2025

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.

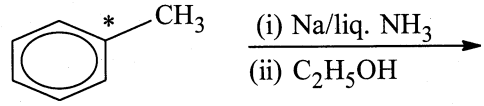
Answer ***question nos.* 1, 2, 3, 4 (compulsory)** and ***any four questions*** from the rest (***question nos.* 5** to **10**)

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

(a) Halogens are deactivators towards aromatic electrophilic substitution but are *o* -, *p* - orienting groups. Explain.

(b) What are benzynes? Why is it so reactive?

(c) Predict the product of the following reaction (no mechanism required) :



(d) What do you mean by proton sponge? Give one example.

(e) Arrange the following compounds with increasing enol content (no explanation needed) :

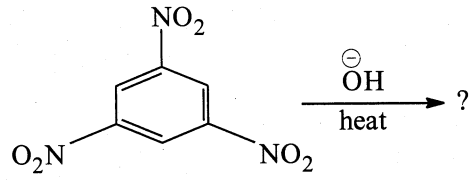
(i) $CH_3COCH_2COOC_2H_5$

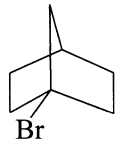
(ii) $CH_2(COOC_2H_5)_2$

(iii) $CH_3COCH_2COCH_3$.

(f) Draw the sawhorse and Newman projections of the staggered conformer of active butane-2, 3-diol.

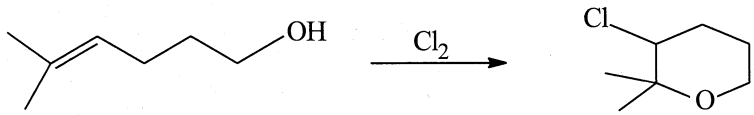
(g) Write down the major product of the following reaction (no mechanism needed) :



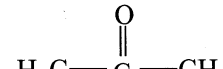
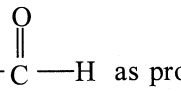
(h)  does not undergo elimination reaction with base. Why?

(i) Predict the products in each case when hex-3-yne and hex-2-yne are separately treated with $HgSO_4$ (catalytic amount) and 20% H_2SO_4 under hot condition (no mechanism required).

(j) Propose a mechanism of the following reaction :



(k) Indicate the positions which are most likely to react in aromatic electrophilic substitution of *o*-nitrotoluene. Give reasons.

(l) Write down the structure of the alkene which on ozonolysis gives  and  as products. Show the mechanism of the reaction.

2. Write short note on (using the points given) :

(a) Aromatic electrophilic *ipso* substitution :

(i) Definition with condition of the reaction.

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

(iii) An example of the formation of a rearranged product preceded by an *ipso* attack. 2+2+1

Or

(b) Nucleophilic aromatic substitution :

(i) Role of substituents on the reaction rate.

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

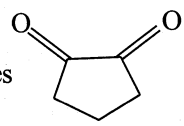
(iii) What is *cine*-substitution? 2+2+1

3. Write short note on (using the points given) :

(a) Tautomerism

(i) Definition

(ii) What is the primary requirement for an aldehyde or ketone to exhibit keto-enol tautomerism?

(iii) Why does  have unusually high enol content? 1+2+2

Or

(b) Aliphatic nucleophilic intramolecular substitution (S_Ni) :

(i) Definition with condition of the reaction.

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

(iii) Comparison with S_N2 type reaction. 1+2+2

4. Write short note on (using the points given) :

(a) E_{1CB} elimination reaction :

(i) Definition with condition of the reaction.

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

(iii) Effect of substituents and solvents on the reaction. 1+2+2

Or

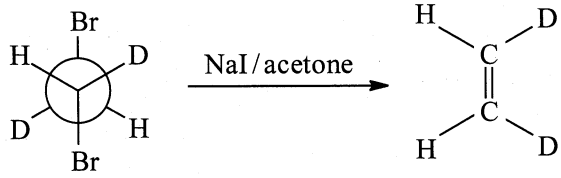
(b) Hydroboration-oxidation of an alkyne

(i) Reagents required

(ii) Write down the mechanism of the reaction taking propyne as the substrate. 2+3

5. (a) Nitration of 1, 4-di-isopropylbenzene gives two products — 1, 4-di-isopropyl-2-nitrobenzene and 4-nitroisopropylbenzene. — Explain.

(b) Explain mechanistically :

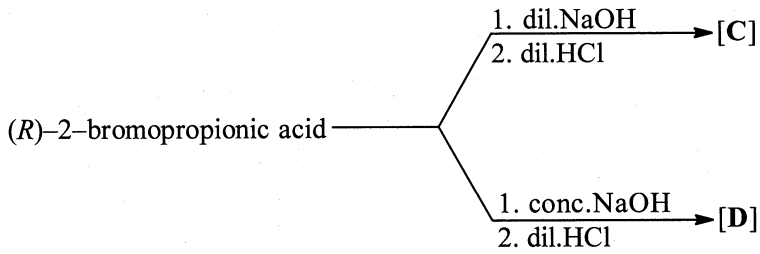


(c) Identify [**A**] and [**B**]. Give mechanism.

$$Me_3C-CH=CH_2 \xrightarrow[THF,\,H_2O]{Hg(OAc)_2} [\mathbf{A}] \xrightarrow[NaOH]{NaBH_4} [\mathbf{B}]$$

Why the formation of [**B**] in this process is superior than the acid-catalyzed hydration process with the same starting material? 4+3+3

6. (a) Identify [**C**] and [**D**] with proper mechanism :



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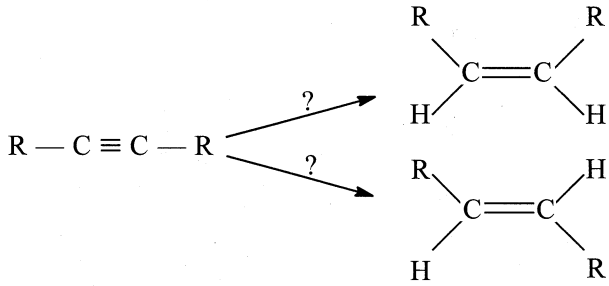
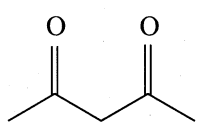
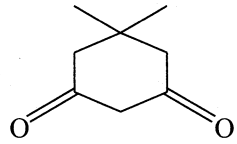
(b) Give the reagents used to carry out the following conversions with mechanism :



(c) The enol content of the following compounds in different solvents are given :



(X)



(Y)

	(X)	(Y)
Toluene	91%	7%
Water	7%	95%

Explain the observations. 4+3+3

7. (a) What is meant by gauche-butane interaction? Depict the most stable conformation of 2, 3-dimethyl butane when viewed through $C_2 - C_3$ bond, citing reasons.

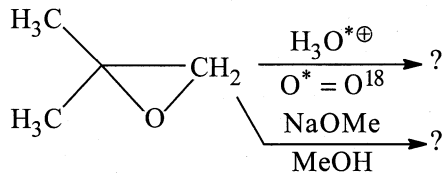
(b) Write down the Birch reduction product of benzoic acid with proper mechanism.

(c) Predict the product with proper stereochemistry. Give mechanism.

$$\textit{trans}\text{-2-pentene} \xrightarrow[\text{ether}]{CH_2I_2 \,/\, Zn-Cu} ?$$ 4+3+3

8. (a) Both *o*-bromoanisole and *m*-bromoanisole give same product with $NaNH_2$/liq. NH_3. Account for this observation giving proper mechanism for each case.

(b) Complete the following reactions showing proper mechanisms—

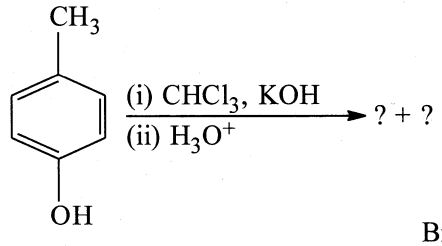


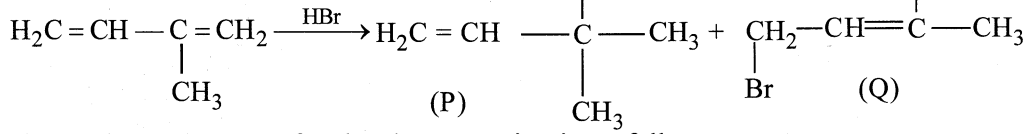
(c) Carry out the following conversions :

(i) $H_3C - CH_2 - C \equiv C - H \longrightarrow H_3C - CH_2 - C \equiv C - CH_3$

(ii) $H_3C - (CH_2)_2 - C \equiv C - (CH_2)_2 - CH_3 \longrightarrow H_3C - (CH_2)_5 - C \equiv C - H$ 4+3+3

9. (a) Give the products of the following reaction along with the mechanism of their formation :



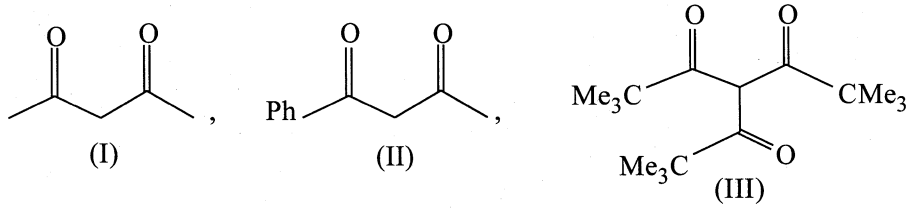
(b) 

The product percentage for the above reaction is as follows :

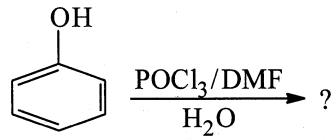
Temp.	(P)	(Q)
−80°C	80 %	20 %
40°C	20 %	80 %

(c) Propene is prepared from 1-chloropropane using $NaOC_2H_5/C_2H_5OH$ on heating for several hours. But if DMSO is used as a solvent, the reaction completes very quickly. – Explain. 4+3+3

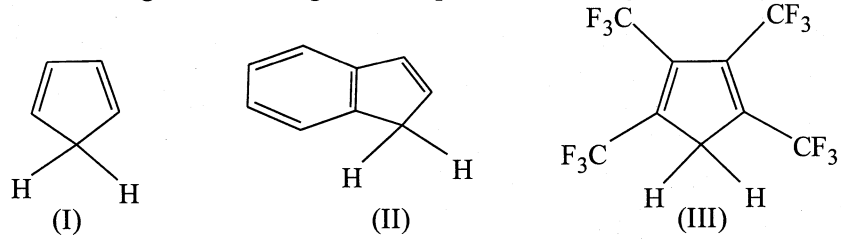
10. (a) Arrange the following in increasing order of enol content giving reasons :



(b) Predict the product in the following reaction with proper mechanism :



(c) Arrange the followings in increasing order of pKa values and justify your answer :



4+3+3