國立清華大學命題紙

八十六學年度<u>化學工程學系</u>系(所)<u>し</u>、組碩士班研究生入學考試 科目<u>有機化學</u> 科號 1702 共 6 貝第 1 頁 *請在試卷【答案卷】內作答

Problem 1 (10%)

Give structures of compounds A through E.

glycerol±NaHSO₄ ,heat → A (C₃H₄O)

A +ethyl alcohol + HC1 \rightarrow B (C₇H₁₅O₂C1)

B + NaOH, heat \rightarrow C (C₇H₁₄O₂)

C + cold neutral KMnO₄ - D(C₇H₁₆O₄)

D + dilute H₂SO₄ → E(C₃H₆O₃) + ethyl alcohol

Problem 2 (10%)

Give the structure of the products from the following reactions.

- (a) benzalacetone + NaOl ----- ?
- (b) ethyl cinnamate + ethyl cyanoacetate $\xrightarrow{OC_2H_5^-}$?
- (c) mesityl oxide + ethyl acetoacetate $\frac{OC_2H_5^-}{}$?
- (d) 1,3 Butadiene + p Benzoquinone $\xrightarrow{\text{benzene, } 35^{\circ}\text{C}}$? quantitative
- (e) 1,3 Butadiene + Maleic anhydride benzene, 20°C → ? quantitative

Problem 3 (20%)

Show intermediate reaction steps for the following reactions.

a)
$$H_2C \longrightarrow CH_2 = CH_2 = CH_2$$

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Problem 4 (3%)

Rank the following species in an order of decreasing basicity, and briefly explain your answer

$$NH_2$$
 NH_2 $H_3C-C\equiv N$

Problem 5 (3%)

Propose a stepwise reaction mechanism for the following transformation.

Problem 6 (14%)

Provide necessary reagent(s) to complete each of the following conversions and show all reaction intermediates.

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Problem 7 (20%)

L 選擇題(單選題)

- 2% 1. Which of the following cycloalkanes exhibits the greatest molar heat of combustion?
 - A. cyclopropane
 - B. cyclobutane
 - C. cyclopentane
 - D cyclohexane
 - E cycloheptane
- 2% 2. Which of the following is a bridged bicyclic alkane?
 - A. cis-decalin
 - B. bicyclo[2.2.1]heptane
 - C. bicyclo[3.2.0]heptane
 - D bicyclo[4.1.0]heptane
 - E none of the above

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- 2% 3. Which of the species below is less basic than acetylide?
 - A. CH₃Li
 - B. CH₃ONa
 - C. NaOH
 - Do both bland c
 - E. all of the above
- 296 4. Which of the following molecules is chiral?
 - A. 2,3-pentadiene
 - B. 1,2-pentadiene
 - C. 2-methyl-2,3-pentadiene
 - D 2-chloro-4-methyl-2,3-pentadiene
 - E none of the above molecules is chiral
- 2% 5. Consider the equilibrium of each of the carbonyl compounds with HCN to produce cyanohydrins. Which is the correct ranking of compounds in order of increasing Keq for this equilibrium?
 - A. H₂CO < cyclohexanone < CH₃CHO < 2-methylcyclohexanone
 - B. CH₃CHO < 2-methylcychlohexanone < cyclohexanone < H₂CO
 - C. cyclohexanone < 2-methylcyclohexanone < H₂CO < CH₃CHO
 - D cyclohexanone < 2-methylcyclohexanone < CH₃CHO < H₂CO
 - E 2-methylcyclohexanone < cyclohexanone < CH3CHO < H2CO
- 3% II. Deduce the identity of the following compound from the spectral data given.

C₉H₁₀O₂: ¹³C NMR, δ 18.06 (quartet), 45.40 (doublet), 127.32 (doublet), 127.55 (doublet), 128.61 (doublet), 139.70 (singlet), 180.98 (singlet); IR, broad 3500-2800, 1708 cm⁻¹.

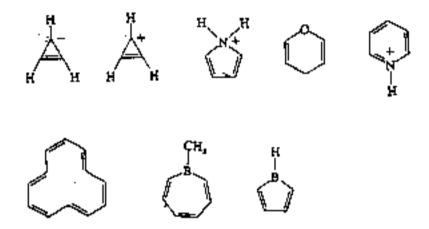
3% III. When deuterated acetone is used as the solvent for ¹H NMR spectroscopy study, a set of quintet signal always appears at δ 2.2. Please explain why?

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4% IV. For the following compounds, please classify each as aromatic, antiaromatic, or nonaromatic.



Problem B (20%)

Write stepwise reaction mechanisms for following reactions:

4% (a)
$$(1) \frac{NH_2}{(1) \frac{N_3NO_2}{(2) \frac{N}{2}}}$$
 $(2) \frac{N}{CH_3}$ $(2) \frac{N}{CH_3}$

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496 (c) H H
$$\frac{H}{H}$$
 $\frac{\text{large excess}}{D_2O}$ $\frac{D}{D}$