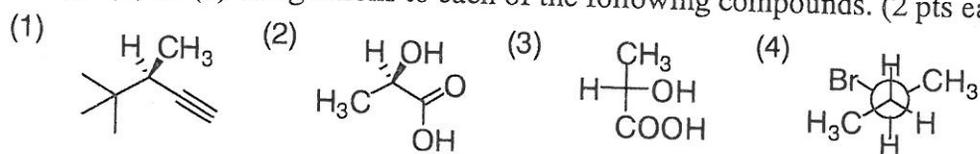
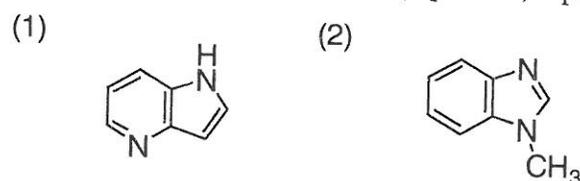


『有機化學』部份 總分 50 分

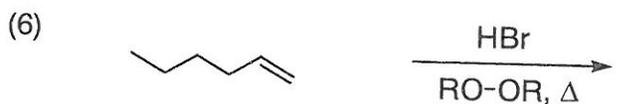
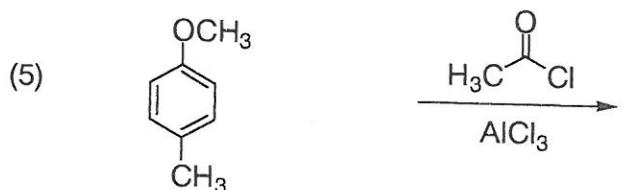
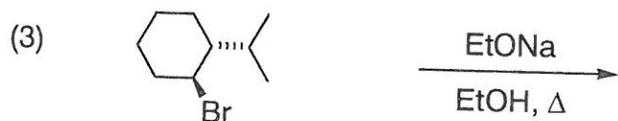
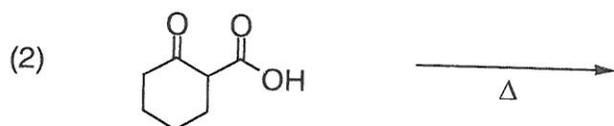
1. Assign (*R*) or (*S*) designations to each of the following compounds. (2 pts each, 8 pts)

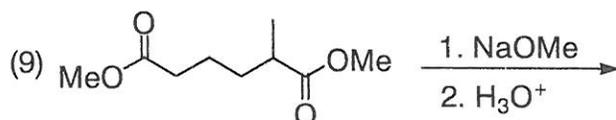
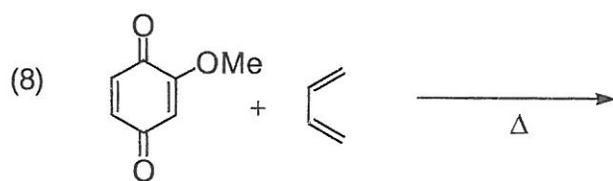


2. Write the structure of the product formed when each of the following compounds reacts with one molar equivalent of HCl. (1 pt each, 2 pts)

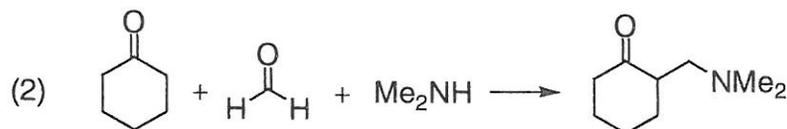
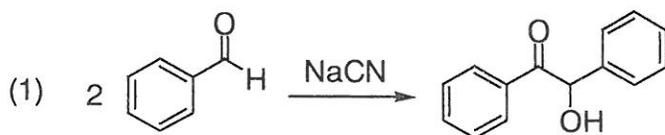


3. Give the expected major product with appropriate stereochemistry, if necessary. (2 pts each, 18 pts)

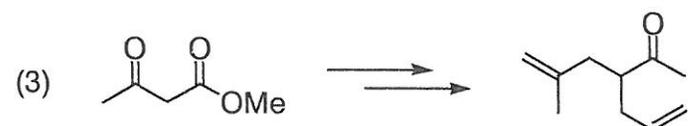
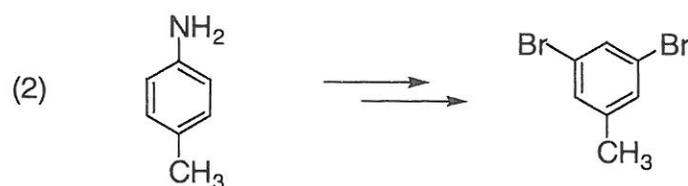
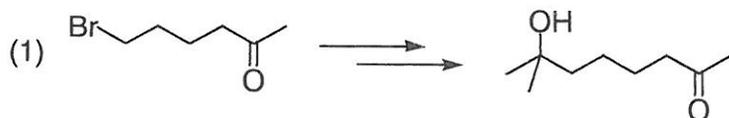




4. Propose a mechanism for the following reactions. (4 pts each, 8 pts)



5. Propose a synthetic scheme for each of the following compounds from the readily available starting materials. (3 pts each, 9 pts)



6. When dissolved in CDCl_3 , a compound (A) with the molecular formula $\text{C}_4\text{H}_8\text{O}_2$ gives a ^1H NMR spectrum that consists of a doublet at δ 1.35, a singlet at δ 2.15, a broad singlet at δ 3.75 (1H), and a quartet at δ 4.25 (1H). When dissolved in D_2O , the compound gives a similar ^1H NMR spectrum, with the exception that the signal at δ 3.75 has disappeared. The IR spectrum of the compound shows a strong absorption peak near 1720 cm^{-1} .

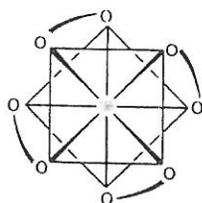
(1) Propose a structure for compound A. (3 pts)

(2) Explain why the NMR signal at δ 3.75 disappears when D_2O is used as the solvent. (2 pts)

無機化學部分 (20 題單選題，每題 2.5 分，共五十分)

1. Select the appropriate point group for the following structure:

- (A) D_{4h}
 (B) C_{4v}
 (C) D_4
 (D) C_4



2. Which of the following selection is correct?

- (i) $C_2^2 = S_4^2$ (ii) $iC_2 = \sigma$ (iii) $C_3 \times \sigma_v = S_6$ (iv) $D_1 \equiv C_2$
 (v) $C_2\sigma_v(xz) = \sigma_v'(yz) \times h$
 (A) (ii), (iv), (v)
 (B) (i), (iii), (v)
 (C) (ii), (iii), (v)
 (D) (i), (ii), (v)

3. Select the correct order for the bond angles, $\angle O-X-O$ of the following ions: XO_3^- , where X = Cl, Br, and I.

- (A) $\angle O-Cl-O < \angle O-Br-O < \angle O-I-O$
 (B) $\angle O-I-O < \angle O-Br-O < \angle O-Cl-O$
 (C) $\angle O-Cl-O < \angle O-Br-O < \angle O-I-O$
 (D) $\angle O-Br-O < \angle O-I-O < \angle O-Cl-O$

4. Select the best choice.

- (A) greatest volume: $S^{2-} < Ar < Ca^{2+}$
 (B) lowest ionization energy: $K < Rb < Cs$
 (C) highest electron affinity: $I > Br > Cl$
 (D) most energy necessary to remove an electron: $Cu > Cu^+ > Cu^{2+}$

5. The $4f_{z(x^2-y^2)}$ orbital has the angular function $\gamma = A z(x^2-y^2) / r^3$, where A = constant. Which of the following statement is true?

- (A) There are 3 angular nodes, 0 radial node, possible quantum numbers for a 4f electron:
 $l = 3, m_l = -3, -2, -1, 0, 1, 2, 3$.
 (B) There are 2 angular nodes, 2 radial nodes, possible quantum numbers for a 4f electron:
 $l = 2, m_l = -2, -1, 0, 1, 2$.
 (C) There are 0 angular nodes, 3 radial node, possible quantum numbers for a 4f electron:
 $l = 3, m_l = -3, -2, -1, 0, 1, 2, 3$.
 (D) There are 0 angular nodes, 2 radial nodes, possible quantum numbers for a 4f electron:
 $l = 2, m_l = -2, -1, 0, 1, 2$.

6. Which of the following statement is true?

- (A) The ratio of ionization energy (IE) of $He^+ : Li^{2+} = 2 : 3$
 (B) The 2nd IE of He is almost exactly twice the IE of H.
 (C) The 3rd IE of Li is almost nine times the IE of H.
 (D) The Bohr equation is given as $E = R_H \left(\frac{1}{n_l^3} - \frac{1}{n_h^3} \right)$.

7. How many unpaired electrons do you predict for the following complexes:

- (i) tetrahedral $[\text{CoCl}_4]^{2-}$ (ii) high-spin $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
(iii) tetrahedral $[\text{NiCl}_4]^{2-}$ (iv) square planar $[\text{Ni}(\text{CN})_4]^{2-}$

- (A) 3, 1, 2, 2
(B) 3, 5, 2, 0
(C) 4, 1, 0, 2
(D) 4, 5, 2, 2

8. Which complex should absorb light of the highest frequency?

$[\text{CrCl}_6]^{3+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, or $[\text{Cr}(\text{en})_3]^{3+}$

- (A) $[\text{CrCl}_6]^{3-}$
(B) $[\text{Cr}(\text{en})_3]^{3+}$
(C) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
(D) all the same

9. On the basis of VSEPR, assign the point group for XeO_2F_2 .

- (A) D_{4h}
(B) D_{2d}
(C) C_{4v}
(D) C_{2v}

The diatomic cations Br_2^+ and I_2^+ are both known. Answer Questions 11-13.

10. Based on the molecular orbital model, what would you predict for the bond orders of these ions?

- (A) 0.5 for both
(B) 1.0 for both
(C) 1.5 for both
(D) 1.0 for Br_2^+ and 1.5 for I_2^+

11. Br_2^+ is red and I_2 ions? Which ion has the more closely spaced HOMO and LUMO?

- (A) $\pi^* \rightarrow \sigma^*$; closer HOMO-LUMO spacing for I_2^+
(B) $\pi^* \rightarrow \sigma^*$; closer HOMO-LUMO spacing for Br_2^+
(C) $\pi \rightarrow \pi^*$; closer HOMO-LUMO spacing for Br_2^+
(D) $\sigma \rightarrow \sigma^*$; closer HOMO-LUMO spacing for I_2^+

12. Since I_2^+ is blue, predict the color of I_2 molecule based on the basis of frontier orbitals.

- (A) red
(B) green
(C) brown
(D) violet

13. List the following acids in order of their acid strength in aqueous solution.

HMnO_4 ; H_2AsO_4 ; H_2SO_3 ; H_2SO_4

- (A) $\text{H}_3\text{AsO}_4 < \text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4 < \text{HMnO}_4$
(B) $\text{H}_3\text{AsO}_4 > \text{H}_2\text{SO}_3 > \text{H}_2\text{SO}_4 > \text{HMnO}_4$
(C) $\text{H}_2\text{SO}_4 < \text{H}_2\text{SO}_3 < \text{H}_2\text{AsO}_4 < \text{HMnO}_4$
(D) $\text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3 > \text{H}_2\text{AsO}_4 > \text{HMnO}_4$

14. Solvents can change the acid-base behavior of solutes. Compare the acid-base properties of dimethylamine in water, acetic acid, and 2-butanol.
- (A) Dimethylamine acts as a weak base in water.
(B) Dimethylamine acts as a stronger base in acetic acid.
(C) Dimethylamine has no significant acid-base behavior in 2-butanol.
(D) all of the above.
15. Predict the order of solubility in water for the following compounds:
 PbCl_2 ; PbBr_2 ; PbI_2 ; PbS
- (A) $\text{PbI}_2 > \text{PbS} > \text{PbBr}_2 > \text{PbCl}_2$
(B) $\text{PbS} > \text{PbI}_2 > \text{PbBr}_2 > \text{PbCl}_2$
(C) $\text{PbS} < \text{PbI}_2 < \text{PbBr}_2 < \text{PbCl}_2$
(D) $\text{PbI}_2 < \text{PbS} < \text{PbBr}_2 < \text{PbCl}_2$
16. ZrO_2 adopts fluorite (CaF_2) structure type, with Zr^{4+} ions in a cubic close packing, fcc lattice and with O^{2-} ions occupying all the tetrahedral holes. The cell parameters of ZrO_2 are $a = b = c = 4.925 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. Atomic weights: Zr (91.224), O (15.999). Calculate the density of ZrO_2 .
- (A) 6.85 g/cm^3
(B) 5.14 g/cm^3
(C) 3.43 g/cm^3
(D) 1.71 g/cm^3
17. (i) Free N_2 has a stretching vibration of $\nu = 2331 \text{ cm}^{-1}$. Would you expect the stretching vibration for coordinated N_2 to be at higher or lower energy? (ii) The molecular orbitals of N_2 are similar to those of CO. Is N_2 a stronger or weaker π -acceptor than CO.
- (A) (i) The coordinated N_2 has higher energy ; (ii) π -acceptor quality: $\text{N}_2 > \text{CO}$
(B) (i) The coordinated N_2 has higher energy ; (ii) π -acceptor quality: $\text{N}_2 < \text{CO}$
(C) (i) The coordinated N_2 has lower energy ; (ii) π -acceptor quality: $\text{N}_2 < \text{CO}$
(D) (i) The coordinated N_2 has lower energy ; (ii) π -acceptor quality: $\text{N}_2 > \text{CO}$
18. The metallocene complex MnCp_2 ($\text{Cp}^- = \text{cyclopentadienyl}$, C_5H_5^- , a very strong field ligand) adopts an octahedral geometry with a very slight distortion on the d_π orbitals. What is the spin multiplicity for this complex?
- (A) 2
(B) 6
(C) 1
(D) 5
19. Select the highest IR C-O stretching frequency: $\text{Cr}(\text{CO})_5(\text{PX}_3)$, X = F, Cl, Br, I.
- (A) $\text{Cr}(\text{CO})_5(\text{PI}_3)$
(B) $\text{Cr}(\text{CO})_5(\text{PF}_3)$
(C) $\text{Cr}(\text{CO})_5(\text{PCl}_3)$
(D) $\text{Cr}(\text{CO})_5(\text{PBr}_3)$
20. Propose a mechanism for the reaction of $[\text{Co}(\text{NH}_3)_6]^{3+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+}$.
- (A) an inner-sphere reaction
(B) a dissociation reaction
(C) an association reaction
(D) an outer sphere reaction

