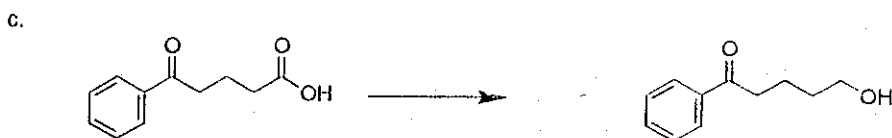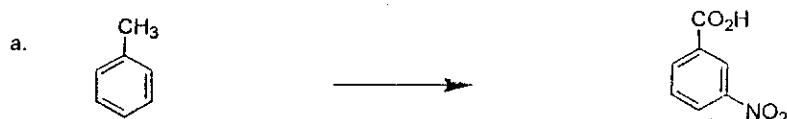Organic Chemistry   有機化學

1. Write the stereo structure of the following compound. (4pts)
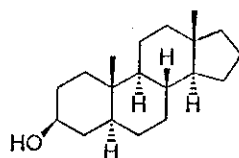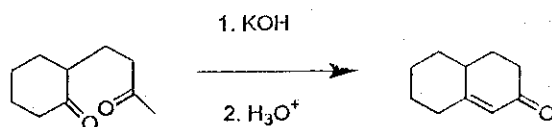


2. Use appropriate reagents to finish each transformation.   Several steps may be needed for each transformation. (16 pts)

a.



b.



c.



d.

有機化學

3. Write down the reaction mechanism for the following transformations. (10 pts)

a.



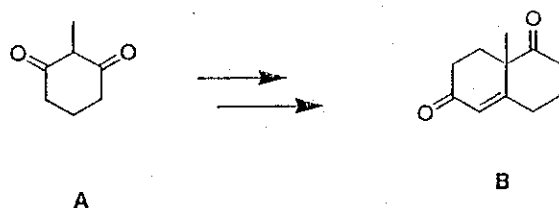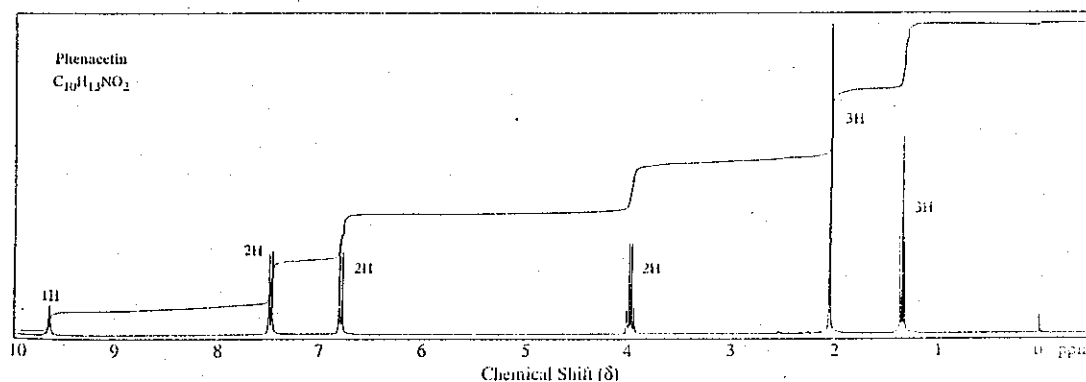1. KOH

2. $H_3O^+$

b.



heat
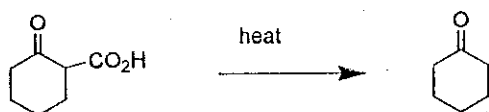
4. Complete the synthesis of compound B by using compound A as a starting material . (10 pts)



A

B

5. Propose a structural formula for the analgesic phenacetin, a molecular formula $C_{10}H_{13}NO_2$ based on the $^1H$ NMR spectrum. (10 pts)
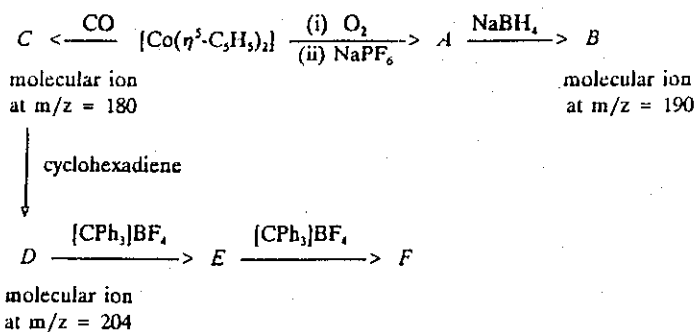
# 無機化學

I. Answer briefly the following questions (5% each):

(1) Why is $[Cu(I)L_4]^+$ often tetrahedral while $[Cu(II)L_4]^{+2}$ often square-planar? (L = neutral ligand)

(2) What is the most possible reason for a dinuclear Cu(II) complex that produces no EPR signal?

(3) Why is CO always coordinated to metal centers via its carbon end but not its oxygen end in metal carbonyl complexes?

(4) Is $^3O_2$ paramagnetic or diamagnetic? Explain your answer.

(5) Account for the trend in acidity: $[Fe(OH_2)_6]^{2+} < [Fe(OH_2)_6]^{3+} < [Al(OH_2)_6]^{3+}$.

(6) Use VSEPR theory to predict the molecular shape and point group of the following compounds: $ClF_3$, $BrF_5$, $SF_4$, $B_2H_6$.

(7) Provide a plausible reason for the difference in IR wavenumbers for the following pair:
$Mo(PF_3)_3(CO)_3$: 2090,2055 $cm^{-1}$, versus $Mo(PEt_3)_3(CO)_3$: 1937,1841 $cm^{-1}$

II. (15%) Some chemistry of cobaltocene is given below. Complexes **A**, **E**, and **F** are salts. Complexes **B**, **C**, and **D** are neutral. Using the data given, identify Compounds A-F and draw their structures.

Hint: Trityl ($CPh_3^+$) is a hydride abstracting reagent.

$$C \xleftarrow{\quad CO \quad} [Co(\eta^5\text{-}C_5H_5)_2] \xrightarrow[\text{(ii) } NaPF_6]{\text{(i) } O_2} A \xrightarrow{\quad NaBH_4 \quad} B$$

molecular ion at m/z = 180          molecular ion at m/z = 190

$[Co(\eta^5\text{-}C_5H_5)_2]$ ↓ cyclohexadiene

$$D \xrightarrow{\quad [CPh_3]BF_4 \quad} E \xrightarrow{\quad [CPh_3]BF_4 \quad} F$$

molecular ion at m/z = 204

Proton NMR data (δ relative to TMS, ppm)

**A**    2.8

**B**    5.2 (2H), 4.6 (5H), 2.7 (2H), 2.6 (1H), 2.0 (1H)

**C**    5.0

**D**    4.2 (2H), 4.0 (5H), 2.4 (2H), 0.9 (2H), 0.3 (2H)

**E**    7.3 (1H), 5.6 (5H), 5.4 (2H), 4.0 (2H), 2.7 (1H), 1.0 (1H)

**F**    7.9 (6H), 7.0 (5H)

| 1 1A | 2 2A | 3 3B | 4 4B | 5 5B | 6 6B | 7 7B | 8 | 9 8B | 10 | 11 1B | 12 2B | 13 3A | 14 4A | 15 5A | 16 6A | 17 7A | 18 8A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.008 | | | | | | | | | | | | | | | | | 2 He 4.003 |
| 3 Li 6.941 | 4 Be 9.012 | | | | | | | | | | | 5 B 10.81 | 6 C 12.01 | 7 N 14.01 | 8 O 16.00 | 9 F 19.00 | 10 Ne 20.18 |
| 11 Na 22.99 | 12 Mg 24.31 | | | | | | | | | | | 13 Al 26.98 | 14 Si 28.09 | 15 P 30.97 | 16 S 32.07 | 17 Cl 35.45 | 18 Ar 39.95 |
| 19 K 39.10 | 20 Ca 40.08 | 21 Sc 44.96 | 22 Ti 47.88 | 23 V 50.94 | 24 Cr 52.00 | 25 Mn 54.94 | 26 Fe 55.85 | 27 Co 58.93 | 28 Ni 58.69 | 29 Cu 63.55 | 30 Zn 65.39 | 31 Ga 69.72 | 32 Ge 72.59 | 33 As 74.92 | 34 Se 78.96 | 35 Br 79.90 | 36 Kr 83.80 |
| 37 Rb 85.47 | 38 Sr 87.62 | 39 Y 88.91 | 40 Zr 91.22 | 41 Nb 92.91 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.1 | 45 Rh 102.9 | 46 Pd 106.4 | 47 Ag 107.9 | 48 Cd 112.4 | 49 In 114.8 | 50 Sn 118.7 | 51 Sb 121.8 | 52 Te 127.6 | 53 I 126.9 | 54 Xe 131.3 |
| 55 Cs 132.9 | 56 Ba 137.3 | 57 La 138.9 | 72 Hf 178.5 | 73 Ta 180.9 | 74 W 183.9 | 75 Re 186.2 | 76 Os 190.2 | 77 Ir 192.2 | 78 Pt 195.1 | 79 Au 197.00 | 80 Hg 200.6 | 81 Tl 204.4 | 82 Pb 207.2 | 83 Bi 209.0 | 84 Po (210) | 85 At (210) | 86 Rn (222) |
| 87 Fr (223) | 88 Ra (226) | 89 Ac (227) | 104 Unq (257) | 105 Unp (260) | 106 Unh (263) | 107 Uns (262) | 108 Uno (265) | 109 Une (266) | | | | | | | | | |

## 分析化學

### ANALYTICAL CHEMISTRY

Note: Always use the correct significant figures in your calculations!!

(15%)1.Define the following terms:

    (a) Beer's Law         (b) buffer capacity         (c) systematic error

(8%) 2. The diprotic acid $H_2A$ has $pK_1 = 4.00$ and $pK_2 = 8.00$.

    (a) At what pH is $[HA^-] = [A^{2-}]$? Why?
    (b) Which is the principal species at pH 2.00: $H_2A$, $HA^-$, or $A^{2-}$? Why?
    (c) Which is the principal species at pH 6.00? Why?

(6%) 3.(a) 96.3 MHz = ? Hz   (b) 12.3 nm = ? cm   (c) 6.80 $\mu$L = ? mL

    (d) how many significant figures are there in 0.03950 ?

(7%) 4.(a) What is fluorescene?

    (b) Explain the difference between a fluorescene emission spectrum and a fluorescene excitation spectrum. Which more closely resembles an absorption spectrum? Why?

(7%) 5.(a) What is Ion Chromatography (IC)?

    (b) Predict the elution order of nitrate, chloride, and sulfate ions in IC. Why?

(7%) 6.(a) What is Anodic Stripping Voltammetry (ASV)?

    (b) ASV is the most sensitive electroanalytical chemistry method for analysis of trace metal ions (e.g., $Pb^{2+}$, $Cu^{2+}$) in river water samples. Why?

Physical Chemistry    物理化學

1. Describe how variation method and perturbation method dealing with the time-independent Schrödinger equation for systems of several interacting particles.(10%)

2. Write the partition function for a two-level system, the lower state (at energy 0) being non-degenerate, and the upper state (at an energy ε) doubly degenerate. (10%)

3. The vapor pressure of nitric acid is as follows:

| T/ °C | 0 | 20 | 40 | 50 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|
| P/ Torr | 14.4 | 47.9 | 133 | 208 | 467 | 670 | 937 | 1282 |

What is the normal boiling point and the enthalpy of vaporization of nitric acid? (10%)

4. Why is "Gibbs energy" also named as "Free energy"? (10%)

5. Does the solubility of a solid in a liquid exhibit appreciable pressure dependence? Why?(10%)