

Total number of printed pages-11

3 (Sem-3/CBCS) CHE HC 2

2023

**CHEMISTRY**

(Honours Core)

Paper : CHE-HC-3026

**(Organic Chemistry-II)**

Full Marks : 60

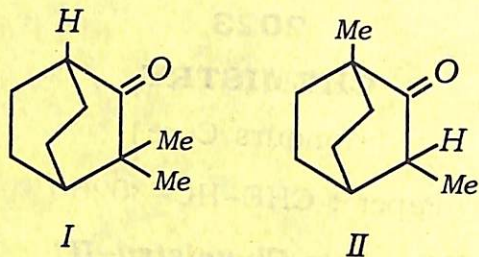
Time : Three hours

**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  
 $(\text{CH}_3)_2\text{CHO}^\ominus$ ,  $\text{PhO}^\ominus$ ,  $\text{CH}_3\text{O}^\ominus$ ,  $\text{OH}^\ominus$
  - (b) Draw the energy profile diagram of  $E|CB$  mechanism of  $\beta$ -elimination reaction.

Contd.

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



- (d) DMF and DMSO favours  $S_N2$  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.

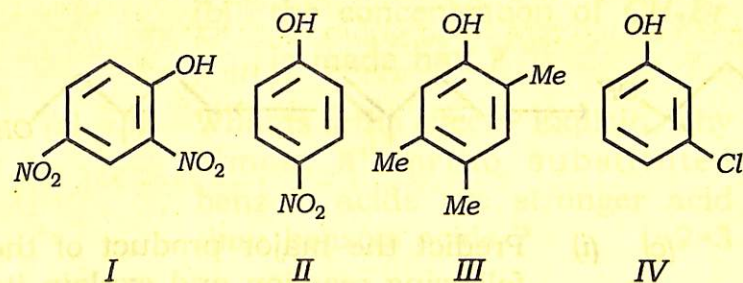
2. Answer the following questions :  $2 \times 4 = 8$

(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  $pK_a$  value of 4, 7, 9 and 11. Suggest with explanation which  $pK_a$  value belong to which phenol :



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

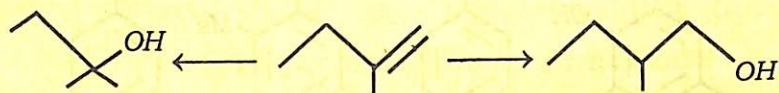


3. Answer **any three** questions :  $5 \times 3 = 15$

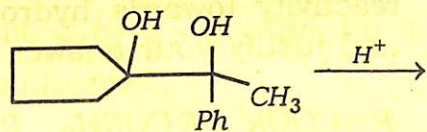
(a) Write the mechanism of Benzoin condensation. Explain why *p*-dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde the condensation occurs.  $3+2=5$

(b) (i) Explain why alcohols are weaker acids than phenols but phenols are stronger nucleophiles. 2

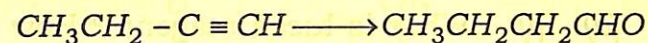
(ii) Provide the required reagents and conditions for the following conversion :  $1\frac{1}{2} \times 2 = 3$



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

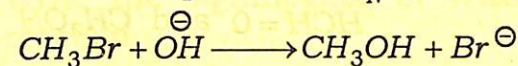


(ii) How do you carry out the following conversion ? 2



(d) (i) Why are vinylic and aryl halides unreactive towards both  $S_N1$  and  $S_N2$  reactions ? 3

(ii) The rate equation of  $S_N2$  reaction



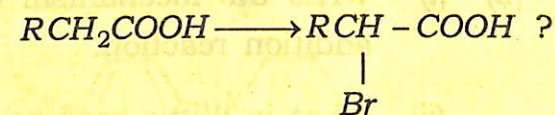
$$\text{Rate} = k[CH_3Br][OH^-]$$

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



4. Answer **any three** questions :  $10 \times 3 = 30$

(a) (i) What is Lucas reagent ? How is it used to distinguish between  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  alcohols ?  $1+2=3$

(ii) Methyl chloromethyl ether is readily hydrolysed by water to  $\text{HCHO}$  and  $\text{CH}_3\text{OH}$  but  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{Cl}$  does not.

Explain.  $2$

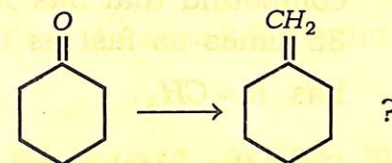
(iii) Picric acid liberates  $\text{CO}_2$  from aqueous  $\text{Na}_2\text{CO}_3$  but phenol does not. Explain.  $2$

(iv) Give the products of Reimer-Tiemann reaction on *p*-Cresol. Explain the reaction with mechanism.  $3$

(b) (i) Write the mechanism of Michael addition reaction.  $3$

(ii) What is Wittig reagent ?  $1$

(iii) How will you convert



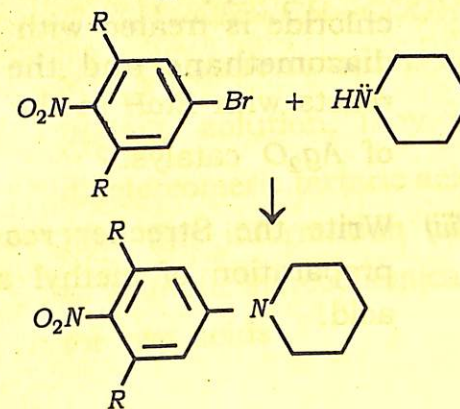
Write the mechanism of the reaction involved.  $3$

(iv) Write the significance of Wittig reaction.  $2$

(v) What do you mean by ylides ?  $1$

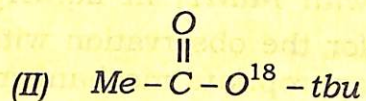
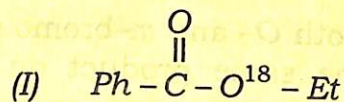
(c) (i) Both *o*- and *m*-bromo anisole give the same product on treatment with  $\text{NaNH}_2$  in  $\text{liq. NH}_3$ . Account for the observation with appropriate mechanism.  $5$

(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

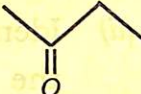
- (d) (i) Give the mechanism of alkaline hydrolysis of the following ester in ordinary water ( $H_2O^{16}$ ) and indicate the distribution  $O^{18}$  is the products in each case. 4



- (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? 2
- (iii) Write the Strecker reaction for preparation of methyl sulphonic acid. 2

- (iv) How can  $CH_3CH_2SH$  be prepared from thiourea? Write the reactions. 2

- (e) (i) What are active methylene compounds? 1

- (ii) Convert EAA to  3

- (iii) 7-chloro cyclohepta-1, 3, 5-triene readily forms white  $AgCl$  ppt. When boiled with  $AgNO_3$  solution but 5-chlorocyclopenta-1, 3-diene does not give reason. 2

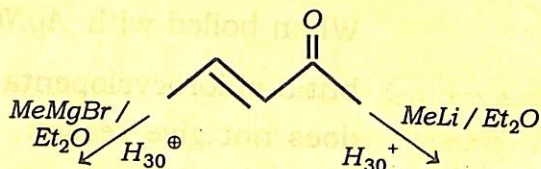
- (iv) Two dicarboxylic acids have the general formula  $COOH - CH = CH - COOH$ . On treatment with cold dil.  $KMnO_4$  solution, they yield two diastereomeric tartaric acids. Show how this information allows one to write the stereochemical formula for two acids. 4

(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.

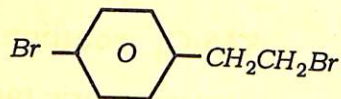
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(ii) Identify the product/products for the following reaction and offer explanation :

3



(iii) Write the Grignard reagent that is formed when



is treated with one mole of  $\text{Mg}$  in dry ether.

2

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

2