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 CH₃CHO and HCHO is treated with Al(OEt)₃? 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
$$HC \equiv C - CH_2 - CH_2 - CH_3 \longrightarrow H_2C = CH - CH = CH - CH_3$$
 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) $CH_3O - CH = CH_2$.

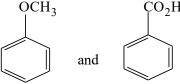
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T(II)-Chemistry-H-3A

(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 KMnO₄.
 - (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:

Which method is better and why?

(b) Account for the following observation:

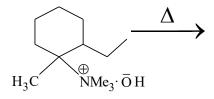
$$O_2$$
 OMe OMe OMe/MeOH O_2 NO2 O_2 N NO2

3+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.

$$\begin{array}{c|c}
OCH_3 \\
& \downarrow \\
+ H_3C - N - C = O \xrightarrow{POCl_3 \\
heat}
\end{array}$$
?

- **8.** (a) Both *o*-bromoanisole and *m*-bromoanisole give same product on treatment with $NaNH_2/liq \cdot NH_3$. 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 EtNH₂. Why can we not prepare a primary amine like Et₃C-NH₂ 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)
$$CH_2N_2 + \bigcirc$$
 OH

OH

OH

CH2N2+ R—C—CI

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

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:

3+2

- 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:

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