

國立清華大學 命題紙

97 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__0302、0506__共__8__頁第__1__頁 *請在【答案卷卡】內作答

I. Choose one correct answer from each of the following questions.

(34%, 2% each)

1. Which of the following alkanes has the lowest boiling point?

- (A) propane (B) cyclobutane (C) hexane (D) cyclohexane

2. Give the following compounds in their order of decreasing boiling points.

I. $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$

II. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

III. $\text{CH}_3\text{CH}_2\text{OH}$

IV. $\text{CH}_3\text{CO}_2\text{H}$

- (A) I, II, III, IV (B) I, IV, II, III (C) I, IV, III, II (D) II, III, IV, I

3. A solution of sucrose in water at 25°C in a tube that is 10.0 cm long gives an observed optical rotation of $+2.00^\circ$. The specific rotation of sucrose in water at the same condition is $+66.4^\circ$. What is the concentration of sucrose in g/100 mL?

- (A) 33.2 (B) 3,320 (C) 3.01 (D) 0.03

4. Which of the following reactions gives a positive iodine test?

- (A) A freshly prepared glucose solution in water
(B) A freshly prepared glycogen solution in water
(C) A freshly prepared starch solution in water
(D) Solution C in the presence of human saliva

5. Which of the following compounds are meso compounds?

I. *cis*-1,2-cyclohexanediol

II. *trans*-1,2-cyclohexanediol

III. *cis*-1,3-cyclohexanediol

IV. *trans*-1,3-cyclohexanediol

V. *cis*-1,4-cyclohexanediol

VI. *trans*-1,4-cyclohexanediol

- (A) I, III, V (B) II, IV, VI (C) III, IV, V, VI (D) II, IV

6. When isopropyl bromide is treated with sodium ethoxide in ethanol, propylene and ethyl isopropyl ether are formed in a 3:1 ratio. If the hexadeuteroisopropyl bromide, $\text{CD}_3\text{CHBrCD}_3$ is used, what is the ratio of $\text{CD}_3\text{CH}=\text{CD}_2$ versus $(\text{CH}_3)_2\text{CHOC}_2\text{H}_5$?

- (A) 1/2 (B) 1/3 (C) 1/4 (D) 1/6

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7. An unknown compound A rapidly decolorized a solution of bromine in carbon tetrachloride. When A was subjected to ozonolysis, the products were butanone and propanal. What is the name of A?
 (A) *cis*-2-methyl-2-hexene (B) *trans*-3-methyl-3-hexene
 (C) *cis*-4-methyl-4-hexene (D) *trans*-5-methyl-5-hexene
8. Which of the following compounds is expected to lose chloride ion most readily to form a carbonium ion?
 (A) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2\text{Cl}$ (B) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl}$
 (C) $\text{CH}_2=\text{CH}-\text{CHCl}-\text{CH}=\text{CH}_2$ (D) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$
9. Arrange the following compounds in decreasing order of reactivity toward ring nitration.
 I. $\text{C}_6\text{H}_5\text{NHCOCH}_3$ II. acetophenone III. aniline IV. benzene
 (A) I, II, III, IV (B) II, I, III, IV (C) III, I, IV, II (D) IV, III, II, I
10. Under $\text{S}_{\text{N}}1$ conditions, 2-bromooctane, of specific optical rotation -20.8° , was found to yield 2-octanol of specific optical rotation $+3.96^\circ$. If optically pure 2-bromooctane has a specific rotation of -34.6° and optically pure 2-octanol has a specific rotation of -9.9° . Calculate the percentage of the product.
 (A) 40% (B) 50% (C) 60% (D) 75%
11. Enkephalins are pentapeptide components of endorphins in the brain. Deduce the amino acid sequence of an enkephalin X from the following data:
 1) The amino acids identified by complete hydrolysis are: Gly, Phe, Leu, and Tyr.
 2) Gly-Gly-Phe and Tyr-Gly are isolated from its partial hydrolysis.
 3) Upon reaction with dansyl chloride, followed by peptide hydrolysis, the dansyl derivative of Tyrosine is identified by thin-layer chromatography.
 (A) Gly-Gly-Phe-Tyr-Gly (B) Leu-Tyr-Gly-Gly-Phe
 (C) Tyr-Gly-Gly-Gly-Phe (D) Tyr-Gly-Gly-Phe-Leu
12. Place the following benzyl alcohols in decreasing order of reaction rate with HBr.
 I. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ II. $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{OH}$
 III. $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{OH}$ IV. $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{OH}$.
 (A) I, II, III, IV (B) II, I, IV, III (C) IV, III, II, I (D) III, IV, I, II
13. What is the reaction mechanism for the above transformation in question 12?
 (A) $\text{S}_{\text{N}}1$ (B) $\text{S}_{\text{N}}2$ (C) $\text{E}1$ (D) $\text{E}2$

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14. Arrange the following acids in increasing order of the rate of esterification in the presence of methanol.

I. $(i\text{-Pr})_2\text{CHCOOH}$ II. Et_3CCOOH III. MeCH_2COOH

IV. Me_2CHCOOH V. Me_3CCOOH

(A) I, II, III, IV, V (B) I, II, V, IV, III (C) III, IV, V, II, I (D) V, IV, III, II, I

15. Arrange the following chemicals according to increasing basicities.

I. $\text{C}_6\text{H}_5\text{NH}_2$ II. $m\text{-NO}_2\text{C}_6\text{H}_5\text{NH}_2$ III. $o\text{-NO}_2\text{C}_6\text{H}_5\text{NH}_2$ IV. $p\text{-NO}_2\text{C}_6\text{H}_5\text{NH}_2$

(A) I, II, III, IV (B) II, III, IV, I (C) III, IV, II, I (D) IV, III, II, I

16. Which of the following methods is suitable for removal of a protecting group, *p*-toluenesulfonyl, for NH_2 ?

(A) H_2/Pd (B) weak alkali (C) CF_3COOH (D) Na in liq. NH_3

17. A 9.6×10^{-5} M solution of **X** in a 10-mm cell at $\lambda_{\text{max}} = 235$ nm has an $A = 1.6$. Calculate ϵ_{max} for this transition.

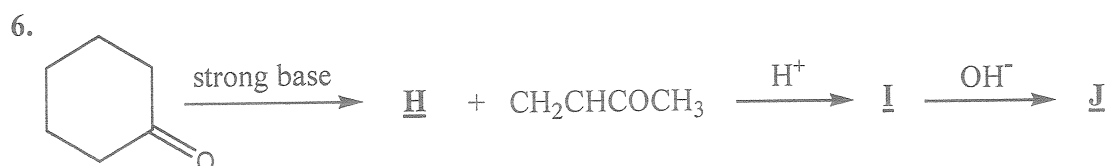
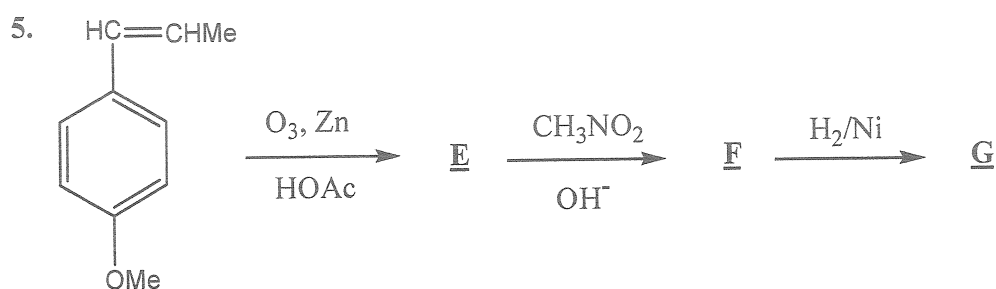
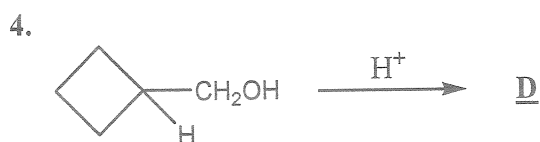
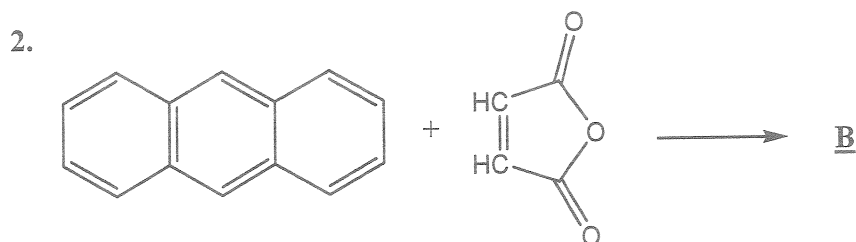
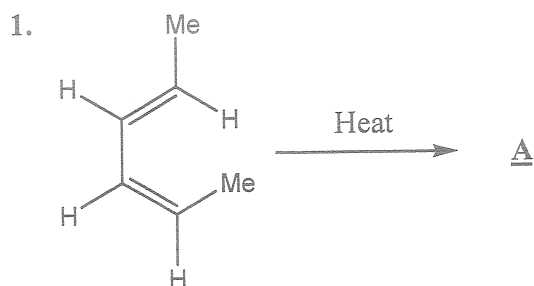
(A) 6×10^5 M/cm (B) $23.5 \text{ M}^{-1}\text{cm}^{-1}$ (C) $1.7 \times 10^5 \text{ M}^{-1}\text{mm}^{-1}$ (D) $1.7 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$

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II. Predict major products A to J in the following reactions.

(20%, 2% each)



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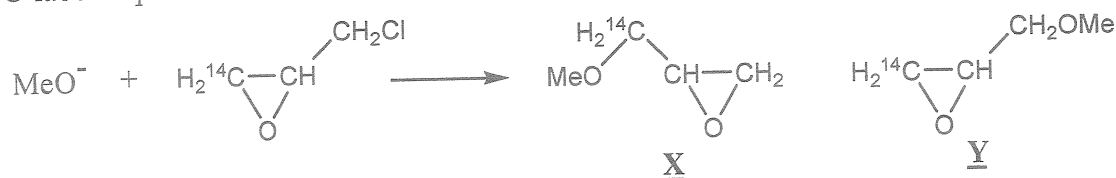
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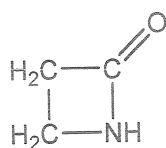
III. Give a rational mechanism to account for each of the following reactions. (20%, 5% each)

1. $\text{C}_6\text{H}_5\text{Cl}$ labeled at C^1 with ^{14}C reacts with KNH_2 to give $\text{C}_6\text{H}_5\text{NH}_2$ labeled at both C^1 and C^2 .

2. The ^{14}C -labeled product from the following reaction is X, but NOT Y.



3. β -Lactams are found in two important classes of antibiotics, the penicillins and cephalosporins. Based on the structure of β -propiolactam,



(a) Account for its unusual reactivity to nucleophiles.

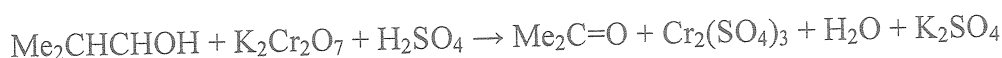
(b) Penicillins react with the amino group of β -lactamase, a key enzyme involved in the synthesis of the bacterial cell wall protein, thus deactivating it. Show the reaction between β -propiolactam and the enzyme, designated as Enz-NH_2 .

4. 5,5-Dimethyl-3-ethoxycyclohex-2-enone reacts with MeMgI followed by H^+ to give 3,5,5-trimethylcyclohex-2-enone. Give

(a) a 1,2-addition pathway for the reaction.

(b) a 1,4-addition pathway for the reaction.

IV. Balance the following redox reaction by the ion-electron (half-cell) method. (5%)



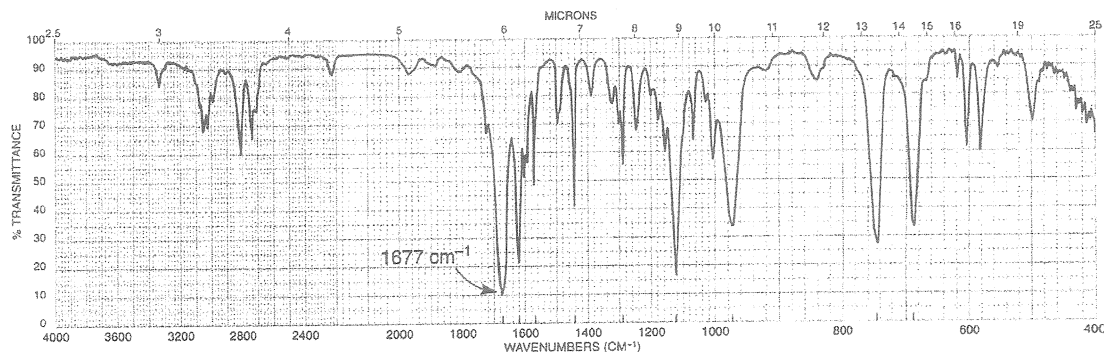
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V. Spectroscopy

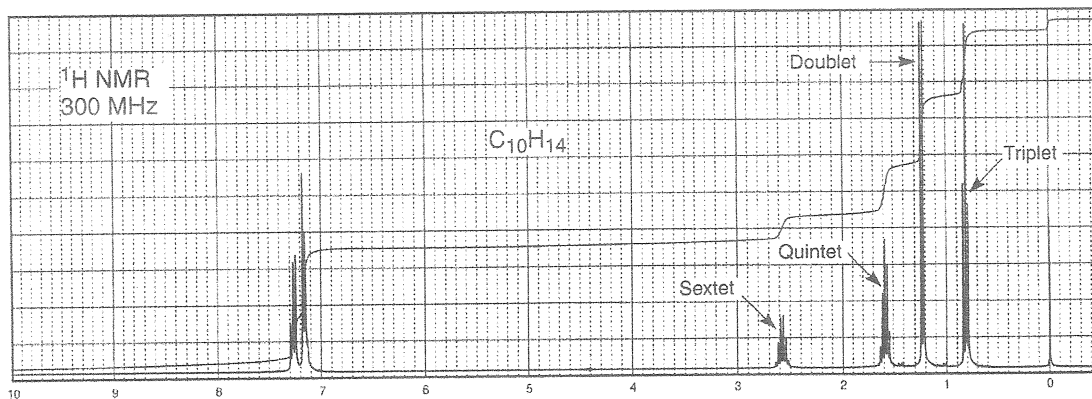
(21%)

1. The main constituent of cinnamon oil has the formula C_9H_8O . From the following infrared spectrum, deduce the structure of this component. (3%)

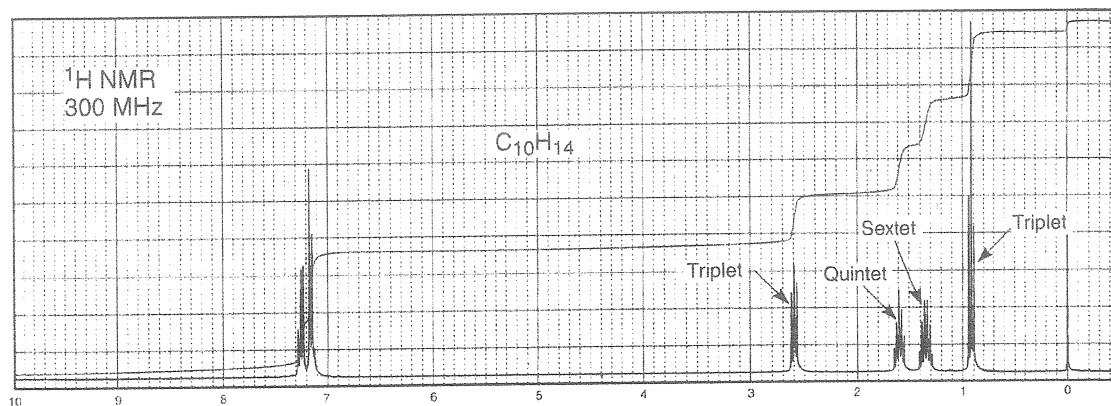


2. The following NMR spectra are of monosubstituted aromatic hydrocarbon compounds with the formula $C_{10}H_{14}$. Draw structures for these compounds.

(a) (3%)



(b) (3%)

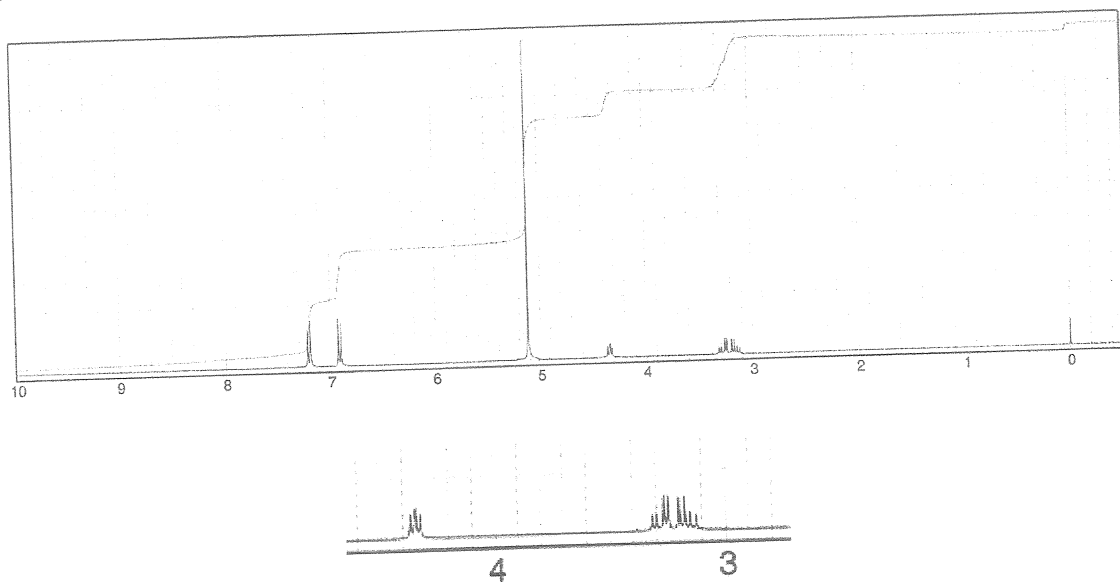


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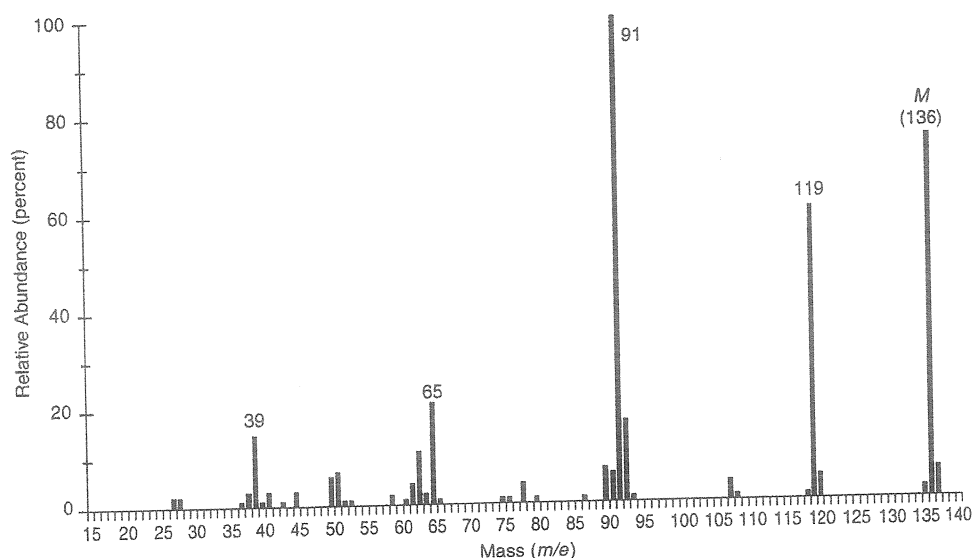
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3. A naturally occurring amino acid with the formula $C_9H_{11}NO_3$ gives the following proton NMR spectrum when determined in deuterium oxide solvent with DCl added. The amino, carboxyl, and hydroxyl protons merge into a single peak at 5.1 ppm in D_2O . Determine the structure of this amino acid (3%) and explain the pattern that appears in the range 3.17 to 3.40 ppm (3%).



4. The ^{13}C NMR spectrum of the unknown compound shows only 4 peaks in the region 125-145 ppm (there are six peaks in the entire spectrum). The infrared spectrum shows a very strong, broad peak extending from 2,500 to 3,500 cm^{-1} , as well as a strong and somewhat broadened peak at 1,680 cm^{-1} . The mass spectrum of this unknown compound is shown below. Determine the structure of this compound. (3%)



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5. Determine the structure of the unknown compound $C_{10}H_9NO_2$ with the following spectra.

(3%)

