

বিদ্যাসাগর বিশ্ববিদ্যালয় VIDYASAGAR UNIVERSITY

Question Paper

B.Sc. Honours Examinations 2021

(Under CBCS Pattern)

Semester - III

Subject: CHEMISTRY

Paper: C-7 T & P Organic Chemistry - III

Full Marks: 60 (Theory-40 + Practical-20)

Time: 3 Hours

Candiates are required to give their answer in their own words as far as practicable.

The figures in the margin indicate full marks.

THEORY (Marks: 40)

Group - A

Answer any three questions:

12×3=36

- 1. (a) Two ozonides are formed when $Me_2C = CMe_2$ is treated with ozone in presence of HCHO. Give mechanism of the formation of two products.
 - (b) What product can you expect from the following reaction? Depict the stereochemical outcome at every step.

$$CO_2H$$
 $\xrightarrow{Br_2 / Aq. NaOH}$?

- (c) What is meant by σ -complex and π -complex? Draw the energy profile diagram of an aromatic electrophilic substitution reaction which passes through σ -complex and π -complex and formation of σ -complex is rate-limiting. Give experimental evidence for the formation of σ -complex and π -complex.
- (d) Complete the following reaction sequence and give mechanism of formation of B from A.

$$Ph - CH_2 - CHO \xrightarrow{SeO_2} \quad [A] \quad \xrightarrow{1. \text{Conc. NaOH/heat}} \quad [B] \quad 2 + 3 + 5 + 2$$

- 2. (a) Write down the mechanism of cyanide catalyzed benzoin condensation? Why is this reaction hazardous to health? Taking an example show the green alternative reaction of benzoin condensation with mechanism involved.
 - (b) Predict product of the following reaction giving proper justification.

$$\frac{1. \text{Na/liq. NH}_3 \cdot \text{EtOH}}{2. \text{H}_3 \text{O}^+}$$

(c) Explain why ethyl formate condenses with 2-methyl cyclohexanone in the presence of a base to yield (A) and not (B):

3. (a) Why Friedel-Craft alkylation of benzene with 1-chloropropane gives isopropyl benzene? How would you prepare n-propyl benzene from benzene?

(b) Write mechanisms to show the products in the following reaction when:

(i)
$$X = -NO_2$$
 (ii) $X = -OMe$

$$X \longrightarrow Cl$$
 $NaNH_2$ Liq. NH_3

Give Evidences in favour of the mechanisms proposed.

(c) The nitrile (A) can be hydrolyzed very readily to the corresponding amide, B, which is extremely difficult to hydrolyze further. Explain

(d) Identify the structure of A to D in the following reactions schemes.

I) O

OEt

$$(CH_2OH)_2/H^+$$

[A]

 $i. LiAlH_4/THF$
 $ii. H^+/H_2O$

[B]

II)
$$\stackrel{\text{HCHO (excess)}}{\stackrel{\text{NaOH}}{\longrightarrow}} [C] \xrightarrow{\text{HCHO/H}^+} [D]$$
 $2+4+2+4$

4. (a) Suggest plausible mechanism for the following reaction.

(b) Predict the product (s) for the following reaction with plausible mechanism.

(c) Predict the product(s) and give plausible mechanism for its formation:

- (d) How would you introduce aldehyde group in the aromatic nucleus by a reaction involving carbene intermediate? Give mechanism.
- (e) Carry out the following stereospecific transformation.

$$Ph \xrightarrow{\qquad \qquad Ph \qquad \qquad Ph \qquad \qquad Ph \qquad \qquad Ph \qquad \qquad 2+4+2+2+2$$

- 5. (a) Dimethoxy carbene does not readily react with alkenes unless the alkene is substituted with electron withdrawing groups. Propose a suitable explanation for this behaviour.
 - (b) Rationalize the observation that sterically hindered esters are more likely to react via acylium ions than are unhindered ketones.
 - (c) Give necessary reagents to carry out the following transformations and show mechanism.

- (d) Explain the role of Na^+ in NaBH_4 reduction of a ketone i) in aqueous medium and ii) in dry THF medium. 2+2+6+2
- 6. (a) Identify the missing structure of intermediate compound and product for the following reactions.

OMe

s-BuLi, THF

$$-78 \, ^{\circ}\text{C}$$

?

 Ph
 H
 $2. \, H^{+} / \, H_{2}\text{O}$
?

- (b) A student used one mole of PhMgBr and two moles of PhCHO in anhydrous ether to get good yields of benzhydrol, Ph_2CHOH . On working up the reaction mixture with aqueous NH_4Cl , he found different product(s). Identify the product(s) and explain the cause of the reaction.
- (c) By choice reagent, how would you carry out the direct addition (route A) and conjugate addition (route B)?

(d) Write down the products of the following reactions showing the plausible mechanism in each case.

(I)
$$\stackrel{i) \text{ Na/Xylene}}{\longleftarrow}$$
 $\stackrel{O}{\longleftarrow}$ OR^1 $\stackrel{i) \text{ Na/EtOH/heat}}{\longmapsto}$ (II)

(III)
$$\stackrel{\text{i) Zn/THF/reflux}}{\text{ii) H}_3\text{O}^+}$$
 $\stackrel{\text{O}}{\text{Ph}}$ $\stackrel{\text{H}}{\text{H}}$ $\stackrel{\text{Er}}{\text{CO}_2\text{Et}}$ $\stackrel{\text{i) NaOEt}}{\text{ii) H}_3\text{O}^+}$ (IV)

2+3+3+4

Group - B

7. Answer any **two** questions:

 $2 \times 2 = 4$

(a) Predict the product of the following reaction with mechanism.

- (b) What happens when PhMgBr is reacted with excess oxygen followed by acidification with dilute aq. Acid?
- (c) Taking an example write down the mechanism of Vilsmeier-Haack formylation reaction.
- (d) Identify the structure of A and B in the following reaction.

$$A \stackrel{\text{Me}_2\text{CuLi}}{\longleftarrow} B$$

$$O \longrightarrow O \longrightarrow O$$

$$O \longrightarrow O$$

PRACTICAL (Marks: 20)

Paper: C-7 P

Group - A

Answer any one question:

 $15 \times 1 = 15$

1. Analyse any one of the following compounds (marked as O_i) covering the points given below :

$$O_1$$
: O_2 : O_3 : O_3 : O_3 : O_3 :

- (i) Detection of special element (write positive test only) with concluding remarks.
- (ii) Solubility tests and concluding remarks.
- (iii) Identification of functional groups (write positive test only) with concluding remarks.
- (iv) Preparation of suitable derivative: Name of derivative, chemical reaction involved and its experimental procedure.

Group - B

Answer any one question:

 $5 \times 1 = 5$

- 2. During determination of melting point, why an organic compound melts over a 3-4-degree range (for example, m. pt. = 54-54 °C) and how is the melting point indicating purity of compound?
- 3. Why is it necessary to prepare suitable "derivative" of unknown organic compounds for its identification? What are the criteria considered for choosing suitable derivative of an organic compound?
- 4. Two compounds, A and B, have the same melting point. How can you determine if they are the same without using spectroscopic method of identification? Explain in detail.