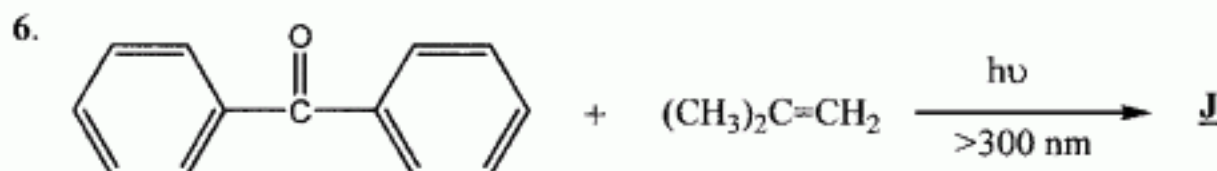
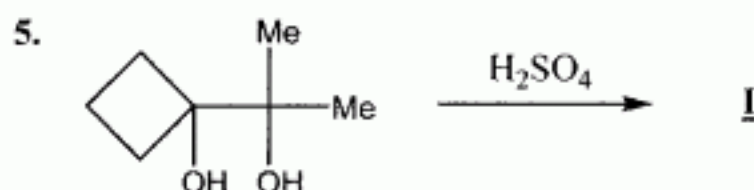
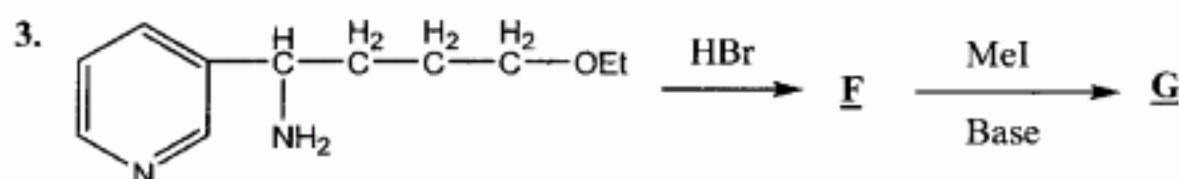
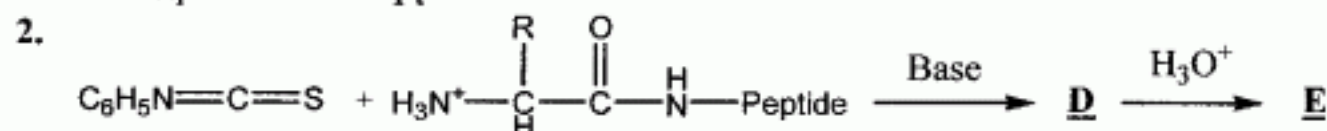
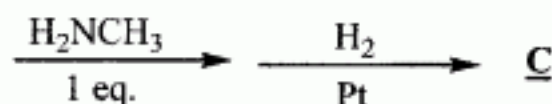
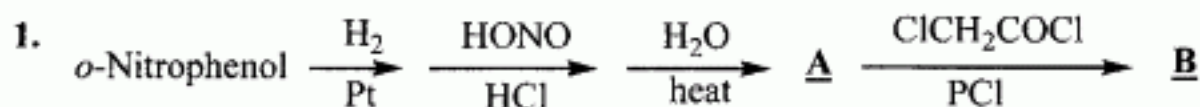


九十三學年度 生科院乙組、生科院(結構生物學程)甲組 碩士班入學考試

科目 有機化學 科號 0902、1106 共 4 頁第 1 頁 \*請在試卷【答案卷】內作答

I. Draw the structures of the major product in each of the following reactions. (20%, 2% each)



II. Choose a correct answer for each of the following questions. (30%, 2% each)

1. Which of the following molecules possesses covalent bonds based on their physical properties?

	I. $\text{Cl}_2$	II. $\text{NaCl}$	III. $\text{ICl}$	IV. $\text{H}_2\text{O}$
Melting Point ( $^\circ\text{C}$ )	-101.6	800.4	27.2	0
Boiling Point ( $^\circ\text{C}$ )	34.6	1413	97	100

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

2. How many structural isomers exist for a cyclic compound  $\text{C}_5\text{H}_{10}$ ?

(A) 3 (B) 4 (C) 5 (D) 6

九十三學年度 生科院乙組、生科院(結構生物學程)甲組 碩士班入學考試

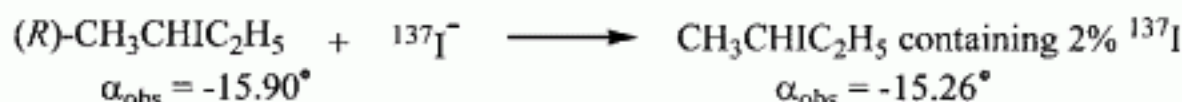
科目 有機化學 科號 0902、1106 共 4 頁第 2 頁 \*請在試卷【答案卷】內作答

- The molecular weight of a compound A is determined to be 78.11 g/mol. Analysis of compound A gives of 92.25% C and 7.743% H. Calculate the molecular formula of A.  
(A)  $C_3H_8S$  (B)  $C_4NO$  (C)  $C_5H_4N$  (D)  $C_6H_6$
- Compare the  $pK$  values of the following organic compounds in the increasing order.  
I.  $CH_3NH_2$ ,  $K_b = 4.5 \times 10^{-4}$  II.  $CH_3COOH$ ,  $K_a = 1.8 \times 10^{-5}$   
III.  $CH_3OH$ ,  $K_a = 3.1 \times 10^{-16}$  IV.  $CH_3NO_2$ ,  $K_a = 9 \times 10^{-11}$   
(A) I, II, III, IV (B) I, II, IV, III (C) II, I, IV, III (D) III, IV, II, I
- A solution shows an observed rotation  $+1.2$  at  $25^\circ C$  (D line) in a 10 cm polarimeter tube containing 0.75 g/10mL coniine, a toxic component of poison hemlock. What is the specific rotation of the enantiomer of coniine?  
(A) 1.6 (B) -1.6 (C) -16 (D) -0.9
- Compare the boiling points of the following compounds in the decreasing order.  
I. ethyldimethylamine II. *n*-butylamine III. diethylamine  
(A) I, II, III (B) I, III, II (C) II, III, I (D) III, II, I
- Compare the basicities of the following compounds in the decreasing order.  
I. *p*- $CH_3OC_6H_4NH_2$  II.  $C_6H_5NH_2$  III. *o*- $CH_3OC_6H_4NH_2$  IV. *m*- $CH_3OC_6H_4NH_2$   
(A) I, II, III, IV (B) II, I, III, IV (C) III, I, IV, II (D) IV, II, I, III
- Which of the following compounds has the least enol content?  
(A)  $CH_3COCH_2COOEt$  (B)  $CH_3COCH_2COCH_3$  (C)  $(EtOCO)_2CH_2$  (D)  $PhCOCH_2COCH_3$
- Compare the stretching frequencies of  $C=O$  in an IR spectrum in the increasing order.  
I. acyl chloride II. ester III. amide IV. ketone  
(A) I, II, III, IV (B) II, IV, I, III (C) III, IV, II, I (D) IV, III, II, I
- Which of the following compounds do not react with  $Ag(NH_3)_2^+$ ?  
I.  $CH_3CH_2CHO$  II.  $CH_3COCH_3$  III.  $CH_3CH=CHCHO$  IV.  $C_6H_5CHO$  V.  $C_6H_5CH_2OH$   
(A) I, III, IV (B) II, V (C) III, IV, V (D) IV, V
- In nonpolar solvents equal amounts of (*a,a*) and (*e,e*) conformers of *trans*-1,2-dibromocyclohexane exist, but in polar solvents only the (*e,e*) conformer predominates. What is the major factor that governs the conformational variation?  
(A) ring strain (B) dipole-dipole repulsion (C) electronegativity (D) inductive effect

九十三學年度 生科院乙組、生科院(結構生物學程)甲組 碩士班入學考試

科目 有機化學 科號 0902、1106 共 4 頁第 3 頁 \*請在試卷【答案卷】內作答

12. What is the reaction mechanism that contributes to the change of observed rotation?



(A) E1 (B) E2 (C) S<sub>N</sub>1 (D) S<sub>N</sub>2

13. What is a characteristic fragmentation peak in mass spectra for 2,2,4-trimethylpentane?

(A) 28 (B) 43 (C) 57 (D) 84

14. What are the charges on lysine at pH2 and pH11?

(A) +2, -1 (B) +2, 0 (C) +1, -1 (D) 0, -1

15. The extinction coefficient of a compound having the molecular weight of 107 is 13,100. How many milligrams of this material must be dissolved in 1 mL to give an absorbance of 0.16 in a light path of 1.0 cm?

(A) 1.3 (B) 131 (C) 0.13 (D) 22

III. Carbocation, carbanion, radical, singlet carbene, and radical cation are common reactive carbon intermediates, answer the following questions: (10%, 5% each)

- Draw chemical structure of each intermediate.
- Describe the shape of each structure.

IV. Two optically active alkenes, **A** and **B**, have the same molecular formula, C<sub>5</sub>H<sub>9</sub>Cl. After addition of one mole of H<sub>2</sub> to each, **A** is converted to an achiral product **C**, and **B** forms an optically active product **D**.

Give the structures of **A**, **B**, **C**, and **D**.

(4%)

V. Oxytocin is a nonapeptide hormone secreted by the pituitary gland, functions by stimulating uterine contraction and lactation during childbirth. Its sequence was determined from the following evidence:

- Oxytocin is a cyclic compound containing a disulfide bridge between two cysteine residues.
- When the disulfide bridge is reduced, oxytocin has the constitution Asn, Cys<sub>2</sub>, Gln, Gly, Ile, Leu, Pro, Tyr.
- Partial hydrolysis of reduced oxytocin yields seven fragments:  
Asp-Cys, Ile-Glu, Cys-Tyr, Leu-Gly, Tyr-Ile-Glu, Glu-Asp-Cys, Cys-Pro-Leu
- Carboxypeptidase treatment initially releases Gly.
- Both Glu and Asp are present as their side-chain amides rather than as free side-chain acids.

Based on the evidence, answer the following questions and briefly explain.

a. What is the amino acid sequence of reduced oxytocin?

(3%)

b. What is the structure of oxytocin itself?

(3%)



九十三學年度 生科院乙組、生科院（結構生物學程）甲組 碩士班入學考試

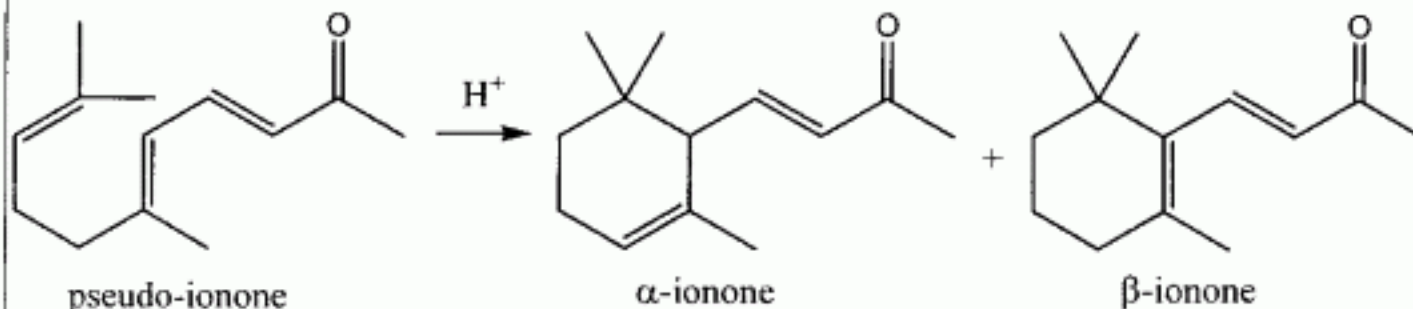
科目 有機化學 科號 0902、1106 共 4 頁第 4 頁 \*請在試卷【答案卷】內作答

VI. Both *cis*- and *trans*-1,2-cyclohexanedicarboxylic acids form anhydrides on heating, but the anhydride forms from the *cis*-1,2-cyclohexanedicarboxylic acid only.

- Draw stereo structures of all anhydrides. (3%)
- Give a rational explanation for the observation. (1%)

VII. Draw a plausible reaction mechanism to explain the fact that (*R*)- $\text{CH}_3\text{CHBrCOO}^-\text{Na}^+$  reacts with  $\text{NaOH}$  to give (*R*)- $\text{CH}_3\text{CHOHCOO}^-\text{Na}^+$ . Specifically show the intermediate formed in the reaction. (4%)

VIII.  $\beta$ -Ionone is an important chemical in the synthesis of vitamin A. It is prepared by the reaction of pseudo-ionone with sulfuric acid to produce more  $\beta$ -ionone than  $\alpha$ -ionone.



- Suggest a mechanism for the acid-catalyzed reaction. (3%)
- Why more  $\beta$ -ionone than the  $\alpha$  isomer is produced? (1%)

IX. Distinguish among (I)  $\text{MeCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ , (II)  $\text{MeCH}_2\text{CHMeCOOH}$ , and (III)  $\text{Me}_3\text{CCOOH}$  by

- PMR (3%)
- Decoupled CMR (3%)

X. Determine the structures with detailed assignment for each of the following compounds.

(12%)

(A)  $\text{C}_7\text{H}_{12}\text{O}_3$

UV:  $\lambda_{\text{max}}=275 \text{ nm}$

IR ( $\text{cm}^{-1}$ ): 1730, 1130

$^1\text{H}$ NMR (ppm): 1.2 (3H, triplet), 2.1 (3H, singlet), 2.5 (4H, multiplet), 4.0 (2H, quartet)

(B)  $\text{C}_5\text{H}_8\text{Br}_2$

IR ( $\text{cm}^{-1}$ ): 1,460 (sharp), 1330, 1230

$^1\text{H}$ NMR (ppm): 0.85 (singlet), 3.5 (singlet), 1:1 ratio of two peaks.

(C)  $\text{C}_9\text{H}_{11}\text{NO}$

$^1\text{H}$ NMR (ppm): 1.9 (singlet), 3.5 (singlet), 7.3 (multiplet), with intensities of 1:1:1.67.