(2)

Odd Semester, 2020

(Held in March, 2021)

CHEMISTRY

(Honours)

(Chem-H-501)

(Part-B : Organic Chemistry-I)

Marks: 37

Time: 2 hours

The figures in the margin indicate full marks for the questions

- **1.** (a) *p* and *o*-nitrophenols are much more acidic than *m*-nitrophenols. Explain.
 - (b) The pK_b values of the amines are as follows:

Amines	pK_{b}
$\mathrm{CH_3NH_2}$	3.83
$(CH_3)_2NH$	3.28
$(CH_3)_3N$	4.28

Arrange the amines in order of increasing basic strength with proper justification. $1\frac{1}{2}$

(c) Compare the acidity of the following acids giving suitable explanations:
 2 CH₃CH₂—COOH, CH₂=CH—COOH, CH≡C—COOH

(d) Give the products of the following reactions:

(i)
$$\frac{\text{conc. H}_2\text{SO}_4}{160 \text{ °C}}$$
?

(ii)
$$+ \bigcirc O \xrightarrow{\text{xylene}} ?$$

(e) Chloroacetic acid is a stronger acid than acetic acid. Explain. 1½

OR

- **2.** (a) Salicylic acid is a much stronger acid than p-hydroxy benzoic acid. Explain. 2
 - (b) Giving suitable reason, arrange the following dicarboxylic acids in order of increasing acid strength: 1½

 HOOC—COOH, HOOC—CH₂—COOH,
 HOOC—CH₂CH₂—COOH
 - (c) Explain why the C_1 — C_2 bond length of naphthalene is 1·36 Å while the C_2 — C_3 bond length is 140 Å.

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- (d) Prove that naphthalene contains two benzene rings fused together at orthopositions.
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- (e) Starting from naphthalene, how can you prepare 1-naphthol? Give chemical equations.
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- **3.** (a) Draw all the conformers of 1,2-dimethyl cyclohexane. Comment on their relative stability.
 - (b) Explain by using chair conformation, why *t*-butyl group in *t*-butyl cyclohexane always exists in the equatorial form.
 - (c) What are cumulated dienes? Give two examples.
 - (d) Write the structure of the monomers that are employed in the synthesis of terylene.
 - (e) Write the preparation of Nylon-6 from caprolactam. 1½

OR

4. (a) Discuss the stereochemistry of bromine addition to Z-2-butene.

- (b) Assign R- and S-configurations to the following optical isomers: 1+1=2
 - (i) H //////OH
 - СНО (ii) Н — ОН НО — Н СН₂ОН
- (c) Why does HBr add to 1,3-butadiene to give both 1,2- and 1,4-addition products?
- (d) Outline a mechanistic pathway for the acid catalysed cationic addition polymerization of alkylated ethylene.
- (e) What is natural rubber? Write the synthesis of Buna-S rubber. 1½
- **5.** (a) Suggest an acid-catalysed mechanism for the hydrolysis of ester. 2
 - (b) Write the products of the following reactions with mechanisms (any *two*): $1\frac{1}{2}\times2=3$
 - (i) $\begin{array}{c} O \\ \hline O \\ \hline \end{array} \begin{array}{c} (1) \text{ NaOH} \\ \hline (2) \text{ H}_3\text{O}^+ \end{array} ?$

4-21**/470**

(Turn Over)

4-21**/470**

 $1\frac{1}{2}$

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(ii)
$$\stackrel{OH}{\longleftarrow}_{Me} \xrightarrow{H^+}$$
 ?

(iii)
$$+ N_3H \xrightarrow{H_2SO_4}$$
?

(c) What is a Mannich base? Synthesize the following compound by using Mannich reaction:

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(d) Complete the following reaction giving mechanism:

$$\begin{array}{c}
Al(OCHMe_2)_3 \\
\hline
O \\
Me_2CHOH
\end{array}$$

OR

- **6.** (a) How will you synthesize the following compounds? Write mechanisms (any two): $1\frac{1}{2}\times2=3$
 - (i) C_6H_5 C=C COOH by Knoevenagel reaction

(ii)
$$\begin{array}{c} \text{CH}_2\text{CH}_2\text{--CH=O} \\ \text{CH}(\text{COOC}_2\text{H}_5)_2 \end{array}$$
 by Michael addition

(b) What are acetals? Write the product and mechanism of the following reaction: $1+1\frac{1}{2}=2\frac{1}{2}$

$$R C O + H_2O \stackrel{H^+}{\longleftarrow} ?$$

(c) How are the following transformations carried out? Give the mechanism (any one): 1½

(ii)
$$CH_3$$
 OH CCH_3

(d) Complete the following reactions with mechanism (any *one*):

(i) $H_{M_{1}} \stackrel{O}{\longrightarrow} ?$ (ii) $Ph \stackrel{O}{\longrightarrow} C = C \stackrel{HIO_{4}}{\longrightarrow} ?$ $Ph \stackrel{O}{\longrightarrow} Ph \stackrel{O}{\longrightarrow} Ph \stackrel{O}{\longrightarrow} ?$

- **7.** (a) Outline the various steps involved in the synthesis of 1-alkyl iso-quinoline by Bischler-Napieralski method.
 - (b) Write down the products and mechanism of the following reactions:

(i)
$$+ CH_3CH_2CH_2CH_2Li \xrightarrow{CO_2}$$
?

- (c) Why are substitution reactions not atom economical? Illustrate by taking a suitable example. 1+1=2
- (d) How will you carry out the following conversions (any two)? $1\frac{1}{2}\times2=3$

(i)
$$\longrightarrow$$
 \longrightarrow \bigcirc

(ii) $CH_3CH_2NH_2 \xrightarrow{?} CH_3COOH$

(iii)
$$C_6H_5Br \xrightarrow{?} C_6H_5COOH$$

OR

8. (a) Outline the mechanism of the following conversion: $2\frac{1}{2}$

- (b) What are the advantages of using ionic liquids? Give one example of a reaction carried out using ionic liquids. 2+1=3
- (c) Why quinoline does not undergo Friedel-Crafts reaction? 1½
- (d) Identify the missing products in the following reactions: $1\frac{1}{2} \times 2=3$

(i)
$$Sn/HCl > A \frac{NaNO_2/HCl}{0-5 °C} > B \frac{KI}{C} > C$$

(ii)
$$CH_3Cl \xrightarrow{KCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{PCl_5} C$$

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