

國 立 清 華 大 學 命 題 紙

95 學年度__生命科學院、生命科學院醫學生物科技學程__系(所)__乙__組碩士班入學考試

科目__有機化學__ 科目代碼__0902、1106__共__8__頁第__1__頁 *請在【答案卷卡】內作答

I. Multiple choice

(30%, 2% each)

- Which of the following names matches with the formula?
(A) $\text{CH}_3\text{PHCH}_2\text{CH}_3$, ethylmethylphosphine (B) $\text{P}(\text{OC}_2\text{H}_5)_3$, triethyl phosphite
(C) CH_3PHCl , methylphosphorus chloride (D) $\text{O}=\text{P}(\text{OC}_2\text{H}_5)_3$, triethylphosphine
- Which of the following chemical tests can be used to distinguish the indicated pair of compounds?
 - Zinc/Ethanol, $(\text{CH}_3\text{CH}_2\text{S})_2$ and CH_3SCH_3
 - Weak base, $\text{CH}_3\text{S}(\text{O})\text{OCH}_3$ and $\text{CH}_3\text{CH}_2\text{SO}_3\text{H}$
 - Hydrolysis, $\text{CH}_3\text{S}(\text{O})\text{OCH}_3$ and $\text{CH}_3\text{S}(\text{O})_2\text{CH}_3$
 - Mercury, $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ AND $\text{CH}_3\text{OCH}_2\text{CH}_2\text{SH}$(A) I, III (B) II, IV (C) I, II, III (D) I, II, III, IV
- Methionine is the active agent for many biological methylations, particularly on nitrogen. In general, transmethylation takes place by activating methionine with ATP, followed by nucleophilic attack. What reaction is involved in binding between methionine and ATP?
(A) Adenylation (B) Nitration (C) Phosphorylation (D) Pyrophosphorylation
- What property of hydroquinone is used to photographic developers to aid in the conversion of silver ion into free silver?
(A) Reduction (B) Oxidation (C) Hydroxylation (D) Polymerization
- In which of the following compounds would you expect intra-molecular hydrogen bonding to occur?
 - o*-nitroaniline
 - o*-hydroxybenzoic acid (salicylic acid)
 - o*-fluorophenol
 - o*-hydrobenzaldehyde (salicylaldehyde)(A) I, II, III, IV (B) I, II, IV (C) II, III, IV (D) I, III
- Rank the following compounds in increasing order of relative acid strengths:
 - p*-methoxybenzoic acid
 - benzoic acid
 - m*-fluorobenzoic acid
 - p*-trifluoromethylbenzoic acid(A) $\text{I} < \text{II} < \text{III} < \text{IV}$ (B) $\text{II} < \text{III} < \text{I} < \text{IV}$ (C) $\text{IV} < \text{II} < \text{III} < \text{I}$ (D) $\text{IV} < \text{III} < \text{II} < \text{I}$
- Rank the following compounds in decreasing order of relative base strengths:
 - p*-methoxy nitrobenzene
 - nitrobenzene
 - m*-methoxynitrobenzene
 - m*-trifluoronitrobenzene(A) $\text{IV} > \text{III} > \text{II} > \text{I}$ (B) $\text{III} > \text{II} > \text{I} > \text{IV}$ (C) $\text{II} > \text{IV} > \text{I} > \text{III}$ (D) $\text{I} > \text{II} > \text{III} > \text{IV}$

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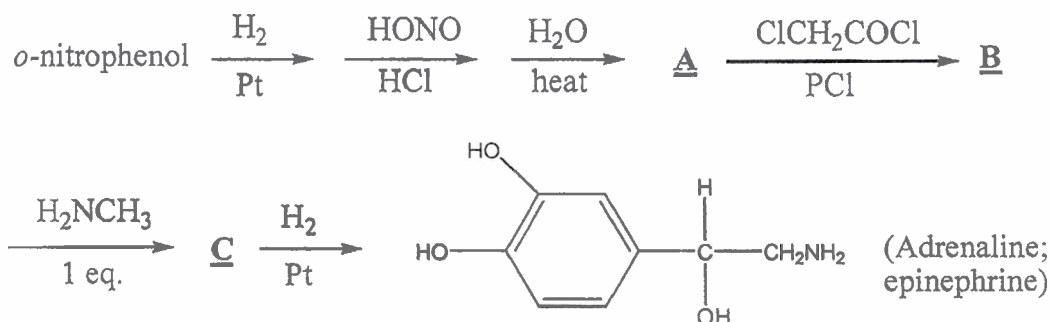
科目__有機化學__ 科目代碼__0902、1106__共__8__頁第__2__頁 *請在【答案卷卡】內作答

8. Which of the following compounds has a chiral center?
(A) 2-Aminoethanol (B) Isopropylamine
(C) Methylethylamine (D) 2-(*N*-Methylamino)heptane
9. The particular wavelengths of electromagnetic radiation that are absorbed by rhodopsin are, by definition, "visible light". Imagine a creature whose vision depended upon the *cis-trans* isomerization, not of a highly conjugated compound like retinal, but of a simple unconjugated alkene. What wavelengths of radiation would constitute "visible light" to such a creature?
(A) far UV (B) Infrared (C) Visible (D) UV
10. When methyl ethyl ketone undergoes Claisen condensation with ethyl benzoate in the presence of NaOC_2H_5 , what is the major product?
(A) 2-methyl-1-phenyl-1,3-butanedione (B) 1-phenyl-1,3-pentanedione
(C) 1-methyl-2-phenyl-1,3-butanedione (D) 2-phenyl-1,3-pentanedione
11. Which location of a proton is required to trigger the decarboxylation of an α,β -unsaturated acid?
(A) α (B) β (C) γ (D) δ
12. Rank the following radicals in increasing order of stability.
I. $\cdot\text{CH}_3$ II. $\cdot\text{CH}_2\text{CH}_3$ III. $\cdot\text{CH}(\text{CH}_3)_2$ IV. $\cdot\text{C}(\text{CH}_3)_3$
(A) I < II < III < IV (B) II < III < IV < I (C) III < IV < I < II (D) IV < III < II < I
13. Which of the following compounds are truly meso compounds?
I. *cis*-1,2-cyclohexanediol II. *trans*-1,2-cyclohexanediol
III. *cis*-1,3-cyclohexanediol IV. *trans*-1,3-cyclohexanediol
(A) I, II (B) I, III (C) II, III (D) II, IV
14. Which of the following methods can be used to determine the molecular weight of an organic compound?
I. IR II. Mass spectroscopy III. NMR IV. UV
(A) I, II, III, IV (B) I, III, IV (C) I, IV (D) III, IV
15. What reaction is carried out to synthesize a bridged bicyclic alkene from cyclopentadiene and ethylene at high temperature?
(A) Hydrogenation (B) Aldol condensation
(C) Hoffman rearrangement (D) Diels-Alder

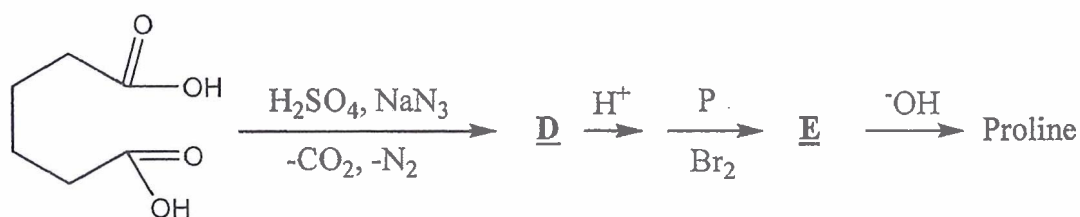
II. Draw the major product for each of the following reactions.

(20%, 2% each)

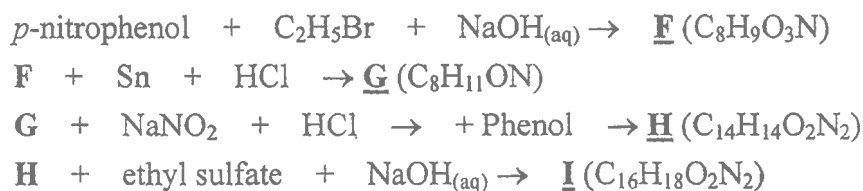
1.



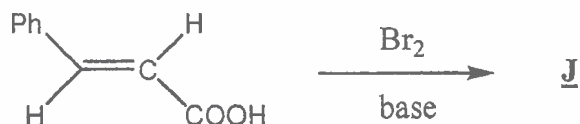
2.



3.



4.

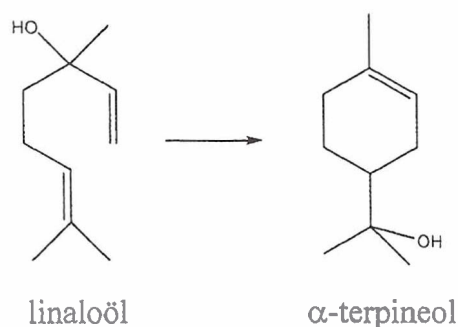


III. Propose the mechanisms accounting for the following observations.

(18%)

a. The cyclization of optically active linalool produces optically active α -terpineol.

(4%)

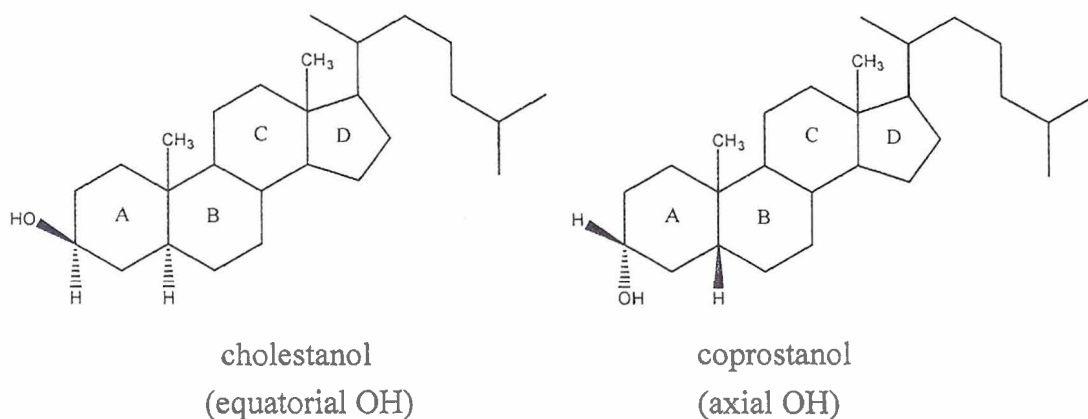


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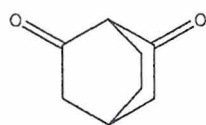
- b. Cholesterol can be reduced either to cholestanol or coprostanol. Equilibration of cholesterol with a trace amount of cholestanone and base gives 90% cholestanol and 10% of its stereoisomer known as epicholestanol. However, similar equilibration of coprostanol (in the presence of coprostanone) gives 10% coprostanol and 90% epicoprostanol. (To explain such observation, you must draw the boat form configurations of each of the compounds accompanied with description) (6%)



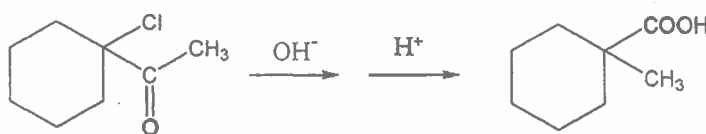
- c. 2,6-Bicyclo[2,2,2]octanedione exhibits no enolic properties.

The structures of two potential isomers have to be shown and discussed.

(4%)



- d.



(4%)

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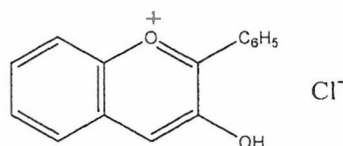
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IV. Briefly answer each of the following questions. (8%)

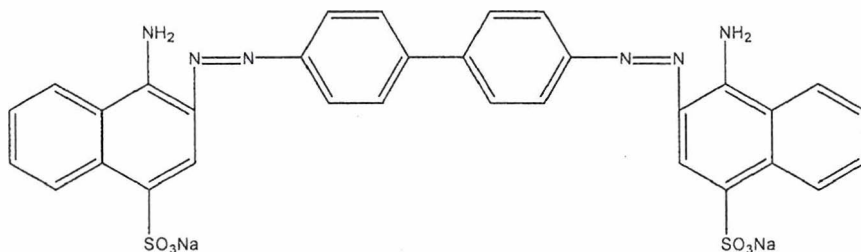
- a. Many of the beautiful colors of butterflies' wings are due to the presence of flavone derivatives called anthocyanins. When anthocyanins are hydrolyzed in hydrochloric acid to remove sugar residues, they produce aromatic oxygen-containing salts. One of these is delphinidin chloride as shown in the structure below. (2%)

Why is this compound aromatic?

What is the hybridization of the heterocyclic oxygen in this compound?



- b. Congo Red is a common pH indicator and also an azo dye. It is red in basic or neutral solution, and blue in acid solution. The neutral (red) form is shown below. Suggest a structure for the blue form of the dye, assuming that it is a dication. (2%)



- c. The pKa of aspartic acid is 2.8. Show detailed calculations to answer (1) and (2).

(1) What is the aspartic acid concentration of a 1 M aspartic acid solution maintained at pH 2.8? (2%)

(2) What is the aspartate ion concentration if the pH is raised to 3.8? (2%)

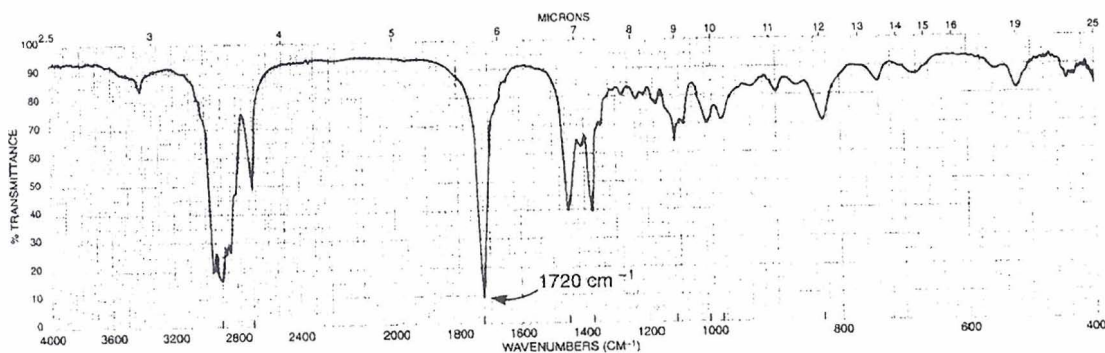
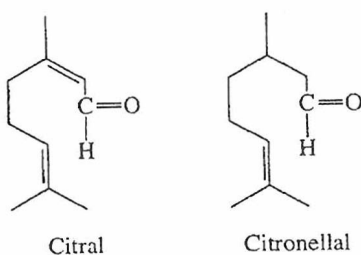
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V. **Spectroscopy:** Detailed calculation and assignment on the functional groups in each spectrum have to be shown in each answer. (24%)

a. Ants emit tiny amounts of chemicals called alarm pheromones to warn other ants of the same species of the presence of an enemy. Several of the components of the pheromone in one species have been identified, and two of their structures follow. Which compound has the infrared spectrum shown below? Explain why? (5%)



b. At room temperature, the proton NMR spectrum of 2,2,3,3-tetrachlorobutane shows a single sharp peak. Lowering the temperature causes a broadening of this peak until finally, at about -45 °C, it separates into two peaks (singlets) of unequal intensities.

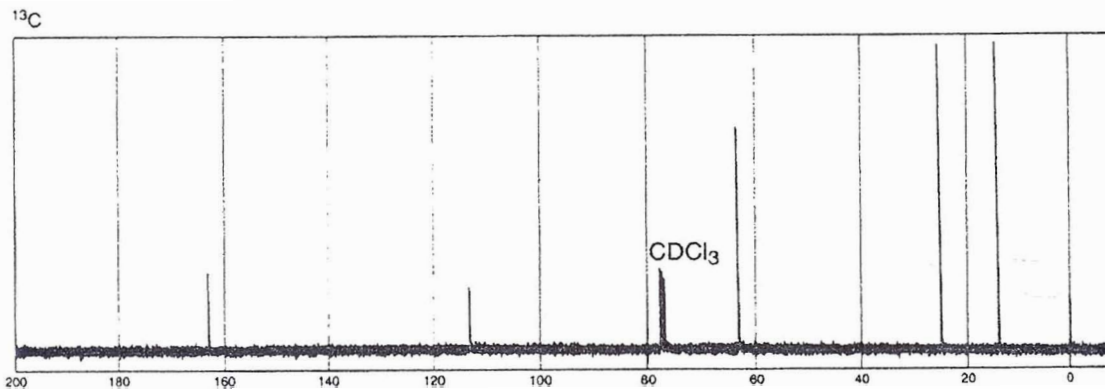
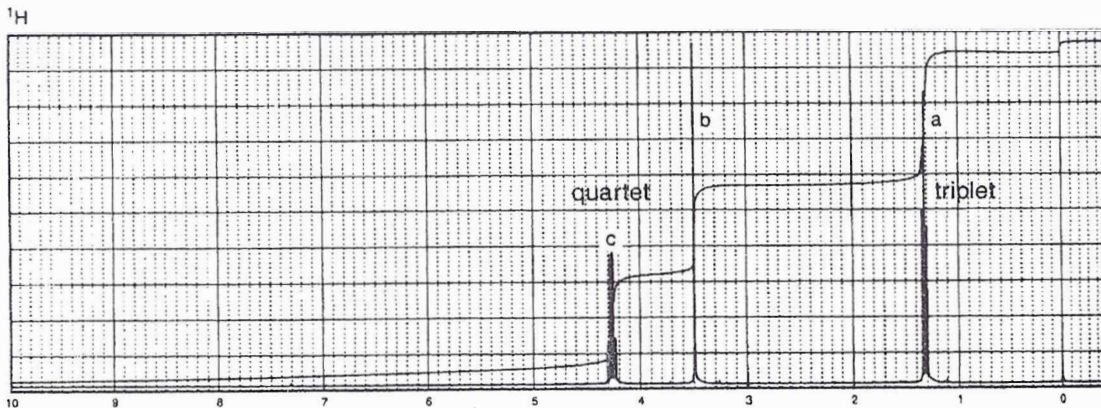
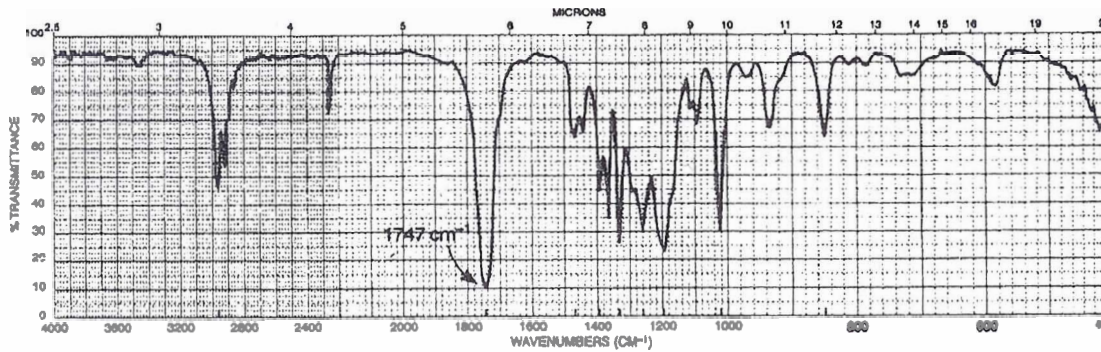
- (1) Account for the effect of temperature. (3%)
- (2) What is the significance of the unequal intensities in the low-temperature spectrum? (3%)

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c. A compound has the molecular formula $C_5H_7NO_2$. Deduce its molecular structure from the following infrared, proton NMR and carbon NMR spectra. (8%)



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d. A naturally occurring amino acid with the formula $C_3H_7NO_2$ gives the following proton NMR spectrum when determined in deuterium oxide solvent. The amino and carboxyl protons merge into a single peak at 4.9 ppm in the D_2O solvent (not shown); the peaks of each multiplet are separated by 7 Hz.

(1) Determine the structure of this amino acid. (4%)

(2) What is the name of this amino acid? (1%)

