The -C-OH group, which apparently contains a carbonyl group, fails to show the reactivities of carbonyl compounds and acts as a separate functional group called carboxylic acid group.

1. Nomenclature

0

These are normally suffixed as "oic acid", when CO₂H is the principal functional group and its carbon is counted while numbering longest chain. The carboxyl carbon is assigned number 1 in the IUPAC nomenclature. For example,

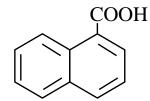
4-Methylhexanoic acid

Name of the alkane without (-e)

Formic acid is called as methanoic acid and CH₃CH=CHCH₂COOH is called as 4–hexenoic acid.

When CO₂H group is the main functional group but its carbon is not counted while selecting longest chain, then the suffix used is "carboxylic acid". For example,

Benzene carboxylic acid



Naphthalene-1-carboxylic acid

Naphthalene-2-carboxylic acid

$$CO_2H$$

Cyclohexane carboxylic acid

If an unbranched chain is directly linked to more than 2 CO₂H groups, these groups are named from the parent hydride by substitutive use of a suffix such as "tricarboxylic acid".

$$CO_2H$$
 CO_2H

Pentane-1,3,5-tricarboxylic acid

When all carboxylic acid groups cannot be described in the suffix, a carboxylic acid group is indicated by the prefix "carboxy".

3-(Carboxymethyl)heptanedioic acid

Dicarboxylic acids are named as "alkanedioic acids". For example, COOH is named as ethanedioic acid, HO₂C-CH₂-CO₂H is named as propanedioic acid and HO₂C-CH₂-CO₂H is named as butane-1,4-dioic acid.

Esters:

According to IUPAC nomenclature, esters are named as "alkyl alkanoate". For example,

$$\begin{array}{c} O \\ II \\ CH_3-C-OCH_2CH_3 \\ Ethyl \ ethanoate \\ \end{array} \begin{array}{c} O \\ II \\ CH_3CH_2-C-O-C_-CH_3 \\ CH_3 \\ \end{array}$$

$$NO_2 \stackrel{4}{\swarrow} \stackrel{O}{\underset{3}{\swarrow}} \stackrel{O}{\underset{2}{\swarrow}} C-OCH_3 \quad C_2H_5 \stackrel{O}{\longleftrightarrow} O \stackrel{O}{\longleftrightarrow} CH_3$$

Methyl-4-nitrobenzoate

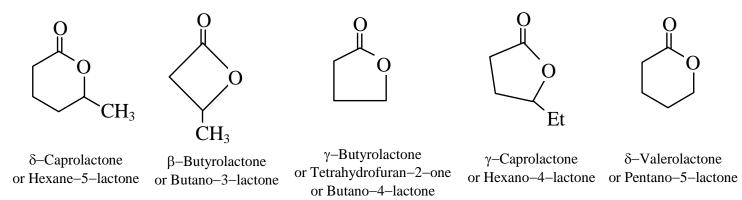
Ethyl methyl malonate

When ester is the main functional group but its carbon is not counted while selecting the longest chain, then the name of the ester is written as "Alkyl alkane carboxylate".

$$CO-OC_2H_5$$

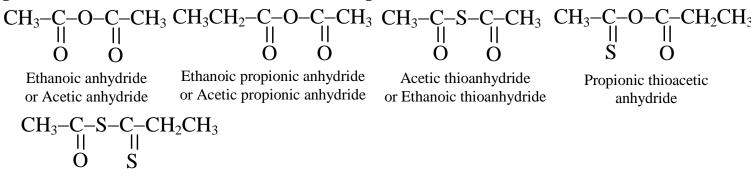
Ethyl cyclohexane carboxylate

Lactones are named by replacing "lactone" for the "ic acid" ending of a systematic "-oic acid" name for the non-hydroxylated parent acid and inserting a locant designating the position of OH group between the "o" and "lactone".



Carboxylic acid anhydride:

Carboxylic acid anhydrides are named as "alkanoic anhydride" (if only one type of alkyl group is present) but when two different alkyl groups are present, then alkanoic are named in alphabetical order.



Acetic thiopropionic thioanhydride

When anhydride group is the main functional group but its carbon is not counted while selecting longest chain, then the suffix used is "carboxylic anhydride". For example,

$$\left(\begin{array}{c} \\ \\ \end{array} \right)$$
 CO $\left(\begin{array}{c} \\ \\ \end{array} \right)$ O

Cyclohexanecarboxylic anhydride

Acid halide:

According to IUPAC nomenclature, acid halides are named as "alkanoyl halide". For example, CH₃COCl is named ethanoyl chloride or acetyl chloride and CH₃CH₂COCl is called propanoyl chloride.

$$CH_3$$
 CH_3
 CH_3
 CH_2
 CH_3
 CH_3

Acetyl chloride or Ethanoyl chloride

Hexanoyl bromide

Malonyl bromide chloride

When COX group is the main functional group but its carbon is not counted while selecting the longest chain, then the suffix used is "carbonyl halide". For example,



Cyclopentane carbonyl chloride

Cyclohexane carbothioyl chloride

Acid amide:

According to IUPAC nomenclature, primary acid amides are named as "alkanamide".

For example, CH₃CONH₂ is named acetamide or ethanamide and CH₃CH₂CONH₂ is called propanamide.

$$CH_3$$

Hexanamide

When CONH₂ group is the main functional group but its carbon is not counted while selecting the longest chain, then the suffix used is "carboxamide". For example,

$$CONH_2$$
 $CONH_2$ Cyclohexanecarboxamide

According to IUPAC nomenclature, secondary acid amides are named as N-alkyl alkanamide and tertiary acid amides are named as N,N-dialkyl alkanamide, if identical substituents are present but when the substituents present are different they are to be named in alphabetical order.

$$CH_{3}CH_{2}-C-NH - \bigcirc$$

$$N-Cyclohexylpropanamide$$

$$O CH_{2}CH_{3}$$

$$CH_{3}CH_{2}CH_{2}-C-N-CH_{2}CH_{3}$$

$$N,N-Diethylbutanamide$$

$$CH_{3}CH_{2}-CH_{2}-C-N-CH_{2}CH_{3}$$

$$CH_{3}CH_{2}-CH_{2}-C-N-CH_{2}CH_{3}$$

$$CH_{3}$$

$$N-Ethyl-N-methylpentanamide$$

Cyclic amides (lactam) are named just as lactones by replacing "lactone" in the name by "lactam".

$$\begin{array}{c} O \\ \hline NH \\ \hline \delta-Valerolactam \\ or \ Pentano-5 \ -lactam \\ \end{array}$$

Tautomeric forms of lactam are called "lactim".

2. Carboxylic Acids

2.1 Preparation of Carboxylic Acids

1. By oxidation of alkenes

When alkenes are treated with an oxidising agent such as KMnO₄ or on oxidative ozonolysis, it forms carboxylic acids.

RCH=CHR'
$$\xrightarrow{\text{(i) KMnO}_4/\text{OH}^-, heat}$$
 RCO₂H + R'CO₂H

RCH=CHR'
$$\xrightarrow{\text{(i) O}_3}$$
 RCO₂H + R'CO₂H

2. By oxidation of aldehydes or primary alcohols

When aldehydes are reacted with Ag₂O, H₃O⁺ or with acidified of alkaline KMnO₄, it forms carboxylic acids.

$$\text{R-CHO} \xrightarrow{\text{(i) Ag}_2\text{O}} \text{RCOOH} \; ; \; \text{RCHO} \xrightarrow{\text{(i) KMnO}_4/\text{OH}^-} \text{RCO}_2\text{H}$$

Primary alcohols can be oxidised to carboxylic acids by acidified K₂Cr₂O₇ or acidified/alkaline KMnO₄.

$$RCH_2OH \xrightarrow{(i) \text{ KMnO}_4/OH^-} RCO_2H$$

3. By oxidation of alkyl benzene (for aromatic acids)

When the arenes containing an α -hydrogen atom are reacted with a strong oxidising agent like alkaline KMnO₄, it forms benzoic acid.

$$\begin{array}{c}
CH_{3} & COOH \\
\hline
(i) \text{ KMnO}_{4} / \text{OH}^{-} \\
\hline
(ii) \text{ H}_{3}\text{O}^{\oplus} \\
\hline
(ii) \text{ KMnO}_{4} / \text{OH}^{-} \\
\hline
(ii) \text{ H}_{3}\text{O}^{\oplus} \\
\hline
(ii) \text{ H}_{3}\text{O}^{\oplus} \\
\hline
(ii) \text{ KMnO}_{4} / \text{OH}^{-} \\
\hline
(ii) \text{ KMnO}_{4} / \text{OH}^{-} \\
\hline
(ii) \text{ KMnO}_{4} / \text{OH}^{-} \\
\hline
(iii) \text{ H}_{3}\text{O}^{\oplus} \\
\hline
\end{array}$$

4. Using Grignard reagent

When Grignard reagent is reacted with CO₂, the alkyl part of RMgX reacts at the carbon of CO₂ to form magnesium salt of carboxylate, which on acid hydrolysis gives carboxylic acid.

$$R-Br \xrightarrow{Mg} R-MgBr \xrightarrow{CO_2} RCO_2^{\ominus}MgBr \xrightarrow{H_3O^{\oplus}} RCO_2H$$

For example,

$$CH_3$$
-Br \xrightarrow{Mg} CH_3 -MgBr

$$CH_{3}-MgBr + O=C=O$$

$$CH_{3}-C-O^{-}MgBr \xrightarrow{H_{3}O^{+}} CH_{3}-C-OH$$

5. By cyanide formation and hydrolysis

$$R-Br \xrightarrow{CN^{\Theta}} R-CN \xrightarrow{H_3O^{\oplus}} R-CONH_2 \xrightarrow{H_3O^{\oplus}} R-CO_2H$$
hydrolysis

The alkyl cyanides can be hydrolysed by acids as well as by bases to give carboxylic acid and acid carboxylate respectively.

The mechanism of acid–catalysed hydrolysis of R–CN is as follows:

$$R-C \equiv N \xrightarrow{H^{\oplus}} R-C \stackrel{\bigoplus}{=} NH \xrightarrow{H_2O:} R-C = NH \xrightarrow{H_2O:} R-C = NH_2 \xrightarrow{\bigoplus} R$$

6. Decarboxylation of gemdicarboxylic acid

Monocarboxylic acids may also result from the decarboxylation of dicarboxylic acids (when the two CO₂H groups are present on same carbon). Acetic acid is thus obtained by heating/warming malonic acid.

$$H_2C$$
 $COOH$
 $COOH$
 $COOH$
 $COOH$
 $COOH$

7. Hydrolysis of acid derivatives

Another useful method constitutes the hydrolysis of carboxylic acid derivatives such as acyl halides, acid amides, acid anhydrides or esters.

$$CH_{3}CH_{2}-C-CI \xrightarrow{H_{2}O/H^{+}} CH_{3}CH_{2}COOH + HCI$$

$$CH_{3}CH_{2}-C \xrightarrow{H_{2}O/H^{+}} CH_{3}CH_{2}COOH + NH_{4}^{+}$$

$$CH_{3}CH_{2}-C-O-C-CH_{2}CH_{3} \xrightarrow{H_{2}O/H^{+}} 2CH_{3}CH_{2}CO_{2}H$$

$$CH_{3}CH_{2}-C-OCH_{3} \xrightarrow{H_{2}O/H^{+}} CH_{3}CH_{2}CO_{2}H + CH_{3}OH$$

$$CH_{3}CH_{2}-C-OCH_{3} \xrightarrow{H_{2}O/H^{+}} CH_{3}CH_{2}CO_{2}H + CH_{3}OH$$

8. By the Oxidation of Methyl Ketones

Oxidation of -C-CH₃ group with sodium hypochlorite (NaOH + Cl₂) results in a carboxyl group formation.

It is a specific reagent for this group. The reaction is commonly called "haloform reaction".

2.3 Chemical Reactions

The most important properties of carboxylic acids are their conversion to important functional derivatives. The reactions of carboxylic acids may be discussed under the following categories.

(a) Reactions involving the -OH group.

- (b) Reactions involving the C=O group.
- (c) Reactions involving the –COOH group.
- (d) Reactions involving the aliphatic moiety.
- **1.** Carboxylic acids react rapidly with aqueous solutions of sodium hydroxide or potassium carbonate to form soluble salts.

$$CH_3CH_3COOH + NaOH \longrightarrow CH_3CH_2COO^-Na^+ + H_2O$$

Propionic acid

Sodium propionate

$$2CH_3CH_2COOH + K_2CO_3 \longrightarrow 2CH_3CH_2COO^-K^+ + H_2O + CO_2$$

Propionic acid

Potassium propionate

Aqueous solutions of these salts are alkaline, they being salts of a strong base and a weak acid. The sodium or potassium salts of long chain fatty acids are known as "soaps".

2. Symmetrical anhydrides are obtained by heating together a carboxylic acid and acetic anhydride. Acetic anhydride, however, is prepared by a special method from ketene and acetic acid.

$$2CH_{3}CH_{2}-C \xrightarrow{O} \xrightarrow{Ac_{2}O, 140^{\circ}} CH_{3}CH_{2}-C \xrightarrow{O} CH_{3}CH_{2}-C \xrightarrow{O} CH_{3}CH_{2}-C \xrightarrow{O} CH_{3}CH_{2}-C \xrightarrow{O} CH_{3}-C \xrightarrow{O} CH_{3$$

Acetic anhydride

3. Reaction with Diazomethane:

A synthetically useful reaction of carboxylic acid is the formation of methyl esters by reaction with diazomethane (CH_2N_2) .

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2 \uparrow$$

4. With LiAlH₄ or NaBH₄

R-COOH
$$\xrightarrow{\text{LiAlH }_4}$$
 RCH₂OH
CH₃CH=CHCH₂COOH $\xrightarrow{\text{LiAlH }_4}$ CH₃CH=CHCH₂CH₂OH

5. With PCl₃ or PCl₅ or SOCl₂

$$\begin{array}{ccc}
O \\
R-C-OH & \xrightarrow{PCl_3 \text{ or } PCl_5} & O \\
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With PCl₃, H₃PO₃; with PCl₅, POCl₃ and with SOCl₂, SO₂ are the other products.

6. With ROH and NH₃

PhCH₂COOH
$$\xrightarrow{\text{CH}_3\text{OH}}$$
 PhCH₂-C-OCH₃ Methyl ester

PhCH₂COO⁺NH₄
$$\xrightarrow{\text{NH}_3}$$
 PhCH₂COO⁻NH₄ $\xrightarrow{\text{Heat}}$ PhCH₂CONH₂ + H₂O.

Mechanism of esterification by acid catalysis:

A direct reaction between a carboxylic acid and alcohol under the catalytic effect of sulphuric acid yields an ester. This is a reversible reaction and is known as the "Fischer esterification".

$$R-C \stackrel{\ddot{O}:}{\bigcirc OH} + H^{+} \stackrel{Fast}{=} \stackrel{\bullet}{\longrightarrow} \stackrel{\bullet}{R-C} \stackrel{\bullet}{\longleftrightarrow} \stackrel{O-H}{\longleftrightarrow} \stackrel{O-H}{\longleftrightarrow} \stackrel{OH}{\longleftrightarrow} \stackrel{OH}{\longleftrightarrow} \stackrel{O-H}{\longleftrightarrow} \stackrel{$$

Base catalysed esterification is very rare. Molecularity of the above esterification reaction is two.

7. Conc. H₂SO₄ treatment

$$\begin{array}{c} \text{CH}_{3}\text{--}\text{C} \stackrel{O}{\longleftrightarrow} \frac{\text{H}_{2}\text{SO}_{4}}{\text{Warming}} & \text{No reaction}; \\ \text{H--C} \stackrel{O}{\longleftrightarrow} \frac{\text{H}_{2}\text{SO}_{4}}{\text{Warming}} & \text{CO} \uparrow + \text{H}_{2}\text{O} \\ \\ \text{Glacial CH}_{3}\text{COOH} & \xrightarrow{700^{\circ}\text{C}} \text{CH}_{2} = \text{C} = \text{O} + \text{H}_{2}\text{O} \\ \text{Ketene} \end{array}$$

8. Hell-Volhard-Zelinsky (HVZ) reaction

This is a reaction affecting α -halogenation of carboxylic acid.

$$R-CH_2-C-OH \xrightarrow{\text{Red P/Br}_2} R-CH-C-OH \xrightarrow{\parallel} O$$

$$\alpha-\text{bromo acid}$$

The possible mechanism for the reaction is

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$$R-COOH \xrightarrow{Ag_2O} R-CO_2^{\bullet}Ag^+ \xrightarrow{Br_2} R-Br + AgBr \downarrow + CO_2^{\uparrow}$$

The mechanism of the reaction is via free radical and various steps in the mechanism are shown as below.

Chain propagation step:
$$R \cup C \cup O \longrightarrow R + CO_2$$

$$R \cdot + R - C - O - Br \longrightarrow R - Br + R - C \cup O$$

Then both the propagation steps are repeated till either the reactants are consumed or any two radicals collide.

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10. With excess of organometallic compounds:

RCOOH
$$\xrightarrow{\text{CH}_3\text{MgBr}}$$
 RCOO $\stackrel{\oplus}{\text{(MgBr)}}$ $\stackrel{\oplus}{+}$ CH₄ \uparrow

$$\downarrow^{\text{CH}_3\text{Li}}$$
RCOO $\stackrel{-}{\text{Li}}^+$ $+$ CH₄ \uparrow

$$\downarrow^{\text{CH}_3\text{Li}}$$
R-C(O $\stackrel{-}{\text{Li}}^+$)₂ $\xrightarrow{\text{2H}_2\text{O}}$ RCOCH₃

$$\stackrel{\oplus}{\text{CH}_3\text{Li}}$$
RCOO $\stackrel{\oplus}{\text{(Ketone)}}$

11. Action of heat on dicarboxylic acids:

12. Heating of α , β and γ -hydroxy carboxylic acids

(i)

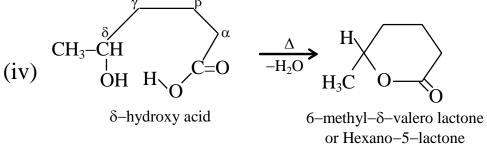
$$2CH_{3}-\stackrel{\alpha}{CH}-COOH \xrightarrow{\Delta} \stackrel{H_{3}C}{\longrightarrow} O \stackrel{CH_{3}}{\longrightarrow} + H_{3}C \stackrel{O}{\longrightarrow} O \stackrel{H}{\longrightarrow} H$$

$$\alpha-\text{hydroxy acid} + H_{3}C \stackrel{O}{\longrightarrow} O \stackrel{H}{\longrightarrow} O$$

$$\text{cis-lactide (racemic)} + H_{3}C \stackrel{O}{\longrightarrow} O \stackrel{H}{\longrightarrow} O$$

$$\text{centre of symmetry}$$

(ii)
$$CH_3$$
— CH $C=O$ A CH_3 — $CH=CH-CO_2H$ CH_3 — CH CH_3 — CH CH_3 — CH CH_2 — CH_2 CH_3 — CH CH_3 CH_3 — CH CH_3 — CH CH_3 CH_3



13. Treatment of α , β and γ -halo carboxylic acid with aqueous NaOH

$$\begin{array}{ccc} CH_{3}-\overset{\alpha}{C}H-COOH & \xrightarrow{OH^{-}} & CH_{3}-CH-COO^{-} \\ Br & OH \\ \alpha-Bromo \ acid & (With \ retention \ of \ configuration) \end{array}$$

$$CH_{3}\text{-}CH\text{-}CH\text{-}COOH \xrightarrow{E_{2}} CH_{3}CH\text{-}CH\text{-}COO^{-}$$

$$Br \ H \qquad (trans product)$$

$$(\beta-Bromo acid) \qquad \alpha,\beta-unsaturated carboxylate$$

$$CH_{2} \xrightarrow{\beta} CH_{2} \xrightarrow{\alpha} CH_{2} \xrightarrow{OH^{-}} CH_{2} \xrightarrow{C} O$$

$$Br \ CH_{2} \xrightarrow{\beta} CH_{2} \xrightarrow{\alpha} CH_{2} \xrightarrow{C} CH_{2} CH_{2} \xrightarrow{C} CH_{2} \xrightarrow{C} CH_{2} \xrightarrow{C} CH_{2} \xrightarrow{C} CH_{2} CH_{2} \xrightarrow{C} CH_{2} CH_{2} \xrightarrow{C} CH_{2} CH_{2$$

14. Decarboxylation

 β -keto acids on slightest warming alone or in presence of a base undergoes ready loss of CO_2 . The process of loss of CO_2 is called "decarboxylation". For example,

Mechanism:

$$Y-C$$

$$CH_{2}$$

$$C=O$$

$$CH_{2}$$

$$Y-C=CH_{2}$$

$$OH$$

$$Enol form$$

$$Transition state$$

$$(6-membered)$$

$$Y-C-CH_{3}$$

$$O$$

$$Keto form$$

Here Y can be substituents like CH₃, OH etc.

$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

$$COOH$$

cis and trans anhydride

15. In the carboxyl group, the carbonyl and the hydroxyl groups are in close association. This tends to modify the chemistry associated with either group alone. In particular, the type of nucleophilic addition reactions identified with the carbonyl group in aldehydes or ketones are commonly not observed with acids. This may be accounted for by the fact that an attacking base preferentially abstracts an H⁺ ion. Because of its negative charge and large resonance energy, resists the addition of a second molecule of the attacking base. It thus does not form an oxime or phenyl hydrazone.

Lithium aluminium hydride reduces a carboxyl group to a primary alcohol. The reduction, however, does not take place with NaBH₄.

Cyclobutane carboxylic acid Cyclobutane carbinol
$$CH_2OH$$

Reduction of the carboxyl group with LiAlH₄ also takes place to an aldehyde at low temperature.

$$RCOOH \xrightarrow{SOCl_2} RCOC1 \xrightarrow{NH_3} RCONH_2 \xrightarrow{POCl_3}$$

LiAlH₄ can also reduce cyamides to aldehydes (after hydrolysis).

Sodium salts of the acid, on fusion with soda lime (NaOH + CaO) also suffer loss of carbon dioxide and the corresponding hydrocarbon is obtained.

$$CH_3CH_2COO^-Na^+ \xrightarrow{Soda lime} CH_3CH_3 \uparrow + CO_2 \uparrow$$

A carboxylic acid can be decarboxylated without soda lime if it contains a β -carbonyl group or a ' β , γ ' -C=C- bond.

16. Cacodyl oxide test

Acetate salt on heating with solid As_2O_3 gives cacodyl oxide, which have an extremely nauseating odour. The cacodyl oxide is poisonous also.

$$4CH_3CO_2Na + As_2O_3 \xrightarrow{CH_3} As-O-As \xrightarrow{CH_3} + 2Na_2CO_3 + 2CO_2 \uparrow$$

$$CH_3 \xrightarrow{CH_3} + 2Na_2CO_3 + 2CO_2 \uparrow$$

Cacodyl oxide (nauseating odour)

Comparison of The Reactivity of Various Acid Derivatives

Partial positive charge of –C– bonds in esters, anhydride, amide and acyl halides determine how fast a nucleophile will attack on these compounds. The order of nucleophilic attack is,

 $RCOCl > (RCO)_2O > RCOOR' > RCONH_2$.

The above consideration is drawn on the fact that +R effect reduces in the order

But – I effect is in the order

Therefore, stronger the – I effect and lesser is the +R effect, stronger will

be the electrophilicity of carbon in $-\dot{C}$ and more easily the nucleophile will attack that carbon.

3. Acid Derivatives

ACID HALIDES

(a) Preparation of acid halides

(i)
$$R-COOH + SOCl_2 \longrightarrow RCOCl + SO_2 \uparrow + HCl \uparrow$$

(ii)
$$3R-COOH + PBr_3 \longrightarrow 3RCOBr + H_3PO_3$$

(iii)
$$R-C \stackrel{O}{\underset{O^{-}}{\overset{NaF + Anhydrous HF}{\longleftrightarrow}}} R-C \stackrel{O}{\underset{F}{\longleftrightarrow}}$$

(iv) RCOOH + PCl₅
$$\longrightarrow$$
 RCOCl + POCl₃ + HCl

The lower acyl chlorides are colourless liquids with irritating odour. Higher members are colourless solids.

(b) Reactions of acid halides

(i) Formation of other acid derivatives

Acyl chlorides are the most reactive acid derivatives. Acyl chlorides may be converted into other acid derivatives as shown below:

RCOC1 + CH₃OH
$$\longrightarrow$$
 R-C-OCH₃ + HCl

O

RCOC1 + 2NH₃ \longrightarrow R-C-NH₂ + NH₄Cl

O

RCOC1 + C₆H₅OH \longrightarrow R-C-OC₆H₅ + HCl

where R may be an alkyl or aryl group.

Acyl chlorides react rapidly with the above reagents. The reaction, however, with aliphatic acid chlorides is much more vigorous than with

the aromatic acid chlorides. In the former, the carbonyl carbon atom is a centre of low electron density while in the latter this is not so because of resonance with the ring

Benzoyl chloride, for instance, is so much less reactive that it can be used as water suspension.

(ii) Formation of ketones

Alkyl Grignard reagent react with anhydrous cadmium chloride, CdCl₂ to form a dialkylcadmium compound, R₂Cd. This intermediate, on reaction with an acyl chloride, yields a ketone. Organo cadmium compounds are less reactive than Grignard reagents and are thus more selective in their attack as nucleophiles.

$$2R-MgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$$

$$O \qquad O$$

$$2CH_3-C-Cl + R_2Cd \longrightarrow 2CH_3-C-R + CdCl_2$$

Both aliphatic and aromatic ketones can be prepared in this manner.

$$2O_2N$$
 — COCl + $(CH_3)_2Cd$ \longrightarrow $2O_2N$ — C-CH₃ + $CdCl_2$ p-Nitrobenzoyl chloride

(iii) Rosenmund Reduction

This reaction requires hydrogen and Pd, which is a catalyst, adsorbed on BaSO₄ and a catalytic poison like quinoline to slow down the reaction. The result is the formation of an aldehyde. If the given catalytic poison is not employed the product would have been a primary alcohol.

$$C_2H_5$$
-C-Cl $\xrightarrow{H_2/Pd-BaSO_4}$ C_2H_5 CHO + HCl

(iv) Friedel-Crafts reaction

Preparation of aromatic ketones by the Friedel–Crafts reaction of acyl chlorides is an important method.

$$C_{6}H_{6} + CH_{3}-C-Cl \xrightarrow{AlCl_{3}} C_{6}H_{5}-C-CH_{3} \text{ (Acetophenone)}$$

$$C_{6}H_{6} + C_{6}H_{5}-C-Cl \xrightarrow{AlCl_{3}} C_{6}H_{5}-C-C_{6}H_{5} \text{ (Benzophenone)}$$

(v) Acid Hydrazides

RCOCl on treatment with hydrazine yields acid hydrazides.

$$RCOCl + 2NH_2-NH_2 \longrightarrow RCONHNH_2 + NH_2 NH_3Cl^-$$

The acid halide, on heating with the salt of the corresponding acid, yields an anhydride.

$$RCOCI + RCOO^{-}Na^{+} \longrightarrow R-C-O-C-R + NaCI$$

(vii) Hydrolysis of $R-C \stackrel{O}{<}_{Cl}^{O}$ by base catalysis

$$R-C = \begin{array}{c} O \\ \vdots \\ OH \end{array} \longrightarrow \begin{array}{c} O \\ -CI \\ CI \end{array} \longrightarrow \begin{array}{c} CI \\ -CI \\ -CH \end{array} \longrightarrow \begin{array}{c} CI \\ -CI \\ -CI \\ -CH \end{array} \longrightarrow \begin{array}{c} CI \\ -CI \\ -CI \\ -CI \end{array} \longrightarrow \begin{array}{c} CI \\ -CI \\ -CI \\ -CI \\ -CI \end{array} \longrightarrow \begin{array}{c} CI \\ -CI \\$$

Acid Anhydrides

Acid anhydrides are formed by the removal of a molecule of water from two molecules of a carboxylic acid. Most acid anhydrides are symmetrical. Unsymmetrical or mixed anhydrides are also known but are not much used. Acid anhydrides are also very reactive like the acid chlorides and

have penetrating odour. They are useful for synthetic purposes because of their less corrosive action and greater stability.

(a) Preparation of acid anhydrides

- (i) $CH_3COOH + CH_2 = C = O \xrightarrow{\Delta} (CH_3CO)_2O$
- (ii) $2RCOOH + (CH_3CO)_2O \xrightarrow{\Delta} (RCO)_2O + CH_3COOH$
- (iii) Heating of 2 moles of $R-C \lesssim_{OH}^{O}$ with dehydrating agents also produces (RCO)₂O.

$$\begin{array}{c} \text{CH-COOH} & \xrightarrow{150^{\circ}\text{C}} & \xrightarrow{\text{CH-C}} & \text{O} \\ \text{CH-COOH} & \xrightarrow{150^{\circ}\text{C}} & \xrightarrow{\text{CH-C}} & \text{O} \\ \text{Maleic acid} & \text{Maleic anhydride} \\ \text{CH}_2\text{-COOH} & \xrightarrow{300^{\circ}\text{C}} & \text{CH}_2\text{-C} & \text{O} \\ \text{CH}_2\text{-COOH} & \xrightarrow{\text{Succinic acid}} & \text{Succinic anhydride} \\ \text{Succinic acid} & \text{Succinic anhydride} \\ \text{COOH} & \xrightarrow{\text{COOH}} & \xrightarrow{\text{COOH}} & \xrightarrow{\text{COOH}} & \text{O} \\ \text{Phthalic acid} & \text{Phthalic anhydride} \\ \text{O} & \xrightarrow{\text{O}^{-}\text{Na}^{+}} & \text{O} & \text{O} \\ \text{IV)} & \text{R-C-Cl} + \text{CH}_3\text{-C=O} & \xrightarrow{\text{R-C-O-C-CH}_3\text{+ NaCl}} \end{array}$$

Acetic anhydride is a colourless liquid with irritating smell, slightly soluble in water but readily soluble in ether and benzene.

(b) Reactions of acid anhydrides

(i) Formation of acid and other acid derivatives

Acid anhydrides contain carbonyl groups and thus undergo nucleophilic attack by various electron donors to yield the corresponding products.

$$CH_{3}-C-O-C-CH_{3} + H_{2}O \longrightarrow 2CH_{3}COOH$$

$$CH_{3}-C-O-C-CH_{3} + CH_{3}OH \longrightarrow CH_{3}-COOCH_{3} + CH_{3}COOH$$

$$CH_{3}-C-O-C-CH_{3} + 2NH_{3} \longrightarrow CH_{3}CONH_{2} + CH_{3}COONH_{4}$$

$$CH_{3}-C-O-C-CH_{3} + C_{6}H_{5}OH \longrightarrow CH_{3}CO_{2}C_{6}H_{5} + CH_{3}COOH$$

(ii) Friedel Crafts acylation

Ketones are obtained by the Friedel-Crafts acylation of aromatic hydrocarbons. Acetophenone is formed from acetic anhydride and benzene in presence of anhydrous AlCl₃.

$$\begin{array}{c|c}
O & O \\
\parallel & \parallel \\
+ CH_3-C-O-C-CH_3
\end{array}
\xrightarrow{AlCl_3}
\begin{array}{c}
O \\
\parallel \\
C-CH_3
\end{array}$$

(iii) Reaction with hydroxylamine

Acid anhydrides react with hydroxylamine to yield hydroxamic acid.

$$RCOCl + NH_2OH \longrightarrow RCONHOH + HCl$$

Hydroxamic acid

(iv) Formation of phenolphthalein

Phthalic anhydride condenses with two moles of phenol in the presence of concentrated H₂SO₄ to form phenolphthalein.

(v) Formation of cyclic imides

Cyclic acid anhydrides react with ammonia to form amides, which on heating lose a molecule of water with the resultant formation of cyclic imides.

CONH₂

$$CONH_2$$

$$COO^- NH_4^+$$

$$COOH$$
Phthalic anhydride
$$COO^- NH_4^+$$

$$COOH$$

Succinic anhydride with ammonia forms succinamic acid.

$$\begin{array}{c|c} CH_2-C \\ & \\ CH_2-C \\ \hline \\ CH_2-C \\ \hline \end{array} \qquad \begin{array}{c} CH_2-CONH_2 \\ \\ CH_2-COOH \\ \end{array}$$

(vi) Reduction

$$\begin{array}{c}
O \\
\hline
CH_2OH \\
CH_2OH
\end{array}$$

(vii) Hydrolysis

Acetic anhydride is hydrolysed in water slowly but rapidly by alkali.

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH.$$

With HCl: $(CH_3CO)_2O + HCl \longrightarrow CH_3COCl + CH_3COOH$.

Esters

Esters probably constitute the most important class of carboxylic acid derivatives. They occur widely in nature and are responsible for the fragrance of many fruits and flowers.

(a) Preparation of esters

(i)
$$R-C \stackrel{O}{\underset{OH}{\longleftarrow}} + R'OH \xrightarrow{Conc. H_2SO_4} R-C \stackrel{O}{\underset{OR'}{\longleftarrow}} + H_2O$$

The mechanism of acid catalysed esterification has already been discussed.

(ii)
$$(CH_3)_2C=CH_2 + CH_3COOH \xrightarrow{Conc. H_2SO_4} CH_3-C-OC(CH_3)_3$$

(iii)
$$CH_3COO: + CH_2CH_2CH_3 \xrightarrow{-Br_{-}} CH_3-C-OCH_2CH_2CH_3$$

$$(iv) \xrightarrow{R-C-Cl} + R'OH \xrightarrow{Pyridine} \xrightarrow{R-C-OR'} + HCl$$

$$(iv) \xrightarrow{R-C-Cl} + R'OH \xrightarrow{Pyridine} \xrightarrow{R-C-OR'} + HCl$$

$$(v) \xrightarrow{R-C} \xrightarrow{O} + \overset{\oplus}{CH_2-N_2} \xrightarrow{\oplus} \xrightarrow{R-C} \overset{\oplus}{O} + \overset{\oplus}{CH_3-N_2} \xrightarrow{S_{N^2}} \xrightarrow{R-C-OCH_3} + N_2 \uparrow$$

(vi) Cyclic esters (lactones) may be obtained by intramolecular esterification of hydroxy acids.

$$R-CH-CH_{2}CH_{2}-C-O^{-}Na^{+} \xrightarrow{H^{+}} O + H_{2}O + Na^{+}$$

$$OH$$

(vii) Transesterification

This is basically a process called as "alcoholysis". This is carried out by refluxing the ester with large excess of alcohol, preferably in the presence of small amount of acid or

sodium alkoxide as catalyst. Alcoholysis is usually effective in replacing a higher alcohol by a lower one.

For example:

CH₃CO₂C₄H₉ + C₂H₅O Na
$$\stackrel{C_2H_5O \text{ Na}}{=}$$
 CH₃CO₂C₂H₅ + C₄H₉-OH. Plausible base catalysed mechanism of the reaction is

$$R^{1}-C \xrightarrow{} + EtO^{\bullet} \rightleftharpoons R^{1}-C-OEt \rightleftharpoons R^{1}-C-OEt + R^{2}O^{\bullet}$$

$$R^{2}O^{+} EtOH \rightleftharpoons R^{2}OH + EtO.^{\bullet}$$

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(b) Reaction of esters

(i) Acyloin condensation

$$2R-C \xrightarrow{O} \xrightarrow{Na / Ether} \xrightarrow{R-C=O} \\ R-CHOH \\ (\alpha-hydroxy ketone)$$

$$Na \longrightarrow Na^{+} + e^{-}$$

$$O \xrightarrow{O} \\ R-C-OR + e^{-} \longrightarrow R-C \xrightarrow{I} \\ OR$$

$$(Radical anion)$$

(ii) Claisen ester condensation

(iii) Reduction of ester

Esters can be reduced by LiAlH₄ in a manner similar to carboxylic acid. The process results in the formation of two alcohols and is known as "hydrogenlysis". One of the alcohols is essentially a primary alcohol while other alcohol unit could be 1°, 2° or 3°. Esters are the only compound, which on reduction with LiAlH₄ gives 2 units of alcohol.

$$COOC_2H_5$$
 $LiAlH_4$
 $+ C_2H_5OH$

 $MeCOCH_2CO_2C_2H_5 \xrightarrow{LiAlH_4} MeCH(OH)CH_2CH_2OH + C_2H_5OH$

(iv) Reaction of NH₃ with ester and keto ester

$$R-C \stackrel{O}{\underset{OC_2H_5}{\longleftarrow}} + NH_3 \longrightarrow R-C \stackrel{O}{\underset{NH_2}{\longleftarrow}} + EtOH$$

$$RCOCH_2CO_2C_2H_5 + NH_3 \longrightarrow R-C=CHCO_2C_2H_5 + H_2O$$

$$(1 \text{ equivalent}) \qquad NH_2$$

(v) Hydrolysis

The basic feature of acid catalysed mechanism is

The basic feature of base catalysed mechanism is

$$\begin{array}{ccc}
O & O & O \\
\parallel & \parallel & \parallel & \square \\
R-C-G & \xrightarrow{Nu^{\Theta}} & R-C \xrightarrow{G} G & \rightleftharpoons G^{\Theta} + R-C-Nu \\
Nu & O
\end{array}$$

Esters undergo nucleophilic substitution reactions very slowly because their leaving groups are quite basic. The rate of hydrolysis of an ester can be increased by carrying out the reaction in the presence of a catalyst. Either H⁺ or OH⁻ can be used to increase the rate of reaction.

In an acid-catalysed reaction all organic reactants, intermediates and products are positively charged or neutral; there are no negatively charged organic reactants, intermediates or products in acidic solution. Also, in a reaction in which OH⁻ is used to increase the rate of the reaction, all organic reactants, intermediates and products are negatively charged or

neutral; there are no positively charged organic reactants, intermediates or products in basic solution.

Ester hydrolysis can be carried out in 8 possible ways. $A_{AC}1$, $A_{AC}2$, $B_{AC}1$, $B_{AC}2$, $A_{AL}1$, $A_{AL}2$, $B_{AL}1$, $B_{AL}2$. Out of these possible mechanistic pathways, most common examples are

$$A_{AC}1$$
, $A_{AC}2$, $A_{AL}1$, $B_{AC}2$

Here A or B stands for acid or base catalysed and AC or AL stands for acyl-oxygen or alkyl-oxygen cleavage and 1 or 2 stands for unimolecular or bimolecular.

$A_{AC}1$:

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{fast} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{C} CH_{3} CH_{3} \xrightarrow{C} C$$

$$CH_{3} \xrightarrow{\oplus} CH_{2}O$$

$$CH_{3} \xrightarrow{\oplus} CH_{3}$$

$$CH_{3} \xrightarrow{\oplus} CH_{3}$$

$$CH_{3} \xrightarrow{\oplus} CH_{3}$$

$$CH_{3} \xrightarrow{\oplus} CH_{3}$$



2:
$$CH_{3}-C-OC_{2}H_{5} \xrightarrow{fast} CH_{3}-C-OC_{2}H_{5} \longleftrightarrow CH_{3}-C-OC_{2}H_{5} \xrightarrow{OH} CH_{3}-C-OC_{2}H_{$$

$$A_{AL}1$$
:

$$CH_{3}-C-O-C$$

$$CH_{3}$$

$$CH_{3}-C \bigoplus_{CH_{3}}^{CH_{3}} \quad CH_{3}-C \bigoplus_{CH_{3}}^{CH_{3}} \quad CH_{3}-C \bigoplus_{CH_{3}}^{CH_{3}} \quad CH_{3}-C \bigoplus_{CH_{3}}^{CH_{3}} + \quad CH_{3}-C-OH \bigoplus_{CH_{3}}^{CH_{3}} + \quad CH_{3}-C-O$$

$B_{AC}2$:

$$CH_{3}-C \xrightarrow{Solw} CH_{3}-C \xrightarrow{Solw} CH_{3}-C \xrightarrow{O} H \xrightarrow{fast} CH_{3}-C \xrightarrow{O} H \xrightarrow{Foton} exchange$$

$$CH_{3}-C \xrightarrow{O} CH_{3}-C \xrightarrow{O} CH_{3}-C \xrightarrow{O} H \xrightarrow{fast} CH_{3}-C \xrightarrow{O} H \xrightarrow{O} H$$

Acid Amides

(a) Preparation of acid amides

(i)
$$RCOCl + NH_3 \longrightarrow RCONH_2 + HCl$$

1° amide

(ii) RCOCl + R'NH₂
$$\longrightarrow$$
 RCONHR' + HCl 2° amide

(iii) RCOCl +
$$R'_2NH \longrightarrow RCONR'_2 + HCl$$

3° amide

(iv) R-COOH + MeNH₂
$$\longrightarrow$$
 RCOO⁻ $\stackrel{\oplus}{NH_3}$ $\stackrel{heat}{\longrightarrow}$ RCONHMe + H₂O

(2° amide)

Mechanism of amide formation from acyl halide.

$$R-C-Cl+:NH_{3} \Longrightarrow R-C-Cl \xrightarrow{-Cl^{-}} R-C-NH_{3} \xrightarrow{-H^{+}} R-C-NH_{2}$$

$$(V) COOH \xrightarrow{2NH_{3}} COO^{-}NH_{4}^{+} \xrightarrow{Heat} Phthalimide$$

H-bonding makes the boiling points and melting points of amides higher than other acid derivatives.

(b) Properties of Amides

Amides are the least reactive of all the acid derivatives. Amides do not react with halide ions, carboxylate ions, alcohols or water because in each case the incoming nucleophile is a weaker base than the leaving group of the amide.

(i) Acidity of amides:

Although amides are considered to be weakly acidic (for instance, K_a for acetamide is ~ 10^{-15}), they react with alkali metals to form salts. The

reason for the acidity is that the resulting anion can be stabilized by resonance as shown below:

$$\begin{array}{ccc}
O & O^{-} \\
R-C-NH_{2} \xrightarrow{Na} H^{+} + R-C-NH & \longrightarrow R-C=NH
\end{array}$$

(ii) Hydrolysis

Amides, however, may be hydrolyzed in the presence of either an acid or a base leading to the formation of the parent acid.

RCONH₂
$$\xrightarrow{H^+/H_2O}$$
 R-C-OH + NH₄⁺
RCONH₂ $\xrightarrow{OH^-/H_2O}$ RCOO⁻ + NH₃

$$\overset{O}{\underset{||}{O}}$$
2C₆H₅-C-NH₂ + H₂SO₄ + 2H₂O \longrightarrow 2C₆H₅COOH + 2NH₄⁺ + SO₄⁻

(iii) Reaction with alcohol

Esters are obtained on heating amides with alcohols in the presence of a mineral acid.

(iv) Dehydration

Amides lose a molecule of water in the presence of an efficient dehydrating agent such as phosphorus pentoxide to form a nitrile.

$$R-C-NH_2 \xrightarrow{P_2O_5} R-C \equiv N + H_2O$$

(iv) Hoffmann degradation reaction

A primary amide (aliphatic or aromatic) on treatment with bromine in the presence of an aqueous base forms an amine. The reaction is referred to as "Hoffmann reaction".

$$C_{6}H_{5}CH_{2}-C-NH_{2} + Br_{2} + NaOH \longrightarrow C_{6}H_{5}CH_{2}-NH_{2} + 2NaBr + Na_{2}CO_{3} + 2H_{2}O$$

$$R \searrow NH_{2} + Br_{2} + 4KOH \xrightarrow{\Delta} RNH_{2} + 2KBr + K_{2}CO_{3} + 2H_{2}O$$
The most plausible mechanism of the Hoffmann's degradation is

The most plausible mechanism of the Hoffmann's degradation is

(v) Acid catalysed hydrolysis

(v) Acid catalysed hydrolysis

O:
$$CH_3-C-NH_2 \xrightarrow{+H^+} CH_3-C-NH_2 + H_2O: \longrightarrow CH_3-C-NH_2 \xrightarrow{+H^+} CH_3-C-NH_3$$

$$OH \xrightarrow{-H^+} CH_3-C-NH_2 \xrightarrow{+H^+} CH_3-C-NH_2 \xrightarrow{+H^+} CH_3-C-NH_3$$

$$OH \xrightarrow{-H^+} CH_3-C-NH_2 \xrightarrow{+H^+} CH_3-C-NH_3$$

$$OH \xrightarrow{-H^+} CH_3-C-NH_3 \xrightarrow{-H^+} CH_3-C-NH_3$$

$$OH \xrightarrow{-H^+} CH_3-C-NH_3 \xrightarrow{-H^+} CH_3-C-NH_3$$

The hydrolysis of an amide doesnot occur without a catalyst. In the nonacid catalysed reaction, the amide is not protonated. Therefore, water, a very poor nucleophile, must attack a neutral amide that is much less susceptible to nucleophilic attack than a protonated amide would be. Consequently, the tetrahedral intermediate is formed very slowly. In addition, the NH₂ group of the tetrahedral intermediate is not protonated in the non-acid catalysed reaction. As a result, the two leaving groups of the

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tetrahedral intermediate are HO⁻ and ⁻NH₂. Because ⁻OH is the weaker base, it is more easily expelled, which reforms the amide. Base catalysed hydrolysis:

In the hydroxide ion promoted hydrolysis of an amide, ⁻OH rather than water is the nucleophile. Because ⁻OH is a better nucleophile than water, it is better at forming the tetrahedral intermediate. The two leaving groups of the tetrahedral intermediates are ⁻OH and ⁻NH₂. Because ⁻OH is the weaker base, it is more easily expelled, but occasionally an ⁻NH₂ is ejected. When this happens, the carboxylic acid that is formed immediately loses a proton. Since this step is irreversible, it disturbs the equilibrium and drives the reaction towards products.

In strongly basic solutions, the hydrolysis reaction is second order in hydroxide ion. In other words, two equivalents of hydroxide ion participate in the reaction. When the new tetrahedral intermediate collapses, the possible leaving groups are O²⁻ or ⁻NH₂. Because ⁻NH₂ is the weaker base, it is expelled and the hydrolysis reaction occurs.

An amide reacts with an alcohol in the presence of H^+ for the same reason it reacts with water in the presence of H^+ .

(v) Reduction of Amide

Amides are reduced to amines.

$$\begin{array}{c} O \\ R-C-NH_2 & \xrightarrow{Na/C_2H_5OH} & RCH_2NH_2 + H_2O \end{array}$$

(vi) Reaction with nitrous acid

$$R-CONH_2 + HNO_2 \xrightarrow{\Delta} R-C \stackrel{O}{\underset{O-H}{\longleftarrow}} + N_2 \uparrow + H_2O$$

The reaction proceeds via the attack of electrophilic species NO⁺ generated from HNO₂.

Fundamental Solved Examples

Example 1.

Predict the stereochemistry at α –C for β –bromo acid (optically active) when treated with NaOH.

Solution:

The configuration (if chiral carbon) at α -carbon remains same i.e. reaction proceeds with retention of configuration.

Example 2.

Write the possible mechanism for the given reaction.

$$Ph-COCOOH \xrightarrow{H^+} PhCOOH + CO.$$

Solution:

Example 3.

Predict the products of given reaction.

$$\begin{array}{c}
\text{Ph-CH=CH-Ph} \xrightarrow{\text{Hot KMnO}_4} & \text{(A)} \\
\downarrow^{\text{cold KMnO}_4} & \text{(B)}
\end{array}$$

Solution:

(A): PhCO₂H (B): Ph-CH-CH-Ph | | OH OH

Example 4.

- (a) Why are both p–Me and m–Me substituted acids weaker than PhCO₂H with the p–acid being the weakest one?
- (b) Why is the p-OH acid weaker than PhCO₂H while the m-OH acid is stronger?

Solution:

- (a) Both p-Me and m-Me are electron-donating and acid weakening. m-Me is electron donating by induction while p-Me is electron-donating by induction as well as hyperconjugation. p-Me being more electron releasing is more acid weakening and p-Me and m-Me substituted acids both are weaker than PhCO₂H.
- (b) OH group shows –I effect from m–position while from p–position it shows –I and +R effects. Electron–donation by resonance (+R) is more prominent than electron withdrawal by induction (–I) for OH group. So m–OH is electron–withdrawing and acid strengthening, thus m–OH acid is stronger than PhCO₂H. p–OH is electron–donating and acid weakening, thus p–OH acid is weaker than PhCO₂H.

Example 5.

Reductive ozonolysis of (A) having molecular formula $C_{11}H_{12}O$ gives CH_2O and (B) with molecular formula $C_{10}H_{10}O_2$. Both (A) and (B) gives a precipitate from reaction with NaOI. (B) on reaction with NaOI gives a precipitate of CHI_3 along with the formation of compound (C) as sodium salt. Compound (C) on acidification gives a compound which on mononitration gives only one product. Identify compound (A), (B) & (C).

Solution:

Compounds (A) and (B) responding positively to iodoform reaction reveals that they have either CH₃CO- or CH₃CH(OH)- structural unit. Compound (A) has 6° of unsaturation while (B) has 5° of unsaturation. Compound (A) has a benzene ring (accounting for 4 degree of unsaturation), a CH₃CO- unit and a double bond in the side chain (accounting for rest two degree of unsaturation). CH₃CO- unit and side chain with a double bond (=CH₂ unit) must be at para position since (C) on mononitration gives only one product.

$$CH_{3}-C=CH_{2}$$

$$O_{3}/H_{2}O$$

$$CH_{3}$$

$$CH_{2}=O$$

$$CH_{3}$$

$$CH_{2}=O$$

$$CH_{3}$$

$$CH_{2}=O$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{2}=O$$

$$CH_{3}$$

$$CH_{3}$$

$$CH_{2}=O$$

$$CH_{3}$$

$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

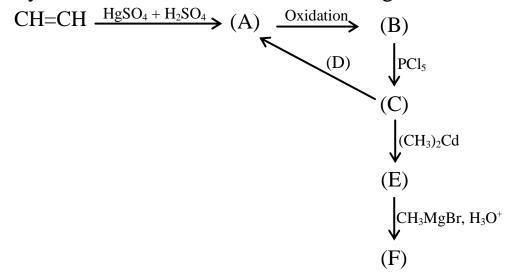
$$CO_{2}H$$

$$CO_{2}H$$

$$CO_{2}H$$

Example 6.

Identify A, B, C, D, E and F in the following reactions



Solution:

$$CH = CH \xrightarrow{HgSO_4 + H_2SO_4} CH_3 - C - H \xrightarrow{oxidation} CH_3 - C - OH \xrightarrow{PCl_5} CH_3 - C - Cl$$

$$(A) \qquad (B) \qquad (C)$$

$$Pd, BaSO_4, H_2 \qquad (CH_3)_2Cd$$

$$(D) \qquad CH_3 - C - CH_3 \qquad CH_3MgBr \qquad CH_3 - C - CH_3$$

$$CH_3 - C - CH_3 \qquad (E)$$

Example 7.

An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) doesnot show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). Compound (E) gives a positive Schiffs test but (F) does not. Give structures of (A) to (F) with reasons.

Solution:

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH-CH}_{2}\text{COOH} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \end{array} \xrightarrow[]{P + Br_{2}} \begin{array}{c} \text{CH}_{3} \\ \text{CH-CHBr-COOH} \\ \text{CH}_{3} \\ \text{CH}_{3} \end{array} \xrightarrow[]{P + Br_{2}} \begin{array}{c} \text{CH-CHBr-COOH} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \end{array} \xrightarrow[]{CH_{3} - C = COOH} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} - C = O + HCHO \\ \text{(F)} \\ \text{(E)} \\ \text{Does not give Schiff's Test} \end{array} \xrightarrow[]{CH_{3} - C = COOH} \\ \text{(D)} \\ \text{$$

Example 8.

An organic compound (A) C₆H₁₂O₃ on treatment with concentrated H₂SO₄ gives CO, H₂O and (B). Compound (B) can be prepared by passing vapours of 1–pentanol over heated copper at 570 K. Compound (A) on heating gives (C) C₁₂H₂₀O₄. Give structures of (A) to (C) with proper reasoning.

Solution:

$$CH_{3}(CH_{2})_{3}CH_{2}OH \xrightarrow{Cu} CH_{3}(CH_{2})_{3}-CHO + H_{2}O$$

$$OH$$

$$CH_{3}(CH_{2})_{3}-CH-COOH \xrightarrow{Conc. H_{2}SO_{4}} CH_{3}(CH_{2})_{3}CHO + CO_{2} + H_{2}O$$

$$CH_{3}(CH_{2})_{3}CHOH + HOOC$$

$$COOH + HO-CH-(CH_{2})_{3}CH_{3}$$

$$CH_{3}(CH_{2})_{3}CH \xrightarrow{O-CO} CH(CH_{2})_{3}CH_{3}$$

$$CH_{3}(CH_{2})_{3}CH \xrightarrow{O-CO} CH(CH_{2})_{3}CH_{3}$$

$$CO-O \xrightarrow{CO-CO} CH(CH_{2})_{3}CH_{3}$$

Example 9.

An optically active organic compound (A) ($C_8H_{13}Cl$) does not decolourise bromine water solution. (A) on treatment with alcoholic KOH can produce 2 products in principle but infact only one product (B) (C_8H_{12}) is obtained. (B) on treatment with ozone followed by work up with H_2O_2 yields (C) ($C_8H_{12}O_4$) which cannot be resolved into enantiomers. (C) on heating with NaOH/CaO yields (D) (C_6H_{12}) which on monochlorination yields $C_6H_{11}Cl$ single isomer. Deduce structures of (A) to (D).

Solution:

Example 10.

A cyclobutandicarboxylic acid exists in two stereo-isomeric forms in which one is polar but non-resolvable while other is non-polar but resolvable into enantiomers. Deduce structures of all these compounds.

Solution:

The compound must be 1,2–cyclobutandicarboxylic acid since all other constitutional isomers are non–resolvable.

