2024

CHEMISTRY — HONOURS

Paper : DSCC-4

(Organic Chemistry - I)

Full Marks : 75

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question numbers* 1, 2, 3, 4 (compulsory)** and ***any four questions*** from the rest (***question nos.* 5** to **10**).

1. Answer ***any ten*** questions : 2×10

(a) Explain why nitrobenzene is used as a solvent in Friedel-Crafts alkylation reaction.

(b) Write down the products of ozonolysis of $CH_3 — CH = CH — CH_2 — CH = CH_2$.

(c) What happens when *cis*-2-butene reacts with *mcpba* (*meta*-chloroperbenzoic acid)?

(d) $PhCH_2Cl$ is a good substrate for both S_N1 and S_N2 mechanism. Explain.

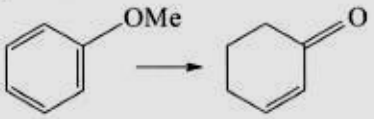
(e) Between *p*-chlorophenol and *p*-fluorophenol, which one is a stronger acid and why?

(f) Convert (*E*)-2-butene into (*Z*)-2-butene.

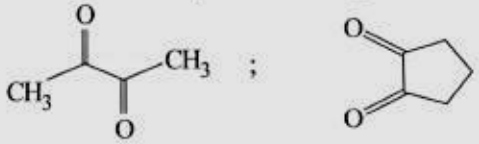
(g) Draw the structures and indicate with arrow(s) the favoured position(s) of electrophilic substitution of the following compounds :

(i) Benzoic acid; (ii) 4-Chlorobenzoic acid; (iii) 3-Methylbenzoic acid; (iv) Anilinium chloride.

(h) How can you convert?

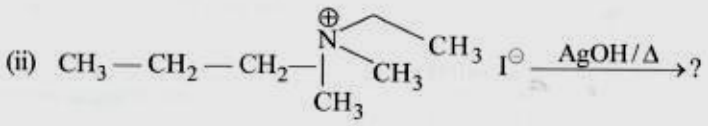


(i) Which of the following two compounds has higher enol content and why?

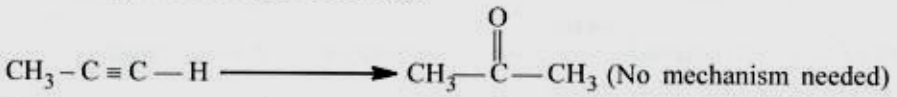


(j) Write the products of the following reactions (No mechanism needed) :

(i) $CH_3-CH-(CH_3)-CH(OH)CH_3 \xrightarrow{\text{conc. } H_2SO_4} ?$

(ii)  $I^{\ominus} \xrightarrow{AgOH/\Delta} ?$

(k) How can you convert the following?



(l) How can you convert benzene to *n*-propylbenzene?

2. Write short note on :

(a) Friedel-Crafts reaction using the following points :

(i) Mechanisms of Friedel-Crafts acylation and alkylation reaction taking any suitable example.

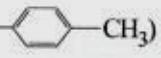
(ii) Any two limitations of Friedel-Crafts alkylation reaction. 3+2

Or,

(b) Reimer-Tiemann reaction using the following points :

(i) Definition with conditions for the reaction.

(ii) Mechanism of the reaction taking any suitable example.

(iii) Products of Reimer-Tiemann reaction on *p*-cresol. (HO—  —CH_3) (No mechanism needed). 1+2+2

3. Write short note on :

(a) Nucleophilic aromatic substitution (S_NAr) reaction using the following points :

(i) Definition with conditions for the reaction.

(ii) Mechanism of S_NAr reaction taking any suitable example.

(iii) Difference between S_NAr and *cine*-substitution. 1+2+2

Or,

(b) Bimolecular elimination reaction (E2) using the following points :

(i) Definition of E2 reaction along with conditions.

(ii) Mechanism of E2 reaction taking any suitable example.

(iii) One example of E2 reaction following Saytzeff elimination rule.

(iv) Difference between Saytzeff and Hofmann elimination taking suitable examples. 1+1+1+2

4. Write short note on :

(a) Addition to alkenes using the following points :

(i) Statement of Markownikoff's rule with an example.

(ii) Mechanism of Markownikoff's addition of HBr to propene.

(iii) Condition and mechanism of anti-Markownikoff's addition of HBr to propene. 1+2+2

Or,

(b) Tautomerism using the following points :

(i) Two differences between tautomerism and resonance.

(ii) One example for each of valence and ring tautomerism.

(iii) Explanation of no keto form of phenol in the equilibrium. 2+2+1

5. (a) Write down the products **[A]**, **[B]**, **[C]** and **[D]** along with plausible mechanism.

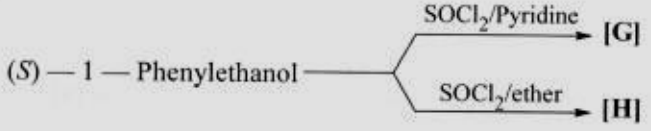
$$PhO^{\ominus}Na^{\oplus} + CO_2 \xrightarrow{125^{\circ}C} [A] \xrightarrow{H_2SO_4} [B]$$

$$PhO^{\ominus}K^{\oplus} + CO_2 \xrightarrow[\text{and pressure}]{\text{High temp.}} [C] \xrightarrow{H_2SO_4} [D]$$

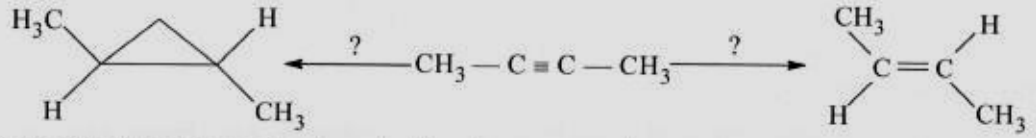
(b) Which of the following pair of compounds Me_2CHBr and Me_3CBr, results in higher ratio of elimination (E2) to substitution (S_N2) when treated with NaOEt/EtOH?

(c) $C_5H_{11}CH_2CH_2OH \xleftarrow{F} C_5H_{11}CH=CH_2 \xrightarrow{E} C_5H_{11}CH(OH)CH_3$.
Identify the reagents **E** and **F**. Give mechanism of the reaction using the reagent **F** only. 4+3+3

6. (a) Give the structures of **[G]** and **[H]** and explain their formation with plausible mechanism.



(b)



Give also plausible mechanisms for the above conversions.

(c) Write the structures of the possible enol forms of ethyl methyl ketone and comment on their stability. 4+3+3

7. (a) (i) The torsional barrier of fluoroethane and iodoethane are remarkably similar (3.3–3.5 Kcal mol^{-1}). Give reason.

(ii) Draw the most stable conformation of 1, 2-dibromoethane and ethylene glycol in Newman projection formula.

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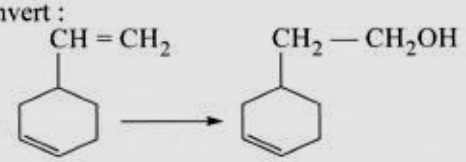
(b) Both *o*- and *m*- bromoanisole on treatment with $NaNH_2$ in liquid ammonia yield the same major product *m*-anisidine. Explain with the help of mechanism.

(c) Explain what happens when a mixture of 1 mole of acetylene and 1 mole of ethylene is treated with 1 mole of Br_2 in CCl_4. Show the plausible mechanistic pathway for the reaction also. 4+3+3

8. (a) When a trace amount of KNH_2 is added to a solution of chlorobenzene and Ph_3CK in liquid ammonia, a product with molecular formula $C_{25}H_{20}$ is obtained. Give the mechanism of the reaction.

(b) $CH_3CH(OH)CH_2SEt$ and $CH_3CH(SEt)CH_2OH$ give same product when treated with dry HCl. Give the structure of the product and account for its formation.

(c) Convert :

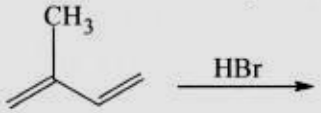
(i) 

(ii) $CH_3CH_2-C\equiv C-H \longrightarrow CH_3-CH_2-CH_2-CHO.$ 4+3+3

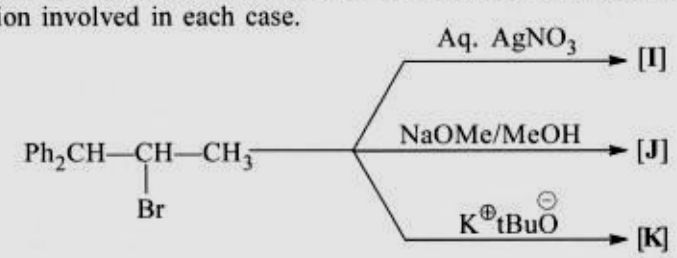
9. (a) Give the products and mechanism of nitration in

(i) Phenol and (ii) Nitrobenzene.

(b) Predict the product of the following reaction showing mechanism :

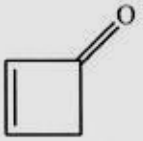


(c) Write down the major products **[I]**, **[J]** and **[K]** of the following reactions. Also mention the type of reaction involved in each case. 4+3+3



10. (a) (i) Acetylacetone shows 15% enol content in water and 92% in *n*-hexane. Explain.

(ii) The following compound exists in 100% Keto form in the equilibrium. Explain.



(b) Compare the basicities and nucleophilicities of NH_3, NH_2NH_2 and NH_2OH. Give reasons.

(c) Between *p*-hydroxybenzoic acid and *p*-nitrobenzoic acid, which one is stronger acid and why? 4+3+3