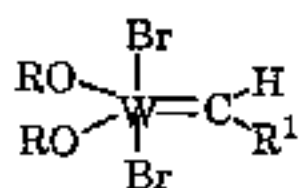


八十五學年度 化學系 化學、應用化學 組碩士班研究生入學考試

科目 無機化學及有機化學 科號 0602 0702 共 8 頁第 1 頁 *請在試卷【答案卷】內作答

1. The tungsten carben complex **1** in the presence of GaBr_3 catalyzes the ring-opening polymerization of norbornene **2**. (5%)



1

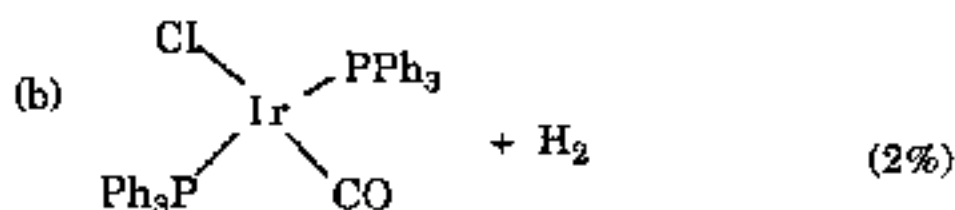
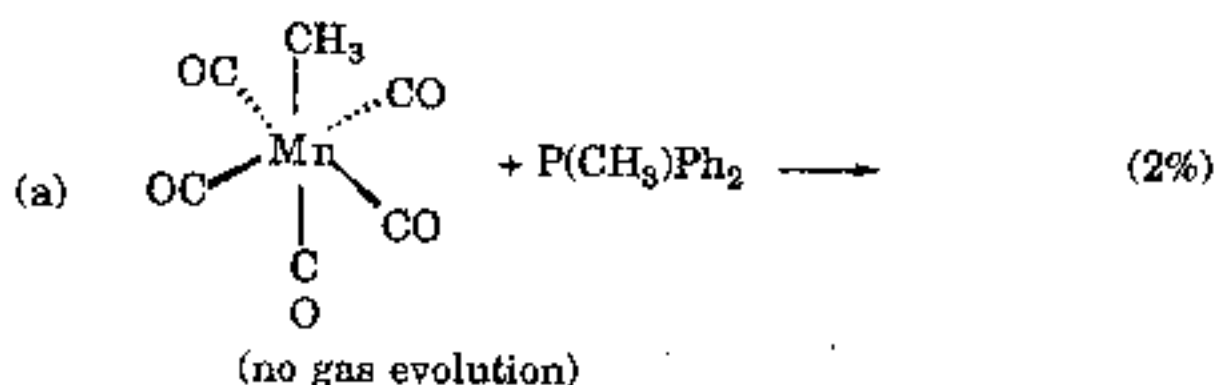


2

propose a mechanism for this catalytic reaction.

2. $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{H}$ eliminates a colorless gas **A**, forming a purple-brown solid **B** with the empirical formula $\text{C}_7\text{H}_5\text{O}_2\text{Fe}$. Reaction of **B** with I_2 gives a brown solid **C** of empirical formula $\text{C}_7\text{H}_5\text{O}_2\text{FeI}$. Treatment of **C** with $\text{Tl}(\text{C}_5\text{H}_5)$ affords a solid **D** of formula $\text{C}_{12}\text{H}_{10}\text{O}_2\text{Fe}$, which gives off a colorless gas and produces an orange solid **E** of formula $\text{C}_{10}\text{H}_{10}\text{Fe}$. Propose structures for **A-E**. (5%)

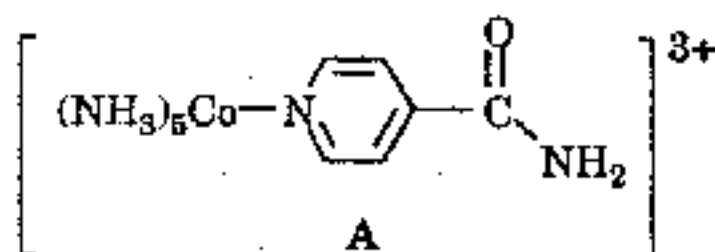
3. Predict the structures of the reaction products.



八十五學年度 化學系 化學、應用化學組碩士班研究生入學考試

科目 無機化學及有機化學 科號 0602 共 8 頁第 2 頁 *請在試卷【答案卷】內作答

4. $\text{Co}(\text{NH}_3)_6^{3+}$ is reduced slowly by $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ ($k = 8.9 \times 10^{-5} \text{M}^{-1}\text{S}^{-1}$), but A is reduced much more rapidly by $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ ($k = 17.6 \text{M}^{-1}\text{S}^{-1}$). What are the mechanisms for these redox reactions and predict the structures of the final products. (5%)



5. Draw all the possible isomers for $\text{Co}(\text{en})_2\text{Cl}_2^+$ and assign absolute configurations for the isomers. (6%)

6. If one does not take into account Jahn-Teller effect, please show spectrum terms and possible d-d transition bands for the giving complexes below. (9%)

(a) CrF_6^{3-} (weak-field) (b) NiF_4^{2-} (c) $\text{Co}(\text{H}_2\text{O})_6^{2+}$ (weak-field)

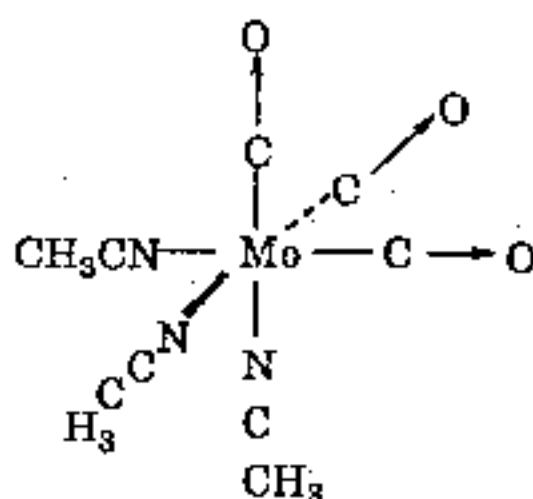
7. Of the complexes below, which will show the strongest absorption intensities in d-d transitions? Give your answer. (3%)

MnF_4^{2-} , $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, NiF_4^{2-} , $\text{Ni}(\text{H}_2\text{O})_6^{2+}$

8. Determine the number of IR active C-O stretching modes for fac- $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$. Show clearly your calculation procedure. (5%)

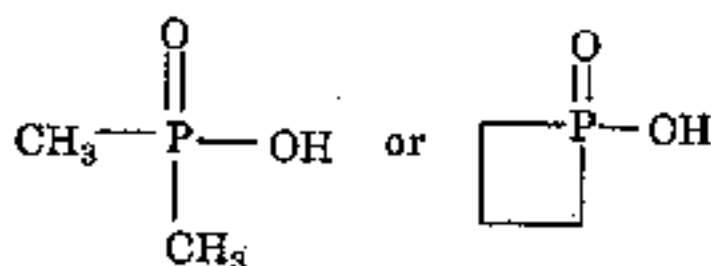
八十五學年度 化學系 化學・應用化學 組碩士班研究生入學考試

科目 無機化學及有機化學 科號 0602 0702 共 8 頁第 3 頁 *請在試卷【答案卷】內作答



C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y), (R_x, R_y)	$(x^2-y^2, xy), (xz, yz)$

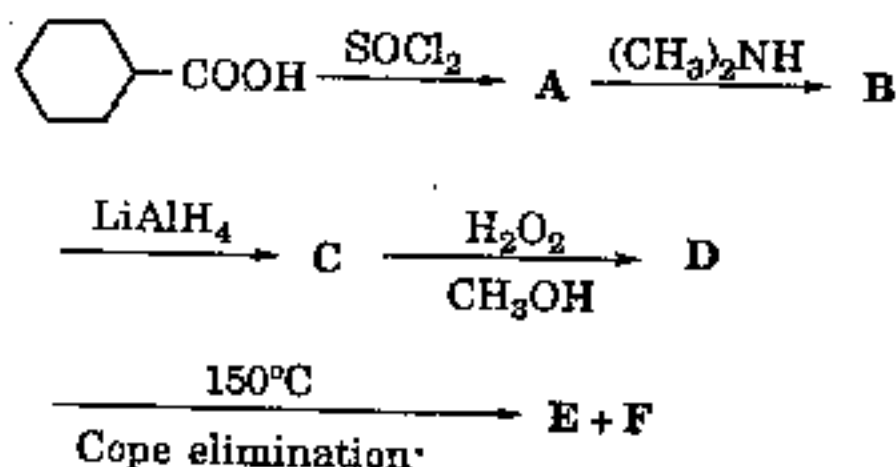
9. Show the structure and point groups for $(\text{Me}_3\text{Si})_3\text{N}$. Why is the structure different from that of $(\text{Me}_3\text{C})_3\text{N}$? Give your reason. (3%)
10. Which do you expect to be more acidic? Give your answer. (3%)



11. Explain the term "proton affinity". Give the a clear definition. (2%)

八十五學年度 化學系 化學、應用化學 組碩士班研究生入學考試
 科目 無機化學及有機化學 科號 0602 0702 共 8 頁第 4 頁 *請在試卷【答案卷】內作答

12. Give the structures of the major products for the following transformations, and propose a mechanism for the Cope elimination of compound D. (6%)

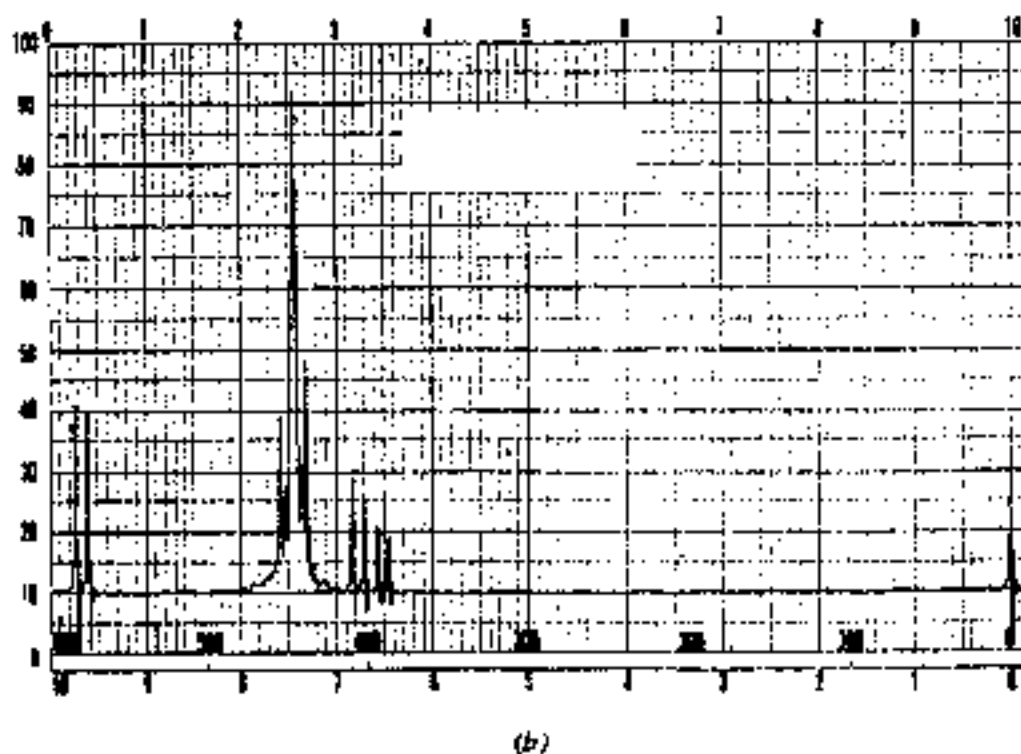
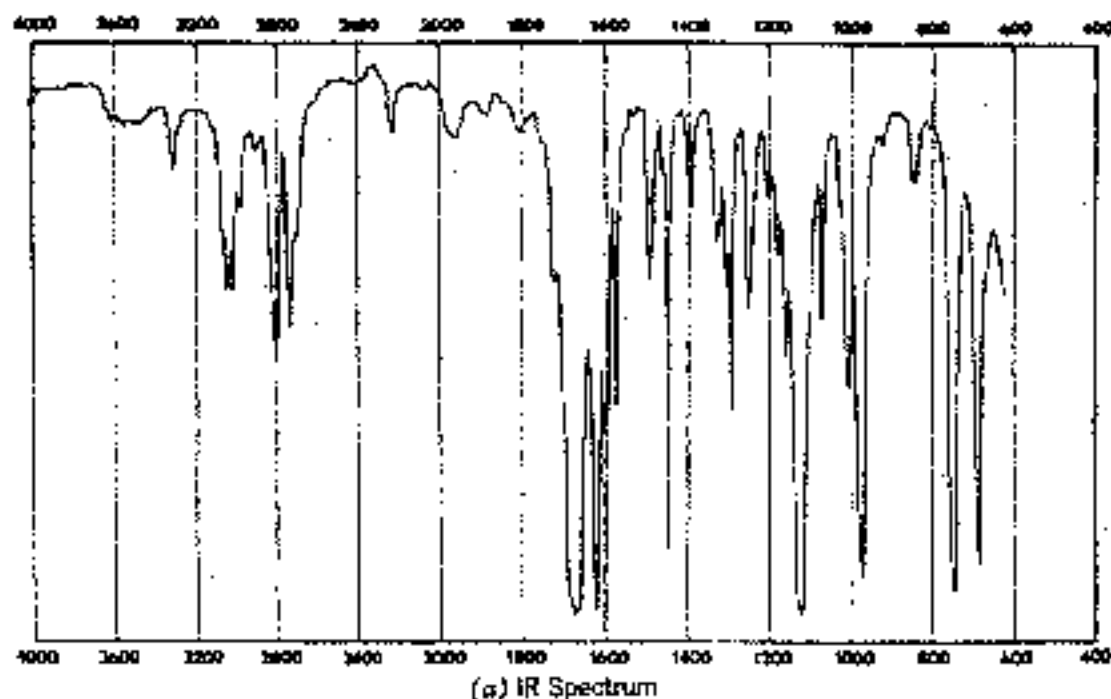


13. How many hydrogens are replaced by deuterium when each of the following compounds is treated with NaOD in D_2O ? Write an equation for the reaction. (4%)
- Cyclohexanecarbaldehyde
 - 3-methylcyclopentadecanone (muscone)
14. Muscone (I) (Problem 13-b), an odorous principle of natural musk from the musk deer, is optically active and has (*R*)-(-)- form. It is heated with hydrazine hydrate and sodium hydroxide in diethylene glycol to give compound II, which is optically inactive. Write the structures of compounds I and II and show the absolute configuration for I, and also explain why compound I is optically active and II is inactive. (4%)
15. Compound X (C_7H_{12}) reacts with dry HCl at -20°C to give Y ($\text{C}_7\text{H}_{13}\text{Cl}$), which reacts with potassium *t*-butoxide in *t*-butyl alcohol to give a small amount of X and mainly Z (C_7H_{12}). Ozonolysis of Z gives cyclohexanone and formaldehyde. What are compounds X through Z? (6%)

八十五學年度 化學系 化學、應用化學組碩士班研究生入學考試

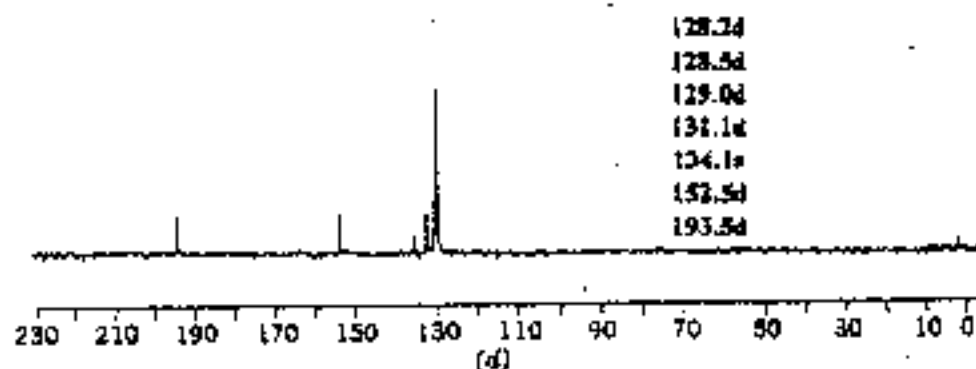
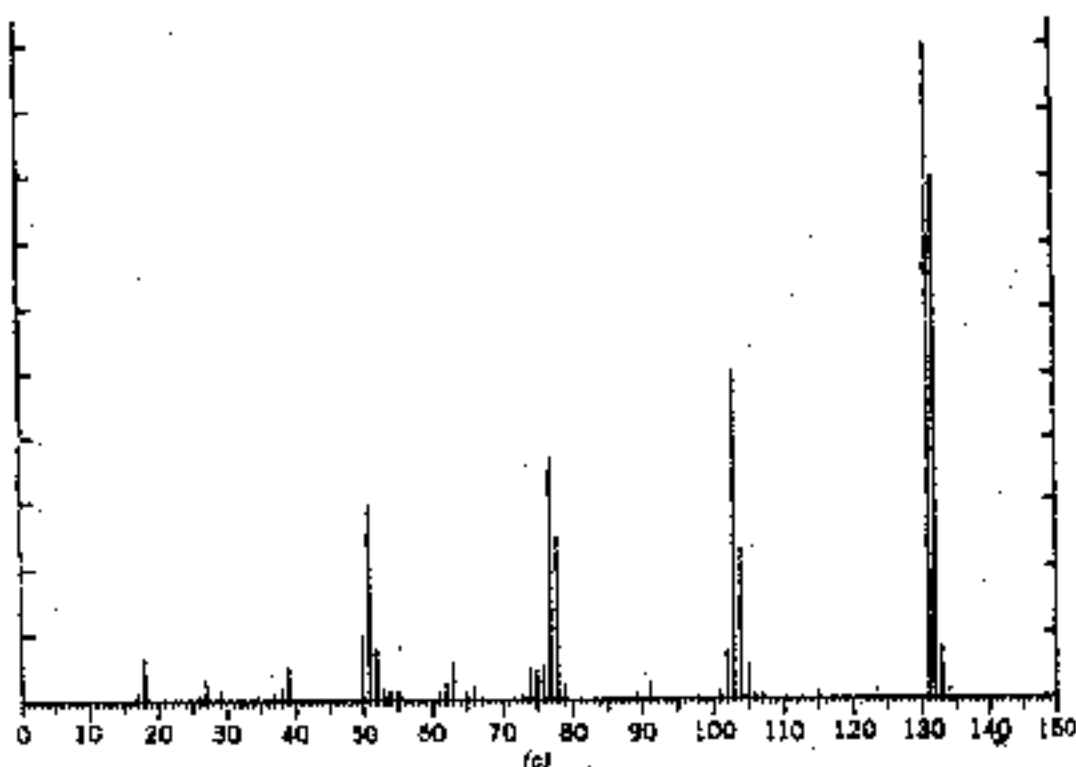
科目 無機化學及有機化學 科號 0602 0702 共 8 頁第 5 頁 *請在試卷【答案卷】內作答

16. Give the structure of a compound having a molecular weight of 182.0575, and UV $\lambda_{\text{max}} = 248 \text{ nm}$ ($\epsilon = 15000$) on the basis of its IR, PMR, Mass and ^{13}C NMR spectra shown below. Please indicate the possible assignments. (5%)

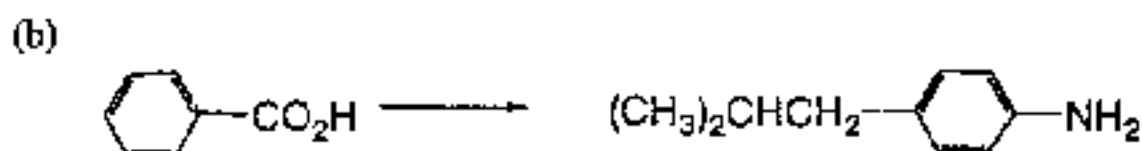
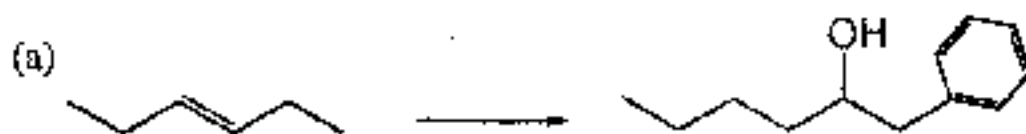


八十五學年度 化學系 化學、應用化學組碩士班研究生入學考試

科目 無機化學及有機化學 科號 0602 共 8 頁第 6 頁 *請在試卷【答案卷】內作答

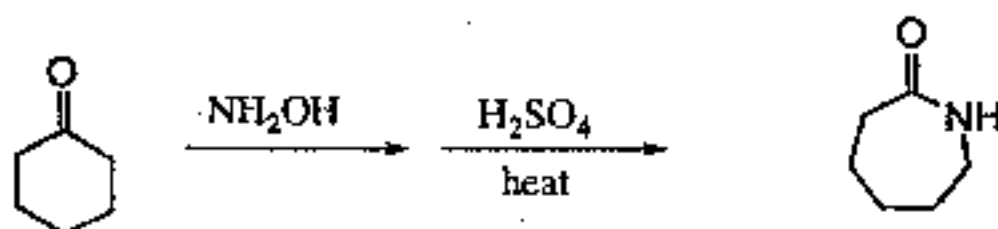


17. Show how you would accomplish each of the following multistep synthetic transformations in good yield. (12%)

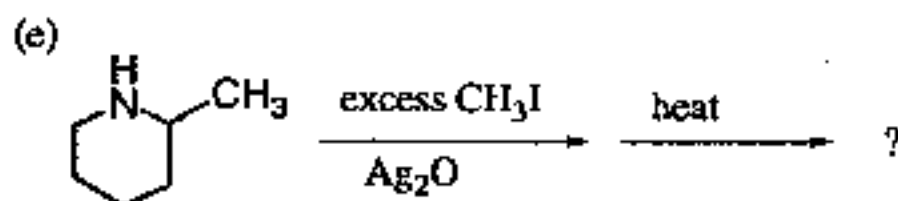
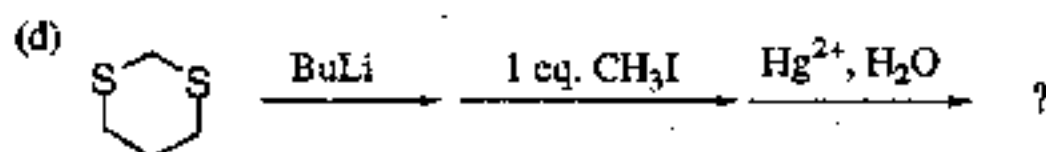
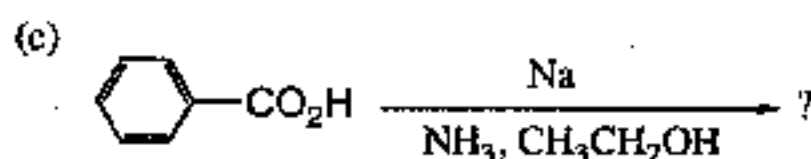
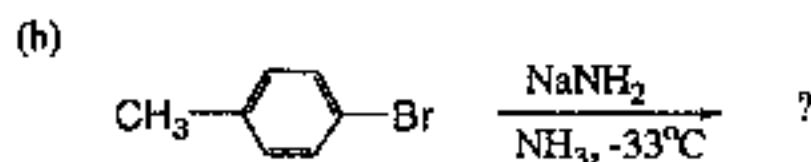
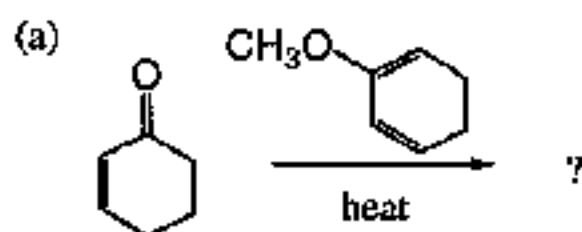


八十五學年度 化學系 化學、應用化學組碩士班研究生入學考試
 科目無機化學及有機化學 科號 0602 0702 共 8 頁第 7 頁 *請在試卷【答案卷】內作答

18. Give a stepwise arrow pushing mechanism for the following transformation. (3%)



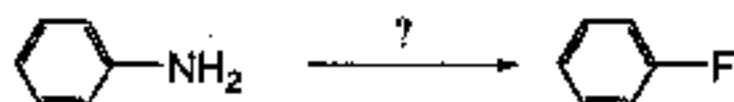
19. Give the structure of major product(s), clearly indicate the stereochemistry if necessary, or provide necessary reagent(s) to complete each of the following transformations. (10%)



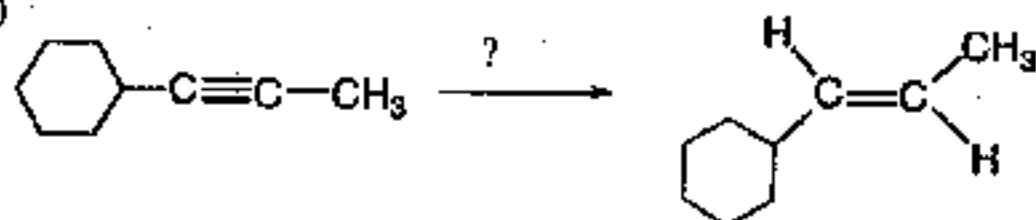
八十五學年度 化學系 化學、應用化學 組碩士班研究生入學考試

科目 無機化學及有機化學 科號 0602 共 8 頁第 8 頁 *請在試卷【答案卷】內作答

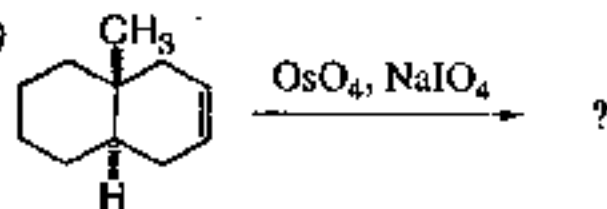
(f)



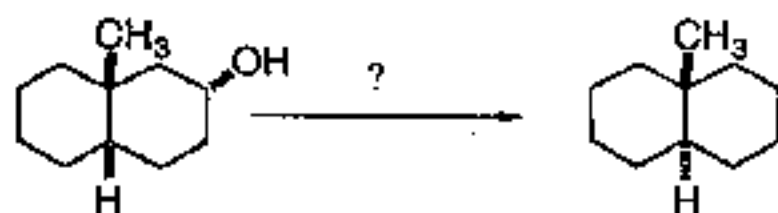
(g)



(h)



(i)



(j)

