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3 (Sem-3/CBCS) CHE HC 2

2023

CHEMISTRY

(Honours Core)

Paper : CHE-HC-3026

(Organic Chemistry-II)

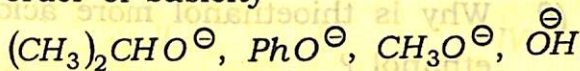
Full Marks : 60

Time : Three hours

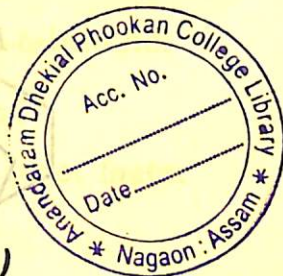
The figures in the margin indicate full marks for the questions.

1. Answer the following questions : 1×7=7

(a) Arrange the following in increasing order of basicity

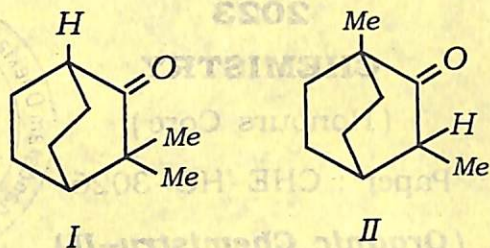


(b) Draw the energy profile diagram of $E|CB$ mechanism of β -elimination reaction.



Contd.

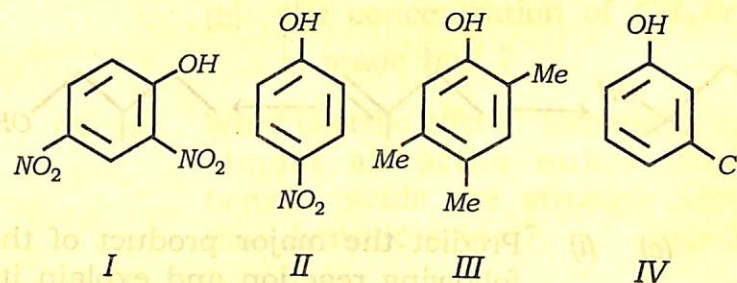
- (c) Which one of the following bridged bicyclic compounds will exhibit Keto-Enol tautomerism.



- (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-butenediol.

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 : $5 \times 3 = 15$

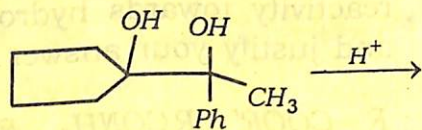
(a) Write the mechanism of Benzoin condensation. Explain why *p*-dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde the condensation occurs. $3+2=5$

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

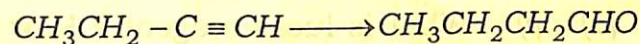
(ii) Provide the required reagents and conditions for the following conversion : $1\frac{1}{2} \times 2 = 3$



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

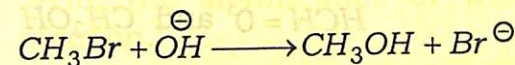


(ii) How do you carry out the following conversion ? 2



(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



$$\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

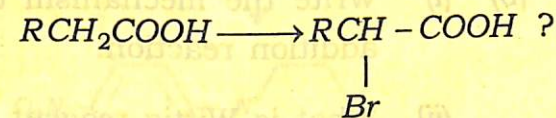
What type of changes are expected in the rates of the reaction if

(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 : 10×3=30

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

(ii) Methyl chloromethyl ether is readily hydrolysed by water to $HCHO$ and CH_3OH but $CH_3OCH_2CH_2Cl$ does not.

Explain. 2

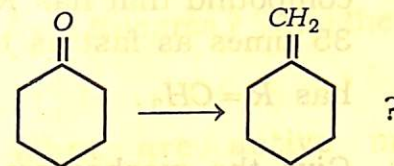
(iii) Picric acid liberates CO_2 from aqueous Na_2CO_3 but phenol does not. Explain. 2

(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



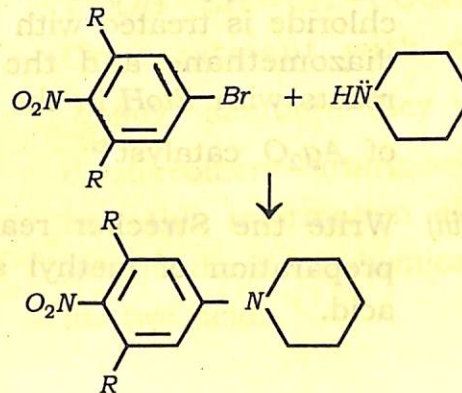
Write the mechanism of the reaction involved. 3

(iv) Write the significance of Wittig reaction. 2

(v) What do you mean by ylides ? 1

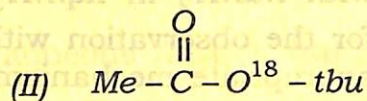
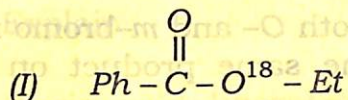
(i) Both *o*- and *m*-bromo anisole give the same product on treatment with $NaNH_2$ in $liq. NH_3$. Account for the observation with appropriate mechanism. 5

(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

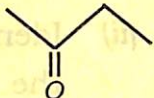
- (d) (i) Give the mechanism of alkaline hydrolysis of the following ester in ordinary water (H_2O^{16}) and indicate the distribution O^{18} is the products in each case. 4



- (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

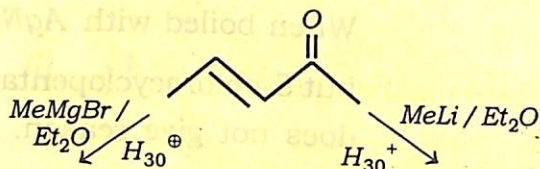
- (iv) Two dicarboxylic acids have the general formula $COOH - CH = CH - COOH$. On treatment with cold dil. $KMnO_4$ solution, they yield two diastereomeric tartaric acids. Show how this information allows one to write the stereochemical formula for two acids. 4

(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.

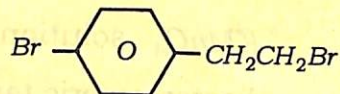
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(ii) Identify the product/products for the following reaction and offer explanation :

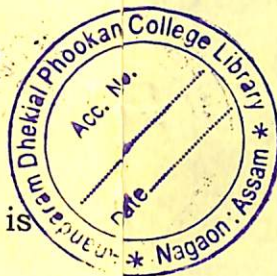
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(iii) Write the Grignard reagent that is formed when



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 ?

2