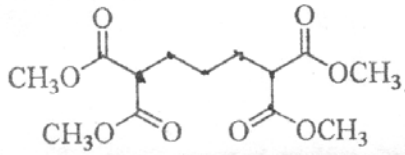
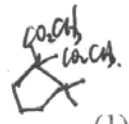
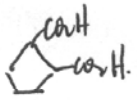
南开大学 2007 年硕士研究生入学考试试题

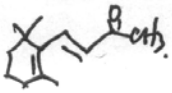
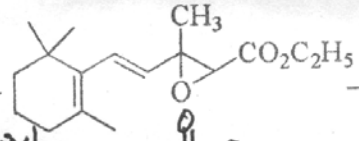
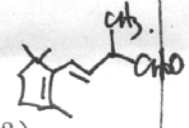
学　院：　化学学院

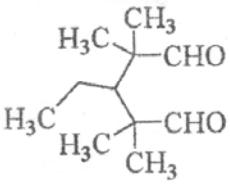
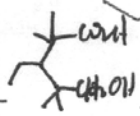
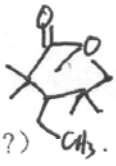
考试科目：　有机化学　　专 业：　有机化学、高分子化学与物理、精细化学品化学、化学生物学、应用化学、农药学

注意：请将答案写在专用答题纸上，答在此试题上无效！

一、完成下列反应式（36 分）

1. 
(1) $NaOC_2H_5$ (2 mol)
(2) Br_2

(?)
(1) OH^-/H_2O
(2) $H^+/\triangle$
(?)


2. 
(?) + $ClCH_2CO_2C_2H_5$
$NaOC_2H_5$

(1) OH^-/H_2O
(2) $H^+/\triangle$
(?)


3. 
(1) 浓 OH^-
(2) H_3^+O

(?)
H^+
$\triangle$

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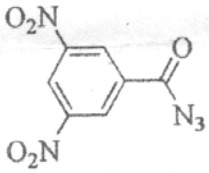
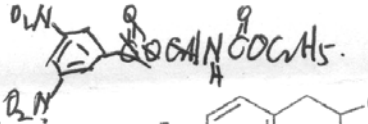
4. 
+ HOC_2H_5

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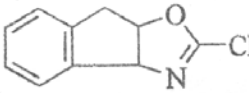
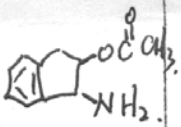
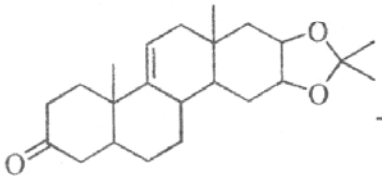
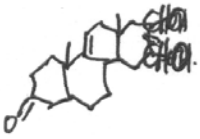
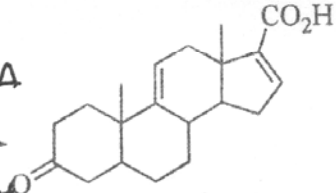
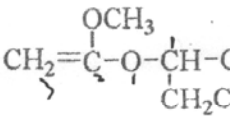
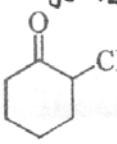
5. 
H_3^+O
(?)


6. 
(1) H_3^+O
(2) HIO_4

(?)
(1) (?)
(2) (?)
$OH^-/\triangle$
$Ag(NH_3)_2^+/\triangle$


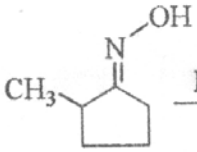
7. 

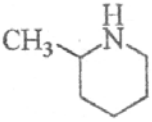
$\triangle$
(?)

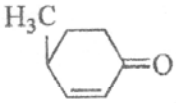
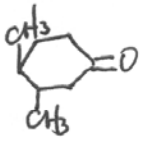
8. 
(1) LDA
(2) PhSeCl

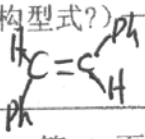
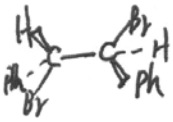
(?)
H_2O_2

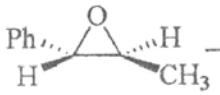
(?)

9. 
PCl_5

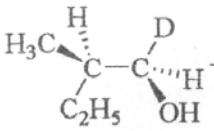
(?)
(?)


10. 
(1) $(CH_3)_2CuLi$
(2) H_3^+O
（构型式?）


11. Ph−C≡C−Ph
Li
NH_3 (液)
（构型式?）

Br_2
（构型式?）


12. 

$\xrightarrow{Ph_3P}$（构型式?）+ $Ph_3P{=}O$

13. 

$\xrightarrow[H^+]{CH_3CO_2H}$（构型式?）$\xrightarrow{500℃}$（构型式?）

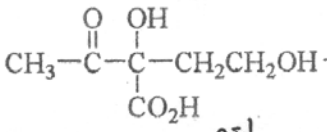
二、简要回答问题（22 分）

1. 叔丁基氯与 0.01M 的 NaCN 乙醇溶液加热反应得到两种不含有氮的有机产物。① 写出这两种产物的结构式；② 用文字表示两种产物生成的历程（不用正常书写历程的方式）。（5 分）

2. ① 写出 (1R, 2S, 4R, 5S)-1,2,4-三甲基-5-氯环己烷平面构型式，并用英文命名该化合物。② 写出该化合物的稳定构象。（5 分）

3. 1mol 邻氯苯酚和 1mol 邻甲基苯甲酸混合物与过量 LDA 反应后加入 1mol 正溴丁烷，反应后酸化，只得到一种与正溴丁烷反应的产物，写出其结构。（3 分）

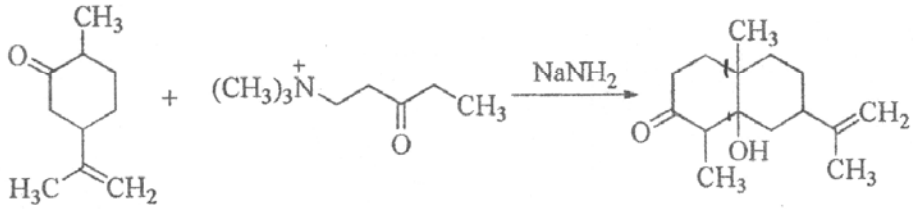
4. 下列化合物 **A** 加热得到中间体 **B**，**B** 很快转化为 **C** 和 **D**。写出 **B**、**C**、**D** 的结构式。（4 分）

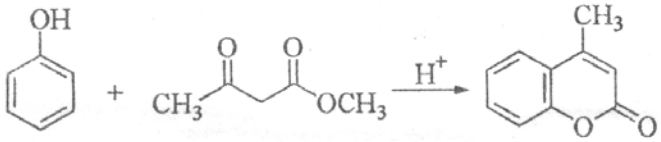


$\xrightarrow{\triangle}$ [**B**]（$C_5H_{10}O_3$）→ **C**，**D**

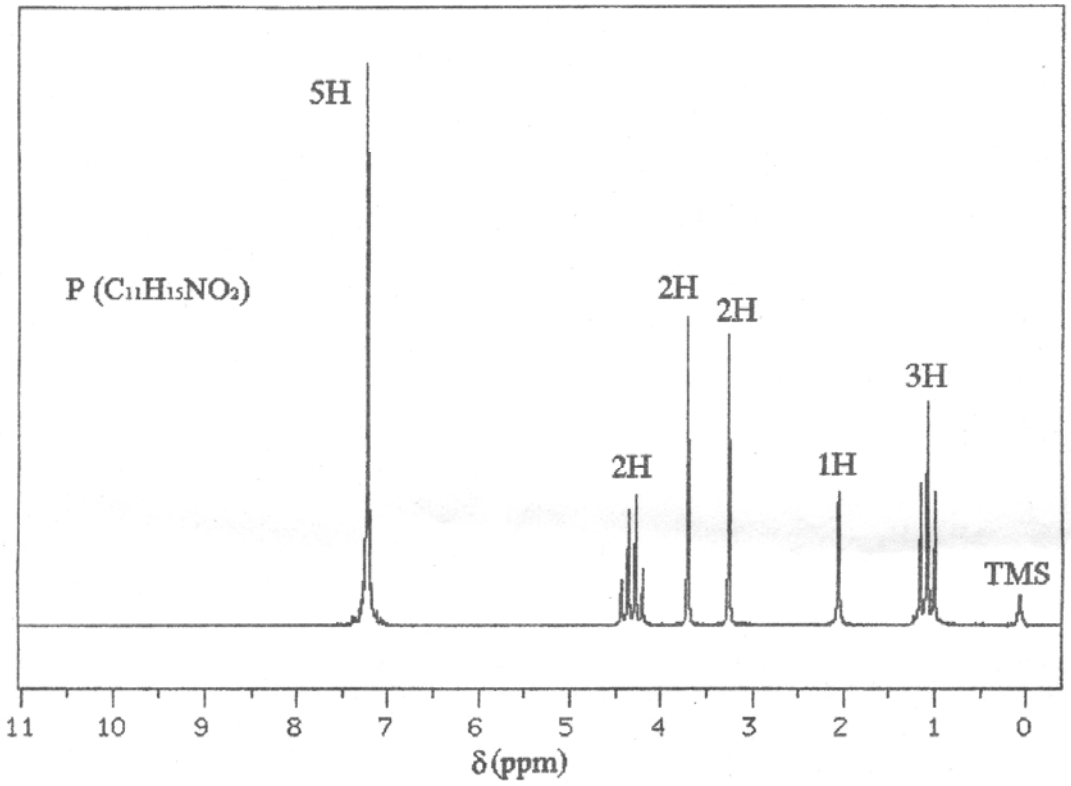
5. 具旋光活性的化合物 **X**（$C_3H_6O_2$）的 IR 在 3240~3550 cm^{-1} 有特征吸收峰，在 1600~1800 cm^{-1} 无吸收峰。**X** 在酸存在下与水反应得到无旋光性、也不可拆分的化合物 **Y**。写出 **X** 和 **Y** 的结构。（5 分）

三、写出下列反应历程（16 分）

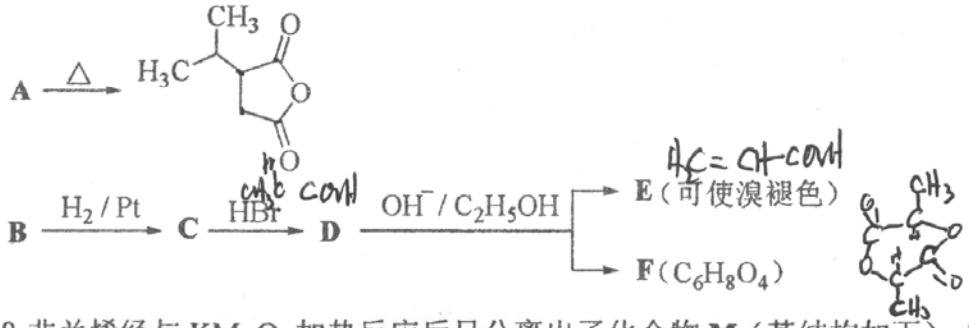
1. 

2. 

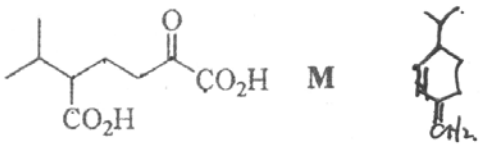
四、化合物 **P**（$C_{11}H_{15}NO_2$）可溶于稀酸，与 HNO_2 作用生成不溶于酸的黄色油状物。当 **P** 与氢氧化钠水溶液共热后酸化得到化合物 **Q**（$C_9H_{11}NO_2$）。**Q** 可以内盐形式存在，**Q** 既可溶于酸，又可溶于碱。**P** 的 IR 在 750 cm^{-1} 和 700 cm^{-1} 有特征吸收，**P** 的 ^1H NMR 谱图如下，写出 **P**、**Q** 的结构。（10 分）



五、薄荷油中含有少量 α-非兰烯和 β-非兰烯，两者都只含碳和氢，并互为同分异构体，分子量为 136。它们催化加氢均得到 1-甲基-4-异丙基环己烷。α-非兰烯经 $KMnO_4$ 加热氧化得 **A** 和 **B**，**A** 与 **B** 的反应如下：

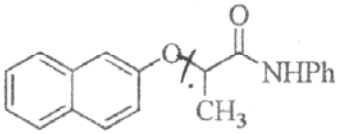


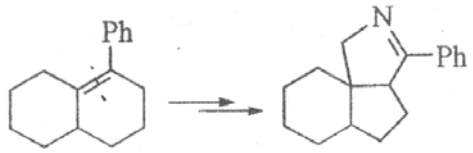
β-非兰烯经与 $KMnO_4$ 加热反应后只分离出了化合物 **M**（其结构如下）。写出 α-非兰烯、β-非兰烯和 **B**、**C**、**D**、**E**、**F** 的结构式。（14 分）



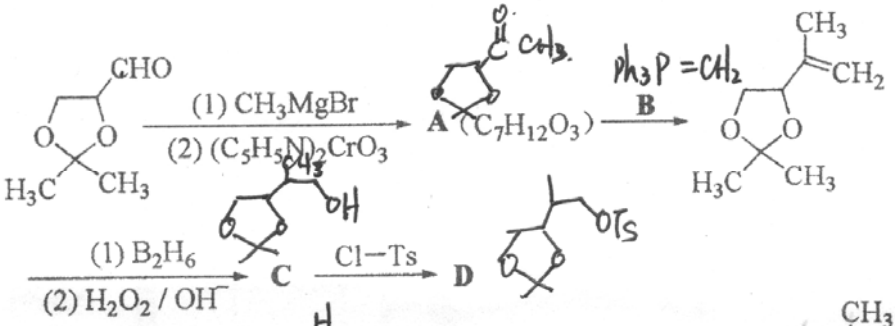
六、完成下列转化（除指定原料必用外，可选用任何原料和试剂）（18 分）

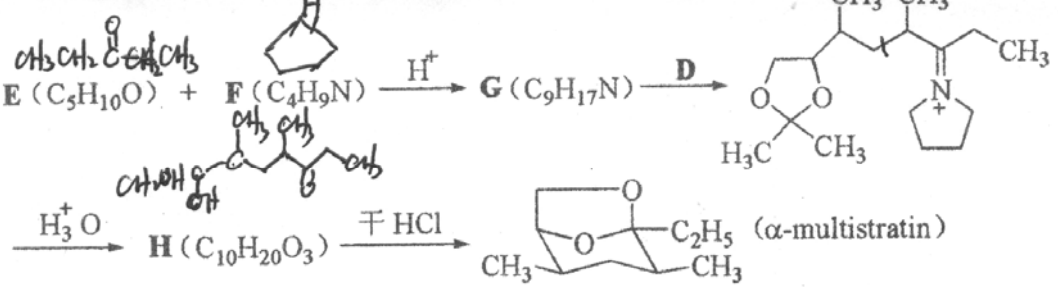
1. $CH_3CH_2CO_2H$ ⟶



2. 

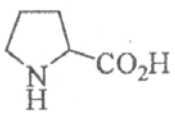
七、天然信息素 α-multistratin 合成路线如下，写出合成中英文字母代表的化合物结构式。（12 分）

1. 

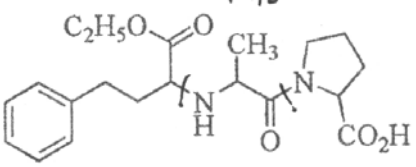
2. 

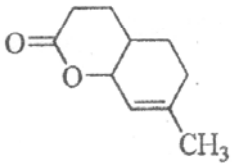
八、合成（22 分）

1. 依那普利（enalapri）是医治高血压的药物。请由 4-苯基丁酸、丙氨酸和脯氨酸及必要的原料和试剂合成依那普利。



脯氨酸



依那普利（enalapri）

2、由三乙、丙烯酸乙酯和不超过 4 碳的原料及必要试剂合成：