

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc DEGREE PROGRAMME / STAND ALONE COURSE 2006/2007

LEVEL 4 - FINAL EXAMINATION

CHU 2221 / CHE 4221 - ORGANIC CHEMISTRY - PAPER II

DURATION: 2 1/2 HOURS

Wednesday, 27th June 2007

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1.30 - 4.00 p.m.

Answer any FOUR (04) questions.

If you have answered more than four questions, only the first four answers will be marked.

(a) An acidic compound A (C₁₀H₁₈O₂) on ozonolysis in the presence of Zn/H₂O gave a neutral compound B (C₅H₁₀O) and an acidic compound C (C₅H₈O₃). Both B and C gave orange precipitates with Brady's reagent. B gave silver mirror with Tollen's reagent while C did not. B was found to be optical active. C when reacted with NaOH / I₂ followed by acidification gave D (C₄H₆O₄). D showed a singlet for 4H and a broad singlet for 2H.
 Deduce the structures of A, B, C and D.

(60 Marks)

(b) Give the structures of compounds E - I in the following reaction scheme.

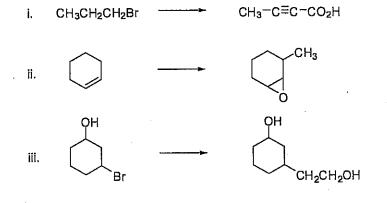


(25 Marks)

(c) Giving the mechanism predict the product J of the following reaction.

(15 Marks)

2. (a) Giving necessary reagents and conditions show how you would perform any two (02) of the following conversions.



(30 Marks)

(b) Giving appropriate mechanisms explain the following observations.

i.
$$\frac{H}{Me}$$
 CI $\frac{H_2O}{Ph}$ HO $\frac{H}{Ph}$ $\frac{H}{Me}$ OH Ph (51%) (49%)

ii. The relative rates of nucleophilic substitution of chlorocyclohexanes in ethanol – water as follows.

(40 Marks)

(c) Predict the product(s) with its stereochemistry of the following reaction giving appropriate mechanisms.

(20 Marks)

(d) Predict the product(s) of the following reaction giving appropriate mechanisms.

(10 Marks)

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3. (a) Deduce the following with respect to the mass spectrum of compound K.

i. The structure of the fragment corresponding to the base peak.

(10 Marks)

ii. The m/z value of the base peak expected in the spectrum.

(05 Marks)

Whether there are isotopic peaks corresponding to the base peak and if there iii. are isotopic peak the m/z values and the relative abundance of these peaks.

(25 Marks)

(b) Ethylene (H₂C=CH₂) and butadiene (H₂C=CH-CH=CH₂) show UV absorption at 165 nm and 217 nm respectively. Draw the energy diagram for butadiene and ethylene and explain why the absorption of butadiene is shifted to longer wavelength.

(15 Marks)

(c) Explain why the ¹H NMR spectrum of CH₃COOH show a resonance signals at $\delta = 10 - 13$ ppm corresponding to the H atom attached to the OH group.

(20 Marks)

- (d) In dilute solution RCOOH shows IR absorptions at 3100 cm⁻¹ and 1760 cm⁻¹ but in concentrated solution the absorptions are at 3077 cm⁻¹ and 1710 cm⁻¹ respectively.
 - i. Identify the bond/s responsible for each of the absorbance.

ii. Explain the above statement.

(25 Marks)

4. (a) Give three reasons to show that benzene cannot be fully described by the Kekule structure of benzene.

(15 Marks)

(b) Explain why [10] annulene is not aromatic as expected by the Hükel's rule.



[10] annulene

(15 Marks)

(c) Explain why the order of boiling points of butane (MW 58), propanal (MW 58) and propanol (MW 60) is as follows.

Boiling points:

butane < propanal < propanol

(10 Marks)

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(d) Give the structures of compounds $\mathbf{L} - \mathbf{Q}$ in the following reactions.

i.
$$O \longrightarrow CO_2$$
Et $H^+/HO \longrightarrow OH$ L $\frac{1. \text{ MeMgBr}}{2. \text{ hydrolysis}}$ M

ii. CHO
$$\frac{1. \text{ OH7 H}_2\text{O}}{\text{CHO}}$$
 N $\frac{\text{CrO}_3 / \text{H}^+}{\text{O}}$

(30 Marks)

(e) Give the mechanism of each of the following reactions.

i.
$$NH_2OH$$
 OH

(30 Marks)

5. (a) Consider the following reaction.

$$CH_3$$
 CH_3 CH_2 CH_3 CH_3

Give the mechanism of the above reaction.

(20 Marks)

ii. Compound A decolourizes bromine water. B on oxidation with $K_2Cr_2O_7$ gives a compound which evolves CO2 from Na2CO3 while C does not undergo oxidation. Deduce the structures of A, B and C.

(15 Marks)

(b) Explain why p K_b value of N,N-dimethylaniline is greater than that of N,N-dimethyl-2,6-dimethylaniline.

N,N-dimethyl-2,6-dimethylaniline

(25 Marks)

(c) Identify the products (D - F) of the following reactions.

i.
$$C_2H_5$$
 N- CH_3 NaNO₂/HCI D

ii. C_2H_5 C- CI NaN₃ E Δ F

(20 Marks)

(d) 'Cyclopropane is subjected to angle strain and torsional strain.' Explain the above statement.

(20 Marks)

(10 Marks)

6. (a) Giving necessary reagents and reaction conditions indicate how you would effect the following conversions.

N. B. Conversions may involve more than one step.

i.
$$CH_3$$
 CO_2H Br SO_3H SO_3H (25 Marks)

iii.
$$Br$$
 Br Br Br Br Br (20 Marks)

(b) Explain why p-nitrophenol gives effervescence (evolves CO_2) with Na_2CO_3 while phenol does not.

(25 Marks)

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