## 95 學年度 <u>化學系 化學組、應用化學組</u> 碩士班入學考試 科目 無機化學及有機化學 科目代碼 0602、0702 共 6 頁第 1 頁 \*請在【答案卷】內作答

1. Predict the structure of the major product with appropriate stereochemistry, if necessary, for each of the following reactions. (6 %)

(a) 
$$H_7C_3-C\equiv C-C_3H_7$$
 Na, liq.  $NH_3$  ?

(b) 
$$CH_3$$
  $CH_3$   $CH_3$   $CH_3$  ?

(c) CH<sub>3</sub> + CH<sub>3</sub> HO<sup>-</sup>, 
$$\triangle$$
 ?

2. Propose a stepwise mechanism for each of the following transformations. (9 %)

(c) 
$$CH_2N_2$$
 +  $N_2$ 

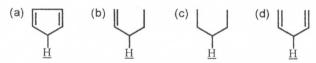
3. Provide a synthetic scheme for each of the following compounds from the readily available starting materials. (9 %)

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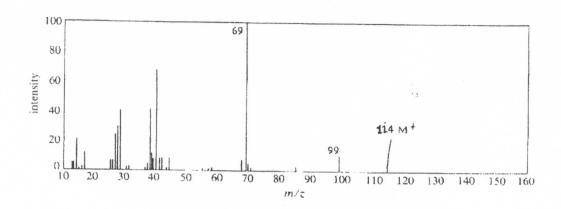
4. Draw the reaction coordinate diagram of the following reaction and predict the favorable route using Hammond Postulate. Which is the rate-limiting step? (4 %)

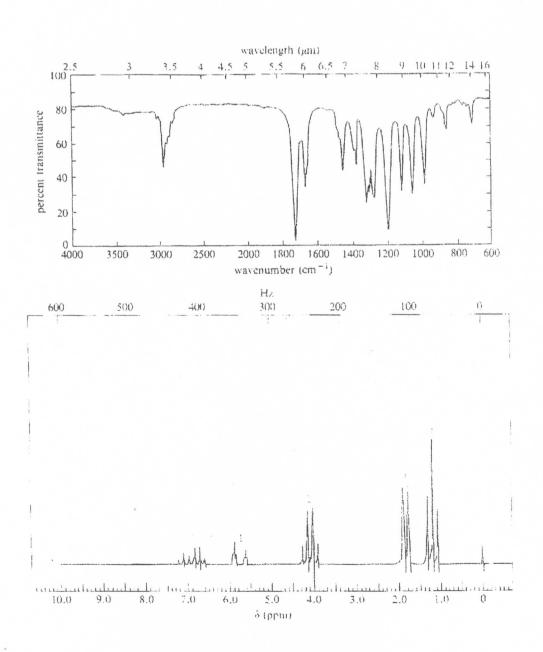
5. Arrange the following compounds in an order of increasing acidity and give a brief explanation of your arrangement. (2 %)



6. An unknown compound gives the NMR, IR, and mass spectra shown below. Propose a structure and show how it is consistent with the observed absorptions. Show fragmentations that account for the prominent ion at m/z 69 and the smaller peak at m/z 99. (8%)

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7. With the following molecules presented in Fischer projection:

glyceraldehyde

Alanine (Ala)

$$\begin{array}{c|c} + & COO \\ \hline + & H_3N \\ \hline & C \\ \hline & H_2 \\ \hline & C \\ \hline & CH_2 \\ \hline & SH \\ \end{array}$$

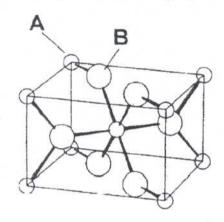
Tyrosine (Tyr)

Cysteine (Cys)

- a. Which structures are in "S" configuration?
- b. Which structures are in "R" configuration?
- c. Which structures are in "D" configuration?
- d. Which structures are in "L" configuration?
- e. With above amino acids, draw the complete structure of Ala-Phe-Cys peptide. Show the absolute configuration in each  $\alpha$ -carbon. (12%)
- 8. Select the compound with the named characteristic and briefly state the reason for your choice. (5%)
  - (I) Strongest Lewis acid:
  - (a) BF<sub>3</sub> BCl<sub>3</sub> BBr<sub>3</sub>
  - (b) BeCl<sub>2</sub> BCl<sub>3</sub>
  - (c)  $B(n-Bu)_3$   $B(t-Bu)_3$
  - (II) More basic toward B(CH<sub>3</sub>)<sub>3</sub>:
  - (d) Me<sub>3</sub>N Et<sub>3</sub>N
  - (e) 2-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N 4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>N
- For each of the following pairs of complexes, choose the one that has the larger LFSE (ligand field stabilization energy), and briefly explain your choice.
   (5%)
  - (a)  $[CrCl_6]^4$  or  $[MnCl_6]^4$  (b)  $[Mn(OH_2)_6]^{2+}$  or  $[Fe(OH_2)_6]^{3+}$

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- (c)  $[Fe(OH_2)_6]^{3+}$  or  $[Fe(CN)_6]^{3-}$  (d)  $[Fe(CN)_6]^{3-}$  or  $[Ru(CN)_6]^{3-}$
- (e)  $Td [FeCl_4]^2$  or  $Td [CoCl_4]^2$
- 10. For complexes of Fe<sup>3+</sup> and Ag<sup>+</sup> with SCN<sup>-</sup>, would you expect coordination of SCN<sup>-</sup> through S or N to these cations? (5%)
- 11. For the structure as shown below, give the empirical formula of the solid and coordination number of each ion.(A and B).. (5%)



- 12. Write equations for the preparation of solutions containing potasside and electride (one equation for each). (5%)
- (a). What kind of transitions is responsible for the observed color for each of the following transition metal complexes? Which of them are paramagnetic?
  MnO<sub>4</sub>, MnO<sub>4</sub>, Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>, Ru(bipy)<sub>3</sub><sup>2+</sup> (5%)
- 14. The half lives of substitution reaction (H<sub>2</sub>O exchange reaction) of the following pair of cobalt complexes are shown below. Explain the rate difference in terms of the electronic structures. (5%)

$$Co(H_2O)_6^{2+}$$
 (< 1 min),  $Co(NH_3)_5(H_2O)^{3+}$  (> 1 day)

15. (a) What is the mechanism for the following substitution reactions? (b) Propose intermediates of the substitution. (c) Draw the structure of the reaction product in (2). (5%)

$$Pt(NH_3)_4^{2+} + Cl^- \longrightarrow Pt(NH_3)_3Cl^+$$
 (1)

$$Pt(NH_3)_3 Cl^+ + Cl^- \longrightarrow Pt(NH_3)_2 Cl_2$$
 (2)

16. Based on the 18-electron rule, determine the number of carbonyl groups, x, y and z values in the following iron carbonyl complexes. Draw the possible structures of these complexes. (5%)

 $Fe(CO)_x$ ,  $Fe_2(CO)_y$  (having symmetry elements:  $C_3$ ,  $\sigma_v$ ,  $\sigma_h$ ) and  $Fe_3(CO)_z$ . (having

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symmetry elements:  $C_2$ ,  $\sigma_v$ )

17. Olefin metathesis uses a metal carbene (M=CRR') as the catalyst. Last year's Nobel Prize in chemistry was given to Grubbs, Schrock and Chauvin who had great contribution to this chemistry. Predict the olefin metathesis products of the following reaction. Propose a mechanism to account for this reaction. (5%)

2 
$$CH_2$$
= $CHCH_2$ Ph  $M$ = $CH_2$  ?