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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

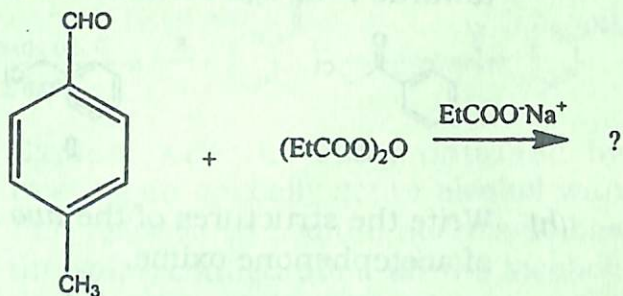
- (a) What are the reagents used in Bouveault-Blanc reduction reaction ?
- (b) Why thiols are also called as mercaptans ?
- (c) Why are oxiranes reactive in comparison to other cyclic ethers ?

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

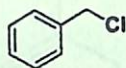
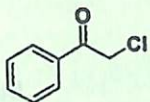
- (a) Predict the product obtained in the following reaction. Give the name of this reaction :



- (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*-methylpropanamide 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?



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

3. Answer the following questions (**any three**):
 $5 \times 3 = 15$

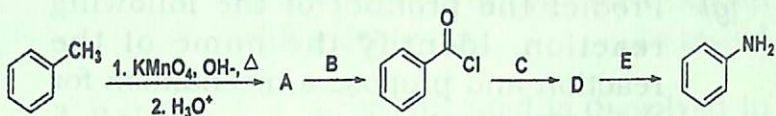
(a) What is Swern oxidation? What is the active species that helps in the oxidation process? Explain the mechanism by considering a suitable example.

$1 + 1 + 3 = 5$

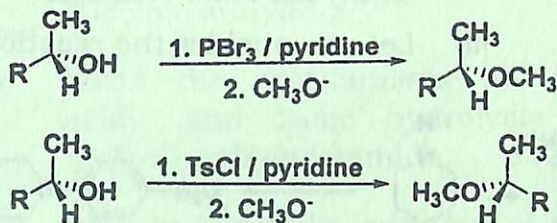
(b) What are arene sulfonic acids? Why they are much stronger than comparably substituted carboxylic acids? Write the reaction for *any one* method of synthesis of arene sulphonic acid? How can they be converted to sulphonyl chlorides?

$1 + 2 + 1 + 1 = 5$

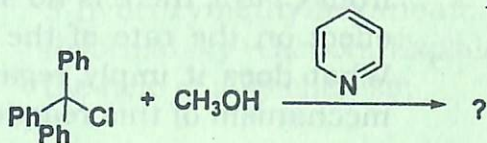
- (c) The reaction sequence given below shows how a methyl group on a benzene ring can be replaced by an amino group. Identify the missing reagents and intermediates with proper justification.



- (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 :

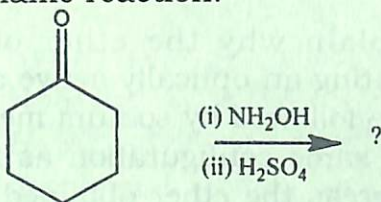


- (f) Write the steps involved in a Benzyne mechanism. Provide evidence (*any one*) in support of the proposed mechanism.

3+2=5

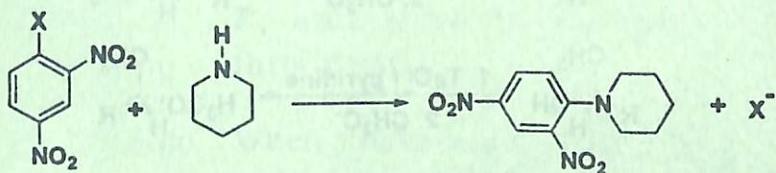
- (g) Predict the product of the following reaction. Identify the name of the reaction and propose a mechanism for the name reaction.

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 ($\text{CH}_3^{18}\text{OH}$) 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

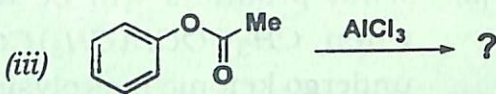
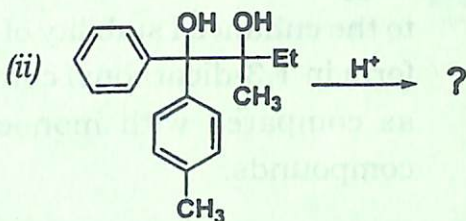
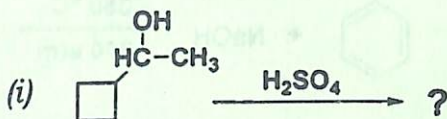
(b) (i) Write the mechanisms for the acidic and basic hydrolysis of *N,N*-dimethylacetamide. 3+2=5

(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

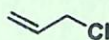
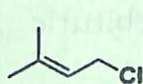
(c) (i) Compound **A** ($C_7H_{11}Br$) is treated with magnesium in ether to give **B** ($C_7H_{11}MgBr$), which reacts violently with D_2O to give 1-methylcyclohexene with a deuterium atom on the methyl group **C**. Reaction of **B** with acetone (CH_3COCH_3) followed by hydrolysis gives **D** ($C_{10}H_{18}O$). 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 isobutylcyclohexane. 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

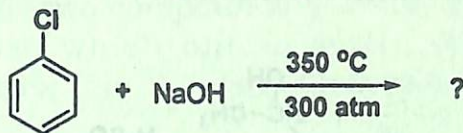


- (e) (i) Arrange the following in decreasing order of hydrolysis in 50% aqueous *EtOH* at 45°C. 2



- (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

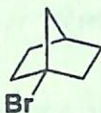
(b) Ethylacetoacetate to Crotonic acid

(c) Ethylacetoacetate to Heptan-2-one

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

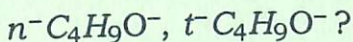
(g) (i) Write in detail the steps involved in a S_N1 mechanism. Explain the observation that the rate of the S_N1 reaction of many RX derivatives is retarded by the addition of X^- ? 3+1=4

(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



(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.

