3 (Sem–3/CBCS) CHE HC 2

2021

(Held in 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 : 1×7=7

   (a) Write the name of a thiol compound that can be used as an antidote for mercury poisoning.

   (b) Arrange the following compounds in order of reactivity toward S_N2 reaction :

   1-Bromobutane,
   1-Bromo-2,2-Dimethylpropane
   1-Bromo-2-Methylbutane
   1-Bromo-3-Methylbutane

(c) With increasing temperature, elimination is favoured over substitution. Why?

(d) What is meant by cine-substitution?

(e) Name a reagent used to convert cyclohexylmethanol to cyclohexanecarboxaldehyde.

(f) Give *two* ways in which you can convert the poor leaving group in ROH to a good leaving group.

(g) What happens when diethylsulfide reacts with hydrogen peroxide and acetic acid?

2. Answer the following questions : 2×4=8

(a) How can you prepare lactic acid from propanoic acid?

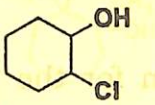
(b) Why is Ethylacetoacetate (EAA) called an active methylene compound?

(c) Explain why the boiling point of ethylene glycol is much lower than that of glycerol.

(d) Between thiol and alcohol, which one is more acidic and why?

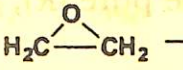
3. Answer ***any three*** of the following questions : 5×3=15

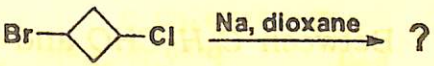
(a) Predict the major product in each of the given reactions : 1×5=5

(i) 

(ii) $CH_3SCH_3 + CH_3I \longrightarrow ?$

(iii) $(C_6H_5)_3P + C_6H_5CH_2Br \longrightarrow ?$

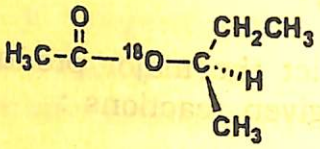
(iv) $n\text{-}C_6H_9MgBr +$  $\xrightarrow[\text{II) } H_3O^+]{\text{I) } Et_2O}$?

(v) 

(b) What product(s) is/are obtained when *m*-chlorotoluene is treated with sodium amide in liquid NH_3? Propose a mechanism to justify the product(s) formed. 1+4=5

(c) What is Bouveault-Blanc reaction? Explain the mechanism of the reaction by considering a suitable example. 1+4=5

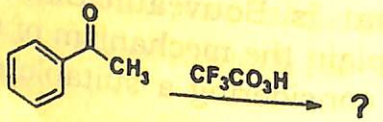
(d) Suppose we have some optically pure (*R*)-2-butyl acetate that has been 'labeled' with the heavy ^{18}O isotope at one oxygen atom as shown.



Draw a mechanism for the hydrolysis of this compound under basic conditions. Predict which of the products will contain the ^{18}O label. Also predict whether the butan-2-ol product will be pure (*R*), pure (*S*) or racemized. 3+1+1=5

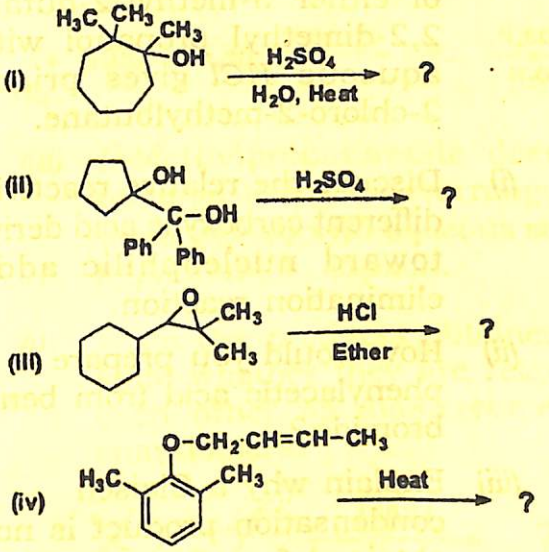
(e) (i) Between C_6H_5CHO and CH_3CHO, which one is less reactive towards nucleophiles and why? 2

(ii) Predict the product and propose a mechanism of the following reaction : 3



4. Answer ***any three*** of the following : 10×3=30

(a) Predict the product and propose mechanisms of the following reactions : 3+3+2+2=10



(b) (i) 2,3-Epoxypropane when reacts with methanol under acidic conditions yield 2-Methoxy-propan-1-ol as major product, but under basic conditions yield 1-Methoxy-propan-2-ol. Explain. 5

(ii) Explain why the acid-catalyzed condensation is a poor method for the synthesis of an unsymmetrical ether such as ethyl methyl ether. 2

(iii) Provide a mechanistic explanation for the observation that treatment of either 3-methyl-2-butanol or 2,2-dimethyl propanol with hot aqueous *HCl* gives principally 2-chloro-2-methylbutane. 3

(c) (i) Discuss the relative reactivities of different carboxylic acid derivatives toward nucleophilic addition-elimination reaction. 5

(ii) How would you prepare phenylacetic acid from benzyl bromide ? 2

(iii) Explain why a Claisen condensation product is not obtained from ester such as ethyl 2-methylbutanoate. 3

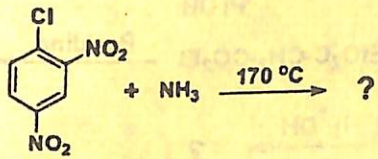
(d) (i) Compare S_N1 and S_N2 reactions with regard to

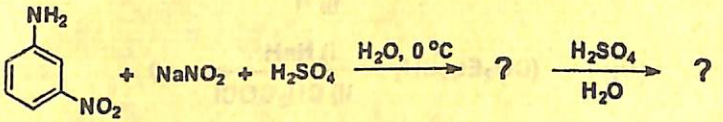
(1) stereochemistry ;

(2) kinetic order ;

(3) occurrence of rearrangements. 2+2+1=5

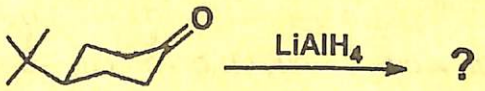
(ii) Complete the following reaction and write the mechanism : ***(any one)*** 3

(a) 

(b) 

(iii) *N*-Methylpropanamide does not undergo Hofmann rearrangement when treated with aqueous sodium hypobromite. Explain. 2

(e) (i) Write the products obtained and state whether they are related to each other as diastereomers or enantiomers. 2



(ii) How can you convert cyclohexanone to nylon ? Write the reaction. 2

(iii) Predict the products formed : 1×6=6

(i) $C_6H_5CHO \xrightarrow[\text{ii) } H_3O^+]{\text{i) 60\% KOH}}$?

(ii) $C_6H_5CHO \xrightarrow{KCN} ?$

(iii) $CH_3\text{-}CH{=}CH\text{-}CHO \xrightarrow[{}^{i}PrOH]{Al(O^{i}Pr)3} ?$

(iv) $CH_3CHO + EtO_2C\text{-}CH_2\text{-}CO_2Et \xrightarrow{Pyridine} ?$

(v) $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph \xrightarrow[II)\ H^+]{I)\ ^-OH} ?$

(vi) $(CO_2Et)_2CH_2 \xrightarrow[II)\ CH_3COCl]{I)\ NaH} ?$

(f) (i) What are ylides? How can you prepare methylenecyclohexane using Wittig reaction? Propose a mechanism for the reaction clearly stating the steps involved. 1+1+3=5

(ii) Identify the product in the following reaction :

$$H_3C{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OEt \xrightarrow{NaOEt} ?$$

In this reaction which substrate is the Michael acceptor and which one is the Michael donor? 2

(iii) Propose a mechanism for acid-catalysed aldol condensation involving the reaction of acetone with *HCl*. 3