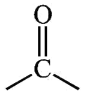
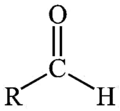
ALDEHYDES & KETONES

1. INTRODUCTION

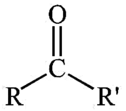
Aldehydes and Ketones are organic compounds belonging to the class of **carbonyl compounds**. Aldehydes have a general formula of RCHO and ketones have a general formula of RCOR′. Carbonyl compounds have a common group $C{=}O$.



Carbonyl Group



Aldehyde



Ketone

In chemical industry ketones and aldehydes are used as solvents, starting materials, and reagents for the synthesis of other products.

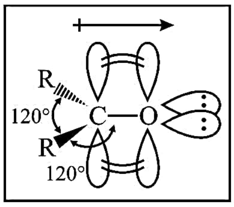
Formaldehyde is well known as the **formalin** solution used to preserve biological specimens and is also used in formation of several important polymers such as **Bakelite**. Ketones dissolve a wide range of organic materials having convenient boiling points for easy distillation, and have low toxicities.

Many other ketones and aldehydes are used as flavourings and additives to foods, drugs and other products.

Benzaldehyde is the primary component of almond extract, and (–) carvone gives spearmint chewing gum its minty flavour.

2. PHYSICAL PROPERTIES

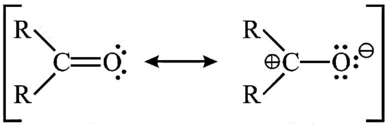
The carbonyl carbon atom is sp^2 hybridized and bonded to three other atoms through coplanar sigma bonds oriented about 120° apart. The unhybridized p orbital overlaps with a p orbital of oxygen to form a pi bond.



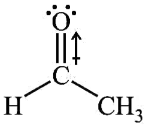
Functional Group	Length	Energy
Ketone C=O bond	1.23 Å	745 kJ/mol (178 kcal/mol)
Alkene C=O bond	1.34 Å	611 kJ/mol (146 kcal/mol)

2.1 Dipole Moment

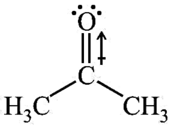
The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon, and the bonding electrons are not shared equally. In particular, the less tightly held pi electrons are pulled more strongly toward the oxygen atom, giving ketones and aldehydes larger dipole moments than most alkyl halides and ethers. We can use resonance forms to symbolize this unequal sharing of the pi electrons.



The first resonance form is more important because it involves more bonds and less charge separation. The contribution of the second structure is evidenced by the large dipole moments of the ketones and aldehydes shown here.



$\mu = 2.7$ D
Acetaldehyde



$\mu = 2.9$ D
Acetone

The positively polarized carbon atom acts as an electrophile (Lewis acid), and the negatively polarized oxygen acts as a nucleophile (Lewis base).

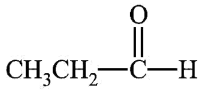
2.2 Boiling Point

Ketones and aldehydes have no $O{-}H$ or $N{-}H$ bonds, however, so their molecules cannot form hydrogen bonds with each other. Their boiling points are therefore lower than those of alcohols of similar molecular weight.

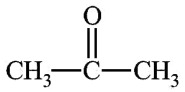
The ketone and the aldehyde are more polar and higher-boiling than the ether and the alkane, but lower-boiling than the hydrogen-bonded alcohol.

$CH_3CH_2CH_2CH_3$
Butane
BP 0°C

$CH_3{-}O{-}CH_2CH_3$
Methoxyethane
BP 8°C



$CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$
Propanal
BP 49°C

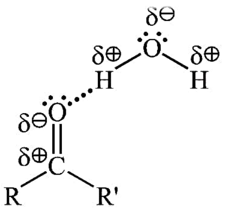


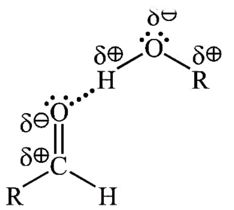
$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$
Acetone
BP 56°C

$CH_3CH_2CH_2{-}OH$
1-Propanol
BP 97°C

2.3 Solubility

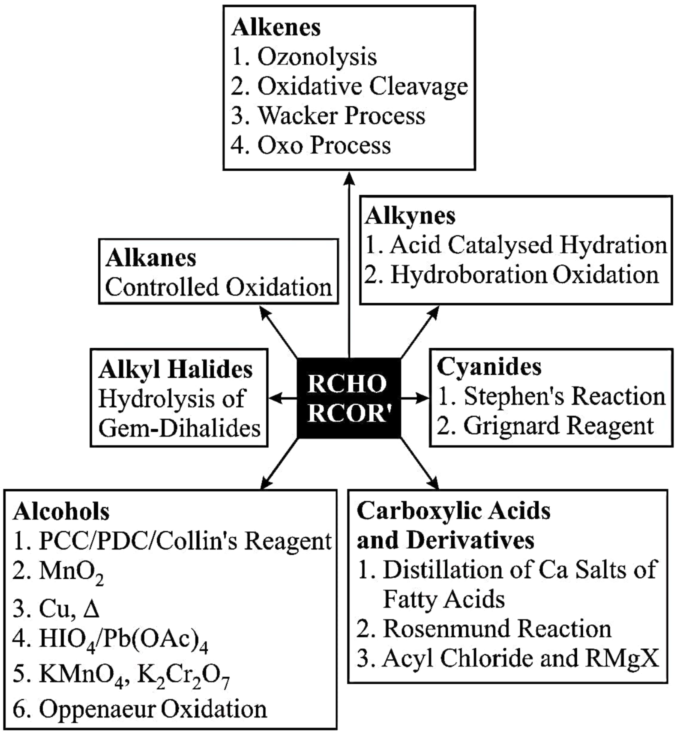
Although pure ketones and aldehydes cannot engage in hydrogen bonding with each other, they have lone pairs of electrons and can act as hydrogen bond acceptors with other compounds having $O{-}H$ or $N{-}H$ bonds. For example, the –OH hydrogen of water or an alcohol can form a hydrogen bond with the unshared electrons on a carbonyl oxygen atom.





Because of this hydrogen bonding, ketones and aldehydes are good solvents for polar hydroxylic substances such as alcohols. They are also remarkably soluble in water. Acetaldehyde and acetone are miscible (soluble in all proportions) with water. Other ketones and aldehydes with up to four carbon atoms are fairly soluble in water. These solubility properties are similar to those of ethers and alcohols, which also engage in hydrogen bonding with water.

3. PREPARATION OF CARBONYL COMPOUNDS



3.1 Alkanes

Controlled oxidation of alkanes under high temperature and pressure in the presence of a catalyst gives carbonyl compounds.

Example - 1

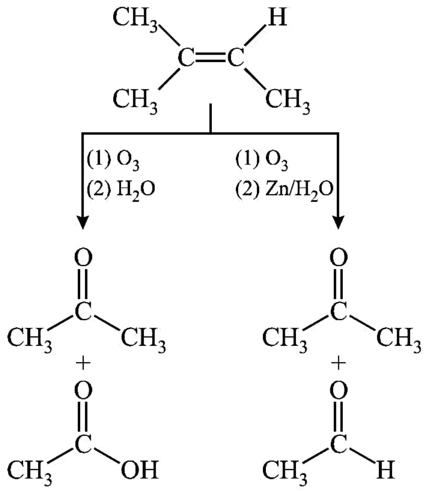
$$CH_4 + O_2 \xrightarrow{\text{Molybdenum Oxide}} HCHO + H_2O$$

3.2 Alkenes

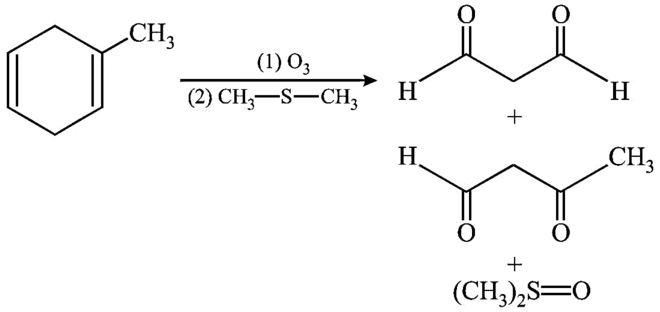
3.2.1 Ozonolysis

Alkenes can be oxidized to aldehydes and ketones if reacted with O_3 and then reduced with Zn or dimethyl sulphide, $(CH_3)_2S$. If a reducing agent is not used, the aldehyde formed cannot be isolated as it is further oxidized to carboxylic acids.

Example - 2



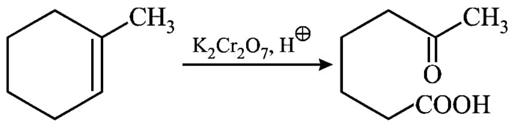
Example - 3



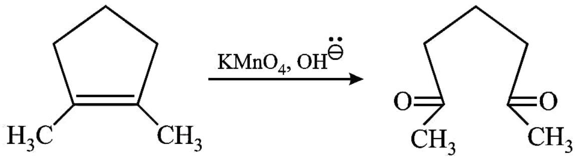
3.2.2 Oxidative Cleavage

Strong oxidizing agents such as acidic $K_2Cr_2O_7$ or alkaline $KMnO_4$ cause oxidative cleavage of double bond to form ketones and carboxylic acids.

Example - 4



Example - 5



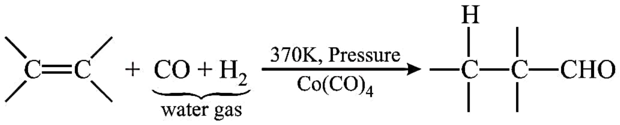
3.2.3 Wacker Process

It is the industrial method to prepare **acetaldehyde**.

$$CH_2{=}CH_2 + \frac{1}{2}O_2 \xrightarrow[H_2O]{PdCl_2.CuCl_2} CH_3CHO$$

3.2.4 Oxo Process

This reaction is also called **hydroformylation**. Carbon mono-oxide and H_2 under high pressure is passed over catalyst $Co(CO)_4$.

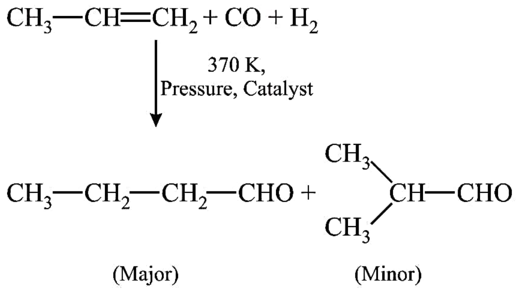


Product formed is a mixture of isomeric chain (predominant) and branched chain aldehydes.

Example - 6

$$CH_2{=}CH_2 + CO + H_2 \xrightarrow[Catalyst]{100°\text{-}150°C} CH_3CHO$$

Example - 7



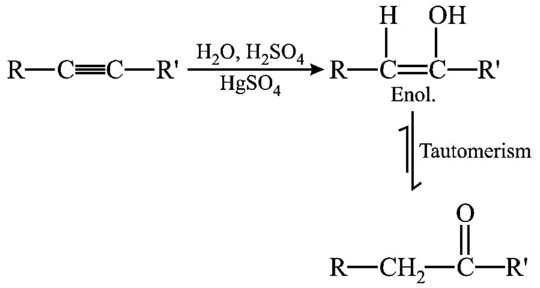
$$CH_3{-}CH{=}CH_2 + CO + H_2 \xrightarrow{370\ K,\ Pressure,\ Catalyst} CH_3{-}CH_2{-}CH_2{-}CHO + (CH_3)_2CH{-}CHO$$

(Major) (Minor)

3.3 Alkynes

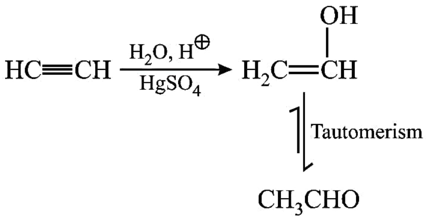
3.3.1 Acid Catalyszed Hydration in presence of Mercuric Salt

This reaction follows Markovnikov addition.



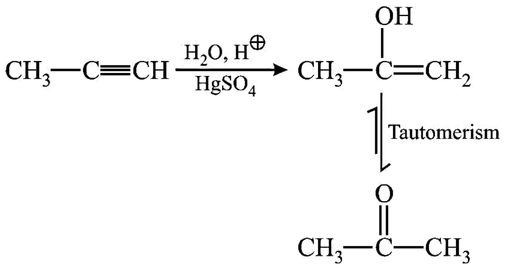
$$R{-}C{\equiv}C{-}R' \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4} \underset{\text{Enol.}}{R{-}\overset{H}{C}{=}\overset{OH}{C}{-}R'} \xrightleftharpoons{\text{Tautomerism}} R{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}R'$$

Example - 8



$$HC{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H^{\oplus}} H_2C{=}\overset{OH}{CH} \xrightleftharpoons{\text{Tautomerism}} CH_3CHO$$

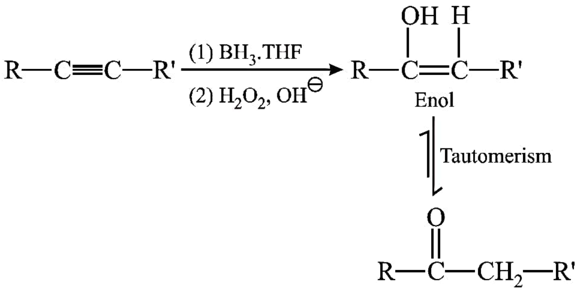
Example - 9



$$CH_3{-}C{\equiv}CH \xrightarrow[HgSO_4]{H_2O,\ H^{\oplus}} CH_3{-}\overset{OH}{C}{=}CH_2 \xrightleftharpoons{\text{Tautomerism}} CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

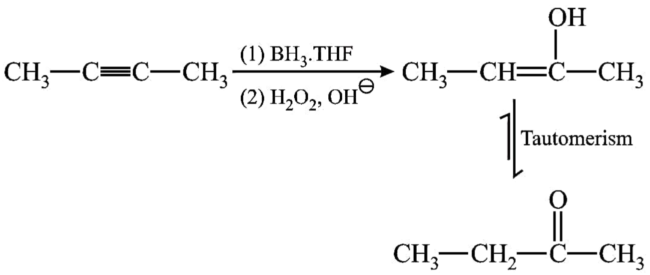
3.3.2 Hydroboration Oxidation

This reaction follows Anti-Markonikov addition. The reagent that can be used are BH_3 or Sia_2BH (Disiamylborane).



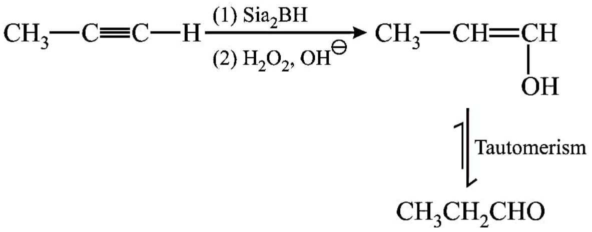
$$R{-}C{\equiv}C{-}R' \xrightarrow[(2)\ H_2O_2,\ OH^{\ominus}]{(1)\ BH_3.THF} \underset{\text{Enol}}{R{-}\overset{OH}{C}{=}\overset{H}{C}{-}R'} \xrightleftharpoons{\text{Tautomerism}} R{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}R'$$

Example - 10



$$CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow[(2)\ H_2O_2,\ OH^{\ominus}]{(1)\ BH_3.THF} CH_3{-}CH{=}\overset{OH}{C}{-}CH_3 \xrightleftharpoons{\text{Tautomerism}} CH_3{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3$$

Example - 11



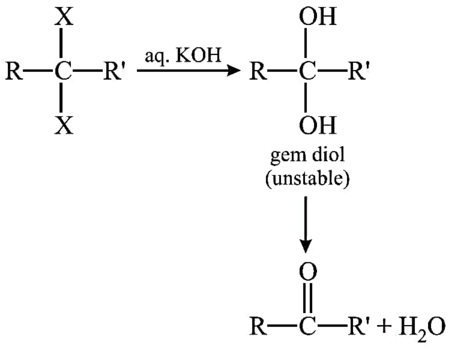
$$CH_3{-}C{\equiv}C{-}H \xrightarrow[(2)\ H_2O_2,\ OH^{\ominus}]{(1)\ Sia_2BH} CH_3{-}CH{=}\underset{OH}{CH} \xrightleftharpoons{\text{Tautomerism}} CH_3CH_2CHO$$

Note...

1. Formation of aldehydes from terminal alkynes requires the use of sterically hindered alkyl borane reagent such as Sia_2BH otherwise the reaction will not terminate at the vinyl borane stage and yield of aldehyde is not satisfactory.
2. Hydration of an internal alkyne always yields a ketone.
3. Acid catalyzed hydration of acetylene yields acetaldehyde. All other terminal alkynes yield ketone.
4. Hydroboration oxidation of terminal alkynes always yields an aldehyde.

3.4 Alkyl Halides

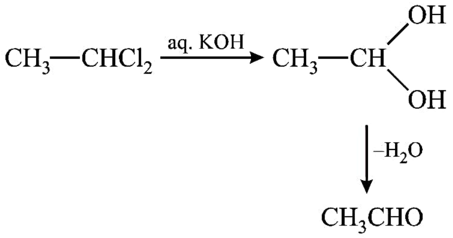
Hydrolysis of geminal dihalides yields carbonyl compounds.



$$R-\overset{X}{\underset{X}{C}}-R' \xrightarrow{\text{aq. KOH}} R-\overset{OH}{\underset{OH}{C}}-R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-R' + H_2O$$

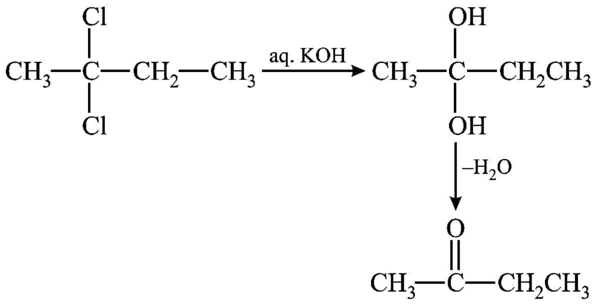
gem diol (unstable)

Example - 12



$$CH_3-CHCl_2 \xrightarrow{\text{aq. KOH}} CH_3-CH(OH)_2 \xrightarrow{-H_2O} CH_3CHO$$

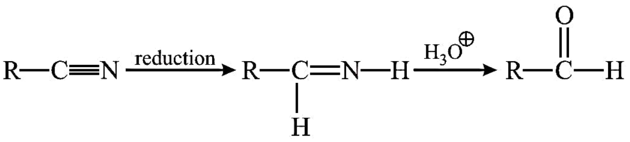
Example - 13



$$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_2-CH_3 \xrightarrow{\text{aq. KOH}} CH_3-\overset{OH}{\underset{OH}{C}}-CH_2CH_3 \xrightarrow{-H_2O} CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

3.5 Alkyl Cyanides

3.5.1 Reduction of Cyanides

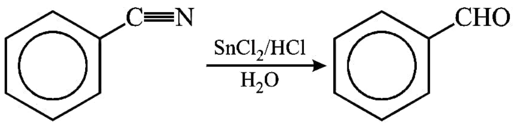


$$R-C\equiv N \xrightarrow{\text{reduction}} R-\underset{H}{C}=N-H \xrightarrow{H_3O^{\oplus}} R-\overset{O}{\overset{\|}{C}}-H$$

Note...

1. If reduction is carried out with $SnCl_2/HCl$, the reaction is called **Stephen's Reduction**.
2. The reduction can also be carried out with **DIBAL-H** (Di-Isobutyl Aluminium Hydride).
3. Only aldehydes are prepared by this method.

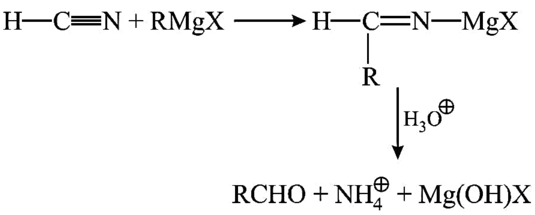
Example - 14



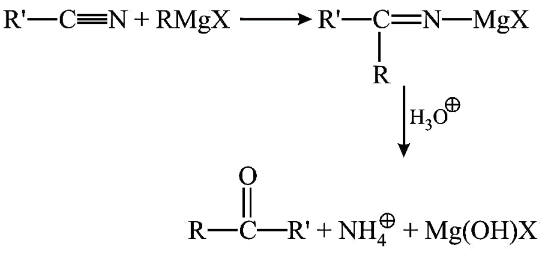
Example - 15

$$CH_3-C\equiv N \xrightarrow[\text{(2) } H_3O^{\oplus}]{\text{(1) DIBAL-H}} CH_3-CHO$$

3.5.2 Grignard Reagent

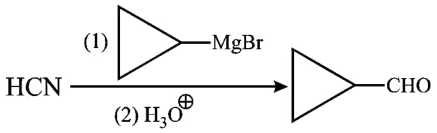


$$H-C\equiv N + RMgX \longrightarrow H-\underset{R}{C}=N-MgX \xrightarrow{H_3O^{\oplus}} RCHO + NH_4^{\oplus} + Mg(OH)X$$

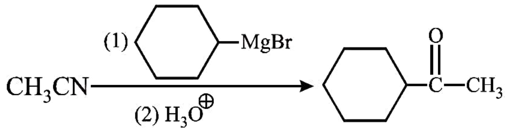


$$R'-C\equiv N + RMgX \longrightarrow R'-\underset{R}{C}=N-MgX \xrightarrow{H_3O^{\oplus}} R-\overset{O}{\overset{\|}{C}}-R' + NH_4^{\oplus} + Mg(OH)X$$

Example - 16



Example - 17



Note...

1. Reaction of Grignard reagent with HCN gives aldehyde.
2. Reaction of Grignard reagent with alkyl cyanide (RCN) gives ketone.

3.6 Alcohols

Primary alcohols (1°) are oxidized to aldehydes whereas secondary alcohols (2°) are oxidized to ketones using suitable reagents. Tertiary alcohols (3°) cannot be oxidized using following methods.

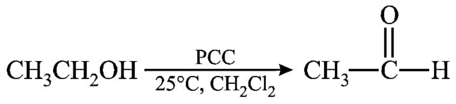
3.6.1 PCC/PDC/Collin's Reagent

Pyridinium chlorochromate (PCC) and Pyridinium dichromate (PDC) oxidize 1° alcohols and 2° alcohols to aldehydes and ketones respectively.

Note...

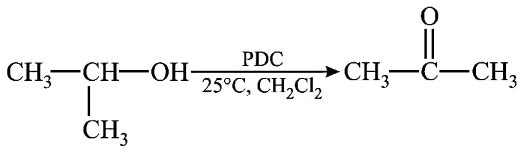
1. Collin's Reagent-Dipyridine Chromium (VI) oxide. $CrO_3.2C_5H_5N$ in CH_2Cl_2.
2. Corey's Reagent - PCC in CH_2Cl_2.
3. Cr (VI) oxidizes 1° alcohols to aldehydes in anhydrons medium and to carboxylic acids in aqueous medium.

Example - 18



$$CH_3CH_2OH \xrightarrow[25°C,\ CH_2Cl_2]{PCC} CH_3-\overset{\overset{O}{\|}}{C}-H$$

Example - 19

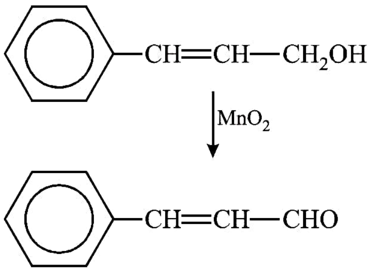


$$CH_3-\underset{\underset{CH_3}{|}}{CH}-OH \xrightarrow[25°C,\ CH_2Cl_2]{PDC} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

3.6.2 MnO_2

Allylic, benzylic and propargylic alcohol are oxidized to aldehydes and ketones by MnO_2.

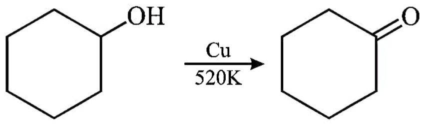
Example - 20



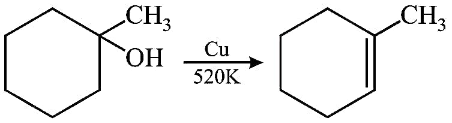
3.6.3 Cu, Δ - Vapour Phase Dehydrogenation

Vapours of alcohol are passed over heated copper to convert them into aldehydes and ketones. 3° alcohols are oxidized to alkenes.

Example - 21



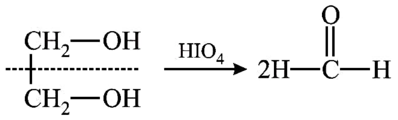
Example - 22



3.6.4 Periodic Acid/Lead Tetraacetate

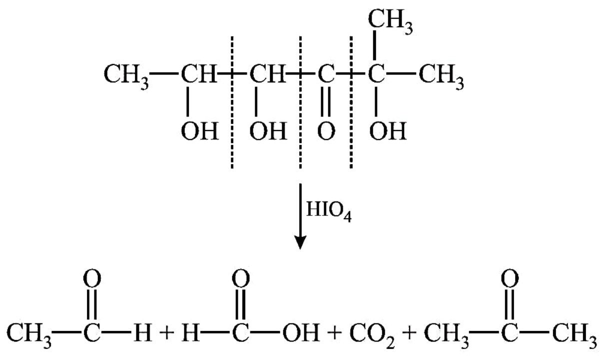
Oxidation of vicinal diols can be carried out with oxidizing agents such as **periodic acid, HIO_4** and **lead tetra acetate, $(CH_3COO)_4Pb$.** These oxidizing agents also cleave vicinal diketo compounds to carboxylic acids.

Example - 23



$$\begin{matrix}CH_2-OH\\ |\\ CH_2-OH\end{matrix} \xrightarrow{HIO_4} 2H-\overset{\overset{O}{\|}}{C}-H$$

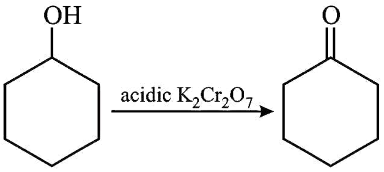
Example - 24



3.6.5 $KMnO_4$, $K_2Cr_2O_7$, Jones Reagent

Oxidizing agents such as alkaline $KMnO_4$, acidic $K_2Cr_2O_7$ and Jones Reagent ($CrO_3 + H_2O$/Acetone) oxidize secondary alcohols to ketones. With primary alcohols, they yield carboxylic acids.

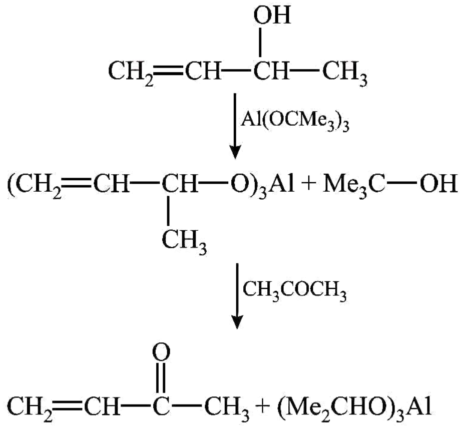
Example - 25



3.6.6 Oppenauer Oxidation

Secondary Alcohols are oxidized to ketones by refluxing them with aluminium tert-butoxide and then acetone is added. The reaction is selective and is particularly used to oxidize unsaturated secondary alcohols.

Example - 26

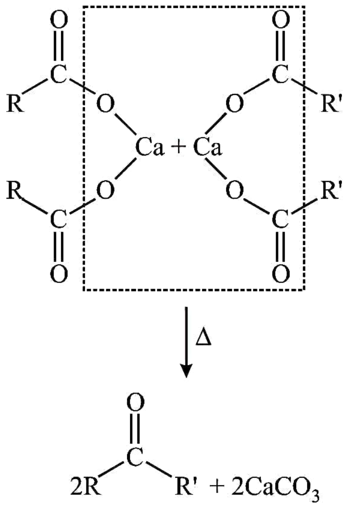


$$CH_2{=}CH{-}\underset{}{\overset{OH}{\overset{|}{C}}}H{-}CH_3 \xrightarrow{Al(OCMe_3)_3} (CH_2{=}CH{-}\underset{\underset{CH_3}{|}}{C}H{-}O)_3Al + Me_3C{-}OH \xrightarrow{CH_3COCH_3} CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3 + (Me_2CHO)_3Al$$

3.7 Carboxylic Acids and Derivatives

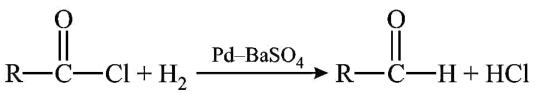
3.7.1 Decarboxylation of Ca Salts

A calcium salt of monocarboxylic acids on heating gives ketone. If heated with calcium salt of formic acid, the product is an aldehyde.



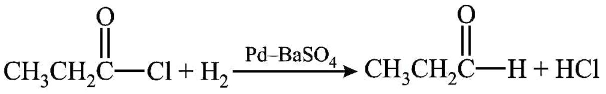
3.7.2 Rosenmund's Reduction

Acid chloride is reduced in boiling xylene using **palladium catalyst supported on barium sulphate**. Small amounts of quinoline and sulphur are also added to increase poisoning. **Lithium tri-t-butoxyaluminium hydride** can also reduce acid chloride to aldehyde.



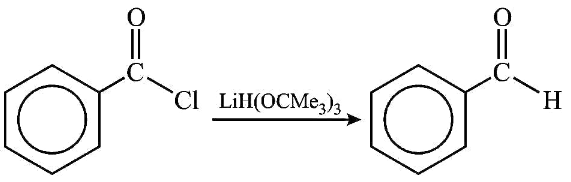
$$R{-}\overset{\overset{O}{\|}}{C}{-}Cl + H_2 \xrightarrow{Pd{-}BaSO_4} R{-}\overset{\overset{O}{\|}}{C}{-}H + HCl$$

Example - 27

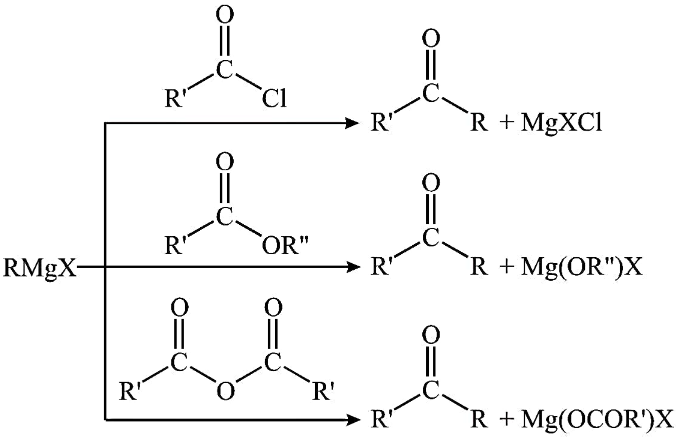


$$CH_3CH_2\overset{\overset{O}{\|}}{C}{-}Cl + H_2 \xrightarrow{Pd{-}BaSO_4} CH_3CH_2\overset{\overset{O}{\|}}{C}{-}H + HCl$$

Example - 28



3.7.3 Acid Derivatives and Grignard Reagent



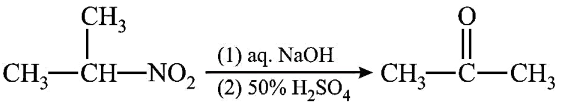
3.8 Nitro Alkanes – NEF Carbonyl Synthesis

Nitro compounds dissolve in aqueous sodium hydroxide to form salts. When this salt is acidified with 50% H_2SO_4, aldehydes (from 1°) and ketones (from 2°) are formed.

Example - 29

$$CH_3CH_2NO_2 \xrightarrow[\text{(2) 50\% } H_2SO_4]{\text{(1) aq. NaOH}} CH_3CH_2CHO$$

Example - 30

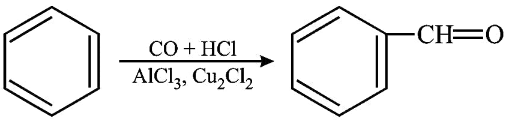


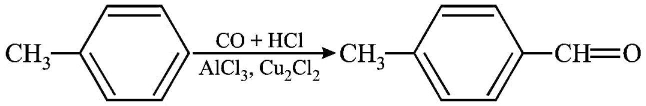
$$CH_3-\underset{\displaystyle CH_3}{CH}-NO_2 \xrightarrow[\text{(2) 50\% } H_2SO_4]{\text{(1) aq. NaOH}} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

3.9 Aromatic Aldehydes

3.9.1 Gattermann Koch Aldehyde Synthesis

Carbon monoxide and HCl are passed through benzene solution in ether in the presence of $AlCl_3$ (catalyst) to produce benzaldehyde.

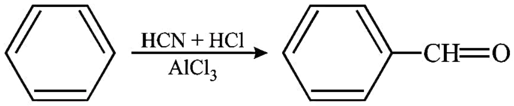




(Predominating product)

3.9.2 Gattermann Aldehyde Synthesis

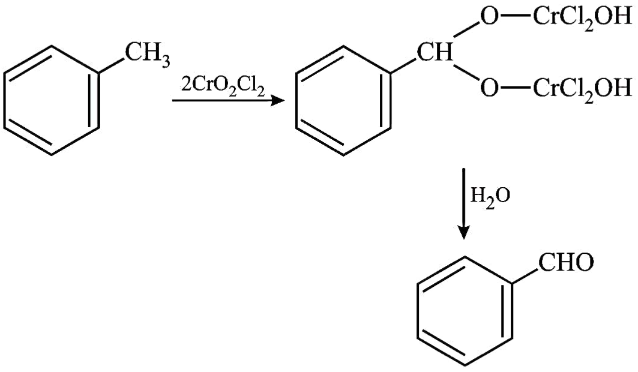
Benzene on treatment with hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride initially gives imine which is hydrolysed into benzaldehyde.



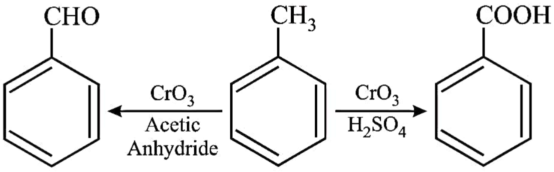
3.9.3 Etard Reaction

Toluene on treatment with chromyl chloride in CCl_4, and on following hydrolysis gives benzaldehyde.

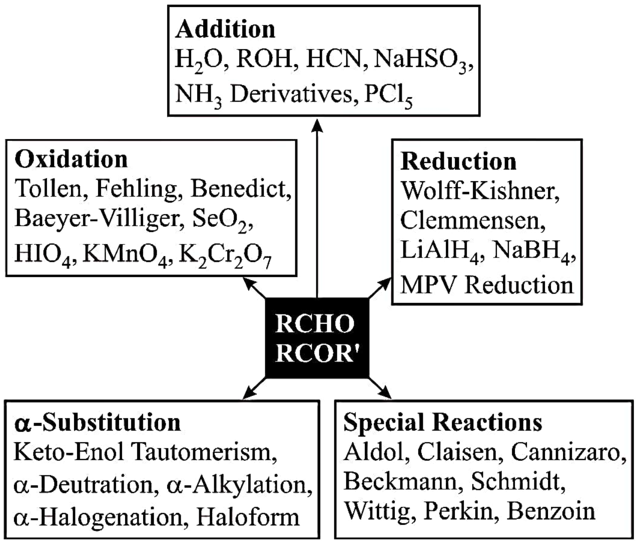
Toluene on treatment with CrO_3 in acetic anhydride also gives benzaldehyde. The formation of benzalidene acetate as intermediate prevents further oxidation to acid.



Example - 31



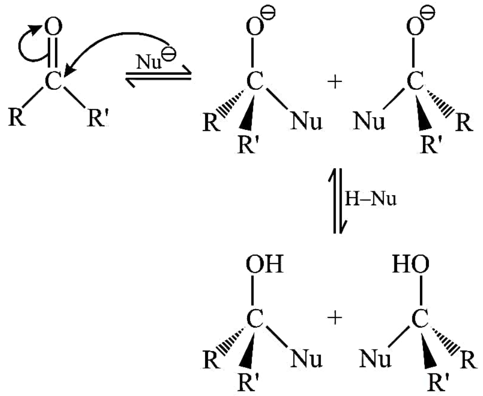
4. REACTIONS OF CARBONYL COMPOUNDS



4.1 Addition Reactions

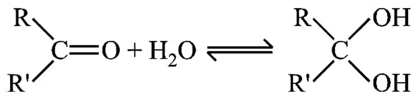
4.1.1 General Mechanism

Trigonal carbonyl compound gets converted into a tetrahedral product. Electronic as well as steric factor suggest that aldehyde is more reactive in comparison to ketone. Racemisation may proceed.



4.1.2 Addition of H_2O – Hydrate Formation

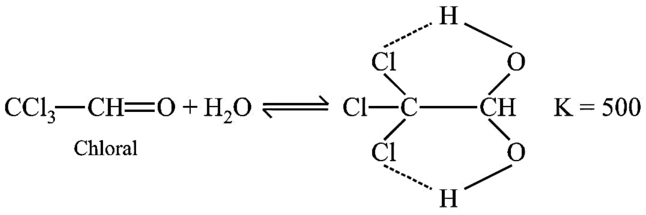
Hydrate is a geminal diol, which is usually unstable, that's why it cannot be isolated from the aqueous solution. Formation depends on the equilibrium constant, which reflects the stability of the corresponding hydrate.



R' = H or alkyl or aryl Hydrate

Electron withdrawing groups stabilize the hydrate.

Example - 32

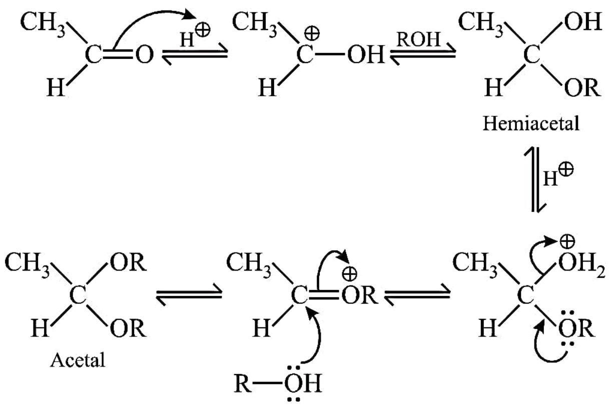


Chloral Chloral Hydrate (solid)

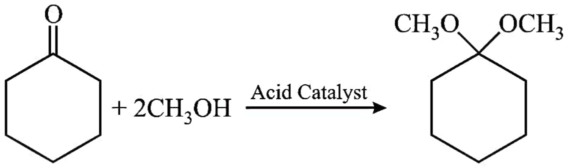
4.1.3 Addition of ROH – Hemiacetal/Acetal Formation

Addition of one alcohol gives hemiacetal and two alcohol molecules gives acetal. Acetal formation involves - acid-catalysed nucleophilic addition to the carbonyl and following unimolecular substitution (S_N1) – protonation, loss of $OH^\ominus$ and attack of alcohol.

Usually reactions are reversible. Simple aldehydes favour the formation of acetal but the hindered aldehydes and most of the ketones do not favour such a formation.

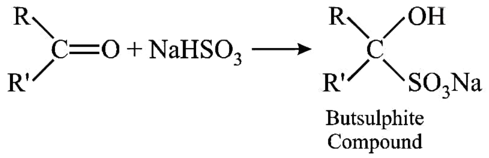


Example - 33

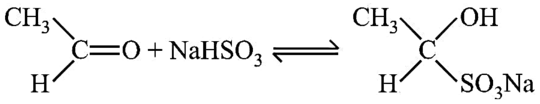


4.1.4 Addition of $NaHSO_3$ – Bisulphite formation

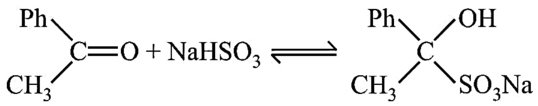
Aldehydes and ketones add on sodium hydrogen sulphite to form a bisulphite compound (hydroxy sulphonic acid salts). Most of ketones, especially hindered ketones have very less tendency to form bisulphites. Bisulphite compounds are usually crystalline solids insoluble in sodium hydrogen sulphite solution.



Example - 34



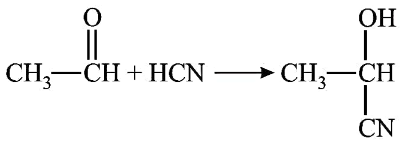
Example - 35



4.1.5 Addition of HCN – Cyanohydrin formation

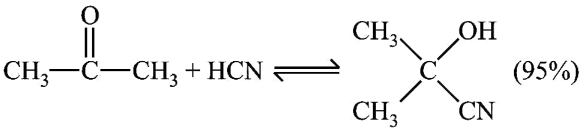
Addition of HCN to aldehyde or ketone gives cyanohydrin (α-hydroxynitrile). HCN (Hydrocyanic acid) is a weak $Nu^{\ominus}$ provider, reaction is usually acid or base catalysed. Presence of $H^{\oplus}$ increases reactivity of carbonyl group while $OH^{\ominus}$ increases reactivity of $CN^{\ominus}$, but in both the conditions, the reaction is a nucleophilic addition. Reaction is usually reversible, cyanohydrin formation depends on the extent of equilibrium (equilibrium constant).

Example - 36



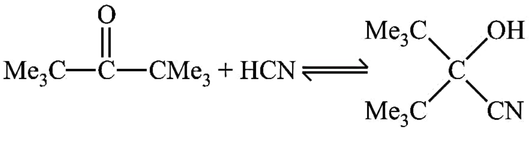
$$CH_3-\overset{\overset{O}{\|}}{C}H + HCN \longrightarrow CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}H}$$

Example - 37



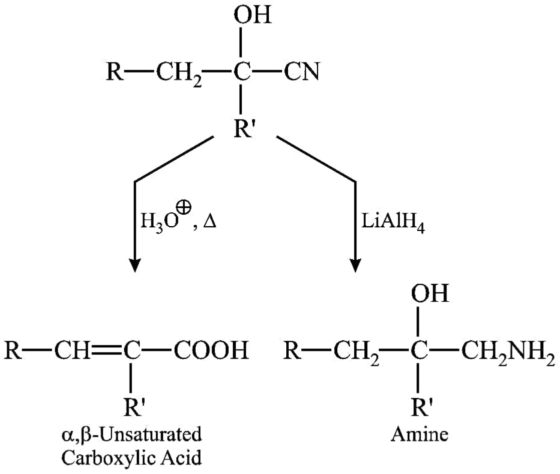
(95%)

Example - 38

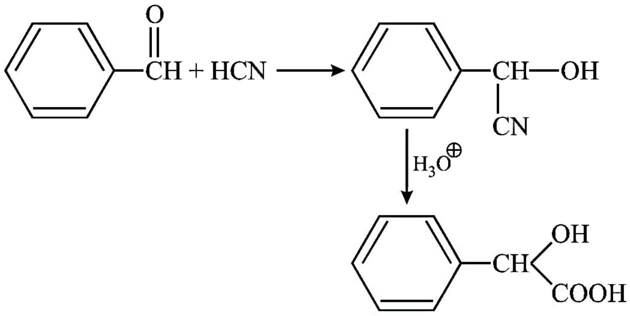


(≈ 5%)

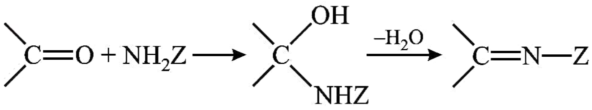
Applications of Cyanohydrins



Example - 39

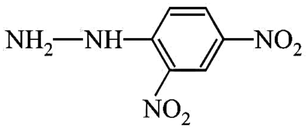
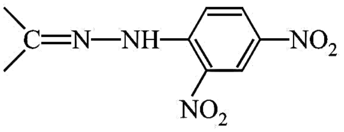
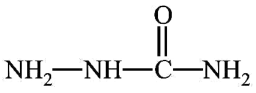
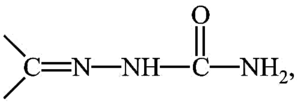


4.1.6 Addition of NH_3 Derivatives



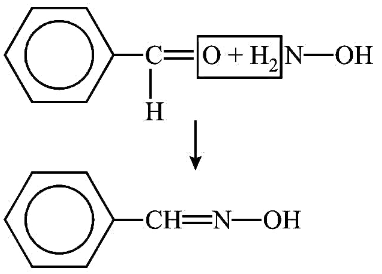
Usually, the reaction is acid catalysed.

The product can demonstrate geometrical isomerism (syn-anti). It is a crystalline solid.

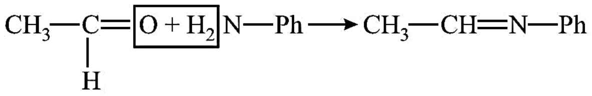
Reagent	Reagent Name	Product	Product Name
NH_2-R	Primary (1°) Amine	$>C=N-R,$	Imine (Schiff Base)
NH_2-OH	Hydroxylamine	$>C=N-OH,$	Oxime
NH_2-NH_2	Hydrazine	$>C=N-NH_2,$	Hydrazone
NH_2-NHPh	Phenyl Hydrazine	$>C=N-NHPh,$	Phenyl Hydrazone
	2, 4-Dinitrophenyl Hydrazine (Brady's Reagent)		2, 4-Dinitrophenyl Hydrazone
 $NH_2-NH-\overset{\overset{\displaystyle O}{\Vert}}{C}-NH_2$	Semicarbazine	 $>C=N-NH-\overset{\overset{\displaystyle O}{\Vert}}{C}-NH_2,$	Semicarbazone

Note... The reaction with Brady's reagent is known as **DNP Test** and is used as a test for detection of carbonyl compounds.

Example - 40



Example - 41



$$CH_3-\underset{\underset{\displaystyle H}{|}}{C}=\boxed{O+H_2}N-Ph \longrightarrow CH_3-CH=N-Ph$$

4.1.7 Addition of Grignard Reagent – Alcohol Formation

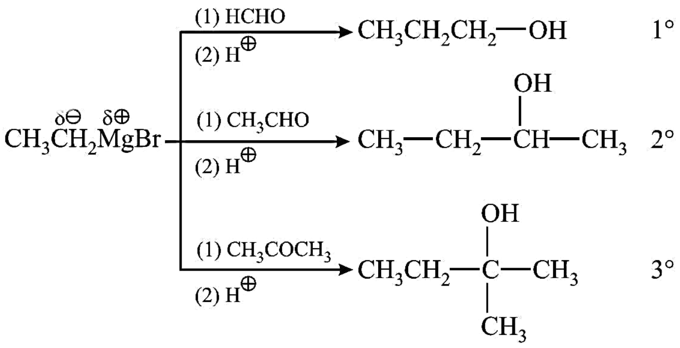
A Grignard reagent (a strong nucleophile resembling a carbanion $R^{\ominus}$) attacks on an aldehyde or a ketone, the subsequent protonation gives the alcohol.

HCHO ⟶ 1° alcohol

RCHO ⟶ 2° alcohol

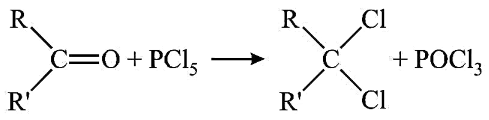
RCOR′ ⟶ 3° alcohol

Example - 42



4.1.8 Addition of PCl_5

On reaction with PCl_5, carbonyl compounds give gem-dihalide.



4.2 Reduction Reactions

4.2.1 Reduction to Alkanes

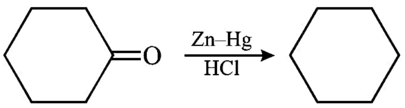
(A) Wolff-Kishner Reduction

Hydrazone or semicarbazone when heated at 180°C with sodium ethoxide, gives out nitrogen and hydrocarbon.

(B) Clemmensen Reduction

Aldehydes and ketones which are not acid sensitive when heated with excess of amalgamated zinc (Zn–Hg) and HCl, give the corresponding alkanes.

Example - 43



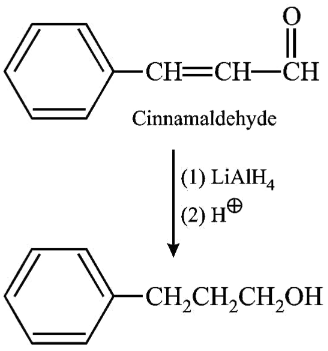
4.2.2 Reduction to Alcohols

(A) Metal Hydrides and Hydrogenation

Aldehydes and ketones are reduced to 1° and 2° alcohols respectively by various reagents, e.g., H_2/Ni, B_2H_6, $LiAlH_4$, $NaBH_4$, etc. Usually $LiAlH_4$ doesn't affect the double and triple bonds. It selectively reduces carbonyl group but reduces even the double bond in the cinnamyl system.

Example - 44

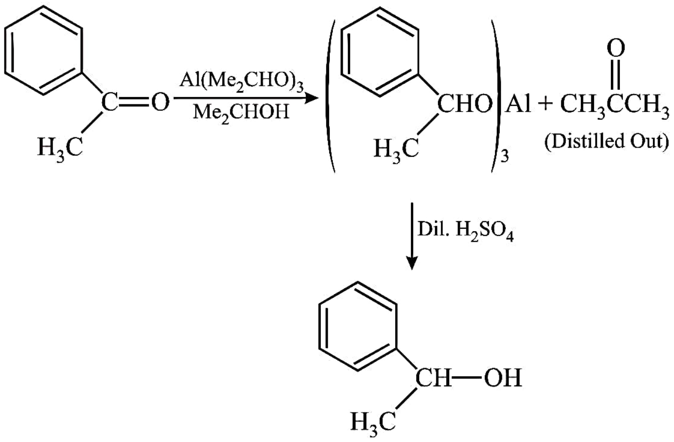
Example - 45



(B) Meerwein-Ponndorf-Verley Reduction

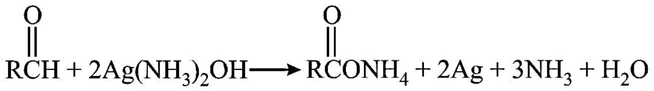
Carbonyl compound is heated with aluminium isopropoxide in isopropanol. Isopropoxide is oxidised to acetone. Without affecting double or triple bonds and some other functional groups, selectively carbonyl group is reduced to the corresponding alcohol.

Example - 46

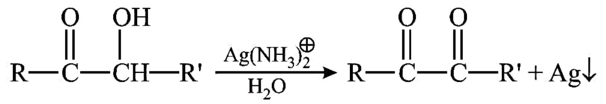


4.3 Oxidation Reactions

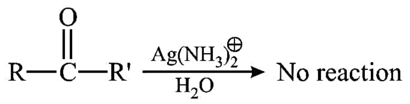
Aldehydes are easily oxidised and hence, are powerful reducing agents. Aldehydes reduce Fehling's solution (alkaline solution of Cu^{2+} with tartaric acid) to red cuprous oxide, Tollen's reagent (ammoniacal silver nitrate) to metallic silver. Benzaldehyde do not reduce Cu^{2+} salt (Fehling solution). Ketones (except α-hydroxy ketones) don't reduce Tollen's reagent and the Fehling solution. Benzaldehyde gives positive Tollen's test. All aldehydes and ketones are oxidised by permanganate, acid dichromates etc. These strong oxidising agents oxidise adjacent carbon atom of ketonic carbonyl and the carbonyl group remains chiefly with smaller alkyl group. **(Popoff's rule)**



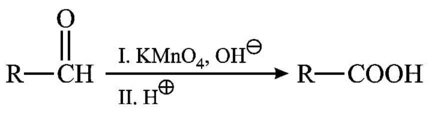
$$R\overset{\overset{O}{\|}}{C}H + 2Ag(NH_3)_2OH \longrightarrow R\overset{\overset{O}{\|}}{C}ONH_4 + 2Ag + 3NH_3 + H_2O$$



$$R—\overset{\overset{O}{\|}}{C}—\overset{\overset{OH}{|}}{C}H—R' \xrightarrow[H_2O]{Ag(NH_3)_2^{\oplus}} R—\overset{\overset{O}{\|}}{C}—\overset{\overset{O}{\|}}{C}—R' + Ag\downarrow$$



$$R—\overset{\overset{O}{\|}}{C}—R' \xrightarrow[H_2O]{Ag(NH_3)_2^{\oplus}} \text{No reaction}$$

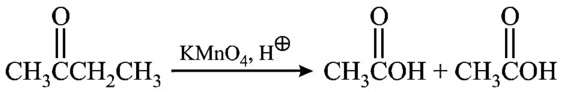


$$R—\overset{\overset{O}{\|}}{C}H \xrightarrow[II.\ H^{\oplus}]{I.\ KMnO_4,\ OH^{\ominus}} R—COOH$$

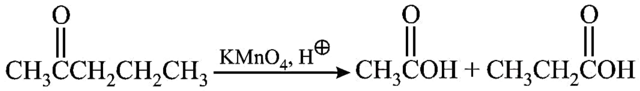
Example - 47

$$C_6H_5CH{=}O \xrightarrow[H_2O]{Ag(NH_3)_2^{\oplus}} C_6H_5COO^{\ominus} + Ag\downarrow$$

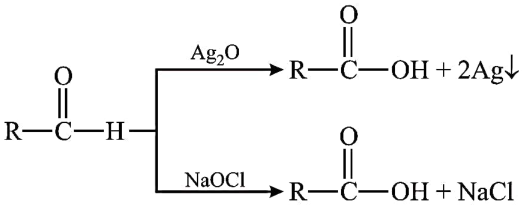
Example - 48



$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow{KMnO_4,\ H^{\oplus}} CH_3\overset{O}{\overset{\|}{C}}OH + CH_3\overset{O}{\overset{\|}{C}}OH$$



$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow{KMnO_4,\ H^{\oplus}} CH_3\overset{O}{\overset{\|}{C}}OH + CH_3CH_2\overset{O}{\overset{\|}{C}}OH$$



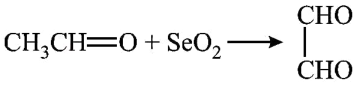
$$R{-}\overset{O}{\overset{\|}{C}}{-}H \xrightarrow{Ag_2O} R{-}\overset{O}{\overset{\|}{C}}{-}OH + 2Ag\downarrow$$

$$R{-}\overset{O}{\overset{\|}{C}}{-}H \xrightarrow{NaOCl} R{-}\overset{O}{\overset{\|}{C}}{-}OH + NaCl$$

4.3.1 Oxidation by SeO_2

Methyl or methylene adjacent to carbonyl group is oxidised to carbonyl group by SeO_2.

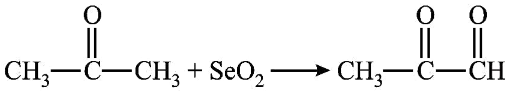
Example - 49



$$CH_3CH{=}O + SeO_2 \longrightarrow \begin{array}{c}CHO\\ |\\ CHO\end{array}$$

Glyoxal

Example - 50



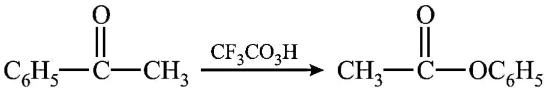
$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 + SeO_2 \longrightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}H$$

Methyl glyoxal

4.3.2 Baeyer-Villiger Oxidation of Ketones

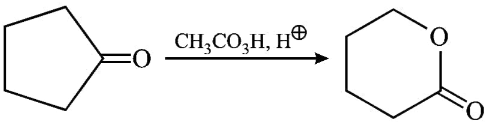
Ketones on treatment with peracids such as perbenzoic acid or peracetic acid or with other peroxy compounds in the presence of acid catalysts, give carboxylic esters by insertion of oxygen. The reaction involves rearrangement at electron deficient oxygen. For unsymmetrical ketones the approximate order of migratory aptitude is : 3° alkyl > 2° alkyl, phenyl > 1° alkyl.

Example - 51



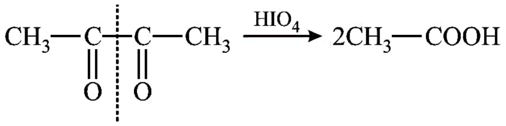
$$C_6H_5{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xrightarrow{CF_3CO_3H} CH_3{-}\overset{O}{\overset{\|}{C}}{-}OC_6H_5$$

Example - 52



4.3.3 Oxidation by $HIO_4/Pb(CH_3COO)_4$

Example - 53



$$CH_3{-}\underset{O}{\underset{\|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}CH_3 \xrightarrow{HIO_4} 2CH_3{-}COOH$$

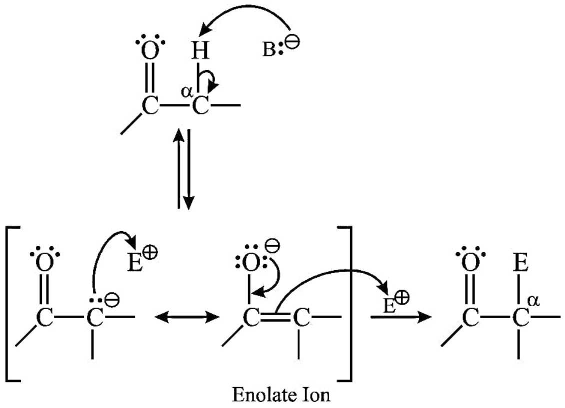
4.4 Alpha Substitutions

Alpha (α) substitutions involve the replacement of a hydrogen atom at the α carbon atom (the carbon next to the carbonyl group) by some other group. The α hydrogen is more acidic because the enolate ion that results from its removal is resonance-stabilized, with the negative charge delocalized over the α carbon atom and the carbonyl oxygen atom.

Base Catalyzed α-Substitution

Step 1: Deprotonation of α carbon to form an enolate.

Step 2: Nucleophilic attack on an electrophile.

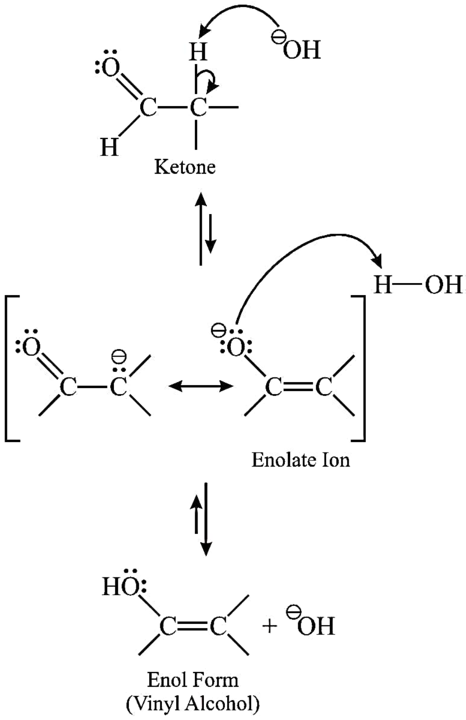


4.4.1 Keto-Enol Tautomerism

(A) Base-Catalyzed Mechanism

Step 1: Deprotonation of α C.

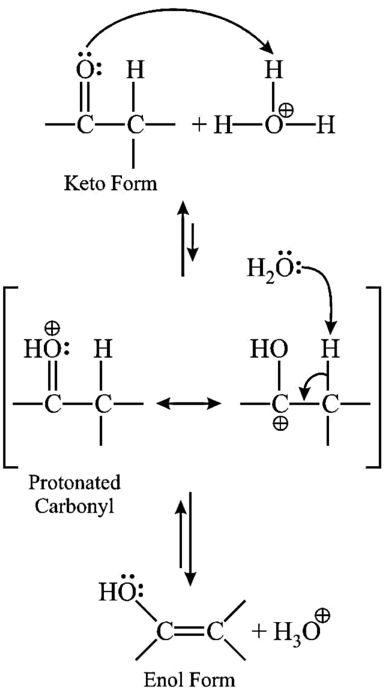
Step 2: Reprotonation on O.



(B) Acid-Catalyzed Mechanism

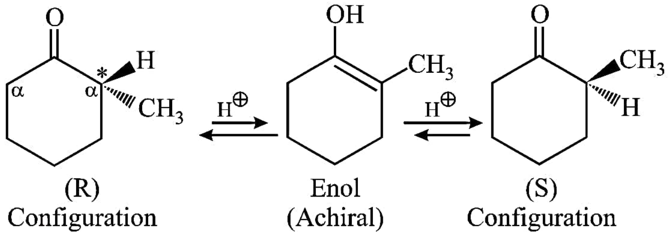
Step 1: An acid protonates the carbonyl oxygen.

Step 2: Deprotonation on C gives the enol form.

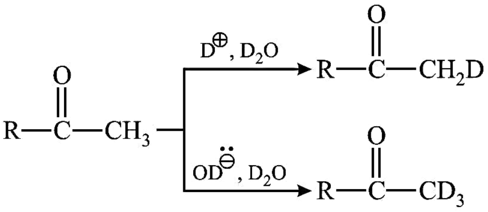


Note...

1. Acid catalyzed mechanism is slower than the base catalyzed mechanism.
2. If an asymmetric carbon atom has an enolizable hydrogen atom, a trace of acid or base allows that carbon to invert its configuration, with the enol serving as the intermediate. A racemic mixture (or an equilibrium mixture of diastereomters) is the result.



4.4.2 α-Deutration



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{D^{\oplus},\ D_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2D$$

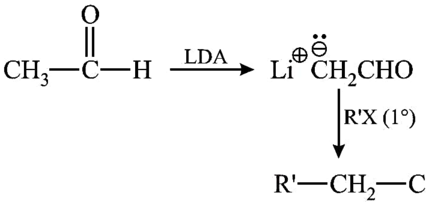
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{\ddot{O}D^{\ominus},\ D_2O} R-\overset{\overset{\displaystyle O}{\|}}{C}-CD_3$$

Note...

1. In acid-catalyzed alpha substitution, only mono substitution is observed.
2. In base-catalyzed alpha substitution, all α-H are substituted.

4.4.3 α-Alkylation

Example - 54

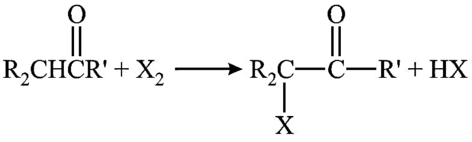


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{LDA} Li^{\oplus}\overset{\ominus}{C}H_2CHO \xrightarrow{R'X\ (1^\circ)} R'-CH_2-CHO$$

LDA - Lithium Diisopropyl amide $LiN(iPr)_2$

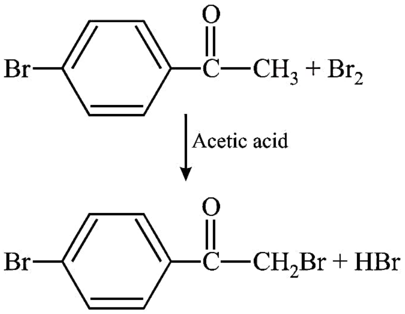
4.4.4 α-Halogenation

Chlorine or bromine replaces one or more α-hydrogen atoms in aldehydes and ketones. Acetone may be brominated in glacial acetic acid to give monobromoacetone. Reaction occurs by electrophilic attack of the halogen on the carbon-carbon double bond of the enol form. The halogenation is catalysed by acids and bases.



$$R_2CH\overset{\overset{\displaystyle O}{\|}}{C}R' + X_2 \longrightarrow R_2\underset{\underset{\displaystyle X}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-R' + HX$$

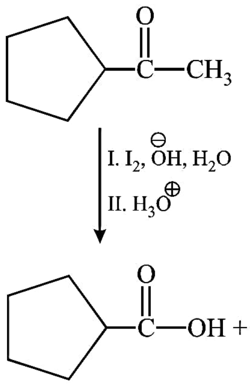
Example - 55



4.4.5 Haloform Reaction

Methyl ketones are cleaved on reaction with excess halogen in the presence of a base. The products are a trihalomethane (haloform) and a carboxylate salt. In aqueous sodium hydroxide, **the rate has been shown to be independent of the bromine concentration**. The reaction is used for structural determinations. The positive iodoform (bright yellow ppt) confirms $CH_3\underset{\underset{O}{\|}}{C}—$ part usually.

Example - 56

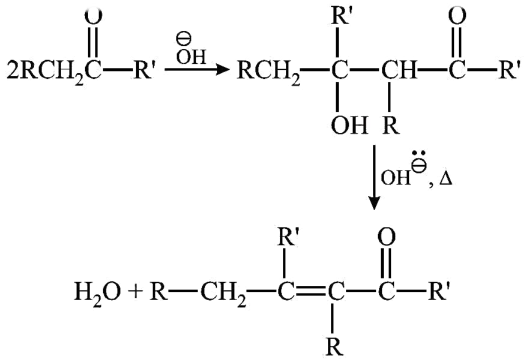


4.5 Special Reactions

4.5.1 Aldol Condensation

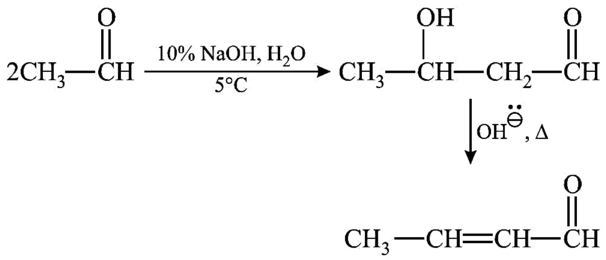
(A) Self-Aldol Condensation

The enolisable carbonyl compound in the presence of $H^{\oplus}$ or $\ddot{OH}^{\ominus}$ (at or below room temp.) undergoes dimerisation, producing aldol. The following dehydration gives α,β-unsaturated aldehyde or ketone. Actually reaction involves nucleophilic addition of an enolate ion to the carbonyl group. Aldehydes are more suitable for aldol condensation than ketones.



$$2RCH_2\overset{\overset{O}{\|}}{C}—R' \xrightarrow{\overset{\ominus}{OH}} RCH_2—\underset{\underset{OH}{|}}{\overset{\overset{R'}{|}}{C}}—\underset{\underset{R}{|}}{CH}—\overset{\overset{O}{\|}}{C}—R' \xrightarrow{\ddot{OH}^{\ominus},\ \Delta} H_2O + R—CH_2—\overset{\overset{R'}{|}}{C}=\underset{\underset{R}{|}}{C}—\overset{\overset{O}{\|}}{C}—R'$$

Example - 57

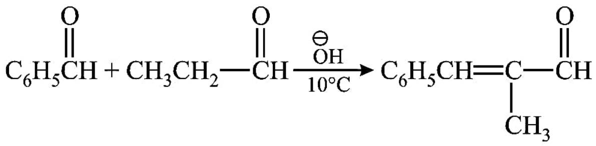


$$2CH_3—\overset{\overset{O}{\|}}{C}H \xrightarrow[5°C]{10\%\ NaOH,\ H_2O} CH_3—\overset{\overset{OH}{|}}{C}H—CH_2—\overset{\overset{O}{\|}}{C}H \xrightarrow{\ddot{OH}^{\ominus},\ \Delta} CH_3—CH=CH—\overset{\overset{O}{\|}}{C}H$$

(B) Cross-Aldol Condensation (Claisen-Schmidt Reaction)

A mixed aldol condensation, more precisely the condensation of aromatic aldehyde (or aldehyde without α-Hs) with an enolisable aldehyde and ketone, which is most suitable.

Example - 58

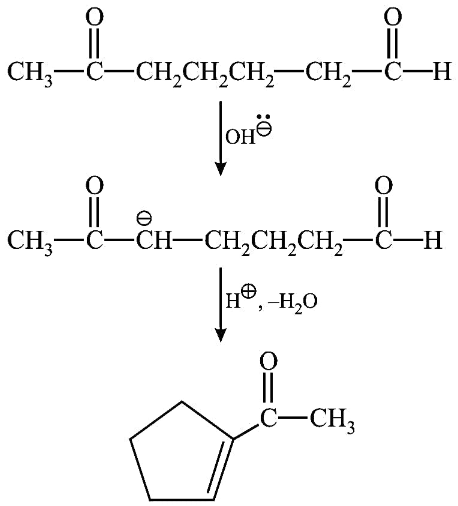


$$C_6H_5\overset{\overset{O}{\|}}{C}H + CH_3CH_2—\overset{\overset{O}{\|}}{C}H \xrightarrow[10°C]{\overset{\ominus}{OH}} C_6H_5CH=\underset{\underset{CH_3}{|}}{C}—\overset{\overset{O}{\|}}{C}H$$

(C) Intramolecular Aldol Condensation

Dicarbonyl compounds give this reaction and undergo cyclization. The formation of the product depends upon the size of the ring (usually 5 or 6 membered rings are formed).

Example - 59

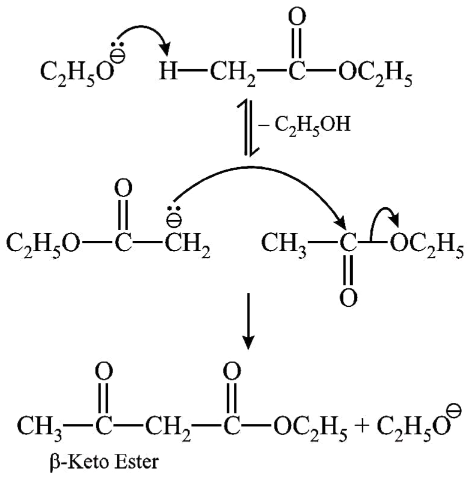


4.5.2 Claisen Condensation

Esters having α-hydrogens on treatment with a strong base such as C_2H_5ONa undergo condensation reactions to produce β-keto esters.

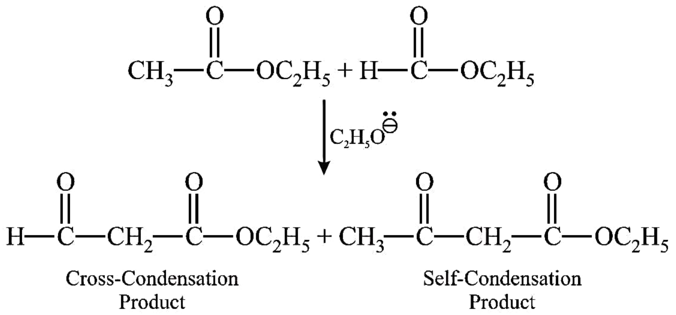
(A) Self-Claisen Condensation

Example - 60



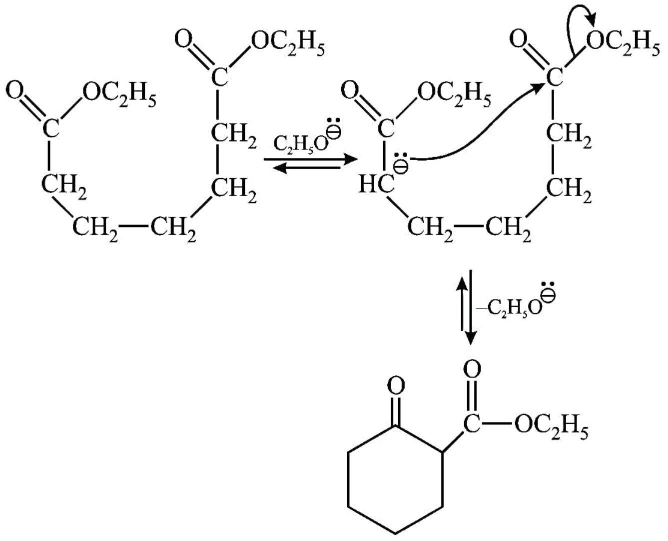
(B) Cross-Claisen Condensation

Example - 61



(C) Intramolecular-Claisen Condensation

(Dieckmann Condensation)

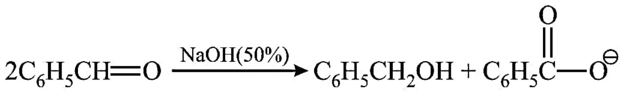


4.5.3 Cannizaro Reaction

It is a characteristic of aldehydes having no α hydrogens e.g., aromatic aldehydes, formaldehydes, etc. It involves oxidation and reduction of molecuels in the presence of highly concentrated $OH^\ominus$ (50%). Reaction is intermolecular. The hydride transfer is the rate determining step.

(A) Self-Cannizaro Reaction

Example - 62

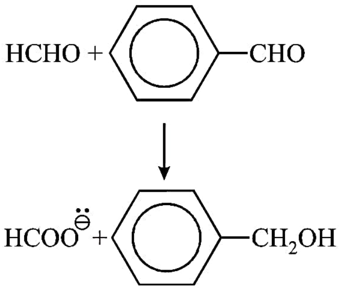


$$2C_6H_5CH{=}O \xrightarrow{NaOH(50\%)} C_6H_5CH_2OH + C_6H_5\overset{\overset{O}{\|}}{C}-O^\ominus$$

(B) Cross-Cannizaro Reaction

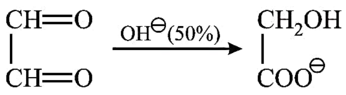
In cross-cannizaro reaction, acid is formed from that molecule which has more electron deficient carbon.

Example - 63



(C) Intramolecular Cannizaro Reaction

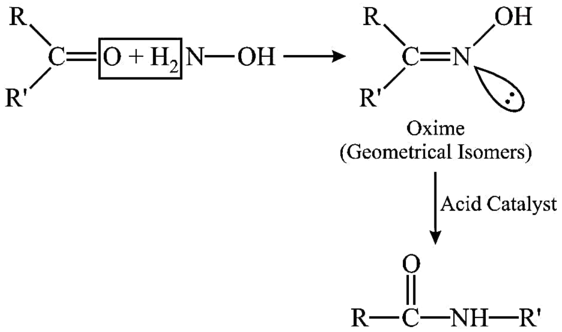
Example - 64



$$\begin{array}{l}CH{=}O\\ |\\ CH{=}O\end{array} \xrightarrow{OH^{\ominus}(50\%)} \begin{array}{l}CH_2OH\\ |\\ COO^{\ominus}\end{array}$$

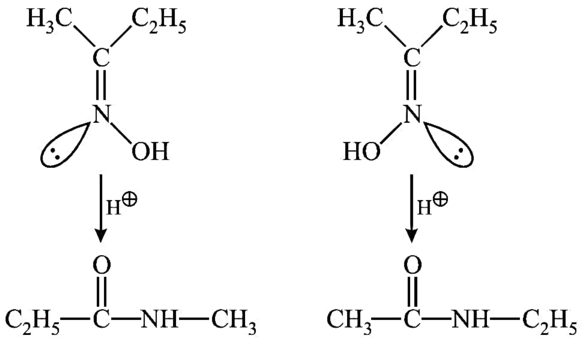
4.5.4 Beckmann Rearrangement

It is the rearrangement of oximes to form substituted amides in the presence of acid catalyst such as H_2SO_4, P_2O_5, BF_3, etc.



> *Note..* The alkyl group that migrates must be **anti** to the OH group.

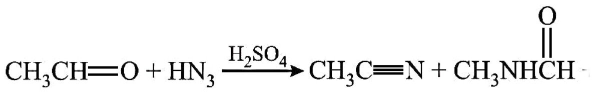
Example - 65



4.5.5 Schmidt Reaction

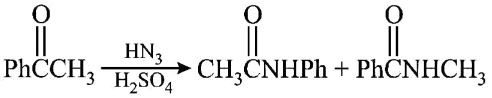
The reaction involves treatment of hydrazoic acid (HN_3) with carbonyl compounds, in the presence of concentrated sulphuric acid. It is a rearrangement at electron deficient nitrogen and is intramolecular in nature.

Example - 66



$$CH_3CH{=}O + HN_3 \xrightarrow{H_2SO_4} CH_3C{\equiv}N + CH_3NH\overset{\overset{O}{\|}}{C}H$$

Example - 67



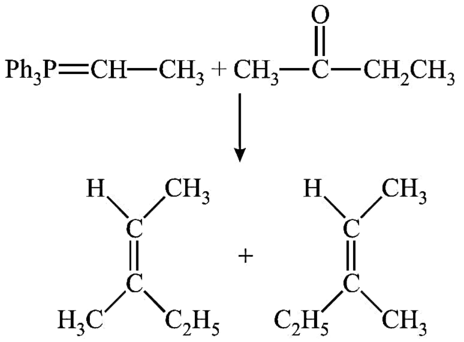
$$Ph\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[H_2SO_4]{HN_3} CH_3\overset{\overset{O}{\|}}{C}NHPh + Ph\overset{\overset{O}{\|}}{C}NHCH_3$$

4.5.6 Wittig Reaction

Carbonyl compounds react with phosphorus ylides (phosphoranes) to yield alkenes and triphenyl phosphine oxide. Reaction involves : First, S_N2 attack of triphenyl phosphine (PPh_3) over 1° and 2° alkyl halide – alkyltriphenyl phosphonium salt. Second, alkyl lithium or phenyl lithium removes a proton (acid-base reaction) from salt to give ylide. Third, the combination of ylide with carbonyl group.

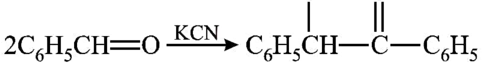
Mixture of E and Z forms are observed.

Example - 68



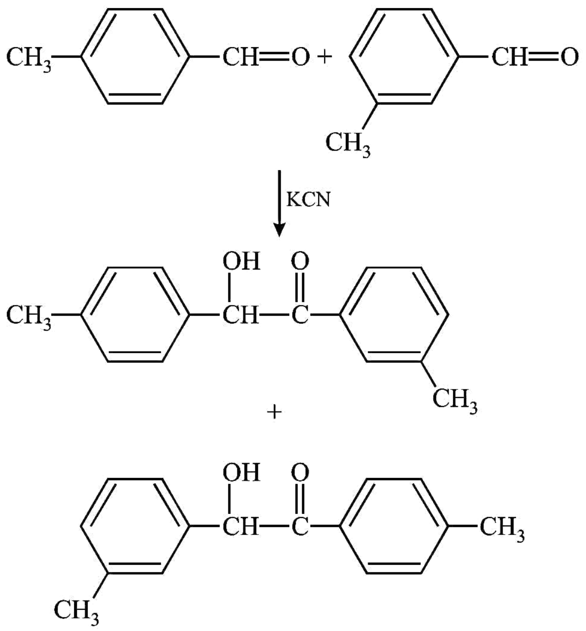
4.5.7 Benzoin Condensation

Benzaldehyde on treatment with aqueous ethanolic potassium cyanide gives benzoin. Mixture of aldehydes give mixed benzoins. Aliphatic aldehydes do not undergo the benzoin condensation. Benzoin is an α-hydroxyketone, hence it reduces Fehling's solution.



$$2C_6H_5CH{=}O \xrightarrow{KCN} C_6H_5\overset{\overset{OH}{|}}{C}H-\overset{\overset{O}{\|}}{C}-C_6H_5$$

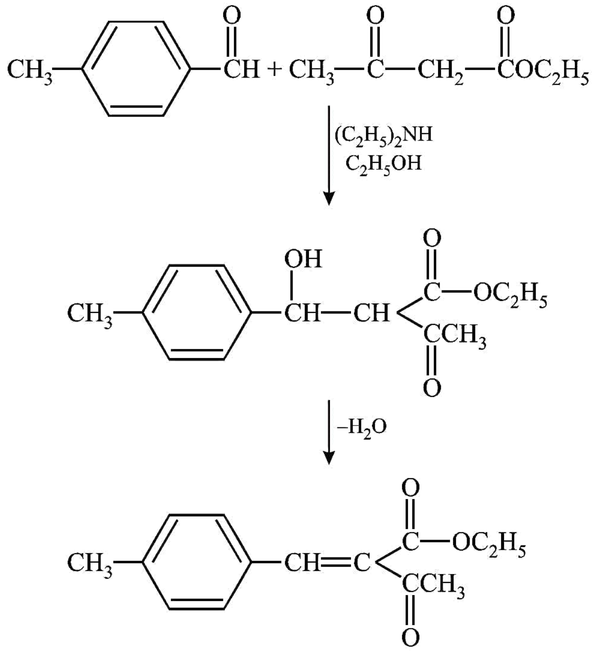
Example - 69



4.5.8 Knoevenagel Condensation

Compounds containing active CH_2 group condense with aldehydes and ketones. It proceeds like aldol condensation and usually aldehydes and ketones do not have α-hydrogens. A CH_2 group is active if it is adjacent to the C=O group.

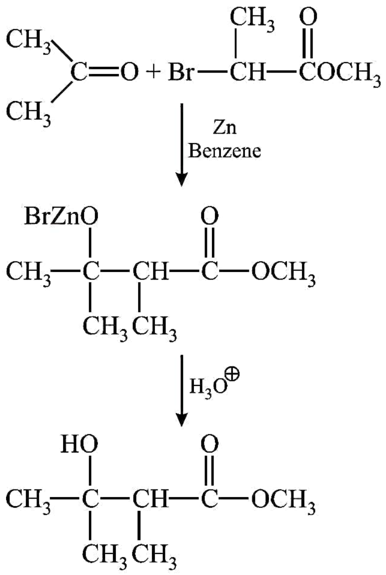
Example - 70



4.5.9 Reformatsky Reaction

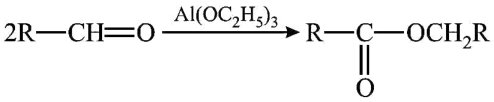
The addition of an organozinc reagent to the carbonyl Actually the intermediate in the reaction appears to organozinc that adds to the carbonyl group in a manner analo to that of a Grignard reagent.

Example - 71



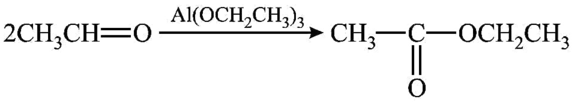
4.5.10 Tischenko Reaction

All aldehydes undergo disproportionation giving ester as the final product (instead of acid and alcohol) in the presence of aluminium ethoxide. Acetaldehyde gives ethyl acetate and propionaldehyde gives propylpropionate.



$$2R{-}CH{=}O \xrightarrow{Al(OC_2H_5)_3} R{-}\underset{\underset{O}{\|}}{C}{-}OCH_2R$$

Example - 72

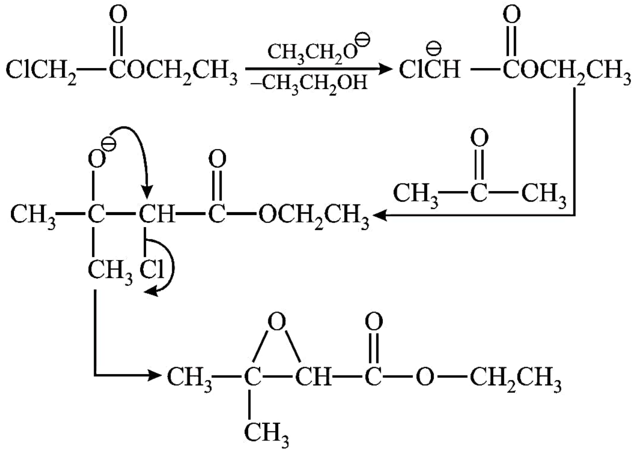


$$2CH_3CH{=}O \xrightarrow{Al(OCH_2CH_3)_3} CH_3{-}\underset{\underset{O}{\|}}{C}{-}OCH_2CH_3$$

4.5.11 Darzen's Glycidic Ester Condensation

The reaction involves the condensation of an aldehyde or ketone with an α-halogen-ester to produce an α, β-epoxy-ester (glycidic ester) in the presence of sodium ethoxide or sodamide.

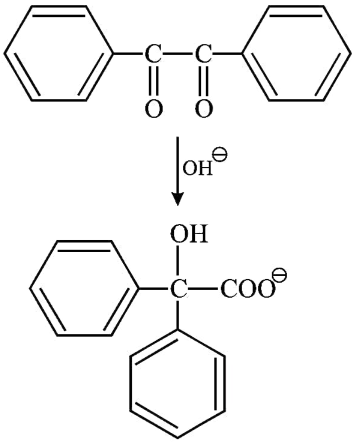
Example - 73



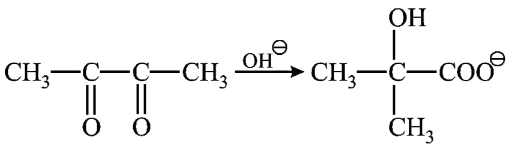
4.5.12 Benzil-Benzilic Acid Rearrangement

α-diketones on treatment with base rearrange to give the salts of α-hydroxyacids. Most known examples are aromatic but can also be applied to aliphatic diketones and to α-keto aldehydes.

Example - 74



Example - 75

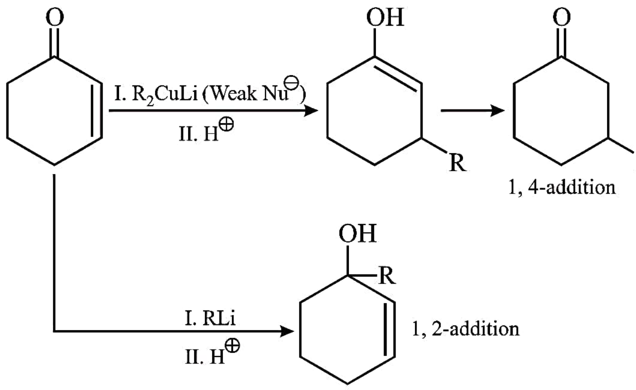


$$CH_3-\underset{\overset{\|}{O}}{C}-\underset{\overset{\|}{O}}{C}-CH_3 \xrightarrow{OH^{\ominus}} CH_3-\overset{OH}{\underset{CH_3}{C}}-COO^{\ominus}$$

4.5.13 Michael Addition

The strong $\overset{\ominus}{Nu}$ (nucleophile) gives 1, 2-addition (across carbonyl group) and weaker nucleophile gives 1, 4-addition. Active methylene carbanion ($Z-CH_2-Z$, i.e., Z = electron withdrawing group) is considered a weak nucleophile. The conjugate addition of enolate anions to α, β-unsaturated carbonyl compounds is known as **Michael Additions**.

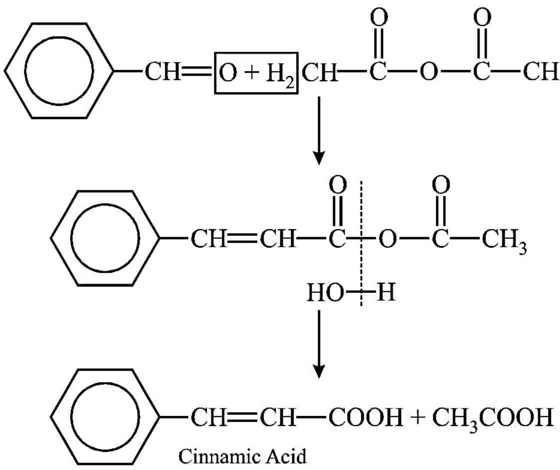
Example - 76



4.5.14 Perkin Addition

It is the condensation of an aromatic aldehyde with an acid anhydride to form α,β-unsaturated carboxylic acids.

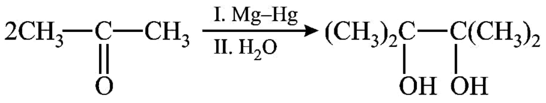
Example - 77



4.5.15 Reduction with Metals

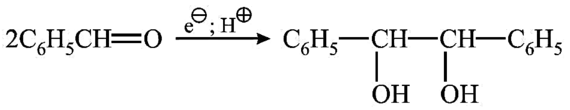
The reduction of ketones with magnesium amalgam gives pinacol. Similarly, benzaldehyde on treatment with zinc and hydrochloric acid or with sodium amalgam gives hydrobenzoin.

Example - 78



$$2CH_3-\underset{\overset{\|}{O}}{C}-CH_3 \xrightarrow[\text{II. } H_2O]{\text{I. Mg–Hg}} (CH_3)_2\underset{OH}{C}-\underset{OH}{C}(CH_3)_2$$

Example - 79

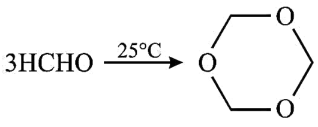


$$2C_6H_5CH{=}O \xrightarrow{e^{\ominus};\,H^{\oplus}} C_6H_5\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}C_6H_5$$

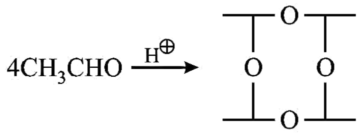
4.5.16 Polymerisation

Formaldehyde solution is evaporated to dryness – a solid polymeric formaldehyde in the form of polymethylene glycol appears, called paraformaldehyde. In the gaseous stage, at room temperature a white crystalline solid metaformaldehyde forms. Acetaldehyde forms metaldehyde and paraldehyde.

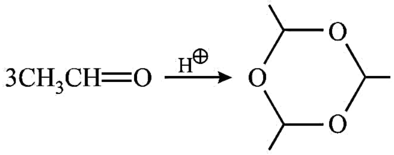
$$nHCHO \longrightarrow \underset{\text{Paraformaldehyde}}{(CH_2O)_n} \qquad n = 6 - 50$$



Trioxane



Metaldehyde



Paraldehyde

5. ANALYSIS OF ALDEHYDES AND KETONES

Aldehydes and ketones are characterized through the addition to the carbonyl group of nucleophilic reagents, especially derivatives of ammonia. An aldehyde or ketone will, for example, react with 2, 4-dinitrophenylhydrazine to form an insoluble yellow or red solid.

Aldehydes are characterized, and in particular are differentiated from ketones, through their ease of oxidation : aldehydes give a positive test with Tollens' reagent ; ketones do not. A positive Tollen's test is also given by a few other kinds of easily oxidized compounds, e.g., certain phenols and amines; these compounds do not, however, give positive tests with 2, 4-dinitrophenylhydrazine.

Aldehydes are also, of course, oxidized by many other oxidizing agents : by cold, dilute, neutral $KMnO_4$ and by CrO_3 in H_2SO_4.

A highly sensitive test for aldehydes is the Schiff test. An ald reacts with the fuchsin-aldehyde reagent to form a charact magenta color.

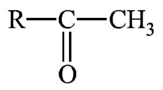
Aliphatic aldehydes and ketones having an α-hydrogen with Br_2 in CCl_4. This reaction is generally too slow to be confused with a test for unsaturation, and moreover it liberates HBr.

Aldehydes and ketones are generally identified through the melting points of derivatives like 2, 4-dinitrophenylhydrazones, oximes, and semicarbazones.

Methyl ketones are characterized through the iodoform test.

5.1 Iodoform Test

Whether or not a ketone is a methyl ketone is shown by the iodoform test. The ketone is treated with iodine and sodium hydroxide (sodium hypoiodite, NaOI); a ketone of the structure.

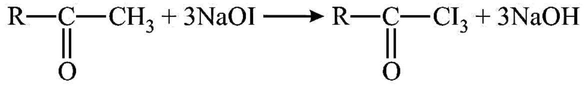


$$R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}CH_3$$

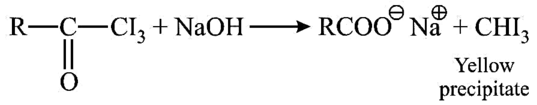
where R is H
or an alkyl
or aryl group.

yields a yellow precipitate of iodoform (CHI_3, m.p. 119°C).

The reaction involves halogenation and cleavage :



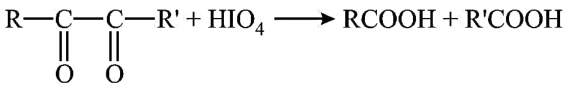
$$R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}CH_3 + 3NaOI \longrightarrow R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}CI_3 + 3NaOH$$



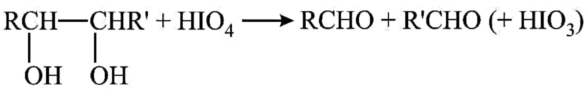
$$R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}CI_3 + NaOH \longrightarrow RCOO^{\ominus}\,Na^{\oplus} + \underset{\substack{\text{Yellow}\\ \text{precipitate}}}{CHI_3}$$

5.2 Periodic Acid Oxidation

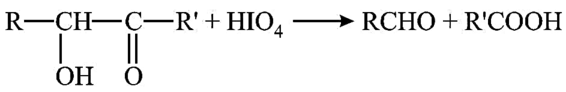
Upon treatment with periodic acid, HIO_4, compounds containing two or more $=O$ or $—OH$ groups attached to adjacent carbon atoms undergo oxidation with cleavage of carbon-carbon bonds. For example :



$$R\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}R' + HIO_4 \longrightarrow RCOOH + R'COOH$$



$$\underset{\displaystyle OH}{\underset{|}{RCH}}\text{—}\underset{\displaystyle OH}{\underset{|}{CHR'}} + HIO_4 \longrightarrow RCHO + R'CHO\ (+\ HIO_3)$$



$$R\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}\underset{\displaystyle O}{\underset{\|}{C}}\text{—}R' + HIO_4 \longrightarrow RCHO + R'COOH$$

The oxidation is particularly useful in determination of structure, as we shall find in our study of carbohydrates. Qualitatively, oxidation by HIO_4 is indicated by formation of a white precipitate ($AgIO_3$) upon addition of silver nitrate. Since the reaction is usually quantitative, valuable inforamtion is given by the nature and amounts of the products, and by the quantity of periodic acid consumed.

6. IMPORTANT CARBONYL COMPOUNDS

6.1 FORMALDEHYDE – HCHO

It is present in green leaves of plants where its presence is supposed to be due to the reaction of CO_2 with water in presence of sunlight and chlorophyll.

$$CO_2 + H_2O \longrightarrow HCHO + O_2$$

Traces of formaldehyde and formed when incomplete combustion of wood, sugar, coal, etc., occurs.

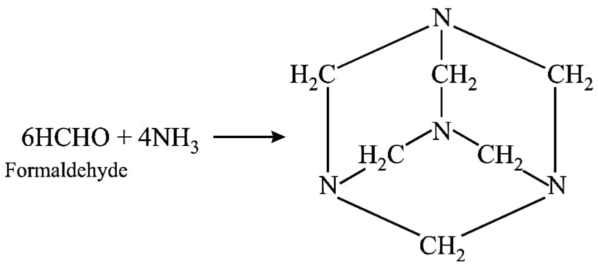
Formaldehyde is prepared in laboratory by catalytic oxidation of methyl alcohol.

Excess of methyl alcohol is removed by fractional distillation. The resulting mixture is called formalin which contains 40% formaldehyde, 8% methyl alcohol and 52% water.

6.1.1 Important Reactions

Reaction with ammonia

Like other aldehydes, formaldehyde does not form addition product with ammonia but crystalline compound, hexamethylene tetramine (Urotropine).

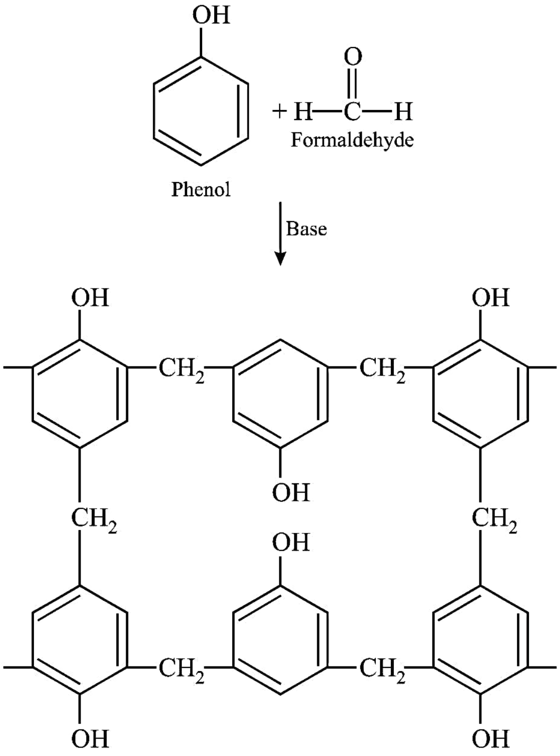


Hexamethylene Tetramine (Urotropine)

It is used as medicine in case of urinary troubles under the name of **Urotropine** or hexamine. Nitration of urotropine under controlled conditions gives an explosive **RDX (Research and Development Explosive).**

Condensation with phenol

Formaldehyde condenses with phenol to give a synthetic plastic, bakelite. The condensation occurs in presence of dilute sodium hydroxide or ammonia at 80°-90°C. Bakelite is used for preparing electrical insulators, electric switches and toys, etc.



6.1.2 Uses

(i) The 40% solution of formaldehyde in water (formalin) is used as disinfectant, germicide and antiseptic. It is used for the preservation of biological specimens.

(ii) It is used in the preparation of hexamethylene tetramine (urotropine) which is used as an antiseptic and germicide.

(iii) It is used in silvering of mirror and decolouring vat dyes.

(iv) It is employed in the manufacture of synthetic dyes such as para-rosaniline, indigo, etc.

(v) It is used in the manufacture of **formamint** (by mixing formaldehyde with lactose) – a throat lozenge.

6.2 ACETALDEHYDE – CH_3CHO

6.2.1 Important Reactions

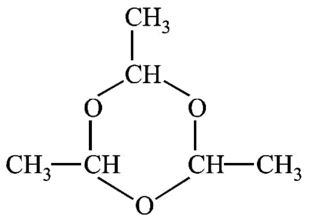
Polymerisation

Acetaldehyde undergoes polymerisation forming different products under different conditions.

Paraldehyde

It is formed, when anhydrous acetaldehyde is treated with a few drops of conc. sulphuric acid.

$$\underset{\text{Acetaldehyde}}{3CH_3CHO} \rightleftharpoons \underset{\text{Paraldehyde, (trimer)}}{(CH_3CHO)_3} \;;$$



Paraldehyde
(A cyclic trimer)

It is a pleasant smelling liquid (B.P. 124°C). It has cyclic structure and when heated with dilute sulphuric acid, it changes again into acetaldehyde. It is used in the medicine as a hypnotic and soporific (sleep producing).

6.2.2 Uses

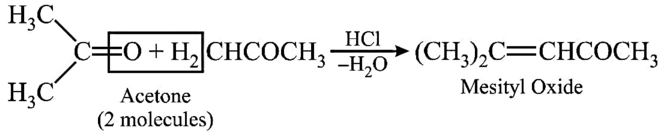
Acetaldehyde is used :

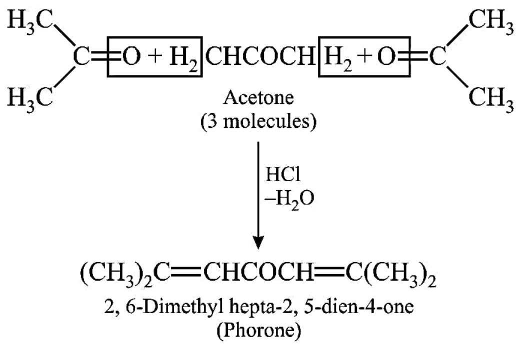
- (i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, buta-1,3-diene (used in rubbers), dyes and drugs.
- (ii) As an antiseptic inhalant in nose troubles.
- (iii) In the preparation of paraldehyde (hypnotic) and metaldehyde (solid fuel).
- (iv) In the preparation of acetaldehyde ammonia (a rubber accelerator).
- (v) As a reducing agent in silvering of mirror.

6.3 ACETONE – CH_3COCH_3

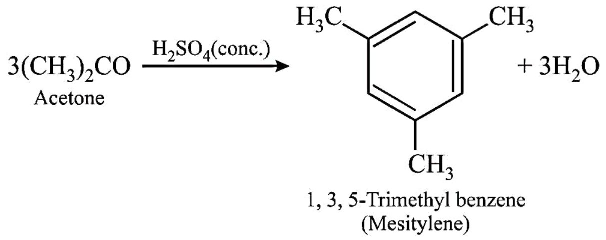
6.3.1 Important Reactions

When acetone saturated with HCl gas is kept at low temperature for few days, it forms mesityl oxide and phorone which can be separated by distillation.





When acetone is distilled with concentrated sulphuric acid it forms mesitylene.



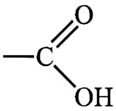
6.3.2 Uses

- (i) As a solvent for cellulose acetate, cellulose nitrate, celluloid, lacquers, resins, etc.
- (ii) For storing acetylene.
- (iii) In the manufacture of cordite–a smokeless powder explosive.
- (iv) In the preparation of chloroform, iodoform, sulphonal and chloretone.
- (v) As a nail polish remover.
- (vi) In the preparation of an artificial scent (ionone), plexiglas (a tough transparent plastic) and synthetic rubber.

CARBOXYLIC ACIDS & DERIVATIVES

1. INTRODUCTION

Carboxylic acids are the compounds containing the **carboxyl functional group.**



The carboxylic acids may be **aliphatic** (R–COOH) or **aromatic** (Ar–COOH) depending upon whether –COOH group is attached to aliphatic alkyl chain or aryl group respectively.

The general formula for carboxylic acids is $C_nH_{2n}O_2$.

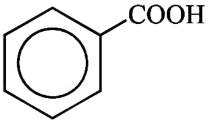
Carboxylic acids are used in the production of polymers, pharmaceuticals, solvents, and food additives. Industrially important acids include acetic acid (component of vinegar, precursor to solvents and coatings), acrylic and methacrylic acids (pre cursors to polymers, adhesives), adipic acid (polymers), citric acid (beverages), ethylene diaminetetraacetic acid (chelating agent), fatty acids (coatings), maleic acid (polymers), propionic acid (food preservatives), terephthalic acid (polymers). Esters of fatty acids are the main components of lipids and polyamides of aminocarboxylic acids are the main components of proteins.

The carboxylic acids ionize in water to give $H^{\oplus}$ ions and hence they are acidic in nature.

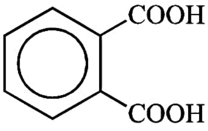
Important Aliphatic Acids

$HCOOH$	Formic Acid
CH_3COOH	Acetic Acid
$CH_2{=}CHCOOH$	Acrylic Acid
$CH_3COCOOH$	Pyruvic Acid (α-keto acid)

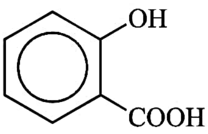
Important Aromatic Acids



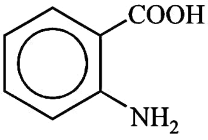
Benzoic Acid



Phthalic Acid



Salicylic Acid



Anthranilic Acid

These are further classified as mono, di, tri carboxylic acids depending upon number of carboxylic groups present in their molecules.

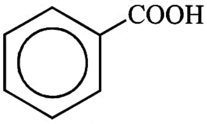
Mono Carboxylic Acids

$HCOOH$

Formic Acid

CH_3COOH

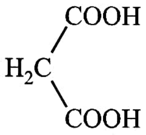
Acetic Acid



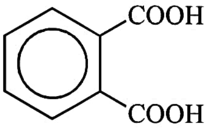
Benzoic Acid

Di Carboxylic Acids

Oxalic Acid



Malonic Acid

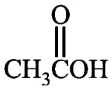


Phthalic Acid

2. PHYSICAL PROPERTIES & ACIDIC CHARACTER

2.1 Boiling Point

Carboxylic acids boil at considerably higher temperatures than do alcohols, ketones, or aldehydes of similar molecular weights.

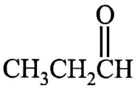


$CH_3\overset{\overset{\large O}{||}}{C}OH$

Acetic Acid, bp 118°C

$CH_3CH_2CH_2OH$

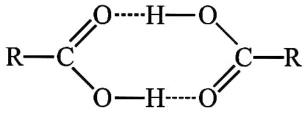
1-Propanol, bp 97°C



$CH_3CH_2\overset{\overset{\large O}{||}}{C}H$

Propionaldehyde, bp 49°C

The high boiling points of carboxylic acids result from formation of a stable, hydrogen-bonded dimer. This dimer contains an eight-membered ring joined by two hydrogen bonds, effectively doubling the molecular weight of the molecules leaving the liquid phase.



Hydrogen-Bonded Acid Dimer

2.2 Melting Point and Physical State

Aliphatic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax-like solids and are practically odourless due to low volatility. They exist as dimer in aprotic and non-polar solvents.

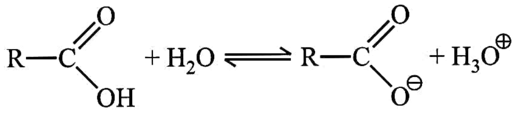
Unbranched acids made up of an even number of carbon atoms have melting points higher than the odd numbered homologs having one more or one less carbon. This oscillating behaviour in melting point is explained by the differences in the intermolecular attractive forces in the crystalline state.

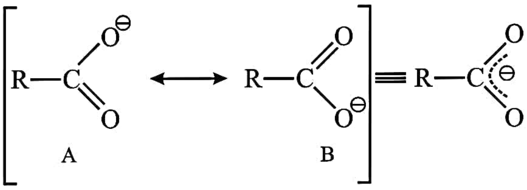
2.3 Solubility

Carboxylic acids form hydrogen bonds with water, and the lower-molecular-weight carboxylic acids (up through 4 carbon atoms) are miscible with water. As the length of the hydrocarbon chain increases, water solubility decreases until acids with more than 10 carbon atoms are essentially insoluble in water.

Carboxylic acids are very soluble in alcohols because the acids form hydrogen bonds with alcohols. Also, alcohols are not as polar as water, so the longer-chain acids are more soluble in alcohols than they are in water. Most carboxylic acids are quite soluble in relatively nonpolar solvents such as chloroform because the acid continues to exist in its dimeric form in the nonpolar solvent. Thus, the hydrogen bonds of the cyclic dimer are not disrupted when the acid dissolves in a nonpolar solvent.

2.4 Acidity of Carboxylic Acids

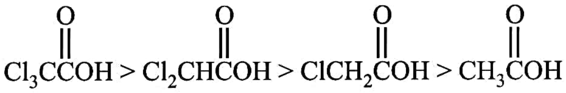




Carboxylate ion exists as two equivalent canonical structure A and B. Due to more stability of carboxylate ion, carboxylic acid is acidic in nature because the equilibrium in reaction favors the formation of stable ion.

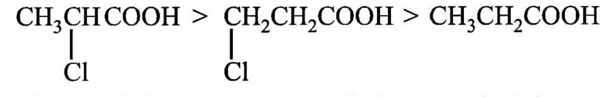
Effect of Substituents on Acidity

Electron withdrawing groups (–I effect) stabilise the anion and hence increase acidic nature. As the no. of –I effect groups increases, acid strength increases and vice versa.



$$Cl_3C\overset{O}{\overset{\|}{C}}OH > Cl_2CH\overset{O}{\overset{\|}{C}}OH > ClCH_2\overset{O}{\overset{\|}{C}}OH > CH_3\overset{O}{\overset{\|}{C}}OH$$

Strength of –I group decreases with increase in distance with –COOH group.



$$CH_3\underset{Cl}{\underset{|}{C}}HCOOH > \underset{Cl}{\underset{|}{C}}H_2CH_2COOH > CH_3CH_2COOH$$

α-Chloropropionic Acid β-Chloropropionic Acid Propionic Acid

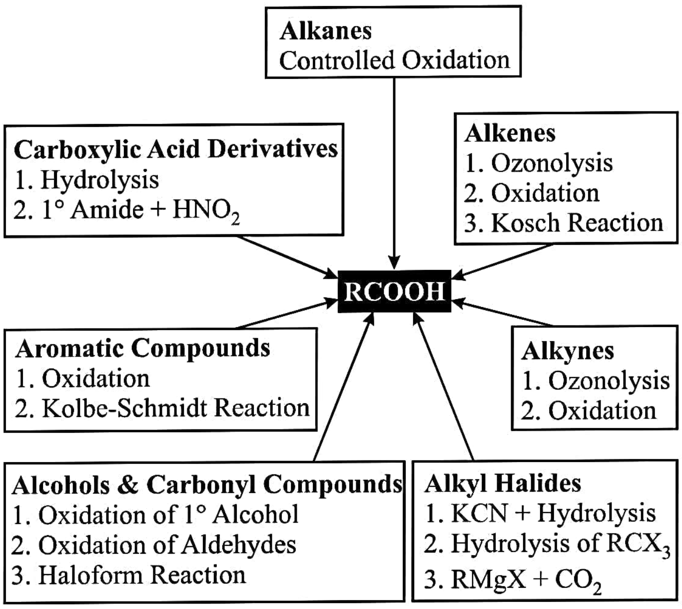
Negative inductive effect of F, Cl, Br, I is in order : F > Cl > Br > I. Hence acid strength is

$$F\text{–}CH_2COOH > Cl\text{–}CH_2COOH > Br\text{–}CH_2COOH > I\text{–}CH_2COOH$$

Relative acid strength is as follows :

$$RCOOH > HOH > ROH > HC{\equiv}CH > NH_3 > RH$$

3. PREPARATION OF CARBOXYLIC ACIDS



3.1 Alkanes

Long chain alkanes are oxidized by air at 120°C in presence of catalyst manganese acetate or manganous stearate.

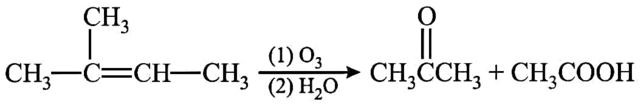
$$\underset{\text{Long Chain Alkane}}{2CH_3(CH_2)_nCH_3 + 3O_2} \xrightarrow[\text{100–160°C}]{\text{Manganous Stearate}} \underset{\text{Mono Carboxylic Acid}}{2CH_3(CH_2)_nCOOH + 2H_2O}$$

3.2 Alkenes

3.2.1 Ozonolysis

Monosubstituted alkenes give carboxylic acid on oxidative ozonolysis.

Example – 1



$$CH_3\text{—}\overset{CH_3}{\overset{|}{C}}{=}CH\text{—}CH_3 \xrightarrow[(2)\,H_2O]{(1)\,O_3} CH_3\overset{O}{\overset{\|}{C}}CH_3 + CH_3COOH$$

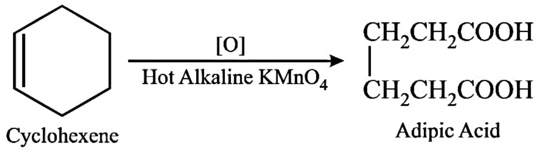
3.2.2 Oxidation

Oxidising agents used are acidified or hot alkaline $KMnO_4$ and $K_2Cr_2O_7$.

$$RCH{=}CHR' + 4[O] \xrightarrow[\Delta]{K_2Cr_2O_7/H_2SO_4} RCOOH + R'COOH$$

Cyclic alkenes can be oxidized to dicarboxylic acids.

Example – 2



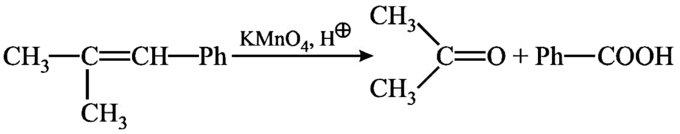
Note... 1. In oxidative cleavage, each C of multiple bond becomes the carbon atom of the carbonyl group and a hydrogen substituent on the double bond is replaced by a hydroxyl group.

2. The terminal $-CH_2$ group of 1-Alkene is completely oxidized to CO_2 and H_2O.

Example – 3

$$CH_3CH_2CH{=}CH_2 \xrightarrow[H_3O^{\oplus}]{KMnO_4,\ OH^{\ominus},\ \Delta} CH_3CH_2COOH + CO_2 + H_2O$$

Example – 4



$$CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH-Ph \xrightarrow{KMnO_4,\ H^{\oplus}} (CH_3)_2C{=}O + Ph-COOH$$

3.2.3 Kosch Reaction – Hydrocarbonylation

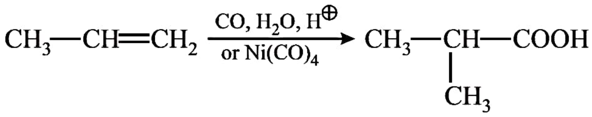
Example – 5

Alkene on treatment with CO, H_2O at high temperature and pressure causes carbonylation. Usually, H_3PO_4 is used as the acid catalyst. The similar effect is observed when $Ni(CO)_4$ is treated independently.

Example – 6

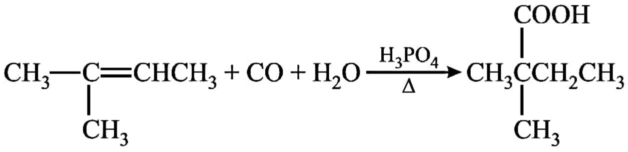
$$\underset{\text{Ethene}}{H_2C{=}CH_2} + CO + \underset{\text{Steam}}{H_2O} \xrightarrow[\text{Pressure, 350°C}]{H_3PO_4} \underset{\text{Propionic Acid}}{CH_3CH_2COOH}$$

Example – 7



$$CH_3-CH{=}CH_2 \xrightarrow[\text{or } Ni(CO)_4]{CO,\ H_2O,\ H^{\oplus}} CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$$

Example – 8



$$CH_3-\underset{\underset{CH_3}{|}}{C}{=}CHCH_3 + CO + H_2O \xrightarrow[\Delta]{H_3PO_4} CH_3\overset{\overset{COOH}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_3$$

Number of carbons is one more than parent alkene.

3.3 Alkynes

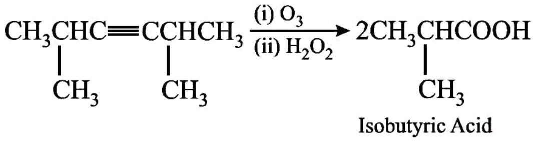
3.3.1 Ozonolysis

Alkynes on ozonolysis give carboxylic acids.

$$\underset{\text{Alkyne}}{RC{\equiv}CR'} + 3[O] + H_2O \xrightarrow{KMnO_4/H^{\oplus}} RCOOH + R'COOH$$

$$R-C{\equiv}C-R' \xrightarrow[\text{(ii) } H_2O_2]{\text{(i) } O_3} R-COOH + R'-COOH$$

Example – 9



$$CH_3\underset{\underset{CH_3}{|}}{CH}C{\equiv}C\underset{\underset{CH_3}{|}}{CH}CH_3 \xrightarrow[\text{(ii) } H_2O_2]{\text{(i) } O_3} 2CH_3\underset{\underset{CH_3}{|}}{CH}COOH$$

Isobutyric Acid

3.3.2 Oxidation

The use of strong oxidising agents such as $KMnO_4/H^{\oplus}$, $KMnO_4/OH^{\ominus}/\Delta$, CrO_3 etc. directly gives the carboxylic acid.

Example – 10

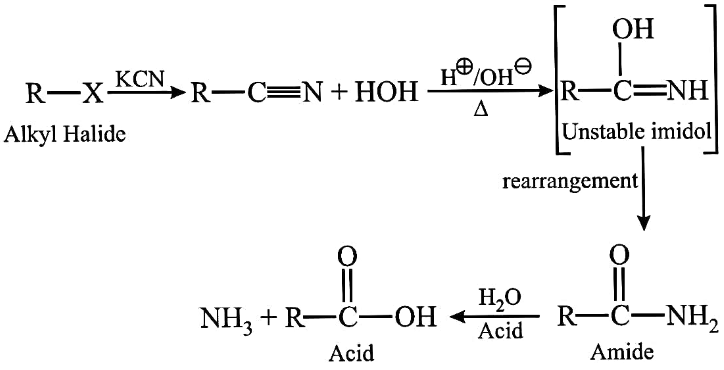
$$CH_3-C{\equiv}C-CH_3 \xrightarrow[\Delta]{KMnO_4,\ OH^{\ominus}} 2CH_3COO^{\ominus}$$

Example – 11

$$Ph-C{\equiv}C-CH_2Ph \xrightarrow[AcOH]{CrO_3} PhCOOH + PhCH_2COOH$$

3.4 Alkyl Halides

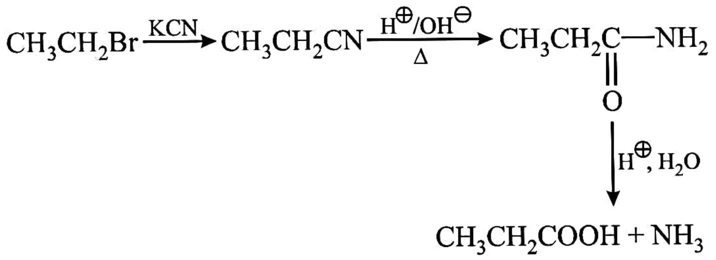
3.4.1 KCN + Hydrolysis



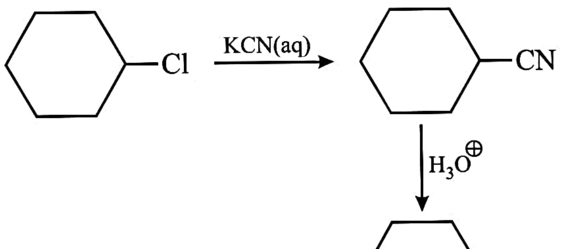
Note...

1. In acidic medium, the products are RCOOH and $NH_4^{\oplus}$ while in alkaline hydrolysis, $RCOO^{\ominus}$ and NH_3 are products.
2. The acid formed contains one more C than parent alkyl halide. The order of reactivity of alkyl halides is 1° > 2° > 3°.
3. In case of 3° alkyl halide, elimination takes place.
4. Vinylic, arylic halides are not appropriate as substitution is difficult.

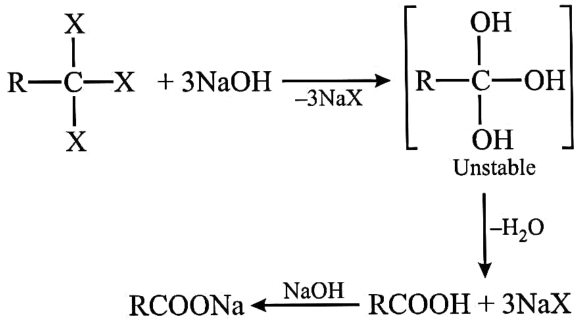
Example – 12



Example – 13

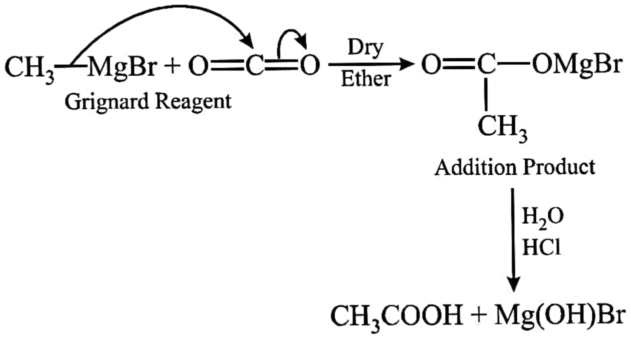


3.4.2 Hydrolysis of terminal trihalogen derivatives of Alkanes



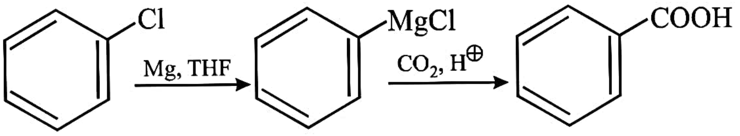
3.4.3 Grignard Reagent + CO_2

Example – 14



Carboxylic acid formed has one C atom more than Grignard Reagent.

Example – 15



3.5 Alcohols

Oxidization of 1° alcohols yields carboxylic acids.

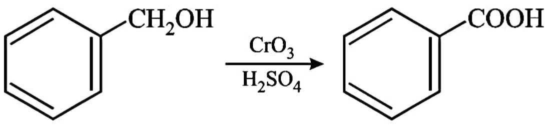
$$RCH_2OH \xrightarrow{[O]} RCOOH$$

Note...

1. **Strong Oxidizing Agents :** $K_2Cr_2O_7/H^{\oplus}$ or $KMnO_4/H^{\oplus}$.
2. **Mild Oxidising Agents :** MnO, CuO (Fehling's Solution), (CrO_3, H_2SO_4) in acetone solution, Ag_2O (Tollen's reagent). $FeSO_4$ + H_2O_2 (Fenton's reagent). These are used for preparing unsaturated acids.

$$RCH{=}CHCH_2OH \xrightarrow{PCC} RCH{=}CHCHO \xrightarrow{Ag_2O} RCH{=}CHCOOH$$

Example – 16



3.6 Aldehydes and Ketones

3.6.1 Oxidation

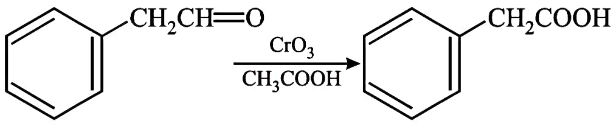
Oxidation of aldehydes and ketones give carboxylic acids.

$$RCHO \xrightarrow{[O]} RCOOH$$

$$RCOR' \xrightarrow{[O]} RCOOH + R'COOH$$

Ketones are oxidized under vigorous conditions such as hot $K_2Cr_2O_7/H^{\oplus}$ and give mixture of acids.

Example – 17



Example – 18

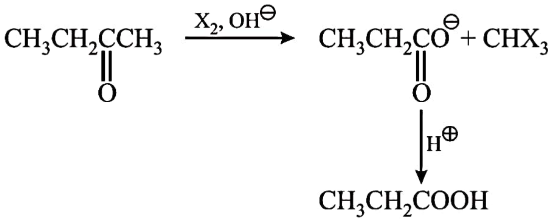
$$CH_3\overset{*}{C}OCH_2CH_2CH_3 \xrightarrow[\Delta]{O} CH_3\overset{*}{C}OOH + CH_3CH_2COOH$$

Keto group (with C*) remains with smaller alkyl group.

3.6.2 Haloform Reaction

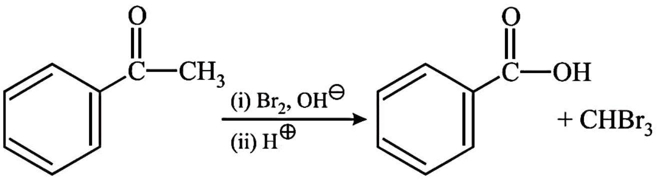
Methyl ketone on treatment with $X_2/OH^{\ominus}$, gives carboxylate having one carbon atom less than the original ketone – **Haloform Reaction.**

Example – 19



$$CH_3CH_2\underset{\underset{O}{\|}}{C}CH_3 \xrightarrow{X_2,\ OH^{\ominus}} CH_3CH_2\underset{\underset{O}{\|}}{C}O^{\ominus} + CHX_3 \xrightarrow{H^{\oplus}} CH_3CH_2COOH$$

Example – 20



3.7 Carboxylic Acid Derivatives

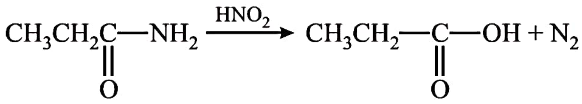
Acyl halide, carboxylic ester, anhydride and amide all on acidic or basic hydrolysis give carboxylic acids.

1° amide on treatment with nitrous acid.

$$RCOOR' \xrightarrow{H^{\oplus},\ H_2O} RCOOH + R'OH$$

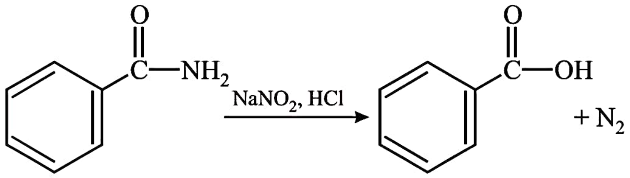
$$RCONH_2 \xrightarrow[\Delta]{OH^{\ominus},\ H_2O} RCOO^{\ominus} + NH_3$$

Example – 21



$$CH_3CH_2\underset{\underset{O}{\|}}{C}—NH_2 \xrightarrow{HNO_2} CH_3CH_2—\underset{\underset{O}{\|}}{C}—OH + N_2$$

Example – 22

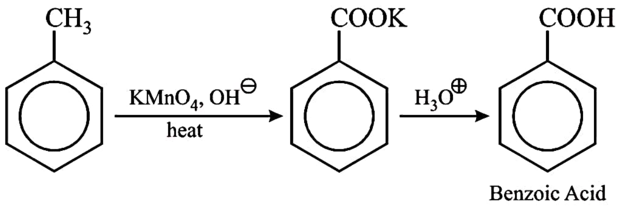


3.8 Preparation of Aromatic Acids

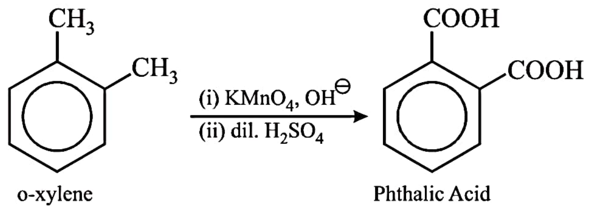
3.8.1 Oxidation of Alkyl Benzenes

Alkyl side chain of benzene ring can be easily oxidized to carboxylic group, irrespective of the length with acidic or alkaline $KMnO_4$, chromic acid or conc HNO_3.

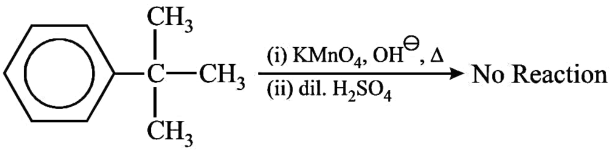
Example – 23



Example – 24



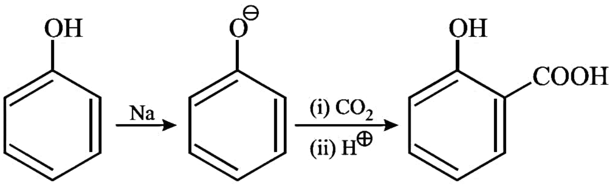
For conversion to carboxylic group, presence of α-hydrogen is necessary. That is why tertiary alkyl side chains are not oxidized.



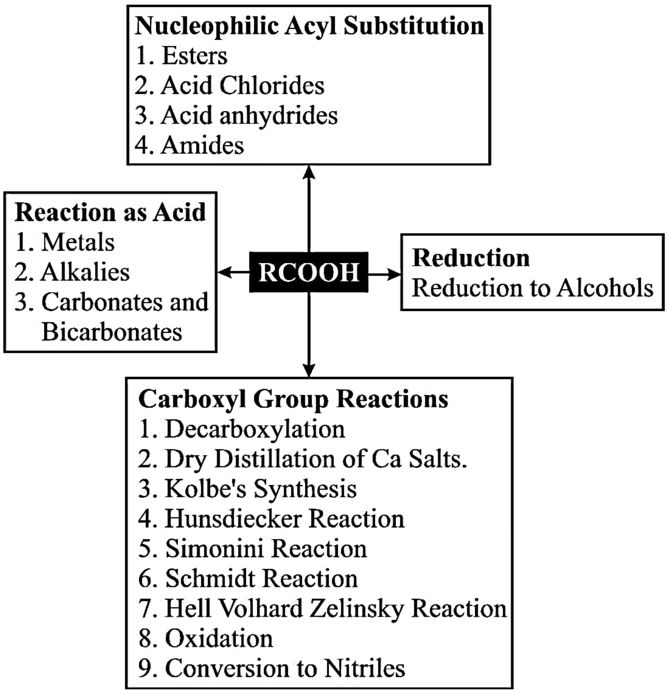
3.8.2 Kolbe - Schmidt Reaction

Sodium phenoxide is carboxylated by treatment of CO_2 in the ortho-position, mostly.

Example – 25



4. REACTIONS OF CARBOXYLIC ACIDS



4.1 Reactions as an Acid

4.1.1 Reaction with Strongly Electropositive Metals

Monocarboxylic acids react with strong electropositive metals (such as Na, K, Zn etc.) evolving hydrogen and forming corresponding salts (acidic character).

$$\underset{\text{Acid}}{2RCOOH} + Na \longrightarrow \underset{\text{Sodium Salt of Acid}}{2RCOONa} + H_2$$

4.1.2 Reaction with Alkalies

Monocarboxylic acids neutralize hydroxides to form corresponding salt and water.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

These salts, on being treated with dilute mineral acids regenerate carboxylic acids.

$$CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$$

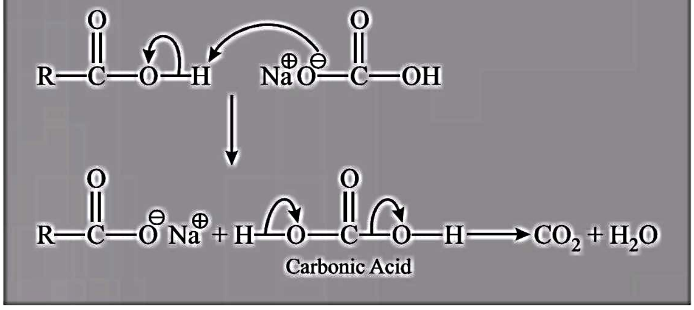
4.1.3 Reaction with Carbonates & Bicarbonates

This reaction is laboratory test of carboxylic group (–COOH) due to effervescence of CO_2.

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COONa + CO_2 + H_2O$$

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

Note... CO_2 evolves from carbonate or bicarbonate, not from acid.



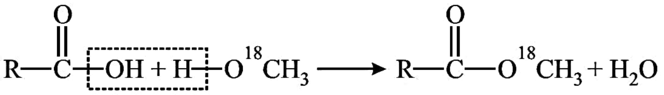
4.2 Nucleophilic Acyl Substitution

4.2.1 Formation of Esters

$$R{-}COOH + HOR' \underset{H_2SO_4}{\overset{conc.}{\rightleftharpoons}} RCOOR' + H_2O$$

This reaction is called esterification and is catalyzed by small amount of inorganic acids.

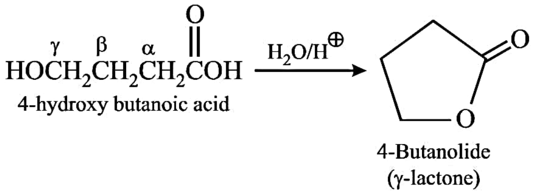
In esterification C–OH bond of acid and O–H bond of alcohol breaks.



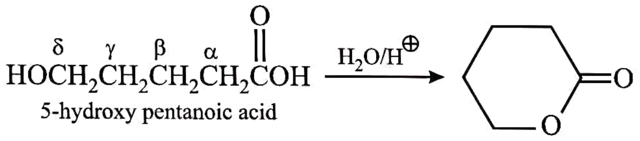
$$R-\overset{\overset{O}{\|}}{C}-\boxed{OH + H}-{}^{18}OCH_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}-{}^{18}OCH_3 + H_2O$$

Hydroxy acids undergo intramolecular esterification and makes cyclic esters called as Lactones.

Example – 26



Example – 27

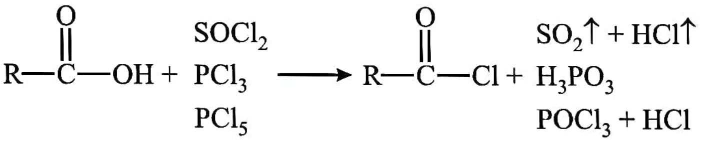


5-hydroxy pentanoic acid

5-Pentanolide
(δ-lactone)

5 membered ring is called ***γ-lactone*** and 6 membered ring is called ***δ-lactone***.

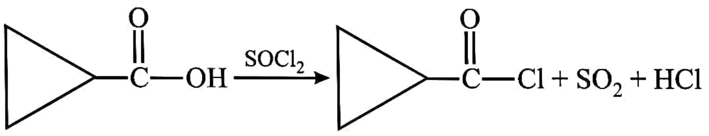
4.2.2 Formation of Acid Chlorides

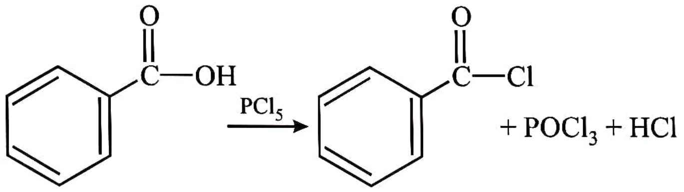


$$R-\overset{O}{\overset{\|}{C}}-OH + \begin{array}{l}SOCl_2\\PCl_3\\PCl_5\end{array} \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + \begin{array}{l}SO_2\uparrow + HCl\uparrow\\H_3PO_3\\POCl_3 + HCl\end{array}$$

Example – 28

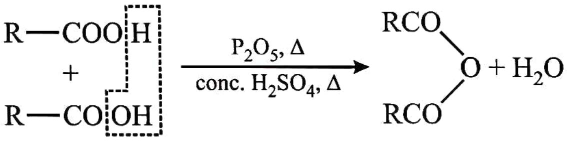
$$3CH_3COOH + PCl_3 \xrightarrow{\Delta} 3CH_3COCl + H_3PO_3$$





Out of these three, $SOCl_2$ method is preferred because here other two products are gases that can easily escape.

4.2.3 Formation of Acid Anhydrides

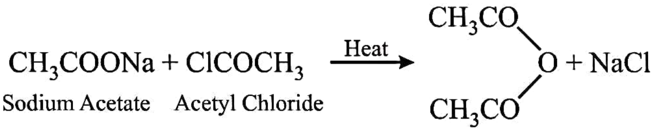


$$\begin{array}{l}R-COOH\\ \quad +\\R-COOH\end{array} \xrightarrow[\text{conc. }H_2SO_4,\,\Delta]{P_2O_5,\,\Delta} \begin{array}{l}RCO\\ \qquad O + H_2O\\RCO\end{array}$$

Acid

Acid Anhydride

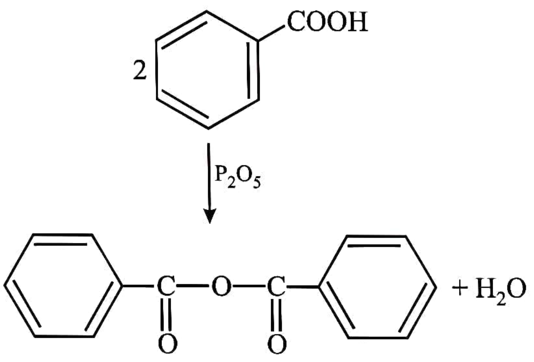
Example – 29



$$\underset{\text{Sodium Acetate}}{CH_3COONa} + \underset{\text{Acetyl Chloride}}{ClCOCH_3} \xrightarrow{\text{Heat}} \begin{array}{l}CH_3CO\\ \qquad O + NaCl\\CH_3CO\end{array}$$

Acetic Anhydride

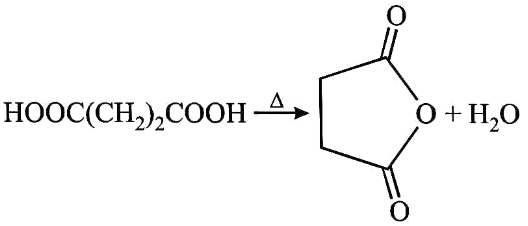
Example – 30



Benzoic Anhydride

Dicarboxylic acids on heating give cyclic anhydride (5 and 6 membered rings).

Example – 31



Note... Formic Acid (HCOOH) does not form anhydride.

4.2.4 Formation of Amides

$$\underset{\text{Acid}}{RCOOH} + NH_3 \longrightarrow \underset{\text{Ammonium Salt}}{RCOONH_4} \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Amide}}{RCONH_2}$$

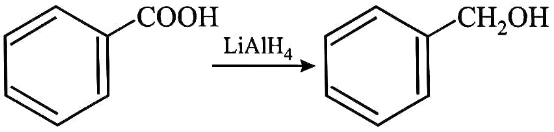
4.3 Reduction

4.3.1 Reduction to Alcohols

Reducing Agents : $LiAlH_4$ in ether solution or with H_2 in presence of copper chromite ($CuCr_2O_4$) catalyst or BH_3/THF (or diborane, B_2H_6) or H_2, Ru etc.

$$\underset{\text{Acid}}{RCOOH} + 2H_2 \xrightarrow{CuO-Cr_2O_3} \underset{1^\circ\text{ Alcohol}}{R-CH_2OH} + H_2O$$

Example – 32



Example - 33

$$CH_3-CH_2-CH_2COOH \xrightarrow[\Delta]{H_2,\ Ru-C} CH_3CH_2CH_2CH_2OH$$

4.4 Carboxyl Group Reactions

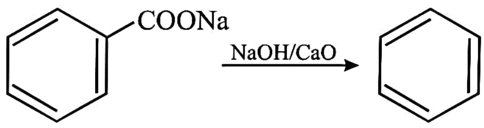
4.4.1 Decarboxylation

When anhydrous alkali salt of a carboxylic acid is heated with soda lime (NaOH : CaO in ratio 3 : 1), an alkane is formed.

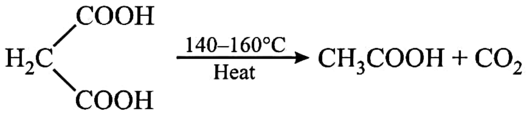
$$\underset{\text{Sodium Salt}}{RCOONa} + NaOH \xrightarrow[\text{Heat}]{CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

The reaction proceeds through **carbanion intermediate**. Greater the stability of carbanion, greater the rate of decarboxylation.

Example - 34

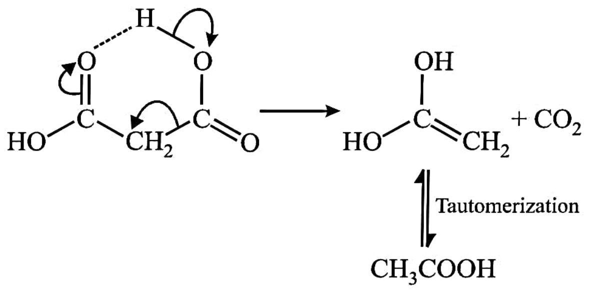


Gem dicarboxylic acids decarboxylate simply on heating.

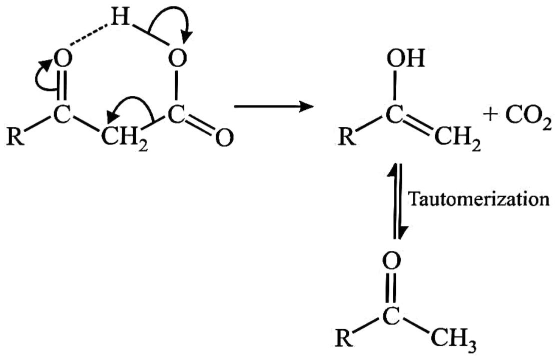


$$H_2C(COOH)_2 \xrightarrow[\text{Heat}]{140-160°C} CH_3COOH + CO_2$$

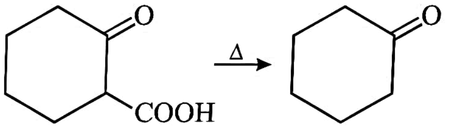
Malonic Acid



β-keto acids undergo decarboxylation through a cyclic transition state, giving ketone.



Example - 35



β-unsaturated acids decarboxylate on heating giving alkenes.

$$H_2\overset{\gamma}{C}=\overset{\beta}{C}H-\overset{\alpha}{C}H_2-COOH \xrightarrow{\text{Heat}} H_2C=CH-CH_3 + CO_2\uparrow$$

4.4.2 Dry Distillation of Calcium Salts of Carboxylic Acids

$$\underset{\text{Calcium Salt}}{(RCOO)_2Ca} \xrightarrow{\Delta} \underset{\text{Ketone}}{RCOR} + CaCO_3$$

When calcium formate is heated, formaldehyde is evolved.

$$(HCOO)_2Ca \xrightarrow{\text{Heat}} \underset{\text{Formaldehyde}}{HCHO} + CaCO_3$$

When a mixture of calcium salt of an acid (other than formic acid) and calcium formate is heated an aldehyde is formed.

$$\underset{\text{Calcium Acetate}}{(CH_3COO)_2Ca} + \underset{\text{Calcium Formate}}{(HCOO)_2Ca} \xrightarrow{\text{Heat}} \underset{\text{Acetaldehyde}}{2CH_3CHO} + CaCO_3$$

4.4.3 Kolbe's Synthesis

Electrolysis of sodium or potassium salts (concentrated aq. solution) of fatty acids yield alkanes.

$$RCOONa \rightleftharpoons RCOO^{\ominus} + Na^{\oplus}$$

At anode : $2RCOO^{\ominus} \longrightarrow R-R + 2CO_2 + 2e^{\ominus}$

At cathode : $2Na^{\oplus} + 2e^{\ominus} \longrightarrow 2Na \xrightarrow{2H_2O} 2NaOH + H_2$

Reaction involves radical intermediates.

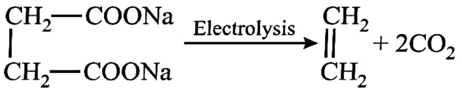
Example - 36

$$2CH_3CH_2-\overset{\overset{O}{||}}{C}-ONa \longrightarrow CH_3CH_2CH_2CH_3$$

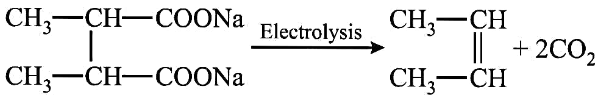
Electrolysis of salt of succinic acid and its derivative give alkene.

Electrolysis of maleic acid/fumaric acid or their salts gives corresponding alkynes.

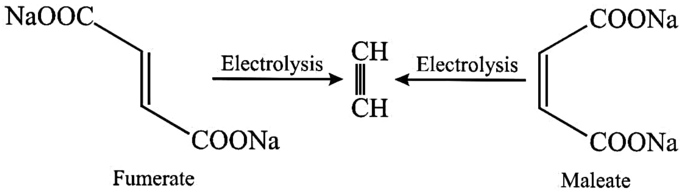
Example - 37



$$\begin{matrix} CH_2-COONa \\ | \\ CH_2-COONa \end{matrix} \xrightarrow{\text{Electrolysis}} \begin{matrix} CH_2 \\ || \\ CH_2 \end{matrix} + 2CO_2$$



$$\begin{matrix}CH_3-CH-COONa\\ |\\ CH_3-CH-COONa\end{matrix} \xrightarrow{\text{Electrolysis}} \begin{matrix}CH_3-CH\\ \|\\ CH_3-CH\end{matrix} + 2CO_2$$



4.4.4 Hunsdiecker Reaction

An alkyl halide is formed when the silver salt of monocarboxylic acid is heated with halogen. This is a step down reaction.

$$CH_3COOAg + Br_2 \xrightarrow[\text{Heat}]{CCl_4} \underset{\text{Methyl Bromide}}{CH_3Br} + AgBr + CO_2\uparrow$$

4.4.5 Simonini Reaction

The reaction of silver salts of carboxylic acids with iodine is called Simonini Reaction.

$$2RCOOAg \xrightarrow[-CO_2]{I_2} RCOOR$$

Note... The ratio of reagents play an important role in determination of products, namely.

1 : 1 ratio of salt and I_2 – RI is formed

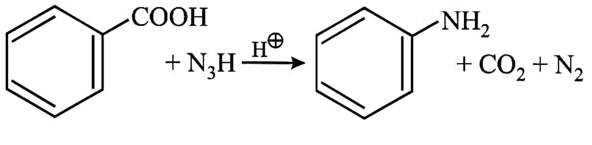
2 : 1 ratio of salt and I_2 – RCOOR is formed

3 : 2 ratio of salt and I_2 – Both the products are obtained

4.4.6 Schmidt Reaction

It involves treatment of hydrazoic acid with carboxylic acids. Alkyl isocyanate is the intermediate. Primary amine formed contains one carbon less than parent acid.

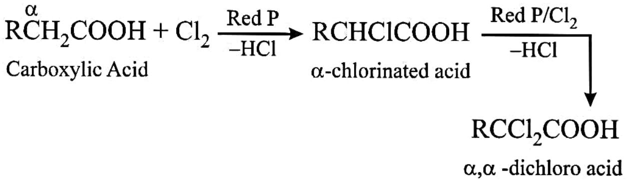
Example – 38



$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Hydrazoic Acid}}{N_3H} \xrightarrow{H_2SO_4\text{ (conc.)}} \underset{\text{Primary Amine}}{RNH_2} + CO_2 + N_2$$

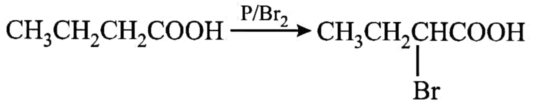
4.4.7 Hell-Volhard Zelinsky Reaction

When carboxylic acid containing an α-hydrogen is treated with Cl_2 or Br_2 in presence of a catalyst. The α-hydrogen is replaced by chlorine or bromine atoms.

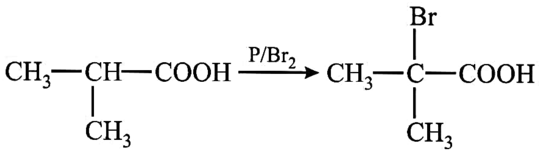


$$\underset{\text{Carboxylic Acid}}{R\overset{\alpha}{C}H_2COOH} + Cl_2 \xrightarrow[-HCl]{\text{Red P}} \underset{\alpha\text{-chlorinated acid}}{RCHClCOOH} \xrightarrow[-HCl]{\text{Red P/Cl}_2} \underset{\alpha,\alpha\text{ -dichloro acid}}{RCCl_2COOH}$$

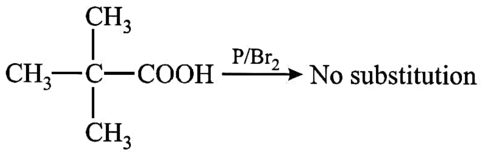
Example – 39



$$CH_3CH_2CH_2COOH \xrightarrow{P/Br_2} CH_3CH_2\underset{\underset{Br}{|}}{C}HCOOH$$



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH \xrightarrow{P/Br_2} CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-COOH$$



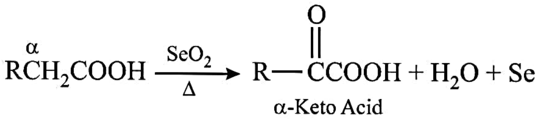
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-COOH \xrightarrow{P/Br_2} \text{No substitution}$$

4.4.8 Oxidation

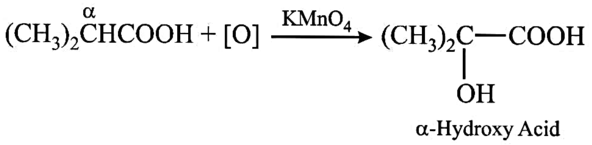
Prolonged heating with powerful oxidising agents oxidises acids into CO_2 and H_2O.

With 3% H_2O_2, they are oxidised to β-hydroxy acids.

$$\underset{\text{Butyric Acid}}{\overset{\gamma}{C}H_3\overset{\beta}{C}H_2\overset{\alpha}{C}H_2COOH} \xrightarrow[H_2O_2]{[O]} \underset{\beta\text{-hydroxy butyric acid}}{CH_3CHOHCH_2COOH}$$



$$R\overset{\alpha}{C}H_2COOH \xrightarrow[\Delta]{SeO_2} \underset{\alpha\text{-Keto Acid}}{R-\overset{\overset{O}{\|}}{C}COOH} + H_2O + Se$$

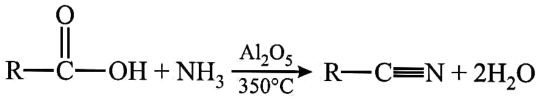


$$(CH_3)_2\overset{\alpha}{C}HCOOH + [O] \xrightarrow{KMnO_4} \underset{\alpha\text{-Hydroxy Acid}}{(CH_3)_2\underset{\underset{OH}{|}}{C}-COOH}$$

4.4.9 Conversion to Nitriles

When mixture of acid and NH_3 are passed over heated alumina, alkane nitrile forms.

Example – 40



$$R-\overset{\overset{O}{\|}}{C}-OH + NH_3 \xrightarrow[350°C]{Al_2O_5} R-C\equiv N + 2H_2O$$

5. IMPORTANT CARBOXYLIC ACIDS

5.1 Formic Acid (HCOOH)

Naturally it occurs in sting of bees, wasps, redant stinging nettles and fruits.

It was first prepared by the distillation of red ants and hence it is called as **Formic Acid** (*Latin* formica : ant)

5.1.1 Preparation

Industrial Preparation

$$CO + NaOH \xrightarrow[100\text{ Atm}]{473\text{ K}} HCOONa \xrightarrow{H^{\oplus}} \underset{\text{Formic Acid}}{HCOOH}$$

Acid is regenerated by the action of H_2SO_4.

5.1.2 Chemical Properties

(A) Acidic Nature

$$HCOOH \rightleftharpoons HCOO^{\ominus} + H^{\oplus}$$

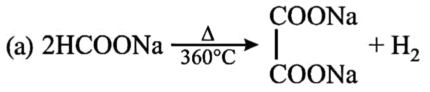
(B) Action of Heat

$$HCOOH \xrightarrow{\Delta} CO_2 + H_2$$

(C) Dehydration

$$HCOOH \xrightarrow{H_2SO_4} CO + H_2O$$

(D) Action of Heat on Formates



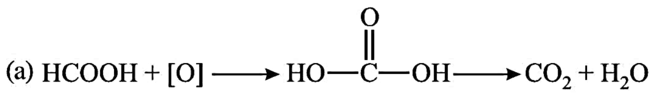
(a) $$2HCOONa \xrightarrow[360°C]{\Delta} \begin{array}{c} COONa \\ | \\ COONa \end{array} + H_2$$

(b) $$HCOONa + NaOH \xrightarrow[CaO]{\Delta} Na_2CO_3 + H_2$$

(c) $$(HCOO)_2Ca \xrightarrow{\Delta} \underset{\text{Formaldehyde}}{HCHO} + CaCO_3$$

(d) $$HCOONH_4 \xrightarrow{\Delta} \underset{\text{Formamide}}{HCONH_2} + H_2O$$

(E) Reducing Properties



(a) $$HCOOH + [O] \longrightarrow HO-\overset{\overset{\displaystyle O}{\|}}{C}-OH \longrightarrow CO_2 + H_2O$$

(b) $$5HCOOH + 2KMnO_4 + 3H_2SO_4 \xrightarrow{\text{Purple}} \underset{\text{Colourless}}{K_2SO_4 + 2MnSO_4 + 5CO_2 + 8H_2O}$$

(c) $$HCOOH + 2HgCl_2 \longrightarrow Hg_2Cl_2 + 2HCl + CO_2$$

$$HCOOH + Hg_2Cl_2 \longrightarrow \underset{\text{Black}}{2Hg} + 2HCl + CO_2$$

(d) Tollen's Reagent

$$HCOOH + Ag_2O \xrightarrow{\Delta} \underset{\text{Silver Mirror}}{2Ag} + CO_2 + H_2O$$

(e) Fehling's Solution

$$HCOOH + 2CuO \longrightarrow \underset{\text{Red Precipitate}}{Cu_2O\downarrow} + CO_2 + H_2O$$

5.1.3 Tests for HCOOH

1. Its aqueous solution turns blue litmus red.
2. It forms silver mirror with Tollens' reagent.
3. It forms black ppt with $HgCl_2$.
4. Heated with H_2SO_4, it evolves CO which burns with blue flame on mouth of test tube.
5. On reacting with neutral solution of $FeCl_3$, it gives red colour which converts in brown ppt on heating.

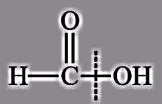
$$HCOOH \xrightarrow[FeCl_3]{\text{Fresh}} \text{Red colour} \xrightarrow{\text{Heating}} \text{Brown ppt}$$

5.1.4 Uses

1. In lab preparation of CO.
2. Textile dyeing and finishing.
3. Leather tanning.
4. Coagulating agent for rubber latex.
5. As an antiseptic and treatment for gout.
6. As a strong irritant.

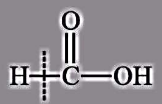
Note... 1. It is the strongest carboxylic acid.

2. Its unique nature is due to the presence of both carboxyl and carbonyl group.



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Carbonyl Group



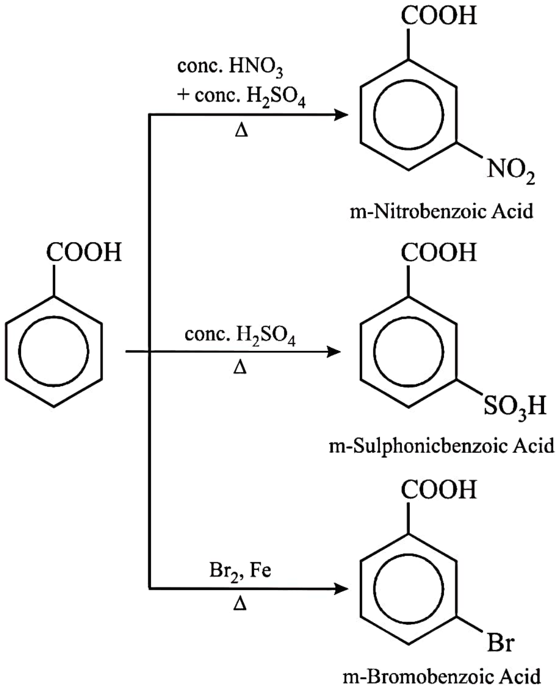
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Carboxyl Group

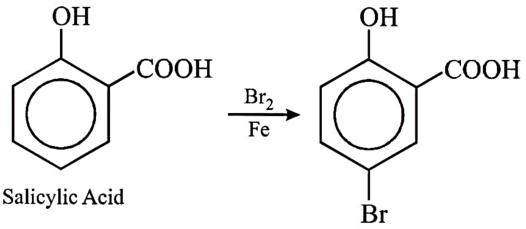
5.2 Acetic Acid (CH_3COOH)

In free state it is found in fermented fruit juices and in bound state it is found in biological fluids and plant extracts.

It is a by-product of alcohol industry.



Example – 41



5.3.3 Uses

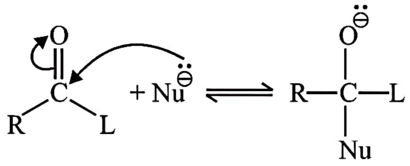
1. Used as food preservative.
2. Used as precursor for many compounds.
3. Used in making medicines for fungal diseases.

6. FUNCTIONAL DERIVATIVES OF ACIDS

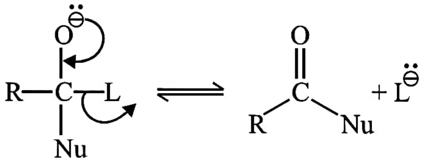
Carboxylic acids form esters, acid halides, amides and acid anhydrides as a functional derivatives. All these derivatives have a carbonyl group and yield carboxylic acids on hydrolysis. Among these derivatives, **acyl chlorides are the most reactive towards nucleophilic acyl substitution reactions and amides are least reactive.**

General Mechanism of Nucleophilic Acyl Substitution

Step1 : Addition of Nucleophile



Step2 : Loss of Leaving Group



Leaving groups L : Cl, NH_2, RO, RCOO

The weaker is the base, the better is the leaving group. The basic nature of the above groups is in the order :

$$Cl^{\ominus} < RCOO^{\ominus} < OH^{\ominus} < RO^{\ominus} < NH_2^{\ominus}$$

Hence, the leaving tendency of the groups is in order :

$$NH_2^{\ominus} < RO^{\ominus} < OH^{\ominus} < RCOO^{\ominus} < Cl^{\ominus}$$

Therefore, the reactivity of the acids and their derivatives follows the order :

$$RCOCl > (RCO)_2O > RCOOH > RCOOR > RCONH_2$$

6.1 Acyl Chlorides

6.1.1 Preparation

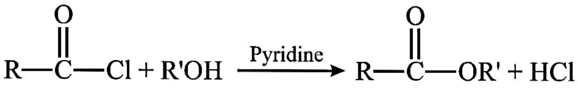
(A) $RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl\uparrow$

(B) $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2\uparrow + HCl\uparrow$

(C) $RCOOH + PCl_3 \longrightarrow RCOCl + H_3PO_3$

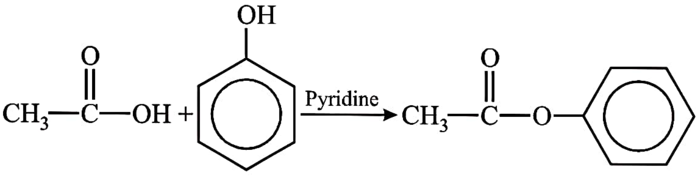
6.1.2 Reactions

(A) Esterification



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + R'OH \xrightarrow{\text{Pyridine}} R-\overset{\overset{\displaystyle O}{\|}}{C}-OR' + HCl$$

Example – 42



5.2.1 Preparation

$$CH_3OH + CO \xrightarrow[\text{heat, pressure}]{\text{Rh Catalyst}} CH_3COOH$$

$$\begin{tikzcd}
\text{Sugar and Starches} \arrow[r, "\text{Fermentation}"] & CH_3CH_2OH \arrow[d, "O_2\text{, Enzyme}", "\text{Acetobacter}"'] \\
 & CH_3COOH
\end{tikzcd}$$

$$\begin{tikzcd}
CH\equiv CH \arrow[r, "H_2O\text{, }HgSO_4", "H_2SO_4"'] & CH_3CHO \arrow[d, "O_2\text{, Cobalt Acetate}", "353\text{ K}"'] \\
 & CH_3COOH
\end{tikzcd}$$

$$CH_3CHO \xrightarrow[H_2SO_4[O]]{Na_2Cr_2O_7} CH_3COOH$$

5.2.2 Chemical Properties

Acetic Acid is a typical member of fatty acids. It shows all the general characteristics of mono carboxylic acids listed earlier.

5.2.3 Tests for CH_3COOH

1. Its aqueous solution turn blue litmus red.
2. Its aqueous solution gives effervescences of CO_2 with $NaHCO_3$.
3. Neutral $CH_3COOH \xrightarrow[FeCl_3]{\text{Neutral}}$ red colour
4. It does not affect Tollen's reagent, Fehling solution and $HgCl_2$. These reactions are used to differentiate it form HCOOH.

5.2.4 Uses

1. Good solvent and lab reagent.
2. As vinegar and table purposes in houses.
3. In manufacturing pickles.
4. Making Al, Cr, Fe acetates which are used as mordants in dyeing.

5.3 Benzoic Acid (C_6H_5COOH)

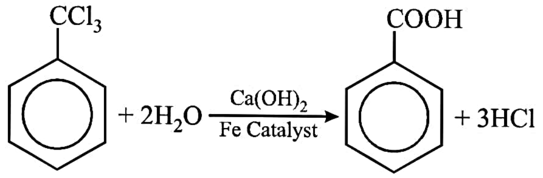
Naturally it is obtained from Benzoin resin. It is a benzene derivative and aromatic compound.

5.3.1 Preparation

(A) $Ph—CH_3 \xrightarrow[KOH, \Delta]{KMnO_4} Ph—COOK \xrightarrow{H_3O^{\oplus}} PhCOOH$

(B) $2C_6H_5CH_3 + 3O_2 \xrightarrow[170°C]{\text{Co-Mn Acetate}} 2C_6H_5COOH + 2H_2O$

(C)

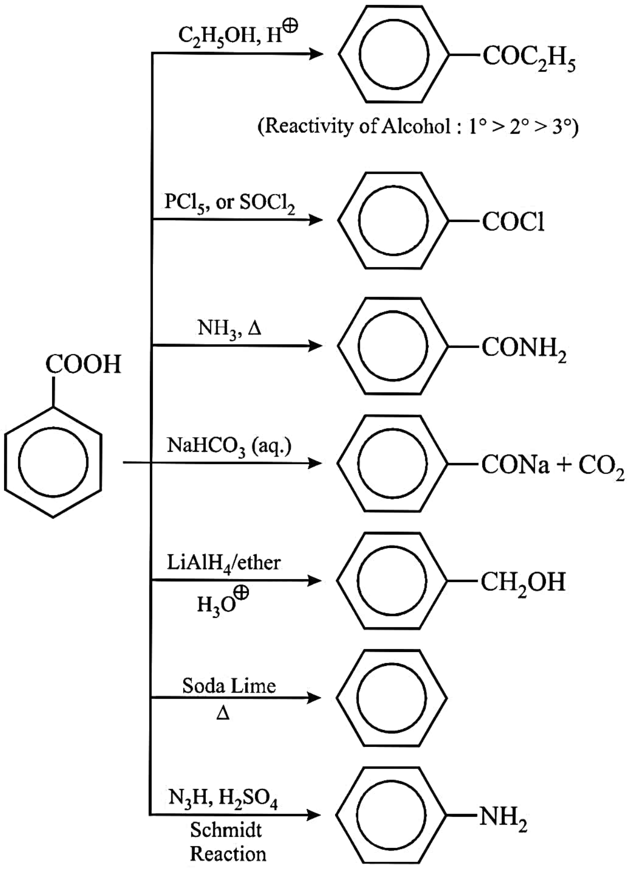


(D)

$$\begin{tikzcd}
C_6H_5NH_2 \arrow[r, "NaNO_2/HCl", "0\text{–}5°C"'] & C_6H_5N_2^{\oplus}Cl^{\ominus} \arrow[d, "CuCN"] \\
C_6H_5COOH & C_6H_5CN \arrow[l, "H_3O^{\oplus}"']
\end{tikzcd}$$

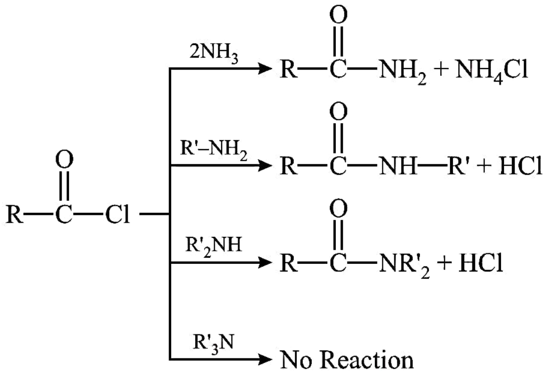
5.3.2 Reactions of Benzoic Acid

Benzoic acid, C_6H_5COOH shows all typical reactions of –COOH group just like aliphatic acids. The properties of the derivatives of benzoic acid are also similar to the properties of aliphatic acids.



COOH group attached to benzene nucleus in m-directing and a deactivating group. It also gives electrophilic substitution (S_E) reactions.

Conversion to Amides



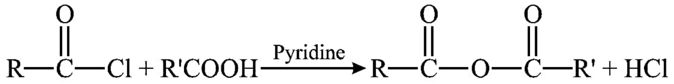
$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{2NH_3} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}NH_2 + NH_4Cl$$

$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{R'\text{–}NH_2} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}NH\text{—}R' + HCl$$

$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{R'_2NH} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}NR'_2 + HCl$$

$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{R'_3N} \text{No Reaction}$$

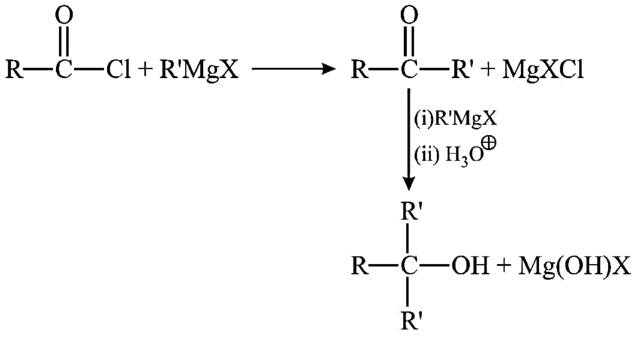
(C) Conversion to Anhydrides



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl + R'COOH \xrightarrow{\text{Pyridine}} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}O\text{—}\overset{O}{\overset{\|}{C}}\text{—}R' + HCl$$

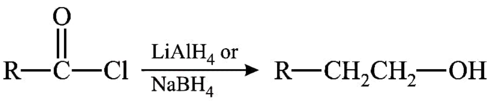
(D) Conversion to Alcohols

(i) Grignard Reagent



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl + R'MgX \longrightarrow R\text{—}\overset{O}{\overset{\|}{C}}\text{—}R' + MgXCl \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i)}R'MgX} R\text{—}\overset{R'}{\underset{R'}{C}}\text{—}OH + Mg(OH)X$$

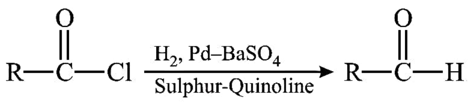
(ii) Metal Hydrides



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow[NaBH_4]{LiAlH_4 \text{ or}} R\text{—}CH_2CH_2\text{—}OH$$

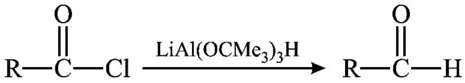
(E) Conversion to Aldehydes

(i) Rosenmund's Reduction



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow[\text{Sulphur-Quinoline}]{H_2,\ Pd\text{–}BaSO_4} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}H$$

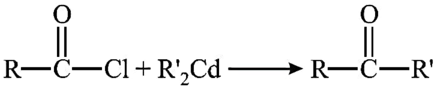
(ii) Metal Hydride $LiAl(OCMe_3)_3H$



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{LiAl(OCMe_3)_3H} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}H$$

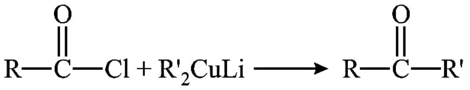
(F) Conversion to Ketones

(i) Dialkyl Cadmium



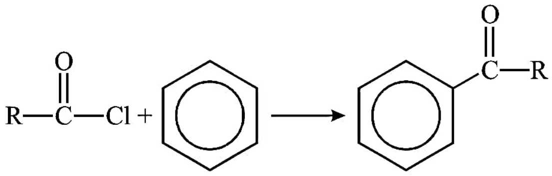
$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl + R'_2Cd \longrightarrow R\text{—}\overset{O}{\overset{\|}{C}}\text{—}R'$$

(ii) Gilman's Reagent

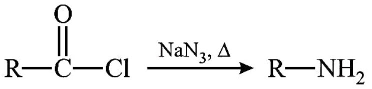


$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl + R'_2CuLi \longrightarrow R\text{—}\overset{O}{\overset{\|}{C}}\text{—}R'$$

(G) Friedel-Craft's Acylation

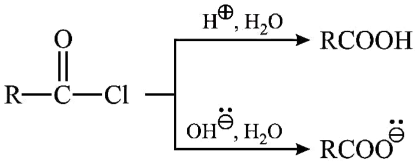


(H) Curtius Reaction



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{NaN_3,\ \Delta} R\text{—}NH_2$$

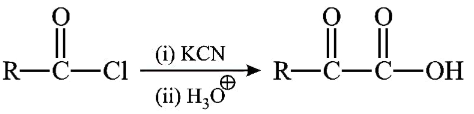
(I) Hydrolysis



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{H^{\oplus},\ H_2O} RCOOH$$

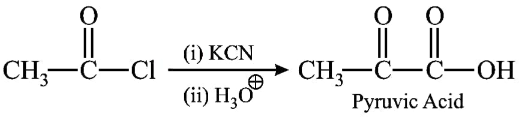
$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow{\ddot{O}H^{\ominus},\ H_2O} RCO\ddot{O}^{\ominus}$$

(J) Formation of α-Keto Acids



$$R\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) KCN}} R\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}OH$$

Example – 43

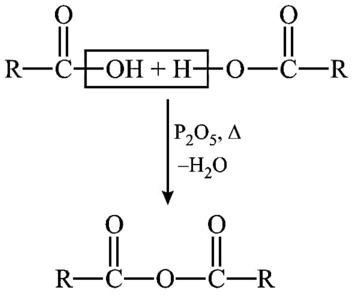


$$CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}Cl \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) KCN}} \underset{\text{Pyruvic Acid}}{CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{O}{\overset{\|}{C}}\text{—}OH}$$

6.2 Acid Anhydrides

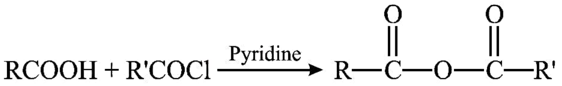
6.2.1 Preparation

(A)



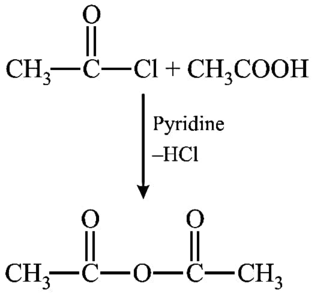
$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}\boxed{OH + H}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow[-H_2O]{P_2O_5,\ \Delta} R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R}$$

(B)



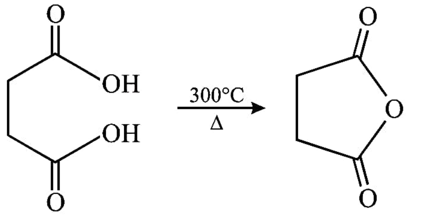
$$\mathrm{RCOOH + R'COCl \xrightarrow{Pyridine} R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'}$$

Example – 44

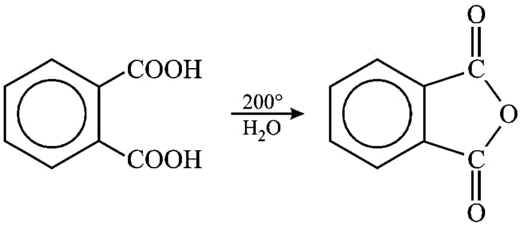


$$\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}Cl + CH_3COOH \xrightarrow[-HCl]{Pyridine} CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_3}$$

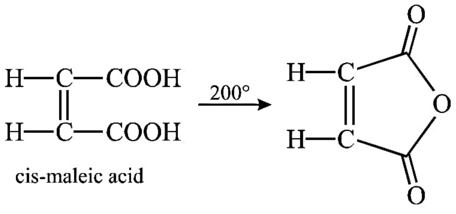
(C)



Succinic Anhydride



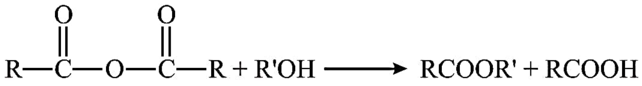
Phthalic Anhydride



Maleic Anhydride

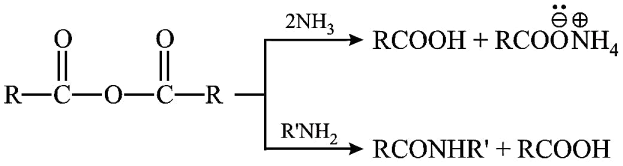
6.2.2 Reactions

(A) Esterification



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R + R'OH \longrightarrow RCOOR' + RCOOH}$$

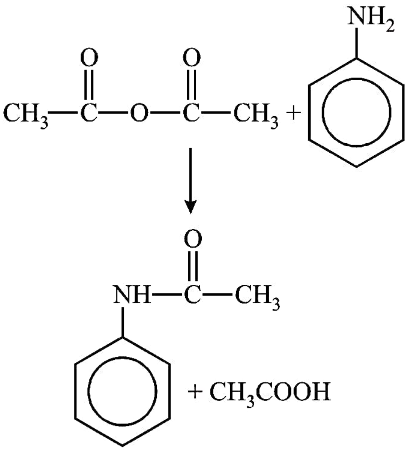
(B) Conversion to Amides



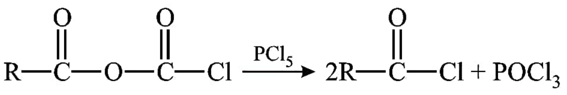
$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{2NH_3} RCOOH + RCO\ddot{\overset{\ominus}{O}}\overset{\oplus}{N}H_4}$$

$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow{R'NH_2} RCONHR' + RCOOH}$$

Example – 45

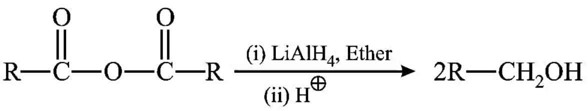


(C) Conversion to Acyl Chlorides



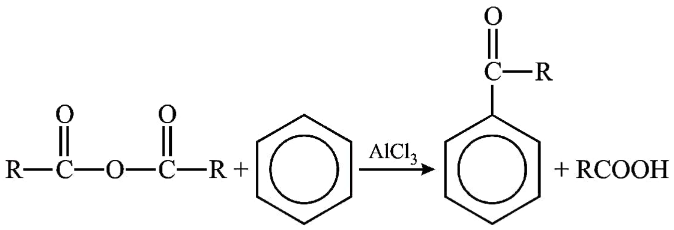
$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow{PCl_5} 2R{-}\overset{O}{\overset{\|}{C}}{-}Cl + POCl_3}$$

(D) Conversion to Alcohols

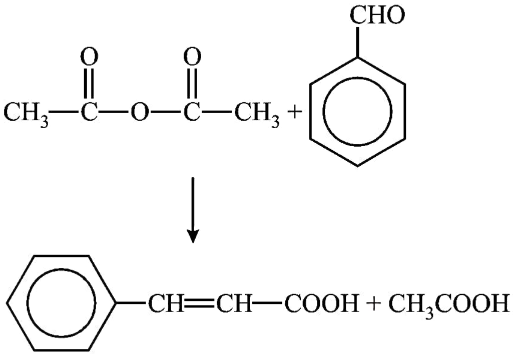


$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R \xrightarrow[(ii)\ H^{\oplus}]{(i)\ LiAlH_4,\ Ether} 2R{-}CH_2OH}$$

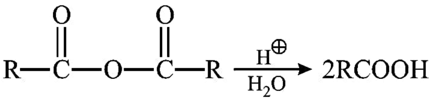
(E) Friedel-Craft's Acylation



(F) Perkin Reaction



(G) Hydrolysis



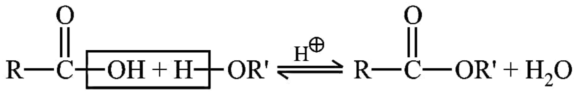
$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow[H_2O]{H^\oplus} 2RCOOH$$

6.3 Esters

6.3.1 Preparation

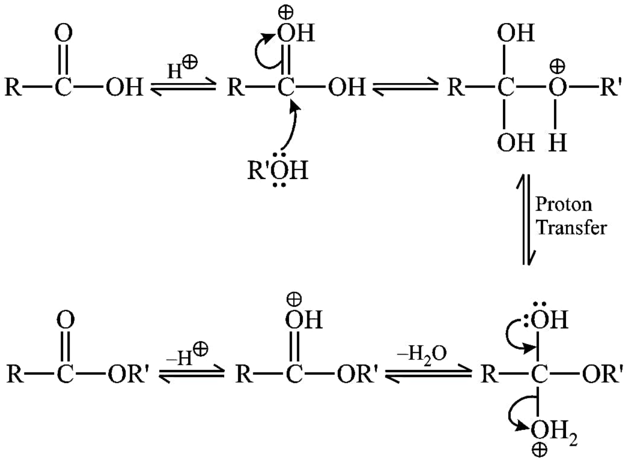
(A) Esterification

The esters are formed by the reaction between an acid, RCOOH and an alcohol by warming with mineral acid in a reaction called as Esterification.



$$R-\overset{O}{\overset{\|}{C}}\boxed{-OH + H-}OR' \overset{H^\oplus}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

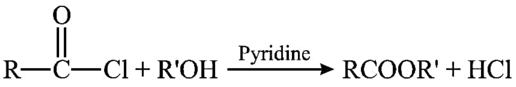
Mechanism



Since a tetrahedral intermediate occupies more space than a planar carbonyl group, we would expect the rate of this reaction to be retarded when bulky reactants are used. When the esterification of acetic acid was compared with that of 2, 2-dimethylpropanoic acid, $(CH_3)_3C—COOH$, the relatively small methyl group of acetic acid is replaced by a larger *tert*-butyl group, and the bulkier acid reacted fifty times slower than acetic acid. Similarly, increasing the size of the alcohol reactant results in a similar rate reduction.

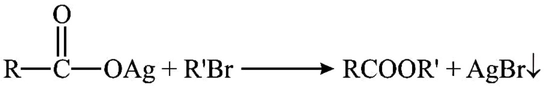
In its formation, steric factor is most important both in acids and alcohols. If acid chlorides or acid anhydrides are esterified with alcohols, it is considered as the better method.

(B)



$$R-\overset{O}{\overset{\|}{C}}-Cl + R'OH \xrightarrow{\text{Pyridine}} RCOOR' + HCl$$

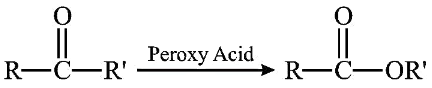
(C)



$$R-\overset{O}{\overset{\|}{C}}-OAg + R'Br \longrightarrow RCOOR' + AgBr\downarrow$$

(D) $R—CH=C=O + R'OH \longrightarrow RCH_2COOR'$

(E) Baeyer-Villiger Oxidation of Ketones



$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{\text{Peroxy Acid}} R-\overset{O}{\overset{\|}{C}}-OR'$$

Oxygen is introduced on that side which has more electron donating alkyl group.

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$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3 \xrightarrow{\text{MCPBA}} CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$$

(F) Carbonylation of Ethers

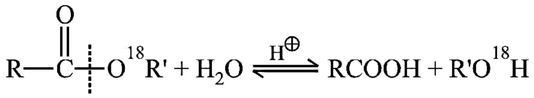
$$R-O-R + CO \xrightarrow[\text{Pressure}]{BF_3,\ 150°\text{-}200°C} R-COOR$$

(G) Diazomethane CH_2N_2

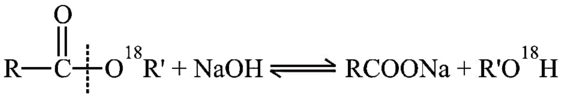
$$R-COOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

6.3.2 Reactions

(A) Hydrolysis



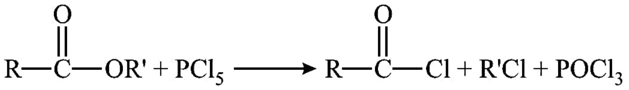
$$R-\overset{\overset{O}{\|}}{C}-O^{18}R' + H_2O \xrightleftharpoons{H^{\oplus}} RCOOH + R'O^{18}H$$



$$R-\overset{\overset{O}{\|}}{C}-O^{18}R' + NaOH \rightleftharpoons RCOONa + R'O^{18}H$$

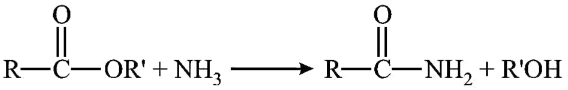
Base catalysed hydrolysis is not reversible as carboxylate ion formed is resonance stabilised.

(B) Conversion to Acyl Chlorides



$$R-\overset{\overset{O}{\|}}{C}-OR' + PCl_5 \longrightarrow R-\overset{\overset{O}{\|}}{C}-Cl + R'Cl + POCl_3$$

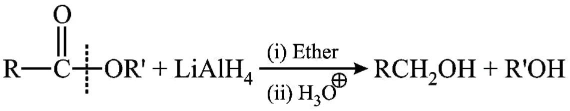
(C) Conversion to Amides



$$R-\overset{\overset{O}{\|}}{C}-OR' + NH_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}-NH_2 + R'OH$$

(D) Conversion to Alcohols

(i) Metal Hydrides

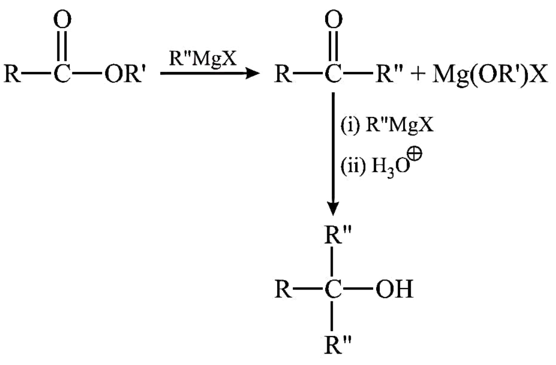


$$R-\overset{\overset{O}{\|}}{C}-OR' + LiAlH_4 \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) Ether}} RCH_2OH + R'OH$$

(ii) Bouveault-Blanc Reduction

$$RCOOR' \xrightarrow[C_2H_5OH]{Na} RCH_2OH + R'OH$$

(iii) Grignard Reagent

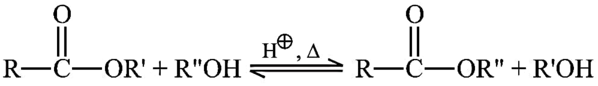


$$R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow{R''MgX} R-\overset{\overset{O}{\|}}{C}-R'' + Mg(OR')X \xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) } R''MgX} R-\underset{\underset{R''}{|}}{\overset{\overset{R''}{|}}{C}}-OH$$

3° Alcohol

(E) Transesterification

Trans esterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. These reactions are often catalyzed by the addition of an acid or base.



$$R-\overset{\overset{O}{\|}}{C}-OR' + R''OH \xrightleftharpoons{H^{\oplus},\ \Delta} R-\overset{\overset{O}{\|}}{C}-OR'' + R'OH$$

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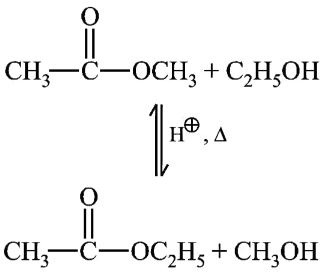
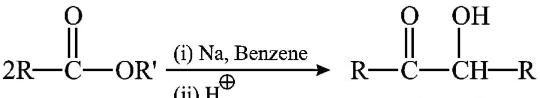


$$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3 + C_2H_5OH \xrightleftharpoons{H^{\oplus},\ \Delta} CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + CH_3OH$$

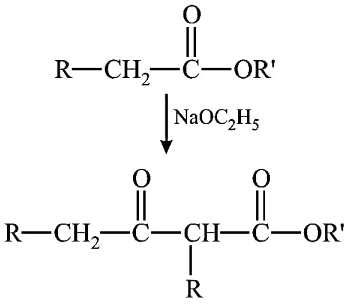
(F) Acyloin Formation



$$2R-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) Na, Benzene}} R-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{C}H-R$$

α-Hydroxy Ketone
(Acyloin)

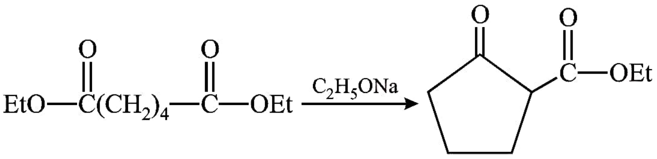
(G) Claisen Condensation



$$R-CH_2-\overset{\overset{O}{\|}}{C}-OR' \xrightarrow{NaOC_2H_5} R-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{R}{|}}{C}H-\overset{\overset{O}{\|}}{C}-OR'$$

Intramolecular claisen condensation is called as ***Dieckmann Condensation***.

Example – 48



6.4 Amides

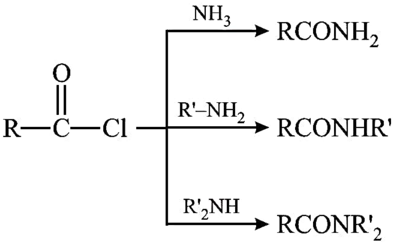
$RCONH_2$	$RCONHR$	$RCONR_2$
1° amides Alkanamides	2° amides N-Alkyl Alkanamides	3° amides N, N-Dialkyl Alkanamides

6.4.1 Preparation

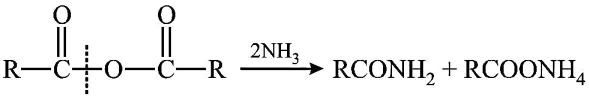
(A) $RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2$

(B) $RCOOH + PCl_5 \longrightarrow RCOCl \xrightarrow{NH_3} RCONH_2$

(C)



(D)



$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow{2NH_3} RCONH_2 + RCOONH_4$$

6.4.2 Reactions

(A) Hydrolysis

$$RCONH_2 + H_2O \xrightarrow{H_2SO_4} RCOOH + NH_3$$

$$RCONH_2 + NaOH \xrightarrow{H_2O} RCOONa + NH_3$$

This is typical of 1° amides to give off NH_3.

$$RCONHR + H_2O \xrightarrow{H^{\oplus}} RCOOH + \underset{1° \text{ amine}}{RNH_2}$$

$$RCONR_2 + H_2O \xrightarrow{H^{\oplus}} RCOOH + \underset{2° \text{ amine}}{R_2NH}$$

(B) Conversion to Cyanides

$$RCONH_2 \xrightarrow[\Delta]{P_4O_{10}} RC{\equiv}N + H_2O$$

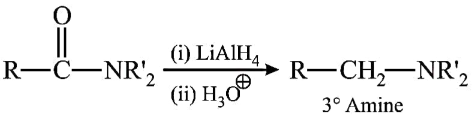
Dehydrating Reagents such as P_2O_5, $SOCl_2$ or $POCl_3$ is used.

(C) Conversion to Amines

Amides are reduced to amines by reaction with reducing agents such as $LiAlH_4$ or Na/C_2H_5OH.

$$RCONH_2 \xrightarrow[(2)\ H_3O^{\oplus}]{(1)\ LiAlH_4/\text{ether}} \underset{1° \text{ Amine}}{RCH_2NH_2}$$

$$RCONHR' \xrightarrow[(2)\ H_3O^{\oplus}]{(1)\ LiAlH_4/\text{ether}} \underset{2° \text{ Amine}}{RCH_2NHR'}$$



$$R-\overset{O}{\overset{\|}{C}}-NR'_2 \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ LiAlH_4} \underset{3° \text{ Amine}}{R-CH_2-NR'_2}$$

(D) Reaction with HNO_2

$$RCONH_2 + HNO_2 \longrightarrow RCOOH + N_2\uparrow + H_2O$$

(E) Hofmann Bromamide Degradation

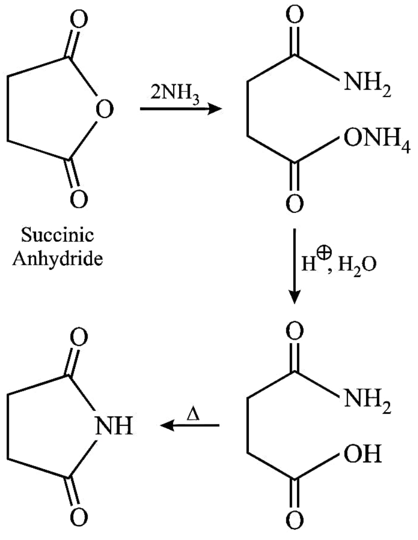
$$RCONH_2 + 4NaOH + Br_2 \Big\downarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Substituted amides do not give this reaction.

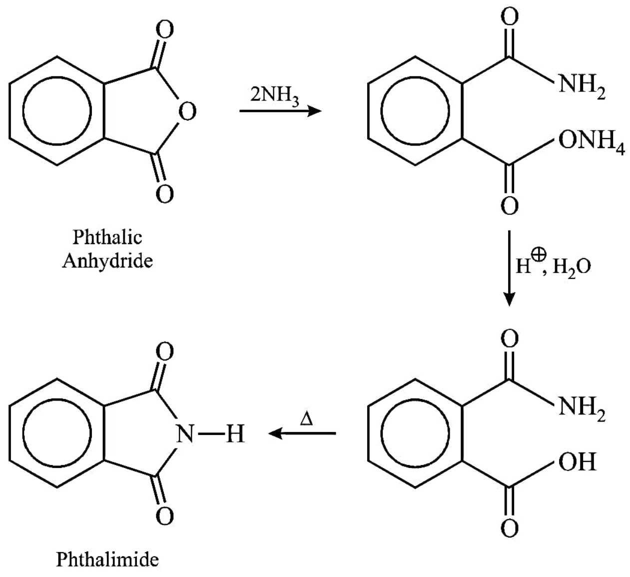
(F) Conversion to Imides

Cyclic anhydrides are converted first into an amide on reaction with NH_3 and then heated to form **imides**.

Example – 49



Example – 50

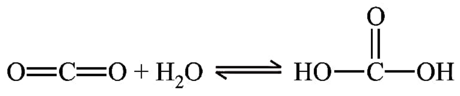


Phthalic Anhydride

Phthalimide

6.5 Carbonic Acid Derivatives

Aqueous carbonic acid (CO_2 gas dissolved in H_2O) is unstable and behaves as dibasic acid.

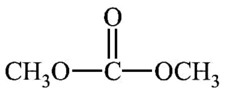


$$O{=}C{=}O + H_2O \rightleftharpoons HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^{\ominus} + H_3O^{\oplus}$$

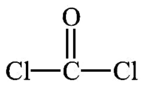
$$HCO_3^{\ominus} + H_2O \rightleftharpoons CO_3^{2\ominus} + H_3O^{\oplus}$$

Derivatives of Carbonic Acid



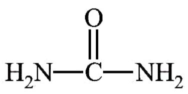
$$CH_3O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3$$

Dimethylcarbonate



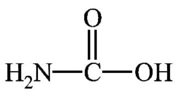
$$Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl$$

Phosgene



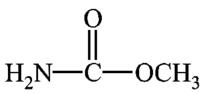
$$H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2$$

Urea



$$H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

Carbamic Acid



$$H_2N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3$$

Methylcarbamate