2019

CHEMISTRY

(Major)

Paper: 5.3

(Organic Chemistry)

Full Marks: 60

Time: 3 hours

The figures in the margin indicate full marks for the questions

1. Answer any seven of the following: $1 \times 7 = 7$

(a) What is the name of the following reaction?

$$RCOOH + HN_3 \xrightarrow{H_2SO_4} RNH_2 + CO_2 + N_2$$

(b) Complete the following reaction:

$$\begin{array}{c|ccccc} CH_3 & CH_3 & \\ CH_3 & CH_3 & \\ & & C \\ &$$

(c) Complete the following reaction:

$$CH_3CH_2COCH_2CH_3 \xrightarrow{?} CH_3CH_2CH_0OH_2CH_3$$

(d) Name the type of the following reaction:

- (e) What is the full form of HOMO?
- (f) Which one is more acidic RSH or ROH?
- (g) Why is furan least aromatic than thiophene?
- (h) Which position of pyridine undergoes electrophilic substitution reaction?
- (i) Why is nitromethane acidic?
- 2. Answer any four of the following questions:

2×4=8

- (a) What happens on boiling an aqueous solution of sodium nitrite with an α-halogen carboxylic acid? Write the reaction.
- (b) What happens when secondary amines react with HNO₂? Write the reaction.
- (c) What happens when aryldiazonium salt is treated with β-naphthol? Write the reaction.

(d) Complete the following reaction:

$$\frac{\text{conc. HNO}_3}{\text{conc. H}_2\text{SO}_4} ?$$

Give the mechanism.

- (e) Draw the tautomers of acetoacetic ester. Which one is more stable and why?
- 3. Answer any three of the following questions:

5×3=15

- (a) How does phenyl acetate undergo intramolecular rearrangement reaction in the presence of AlCl₃? Give mechanism of this reaction. What are the factors on which relative amount of product depends?

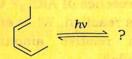
 1+3+1=5
- (b) Complete the following reactions: 1×5=5

(i)
$$H_3C$$
 CH_3 $Pb(OAc)_4$?

Pinacol

20A/281

- OH Pb(OAc)₄ ?
- (iv) $CH_3(CH_2)_4CHO \xrightarrow{?} CH_3(CH_2)_4CH_2OH$
- (v) $CH_3COCI \xrightarrow{LAH}$?
- (c) Which cycloaddition reaction is known as Diels-Alder reaction? Write the product of the following reaction and justify the stereochemistry of the product using FMO method: 1+4=5



- (d) What do you mean by active methylene compound? From ethyl acetoacetate, how will you prepare the following compounds?
 - (i) Cinnamic acid
 - (ii) Monocarboxylic acid
 - (iii) A heterocyclic compound
 - (iv) Butanone

4. Answer the following questions:

10×3=30

5

5

Either

- (a) (i) What happens when ethanal treated with nitroethane in the presence of a base? Write the reaction and give the mechanism.

 Write the Mannich reaction. 1+3+1=5
 - (ii) What are the different products you obtain when nitrobenzene undergoes reduction in alkaline medium? Write the reactions.

Or

- (b) (i) What is exhaustive methylation of amines and Hoffmann's elimination? Discuss with a suitable example.
 - (ii) Explain the following: 1+1+1+2=5
 - 1. Aniline is less basic than N-methyl aniline.
 - 2. Diphenyl amine is a much weaker base than aniline.
 - 3. 2,4,6-trinitroaniline is termed Picramide even though it contains no amide linkage.

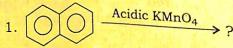
4. Triphenyl amine and N,N-dimethyl aniline are both tertiary amines. Triphenyl amine is insoluble in HCl but N,N-dimethyl aniline readily dissolves in HCl.

Either

- (i) Explain why the electrophilic substitution takes place preferably at α-position in furan, thiophene and pyrrole.
 - (ii) Pyrrole is acidic in character like phenol. Explain. 2
- (iii) Describe nitration of pyridine and justify mechanism of that substitution takes place at position 3.

- Or (d) (i) What are polynuclear hydrocarbons? What are the different types? 1+2=3
 - (ii) Write the Haworth's synthesis of naphthalene. 3

(iii) Give the product with name of the following: $1 \times 4 = 4$



Either

Complete the following, specifying the transformation oxidation as reduction: or $2 \times 5 = 10$

Ph—CH=CH—COOEt AlH₃

(iv) ?
$$\xrightarrow{\text{Pd/H}_2}$$
 RCHC

(v)
$$C = C$$
 $C_2H_5OH \Rightarrow ?$

3

- omen may or (f) (i) Predict the structures for compounds I, II and III: 3 1,3-butadine
 - (ii) What is sigmatropic rearrangement? What do you mean by the order [i, j] of a sigmatropic rearrangement? Give example. 1+1+1=3
 - (iii) Discuss the FMO method of 2 (4+2) cycloaddition reaction.
 - (iv) Write down the Woodward-Hoffmann rules for electrocyclic 2 reaction.