## 2021

## **CHEMISTRY — HONOURS**

Paper: CC-8

[Organic Chemistry-4]

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.

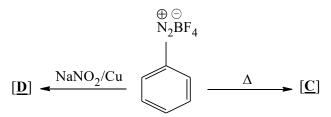
Answer question no. 1 and any eight questions from the rest (Q. Nos. 2-13).

1. Answer any ten questions:

 $1 \times 10$ 

(a) Give the structures of  $[\underline{\mathbf{A}}]$  and  $[\underline{\mathbf{B}}]$  in the following reaction:

- (b) Convert PhCHO to PhCOCH<sub>3</sub> using umpolung technique.
- (c) Give one example of each of the following:
  - (i) Illogical electrophile
  - (ii) Illogical nucleophile.
- (d) 2-Butyne does not show  $C \equiv C$  stretching frequency in its IR spectrum. Explain.
- (e) The UV spectrum of aniline in dilute acid solution is very similar to that of benzene. Explain.
- (f) Give the structures  $[\underline{\mathbf{C}}]$  and  $[\underline{\mathbf{D}}]$  in the following reaction:



- (g) Give examples of two NMR active nuclei.
- (h) What is the range of infrared radiations for organic compounds?

## T(4th Sm.)-Chemistry-H/CC-8/CBCS

(2)

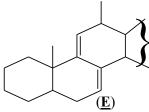
(i) Carry out the following conversion:

(j) Write synthetic equivalents corresponding to the following synthons:

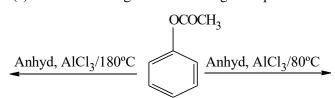
 $\odot$  (i) COOH ; (ii)  $\mathrm{CH_2CH_2OH}$ 

- (k) Suggest a reason for the use of excess mineral acid in the diazotisation reaction.
- (l) Give the product of the following reaction along with the plausible mechanism.

- 2. (a) An isomeric dinitrobenzene shows three signals in its  ${}^{1}H$  NMR spectrum. Identify the compound. Compare the relative  $\delta$  values of the protons and give reasons.
  - (b) Calculate  $\lambda_{\text{max}}$  for the following compound ( $\underline{\mathbf{E}}$ ) using Woodward's diene rules. 3+2



- **3.** (a) p Toluidine reacts with benzenediazonium chloride to form a compound, which on boiling with  $H_2SO_4$  gives four products (excluding nitrogen). Discuss.
  - (b) R-CONHMe does not undergo Hofmann amine formation reaction. Offer an explanation. 3+2
- **4.** (a) Compare the reaction behaviour of aniline, N-methylaniline, and N, N-dimethylaniline towards NaNO<sub>2</sub> and dilute HCl. Explain the reactions.
  - (b) What happens when PhCH<sub>2</sub>COCl is treated with CH<sub>2</sub>N<sub>2</sub> and the resultant product is allowed to react with Ag<sub>2</sub>O in water? Give mechanism for the second step of the reaction. 3+2
- 5. (a) Give the product(s) of the following reactions along with plausible mechanisms.



How do you justify the formation of different products with the change in reaction temperature?

3+2

(b) Give the product(s) of the following reaction along with the mechanism involved in it.

**6.** (a) Give the product(s) of the following reaction along with the plausible mechanism.

$$CH_3$$
 $*$ 
 $H^{\oplus}$ 

- (b) Give any two reasons for use of TMS as a reference compound in <sup>1</sup>H NMR spectroscopy. 3+2
- 7. (a) Distinguish between the following compounds with the help of spectroscopic methods given within the parenthesis.

(b) In the following reaction, use *Felkin-Anh's model* to determine the stereochemistry of the major product.

O

3+2

Please Turn Over

## T(4th Sm.)-Chemistry-H/CC-8/CBCS

(4)

**8.** (a) Suggest structures  $[\underline{\mathbf{F}}]$ ,  $[\underline{\mathbf{G}}]$  and  $[\underline{\mathbf{H}}]$ . Also suggest a mechanism of conversion from  $[\underline{\mathbf{G}}]$  to  $[\underline{\mathbf{H}}]$ .

$$\begin{array}{c|c}
\hline
CH_3NO_2/OEt \\
\hline
\end{array} & \underline{[\mathbf{F}]} & \underline{Sn/conc. \ HCl/\Delta} \\
\hline
\end{array} & \underline{[\mathbf{G}]} & \underline{NaNO_2/dil.HCl} \\
\hline
0^{\circ}-5^{\circ}C \\
\hline
\end{array} & \underline{[\mathbf{H}]}$$

(b) Mention two chemical differences between RCN and RNC.

3+2

- **9.** (a) A compound C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> shows a very strong IR peak at 1720 cm<sup>-1</sup> and only a 6H,s in its <sup>1</sup>H NMR spectrum. Analyse the structure of the compound with proper justification.
  - (b) What type of change is observed in the UV spectrum of mesityl oxide when the solvent is changed from octane to methanol? Justify your answer.

    3+2
- **10.** (a) Mention two criteria for a good protecting group. Using protection and deprotection techniques, outline the following transformation:

(b) Benzaldehyde fails to undergo Dakin's reaction. Account for the observation.

3+2

- 11. (a) Alkyl halides give mainly cyanides with aqueous ethanolic KCN, but with AgCN, isocyanides become the major products. Account for these observations.
  - (b) Very dilute solution of ω-bromo aliphatic acids in butanone on boiling in presence of potassium carbonate give lactones, but concentrated solution of the same give polymeric compounds. Explain.
- 12. (a) Give retrosynthesis and efficient synthesis of the following target molecules:



(b) Depict both retrosynthesis and an efficient forward synthesis of the following compound:

 $(1\frac{1}{2}+1\frac{1}{2})+2$ 

13. (a) Give the product and mechanism of the following reaction:

$$(CH_2)_{16} \underbrace{CO_2Me}_{CO_2Me} \underbrace{Na/xylene}_{Na/xylene}$$

Explain how the addition of Me<sub>3</sub>SiCl benefits the formation of product in the reaction.

(b) Benzidine rearrangement is intramolecular in nature. Justify the statement.

3+2