ORGANIC CHEMISTRY

COURSE OUTLINE:

- Definition of organic Chemistry
- Properties of organic compounds
- Functional groups of organic compounds
- Molecular empirical structural formulae
- Homologous series (Groups of organic compounds)
- Alkanes
- Alkener
- Alkynes

  Hydro carbons
- Alkyl halides (Halogeno alkanes)
- Alcohols
- Ethers
- Phenols
- Benzene
  - ✓ Methy/Benzene
  - ✓ Nitrobenzene
  - ✓ Chlorobenzene

  Aromatics
- Carbons/compounds
  - ✓ Aldehydes (Alkanals)
  - ✓ Ketones (Alkanones)
- Carboxylic acids
  - ✓ Acidic halides (Alkanoy chlorides)
  - ✓ Amides
- Esters
- Amines
- Diazonium salts
- Applied organic chemistry
- Practical organic chemistry

Reference books:

Principles of Organic Chemistry

A′ level Chemistry – Ramsden.

INTRODUCTION:

Definition of Organic Chemistry:

Organic Chemistry is the Chemistry of Carbon and related elements. It does not involve inorganic compounds of carbon like CO_2, $CO_3^{2-}s$, HCO_3^{-}s.

Organic Chemistry started when the first organic compounds were largely obtained from living things. This therefore makes carbon as the most abundant element in living organisms.

PROPERTIES OF ORGANIC COMPOUNDS:

Organic compounds are characterized by the following properties:

- They are made up of carbon and other elements like H_2, O_2, N_2, S, P and Cl_2.
- They are complex in structure e.g. some are made up of long chains of carbon, highly branched chain, rings of carbon.
- They exhibit isomerism a condition in which several structures can be written from one molecular formula.
- All organic compounds are bonded by covalent bonding.
- Most organic compounds undergo slower reactions.
- From the above properties, organic chemistry places a lot of interest in the behaviour of carbon.

Carbon as an element in organic chemistry:

C(6) = 2:4 $1S^2 2S^2 2P^2$

Electronic configuration

From the above configuration, carbon has got two principle equation numbers, a total of 6 electrons.

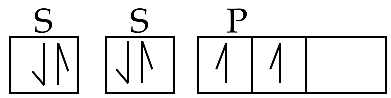
2 electrons in the S-orbital (inner energy level).

4 electrons in the 2^{nd} principle quantum number distributed as 2 in the S-orbital and 2 in P-orbital.

When carbon undergoes a chemical reaction, it uses all the four electrons in the P-quantum number which gives it a tetravalent.

Since bonding in organic compounds occurs in covalent bond (sharing electrons), it means each carbon atom should contribute four (2 pairs of electrons). Carbon then forms 4 covalent bonds by molecular mixing of orbitals a process known as Hybridization.

HYBRIDIZATION OF ORBITALS IN CARBON

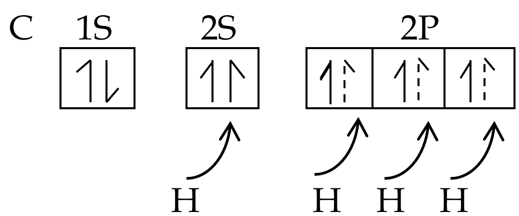
C(ground state-uncreative) 

When carbon atom is excited, one electron from the 2S – orbital is sent to the 2P giving in total four unpaired electrons which now become the tetravalent of carbon.

Bonding in carbon thereof involves the mixing of the S – and the P-orbitals.

(i) Formation of alkanes (Example methane).
Bonding in alkanes involves $2SP^3$ hybridization.

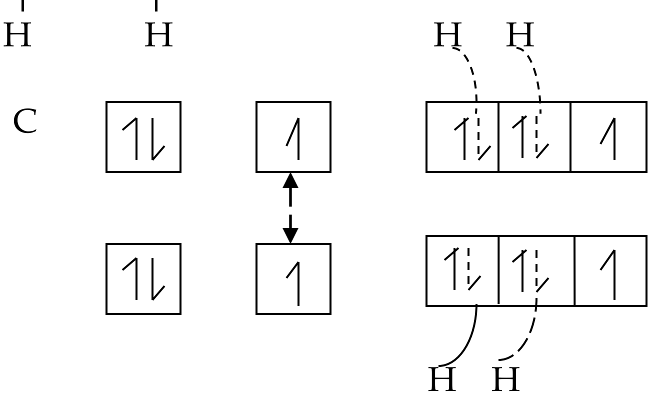
```
    H
    |
H — C — H
    |
    H
```



(ii) **Bonding in alkenes**
In alkenes, bonding involves 2Ps hybridization.

Ethene:

```
H       H
|       |
C   =   C
|       |
H       H
```



(iii) Bonding in alkynes

2SP hybridization e.g. ethyne

i.e. 1 electron in 2S of each carbon atom combines to form a normal sigma bond while each hydrogen combines with each of the 2SP electron leaving 2 unpaired electrons in the 2P which will overlap to form 2π bonds.

H – C – C – H

H – C≡C – H

UNIQUE PROPERTIES OF CARBON

Carbon is generally a unique element and it displays the following properties:

(i) If forms multiple bonds with other elements or itself. E.g.

– double bond C = C (alkene); C = O (carbons)

- triple bond C≡C (alkynes); C≡N (Nitrates)

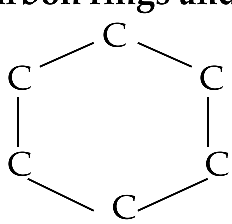
Carbon forms up to 4 covalent bonds and this is always exhibited in all its compounds.

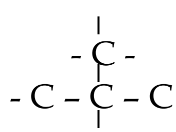
- C - -C = C - -C ≡ C – - C ≡ N.

Carbon forms long chain compounds a process known as catenation, e.g.

- C – C – C – C -.

Carbon rings and branded compounds.





FUNCTIONAL GROUP:

Is an atom of groups of atoms in an organic compound that determines the chemical properties of that compound.

Most of the chemical reactions of organic compounds are determined by their functional group.

Families of organic compounds known as homologous series are also determined by functional group.

No.	Homologous series (class)	Functional group	Examples
1.	Alkanes C_nH_{2n+2} (R – H)	- C – C – (Carbon single bond)	H_4 (Methane)
2.	Alkenes (C_nH_{2n})	- C = C – (Carbon double bond)	C_2H_4 (Ethene)
3.	Alkynes (C_nH_{2n-2})	- C ≡ C – (Carbon triple bond)	C_2H_2 (Ethyne)
4.	Alkyl halides/halogenal alkaner (R–x) C_nH_{2n+1}X Where X is a halogen e.g. Cl_2, Br.	Halogen(X)	C_2H_5Cl(Chloro ethane)
5.	Alkanals (alcohols) $(C_nH_{2n+1}OH)(R-OH$	Hydroxyl group (-OH)	C_3H_7OH(Propanol)
6.	Ethers (R-OR)	- O – (Oxygen)	C_2H_6O H H H – C – O – C – H H H (di methyl) (ether of methoxyl)
7.	Carbons/Compounds (i) Alkanals (aldehydes)	O ‖ - C – H (Carbony/Carbon & H_2)	C_2H_4 H O H – C – C – H H (Ethanal)
	(ii) Alkanones (Ketone) O ‖ R – C – R	O ‖ - C – (Carbony/Carbon)	C_3H_6O (Propanone) H H H – C – C – C – H H O H

8.	Carboxylic acid R – COOH	O ‖ - C – O – H Carboxylic acid group	$C_2H_4O_2(Ethanoic\ acid)$ H O | ‖ H – C – C – O – H | H
9.	Esters (ROOR)	O ‖ - C – O – /	$C_3H_6O_2(Methyl\ ethanoate)$ H O H | ‖ | H – C – C - O – C – H | | | H H H
10.	Nitro compound R - NO_2	$-NO_2(Nitro\ group)$	$C_2H_4NO_2(Nitro\ ethane)$ H H | | H – C – C - NO_2 | | H H
11.	Nitriles (Cyanohydrins) R - C≡N	$-C \equiv N(Nitrile\ group)$	Ethanitrile C_2H_3N H | H – C – C ≡ N | H
12.	(Acido halides) O ‖ R – CO – X	O ‖ — C – X	$C_2H_3O_4Cl$ H O | ‖ H – C – C – X | H (Ethanoyl)
13.	Amides O ‖ R – C - NH_2	O ‖ - C - NH_2 (Amide group)	$C_2H_5 - ON$ H O | ‖ H – C – C NH_2 | H (Ethanimide)
14.	Amines $(R - NH_2)$	$-NH_2\ (Amino\ group)$	H | H – C - NH_2 | H $CH_5N\ (Methyl\ amine)$

EMPIRICAL MOLECULAR AND STRUCTURAL FORMULAE

Empirical formula is the simplest formula which expresses the ratio of the number of atoms present in a molecular or compound. E.g.
A certain organic compound has 39.13% by mass Carbon 52.23%, Oxygen and the rest hydrogen, determine its empirical formula.
39.13 + 52.23
100 – 91. 36 = 8.64

Element	C	H	O			
Percentage composition	39.13	8.64	52.23			
Composition / Rfm	$\frac{39.13}{12}$	$\frac{8.64}{1}$	$\frac{52.23}{16}$			
Number of moles	3.2608	8.64	3.2644			
Divide by smallest	$\frac{3.2608}{3.2608}$	$\frac{8.64}{3.2608}$	$\frac{3.2644}{3.2608}$			
Mole ratio	1 x 2	2.6 x 2	1 x 2	1 x 3	2. 6 x 3	1 x 3
	1	5.3	1	$C_3H_8O_3$		

∴ Empirical formula = $C_2H_5O_{2.}$

Molecular formula expresses the true or actual number of each atom present in 1mole of a compound. It is also a multiple of an empirical formular.

$\frac{Molecular\ formula\ mass}{Empirical\ formular\ mass} = n$ n = simple whole number.

Molecular formula = [Empirical formula].

MOLECULAR FORMULA MASSES:
They can be determined from;
(i) Vapour density:
When a compound is vapourized and weighed, its mass is twice the molecular formula mass.
2 x V.P = MFM.

(ii) Rates of diffusion (Graham's law)

$MFM_A = \left(\frac{R_A}{R_B}\right)^2 \text{ x } MFM_B$

(iii) Ideal gas equation

PV = nRT; PV = $\frac{mRT}{mR}$

Mr = $\frac{mRT}{PV}$

GASEOUS HYDROCARBONS (EUDIOMETRY)

Eudiometry is a technique used to determine molecular formula of gaseous hydrocarbons.

When a gaseous hydrocarbon is exploded with excess oxygen, it readily burns forming $CO_{2\ and}\ H_2O$ as the only product.

If the gases are passed over an alkali e.g. (KOH or NaOH), all the CO_2 formed is absorbed and the diminution (reduction) in the volume of the gases is due to CO_2.

The residual gas at that point will now be excess O_2.

The volume of H_2O formed is regarded as negligible.

$$C_xH_y(g) + \frac{x+y}{4}O_2(g) \longrightarrow XCO_2(g) + \frac{x}{2}H_2O_{(l)}$$

From the above equation, everyone mole of a hydrocarbon is equivalent to X moles of CO_2 produced.

Similar when the volumes are related, the volume at CO_2 is equivalent to (X) x volume of CO_2 produced.

X(Volume of HC) = Volume of CO_2 produced.

Then the volume of O_2 used can also be related to the volume of the hydrocarbon by volume of;

Oxygen used = $\left(\frac{x+y}{4}\right)$(Volume of hydrocarbon).

Example:

$15cm^3$of a gaseous hydrocarbon were exploded with $105cm^3$of oxygen in a sealed vessel after cooling, the residual volume occupies $75cm^3$. On addition of caustic potash, there was a final diminution/decrease of volume to $30cm^3$. Determine the molecular mass of a hydrocarbon.

Let the hydrocarbon be C_xH_y.

$$C_xH_{y(g)} + \left(\frac{x+y}{4}\right) O_{2(g)} \longrightarrow XCO_{2(g)} + \frac{y}{2}H_2O_{(l)}$$

Volume of O_2 used = 105 – 30 = $75cm^3$
Volume of CO_2 produced = 75 – 30 = 45cm^3
C_xH_y = volume of CO_2 produced.
= 45.

$\frac{45}{15} = 3.$

$(Volume\ of\ HC)\left(x + \frac{y}{4}\right)$ = Volume of O_2used.

$15\left(3 + \frac{y}{4}\right) = 75$

$3 + \frac{y}{4} = \frac{75}{15}$

$3 + \frac{y}{4} = 5$

$\frac{y}{4} = 2$

y = 8.

Molecular formula is C_3H_8
12 x 3 + 8 x 1 = **449**.

DETERMINATION OF MOLECULAR FORMULA OF ORGANIC COMPOUND USING MASS OF $CO_{2\ and}\ H_2O$.

When an organic compound is burnt, the masses of the products, carbon dioxide and H_2O together with the initial mass of the organic compound can be used to determine the molecular formula.

Example:
0.464g of an organic compound Q when burnt gave 1.32g of CO_2, 0.315g of H_2O. When 0.2325g of Q were separately burnt, 7.08 cm^3 of N_2 gas at s.t.p was produced. Determine the molecular formula of Q and draw its structure. Vapour density = 46.5.

Organic cpd + $O_2 \longrightarrow CO_2 + H_2O$
12g of C 44g of CO_2
2g of H 18g of H_2O.

12g of carbon produces 44g of CO_2.
Xg of carbon produce 1.32g of CO_2.

$\left(\frac{12}{44}\ x\ 1.32\right) g$ of carbon inorganic compound.
= 0.36g.
Percentage of carbon = $\frac{0.36}{0.464}\ x\ 100$
= 77.6%

2g of H_2 in Q produces 18g of H_2O.
y of H_2 in Q produces 0.315g of H_2O.
y = $\left(\frac{2}{18}\ x\ 0.315\right) g$ of H_2
= 0.035g.

Percentage of H in Q = $\frac{0.035}{0.464}\ x\ 100$

= 7.5%

Mass of Nitrogen = 0.36 + 0.035 = 0.395
0.464 – 0.395
= 0.069g of N_2.

Percentage of N_2 = 77.6 + 7.5 = 85.1g
(100 – 85.1)
= 14.9%

1moleof a gas contains 22400cm^3 at s.t.p.
Xmoles of N_2 contains 7.08cm^3.

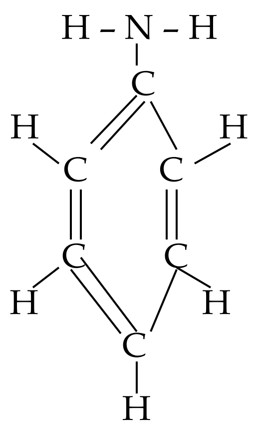
$\frac{7.08}{22400} = 3.16 \times 10^{-4}$moles.

0.2325g of Q produces 3.16 x 10^{-4} moles of N_2.
Xg of Q produced by 1mole of N_2.

Elements	C	H	N
Percentage composition	776.	7.5	14.9
Relative atoms	$\frac{77.6}{12}$	$\frac{7.5}{1}$	$\frac{14.9}{14}$
Moles	6.47	7.5	1.06
Simple ratio	$\frac{6.47}{1.06}$	$\frac{7.5}{1.06}$	$\frac{1.06}{1.06}$
Simple ratio	6	7	1

Empirical formula C_6H_7N
$(C_6H_7N)n = 46.5\ x\ 2$
n(12 x 6) + 7 x 1 + 14 = 93
93n = 93
n = 1.

Molecular formula = C_6H_7N

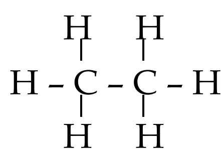


Phenyl-amine.

STRUCTURAL FORMULA

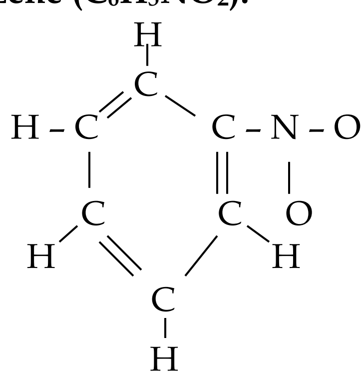
It shows the different atoms and how they are connected in one molecule of a compound e.g.

1. **Ethane structure.**

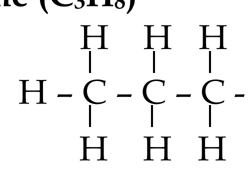


or $H_3C.CH_3$

2. **Nitrobenzene ($C_6H_5NO_2$).**



3. **Propane (C_3H_8)**



or $H_3C - C\,H_2.CH_3$

4. But-2-end (C_4H_8)

```
        H   H   H   H
        |   |   |   |
    H – C – C = C – C – H        or      H3C.CH = CH.CH3
        |           |
        H           H
```

5. Buta-3-diene

```
         H    H   H
         |    |   |
    H – C = C – C = C – H        or      H2C = CH.CH = CH2
                    |
                    H
```

ORGANIC COMPOUNDS

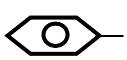
Organic compounds are generally classified according to the functional groups they do have and its very important that all the organic compounds are given names.

NOMENCLATURE OF ORGANIC COMPOUNDS

Naming of organic compounds follows a strict system of nomenclature where names are assigned.

NAMING OF HYDRO CARBONS

They are named using "stem" names that indicate the alkyl groups. E.g.

Alkyl group:		**Name:**
$\pm CH_3$	1	Methyl
$\pm CH_2CH_3$	2	Ethyl
$\pm CH_2CH_2CH_3$	3	Propyl
$\pm CH_2CH_2CH_2CH_3$	4	Butyl
$-C_6H_5$ or 	6	Phenyl

RULES GOVERNING NOMENCLATURE (Guidelines)

(i) Hydrocarbons are named as derivatives of alkanes. Where the suffic-ane- is added to the stem name.

(ii) Always identify the longest continuous chain in the compound and this gives the parent name. Other things attached to that chain are regarded as branches. E.g.

$H_3C\ \underset{\underset{CH_3}{|}}{CH}.CH_2CH_3$ Branch   but-4carbon atoms.

(iii) Number – the carbon parent chain from one end to the other end giving the position of the branch the lowest number. E.g.

$H_3C\ \underset{\underset{CH_3}{|}}{CH}\ CH_2\ CH_3$

(iv) If there are more than one substituent branch, the numbering has to consider the lowest sum of the positions. E.g.

$H_3C\ \underset{\underset{CH_3}{|}}{CH}\ \overset{\overset{CH_3}{|}}{CH}\ CH\ CH\ CH_3$

R – L – sum of branches = 4 + 5 = 9.

L – R, sum of branches = 2 + 3 ⟶ selected.
= 5

The sum of the locants moving from left to right is the lowest and therefore it is preferred.

(v) All the positions of the locants are identified and they are put as prefix separated with a (-) in the branch. E.g.
2 – methyl & 3 – methyl

(vi) When there are more than one substituent, the following is noted:

(a) Similar substituents are given a prefix di – 2, tri – 3, tetra – 4 ---- and their locants are also indicated before the prefix but the locant separated by a comma(,). E.g. 2, 3-dimethyl.
The numerical order of the locants is followed.

$H_3C\ \underset{\underset{CH_3}{|}}{CH} – \overset{\overset{CH_2\ CH_3}{|}}{CH}\ CH_2\ CH_2\ CH_3$ hex – 6 carbon atoms.

3 – Ethyl
2 – Methyl

The alphabets in the beginning letter of the names of the substituent has got to be followed.

(vii) The last name to be written is the parent name which indicates the number of carbon atoms in the chain.

$$\begin{array}{l} \quad\quad\quad\;\; CH_3 \quad CH_2\,CH_3 \\ \quad\quad\quad\;\;\; | \quad\quad\;\; | \\ H_3CCH_2\,C\,CH_2\,CH\,CH_2\,CH_3 \\ \quad\quad\quad\;\;\; | \\ \quad\quad\quad\;\; CH_3 \end{array}$$

3, 3-dimethyl -5-ethyl heptanes.

If a multiple bond (triple or double bond) is present, then the longest chain identified must involve the (double or triple) bond.

The multiple bond must be given the lowest number within the stem name.

$$\begin{array}{l} H_3C\,CH_2\,CH = C - CH_2CH_3 \\ \quad\quad\quad\quad\quad\quad\;\; | \\ \quad\quad\quad\quad\quad\quad CH_2 \\ \quad\quad\quad\quad\quad\quad\;\; | \\ \quad\quad\quad\quad\quad\quad CH_2 \\ \quad\quad\quad\quad\quad\quad\;\; | \\ \quad\quad\quad\quad\quad\quad CH_7 \end{array}$$

4-ethyl heft-3-ene.

(viii) When there are other functional groups, their positions, names are indicated. E.g. Halogen (Cl, F, Br, I)= Chloro, Fluoro, Bromo, Iodo.

OH = (alcohol) – O*l*

C = C (double bond) – ene

C≡C (triple bond) – yne.

$$\begin{array}{l} O \\ \| \\ C - H \end{array}$$ (aldehyde) – anal

$$\begin{array}{c} O \\ \| \\ \diagup C \diagdown \end{array}$$ (Ketone) – one

$-NH_2$ (amine) – amine.

(ix) **VOWEL/CONSONANT RULE**

When naming a compound where a locant is included within the stem name, the two letters close to the locant must be a vowel and a consonant and not all vowels or all consonants. E.g.

$CH_3CH\,CH_3$ | OH — Propan – 2 - O*l* (Consonant ↑ n, Vowel ↑ O)

$CH_3\,CH = CHCH = CH_2$ Penta – 1, 3-diene.

$HOCH_2CH_2\,OH$ Ethane-1, 2-diol.

$HOOC.COOH$ Ethane-1, 2-dioc acid.

CH_3COOH Ethanoic acid.

(x) When naming compounds with very many functional groups (poly functional compounds), the functional groups are assigned an order depending of the seniority order and this order is the carboxylic acid, carbonyl, cyanide, ketone, alcohol, amines, double bond, triple bond, nitro group and halogen.

$-COOH > \overset{O}{\overset{|}{C}} - H > C{\equiv}N > \underset{\textbf{Katone}}{\overset{O}{\overset{|}{C}}} > \underset{\textbf{Hydroxyl}}{-OH} > -NH_2 > -C{=}C->$

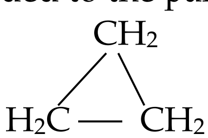
$C{\equiv}C > NO_2 > X$(halogen).

E.g. $CH_3\underset{Cl}{\underset{|}{C}}H\,CH_2\,COOH$ 3 – chloro butanoic acid.

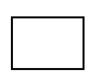
$CH_3\underset{Cl}{\underset{|}{C}}H - \overset{NH_2}{\overset{|}{C}}H\,CH = CH_2$ 4-chloro-3-amino pentene.

$H_2C = CHCH_2CH_2C{\equiv}CH$ Hexane-5-yne.

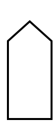
For the case of cyclic compounds (ringed compounds), the prefix "cyclo) is added to the parent alkane name.

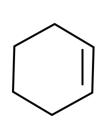


Cyclopropane

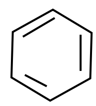


Cyclobutane





Cyclopentane Cyclohexene



Cyclohexa-1, 3, 5 – triene.
Or
Benzene (Phenyl group)

STRUCTURES OF ORGANIC COMPOUNDS FROM NAMES:
Structures can be written from the names.

Example:
Butane

H H H H
| | | |
H – C – C – C – C – H Or $H_3C\ CH_2\ CH_3\ CH_3$
| | | |
H H H H

2-Methyl propane.

H
|
H H- C - H
| | |
H - C – C – C – H
| | |
H H H

CH_3
|
Or $H_3C\ CH\ CH_3$

5-methyl heft-3-ene.

H
|
H H H H – C – H H
| | | | | |
H – C – C – C = C – C – C – C – H
| | | | | |
H H H H H H

CH_3
|
$H_3C\ CH_2\ CH = CH\ CHCH_2\ CH_3$

3, 4-dimethyl pentanol.

H H
| |
H H H – C – H H – C – H
| | | | |

$$
\begin{array}{cccccccc}
OH - & C & - & C & - & C & - & C & - & C - H \\
 & | & & | & & | & & | & & | \\
 & H & & H & & H & & H & & H
\end{array}
$$

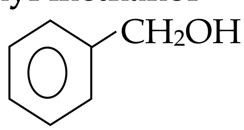
4, 5-dimethyl hex-2-yne.

$$
\begin{array}{ccccccccc}
 & & & & & H & & & \\
 & & & & & | & & & \\
 & H & & & H - & C & - H & H & & H \\
 & | & & & & | & & | & & | \\
H - & C & - C \equiv & C - & & C & - & C & - & C - H \\
 & | & & & & | & & | & & | \\
 & H & & & & H & H - & C & - H & H \\
 & & & & & & & | & & \\
 & & & & & & & H & &
\end{array}
$$

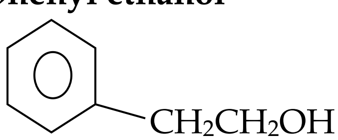
Ethane-1, 2 – diol

$$
\begin{array}{ccccc}
 & H & & H & \\
 & | & & | & \\
OH - & C & - & C & - OH \\
 & | & & | & \\
 & H & & H &
\end{array}
$$

Phenyl methanol



2-phenyl ethanol



2, 2 –dimethyl propane

$$
\begin{array}{c}
CH_3 \\
| \\
H_3C.C.CH_3 \\
| \\
CH_3
\end{array}
$$

Propane- 1, 2, 3 – triol.

$$
\begin{array}{ccc}
HO.CH_2 & CH & CH_2 \\
 & | & | \\
 & OH & OH
\end{array}
$$

Or: $H_2C(OH)CH(OH)CH_2.OH$

Or:

$$
\begin{array}{cccccc}
 & H & & H & & H \\
 & | & & | & & | \\
H - & C & - & C & - & C - H \\
 & | & & | & & | \\
 & OH & & OH & & OH
\end{array}
$$

International Union of Pure and Applied Chemistry.

N.B: Name organic compounds should always consider the IUPAC system. Where names and systematically written and this is the most universally known way of naming. However, trivial names may be found in a number of books and these should not be used for exam purposes.

E.g. CH≡CH (Ethyne) = (Acetylene) trivial name.
$CH_3CH_2CH_2OH$ Propanol = (Propyl alcohol) trivial name.

ISOMERISM
This is the existence of compounds with the same molecular formula but different structural formulae. These compounds are known as **Isomers**.

Types of isomerism
There are two types of isomerism with a number of subtypes.

1. **Structural isomerism**
   The type of isomerism where compounds differ in the arrangement of atoms within the molecule i.e. isomers under structural isomerism differ in the carbon skeleton.

2. **Stereo isomerism**
   Type of isomerism where compounds of the same molecular formula and structural formula differ in the spatial arrangement of atoms.

STRUCTURAL ISOMERISM
Structural isomers can be further subdivided into:

(i) **Chain structural isomerism**
   This is where compounds differ in the arrangement of carbon atoms in a molecule.

Note: The position of the functional group in the chain must remain the same.
E.g. (C_4H_{10})
$H_3C\ CH_2\ CH_2\ CH_3$ *n*-Butene

```
      CH3
      |
H3C CH CH3
```
2-methyl (propane).

C_5H_{12}

$H_3C\ CH_2\ CH_2\ CH_2\ CH_3$ *n*- pentane

$$\begin{array}{l} H_3C\ CH_2\ \underset{\displaystyle |\atop \displaystyle CH_3}{CH}\ CH_3 \end{array}$$ 3-methyl (butane)

$$\begin{array}{c} CH_3 \\ | \\ H_3C - C - CH_3 \\ | \\ CH_3 \end{array}$$

(ii) **Functional isomerism**

Type of isomerism where the isomers differ by the functional group. Such isomers also differ in both physical and chemical properties. E.g. Alcohols.

- **Ethers are isomeric.**

  C_2H_6O

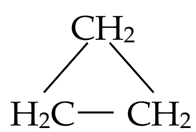
  $H_3C\ CH_2\ OH$ Ethanol.

  H_3COCH_3 Dimethy ether (methoxy ethane)

- **Alkenes and cyclicalkanes**

  (C_3H_6)

  $H_3C\ CH = CH_2$ Propane

  Cyclopropane.

- **Carboxylic acids and esters.**

  $C_4H_8O_2$

  $H_3C\ CH_2\ CH_2\ COOH$ Butanoic acid

  $$H_3C\ \overset{\displaystyle O\atop \displaystyle ||}{C} - O\ CH_2\ CH_3$$ Ethyl ethanoate (ester)

(iii) **Positional isomerism**

Type of isomerism where the compounds with the same molecular formula differ in position of the functional group within the same carbon skeleton.

- **(C_3H_7OH)**

  $H_3C\ CH_2\ CH_2OH$ Propan-1-O*l*

  $$\begin{array}{l} H_3C\ \underset{\displaystyle |}{C}H\ CH_3 \\ \quad\ \ \ OH \end{array}$$ Propan-2-O*l*

- C_4H_8

  $H_3C\ CH_2 = CH_2\ CH_3$ But-2-ene

  $H_2C = CH\ CH_2\ CH_3$ But-1-ene

- (C_4H_9Cl)

  $H_3C\ CH\ CH\ CH - Cl$ Chloro butane

  $H_3C\ CH(Cl)\ CH_2\ CH_3$ 2-Chloro butane

Question:

Write all the isomers of the compounds with molecular formula $C_5H_{12}O$.

1. $H_3C\ CH_2\ CH_2\ CH_2\ CH_2\ OH$ *n* – Pent-1-o*l*

2. $$\begin{array}{l} CH_3\ CH_2\ CH_2\ \underset{\displaystyle |}{C}H\ CH_3 \\ \qquad\qquad\qquad\ \ OH \end{array}$$ Pentan-2-o*l*

3. $$\begin{array}{l} CH_3\ CH_2\ \underset{\displaystyle |}{C}H\ CH_2\ CH_3 \\ \qquad\quad\ \ OH \end{array}$$ Pentan-3-ol

4. $$\begin{array}{l} CH_3\ \underset{\displaystyle |}{C}H\ CH_2\ CH_2\ OH \\ \qquad CH_3 \end{array}$$ 3-methyl butanol

5. $$CH_3\ \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}.CH_2\ OH$$ 2, 2-dimethyl propanol

6. $$\begin{array}{l} CH_3\ CH_2\ \underset{\displaystyle |}{C}H\ CH_2\ OH \\ \qquad\quad\ \ CH_3 \end{array}$$ 2-methyl butanol

7. $CH_3\,CH_2\,O\,CH_2\,CH_2\,CH_3$ Ethoxy propane.

8. $CH_3\,O\,CH_2\,CH_2\,CH_2\,CH_3$ Methoxy butane.

Note: 1, 2, 3 are positional isomers.
4, 5, 6 are chain isomers.
7 and 8 are functional isomers.

STEREO-ISOMERISM

The compounds differ by spatial arrangement of atoms. There are two types i.e. geometrical steroisomerism and optical steroisomerism.

GEOMETRICAL STEROISOMERIM

Is where isomers have the same structural formula but differ in the spatial arrangement of the groups around a double bond.

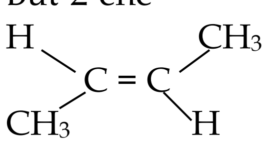
Geometrical isomers arise as a result of a double bond which is planar and does not allow free rotation (restricted rotation) unlike a single carbon bond which freely allows rotation.

Geometrical isomers can therefore be;

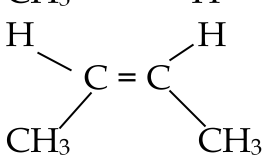
(i) **Cis-geometrical isomer.**
Is when identical groups of atoms are on the same plane of the double bond.

(ii) **Trans-geometrical isomer.**
Is when identical atoms are rotated on opposite planes of the double bond.

But-2-ene

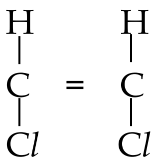


Trans but-2-ene.

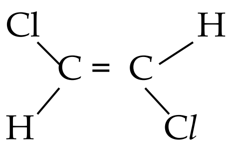


Bis but-2-ene

1, 2-dichloro ethene.

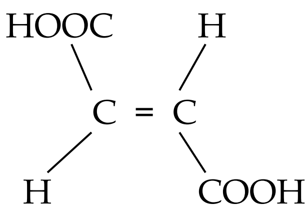


Cis 1,2 dichloro ethene.

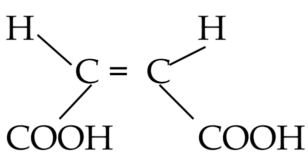


Trans 1, 2 dichloro ethene

Butene-1, 4-dioc acid



Trans butane-1, 4-dioc acid.



Cis butane- 1, 4-dioc acid

OPTICAL ISOMERISM

Type of isomerism that arises when two or more compounds with the same molecular or structural formula have got different optical properties in rotating the plane of polarized light.

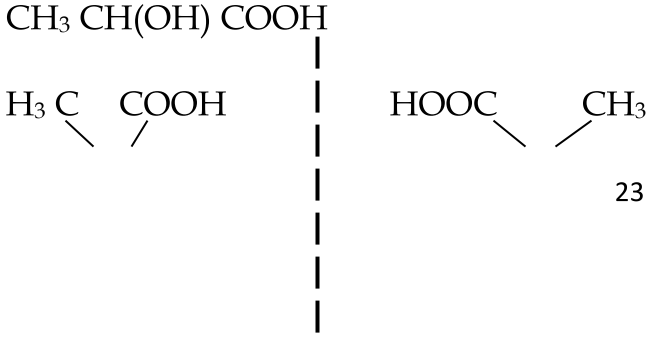
The optical isomers are usually not super imposable onto each other and they have got marked differences in the physical and chemical properties.

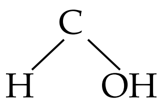
For any optical isomers to exist, they must have a must have a mirror image of each other and rotating a plane of polarized light either to the right or to the left.

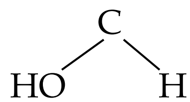
When an isomer rotates light to the right, it is known as **DEXTROROTARY** (D-isomer) (+ve isomer).

When it rotates light to the left, it is known as **LEVOROTARY** (L-isomer or –ve isomer). E.g. lactic acid (2-hydroxy propanoic acid).

CH_3 CH(OH) COOH



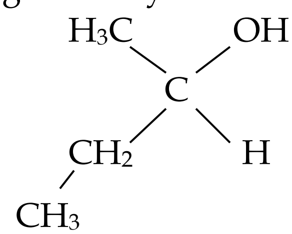




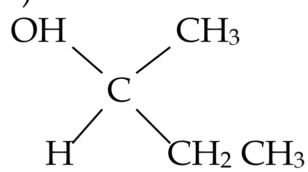
D-isomer (L-isomer)

CONDITIONS OF GEOMETRICAL ISOMERS

A compound must have asymmetrical centre. This is a centre joined by four different groups of atoms and that carbon centre is said to be asymmetric carbon. E.g. 2-methyl butan-2-ol (amyl alcohol).



L-isomer



D-isomer

Ways of writing organic compounds

(i) Using carbon-carbon bonds.

$H_3C - CH_2 - CH_2 - CH_3$ Butane.

$H_3C - CH = CH - CH_2 - CH_3$ Pent-2-ene.

(ii) Plainly illustrating atom.

$CH_3\ CH_2\ CH_2\ CH_3$ Butane.

$CH_3(CH_2)_2\ CH_3$ Butane.

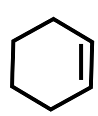
(iii) Using the molecular formula.

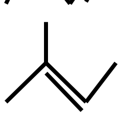
C_4H_8	Butene
C_6H_6	Benzene
$C_6H_5NO_2$	Nitrobenzene.

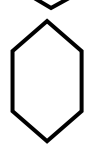
(iv) Using skeletal structure.

(a)  Pentane

(b)  Hex-3-ene.

 Cyclohexene.

(c)  2-methyl but-2-ene

 Cyclohexane.

Note: No. (iv) is not commonly used at A′ level.

ORGANIC REACTIONS

Generally most organic reactions are slow compared to inorganic reactions. At the same time, they yield different product depending on the conditions of reaction. When considering a particular organic reaction, conditions at which it takes place must be specified.

TYPES OF ORGANIC REACTIONS.

There are several types of organic reactions, categorized under different ways.

Bond breaking in organic reaction.

There are two ways in which bonds can be broken in organic reactions.

(a) **Heterolytic fission.**

Here an organic bond is broken and the resulting electrons within a broken bond are then taken up by one atom giving rise to ions. E.g.

Ione pair of electrons.

$$CH_3 - Cl \longrightarrow {}^{+}CH_3 + :Cl^-$$

$$A \div B \longrightarrow \underbrace{A^+ + :B^-}_{\text{Ions.}}$$

(b) **Homolytic fission**

Type of bond breaking where by the resulting electrons in the broken bond are equally shared by the two atoms. This results into atoms with unpaired electrons which are called free radicals. E.g.

$$A - B \longrightarrow \underbrace{A^{\bullet} + B^{\bullet}}_{\text{Free radicals}}$$

$$CH_3 - H \longrightarrow \underbrace{{}^{\bullet}CH_3 + H^{\bullet}}_{\text{Free radicals.}}$$

TYPES OF ORGANIC REACTIONS

1. **ELECTROPHILLIC ADDITION REACTIONS**

Electrophillic addition reactions are reactions in which an electrophille is added to a reacting substrate (molecule).

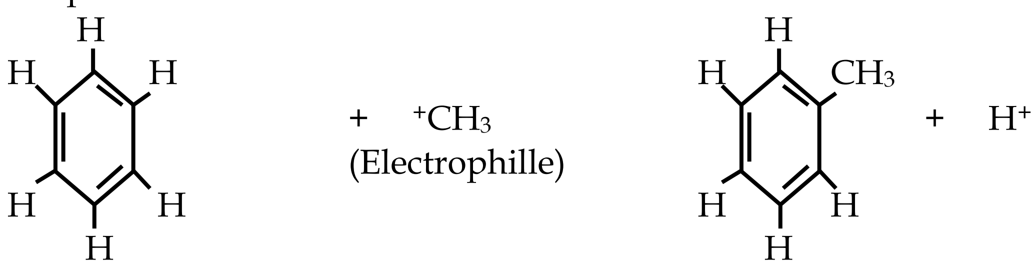
An electrophille is an electron seeking species or atoms. Electrophilles are usually positively charged. E.g. $^{+}NO_3$, ^{+}Cl, $^{+}CH_3$.

Examples:

$CH_2 = CH_2 + Cl - Cl \longrightarrow Cl\text{-}CH_2 - CH_2 - Cl.$

2. **ELECTROPHILLIC SUBSTITUTION REACTION.**

Type of organic reaction where an electrophille is substituted by another electrophille.



$^{+}CH_3$ substitutes H^{+}.

3. **SUBSTITUTION NUCLOEPHILLIC REACTIONS**

Type of organic reaction where a nucleophille replaces another nucleophille in a reacting molecule.

A nucleophille is a species or group of atoms that seek for the positive centre of the reacting molecule. They either be negatively charged e.g. $:\bar{O}H$, $:Cl^{-}$, $:Br^{-}$ or neutral (uncharged). E.g. $H_2O:$, $:NH_3$.

All nucleophilles must have a lone pair of electrons.

$CH_3\,CH_2\,CH_2 - Cl + :\bar{O}H \longrightarrow CH_3\,CH_2\,CH_2 - OH + :Cl^{-}.$

Nucleophillic substitution reactions can either be;

(i) Substitution nucleophillic biomelecular (SN_2). Here two molecules are involved in the rate determining step of the reaction.

OR:

(ii) Substitution nucleophillic unimilecular (SN_1). Here only one molecule is involved in the rate determining step of the rnx.

4. Elimination reactions (E).

These are reactions where an atom is completely removed from the molecule. This always results into the formation of a double or multiple bond. E.g.

$$CH_3\overset{\overset{Cl}{|}}{C}H\,CH_3 \longrightarrow CH_2 = CH\,CH_3 + Cl^- + H^+.$$

NOTE: Elimination reactions can also be biomolecular (E_2) or unimolecular (E_1).

FACTORS THAT AFFECT ORGANIC REACTIONS.

(i) Conditions of temperature.

Temperature affects a number of organic reactions and therefore when writing those reactions, temperature has got to be specified.

(ii) **Nature of the solvent.**

The nature of the solvent used affects the type of organic reaction e.g. aqueous condition, organic solvent condition. E.g.

$$CH_3CH_2 - Cl + \overset{-}{O}H_{(aq)} \xrightarrow{heat} CH_3CH_2OH + :Cl^-$$

$$CH_3CH_2 - Cl + \overset{-}{O}H \xrightarrow[Heat]{Ethanol} CH_2 = CH_2.$$

(iii) **The structure of the reacting molecule**.

The structure of the reacting molecule can affect the organic reaction in several ways like.

(a) Steric hindrance.

A condition in which the surrounding alkyl groups prevent a reagent from attaching the reaction centre e.g.

$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}} \quad < \quad H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C^+}} \quad < \quad H-\overset{\overset{CH_3}{|}}{C^+}-H$$

Tertiary Carbocation	Secondary Carbocation	Primary Carbocation

(b) Electronegativity

$$\overset{\delta+}{CH_3} - \overset{\delta-}{Cl} > \overset{\delta+}{CH_3} - Br > \overset{\delta+}{CH_3} - \overset{\delta-}{I}$$

(c) Bond length.

Usually longer bonds are easily broken than the shorter ones. If a reaction proceeds by breaking a particular bond, a longer bond can then easily be broken than a smaller one.

MECHANISM OF REACTIONS

A mechanism of an organic reaction is an illustration by showing the flow of electrons from one centre to another. This flow is normally illustrated by means of curled arrows.

When a double headed arrow is used, it implies two electrons flowing i.e. and when a single headed arrow is used, it implies one electron i.e. .

The arrow must always begin at the centre of the double bond where electrons are positioned and ends where electrons are deficient or it must begin at the centre of a lone pair of electrons. E.g.

Electron rich

(i) $CH_2 = CH_2$ $\quad Br^+$ - Electron deficient centre.

(ii) $Cl - Cl \longrightarrow 2Cl^{\bullet}$

(iii) $H_2O\!:$

$\quad {}^{+}CH_2 - CH_3 \longrightarrow H_2O^+CH_2CH_3$

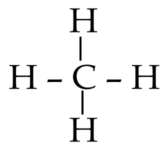
ALKANES

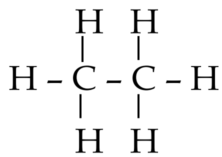
These are saturated hydrocarbons containing carbon and hydrogen elements only joined by a single covalent bond.

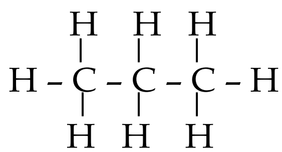
The open chain hydrocarbons (alkanes) have got a general formula of C_nH_{2n+2} where n = a whole number.

Functional group of all alkanes is a carbon - carbon "C- C" single bond where all the four valency electrons of carbon are involved in the bonding.

Examples:

n = 1 CH_4  Methane

n = 2 C_2H_6  Ethane

n = 3 C_3H_8  Propane

NOMENCLATURE

Alkanes are named as saturated hydrocarbons by adding the suffix-ane on the stem name of the parent hydrocarbon.

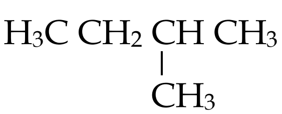
The parent hydrocarbon indicates the number of carbon atoms.

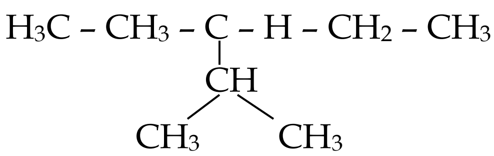
Number of carbon atoms	Parent name	Alkane
n = 1	Meth	Methane
n = 2	Eth	Ethane
n = 3	Prop	Propane
n = 4	But	Butane
n = 5	Pent	Pentane
n = 6	Hex	Hexane

The branches on the parent chain must be indicated together with their positions.

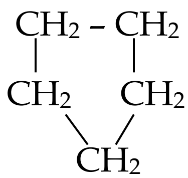
For cyclic alkanes, the word cyclo has got to be written before the parent name.

$H_3C\ CH_2\ CH_2\ CH_3$ n – Butane.

 2-methyl butane.



3-isoprophyl pentane

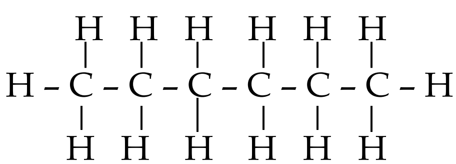


Cyclo pentane

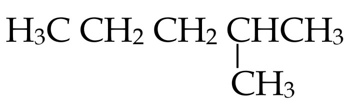
ISOMERISM IN ALKANES

Alkanes exhibit structural isomerism specifically chain isomerism where the isomers differ in the chain.

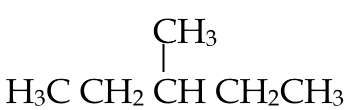
C_6H_{14}



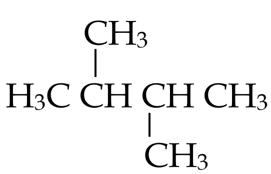
n - hexane



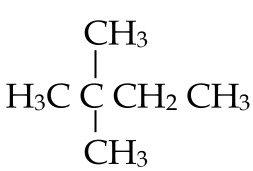
2-methyl pentane



3-methyl pentane



2, 3-dimethyl butane



2, 2-dimethyl butane

PREPARATIONS OF ALKANES

1. **FROM UNSATURATED HYDROCARBONS**

Alkanes are prepared by reduction of unsaturated hydrocarbons e.g. alkenes and alkynes.

When an alkene is reacted with H_2, in the presence of a suitable catalyst like nickel at 150^oC, platinum (Pt) and paradium (Pd) at room temperature, an alkane is formed.

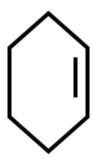
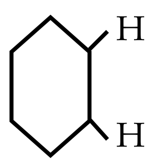
Alkynes also undergo the same reaction except that excess H_2 is required.

$CH_2 = CH_2 + H_2 \xrightarrow[150^oC]{Ni} CH_3{}^-CH_3$

Ethene Ethane

$CH_3CH = CH_2 + H_2 \xrightarrow[r.t.p]{Pt} CH_3CH_2CH_3$

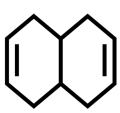
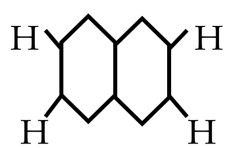
Propene Propane

 + $H_2 \xrightarrow[r.t.p]{pd}$ 

Cyclohexene Cyclohexane

$CH_3C{\equiv}CH \ + \ 2H_2 \xrightarrow{Pt} CH_3CH_2CH_3$

Propyne Propane

 $+ \ 2H_2 \xrightarrow[150^oC]{Ni}$ 

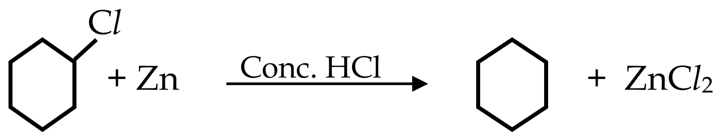
Bicyclo hexa-1, 6-diene Bicyclo hexane

2. **FROM HALOGENO ALKANES (ALKYL HALIDES) (R-X)**

(i) When alkyl halides are reduced with zinc in the presence of conc. HC*l* acid, alkanes are formed.

$CH_3\ CH_2 - Cl + Zn \xrightarrow{Conc.\ HCl} CH_3CH_3 \ + ZnCl_2$

Chloro ethane Ethane



Cyclochloro hexane Cyclohexane

$$CH_3 - \underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3 \xrightarrow{Zn/Conc.HCl} CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_3 + ZnCl_2.$$

2-chlor-2-methyl propane 2-methyl propane.

(ii) When alkyl halides are heated with sodium metal in ether (diethyl ether) alkanes are formed but with increase in carbon chain (doubling the carbon chain). This reaction is known as **Wurtz** reaction and its usually important in organic synthesis when doubling the carbon chain.

$$2CH_3Br \xrightarrow{2Na/ether} CH_3CH_3 + 2NaBr$$

Bromo methane Ethane

$$2CH_3CH_2 - Cl + 2Na \xrightarrow[Heat]{ether} CH_3CH_2CH_2CH_3 + 2NaCl$$

Chloro ethane Butane

$$2CH_3\underset{\underset{CH_3}{|}}{CH} - CH_2 - Cl + 2Na \xrightarrow[heat]{ether} CH_3\underset{\underset{CH_3}{|}}{CH}CH_2CH_2CHCH_3 + 2NaCl$$

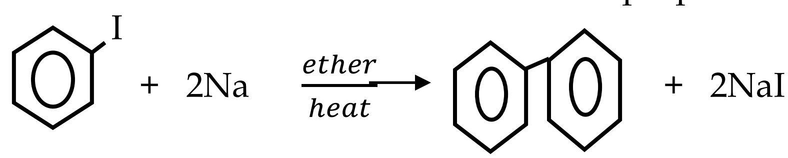
Chloro-3-methyl Propane 2-methyl pentane

$$2CH_3\underset{\underset{CH_3}{|}}{CH}\ CH_2Cl + 2Na \xrightarrow[heat]{ether} CH_3\underset{\underset{CH_3}{|}}{CH}\ CH_2\ CH_2\ \underset{\underset{CH_3}{|}}{CH}\ CH_3 + 2NaCl$$

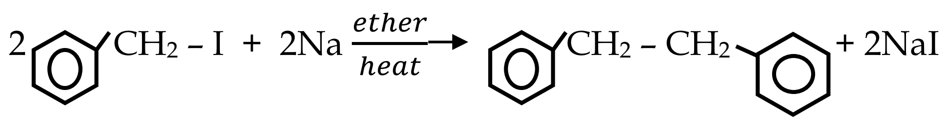
2, 5-dimethyl hexane.

$$CH_3CH_2-Cl + CH_3Cl \xrightarrow[heat]{2NaI\ ether} CH_3CH_2CH_3 + 2NaCl$$

n – propane



Biphenyl

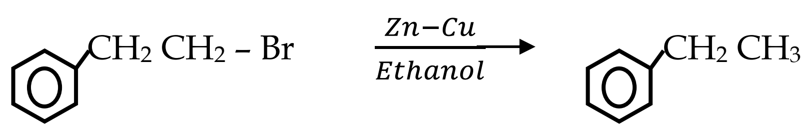


1, 2 biphenyl ethane.

(iii) Reduction using zinc – copper couple.

Alky halides can be reduced using zinc-copper couple in presence of ethanol to give alkane.

$$CH_3CH_2-Cl \xrightarrow[Ethanol]{Zn-Cu} CH_3\,CH_3$$



2 phenyl ethane.

3. **FROM CARBOXYLIC ACIDS AND THEIR SALTS**

Alkanes can be prepared from carboxylic acids or salts of carboxylic acids by reacting with fused sodium hydroxide or soda lime.

(i) From carboxylic acids.

Step I:

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} + NaOH \longrightarrow \underset{\text{Sodium propanoate}}{CH_3\,CH_2\,CO\bar{O}Na^+} + H_2O$$

Step II:

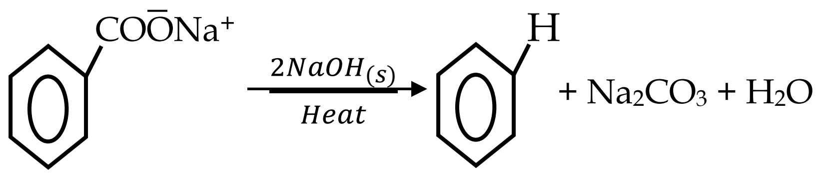
$$CH_3\,CH_2\,CO\bar{O}Na^+ + NaOH_{(s)} \xrightarrow{\Delta} CH_3CH_3 + Na_2CO_3.$$

Ethane

Overall equation:

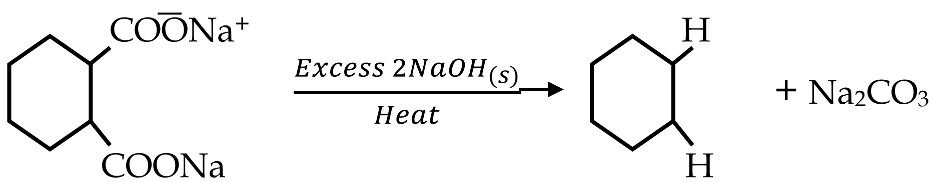
$$CH_3CH_2COOH \xrightarrow[Heat]{Excess\ 2NaOH_{(s)}} CH_3CH_3 + Na_2CO_3 + H_2O.$$

Note: This reaction is very important in organic synthesis by reduction of the carbon chain length by one carbon atom.



Benzene

$$CH_3COOH \xrightarrow[Heat]{Excess\ 2NaOH_{(s)}} \underset{\text{Methane}}{CH_4} + Na_2CO_3 + H_2O$$



Cyclohexane

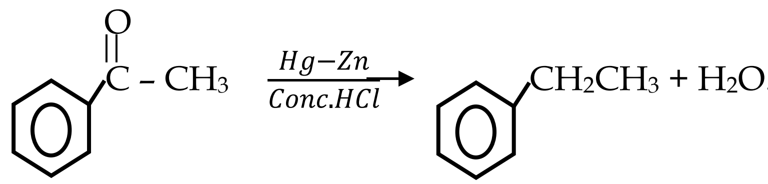
4. **FROM CARBONYL COMPOUNDS**

Reduction of carbonyl compounds using amalgamated zinc produces alkanes in the presence of conc. HC*l*.

Carbonyl compounds are aldehydes and ketones containing an oxygen atom in the carbonyl carbon, (C = O) which is removed by zinc and then given to hydrogen to form H_2O. e.g.

$$\underset{\text{(Ethanal aldehyde)}}{CH_3 - \overset{\overset{O}{||}}{C} - H} \xrightarrow[Conc.HCl]{Hg-Zn} \underset{\text{Ethane}}{CH_3CH_3 + H_2O.}$$

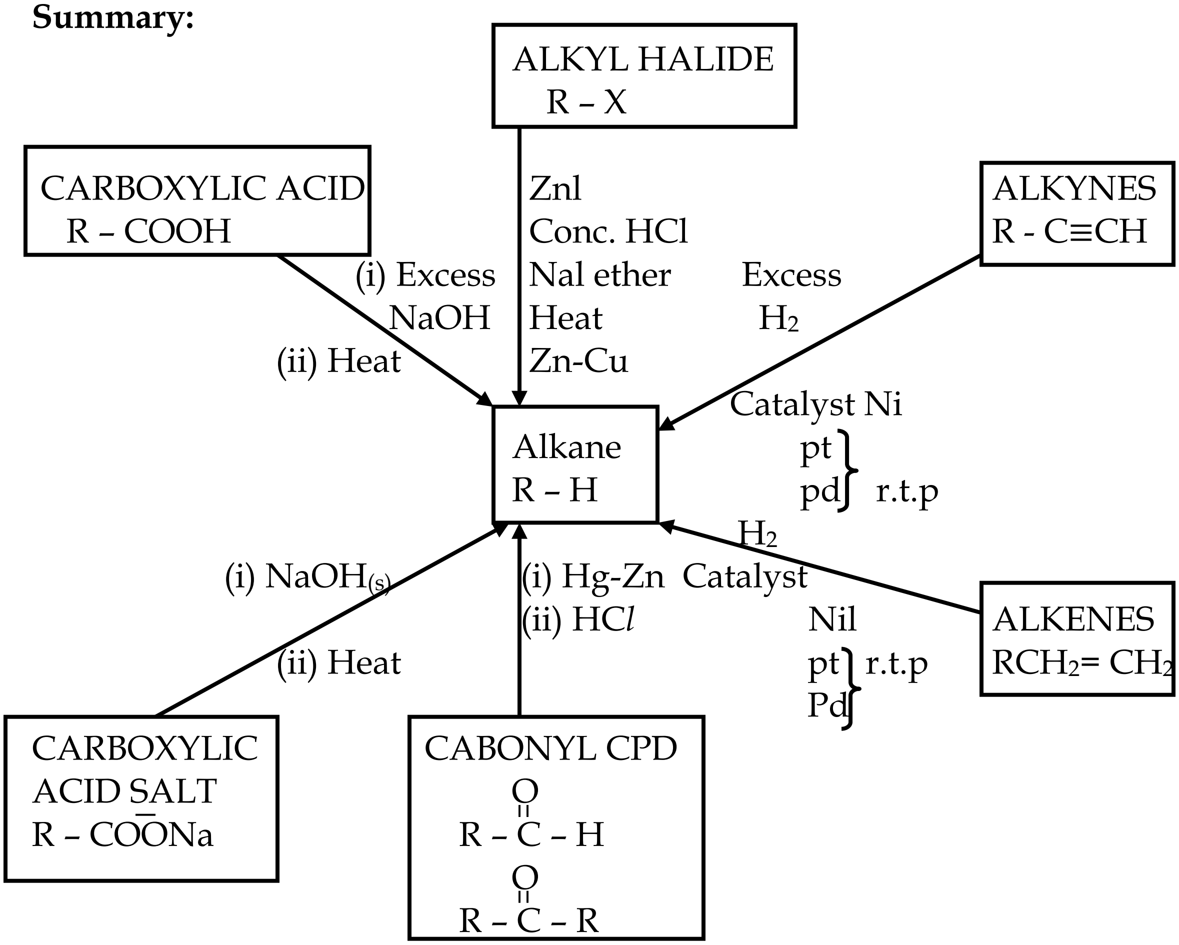
$$CH_3-\overset{\overset{\large O}{||}}{C}-CH_3 \xrightarrow[Conc.HCl]{Hg-Zn} CH_3CH_2CH_3 + H_2O.$$



5. **CRACKING OF HIGHER ALKANES**

When higher alkanes are heated under high temperatures, they break down into shorter alkanes and sometimes alkenes are also formed.

Summary:



Question:

Convert $CH_2 = CH_2$ to CH_4.

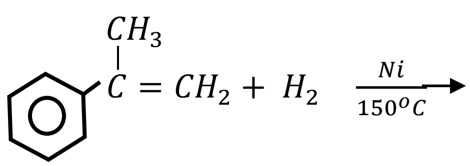
$$CH_2 = CH_2 + HCl \longrightarrow CH_3CH_2Cl \xrightarrow[Heat]{NaOH_{(s)}} CH_3CH_2OH \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+(aq)} CH_3COOH \xrightarrow[Heat]{Excess\ NaOH} \boxed{CH_4 + Na_2CO_3}$$

$$CH_2 = CH_2 \xrightarrow[Heat]{H_2O/H^+} CH_3CH_2OH \xrightarrow[Heat]{Cr_2O_7^{2-}(aq)\ H^+(aq)} CH_3COOH \xrightarrow[Heat]{Excess\ NaOH_{(s)}} \boxed{CH_4 + Na_2CO_3}$$

Complete the following equations, writing the IUPAC name of the main product.

1. $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COOH \xrightarrow[Heat]{Excess\ NaOH_{(s)}}$

2. $CH_3CH_2Cl + 2Na \xrightarrow[heat]{ether}$

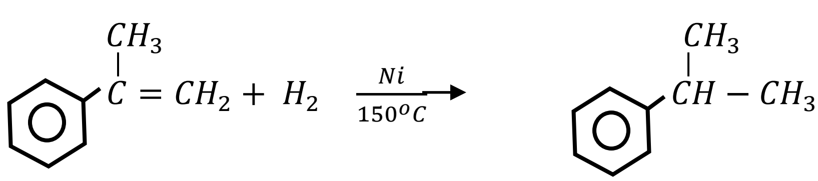
3. 

4. $CH_3CH_2 - Br \xrightarrow[Ethanol]{Zn-Hg}$

Solutions:

1. $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COOH \xrightarrow[Heat]{Excess\ NaOH_{(s)}} CH_3 + CH_2 + CH_3 + Na_2CO_3 + H_2O.$
   n - propane

2. $CH_3CH_2Cl + 2Na \xrightarrow[heat]{ether} CH_3CH_2CH_2CH_3 + 2NaCl.$
   n – Butane

3. 

2-methyl-2-phenyl ethane

4. $CH_3CH_2 - Br \xrightarrow[Ethanol]{Zn-Hg}$ CH_3CH_3

n – ethane.

PROPERTIES OF ALKANES

PHYSICAL PROPERTIES

(a) **Nature:**

Lower alkanes exist as gases ($C_1 - C_3$) exist as gases at room temperature. This is because they have got low boiling points.

The medium ($C_4 - C_9$) exist as liquids. Higher alkanes are greater than C_{10} exist as solids at room temperature.

(b) **Boiling and melting points:**

Generally the boiling points and melting points of alkanes are lower than corresponding compounds like alcohols, carboxylic acids.

Explanation:

Alkane molecules are held by weak Vander Waal's forces of attraction while corresponding alcohols and carboxylic acids are held by relatively strong hydrogen bonding.

Within alkanes, the boiling point generally increases with the increase in molecular weight.

Ethane (30) boils at lower temperature than Butane (56).

Explanation:

Increase in the molecular weight increases the size of the molecules which correspondingly increases the Vander Waal's forces of attraction. That is why butane (56) boils at a higher temperature than ethane (30).

However, when branching is considered e.g. pentane.

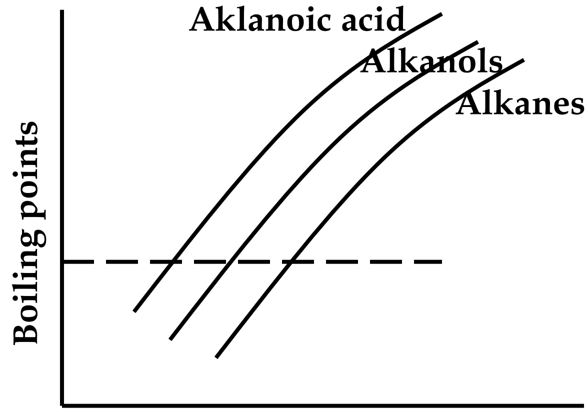
$CH_3CH_2CH_2CH_2CH_3$ *and* $H_3C - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - CH_3$

mm = 72 (n – pentane) mm = 72 (2, 2-dimethyl propane)

2, 2-dimethyl propane boils at a lower temperature than n-pentane yet both are of the same molecular weight.

Explanation:
2, 2-dimethyl propane is highly branched giving it a spherical shape which reduces its size and weaker Vander Waal's forces of attraction will exist between the molecules. While normal pentane is a straight chain molecule which gives the molecule an extended structure resulting into relatively stronger Vander Waal's forces.

A SKETCH SHOWING BOILING POINTS OF ALKANES, ALCOHOL AND CARBOXYLIC ACIDS



Assignment:
The boiling points of alkanes with even and odd number of carbon atoms are not the same.
(i) Identify how they differ
(ii) Explain the above difference.

COMBUSTION OF ALKANES
Alkanes usually burn in air to give CO_2 *and* H_2O only and a lot of heat is produced. This explains why alkanes are used as fuels in domestic and industrial use. E.g. methane is an example of a bio gas that explodes readily to give heat.

Gasoline usually contains propane or butane used in domestic and industrial heating and also to run auto-mobile.

$CH_4 + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)} + Heat$

$$C_3H_8 + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(l)} + Heat$$

REACTIONS WITH HALOGENS IN PRESENCE OF (UV) LIGHT OR HEAT

Alkanes are generally unreactive but in the presence of UV radiations (like sunlight), alkanes react with chlorine to form chloro alkane. This is an example of a substitution reaction where H_2 atoms are substituted by chlorine atoms following a free radical mechanism.

A free radical mechanism is a type of reaction where free radicals are involved.

A free radical is a chemical species with unpaired electrons and it is always very unstable but reactive. E.g.

$$CH_4 + \overset{\textbf{Excess}}{4Cl_2} \xrightarrow{UV} CCl_4 + 4HCl$$

$$CH_3CH_3 + \overset{\textbf{Excess}}{Cl_2} \xrightarrow{UV} CH_3\,CCl_3 + 3HCl$$

$$CH_4 + \overset{\textbf{Limited}}{Cl_2} \xrightarrow{\text{UV}} CH_3Cl + HCl$$

The above reaction is a chain reaction where the products formed become the reactants of the next step.

Therefore, the reaction can then be divided into three;

(i) Initiation step
(ii) Propagation step
(iii) Termination step

INITIATION STEP

$$CL_{2(g)} \xrightarrow{UV} 2Cl^{\bullet}$$

Formation of free radicals using UV. i.e.

$$Cl - Cl \xrightarrow{\text{UV}} \underset{\text{(Free radical)}}{2Cl^{\bullet}}$$

PROPAGATION STEP

Here the free radicals generated react with neutral molecules to form new radicals.

$$H-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H + Cl^{\bullet} \longrightarrow {}^{\bullet}CH_3 + HCl$$

$${}^{\bullet}CH_3 + Cl-Cl \longrightarrow CH_3Cl + Cl^{\bullet}$$

$$Cl-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-H + Cl^{\bullet} \longrightarrow {}^{\bullet}CH_2 + HCl$$

$${}^{\bullet}CH_2 + Cl-Cl \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

$$H-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-H + Cl \longrightarrow {}^{\bullet}CH\,Cl_2 + HCl$$

$${}^{\bullet}CHCl_2 + Cl-Cl \longrightarrow CH\,Cl_3 + Cl^{\bullet}$$

$$Cl-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-H + Cl-Cl \longrightarrow {}^{\bullet}CCl_3 + HCl$$

TERMINATION

$${}^{\bullet}CCl_3 + {}^{\bullet}Cl \longrightarrow CCl_4$$

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$${}^{\bullet}CCl_3 + {}^{\bullet}CCl_3 \longrightarrow Cl_3CCCl_3$$

Note: The above reaction yields a mixture of products and therefore it might be very good in the synthesis of organic compounds. E.g. the above produces a mixture of compounds like chloro methane, Di chloro methane, tri chloro methane, tetra chloro methane.

However, the extent of reaction is determined by the amount of chlorine present.

NITRATION

Alkanes react with HNO_3acid vapour (heated HNO_3acid) to form Nitro alkanes, unlike chlorination, in this reaction only one hydrogen atom is substituted by the nitro group.

$$CH_4 + HNO_3 \xrightarrow{\text{Heat}} \underset{\text{Nitro methane}}{CH_3NO_2} + H_2O$$

$$CH_3CH_3 + HNO_3 \xrightarrow{\text{Heat}} \underset{\text{Nitro ethane}}{CH_3CH_2NO_2} + H_2O$$

MECHANISM

$$HO - NO_2 \xrightarrow{Heat} \underbrace{HO^{\bullet} + {}^{\bullet}NO_2}_{\text{Free radicals}}$$

$$\text{C} - \underset{\text{H}}{\overset{\text{H}}{\text{C}}} - \text{H} + {}^{\bullet}\text{OH} \longrightarrow \text{H}_3\text{C}^{\bullet} + \text{H}_2\text{O}$$

$$H_3C^{\bullet} + NO_2 \longrightarrow CH_3NO_2$$

Petroleum industry

- How petrol is formed (distribution of petroleum)
- Cracking of alkanes (thermal cracking)
- Products of a petro – chemical industry.
- Uses of alkanes – fuels, solvents.

ALKENES

Alkene are unsaturated hydro carbons consisting of a carbon-carbon double bond (- C = C -) as the functional group.

All members in alkene homologous series conform to the general formula C_nH_{2n}.

```
H       H
 \     /
  C = C
 /     \
H       H
```

Ethene

C_2H_4

```
    H   H   H
    |   |   |
H – C – C = C
    |       |
    H       H
```

Propene

C_3H_6

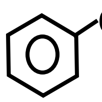
NOMENCLATURE

Alkenes are named as derivations of alkanes by removing the suffix "ane" and replacing it with "ene". E.g.

$CH_2 = CH_2$ Ethene

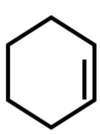
$CH_3\ CH = CH_2$ Propene

$CH_3\underset{|}{C}H\ CH = CH_2$ $3 - $methyl butene
$\quad CH_3$

 $CH = CH_2$ n – phenyl ethene

```
      CH3
      |
H3C – C = C – CH3
  |
  CH3
```

2, 3-dimethyl but-2-ene

 Cyclo Hexene

$CH_3CH = CH\ CH_3$ but-2-ene

$CH_3CH_2CH_2CH = CH_2$ n – pentene

ISOMERISM

Alkenes exhibit four types of isomerism i.e.

(i) **Chain isomerism**

Examples: C_4H_8

$CH_3CH_2CH = CH_2$ n – but-1-ene

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$ 2-methyl prop-l-ene

(ii) **Position isomerism**

These differ by the position of the double bond.

E.g. C_5H_{10}.

$CH_3CH_2CH_2CH = CH_2$ pent-l-ene

$CH_3CH = CH\ CH_2\ CH_3$ pent-2-ene

(iii) Ring isomerism

Isomers differ by the shape of the carbon skeleton. Alkene and clyclo-alkanes are isomeric.

E.g. C_4H8

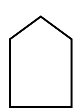
$CH_3CH_2CH = CH_2$ But ene

$$\begin{array}{ccc} CH_2 & - & CH_2 \\ | & & | \\ H_2C & - & CH_2 \end{array}$$

Cyclo butane

C_5H_{10}

$CH_3CH_2CH_2CH = CH_2$ Pentene

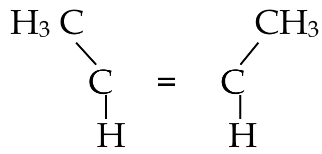


Cyclo-pentane

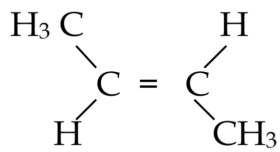
(iv) **Geometrical isomerism**

Compounds differ by the different ways in which the atoms are arranged by the double bond. (restricted rotation of a double bond).

Example: But-2-ene.



Cis but-2-ene

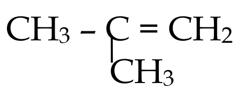


Tans but-2-ene

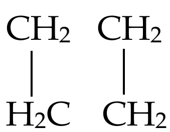
Exercise:

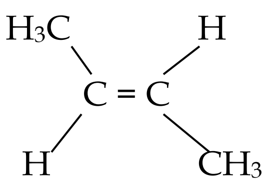
Write all the isomers of C_4H_8

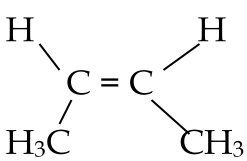
1. $CH_3\ CH_2\ CH = CH_2$ n – but-l-ene

2.  2-methyl prop-l-ene

3. $CH_3CH = CH\ CH_3$ but-2-ene

4.  Cyclobutane

5. 

6. 

1 and 2 are chain isomers
3 and 4 are position isomers
5 is a ring isomers
6 is geometrical isomers

METHODS OF PREPARATION OF ALKENES

Alkenes are prepared from a number of ways:

(i) **From Alkyl halides (Halogeno alkanes)**

When halogeno alkanes are heated with an alcoholic alkaline solution like NaOH or KOH, this reaction is an elimination reaction when both H_2 and the halogen are removed from an alkyl halide to form an alkene as a major product and hydrogen halide as a minor product.

Conditions:

Heat

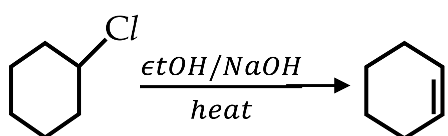
Alcoholic alkali (NaOH or KOH)

E.g. $CH_3CH_2Cl \xrightarrow[heat]{Alcoholic\ /\ KOH} CH_2 = CH_2 + HCl$

Chloro ethane

$CH_3CH_2CH_2\ Br \xrightarrow[Heat]{C_2H_5OH\ /\ KOH} CH_3CH = CH_2 + H\ Br$

Bromo propane — Propene



+ HCl

Cyclo hexene

$$\begin{array}{l} \quad\ CH_3 \\ \quad\ \ | \\ CH_3\text{–}CHCH_2CH_2CH2Br \xrightarrow[heat]{\epsilon t\bar{O}/\epsilon tOH} CH_3CHCH_2CH = CH_2 + HBr \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\ \ | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3 \end{array}$$

(ii) **Dehydration of alcohols**

When alcohol is heated with conc. H_2SO_4 or H_3PO_4 acid in either liquid or vapour phase, an alkene is formed.

Conditions:

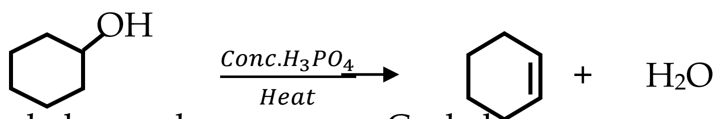
Heat at appropriate temperature depending on the type of alcohol (170 – 180^{o}C).

Concentrated acid

E.g. Liquid phase

$$CH_3CH_2OH \xrightarrow[(175-180)^oC]{Conc.H_2SO_4} CH_2 = CH_2 + H_2O$$

Ethene



Cyclo hexanol Cyclo hexene

$$\underset{\underset{CH_3}{|}}{CH_3\,CH} - OH \xrightarrow[(170-180)^oC]{Conc.H_2SO_4} CH_3CH = CH_2 + H_2O$$

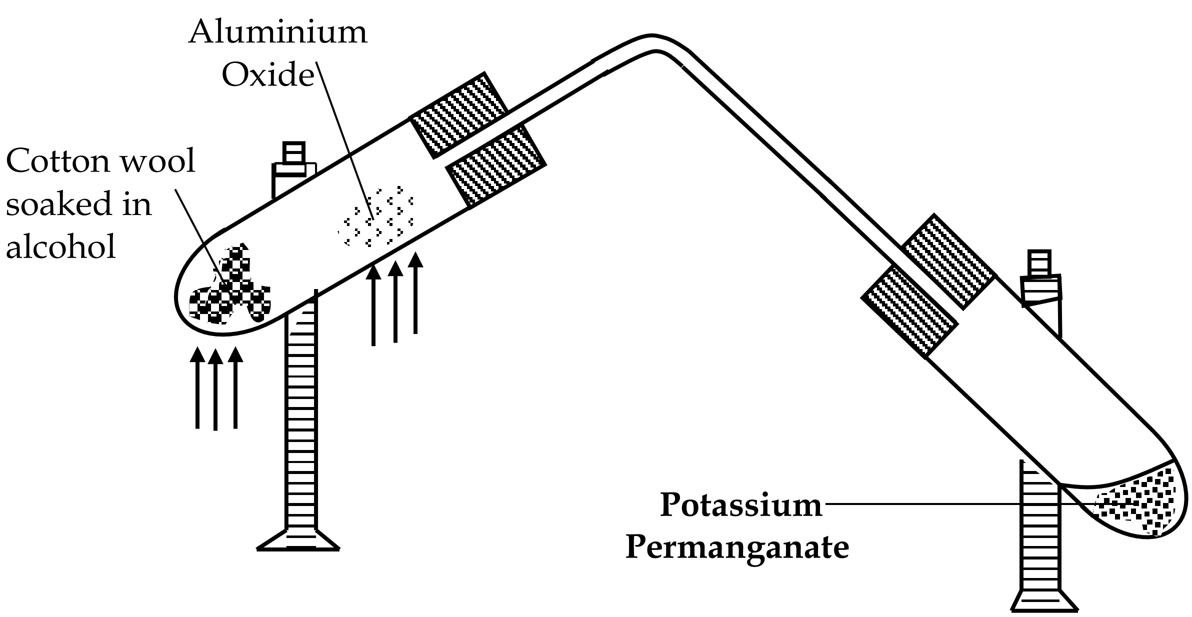
Propan-2-o*l* Propene

$$CH_2CH_2\,\underset{\underset{OH}{|}}{CH}\,CH_3 \xrightarrow[(175-180)^oC]{Conc.H_2SO_4} CH_3CH_2CH = CH_2 + H_2O$$

Butanol butene

VAPOUR PHASE:

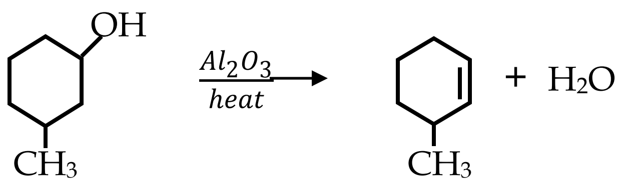
When the vapour of an alcohol generated by heating, the alcohol is passed over heated A*l*$_2$O$_3$ as a catalyst, an alkene is formed.



Observation:
The purple solution of potassium permanganate is decolourised.

E.g.

$$CH_3CH_2OH_{(g)} \xrightarrow[heat]{Al_2O_3} CH_2 = CH_2 + H_2O.$$



3-methyl cyclo hexanol 3-methyl cyclo hexene.

The above reaction is also known as elimination reaction because an alcohol loses a water molecule and it forms an unsaturated compound.

(iii) **Dehydro Halogenations of Vicinal Dihalides**

This is a reaction where there is removal of both hydrogen and halogen atoms from one molecule to form unsaturated compound.

A Vicinal dihalide is a compound with two halogen atoms positioned at adjacent carbon atoms. The structure is shown below.

$$\begin{array}{ccc} X & & X \\ | & & | \\ -C & - & C- \\ | & & | \end{array}$$

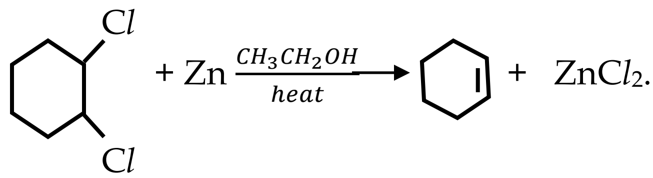
Vicinal is different from a Gem-dihalide.
A Gem-dihalide has got two halogen atoms positioned within the same carbon atom. E.g.

$$\begin{array}{c} X \\ | \\ -C-X \\ | \end{array} \text{ Gem-dihalide}$$

(a) When a vicinal dihalide is heated with zinc in presence of an alcohol, an alkene is formed. E.g.

$$CH_3\underset{}{\overset{\overset{Cl}{|}}{CH}} = \underset{\underset{Cl}{|}}{CHCH_3} + Zn \xrightarrow[heat]{CH_3CH_2OH} CH_3CH = CHCH_3 + ZnCl_2$$

2, 3-dichloro butane



$$CH_3\underset{\underset{Br}{|}}{C}H_3\ \overset{\overset{Br}{|}}{C}H\ CH_3 \xrightarrow[heat]{Zn/Ethanol} CH_3CH = CHCH_3 + ZnBr_2$$

Note: Sodium metal can also be used to give the same products that atoms of sodium are required. E.g.

$$CH_3\underset{\underset{Cl}{|}}{C}H\ \overset{\overset{Cl}{|}}{C}H_2 + 2Na \xrightarrow[heat]{Ethanol} CH_3CH = CH_2 + 2NaCl.$$

(b) **Using gem dihalides**

Higher alkenes are produced but with an increased number of carbon atoms and this reaction is useful in increasing the carbon length during organic synthesis.

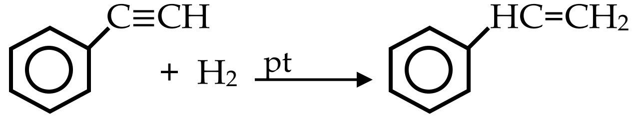
$$2CH_3CHCHCl_2 + 2Zn \xrightarrow{Ethanol} CH_3CH = CHCH_3 + 2ZnCl_2$$

$$2CH_2Cl_2 + 4Na \xrightarrow{Ethanol} CH_2 = CH_2 + 4NaCl$$

(iv) **Partial reduction of alkynes**

When Alkynes are reacted with hydrogen in equi-molar ratio in presence of a heated catalyst like nickel at 150^oC or platinum and palladium at room temperature, an alkene is formed.

$$CH \equiv CH \xrightarrow[150^oC]{Ni\ /\ H_2} CH_2 = CH_2$$



$$CH_3 - \underset{\underset{CH_3}{|}}{C}HC \equiv CH + H_2 \xrightarrow[150^oC]{Ni} CH_3\ \underset{\underset{CH_3}{|}}{C}H\ CH = CH_2$$

CHEMICAL REACTIONS OF ALKENES

Alkenes are generally very reactive compared to alkanes. This is so because alkenes have a double bond consisting of π electrons which can be easily donated to reactants (electrophiles).

A double bond in alkenes is also shorter and stronger; that means its releases high energy compared to a single bond.

Bond	**Energy KJ mol^{-1}**	**Length (mm)**
C – C	346	0.154
C = C	598	0.134

The above make alkenes reactive to electrophiles.

TYPES OF REACTIONS

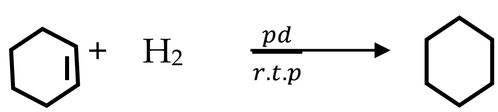
(a) **Addition reactions**

Alkenes undergo addition reactions where a double bond is converted to a single bond.

(i) Hydrogenation (Reduction)

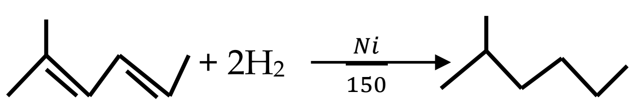
Alkenes react with H_2 in presence of heated catalyst of Nickel at 150^{o}C or platinum and palladium of at room temperature to form alkanes. In this reaction all the hydrogen atoms are added across a double bond.

$$CH_2 = CH_2 + H_2 \xrightarrow[150^oC]{Ni} CH_3CH_3$$



Cyclo hexene Cyclo hexane

$$CH_3\,CH_2\,CH = CH_2 + H_2 \xrightarrow{Pt} CH_3\,CH_2\,CH_2\,CH_3$$



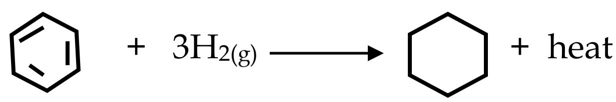
This reaction forms the basis of synthesizing saturated compounds from unsaturated e.g. formation of margarine when unsaturated fats are heated with H_2 in presence of a catalyst to form a fat (margarine).

Determination of stability of compounds like Cis and trans-forms of alkenes, benzene and cyclo – 1, 3, 6 – triene.

$$\underset{\substack{|\\H}}{CH_3\,C} = \underset{\substack{|\\H}}{C}\,CH_3 + H_{2(g)} \xrightarrow[150]{Ni} CH_3CH_2CH_2CH_3 + \text{heat}(28.6KJ)$$

$$CH_3\,\overset{\substack{H\\|}}{C} = CCH_3 + H_{2(g)} \xrightarrow[150]{Ni} CH_3CH_2CH_2CH_3 + \text{heat}(27.6KJ)$$

The Cis form is unstable compared to the trans form.



Mechanism:

$CH_2 = CH_2 + H^{\delta-} - H^{\delta-}\,Pt \longrightarrow CH_3 + +_{CH_2} +\!: H^{-}Pt$

Carbon cation ion

$CH_3 - \overset{+}{C}H_2 \longrightarrow CH_3CH_3$

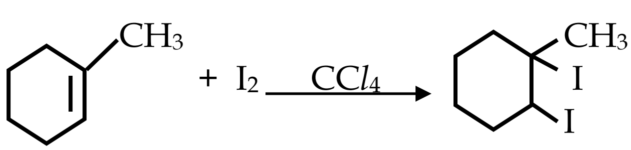
$:H^-$

(ii) Halogenation

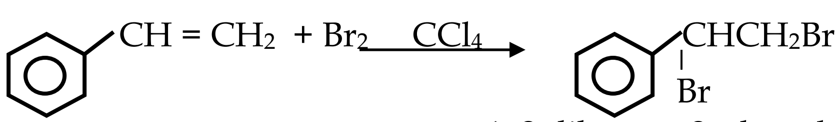
Alkenes react with halogens like Cl_2, Br_2, I_2 in presence of an organic solvent like carbon tetra-chloride to form a dihalide compound.

$$CH_3\,CH = CH_2 + Cl_2 \xrightarrow{CCl_4} CH_3\underset{\substack{|\\Cl}}{C}HCH_2Cl$$

1,2-dichloro propane.



1, 2-di iodo -2-methyl cyclo hexane.

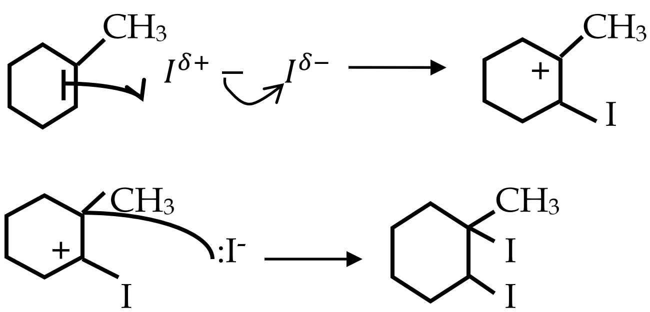


1, 2 dibromo-2-phenyl ethane.

Mechanism:

$$CH_3CH = CH_2 \quad Cl^{\delta+} - Cl^{\delta-} \longrightarrow CH_3{}^{+}CHCH_2Cl + :Cl^{-}$$

$$CH_3{}^{+}CHCH_2Cl \quad :Cl^{-} \longrightarrow CH_3CH(Cl)\,CH_2Cl$$



If the same reaction is done in the presence of H_2O, then the product formed is an hydroxyl halogeno alkane. This is because the OH generated from water is a better nucleophile than the halogen in addition to its presence in excess.

$$CH_2 = CH_2 \xrightarrow{H_2O/Br_2} HOCH_2\,CH_2\,Br$$

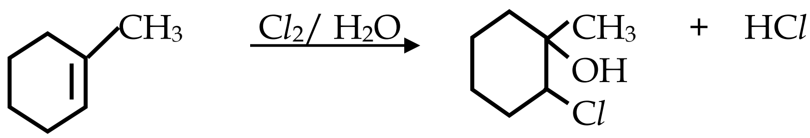
2-bromo ethanol

Mechanism

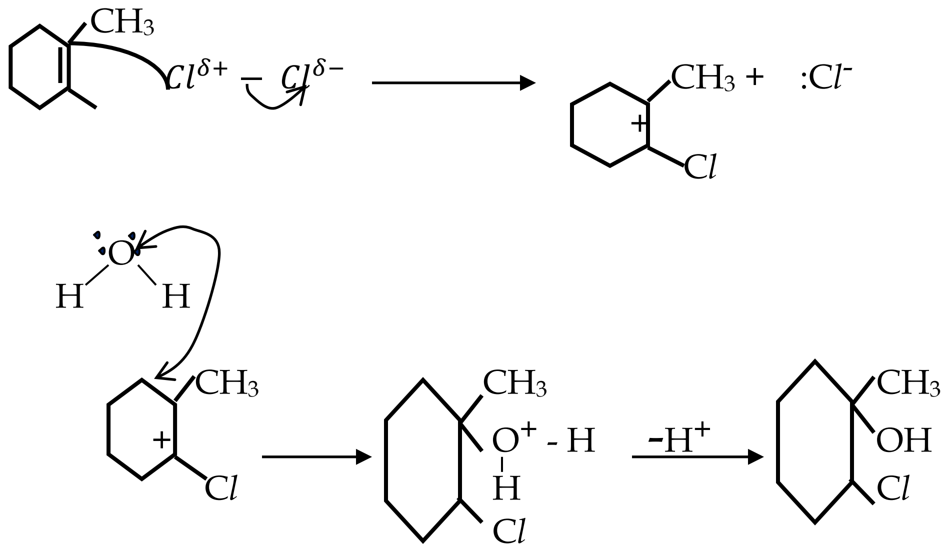
$$CH_2 = CH_2 \quad Br^{\delta+} - Br^{\delta-} \longrightarrow {}^{+}CH_2CH_2Br + :Br^{-}$$

$${}^{+}CH_2 - CH_2\,Br \quad H_2\ddot{O}: \longrightarrow H_2O^{+} - CH_2CH_2Br \xrightarrow{-H+} HOCH_2CH_2Br + H^{+}$$

$$H^{+} + Br^{-} \longrightarrow HBr.$$



Mechanism:



$H^+ + Cl^- \longrightarrow HCl.$

$CH_3CH = CH_3 \xrightarrow{Br_2/H_2O} CH_3CH - CH_2 + HBr.$

Mechanism:

$CH_3CH = CH_2 \longrightarrow CH_3{}^+CH\ CH_2\ Br + Br^-$

$Br^{\delta+} - Br^{\delta-}$

$CH_3{}^+CH\ CH_2\ Br \longrightarrow CH_3\ CH\ CH_2\ Br \xrightarrow{-H^+} CH_3CHCH_2\ Br + H^+$

$:OH_2$ $\qquad$ $H-O-H$ $\qquad$ OH

Alternatively:

$$H_2O + Br_2 \longrightarrow HOBr + HBr$$

$$CH_3\,CH = CH_2 \longrightarrow CH_3\overset{+}{C}HCH_2\,Br + :\bar{O}H$$

$$Br - OH$$

$$\underset{:OH}{CH_3\overset{+}{C}HCH_2Br} \longrightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2Br$$

Reactions with halogen acids (HX)

Alkenes react with halogen acids to form alkyl halides. This reaction is an addition reaction that can proceed into two ways according to the conditions of reaction.

(i) **Electrophillic addition**

This reaction occurs readily in the absence of a peroxide following an ionic mechanism.

(ii) **Free radical mechanism**

This occurs in the presence of a peroxide. In both types of reaction, the products formed are different.

$$CH_2 = CH_2 + HBr \longrightarrow CH_3CH_2Br.$$

Bromo ethane.

$$CH_3CH = CH_2 + HBr \longrightarrow CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$

2-bromo-propane (ionic mechanism)

$$CH_3CH = CH_2 + HBr \xrightarrow[(ROOR)]{peroxide} CH_3CH_2CH_2Br.$$

1-bromo propane (free radical mechanism)

MARKWONIKOFF RULE

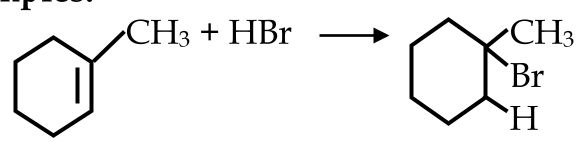
Markwonikoff rule predicts the products formed when halogen acid is reacted with unsymmetrical alkene.

The rule states that addition of a halogen acid to unsymmetrical alkene gives a product where the hydrogen is added to the carbon atom with the lower number of hydrogens and the halogen atom is added to the hydrogen atom across a double bond to a carbon atom with few H_2 atoms.

This reaction is followed in the absence of a peroxide. E.g.
CH_3OOCH_3 (peroxide) or ROOR.

In the presence of a peroxide, anti Makwonikoff's rule applied where the hydrogen from the halogen acid is added to the carbon atom across the double bond with the highest hydrogen atom and the halogen goes to the carbon atom with the least hydrogens.

Examples:

1. 

2. $$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}} = CHCH_3 + HCl \longrightarrow CH_3\,\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}}\,CH_2\,CH_3$$

3. $$CH_3\,CH = CH_2 + HBr \xrightarrow{ROOR} CH_3CH_2CH_2Br$$

4. $$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + HCl \xrightarrow{ROOR} CH_3\,\overset{\displaystyle CH_3}{\overset{|}{CH}}\,CH_2\,Cl$$

MECHANISM (MARKWONIKOFF RULE)

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}} = CH\ CH_3 + HCl \longrightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}} - CH_2\ CH_3$$

$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}} = CH\ CH_3 \quad H - Cl \xrightarrow{\text{slow}} CH_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}} - CH_2CH_3 + :Cl^-$$

$$:Cl^- \qquad CH_3\ \underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}\ CH_2\ CH_3 \longrightarrow CH_3\ \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle Cl}{\overset{|}{C}}}} - CH_2\ CH_3$$

$$CH_3\ \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + HCl \xrightarrow{\text{ROOR}} CH_3\ \overset{\displaystyle CH_3}{\overset{|}{CH}}\ CH_2Cl$$

MECHANISM (ANTI MARKWONIKOFF)

$$\text{ROOR} \xrightarrow{\text{heat}} 2RO^{\bullet}$$

$$RO^{\bullet} + H - Cl \longrightarrow ROH + Cl^{\bullet}$$

$$CH_3\ \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + Cl^{\bullet} \longrightarrow CH_3\ \overset{\displaystyle CH_3}{\overset{|}{\underset{\bullet}{C}}} - CH_2Cl$$

$$CH_3\ \overset{\displaystyle CH_3}{\overset{|}{\underset{\bullet}{C}}}\ CH_2Cl + H - Cl \longrightarrow CH_3\overset{\displaystyle CH_3}{\overset{|}{CH}}\ CH_2Cl + {}^{\bullet}Cl$$

The reactions follow a more stable carbo cation ions in the order of
$3^{\bullet} > 2^{\bullet} > 1^{\bullet}$.

REACTIONS OF ALKENES WITH H_2O IN PRESENCE OF AN ACID(H_2O/H^+(aq)

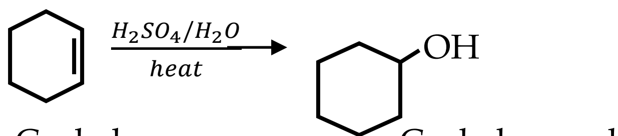
MINERAL ACID WATER

When an alkene is heated with H_2O in presence of H_2SO_4 acid, an alcohol is formed. This reaction is known as hydration of alkenes and is used in the preparation of alcohols.

Example:

1. $CH_3CH = CH_2 \xrightarrow[Warm]{H_2O/H^+} CH_3\underset{\substack{|\\OH}}{CH}CH_3$

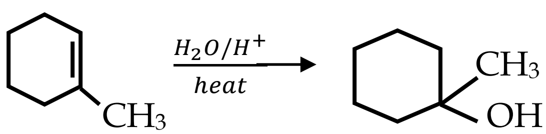
Propane — Propan-2-ol

2. 

Cyclo hexene — Cyclo hexanol

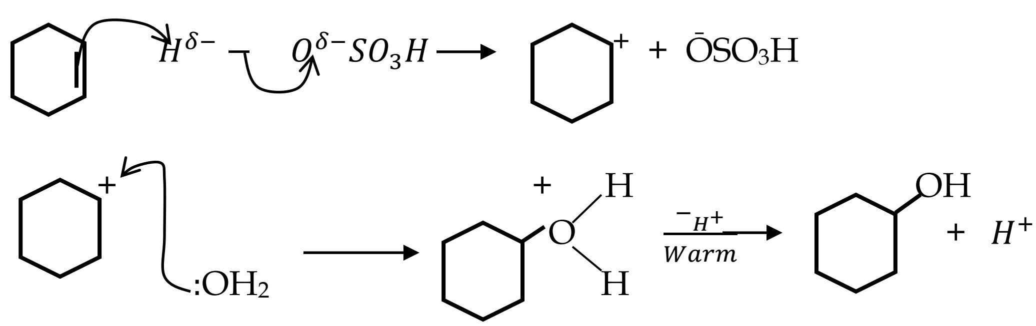
3. $CH_3\underset{\substack{|\\CH_3}}{C} = \overset{\substack{CH_3\\|}}{C}CH_3 + H_2O \xrightarrow[heat]{H^+} CH_3 - \overset{\substack{OH\\|}}{\underset{\substack{|\\CH_3}}{C}} - \overset{\substack{CH_3\\|}}{CH}CH_3$

2-3-dimethyl but-2-ene — 2, 3-dimethyl butan-2-ol

4. 

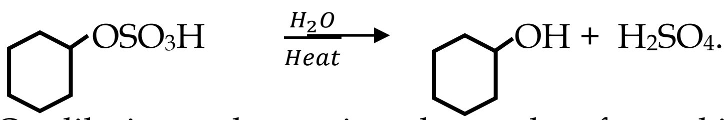
2-methyl cyclo hexene — methyl cyclo hexan-1-ol

Mechanism:



H+ $+ \bar{O}SO_3H \longrightarrow H_2SO_4$.

NOTE: If the reaction is done by first reacting the alkene with the sulphuric acid, the intermediate formed is (Alkyl hydrogen sulphate).



On diluting and warming, the product formed is the alcohol.

$$CH_3\,CH = CH_2 \xrightarrow[heat]{H_2O/H^+(aq)} CH_3\,\underset{\underset{OH}{|}}{C}H\,CH_3$$

Propan-2-ol

Mechanism:

$$CH_3\,CH = CH_2 \;\bullet\; H^+ \longrightarrow CH_3\,{}^+CH\,CH_3$$

$$CH_3\,{}^+CH\,CH_3 \quad :OH_2 \longrightarrow CH_3\,\underset{\underset{H\ +\ H}{\overset{|}{O}}}{C}H\,CH_3 \xrightarrow[Warm]{-H^+} CH_3\,\underset{\underset{OH}{|}}{C}H\,CH_3$$

REACTIONS WITH MOLECULAR O_2.

Alkenes react with molecular O_2 in presence of a heated silver catalyst to form Expoxides. Hydrolysis of expoxides with water produced d-ols.

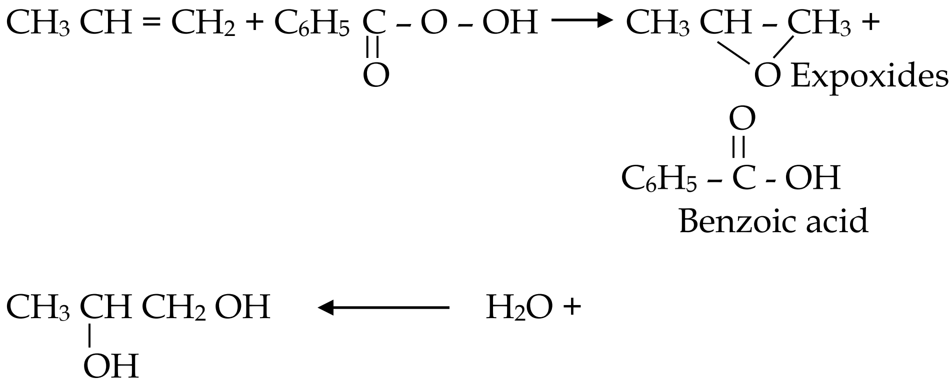
$$CH_3\,CH = CH_2 + O_2 \xrightarrow[250^oC]{2AG} CH_3\,CH - CH_2 + Ag_2O$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \diagdown\ \diagup$$
$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad O$$

Propane expoxide

$$\underset{\diagdown O \diagup}{CH_3\,CH - CH_3} \xrightarrow{H_2O} CH_3\,\underset{\underset{OH}{|}}{C}H\;CH_2\;OH$$

Propanes 1, 2-diol.

This reaction can also occur, when alkenes are reacted with peroxo acids. E.g. Benzene peroxo acid.

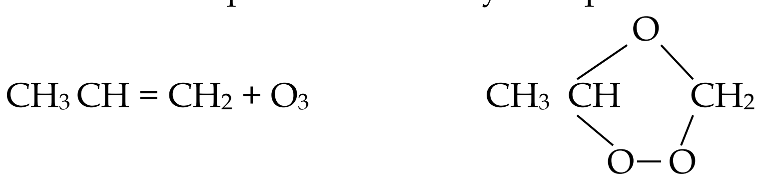


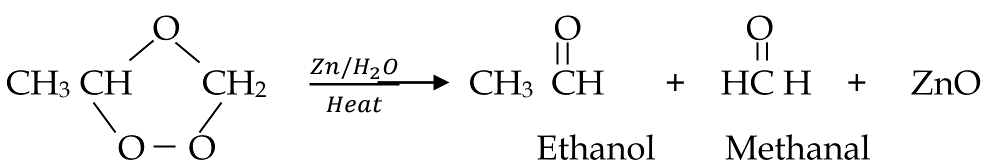
REACTIONS WITH OZONE (O_3)

Alkenes react with ozone to form ozonides hydrolysis of ozonides in the presence of;

$$NaPab \xrightarrow{H_2O} Na^+ + Pab^-$$

Zinc and H_2O produces carbonyl compounds.

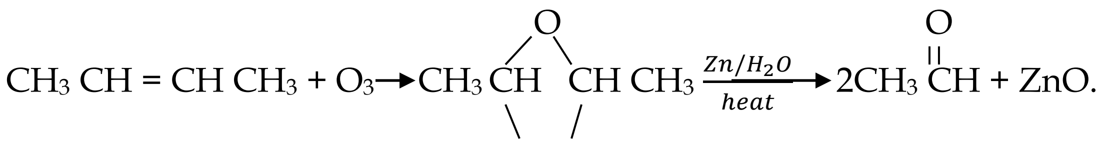




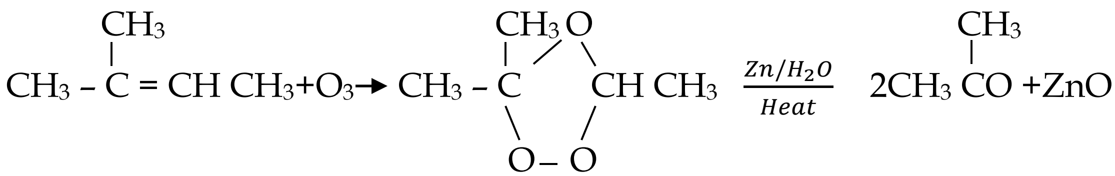
The above reaction is very important in two main ways.

(i) In organic synthesis of converting an alkene to a carbonyl compounds of aldehyde and ketone.

(ii) It is important in the analysis of the structure of the original alkene. If one product is formed after the hydrolysis of the ozonide, then the alkene used is asymmetrical where the double bond is at the centre. But if two products are formed, then the alkene is unsymmetrical.

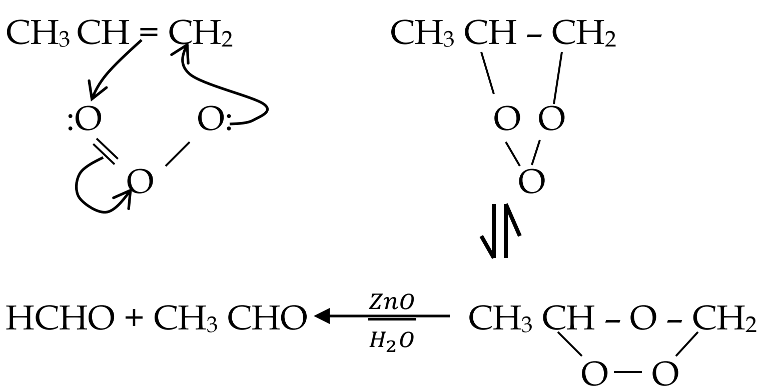


ethanol



$CH_3C(CH_3)=O$ + CH_3CHO

Propanone (Ketone) + aldehyde (Ethanal)



OXIDATION REACTION OF ALKENES

Alkenes undergo oxidation reaction using mild oxidizing agents like Alkaline potassium permanganate to form di-ols.

During this reaction, observation made is that the purple solution mixture, turns colourless (purple solution decolourised).

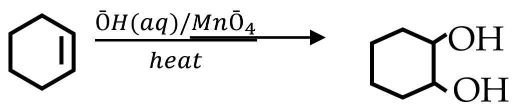
This test indicates the presence of a double bond which is converted to a saturated compound.

$$CH_2 = CH_2 \xrightarrow[heat]{\bar{O}H(aq)/Mn\bar{O}_4} HO - CH_2\,CH_2\,OH$$

Ethene → Ethane-1, 2-diol

$$CH_3\,CH = CH_2 \xrightarrow[heat]{KMnO_4/\bar{O}H} CH_3\,\underset{\large |\atop OH}{CH}\,CH_2\,OH$$

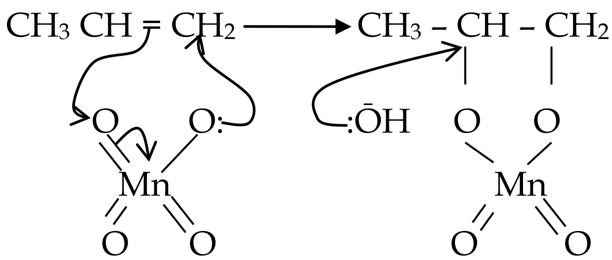
Propane -1, 2- diol



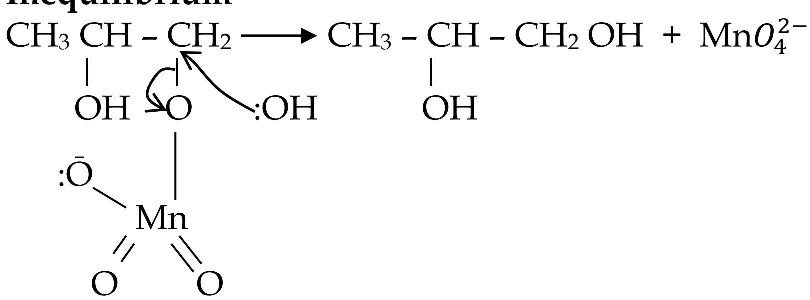
Cyclo hexane-1, 2-diol.

MECHANISM:

$KMnO_4 \longrightarrow K^+_{(aq)}\ Mn\bar{O}_4(aq)$



Inequilibrium



POLYMERISATION
Alkenes undergo polymerisation known as addition polymerisation due to the presence of a double bond, enabling the monomer units to repeatedly combine to form high molecular mass products known as polymers.

During polyermerisation, a catalyst is required in order to initiate the formation of free radicals.

Catalysts popularly used include;
(i) Molecular oxygen/peroxide
(ii) Metallic catalyst.

Example:

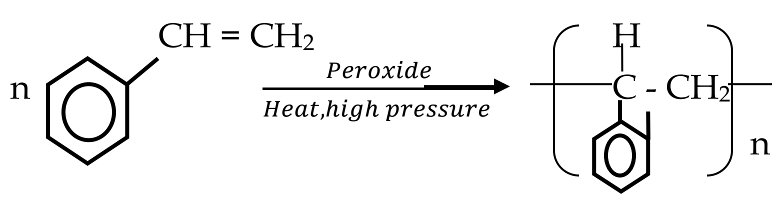
1. $n\ CH_2 = CH_2 \xrightarrow[\substack{Heat\ (high\ temp.)\\ High\ pressure}]{O_2\ Catalyst} +\!\!(CH_2 - CH_2)\!\!+_n$

   Ethene (Monomer) — Polythene (Polymer)

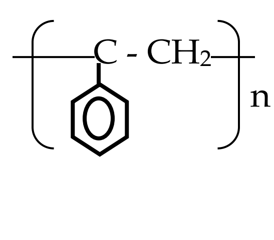
2. $n\ CH_3\underset{\underset{Cl}{|}}{C} = CH_3 \xrightarrow[\substack{High\ temp.\\ High\ pressre}]{O_2 catalyst} \left(\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2\right)_n$

3. $C_l\ CH = CH \xrightarrow[\substack{High\ temp.\\ High\ pressure}]{Peroxide} \left(\underset{\underset{Cl}{|}}{CH} - CH_2\right)_n$

   Xinyl chloride

4. 

   Styrene — Polystyrene



5. $$n\,CH_3\,CH = CH - CH = CH_2 \xrightarrow[Heat]{Catalyst} \left[\underset{\displaystyle CH_3}{\underset{|}{CH}} - CH = CH - CH_2 \right]_n$$

Penta-1, 3-diene — Rubber

6. $$CH_3\,\overset{\displaystyle CH_3}{\overset{|}{C}} = CH - CH_3 \xrightarrow[heat,pressure]{Catalyst} \left[\begin{matrix} CH_3 & \\ | & \\ C & - CH \\ | & | \\ CH_3 & CH_3 \end{matrix} \right]_n$$

7. $$CH_2 = \overset{\displaystyle CH_3}{\overset{|}{C}} - CH = CH_2 \longrightarrow \left[CH\text{-}\ \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2 \right]_n$$

2-methyl Buta-1, 3-diene (Isoprene) — Poly methyl Buta-1, 3-diene.

Mechanism:

$$ROOR \xrightarrow{Heat} 2RO^{\bullet}$$

$$RO^{\bullet}\quad CH_2 = CH_2 \longrightarrow RO - CH_2 - {}^{\bullet}CH_2$$

$$RO\,CH_2\,{}^{\bullet}CH\quad CH_2 = CH_2 \longrightarrow RO\,CH_2CH_2CH_2{}^{\bullet}CH_2$$

$$RO\,CH_2\,CH_2\,CH_2\,{}^{\bullet}CH_2\quad CH_2 = CH_2 \longrightarrow RO\,CH_2\,CH_2\,CH_2\,CH_2\,CH_2{}^{\bullet}CH_2$$

Termination:

$$RO\,CH_2\,CH_2 ---- {}^{\bullet}CH_2\quad {}^{\bullet}CH_2 ---- CH_2\,CH_2\,OR$$

$$RO\,CH_2\,CH_2 --- CH_2\,CH_2 --- CH_2\,CH_2\,OR.$$

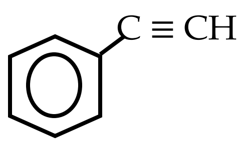
ALKYNES

Alkynes are unsaturated hydro carbons which contain a triple bond in the carbon skeleton as their functional group.

They have a general formula C_nH_{2n-2} where $n \geq 2$.

NOMENCLATURE AND ISOMERISM OF ALKYNES

The name of alkyne is formed by replacing the end n, from the corresponding "ane" with "yne" as shown below.

Alkyne	**IUPAC name:**
$HC \equiv CH$	Ethyne
$CH_3C \equiv CH$	Propyne
$CH_3C \equiv C\ CH$	Butyne
	Phenyl ethyne.
$HC \equiv CC \equiv CH$	Buta-1, 3- diyne.
$CH_3\ \underset{|}{\overset{CH_3}{C}}H\ C\ \ CH$	3-methyl butyne

Alkynes show chain, functional and position isomerism.

PREPARATION OF ALKYNES

(a) Only ethyne can be prepared by the following methods:

(i) Partial combustion of methane, yields ethyne.

$$2CH_4 + O_2 \longrightarrow HC \equiv CH + 4H_2O.$$

(ii) Heating of methane in absence of air at 1500°C also yields ethyne.

$$CH_4 \xrightarrow{1500^oC} C_2H_2$$

(iii) Hydrolysis of calcium carbide also yields ethyne.

$$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2.$$

GENERAL METHODS FOR PREPARATION OF ALKYNES

DIHALOGENATION OF DIHALOGENATED ALKENES

This is done by using alcoholic KOH. It is an elimination reaction in which two moles of halogen acids (HX) are lost e.g.

$$CH_3CH_2\ CH\ CH_2 \xrightarrow[Heat]{KOH/Alcohol} CH_3\ C \equiv CH + KCl + H_2O.$$

$$CH_3\ \underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}\ CH_3 \xrightarrow[Heat]{KOH/Alcohol} CH_3\ C \equiv CH + KCl + H_2O.$$

Mechanism:

$$KOH \longrightarrow K+ \ + \ \bar{O}H.$$

$$CH_3\ CH_2OH + \bar{O}H \longrightarrow CH_3CH_2\ \bar{O} \ + H_2O.$$

$$CH3\ \ \underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}\!-CH_3 \longrightarrow CH_3\ \underset{Cl}{\underset{|}{C}} = CH \longrightarrow CH_3\ C \equiv CH$$

$$H\ \ \bar{O}\ CH_2CH_3 \qquad\qquad H\ \ \bar{O}\ CH_2CH_3$$

TYPES OF ALKYNES

Alkynes are classified according to the position of the triple bond.

(i) Terminal
(ii) Symmetrical
(iii) Unsymmetrical

Examples:

$$\left.\begin{array}{l} CH_3C \equiv CH \\ CH_3CH_2C \equiv CH \end{array}\right\} \begin{array}{l} \text{Terminal/unsymmetrical} \\ \text{Butyne} \end{array}$$

$CH_3C \equiv CCH_3$ Symmetrical but not terminal buta-2-yne.

$CH_3\ C \equiv CCH_2CH_3$ Unsymmetrical but non terminal penta-2-yne.

$CH_3C \equiv CCH_2C \equiv CCH_3$ Hepta-2, 5-diyne.

$CH_3\ \equiv CC\ \equiv CH$ buta-1, 3-diyne.

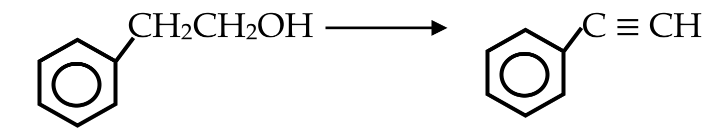
PREPARATION OF ALKYNES

FROM DIHALOGENO ALKANES

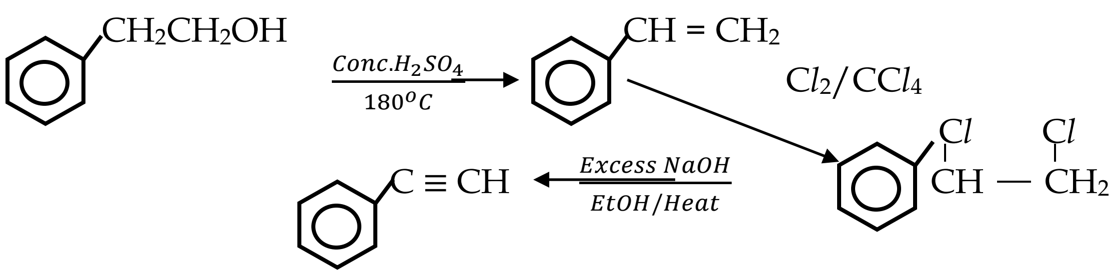
When dihalogeno alkanes are heated with excess alkali in the presence of an organic solvent like ethanol, dehydrohalogenation occurs giving an alkyne.

$$ClCH_2CH_2Cl \xrightarrow[EtOH/heat]{Excess\ KOH} HC \equiv CH.$$

Convert



Phenyl ethynol Phenyl ethyne



Mechanism:

$$CH_3-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_2Cl \xrightarrow[NaOH/Heat]{Excess\ alcholic} CH_3C \equiv CH$$

$$NaOH + EtOH \rightleftharpoons Et\bar{O}Na^+ + H_2O$$

$$Et\bar{O}Na^+ \longrightarrow Et\bar{O}: + Na^+.$$

$$CH_3\ \overset{Cl}{\underset{H}{C}}-\ CH_2-Cl \longrightarrow CH_3-\overset{Cl}{C}=\overset{H}{\underset{H}{C}} \longrightarrow CH_3C \equiv CH$$

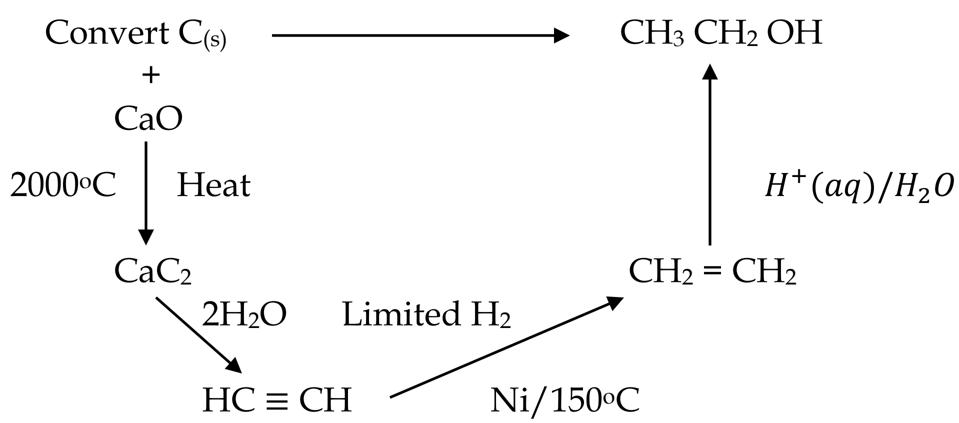
$Et\bar{O}:$ $Et\bar{O}:$

(ii) **From CaO.**

This method is specifically for ethyne.

$$CaO_{(s)} + 3C_{(s)} \xrightarrow[2000^oC]{Heat} CaC_2 + CO_{(g)}$$

$$CaC_{2(s)} + 2H_2O_{(s)} \longrightarrow HC\equiv CH + Ca(OH)_2$$



(iii) **From alkane (CH ≡ CH)**

Partial oxidation of alkanes.

$$CH_4 + \tfrac{1}{2}\,O_2 \longrightarrow HC\equiv CH + H_2O$$

$$2CH_4 \xrightarrow[1500^oC]{} CH\equiv CH + 3H_2$$

Thermal cracking

REACTIONS OF ALKYNES

(i) **Electrophilic addition**

Is where an electron seeking species is added across a triple bond. Alkynes are very reactive because of the presence of π electrons in a triple bond. This reaction is essentially like that of alkenes, however, 2moles of the electrophile are required to saturate an alkyne.

(ii) **Addition of halogen (X_2)**

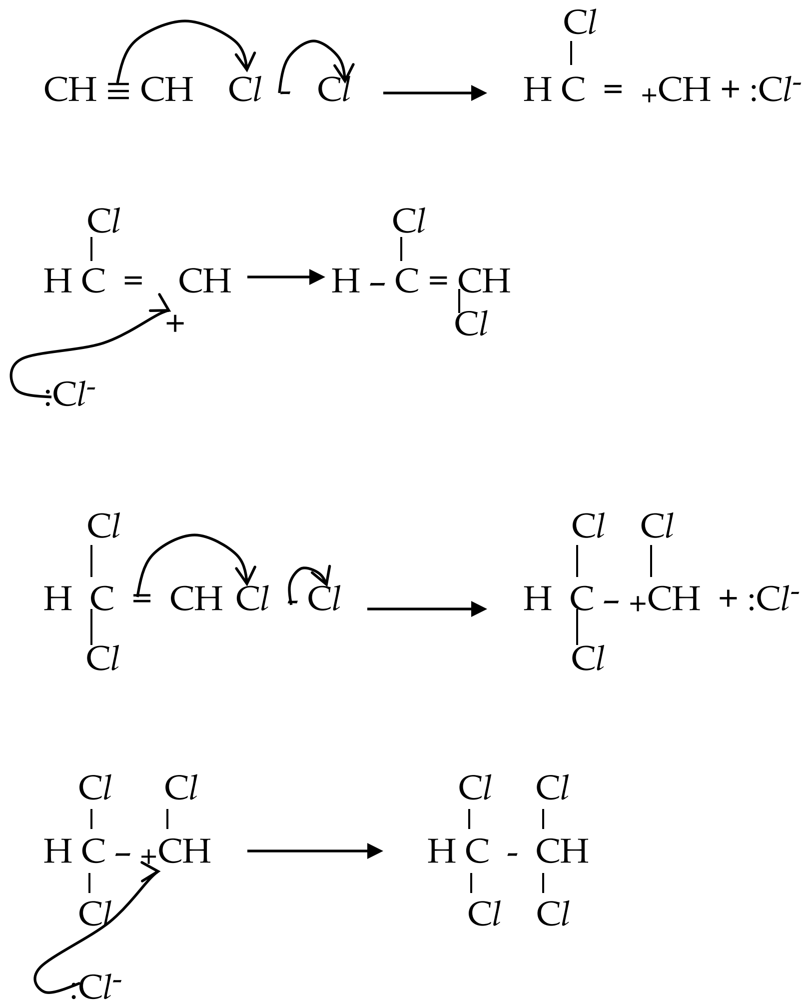
$$CH\equiv CH + Cl_2 \xrightarrow{CCl_4} ClCH = CHCl \xrightarrow{Cl_2/CCl_2} Cl_2CH - CHCl_2$$

Overall

$$CH \equiv CH + 2Cl_2 \xrightarrow{CCl_4} Cl_2CHCHCl_2$$

1, 1, 2, 2 tetrachloro ethane.

Mechanism:



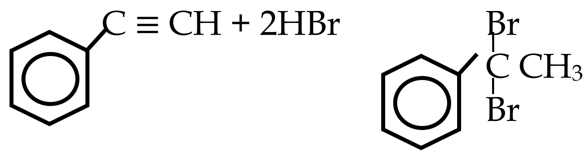
$$CH_3\,C\,CH + 2Br_2 \xrightarrow{CCl_4} CH_3\,\underset{\displaystyle Br}{\overset{\displaystyle Br}{C}}\,\underset{\displaystyle Br}{CH}\;Br$$

(iii) **Halogen acids (HX)**

Alkynes react with halolgen acids to give dihalides depending on the structure of an alkyne, the dihalide can either be a gem or vicinal due to Makwonikoff’s rule.

$$\left.\begin{array}{l} CH \equiv CH + 2Br \longrightarrow CH_3CHBr_2 \\ CH_3C \equiv CH + 2HCl \longrightarrow CH_3\overset{Cl}{\underset{Cl}{C}}CH_3 \end{array}\right\} \text{Gem dihalides}$$

$$CH_3C \equiv CH + 2HBr \xrightarrow{ROOR} CH_3\,CH_2\,CH\,Br.$$



(iv) With H_2O.

Alkynes react with H_2O in the presence of H_2SO_4 acid and $HgSO_4$ with a temperature of about 60^oC to form carbonyl compounds. A symmetrical alkyne forms a ketone.

$$CH_3C\equiv CCH_3 + H_2O \xrightarrow[60^oC]{H_2SO_4/HgSO_4} CH_3\overset{O}{\overset{\|}{C}}CH_2\,CH_3$$

Butan-2-one

$$CH_3C \equiv CH + H_2O \xrightarrow[60^oC,ROOR]{H_2SO_4/HgSO_4} CH_3CH_2CHO$$

Propanal

(v) Reactions with H_2.

Alkynes just like alkenes react with H_2 when passed over a suitable catalyst like Ni/150^{o}C, pt/r.t.p to form an alkane.

$$CH \equiv CH + 2H_2 \xrightarrow[150^oC]{Ni} CH_3CH_3$$

$$CH_3C \equiv CH + 2H_2 \xrightarrow[r.t.p]{pt} CH_3CH_2CH_2$$

(vi) Nitrile formation

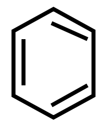
When little NH_3 is passed over an alkyne heater over an Al catalyst at 573^{o}C, a nitrile is formed.

$$CH \equiv CH + NH_3 \xrightarrow[573^oC]{Al_{(s)}} CH_3\,CN + H_2$$

Ethanonitrile

(vii) Polymerisation

Due to the presence of a triple bond, alkynes polymerise to form cyclic or aromatic compounds. This occurs when an alkyne is heated in a glass tube containing Fe catalyst (4000^oC).

$3CH \equiv CH \xrightarrow[4000^oC]{Fe}$ 

When two molecules of ethyne combine by passing them through a saturated solution of copper(I) chloride in ammonium chloride, vinyl ethyne is formed.

Vinyl ethyne is a good starting material for linear polymers.

$$2CH \equiv CH \xrightarrow[NH_4Cl]{CuCl} CH_2 = CHC \equiv CH$$

Vinyl ethyne.

$$CH_2 = CHC \equiv CH \ + \ CH \equiv CH \rightarrow CH_2 = CH\,CH = CHC \equiv CH$$

A terminal proton of an alkyne can be substituted by other electropositive metals. This indicates that, such alkynes are acidic.

NOTE: Only terminal alkynes behave this way. Non terminal do not.

$$CH\,CH + 2Na \xrightarrow{\text{Liquid } NH_3} \overset{+}{N}a\bar{C} \equiv \bar{C}Na^+ + H_2.$$

$$2CH_3C \equiv CH + 2Na \xrightarrow{\text{Liquid } NH_3} 2CH_3C \equiv \bar{C}\,Na^+ + H_2.$$

WITH AMMONIACAL COPPER(I) CHLORIDE SOLUTION

Similary, H_2 in alkynes can be substituted when its passed in solution of CuC_l NH_3 giving a red precipitate of Cu^+ alkyne derivative. This reagent is called ammoniacal copper(I) chloride solution, $CuCl/NH_{3(aq)}$.

$$HC \equiv CH + CuCl \xrightarrow{NH_{3(aq)}} CuC \equiv C\,Cu + 2HCl.$$

Red ppt.

Copper(I) ethyne (or Copper acetylide)

WITH AMMONIACAL SILVER NITRATE SOLUTION.

When a terminal alkyne is bubbled through a solution of ammonial $AgNO_3$, a white precipitate of silver dicarbide is formed.

$$HC\equiv CH + 2\,AgNO_3 + 2NH_{3(aq)} \longrightarrow \underset{\text{White ppt}}{Ag\,C \equiv C\,Ag_{(s)}} + 2NH_4NO_3.$$

Differentiate between $CH_3\,C \equiv CH$ and $CH_3\,C \equiv CCH_3$

Reagent: Ammoniacal copper(I) chloride solution.

With $CH_3C \equiv CH$: No observable change.

With $CH_3C \equiv CCH_3$: A red precipitate is observed.

The above reactions are used for distinguishing between terminal alkynes and non terminal

SYNTHESIS OF HIGHER ALKYNES

When an alkyne is passed through liquid NH_3 in presence of Na metal and the derivative formed is reacted with an alkyl halide, the chain is increased giving a higher alkyne.

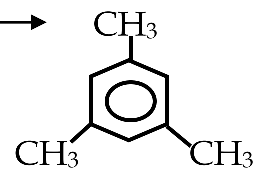
$$HC \equiv CH + 2Na \xrightarrow{\text{Liquid } NH_3} \overset{+}{N}a\bar{C} \equiv \bar{C}Na^+ + 2CH_3Cl \longrightarrow CH_3C \equiv C\,CH_3 + 2NaCl$$

$$CH_3C\,CH + Na \xrightarrow{NaNH_2} CH_3C \equiv \bar{C}\,Na^+$$

$$CH_3C \equiv \bar{C}Na^+ + CH3CH2Cl \qquad CH_3\,C \equiv CCH_2\,CH_2 + NaCl$$

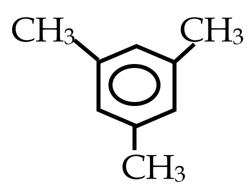
Physical properties of alkynes

- They are insoluble in H_2O.
- They are very soluble in organic solvents like benzene, CCl_4.
- They are less dense than H_2O.
- Their boiling points increase in number of carbon atoms. E.g. Ethyne boils at -75, propane -43, butyne at 91.
- They have got almost the same boiling points as those of corresponding alkenes.
- They have got the same vanderwaal's forces of attraction.

Convert $CH \equiv CH \longrightarrow$ 

$$2CH \equiv CH + Na \xrightarrow{NaNH_2} 2CH \equiv \bar{C}Na^+ + H_2$$

$$CH \equiv \bar{C}Na^+ + CH_3Cl \longrightarrow CH \equiv CCH_3$$

$3CH_3C \equiv CH \xrightarrow[400^oC]{Fe}$ 

AROMATIC COMPOUNDS (ARENES)

The term aromatic is derived from the Greek work Aroma to mean sweet smell. This term has been carried forward by modern Chemists used as aromatic to mean or describe the study of compounds with benzene ring.

Benzene is a parent compound of aromatic compounds.

STRUCTURE AND BONDING OF BENZENE

Structure and bonding of benzene was made clear by analysis made by Chemists. They found out that a clear colourless compound was isolated from distillation of crude oil and on analysis, it was found to contain 92.3% carbon and 7.7% hydrogen only.

When 0.250g of this liquid was vapourized at 100°C, they found out that the liquid occupies 98cm³. The results were subjected to analysis.

Element	**C**	**H**
Percentage composition	92.3	7.7
Relative atoms	$\frac{92.3}{12}$	$\frac{7.7}{1}$
Moles	7.69	7.70
Mole ratio	$\frac{7.69}{7.69}$	$\frac{7.70}{7.69}$
	1	1

Empirical formula = CH

Volume of gas at 100(373)K

$$= \frac{24 \times 373}{293}$$

$$= 30.04\ dm^3$$

98cm³ of liquid contain 0.25g at 100°C.

Mass of 1mol $\left(\frac{6.25 \times 30040}{98}\right) g$

$$= 76.6 \doteq 77g.$$

$(CH)_n = 77$

$12n + n = 77$

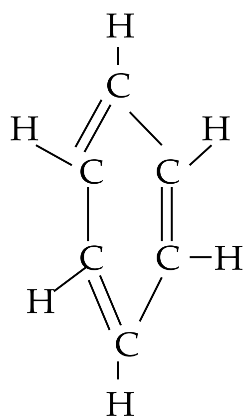
$n = \frac{77}{13}$

$n = 5.0 \bumpeq 6.$

Molecular formula is C_6H_6.

The structure proposed was C_6H_6 with all its isomers.

In 1865, Kekule proposed that the structure of benzene molecule is not a straight chain but an hexagonal ring consisting of alternating double bonds.



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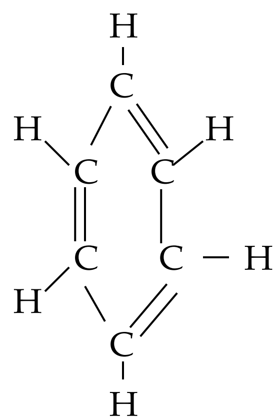


But a number of evidences proved out that the above structure, proposed by Kekule was not true. Benzene does not have true double bonds since it does not undergo addition reaction with bromine in darkness.

EVIDENCE PUT TO EXPLAIN BENZENE STRUCTURE.

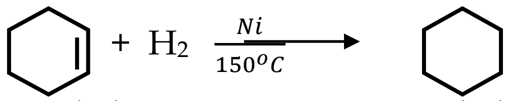
(i) X-ray structure determination to measure the length of carbon-carbon bonds.

Compound	**Bond**	**Length/nm**
Cyclo hexane	C – C	0.154
Cyclo hexene	C = C	0.134
Benzene	C$\overset{\cdots}{-}$C	0.140

The measurements of the bond length showed that, the bond length of benzene are between single and double, therefore are not true double bonds ruling out Kekule's structure of double bonds.

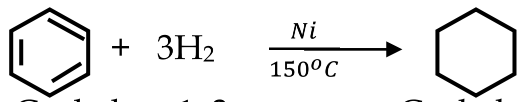
(ii) **Thermodynamic measurements:**

(a) Enthalpy of hydrogenation.



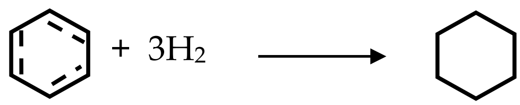
ΔH = -119 KJ mol^{-1}.

Cyclo hexene   Cyclo hexane



ΔH = 3(119)

Cyclo hex-1, 3, 5-triene   Cyclo hexane   -357 KJ mol^{-1}.



ΔH = -207 KJ mol^{-1}.

Benzene

Conclusion:

The double bonds of benzene are not true double bonds.

Benzene is more stable than cyclo hex-1, 3, 5, triene by an extra 150 KJmol^{-1}

(b) Enthalpy of formation of benzene.

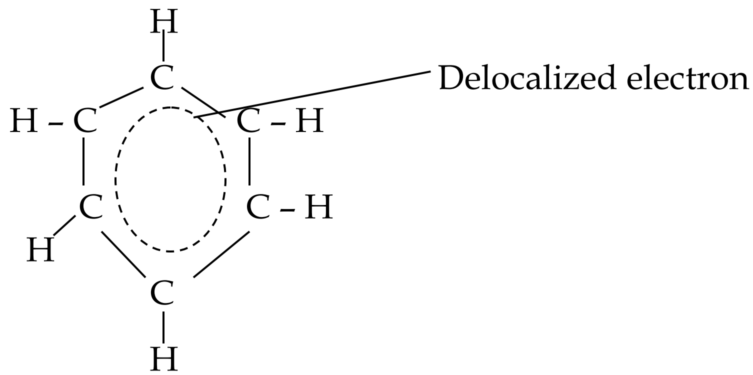
The theoretical/calculated enthalpy of formation of benzene is 252 KJ mol^{-1} but the practical value of this energy is 82 KJ mol^{-1}. This means benzene is more stable by 170 KJ mol^{-1} of energy.

$$6C_{(s)} + 3H_{2(g)} \longrightarrow C_6H_{6(g)} \quad \Delta H = 82 \text{ KJ mol}^{-1}.$$

(c) Reactions of benzene

Benzene does not undergo addition reactions but undergoes substitution reactions implying it does not have double bonds but a system of delocalized electrons or the pie (π system).

DELOCALIZATION OF BENZENE STRUCTURE

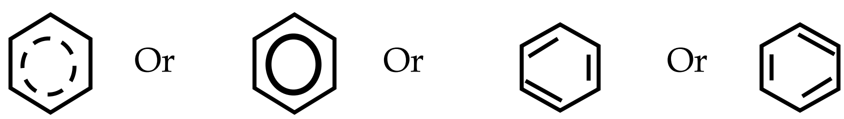


Benzene structure has got six δ carbon – carbon bonds.

It has got 3-π carbon – carbon bonds.

The π bonds are not localized but they are shared by the six carbon atoms giving a π system of electrons and this is called delocalization.

STRUCTURE OF BENZENE.



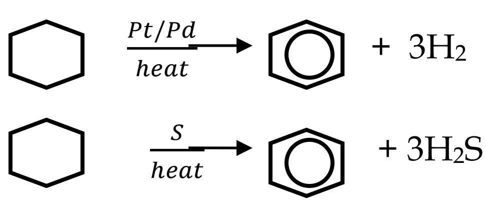
I II III IV

BENZENE

Is the parent aromatic compound with a hexagonal ring of carbon atoms having a π system of electrons.

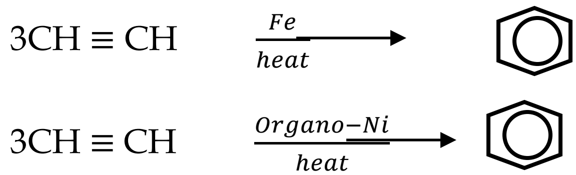
FORMATION OF BENZENE

(i) From dehydrogenation of cyclo hexane when heated with Pt/Pd or heated with sulphur. Cyclo hexane loses H_2 atoms to form benzene.

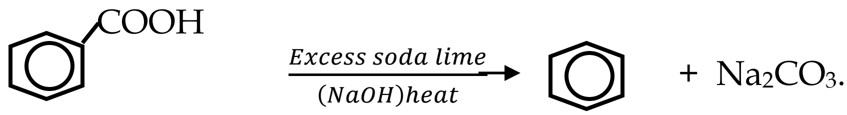


(ii) **Polymerisation of ethyne**

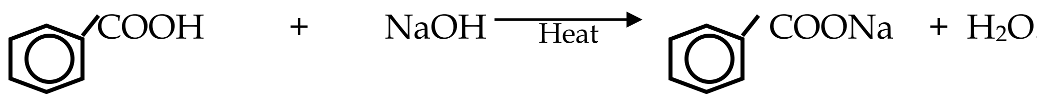
When ethyne is heated with an organo iron or Nickel, it undergoes cyclisation to form benzene.

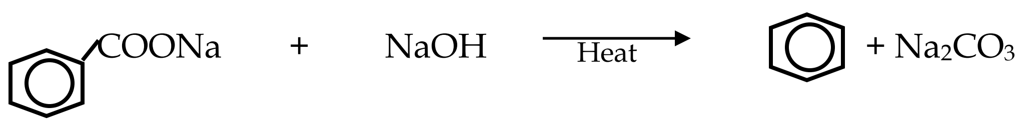


(iii) **Decaboxylation of benzoic acid**
When benzoic acid is heated with soda lime (a mixture of (NaOH and CaO).



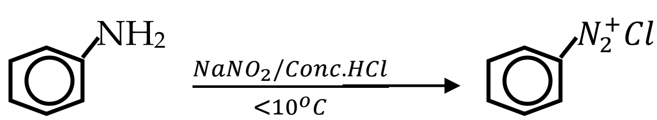
Two step reaction



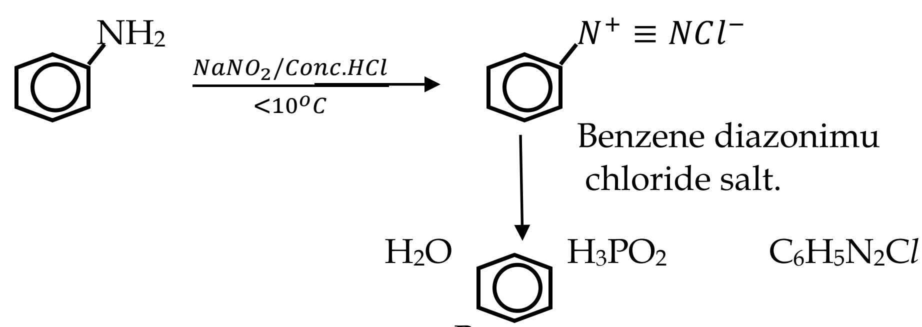


(iv) **From benzene diazonium SaH.**
When benzene diazonium salt is reacted with pypophosphorus acid in presence of water, benzene is formed.

The formation of benzene diazonium alt can be started from phenyl amine which is reacted with a mixture of $NaNO_2$ and HCl (HNO_2 acid) at a temperature <10.

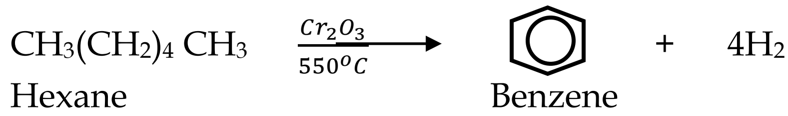


Benzene diazonium salt.

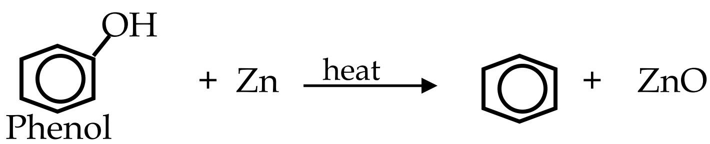


Benzene.

(v) Catalytic reformation of petroleum under heat of about 550°C in the presence of Cr_2O_3/Al_2O_3.



(vi) **From phenol**
When phenol is heated with zinc dust, benzene is formed.



PROPERTIES OF BENZENE

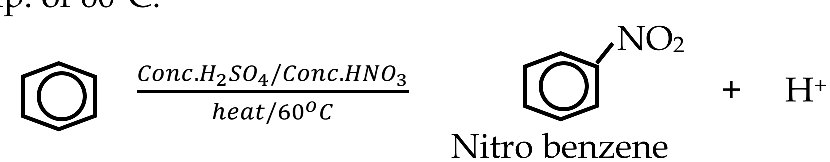
PHYSICAL PROPERTIES

- ✓ It is a colourless liquid.
- ✓ It has got a x-tic smell.
- ✓ It is insoluble in water but dissolves in organic solvents e.g. CCl_4, methyl benzene.
- ✓ It burns with a highly sooty flame.

CHEMICAL PROPERTIES

Benzene undergoes electrophillic substitution reaction where the hydrogen atom on the ring is replaced by another electrophille. Benzene therefore reacts mainly with electrophilles (Positively charged species) to form substituted products on the benzene ring.

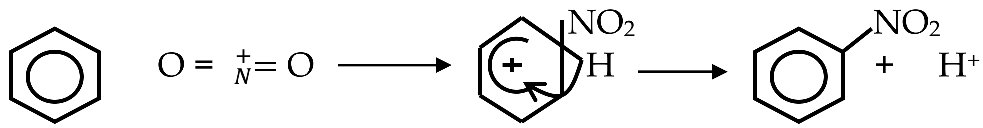
(i) **Nitration reaction**
Is a reaction where the nitronium ion $^+NO_2$, $O = {}^+N = O$) substitutes the hydrogen in the benzene ring. The electrophille of the nitronium ion is generated from a mixture of Conc. H_2SO_4 and Conc. HNO_3 acid heated at a temp. of 60°C.



Mechanism:

$H_2SO4 + NO - NO_2 \xrightarrow{\text{Protonation}} H_2O^+ = NO_2 + HSO_4^-$

$H_2O^+ - NO_2 \longrightarrow H_2O + \overset{+}{N}O_2$



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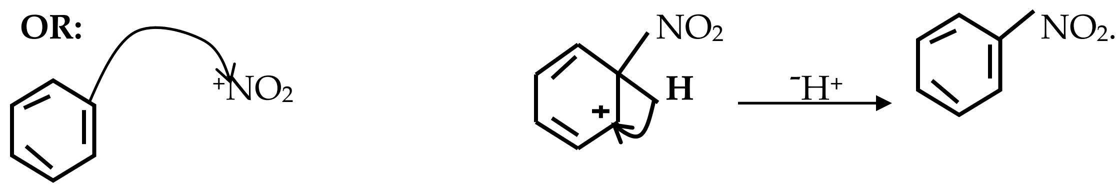
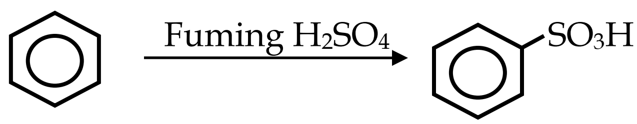


(ii) **Sulphonation:**

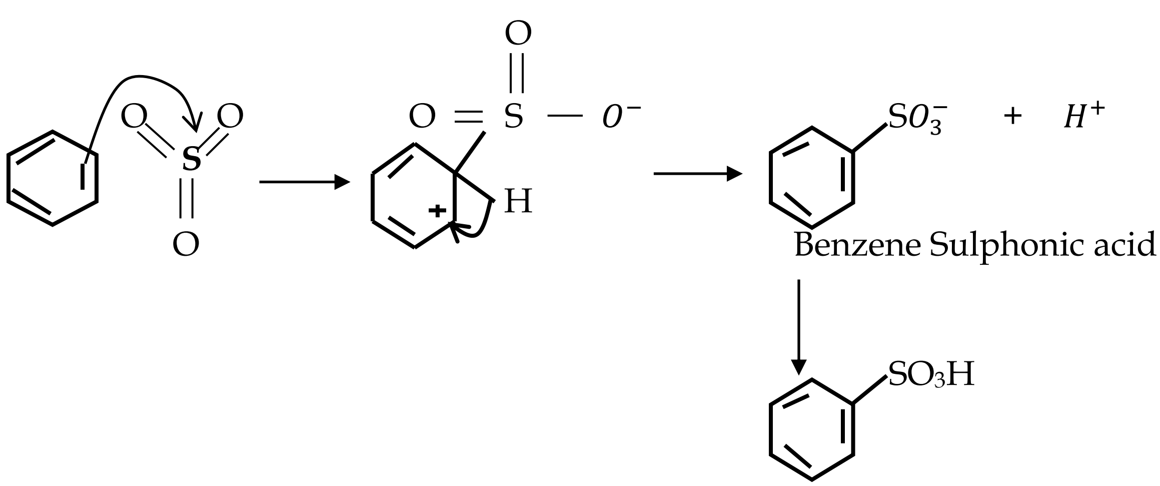
This is a reaction where benzene reacts with Conc. Or fuming H_2SO_4 acid to form benzene sulphuric acid.

The electrophille in this reaction is SO_3 which is a neutral electrophille generated from fuming sulphuric acid.



Mechanism:

$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$



(iii) **Halogenations**

Benzene reacts with halogens like Cl_2, Br_2 only in the presence of halogen carrier which polarizes the halogen molecule by accepting the lone pair of electrons so that the eletrophille is generated.

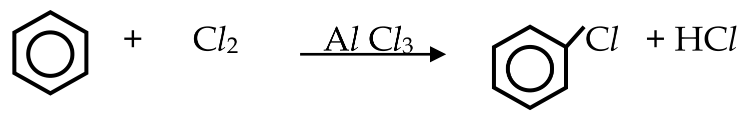
In the absence of the halogen carrier, benzene does not react with halogens.

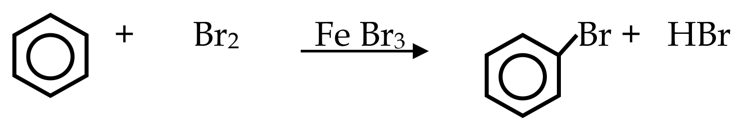
Examples of halogen carries used are:

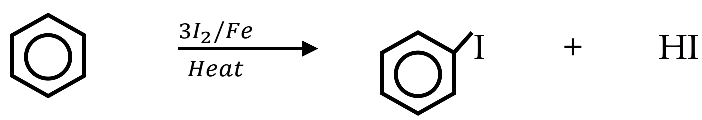
$AlCl_3$ $\quad$ CH_3COOH

$FeCl_3$

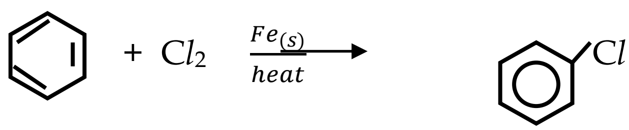
BF_3 $\quad$ Fe, Cl_2/Heat







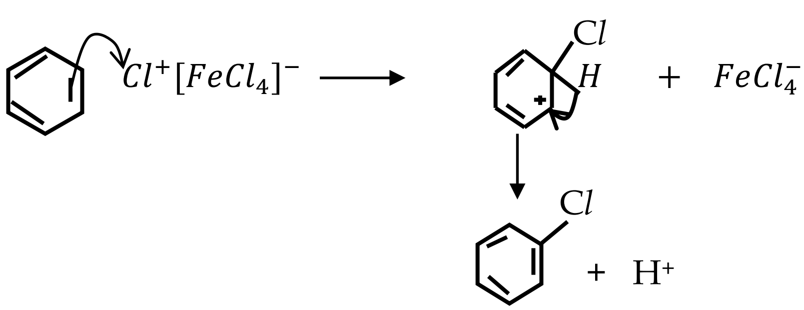
Mechanism:



Mechanism:

$$3Cl_{2(s)} + 2Fe_{(s)} \xrightarrow{heat} 2FeCl_3$$

$$Cl^{\delta+} - Cl^{\delta-} --- FeCl_3 \rightleftharpoons [FeCl_4]^- Cl^+$$

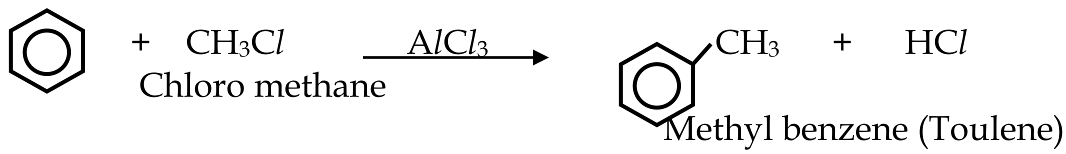


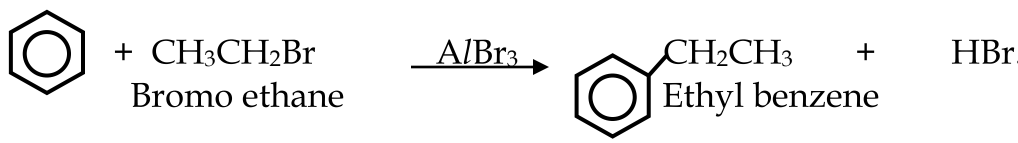
$$FeCl_4^- + H^+ \longrightarrow FeCl_3 + HCl$$

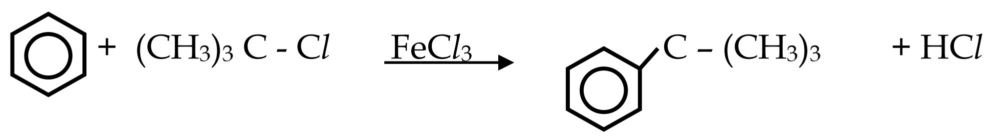
Alkylation of Benzene

This is the reaction where an aromatic compound reacts with an alkyl halide in the presence of a halogen carrier to form an alkyl aromatic compound.

This reaction was first identified by **Friedel craft**. It is also called Friedel Craft alkylation.

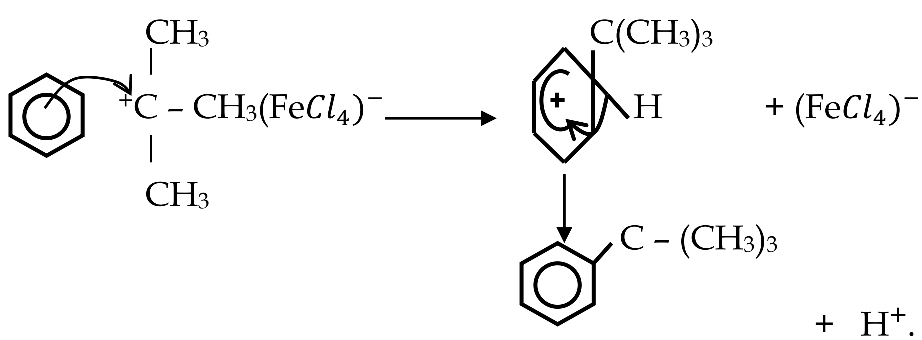




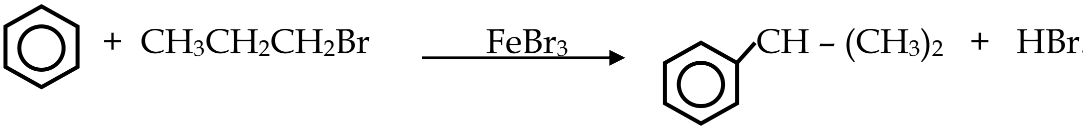


Mechanism

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl \text{ -------- } FeCl_3 \rightleftharpoons H_3C-\underset{CH_3}{\overset{CH_3}{C^+}}\,(FeCl_4)^-$$



$$FeCl_4^- + H^+ \longrightarrow FeCl_3 + HCl.$$

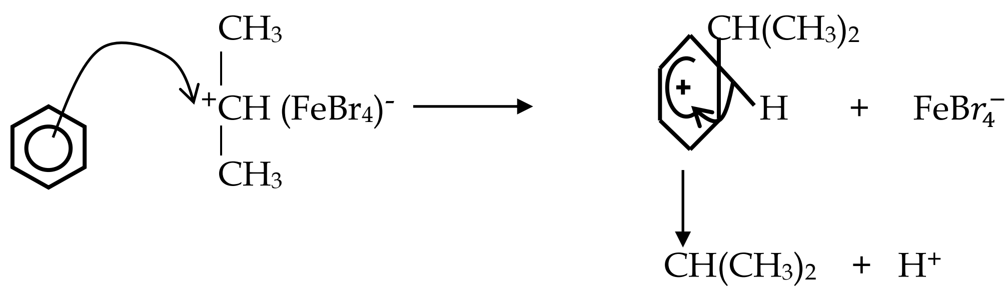


Mechanism:

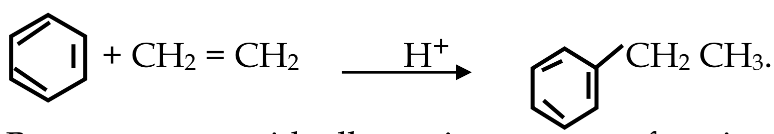
$$CH_3CH_2CH_2{-}Br \ldots\ldots\ldots\ldots FeBr_3 \rightleftharpoons CH_3CH_2{}^{+}CH_2\,(FeBr_4)^-$$

Re-arrangement.

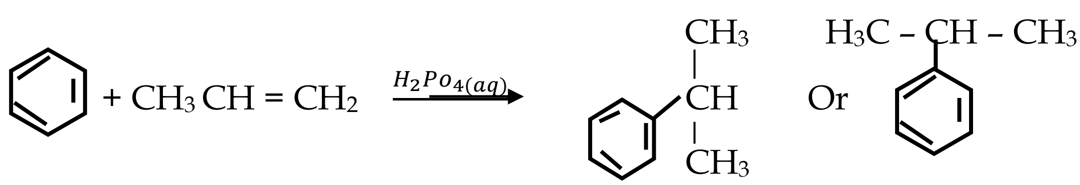
$$CH_3\,{}^{+}CHCH_3\,(FeBr_4)^-$$



$$H^+ + FeBr_4^- \longrightarrow Fe\,Br_3 + HBr.$$

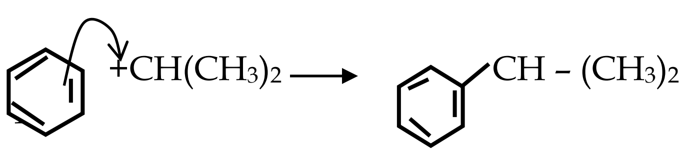


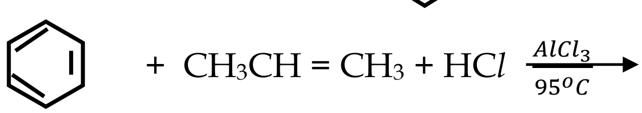
Benzene reacts with alkenes in presence of a mineral acid.
The mineral acid is necessary to form an elctrophille.



Mechanism:

$$CH_3CH = CH_2 + H^+ \longrightarrow CH_3\ {}^{+}CH\ CH_3$$

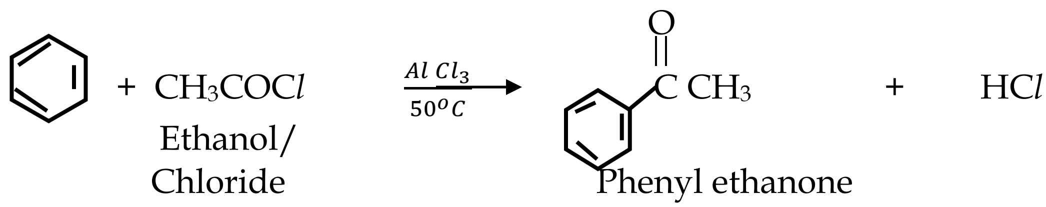




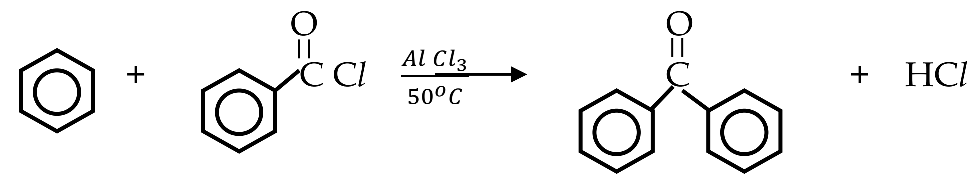
Acylation

Is a reaction of benzene with acid halides in the presence of halogen carriers to form aromatic ketones at a temperature of 50°C.

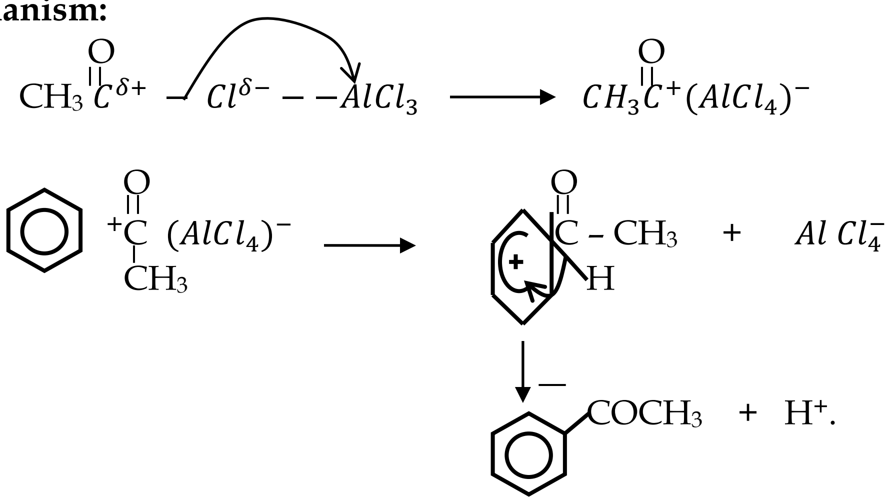
1.



2.



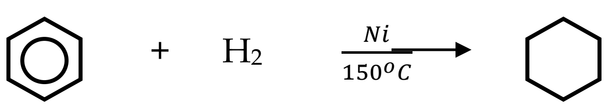
Mechanism:



$Al\ Cl_4^- + H^+ \longrightarrow Al\ Cl_3 + HCl.$

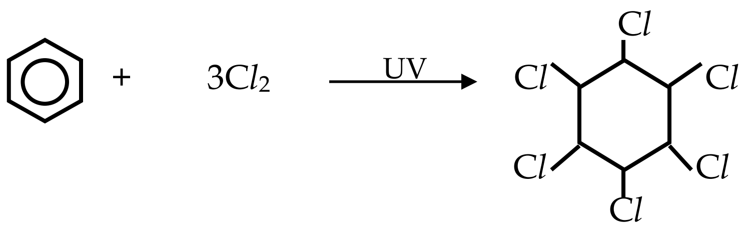
Hydrogenation:

Benzene react with hydrogen in presence of Ni catalyst when heated at 150°C to form cyclo hexane.



Halogen in presence of light (uv).

When chlorine is mixed with benzene in the presence of sun light or uv rays, the benzene ring becomes highly substituted with chlorine atoms to form 1, 2, 3, 4, 5, 6 hexa chloro benzene.



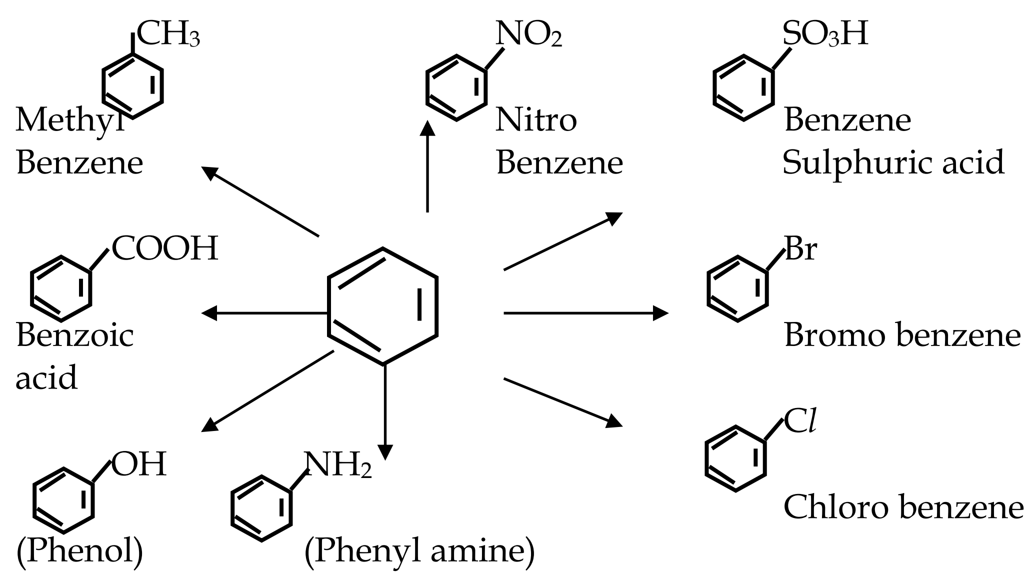
1, 2, 3, 4, 5, 6 – hexa chloro
Cyclo hexane.

Combustion

Benzene burns in air with a sooty flame to form CO_2 and H_2O.

$$+ \quad \frac{1}{2}O_{2(g)} \longrightarrow 6CO_{2(g)} + 3H_2O_{(l)}.$$

DERIVATIVES OF BENZENE



Derivatives of benzene react differently depending on the behaviour of the group of atom(s). the chemical behaviour of these groups are divided into three groups.

(i) The group which substitutes the benzene ring directing any incoming group 2(ortho) and 4(para) position directors. E.g.

(a) OH-group, ethoxide group OCH_3, CH_3-gp, NH_2-nitro group, amides gp-HN- $\overset{\overset{O}{||}}{C}$ CH_3.

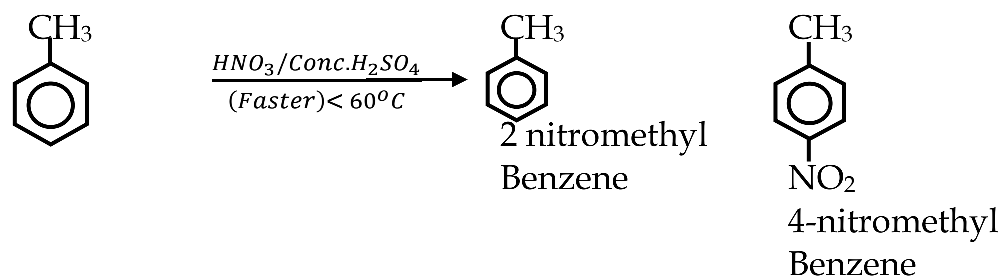
These groups have got positive inductive effect by pushing the electrons towards the ring, activating the benzene ring so that the electrons are available at positions 2, 4, and 6 where the incoming electrophille are added.

By activating the ring, they increase the electron density on the ring so that the electrophilles are added faster.

Usually two products are given, i.e. position 2 and position 4 products.

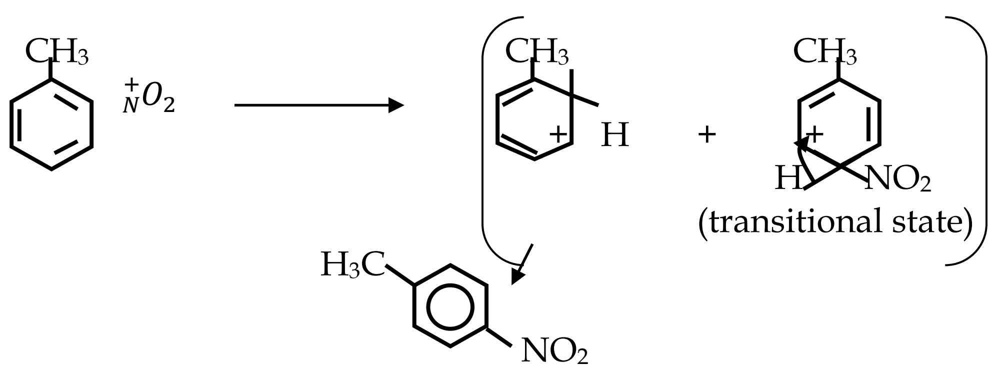
METHYL BENZENE

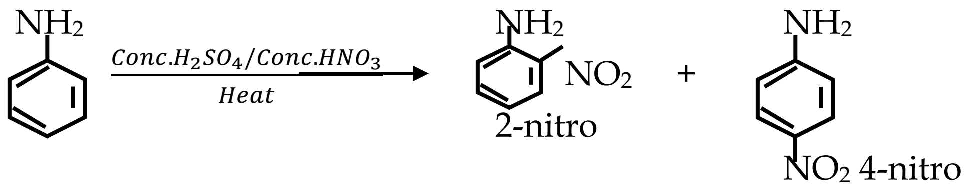
1.

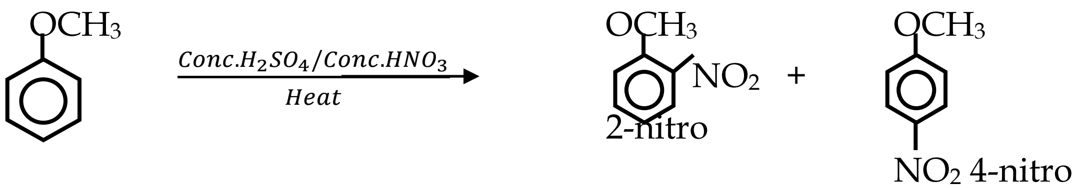


$HNO_3 + H_2SO_4 \longrightarrow H_2O^+ - NO_2 + HSO_4^-$

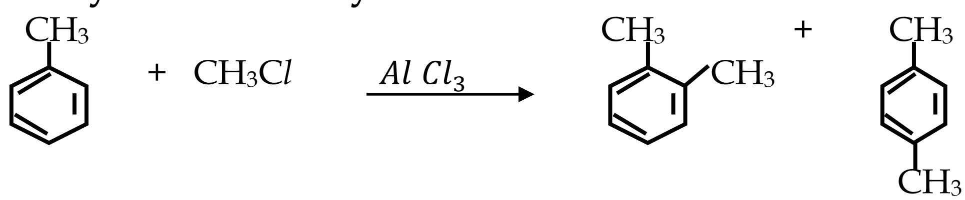
$H_2O^{\pm} - NO_2 \longrightarrow H_2O \quad + \quad \overset{+}{N}O_2$



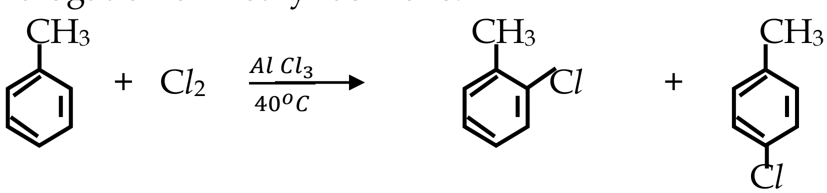
2. 

3. 

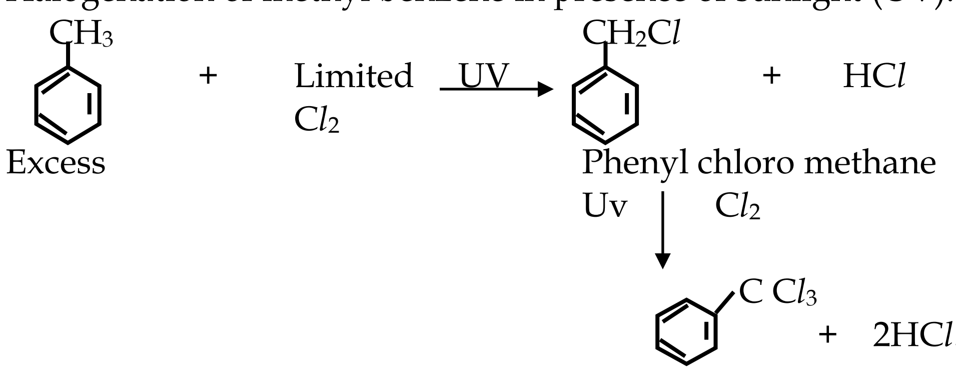
Alkylation of methyl benzene.



(a) Halogation of methyl benzene.

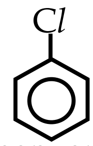


(b) Halogenation of methyl benzene in presence of sunlight (UV).

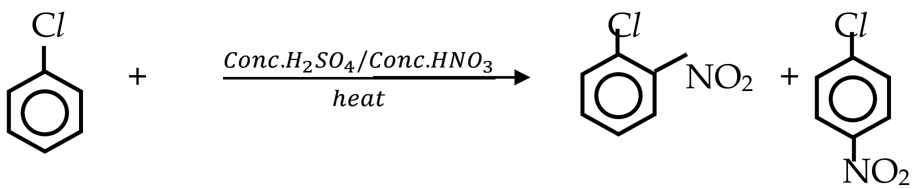


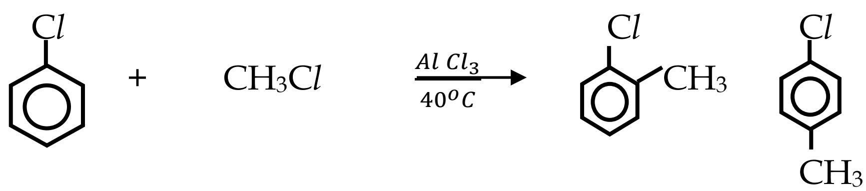
This reaction follows a free radical mechanism.

CHLORO BENZENE



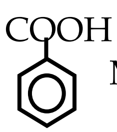
Chloro benzene or other halogeno benzene compounds can substitute the ring at position 2 and 4 but at a much slower rate. This is because halogens have got a negative inductive effect (electronegative) and withdrawal electrons from the ring towards themselves so that the pie electrons on the ring can be availed to electropilles at position 2 or 4 where there is a high electron density.





Groups that direct further substitution at position 3 of the ring do so at a much slower rate including COOH, NO_2, CN, SO_3H.

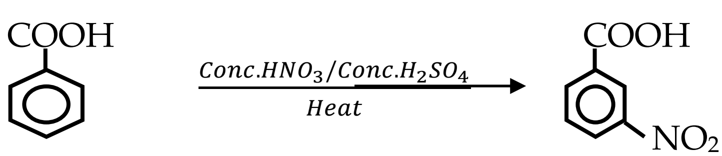
BENZOIC ACID



Meta(3) position directors.

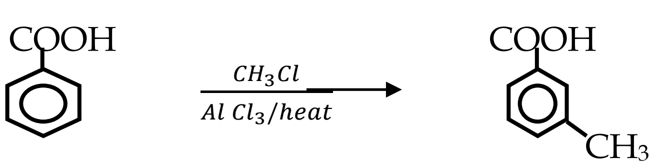
Carboxylic acid on benzoic acid directs the incoming substituents at position 3 so that one major product is formed.

(i)

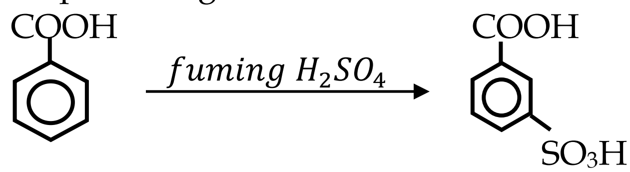


3-nitro benzoic acid.

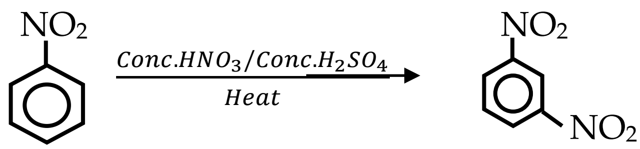
(ii)



(iii) Sulphonating



(iv)

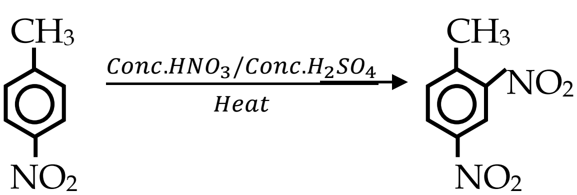


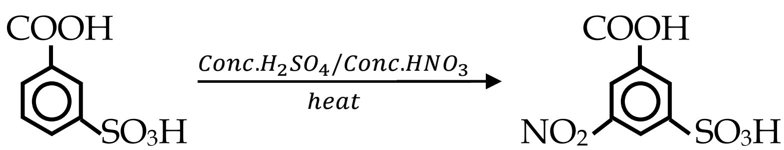
The above are Meta (3) directors because they pull electrons away from the ring and decreasing electron density at position 2 or 4 and the only place where the electrons are available is the Meta position.

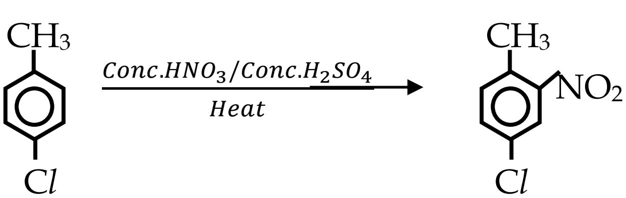
DISTRIBUTED COMPOUNDS

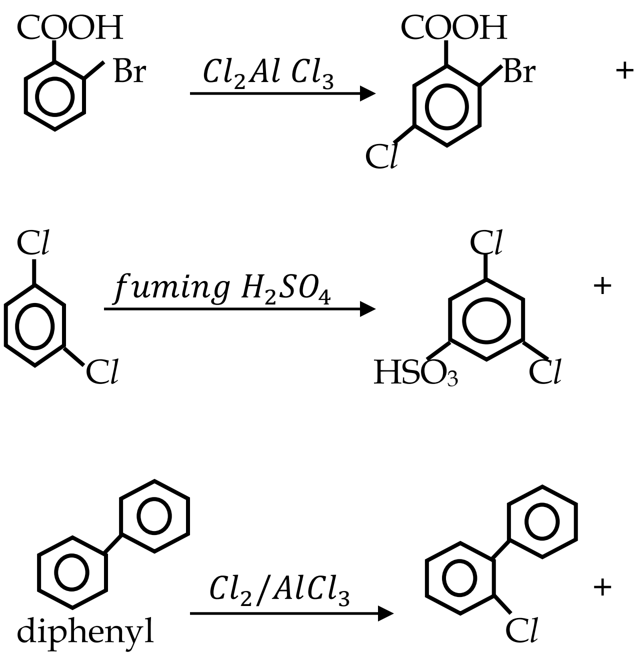
When there are two substituents on the benzene ring, the orientation effect of these two will be determined or predicted by their reinforcing effects or the order of their superiority. The following order is normally observed.

- OR > NR_2 > Alkyl group > halogen > Meta directors.







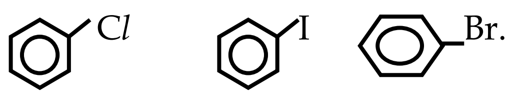

COOH
Br
$Cl_2Al\ Cl_3$
COOH
Br
Cl
+
Cl
fuming H_2SO_4
Cl
Cl
HSO3
Cl
+
diphenyl
$Cl_2/AlCl_3$
Cl
+

ALKYL HALIDES
(Halogeno alkanes)

Alkyl halides are compounds in which halogen atoms are directly attached onto the hydro carbon chain or aromatic ring.

R – X where R = Alkyl or Aryl group.
X = Halogen atom (C*l*, Br, I, F)

When the halogen is attached to the aromatic ring, it is called aromatic halide. e.g.



When the halogen is directly attached to the hydro carbon, it is called alkyl halide / halogen alkane. E.g.

CH^3CH_2Cl,	CH_3Br,	$CH_3\underset{\substack{\vert \\ I}}{C}HCH_3$
Chloro ethane	Bromo methane	2-Iodo propane.

ALKYL OR HALOGENO ALKANES

Nomenclature:
Alkyl halides are named as derivatives of corresponding alkanes y inserting the number and the prefix, chloro, Bromo, Iodi, Fluoro, to the alkane name.

Example:

CH_3Cl	Chloro methane
CH_3CH_2Br	Bromo ethane
$CH_3\underset{\substack{\vert \\ I}}{C}HCH_3$	2-Iodo propane.
$CH_3\overset{\substack{CH_3 \\ \vert}}{C}H\ \overset{\substack{Cl \\ \vert}}{C}HCH_3$	2-chloro-3-methyl butane.
$CH_3 - \overset{\substack{CH_3 \\ \vert}}{\underset{\substack{\vert \\ CH_3}}{C}} - Br$	2-Bromo, 2-methyl propane.

ISOMERISM

Alkyl halides exhibit two types of isomerism.

(i) Chain isomerism

(ii) Positional isomerism

CHAIN ISOMERISM:

These arise as a result of difference in the arrangement of carbon atoms giving different carbon skeleton but the position of the halogen atom remains the same.

$C_4 H_9 Br$.

1. $CH_3 CH_2 CH_2 CH_2 Br$ 1-Bromo butane.

2. $CH_3 \underset{\underset{CH_3}{|}}{C}H CH_2 Br$ 1-Boromo-2-methyl propane.

POSITIONAL ISOMERISM:

These arise as a result of the different positions taken by the halogen atom on the same chain. E.g.

$C_4 H_9 Br$.

$CH_3 CH_2 CH_2 CH_2 Br$ 1-Bromo butane

$CH_3 CH_2 \underset{\underset{Br}{|}}{C}H CH_3$ 2-Brobom butane

METHODS OF PREPARATION:

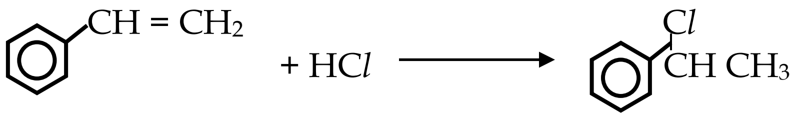
Alkyl halides are prepared from the following:

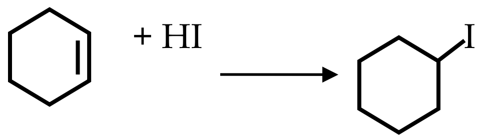
(i) **From Alkenes:**

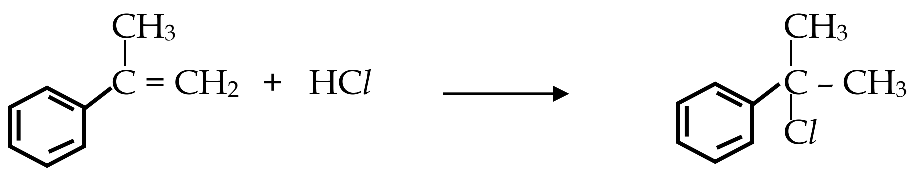
Addition of an halogen acid to an alkene at room temperature gives an alkyl halide. When unsymmetrical alkene is used, addition of an halogen acid gives a product predicted by Makwonikoff's rule. But if a peroxide used, then the product will be that of anti Makwonikoff's rule.

1. $CH_3CH = CH_2 + HBr \xrightarrow{r.t.p} CH_3 \overset{\overset{Br}{|}}{C}H CH_3$

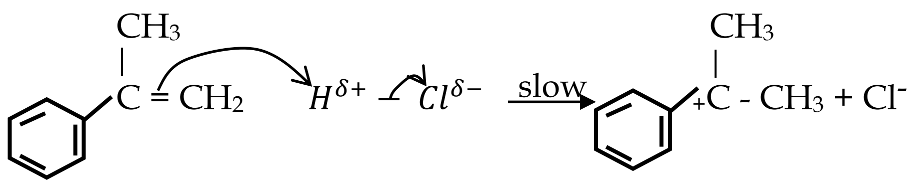
2. $CH_3 CH = CH_2 + HBr \xrightarrow[Heat]{ROOR} CH_3 CH_2 CH_2 Br$.

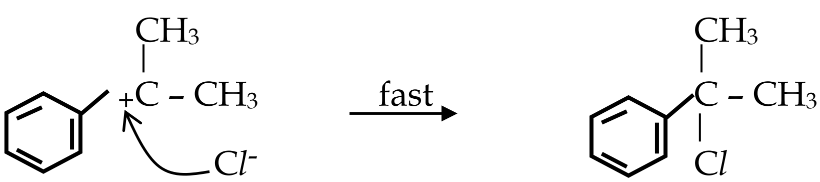
3. 

4.  Iodo cyclo hexane.

5. 

Mechanism:



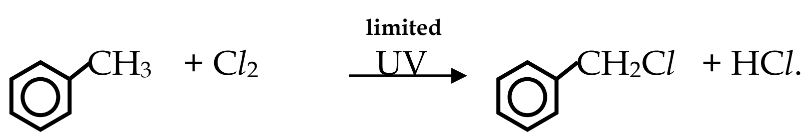


(ii) **From Alkanes**

When alkanes are reacted with a halogen molecule in presence of UV rays of sunlight. A mixture of alkyl halides are formed but if the reaction conditions are controlled by using excess alkane or limited halogen molecule, then the product formed would be one type of alkyl halide.

Excess:

$$CH_3\,CH_2\,CH_3 + Cl_2 \xrightarrow[Sunlight]{U.V} CH_3CH_2CH_2Cl + HCl.$$



(iii) From Alcohols:

Alcohols are the most important source of preparing alkly halides in reaction where hydroxyl groups of alcohol are replaced by halogen atoms which could be derived from:
- halogen acids (HX).
- Phosphorus tri or penta halides (PX_3/PX_5)
- Thiony chloride ($SOCl_2$).

(a) **Action of halogen acid on the alcohol**:

When a halogen acid is heated with an alcohol in presence of a dehydrating agent e.g.
- $ZnCl_2$ (anhydrous)
- Conc. H_2SO_4.
- Al_2O_3 (Dry)

An alkyl halide is formed. Sometime the halogen acid is generated "insitu."

$$R - OH + HX \longrightarrow R - X + H_2O.$$

$$CH_3\,CH_2\,OH \xrightarrow{NaCl/Conc.H_2SO_4} CH_3CH_2 - Cl + H_2O.$$

$$CH_3\,\underset{\displaystyle OH}{\underset{|}{CH}}\,CH_3 + H + HCl \xrightarrow[ZnCl_2]{\text{anhydrous}} CH_3\,\underset{\displaystyle Cl}{\underset{|}{CH}}\,CH_3 + H_2O$$

$$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - OH \xrightarrow[Anhydrous\ Zn\ Cl_2]{Conc.HCl} CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - Cl + H_2O$$

A solution of anhydrous $ZnCl_2$ in Conc.HCl (Lucas reagent) is an important reagent for distinguishing the three classes of alcohols i.e.
- Primary.
- Secondary and tertiary alcohols.

The tertiary alcohol gives an immediate cloudy solution of an alkyl halide. (0.5 minutes).

The secondary alcohol gives cloudy solution between 5 and 10 minutes.

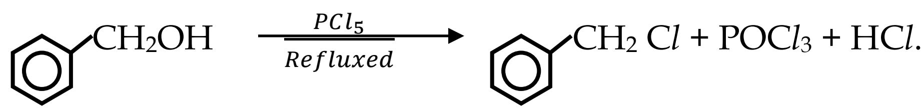
The primary alcohol does not give a cloudy solution at room temperature.

(b) Action of phosphorous halides:

When alcohols are refluxed with phosphorous halide like phosphorous tri chloride or phosphorous penta chloride, the halogeno alkanes or alkyl halides are formed.

$$R - OH + PCl_5 \xrightarrow{\text{refluxed}} R - Cl + POCl_3 + HCl.$$

$$CH_3\,CH_2\,OH + PCl_5 \xrightarrow{\text{refluxed}} CH_3\,CH_2\,Cl + POCl_3 + HCl$$



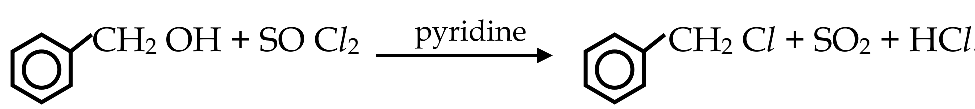
$$3CH_3\,CH_2\,OH + PCl_3 \xrightarrow{\text{reflux}} 3CH_3\,CH_2\,Cl + H_3PO_3.$$

(c) Action of thionyl chloride ($SOCl_2$):

When alcohols are refluxed in presence of thionyl chloride in the presence of an organic base pyridine to neutralize the mixture of toxic gases, an alklyl halide is formed.

This is a very convenient way of preparing alkyl halides.

$$CH_3CH_2OH + SOCl_2 \xrightarrow[heat]{pyridine} CH_3\,CH_2\,Cl + SO_2 + HCl$$



REACTIONS OF ALKYL HALIDES

CLASSES OF HALOGENO ALKANES

(i) **Primary Alkyl halides $RCH_2\,CH_2 - X$.**

Here the halogen atom is attached to a carbon is which bonded to only one another.

(ii) Secondary alkly halide. $\begin{array}{c} R - CH - R^2 \\ \qquad\quad | \\ \qquad\quad X \end{array}$

Here the halogen atom is attached to a carbon atom which is bonded to two other carbon atoms.

(iii) Tertiary alkly halide: $\begin{array}{c} R^1 \\ | \\ R^2 - C - X \\ | \\ R^3 \end{array}$

Here the halogen atom is attached to a carbon atom which is bonded to three other carbon atoms.

The three classes of alkly halides given above react differently due to the stability of the carbo cation ion which is formed as an intermediate during the reaction. The stability is governed by the order that tertiary > secondary > primary.

$$\begin{array}{ccccc} \begin{array}{c} R^1 \\ | \\ R^2 - C^+ \\ | \\ R^3 \end{array} & > & \begin{array}{c} R^1 \\ | \\ H - C^+ \\ | \\ R^2 \end{array} & > & \begin{array}{c} H \\ | \\ R^1 - C - C \\ | \\ H \end{array} \\ \textbf{Tertiary} & & \textbf{Secondary} & & \textbf{Primary} \end{array}$$

PHYSICAL PROPERTIES:

Lower alkyl halides are gases at room temperature.

The medium ones are liquids and the higher ones are solids.

The boiling points of alkyl halides with the same number of carbon atoms is determined by the atomic size of the halogen which later is as a result of the Van de Waal's forces of attraction.

$I^- > Br^- > Cl^- > F^-$.

$$\begin{array}{c} CH_3 \\ | \\ H_3C - C - I \\ | \\ CH_3 \end{array} > \begin{array}{c} CH_3 \\ | \\ H_3C - C - Br \\ | \\ CH_3 \end{array} > \begin{array}{c} CH_3 \\ | \\ H_3C - C - Cl \\ | \\ CH_3 \end{array}$$

CHEMICAL PROPERTIES:

Halogen atoms being more electronegative than carbon means that the C – X bond is highly polar due to the presence of partial induced charge where the halogen is partially negative and carbon is partially positive.

The polarity of the C – X bond makes alkyl halides to be very reactive to the nucleoptile thus necleophillic substitution.

$$\begin{array}{c} | \\ -C^{\delta+} - X^{\delta-} \\ | \\ :Nu \end{array} \longrightarrow \begin{array}{c} | \\ -C- \\ | \\ Nu \end{array} + X^-$$

The type of halogen present also determines the reaction.

The electronegativity difference between the halogen together with the bond length determines overall the reactivity. Down the group of the halogens there is decrease in electronegativity and at the same time increase in the bond length.

The reaction becomes faster with Iodo-alkanes than Bromo chloro fluoro alkanes because of low electronegativity in the iodides.

NUCLEOPHILLIC SUBSTITUTION REACTIONS

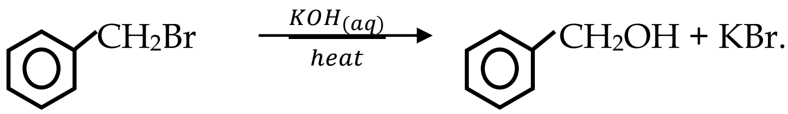
(i) **Reaction with alkalis:**

Alkalis react with alkly halides to form alcohols when they are refluxed.

$$CH_3Cl + \bar{O}H_{(aq)} \xrightarrow{\text{Reflux}} CH_3OH + Cl^-(aq)$$

$$\begin{array}{c} CH_3\,CH\,CH_3 \\ | \\ I \end{array} + NaOH_{(aq)} \xrightarrow{\text{Reflux}} \begin{array}{c} CH_3\,CH\,CH_3 \\ | \\ OH \end{array} + NaI$$

$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[heat]{\bar{O}H_{(aq)}} H_3C-\underset{CH_3}{\overset{CH_3}{C}}-OH + Br^-_{(aq)}$$



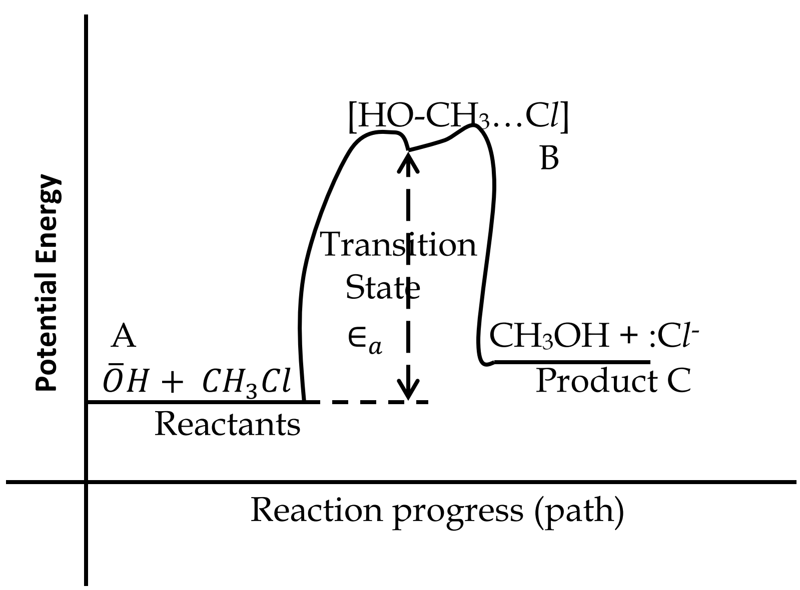
Primary alkyl halides with aqueous alkali.

Primary alkyl halides follow nucleophillic substitution bimolecular (SN_2) mechanism. Is a type of reaction where two molecules involve the rate determining step.

$-\overset{|}{C}$ - + : X – Alkyl halide
| - hydroxide group
Nu

Mechanism:

$$:\bar{O}H \quad CH_3^{\delta+} - Cl^{\delta-} \xrightarrow{slow} [HO \ldots . CH_3 \ldots Cl] \xrightarrow{fast} HO - CH_3 + :Cl^-$$



The nucleophille which is $\bar{O}H$ approaches the carbon atom carrying halogen from the opposite side.

This partially forms a nucleophille carbon bond and at the same time, a carbon halogen bond partly breaks. This leads to the increase in potential energy from A to B.

At B, there is partial halogen bond broken and partial nucleophille bond formed. This state is known as **activation complex** or **transition state**.

The energy level between the reactants and the activation complex is called the **activation energy**.

Later, the potential energy of the system increases when all the carbon halogen bonds are broken and the carbon nucleophille bonds are formed.

The energy of the system finally decreases until point C where the product of the alcohol is finally formed. This type of reaction is categorized as SN_2 reactions mechanism because there are two molecules involved at the activated complex.

(ii) Secondary alkyl halide

$$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3 + NaOH_{(aq)} \xrightarrow{\text{Heat}} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 + NaCl$$

Mechanism:

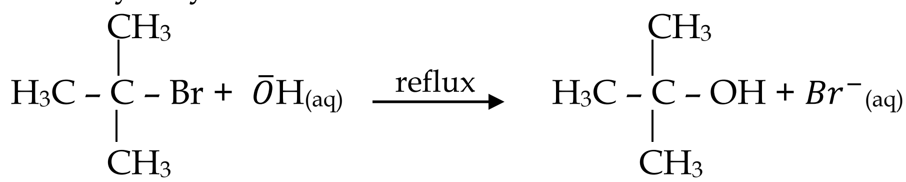
$H\bar{O}:$

$$CH_3 - \underset{\displaystyle Cl^{\delta-}}{\underset{|}{CH^{\delta+}}} - CH_3 \longrightarrow CH_3 - \overset{\displaystyle OH}{\overset{|}{CH}} - CH_3 + :Cl^-$$

$$:Cl^- + Na^+_{(aq)} \longrightarrow NaCl.$$

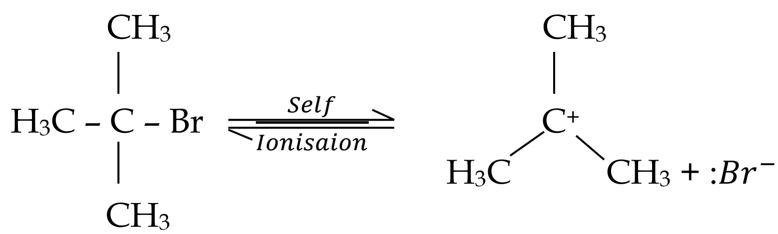
The mechanism followed by secondary alkyl halides is always between SN_1 and SN_2.

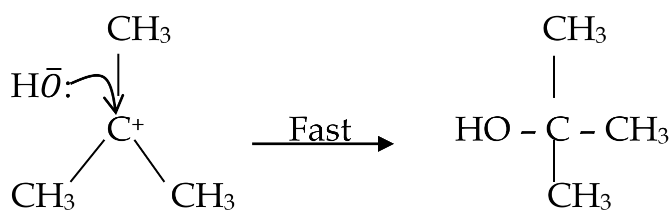
(iii) Tertiary alkyl halides



Tertiary alkyl halides follow SN_1 mechanism. Here only the alkyl halide molecule is involved in the activated complex and thus its concentration alone determines the order of reaction.

Mechanism:



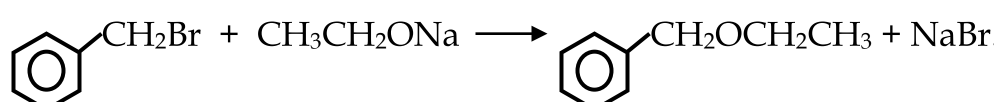


REACTIONS WITH ALKA OXIDES (Na, K)

Alkyl halides react with sodium or potassium alka oxides to form ethers under heat.

$$CH_3CH_2Cl + CH_3\bar{O}Na^{+} \xrightarrow{heat} CH_3CH_2OCH_3 + NaCl.$$

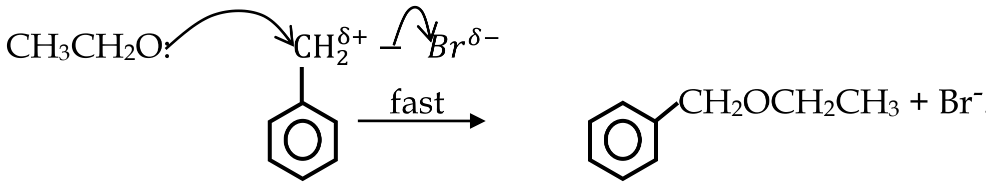
Ethoxy methane.



Bromo phenyl methane Phenyl methoxy ethane

Mechanism:

$$CH_3CH_2\bar{O}Na^+ \xrightarrow{slow} CH_3CH_2\bar{O}_{(aq)} + Na^+$$



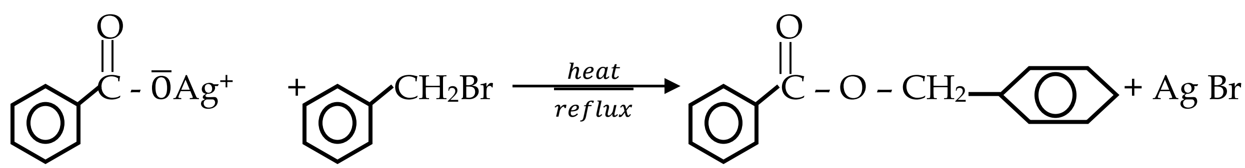
$$Na^+_{(aq)} + Br^-_{(aq)} \longrightarrow NaBr.$$

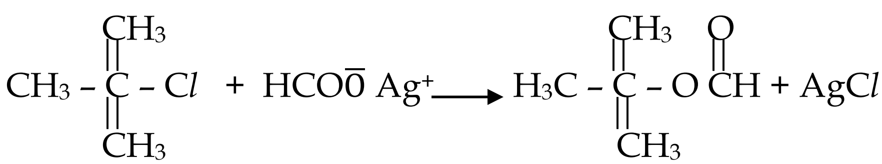
REACTIONS WITH SILVER SALTS OF CARBOXYLIC ACIDS

Alkyl halides react with silver salts of carboxylic acids when refluxed to form esters. This reaction uses the alkanoate ion as the nucleophille.

$$CH_3\,CO\bar{O}Ag^+ + CH_3CH_2\,Cl \xrightarrow{Reflux} CH_3\overset{O}{\overset{||}{C}}OCH_2\,CH_3 + AgCl$$

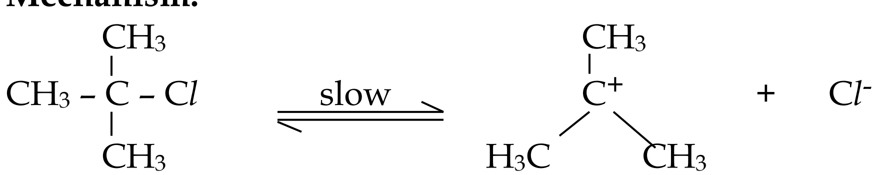
Ethyl Ethanoate



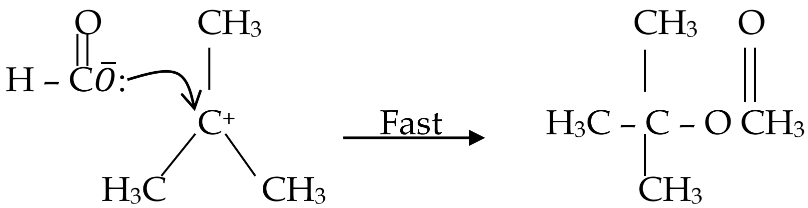


2, 2 dimethyl, ethyl methanoate.

Mechanism:



$$H\overset{O}{\overset{||}{C}}\,\bar{O}\,Ag^+ \longrightarrow H\overset{O}{\overset{||}{C}}-\bar{O} + Ag^+.$$



$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)}$.

REACTIONS WITH POTASSIUM CYANIDE (KCN)

Alkyl halides react with KCN in presence of an alcohol when refluxed to form alkyl nitriles.

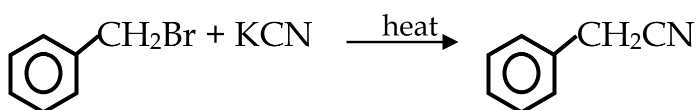
Condition (reflux) – alcohol present.

Nucleophile $\bar{C} \equiv N$ or $\bar{C}N$.

Example:

$CH_3CH_2CH_2Cl + KCN \xrightarrow[reflux]{heat} CH_3CH_2CH_2CN + KCl$

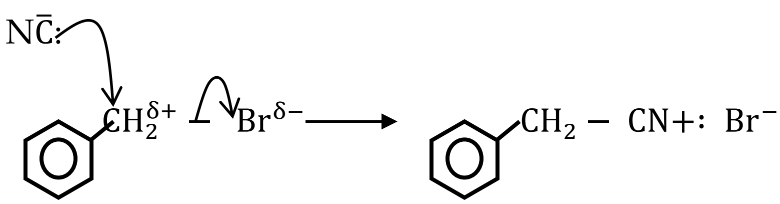
Propy nitrile.



Phenyl methyl nitrile.

Mechanism:

$KCN \longrightarrow K^{+} + \bar{C}N$.



$K^{+}_{(aq)} + Br^{-}_{(aq)} \longrightarrow KBr$.

Note:

(i) The above reaction is important inorganic synthesis, more especially increasing the carbon length (chain) by a single carbon.

(ii) Silver cyanide can also be used instead of potassium cyanide.

Convert CH_3COOH to CH_3CH_2COOH.

REACTIONS WITH SILVER NITRITE ($AgNO_2$).

Alky halides react with $AgNO_2$ when refluxed to form a mixture of nitro alkanes and alkyl nitrite. Such types of reactions are not important in synthesis since they yield a mixture of products.

$$CH_3\,Cl + AgNO_2 \xrightarrow[reflux]{heat} CH_3\,NO_2 \text{ Nitro methane}$$

$$CH_3\,Cl + AgNO_2 \xrightarrow[reflux]{heat} CH_3O - N = O \text{ Methyl nitrite.}$$

Mechanism:

$$AgNO_2 \longrightarrow Ag^+ + N\bar{O}_2.$$

$$O = N\text{-}\bar{O}:$$

$$CH_3^{\delta+} - Cl^{\delta-} \longrightarrow CH_3O - N = O + Cl^-$$

Methyl nitrite

$$Ag^+ + Cl^- \longrightarrow Ag\,Cl^-_{(aq)}$$

Or:

$$O = \ddot{N} - \bar{O}:$$

$$CH_3^{\delta+} - Cl^{\delta-} \longrightarrow CH_3NO_2 = O + Cl^-$$

Nitro methane

$$Ag^+ + Cl^- \longrightarrow AgCl.$$

REACTIONS WITH AMMONIA AND AMINES

Alkyl halides react with conc. NH_3 to form a mixture of amines when heated in a sealed tube. A mixture of amines are produced because a product at one stage become a nucleophille for the next stage. The nucleophille is ammonia and the amines.

$$CH_3\,CH_2 - I + NH_3 \xrightarrow[sealed\ tube]{heat\ in} CH_3\,CH_2\,NH_2 + HI$$

Ethyl amine (Primary)

$$CH_3\,CH_2 - I + CH_3\,CH_2\,NH_2 \xrightarrow[sealed\ tube]{heat} CH_3\,CH_2\,NH\,CH_2\,CH_3 + HI$$

Diethyl amine (Secondary)

$$CH_3\,CH_2 - I + CH_3\,CH_2\,NH\,CH_2\,CH_3 \xrightarrow[sealed\ tube]{heated} CH_3\,CH_2\overset{\overset{CH_2\,CH_3}{|}}{\underset{\bullet\bullet}{N}} - CH_2\,CH_3$$

Triethyl amine (Tertiary)

$$CH_3\,CH_2 - I + (CH_3\,CH_2)_3N \xrightarrow[sealed\ tube]{heat} (CH_3\ CH2)_{\bar{4}}\ +_{N}$$

Tetra ethyl amine
(Quaternary amine)

ELIMINATION REACTIONS OF ALKYL HALIDES

These are reactions that will result into the formation of unsaturated compound with elimination of a water molecule. Alkyl halides when refluxed or heated with an alkali (KOH, NaOH) in the presence of an alcohol, they from alkene. The reaction can also be effected by using a strong base which is an alka oxide.

Strong base (Alka oxide)

Ethanoxide / $\epsilon t\bar{O}$
Methoxide / met $\bar{O}$

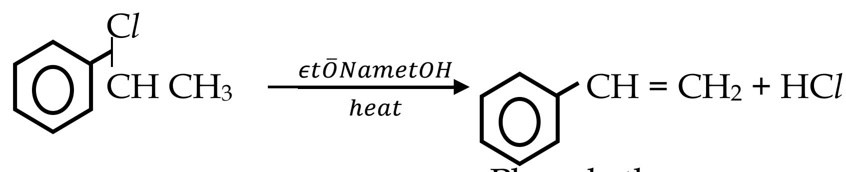
DEHYDROHALOGENTION

$$CH_3\,CH_2\,Cl \xrightarrow[\epsilon t\bar{O}]{NaOH_{(aq)}} CH_2 = CH_2 + HCl$$

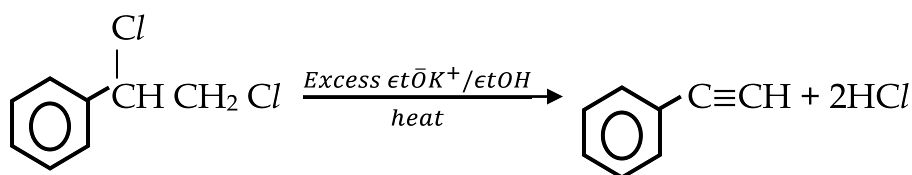
$$CH_3\,\underset{\underset{Br}{|}}{C}H\,CH_3 \xrightarrow[heat]{\bar{O}H_{(aq)}/\epsilon tOH} CH_2 = CH\,CH_3 + HBr.$$

$$H_3C-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl \xrightarrow[heat]{\epsilon t\bar{O}/met\bar{O}H} CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3\ HCl$$

2-methyl/prop-1-ene.



Phenyl ethene



Phenyl ethyne

Mechanisms:
Elimination bimolecular (ϵ_2).

$$\epsilon t\bar{O}Na^+ \;+\; \bar{O}H_{(aq)} \longrightarrow \epsilon t\bar{O}Na^+ + H_2O$$

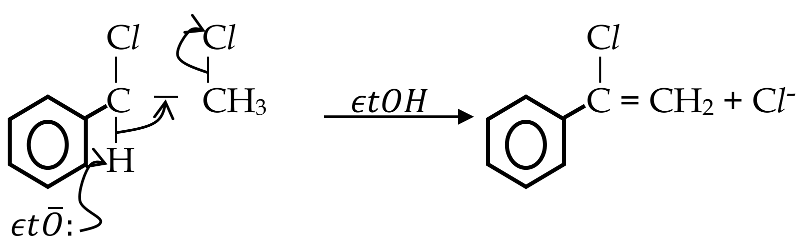
$$\epsilon t\bar{O}Na^+ \rightleftharpoons \epsilon t\bar{O}: + Na^+.$$

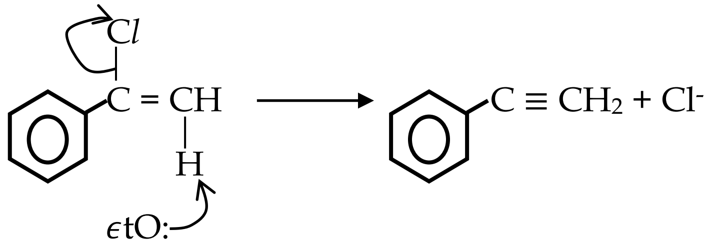
$$\underset{\underset{H}{|}}{H_3C} - \underset{\underset{Br}{|}}{CH}\ CH_3 \longrightarrow H_2C = CH\ CH_3 + Br^- + \epsilon tOH$$

$\epsilon t\bar{O}$:

Na^+ + Br- $\longrightarrow$ NaBr.

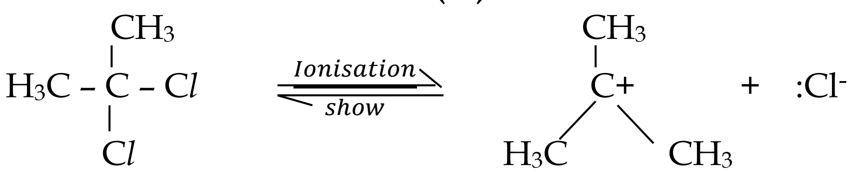
$$\epsilon t\bar{o}K^+(aq) \rightleftharpoons \epsilon t\bar{O}(aq) + K^+(aq).$$

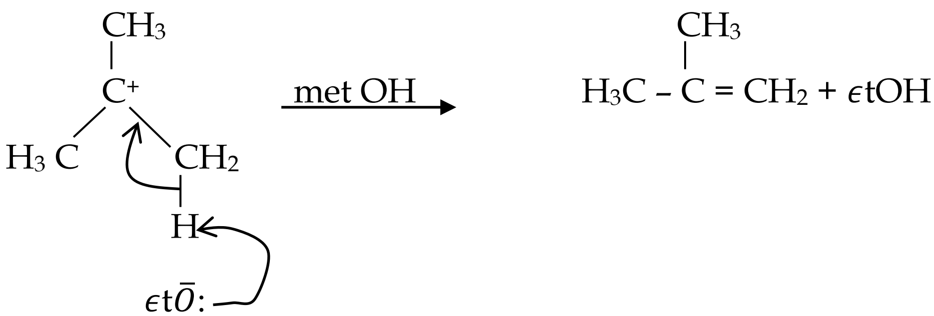




$Cl^{-}_{(aq)} + K^{+} \longrightarrow KCl$

Elimination uimolecular (ϵ_1)





Research: Discus all the reactions of chloro ethane with NaOH. (25mks)

Wurtz reaction:

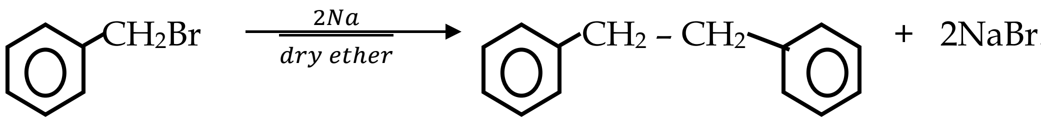
When alkyl halides are reacted with Na metal in the presence of ether, alkanes are formed. The product will have an increased carbon atom by 2 i.e. the carbon number doubles.

$$2\,R - X + 2Na \xrightarrow{\text{dry ether}} \underset{\text{Akane.}}{R - R} + 2NaX.$$

$$2CH_3Cl + 2Na \xrightarrow{\text{dry ether}} CH_3\,CH_3 + 2NaCl.$$

$$CH_3\,\overset{\overset{CH_3}{|}}{CH}\,Cl \xrightarrow{\text{Na/dry ether}} CH_3\,\overset{\overset{CH_3}{|}}{CH}\;\overset{\overset{CH_3}{|}}{CH}\;\overset{\overset{CH_3}{|}}{CH_3} + 2NaCl$$

$$CH_3\,\overset{\overset{CH_3}{|}}{CH}\,\overset{\overset{CH_3}{|}}{CH}\,CH_3$$



DIHALIDES COMPOUNDS

There are compounds that have got two halogen atoms within the same carbon chain.

There are two types of dihalides;

(i) **Vicinal dihalide**

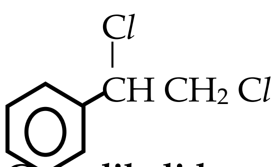
This contains two halogen atoms located on any adjacent carbon atom i.e.

$H_2C - CH_2$
$\;\;\;\;|\;\;\;\;\;\;|$
$\;\;\;\;X\;\;\;\;X$

Example:

$CH_2\,Cl\,CH_2\,Cl$ — 1, 2-dichloro ethane.

$\;\;\;\;\;\;\;\;\;\;\;\;Br$
$\;\;\;\;\;\;\;\;\;\;\;\;|$
$CH_3\,CH\,CH\,CH_3$ — 2, 3-dibromo butane.
$\;\;\;\;\;\;\;\;|$
$\;\;\;\;\;\;\;Br$



1, 2-dichlorophenyl ethane.

(ii) **Gem dihalides**

These contain the two halogen atoms located on the same carbon atoms.

i.e.
$$\begin{array}{c} X \\ | \\ CH_3 - C - CH_3 \\ | \\ X \end{array}$$

Example:

$$\begin{array}{c} Cl \\ | \\ CH_3\;C - CH_3 \\ | \\ Cl \end{array}$$

2, 2 dichloro propane

$CH_3\ CH\ Cl_2$ 1, 1-dichloro ethane.

PREPARATION OF DIHALIDES

Dihalides are prepared from the following reactions:

(i) **From Alkenes**

When alkenes are reacted with halogens in presence of CCl_4 (organic base) at room temperature, a vicinal dihalide is formed.

$$CH_2 = CH_2 + Cl_2 \xrightarrow[R.T]{CCl_4} Cl\ CH_2\ CH_2\ Cl.$$

(ii) From alkynes and halogen acids

When alkynes react with halogen acids (excess), a gem dihalide is formed.

$$CH_3\ C \equiv CH + 2HBr \xrightarrow[\text{heat}]{} CH_3\ \underset{\large Br}{\overset{\large Br}{\underset{|}{\overset{|}{C}}}} - CH_3$$

$$HC \equiv CH + 2HCl \xrightarrow[heat]{ROOR} H_3C - C\ Cl_2.$$

(iii) **From carbonyl compounds (Aldehydes and Ketones).**

When a carbonyl compound is reacted with phosphorous pental tri chloride, a dihalide is formed. Usng aldehydes, will produce a gem dihalide and ketones also produce gem dihalide.

$$CH_3\ \overset{\large O}{\overset{||}{C}} - H + PCl_5 \longrightarrow CH_3\ CH\ Cl_2 + POCl_3$$

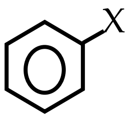
$$CH_3\ \overset{\large O}{\overset{||}{C}}\ CH_3 + PCl_5 \longrightarrow CH_3 - \underset{\large Cl}{\overset{\large Cl}{\underset{|}{\overset{|}{C}}}} - CH_3 + POCl_3$$

POLYHALIDES

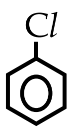
These are halogen compound with more than two halogen atoms on the same carbon chain.

AROMATIC HALIDES

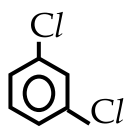
These are compounds with one or more halogen atoms directly attached to the aromatic ring.



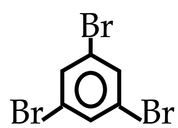
or Ar – X



Chloro benzene

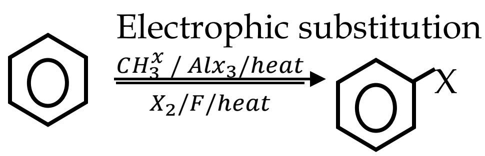


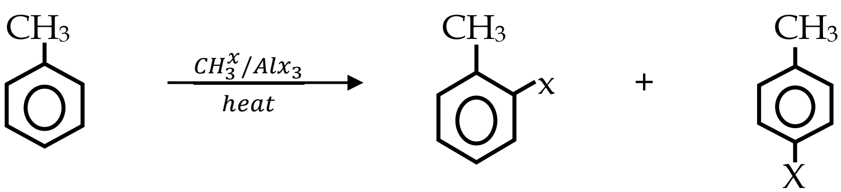
1, 3-dichloro benzene



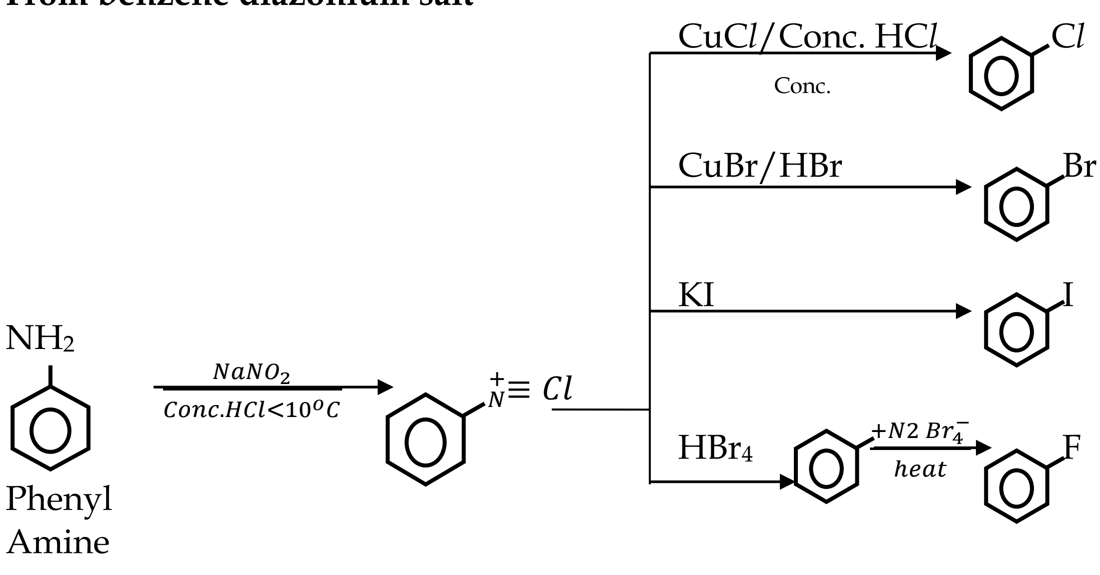
1, 3, 3-tribromo benzene.

PREPARATION





From benzene diazonium salt

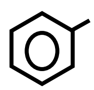
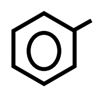


PHYSICAL PROPERTIES OF AROMATICS

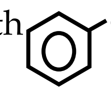
They are colourless liquids or solids with characteristic flame.

They are insoluble in H_2O but soluble in organic solvents like CCl_4.

NOTE:
They do not easily undergo necleophillic substitution unlike alkyl halide.

Distinguish between  Cl and  CH_2Cl

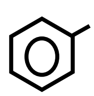
Reagent: Hot aqueous NaOH in dil HNO_3 and $AgNO_3$.

Observations:
- A white precipitate forms with CH_2Cl.
- No observable change with  Cl.

ALCOHOLS AND PHENOLS:

These are compounds that contain hydroxyl group. Therefore the functional group is hydroxyl group. The difference between alcohol or alkanols and phenol is that the hydroxyl group is directly attached to the aromatic ring in phenols.

Alkanol	Phenol
R – OH	Ar – OH



OH

ALKANOLS OR ALCOHOLS

Alcohols are organic compounds derived from hydro carbons but where one or more hydrogens is/are replaced by hydroxyl group. The general formula is R – OH where R is an alkyl group or simply represented as $C_nH_{2n+1}OH$. Where n = simple number.

They are also called alkanols simply because a hydroxyl group replaces a hydrogen.

TYPES OF ALCOHOLS

There are basically three types of alcohols:

(i) Monohydric alcohol

This is one that has got one hydroxyl group.

(ii) Dihydric alcohol

This is one that has got two hydroxyl groups.

(iii) Polyhydric alcohol

These have got more than two hydroxyl groups e.g.

$$\begin{array}{l} HO - CH_2\ \underset{\displaystyle OH}{\underset{|}{CH}}\ CH_2\ OH \end{array}$$

NOMENCLATURE

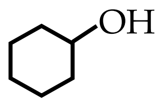
Alcohols are named as alkanols according to the IUPAC. This is done by replacing the last "e" in alkane name with suffix "ol" (functional group name).

The position of the functional group has to be indicated just before the suffix "ol.

If the stem name has got a vowel, then a consonant letter must be added just before the position of the functional group.

E.g.	$CH_3\ CH_2\ OH$	Ethano-1-ol
	$CH_3\underset{\displaystyle OH}{\underset{\vert}{C}}H\ CH_3$	Propan-2-ol
	$CH_3\ \ \overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle OH}{\underset{\vert}{C}}}}\ \ CH_2\ \ CH_3$	2-methyl butan-2-ol.
	$HO - CH_2CH_2OH$	Ethane-1, 2 – diol

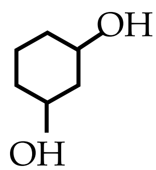
$HO - CH_2CH(OH)CH_2OH$ Propane – 1, 2, 3 – triol.



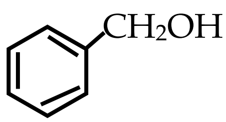
Cyclohexan-1-ol

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

2-methyl propan-2-ol



Cyclohexan-1, 3-diol
Xyclohexane-1, 3-diol



Phenyl methan-1-ol.

NOTE: Loot at isomerism in alcohols.
Types – structural:
(i) Chain
(ii) Position
- Functional (alcohol and others are isomeric).

CLASSES OF ALCOHOLS

Monohydric alcohols are classified into three classes.

(i) **Primary alcohol**

This has one alkyl group attached to the carbon atom carrying the –OH group. E.g. $-\underset{\displaystyle H}{\underset{|}{C}} - OH$

$CH_3CH_2 - OH$

(ii) **Secondary alcohol**

This has got two alkyl groups attached to the carbon atom carrying the OH group.

$$\begin{array}{c} \diagdown \\ H - C - OH \\ \diagup \end{array}$$

E.g: $\begin{array}{l} CH_3\ CH\ CH_3 \\ \quad\ \ | \\ \quad\ OH \end{array}$

(iii) **Tertiary alcohol**

This has three alkyl groups attached to the carbon atom carrying the OH group.

$$\begin{array}{c} | \\ - C - OH \\ | \end{array}$$

E.g.

$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3 - & C & - OH \\ & | & \\ & CH_3 & \end{array}$$

METHODS OF PREPARATION

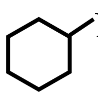
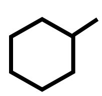
(i) **From alkyl halide (SN reaction)**

When alkyl halides are refluxed with aqueous alkali IKOH or NaOH) or with moist silver oxide, alcohols are formed.

This is a hydrolysis reaction that occurs by nucleophillic substitution reaction.

$$CH_3\ CH_2\ Cl + NaOH_{(aq)} \xrightarrow{warm} CH_3\ CH_2\ OH + NaCl$$

$$\begin{array}{c} I \\ | \\ CH_3 - C - CH_3 \\ | \\ CH_3 \end{array} + \bar{O}H_{(aq)} \xrightarrow{heat} \begin{array}{c} OH \\ | \\ CH_3 - C - CH_3 \\ | \\ CH_3 \end{array} + I^-$$

Br + $KOH_{(aq)} \xrightarrow{heat}$ OH + KBr.

$$\begin{array}{c} Cl \\ | \\ CH_3\ CH\ CH_3 \end{array} + AgOH_{(aq)} \longrightarrow \begin{array}{c} OH \\ | \\ CH_3\ CH\ CH_3 \end{array} + AgCl.$$

(ii) **From alkenes**

When alkenes are reacted with dilute mineral acid water and heated, an alcohol is formed. They usually used acid is H_2SO_4 acid.

If the mixture is not heated, then an alkyl hydrogen sulphate is formed.

$$CH_2 = CH\,CH_3 \xrightarrow[heat]{H^+/H_2O} H - CH_2\,\underset{}{\overset{OH}{|}}{CH_2} - CH_3$$

$$CH_2 = CH\,CH_3 \xrightarrow{H_2SO_4/H_2O} CH_3\underset{HSO_4}{\underset{|}{C}}H_2\,CH_3$$

Mechanism:

$H^{\delta+} - O^{\delta-}SO_3H$

$$CH_3\,CH = CH_2 \quad H^+ \longrightarrow CH_3 - {}^+CH\,CH_3.$$

$$CH_3\,{}^+CH\,CH_3 \longrightarrow CH_3 - \underset{\underset{H\quad H}{O^+}}{\underset{|}{CH}} - CH_3 \xrightarrow{-H^+} CH_3\,\underset{OH}{\underset{|}{CH}}\,CH_3 + H^+$$

$\ddot{O}H_2$

OR:

$$CH_3\,CH = CH_2 \quad H^{\delta+} - O^{\delta-}SO_3H \longrightarrow CH_3\,{}^+CH\,CH_3 + \bar{O}SO_3H$$

$$CH_3{}^+CH\,CH_3 \longrightarrow CH_3\,\underset{OSO_3H}{\underset{|}{CH}}\,CH_3$$

$:\bar{O}SO_3H$

$\downarrow$ H_2O/heat

NOTE:

H_2O acts as a nucleophile that will react with the alkyl hydrogen sulphate in the last step to form an alcohol. i.e.

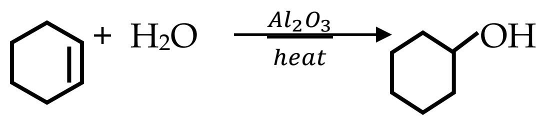
$:OH_2$

$$CH_3\,\underset{OSO_3H}{\underset{|}{CH}}\,CH_3 \longrightarrow CH_3 - \overset{\overset{H\quad H}{O^+}}{\overset{|}{CH}}\,CH_3 \xrightarrow{-H^+} OH$$

$CH_3\,CH\,CH_3$

When alkenes are reacted with H_2O in presence of Al_2O_3, an alcohol is formed. E.g.

$$CH_3CH = CH_2 + H_2O \xrightarrow[heat]{Al_2O_3} \underset{\displaystyle CH_3\ CH\ CH_3}{\overset{\displaystyle OH}{|}}$$



$$CH_3\ \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + H_2O \xrightarrow[heat]{Al_2O_3} CH_3\ \underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_3$$

(iii) **From carbonyl compounds (Aldehydes and ketones)**

Carbonyl compounds are reduced in the presence of a suitable reducing agent to alcohols.

$$\text{Aldehydes} \xrightarrow{[H]} \text{Primary alcohols}$$

$$\text{Ketones} \xrightarrow{[H]} \text{Secondary alcohols}$$

Reducing agents normally used:

Hydrogen in presence of catalyst, Ni/150, Pt/pd, r.t.p.

Using Li Al H_4 (Lithium, Aluminium, Tetra hydride) in presence of dry ether.

Sodium boron tetrahydride ($NaBH_4$)

E.g.

$$CH_3\ CH_2\ \overset{\overset{\displaystyle O}{||}}{C}H + H_2 \xrightarrow[150^oC]{Ni} H_3\ CH_2\ CH_2OH$$

Propanal Propanol

$$CH_3\ \overset{\overset{\displaystyle O}{||}}{C}\ CH_3 + H_2 \xrightarrow{Ni\ /150^oC} CH_3\ \underset{\underset{\displaystyle OH}{|}}{CH}\ CH_3$$

$$CH_3\overset{O}{\overset{||}{C}}H \xrightarrow[dry\ ether]{LiAlH_4} CH_3\,CH_2\,OH$$

$$CH_3\,\underset{O}{\underset{||}{C}}\,CH_2\,CH_3 \xrightarrow{NaBH_4} CH_3\,\underset{OH}{\underset{|}{C}}H\,CH_2\,CH_3$$

$$CH_3\,CH = CH\,\overset{O}{\overset{||}{C}}H \xrightarrow[Dry\ ether]{Li\ AlH_4} CH_3CH = CH_2\,CH_2\,OH$$

$$CH_3\,CH = CH\,\overset{O}{\overset{||}{C}}H \xrightarrow[150^oC]{H_2/Ni} CH_3\,CH_2\,CH_2\,CH_2\,OH$$

(iv) **Hydrolysis of esters**

Esters are hydrolyzed in presence of mineral acids or alkalis to form corresponding alcohols and carboxylic acids. This reaction is not very useful for synthesizing alcohols because of the mixture of alcohol and acid.

$$CH_3\,\overset{O}{\overset{||}{C}}\,OO\,CH_2\,CH_3 \underset{heat}{\overset{H^+(aq)}{\rightleftharpoons}} CH_3\,COOH + CH_3\,CH_2\,OH$$

$$CH_3\,O\,\overset{O}{\overset{||}{C}}\,CH_3 \underset{heat}{\overset{OH(aq)}{\rightleftharpoons}} CH_3\,OH + CH_3\,COOH$$

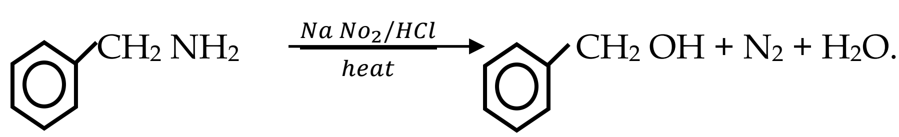
Ethyl ethanoate

Mechanism: (look for acid/base hydrolysis of esters).

(v) **From primary amines**

They react with HNO_2 acid which is generated "insitu" by reacting sodium nitrite and conc. HC*l* to form alcohols. This reaction is only for primary amines and not secondary or tertiary.

$$CH_3\,NH \xrightarrow[heat]{Na\,No_2/HCl} CH_3OH + N_2 + H_2O$$



(vi) **From fermentation of carbohydrates.**

PROPERTIES OF ALCOHOLS

PHYSICAL PROPERTIES

Lower members are liquids, higher members are solids at r.t.p with x-tic smell.

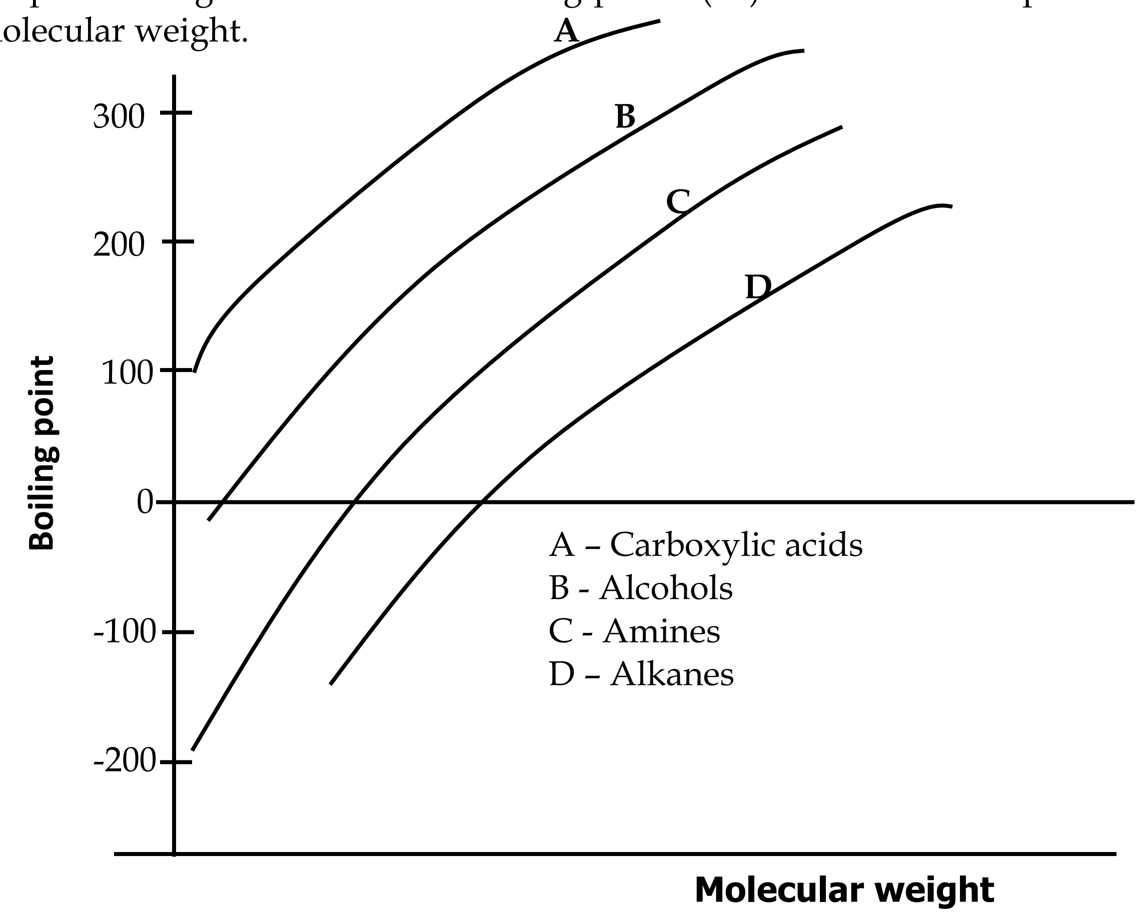
The lower members are very soluble in H_2O but the solubility decreases with the molecular mass.

Alcohols have got relatively higher boiling points compared to similar hydro carbons of approximately the same molecular mass.

Examples:

	Molecular weight	**Boiling points**
Ethane	30	-42
Methanol	32	46
Butane	58	-0.5
Propan-ol	60	98

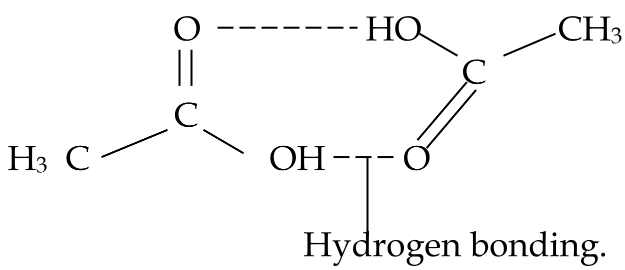
Graph showing the variation of boiling points (^oC) of different compounds with molecular weight.



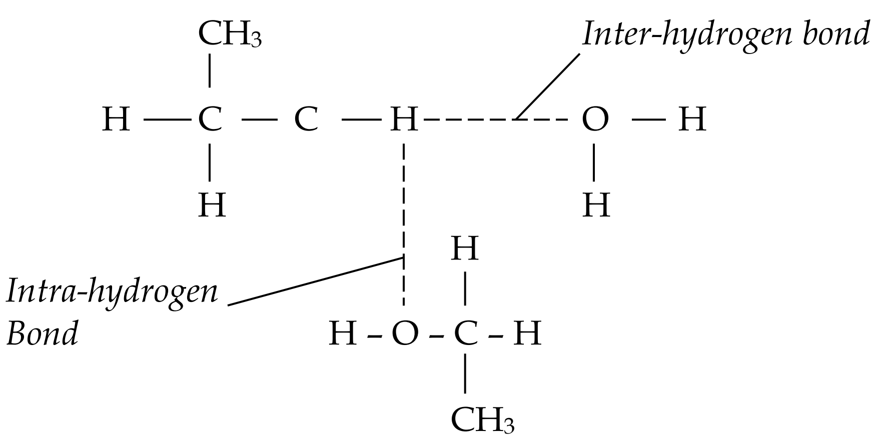
Note:
The boiling points increase generally with increase in molecular weight.
Increase in molecular weight increases the Van Der Waal's forces of attraction. This makes the compound stronger hence high boiling points.

Explanation:
The boiling points of the compounds above on the graph are determined by hydrogen boding.

Carboxylic acids have got the highest boiling points due to extensive hydrogen bonds which makes molecules to dimerise in a liquid hence difficult to separate them during boiling so that they escape to vapour.



Alcohols' boiling point is higher than that of alkanes but lower than that of carboxylic acid because of inter and intramolecular hydrogen bonding. Molecules will interact in liquids and aqueous phases and high boiling point.



Amines boil at a lower temperature than alcohols of the corresponding molecular weight because nitrogen is less electronegative than oxygen so the hydrogen bonds formed in amines are weaker than in alcohols thus amines boil at a lower temperature.

Alkanes have the least boiling point because of the absence of hydrogen with only Van der Waal's forces of attraction which are weaker and easily broken during boiling.

In summary:
The solubility in water and the boiling points of alcohols are due to hydrogen bonding.

Questions:

1. Methyl amine (mm = 31) boils at -6.3^{o}C while methanol (mm = 32) boils at 46^{o}C. Explain.

2. 2-methyl propan-2-ol boils at a lower temperature than butan-1-ol yet they all have the same molecular weight.

$$\begin{array}{ccc} & OH & \\ & | & \\ CH_3 & C & CH_3 \\ & | & \\ & CH_3 & \end{array} \qquad \text{and} \qquad CH_3\,CH_2\,CH_2\,CH_2\,OH$$

2 methyl propan-2-ol is highly branched giving it a spherical shape which decreases on the size and weakens the Van der Waal's forces of attraction existing between the molecules.

Butan-1-ol is a straight chain molecule which gives it an extended structure resulting in relatively stronger Van der Waal's forces.

CHEMICAL PROPERTIES OF ALCOHOLS

Alcohols consists of three major bonds that are involved in a chemical reaction.

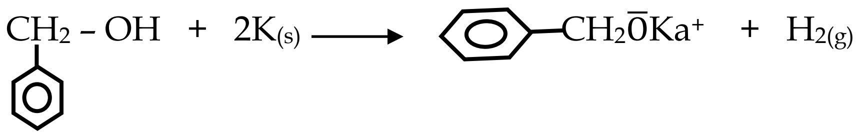
(i) Functional group – OH group.
Where the O – H bond is involved in the reaction.
(ii) Oxygen-carbon bond which is highly polarized.
(iii) Alkyl groups – R group.

REACTION INVOLVING CLEAVAGE OF THE O – H BOND

Reactions with electropositive metals:
When an alcohol is reacted with a metal like sodium or potassium, an alka oxide and H_2 gas are formed.

$$2R - OH + 2Na_{(s)} \longrightarrow 2R - \bar{O}Na^{+} + H_2$$

$$CH_3CH_2OH + Na_{(s)} \xrightarrow{r.t.p} 2CH_3CH_2\bar{O}Na^{+} + H_{2(g)}$$



Observation:
Effervescence of a colourless gas that burns with a pop sound.

Reactions with mineral acids:
When an alcohol is reacted with a mineral acid, a salt is formed.

$$R - OH + HCl \longrightarrow R - \overset{+}{O}H_2Cl$$

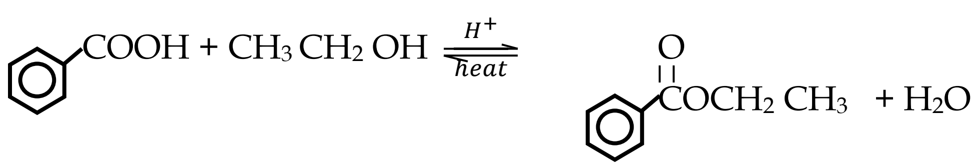
$$CH_3CH_2OH + HCl \longrightarrow CH_3CH_2\overset{+}{O}H_2Cl$$

From the two reactions above, alcohols are regarded as amphoteric because they react with acids and bases to show both acidic and basic.

Esterification
Alcohols react with carboxylic acids in presence of mineral acids to form esters. This reaction is known as esterification.

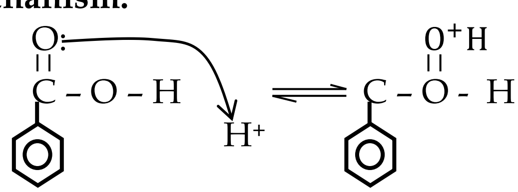
$$CH_3CH_2OH + CH_3CH_2COOH \underset{heat}{\overset{H^+}{\rightleftharpoons}} CH_3CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_3 + H_2O$$

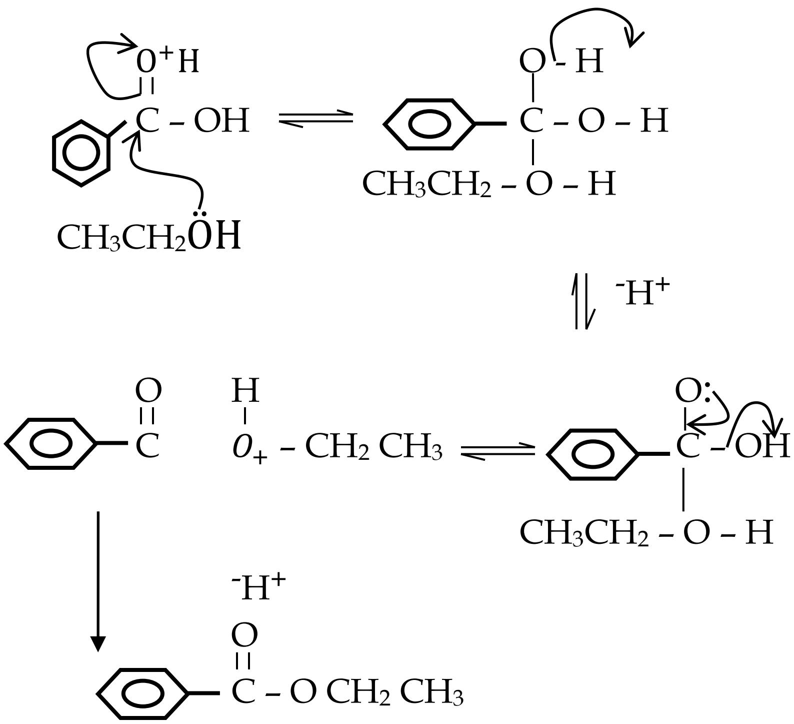
Ethyl propanoate



Ethyl benzoate.

Mechanism:



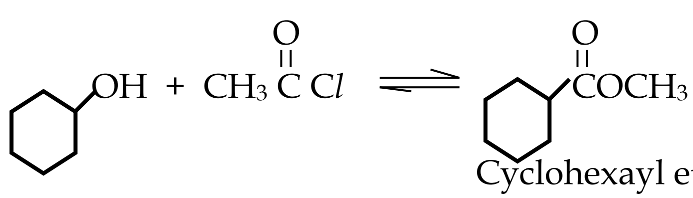


Alcohols react with acid chlorides to form esters.

$$CH_3CH_2OH + CH_3\overset{\overset{O}{\|}}{C}Cl \rightleftharpoons CH\overset{\overset{O}{\|}}{C}OCH_2CH_3 + HCl$$

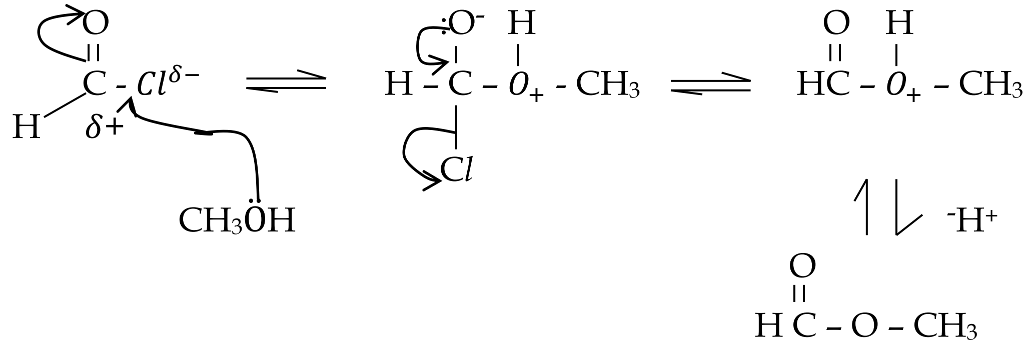
Ethanol
Chloride

$$CH_3OH + HCOCl \rightleftharpoons H\overset{\overset{O}{\|}}{C}OCH_3 + HCl$$



Cyclohexayl ethanoate.

Mechanism:



Alcohols react with acid anhydrides to form esters.

$$R^1 - \overset{O}{\overset{\|}{C}} - O - \overset{O}{\overset{\|}{C}} - R^2 + R^3 - OH \underset{}{\overset{H^+}{\rightleftharpoons}} R^1 - \overset{O}{\overset{\|}{C}} - OR^3 + R^2 - \overset{O}{\overset{\|}{C}} - OH$$

$$CH_3\overset{O}{\overset{\|}{C}} - O\overset{O}{\overset{\|}{C}}H_3 + CH_3OH \overset{H^+}{\rightleftharpoons} CH_3\overset{O}{\overset{\|}{C}} - OCH_3 + CH_3COOH$$

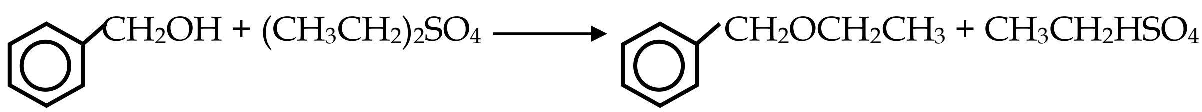
Ethanoic acid anhydride — Methyl ethanoate

Alkylation of alcohols

Alcohols react with dialkyl sulphates to form ethers and alky derivatives. This reaction involves replacement of hydrogen in the alcohol with alkyl group.

$$R - OH + R_2SO_4 \longrightarrow R - O - R + RHSO_4$$

$$\underset{}{CH_3CH_2OH} + \underset{\text{Dimethyl Sulphate}}{(CH_3)_2SO_4} \longrightarrow \underset{\text{Ethoxy methane}}{CH_3CH_2OCH_3} + \underset{\text{Methyl hydrogen sulphate}}{CH_3HSO_4}$$



REACTIONS INVOLVING CLEAVAGE OF A CARBON OXYGEN BOND

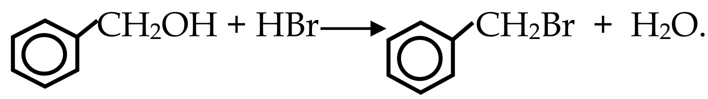
In these reactions, we are removing both oxygen and hydrogen atoms from the alcohol.

Reactions with halogen acids (Hx)

Alcohols react with halogen acids to form alkyl halides.

$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O.$$

$$CH_3CH_2OH + HI \longrightarrow CH_3CH_2I + H_2O.$$



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + HCl \longrightarrow CH_3\,\underset{\displaystyle CH_3}{\underset{|}{CH}}-Cl + H_2O$$

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH + HCl \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-Cl + H_2O$$

Mechanism:

Primary and secondary alcohols follow SN_2 mechanism because of the fairly unstable carbon cation ion, while the tertiary alcohols follow SN_1 because of the stability of the carbon cation ion formed.

SN_2:

$$CH_3\,CH_2\,\ddot{O}H + H^{\delta+} - Cl^{\delta-} \xrightarrow[\text{slow}]{} CH_3CH_2O^{+}H_2 + Cl^{-}$$

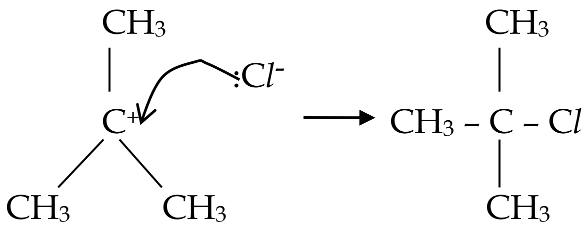
$$CH_3CH_2 - \overset{+}{O}H_2 \xrightarrow{\text{fast}} CH_3CH_2 - Cl + H_2O$$

$$:Cl^{-}$$

SN_1:

$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH \rightleftharpoons \overset{\displaystyle CH_3}{\overset{|}{\underset{H_3C\;\diagup\;\;\diagdown\;CH_3}{C^{+}}}} + \bar{O}H_{(aq)}$$

$$H - Cl \longrightarrow H^{+} + Cl^{-}$$



$H^+ + \overline{O}H \longrightarrow H_2O.$

PRACTICAL IMPORTANCE OF THE REACTION

The practical importance of the above reaction is to distinguish between the three classes of alcohol.

Reagent: An hydrous zinc chloride in concentrated hydrochloric acid.

Observation:

- An immediate cloudy solution at room temperature forms with a tertiary alcohol.
- Within 5 minutes at room temperature, a cloudy solution is formed with a secondary alcohol.
- No cloudy solution forms at room temperature with primary alcohol.

Equations:

$$CH_3\underset{\underset{\displaystyle OH}{|}}{CH}CH_3 + \underset{\text{Conc.}}{HCl} \xrightarrow{\text{Anhydrous } ZnCl_2} CH_3\overset{\overset{\displaystyle Cl}{|}}{CH}CH_3 + H_2O$$

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-OH + \underset{\text{Conc.}}{HCl_{(l)}} \xrightarrow{ZnCl_{2(s)}} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl + H_2O$$

REACTIONS WITH PHOSPHORUS HALIDES

Alcohols react with PX_5 and PX_3 to form alky halides where X is a halogen.

$$3CH_3\,CH_2\,OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + HCl + POCl_3$$

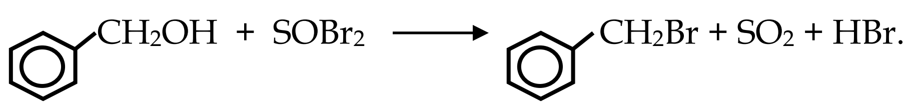
Others: PI_3/PI_5
PBr_3/PBr_5.

NOTE:
Evolution of HCl or fuming whenPCl_5 is added to a compound suggests the presence of OH group in that compound.

REACTION WITH THINLY CHLORINE

Alcohols react with $SOCl_2$ or $SOBr_2$ to form alkyl halides. An organic base like pyridine must be included to neutralize toxic and poisonous gases liberated.

$$CH_3CH_2\,OH + SOCl_2 \xrightarrow{\text{pryridine}} CH_3CH_2Cl + SO_2 + HCl.$$



Mechanism:

REACTION WITH H_2SO_4 ACID

Alcohols react with H_2SO_4 giving different products depending on the conditions of reaction.

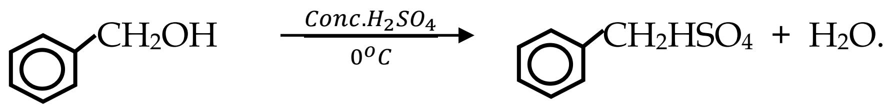
Conditions:

A. (i) Conc. H_2SO_4 Products got are substituted products.
(ii) Excess alcohol
(iii) Low temperatures.
Substituted products.
Alky hydrogen sulphate – 0^oC.
Ether – warm (140^oC)

B. (i) Conc. H_2SO_4.
(ii) High temperatures (heat) - Elimination product.
(iii) Limited alcohol.

Example:

$$CH_3CH_2OH \xrightarrow[0^oC]{Conc.H_2SO_4} CH_3CH_2HSO_4 + H_2O.$$



Phenyl methyl
Hydrogen sulphate.

Mechanism:

$$CH_3\ CH_2\ \ddot{O}H \quad H^{\delta+} - {}^{\delta-}_{O}SO_3H \longrightarrow CH_3CH_2\overset{+}{O}H_2 + \bar{O}SO_3H$$

$$CH_3\ CH_2 - \overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3\ {}^{+}CH_2 + H_2O.$$

$$CH_3\ {}^{+}CH_2 \longrightarrow CH_3CH_2HSO_4$$

$$:OSO_3H.$$

Excess

$$2CH_3CH_2OH \xrightarrow[140^oC]{Conc.H_2SO_4} CH_3CH_2O\ CH_2\ CH_3 + H_2O$$

Diethyl ethers

$$2CH_3OH \xrightarrow[140^oC]{Conc.H_2SO_4} CH_3\ O\ CH_3 + H_2O.$$

Mechanism:

$$CH_3\ CH_2\ \ddot{O}H \quad H^{\delta+} - {}^{\delta-}_{O}SO_3H \longrightarrow CH_3CH_2\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3\ {}^{+}CH_2$$

$[CH_3\ CH_2\ OH] >> [\bar{O}SO_3]$ therefore CH_3CH_2OH is a better nucleophile.

$$CH_3\ CH_2\ddot{O}H \quad {}^{+}CH_3CH_2 \longrightarrow CH_3CH_2 - O - CH_2\ CH_3$$

$$\downarrow {}^{-}H^{+}$$

$$CH_3CH_2\ O\ CH_2\ CH_3$$

Alcohols are dehydrated when heated with conc. H_2SO_4 and H_3PO_4 acid to form alkenes in a liquid phase or when the alcohol is passed over heated Al_2O_3 at 300^o in a vapour phase.

Water molecule is eliminated and therefore this type of reaction is known as elimination or dehydration.

The reactivity in the liquid phase is determined by the type of carbon cation ion formed.

Elimination reactions occur under the following conditions:

(i)	Heat:	[170 – 185^{o}C]	Primary alcohol
		[150 – 180^{o}C]	Secondary alcohol
		[90 – 150^{o}C]	Tertiary alcohol.

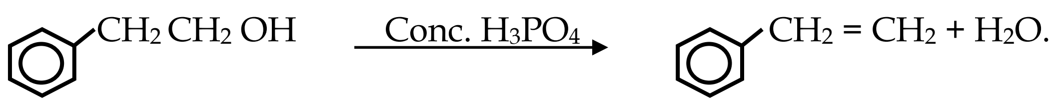
(ii) Conc. H_2SO_4: [>60%].

Example:

$$CH_3CH_2CH_2OH \xrightarrow[175-185^oC]{Conc.H_2SO_4} CH_3\ CH = CH_2 + H_2O$$

$$CH_3\ \underset{\displaystyle OH}{\underset{|}{CH}}\ CH_3 \xrightarrow[heat]{Conc.H_3PO_4} CH_3CH = CH_2 + H_2O$$

$$H_3C - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - OH \xrightarrow[150^oC]{Conc.H_2SO_4} H_3C\ \overset{\displaystyle CH_3}{C} = CH_2 + H_2O$$

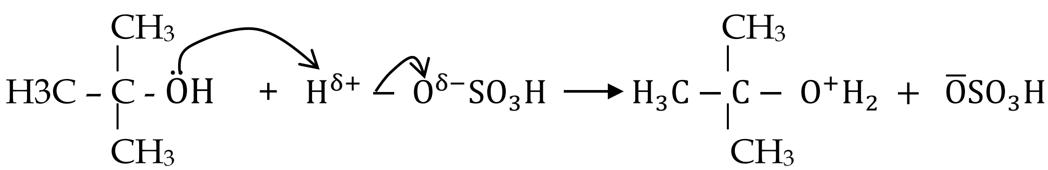


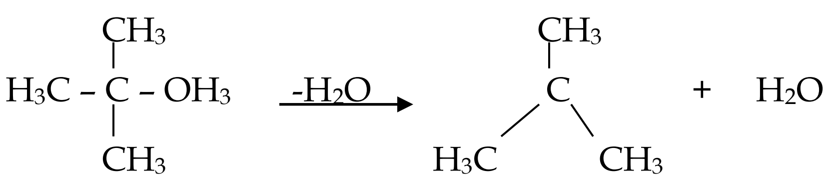
$$CH3CH_2CH_2CH_2OH \xrightarrow[175^o-185^oC]{Conc.H_2SO_4} CH_3CH = CH\ CH_3 + H_2O.$$

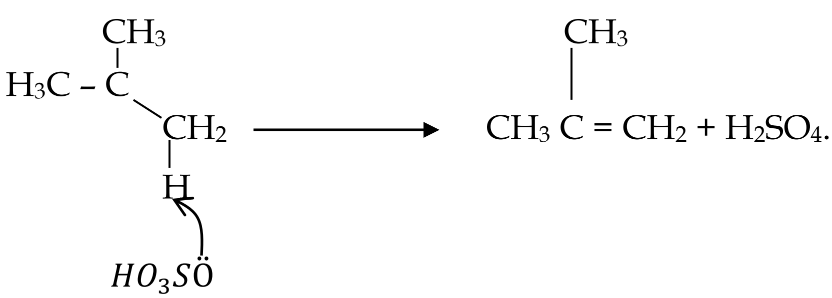
$$CH_3\ CH_2\underset{\displaystyle OH}{\underset{|}{C}}H_2CH_3 \xrightarrow[175]{Conc.H_2SO_4} CH_3CH = CH\ CH_3 + H_2O.$$

Mechanism:

1. Protonation of alcohol
2. Loss of H_2O to form carbo cation ion.
3. Re-arrangement of the carbo cation to a more stable form.
4. Loss of the proton to form alkene.





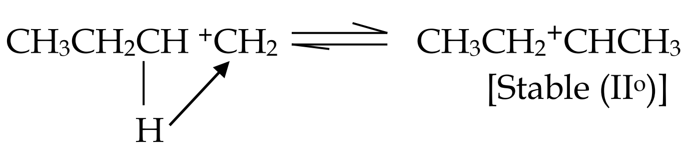


$$CH_3CH_2CH_2CHOH \xrightarrow[175-185^{o}C]{Conc.H_2SO_4} CH_3CH = CH\ CH_3 + H_2O$$

$$CH_3CH_2CH_2CH_2\ddot{O}H \quad H^+ \longrightarrow CH_3CH_2CH2CH_2\overset{+}{O}H_2$$

$$CH_3CH_2CH_2CH_2 \overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3CH_2CH_2{}^+CH_2 + H_2O$$

[Unstable(I°1)]

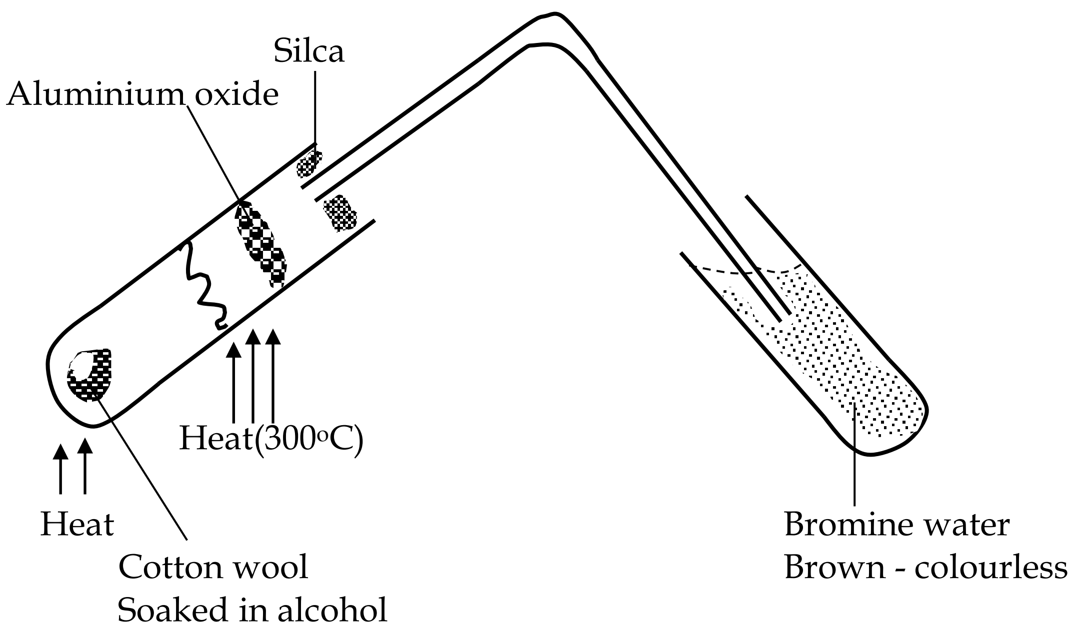


$$CH_3\underset{\begin{array}{c}|\\H\end{array}}{C}H\ \overset{+}{C}H\ CH_3 \longrightarrow CH_3CH = CHCH_3 + H_2SO_4.$$

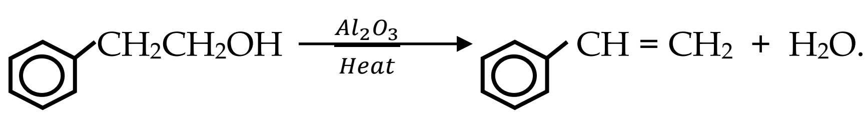
$HO_3S\bar{O}:$

DEHYDRATION IN VAPOUR PHASE

When an alcohol is heated and its vapour is passed over heated Al_2O_3 at 300^o, an alkene is formed which is detected by turning bromine water colourless.



$$CH_3CH_2OH \xrightarrow[Heat(300^oC)]{Al_2O_3} CH_2 = CH_2 + H_2O.$$



N.B: Elimination reactions in alcohols compete with substitution reactions. The difference is due to the conditions provided.

$$CH_3CH_2OH \xrightarrow[\text{Heat}]{\text{Conc.}H_2SO_4(180^o)} CH_2{=}CH_2 + H_2O$$

$$CH_3CH_2OH \xrightarrow[\text{Excess alcoho }(140^o)]{Conc.H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

OXIDATION REACTIONS

Primary alcohol $\xrightarrow{[O]}$ Aldehyde $\xrightarrow{[O]}$ Carboxylic acid.

Secondary alcohol $\xrightarrow{[O]}$ Ketones $\xrightarrow{[O]}$ No product

Tertiary alcohols $\xrightarrow{[O]}$ No product.

Oxidation of alcohols is effected by oxidizing agents such as:

(i) Acidified $K_2Cr_2O_7$/ $H^+_{(aq)}$

(ii) Acidified $Na_2Cr_2O_7/H^+_{(aq)}/Cr_2O^{2-}_{7(aq)}$

(iii) Chromic acid, CrO_3.

Acidification is done by use of sulphuric acid.

$$CH_3CH_2OH + Na_2Cr_2O_7 + H_2SO_4 \xrightarrow{\text{heat}} CH_3CHO + Na_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

$$3CH_3CH_2OH + Na_2Cr_2O_7 + 4H_2SO_4 \xrightarrow{\text{heat}} 3CH_3CHO + Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

Orange solution ($Cr_2O_7^{2-}$) — Green solution (Cr^{3+})

During the process, the solution mixture turns from orange to green indicating the conversion of the dichromate to chromium(III) ion.

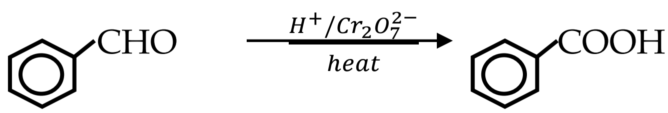
Excess oxidizing agent.

$$CH_3CHO + Na_2Cr_2O_{7(aq)} + H_2SO_{4(aq)} \rightarrow CH_3COOH + Na_2SO_{4(aq)} + Cr_2(SO_4)_3 + H_2O_{(l)}$$

Simply:

$$CH_3\underset{\large OH}{\underset{|}{C}}HCH_3 \xrightarrow[heat]{H^+(aq)/Cr_2O_7^{2-}(aq)} CH_3\ C\ CH_3$$

$$CH_3OH \xrightarrow[heat]{Excess\ H^+(aq)/Cr_2O_7^{2-}(aq)} HCOOH$$



IODO FORM/HALO FORM TEST

This test is usually performed to confirm for the presence of compounds that have got a methyl group.

Example:

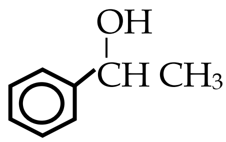
Methyl alcohol	$H_3C - \overset{\displaystyle OH}{\overset{|}{C}}H$
Methyl at dehydes	$H_3C - \underset{\displaystyle O}{\underset{\|}{C}} - H$
Methyl ketones	$H_3C - \underset{\displaystyle O}{\underset{\|}{C}} -$
Product formed	CHI_3 - Tri iodo methane (Yellow ppt)

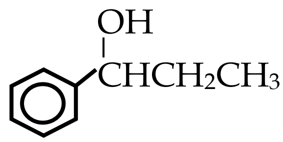
This test confirms / differentiates methyl / alcohols from the rest. Methy alcohols form tri iodo methane when oxidized which is observed as a yellow ppt, while the rest of the alcohols no observable change.

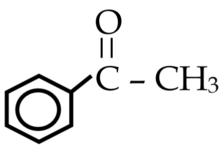
Reagent: Hot NaOH in Iodine solution.

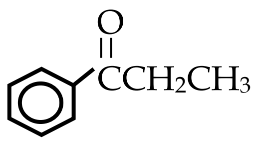
Question: *Give a reagent that can be used to distinguish between pairs of the compounds below and state what is observed in each case. Write the equation for the reaction(s) that take place.*

(a) CH_3CH_2OH and $CH_3CH_2CH_2OH$

(b) 

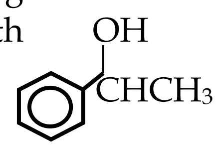
and 

(c) 

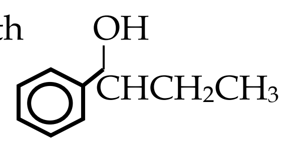
and 

Solutions:

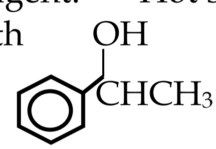
(a) Hot sodium hydroxide solution.
With CH_3CH_2OH - A yellow precipitate is observed.
With $CH_3CH_2CH_2OH$ - No observable change.

(b) Reagent: Hot sodium hydroxide in iodine solution.
With 

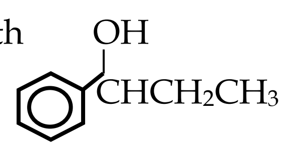
- A yellow precipitate is observed.

With 

- No observable change.

(c) Reagent: Hot sodium hydroxide in iodine solution.
With 

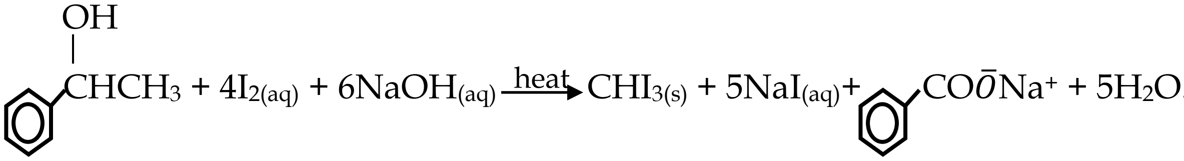
- A yellow precipitate is observed.

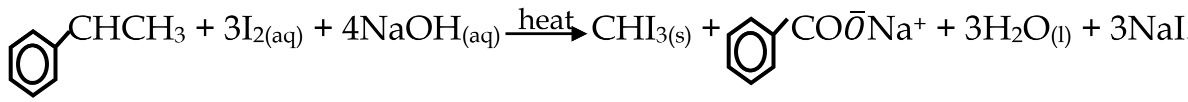
With 

- No observable change.

Equations:

$CH_3CH_2OH + 4I_{2(aq)} + 6NaOH_{(aq)} \xrightarrow{heat} CHI_3 + 5NaI_{(aq)} + HCO\bar{O}Na^+ + 5H_2O.$





Rule: Alcohols; $4I_2$; 6NaOH

Aldehydes/ketones, $3I_2$; 4NaOH.

Example:

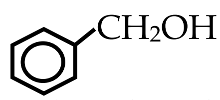
$$CH_3\overset{\overset{O}{||}}{C}\ CH_2CH_3 + 3I_{2(aq)} + 4NaOH_{(aq)} \rightarrow CHI_{3(s)} + CH_3CH_2CO\bar{O}Na^+ + 3NaI + 3H_2O.$$

AROMATIC ALCOHOLS

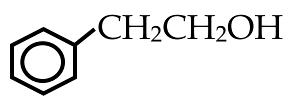
These are aromatic compounds with hydroxyl groups. They are divided into two: Aromatic alcohols and phenols.

(i) **Aromatic Alcohols:**

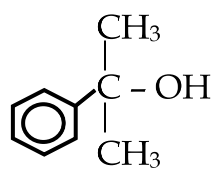
These contain an aromatic ring and then the hydroxyl group which is not directly attached to a ring but attached via the chain on the ring.



2-phenyl methanol



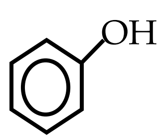
2-phenyl ethanol.



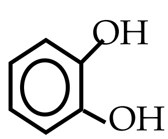
2-phenyl propan-2-ol

(ii) **Phenols:**

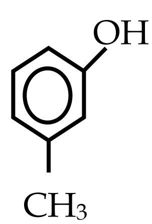
These contain an aromatic ring with one or more OH group directly attached to the ring.



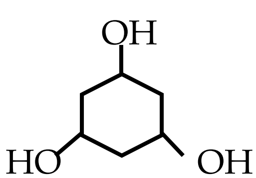
Phenol



Diphenol



3-methyl phenol.

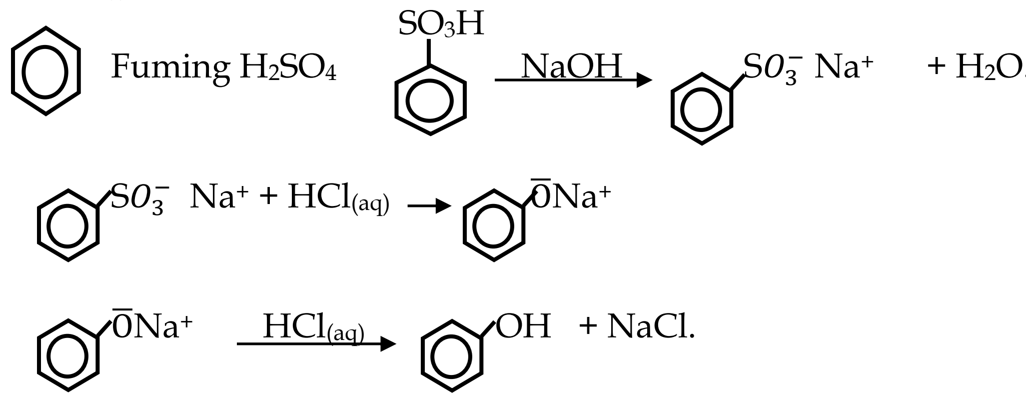


PHENOLS

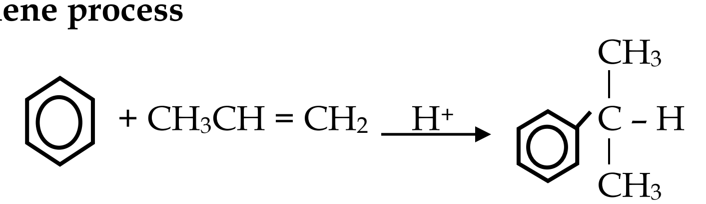
Is a class of compounds named as phenols and one or more OH groups are directly attached to the ring.

METHODS OF PREPARATION

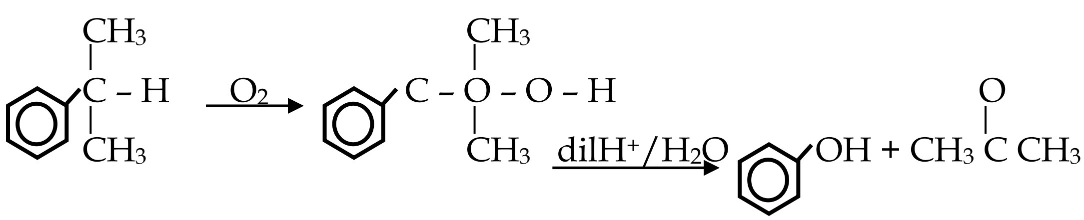
1. **Benzene sulphonic acid**



2. **Cumene process**



2-pheny propane.



3. **Aromatic halides**

In cumene process, Benzene is reacted with propene in presence of an acid or halogen carrier like $AlCl_3$ to form two phenyl propane.

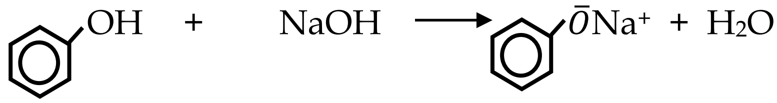
Molecular O_2 is blown into this product and the intermediate is acid hydrolysed to give a phenol.

When an aromatic halide is treated with alkali at extremely harsh conditions like 300°C, 200 atm of pressure and copper, a phenol is formed.

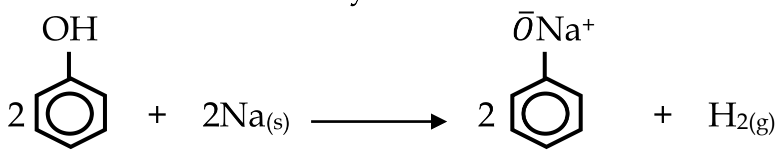
This subsequently strengthens the C – O bond by developing a partial double bond between C and C and at the same time weakening the O – H bond by decreasing the electron density and releases a proton easily. This does not occur in aliphatic aromatic alcohols as ordinary alcohols.

Subsequently, phenols being slightly acidic, under the following:

(i) Very soluble in NaOH or KOH

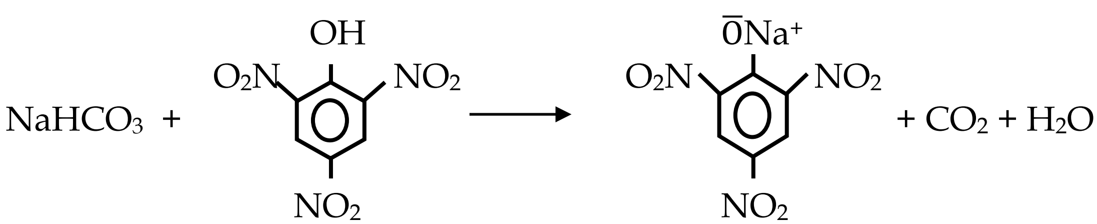


(ii) Phenols react with very reactive metals like Na to form salt and H_2.



Acid properties of phenols can be improved by;

Adding electrons with a………..which de-active the ring. Such groups include the Nitro groups. 2, 4, 6-trinitrophenol is more acidic than phenol. It liberates CO_2 from saturated $NaHCO_3$.



Carboxylic acids are more acidic than phenols. [Give the reactions that distinguish acidic character of phenols and carboxylic acids.

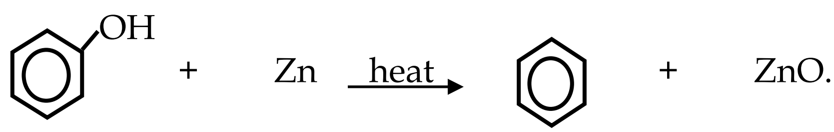
COMPLEX FORMATION WITH NEUTRAL FECL$_3$.

Phenols form a complex with aqueous neutral $FeCl_3$ and the colour of the complex product is violet colouration (purple). This reaction is important in confirming the presence of a phenolic group and it is also useful in distinguishing between phenol and aromatic alcohols.

Question: Distinguish between HCOOH and CH_3COOH.
(We use the Iodo form test).

OR:
Using neutral (iron III) chloride) solution.
A purple colouration with HCOOH.
No observable change with CH_3COOH.

REACTION WITH ZICN DUST:
Phenol when heated with Zinc dust forms benzene.

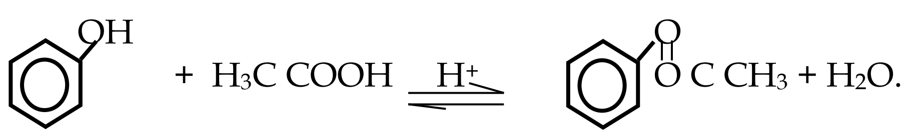


ALCOHOL REACTIONS OF PHENOLS RESEMBLING
This involves cleavage of C - O bond.

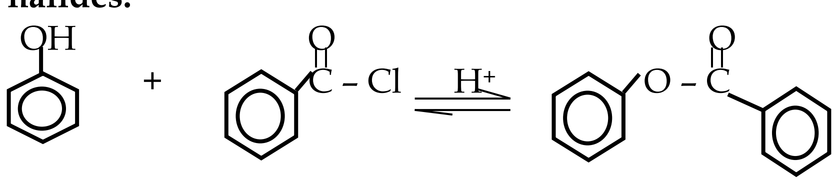
Phenols undergo some reactions resembling alcohol where the C – O bond is involved.

Esterification:
Phenols react with carboxylic acids, halides and acid an hydrides to form an ester.

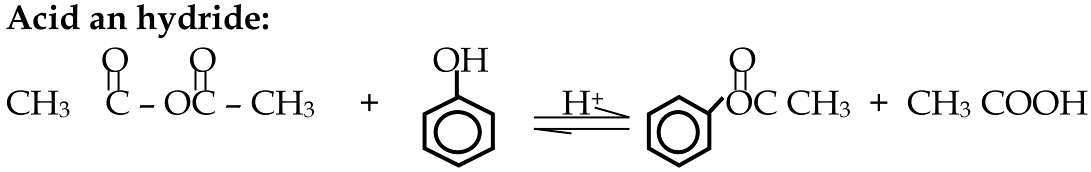
Carboxylic acids:



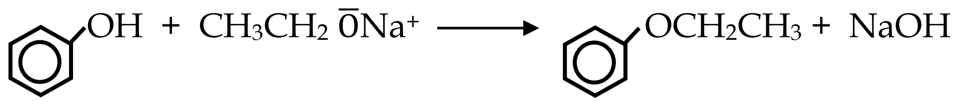
Acid halides:



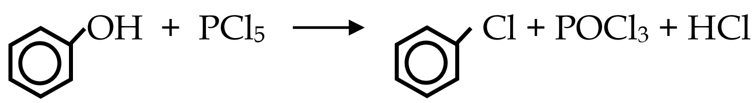
Acid an hydride:



Ether formation:
Phenols react with alka oxides to form ethers.



Phosphorous penta halides:
Phenols react with PCl_5 liberating HCl gas which fumes in air.

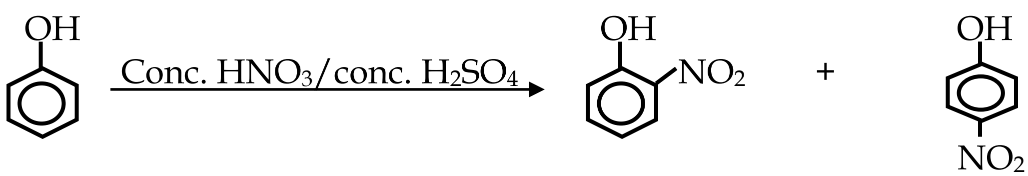


Reactions with liquid NH_3.

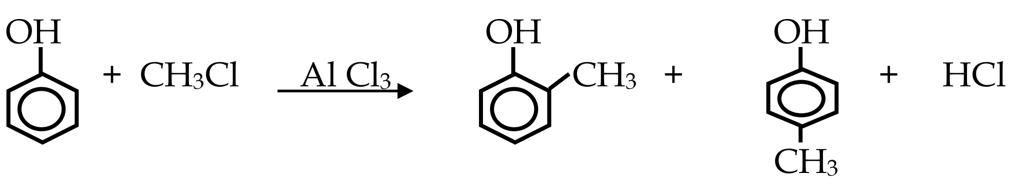
REACTIONS OF THE RING IN PHENOL

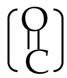
Due to the presence of the OH group in phenol, phenol undergoes a number of reactions where delocalized electrons on the ring are involved.

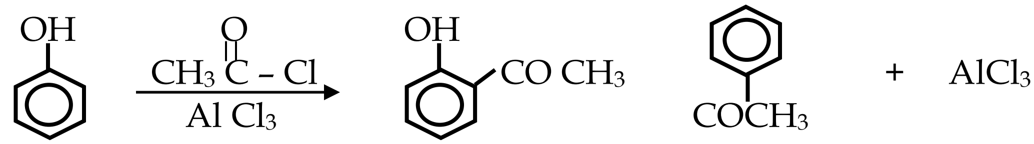
Nitration:
Phenol reacts with conc. H_2SO_4 and conc. HNO_3 acids to form 2-nitro phenol and 4-nitrophenol.



Alkylation:
Phenol reacts with alkyl halides in presence of a halogen carrier to form alkylated product phenol.

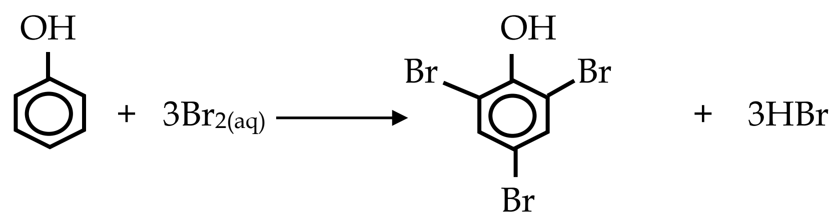


A cylation 

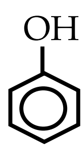
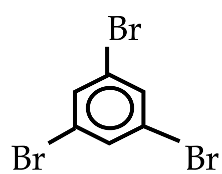


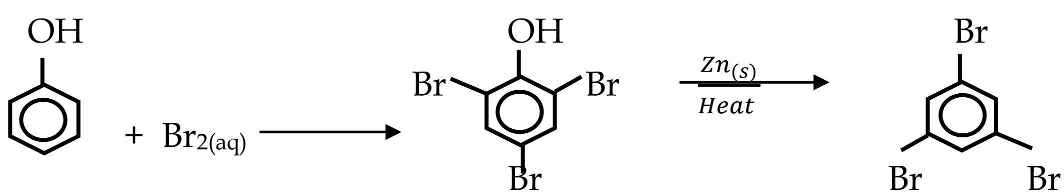
Bromine H_2O.
When reacted with bromine, H_2O phenol forms a substituted poly product of 2, 4, 6 tri bromo phenol which is a white precipitate.

The presence of OH makes phenol to be very reactive. This reaction is very important in confirming the presence of phenol together with the neutral iron (III) chloride test.



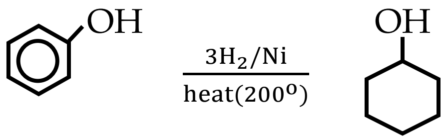
White ppt.

Convert  to 



Hydrogen in presence of heated Ni catalyst.

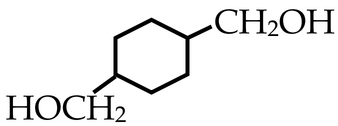
Phenol can be hydrogenated into cyclo hexanol when reacted with H_2 in the presence of a heated catalyst.



POLYHYDRIC ALCOHOLS

These are alcohols with more than one OH group attached to the same carbon chain as:

$HOCH_2CH_2OH$



$$\begin{array}{c} HOCH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 \end{array}$$

The chemical and physical properties of these types of alcohols are slightly the same; however, there are slight differences.

Ethane-1, 2-diol boils at a higher temperature.

Ethane-1, 2-diol has two OH group which results into formation of extensive hydrogen bonds which is difficult to break hence high boiling point.

PREPARATION OF DIOLS

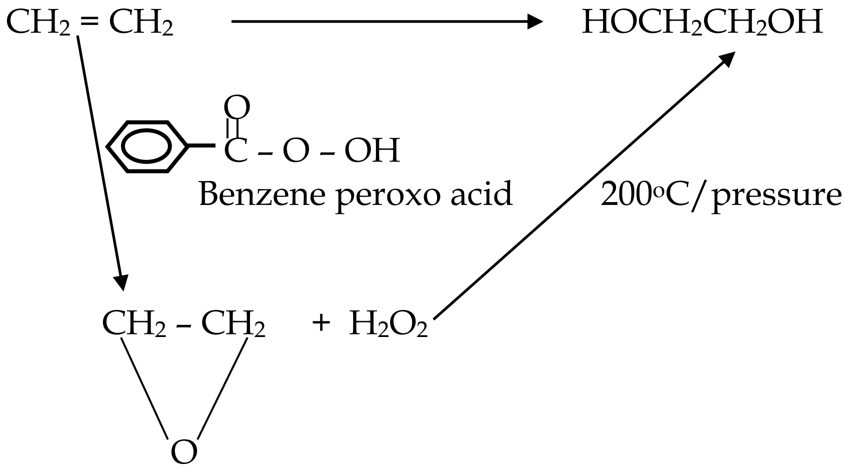
They can be prepared from alkyl halides.

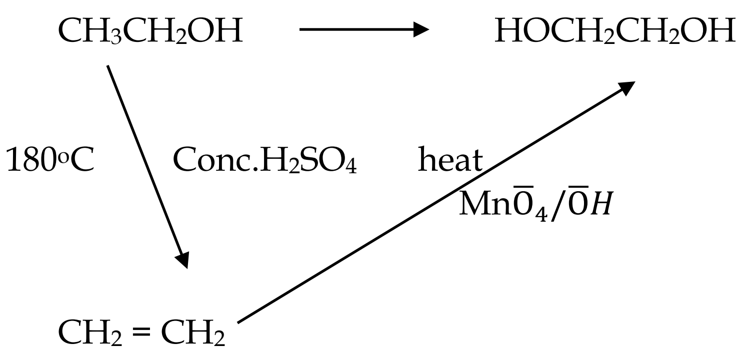
$CH_3CH_2Cl \longrightarrow HO\ CH_2CH_2OH$ ethane-1, 2-diol

Heat $\downarrow$ $\epsilon t\bar{O}\ /\epsilon tOH$

$CH_2 = CH_2 \xrightarrow[\text{heat}]{MNO_4^-/\bar{O}H}$ ethane-1, 2-diol

Alkenes





Reactions of diols are the same as those of monohydric alcohols.
The difference is that excess of the reagent is used.

$CH_3\,CH_2\,CH_2\,OH$

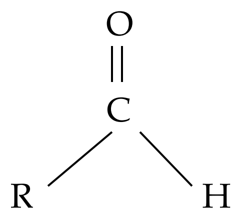
$$\downarrow \text{heat, } 175^{o}C, \text{ Conc.}H_2SO_4$$

$$CH_3CH = CH_2 \xrightarrow[Mn\bar{O}_4/\bar{O}H]{heat} CH_3\underset{}{\overset{OH}{\overset{|}{C}}}H\ CH_2OH$$

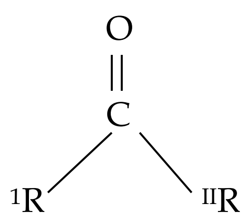
CARBONYL COMPOUNDS

These are compounds containing a carbonyl functional group. They are alkanal (Aldehydes) and alkanones (Ketones).

These two belong to a group of organic compounds known as carbonyl compounds with a general formula $C_nH_{2n}O$.



- Aldehyde



- Ketone

The major difference between aldehyde and ketone is in the presence or absence of H_2 attached onto the carbonyl carbon.

In aldehydes, "H" is to the carbonyl carbon while in a ketone, similar or different alkly groups are attached to the carbonyl carbon as shown above.

NOMENCLATURE

IUPAC system is used in the naming of both aldehydes and ketones. Generally, aldehydes are named as alkanals by replacing "e" in the alkane name with –"als" while ketones are named as alkanones by replacing –"e" with –"ones".

	Alkanals		**Alkanones**	
(Formaldehyde)	$H\overset{O}{\overset{\parallel}{C}}-H$	Methanal	$CH_3\overset{O}{\overset{\parallel}{C}}CH_3$	Propan-2-ones
(Acetaldehyde)	$CH_3\overset{O}{\overset{\parallel}{C}}-H$	ethanol	$CH_3\overset{O}{\overset{\parallel}{C}}CH_2CH_3$	butan-2-ones

$CH_3\,CH_2\,\overset{\overset{\displaystyle O}{\|}}{C}\,-H$ Propanal

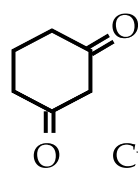
$CH_3\,\overset{\overset{\displaystyle O}{\|}}{C}\,\underset{\underset{\displaystyle CH_3}{|}}{CH}\,CH_3$ 3-methyl butan-2-ones

$CH_3CH_2CH_2\,\overset{\overset{\displaystyle O}{\|}}{C}-H$ – Butanal

$CH_3\,\underset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_3$

2-methyl hexan-3-one

$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}\,\overset{\overset{\displaystyle O}{\|}}{C}H$ 2-methyl propanal



Cyclohexa-1, 3-dione.

ISOMERISM

Both aldehydes and ketones exhibit structural and functional isomerism.

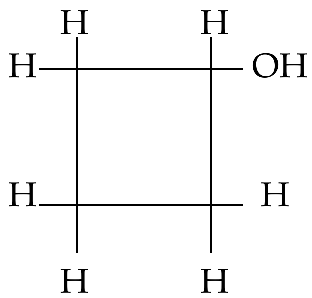
In structural isomerism, they show position and chain isomers.

In functional isomerism, both aldehydes and ketones are isomeric within themselves and with other classes of organic compounds like alcohols and cyclic ethers.

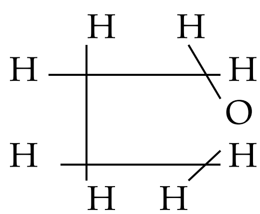
C_4H_8O

$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H$ Butanal

$CH_3CH\,\overset{\overset{\displaystyle O}{\|}}{C}\,CH_3$ Butan-2-one



Cyclic butanol (cyclic alcohol)



Cyclic ether (Tetacfuran)

C_4H_8O

$CH_3CH_2CH_2CHO$ Butanal

$CH_3CH(CH_3) - CHO$ 2-methyl propanal (Aldehyde)

$CH_3\ C(=O)\ CH_2\ CH_3$ Butan-2-one (Ketone)

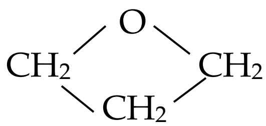
$CH_2 - CH_2 - O - CH_2 - CH_2$ (ring) Tetrahydrofuran (furan)

$CH_2 = CH\ CH_2 - CH_2\ OH$ But-en-4-ol
(Usaturated alcohol)

Write all the isomers of the compounds with the molecular formula C_3H_6O.
CH_3CH_2CHO Propanal (Aldehyde)

$CH_3\ C(=O)\ CH_3$ Propanone (Ketone)

$CH_2 = CH\ CH_2OH$ Prop-1-en-3-ol.



Trihyrofuran

PREPARATION OF CARBONYL COMPOUNDS

They can be prepared from the following:

i) Mild oxidation of alkanol (alcohols)
ii) Carboxylic acids or their salts.
iii) Ozonolysis of alkenes followed by hydrolysis.
iv) Acid hydrolysis of alkynes.
v) Hydrogenation of acid chlorides.
vi) Acylation (aromatic ketones)

OXIDATION OF ALCOHOLS

Primary and secondary alcohols are oxidized in liquid phase using $K_2Cr_2O_7$ /H^+ or $Na_2Cr_2O_7$/H^+, CrO_3/H^+ to form aldehydes and ketones respectively.

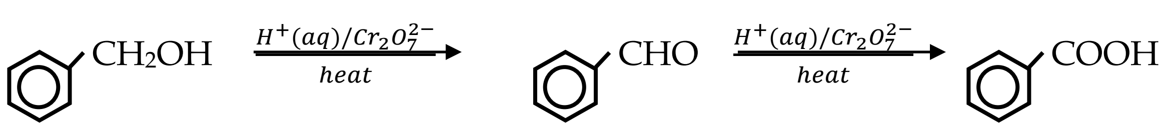
During oxidation process, a colourless solution turns to green solution.

Examples:

$$CH_3CH_2OH \xrightarrow[warm]{H^+/Cr_2O_7^{2-}(aq)} CH_3CHO \xrightarrow[heat]{H^+(aq)/Cr_2O_7^{2-}} CH_3COOH$$

Alcohol   Ethanal Aldehyde   Carboxylic acid

$$CH\ \underset{|}{\overset{OH}{}}\!\!CH\ CH_3 \xrightarrow[heat]{H^+(aq)/Cr_2O_7^{2-}} CH_3\ \overset{\overset{O}{||}}{C}\ CH_3$$



During the oxidation process, especially for primary alcohols, there will be further oxidation to carboxylic acid which renders this method ineffective but this further oxidation can be avoided by carrying out a reaction under low heat (temperatures) or limiting the amount of the oxidant used.

Oxidation can also be effected under vapour phase. When an alcohol vapour is passed over heated Cu at 300°C, it is oxidized to an aldehyde or ketone.

$$CH_3CH_2OH_{(g)} \xrightarrow[300^oC]{Cu} CH_3CHO + H_2$$

$$CH_3\underset{\underset{OH}{|}}{C}H\,CH_3 \xrightarrow[300^oC]{Cu} CH_3\underset{\underset{O}{|}}{C}CH_3 + H_2$$

Oxidation under vapour phase can also be brought about when an alcohol together with limited O_2 is passed over heated Ag at 500°C.

$$CH_3CH_2OH + \tfrac{1}{2}O_2 \xrightarrow[500^oC]{Ag_{(S)}} CH_3CHO + H_2O$$

$$CH_3C(OH)CH_3 + \tfrac{1}{2}O_2 \xrightarrow[500^oC]{Ag_{(S)}} CH_3COCH_3 + H_2O$$

CARBOXYLIC ACIDS

When a carboxylic acid salt of calcium is heated, an aldehyde id formed. More specially methanol is formed.

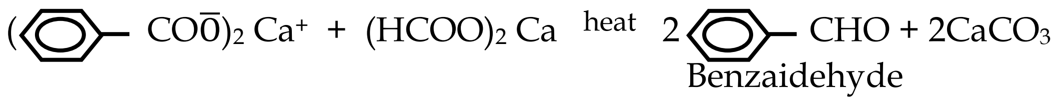
$$Ca(COO)_2 \xrightarrow{heat} CaCO_3 + H\overset{\overset{O}{||}}{C}H$$

With other higher aldehydes, Ca salt of a carboxylic acid is heated with calcium methanoate.

Examples:

$$(CH_3COO)_2Ca_{(s)} + (HCOO)_2Ca_{(s)} \xrightarrow{heat} \underset{\text{Ethanal}}{2CH_3CHO} + 2CaCO_3$$

$$(CH_3CH_2CO\bar{O})_2Ca^+ + (HCOO)_2Ca \xrightarrow{heat} \underset{\text{Propanal}}{2CH_3CH_2CHO} + 2CaCO_3$$



Ketones can be prepared by heating Ca salts of higher carboxylic acids.

$(CH_3COO)_2Ca \xrightarrow{heat} CH_3\ CO\ CH_3 + CaCO_3$

$(CH_3CH_2COO)_2Ca^+ \xrightarrow{heat} CH_3CH_2COCH_2CH_3 + CaCO_3$

Convert $CH_3CH_2OH \longrightarrow CH_3COCH_3$

$CH_3CH_2OH \xrightarrow[heat]{Excess\ H^+(aq)/Cr_2O_7^{2-}} CH_3COOH + Ca(OH)_2$

$\downarrow$

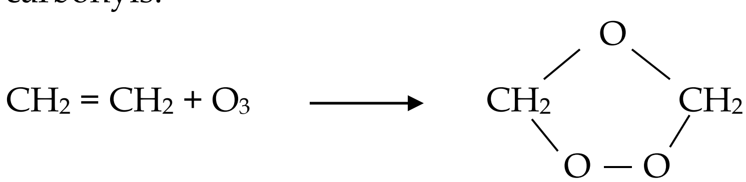
$(CH_3COO)_2Ca + H_2O$

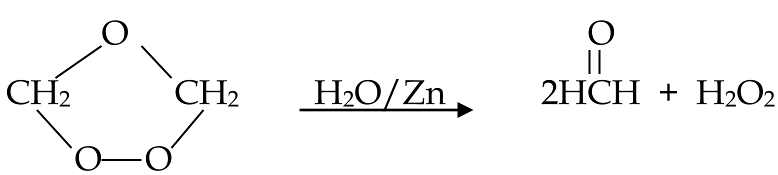
$CH_3COCH_3 \xleftarrow{} heat$

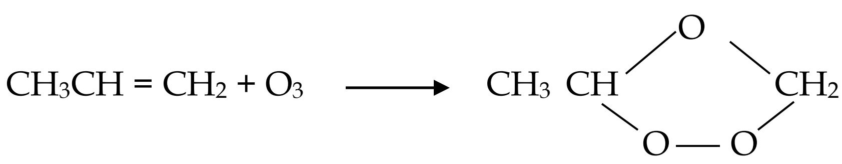
OZONOLYSIS

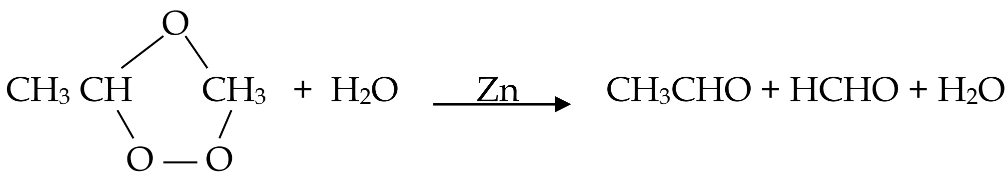
When an alkene is reacted with ozone, an ozonide id formed. When the ozonide is diluted in H_2O in presence of some zinc, a carbonyl compound is formed. Zinc dust is used to decompose H_2O_2.

Note: Aldehydes formed depends on the types of alkene used. Symmetrical alkene gives one type of aldehyde while unsymmetrical will give you both carbonyls.









$$CH_3C(CH_3) = C(CH_3) - CH_3 + O_3 \longrightarrow 2CH_3\,CO\,CH_3$$

$$CH_3C(CH_3) = CH\,CH_3 + O_3 \longrightarrow CH_3COCH_3 + CH_3CHO$$

The above method has the disadvantage of yielding a mixture of products which may not be good in organic synthesis.

HYDROLYSIS (ACID) OF ALKYNES

When an alkyne is passed through hot H_2SO_4 in presence of mercury sulphate, the carbonyl carbon is formed.

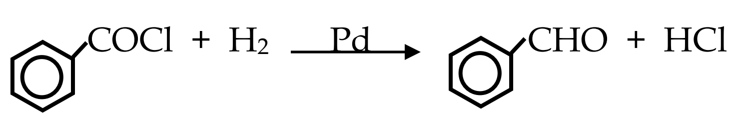
$$CH \equiv CH + H_2O \xrightarrow[60^oC]{H_2SO_4/H_gSO_4} \underset{\text{Ethanal}}{CH_3CHO}$$

$$CH_3C \equiv CH + H_2O \xrightarrow[60^oC]{H_2SO_4/H_gSO_4} CH_3COCH_3$$

HYDROGENATION OF ACID CHLORIDES

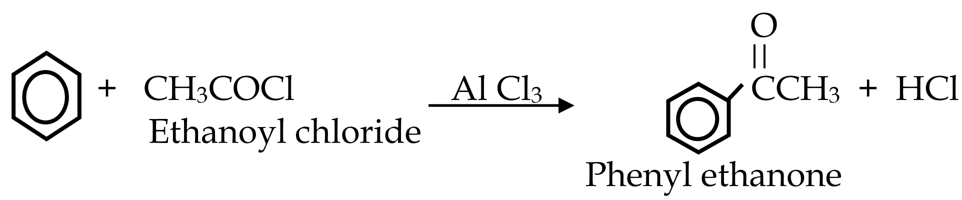
Acid chlorides are reduced by hydrogen in presence of catalysts like pd to form aldehydes.

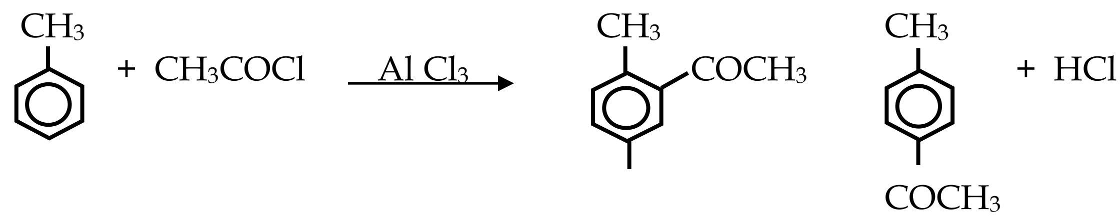
$$CH_3COCl + H_2 \xrightarrow{Pd} CH_3CHO + HCl$$



ACYLATION

Alkyl acylation is a reaction between acid halides with a benzene ring compound. This reaction produces aromatic ketones when it is carried out in presence of a halogen carrier (Al Cl_3, $FeCl_3$)





PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS

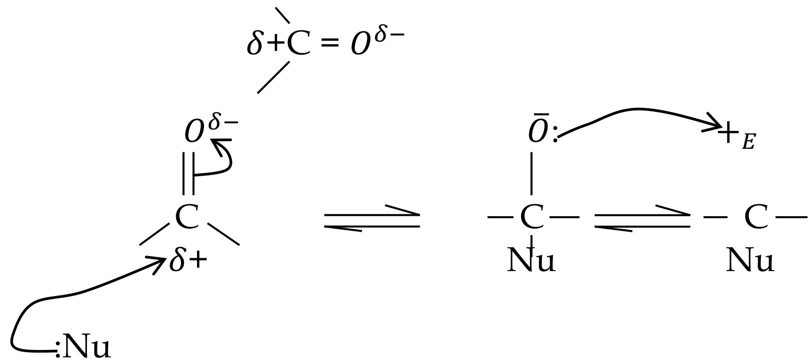
Lower members of aldehydes and ketones are liquids and are miscible with H_2O forming neutral solutions. The miscibility in H_2O is due to the polar carbonyl carbon.

They have higher boiling points than their hydrocarbon counterparts. This is because of the polar nature of the carbonyl carbon that results into the intermolecular attractions but their boiling points are lower than those of alcohols and carboxylic acids due to the lack of H_2 bonding.

CHEMICAL PROPERTIES OF CARBONYL COMPOUNDS

Carbonyl compounds chemically react because of the property of the carbonyl carbon which is a common functional group present in both aldehydes and ketones.

A carbonyl carbon contains more electronegative oxygen bonded to carbon which pulls electrons towards itself and attains a δ^- charge while the carbon remains δ^+. Therefore, the carbon oxygen bond is polarised creating a good condition for nucleophillic reagents to be added across the carbonyl carbon. The intermediate formed with a negative on oxygen reacts with an electrophille to form the final end product.



Carbonyl group in aldehyde is more reactive than in ketones.

Explanation:
In ketones, the presence of two alkyl groups having a positive inductive effect highly neutralizes the positive charge in the carbon resulting into a less attraction of a nucleophile.

$$\underset{\delta+}{R-\overset{O^{\delta-}}{\overset{\|}{C}}-H} \quad > \quad \underset{\delta+}{R-\overset{O^{\delta-}}{\overset{\|}{C}}-R}$$

Methanol is more reactive than other aldehydes. Explain.
In methanol only hydrogen is bonded to the carbonyl carbon that the partial positive charge formed is not neutralized making methanol more reactive.

Therefore, the more number of alkyl groups added to a carbonyl carbon, the les the reaction due to the following reasons:

(i) The alkyl groups have got electron pushing (positive inductive) effect which neutralizes the partial) positive charge on the carbon.

(ii) Several alkly groups will have a crowding effect preventing a nucleophile from being attached to the carbon.

Order of the reactivity of the following:

$$H-\underset{H}{\underset{|}{C}}=O > CH_3\underset{H}{\underset{|}{C}}=O > \underset{\text{Neutralization of charges}}{CH_3\overset{O}{\overset{|}{C}}-CH_3} > \underset{\text{Steric hinderance}}{CH_3CH_2-\overset{O}{\overset{|}{C}}-CH_2CH_3} > C_3H_7\overset{O}{\overset{|}{C}}C_3H_7.$$

When other atoms of a more electronegative effect are added next to the carbonyl group, the reactivity of the carbonyl carbon compound increases. E.g. if a hydrogen on the carbon atom next to the carbonyl group is replaced with a halogen, the reactivity increases.

$$CH_3CH_2\overset{\overset{O}{||}}{C}-H \;<\; CH_3\underset{\underset{Cl}{|}}{CH}-\overset{\overset{O^{\delta-}}{||}}{\underset{\delta+}{C}}-H \;<\; CH_3\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{O^{\delta-}}{\underset{\delta+}{C}}-H$$

REACTION OF CARBONYL COMPOUNDS
GENERAL REACTION (BOTH KETONES AND ALDEHYDES)

(i) **Reactions of alkyl groups:**
Both aldehydes and ketones containing alpha hydrogen i.e. hydrogens on the carbons next to be carbonyl group undergo halogenations reaction, when reacted with a halogen to form substituted products. Substitution proceeds until the alpha hydrogens are replaced.

$$CH_3\overset{\overset{O}{||}}{C}H + Cl_2 \longrightarrow CH_2Cl\overset{\overset{O}{||}}{C}-H + HCl$$

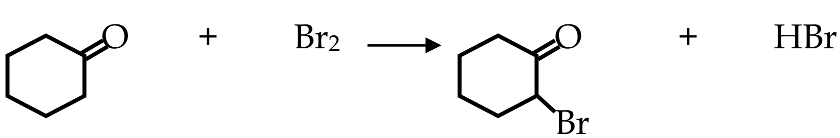
$$\downarrow Cl_2$$

$$HCl + CCl\overset{\overset{O}{||}}{C}H \xleftarrow{Cl_2} CHCl_2\overset{\overset{O}{||}}{C}H + HCl$$

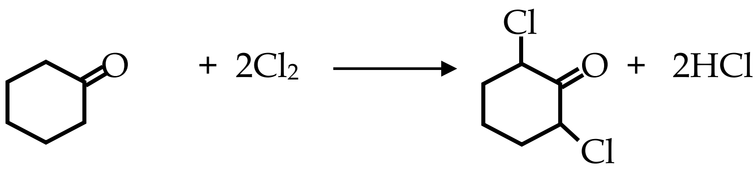
$$CH_3\overset{\overset{O}{||}}{C}CH_3 + Br_2 \longrightarrow CH_2Br\,C\,CH_3 + HBr$$

$$Br_2$$

$$CBr_3COCH_3 \xleftarrow{Br_2} CH\,Br_2\overset{\overset{O}{||}}{C}CH_3 + HBr$$



$$CH_3COCH_3 + 3Cl_2 \longrightarrow CCl_3\overset{\overset{O}{||}}{C}CH_3 + 3HCl$$



(ii) **Reactions due to carbonyl group:**

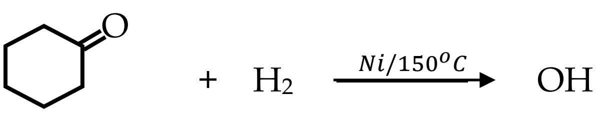
Both aldehydes and ketones containing a carbonyl group undergo the following reactions:

Reduction (Reaction with H_2)

Aldehydes and ketones are reduced by H_2 in presence of a suitable catalyst e.g. Ni/150^{o}C, pt/pd into primary and secondary alcohols respectively.

$$CH_3CHO + H_2 \xrightarrow{Ni/150^oC} CH_3CH_2OH$$

$$CH_3COCH_3 + H_2 \xrightarrow{Pt} CH_3\underset{\underset{OH}{|}}{CH}CH_3$$



Using reducing agents:

Similarly strong reducing agents such as Aluminium, Na, Lithium tetrahydride, Na/Ethanol can also be used to effect reduction.

$$CH_3COCH_3 \xrightarrow[Dry\ ether]{Li\ AlH_4} CH_3CH(OH)CH_3$$

$$CH_3CHO \xrightarrow{Na/Ethanol} CH_3CH_2OH$$

Mechanism of reduction:

$$H_2 \xrightarrow{Pt} H^+ + :H^-$$

$$CH_3\overset{\overset{O^{\delta-}}{||}}{C_{\delta+}}CH_3 \;(H^-:) \longrightarrow CH_3-\overset{\overset{\bar{O}:}{||}}{\underset{\underset{H}{|}}{C}}-CH \xrightarrow{H^+} CH_3-\overset{\overset{OH}{||}}{\underset{\underset{H}{|}}{C}}-CH_3$$

Addition of HCN (hydrogen cyanide)

Both carbonyl compounds react with HCNs to form 2 hydroxyl nitrates or cyanohydrins. The HCN is generated insitu from the reaction between NaCN and Conc. H_2SO_4.

$$CH_3CHO + NaCN + H_2SO_4 \longrightarrow CH_3CH(OH)CN$$

2-hydroxy propanitrile.

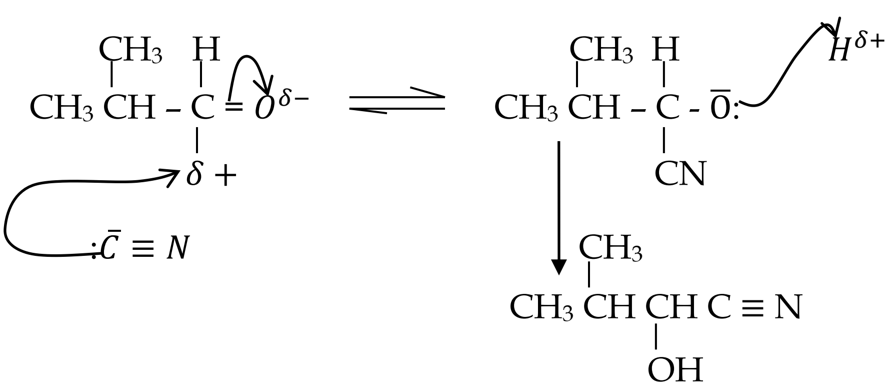
$$CH_3COCH_3 \xrightarrow{Conc.H_2SO_4/NaCH} CH_3C(OH)(CN)CH$$

$$CH_3CH(CH_3)CHO + KCN/H_2SO_4 \longrightarrow CH_3CH(CH_3)CH(OH)CN$$

$$CH_3C(CH_3)(CH_3)CHO \xrightarrow{HCN} CH_3C(CH_3)(CH_3)CH(OH)CN$$

Mechanism:

$$2KCN + H_2SO_4 \longrightarrow 2HCN + K_2SO_4$$



2-hydroxyl, 3-methyl butanitrile.

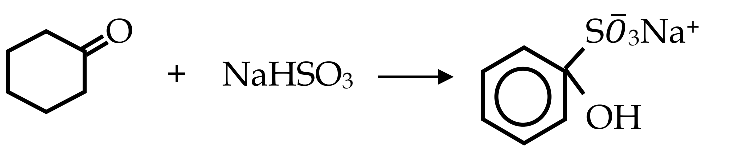
REACTION WITH $NaHSO_3$

Both carbonyl compounds react with a saturated solution of $NaHSO_3$ to give crystalline solids of $NaHSO_3$ derivatives.

$$CH_3CHO + \underset{\text{(saturated)}}{NaHSO_3} \longrightarrow CH_3\underset{\substack{|\\OH}}{C}H\,S\bar{O}_3Na^+$$

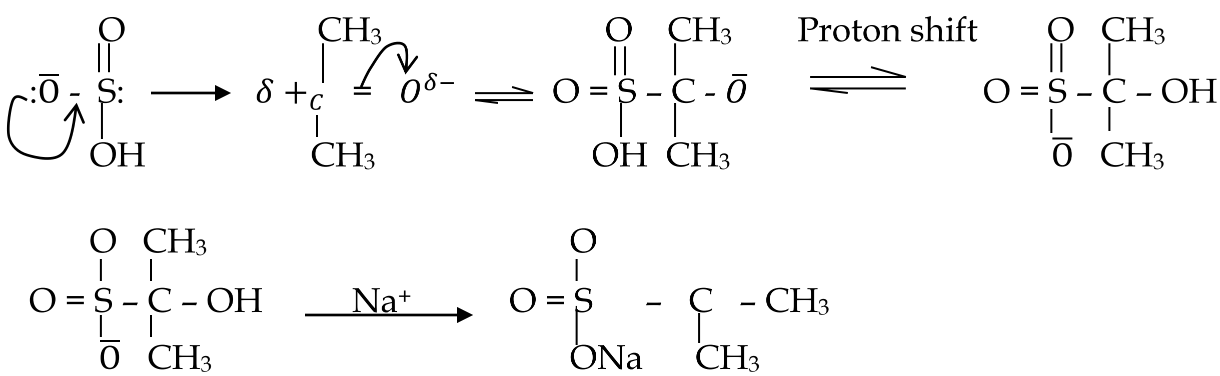
Ethanal sodium hydrogen sulphite.

$$CH_3COCH_3 + NaHSO_3 \longrightarrow (CH_3)_2\overset{\substack{OH\\|}}{C} - S\bar{O}_3Na^+$$



Mechanism:

$$NaHSO_3 \longrightarrow Na^+ + HS\bar{O}_3.$$



ADDITION REACTION WITH PCl_5.

Both carbonyl compounds react with PCl_5 to give gem-dihalides with no steaming in moist air i.e. (No hydrogen halide formed) which distinguishes between alcohols and carbonyl compounds.

$$CH_3CHO + PCl_5 \longrightarrow CH_3\overset{\substack{Cl\\|}}{\underset{\substack{|\\Cl}}{C}}H + POCl_3$$

$$CH_3\,COCH_3 + PCl_5 \longrightarrow CH_3\,\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}} - CH_3 + POCl_3$$

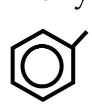
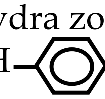
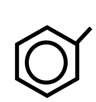
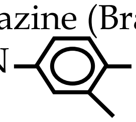
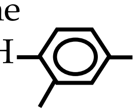
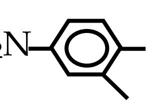
CONDENSATION REACTIONS

Aldehydes and ketones react with compound containing amino groups to form condensations products and loss of H_2O molecule. These products formed have got sharp melting points which are used in identification of the original compounds.

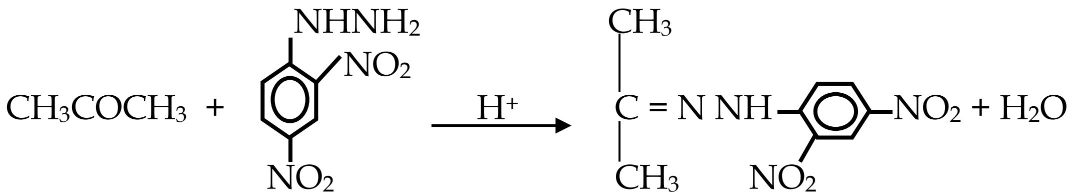
These types of reactions are condensation because there is elimination of a H_2O molecule.

$$\rangle C = O + R - NH_2 \longrightarrow C = N - R + H_2O.$$

$$CH_3\,\underset{\displaystyle O}{\underset{||}{C}}\,CH_3 + R - NH_2 \longrightarrow CH_3\,\underset{\displaystyle N\text{-}R}{\underset{||}{C}}\,CH_3 + H_2O$$

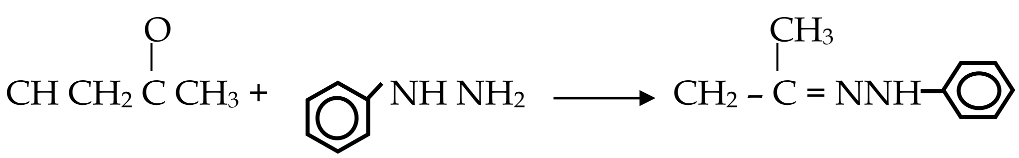
	Reagents	**Product**	**R – group**
1.	Hydroxyl amine $HO - NH_2$	Oxime $\rangle C = N - OH$	-OH
2.	Hydrazine $NH_2 - NH_2$	Hydra zone $\rangle C = N\,NH_2$	$-NH_2$
3.	Phenyl hydrazine  NH NH_2	Phenyl hydra zone $\rangle C = N\,NH-$ 	 NH
4.	Semi carbazine $NH_2\,NH\,CONH_2$	Semi carbazone $\rangle C = N - NHCONH_2$	$NH - CONH_2$
5.	2, 4 dinitrophenyl Hydrazine (Brady's reagent) NO_2N-  $NHNH_2$ NO_2	2, 4 dinitrophenyl hydrazone $\rangle C = N\,NH-$  $-NO_2$ NO_2	O_2N-  NH NO_2

Mechanism:



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}H + HO - NH_2 \longrightarrow CH_3\,CH = N - OH + H_2O.$$

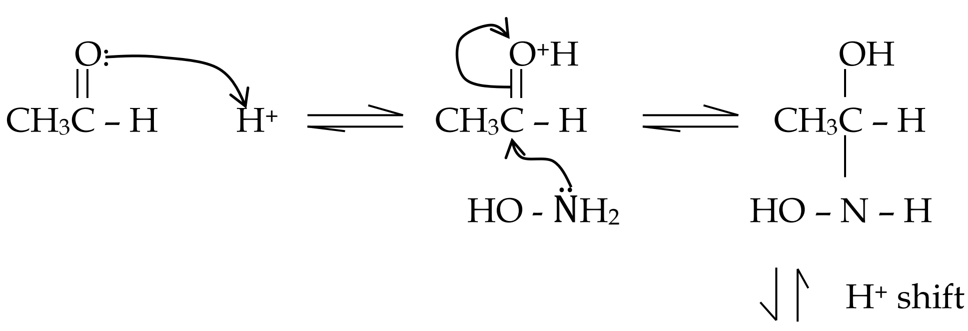
$$CH_3\,\overset{\overset{\displaystyle O}{\|}}{C}\,CH_3 + NH_2 - NH_2 \longrightarrow (CH_3)_2C = N\,NH_2 + H_2O$$

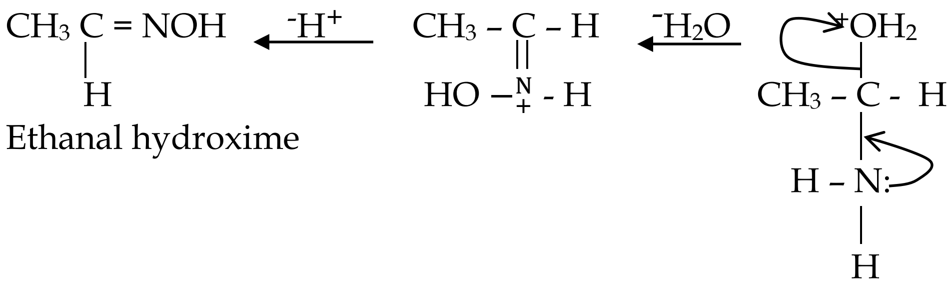


$$CH_3\,CH_2\,CH_2\,CHO + NH_2\,NH\,CONH_2 \longrightarrow CH_3CH_2CH_2\,CH = N\,NHCONH_2$$

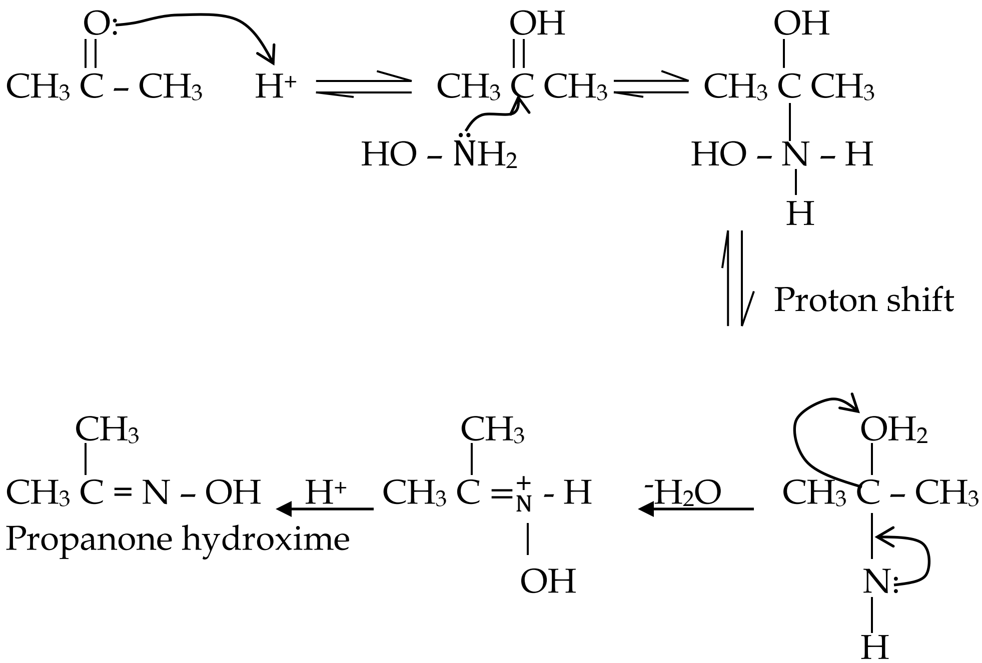
Mechanisms of condensation reactions of carbonyl compounds

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}H + HO - NH_2 \xrightarrow{H^+} CH_3\,CH = N - OH + H_2O$$

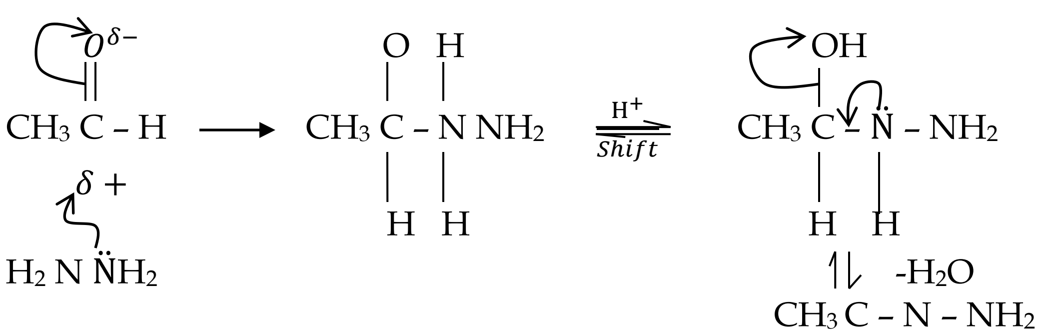


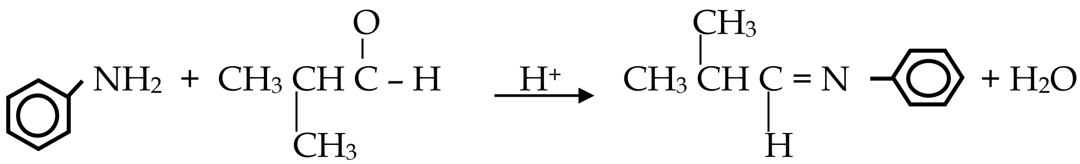


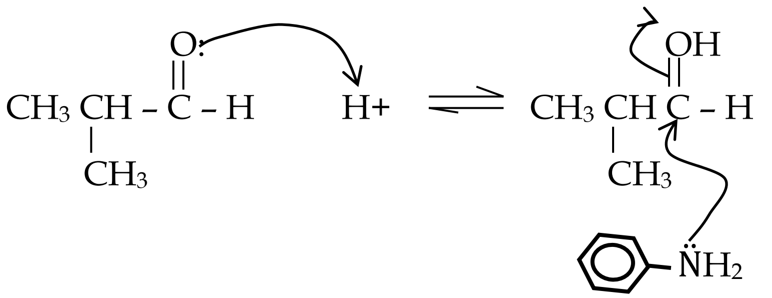
$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + HO-NH_2 \xrightarrow{H^+} CH_3\overset{\overset{CH_3}{|}}{C}=N-OH + H_2O$$

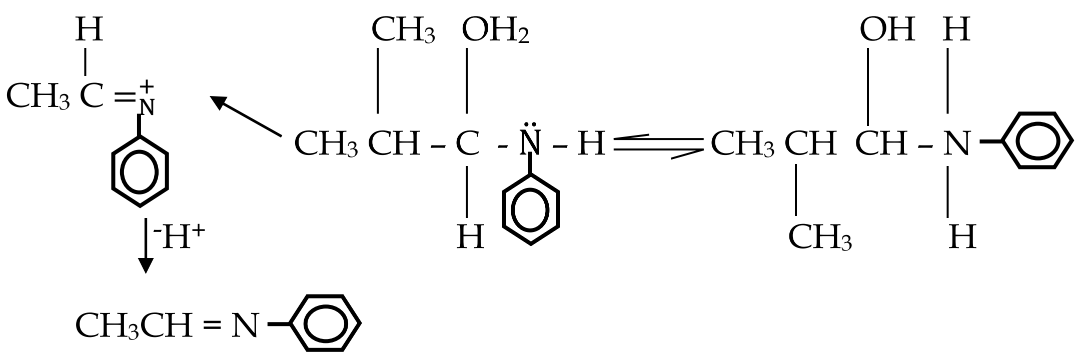


$$CH_3\overset{\overset{O}{\|}}{C}H + H_2N-NH_2 \longrightarrow CH_3\overset{\overset{H}{|}}{C}=NNH_2 + H_2O$$









Reactions with dilute NaOH

Aldehydes containing ∝-hydrogens and ketones react with dilute NaOH to form hydroxyl alkanals or alkanones which are compounds containing both hydroxyl group and carbonyl carbon but with doubling of the chain.

When these compounds are heated, H_2O is lost and a double bond is formed.

$$2CH_3\,CHO \xrightarrow{\bar{O}H_{(aq)}} CH_3\,\underset{\displaystyle |\atop\displaystyle OH}{CH}\,CH_2\,CHO \quad \text{2 hydroxy butane.}$$

$$2CH_3CH_2CHO \xrightarrow{\bar{O}H_{(aq)}} CH_3\,CH_2\,\underset{\displaystyle |\atop\displaystyle OH}{CH}\,CH_2CH_2\,CHO$$

$$2CH_3\overset{\overset{O}{||}}{C}CHO \xrightarrow{\bar{O}H_{(aq)}} CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2\underset{\underset{O}{||}}{C}-CH_3$$

Mechanism:

$$\underset{\underset{H}{|}}{CH_2}-\overset{\overset{O}{||}}{C}-H \longrightarrow \bar{C}H_2\overset{\overset{O}{||}}{C}-H + H_2O$$

$$:\bar{O}H$$

$$H\overset{\overset{O}{||}}{C}-CH_2 \quad \delta+\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}=O^{\delta-} \longrightarrow CH_3\overset{\overset{\bar{O}}{|}}{C}H-CH_2-\overset{\overset{O}{||}}{C}-H$$

$$\big\downarrow {}^{+}H^{+}\ (H_2O)$$

$$CH_3\underset{\underset{OH}{|}}{C}H\ CH_2\overset{\overset{O}{||}}{C}-H$$

Reactions with conc. NaOH

This reaction is possible only with aldehydes having ∝-hydrogens and not with ketones to give brown resinious compounds formed by a series of condensation.

$$2CH_3CHO \xrightarrow{\text{Conc.}} \bar{O}H\ CH_3\underset{\underset{OH}{|}}{C}H\ \underset{\underset{H}{|}}{C}H\ CHO \xrightarrow{-H_2O} CH_3CH=CH\ CHO$$

$$CH_3CH=CH\ CHO + CH_3CHO \xrightarrow{\bar{O}H} CH_3CH=CH\overset{\overset{OH}{|}}{C}H-CH_2CHO$$

$$CH_3CH=CH\overset{\overset{OH}{|}}{C}H-CH_2CHO \xrightarrow{-H_2O} CH_3CH=CH-CH=CHCHO$$

Polymerization:
i.e. $nCH_3CHO \xrightarrow{\text{Conc. } \bar{O}H} CH_3(CH = CH)_n CHO$.

Reaction that distinguish between aldehydes and ketones.

Oxidation:
Aldehydes are oxidized by oxidizing agents e.g. $H^+_{(aq)}/K_2Cr_2O_{7(aq)}$ H^+/CrO_3 to carboxylic acid.

Ketones are resistant to oxidation and therefore they never yield any product with the same reagents.

Test:
Add 2 drops of an aldehyde into 2cm^3 of $H^+_{(aq)}/K_2Cr_2O_{7(aq)}$ and warm.

An orange solution turns to green, the resultant solution becomes acidic.

$$CH_3\,CHO \xrightarrow{H^+_{(aq)}/Cr^2O_7^{2-}(aq)} CH_3COOH + Cr^{3+}_{(aq)} + H_2O.$$

Benedicts or Fehling's solution:
Increases a solution containing Cu^{2+} ions. This solution is blue in colour but when reacted with an aldehyde under heat, the aldehyde decreases Cu^{2+} to Cu^+ resultant into a red-brown precipitate of $Cu_2O_{(s)}$.

This property of aldehyde is reduction.
Ketones do not give a red-brown precipitate.

$$CH_3CHO + Cu^{2+} + H_2O \xrightarrow{\text{heat}} CH_3COOH + Cu_2O_{(s)}.$$

Ammoniacal silver nitrate (Tolleris reagents)
Ammoniacal silver nitrate solution is a solution of silver nitrate in NH_3.

Aldehydes unlike ketones are oxidized by this mild oxidizing agent to a carboxylic acid.

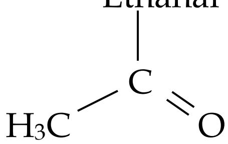
The Ag^+ in the $AgNO_3$ is reduced to Ag metals. Therefore, the observation made in practicals is; a grey deposit or silvery coating on the sides of the test tube.

$$CH_3\,CHO + Ag\,(NH_3)_2\,NO_3 + H_2O_{(l)} \xrightarrow{\text{heat}} CH_3CO\bar{O}NH_4^+ + Ag + NH_4NO_3.$$

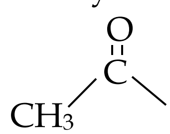
Note that atmospheric O_2 can also oxidize aldehydes. This is why samples of aldehydes are normally contaminated when exposed to the atmosphere.

Iodoform / haloform reaction:
This reaction is only possible for methyl aldehydes and ketones. Since we have only one methyl aldehyde, ethanal, the reaction is strictly positive for ethanol and methyl ketones with the following structure.

Ethanal



Methyl ketones



The reaction is useful in practicals in determining the structure of carbonyl compounds.

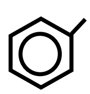
Test:
When iodine and NaOH is added to ethanol or a methyl ketone and warmed, a yellow precipitate of tri iodo methane is formed.

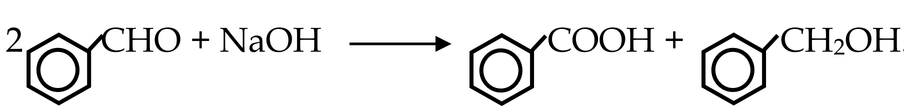
$$CH_3CHO + I_{2(g)} + NaOH_{(aq)} \longrightarrow CHI_{3(s)} + NaI + HCO\bar{O}Na^+ + H_2O_{(l)}$$

$$CH_3\overset{\overset{\large O}{||}}{C}CH_3 + I_{2(aq)} + NaOH_{(aq)} \xrightarrow{\text{warm}} CHI_3 + CH_3COONa^+ + NaI_{(aq)} + H_2O.$$

CARNIZARO REACTIONS:
This reaction is only possible for aldehydes withour ∝-hydrogen ketones.

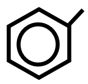
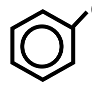
When NaOH is reacted with an aldehyde without an alpha-hydrogen of general formula.

HCHO,  CHO, the aldehyde is oxidized to carboxylic acid and the other half is decreased to the alcohol.

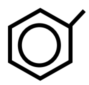


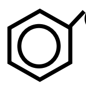
$2HCHO \xrightarrow{NaOH} HCOOH + CH3OH.$

Name the reagent that can be used to distinguish between the following pairs of compounds and in each case, state what would be observed when the reagent it separately treated with each compound.

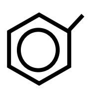
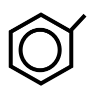
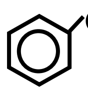
(i)  $COCH_3$ and  $COCH_2CH_3$.

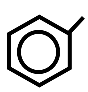
Reagent: Hot iodine solution in aqueous sodium hydroxide.

With  $COCH_3$: A yellow precipitate.

With  $COCH_2CH_3$: No observable change.

(ii) CH_3COCH_3 and HCHO
Reagent:
With CH_3COCH_3
With HCHO

(iii)  CHO and  $COCH_2CH_3$
Reagent:
With  CHO

With  $COCH_2CH_3$

(iv) $CH_3CH_2COCH_3$ and HCHO
Reagent:
With CH_3 CH_2 CO CH_2 CH_3
With HCHO

CARBOXYLIC ACIDS
CARBOXYLIC ACIDS/ALKANOIC ACIDS

Carboxyclic acids are organic compounds with a general formula,

```
  O
  ‖
R C – OH
```

($C_nH_{2n}O_2$) if they are saturated. They contain two functional groups:

```
 O Carbonyl carbon group
 ‖
/C\
- OH – hydroxyl group
```

Carboxylic acid group

```
 O
 ‖
/C – O – H
```

Carboxylic acids can be roughly categorized into the following:

(i) **Monobasic acid:**

Contains a single carboxylic acid group.

```
  O
  ‖
R C – OH
```

(ii) **Diabasic acid**

Contains two carboxylic acid groups joined to the same carbon chain.

```
                O
                ‖
HO – C – R – C – OH
     ‖
     O
```

(iii) **Tribasic acid**

Contains three carboxylic acid groups joined to the same carbon chain.

```
     O       O
     ‖       ‖
HO – C – R – C – OH
         |
         C – OH
         ‖
         O
```

Nature of the alkyl group

Saturated carboxylic acid

Contains the R group with single carbon-carbon bond.

```
    H   H   O
    |   |   ‖
H – C – C – C – OH
    |   |
    H   H
```

$\underbrace{\qquad\qquad}$ Alky group.

Unsaturated carboxylic acid

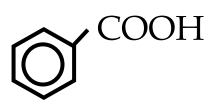
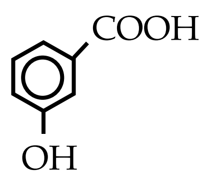
Contains atleast a double bond in the alkyl chain.

$$H_2C = CH\overset{\overset{\displaystyle O}{\|}}{C} - OH$$ Propenoic

Alkyl group.

NOMENCLATURE

According to the IUPAC system, carbonxylic acids are named after their corresponding alkanes. This is usually done by replacing a suffix-ane by OIC.

HCOOH	Methanoic acid
CH_3COOH	Ethanoic acid
$CH_3CH\ COOH$ CH_3	2-methyl propan-1-oic
	Benzoic acid
	3-hydroxy benzoic acid
$CH_3CH = CH\ CHOO$	Buten-2-oic acid
$CH_2\ COOH$	2-phenyl ethanoic acid.
HOOC-CH-COOH COOH	Butane-1, 2, 3-trioc acid.

$CH_3(CH_2)_4\ CH = CH - (CH_2)_2\ COOH$ Dec-4-enoic acid.

MONOBASIC CARBOXYLIC ACIDS

These contain a single carboxylic acid group. They are largely found in nature. E.g.

Citric acid – in citrus fruits

Lactic acid $\left(\begin{array}{l} CH\ CH\ COOH \\ \quad\ \ \ | \\ \quad\ \ OH \end{array}\right)$

Formic acid (HCOOH) – insect bites.

ISOMERISM

Monobasic acids show both structural and functional isomerism.

STRUCTURAL

Chain isomerism:

Isomers differ from nature of the carbon chain $C_5H_{10}O_2$.

$CH_3CH_2CH_2CH_2COOH$	-	Pentanoic acid
$\begin{array}{l} CH_2\ CH_2\ CH\ COOH \\ \qquad\qquad\ \ | \\ \qquad\qquad CH_3 \end{array}$	-	3-methyl butanoic acid
$\begin{array}{l} CH_3\ CH\ CH_2\ COOH \\ \qquad\ \ | \\ \qquad CH_3 \end{array}$	-	2-methyl butanoic acid
$\begin{array}{c} CH_3 \\ | \\ H_3C - C - COOH \\ | \\ CH_3 \end{array}$	-	2, 2-dimethy propanoic acid

FUNCTIONAL

Monocarboxylic acids are isomeric with esters e.g. $C_3H_6O_2$

$CH_3\,CH_2\,COOH$	$CH_3\overset{\overset{O}{\parallel}}{C}O\,CH_3$
Propanoic acid	Methyl ethanoate

METHODS OF PREPARATION OF MONOCARBOXYLIC ACIDS

Monocarboxylic acids can be prepared from the following:

(i) **Oxidation of primary alcohola and aldehydes:**

Primary alcohols are oxidized by excess oxidizing agents until carboxylic acids are formed.

Aldehydes are also oxidized to carboxylic acids.

$$\text{Primary alcohol} \xrightarrow[heat]{Excess\ oxidising\ agent} \text{carboxylic acid}$$

$$\text{Aldehydes} \xrightarrow[agent/heat]{oxidising} \text{carboxylic acid}$$

The main lab. Oxidizing agents used in this case are acidified $K_2/Na_2Cr_2O_7$/ $H^+_{(aq)}$ / $CrO_{3(aq)}$, $H^+_{(aq)}$ / $KMnO_{4(aq)}$

$$CH_3\,CH_2\,OH \xrightarrow[heat]{\substack{Excess \\ H^+(aq)/Cr_2O_7^{2-}(aq)}} CH_3\,COOH$$

$$CH_3\,CHO \xrightarrow[heat]{H^+(aq)/Cr_2O_7^{2-}} CH_3\,COOH$$

(ii) **Hydrolysis of acid nitriles and acid amides with alkaline or acid.**

When a nitrile is heated under reflux with mineral acid or alkali, an amide is first formed which later is further hydrolyzed to a carboxylic acid.

$$\underset{\text{Ethanitrile}}{CH_3\,C\equiv N} \xrightarrow[\bar{O}H/\,H_2O]{H^+/H_2O} \underset{\text{Ethanamide}}{CH_3\overset{\overset{O}{||}}{C} - NH_2}$$

Heat

$$\xrightarrow[heat]{H^+/H_2O} CH_3\,COOH + NH_2$$

$$\underset{\text{Propanamide}}{CH_3\,CH_2\,\overset{\overset{O}{||}}{C}\,NH_2} \xrightarrow[heat]{H^+/H_2O} CH_3\,CH_2\,COOH + NH_3$$

The usefulness of this reaction is, increase of the carbon chain of one carbon. E.g.
Convert $CH_2 = CH_2 \longrightarrow CH_3CH_2CH_2OH$

$$CH_2 = CH_2 \xrightarrow{HCl} CH_3CH_2Cl \xrightarrow[heat]{KCN/\epsilon tOH} CH_3CH_2CN$$

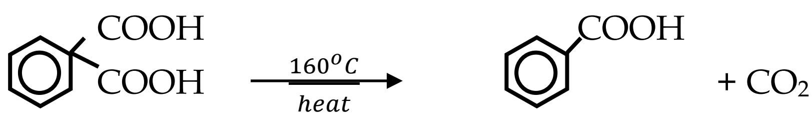
$$CH_3CH_2CH_2OH \xrightarrow[Dry\ ether]{LiAlH_4} CH_3CH_2COOH$$

(iii) **From dicaboxylic acids**

When dicarboxylic acids are heated, they are decomposed by loss of CO_2 to form a monocarboxylic acid. This reaction is important in reducing the carbon chain by one carbon.

$$HOOCCOOH \xrightarrow{heat} HCOOH + CO_2$$

$$HOOCCH_2COOH \xrightarrow{heat} CH_3COOH + CO_2$$



PROPERTIES OF CARBOXYLIC ACIDS

Physical properties:

Lower members ($C_1 - C_4$) are colourless liquids very soluble in H_2O.

Medium members ($C_5 - C_9$) are solids only partially soluble in H_2O.

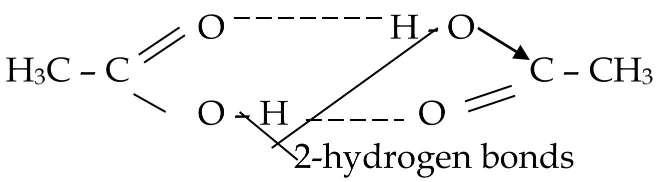
SOLUBILITY OF CARBOXYLIC ACIDS IN H_2O.

Solubility of carboxylic acids decreases with the increase in the carbon chain. This is because the more number of carbon chains which are hydrophobic outweighs the carboxylic acid group, which is responsible for forming H_2 bonds with H_2O hence low solubility.

Melting and boiling points:

Carboxylic acids show high values of melting and boiling points compared to their corresponding alcohols and alkanes. This is because a single molecule of a carboxylic acid dimerises via H_2 bonds which makes their melting and boiling points to be higher.

By them undergoing dimerisation, their apparent molecular masses when determined by **cryoscopic method** to be twice the actual molecular mass.



Apparent Mw = 120
Dimes
Real Mw = 60

The formation of H_2 bonds also make them to be very soluble in H_2O.

CHEMICAL PROPERTIES

Acid nature:

Carboxylic acids are acidic in nature. They are more acidic than phenol but less acidic compared to mineral acids. Aqueous solutions of carboxylic acids turn litmus paper red.

When dissolved in H_2O, they dissociate. An equation is established as shown.

$$R-\overset{\overset{O}{\|}}{C}-OH + H_2O \rightleftharpoons R\overset{\overset{O}{\|}}{C}-\bar{O}_{(aq)} + H_3O^+_{(aq)}$$

$$Ka = \frac{[RCO\bar{O}]\,[H_3O^+]}{[RCOOH]}$$

Moldm^{-3}.

The Ka value is then used to denote the strength of the acid. The bigger the Ka value, the more stronger the acid.

Acid	Ka	PKa
Methanoic, HCOOH	1.77×10^{-4} mol dm^{-3}	3.75
Ethanoic, CH_3 COOH	1.75×10^{-5} mol dm^{-3}	4.82

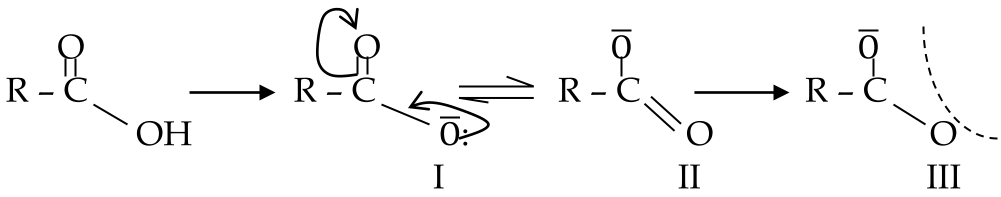
Another important value is PKa, therefore the higher the PKa value, the weaker the acid.

Explanation/reason for acid strength

Acidity of carboxylic acids is determined by a number of factors;

(i) **Resonance of the carboxylic ion**

When the carboxylic acid group ionizes, it forms the carboxylic ion and this ion may show several resonance structures in order to attain a more stable form. The more stable the carboxylate, the stronger the acid.



I, II and III are resonance structures of carboxylic acid.

(ii) **Inductive effect:**

Inductive effect is a tendency of an atom or groups of atoms to donate or withdraw electrons from a certain group.

Adjacent electron withdrawing substituents increase the acidity by further stabilizing the carboxylate. E.g.

Acids	**Structure**	**PKa**
Ethanoic acid	CH_3CO_2H	4.7
Fluoro ethanoic	FCH_2CO_2H	2.6
Dichloro ethanoic	$ClCH_2CO_2H$	1.3
Chloro ethanoic	Cl_2CHCO_2H	2.9
Tri-chloro ethanoic	Cl_3CCO_2H	0.9
Nitro ethanoic	$NO_2CH_2CO_2H$	1.7

The above table shows that the presence of an electron withdrawing atom pulls electrons from the bond decreasing electron density of that bond (O–H) and the ease of a proton release.

More atoms of such groups decreases the electron density of the O – H bond further and stabilizing the carboxylate thus high acidity.

The data below shows the PKa of the following acids. Explain.

Acid	**PKa**
CH_3 COOH	4.7
CH_3 CH_2 COOH	4.9

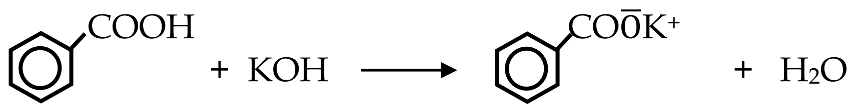
REACTIONS OF CARBOXYLIC ACIDS

They react as weak acids.

They react with bases e.g. (KOH and NaOH) to form a salt and H_2O.

$$R\overset{\overset{\large O}{||}}{C} - OH \ + \ NaOH \longrightarrow R\overset{\overset{\large O}{||}}{C}\bar{O}Na^{+} \ + H_2O.$$

$$CH_3CO_2H \ + \ OH \longrightarrow CH_3CO\bar{O}_{(aq)} \ + H_2O.$$

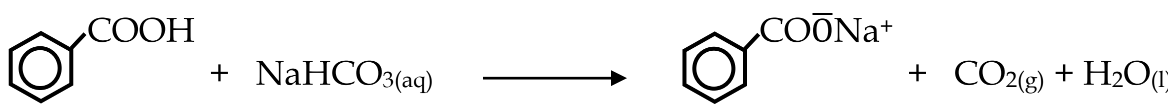


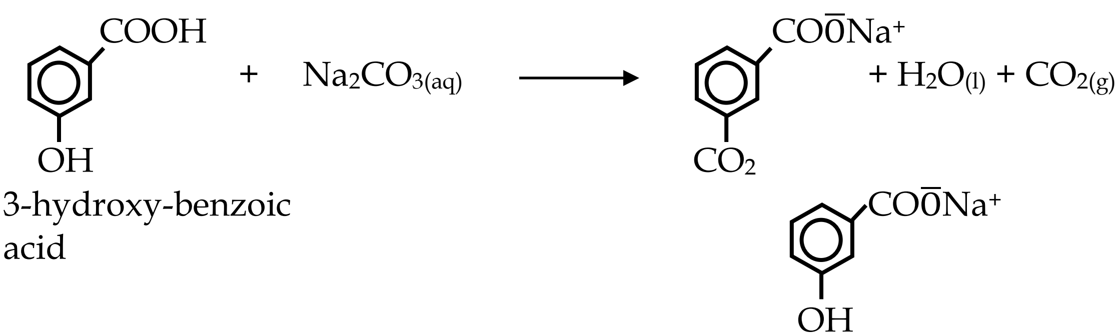
REACTION WITH SODIUM CARBONATE (NA_2CO_3)

Carboxylic acids unlike phenol react with Na_2CO_3 very slowly to liberate $CO_{2(g)}$. This reaction is of practical importance in distinguishing carboxylic acids from phenols. The reagent used is saturated Na_2CO_3.

$$CH_3COOH + Na_2CO_{3(aq)} \longrightarrow 2CH_3COONa^{+} \ + \ H_2O_{(l)} + CO_{2(g)}$$

Similarly, CO_2 can also be evolved from saturated $NaHCO_3$.





3-hydroxy-benzoic acid

OTHER REACTIONS:

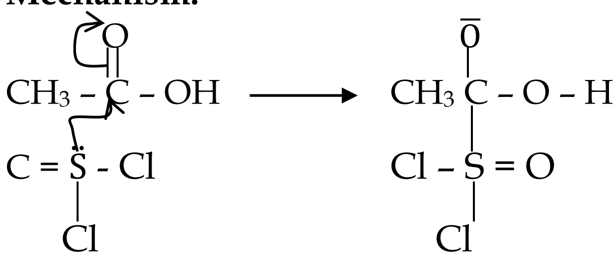
With $SOCl_2$.

Carboxylic acids react with $SOCl_2$ in presence of an organic base e.g. pyridine to form an acid chloride and SO_2. This is one useful way of preparing acid chlorides.

$$RCOOH + SOCl_2 \xrightarrow[pyridine]{\bar{t}t3N} R - \overset{\overset{O}{||}}{C} - Cl + SO_{2(g)} + HCl_{(g)}$$

$$CH_3COOH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3COCl + SO_2 + HCl$$

Mechanism:



Reaction with PCl_5.

Carboxylic acids react with PCl_3 or PCl_5 to form acid halides.

$$R\overset{\overset{O}{||}}{C} - OH + PCl_5 \xrightarrow{RT} R\overset{\overset{O}{||}}{C}Cl + POCl_3 + HCl$$

$$CH_3\,COOH + PCl_5 \longrightarrow CH_3COCl + PO\,Cl_2 + HCl$$

Reaction with alcohols

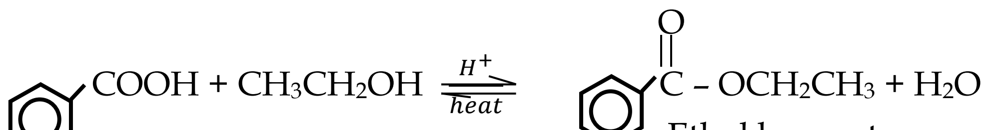
React with alcohols in presence of a mineral acid to form an ester under heat. This is called esterification where an ester is formed by refluxing a carboxylic acid and alcohol in presence of an acid catalyst.

To complete the reaction, one of the components either an acid or an alcohol has to be in excess or to remove an ester at a certain interval once it is formed.

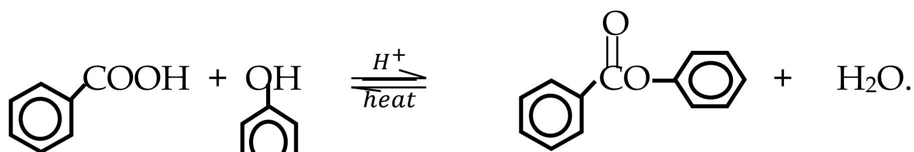
$$R - \overset{\overset{O}{||}}{C}\,OH + R - CH_2OH \;\underset{heat}{\overset{H^+(aq)}{\rightleftharpoons}}\; R\overset{\overset{O}{||}}{C}\,O - CH_2 - R + H_2O_{(s)}$$

$$CH_3COOH + CH_3OH \xrightleftharpoons[heat]{H^+} CH_3\overset{\overset{O}{||}}{C}OCH_3 + H_2O$$

Methyl ethanoate



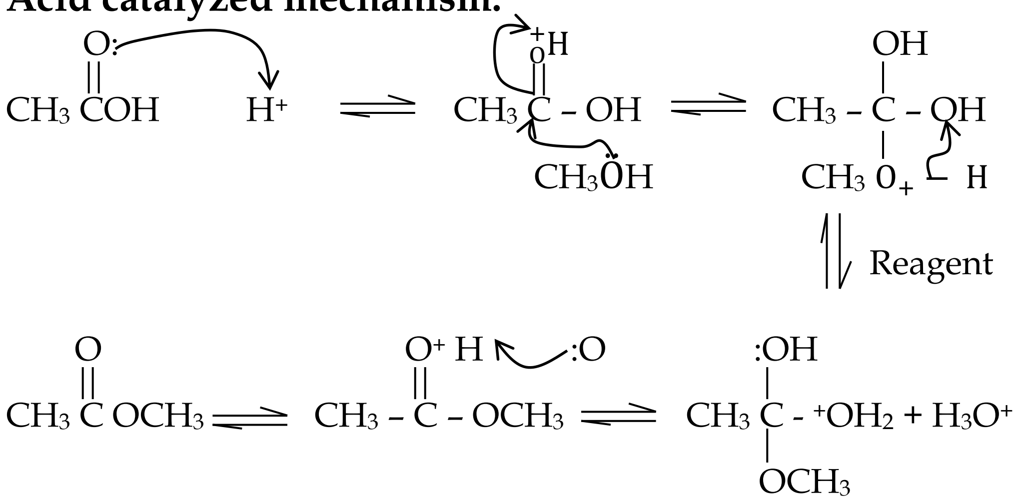
Ethyl benzoate



Phenyl benzoate

The mechanism for this reaction depends on the catalyst used/base catalysed or acid catalysed.

Acid catalyzed mechanism.



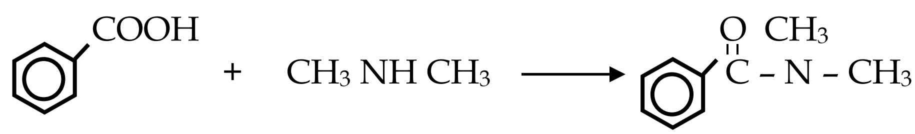
Reaction with amides:

Carboxylic acids react with amides to form substituted amines. With amines, they form amides.

$$R\overset{\overset{O}{||}}{C}OH + R_2NH \longrightarrow R\overset{\overset{O}{||}}{C}-NR_2 + H_2O.$$

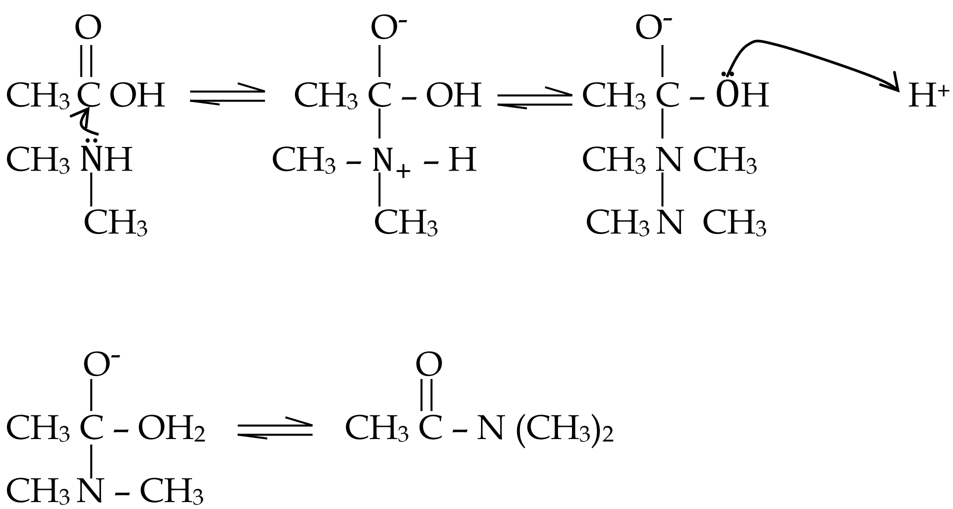
$$CH_3COOH + (CH_3)_2NH \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}\underset{\displaystyle CH_3}{N} - CH_3 + H_2O$$

$$CH_3\,COOH + CH_3NH_2 \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}} - NH\,CH_3 + H_2O$$



This reaction occurs because of the presence of a proton on the amine which are substituted by the carboxylate.

Mechanism:



REDUCTION OF CARBOXYLIC ACIDS

Carboxylic acids are usually reduced by reducing agents e.g. $LiAlH_4$/ether (THF) to form aldehydes and later alcohols (primary).

Note: ***$NaBH_4$ is not commonly used to decrease carboxylic acids because it s less reactive.***

$$CH_3\,COOH \xrightarrow[dry\ ether]{Li\,Al\,H_4} CH_3CHO \xrightarrow[dry\ ether]{Li\,Al\,H_4} CH_3\,CH_2\,OH + H_2O.$$

OR:

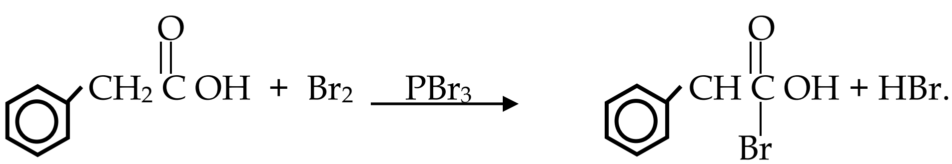
$$CH_3\,COOH \xrightarrow[dry\ ether]{Excess\ Li\,Al\,H_4} CH_3\,CH_2\,OH + H_2O$$

REACTIONS WITH HALOGENS (∝- HALOGENATIONS)

Carboxylic acids can be halogenated at the carbon atom adjacent to the carboxylic group when reacted with reagents like Br_2, PCl_5. This reaction depends on the character of the carbonyl compound where the product of the reaction known as ∝-bromo carboxylic acid, is converted to ∝-hydroxy or ∝-amino carboxylic acid.

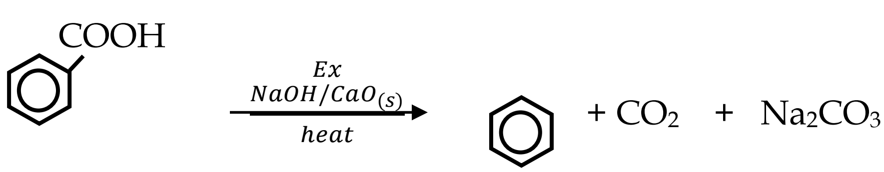
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH + Br_2 \xrightarrow{PBr_3} BrCH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}-OH + HBr$$

∝-bromo ethanoic acid



DECARBOXYLATION

Carboxylic acids with a carbonyl group at the third position readily undergoes thermal decarboxylation where CO_2 is lost to form a simple alkane when heated in the presence of dry soda lime.



$$CH_3COOH \xrightarrow[heat]{Ex\ NaOH/CaO_{(s)}} CH_4 + CO_2 + Na_2CO_3$$

$$HO\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{heat} CH_3\overset{\overset{\displaystyle O}{\|}}{C}OH + CO_2$$

Malonic acid
(Propane -1, 3-dioic)

Carboxylic acid derivatives

Esters $R\overset{O}{\overset{\|}{C}}-OR$

Amides $R\overset{O}{\overset{\|}{C}}-NH_2$

Anhydrides $R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}-R.$

Acid halides $R\overset{O}{\overset{\|}{C}}-X$

ACID HALIDES

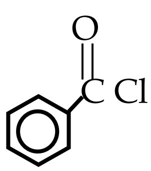
These are compounds derived from carboxylic acids by reacting an acid with a halogen. The commonest examples are acid chlorides.

$R\overset{O}{\overset{\|}{C}}-X$ where x = halogen atom.

Nomenclature:

Acid chlorides are named by replacing the suffix –ic in acids with –oyl.

$CH_3\overset{O}{\overset{\|}{C}}Cl$ Ethanoyl chloride



Benzoyl chloride

$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}Cl$ 2-methyl propanyl chloride

PREPARATION

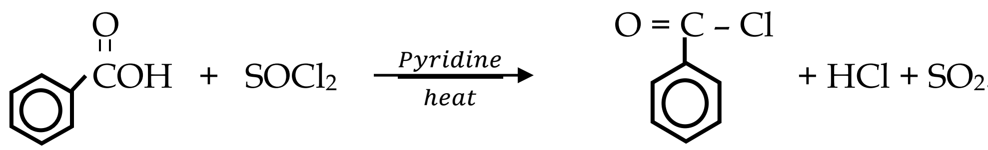
i) **Reacting carboxylic acids with phosphorous halides.**

$$CH_3COOH + PCl_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}\,Cl + H_3PO_3$$

$$CH_3COOH + PCl_5 \longrightarrow CH_3\,\overset{O}{\overset{\|}{C}}\,Cl + HCl + POCl_3$$

ii) **Reaction of carboxylic acid with thionyl chloride**

This reaction should occur in a fume cupboard due to evolution of toxic acids or should occur in the presence of pyridine which absorbs.



PROPERTIES OF ACID HALIDES

Physical:

They are colourless volatile liquids with irritating smells. They fume easily in moist air due to evolution of HCl gas.

Have low boiling points than the corresponding acids.

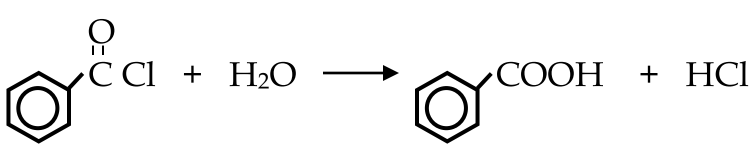
Chemical properties:

They undergo a number of reactions making them suitable for organic synthesis.

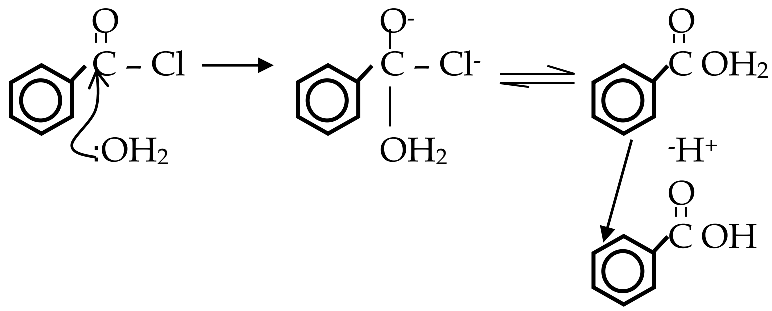
Hydrolysis using H_2O.

Acid halides react with H_2O to form their parent carboxylic acids.

$$CH_3\,\overset{O}{\overset{\|}{C}}\,Cl + H_2O \xrightarrow{RT} CH_3\,\overset{O}{\overset{\|}{C}} - OH + HCl$$

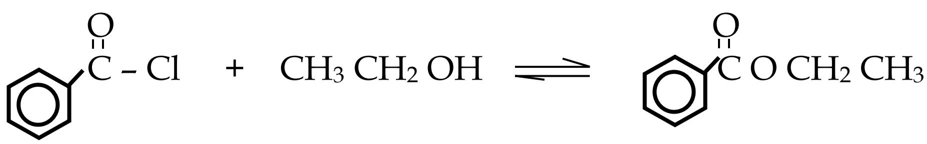


Mechanism:

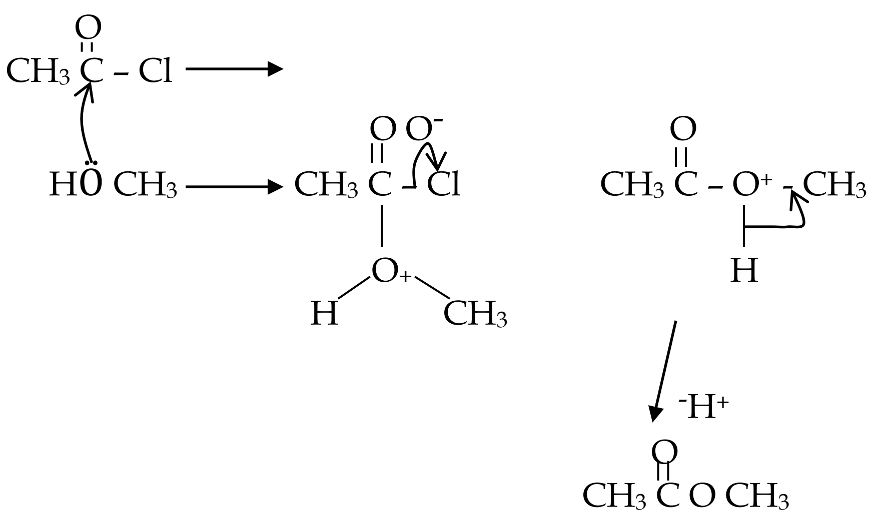


Reaction with alcohols:
Acid halides react with alcohols to form esters.

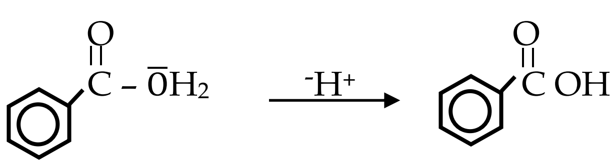
$$CH_3\overset{O}{\overset{\|}{C}}Cl + CH_3OH \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}OCH_3 + HCl$$



Mechanism:

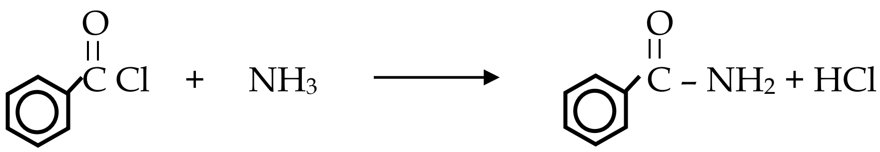


Reaction with NH_3 and amines:
Acid chlorides react with NH_3 to form amides. This reaction is responsible with primary/secondary amines to form amides.



$$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}Cl + NH_3 \longrightarrow CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}NH_3 + HCl$$

2-methyl propanamide



Benzanamide

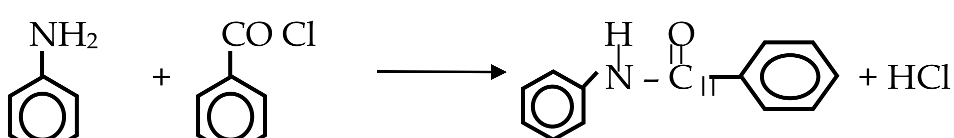
$$CH_3\overset{\overset{O}{\|}}{C}Cl + CH_3NH_2 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-NHCH_3 + HCl$$

$$CH_3\underset{\underset{O}{\|}}{C}Cl + CH_3NHCH_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{N}-CH_3 + HCl$$

N, N-dimethyl ethanamide.

Mechanism:

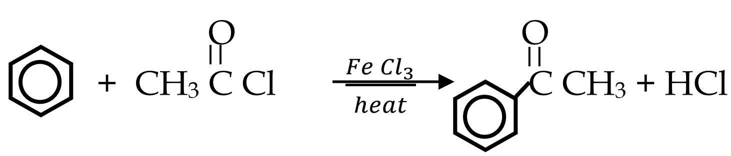
$$CH_3\overset{\overset{O}{\|}}{C}Cl \quad \underset{\underset{CH_3}{|}}{H\ddot{N}-CH_3} \longrightarrow CH_3\overset{\overset{O^-}{|}}{\underset{\underset{\underset{\underset{CH_3}{|}}{H-N-CH_3}}{|}}{C_+}}-Cl \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\underset{\underset{H}{|}}{N}(CH_3)_2 \xrightarrow{-H^+} CH_3\underset{\underset{O}{\|}}{C}-N(CH_3)$$

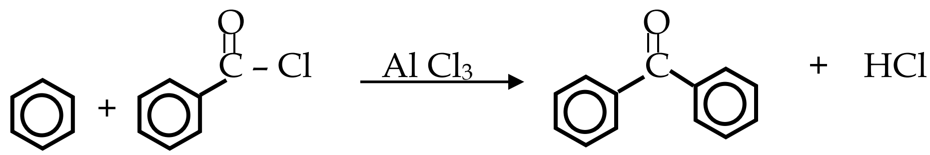


Phenyl benzanamide.

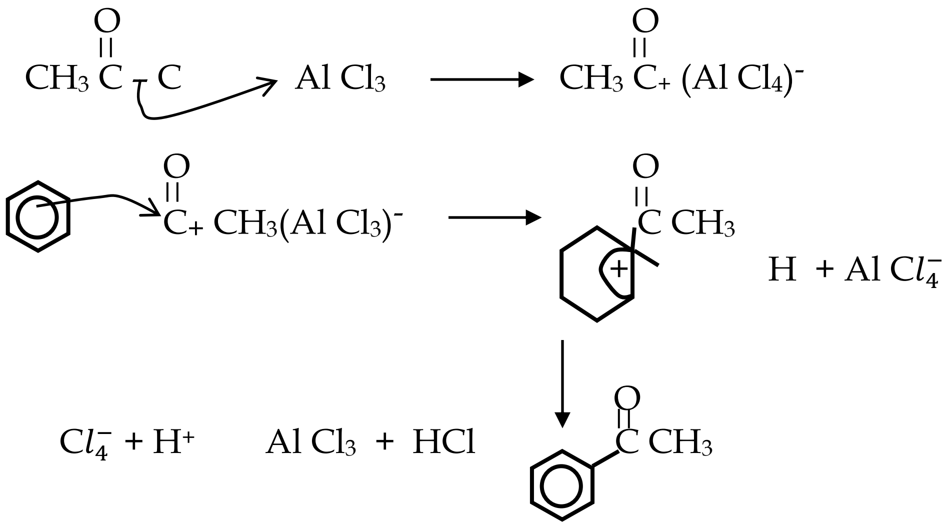
Reaction with benzene:

Acid halides react with benzene in presence of a hydrogen carrier.





Mechanism:



AMIDES

Amides are compounds derived from carboxylic acid and nitrogen containing compound like amine or NH_3 with a general formula $R\overset{O}{\overset{||}{C}}NH_2$.

Unlike amines, they contain a carbonyl carbon directly attached to the nitrogen.

Naturally, such compounds are found in proteins.

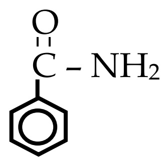
Nomenclature:

Amides are named as derivatives of parent hydrocarbons alkane, replacing – e – amide.

E.g.

$H\overset{O}{\overset{||}{C}} - NH_2$ Methanamide

$CH_3\ \overset{O}{\overset{||}{C}} - NH_2$ Ethanamide



Benzenamide

$CH_3CONH(CH_3)_2$ N, N-dimethyl ethanamide

$CH_3CH_2C(=O)-N(CH_3)_3$ N, N , N – trimethyl propanamide.

PROPERTIES OF AMIDES

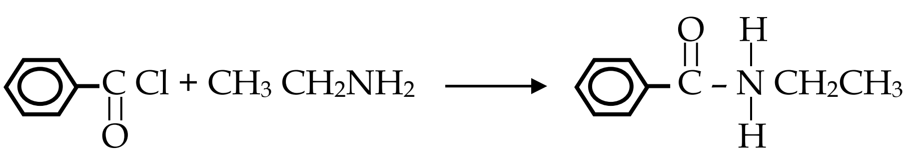
Physical:

All amides are colourless crystalline solids except ethanamide. They have got higher boiling points than corresponding carboxylic acids due to the formation of H_2 bonding.

PREPARATION

Reaction between acid halides and NH_3 or amines.

$$CH_3C(=O)Cl + NH_3 \longrightarrow CH_3C(=O)-NH_2$$



Esters and ammonia

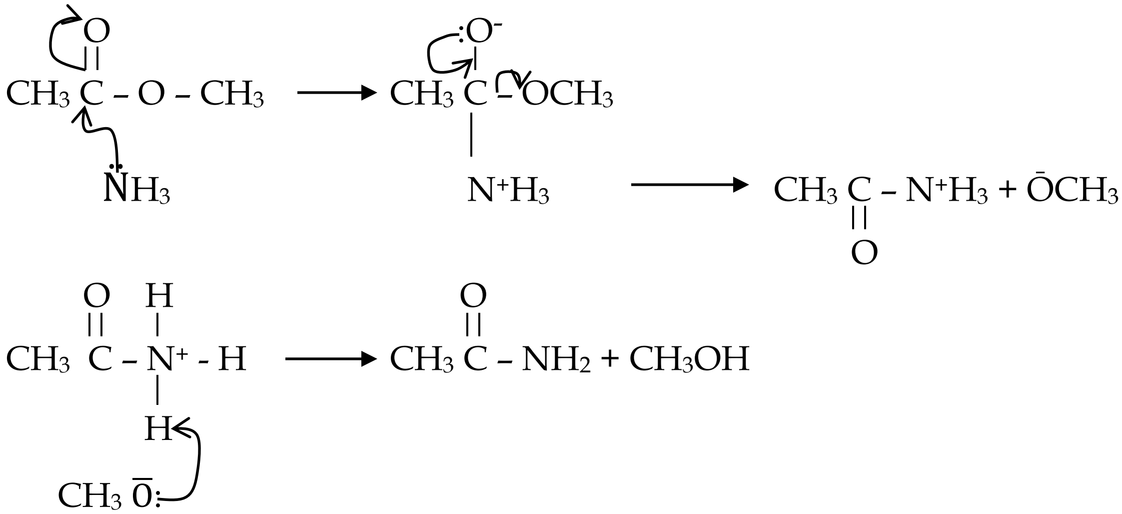
$$CH_3C(=O)OCH_3 + NH_3 \xrightarrow{heat} CH_3C(=O)NH_2 + CH_3OH$$

Acid anhydrides and ammonia

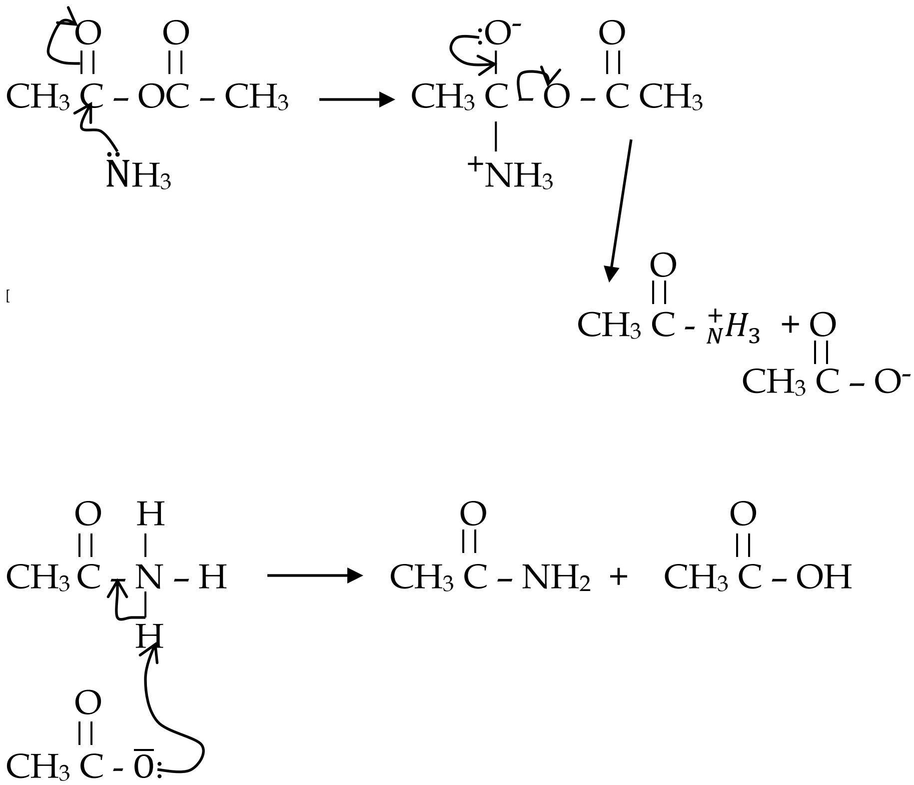
$$CH_3C(=O)O-C(=O)CH_3 + 2NH_3 \xrightarrow{heat} 2CH_3C(=O)ONH_2 + H_2O$$

Ethanoic acid anhydride.

Mechanism:



With anhydrides



Amides are reduced by reducing agents such as sodium tetrahydride borate, $LiAlH_4$.

$$CH_3\,CH(CH_3)\,\overset{O}{\overset{||}{C}}\,NH_2 \xrightarrow{\in tOH\ /\ Na} CH_3\,CH(CH_3)\,CH_2\,NH_2 + H_2O$$

2-methyl propanamide 2-methyl propyl amide

Hydrolysis

Amides are hydrolysed in presence of a mineral acid or an alkali to form a carboxylic acid.

For example:

$$CH_3\,CH_2\,\overset{O}{\overset{||}{C}}\,NH_2 + H_2O \xrightarrow[heat]{H+\ /\ \bar{O}H} CH_3CH_2\,COOH + NH_4^+$$

$$CH_3\,\overset{CH_3}{\overset{|}{CH}}\ \overset{O}{C}\ \ NH_2 + H_2O \xrightarrow[heat]{H+\ /\ (aq)} CH_3\,\overset{CH_3}{\overset{|}{CH}}\,COOH + NH_4^+$$

For distributed amides, hydrolysis produces a carboxylic acid and on amine.

Example:

$$CH_3\,\overset{O}{\overset{||}{C}}\,NH\,CH_3 \xrightarrow[heat]{H_2O/H^+} CH_3COOH + CH_3\,NH_2$$

N-methyl ethanamide Primary amine

For trisubstituted.

$$CH_3\,CON\,(CH_3)_2 + H_2O \xrightarrow[heat]{\bar{O}H} CH_3COOH + NH(CH_3)_2$$

N-N-dimethylethanamide Secondary amine.

ACID CATALYZED HYDROLYSIS (MECHANISMS)

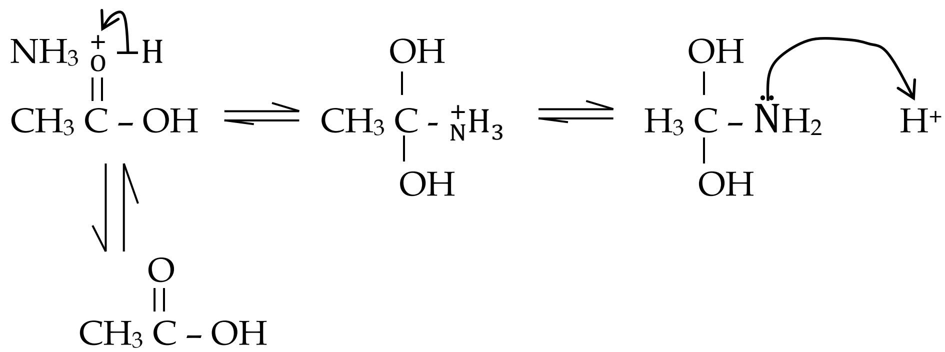
1.

$$CH_3\,\overset{O:}{\overset{||}{C}} - NH_2 \quad H^+ \rightleftharpoons CH_3\,\overset{^+OH}{\overset{||}{C}} - NH_2 \quad :OH_2 \rightleftharpoons CH_3\,\overset{OH}{\overset{|}{C}} - NH_2$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$

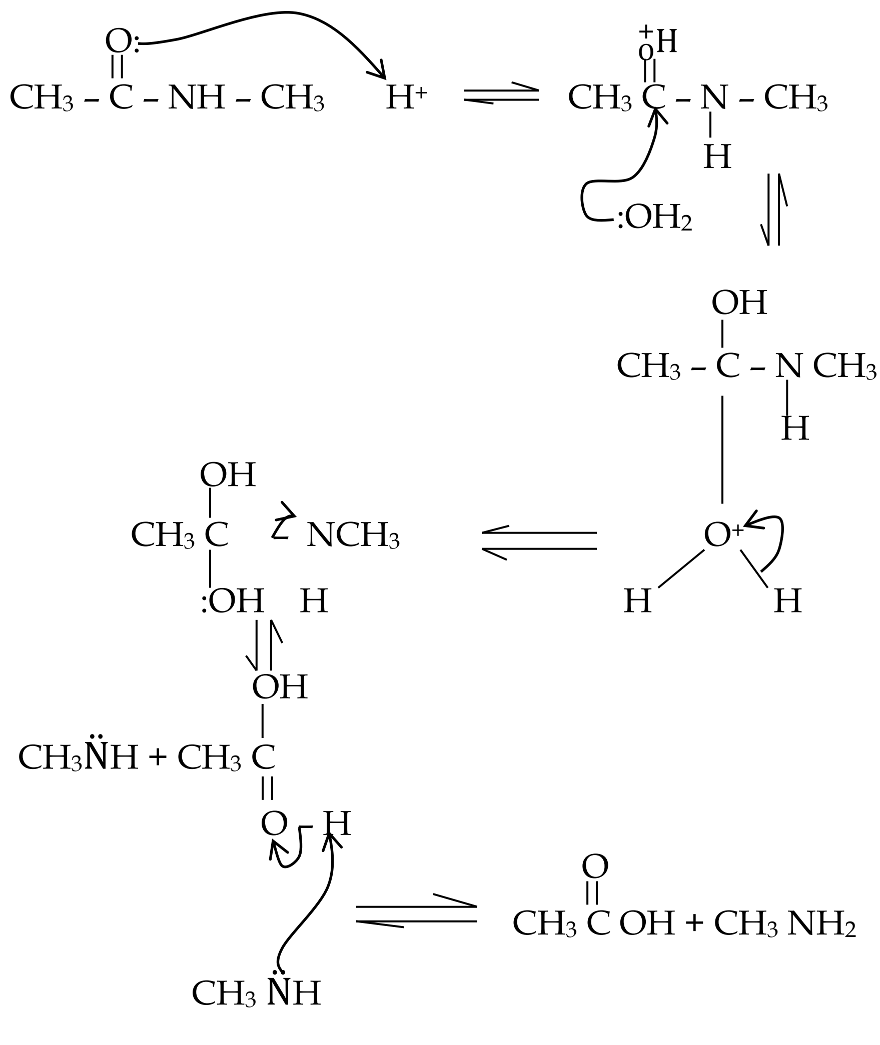
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H - O^+ - H$$

$$\rightleftharpoons\ ^-H^+$$



$$NH_3 + H^+ \longrightarrow NH_4^+$$

2.



HOFFMAN'S DEGRADATION

When an amide is heated with Br_2 and an alkali, a primary amine id produced which is less than one carbon from the original amide; this reaction is known as Hoffman's degradation because it involves reduction of the carbon chain by one carbon atom.

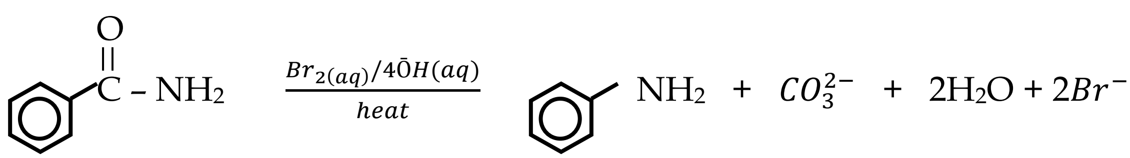
(i)

$$CH_3\overset{O}{\overset{||}{C}}NH_2 \xrightarrow[heat]{Br_2/KOH} CH_3NH_2$$

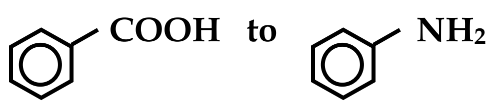
Equation:

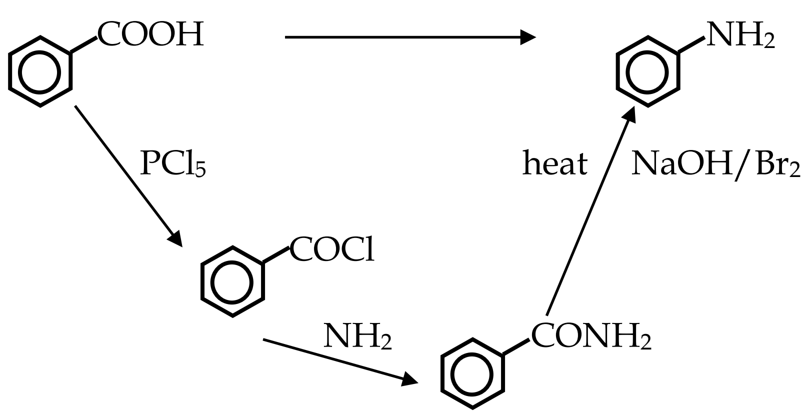
$$CH_3\overset{O}{\overset{||}{C}}NH_2 + Br_2 + 4KOH_{(aq)} \xrightarrow{heat} CH_3NH_2 + K_2CO_3 + 2KBr + H_2O.$$

(ii)



Convert





ESTERS

Esters are derivatives of carboxylic acids. Are highly volatile compounds with a fruity smell. They conform to a general formula: $R\overset{O}{\overset{||}{C}} - O - R$

NOMENCLATURE

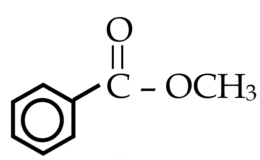
Esters are named using their parent acid name but adding the suffix –ate.

$CH_3\ \overset{O}{\overset{||}{C}}\ O\ CH_3$ - methyl ethanoate

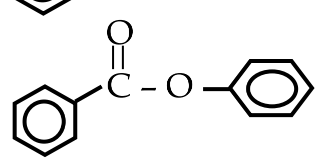
$CH_3\ CH_2\ \overset{O}{\overset{||}{C}}\ O\ CH_3$ - methyl propanoate

$CH_3\ O\ \overset{O}{\overset{||}{C}}\ CH_3\ CH_2\ CH_3$ - methyl butanoate

$CH_3\ \overset{O}{\overset{||}{C}} - O\ CH_2\ CH_3$ - ethyl methanoate



- methyl benzoate



- phenyl benzoate

Isomerism

Esters show structural isomerism and functional isomerism.
Functionally esters are isomeric with carboxylic acids.

$C_4H_8O_2$

$CH_3CH_2CH_2COOH$ – Alcohol

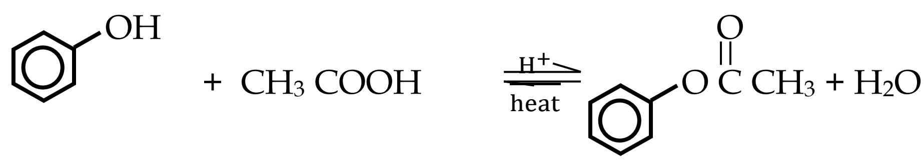
$$CH_3CH_2\overset{\overset{\displaystyle O}{||}}{C}OCH_3$$ - Ester

PREPARATION OF ESTERS

(i) **Esterification:**

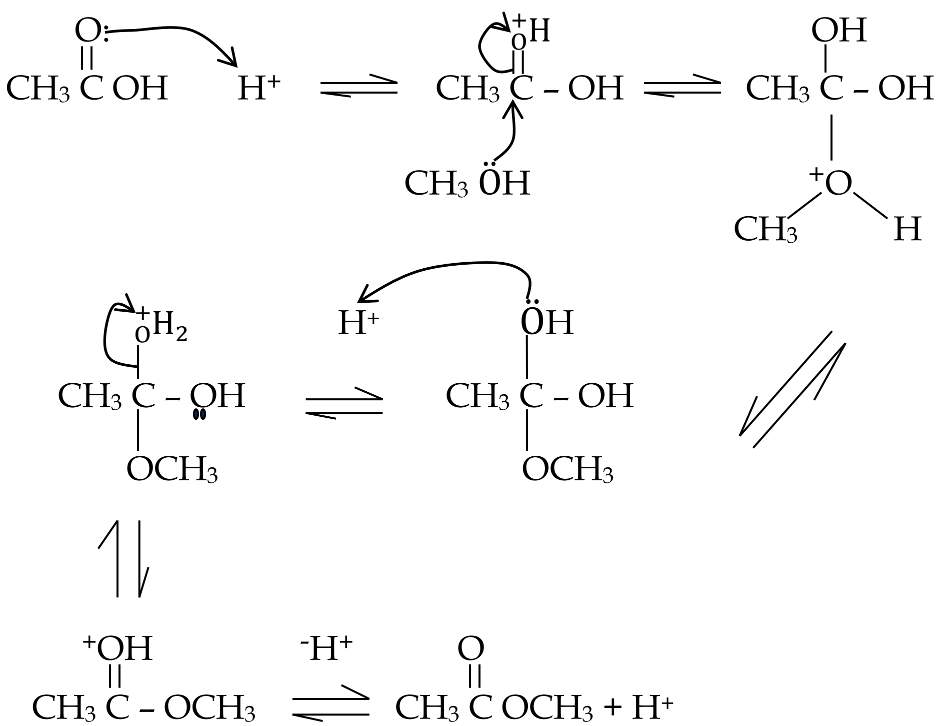
From carboxylic acids and an alcohol. This reaction is catalyzed by a mineral acid or an alkali.

$$CH_3COOH + CH_3OH \underset{heat}{\overset{H^+}{\rightleftharpoons}} CH_3\overset{\overset{\displaystyle O}{||}}{C}OCH_3 + H_2O$$



Phenyl ethanoate

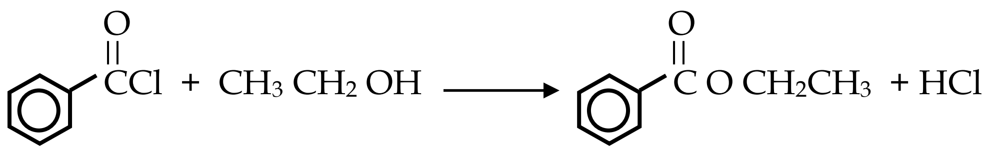
Mechanism:



From acid chlorides and acid anhydrides

When alcohols are reacted with acid chlorides or acid anhydrides, an ester is formed.

$$CH_3\overset{\overset{O}{\|}}{C}\,Cl + CH_3\,OH \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}\,O\,CH_3 + HCl$$



$$CH_3\overset{\overset{O}{\|}}{C}\,O\,\overset{\overset{O}{\|}}{C} - CH_3 + CH_3OH \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\,O\,CH_3 + CH_3\,COOH$$

Ethanoic acid anhydride.

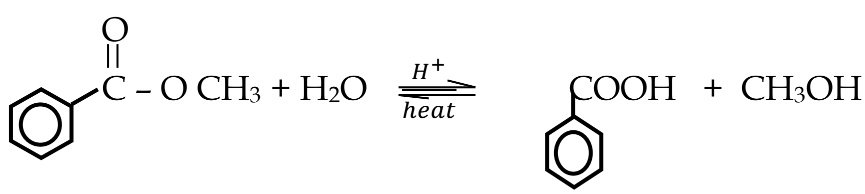
REACTIONS OF ESTERS

Esters undergo the following reactions:

i) **Hydrolysis**

Esters are hydrolyzed in presence of a mineral acid to a corresponding carboxylic acid and alcohol.

$$CH_3\overset{\overset{O}{\|}}{C}\,O\,CH_2\,CH_3 \xrightarrow[heat]{H^+/H_2O} CH_3\,COOH + CH_3\,OH$$



NOTE:

Hydrolysis involves cleavage at

$$R - \overset{\overset{O}{\|}}{C} - O - R$$

The position of this cleavage is useful in radiolabelling to trace for the reaction mechanisms.

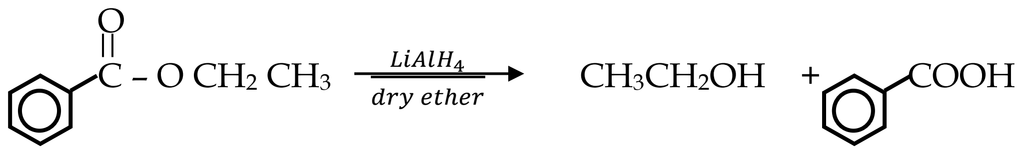
Example:

$$R\overset{\overset{O}{\|}}{C} - {}^{18}O - R + H_2{}^{16}O \rightleftharpoons R\overset{\overset{O}{\|}}{C} - {}^{16}OH + R - {}^{18}OH$$

ii) **Reduction**

Esters are reduced with $LiAlH_4$ in presence of ether to carboxylic acid and the alcohol.

Example:

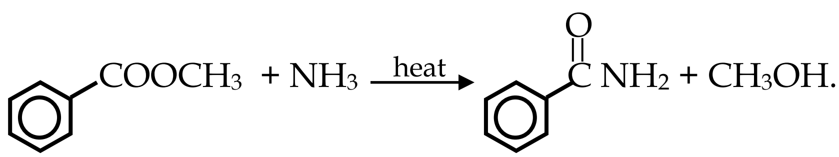


iii) **Reaction with NH_3**

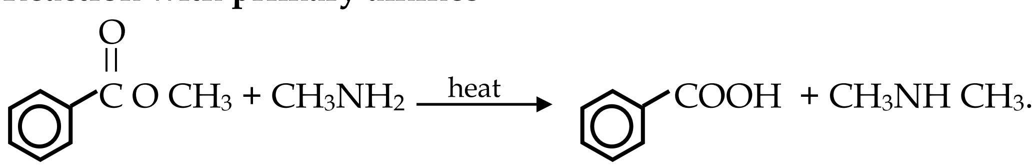
Esters react with NH_3 to give amides and alcohols.

Example:

$$CH_3\,CH_2\,\overset{\overset{O}{||}}{C}\,O\,CH_3 + NH_3 \xrightarrow{\text{heat}} CH_3\,CH_2\,\overset{\overset{O}{||}}{C} - NH_2 + CH_3OH$$



iv) **Reaction with primary amines**



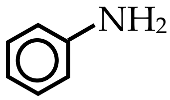
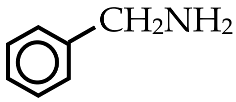
AMINES

These are compounds that are derived from ammonia base by replacing one hydrogen with an amino group. They therefore have a general formula.
$RCH_2 - NH_2$.

The functional group of amines is $- NH_2$ (amino group).

NOMENCLATURE

Amines are named as derivatives of alkanes by adding amine suffix to the stem name.

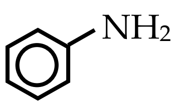
CH_3NH_2	methyl amine
$CH_3CH_2NH_2$	ethyl amine
$CH_3CH_2CH_2NH_2$	propyl amine
	phenyl-amine (aniline)
	phenyl methyl amine

CLASSES OF AMINES

Amines are classified into four groups or four classes.

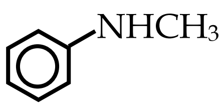
i) **Primary amines**

Is formed when only one hydrogen is replaced from the NH_3.

$CH_3CH_2NH_2$	Ethyl amine
	Phenyl amine (primary aromatic)

ii) **Secondary amines**

Is formed when two hydrogens of NH_3 are replaced by alkyl or anyl groups.

$(CH_3)_2NH$	Dimethyl amine or N-N-dimethyl amine
$CH_3NHCH_2CH_3$	Ethyl methyl amine
	Phenyl methyl amine

iii) **Tertiary amines**

Are formed when all the hydrogens in the NH_3 are replaced by the alkyl group.

$(CH_3)_3N$	Trimethyl amine
$(CH_3)_2NCH_2CH_3$	Phenyl dimethyl amine.

iv) **Quartenary amines**

Are salts formed when the lone pair on the Nitrogen is donated to an alkyl group.

$(CH_3)_3\overset{+}{N}CH_3$ Tetramethyl amine.

Isomerism

Amines exhibit all the three types of isomerism, chain, positional and functional.

Write all isomers of $C_4H_{11}N$.

1. $CH_3\,CH_2\,CH_2\,CH_2\,NH_2$ n-butylamine

2. $$\begin{array}{l} CH_3\,\underset{\displaystyle CH_3}{\underset{|}{C}}H\,CH_2\,NH_2 \end{array}$$ 2-methyl propylamine

3. $$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & C & - & NH_2 \\ & & | & & \\ & & CH_3 & & \end{array}$$ 2-amino-2-methyl propane.

4. $CH_3\,CH_2\,CH\,CH_3$ 2-amino butane

1 and 2 are chain isomers.
3 and 4 are position isomers.

5. $$CH_3\,CH_2\,\overset{\displaystyle H}{\overset{|}{N}}\,CH_2\,CH_3$$ N-diethyl amine (functional)

6. $$CH_3\,\overset{\displaystyle CH_3}{\overset{|}{N}}\,CH_2\,CH_3$$ (Functional)

METHODS OF PREPARATION

From alkyl halides

When alkyl halides are heated with NH_3 in a sealed tube at a temperature of 100^oC, the reaction gives a mixture of amines. This method is not suitable for producing a specific amine because of a mixture of amines.

Although the products produced may be controlled by using excess NH_3 and at the same time separating each product by functional distillation.

$$CH_3CH_2Cl + NH_{3(l)} \xrightarrow[100^oC]{sealed\ tube} CH_3CH_2NH_2 + HCl.$$

Primary

$$CH_3CH_2NH_2 + CH_3CH_2Cl \xrightarrow[100^oC]{sealed\ tube} (CH_3CH_2)_2NH + HCl$$

Secondary

$$(CH_3CH_2)_2NH + CH_3CH_2Cl \xrightarrow[100^oC]{sealed\ tube} (CH_3CH_2)_3N + HCl$$

Tertiary

NOTE:
When excess NH_3 is used,

$$CH_3CH_2Cl + {}^{Excess}_{NH_3}(l) \xrightarrow[100^oC]{sealed\ tube} CH_3CH_2NH_2 + HCl$$

Mechanism:
Excess NH_3

$$H_3N: \; \underset{\displaystyle CH_3}{\overset{\delta+}{CH_2}} - \overset{\delta-}{Cl} \rightleftharpoons \underset{\displaystyle CH_3}{CH_2} - \overset{+}{N}H_3 \xrightarrow{-H^+} CH_3CH_2NH_2 + H^+$$

$$H^+ + Cl^- \longrightarrow HCl.$$

From alkyl cyanides

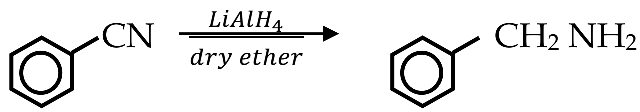
When an alkyl cyanide also known as a nitrile is reduced with reducing agents such as $LiAlH_4$ or $NaBH_4$. Or simply sodium in an alcohol, dry ether a primary amine is formed.

$$CH_3C \equiv N \xrightarrow[dry\ ether]{LiAlH_4} CH_3CH_2NH_2$$

Ethanitrile

$$CH_3CH_2CN \xrightarrow[ethanol]{Na} CH_3CH_2CH_2NH_2$$

Propanitrile



Benzenitrile

From acid amides

When an acid amide is reduced using reducing agents like $LiAlH_4$/dry ether, primary amines are formed.

$$CH_3\overset{\overset{\displaystyle O}{||}}{C}NH_2 \xrightarrow[dry\ ether]{LiAlH_4} CH_3CH_2NH_2 + H_2O$$

$$CH_3\overset{\overset{\displaystyle O}{||}}{C} - NHCH_3 \xrightarrow[dry\ ether]{LiAlH_4} CH_3CH_2NHCH_3$$

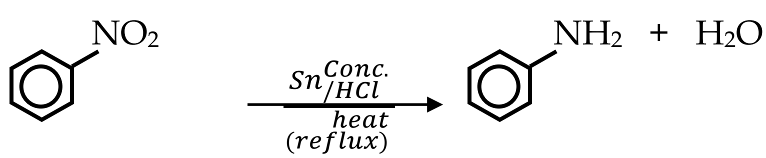
HOFFMAN'S DEGRADATION

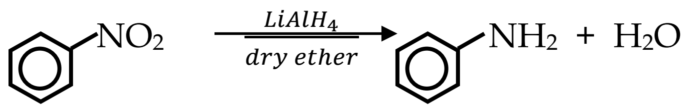
When amines are reacted with Br_2 in a solution of KOH or NaOH, a primary amine is formed which is one carbonless from the parent amide. This reaction shortens the chain by one carbon and it is known a Hoffman's degradation.

$$CH_3\overset{\overset{\displaystyle O}{||}}{C}NH_2 + Br_2 + KOH \xrightarrow{heat} CH_3NH_2 + KBr + K_2CO_3 + H_2O$$

From nitro compounds

When a nitro compound preferably aromatic nitro compound is reacted with tin in conc. HCl or $LiAlH_4$/ether, aromatic amine is formed.





This method is suitable for preparing aromatic amines.

HYDROLYSIS OF TERTIARY AND SECONDARY AMINES

This produces primary and secondary amines respectively. When they are heated with mineralized acid H_2O or a base.

$CH_3\,NH\,CH_3 + H_2O \xrightarrow[heat]{H^+} CH_3OH + CH_3\,NH_2$

Secondary Primary

$CH_3\,CH_2N(CH_3)_2 + H_2O \xrightarrow[heat]{H^+} CH_3\,CH_2OH + CH_3NHCH_3$

Tertiary Secondary

$CH_3CH_2NHCH_3 + OH \xrightarrow[H_2O]{H^+} CH_3\,CH_2\,NH_2 + CH_3OH$

Mechanism: (Base catalysed)

PHYSICAL PROPERTIES OF AMINES

i. Lower amines up to C_2 are gases while those with $C_3 = C_{11}$ are liquids, higher amines are solids at room temperature.
ii. Lower amines have got a fishy ammoniacal smell or odour.
iii. Boiling points of amines are higher than those of corresponding alkanes.
iv. Lower members are soluble in H_2O but the solubility decreases with increase in molecular weight.

Explanations for boiling points and solubility

Question:

Methyl amine CH_3NH_2	Molecular	Boiling point ^oC
	31	-7
CH_3CH_3	30	-89

Methyl amine boils at a high temperature than ethane because of the presence of intramolecular hydrogen bonding which holds methylamine molecules together in the liquid phase and difficult to escape to vapour phase during boiling and more heat required to boil while in ethane, the weak Van der Waal's forces are easily broken and loss heat required to boil.

Comparing three classes of amines, primary amine boils at a higher temperature than the secondary followed by tertiary.

Amine	Molecular weight	Boiling point ^oC
$CH_3\ CH_2\ CH_2\ NH_2$	59	49
$CH_3\ CH_2\ NH\ CH_3$	59	35
$\begin{array}{l} CH_3 - \ddot{N} - CH_3 \\ \qquad\ \, \vert \\ \qquad CH_3 \end{array}$	59	3.5

Primary amine forms atleast two intramolecular hydrogen bonding due to the presence of more hydrogen atoms on the nitrogen and hence boiling at a higher temperature.

The secondary amine forms only one hydrogen bond since it has only one hydrogen in the nitrogen while the tertiary amine has not hydrogen on the nitrogen and therefore forming no hydrogen bonding and ends boiling at the lowest temperature.

Assignment (Research work)
Carboxylic acids boil at higher temperatures than alcohols which also boils at a higher temperature than an amine and an alkane has the least boiling point. Explain.

BASICITY OF AMINES

Amines are bases which form weak alkaline solutions when dissolved in H_2O. Such solutions turn litmus paper to blue.

The basic strength of an amine is determined by the extent of ionization denoted as Kb. The greater the Kb value, the more basic the amine. The basic character of an amine can be explained by the presence of lone pair of electrons on the nitrogen atom which are always donated.

The more available these lone pair of electrons are, the more basic an amine is.

The availability of electrons on the nitrogen atom is determined by the atoms that are bonded onto it.

Groups of atoms that have got positive inductive effect will push electrons towards nitrogen making them available while those with negative inductive effect will lower the electron density on the nitrogen atom making them less available.

$$CH_3\,NH_2 + H_2O \rightleftharpoons CH_3\,\overset{+}{N}H_3 + OH$$

$$Kb = \frac{[CH_3\overset{+}{N}H_3][\bar{O}H]}{[CH_3NH_2]}$$

Questions:

1. Methylamine is a stronger base than ammonia.
2. Phenylamine is a weaker base than methylamine.
3. Ethylmethylamine is a stronger bases than trimethyl amine.

   Trend:
   Secondary amine > Primary > Tertiary > ammonia

4. Amino benzene is a weaker base than aliphatic primary amine. Explain.

The final of Basicity will be;

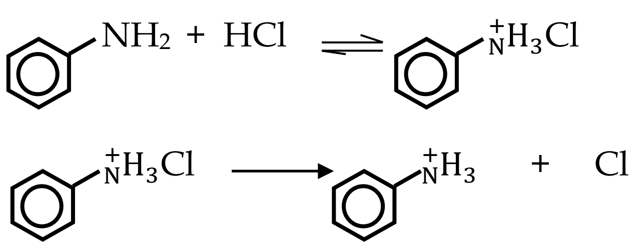
Secondary > Primary > Tertiary > Ammonia > Aromatic

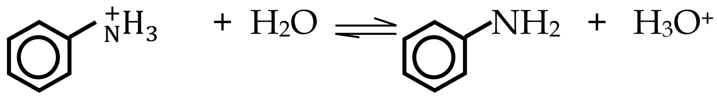
Being basic amines, they react with mineral acids to produce salts. These salts are strong electrolytes because they fully get ionized and their pH is slightly less than 7.

1. $CH_3CH_2NH_2 + HCl \rightleftharpoons CH_3\,CH_2\,\overset{+}{N}H_3 + Cl$

   $CH_3\,CH_2\overset{+}{N}H_3Cl \longrightarrow CH_3CH_2\overset{+}{N}H_3 + Cl^-$

   $CH_3\,CH_2\overset{+}{N}H_3 + H_2O \rightleftharpoons \underbrace{CH_3\,CH_2\,NH_2 + H_3O^+}_{\text{Acidic}}$

2. 



REACTIONS OF AMINES

1. With nitrous acid:

Nitrous acid being liable is generated insitu. Primary amines react with nitrous acid to form a colourless solution of alcohol and a colourless gas of nitrogen.

$$CH_3CH_2NH_2 \xrightarrow{NaNO_2/Conc.HCl} CH_3CH_2OH + N_{2(g)} + H_2O.$$

Secondary amines will produce a yellow oily substances known as nitroso amines.

$$CH_3CH_2NH_2 \xrightarrow{NaNO_2/HCl} CH_3CH_2\text{-}\underset{\displaystyle |\atop CH_3}{N}\text{-}N{=}O$$

Ethyl methyl nitroso amine

$$(CH_3CH_2)_2 \xrightarrow{NH\ \ NaNO_2/HCl} CH_3CH_2\text{-}\underset{\displaystyle |\atop CH_3}{N}\text{-}N{=}O$$

Diethyl nitosoamine.

Tertiary amines when dissolved in HNO acid to form NH_4NO_2 which when warmed forms a nitrosoamine and an alcohol by decomposition.

$$(CH_3)_3N \xrightarrow{NaNO_2/Conc.\ HCl} (CH_3)_3\overset{+}{N}H\ NO_2^-$$

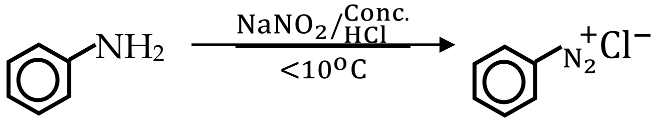
Trimethy ammonium nitrite.

$$(CH_3)_3\overset{+}{N}H\ NO_2^- \xrightarrow{Warm} (CH_3)_2N\text{-}N{=}O + CH_3OH$$

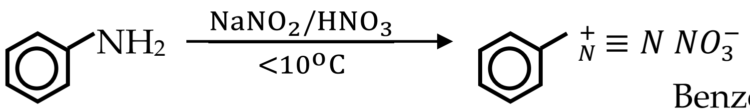
Diethyl nitrosoamine.

Aromatic primary amines react with nitrous acid giving different products depending on the temperatures.

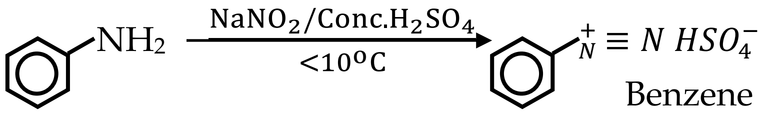
At temperatures below 10°C, aromatic primary amines with nitrous acid to form diazonium salts.



Benzene diazonium chloride.

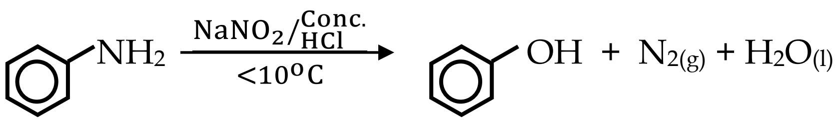


Benzene diazonium nitrate.



Benzene diazonium hydrogen sulphate.

At temperatures above ten (>10°C), the major product formed is a phenol.



The above reaction is of practical importance in distinguishing the classes of amines.

In summary:

i) 1° amines : Yield a colourless solution and effervescence of a colourless gas.

ii) 2° amines : Yield a yellow oily substance which when phenol and conc. H_2SO_4 is added and the mixture made alkaline. This yields an ***intense blue colour***.

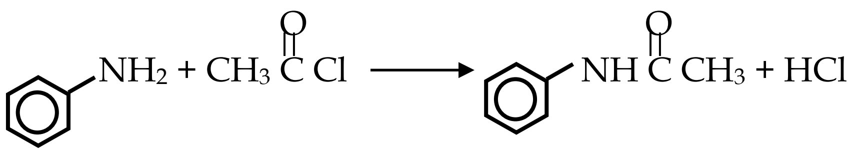
iii) 3° amines : A yellow oily substance persists.

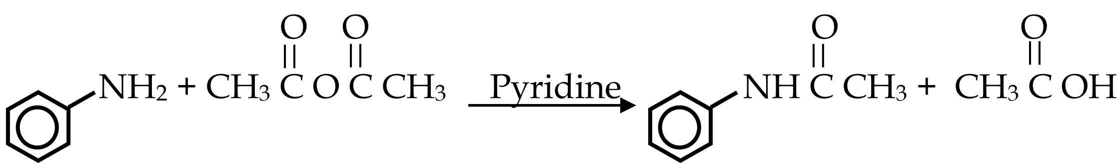
iv) Aromatic amine : A brightly coloured compound known as an azo dye is produced when 2-napthol (OH) is added.

2. **Reactions with acid chlorides and acid anhydrides**.

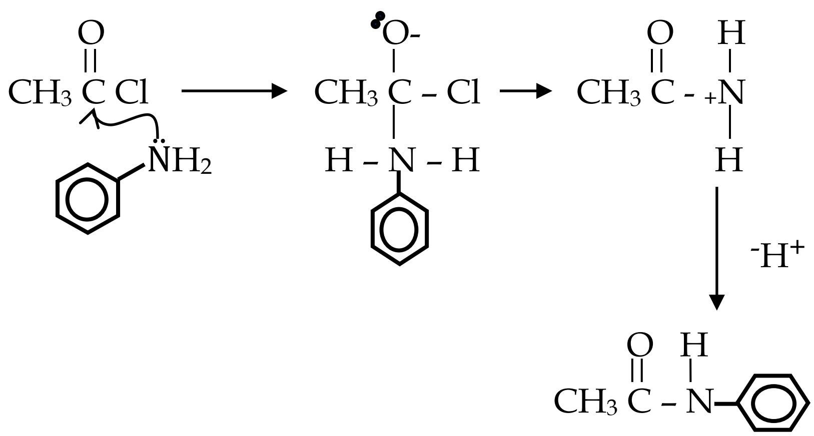
1^o and 2^o amines react with acid chlorides and acid anhydrides to form amides.

$$CH_3CH_2CH_2NH_2 + CH_3\overset{O}{\overset{\parallel}{C}}Cl \longrightarrow CH_3CH_2NH\overset{O}{\overset{\parallel}{C}}CH_3 + HCl$$





Mechanism:



3. **Reactions with sodium metal**

Amines react with Na when heated to produce H_2. This reaction is only possible with 1^o and 2^o amines which do have H_2. The tertiary ones without H_2 do not.

$CH_3\,CH_2\,NH_2 + Na$ heat $CH_3\,CH_2\,NH\,Na + \frac{1}{2}H_2$

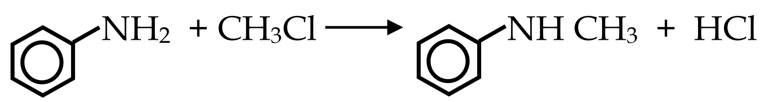
$(CH_3CH_2)_2NH + Na$ heat $CH_3CH_2\,Na + \frac{1}{2}H_2$

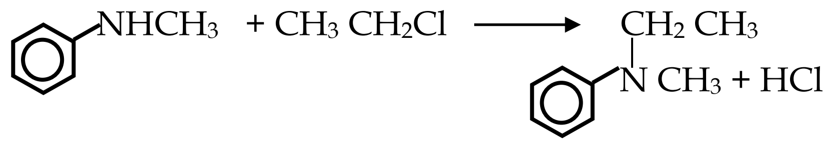
4. **Reactions with alkyl halides**

Aromatic and alkyl amines react with alky halides to form higher amines.

$$CH_3NH_2 + CHCl \longrightarrow NH_3NHCH_3 + HCl$$

$$CH_3NHCH_3 + CH_3CH_2Cl \longrightarrow (CH_3)_2NCH_2CH_3 + HCl$$

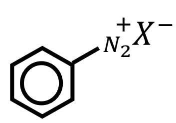




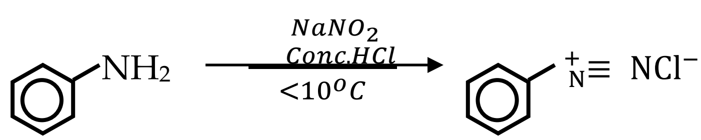
DIAZONIUM SALTS

These are salts formed from primary aromatic amine when reacted with an inorganic mineral acid. The process of forming these salts is diazotization.

Temperature is critical in the formation of a diazonium salt and the temperature always has to be <10°C. Where X is the halogen or NO_3^-, HSO_4^-.



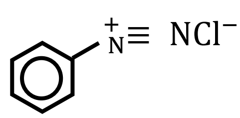
Benzene diazonium chloride.



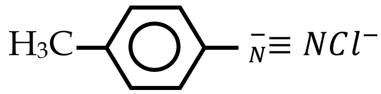
What determines the anion is the acid used.

Nomenclature

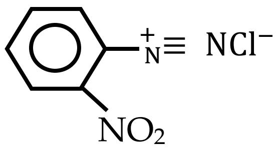
Diazonium salts are named as benzene diazonium.



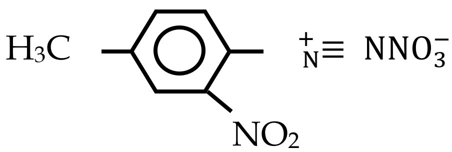
Benzene diazonium chloride.



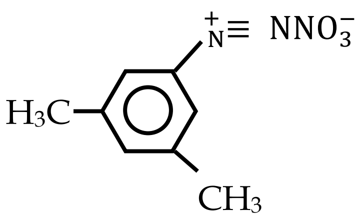
4-methyl benzene diazonium chloride.



2-nitro benzene diazonium chloride.



- 4-methyl-2-nitro-benzene
Diazonium nitrate.



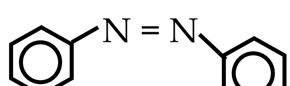
3, 5-dimethyl benzene diazonium
Hydrogen sulphate.

Physical properties of diazonium salts
Are a colourless crystalline solids which turn brown on exposure to air.

Their solutions are neutral to litmus but very soluble in H_2O to give an ionic solution that has got good electrolytic conductivity.

Chemical reactions
Diazonium salts are very useful in organic synthesis reacting with different substances to form different products.

Coupling reaction
Benzene diazonium salts react with phenols to form brightly coloured compounds known as azo compounds by adding an aromatic ring to the nitronium ion a reaction known as coupling.

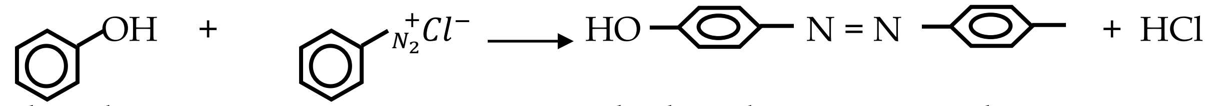
Ar – N = N – Ar or 

Azo compounds.

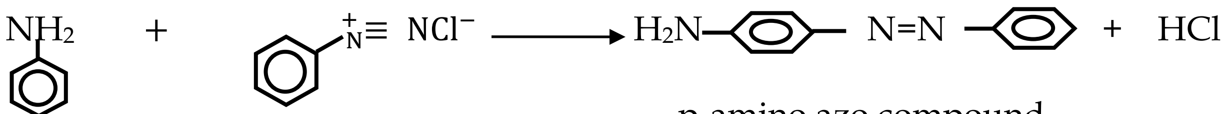
For coupling to occur, the aromatic ring must have a strong electron releasing groups such as hydroxyl, NH_2 – (amino), OR group and NHR group.

These groups will activate the ring making the electrons available at the para position for diazotization.

If the para position is already occupied, then diazoti-phenol.

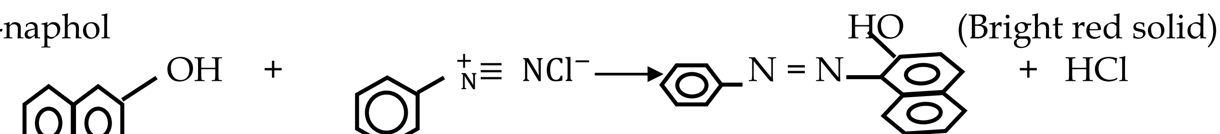


Phenyl amine p-hydroxyl azo compound

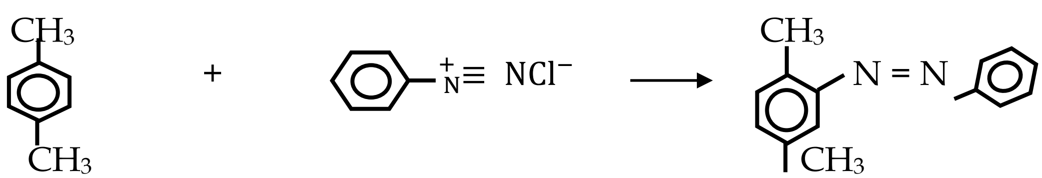


p-amino azo compound.

2-naphol



2-napthol azo compound.

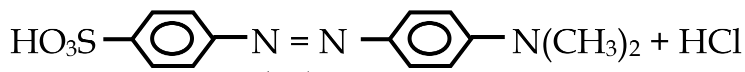


1, 4-dimethyl benzene.

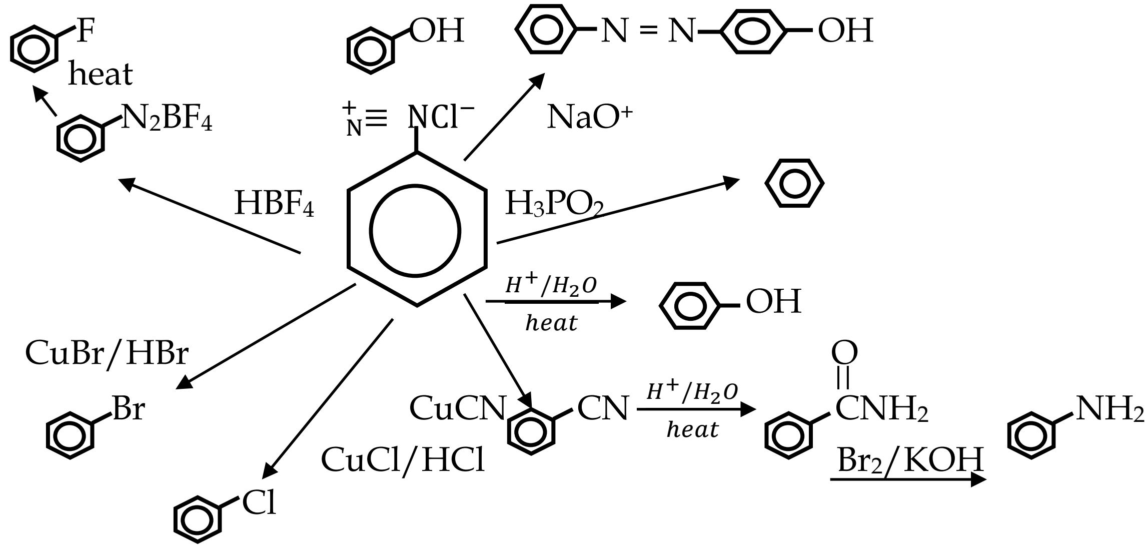
The importance of coupling

i) **Test for primary aromatic amines**:
If a primary aromatic amine is treated with a mixture of $NaNO_2$ and HCl, 2-napthol, a bright red solid is formed due to the reaction of diazonium salt with 2-napthol at a temperature below 10^{o}C.

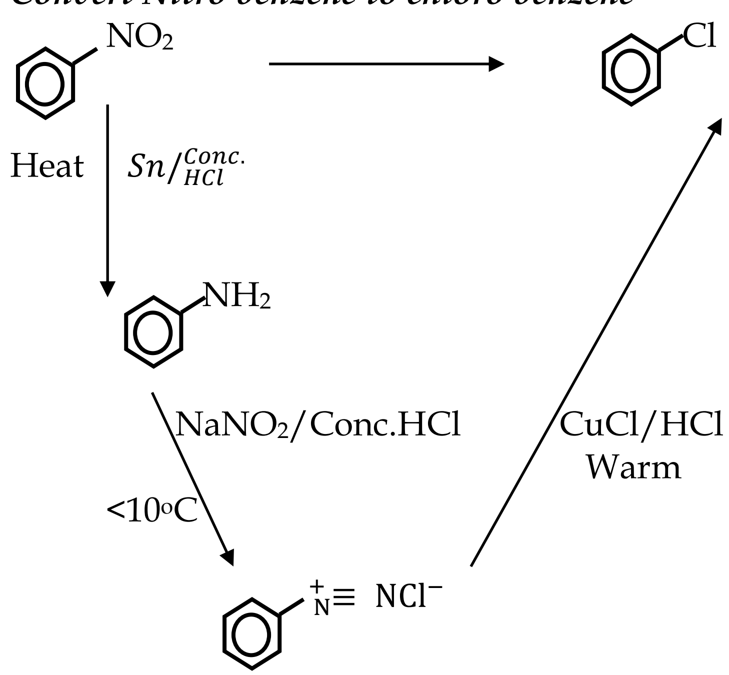
ii) It is used in preparation of dyes (coloured compounds) e.g. methyl orange indicator is prepared by coupling 4-hydrogen sulphite benzene, diazonium chloride and dimethyl phenyl amine.



Methyl orange.



Convert Nitro benzene to chloro benzene



APPLIED ORGANIC CHEMISTRY

1. Polymers (plastic)
2. Lipids – Soap and detergents
3. Hydro carbon – petroleum

POLYMER AND POLYMERISATION

Definition:

A polymer is a compound of high molecular mass made up of small repeated units known as monomers. These molecules are formed by a process known as polymerization.

Polymerization is process of combining low molecular weight molecules repeatedly in some regular manner to forma high molecular mass compound. In polymerization, the low molecular mass molecules are always known as monomers.

These are simple molecules which when combined can form a dimer, trimer or a polymer when many.

POLYMERS:

There are two types of polymers depending on how they are formed.

i) **Natural polymers**

Are naturally occurring polymers not made by man e.g. cotton, wool, protein, rubber, starch e.t.c.

ii) **Artificial polymers (Synthetic)**

These are man-made polymers.

Example: Polythene, Poly vinyl chloride (PVC), Polyester, Terylene, Nylon e.t.c.

Advantages of synthetic polymers over natural

- They can be produced in large quantities within a short period of time.
- Are recyclable
- Have got improved properties e.g. cross linkages for toughness, high density for tensile strain.

Advantages of natural polymers over artificial polymers

- They are biodegradable
- They are cheap since no process involved in producing them.

Properties of polymers

A polymer is judged by some of these properties:

i) **The length of a polymer**

This determines its strength and the melting point. The longer the length, the stronger the polymer would be and a high melting point it will have.

ii) **Cross linkages**

A cross link is a force that joins molecules within a polymer. When a polymer has got several cross linkages, it will have an increased strength.

iii) **Branching**

Increased branches within a polymer decreases its strength and lowers its melting point.

iv) **Intermolecular forces**

If a polymer has got several intermolecular forces within itself, then it will have increased strength than when there are few intermolecular forces.

CLASSIFICATION OF POLYMER

There are several ways of classifying polymers:

i) **Addition polymers**

These are polymers made by directly adding monomers without loss of any simple molecule.

Example:

$$\underset{\text{(ethene)}}{n\,CH_2 = CH_2 + CH_2 = CH_2} \longrightarrow \underset{\text{Polymer (Polythene)}}{\left\{CH_2 - CH_2\right\}_n}$$

ii) Condensation polymers

These are polymers made by combining monomer units but splitting out a small molecule which is usually H_2O. E.g. Terylene

PET (Polythene terathalein)

iii) **Thermoplastic polymers**

These are polymers that can soften and flow when heated and harden when they cool. In other words, they can be remolded into any shape by heat. E.g. polythene.

iv) **Thermosetting polymers**

these are polymers which when heated cannot melt but instead burn away. Such polymers cannot be remolded since they are initially set to a solid. E.g. Formica.

Other terminologies include:

i) **Copolymer**

A copolymer is a type of polymer made by having one or more different monomers. E.g. SBR (Styrene Butadiene Rubber). This is made from styrene and buta-1, 3-diene.

ii) **A fibre**

Is a form of polymer consisting of strings or bundles of strings that settle up during its formation.

iii) **Elastomers**

Is a type of polymer which when stress is applied, and released, it springs back to its original position e.g. rubber.

ADDITION POLYMERIZATION

Addition polymers

Definition: Addition polymerization

Examples:

Monomers	Formula	Polymer and trade name	Uses
Ethene (ethylene)	$CH_2 = CH_2$	Polythene (Polyethylene)	Making bags, squeeze bottles, films, toys, moulded objects, shoes, electrical insulators e.t.c.
Propene (propylene)	$CH_3CH = CH_2$	Poly propene (polypropylene) (Vectra)	Making bottles, films, indoor and outdoor carpets.

Polypropene is formed when propene is heated at various pressures and catalytic temperatures.

$$CH_3CH = CH_2 + CH_3CH = CH_2 \xrightarrow[\text{catalyst, high pressure}]{\text{high temperatures}} \left[\begin{array}{c} CH_3 \\ | \\ CH - CH_2 \end{array} \right]_n$$

(Polypropene)

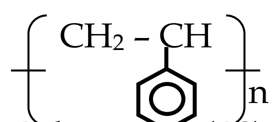
Vinyl chloride (Chloroethene)	$CH_2 = CHCl$	Poly vinyl chloride (PVC)	- Making of floor tiles. - Making pipes, raincoats, insulator tapes.

By modifying ethene, several polymers with better properties can be formed by adding groups of atoms with either –OH group (polar) or  (non polar, giving polymers such as poly viny alcohol and polystyrene respectively. i.e.

$$n\,CH_2 = \underset{}{\overset{\displaystyle OH \atop |}{CH}} \xrightarrow[\text{catalyst}]{\text{high temperature/high pressure}} \left[CH_2 - \overset{\displaystyle OH \atop |}{CH} \right]_n$$

(Poly viny alcohol)[PVA]

$$nCH_2 = CH_2 \; \frac{\text{high temperature/high pressure}}{\text{catalyst}}$$



Polystyrene (PS)

Styrene	$CH_2 = CH$ 	Polystyrene (Styre form) or styrone	Making food and drink containers, coolers, construction materials, mattresses e.t.c.
Acryonitrile	$CH_2 = CHCN$	Polyacrylonitrile (Acrilan)	Fabrics, rugs e.t.c.
Vinyl acetate	$CH_2 = CHOCOCH_3$	Poly vinyl acetate (PVA)	Latex paint, coatings, textiles, adhesives.

Emphasis: Structure of the polymer and its monomer.

1.

$$\left[\begin{array}{cccc} & H & Cl & OCOCH_3 \\ & | & | & | \\ CH - & C - & CH - & C \\ | & | & & | \\ Cl & OCOCH_3 & & H \end{array}\right]_n$$

Polymer

Rules of writing monomers from polymers

Examine whether you are going to see the repeating units.

$\downarrow$

$CH = CHOCOCH_3$ (Monomer)

2.

$$\left[\begin{array}{c} CH_2 - CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_2 \end{array}\right]_n$$

Polymer

$\downarrow$

Monomer

$$CH_2 = CH\ \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$$ (2-methyl buta-1, 3-diene)

HIGH DENSITY POLYTHENE AND LOW DENSITY POLYTHENE (HDPE & LDPE)

On the other hand, if ethene is polymerized giving branches, it will end up producing a low density polymer of 0.92g/mc and this polymer will be known as LDPE which is soft and flexible.

CONDENSATION POLYMERS

These are formed by splitting monomers to eliminate a small molecule which is usually H_2O. This reaction is known as condensation reaction.

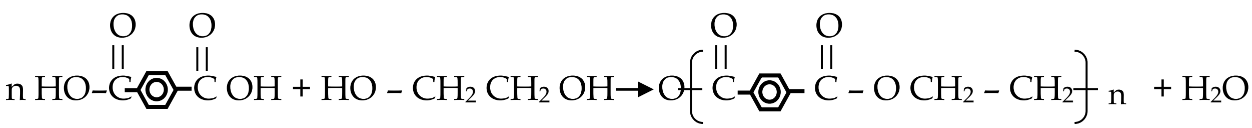
The empirical formula of the polymer in condensation polymerization is not the same as that of a monomer.

Example:

i) **Polyester (Dacron)**

Are formed by reacting a carboxylic acid and an alcohol monomers to form a polyester and H_2O molecule. E.g.

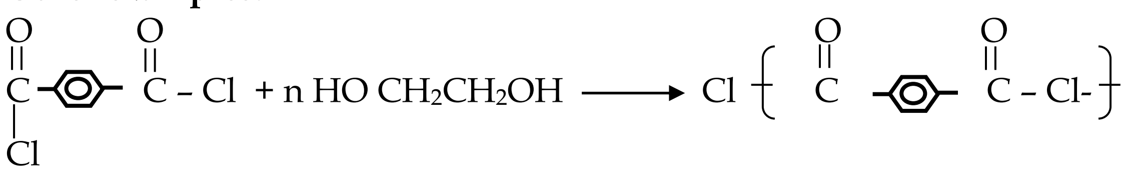
Benzene-1, 4-dioic (Terathepthalic acid) and Ethane-1, 2-diol.

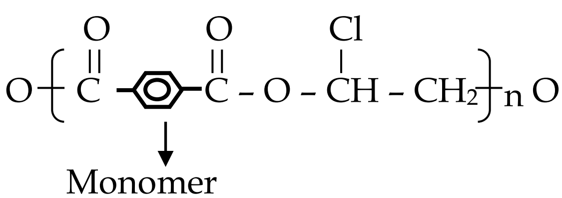


Uses of polyesters

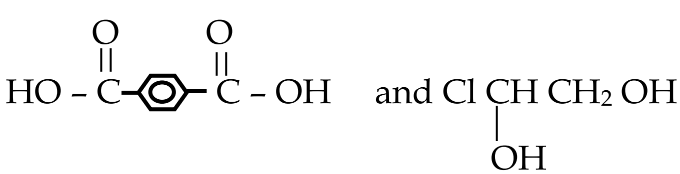
- Used in making of textile fabrics.
- Making films, magnetic coated films using audio and video tapes.
- In heart/cardiac operations to replace some heart blood vessels because it is non toxic, inert and non inflammatory.

Other examples:

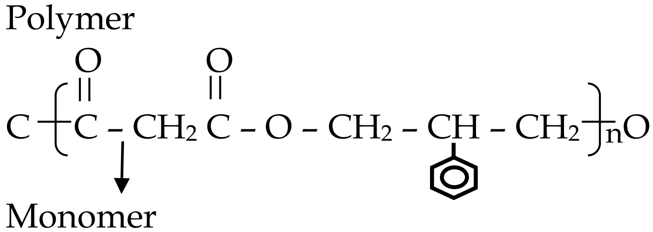




Polymer



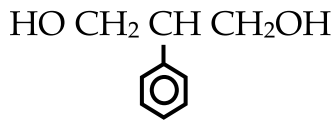
Polymer



$$HO\overset{O}{\overset{||}{C}}CH_2\overset{O}{\overset{||}{C}} - OH$$

Papan-, 3-dioic

and



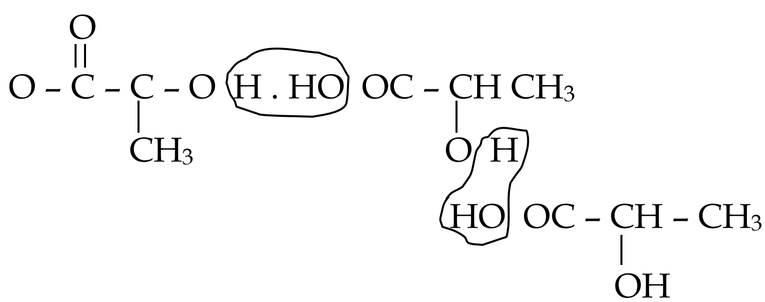
2-phenyl propane -1, 3-diol.

ii) **Lactic acid (2-hydroxy propanoic acid) polymer**

Is a polymer made up of one monomer of 2-dydroxy propanoic acid which undergoes self-condensation. The uses of this polymer are of great importance in surgery and stitching broken deep wounds.

The advantage is that the polymer threads get dissolved in the body.

$$n\,CH_3\overset{O}{\overset{|}{C}}H - COOH \longrightarrow \left[O - \underset{CH_3}{\underset{|}{CH}} - \overset{O}{\overset{||}{C}} \right]_n O + H_2O$$



$$O\left[\overset{O}{\overset{||}{C}} - \underset{CH_3}{\underset{|}{CH}} - O - \overset{O}{\overset{||}{C}} - \underset{CH_3}{\underset{|}{CH}} - O - \overset{O}{\overset{||}{C}} - \underset{CH_3}{\underset{|}{CH}} \right]_n OH$$

iii) **Polyamides**

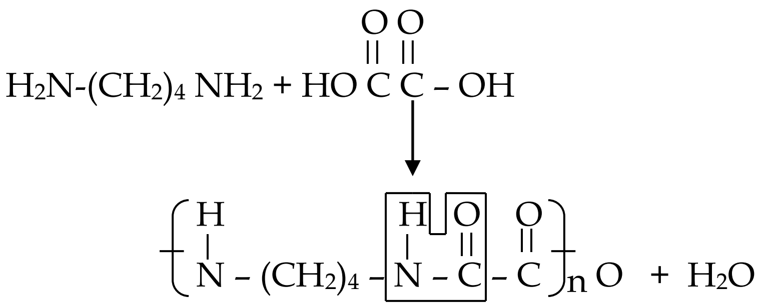
These re polymers formed by condensing a dicarboxylic acid or carboxylic acid chloride with a diamine to form an amide bond or link.

Examples:

Ethane -1, 4-dicarboxylic acid

Hexane -1, 6-diamine

Ethane-1, 2- dioic

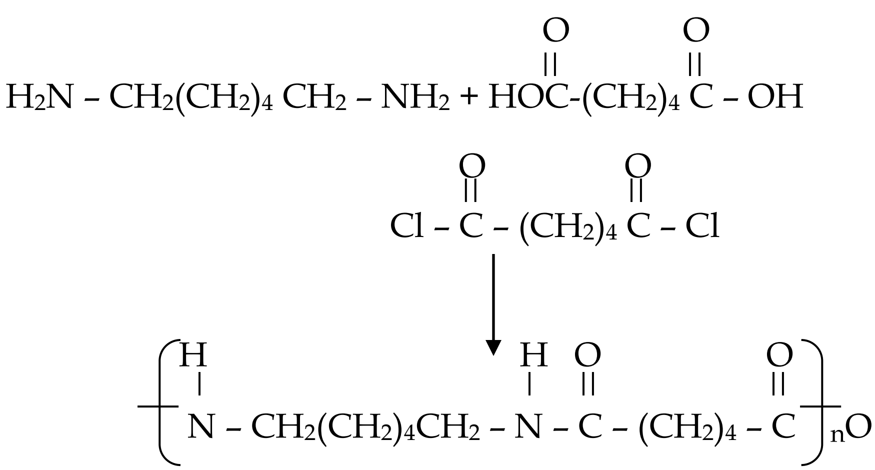


Peptide or amide bond.

Other examples

i) **Nylon-6 6:**

Is a polymer of Hexane-1, 6-dioic or its acid chloride and Hexane-1, 6-diamine. It is called so because its monomers are made up of 6 carbon atoms each.



Uses:

- Made of high quality fabric for the making of clothes.
- Used in parachutes.
- Used in military gear.

The advantage of nylon-6, 6 is that it has got a good tensile strength, H_2O repellant, however, it has got a disadvantage of burning easily when put on fire.

Polymer

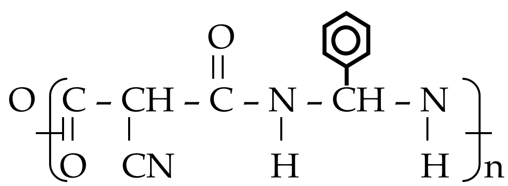
$$\left[O - \overset{O}{\overset{\|}{C}} - CH = CH - \overset{O}{\overset{\|}{C}} - \overset{H}{\overset{|}{N}} - CH\,CH_2 - \overset{H}{\overset{|}{N}} \right]_n$$

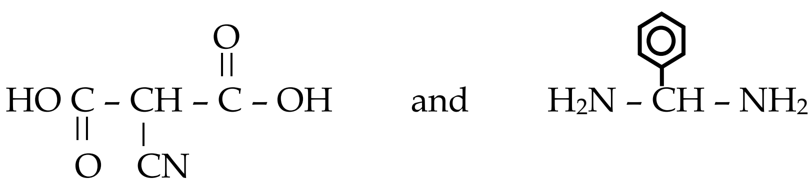
Monomer

$$HO - \overset{O}{\overset{\|}{C}}\,CH = CH\,\overset{O}{\overset{\|}{C}} - OH \quad \text{and} \quad H_2N(CH_2)_2\,NH_2$$

But-2-ene-1, 4-dioic Ethane-1, 2-diamine

Polymer





2-cyanopropane-1, 3-dioic 2-pl

NATURAL POLYMERS

These are polymers not made by man.

Examples:

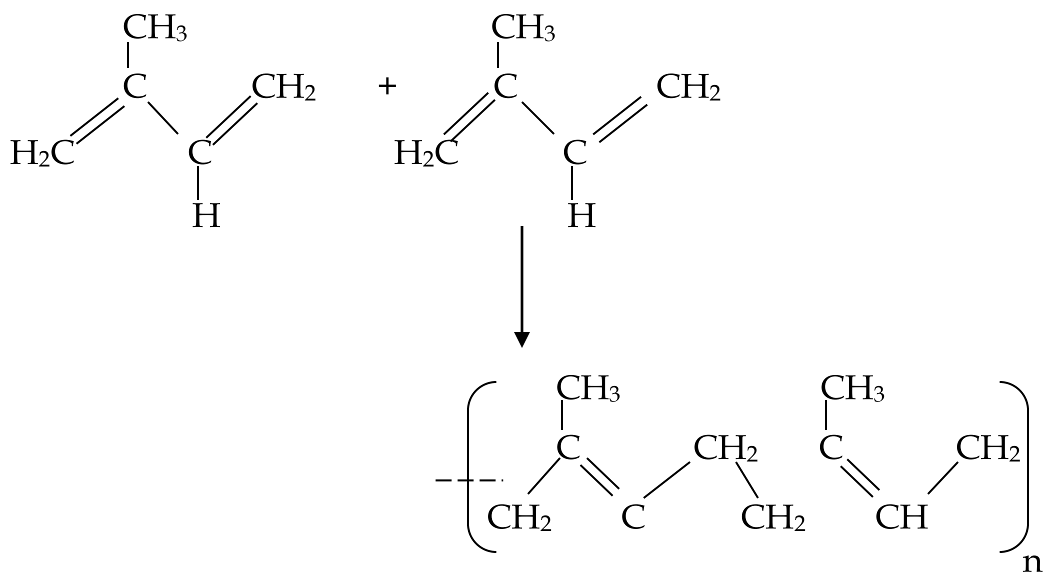
Cotton	
Wool	(Polyamides)
Proteins	
Carbohydrates	(Polysaccharide)
Lipids	(Polyesters)
Rubber	

RUBBER

NATURAL RUBBER

Is a polymer of 2-methyl buta-1, 3-diene which is simply known as isoprene unit.

Natural rubber is obtained from the rubber tree. Naturally, the rubber tree polymerizes the isoprene units by linking carbon 1 and carbon 4 and this leaves a double bond between carbon 2 and carbon 3 which double bond is in a cis – configuration.



Rubber

OR:

$$\left[H_2C - \overset{CH_3}{\overset{|}{C}} = \underset{\overset{|}{H}}{C} - CH_2 \right]_n$$

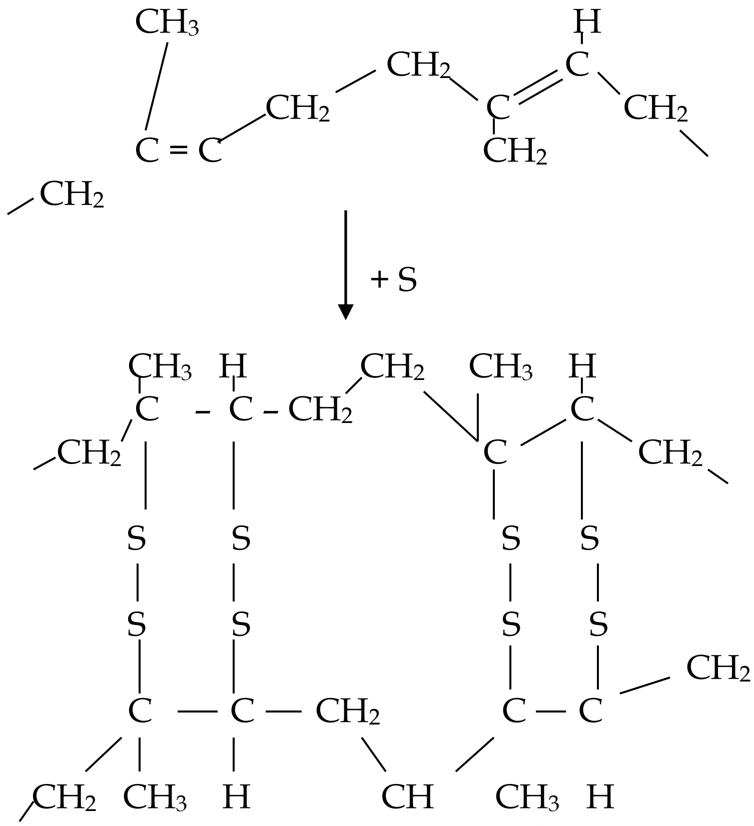
Natural rubber is weak due to a few cross linkages and therefore it is less elastic but it can be improved by the process called Vulcanization.

Definition:

Vulcanization is a process of making rubber, hard, tough and resistant to wearing so that it is made useful. This is done by cross linking monomers using disulphide bonds, S-S-bridge linkage.

When rubber is heated with sulphur, it forms S-S linkages which make it tough.

Natural rubber



Vulcanized rubber

Vulcanized rubber is useful in the following ways:

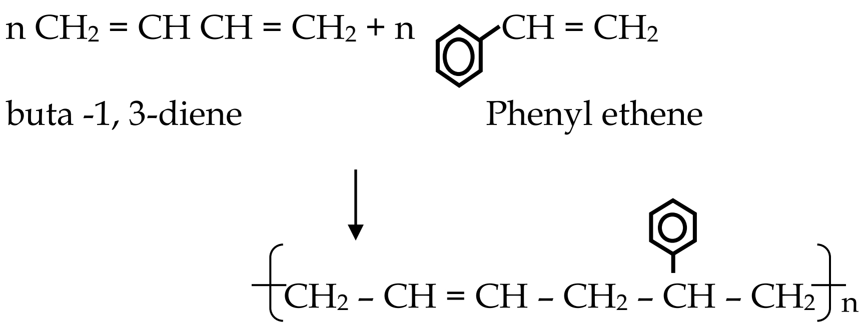
- Manufacturing of carlyres
- Manufacture of balls, bags, shoe soles e.t.c.
- Used ion insulation e.t.c.

Synthetic rubber

The knowledge of composition and structure of rubber has given rise to synthetic rubber. This has made polymer by polymerizing elastomers to give rise to a copolymer which has got some properties of natural rubber.

One of the examples is:

Stfren buta-diene rubber (SBR) which is made by polymerizing buta-1, 3-diene and styrene.



FATS AND OILS

- Triglycerides / trimesters
- Differences between the oils and fats
- Components of a triglyceride (glycerol and fatty acid)
- Saponification
- Additives of soap
- Properties of soap.

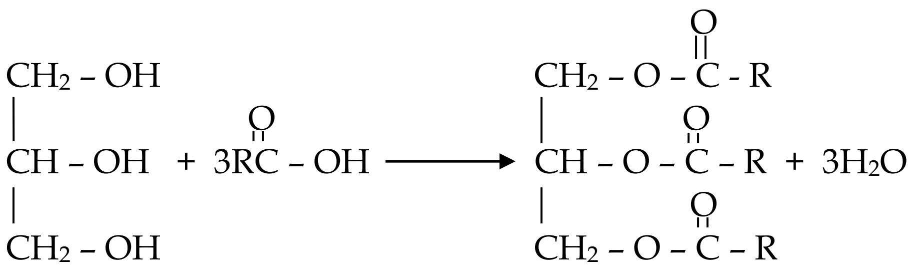
FATS AND OILS

Fats and oil are trimesters made from glycerol (propane-1, 2, 3-triol) and long chain carboxylic acids called fatty acids. The R – groups of the acids, which can be the same or different within the same molecule, can be saturated or unsaturated, i.e. they may contain one or more carbon-carbon double bonds.

COMMON FATTY ACIDS

Name	**Number of carbon atoms**	**Formula**
Saturated acids		
Butanoic	C_4	$CH_3CH_2CH_2CO_2H$
Lauric	C_{12}	$CH_3(CH_2)_{10}CO_2H$
Myristic	C_{14}	$CH_3(CH_2)_{12}CO_2H$
Palmitic	C_{16}	$CH_3(CH_2)_{1}4CO_2H$
Stearic	C_{18}	$CH_3(CH_2)_{16}CO_2H$
Unsaturated acids		
Oleic	C_{18}	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$
Linolenic	C_{18}	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$

A fatty acid – R group may be unsaturated, monounsaturated or polyunsaturated, depending on whether one or more double bonds is present.

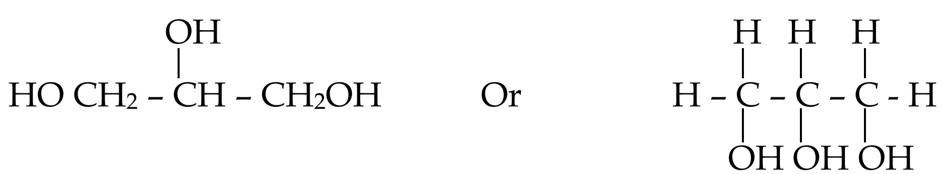


Glycerol ***Fatty acid*** ***Fat or oil***

TRIGLYCERIDES (Triesters)
Common fats and oils made of a glycerol and fatty acids (act as components). Triglycerides consist of three fatty acids and one glycerol.

FATTY ACIDS AND GLYCEROL
(Components of a triglyceride)

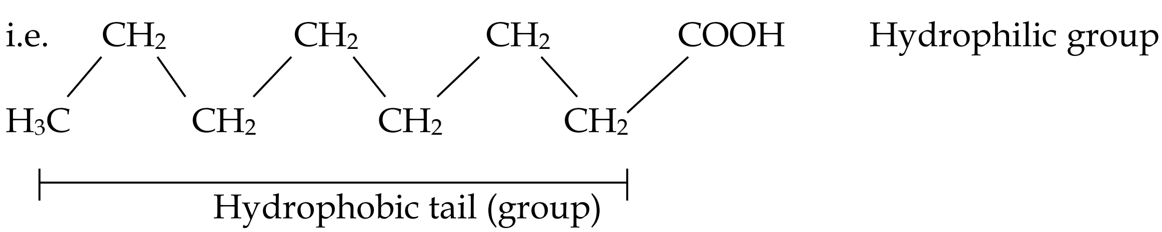
GLYCEROL
Is a polyhydric alcohol made up of three carbon atoms and 3 hydroxyl groups. It is therefore a small molecule.



Glycerol

FATTY ACIDS
A fatty acid is a long carbon chain molecule consisting of a carboxylic acid group at one end. The long carbon chain makes it to be hydrophobic and the carboxylic acid group makes it to be hydrophilic.

i.e.



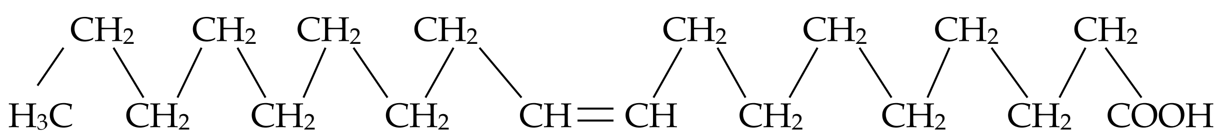
If there are no double bond in the hydrocarbon chain, then the fatty acid is said to be ***saturated fatty acid***.

Example: Stearic acid (Octadecanoic acid)
$CH_3(CH_2)_{16}COOH$

Started fatty acids from straight chains and their physical state is largely solid at room temperature because of their high melting points.

On the other hand, fatty acids that have got one or more double bonds within the hydrocarbon chain are said to be ***unsaturated fatty acids.***

Example:
Oleic acid (Octadec-cis-a-enoic acid)
C_{18} – $[CH_3(CH_2)_7CH = CH(CH_2)_7CO_2H]$



The presence of a double bond in the hydrocarbon chain results into the formation of a bend, which prevents the molecules from close packing resulting into the fatty acids having low melting points.

Those with trans double bond will tend to have fairly straight or linear carbon chain and the molecules will closely pack easily with high melting points making them solids at room temperature.

Fatty acids with more than one double bond are called **polyunsaturated fatty acids (PUFAS).**

Example: Linolenic acid – C_{18}.

$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH\ (CH_2)_7CO_2H$

SPONIFICATION

Saponification is the process of making soap.

SOAPS AND DETERGENTS
SOAP
Soap is sodium or potassium salt of long chain carboxylic acids obtained by boiling fat or oil with NaOH or KOH solution.

MANUFACTURE OF SOAP
Oil or fat is put on a pan, sodium hydroxide solution is added and the mixture boiled.

Sodium chloride (Common salt) is added to precipitate out the soap a process known as salting out. Soap precipitates out as a hard cake.

It is then removed and processed into various shapes. Perfumes and dyes are also added to add value to the soap.

$$
\begin{array}{lccll}
CH_2-O-\overset{\overset{O}{||}}{C}-R & & & CH_2-O-H & \\
| & & & | & \\
CH-O-\overset{\overset{O}{||}}{C}-R & +\ 3NaOH & \longrightarrow & CH-O-H & +\ 3R\overset{\overset{O}{||}}{C}-\bar{O}Na^{+} \\
| & & & | & \\
CH_2-O-\overset{\overset{O}{||}}{C}-R & & & CH_2-O-H & \text{Sodium stearate} \\
\text{Glycerol/stearate} & & & \text{Glycrol} & \text{(Soap)} \\
\text{(a fat)} & & & &
\end{array}
$$

$R = (CH_2)_{16}CH_3$

SOURCES OF OILS

i) **Vegetable oils:**

These can be obtained from cotton seeds, sunflower, simsim, castor, groundnuts e.t.c.

In extraction of vegetable oil after removing the husks, the seeds are then crushed in power form and then boiled with H_2O for some time. The oil floats on top of the H_2O.

ii) **Animal oil:**
These are esters obtained from animals e.g. from whale, fish (sardines) and lard oil.

SOURCES OF FATS:

i) **Vegetable fats:**
Are obtained from plants like coconut or palm trees.

ii) **Animal fats:**
Are obtained from animals e.g. butter from milk and lard.

Uses of fats and oils

- Are used for food.
- In the manufacture of soap, candles and hair oils.
- In the manufacture of paints and vanishes.
- Ground nut oil is used to make vegetable ghee.

DISADVANTAGES OF USING ORDINARY SOAP

Soap forms scum with hard H_2O. Hard H_2O contains dissolved Ca^{2+} or Mg^{2+} which reacts with soap forming insoluble Ca^{2+} salt called scum.

$$2\,R\overset{\overset{O}{||}}{C}ONa_{(aq)} + Ca^{2+} \longrightarrow (RCO\bar{O})_2Ca^{2+}{}_{(s)} + 2Na^{+}{}_{(aq)}$$

$$2\,C_{17}H_{35}\overset{\overset{O}{||}}{C}ONa_{(aq)} + Ca^{2+}{}_{(aq)} \longrightarrow (C_{17}H_{35}COO)_2Ca^{2+}{}_{(s)} + 2Na^{+}{}_{(aq)}$$

Formation of scum is expensive in that much soap has to be used to produce enough later for washing.

It also stains clothes.

THE CLEANING ACTION OF SOAP

A molecule of soap contains a water loving part which is polar $CO\bar{O}$ called hydrophilic part and the non polar ware insoluble (dirt soluble) part $R - CH_2$ called the hydrophocic part.

During washing, these molecules are dispersed and they form a spherical cluster around grease or dirt called micelle with the polar end attracted by H_2O. The dirt combines with the hydrophobic part while H_2O dissolves in the hydrophilic part.

As H_2O molecules attract the polar end, the surface tension of H_2O is lowered. Repulsion between the polar end of soap and rinsing help remove the dirt.

DETERGENTS

Synthetic detergents solve the problem of scum formation.

Synthetic detergents are surface active agents and are called "**soapless soaps**."

Like soap, detergents contain both hydrophilic (H_2O soluble) and hydrophobic (oil solution) parts.

An example of a detergent is alkyl benzene sulphonates i.e.

$CH_3 - (CH_2)_n - CH_2$  $SO_3^- Na^+$

However, the major disadvantage of alky benzene sulphonate detergents it that, they contain so many branches which are non-biodegrable and this can be dangerous if re-supplied into drinking H_2O.

This can be solved by making detergents with no branching (i.e. linear alkyl group).

TYPES OF DETERGENTS

i) **CATIONIC DETERGENTS**

These carry positive heads e.g. hexadecyl trimethyl ammonium bromide. They are made by reacting amines with alkyl halides.

They are used in making air conditioners.

Example:

$C_{15}H_{31}CH_2NH_2 - Br + 3CH_3Br \longrightarrow C_{15}H_{31}CH_2^+N\ (CH_3)\ Br^- + 2HBr$

In H_2O it behaves as;

$C_{15}H_{31}CH_2^+N\ (CH_3)\ Br^- \longrightarrow C_{15}H_{31}CH_2^+N(CH_3)_3 + Br^-$

ii) **ANIONIC DETERGENTS**

These carry negative heads. They are made from benzene by alkylation, sulphonation and neutralization reaction e.g. sodium-4-dodecyl benzene sulphonate.

These are used in the manufacture of both pastes and shampoos.

Anionic detergents can also be made from straight chain alcohol (C_{10} – C_{14})

iii) **NON-IONIC DETERGENTS**

These are neutral in H_2O i.e. the head carries no charge i.e. they are not dissociated e.g. $CH_3(CH_2)_{10}CH_2 - (OCH_2CH_2)_8\ ^{-}OH$, ethoxylate made from long chain alcohols with ethoxides.

Example:

$$CH_3(CH_2)_{10}CH_2\text{-}OH + 8\underset{\diagdown\ O\ \diagup}{CH_2CH_2} \longrightarrow CH_3(CH_2)_{10}(OCH_2CH_3)_8\ –OH$$

They are used as liquid detergents.

The action of detergents can be improved by addition of the following which constitute the bulk of the detergents.

a) **Inorganic phosphates:** Are added to soaps to remove any soluble Ca^{2+} or Mg^{2+} in H_2O as Ca^{2+} or $Mg^{2+}PO_4^{3-}$.

b) **Sodium peroxoborate:** This is added to act as a bleaching agent. They make clothes appear bright. They release H_2O_2 in H_2O which bleaches.

c) Sodium sulphate: This is added mainly to increase the bulk of the powder.

Note:

i) The major disadvantage of detergents containing phosphates is that they cause pollution in rivers, dams, and lakes. (Phosphates are used as food by algae so their presence promote the growth of algae causing foaming of H_2O thus polluting it.

ii) Detergents are better than soaps because the can be used in any type of H_2O i.e. there is no formation of scum.

END