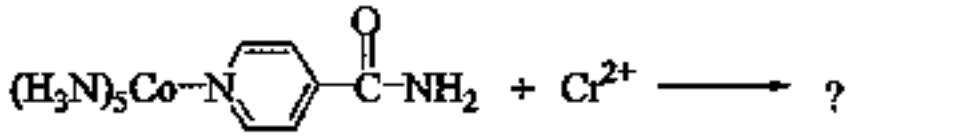
1. The oxidation-reduction reactions and the rate constants are shows below

(a)  + Cr^{2+} ⟶ ?

($k_2 = 17.6\ (M^{-1}S^{-1})$)

(b) $Co(NH_3)_6^{3+} + Cr^{2+} \longrightarrow$?

($k_2 = 8.9\times10^{-5}(M^{-1}S^{-1})$)

(i) Predict the products of the reactions (ii) what are the mechanisms for the above two reactions? (iii) Explain why the rate constant of (a) is much faster than that of (b) (hint, inner and outer-sphere electron transfer). (7%)

2. Propose a reasonable structure for $Cu(H_2O)_6^{2+}$. This complex was found to have two types of Cu-O distance and two separate water exchange rates in aqueous solution. Why? (6%)

3. (a) Describe the bonding between CO and a meal center. (2%)

(b) Compare the ν(CO) frequencies of $V(CO)_6$ and $V(CO)_6^-$ in the IR spectra. Which gives higher ν(CO)? (2%)

(c) The V-C distance in $V(CO)_6$ is 200 pm, but only 193 pm in $V(CO)_6^-$. Explain. (2%)

4. Give the most likely metals of first-row transition metals for each of the following. Explain why. (6%)

(a) $M(CO)_6$ (b) $[(\eta^5\text{-}C_5H_5)_2M]^+$

(c) $[M(CO)_3(NO)]^-$ (d) $[\eta^5\text{-}C_5H_5M(CO)_3]_2$

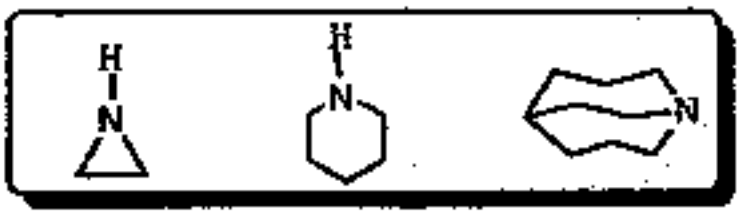
(NO: linear) (containing single M-M bond)

5. Draw the detailed structures and assign the point groups of the following complexes. (6%)

(a) $N(SiMe_3)_3$ (b) B_2H_6 (c) $(B_3N_3H_6)Cr(CO)_3$ (d) $Re_2Cl_8^{2-}$

6. Answer the following questions **with a brief reason.**

(a) In the reaction of the following amines with proton in gaseous phases, arrange the energy released from these amines by an increasing order. (2%)



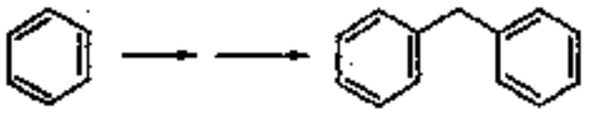
(b) Among the following complexes, which one has the largest 10 Dq values? And which one has the smallest 10 Dq value? How many of them will have perfect octahedral geometries? (5%)

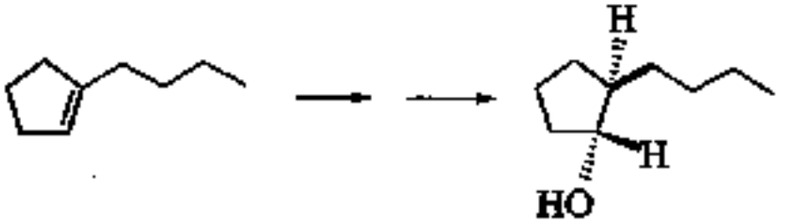
$Ir(CN)_6^{3-}$, $Co(CN)_6^{3-}$, $Co(NH_3)_6^{3+}$, $Ir(NH_3)_6^{3+}$, $Ir(CN)_6^{2-}$, $Co(NH_3)_6^{2+}$

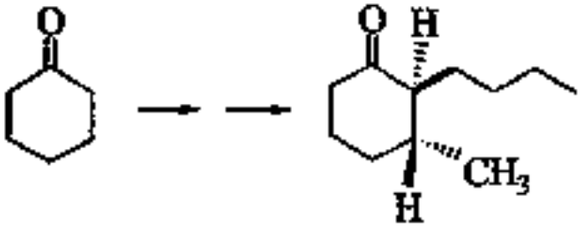
7. Draw the molecular orbitals of B_2 and C_2 complexes. Show the term symbols for the first two absorptions in the photoelectron spectra of B_2. (6%)

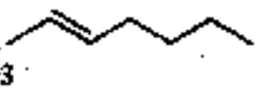
8. Show the number of d-d transition bands for weak-field CrF_6^{3-} and tetrahedral NiF_4^{2-} give the transitions in term of term symbols. (6%)

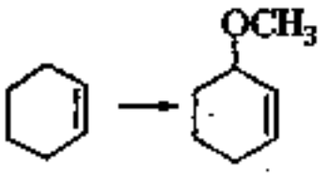
9. Propose a synthetic scheme for each of the following compounds from the readily available starting materials. (15%)

(a) 

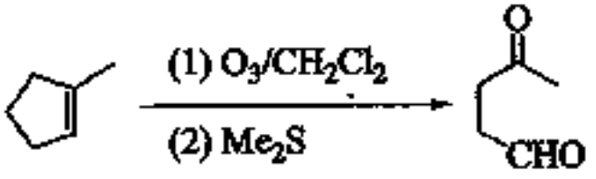
(b) 

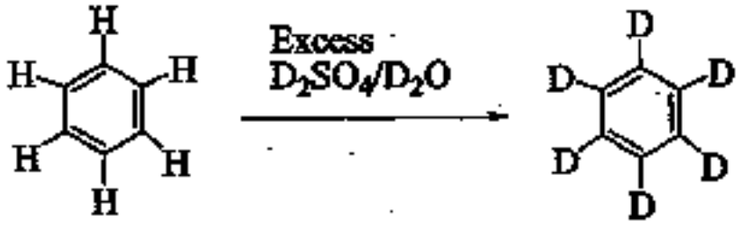
(c) 

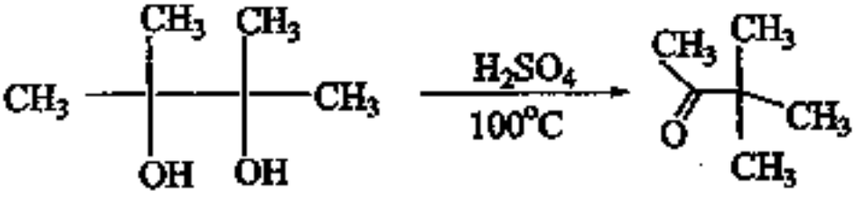
(d) CH_3-C≡CH ⟶ ⟶ 

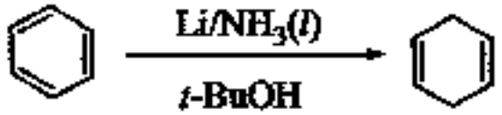
(e) 

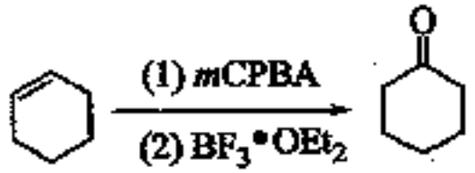
10. Write the reaction mechanism for the following transformation (use ⌒ to show electron flow) (10%)

(a) 

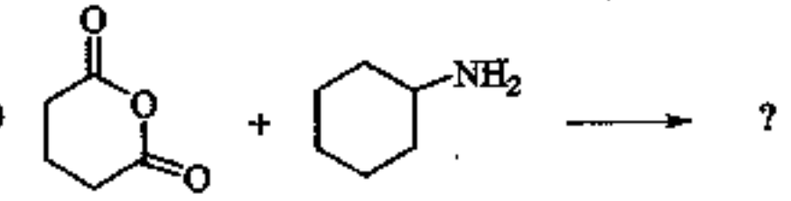
(b) 

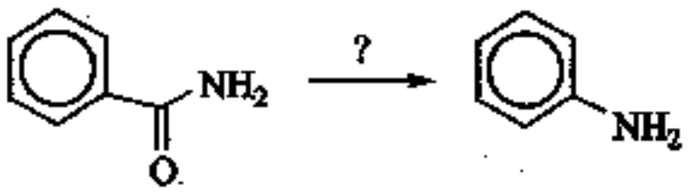
(c) 

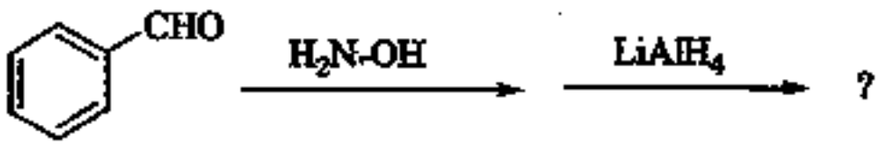
(d) 

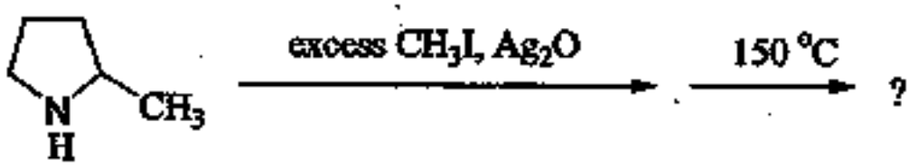
(e) 

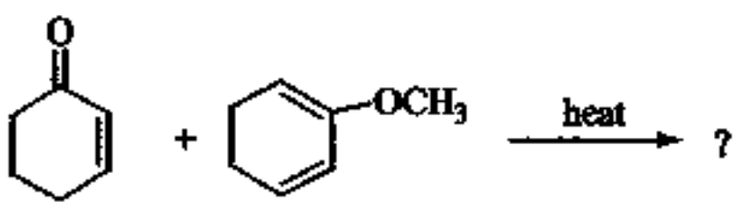
11. Predict the structure, including stereochemistry, of the major product or provide necessary reagent(s) to complete each of the following transformations.(15%)

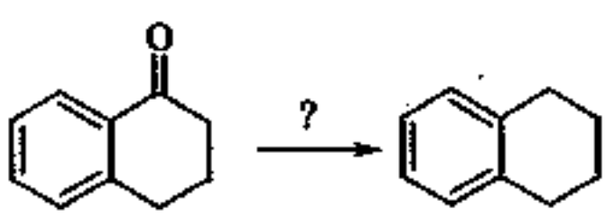
(a) 

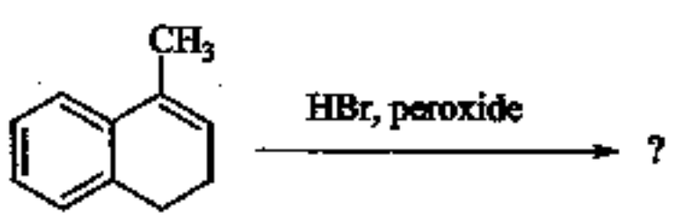
(b) 
NH2
?
NH2
O

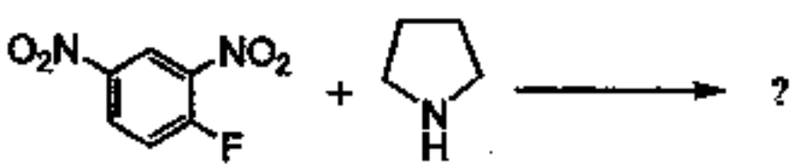
(c) 
CHO
H2N-OH
LiAlH4
?

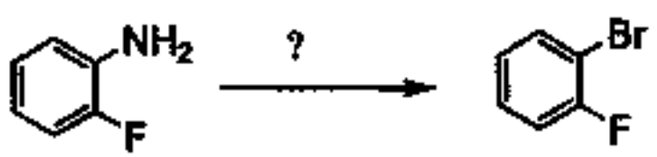
(d) 
N
H
CH3
excess CH3I, Ag2O
150 °C
?

(e) 
O
+
OCH3
heat
?

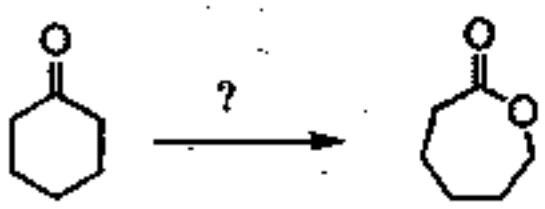
(f) 
O
?

(g) 
CH3
HBr, peroxide
?

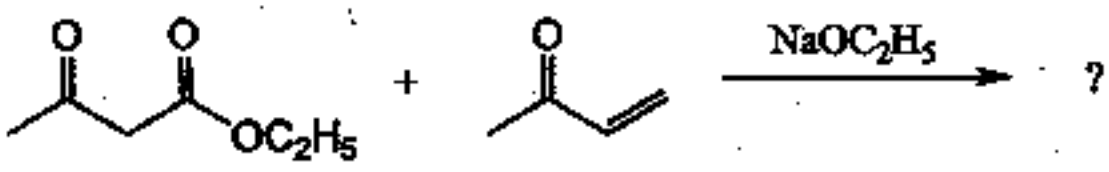
(h) 
O2N
NO2
F
+
N
H
?

(i) 
NH2
F
?
Br
F

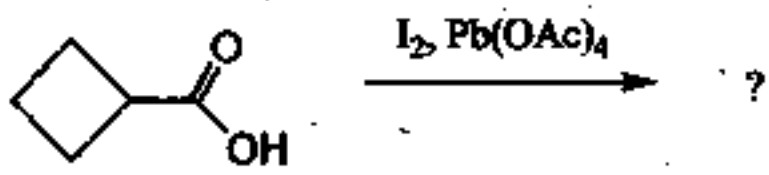
(j)



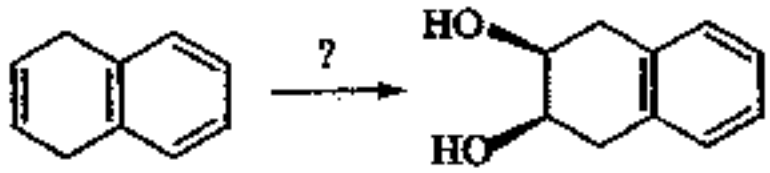
(k)



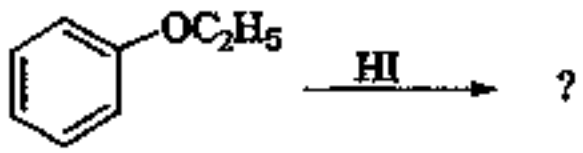
(l)



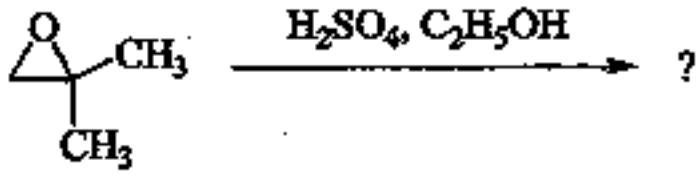
(m)



(n)



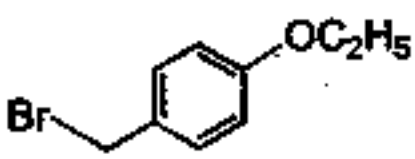
(o)

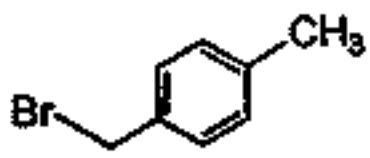


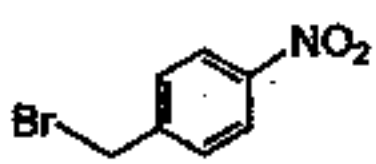
12. Answer the following questions and give a brief explanation for your answer. (3%)
(a) Which of the following compounds is the most unstable one?

cyclopropenone, cyclopentadienone, cycloheptatrienone

(b) Which of the following compounds is the easiest one to react through S_N1 mechanism?







13. Deduce the molecular structure for the compound that consistent with the provided spectral information. (7%)