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

   $(CH_3)_2CHO^{\ominus}$, $PhO^{\ominus}$, $CH_3O^{\ominus}$, $\overset{\ominus}{O}H$

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

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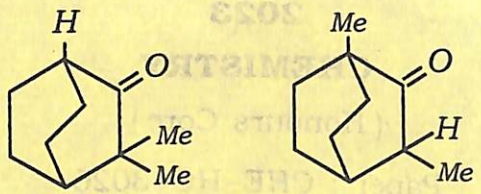
(c) Which one of the following bridged bicyclic compounds will exhibit Keto-Enol tautomerism.



I *II*

(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 ?

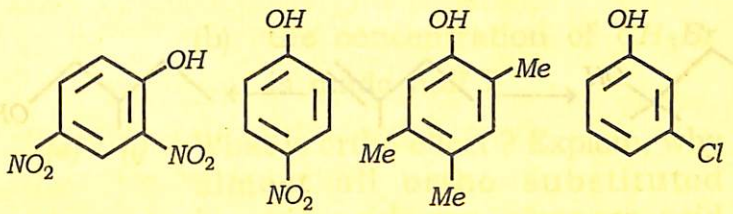
(g) Name the reagent that can be used to convert Cis – 2 – butene to racemic 2,3 – butanediol.

2. Answer the following questions : 2×4=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 *pKa* value of 4, 7, 9 and 11. Suggest with explanation which *pKa* value belong to which phenol :



I *II* *III* *IV*

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

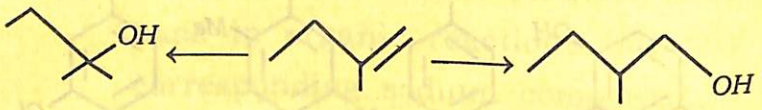
$R-COOR'$, $RCONH_2$, $RCOCl$

3. Answer ***any three*** questions : 5×3=15

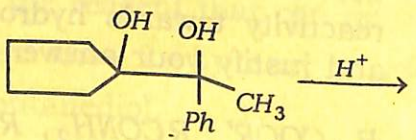
(a) Write the mechanism of Benzoin condensation. Explain why *p*-dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde the condensation occurs. 3+2=5

(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



(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

$$CH_3CH_2-C\equiv CH \longrightarrow CH_3CH_2CH_2CHO$$

(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

$$CH_3Br + \overset{\ominus}{O}H \longrightarrow CH_3OH + Br^{\ominus}$$

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

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

$$RCH_2COOH \longrightarrow \underset{\displaystyle Br}{\underset{|}{RCH}}-COOH \ ?$$

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 hydralysed by water to $HCH=0$ and CH_3OH but $CH_3OCH_2CH_2Cl$ does not. Explain. 2

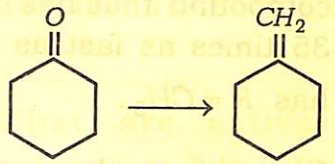
(iii) Picric acid liberates CO_2 from aqueous Na_2CO_3 but phenol does not. Explain. 2

(iv) Give the products of Reimen-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



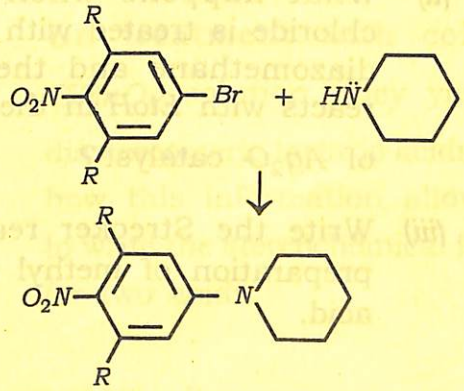
Write the mechanism of the reaction involved. 3

(iv) Write the significance of Wittig reaction. 2

(v) What do you mean by ylides ? 1

(c) (i) Both *O*– and *m*–bromo misole 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

(I) $Ph - \overset{\overset{O}{\|}}{C} - O^{18} - Et$

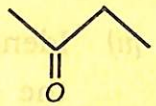
(II) $Me - \overset{\overset{O}{\|}}{C} - O^{18} - tbu$

(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

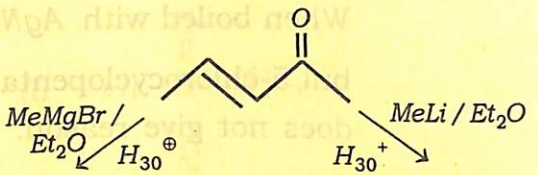
(ii) Convert EAA to  3

(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

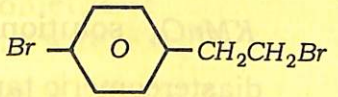
(iv) Two dicarboxylic acids have the genral formula $COOH - CH = CH - COOH$. On treatment with cold dil. $KMnO_4$ solution, they yield two diastereomeric tartaric acids. Show how this information allows one to write the stereochemical formula for two acids. 4

(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. 3

(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 *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

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