3 (Sem-3/CBCS) CHE HC 2

2023 CHEMISTRY

(Honours Core)

Paper: CHE-HC-3026

(Organic Chemistry-II)

Full Marks: 60

Time: Three hours

The figures in the margin indicate full marks for the questions.

- 1. Answer the following questions: 1×7=7
 - (a) Arrange the following in increasing order of basicity $(CH_3)_2 CHO^{\Theta}$, PhO^{Θ} , CH_3O^{Θ} , OH
 - (b) Draw the energy profile diagram of $E \mid CB$ mchanism of β -elimination reaction.

(c) Which one of the following bridged bicyclic compounds will exhibit Keto-Enol tautomerism.

- (d) DMF and DMSO favours $S_N 2$ reaction although they are polar solvents. Explain.
- (e) Potassium t butoxide is a widely used base in organic reactions but the corresponding sodium compound is unknown. Give reason.
- (f) Why is thioethanol more acidic than ethanol?
- (g) Name the reagent that can be used to convert Cis-2-butene to racemic 2,3-butanediol.

- 2. Answer the following questions: $2\times4=8$
 - (a) Arrange the following compounds in increasing boiling point and give reason for your answer.

 n-hexanol, n-butanol and t-butanol
 - (b) Between $CH_3CH_2CH_2Cl$ and CH_3OCH_2Cl , which would react faster in S_N1 solvolysis. Explain.
 - (c) The phenols shown have approximate pKa value of 4, 7, 9 and 11. Suggest with explanation which pKa value belong to which phenol:

$$OH OH OH OH OH OH$$

$$NO_2 NO_2 Me Me$$

$$NO_2 Me$$

(d) Arrange the following carboxylic acid derivatives in order of increasing reactivity towards hydrolysis reaction and justify your answer:

R-COOR', $RCONH_2$, RCOCI

- 3. Answer any three questions: 5×3=15
 - (a) Write the mechanism of Benzoin condensation. Explain why p-dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde the condensation occurs.

 3+2=5
 - (b) (i) Explain why alcohols are weaker acids than phenols but phenols are stronger nucleophiles. 2
 - (ii) Provide the required reagents and conditions for the following conversion: 1½×2=3

$$\bigcirc$$
OH \longleftarrow \bigcirc OH

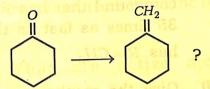
(c) (i) Predict the major product of the following reaction and explain its formation mechanistically. 3

$$CH_3$$
 CH_3 H^+

- (ii) How do you carry out the following conversion? 2 $CH_3CH_2 C \equiv CH \longrightarrow CH_3CH_2CH_2CHO$
- (d) (i) Why are vinylic and aryl halides unreactive towards both $S_N 1$ and $S_N 2$ reactions?
 - (ii) The rate equation of $S_N 2$ reaction O $CH_3Br + OH \longrightarrow CH_3OH + Br^O$ Rate = $k[CH_3Br][OH]$ What type of changes are expected in the rates of the reaction if
 - (a) the concentration of each of the reactants is made double?
 - (b) the concentration of CH_3Br is made half?
 - (e) (i) What is ortho effect? Explain, why almost all ortho substituted benzoic acids are stronger acid than benzoic acids? 1+2=3
 - (ii) How can you convert: 2 $RCH_2COOH \longrightarrow RCH COOH ?$ | Br

- 4. Answer any three questions: 10×3=30
 - (a) (i) What is lucas reagent? How is it used to distinguish between 1°, 2° and 3° alcohols?
 - (ii) Methyl chloromethyl ether is readily hydralysed by water to HCH=0 and CH_3OH but $CH_3OCH_2CH_2Cl$ does not. Explain.
 - (iii) Picric acid liberates CO_2 from aqueous Na_2CO_3 but phenol does not. Explain.
 - (iv) Give the products of Reimen-Tiemann reaction on p-Cresol. Explain the reaction with mechanism.
 - (b) (i) Write the mechanism of Michael addition reaction.
 - (ii) What is Wittig reagent?

(iii) How will you convert



Write the mechanism of the reaction involved.

- (iv) Write the significance of Wittig reaction.
- (v) What do you mean by ylides? 1
- (c) (i) Both O- and m-bromo misole give the same product on treatment with $NaNH_2$ in liq. NH_3 . Account for the observation with appropriate mechanism.
 - (ii) Write down the mechanism of the following reaction:

Account for the fact that the compound that has R = H reacts 35 times as fast as the one that has $R = CH_3$. 3+2=5

- (d) (i) Give the mechanism of alkaline hydrolysis of the following ester in ordinary water (H_2O^{16}) and indicate the distribution O^{18} is the products in each case.

 - (ii) What happens when an acid chloride is treated with excess of diazomethane and the product reacts with *EtoH* in the presence of Ag_2O catalyst?
 - (iii) Write the Strecker reaction for preparation of methyl sulphonic acid.

- (iv) How can CH_3CH_2SH be prepared from thiourea? Write the reactions.
- (e) (i) What are active methylene compounds?
 - (ii) Convert EAA to
 - (iii) 7-chloro cyclohepta -1, 3, 5-triene readily forms white AgCl ppt.

 When boiled with AgNO₃ solution but 5-chlorocyclopenta -1, 3-diene does not give reason.
- (iv) Two dicarboxylic acids have the genral formula

 COOH-CH=CH-COOH.

 On treatment with cold dil.

 KMnO₄ solution, they yield two diastereomeric tartaric acids. Show how this information allows one to write the stereochemical formula for two acids.

(f) (i) When an alkyl halide is converted to a Grignard reagent then the carbon atom linked to halogen atom changes its polarity. Justify this statement with an example.

(ii) Identify the product/products for the following reaction and offer explanation:

$$\begin{array}{c} O \\ \parallel \\ Et_2O \\ H_{30} \end{array} \oplus \begin{array}{c} MeLi \, / \, Et_2O \\ H_{30} \end{array}$$

(iii) Write the Grignard reagent that is formed when

$$Br - O - CH_2CH_2Br$$

is treated with one mole of Mg in dry ether.

(iv) Why Clemmensen reduction of 4-methyl-5-hydroxyhexan-3-one to 3-methylhexan-2-ol cannot be carried out?