# Aliphatic Chemistry

## 1st Year Biology Students

## Faculty of Science

## 2022/2023

Prepared by

**Dr/ Entesar A. Hassan**

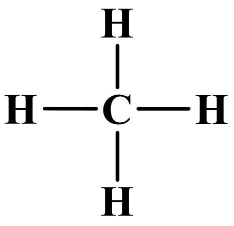
# Contents

# Hydrocarbons

**The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called hydrocarbons. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons.**

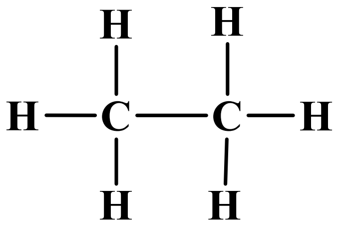
**Aliphatic hydrocarbons are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons.**

**A- Alkanes are aliphatic hydrocarbons with only single covalent bonds.**



$CH_4$

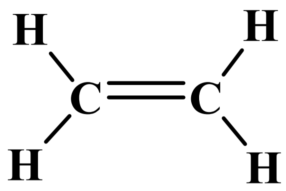
methane



$C_2H_6$

ethane

**B- Alkenes are hydrocarbons that contain at least one C– C double bond.**



$C_2H_4$

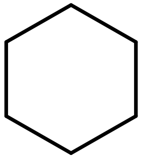
ethylene

**C- Alkynes are hydrocarbons that contain C-C triple bond.**

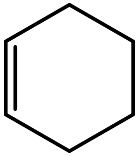
$$H-C\equiv C-H$$

$C_2H_2$
acetylene

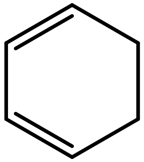
**D- An aliphatic hydrocarbon with a ring or C atoms; these hydrocarbons are called cycloalkanes (or cycloalkenes or cycloalkynes).**



cyclohexane



cyclohexene



cyclohexadiene

**Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as saturated hydrocarbons.**

# 1-Hydrocarbons

# (A) Alkanes

**All bonds between carbon atoms are single.**

## 1- Synthesis of alkanes

**1- From alkenes (by catalytic hydrogenation):-**

$$CH_2{=}CH_2 \xrightarrow{H_2\ /\ Ni} CH_3\text{-}CH_3$$

**2- From alkynes (by catalytic hydrogenation):-**

$$CH{\equiv}CH \xrightarrow{2H_2\ /\ Pt} CH_3\text{-}CH_3$$

# 3- From alkyl halides (by reduction):-

$$\text{i) RX (X; Br; I)} \xrightarrow[\text{or } H_2\text{/ Pd-C}]{\text{Zn/ HCl}} \text{RH} + \text{HX}$$

$$\text{e.g. } CH_3Br \xrightarrow{\text{Zn/ HCl}} CH_4 + HBr$$

$$\text{ii) RX} \xrightarrow{\text{Mg / ether}} \text{RMgX} \xrightarrow{H^+} \text{RH}$$

$$\text{e.g. } CH_3I \xrightarrow{\text{Mg / ether}} CH_3MgI \xrightarrow{H^+} CH_4$$

**iii) From Wurtz reaction**

$$2RX + 2Na \xrightarrow{\text{ether}} R\text{-}R + 2NaX$$

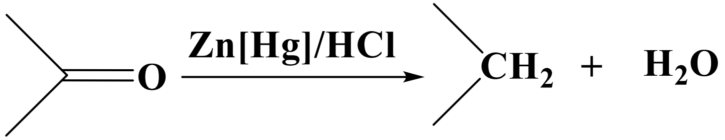
$$\text{e.g. } 2CH_3Br + 2Na \longrightarrow CH_3\text{-}CH_3 + 2NaBr$$

## 4- From alcohols (by reduction):-

$$ROH + 2HI \xrightarrow{150\ ^{o}C} RH + I_2 + H_2O$$

e.g. $CH_3CH_2OH + 2HI \longrightarrow CH_3CH_3 + I_2 + H_2O$

## 5- From aldehydes and ketones (Clemensen reduction):-



e.g $CH_3CHO \xrightarrow{Zn[Hg]/HCl} H_3C—CH_3 + H_2O$

## 6- From carboxylic acids:-

## i) By reduction:-

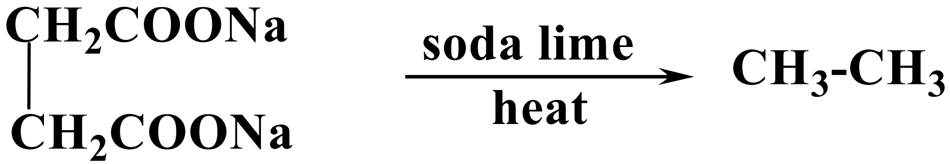
$$RCOOH \xrightarrow[200^{o}C]{HI/P} RCH_3$$

e.g $CH_3COOH \xrightarrow[200^{o}C]{HI/P} CH_3\text{-}CH_3$

## ii) By decarboxylation:-

$$RCOONa \xrightarrow[\text{heat}]{\text{soda lime}} RH + Na_2CO_3$$

e.g $$CH_3COONa \xrightarrow[\text{heat}]{\text{soda lime}} CH_4 + Na_2CO_3$$



$$\begin{array}{l} CH_2COONa \\ | \\ CH_2COONa \end{array} \xrightarrow[\text{heat}]{\text{soda lime}} CH_3\text{-}CH_3$$

sodium succinate

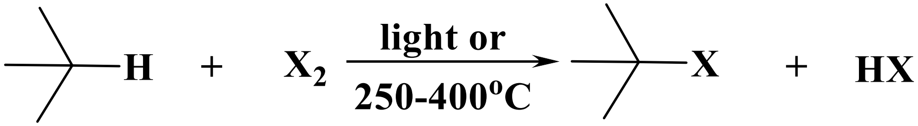
## iii) By Kolb's synthesis:-

$$2RCOOK + 2H_2O \xrightarrow{\text{electrolysis}} R\text{-}R + 2CO_2 + H_2 + 2KOH$$

e.g. $$2CH_3COOK + 2H_2O \longrightarrow CH_3\text{-}CH_3 + 2CO_2 + H_2 + 2KOH$$

# 2- Reactions of alkanes

## 1- Halogenation:-



e.g. $$CH_4 \xrightarrow{Cl_2/\,h\nu} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

## 2- Nitration:-

$$R\text{-}H + HNO_3 \xrightarrow[150\text{-}475^oC]{\text{vap. phase}} RNO_2 + H_2O$$

## 3- Pyrolysis:-

$$\text{Alkane} \xrightarrow[\text{with or without catalyst}]{400\text{-}600^oC} \text{smaller alkanes} + \text{alkenes} + H_2$$

$$\underset{\text{n-propane}}{2CH_3\text{-}CH_2CH_3} \xrightarrow{500^oC} \underset{\text{methane}}{CH_4} + \underset{\text{ethylene}}{CH_2{=}CH_2} + \underset{\text{propylene}}{CH_3\text{-}CH{=}CH_2} + H_2$$

# B- Alkenes

**Unsaturated hydrocarbons (contain double bonds)**

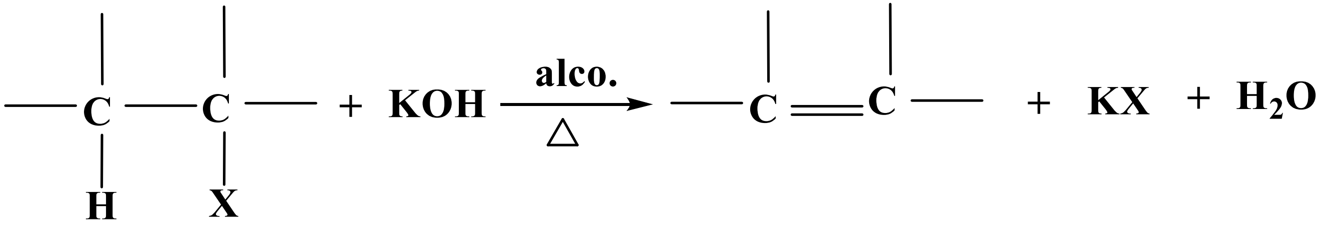
## 1- Synthesis of alkenes

**1- From alkynes:- (via catalytic hydrogenation)**

$$R\text{-}C\equiv C\text{-}R \xrightarrow{H_2/Pd} R\text{-}CH{=}CH\text{-}R$$

e.g. $$H\text{-}C\equiv C\text{-}H \xrightarrow{H_2/Pd} CH_2{=}CH_2$$

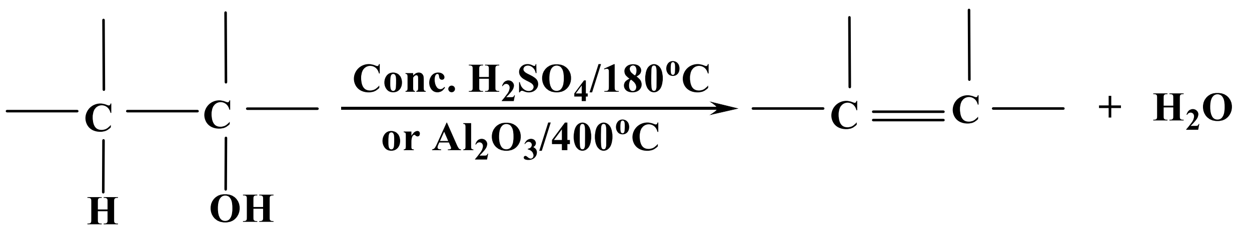
**2- From alkyl halides:- (via dehydrohalogenation)**



$$-\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{|}{C}}}- + KOH \xrightarrow[\triangle]{alco.} -\overset{|}{C}{=}\overset{|}{C}- + KX + H_2O$$

e.g. $$CH_3CH_2\text{-}Br + KOH \xrightarrow[\triangle]{alco.} CH_2{=}CH_2 + KBr + H_2O$$

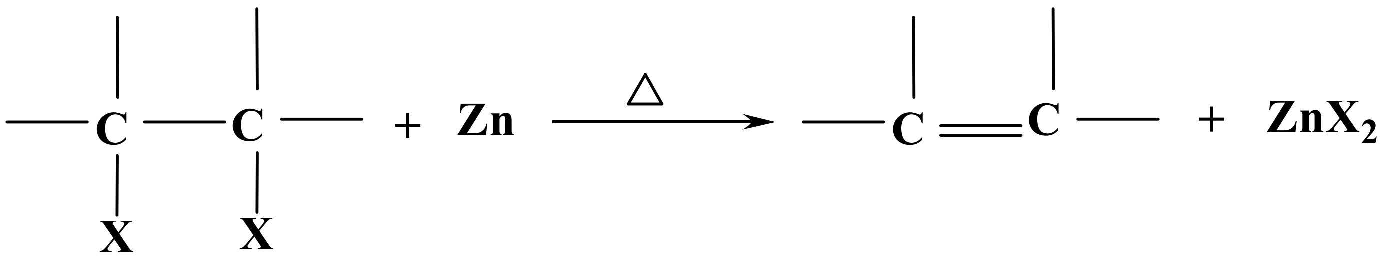
# 3- From alcohols:- (via dehydation)



$$-\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OH}{|}}{\overset{|}{C}}- \xrightarrow[\text{or } Al_2O_3/400^oC]{\text{Conc. } H_2SO_4/180^oC} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

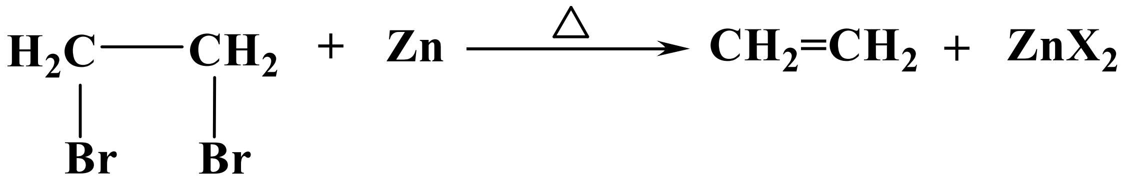
e.g. $CH_3CH_2\text{-}OH \xrightarrow[\text{or } Al_2O_3/400^oC]{\text{Conc. } H_2SO_4/180^oC} CH_2{=}CH_2 + H_2O$

# 4- From vicinal dihalides:- (via dehalogenation)



$$-\underset{\underset{X}{|}}{\overset{|}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}- + Zn \xrightarrow{\triangle} -\overset{|}{C}=\overset{|}{C}- + ZnX_2$$

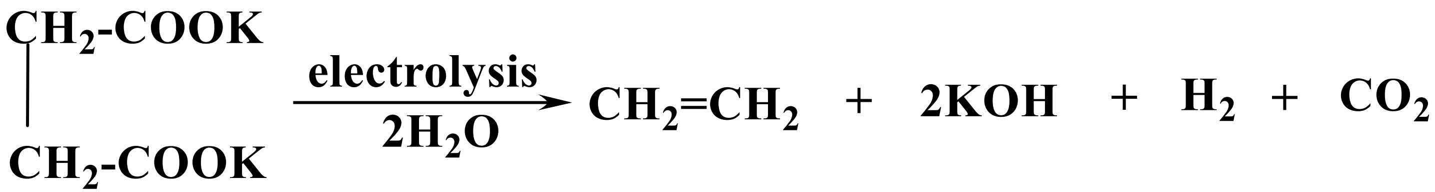
e.g.



$$\underset{\underset{Br}{|}}{H_2C}-\underset{\underset{Br}{|}}{CH_2} + Zn \xrightarrow{\triangle} CH_2{=}CH_2 + ZnX_2$$

1,2-dibromoethan

## 5- From dicarboxylic acids:- (via Kolb’s synthesis)

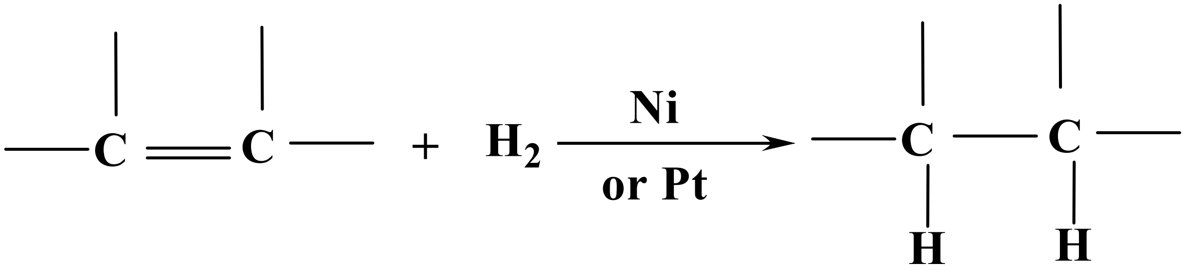


$$\begin{array}{l} CH_2\text{-}COOK \\ | \\ CH_2\text{-}COOK \end{array} \xrightarrow[2H_2O]{\text{electrolysis}} CH_2{=}CH_2 + 2KOH + H_2 + CO_2$$

Potassium succinate

# 2- Reactions of alkenes

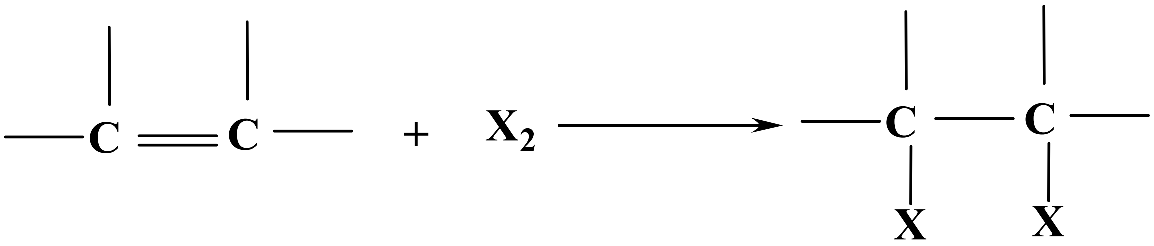
## 1- Addition of hydrogen:-



$$-\overset{|}{C}=\overset{|}{C}- + H_2 \xrightarrow[\text{or Pt}]{\text{Ni}} -\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{H}{\underset{|}{\overset{|}{C}}}-$$

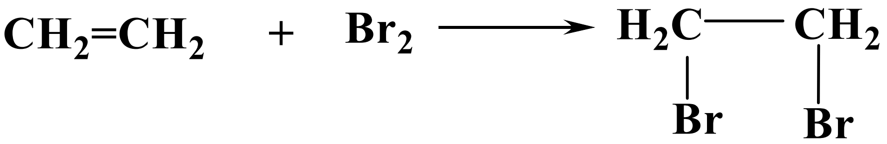
e.g. $CH_2{=}CH_2 + H_2 \longrightarrow CH_3-CH_3$

# 2- Addition of halogens:-



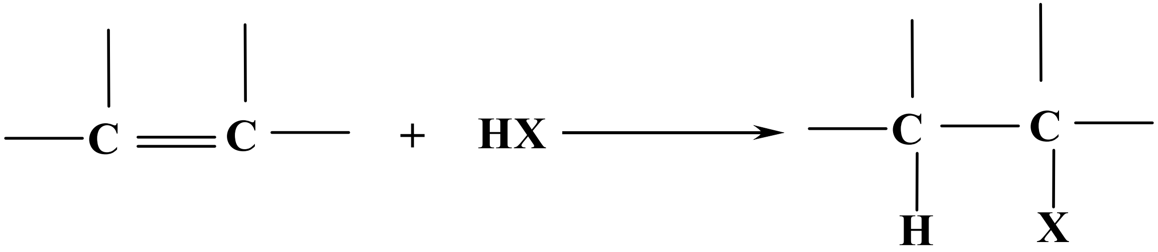
(vicinal halides)
(X= Cl; Br)

e.g.



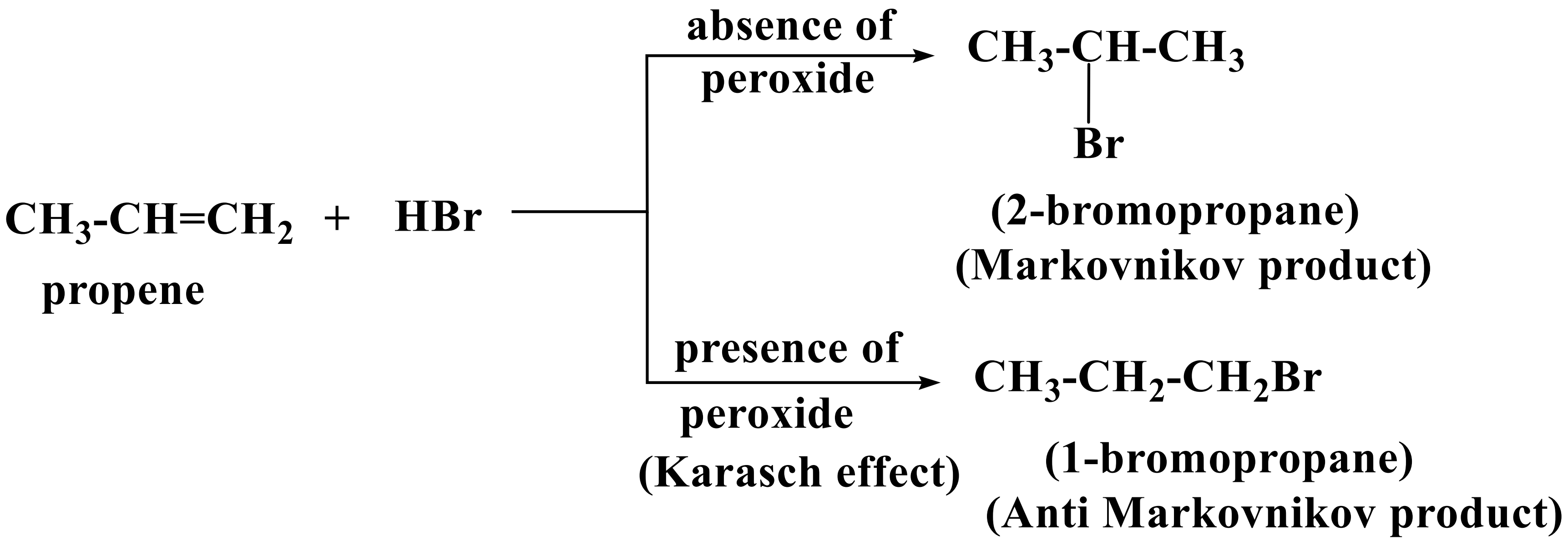
$$CH_2{=}CH_2 + Br_2 \longrightarrow H_2C(Br){-}CH_2(Br)$$

# 3- Addition of halogen acids:-



(Alkyl halides)

e.g. $CH_2{=}CH_2 + HBr \longrightarrow CH_3{-}CH_2Br$ (Ethyl bromide)



$CH_3\text{-}CH{=}CH_2$ + HBr

propene

absence of peroxide → $CH_3\text{-}\underset{\displaystyle Br}{\underset{|}{CH}}\text{-}CH_3$

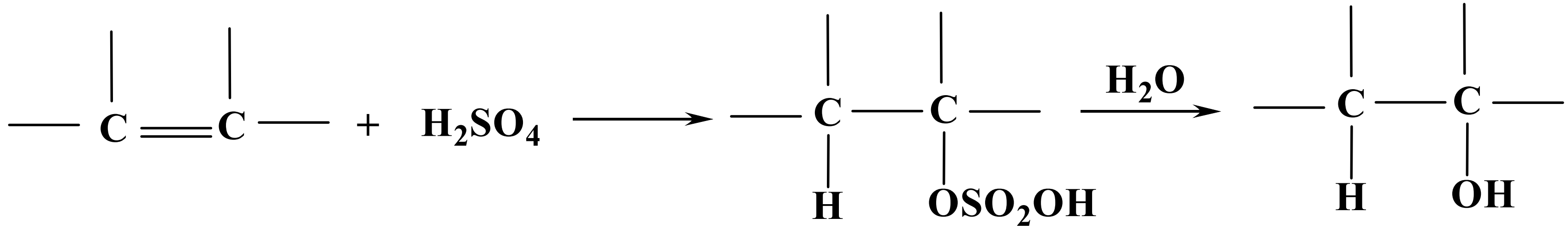
(2-bromopropane)
(Markovnikov product)

presence of peroxide (Karasch effect) → $CH_3\text{-}CH_2\text{-}CH_2Br$

(1-bromopropane)
(Anti Markovnikov product)

# 4- Hydration:-

i)

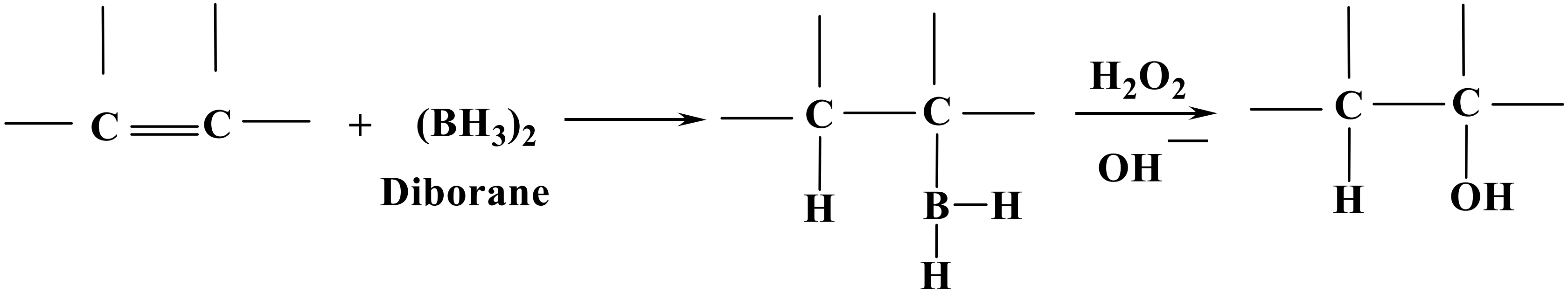


$$-\overset{|}{C}=\overset{|}{C}- + H_2SO_4 \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{OSO_2OH}{\overset{|}{C}}- \xrightarrow{H_2O} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

e.g. $CH_2{=}CH_2 \xrightarrow{H_2SO_4} CH_3CH_2OSO_2OH \xrightarrow{H_2O} CH_3CH_2OH$

(Ethyl hydrogen sulphate) (Ethanol)

ii)



$$-\overset{|}{C}=\overset{|}{C}- + (BH_3)_2 \longrightarrow -\underset{H}{\overset{|}{C}}-\underset{\underset{H}{B-H}}{\overset{|}{C}}- \xrightarrow[OH^-]{H_2O_2} -\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

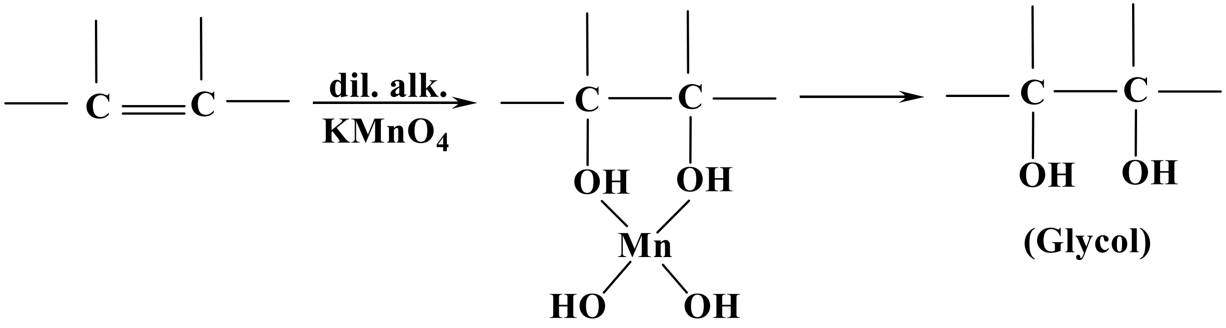
Diborane

e.g. $CH_2{=}CH_2 \xrightarrow[2)\ H_2O_2/OH^-]{1)\ (BH_3)_2} CH_3CH_2OH$

(Ethanol)

# 5- Oxidation:-

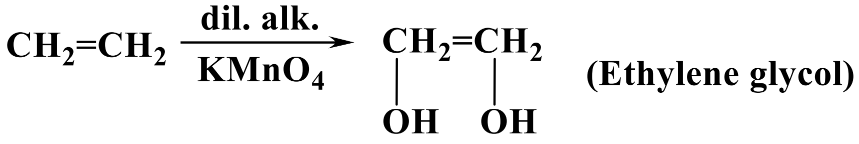
## i) In dilute alkaline solution:-



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow[KMnO_4]{dil.\ alk.} -\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \text{ (Mn(OH)}_2\text{ ester) } \longrightarrow -\underset{OH}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-$$

(Glycol)

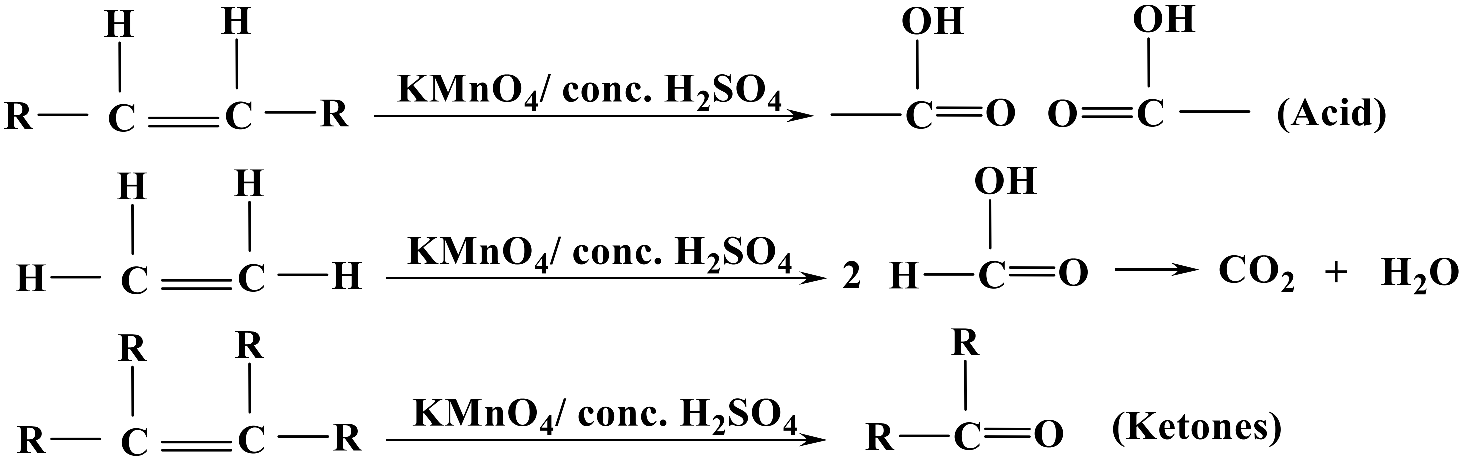
e.g.



$$CH_2=CH_2 \xrightarrow[KMnO_4]{dil.\ alk.} \underset{OH}{CH_2}=\underset{OH}{CH_2}$$

(Ethylene glycol)

## ii) In conc. $H_2SO_4$:-

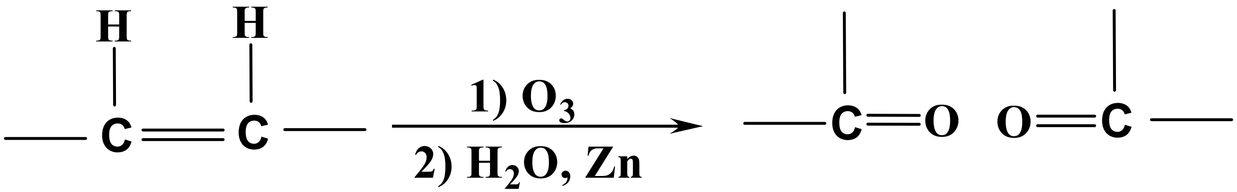


$$R-\overset{H}{C}=\overset{H}{C}-R \xrightarrow{KMnO_4/\ conc.\ H_2SO_4} -\overset{OH}{C}=O \quad O=\overset{OH}{C}- \text{ (Acid)}$$

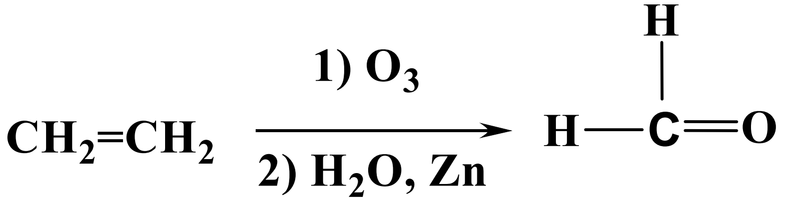
$$H-\overset{H}{C}=\overset{H}{C}-H \xrightarrow{KMnO_4/\ conc.\ H_2SO_4} 2\ H-\overset{OH}{C}=O \longrightarrow CO_2 + H_2O$$

$$R-\overset{R}{C}=\overset{R}{C}-R \xrightarrow{KMnO_4/\ conc.\ H_2SO_4} R-\overset{R}{C}=O \text{ (Ketones)}$$

# 6- Ozonolysis:-

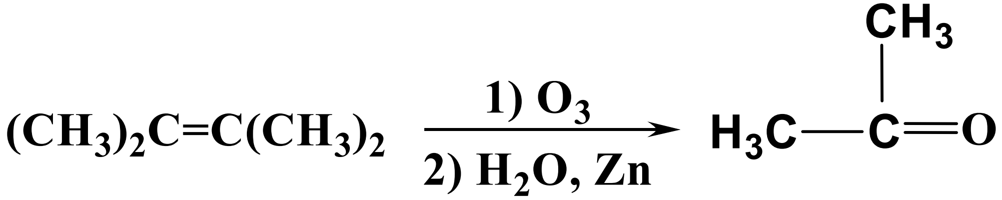


$$-\overset{H}{\underset{}{C}}=\overset{H}{C}- \xrightarrow[2)\ H_2O,\ Zn]{1)\ O_3} -\overset{|}{C}=O \quad O=\overset{|}{C}-$$

e.g. 

$$CH_2=CH_2 \xrightarrow[2)\ H_2O,\ Zn]{1)\ O_3} H-\overset{H}{C}=O$$

(Formaldehyde)

e.g. 

$$(CH_3)_2C=C(CH_3)_2 \xrightarrow[2)\ H_2O,\ Zn]{1)\ O_3} H_3C-\overset{CH_3}{C}=O$$

(Acetone)

# 7- Pyrolysis:-

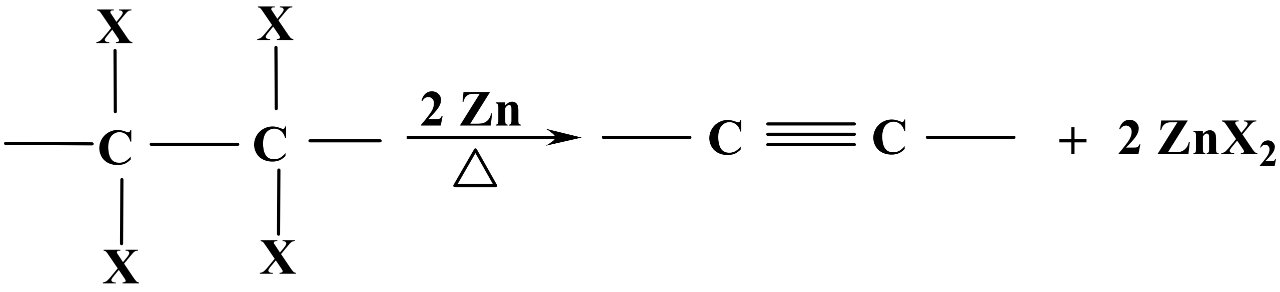
$$n(CH_2=CH_2) \xrightarrow[O_2/\ heat,\ P]{Polymerization} -(CH_2\text{-}CH_2)_n- \quad \text{(Polyethylene)}$$

# C-Alkynes

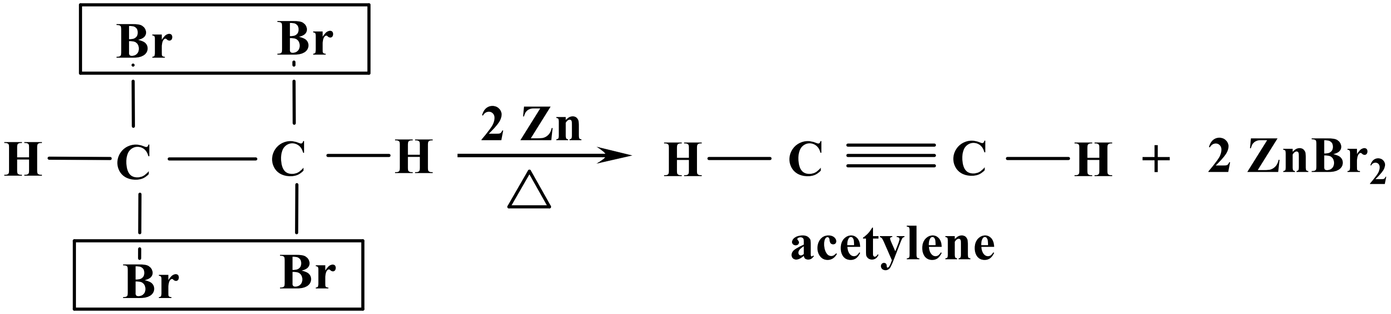
**Unsaturated hydrocarbons (contain triple bond).**

## 1- Synthesis of alkynes

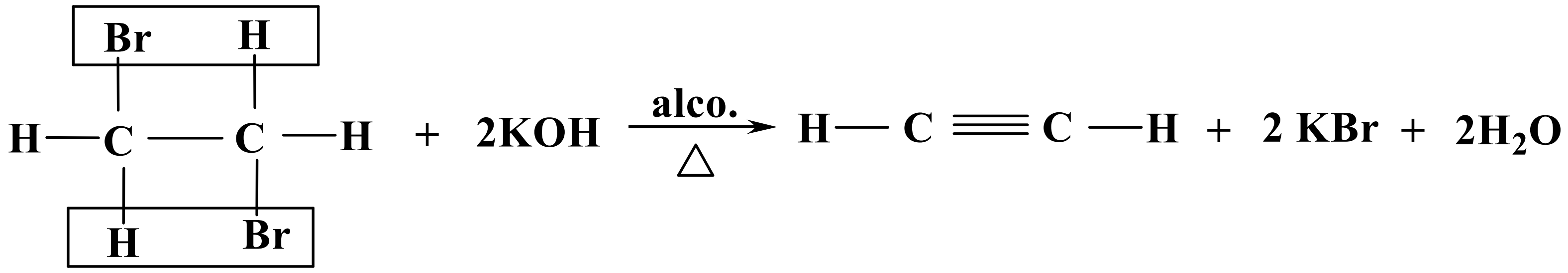
1-



$$-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}- \xrightarrow[\triangle]{2\,Zn} -C\equiv C- + 2\,ZnX_2$$

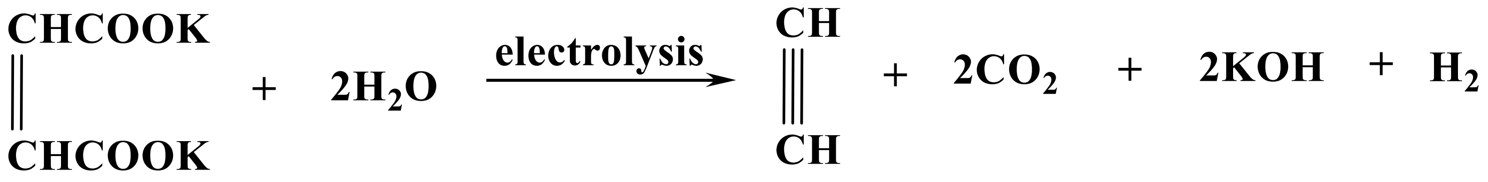


$$H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H \xrightarrow[\triangle]{2\,Zn} H-C\equiv C-H + 2\,ZnBr_2$$

2- 

$$H-\underset{\boxed{H}}{\overset{\boxed{Br}}{C}}-\underset{\boxed{Br}}{\overset{\boxed{H}}{C}}-H + 2KOH \xrightarrow[\triangle]{alco.} H-C\equiv C-H + 2\,KBr + 2H_2O$$

(1,2-dibromoethane)

3- 

$$\begin{array}{c}CHCOOK\\ \|\\ CHCOOK\end{array} + 2H_2O \xrightarrow{electrolysis} \begin{array}{c}CH\\ |||\\ CH\end{array} + 2CO_2 + 2KOH + H_2$$

(Pot. maleiate)

4- $CaC_2 + 2H_2O \xrightarrow{\triangle} CH\equiv CH + 2Ca(OH)_2$

(Calcium carbide)

5- $—C\equiv C—H \xrightarrow[- NH_3]{NaNH_2} —C\equiv \overset{-}{C}\ Na^+ \xrightarrow{RX} —C\equiv C—R + NaX$

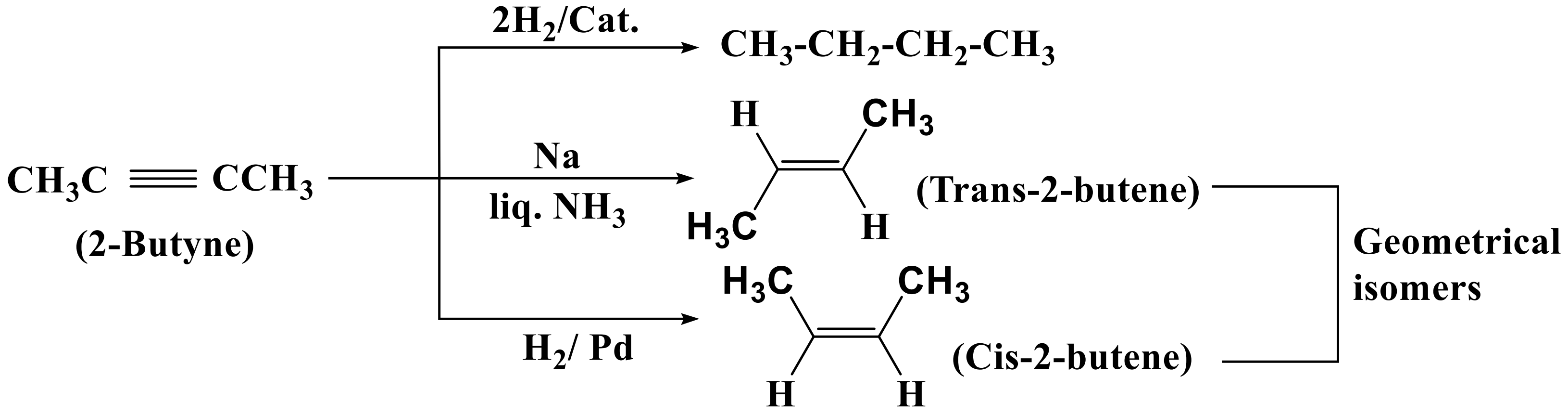
6- $2CH_4 \xrightarrow{1400\text{-}1600^oC} CH\equiv CH + 3H_2$

# 2- Reactions of alkynes

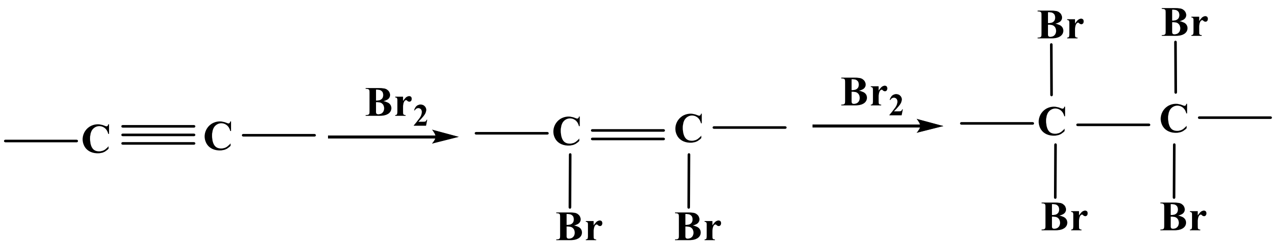
## 1- Addition of hydrogen:-

1- $CH \equiv CH \xrightarrow{2H_2/Cat.} CH_3\text{-}CH_3$

e.g. $CH \equiv CH \xrightarrow{H_2/Pd} CH_2 = CH_2$

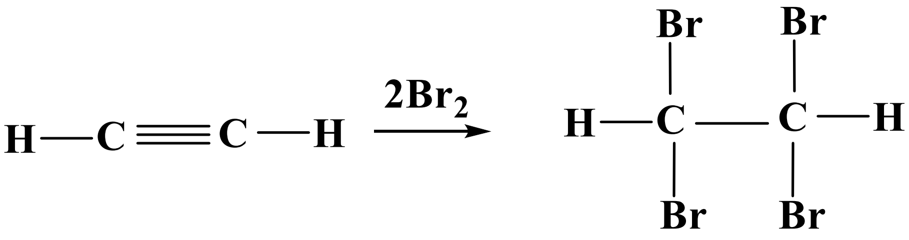


## 2- Addition of bromine:-



$$-C\equiv C- \xrightarrow{Br_2} -C(Br)=C(Br)- \xrightarrow{Br_2} -CBr_2-CBr_2-$$

e.g.

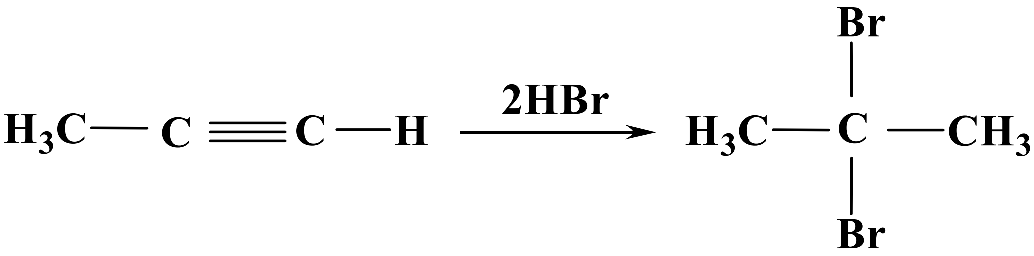


$$H-C\equiv C-H \xrightarrow{2Br_2} H-CBr_2-CBr_2-H$$

## 3- Addition of (HBr):-

$$H-C\equiv C-H \xrightarrow{HBr} CH_2{=}CH-Br \xrightarrow{HBr} CH_3CH_2Br$$

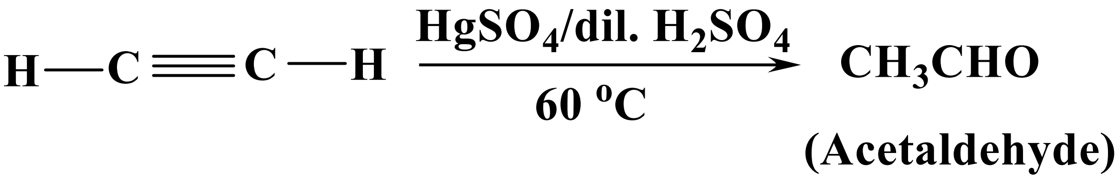
(Vinyl bromide) (1,1-dibromoethane)



$$H_3C-C\equiv C-H \xrightarrow{2HBr} H_3C-CBr_2-CH_3$$

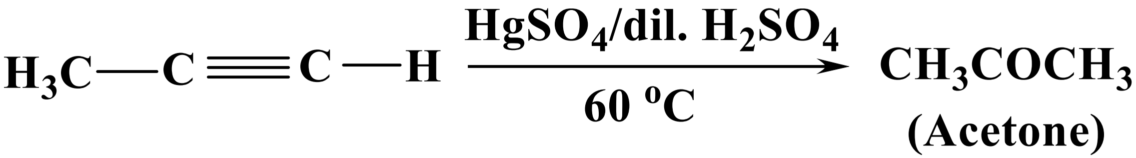
(2,2-dibromopropane)

# 4- Catalytic hyrdration:-



$$H-C\equiv C-H \xrightarrow[60\ ^{o}C]{HgSO_4/dil.\ H_2SO_4} CH_3CHO$$

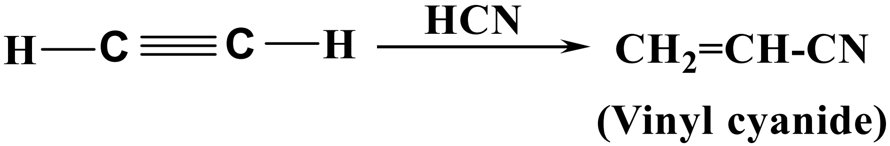
(Acetaldehyde)



$$H_3C-C\equiv C-H \xrightarrow[60\ ^{o}C]{HgSO_4/dil.\ H_2SO_4} CH_3COCH_3$$

(Acetone)

# 5- Addition of HCN:-



$$H-C\equiv C-H \xrightarrow{HCN} CH_2{=}CH\text{-}CN$$

(Vinyl cyanide)

## 6- Cyclic trimeriztion:-

$$3\ H-C\equiv C-H \xrightarrow[\text{hot tube}]{\text{red.}} C_6H_6$$

benzene

## 7- Polymerzition:-

$$2\ H-C\equiv C-H \xrightarrow{Cu_2Cl_2} CH_2=CH-C\equiv CH$$

(Vinyl acetylene)

## 8- Salt formation:-

i) $$H-C\equiv C-H \xrightarrow[\text{(molten)}]{110^oC \quad Na^+} H-C\equiv C^-\ Na^+ \quad + \quad H$$

(Sodium acetylide)

ii) $$H-C\equiv C-H \xrightarrow{Ag^+} H-C\equiv C^-\ Ag^+ \xrightarrow{Ag^+} Ag^+\ {}^-C\equiv C^-\ Ag^+$$

(Silver acetylide) (Silver carbide)

iii) $$H-C\equiv C-H \xrightarrow{Cu^+} H-C\equiv C^-\ Cu^+ \xrightarrow{Cu^+} Cu^+\ {}^-C\equiv C^-\ Cu^+$$

(Cuperous acetylide) (Cuperous carbide)

# 2- Halogen derivatives of saturated hydrocarbons (alkyl halides)

# RX

# Alkyl halides

**Alkyl halides are also known as haloalkanes.**

**Alkyl halides are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine).**

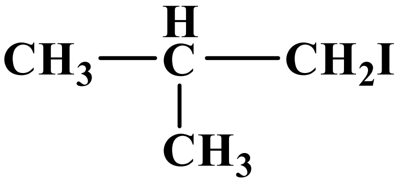
**Alkyl halides can be classified as primary, secondary, or tertiary.**

$CH_3-CH_2Br$

bromoethane

$CH_3-CH_2-CH_2Cl$

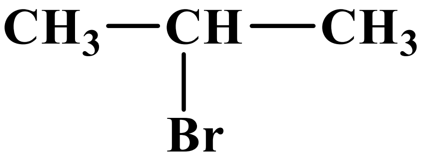
1-chloropropane



$CH_3-\overset{H}{\underset{CH_3}{C}}-CH_2I$

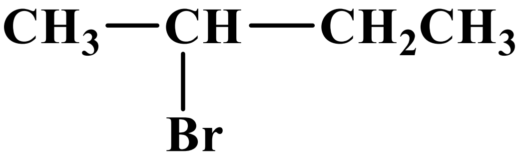
1-iodo-2-methylpropane

primary alkyl halide



$CH_3-\underset{Br}{CH}-CH_3$

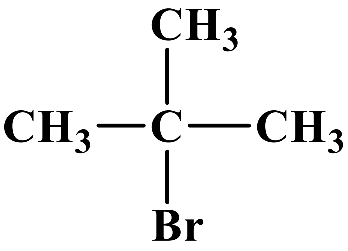
2-bromopropane



$CH_3-\underset{Br}{CH}-CH_2CH_3$

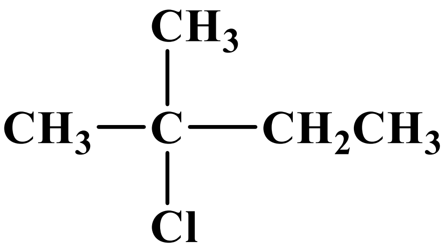
2-bromobutane

secondary alkyl halide



$CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_3$

2-bromo-2-methylpropane

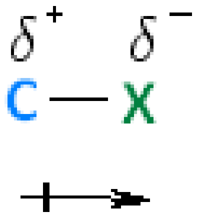


$CH_3-\overset{CH_3}{\underset{Cl}{C}}-CH_2CH_3$

2-chloro-2-methylbutane

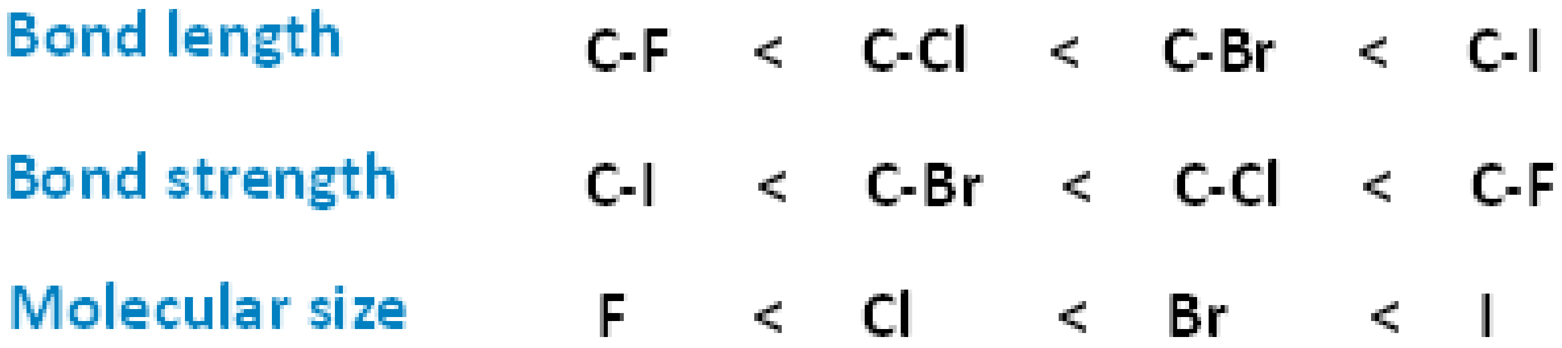
tertiary alkyl halide

**With respect to electronegativity, halogens are more electronegative than carbons. This results in a carbon-halogen bond that is polarized. As shown in the image below, carbon atom has a partial positive charge, while the halogen has a partial negative charge.**



The Polar C-X Bond

The following image shows the relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Bond length | C-F | < | C-Cl | < | C-Br | < | C-I |
| Bond strength | C-I | < | C-Br | < | C-Cl | < | C-F |
| Molecular size | F | < | Cl | < | Br | < | I |

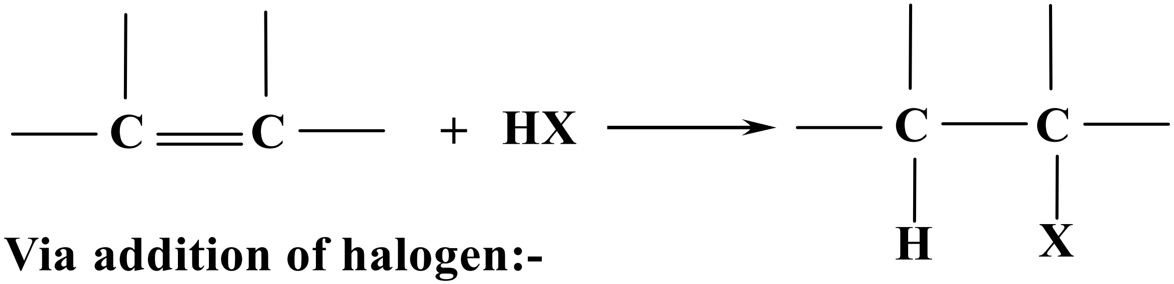
# 1- Synthesis

## 1- From alkanes:-

$$RH + X_2 \xrightarrow{h\nu} RX + HX$$

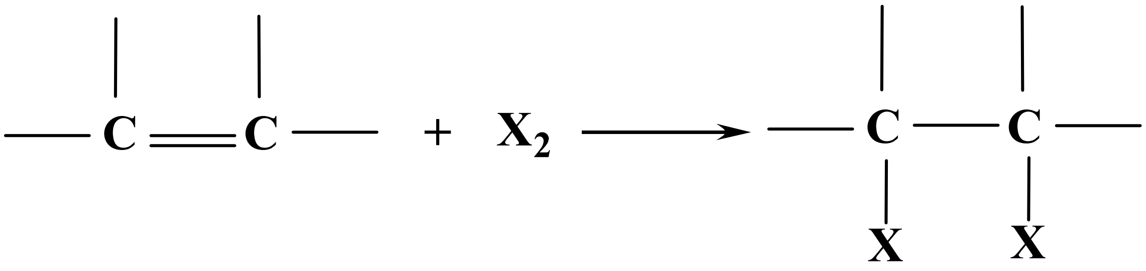
## 2- From alkenes:-

### i) Via addition of halogen acids:-



$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\overset{|}{\underset{H}{\underset{|}{C}}}-\overset{|}{\underset{X}{\underset{|}{C}}}-$$

### ii) Via addition of halogen:-



$$-\overset{|}{C}=\overset{|}{C}- + X_2 \longrightarrow -\overset{|}{\underset{X}{\underset{|}{C}}}-\overset{|}{\underset{X}{\underset{|}{C}}}-$$

**(Vicinal dihalides)**

# 3- From alcohols:-

$$\mathrm{ROH} + \mathrm{HX} \longrightarrow \mathrm{R{-}X} + \mathrm{H_2O}$$

e.g. $$\underset{\text{(ethanol)}}{\mathrm{CH_3CH_2OH}} + \mathrm{HBr\ (conc.)} \longrightarrow \underset{\text{(ethyl bromide)}}{\mathrm{CH_3CH_2Br}} + \mathrm{H_2O}$$

# 4- Halides exchange:-

$$\mathrm{RX} + \mathrm{I}^{-} \xrightarrow{\text{acetone}} \mathrm{R{-}I} + \mathrm{X}^{-}$$

# 2- Reactions

## 1- Nucleophilic substitution:-

$$\boxed{RX + Z^- \longrightarrow RZ + X^-}$$

$$Na^+OH^- \longrightarrow ROH\ \text{(alcohols)} + NaX$$

$$Na^+R^- \longrightarrow R\text{-}R\ \text{(alkanes)} + NaX$$

$$Na^+\,C^- \equiv C - R' \longrightarrow \underset{\text{(alkynes)}}{R - C \equiv C - R'} + NaX$$

$$K^+I^- \longrightarrow RI\ \text{(alkyl halides)} + KX$$

$$Na^+OR^- \longrightarrow ROR\ \text{(ethers)} + NaX$$

$$NH_3 \longrightarrow RNH_2\ \text{(amines)} + HX$$

$$\mathrm{R'CO\overline{O}\ Ag^{+}} \longrightarrow \mathrm{R'COOR}\quad \text{(esters)} + \mathrm{AgX}$$

$$\mathrm{K^{+}\ S\overline{H}} \longrightarrow \mathrm{RSH}\quad \text{(thioalcohols)} + \mathrm{KX}$$

$$\mathrm{K^{+}\overline{S}R} \longrightarrow \mathrm{RSR}\quad \text{(thioethers)} + \mathrm{KX}$$

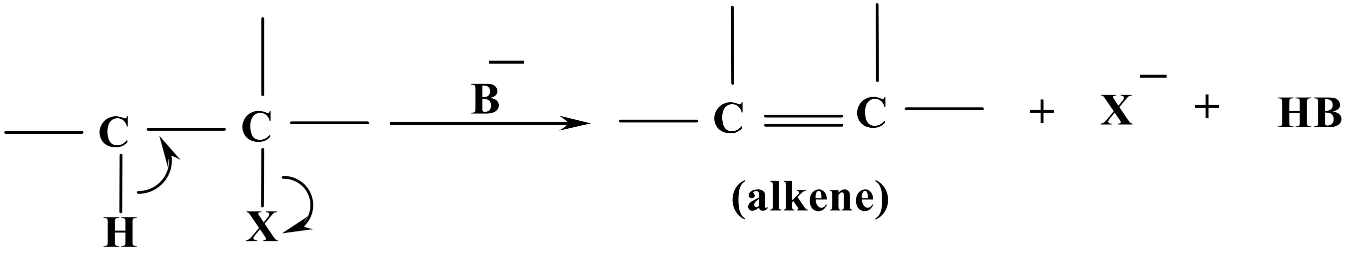
$$\mathrm{Na^{+}C\overline{N}} \longrightarrow \mathrm{RCN}\quad \text{(nitriles)} + \mathrm{NaX}$$

$$\mathrm{Ag^{+}C\overline{N}} \longrightarrow \mathrm{RNC}\quad \text{(isonitriles)} + \mathrm{AgX}$$

$$\mathrm{Na^{+}\overline{N}O_2} \longrightarrow \mathrm{RNO_2}\quad \text{(nitroalkanes)} + \mathrm{NaX}$$

$$\mathrm{\overline{A}rH^{+}} \xrightarrow{\mathrm{AlCl_3}} \mathrm{ArR}\quad \text{(Friedel-Crafts reaction)} + \mathrm{HX}$$

## 2- Elimination:- formation of alkenes:-



$$\text{e.g.}\quad CH_3CH_2Br \xrightarrow{\text{alco. KOH}} CH_2{=}CH_2 + KBr + H_2O$$

## 3- Reduction to alkanes:-

$$RX + H_2 \xrightarrow[\text{or Zn/HCl}]{\text{Pd/C}} RH + HX$$

## 4- Reaction with magnesium in ethers:-

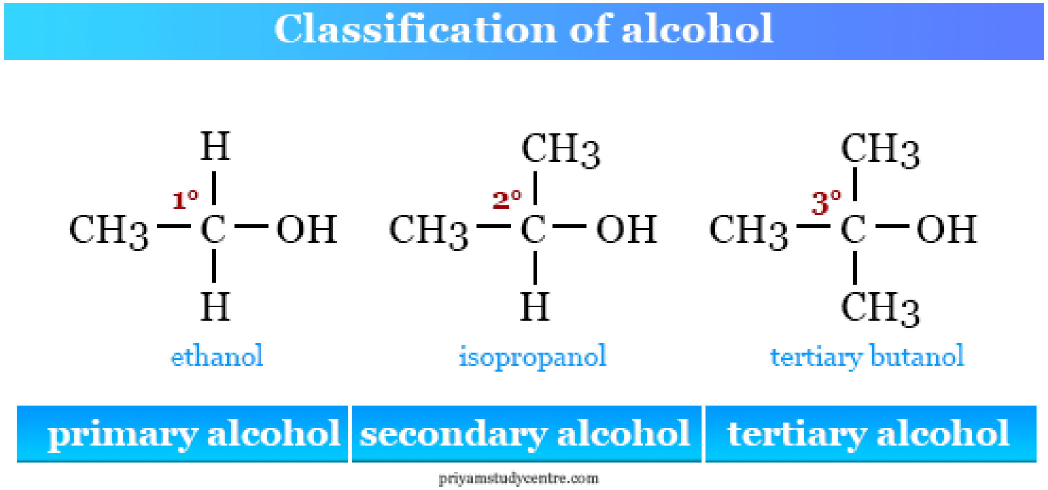
$$RX \xrightarrow{\text{Mg/ethers}} RMgX \quad \text{(Grignard reagent)}$$

# 3- Alcohols

# ROH

# Alcohols

**Aliphatic alcohols are organic chemical compounds. They are flammable liquids and are highly soluble in water and many organic solvents. Highly volatile liquids, they are stable in water under typical use conditions.**



-Types of aliphatic alcohol

1- Methanol, ethanol, propanol, isopropyl alcohol, butanol, isobutanol, etc are examples of monohydric alcohols because these contain only one hydroxyl group.

2- Ethylene glycol, trimethylene glycol, pentamethylene glycol, isobutene glycol are dihydric types of aliphatic alcohols. These chemicals contain two alcoholic groups.

**3-The only important trihydric aliphatic organic compound is glycerol or propane-1-2-2-triol because these contain three alcoholic groups. Glycerol occurs in almost all animals and vegetable oils.**

**4- D-sorbitol, D-mannitol, and dulcitol are the polyhydric aliphatic alcohols that occur naturally contain more than three hydroxyl groups.**

# Examples of alcohol Names and Formula

**methanol $CH_3OH$**

***n*-propanol $CH_3CH_2CH_2OH$**

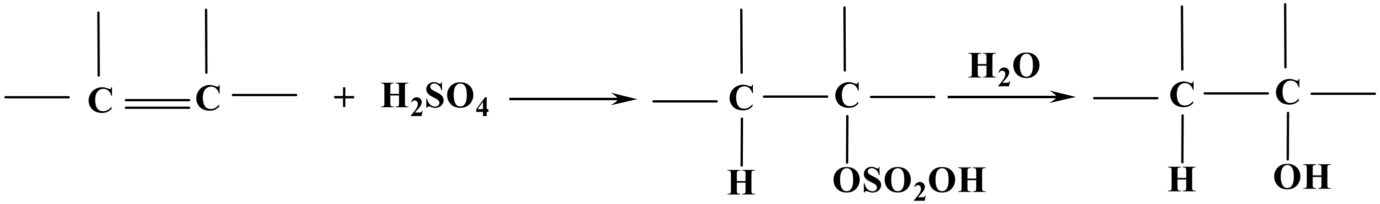
***iso*-propanol$CH_3CH(OH)CH_3$**

***t*-butanol $(CH_3)_3COH$**

# 1- Synthesis

## 1- From alkenes:- (by hydration)

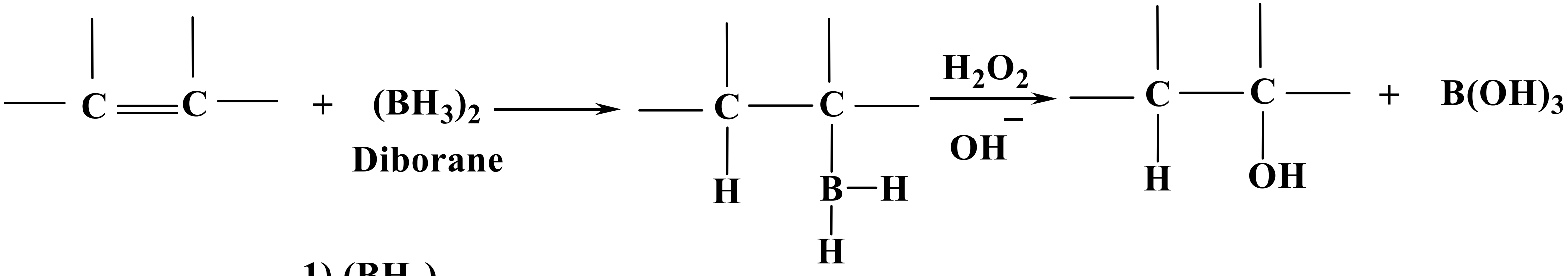
**i) With dil. sulfuric acid:-**



$$-\overset{|}{C}=\overset{|}{C}- \;+\; H_2SO_4 \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OSO_2OH}{C}}- \xrightarrow{H_2O} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}-$$

e.g. $CH_2{=}CH_2 \xrightarrow{H_2SO_4} \underset{\text{(Ethyl hydrogen sulphate)}}{CH_3CH_2OSO_2OH} \xrightarrow{H_2O} \underset{\text{(Ethanol)}}{CH_3CH_2OH}$

**ii) Hydroboration followed by oxidation:-**



$$-\overset{|}{C}=\overset{|}{C}- \;+\; \underset{\text{Diborane}}{(BH_3)_2} \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{\underset{H}{|}\atop{B-H}}{C}}- \xrightarrow[\overset{-}{OH}]{H_2O_2} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- \;+\; B(OH)_3$$

e.g. $CH_2{=}CH_2 \xrightarrow[2)\ H_2O_2/\overset{-}{OH}]{1)\ (BH_3)_2} \underset{\text{(Ethanol)}}{CH_3CH_2OH}$

# 2- From alkyl halides by hydrolysis:-

$$\boxed{RX + Z^{-} \longrightarrow RZ + X^{-}}$$

$$Na^{+}OH^{-} \longrightarrow ROH\ \text{(alcohols)} + NaX$$

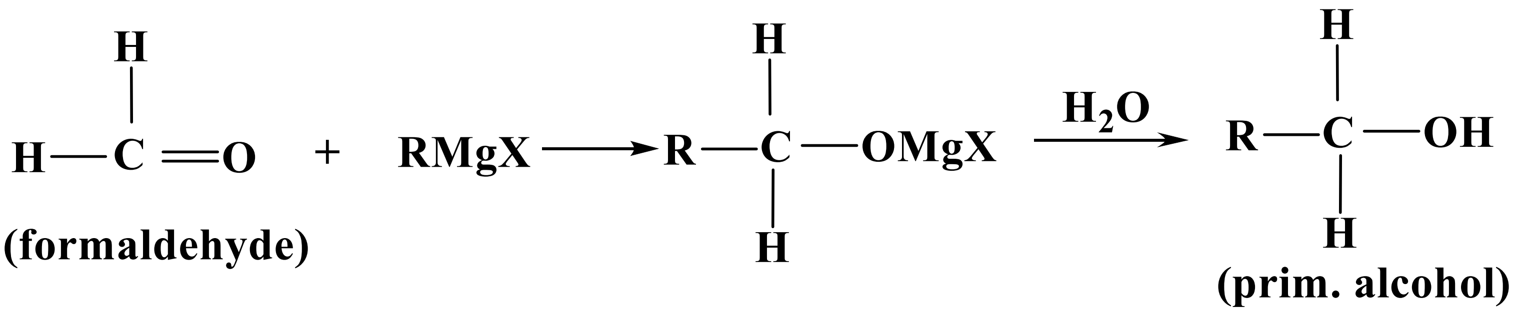
# 3- From aldehydes and ketones:-

## i) By reduction:-

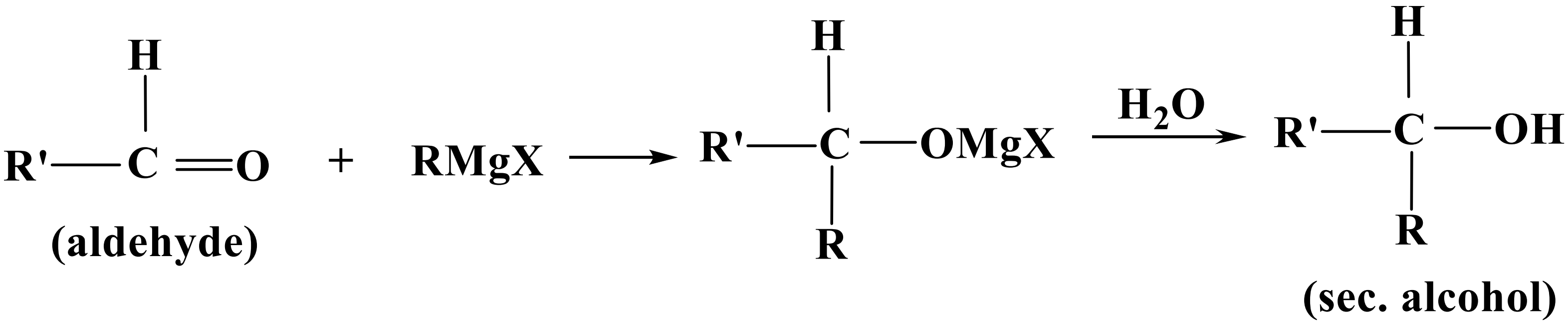
$$4RCHO + LiAlH_4 \longrightarrow (RCH_2O)_4LiAl \xrightarrow{H_2O} \underset{\text{(prim. alcohol)}}{4RCH_2OH} + LiOH + Al(OH)_3$$

$$4R_2CO + LiAlH_4 \longrightarrow (R_2CHO)_4LiAl \xrightarrow{H_2O} \underset{\text{(sec. alcohol)}}{4R_2CHOH} + LiOH + Al(OH)_3$$

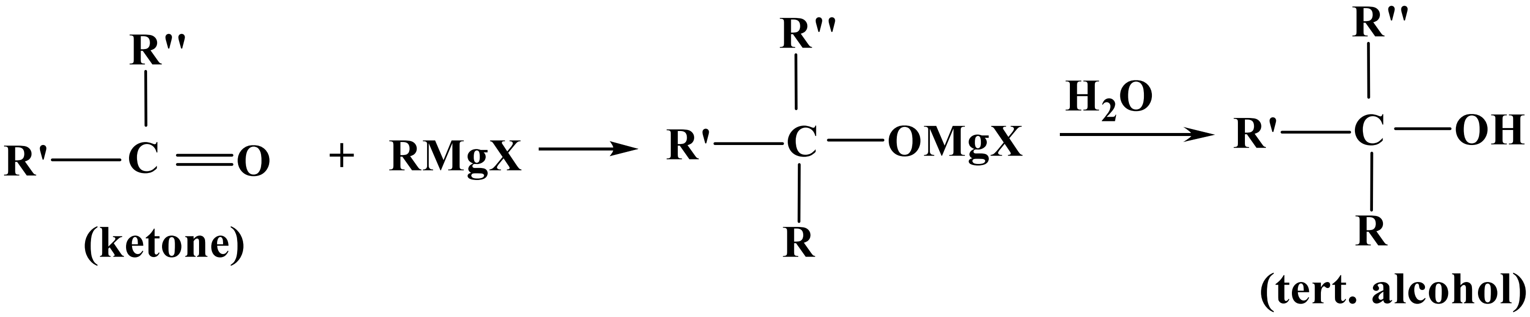
# ii) By addition of Grignard reagents:-



$$H-\overset{H}{C}=O + RMgX \longrightarrow R-\underset{H}{\overset{H}{C}}-OMgX \xrightarrow{H_2O} R-\underset{H}{\overset{H}{C}}-OH$$



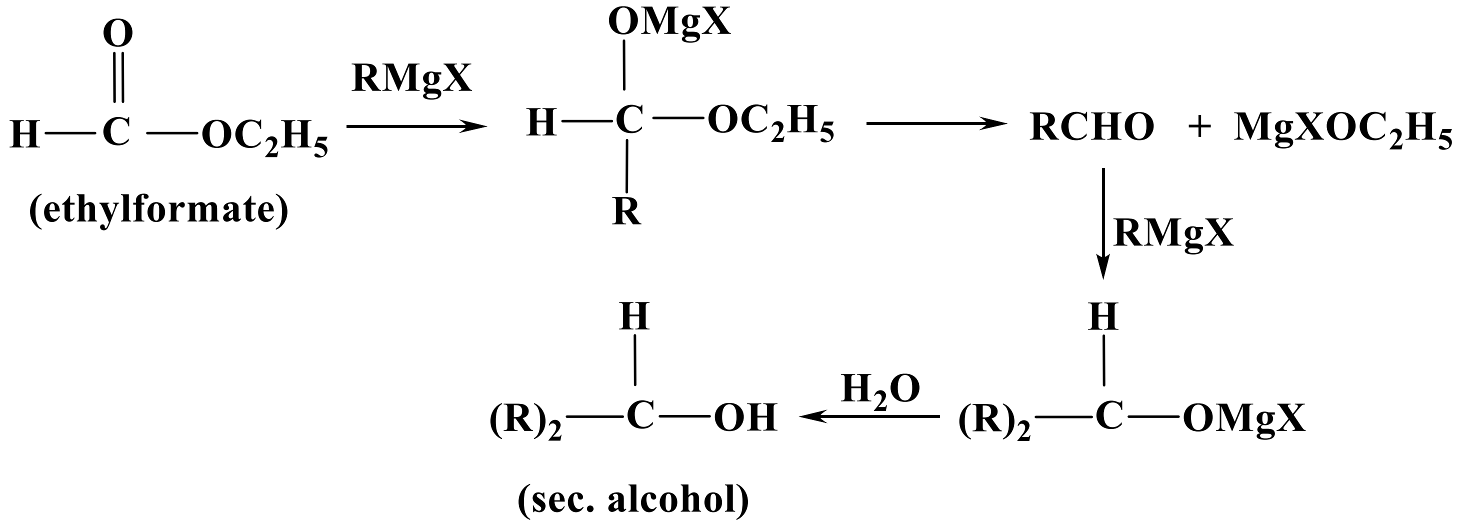
$$R'-\overset{H}{C}=O + RMgX \longrightarrow R'-\underset{R}{\overset{H}{C}}-OMgX \xrightarrow{H_2O} R'-\underset{R}{\overset{H}{C}}-OH$$

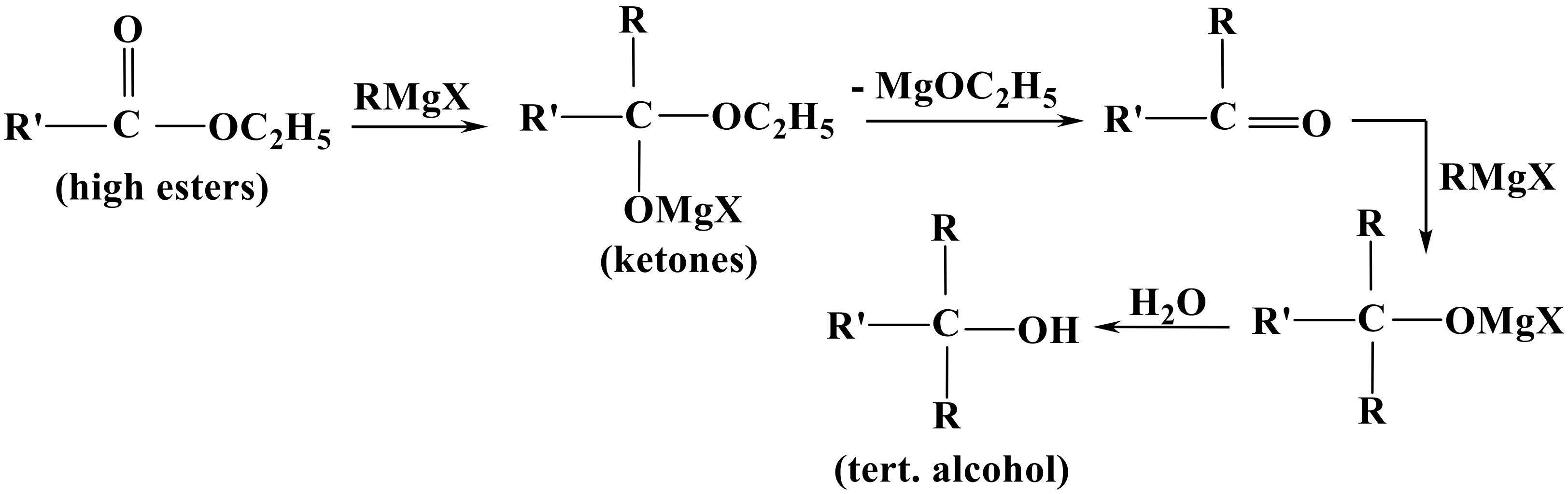


$$R'-\overset{R''}{C}=O + RMgX \longrightarrow R'-\underset{R}{\overset{R''}{C}}-OMgX \xrightarrow{H_2O} R'-\underset{R}{\overset{R''}{C}}-OH$$

# 4- From esters:-

## i) By addition of Grignard reagent:-





**ii) By reduction:-**

$$RCOOR' \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

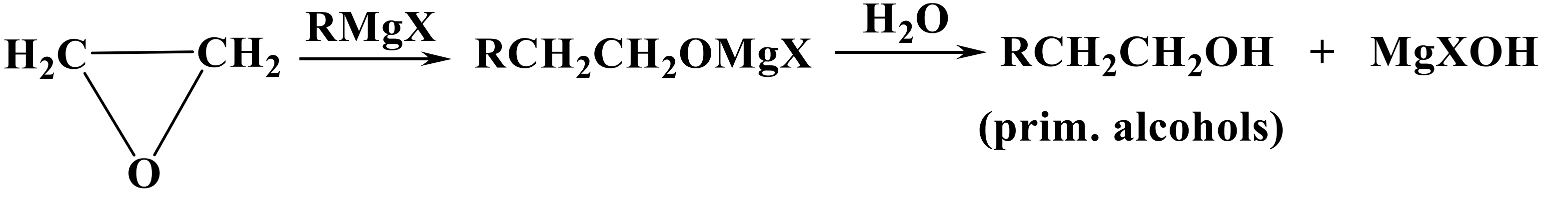
**iii) By hydrolysis:-**

$$RCOOR' + KOH \longrightarrow RCOOK + R'OH$$

## 5) From acids:- (by reduction with boranes)

$$RCOOH \xrightarrow{BH_3/2H_2O} RCH_2OH + B(OH)_3 + H_2$$

## 6) From ethylene oxide (epoxide):- by addition of Grignard reagents



$$H_2C\text{—}CH_2(\text{—O—}) \xrightarrow{RMgX} RCH_2CH_2OMgX \xrightarrow{H_2O} RCH_2CH_2OH + MgXOH$$

(prim. alcohols)

# 2- Reactions

## 1- Reaction with halogen acids:-

$$ROH \quad + \quad HX \longrightarrow R-X \quad + \quad H_2O$$

e.g. $$CH_3CH_2OH \quad + \quad HBr\ (conc.) \longrightarrow CH_3CH_2Br \quad + \quad H_2O$$

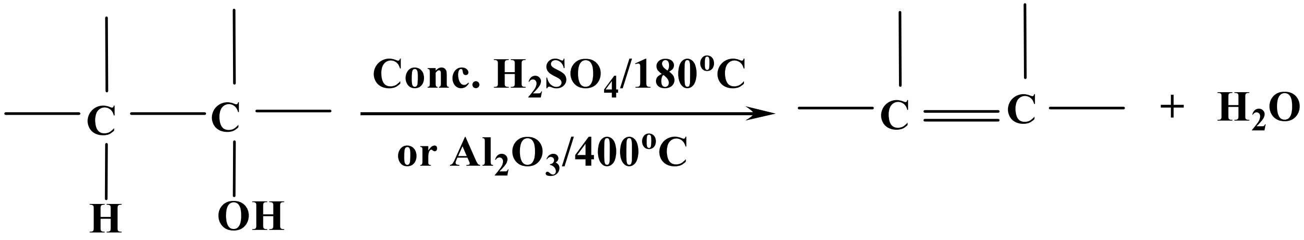
(ethanol) (ethyl bromide)

## 2- Reaction with thionyl chloride:-

$$ROH \quad + \quad SOCl_2 \longrightarrow RCl \quad + \quad SO_2 \quad + \quad HCl$$

## 3- Reaction with conc. Sulphoric acid (dehydration):-

### i) In the presence of conc. ($H_2SO_4/180^oC$)



$$-\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{OH}{\underset{|}{\overset{|}{C}}}- \xrightarrow[\text{or } Al_2O_3/400^oC]{\text{Conc. } H_2SO_4/180^oC} -\overset{|}{C}=\overset{|}{C}- \quad + \quad H_2O$$

e.g. $$CH_3CH_2\text{-}OH \xrightarrow[\text{or } Al_2O_3/400^oC]{\text{Conc. } H_2SO_4/180^oC} CH_2=CH_2 \quad + \quad H_2O$$

### ii) Dehydration with conc. $H_2SO_4$ acid at 140°C:-

$$2ROH \xrightarrow[\triangle]{Conc.\ H_2SO_4} ROR + H_2O$$

## 4- Esterification:-

$$ROH + R'COOH \overset{H^+}{\rightleftharpoons} R'COOR + H_2O$$

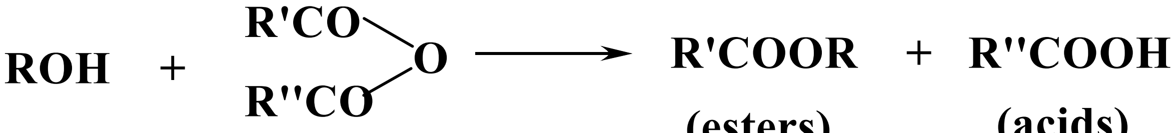
e.g. $$CH_3CH_2OH + CH_3COOH \xrightleftharpoons{conc.\ H_2SO_4} CH_3COOC_2H_5 + H_2O$$

(ethyl acetate)

## 5- Reaction with acid chlorides and anhydrides:-

$$ROH + R'COCl \longrightarrow R'COOR + HCl$$

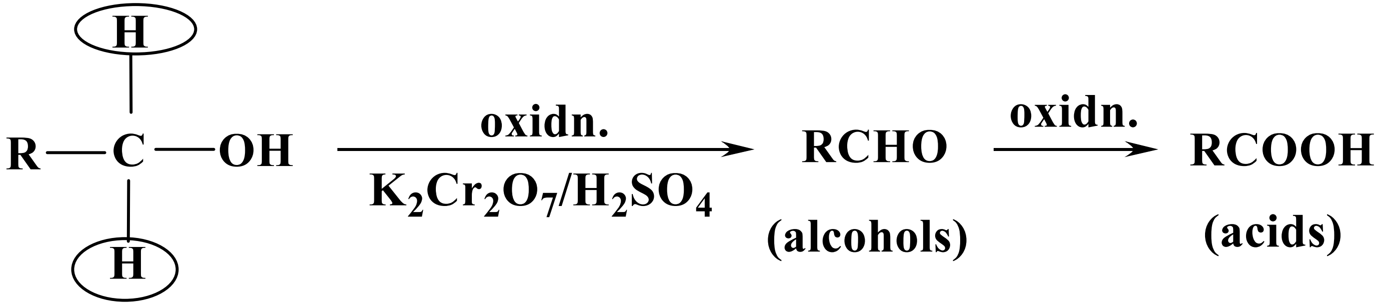
(acid chloride) (estrers)



$$ROH + \begin{matrix} R'CO \\ R''CO \end{matrix}\!\!>\!O \longrightarrow R'COOR + R''COOH$$

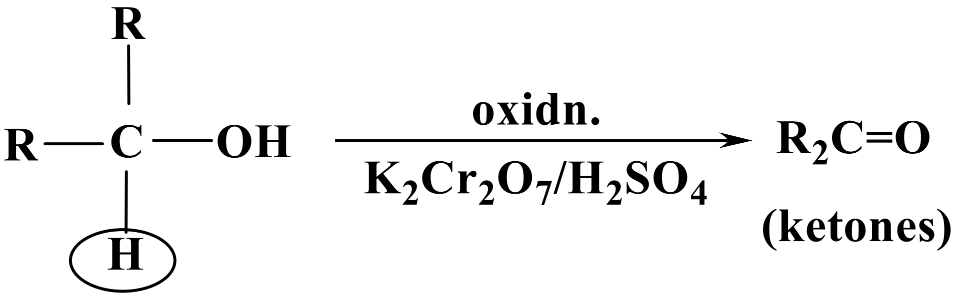
(anhydrides) (esters) (acids)

# 6- Oxidation:-



$$\mathrm{R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{oxidn.} \underset{(alcohols)}{RCHO} \xrightarrow{oxidn.} \underset{(acids)}{RCOOH}}$$

(prim. alcohols)

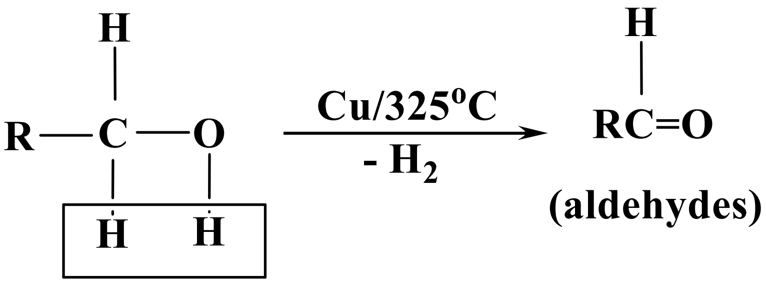


$$\mathrm{R-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{oxidn.} \underset{(ketones)}{R_2C{=}O}}$$

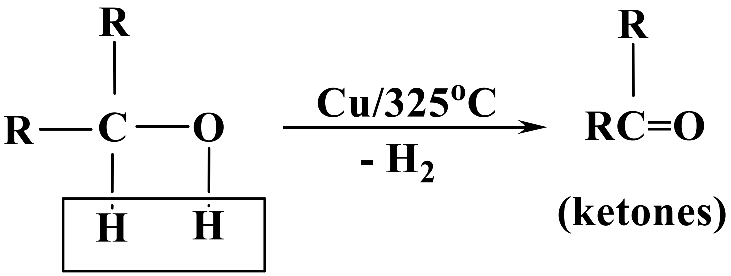
(sec. alcohols)

$$\text{Tert. alcohols} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{oxidn.} \text{No reaction}$$

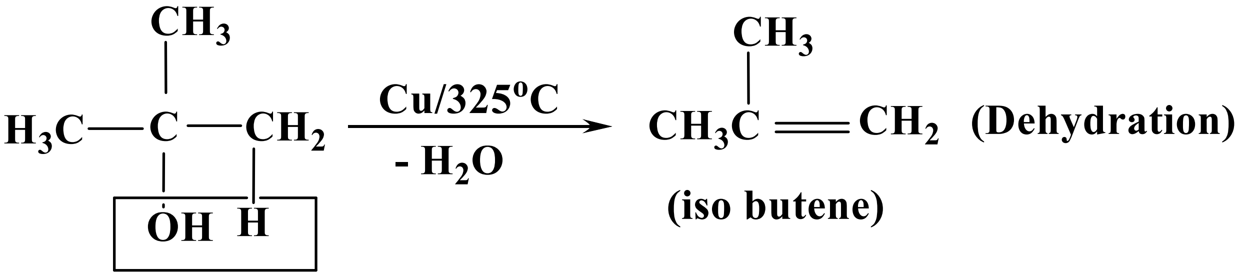
# 7- Dehydrogenation:-



(prim. alcohols)



(sec. alcohols)



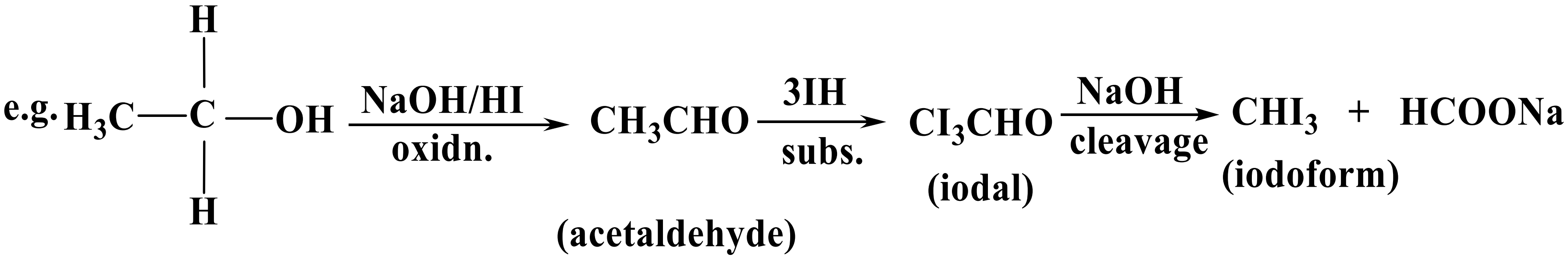
(Tert. alcohols) (tert. butanol)

# 8- Haloform test:-

$$R\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[\text{(oxidn.)}]{NaOH/HI} RCOCH_3 + NaI + H_2O$$

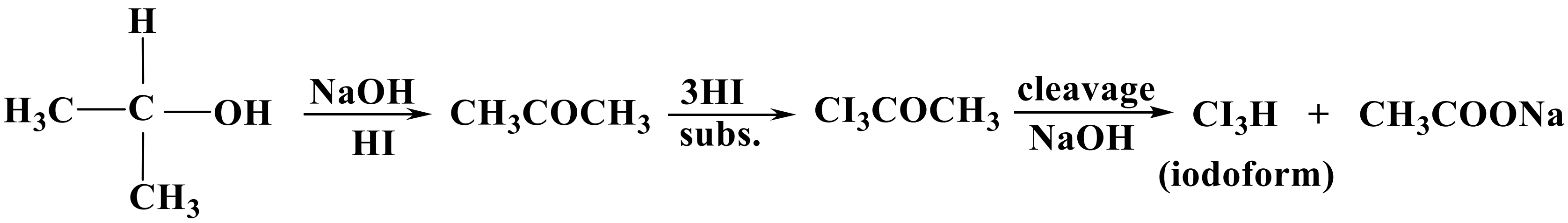
$$RCOCH_3 + 3IH \xrightarrow{\text{substitution}} RCOCI_3 + 3NaOH$$

$$RCOCI_3 + NaOH \xrightarrow{\text{cleavage}} RCOONa + HCI_3 \text{ (iodoform)}$$



$$\text{e.g. } H_3C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH \xrightarrow[\text{oxidn.}]{NaOH/HI} \underset{\text{(acetaldehyde)}}{CH_3CHO} \xrightarrow[\text{subs.}]{3IH} \underset{\text{(iodal)}}{CI_3CHO} \xrightarrow[\text{cleavage}]{NaOH} \underset{\text{(iodoform)}}{CHI_3} + HCOONa$$

**The requirements for iodoform reaction is the presence of alpha $CH_3$ and one hydrogen attached to carbinol (C-OH)**



$$H_3C-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[HI]{NaOH} CH_3COCH_3 \xrightarrow[subs.]{3HI} CI_3COCH_3 \xrightarrow[NaOH]{cleavage} \underset{(iodoform)}{CI_3H} + CH_3COONa$$

(isopropanol)

## 9- Reaction with ammonium:-

$$ROH + NH_3 \xrightarrow{pressure} \underset{(prim.\ amines)}{RNH_2} + H_2O$$

$$RNH_2 + ROH \xrightarrow{pressure} \underset{(sec.\ amines)}{R_2NH} + H_2O$$

$$(R)_2NH + ROH \xrightarrow{pressure} \underset{(tert.\ amines)}{R_3N} + H_2O$$

## 10- Reaction with phosphorus pentasulphide:-

$$5ROH + P_2S_5 \longrightarrow \underset{(thiol)}{5RSH} + P_2O_5$$

# 4- Ethers

# ROR

# Ethers

**Ethers are a class of organic compounds that contain an ether group - an oxygen atom connected to two alkyl or aryl groups. They have the general formula R–O–R′, where R and R′ represent the alkyl or aryl groups.**

**Ethers can again be classified into two varieties: if the alkyl groups are the same on both sides of the oxygen atom, then it is simple or symmetrical ether, whereas if they are different, the ethers are called mixed or unsymmetrical ethers. A typical example of the first group is the solvent and anaethetic diethyl ether, commonly referred to simply as "ether" ($CH_3$–$CH_2$–O–$CH_2$–$CH_3$).**

# 1- Synthesis

## 1- From alkyl halides:-

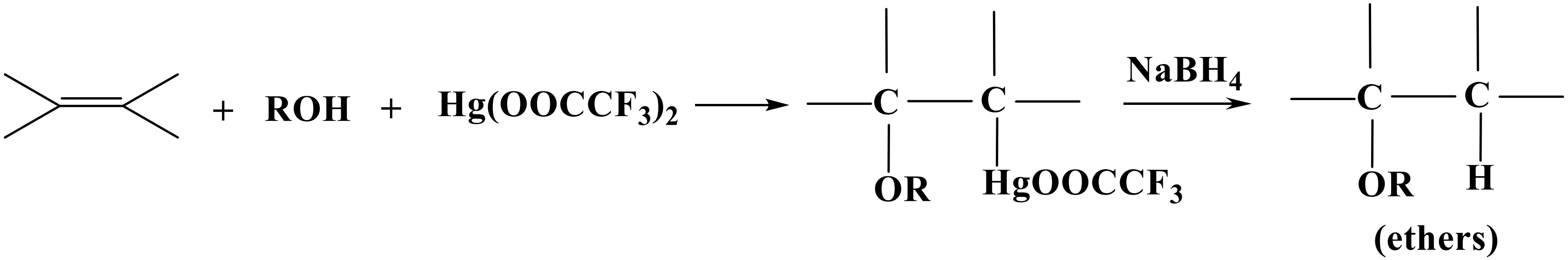
$$\boxed{RX + Z^{-} \longrightarrow RZ + X^{-}}$$

$$Na^{+}\overline{OR} \longrightarrow ROR \text{ (ethers)} + NaX$$

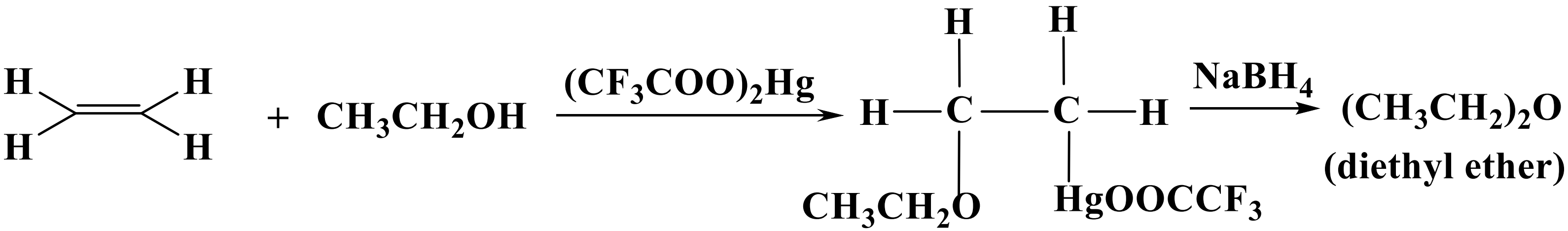
## 2- From alcohols:- via dehydration:-

$$2ROH \xrightarrow[\triangle]{\text{Conc. } H_2SO_4} ROR + H_2O$$

## 3- From olefines:- by alkoxy mercuration, demercuration



e.g.



# 2- Reactions

## 1- Cleavage by halogen acids:-

$$\text{ROR} + \text{HX} \xrightarrow[\text{high temp.}]{\text{conc.}} \text{RX} + \text{ROH}$$

and $$\text{ROH} + \text{HX} \xrightarrow[\text{high temp.}]{\text{conc.}} \text{RX} + H_2O$$

(or) $$\text{ROR} + 2\text{HX} \xrightarrow[\text{high temp.}]{\text{conc.}} 2\text{RX} + H_2O$$

XH usually (HI, HBr)

e.g. $$(CH_3CH_2)_2O + HI \xrightarrow{\text{high temp.}} CH_3CH_2I + CH_3CH_2OH$$

$$(CH_3CH_2)_2O + 2HI\ (\text{conc.}) \xrightarrow{\text{high temp.}} 2CH_3CH_2I + H_2O$$

# 2- Reaction with phosphorus pentasulphide:-

$$5ROR + P_2S_5 \xrightarrow{\triangle} 5RSR + P_2O_5$$

(dialkylthioether)

e.g. $5C_2H_5OC_2H_5 + P_2S_5 \xrightarrow{\triangle} 5C_2H_5SC_2H_5 + P_2O_5$

(diethylthioether)

# 5- Thioalcohols and thioethers
# RSH and RSR

# A- Thioalcohols

## (Thioles)

## RSH

# Thioalcohols

**A thiol or thiol derivative is any organosulfur compound with the form R−SH, where R represents an alkyl or other organic substituent. The –SH functional group itself is referred to as either a thiol group or a sulfhydryl group, or a sulfanyl group. Thiols are the sulfur analogue of alcohols (that is, sulfur takes the place of oxygen in the hydroxyl group of an alcohol). Thiols are sometimes referred to as mercaptans.**

# 1- Synthesis

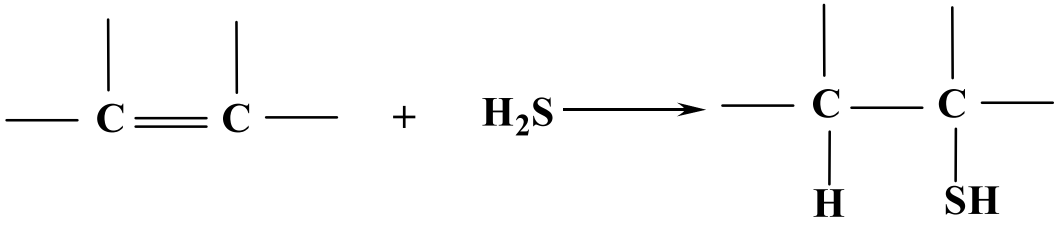
## 1- From alkyl halides:-

$$RX + K^{+}SH^{-} \longrightarrow RSH \text{ (thioalcohols)} + KX$$

## 2- From alcohols:-

$$5ROH + P_2S_5 \longrightarrow 5RSH + P_2O_5$$

## 3- From alkenes:-

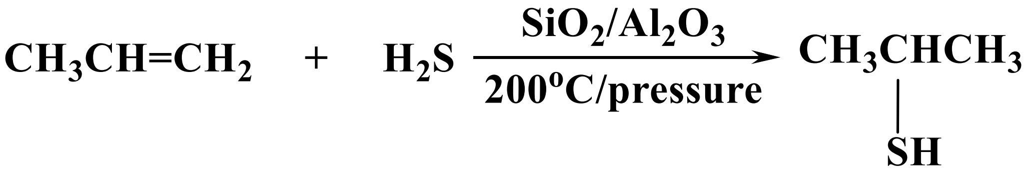


$$-\overset{|}{C}=\overset{|}{C}- \quad + \quad H_2S \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{SH}{\overset{|}{\underset{|}{C}}}-$$

e.g. $CH_2{=}CH_2 + H_2S \xrightarrow{\text{light}} CH_3CH_2SH$

$$CH_3CH{=}CH_2 + H_2S \xrightarrow{\text{light}} CH_3CH_2CH_2SH$$

(anti-Markovnikov addition)



$$CH_3CH{=}CH_2 + H_2S \xrightarrow[200^{o}C/\text{pressure}]{SiO_2/Al_2O_3} CH_3\underset{SH}{\underset{|}{C}}HCH_3$$

(Markovnikov addition)

# 2- Reactions

## 1- With sodium:-

$$\mathrm{2RSH + 2Na \longrightarrow 2RSNa + H_2\uparrow}$$

e.g. $\mathrm{2C_2H_5SH + 2Na \longrightarrow 2C_2H_5SNa}$

## 2- With acids:-

$$\mathrm{RCOOH + R'SH \xrightleftharpoons{H^+} \underset{\text{(thioester)}}{RCOSR'} + H_2O}$$

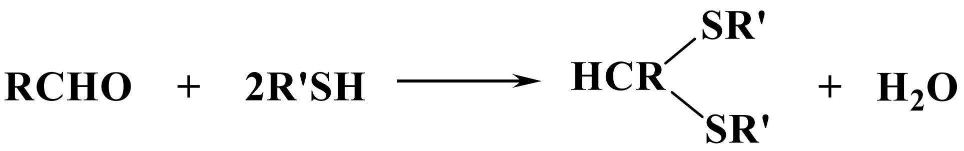
e.g. $\mathrm{CH_3COOH + C_2H_5SH \xrightleftharpoons{H^+} CH_3COSC_2H_5}$

## 3- Oxidation:-

$\mathrm{2RSH \xrightarrow{H_2O_2} RSSR}$ (dialkyl sulphide)

$\mathrm{RSH \xrightarrow{HNO_3} RSO_3H}$

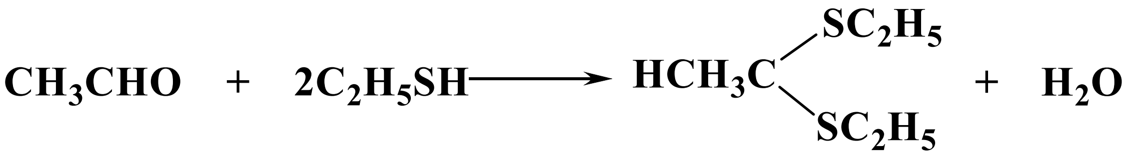
# 4- Reaction with aldehydes and ketones:-



$$RCHO + 2R'SH \longrightarrow HCR\genfrac{}{}{0pt}{}{SR'}{SR'} + H_2O$$

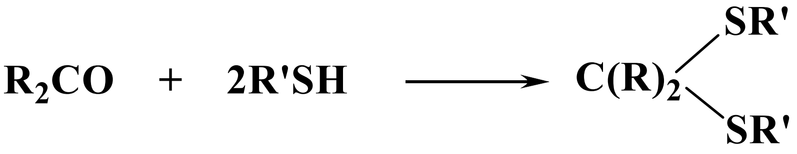
(thioacetal)

e.g.



$$CH_3CHO + 2C_2H_5SH \longrightarrow HCH_3C\genfrac{}{}{0pt}{}{SC_2H_5}{SC_2H_5} + H_2O$$

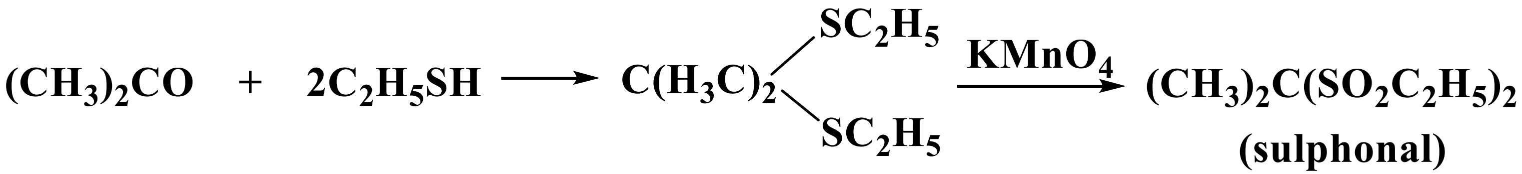
(thioacetal)



$$R_2CO + 2R'SH \longrightarrow C(R)_2\genfrac{}{}{0pt}{}{SR'}{SR'}$$

(thioketal)

e.g.



$$(CH_3)_2CO + 2C_2H_5SH \longrightarrow C(H_3C)_2\genfrac{}{}{0pt}{}{SC_2H_5}{SC_2H_5} \xrightarrow{KMnO_4} (CH_3)_2C(SO_2C_2H_5)_2$$

(sulphonal)

## 5- Reaction with lead acetate:-

$$2RSH + (CH_3COO)_2Pb \longrightarrow (RS)_2Pb\downarrow + 2CH_3COOH$$

**(lead mercaptide)**

## 6- Reaction with alumina/zinc sulphide:-

$$2RSH \xrightarrow[ZnS/300^{o}C]{Al_2O_3/} RSR + H_2S$$

$$\text{e.g.}\quad CH_3CH_2SH \xrightarrow[ZnS/300^{o}C]{Al_2O_3/} (CH_3CH_2)_2S + H_2S$$

## 7- Desulphurization:-

$$RSH \xrightarrow{H_2/Ni} RH + H_2S$$

# B- Thioethers

# (Alkyl sulphide)

# RSR

# Thioethers

## (Alkyl sulphides)

**An organic sulfide or thioether is a functional group in organosulfur chemistry with the connectivity C–S–C. Like many other sulfur-containing compounds, volatile sulfides have foul odors. A sulfide is similar to an ether except that it contains a sulfur atom in place of the oxygen. The grouping of oxygen and sulfur in the periodic table suggests that the chemical properties of ethers and sulfides are somewhat similar.**

# 1- Synthesis

## 1- From alkyl halides:-

**- Via heating with $K_2S$.**

$$RX + K^+SR^- \longrightarrow RSR \quad \text{(thioethers)} + KX$$

**- Via heating with sodium mercaptide.**

$$RX + R'SNa \longrightarrow RSR' + NaX$$

## 2- From ethers:-

**Via reaction with $P_2S_5$.**

$$5ROR + P_2S_5 \longrightarrow 5RSR + P_2O_5$$

# 3- From thioalcohols:-

- By passing thiol over $Al_2O_3/ZnS(300^oC)$

$$2RSH \xrightarrow[ZnS/300^oC]{Al_2O_3/} RSR \quad + \quad H_2S$$

$$\text{e.g.} \quad 2CH_3CH_2SH \xrightarrow[ZnS/300^oC]{Al_2O_3/} (CH_3CH_2)_2S \quad + \quad H_2S$$

# 4- From alkenes:-

$$RCH{=}CH_2 \quad + \quad R'SH \xrightarrow{peroxide} RCH_2\text{-}CH_2SR'$$

$$\text{e.g} \quad CH_3CH{=}CH_2 \quad + \quad C_2H_5SH \xrightarrow{peroxide} CH_3CH_2CH_2S\text{-}CH_2CH_3$$

(anti-Markovnikov addition)

# 2- Reactions

## 1- Desulphurization:-

$$\text{R-S-R'} + H_2 \xrightarrow{\text{Ni}} \text{RH} + \text{R'H} + \text{NiS}$$

e.g. $$(CH_3CH_2)_2S + H_2 \xrightarrow{\text{Ni}} 2CH_3CH_3 + \text{NiS}$$

## 2- Oxidation:-

$$(C_2H_5)_2S \xrightarrow{H_2O_2} (C_2H_5)_2S{=}O \xrightarrow{H_2O} (C_2H_5)_2SO_2$$

(diethylsulphoxide) (diethylsulphone)

## 3- Reaction with alkyl halides:-

$$R_2S + RX \longrightarrow R_3S^+X^-$$

(sulphonium salt)

e.g. $$(C_2H_5)_2S + C_2H_5I \longrightarrow [(C_2H_5)_3S]^+I^- \xrightarrow{H_2O} [(C_2H_5)_3S]^+OH^-$$

triethyl sulphonium hydroxide

# 6- Aldehydes and ketones

# RCHO and RCOR

# Aldehydes and ketones

**Aliphatic aldehydes and ketones are essential building blocks for the synthesis of more complex organic compounds.**

**e.g.**

**Formaldehyde HCHO**

**Acetaldehyde $CH_3CHO$**

**Acetone $CH_3COCH_3$**

# A- Aldehydes

# RCHO

# A- Aldehydes

**Chemically, an aldehyde is a compound containing a functional group with the structure -CHO, consisting of a carbonyl center (a carbon double-bonded to oxygen) with the carbon atom also bonded to hydrogen and to any generic alkyl or side chain R group. The functional group itself (i.e. without the "R" side chain) is known as an aldehyde or formyl group. Aldehydes,**

**which are generally created by removing hydrogen from an alcohol, are common in organic chemistry; the most well-known is formaldehyde. As they are frequently strongly scented, many fragrances are or contain aldehydes.**

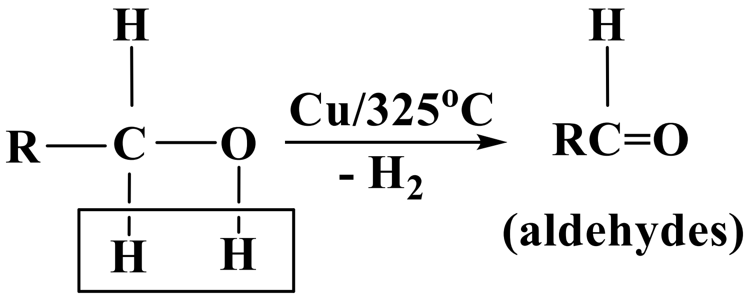
# 1- Synthesis

## 1- Via catalytic hydration of alkynes:-

$$H-C\equiv C-H \xrightarrow[60\ ^oC]{HgSO_4/dil.\ H_2SO_4} CH_3CHO$$

(Acetaldehyde)

## 2- Via dehydrogenation of alcohols:-



$$R-\underset{H}{\overset{H}{C}}-\underset{H}{O} \xrightarrow[-\ H_2]{Cu/325^oC} R\overset{H}{C}=O$$

(prim. alcohols)

(aldehydes)

# 3- From carboxylic acids:-

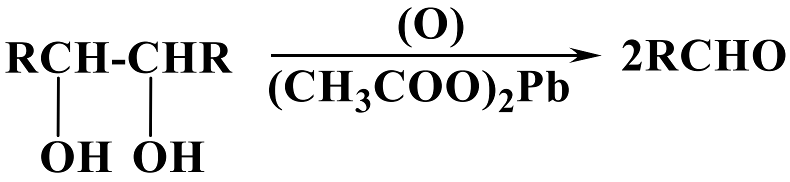
$$3RCOOH + 3HCOOH \xrightarrow[MnO/300^oC]{vap.\ over} RCHO + \underbrace{(R_2C{=}O + HCHO)}_{by\ products} + 3CO_2 + 3H_2O$$

# 4- From calcium salt of carboxylic acids:-

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{\triangle} 2RCHO + 2CaCO_3$$

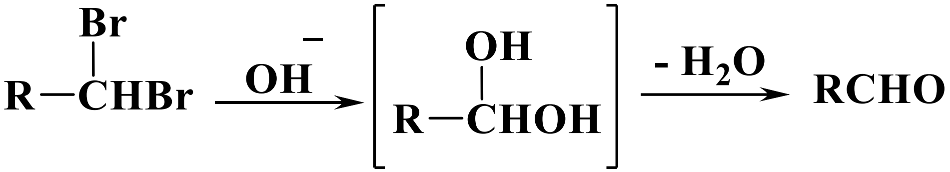
e.g. $(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow{\triangle} 2CH_3CHO + 2CaCO_3$

# 5- From glycoles:-



$$\underset{OH}{RCH}-\underset{OH}{CHR} \xrightarrow[(CH_3COO)_2Pb]{(O)} 2RCHO$$

# 6- From Gem-dihalides:- (hydrolysis)



$$\mathrm{R-\overset{Br}{\overset{|}{C}}HBr} \xrightarrow{\mathrm{OH^-}} \left[\mathrm{R-\overset{OH}{\overset{|}{C}}HOH}\right] \xrightarrow{-\mathrm{H_2O}} \mathrm{RCHO}$$

# 7- From acid derivatives:-

## a- From esters:-

$$\mathrm{HCOOC_2H_5} + \mathrm{RMgX} \longrightarrow \mathrm{RCHO} + \mathrm{MgOC_2H_5X}$$

## b- From acyl chlorides:-

$$\mathrm{RCOCl} \xrightarrow{\mathrm{H_2/Pd}} \mathrm{RCHO} + \mathrm{HCl}$$

e.g. $\mathrm{CH_3COCl} \xrightarrow{\mathrm{H_2/Pd}} \mathrm{CH_3CHO} + \mathrm{HCl}$

# 2- Reactions

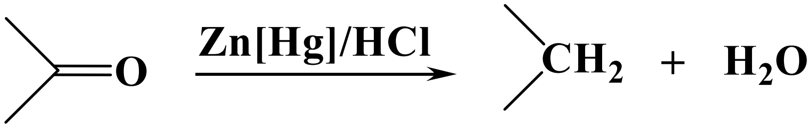
## I- Simple addition reactions:-

## 1- Addition of hydrogen:-

### a- Reduction to alcohols:- via $LiAlH_4$

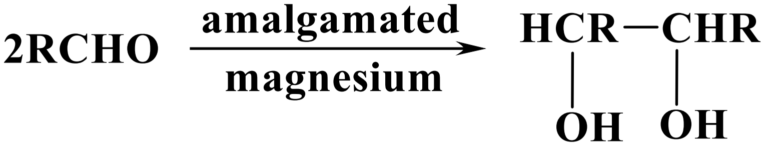
$$4RCHO + LiAlH_4 \longrightarrow (RCH_2O)_4LiAl \xrightarrow{H_2O} \underset{\text{(prim. alcohol)}}{4RCH_2OH} + LiOH + Al(OH)_3$$

### b- Reduction to alkanes:- via Clemensen reduction



$$\text{e.g} \quad CH_3CHO \xrightarrow{Zn[Hg]/HCl} H_3C{-}CH_3 + H_2O$$

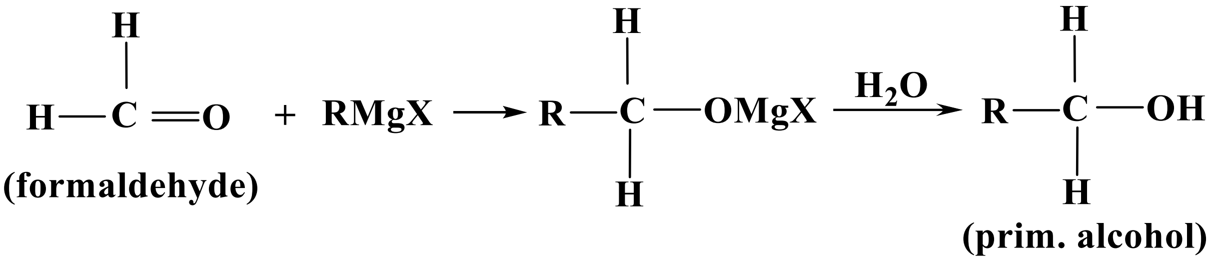
### c- Reduction to glycols:-



$$2RCHO \xrightarrow[\text{magnesium}]{\text{amalgamated}} \underset{OH}{HCR}{-}\underset{OH}{CHR}$$

Glycols

## 2- Addition of Grignard reagents:-

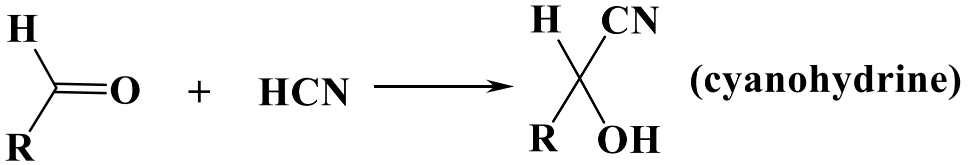


$$H-\overset{H}{\underset{}{C}}=O + RMgX \longrightarrow R-\overset{H}{\underset{H}{C}}-OMgX \xrightarrow{H_2O} R-\overset{H}{\underset{H}{C}}-OH$$

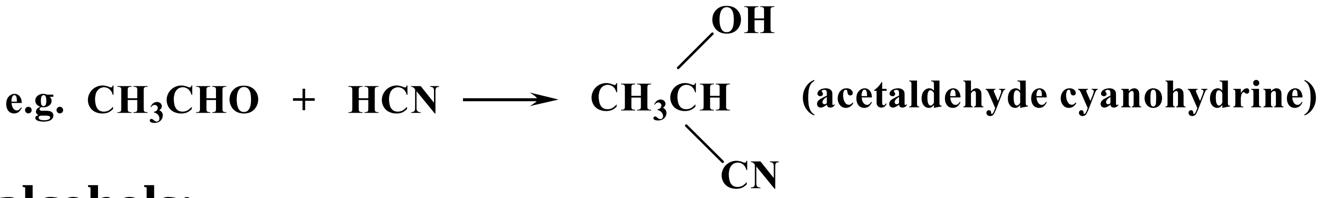
(formaldehyde)

(prim. alcohol)

## 3- Addition of hydrogen cyanide:-

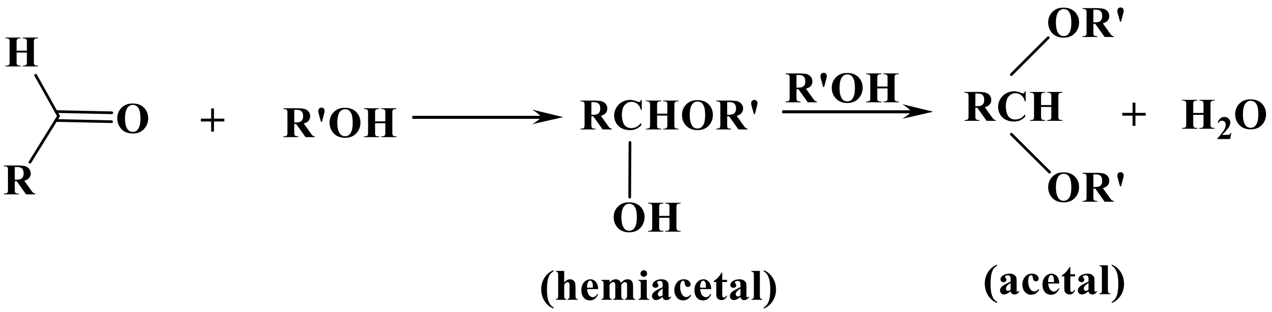


(cyanohydrine)



e.g. $CH_3CHO + HCN \longrightarrow CH_3CH(OH)(CN)$ (acetaldehyde cyanohydrine)

## 4- Addition of alcohols:-

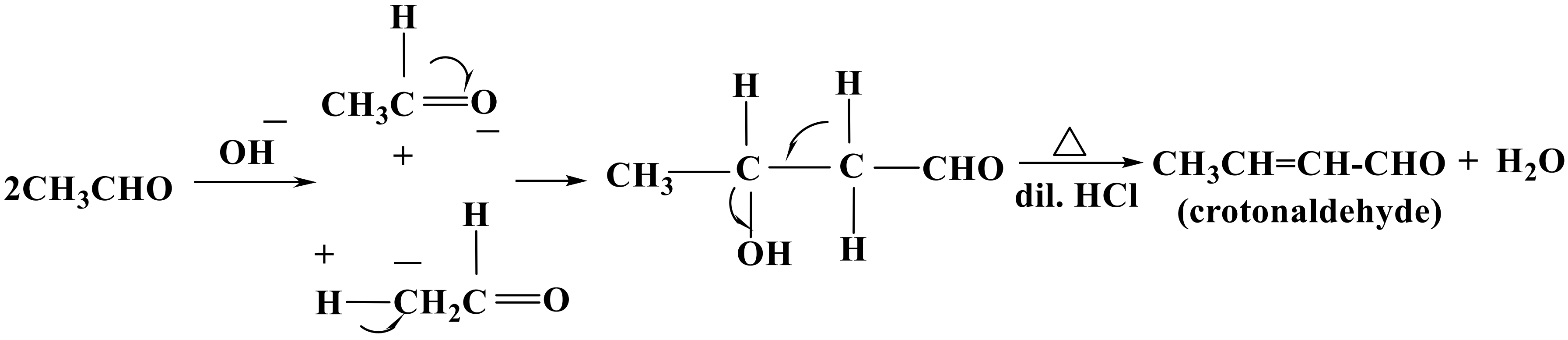


$$RCHO + R'OH \longrightarrow \underset{OH}{RCHOR'} \xrightarrow{R'OH} RCH(OR')_2 + H_2O$$

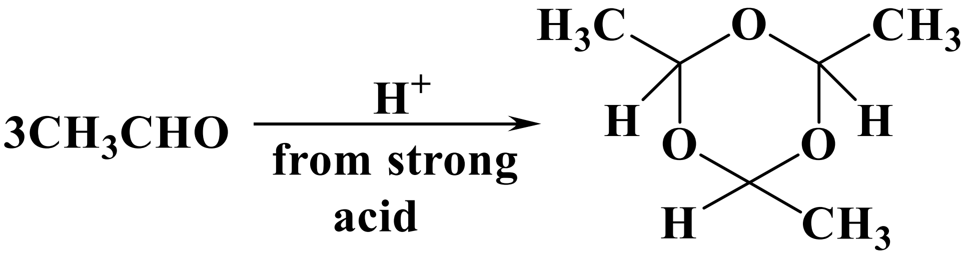
(hemiacetal)

(acetal)

## 5- Aldol’s reaction:-

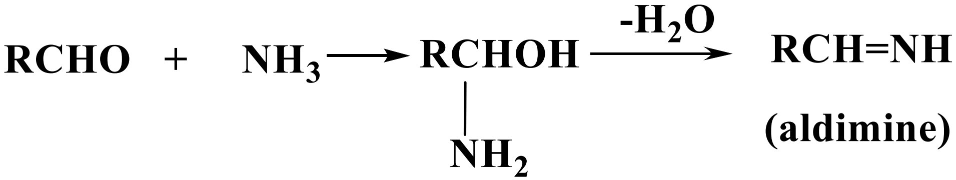


## 6- Cyclic trimerization:-



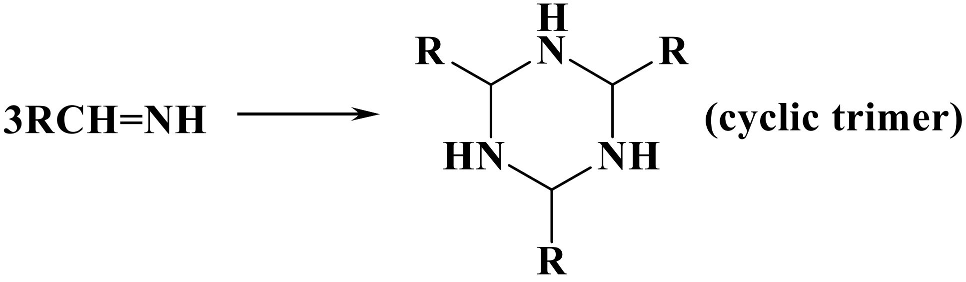
# II- Addition followed by dehydration (condensation reactions):-

## a- With ammonia:-



$$RCHO + NH_3 \longrightarrow \underset{\displaystyle NH_2}{\underset{|}{RCHOH}} \xrightarrow{-H_2O} RCH{=}NH$$

(aldimine)

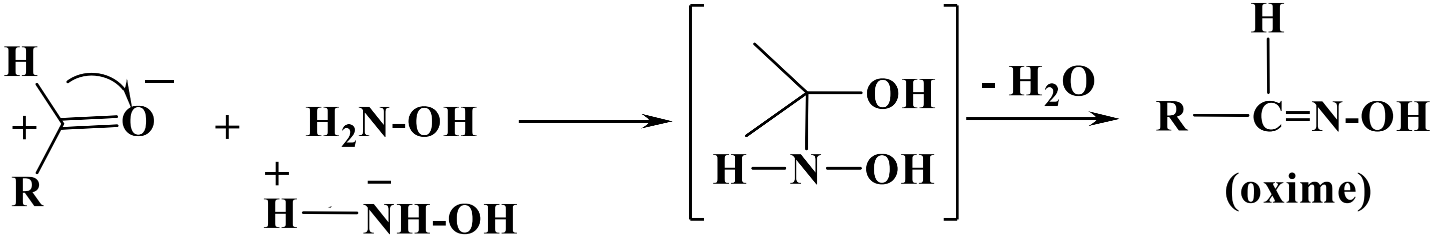


$$3RCH{=}NH \longrightarrow$$

(cyclic trimer)

## b- With ammonia derivatives:-

## i- Hydroxylamine ($H_2N\text{-}OH$)

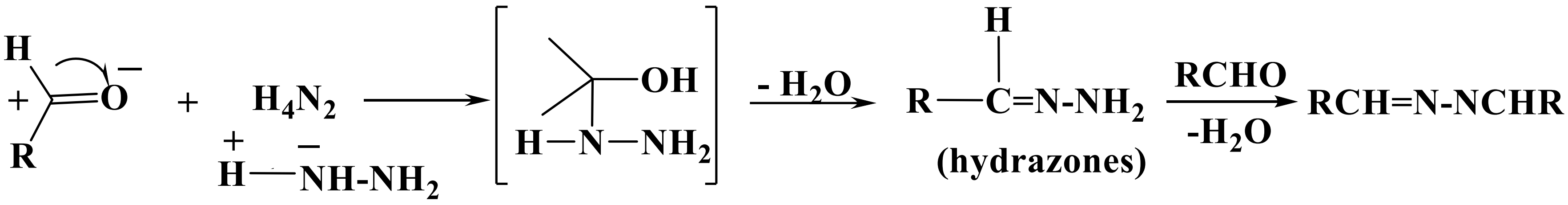


(oxime)

e.g. $CH_3CHO + H_2NOH \longrightarrow CH_3CH{=}NOH + H_2O$

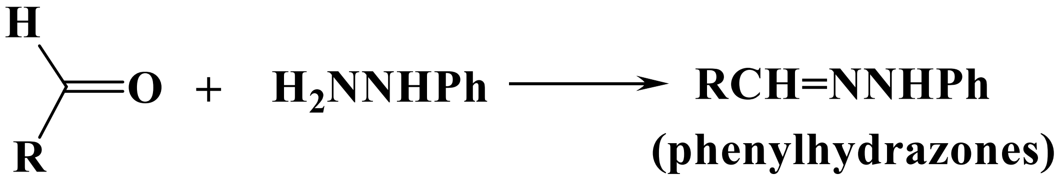
(acetaldoxime)

## ii- Hydrazine hydrate:- ($H_2N-NH_2$)

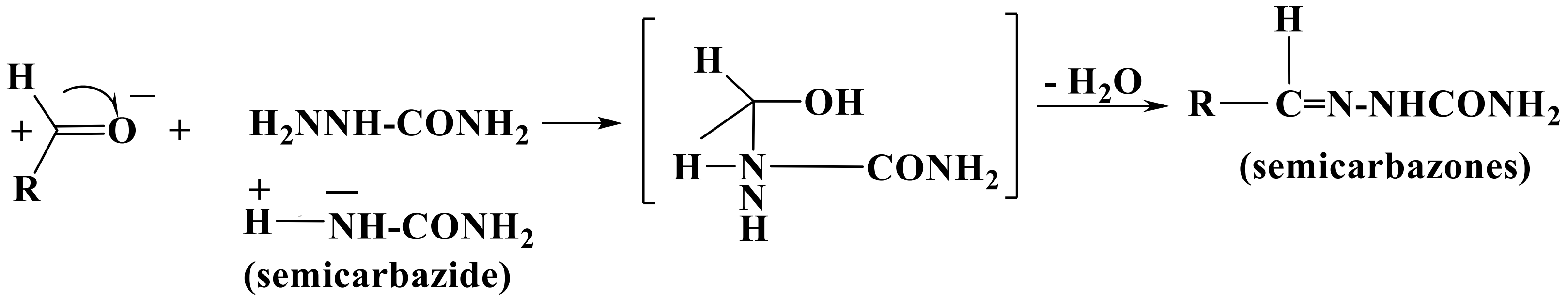


e.g. $CH_3CHO + H_2NNH_2 \longrightarrow CH_3CH{=}NNH_2 + H_2O \xrightarrow{CH_3CHO} CH_3CH{=}N\text{-}NCHCH_3$

## iii- Phenylhydrazine:-



### iv- Semicarbazide:-



## III- Oxidation:-

$$RCHO \xrightarrow{K2Cr_2O_7/\text{ conc } H_2SO_4} RCOOH$$

## IV- Intramolecular oxidation and reduction (Cannizzaro's reaction):-

$$2RCHO + NaOH \longrightarrow RCOONa + RCH_2OH$$

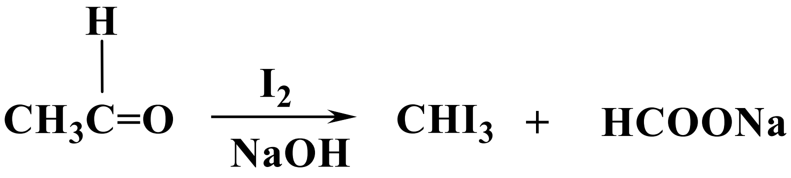
e.g. $2HCHO + NaOH \longrightarrow HCOONa + CH_3OH$

# Tests for aldehydes

## 1- Schiff's reagent:-

**Gives magenta red colour.**

## 2- Haloform test (Iodoform test ):-



$$CH_3\overset{H}{\overset{|}{C}}=O \xrightarrow[NaOH]{I_2} CHI_3 + HCOONa$$

**(yellow crystals)**

## 3- Tollen's colour:-

**Mild oxidizing agent oxidizes aldehydes not ketones.**

$$RCHO + 2[Ag(NH_3)_2]OH \longrightarrow RCOONH_4 + 2Ag\downarrow + H_2O + 2NH_3$$

**(ammonical silver hydroxide)** **(silver mirror)**

# B- Ketones

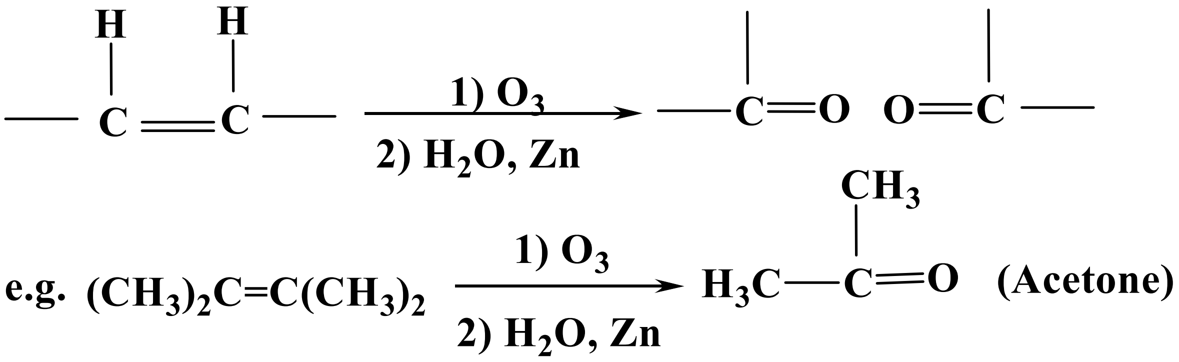
# B- Ketones

In chemistry, a ketone is a functional group with the structure $R_2C=O$, where R can be a variety of carbon-containing substituents. Ketones contain a cabonyl group (a carbon-oxygen double bond). The simplest ketone is acetone (R= R'= methyl), with the formula $CH_3C(O)CH_3$. Many ketones are of great importance in biology and in industry.

Examples include many sugars (ketones), many steroids (e.g., testosterone), and the solvent acetone.

# Synthesis

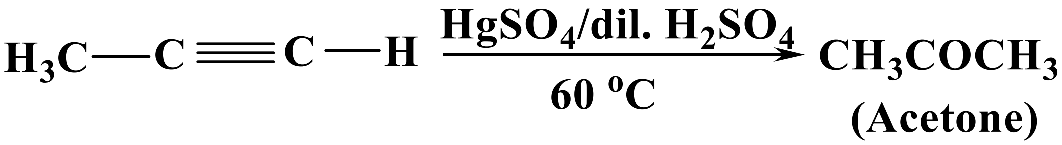
## 1- From alkenes:- (via ozonolysis)



$$-CH=CH- \xrightarrow[\text{2) } H_2O,\ Zn]{\text{1) } O_3} -CH=O \quad O=CH-$$

e.g. $$(CH_3)_2C=C(CH_3)_2 \xrightarrow[\text{2) } H_2O,\ Zn]{\text{1) } O_3} H_3C-C(CH_3)=O$$ (Acetone)

## 2- From alkynes:- (via catalytic hydration)

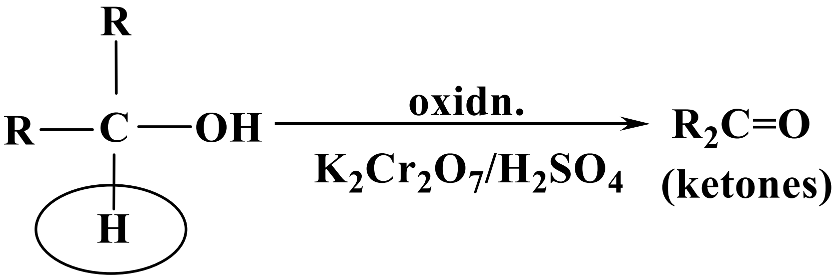


$$H_3C-C\equiv C-H \xrightarrow[60\ ^oC]{HgSO_4/\text{dil. } H_2SO_4} CH_3COCH_3$$

(Acetone)

# 3- From alcohols:-

## a- Via oxidation.

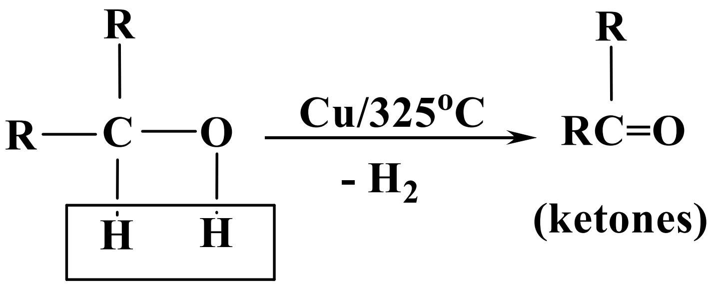


$$R-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{oxidn.}} R_2C=O$$

(sec. alcohols)

(ketones)

## b- Via dehydrogenation.



$$R-\overset{\displaystyle R}{\underset{\displaystyle H}{C}}-\underset{\displaystyle H}{O} \xrightarrow[-\,H_2]{Cu/325^oC} \overset{\displaystyle R}{RC}=O$$

(ketones)

(sec. alcohols)

# 4- From carboxylic acids:-

$$2RCOOH \xrightarrow[\text{MnO/300}^{o}\text{C}]{\text{vap. over}} R_2CO + CO_2 + H_2O$$

$$\text{e.g.} \quad 2CH_3COOH \longrightarrow (CH_3)_2CO + CO_2 + H_2O$$

$$RCOOH + R'COOH \xrightarrow[\text{MnO/300}^{o}\text{C}]{\text{vap. over}} RCOR' + CO_2 + H_2O$$

(by products $R_2CO$, $R'_2CO$)

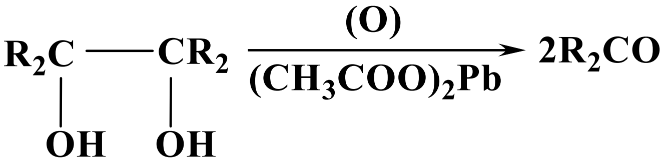
# 5- From calcium salts of carboxylic acids:-

$$(RCOO)_2Ca \xrightarrow{\triangle} R_2CO + CaCO_3$$

(ketones)

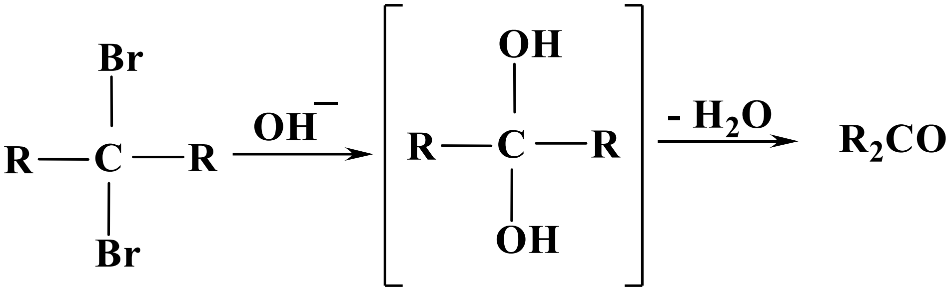
$$\text{e.g.} \quad (CH_3COO)_2Ca \xrightarrow{\triangle} (CH_3)_2CO + CaCO_3$$

# 6- From glycols:-



$$\underset{\text{OH}}{R_2C}-\underset{\text{OH}}{CR_2}\xrightarrow[(CH_3COO)_2Pb]{(O)}2R_2CO$$

# 7- From gem-dihalides:-



$$R-\overset{Br}{\underset{Br}{C}}-R\xrightarrow{OH^{-}}\left[R-\overset{OH}{\underset{OH}{C}}-R\right]\xrightarrow{-\,H_2O}R_2CO$$

# 8- From acyl chlorides:-

## a- Via Grignard reagents:-

$$RCOCl + R'MgX \xrightarrow[\text{temp.}]{\text{low}} RCOR' + MgXCl$$

e.g. $CH_3COCl + CH_3MgX \xrightarrow[\text{temp.}]{\text{low}} (CH_3)_2CO + MgXCl$

*** If the reaction was carried out at room temperature *t*-alcohols were obtained.**

**b- Via addition of organocadmium compounds.**

$$2RCOCl \quad + \quad R_2Cd \longrightarrow RCOR \quad + \quad CdCl$$

$$2RCOCl \quad + \quad R'_2Cd \longrightarrow 2RCOR' \quad + \quad CdCl_2$$

$$\text{e.g.} \quad 2CH_3COCl \quad + \quad (CH_3CH_2)_2Cd \longrightarrow \underset{\text{(ethyl methyl ketone)}}{2CH_3COCH_2CH_3} \quad + \quad CdCl_2$$

# Reactions

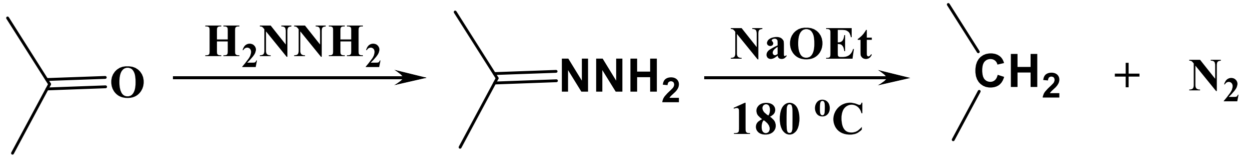
## I- Simple addition reactions:-

### a- Addition of hydrogen (reduction): (formation of alcohols)

$$4R_2CO + LiAlH_2 \longrightarrow (R_2CHO)_4LiAl \xrightarrow{H_2O} 4R_2CHOH + LiOH + Al(OH)_3$$

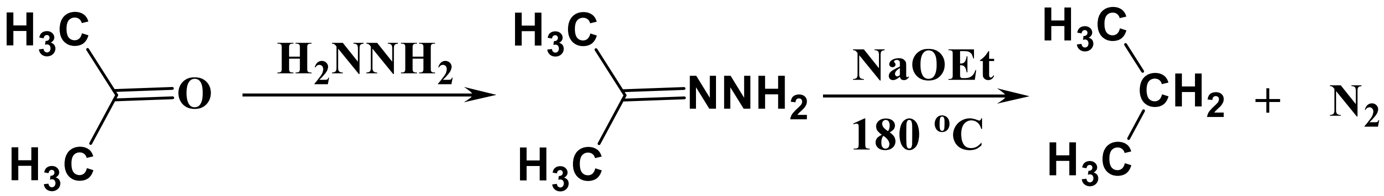
(sec. alcohol)

### b- Reduction to alkanes: (via Wolff-Kishner reduction)



(alkane)

e.g.



(propane)

# II- Addition followed by dehydration (condensation reaction):-

## a- Addition of ammonia derivatives:-

### i- With hydroxyl amine.

$$(CH_3)_2CO + H_2NOH \longrightarrow (CH_3)_2C{=}NOH \quad \text{(acetoxime)}$$

### b- With hydrazine.

$$(CH_3)_2CO + H_2NNH_2 \longrightarrow (CH_3)_2C{=}NNH_2 \xrightarrow{(CH_3)_2CO} (CH_3)_2C{=}NNC{=}(CH_3)_2$$

(hydrazone) (azine)

### c- With phenylhydrazine.

$$(CH_3)_2CO + PhNHNH_2 \longrightarrow (CH_3)_2C{=}NNHPh$$

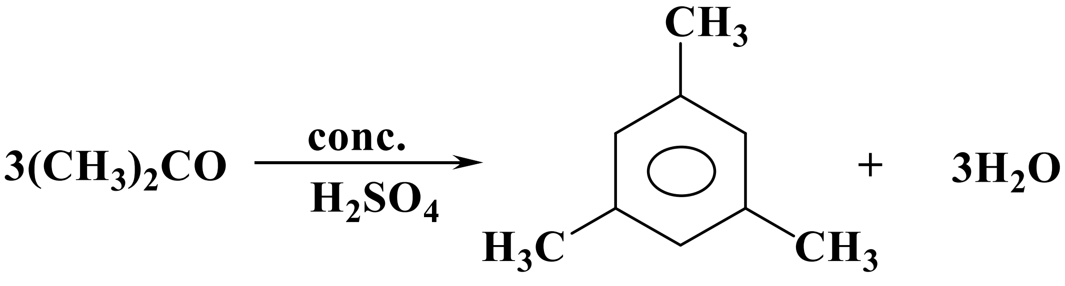
### d- With semicarbazide.

$$(CH_3)_2CO + NH_2NHCONH_2 \longrightarrow (CH_3)_2C{=}NNHCONH_2$$

(semicarbazone)

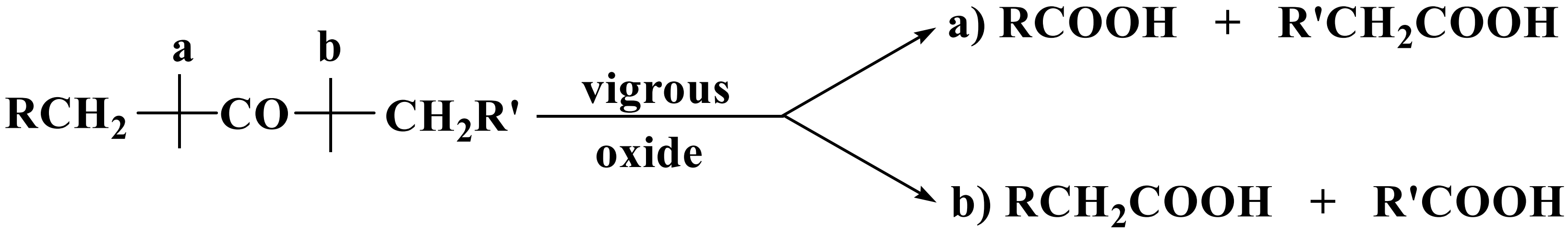
### c- With active methylene compounds.

$$3(CH_3)CO \xrightarrow[ZnCl_2]{\text{dry HCl}} (CH_3)_2{=}CHCOCH{=}C(CH_3)_2$$



(mesitylene)

## III- Oxidation:- (by using strong oxidizing reagent)



# ***Notes

**1- Schiff’s reagents is negative with Ketones.**

**2- Haloform test:- (Iodoform test)**

$$CH_3COCH_3 \xrightarrow[NaOH]{I_2} CI_3H \quad + \quad CH_3COONa$$

**3- Tollent’s reagent is negative with ketones.**

**Tollens’ test, also known as silver-mirror test, is a qualitative laboratory test used to distinguish between an aldehyde and a ketone. It exploits the fact that aldehydes are readily oxidized (see oxidation), whereas ketones are not.**

# 7- Carboxylic acids and their derivatives

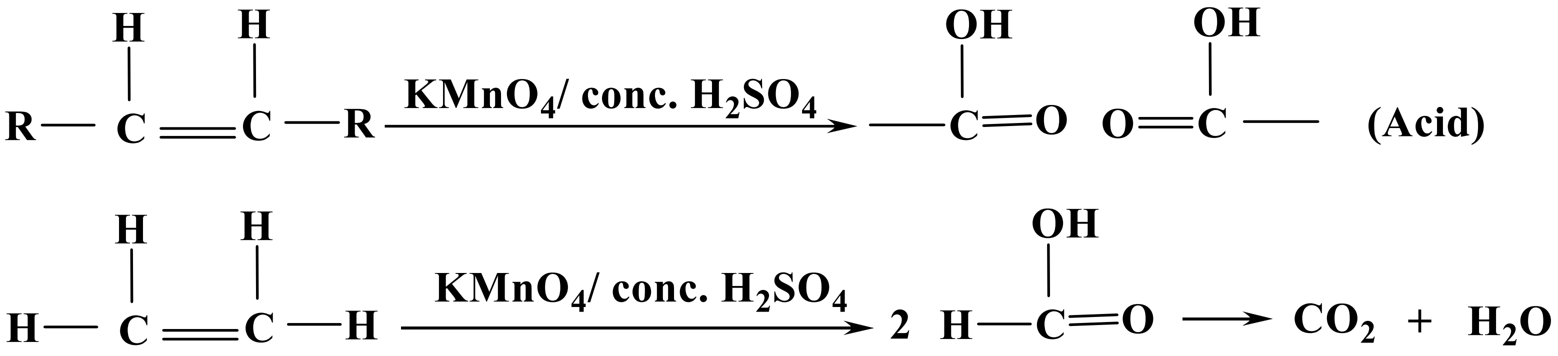
# A- Carboxylic acids

# A-Carboxylic acids

**A carboxylic acid is an organic acid that contains a carboxyl group (C(=O)OH) attached to a R-group. The general formula of a carboxylic acid is R−COOH or R−$CO_2$H, with R referring to the alkyl, alkenyl, aryl, or other group. Carboxylic acids occur widely. Important examples include the amino acids and fatty acids. Deprotonation of a carboxylic acid gives a carboxylate anion $COO^-$.**

# 1- Synthesis

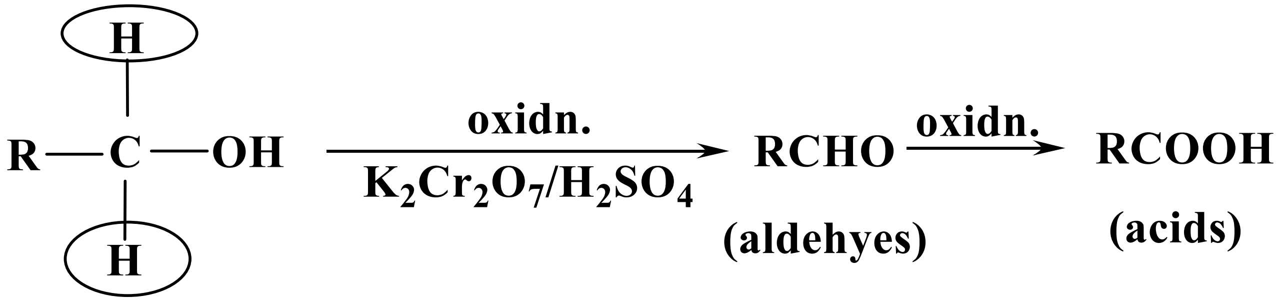
## 1- From alkanes:- (via oxidation)



$$R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-R \xrightarrow{KMnO_4/\text{ conc. } H_2SO_4} -\overset{OH}{\overset{|}{C}}=O \quad O=\overset{OH}{\overset{|}{C}}- \quad \text{(Acid)}$$

$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H \xrightarrow{KMnO_4/\text{ conc. } H_2SO_4} 2\ H-\overset{OH}{\overset{|}{C}}=O \longrightarrow CO_2 + H_2O$$

## 2- From primary alcohols:- (via oxidation)



$$R-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-OH \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{oxidn.}} RCHO \xrightarrow{\text{oxidn.}} RCOOH$$

(prim. alcohols) (aldehyes) (acids)

## 3- From aldehydes :- (Via oxidation)

$$RCHO \xrightarrow{K_2Cr_2O_7/\text{ conc } H_2SO_4} RCOOH$$

## 4- Hydrolysis of acid derivatives:-

### a- From acylchlorides:- via hydrolysis

$$RCOOCOR + H_2O \xrightarrow{\triangle} 2RCOOH$$

### b- From anhydrides:-

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

e.g. $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

(acetyl chloride)

**c- From amides:-**

**i- Via acid-or base catalyzed hydrolysis.**

$$RCONH_2 \xrightarrow[H_2O]{H^+} RCOOH + NH_4^+$$

$$RCONH_2 \xrightarrow{OH^-} RCOO^- + NH_3\uparrow$$

**ii- Action of nitrous acid.**

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

## 5- From Grignard reagents:-

$$RMgX + CO_2 \longrightarrow RCOOMgX \xrightarrow{H^+} RCOOH$$

$$\text{e.g. } CH_3MgX + CO_2 \longrightarrow CH_3COOMgX \xrightarrow{H^+} CH_3COOH$$

## 6- From nitriles: via boiling with acids or alkalies (hydrolysis)

$$RC\equiv N \quad + \quad 2H_2O \xrightarrow{H^+} RCOOH \quad + \quad NH_4^+$$

$$CH_3C\equiv N \quad + \quad 2H_2O \xrightarrow{H^+} CH_3COOH \quad + \quad NH_4^+$$

# 2- Reactions

## 1- Salt formation:-

**Acids react with metals, metal oxides, hydroxides, carbonates to form salts of carboxylic acids.**

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2\uparrow$$

$$2CH_3COOH + CuO \longrightarrow (CH_3COO)_2Cu + H_2O$$

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

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

## 2- Replacement of hydroxyl group by halogen: [acyl halides formation]:

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

e.g. $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

## 3- Esterification:-

$$CH_3CO\boxed{OH} + \boxed{H}OCH_3 \longrightarrow CH_3COOCH_3 + H_2O$$

## 4- Reduction:-

### a- To alcohols.

$$RCOOH \xrightarrow{BH_3/2H_2O} RCH_2OH + B(OH)_3 + H_2$$

### b- To alkanes.

$$RCOOH \xrightarrow[200^oC]{HI/P} RCH_3$$

e.g $CH_3COOH \xrightarrow[200^oC]{HI/P} CH_3\text{-}CH_3$

# 5- Pyrolysis:-

$$3RCOOH + 3HCOOH \xrightarrow[\text{MnO/300}^{o}\text{C}]{\text{vap. over}} RCHO + \underset{\text{by products}}{(R_2C{=}O + HCHO)} + 3CO_2 + 3H_2O$$

# 6- Halogenation:-

$$CH_3COOH \xrightarrow{Cl_2/P} \underset{\text{(monochloroacetic acid)}}{ClCH_2COOH} \xrightarrow{Cl_2/P} \underset{\text{(dichloroacetic)}}{Cl_2CHCOOH} \xrightarrow{Cl_2/P} \underset{\text{(trichloroacetic acid)}}{Cl_3CCOOH}$$

# 7- Oxidation:- (only formic acid)

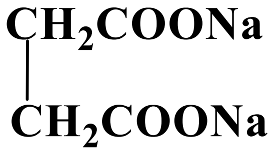
$$HCOOH \xrightarrow{\text{oxidn.}} CO_2 + H_2O$$

# Reactions on carboxylic acid salts

## 1- Sodium salts:-

$$\mathrm{RCOONa} \xrightarrow[\text{heat}]{\text{soda lime}} \mathrm{RH} + \mathrm{Na_2CO_3}$$

e.g $$\mathrm{CH_3COONa} \xrightarrow[\text{heat}]{\text{soda lime}} \mathrm{CH_4} + \mathrm{Na_2CO_3}$$



$$\begin{array}{l}\mathrm{CH_2COONa}\\ |\\ \mathrm{CH_2COONa}\end{array} \xrightarrow[\text{heat}]{\text{soda lime}} \mathrm{CH_3\text{-}CH_3}$$

sodium succinate

## 2- Potassium salts:- (Kolbe's synthesis)

$$\mathrm{2RCOOK} + \mathrm{2H_2O} \xrightarrow{\text{electrolysis}} \mathrm{R\text{-}R} + \mathrm{2CO_2} + \mathrm{H_2} + \mathrm{2KOH}$$

e.g. $$\mathrm{2CH_3COOK} + \mathrm{2H_2O} \longrightarrow \mathrm{CH_3\text{-}CH_3} + \mathrm{2CO_2} + \mathrm{H_2} + \mathrm{2KOH}$$

## 3- Silver salts:-

$$\mathrm{RX} + \mathrm{R'COO^{-}\,Ag^{+}} \longrightarrow \mathrm{R'COOR}\ \ \text{(esters)} + \mathrm{AgX}$$

## 4- Heating of calcium salts:-

$$\mathrm{(RCOO)_2Ca} + \mathrm{(HCOO)_2Ca} \xrightarrow{\triangle} \mathrm{2RCHO} + \mathrm{2CaCO_3}$$

e.g. $\mathrm{(CH_3COO)_2Ca} + \mathrm{(HCOO)_2Ca} \xrightarrow{\triangle} \mathrm{2CH_3CHO} + \mathrm{2CaCO_3}$

## 5- Heating of ammonium salts:-

$$\mathrm{RCOONH_4} \xrightarrow{\triangle} \underset{\text{(amide)}}{\mathrm{RCONH_2}} + \mathrm{H_2O}$$

# B- Acid derivatives

## (1- Esters)

# 1- Esters

**An ester is a chemical compound derived from an acid (organic or inorganic) in which at least one –OH hydroxyl group is replaced by an –O– alkyl (alkoxy) group, as in the substitution reaction of a carboxylic acid and an alcohol.**

# 1- Synthesis

## 1- From acids:-

$$ROH + R'COOH \xrightleftharpoons{H^+} R'COOR + H_2O$$

$$\text{e.g. } CH_3CH_2OH + CH_3COOH \xrightleftharpoons{\text{conc. } H_2SO_4} CH_3COOC_2H_5 + H_2O$$

(ethyl acetate)

## 2- From acylhalides:-

$$ROH + R'COCl \longrightarrow R'COOR + HCl$$

(acid chloride) (estrers)

## 3-From anhydrides:-

$$ROH + R'COOCOR'' \longrightarrow R'COOR + R''COOH$$

(anhydrides) (esters) (acids)

## 4- From alkylhalides:-

$$RX + R'COOAg \longrightarrow R'COOR + AgX$$

# 2- Reactions

## 1- Ammonolysis:-

$$RCOOR' + NH_3 \longrightarrow RCONH_2 + R'OH$$

(amide)

$$\text{e.g.}\quad CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$$

(acetamide)

## 2- Aminolysis:-

$$RCOOR' + R''NH_2 \longrightarrow RCONHR' + R'OH$$

(anilides)

$$\text{e.g.}\quad CH_3COOC_2H_5 + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + C_2H_5OH$$

(acetanilide)

# 4- Transesterfication:- (with lower alcohols)

$$RCOOR' + R''OH \longrightarrow RCOOR'' + R'OH$$

e.g. $CH_3COOC_4H_9 + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + C_4H_9OH$

(n-butanol)

# 5- Reduction:-

$$RCOOR' \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

# (2- Acylchlorides)

# 2- Acylchlorides

**In organic chemistry, an acyl chloride (or acid chloride) is an organic compound with the functional group -COCl. Their formula is usually written RCOCl, where R is a side chain. They are reactive derivatives of carboxylic acids. A specific example of an acyl chloride is acetyl chloride, $CH_3COCl$. Acyl chlorides are the most important subset of acyl halides.**

# 1- Synthesis

## From acids:-

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

e.g. $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$

# 2- Reactions

## 1- Hydrolysis to acids:-

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

e.g. $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

(acetyl chloride)

## 2- Alcoholysis to esters:-

$$ROH + R'COCl \longrightarrow R'COOR + HCl$$

(acid chloride) (estrers)

## 3- Ammonolysis:-

$$RCOCl + 2NH_3 \xrightarrow{} RCONH_2 + NH_4Cl$$

e.g. $CH_3COCl + 2NH_3 \xrightarrow{} CH_3CONH_2 + NH_4Cl$

## 4- Aminolysis:-

$$RCOOR' + R''NH_2 \xrightarrow{} RCONHR'' + R'OH$$

(anilides)

e.g. $CH_3COOC_2H_5 + CH_3NH_2 \xrightarrow{} CH_3CONHCH_3 + C_2H_5OH$

(acetanilide)

## 5- Reaction with sodium salts:-

$$RCOCl + RCOONa \xrightarrow{} (RCO)_2O + NaCl$$

(anhydrides)

# 6- Reduction:-

## a- To alcohols: (LAl$H_4$)

$$RCOCl \xrightarrow[HCl]{LiAlH_4} RCH_2OH$$

## b- To aldehydes:-

$$RCOCl \xrightarrow{H_2/Pd} RCHO + HCl$$

e.g. $CH_3COCl \xrightarrow{H_2/Pd} CH_3CHO + HCl$

# (3-Anhydrides)

# 3-Anhydrides

An acid anhydride is a compound that has two acyl groups bonded to the same oxygen atom. A common type of organic acid anhydride is a carboxylic anhydride, where the parent acid is a carboxylic acid, the formula of the anhydride being $(RC(O))_2O$. Symmetrical acid anhydrides of this type are named by replacing the word acid in the name of the parent carboxylic acid by the word anhydride. Thus, $(CH_3CO)_2O$ is called acetic anhydride. Mixed (or unsymmetrical) acid anhydrides, such as acetic formic anhydride, are known, whereby reaction occurs between two different carboxylic acids. Nomenclature of unsymmetrical acid anhydrides list the names of both of the reacted carboxylic acids before the word "anhydride" (for example, the dehydration reaction between benzoic acid and propanoic acid would yield "benzoic propanoic anhydride").

# 1- Synthesis

## 1- From acyl halides:-

$$RCOCl \quad + \quad RCOONa \longrightarrow (RCO)_2O \quad + \quad NaCl$$

(anhydrides)

## 2- From carboxylic acids:-

$$2RCOOH \quad + \quad AC_2O \xrightarrow{heat} (RCO)_2O \quad + \quad 2CH_3COOH$$

## 3- From ketenes:-

$$CH_2{=}C{=}O \quad + \quad CH_3COOH \longrightarrow (CH_3CO)_2O$$

(acetic anhydride)

# 2- Reactions

## 1- Hydrolysis to acids:-

$$RCOOCOR + H_2O \xrightarrow{\triangle} 2RCOOH$$

## 2- Alcoholysis to esters:-

$$ROH + \underset{\text{(anhydrides)}}{R'COOCOR''} \longrightarrow \underset{\text{(esters)}}{R'COOR} + \underset{\text{(acids)}}{R''COOH}$$

## 3- Ammonolysis with ammonia:-

$$(RCO)_2O + 2NH_3 \longrightarrow \underset{\text{(amides)}}{RCONH_2} + RCOONH_4$$

## 4- Aminolysis with amines:-

$$(RCO)_2O + RNH_2 \longrightarrow \underset{\text{(anilides)}}{RCONHR} + RCOOH$$

# 4- Aminolysis with amines:-

$$(RCO)_2O + RNH_2 \longrightarrow \underset{\text{(anilides)}}{RCONHR} + RCOOH$$

# (4- Amides)

# 4- Amides

**In organic chemistry, an amide also known as an organic amide or a carboxamide, is a compound with the general formula RC(=O)NR′R″, where R, R', and R″ represent organic groups or hydrogen atoms. It can be viewed as a derivative of a carboxylic acid RC(=O)OH with the hydroxyl group –OH replaced by an amine group –NR′R″; or, equivalently, an acyl (alkanoyl) group RC(=O)– joined to an amine group. Common examples of amides are acetamide $H_3C–CONH_2$, benzamide $C_6H_5–CONH_2$, and dimethylformamide $HCON(–CH_3)_2$. Amides are qualified as primary, secondary, and tertiary according to whether the amine subgroup has the form $–NH_2$, –NHR, or –NRR', where R and R' are groups other than hydrogen. The core –C(=O)N= of amides is called the amide group (specifically, carboxamide group).**

# Synthesis

## 1- From other acid derivatives. via ammonolysis

$$(RCO)_2O + 2NH_3 \longrightarrow \underset{\text{(amides)}}{RCONH_2} + RCOONH_4$$

## 2- From ammonium salts. via pyrolysis

$$RCOONH_4 \xrightarrow{\triangle} \underset{\text{(amide)}}{RCONH_2} + H_2O$$

## 3- Partial hydrolysis of nitriles

$$RC \equiv NH_3 + H_2O \xrightarrow{HCl} RCONH_2$$

# Reactions

## 1- Hydrolysis to acids:-

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

## 2- Reduction to primary amines:-

$$RCONH_2 \xrightarrow[(2H_2)]{Na/EtOH} RCH_2NH_2 + H_2O$$

## 3- Dehydration to nitrils:-

$$RCONH_2 \xrightarrow{P_2O_5} RC\equiv N + H_2O$$

# 4- reaction with nitrous acid:-

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

# 5- Hofmann rearrangement:-

$$RCONH_2 \xrightarrow{Br_2/\ KOH} RNH_2$$

# 7- Amines

# Amines

In organic chemistry, amines are compounds and functional groups that contain a basic nitrogen atom with a lone pair. Amines are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (these may respectively be called alkylamines and arylamines; amines in which both types of substituent are attached to one nitrogen atom may be called alkylarylamines). Important amines include amino acids, biogenic amines, trimethylamine, and aniline; inorganic derivatives of ammonia are also called amines, such as monochloramine ($NClH_2$). The substituent $-NH_2$ is called an amino group. Compounds with a nitrogen atom attached to a carbonyl group, thus having the structure R–CO–NR′R″, are called amides and have different chemical properties from amines.

# Synthesis

## 1- Synthesis of primary, secondary and tertiary amines from alcohols (mixture):-

$$\mathrm{ROH} + \mathrm{NH_3} \xrightarrow{\text{pressure}} \mathrm{RNH_2} + \mathrm{H_2O}$$

$$\mathrm{ROH} + \mathrm{RNH_2} \xrightarrow{\text{pressure}} \mathrm{R_2NH} + \mathrm{H_2O}$$

$$\mathrm{ROH} + \mathrm{R_2NH} \xrightarrow{\text{pressure}} \mathrm{R_3N} + \mathrm{H_2O}$$

# Reactions

## 1- Acylation:-

$$\begin{tikzcd}
RNH_2 + RCOCl \arrow[r] & RNHCOR + HCl \arrow[d, "RCOCl"] \\
& RN(COR)_2
\end{tikzcd}$$

## 2- Oxidation:-

### 1- Primary amines:-

$$RCH_2NH_2 \xrightarrow{KMnO_4} RCH{=}NH \xrightarrow{H^+} RCHO$$

(imine)

### 2- Secondary amines:-

$$R_2NH \xrightarrow{KMnO_4} R_2N{-}NR_2$$

### 3- Tertiary amines:-

$$R_3N \xrightarrow{H_2O_2} R_3N \longrightarrow H_2O$$ (amine oxide)

# References

1- https://chem.libretexts.org/Courses/Sacramento_City_College/SCC%3A_CHEM_330_Adventures_in_Chemistry_(Alviar-Agnew)/09%3A_Organic_Chemistry/9.02%3A_Aliphatic_Hydrocarbons.

2- https://profiles.uonbi.ac.ke/andakala/files/sch_102__2019_synthesis_and_reactions_of_alkanes.pdf

3-https://chemed.chem.purdue.edu/genchem/topicreview/bp/1organic/reaction.html

4- https://kpu.pressbooks.pub/organicchemistry/chapter/10-1-synthesis-of-alkenes/

5- https://www.cliffsnotes.com/study-guides/chemistry/organic-chemistry-i/structure-and-properties-of-alkenes/alkenes-preparations

**6- https://crab.rutgers.edu/~alroche/Ch08.pdf**

**7- https://pubs.rsc.org/en/content/articlelanding/2020/ob/d0ob00325e**

**8- https://chem.libretexts.org/Courses/Sacramento_City_College/ SCC%3A_Chem_420-Organic_Chemistry_I/Text/10%3A_Alkynes/10.03%3A_Reactions_of_Alkynes_-Addition_of_HX _and_X%E2%82%82**

**9- https://www.cliffsnotes.com/study-guides/chemistry/organic-chemistry-ii/alkyl-halides/preparation-of-alkyl-halides**

**10-https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Wade)/07%3A_Alkyl_Halides%3A_Nucleophilic_Substitution_and_Elimination/7.01%3A_Nomenclature_of_Alkyl_Halides**

11- https://www.priyamstudycentre.com/2020/02/ types-alcohol-uses. html

12- https://en.wikipedia.org/wiki/Ether

13- IUPAC, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book") (1997). Online corrected version: (2006–) "ethers". doi:10.1351/goldbook.E02221

14- https://www.toppr.com/guides/chemistry/ alcohols-phenols-and-ethers/chemical-reactions-of-ethers/

15- https://www.rbchannel2020.info/2020/07/ Naming-and-preparing-ethers.html

**16- https://en.wikipedia.org/wiki/Thiol**

**17- https://en.wikipedia.org/wiki/Sulfide_(organic)**

**18- https://www.google.com/search?q=Reactions+of+thiols&client= firefox-b-d&sa=X&biw=1366&bih=643&tbm=isch&source=iu&ictx =1&fir=AypfqzFGOwZXwM%252CHueqf3o6asulaM%252C_%253BPq854R8d82PqMM%252Cq5ftVcJtqDAtnM%252C_%253BX1uVrugLIPwDAM%252CzSGqvaivYuas1M%252C_&vet=1&usg=AI4_-kQNrIfouAJh1Ju9O4I8bz0cERSTkg&ved=2ahUKEwicu4b8rb3zAhUp8uAKHXJbCo4Q_h16BAgJEAE#imgrc=_dSzuoig2SAe7M**

**19- https://www.google.com/search?client=firefox-b-d&q= aliphatic+adehydes+and+ketones**

**20- https://en.wikipedia.org/wiki/Aldehyde#Synthesis**

**21- https://en.wikipedia.org/wiki/Stephen_aldehyde_synthesis**

**22- https://en.wikipedia.org/wiki/Geminal_halide_hydrolysis**

**23- https://en.wikipedia.org/wiki/Ketone**

**24- https://www.google.com/search?client=firefox-b-d&q=Carboxylic+acids**

**25- https://en.wikipedia.org/wiki/Carboxylic_acid.**