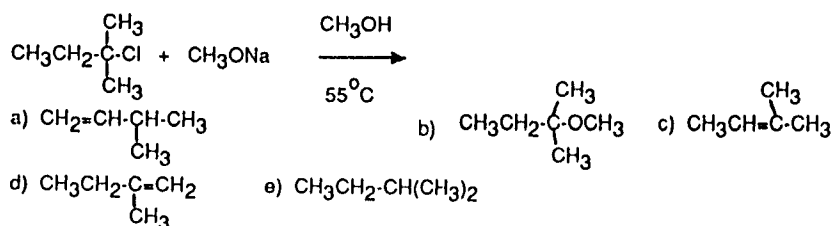


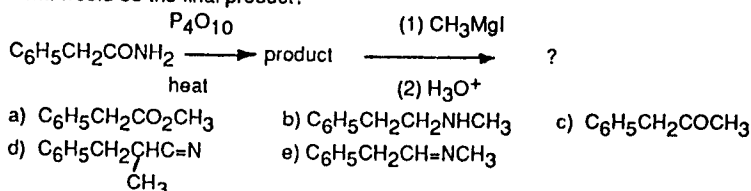
I. Answer the following problems(20%):

- ( ) 1. Which reagent(s) would you use to carry out the following transformation? (a.)  $\text{Br}_2$ , heat, and light (b.)  $\text{Cl}_2$ ,  $\text{FeCl}_3$  (c)  $\text{KMnO}_4$ ,  $\text{OH}^-$ , heat (then  $\text{H}_3\text{O}^+$ ) (d)  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (e)  $\text{SO}_3/\text{H}_2\text{SO}_4$
- ( ) 2. Which of the following procedures would not yield 3-pentanone as a major product?  
 a)  $\text{CH}_3\text{CH}_2\text{CN} + \text{CH}_3\text{CH}_2\text{MgBr} \xrightarrow{\text{H}_3\text{O}^+}$   
 b)  $\text{CH}_3\text{CH}_2\text{COOH} + 2 \text{CH}_3\text{CH}_2\text{Li} \xrightarrow{\text{H}_2\text{O}}$   
 c)  $\text{CH}_3\text{CH}_2\text{CN} + \text{CH}_3\text{CH}_2\text{Li} \xrightarrow{\text{H}_3\text{O}^+}$   
 d)  $\text{CH}_3\text{CH}_2\text{COCl} + (\text{CH}_3\text{CH}_2)_2\text{CuLi} \xrightarrow{\quad}$   
 e)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{MgBr} \xrightarrow{\text{H}_3\text{O}^+}$
- ( ) 3. In the reaction of carbonyl compounds with  $\text{LiAlH}_4$ , the effective reducing species is:  
 a)  $\text{Li}^+$  b)  $\text{Al}^{+3}$  c)  $\text{AlH}_4^-$  d)  $\text{AlH}_3$  e)  $\text{H}^-$
- ( ) 4. What would be the major product of the following reaction?

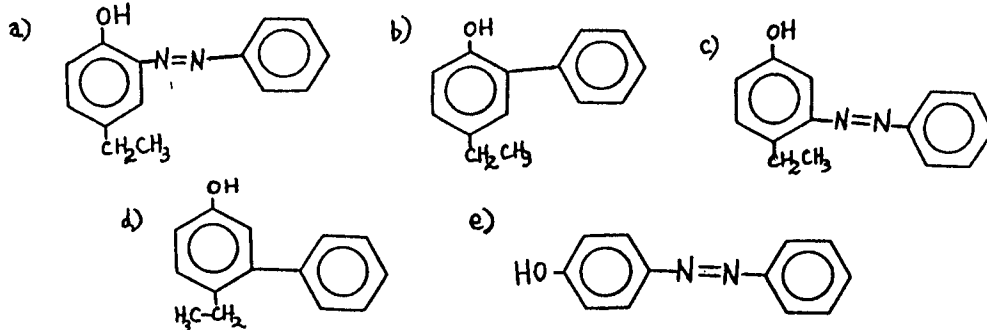


- ( ) 5. Treating  $(\text{Me})_3\text{C}-\text{Cl}$  with a mixture of  $\text{H}_2\text{O}$  and  $\text{MeOH}$  at room temperature would yield:  
 a)  $\text{CH}_2=\text{C}(\text{CH}_3)_2$  b)  $(\text{CH}_3)_3\text{COH}$  c)  $(\text{CH}_3)_3\text{COCH}_3$  d) All of these e) None of these
- ( ) 6.  $\text{S}_{\text{N}}1$  reactions of the type,  $\text{Nu}^- + \text{RL} \longrightarrow \text{Nu-R} + \text{L}^-$ , are favored:  
 a) when tertiary substrates are used.  
 b) by using a high concentration of the nucleophile.  
 c) when  $\text{L}^-$  is a strong base.  
 d) by use of a non-polar solvent.  
 e) by none of the above.
- ( ) 7. How many  $^{13}\text{C}$  signals would you expect from  $\text{C}_6\text{H}_5\text{OCH}_3$ ?  
 a) Four b) Two c) Three d) Seven e) Five
- ( ) 8. A compound with the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  gives a  $^1\text{H}$  NMR spectrum consisting only of a quartet centered at  $\delta$  3.5 and a triplet at  $\delta$  1.1. The most likely structure for the compound is:  
 a)  $(\text{CH}_3)_3\text{C}-\text{OH}$  b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  c)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  d)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$   
 e)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$        $\text{CH}_3\text{OCH}(\text{CH}_3)\text{CH}_3$

( ) 9. What would be the final product?



( ) 10. What is the principal product when aniline is treated with sodium nitrite and hydrochloric acid at  $0-5^\circ\text{C}$  and this mixture is added to *p*-ethylphenol?



- II. When a solution of 1,3-butadiene in  $\text{CH}_3\text{OH}$  is treated with chlorine, the products are  $\text{ClCH}_2\text{CH}=\text{CHCH}_2\text{OCH}_3$  (30%) and  $\text{ClCH}_2\text{CH}(\text{OCH}_3)\text{CH}=\text{CH}_2$  (70%). Write a mechanism that accounts for their formation. (6%)

- III. What would be the major product formed in the Baeyer-Villiger oxidation of 3-methyl-2-butanone?(4%)
- IV. a) Write resonance structures for the phthalimide anion that will account for the acidity of phthalimide. b) Would you expect phthalimide to be more or less acidic than benamide? Why? (6%)
- V. When acrolein reacts with hydrazine, the product is a dihydropyrazole:  
 $\text{CH}_2=\text{CHCHO} + \text{H}_2\text{N-NH}_2 \longrightarrow$

Suggest a mechanism that explains this reaction. (6%)

- VI. Propose a structure for compound I whose  $^1\text{H}$  NMR and IR spectra are given in the following Figs. (8%)

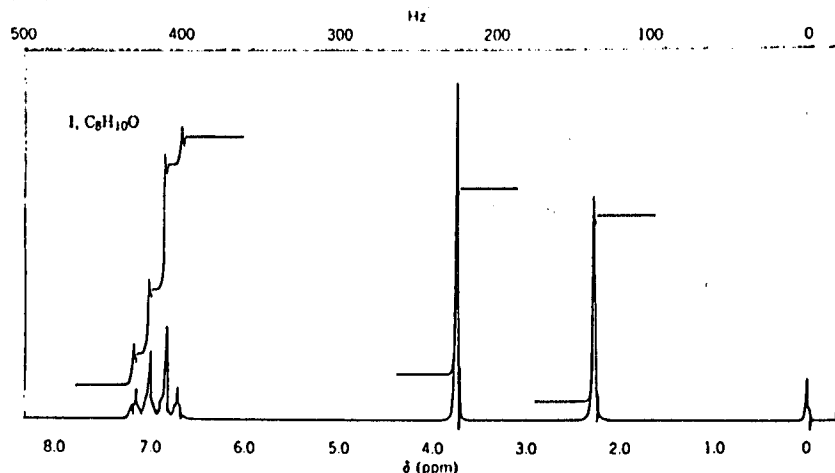


FIGURE 1. The  $^1\text{H}$  NMR spectrum of compound I

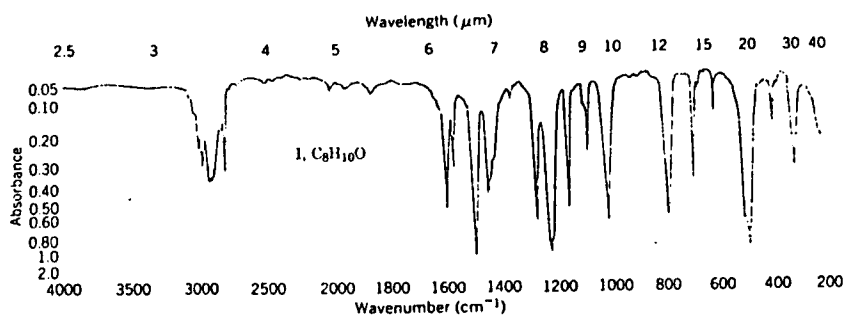
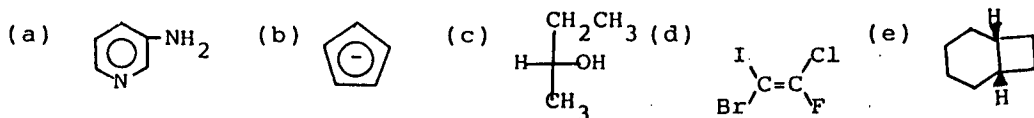


FIGURE 2. The IR spectrum of compound I

- VII. Name (IUPAC system in English) or draw the structure of each of the following compounds or ion. (20%).



- (f) 18-crown-6 (g) DMF (h) trans-2-methylcyclohexanecarboxylic acid  
 (i) NBS (j) Tetrakis(1,1-dimethylethyl)tetrahedrane

- VIII. For each of the following questions, assume that all measurements are made in 10-cm polarimeter sample containers. (4%).
- (a) A solution of 0.4 g of optically active 2-butanol in 10 ml of water displays an optical rotation of  $-0.56^\circ$ . What is its specific rotation?
- (b) The specific rotation of sucrose is  $+66.4^\circ$ . What would be the observed optical rotation containing 3 g of sucrose in 10 ml of water?

- IX. Outline a simple chemical test that would distinguish between the members of each of the following compounds: 1,3-butadiene, butane, 1-butyne and 4-bromobutene. (8%).

- X. Cyclohexane has two stable conformations; chair and boat form, which one is more stable? Please describe with Newman's projection. (6%).

XI. Rank the members of each species below in the order of (1) basicity, (2) nucleophilicity, and (3) leaving-group ability. Briefly explain your answers.  $\text{H}_2\text{O}$ ,  $\text{HO}^-$ ,  $\text{CH}_3\text{CO}_2^-$ . (6%)

XII. Indicate whether each of the following compounds or ions would or would not be aromatic. Explain your answer in each instance. (6%)

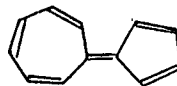
(a)



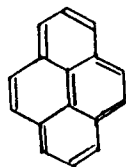
(b)



(c)



(d)



(e)



(f)

