## 2022

## CHEMISTRY — HONOURS MURALIDHAR GIRLS' COLLEGE

Paper: CC-7

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(Organic Chemistry)

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 number 1 (compulsory) and any eight (08) questions from the rest (from question number 2 to question number 12).

## 1. Answer any ten questions:

1×10

- (a) Acetals are stable to bases. Explain.
- (b) Explain why the following ylide does not participate in Wittig reaction:

(c) Identify the product [A] in the following reaction:

$$\begin{array}{c}
\text{CHO} & 50\% \\
\hline
\text{NaOH} & [A]
\end{array}$$

- (d) What will be the major product when ketene is made to react with HCl?
- (e) In Kolbe's reaction for the synthesis of salicylic acid, NaOH is preferred over KOH. Why?
- (f) Explain why  $\beta$ -hydroxyesters can be prepared by the Reformatsky reaction and not by Grignard reaction.
- (g) How can you accomplish the following conversion?

$$CH = CH_2$$
  $CH_2CH_2OH$ 

(h) Indicate the reagents required for the following conversion:

$$CH_3(CH_2)_4C \equiv CH \rightarrow CH_3(CH_2)_5CHO$$

(i) CF<sub>3</sub>CHO gives a stable hydrate. Explain.

(2)

- (j) When aniline is subjected to Friedel-Crafts alkylation in the presence of catalytic amount of AlCl<sub>3</sub>, alkylation does not occur; while in presence of large excess of AlCl<sub>3</sub>, a very small amount of *m*-alkylaniline is obtained. Explain precisely.
- (k) Ph COOC Me<sub>3</sub>  $\xrightarrow{\text{H}_2\text{O}^{18}}$ ?

Identify the product(s). (Mechanism not needed)

- (1) How can you convert R<sub>2</sub>CHCOOH to R<sub>2</sub>CBrCOOH? (No mechanism required)
- 2. (a) *cis*-2-Butene produces optically inactive racemic 2, 3-butanediol (resolvable) on treatment with *mcpba* followed by acid catalysed hydrolysis; whereas *trans*-2-butene produces optically inactive *meso*-2,3-butanediol (non-resolvable). Justify with plausible mechanism.
  - (b) A six membered cyclic compound gives  $CH_2(CHO)_2$  as the only product of ozonolysis. Identify the compound.
- 3. (a) Reaction of acetone with equivalent proportion of bromine yields monobromoacetone under an acid catalysed condition. Explain with proper reaction mechanism.
  - (b) Predict the product of the following reaction with proper reasonings.

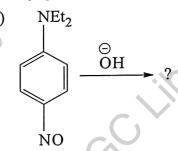
$$CH_2 = C = CH_2 \xrightarrow{HBr} ?$$

3+2

- 4. (a) Give two Wittig alkene synthesis of 2-methyl-1-hexene. Is one synthesis preferred over the other? Why?
  - (b) Carry out the following conversion:

3+2

5. (a) Arrange the following halobenzenes in increasing rate for nitration reaction. Justify your answer.  $C_6H_5$  Br,  $C_6H_5Cl$ ,  $C_6H_5F$ 



Identify the product(s) with proper justification.

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6. (a) Benzene reacts with trimethylacetyl chloride in the presence of anhydrous AlCl<sub>3</sub> at elevated temperatures to give p-tertiarybutylbenzene as one of the products; but toluene with the same reagent, at a lower temperature gives, p-tertiarybutyl acylated product only. Explain the facts showing proper reactions.

(3)

X(3rd Sm.)-Chemistry-H/CC-7/CBCS

(b) Write down the product of the following reaction showing mechanism:

3+2

- 7. (a) Justify with proper mechanism, why m-chlorotoluene on treatment with  $KNH_2/NH_3(l)$  yields m-toluidine in large excess over o- and p-toluidines.
  - (b) Show mechanistically how o-xylene when heated at 80°C with anhydrous AlCl<sub>3</sub> and HCl converts to m-xylene.
- 8. (a) Explain the following reactions:

$$(i) CH_3MgI/dry Et_2O + some$$

$$(i) CH_3MgI/CuCl in Et_2O + (ii) H_3O^{\oplus}$$

(b) Predict the product(s) in each of the following reactions giving plausible mechanistic steps: 3+2

9. (a) Explain the formation of following products with plausible mechanism.

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(4)

(b) Predict the products expected to be formed from the following alkene on treatment with ozone followed by oxidative work up with H<sub>2</sub>O<sub>2</sub>.

- 10. (a) Suggest Corey-House synthesis of 3-methyloctane using Gilman reagent. Why can't alkyllithium reagent be used for this synthesis?
  - (b) Suggest mechanistic steps for the following conversion:

$$\begin{array}{c}
O \\
Me - C - CH = CH - Me + Me
\end{array}$$

$$\begin{array}{c}
O \\
NaOEt
\end{array}$$

$$Me$$

11. (a) Carry out the following transformation mentioning proper reagents and show the plausible mechanism.

- (b) Explain why o-nitrobenzaldehyde undergoes benzoin condensation but p-nitrobenzaldehyde does not. 3+2
- 12. (a) When o-hydroxybenzoic acid is treated with excess Br<sub>2</sub>/H<sub>2</sub>O, a heavy white precipitate settles down with the evolution of a colourless gas. Explain mechanistically the products formed along with proper justification of the course of the reaction.
  - (b) Identify the product with proper mechanism.

PhCHO + BrCH<sub>2</sub>CO<sub>2</sub>Me 
$$\xrightarrow{K^{\oplus} \text{tBu O}/t \text{BuOH}}$$