Total number of printed pages–12

3 (Sem–3/CBCS) CHE HC 2

2022

CHEMISTRY

(Honours)

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 ***(any seven)*** : 1×7=7

   (a) What are the reagents used in Bouveault-Blanc reduction reaction ?

   (b) Why thiols are also called as mercaptans ?

   (c) Why are oxiranes reactive in comparison to other cyclic ethers ?

Contd.

(d) Name *two* acids which can cleave an ether linkage.

(e) Why it is more advantageous to use thionyl chloride in place of phosphorous pentachloride in the preparation of acid chlorides ?

(f) What is saponification ?

(g) Draw the orbital diagram of a S_N2 transition state.

(h) Arrange the following in order of increasing nucleophilicity :

PhO^-, ^-OH, AcO^-, TsO^-

(i) Name *one* reagent that can convert an acid chloride to aldehyde.

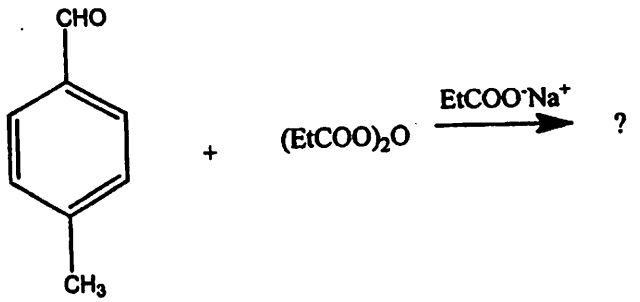
(j) Compound $A(C_5H_{10}O)$ forms a phenylhydrazone, gives negative Tollen's and iodoform test and can be reduced to pentane. What is the compound ?

(k) What is Fremy's salt ? Write its structure.

(l) Why don't *N*-nitrosoamines which form from secondary amines lead to diazonium ions ?

2. Answer the following questions : ***(any four)*** 2×4=8

(a) Predict the product obtained in the following reaction. Give the name of this reaction :



(b) What is cumene ? How is it being utilized for the synthesis of phenol ?

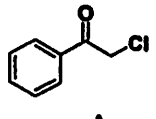
(c) If propionyl chloride is added to one equivalent of methylamine, only a 50% yield of *N*-methylpropanamide is obtained. If, however, the acyl chloride is added to two equivalents of methylamine, the yield of *N*-methyl-propanamide is almost 100%. Explain.

(d) Propose a synthesis of *n*-propylbenzene using organolithium compound.

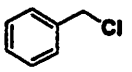
(e) Explain why a Claisen condensation product is not obtained from ester such as ethyl benzoate.

(f) What do you mean by stabilized ylides ? Give an example.

(g) Of the two compounds A and B shown below, which one is more reactive towards I^- in S_N2 conditions and why ?



A



B

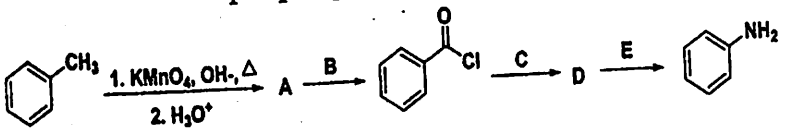
(h) Write the structures of the *two* isomers of acetophenone oxime.

3. Answer the following questions ***(any three)*** : 5×3=15

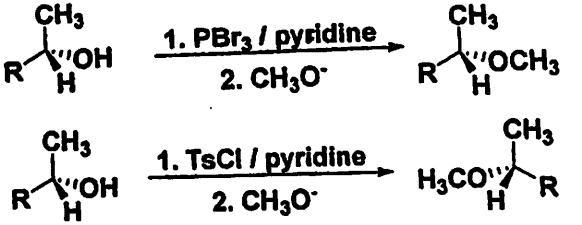
(a) What is Swern oxidation ? What is the active species that helps in the oxidation process ? Explain the mechanism by considering a suitable example. 1+1+3=5

(b) What are arene sulfonic acids ? Why they are much stronger than comparably substituted carboxylic acids ? Write the reaction for *any one* method of synthesis of arene sulphonic acid ? How can they be converted to sulphonyl chlorides ? 1+2+1+1=5

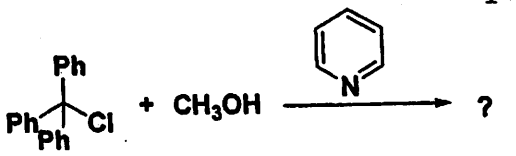
(c) The reaction sequence given below shows how a methyl group on a benzene ring can be replaced by an amino group. Identify the missing reagents and intermediates with proper justification.



(d) Explain why the ether obtained by treating an optically active alcohol with PBr_3 followed by sodium methoxide has the same configuration as the alcohol, whereas the ether obtained by treating the alcohol with tosyl chloride followed by sodium methoxide has a configuration opposite that of the alcohol.

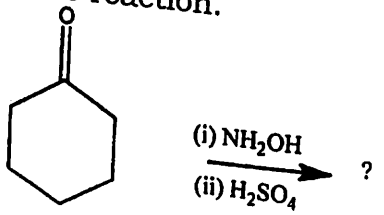


(e) Complete the following reaction and propose a mechanism for the same : 1+4=5



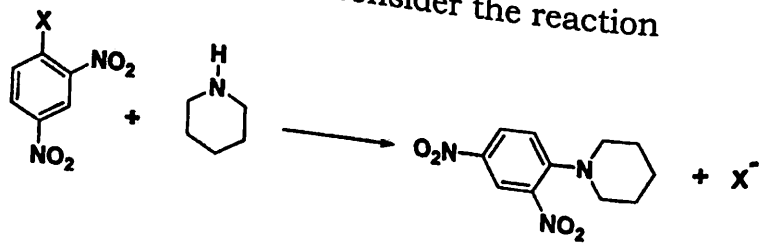
(f) Write the steps involved in a Benzyne mechanism. Provide evidence *(any one)* in support of the proposed mechanism. 3+2=5

(g) Predict the product of the following reaction. Identify the name of the reaction and propose a mechanism for the name reaction. 1+1+3=5



(h) (i) Propose a mechanism for acid catalyzed aldol reaction. 3

(ii) Let us consider the reaction



When the substituent *X* is changed from *Cl* to *I*, there is no significant effect on the rate of the reaction. What does it imply regarding the mechanism of this reaction ? 2

4. Answer following questions : ***(any three)*** 10×3=30

(a) (i) Write a reaction for the preparation of an acyl azide. How can you convert an acyl azide to isocyanate ? Explain with mechanism. 1+1+2=4

(ii) If a carboxylic acid is dissolved in isotopically labelled methanol ($CH_3{}^{18}OH$) and an acid catalyst is added, where will the label reside in the product ? Explain. 3

(iii) Write a reaction for the formation of succinic anhydride in the presence of acetic anhydride. How does acetic anhydride help in the formation of succinic anhydride ? 3

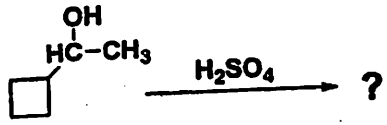
(b) (i) Write the mechanisms for the acidic and basic hydrolysis of *N, N*-dimethylacetamide. 3+2=5

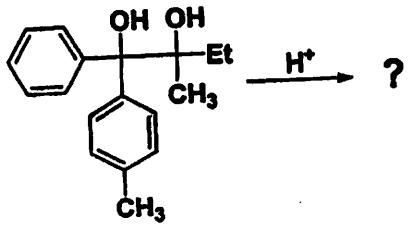
(ii) Why nucleophilic addition of the organozinc compound does not occur to the ester group in Reformatsky reaction ? How can you prepare 3-hydroxymethylhexanoate using Reformatsky reaction. Explain with the help of a mechanism. 5

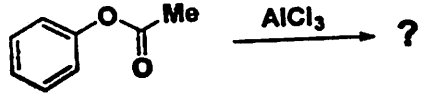
(c) (i) Compound **A** ($C_7H_{11}Br$) is treated with magnesium in ether to give **B** ($C_7H_{11}MgBr$), which reacts violently with D_2O to give 1-methylcyclohexene with a deuterium atom on the methyl group **C**. Reaction of **B** with acetone (CH_3COCH_3) followed by hydrolysis gives **D** ($C_{10}H_{18}O$). Heating **D** with concentrated H_2SO_4 gives **E** ($C_{10}H_{16}$), which decolorizes two equivalents of Br_2 to give **F** ($C_{10}H_{16}Br_4$). **E** undergoes hydrogenation with excess H_2 and a *Pt* catalyst to give iso-butylcyclohexane. Determine the structures of compounds **A** through **F**, and show your reasoning throughout. 7

(ii) When ethylene oxide is treated with anhydrous *HBr* gas, the major product is 1,2-dibromoethane. When ethylene oxide is treated with concentrated aqueous *HBr*, the major product is ethylene glycol. Explain these observations. 3

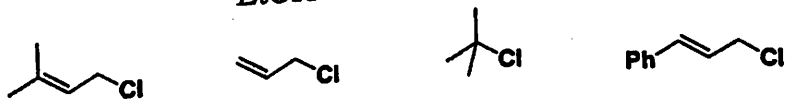
(d) Predict the products of the following transformations and justify your answer with mechanism : 3+4+3=10

(i) 

(ii) 

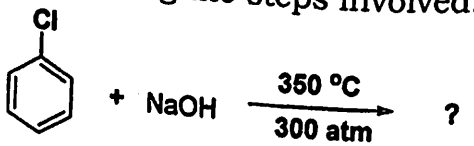
(iii) 

(e) (i) Arrange the following in decreasing order of hydrolysis in 50% aqueous *EtOH* at 45°*C*. 2



(ii) Propose a mechanism for acid catalyzed hemiacetal formation from aldehyde and ethanol. 3

(iii) Complete the reaction. Propose a mechanism for the same clearly mentioning the steps involved. 5



(f) (i) Suggest *one* factor that contributes to the enhanced stability of the enol form in 1,3-dicarbonyl compounds as compared with monocarbonyl compounds. 2

(ii) What products will be obtained when $CH_3COCH(CH_3)COOC_2H_5$ undergo ketonic hydrolysis ? Write the reactions involved. 2

(iii) Write the reactions involved in the conversion of *(any two)* 2+2=4

(a) Diethylmalonate to Barbituric acid

(b) Ethylacetoacetate to Crotonic acid

(c) Ethylacetoacetate to Heptan-2-one

(iv) Between organolithium and Grignard reagent which one is more reactive and why ? 2

(g) (i) Write in detail the steps involved in a S_N1 mechanism. Explain the observation that the rate of the S_N1 reaction of many *RX* derivatives is retarded by the addition of X^-? 3+1=4

(ii) Predict whether the following substrate is likely to undergo S_N1 and/or S_N2 reaction or neither ? Explain. 3

(iii) Use *either* Wedge formula *or* Fischer projection to show the reaction of *S*-2-bromobutane reacts with hydroxide proceeding by S_N2 mechanism ? 2

(iv) Which is a better nucleophile and why 1

$n\text{-}C_4H_9O^-$, $t\text{-}C_4H_9O^-$?

(h) How can you carry out the following conversions? 1+4+1+4=10

(a) Cyclohexanone to ε-Caprolactam

(b) Benzil to Benzilic acid

Write the reactions involved and propose mechanisms for each of the conversions.