# 2021

# CHEMISTRY — HONOURS

**Third Paper** 

(Group - A)

Full Marks: 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

### CHT-22a

### Unit - I

Answer any three questions.

1. (a) What are the products obtained when a mixture of CH<sub>3</sub>CHO and HCHO is treated with Al(OEt)<sub>3</sub>? Explain with mechanism.

(b) Convert 
$$H_3C - C \equiv C - CH_3$$
 to  $H_3C - CH(D)COCH_3$ .

- **2.** (a) Cyclopentadiene reacts with maleic anhydride much faster than 1, 3-butadiene in a thermal Diels-Alder reaction. Explain this observation showing the adducts.
  - (b) Identify A to D of the following reaction sequence (mechanism not required):

$$CH_{3}$$

$$\xrightarrow{LDA} A \xrightarrow{CH_{3}CHO} B \xrightarrow{H_{3}O^{+}} C \xrightarrow{\Delta} D$$

$$3+2$$

**3.** (a) Write down the structures of the ozonides formed when 2,3-dimethyl-2-butene is subjected to ozonolysis. Give also the mechanism of ozonide formation.

(b) Convert 
$$HC = C - CH_2 - CH_2 - CH_3 \longrightarrow H_2C = CH - CH = CH - CH_3$$
 3+2

**4.** (a) Explain the following reaction with mechanism:

$$\begin{array}{c|cccc}
CHO & CH_2OH & C - ONa \\
\hline
OH & CH_3 & CH_3
\end{array}$$

(b) Predict the products of the reaction of HBr with (i)  $F_3C - CH = CH_2$  and (ii)  $CH_3O - CH = CH_2$ .

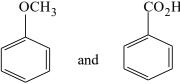
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# T(II)-Chemistry-H-3A

(2)

- **5.** (a) Indicate the product stereochemistry along with mechanism, in each case, for the reactions of *cis*-2-butene and *trans*-2-butene with alkaline KMnO<sub>4</sub>.
  - (b) Predict the major product in each case of Birch reduction of the following compounds (mechanism not required):

    3+2



Unit - II

Answer any two questions.

**6.** (a) Ethylbenzene can be prepared by the following two methods:

(i) 
$$\begin{array}{c} C_2H_5Cl \\ \hline anhydrous AlCl_3 \end{array}$$
 O 
$$C_2H_5 \\ \hline C \\ \hline CH_3COCl \\ \hline anhydrous AlCl_3 \end{array}$$
 C 
$$\begin{array}{c} C_2H_5 \\ \hline C \\ \hline CH_3 \\ \hline C \\ \hline \end{array}$$
 (ii) 
$$\begin{array}{c} C_1H_5 \\ \hline C \\ \hline CH_3 \\ \hline C \\ \hline \end{array}$$

Which method is better and why?

(b) Account for the following observation:

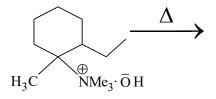
$$O_2$$
 OMe OMe OMe/MeOH  $O_2$  NO  $O_2$ 

- 7. (a) In presence of pyridine, the *threo* isomer of 1, 2-dibromo-1, 2-diphenylethane undergoes dehydrobromination to give (*Z*)-1-bromo-1, 2-diphenylethene, whereas the *erythro* isomer undergoes debromination to give (*E*)-1, 2-diphenylethene. Account for this observation.
  - (b) Predict the product with suitable mechanism.

$$\begin{array}{c|c}
CH_3 & \\
& & \\
& & \\
+ H_3C & -N - C = O \xrightarrow{POCl_3} ?
\end{array}$$

3+2

- **8.** (a) Both *o*-bromoanisole and *m*-bromoanisole give same product on treatment with NaNH<sub>2</sub>/liq·NH<sub>3</sub>. Account for the following observation.
  - (b) Write down the major product in the following reaction and explain its formation: 3+2



### CHT-22b

### Unit - I

Answer any three questions.

- 9. (a) Use Reformatsky reaction to synthesize  $PhC(Me) = C(Me)CO_2H$ . Why can we not use magnesium in place of zinc in this synthesis?
  - (b) Alkaline hydrolysis of benzonitrile affords the salt of an acid but in presence of hydrogen peroxide, an amide is formed. Explain. 3+2
- **10.** (a) Show how you would prepare the following compounds employing Grignard's reaction on bromobenzene:
  - (i) 1-phenylethanol
  - (ii) 2-phenylpropene
  - (iii) benzyl bromide.
  - (b) Convert Aniline  $\rightarrow$  1, 2, 3-Tribromobenzene.

3+2

- 11. (a) Write down Gabriel Phthalimide Synthesis for the preparation of EtNH<sub>2</sub>. Why can we not prepare a primary amine like Et<sub>3</sub>C-NH<sub>2</sub> by this method?
  - (b) Convert using an organometallic compound:

p-Nitrotoluene  $\longrightarrow p$ -Nitroacetophenone

3+2

- 12. (a) Explain mechanistically the difference in the pattern of coupling of benzene diazonium cation with (i) aniline and (ii) N,N-dimethyl aniline.
  - (b) Explain why diazoacetic ester is more stable than diazomethane.

3+2

13. (a) Complete the reactions:

(i) 
$$CH_2N_2 + C_2H_5OH \rightarrow$$

### T(II)-Chemistry-H-3A

(4)

(ii) 
$$CH_2N_2 + OH$$

O

(iii)  $CH_2N_2 + R - C - CI$ 

(b) Give the products showing plausible mechanism of the following reaction:

3+2

3+2

 $R_2NH + HCHO + HCOOH \rightarrow$ 

# Unit - II

Answer any two questions.

- **14.** (a) How will you prepare phenol from benzene via cumene? Give the mechanism of the reactions involved.
  - (b) Predict the product of the following reaction with plausible mechanism:

 $\begin{array}{c}
\text{CHO} \\
\xrightarrow{\text{(i) H}_2\text{O}_2/\text{NaOH}} \\
\xrightarrow{\text{(ii) H}_3\text{O}^{\oplus}}
\end{array}$ 

- 15. (a) Both  $Ph_2C(OH) C(OH)Me_2$  and Ph(Me)C(OH) C(Me)(OH)Ph on treatment with conc.  $H_2SO_4$  gives the same ketone. Explain mechanistically.
  - (b) What happens when diazoamino benzene is treated with dil.HCl? Explain mechanistically. 3+2
- 16. (a) Predict the products of the following reactions and give the mechanism:

(b) Predict the products of the following reaction and explain their formation:

$$\begin{array}{c|c} CONH_2 & CO^{15}NH_2 \\ \hline & & \\ \hline & &$$