國立成功大學八十二學年度化学研究所考試(有機化学 試題) 第1頁

I. Answer the following problems(20%):) 1. Which reagent(s) would you use to carry out the following transformation? (a.) Br2, heat, and light (b.) Cl_2 , FeCl_3 (c) KMnO_4 , OH^- , heat (then H_3O^+) (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) CH₃CH₂CN + CH₃CH₂MgBr→ H₃O→ b) CH3CH2COOH + 2 CH3CH2Li - H2O, c) CH3CH2CN + CH3CH2Li -→ H³O+ d) $\text{CH}_3\text{CH}_2\text{COCI} + (\text{CH}_3\text{CH}_2)_2 \text{ CuLi}$ e) CH₃CH₂COOH + CH₃CH₂MgBr→→ H₃O[†]→ () 3. In the reaction of carbonyl compounds with LiAlH $_{
m 4}$, the effective reducing species is: a) Li⁺ b) Ai⁺³ c) AiH4⁻ d) AiH₃ e) H⁻ (*) 4. What would be the major product of the following reaction? СН3ОН + CH₃ONa 55°C ĊΗ3 d) CH₃CH₂-C=CH₂ CH₃ e) CH_3CH_2 - $CH(CH_3)_2$ () 5. Treating (Me)₃C-Cl with a mixture of H₂O and MeOH at room temperature would yield: a) CH₂=C(CH₃)₂ b) (CH₃)₃COH c) (CH₃)₃COCH₃ d) All of these e) None of these () 6. S_N1 reactions of the type, $Nu^+ + RL \longrightarrow Nu-R + L^+$, are favored: a) when tertiary substrates are used. b) by using a high concentration of the nucleophile.
c) when L⁻ is a strong base. d) by use of a non-polar solvent. e) by none of the above. () 7. How many $^{13}{\rm C}$ signals would you expect from ${\rm C_6H_5OCH_3}$? a) Four b) Two c) Three d) Seven e) Five () 8. A compound with the molecular formula C4H10O gives a 1H NMR spectrum consisting only of a quartet centered at δ 3.5 and a triplet at δ 1.1. The most likely structure for the compound is: a) (CH₃)₃C-OH b) c) CH3CH2CH2CH2OH d) CH3CH2OCH2CH3 ĆH3 e) CH₃CHCH₂OH CH₃ снзосненз () 9. What would be the final product? P4O10 (1) CH₃MgI C6H5CH2CONH2 - product heat $(2) H_3O^+$ a) C₆H₅CH₂CO₂CH₃ $^{\rm b)\,C_6H_5CH_2CH_2NHCH_3}$ c) C₆H₅CH₂COCH₃ d) C₆H₅CH₂CHC=N e) C₆H₅CH₂CH=NCH₃ снз () 10. What is the principal product when aniline is treated with sodium nitrite and hydrochloric acid at 0.5° C and this mixture is added to p-ethylphenol? HJCH₂

II. When a solution of 1,3-butadiene in CH₃OH is treated with chlorine, the products are CICH₂CH=CHCH₂OCH₃ (30%) and CICH₂CH(OCH₃)CH=CH₂ (70%). Write a mechanism that accounts for their formation. (6%) 040

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- 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%)

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

 Propose a strcture for compound I whose ¹H NMR and IR spectra are given in the following Figs. (8%)

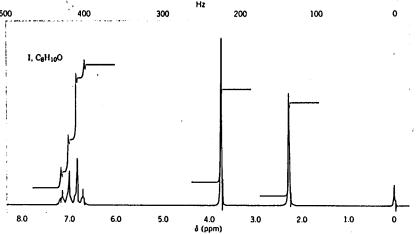


FIGURE 4. The ¹H NMR spectrum of compound I

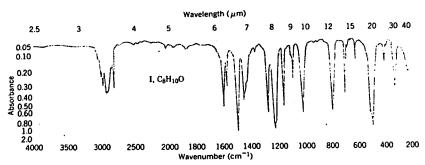


FIGURE 2. The IR spectrum of compound I

- VII. Name (IUPAC system in English) or draw the structure of each of the following compounds or ion. (20%).
 - (a) \bigcirc NH₂ (b) \bigcirc (c) \bigcirc CH₂CH₃ (d) \bigcirc (e) \bigcirc H \bigcirc C=C \bigcirc H
 - (f) 18-crown-6 (g) DMF (h)trans-2-methylcyclohexanecarboxylic acid
 - (i) NBS (j)Tetrakis(1,1-dimethyethyl)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°. What is its specific rotation?

 (b) The specific rotation of sucrose is +66.4°. 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%).

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- Rank the members of each species below in the order of (1) basicity, (2) nucleophilicity, and (3) leaving-group ability. Briefly explain you answers. $\rm H_2^{O}$, $\rm HO^-$, $\rm CH_3^{CO}_2^-$. (6%)
- XII. Indicate whether each of the following compounds or ions would or would not be aromatic. Explaine you anser in each instance. (6%)
 (a) (b) (c)

(e) (f)