CHEMISTRY — HONOURS

Paper: CC-3

(Organic Chemistry - 2)

Full Marks: 50

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 no. 1 and any eight questions from the rest.

1. Answer any ten questions:

1×10

- (a) Write down the structure of conformers of optically active butane-2, 3-diol.
- (b) E-But-2-ene has enantiotopic faces. Justify the statement.
- (c) Write down the s-cis and s-trans conformational isomers of methyl acrylate.
- (d) Draw the structure of stilbene in Re-Si face.
- (e) 18-crown-5 binds ammonium cation more than 1000 times weaker than 18-crown-6. Explain.
- (f) Write the type of tautomerism involved in the following cases:

(i)
$$CN$$
 CF_3

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OH

- (g) Draw the most stable conformer of 1, 2-dibromoethane and ethylene glycol in Newman Projection formula.
- (h) Between NH₃ and NH₂NH₂, which one is more nucleophilic? Justify.
- (i) Alkaline hydrolysis of methyl chloride takes place at a much faster rate in presence of sodium iodide. Explain.

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X(2nd Sm.)-Chemistry-H/CC-3/CBCS

(2)

VCC / ilo,

(j) Write down the products of the following reactions:

(k) Write the correct order of pka values for the following compounds:

OH OH COOH OH OH OH
$$NO_2$$

- (l) Compare the base strengths of 4-Nitroaniline and 2,3,5,6 tetramethyl-4-Nitroaniline.
- 2. (a) Designate R/S in the following compounds showing the priority of the ligands.

(i)
$$H_3C$$
 $C=C=C$ (ii) H_3C $COOH$ NO_2 $COOH$ (iii) H_2 NO_2 $COOH$

- (b) Between ethanol and trifluoroethanol, which is more efficient solvent for S_N1 reaction? Explain.
- 3. (a) Identify the underlined atoms as homotopic, enantiotopic or diastereotopic with explanation.

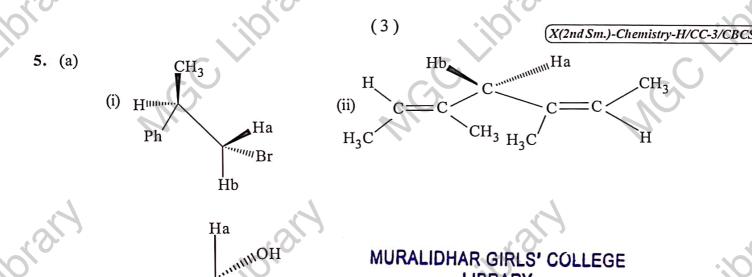
(i)
$$\underline{\underline{H}}$$
 (ii) $\underline{\underline{H}}$ (iii) $\underline{\underline{H}}$ $\underline{\underline{H}}$ $\underline{\underline{H}}$

- (b) Between allyl chloride and trityl chloride, which one will react faster in S_N1 reaction? Explain. 3+2
- 4. (a) Predict the major product in the following reaction with mechanism. Offer explanation.

$$PhCH_{2}CHBrCH_{3} \xrightarrow{NaOEt}$$

$$EtOH$$

(b) Write in increasing order of the following leaving groups affecting the rate of an E₁cB reaction. Give explanation. MeO[⊙], CN[⊙], PhS[⊙]. 3+2



(iii)

(b) Which form of diethyl malonate is stable in n-hexane? What happens when methanol is added 3+2 to it? Explain on the basis of entropy change of the equilibrium.

Identify the pro-R and pro-S hydrogen atoms (marked) in each of the above molecules.

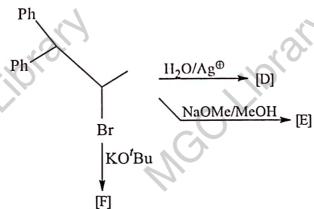
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6. (a) Give the structures of [A], [B] and [C] and explain their relative amounts.

$$CH_3$$
 $\xrightarrow{\Delta}$ [A]+[B]+[C]
 H_3C $N(CH_3)_3OH$

(b) Predict the product and explain the following reaction with mechanism.

7. (a) Write down the major products [D], [E] and [F] in the following reaction with proper justification.



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- (b) Treatment of alkyl iodide with AgNO₃ yields alkyl nitrite as the major product whereas alkyl iodides gives nitro alkane mainly on treatment with NaNO₂.— Explain. 3+2
- 8. (a) Explain the following experimental observations.

$$CH_{3} - CH_{2} - CH_{2} - CH - CH_{3} \xrightarrow{\text{EtOH}/\Delta} 1\text{-Pentene} + 2\text{-Pentene}$$

$$X = -Br - OTs - SMe_{2} - SO_{2}Me - NMe_{3}$$

$$\frac{[1\text{-Pentene}]}{[2\text{-Pentene}]} = 0.45 \quad 0.92 \quad 6.7 \quad 8.1 \quad 49$$

(b) Account for the following observation of scrambling of radioactivity $(C^* = {}^{14}C)$

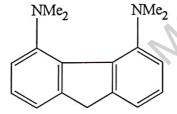
9. (a) Predict the products and explain the stereochemical course of the reaction:

Erythro – PhCDH – CHPh – OCOCH₃
$$\xrightarrow{\Delta}$$
?

- (b) When optically active -1, 2-dichloro -1, 2-diphenyl ethane is heated with pyridine gives an alkene, but *meso* compound does not react.— Explain.

 3+2
- (a) Arrange the following compounds in increasing order of enol content and justify. CH₃COCH₂COCH₃, [(CH₃)₃CCO]₃CH, PhCH₂COCH₂COCH₃
 - (b) The following compound is an extremely strong base.— Explain.

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11. (a) $H_3C-CH_2-CH_2-CH_2-OBs + X^{\odot} \xrightarrow{acetone} CH_3-CH_2-CH_2-CH_2-X + BsO^{\odot}$ When LiX is used, the order of nucleophilicity of above reaction is $I^{\odot} > Br^{\odot} > Cl^{\odot}$ but the order is $CI^{\odot} > Br^{\odot} > l^{\odot}$ when $Bu_4 N^{\odot} X^{\odot}$ is used.— Justify.

(b) Compare the relative stability of different conformers of *n*-propyl chloride (on rotation around $C_1 - C_2$ bond) with proper justification.

- 12. (a) What happens when (R)-2-bromobutanoic acid is treated with alkali? Predict the configuration of the product with mechanism and explanation.
 - (b) Calculate the enthalpy change (ΔH) for the following reaction.

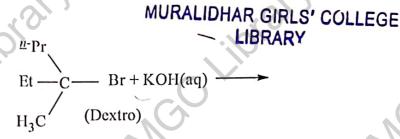
$$CH_4 + Br_2 \xrightarrow{hv} CH_3Br + HBr$$

C-II, C-Br, H-Br and Br-Br bond energies are 102 kcal/mole, 70 kcal/mole, 88 kcal/mole and 46 kcal/mole respectively.

Is the reaction endothermic or exothermic?

3+2

3. (a) For the reaction,



Draw the energy profile diagram for the reaction. Draw the structure of the intermediate. What is the optical activity of the product?

(b) If in the above reaction, the concentration of KOH is doubled, what will be the effect on the rate? If aqueous KOH is replaced by alcoholic KOH, write the structure of the product formed.

3+2