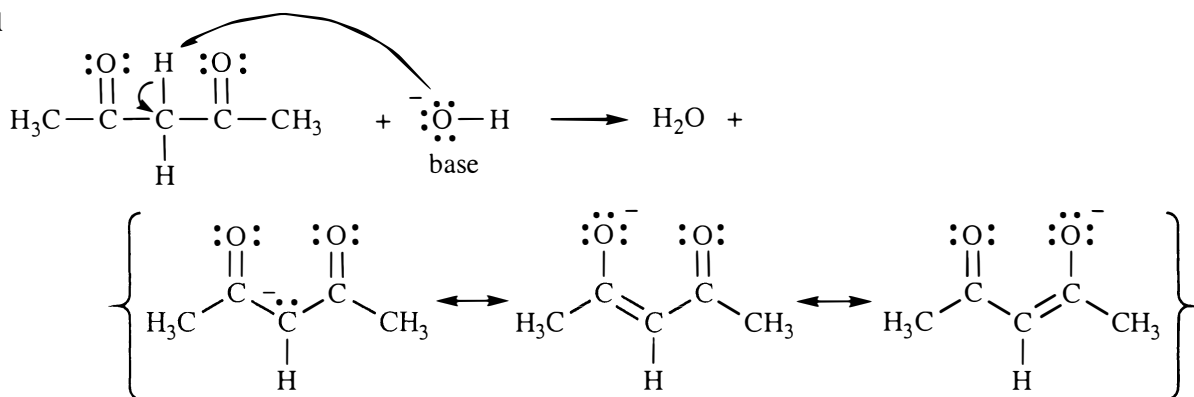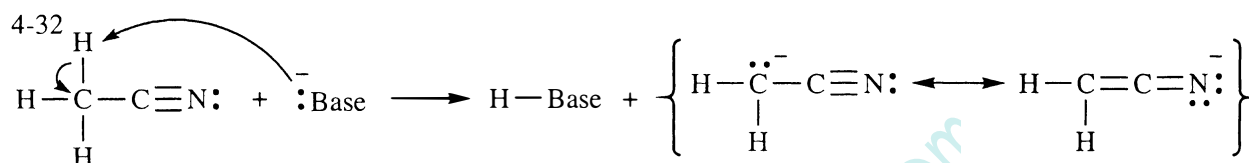
many more

4-29   most stable (c) > (b) > (a) least stable

(c) $CH_3-\overset{+}{\underset{CH_3}{C}}CH_2CH_3$ (b) $CH_3-\overset{+}{\underset{CH_3}{C}}HCHCH_3$ (a) $CH_3-\underset{CH_3}{C}HCH_2\overset{+}{C}H_2$

       3°   2°   1°

4-30   most stable (c) > (b) > (a) least stable

(c) $CH_3-\overset{\bullet}{\underset{CH_3}{C}}CH_2CH_3$ (b) $CH_3-\overset{\bullet}{\underset{CH_3}{C}}HCHCH_3$ (a) $CH_3-\underset{CH_3}{C}HCH_2\overset{\bullet}{C}H_2$

       3°   2°   1°

4-31

$$H_3C-C-C-C-CH_3 \quad + \quad {}^-\!:\!\overset{..}{O}-H \quad \longrightarrow \quad H_2O \quad +$$

base

$$\left\{ \begin{array}{ccc} & & \end{array} \right.$$ H_3C, C, C, CH_3 ... H

4-32

$$H-\overset{H}{\underset{H}{C}}-C\equiv N: \quad + \quad :Base^- \quad \longrightarrow \quad H-Base \quad + \quad \left\{ H-\overset{..}{\underset{H}{C}}{}^-\!-C\equiv N: \longleftrightarrow H-\overset{}{\underset{H}{C}}=C=\overset{..}{\underset{..}{N}}:^- \right\}$$

4-33

$$\underset{\overset{..}{\underset{..}{C}}}{\overset{\overset{O}{\parallel}}{H}}\,\,\overset{O}{\underset{}{C}}-O-CH_2CH_3$$

4-34 Please refer to solution 1-20, page 12 of this Solutions Manual.

4-35

(a) and (c)

(b) $\Delta H°$ is negative (decreases), so the reaction is exothermic.

(d) The first transition state determines the rate since it is the highest energy point. The *structure* of the first transition state resembles the *structure* of the intermediate since the *energy* of the transition state is closest to the *energy* of the intermediate.

transition states

E_{a1}

E_{a2}

intermediate

reactants

$\Delta H°$

products

energy

reaction coordinate ⟶

4-36

transition state

activation energy

reactants

heat of reaction

products

energy

reaction coordinate ⟶

4-37

4-38
The rate law is first order with respect to the concentrations of hydrogen ion and of *t*-butyl alcohol, zeroth order with respect to the concentration of chloride ion, second order overall.
rate = k_r [$(CH_3)_3COH$] [H^+]

4-39 (a) $CH_3CH_2CH(CH_3)_2$
1° 2° 3° 1°

(b) $(CH_3)_3CCH_2C(CH_3)_3$
1° 2° 1°

(c)
all are 2° H except for the two types labeled

(d)
3°
all are 2° H except for the two types labeled

(e)
all are 2° H except as labeled

4-40

(a) break $H–CH_2CH_3$ and $I–I$, make $I–CH_2CH_3$ and $H–I$
kJ/mole: (+ 410 + + 151) + (− 222 + − 297) = **+ 42 kJ/mole**
kcal/mole: (+ 98 + + 36) + (− 53 + − 71) = **+ 10 kcal/mole**

(b) break $CH_3CH_2–Cl$ and $H–I$, make $CH_3CH_2–I$ and $H–Cl$
kJ/mole: (+ 339 + + 297) + (− 222 + − 431) = **− 17 kJ/mole**
kcal/mole: (+ 81 + + 71) + (− 53 + − 103) = **− 4 kcal/mole**

4-40 continued

(c) break $(CH_3)_3C-OH$ and $H-Cl$, make $(CH_3)_3C-Cl$ and $H-OH$

kJ/mole: $(+381 + +431) + (-331 + -498) = $ **−17 kJ/mole**

kcal/mole: $(+91 + +103) + (-79 + -119) = $ **−4 kcal/mole**

(d) break $CH_3CH_2-CH_3$ and $H-H$, make CH_3CH_2-H and $H-CH_3$

kJ/mole: $(+356 + +435) + (-410 + -435) = $ **−54 kJ/mole**

kcal/mole: $(+85 + +104) + (-98 + -104) = $ **−13 kcal/mole**

(e) break CH_3CH_2-OH and $H-Br$, make CH_3CH_2-Br and $H-OH$

kJ/mole: $(+381 + +368) + (-285 + -498) = $ **−34 kJ/mole**

kcal/mole: $(+91 + +88) + (-68 + -119) = $ **−8 kcal/mole**

4-41 Numbers are bond dissociation energies in kcal/mole in the top line and kJ/mole in the bottom line.

85	87	91	95	98	104
356	364	381	397	410	435

most stable   least stable

4-42

(a) Only one product; chlorination would work. Bromination on a 2° carbon would not be predicted to be a high-yielding process.

(b)

Chlorination would produce four constitutional isomers and would not be a good method to make only one of these. Monobromination at the 3° carbon would give a reasonable yield.

(c)

Chlorination would produce two constitutional isomers and would not be a good method to make only one of these. Monobromination would be selective for the 3° carbon and would give an excellent yield.

(d) Only one product; chlorination would give a high yield. Monobromination would be very difficult since all hydrogens are on 1° carbons.
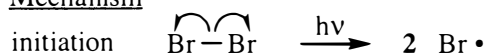
4-43

initiation (1)

propagation

(2)

(3)

Termination steps are any two radicals combining.

71

4-44

(a) $CH_2=CH-\overset{\bullet}{C}H_2 \longleftrightarrow \overset{\bullet}{C}H_2-CH=CH_2$

(b)

(c)

(d)   (e)

4-45

(a) <u>Mechanism</u>

initiation $\overset{\frown\frown}{Br-Br} \xrightarrow{h\nu} 2\ Br\bullet$

propagation

The 3° allylic H is abstracted selectively (faster than any other type in the molecule), forming an intermediate represented by two *non-equivalent* resonance forms. Partial radical character on two different carbons of the allylic radical leads to two different products.

(b) There are two reasons why the H shown is the one that is abstracted by bromine radical: the H is 3° and it is allylic, that is, neighboring a double bond. Both of these factors stabilize the radical that is created by removing the H atom.

4-46 Where mixtures are possible, only the major product is shown.

(a)   only one product possible

(b)   3° hydrogen abstracted selectively, faster than 2° or 1°

(c)   3° hydrogen abstracted selectively, faster than 1°

72

4-46 continued

(d) 3° hydrogen abstracted selectively, faster than 2°

decalin

(e) 3° hydrogen abstracted selectively, faster than 2° or 1°

(f) both 2°—formed in equal amounts

(g) from resonance-stabilized benzylic radical

(h) All hydrogens at the starred positions are equivalent and *allylic*. The H from the lower right carbon has been removed to make an intermediate with two non-equivalent resonance forms, giving the two products shown. *Drawing the resonance forms is the key to answering this question correctly.*

4-47

(a) As CH_3Cl is produced, it can compete with CH_4 for available $Cl \cdot$, generating CH_2Cl_2. This can generate $CHCl_3$, *etc*.

propagation steps

$$CH_4 + Cl \cdot \longrightarrow HCl + \cdot CH_3$$
$$\cdot CH_3 + Cl_2 \longrightarrow ClCH_3 + Cl \cdot$$
$$ClCH_3 + Cl \cdot \longrightarrow HCl + \cdot CH_2Cl$$
$$\cdot CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl \cdot$$
$$CH_2Cl_2 + Cl \cdot \longrightarrow HCl + \cdot CHCl_2$$
$$\cdot CHCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl \cdot$$
$$CHCl_3 + Cl \cdot \longrightarrow HCl + \cdot CCl_3$$
$$\cdot CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl \cdot$$

(b) To maximize CH_3Cl and minimize formation of polychloromethanes, the ratio of methane to chlorine must be kept high (see problem 4-2).

To guarantee that all hydrogens are replaced with chlorine to produce CCl_4, the ratio of chlorine to methane must be kept high.

73

4-48

(a) *n*-Pentane can produce three monochloro isomers. To calculate the relative amount of each in the product mixture, multiply the numbers of hydrogens which could lead to that product times the reactivity for that type of hydrogen. Each relative amount divided by the sum of all the amounts will provide the percent of each in the product mixture.

```
            ┌--- equivalent----┐
            │   ┌equivalent┐   │
            ↓   ↓          ↓    ↓
          CH₃CH₂CH₂CH₂CH₃
```

$$CH_3CH_2CH_2CH_2CH_3$$

Cl–CH₂CH₂CH₂CH₂CH₃

(6 1° H) x (reactivity 1.0)
= 6.0 relative amount

            Cl
            |
CH₃–CHCH₂CH₂CH₃

(4 2° H) x (reactivity 4.5)
= 18.0 relative amount

                Cl
                |
CH₃CH₂–CHCH₂CH₃

(2 2° H) x (reactivity 4.5)
= 9.0 relative amount

total amount = 33.0

(b) $\frac{6.0}{33.0}$ x 100 = **18%** $\frac{18.0}{33.0}$ x 100 = **55%** $\frac{9.0}{33.0}$ x 100 = **27%**

4-49

(a) The second propagation step in the chlorination of methane is highly exothermic ($\Delta H° = -109$ kJ/mole (-26 kcal/mole)). The transition state resembles the reactants, that is, the Cl–Cl bond will be slightly stretched and the Cl–CH₃ bond will just be starting to form.

$$\delta\bullet \qquad\qquad \delta\bullet$$
$$Cl\cdots\cdots Cl\cdots\cdots\cdots\cdots CH_3$$
stronger   weaker

(b) The second propagation step in the bromination of methane is highly exothermic ($\Delta H° = -101$ kJ/mole (-24 kcal/mole)). The transition state resembles the reactants, that is, the Br–Br bond will be slightly stretched and the Br–CH₃ bond will just be starting to form.

$$\delta\bullet \qquad\qquad \delta\bullet$$
$$Br\cdots\cdots Br\cdots\cdots\cdots\cdots CH_3$$
stronger   weaker

4-50 Two mechanisms are possible depending on whether HO • reacts with chlorine or with cyclopentane.

Mechanism 1

initiation {
(1)   HO – OH ⟶ 2 HO •
(2)   HO • + Cl – Cl ⟶ HO – Cl + Cl •

propagation {
(3)   Cl • + ⟶ H – Cl +
(4)   Cl – Cl + ⟶ + Cl •

Mechanism 2

initiation {
(1)   HO – OH ⟶ 2 HO •
(2)   HO • + ⟶ H – OH +

propagation {
(3)   Cl – Cl + ⟶ + Cl •
(4)   Cl • + ⟶ H – Cl +

The energies of the propagation steps determine which mechanism is followed. The bond dissociation energy of HO—Cl is about 210 kJ/mole (about 50 kcal/mole), making initiation step (2) in mechanism 1 *endothermic* by about 30 kJ/mole (about 8 kcal/mole). In mechanism 2, initiation step (2) is *exothermic* by about 101 kJ/mole (24 kcal/mole); mechanism 2 is preferred.

4-51

a carbene

4-52 This critical equation is the key to this problem: $\Delta G = \Delta H - T \Delta S$

At 1400 K, the equilibrium constant is 1; therefore:

$$K_{eq} = 1 \implies \Delta G = 0 \implies \Delta H = T \Delta S$$

Assuming ΔH is about the same at 1400 K as it is at calorimeter temperature:

$$\Delta S = \frac{\Delta H}{T} = \frac{-137 \text{ kJ/mole}}{1400 \text{ K}} = \frac{-137,000}{1400} \text{ J/K-mole}$$

$$= -98 \text{ J/K-mole} \ (-23 \text{ cal/K-mole})$$

This is a large *decrease* in entropy, consistent with two molecules combining into one.

4-53

Assume that chlorine atoms (radicals) are still generated in the initiation reaction. Focus on the propagation steps. Bond dissociation energies are given below the bonds, in kJ/mole (kcal/mole).

$$Cl\bullet \; + \; H-CH_3 \longrightarrow H-Cl \; + \; \bullet CH_3 \qquad \Delta H = +4 \text{ kJ/mole } (+1 \text{ kcal/mole})$$
$$ 435 \,(104) 431 \,(103)$$

$$Cl-Cl \; + \; \bullet CH_3 \longrightarrow Cl-CH_3 + Cl\bullet \qquad \Delta H = -109 \text{ kJ/mole } (-26 \text{ kcal/mole})$$
$$242 \,(58) 351 \,(84)$$

What happens when the different radical species react with iodine?

$$Cl\bullet \; + \; I-I \longrightarrow I-Cl \; + \; \bullet I \qquad \Delta H = -60 \text{ kJ/mole } (-14 \text{ kcal/mole})$$
$$ 151 \,(36) 211 \,(50)$$

$$I-I \; + \; \bullet CH_3 \longrightarrow I-CH_3 + I\bullet \qquad \Delta H = -83 \text{ kJ/mole } (-20 \text{ kcal/mole})$$
$$151 \,(36) 234 \,(56)$$

Compare the second reaction in each pair: methyl radical reacting with chlorine is more exothermic than methyl radical reacting with iodine; this does not explain how iodine prevents the chlorination reaction. Compare the first reaction in each pair: chlorine atom reacting with iodine is very exothermic whereas chlorine atom reacting with methane is slightly endothermic. Here is the key: chlorine atoms will be scavenged by iodine before they have a chance to react with methane. Without chlorine atoms, the reaction comes to a dead stop.

4-54 (a)

(b) All energies are in kJ/mole. The abbreviation "cy" stands for the cyclohexane ring.

Step 2: break H—Sn, make H—Br: +310 + −368 = −58 kJ/mole

Step 3: break cy—Br, make Br—Sn: +285 + −552 = −267 kJ/mole WOW!

Step 4: break H—Sn, make cy—H: +310 + −397 = −87 kJ/mole

The sum of the two propagation steps are: −267 + −87 = −354 kJ/mole —a hugely exothermic reaction.

4-55

Mechanism 1:

(a) Cl• + O₃ ⟶ ClO• + O₂

(b) 2 ClO• ⟶ Cl–O–O–Cl

(c) Cl–O–O–Cl —hν→ O₂ + 2 Cl•

The biggest problem in Mechanism 1 lies in step (b). The concentration of Cl atoms is very small, so at any given time, the concentration of ClO will be very small. The probability of two ClO radicals finding each other to form ClOOCl is virtually zero. Even though this mechanism shows a catalytic cycle with Cl• (starting the mechanism and being regenerated at the end), the middle step makes it highly unlikely.

Mechanism 2:

(d) O₃ —hν→ O₂ + O

Step (d) is the "light" reaction that occurs naturally in daylight. At night, the reaction reverses and regenerates ozone.

(e) Cl• + O₃ ⟶ ClO• + O₂

(f) ClO• + O ⟶ O₂ + Cl•

Step (f) is the crucial step. A low concentration of ClO *will* find a relatively high concentration of O atoms because the "light" reaction is producing O atoms in relative abundance. Cl• is regenerated and begins propagation step (e), continuing the catalytic cycle.

Mechanism 2 is believed to be the dominant mechanism in ozone depletion. Mechanism 1 can be discounted because of the low probability of step (b) occurring, because two species in very low, catalytic concentration are required to find each other in order for the step to occur.

4-56

(a)

$$\left[\begin{array}{c} H \\ | \\ H-C\cdots\cdots H\cdots\cdots Cl \\ | \\ H \end{array} \right]^{\ddagger} \quad \left[\begin{array}{c} D \\ | \\ D-C\cdots\cdots D\cdots\cdots Cl \\ | \\ D \end{array} \right]^{\ddagger}$$

In each case, the bond from carbon to H (D) is breaking and the bond from H (D) to Cl is forming.

(b) C₂H₅—D + Cl₂ ⟶ $\underbrace{C_2H_5—Cl + DCl}_{7\%}$ + $\underbrace{C_2H_4DCl + HCl}_{93\%}$

D replacement: 7% ÷ 1 D = 7 (reactivity factor)
H replacement: 93% ÷ 5 H = 18.6 (reactivity factor)
relative reactivity of H : D abstraction = 18.6 ÷ 7 = 2.7

Each hydrogen is abstracted 2.7 times faster than deuterium.

(c) In both reactions of chlorine with either methane or ethane, the first propagation step is rate-limiting. The reaction of chlorine atom with methane is *endothermic* by 4 kJ/mole (1 kcal/mole), while for ethane this step is *exothermic* by 21 kJ/mole (5 kcal/mole). By the Hammond Postulate, differences in activation energy are most pronounced in *endothermic* reactions where the transition states most resemble the products. Therefore, a change in the methane molecule causes a greater change in its transition state energy than the same change in the ethane molecule causes in its transition state energy. Deuterium will be abstracted more slowly in both methane and ethane, but the rate effect will be more pronounced in methane than in ethane.

CHAPTER 5—STEREOCHEMISTRY

> Note to the student: Stereochemistry is the study of molecular structure and reactions in three dimensions. Molecular models will be especially helpful in this chapter.

5-1 The best test of whether a household object is chiral is whether it would be used equally well by a left- or right-handed person. The chiral objects are the corkscrew, the writing desk, the screw-cap bottle (only for refilling, however; in use, it would not be chiral), the rifle and the knotted rope; the corkscrew, the bottle top, and the rope each have a twist in one direction, and the rifle and desk are clearly made for right-handed users. All the other objects are achiral and would feel equivalent to right- or left-handed users.

5-2

(a) *cis*

H   H   H   H   achiral—
│   │   │   │   identical mirror images
CH₃ CH₃   CH₃ CH₃

mirror

(b) *trans*

H₃C   H   H   CH₃   chiral—
│   │   │   │   enantiomers
H   CH₃   CH₃   H

mirror

(c) *cis* first, then *trans*

H   H   achiral—
H   CH₃   H₃C   H   identical mirror images
CH₃   CH₃

mirror

CH₃   CH₃   achiral—
H   H   H   H   identical mirror images
CH₃   CH₃

mirror

(d)

CH₃   CH₃   chiral—
│   │   enantiomers
CH₃CH₂—C‴H   H‴C—CH₂CH₃
      Br   Br

mirror

79

5-2 continued

(e)

chiral—
enantiomers

mirror

(f)

chiral—
enantiomers

mirror

5-3 Asymmetric carbon atoms are starred.

(a)

no asymmetric carbons—
same structure

(b)

no asymmetric carbons—
same structure

(c)

enantiomers

(d)

no asymmetric carbons—
same structure

(e)

no asymmetric carbon—
same structure

80

5-3 continued

(f) enantiomers

(g) same structure

(h) enantiomers

(i) no asymmetric carbons—
same structure

(j) enantiomers

(k) enantiomers

5-4   You may have chosen to interchange two groups different from the ones shown here. The type of isomer produced will still be the same as listed here.

Interchanging any two groups around a chirality center will create an enantiomer of the first structure.

Interchanging the Br and the H creates an enantiomer of the structure in Figure 5-5.

Interchanging the ethyl and the isopropyl creates an enantiomer of the structure in Figure 5-5.

On a double bond, interchanging the two groups on ONE of the stereocenters will create the other geometric (cis-trans) isomer. However, interchanging the two groups on BOTH of the stereocenters will give the original structure.

original structure is cis

interchange H and CH_3 on top stereocenter to produce trans

81

5-5

(a)

plane of
symmetry

(b)

plane of
symmetry

(c)

chiral—no
plane of
symmetry

(d)

chiral—no
plane of
symmetry

(e)

chiral—no
plane of
symmetry

(f) plane of
symmetry

this view is from
the right side of the
structure as drawn
in the text

(g)

plane of
symmetry

(h)

chiral—no
plane of
symmetry

5-6   ALWAYS place the 4th priority group away from you. Then determine if the sequence 1→2→3 is clockwise (R) or counter-clockwise (S). (There is a Problem-Solving Hint near the end of section 5-3 in the text that describes what to do when the 4th priority group is closest to you.)

(a) R

(b) rotate CH₃ up

 S

(c) only one asymmetric carbon

 R

(d) S → ← S

(e) R → ← S

(f)

(g)

(h) R

(i) S →

see next page for an
explanation of part (i)

82

5-6 continued

Part (i) deserves some explanation. The difference between groups 1 and 2 hinge on what is on the "extra" oxygen.

higher priority   lower priority

5-7 There are no asymmetric carbons in 5-3 (a), (b), (d), (e), or (i).

(c)

(f)

(g)

(h)

(j)

(k)

5-8

2.0 g / 10 mL = 0.20 g/mL ; 100 mm = 1 dm

$$[\alpha]_D^{25} = \frac{+1.74°}{(0.20)(1)} = +8.7° \text{ for (+)-glyceraldehyde}$$

5-9

0.5 g / 10 mL = 0.05 g/mL ; 20 cm = 2 dm

$$[\alpha]_D^{25} = \frac{-5.0°}{(0.05)(2)} = -50° \text{ for (−)-epinephrine}$$

5-10
Measure using a solution of about one-fourth the concentration of the first. The value will be either + 45° or − 45°, which gives the sign of the rotation.

5-11
Whether a sample is dextrorotatory (abbreviated "(+)") or levorotatory (abbreviated "(−)") is determined experimentally by a polarimeter. Except for the molecule glyceraldehyde, there is no direct, universal correlation between direction of optical rotation ((+) and (−)) and designation of configuration (R and S). In other words, one dextrorotatory compound might have R configuration while a different dextrorotatory compound might have S configuration.
(a) Yes, both of these are determined experimentally: the (+) or (−) by the polarimeter and the smell by the nose.
(b) No, R or S cannot be determined by either the polarimeter or the nose.
(c) The drawings show that (+)-carvone from caraway has the S configuration and (−)-carvone from spearmint has the R configuration.

(For fun, ask your instructor if you can smell the two enantiomers of carvone. Some people are unable, presumably for genetic reasons, to distinguish the fragrance of the two enantiomers.)

(+)-carvone (caraway seed)   (−)-carvone (spearmint)

5-12

(R)-2-bromobutane   (R)-2-butanol   (S)-2-butanol
                              one-third of mixture   two-thirds of mixture

Chapter 6 will explain how these mixtures come about. For this problem, the S enantiomer accounts for 66.7% of the 2-butanol in the mixture and the rest, 33.3%, is the R enantiomer. Therefore, the excess of one enantiomer over the racemic mixture must be 33.3% of the S, the enantiomeric excess. (All of the R is "canceled" by an equal amount of the S, algebraically as well as in optical rotation.)

The optical rotation of pure (S)-2-butanol is + 13.5°. The optical rotation of this mixture is:
        33.3% x (+ 13.5°) = + 4.5°

84

5-13 The rotation of pure (+)-2-butanol is +13.5° .

$$\frac{\text{observed rotation}}{\text{rotation of pure enantiomer}} = \frac{+0.45°}{+13.5°} \text{ x } 100\% = 3.3\% \text{ optical purity}$$
$$= 3.3\% \text{ e.e.} = \text{excess of (+) over (–)}$$

To calculate percentages of (+) and (–):   (two equations in two unknowns)

(+) + (–) = 100% ⟹   (–) = 100% – (+)

(+) – (–) = 3.3% ⟹   (+) – (100% – (+)) = 3.3%

2 (+) = 103.3%

(+) = 51.6% (rounded)
(–) = 48.4%

5-14 Drawing Newman projections is the clearest way to determine symmetry of conformations.

(a)

chiral—
optically active

$$H_3C - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} \overset{*}{-} Cl$$

(b)

plane includes Br and Cl

plane of symmetry containing
Br—C—C—Cl; not optically active

$$Br - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - Cl$$

no asymmetric carbons

(c)

chiral—
optically active

$$ClCH_2 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}} \overset{*}{-} Cl$$

(d)

plane of symmetry—not optically
active despite the presence of two
asymmetric carbons

(e)

no plane of symmetry—
optically active
(other chair form is
equivalent—no plane of
symmetry)

(f)

plane of symmetry through
C-1 and C-4—not
optically active

no asymmetric carbons

Part (2) Predictions of optical activity based on asymmetric centers give the same answers as predictions based on the most symmetric conformation.

5-15

(a)

H   C=C=C   H

Cl   Cl

no asymmetric carbons, but the molecule is chiral (an allene); the drawing below is a three-dimensional picture of the allene in (a) showing there is no plane of symmetry because the substituents of an allene are in different planes

(b)

H   C=C=C   H

Cl   CH₃

no asymmetric carbons, but the molecule is chiral (an allene)

(c)

H   C=C=C   CH₃

Cl   CH₃

no asymmetric carbons; this allene has a plane of symmetry between the two methyls (the plane of the paper), including all the other atoms because the two pi bonds of an allene are perpendicular, the Cl is in the plane of the paper and the plane of symmetry goes through it; not a chiral molecule

(d)

H   H
C=C
Cl   H
C=C
H   H

planar molecule—no asymmetric carbons; not a chiral molecule

(e)

plane of symmetry bisecting the molecule; no asymmetric carbons; not a chiral molecule

(f)

CH₃
Br
I
Br

no asymmetric carbons, but the molecule is chiral due to restricted rotation; the drawing below is a three-dimensional picture showing that the rings are perpendicular (hydrogens are not shown)

(g)

D   D

H   H

no asymmetric carbons, and the groups are not large enough to restrict rotation; not a chiral compound

(h)

Cl
*
*

two asymmetric carbons; a chiral compound

86

5-16

(a)

	COOH		COOH		H		CH$_3$
H—|—OH		HO—|—H		CH$_3$—|—COOH		HO—|—H
	CH$_3$		CH$_3$		OH		COOH

enantiomer   enantiomer   same

(b)

	CH$_2$CH$_3$		CH$_3$		CH$_2$CH$_3$		CH$_3$
H—|—Br		Br—|—H		Br—|—H		H—|—Br
	CH$_3$		CH$_2$CH$_3$		CH$_3$		CH$_2$CH$_3$

same   enantiomer   enantiomer

(c)

	CH$_3$		CH$_3$		CH$_3$		CH$_2$CH$_3$
HO—|—H		H—|—OH		HO—|—H		H—|—OH
	CH$_2$CH$_3$		CH$_2$CH$_3$		CH$_2$CH$_3$		CH$_3$

(R)-2-butanol   enantiomer   same   same

Rules for Fischer projections:
1. Interchanging any two groups an odd number of times (once, three times, etc.) makes an enantiomer. Interchanging any two groups an even number of times (e.g. twice) returns to the original stereoisomer.
2. Rotating the structure by 90° makes the enantiomer. Rotating by 180° returns to the original stereoisomer. (The second rule is an application of the first. Prove this to yourself.)

5-17

(a)

	CH$_2$OH
HO—	—H
	CH$_3$

(b)

	CH$_2$OH
H—	—Br
	CH$_2$CH$_3$

(c)

	CH$_2$Br
Br—	—H
	CH$_2$CH$_3$

(d)

	CH$_3$
HO—	—H
	CH$_2$CH$_3$

(e)

	CHO
H—	—OH
	CH$_2$OH

5-18

mirror

(a)

	CHO			CHO
H—	—OH		HO—	—H
	CH$_2$OH			CH$_2$OH

180° rotation of the right structure does not give left structure; no plane of symmetry: chiral—**enantiomers**

(b)

	CH$_2$OH			CH$_2$OH
H—	—Br		----Br—	—H
	CH$_2$OH			CH$_2$OH

180° rotation of the right structure gives same structure as on the left; also has plane of symmetry: **same structure**

(c)

	CH$_2$Br			CH$_2$Br
Br—	—Br		Br—	—Br
	CH$_3$			CH$_3$

plane of symmetry: **same structure**

5-18 continued   mirror

(d)

```
        CHO                    CHO
  H  ──┼── OH          HO ──┼── H
  H  ──┼── OH          HO ──┼── H
       CH₂OH                CH₂OH
```

180 ° rotation of the right structure does not give left structure; no plane of symmetry: chiral—**enantiomers**

(e)

```
        CH₂OH                  CH₂OH
  H  ──┼── OH          HO ──┼── H
  H  ──┼── OH          HO ──┼── H
       CH₂OH                CH₂OH
```

180° rotation of the right structure gives same structure as on the left; also has plane of symmetry: **same structure**

(f)

```
        CH₂OH                  CH₂OH
  HO ──┼── H           H  ──┼── OH
  H  ──┼── OH          HO ──┼── H
       CH₂OH                CH₂OH
```

180 ° rotation of the right structure does not give left structure; no plane of symmetry: chiral—**enantiomers**

5-19 If the Fischer projection is drawn correctly, the most oxidized carbon will be at the top; this is the carbon with the greatest number of bonds to oxygen. Then the numbering goes from the top down.

(a) *R*   (d) *2R,3R*   (g) *R*
(b) no chiral center   (e) *2S,3R* (numbering down) (h) *S*
(c) no chiral center   (f) *2R, 3R*   (i) *S*

5-20
(a) enantiomers—configurations at both asymmetric carbons inverted
(b) diastereomers—configuration at only one asymmetric carbon inverted
(c) diastereomers—configuration at only one asymmetric carbon inverted (the left carbon)
(d) constitutional isomers—C=C shifted position
(e) enantiomers—chiral, mirror images
(f) diastereomers—configuration at only one asymmetric carbon inverted (the top one)
(g) enantiomers—configuration at all asymmetric carbons inverted
(h) same compound—superimposable mirror images (hard question! use a model)
(i) diastereomers—configuration at only one chirality center (the nitrogen) inverted

5-21

(a)

```
           CH₃
  Br ──*── Cl
  Br ──*── Cl
           CH₃
```
plane of symmetry

meso structure
not optically active

```
     Br        Br
  Cl╲  ╱    ╲  ╱Cl
    *          *
  H₃C          CH₃
```
plane of symmetry

88

5-21 continued

(b)

CH₃
Br ─*─ Cl
Cl ─*─ Br
CH₃

CH₃
Cl ─*─ Br
Br ─*─ Cl
CH₃

50:50

Br Cl   Br Cl
*   *
H₃C   CH₃

Cl Br   Cl Br
*   *
H₃C   CH₃

racemic mixture—not optically active, although each enantiomer by itself would be optically active

(c)

planes of
symmetry

CH₃
H ─── H
H ─── H
CH₃

not chiral
not optically active

H H   H H

H₃C   CH₃

(d)

CH₂OH
HO ─*─ H
Br ─*─ H
CH₂OH

optically active

H Br   HO H
*   *
HOH₂C   CH₂OH

(e)

CHO
H ─*─ OH
HO ─*─ H
H ─*─ OH
H ─*─ OH
CH₂OH

optically active

HO H   HO H
*   *
H   H
HO   OH

HO   H
      O

(f)

CH₃
H ─*─   *─ Br
* H   H *
Br ─*   *─ H
CH₃

not optically active—
superimposable on its
mirror image—
technically, this is
a meso structure
(may require models!)

(g)

plane of
symmetry

Br   Br
* H   H *
H   H
* CH₃   CH₃ *
H   H

meso—
not optically active

5-22

(a)

COOH
H ─── OH
H ─── Cl
CH₃

A

COOH
HO ─── H
Cl ─── H
CH₃

B

COOH
H ─── OH
Cl ─── H
CH₃

C

COOH
HO ─── H
H ─── Cl
CH₃

D

enantiomers: A and B; C and D
diastereomers: A and C; A and D; B and C; B and D

89

5-22 continued

(b)

```
        COOH                    COOH                    COOH
  H ──┼── OH   plane of   H ──┼── OH           HO ──┼── H
  ─ ─ ─┼─ ─ ─  symmetry                               
  H ──┼── OH   MESO       HO ──┼── H            H ──┼── OH
        COOH                    COOH                    COOH
         E                       F                       G
```

enantiomers: F and G
diastereomers: E and F; E and G

(c)

```
     COOH          COOH           COOH          COOH
 H ─┼─ OH     HO ─┼─ H       HO ─┼─ H       H ─┼─ OH
 H ─┼─ OH     HO ─┼─ H        H ─┼─ OH     HO ─┼─ H
 H ─┼─ Br     Br ─┼─ H        H ─┼─ Br     Br ─┼─ H
     COOH          COOH           COOH          COOH
      H             I              J             K
```

```
      COOH          COOH           COOH          COOH
 HO ─┼─ H      H ─┼─ OH       H ─┼─ OH     HO ─┼─ H
 HO ─┼─ H      H ─┼─ OH      HO ─┼─ H       H ─┼─ OH
  H ─┼─ Br     Br ─┼─ H       H ─┼─ Br     Br ─┼─ H
      COOH          COOH           COOH          COOH
       L             M              N             O
```

enantiomers: H and I; J and K; L and M; N and O
diastereomers: any pair which is not enantiomeric

(d)

```
      OH              OH              OH              OH
  H   /\   CH3    CH3  /\   H     CH3  /\  CH3     H  /\   H
    \ H /            \ H /            \ H /            \ H /
 CH3 ──── H       H ──── CH3      H ──── H       CH3 ──── CH3
      P               Q               H               H
                                plane of         plane of
                                symmetry         symmetry
                                 MESO             MESO
                                  T                U
```

enantiomers: P and Q
diastereomers: P and T; P and U;
Q and T; Q and U; T and U

5-23 Any diastereomeric pair could be separated by a physical process like distillation or crystallization. Diastereomers are found in parts (a), (b), and (d). The structures in (c) are enantiomers; they could not be separated by normal physical means.

5-24

5-25 Please refer to solution 1-20, page 12 of this Solutions Manual.

5-26

5-26 continued

(i)
$$
\begin{array}{c}
Br \\
C=C=C \\
Cl
\end{array}
\begin{array}{c}
Br \\
Cl
\end{array}
$$
chiral molecule, but
no chiral centers

(j) chiral

(k) achiral == plane of symmetry

(l) == plane of symmetry meso; achiral

(m) chiral

(n) CH$_2$ ... R → chiral

(o) chiral

(p) H$_3$C ... R NH$_2$
(NH$_2$ is group 1, CH$_3$ is group 4) chiral

5-27

(a)
$$
\begin{array}{c}
CH_3 \\
H \blacktriangleright \overset{*}{C} \blacktriangleleft Cl \\
CH_2CH_3
\end{array}
$$
→ enantiomer →
$$
\begin{array}{c}
CH_3 \\
Cl \blacktriangleright \overset{*}{C} \blacktriangleleft H \\
CH_2CH_3
\end{array}
$$
no plane of symmetry
no diastereomer
chiral structure

chiral structure

(b) → enantiomer →
no plane of symmetry
no diastereomer
chiral structure

chiral structure

(c)
$$
\begin{array}{c}
CH_3 \\
Br \blacktriangleright \overset{*}{C} \blacktriangleleft H \\
Br \blacktriangleright \overset{*}{C} \blacktriangleleft H \\
CH_2CH_2CH_3
\end{array}
$$
→ enantiomer →
$$
\begin{array}{c}
CH_3 \\
H \blacktriangleright \overset{*}{C} \blacktriangleleft Br \\
H \blacktriangleright \overset{*}{C} \blacktriangleleft Br \\
CH_2CH_2CH_3
\end{array}
$$
$$
\begin{array}{c}
CH_3 \\
H \blacktriangleright \overset{*}{C} \blacktriangleleft Br \\
Br \blacktriangleright \overset{*}{C} \blacktriangleleft H \\
CH_2CH_2CH_3
\end{array}
$$

no plane of symmetry
chiral structure

chiral structure

chiral structure
(inverting two groups on the
bottom asymmetric carbon
instead of the top one would
also give a diastereomer)

diastereomer

5-27 continued

(d)

Br — H ... Br, H (structure)
no plane of symmetry
chiral structure

enantiomer →

H, Br ... Br, H
chiral structure

diastereomer →

H, Br ... Br, H
not chiral ;
meso structure

(inverting two groups on the
right asymmetric carbon instead
of the left one would also give a
diastereomer)

(e)

CH_2CH_3
H ► C ◄ OH
---- plane of symmetry
H ► C ◄ OH
CH_2CH_3

no enantiomer
a meso structure, not chiral

diastereomer →

CH_2CH_3
HO ► C ◄ H
H ► C ◄ OH
CH_2CH_3

(inverting two groups on the
bottom asymmetric carbon
instead of the top one would
also give a diastereomer)

chiral structure

racemic mixture of enantiomers; each is chiral with no plane of symmetry

(f)

CH_2CH_3
H ► C ◄ OH
HO ► C ◄ H
CH_2CH_3

+

CH_2CH_3
HO ► C ◄ H
H ► C ◄ OH
CH_2CH_3

diastereomer ⟹

⟸ diastereomer

CH_2CH_3
H ► C ◄ OH
---- plane of symmetry
H ► C ◄ OH
CH_2CH_3

this meso structure is a diastereomer of each of the
enantiomers; it is not chiral

5-28

(a)

CH_2OH
H — OH
CH_3

(b)

CHO
H — Br
CH_3

(c)

CH_2OH
H — Br
HO — H
CH_3

(d)

CH_2OH
HO — H
H — OH
CH_3

93

5-29 Your drawings may look different from these and still be correct. Check configuration by assigning *R* and *S* to be sure.

(a) (b) (c) (d)

5-30

(a) same (meso)—plane of symmetry, superimposable
(b) enantiomers—configuration inverted at both asymmetric carbon atoms
(c) enantiomers—configuration inverted at both asymmetric carbon atoms
(d) enantiomers—solve this problem by switching two groups at a time to put the groups in the same positions as in the first structure; it takes three switches to make the identical compound, so they are enantiomers; an even number of switches would prove they are the same structure
(e) enantiomers—configuration inverted at both asymmetric carbon atoms
(f) diastereomers—configuration inverted at only one asymmetric carbon
(g) enantiomers—configuration inverted at both asymmetric carbon atoms
(h) same compound—rotate the right structure 180° around a horizontal axis and it becomes the left structure

5-31 Drawing the enantiomer of a chiral structure is as easy as drawing its mirror image.

(a) (b) (c) (d)

(e)

(f) plane of symmetry—
no enantiomer

(g) (h) (i)

5-32

(a) 1.00 g / 20.0 mL = 0.050 g/mL ; 20.0 cm = 2.00 dm

$$[\alpha]_D^{25} = \frac{-1.25°}{(0.0500)(2.00)} = -12.5°$$

(b) 0.050 g / 2.0 mL = 0.025 g/mL ; 2.0 cm = 0.20 dm

$$[\alpha]_D^{25} = \frac{+0.043°}{(0.025)(0.20)} = +8.6°$$

5-33 The 32% of the mixture that is (–)-tartaric acid will cancel the optical rotation of the 32% of the mixture that is (+)-tartaric acid, leaving only (68 – 32) = 36% of the mixture as excess (+)-tartaric acid to give measurable optical rotation. The specific rotation will therefore be only 36% of the rotation of pure (+)-tartaric acid: (+ 12.0°) x 36% = + 4.3°

5-34
(a)

(b) Rotation of the enantiomer will be equal in magnitude, opposite in sign: $-15.90°$.

(c) The rotation $-7.95°$ is what percent of $-15.90°$?

$$\frac{-7.95°}{-15.90°} \text{ x } 100\% = 50\% \text{ e.e.}$$

There is 50% excess of (R)-2-iodobutane over the racemic mixture; that is, another 25% must be R and 25% must be S. The total composition is 75% (R)-$(-)$-2-iodobutane and 25% (S)-$(+)$-2-iodobutane.

5-35 All structures in this problem are chiral.

(a)

A   B   C   D

enantiomers: **A** and **B**; **C** and **D**
diastereomers: **A** and **C**; **A** and **D**; **B** and **C**; **B** and **D**

(b)

E   F   G   H

enantiomers: **E** and **F**; **G** and **H**
diastereomers: **E** and **G**; **E** and **H**; **F** and **G**; **F** and **H**

5-35 continued

(c) This structure is a challenge to visualize. A model helps. One way to approach this problem is to assign R and S configurations. Each arrow shows a change at one asymmetric carbon.

Summary

$RSSS$ (**K**) is the enantiomer of $RRRS$ (**M**)

$SSSS$ (**L**) is the enantiomer of $RRRR$ (**P**)

The structures with two R carbons and two S carbons (**J**, **N**, and **O**) have special symmetry. **J** is a meso structure; it has chirality centers and is superimposable on its mirror image—see Problem 5-20(h). **N** and **O** are enantiomers, and are diastereomers of all of the other structures. Give yourself a gold star if you got this correct!

5-36

C and D are enantiomers. All other pairs are diastereomers.

*Structures **A** and **B** are both meso structures, but they are clearly different from each other. How can they be distinguished? One of the advanced rules of the Cahn-Ingold-Prelog system says: When two groups attached to an asymmetric carbon differ only in their absolute configuration, then the neighboring (R) stereocenter takes priority. Now the configuration of the central asymmetric carbon can be assigned: S for structure **A**, and R for structure **B**. This rule also applies to problem 5-37. (Thanks to Dr. Kantorowski for this explanation.)

5-37 This problem is similar to 5-36.

(a)

| **A** | diastereomers | **B** | | **C** | enantiomers | **D** |
| meso | | meso | | chiral | | chiral |

(b)   2S,4R   2S,4R   2R,4R   2S,4S
      equivalent   equivalent
      to 2R,4S   to 2R,4S

The configuration of carbon-3 in **A** and **B** can be assigned according the rule described above in the solution to problem 5-36: C-3 in **A** is *S*, and C-3 in **B** is *R*.

(c) According to the IUPAC designation described in text Section 5-2B, a chirality center is "any atom holding a set of ligands in a spatial arrangement which is not superimposable on its mirror image." An asymmetric carbon must have four different groups on it, but in **A** and **B**, C-3 has two groups that are identical (except for their stereochemistry). C-3 holds its groups in a spatial arrangement that is superimposable on its mirror image, so it is not a chirality center. But it is stereogenic: in structure **A**, interchanging the H and Br at C-3 gives structure **B**, a diastereomer of **A**; therefore, C-3 is stereogenic.

(d) In structure **C** or **D**, C-3 is not stereogenic. Inverting the H and the Br, then rotating the structure 180°, shows that the same structure is formed. Therefore, interchanging two atoms at C-3 does *not* give a stereoisomer, so C-3 does not fit the definition of a stereogenic center.

5-38 The Cahn-Ingold-Prelog priorities of the groups are the circled numbers in (a).

(a)

(R)-3,4-dimethyl-1-pentene   (S)-2,3-dimethylpentane

(b) The reaction did not occur at the asymmetric carbon atom, so the configuration has not changed—the reaction went with retention of configuration at the asymmetric carbon.

(c) The *name* changed because the *priority* of groups in the Cahn-Ingold-Prelog system of nomenclature changed. When the alkene became an ethyl group, its priority changed from the highest priority group to priority 2. (We will revisit this anomaly in problem 6-21(c).)

(d) There is no general correlation between *R* and *S* designation and the physical property of optical rotation. Professor Wade's poetic couplet makes an important point: do not confuse an object and its properties with the *name* for that object. (Scholars of Shakespeare have come to believe that this quote from Juliet is a veiled reference to designation of *R,S* configuration versus optical rotation of a chiral molecule. Shakespeare was *way* ahead of his time.)

5-39

(a) The product has no asymmetric carbon atoms but it has three stereocenters: the carbon with the OH, plus both carbons of the double bond. Interchange of two bonds on any of these makes the enantiomer.

(b) The product is an example of a chiral compound with no asymmetric carbons. Like the allenes, it is classified as an "extended tetrahedron"; that is, it has four groups that extend from the rigid molecule in four different directions. (A model will help.) In this structure, the plane containing the COOH and carbons of the double bond is perpendicular to the plane bisecting the OH and H and carbon that they are on. Since the compound is chiral, it is capable of being optically active.

(c) As shown in text Figure 5-16, Section 5-6, catalytic hydrogenation that creates a new chirality center creates a racemic mixture (both enantiomers in a 1:1 ratio). A racemic mixture is not optically active. In contrast, by using a chiral enzyme to reduce the ketone to the alcohol (as in part (b)), an excess of one enantiomer was produced, so the product was optically active.

CHAPTER 6—ALKYL HALIDES: NUCLEOPHILIC SUBSTITUTION AND ELIMINATION

6-1 In problems like part (a), draw out the whole structure to detect double bonds.

(a) vinyl halide   (c) aryl halide   (e) vinyl halide
(b) alkyl halide   (d) alkyl halide   (f) aryl halide

6-2 (a) H   (b) Br   (c)   (d) I   (e) Br
    I – C – I   Br – C – Br   I – C – H
        H   Br   I

    (f)   (g) H   CH₂F   (h)
                          H   —Cl   or   (CH₃)₃CCl
         Br   F

6-3 IUPAC name; common name; degree of halogen-bearing carbon

(a) 1-chloro-2-methylpropane; isobutyl chloride; 1°
(b) diiodomethane; methylene iodide; methyl
(c) 1,1-dichloroethane; no common name; 1°
(d) 2-bromo-1,1,1-trichloroethane; no common name; all 1°
(e) trichloromethane; chloroform; methyl
(f) 2-bromo-2-methylpropane; t-butyl bromide; 3°
(g) 2-bromobutane; sec-butyl bromide; 2°
(h) 1-chloro-2-methylbutane; no common name; 1°
(i) cis-1-bromo-2-chlorocyclobutane; no common name; both 2°
(j) 3-bromo-4-methylhexane; no common name; 2°
(k) 4-fluoro-1,1-dimethylcyclohexane; no common name; 2°
(l) trans-1,3-dichlorocyclopentane; no common name; all 2°

6-4

Kepone®

Chlordane®

99

6-5 From the text, Section 2-9B, the bond dipole moment depends not only on bond length but also on charge separation, which in turn depends on the difference in electronegativities of the two atoms connected by the bond. Because chlorine's electronegativity (3.2) is significantly higher than iodine's (2.7), the C—Cl bond dipole is greater than that of C—I, despite C—I being a longer bond.

6-6

(a) *n*-Butyl bromide has a higher molecular weight and less branching, and boils at a higher temperature than isopropyl bromide.

(b) *t*-Butyl bromide has a higher molecular weight and a larger halogen, and despite its greater branching, boils at a higher temperature than isopropyl chloride.

(c) *n*-Butyl bromide has a higher molecular weight and a larger halogen, and boils at a higher temperature than *n*-butyl chloride.

6-7 From Table 3-2, the density of hexane is 0.66; it will float on the water layer (d 1.00). From Table 6-2, the density of chloroform is 1.50; water will float on the chloroform. Water is immiscible with many organic compounds; whether water is the top layer or bottom layer depends on whether the other material is more dense or less dense than water. (This is an important consideration to remember in lab procedures.)

6-8

(a) Step (1) is initiation; steps (2) and (3) are propagation.

(1) $\quad$ Br — Br $\xrightarrow{\text{hv}}$ 2 Br •

(2) $\quad$ H$_2$C=C(H)—CH$_2$ + Br • $\longrightarrow$ HBr + { H$_2$C=C(H)—ĊH$_2$ $\longleftrightarrow$ H$_2$Ċ—C(H)=CH$_2$ }

(3) $\quad$ H$_2$C=C(H)—ĊH$_2$ + Br—Br $\longrightarrow$ H$_2$C=C(H)—CH$_2$—Br + Br •

(b) Step (2): break allylic C—H, make H—Br: kJ/mole: + 364 – (+ 368) = – 4 kJ/mole

$\qquad$ kcal/mole: + 87 – (+ 88) = – 1 kcal/mole

$\quad$ Step (3): break Br—Br, make allylic C—Br: kJ/mole: + 192 – (+ 280) = – 88 kJ/mole

$\qquad$ kcal/mole: + 46 – (+ 67) = – 21 kcal/mole

ΔH overall = – 4 + – 88 = – 92 kJ/mole $\quad$ (– 1 + – 21 = – 22 kcal/mole)
This is a very exothermic reaction; it is reasonable to expect a small activation energy in step (1), so this reaction should be very rapid.

6-9 $\quad$ (a) propagation steps

repeats chain mechanism

100

6-9   continued

The resonance-stabilized allylic radical intermediate has radical character on both the 1° and 3° carbons, so bromine can bond to either of these carbons producing two isomeric products.

(b) Allylic bromination of cyclohexene gives 3-bromocyclohex-1-ene regardless of whether there is an allylic shift. Either pathway leads to the same product. If one of the ring carbons were somehow marked or labeled, then the two products can be distinguished. (We will see in following chapters how labeling is done experimentally.)

the second structure from an allylic shift is *identical* to the first structure—only one compound is produced

6-10

(a)

This compound has only one type of hydrogen—only one monochlorine isomer can be produced.

(b)

Bromination has a strong preference for abstracting hydrogens (like 3°) that give stable radical intermediates.

(c)

Bromine atom will abstract the hydrogen giving the most stable radical; in this case, the radical intermediate will be stabilized by resonance with the benzene ring.

(d)

the second structure from an allylic shift is *identical* to the first structure—only one compound is produced

Bromine atom will abstract the hydrogen giving the most stable radical; in this case, the radical intermediate will be stabilized by resonance with the benzene ring.

6-11
(a) substitution—Br is replaced
(b) elimination—H and OH are lost
(c) elimination—both Br atoms are lost

6-12

(a) $CH_3(CH_2)_4CH_2 - OCH_2CH_3$ (b) $CH_3(CH_2)_4CH_2 - CN$ (c) $CH_3(CH_2)_4CH_2 - OH$

6-13 The rate law is first order in both 1-bromobutane, C_4H_9Br, and methoxide ion. If the concentration of C_4H_9Br is lowered to one-fifth the original value, the rate must decrease to one-fifth; if the concentration of methoxide is doubled, the rate must also double. Thus, the rate must decrease to 0.02 mole/L per second:

$$\text{rate} = \underset{\text{original rate}}{(0.05 \text{ mole/L per second})} \times \underset{\substack{\text{change in} \\ C_4H_9Br}}{\frac{(0.1 \text{ M})}{(0.5 \text{ M})}} \times \underset{\substack{\text{change in} \\ NaOCH_3}}{\frac{(2.0 \text{ M})}{(1.0 \text{ M})}} = \underset{\text{new rate}}{0.02 \text{ mole/L per second}}$$

A completely different way to answer this problem is to solve for the rate constant k, then put in new values for the concentrations.

rate $= k$ $[C_4H_9Br]$ $[NaOCH_3]$ $\Longrightarrow$ 0.05 mole L^{-1} sec^{-1} = k (0.5 mol L^{-1}) (1.0 mol L^{-1}) $\Longrightarrow$

rate constant k = 0.1 L mol^{-1} sec^{-1}

rate $= k$ $[CH_3I]$ $[NaOH]$ = (0.1 L mol^{-1} sec^{-1}) (0.1 mol L^{-1}) (2.0 mol L^{-1}) = 0.02 mole L^{-1} sec^{-1}

6-14 Organic and inorganic products are shown here for completeness.

(a) $(CH_3)_3C$ — O — CH_2CH_3 + KBr

(b) HC≡C — $CH_2CH_2CH_2CH_3$ + NaCl

(c) $(CH_3)_2CHCH_2$ — $\overset{+}{N}H_3$ $\overset{-}{B}r$ $\xrightarrow{NH_3}$ $(CH_3)_2CHCH_2$ — NH_2 + $\overset{+}{N}H_4$ $\overset{-}{B}r$

(d) CH_3CH_2 — CN + NaI

(e) ⟋⟍⟋⟍^{I} + NaCl

(f) ⟋⟍⟋⟍^{F} + KCl (18-crown-6 is the catalyst and does not change; CH_3CN is the solvent)

6-15 All reactions in this problem follow the same pattern; the only difference is the nucleophile (⁻:Nuc). Only the nucleophile is listed below. (Cations like Na$^+$ or K$^+$ accompany the nucleophile but are simply spectator ions and do not take part in the reaction; they are not shown here.)

⟋⟍⟋^{Cl} + ⁻:Nuc $\longrightarrow$ ⟋⟍⟋^{Nuc} + Cl$^-$

1-chlorobutane

(a) HO$^-$ (b) F$^-$ from KF/18-crown-6 (c) I$^-$ (d) $^-$CN (e) HC≡C$^-$

(f) $^-OCH_2CH_3$ (g) excess NH_3 (or $^-NH_2$)

6-16
(a) $(CH_3CH_2)_2NH$ is a better nucleophile—less hindered
(b) $(CH_3)_2S$ is a better nucleophile—S is larger, more polarizable than O
(c) PH_3 is a better nucleophile—P is larger, more polarizable than N
(d) CH_3S^- is a better nucleophile—anions are better than neutral atoms of the same element
(e) $(CH_3)_3N$ is a better nucleophile—less electronegative than oxygen, better able to donate an electron pair
(f) CH_3S^- is a better nucleophile—anions are generally better than neutral atoms, and S is larger and more polarizable than O
(g) $CH_3CH_2CH_2O^-$ is a better nucleophile—less branching, less steric hindrance
(h) I$^-$ is a better nucleophile—larger, more polarizable

6-17 A mechanism must show *electron movement*.

$$CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH_3 \ + \ H^+ \ \rightleftharpoons \ CH_3-\overset{\overset{H}{|}}{\underset{\cdot\cdot}{\overset{+}{O}}}-CH_3 \ + \ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:^- \ \longrightarrow \ CH_3-\overset{\overset{H}{|}}{\underset{\cdot\cdot}{O}}: \ + \ CH_3-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}}:$$

Protonation converts OCH_3 to a good leaving group.

6-18 The type of carbon with the halide, and relative leaving group ability of the halide, determine the reactivity.

methyl iodide > methyl chloride > ethyl chloride > isopropyl bromide >> neopentyl bromide, *t*-butyl iodide $\Big\}$ *least reactive*

most reactive

Predicting the relative order of neopentyl bromide and *t*-butyl iodide would be difficult because both would be extremely slow.

6-19 In all cases, the less hindered structure is the better S_N2 substrate.

(a) 2-methyl-1-iodopropane (1° versus 3°)

(b) cyclohexyl bromide (2° versus 3°)

(c) isopropyl bromide (no substituent on neighboring carbon)

(d) 2-chlorobutane (even though this is a 2° halide, it is easier to attack than the 1° neopentyl type in 2,2-dimethyl-1-chlorobutane—see below)

(e) isopropyl iodide (same reason as in (d))

a neopentyl halide—hindered to backside attack by neighboring methyl groups

6-20 All S_N2 reactions occur with inversion of configuration at carbon.

(a)

(b)

6-20 continued

(c)

(d)

(e)

(f)

6-21

(a) The best leaving groups are the weakest bases. Bromide ion is so weak it is not considered at all basic; it is an excellent leaving group. Fluoride is moderately basic, by far the most basic of the halides. It is a terrible leaving group. Bromide is many orders of magnitude better than fluoride in leaving group ability.

(b)

transition state

(c) As noted on the structure above, the configuration is inverted even though the designations of the configuration for both the starting material and the product are *S*; the oxygen of the product has a lower priority than the bromine it replaces. Refer to the solution to problem 5-38, p. 97, for the caution about confusing absolute configuration with the *designation* of configuration.

(d) The result is perfectly consistent with the S_N2 mechanism. Even though both the reactant and the product have the *S* designation, the configuration has been inverted: the nomenclature priority of fluorine changes from second (after bromine) in the reactant to first (before oxygen) in the product. While the designation may be misleading, the structure shows with certainty that an inversion has occurred.

6-22

6-23 The structure that can form the more stable carbocation will undergo S_N1 faster.

(a) 2-bromopropane: will form a 2° carbocation
(b) 2-bromo-2-methylbutane: will form a 3° carbocation
(c) allyl bromide is faster than *n*-propyl bromide: allyl bromide can form a resonance-stabilized intermediate.
(d) 2-bromopropane: will form a 2° carbocation
(e) 2-iodo-2-methylbutane is faster than *t*-butyl chloride (iodide is a better leaving group than chloride)
(f) 2-bromo-2-methylbutane (3°) is faster than ethyl iodide (1°); although iodide is a somewhat better leaving group, the difference between 3° and 1° carbocation stability dominates

6-24 Ionization is the rate-determining step in S_N1. Anything that stabilizes the intermediate will speed the reaction. Both of these compounds form resonance-stabilized intermediates.

6-25

105

6-26 It is important to analyze the structure of carbocations to consider if migration of any groups from adjacent carbons will lead to a more stable carbocation. As a general rule, if rearrangement would lead to a more stable carbocation, a carbocation will rearrange. (Beginning with this problem, only those unshared electons pairs involved in a particular step will be shown.)

(a)

nucleophilic attack on unrearranged carbocation

unrearranged product

nucleophilic attack after carbocation rearrangement

Methyl shift to the
2° carbocation forms a
more stable 3° carbocation.

rearranged product

(b)

nucleophilic attack on unrearranged carbocation

unrearranged
product

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6-26(b) continued

nucleophilic attack after carbocation rearrangement

Hydride shift to the
2° carbocation forms a
more stable 3° carbocation.

rearranged
product

(c)

Note: braces are used to indicate
the ONE chemical species represented
by multiple resonance forms.

nucleophilic attack on unrearranged carbocation

unrearranged
product

The most basic species in a mixture is the most likely to remove a proton.
In this reaction, acetic acid is more basic than iodide ion.

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6-26(c) continued

nucleophilic attack after carbocation rearrangement

allylic—resonance-stabilized

rearranged product

(removes H⁺ as on p. 107)

plus two other resonance forms as shown on p. 107

Comments on 6-26(c)

(1) The hydride shift to a 2° carbocation generates an allylic, resonance-stabilized 2° carbocation.

(2) The double-bonded oxygen of acetic acid is more nucleophilic because of the resonance forms it can have after attack. (See Solved Problem 1-5 and Problem 1-16 in the text.)

(3) Attack on only one carbon of the allylic carbocation is shown. In reality, both positive carbons would be attacked in equal amounts, but they would give the identical product *in this case*. In other compounds, however, attack on the different carbons might give different products. ALWAYS CONSIDER ALL POSSIBILITIES.

(d)

The 1° carbocation initially formed is very unstable; some chemists believe that rearrangement occurs at the same time as the leaving group leaves. At most, the 1° carbocation has a very short lifetime.

hydride shift followed by nucleophilic attack

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6-26 (d) continued

alkyl migration (ring expansion) followed by nucleophilic attack

6-27

(a) $CH_3 - \underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - O - \overset{\overset{O}{\|}}{C} - CH_3$

$S_N1, 3°$

(b) $CH_3 - \underset{\underset{CH_3}{|}}{CH}CH_2OCH_3$

$S_N2, 1°$

(c) CH_3 ⟨ ⟩ OCH_2CH_3

$S_N1, 3°$

(d) ⟨ ⟩ OCH_3

S_N1, weak nucleophile

(e) ⟨ ⟩ OCH_2CH_3

S_N2, strong nucleophile

6-28

(R)-2-bromobutane → $\xrightarrow[\substack{S_N2-\\ \text{inversion}}]{H_2O, \Delta}$ (S)-2-butanol

$\xrightarrow[\substack{S_N1-\\ \text{racemization}}]{H_2O, \Delta}$ (R)-2-butanol + (S)-2-butanol

50 : 50 mixture—racemic

If S_N1, which gives racemization, occurs exactly twice as fast as S_N2, which gives inversion, then the racemic mixture (50 : 50 $R + S$) is 66.7% of the mixture and the rest, 33.3%, is the S enantiomer from S_N2. Therefore, the excess of one enantiomer over the racemic mixture must be 33.3%, the enantiomeric excess. (In the racemic mixture, the R and S "cancel" each other algebraically as well as in optical rotation.)

The optical rotation of pure (S)-2-butanol is + 13.5°. The optical rotation of this mixture is:

33.3% x + 13.5° = + 4.5°

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6-29

(a) Methyl shift may occur simultaneously with ionization. The lifetime of 1° carbocations is exceedingly short; some chemists believe that they are only a transition state to the rearranged product.

(b) Alkyl shift may occur simultaneously with ionization.

6-30

(a)

The S_N1 mechanism begins with ionization to form a carbocation, attack of a nucleophile, and in the case of ROH nucleophiles, removal of a proton by a base to form a neutral product.

(b) In the E1 reaction, the solvent (methanol, in this case) serves two functions: it aids the ionization process by solvating both the leaving group (bromide) and the carbocation; and second, it serves as a base to remove the proton from a carbon adjacent to the carbocation in order to form the carbon-carbon double bond. The S_N1 mechanism adds a third function to the solvent: the first step is the same as in E1, ionization to form the carbocation; the second step has the solvent acting as a nucleophile—this step is different from E1; third, the solvent acts like a base and removes a proton, although from an oxygen (S_N1) and not a carbon (E1). Solvents are versatile!

110

6-31 This solution does not show complete mechanisms. Rather, it shows the general sequence of all four pathways leading to five different products.

2-bromo-3-methylbutane

ionization

unrearranged 2° carbocation

hydride shift

rearranged 3° carbocation

S_N1

E1

S_N1

E1

CH₃CH₂

Five unique products shown in the boxes. One alkene can be produced from either the 2° or the 3° carbocation.

two possible E1 products

same compound

two possible E1 products

6-32

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6-33 Substitution products are shown first, then elimination products.

(a)

(b)

(c)

without rearrangement   with rearrangement

(d)

6-34 Et is the abbreviation for ethyl, so EtOH is ethanol.

S_N1 product:

E1—MAJOR product— more substituted alkene

E1—MINOR product— more substituted alkene

6-35   without rearrangement   with rearrangement

6-36

NaOCH₂CH₃

E2—minor
product—less
substituted alkene
(monosubstituted)

E2—major
product—more
substituted alkene
(trisubstituted)

OCH₂CH₃

S_N2—probably
very small amount
because of steric
hindrance

6-37

(a)

Br

NaOCH₃

minor alkene—
monosubstituted

major alkene—
disubstituted
(cis + trans)

OCH₃

S_N2 product—some
will be formed on a
2° carbon

(b)

Br

NaOMe

major alkene—
trisubstituted
(cis + trans)

minor alkene—
disubstituted

No S_N2 product will be
formed; S_N2 cannot
occur at a 3° carbon.

(c)

Br

NaOH

minor alkene—
monosubstituted

major alkene—
trisubstituted

OH

S_N2 product—very
small amount because
2° carbon is hindered

(d)

Br

H,,, CH₃

H

NaOEt

CH₃

minor alkene—
disubstituted

CH₃

major alkene—
trisubstituted

OEt

CH₃

S_N2 product showing
inversion at the
carbon—some of this
product will be formed
●n a 2° carbon

H atoms that are
removed are shown

Br

H

CH₃   S_N2   ⁻:ÖCH₂CH₃

H H

E2—
major

E2—minor

6-38   In systems where free rotation is possible, the H to be abstracted by the base and the leaving group (Br here) must be anti-coplanar. The E2 mechanism is a concerted, one-step mechanism, so the arrangement of the other groups around the carbons in the starting material is retained in the product; there is no intermediate to allow time for rotation of groups. (Models will help.)

H and Br anti-coplanar   transition state

only geometric isomer possible from a concerted mechanism

trans

- - - - - - - = stretched bond being broken or formed

orbital picture of this reaction

transition state

trans

pi bond

The other diastereomer has two groups interchanged on the back carbon of the Newman projection, where it must give the *cis*-alkene.

pi bond

cis

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6-39 Iin this problem, all new internal alkenes form *cis* isomers as well as the *trans* isomers shown.

Section 1

Section 2

Section 3

Section 4

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6-39 continued

Section 5

S_N2

E2 + E2

6-40

(a) Ethoxide is a strong base/nucleophile—second-order conditions. The 1° bromide favors substitution over elimination, so S_N2 will predominate over E2.

substitution—major   elimination—minor

(b) Methoxide is a strong base/nucleophile—second-order conditions. The 2° chloride will undergo S_N2 by backside attack as well as E2 to make a mixture of alkenes.

OCH₃

substitution   elimination—
minor alkene

elimination—
major alkene
(*cis + trans*)

(c) Ethoxide is a strong base/nucleophile—second-order conditions. The 3° bromide is hindered and cannot undergo S_N2 by backside attack. E2 is the only route possible.

$$CH_3-C=CH_2$$
$$|$$
$$CH_3$$

(d) Heating in ethanol is conditions for solvolysis, an S_N1 reaction.

$$OCH_2CH_3$$
$$|$$
$$CH_3-C-CH_3$$
$$|$$
$$CH_3$$

(e) Hydroxide is a strong base/nucleophile—second-order conditions. The 1° iodide is more likely to undergo S_N2 than E2, but both products will be observed.

$$CH_3-CHCH_2OH$$ $$CH_3-C=CH_2$$
$$|$$ $$|$$
$$CH_3$$ $$CH_3$$
substitution—major   elimination—minor

(f) Silver nitrate in ethanol/water is ionizing conditions for 1° alkyl halides that will lead to rearrangement followed by substitution on the 3° carbocation.

$$OCH_2CH_3$$ from ethanol as $$OH$$ from water as
$$|$$ nucleophile $$|$$ nucleophile
$$CH_3-C-CH_3$$ $$CH_3-C-CH_3$$
$$|$$ $$|$$
$$CH_3$$ $$CH_3$$

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6-40 continued

(g) Silver nitrate in ethanol/water is ionizing conditions for 1° alkyl halides that will lead to rearrangement followed by substitution on the 3° carbocation.

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OCH_2CH_3}{|}}{C}} - CH_2CH_3 \quad \text{from ethanol as nucleophile}$$

$$CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}} - CH_2CH_3 \quad \text{from water as nucleophile}$$

(h) Heating a 3° halide in methanol is quintessential first-order conditions, either E1 or S_N1 (solvolysis).

substitution
(S_N1)

(trace)

elimination (E1)

(i) Ethoxide in ethanol on a 3° halide will lead to E2 elimination; there will be no substitution.

major alkene
trisubstituted

minor alkene
disubstituted

6-41 Please refer to solution 1-20, page 12, of this Solutions Manual.

6-42 (a) (b) (c) (d)

$$Cl - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - CH_2OH$$

(e) (f) (g) (h) (i)

$$H - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - H$$

$$Cl - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - H$$

$$I - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_2CH_3}{|}}{C}} - CH_3$$

6-43

(a) 2-bromo-2-methylpentane
(b) 1-chloro-1-methylcyclohexane
(c) 1,1-dichloro-3-fluorocycloheptane

(d) 4-(2-bromoethyl)-3-(fluoromethyl)-2-methylheptane
(e) 4,4-dichloro-5-cyclopropyl-1-iodoheptane
(f) *cis*-1,2-dichloro-1-methylcyclohexane

6-44 Ease of backside attack (less steric hindrance) decides which undergoes S_N2 faster in all these examples except (b).

(a) ⟍⟋⟍Cl   faster than   ⟍⟋⟍ Cl   Primary R-X reacts faster than 2° R-X.

(b) ⟍⟋⟍I   faster than   ⟍⟋⟍Cl   Iodide a better leaving group than chloride.

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6-44 continued

(c) 　faster than　　Less branching on a neighboring carbon.

(d) 　faster than　　Same neighboring branching, so 1° faster than 2°.

(e) —CH$_2$Cl　faster than　 —Cl　Primary R-X reacts faster than 2° R-X.

(f) 　faster than　　Less branching on a neighboring carbon.

6-45 Formation of the more stable carbocation decides which undergoes S_N1 faster in all these examples except (d).

(a) 3° 　faster than　 2°

(b) 2° Cl　faster than　 1°

(c) —Br 2°　faster than　 —CH$_2$Br 1°

(d) —I　faster than　 —Cl　(leaving group ability)

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(e) 3°　faster than　 Br 2°

(f) 2° **allylic**　faster than　 2°

6-46 For S_N2, reactions should be designed such that the nucleophile attacks the least highly substituted alkyl halide. ("X" stands for a halide: Cl, Br, or I.)

(a)

(b)

(c)

(d)

(e) $H_2C = CHCH_2X + \ ^-CN \longrightarrow H_2C = CHCH_2CN$

(f) $(CH_3)_3C-O^- + X-CH_3 \longrightarrow (CH_3)_3C-O-CH_3$

(g) $HC \equiv C^- + X-CH_2CH_2CH_3 \longrightarrow HC \equiv C-CH_2CH_2CH_3$

6-47

(a) (1)

this bond formed

(2)

this bond formed

Synthesis (1) would give a better yield of the desired ether product. (1) uses S_N2 attack of a nucleophile on a 1° carbon, while (2) requires attack on a more hindered 2° carbon. Reaction (2) would give a lower yield of substitution, with more elimination.

(b) CANNOT DO S_N2 ON A 3° CARBON!

bumps into H before it can find C

elimination (E2) competes

6-47 (b) continued on next page

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6-47 (b) continued

Better to do S_N2 on a methyl carbon:

6-48

(a) S_N2—second order: reaction rate doubles
(b) S_N2—second order: reaction rate increases six times
(c) Virtually all reaction rates, including this one, increase with a temperature increase.

6-49 This is an S_N1 reaction; the rate law depends only on the substrate concentration, not on the nucleophile concentration.

(a) no change in rate
(b) the rate triples, dependent only on [t-butyl bromide]
(c) Virtually all reaction rates, including this one, increase with a temperature increase.

6-50 The key to this problem is that iodide ion is both an excellent nucleophile AND leaving group. Substitution on chlorocyclohexane is faster with iodide than with cyanide (see Table 6-3 for relative nucleophilicities). Once iodocyclohexane is formed, substitution by cyanide is much faster on iodocyclohexane than on chlorocyclohexane because iodide is a better leaving group than chloride. So two fast reactions involving iodide replace a slower single reaction, resulting in an overall rate increase.

6-51

6-52

(a)

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6-52 continued

(b)

(i)
equivalent resonance forms

(ii)

(iii)
equivalent resonance forms

(iv)
loss of bromide gives unstable 1° carbocation that quickly rearranges to a 2° allylic carbocation

equivalent resonance forms—same as from part (iii)

(c) Only one substitution product arises from equivalent resonance forms.

(i)

(ii)

(iii)
cis + trans

(iv)
cis + trans   same as part (iii)

6-53

most stable

allylic (+ on 3° and 2° C) > allylic (+ on 1° and 2° C) > 3° > 2° > 1°

least stable

6-54

6-55 Reactions would also give some elimination products; only the substitution products are shown here.

(a)

$N\equiv C\blacktriangleright C\blacktriangleleft H$

CH$_3$

CH$_2$CH$_3$

S$_N$2 gives inversion:
only product:

(b)

CH$_3$

$H\blacktriangleright C\blacktriangleleft OH$

$H\blacktriangleright C\blacktriangleleft CH_3$

CH$_2$CH$_3$

S$_N$2 only
with inversion

(c)

CH$_2$CH$_3$

$CH_3CH_2O\blacktriangleright C\blacktriangleleft CH_3$ + $CH_3\blacktriangleright C\blacktriangleleft OCH_2CH_3$

CH(CH$_3$)$_2$

CH$_2$CH$_3$

CH(CH$_3$)$_2$

solvolysis, S$_N$1, racemization

6-56

(a) CH$_3$CH$_2$OCH$_2$CH$_3$

(b) 〈〉—CH$_2$CH$_2$CN

(c) 〈〉—SCH$_2$CH$_3$

(d) CH$_3$(CH$_2$)$_8$CH$_2$—C≡CH

(e) 〈N$^+$〉-CH$_3$ I$^-$

(f) (CH$_3$)$_3$C—CH$_2$CH$_2$NH$_2$

(g) 〈O〉

(h) HO····〈〉····CH$_3$

6-57   <u>substitution</u>

Regardless of which bromine is substituted on each molecule, the same mixture of products results.

Each of the substitution products has one chiral center inverted from the starting material. The mechanism that accounts for inversion is S_N2. If an S_N1 process were occurring, the product mixture would also contain 2R,3R and 2S,3S diastereomers. Their absence argues against an S_N1 process occurring here.

<u>elimination</u>

The other enantiomer gives the same product (you should prove this to yourself).

The absence of *cis* product is evidence that only the E2 elimination is occurring in one step through an anti-coplanar transition state with no chance of rotation. If E1 had been occuring, rotation around the carbocation intermediate would have been possible, leading to both the *cis* and *trans* products.

6-58

(a) $\dfrac{+15.58°}{+15.90°}$ x 100% = 98% of original optical activity = 98% e.e.

Thus, 98% of the *S* enantiomer and 2% racemic mixture gives an overall composition of 99% *S* and 1% *R*.

(b)   The 1% of radioactive iodide has produced exactly 1% of the *R* enantiomer. Each substitution must occur with inversion, a classic S_N2 mechanism.

6-59

(a) An S_N2 mechanism with inversion will convert *R* to its enantiomer, *S*. An accumulation of excess *S* does not occur because it can also react with bromide, regenerating *R*. The system approaches a racemic mixture at equilibrium.

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6-59 continued

(b) In order to undergo substitution and therefore inversion, HO^- would have to be the leaving group, but HO^- is never a leaving group in S_N2. No reaction can occur.

(c) Once the OH is protonated, it can leave as H_2O. Racemization occurs in the S_N1 mechanism because of the planar, achiral carbocation intermediate which "erases" all stereochemistry of the starting material. Racemization occurs in the S_N2 mechanism by establishing an equilibrium of R and S enantiomers, as explained in 6-59(a).

6-60

(a)

major   minor   trace amount

The carbocation produced in this E1 elimination is 3° and will not rearrange. The product ratio follows the Zaitsev rule.

(b)

trace—from unrearranged 2° carbocation   from either unrearranged 2° carbocation or rearranged 3° carbocation   from rearranged 3° carbocation

The carbocation produced in this E1 elimination is 2° and can either eliminate to give the first two alkenes, or can rearrange by a hydride shift to a 3° carbocation which would produce the last two products. The amounts of the last two products are not predictable as they are both trisubstituted, but the first product will certainly be the least.

(c)

trace—from unrearranged 2° carbocation   major from rearranged 3° carbocation   minor from rearranged 3° carbocation

The carbocation produced in this E1 elimination is 2° and can either eliminate to give the first alkene, or can rearrange by a methyl shift to a 3° carbocation which would produce the last two products. The middle product is major as it is tetrasubstituted versus disubstituted for the last structure and monosubstituted for the first structure.

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6-61 The allylic carbocation has two resonance forms showing that two carbons share the positive charge. The ethanol nucleophile can attack either of these carbons, giving the S_N1 products; or loss of an adjacent H will give the E1 product.

S_N1

E1

6-62

(a)

(b)

S_N1

S_N2

125

6-63 NBS generates bromine which produces bromine radical. Bromine radical abstracts an allylic hydrogen, resulting in a resonance-stabilized allylic radical. The allylic radical can bond to bromine at either of the two carbons with radical character.

$$H_2C=C-\overset{H}{\underset{CH_3}{C}}-CH_3 + Br\cdot \longrightarrow HBr + \left[H_2C=C-\overset{\cdot}{C}-CH_3 \longleftrightarrow \overset{\cdot}{H_2C}-C=C-CH_3 \right]^{allylic}$$

continues propagation

$$\cdot Br + H_2C=C-\overset{Br}{\underset{CH_3}{C}}-CH_3 + H_2C-C=\overset{Br}{\underset{CH_3}{C}}-CH_3$$

with Br_2

6-64 The bromine radical from NBS will abstract whichever hydrogen produces the most stable intermediate; in this structure, that is a benzylic hydrogen, giving the resonance-stabilized benzylic radical.

(Even though three carbons of the ring have some radical character, these are minor resonance contributors. The product is most stable when the ring has all three double bonds intact, necessitating that the bromine bond to the benzylic carbon.)

6-65 Two related factors could explain this observation. First, as carbocation stability increases, the leaving group will be less tightly held by the carbocation for stabilization; the more stable carbocations are more "free" in solution, meaning more exposed. Second, more stable carbocations will have longer lifetimes, allowing the leaving group to drift off in the solvent, leading to more possibility for the incoming nucleophile to attack from the side that the leaving group just left.

The less stable carbocations hold tightly to their leaving groups, preventing nucleophiles from attacking this side. Backside attack with inversion is the preferred stereochemical route in this case.

6-66

ionization $\longrightarrow$ Br^- + 2° carbocation

rearrangement $\longrightarrow$ 3° carbocation

mechanisms continued on next page

6-66 continued

substitution on 2° carbocation

substitution on rearranged 3° carbocation

elimination from rearranged 3° carbocation

6-67

(a) E2—
one step

$H_2C=CH-CH_3 + H_2O + Br^-$

S_N2—
one step

$CH_3-\overset{OH}{\underset{|}{CH}}-CH_3 + Br^-$

(b) In the E2 reaction, a C—H bond is broken. When D is substituted for H, a C—D bond is broken, slowing the reaction. In the S_N2 reaction, no C—H (C—D) bond is broken, so the rate is unchanged.

(c) These are first-order reactions. The slow, rate-determining step is the first step in each mechanism.

Explanation on next page.

E1

S_N1

6-67 (c) continued

The only mechanism of these two involving C—H bond cleavage is the E1, but the C—H cleavage does NOT occur in the slow, rate-determining step. Kinetic isotope effects are observed only when C—H (C---D) bond cleavage occurs in the rate-determining step. Thus, we would expect to observe *no change in rate* for the deuterium-substituted molecules in the E1 or S_N1 mechanisms. (In fact, this technique of measuring isotope effects is one of the most useful tools chemists have for determining what mechanism a reaction follows.)

6-68 Both products are formed through E2 reactions. The difference is whether a D or an H is removed by the base. As explained in Problem 6-67, C—D cleavage can be up to 7 times slower than C—H cleavage, so the product from C—H cleavage should be formed about 7 times as fast. This rate preference is reflected in the 7 : 1 product mixture. ("Ph" is the abbreviation for a benzene ring.)

requires C—D bond cleavage; slow; minor product

requires C—H bond cleavage; 7 times faster; major product

6-69 The energy, and therefore the structure, of the transition state determines the rate of a reaction. Any factor which lowers the energy of the transition state will speed the reaction.

transition state—
developing charge

This example of S_N2 is unusual in that the nucleophile is a neutral molecule—it is not negatively charged. The transition state is beginning to show the positive and negative charges of the products (ions), so the transition state is more charged than the reactants. The polar transition state will be stabilized in a more polar solvent through dipole-dipole interactions, so the rate of reaction will be enhanced in a polar solvent.

nonpolar solvent

polar solvent—
lower energy,
faster reaction

energy →

reaction coordinate →

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6-70 The problem is how to explain this reaction:

$Et_2N:$
|
$H_2C-CH-CH_2CH_3$ $\xrightarrow{HO^-}$
|
Cl **1**

$:NEt_2$
|
$H_2C-CH-CH_2CH_3$ $+$ Cl^-
|
OH **2**

1) second order, but several thousand times faster than similar second order reactions without the NEt_2 group
2) NEt_2 group migrates

Solution

Clearly, the NEt_2 group is involved. The nitrogen is a nucleophile and can do an internal nucleophilic substitution (S_Ni), a very fast reaction for entropy reasons because two different molecules do not have to come together.

$Et_2N:$
|
$H_2C-CH-CH_2CH_3$ $\xrightarrow[\text{very fast}]{S_Ni}$
|
Cl **1**

$Et\overset{+}{\underset{}{N}}Et$
|
$H_2C-CH-CH_2CH_3$ $+$ Cl^-
   3

The slower step is attack of HO^- on intermediate **3**; the N is a good leaving group because it has a positive charge. Where will HO^- attack **3**? On the less substituted carbon, in typical S_N2 fashion.

$Et\overset{+}{N}Et$
|
$H_2C-CH-CH_2CH_3$ $\xrightarrow{S_N2}$
$HO:^-$ **3**

$:NEt_2$
|
$H_2C-CH-CH_2CH_3$
|
OH **2**

This overall reaction is fast because of the *neighboring group assistance* in forming **3**. It is second order because the HO^- group and **3** collide in the slow step (not the *only* step, however). And the NEt_2 group "migrates", although in two steps.

6-71 The symmetry of this molecule is crucial.

(a)

Ph H Ph
| | |
$CH_3-C-C-C-CH_3$
| | |
H Br H

Regardless of which adjacent H is removed by *t*-butoxide, the product will be 2,4-diphenyl-2-pentene.

(b) Here are a Newman projection, a three-dimensional representation and a Fischer projection of the required diastereomer. On both carbons 2 and 4, the H has to be anti-coplanar with the bromine while leaving the other groups to give the same product. Not coincidentally, the correct diastereomer is a meso structure.

H and Br are anti-coplanar

6-72 "Ph" = phenyl

(a)

$$CH_3CHCHCH_3 \xrightarrow[E2]{NaOCH_3} CH_3-C=CHCH_3 + CH_3CHCH=CH_2$$

(with Ph substituent) → major + minor

(b) H and Br must be anti-coplanar in the transition state

2R,3R → NaOCH₃ → methyls *cis*

(c)

2S,3R → methyls *trans*

(d) The 2S,3S is the mirror image of 2R,3R; it would give the mirror image of the alkene that 2R,3R produced (with two methyl groups *cis*). The alkene product is planar, not chiral, so its mirror image is the same: the 2S,3S and the 2R,3R give the same alkene.

6-73 All five products (boxed) come from rearranged carbocations. Rearrangement, which may occur simultaneously with ionization, can occur by hydride shift to the 3° methylcyclopentyl cation, or by ring expansion to the cyclohexyl cation.

hydride shift

alkyl shift (ring expansion)

6-74 Begin with a structure of (S)-2-bromo-2-fluorobutane. Since there is no H on C-2, the lowest priority group must be the CH_3. The Br has highest priority, then F, then CH_2CH_3, and CH_3 is fourth. Sodium methoxide is a strong base and nucleophile, so the reaction must be second order, E2 or S_N2.

(a)

6-74 continued

In regular structural formulas, the reaction would give three products including the stereoisomers shown above.

(b)

In these structures, the numbers 1 to 4 indicate the group's priority in the Cahn-Ingold-Prelog system.

A cursory analysis of the *designation* of configuration would suggest to the uncritical mind that this reaction proceeded with retention of configuration—but that would be wrong! You know by now that a careful analysis is required. In the Cahn-Ingold-Prelog system, the F in the starting material was priority group 2, but in the product, because Br has left, F is now the first priority group. So even though the *designation* of configuration suggests retention of configuation, the molecule has actually undergone inversion as would be expected with an S_N2 reaction. (See the solution to problem 6-21 for a similar example.)

6-75

(a) Only the propagation steps are shown. NBS provides a low concentratin of Br_2 which generates bromine radical in ultraviolet light. In the starting material, all 8 allylic hydrogens are equivalent.

(b) The first step in this first-order solvolysis is ionization, followed by rearrangement.

mechanism continued on next page

132

6-75 (b) continued

E1

S_N1

(c) This first-order solvolysis generates an allylic carbocation in the ionization step.

The E1 is shown on the next page.

These are the S_N1 products.

6-75 (c) continued
  E1

(d) The first step in this first-order solvolysis is ionization, followed by rearrangement.

S_N1 product from unrearranged carbocation

rearrangement by alkyl shift

S_N1 on rearranged carbocation

E1 on rearranged carbocation

CHAPTER 7—STRUCTURE AND SYNTHESIS OF ALKENES

7-1 The number of elements of unsaturation in a hydrocarbon formula is given by:

$$\frac{2(\#C) + 2 - (\#H)}{2}$$

(a) $C_6H_{12} \Rightarrow \frac{2(6) + 2 - (12)}{2} = 1$ element of unsaturation

(b) Many examples are possible. Yours may not match these, but all must have either a double bond or a ring, that is, one element of unsaturation.

7-2 $C_4H_6 \Rightarrow \frac{2(4) + 2 - (6)}{2} = 2$ elements of unsaturation

7-3 Hundreds of examples of C_4H_6NOCl are possible. Yours may not match these, but all must contain two elements of unsaturation.

7-4 Many examples of these formulas are possible. Yours may not match these, but correct answers must have the same number of elements of unsaturation.

(a) $C_3H_4Cl_2 \Rightarrow C_3H_6 = 1$

(b) $C_4H_8O \Rightarrow C_4H_8 = 1$

135

7-4 continued

(c) $C_4H_4O_2 \Rightarrow C_4H_4 = \mathbf{3}$

$$HC \equiv C - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - OCH_3$$

(d) $C_5H_5NO_2 \Rightarrow C_{5.5}H_5 = \mathbf{4}$

$$\underset{O}{\overset{O}{\bigcirc}} \! - C \equiv C - NH_2$$

(e) $C_6H_3NClBr \Rightarrow C_{6.5}H_5 = \mathbf{5}$

$$HC \equiv C - \underset{Br}{C} = \underset{NH}{C} - C \equiv CH$$
$$\underset{Cl}{}$$

$$Br \! - \! \langle \rangle \! - \! N = C = CH_2$$
$$Cl$$

Note to the student: The IUPAC system of nomenclature is undergoing many changes, most notably in the placement of position numbers. The new system places the position number close to the functional group designation, which is what this Solutions Manual will attempt to follow; however, you should be able to use and recognize names in either the old or the new style. Ask your instructor which system to use.

7-5

(a) 4-methylpent-1-ene
(b) 2-ethylhex-1-ene
(c) penta-1,4-diene
(d) penta-1,2,4-triene
(e) 2,5-dimethylcyclopenta-1,3-diene

(f) 4-vinylcyclohex-1-ene ("1" is optional)
(g) 3-phenylprop-1-ene ("1" is optional)
(h) *trans*-3,4-dimethylcyclopent-1-ene ("1" is optional)
(i) 7-methylenecyclohepta-1,3,5-triene

7-6   (b), (e), and (f) do not show *cis,trans* isomerism

(a)

(*Z*)-hex-3-ene
(*cis*-hex-3-ene)

(*E*)-hex-3-ene
(*trans*-hex-3-ene)

(c)

(2*Z*,4*Z*)-hexa-2,4-diene
cis, cis-hexa-2,4-diene

(2*Z*,4*E*)-hexa-2,4-diene
cis, trans-hexa-2,4-diene

(2*E*,4*E*)-hexa-2,4-diene
trans, trans-hexa-2,4-diene

(d)

"*Cis*" and "*trans*" are not clear for this example; "*E*" and "*Z*" are unambiguous.

(*Z*)-3-methylpent-2-ene

(*E*)-3-methylpent-2-ene

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7-7

(a)

2,3-dimethylpent-2-ene
(neither *cis* nor *trans*)

(b)

3-ethylhexa-1,4-diene
(*cis* or *trans* not specified; the vinyl
group is part of the main chain)

(c)

1-methylcyclopentene

(d)

Cl

5-chlorocyclohexa-1,3-diene
(positions of double bonds need
to be specified)

(e)

cis-3,4-dimethylcyclohexene
(could also have drawn *trans*)

(f)

Br

Br

(*E*)-2,5-dibromo-3-ethylpent-2-ene
(*cis* does not apply)

7-8

(a)

Cl

Br

(*E*)-3-bromo-2-chloropent-2-ene

Cl   Br

(*Z*)-3-bromo-2-chloropent-2-ene

(b)

(2*E*,4*E*)-3-ethylhexa-2,4-diene   (2*Z*,4*E*)-   (2*E*,4*Z*)-   (2*Z*,4*Z*)-

(c) no geometric isomers

(d)

(*Z*)-penta-1,3-diene

(*E*)-penta-1,3-diene

(e)

(*E*)-4-*t*-butyl-5-methyloct-4-ene

(*Z*)-4-*t*-butyl-5-methyloct-4-ene

7-8 continued

(f)

(2Z,5E)-3,7-dichloroocta-2,5-diene

(2E,5E)-3,7-dichloroocta-2,5-diene

(2Z,5Z)-3,7-dichloroocta-2,5-diene

(2E,5Z)-3,7-dichloroocta-2,5-diene

(g) no geometric isomers (an *E* double bond would be too highly strained)

(h)

(Z)-cyclodecene

(E)-cyclodecene

(i)

(1E,5E)-cyclodeca-1,5-diene

(1Z,5E)-cyclodeca-1,5-diene

(1Z,5Z)-cyclodeca-1,5-diene

7-9 From Table 7-1, approximate heats of hydrogenation can be determined for similarly substituted alkenes. The energy difference is approximately 6 kJ/mole (1.4 kcal/mole), the more highly substituted alkene being more stable.

gem-disubstituted
117 kJ/mole
(28.0 kcal/mole)

tetrasubstituted
111 kJ/mole
(26.6 kcal/mole)

7-10 Use the relative values in Figure 7-7.

(a)   2 x (*trans*-disubstituted − *cis*-disubstituted) =

2 x (22 − 18) = 8 kJ/mole more stable for *trans,trans*

(2 x (5.2 − 4.2) = 2 kcal/mole)

(b)   *gem*-disubstituted − monosubstituted = 20 − 11 = 9 kJ/mole

(4.8 − 2.7 = 2.1 kcal/mole)

2-methylbut-1-ene is more stable

138

7-10 continued

(c) trisubstituted − *gem*-disubstituted = 25 − 20 = 5 kJ/mole
$$(5.9 − 4.8 = 1.1 \text{ kcal/mole})$$
2-methylbut-2-ene is more stable

(d) tetrasubstituted − *gem*-disubstituted = 26 − 20 = 6 kJ/mole
$$(6.2 − 4.8 = 1.4 \text{ kcal/mole})$$
2,3-dimethylbut-2-ene is more stable

7-11

(a)   strained but stable

(b) could not exist—ring size must be 8 atoms or greater to include *trans* double bond

(c)   Despite the ambiguity of this name, we must assume that the *trans* refers to the two methyls since this compound can exist, rather than the *trans* referring to the alkene, a molecule which could not exist.

(d)   stable—*trans* in 10-membered ring

(e) unstable at room temperature—cannot have *trans* alkene in 7-membered ring (possibly isolable at very low temperature—this type of experiment is one of the challenges chemists attack with gusto)
(f) stable—alkene not at bridgehead
(g) unstable—violation of Bredt's Rule (alkene at bridgehead in 6-membered ring)
(h) stable—alkene at bridgehead in 8-membered ring
(i) unstable—violation of Bredt's Rule (alkene at bridgehead in 7-membered ring)

7-12
(a) The dibromo compound should boil at a higher temperature because of its much larger molecular weight.
(b) The *cis* should boil at a higher temperature than the *trans* as the *trans* has a zero dipole moment and therefore no dipole-dipole interactions.
(c) 1,2-Dichlorocyclohexene should boil at a higher temperature because of its much larger molecular weight and larger dipole moment than cyclohexene.

7-13

(a)

7-13 continued

(b) $\xrightarrow{(CH_3CH_2)_3N:}$

hindered base gives Hofmann product as major isomer

minor
E2

major
E2

(c) $\xrightarrow[CH_3OH]{NaOCH_3}$

major product is difficult to predict for 2° halides

S_N2

E2

(d) $\xrightarrow[(CH_3)_3COH]{NaOC(CH_3)_3}$

NaOC(CH$_3$)$_3$ is a bulky base and a poor nucleophile, minimizing S$_N$2

E2

7-14

cis

7-15 (a)

rotate

HO⁻

E2 elimination

HO⁻

substitution product—since the substrate is a neopentyl halide and highly hindered, the S$_N$2 substitution is slow, and elimination is favored

7-15 continued

(b)

(CH₃CH₂)₃N:

→

$$Ph—C=C—Ph$$ with Br and H

only alkene isomer
E2

+ minor substitution products

(c)

one enantiomer
of the *d,l* pair

(CH₃CH₂)₃N:

→

only alkene isomer
E2

+ minor substitution products

(d)

$$\frac{NaOH}{acetone}$$

→

S_N2 is the only mechanism possible because no H can get coplanar with Cl; an elimination product would violate Bredt's Rule

(e)

$$\frac{(CH_3)_3CO^-}{(CH_3)_3COH}$$

→

See Appendix 1 in this manual for numbering and naming bicyclic systems.

Models show that the H on C-3 cannot be anti-coplanar with the Cl on C-2. Thus, this E2 elimination must occur with a *syn*-coplanar orientation: the D must be removed as the Cl leaves.

7-16 As shown in Solved Problem 7-3, the H and the Br must have trans-diaxial orientation for the E2 reaction to occur. In part (a), the cis isomer has the methyl in equatorial position, the NaOCH₃ can remove a hydrogen from either C-2 or C-6, giving a mixture of alkenes where the most highly substituted isomer is the major product (Zaitsev). In part (b), the *trans* isomer has the methyl in the axial position at C-2, so no elimination can occur to C-2. The only possible elimination orientation is toward C-6.

(a)

either H
can be removed

$$\frac{NaOCH_3}{CH_3OH}$$

→

major

+

minor

Zaitsev orientation

(b)

only this H
can be removed

$$\frac{NaOCH_3}{CH_3OH}$$

→

only alkene formed; stereochemistry of E2 precludes other isomer from forming

141

7-17   E2 elimination requires that the H and the leaving group be anti-coplanar; in a chair cyclohexane, this requires that the two groups be trans diaxial. However, when the bromine atom is in an axial position, there are no hydrogens in axial positions on adjacent carbons, so no elimination can occur.

7-18

(b) Showing the chair form of the decalins makes the answer clear. The top isomer locks the H and the Br into a trans-diaxial conformation—optimum for E2 elimination. The bottom isomer has Br equatorial where it is exceedingly slow to eliminate.

7-19   Models are a big help for this problem.

7-20

both Br anti-coplanar   transition state   only geometric isomer
                                                         possible from a
                                                         concerted mechanism

‑ ‑ ‑ ‑ ‑ ‑ ‑ = stretched bond being broken or formed

transition state   *cis*

7-21

(S,S)

both Br anti-coplanar   transition state   only geometric isomer
                                                         possible from a
                                                         concerted mechanism

‑ ‑ ‑ ‑ ‑ ‑ ‑ = stretched bond being broken or formed

transition state   *cis*

143

7-22
(a)

NaI / acetone → cyclohexene

(b) *(R,R)*

NaI / acetone →

cis-hept-3-ene

(c)

rotate →

I⁻ →

trans-pent-2-ene

(d)

NaI / acetone →

The two bromine atoms must be anti-coplanar in order to eliminate. Only the bromines at C-1 and C-2 fit that requirement; the bromines at C-2 and C-3 cannot eliminate.

(*S*)-3-bromo-1-ethyl-3-methylcyclohexene

(e)

rotation →

NaI, acetone →

trans-cyclodecene

In the first conformation shown, the bromine atoms are not coplanar and cannot eliminate. Rotation in this large ring can place the two bromines anti-coplanar, generating a *trans* alkene in the ring. (Use models!)

7-23 The stereochemical requirement of E2 elimination is anti-coplanar; in cyclohexanes, this translates to *trans*-diaxial. Both dibromides are *trans*, but because the *t*-butyl group must be in an equatorial position, only the left molecule can have the bromines diaxial. The one on the right has both bromines locked into equatorial positions, from which they cannot undergo E2 elimination.

trans-diaxial— can do E2

trans-diequatorial—cannot do E2

144

7-24
(a)

(b)

carbocation rearrangement

same product mixture as in part (a)

145

7-25 In these mechanisms, the base removing the final proton is shown as HSO_4^-. It is equally possible that water removes this proton.

(a)

(b)

cis + trans
major isomer

minor isomer

(c)

from unrearranged 2° carbocation

greatest amount

from rearranged 3° carbocation

greatest amount

least amount

146

7-26

(a) $\Delta G°$ = $\Delta H° - T\Delta S°$

= + 116,000 J/mol − 298 K (117 J/K•mol)

= + 81,100 J/mol = + 81.1 kJ/mol (+19.3 kcal/mole)

$\Delta G°$ is positive, the reaction is **disfavored** at 25°C

(b) ΔG_{1000} = + 116,000 J/mol − 1273 K (117 J/K•mol)

= − 32,900 J/mol = − 32.9 kJ/mol (− 8.0 kcal/mole)

ΔG is negative, the reaction is **favored** at 1000°C

7-27

(a) basic and nucleophilic mechanism: $Ba(OH)_2$ is a strong base
(b) acidic and electrophilic mechanism: the catalyst is H^+
(c) free radical chain reaction: the catalyst is a peroxide that initiates free radical reactions
(d) acidic and electrophilic mechanism: the catalyst BF_3 is a strong Lewis acid

7-28

(a)

This 1° carbocation may or may not exist. It is shown for clarity.

(b)

7-29

(a)

(b)

This 1° carbocation may or may not exist. It is shown for clarity.

Two possible rearrangements

1. Hydride shift

2. Alkyl shift—ring expansion

(c) carbocation formation

continued on next page

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7-29 (c) continued
without rearrangement

with hydride shift

(d)

E1 product from
unrearranged
carbocation

rearrangement by alkyl shift

E1 on rearranged carbocation

7-29 (d) continued
    E1 on rearranged carbocation

7-30 Please refer to solution 1-20, page 12 of this Solutions Manual.

7-31
(a)   (b)   (c) Br, Br   (d)   (e)

(f) Z   (g)   (h) Br, Z   (i) Z E

7-32
(a) 2-ethylpent-1-ene (number the longest chain *containing the double bond*)
(b) 3-ethylpent-2-ene
(c) (3*E*,6*E*)-octa-1,3,6-triene
(d) (*E*)-4-ethylhept-3-ene
(e) 1-cyclohexylcyclohexa-1,3-diene
(f) (3*Z*,5*E*)-6-chloro-3-(chloromethyl)octa-1,3,5-triene

7-33 (a) *E*   (b) neither—two methyl groups on one carbon   (c) *Z*   (d) *Z*

7-34
(a)

(*Z*)-1-fluoro- (*E*)-1-fluoro- 2-fluoro- 3-fluoro- fluorocyclopropane
prop-1-ene   prop-1-ene   prop-1-ene prop-1-ene

(b) C$_4$H$_7$Br has one element of unsaturation, but no rings are permitted in the problem, so all the isomers must have one double bond. Only four isomers are possible with four carbons and one double bond, so the 12 answers must have these four skeletons with a Br substituted in all possible positions.

(b) Cholesterol, C$_{27}$H$_{46}$O, has five elements of unsaturation. If only one of those is a pi bond, the other four must be rings.

150

7-35

(a)	*trans,trans*	*cis,trans*	*trans,cis*	*cis,cis*
(b)	2E,4E	2Z,4E	2E,4Z	2Z,4Z

This problem is intended to show the difficulty of using *cis-trans* nomenclature with any but the simplest alkenes. *Cis* and *trans* are ambiguous: the first alkene in part (a) is *cis* if the two similar substituents are considered, but *trans* if the chain is considered. The *E-Z* nomenclature is unambiguous and is preferred for all four of these isomers.

7-36 (a) and (d) have no geometric isomers

(b)

trans-pent-2-ene   *cis*-pent-2-ene
(*E*)-pent-2-ene   (*Z*)-pent-2-ene

(c)

trans-hex-3-ene   *cis*-hex-3-ene
(*E*)-hex-3-ene   (*Z*)-hex-3-ene

(e)

trans-1,2-dibromopropene
(*E*)-1,2-dibromopropene

cis-1,2-dibromopropene
(*Z*)-1,2-dibromopropene

(f)

trans,trans-hexa-2,4-diene   *cis,trans*-hexa-2,4-diene   *cis,cis*-hexa-2,4-diene
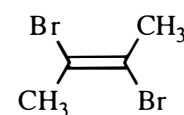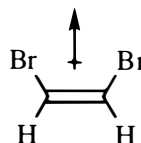(2*E*,4*E*)-hexa-2,4-diene   (2*Z*,4*E*)-hexa-2,4-diene   (2*Z*,4*Z*)-hexa-2,4-diene
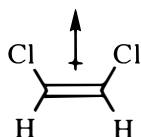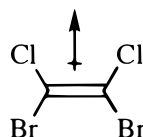
7-37

(a)

dipole moment = 0

(b)

dipole moment = 0

(c)
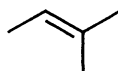

larger dipole moment
(no bromines opposing
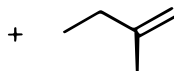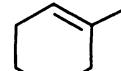the dipole of the chlorines)

7-38

(a)

(b)

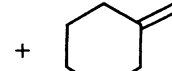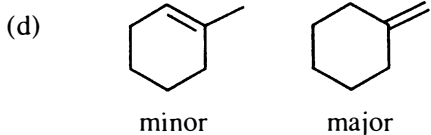major   +   minor

(c)

major   +   minor

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7-38 continued

(d)

minor   major

7-39 Only major alkene isomers are shown. Minor alkene isomers would also be produced in parts (a), (b) and (d).

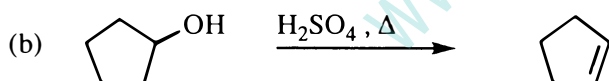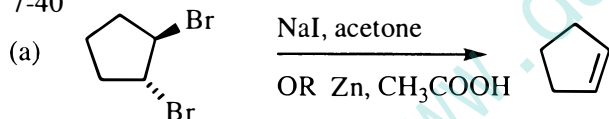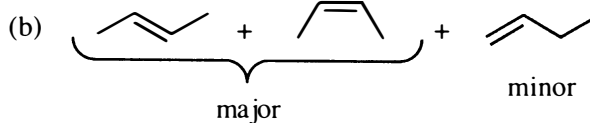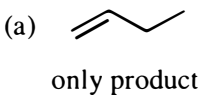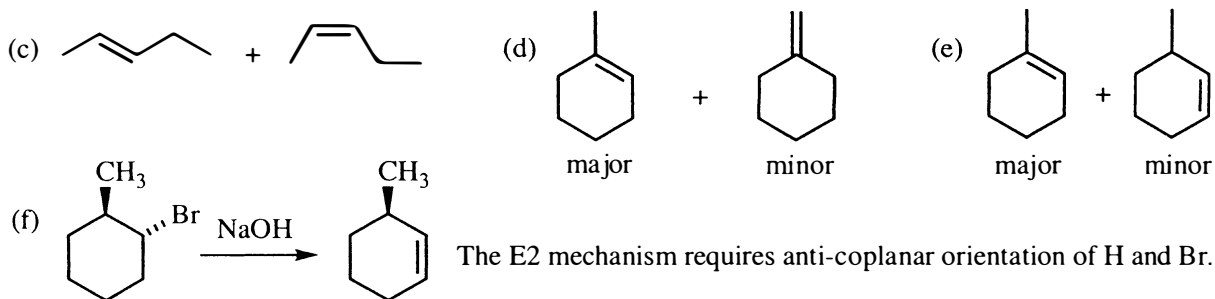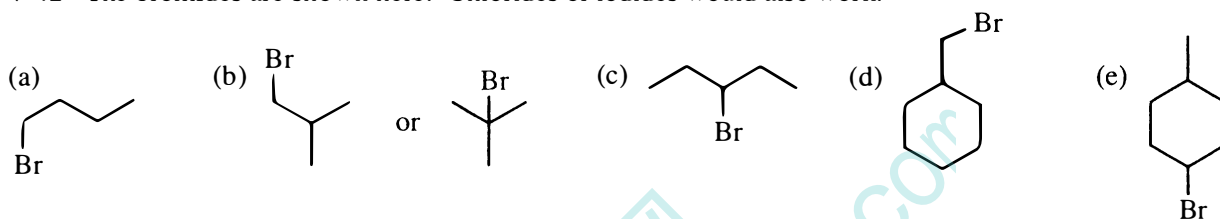(a) $CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_3 + H_2O$

E + Z

(b)

  + NaOC$(CH_3)_3$ →   + NaBr + HOC$(CH_3)_3$

hindered base

(c) $CH_3-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-CH_3 + Zn \xrightarrow{CH_3COOH} CH_3-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_3 + ZnBr_2$

E + Z

(d) $CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{NaOH, \Delta}$ + NaBr + H$_2$O

7-40

(a) $\xrightarrow[\text{OR Zn, CH}_3\text{COOH}]{\text{NaI, acetone}}$

(b) $\xrightarrow{H_2SO_4 , \Delta}$

(c) $\xrightarrow{KOC(CH_3)_3}$

(d) $\xrightarrow{Br_2 , h\nu}$ $\xrightarrow{KOC(CH_3)_3}$

7-41

(a)

only product

(b) +   major   +   minor

152

7-41 continued

(c) +   (d) +   (e) +

major   minor   major   minor

(f) $\xrightarrow{\text{NaOH}}$ The E2 mechanism requires anti-coplanar orientation of H and Br.

7-42   The bromides are shown here.   Chlorides or iodides would also work.

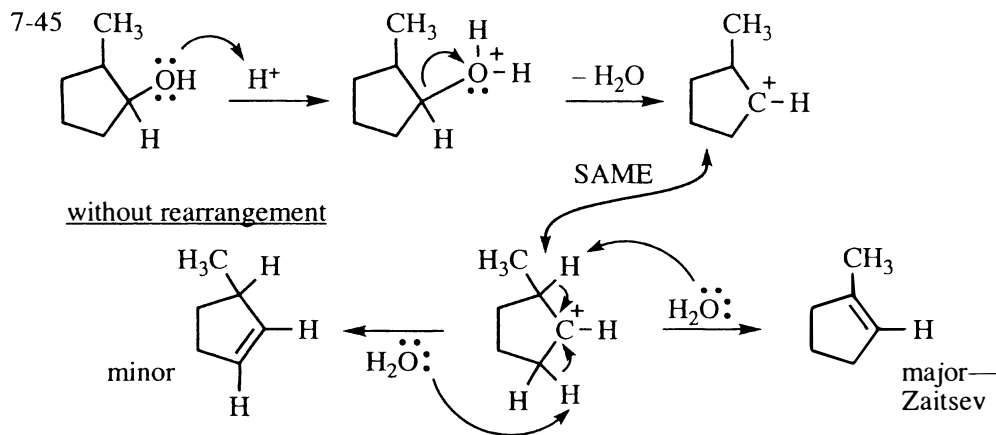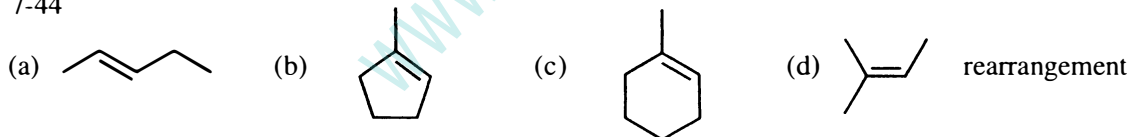(a)   (b) or   (c)   (d)   (e)

7-43

(a) There are two reasons why alcohols do not dehydrate with strong base. The potential leaving group, hydroxide, is itself a strong base and therefore a terrible leaving group. Second, the strong base deprotonates the —OH faster than any other reaction can occur, consuming the base and making the leaving group anionic and therefore even worse.

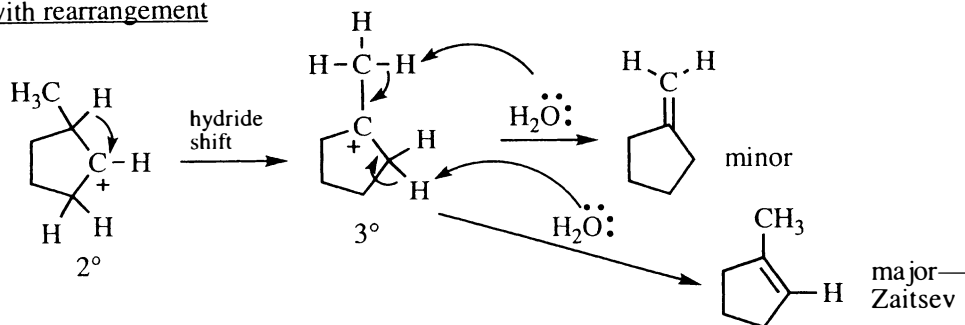$$\text{ROH} + {}^-\text{OC(CH}_3)_3 \rightleftharpoons \text{RO}^- + \text{HOC(CH}_3)_3$$

(b) A halide is already a decent leaving group. Since halides are extremely weak bases, the halogen atom is not easily protonated, and even if it were, the leaving group ability is not significantly enhanced. The hard step is to remove the adjacent H, something only a strong base can do—and strong bases will not be present under strong acid conditions.
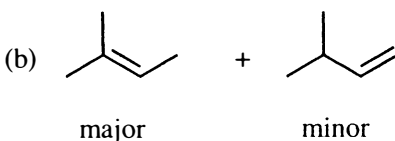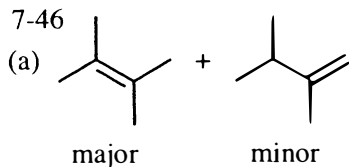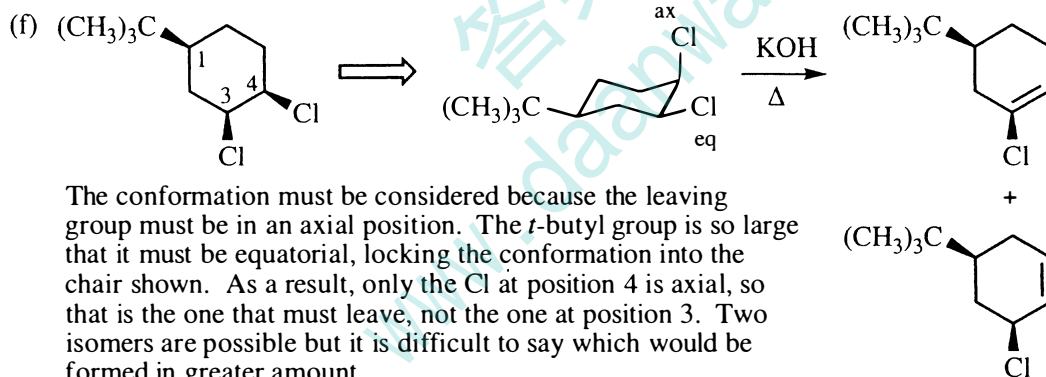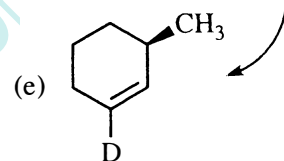
7-44

(a)   (b)   (c)   (d) rearrangement

7-45

without rearrangement

7-45 continued
__with rearrangement__

minor

major—
Zaitsev

7-46

(a) major + minor

(b) major + minor

only product from E2—
anti-coplanar is
possible only from
carbon without CH_3 by
removing H and Cl

(c) major + minor

(d) major + minor

(e)

(f)

The conformation must be considered because the leaving
group must be in an axial position. The *t*-butyl group is so large
that it must be equatorial, locking the conformation into the
chair shown. As a result, only the Cl at position 4 is axial, so
that is the one that must leave, not the one at position 3. Two
isomers are possible but it is difficult to say which would be
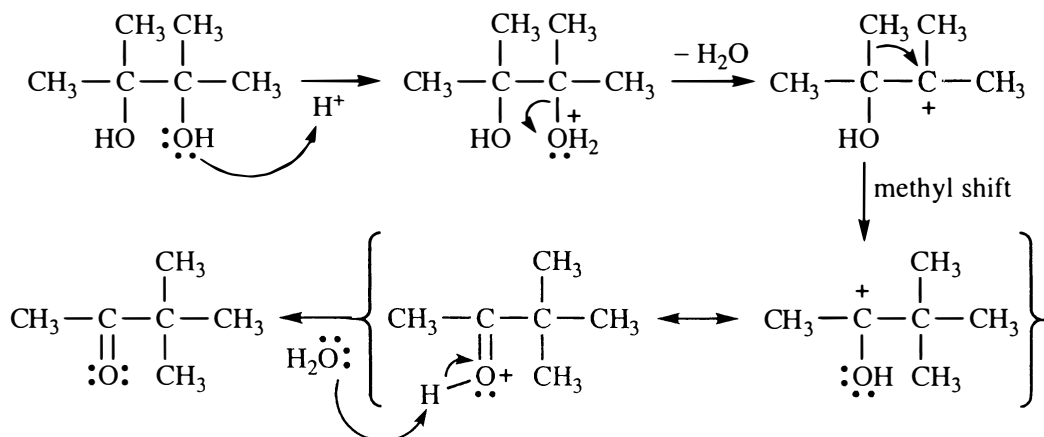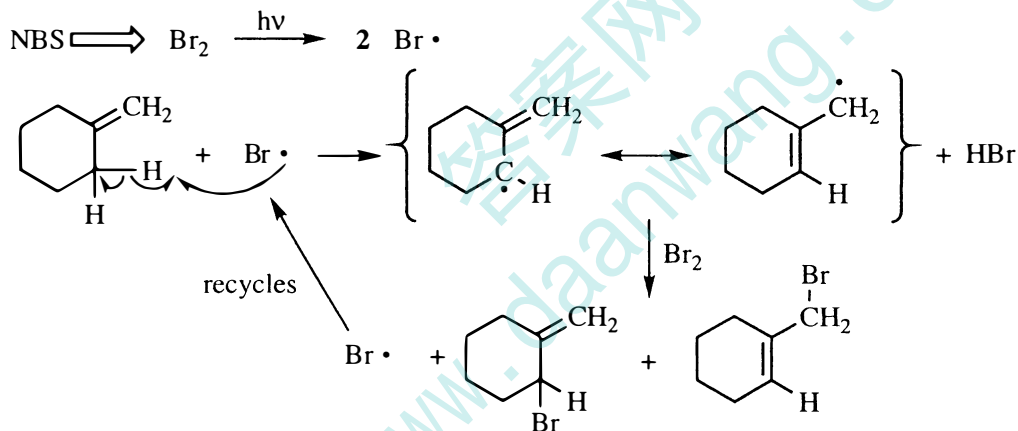formed in greater amount.

7-47

E1 works well because only one carbocation and
only one alkene are possible. Substitution is not a
problem here. The only nucleophiles are water,
which would simply form starting material by a
reverse of the dehydration, and bisulfate anion.
Bisulfate anion is an extremely weak base and poor
nucleophile; if it did attack the carbocation, the
unstable product would quickly re-ionize, with no
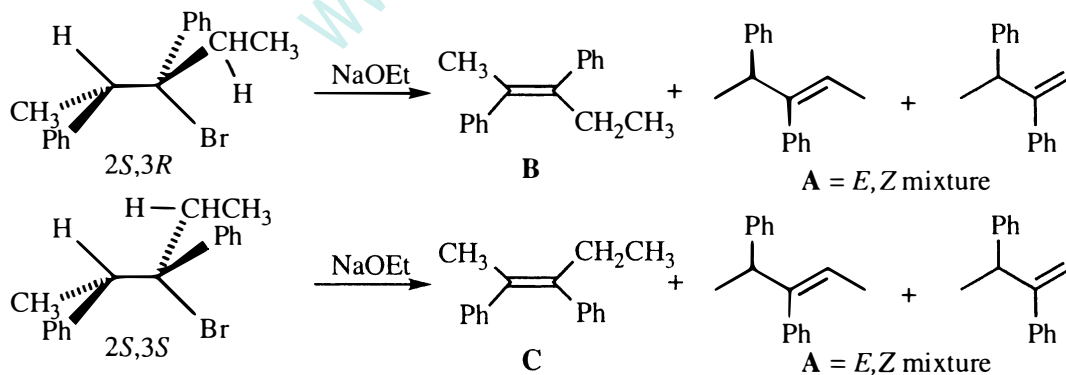net change, back to the carbocation.

154

7-48

The driving force for this rearrangement is the great stability of the resonance-stabilized, protonated carbonyl group.
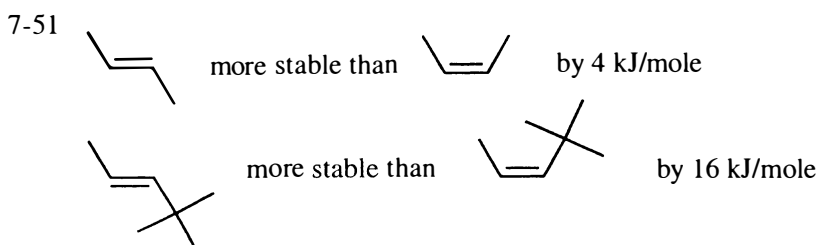
7-49 NBS generates bromine which produces bromine radical. Bromine radical abstracts an allylic hydrogen, resulting in a resonance-stabilized allylic radical. The allylic radical can bond to bromine at either of the two carbons with radical character. See the solution to problem 6-63.
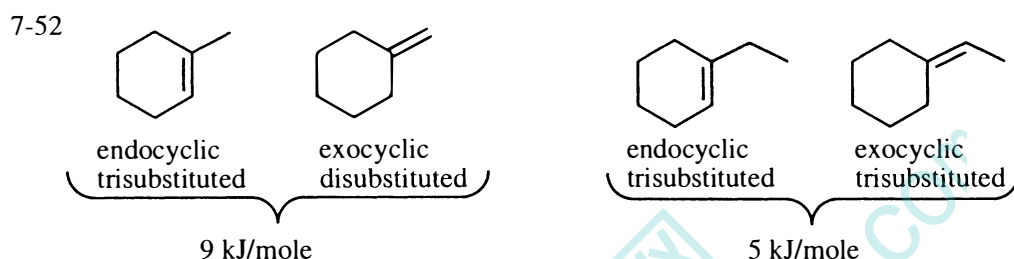

7-50

E2 dehydrohalogenation requires anti-coplanar arrangement of H and Br, so specific cis-trans isomers (**B** or **C**) are generated depending on the stereochemistry of the starting material. Removing a hydrogen from C-4 (achiral) will give about the same mixture of *cis* and *trans* (**A**) from either diastereomer.

7-51

 more stable than by 4 kJ/mole

 more stable than by 16 kJ/mole

Steric crowding by the *t*-butyl group is responsible for the energy difference. In *cis*-but-2-ene, the two methyl groups have only slight interaction. However, in the 4,4-dimethylpent-2-enes, the larger size of the *t*-butyl group crowds the methyl group in the *cis* isomer, increasing its strain and therefore its energy.

7-52

endocyclic trisubstituted | exocyclic disubstituted | endocyclic trisubstituted | exocyclic trisubstituted

9 kJ/mole   5 kJ/mole

A standard principle of science is to compare experiments which differ by only one variable. Changing more than one variable clouds the interpretation, possibly to the point of invalidating the experiment.
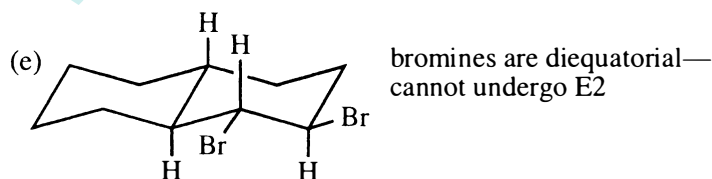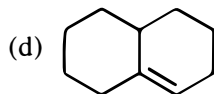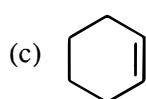
The first set of structures compares endo and exocyclic double bonds, but the degree of substitution on the alkene is also different, so this comparison is not valid—we are not isolating simply the exo or endocyclic effect.

The second pair is a much better measure of endo versus exocyclic stability because both alkenes are trisubstituted, so the degree of substitution plays no part in the energy values. Thus, 5 kJ/mole is a better value.
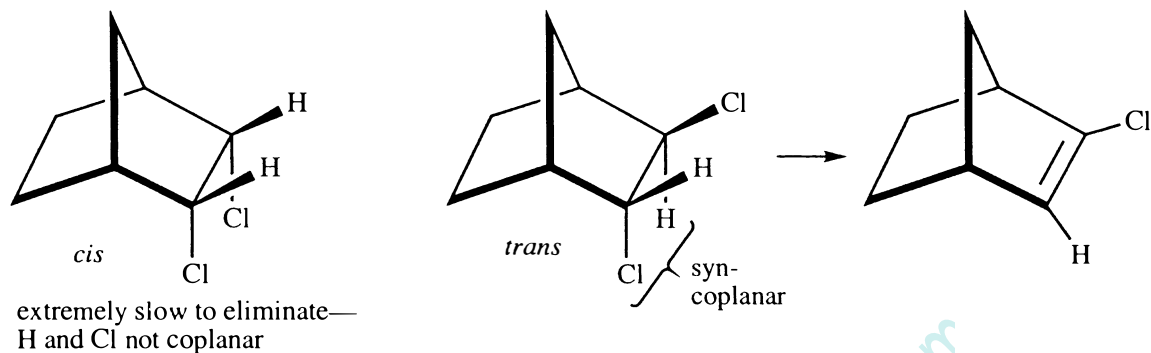
7-53

(a) $CH_3CH_2CH=CH_2$

(b) No reaction—the two bromines are not trans and therefore cannot be trans-diaxial.

(c)

(d)

(e)

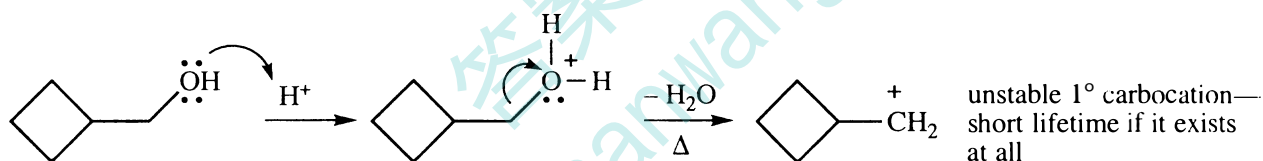bromines are diequatorial—cannot undergo E2

No reaction—the bromines are trans, but they are diequatorial because of the locked conformation of the trans-decalin system. E2 can occur only when the bromines are trans diaxial.

7-54 In E2, the two groups to be eliminated must be coplanar. In conformationally mobile systems like acyclic molecules, or in cyclohexanes, anti-coplanar is the preferred orientation where the H and leaving group are 180° apart. In rigid systems like norbornanes, however, SYN-coplanar (angle 0°) is the only possible orientation and E2 will occur, although at a slower rate than anti-coplanar.
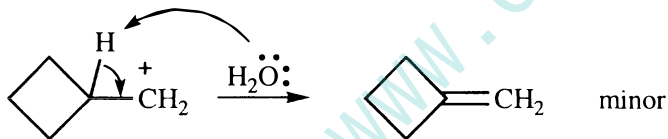
The structure having the H and the Cl syn-coplanar is the *trans*, which undergoes the E2 elimination. (It is possible that the *other* H and Cl eliminate from the *trans* isomer; the results from this reaction cannot distinguish between these two possibilities.)

cis

extremely slow to eliminate—
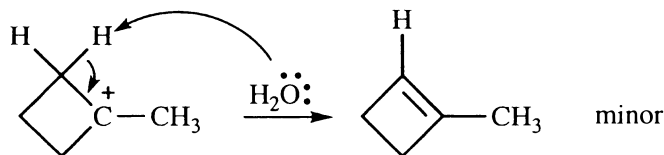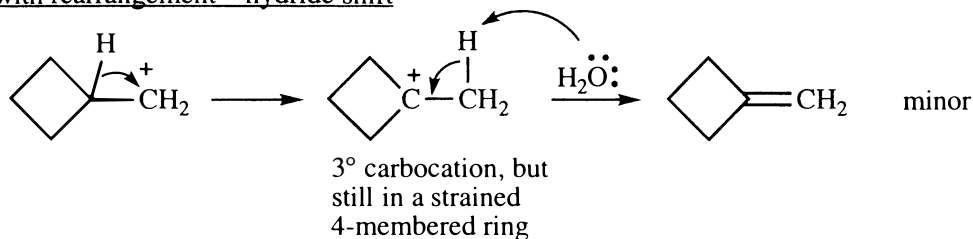H and Cl not coplanar

trans

syn-coplanar

7-55 It is interesting to note that even though three-membered rings are more strained than four-membered rings, three-membered rings are far more common in nature than four-membered rings. Rearrangement from a four-membered ring to something else, especially a larger ring, will happen quickly.

unstable 1° carbocation—
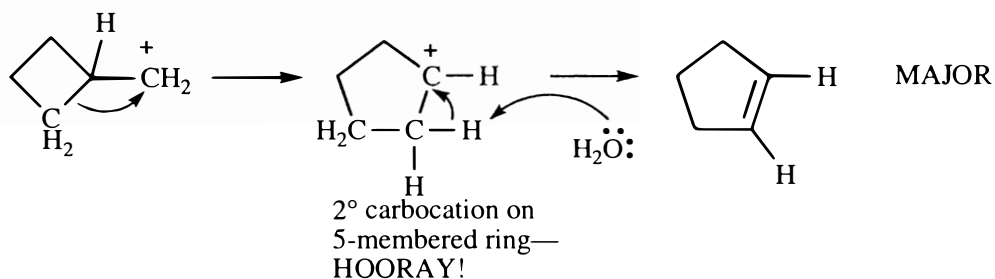short lifetime if it exists
at all

without rearrangement

minor

with rearrangement—hydride shift

minor
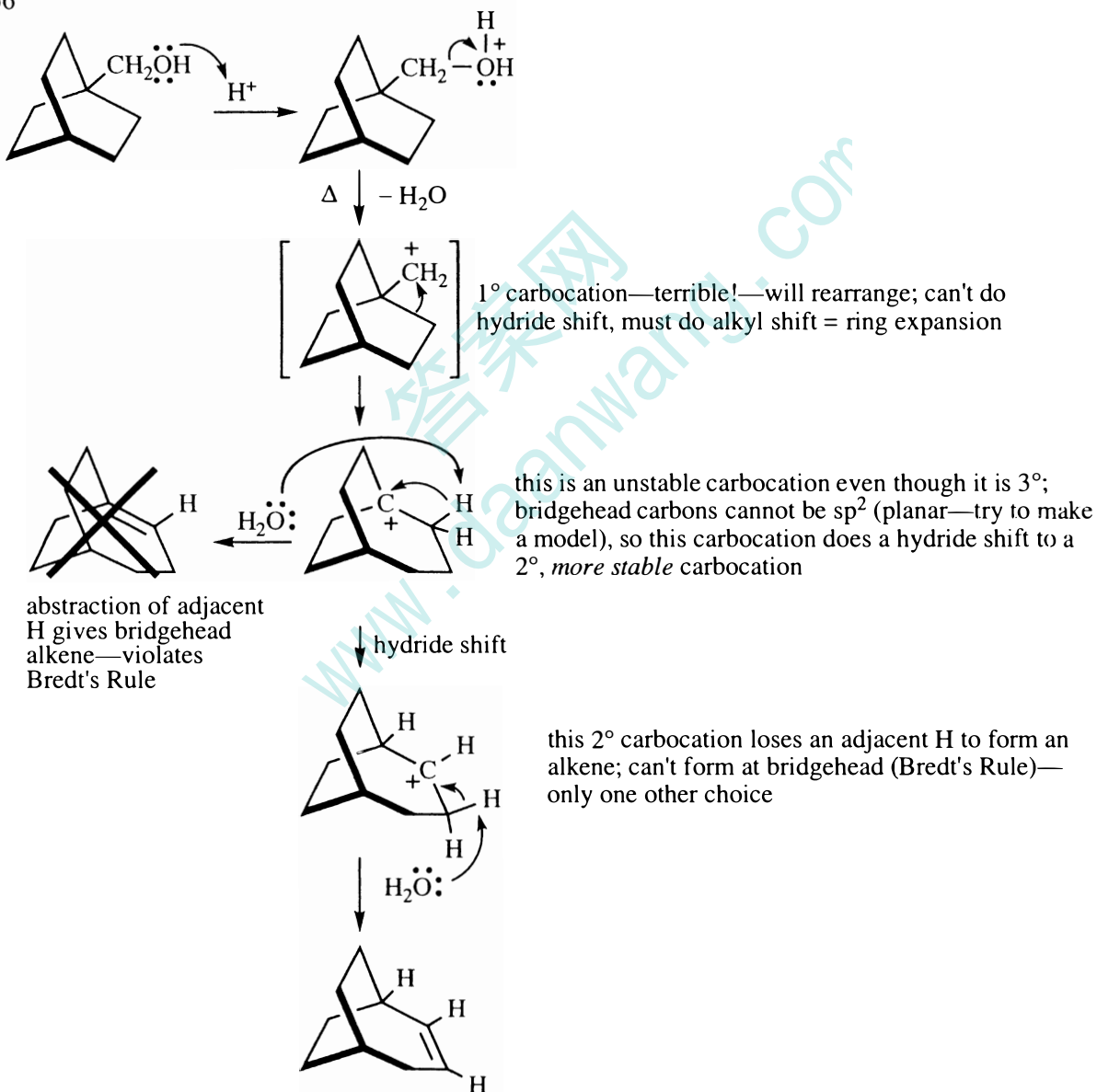
3° carbocation, but
still in a strained
4-membered ring

minor

7-55 continued

<u>with rearrangement—alkyl shift—ring expansion</u>

2° carbocation on
5-membered ring—
HOORAY!

7-56

Δ ↓ − H₂O

1° carbocation—terrible!—will rearrange; can't do hydride shift, must do alkyl shift = ring expansion

this is an unstable carbocation even though it is 3°; bridgehead carbons cannot be sp² (planar—try to make a model), so this carbocation does a hydride shift to a 2°, *more stable* carbocation

abstraction of adjacent
H gives bridgehead
alkene—violates
Bredt's Rule

↓ hydride shift

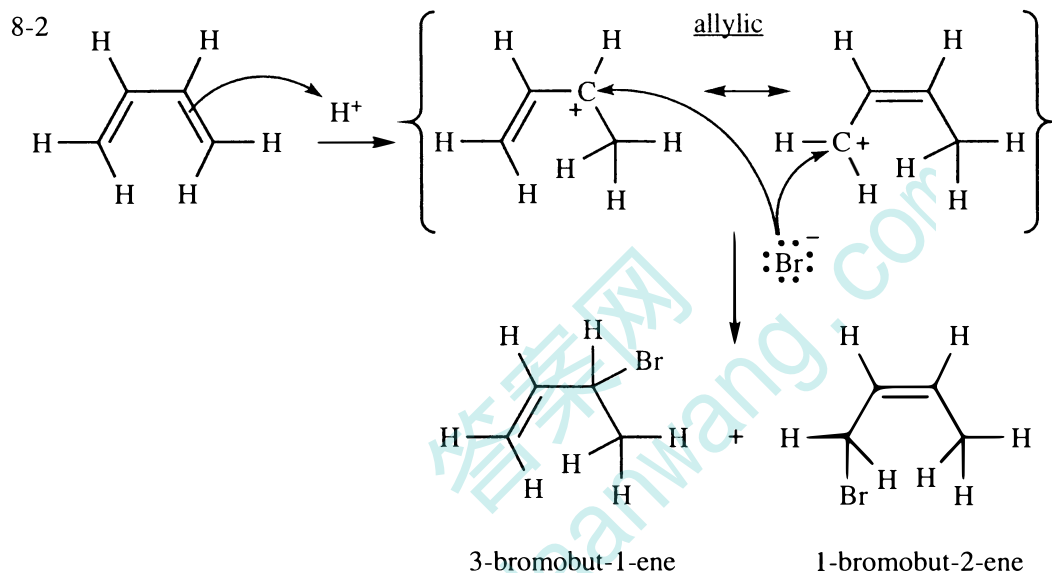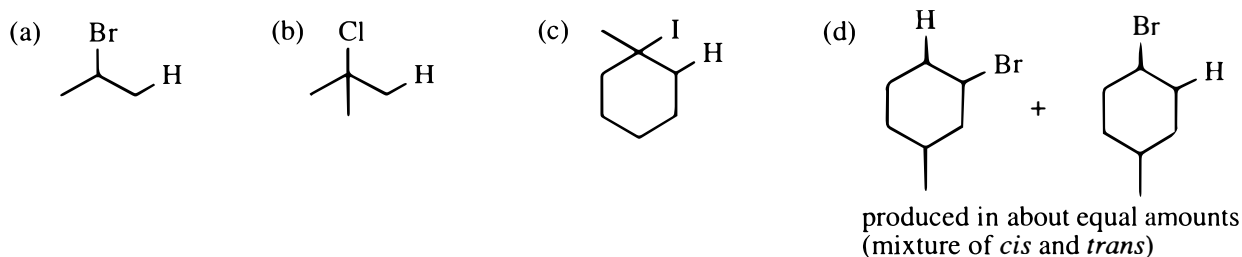this 2° carbocation loses an adjacent H to form an alkene; can't form at bridgehead (Bredt's Rule)—only one other choice
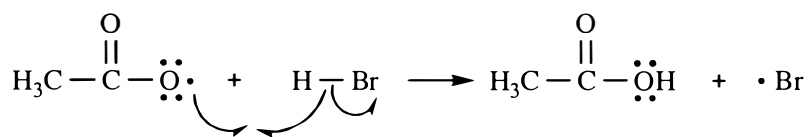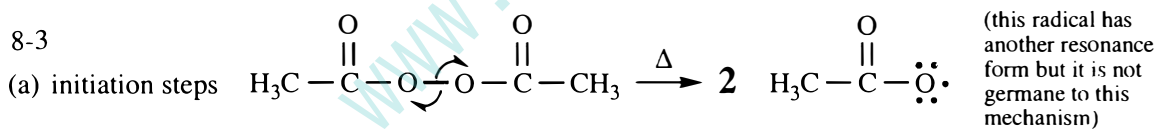
CHAPTER 8—REACTIONS OF ALKENES
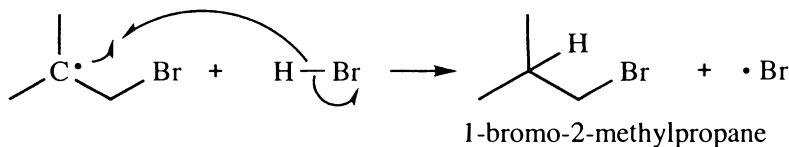
8-1 *Major* products are produced in greatest amount; they are not necessarily the *only* products produced.

(a), (b), (c), (d) structures

produced in about equal amounts
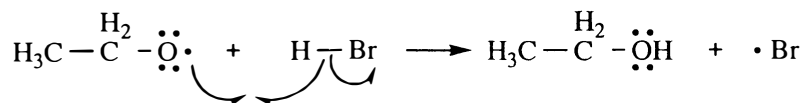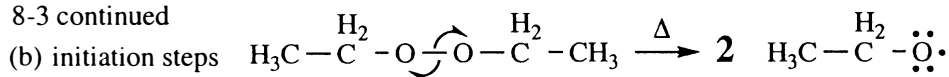(mixture of *cis* and *trans*)

8-2

allylic

Because the allylic carbocation has partial positive charge at two carbons, the bromide nucleophile can bond at either electrophilic carbon, giving two products.
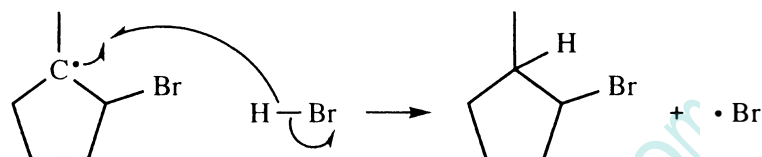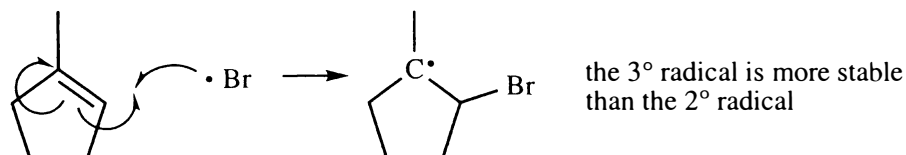
3-bromobut-1-ene   1-bromobut-2-ene
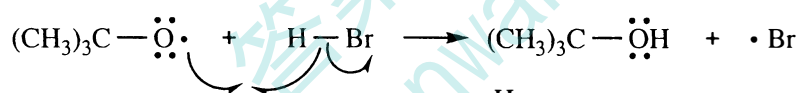
8-3

(a) initiation steps

(this radical has another resonance form but it is not germane to this mechanism)

propagation steps

the 3° radical is more stable than the 1° radical

1-bromo-2-methylpropane

159

8-3 continued
(b) initiation steps

$$H_3C-\overset{H_2}{C}-O \frown O-\overset{H_2}{C}-CH_3 \xrightarrow{\Delta} 2 \quad H_3C-\overset{H_2}{C}-\ddot{\underset{..}{O}}\cdot$$

$$H_3C-\overset{H_2}{C}-\ddot{\underset{..}{O}}\cdot \;+\; H\frown Br \longrightarrow H_3C-\overset{H_2}{C}-\ddot{\underset{..}{O}}H \;+\; \cdot Br$$

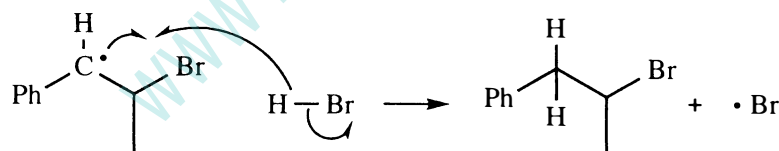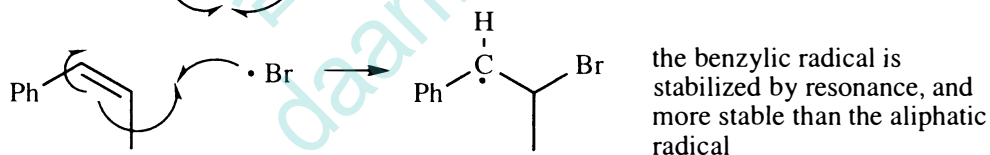propagation steps

the 3° radical is more stable than the 2° radical

1-bromo-2-methylcyclopentane (*cis + trans*)

(c) initiation steps

 $\xrightarrow{\Delta}$ **2** $(CH_3)_3C-\ddot{\underset{..}{O}}\cdot$

$$(CH_3)_3C-\ddot{\underset{..}{O}}\cdot \;+\; H\frown Br \longrightarrow (CH_3)_3C-\ddot{\underset{..}{O}}H \;+\; \cdot Br$$

propagation steps

the benzylic radical is stabilized by resonance, and more stable than the aliphatic radical
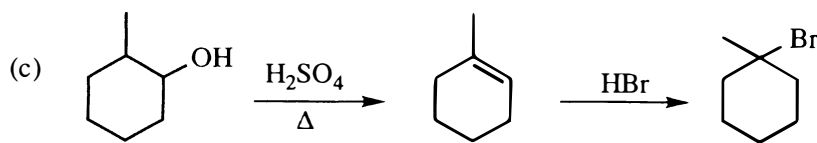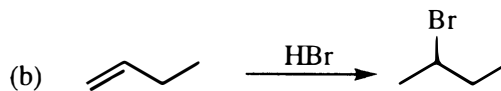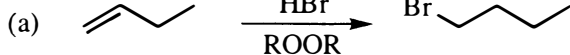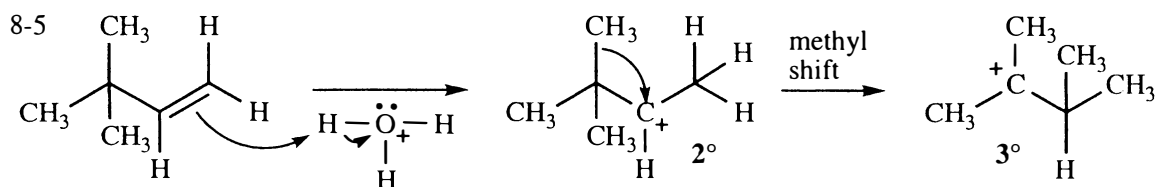

2-bromo-1-phenylpropane
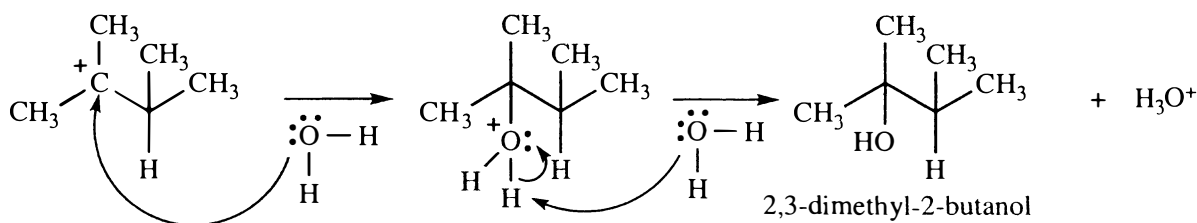(recall that "Ph" is the abbreviation for "phenyl")
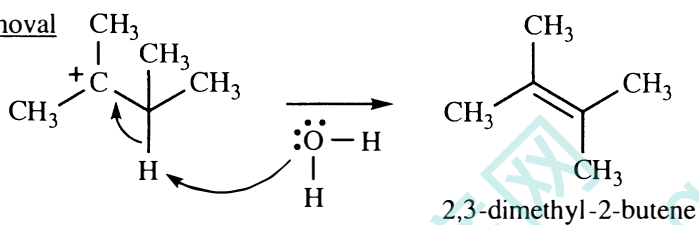
8-4
(a)

(b)

(c)

(d)

Note: A good synthesis uses major products as intermediates, not minor products. Knowing orientation of addition and elimination is critical to using reactions correctly.

160

8-5

nucleophilic attack by water

2,3-dimethyl-2-butanol   + H_3O^+

proton removal

2,3-dimethyl-2-butene   + H_3O^+

8-6

(a)

from 3° carbocation

(b)

(c)

from 3° benzylic carbocation

8-7

(a)

(b)

$\begin{array}{c} O \\ \parallel \\ H_3C-C \end{array}$

"Ac" = acetyl

$\begin{array}{c} O \\ \parallel \\ H_3C-C-O^- \end{array}$

"OAc" or "AcO" = acetate

161

8-8

(a)

(b)

(c)

(d)

8-9

(a)

(b)

(c)

Using an acid-catalyzed hydration in part (c) would initially form a 2° carbocation that would quickly rearrange to 3° on carbon-3. The desired product would not be synthesized.

8-10

(a), (b)

(c), (d)

(e), (f)

8-11

(a)

(b)

(c)

8-12 Instead of borane attacking the bottom face of 1-methylcyclopentene, it is equally likely to attack the top face, leading to the enantiomer.

8-13

(a)

(b)

major   minor—steric hindrance to attack of BH_3

(c)

8-14

(a)

enantiomers

(b)

enantiomers

The enantiomeric pair produced from the Z-alkene is diastereomeric with the other enantiomeric pair produced from the E-alkene. Hydroboration-oxidation is stereospecific, that is, each alkene gives a specific set of stereoisomers, not a random mixture.

8-15

(a)

(b)

163

8-15 continued

(c)

8-16

empty p orbital in
planar carbocation

The *planar* carbocation is responsible for non-stereoselectivity. The bromide nucleophile can attack from the top or bottom, leading to a mixture of stereoisomers. The addition is therefore a mixture of syn and anti addition.

8-17 During bromine addition to either the *cis-* or *trans-*alkene, two new chiral centers are being formed. Neither alkene (nor bromine) is optically active, so the product cannot be optically active.
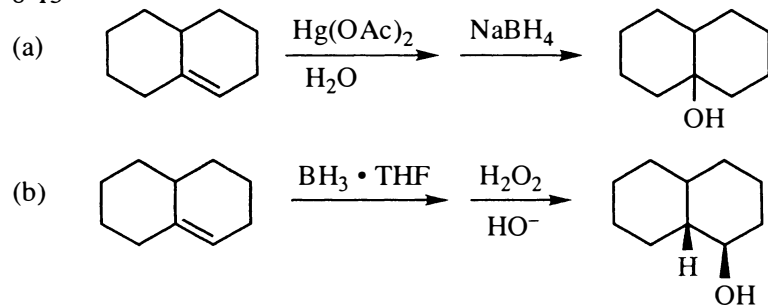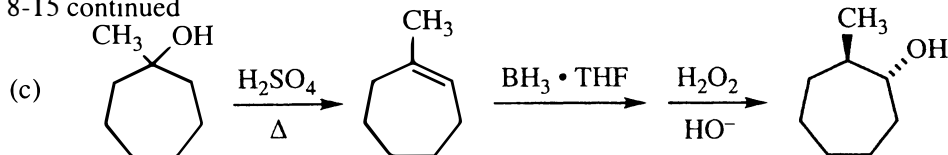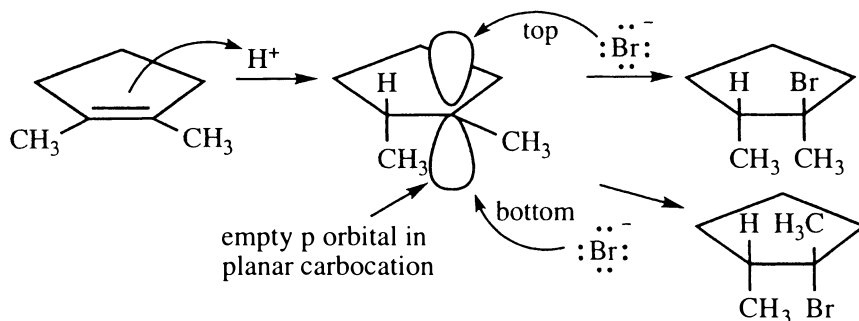
The *cis*-but-2-ene gives two chiral products, a racemic mixture. However, *trans*-but-2-ene, because of its symmetry, gives only one *meso* product which can never be chiral. The "optical *in*activity" is built into this symmetric molecule.

This can be seen by following what happens to the configuration of the chiral centers from the intermediates to products, below. (The key lies in the symmetry of the intermediate and *inversion* of configuration when bromide attacks.)

IDENTICAL—SYMMETRIC

CIS

a Br⁻ nucleophile could
attack at either carbon

2S,3S   ENANTIOMERS   2R,3R

8-17 continued

ENANTIOMERIC

TRANS

a Br⁻ nucleophile could
attack at either carbon

bromide attack on this
bromonium ion gives the
same results

:Br: ⁻ OR :Br: ⁻

2R,3S IDENTICAL—MESO 2R,3S

CONCLUSION: anti addition of a symmetric reagent to a symmetric *cis*-alkene gives racemic product, while anti addition to a *trans*-alkene gives meso product. (We will see shortly that syn addition to a *cis*-alkene gives meso product, and syn addition to a *trans*-alkene gives racemic product. Stay tuned.)

8-18 Enantiomers of chiral products are also produced but not shown.

(a)

(b)

Bromide will attack
the other carbon of the
bromonium ion as well.

(c)

8-18 continued

(d) Three new asymmetric carbons are produced in this reaction. All stereoisomers will be produced with the restriction that the two adjacent chlorines on the ring must be *trans*.

8-19   The *trans* product results from water attacking the bromonium ion from the face opposite the bromine. Equal amounts of the two enantiomers result from the equal probability that water will attack either C-1 or C-2.

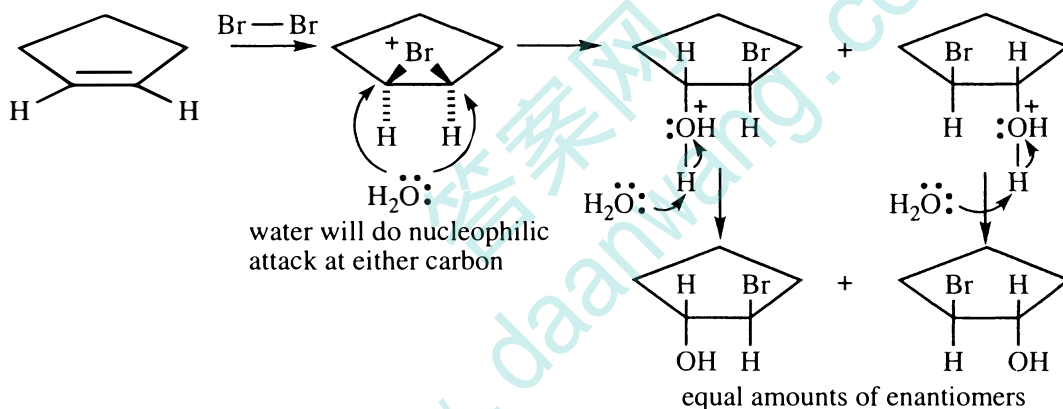water will do nucleophilic
attack at either carbon

equal amounts of enantiomers

8-20

from Solved Problem 8-5

the bromonium ion
shown here is the
enantiomer of the one
shown in Solved
Problem 8-5

enantiomer of product
in Solved Problem 8-5

from Solved Problem 8-6: the bromonium ion shown is meso as it has a plane of symmetry; attack by the nucleophile at the other carbon from what is shown in the text will create the enantiomer

show products from
both nucleophiles
attacking at this carbon

these are the enantiomers of the
structures shown in the text

166

8-21 The chiral products shown here will be racemic mixtures.
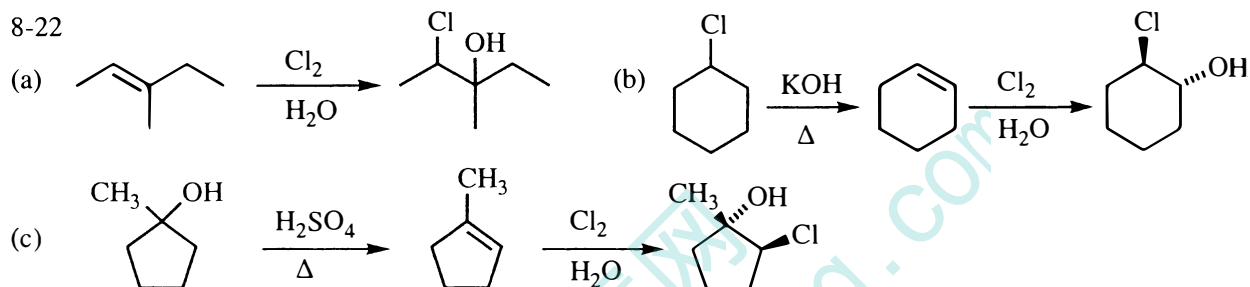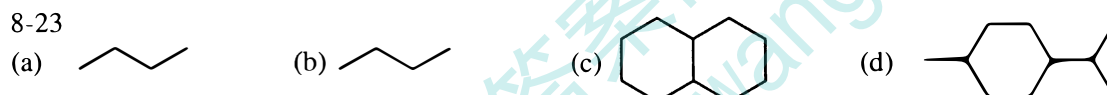
(a) CH₃ OH
Cl

plus enantiomer

(b)

HO Br

(c) H₃C H Cl

HO H CH₃

plus enantiomer

(d) H₃C H Cl

HO H CH₃

plus enantiomer

(e) CH₃ OH Br + CH₃ Cl Br

plus enantiomers

8-22

(a) →(Cl₂ / H₂O)→ Cl OH

(b) →(KOH / Δ)→ →(Cl₂ / H₂O)→ Cl OH

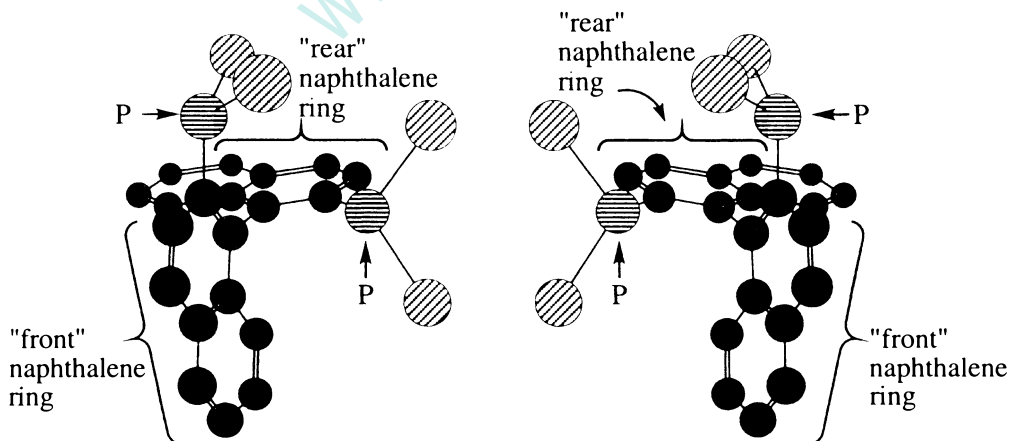(c) CH₃ OH →(H₂SO₄ / Δ)→ CH₃ →(Cl₂ / H₂O)→ CH₃ OH Cl
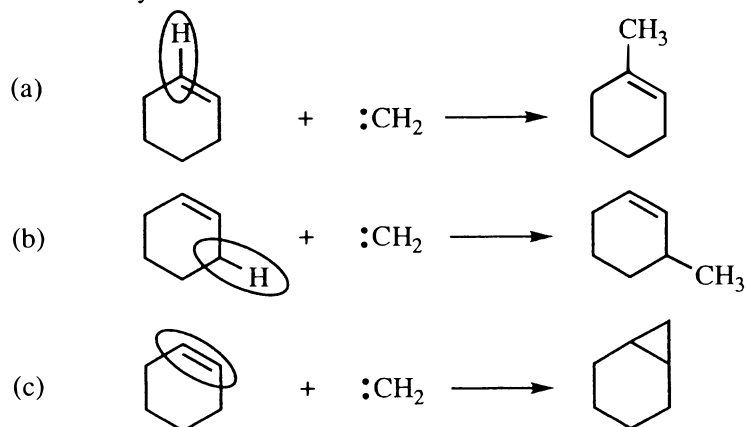
8-23

(a)   (b)   (c)   (d)

8-24 Limonene, $C_{10}H_{16}$, has three elements of unsaturation. Upon catalytic hydrogenation, the product, $C_{10}H_{20}$, has one element of unsaturation. Two elements of unsaturation have been removed by hydrogenation—these must have been pi bonds, either two double bonds or one triple bond. The one remaining unsaturation must be a ring. Thus, limonene must have one ring and either two double bonds or one triple bond. (The structure of limonene is shown in the text in Problem 8-23(d), and the hydrogenation product is shown above in the solution to 8-23(d).)

8-25 The BINAP ligand is an example of a conformationally hindered biphenyl as described in text section 5-9A and Figure 5-17. The groups are too large to permit rotation around the single bond connecting the rings, so the molecules are locked into one chiral twist or its mirror image.

"rear" naphthalene ring

P →

P

"front" naphthalene ring

"rear" naphthalene ring
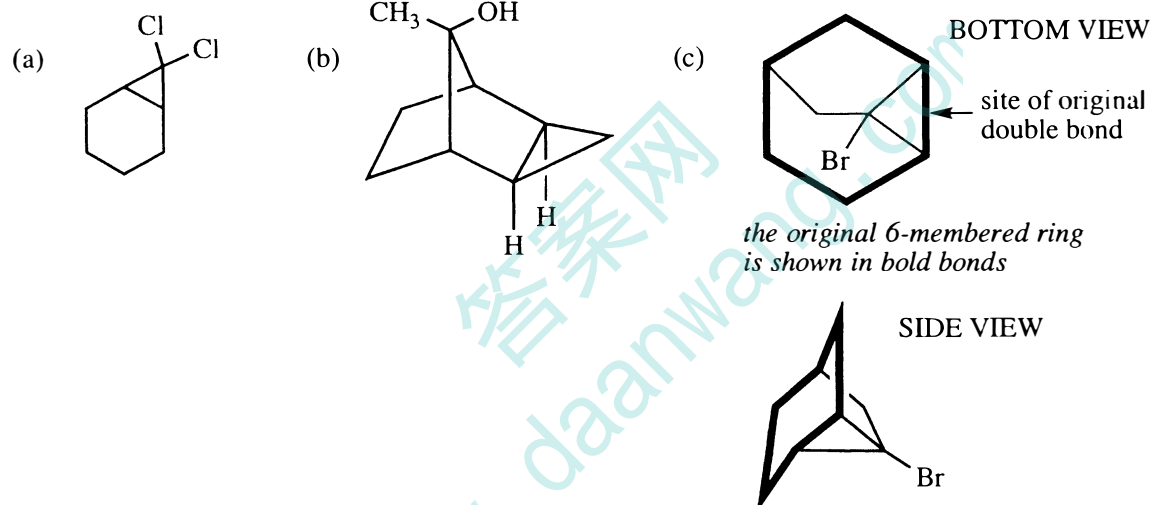
← P

P

"front" naphthalene ring

These simplified three-dimensional drawings of the enantiomers show that the two naphthalene rings are twisted almost perpendicular to each other, and the large —P(Ph)₂ substituents prevent interconversion of these mirror images.

167

8-26 Methylene inserts into the circled bonds.

(a)

(b)

(c)

8-27

(a)

(b)

(c)

BOTTOM VIEW

site of original
double bond

*the original 6-membered ring
is shown in bold bonds*

SIDE VIEW

8-28

(a)

$$\xrightarrow[\text{Zn(Cu)}]{\text{CH}_2\text{I}_2}$$

(b)

$$\xrightarrow[\text{50\% NaOH (aq)}]{\text{CH}_2\text{Br}_2}$$

(c)

$$\xrightarrow[\Delta]{\text{H}_2\text{SO}_4}$$

$$\xrightarrow[\text{50\% NaOH (aq)}]{\text{CHCl}_3}$$

8-29

(a)

(b)

(c)

(d)

168

8-30

(a)

ENANTIOMERS

(b)

IDENTICAL—MESO
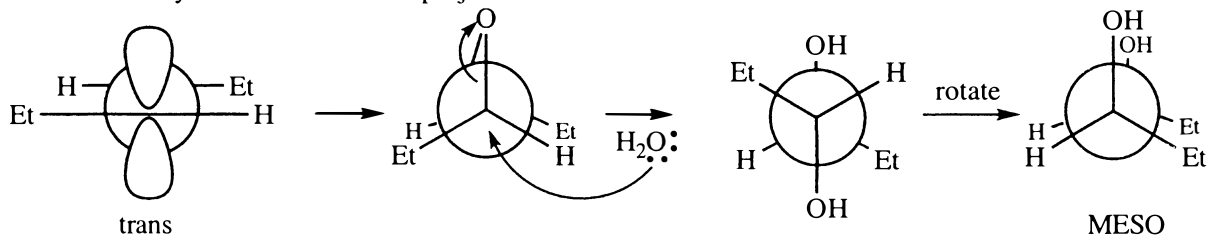
stereochemistry shown in Newman projections:

trans

rotate

MESO

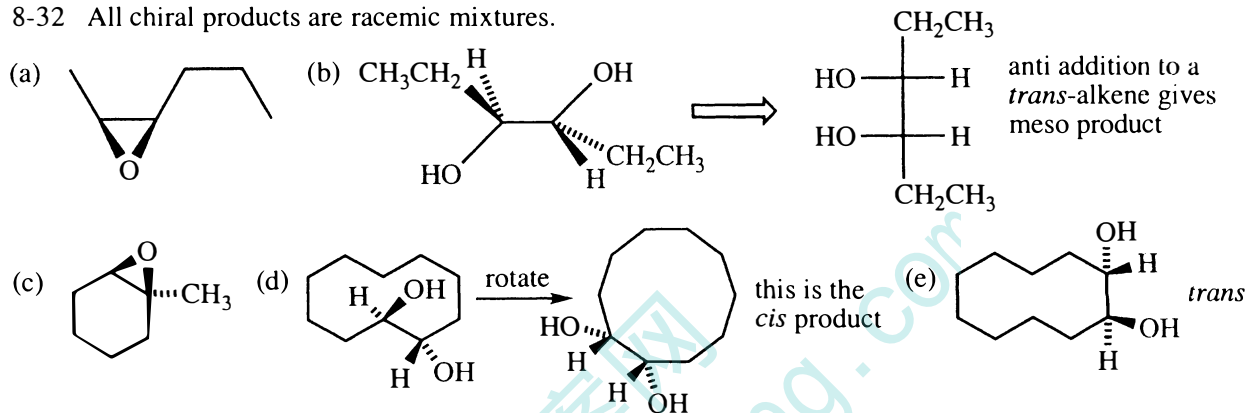Remember the lesson from Problem 8-17: anti addition of a symmetric reagent to a symmetric *cis*-alkene gives racemic product, while anti addition to a *trans*-alkene gives meso product. This fits the definition of a *stereospecific* reaction, where different stereoisomers of the starting material (*cis* and *trans*) are converted into different stereoisomers of product (a *dl-pair* and *meso form*).

8-31

8-32 All chiral products are racemic mixtures.

(a)

(b)

anti addition to a *trans*-alkene gives meso product

(c)

(d)

rotate

this is the *cis* product

(e)

trans

8-33

enantiomers

8-34 All these reactions begin with achiral reagents; therefore, all the chiral products are racemic.

(a)

(b)

(c)

(d)

(e)

same as (d)!

(f)

same as (c)!

Refer to the observation *in* the solution to Problem 8-35 on the next page.

8-35

(a) meso

(b) racemic (*d,l*)

(c) meso

(d) racemic (*d,l*)

Have you noticed yet? For symmetric alkenes and symmetric reagents (addition of two identical X groups):
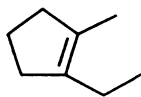
cis-alkene + **syn** addition → meso
cis-alkene + **anti** addition → racemic
trans-alkene + **syn** addition → racemic
trans-alkene + **anti** addition → meso

Assume that cis/syn/meso are "same", and trans/anti/racemic are "opposite". Then any combination can be predicted, just like math!
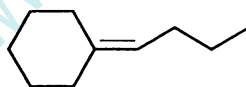
$+1 \times +1 = +1$
$+1 \times -1 = -1$
$-1 \times +1 = -1$
$-1 \times -1 = +1$

8-36 Solve these ozonolysis problems by working backwards, that is, by "reattaching" the two carbons of the new carbonyl groups into alkenes. Here's a hint. When you cut a circular piece of string, you still have only one piece. When you cut a linear piece of string, you have two pieces. Same with molecules. If ozonolysis forms only one product with two carbonyls, the alkene had to have been in a ring. If ozonolysis gives two molecules, the alkene had to have been in a chain.
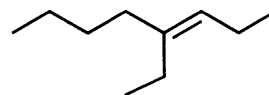
(a) two carbonyls from ozonolysis are in a chain, so alkene had to have been in a ring

(b) two carbonyls from ozonolysis are in two different products, so alkene had to have been in a chain, not a ring
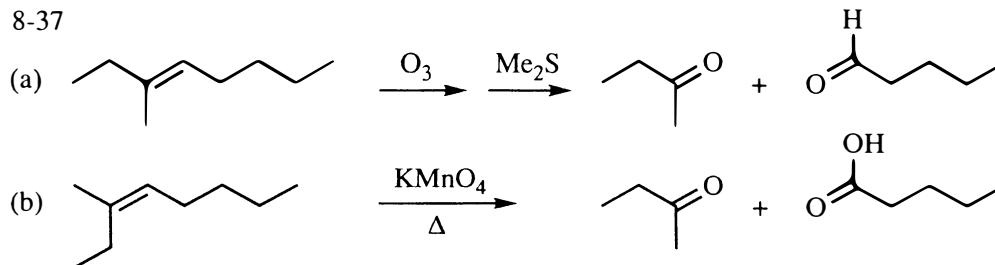
(c) two carbonyls from ozonolysis are in two different products, so alkene had to have been in a chain, not a ring

E or *Z* of alkene cannot be determined from products

8-37

(a)

(b)

8-37 continued

(c) $\xrightarrow{O_3}$ $\xrightarrow{Me_2S}$ =O + O=

(d) $\xrightarrow{O_3}$ $\xrightarrow{Me_2S}$

(e) $\xrightarrow[\Delta]{KMnO_4}$

(f) $\xrightarrow[cold]{KMnO_4}$

8-38 The representation for a generic acid will be H—B, where B is the conjugate base.

8-39 Catalytic BF_3 reacts with trace amounts of water to form the probable catalyst:

8-40   H—B is used here to symbolize a generic acid.

alkenes

polymers
(colored)

Note: the dashed bond symbol is used here to indicate the continuation of a polymer chain.

8-41

1° radical, and *not* resonance-stabilized—
this orientation is not observed

Orientation of addition always generates the more stable intermediate; the energy difference between a 1° radical (shown above) and a benzylic radical is huge. The phenyl substituents must necessarily be on alternating carbons because the orientation of attack is always the same—not a random process.

8-42   For clarity, the new bonds formed in this mechanism are shown in bold.

8-43

Dashed bonds mean that the chain continues.

8-44

8-45 In the spirit of this problem, all starting materials will have six carbons or fewer and only one carbon-carbon double bond. Reagents may have other atoms.

(a)

major product from resonance stabilized radical on 1° and 3° C

(b)

(c)

8-46 Please refer to solution 1-20, page 12 of this Solutions Manual.

8-47

(f) peroxides do not affect HCl addition

8-47 continued

(h)

(i)

(j)

(k)

(l)

(m)

(n)

(o)

intermediate

(p)

8-48

(a)

initiation

propagation

(b)

8-48 continued

(c)

(d)

(e)

(f)

8-48 continued

(g)

Recall that "Ph" is the abbreviation for phenyl.

8-49

(a)

$$\xrightarrow[\text{H}_2\text{O}]{\text{Hg(OAc)}_2} \xrightarrow{\text{NaBH}_4}$$

(b)

$$\xrightarrow[\text{ROOR}]{\text{HBr}}$$

(c)

$$\xrightarrow{\text{BH}_3 \cdot \text{THF}} \xrightarrow[\text{HO}^-]{\text{H}_2\text{O}_2}$$

(d)

$$\xrightarrow{\text{O}_3} \xrightarrow{\text{Me}_2\text{S}}$$

or KMnO$_4$, Δ

(e)

$$\xrightarrow[\text{CH}_3\text{OH}]{\text{Hg(OAc)}_2} \xrightarrow{\text{NaBH}_4}$$

(f)

$$\xrightarrow[\text{H}_2\text{O}_2]{\text{OsO}_4}$$

or cold, dilute KMnO$_4$

(g)

$$\xrightarrow[\text{Zn(Cu)}]{\text{CH}_2\text{I}_2}$$

(h)

$$\xrightarrow[\text{H}_2\text{O}]{\text{Cl}_2}$$

(i)

$$\xrightarrow[\text{50\% NaOH (aq)}]{\text{CHBr}_3}$$

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8-50

(a) [structure: CH₃-substituted cyclohexane with HO and a side chain bearing CH₂OH]

(b) [structure: CH₃-substituted cyclohexane with two epoxide (O) groups]

(c) [structure: diketone-aldehyde] + $CH_2=O$

(d) [structure: HO, HO, CH₃-substituted cyclohexane with side chain bearing OH and CH₂OH]

(e) [structure: HOOC diketone] + CO_2

(f) [structure: HO, HO, CH₃-substituted cyclohexane with side chain bearing OH and CH₂OH]

(g) [structure: isopropyl-substituted cyclohexane]

(h) [structure: Br, cyclohexane with C(CH₃)₂Br side group]

(i) [structure: Br, cyclohexane with CH₂Br side chain]

(j) [structure: Br, HO, CH₃-cyclohexane with C(CH₃)(OH)CH₂Br side chain]

(k) [structure: Cl, Cl, CH₃-cyclohexane with C(CH₃)(Cl)CH₂Cl side chain]

(l) [structure: CH₃O-cyclohexane with C(CH₃)₂OCH₃ side group]

(m) [structure: CH₃-cyclohexane with 1-methylcyclopropyl group]

8-51 Each monomer has two carbons in the backbone, so the substituents on the monomer will repeat every two carbons in the polymer. Dashed bonds indicate continuation of the polymer chain.

line formula representation

[structure: vinyl chloride monomer with Cl] → ----$CH_2CHCH_2CHCH_2CHCH_2CH$---- (with Cl substituents)
polyvinyl chloride, PVC

[structure: tetrafluoroethylene monomer] → ----C—C—C—C—C—C---- (with F substituents)
polytetrafluoroethylene, PTFE, Teflon

[structure: acrylonitrile monomer with C≡N] → ----$CH_2CHCH_2CHCH_2CHCH_2CH$---- (with C≡N substituents)
polyacrylonitrile, Orlon

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8-52   Without divinylbenzene, individual chains of polystyrene are able to slide past one another. Addition of divinylbenzene during polymerization forms bridges, or "crosslinks", between chains, adding strength and rigidity to the polymer. Divinylbenzene and similar molecules are called crosslinking agents.

two polystyrene chains crosslinked by a divinylbenzene monomer shown in the dashed oval

8-53   A peroxy radical is shown as the initiator. Newly formed bonds are shown in bold.

8-54

ethyl acrylate

8-55   In each case, the compound (boxed) that produces the more stable carbocation is more reactive.

(a)

(b)

(c)

180

8-56 Once the bromonium ion is formed, it can be attacked by either nucleophile, bromide or chloride, leading to the mixture of products.

8-57   Two possible orientations of attack of bromine radical are possible:

(A) anti-Markovnikov

(B) Markovnikov

The first step in the mechanism is endothermic and rate determining. The 3° radical produced in anti-Markovnikov attack (A) of bromine radical is several kJ/mole more stable than the 1° radical generated by Markovnikov attack (B). The Hammond Postulate tells us that it is reasonable to assume that the activation energy for anti-Markovnikov addition is lower than for Markovnikov addition. This defines the first half of the energy diagram.

The relative stabilities of the final products are somewhat difficult to predict. (Remember that stability of final products does not necessarily reflect relative stabilities of intermediates; this is why a thermodynamic product can be different from a kinetic product.) From bond dissociation energies (kJ/mole) in Table 4-2:

anti-Markovnikov		Markovnikov	
H to 3° C	381	H to 1° C	410
Br to 1° C	285	Br to 3° C	272
	666 kJ/mole		682 kJ/mole

If it takes more energy to break bonds in the Markovnikov product, it must be lower in energy, therefore, more stable—OPPOSITE OF STABILITY OF THE INTERMEDIATES!

Now we are ready to construct the energy diagram; see the next page.

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8-57 continued

It is the anti-Markovnikov product that is the kinetic product, not the thermodynamic product; the anti-Markovnikov product is obtained since its rate-determining step has the lower activation energy.

8-58   Recall these facts about ozonolysis: each alkene cleaved by ozone produces two carbonyl groups; an alkene in a chain produces two separate products; an alkene in a ring produces one product in which the two carbonyls are connected.

(a)   + CH$_2$=O

(b)

(c)

(d)

8-59

(a)

(b)

(or cold, dilute KMnO$_4$)

cis + **syn**
(*cis* double bond plus
syn stereochemistry of addition)

trans + **anti**
(*trans* double bond plus
anti stereochemistry of addition)

8-59 continued

(c)

anti addition of Br$_2$ *requires trans* alkene to give meso product

This structure shows a *trans* alkene in a 10-membered ring, just the rotated view of the structure to the right.

rotate around C-2

trans-cyclodecene

(d)

(e)

(f)

8-60

A) Unknown X, C$_5$H$_9$Br, has one element of unsaturation. X reacts with neither bromine nor KMnO$_4$, so the unsaturation in X cannot be an alkene; it must be a ring.

B) Upon treatment with strong base (*t*-butoxide), X loses H and Br to give Y, C$_5$H$_8$, which does react with bromine and KMnO$_4$; it must have an alkene and a ring. Only one isomer is formed.

C) Catalytic hydrogenation of Y gives methylcyclobutane. This is a BIG clue because it gives the carbon skeleton of the unknown. Y must have a double bond in the methylcyclobutane skeleton, and X must have a Br on the methylcyclobutane skeleton.

D) Ozonolysis of Y gives a dialdehyde Z, C$_5$H$_8$O$_2$, which contains all the original carbons, so the alkene cleaved in the ozonolysis had to be in the ring.

Let's consider the possible answers for X and see if each fits the information.

1)

if this is X — KO-*t*-Bu ⟹ this must be Y; only one product — ozonolysis ⟹ + O=CH$_2$ DOES NOT FIT OZONOLYSIS RESULTS so this cannot be X and Y

more possibilities on the next page

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8-60 continued

2) KO-*t*-Bu ⟹ +

if this is X   major   minor

Y would be a mixture of alkenes, but the elimination gives only one product. We already saw in example 1 that the exocyclic double bond does not fit the ozonolysis results so this structure cannot be X.

3) KO-*t*-Bu ⟹ +

if this is X   major   minor

Y would be a mixture of alkenes, but the elimination gives only one product, so this structure of X is not consistent with the information provided.

4) KO-*t*-Bu ⟹ + ozonolysis ⟹

if this is X

SAME COMPOUND; this must be Y; only one product

Z, a dialdehyde

The correct structures for X, Y, and Z are given in the fourth possibility. The only structural feature of X that remains undetermined is whether it is the *cis* or *trans* isomer.

8-61 The clue to the structure of α-pinene is the ozonolysis. Working backwards shows the alkene position.

backwards ⟹ became carbonyl carbons

α-pinene

After ozonolysis, the two carbonyls are still connected; the alkene must have been in a ring, so reconnect the two carbonyl carbons with a double bond.

8-62 The two products from permanganate oxidation must have been connected by a double bond at the carbonyl carbons. Whether the alkene was *E* or *Z* cannot be determined by this experiment.

$$CH_3(CH_2)_{12}CH=CH(CH_2)_7CH_3$$

shown here as *Z* which is the naturally-occurring isomer

8-63

Unknown X $\xrightarrow[\text{Pt}]{3\ H_2}$ must have three alkenes in this skeleton

Unknown X $\xrightarrow{O_3}\xrightarrow{Me_2S}$ $CH_2=O$ + ... + ...

There are several ways to attack a problem like this. One is the trial-and-error method, that is, put double bonds in all possible positions until the ozonolysis products match. There are times when the trial-and-error method is useful (as in simple problems where the number of possibilities is few), but this is not one of them.

Let's try logic. Analyze the ozonolysis products carefully—what do you see? There are only two methyl groups, so one of the three terminal carbons in the skeleton (C-8, C-9, or C-10) has to be a $=CH_2$. Do we know which terminal carbon has the double bond? Yes, we can deduce that. If C-10 were double-bonded to C-4, then after ozonolysis, C-8 and C-9 must still be attached to C-7. However, in the ozonolysis products, there is no branched chain, that is, no combination of C-8 + C-9 + C-7 + C-1. What if C-7 had a double bond to C-1? Then we would have acetone, CH_3COCH_3, as an ozonolysis product—we don't. Thus, we can't have a double bond from C-4 to C-10. One of the other terminal carbons (C-8) must have a double bond to C-7.

The other two double bonds have to be in the ring, but where? The products do not have branched chains, so double bonds must appear at both C-1 and C-4. There are only two possibilities for this requirement.

Ozonolysis of **I** would give fragments containing one carbon, two carbons, and seven carbons. Ozonolysis of **II** would give fragments containing one carbon, four carbons, and five carbons. Aha! Our mystery structure must be **II**.

(Editorial comment: Science is more than a collection of facts. The application of observation and logic to solve problems by *deduction* and *inference* are critical scientific skills, ones that distinguish humans from algae.)

8-64 In this type of problem, begin by determining which bonds are broken and which are formed. These will always give clues as to what is happening.

H⁺ goes to most electronegative atom

protonated epoxide opens to give the most stable carbocation (3°)

3° carbocation looks for electrons, finds them at nearby alkene, forming a 6-membered ring (yes!)—leaves a 3° carbocation

8-65 See the solution to Problem 8-35 for simplified examples of these reactions.

(a)

trans + **syn** → racemic

(b)

trans + **anti** → meso

(c)

cis + **anti** → racemic

(d)

cis + **syn** → meso

186

8-66

8-67 By now, these rearrangements should not be so "unexpected".

alkyl migration with ring expansion gives 3° carbocation in 6-membered ring—carbocation nirvana!

You must be asking yourself, "Why didn't the methyl group migrate?" To which you answered by drawing the carbocation that would have been formed:

The new carbocation is indeed 3°, but it is only in a 5-membered ring, not quite as stable as in a 6-membered ring. In all probability, some of the product from methyl migration would be formed, but the 6-membered ring would be the major product.

8-68 Each alkene will produce two carbonyls upon ozonolysis or permanganate oxidation. Oxidation of the unknown generated four carbonyls, so the unknown must have had two alkenes. There is only one possibility for their positions.

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8-69

(a) Fumarase catalyzes the addition of H and OH, a hydration reaction.

(b) Fumaric acid is planar and cannot be chiral. Malic acid does have a chiral center and is chiral. The enzyme-catalyzed reaction produces only the *S* enantiomer, so the product must be optically active.

(c) One of the fundamental rules of stereochemistry is that optically inactive starting materials produce optically inactive products. Sulfuric-acid-catalyzed hydration would produce a racemic mixture of malic acid, that is, equal amounts of *R* and *S*.

(d) If the product is optically active, then either the starting materials or the catalyst were chiral. We know that water and fumaric acid are not chiral, so we must infer that fumarase is chiral.

(e) The D and the OD are on the "same side" of the Fischer projection (sometimes called the "erythro" stereoisomer). These are produced from either: (1) syn addition to *cis* alkenes, or (2) anti addition to *trans* alkenes. We know that fumaric acid is *trans*, so the addition of D and OD must necessarily be anti.

(f) Hydroboration is a syn addition.

As expected, *trans* alkene plus syn addition puts the two groups on the "opposite" side of the Fischer projection (sometimes called "threo").

8-70

(a)

(b)

8-71 The addition of BH_3 to an alkene is reversible. Given heat and time, the borane will eventually "walk" its way to the end of the chain through a series of addition-elimination cycles. The most stable alkylborane has the boron on the end carbon; eventually, the series of equilibria lead to that product which is oxidized to the primary alcohol.

8-72 First, we explain *how* the mixture of stereoisomers results, then *why*.

We have seen many times that the bridged halonium ion permits attack of the nucleophile only from the opposite side.

A mixture of *cis* and *trans* could result only if attack of chloride were possible from both top and bottom, something possible only if a *carbocation* existed at this carbon.

This picture of the p orbitals of benzene show resonance overlap with the p orbital of the carbocation. The chloride nucleophile can form a bond to the positive carbon from either the top or the bottom.

Why does a carbocation exist here? Not only is it 3°, *it is also next to a benzene ring (benzylic) and therefore resonance-stabilized.* This resonance stabilization would be forfeited in a halonium ion intermediate.

CHAPTER 9—ALKYNES

9-1   Other structures are possible in each case.

(a) C_6H_{10} $CH_3CH_2C\equiv CCH_2CH_3$ $CH_3CH_2CH_2CH_2C\equiv CH$

(b) C_8H_{12} ⬡—$C\equiv CH$ $HC\equiv C—CH_2CH=CHCH_2CH_2CH_3$

(c) C_7H_{10} ⬠—$C\equiv CH$ $CH_2=CH—C\equiv C—CH_2CH_2CH_3$

9-2   New IUPAC names are given. The asterisk (*) denotes acetylenic hydrogens of terminal alkynes.

(a) $CH_3CH_2—C\equiv C—\overset{*}{H}$ $CH_3—C\equiv C—CH_3$
            but-1-yne   but-2-yne

(b) $CH_3CH_2CH_2—C\equiv C—\overset{*}{H}$ $CH_3CH_2—C\equiv C—CH_3$ $CH_3\overset{\displaystyle CH_3}{\overset{|}{CH}}—C\equiv C—\overset{*}{H}$
            pent-1-yne   pent-2-yne   3-methylbut-1-yne

9-3   The decomposition reaction below is exothermic ($\Delta H° = -234$ kJ/mole) as well as having an increase in entropy. Thermodynamically, at 1500°C, an increase in entropy will have a large effect on ΔG (remember $\Delta G = \Delta H - T\Delta S$). Kinetically, almost any activation energy barrier will be overcome at 1500°C. Acetylene would likely decompose into its elements:

$$HC\equiv CH \xrightarrow{1500°\,C} 2\ C\ +\ H_2$$

9-4   Adding sodium amide to the mixture will produce the sodium salt of hex-1-yne, leaving hex-1-ene untouched. Distillation will remove the hex-1-ene, leaving the non-volatile salt behind.

$$\left.\begin{array}{l}CH_2=CHCH_2CH_2CH_2CH_3\\ H—C\equiv C—CH_2CH_2CH_2CH_3\end{array}\right\} \xrightarrow{NaNH_2} \left\{\begin{array}{l}CH_2=CHCH_2CH_2CH_2CH_3\\ Na^+\ ^-\!:C\equiv C—CH_2CH_2CH_2CH_3 \quad \text{non-volatile salt}\end{array}\right.$$

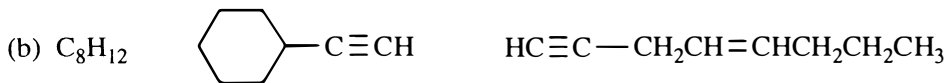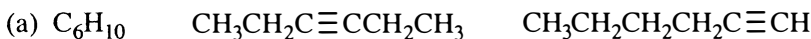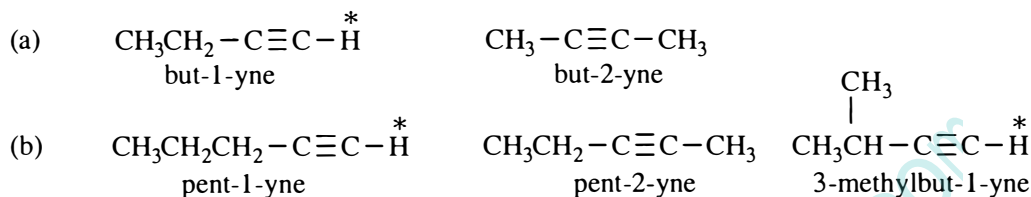9-5 The key to this problem is to understand that *a proton donor will react only with the conjugate base of a weaker acid*. See Appendix 2 at the end of this Solutions Manual for an in-depth discussion of acidity.

(a) $H—C\equiv C—H\ +\ NaNH_2\ \longrightarrow\ H—C\equiv C\!:^-\ Na^+\ +\ NH_3$

(b) $H—C\equiv C—H\ +\ CH_3Li\ \longrightarrow\ H—C\equiv C\!:^-\ Li^+\ +\ CH_4$

(c) no reaction: $NaOCH_3$ is not a strong enough base

(d) no reaction: NaOH is not a strong enough base

(e) $H—C\equiv C\!:^-\ Na^+\ +\ CH_3OH\ \longrightarrow\ H—C\equiv C—H\ +\ NaOCH_3$ (opposite of (c))

(f) $H—C\equiv C\!:^-\ Na^+\ +\ H_2O\ \longrightarrow\ H—C\equiv C—H\ +\ NaOH$ (opposite of (d))

(g) no reaction : $H—C\equiv C\!:^-\ Na^+$ is not a strong enough base

(h) no reaction: $NaNH_2$ is not a strong enough base

(i) $CH_3OH\ +\ NaNH_2\ \longrightarrow\ NaOCH_3\ +\ NH_3$

9-6

$$H-C\equiv C-H \xrightarrow{NaNH_2} H-C\equiv C:^- Na^+ \xrightarrow{CH_3CH_2Br} H-C\equiv C-CH_2CH_3$$

$$\downarrow NaNH_2$$

$$CH_3(CH_2)_5-C\equiv C-CH_2CH_3 \xleftarrow{CH_3(CH_2)_5Br} Na^+ {}^-:C\equiv C-CH_2CH_3$$

9-7

(a) $H-C\equiv C-H \xrightarrow[\text{2) } CH_3CH_2CH_2CH_2Br]{\text{1) } NaNH_2} H-C\equiv C-CH_2CH_2CH_2CH_3$

(b) $H-C\equiv C-H \xrightarrow[\text{2) } CH_3CH_2CH_2Br]{\text{1) } NaNH_2} H-C\equiv C-CH_2CH_2CH_3 \xrightarrow[\text{2) } CH_3I]{\text{1) } NaNH_2} CH_3-C\equiv C-CH_2CH_2CH_3$

(c) $H-C\equiv C-H \xrightarrow[\text{2) } CH_3CH_2Br]{\text{1) } NaNH_2} H-C\equiv C-CH_2CH_3 \xrightarrow[\text{2) } CH_3CH_2Br]{\text{1) } NaNH_2} CH_3CH_2-C\equiv C-CH_2CH_3$

(d) cannot be synthesized by an S_N2 reaction—would require attack on a 2° alkyl halide

$$CH_3-C\equiv C:^- Na^+ \quad + \quad \underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{CH}}CH_2CH_3 \quad \overset{2°}{\bcancel{\longrightarrow}} \quad CH_3-C\equiv C-\underset{\underset{CH_3}{|}}{CH}CH_2CH_3$$

strong nucleophile;
must be second order

low yields; not practical

(e) $H-C\equiv C-H \xrightarrow[\text{2) } CH_3I]{\text{1) } NaNH_2} CH_3-C\equiv C-H \xrightarrow[\text{2) } BrCH_2\underset{\underset{CH_3}{|}}{CH}CH_3]{\text{1) } NaNH_2} CH_3-C\equiv C-CH_2\underset{\underset{CH_3}{|}}{CH}CH_3$

(f) $H-C\equiv C-H \xrightarrow[\text{2) } Br(CH_2)_8Br]{\text{1) } NaNH_2}$

$$\downarrow NaNH_2$$

Intramolecular cyclization of large rings must be carried out in dilute solution so the last S_N2 displacement will be *intra*molecular and not *inter*molecular.

9-8

(a) $H-C\equiv C-H \xrightarrow[\text{2) } H_2C=O]{\text{1) } NaNH_2} \xrightarrow{H_2O} H-C\equiv C-CH_2OH$

192

9-8 continued

(b) $H-C\equiv C-H$ $\xrightarrow[\text{2) } Ph\diagdown C\diagup CH_3]{\text{1) NaNH}_2}$ $\xrightarrow{H_2O}$ $H_3C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}-C\equiv C-H$

                                     O

(c) $H-C\equiv C-H$ $\xrightarrow[\text{2) CH}_3I]{\text{1) NaNH}_2}$ $CH_3-C\equiv C-H$ $\xrightarrow[\substack{\text{2) HCCH}_2CH_2CH_3 \\ \quad\| \\ \quad O \\ \text{3) H}_2O}]{\text{1) NaNH}_2}$ $CH_3-C\equiv C-\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CH_2CH_3$

(d) $H-C\equiv C-H$ $\xrightarrow[\text{2) CH}_3I]{\text{1) NaNH}_2}$ $CH_3-C\equiv C-H$ $\xrightarrow[\substack{\text{2) CH}_3CCH_2CH_3 \\ \quad\| \\ \quad O \\ \text{3) H}_2O}]{\text{1) NaNH}_2}$ $CH_3-C\equiv C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2CH_3$

9-9

9-10 To determine the equilibrium constant in the reaction:

terminal alkyne $\rightleftharpoons$ internal alkyne $\Delta G = -RT \ln K_{eq}$

$\Delta G = -17.0$ kJ/mole

      $(-4.0$ kcal/mole$)$

R = 8.314 J/K•mole

$$K_{eq} = e^{\left(-\frac{\Delta G}{RT}\right)} = e^{\left(\frac{-(-17,000)}{(8.314)(473)}\right)} = e^{4.32} = 75$$

$$\frac{[\text{internal}]}{[\text{terminal}]} = \frac{75}{1} = \frac{98.7\% \text{ internal}}{1.3\% \text{ terminal}}$$

9-11 (a) This isomerization is the reverse of the mechanism in the solution to 9-9.

(b) All steps in part (a) are reversible. With a weaker base like KOH, an equilibrium mixture of pent-1-yne and pent-2-yne would result. With the strong base $NaNH_2$, however, the final terminal alkyne is deprotonated to give the acetylide ion:

$$H-C\equiv C-CH_2CH_2CH_3 \; + \; NaNH_2 \longrightarrow Na^+ \; {}^-\!{:}C\equiv C-CH_2CH_2CH_3 \; + \; NH_3$$
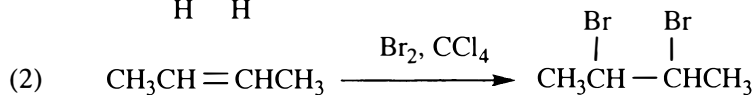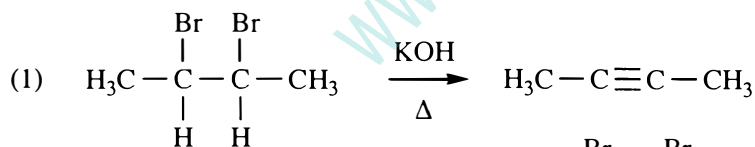
Because pent-1-yne is about 10 pK units more acidic than ammonia, this deprotonation is *not reversible*. The acetylide ion is produced and can't go back. Le Châtelier's Principle tells us that the reaction will try to replace the pent-1-yne that is being removed from the reaction mixture, so eventually all of the pent-2-yne will be drawn into the pent-1-yne anion "sink".
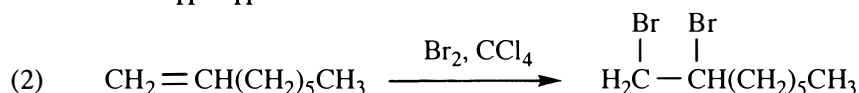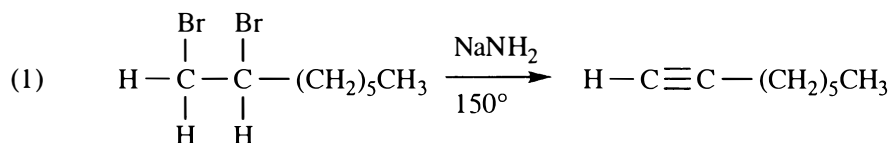
(c) Using the weaker base KOH at 200°C will restore the equilibrium between the two alkyne isomers with pent-2-yne predominating.
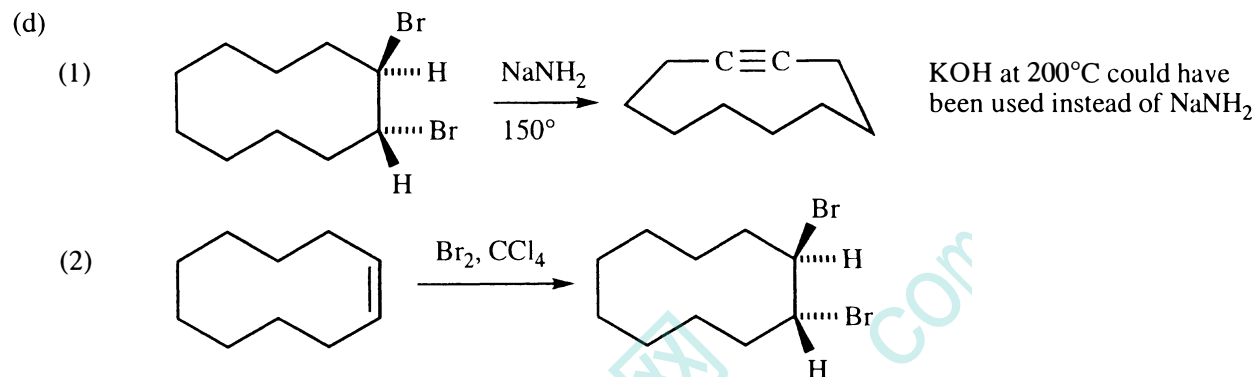
9-12

(a)

(b)

9-12 continued

(c)

(1)

(2)

(d)

(1)

KOH at 200°C could have been used instead of NaNH$_2$

(2)

9-13

(a) $CH_3CH_2 - C \equiv C - CH_2CH_2CH_2CH_3$ $\xrightarrow[\text{Lindlar catalyst}]{H_2}$

(b) $H_3C - C \equiv C - CH_2CH_3$ $\xrightarrow[\text{NH}_3]{\text{Na}}$

(c)

One of the useful "tricks" of organic chemistry is the ability to convert one stereoisomer into another. Having a pair of reactions like the two reductions shown in parts (a) and (b) that give opposite stereochemistry is very useful, because a common intermediate (the alkyne) can be transformed into either stereoisomer. This principle is used again in part (d).

195

9-13 continued

(d)

9-14   The goal is to add only one equivalent of bromine, always avoiding an excess of bromine, because two molecules of bromine could add to the triple bond if bromine was in excess. If the alkyne is added to the bromine, the first drops of alk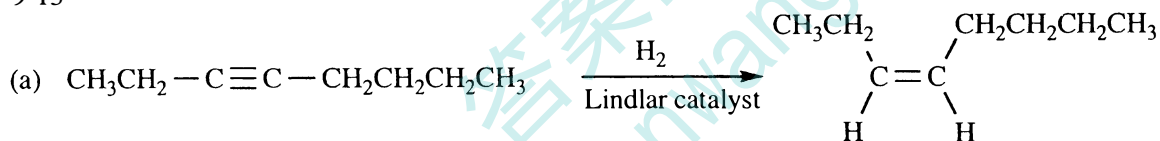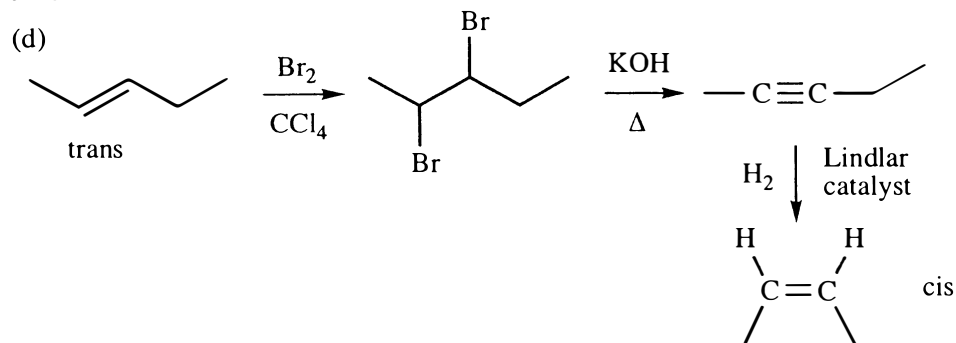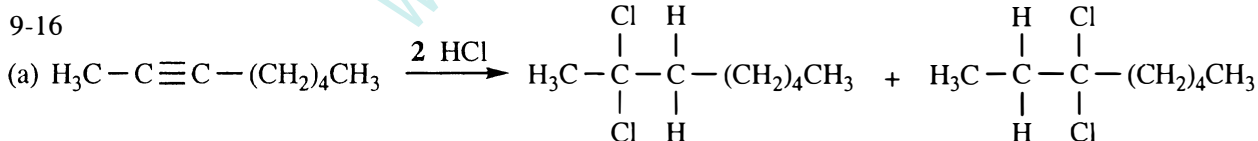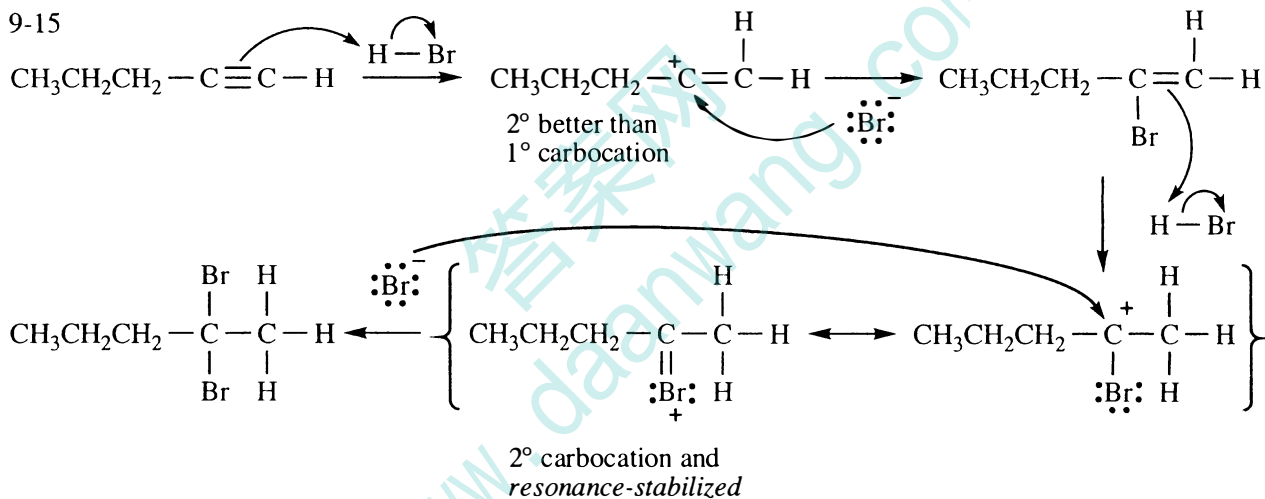yne will encounter a large excess of bromine. Instead, adding bromine to the alkyne will always ensure an excess of alkyne and should give a good yield of dibromo product.

9-15

9-16

(a) $H_3C-C\equiv C-(CH_2)_4CH_3$ $\xrightarrow{2\ HCl}$ $H_3C-\overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-(CH_2)_4CH_3$ + $H_3C-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{Cl}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-(CH_2)_4CH_3$

(b) The second addition occurs to make the carbocation intermediate at the carbon with the halogen because of *resonance stabilization.*

9-17

<u>initiation</u>: RO–OR $\xrightarrow{h\nu}$ 2 RO•

RO• + H—Br $\longrightarrow$ RO—H + Br•

<u>propagation</u>:

Br• + H—C≡C—CH₂CH₂CH₃ $\longrightarrow$ H—C=C•—CH₂CH₂CH₃
|
Br

H—C=C•—CH₂CH₂CH₃ + H—Br $\longrightarrow$ H—C=C—CH₂CH₂CH₃ + Br•
| | |
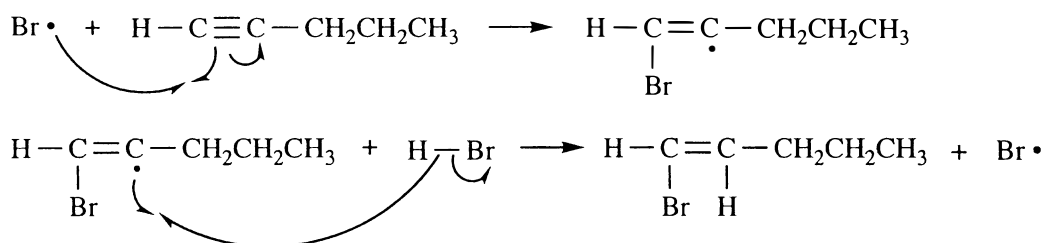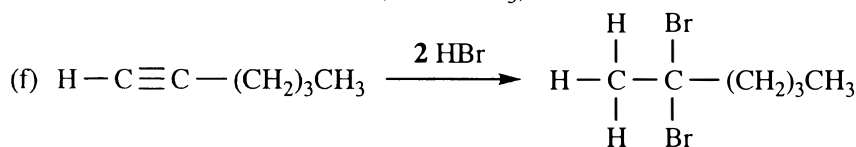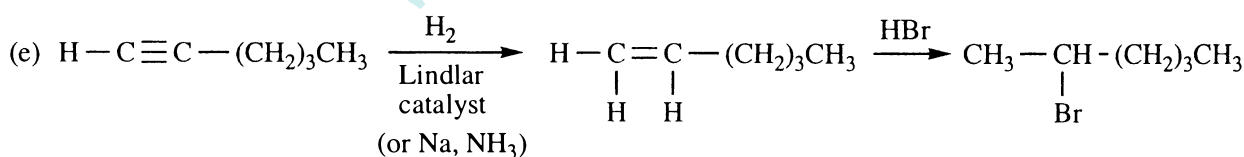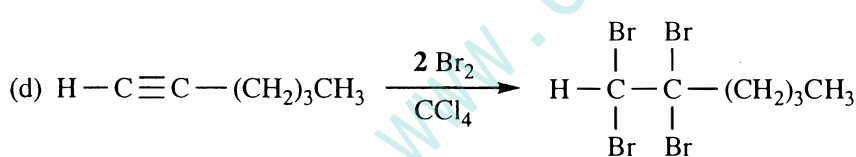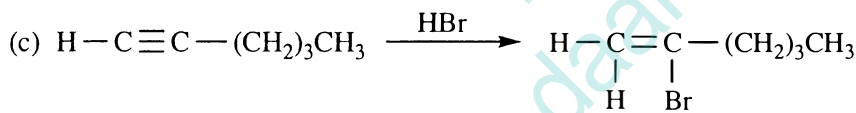Br   Br H

The 2° radical is more stable than 1°. The anti-Markovnikov orientation occurs because the bromine radical attacks first to make the most stable radical, which is contrary to electrophilic addition where the H⁺ attacks first (see the solution to 9-15).

9-18

(a) H—C≡C—(CH₂)₃CH₃ $\xrightarrow{\text{1 eq. Cl}_2}$ H—C=C—(CH₂)₃CH₃ $E + Z$
| |
Cl Cl

(b) H—C≡C—(CH₂)₃CH₃ $\xrightarrow[\text{ROOR}]{\text{HBr}}$ H—C=C—(CH₂)₃CH₃ $E + Z$
| |
Br H

(c) H—C≡C—(CH₂)₃CH₃ $\xrightarrow{\text{HBr}}$ H—C=C—(CH₂)₃CH₃
| |
H Br

(d) H—C≡C—(CH₂)₃CH₃ $\xrightarrow[\text{CCl}_4]{\text{2 Br}_2}$
Br Br
| |
H—C—C—(CH₂)₃CH₃
| |
Br Br

(e) H—C≡C—(CH₂)₃CH₃ $\xrightarrow[\substack{\text{Lindlar}\\\text{catalyst}\\\text{(or Na, NH}_3)}]{\text{H}_2}$ H—C=C—(CH₂)₃CH₃ $\xrightarrow{\text{HBr}}$ CH₃—CH-(CH₂)₃CH₃
| | |
H H   Br

(f) H—C≡C—(CH₂)₃CH₃ $\xrightarrow{\text{2 HBr}}$
H Br
| |
H—C—C—(CH₂)₃CH₃
| |
H Br

9-19

$$CH_3-C\equiv C-CH_2CH_3$$

H⁺   H⁺

$$CH_3-\overset{+}{C}=C-CH_2CH_3 \qquad CH_3-\overset{+}{C}=C-CH_2CH_3$$
$$\overset{|}{H} \qquad\qquad\qquad\qquad \overset{|}{H}$$

both 2° *vinyl* carbocations

$H_2\ddot{O}:$ $H_2\ddot{O}:$

$$CH_3-C=C-CH_2CH_3 \qquad CH_3-C=C-CH_2CH_3$$
$$\overset{|}{H}\ \overset{|+}{:OH} \qquad\qquad HO:\ \overset{|}{H}$$
$$\overset{|}{H} \qquad\qquad\qquad \overset{|}{H}$$

$H_2\ddot{O}:$ $H_2\ddot{O}:$

$$CH_3-C=C-CH_2CH_3 \qquad CH_3-C=C-CH_2CH_3$$
$$\overset{|}{H}\ :\ddot{O}H \qquad\qquad HO:\ \overset{|}{H}$$

H⁺   H⁺

$$CH_3-\overset{|}{\underset{|}{C}}-\overset{+}{C}-CH_2CH_3 \qquad CH_3-\overset{+}{C}-\overset{|}{\underset{|}{C}}-CH_2CH_3$$
$$\overset{H}{|}\quad :\ddot{O}-H \qquad\qquad H-\ddot{O}:\ H$$

resonance-stabilized carbocations

(resonance forms not shown)

$H_2\ddot{O}:$ $H_2\ddot{O}:$

$$CH_3-\overset{H}{\underset{H}{C}}-\overset{}{\underset{O}{\overset{||}{C}}}-CH_2CH_3 \qquad CH_3-\overset{}{\underset{O}{\overset{||}{C}}}-\overset{H}{\underset{H}{C}}-CH_2CH_3$$
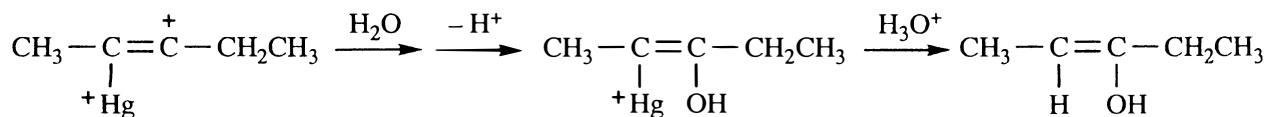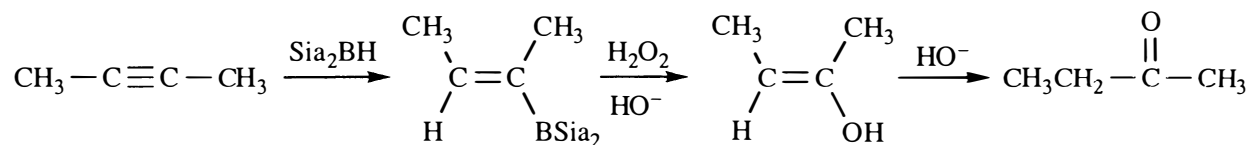
3-pentanone   2-pentanone

The role of the mercury catalyst is not shown in this mechanism. As a Lewis acid, it may act like the proton in the first step, helping to form vinyl cations; the mercury is replaced when acid is added.

$$CH_3-C=\overset{+}{C}-CH_2CH_3 \xrightarrow{H_2O} \xrightarrow{-H^+} CH_3-C=C-CH_2CH_3 \xrightarrow{H_3O^+} CH_3-C=C-CH_2CH_3$$
$$\quad\ \ \overset{|}{{}^+Hg} \qquad\qquad\qquad\qquad\qquad {}^+Hg\ \ OH \qquad\qquad\qquad H\ \ OH$$
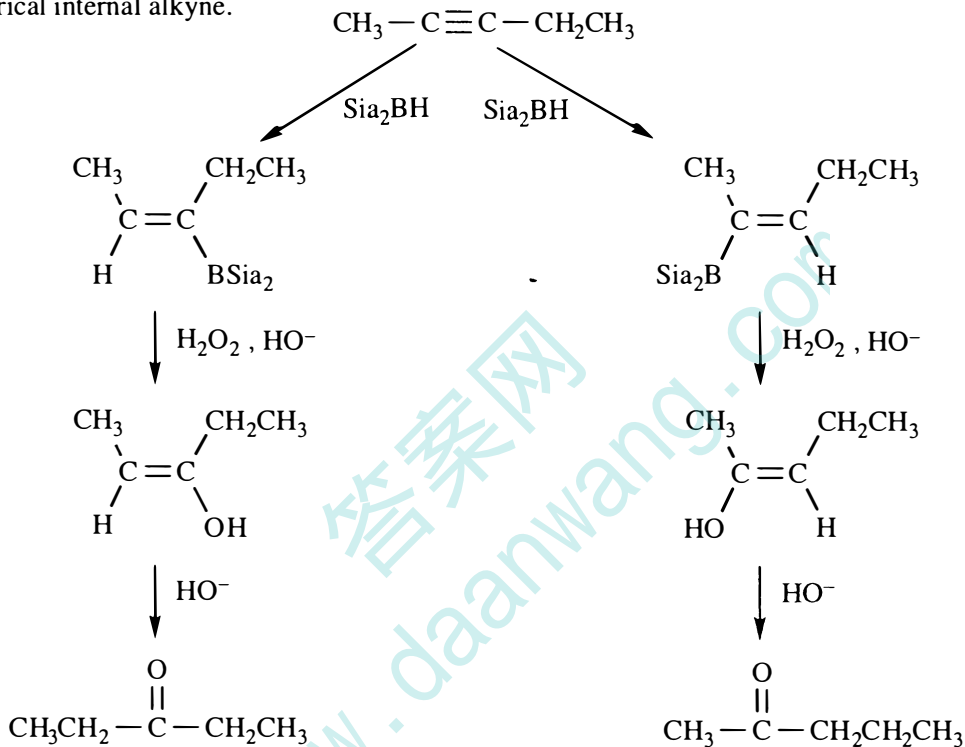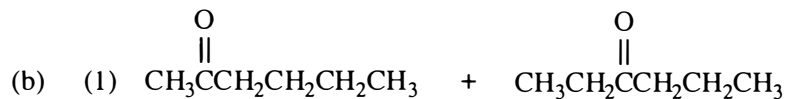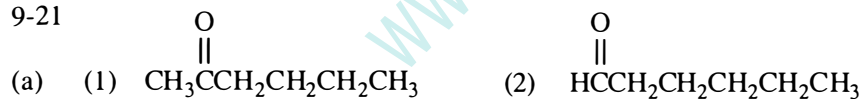
9-20

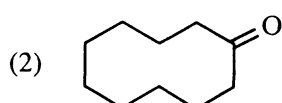(a) But-2-yne is symmetric. Either orientation produces the same product.
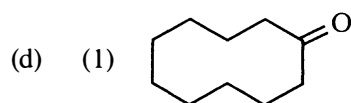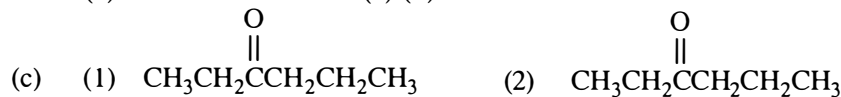

(b) Pent-2-yne is not symmetric. Different orientations of attack will lead to different products on any unsymmetrical internal alkyne.

9-21
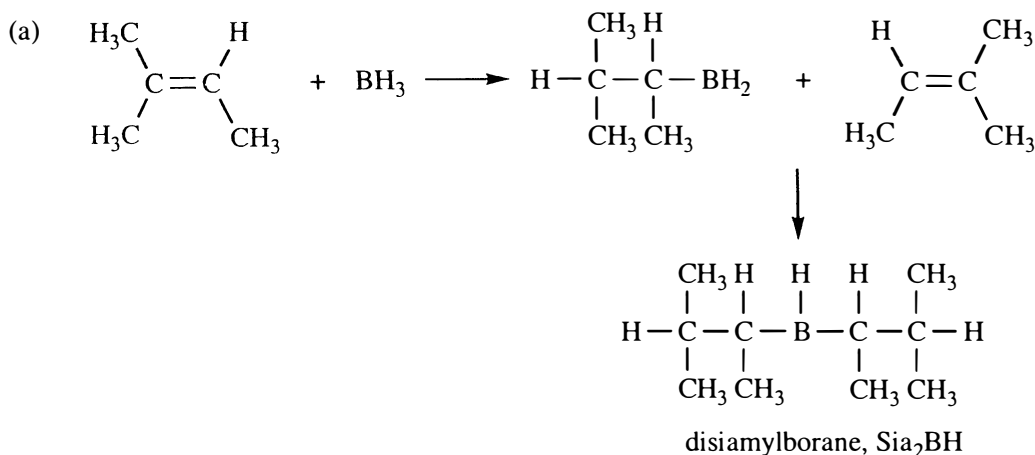
(a) (1) $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$ (2) $H\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2CH_3$

(b) (1) $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$ + $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$

(2) same mixture as in (b) (1)

(c) (1) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$ (2) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$

(d) (1)   (2)

199

9-22

(a)

disiamylborane, Sia$_2$BH
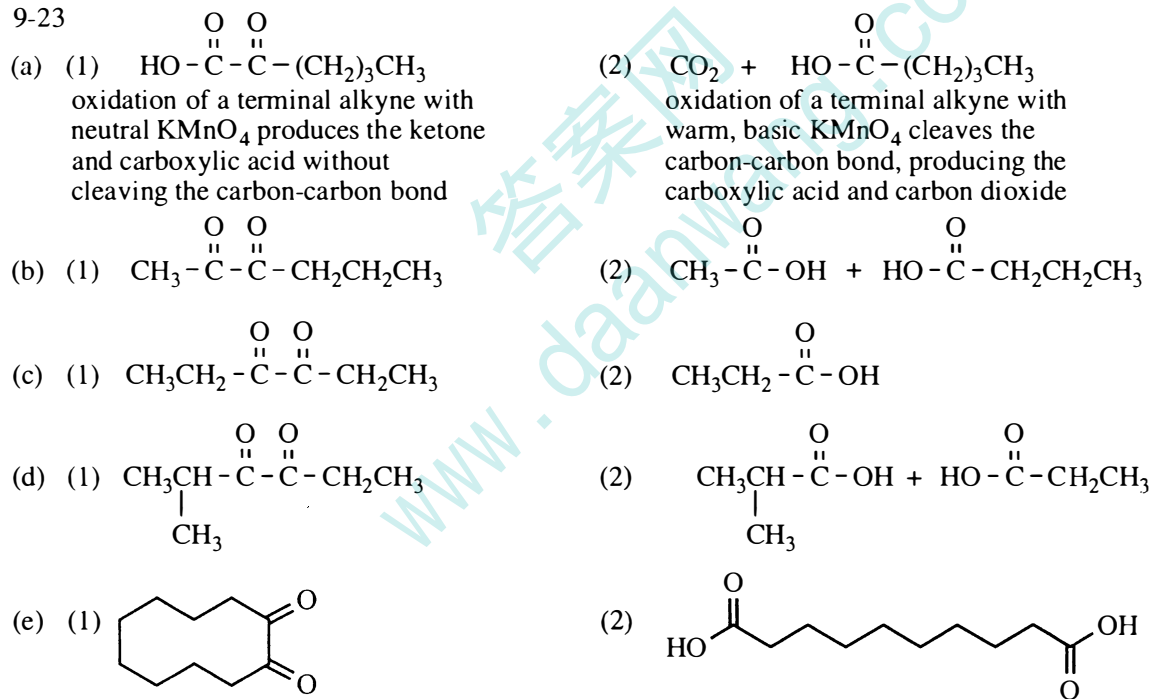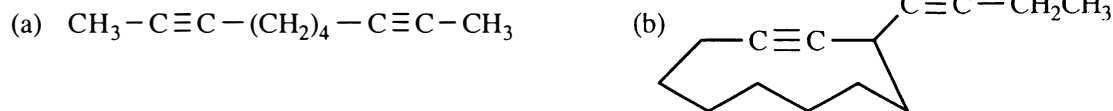
(b) There is too much steric hindrance in Sia$_2$BH for the third B—H to add across another alkene. The reagent can add to alkynes because alkynes are linear and attack is not hindered by bulky substituents.
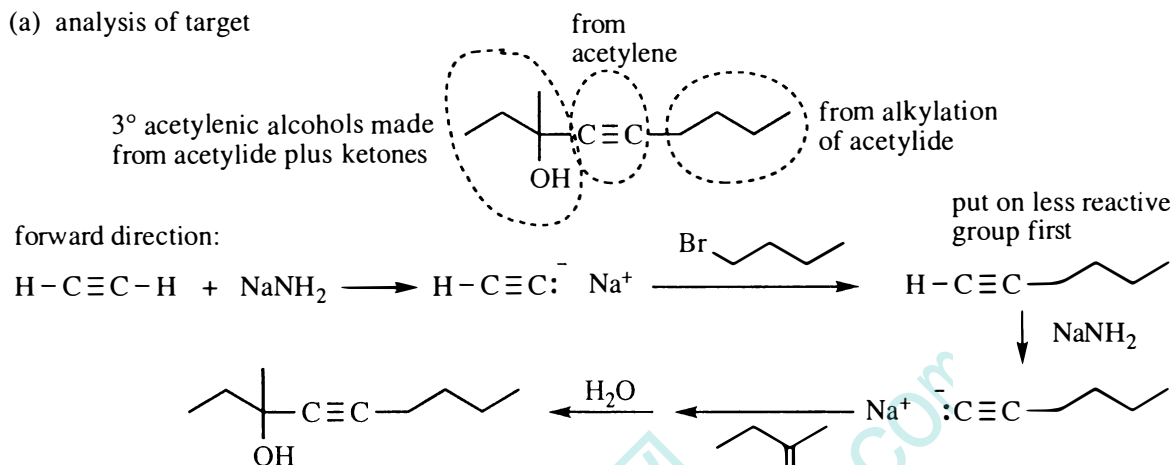
9-23

(a) (1) HO–C(=O)–C(=O)–(CH$_2$)$_3$CH$_3$
oxidation of a terminal alkyne with neutral KMnO$_4$ produces the ketone and carboxylic acid without cleaving the carbon-carbon bond

(2) CO$_2$ + HO–C(=O)–(CH$_2$)$_3$CH$_3$
oxidation of a terminal alkyne with warm, basic KMnO$_4$ cleaves the carbon-carbon bond, producing the carboxylic acid and carbon dioxide

(b) (1) CH$_3$–C(=O)–C(=O)–CH$_2$CH$_2$CH$_3$

(2) CH$_3$–C(=O)–OH + HO–C(=O)–CH$_2$CH$_2$CH$_3$

(c) (1) CH$_3$CH$_2$–C(=O)–C(=O)–CH$_2$CH$_3$

(2) CH$_3$CH$_2$–C(=O)–OH

(d) (1) CH$_3$CH(CH$_3$)–C(=O)–C(=O)–CH$_2$CH$_3$

(2) CH$_3$CH(CH$_3$)–C(=O)–OH + HO–C(=O)–CH$_2$CH$_3$

(e) (1)

(2)

9-24

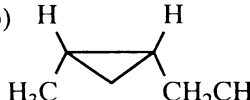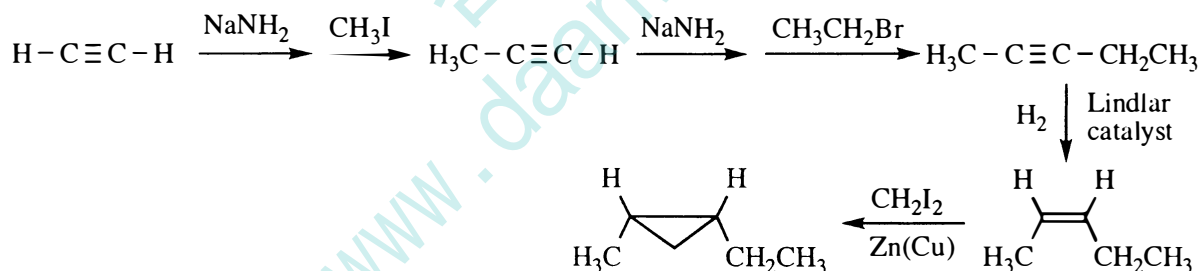(a) CH$_3$–C≡C–(CH$_2$)$_4$–C≡C–CH$_3$

(b)

200

9-25 When proposing syntheses, begin by analyzing the target molecule, looking for smaller pieces that can be combined to make the desired compound. This is especially true for targets that have more carbons than the starting materials; immediately, you will know that a carbon-carbon bond forming reaction will be necessary.
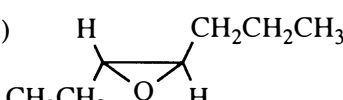
People who succeed at synthesis *know the reactions*—there is no shortcut. Practice the reactions for each functional group until they become automatic.
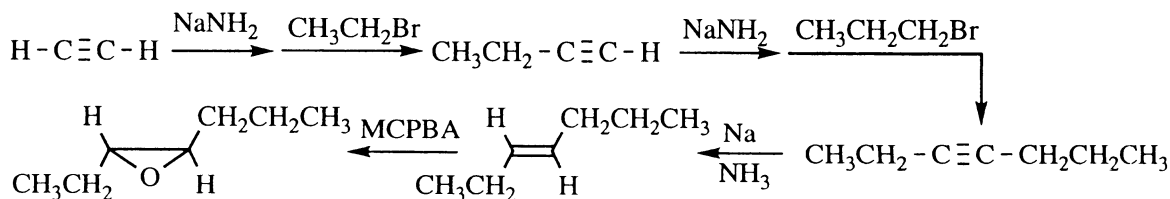
(a) analysis of target

3° acetylenic alcohols made from acetylide plus ketones

from acetylene

from alkylation of acetylide

forward direction:

put on less reactive group first

$$H-C\equiv C-H + NaNH_2 \longrightarrow H-C\equiv C:^- \ Na^+ \longrightarrow H-C\equiv C-\text{(butyl)}$$

$$\downarrow NaNH_2$$

(3° acetylenic alcohol) $\xleftarrow{H_2O}$ $\xleftarrow{}$ $Na^+ \ :C\equiv C-\text{(butyl)}$

(b)

analysis of target: cyclopropanes are made by carbene insertion into alkenes; to get *cis* substitution around cyclopropane, stereochemistry of alkene must be *cis; cis* alkene comes from catalytic hydrogenation of an alkyne
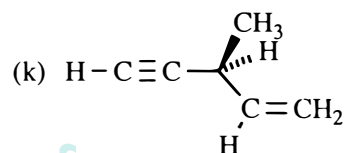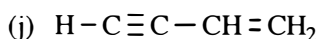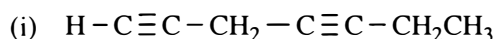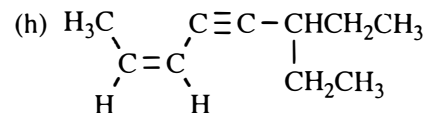
$$H-C\equiv C-H \xrightarrow{NaNH_2} \xrightarrow{CH_3I} H_3C-C\equiv C-H \xrightarrow{NaNH_2} \xrightarrow{CH_3CH_2Br} H_3C-C\equiv C-CH_2CH_3$$

$$H_2 \ \Big\downarrow \ \begin{array}{c}\text{Lindlar}\\\text{catalyst}\end{array}$$

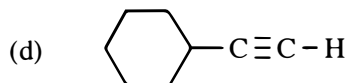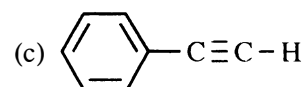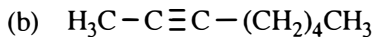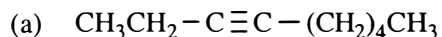(cyclopropane product) $\xleftarrow{\begin{array}{c}CH_2I_2\\Zn(Cu)\end{array}}$ (cis alkene)

(c)

analysis of target: epoxides are made by direct epoxidation of alkenes; to get *trans* substitution around epoxide, stereochemistry of alkene must be *trans*; *trans* alkene comes from sodium/ammonia reduction of an alkyne

$$H-C\equiv C-H \xrightarrow{NaNH_2} \xrightarrow{CH_3CH_2Br} CH_3CH_2-C\equiv C-H \xrightarrow{NaNH_2} \xrightarrow{CH_3CH_2CH_2Br}$$

(epoxide product) $\xleftarrow{MCPBA}$ (trans alkene) $\xleftarrow[NH_3]{Na}$ $CH_3CH_2-C\equiv C-CH_2CH_2CH_3$

9-26 Please refer to solution 1-20, page 12 of this Solutions Manual.

9-27

(a) $CH_3CH_2-C\equiv C-(CH_2)_4CH_3$ (b) $H_3C-C\equiv C-(CH_2)_4CH_3$ (c) —$C\equiv C-H$

(d) —$C\equiv C-H$ (e) $CH_3CH_2-C\equiv C-\underset{\underset{CH_3}{|}}{C}HCH_2CH_2CH_3$

(f) (g) $CH_3\underset{\underset{OH}{|}}{C}H-C\equiv C-(CH_2)_3CH_3$ (h) $\underset{\underset{H}{|}}{H_3C}\underset{}{\overset{}{C}}=\underset{\underset{H}{|}}{\overset{}{C}}-\overset{}{C}\equiv C-\underset{\underset{CH_2CH_3}{|}}{C}HCH_2CH_3$

(i) $H-C\equiv C-CH_2-C\equiv C-CH_2CH_3$ (j) $H-C\equiv C-CH=CH_2$ (k) $H-C\equiv C-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}\overset{\cdots H}{\underset{}{}} \, C=CH_2$

9-28

(a) ethylmethylacetylene
(b) phenylacetylene
(c) *sec*-butyl-*n*-propylacetylene
(d) *sec*-butyl-*t*-butylacetylene

9-29

(a) 4-phenylpent-2-yne
(b) 4,4-dibromopent-2-yne
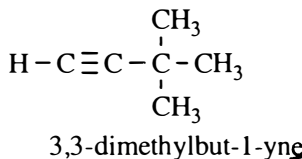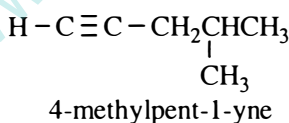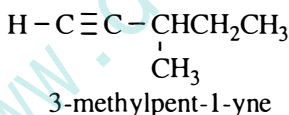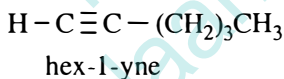(c) 2,6,6-trimethylhept-3-yne
(d) (*E*)-3-methylhept-2-en-4-yne
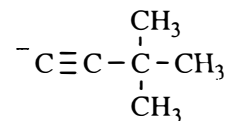(e) 3-methylhex-4-yn-3-ol
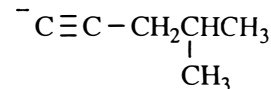(f) cycloheptylprop-1-yne

9-30

(a) <u>internal alkynes</u>   <u>terminal alkynes</u>   <u>acetylide ions</u>

$CH_3-C\equiv C-CH_2CH_2CH_3$
hex-2-yne

$CH_3CH_2-C\equiv C-CH_2CH_3$
hex-3-yne

$CH_3-C\equiv C-\underset{\underset{CH_3}{|}}{C}HCH_3$
4-methylpent-2-yne

$H-C\equiv C-(CH_2)_3CH_3$
hex-1-yne

$H-C\equiv C-\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$
3-methylpent-1-yne

$H-C\equiv C-CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$
4-methylpent-1-yne

$H-C\equiv C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$
3,3-dimethylbut-1-yne

$\xrightarrow{NaNH_2}$

$^-C\equiv C-(CH_2)_3CH_3$

$^-C\equiv C-\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$

$^-C\equiv C-CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$

$^-C\equiv C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$
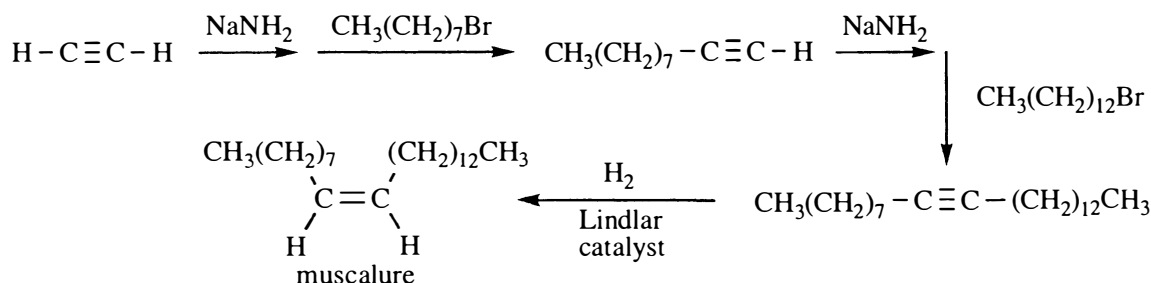
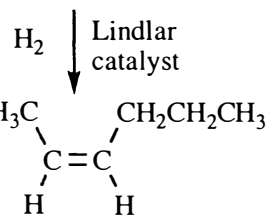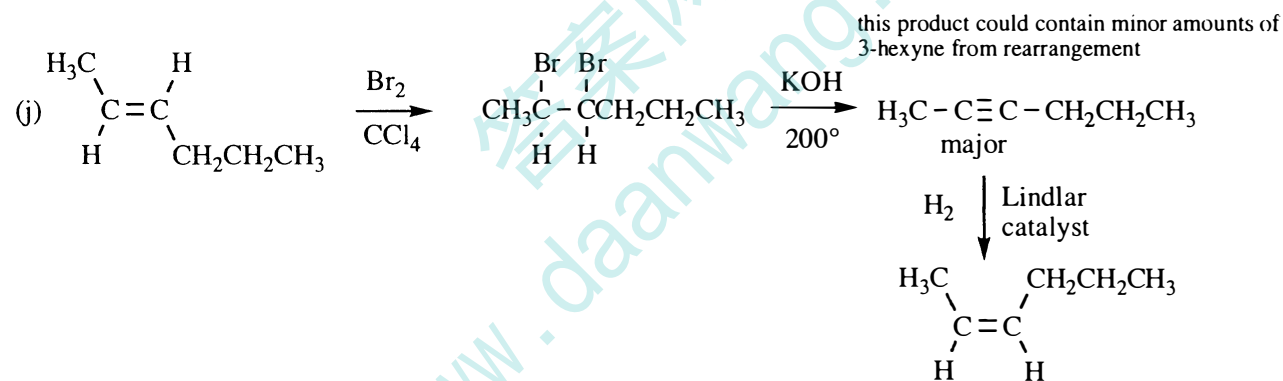(b) All four terminal alkynes will be deprotonated with sodium amide.

9-31

$CH_3CH_2-\overset{\overset{O}{||}}{\underset{\underset{HC}{}}{C}}\underset{\underset{CHCl}{\diagdown}}{} \quad {}^-:C\equiv CH \xrightarrow{\quad NaNH_2 \quad} HC\equiv CH$

$\xrightarrow{H_2O}$

$CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{HC}{}}{C}}\underset{\underset{CHCl}{\diagdown}}{}-C\equiv CH$ ethchlorvynol

202

9-32

$$H-C\equiv C-H \xrightarrow{\text{NaNH}_2} \xrightarrow{\text{CH}_3(\text{CH}_2)_7\text{Br}} CH_3(CH_2)_7-C\equiv C-H \xrightarrow{\text{NaNH}_2}$$

$$\xrightarrow{\text{CH}_3(\text{CH}_2)_{12}\text{Br}}$$

$$CH_3(CH_2)_7-C\equiv C-(CH_2)_{12}CH_3$$

$$\xrightarrow[\substack{\text{Lindlar}\\\text{catalyst}}]{\text{H}_2}$$

muscalure

9-33

(a) $CH_2=\overset{\underset{|}{Cl}}{C}CH_2CH_2CH_3$

(b) $H_3C-\overset{\underset{|}{Cl}}{\overset{|}{\underset{Cl}{C}}}-CH_2CH_2CH_3$

(c) $CH_3CH_2CH_2CH_2CH_3$

(d) $CH_2=CHCH_2CH_2CH_3$

(e) $\overset{H}{\underset{Br}{}}C=C\overset{Br}{\underset{CH_2CH_2CH_3}{}}$

(f) $H-\overset{\underset{|}{Br}}{\underset{Br}{C}}-\overset{\underset{|}{Br}}{\underset{Br}{C}}-CH_2CH_2CH_3$

(g) $HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

(h) $CO_2 + HO-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

(i) $H_2C=CHCH_2CH_2CH_3$

(j) $Na^+\ \ ^-:C\equiv C-CH_2CH_2CH_3$

(k) $H_3C-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

(l) $H-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_3$

9-34

(a) $H_3C-\overset{\underset{|}{Br}}{\underset{Br}{C}}-CH_2CH_3 \xrightarrow[150°]{\text{NaNH}_2} \xrightarrow{\text{H}_2\text{O}} H-C\equiv C-CH_2CH_3$

(b) $H_3C-\overset{\underset{|}{Br}}{\underset{Br}{C}}-CH_2CH_3 \xrightarrow[200°]{\text{KOH}} H_3C-C\equiv C-CH_3$

(c) $CH_3CH_2-C\equiv C-H \xrightarrow{\text{NaNH}_2} CH_3CH_2-C\equiv C:^-\ Na^+$

$$\downarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$$

$$CH_3CH_2-C\equiv C-CH_2CH_2CH_2CH_3$$
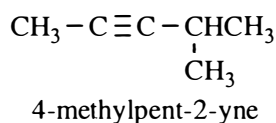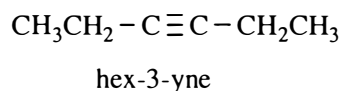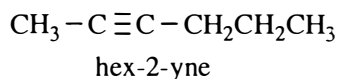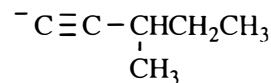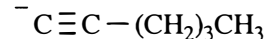
(d) $\overset{H_3C}{\underset{H}{}}C=C\overset{H}{\underset{CH_2CH_2CH_3}{}} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \overset{Br\ \ Br}{\underset{H\ \ \ H}{CH_3C-CCH_2CH_2CH_3}} \xrightarrow[200°]{\text{KOH}} H_3C-C\equiv C-CH_2CH_2CH_3$

this product could contain minor amounts of 3-hexyne from rearrangement

(e) $\overset{H}{\underset{H_3C}{}}C=C\overset{H}{\underset{CH_2CH_2CH_3}{}} \xrightarrow[\text{CCl}_4]{\text{Br}_2} \overset{Br\ \ Br}{\underset{H\ \ \ H}{CH_3C-CCH_2CH_2CH_3}} \xrightarrow[\substack{2)\ \text{H}_2\text{O}}]{\substack{1)\ \text{NaNH}_2\\150°}} H-C\equiv C-CH_2CH_2CH_2CH_3$

203

9-34 continued

(f)

H₂ / Lindlar catalyst → cis

(g)

Na / NH₃ → trans

(h) $HC \equiv C - CH_2CH_2CH_2CH_3$ $\xrightarrow[\substack{H_2SO_4 \\ HgSO_4}]{H_2O}$ $\left[\substack{OH \\ | \\ CH_2 = CCH_2CH_2CH_2CH_3} \right]$ → $H_3C - \overset{O}{\overset{||}{C}}CH_2CH_2CH_2CH_3$

unstable enol

(i) $HC \equiv C - CH_2CH_2CH_2CH_3$ $\xrightarrow[\substack{2) H_2O_2, \\ HO^-}]{1) Sia_2BH}$ $\left[\substack{OH \\ | \\ CH = CHCH_2CH_2CH_2CH_3} \right]$ → $H - \overset{O}{\overset{||}{C}}CH_2CH_2CH_2CH_2CH_3$

unstable enol

(j) $\xrightarrow{\substack{Br_2 \\ CCl_4}}$ $\substack{Br\ Br \\ | \ \ | \\ CH_3\overset{.}{C} - CCH_2CH_2CH_3 \\ | \ \ | \\ H\ \ H}$ $\xrightarrow[200°]{KOH}$ $H_3C - C \equiv C - CH_2CH_2CH_3$

major

this product could contain minor amounts of 3-hexyne from rearrangement

$\xrightarrow[\substack{Lindlar \\ catalyst}]{H_2}$

9-35

 $\xrightarrow[200°]{KOH}$ $HC \equiv$ ⋯ + ⋯ } Mixture **A**

from rearrangement— could contain 3-hexyne

only the terminal alkyne reacts with NaNH₂ and acetone

1) NaNH₂   2) (acetone)   3) H₃O⁺

 + } Mixture **B**

distill

Compound **D**
b.p. 140-150°C
under vacuum

Compound **C**
b.p. 80-84°C

204
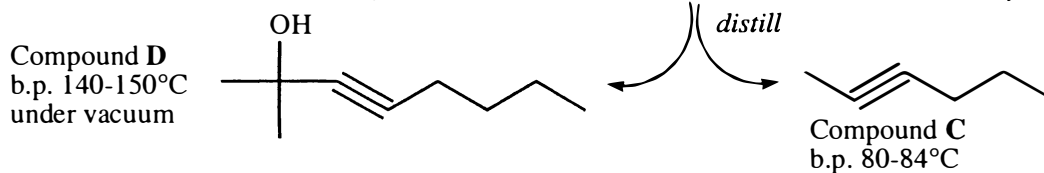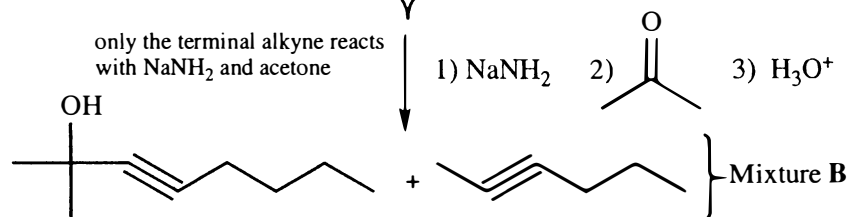
9-36

(a) $CH_3CH_2-C\equiv C-CH_2CH_3$

(b) $CH_3CH_2-C\equiv C-H$ + $CH_2=C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ elimination on 3° halide

(c) $CH_3CH_2-C\equiv C-CH_2OH$
(after H_2O workup)

(d) $CH_3CH_2-C\equiv C-$ (cyclohexane with OH)
(after H_2O workup)

(e) $CH_3CH_2-C\equiv C-\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CH_2CH_3$
(after H_2O workup)

(f) $CH_3CH_2-C\equiv C-H$ + Na^+ $^-O-$ (cyclohexane)

(g) $CH_3CH_2-C\equiv C-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3$
(after H_2O workup)

9-37

(a) $HC\equiv C-H \xrightarrow{NaNH_2} HC\equiv C:^- \ Na^+ \xrightarrow{CH_3CH_2CH_2CH_2Br} HC\equiv C-CH_2CH_2CH_2CH_3$

(b) $HC\equiv C-H \xrightarrow{NaNH_2} HC\equiv C:^- \ Na^+ \xrightarrow{CH_3CH_2CH_2Br} HC\equiv C-CH_2CH_2CH_3$

$H_3C-C\equiv C-CH_2CH_2CH_3 \xleftarrow[CH_3I]{NaNH_2}$

(c) $H_3C-C\equiv C-CH_2CH_2CH_3 \xrightarrow[\substack{Lindlar\\catalyst}]{H_2}$ $\begin{smallmatrix}H_3C\\ \\H\end{smallmatrix}C=C\begin{smallmatrix}CH_2CH_2CH_3\\ \\H\end{smallmatrix}$
synthesized in part (b)

(d) $H_3C-C\equiv C-CH_2CH_2CH_3 \xrightarrow[NH_3]{Na}$ $\begin{smallmatrix}H_3C\\ \\H\end{smallmatrix}C=C\begin{smallmatrix}H\\ \\CH_2CH_2CH_3\end{smallmatrix}$
synthesized in part (b)

(e) $H_3C-C\equiv C-CH_2CH_2CH_3 \xrightarrow[Pt]{\substack{2\ equiv.\\H_2}}$ $CH_3CH_2CH_2CH_2CH_2CH_3$
synthesized in part (b)

(f) $HC\equiv C-CH_2CH_2CH_2CH_3 \xrightarrow{2\ HBr}$ $H_3C-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_2CH_2CH_2CH_3$
synthesized in part (a)

9-37 continued

(g) $H-C\equiv C-CH_2CH_2CH_3$ $\xrightarrow[\text{2) } H_2O_2,\ HO^-]{\text{1) } Sia_2BH}$ $\underset{\overset{\parallel}{O}}{H-C}CH_2CH_2CH_2CH_3$
      from (b)

(h) $H-C\equiv C-CH_2CH_2CH_3$ $\xrightarrow[\substack{H_2SO_4 \\ HgSO_4}]{H_2O}$ $\underset{\overset{\parallel}{O}}{H_3C-C}CH_2CH_2CH_3$
      from (b)

(i) $HC\equiv C-H$ $\xrightarrow{NaNH_2}$ $HC\equiv C\!:^-\ Na^+$ $\xrightarrow{CH_3CH_2Br}$ $HC\equiv C-CH_2CH_3$ $\xrightarrow{NaNH_2}$

$\xrightarrow{CH_3CH_2Br}$

$CH_3CH_2-C\equiv C-CH_2CH_3$ $\xrightarrow[\substack{\text{Lindlar} \\ \text{catalyst}}]{H_2}$ $\underset{\substack{H \qquad\quad H}}{\overset{CH_3CH_2 \qquad CH_2CH_3}{C=C}}$ $\xrightarrow{Br_2}$ [structure with CH₃CH₂ ... CH₂CH₃, H, Br, H, Br]
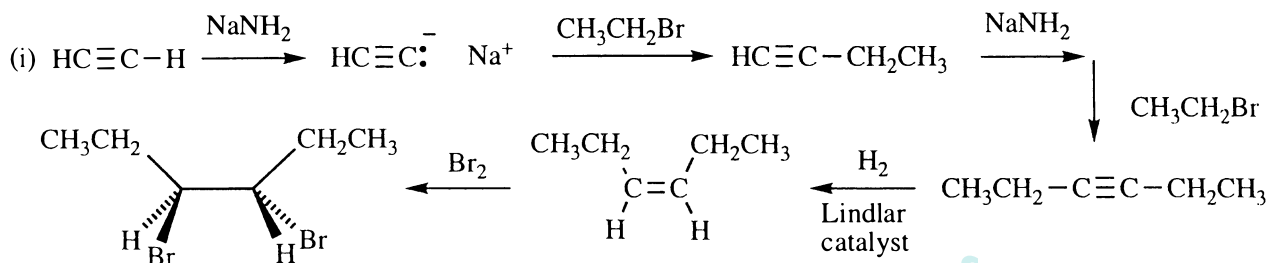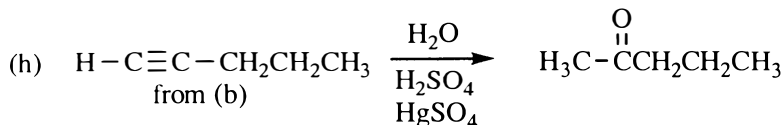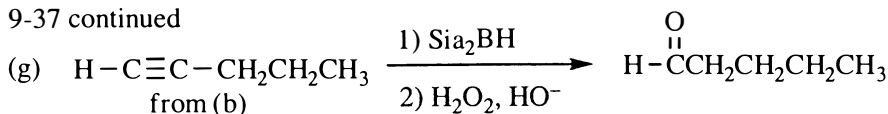
alkene must be cis to
produce the (±) product
from anti addition

*Review the stereochemistry in the
solution to Problem 8-35, p. 171 of
this Solutions Manual.*

(j) $HC\equiv C-H$ $\xrightarrow{NaNH_2}$ $HC\equiv C\!:^-\ Na^+$ $\xrightarrow{CH_3I}$ $HC\equiv C-CH_3$ $\xrightarrow[\text{2) } CH_3I]{\text{1) } NaNH_2}$ $H_3C-C\equiv C-CH_3$

$\xrightarrow[\substack{\text{Lindlar} \\ \text{catalyst}}]{H_2}$ $\underset{\substack{H \qquad\quad H}}{\overset{H_3C \qquad\quad CH_3}{C=C}}$
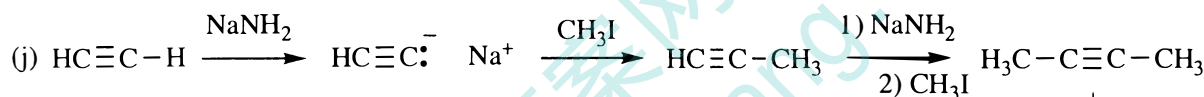
Alternatively, *trans*-but-2-ene could be
anti-hydroxylated with aqueous peracetic acid.

*Review the stereochemistry in the
solution to Problem 8-35, p. 171 of
this Solutions Manual.*

[meso structure with H₃C, CH₃, H, OH, HO, H] $\xleftarrow[H_2O_2]{OsO_4}$

meso

alkene must be cis to produce the
meso product from syn addition

9-38

Compound **X** $\xrightarrow[\text{Pt}]{5\ H_2}$ [cyclohexyl]$-CH_2CH_2CH_2CH_3$

$\downarrow$ $\substack{O_3 \\ Me_2S}$
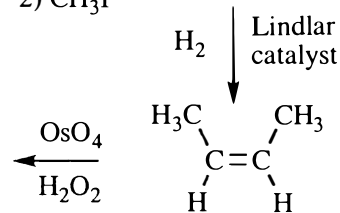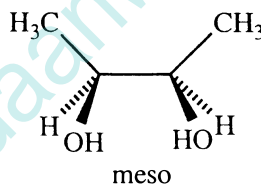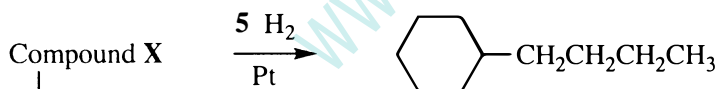
$\Longrightarrow$ the fact that five equivalents of hydrogen are consumed
says that **X** must have five pi bonds in the above
carbon skeleton

$\underset{\overset{\parallel}{O}}{H-C}-CH_2CH_2-\underset{\overset{\parallel}{O}}{C}-\underset{\overset{\parallel}{O}}{C}-H\ +\ \underset{\overset{\parallel}{O}}{H-C}-\underset{\overset{\parallel}{O}}{C}-H\ +\ \underset{\overset{\parallel}{O}}{H-C}-\underset{\overset{\parallel}{O}}{C}-OH\ +\ \underset{\overset{\parallel}{O}}{H-C}-OH$

from C≡C
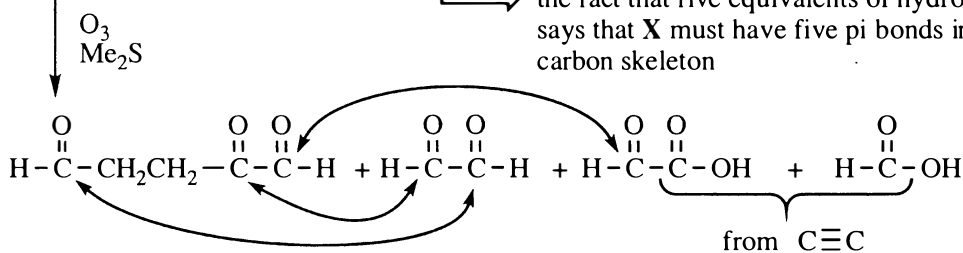
6 carbonyls $\Longrightarrow$ 3 alkenes   2 carboxylic acids $\Longrightarrow$ 1 alkyne

[phenyl]$-CH=CH-C\equiv CH$
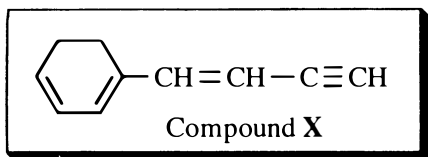
Compound **X**

Whether the alkene is cis or trans cannot
be determined from these results.

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9-39 Compound **Z**

ozonolysis ⇒ $CH_3(CH_2)_4-\overset{\overset{O}{\|}}{C}-H$ $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OH$ $HO-\overset{\overset{O}{\|}}{C}-H$

from alkene   from alkyne
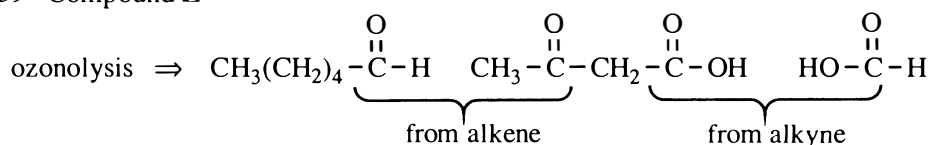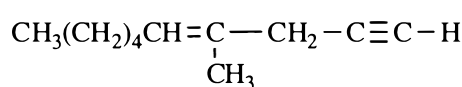
Compound **Z**: $CH_3(CH_2)_4CH=\underset{\underset{CH_3}{|}}{C}-CH_2-C\equiv C-H$ Whether the alkene is E or Z cannot be determined from this information.

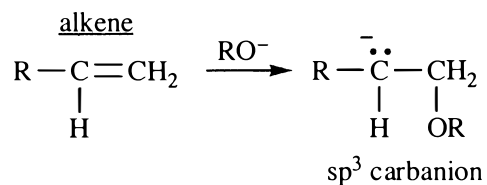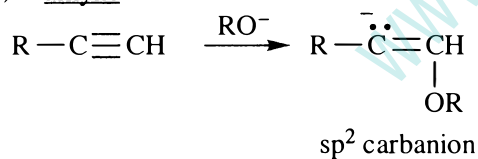9-40 All four syntheses in this problem begin with the same reaction of benzyl bromide with acetylide ion:

$HC\equiv CH$ $\xrightarrow{NaNH_2}$ $HC\equiv C:^-$ + ⟍CH$_2$Br $\longrightarrow$ $PhCH_2-C\equiv CH$ $\xrightarrow{NaNH_2}$ $PhCH_2-C\equiv C:^-$

benzyl bromide

use this below

(a) $PhCH_2-C\equiv C:^-$ + Br⟍⟋ $\longrightarrow$ $PhCH_2-C\equiv C$⟍⟋   6-phenylhex-1-en-4-yne

allyl bromide

(b) $PhCH_2-C\equiv C:^-$ + Br⟍⟋ $\longrightarrow$ $PhCH_2-C\equiv C$⟍ $\xrightarrow[\substack{Pd/BaSO_4 \\ quinoline}]{H_2}$ Ph⟍⟋

ethyl bromide

Lindlar catalyst   *cis*-1-phenylpent-2-ene

(c) $PhCH_2-C\equiv C:^-$ + Br⟍⟋ $\longrightarrow$ $PhCH_2-C\equiv C$⟍ $\xrightarrow[NH_3]{Na}$ Ph⟍⟋

ethyl bromide

trans-1-phenylpent-2-ene
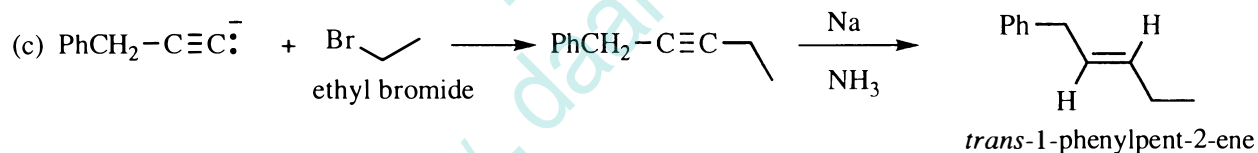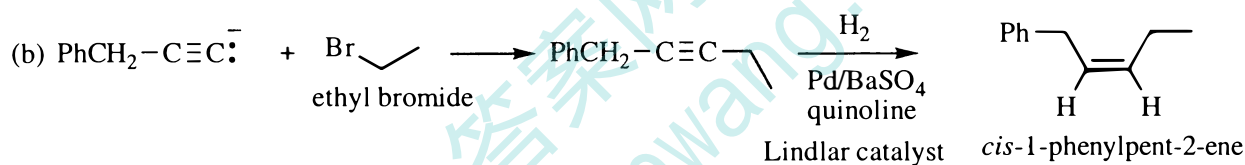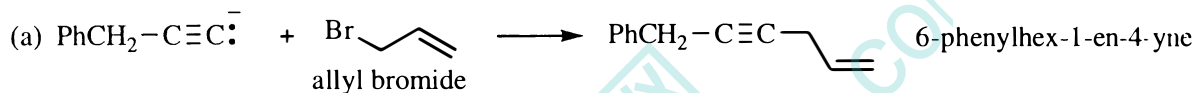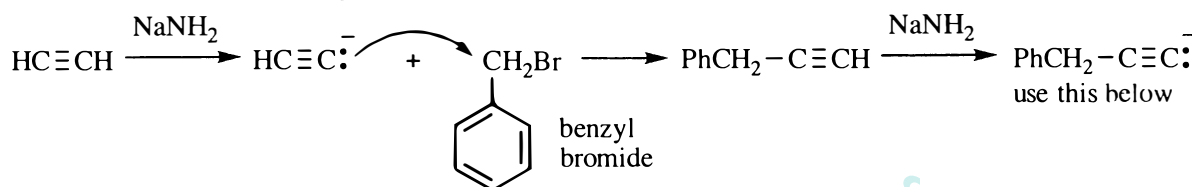
(d) The diol with the two OH groups on the same side in the Fischer projection is the equivalent of a meso structure, although this one is not meso because the top and bottom group are different. Still, it gives a clue as to its synthesis. The "meso" diol can be formed by either a syn addition to a cis double bond, or by an anti addition to a trans double bond. We saw the same thing in the solution to 9-37 (j).

Ph⟍⟋ $\xrightarrow[H_2O_2]{OsO_4}$ [structure] $\xleftarrow[H_3O^+]{HCO_3H}$ Ph⟍⟋

cis product from part (b)   syn addition   anti addition   *trans* product from part (c)

CH_2Ph
$H-\!\!\!\!-OH$
$H-\!\!\!\!-OH$
CH_2CH_3
racemic

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9-41

(a) $CH_3CH_2-C\equiv C-H$ $\xrightarrow[\text{2) }H_2O_2,\ HO^-]{\text{1) }Sia_2BH}$ $CH_3CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

(b)

(c) alkyne

$R-C\equiv CH$ $\xrightarrow{RO^-}$ $R-\overset{..}{\overset{\displaystyle -}{C}}=CH$
$\qquad\qquad\qquad\qquad\qquad\ \ |$
$\qquad\qquad\qquad\qquad\qquad\ OR$

sp^2 carbanion

alkene

$R-\underset{H}{\overset{|}{C}}=CH_2$ $\xrightarrow{RO^-}$ $R-\underset{H}{\overset{\overset{\displaystyle ..}{\overset{\displaystyle -}{|}}}{C}}-\underset{OR}{\overset{|}{C}}H_2$
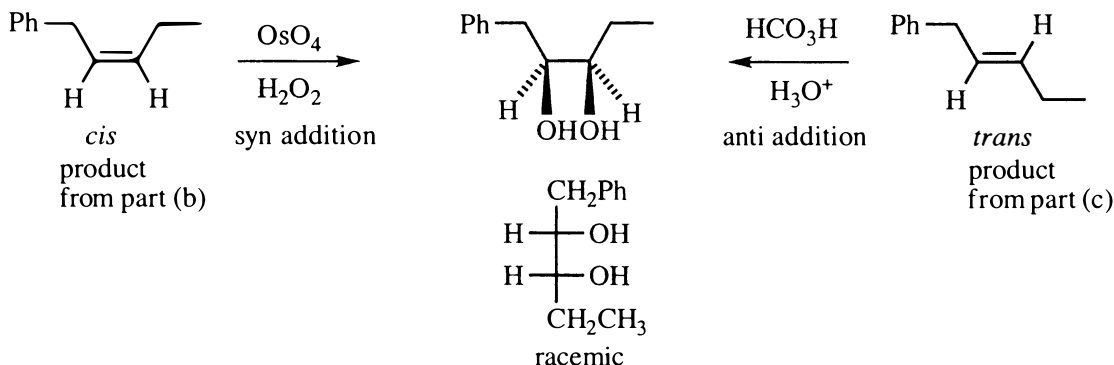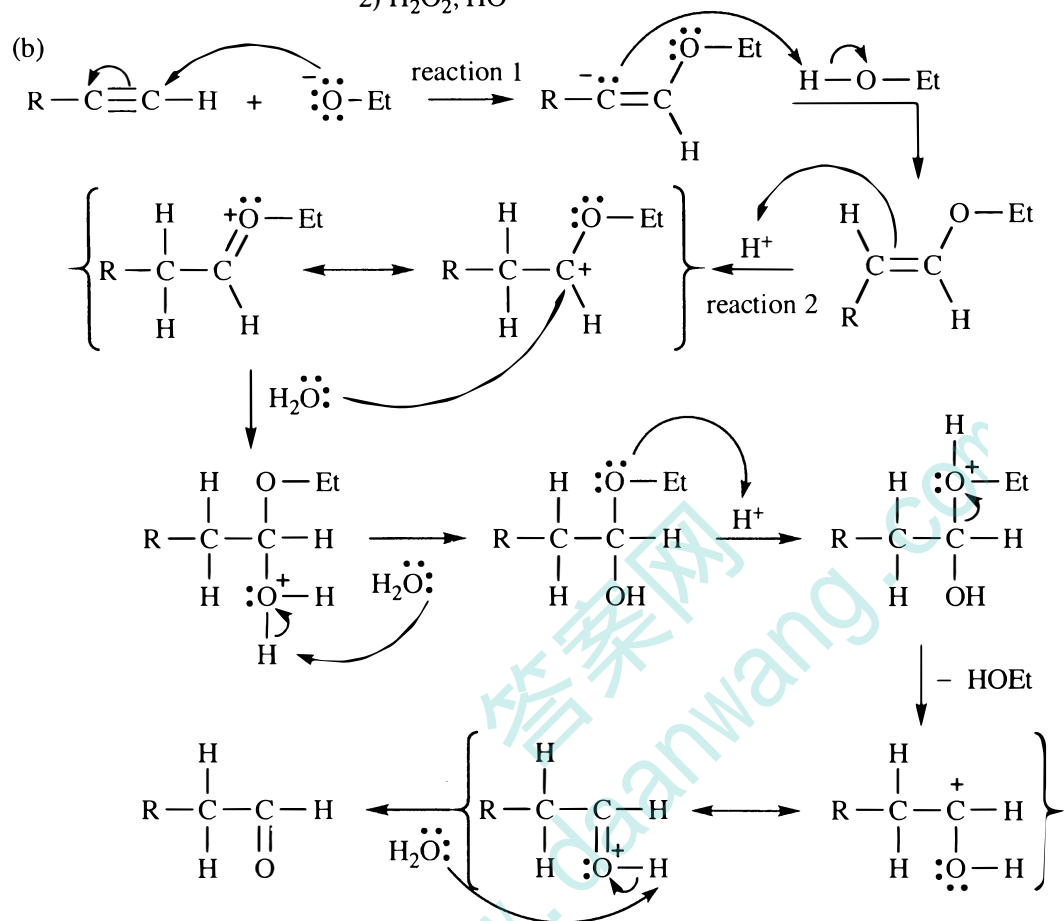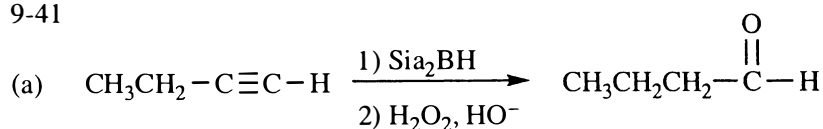
sp^3 carbanion

The closer that electrons are to the nucleus, the more stable. An s orbital is closer to a nucleus than a p orbital is, as p orbitals are elongated away from the nucleus. An sp^2 carbanion is more stable than an sp^3 carbanion because the sp^2 carbanion has 33% s character and and the electron pair is closer to the positive nucleus than in an sp^3 carbanion which is only 25% s character. The sp^2 carbanion is easier to form because of its relative stability.

9-42 Diols are made by two reactions from Chapter 8 and revisited in 9-41 (d): either syn-dihydroxylation with OsO_4, or anti-dihydroxylation via an epoxide using a peroxyacid and water. As this problem says to use inorganic reagents, the solution shown here will use OsO_4.

Recall the stereochemical requirements of syn addition as outlined in this Solutions Manual, p. 171, Problem 8-35:

cis-alkene + **syn** addition → meso

cis-alkene + **anti** addition → racemic (±)

trans-alkene + **syn** addition → racemic (±)

trans-alkene + **anti** addition → meso

Part (a) asks for the synthesis of the meso isomer, so syn addition will have to occur on the cis-alkene. Part (b) will require syn addition to the trans-alkene to give the (±) product.

(a)
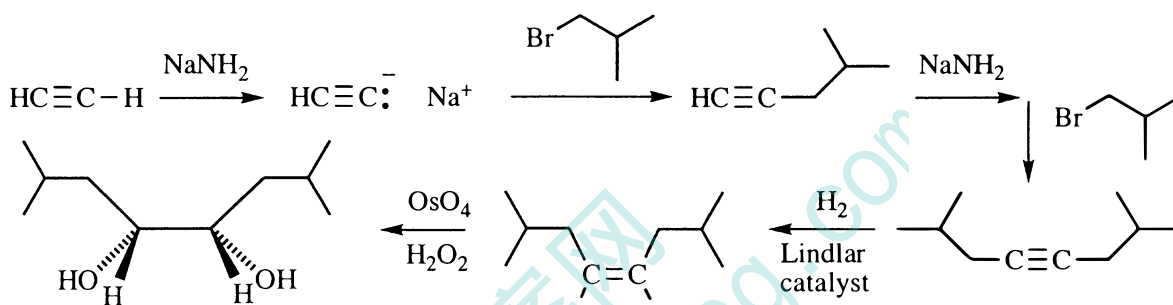
alkene must be cis to
produce the meso product
from syn addition, so
reduction is done with
Lindlar catalyst to produce
the cis alkene

(b)
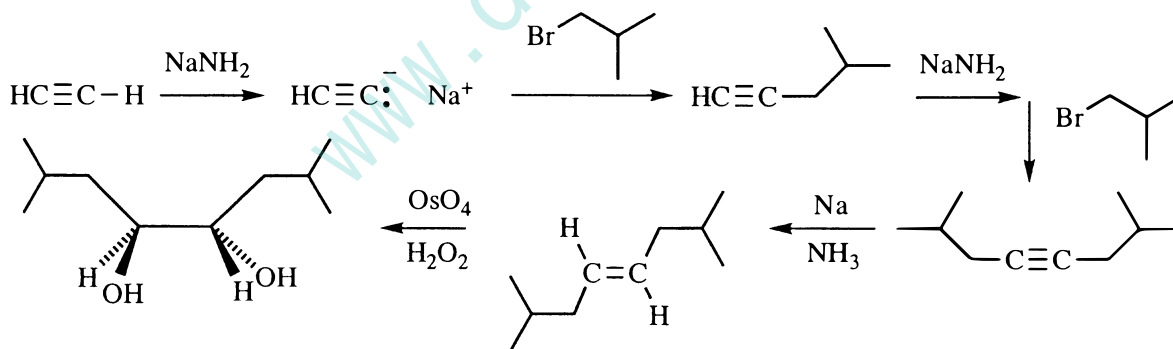
alkene must be trans to
produce the (±) product from
syn addition, so reduction is
done with Na/NH$_3$

9-43   This synthesis begins the same as the solution to problem 9-40:
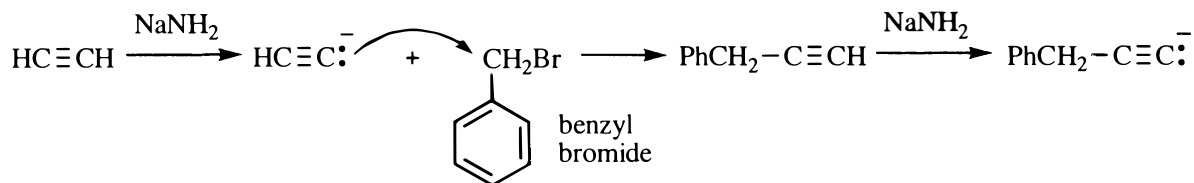
The anion will add across the carbonyl group of the aldehyde:

acid-catalyzed dehydration

H_2SO_4, Δ

MCPBA
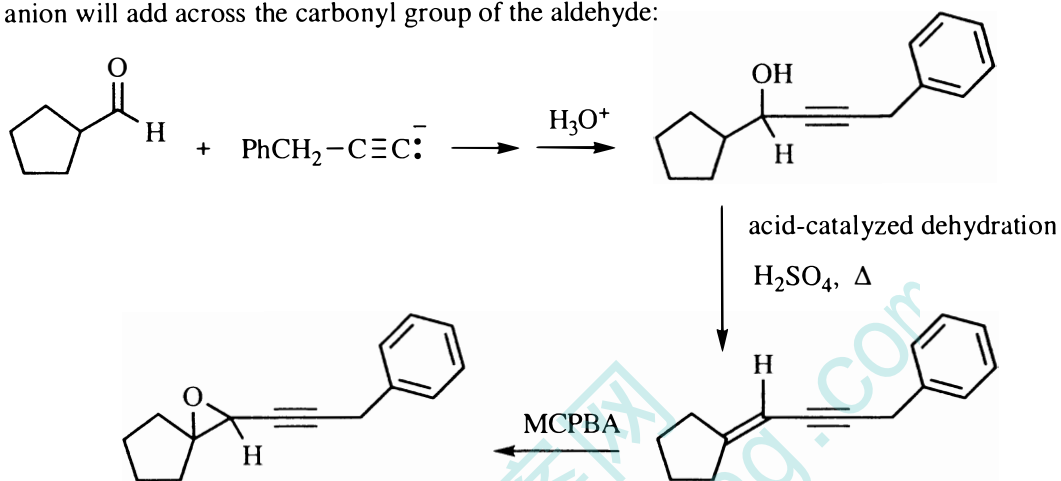
CHAPTER 10—STRUCTURE AND SYNTHESIS OF ALCOHOLS
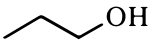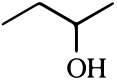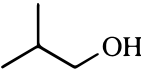
10-1 Please see the note on p. 136 of this Solutions Manual regarding placement of position numbers.

(a) 2-phenylpropan-2-ol
(b) 5-bromoheptan-2-ol
(c) 4-methylcyclohex-3-en-1-ol ("1" is optional)

(d) *trans*-2-methylcyclohexan-1-ol ("1" is optional)
(e) (*E*)-2-chloro-3-methylpent-2-en-1-ol
(f) (2*R*,3*S*)-2-bromohexan-3-ol
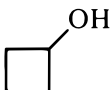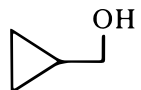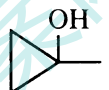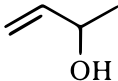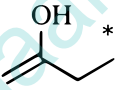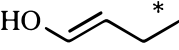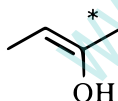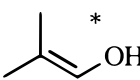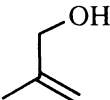
10-2 IUPAC name first, then common name.

(a) cyclopropanol; cyclopropyl alcohol
(b) 2-methylpropan-2-ol; *t*-butyl alcohol

(c) 1-cyclobutylpropan-2-ol; no common name
(d) 3-methylbutan-1-ol; isopentyl alcohol
      (also isoamyl alcohol)
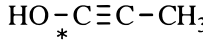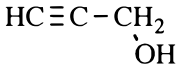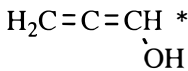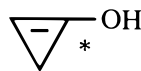
10-3 Only constitutional isomers are requested, not stereoisomers, and only structures with an alcohol group.

(a) C_3H_8O ⟋⟍OH propan-1-ol   OH propan-2-ol

(b) $C_4H_{10}O$

butan-1-ol   butan-2-ol   2-methylpropan-1-ol   2-methylpropan-2-ol

(c) C_4H_8O has one element of unsaturation, either a double bond or a ring.

cyclobutanol   cyclopropylmethanol   1-methylcyclopropanol   2-methylcyclopropanol
cis or *trans*

but-3-en-1-ol   but-3-en-2-ol   but-1-en-2-ol   but-1-en-1-ol (*E* or *Z*)

but-2-en-1-ol   but-2-en-2-ol   2-methyl-   2-methylprop-2-en-1-ol
(*E* or *Z*)   (*E* or *Z*)   prop-1-en-1-ol

(d) C_3H_4O has two elements of unsaturation, so each structure must have either a triple bond, or two double bonds, or a three-membered ring and a double bond. All structures must contain an OH. (In the name, the "e" is dropped from "yne" because it follow by a vowel in "ol".)

$HO-C\equiv C-CH_3$ $HC\equiv C-CH_2$ $H_2C=C=CH$ *   OH   OH
prop-1-yn-1-ol   OH   OH   cycloprop-1-en-1-ol   cycloprop-2-en-1-ol
                        prop-2-yn-1-ol   propa-1,2-dien-1-ol

*These compounds with the OH bonded directly to the carbon-carbon double bond are called "enols" or "vinyl alcohols." The structure with OH on a carbon-carbon triple bond is called an ynol. These are unstable, although the structures are legitimate.

10-4 (a) 8,8-dimethylnonane-2,7-diol
(b) octane-1,8-diol
(c) *cis*-cyclohex-2-ene-1,4-diol
(d) 3-cyclopentylheptane-2,4-diol
(e) *trans*-cyclobutane-1,3-diol

10-5 There are four structural features to consider when determining solubility in water: 1) molecules with fewer carbons will be more soluble in water (assuming other things being equal); 2) branched or otherwise compact structures are more soluble than linear structures; 3) more hydrogen-bonding groups will increase solubility; 4) an ionic form of a compound will be more soluble in water than the nonionic form.

(a) Cyclohexanol is more soluble because its alkyl group is more compact than in 1-hexanol.
(b) 4-Methylphenol is more soluble because its hydrocarbon portion is more compact than in 1-heptanol, and phenols form particularly strong hydrogen bonds with water.
(c) 3-Ethylhexan-3-ol is more soluble because its alkyl portion is more spherical than in octan-2-ol.
(d) Cyclooctane-1,4-diol is more soluble because it has two OH groups which can hydrogen bond with water, whereas hexan-2-ol has only one OH group. (The ratio of carbons to OH is 4 to 1 in the former compound and 6 to 1 in the latter; the smaller this ratio, the more soluble.)
(e) These are enantiomers and will have identical solubility.

10-6 Dimethylamine molecules can hydrogen bond among themselves so it takes more energy (higher temperature) to separate them from each other. Trimethylamine has no N-H and cannot hydrogen bond, so it takes less energy to separate these molecules from each other, despite its higher molecular weight.

10-7 See Appendix 2 at the back of this Solutions Manual for a review of acidity and basicity.
(a) Methanol is more acidic than *t*-butyl alcohol. The greater the substitution, the lower the acidity.
(b) 2-Chloropropan-1-ol is more acidic because the electron-withdrawing chlorine atom is closer to the OH group than in 3-chloropropan-1-ol.
(c) 2,2-Dichloroethanol is more acidic because two electron-withdrawing chlorine atoms increase acidity more than just the one chlorine in 2-chloroethanol.
(d) 2,2-Difluoropropan-1-ol is more acidic because fluorine is more electronegative than chlorine; the stronger the electron-withdrawing group, the more acidic the alcohol.

10-8

most acidic							least acidic
sulfuric acid	>>	2-chloroethanol	> water	> ethanol	> *t*-butyl alcohol	> ammonia	> hexane
H_2SO_4		$ClCH_2CH_2OH$	H_2O	CH_3CH_2OH	$(CH_3)_3COH$	NH_3	C_6H_{14}

Sulfuric acid is one of the strongest acids known. On the other extreme, alkanes like hexane are the least acidic compounds. The N–H bond in ammonia is less acidic than any O–H bond. Among the four compounds with O–H bonds, the tertiary alcohols are the least acidic. Water is more acidic than most alcohols including ethanol. However, if a strong electron-withdrawing substituent like chlorine is near the alcohol group, the acidity increases enough so that it is more acidic than water. (Determining exactly where water appears in this list is the most difficult part.)

10-9 Resonance forms of phenoxide anion show the negative charge delocalized onto the ring only at carbons 2, 4, and 6:
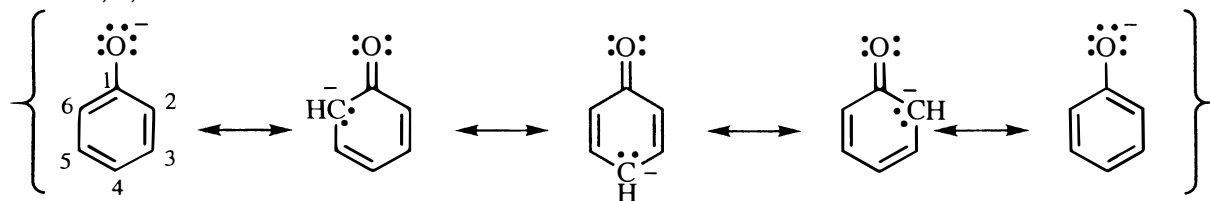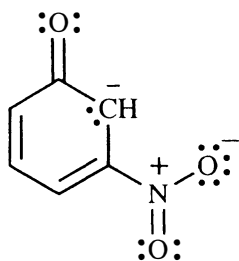
10-9 continued

Nitro group at position 2

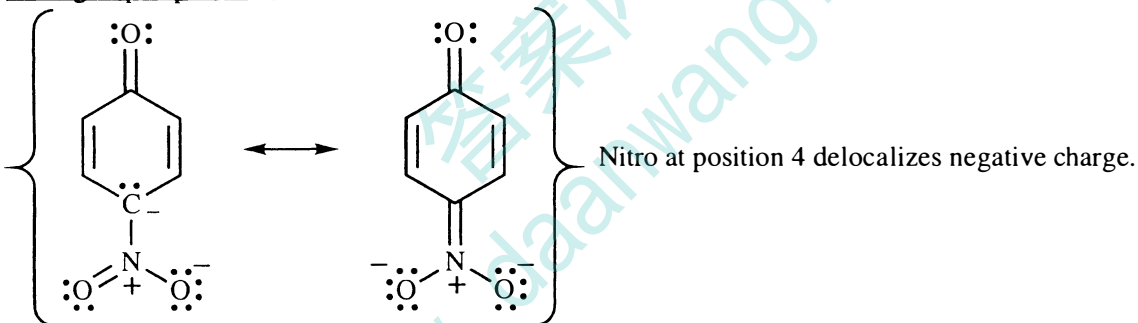Nitro at position 2 delocalizes negative charge.
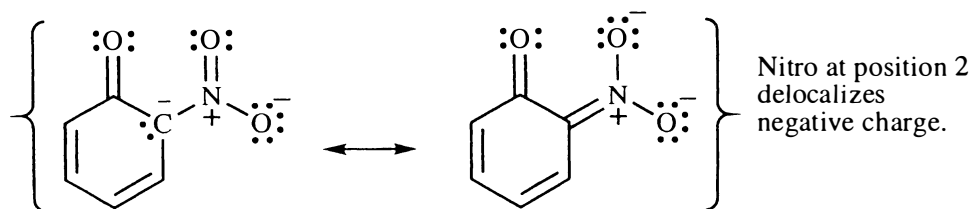
Nitro group at position 3

Nitro at position 3 cannot delocalize negative charge at position 2 or 4—no resonance stabilization.

Nitro group at position 4

Nitro at position 4 delocalizes negative charge.

Only when the nitro group is at one of the negative carbons will the nitro have a stabilizing effect (via resonance). Thus, 2-nitrophenol and 4-nitrophenol are substantially more acidic than phenol itself, but 3-nitrophenol is only slightly more acidic than phenol (due to the inductive effect).

10-10
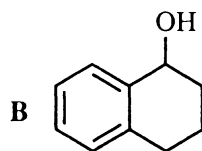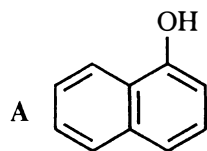
(a) Structure **A** is a phenol because the OH is bonded to a benzene ring. As a phenol, it will be acidic enough to react with sodium hydroxide to generate a phenoxide ion that will be fairly soluble in water. Structure **B** is a 2° benzylic alcohol, not a phenol, not acidic enough to react with NaOH.
(b) Both of these organic compounds will be soluble in an organic solvent like dichloromethane. Shaking this organic solution with aqueous sodium hydroxide will ionize the phenol **A**, making it more polar and water soluble; it will be extracted from the organic layer into the water layer, while the alcohol will remain in the organic solvent. Separating these immiscible solvents will separate the original compounds. The alcohol can be retrieved by evaporating the organic solvent. The phenol can be isolated by acidifying the basic aqueous solution and filtering if the phenol is a solid, or separating the layers if the phenol is a liquid.

10-11 The Grignard reaction needs a solvent containing an ether functional group: (b), (f), (g), and (h) are possible solvents. Dimethyl ether, (b), is a gas at room temperature, however, so it would have to be liquefied at low temperature for it to be a useful solvent.

10-12

(a) CH_3CH_2MgBr (b) Li + LiI   (c) F—⬡—MgBr   (d) + LiCl
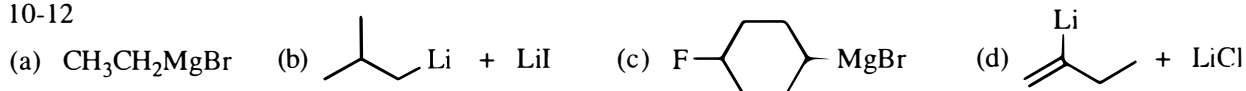
10-13 Any of three halides—chloride, bromide, iodide, but not fluoride—can be used. Ether is the typical solvent for Grignard reactions.

(a)

(b)

(c)
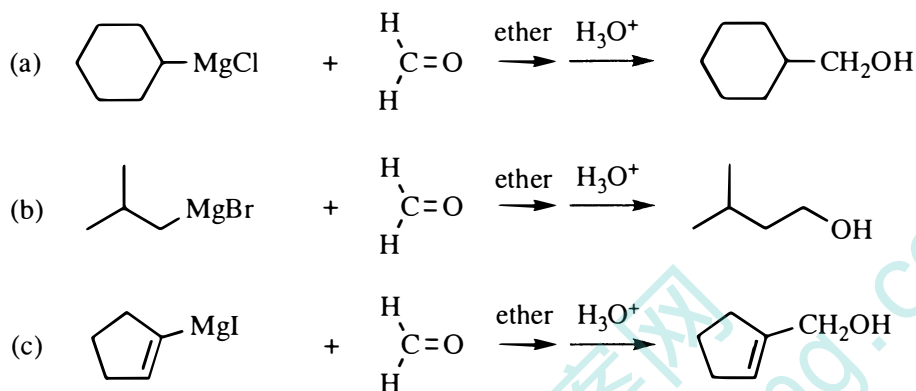
Note: the alternative arrow symbolism could also be used, where the two steps are numbered around one arrow:
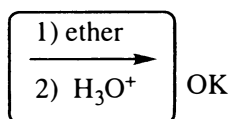
1) ether
2) H_3O^+ OK

NO! Me BAD!
This means that water is present with ether during the Grignard reaction.
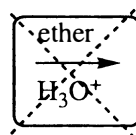
ether
H_3O^+

10-14 Any of three halides—chloride, bromide, iodide, but not fluoride—can be used. Grignard reactions are always performed in ether solvent; ether is not shown here.

(a) two methods
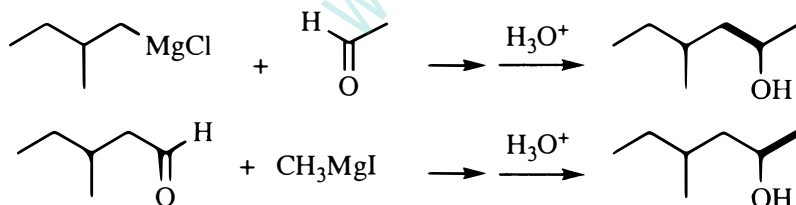
Where two methods can be used to form the target compound, the newly formed bond is shown in bold.

(b) two methods

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10-14 continued

(c)
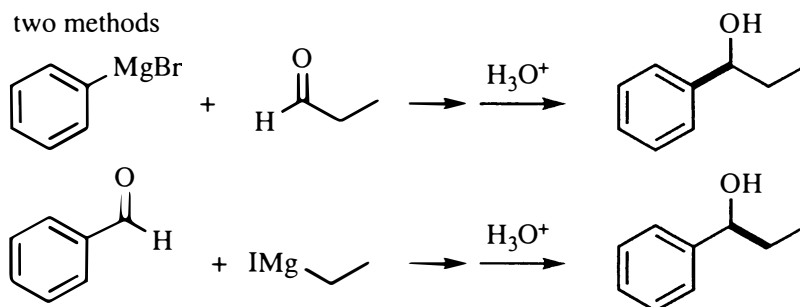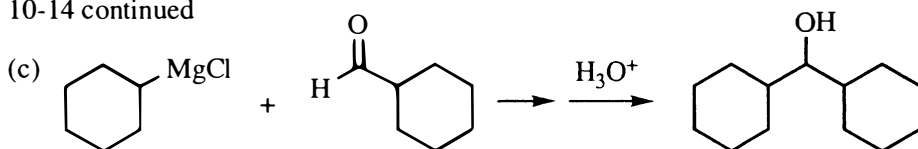
10-15 Grignard reactions are always performed in ether. Here, the ether is not shown.

(a) Any of the three bonds shown in bold can be formed by adding a Grignard reagent across a ketone.

(i) CH_3CH_2MgBr
+

(ii)

+ PhMgBr

(iii) $CH_3CH_2CH_2MgBr$
+

(b)

Ph—MgBr + $\overset{Ph}{\underset{Ph}{\diagdown}}$C=O $\xrightarrow{H_3O^+}$ Ph—$\overset{Ph}{\underset{Ph}{C}}$—OH

(c) CH_3—MgI

(d) two methods

Cy = cyclohexyl

10-16

(This is just a nucleophilic substitution where Cl is the leaving group. The unusual feature is that it occurs at a carbonyl carbon.)

ketone intermediate

Ph—MgBr

$\begin{array}{c} OH \\ | \\ CH_3-C-Ph \\ | \\ Ph \end{array}$ $\xleftarrow[\text{step}]{H_3O^+ \text{ work-up}}$ $\begin{array}{c} :\overset{..}{O}:^- \\ | \\ CH_3-C-Ph \\ | \\ Ph \end{array}$

215
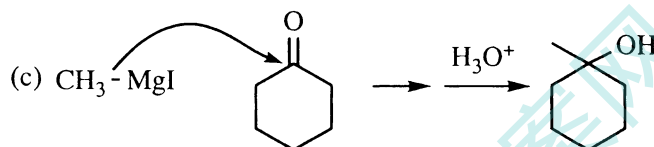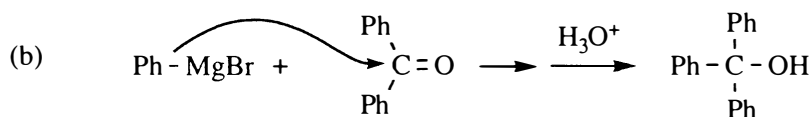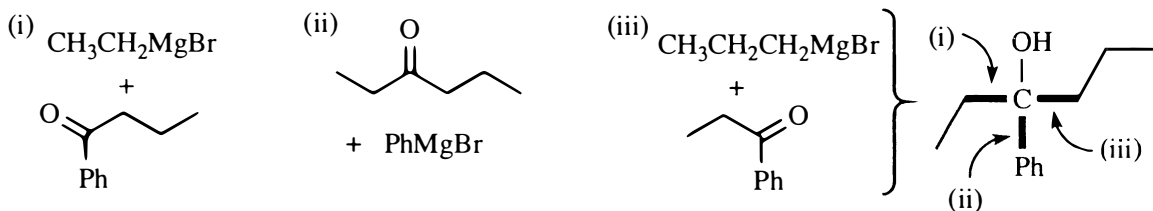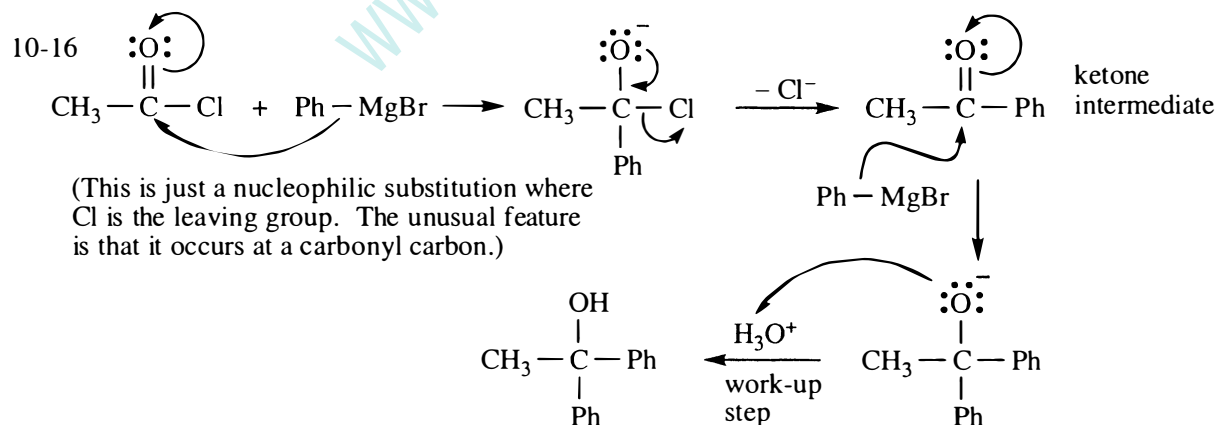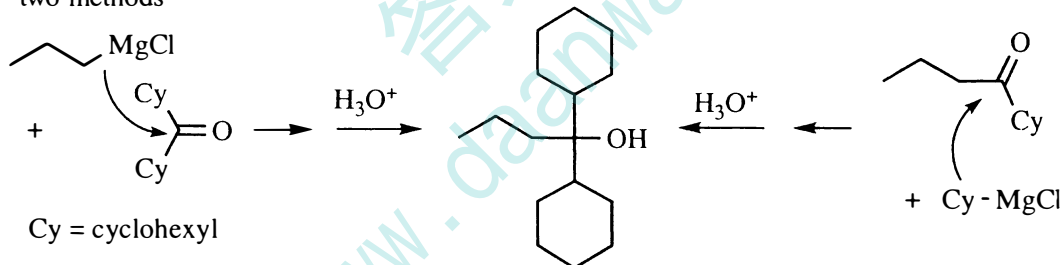
10-17 Acid chlorides or esters will work as starting materials in these reactions. The typical solvent for Grignard reactions is ether; it is not shown here.

(a) Ph−C(=O)−Cl   + 2 PhMgBr $\xrightarrow{}$ $\xrightarrow{H_3O^+}$ Ph−C(Ph)(Ph)−OH

(b) (CH₃)₂CH−C(=O)−OCH₃   + 2 CH₃CH₂MgI $\xrightarrow{H_3O^+}$ product with OH

(c) Ph−C(=O)−Cl   + 2 cyclohexyl−MgCl $\xrightarrow{H_3O^+}$ product with OH

10-18

(a) H−C(=O)−OEt + allyl−MgBr $\longrightarrow$ H−C(O⁻)(OEt)(allyl) $\xrightarrow{-\,EtO^-}$ H−C(=O)−allyl   aldehyde intermediate

MgBr ↓

allyl−C(O⁻)(H)−allyl $\xrightarrow{H_3O^+}$ allyl−C(OH)(H)−allyl

(b) (i) HC(=O)−OEt + 2 CH₃CH₂MgBr $\xrightarrow{H_3O^+}$ product with OH

(ii) HC(=O)−OEt + 2 Ph−MgBr $\xrightarrow{H_3O^+}$ diphenylmethanol

(iii) HC(=O)−OEt + 2 CH₃CH=CH−CH₂−MgBr $\xrightarrow{H_3O^+}$ product with OH

10-19 Ether is the typical solvent in Grignard reactions.

(a) Ph−MgBr + epoxide $\xrightarrow{H_3O^+}$ Ph−CH₂CH₂−OH

216

10-19 continued

(b)

(c)

10-20

(a)

(b)
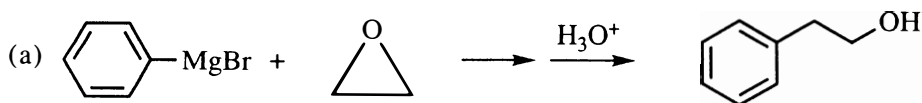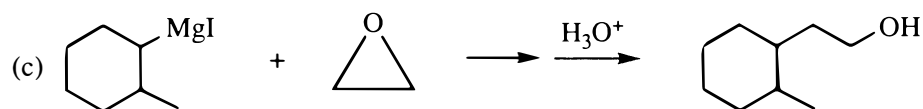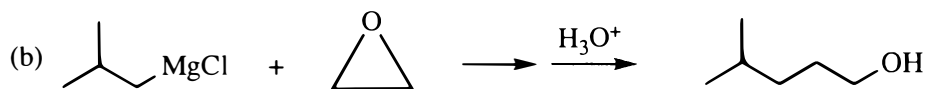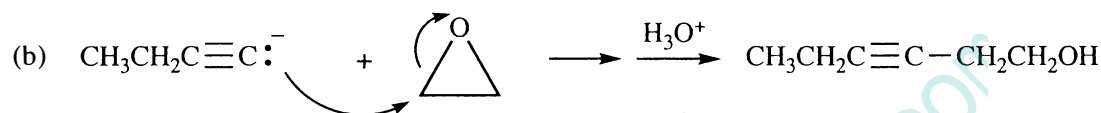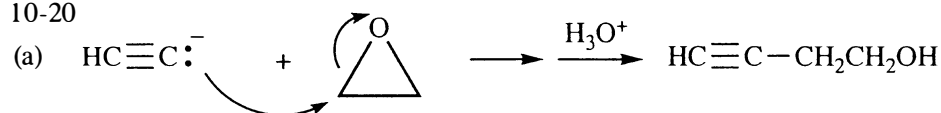
10-21 There are more than one synthetic route to each structure; the ones shown here are representative. The new bonds formed are shown here in bold. Your answers may be different and still be correct.

(a)

(b)

(c)
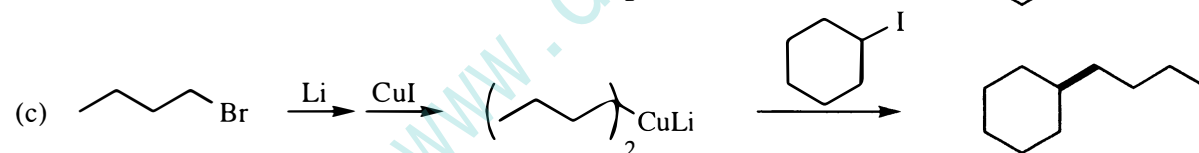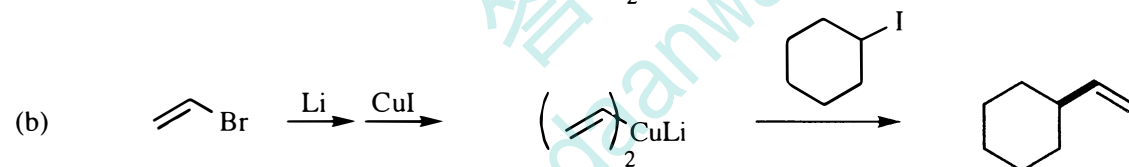
Alternatively, coupling lithium dicyclohexylcuprate with 1-bromobutane would also work. As this mechanism is not a typical S_N2, it is not as susceptible to steric hindrance like acetylide ion substitution or a similar S_N2 reaction.

(d)
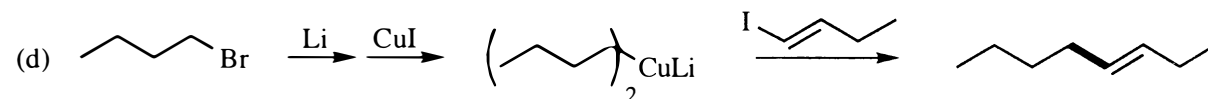
10-22 These reactions are acid-base reactions in which an acidic proton (or deuteron) is transferred to a basic carbon in either a Grignard reagent or an alkyllithium.

(a) CH_3D + $Mg(OD)I$ (b) $CH_3CH_2CH_2CH_3$ + $LiOCH_2CH_3$

(c)   (d)   (e)

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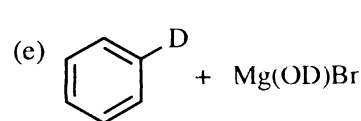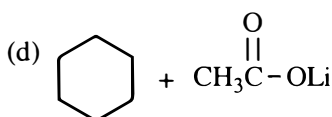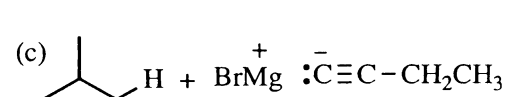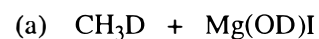
10-23 Grignard reagents are incompatible with acidic hydrogens and with electrophilic, polarized multiple bonds like C=O, NO_2, etc.

(a) As Grignard reagent is formed, it would instantaneously be protonated by the N—H present in other molecules of the same substance.

(b) As Grignard reagent is formed, it would immediately attack the ester functional group present in other molecules of the same substance.

(c) Care must be taken in how reagents are written above and below arrows. If reagents are numbered "1. ... 2. ... *etc.*", it means they are added in separate steps, the same as writing reagents over separate arrows. If reagents written around an arrow are not numbered, it means they are added all at once in the same mixture. In this problem, the ketone is added in the presence of aqueous acid. The acid will immediately protonate and destroy the Grignard reagent before reaction with the ketone can occur.

(d) The ethyl Grignard reagent will be immediately protonated and consumed by the OH. This reaction *could* be made to work, however, by adding two equivalents of ethyl Grignard reagent—the first to consume the OH proton, the second to add across the ketone. Aqueous acid will then protonate both oxygens.

10-24 Sodium borohydride does not reduce esters.

(a) $CH_3(CH_2)_8CH_2OH$ (b) no reaction   (c) no reaction (PhCOO⁻ before acid work-up)   (d)

(e)   (f) ester —{
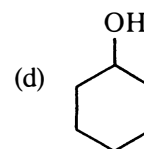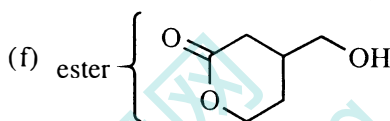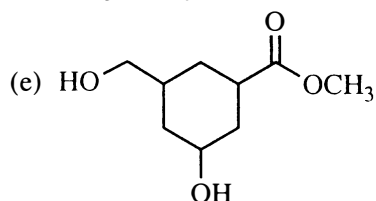
10-25 Lithium aluminum hydride reduces esters as well as other carbonyl groups.

(a) $CH_3(CH_2)_8CH_2OH$ (b) $CH_3CH_2CH_2OH$ + $HOCH_3$ (c) $PhCH_2OH$ (d)

(e) + $HOCH_3$ (f)

10-26
(a)

OR

OR

(b)

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10-26 continued

(c)

NaBH₄ / CH₃OH →

OR

1) LiAlH₄
2) H₃O⁺

(d)

NaBH₄ / CH₃OH →

LiAlH₄ will NOT give the desired product. LiAlH₄ will also reduce the ester in addition to the ketone.
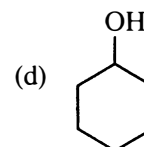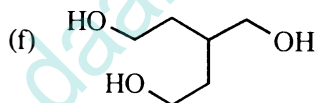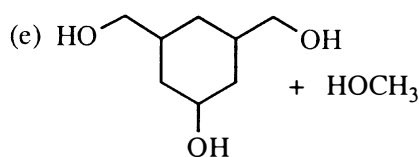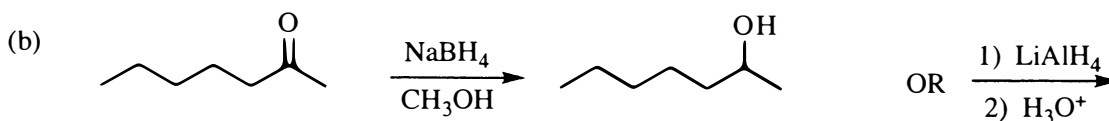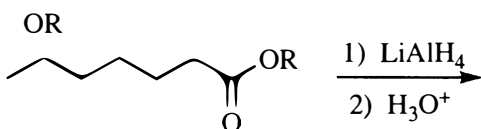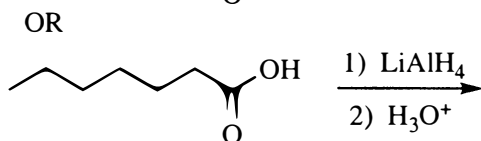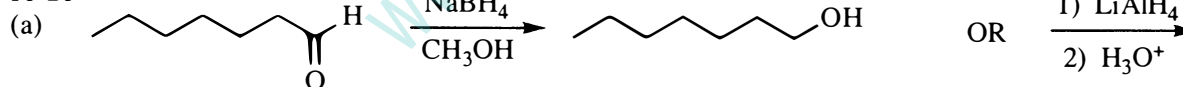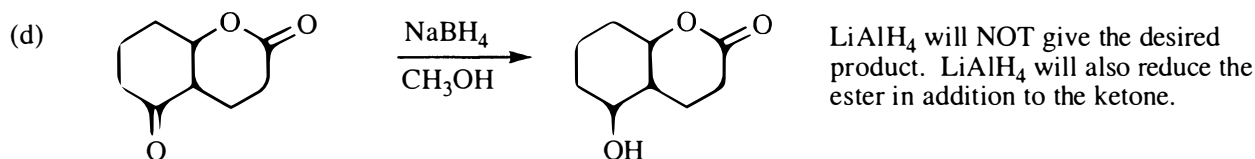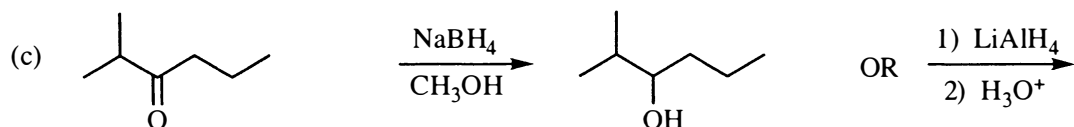
10-27 Approximate pKa values are shown below each compound. Refer to text Tables 1-5, 9-2, and 10-3, and Appendix 5 at the back of the text.

CH_3SO_3H > CH_3COOH > CH_3SH > CH_3OH > $CH_3C\equiv CH$ > CH_3NH_2 > CH_3CH_3

< 0   4.74   ≈ 10.5   15.5   25   ≈ 35   50

 most acidic   least acidic
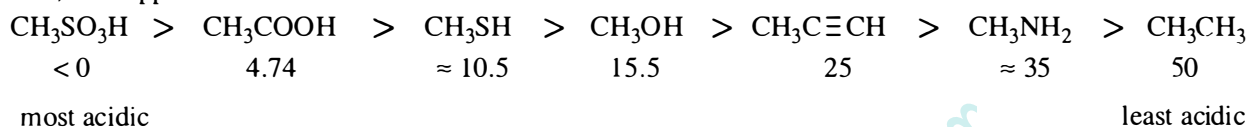
10-28
(a) 4-methylpentane-2-thiol
(b) (Z)-2,3-dimethylpent-2-ene-1-thiol ("1" is optional)
(c) cyclohex-2-ene-1-thiol ("1" is optional)

10-29

HBr / ROOR →

NaSH →

3-methylbutane-1-thiol

NBS →

NaSH →

2-butene-1-thiol
(but-2-ene-1-thiol)

OR

HBr, 40° C
(see Problem 8-2)
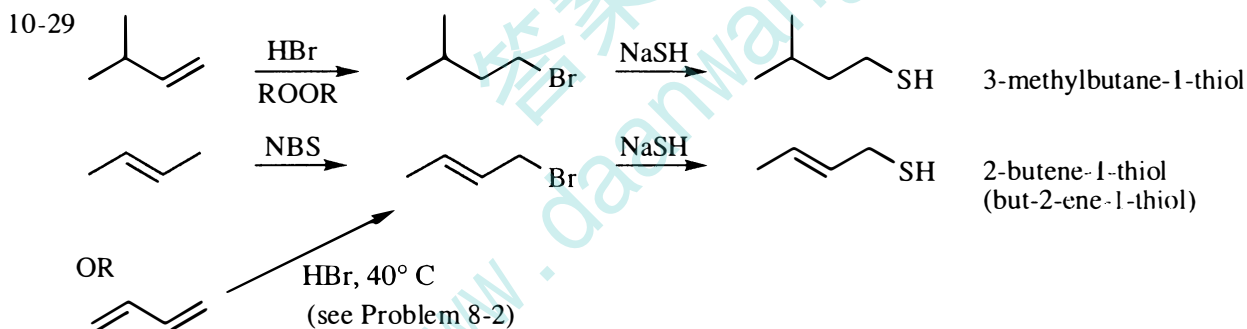
10-30 Please refer to solution 1-20, page 12 of this Solutions Manual.

10-31
(a) 5-methyl-4-*n*-propylheptan-2-ol; 2°
(b) 4-(1-bromoethyl)heptan-3-ol; 2°
(c) (*E*)-4,5-dimethylhex-3-en-1-ol; 1°
(d) 3-bromocyclohex-3-en-1-ol; 2° ("1" is optional)
(e) *cis*-4-chlorocyclohex-2-en-1-ol; 2° ("1" is optional)
(f) 6-chloro-3-phenyloctan-3-ol; 3°
(g) (1-cyclopentenyl)methanol; 1°

10-32
(a) 4-chloro-1-phenylhexane-1,5-diol
(b) *trans*-cyclohexane-1,2-diol
(c) 3-nitrophenol
(d) 4-bromo-2-chlorophenol

10-33

(a) [structure: triphenylmethanol, C-OH with three phenyl groups]

(b) [structure with OH and Br]

(c) [cyclopentenol structure with OH]

(d) [structure with OH and cyclohexyl]

(e) [structure: OH OH with H,,, H]

(f) [cyclopentane with OH and OH]

(g) [phenol with OH and I, para-iodophenol]

(h) [structure: HO H, H,,, OH]

(i) [cyclopentene with SH]

(j) CH₃S—SCH₃

(k) [structure with OH and alkyne, CH₃]
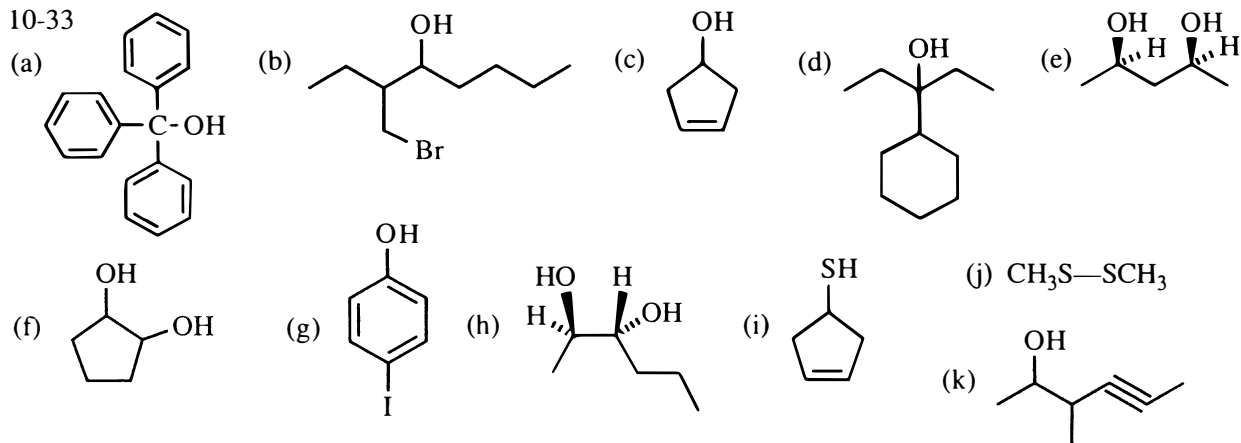
10-34

(a) Hexan-1-ol will boil at a higher temperature as it is less branched than 3,3-dimethylbutan-1-ol.

(b) Hexan-2-ol will boil at a higher temperature because its molecules hydrogen bond with each other, whereas molecules of hexan-2-one have no intermolecular hydrogen bonding.

(c) Hexane-1,5-diol will boil at a higher temperature as it has two OH groups for hydrogen bonding. Hexan-2-ol has only one group for hydrogen bonding.

(d) Hexan-2-ol will boil at a higher temperature because it has a higher molecular weight than pentan-2-ol. All other structural features of the two molecules are the same, so they should have the same intermolecular forces.

10-35

(a) 3-Chlorophenol is more acidic than cyclopentanol. In general, phenols are many orders of magnitude more acidic than alcohols.

(b) 2-Chlorocyclohexanol is slightly more acidic than cyclohexanol; the proximity of the electronegative chlorine to the OH increases its acidity.

(c) Cyclohexanecarboxylic acid is more acidic than cyclohexanol. In general, carboxylic acids are many orders of magnitude more acidic than alcohols.

(d) 2,2-Dichlorobutan-1-ol is more acidic than butan-1-ol because of the two electron-withdrawing substituents near the acidic functional group.

10-36

(a) Propan-2-ol is the most soluble in water as it has the fewest carbons and the most branching.

(b) Cyclohexane-1,2-diol is the most soluble as it has two OH groups for hydrogen bonding. Cyclohexanol has only one OH group; chlorocyclohexane cannot hydrogen bond and is the least soluble.

(c) Cyclohexanol is the most soluble as it can hydrogen bond. Chlorocyclohexane cannot hydrogen bond, and 4-methylcyclohexanol has the added hydrophobic methyl group, decreasing its water solubility.

10-37

(a) [structure: pent-1-ene] $\xrightarrow[H_2O]{Hg(OAc)_2}$ $\xrightarrow{NaBH_4}$ [structure with OH]

(b) [methylcyclohexene structure] $\xrightarrow[HO^-]{BH_3 \cdot THF \quad H_2O_2}$ [cyclohexane with CH₃, H and OH]

10-37 continued

(c) $\xrightarrow{BH_3 \cdot THF} \xrightarrow[HO^-]{H_2O_2}$

(d) $\xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4}$

10-38

(a)

(b)

(c)
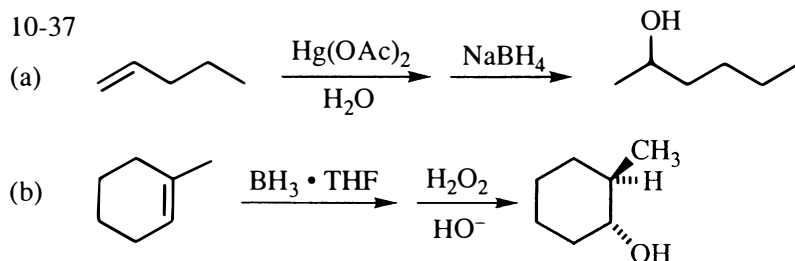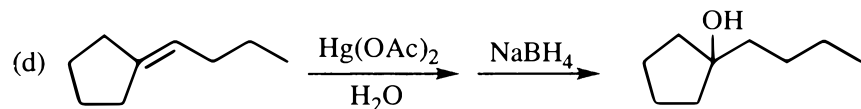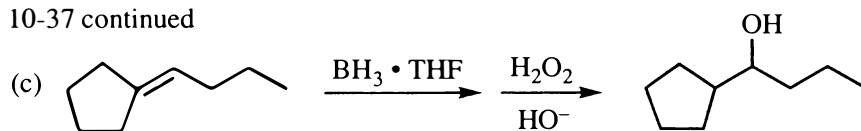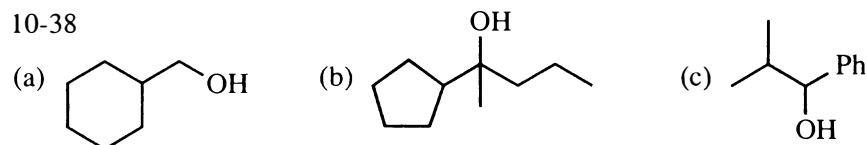
(d) This problem confuses a lot of people. When a Grignard reagent is added to a compound that has an OH group, the first thing that happens is that the Grignard reacts by removing the H^+ from the O^-.
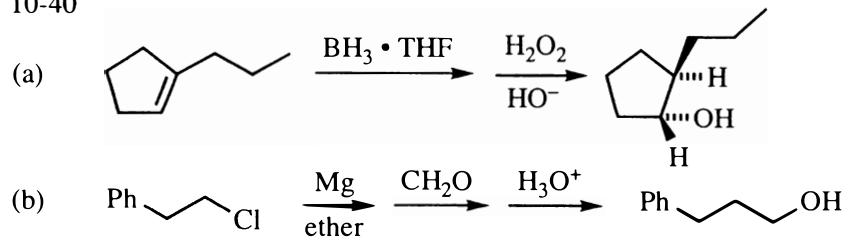

$+$ **1** CH_3MgI $\xrightarrow{ether}$

(only one equivalent of Grignard reagent added)

$+$ CH_4

If no more Grignard reagent is added before acid hydrolysis, then the starting material is recovered.

H_3O^+

$\xrightarrow[ether]{CH_3MgI}$

If a second equivalent (or excess) of Grignard reagent is added before hydrolysis, then it will add at the ketone. Acid hydrolysis will give the diol.

$\xrightarrow{H_3O^+}$

(e)

(f)

(g)

(h)

(i)

(j)

(k)

(l)

(m)

(n)

(o)

221
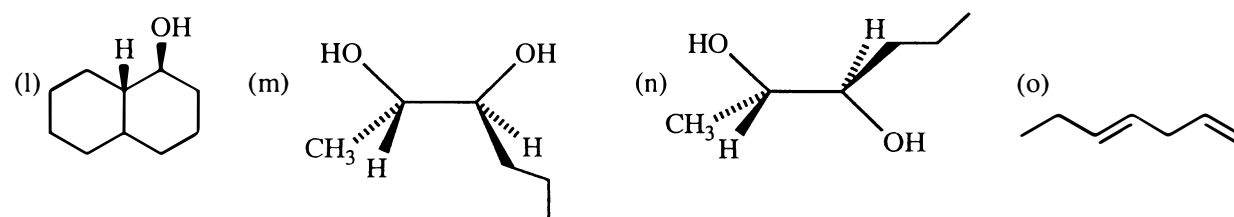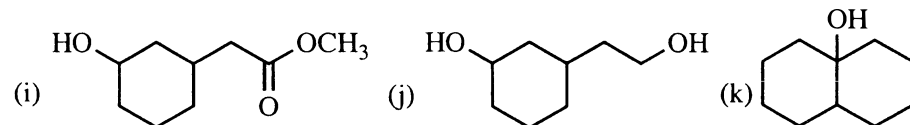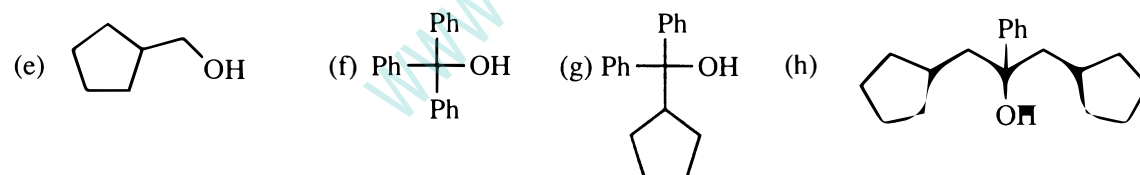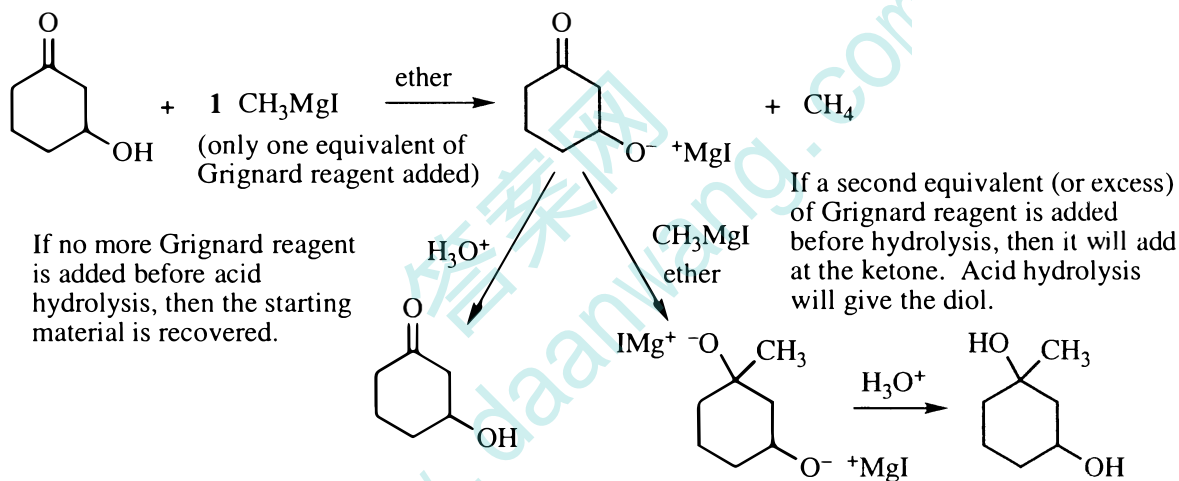
10-39 All Grignard reactions are run in ether solvent. Two arrows are shown indicating that the Grignard reaction is allowed to proceed, and then in a second step, dilute aqueous acid is added.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)
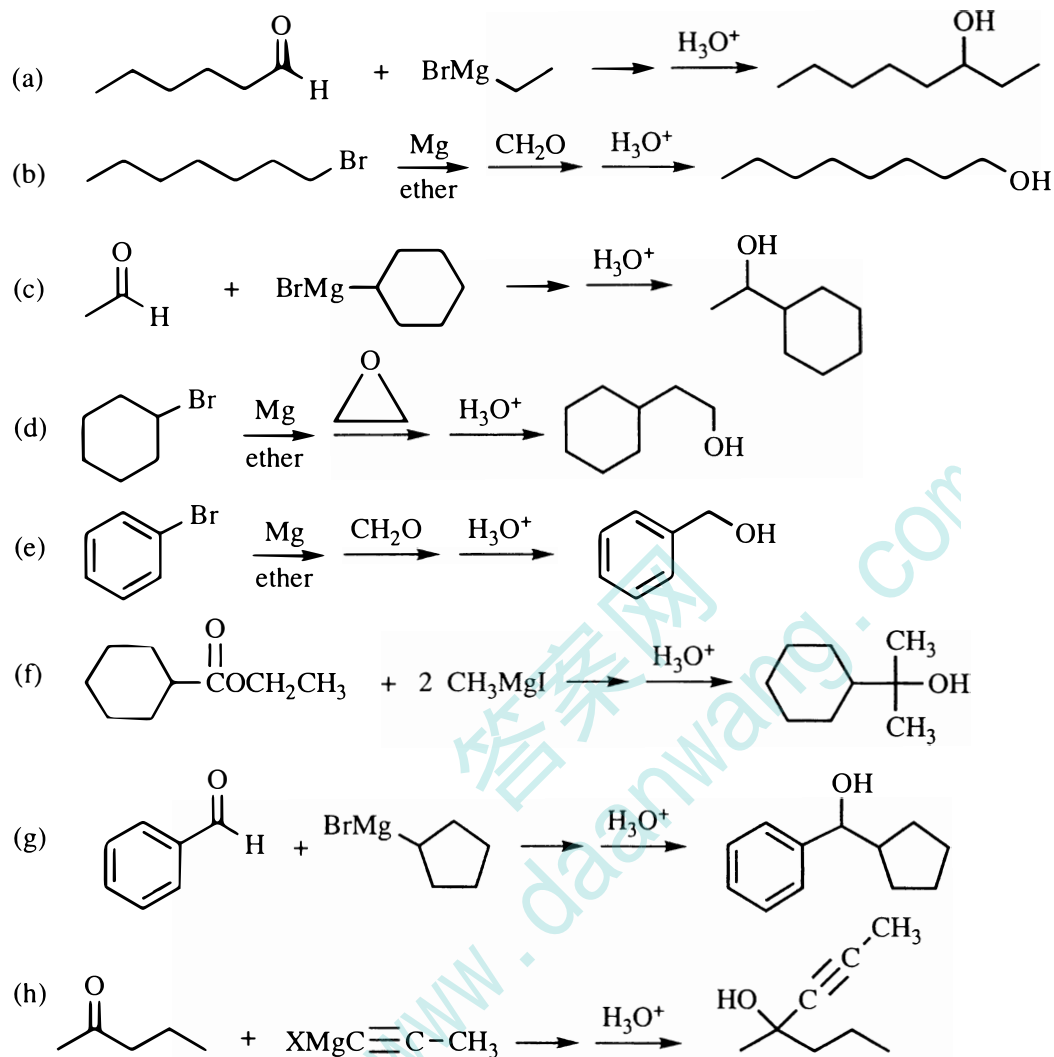
RMgX + H−C≡C−CH₃

any Grignard reagent where R is alkyl or alkenyl

Technically, XMgC≡CCH₃ is a Grignard reagent because it is an organometallic compound of magnesium. However, it is not made in the usual fashion; it is made by deprotonating the terminal alkyne as shown.

10-40

(a)

(b)

10-40 continued

(c)
$\xrightarrow[\text{CH}_3\text{OH}]{\text{NaBH}_4}$

(d)
$\xrightarrow[\text{Pt}]{\text{1 eq. H}_2}$

(e)
$\xrightarrow[\text{CH}_3\text{OH}]{\text{NaBH}_4}$

(f)
$\xrightarrow{\text{LiAlH}_4}$ $\xrightarrow{\text{H}_3\text{O}^+}$

10-41

(a) $+$ CH$_2$O $\xrightarrow{\text{ether}}$ $\xrightarrow{\text{H}_3\text{O}^+}$

(b) $\xrightarrow[\text{HO}^-]{\text{BH}_3 \bullet \text{THF} \quad \text{H}_2\text{O}_2}$

(c) $\xrightarrow{\text{NaOH}}$

(d) $\xrightarrow[\text{ether}]{\text{Mg}}$ $\xrightarrow{\text{H}_3\text{O}^+}$

(e) $+$ NaSH $\longrightarrow$

(f)
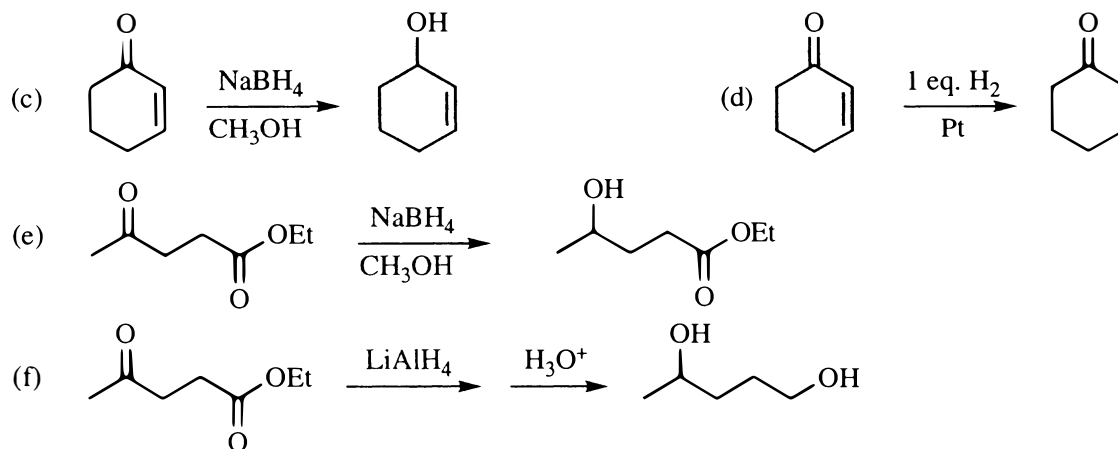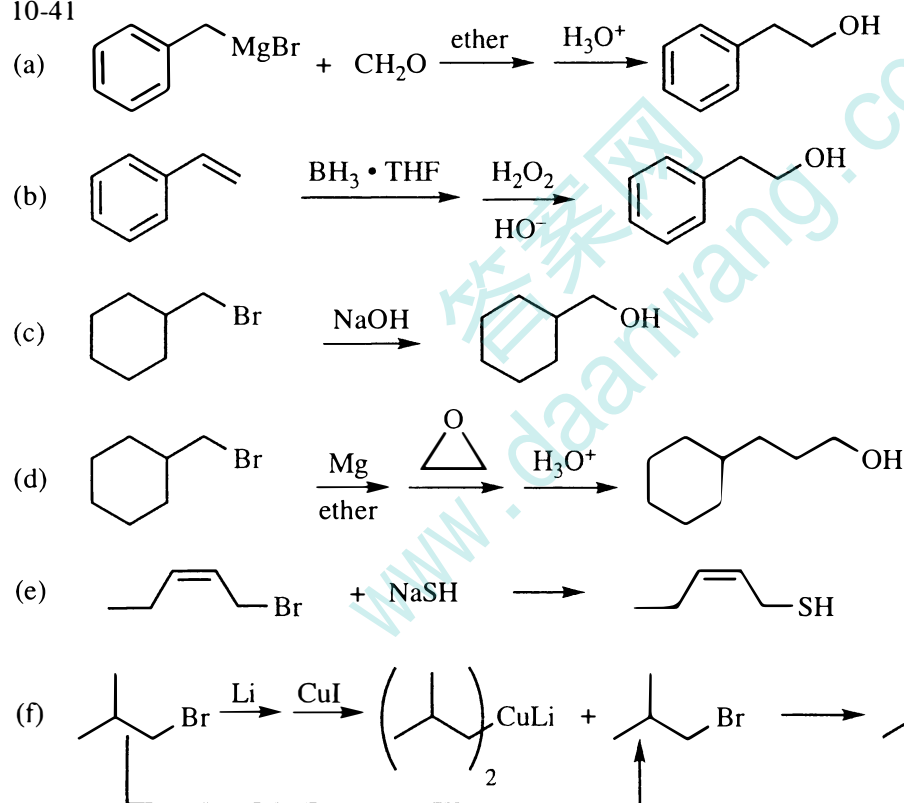
10-42 The position of the equilibrium can be determined by the strength of the acids or the bases. The stronger acid and stronger base will always react to give the weaker acid and base, so the side of the equation with the weaker acid and base will be favored at equilibrium. See Appendix 2 in this Solutions Manual for a review of acidity.

(a) CH$_3$CH$_2$O$^-$ $+$ —OH $\rightleftharpoons$ CH$_3$CH$_2$OH $+$ —O$^-$

stronger   stronger   weaker   weaker
base   acid   acid   base

products favored

10-42 continued

(b) KOH + [4-chloro-2-chlorophenol structure] OH ⇌ H₂O + [4-chloro-2-chlorophenoxide] O⁻ K⁺

stronger base ——— stronger acid ——— weaker acid ——— weaker base

products favored

(c) [1-naphthol] OH + CH₃O⁻ ⇌ [1-naphthoxide] O⁻ + CH₃OH

stronger acid ——— stronger base ——— weaker base ——— weaker acid

products favored

(d) [cyclopentanol] OH + KOH ⇌ H₂O + [cyclopentoxide] O⁻ K⁺

weaker acid ——— weaker base ——— stronger acid ——— stronger base

reactants favored

(e) (CH₃)₃CO⁻ + CH₃CH₂OH ⇌ (CH₃)₃COH + CH₃CH₂O⁻

stronger base ——— stronger acid ——— weaker acid ——— weaker base

products favored

(f) (CH₃)₃CO⁻ + H₂O ⇌ (CH₃)₃COH + HO⁻

stronger base ——— stronger acid ——— weaker acid ——— weaker base

products favored

(g) KOH + CH₃CH₂OH ⇌ H₂O + CH₃CH₂O⁻ K⁺

weaker base ——— weaker acid ——— stronger acid ——— stronger base

reactants favored

10-43

(a) [aldehyde structure] H, O $\xrightarrow[\text{CH}_3\text{OH}]{\text{NaBH}_4}$ [alcohol structure] OH OR $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) LiAlH}_4}$

OR

[carboxylic acid structure] OH, O $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) LiAlH}_4}$

OR

[ester structure] OR, O $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) LiAlH}_4}$

224

10-43 continued

(b)

$\xrightarrow[\text{CH}_3\text{OH}]{\text{NaBH}_4}$

OR $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) LiAlH}_4}$

(c)

$\xrightarrow[\text{CH}_3\text{OH}]{\text{NaBH}_4}$

OR $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) LiAlH}_4}$

(d)

$\xrightarrow[\text{CH}_3\text{OH}]{\text{NaBH}_4}$

OR $\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) LiAlH}_4}$

(e)

$\xrightarrow[\text{CH}_3\text{OH}]{\text{NaBH}_4}$

(f)

$\xrightarrow[\text{2) H}_3\text{O}^+]{\text{1) LiAlH}_4}$

  + HOCH$_2$CH$_3$

10-44 The goal is to synthesize the target compound (boxed) from starting materials of six carbons or fewer. The product has 12 carbons, so the logical "disconnection" in working backwards is two six carbon fragments which could be joined in a Grignard reaction. The best way to make epoxides is from the double bond, and double bonds are made from alcohols which are the products of Grignard reactions.
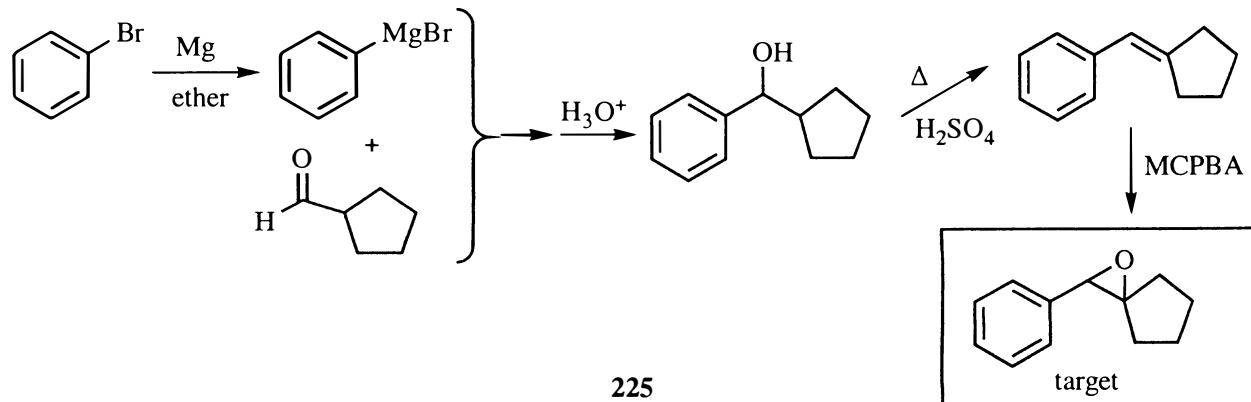
10-45 All steps are reversible.
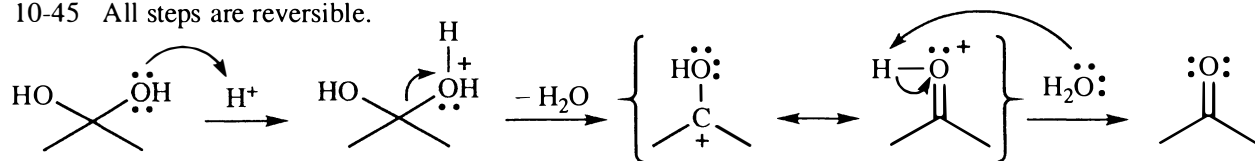
10-46 The symbol H—B represents a generic acid, where B⁻ is the conjugate base.

(a)

(b)

(c)

10-47

isobutylcyclohexane
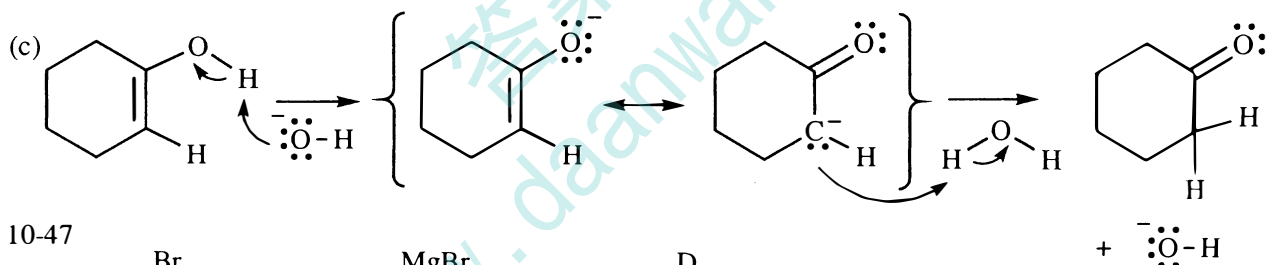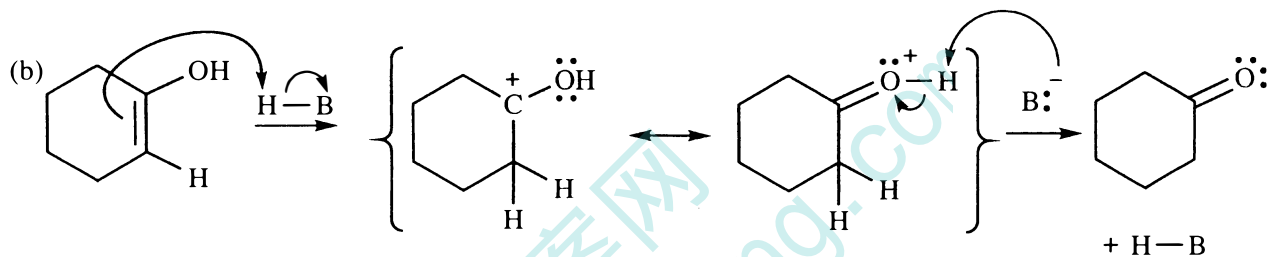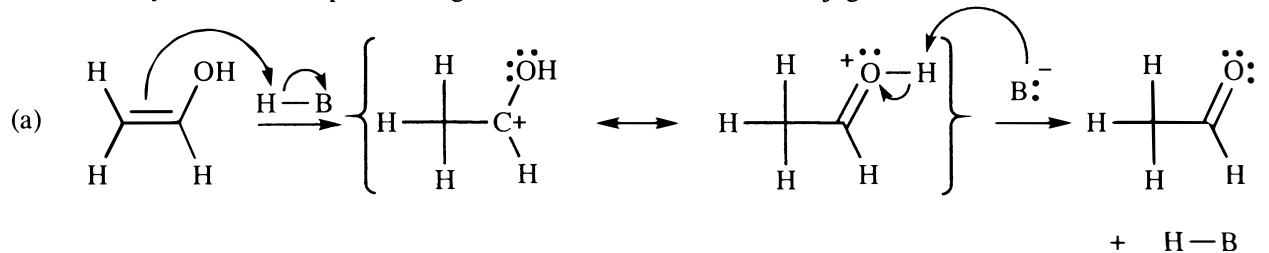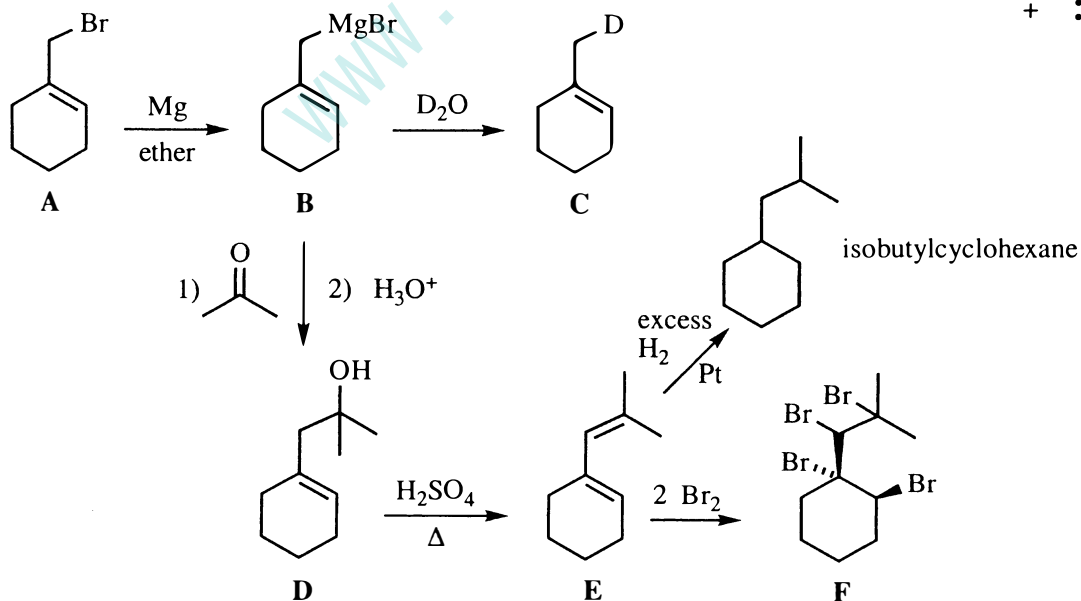
10-48 This mechanism is similar to cleavage of the epoxide in ethylene oxide by Grignard reagents. The driving force for the reaction is relief of ring strain in the 4-membered cyclic ether, which is why it will undergo a Grignard reaction whereas most other ethers will not.
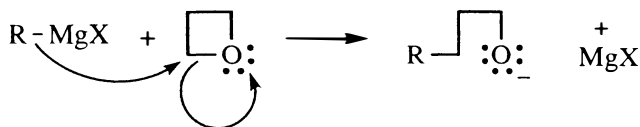
10-49 When mixtures of isomers can result, only the major product is shown.
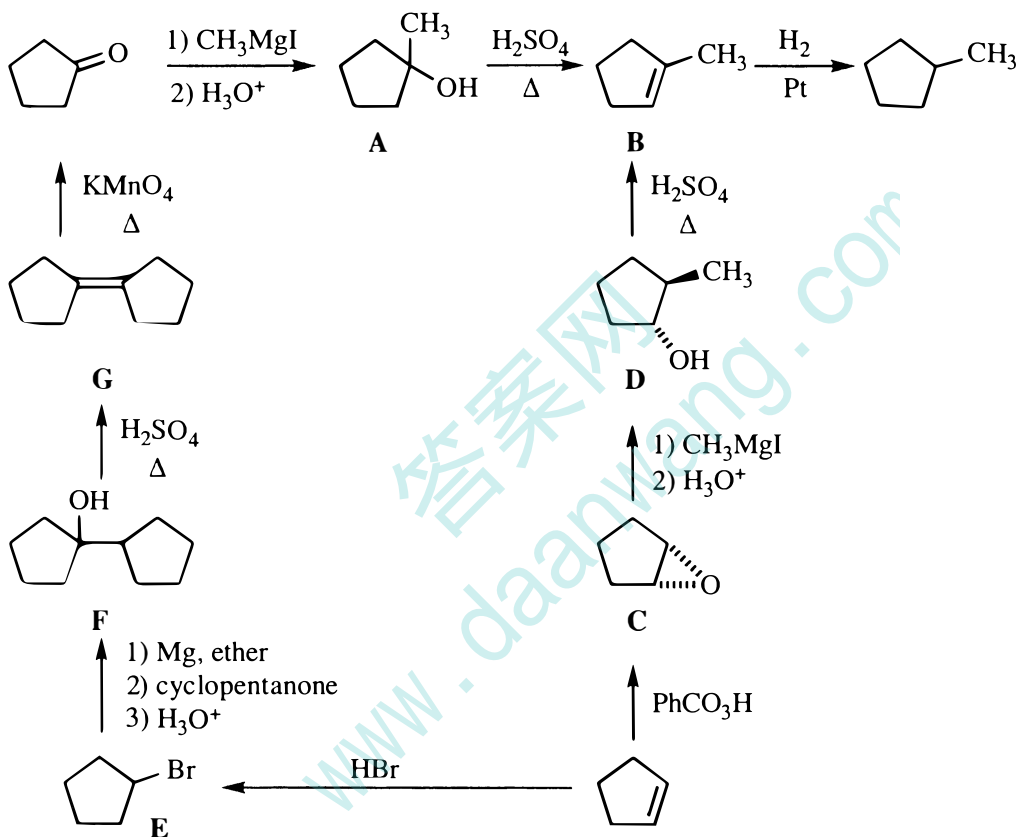
10-50 The most important reactant in the deskunking mixture is hydrogen peroxide. Thiols are oxidized to structures having one, two, or three oxygens on the sulfur; all of these functional groups are acidic. The sodium bicarbonate is basic enough to ionize these acids, making them water soluble where the soap can wash them away.

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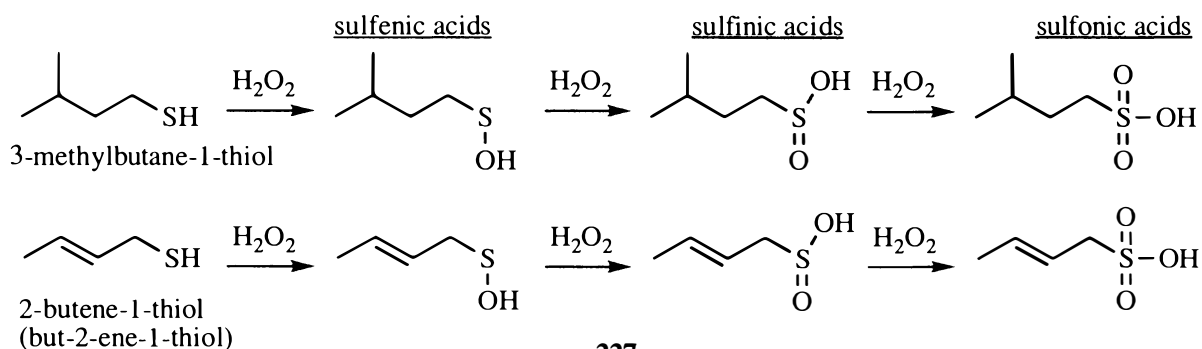
10-51
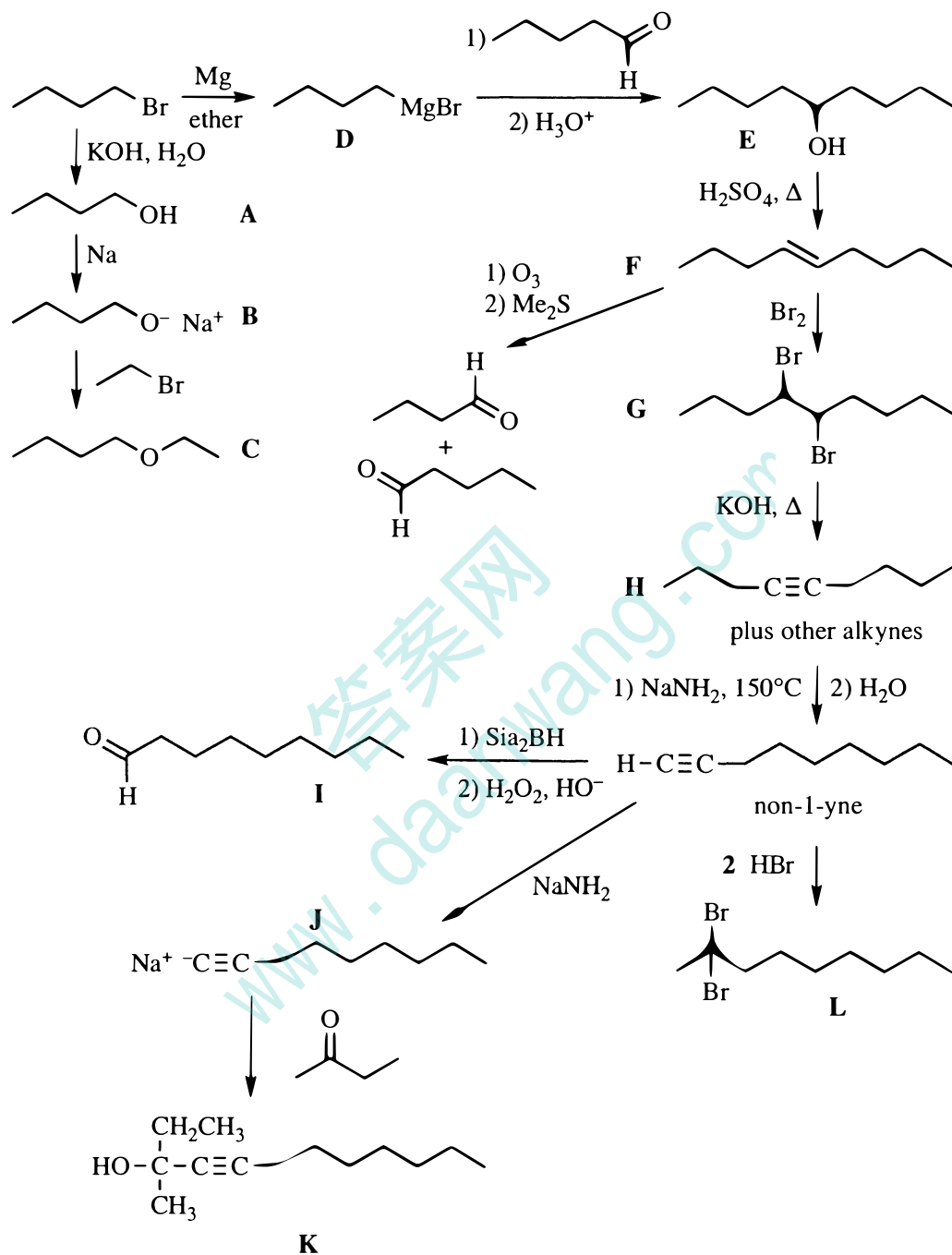
CHAPTER 11—REACTIONS OF ALCOHOLS

11-1
(a) both reactions are oxidations
(b) oxidation, oxidation, reduction, oxidation
(c) one carbon is oxidized and one carbon is reduced—no net change
(d) reduction: C—O is replaced by C—H
(e) neither oxidation nor reduction—the C still has two bonds to O
(f) oxidation (addition of X_2)
(g) neither oxidation nor reduction (addition of HX)
(h) neither oxidation nor reduction (elimination of H_2O)
(i) oxidation: adding an O to each carbon of the double bond
(j) the first reaction is oxidation as a new C—O bond is formed to each carbon of the alkene; the second reaction is neither oxidation nor reduction, as H_2O is added to the epoxide, and each carbon still has one bond to oxygen
(k) neither oxidation nor reduction: H—B is added in the first reaction, and B is replaced by O in the second reaction; overall, only H and OH are added, so there is no net oxidation nor reduction. (Note that in functional groups involving two carbons like alkenes or alkynes, both carbons have to be oxidized or reduced before the *net* change to the functional group is classified as oxidation or reduction.)

11-2

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

229
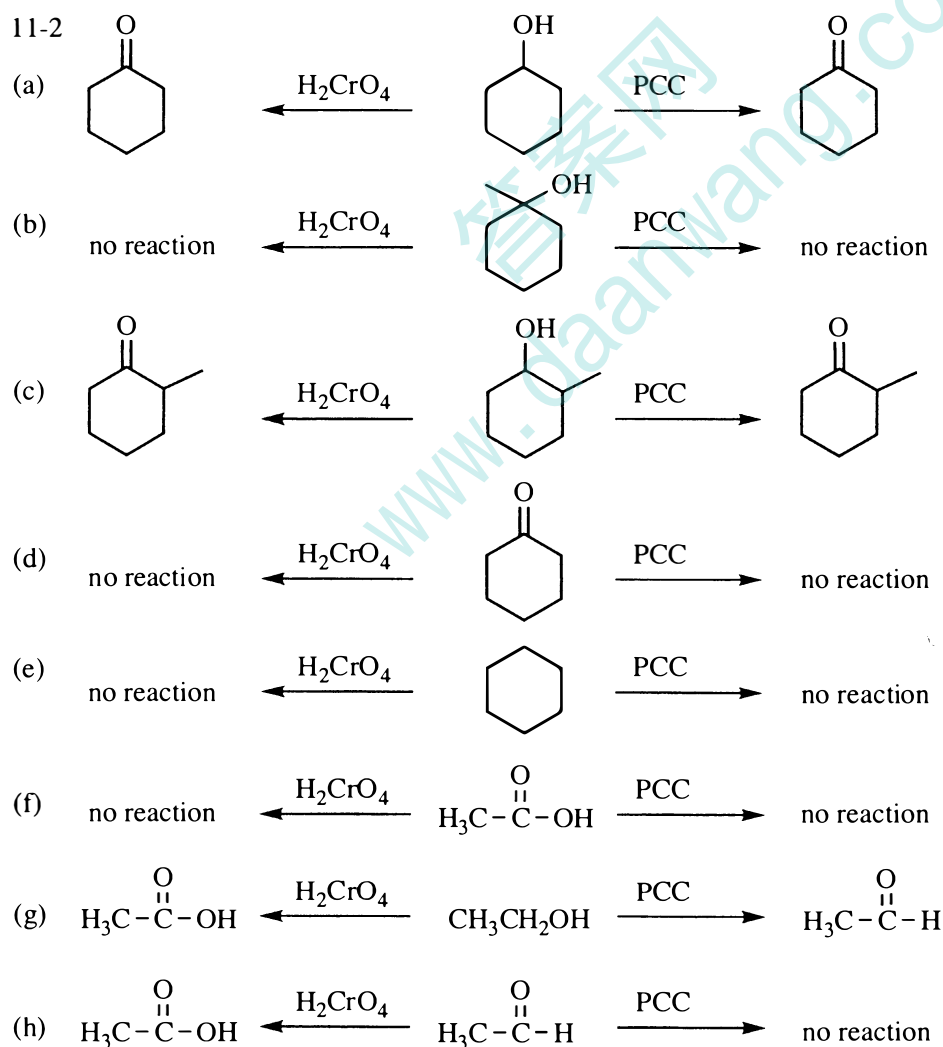
11-3
(a) A 1° alcohol loses two hydrogens when transformed to the aldehyde, and a 2° alcohol loses one hydrogen in forming a ketone; each alcohol is oxidized. DMSO loses an oxygen from the sulfur; it is clearly reduced. (If you got those two, you did the problem correctly.) To be rigorous, oxalyl chloride undergoes a disproportionation reaction: one C is oxidized to CO_2 and the other C is reduced to CO; however, the net effect on the elements in oxalyl chloride is "no change".
(b) Text section 8-15B shows that dimethyl sulfide reduces an ozonide. In the process, dimethyl sulfide is oxidized to DMSO.

11-4
(a) Dehydrogenation does not occur at 25° C—either: 1) there is a high kinetic barrier (a high activation energy) for this reaction, or 2) it is thermodynamically unfavorable, with $\Delta G > 0$. The latter possibility is supported by the fact that the reverse reaction (catalytic hydrogenation of a carbonyl) *is* spontaneous at 25° C (see text section 10-11C) and therefore has $\Delta G < 0$. This makes the question of kinetics academic—a reaction that cannot proceed must be uselessly slow.
(b) and (c) Kinetics will improve with increasing temperature for virtually all reactions, so both the hydrogenation and dehydrogenation reactions will go faster. In this case, however, the question is how to favor the dehydrogenation reaction. The answer is that thermodynamics will favor this reaction as the temperature is raised. The key is the fundamental thermodynamic equation $\Delta G = \Delta H - T\Delta S$. We can estimate that $\Delta H > 0$ since the product ketone plus hydrogen is less stable than the starting alcohol. Also, $\Delta S > 0$ since one molecule is converted to two: therefore, $-T\Delta S < 0$. At low temperature (25° C), ΔH dominates because T is so small, so $\Delta G > 0$. At a high enough temperature, the $-T\Delta S$ term will begin to overwhelm ΔH, and ΔG will become negative. For the reaction in question, this must be the case at 300° C.

11-5
(a)
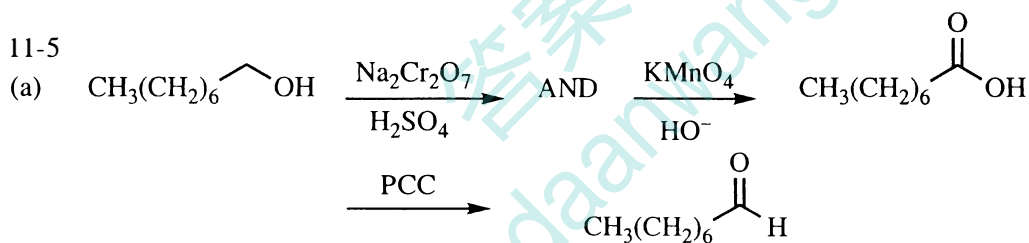
(b) all three reagents give the same ketone product with a secondary alcohol

(c)
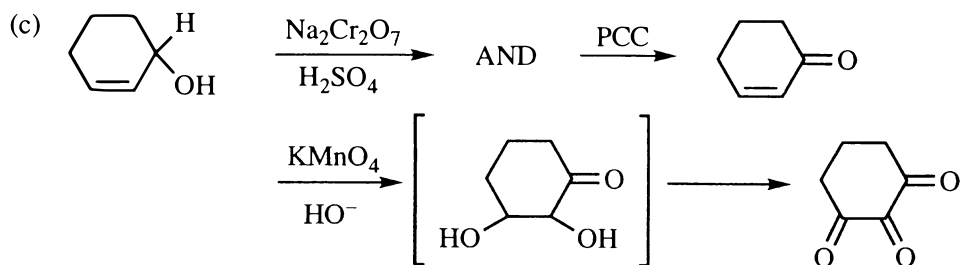
(d) all three reagents give no reaction with a tertiary alcohol

230
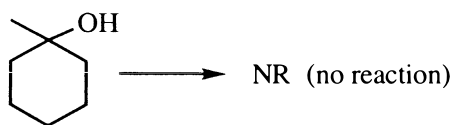
Note to the student: For simplicity, this book will use these standard laboratory methods of oxidation:

— PCC (pyridinium chlorochromate) to oxidize 1° alcohols to aldehydes;
— H_2CrO_4 (chromic acid) to oxidize 1° alcohols to carboxylic acids;
— CrO_3, H_2SO_4, acetone (Jones reagent) to oxidize 2° alcohols to ketones.

Understand that other choices are legitimate; for example, Swern oxidation works about as well as PCC in the preparation of aldehydes, and Collins reagent or PCC will oxidize a 2° alcohol to a ketone as well as chromic acid. If you have a question about the appropriateness of a reagent you choose, consult the table in the text before Problem 11-2.

11-6

(a)

(b)

(c)

(d)

(e)

(f)
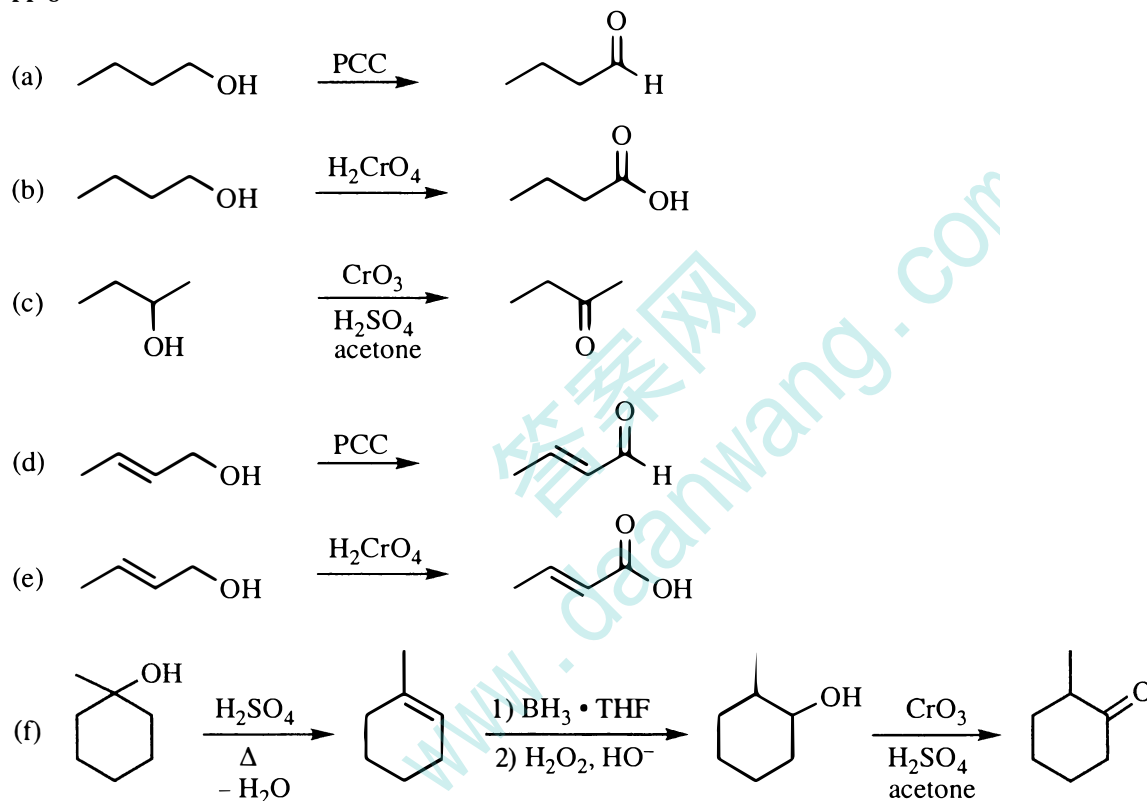
11-7 A chronic alcoholic has induced more ADH enzyme to be present to handle large amounts of imbibed ethanol, so requires more ethanol "antidote" molecules to act as a competitive inhibitor to "tie up" the extra enzyme molecules.

11-8

pyruvic acid is a normal metabolite
in the breakdown of glucose ("blood sugar")

231
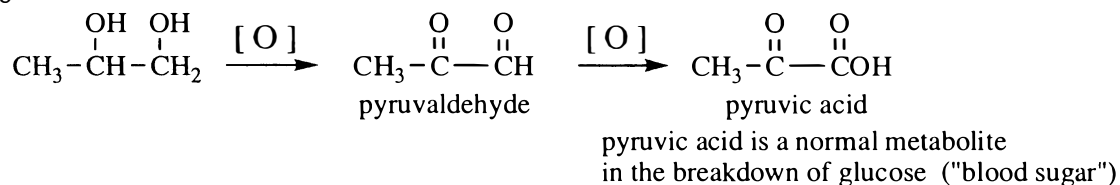
11-9 From this problem on, "Ts" will refer to the "tosyl" or "p-toluenesulfonyl" group:

$Ts \implies$

(a) CH_3CH_2-OTs + $KO-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$ $\longrightarrow$ $CH_3CH_2O-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$ +   KOTs
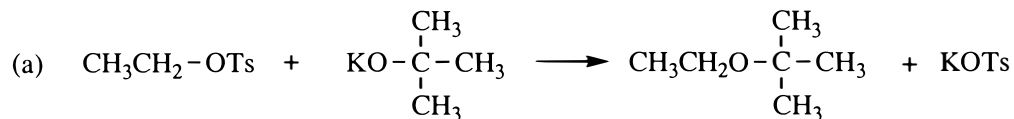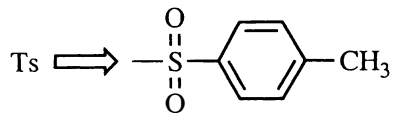
(E2 is also possible with this hindered base; the product would be ethylene, $CH_2=CH_2$.)

(b) OTs   +   NaI $\longrightarrow$ I   +   NaOTs

(c)   +   NaCN $\longrightarrow$ +   NaOTs   inversion—S_N2

(d) $\xrightarrow{NH_3}$ $\xrightarrow[NH_3]{excess}$ $+ \overset{+}{N}H_4 \ \overset{-}{O}Ts$

(e) OTs   + Na^+ $:\!\bar{C}\!\equiv\!CH$ $\longrightarrow$ $C\equiv CH$ +   NaOTs

11-10
(a) OH $\xrightarrow[\text{pyridine}]{TsCl}$ OTs $\xrightarrow{NaBr}$ Br

(b) OH $\xrightarrow[\text{pyridine}]{TsCl}$ OTs $\xrightarrow[NH_3]{\text{excess}}$ NH_2

(c) OH $\xrightarrow[\text{pyridine}]{TsCl}$ OTs $\xrightarrow{NaOCH_2CH_3}$ O

(d) OH $\xrightarrow[\text{pyridine}]{TsCl}$ OTs $\xrightarrow{KCN}$ CN

11-11
(a) $-CH_2OH$ $\xrightarrow[\text{pyridine}]{TsCl}$ $-CH_2OTs$ OR

11-11 continued

(b)

(c)

major + minor
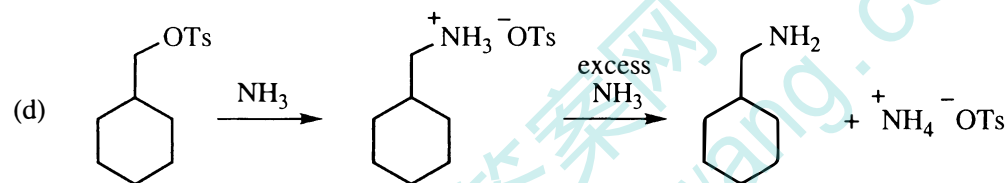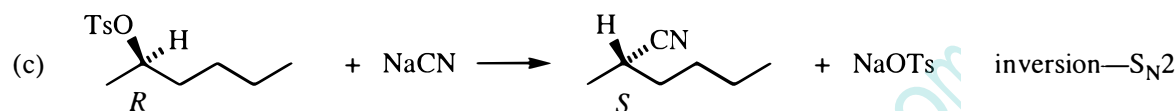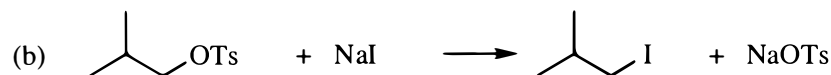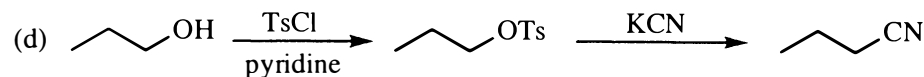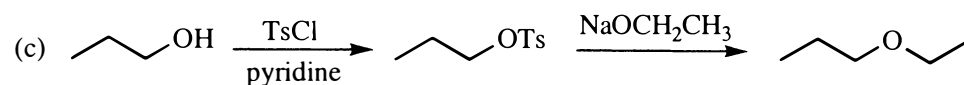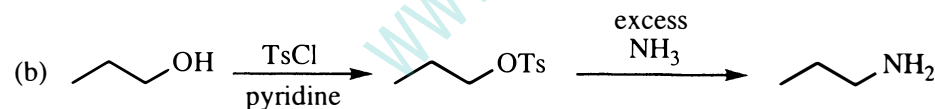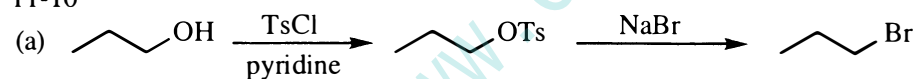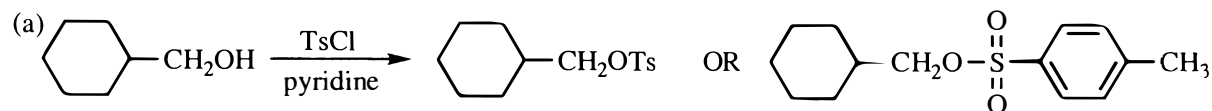
(d)
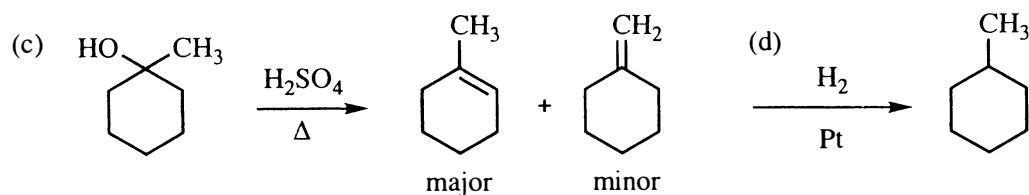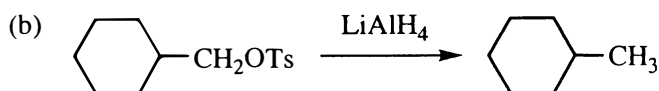
11-12

(a) either S_N1 or S_N2 on 2° alcohols

(b) S_N2 on 1° alcohols

11-13

carbocation
intermediate
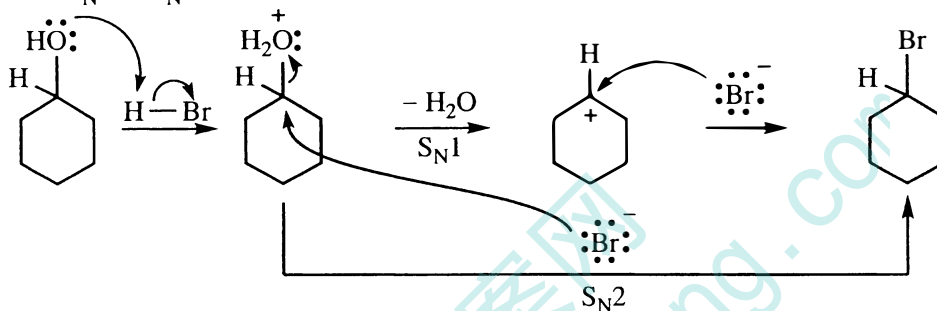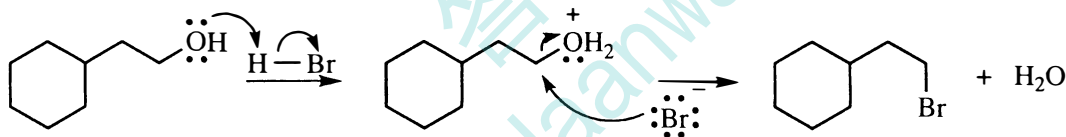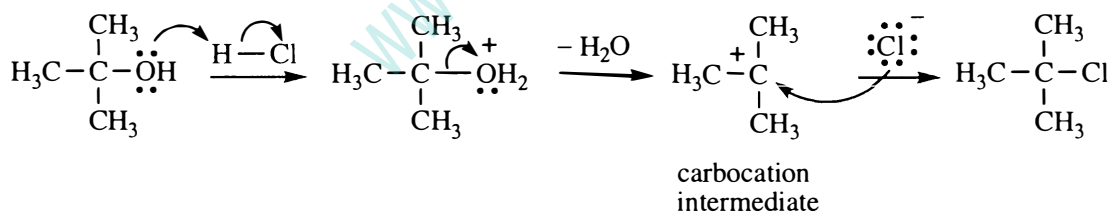
11-14 The two standard qualitative tests are:

1) chromic acid—distinguishes 3° alcohol from either 1° or 2°
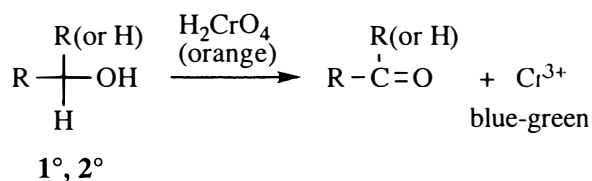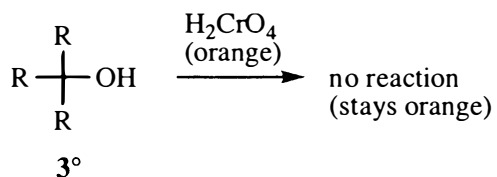
11-14 continued

2) <u>Lucas test</u>—distinguishes 1° from 2° from 3° alcohol by the rate of reaction

3° R—C(R)(R)—OH + HCl $\xrightarrow{ZnCl_2}$ R—C(R)(R)—Cl + H_2O insoluble—"cloudy" in < 1 minute
soluble

2° R—C(R)(H)—OH + HCl $\xrightarrow{ZnCl_2}$ R—C(R)(H)—Cl + H_2O insoluble—"cloudy" in 1-5 minutes
soluble

1° R—C(H)(H)—OH + HCl $\xrightarrow{ZnCl_2}$ R—C(H)(H)—Cl + H_2O insoluble—"cloudy" in > 6 minutes
soluble   (no observable reaction at room temp.)

- -

(a)

Lucas: cloudy in 1-5 min.   cloudy in < 1 min.
H_2CrO_4:   immediate blue-green   no reaction—stays orange

(b)

Lucas: cloudy in 1-5 min.   no reaction
H_2CrO_4:   immediate blue-green   no reaction—stays orange

(c)

Lucas: no reaction   cloudy in 1-5 min.
H_2CrO_4:   DOES NOT DISTINGUISH—immediate blue-green for both

(d)

Lucas: cloudy in < 1 min. **   no reaction
H_2CrO_4:   DOES NOT DISTINGUISH—
                immediate blue-green for both

(**Remember that allylic cations are resonance-stabilized and are about as stable as 3° cations. Thus, they will react as fast as 3° in the Lucas test, even though they may be 1°. Be careful to notice subtle but important structural features!)

(e)

Lucas: no reaction   cloudy in < 1 min.
H_2CrO_4:   DOES NOT DISTINGUISH—stays orange for both

11-15

Even though 1°, the neopentyl carbon is hindered to backside attack, so S_N2 cannot occur easily. Instead, an S_N1 mechanism occurs, with rearrangement.

11-16

This 3° carbocation is planar at the C⁺ so that the Cl⁻ can approach from the top or bottom giving both the cis and trans isomers.

11-17

11-18

$$3 \quad \text{(CH}_3\text{)}_3\text{CCH}_2\text{OH} + \text{PBr}_3 \longrightarrow 3 \quad \text{(CH}_3\text{)}_3\text{CCH}_2\text{Br} + \text{P(OH)}_3$$

$$6 \; CH_3(CH_2)_{14}CH_2OH + 2 \; P + 3 \; I_2 \longrightarrow 6 \; CH_3(CH_2)_{14}CH_2I + 2 \; P(OH)_3$$

11-19

(a)

retention

(b)

S_N2—inversion

Another possible answer would be to use PCl_3.

235

11-20

(a)
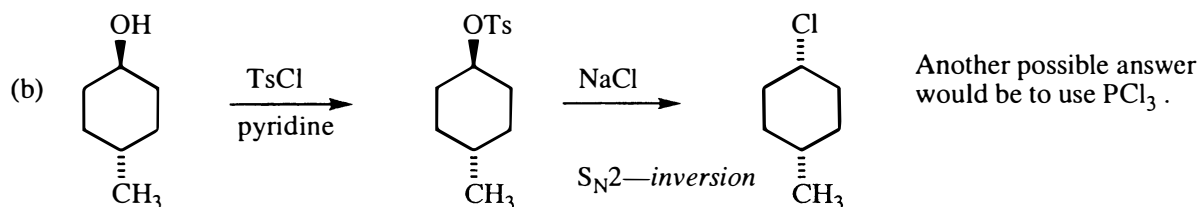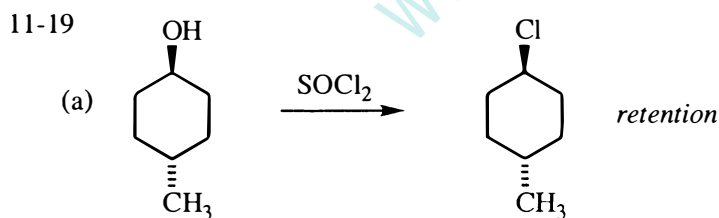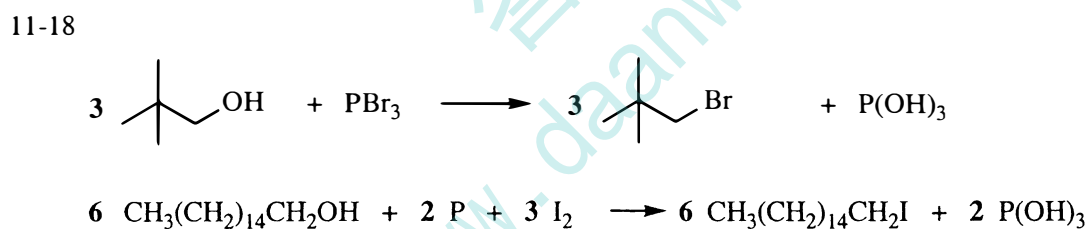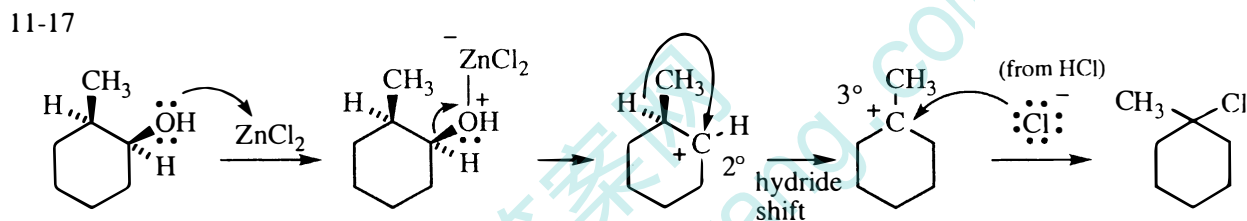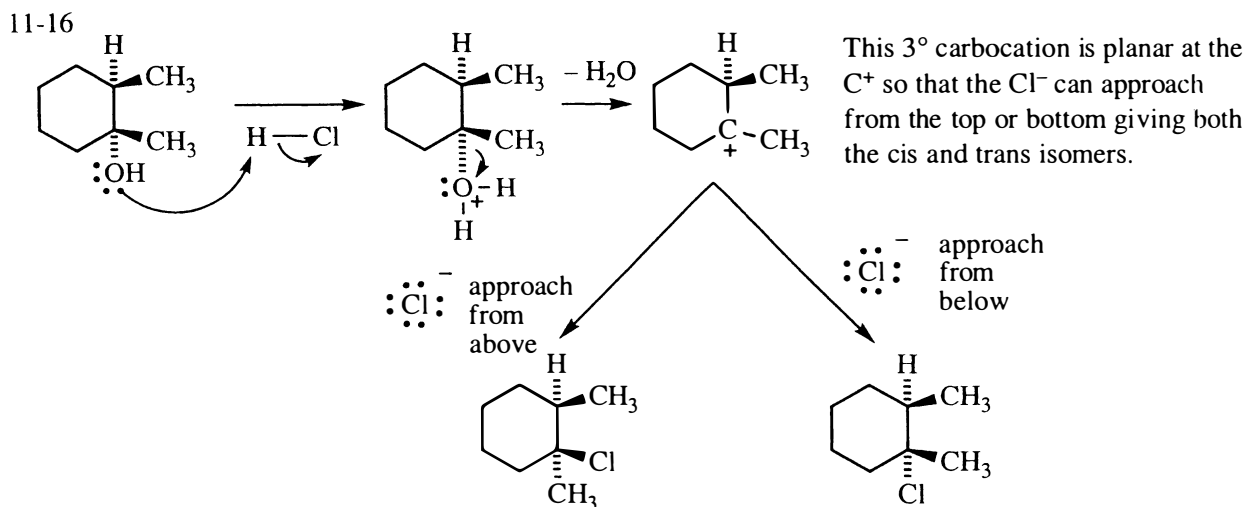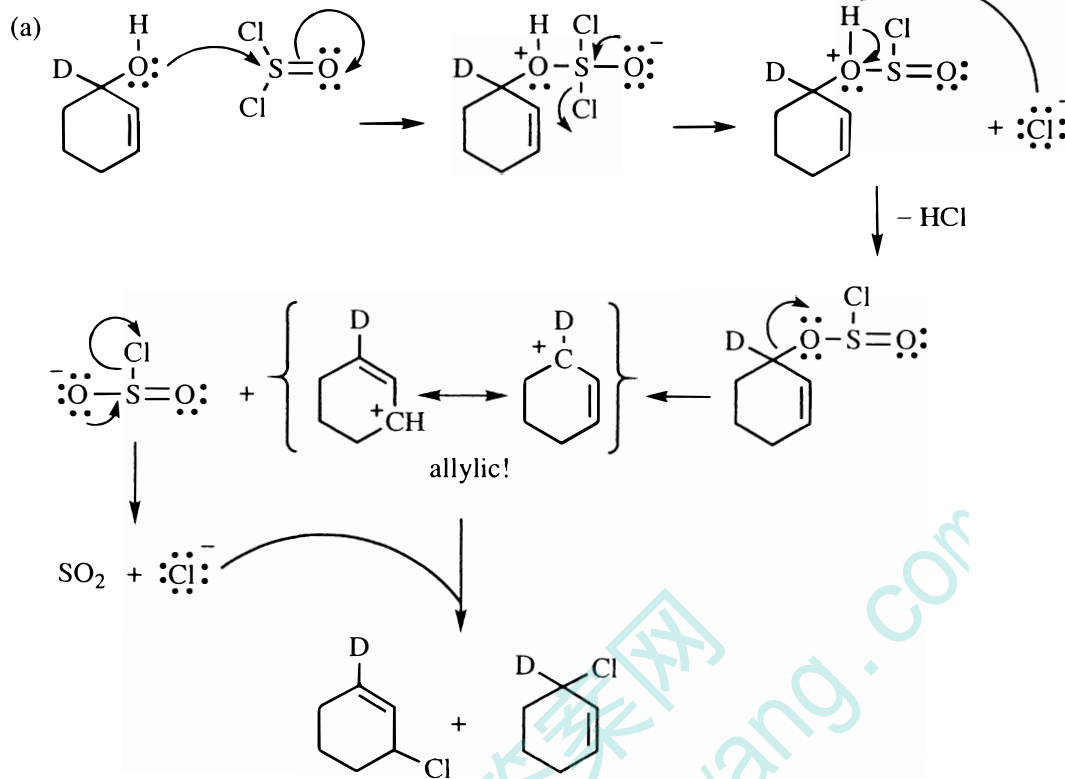
(b) The key is that the intermediate carbocation is allylic, very stable and relatively long-lived. It can therefore escape the ion pair and become a "free carbocation". The nucleophilic chloride can attack any carbon with positive charge, not just the one closest. Since two carbons have partial positive charge, two products result.

11-21

(a)

11-21 continued

(b)

(c)

(poor reaction on 3°)

(poor reaction on 3°)

(poor reaction on 3°)

(d)

1°, neopentyl

HCl / ZnCl₂ → no reaction unless heated, then S$_N$1—rearrangement

HBr → S$_N$2—minor (hindered) + S$_N$1—rearrangement

PBr₃ →

P / I₂ →

SOCl₂ →

11-21 continued

(e)

HCl / ZnCl₂ → S_N1; carbocation intermediate can be attacked from either side by chloride

HBr → S_N2 with inversion of configuration

PBr₃ → S_N2 with inversion of configuration

P / I₂ → S_N2 with inversion of configuration

SOCl₂ → retention of configuration

11-22

(a)

H₂SO₄, Δ → major + minor

(b)

H₂SO₄, Δ → major (cis + trans) + minor

(c)

H₂SO₄, Δ → major (cis + trans) + minor

(d)

H₂SO₄, Δ → major + minor

(e)

H₂SO₄, Δ → major + minor + trace

238

11-23

good leaving group

cyclohexene was formed
without a carbocation
intermediate

this product can react with two
more alcohols to become leaving
groups in the E2 elimination

11-24

Both mechanisms begin with protonation of the oxygen.
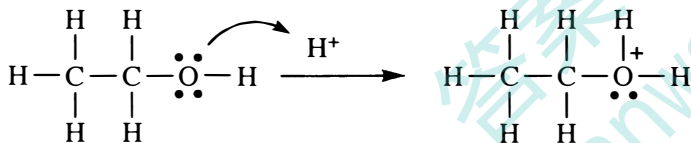
One mechanism involves another molecule of ethanol acting as a base, giving elimination.
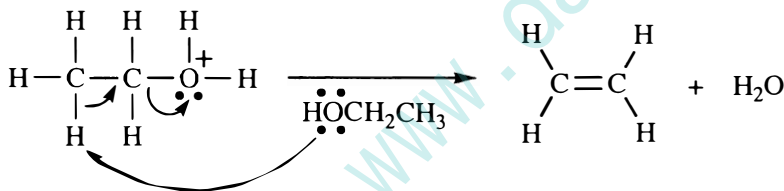
The other mechanism involves another molecule of ethanol acting as a nucleophile, giving substitution.
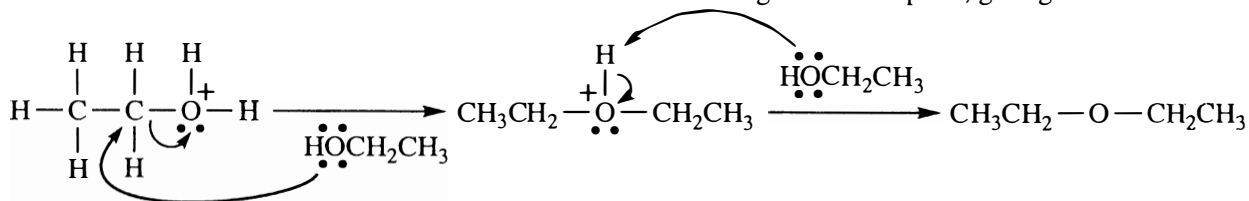
11-25   An equimolar mixture of methanol and ethanol would produce all three possible ethers. The difficulty in separating these compounds would preclude this method from being a practical route to any one of them. This method is practical only for symmetric ethers, that is, where both alkyl groups are identical.

$$CH_3CH_2OH + HOCH_3 \xrightarrow[\Delta]{H^+} H_2O + CH_3CH_2OCH_3 + CH_3OCH_3 + CH_3CH_2OCH_2CH_3$$

239

11-26

11-27

(a)

(b)

(c)

ring expansion

hydride shift

240

11-27 continued

(d)

11-28

(a)
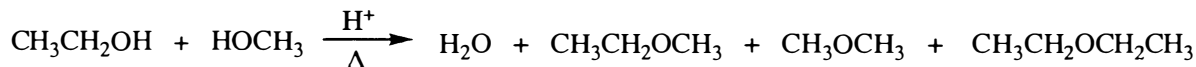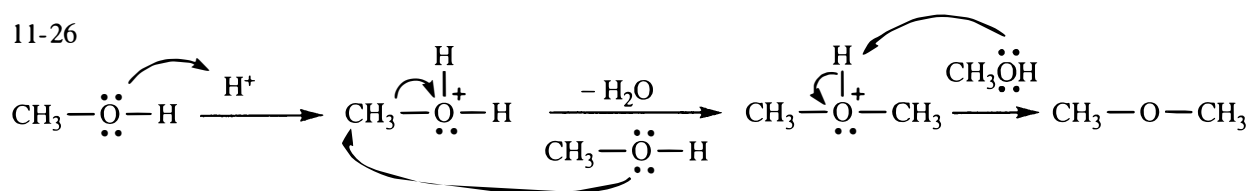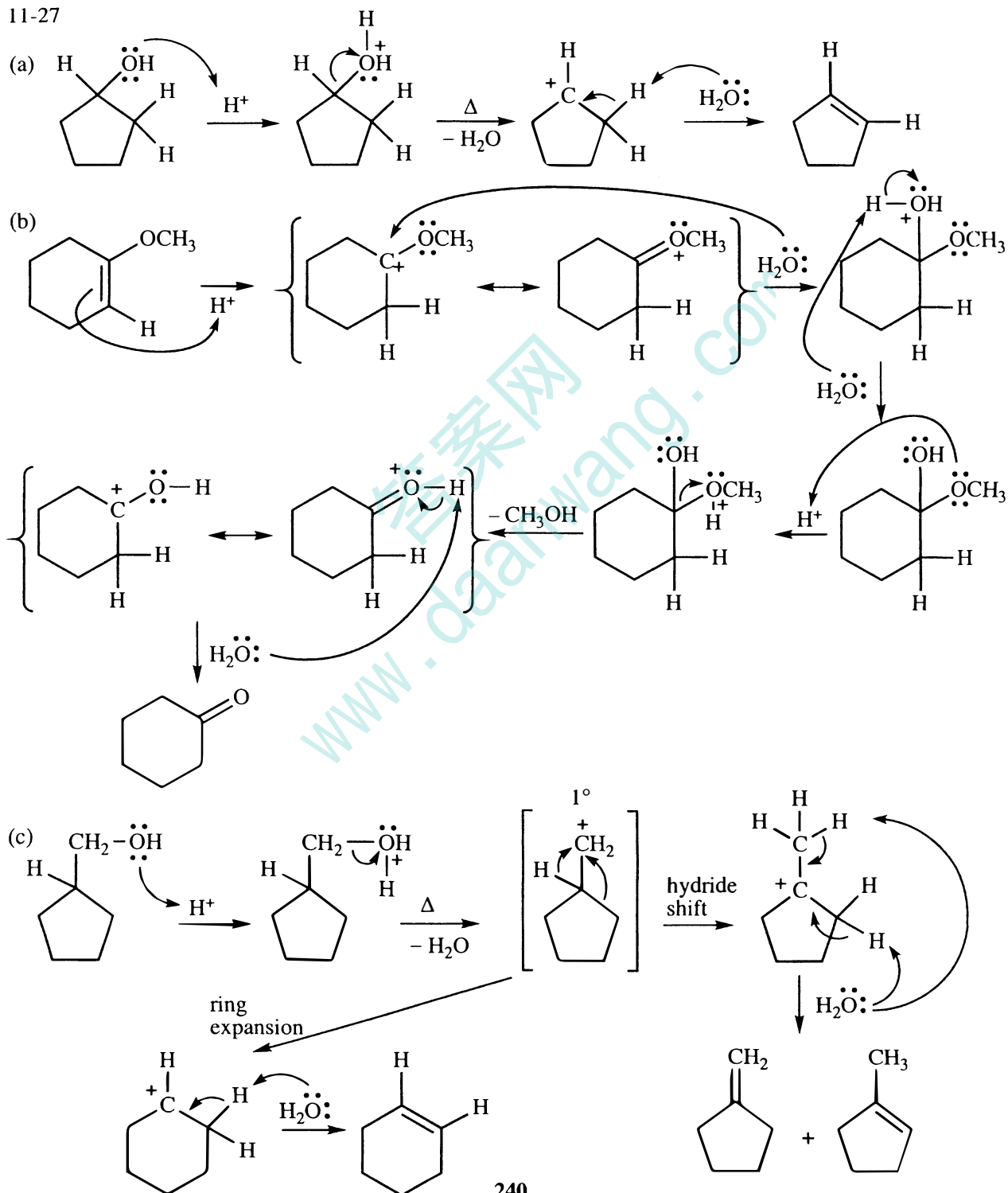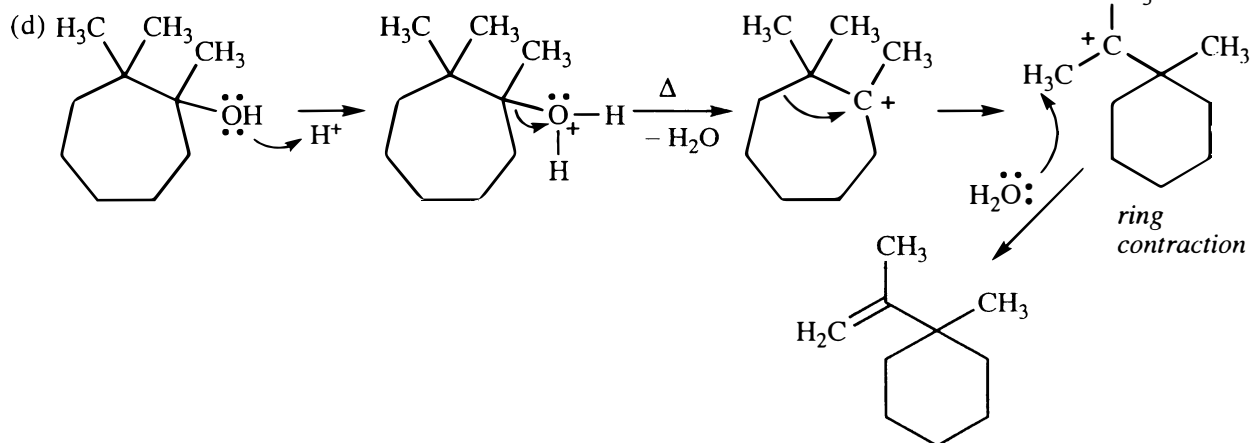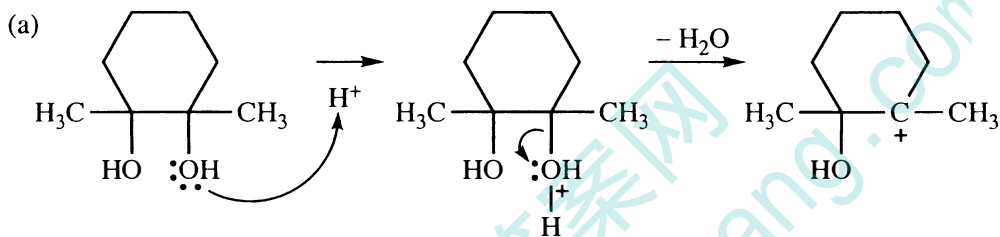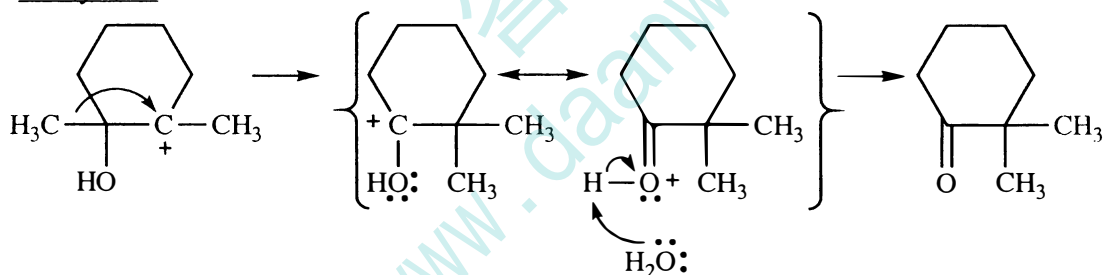
Methyl shift

Alkyl shift—ring *contraction*

241

11-28 continued

(b)

3° and doubly benzylic carbocation

ring expansion

11-29

ring expansion

Similar to the pinacol rearrangement, this mechanism involves a carbocation next to an alcohol, with rearrangement to a protonated carbonyl. Relief of some ring strain in the cyclopropane is an added advantage of the rearrangement.

HSO_4^-

11-30

(a) 2 $H_3C - \overset{O}{\underset{||}{C}} - H$

(b) + $CH_2 = O$

(c) + $H - \overset{O}{\underset{||}{C}} -$

(d)

11-31

(a) $Cl - \overset{O}{\underset{||}{C}} - CH_2CH_2CH_3$ + $HOCH_2CH_2CH_3$

(b) $CH_3(CH_2)_3OH$ + $Cl - \overset{O}{\underset{||}{C}}CH_2CH_3$

(c) $H_3C - \bigcirc - OH$ + $Cl - \overset{O}{\underset{||}{C}}CH(CH_3)_2$

(d) $\triangleright - OH$ + $Cl - \overset{O}{\underset{||}{C}} - \bigcirc$

11-32

11-33 Proton transfer (acid-base) reactions are much faster than almost any other reaction. Methoxide will act as a base and remove a proton from the oxygen much faster than methoxide will act as a nucleophile and displace water.

11-34

(a)
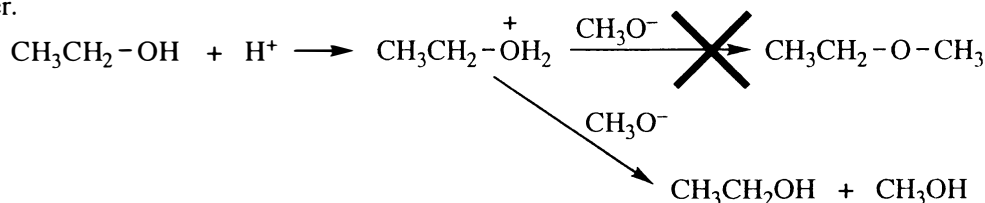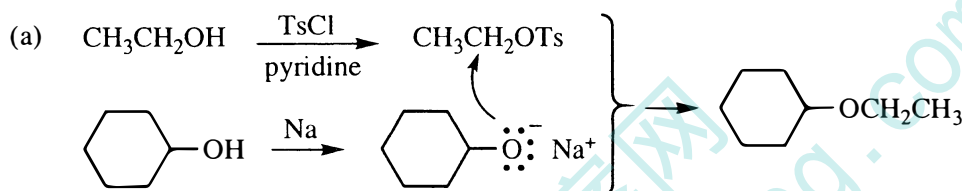
(b) There are two problems with this attempted bimolecular dehydration. First, all three possible ether combinations of cyclohexanol and ethanol would be produced. Second, hot sulfuric acid are the conditions for dehydrating secondary alcohols like cyclohexanol, so elimination would compete with substitution.

11-35

(a) What the student did:

sodium *(S)*-2-butoxide   *(S)*-2-ethoxybutane
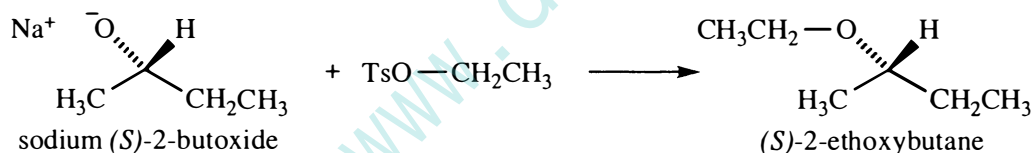
The product also has the *S* configuration, not the *R*. Why? The substitution is indeed an S_N2 reaction, but the *substitution did not take place at the chiral center*, so the configuration of the starting material is retained, not inverted.

(b) There are two ways to make *(R)*-2-ethoxybutane. Start with *(R)*-2-butanol, make the anion, and substitute on ethyl tosylate similar to part (a), or do an S_N2 inversion at the chiral center of *(S)*-2-butanol. S_N2 works better at 1° carbons so the former method would be preferred to the latter.

(c) This is not the optimum method because it requires S_N2 at a 2° carbon, as discussed in part (b).

(S)-2-butanol   *(S)*-2-butyl tosylate   *(R)*-2-ethoxybutane
                                no inversion yet   INVERSION!

243

11-36

11-37

(a) $CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH$ $\xrightarrow{SOCl_2}$ $CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl$ $\xrightarrow[2)\ H_3O^+]{1)\ \mathbf{2}\ CH_3CH_2MgBr}$ $CH_3CH_2-\overset{CH_2CH_3}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-CH_2CH_3$

$\downarrow H_2SO_4$

$CH_3\overset{CH_2CH_3}{\underset{|}{C}}HCHCH_2CH_3$ $\xleftarrow[2)\ H_2O_2,\ HO^-]{1)\ BH_3\cdot THF}$ $CH_3CH=\overset{CH_2CH_3}{\overset{|}{C}}-CH_2CH_3$
$\underset{OH}{|}$

(b) $CH_3CH_2CH_2OH$ $\xrightarrow{PCC}$ $CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$ $\xrightarrow[2)\ H_3O^+]{1)\ CH_3CH_2MgBr}$ (OH) $\xrightarrow[acetone]{CrO_3\ H_2SO_4}$ (O)

11-38

(a) (OH) $\xrightarrow[\Delta]{H^+}$ ( ) $\xrightarrow[H_3O^+]{HCO_3H}$ (OH, OH) any peroxy acid can be used to form the epoxide which is cleaved to the *trans*-diol in aqueous acid

(b) (OH) $\xrightarrow{CrO_3\ H_2SO_4}$ (=O) $\xrightarrow{CH_3CH_2MgBr}$ $\xrightarrow{H_3O^+}$ (OH, ethyl) $\xrightarrow{HCl}$ (Cl, ethyl)

CH_3CH_2OH $\xrightarrow{PBr_3}$ CH_3CH_2Br $\xrightarrow{Mg,\ ether}$

(c) (OH) $\xrightarrow{PBr_3}$ (Br) $\xrightarrow[ether]{Mg}$ (MgBr) $\xrightarrow[from\ part\ (b)]{}$ $\xrightarrow{H_3O^+}$ (OH) $\xrightarrow[\Delta]{H^+}$ ( )

OR: (OH) $\xrightarrow{PBr_3}$ (Br) $\xrightarrow[ether]{Mg}$ ( ) $\xrightarrow{H_3O^+}$ (OH) $\xrightarrow[\Delta]{H^+}$ $\xrightarrow{MCPBA}$ (epoxide)

$\xrightarrow{CrO_3\ H_2SO_4}$ (=O)

(d) (OH) $\xrightarrow{PBr_3}$ (Br) $\xrightarrow[from\ (c)]{Mg\ ether}$ ( ) (O$^-$ $\overset{+}{MgBr}$) $\xrightarrow[CH_3OH\ \ PBr_3]{CH_3Br}$ (OCH$_3$)

see the next page for an alternative ending

11-38 continued

(d) continued from the previous page
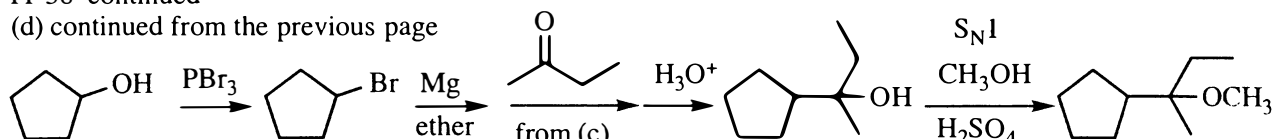
(e) There are several possible combinations of Grignard reactions on aldehydes or ketones. This is one example. Your example may be different and still be correct.

11-39 Please refer to solution 1-20, page 12 of this Solutions Manual.

11-40

(a)

(b)

(c)

(d)

11-41

(a) [structure: H, OTs stereocenter with ethyl] R

(b) [structure: H, Br stereocenter] R (from inversion)

(c) [cyclooctanone structure]

(d) [cyclopentanecarbaldehyde structure]

(e) [cyclopentane-COOH structure]

(f) [cyclopentyl-Cl structure]

(g) [butyl-Br structure]

(h) [cyclooctane-CH₂OMgBr structure] + CH₃CH₃

(i) [structure with OCH₃]

(j) [isobutylene structure] + CH₃OH

(k) [cyclopentene structure]

(l) [dialdehyde structure: H–C(=O)...C(=O)–H]

(m) [structure: CH₃CH₂CH₂–O–CH₂CH₃]

(n) [alkene structure] major + [alkene structure] minor + EtOH

11-42

(a) [cyclohexanol] →Na→ [cyclohexanolate O⁻Na⁺] →CH₃CH₂Br→ [cyclohexyl OCH₂CH₃] Williamson ether synthesis

(b) [benzyl bromide] →NaOH→ [benzyl alcohol OH] →PCC→ [benzaldehyde, O, H] + [benzyl MgBr] ←Mg/ether← [benzyl bromide Br]

↓ H₃O⁺

[1,2-diphenylethanol, OH] →H₂SO₄, Δ→ [stilbene / diphenylethene]

(c) [cyclohexyl Br] →Mg/ether→ [cyclohexyl MgBr] →1) H–C(=O)–propyl 2) H₃O⁺→ [cyclohexyl-CH(OH)-propyl] →CrO₃, H₂SO₄, acetone→ [cyclohexyl-C(=O)-propyl]

(d) [cyclohexyl-CH₂OH] →PCC→ [cyclohexanecarbaldehyde, H, O] →1) CH₃CH₂MgBr 2) H₃O⁺→ [cyclohexyl-CH(OH)-ethyl]

11-43 Major product for each reaction is shown.

(a)
cis + trans—rearranged

(b)
cis + trans

(c)
cis + trans

(d)

(e)
rearranged

(f)
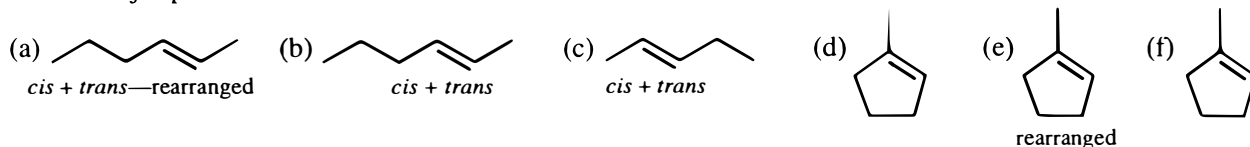
Note that (d), (e), and (f), produce the same alkene.

11-44

(a) $CH_3CH_2CH_2COOCH_3$

(b)

(c)

(d)

(e) CH_3ONO_2

11-45

methanesulfonyl
chloride

11-46

(a)

(b)
Alternatively, PBr₃ could be used.

(c)
could use NaOH if kept cold to avoid elimination

11-47

(a)
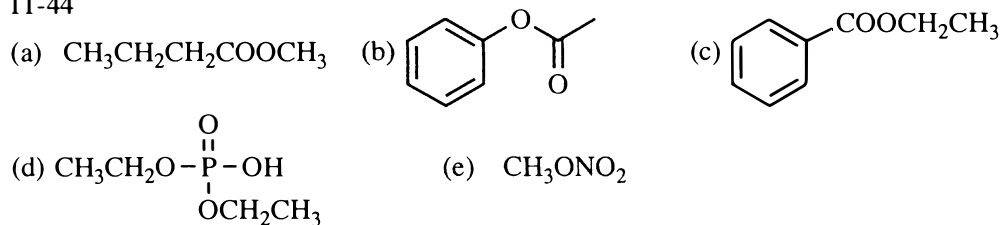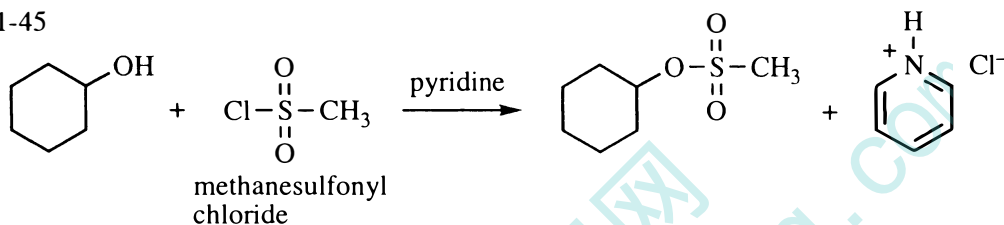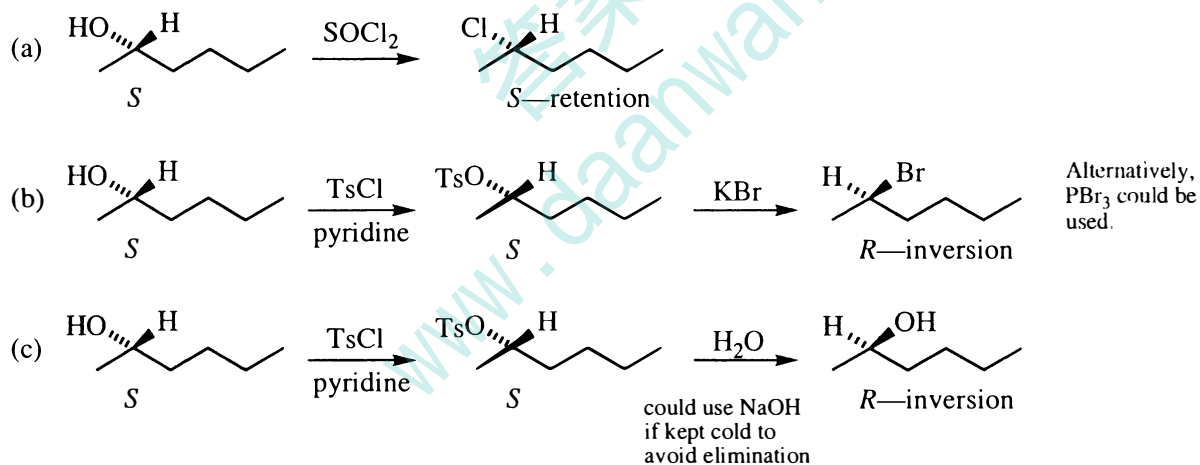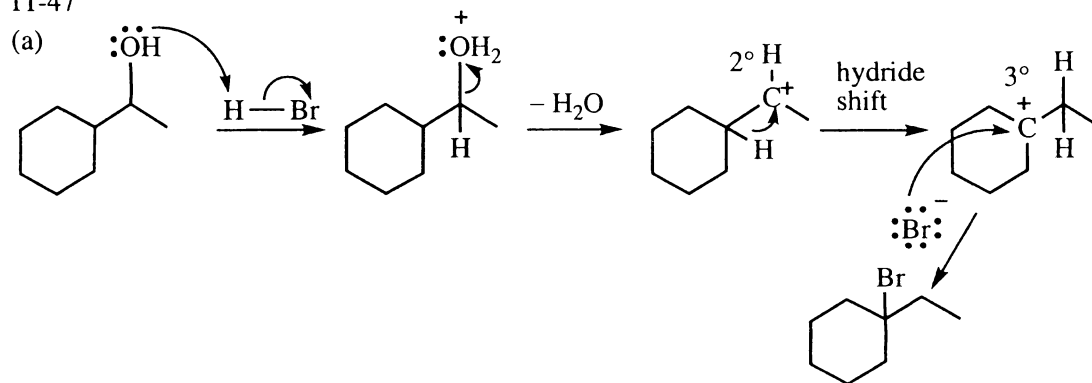
11-47 continued

(b) PBr$_3$ converts alcohols to bromides without rearrangement because no carbocation intermediate is produced.

11-48

(a) PCC →

(b) PBr$_3$ →

(c) Na → O$^-$ Na$^+$ CH$_3$I → OCH$_3$

(d) SOCl$_2$ → *retention*   OR   TsCl pyridine → Cl$^-$ S$_N$2 → *inversion*

(e) H$_2$SO$_4$ Δ → 1) O$_3$ 2) Me$_2$S → HIO$_4$ ← OH OH

(f) CH$_2$OH H$_2$CrO$_4$ → COOH

(g) OH CrO$_3$ H$_2$SO$_4$ acetone → =O

(h) OH H$_2$SO$_4$ Δ →

(i) TsCl pyridine → *cis*

(j) OH P, I$_2$ → I

248

11-49

(a)

$$\text{OH} \xrightarrow{\text{PBr}_3} \text{Br} \quad \textit{inversion}$$

(b)

$$\text{OH} \xrightarrow{\text{SOCl}_2} \text{Cl} \quad \textit{retention}$$

(c)

$$\text{OH} \xrightarrow[\text{ZnCl}_2]{\text{HCl}} \text{Cl} \quad S_N1$$

cis and trans

(d)

$$\text{OH} \xrightarrow{\text{HBr}} \text{Br} \quad S_N1$$

cis and trans

(e)

$$\text{OH} \xrightarrow[\text{2) NaBr}]{\text{1) TsCl, pyridine}} \text{Br} \quad \textit{inversion, } S_N2$$

11-50

(a)

Lucas:	no reaction	cloudy in 1-5 min.

(b)

Lucas:	cloudy in 1-5 min.	cloudy in < 1 min.
H_2CrO_4:	immediate blue-green	no reaction—stays orange

(c)

Lucas:	cloudy in 1-5 min.	no reaction
H_2CrO_4:	immediate blue green	no reaction—stays orange

(d)

Lucas:	cloudy in 1-5 min.	no reaction
H_2CrO_4:	immediate blue green	no reaction—stays orange

(e)

Lucas:	no reaction	cloudy in < 1 min.

249

11-51

(a)

(b)

The last three resonance forms are similar to the first three; the change is that the electrons are shown in alternate positions in the benzene ring. To be rigorously correct, these three resonance forms should be included, but most chemists would not write them since they do not reveal extra charge delocalization; understand that they would still be significant, even if not written with the others.

(c)

11-52

11-53

11-54

alkyl shift—
ring expansion

recall that 1° carbocations
probably do not exist; this could
be considered a transition state

ring expansion from 1°
carbocation to 2°, *resonance-
stabilized* carbocation

NOTE:

The migration directly above does NOT occur
as the cation produced is not resonance-stabilized.
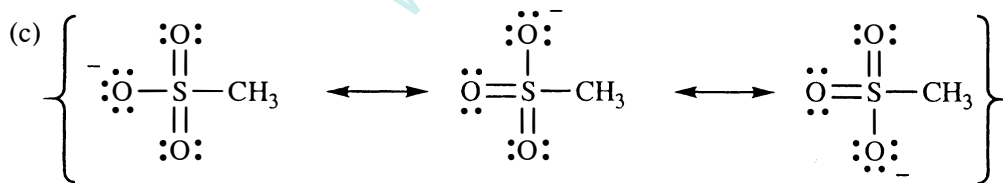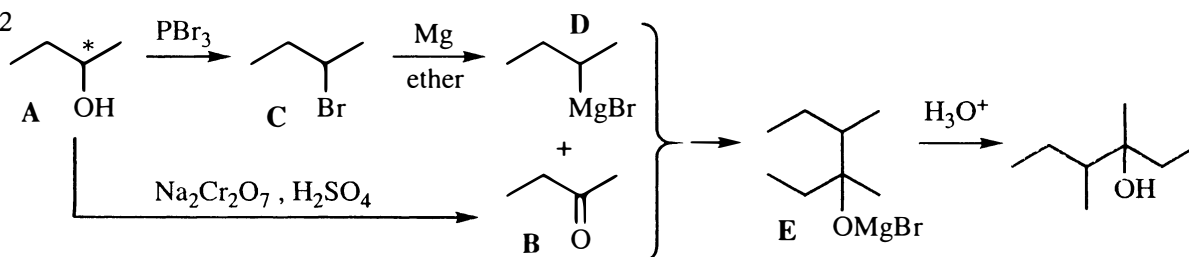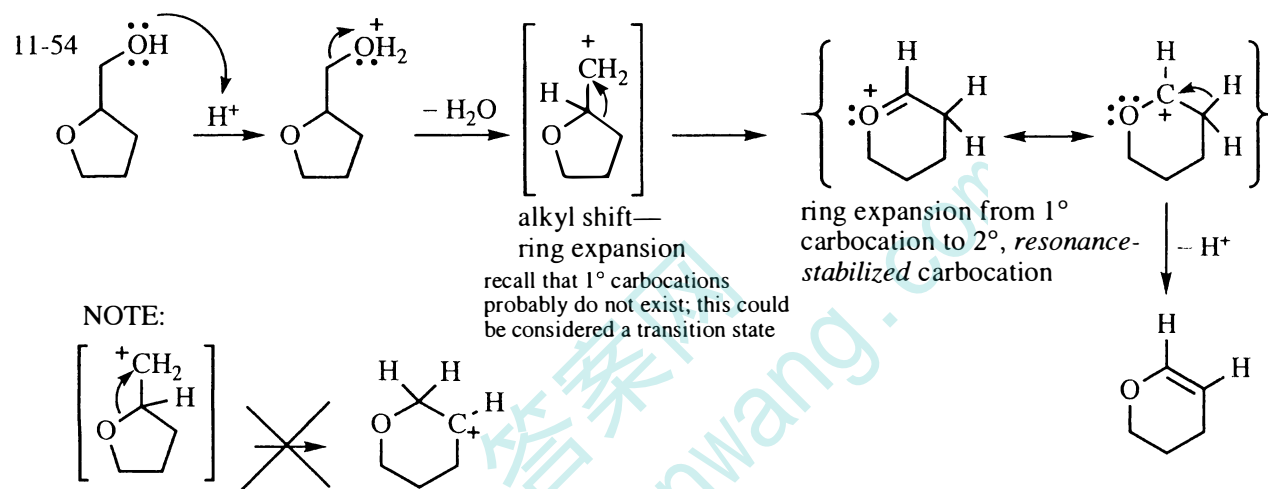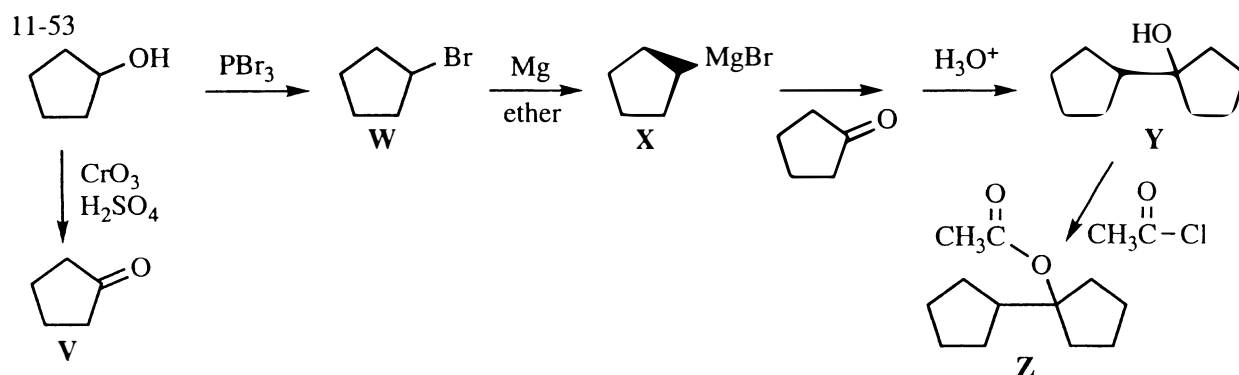
*An alternative mechanism could be proposed: protonate the ring oxygen, open the ring to a 2°
carbocation followed by a hydride shift to a resonance-stabilized cation, ring closure, and dehydration.*

hydride shift to resonance
stabilized cation

2° carbocation

H⁺ off one O, H⁺
on the other O

11-55

(a)

In this presentation of the mechanism, the rearrangement is shown concurrently with cleavage of the C-O bond with no 1° carbocation intermediate.

$+ HO - \bar{Z}nCl_2$

$H - Cl$

$Cl^- + H_2O + ZnCl_2$

(b)

$+ H_2O$

Once this carbocation is formed, removal of adjacent protons produces the compounds shown.
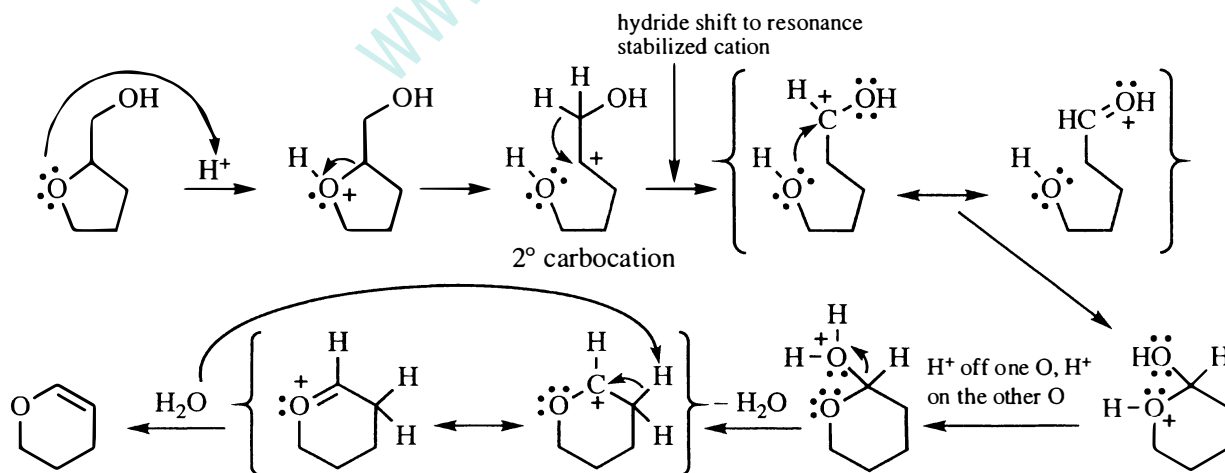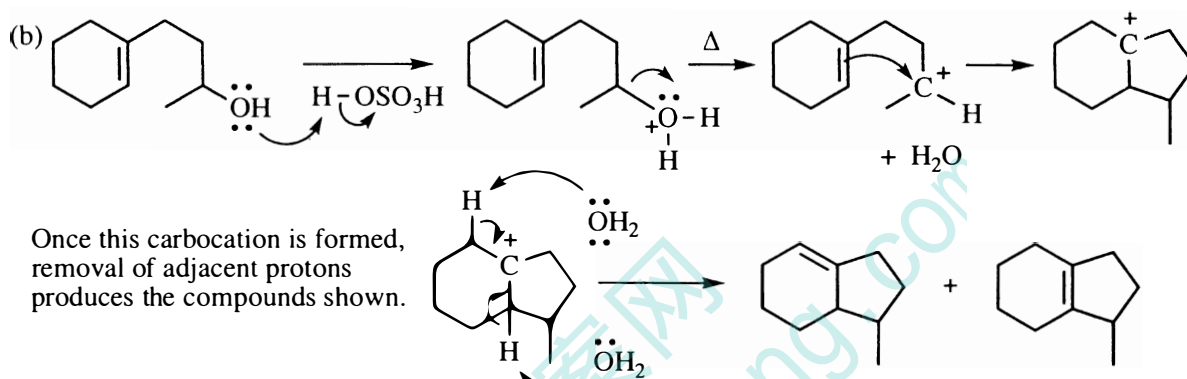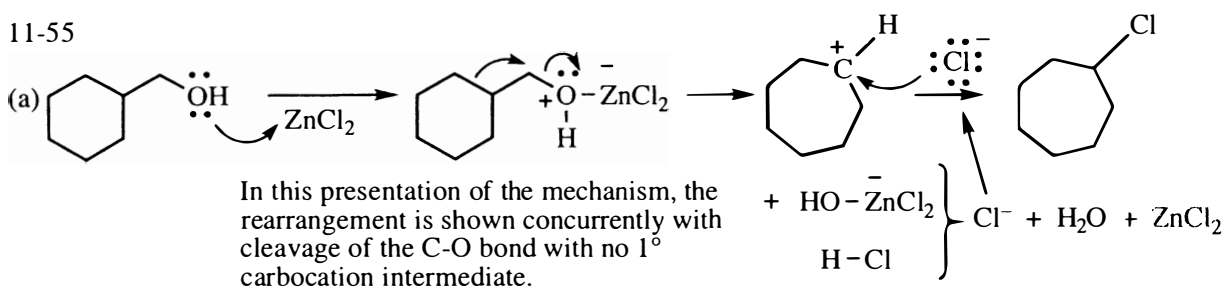
(c) All three of the products go through a common carbocation intermediate.

rearrangement

$- H_2O$

$+ H_2O$:

This is the product from a pinacol rearrangement.

11-56

(a)

OR: alternative ending

after hydrolysis of
Grignard product

(b)

(c)

or use the S_N1 method
shown in part (a)

(d) **2**

two RMgX can add to an
ester, making a 3° alcohol
with two equivalent R
groups; see solution to
problem 10-18

(e)

from (b)

11-56 continued

(f)

(g)

(h)

11-57 For a complicated synthesis like this, begin by working backwards. Try to figure out where the carbon framework came from; in this problem we are restricted to alcohols containing five or fewer carbons. The dashed boxes show the fragments that must be assembled. The most practical way of forming carbon-carbon bonds is by Grignard reactions. The epoxide must be formed from an alkene, and the alkene must have come from dehydration of an alcohol produced in a Grignard reaction.

major
isomer

avoid carbocation conditions
to *prevent rearrangement*

11-58

(a) Both of these pseudo-syntheses suffer from the misconception that incompatible reagents or conditions can co-exist. In the first example, the S_N1 conditions of ionization cannot exist with the S_N2 conditions of sodium methoxide. The tertiary carbocation in the first step would not wait around long enough for the sodium methoxide to be added in the second step. (The irony is that the first step by itself, the solvolysis of *t*-butyl bromide in methanol, would give the desired product without the sodium methoxide.)

In the second reaction, the acidic conditions of the first step in which the alcohol is protonated are incompatible with the basic conditions of the second step. If basic sodium methoxide were added to the sulfuric acid solution, the instantaneous acid-base neutralization would give methanol, sodium sulfate, and the starting alcohol. No reaction on the alcohol would occur.

(b)

S_N1 solvolysis conditions
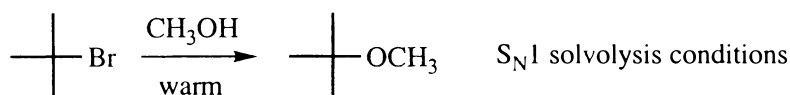
Several synthetic sequences are possible for the second synthesis.
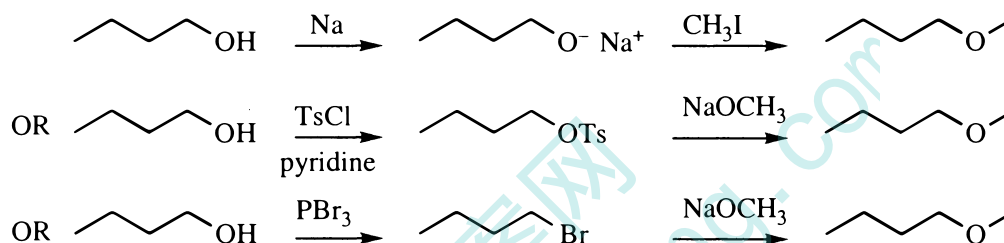
11-59

Compound X : —must be a 1° or 2° alcohol with an alkene; no reaction with Lucas leads to a 1° alcohol; can't be allylic as this would give a positive Lucas test

Compound Y : —must be a cyclic ether, not an alcohol and not an alkene; other isomers of cyclic ethers possible

11-60

this reaction works fine, but wait.......
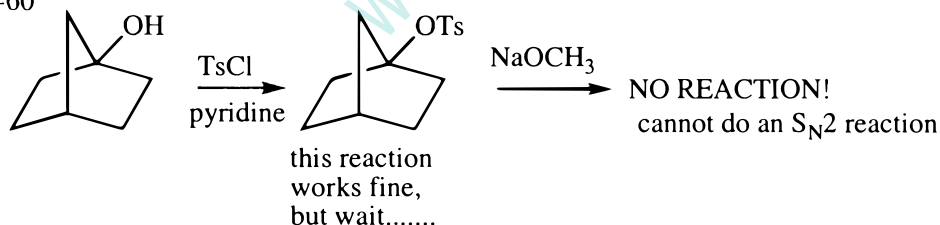
The Williamson ether synthesis is an S_N2 displacement of a leaving group by an alkoxide ion. There are two reasons why this tosylate cannot unergo an S_N2 reaction. First, backside attack cannot occur because the back side of the bridgehead carbon is blocked by the other bridgehead. Second, the bridgehead carbon cannot undergo inversion because of the constraints of the bridged ring system.

backside attack is blocked

side view

this carbon cannot invert which is required in the S_N2 mechanism

side view
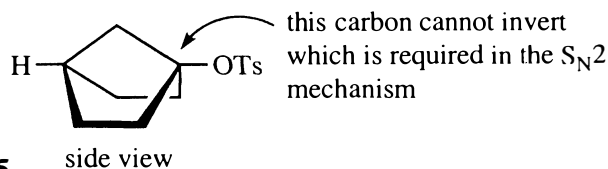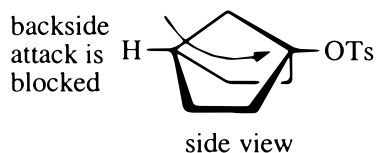
11-61 Let's begin by considering the facts.

The axial alcohol is oxidized ten times as fast as the equatorial alcohol. (In the olden days, this observation was used as evidence suggesting the stereochemistry of a ring alcohol.)
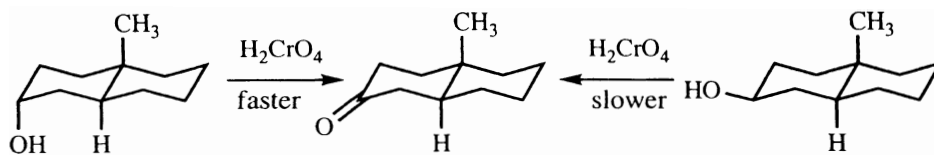
Second, it is known that the oxidation occurs in two steps: 1) formation of the chromate ester; and 2) loss of H and chromate to form the C=O. Let's look at each mechanism.
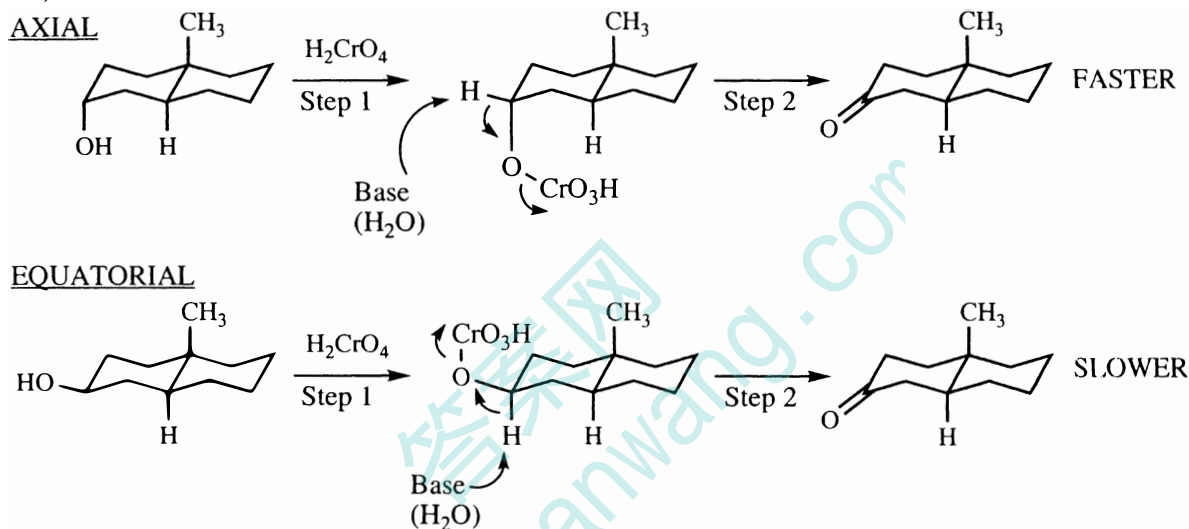
AXIAL

EQUATORIAL

So what do we know about these systems? We know that substituents are more stable in the equatorial position than in the axial position because any group at the axial position has 1,3-diaxial interactions. So what if Step 1 were the rate-limiting step? We would expect that the equatorial chromate ester would form faster than the axial chromate ester; since this is contrary to what the data show, Step 1 is not likely to be rate-limiting. How about Step 2? If the elimination is rate limiting, we would expect the approach of the base (probably water) to the equatorial hydrogen (axial chromate ester) would be faster than the approach of the base to the axial hydrogen (equatorial chromate ester). Moreover, the axial ester is more motivated to leave due to steric congestion associated with such a large group. This is consistent with the relative rates of reaction from experiment. Thus, it is reasonable to conclude that the second step of the mechanism is rate-limiting.

11-62
(a)

256

11-62 (a) continued

(b)
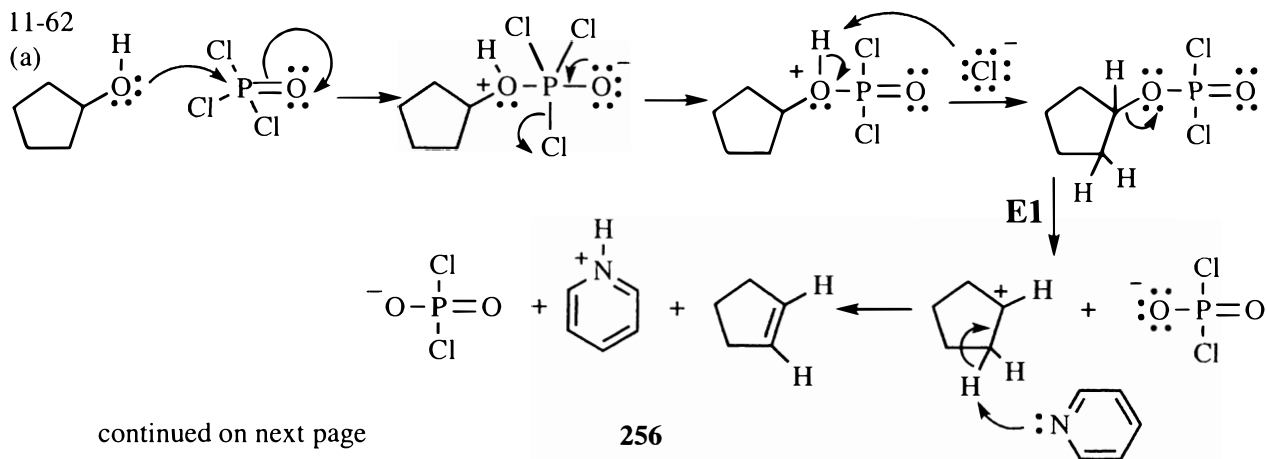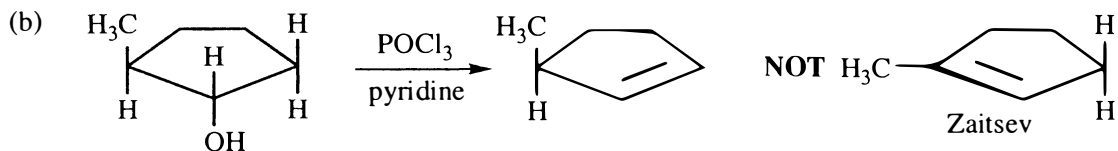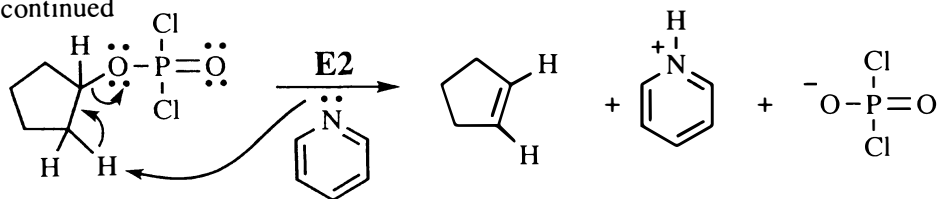
There must be a stereochemical requirement in this elimination. If the Saytzeff alkene is not produced because the methyl group is *trans* to the leaving group, then the H and the leaving group must be *trans* and the elimination must be anti—the characteristic stereochemistry of E2 elimination. This evidence differentiates between the two possibilities in part (a).

11-63

(a)
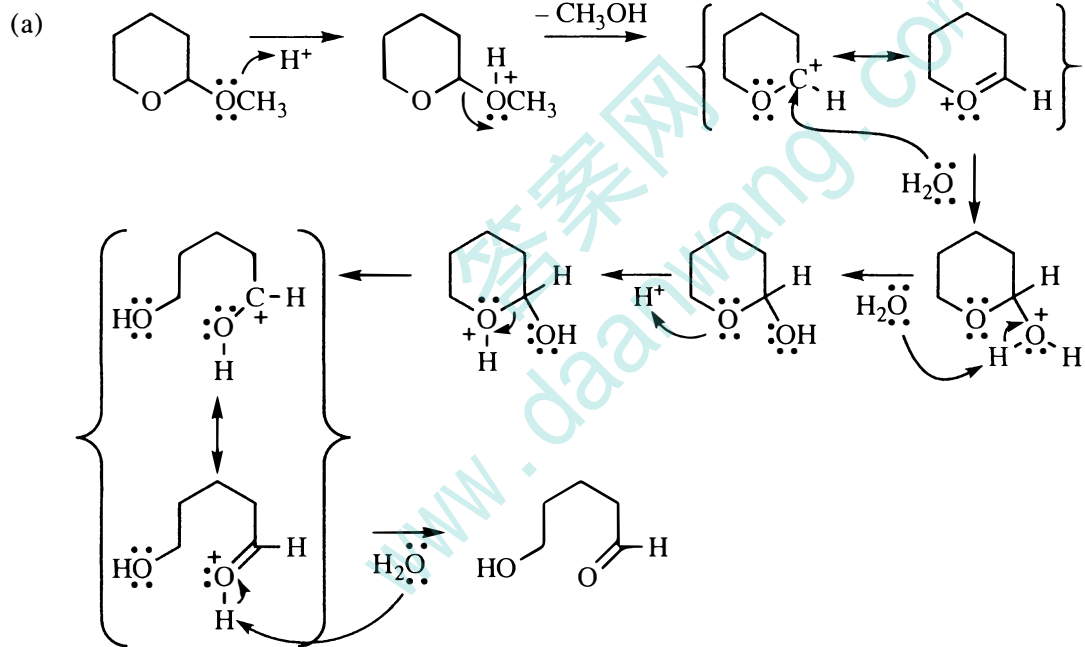
It is equally likely for protonation to occur first on the ring oxygen, followed by ring opening, then replacement of OCH₃ by water.

Dr. Kantorowski suggests this alternative. He and I will arm wrestle to determine which mechanism is correct.
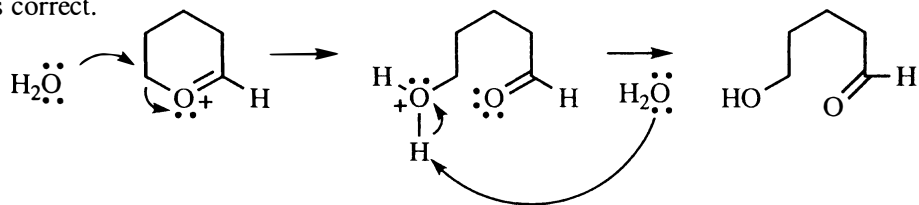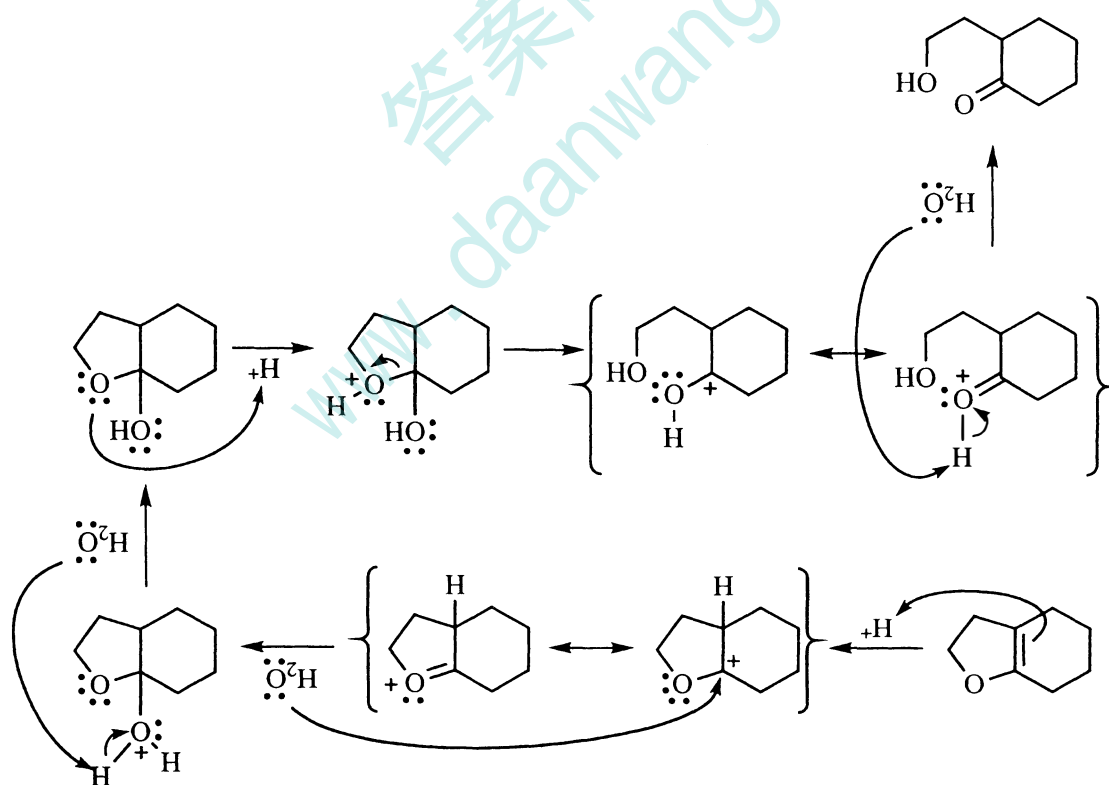
CHAPTER 12—INFRARED SPECTROSCOPY AND MASS SPECTROMETRY

See p. 270 for some useful web sites with infrared and mass spectra.

12-1   The table is completed by recognizing that: $(\overline{v})(\lambda) = 10{,}000$

$\overline{v}$ (cm^{-1})	4000	**3300**	**3003**	**2198**	1700	1640	1600	400
λ (μm)	2.50	3.03	3.33	4.55	**5.88**	**6.10**	**6.25**	25.0

12-2 In general, only bonds with dipole moments will have an IR absorption.
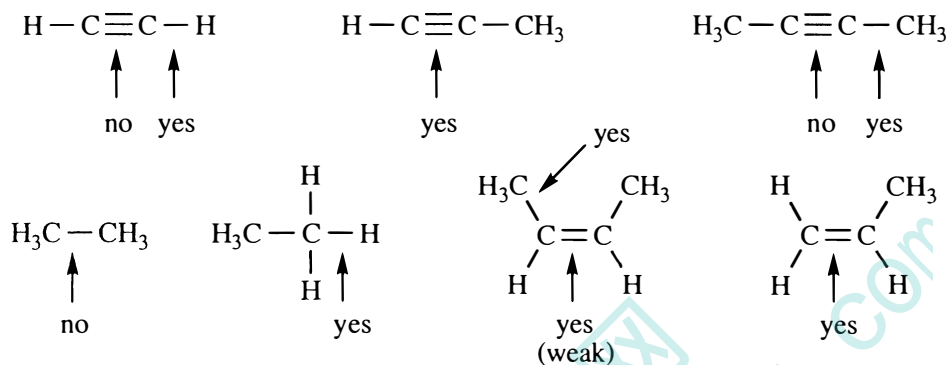
12-3

(a) alkene: C=C at 1640 cm^{-1} , =C—H at 3080 cm^{-1}

(b) alkane: no peaks indicating sp or sp^2 carbons present

(c) This IR shows more than one group. There is a terminal alkyne shown by: C≡C at 2100 cm^{-1} , ≡C—H at 3300 cm^{-1} . These signals indicate an aromatic hydrocarbon as well: =C—H at 3050 cm^{-1}, C=C at 1600 cm^{-1} .

12-4

(a) 2° amine, R—NH—R: one peak at 3300 cm^{-1} indicates an N—H bond; this spectrum also shows a C=C at 1640 cm^{-1}

(b) carboxylic acid: the extremely broad absorption in the 2500-3500 cm^{-1} range, with a "shoulder" around 2500-2700 cm^{-1} , and a C=O at 1710 cm^{-1} , are compelling evidence for a carboxylic acid

(c) alcohol: strong, broad O—H at 3330 cm^{-1}

12-5

(a) conjugated ketone: the small peak at 3030 cm^{-1} suggests =C—H, and the strong peak at 1685 cm^{-1} is consistent with a ketone conjugated with the alkene. The C=C is indicated by a very small peak around 1600 cm^{-1} .

(b) ester: the C=O absorption at 1738 cm^{-1} (higher than the ketone's 1710 cm^{-1}), in conjunction with the strong C—O at 1200 cm^{-1}, points to an ester

(c) amide: the two peaks at 3160-3360 cm^{-1} are likely to be an NH$_2$ group; the strong peak at 1640 cm^{-1} is too strong for an alkene, so it must be a different type of C=X, in this case a C=O, so low because it is part of an amide

12-6

(a) The small peak at 1642 cm^{-1} indicates a C=C, consistent with the =C—H at 3080 cm^{-1} . This appears to be a simple alkene.

(b) The strong absorption at 1691 cm^{-1} is unmistakably a C=O. The smaller peak at 1626 cm^{-1} indicates a C=C, probably conjugated with the C=O. The two peaks at 2712 cm^{-1} and at 2814 cm^{-1} represent H—C=O confirming that this is an aldehyde.

259

12-6 continued

(c) The strong peak at 1650 cm^{-1} is C=C, probably conjugated as it is unusually strong. The 1703 cm^{-1} peak appears to be a conjugated C=O, undeniably a carboxylic acid because of the strong, broad O—H absorption from 2400-3400 cm^{-1}.

(d) The C=O absorption at 1742 cm^{-1} coupled with C—O at 1220 cm^{-1} suggest an ester. The small peak at 1604 cm^{-1}, peaks above 3000 cm^{-1}, and peaks in the 600-800 cm^{-1} region indicate a benzene ring.

12-7

(a) The M and M+2 peaks of equal intensity identify the presence of bromine. The mass of M (156) minus the weight of the lighter isotope of bromine (79) gives the mass of the rest of the molecule: $156 - 79 = 77$. The C_6H_5 (phenyl) group weighs 77; this compound is bromobenzene, C_6H_5Br.

(b) The m/z 127 peak shows that iodine is present. The molecular ion minus iodine gives the remainder of the molecule: $156 - 127 = 29$. The C_2H_5 (ethyl) group weighs 29; this compound is iodoethane, C_2H_5I.

(c) The M and M+2 peaks have relative intensities of about 3:1, a sure sign of chlorine. The mass of M minus the mass of the lighter isotope of chlorine gives the mass of the remainder of the molecule: $90 - 35 = 55$. A fragment of mass 55 is not one of the common alkyl groups (15, 29, 43, 57, etc., increasing in increments of 14 mass units (CH_2)), so the presence of an atom like oxygen must be considered. In addition to the chlorine atom, mass 55 could be C_4H_7 or C_3H_3O. Possible molecular formulas are C_4H_7Cl or C_3H_3ClO.

(d) The odd-mass molecular ion indicates the presence of an odd number of nitrogen atoms (always begin by assuming *one* nitrogen). The rest of the molecule must be: $115 - 14 = 101$; this is most likely C_7H_{17}. The formula $C_7H_{17}N$ is the correct formula of a molecule with no elements of unsaturation. The seven carbons probably include alkyl groups like ethyl or propyl or isopropyl.

12-8 Recall that radicals are not detected in mass spectrometry; only positively-charged ions are detected.

12-9

260
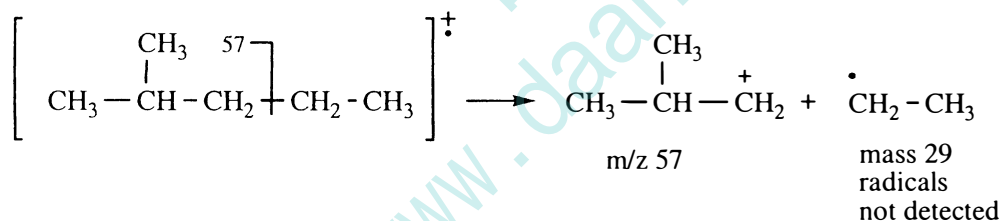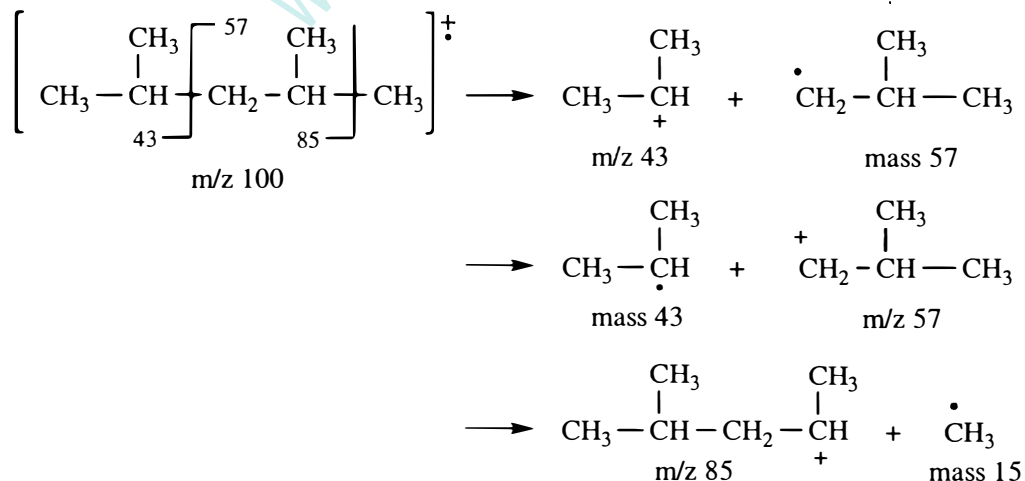
12-10 The molecular weight of each isomer is 116 g/mole, so the molecular ion appears at m/z 116. The left half of each structure is the same; loss of a three carbon radical gives a stabilized cation, each with m/z 73:

m/z 73   m/z 73
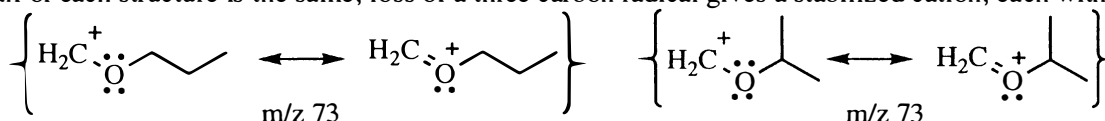
Where the two structures differ is in the alpha-cleavage on the right side of the oxygen. Alpha-cleavage on the left structure loses two carbons, whereas alpha-cleavage on the right structure loses only one carbon.

alpha-cleavage   loss of $\dot{C}H_2CH_3$ alpha-cleavage   loss of $\dot{C}H_3$

m/z 87   m/z 101
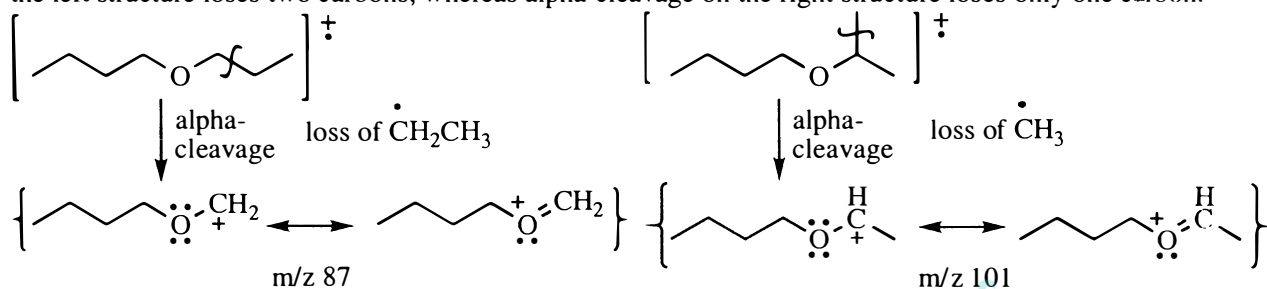
12-11 2,6-Dimethylheptan-4-ol, $C_9H_{20}O$, has molecular weight 144. The highest mass peak at 126 is *not* the molecular ion, but rather is the loss of water (18) from the molecular ion.

m/z 144   m/z 126
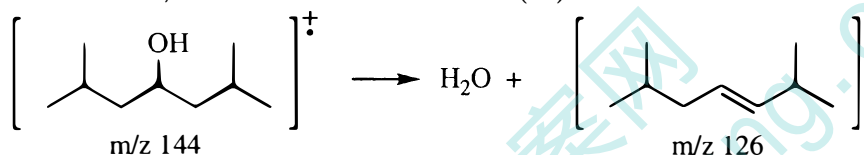
The peak at m/z 111 is loss of another 15 (CH_3) from the fragment of m/z 126. This is called allylic cleavage; it generates a 2°, allylic, resonance-stabilized carbocation.

m/z 126   m/z 111 $\dot{C}H_3$
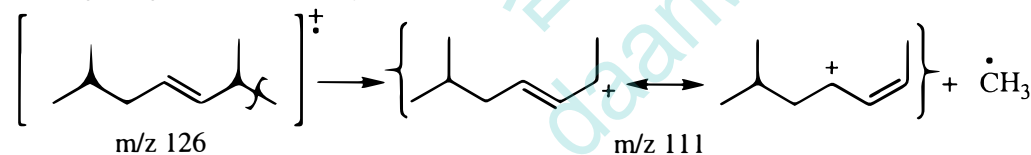
The peak at m/z 87 results from fragmentation on one side of the alcohol:

m/z 144   alpha-cleavage   m/z 87   mass 57
                                          resonance-stabilized

12-12 Please refer to solution 1-20, page 12 of this Solutions Manual.

12-13 Divide the numbers into 10,000 to arrive at the answer.

(a) 1603 cm^{-1} (b) 2959 cm^{-1} (c) 1709 cm^{-1} (d) 1739 cm^{-1} (e) 2212 cm^{-1} (f) 3300 cm^{-1}

12-14

(a)

or

1660 cm^{-1} 1710 cm^{-1}
                          stronger absorption—larger dipole

261

12-14 continued

(b)

1660 cm⁻¹

or

1640 cm⁻¹
stronger absorption—larger dipole

(c)

1660 cm⁻¹
stronger absorption—
larger dipole

or

1660 cm⁻¹

(d)

1660 cm⁻¹
(no dipole moment)

or

1660 cm⁻¹
stronger absorption—larger dipole

12-15

(a)

1660 cm⁻¹
weak or non-existent

and

3000-
3100 cm⁻¹

1660 cm⁻¹
moderate intensity

(b)

 1620 cm⁻¹

conjugated

and

1645 cm⁻¹

not conjugated

(c) both carbonyls show strong absorptions around 1710 cm⁻¹

$CH_3(CH_2)_3 - \overset{\overset{O}{\|}}{C} - H$

2700-2800 cm⁻¹
two small peaks

and

$CH_3(CH_2)_2 - \overset{\overset{O}{\|}}{C} - CH_3$

(d)

3300 cm⁻¹
broad, strong

1200 cm⁻¹

and

1710 cm⁻¹
strong

262

12-15 continued

(e) $CH_3(CH_2)_5 - C \equiv C - H$ 3300 cm^{-1} and $CH_3(CH_2)_6 - C \equiv N$

2100-2200 cm^{-1}
weak to moderate intensity

2200-2300 cm^{-1}
moderate to strong intensity

(f) both carbonyls show strong absorptions around 1710 cm^{-1}

3300 cm^{-1}
broad, strong

$CH_3CH_2CH_2 - \overset{O}{\underset{}{C}} - OH$ and $CH_3 - \overset{O-H}{\underset{}{CH}} - CH_2 - \overset{O}{\underset{}{C}} - H$

2500-3500 cm^{-1}
very broad

2700-2800 cm^{-1}
two small peaks

(g) $CH_3CH_2CH_2 - \overset{O}{\underset{}{C}} - \overset{}{\underset{H}{N}} - H$ 1650 cm^{-1} and $CH_3CH_2 - \overset{O}{\underset{}{C}} - CH_2CH_3$ 1710 cm^{-1}

3300 cm^{-1}
two peaks

12-16

(a)
$\overset{H}{\underset{H}{>}}C = C\overset{\overset{O}{\underset{}{C}} - OH}{\underset{CH_3}{<}}$

1700 cm^{-1}
2400-3400 cm^{-1}
1640 cm^{-1}

(b) $CH_3 - \underset{CH_3}{\overset{}{CH}} \cdot \overset{O}{\underset{}{C}} - CH_3$ 1715 cm^{-1}

(c)
$CH_2 \cdot C \equiv N$

3000-3100 cm^{-1}
2250 cm^{-1}
1600 cm^{-1}

(d)
$N \overset{H}{\underset{CH_2CH_3}{<}}$

3000-3100 cm^{-1}
3400 cm^{-1}
2900-3000 cm^{-1}
1600 cm^{-1}

12-17

(a) $\left[CH_3 \overset{\overset{71}{\overset{CH_3}{\underset{}{|}}}}{\underset{\underset{43}{}}{C}H} \right. \left. CH_2CH_2CH_3 \right]^{\ddagger}$

m/z 86

$\longrightarrow$ $^+CH \overset{CH_3}{\underset{}{|}} - CH_2CH_2CH_3$

m/z 71

$\longrightarrow$ $CH_3 - \overset{CH_3}{\underset{+}{CH}}$ m/z 43

263

12-17 continued

(b) $\left[CH_3 \cdot CH = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 \!+\! CH_2CH_3 \right]^{+\cdot} \longrightarrow \left\{ CH_3 \cdot CH = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{+}{C}H_2 \longleftrightarrow CH_3 - \overset{+}{C}H - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 \right\}$

m/z 98—allylic cleavage   m/z 69

(c) $\left[CH_3 \!+\! \overset{\overset{\displaystyle \overset{87}{OH}}{|}}{CH} \!+\! CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} \cdot CH_3 \right]^{+\cdot}$ m/z 102

$\xrightarrow[\text{cleavage}]{\text{alpha-}}$ $\left\{ \overset{\overset{\displaystyle \overset{\cdot\cdot}{OH}}{|}}{+CH} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} \cdot CH_3 \longleftrightarrow \overset{\overset{\displaystyle \overset{+}{OH}}{||}}{CH} - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} \cdot CH_3 \right\}$

m/z 87

$\xrightarrow[]{\text{alpha-cleavage}}$ $\left\{ CH_3 - \overset{\overset{\displaystyle \overset{\cdot\cdot}{OH}}{|}}{\underset{+}{CH}} \longleftrightarrow CH_3 - \overset{\overset{\displaystyle \overset{+}{OH}}{||}}{CH} \right\}$

m/z 45

$\xrightarrow{- H_2O}$ $\left[CH_3 \cdot CH = CH - \overset{\overset{\displaystyle CH_3}{|}}{CH} \cdot CH_3 \right]^{+\cdot}$ m/z 84

(d) m/z 134 $\longrightarrow$ benzyl cation $\xrightarrow{\text{rearrange}}$ m/z 91

The *tropylium ion* is a characteristic fragment from phenylalkanes.

m/z 77

$\overset{\overset{\displaystyle CH_3}{|}}{HC+}$ m/z 43 $H_2\overset{+}{C}$ $\xrightarrow{\text{rearrange}}$ $H_3C - \overset{\overset{\displaystyle +}{C}}{\underset{\underset{\displaystyle CH_3}{|}}{}} - CH_3$ m/z 57

$\overset{\overset{\displaystyle CH_3}{|}}{CH_3}$

(e) $\left[\text{(cyclohexyl)} - O - \text{(isopropyl)} \right]^{+\cdot}$ m/z 144   85   43   129

$\longrightarrow$ $+CH$ m/z 85 $\overset{\overset{\displaystyle CH_3}{/}}{HC+}\underset{\underset{\displaystyle CH_3}{}}{}$ m/z 43

$\xrightarrow{\text{alpha-cleavage}}$ $\left\{ \text{(cyclohexyl)} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - \overset{+}{C}H \overset{CH_3}{} \longleftrightarrow \text{(cyclohexyl)} - \overset{+}{\underset{\cdot\cdot}{O}} = CH \overset{CH_3}{} \right\}$

m/z 129

12-18

(a)

$$\left[\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \overset{57}{|} \text{CH}_2 \overset{71}{|} \text{CH}_2 \overset{85}{|} \text{CH}_2\text{CH}_3 \right]^{+\cdot}$$

m/z 114

$\longrightarrow$

CH$_2$ m/z 85 + H$_2$Ċ–CH$_3$ mass 29

CH$_2$ m/z 71 + H$_2$Ċ mass 43

CH$_2$ m/z 57 + H$_2$Ċ mass 57

(b)

$$\left[\begin{array}{c} \text{CH}_3 \\ \text{cyclohexane} \end{array} \right]^{+\cdot}$$

m/z 98

$\longrightarrow$

$\overset{H}{\underset{+}{C}}$ (ring) m/z 83 + •CH$_3$ mass 15

(c)

$$\left[\begin{array}{c} \text{CH}_3 \quad 69 \\ \text{CH}_3-\text{C}=\text{CH}-\text{CH}_2 | \text{CH}_3 \end{array} \right]^{+\cdot}$$

m/z 84

$\longrightarrow$

$$\left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3-\text{C}=\text{CH}-\overset{+}{\text{CH}_2} \end{array} \longleftrightarrow \begin{array}{c} \text{CH}_3 \\ \text{CH}_3-\overset{+}{\text{C}}-\text{CH}=\text{CH}_2 \end{array} \right\}$$

m/z 69

+ •CH$_3$ mass 15

(d)

$$\left[\begin{array}{c} \text{OH} \\ \text{CH}_2 | \text{CH}_2-\text{CH}_2\text{CH}_2\text{CH}_3 \\ 31 \end{array} \right]^{+\cdot}$$

m/z 88

$\longrightarrow$

$$\left\{ \begin{array}{c} :\ddot{\text{O}}\text{H} \\ \text{CH}_2 \\ + \end{array} \longleftrightarrow \begin{array}{c} +\ddot{\text{O}}\text{H} \\ \parallel \\ \text{CH}_2 \end{array} \right\}$$

m/z 31

+ •CH$_2$CH$_2$CH$_2$CH$_3$ mass 57

$\downarrow$ – H$_2$O

$$\left[\text{CH}_2=\text{CH}-\text{CH}_2 \overset{41}{|} \text{CH}_2 \overset{55}{|} \text{CH}_3 \right]^{+\cdot}$$

m/z 70

$\longrightarrow$

CH$_2$=CH–CH$_2$–$\overset{+}{\text{CH}_2}$ m/z 55 + •CH$_3$ mass 15

$\downarrow$

$$\left\{ \text{CH}_2=\text{CH}-\overset{+}{\text{CH}_2} \longleftrightarrow \overset{+}{\text{CH}_2}-\text{CH}=\text{CH}_2 \right\}$$

m/z 41

+ •CH$_2$CH$_3$ mass 29

(e)

$$\left[\begin{array}{c} 77 \quad \overset{H}{N} \\ \text{C}_6\text{H}_5-\text{NH}-\text{CH}_2\text{CH}_3 \\ 106 \end{array} \right]^{+\cdot}$$

m/z 121

$\longrightarrow$

$\text{C}_6\text{H}_5\overset{+}{\text{C}}$ m/z 77 + •NHCH$_2$CH$_3$ mass 44

265

12-18 (e) continued

m/z 121 → alpha-cleavage → m/z 106 + •CH₃ (mass 15)

12-19

(a) The characteristic frequencies of the OH absorption and the C=C absorption will indicate the presence or absence of the groups. A spectrum with an absorption around 3300 cm^{-1} will have some cyclohexanol in it; if that same spectrum also has a peak at 1645 cm^{-1}, then the sample will also contain some cyclohexene. Pure samples will have peaks representative of only one of the compounds and not the other. Note that *quantitation* of the two compounds would be very difficult by IR because the strength of absorptions are very different. Usually, other methods are used in preference to IR for quantitative measurements.

3300 cm^{-1} broad, strong

1200 cm^{-1}

1645 cm^{-1} moderate
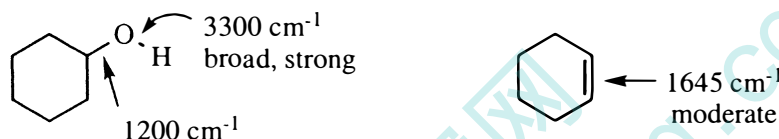
(b) Mass spectrometry can be misleading with alcohols. Usually, alcohols dehydrate in the inlet system of a mass spectrometer, and the characteristic peaks observed in the mass spectrum are those of the alkene, not of the parent alcohol. For this particular analysis, mass spectrometry would be unreliable and perhaps misleading.

12-20

(a) The "student prep" compound must be 1-bromobutane. The most obvious feature of the mass spectrum is the pair of peaks at M and M+2 of approximately equal heights, characteristic of a bromine atom. Loss of bromine (79) from the molecular ion at 136 gives a mass of 57, C_4H_9, a butyl group. Which of the four possible butyl groups? The peaks at 107 (loss of 29, C_2H_5) and 93 (loss of 43, C_3H_7) are consistent with a linear chain, not a branched chain.

(b) The base peak at 57 is so strong because the carbon-halogen bond is the weakest in the molecule. Typically, loss of halogen is the dominant fragmentation in alkyl halides.

m/z 136 →

m/z 107 Br + H₂C•CH₃ mass 29

H₂C•Br m/z 93 + H₂C mass 43

m/z 57 + •Br mass 79

266
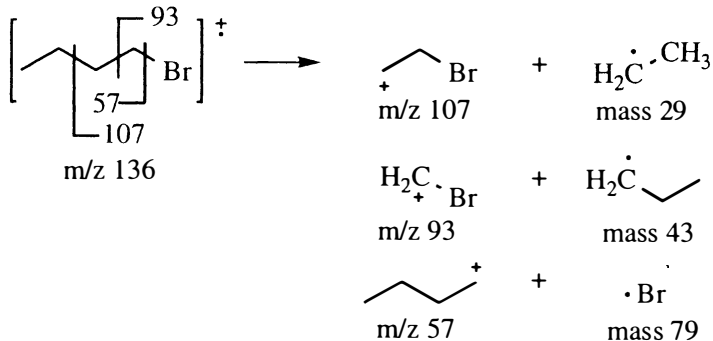
12-21

(a) Deuterium has twice the mass of hydrogen, but similar spring constant, k. Compare the frequency of C—D vibration to C—H vibration by setting up a ratio, changing only the mass (substitute 2m for m).

$$\frac{\nu_D}{\nu_H} = \frac{\sqrt{k/2m}}{\sqrt{k/m}} = \frac{\sqrt{1/2} \ \sqrt{k/m}}{\sqrt{k/m}} = \sqrt{1/2} = 0.707$$

$$\nu_D = 0.707 \ \nu_H = 0.707 \ (3000 \ cm^{-1}) \approx \mathbf{2100 \ cm^{-1}}$$

(b) The functional group most likely to be confused with a C—D stretch is the alkyne (carbon-carbon triple bond), which appears in the same region and is often very weak.

12-22

a 1° carbocation—not favorable

m/z 114   m/z 57

a 2° carbocation—reasonable

m/z 114   m/z 57

a 3° carbocation—the best

m/z 114   m/z 57
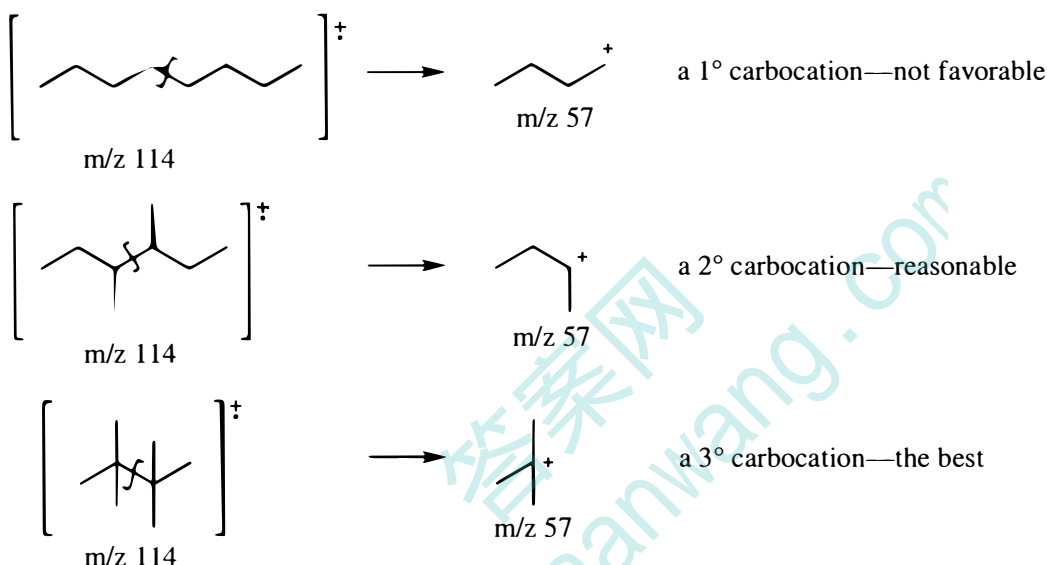
The most likely fragmentation of 2,2,3,3-tetramethylbutane will give a 3° carbocation, the most stable of the common alkyl cations. The molecular ion should be small or non-existent while m/z 57 is likely to be the base peak, whereas the molecular ion peaks will be more prominent for n-octane and for 3,4-dimethylhexane.

12-23

(a) The information that this mystery compound is a hydrocarbon makes interpreting the mass spectrum much easier. (It is relatively simple to tell if a compound has chlorine, bromine, or nitrogen by a mass spectrum, but oxygen is difficult to determine by mass spectrometry alone.) A hydrocarbon with molecular ion of 110 can have only 8 carbons (8 x 12 = 96) and 14 hydrogens. The formula C_8H_{14} has two elements of unsaturation.

(b) The IR will be useful in determining what the elements of unsaturation are. Cycloalkanes are generally not distinguishable in the IR. An alkene should have an absorption around 1600-1650 cm^{-1}; none is present in this IR. An alkyne should have a small, sharp peak around 2200 cm^{-1}—PRESENT AT 2120 cm^{-1}! Also, a sharp peak around 3300 cm^{-1} indicates a hydrogen on an alkyne, so the alkyne is at one end of the molecule. Both elements of unsaturation are accounted for by the alkyne.

12-23

(c) The only question is how are the other carbons arranged. The mass spectrum shows a progression of peaks from the molecular ion at 110 to 95 (loss of CH_3), to 81 (loss of C_2H_5), to 67 (loss of C_3H_7). The mass spectrum suggests it is a linear chain. The extra evidence that hydrogenation of the mystery compound gives n-octane verifies that the chain is linear. The original compound must be oct-1-yne.

(d) The base peak is so strong because the ion produced is stabilized by resonance.
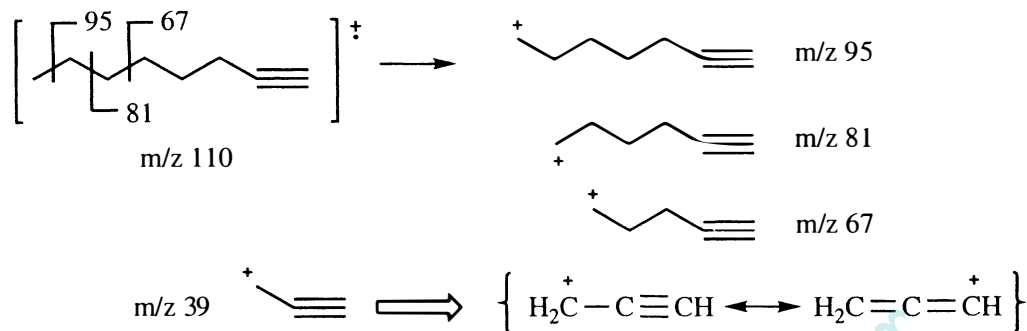
12-24

(a) and (b) The mass spec is consistent with the formula of the alkyne, C_8H_{14}, mass 110. The IR is not consistent with the alkyne, however. Often, symmetrically substituted alkynes have a miniscule C≡C peak, so the fact that the IR does not show this peak does not prove that the alkyne is absent. The important evidence in the IR is the significant peak at 1620 cm^{-1}; this absorption is characteristic of a conjugated diene. Instead of the alkyne being formed, the reaction must have been a double elimination to the diene.

12-25

(a)

(b)

(c)

268

12-26
(a)

2-methylhexan-2-ol
$C_7H_{16}O$ mol. wt. 116
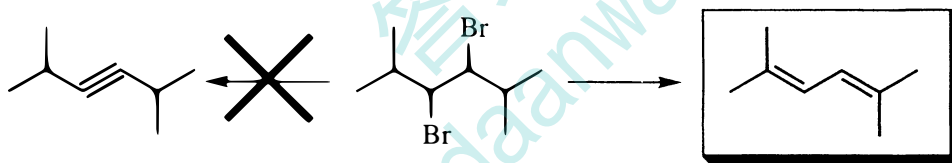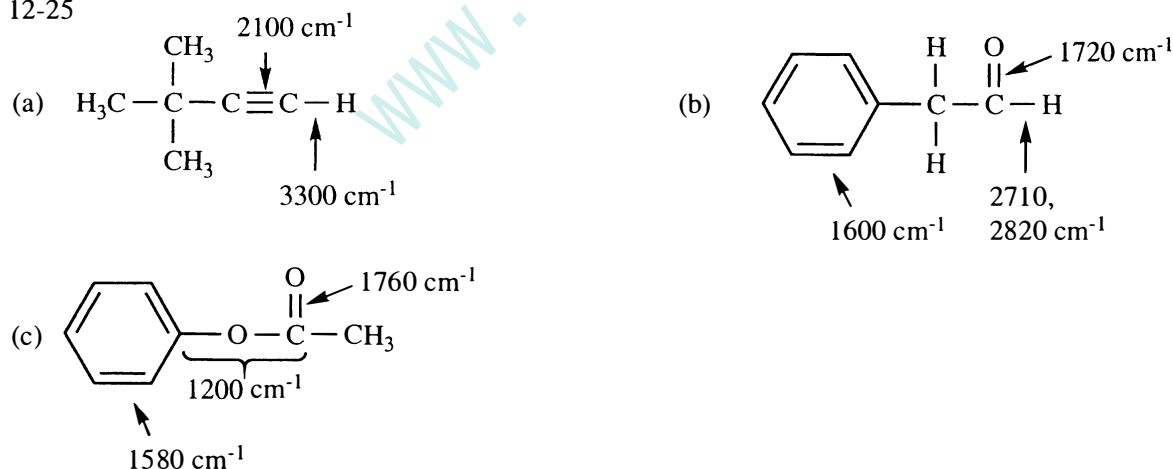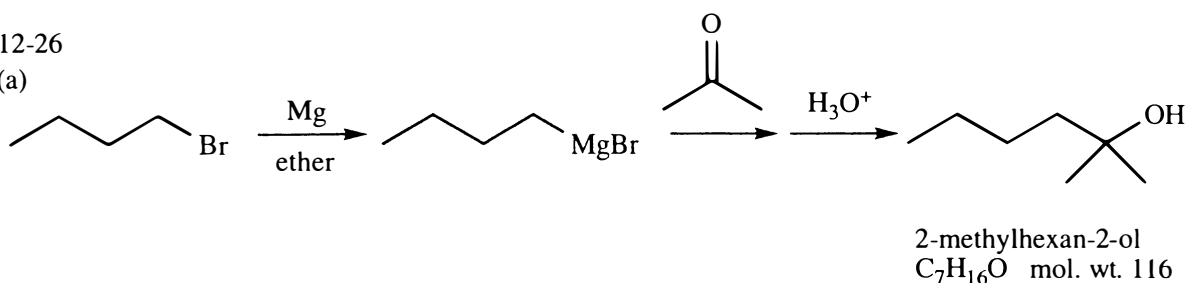
(b) The molecular ion is not visible in the spectrum. Alcohols typically dehydrate in the hot inlet system of the mass spectrometer, especially true for 3° alcohols that are the easiest type to dehydrate. The two fragmentations that produce a resonance-stabilized carbocation give the major peaks in the spectrum at m/z 59 and 101.

mass 116   m/z 59

m/z 101
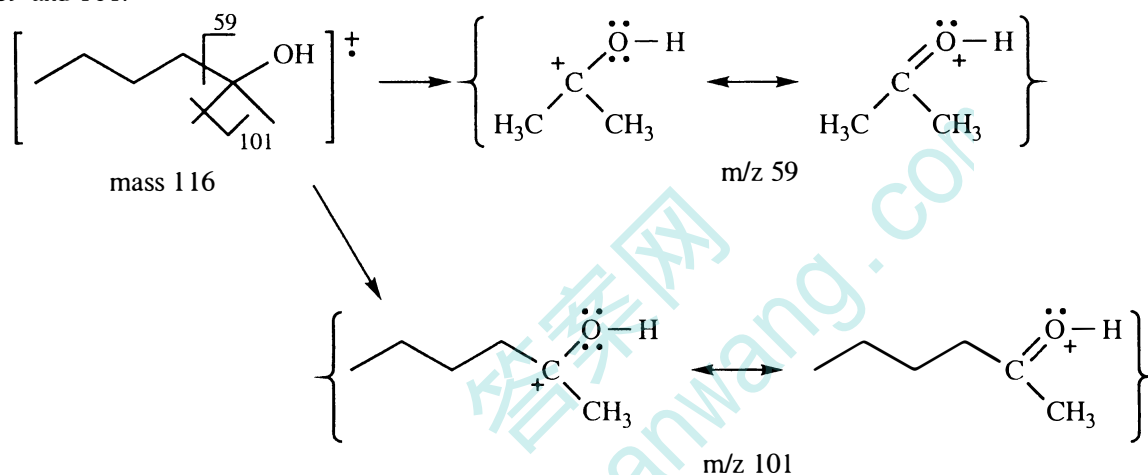
12-27 The unknown compound has peaks in the mass spec at m/z 198, 155, 127, 71, and 43. It is helpful that the masses of two of the fragments, 155 and 43, sum to 198, as do the other two fragment masses, 127 and 71. We can say with certainty that the molecular ion is at m/z 198, and that the unknown is a relatively simple molecule with two main fragmentations.

This is a fairly high mass for a simple compound; some heavy group must be present. What is NOT present is N because of the even molecular ion mass, nor Cl nor Br because of the lack of isotope peaks, nor a phenyl group because of no peak at 77. The progression of alkyl group masses: 15, 29, **43**, 57, **71**, 85, 99—includes two of the peaks, so it appears that the unknown contains a propyl group and a pentyl group (the propyl could be part of the pentyl group). The 127 fragment is key; the fragment C_9H_{19} has this mass, but we would expect much more fragmentation from a nine carbon piece. There must be some other explanation for this 127 peak.

And there is! There is one piece—more specifically, one atom—that has mass 127: iodine! In all probability, the iodine atom is attached to a fragment of mass 71 which is C_5H_{11}, a pentyl group. We cannot tell with certainty what isomer it is, so unless there is some other evidence, let's propose a straight chain isomer, 1-iodopentane.
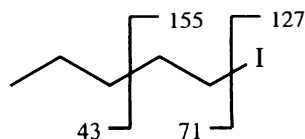
The 155 fragment probably has this bridged structure because iodine is so big:

269

12-28

(a)

$H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

broad, strong OH peak
around 3300 cm^{-1}

$H_3C-\underset{O}{\overset{\overset{CH_3}{|}}{C}}=\underset{CH_3}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

strong peak around
1715 cm^{-1}

(b)

strong peak around
1690 cm^{-1}

two peaks at
2700 and 2800 cm^{-1}

OH   broad, strong OH peak
around 3300 cm^{-1}

(c)

very broad
2500-3500 cm^{-1}
with a "shoulder"
around 2700 cm^{-1}

broad COOH band
missing

still has a strong
OH at 3300 cm^{-1}
but different from
COOH
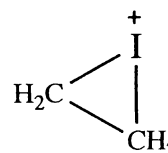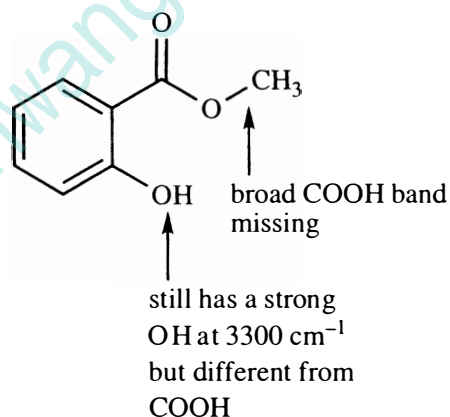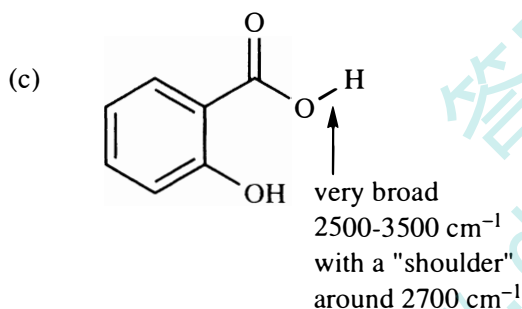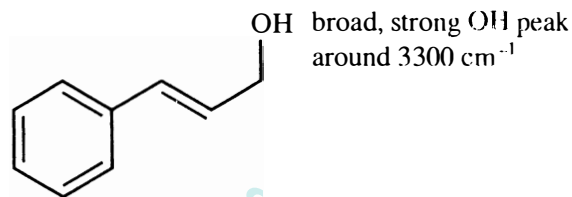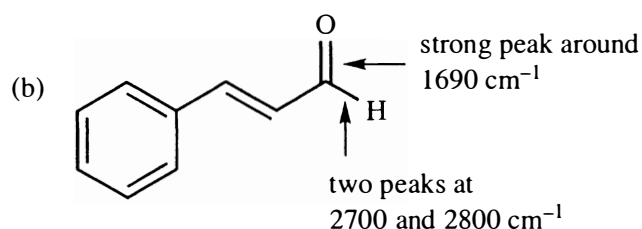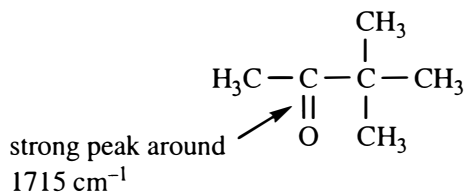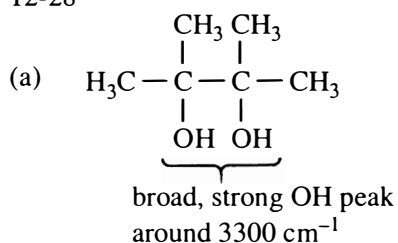
If you wish to find IR spectra and mass spectra of common compounds, there are two web sites that are very helpful. Entering a name or molecular formula will give isomers from which to choose the desired structure and the IR or MS if available in their database.

http://webbook.nist.gov/
"NIST" is the U.S. National Institute of Standards and Technology.

http://www.aist.go.jp/RIODB/SDBS/menu-e.html
This is from the National Institute of Advanced Industrial Science and Technology of Japan.

CHAPTER 13—NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A benzene ring can be written with three alternating double bonds or with a circle in the ring. All of the carbons and hydrogens in an unsubstituted benzene ring are equivalent, regardless of which symbolism is used.

equivalent to
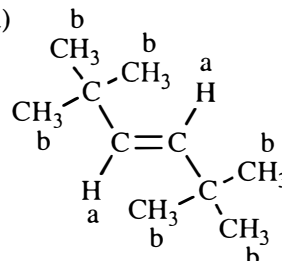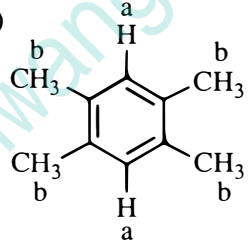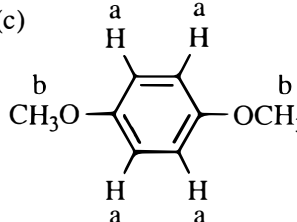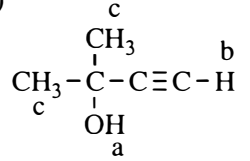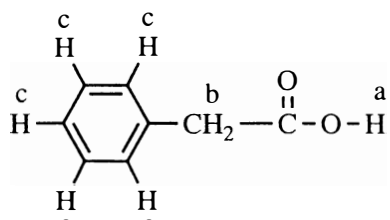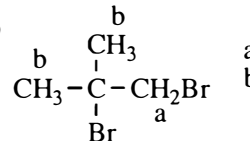
The Japanese web site listed at the bottom of p. 270 also gives proton and carbon NMR spectra.

Reminder: The word "spectrum" is singular; the word "spectra" is plural.

13-1

(a) $\dfrac{650\ \text{Hz}}{300 \times 10^6\ \text{Hz}} = 2.17 \times 10^{-6} = 2.17$ ppm downfield from TMS

(b) Difference in magnetic field $= 70{,}459$ gauss $\times (2.17 \times 10^{-6}) = 0.153$ gauss

(c) The chemical shift does not change with field strength: $\delta\ 2.17$ at both 60 MHz and 300 MHz.

(d) $(2.17\ \text{ppm}) \times (60\ \text{MHz}) = (2.17 \times 10^{-6}) \times (60 \times 10^6\ \text{Hz}) = 130$ Hz

13-2 Numbers are chemical shift values, in ppm, derived from Table 13-3 and the Appendix in the text.
Your predictions should be in the given range, or within 0.5 ppm of the given value.

(a)
a = δ 5-6
b = δ 0.9

(b)
a = δ 7.2
b = δ 2.3

(c)
a = δ 7.2
b = δ 3.6

(d)
a = δ 2-5
b = δ 2.5
c = δ 1-2

(e)
a = δ 10-12
b ≈ δ 3 (between two deshielding groups)
c = δ 7.2 (The hydrogens labeled "c" are not equivalent.
They appear at roughly the same chemical shift
because the substituent is neither strongly electron-
donating nor withdrawing.) **271**

(f)
a = δ 3-4
b = δ 1-2

13-3

(a) CH₃CH₂CH₂Cl
(with labels c b a)

three types of H

(b) CH₃CHCH₃
(with labels b a b, Cl below)

two types of H

(c) CH₃–C–CH₂CH₃
(with CH₃ above and CH₃ below, labels a CH₃ b c, a for lower CH₃)

three types of H

(d) aromatic ring with CH₃ and Br substituents (labels b, H, a, e, H, c, H, d)

five types of H

13-4

(a) toluene ring with CH₃ (labels a CH₃, b H, b H, H c, H c, H d)

four types of H
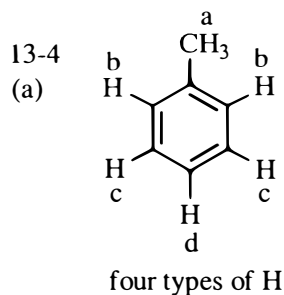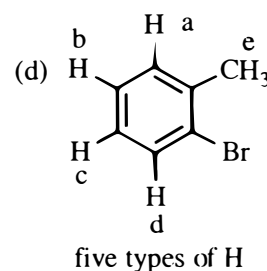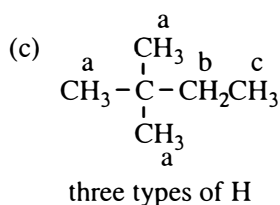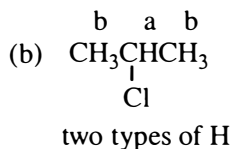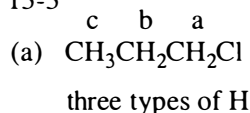
(b) The three types of aromatic hydrogens appear in a relatively small space around δ 7.2. The signal is complex because all the peaks from the three types of hydrogens overlap.

Note: NMR spectra drawn in this Solutions Manual will represent peaks as single lines. These lines may not look like "real" peaks, but this avoids the problem of variation among spectrometers and printers. Individual spectra may look different from the ones presented here, but all of the important information will be contained in these representational spectra.

13-5

$$H_3C-\underset{\underset{c}{CH_3}}{\overset{\overset{c}{CH_3}}{C}}-O-\underset{a}{\overset{O}{C}}-CH_2-\underset{b}{\overset{O}{C}}-CH_3$$

(NMR spectrum showing peaks: c 9H, b 3H, a 2H, TMS, with δ(ppm) axis from 10 to 0)

δ (ppm)
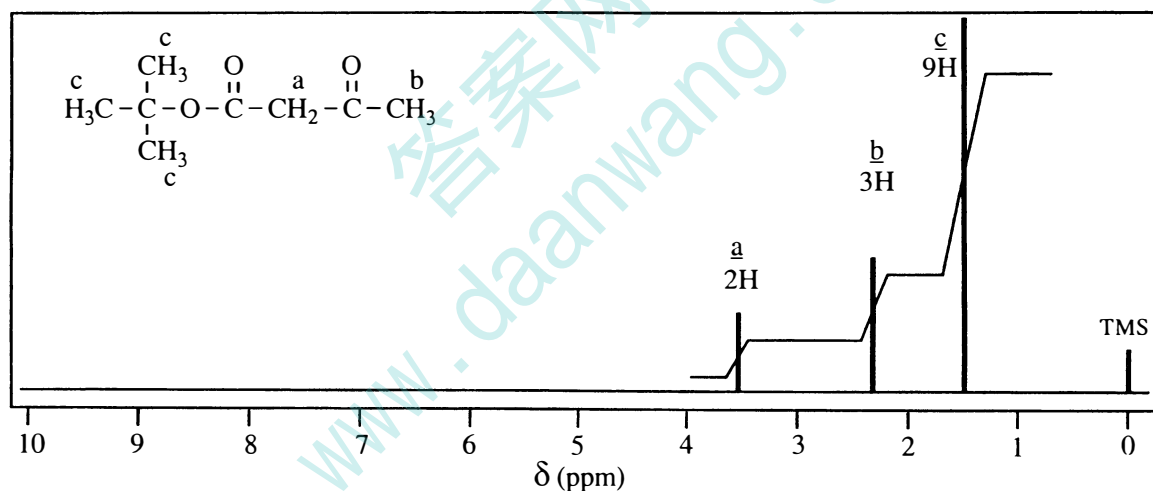
13-6 The three spectra are identified with their structures. Data are given as chemical shift values, with the integration ratios of each peak given in parentheses.

Spectrum (a)

CH₃–C–C≡C–H
(with OH above, CH₃ below, labels c, b OH, a, c CH₃)

a = δ 2.4 (1) (1H)
b = δ 2.6 (1) (1H)
c = δ 1.5 (6) (6H)

Spectrum (b)

CH₃O— benzene ring —OCH₃
(labels a H, a H, b, b, H a, H a)

a = δ 6.8 (2) (4H)
b = δ 3.7 (3) (6H)

Spectrum (c)

CH₃–C–CH₂Br
(with CH₃ above, Br below, labels b CH₃, b, a, Br)

a = δ 3.9 (1) (2H)
b = δ 1.9 (3) (6H)

(This is the compound in Problem 13-2(f). You may wish to check your answer to that question against the spectrum.)
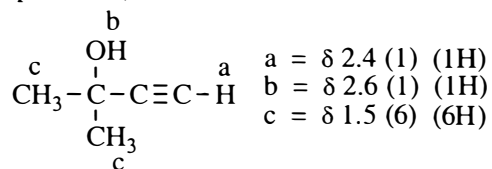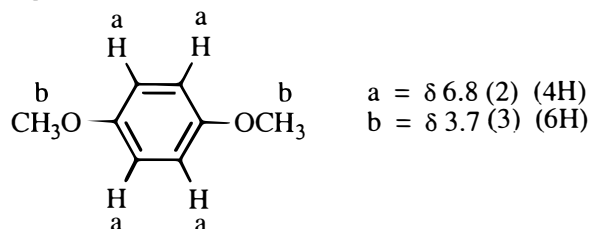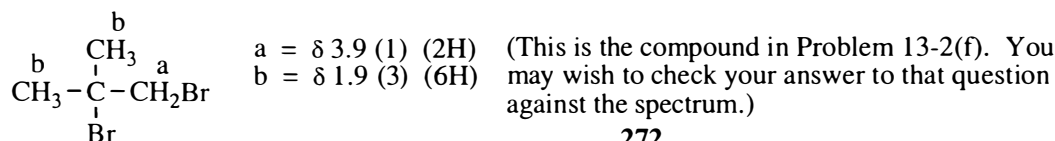
13-7 Chemical shift values are approximate and may vary slightly from yours. The splitting and integration values should match exactly, however.

(a)

(b)

(c)

Note: the three types of aromatic protons above are *accidentally equivalent* because the isopropyl group has little effect on their chemical shifts.

13-7 continued

(d)

$\underline{a}$
4H

All four aromatic
protons are
equivalent.

a H   H a
c   b   b   c
CH_3CH_2O —⟨ ⟩— OCH_2CH_3
a H   H a

$\underline{b}$
4H

$\underline{c}$
6H

TMS

10   9   8   7   6   5   4   3   2   1   0
δ (ppm)

(e)

$\underline{b}$
4H

$\underline{c}$
6H

c   a   O   b   b   O   a   c
             ∥   ∥
$CH_3CH_2O - C - CH_2CH_2 - C - OCH_2CH_3$

No splitting is observed when *chemically
equivalent* hydrogens are adjacent to each
other, as with hydrogens "b" above.

$\underline{a}$
4H

TMS

10   9   8   7   6   5   4   3   2   1   0
δ (ppm)

13-8
(a)

δ 2.4 H_2C
δ 1.8 H_2C
     H_3C CH_3
        δ 1.2

O
H δ 5.8
H δ 6.7

The signals at 1.8 and 2.4 are
triplets because each set of
protons has two neighboring
hydrogens. The N+1 rule
correctly predicts each to be a
triplet.

(b)

δ 1.1
H_3C CH_3 δ 7.3   H
δ 1.5 H_2C
δ 1.65 H_2C C
            H_2
      δ 2.1
      allylic

O
CH_3 δ 2.3
H δ 6.2
CH_3
δ 1.7
allylic
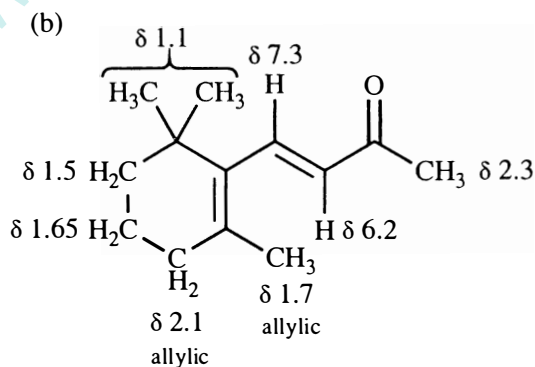
The three CH_2 groups can be distinguished by chemical shift
and by splitting. The allylic CH_2 will be the farthest downfield
of the three, at 2.1. The signal at 1.5 is a triplet, so that must be
the one with only two neighboring protons. The CH_2 showing
the multiplet at 1.65 must be the one between the other two
CH_2 groups.

13-9

(a)

The three types of aromatic protons are *accidentally equivalent.*

<u>a</u> 5H

<u>b</u> 1H J = 15 Hz

<u>c</u> 1H J = 15 Hz

<u>d</u> 9H

TMS

10 9 8 7 6 5 4 3 2 1 0

δ (ppm)

(b)

CH₃O b ... CH₃ c
C=C
Cl ... H a

<u>a</u> 1H

<u>b</u> 3H

<u>c</u> 3H

TMS

10 9 8 7 6 5 4 3 2 1 0

δ (ppm)

(c)

(CH₃)₃C e ... C-OCH₂CH₃
C=C
H a ... H b

<u>a</u> 1H

<u>b</u> 1H

<u>c</u> 2H

<u>d</u> 3H

<u>e</u> 9H

TMS

10 9 8 7 6 5 4 3 2 1 0

δ (ppm)

13-9 continued

(d)

a
1H

11

The chemical shift
of —COOH is
variable. It is
usually a broad
peak.

b
2H

c
2H

The electron-withdrawing
carbonyl group deshields the
protons adjacent to it, moving
them downfield from their
usual position at δ 7.2.

d
CH₃

c
H   c
          H

b
H   b
          H

$O=\overset{}{\underset{}{C}}-OH$
a

d
3H

TMS

10   9   8   7   6   5   4   3   2   1   0

δ (ppm)

13-10 The formula C_3H_2NCl has three elements of unsaturation. The IR peak at 1650 cm⁻¹ indicates an
alkene, while the absorption at 2200 cm⁻¹ must be from a nitrile (not enough carbons left for an alkyne).
These two groups account for the three elements of unsaturation. So far, we have:

$$\underset{/}{\overset{\backslash}{C}}=\underset{\backslash}{\overset{/}{C}}\!\!-\!\!C\!\equiv\!N \quad + \; 2\,H \; + \; Cl$$

The NMR gives the coupling constant for the two protons as 14 Hz.
This large J value shows the two protons as *trans* (*cis*, J = 10 Hz;
geminal, J = 2 Hz). The structure must be the one in the box.

$$\underset{Cl}{\overset{H}{\backslash}}C=C\underset{H}{\overset{C\equiv N}{/}}$$
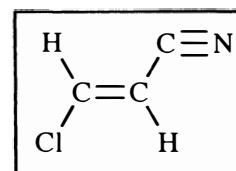
13-11

(a) C_3H_7Cl—no elements of unsaturation; 3 types of protons in the ratio of 2 : 2 : 3 .

$Cl-\overset{a}{C}H_2\overset{b}{C}H_2\overset{c}{C}H_3$ a = δ 3.8 (triplet, 2H); b = δ 2.1 (multiplet, 2H);
c = δ 1.3 (triplet, 3H)

(b) $C_9H_{10}O_2$—5 elements of unsaturation; four
protons in the aromatic region of the NMR
indicate a disubstituted benzene; the pair of
doublets with J = 8 Hz indicate the
substituents are on opposite sides of the ring
(*para*).

 + 3 C + 6 H + 2 O +
1 element of unsaturation
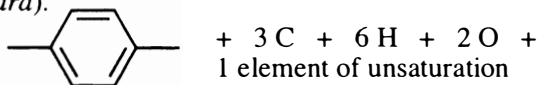
The other NMR signals are two 3H singlets,
two CH₃ groups. One at δ 3.9 must be a CH₃O
group. The other at δ 2.4 is most likely a CH₃
group on the benzene ring.

CH_3- + OCH₃ + C + O +
1 element of unsaturation
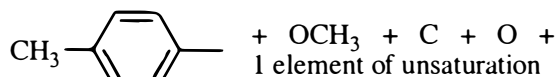
One way to assemble these pieces consistent with the NMR is:

b   a
H   H   O
                      ‖
d   c
CH₃—   —C—OCH₃
H   H
b   a

a = δ 7.9 (doublet, 2H)
b = δ 7.2 (doublet, 2H)
c = δ 3.9 (singlet, 3H)
d = δ 2.4 (singlet, 3H)
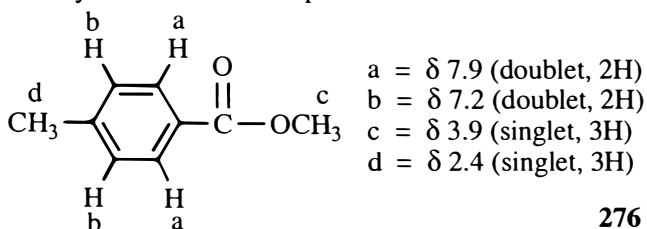
(Another plausible structure is to have the
methoxy group directly on the ring and to put
the carbonyl between the ring and the methyl.
This does not fit the chemical shift values
quite as well as the above structure, as the
methyl would appear around δ 2.1 or 2.2
instead of 2.4.)

276

13-12　　H_c , δ 5.1

δ 5.1

J_{ac} = 11 Hz

J_{bc} = 1.4 Hz　　J_{bc} = 1.4 Hz

13-13

(a)
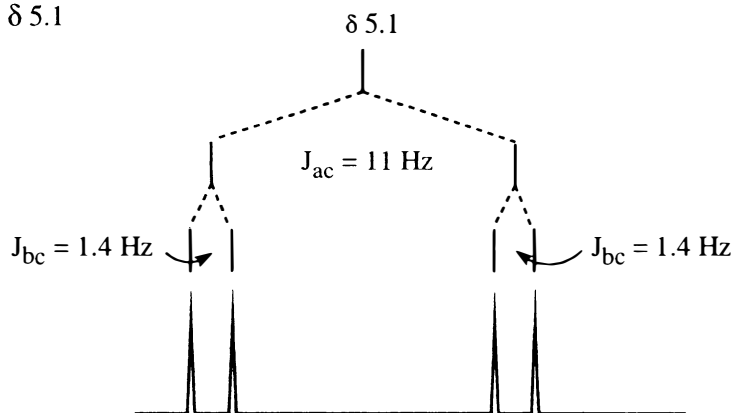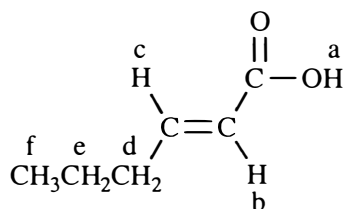
a = δ 12.1 (broad singlet, 1H)
b = δ 5.8 (doublet, 1H)
c = δ 7.1 (multiplet, 1H)
d = δ 2.2 (quartet, 2H)
e = δ 1.5 (sextet, 2H)
f = δ 0.9 (triplet, 3H)

(b)　The vinyl proton at δ 7.1 is H_c; it is coupled with H_b and H_d, with two different coupling constants, J_{bc} and J_{cd}, respectively. The value of J_{bc} can be measured most precisely from the signal for H_b at δ 5.8; the two peaks are separated by about 15 Hz, corresponding to 0.05 ppm in a 300 MHz spectrum. The value of J_{cd} appears to be about the standard value 8 Hz, judging from the signal at δ 7.1. The splitting tree would thus appear:

δ 7.1

J_{bc} = 15 Hz

J_{cd} = 8 Hz　J_{cd} = 8 Hz　J_{cd} = 8 Hz　J_{cd} = 8 Hz

overlap in NMR
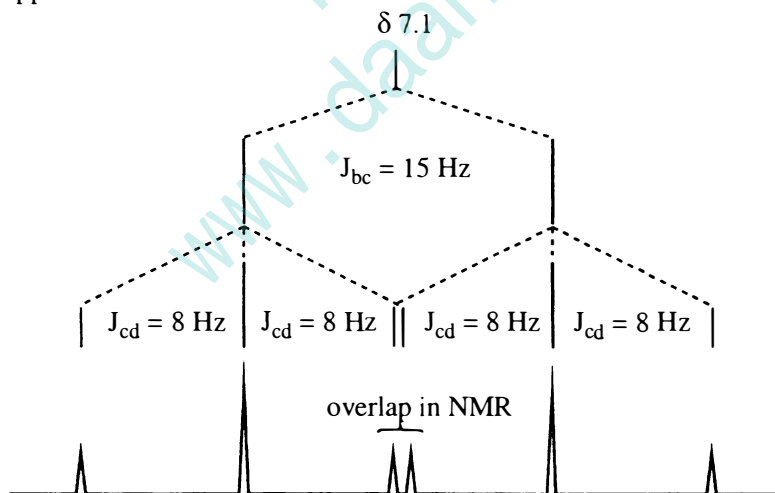
13-14
(a)
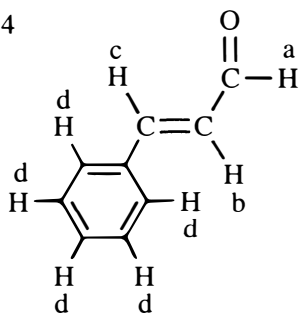
a = δ 9.7 (doublet, 1H)
b = δ 6.7 (doublet of doublets, 1H)
c = δ 7.5 (doublet, 1H)
d = δ 7.4 (multiple peaks, 5H)

The doublet for H$_c$ at δ 7.4 OVERLAPS the 5H peaks of H$_d$.

(b) J$_{ab}$ can be determined most accurately from H$_a$ at δ 9.7: J$_{ab}$ ≈ 8 Hz, about the same as "normal" alkyl coupling.

J$_{bc}$ can be measured from H$_b$ at δ 6.7, as the distance between either the first and third peaks or the second and fourth peaks (see diagram below): J$_{bc}$ ≈ 18 Hz, about double the "normal" alkyl coupling.

(c)

δ 6.7

J$_{bc}$ = 18 Hz

J$_{ab}$ = 8 Hz   J$_{ab}$ = 8 Hz
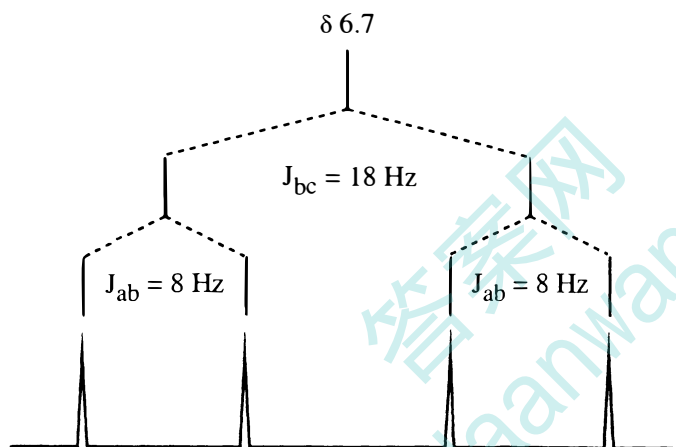
13-15
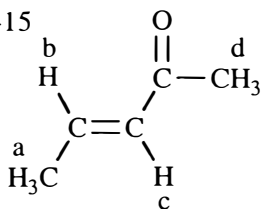
(a) a = δ 1.7   (b) a = doublet
     b ≈ δ 6.8   b = multiplet (two overlapping quartets—see part (c))
     c = δ 5-6   c = doublet
     d = δ 2.1   d = singlet

(c) using J$_{bc}$ = 15 Hz and J$_{ab}$ = 7 Hz: δ 6.8

J$_{bc}$ = 15 Hz

J$_{ab}$ = 7 Hz

278

13-16

cis diastereomer

trans diastereomer

13-17

(a)

non-superimposable mirror images = enantiomers; therefore, H_a and H_b are *enantiotopic* and are not distinguishable by NMR

(b)

enantiomers
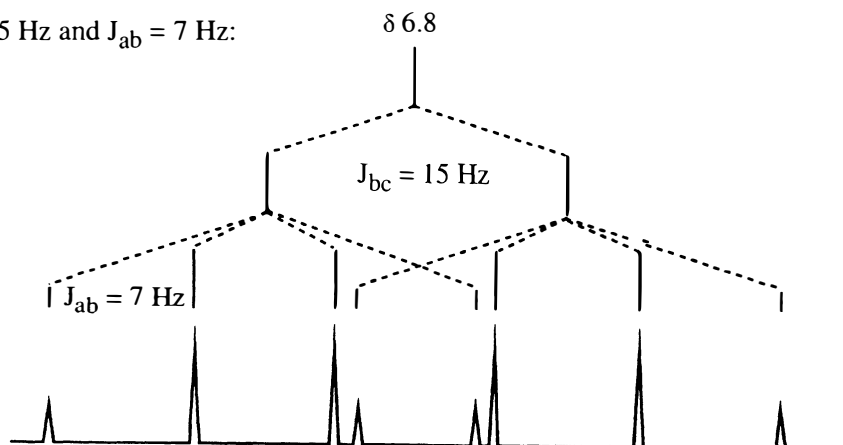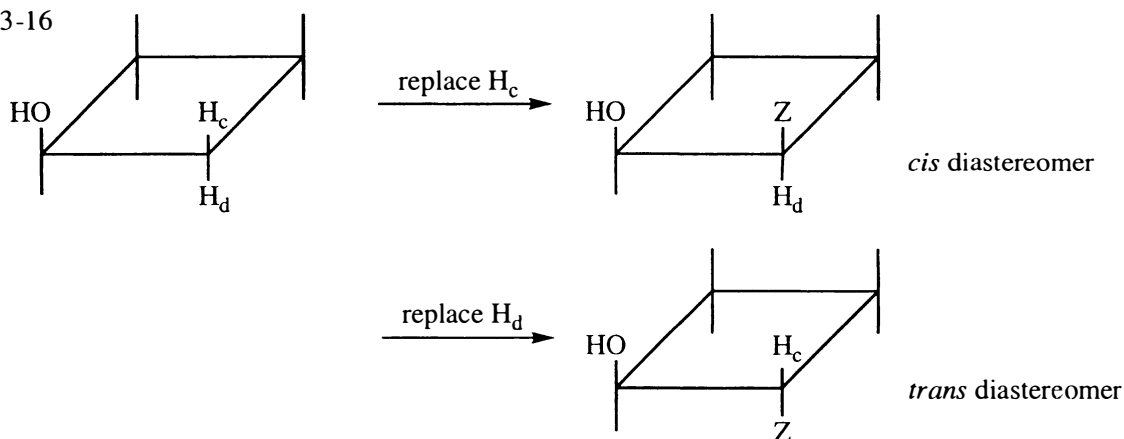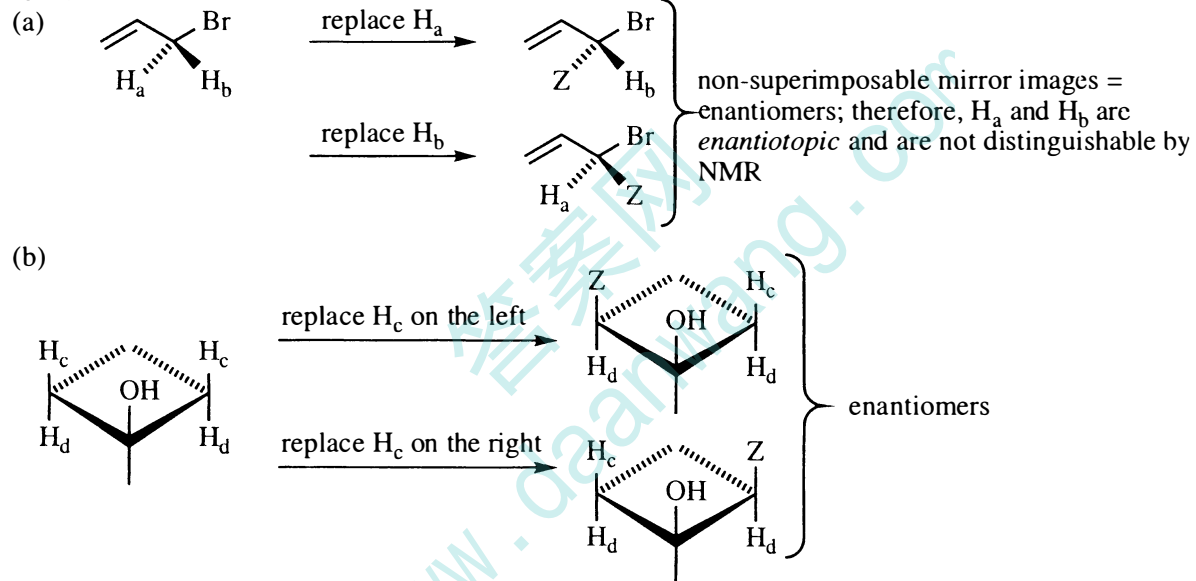
(c) The H_d protons are also enantiotopic.

13-18

(a)
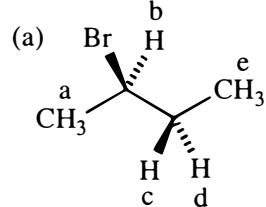
This compound has five types of protons. H_c and H_d are diastereotopic. a = δ 1.5; b = δ 3.6; c,d = δ 1.7; e = δ 1.0

(b)
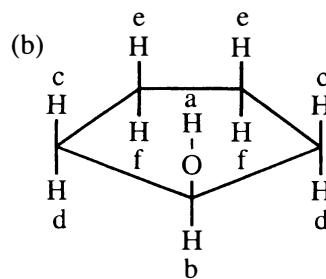
This compound has six types of protons. H_c and H_d are diastereotopic, as are H_e and H_f. a = δ 2-5; b = δ 3.9; c,d = δ 1.6; e,f = δ 1.3

13-18 continued

(c)
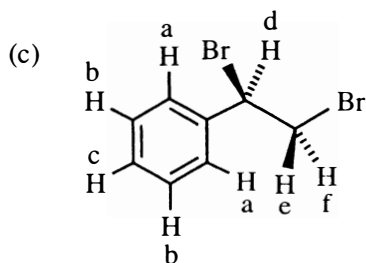
This compound has six types of protons.
H_e and H_f are diastereotopic. a,b,c = δ 7.2;
d ≈ δ 5.0; e,f = δ 3.6

(d)
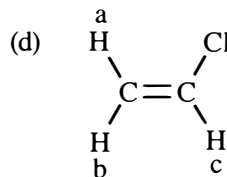
This compound has three types of
protons. H_a and H_b are diastereotopic.
a,b = δ 5-6; c = δ 7-8

13-19

(a)

(b)
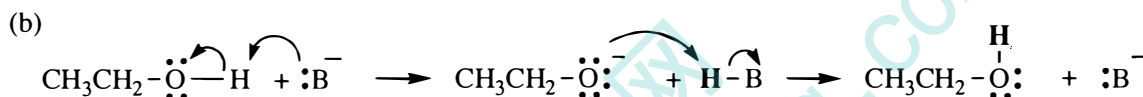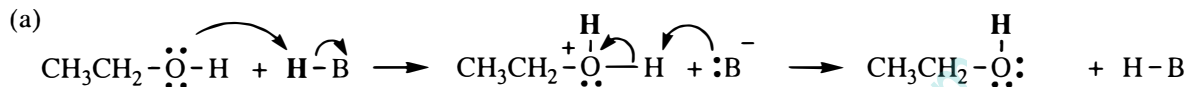
13-20   The protons from the OH in ethanol exchange with the deuteriums in D_2O. Thus, the OH in ethanol
is replaced with OD which does not absorb in the NMR. What happens to the H? It becomes HOD which
can usually be seen as a broad singlet around δ 5.25. (If the solvent is $CDCl_3$, the immiscible HOD will
float on top of the solvent, out of the spectrometer beam, and its signal will be missing.)

$$ROH + D_2O \longrightarrow ROD + HOD$$

280
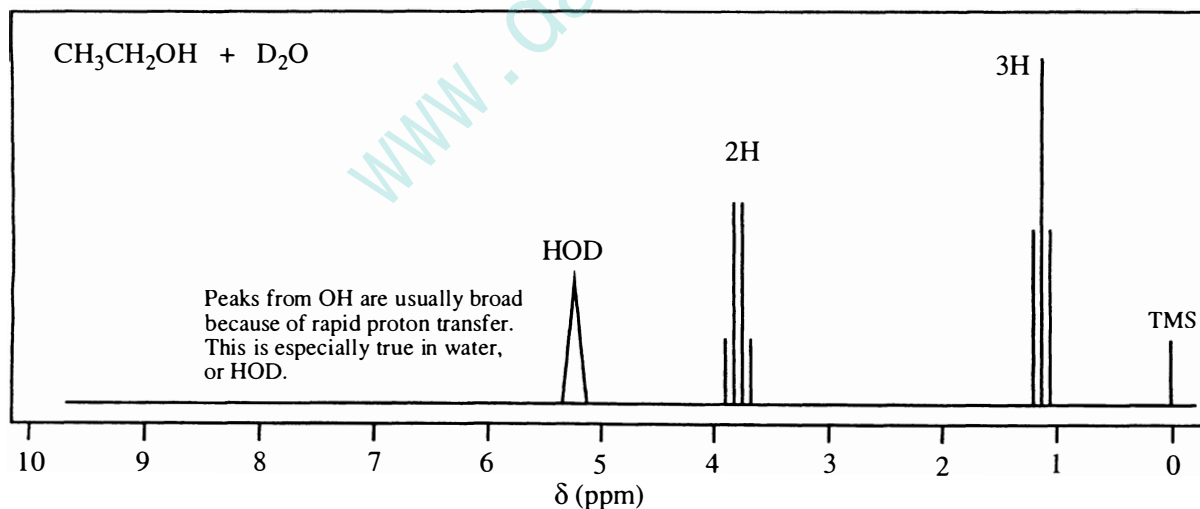
13-21

(a) The formula $C_4H_{10}O_2$ has no elements of unsaturation, so the oxygens must be alcohol or ether functional groups. The doublet at δ 1.2 represents 3H and must be a CH_3 next to a CH. The peaks centered at δ 1.65 integrating to 2H appear to be an uneven quartet and signify a CH_2 between two sets of non-equivalent protons; apparently the coupling constants between the non-equivalent protons are not equal, leading to a complicated pattern of overlapping peaks. The remaining five hydrogens appear in four groups of 1H, 1H, 1H, and 2H, between δ 3.7 and 4.2. The 2H multiplet at δ 3.75 is a CH_2 next to O, with complex splitting (doublet of doublets) due to diastereotopic neighbors. The 1H multiplet at δ 4.0 is a CH between many neighbors. The two 1H signals at δ 4.1-4.2 appear to be OH peaks in different environments, partially split by adjacent CH groups.

The 3-dimensional view shows clearly that the two Hs on a CH_2 are not equivalent

Of the two possible structures:

$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_2OH}{|}}{C}}-CH_2OH$$

OR

4.0
1.2 H 1.65 3.75
$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH \leftarrow 4.1-4.2}{|}}{C}}-CH_2CH_2OH$

CORRECT!

this one has no chiral centers and would not display such complex splitting

If the possibility of intramolecular H-bonding is considered, the differences in the environments for each H become even more obvious.

(b) The formula C_2H_7NO has no elements of unsaturation. The N must be an amine and the O must be an alcohol or ether. Two triplets, each with 2H, are certain to be $-CH_2CH_2-$. Since there are no carbons left, the N and O, with enough hydrogens to fill their valences, must go on the ends of this chain. The rapidly exchanging OH and NH_2 protons appear as a broad, 3H hump at δ 2.8.

$HOCH_2CH_2NH_2$
δ 3.7 — — δ 2.9
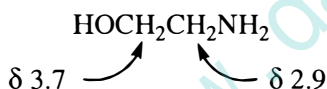
13-22
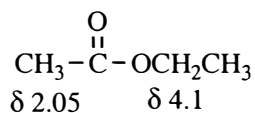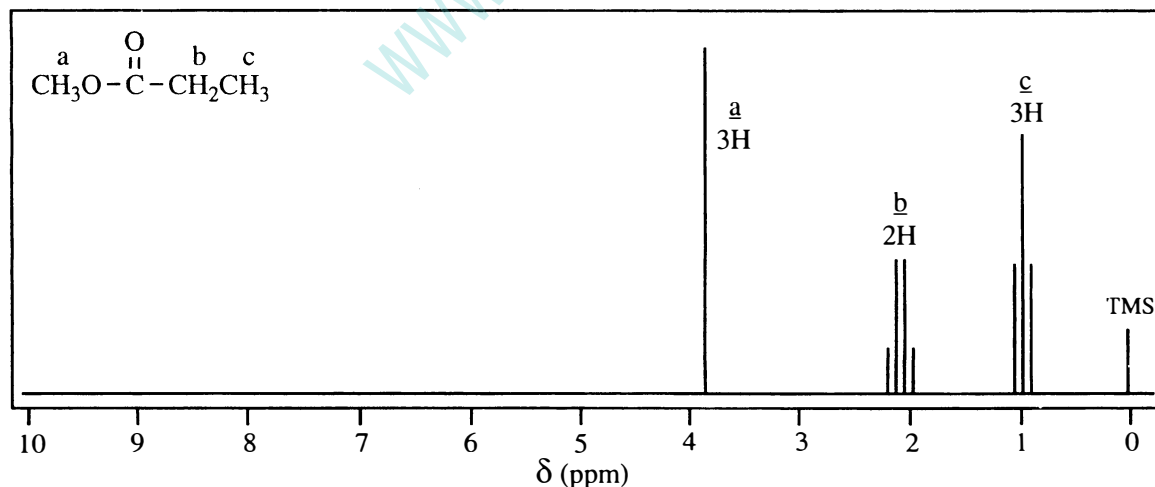
The key is what protons are adjacent to the oxygen. The CH_3O in methyl propanoate, above, absorbs at δ 3.9, whereas the CH_2 next to the carbonyl absorbs at δ 2.2. This is in contrast to ethyl acetate, at the left.

$$CH_3-\overset{O}{\overset{||}{C}}-OCH_2CH_3$$
δ 2.05   δ 4.1

281

13-23

H_a = δ 2.4 (singlet, 1H)
H_b = δ 3.4 (doublet, 2H)
H_c = δ 1.8 (multiplet, 1H)
H_d = δ 0.9 (doublet, 6H)

$$d$$
$$CH_3$$
$$H_2 \quad |$$
$$H-O-\underset{a}{\overset{b}{C}}-\underset{\underset{d}{CH_3}}{\overset{|}{C}}-\underset{c}{H}$$
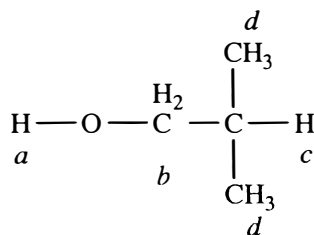
13-24
(a) The formula $C_4H_8O_2$ has one element of unsaturation. The 1H singlet at δ 12.1 indicates carboxylic acid. The 1H multiplet and the 6H doublet scream isopropyl group.

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}CH-\overset{\overset{O}{\parallel}}{C}-OH$$
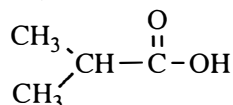
(b) The formula $C_9H_{10}O$ has five elements of unsaturation. The 5H pattern between δ 7.2-7.4 indicates monosubstituted benzene. The peak at δ 9.85 is unmistakably an aldehyde, trying to be a triplet because it is weakly coupled to an adjacent CH_2. The two triplets at δ 2.7-3.0 are adjacent CH_2 groups.

$$\text{benzene}-\underset{\underset{H_2}{C}}{\overset{\overset{H_2}{C}}{}}-\overset{\overset{O}{\parallel}}{C}-H$$
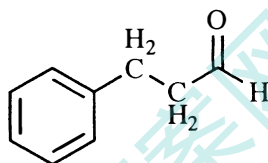
(c) The formula $C_5H_8O_2$ has two elements of unsaturation. A 3H singlet at δ 2.3 is probably a CH_3 next to carbonyl. The 2H quartet and the 3H triplet are certain to be ethyl; with the CH_2 at δ 2.7, this also appears to be next to carbonyl.

$$CH_3CH_2-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-CH_3$$
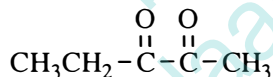
(d) The formula C_4H_8O has one element of unsaturation, and the signals from δ 5.0-6.0 indicate a vinyl pattern (CH_2=CH—). The complex quartet for 1H at δ 4.3 is a CH bonded to an alcohol, next to CH_3. The OH appears as a 1H singlet at δ 2.5, and the CH_3 next to CH is a doublet at δ 1.3. Put together:

$$\underset{}{\overset{OH}{|}}$$
$$CH_2=CH-CH-CH_3 \qquad \text{but-3-en-2-ol}$$
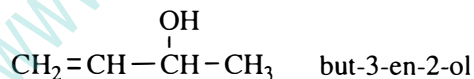
(e) The formula $C_7H_{16}O$ is saturated; the oxygen must be an alcohol or an ether, and the broad 1H peak at δ 1.2 is probably an OH. Let's analyze the spectrum from left to right. The expansion of the 1H multiplet at δ 1.7 shows seven peaks—an isopropyl group! Six of the nine H in the pattern at δ 0.9 must be the doublet from the two methyls from the isopropyl. The 2H quartet at δ 1.5 must be part of an ethyl pattern, from which the methyl triplet must be the other 3H of the pattern at δ 0.9. This leaves only the 3H singlet at δ 1.1 which must be a CH_3 with no neighboring Hs.

$$-OH \ + \ -CH_2CH_3 \ + \ CH_3-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}- \ + \ -CH_3 \ + \ 1\,C$$

These pieces can be assembled in only one way:

$$HO-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2CH_3}{|}}{C}}-CH(CH_3)_2 \quad \text{2,3-dimethylpentan-3-ol}$$
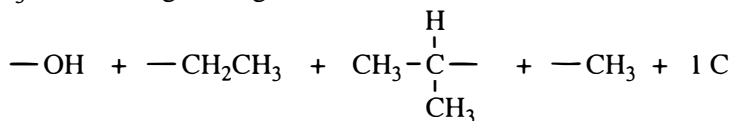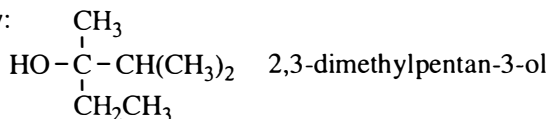
13-25 Chemical shift values are estimates from Figure 13-41 and from Appendix 1C, except in (c) and (d), where the values are exact.

(a) estimated

a
δ 130

b
δ 70

TMS

Carbon -13 δ (ppm)

(b) estimated

a
δ 125

b
δ 30

c
δ 22

TMS

Carbon -13 δ (ppm)

(c) exact values

a
δ 200

b
δ 145

c
δ 126

d
δ 26

e
δ 17

TMS

Carbon -13 δ (ppm)

13-25 continued

(d) exact values

b
δ 136

c
δ 135

a
δ 192

TMS

Carbon -13 δ (ppm)

13-26

(a) δ 37 O

δ 8 →

δ 30

δ 209

(b) 30 ÷ 2 = **15**
37 ÷ 2.7 = **14**
8 ÷ 1 = **8**

As a *general* rule,
the 15-20 rule works
fairly well.

b
3H

a
2H

c
3H

TMS

O
‖
H₃C — C — CH₂ — CH₃
b   a   c

δ (ppm)

13-27

(a)

a   a
C = C
/   \
C   C
b   O   b

a
δ 130

b
δ 70

TMS

Carbon -13 δ (ppm)

284

13-27 continued

(b)

$\underline{a}$
δ 125

$\underline{b}$
δ 30 $\underline{c}$
δ 22

TMS

200 180 160 140 120 100 80 60 40 20 0

Carbon -13 δ (ppm)

(c)

$\underline{b}$
δ 145

$\underline{a}$
δ 200 $\underline{c}$
δ 126 $\underline{d}$
δ 26 $\underline{e}$
δ 17

TMS

200 180 160 140 120 100 80 60 40 20 0

Carbon -13 δ (ppm)

(d)

$\underline{a}$
δ 192 $\underline{b}$
δ 136

$\underline{c}$
δ 135

TMS

200 180 160 140 120 100 80 60 40 20 0

Carbon -13 δ (ppm)

285

13-28 The full carbon spectrum of phenyl propanoate is presented below.
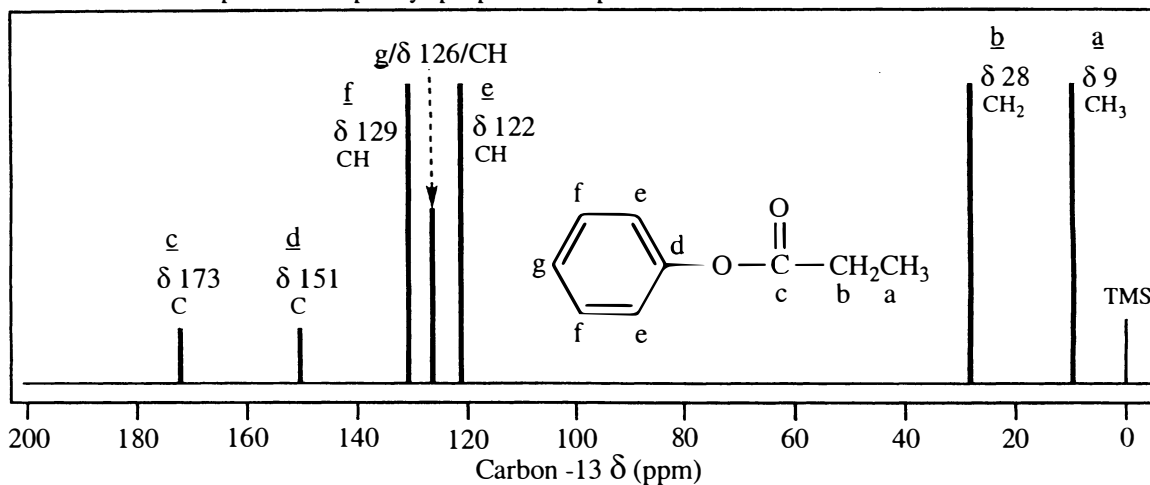
The DEPT-90 will show only the methine carbons, i.e., CH. All other peaks disappear.
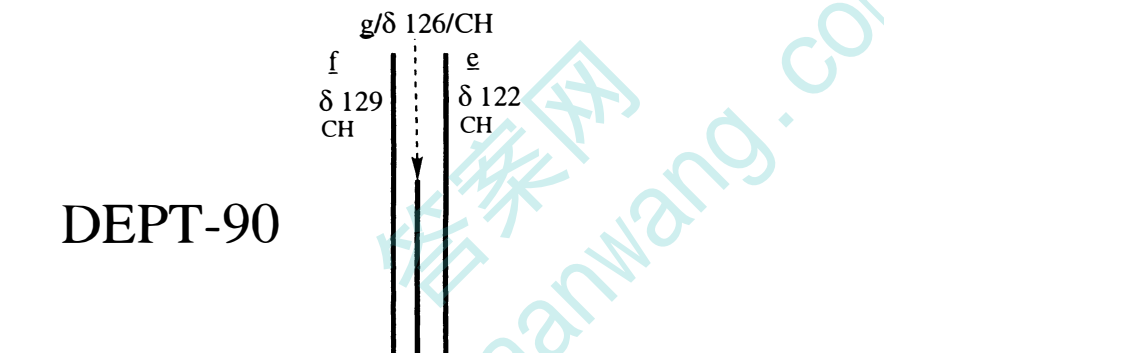
The DEPT-135 will show the methyl, CH_3, and methine, CH, peaks pointed up, and the methylene, CH_2, peaks pointed down.
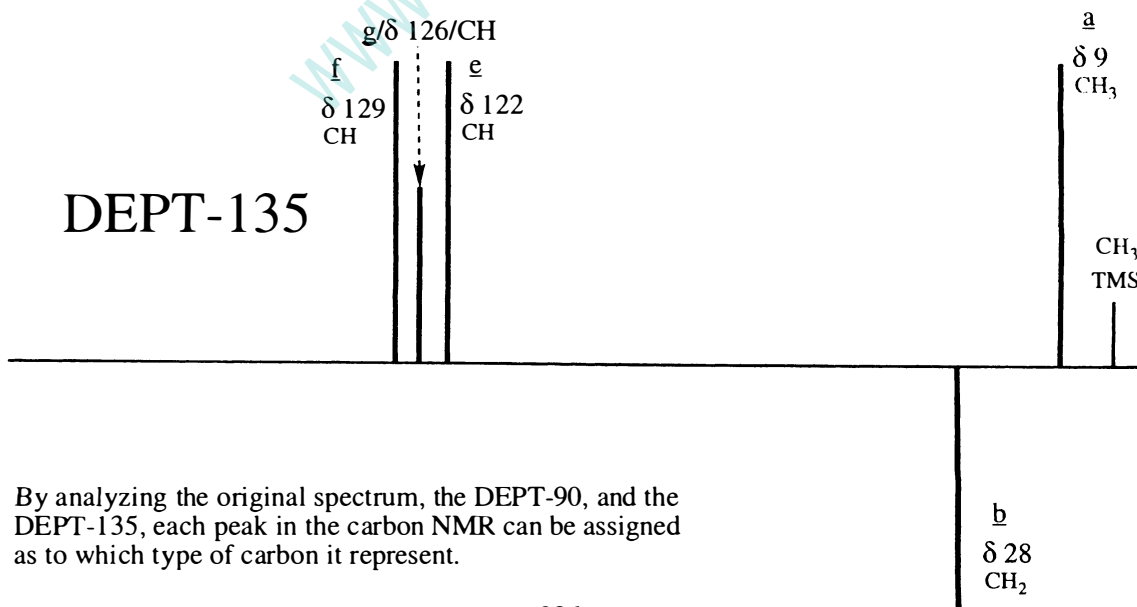
By analyzing the original spectrum, the DEPT-90, and the DEPT-135, each peak in the carbon NMR can be assigned as to which type of carbon it represent.

13-29

Since allyl bromide was the starting material, it is reasonable to expect the allyl group to be present in the impurity: the triplet at 115 is a $=CH_2$, the doublet at 138 is $=CH-$, and the triplet at 63 is a deshielded aliphatic CH_2; assembling the pieces forms an allyl group. The formula has changed from C_3H_5Br to C_3H_6O, so OH has replaced the Br.

$$H_2C=CH-CH_2OH$$

δ 115
triplet

δ 138
doublet

δ 63
triplet
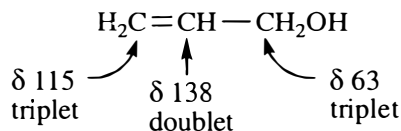
Allyl bromide is easily hydrolyzed by water, probably an S_N1 process.

$$H_2C=CH-CH_2Br \xrightarrow{H_2O} H_2C=CH-CH_2OH + HBr$$
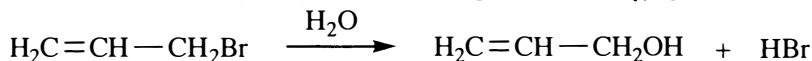
13-30
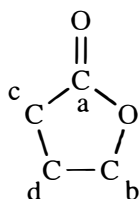
a = δ 180, singlet
b = δ 70, triplet
c = δ 28, triplet
d = δ 22, triplet

Two elements of unsaturation in $C_4H_6O_2$, one of which is a carbonyl, and no evidence of a C=C, prove that a ring must be present.

13-31
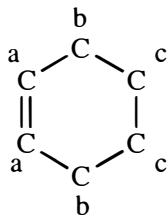
a = δ 128, doublet
b = δ 25, triplet
c = δ 23, triplet

Two elements of unsaturation in C_6H_{10} must be a C=C and a ring. Only three peaks indicates symmetry.

Using PBr_3 instead of $H_2SO_4/NaBr$ would give a higher yield of bromocyclohexane.

13-32   Compound 2

Mass spectrum: the molecular ion at m/z 136 shows a peak at 138 of about equal height, indicating a bromine atom is present: 136 – 79 = 57. The fragment at m/z 57 is the base peak; this fragment is most likely a butyl group, C_4H_9, so a likely molecular formula is C_4H_9Br.
Infrared spectrum: Notable for the absence of functional groups: no O—H, no N—H, no =C—H, no C=C, no C=O ⇒ most likely an alkyl bromide.
NMR spectrum: The 6H doublet at δ 1.0 suggests two CH_3's split by an adjacent H—an isopropyl group. The 2H doublet at δ 3.2 is a CH_2 between a CH and the Br.

Putting the pieces together gives isobutyl bromide.

$$Br-CH_2-CH \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$
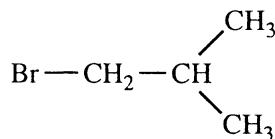
13-33

The formula $C_9H_{11}Br$ indicates four elements of unsaturation, just enough for a benzene ring.

Here is the most accurate method for determining the number of protons per signal from integration values *when the total number of protons is known.* Add the integration heights: 4.4 cm + 13.0 cm + 6.7 cm = 24.1 cm. Divide by the total number of hydrogens: 24.1 cm ÷ 11H = 2.2 cm/H. Each 2.2 cm of integration height = 1H, so the ratio of hydrogens is 2 : 6 : 3.

The 2H singlet at δ 7.1 means that only two hydrogens remain on the benzene ring, that is, it has 4 substituents. The 6H singlet at δ 2.3 must be two CH_3's on the benzene ring in identical environments. The 3H singlet at δ 2.2 is another CH_3 in a slightly different environment from the first two. Substitution of the three CH_3's and the Br in the most symmetric way leads to the structures on the next page.

13-33 continued

a   b
H   CH₃

c
CH₃ ──── Br

H   CH₃
a   b
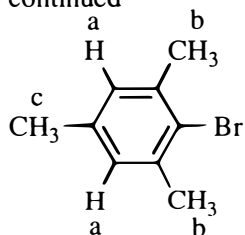
a = δ 7.1 (singlet, 2H)
b = δ 2.3 (singlet, 6H)
c = δ 2.2 (singlet, 3H)

a second structure is also possible although it is less likely because the Br would probably deshield the Hs labeled "a" to about 7.3-7.4

b H₃C   H a

c
CH₃ ──── Br

b H₃C   H a
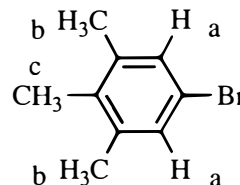
13-34 The numbers in italics indicate the number of peaks in each signal.

(a)   CH₃──CH₂──CCl₂──CH₃
       3   *4*   *1*

(b)   CH₃──CH──OH⁷   (assume OH exchanging rapidly—no splitting)
            | *1*
            CH₃
            2

(c)   *10*
      CH₃──CH──CH₃
            | *2*
            CH₃

(d) H──⟨benzene ring with H, H, CH₃, H, H⟩──CH₃
              1

      1
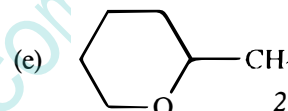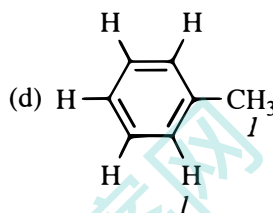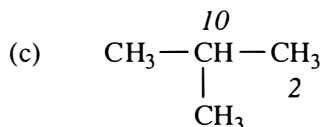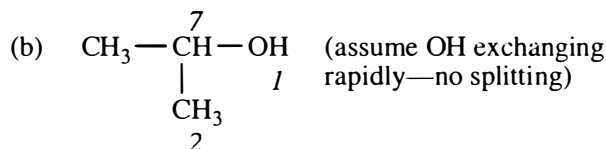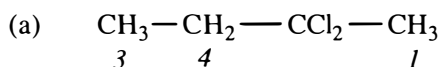
(all of these benzene H's are accidentally equivalent and do not split each other)

(e) ⟨tetrahydropyran ring⟩──CH₃
                            2

13-35 Consult Appendix 1 in the text for chemical shift values. *Your predictions should be in the given range, or within 0.5 ppm of the given value.*

(a) ⟨benzene⟩──H   all at δ 7.2

(b) ⟨cyclohexane with H, H⟩   all at δ 1.3

(c)   δ 1.6
      CH₃──O──CH₂──CH₂──CH₂Cl
      δ 3.4   δ 3.8   δ 3.2

(d)   CH₃──CH₂──C≡C──H
       δ 1.2   δ 2.2   δ 2.5

(e)   O
                 ‖
      CH₃──CH₂──C──CH₃
      δ 1.0   δ 2.5   δ 2.0

(f)   CH₃ δ 4.3   δ 2-5
          ＼
           CH──O──CH₂──CH₂──OH
          ╱   δ 3.8   δ 3.8
      CH₃
      δ 0.9

(g)   O
                 ‖
      H──⟨benzene ring⟩──C──H
      δ 8.0   δ 9-10

      H   H
      δ 7.5   δ 8.0
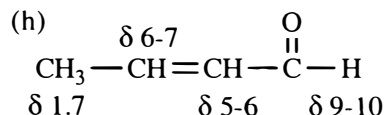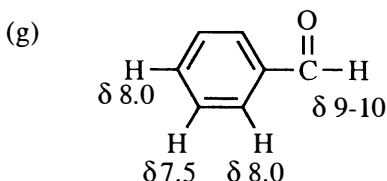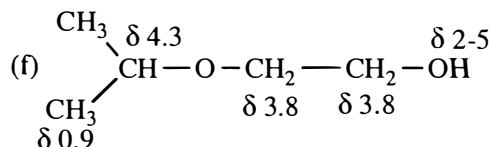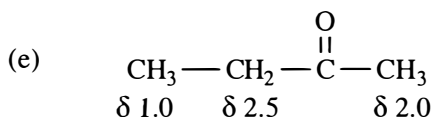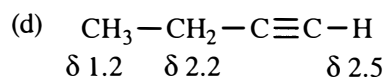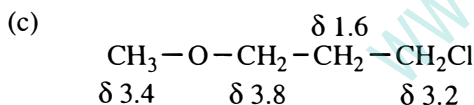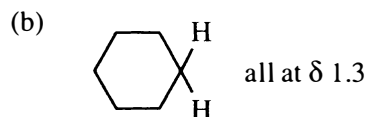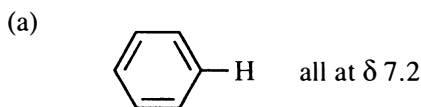
The C=O has its strongest deshielding effect at the adjacent H (ortho) and across the ring (para). The remaining H (meta) is less deshielded.

(h)   δ 6-7   O
                        ‖
      CH₃──CH═CH──C──H
      δ 1.7   δ 5-6   δ 9-10

288

13-35 continued

(i)

$$HOOC - CH_2 - CH_2 - C(=O) - O - CH(CH_3)_2 \leftarrow \delta 4.0$$

δ 10-12 δ 2.3 δ 2.3   CH$_3$ δ 1.1

(j) δ 1.3 δ 4.5 δ 1.3 δ 1.7 allylic

(k) δ 1.4 δ 7.2 δ 2.5 benzylic

(l) δ 6.0 δ 7.2 δ 3.0 allylic and benzylic

13-36

$$CH_3 - \underset{|}{\overset{a}{CH}} - CH_3$$
  $\quad\quad$ OH (b), c CH$_3$ groups

a = δ 4.0 (septet, 1H)
b = δ 2.5 (broad singlet, 1H) (rapidly exchanging)
c = δ 1.2 (doublet, 6H)
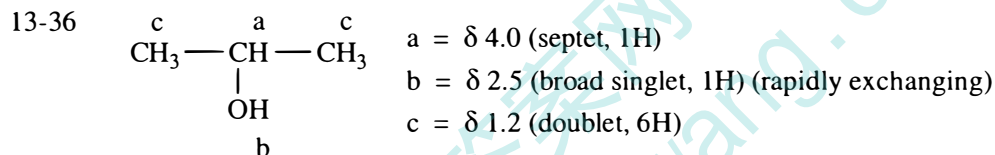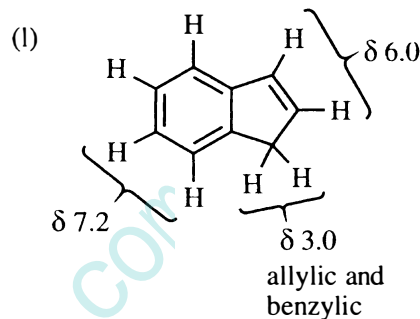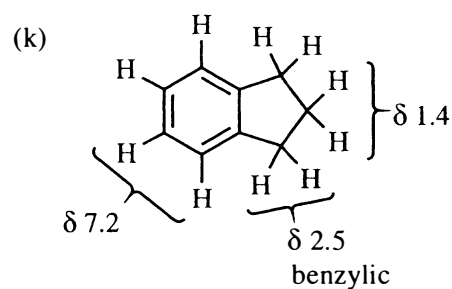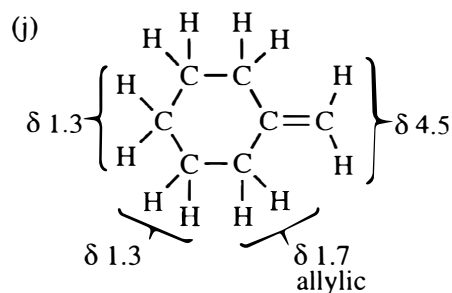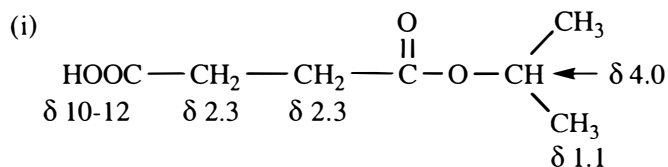
13-37

(a) The chemical shift *in ppm* would not change: δ 4.00.

(b) Coupling constants do not change with field strength: J = 7 Hz, regardless of field strength.

(c) At 60 MHz, δ 4.00 = 4.00 ppm = $(4.00 \times 10^{-6}) \times (60 \times 10^6 \text{ Hz})$ = 240 Hz

The signal is 240 Hz downfield from TMS in a 60 MHz spectrum.

At 300 MHz, $(4.00 \times 10^{-6}) \times (300 \times 10^6 \text{ Hz})$ = 1200 Hz

The signal is 1200 Hz downfield from TMS in a 300 MHz spectrum.
Necessarily, 1200 Hz is exactly 5 times 240 Hz because 300 MHz is
exactly 5 times 60 MHz. They are directly proportional.

13-38

Phenyl—$\overset{c}{CH_2} - \overset{b}{CH_2} - O - \overset{O}{\overset{||}{C}} - \overset{d}{CH_3}$

a = δ 7.2-7.3 (multiplet, 5H)
b = δ 4.3 (triplet, 2H)
c = δ 2.9 (triplet, 2H)
d = δ 2.0 (singlet, 3H)

13-39

(a)

$$CH_3 - O - CH_2CH_3$$
b   a   c

b 3H

c 3H

a 2H

TMS

δ (ppm)

(b)

$$(CH_3)_2CH - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$
c   a   b

b 3H

c 6H

a 1H

(To show the pattern
of peaks, this multiplet
is larger than it would
appear on a real spectrum.)

TMS

δ (ppm)

(c)

$$ClCH_2CH_2CH_2Cl$$
a   b   a

a 4H

b 2H

TMS

δ (ppm)

290

13-39 continued

(d)

b d
H NH₂

a
H

c
H

H NH₂
b d

The NH₂ group
shields nearby
protons on benzene.

a
1H

b
2H

c
1H

d
4H
very
broad
and
variable

TMS

10 9 8 7 6 5 4 3 2 1 0
δ (ppm)

(e)

a H   H b   d
                        CH₃

O₂N—⟨ ⟩—O—CH c

a H   H b   CH₃
                        d
              c
              1H

a
2H

b
2H

(To show the pattern
of peaks, this multiplet
is larger than it would
appear on a real spectrum.)

d
6H

TMS

10 9 8 7 6 5 4 3 2 1 0
δ (ppm)

(f)

Signal (a) is split into a quartet because of the adjacent
CH₃ with J = 7 Hz. Each of those peaks is then split
into a doublet because of the coupling with the trans
H, J = 15 Hz. This is called a doublet of quartets, and
it is drawn here as two quartets. In a real spectrum,
these peaks would overlap and would not be a clean
doublet of quartets. See the splitting tree for problem
13-15.

a H   O
          ‖
d   c
H₃C   CH₃

b H

c
3H

d
3H

a
1H

b

TMS

10 9 8 7 6 5 4 3 2 1 0
δ (ppm)

291

13-40

(a) The NMR of 1-bromopropane would have three sets of signals, whereas the NMR of 2-bromopropane would have only two sets (a septet and a doublet, the typical isopropyl pattern).

(b) Each spectrum would have a methyl singlet at δ 2. The left structure would show an ethyl pattern (a 2H quartet and a 3H triplet), whereas the right structure would exhibit an isopropyl pattern (a 1H septet and a 6H doublet).

(c) The most obvious difference is the chemical shift of the CH_3 singlet. In the compound on the left, the CH_3 singlet would appear at δ 2.1, while the compound on the right would show the CH_3 singlet at δ 3.8. Refer to the solution of 13-22 for the spectrum of the second compound.

(d) The splitting and integration for the peaks in these two compounds would be identical, so the chemical shift must make the difference. As described in text section 13-5B, the alkyne is not nearly as deshielding as a carbonyl, so the protons in pent-2-yne would be farther upfield than the protons in butan-2-one, by about 0.5 ppm. For example, the methyl on the carbonyl would appear near δ 2.1 while the methyl on the alkyne would appear about δ 1.7.

13-41 The multiplicity in the off-resonance decoupled spectrum is given below each chemical shift: s = singlet; d = doublet; t = triplet; q = quartet. It is often difficult to predict exact chemical shift values; your predictions should be in the right vicinity. There should be no question about the multiplicity and DEPT spectra, however.
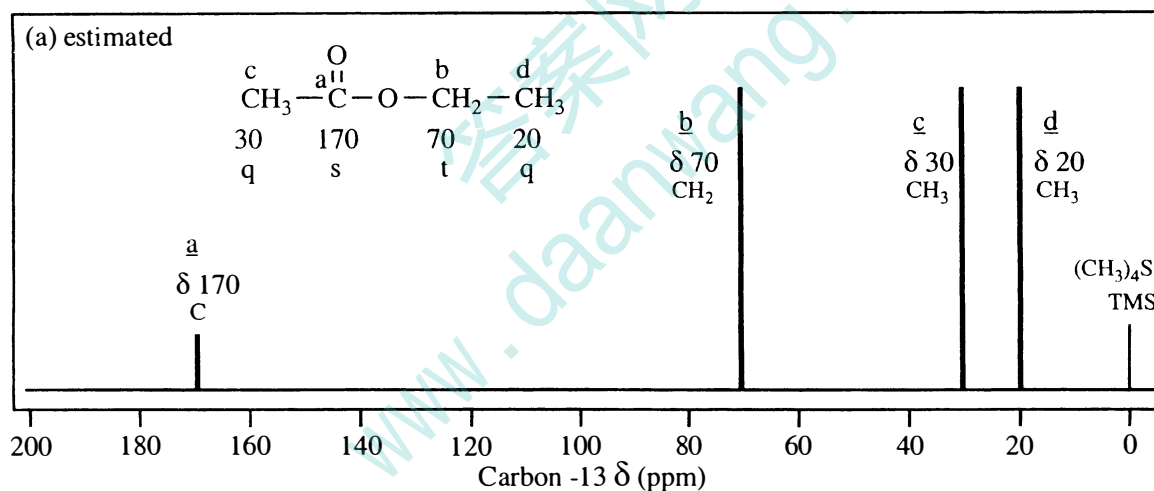
The DEPT-90 spectrum for ethyl acetate would have no peaks because there are no CH groups.

13-41 continued

(b) actual values

b   a   c
H₂C = CH — CH₂Cl
118 134   45
t   d   t

b
δ 118
CH₂

c
δ 45
CH₂

a
δ 134
CH

(CH₃)₄Si
TMS

Carbon -13 δ (ppm)
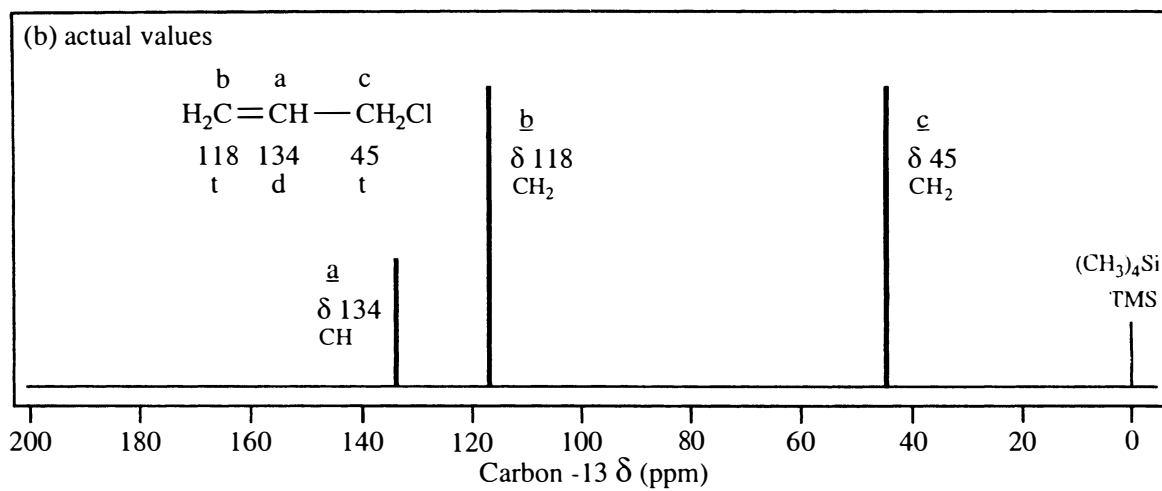
DEPT-90

CH

DEPT-135

CH

CH₃

CH₂

CH₂

(c) actual values

Carbons b and c
are accidentally
equivalent.

b,c
δ 129
CH

d
127
d

c
b
a
139/s
H₂ H₂
C — C — Br
e   f
39   33
t   t

e
δ 39
CH₂

f
δ 33
CH₂

a
δ 139
C

d
δ 127
CH

c
129
d

b
129
d

(CH₃)₄Si
TMS

Carbon -13 δ (ppm)
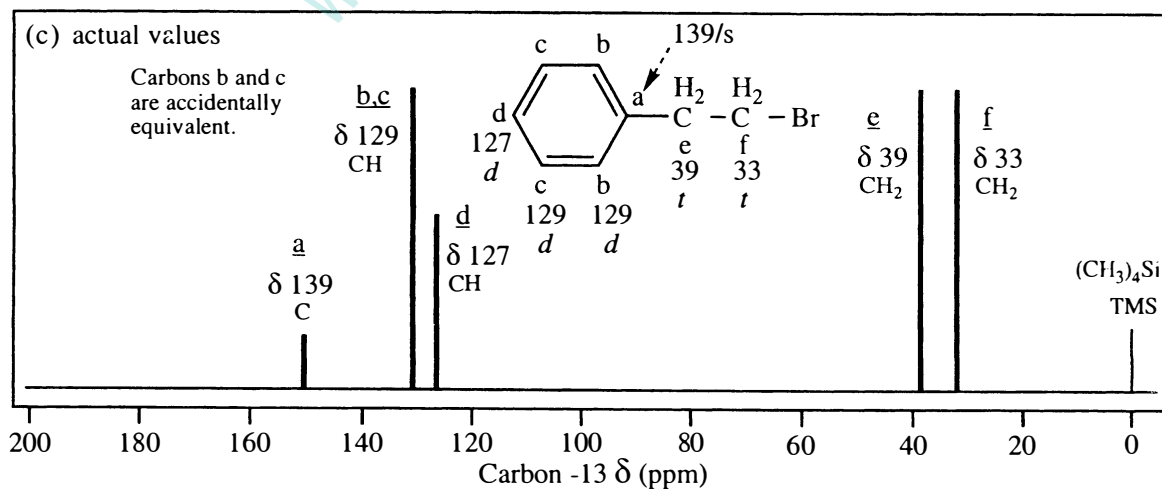
DEPT-90 and DEPT-135 on next page

13-41 (c) continued

DEPT-90 $\quad$ CH $\quad$| CH

DEPT-135 $\quad$ CH $\quad$| CH $\qquad$ CH$_3$ | $\qquad$ CH$_2$
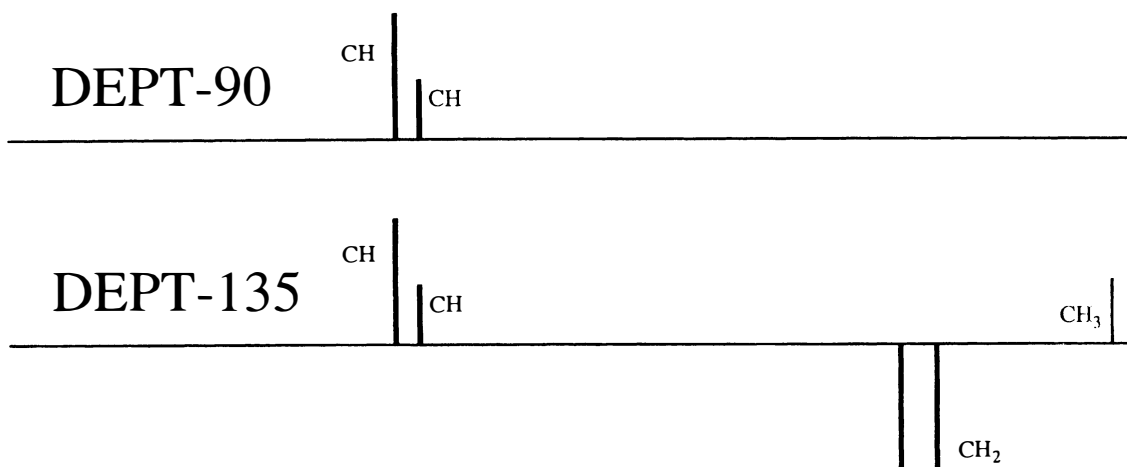
13-42 The multiplicity of the peaks in this off-resonance decoupled spectrum show two different CH's and a CH$_3$. There is only one way to assemble these pieces with three chlorines.

$$\delta\,20 \longrightarrow \text{CH}_3 - \overset{\overset{\text{Cl}}{|}}{\underset{\uparrow}{\text{CH}}} - \overset{\overset{\text{Cl}}{|}}{\underset{\underset{\text{Cl}}{|}}{\text{CH}}}$$

δ 20 → CH$_3$ — CH — CH
q

δ 60
d

δ 75
d
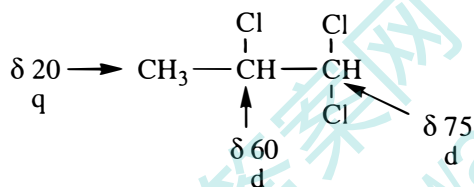
13-43 There is no evidence for vinyl hydrogens, so the double bond is gone. Integration gives eight hydrogens, so the formula must be C$_4$H$_8$Br$_2$, and the four carbons must be in a straight chain because the starting material was but-2-ene. From the integration, the four carbons must be present as one CH$_3$, one CH, and two CH$_2$ groups. The methyl is split into a doublet, so it must be adjacent to the CH. The two CH$_2$ groups must follow in succession, with two bromine atoms filling the remaining valences. (The spectrum is complex because the asymmetric carbon atom causes the neighboring protons to be diastereotopic.)

$$\text{H} - \overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}} - \overset{\overset{\text{Br}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}} - \overset{\overset{\text{H}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}} - \overset{\overset{\text{Br}}{|}}{\underset{\underset{\text{H}}{|}}{\text{C}}} - \text{H}$$

$\qquad$ d $\quad$ a $\quad$ c $\quad$ b

a = δ 4.3 (sextet, 1H)
b = δ 3.6 (triplet, 2H)
c = δ 2.3 (multiplet, 2H)
d = δ 1.7 (doublet, 3H)
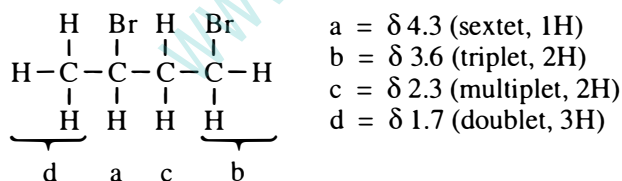
13-44 There is no evidence for vinyl hydrogens, so the compound must be a small, saturated, oxygen-containing molecule. Starting upfield (toward TMS), the first signal is a 3H triplet; this must be a CH$_3$ next to a CH$_2$. The CH$_2$ could be the signal at δ 1.5, but it has six peaks: it must have five neighboring hydrogens, a CH$_3$ on one side and a CH$_2$ on the other side. The third carbon must therefore be a CH$_2$; its signal is a quartet at δ 3.6, split by a CH$_2$ and an OH. To be so far downfield, the final CH$_2$ must be bonded to oxygen. The remaining 1H signal must be from an OH. The compound must be propan-1-ol.
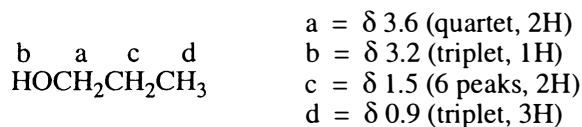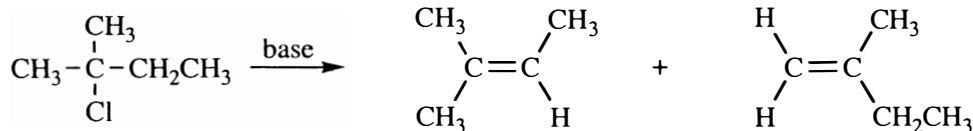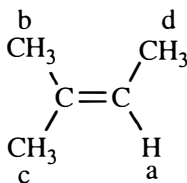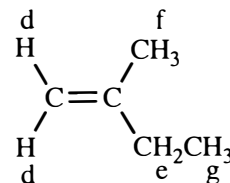
b $\quad$ a $\quad$ c $\quad$ d
HOCH$_2$CH$_2$CH$_3$

a = δ 3.6 (quartet, 2H)
b = δ 3.2 (triplet, 1H)
c = δ 1.5 (6 peaks, 2H)
d = δ 0.9 (triplet, 3H)

294

13-45

(a)

a = δ 5.2 (quartet, 1H)
b = δ 1.7 (singlet, 3H)
c = δ 1.6 (singlet, 3H)
d = δ 1.5 (doublet, 3H)

d = δ 4.7 (singlet, 2H)
e = δ 2.0 (quartet, 2H)
f = δ 1.7 (singlet, 3H)
g = δ 1.0 (triplet, 3H)

(b) With NaOH as base, the more highly substituted alkene, Isomer A, would be expected to predominate -- the Zaitsev Rule. With KO-*t*-Bu as a hindered, bulky base, the less substituted alkene, Isomer B, would predominate (the Hofmann product).

13-46 "Nuclear waste" is comprised of radioactive products from either nuclear reactions, for example, from electrical generating stations powered by nuclear reactors, or residue from medical or scientific studies using radioactive nuclides as therapeutic agents (like iodine for thyroid treatment) or as molecular tracers (carbon-14, tritium H-3, phosphorus-32, nitrogen-15, and many others). The physical technique of *nuclear* magnetic resonance neither uses nor generates any radioactive elements, and does not generate "nuclear waste". (Some people assume that the medical application of NMR, medical resonance imaging or MRI, purposely dropped the word "nuclear" from the technique to avoid the confusion between "nuclear" and "radioactive".)

13-47

Mass spectrum: The molecular ion of m/z 117 suggests the presence of an odd number of nitrogens.
Infrared spectrum: No NH or OH appears. Hydrogens bonded to both sp^2 and sp^3 carbon are indicated around 3000 cm^{-1}. The characteristic C≡N peak appears at 2250 cm^{-1} and aromatic C=C is suggested by the peak at 1600 cm^{-1}.
NMR spectrum: Five aromatic protons are shown in the NMR at δ 7.3. A CH$_2$ singlet appears at δ 3.7. Assemble the pieces:
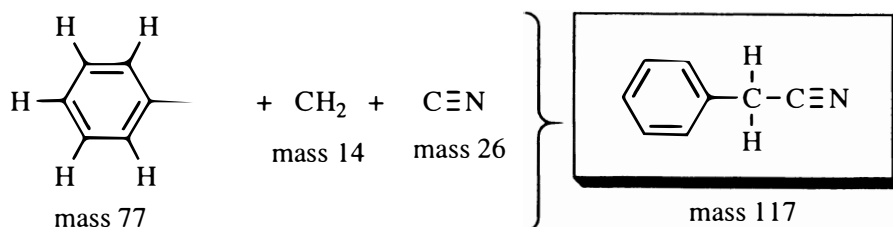
13-48 This is a challenging problem, despite the molecule being relatively small.

Mass spectrum: The molecular ion at 96 suggests no Cl, Br, or N. The molecule must have seven carbons or fewer.

Infrared spectrum: The dominant functional group peak is at 1685 cm^{-1}, a carbonyl that is conjugated with C=C (lower wavenumber than normal, very intense peak). The presence of an oxygen and a molecular ion of 96 lead to a formula of C_6H_8O, with three elements of unsaturation, a C=O and one or two C=C.

Carbon NMR spectrum: The six peaks show, by chemical shift, one carbonyl carbon (196), two alkene carbons (129, 151), and three aliphatic carbons (23, 26, 36). By off-resonance decoupling multiplicity, the groups are: three CH_2 groups, two alkene CH groups, and carbonyl.

Since the structure has one carbonyl and only two alkene carbons, the third element of unsaturation must be a ring.

$$C=C \underset{H}{\overset{H}{\diagdown}} \overset{C=O}{\diagup} \qquad CH_2 + CH_2 + CH_2 + 1 \text{ ring}$$
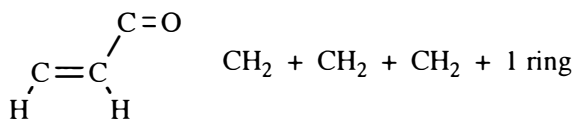
Since the structure has no methyl group, and no $H_2C=$, all of the carbons must be included in the ring. The only way these pieces can fit together is in cyclohex-2-enone. Notice that the proton NMR was unnecessary to determine the structure, fortunately, since the HNMR was not easily interpreted except for the two alkene hydrogens; the hydrogen on carbon-2 appears as the doublet at 6.0.
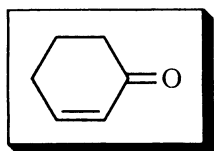
cyclohex-2-enone
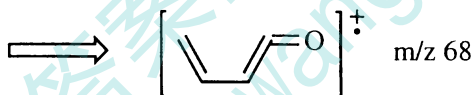
The mystery mass spec peak at m/z 68 comes from a fragmentation that will be discussed later; it is called a retro-Diels-Alder fragmentation.

13-49 The key to the carbon NMR lies in the symmetry of these structures.

ortho-xylene　　*meta*-xylene　　*para*-xylene
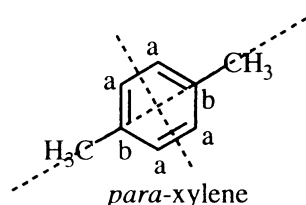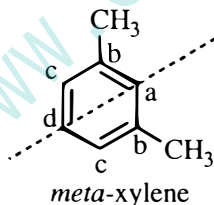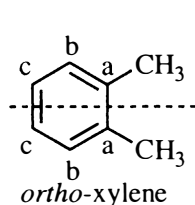
(a) In each molecule, the methyl carbons are equivalent, giving one signal in the CNMR. Considering the ring carbons, the symmetry of the structures shows that *ortho*-xylene would have 3 carbon signals from the ring (total of 4 peaks), *meta*-xylene would have 4 carbon signals from the ring (total of 5 peaks), and *para*-xylene would have only 2 carbon signals from the ring (total of 3 peaks). These compounds would be instantly identifiable simply by the number of peaks in the carbon NMR.

(b) The proton NMR would be a completely different problem. Unless the substituent on the benzene ring is moderately electron-withdrawing or donating, the ring protons absorb at roughly the same position. A methyl group has essentially no electronic effect on the ring hydrogens, so while the *para* isomer would give a clean singlet because all its ring protons are equivalent, the *ortho* and *meta* isomers would have only slightly broadened singlets for their proton signals. (Only a very high field NMR, 500 MHz or higher, would be able to distinguish these isomers in the proton NMR.)

13-50 (a), (b) and (c) The six isomers are drawn here. Below each structure is the number of proton signals and the number of carbon signals. (Note that splitting patterns would give even more clues in the proton NMR.)

1xH	3xH*	2xH	2xH	2xH	5xH
1xC	3xC	3xC	2xC	2xC	4xC
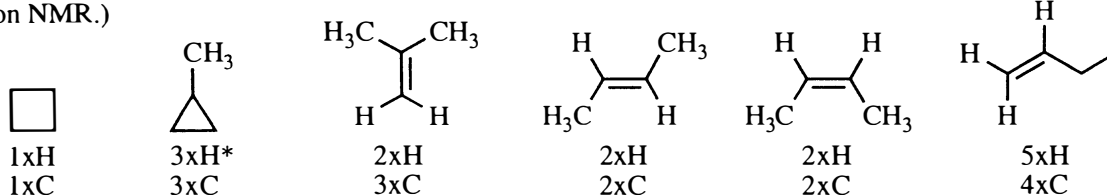
*Rings always present challenges in stereochemistry. When viewed in three dimensions, it becomes apparent that the two hydrogens on a CH_2 are not equivalent: on each CH_2, one H is cis to the methyl and one H is trans to the methyl. These are diastereotopic protons. A more correct answer to part (b) would be four types of protons; whether all four could be distinguished in the NMR is a harder question to answer. For the purpose of this problem, whether it is 3 or 4 types of H does not matter because either one, in combination with three types of carbon, will distinguish it from the other 5 structures.
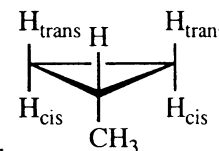
(d) Two types of H and three types of C can be only one isomer: 2-methylpropene (isobutylene). (The only isomers that would not be distinguished from each other would be *cis*- and *trans*-but-2-ene.)

13-51 For DEPT to be useful in distinguishing isomers, there should be different numbers of CH_3, CH_2, CH, and C signals in the carbon NMRs.

A	**B**	**C**
6 C signals	5 C signals	5 C signals
one CH_3 peak	one CH_3 peak	one CH_3 peak
four CH_2 peaks	two CH_2 peaks	two CH_2 peaks
one CH peak	two CH peaks	one CH peak
		one C peak
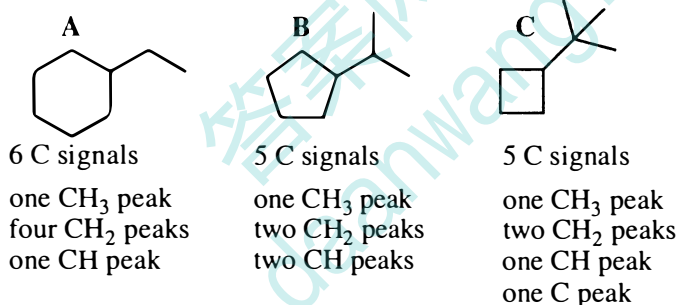
A carbon NMR could not distinguish isomers **B** and **C**, and if there is any overlap in the signals, it might have a difficult time distinguishing **A**. Fortunately, the patterns that would appear in the DEPT-90 would distinguish **B** (two CH peaks up) from the other two (1 CH peak up), and the DEPT-135 would instantly distinguish **A** (4 CH_2 peaks down) from **C** (2 CH_2 peaks down).

13-52

(a) MS or IR could not easily distinguish these isomers: same molecular weight and same functional group. They would give dramatically different proton and carbon NMRs however.

2 singlets in HNMR
3 singlets in CNMR

4 signals, all with splitting, in HNMR
4 singlets in CNMR
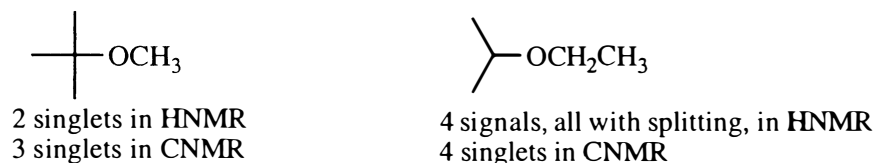
13-52 continued

(b) The only technique that would not readily distinguish these isomers would be MS because they have the same molecular weight and would have similar, though not identical, fragmentation patterns.
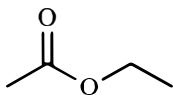
IR: C=O about 1730 cm^{-1}
HNMR: methyl singlet and ethyl pattern
CNMR: ester C=O about δ 170
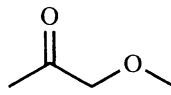
IR: C=O about 1710 cm^{-1}
HNMR: 3 singlets
CNMR: ketone C=O about δ 200

(c) The big winner here is MS: they have different molecular weights, plus the Cl has the two isotope peaks that make a Cl atom easily distinguished. The other techniques would have minor differences and would require having a detailed table of frequencies or chemical shifts to determine which is which.
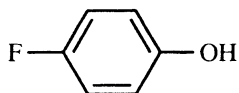
M$^+$ = m/z 112
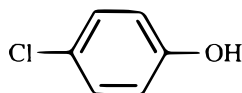
M$^+$ = m/z 128, 130

CHAPTER 14—ETHERS, EPOXIDES AND SULFIDES

14-1
The four solvents decrease in polarity in this order: water, ethanol, ethyl ether, and dichloromethane. The three solutes decrease in polarity in this order: sodium acetate, 2-naphthol, and naphthalene. The guiding principle in determining solubility is, "Like dissolves like." Compounds of similar polarity will dissolve (in) each other. Thus, sodium acetate will dissolve in water, will dissolve only slightly in ethanol, and will be virtually insoluble in ethyl ether and dichloromethane. 2-Naphthol will be insoluble in water, somewhat soluble in ethanol, and soluble in ether and dichloromethane. Naphthalene will be insoluble in water, partially soluble in ethanol, and soluble in ethyl ether and dichloromethane. (Actual solubilities are difficult to predict, but you should be able to predict *trends*.)

14-2
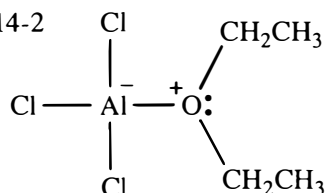
Oxygen shares one of its electron pairs with aluminum; oxygen is the Lewis base, and aluminum is the Lewis acid. An oxygen atom with three bonds and one unshared pair has a positive formal charge. An aluminum atom with four bonds has a negative formal charge.

14-3

The crown ether has two effects on $KMnO_4$: first, it makes $KMnO_4$ much more soluble in benzene; second, it holds the potassium ion tightly, making the permanganate more available for reaction. Chemists call this a "naked anion" because it is not complexed with solvent molecules.

18-crown-6
a "crown ether"

$+ KMnO_4$ $\xrightarrow{benzene}$
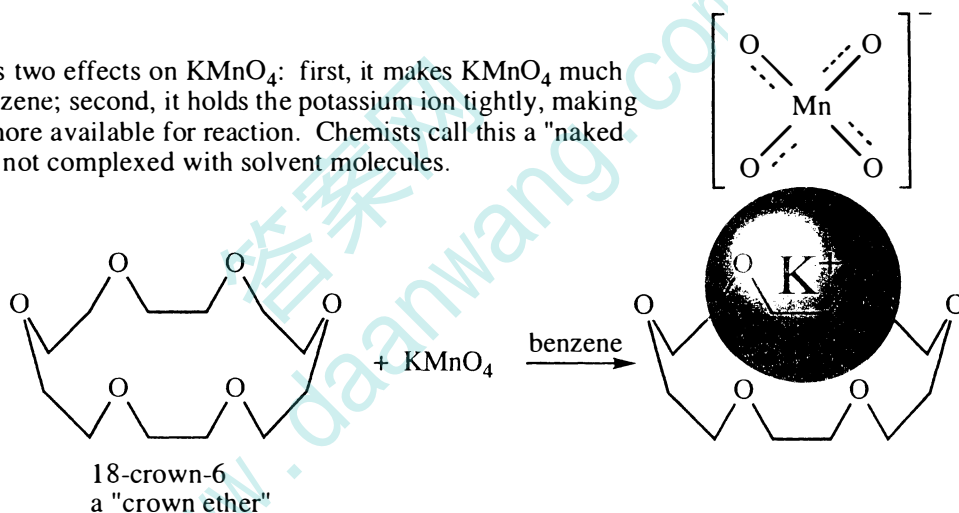
Please see the note on p. 13 of this Solutions Manual regarding placement of position numbers.

14-4 IUPAC name first; then common name (see Appendix 1 in this Solutions Manual for a summary of IUPAC nomenclature)

(a) methoxycyclopropane; cyclopropyl methyl ether
(b) 2-ethoxypropane; ethyl isopropyl ether
(c) 1-chloro-2-methoxyethane; 2-chloroethyl methyl ether
(d) 2-ethoxy-2,3-dimethylpentane; no common name
(e) 2-*t*-butoxybutane; *sec*-butyl *t*-butyl ether
(f) *trans*-2-methoxycyclohexan-1-ol; no common name

14-5

(a) $\xrightarrow{H^+}$ $+ \ 2 \ H_2O$
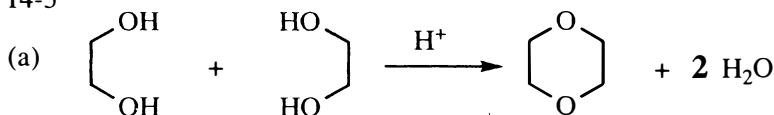
The alcohol is ethane-1,2-diol; the common name is ethylene glycol.

299

14-5 continued

(b)
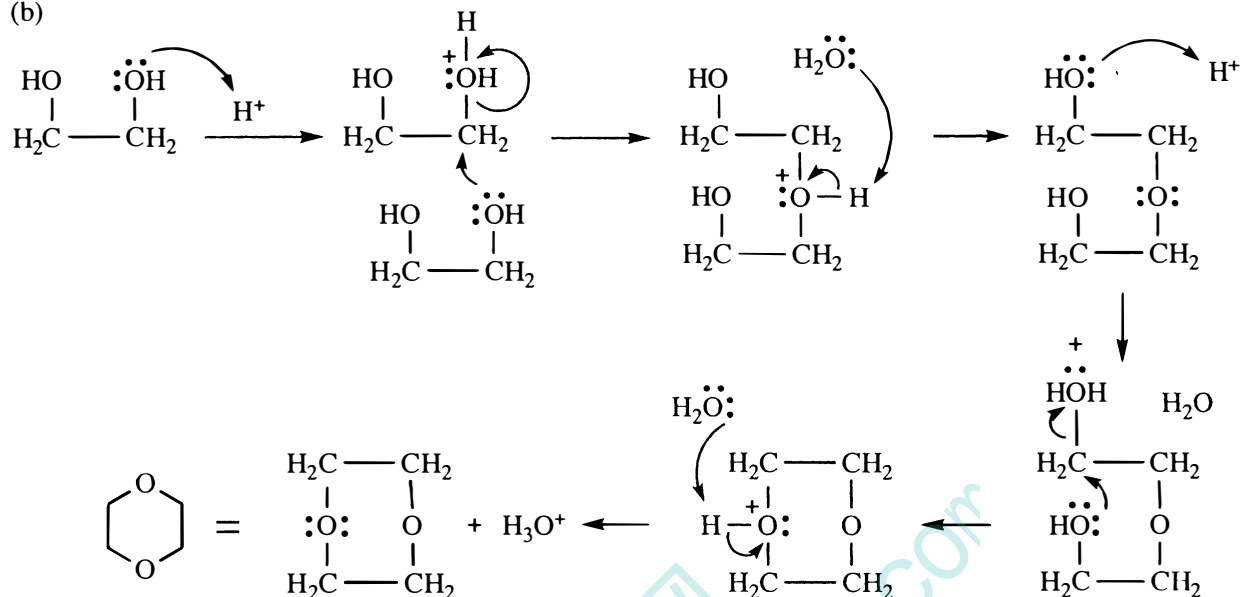
The mechanism shows that the acid catalyst is regenerated at the end of the reaction.

14-6
(a) dihydropyran
(b) 2-chloro-1,4-dioxane
(c) 3-isopropylpyran
(d) *trans*-2,3-diethyloxirane; *trans*-3,4-epoxyhexane; *trans*-3-hexene oxide
(e) 3-bromo-2-ethoxyfuran
(f) 3-bromo-2,2-dimethyloxetane

14-7
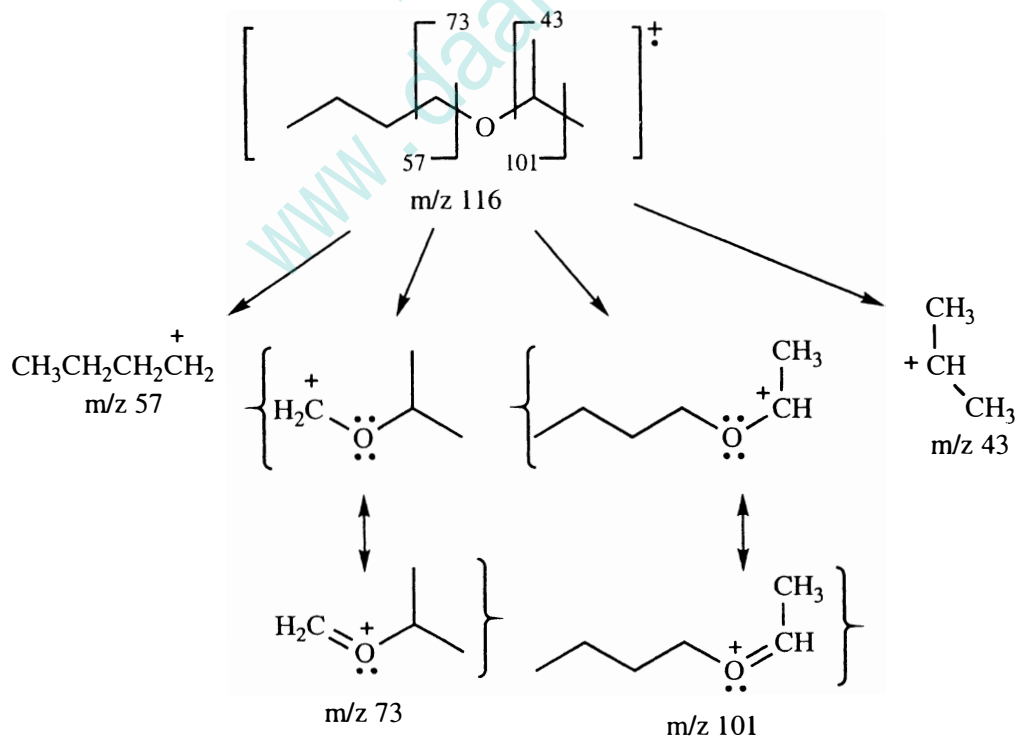
14-8 S_N2 reactions, including the Williamson ether synthesis, work best when the nucleophile attacks a 1° or methyl carbon. Instead of attempting to form the bond from oxygen to the 2° carbon on the ring, form the bond from oxygen to the 1° carbon of the butyl group.

The OH must first be transformed into a good leaving group: either a tosylate, or one of the halides (not fluoride).

14-9

(a)

(b)

(c)

(d) $CH_3CH_2CH_2OH \xrightarrow{Na} \xrightarrow{CH_3CH_2Br} CH_3CH_2CH_2OCH_2CH_3$

$CH_3CH_2OH \xrightarrow{Na} \xrightarrow{CH_3CH_2CH_2Br} CH_3CH_2CH_2OCH_2CH_3$

(e)

14-10

(a) (1)

(2)

14-10 continued

(b) (1)

(2)
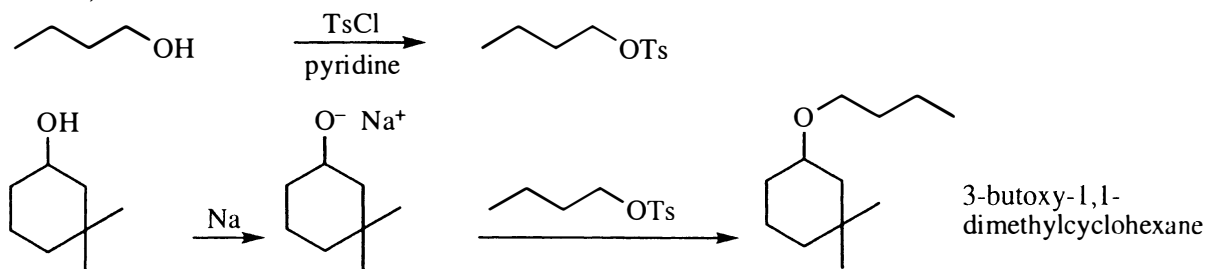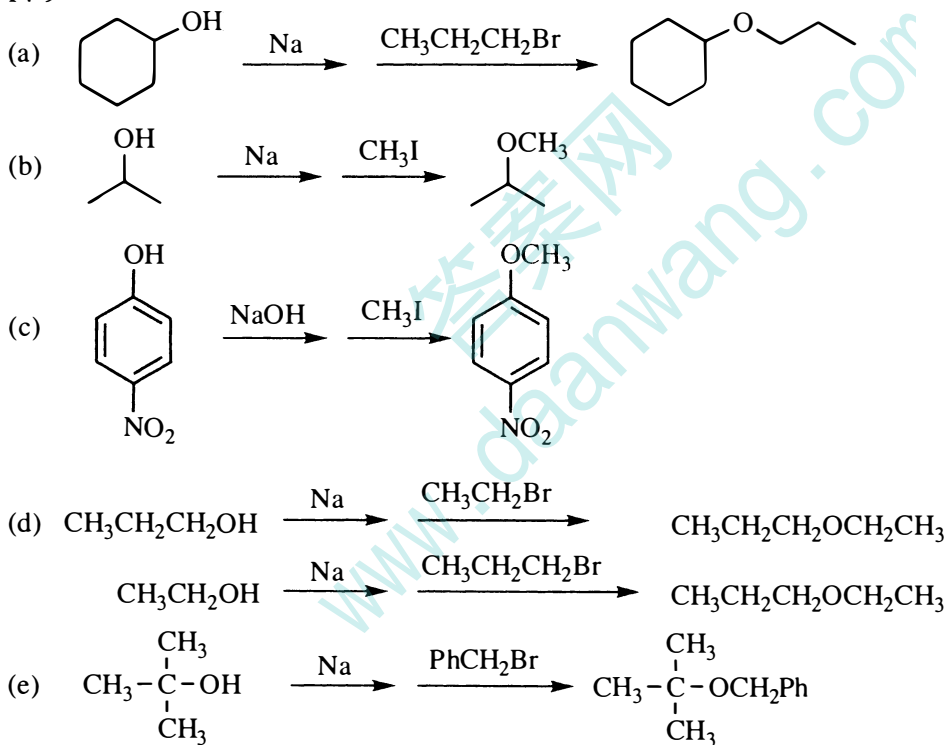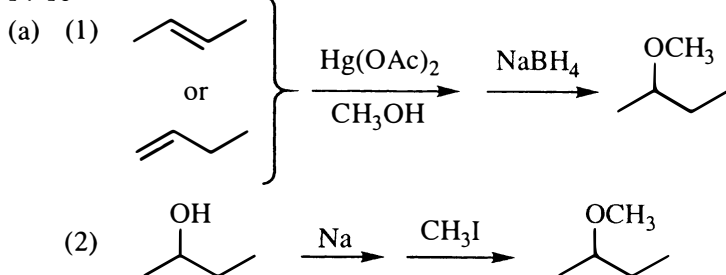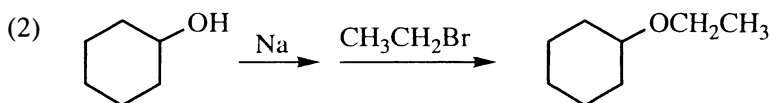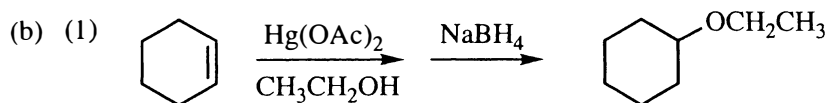
(c) (1) Alkoxymercuration is not practical here; the product does not have Markovnikov orientation.

(2)

(d) (1)

(2)

(e) (1)
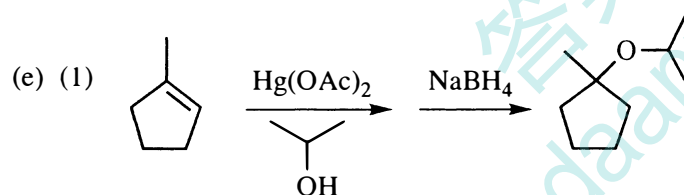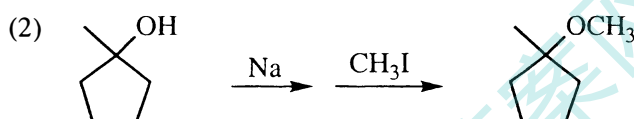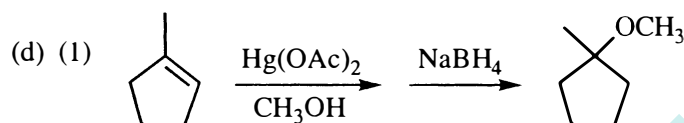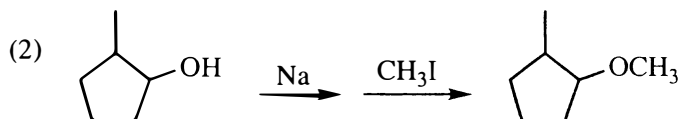
(2) Williamson ether synthesis would give a poor yield of product as the halide is on a 2° carbon.

(f) (1)
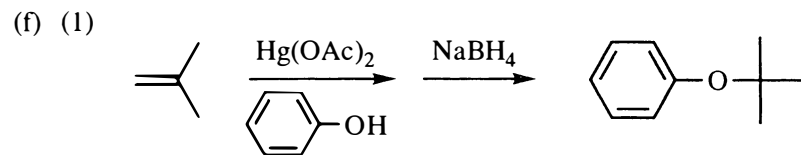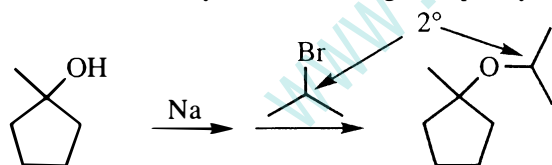
(2) Williamson ether synthesis is not feasible here. S_N2 does not work on either a benzene or a 3° halide.

14-11 An important principle of synthesis is to avoid mixtures of isomers wherever possible; minimizing separations increases recovery of products. Bimolecular dehydration is a random process. Heating a mixture of ethanol and methanol with acid will produce all possible combinations: dimethyl ether, ethyl methyl ether, and diethyl ether. This mixture would be troublesome to separate.

14-12

Ether formation
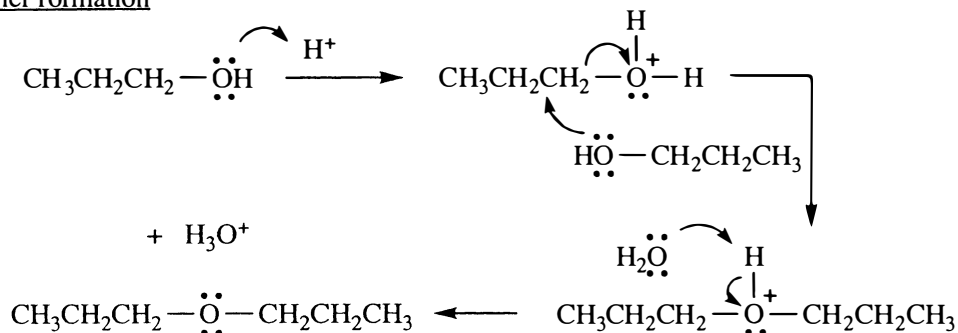
Dehydration
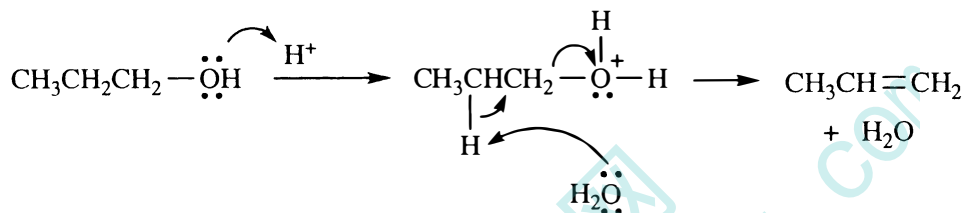
Remember $\Delta G = \Delta H - T\Delta S$? Thermodynamics of a reaction depend on the sign and magnitude of ΔG. As temperature increases, the entropy term grows in importance. In ether formation, the ΔS is small because two molecules of alcohol give one molecule of ether plus one molecule of water—no net change in the number of molecules. In dehydration, however, one molecule of alcohol generates one molecule of alkene plus one molecule of water—a large increase in entropy. So $T\Delta S$ is more important for dehydration than for ether formation. As temperature increases, the competition will shift toward more dehydration.

14-13

(a) This symmetrical ether at 1° carbons could be produced in good yield by bimolecular dehydration.

(b) This unsymmetrical ether could not be produced in high yield by bimolecular dehydration. Williamson synthesis would be preferred.
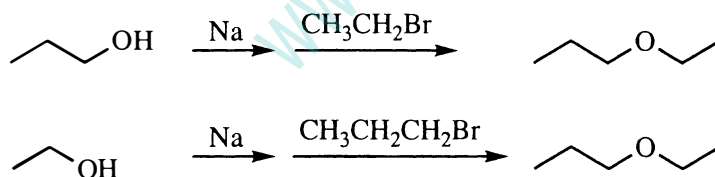
(c) Even though this ether is symmetrical, both carbons are 2°, so bimolecular dehydration would give low yields. Unimolecular dehydration to give alkenes would be the dominant pathway. Alkoxymercuration-demercuration is the preferred route.

14-14

14-15

(a) $\xrightarrow{HBr}$ —Br + Br—CH$_2$CH$_3$ + H$_2$O

(b) $\xrightarrow{HI}$ I—⌐—I + H$_2$O

(c) —OCH$_3$ $\xrightarrow{HBr}$ —OH + CH$_3$Br

(d) $\xrightarrow{HI}$

(e) —O—CH$_2$CH$_2$—CH—CH$_2$—O—CH$_2$CH$_3$ $\xrightarrow{HBr}$
|
CH$_3$

—OH + BrCH$_2$CH$_2$—CH—CH$_2$—Br + BrCH$_2$CH$_3$ + H$_2$O
|
CH$_3$

14-16

nucleophilic attach on CH$_3$ faster than on 1° carbon

two proton transfers happen here: one H$^+$ comes off of oxygen, another H$^+$ goes on the other oxygen; several different scenarios of how this happens could be proposed

B(OH)$_3$ + 2 HBr

304
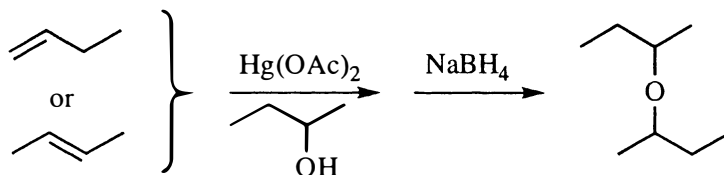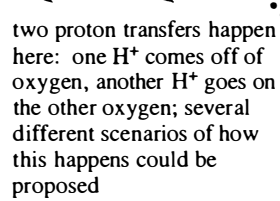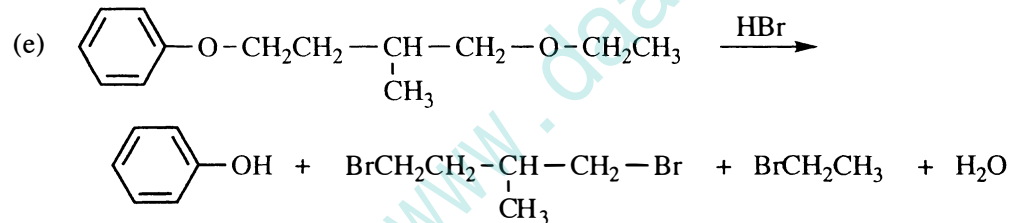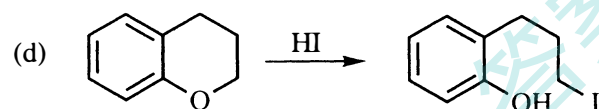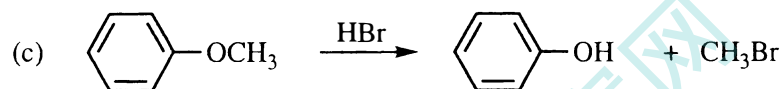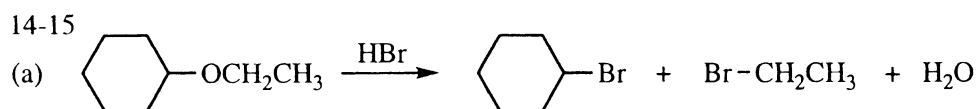
14-17 Begin by transforming the alcohols into good leaving groups like halides or tosylates:
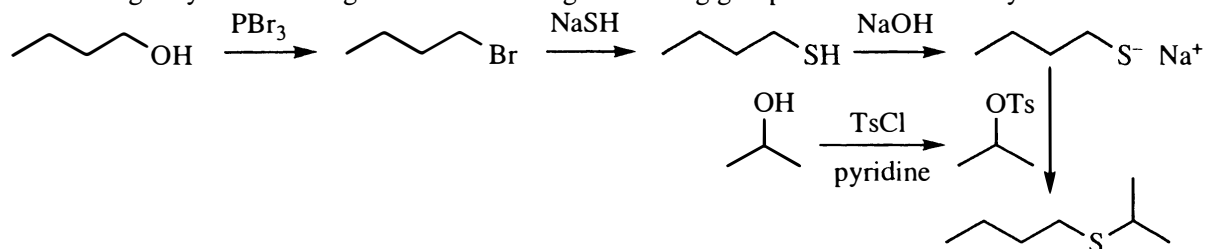
14-18 The sulfur at the center of mustard gas is an excellent nucleophile, and chloride is a decent leaving group. Sulfur can do in *internal* nucleophilic subsitution to make a reactive sulfonium salt and the sulfur equivalent of an epoxide.

(a)
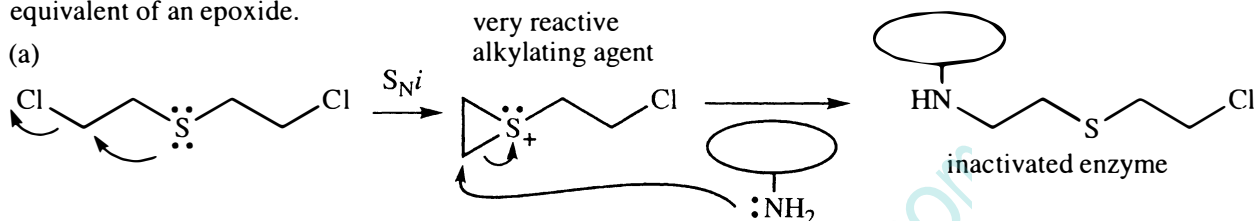
(b) NaOCl is a powerful oxidizing agent. It oxidizes sulfur to a sulfoxide or more likely a sulfone, either of which is no longer nucleophilic, preventing formation of the cyclic sulfonium salt.
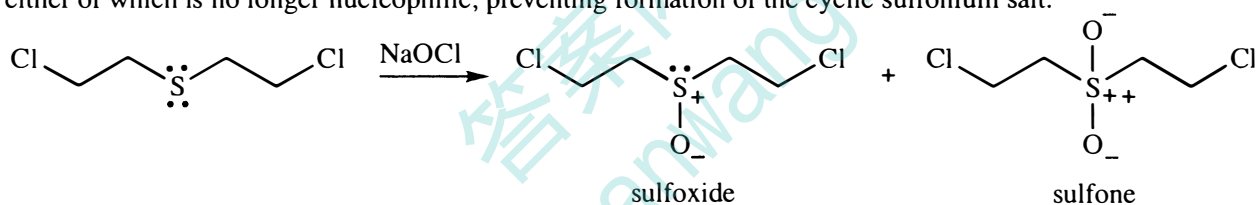
14-19

Generally, chemists prefer the peroxyacid method of epoxide formation to the halohydrin method. Reactions (a) and (b) show the peroxyacid method, but the halohydrin method could also be used.

(a)

(b)

(c)

(d)

(e)
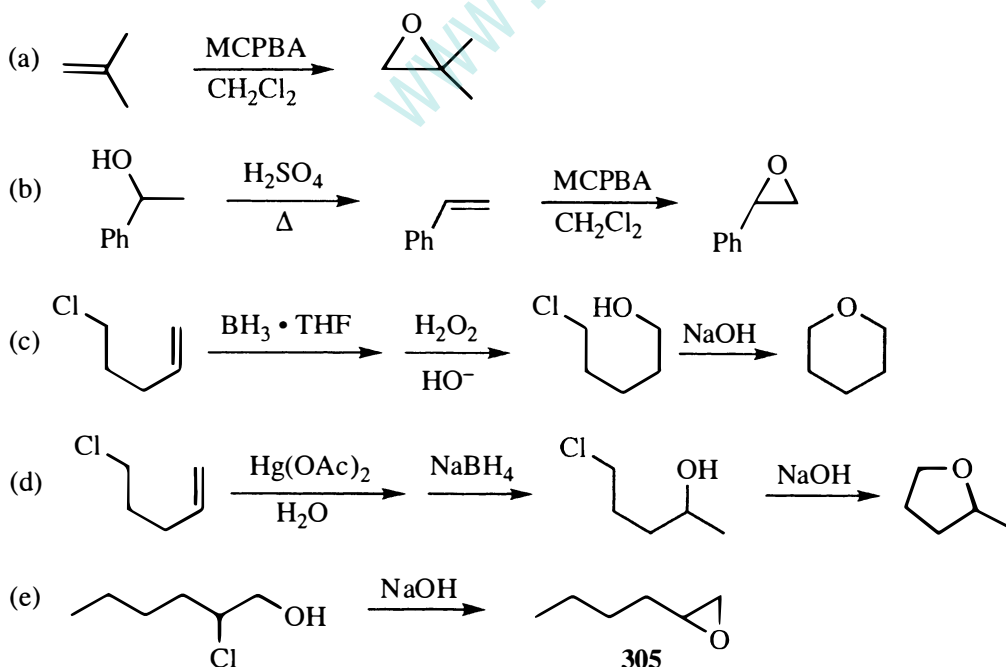
14-20

(a) 1) *tert*-Butyl hydroperoxide is the oxidizing agent. The $(CH_3)_3COOH$ contains the O—O bond just like a peroxyacid. 2) Diethyl tartrate has two asymmetric carbons and is the source of asymmetry; its function is to create a chiral transition state that is of lowest energy, leading to only one enantiomer of product. This process is called *chirality transfer*. 3) The function of the titanium (IV) isopropoxide is to act as the glue that holds all of the reagents together. The titanium holds an oxygen from each reactant—geraniol, *t*-BuOOH, and diethyl tartrate—and tethers them so that they react together, rather than just having them in solution and hoping that they will eventually collide.

(b) All three reactants are required to make Sharpless epoxidation work, but the key to *enantioselective* epoxidation is the chiral molecule, diethyl tartrate. When it complexes (or *chelates*) with titanium, it forms a large structure that is also chiral. As the *t*-BuOOH and geraniol approach the complex, the steric requirements of the complex allow the approach in one preferred orientation. When the reaction between the alkene and *t*-BuOOH occurs, it occurs preferentially from one face of the alkene, leading to one major stereosiomer of the epoxide. Without the chiral diethyl tartrate in the complex, the alkene could approach from one side just as easily as the other, and a racemic mixture would be formed.

(c) Using the enantiomer of diethyl L-tartrate, called diethyl D-tartrate, would give exactly the opposite stereochemical results.
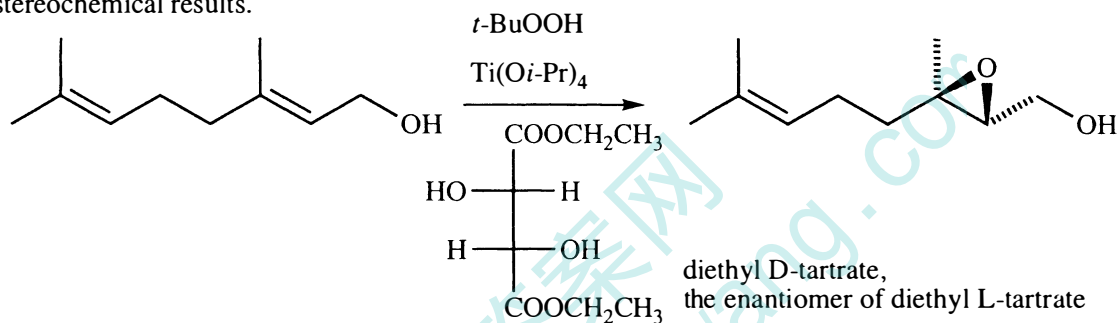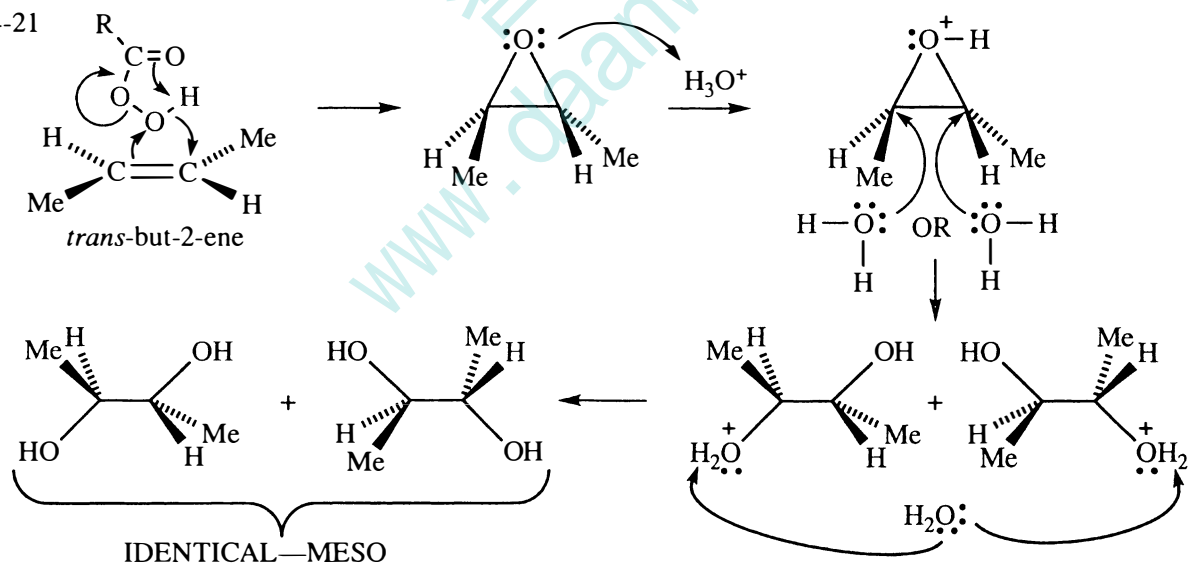
diethyl D-tartrate,
the enantiomer of diethyl L-tartrate

14-21

trans-but-2-ene

IDENTICAL—MESO

stereochemistry shown in Newman projections:

trans

MESO

14-21 continued

cis-2-butene

ENANTIOMERS

stereochemistry shown in Newman projections:

cis

rotate

CHIRAL—
RACEMIC
MIXTURE

14-22

$$H_2C=CH_2 \xrightarrow[\text{H}_2\text{O}]{\text{H}_2\text{SO}_4} CH_3CH_2OH$$

$$H_2C=CH_2 \xrightarrow{\text{RCO}_3\text{H}} H_2C\text{—}CH_2$$

$$\xrightarrow{\text{H}^+} CH_3CH_2OCH_2CH_2OH$$
Cellosolve®
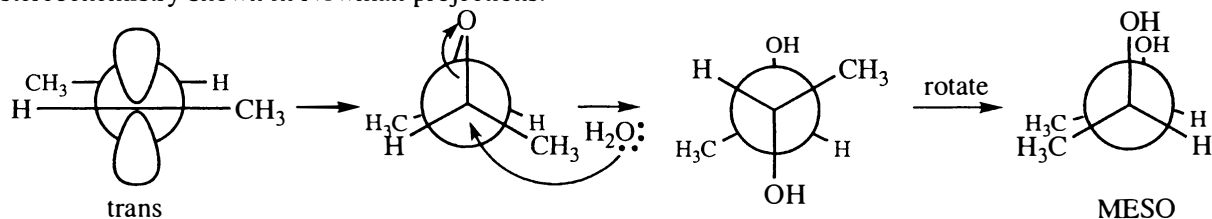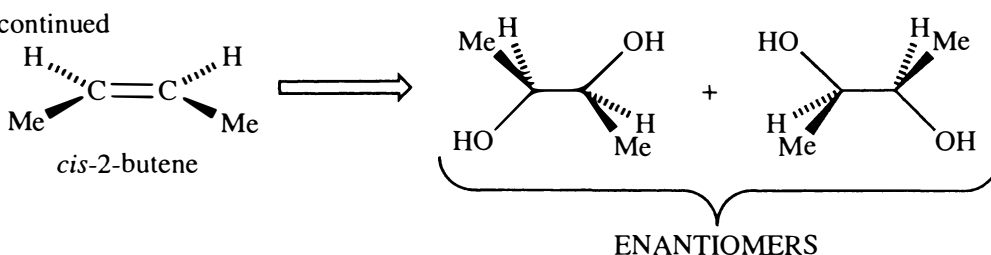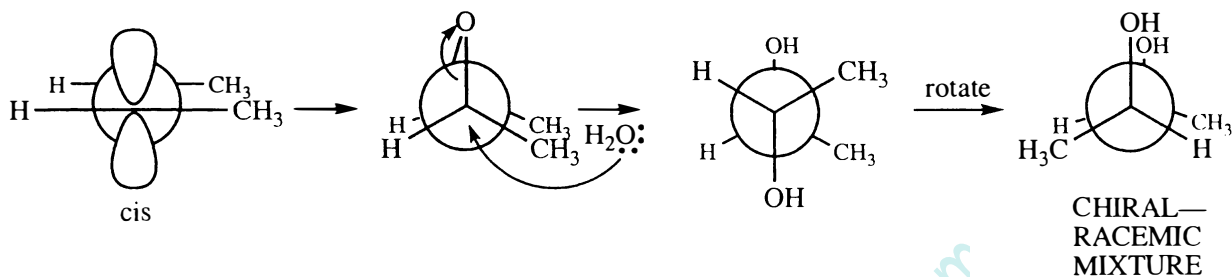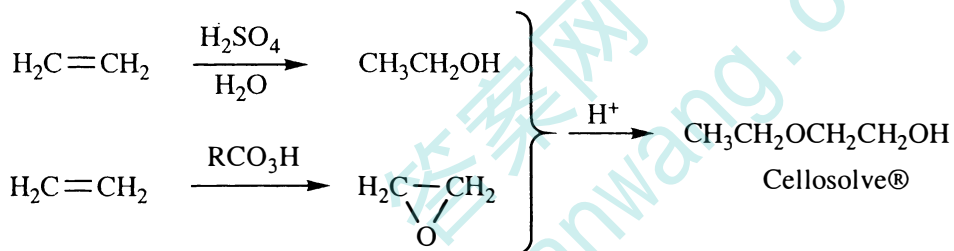
14-23

anhydrous HBr—only Br⁻ nucleophiles present

$$BrCH_2CH_2Br + H_2O$$
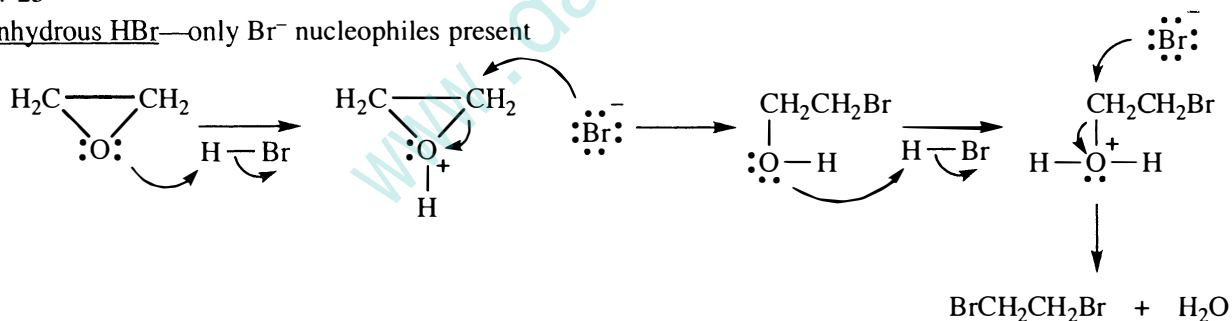
aqueous HBr—many more H_2O nucleophiles than Br⁻ nucleophiles

$$+ H_3O^+$$
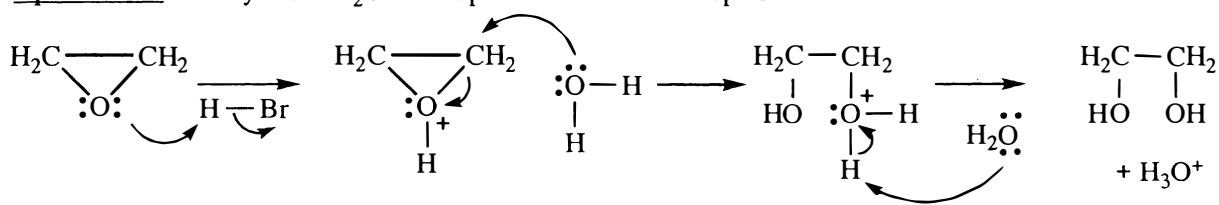
14-24 The cyclization of squalene via the epoxide is an excellent (and extraordinary) example of how Nature uses organic chemistry to its advantage. In one enzymatic step, Nature forms four rings and eight chiral centers! Out of 256 possible stereoisomers, only one is formed!

$\int$ = bonds formed

14-25

14-26

(a)

(b)

(c)

(d)

(e)

(f)

14-27

(a)

(b)

(c)

(d)

308
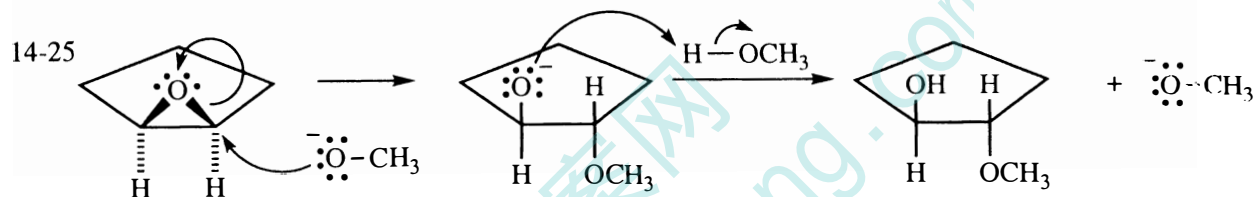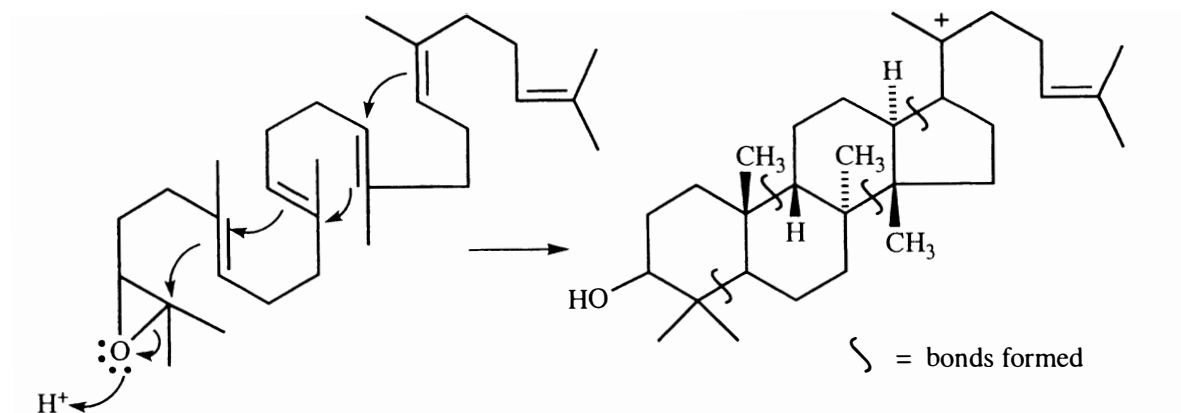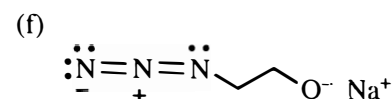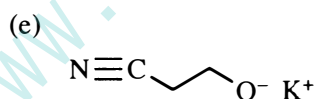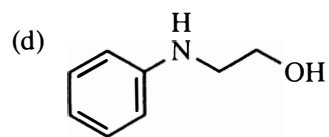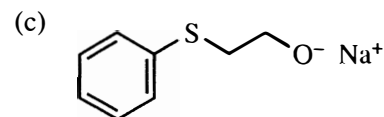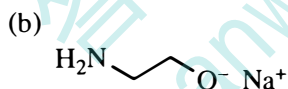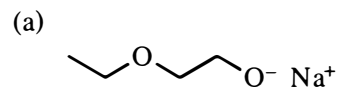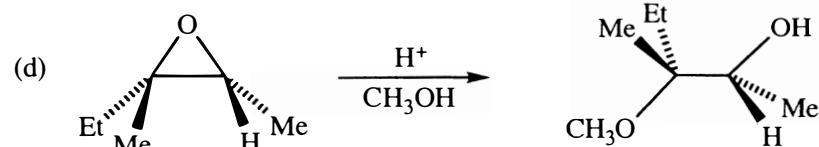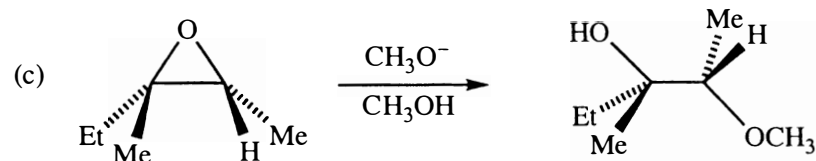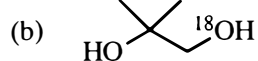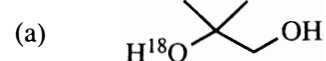
14-28 Newly formed bonds are shown in bold.

(a)

(b)

(c)
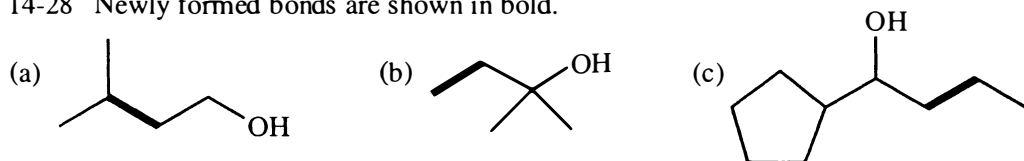
14-29 Please refer to solution 1-20, page 12 of this Solutions Manual.

14-30

(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)
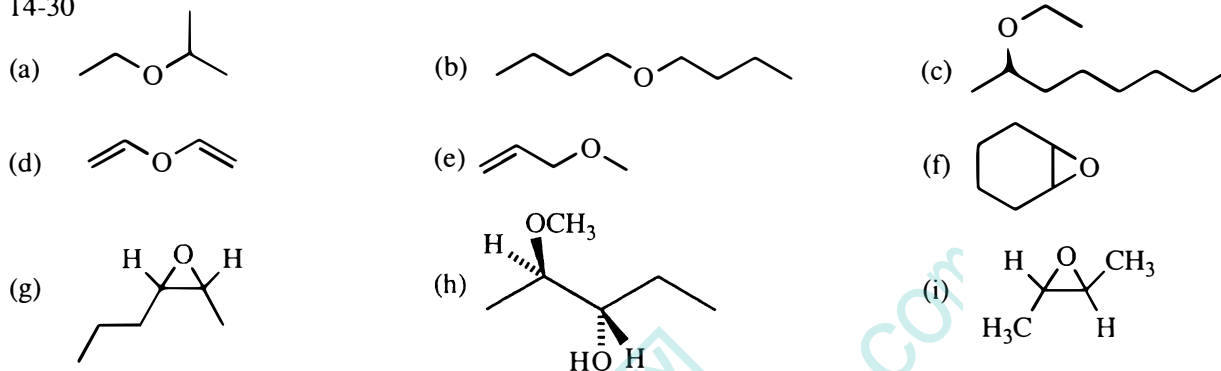
14-31
(a) *sec*-butyl isopropyl ether
(b) *t*-butyl isobutyl ether
(c) ethyl phenyl ether
(d) chloromethyl *n*-propyl ether

(e) *trans*-cyclohexene glycol
(f) cyclopentyl methyl ether
(g) propylene oxide
(h) cyclopentene oxide

14-32
(a) 2-methoxypropan-1-ol
(b) ethoxybenzene or phenoxyethane
(c) methoxycyclopentane
(d) 2,2-dimethoxycyclopentan-1-ol
(e) *trans*-1-methoxy-2-methylcyclohexane

(f) *trans*-3-chloro-1,2-epoxycycloheptane
(g) *trans*-1-methoxy-1,2-epoxybutane; or,
    trans-2-ethyl-3-methoxyoxirane
(h) 3-bromooxetane
(i) 1,3-dioxane

14-33

(a) + + H_2O

(b) + + H_2O

(c) and (d)   no reaction

(e) $-OH + CH_3CH_2I$

(f)

(g)

(h)

(i)

309

14-33 continued

(j)

(k)

(l)

(m)

(n)
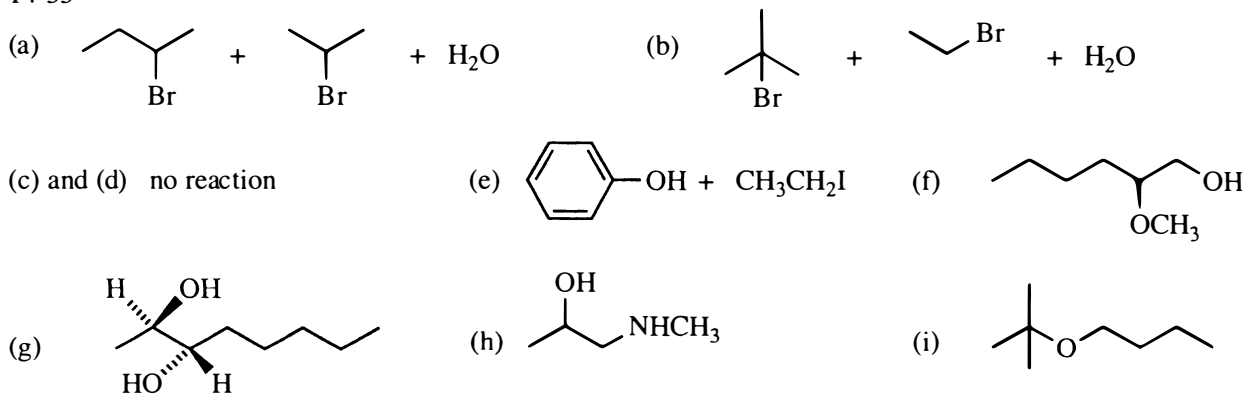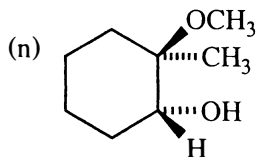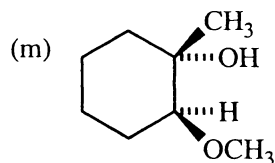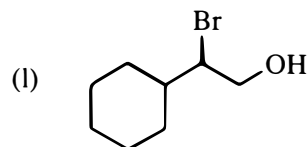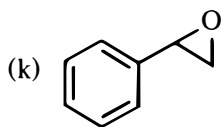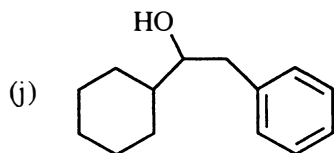
14-34

(a) On long-term exposure to air, ethers form peroxides. Peroxides are explosive when concentrated or heated. (For exactly this reason, ethers should *never* be distilled to dryness.)

(b) Peroxide formation can be prevented by excluding oxygen. Ethers can be checked for the presence of peroxides, and peroxides can be destroyed safely by treatment with reducing agents.

14-35

(a) Beginning with *(R)*-butan-2-ol and producing the *(R)* sulfide requires two inversions of configuration.
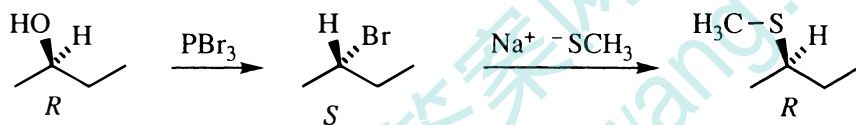
An alternative approach would be to make the tosylate, displace with chloride or bromide (S_N2 with inversion), then do a second inversion with $NaSCH_3$.

(b) Synthesis of the *(S)* isomer directly requires only one inversion.

14-36

(a)

molecular ion m/z 102

m/z 73

$CH_3CH_2CH_2^+$ m/z 43

14-36 continued
(b)

molecular ion m/z 102

m/z 31
(after H migration)

m/z 71

m/z 59

m/z 87

14-37

+ H$_3$O$^+$

14-38

(a)

$\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{MCPBA}}$ $\xrightarrow[\text{2) H}_2\text{O}]{\text{1) PhMgBr}}$

(b)

$\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{MCPBA}}$ $\xrightarrow[\text{CH}_3\text{OH}]{\text{NaOCH}_3}$

(c)

$\xrightarrow[\text{CH}_2\text{Cl}_2]{\text{MCPBA}}$ $\xrightarrow[\text{CH}_3\text{OH}]{\text{H}^+}$

14-39
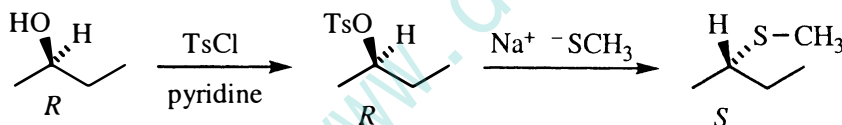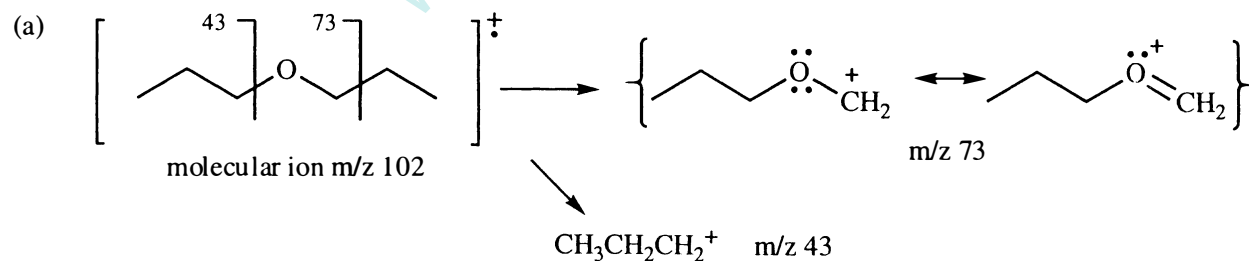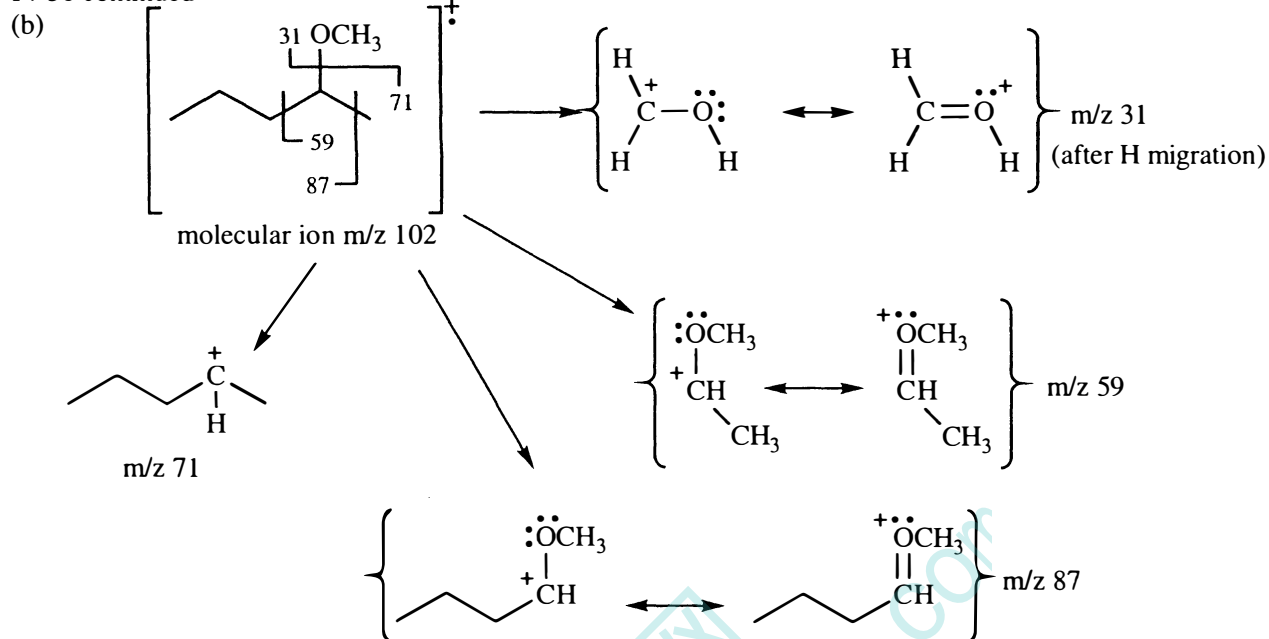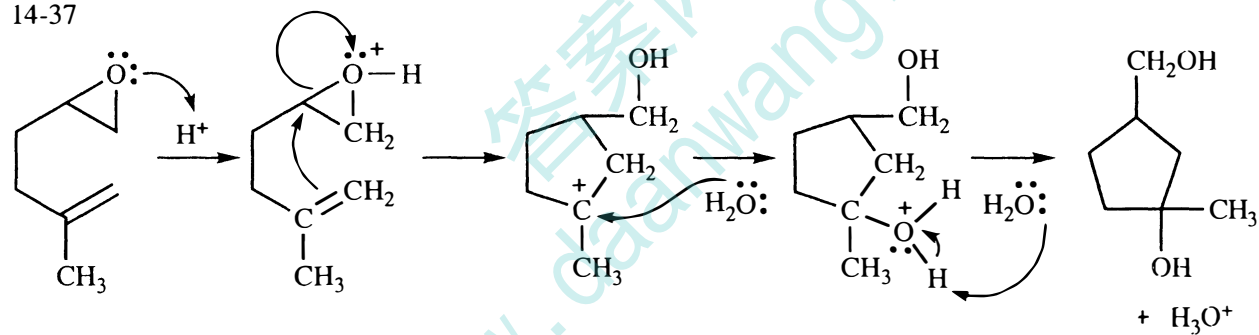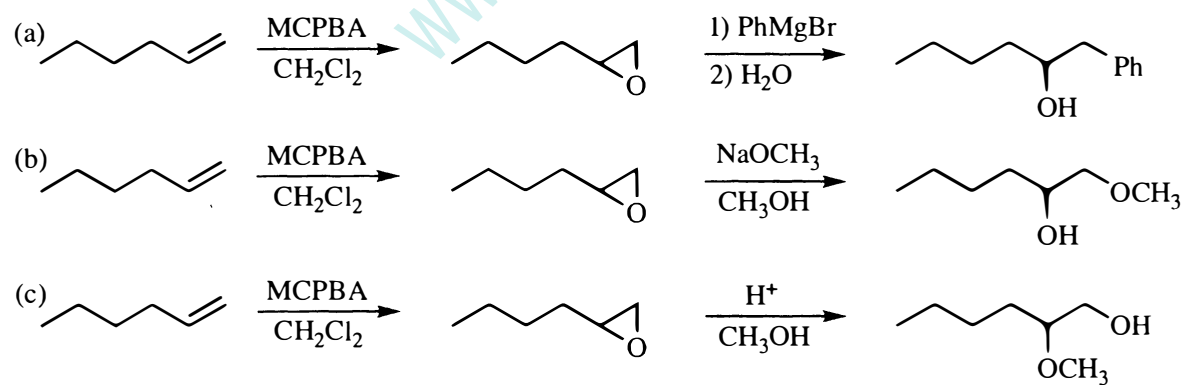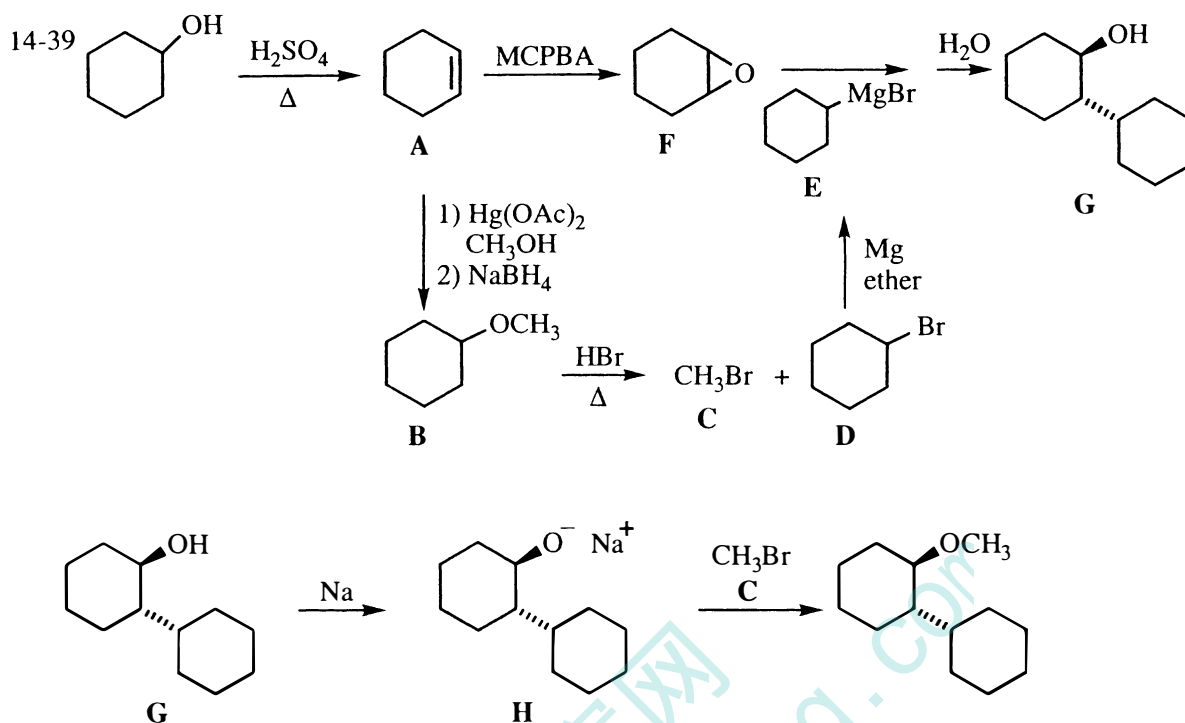
14-40 The student turned in the wrong product! Three pieces of information are consistent with the desired product: molecular formula $C_4H_{10}O$; O—H stretch in the IR at 3300 cm^{-1} (although it should be strong, not weak); and mass spectrum fragment at m/z 59 (loss of CH_3). The NMR of the product should have a 9H singlet at δ 1.0 and a 1H singlet between δ 2 and δ 5. Instead, the NMR shows CH_3CH_2 bonded to oxygen. The student isolated diethyl ether, *the typical solvent used in Grignard reactions.*

Predicted product
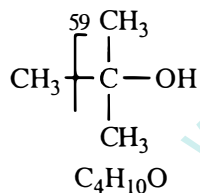
$C_4H_{10}O$

O—H at 3300 cm^{-1}

Isolated product
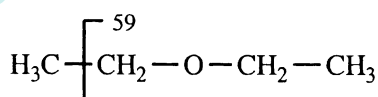
$C_4H_{10}O$

O—H at 3300 cm^{-1} due to water contamination

14-41

(a)

(b)

14-41 continued

(c)

(d)

(e)   (f)
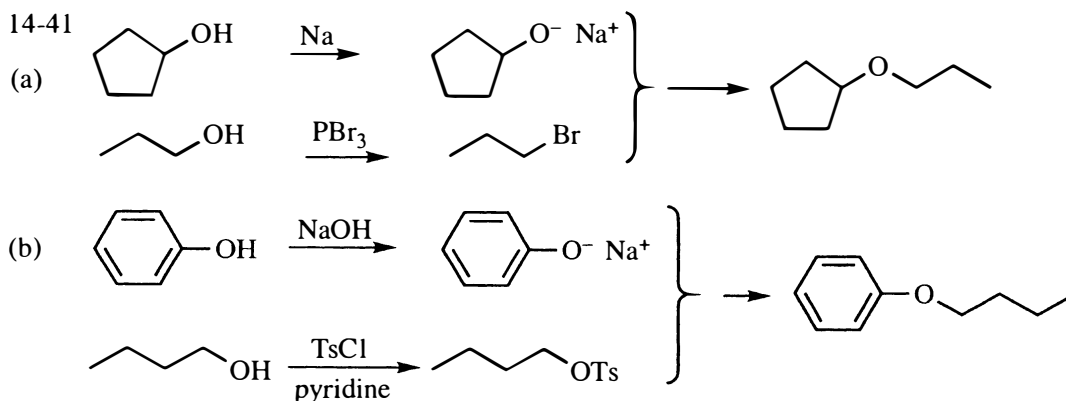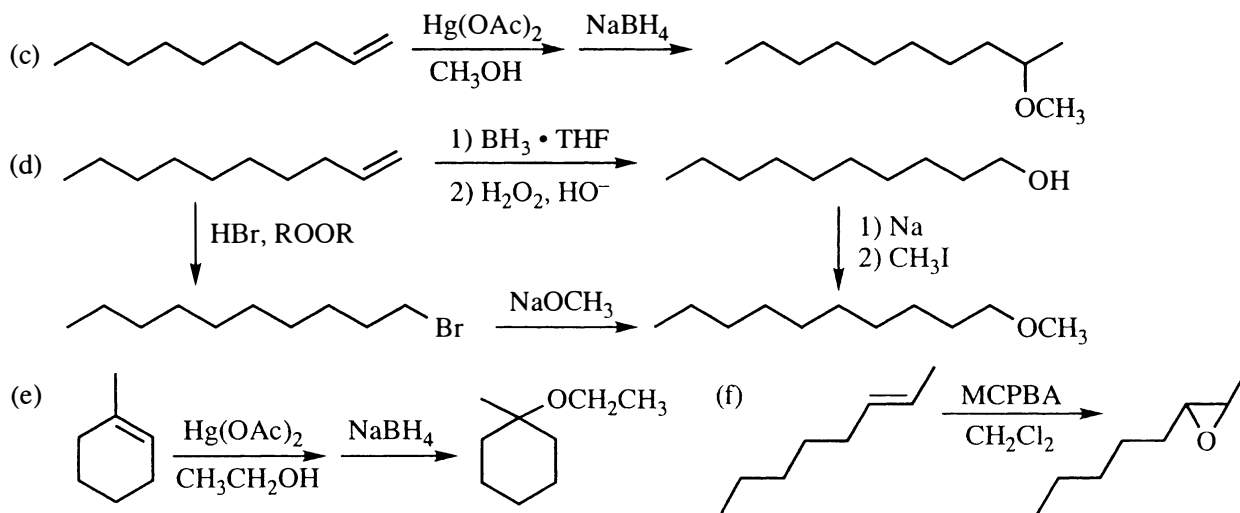
14-42 In the first sequence, no bond is broken to the chiral center, so the configuration of the product is the same as the configuration of the starting material.

$[\alpha]_D = -8.24°$

(Assume the enantiomer shown is levorotatory.)

$[\alpha]_D = -15.6°$

In the second reaction sequence, however, bonds to the chiral carbon are broken twice, so the stereochemistry of each process must be considered.

RETENTION OF CONFIGURATION

Undoubtedly, some E2 products will also form in this reaction.
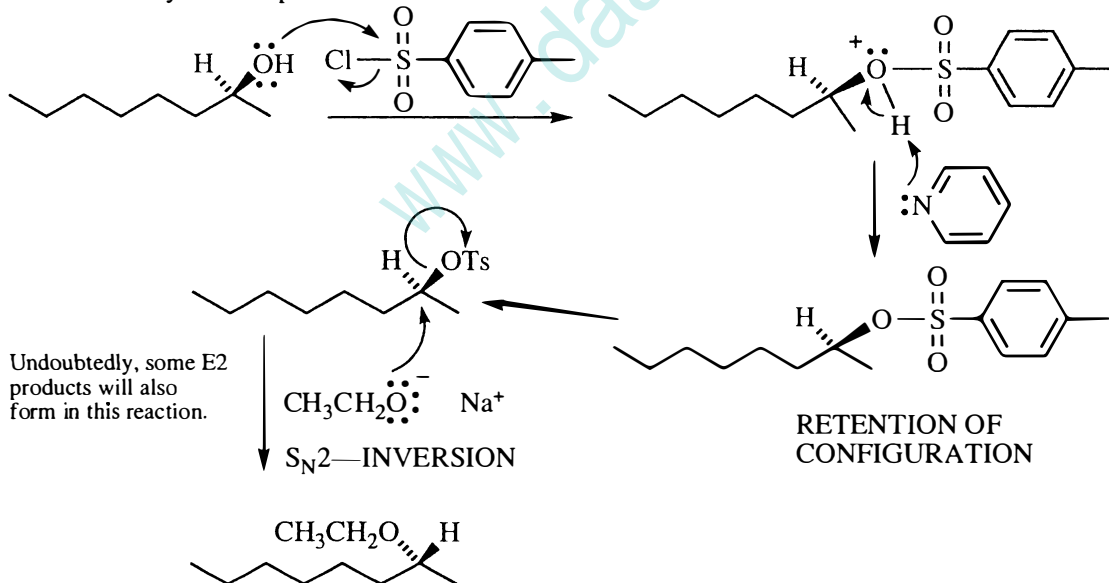
S_N2—INVERSION

The second sequence involves *retention* followed by *inversion*, thereby producing the *enantiomer* of the 2-ethoxyoctane generated by the first sequence. The optical rotation of the final product will have equal magnitude but opposite sign, $[\alpha]_D = +15.6°$.

313

14-43
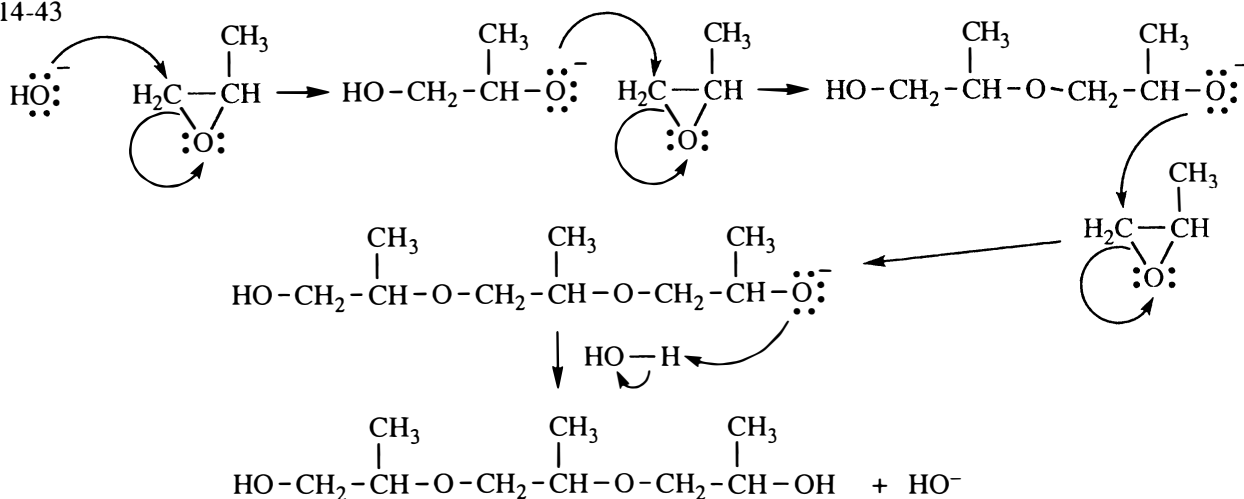
14-44 The text uses HA to indicate an acid; A$^-$ is the conjugate base.

Note that all three carbocation intermediates are 3°!
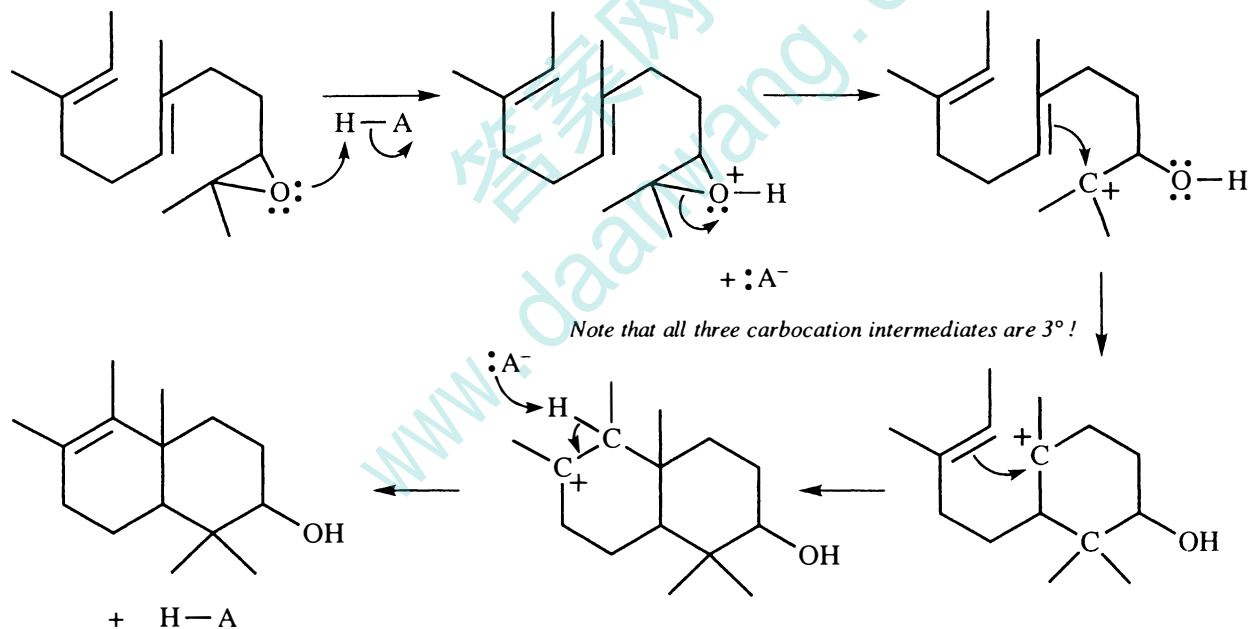
This process resembles the cyclization of squalene oxide to lanosterol. (See the solution to problem 14-24.) In fact, pharmaceutical synthesis of steroids uses the same type of reaction called a "biomimetic cyclization".

14-45

(a)
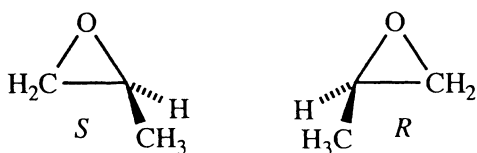
(b)
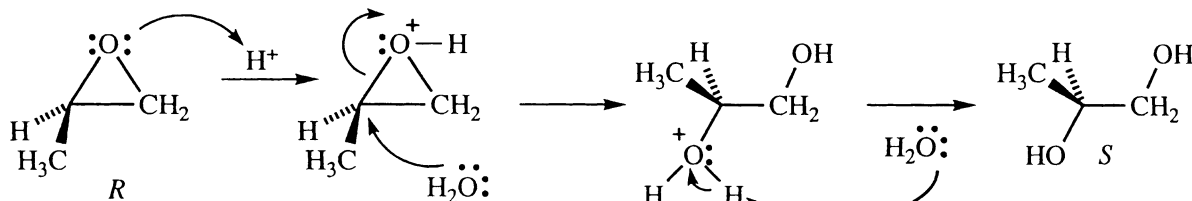
Attack of water gave *inversion* of
configuration at the chiral center; R became S.

(c)

+ HO⁻

No bond to the chiral center
was broken. Configuration
is retained; R stays as R.
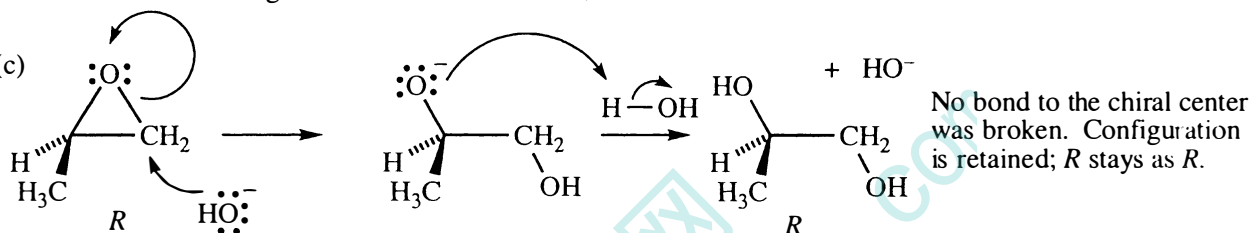
(d) The difference in these mechanisms lies in where the nucleophile attacks. Attack at the chiral carbon gives inversion; attack at the achiral carbon retains the configuration at the chiral carbon. These products are enantiomers and must necessarily have optical rotations of opposite sign.

14-46   methyl cellosolve $CH_3OCH_2CH_2OH$

To begin, what can be said about methyl cellosolve? Its molecular weight is 76; its IR would show C—O in the 1000-1200 cm⁻¹ region and a strong O—H around 3300 cm⁻¹; and its NMR would show four sets of signals in the ratio of 3:2:2:1.

The unknown has molecular weight 134; this is double the weight of methyl cellosolve, minus 18 (water). The IR shows no OH, only ether C—O. The NMR shows no OH, only H—C—O in the ratio of 3:2:2. Apparently, two molecules of methyl cellosolve have combined in an acid-catalyzed, bimolecular dehydration.

$CH_3OCH_2CH_2\text{—}O\text{—}CH_2CH_2OCH_3$

(this compound is called "diethylene
glycol dimethyl ether", or a shortened,
common name is "diglyme")
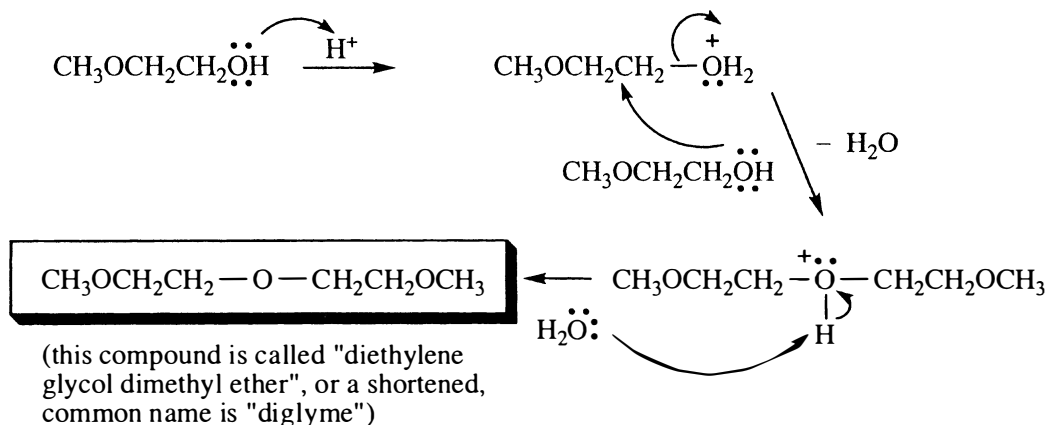
14-47
The formula C_8H_8O has five elements of unsaturation (enough (4) for a benzene ring). The IR is useful for what is does *not* show. There is neither OH nor C=O, so the oxygen must be an ether functional group.

The NMR shows a 5H signal at δ 7.2, a monosubstituted benzene. No peaks in the δ 4.5-6.0 range indicate the absence of an alkene, so the remaining element of unsaturation must be a ring. The three protons are non-equivalent, with complex splitting.
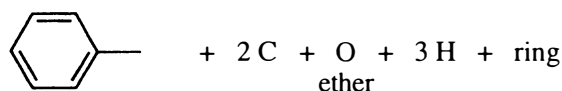
These pieces can be assembled in only one manner consistent with the data.
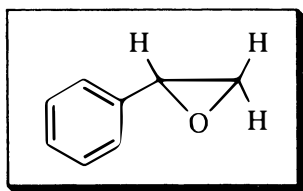
(Note that the CH_2 hydrogens are not equivalent (one is *cis* and one is *trans* to the phenyl) and therefore have distinct chemical shifts.)

14-48 The key concept is that reagents always go to the less hindered side of a molecule first. In this case, the "underneath" side is less hindered; the "top" side has a CH_3 hovering over the double bond and approach from the top will be much more difficult, and therefore slower, than approach from underneath.
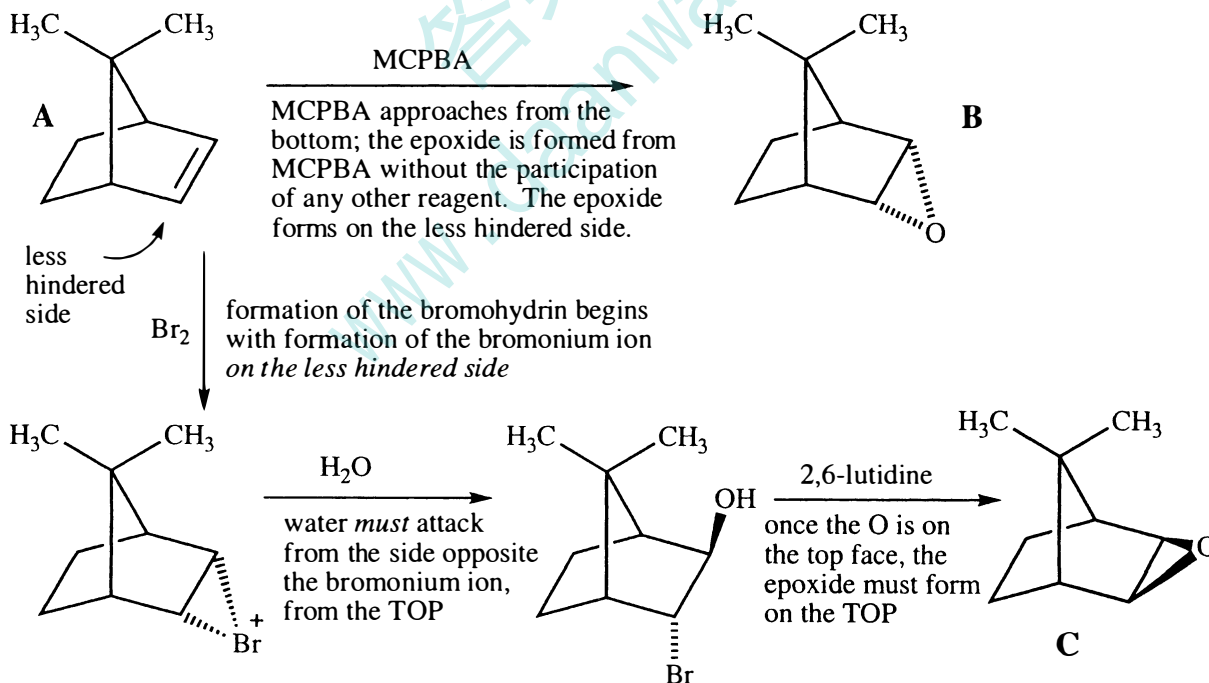
Epoxides **B** and **C** are diastereomers; they will have different chemical and physical properties. Nucleophiles can react with **C** much faster than with **B** for precisely the same reason that explained their formation: approach from underneath is less hindered and is faster than approach from the top.

316

CHAPTER 15—CONJUGATED SYSTEMS, ORBITAL SYMMETRY, AND

ULTRAVIOLET SPECTROSCOPY

15-1   Look for: 1) the number of double bonds to be hydrogenated—the fewer C=C, the smaller the ΔH; 2) conjugation—the more conjugated, the more stable, the lower the ΔH; 3) degree of substitution of the alkenes—the more substituted, the more stable, the lower the ΔH.

(a)

smallest ΔH <   <   <

<   =C=   <   biggest ΔH

(b)

smallest ΔH <   <   <   <   biggest ΔH
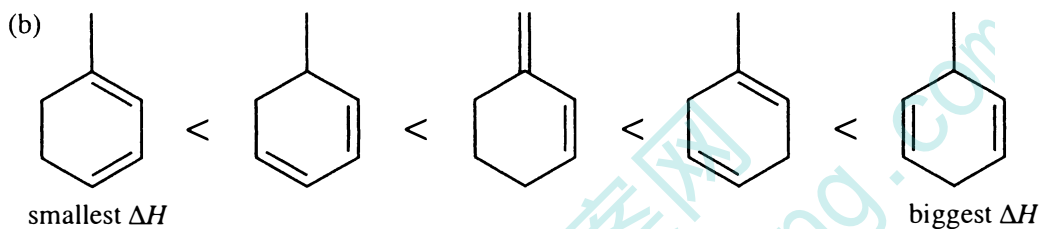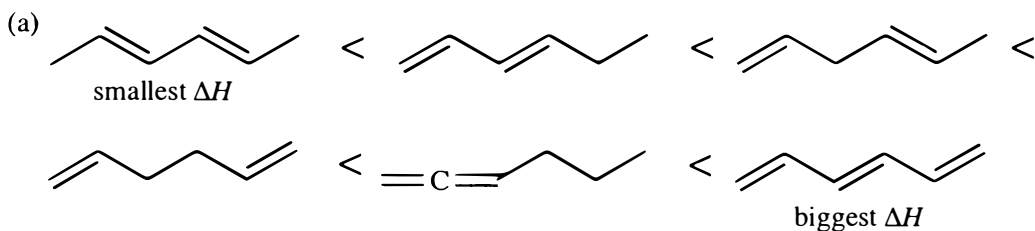
15-2   Reminder: H—B is used to symbolize the general form for an acid, that is, a protonated base; B⁻ is the conjugate base.

hydride shift

allylic

B:⁻

The key step is hydride shift from a 2° carbocation to a 2° *allylic*, resonance-stabilized carbocation, which can subsequently lose a proton to form a *conjugated* diene.

317
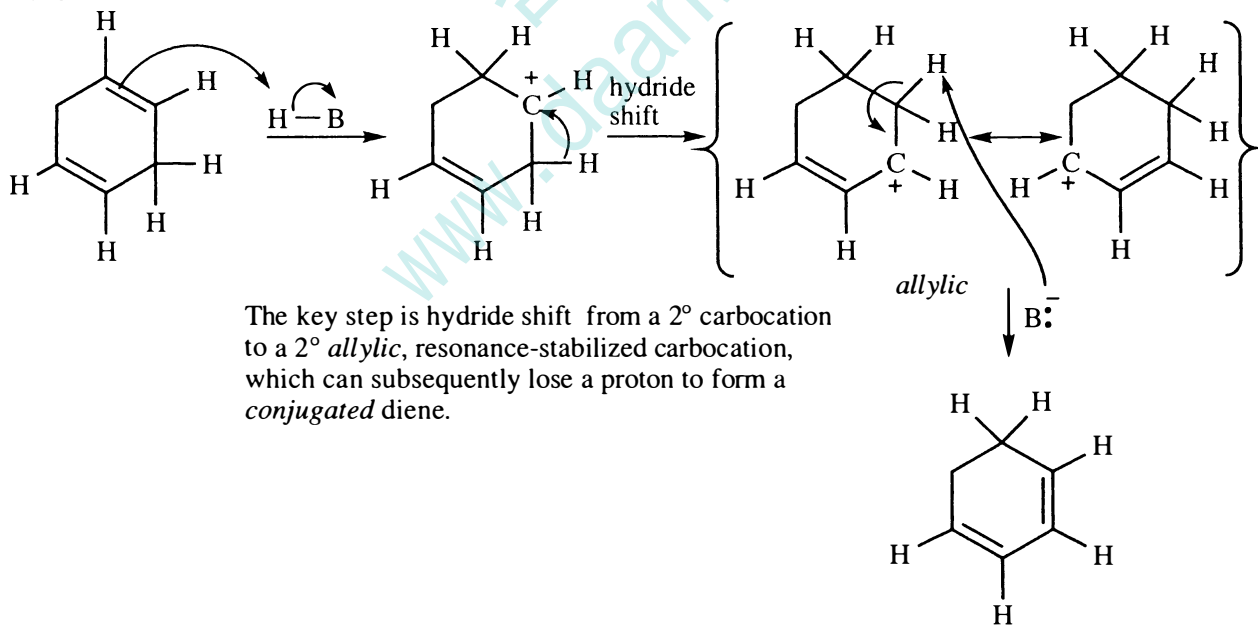
15-3 (You may wish to refer to problem 2-6.)   orbital picture

(a)
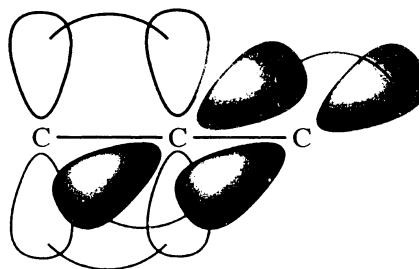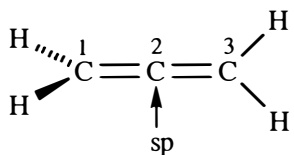
The central carbon atom makes two π bonds with two p orbitals. These p orbitals must necessarily be perpendicular to each other, thereby forcing the groups on the ends of the allene system perpendicular.

(b)
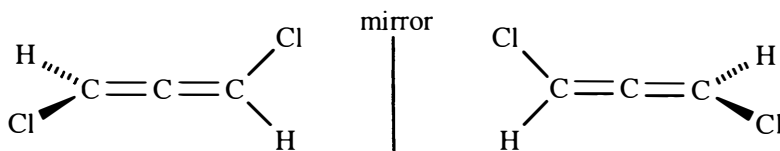
non-superimposable mirror images = enantiomers

15-4 Carbocation stability depends on conjugation (benzylic, allylic), then on degree of carbon carrying the positive charge.

less significant contributor

more significant contributor

2°   equivalent to the
                     first resonance form

318

15-5
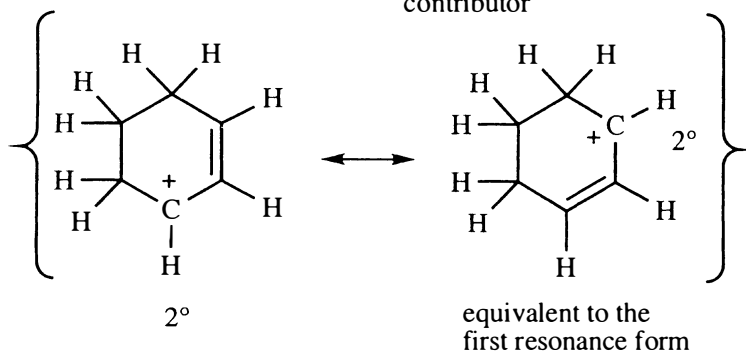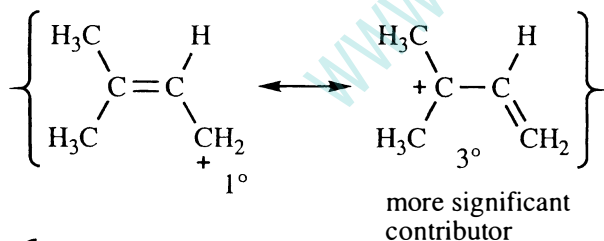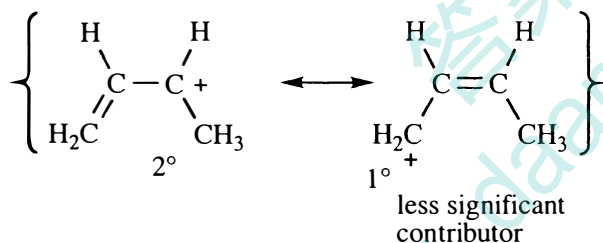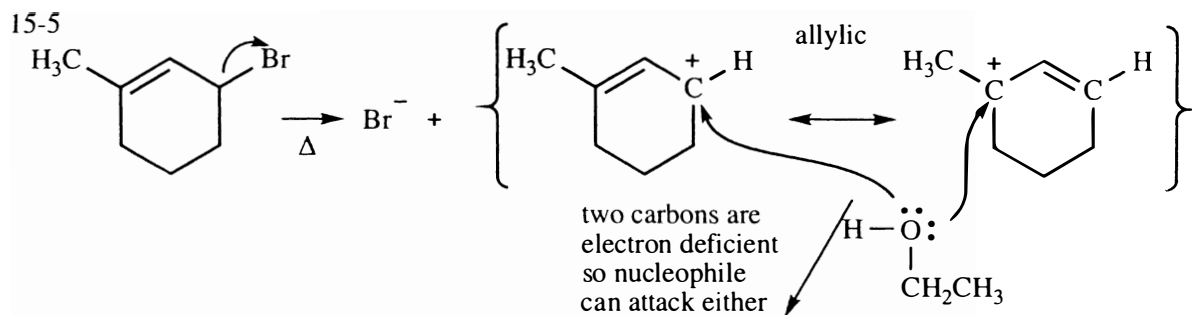
The most basic species in the reaction mixture will remove this proton. The oxygen of ethanol is more basic than bromide ion.

15-6

319

15-7

(a)

(b)

two carbons are
electron deficient
so nucleophile
can attack either

same carbocation
as in (a)

allylic

two carbons are
electron deficient
so nucleophile
can attack either

15-7 continued
(c)

$H_2C=C-C=CH_2$ (with H, H below) $\xrightarrow{Br-Br}$ [allylic resonance structures]

$H_2C-\overset{+}{C}-C=CH_2$ (Br above, H H below) $\longleftrightarrow$ $H_2C-C=C-\overset{+}{CH_2}$ (Br above, H H below)

:Br:⁻

two carbons are electron deficient so nucleophile can attack either

$H_2C-C-C=CH_2$ (Br Br above, H H below) + $H_2C-C=C-CH_2$ (Br above, Br above, H H below)

While the bromonium ion mechanism is typical for isolated alkenes, the greater stability of the resonance-stabilized carbocation will make it the lower energy intermediate for conjugated systems.

(d)

$H_3C-C=C-CH_2$ (Cl above, H H below) $\xrightarrow[-\,AgCl]{Ag^+}$ [$H_3C-C=C-\overset{+}{CH_2}$ (H H below) $\longleftrightarrow$ $H_3C-\overset{+}{C}-C=CH_2$ (H H below)] allylic

$H_2\overset{..}{O}$ .... $H_2\overset{..}{O}$

two carbons are electron deficient so nucleophile can attack either

$H_3C-C=C-CH_2$ (with $H-\overset{+}{\underset{|}{O}}-H$ above, H H below) + $H_3C-C-C=CH_2$ (with $H-\overset{+}{\underset{|}{O}}-H$ above, H H below)

$H_2\overset{..}{O}$ .... $H_2\overset{..}{O}$

$H_3C-C=C-CH_2$ (OH above, H H below) + $H_3C-C-C=CH_2$ (OH above, H H below)

321

15-7 continued

(e)

same carbocation as in (d)

two carbons are
electron deficient
so nucleophile
can attack either

15-8

(a)

(b)

two carbons are
electron deficient
so nucleophile
can attack either

(c) The resonance form **A⁺**, which eventually leads to product **A**, has positive charge on a 2° carbon and is a more significant resonance contributor than structure **B⁺**. With greater positive charge on the 2° carbon than on the 1° carbon, we would expect bromide ion attack on the 2° carbon to have lower activation energy. Therefore, **A** must be the *kinetic* product. At higher temperature, however, the last step becomes reversible, and the stability of the products becomes the dominant factor in determining product ratios. As **B** has a disubstituted alkene whereas **A** is only monosubstituted, it is reasonable that **B** is the major, *thermodynamic* product at 60° C.

15-8 continued

(d) At 60° C, ionization of **A** would lead to the same allylic carbocation as shown in (b), which would give the same product ratio as formation of **A** and **B** from butadiene.

15-9

(a)

(b)

recycles in chain mechanism
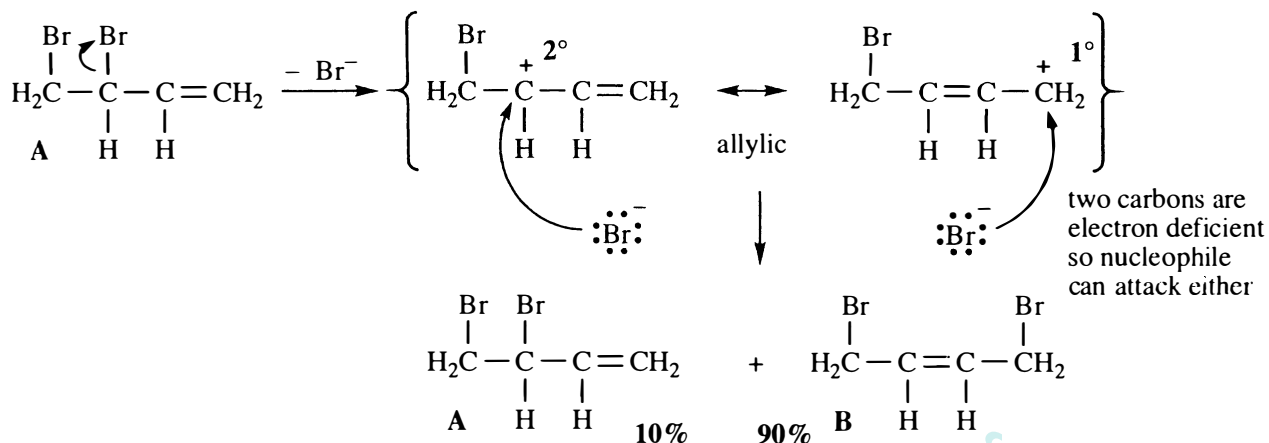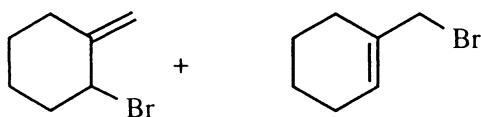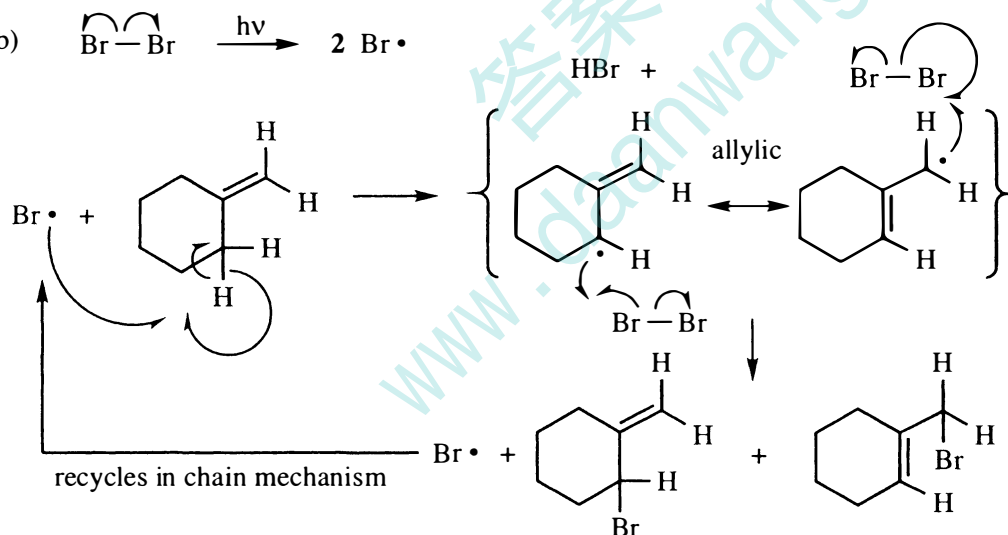
15-10   ("Pr" is the abbreviation for *n*-propyl, used below.)
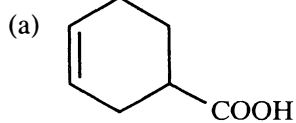
NBS generates a low concentration of Br$_2$

323
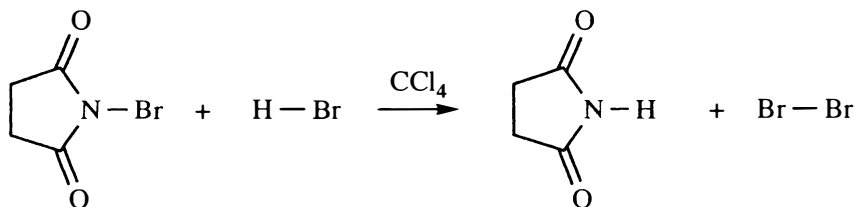
15-10 continued

<u>initiation</u>

$$Br-Br \xrightarrow{h\nu} 2\ Br\bullet$$
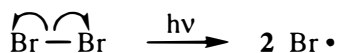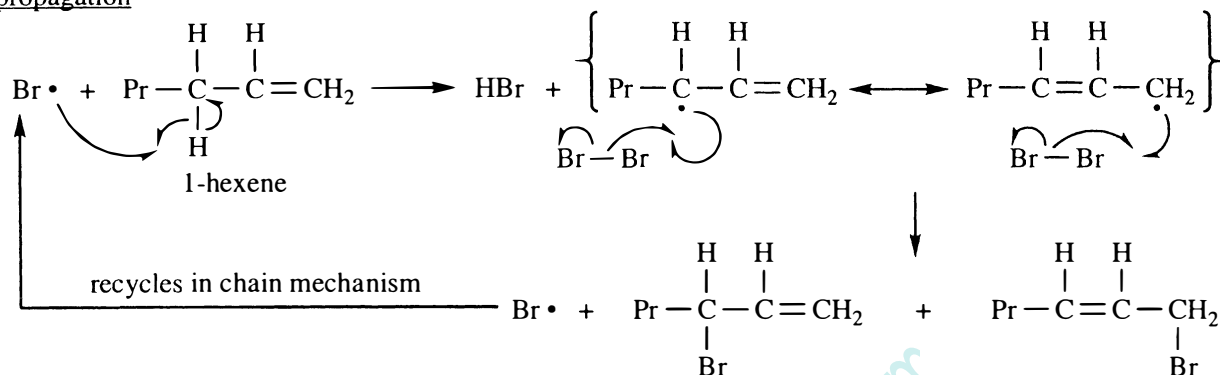
<u>propagation</u>

The HBr generated in the propagation step combines with NBS to produce more Br_2, continuing the chain mechanism.

15-11

(a)

(b)
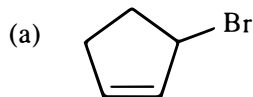
These are the major products from abstraction of a 2° allylic H.

(c)
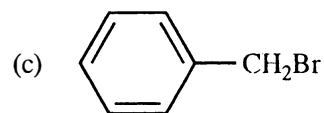
benzylic radicals are even more stable than allylic

15-12   Both halides generate the same allylic carbanion.

15-13

(a) $CH_3CH_2CH_2CH_2Br \xrightarrow[\text{ether}]{Mg} CH_3CH_2CH_2CH_2MgBr \xrightarrow{H_2C=CHCH_2Br} H_2C=CHCH_2(CH_2)_3CH_3$

(b)

15-13 continued

(c) $CH_3CH_2CH_2Br \xrightarrow[\text{ether}]{Mg} CH_3CH_2CH_2MgBr$

dec-5-ene

This synthesis could also
be performed sequentially.

add one-half equivalent

15-14

(a)

(b)

(c)

(d)

(e)

(f)

15-15

(a)

(b)

(c)

(d)

(e)

(f)

15-16

(a)

(b)

(c)

racemic mixture; wedge and
dashed bonds show relative
stereochemistry

325
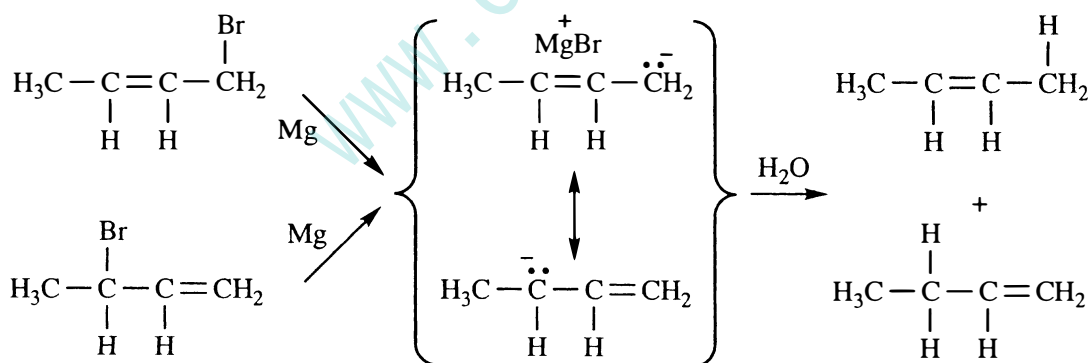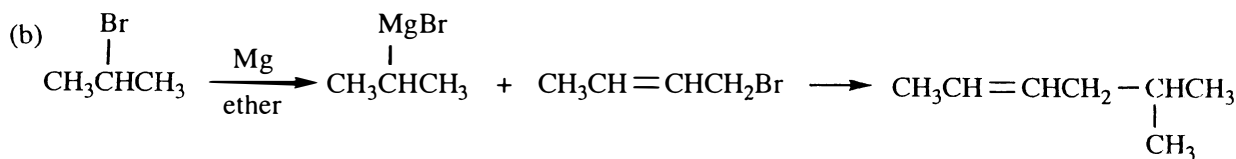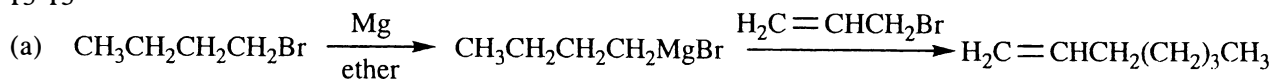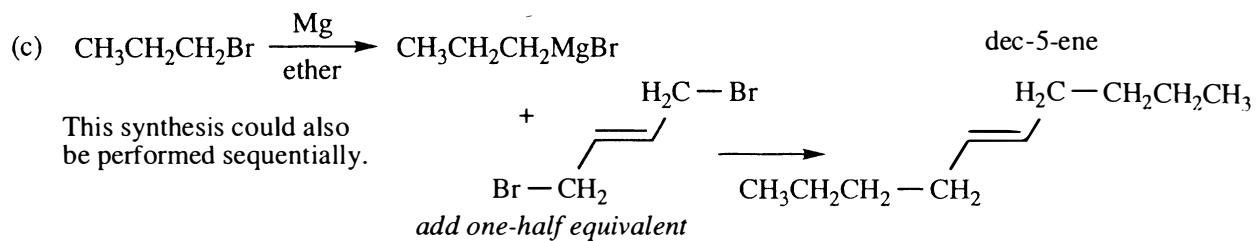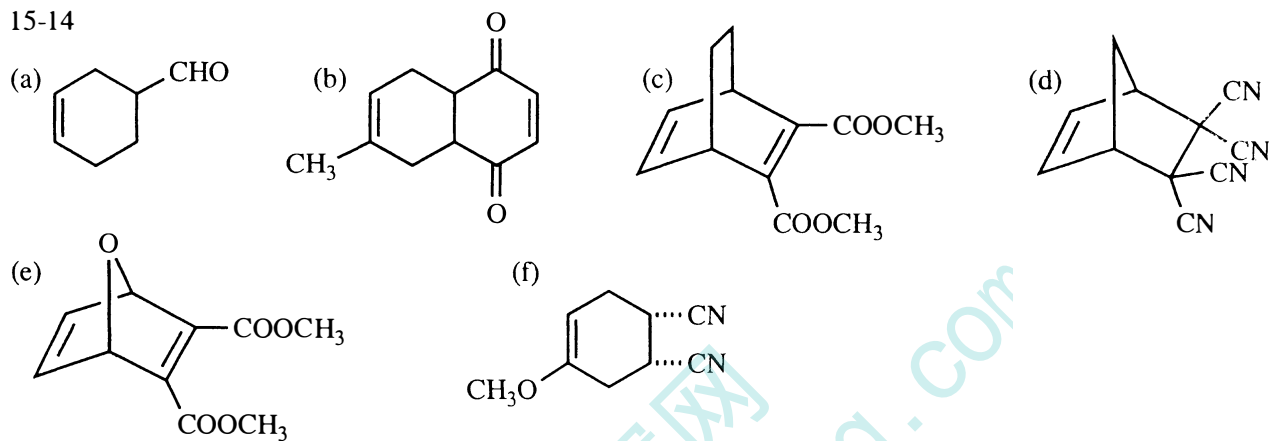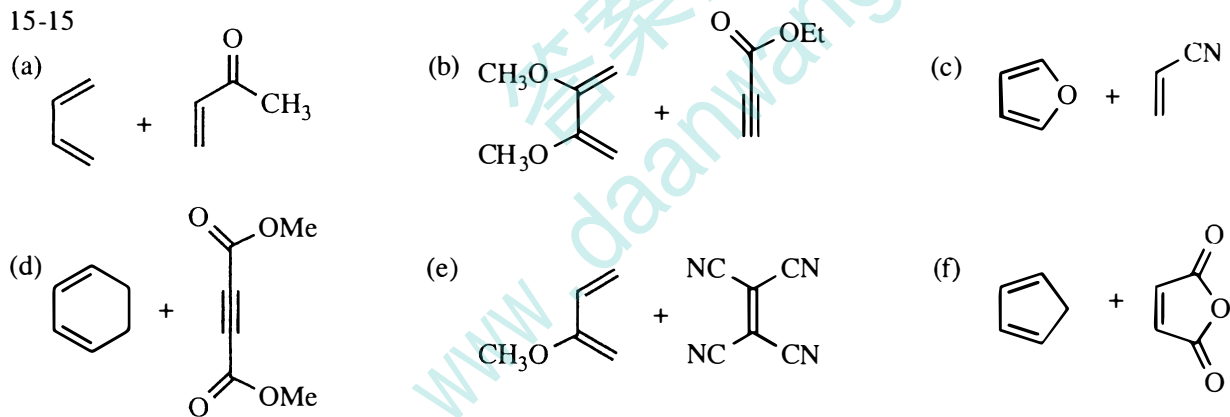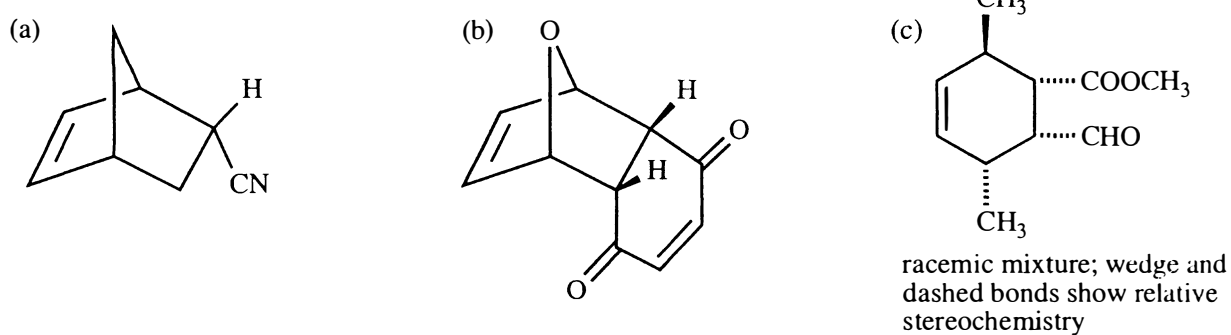
15-17 These structures show the alignment of diene and dienophile in the Diels-Alder transition state, leading to 1,4-orientation in (a) and 1,2-orientation in (b).

(a)
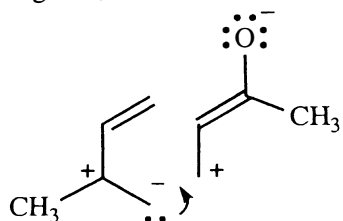
this left structure is a VERY minor resonance contributor; however, it explains the orientation for the diene as carbon-1 is more negative and carbon-2, a 3°C, is slightly more positive because of methyl group stabilization

(b)
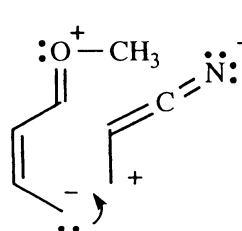
15-18 For clarity, the bonds formed in the Diels-Alder reaction are shown in bold.

(a)
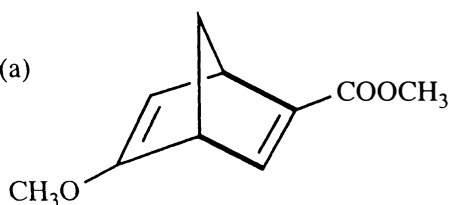
(b)
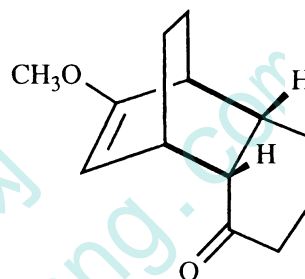
(c)
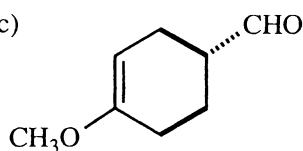
(d)
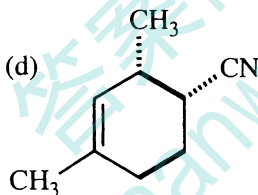
15-19 For a photochemically *allowed* process, one molecule must use an excited state in which an electron has been promoted to the first antibonding orbital. All orbital interactions between the excited molecule's HOMO* and the other molecule's LUMO must be bonding for the interaction to be allowed; otherwise, it is a forbidden process.

HOMO*
excited state of
diene HOMO

π_3*

bonding interaction
(constructive overlap)

antibonding interaction
(destructive overlap)

π*
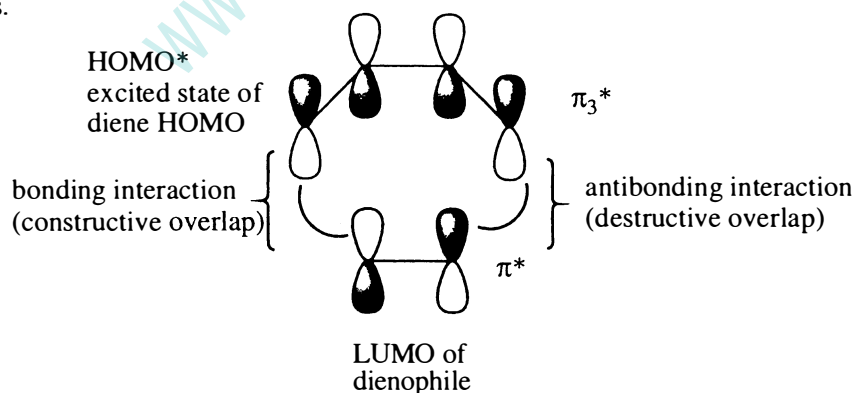
LUMO of
dienophile

In the Diels-Alder cycloaddition, the LUMO of the dienophile and the excited state of the HOMO of the diene (labeled HOMO*) produce one bonding interaction and one antibonding interaction. Thus, this is a photochemically forbidden process.

15-20 For a [4 + 4] cycloaddition:

(a)

Thermal

HOMO

π_2

π_3

LUMO

antibonding
interaction

bonding
interaction

one interaction is antibonding
⇒ **forbidden**

Photochemical

HOMO*
π_3

π_3

LUMO

both interactions are bonding
⇒ **allowed**
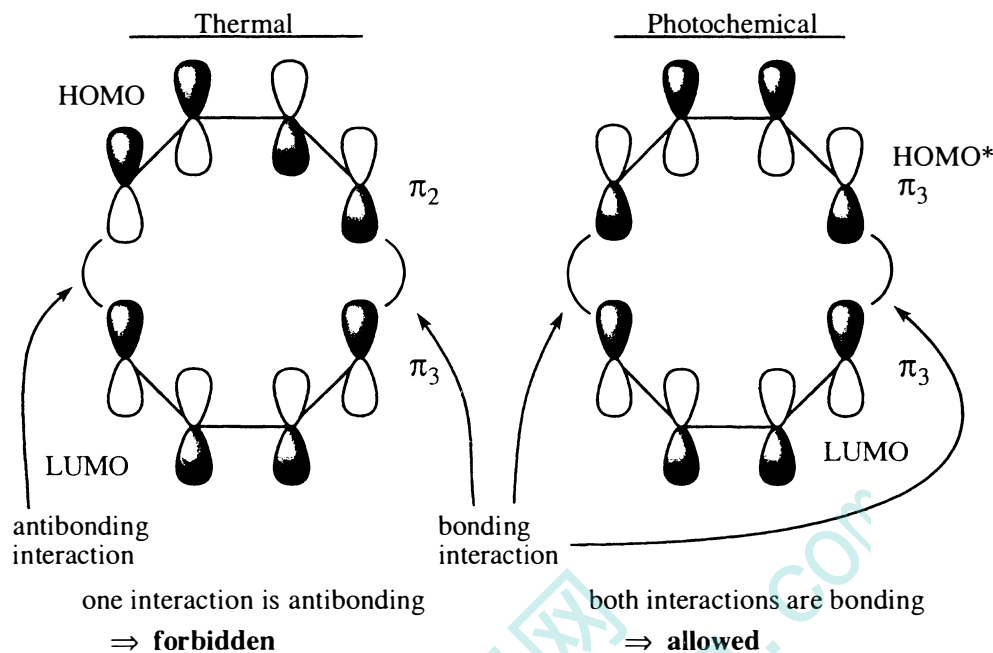
(b) A [4 + 4] cycloaddition is not thermally allowed, but a [4 + 2] (Diels-Alder) is!

HOMO

π_2

bonding
interaction

bonding
interaction

π_3

LUMO
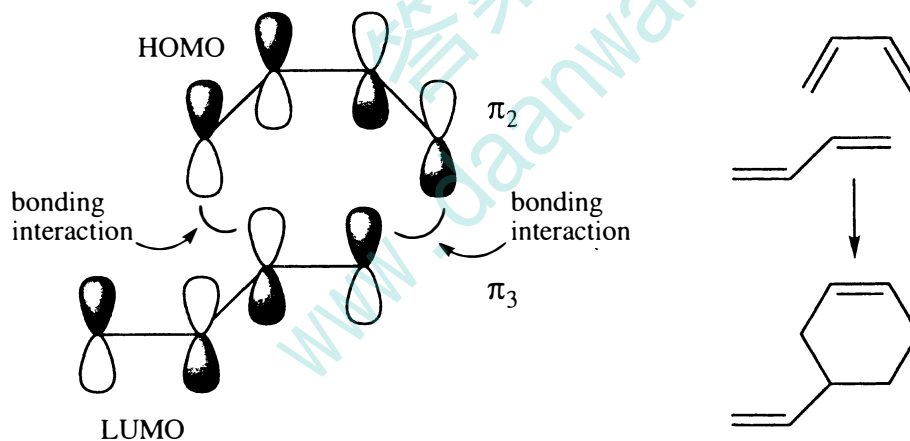
15-21

$$A = \varepsilon c\, l \qquad \varepsilon = \frac{A}{c\, l} \qquad l = 1 \text{ cm} \qquad A = 0.50$$

convert mass to moles: $1 \text{ mg} \times \dfrac{1 \text{ g}}{1000 \text{ mg}} \times \dfrac{1 \text{ mole}}{160 \text{ g}} = 6 \times 10^{-6} \text{ moles}$

$$c = \frac{6 \times 10^{-6} \text{ moles}}{10 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 6 \times 10^{-4} \text{ M}$$

$$\varepsilon = \frac{0.50}{(6 \times 10^{-4})(1)} = 833 \approx \boxed{800}$$

327
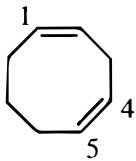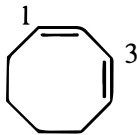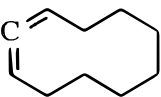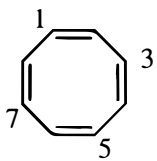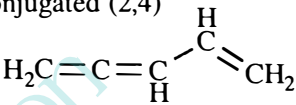
15-22
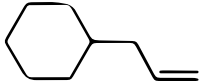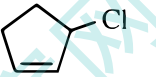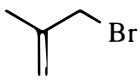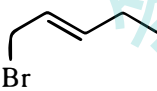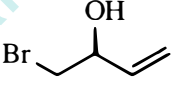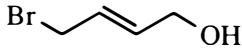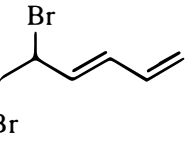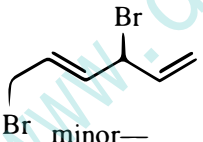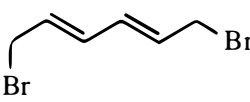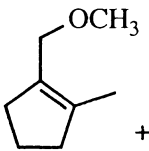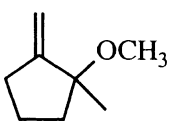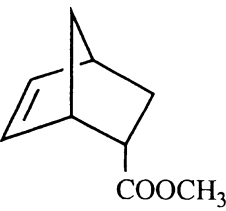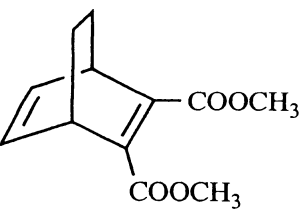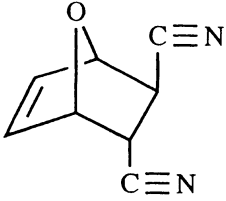
(a) 353 nm: a conjugated tetraene—must have highest absorption maximum among these compounds;
(b) 313 nm: closest to the bicyclic conjugated triene in Table 15-2; the diene is in a more substituted ring, so it is not surprising for the maximum to be slightly higher than 304 nm;
(c) 232 nm: similar to 3-methylenecyclohexene in Table 15-2;
(d) 273 nm: 1,3 cyclohexadiene (256 nm) + 2 alkyl substituents (2 x 5 nm) = predicted value of 266 nm;
(e) 237 nm: like 3-methylenecyclohexene (232 nm) + 1 alkyl group (5 nm) = predicted value of 237 nm

15-23 Please refer to solution 1-20, page 12 of this Solutions Manual.

15-24

(a) isolated   (b) conjugated   (c) cumulated   (d) conjugated   (e) conjugated

(f) cumulated (1,2) and conjugated (2,4)

15-25

(a)

(b) one equivalent of HCl

(c)

(d)

(e)

(f)   minor— not conjugated

(g)

(h)

(i)

(j)

328

15-26 Grignard reactions are performed in ether solvent. For clarity, the bonds formed are shown in bold.

(a)

(b)

(c)

15-27

(a)

(b)

(c)

(d)

329

15-27 continued

(e)

(f)

(g)
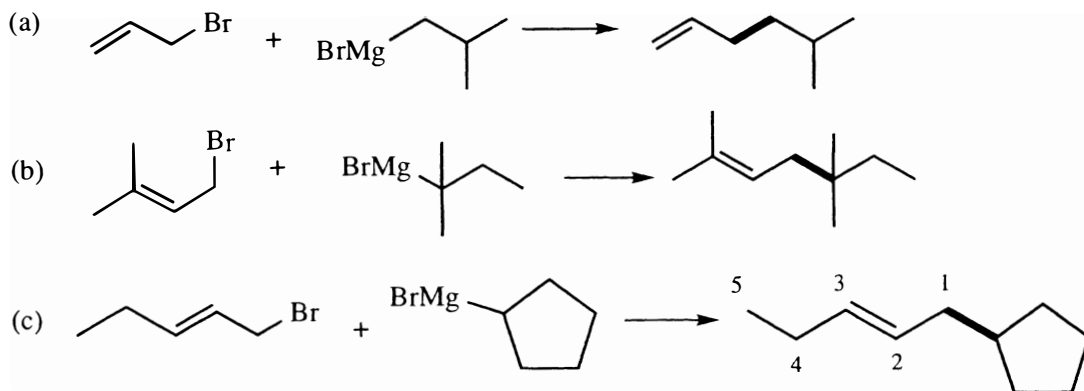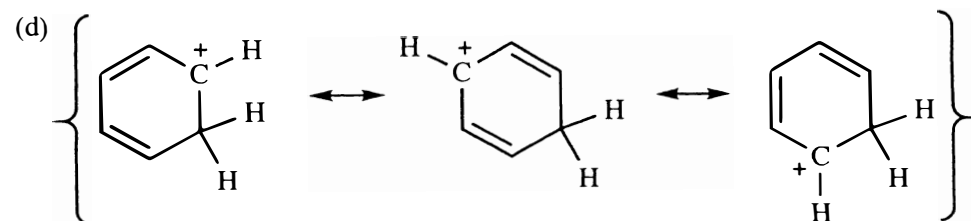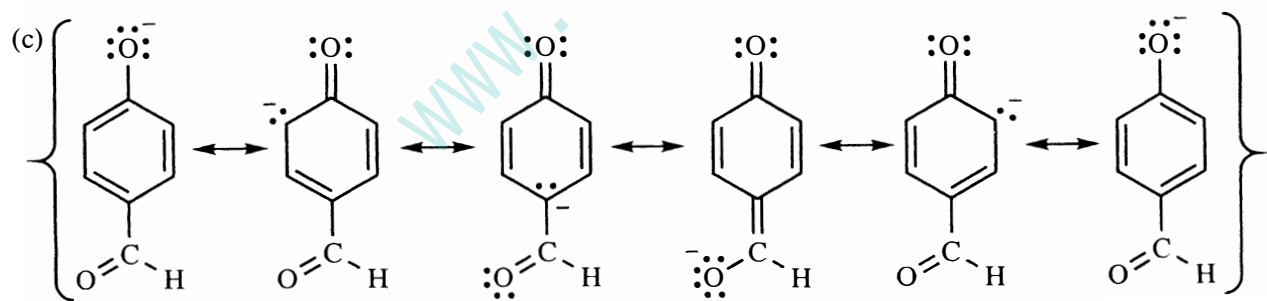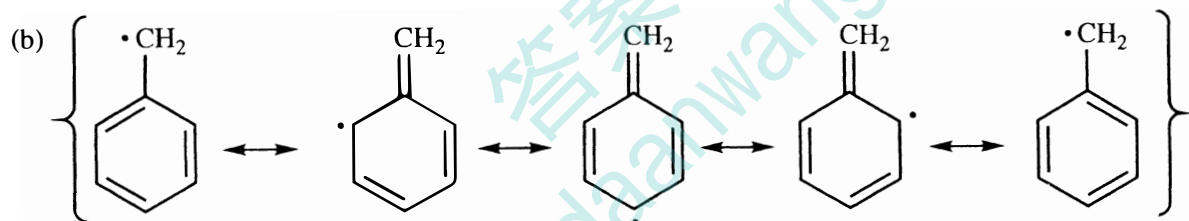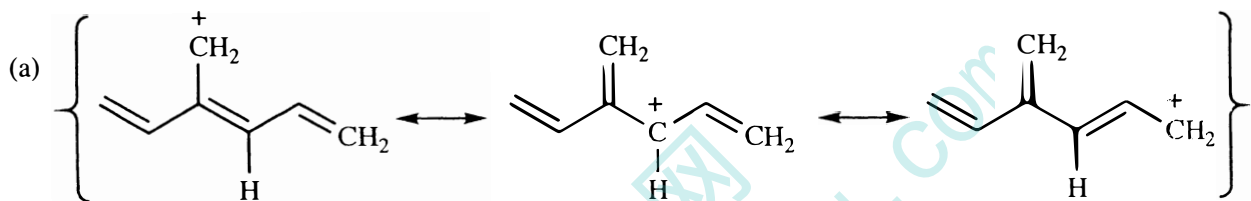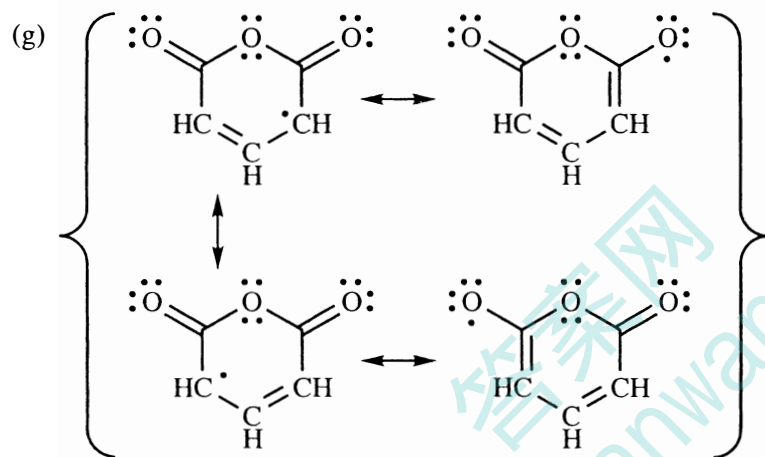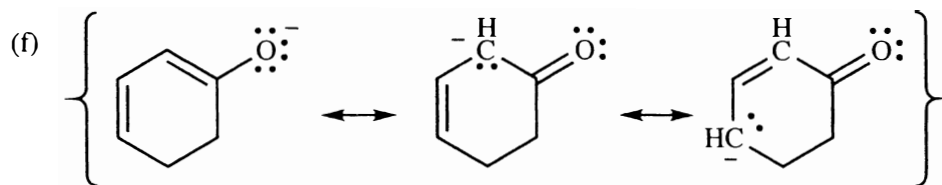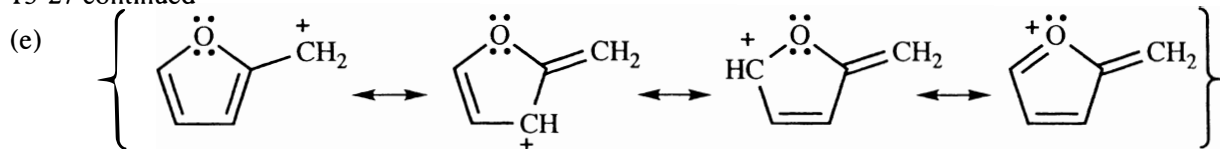
15-28

(a) $A = \varepsilon c l$ $\qquad$ $\varepsilon = \dfrac{A}{c\,l}$ $\qquad$ $l = 1 \text{ cm}$ $\qquad$ $A = 0.74$

convert mass to moles: $0.0010 \text{ g} \times \dfrac{1 \text{ mole}}{255 \text{ g}} = 3.9 \times 10^{-6} \text{ moles}$

$c = \dfrac{3.9 \times 10^{-6} \text{ moles}}{100 \text{ mL}} \times \dfrac{1000 \text{ mL}}{1 \text{ L}} = 3.9 \times 10^{-5} \text{ M}$

$\varepsilon = \dfrac{0.74}{(3.9 \times 10^{-5})(1)} \approx \boxed{19{,}000}$

(b) This large value of ε could only come from a conjugated system, eliminating the first structure. The absorption maximum at 235 nm is most likely a diene rather than a triene. The most reasonable structure is:
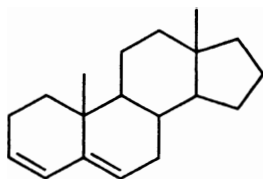
compare with:
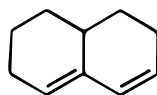
$\lambda_{max} = 235 \text{ nm}$

Solved Problem 15-3
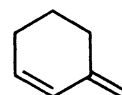
$\lambda_{max} = 232 \text{ nm}$

Table 15-2

15-29
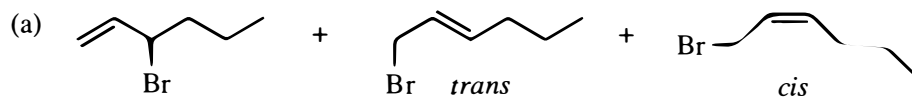
(a)

[structure: 3-bromo-1-hexene (vinyl, CH with Br, propyl chain)] + [structure: 1-bromo-2-hexene, *trans*] + [structure: Br—CH₂ cis alkene, *cis*]

Br   Br   *trans*   *cis*

(b)   ("Pr" is the abbreviation for *n*-propyl, used below.)

NBS generates a low concentration of Br_2

[structure: succinimide N—Br] + H—Br ⟶ [structure: succinimide N—H] + Br—Br

initiation

Br — Br $\xrightarrow{h\nu}$ 2 Br•
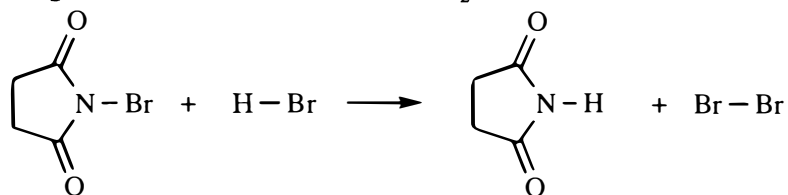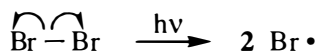
propagation

first step is abstraction of allylic hydrogen to generate allylic radical

Br• + Pr—CH₂—CH=CH₂ ⟶ HBr +   radical will be a
                                          mixture of cis
        1-hexene   and trans

{ Pr—ĊH—CH=CH₂ ⟷ Pr—CH=CH—ĊH₂ }
       Br—Br   Br—Br

Br• + Pr—CH(Br)—CH=CH₂ + Pr—CH=CH—CH₂Br

recycles in   Br   Br
chain mechanism

cis + trans

15-30

(a) [structure: cyclohexene ring with COOH substituent]
      COOH

(b) [bicyclic structure with COOCH₃]
      COOCH₃

(c) [norbornene structure with COOH]
      COOH

15-30 continued

(d)

(e)

(f)
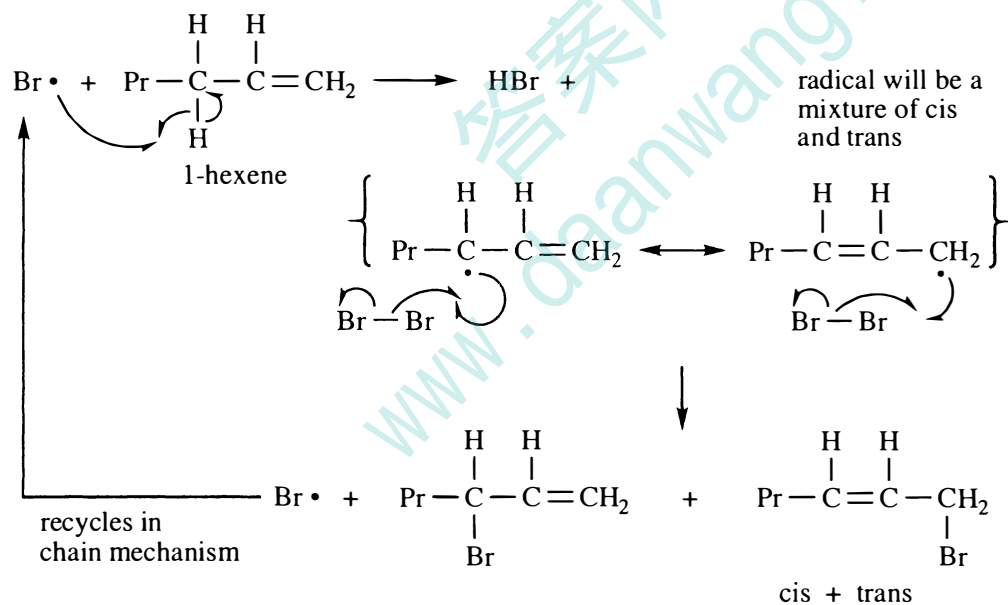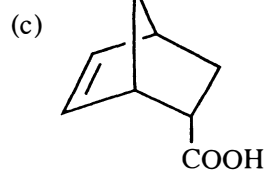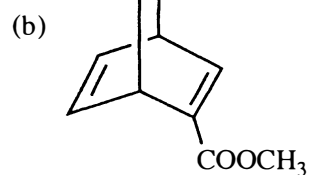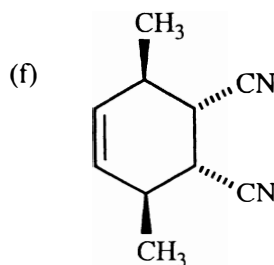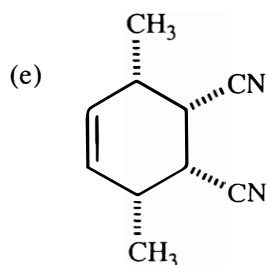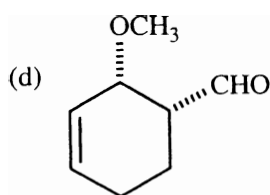
(Note: Yield of the product in (f) would be small or zero due to severe steric interaction in the *s-cis* conformation of the diene. See Figure 15-16.)

15-31

(a)

more significant
contributor: 2°

(b)

more significant
contributor: 2°

(c)

more significant contributor—
negative charge on more electronegative atom

(d)

more significant contributor—
no charge separation

(e)

most significant contributor—
negative charge on more electronegative atom

15-31 continued

(f)

most significant
contributor---all atoms
have full octets

(g)

more significant contributor—
negative charge can be stabilized
by electronegative chlorines

15-32

(a) The absorption at 1630 cm^{-1} suggests a conjugated alkene. The higher temperature allowed for migration of the double bond.

(b)

desired   actual

(c)
expected:

doubly allylic
m/z 122   m/z 79   mass 43

actual:

m/z 122   mass 29
                         m/z 93

15-33

(a)

(b)

(c)

(d)

(e)

(f)

333

15-33 continued

(g) (h) (i)
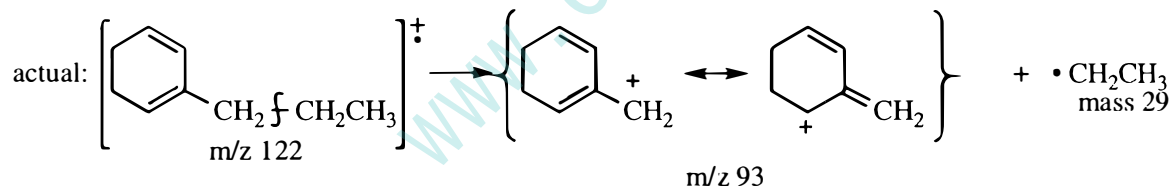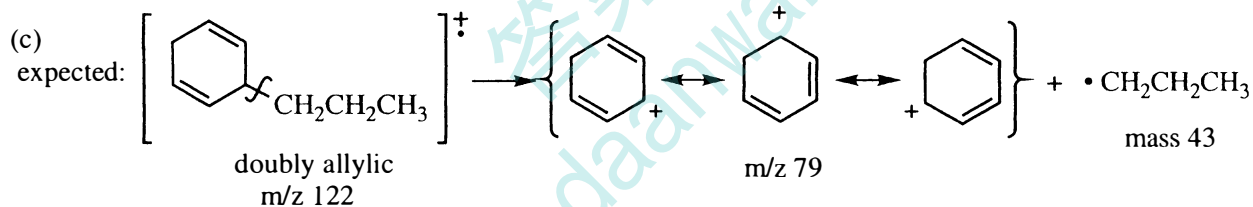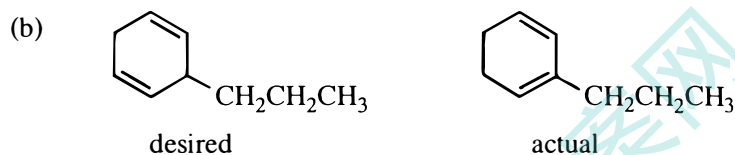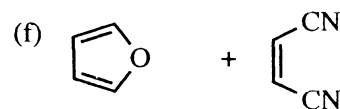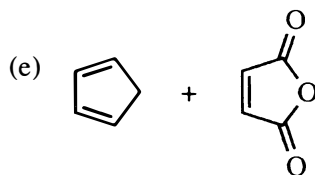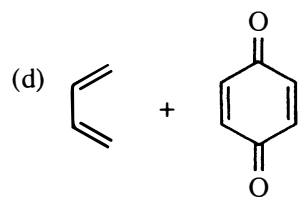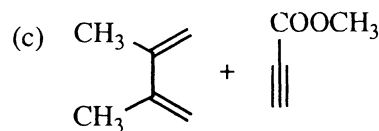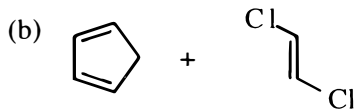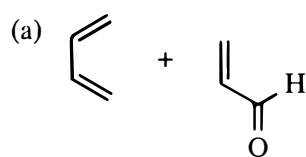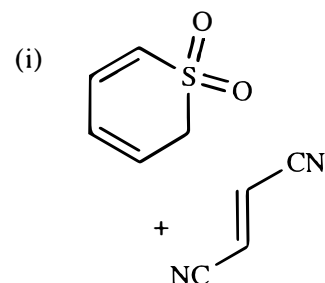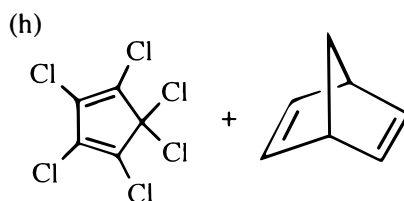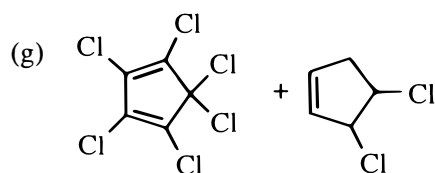
15-34

(a)
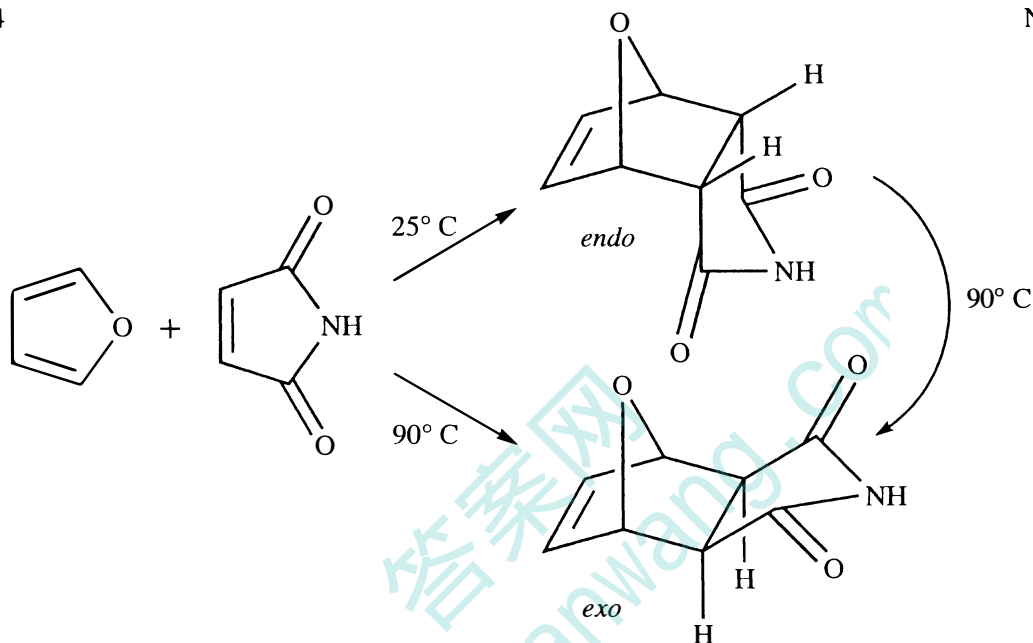
(b) The *endo* isomer is usually preferred because of secondary p orbital overlap of C=O with the diene in the transition state.

(c) The reasoning in (b) applies to stabilization of the transition state of the reaction, not the stability of the product. Arguments based on transition state stability apply to the rate of reaction, inferring that the *endo* product is the kinetic product.

(d) At 25° C, the reaction cannot easily reverse, or at least not very rapidly. The *endo* product is formed faster and is the major product because its transition state is lower in energy—the reaction is under kinetic control. At 90° C, the reverse reaction is not as slow and equilibrium is achieved. The *exo* product is less crowded and therefore more stable—equilibrium control gives the *exo* as the major product.

15-35 Nodes are represented by dashed lines.

(a)

π_6^*

π_5^*

π_4^*

π_3

π_2

π_1

(b)

π_6^*

π_5^*

π_4^*

π_3

π_2

π_1

(c)

335
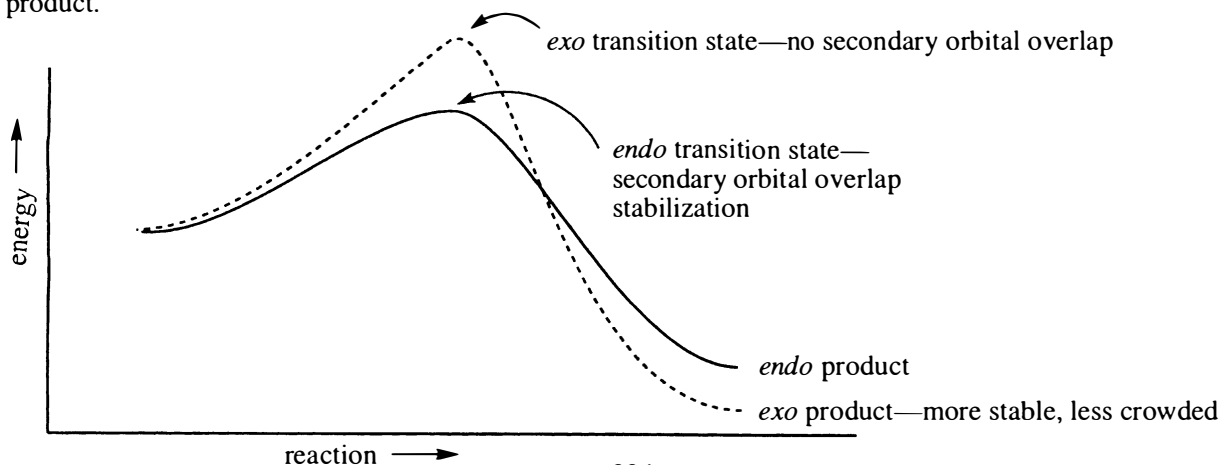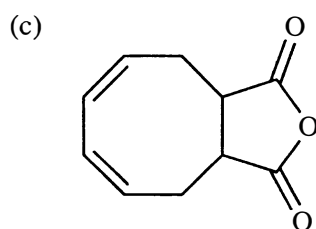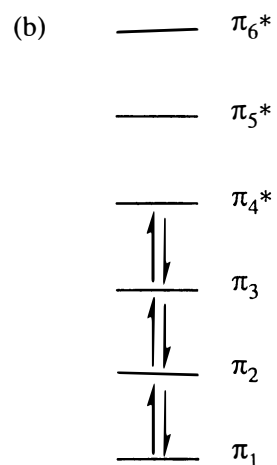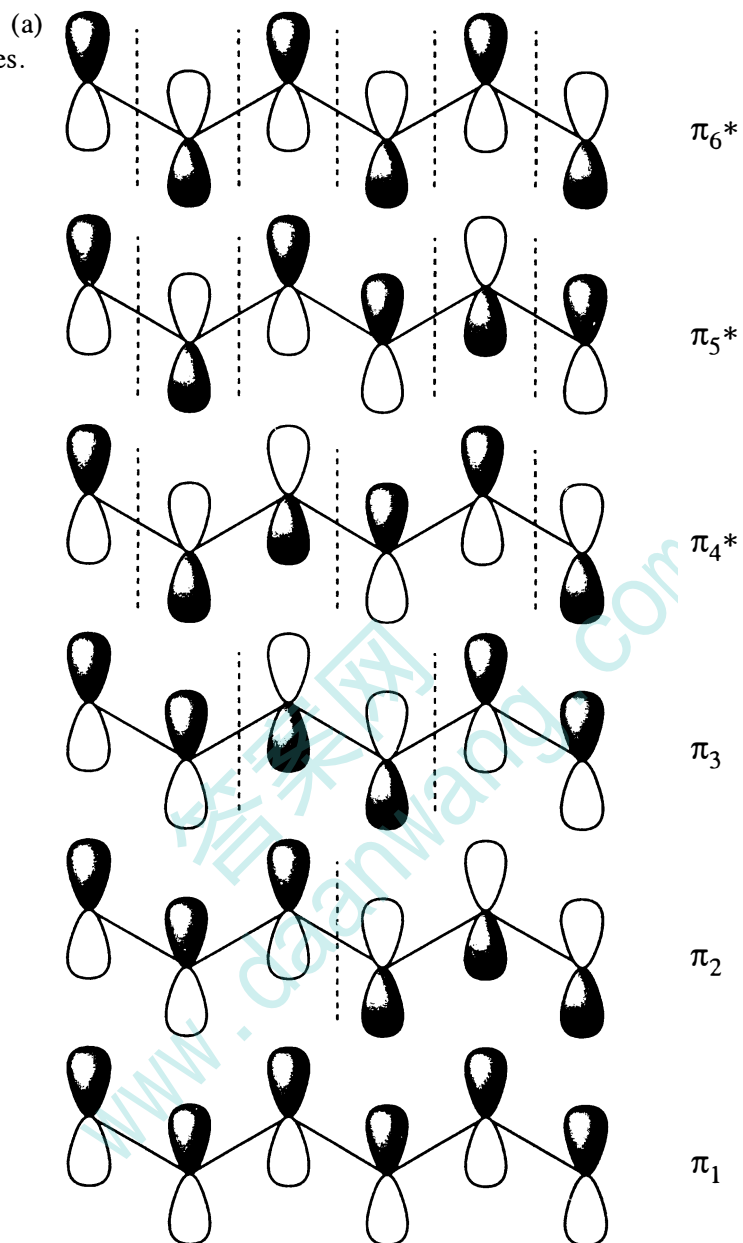
15-35 continued

(d) Whether the triene is the HOMO and the alkene is the LUMO, or *vice versa*, the answer will be the same.

Thermal	Photochemical

HOMO π_3

LUMO

one antibonding interaction

$\Rightarrow$ **forbidden**

HOMO* π_4*

LUMO

two bonding interactions

$\Rightarrow$ **allowed**

(e)

15-36

(a) $\left\{ H_2C=C-C=C-\overset{\bullet}{C}H_2 \longleftrightarrow H_2C=C-\overset{\bullet}{C}-C=CH_2 \longleftrightarrow H_2\overset{\bullet}{C}-C=C-C=CH_2 \right\}$
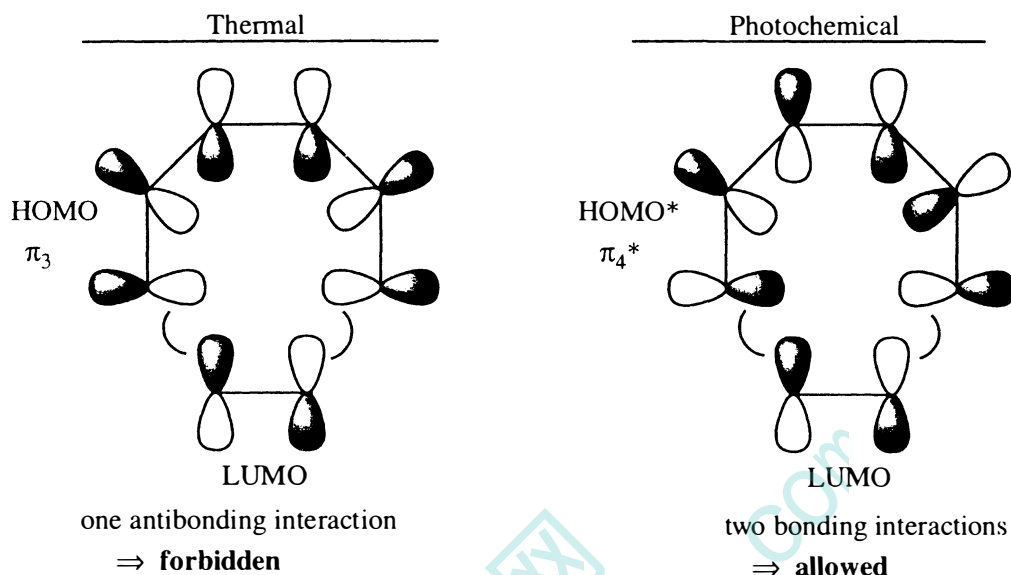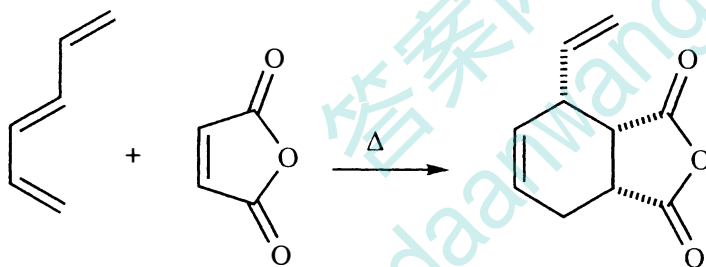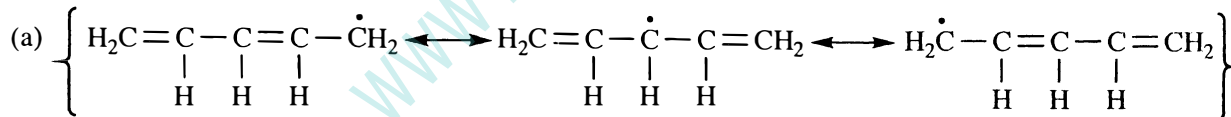
(b) Five atomic orbitals will generate five molecular orbitals.

(c) The lowest energy molecular orbital has no nodes. Each higher molecular orbital will have one more node, so the fifth molecular orbital will have four nodes.

15-36 continued

(d) Nodes are represented by dashed lines.

(e)

π₅*

π₄*

π₃

π₂

π₁
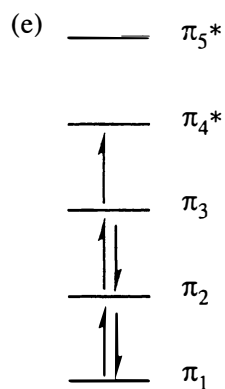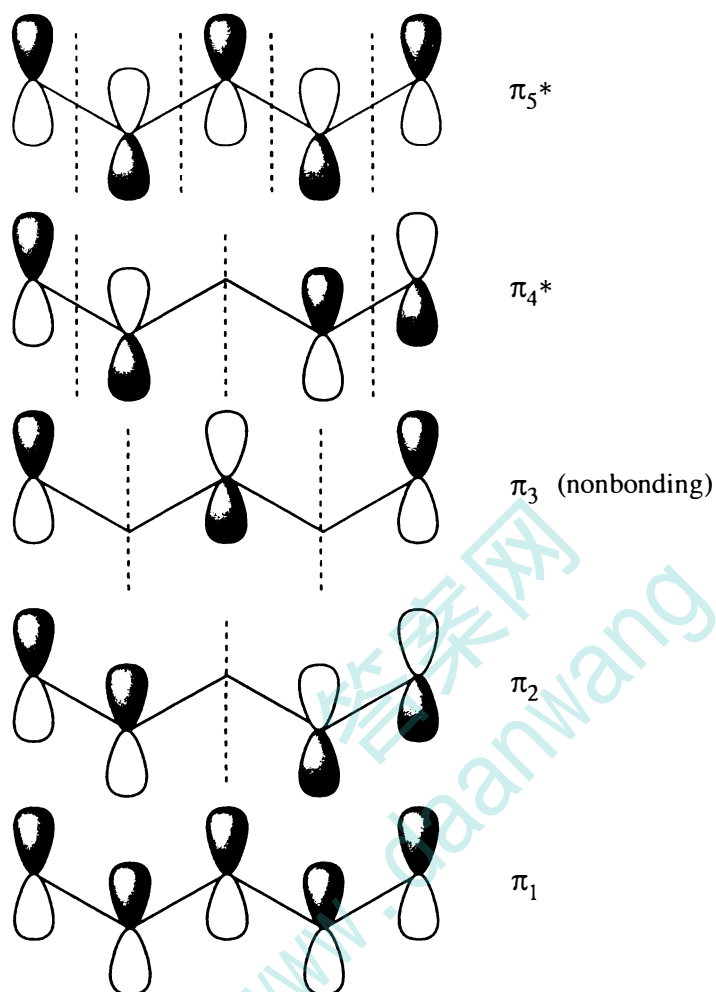
(f) The HOMO, π_3, contains an unpaired electron giving this species its radical character. The HOMO is a non-bonding orbital with lobes only on carbons 1, 3, and 5, consistent with the resonance picture.

15-36 continued

(g)

——— π_5^*

——— π_4^*

——— π_3

⇅ π_2

⇅ π_1
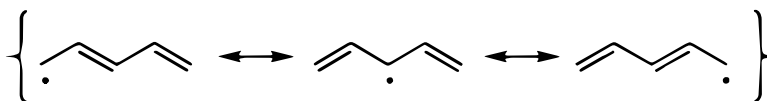
Again, it is π_3 that determines the character of this species. When the single electron in π_3 of the neutral radical is removed, positive charge appears only in the position(s) which that electron occupied. That is, the positive charge depends on the now *empty* π_3, with *empty* lobes (positive charge) on carbons 1, 3, and 5, consistent with the resonance description.

(h)

——— π_5^*

——— π_4^*

⇅ π_3

⇅ π_2

⇅ π_1
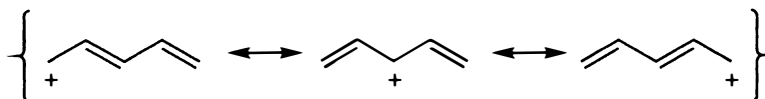
Again, it is π_3 that determines the character of this species. The negative charge depends on the *filled* π_3, with lobes (negative charge) on carbons 1, 3, and 5, consistent with the resonance description.

15-37
(a)
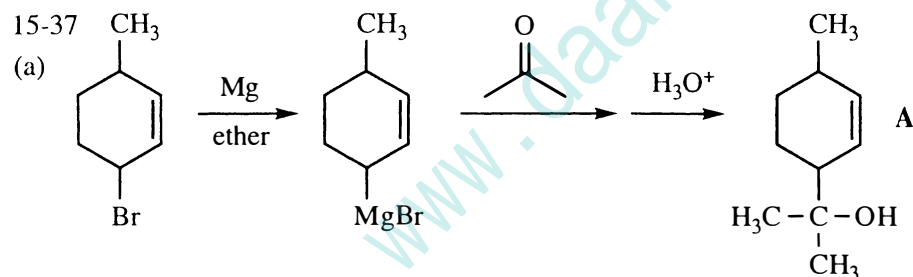
(b) Use Appendix 3 to predict λ_{max} values. Alkyl substituents are circled.
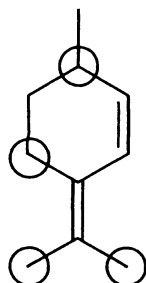
transoid cyclic diene = 217 nm
4 alkyl groups = 20 nm
exocyclic alkene = 5 nm
TOTAL = 242 nm

desired product
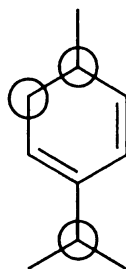
cisoid cyclic diene = 253 nm
3 alkyl groups = 15 nm
TOTAL = 268 nm
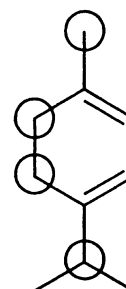
cisoid cyclic diene = 253 nm
4 alkyl groups = 20 nm
TOTAL = 273 nm—AHA!

actual product **B**

338

15-37 continued

(c)

B is produced in preference to the other cisoid diene above because **B**'s diene system is more highly substituted and therefore more stable
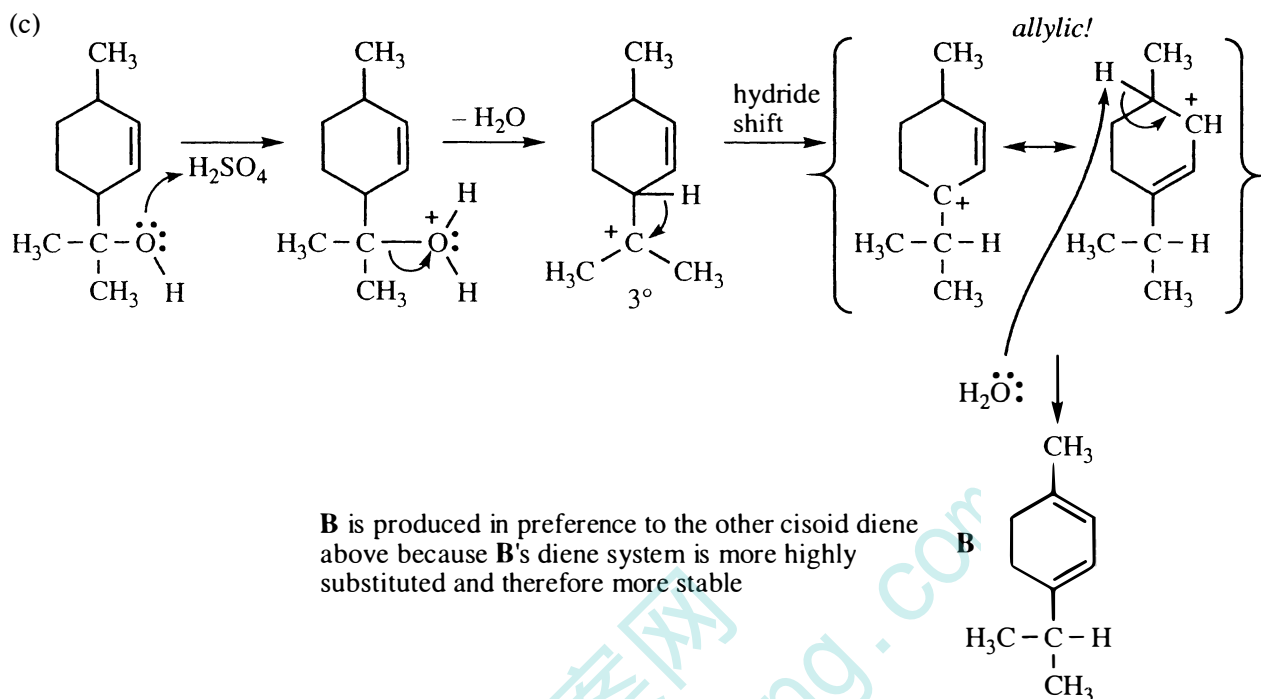
15-38 It is stunningly clever reactions like this that earned E. J. Corey his Nobel Prize.

Diels-Alder

imagine the diene on top of the dienophile in the transition state, leading to the *endo* adduct

endo product

retro-Diels-Alder

same as

amazing!
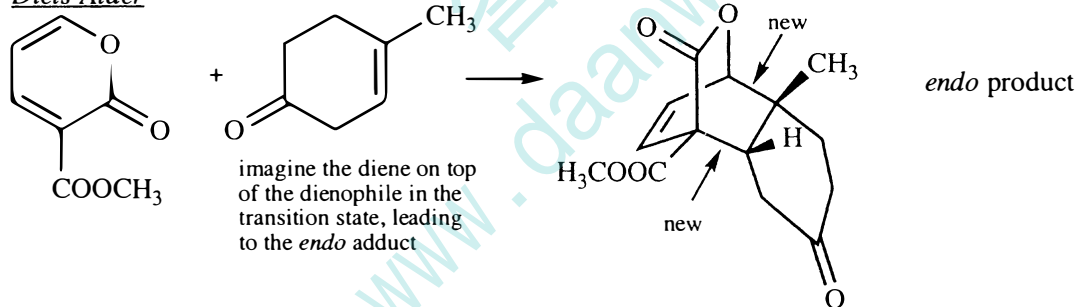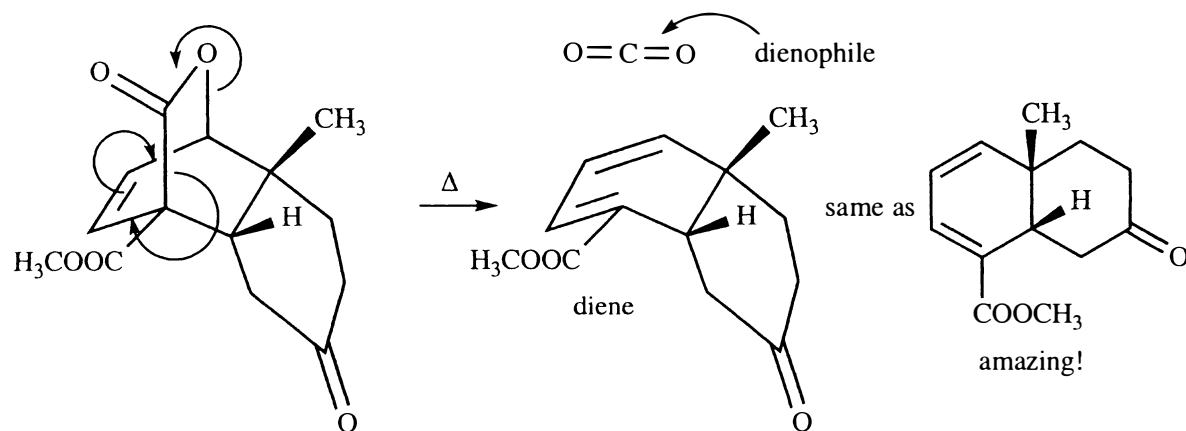
CHAPTER 16—AROMATIC COMPOUNDS

Note: The representation of benzene with a circle to represent the π system is fine for questions of nomenclature, properties, isomers, and reactions. For questions of mechanism or reactivity, however, the representation with three alternating double bonds (the Kekulé picture) is more informative. For clarity and consistency, this Solutions Manual will use the Kekulé form exclusively.

equivalent representations of benzene
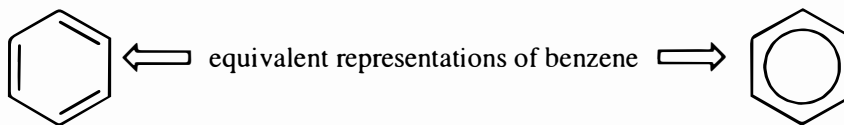
Kekulé form used in
the Solutions Manual

16-1
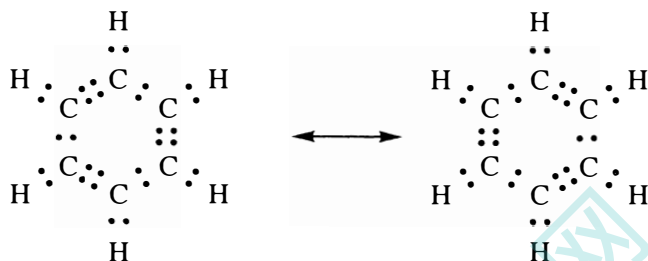
16-2   All values are per mole.

(a)   benzene $- 208$ kJ $- 49.8$ kcal
   $-$ 1,4-cyclohexadiene $- 240$ kJ $- 57.4$ kcal
                          $\Delta H = + 32$ kJ $+ 7.6$ kcal

(b)   benzene $- 208$ kJ $- 49.8$ kcal
   $-$ cyclohexene $- 120$ kJ $- 28.6$ kcal
                          $\Delta H = - 88$ kJ $- 21.2$ kcal

(c)   1,3-cyclohexadiene $- 232$ kJ $- 55.4$ kcal
   $-$ cyclohexene $- 120$ kJ $- 28.6$ kcal
                          $\Delta H = - 112$ kJ -26.8 kcal

16-3

(a)
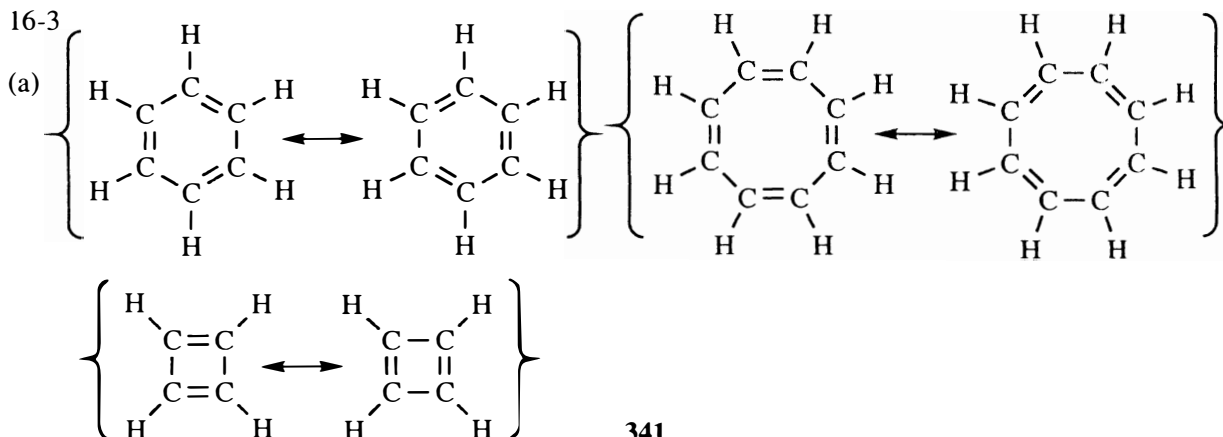
16-3 continued

(b)
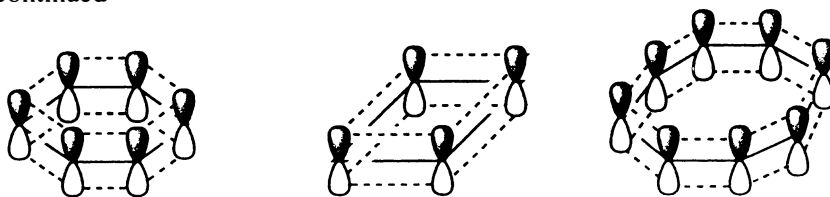
16-4
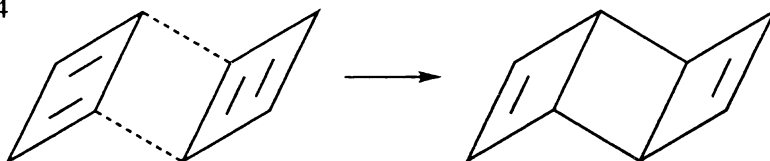
16-5 Figure 16-8 shows that the first 3 pairs of electrons are in three bonding molecular orbitals of cyclooctatetraene. Electrons 7 and 8, however, are located in two different nonbonding orbitals. As in cyclobutadiene, a planar cyclooctatetraene is predicted to be a diradical, a particularly unstable electron configuration.

16-6
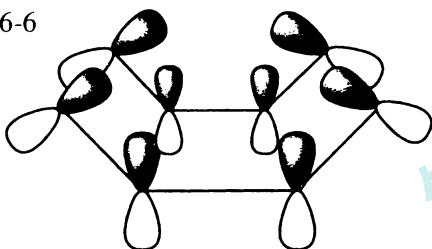
Models show that the angles between p orbitals on adjacent π bonds approach 90°.

16-7
(a) nonaromatic: internal hydrogens prevent planarity
(b) nonaromatic: not all atoms in the ring have a p orbital
(c) aromatic: [14]annulene
(d) aromatic: also a [14]annulene in the outer ring: the internal alkene is not part of the aromatic system

16-8 Azulene satisfies all the criteria for aromaticity, and it has a Huckel number of π electrons: 10. Both heptalene (12 π electrons) and pentalene (8 π electrons) are antiaromatic.

16-9

(a)

nonbonding energy
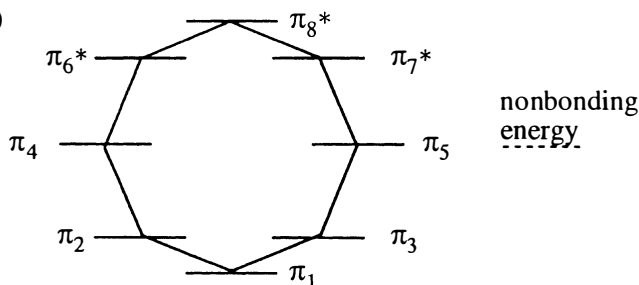
(b)
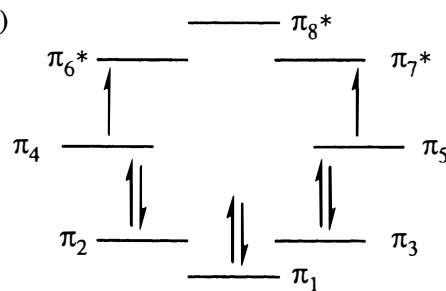
This electronic configuration is antiaromatic.

16-9 continued

(c)

These are TOP views. Nodes
are shown by dashed lines.

π_4 π_5 π_2 π_1 π_3

16-10

(a)

π_2^* π_3^* π_1

(b)

$$\underline{\qquad} \ \pi_2^* \qquad \underline{\qquad} \ \pi_3^*$$

$- -$ nonbonding

$$\underline{\qquad} \ \pi_1$$

π_1 is bonding; π_2^* and π_3^* are antibonding.

(c)

cation—**aromatic** anion—**antiaromatic**

16-11

(a)

π_4^* π_5^*

π_2 π_3

π_1

(b)

π_4^* ———   ——— π_5^* antibonding

————————————————————————————— nonbonding
π_2 ———   ——— π_3

bonding

——— π_1

(c)

π_4^* ———   ——— π_5^*

π_2 ———   ——— π_3

——— π_1

cation—**antiaromatic**

π_4^* ———   ——— π_5^*

π_2 ———   ——— π_3

——— π_1
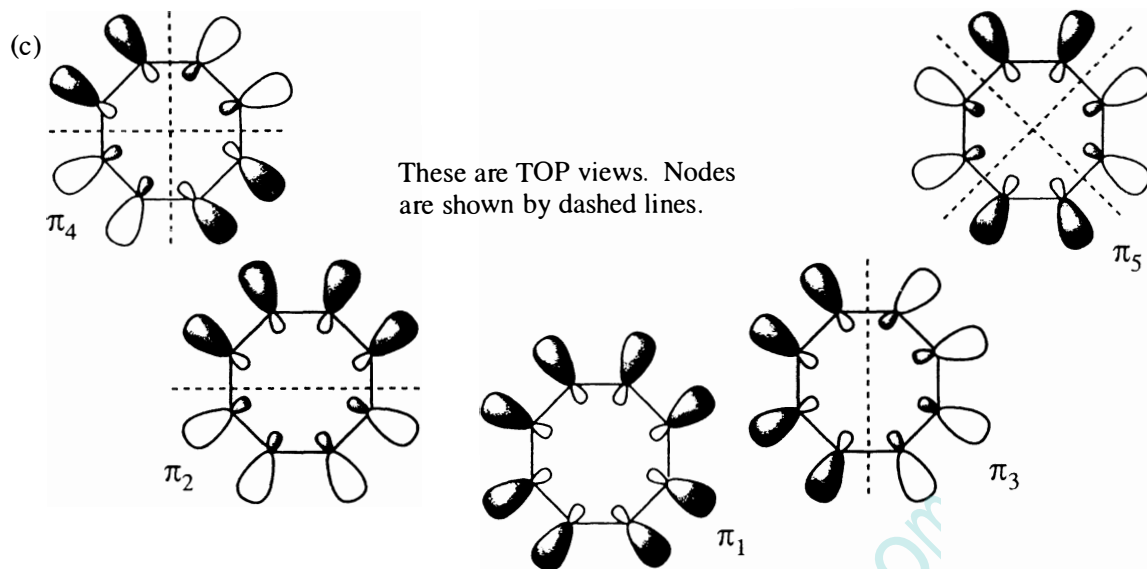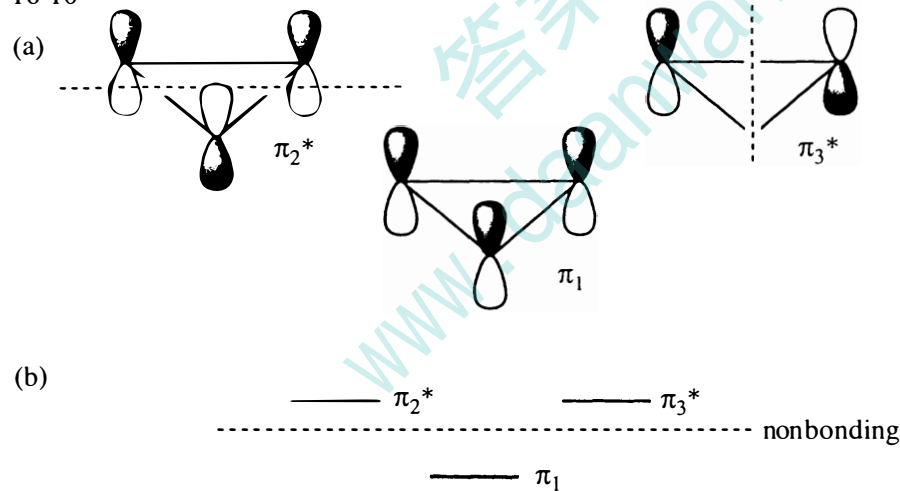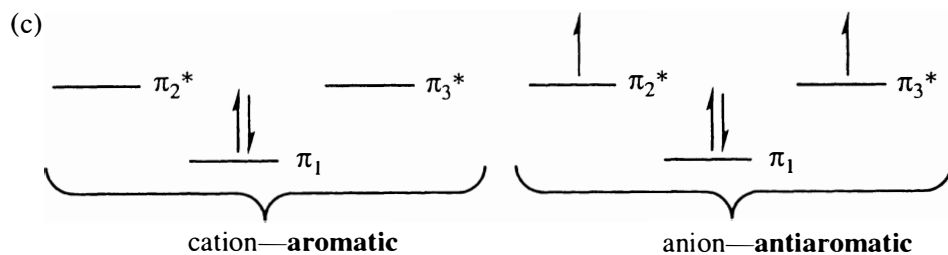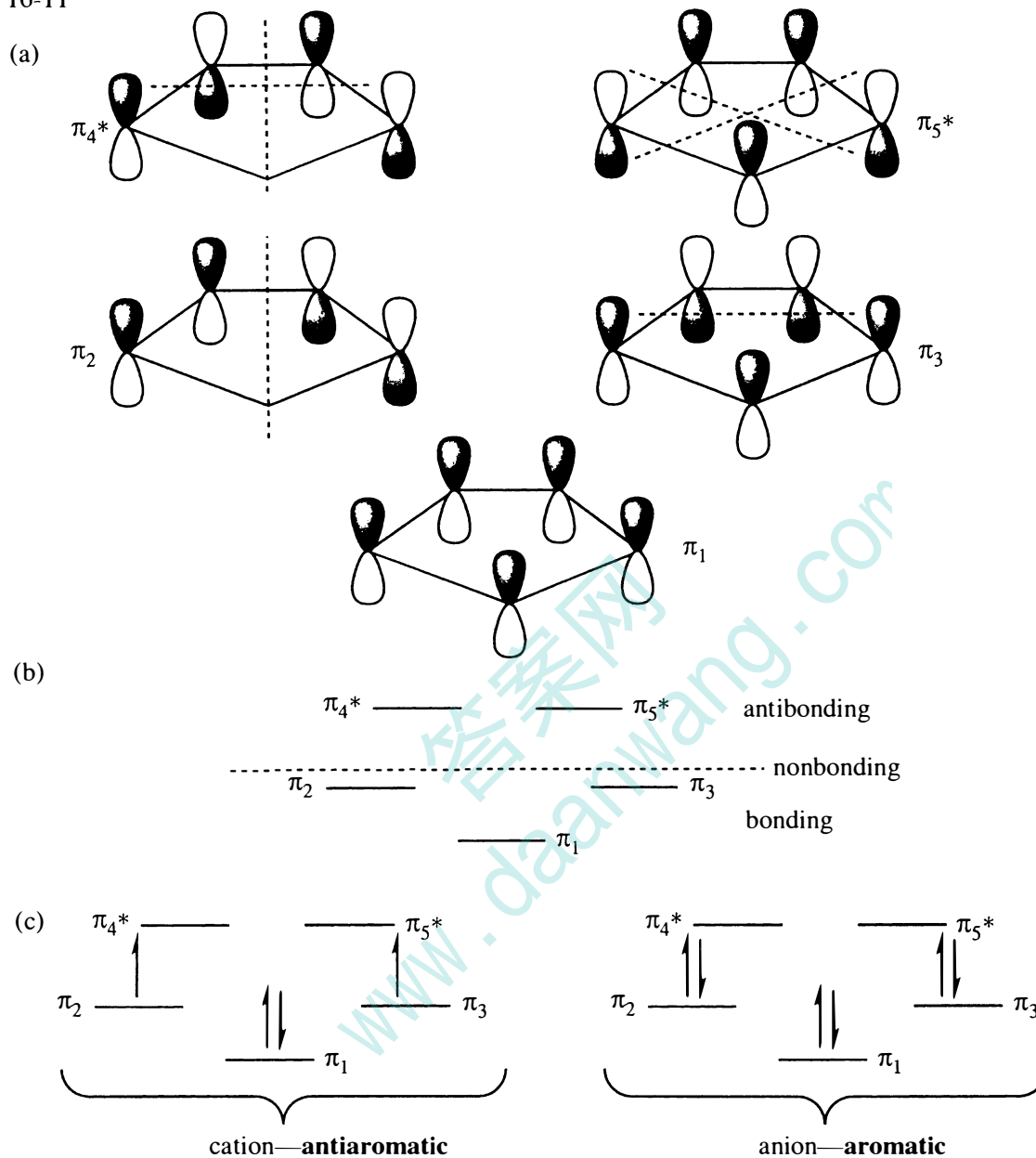
anion—**aromatic**

16-12

(a) antiaromatic: 8 π electrons, not a Huckel number
(b) aromatic: 10 π electrons, a Huckel number
(c) aromatic: 18 π electrons, a Huckel number
(d) antiaromatic: 20 π electrons, not a Huckel number
(e) nonaromatic: no cyclic π system
(f) aromatic: 18 π electrons, a Huckel number

16-13 The reason for the dipole can be seen in a resonance form distributing the electrons to give each ring 6 π electrons. This resonance picture gives one ring a negative charge and the other ring a positive charge.

aromatic tropylium ion
6 π electrons

aromatic cyclopentadienyl anion
6 π electrons

several resonance forms delocalizing the positive charge around the seven-membered ring

several resonance forms delocalizing the negative charge around the five-membered ring

composite resonance picture shows that both rings are aromatic with charge separation

16-14

aromatic cyclopropenium ion

The crystalline material soluble in polar organic solvents is cyclopropenium tetrafluoroborate.

KCl

Cl—◁| + KBF$_4$

16-15 Draw resonance forms showing the carbonyl polarization, leaving a positive charge on the carbonyl carbon.

2 π electrons—
AROMATIC

6 π electrons—
AROMATIC

4 π electrons—
ANTIAROMATIC

The three- and seven-membered rings are aromatic; the five-membered ring is antiaromatic and, not surprisingly, very reactive.

345
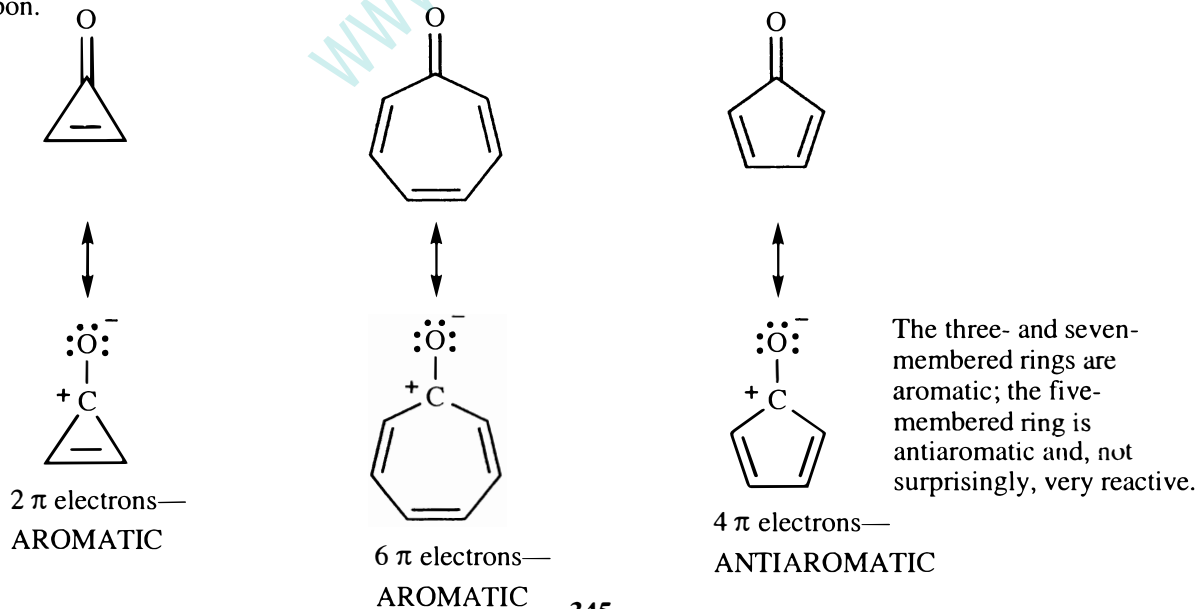
16-16
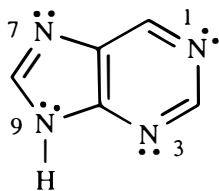
The structure of purine shows two types of nitrogens. One type (N-1, N-3, and N-7) has an electronic structure like the nitrogen in pyridine; the pair of electrons is in an sp^2 orbital planar with the ring. These electrons are available for bonding, and these three nitrogens are basic. The other type of nitrogen at N-9 has an electronic structure like the nitrogen of pyrrole; its electron pair is in a p orbital, perpendicular to the ring system, and more importantly, an essential part of the aromatic pi system. With this pair of electrons, the pi system is aromatic and has 10 electrons, a Huckel number, so the electron pair is not available for bonding and N-9 is not a basic nitrogen.

16-17

(a)   The proton NMR of benzene shows a single peak at δ 7.2; alkene hydrogens absorb at δ 4.5-6. The chemical shifts of 2-pyridone are more similar to benzene's absorptions than they are to alkenes. It would be correct to infer that 2-pyridone is aromatic.

(b)
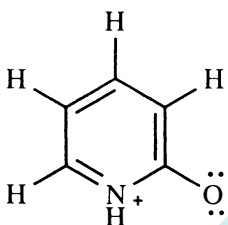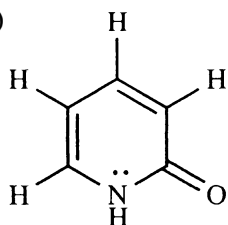
The lone pair of electrons on the nitrogen in the first resonance form is part of the cyclic pi system. The second resonance form shows three alternating double bonds with six electrons in the cyclic pi system, consistent with an aromatic electronic system.
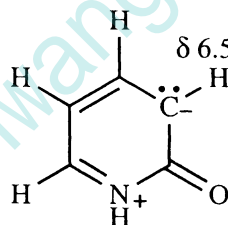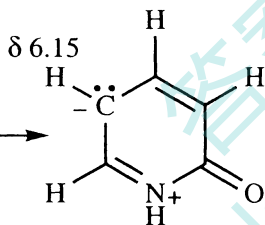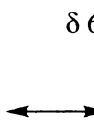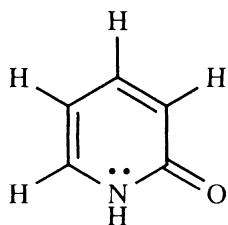
δ 6.15   δ 6.57 These resonance forms show that the hydrogens at positions with greater electron density are shielded, decreasing chemical shift.

H δ 7.26

δ 7.31
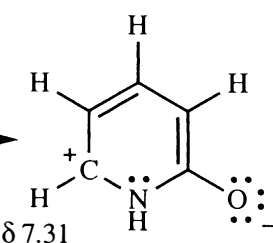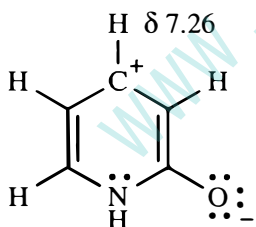
These resonance forms show that the hydrogens at positions with greater positive charge are deshielded, increasing chemical shift.

(c)
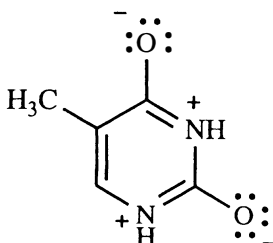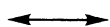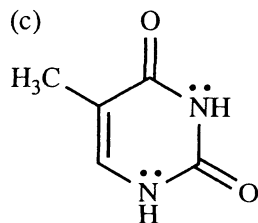
This resonance form of thymine shows a cyclic pi system with 6 pi electrons, consistent with an aromatic system. Four of these electrons came from the two lone pairs of electrons on nitrogens in the first resonance form.

16-18

(a)
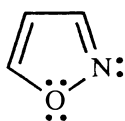
aromatic: 4 π
electrons in
double bonds
plus one pair
from oxygen

(b)
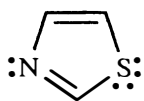
aromatic: 4 π
electrons in
double bonds
plus one pair
from sulfur

(c)
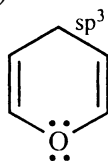
not aromatic:
no cyclic π
system
because of sp³
carbon

(d)
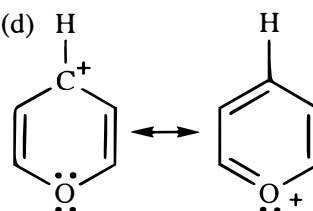
aromatic: cation on carbon-
4 indicates an empty p
orbital; two π bonds plus a
pair of electrons from
oxygen makes a 6 π
electron system

(e)
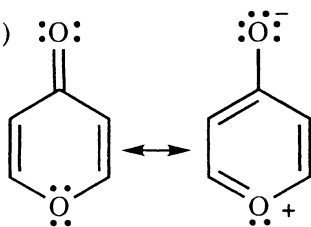
aromatic: resonance form
shows "push-pull" of
electrons from one O to
the other, making a cyclic
π system with 6 electrons

(f)
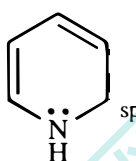
not aromatic:
no cyclic π
system
because of sp³
carbon

(g)
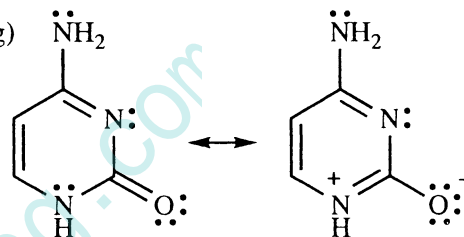
aromatic: resonance form shows
electron pair from N making a cyclic
π system with 6 electrons

16-19
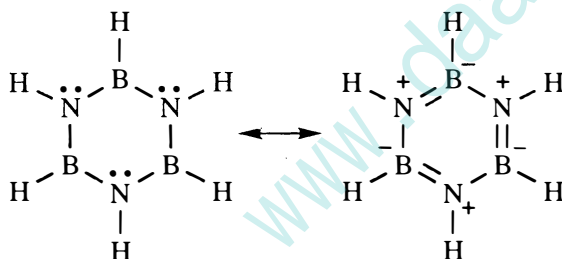
Borazole is a non-carbon equivalent of
benzene. Each boron is hybridized in its
normal sp². Each nitrogen is also sp² with its
pair of electrons in its p orbital. The system
has six π electrons in 6 p orbitals—aromatic!

16-20

(a)
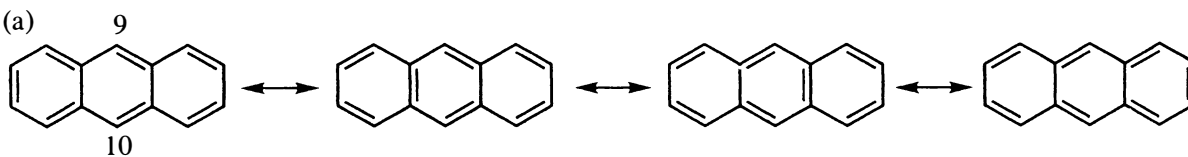
anthracene

phenanthrene

347
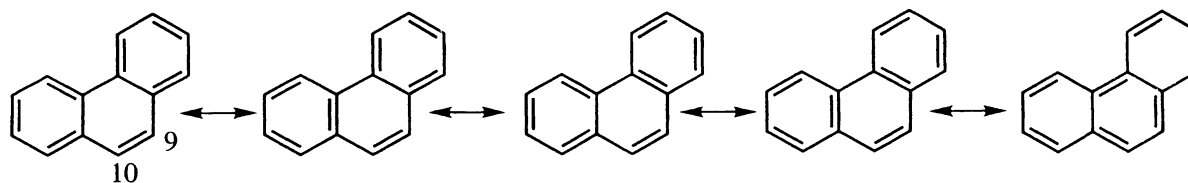
16-20 continued

(b) <u>anthracene</u>

plus many other resonance forms

bromide attack at C-10 leaves two aromatic rings

<u>phenanthrene</u>

plus many other resonance forms

cis and *trans*

bromide attack at C-9 leaves two aromatic rings
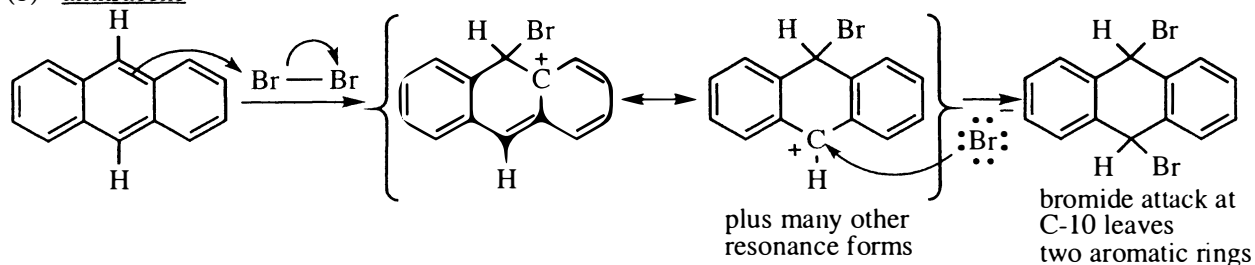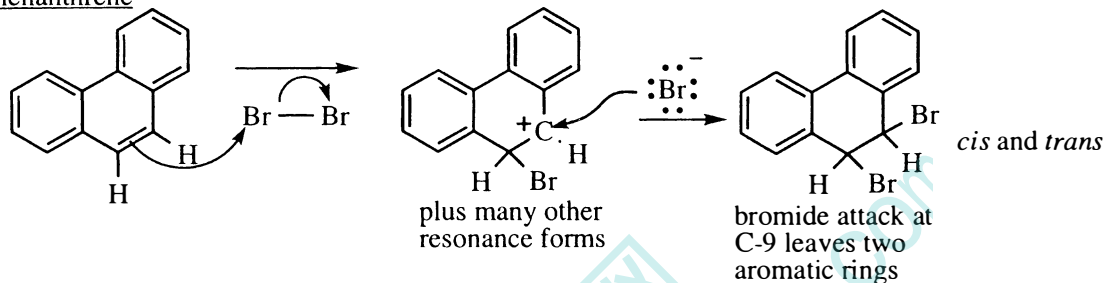
(c) A typical addition of bromine occurs with a bromonium ion intermediate which can give only anti addition. Addition of bromine to phenanthrene, however, generates a free carbocation because the carbocation is benzylic, stabilized by resonance over two rings. In the second step of the mechanism, bromide nucleophile can attack either side of the carbocation giving a mixture of *cis* and *trans* products.

(d)

resonance-stabilized

+ HBr
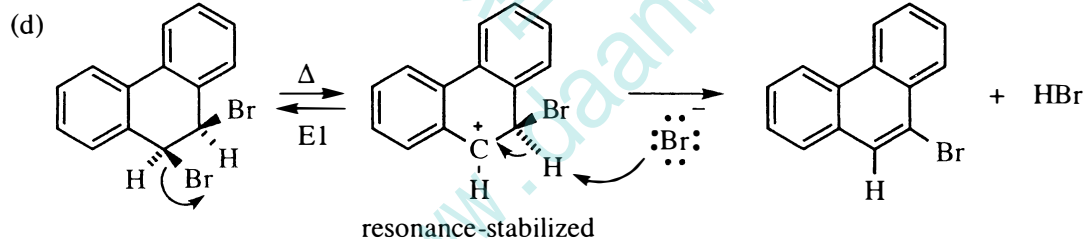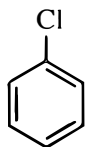
16-21
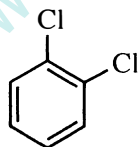
chlorobenzene

o-dichlorobenzene (1,2-dichlorobenzene)
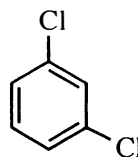
m-dichlorobenzene (1,3-dichlorobenzene)
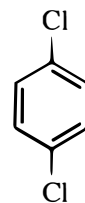
p-dichlorobenzene (1,4-dichlorobenzene)
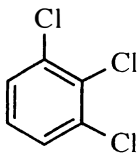
1,2,3-trichlorobenzene
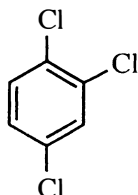
1,2,4-trichlorobenzene
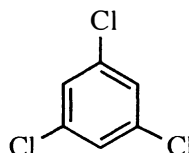
1,3,5-trichlorobenzene
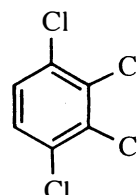
1,2,3,4-tetrachloro-benzene

16-21 continued
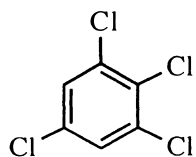
1,2,3,5-tetrachloro-
benzene
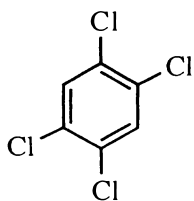
1,2,4,5-tetrachloro-
benzene
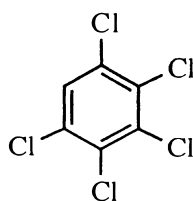
1,2,3,4,5-pentachloro-
benzene
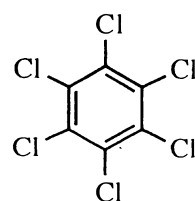
1,2,3,4,5,6-hexachloro-
benzene

16-22

(a) fluorobenzene
(b) 4-phenylbut-1-yne
(c) *m*-methylphenol, or
    3-methylphenol
    (common name: *m*-cresol)

(d) *o*-nitrostyrene
(e) *p*-bromobenzoic acid, or
    4-bromobenzoic acid
(f) isopropoxybenzene, or
    isopropyl phenyl ether

(g) 3,4-dinitrophenol
(h) benzyl ethyl ether, or
    benzoxyethane, or
    (ethoxymethyl)benzene, or
    α-ethoxytoluene

16-23 These examples are representative. Your examples may be different from these and still be correct.

(a)
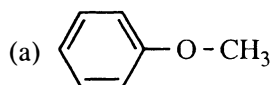
methyl phenyl ether
or methoxybenzene
or anisole

(b)
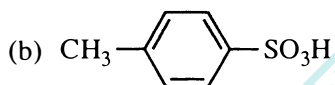
p-toluenesulfonic acid

(c)

phenyllithium

(d)
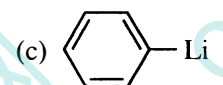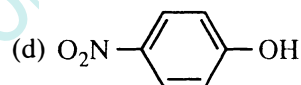
These are *phenols*.
This is 4-nitrophenol.

(e)

diphenylmethanol

(f)
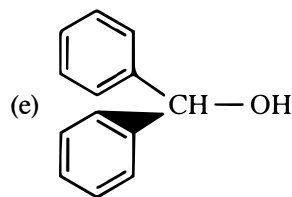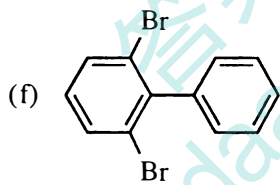
1,3-dibromo-2-phenylbenzene

(g)
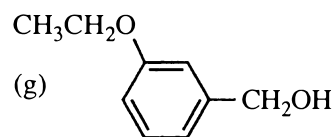
3-ethoxybenzyl alcohol
or 3-ethoxyphenylmethanol

16-24

16-25

λ_{max} 220 nm (strong)
        258 nm (weak)

$- H_2O$

plus resonance forms with positive
charge on the benzene ring

λ_{max} 250 nm (strong)
        290 nm (weak)

electronic systems with extended
conjugation absorb at longer wavelength
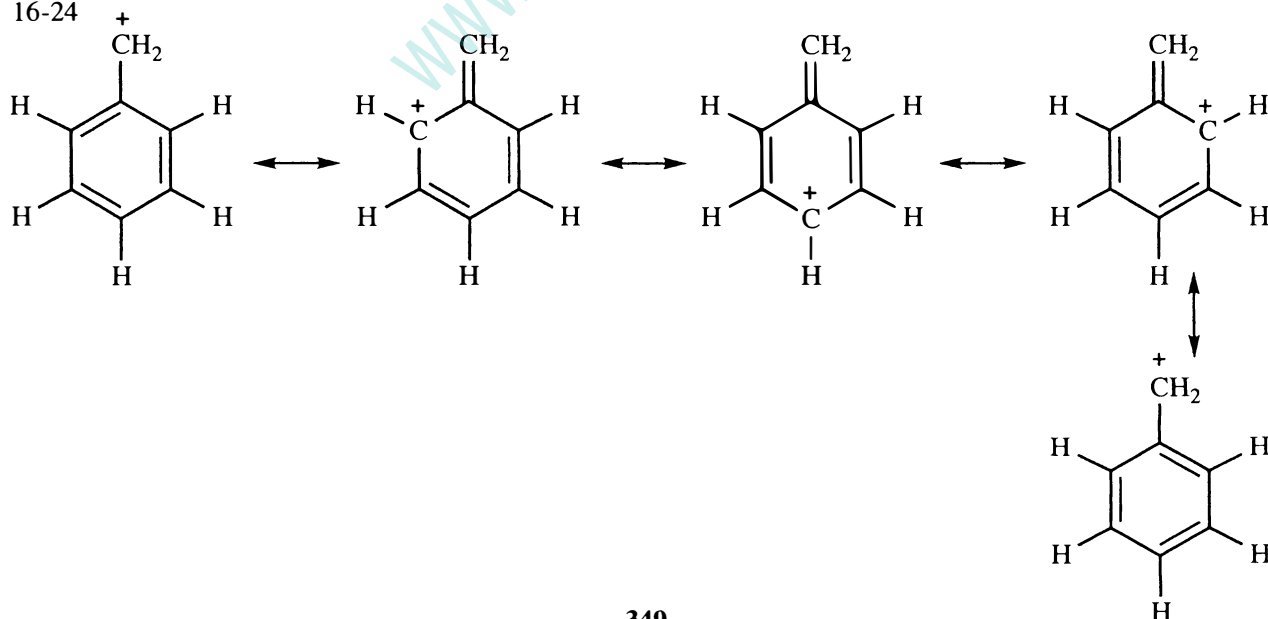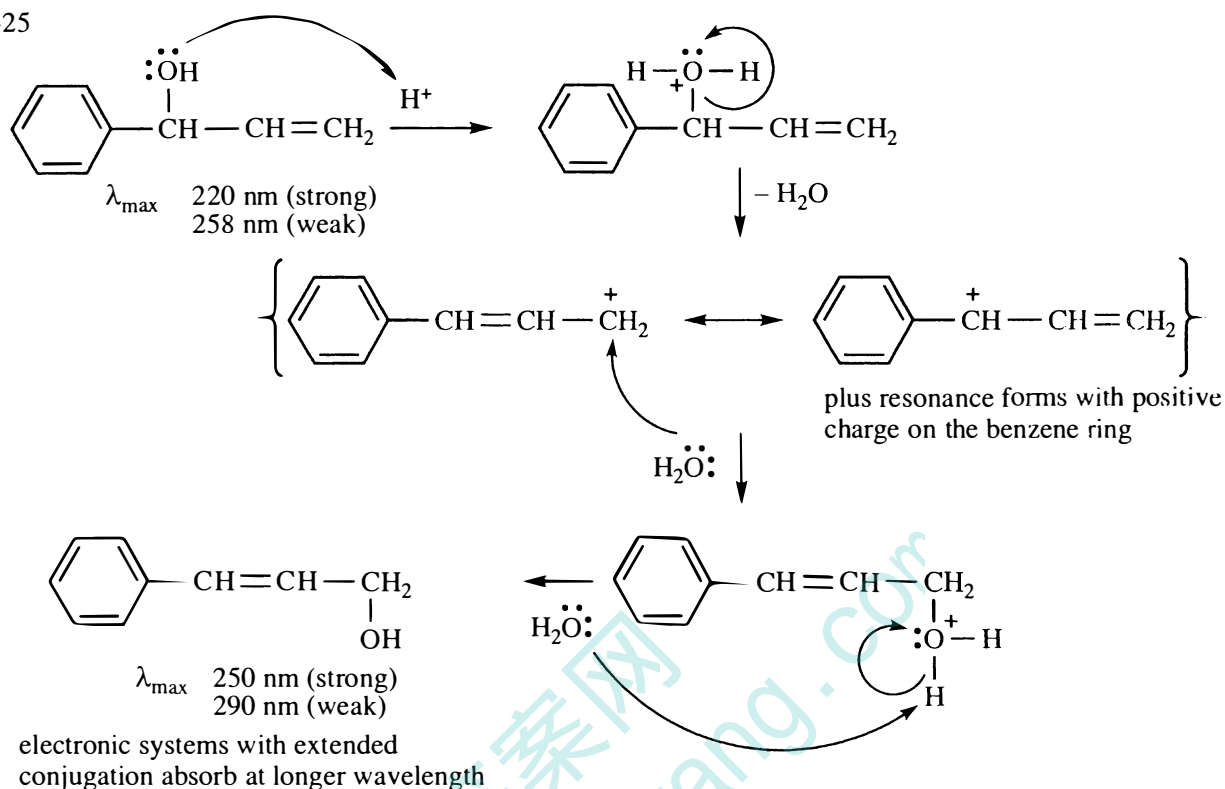
16-26   Please refer to solution 1-20, page 12 of this Solutions Manual.

16-27

350
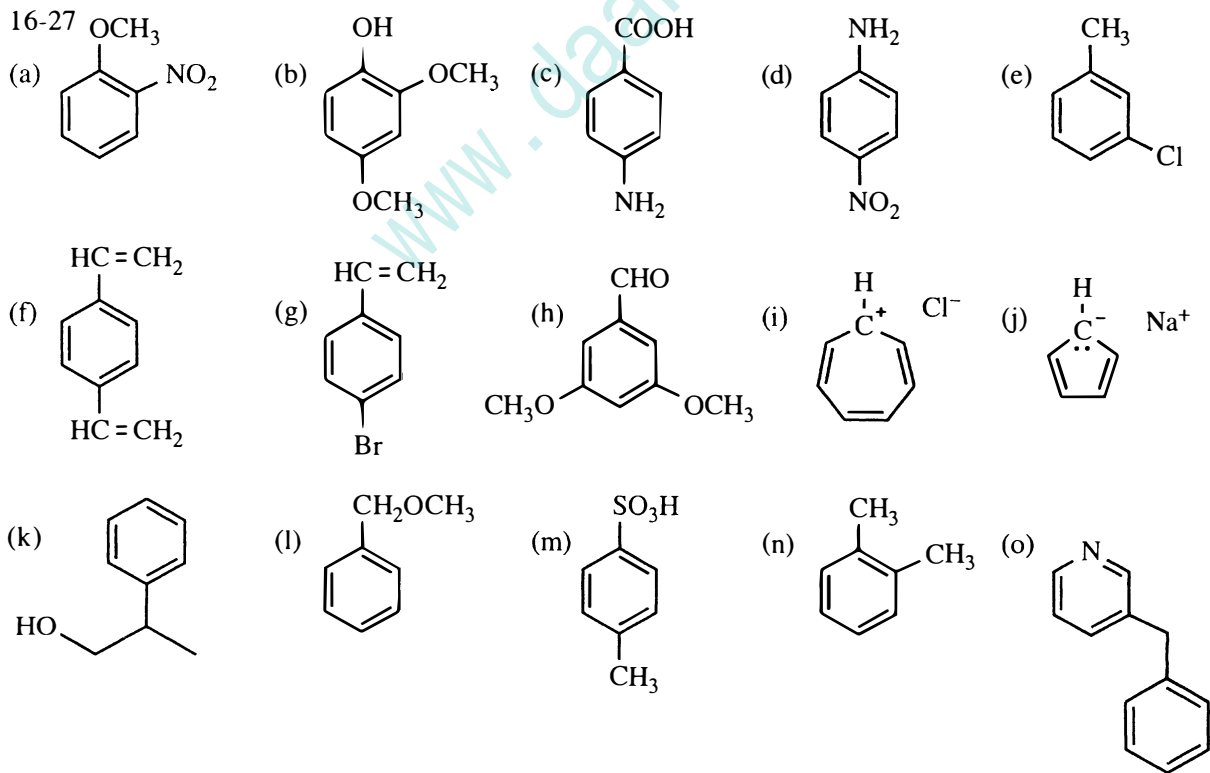
16-28

(a) 1,2-dichlorobenzene (*ortho*)
(b) 4-nitroanisole (*para*)
(c) 2,3-dibromobenzoic acid
(d) 2,7-dimethoxynaphthalene

(e) 3-chlorobenzoic acid (*meta*)
(f) 2,4,6-trichlorophenol
(g) 2-*sec*-butylbenzaldehyde (*ortho*)
(h) cyclopropenium tetrafluoroborate

16-29
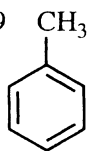
toluene
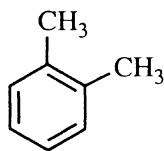
o-xylene
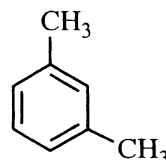
m-xylene
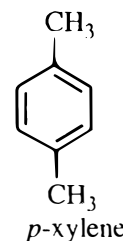
p-xylene
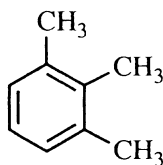
1,2,3-trimethylbenzene
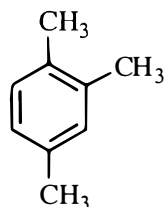
1,2,4-trimethylbenzene
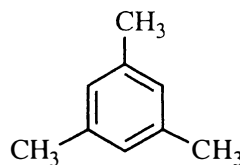
1,3,5-trimethylbenzene
(common name: mesitylene)

16-30 Aromaticity is one of the strongest stabilizing forces in organic molecules. The cyclopentadienyl system is stabilized in the anion form where it has 6 π electrons, a Huckel number. The question then becomes: which of the four structures can lose a proton to become aromatic?

While the first, third, and fourth structures can lose protons from sp^3 carbons to give resonance-stabilized anions, only the second structure can make a cyclopentadienide anion. It will lose a proton most easily of these four structures which, by definition, means it is the strongest acid.

AROMATIC

16-31

(a)

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16-31 continued

(b)

(c)

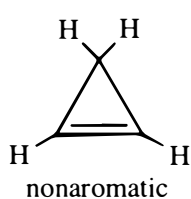different positions
of double bonds

(ignoring enantiomers)
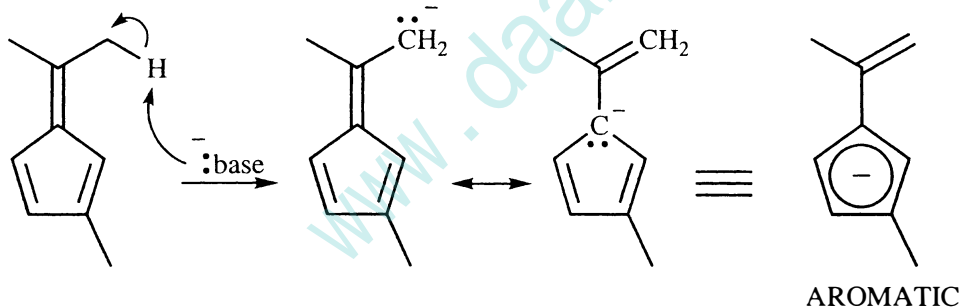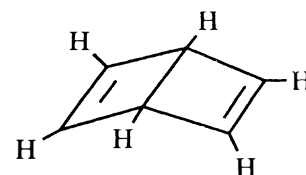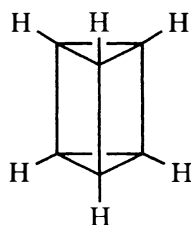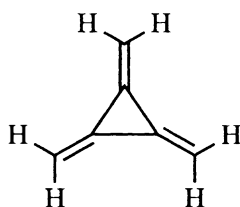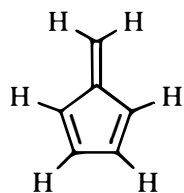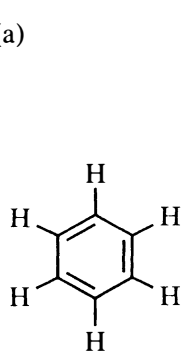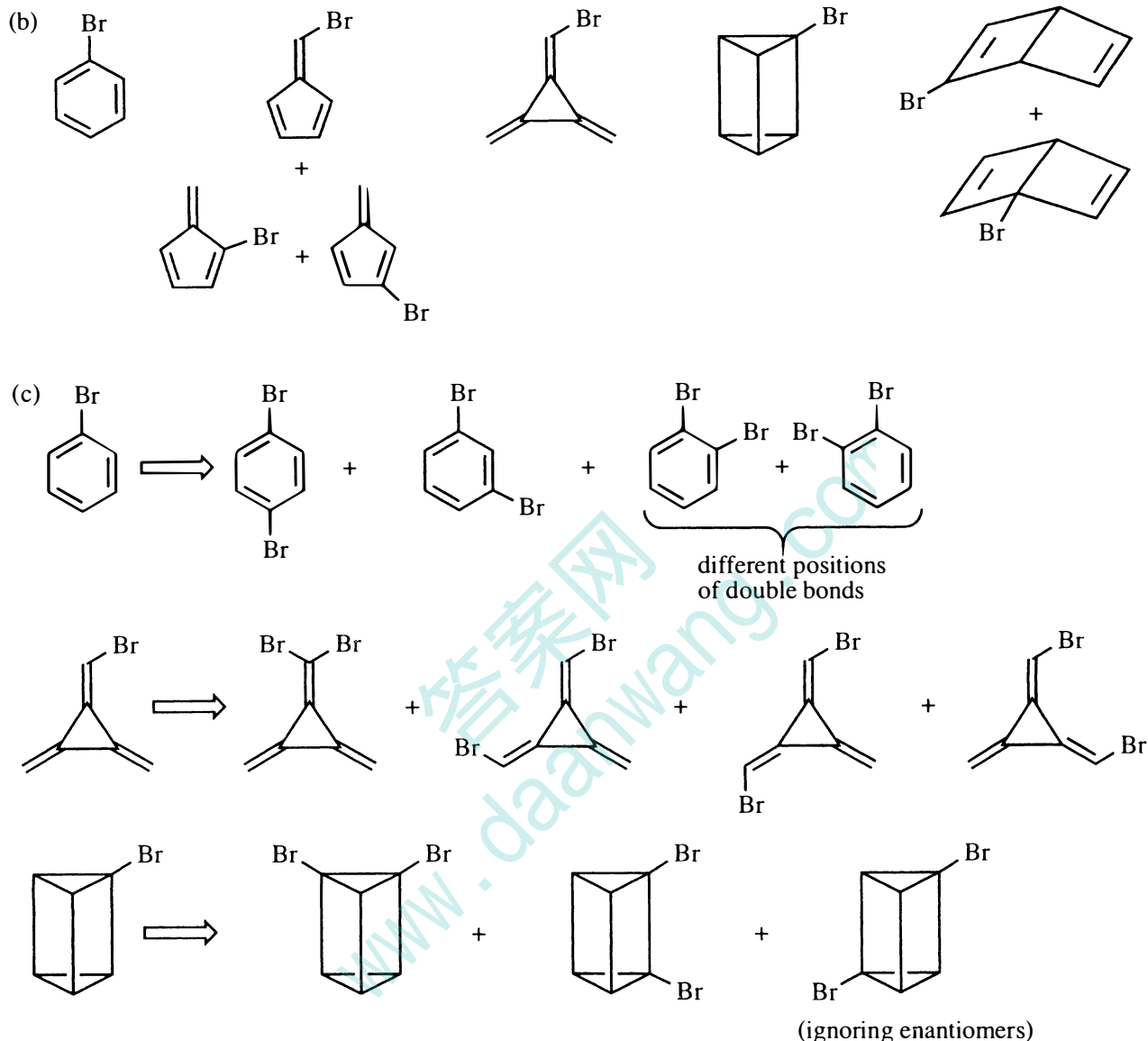
(d) The only structure consistent with three isomers of dibromobenzene is the prism structure, called Ladenburg benzene. It also gives no test for alkenes, consistent with the behavior of benzene. (Kekulé defended his structure by claiming that the "two" structures of *ortho*-dibromobenzene were rapidly interconverted, equilibrating so quickly that they could never be separated.)
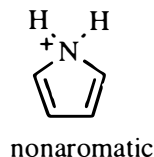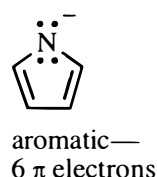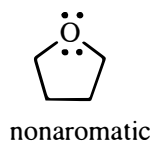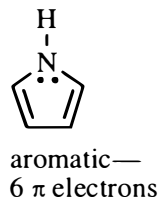
(e) We now know that three- and four-membered rings are the least stable, but this fact was unknown to chemists during the mid-1800s when the benzene controversy was raging. Ladenburg benzene has two three-membered rings and three four-membered rings (of which only four of the rings are independent), which we would predict to be unstable. (In fact, the structure has been synthesized. Called *prismane*, it is NOT aromatic, but rather, is very reactive toward addition reactions.)
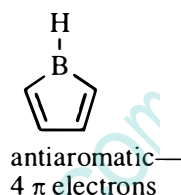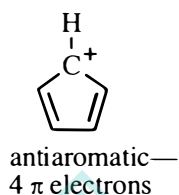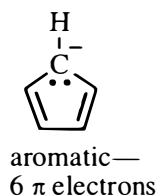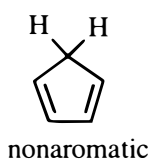
16-32

(a)

nonaromatic   antiaromatic—
4 π electrons   aromatic—
2 π electrons

(b)

aromatic—
6 π electrons   aromatic—
6 π electrons   nonaromatic   aromatic—
6 π electrons   nonaromatic

(c)

nonaromatic   aromatic—
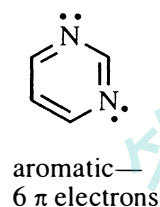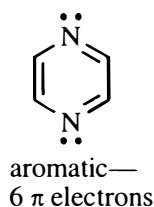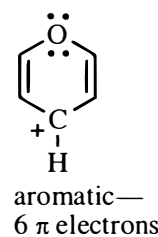6 π electrons   antiaromatic—
4 π electrons   antiaromatic—
4 π electrons
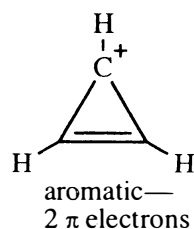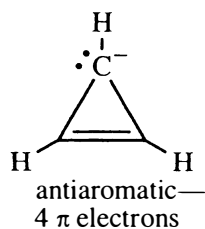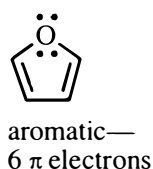
(B is sp², but donates
no electrons to the π
system)

(d)

aromatic—
6 π electrons   aromatic—
6 π electrons   nonaromatic   aromatic—
6 π electrons

(e)

nonaromatic

if oxygen is sp² ⟹ antiaromatic (8 π
electrons); if oxygen is sp³ ⟹ nonaromatic
⟹ not aromatic in either case

aromatic—
6 π electrons

(f)

aromatic—
6 π electrons   aromatic—
6 π electrons   nonaromatic

(g)

antiaromatic—
12 π electrons   aromatic—
10 π electrons   this is a tough call—it has 10 π electrons so it
could be aromatic, but internal H's might
force it out of planarity

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