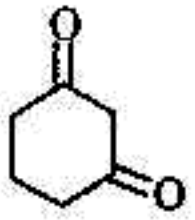
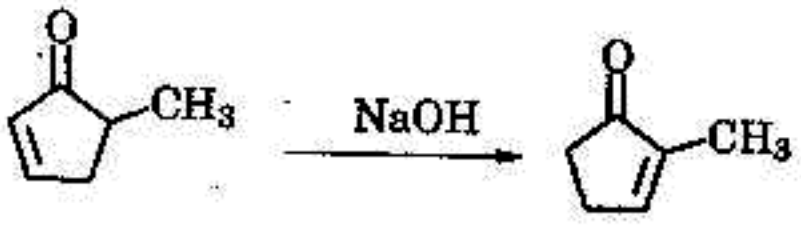
1. Draw Structures for the monoenol forms of 1,3-cyclohexanedione. How many enol forms are possible? Which would you expect to be most stable? Explain. (10%)



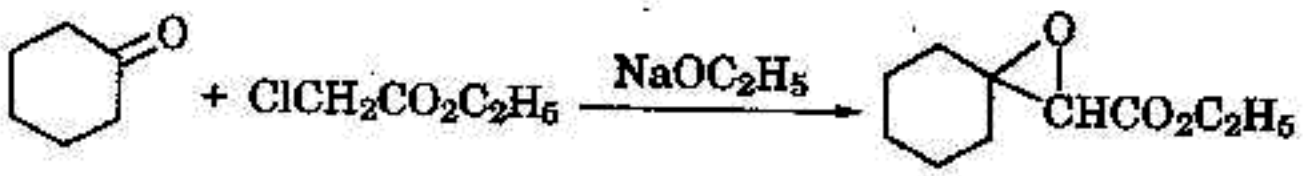
1,3-Cyclohexanedione

2. Provide plausible reaction mechanisms, including the structures of all intermediates, for the following transformations. (10%)

(a)

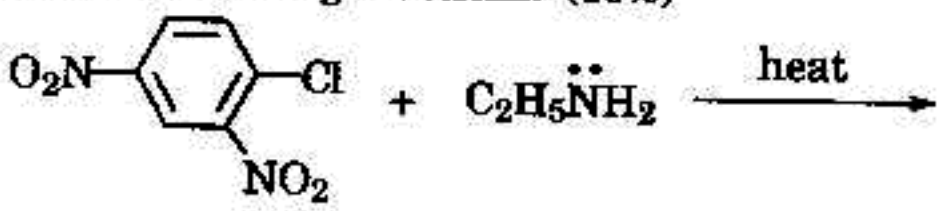


(b)

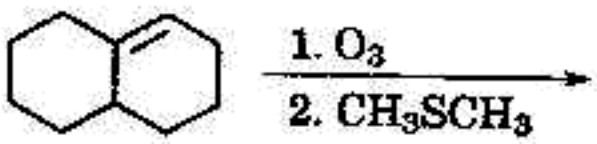


3. Complete the following reactions. (10%)

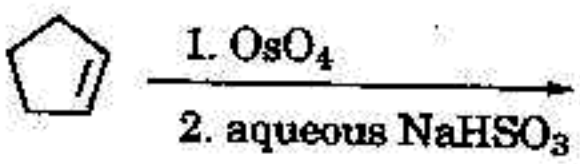
(a)



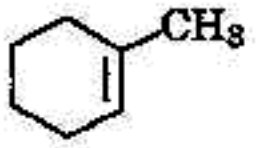
(b)



(c)

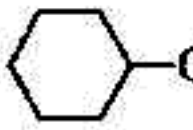


(d)



$\xrightarrow[2.\ H_2O_2,\ NaOH]{1.\ BH_3}$

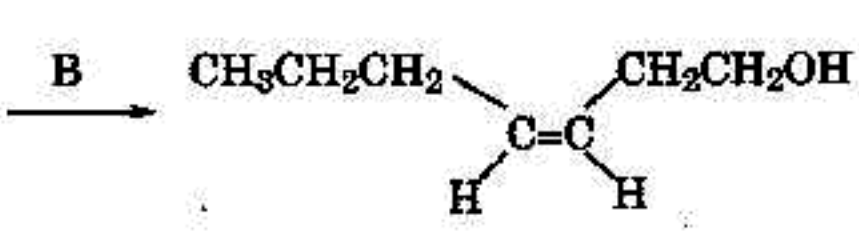
(e)

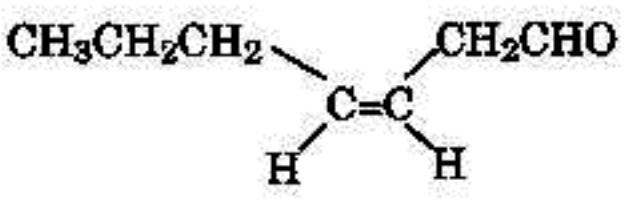


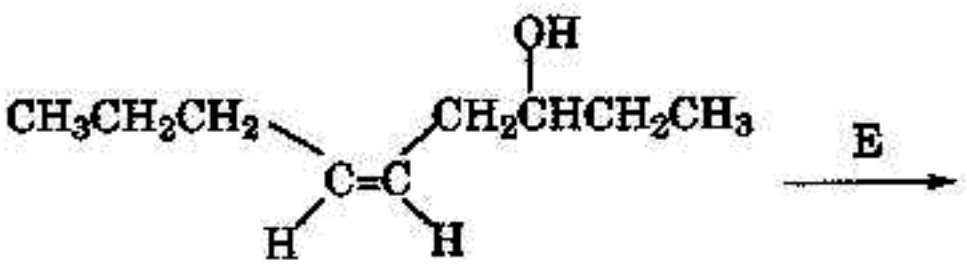
$\xrightarrow[\text{aqueous } H_2SO_4]{HgSO_4}$

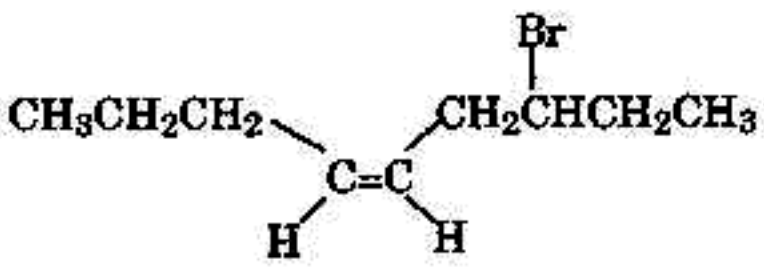
4. Suggest reagents for the following transformations. (10%)

(a) $CH_3CH_2CH_2C{\equiv}CH \xrightarrow{A} CH_3CH_2CH_2C{=}CCH_2CH_2OH$



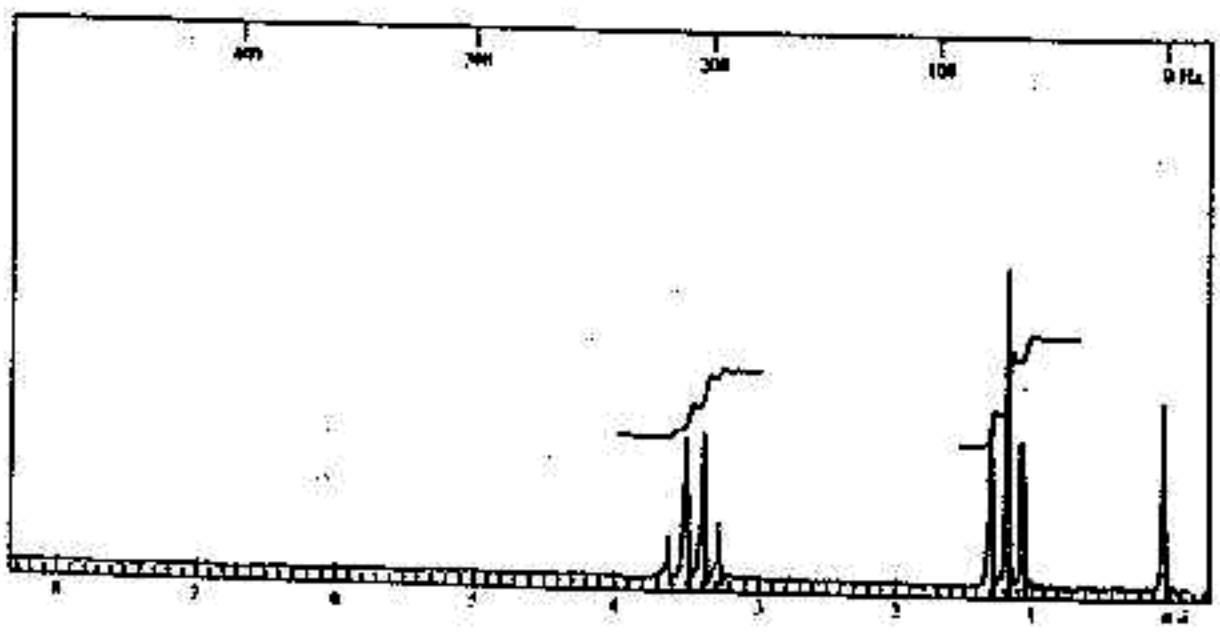




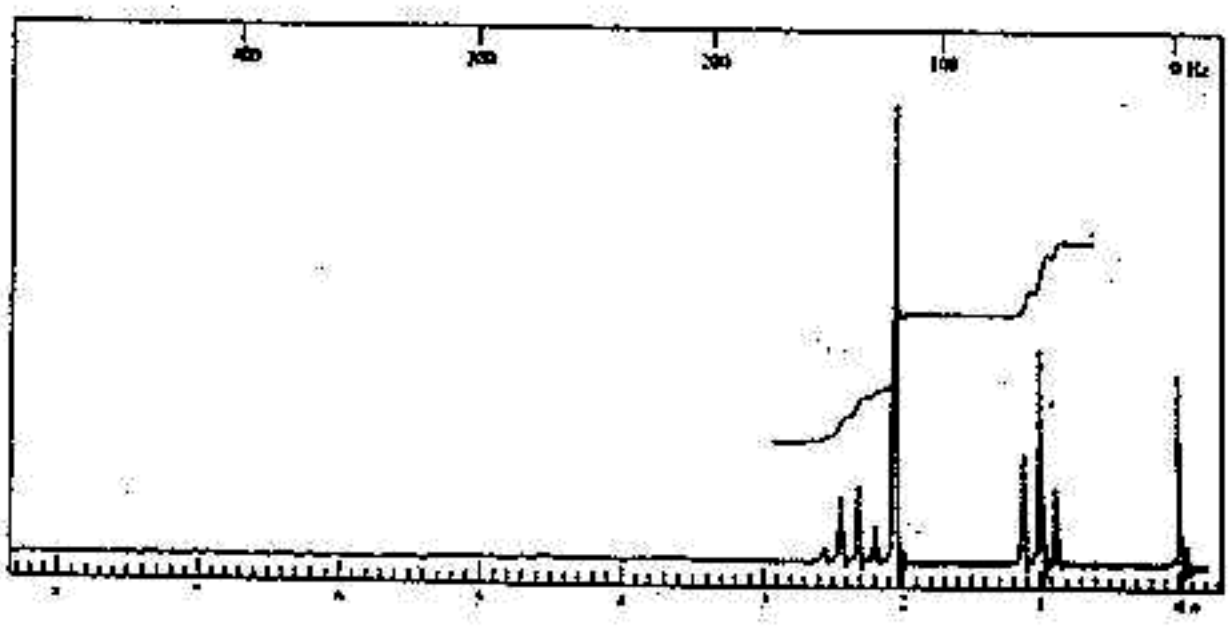


5. Give a structure consistent with each of the proton NMR spectra shown below. (10%)

(a) $C_4H_{10}O$



(b) C_4H_8O



6. The isoelectronic ions VO_4^{3-}, CrO_4^{2-}, and MnO_4^- all have intense charge transfer bands in the visible light region. Arrange the wavelengths of these three complexes in increasing order. Give your answer with a diagram to show the transitions. (6 %)

7. Briefly answer the question with a reason (10%)
   (a) Which ion shows the greatest tendency for square planar complexes Ni^{2+}, Ir^{+1}, Rh^{+1}, Pd^{2+} and Pt^{2+}
   (b) Which ion shows the greatest tendency for square planar complexes Cu(II), Ag(II) and Au(II)
   (c) What are the structure and the point group of $N(SiMe_3)_3$?
   (d) Explain the leveling effect of a acid or a base when it is used as a solvent. Give one example.
   (e) Which complexes will **not** shows Jahn-Teller distortion. Give your reason.
   $Ni(NH_3)_6^{2+}$, $Cu(NH_3)_6^{2+}$, $Mn(H_2O)_6^{2+}$, $Ti(H_2O)_6^{3+}$, $Cr(H_2O)_6^{3+}$, $Co(NH_3)_6^{2+}$, CoF_6^{3-} and MnF_6^{2-},

8. Show the number of d-d transition bands in terms of spectrum terms for CrF_6^{3-}. (3%)

9. For the following two complexes, use the character to predict the number of IR active band of υ(CO) stretching modes in the 2200-1700 cm^{-1}. Here you only consider the stretching mode and forget the bending and other modes of CO group. (6%)
   (a) trans-$M(CO)_4L_2$ (b) cis-$M(CO)_4L_2$

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1		
B_{1u}	1	−1	1	1	−1	−1	1	−1	1	1	z	
B_{2u}	1	−1	1	−1	1	−1	1	−1	−1	1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

10. Fig. 1 shows the rate of exchange of water molecules on aquated metal ions (eq 1)

$$M(H_2O)_6^{n+} + H_2O^* \rightleftharpoons M(H_2O)_5(H_2O^*)^{n+} + H_2O \quad (1)$$

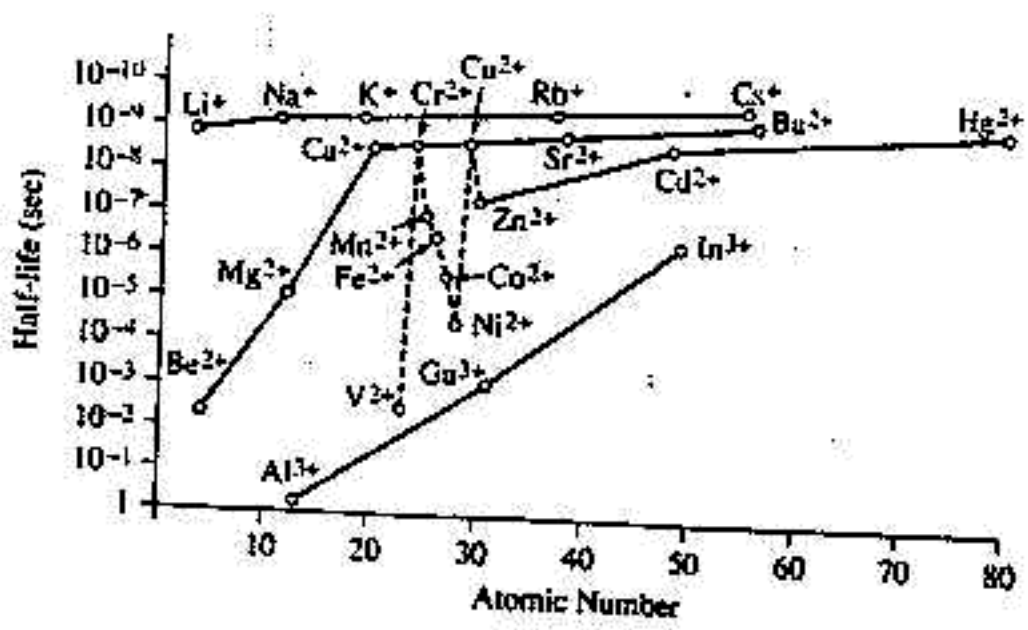


Fig. 1

Explain why (a) $V^{2+} << Cr^{2+}$ (b) $Be^{2+} << Li^+$ (c) $Al^{3+} < Ga^{3+}$ in the rate of exchange of water molecules. (6%)

11. Draw all possible isomers (geometric isomers, linkage isomers and enantiomers) of the following compounds. (4%)

$[Co(en)_2(Cl)_2]^+$, $Pd(en)(NCS)_2$ en = 

Assign the absolute configuration (Δ or Λ) of the enantiomers. (2%)

12. Which of the following molecules or ions may be used as
(a) π-acceptor ligands
(b) π-donor ligands
NH_3, H_2O, PPh_3, CH_2CH_2, CHCH, CO, Cl^- (4%)

13. Choose the most suitable complex from the following that may be used as the catalyst for (5%)
(a) hydrogenation
(b) synthesis of acetic acid from methanol and CO
(c) oxidation of ethylene to CHCHO by O_2
(d) hydroformylation
(e) olefin metathesis
$RhCl(CO)(PPh_3)_2$, $Rh(CO)_2I_2^-$, $RhCl(PPh_3)_3$, $PdCl_4^-$, $NiCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$, $Fe(CO)_5$, $WBr(OCH_2C(CH_3)_3)_2(CHC(CH_3)_3)$

14. Classify the following compounds as closo, nido or arachno and explain why? (4%)
B_5H_9, $B_3H_8Mn(CO)_3$, $C_2B_{10}H_{12}$, $SiC_2B_4H_{10}$