TEXT BOOK OF

ORGANIC CHEMISTRY

(Paper VIII : DSC - D4)
B.Sc. Part II : Semester IV

As per New Revised Choice Based Credit System (CBCS)
Syllabus of Shivaji University, Kolhapur, w.e.f. June 2019

Dr. PRAVINA B. PISTE
M.Sc., Ph.D.
Associate Professor at Y.C. Institute
of Science, Satara.
PG Recognized Teacher, Research Guide.

Dr. ARJUN S. KUMBHAR
M.Sc., Ph.D.
Associate Professor,
P.G. Recognized Teacher, Research Guide,
P.D.V.P. College, Tasgaon. Dist. - Sangli

Dr. DNYANDEV N. ZAMBARE
M.Sc., Ph.D.
Professor,
P.G. Recognized Teacher, Research Guide,
Department of Chemistry,
Kisanveer Mahavidyalaya, Wai.

Dr. AVINASH M. NALAWADE
M.Sc., M.Phil, Ph.D.
Assistant Professor,
P.G. Recognized Teacher, Research Guide,
Lal Bahadur Shastri College, Satara

Dr. C. P. MANE
M.Sc., Ph.D.
Head, P.G. Recognized Teacher,
Research Guide, Department of Chemistry,
Lal Bahadur Shastri College, Satara.

Price : ₹ 60.00

NIRALI PRAKASHAN
ADVANCEMENT OF KNOWLEDGE

N4829

B.Sc. - II : ORGANIC CHEMISTRY (P-VIII) (Sem. - IV)

First Edition : December 2019 **ISBN 978-93-89686-68-5**

Published By :
NIRALI PRAKASHAN
Abhyudaya Pragati, 1312, Shivaji Nagar,
Off J.M. Road, PUNE – 411005
Tel - (020) 25512336/37/39, Fax - (020) 25511379
Email : niralipune@pragationline.com

Polyplate

Printed By :
YOGIRAJ PRINTERS AND BINDERS
Works: Sr. No. 10\1,Ghule Industrial Estate,
Nanded Village Road,
TAL-HAVELI, DIT-PUNE 411041.
Mobile - 9850046517, 9404225254

➢ DISTRIBUTION CENTRES

PUNE

Nirali Prakashan : 119, Budhwar Peth, Jogeshwari Mandir Lane,
Pune 411002, Maharashtra. Tel : (020) 2445 2044,
Email : bookorder@pragationline.com,
niralilocal@pragationline.com

Nirali Prakashan : S. No. 28/27, Dhyari, Near Pari Company, Pune 411041
Tel : (020) 24690204 Fax : (020) 24690316
Email : dhyari@pragationline.com,
bookorder@pragationline.com

MUMBAI

Nirali Prakashan : 385, S.V.P. Road, Rasdhara Co-op. Hsg. Society Ltd.,
Girgaum, Mumbai 400004, Maharashtra
Tel : (022) 2385 6339 / 2386 9976, Fax : (022) 2386 9976
Email : niralimumbai@pragationline.com

➢ DISTRIBUTION BRANCHES

JALGAON

Nirali Prakashan : 34, V. V. Golani Market, Navi Peth, Jalgaon 425001,
Maharashtra, Tel : (0257) 222 0395, Mob : 94234 91860

KOLHAPUR

Nirali Prakashan : New Mahadvar Road, Kedar Plaza, 1st Floor Opp. IDBI Bank
Kolhapur 416 012, Maharashtra. Mob : 9850046155

NAGPUR

Nirali Prakashan : Above Maratha Mandir, Shop No. 3, First Floor,
Rani Jhanshi Square, Sitabuldi, Nagpur 440012, Maharashtra
Tel : (0712) 254 7129;
Email : niralinagpur@pragationline.com

DELHI

Nirali Prakashan : 4593/15, Basement, Agarwal Lane, Ansari Road, Daryaganj
Near Times of India Building, New Delhi 110002
Mob : 08505972553

BENGALURU

Nirali Prakashan : Maitri Ground Floor, Jaya Apartments, No. 99, 6th Cross,
6th Main, Malleswaram, Bangaluru 560 003, Karnataka
Mob : +91 9449043034
Email: niralibangalore@pragationline.com

Other Branches : Hyderabad, Chennai

SYLLABUS

Unit 1 : Carboxylic Acids and their Derivatives (8 L)

1.1 Monocarboxylic acid: Introduction, Methods of Formation from Alcohols, Aldehydes, Ketones, Nitriles and Alkyl benzenes. Chemical Reaction: Hell-Volhard-Zelinsky (HVZ) reaction.

1.2 Formation of Halo Acids: Mono, Di, Tri- chloro acetic acid. Substitution reactions of Monochloro acetic acid by Nucleophile OH^-, I^-, CN^- and NH_3

1.3 Hydroxy acids: Malic and Citric acid. Methods of formation of Malic acid from maleic acid, from Alpha bromo succinic acid and moist Ag_2O. Chemical Reactions: Reactions of Malic acid-Action of heat, oxidation by $KMnO_4$ and reduction reaction with HI. Uses of Malic acid. Method of formation of Citric acid from glycerol. Chemical Reactions: Reaction of citric acid: Acetylation by acetic anhydride, reduction by HI, action of heat. Uses of citric acid.

1.4 Unsaturated acid: Cinnamic acid: Methods of formation from benzaldehyde using diethyl malonate and by using acetic anhydride and sodium acetate. Chemical Reactions-Bromination, Oxidation. Uses of cinnamic acid. Acrylic acid: Method of formation from acrolein and by dehydration of beta hydroxy propionic acid. Chemical Reactions: Addition of water, Reduction by Na/C_2H_5OH. Uses of acrylic acid.

1.5 Dicarboxylic acid: Succinic and phthalic acid. Method of formation of succinic acid from ethylene dibromide, maleic acid. Chemical Reactions: Action of heat, Action of $NaHCO_3$, C_2H_5OH in the presence of acid. Uses of succinic acid. Phthalic acid: Method of formation from o-xylene and Naphthalene. Chemical Reactions: Action of heat, reaction with sodalime, ammonia. Uses of phthalic acid.

1.6 Carboxylic acid derivatives: Introduction Acid halide derivative: Acetyl chloride: formation from acid, by action with PCl_3 and $SOCl_2$, reaction with water, alcohol (Mechanism of esterification is expected) and ammonia. Uses of acetyl choride. Acid anhydride derivative: Method of formation of acetic anhydride by dehydration of acetic acid, reactions with water, alcohol and ammonia. Uses of acetic anhydride.

Unit 2 : Amines and Diazonium Salts (8 L)

2.1 Introduction, Classification, Nomenclature, Structure.

2.2 Methods of preparation: (a) From alkyl halide by ammonolysis, (b) By reduction of nitriles or cyanides, (c) From unsubstituted amides (Hoffmann degradation), (d) By Gabriel synthesis (from phthalimide).

2.3 Reactions: Carbylamine reaction, Schotten-Baumann reaction, Electrophilic substitution (Aniline), Nitration, Bromination, Sulphonation.

2.4 Diazonium salt: Introduction, Preparation of Benzene diazonium chloride.

2.5 Reactions: Replacement by Halogen (Sandmeyer), Replacement by Iodine, Replacement by –OH, C and N. Coupling reactions: Synthesis of Methyl Orange and Congo Red. Reduction of BDC.

Unit 3 : Carbohydrates (8 L)

Classification of carbohydrates, Reducing and non-reducing sugars, General properties of glucose and fructose, their open chain structure. Epimers, mutarotation and anomers.

Determination of configuration of Glucose (Fischer proof). Ring structure of glucose. Determination of size of the ring of Glucose by methylation method. Haworth projections. Cyclic structure of fructose. Linkage between monosachharides, structure of disaccharides (sucrose, maltose, lactose) and polysaccharides (starch and cellulose), excluding their structure elucidation.

Unit 4 : Carbonyl Compounds - Aldehydes and Ketone (6 L)

4.1 Introduction, Nomenclature, Structure.

4.2 Reactivity of Carbonyl group, Mechanism of nucleophilic addition to carbonyl group.

4.3 Reactions: Mechanism and application of Aldol condensation, Perkin reaction, Cannizzaro's reaction, Knoevenagel condensation, Reformatsky reaction.

Unit 5 : Stereochemistry (8 L)

5.1 Conformational isomerism – Introduction.

5.2 Representation of conformations of ethane by using Saw-Horse, Fischer (dotted line wedge) and Newman's projection formulae.

5.3 Conformations and conformational analysis of ethane and n-butane by Newman's projection formula with the help of energy profile diagrams.

5.4 Cycloalkanes relative stability - Baeyer's strain theory, Theory of strainless rings.

5.5 Conformations and stability of cyclohexane and monosubstituted cyclohexanes: Cyclohexanol, bromocyclo-hexane and methyl cyclohexane.

5.6 Locking of conformation in t-butyl cyclohexane.

***

B.Sc. II Revised Syllabus 2018-19

Semester III and IV Nature of Question Paper

Total Marks 50

Q. 1 (a) Answer the following in one sentence: **(5)**

i)

ii)

iii)

iv)

v)

(b) Choose the correct alternative and rewrite the sentence again: **(5)**

I)

II)

III)

IV)

V)

Q. 2 Attempt any TWO of the following (Out of FOUR): **(20)**

a)

b)

c)

d)

Q. 3 Answer any FOUR of the following (Out of SIX): **(20)**

a)

b)

c)

d)

e)

f)

***

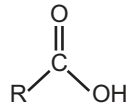
Chapter **1**...

Carboxylic Acids and Their Derivatives

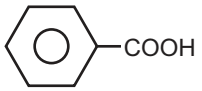
Contents ...

Introduction

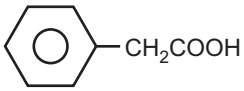
It is a group of an organic compound containing a carboxylic group (−COOH). Carboxylic acid contains a carbonyl group to which the hydroxyl group is attached. The general formula of the group is R−COOH. In the formula, R denotes the rest of the group attached to the functional group. This carboxylic group may be attached to hydrogen (HCOOH), an alkyl group (RCOOH), or an aryl group (ArCOOH). The structure of carboxylic acid is



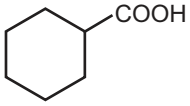
HCOOH	CH_3COOH	$CH_3(CH_2)_{10}COOH$
Formic acid	Acetic acid	Lauric acid
(Methanoic acid)	(Ethanoic acid)	(Dodecanoic acid)



Benzoic acid



Phenyl acetic acid



Cyclohexane carboxylic acid

The classification of carboxylic acids is based on the number of –COOH groups present in the molecule as mono-, di-, tri-, or poly carboxylic acid. If carboxylic acid contain halogen atom then it is called as haloacid and if it contain –OH group then it is called as hydroxy acid. When it contain double bond then it is called as unsaturated acid.

1.1 Monocarboxylic Acid

The molecule which contain only one –COOH group is called as monocarboxylic acid.

Lower straight chain aliphatic carboxylic acids as well as those of even carbon upto C_{18} are commercially available. e.g. acetic acid is produced by methanol carbonylation with carbon monoxide. Whereas long chain carboxylic acids are obtained by the hydrolysis of triglycerides obtained from plant or animal oils. Vinegar, a dilute solution of acetic acid is biologically produced from the fermentation of ethanol.

The aliphatic carboxylic acids have been known from the ancient time and named according to their sources rather than to their chemical structure. e.g. Formic acid adds the sting to the bite of an ant (Latin : Formica – ant), butyric acid gives rancid butter its typical smell (Latin : butyrum – butter); and caproic, caprylic and capric acids all are found in goat fat (Latin : Caper – goat).

Some of the examples of carboxylic acids have been given below in Table 1.1.

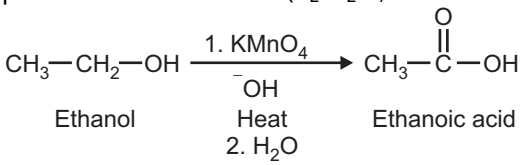
Table 1.1

Name of the compound	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$CH_3.CH_2.COOH$	Propionic acid	Propanoic acid
$CH_3.CH_2.CH_2.COOH$	Butyric acid	Butanoic acid

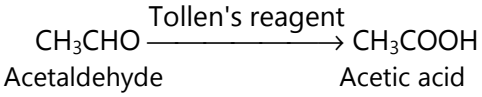
1.1.1 Methods of Formation

There are different methods used in preparation of monocarboxylic acids. Some of them are,

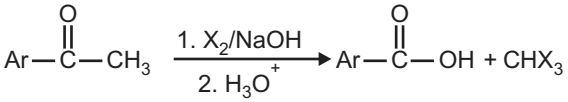
1. From Alcohols: Primary alcohols can undergo oxidation reaction to form corresponding carboxylic acids with the help of oxidizing agents such as potassium permanganate ($KMnO_4$ for neutral or acidic or alkaline media), chromium trioxide (CrO_3 /H_2SO_4 Jones reagent), and potassium dichromate ($K_2Cr_2O_7$ acidic media).



2. From Aldehydes: Aldehydes with mild oxidizing agents such as Tollen's reagents [$Ag(NH_3)_2^+OH^-$] and manganese dioxide (MnO_2) give monocarboxylic acid.



3. Ketones: Methyl ketones can be converted to carboxylic acids via. the haloform reaction.



4. Hydrolysis of Nitriles (Cyanides): Aliphatic nitriles are prepared by treatment of alkyl halides with sodium cyanide in a solvent that will dissolve both reactants. In dimethyl sulfoxide (DMSO), reaction occurs rapidly and exothermically at room temperature. The resulting nitrile is then hydrolysed to the acid by boiling with aqueous alkali or acid.

$$R - C \equiv N \xrightarrow[H^+ / HOH]{\text{Acid hydrolysis}} R \cdot COOH + NH_2$$

Example:

$$Br - CH_2 - CH_2 - CH_2 - Br \xrightarrow{NaCN} NC - CH_2 - CH_2 - CH_2 - CN$$

Pentane dinitrile

$$\xrightarrow{H_3O^+} HO_2C - CH_2 - CH_2 - CH_2 - CO_2H$$

Glutaric acid

This synthetic method is generally limited to the use of primary alkyl halides. Aryl halides (except for those with ortho and para nitro groups) do not react with sodium cyanide. Just like Grignard synthesis, nitrile synthesis also increases the length of carbon chain.

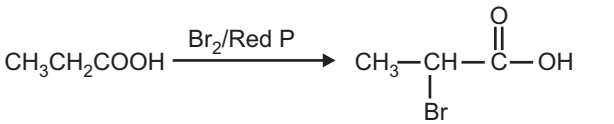
5. Oxidation of Alkyl benzenes: Strong oxidation of alkyl benzenes also result in the formation of carboxylic acids.

$$Ar - R \xrightarrow{KMnO_4} Ar - COOH$$

Example: $NO_2 - C_6H_5 - CH_3 \xrightarrow{KMnO_4} NO_2 - C_6H_5 - COOH$

1.1.2 Chemical Reaction

1. Hell-Volhard-Zelinski reaction: Aliphatic carboxylic acids on reaction with bromine in the presence of phosphorus produce halo acids. This reaction is known as Hell-Volhard-Zelinski (HVZ) reaction.



Propanoic acid 2-Bromopropanoic acid

1.2 Halo Acids

If acid contain halogen atom then it is called as Halo acid. Depending upon the position of halogen atom on α, β, γ carbon atom with respect to carboxylic acid, they are classified as α-halo acid, β-halo acid, γ-halo acid respectively.

1.2.1 Methods of Formation of Halo Acids

Synthesis of mono-, di- and trichloro acetic acid have been carried out by different methods.

(A) Methods of formation of Monochloro acetic acid:

It can be prepared with the help of following methods:

1. Hell-Volhard-Zelinski reaction: The reaction of aliphatic carboxylic acids with bromine/chlorine in the presence of red phosphorus in direct sunlight at 373 K produces α halo acids. This reaction is **Hell-Volhard-Zelinski reaction**.

$$CH_3COOH + Cl_2 \xrightarrow[\text{Direct sunlight}]{\text{Red P / 373 K}} Cl \cdot CH_2 - COOH + HCl$$

Acetic acid Monochloro acetic acid

2. From Ethylene chlorohydrine: This method is used in laboratory or in industry. The oxidation of ethylene chlorohydrine with nitric acid gives monochloro acetic acid.

$$OH - CH_2 - CH_2 - Cl \xrightarrow[HNO_3]{[O]} Cl \cdot CH_2 - COOH$$

Ethylene chlorohydrine Monochloro acetic acid

3. From Trichloro ethylene: When trichloro ethylene agitating with 90% sulphuric acid gives monochloro acetic acid.

$$Cl_2C = CHCl \xrightarrow{90\%\ H_2SO_4} Cl \cdot CH_2 - COOH$$

Trichloro ethylene Monochloro acetic acid

(B) Dichloro acetic acid:

It is a colourless liquid having boiling point 193°C. It is soluble in water and ethanol and having 1.25 pK_a value.

Methods of Formation:

It has been prepared by following methods:

1. Hell-Vohlard-Zelinsky method: When acetic acid is treated with excess amount of chlorine in direct sunlight in the presence of red phosphorus at 373 K, it gives dichloro acetic acid.

$$CH_3COOH + 2Cl_2 \xrightarrow[\text{Direct sunlight}]{\text{Red P / 373 K}} Cl_2 \cdot CH - COOH + 2HCl$$

Acetic acid Dichloro acetic acid

2. From Chloral hydrate: When chloral hydrate is treated with calcium carbonate in the presence of sodium cyanide, it gives Ca-salt of acid which on further acidification with H_2SO_4 gives dichloro acetic acid.

$$2CCl_3\text{-}CH(OH)_2 + 2CaCO_3 \xrightarrow{NaCN} (Cl_2CHCOO)_2Ca + CaCl_2 + H_2O + 2CO_2$$

Chloral hydrate

$$(Cl_2CHCOO)_2Ca \xrightarrow{H_2SO_4 \mid H^+} 2Cl_2CH.COOH + CaSO_4$$

Dichloro acetic acid

(C) Trichloro acetic acid:

It is a colourless deliquescent solid having melting point 57.5°C. It is soluble in water, ethanol and ether. It is strongly corrosive to skin.

Methods of Formation:

It has been prepared by following methods:

1. Hell-Vohlard-Zelinsky method: When acetic acid is treated with excess amount of chlorine in direct sunlight in the presence of red phosphorus at 373 K, it gives trichloro acetic acid.

$$CH_3COOH + 3Cl_2 \xrightarrow[\text{Direct sunlight}]{\text{Red P / 373 K}} Cl_3C - COOH + 2HCl$$

Acetic acid Trichloro acetic acid

2. When oxidation of chloral with nitric acid is carried out it gives trichloro acetic acid.

$$CCl_3CHO \xrightarrow[HNO_3]{[O]} Cl_3C - COOH$$

Chloral Trichloro acetic acid