ORGANIC CHEMISTRY

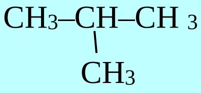
Is about structural formulae, naming [nomenclature], preparation [synthesis], and properties of Compounds formed by carbon excluding carbon monoxide [CO], carbon dioxide [CO_2], metal carbonates, carbon disulphide [CS_2] and hydrogen carbonates which are classified as inorganic compounds.

UNIQUE NATURE OF CARBON

The Carbon atom possesses the unique ability to form multiple bonds between itself and other Carbon atoms i.e. $H_2C = CH_2$ and $HC \equiv CH$ and also with the atoms of certain other elements such as Oxygen $H_2C = O$, $H_2C = S$, and Nitrogen $HC \equiv N$.

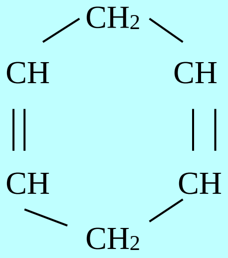
It also has the ability to form chains of identical atoms (CATENATION) which is an essential feature of its chemistry. These chains may exist as short or long open systems, where several modes of branching are possible or as closed ring systems

e.g. $CH_3CH_2CH_2CH_3$,



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

or



etc

NB: To catenate, an element must have a valency of at least two and be able to form fairly strong covalent bonds with itself. Carbon has a valency of four, permitting the existence of multiple bonds in chains of carbon atoms in certain compounds.

It should also show a valiancy of +4 in all stable compounds it forms.

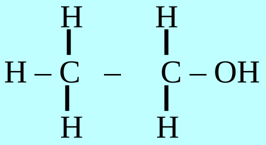
CHARACTERISTICS/ PROPERTIES OF ORGANIC COMPOUNDS

Organic compounds are generally gases, volatile liquids or low melting point solids, they tend to be insoluble in water unless they contain polar groups such as -OH, -COOH, $-SO_3H$ etc, but are usually soluble in organic, non-polar solvents such as tetra chloromethane/carbon tetrachloride, ethoxyethane/ diethyl ether, benzene etc.

On burning in excess oxygen, they yield carbon dioxide and water (except when the compound contains no hydrogen, which is comparatively rare). Organic reactions are generally slow in and often require energy. Some has the ability of possessing the same molecular formula to exist in different forms on account of their having different structural arrangements of atoms.

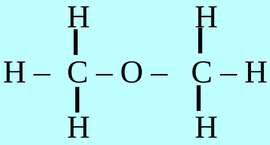
Example;

C_2H_6O applies to two entirely different compounds that is ethanol and methoxymethane which posses distinctly different properties



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$

Ethanol



$H-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-H$

methoxymethane/dimethylether

In organic chemistry we can concentrate on a relatively small group of commonly encountered elements i.e. carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus and the halogens.

NAMING ORGANIC COMPOUNDS

The most universal and systematic method of naming these compounds is that devised by a commission appointed by the International Union of Pure and Applied Chemistry (IUPAC). It provides a convenient and relatively straightforward method for naming even the most complicated molecules and the advantage is that the same basic principles are employed for each series of compounds i.e. it defines the structures more clearly

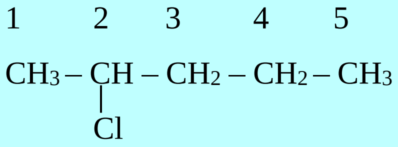
The following provides an outline of the systematic principles adopted.

i) The largest continuous chain of carbon atoms containing the functional group is selected and named according to the parent alkane.

NB. All organic compounds are considered as derivatives of alkanes.

ii) The carbon atoms of the chain are numbered in order to indicate the positions of any substituents in the chain. The end of the chain from which the numbering starts is chosen so as to use the lowest values

Example



$$\overset{1}{CH_3}-\underset{\underset{Cl}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

2-chloropentane

iii) The names of the substituents prefix, the name of the parent alkane alphabetically and the positions of substituent precede the whole.

iv) The numbers assigned to the functional groups are chosen so as to be as small as possible. These are usually placed between the stem and the ending of the name. The functional group numbers are given precedence over those assigned to other substituents.

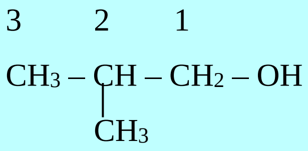
Example:

Simple alcohols are named by dropping the “e” from the end of the name of the parent alkane and adding the suffix “ol”

CH_3CH_2– OH

Ethanol

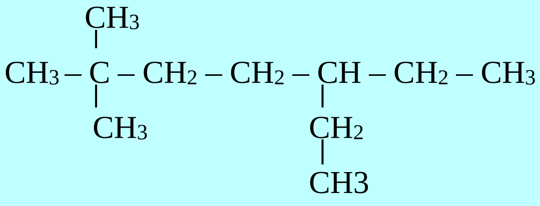
(Parent alkane; ethane)



$$\overset{3}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{2}{CH}}-\overset{1}{CH_2}-OH$$

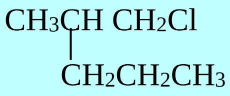
2 methyl propane – 1 – 01

(Parent alkane; propane)



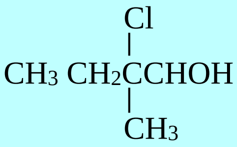
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-\underset{\underset{\underset{\underset{\mathrm{CH3}}{|}}{CH_2}}{|}}{CH}-CH_2-CH_3$$

4 – ethyl – 2, 2 – dimethyl heptane



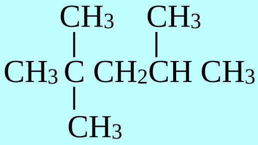
$$CH_3\underset{\underset{CH_2CH_2CH_3}{|}}{CH}\ CH_2Cl$$

1 – chloro – 2 - methyl pentane



$CH_3\ CH_2\overset{Cl}{\underset{CH_3}{C}}CHOH$

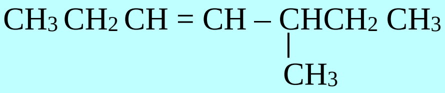
2 – chloro – 2 - methyl butan – 1 – ol



$CH_3\ \overset{CH_3}{\underset{CH_3}{C}}\ CH_2\overset{CH_3}{CH}\ CH_3$

2, 2, 4 – trimethyl pentane

In alkenes the suffix “ene” replaces “ane” of the corresponding alkane, then;

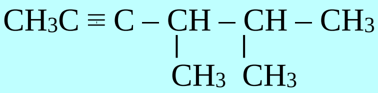


$CH_3\,CH_2\,CH = CH - \underset{CH_3}{CH}CH_2\,CH_3$

5 – methyl – 3- heptene or

5 – methyl hept – 3- ene

And

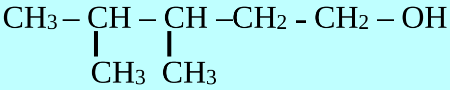


$CH_3C \equiv C - \underset{CH_3}{CH} - \underset{CH_3}{CH} - CH_3$

4, 5 – dimethyl –2- hexyne

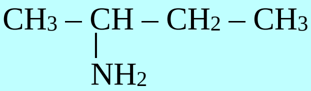
NB: Naming mono functional compound, the longest chain should include the functional group and the carbon are numbered so that the position of the functional group gets the smaller value. The last “e” of the corresponding alkane is then dropped and replaced by the suffix representing the functional group. And the position of the functional group written before the name of the hydrocarbon separated on either side by hyphens.

i.e.



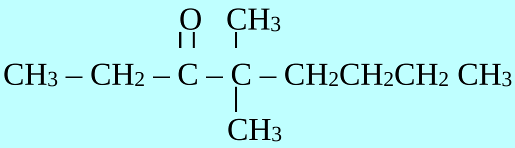
$CH_3 - \underset{CH_3}{CH} - \underset{CH_3}{CH} - CH_2 - CH_2 - OH$

3, 4 dimethyl – 1 – pentanol



$CH_3 - \underset{NH_2}{CH} - CH_2 - CH_3$

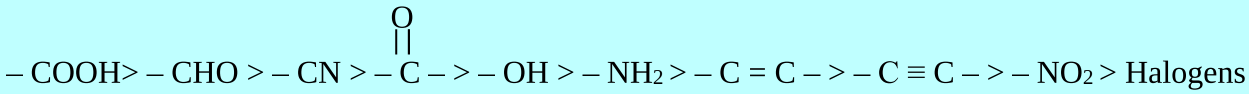
2 – amino butane



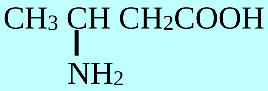
$CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - \overset{CH_3}{\underset{CH_3}{C}} - CH_2CH_2CH_2\,CH_3$

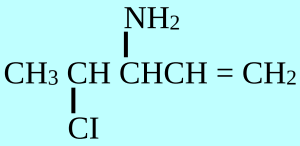
4, 4 dimethyl – 3 – octanone

NB: The order of seniority is

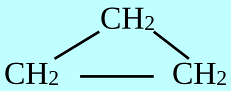

$-COOH > -CHO > -CN > -\overset{O}{\overset{||}{C}}- > -OH > -NH_2 > -C=C- > -C\equiv C- > -NO_2 >$ Halogens

i.e.


$CH_3\underset{NH_2}{\underset{|}{CH}}\,CH_2COOH$ 2 – amino butanoic acid


$CH_3\underset{Cl}{\underset{|}{CH}}\,\overset{NH_2}{\overset{|}{CH}}CH=CH_2$ 4 chloro – 3 – amino – 1 pentene

NB: For cyclic compounds, the prefix cyclo must be put before the name of the parent hydrocarbon i.e.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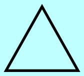
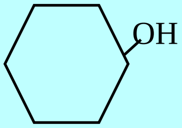
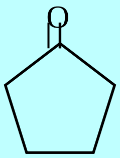

cyclopropane



cyclotamone etc

ISOMERISM

Is the phenomenon whereby certain compounds possessing the same molecular formula exist in different forms because they have different arrangements of atoms. Hence is the existence of compounds with same molecular formula but different structural formulae and the compounds are called **Isomers.**

This concept illustrates the fundamental importance of molecular structure in organic chemistry. There are two main types of isomerism.

- Structural isomerism, in which the atoms are linked together in different ways.
- Stereo Isomerism, in which the atoms have different partial arrangements. Stereo Isomerism will be seen at higher levels.

STRUCTURAL ISOMERISM

Arises from the differences in the arrangement of atoms within the molecule resulting in two or more different structural formulae. Hence structural Isomers have same molecular formula but different structures.

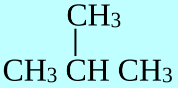
Types of structural Isomerism

1. CHAIN ISOMERISM: Is due to the difference in the structure of carbon chain or the arrangement of carbon atoms in the molecule.

Example:

a) C_4H_{10}

$CH_3\,CH_2CH_2\,CH_3$ Straight chain Isomer

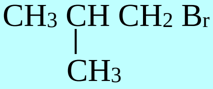


$CH_3\,\overset{CH_3}{\overset{|}{C}H}\,CH_3$

Branched chain Isomer

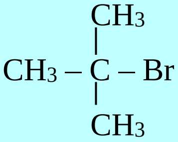
b) C_4H_9Br

$CH_3\,CH_2CH_2CH_2\,B_r$ 1 – bromo - butane



$CH_3\,\underset{CH_3}{\underset{|}{C}H}\,CH_2\,B_r$

1 – bromo – 2 – methyl propane

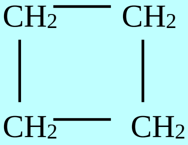


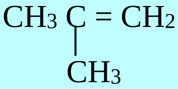
$CH_3 - \overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}} - Br$

2 – bromo – 2 – methyl propane

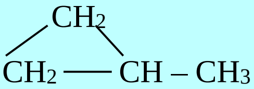
c) C_4H_8

$CH_3\,CH_2\,CH = CH_2$





$CH_3\,\underset{CH_3}{\underset{|}{C}} = CH_2$

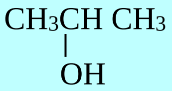


etc

2. **POSITION ISOMERISM:** Is a type of structural isomerism in which the compounds have the same carbon skeleton or chain and the same functional group but the positions on to which the functional groups are attached differ.

e.g.

C_3H_8O

$CH_3CH_2CH_2OH$	propan – 1 – ol
 $CH_3\underset{\overset{\vert}{OH}}{C}H\;CH_3$	propan – 2 – ol

C_5H_{10}

$CH_3CH_2CH_2CH = CH_2$	pent – 1 – ene
$CH_3CH_2CH = CH\;CH_3$	pent – 2 – ene

3. **FUNCTIONAL GROUP ISOMERISM:** Is a type of isomerism in which the compounds have different carbon skeletons and also have different functional groups.

Example:

C_2H_6O

$CH_3\;CH_2\;OH$	Ethanol
CH_3OCH_3	Dimethyl ether / methoxymethane

$C_4H_8O_2$

$CH_3\;CH_2\;COOH$	Butanoic acid
$CH_3COO\;CH_2\;CH_3$	Ethyl ethanoate

STRUCTURE AND PHYSICAL PROPERTIES

Physical properties of a compound depend primarily upon the nature of the bonds holding the atoms in the molecules together and also upon the size and shape of the molecules themselves.

POLARIZATION OF A COVALENT BOND

A covalent bond is formed by the sharing of two electrons, one being contributed by each of the constituent atoms, these electrons are not distributed exactly between the two atoms unless they happen to be identical or possess exactly equal electronegativity values.

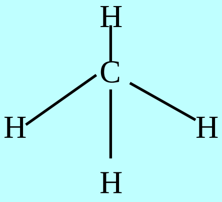
NB: Small atoms attract electrons more readily than do larger ones. And those which have nearly filled shells tend to have higher electronegativity values than those with only partly filled shells. The electrons in a bond joining two atoms A and B are displaced towards the more electronegative atom, which acquires a relatively negative charge (σ-) and the other relatively positive (σ+). Then the bond is said to be POLARIZED

$$A^{\sigma+} \rightarrow B^{\sigma-}$$

A molecule that has an asymmetrical distribution of electrons is said to poses a DIPOLEMOMENT which is the product of the size of the charge and the distance of separation in the molecule.

In methane

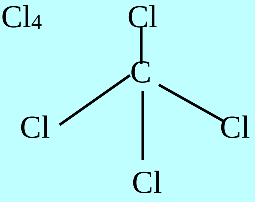
CH_4



Methane

and

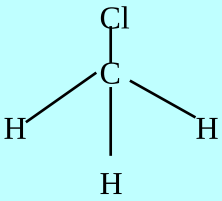
CCl_4



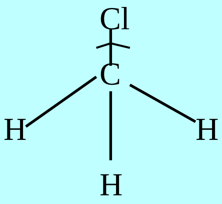
Tetra chloromethane

Dipole moment is zero, because the electron distribution within the molecules is completely symmetrical.

But CH_3Cl



Dipole moment is not zero, because chlorine is more electronegative and the distribution of electrons within the molecule is not symmetrical i.e.



Hence;

The dipole – dipole interaction; Is an attractive force between the relatively positive end of one polar molecule and the relatively negative end of another i.e. $A^{\sigma+} – B^{\sigma-}$ / $B^{\sigma-} – A^{\sigma+}$

MELTING POINT

Organic solids are composed of molecules which are predominantly covalent and are held together by attractive forces between non-bonded atoms (Vanderwaal's forces) which can exist between atoms within a molecule which are not attached to each other or between the atoms of different molecules. These attractions are weak and function only over a short range. So as these non-bonded atoms approach each other more closely the attractive forces vanish and a repulsive force emerges.

And are also held by dipole-dipole interactions which are also weak. Hence these solids have correspondingly lower melting point.

NB: The size and shape of the molecules of a solid are closely related to its melting point, Compounds composed of large molecules tend to have higher melting points than those composed of small ones. And the more symmetrical the molecule the higher the melting point.

Examples:

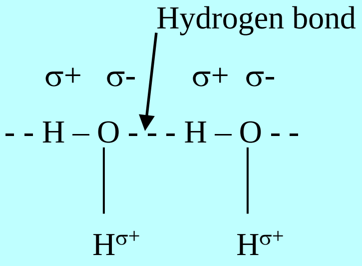
Carboxylic acids with an "even" member of the series has higher melting point than the "odd"

BOILING POINTS

Organic liquids whose molecules contain –OH group tend to have abnormally high boiling points, this is because of hydrogen bonding which limits the formation of a covalent bond with one and holding the other solely by electrostatic forces resulting into a very strong dipole-dipole interaction.

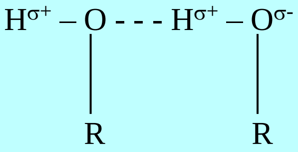
NB: Hydrogen bonding is the bond formed between hydrogen atom and an electronegative atom. Hydrogen bonding has two different forms.

a) **Intermolecular hydrogen bonding** which occurs between separate molecules giving rise to association in the liquid and solid phases. It causes an elevation in the boiling point. Water forms a series of hydrogen bonds which have to be broken down in order to convert the liquid into steam.



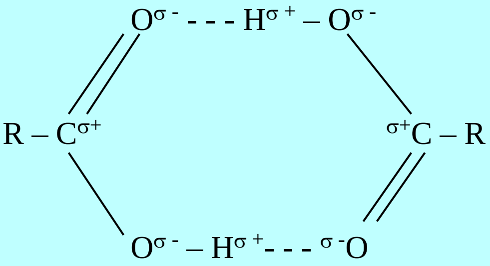
$$- - \overset{\sigma+}{H} - \underset{H^{\sigma+}}{\overset{\sigma-}{O}} - - - \overset{\sigma+}{H} - \underset{H^{\sigma+}}{\overset{\sigma-}{O}} - -$$

Alcohol



$$H^{\sigma+} - \underset{R}{O} - - - H^{\sigma+} - \underset{R}{O^{\sigma-}}$$

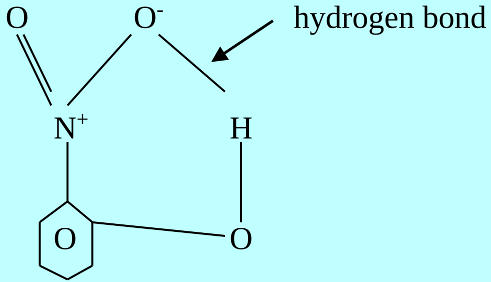
carboxylic acid



The greater polarity of carboxylic acid molecules and the formation of two intermolecular hydrogen bonds give rise to boiling point higher than for the corresponding alcohols.

b) **Intra molecular hydrogen bonding** which occurs between different atoms within the same molecule.

In 2 –nitrophenol, the intramolecular hydrogen bond is formed between one of the oxygen atoms of the nitro group and the hydrogen atom of the hydroxyl group. Hence having a greater volatility than either 3 – nitrophenol or 4 –nitrophenol



2 –nitrophenol

Explain the following

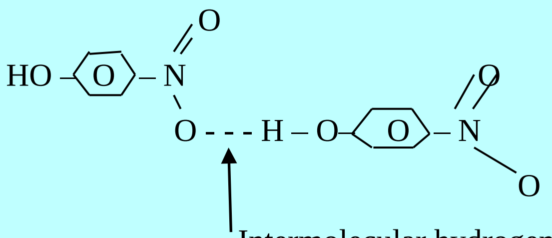
a) Ammonia boils at $-33^{0}C$ whereas Phosphine PH_3 boils at $-88^{0}C$.

Solution: Ammonia has a higher boiling point than Phosphine because the nitrogen atom in ammonia has a high electronegativity power than phosphorus. This allows formation of hydrogen bonding between ammonia molecules and Vanderwaals bonding in phosphine molecules.

However, the hydrogen bonding is stronger and hence need a lot of energy to break compared to one need for weak Vanderwaals.

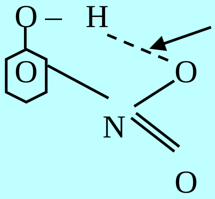
b) The melting point of 4 – nitro phenol is higher than that of 2 – nitrophenol.

Solution: In 4 – nitrophenol molecule, the two functional groups are further apart and thus able to associate via intermolecular hydrogen bonding i.e.



Intermolecular hydrogen bond

Whereas in a 2 – nitro phenol molecule, the functional groups are closer and this causes an intra hydrogen bond to be formed by interaction of the hydrogen on the hydroxyl group with the oxygen atom on the nitro functional group i.e.

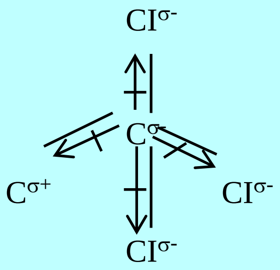


intra hydrogen bond

This leads to the molecules in 2 – nitrophenol to associate with a much weaker vanderwaals forces of attraction which are in fact much easier to break than the intermolecular hydrogen bonds in 4 – nitrophenol. Therefore, the melting point of 4 – nitrophenol is higher than 2 – nitro phenol

c) Carbon tetra chloride molecule is non-polar yet the bonds in carbon tetra chloride are polar.

Solution: Chlorine atom is more electronegative than carbon therefore; it tends to attract the bonding electrons between C – Cl more towards itself so that it acquires partial negative charge while carbon acquires a partial positive change. This un-equal distribution of electrons establishes a dipole moment in the direction of the more electronegative chlorine atom thus making the C – Cl bond in CCl_4 polar. However, the whole molecule of tetra chloromethane is non -polar because the C – Cl bonds are symmetrical and tetrahedrally arranged around the central carbon atom. Therefore, the effect of bond polarity in the opposite directions cancel out with each other so that the net dipole moment in the whole molecule of tetra chloromethane is zero and thus non -polar



Solubility

This depends upon the intermolecular forces between the dissolved substance, irrespective of whether it is a solid or a liquid and the solvent. The solubility of a non-electrolyte in water depends on whether the compound can form hydrogen bonds with water for compounds containing –OH group. The best solvents are those which also contain –OH group

The size of a substance also determines its solubility alkanes are all virtually insoluble in water but the smallest member of the series (methane) is more soluble than any of the larger members.

NB: Any possibility of hydrogen bonding in this instance is deemed unlikely.

Explain the following

1. Phenol (hydroxybenzene) is sparingly soluble in water but very soluble in dilute sodium hydroxide.

Solution: Hydroxybenzene is slightly acidic, therefore it poorly ionizes in water to form a phenoxide ion and a hydrogen ion. i.e.

$$C_6H_5OH_{(aq)} \rightleftharpoons C_6H_5\bar{O}_{(aq)} + H^+_{(aq)}$$

In addition, the phenoxide ion so formed readily combines with sodium ions from sodium hydroxide to form sodium phenoxide (sodium salt of phenol) which is highly soluble. Therefore, phenol is more soluble in dilute sodium hydroxide

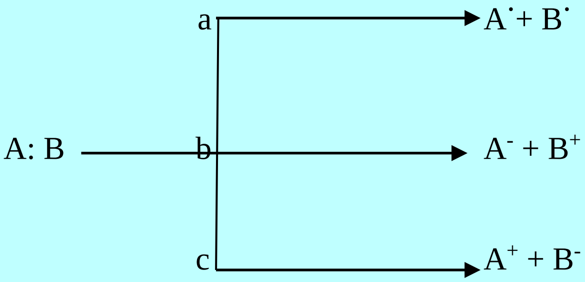
$$C_6H_5O^-_{(aq)} + NaOH_{(aq)} \rightleftharpoons C_6H_5\bar{O}Na^+_{(aq)} + OH^-_{(aq)}$$

REACTANTS AND REACTIONS

In a chemical reaction the reactant molecules undergoing attack is referred to as the SUBSTRATE and the attacking species is the REAGENT these two interact to yield the products of the reaction.

During the process; chemical bonds have to be broken in order that new compounds may be formed. This breaking (fission) of bonds can happen in any of the different ways depending upon the electronegativity values of the two atoms formed by the bond

i.e.



$A^{\cdot} + B^{\cdot}$ A & B hand similar electronegativity values

$A^- + B^+$ A is more electronegative than B

$A^+ + B^-$ B is more electro negative than A

Where the difference in electronegativity between bonded atoms is small, as in a rupturing the bond between them results in the formation of very reactive FREE RADICALS with each atom acquiring one of the bonding electrons. The process is known as HOMOLYTIC FISSION. The movement of a single electron during homolytic fusion is depicted by a half arrow.

E.g. $Cl-Cl \longrightarrow Cl^o + Cl^o$

Where one atom is distinctly more electronegative than the other, there is a tendency for both bonding electrons to remain with the more electronegative atom after rupture of the bond.

The process is HETEROLYTIC FISSION. The more electronegative atom gains a single negative charge owing to the acquisition of an extra electron and the less electronegative atom becomes positively charged.

The shift of a pair of electrons is indicated by a curly arrow

E.g. $C \overset{\curvearrowright}{-} Cl \longrightarrow C^{\sigma+} + Cl^{\sigma-}$

NB. Heterolytic fission is the type most frequently encountered in organic chemistry.

ELECTROPHILES AND NUCLEOPHILES

- Electrophiles are electron loving example H^+, CI^+, I^+, N^+O_2, RN_2^+, R_3C^+.
- Hence electrophiles are donors of protons or acceptors of electron pairs.
- Thus are oxidizing agents.

- Nucleophiles are nucleus loving example; H_2O, ROH, ^-OH, RO^-, Cl^-, Br^-, I^-, NH_3, RNH_2, CN^-.
- Nucleophiles are acceptors of protons or donors of electrons pairs
- Thus are reducing agents.

FUNCTIONAL GROUP AND HOMOLOGOUS SERIES

Organic compounds are categorized according to their functional groups. These are groups of atoms or bonds common to a series or family of compounds and which govern the principal chemical properties of the series.

Each series follows a regular structural pattern in which each member differs from the next by a constant amount and such a series is called a HOMOLOGOUS SERIES and the individual members of it are referred to as HOMOLOGUES.

Alkanes are series of hydrocarbons; they contain only carbon and hydrogen.

General structural formula C_nH_{2n+2}, n = 1, 2…. each homologue differs by the increment $-CH_2-$ and the first member is methane, formula, n = 1, CH_4 followed by n = 2, C_2H_6, ethane, n = 3, C_3H_8 propane and so on.

The table below gives the general structural formulae of the aliphatic homologous series and their functional groups.

Homologous series	General structural formula	Functional group
✓ Alkanes	C_nH_{2n+2}	– single bond

✓ Alkenes	C_nH_{2n} for $n \geq 2$	>C = C< double bond
✓ Alkynes	C_nH_{2n-2} for $n \geq 2$	- C ≡ C- tripple bond
✓ Alcohols	$C_nH_{2n+1}OH$	–OH
Ethers	$C_nH_{2n+1}O$ for $n \geq 2$	– O –
Aldehydes	$C_nH_{2n+1}CHO$ for $n \geq 2$	H$\rangle$C = O
Ketones	$C_nH_{2n+2}CO$ for $n \geq 2$	>C = O
✓ Carboxylic acids	$C_nH_{2n+1}COOH$	$-\underset{\substack{\mid \\ OH}}{C}=O$
Primary amines	$C_nH_{2n+1}NH_2$	$–NH_2$

"R" is the conventional means of representing the general formula of an alkyl group as the formulae RH, ROH, RCHO etc represents the alkanes, alcohol and aldehydes respectively.

NB: Each alkyl group named from the parent alkane by dropping the ending "-ane" and replacing it with "-yl" e.g.

That derived from methane is the methyl group ($-CH_3$).

Ethane is the ethyl group ($-CH_2CH_3$)

Propane is the propyl group etc.

SATURATED AND UNSATURATED HYDROCARBONS

All carbon valences of alkanes are saturated with hydrogen. Alkanes contain only carbon hydrogen and carbon – carbon single bonds, they are said to be SATURATED and are described as saturated hydrocarbons.

Compound possessing carbon-carbon multiple bonds are said to be UNSATURATED and those possessing one set of carbon-carbon double bonds >C=C< are called ALKENES and those possessing a set of carbon-carbon tripple bonds –C≡C– are called ALKYNES and these carbon-carbon multiple bond represents the functional group

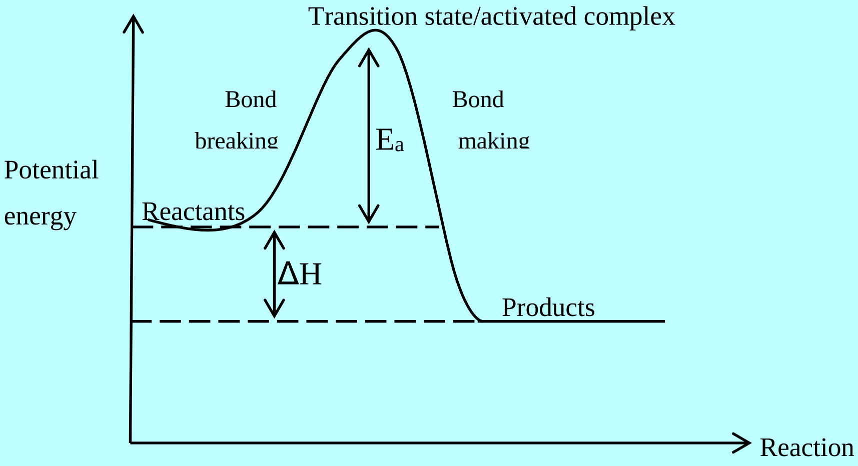
Energetics and Kinetics of a reaction

A detailed description of a chemical reaction outlining each separate stage is called a MECHANISM.

NB: Nucleophiles always attack and the electrophiles are always attacked

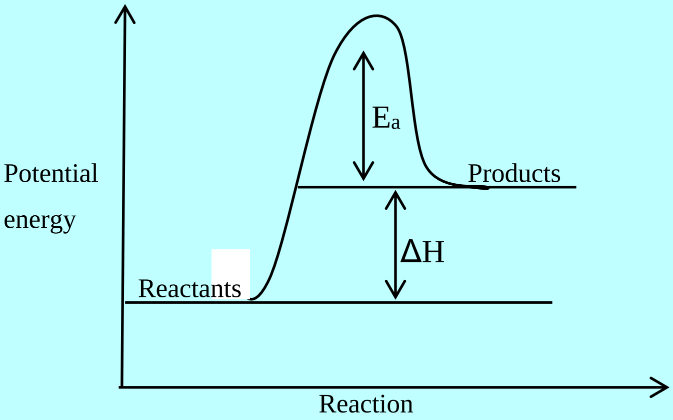
The reactant molecules become activated owing to their greater energy content and are referred to as the TRANSITION STATE or ACTIVATED COMPLEX. The complex is the least stable state through which the reactants pass before forming the products. The quantity of energy required to raise the reactant molecules to this state is referred to as the ACTIVATION ENERGY (E_a) for the reaction. It is in fact, this energy which is the most influential in determining the rate which a reaction precedes.

Exothermic



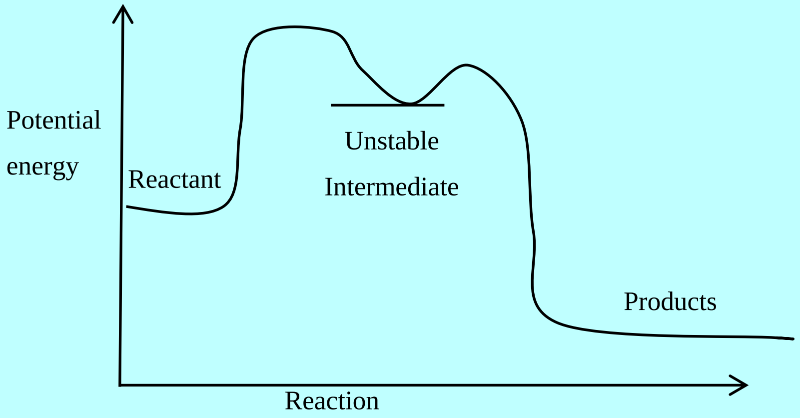
NOTE: Products formed via an exothermic process have lower energy content than the reactants from which they are formed and ΔH is negative.

Endothermic



ΔH is positive

If the activated complex exists as an UNSTABLE INTERMEDIATE which in many instances may actually be isolated, thus observed in a reaction profile as a trough in the activated peak of the curve resulting in a double hump i.e.



As the intermediate becomes more stable, the greater the likelihood of being able to separate the intermediate from the reaction mixture during the course of the reaction.

NB: The majority of organic reactions are complex and processed via the formation of intermediate which corresponds to a trough in the activated part of the reaction profile.

Since the reaction cannot proceed more rapidly than its slowest stage it is this RATE – DETERMINING STEP that governs the rate of the overall reaction.

The molecularity of the reaction describes the number of species involved in bond cleavage in the rate determining step. Reactions in which only one molecule is involved in bond cleavage during this step i.e.

$AB \longrightarrow A + B$ are described as UNIMOLECULAR and those in which two molecules are involved i.e.

$AB + C \longrightarrow A + BC$ are described as BIMOLECULAR and the molecularity must be a whole number

<u>Example:</u> The hydrolysis of a tertiary haloalkane is Unimolecular and the hydrolysis of a primary haloalkane is bimolecular.

<u>Determination of Relative Molecular mass of a compound.</u>

Method:

a) Vapour density measurements example gas syringe

Relative molecular mass = Vapour Density x 2

Having determined the relative molecular mass and empirical formula, the molecular formula of the compound can be found

Molecular formula = (Empirical formula) n

b) The molecular formula of gaseous hydrocarbons can usually be determined by gas explosion reactions (eudiometry). A known volume of the gas is repeatedly sparked in excess oxygen in a eudiometer until no further change in volume is observed. After cooling to the ambient temperature, the volume is noted and the amount of carbon dioxide determined by dissolving in potassium hydroxide. The remaining gas is excess oxygen.

Example:

30cm^3 of a gaseous hydrocarbon C_xH_y were mixed with 140cm^3 of oxygen (in excess) and exploded. After cooling to room temperature, the residue gases occupied 95cm^3. By absorption with potassium hydroxide solution a diminition of 60cm^3 was produced and the remaining gas was shown to be oxygen. Determining the formula of the hydrocarbon.

$$C_xH_y \quad + \quad \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 \quad + \quad \left(\frac{y}{2}\right) H_2O$$

1 molecule $\quad \left(x+\frac{y}{4}\right)$molecules $\quad x$ molecule $\quad \frac{y}{2}$ molecules

By the converse of Avogadro’s hypothesis

1 volume $\quad \left(x+\frac{y}{4}\right)$ volume $\quad x$ volume $\quad \frac{y}{2}$ volume

Assume that the steam will condense to water and occupy negligible volume

The potassium hydroxide solution absorbs the volume of carbon-dioxide produced i.e. 60cm^3

$\therefore$ Volume of excess oxygen is (95 – 60) cm^3 = 35cm^3

$\therefore$ 30cm^3 of C_xH_y combines with (140 – 35) = 105cm^3 of oxygen to give 60cm^3 of carbon dioxide

Now: $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow{\hspace{3em}} xCO_2 + \frac{y}{2}H_2O$

30cm^3 :105cm^3 : 60cm^3

1 :3.5 : 2 (simplest ratio)

$x = 2$

And $\left(x + \frac{y}{4}\right) = 3.5$

$y = 6$

Giving the molecular formula of the hydrocarbon as C_2H_6 (Ethane)

ALKANES (Paraffin)

General formula C_nH_{2n+2}, forms a series of saturated hydrocarbons and successive members differ in composition by – CH_2; they are tetrahedrally surrounded by hydrogen and other carbon atoms, they are very stable and relatively unreactive.

NOMENCLATURE

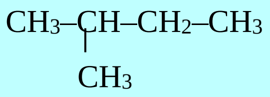
With exception of methane CH_4, ethane C_2H_6, propane C_3H_8, and butane C_4H_{10} straight chain alkanes are named by taking the Greek prefix appropriate to the number of carbon atoms and adding the ending "-ane". For branched alkanes, the largest un branched chain of carbon atom is selected and named accordingly and the name of the alkyl substituents prefix the name of the main chain.

$CH_3–CH_2–CH_2–CH_3$

Butane

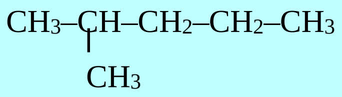
$CH_3-CH_2–CH_2–CH_2–CH_3$

Pentane



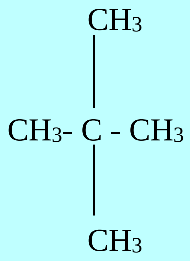
$CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3$

2 – Methyl butane



$CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_2-CH_3$

2 – methyl pentane



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

2, 2 Dimethyl propane

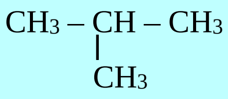
Structural Isomerism in Alkanes

Methane, ethane and propane have no isomers, butane has two, pentane has three and the following higher homologous of the series have a progressively greater number. All isomers are due to branching of the hydrocarbon chain and are referred to as CHAIN/ Branched chain isomers.

Butane C_4H_{10}

$CH_3 – CH_2 – CH_2 – CH_3$,

Butane



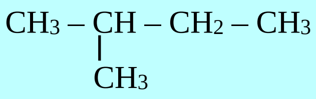
$CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_3$

2 – methyl propane

Pentane C_5H_{12}

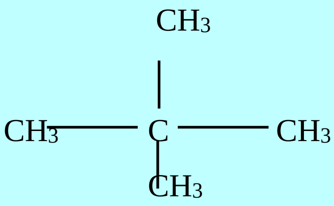
$CH_3 – CH_2 – CH_2 – CH_2 – CH_3$

Pentane



$CH_3-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_3$

2 – methyl butane



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

2, 2 dimethyl propane

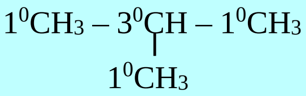
Classification of Carbon

A primary (1^0) carbon is one which is attached to not more than one other carbon atom.
i.e. $-CH_3$

A secondary (2^0) carbon is one which is attached to two other carbon atoms i.e. $-CH_2-$

A tertiary (3^0) carbon is one which is attached to three other carbon atoms i.e. $-\overset{|}{\underset{|}{C}}H$

i.e. $1^0CH_3 - 2^0CH_2 - 2^0CH_2 - 1^0CH_3$



$$1^0CH_3 - 3^0\underset{1^0CH_3}{\underset{|}{C}}H - 1^0CH_3$$

Physical Properties

- The first forms are gases but the C_5 to C_{17} are liquids and the rest are solids at 20^0C.
- The Boiling point and melting point of alkanes increases with increasing relative molecular mass but the branched – chain isomers are more volatile than their straight isomers. Hence the greater the degree of branching in an isomer, the greater is to volatility.
- They are non-polar and immiscible with water but soluble in non-polar organic solvents such as trichloro methane, ether, benzene etc. Methane shows a light tendency to dissolve in water but this is due to its small size of its molecules.

REACTIONS

a) Chlorination

Alkanes undergo chlorination in presence of ultra-violet light (250 – 400^0C) yielding a mixture of chloromethane CH_3Cl, dichloromethane CH_2Cl_2, trichloro methane (chloroform) $CHCl_3$ and tetra chloromethane (carbon tetra chloride) CCl_4

$CH_4 \xrightarrow[UV\ light]{Cl2}$ Mixture of CH3Cl, CH_2Cl_2, $CHCl_3$ & CCl_4

Mechanism

$$\left.\begin{array}{l}
Cl-Cl \xrightarrow{UV} Cl^{\bullet} + Cl^{\bullet} \\
CH_4 + Cl \longrightarrow {}^{\bullet}CH_3 + HCl \\
{}^{\bullet}CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}
\end{array}\right\} \text{Chain initiation step}$$

$$\left.\begin{array}{l}
Cl-Cl \xrightarrow{UV} Cl^{\bullet} + Cl^{\bullet} \\
CH_3Cl + Cl^{\bullet} \longrightarrow {}^{\bullet}CH_2Cl + HCl \\
{}^{\bullet}CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}
\end{array}\right\} \text{Chain propagation}$$

$$\left.\begin{array}{l}
Cl-Cl \xrightarrow{UV} Cl^{\bullet} + Cl^{\bullet} \\
CH_2Cl_2 + Cl^{\bullet} \longrightarrow {}^{\bullet}CHCl_2 + HCl \\
{}^{\bullet}CHCl + Cl_2 \longrightarrow CHCl_3 + Cl^{\bullet} \\
\\
Cl-Cl \xrightarrow{UV} Cl^{\bullet} + Cl^{\bullet} \\
\\
CHCl_3 + Cl^{\bullet} \longrightarrow {}^{\bullet}CCl_3 + HCl \\
{}^{\bullet}CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl^{\bullet} \\
Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2
\end{array}\right\} \text{Chain termination}$$

b) <u>Halogenation using sulphur dichloride dioxide (SO_2Cl_2)</u>

$$RH + SO_2Cl_2 \xrightarrow[\substack{reflux \\ (40-80°c)}]{\substack{di(benzene\ carbonyl)peroxide \\ catylist}} RCl + HCl + SO_2$$

Halo alkane

c) **Nitration**

$$RH + HNO_3 \xrightarrow[150\text{-}400°C]{} RNO_2 + H_2O$$ via a free radical mechanism

Nitro alkane

(Useful commercial solvents)

Mechanism

$$HO-NO_2 \longrightarrow HO^\bullet + {}^\bullet NO_2 \text{ (free radicals)}$$

$$R-H + {}^\bullet OH \longrightarrow R^\bullet + H_2O$$

$$R^\bullet + {}^\bullet NO_2 \longrightarrow R-NO_2$$

Example: $CH_3CH_3 + HNO_3 \xrightarrow[150\text{-}400°C]{} CH_3CH_2-NO_2 + H_2O$

Mechanism

$$HO-NO_2 \longrightarrow HO^\bullet + {}^\bullet NO_2$$

$$CH_3-CH_2-H + {}^\bullet OH \longrightarrow CH_3{}^\bullet CH_2 + H_2O$$

$$CH_3{}^\bullet CH_2 + {}^\bullet NO_2 \longrightarrow CH_3CH_2-NO_2 \text{ (nitro ethane)}$$

Note: Is a substitution reaction because a hydrogen atom of the alkane is substituted by NO_2-group producing nitro alkane.

d) **Combustion**

Burn exothermically in excess oxygen with non-smoky flame to give CO_2 and steam.

$$C_nH_{2n+2} + \frac{3n+1}{2}O_2 \xrightarrow{\text{Burn}} {}_nCO_2 + (n+1)\ H_2O \quad \Delta H = \text{-ve}$$

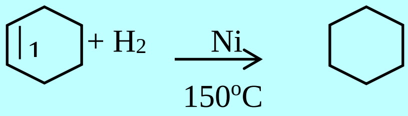
It’s via a high temperature free radical mechanism.

Preparations

1. **Hydrogenation**

$$\underset{\text{Alkene}}{C_nH_{2n} + H_2} \xrightarrow[\text{Ni cat}]{\text{Pt, Pd or}} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

Example;



Cyclohexene → cyclohexane

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

Propyne ⟶ Propane

NB. Reduction with Pt (platinum) and Pd (palladium) occurs at room temperature while these with Ni (Nickel) requires a temperature of about 150°C

2. **Reduction of Haloalkanes**

$$\underset{\text{(Alcohol)}}{ROH} \quad + HX \longrightarrow \underset{\text{(Haloalkanes)}}{RX} + H_2O$$

X = Cl, Br, I

Then; $2Rx + Zn + 2H^+ \xrightarrow{\text{Zn-Cu/aq. alcohol}} \underset{\text{Alkane}}{2RH} + Zn^{2+} + x^-$

e.g. $CH_3CH_2Cl \xrightarrow[\text{Zn-Cu couples}]{\text{Ethanol}} CH_3CH_3$

3. **Grignard reaction**

$$RX \xrightarrow[\text{Dry ether}]{Mg} RMgX$$

Alkyl magnesium alkane

And on treatment with aqueous H^+ liberate the alkane

$$RMgX + H_2O \xrightarrow{H^+ (aq)} R - H + Mg(OH)X$$

E.g.

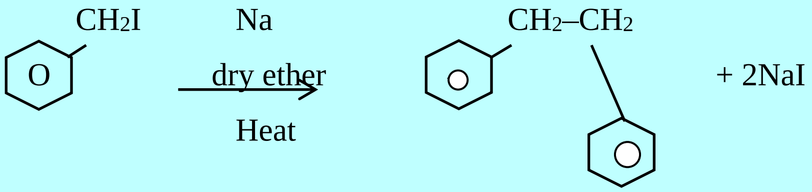
$$\begin{tikzcd} CH_3CH_2CI \arrow[r, "Mg", "\text{Dry ether}"'] & CH_3CH_2^{-}Mg - CI \arrow[d, "aq. H^+"', "H_2O"] \\ & CH_3CH_3 \end{tikzcd}$$

4. Wurtz synthesis

(Alkyl acids when heated with sodium metal in dry ether)

$$2R\text{-}x + 2Na \xrightarrow[\text{Ether / heat}]{\text{dry}} R - R + 2Nax$$

e.g. $$2CH_3Br \xrightarrow[\text{Dry ether/ Heat}]{Na} CH_3CH_3 + 2NaBr$$

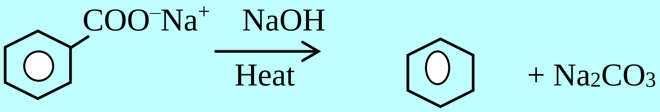


5. From carboxylic acids

When sodium salts of carboxylic acids are heated with soda limes they eliminate a molecule of carbon dioxide to form alkane

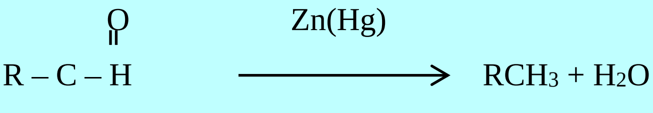
$$R - COO^-Na^+ + NaOH_{(s)} \xrightarrow{Heat} R\text{–}H + Na_2CO_3$$

Example: $$CH_3CH_2CH_2COO^-Na \xrightarrow[\text{Heat}]{\text{Excess } NaOH_{(s)}} CH_3CH_2CH_3$$



6. From Carbonyl compound

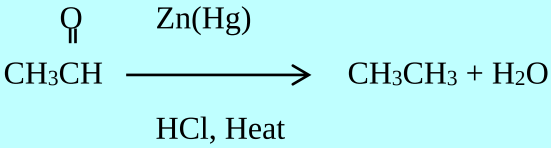
Reduction of carbonyl compounds with amalgamated zinc (Zn (Hg)) and hydrochloric acid



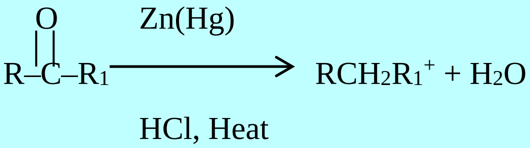
$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{HCl, heat}]{\text{Zn(Hg)}} RCH_3 + H_2O$$

Aldehyde

Example:

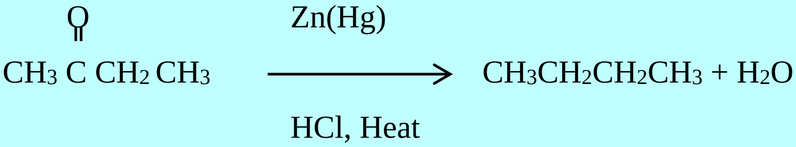


$$CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{HCl, Heat}]{\text{Zn(Hg)}} CH_3CH_3 + H_2O$$



$$R-\overset{O}{\overset{\|}{C}}-R_1 \xrightarrow[\text{HCl, Heat}]{\text{Zn(Hg)}} RCH_2R_1^+ + H_2O$$

e.g.



$$CH_3\ \overset{O}{\overset{\|}{C}}\ CH_2\ CH_3 \xrightarrow[\text{HCl, Heat}]{\text{Zn(Hg)}} CH_3CH_2CH_2CH_3 + H_2O$$

NB: Pyrolysis of alkanes is referred to as CRACKING, particularly where petroleum is involved. Paraffin fraction in the Vapour state are passed through a metal chamber heated to 400 – 700^{0}C using various metallic oxides as catalyst. The starting alkanes are broken down into a mixture of smaller alkanes, alkenes and some hydrogen i.e.

$$\text{Alkane} \xrightarrow{400 - 700^0C} \text{Smaller alkanes + Alkenes} + H_2$$

e.g. $2CH_3CH_2CH_3 \xrightarrow{400 - 700^0C} CH_4 + CH_3CH = CH_2 + CH_2 = CH_2 + H_2$

Propane methane propene ethene

Therefore, CRACKING

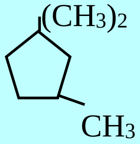
Is a process in which less volatile higher hydrocarbons are converted to more volatile hydrocarbons by application of heat / a catalyst and the products formed will depend on

–structure of the hydrocarbon

– Temperature and pressure applied.

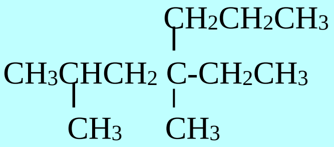
Example: 1. Give the IUPAC name for

a).



1, 1, 3 – trimethyl cyclo pentane

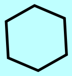
(b)



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2\,\overset{\displaystyle CH_2CH_2CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}\text{-}CH_2CH_3$$

4 – ethyl – 2, 4 – dimethyl heptane

NB: During cracking the following changes may occur.

- Formation of a mixture of hydrocarbon of lower chains
- Saturated hydrocarbon may be converted to unsaturated hydrocarbons
- Cyclisation may occur e.g. $CH_3\ (CH_2)_4CH_3 \xrightarrow[600^0C]{pt\ or\ H_2O_3}$ 

<u>Types of Cracking</u>

- Thermal cracking, here cracking takes place by heating by either liquid of gases hydrocarbon.
- Catalyst cracking; Here cracking takes place by heating in the presence of a mixture of Silica and Aluminum silicate as catalyst

ALKENES (OLEFINS)

General formulae C_nH_{2n}

They possess a double bond; >C = C< which makes them generally much more reactive than the alkanes.

NOMENCLATURE

"–ane" of the alkane is replaced by "-ene" and the position of the double bond is specified by placing the appropriate number between the stem of the name and the "–ene".

Example $CH_2 = CH_2$ ethene

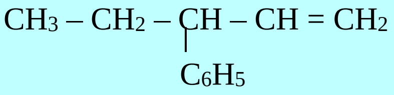
$CH_3 – CH = CH_2$ propene

(4) (3) (2) (1)

$CH_3\ CH_2 –CH =CH_2$ But -1 –ene

(4) (3) (2) (1)

$CH_3CH=CH –CH_3$ But – 2 – ene



$$CH_3 – CH_2 – \underset{\displaystyle C_6H_5}{\underset{|}{CH}} – CH = CH_2$$

3 – phenylpent – 1- ene etc

STRUCTURAL ISOMERISM IN ALKENES

Ethene and propene have no structural Isomers but

C_4H_8

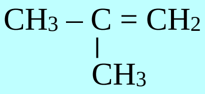
$CH_3 – CH_2 – CH = CH_2$

But – 1 – ene

$CH_3 - CH = CH – CH_3$

But – 2 –ene

These are straight – chain structures with the difference being in the portion of the double bond, hence are positional isomers.



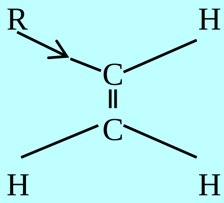
$$CH_3 – \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$$

2 – methyl propane is branched –chain

PHYSICAL PROPERTIES

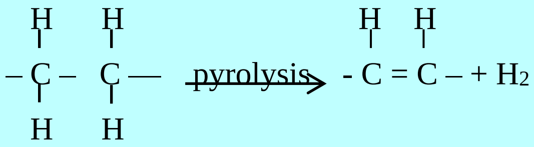
Ethene propene and But-1-ene are gases and the rest are liquids with the exception of higher members with more than fifteen Carbons which are solids. Branching enhances the volatility and their boiling points are generally marginally lower than corresponding alkanes. They are virtually insoluble in water but soluble in non-polar organic solvents such as chloroform, ether, benzene etc.

Unsymmetrical alkene is slightly polar due to the electron donating properties of the alkyl group(s) i.e.



Industrial source

Large alkenes are obtained by the cracking of petroleum



$$-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}- \xrightarrow{\text{pyrolysis}} -\overset{H}{C}=\overset{H}{C}- + H_2$$

And then separated by fractional distillation

Ethane

By passing ethanol Vapour over an aluminium oxide catalyst at 350^0C

$$CH_3CH_2OH \xrightarrow[350^0C]{Al_2O_3} CH_2{=}CH_2 + H_2O$$

Synthetic preparations

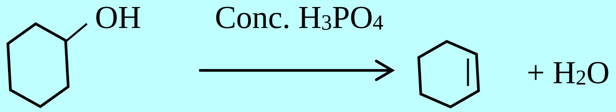
This mainly involves elimination of atoms l groups from two adjacent carbon atoms, mainly from alcohols and halo alkanes.

Dehydration of alcohol using a concentrated sulphiric acid and phosphoric acid

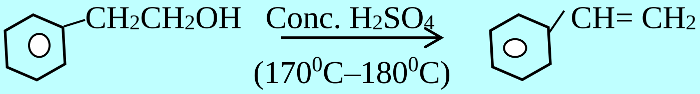
Heating is required and acid must be in excess, temperature required 170 – 180^0C.

$$RCH_2CH_2 - OH \xrightarrow[(170^oC - 180^oC)]{\text{Conc. } H_2SO_4 \text{ or } H_3PO_4} RCH = CH_2 + H_2O$$

Example $$CH_3CH_2OH \xrightarrow[(170^0C - 180^0C)]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$



Cyclohexanol cyclohexane



2 phenyl ethanol 2 phenyl ethane

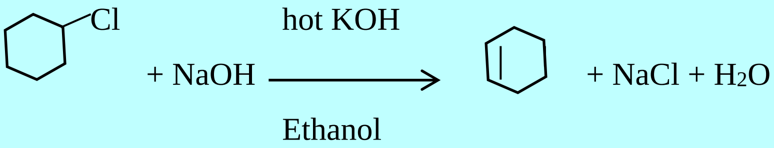
Dehydrohalogenation

Carried out by heating them in an alcoholic solution of potassium hydroxide

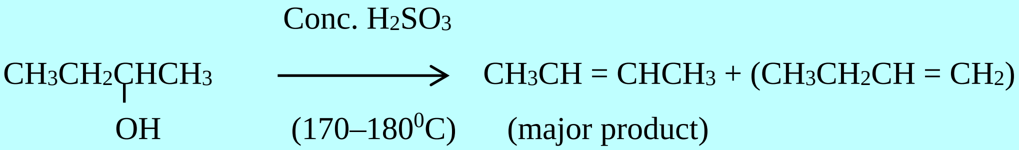
$$RCH_2CH_2X \xrightarrow[\text{Heat}]{\text{Alc .KOH}} RCH = CH_2 + KX + H_2O$$

X = Cl, Br, I

Example;

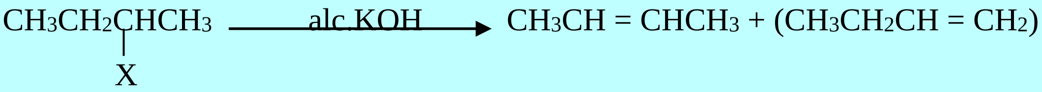


Example;



$$\underset{OH}{CH_3CH_2CHCH_3} \xrightarrow[(170–180^0C)]{\text{Conc. } H_2SO_3} CH_3CH = CHCH_3 + (CH_3CH_2CH = CH_2)$$

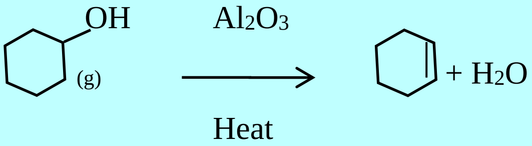
(major product)



$$\underset{X}{CH_3CH_2CHCH_3} \xrightarrow{\text{alc.KOH}} CH_3CH = CHCH_3 + (CH_3CH_2CH = CH_2)$$

By passing alcohol vapours over heated Aluminium oxide as catalyst

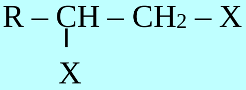
$$CH_3CH_2CH_2OH_{(g)} \xrightarrow[Heat]{Al_2O_3} CH_3CH = CH_2 + H_2O$$



By dehalogenation of Vicinal – dihalides

Vicinal dihalides, Are halogen compounds with two halogen atoms on adjacent carbon atoms. Germ-dihalides, have two halogen atoms on the same carbon atom. This is carried by heating out vicinal-dihalides with zinc in alcohol

i.e.



$$R - \underset{X}{CH} - CH_2 - X \xrightarrow[Heat]{Zn/CH_3OH} RCH \equiv CH + ZnX_2$$

Metallic sodium is also used

Example: $Cl - CH_2 - CH_2 - Cl \xrightarrow{2Na} CH_2 = CH_2 + 2NaCl$

Note: With germ halides higher alkanes are produced by increasing the length of the carbon chain e.g.

$$2RCHX_2 \xrightarrow[Heat]{2Zn / alcohol} RCH = CHR + 2ZnX_2$$

REACTIONS

- **Addition of hydrogen / Hydrogenation**

  Occurs in the presence of Pt, Pd or (Ni at 150^0C) catalyst.

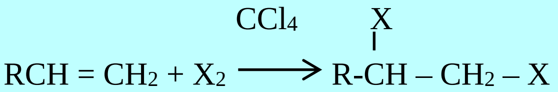
$$RCH = CH_2 + H_2 \xrightarrow[150^0C]{Ni} RCH_2CH_3$$

$$CH_3CH_2 = CH_2 + H_2 \xrightarrow[150^0C]{Ni} CH_3CH_2CH_3$$

$+ H_2 \xrightarrow{Pt}$

This reaction is used in the synthesis of saturated compounds like in the manufacture of margarine.

- **Addition of halogens**

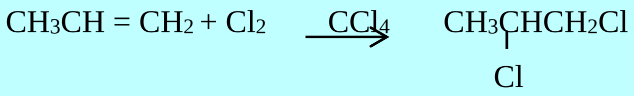


$$RCH = CH_2 + X_2 \xrightarrow{CCl_4} R\text{-}\overset{\overset{X}{|}}{C}H - CH_2 - X$$

(X = Cl, Br, I) which are electrophiles in this case

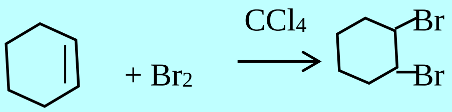
(Dihalogens)

e.g.

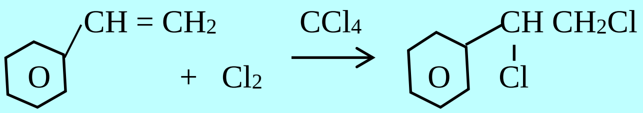


$$CH_3CH = CH_2 + Cl_2 \xrightarrow{CCl_4} CH_3\underset{\underset{Cl}{|}}{C}HCH_2Cl$$

1, 2 –dichloro propane



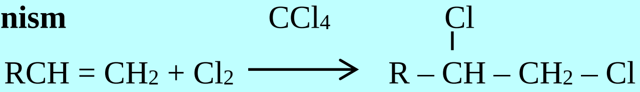
1, 2 – dibromo cyclohexane



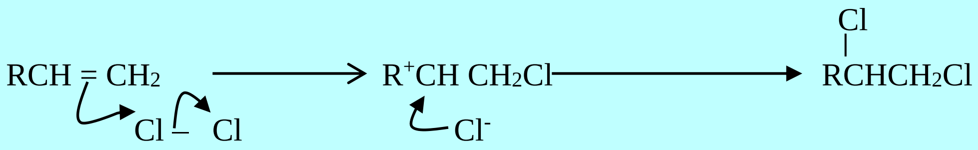
Phenyl ethane

1, 2 –dichloro -2-phenyl ethane

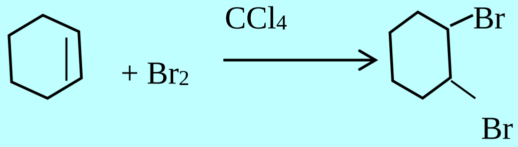
Mechanism



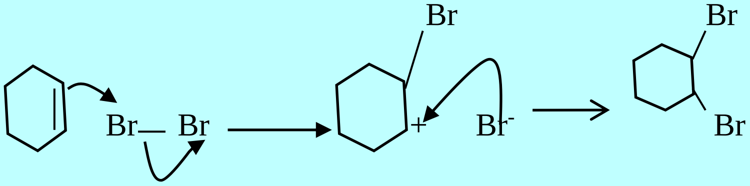
$$RCH = CH_2 + Cl_2 \xrightarrow{CCl_4} R - \overset{\overset{Cl}{|}}{C}H - CH_2 - Cl$$



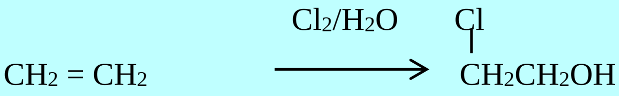
Example:



Mechanism



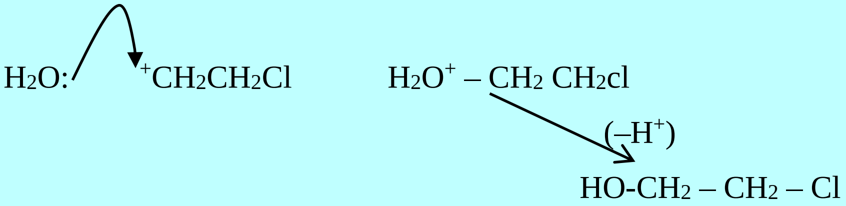
NB: Halogenation may be carried out in presence of water. Then example



$$CH_2 = CH_2 \xrightarrow{Cl_2/H_2O} \overset{Cl}{\overset{|}{C}}H_2CH_2OH$$

Mechanism

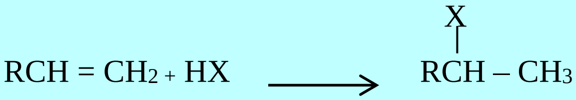
$$CH_2 = CH_2 \longrightarrow {}^{+}CH_2\ CH_2Cl$$



$$H_2O: \quad {}^{+}CH_2CH_2Cl \qquad H_2O^{+} – CH_2\ CH_2cl \xrightarrow{(–H^{+})} HO\text{-}CH_2 – CH_2 – Cl$$

NB: Reaction of Bromine is used to test the presence of multiple bonds where Bromine gets decolourised.

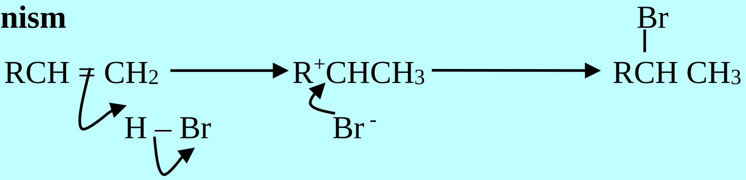
- **<u>Addition of halogen acids (HX) for X = Cl, Br, I</u>**



$$RCH = CH_2 + HX \longrightarrow R\overset{X}{\overset{|}{C}}H – CH_3$$

(Alkene) (Alkyl halide)

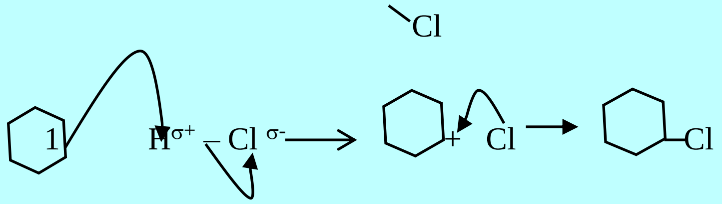
Mechanism



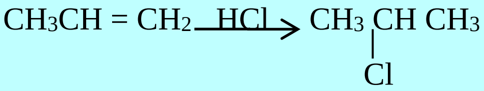
$$RCH = CH_2 \longrightarrow R^{+}CHCH_3 \longrightarrow R\overset{Br}{\overset{|}{C}}H\ CH_3$$

Example

Mechanism

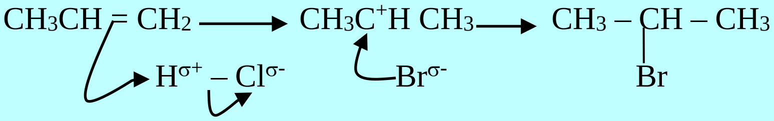


NB:



$$CH_3CH = CH_2 \xrightarrow{HCl} CH_3\underset{\displaystyle Cl}{\underset{|}{C}}H\,CH_3$$

Mechanism



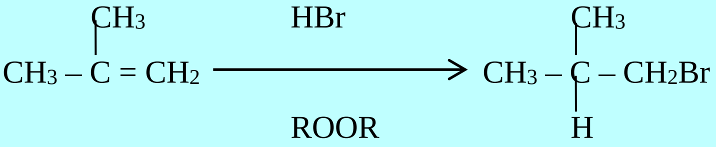
$CH_3CH_2 – {}^+CH_2$; This carbonium ion (1^0) is also possible but it is not very stable. Instead we consider the carbonium ion (2^0) which is more stable $CH_3\text{-}{}^+CH – CH_3$. This is according to <u>Markchonikoff's rule</u>.

In addition, reactions involving a symmetrical alkene (Alkenes with carbon atoms carrying double bond having different number of hydrogens), the hydrogen of the halogen acid adds to the carbon which carries the greater number of hydrogen atoms while the halide atom adds to one with the lesser.

- **<u>Addition of halogeno-acids in presence of a peroxide (RO-OR)</u>**

$$RCH = CH \xrightarrow[\text{Peroxide}]{HBr} RCH_2CH_2Br$$

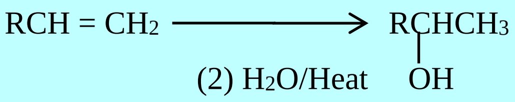
Example:



$$CH_3 – \overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 \xrightarrow[ROOR]{HBr} CH_3 – \underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} – CH_2Br$$

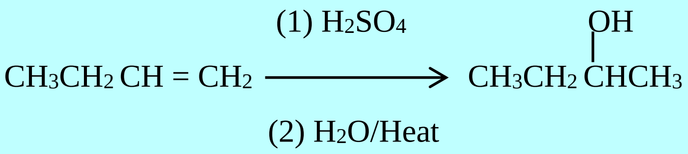
- **<u>Hydration of alkenes (Preparation of alcohols)</u>**

(1) H_2SO_4



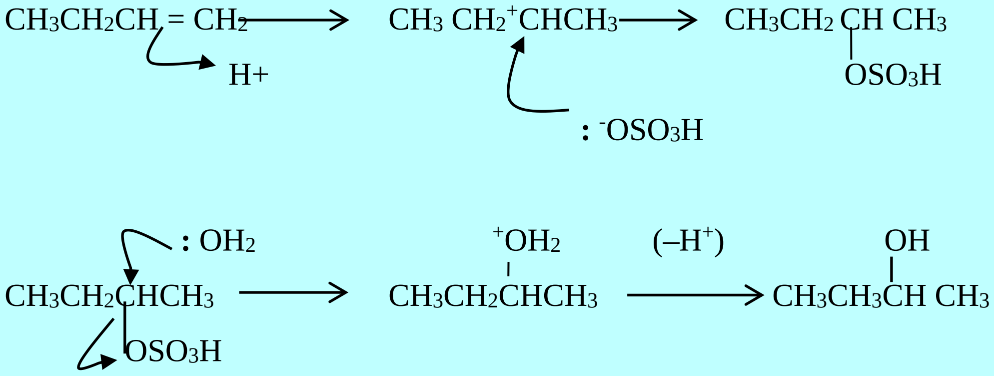
$$RCH=CH_2 \xrightarrow[\text{(2) } H_2O/\text{Heat}]{} \underset{\displaystyle OH}{RCHCH_3}$$

Example;



$$CH_3CH_2CH=CH_2 \xrightarrow[\text{(2) } H_2O/\text{Heat}]{\text{(1) } H_2SO_4} CH_3CH_2\overset{\displaystyle OH}{C}HCH_3$$

Mechanism; $H_2SO_4 \rightleftharpoons H^+ + {}^-OSO_3H$



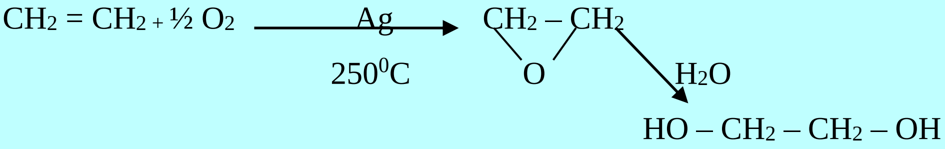
$$CH_3CH_2CH=CH_2 \xrightarrow{H+} CH_3CH_2{}^+CHCH_3 \xrightarrow{:{}^-OSO_3H} CH_3CH_2\underset{\displaystyle OSO_3H}{C}HCH_3$$

$$CH_3CH_2\underset{\displaystyle OSO_3H}{C}HCH_3 \xrightarrow{:OH_2} CH_3CH_2\overset{\displaystyle {}^+OH_2}{C}HCH_3 \xrightarrow{(-H^+)} CH_3CH_3\overset{\displaystyle OH}{C}H\ CH_3$$

- **<u>Reaction with Oxygen</u>**

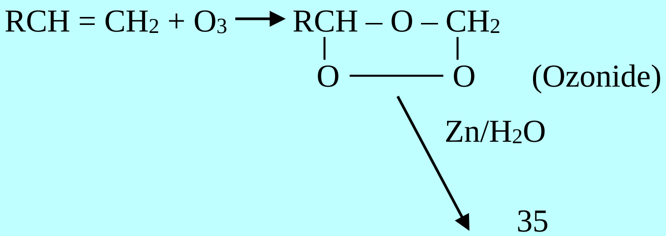
Over heated silver catalyst, they form epoxides. And Diols are produced on hydrolysis of the epoxide.

Example:



$$CH_2=CH_2+\tfrac{1}{2}O_2 \xrightarrow[250^0C]{Ag} CH_2-CH_2\ (O) \xrightarrow{H_2O} HO-CH_2-CH_2-OH$$

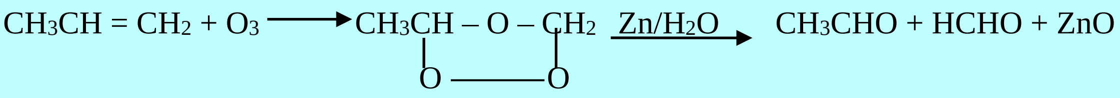
- **<u>Reaction with Ozone / Ozonized Oxygen (O_3)</u>**



$$RCH=CH_2+O_3 \rightarrow \underset{\displaystyle O\text{———}O}{RCH-O-CH_2}\ \text{(Ozonide)} \xrightarrow{Zn/H_2O}$$

$RCHO + HCHO + ZnO$

Example;

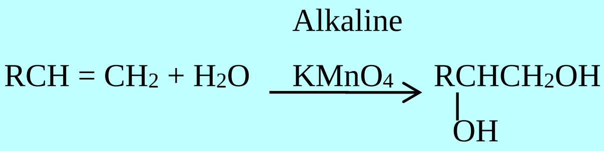


$$CH_3CH = CH_2 + O_3 \longrightarrow \underset{O\text{———}O}{CH_3CH - O - CH_2} \xrightarrow{Zn/H_2O} CH_3CHO + HCHO + ZnO$$

This reaction is important in conversion of an alkene to aldehyde or ketone. It is also used to investigate the position of the double bond for symmetrical alkenes one product is formed and for unsymmetrical alkenes; two different products are formed.

- **Oxidation Reaction**

Undergo oxidation reaction using potassium permanganate to form diols.



$$RCH = CH_2 + H_2O \xrightarrow[KMnO_4]{\text{Alkaline}} \underset{OH}{RCH}CH_2OH$$

Example;

$$CH_2 = CH_2 \xrightarrow[\ddot{O}H]{aq.\ KMnO_4} HO - CH_2 - CH_2\text{-}OH$$

NB: Purple potassium manganate (VII) gets decolourised.

POLYMERIZATION

Polymerization is a process by which many simple molecules join together to form very large molecules.

Simple alkenes polymerize to form a family of long chain addition polymers.

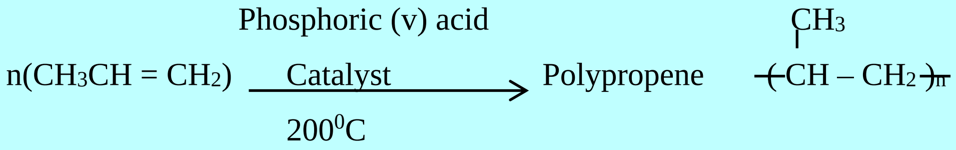
Ethene polymerizes to form polyethene (polythene)

$$nCH_2 = CH_2 \xrightarrow[\text{High pressure and Temp. }(200\text{-}400^0C)]{O_2\text{ catalyst}} -(CH_2 - CH_2)-_n$$

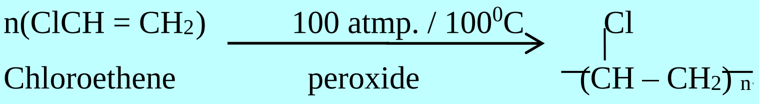
Uses: Making polyethene bags

In a similar way;

Propene forms Polypropene (polypropylene)



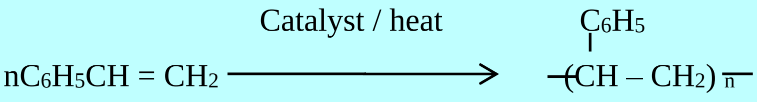
$$n(CH_3CH = CH_2)\xrightarrow[200^0C]{\substack{\text{Phosphoric (v) acid}\\ \text{Catalyst}}}\text{Polypropene}\quad -\!\left(\overset{\overset{CH_3}{|}}{C}H - CH_2\right)_n\!-$$



$$\underset{\text{Chloroethene}}{n(ClCH = CH_2)}\xrightarrow[\text{peroxide}]{100\text{ atmp. / }100^0C}-\!\left(\overset{\overset{Cl}{|}}{C}H - CH_2\right)_n\!-$$

(Polychloroethene)

Uses; Used in making plastic rain coats, curtains, furniture coverings, records, water piping and guttering (polyvinyl chloride).



$$\underset{\text{(Phenyl ethene)}}{nC_6H_5CH = CH_2}\xrightarrow[\text{high pressure}]{\text{Catalyst / heat}}-\!\left(\overset{\overset{C_6H_5}{|}}{C}H - CH_2\right)_n\!-$$

(polyphenylethene)

(Polystyrene)

$$\underset{\text{(Tetrafluoroethene)}}{nCF_2 = CF_2}\xrightarrow[(45-50\text{ atm})]{\text{Peroxide}}-\!\left(CF_2 - CF_2\right)_n\!-$$

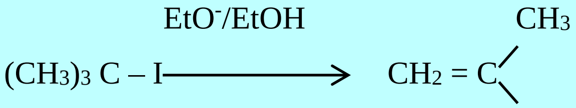
Teylon (PTFE)

Uses; Used in making non-stick cooking utensils and low friction bearings.

NOTE: They burn with a luminous, smoky flame.

Examples

1. Complete the following and write a mechanism

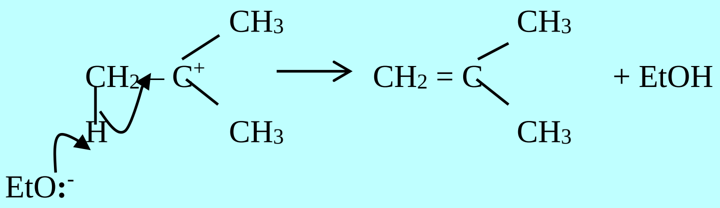
a) 

$$(CH_3)_3C - I\xrightarrow{EtO^-/EtOH}CH_2 = C\begin{matrix}\diagup CH_3\\ \diagdown\end{matrix}$$

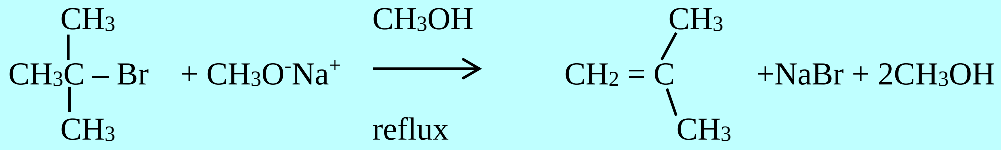
Heat CH3

Mechanism

$$(CH_3)_3C-I \rightleftharpoons (CH_3)_3C^+ + I$$



2.

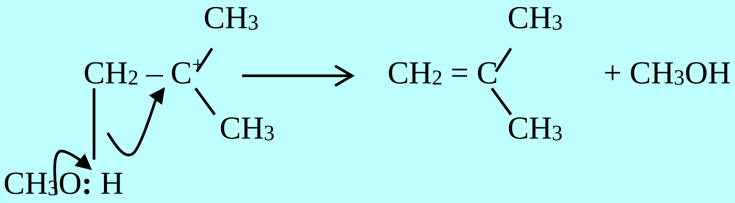


$$CH_3C(CH_3)_2-Br + CH_3O^-Na^+ \xrightarrow[\text{reflux}]{CH_3OH} CH_2=C(CH_3)_2 + NaBr + 2CH_3OH$$

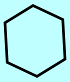
Mechanism

$$CH_3O\text{-}Na^+ \longrightarrow CH_3O^- + Na^+$$

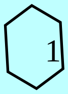
$$(CH_3)_3C\,Br \rightleftharpoons (CH_3)_3C^+ + Br^-$$



2. Name the reagent that can be used to distinguish between the following pairs of compounds.



And

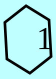


Reagent: 1. Bromine water

2) Potassium manganate (vii) solution

Observation

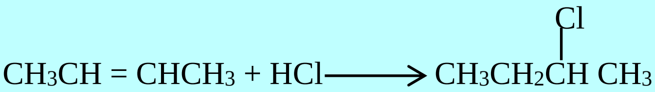
1) Gives o observable change
2) Gives no observable change



1) decolourises bromine water
2) The solution turns from purple to colourless

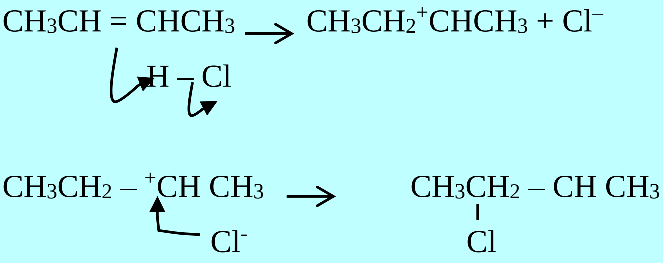
3. Write equations to show the reactions that can take place between the following pairs of compounds and indicate the mechanism for the reaction
   a) But -2- ene and hydrogen chloride
   b) Ethane and iodine
   c) Methyl benzene and chlorine in the presence of sunlight

Solution

a) 

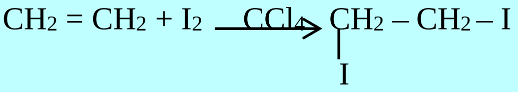
$$CH_3CH = CHCH_3 + HCl \longrightarrow CH_3CH_2\underset{}{\overset{Cl|}{C}}H\ CH_3$$

Mechanism



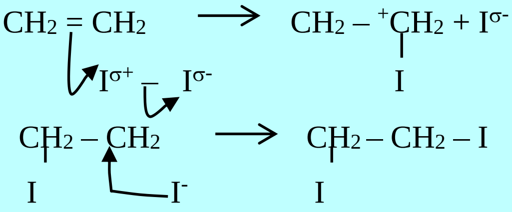
$$CH_3CH = CHCH_3 + H - Cl \longrightarrow CH_3CH_2{}^{+}CHCH_3 + Cl^{-}$$

$$CH_3CH_2 - {}^{+}CH\ CH_3 + Cl^{-} \longrightarrow CH_3\underset{|\ Cl}{CH_2} - CH\ CH_3$$

b) 

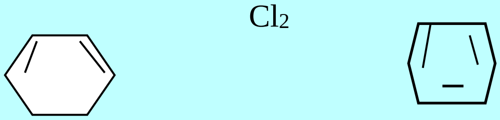
$$CH_2 = CH_2 + I_2 \xrightarrow{CCl_4} \underset{|\ I}{CH_2} - CH_2 - I$$

Mechanism



$$CH_2 = CH_2 + I^{\sigma+} - I^{\sigma-} \longrightarrow CH_2 - {}^{+}\underset{|\ I}{CH_2} + I^{\sigma-}$$

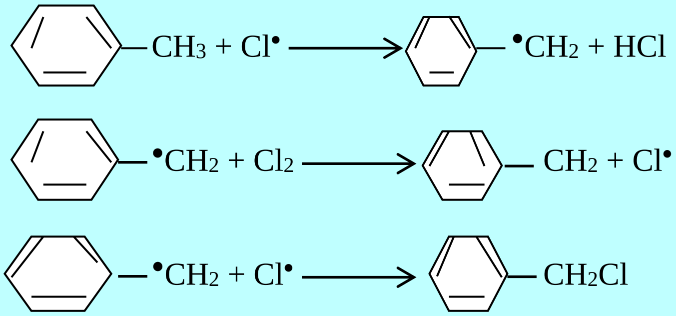
$$\underset{|\ I}{CH_2} - CH_2 + I^{-} \longrightarrow \underset{|\ I}{CH_2} - CH_2 - I$$



$$—CH_3 \xrightarrow{\text{U.V light}} —CH2Cl$$

Mechanism

$$Cl{:}\,Cl \xrightarrow{\text{U.V light}} 2Cl^{\bullet}$$



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

Note that the sequence of reaction is eventually stopped when two of the free radicals collide and form a stable molecule

And if it was excess Cl_2, the phenyltrichloromethane is formed

4. Write equation to show how each of the following compounds can be synthesized

a) $(CH_3)_2\,C = CH$ from 2 – bromo – 2 – methyl propane

Solution

$$(CH_3)_3C – Br \xrightarrow[\text{Heat}]{KOH/C_2H_5OH} (CH_3)_2\,C = CH_2$$

b) $CH_3CH_2CH_2CH_3$ from $CH_2 = CH_2$

Solution

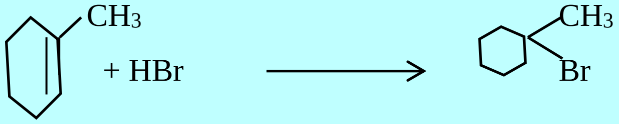
$$CH_2 = CH_2 + HCl \longrightarrow CH_3CH_2Cl \xrightarrow[\text{dry ether, Heat}]{Na} CH_3CH_2CH_2CH_3$$

1. Give the structural formulae and IUPAC name of the product of each of the following reactions

   $CH_3CH = CH_2 + HI \longrightarrow CH_3CHICH_3$ *(2-1odo propane)*

   $(CH_3)_2C = CH_2 + HCl \xrightarrow{peroxide} (CH_3)_2CHCH_2Cl$ *(1-chloro-2-methyl propane)*

   $(CH_3)_2C = CH_2 + HBr \longrightarrow (CH_3)_3CBr$ *(2-bromo-2-methyl propane)*

   1-bromo-1- methyl cyclohexane

2. Write the mechanism for the addition of the following reagents to propene and name the products.
   a) Chlorine in tetra chloromethane *(1, 2-dichloropropane)*
   b) Chlorine water *(2-chloropropane-1-o1)*
   c) Bromine water *(1-bromopropan-2-o1)*

ALKYNES (ACETYLENES)

Form a homologous series of unsaturated hydrocarbons containing a carbon-carbon triple bond. General molecular formula

C_nH_{2n-2}

Nomenclature

The stem of the name of the corresponding alkane is taken and replacing the ending "-ane" of the alkane with the suffix "-yne". The position of the triple bond is indicated by inserting the appropriate number between the stem and the ending e.g.

$CH \equiv CH$ Ethyne

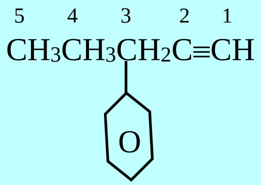
$CH_3C\equiv CH$ Propyne

4 3 2 1

$CH_3CH_2C\equiv CH$ But-1-yne

4 3 2 1

$CH_3C\equiv CCH_3$ But-2-yne



5 4 3 2 1

$CH_3CH_3CH_2C\equiv CH$

3-phenylpent-1-yne

The first three members are gases, and the rest are liquids at 20^0C.

NB: When the triple bond is at the end of the chain e.g. $CH_3CH_2C\equiv CH$, it is called **Terminal triple bond**.

When the triple bond is in the middle of the chain e.g. $CH_3C\equiv CCH_3$, it is called **Internal triple bond**.

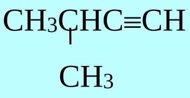
ISOMERISM

Ethyne and propyne do not form isomers but the rest exhibit three types of isomerism.

a) Chain isomerism

The triple bond position does not change, but the chain structure differs.

e.g. C_3H_8 $CH_3CH_2CH_2\ C\equiv CH$ – pentyne



$CH_3\underset{CH_3}{C}HC\equiv CH$ -methyl-3-butyne

b) Position Isomerism

It is due to different positions of the triple bond in the same chain e.g.

C_4H_6

$CH_3CH_2C\equiv CH$ $CH_3C\equiv CCH_3$

1 –butyne 2 –butyne

c) Function Isomerism

Due to the formation of dienes i.e. alkenes with two double bonds

C_4H_6

$CH_3CH_2C\equiv CH$ - 1 –Butyne

$CH_2 = CH–CH=CH_2$ – 1, 3 - butadiene

Alkynes do not show **geometrical isomerism** because the molecule around the triple bond is linear.

Industrial sources

Ethyne is manufactured primarily from natural gas and higher alkanes obtained from petroleum.

$$2CH_4 \xrightarrow[\text{Electric arc}]{1500^0C} CH \equiv CH + 3H_2$$

Also can be obtained by treating calcium dicarbide with water.

1

Calcium dicarbide is obtained by reducing quicklime, obtained from lime stone, with coke in an electric furnace at 2000 – 3000^{0}C

$$\underset{\text{(Lime stone)}}{CaCO_3} \xrightarrow{\text{heat}} \underset{\text{(Quicklime)}}{CaO} + CO_2$$

$$CaO + 3C \xrightarrow{2000–3000^0C} \underset{\text{(Calcium-di-carbide)}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{(Ethyne)}}{CH \equiv CH} + Ca(OH)_2$$

This method is now obsolete owing to high electrical costs involved in maintaining the high temperatures in the furnace.

Synthetic preparations

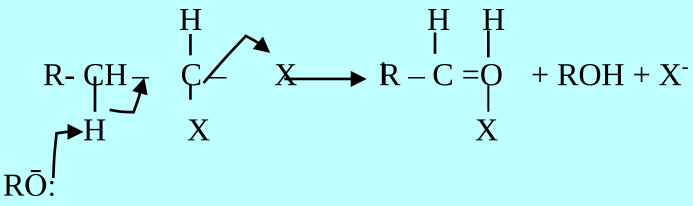
a) From diahalogen compounds.

$$RCH_2\,CH-X_2 \xrightarrow[\text{KOH (excess)}]{\text{Hot alcoholic}} RC\equiv CH + 2HX + H_2O$$

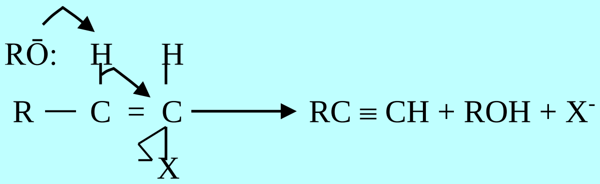
$$R-CX_2CH_3 \xrightarrow[\text{KOH}]{\text{Excess hot alcoholic}} RC\equiv CH + 2HX + H_2O$$

Mechanism; $KOH \rightleftharpoons K^+ + \bar{O}H$

$$ROH + {}^-OH \rightleftharpoons R\bar{O} + H_2O$$



Another RŌ then removes the remaining hydrogen atom



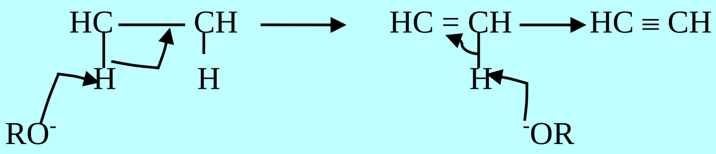
Example.

$$BrCH_2CH_2Br \xrightarrow[\text{KOH}]{\text{Alcohol}} CH\equiv CH$$

Mechanism

$$KOH \rightleftharpoons K^+ + OH^-$$

$$ROH + {-OH} \longrightarrow RO^- + H_2O$$



REACTIONS

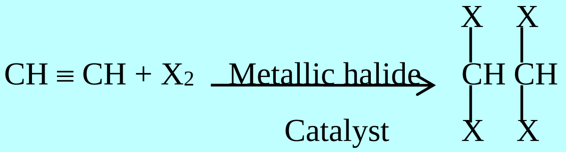
a) Addition of hydrogen

$$CH \equiv CH + H_2 \xrightarrow[\text{Catalyst}]{\text{Pt, Pd, or Ni}} CH_3CH_3$$

Note: - Applies to the rest of Alkynes

- Nickel (Ni) requires heating about (125^0C-250^oC)

b) Addition of Halogens



$$CH \equiv CH + X_2 \xrightarrow[\text{Catalyst}]{\text{Metallic halide}} \begin{matrix} X & X \\ | & | \\ CH & CH \\ | & | \\ X & X \end{matrix}$$

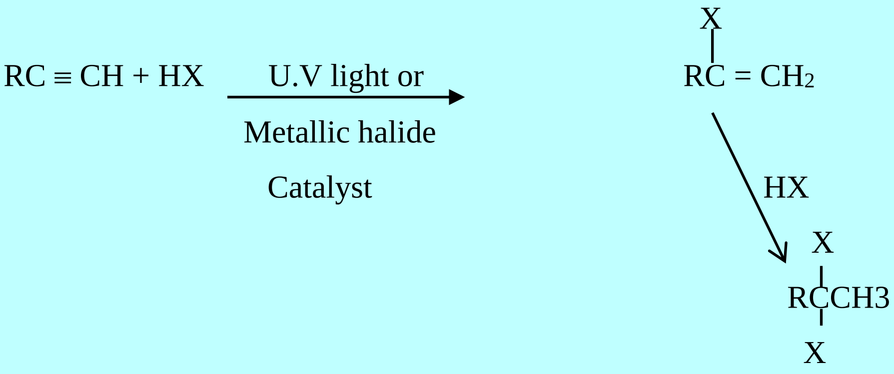
(1, 1, 2, 2 –Tetrahaloethane)

Note: - Applies to the rest of Alkynes

- In the absence of a catalyst, chlorine reacts explosively with ethyne yielding hydrogen chloride and carbon

$$CH \equiv CH + Cl_2 \longrightarrow 2HCl + 2C$$

c) Addition of Hydrogen Halides

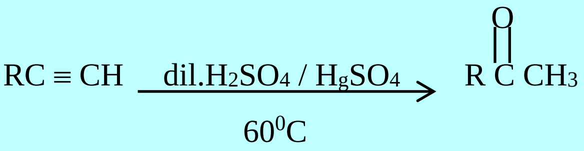


$$RC \equiv CH + HX \xrightarrow[\text{Metallic halide Catalyst}]{\text{U.V light or}} \overset{\overset{X}{|}}{RC} = CH_2 \xrightarrow{HX} \underset{\underset{X}{|}}{\overset{\overset{X}{|}}{RCCH3}}$$

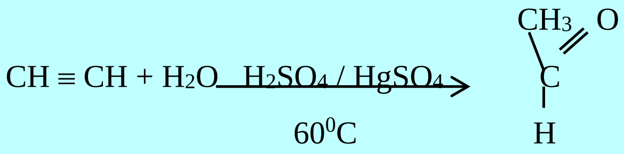
1, 1 dihalo (Alkene)

Note: Rate of reaction HI > HBr > HCl.

d) Addition of water



$$RC \equiv CH \xrightarrow[60^0C]{dil.H_2SO_4 / HgSO_4} RCOCH_3$$

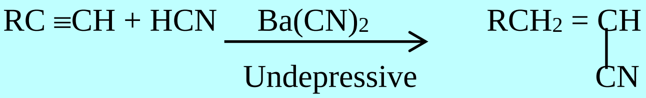


E.g. $$CH \equiv CH + H_2O \xrightarrow[60^0C]{H_2SO_4 / HgSO_4} CH_3CHO$$

Ethanal

The reaction is initiated by nucleophilic attack.

e) Addition of Hydrogen cyanide



$$RC \equiv CH + HCN \xrightarrow[Undepressive]{Ba(CN)_2} RCH_2 = CH(CN)$$

f) Dimerization of Ethyne

Ethyne dimerizes in a solution of copper (1) chloride and ammonium chloride in hydrochloric acid

$$CH \equiv CH + CH \equiv CH \xrightarrow[In\ HCl]{CuCl,\ NH_4Cl} CH_2 = CH \equiv CH$$

(1-Buten-3-yne)

g) Additional of methanol

$$CH \equiv CH + 2HCHO \xrightarrow[High\ pressure]{Cu_2C_2} HOCH_2C \equiv CCH_2OH$$

(Butyne-1, 4, diol)

$$\downarrow H_2/Pt$$

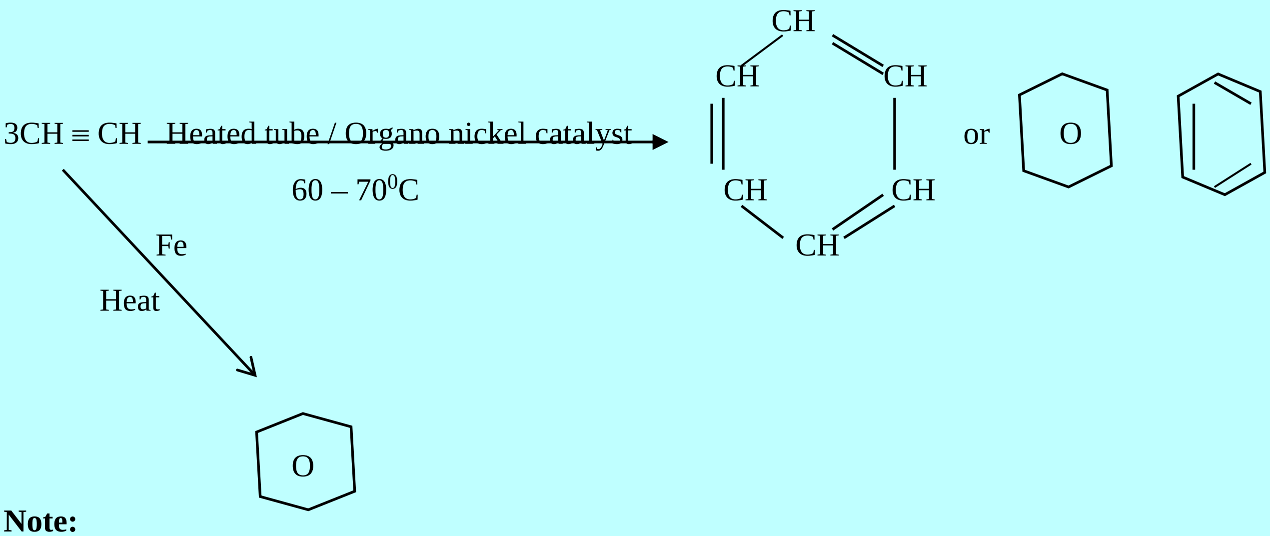
$$CH_2 = CHCH = CH_2 \xleftarrow{Al_2O_3,\ 270^0C} HOCH_2CH_2CH_2CH_2OH$$

(Buta – 1, 3 – diene) $-2H_2O$ (Butane 1, 4, diol)

This is an important reagent in the preparation of synthetic rubbers.

Polymerization of Ethyne.

Polymerizes to benzene when passed through a heated tube containing a complex organo-nickel catalyst.



Note:

Alkynes with terminal triple bonds when passed through a solution of ammoniacal silver nitrate, deposits a white precipitate of silver dicarbide

E.g. Ethyne

$$HC \equiv CH_{(g)} + 2NH_{3\,(aq)} + 2AgNO_{3\,(aq)} \longrightarrow AgC{\equiv}CAg_{(s)} + 2NH_4NO_{3\,(aq)}$$

(White ppt)

And; When passed through a solution of ammoniacal copper (1) chloride, deposits a red ppt of copper (1) dicarbide

E.g. Ethyne

$$HC \equiv CH_{(g)} + 2NH_{3\,(g)} + Cu_2Cl_{2\,(g)} \longrightarrow CuC = CCu_{(g)} + 2NH_4Cl_{(g)}$$

Red ppt

Alkynes of the type RC ≡ CR (with internal triple bond) do not react and therefore these reactions can be used to test for the terminal triple bond.

These heavy metal dicarbides are dangerously sensitive explosives

Formation of Ethenyl sodium

Ethyne reacts with sodium in liquid ammonia to form ethenyl sodium

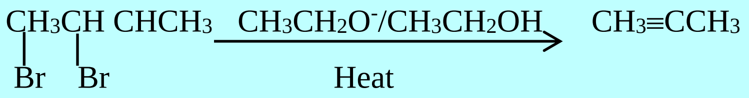
$2\ CH \equiv CH + 2Na \xrightarrow{\text{liquid } NH_3} 2\ CH \equiv {}^{-}CNa^{+} + H_2$

$CH \equiv CNa + CH_3I \longrightarrow CH \equiv CCH_3 + NaI$

(Propyne)

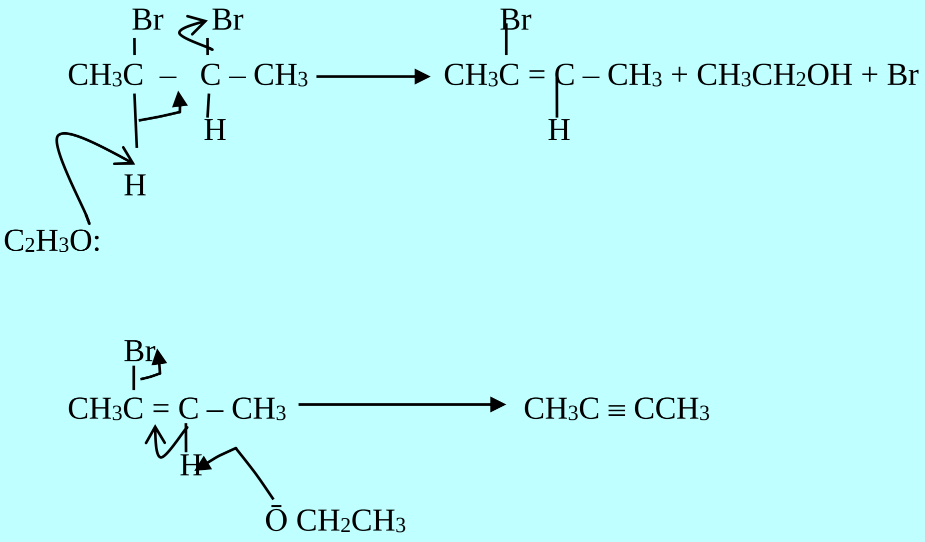
Examples

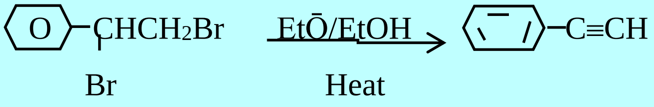
Complete the following and in each case outline a mechanism for the reaction.

a) 

$CH_3\underset{|\atop Br}{CH}\ \underset{|\atop Br}{CH}CH_3 \xrightarrow[\text{Heat}]{CH_3CH_2O^-/CH_3CH_2OH} CH_3\equiv CCH_3$

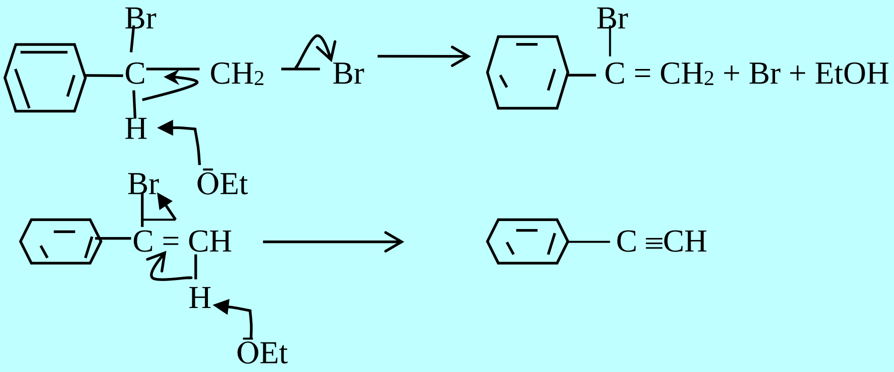
Mechanism



b) 

Mechanism

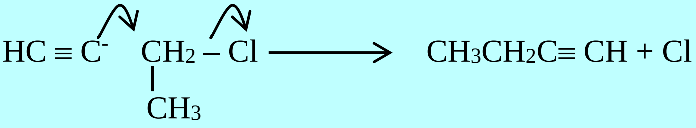
-



c) $CH_3CH_2Cl + HC\equiv Na \xrightarrow{liq.\ NH_3} CH_3CH_2C\equiv CH + Cl^-$

Mechanism

$HC\equiv {}^-CNa^+ \longrightarrow HC\equiv C^- + Na^+$



$$HC \equiv C^- \quad \underset{CH_3}{\underset{|}{CH_2}} - Cl \longrightarrow CH_3CH_2C\equiv CH + Cl$$

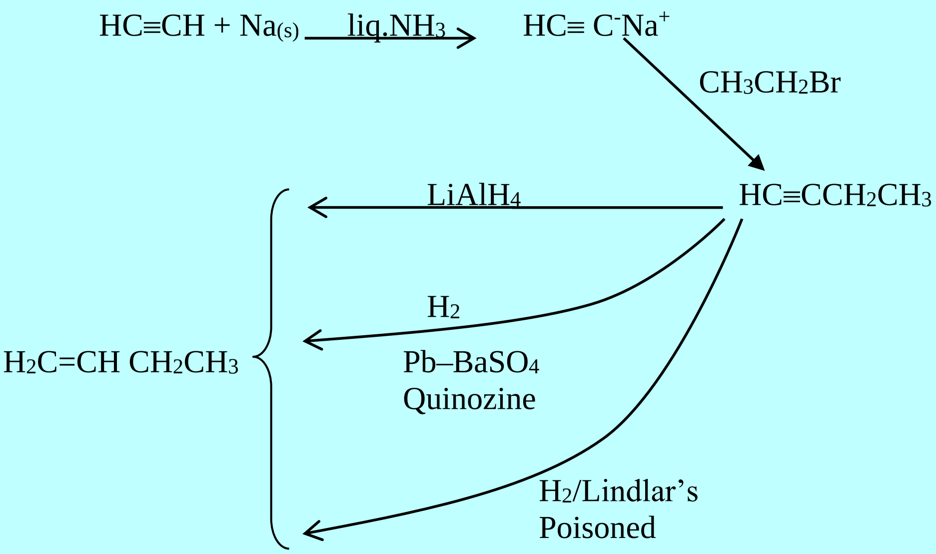
QN: Write equations to show how the following compounds can be synthesized

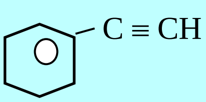
a) CH_3CHO from 1, 2, - dibromoethene

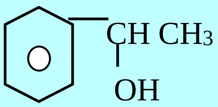
$$CH_2BrCH_2Br \xrightarrow[Heat]{KOH/EtOH} HC\equiv CH$$

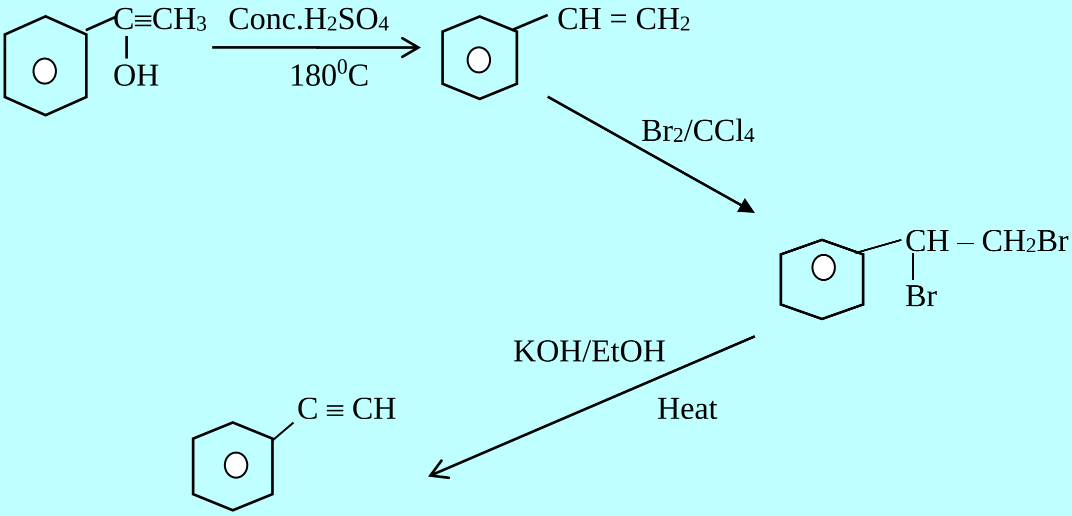
$$HC\equiv CH + H_2O \xrightarrow[60^0C]{H_2SO_4/HgSO_4} CH_3CHO$$

b) $CH_3CH_2CH = CH_2$ from Ethyne



c) 

from 



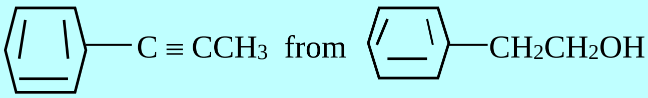
d) $CH_3C\equiv CH$ from Ethene

$$\begin{tikzcd} CH_2{=}CH_2 \arrow[r, "Br_2/CCl_4"] & CH_2BrCH_2Br \arrow[r, "\text{Excess. KOH}/C_2H_5OH", "\text{Heat}"'] & CH{\equiv}CH \arrow[d, "Na"', "\text{Liquid } NH_3"] \\ & CH_3C{\equiv}CH & HC \equiv {}^-CNa^+ \arrow[l, "CH_3Cl"'] \end{tikzcd}$$

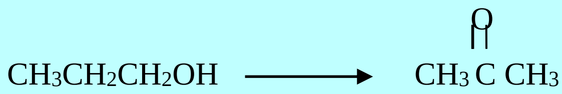
Exercise

a) $CH_3CH_2C{\equiv}CH$ from Ethanol

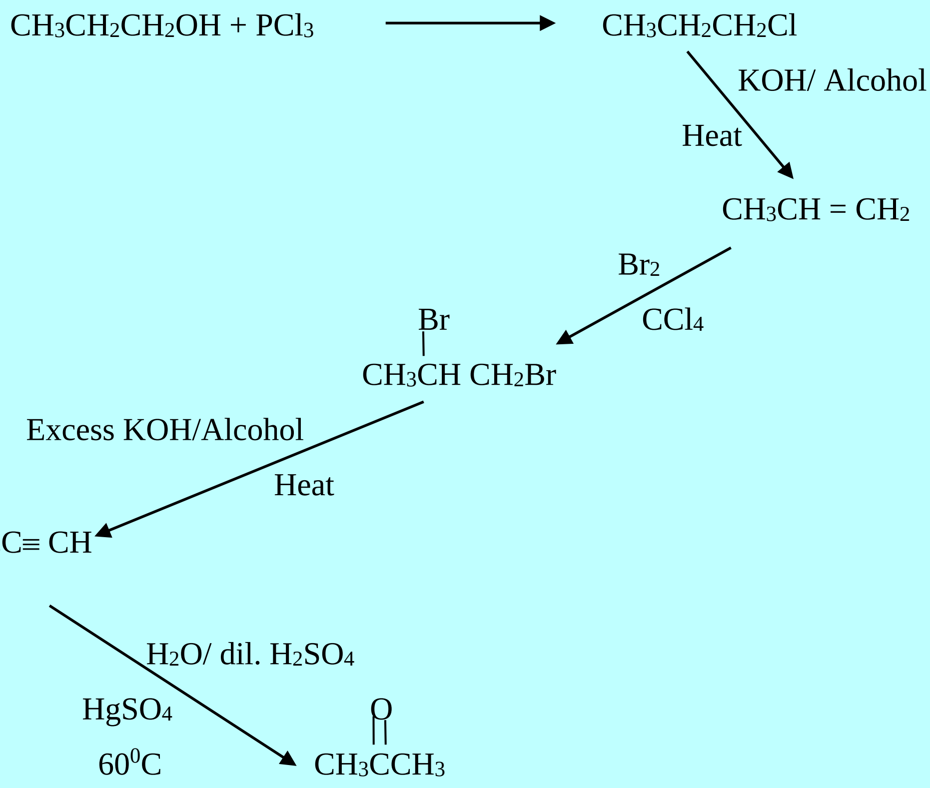
b)



c)



$$CH_3CH_2CH_2OH \longrightarrow CH_3\overset{O}{\overset{||}{C}}CH_3$$



$$CH_3CH_2CH_2OH + PCl_3 \longrightarrow CH_3CH_2CH_2Cl$$

$$CH_3CH_2CH_2Cl \xrightarrow[\text{Heat}]{\text{KOH/ Alcohol}} CH_3CH = CH_2$$

$$CH_3CH = CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\overset{Br}{\overset{|}{C}}H\,CH_2Br$$

$$CH_3\overset{Br}{\overset{|}{C}}H\,CH_2Br \xrightarrow[\text{Heat}]{\text{Excess KOH/Alcohol}} CH_3C{\equiv}\,CH$$

$$CH_3C{\equiv}\,CH \xrightarrow[HgSO_4,\ 60^0C]{H_2O/\ \text{dil. } H_2SO_4} CH_3\overset{O}{\overset{||}{C}}CH_3$$

NB: $CH_3C \equiv CCH_3$ and $CH \equiv CCH_2CH_3$ (Distinguishing them)

(i) <u>Reagent</u>

Tollen’s reagent (silver nitrate solution in ammonia solution)

Observation.

$CH_3\equiv CCH_3$	No observable change
$CH\equiv CCH_2CH_3$	White precipitate forms

Reagent

Fehling’s reagent (copper (1) chloride solution in ammonia solution)

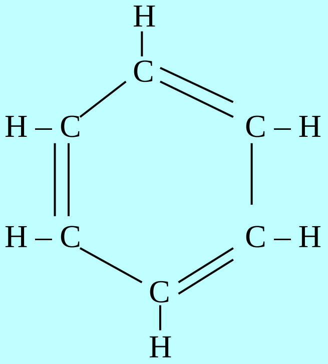
Observation

$CH_3\equiv CCH_3$	No observable change
$CH\equiv CCH_2CH_3$	Red precipitate forms

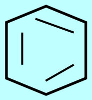
AROMATICITY AND BENZENE

Aromatic compounds are those possessing the ring structures of benzene or other molecular structures that resemble benzene in electronic configuration and chemical behavior.

Benzene

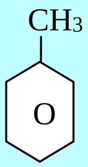


Or

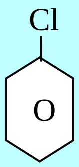


Naming substituted Benzene derivatives

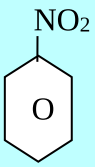
A benzene molecule in which one hydrogen atom has been replaced by an atom / group is referred to as a **Mono-substituted derivative**



Methylbenzene
(Toluene)



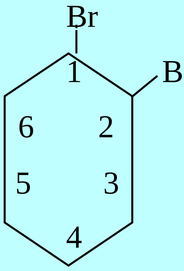
Chlorobenzene



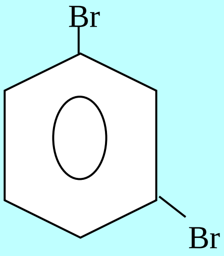
Nitrobenzene

For each di-substituted derivative there are three different Isomers depending upon the position of substitution in the ring

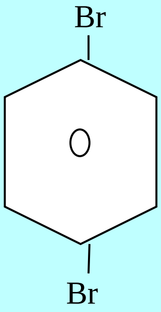
Example



1, 2 – Dibromo benzene
It is ***ortho derivative***, because
two substituents are attached to
adjacent carbon in the ring



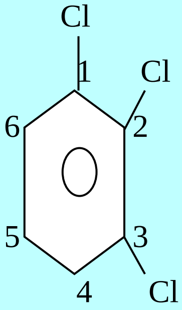
1, 3 Dibromo benzene
It is ***meta derivative***, because
the substituents are in the
next –but-one position



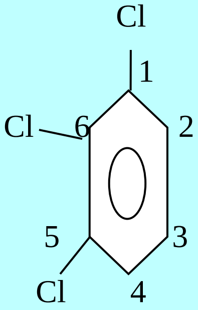
1, 4 – Dibromo benzene
It is ***Para derivative*** because
the two substituents are diametrically opposite

NB: The positions of substitution are indicated by numbering the carbon atoms in the ring and choosing unity so as to give the lowest combination of numbers.

Example

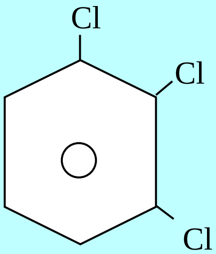


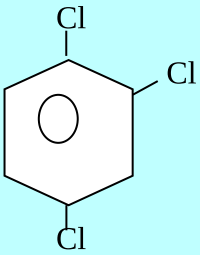
not

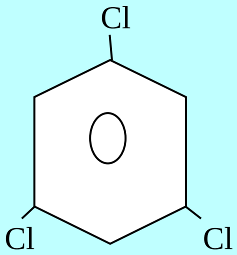


1, 2, 3, Trichlorobenzene

1,5,6 Trichlorobenzene

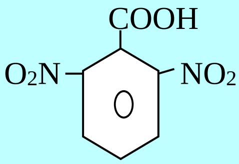






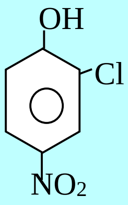
1, 2, 3 – Trichlorobenzene 1, 2, 4 – Trichlorobenzene 1, 3, 5 – Trichlorobenzene

- If one of the groups present gives rise to a compound with a special name, then only two positions of substitution are mentioned.



2, 6- Dinitrobenzene carboxylic acid

2,6 -Dinitro benzoic acid



2 – chloro-4-nitrophenol

NB: For convenience especially when writing complicated structural formulae, the phenyl group is often abbreviated to “ph”.

i.e. $C_6H_5–$ phenyl group “ph”

PHYSICAL PROPERTIES

Benzene is a colourless liquid (b.p 80^0C, m.p 5.5^0C) with a characteristic aromatic smell. It is immiscible with water, (forms upper layer) but it is soluble in organic solvents. It burns with a yellow smoky and luminous flame like other aromatic compounds. It is highly toxic

INDUSTRIAL SOURCE

Benzene can be obtained from coal tar and petroleum.

Petroleum vapour containing hexane and other hydrocarbons is passed over a finely divided platinum catalyst at 500°C and under 10–20 atmospheric pressure. This process is known as “**reforming**”

$$\underset{\text{(Hexane)}}{C_6H_{14}} \xrightarrow[500^0C,\ 10\text{-}20atm]{Pt\ (catalyst)} C_6H_6 + 4H_2$$

SYNTHETIC PREPARATIONS

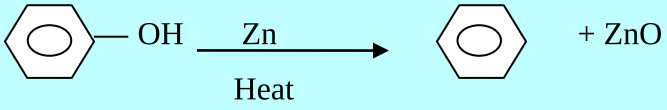
- **Decarboxylation of a sodium salt**

Sodium benzoate is fused with soda lime (NaOH $_{(s)}$)

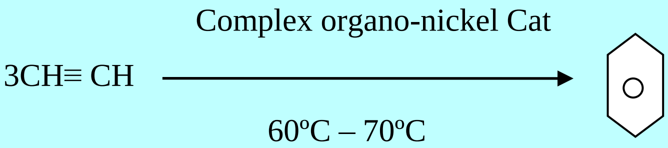
$$C_6H_5COONa \xrightarrow[NaOH]{Fuse} C_6H_6 + Na_2CO_3$$

- **From phenol**

Phenol vapour is passed over heated zinc dust



- **Polymerization of Ethyne**

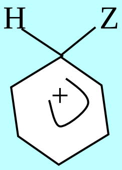


REACTIONS

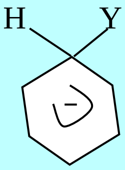
The availability of π- electrons in benzene serves as a source of electrons (a nucleophilic reagent) and its reactions are characterized by electrophilic substitution in the ring.

An unstable intermediate is formed in which the entering atom/group and the leaving hydrogen atom are both momentarily bonded to the ring. This causes a disruption in the symmetry of the delocalized $\pi -$ electrons and may be illustrated by an incomplete circle inside the ring.

If the attacking species is an electrophile, which is most common, then the reaction intermediate will carry a positive charge which is distributed over the bulk of the molecule



Electrophilic
attack



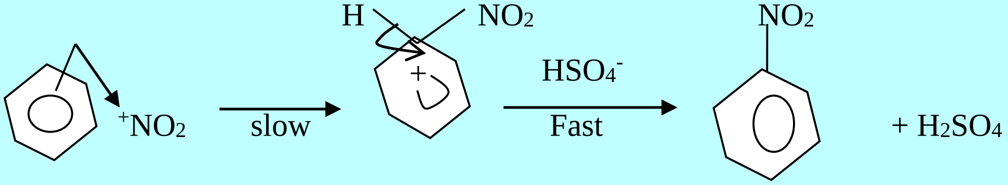
Nucleophilic
attack

In the case of nucleophilic substitution, a negative charge is distributed over the molecule.

- **Nitration**

A nitrating mixture (equal molar quantities of concentrated nitric and sulphuric acids) is carefully added to the benzene and the mixture is then refluxed in a water bath maintained at 55ºC – 60⁰C. Weaker nitric acid functions as a base in highly acidic sulphuric acid medium releasing the Nitronium cation (${}^+NO_2$) which then undergoes substitution in the ring.

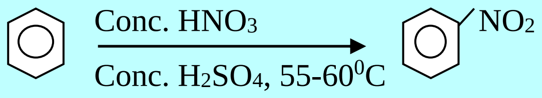
Mechanism: $HNO_3 + 2H_2SO_4 \overset{\text{Slow}}{\rightleftharpoons} {}^+NO_2 + H_3O^+ + 2HSO_4^-$



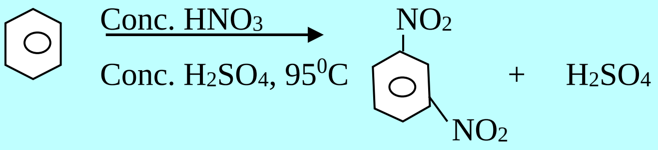
Nitrobenzene

(Pale yellow liquid)

i.e.



But at 95ºC, 1, 3 – dinitrobenzene is obtained



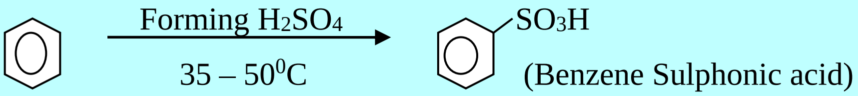
(1, 3 – Dinitrobenzene)

- **Sulphonation**

Sulphonation of benzene to form benzene Sulphonic acid is best carried out using fuming sulphuric acid. The reaction takes place on gently warming to 35 – 50⁰C.

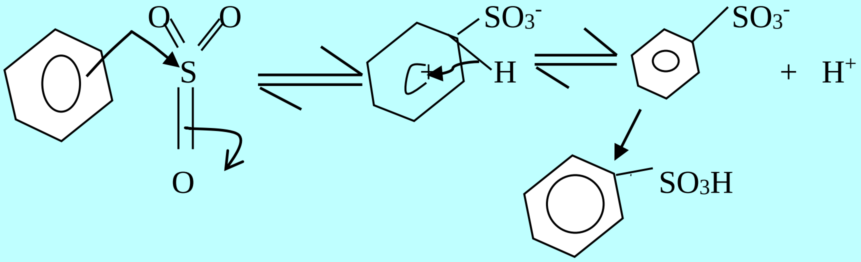
N.B Ordinary concentrated sulphuric acid may be used, but the mixture then requires refluxing for several hours.

The most probable mode of attack seems to be electrophilic substitution by the electron-deficient sulphur (iv) oxide, SO_3, although the SO_3H^+ ion has been considered as a possibility.



Mechanism;

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

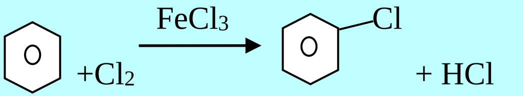


The reaction is reversible with equilibrium tending towards the left.

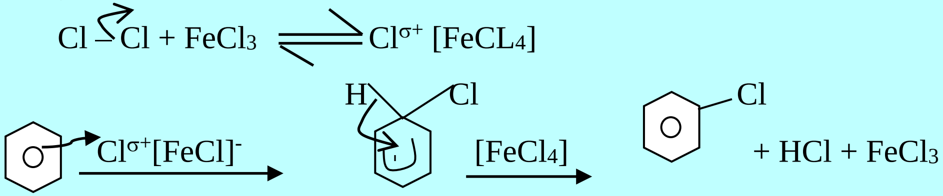
- **Halogenation**

Substitution by chlorine / bromine in benzene takes place readily at room temperature in the presence of a halogen carrier catalyst

E.g. Fe, Al



Mechanism;



(Chlorobenzene)

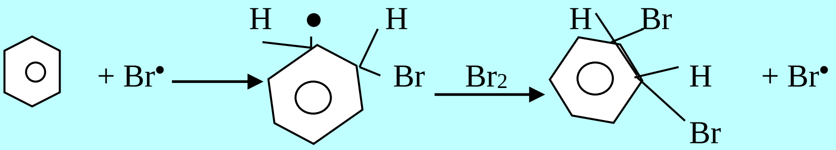
In the presence of direct sunlight or ultra-violet radiation benzene reacts with chlorine or bromine at room temperature to form white crystals of 1, 2, 3, 4, 5, 6- hexachlorocyclohexane or hexabromocyclolexane respectively

$$C_6H_6 + 3Br_2 \xrightarrow[r.t]{U.V} C_6H_6Br_6$$

(Benzene hexabromide)

It is an addition reaction and proceeds via a free-radical mechanism.

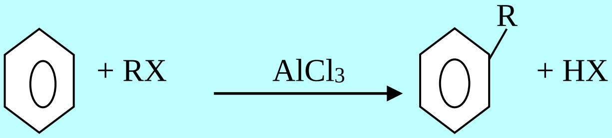
$Br_2 \xrightarrow{U.V} 2\,Br^{\bullet}$ chain initiation



The propagation stages are repeated until $C_6H_6Br_6$ is formed as the major product. The final product has several stereo isomers and in the case of the hexachloride, one of these is a powerful insecticide.

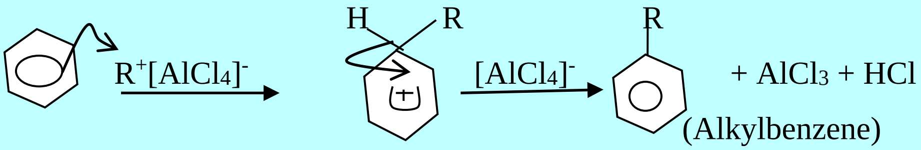
- **Friedel-crafts Alkylation**

Alkylation is a reaction of aromatic compounds with alkyl halides (R–X) in the presence of a halogen carrier to produce alkyl aromatic compound

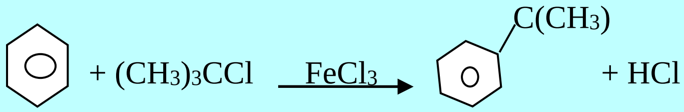


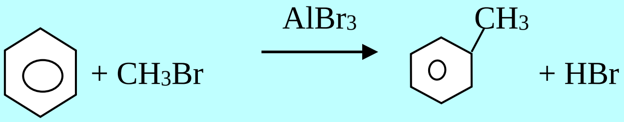
Mechanism

$$R - X + AlCl_3 \rightleftharpoons R^+[AlCl_4]^-$$



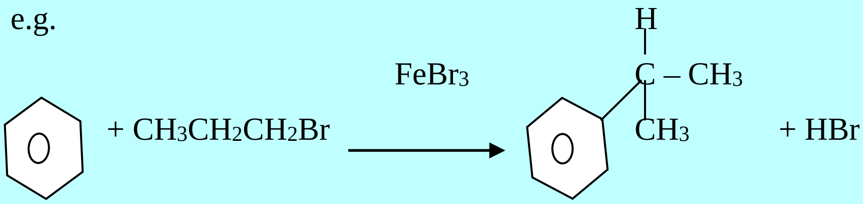
e.g.



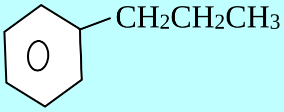


Rearrangement can take place

e.g.



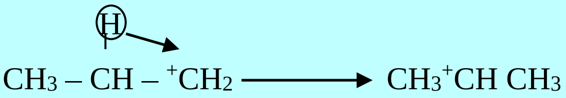
But not



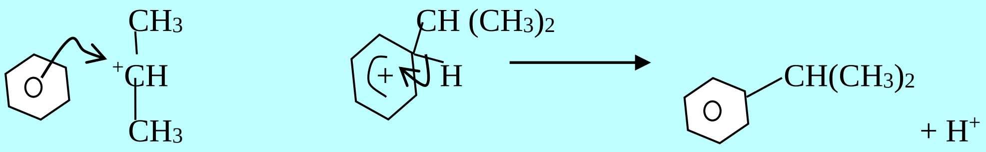
Mechanism

$$CH_3CH_2CH_2 - Br + FeBr_3 \rightleftharpoons CH_3CH_2{}^{+}CH_2 + FeBr_4^{-}$$

The primary carbonium ion formed undergoes rearrangement to give a more stable secondary carbonium ion

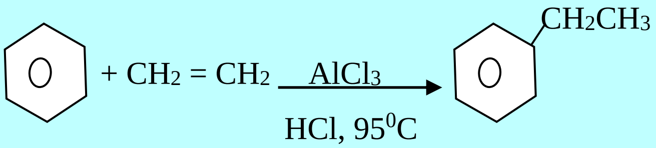


$$CH_3 - \overset{H}{CH} - {}^{+}CH_2 \longrightarrow CH_3{}^{+}CH\ CH_3$$



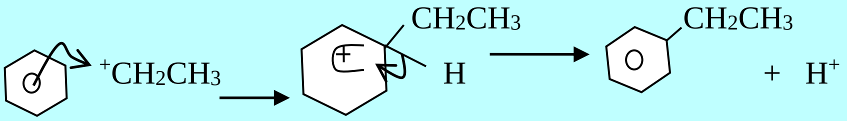
$[FeBr_4^{-} + H^{+} \longrightarrow FeBr_3 + HBr]$

N.B: Alkyl aromatic compound can also be produced using alkenes.

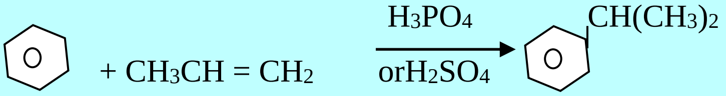


Mechanism;

$$CH_2 = CH_2 + H^{+} \longrightarrow {}^{+}CH_2CH_3$$



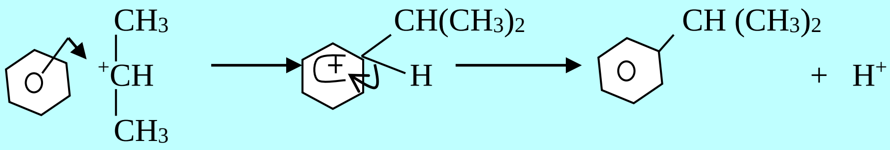
Also:



Mechanism;

$$H_3PO_4 \rightleftharpoons H^+ + {}^-OPO_3H_2$$

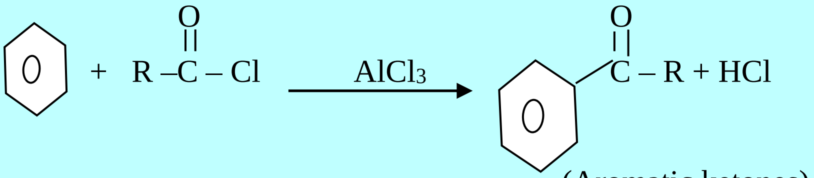
$$CH_3CH = CH_2 + H^+ \longrightarrow CH_3{}^+CH\ CH_3$$



$$[{}^-OPO_3H_2 + H^+ \longrightarrow H_2PO_4]$$

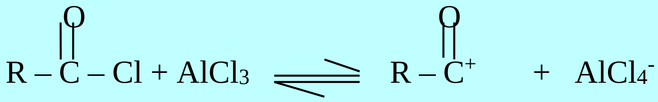
- **<u>Friedel – crafts Acylation.</u>**

Is a reaction where aromatic compounds react with acid chlorides in the presence of a halogen carrier to give aromatic ketones as the products. The mixture is refluxed on a water bath at 50^{0}C (It is a condensation reaction)

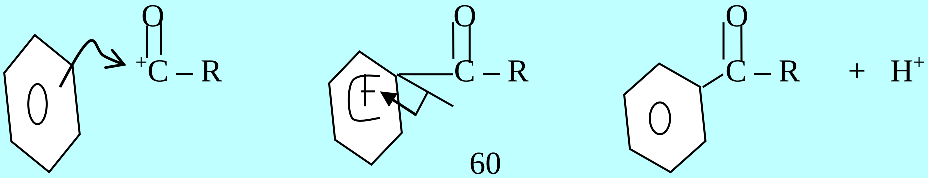


(Aromatic ketones)

Mechanism:



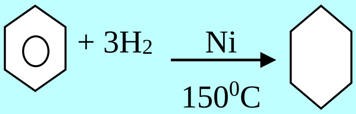
$$R - \overset{\overset{\displaystyle O}{||}}{C} - Cl + AlCl_3 \rightleftharpoons R - \overset{\overset{\displaystyle O}{||}}{C^+} \quad + \quad AlCl_4^-$$



$[H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl]$

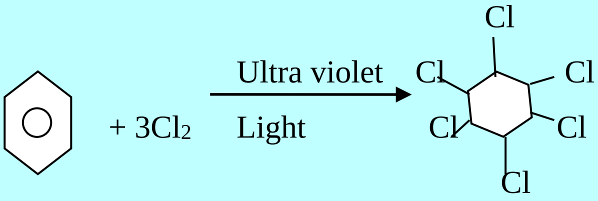
NB: A condensation reaction is one in which a new compound is formed from two or more reactants together with the elimination of a simple molecule such as water, ammonia, hydrogen chloride etc.

- **Reaction with Hydrogen**



(cyclohexane)

- **Reaction with chlorine in the presence of ultra violet light**

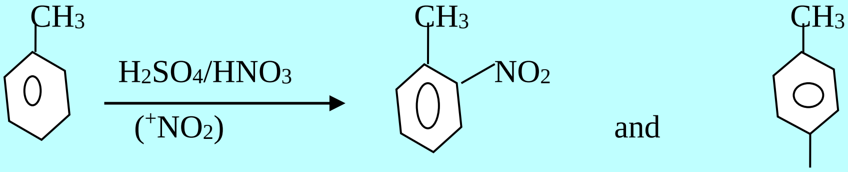


(1, 2, 3, 4, 5, 6, hexa cyclohexane)

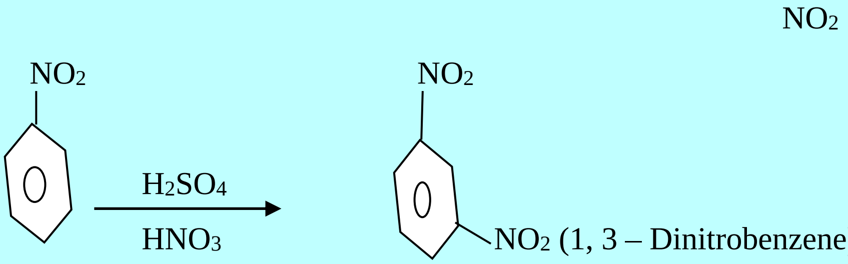
- **Orientation of substitution in a mono substituted benzene nucleus.**

When a second atom / group of atoms is attacked to a monosubstituted benzene ring, the position of substitution is determined by the nature of the substituent already attached to the ring and is not dependent upon the attacking atom or group of atoms

E.g. the Nitration and Bromination of methylbenzene (toluene) and nitrobenzene.



And

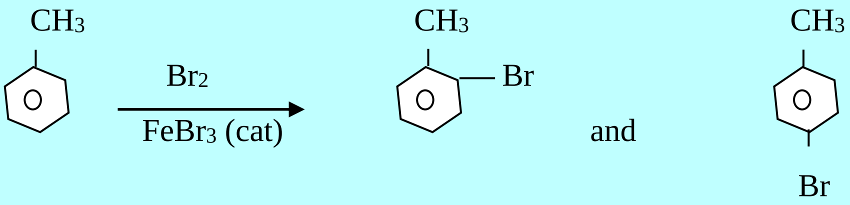


(1, 3 – Dinitrobenzene)

It’s the methyl or nitro group which actually determines the position of a secondary substitution. And the position of substitution of the second substituent is governed largely by whether or not the atom or group already present is donating electrons to the ring or withdrawing electrons from it.

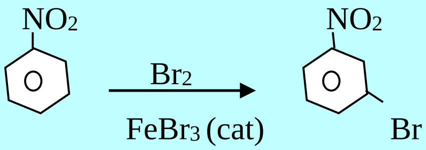
Electron donating substituents enhance the availability of electrons about the ring which is said to be activated. The 2 – and 4 – positions are the sites predominantly affected by the increase in electron density, rendering them more vulnerable to attack by an electrophilic reagent.

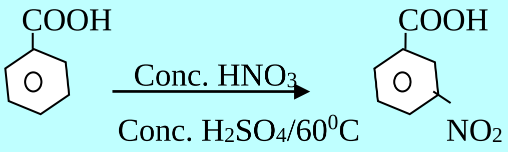
e.g.



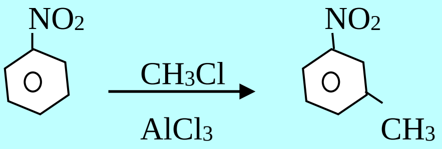
(Bromo – 2 – and Bromo – 4 – methyl benzene)

Electron withdrawing substituents reduce the availability of electrons about the ring, which is said to be deactivated; electrons are withdrawn mainly from the 2 – and 4 positions rendering the 3 – position relatively richer in electrons. And any subsequent attack by an electrophile takes place preferentially in the 3 - position





3 – nitrobenzoic acid



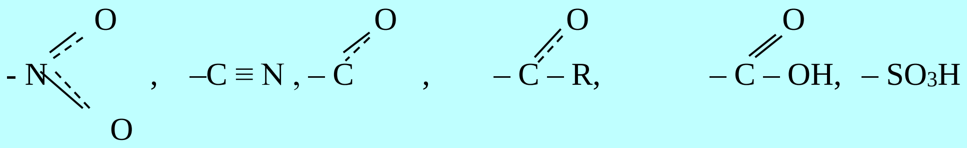
3-methyl nitrobenzene

NOTE: Examples

Ring activating directing to 2- and 4 – positions

$-R$, $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$

Ring deactivating, directing to 3 – position

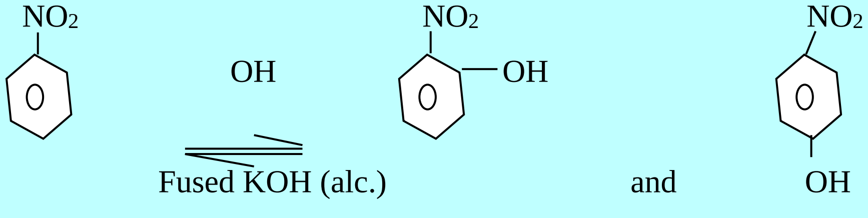


$$-N\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\ ,\quad -C\equiv N\ ,\ -\overset{O}{\overset{\|}{C}}\quad ,\quad -\overset{O}{\overset{\|}{C}}-R,\qquad -\overset{O}{\overset{\|}{C}}-OH,\ \ -SO_3H$$

But Halogens prove an exception to those general rules and direct to the 2 – and 4 – positions despite withdrawing electrons from the ring.

NB:

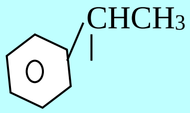
- Saturated group direct predominantly to the 2-and 4- position
- Unsaturated groups direct predominantly to the 3-positions hence halogens are saturated group
- If a strong electron withdrawing substituent is already attacked to the ring, then the relative decrease in the availability of the electrons in the 2- and 4- positions may render these sites sufficiently deficient in electrons as to undergo attack by a nucleophile. E.g. If nitro benzene is fused with potassium hydroxide in the presence of air 2- nitrophenol is formed as the major product, because the electrons with drawing inductive effect of the nitro group makes the 2- position more deficient in electrons than the more distant 4-



Major product

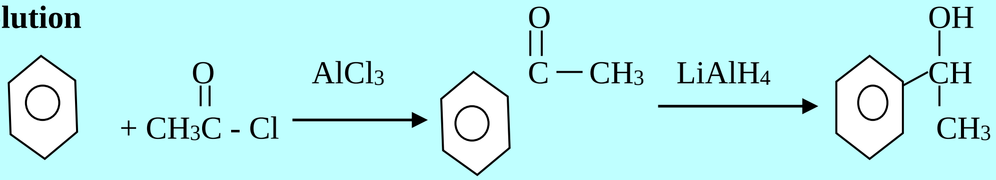
Example;

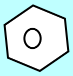
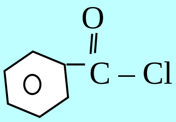
Write equation to show how the following conversions can be carried out



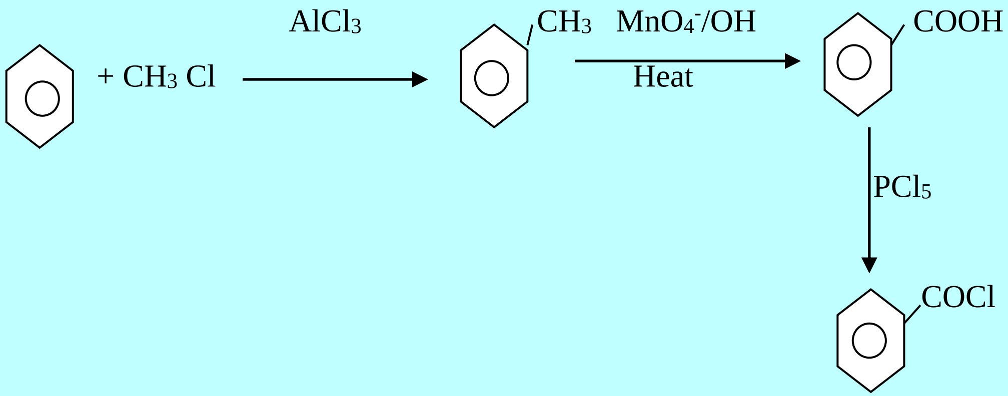
1. Benzene to OH

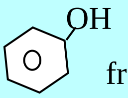
Solution



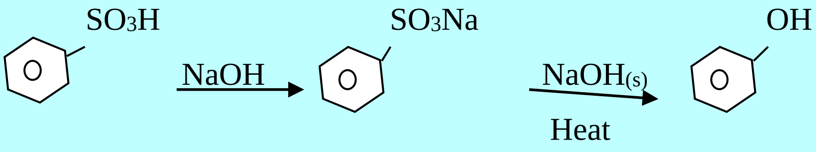
2.  to 

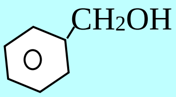
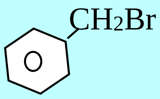
Solution

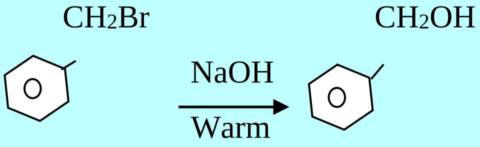


3.  from benzene sulphonic acid

Solution



4.  from 

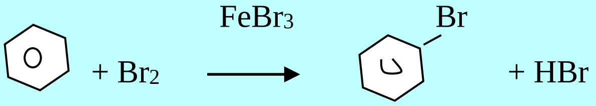


Write notes on the following

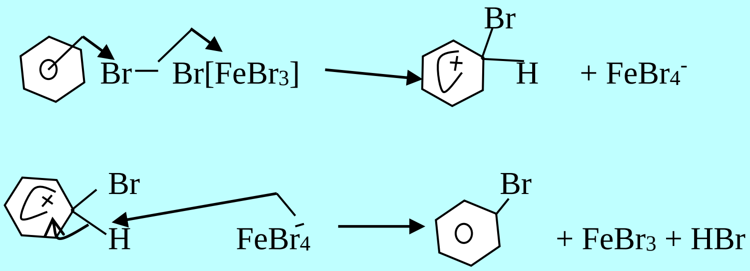
a) Electrophilic substitution reaction

Solution: This is a reaction in which a hydrogen atom in the benzene ring is replaced by another atom or group of atoms.

E.g. Benzene reacts with bromine in the presence of Iron (iii) bromide

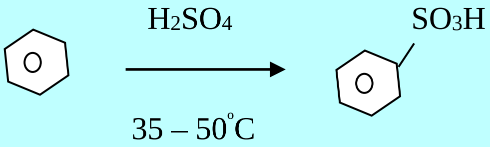


Mechanism

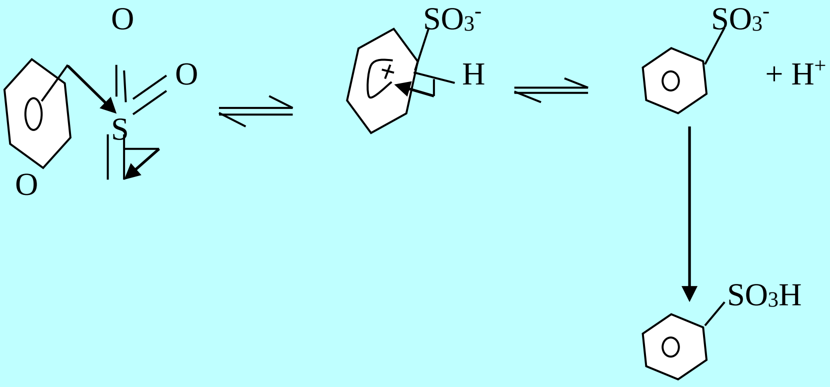


b) **Sulphonation** is the reaction in which aromatic compounds react with forming sulphiric acid

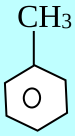
Example: Benzene react with fuming sulphiric acid at a temperature of about 35ºC – 50ºC to form Benzene Sulphonic acid



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



METHYLBENZENE (TOLUENE)

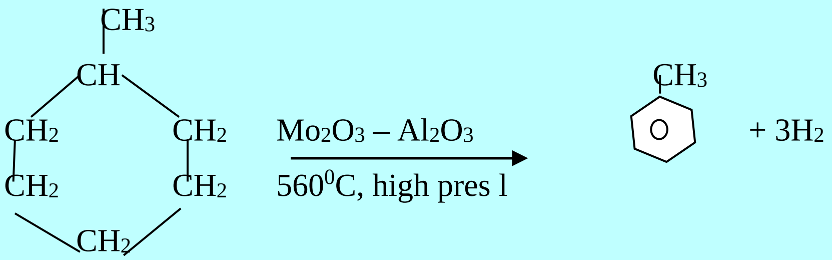


Is a higher homologue of benzene, colourless liquid, insoluble in water but soluble in organic solvents.

It’s a better solvent than benzene since its fumes are less toxic that those of benzene.

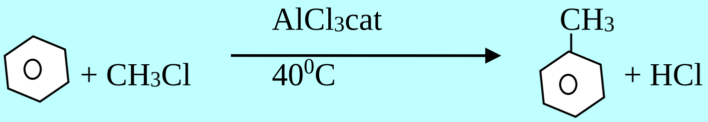
Industrial Source

Methyl cyclohexane is heated under pressure in the presence of molybdenum (III) oxide and Aluminium oxide catalysts where dehydrogenation occurs.



Synthetic preparations

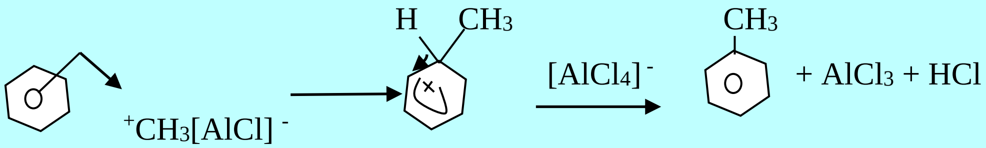
a) **Chloromethane** is bubbled through dry benzene in the presence of an anhydrous aluminium chloride catalyst at a temperature of 40ºC.



A better yield is obtained if the mass of catalyst used is about 1/3 that of benzene

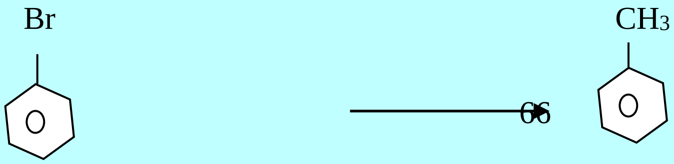
Mechanism

$$CH_3Cl + AlCl \rightleftharpoons {}^{+}CH_3[AlCl_4]^{-}$$



b) **Wurtz synthesis of alkanes**

Sodium is slowly added to a dry ethereal solution of bromobenzene and iodomethane



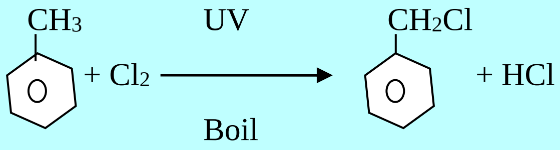
Dry

+ CH_3I + 2Na $(C_2H_5)_2O$ + NaBr + NaI

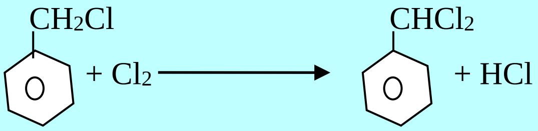
Then methyl benzene is separated by fractional distillation

REACTIONS

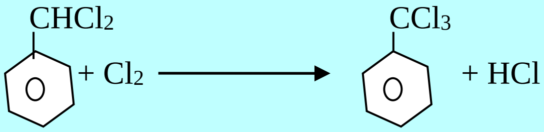
a) Side chain substitution, which proceeds via a free radial mechanism chlorine is bubbled through boiling methylbenzene in the presence of ultra-violet light, substitution occurs in the side chain yielding successively chloromethyl benzene, dichloromethyl benzene and trichrolomethyl benzene.



Chloromethyl benzene
(Benzyl chloride)



Dichloromethyl benzene
(Benzal chloride)



trichloro methyl benzene
(Benzotrichloride)

Also Bromination of methylbenzene takes place under similar conditions

Mechanism

Step 1: Chain initiation

$$Cl_2 \xrightarrow{UV} 2Cl^{\bullet}$$

Step 2: Chain propagation

a) $C_6H_5CH_3 + Cl^{\bullet} \longrightarrow C_6H_5CH_2^{\bullet} + HCl$

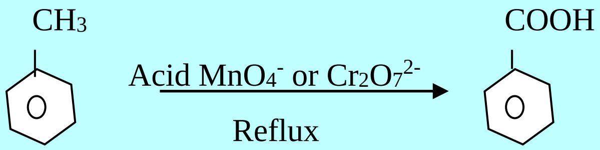
b) $C_6H_5^{\bullet}CH_2 + Cl_2 \longrightarrow C_6H_5CH_2Cl + Cl^{\bullet}$

Step 2 (a) and (b) are repeated to give the further product i.e.

$C_6H_5CHCl_2$ and $C_6H_5CCl_3$

Oxidation (side chain reaction)

Using acidified potassium manganate (vii), potassium dichromate (vi) or dilute nitric acid

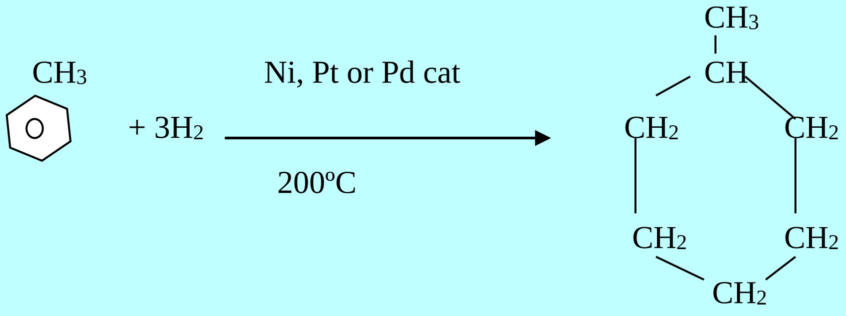


Benzene carboxylic acid (benzoic acid)

NB: If a milder oxidizing agent is used e.g. Manganese (IV) oxide or chromium (VI) dichloride dioxide (chromyl chloride), Methylbenzene is only oxidized as far as benzene carbaldehyde (Benzaldehyde).

<u>Hydrogenation (addition in the ring)</u>

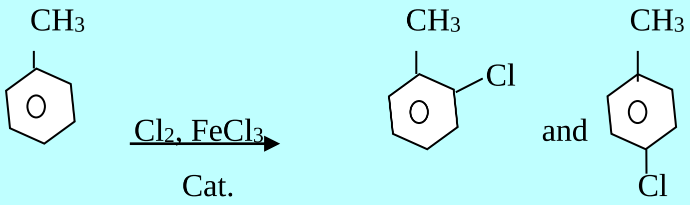
Methylbenzene Vapour is passed over finely divided Nickel, Platinum or Palladium catalyst at 200ºC, addition occurs giving methylcyclohexane.



methylcyclohexane

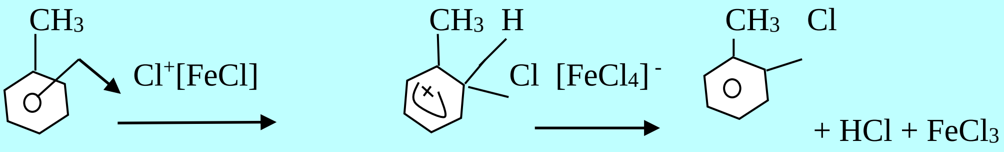
<u>Ring substitution</u>

If methylbenzene is treated with chlorine /bromine in the presence of a suitable halogen carrier at room temperature and in absence of sunlight

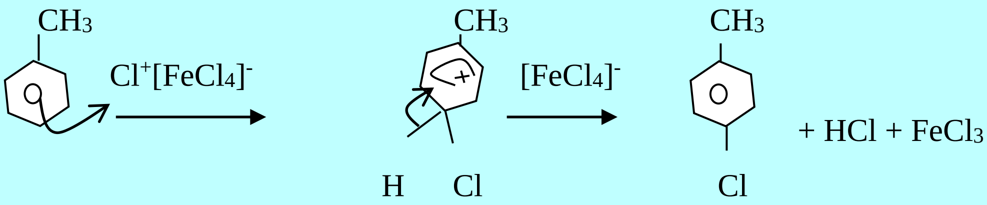


Chloro – 2 – and Chloro – 4 – methylbenzene

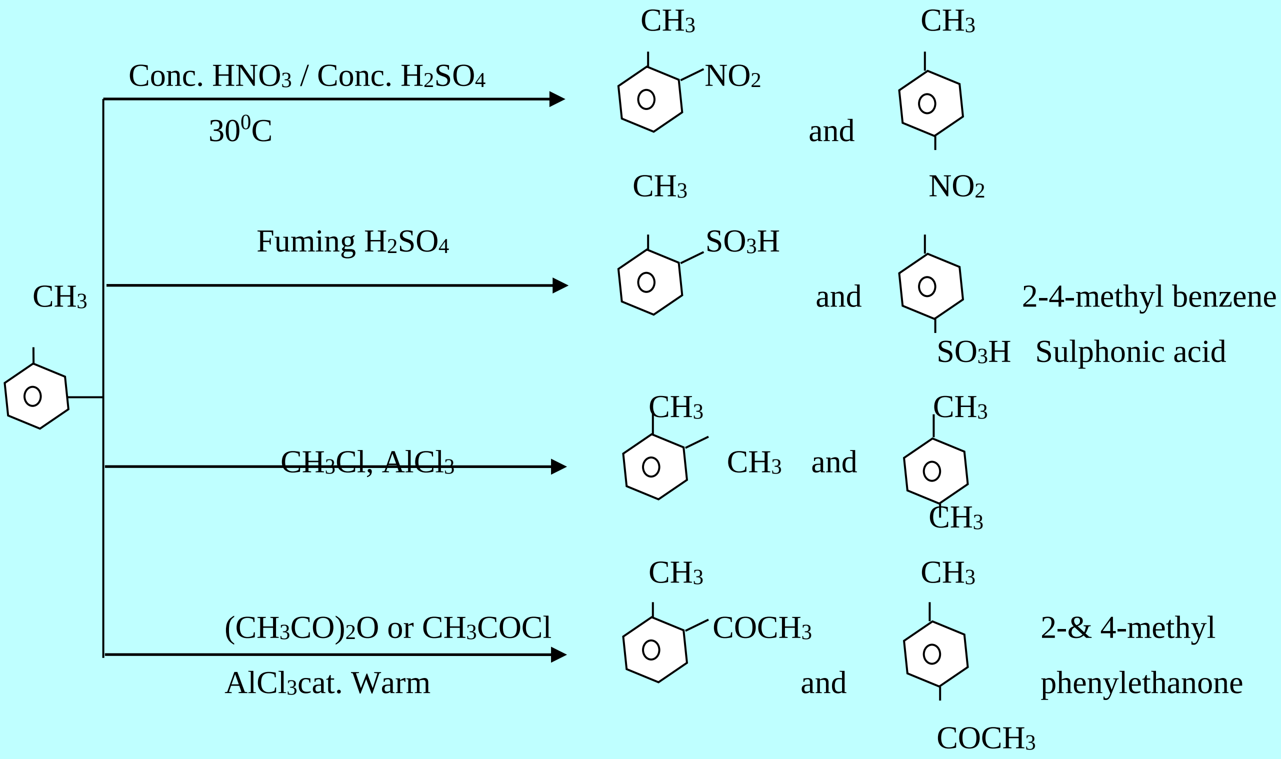
Mechanism $Cl-Cl \quad FeCl_3 \longrightarrow Cl^+[FeCl_4]^-$



And

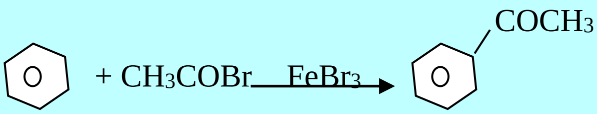


Other ring substitution reactions

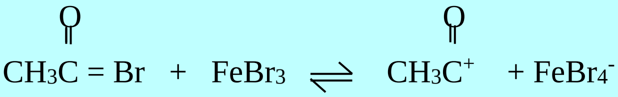


Example 1:

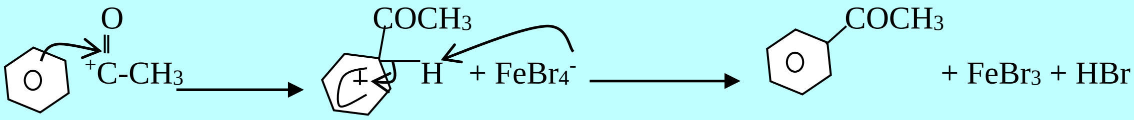
Complete the following and outline a mechanism



Mechanism



$$CH_3\overset{O}{\overset{\|}{C}} = Br \;+\; FeBr_3 \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}{}^+ \;+\; FeBr_4^-$$

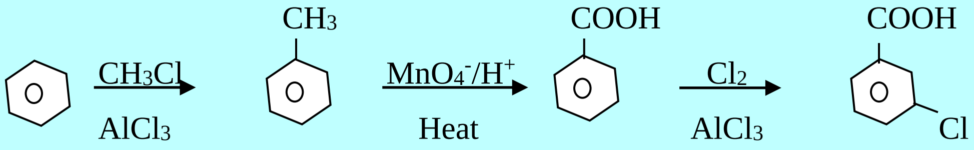


Example 2.

Give a reaction scheme to show how the following conversions can be effected.

2– Chloro benzoic acid from benzene

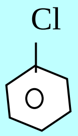
Solution:



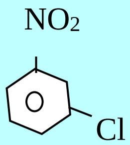
HALOHYDROCARBONS

Are derivatives of alkanes with formula R-X where R is an alkyl group e.g. CH_3CH_2Br and X an halogen such as Cl^-, I^-, Br^-, Fe^-

Alkyl halides are compounds in which the halogen atom is attached directly to an aromatic ring. Formula ArX e.g.



and



Chlorobenzene 3-chloronitro benzene

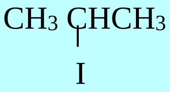
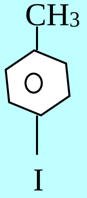
Vinyl halides (halo ethenes) are compounds in which the halogen is attacked directly to a doubly bonded carbon e.g.

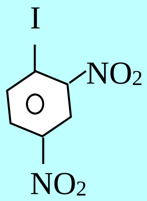
Chloroethene (vinyl chloride) $CH_2 = CHCl$

Unsaturated halogen compounds of the type $CH_2= CHCH_2X$ are called Alkyl halides.

If two halogen atoms are attached to adjacent carbons, the compound is referred to as a VICINAL (VIC) DIHALIDE and if both are attached to the same carbon, then it is known as a GERMINAL (GEM) DIHALIDE

Nomenclature

CH_3Cl	Chloromethane	(Methyl chloride)
 $\underset{\displaystyle I}{CH_3\,CHCH_3}$	2- Iodopropane	(Isopropyl iodide)
$C_6H_5CH_2Cl$	Chloromethyl benzene	(Benzl chloride)
 CH3 I	4-Iodomethyl benzene	



Iodo – 2, 4 –dinitro benzene

Synthetic preparation of halo alkenes

Substitution in Alcohols

$$CH_3CH_2OH + \text{dry } HCl \xrightarrow[\text{Reflux}]{ZnCl_2 \text{ cat}} CH_3CH_2Cl + H_2O$$

Note that in the case of the more reactive tertiary alcohols, the reaction proceeds in the cold.

Chlorination can also be brought about by refluxing with sulphur dichloride oxide (thionyl chloride) $SOCl_2$ in the presence of small amounts of pyridine C_5H_5N which absorbs the hydrogen chloride.

$$CH_3CH_2OH + SOCl_2 \xrightarrow{C_5H_5N} CH_3CH_2Cl + SO_2 + HCl$$

Bromination of tertiary alcohols can be brought about in the cold by treating them with either Hydrogen bromide (NaBr/Conc.H_2SO_4) or red phosphorus and bromine but primary alcohols are less susceptible and require refluxing

$$CH_3CH_2OH + HBr \xrightarrow[\text{Reflux}]{NaBr/\ H_2SO_4} CH_3CH_2Br + H_2O$$

Iodoalkane is prepared by adding iodine to a mixture of the alcohol and red phosphorous and then refluxing on a water bath

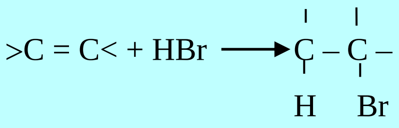
$$CH_3CH_2OH + PI_3 \longrightarrow CH_3CH_2\,I + H_2PO_3$$

NB: An iodine and sulphuric acid cannot be used as the hydrogen Iodide produced, being a powerful reducing agent, would be oxidized to Iodine by the acid.

Therefore, ease of substitution of alcohols

3^0 alcohol > 2^0 alcohol > 1^0 alcohol and is dependent upon the order of stability of the intermediate carbonium ion.

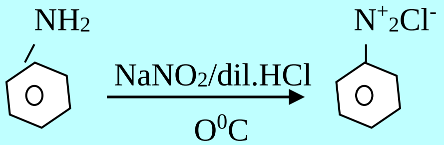
Addition of hydrogen halides to Alkenes



$$>C = C< + HBr \longrightarrow \underset{H}{\overset{|}{C}} - \underset{Br}{\overset{|}{C}} -$$

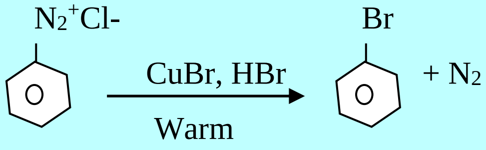
Replacement of a Diazonium salt (Sandmeyer Reaction)

Diazonium salt is obtained by treating a primary aromatic amine such as phenyl amine with $NaNO_2$ /dil. HCI at 0^0C (dilute nitrous acid at 0^0C)



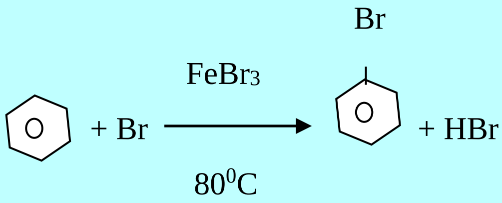
Benzene diazonium chloride

Then



Bromo benzene

Direct halogenations



Note that the bromine molecule is polarized during the reaction, forming complex $Br^+ [FeBr_4]^-$

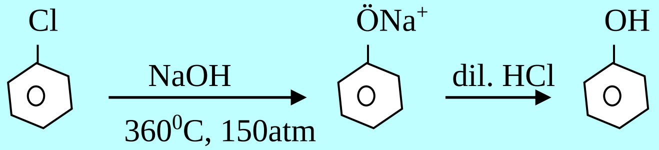
REACTIONS

Alcohol formation

$$R^{\sigma+} - X^{\sigma-} + \ddot{O}H \longrightarrow R - OH + X^{-}$$

Primary and secondary Haloalkanes undergo alkaline hydrolysis to the alcohol.

Aryl halides are not sufficiently reactive to undergo hydrolysis to phenols except under severe conditions; phenol can be obtained by heating Chlorobenzene with aqueous sodium hydroxide at 360ºC at a high pressure and then hydrolyzing the phenoxide formed with hydrochloric acid



Phenol

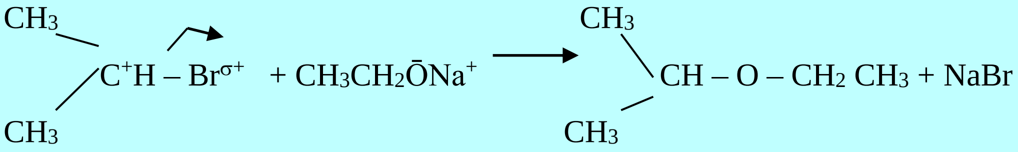
Sodium phenoxide

Ether formation (Williamson's synthesis)

This reaction is suitable for both symmetrical and unsymmetrical ethers as well as alkoxy aromatics and alkoxy alkanes. Sodium or potassium alkoxide (Alkylate) is prepared by dissolving the alkali metal in excess of the appropriate alcohol which reacts with the halo alkane to from the ether

$$CH_3C^{\sigma+}H_2 - Br^{\sigma-} + CH_3CH_2\bar{O}Na^+ \longrightarrow CH_3CH_2 - O - CH_2CH_3 + NaBr$$

Sodium ethoxide — Ethoxyethane (Diethyl ether)

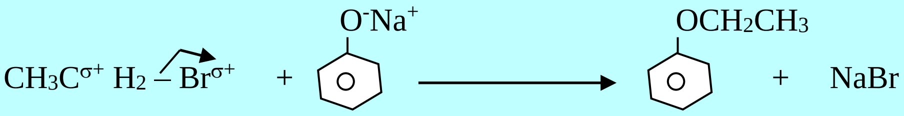


$$(CH_3)_2C^{+}H - Br^{\sigma+} + CH_3CH_2\bar{O}Na^+ \longrightarrow (CH_3)_2CH - O - CH_2CH_3 + NaBr$$

2 – Ethoxy propane

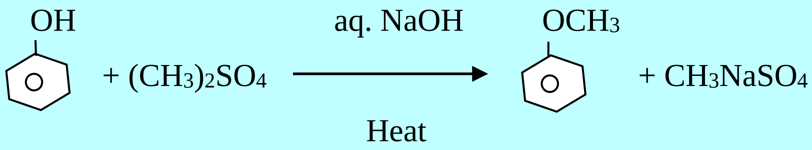
(Ethyl Isopropyl ether)

The reaction may also be performed using the phenoxide



Sodium phenoxide Ethoxy benzene

NB: For methoxy aromatics, it is more usual to use dimethylsulphate $(CH_3)_2SO_4$ and a phenol in aqueous sodium hydroxide

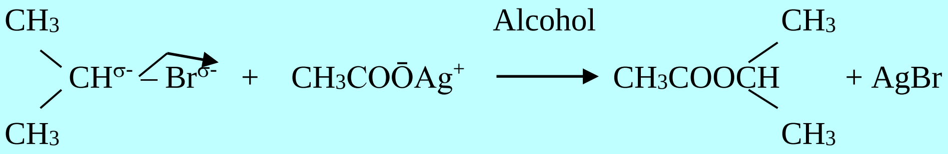


Ester formation

An alcoholic solution of silver (I) salt of a carboxylic acid is warmed with an halo alkane.

$$CH_3C^{\sigma+}H_2 - Br^{\sigma-} + CH_3CO\bar{O}Ag^+ \xrightarrow{\text{Alcohol}} CH_3COOCH_2CH_3 + AgBr$$

Ethyl ethanoate



1 –methylethyl ethanoate

NB: Phenyl esters cannot be obtained by the direct interaction of the aryl halide and the carboxylate ion.

Amine formation

Alkylation of ammonia takes place if an alcoholic solution of ammonia is heated with a haloalkane

$$NH_3 + CH_3CH_2Br \xrightarrow{\text{heat}} CH_3CH_2NH_2 + HBr$$

1^{o} amine

$$CH_3CH_2NH_2 + CH3CH2Br \longrightarrow (CH_3CH_2)_2NH + HBr$$

2^{o} amine

$$(CH_3CH_2)_2NH + CH_3CH_2Br \longrightarrow (CH3CH2)3N + HBr$$

3^{o} amine

$$(CH_3CH_2)_3N + CH_3CH_3Br \longrightarrow (CH_3CH_2)_4N^{+}Br^{-}$$

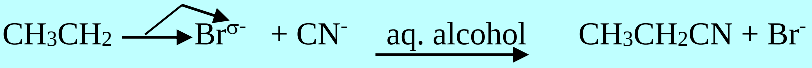
4^{o} quaternary ammonium salt

The reaction has the disadvantage that a mixture of different classes of amines results since the alkyl amines are more reactive than the ammonia.

NB: The reaction tends to be limited to the aliphatic series, although aryl halides will react if electron with drawing substituents are present in the 2 – or 4 positions.

Cyanide formation

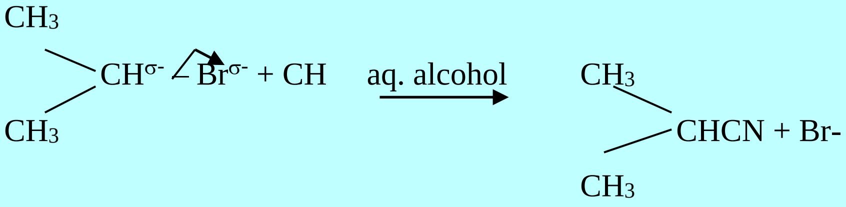
These are prepared by heating the haloalkane with sodium cyanide in a suitable solvent (aqueous alcohol)



$$CH_3CH_2 \longrightarrow Br^{\sigma-} + CN^{-} \xrightarrow{\text{aq. alcohol}} CH_3CH_2CN + Br^{-}$$

Propane nitrite

(Ethyl cyanide)



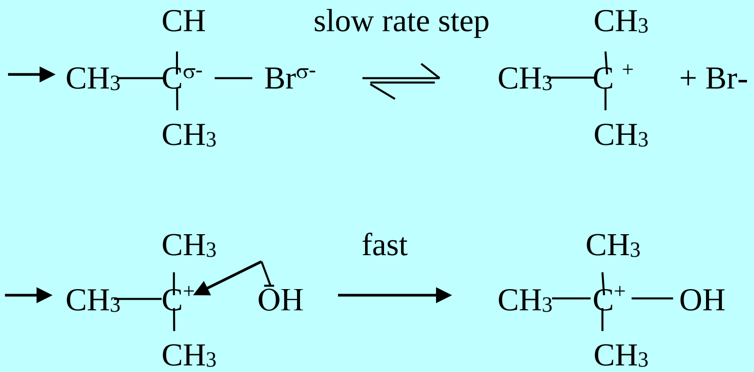
2 – Methyl propane nitrite

NB: Aromatic nitrites are not prepared from the un-reactive aryl halides but from diazonium salts.

NB: The molecularity of the reaction describes the number of species involved in bond cleavage in the rate- determining step i.e.

The substitution Nucleophilic unimolecular (SN1) reaction has a molecularity of one.

I.e. Rate = K [RX]

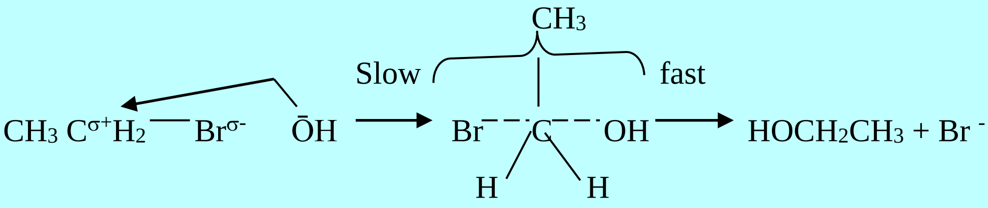


$$CH_3-\overset{CH}{\underset{CH_3}{C^{\sigma-}}}-Br^{\sigma-} \xrightleftharpoons{\text{slow rate step}} CH_3-\overset{CH_3}{\underset{CH_3}{C^{+}}} + Br^-$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C^{+}}} \quad \bar{O}H \xrightarrow{\text{fast}} CH_3-\overset{CH_3}{\underset{CH_3}{C^{+}}}-OH$$

The substitution Nucleophilic bimolecular (SN^2) reaction has a molecularity of two

i.e. Rate = K[R X] [$\bar{O}$H]



$$CH_3\,C^{\sigma+}H_2-Br^{\sigma-} \quad \bar{O}H \xrightarrow{\text{Slow}} \overset{CH_3}{Br---\underset{H\quad H}{C}---OH} \xrightarrow{\text{fast}} HOCH_2CH_3 + Br^-$$

The Grignard reagent

Turnings or granules of Magnesium are treated with a dry ethereal solution of a haloalkane. The formula is usually represented as simply ALKYL MAGNESIUM HALIDE RMgX e.g.

$$CH_3CH_3Br + Mg \xrightarrow[(C_2H_5)_2O]{\text{dry}} \underset{\text{Ethyl Magnesium bromide}}{CH_3CH_2MgBr}$$

The Magnesium – carbon bond is covalent, but the magnesium-Halogen bond is ionic. The Grignard reagent may be employed for preparing alkanes, alkenes, alkynes, alcohols, aldehyde, ketones and carboxylic acids.

NB: Aromatic Grignard reagents are made in the same way and perform exactly similar reactions

Synthetic applications of Grignard reagents

Preparation of alkanes

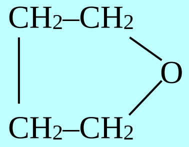
$$RX + Mg \xrightarrow[(C_2H_5)_2O]{\text{dry}} RMgX$$

$$RMgX + H_2O \xrightarrow{\text{dil. acid}} \underset{\text{Alkane}}{RH} + \underset{\text{precipitated}}{MgXOH}$$

Preparation of Alkynes

Suitable for higher homologous of Ethyne

$$CH \equiv CH + RMgX \xrightarrow{\text{Tetrahydroturan}} RH + CH \equiv CMgX$$

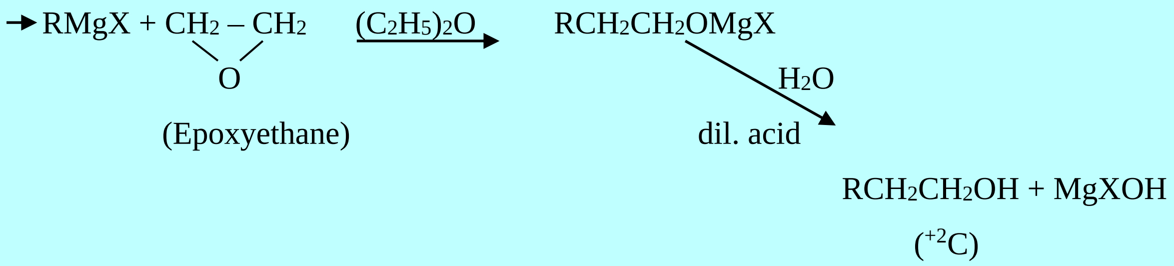


$$CH \equiv CMgX + RX \longrightarrow CH \equiv CR + MgX_2$$

Preparation of Alcohols

Suitable for 1^0, 2^0, and 3^0 alcohols

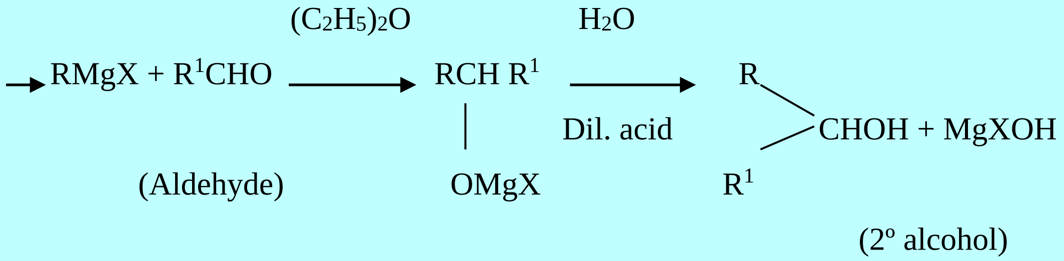
$$\rightarrow RMgX + \underset{\substack{\uparrow \\ \text{Methanol}}}{HCHO} \xrightarrow{(C_2H_5)_2O} RCH_2OMg\,X \xrightarrow[\text{Dil. acid}]{H_2O} \underset{\substack{1^0\text{alcohol} \\ (^+C)}}{RCH_2OH} + MgXOH$$



$$\rightarrow RMgX + \underset{O}{CH_2 - CH_2} \xrightarrow{(C_2H_5)_2O} RCH_2CH_2OMgX \xrightarrow[\text{dil. acid}]{H_2O} RCH_2CH_2OH + MgXOH$$

(Epoxyethane)

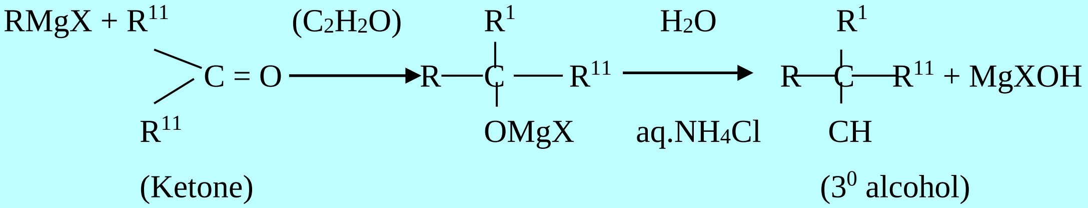
($^{+2}$C)



$$\rightarrow RMgX + R^1CHO \xrightarrow{(C_2H_5)_2O} \underset{OMgX}{RCH\,R^1} \xrightarrow[\text{Dil. acid}]{H_2O} \begin{matrix} R \\ R^1 \end{matrix} > CHOH + MgXOH$$

(Aldehyde)

(2° alcohol)



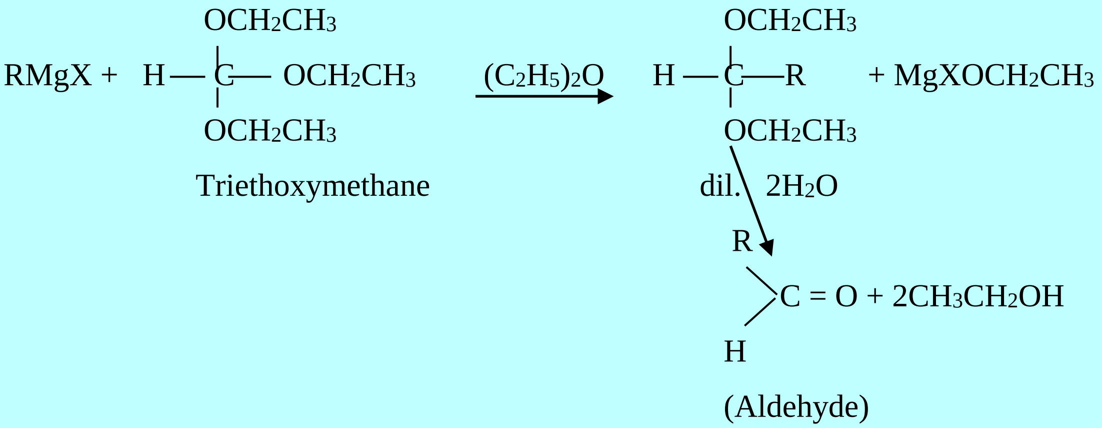
$$RMgX + \begin{matrix} R^{11} \\ R^{11} \end{matrix} > C = O \xrightarrow{(C_2H_2O)} R - \overset{R^1}{\underset{OMgX}{C}} - R^{11} \xrightarrow[\text{aq.}NH_4Cl]{H_2O} R - \overset{R^1}{\underset{CH}{C}} - R^{11} + MgXOH$$

(Ketone)

(3^0 alcohol)

NOTE: Aq. Ammonium chloride (NH_4Cl_4) is used in the hydrolysis to the tertiary alcohol, as the presence of an acid causes dehydration

Preparation of Aldehydes

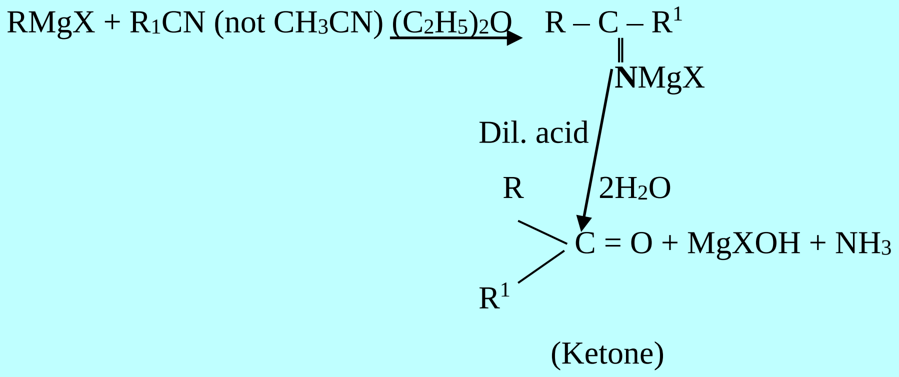


$$RMgX + H - \overset{OCH_2CH_3}{\underset{OCH_2CH_3}{C}} - OCH_2CH_3 \xrightarrow{(C_2H_5)_2O} H - \overset{OCH_2CH_3}{\underset{OCH_2CH_3}{C}} - R + MgXOCH_2CH_3 \xrightarrow[\text{dil.}]{2H_2O} \begin{matrix} R \\ H \end{matrix} > C = O + 2CH_3CH_2OH$$

Triethoxymethane

(Aldehyde)

Preparation of Ketones



Preparation of carboxylic acids

$$RMgX + CO_2 \xrightarrow{(C_2H_5)_3O} RCOOMgX \xrightarrow[\text{Dil. Acid}]{H_2O} RCOOH + MgXOH$$

NB: $(C_2H_5)_3O$ ≡ dry ether

Qn. Show how the following conversions can be affected.

a) Propene to chlorobutane

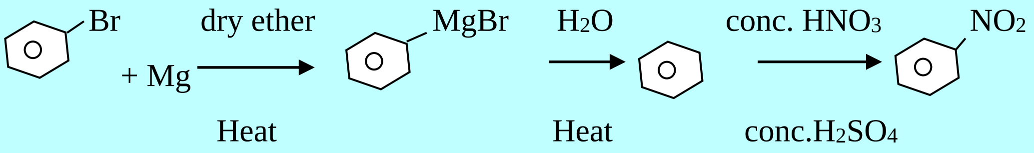
$$CH_3CH = CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br \xrightarrow[\text{Ether}]{Mg} CH_3CH_2CH_2\text{–}MgXOH$$

$$CH_3CH_2CH_2\text{–}MgXOH \xrightarrow{^{+}CH_2O} CH_3CH_2CH_2CH_2\text{-O-}MgBr$$

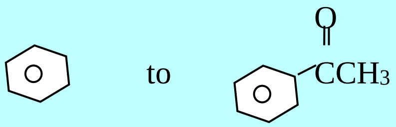
$$CH_3CH_2CH_2CH_2OH \xleftarrow[\text{dil. acid}]{H_2O} CH_3CH_2CH_2CH_2\text{-O-}MgBr$$

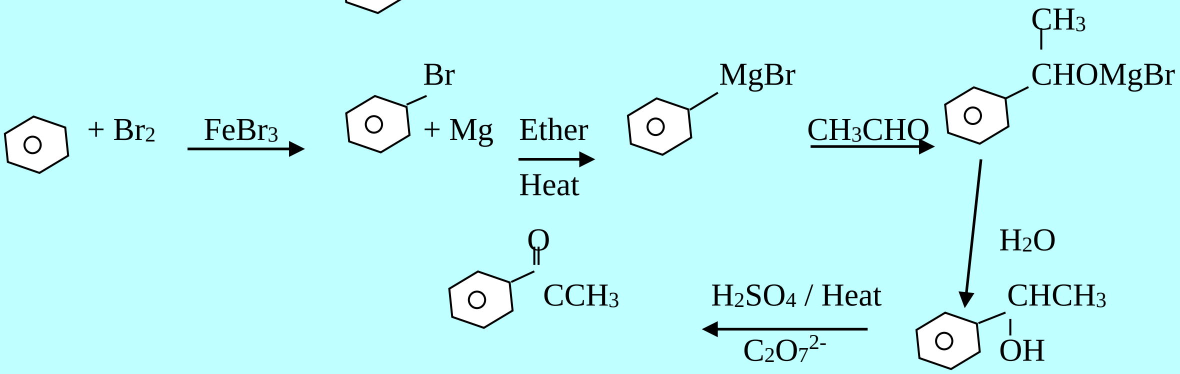
$$CH_3CH_2CH_2CH_2OH \xrightarrow{HCl} CH_3CH_2CH_2CH_2Cl$$

b) Bromobenzene to nitrobenzene

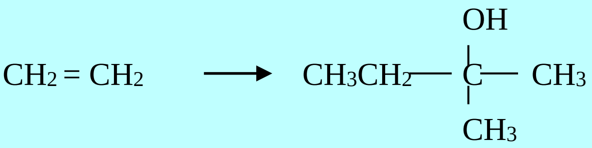


c)

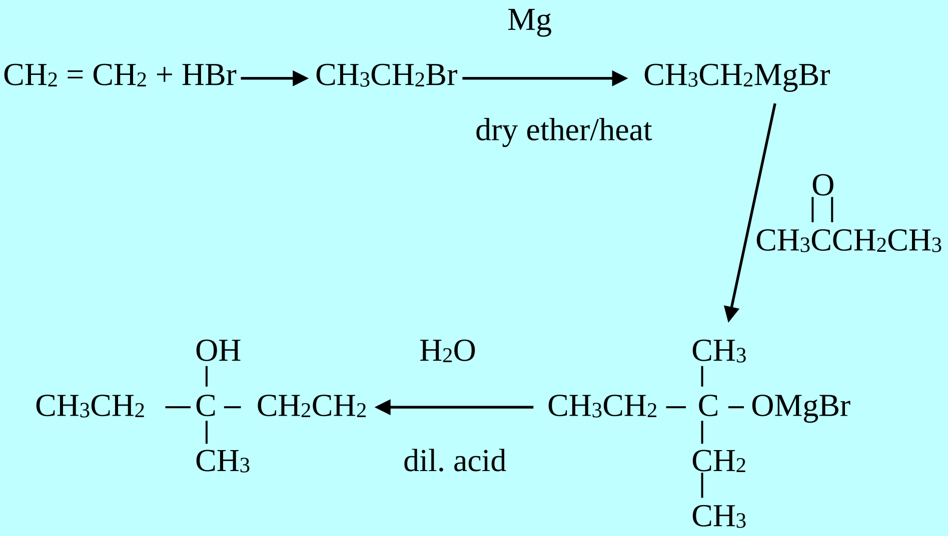




d)



$$CH_2=CH_2 \longrightarrow CH_3CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3$$

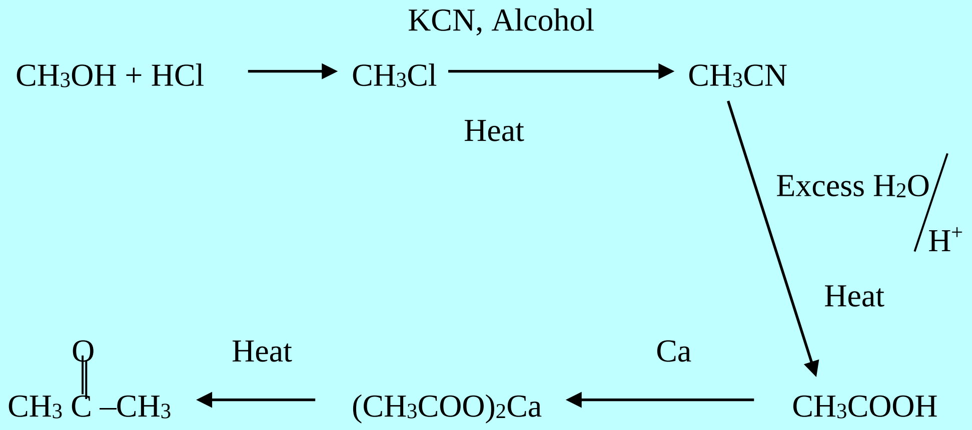


$$CH_2=CH_2 + HBr \longrightarrow CH_3CH_2Br \xrightarrow[\text{dry ether/heat}]{Mg} CH_3CH_2MgBr$$

$$CH_3CH_2MgBr \xrightarrow{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3} CH_3CH_2-\overset{CH_3}{\underset{\substack{CH_2\\|\\CH_3}}{C}}-OMgBr$$

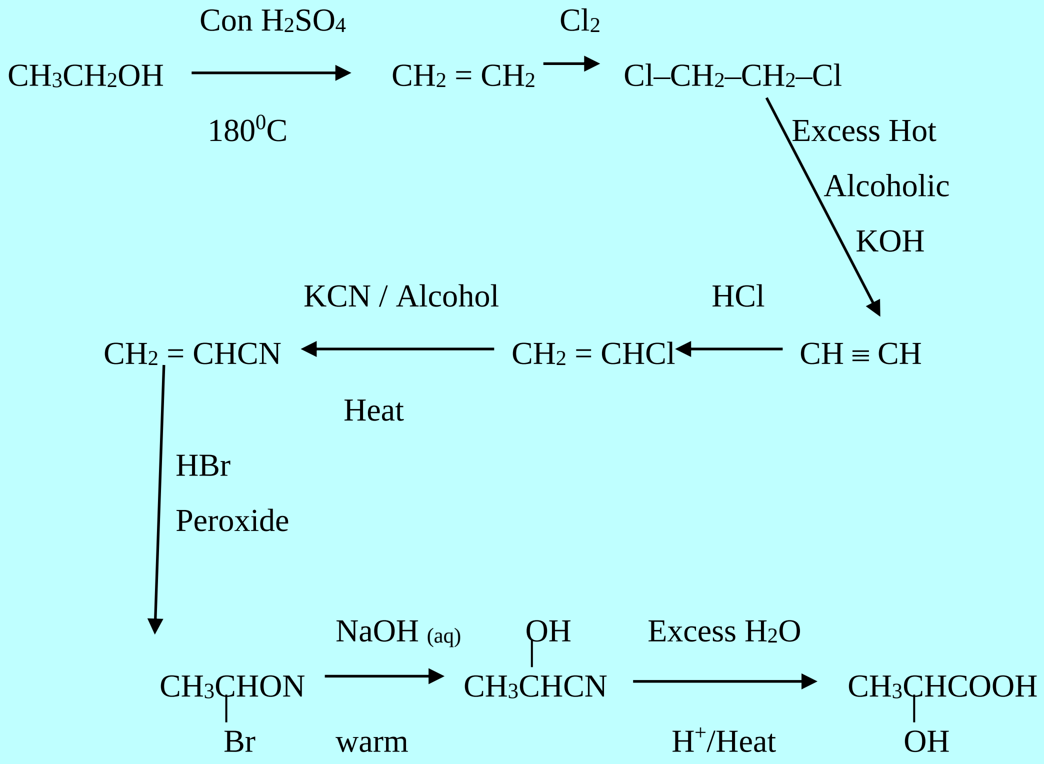
$$CH_3CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_2CH_2 \xleftarrow[\text{dil. acid}]{H_2O} CH_3CH_2-\overset{CH_3}{\underset{\substack{CH_2\\|\\CH_3}}{C}}-OMgBr$$

e) CH_3OH to CH_3COCH_3



$$CH_3OH + HCl \longrightarrow CH_3Cl \xrightarrow[\text{Heat}]{\text{KCN, Alcohol}} CH_3CN \xrightarrow[\text{Heat}]{\text{Excess } H_2O/H^+} CH_3COOH \xrightarrow{\text{Ca}} (CH_3COO)_2Ca \xrightarrow{\text{Heat}} CH_3\overset{\overset{O}{\|}}{C}-CH_3$$

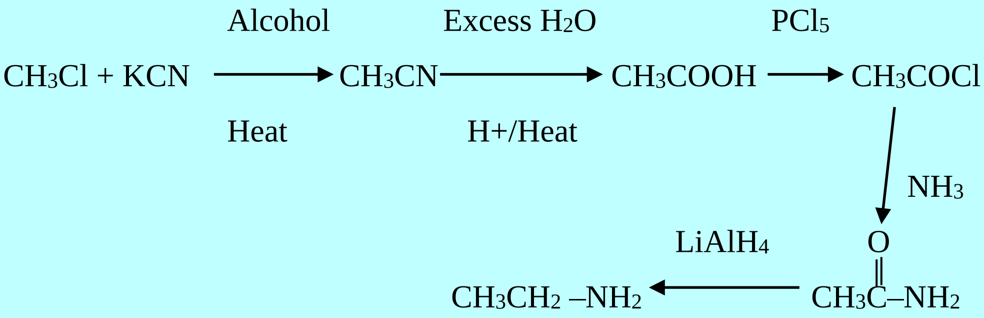
f) CH_3CH_2OH to $CH_3\overset{\overset{OH}{|}}{C}HCOOH$



$$CH_3CH_2OH \xrightarrow[180^0C]{\text{Con } H_2SO_4} CH_2 = CH_2 \xrightarrow{Cl_2} Cl\text{–}CH_2\text{–}CH_2\text{–}Cl \xrightarrow{\text{Excess Hot Alcoholic KOH}} CH \equiv CH \xrightarrow{HCl} CH_2 = CHCl \xrightarrow[\text{Heat}]{\text{KCN / Alcohol}} CH_2 = CHCN$$

$$CH_2 = CHCN \xrightarrow{\text{HBr Peroxide}} CH_3\underset{\underset{Br}{|}}{C}HON \xrightarrow[\text{warm}]{NaOH_{(aq)}} CH_3\overset{\overset{OH}{|}}{C}HCN \xrightarrow[H^+/\text{Heat}]{\text{Excess } H_2O} CH_3\underset{\underset{OH}{|}}{C}HCOOH$$

g) CH_3Cl to $CH_3CH_2-NH_2$



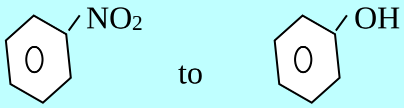
$$CH_3Cl + KCN \xrightarrow[\text{Heat}]{\text{Alcohol}} CH_3CN \xrightarrow[\text{H+/Heat}]{\text{Excess } H_2O} CH_3COOH \xrightarrow{PCl_5} CH_3COCl$$

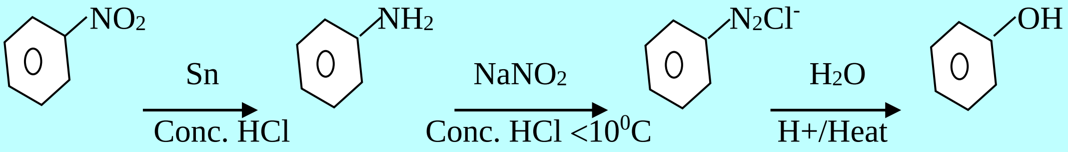
$$CH_3COCl \xrightarrow{NH_3} CH_3\overset{\overset{O}{\|}}{C}-NH_2$$

$$CH_3CH_2-NH_2 \xleftarrow{LiAlH_4} CH_3\overset{\overset{O}{\|}}{C}-NH_2$$

OR

$$CH_3\ Cl + KCN \xrightarrow[\text{Heat}]{\text{Alcohol}} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2-NH_2$$

h) 



ALCOHOLS

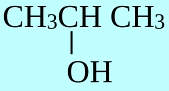
Monohydroxyl derivatives of alkanes are called Aliphatic monohydric compounds containing more than one hydroxyl group are called Polyhydric alcohols

They may be classified as primary (1^0) secondary (2^0) or tertiary (3^0) according to the nature of carbon atom to which the hydroxyl group is attached i.e.

CH_3CH_2OH

Ethanol

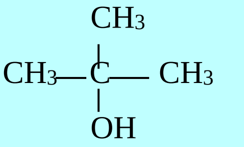
1º



$CH_3\underset{OH}{\underset{|}{CH}}CH_3$

Propan -2-o1

2º

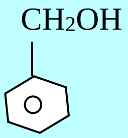


$CH_3-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3$

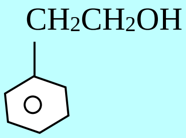
2-methyl propan-2-ol

3º

Aromatic alcohols are aryl substituents of aliphatic alcohols in which the hydroxyl group is separated from the benzene ring by at least one methylene (-CH_2-) group e.g.



Phenyl methanol



2-phenyl ethanol

Industrial source

1st stage: Steam reforming

$$CH_4 + H_2O \xrightarrow[900^oC]{\text{Ni catalyst}} \underbrace{CO + 3H_2}_{\text{Synthesis gas}}$$

2nd stage: Synthesis gas is passed over a chromium (III) oxide /Zinc oxide catalyst at 350^0-400^0C.

$$2H_2 + CO \xrightleftharpoons[350^o–400^oC,\ \text{high pressure}]{Cr_2O_3\ /\ ZnO\ \text{cat}} CH_3OH$$

The equilibrium, is maintained by high pressure

NOTE:

Ordinary commercial alcohol is an azeotropic mixture of 95.6% ethanol and 4.4% water by mass, therefore separation by fractional distillation is not possible as that of Zeotropic mixture which boils at only a marginally lower temperature (78.2ºC) than the absolute that contains 95% ethanol and this is then fractionally distilled.

The distillate being collected in three separate parts.

1st fraction : over at 64.8ºC, Benzene ethanol water

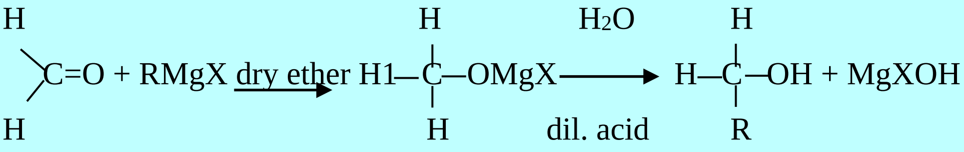
2nd fraction : at 68.2ºC, Benzene / ethanol

Final fraction : at 78.3ºC, is absolute ethanol

Absolute ethanol is highly hydroscopic and must be stored away from atmospheric moisture if its purity is to be maintained.

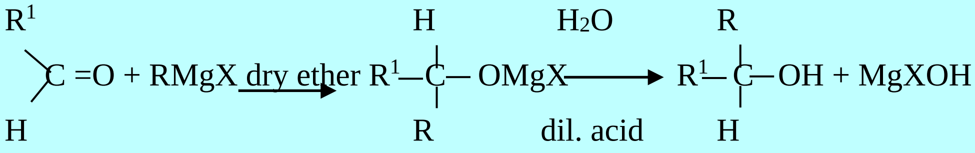
Using: Synthetic preparations of Aliphatic Alcohols

a) Grignard synthesis



$$\overset{H}{\underset{H}{>}}C{=}O + RMgX \xrightarrow{\text{dry ether}} H1{-}\overset{H}{\underset{H}{C}}{-}OMgX \xrightarrow[\text{dil. acid}]{H_2O} H{-}\overset{H}{\underset{R}{C}}{-}OH + MgXOH$$

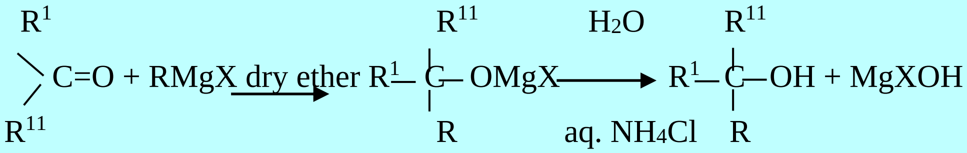
Methanal 1° alcohol



$$\overset{R^1}{\underset{H}{>}}C{=}O + RMgX \xrightarrow{\text{dry ether}} R^1{-}\overset{H}{\underset{R}{C}}{-}OMgX \xrightarrow[\text{dil. acid}]{H_2O} R^1{-}\overset{R}{\underset{H}{C}}{-}OH + MgXOH$$

High aldehyde 2° alcohol

Such as ethanal



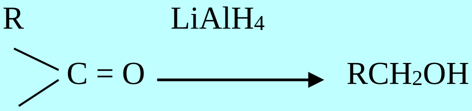
$$\overset{R^1}{\underset{R^{11}}{>}}C{=}O + RMgX \xrightarrow{\text{dry ether}} R^1{-}\overset{R^{11}}{\underset{R}{C}}{-}OMgX \xrightarrow[\text{aq. } NH_4Cl]{H_2O} R^1{-}\overset{R^{11}}{\underset{R}{C}}{-}OH + MgXOH$$

Ketone 3^0alcohol

Such as propanone

b) Lithium Tetrahydrido aluminate (III) in dry water

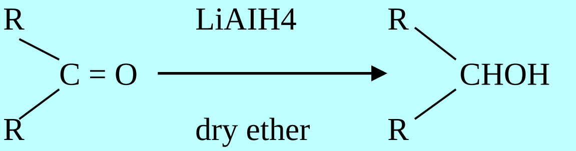
Its suitable for 1° and 2° alcohol, the reactions are performed at 0°C and its use in elementary practical work is not really desirable since it reacts violently with water and moisture.



$$\overset{R}{>}C = O \xrightarrow{LiAlH_4} RCH_2OH$$

H dry ether

Aldehyde 1^0 alcohol



Ketone 2^o alcohol

Hydrolysis of Haloalkanes

$$RX + \bar{O}H \longrightarrow ROH + X^-$$

Preparations of Aromatic Alcohols

(The Carnizzaro reaction)

$$2C_6H_5CHO + KOH \longrightarrow C_6H_5CH_2OH + C_6H_5COOK$$

Phenyl methanol Potassium benzoate

Hydrolysis of chloro methyl benzene (Benzyl chloride)

$$C_6H_5CH_2Cl + KOH \longrightarrow C_6H_5CH_2OH + KCl$$

REACTIONS

Halogenation

Using hydrogen halides

$$CH_3CH_2OH + HCl \xrightarrow[\text{Reflux}]{ZnCl_2\ Cat} CH_3CH_2Cl + H_2O$$

$$CH_3CH_2OH + HBr \xrightarrow[\text{Reflux}]{NaBr\ /Conc.\ H_2SO_4} CH_3CH_2Br + H_2O$$

NB

Bromination may be carried out by treating the alcohol with red phosphorous and bromine

→ An iodine and sulphuric acid cannot be used to bring about iodination as the hydrogen iodide produced, being a powerful reducing agent, it oxidized to iodine by the acid. Instead, the alcohol is treated with red phosphorous and iodine.

→ Tertiary and aromatic alcohols are predictably more readily halogenated by the hydrogen halides, the reactions taking place fairly rapidly on shaking in the cold.

Mechanism

Step I: Donation of lone pair of electrons from the oxygen atom of the alcohol to a proton released from the acid

$$CH_3CH_2 - \ddot{O}H \quad H^+ \rightleftharpoons CH_3CH_2 - O^+H_2$$

Step II: Ions of water molecule form the protonated alcohol to form a carbocation (Carbonium ion)

$$CH_3CH_2 - {}^+OH_2 \rightleftharpoons CH_3{}^+CH_2 + H_2O$$

Step III: Nucleophilic attack by a halide upon the carbocation to form the halo alkane

$$CH_3{}^+CH_2 \quad X^- \longrightarrow CH_3CH_2X$$

Using phosphorous

$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl3 + HCl$$

Phosphorus trichloride reacts similarly, although slightly less readily.

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

Using sulphur Dichloride oxide (Thionyl Chloride)

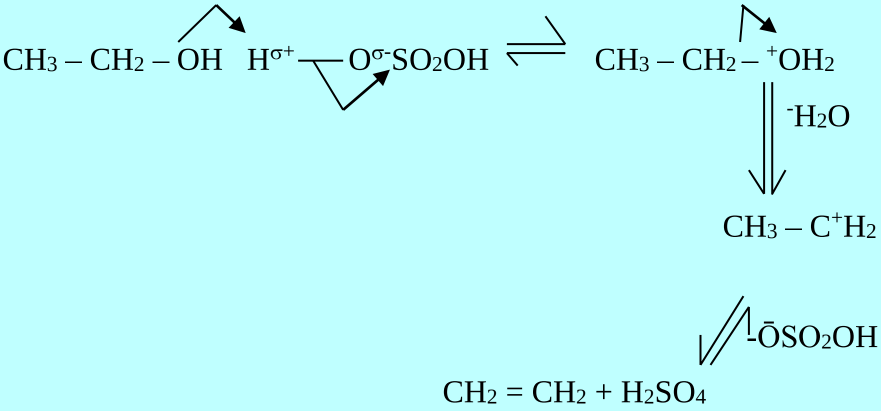
$$CH_3CH_2OH + SOCl_2 \xrightarrow[\text{Pyridine } (C_5H_5N)]{\text{reflux}} CH_3CH_2Cl + SO_2 + HCl$$

Dehydration to Alkenes

Excess Conc. H_2SO_4. 170°C

$$CH_3CH_2OH \xrightarrow[\text{OR}\quad Al_2O_3\ 350^oC]{} CH_2 = CH_2 + H_2O$$

Mechanism



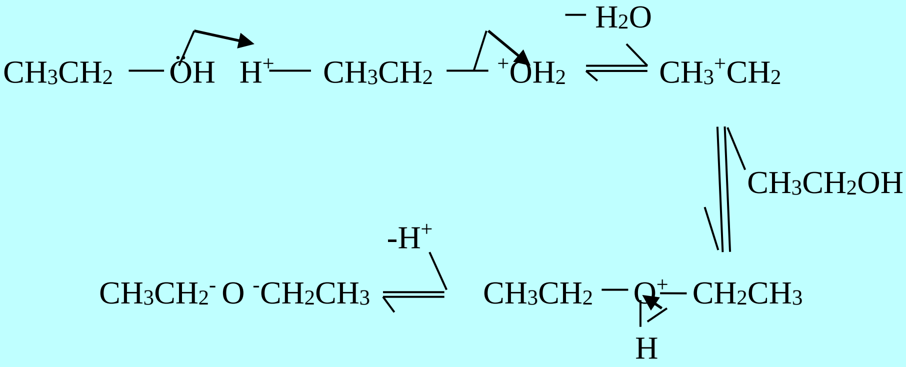
Ether formation

$$2CH_3CH_2OH \underset{140^0C}{\overset{Conc.H_2SO_4}{\rightleftharpoons}} CH_3CH_2OCH_2CH_3 + H_2O$$

Ethoxyethane

“Ether”

Mechanism



With metals

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$$

Esterification

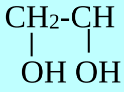
The process whereby an alcohol reacts reversibly with an acid to form an ester is known as esterification. This involves the replacement of a hydroxyl group of an acid by an alkyl group of an alcohol.

E.g. Ethanol reacts with concentrated sulphuric and nitric acid in the cold to form ethyl hydrogen sulphate and ethyl nitrate (dangerous reaction)

$$CH_3CH_2OH + HONO_2 \rightleftharpoons \underset{\text{Ethyl nitrate}}{CH_3CH_2ONO_2} + H_2O$$

Nitrate esters are especially important in manufacturing explosives

- Nitration of propane, 1, 2, 3 triol (glycerol)



$\underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH}}\ CH_2-OH$ yields propane, 1, 2, 3 triyltrinitrate

(Nitroglycerine $CH_2NO_3CHNO_3CH_2NO_3$ which when mixed with finely divided silicon (IV) oxide in the correct proportions is used in manufacturing dynamite.

NB

The most important class of esters is that formed between alcohol and carboxylic acids. The alcohol and the carboxylic acid are boiled under reflux in the presence of 5% concentrated sulphuric acid

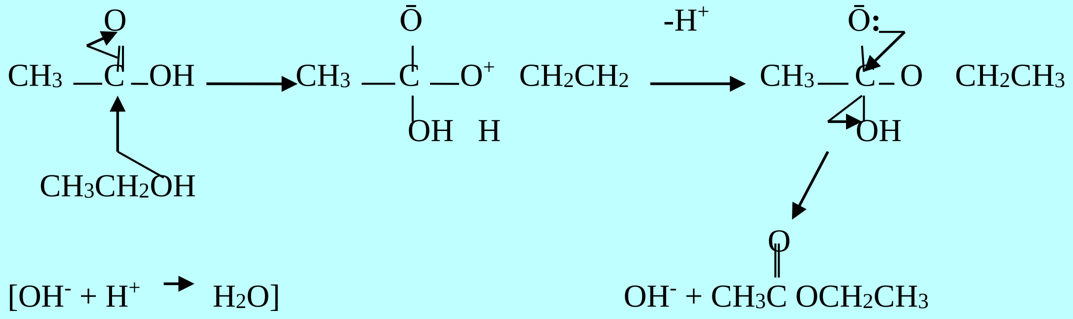
a). $CH_3COOH + HOCH_2CH_3 \underset{\text{Reflux}}{\overset{H^+\ \text{Cat.}}{\rightleftharpoons}} \underset{\text{Ethylethanoate.}}{CH_3\,COOCH_2CH_3} + H_2O$

Esterification may also be accomplished using an acyl or benzene carbonyl (benzoyl) chloride.

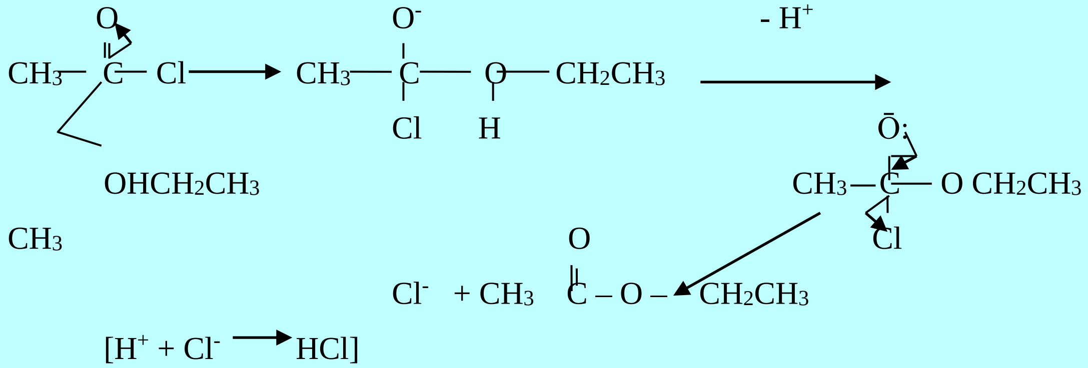
b). $CH_3COCl + CH_3CH_2OH \longrightarrow CH_3COOCH_2CH_3 + HCl$

Ethanoylchloride

Mechanism

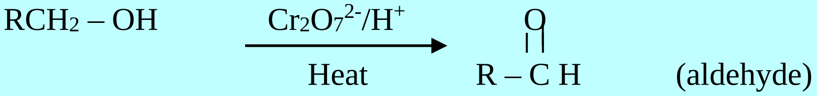


b)

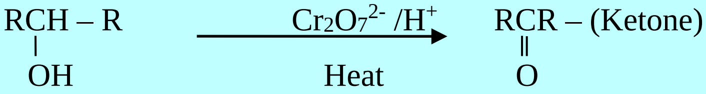


<u>Oxidation</u>

Potassium manganate (VII) (permanganate) and potassium dichromate (VI) are the most popular oxidizing agent. The manganate (VII) can be used in a neutral alkaline or acidic medium whereas the dichromate (VI) functions only in a medium of sulphuric acid



$$RCH_2-OH \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}/H^+} R-\overset{O}{\overset{||}{C}}H \quad \text{(aldehyde)}$$



$$R\underset{\underset{OH}{|}}{C}H-R \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}/H^+} R\underset{\underset{O}{||}}{C}R - \text{(Ketone)}$$

NB: Tertiary alcohols are comparatively stable for oxidation and are not oxidized at all in neutral or alkaline media. But under the same conditions primary and secondary alcohols retain the same carbon skeleton in undergoing oxidation to the aldehyde, acid or Ketone e.g.

$$CH_3CH_2\text{-}OH \xrightarrow[\text{Heat}]{Cr_2O_7/H^+} CH_3\ CHO \xrightarrow[\text{Heat}]{Cr_2O_7/H^+} CH_3CooH$$

TESTS OF ALCOHOLS

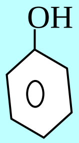
- Lower alcohols dissolve in water to give solution which have no effect on methyl orange and phenolphthalein indicators and are neutral to litmus.
- Addition of acidified solution of potassium dichromate to a primary or secondary alcohol and warming turns the mixture green if the alcohol is primary, unpleasant smelling aldehyde is formed but if it is a secondary alcohol fruity pleasant-smelling Ketone is formed

NB: Tertiary alcohols do not give positive test with acidified potassium dichromate solution. Formation of aldehyde or Ketone in the experiment is confirmed by adding a few drops of Brady's reagent to the product. Formation of a yellow precipitate then confirms

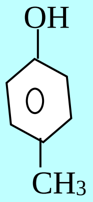
- With ethanoic acid, addition of some ethanoic acid & a few drops of sulphuric acid to primary, secondary or tertiary alcohol and warming the product sweet pleasant smell ester.
- Iodine solution and sodium hydroxide solution (Iodo form test). This gives positive results with only secondary alcohol which have methyl group attached to carbon atom carrying the -OH group i.e. $CH_3\text{-}\overset{\overset{O}{||}}{\ }CH\text{-}R$. Ethanol is the only primary alcohol which gives a positive iodo form test. To the alcohol is added sodium hydroxide followed by iodine. A pale yellow precipitate is formed

PHENOLS

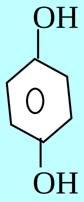
Are compounds containing a hydroxyl group attached directly to an aromatic nucleus.



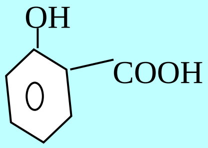
Phenol



4-methyl phenol



Benzene -1,4diol



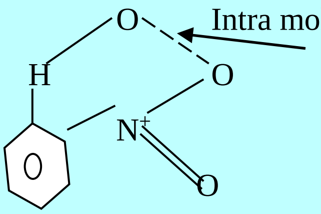
2-Hydrodyl benzene carboxylic acid

(2-hydroxyl benzoic acid)

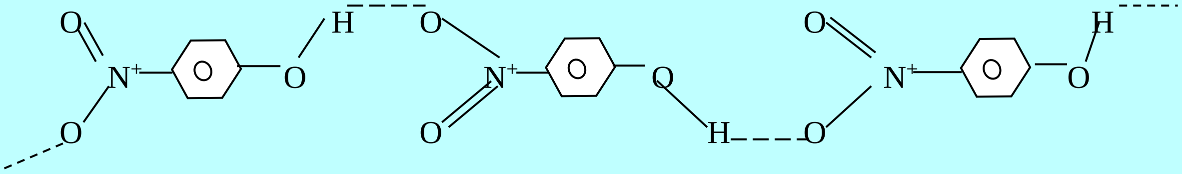
Phenol is a colourless, hygroscopic crystalline solid.

NB:

The greater volatility of 2-nitrophenol is attributed to intramolecular hydrogen bonding, where as the higher boiling points of the 3-and 4- isomers are a direct result of intermolecular hydrogen bonding.

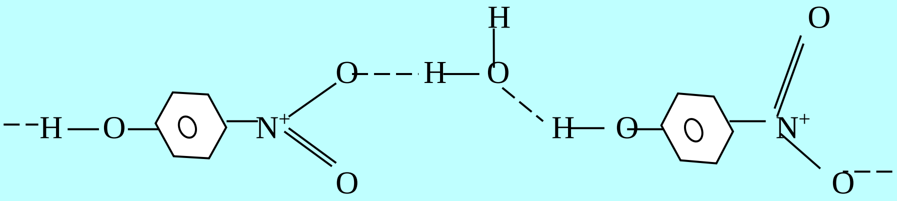


Intra molecular hydrogen bonding in 2 –nitrophenol



Inter molecular hydrogen bonding in 4-nitrophenol

As a result of their ability to associate with themselves and also with water molecules, 3 - and 4 - nitrophenol are appreciably more soluble in water than 2 nitro phenol, which cannot form inter molecular hydrogen bonds.



(Inter molecular hydrogen bonds between water and 4-nitrophenol)

Hence the low miscibility and higher volatility of 2-nitrophenol enables it to be easily separated from other isomers by steam distillation.

PREPARATIONS

Alkali fusion with sodium benzene sulphate

$$C_6H_5SO_3Na + 2NaOH \xrightarrow{300 - 350^0C} C_6H_5ONa + Na_2SO_3 + H_2O$$

$$C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl$$

Hydrolysis of chloro benzene

$$C_6\ H_5Cl \xrightarrow[360^oC,\ 150atm]{aq.\ NaOH} C_6H_5ONa \xrightarrow{dil.\ HCl} C_6H_5OH$$

From Benzene (Rasching process)

$$2C_6H_6 + 2HCr + O_2 \xrightarrow[230^oC]{CuCl_2\ cat} 2C_6H_5Cl + 2H_2O$$

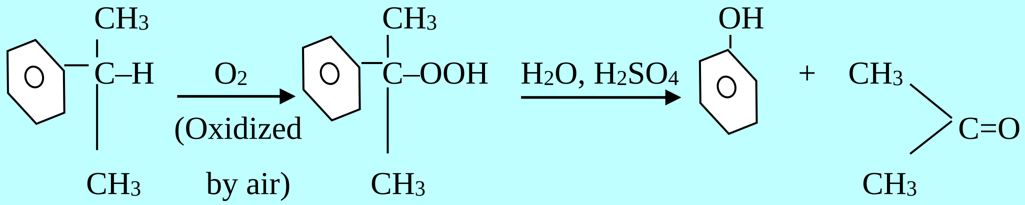
Then

$$C_6H_5Cl + H2O \xrightarrow[425^0C]{Si\ cat.} C_6H_5OH + HCl$$

From petroleum products

$$C_6H_6 + CH_3CH = CH_2 \xrightarrow[250^oC,\ 30atm]{H_3PO_4\ cat} C_6H_5CH\ (CH_3)_2$$

Then



From Coal far

$$2C_6H_5ONa + H_2O + CO_2 \longrightarrow 2C_6H_5OH + Na_2CO_3$$

Hydrolysis of Diazonium salts

$$C_6H_5N_2^+ \; + 2H_2O \xrightarrow[\text{(Warm)}]{50^0C} C_6H_5OH + N_2 + H_3O^+$$

REACTIONS

Phenol undergoes two distinctive types of reaction

- Side –chain substitution, which generally involves replacement of the acidic proton And
- Electrophilic substitution in the ring.

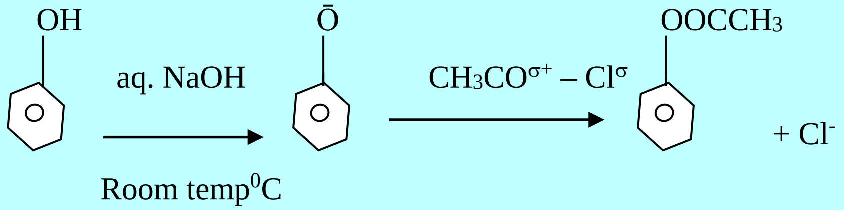
Reactions of the hydroxyl group

Reactions involving the hydroxyl group resemble those of the alcohols to a certain extent, but differ in as much as phenol exhibits much stronger acidic characteristics

$$C_6H_5OH \rightleftharpoons C_6\,H_5\bar{O} + H^+ \overset{-OH}{\rightleftharpoons} H_2O$$

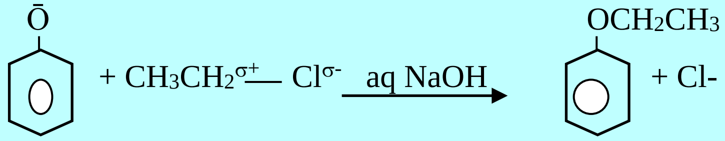
Esterification

Phenol does not esterify with ethanoic acid, but in alkaline solution the nucleophilic phenoxide ion readily attacks the electrophilic acyl RCO-and aroyl, Aro-, centres of ethanoyl chloride, CH_3COCl, benzene carbonyl chloride C_6H_5COCl



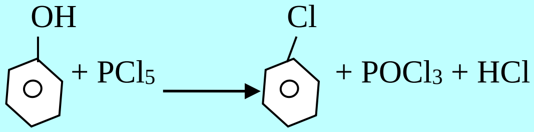
Phenyl ethanoete

Ether formation, Williamson's synthesis



Its nucleophilic substitution. Ethoxybenzene

Displacement of the hydroxyl group

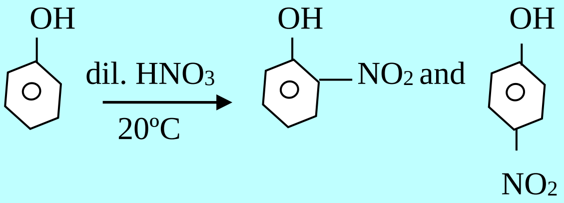


Ring Substitution

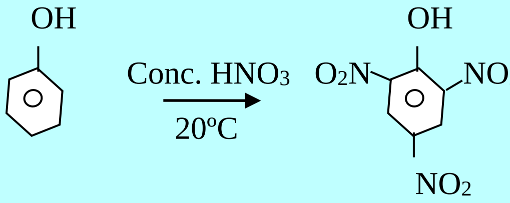
In addition to exhibiting acidic properties phenol is characterized by electrophilic substitution in the 2- and 4- positions of the aromatic ring.

Nitration

The nitration of Phenol is carried out at room temperature using dilute nitric acid.

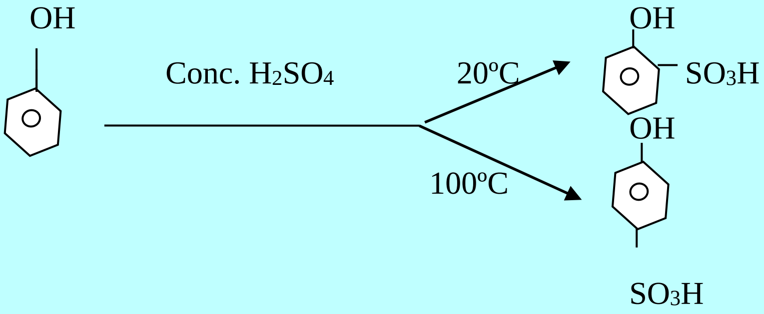


The two isomers can be separated by steam distillation but the use of conc. nitric acid yields 2, 4, 6, - tri nitro product



2, 8, 6, Trinitrophenol

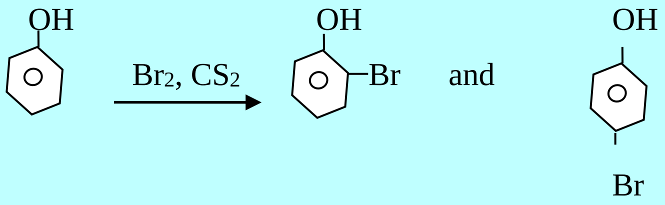
Sulphonation



2 – and 4 – Hydroxybenzene Sulphonic acid

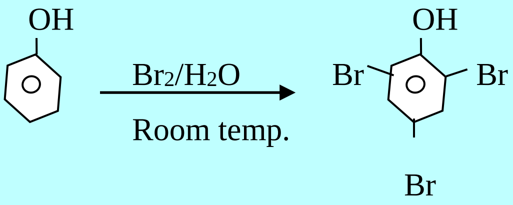
Halogenations

Halogenation of the ring occurs at room temperature and without the use of a halogen carrier catalyst, in order to facilitate the formation of the mono substituted derivatives, Bromination is carried out in a solvent of low polarity e.g. anhydrous carbon disulphide or tetra chloromethane.



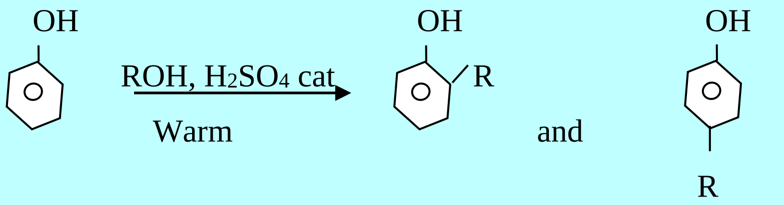
2 - and 4 - Bromophenol

In aqueous solution, bromine forms an immediate white precipitate of 2, 4, 6 tri bromophenol, which is sometimes used as an antiseptic



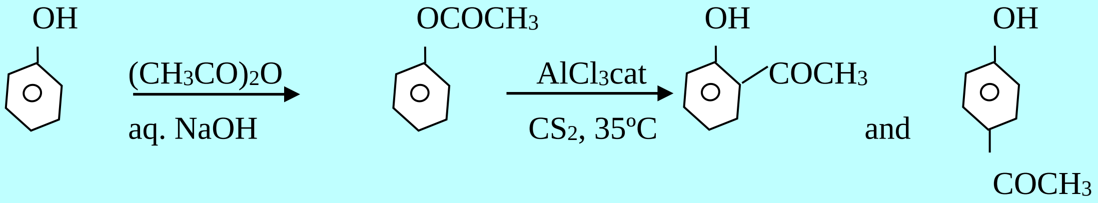
A similar reaction takes place with chlorine water yielding 2, 4, 6, trichlorophenol chlorination of phenol without the use of a solvent at temperatures between 40ºC and 150ºC yields a mixture of 2- and 4- chlorophenol (major product)

Alkylation



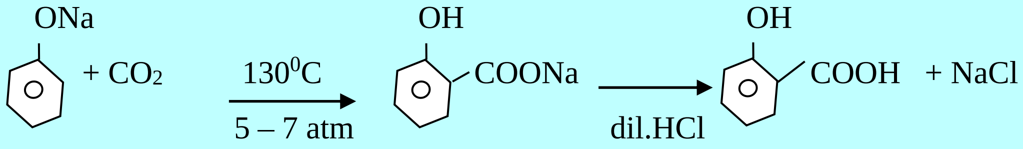
2- and 4- alkylphenol

Acylation

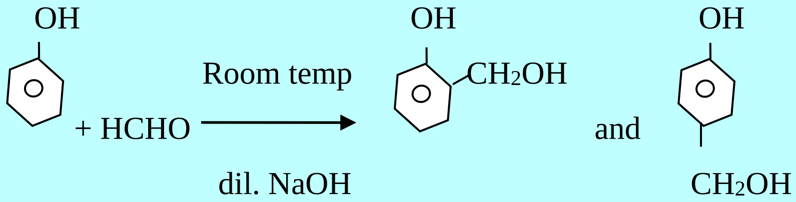


2-and 4- Hydoxyphenoyl ethanone

Carbonation, kolbe-schmitt reaction

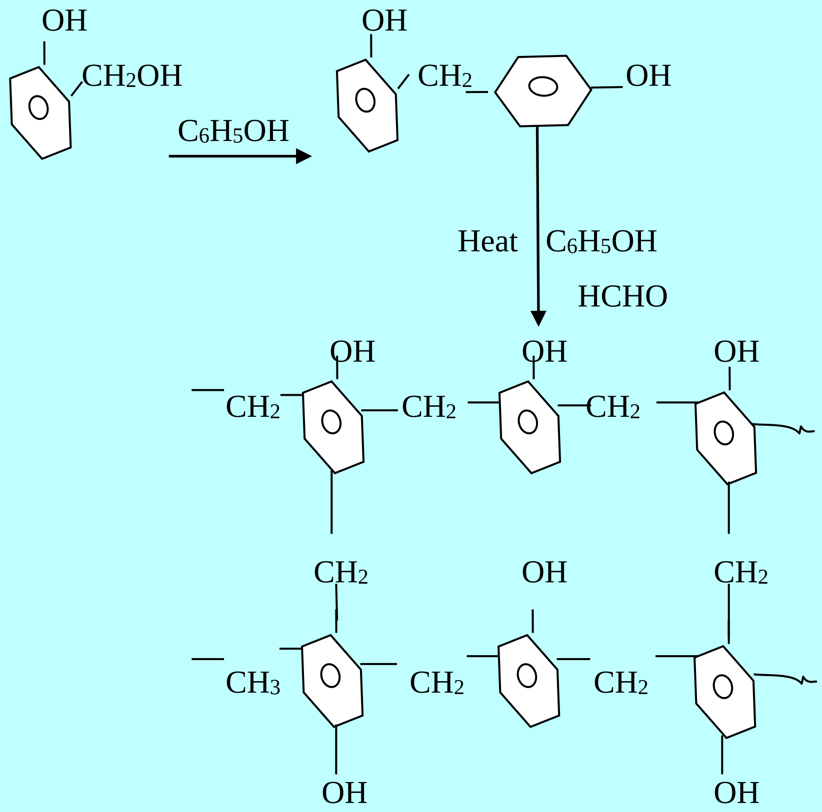


Phenol methanol



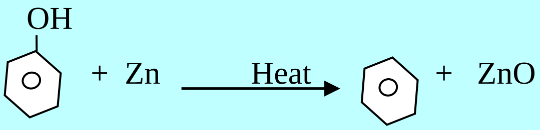
2- and 4- Hydroxymethylphenol

Heating with a larger quantity of methanol in an acidic medium produces rigid, three-dimensional, cross-linked polymers e.g. Bakelite

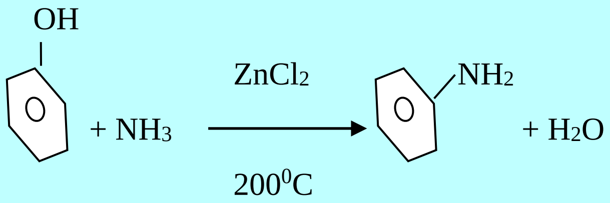


Bakelite

Reaction with Zinc dust



Reaction with ammonia



Differences of reactions between phenol and alcohol

- ✓ Phenol is a stronger acid than alcohol and turns litmus blue red.
- ✓ Phenol does not undergo substitution reactions with HX example HCl, PCI_3 or PCi_5 to form, aryl halides
- ✓ Phenol is not oxidized in a simple way as primary and secondary alcohol

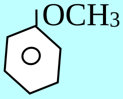
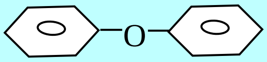
- ✓ Phenol reacts with neutral iron (III) chloride solution to give a purple violet colouration.

Similarities of reactions between phenol and alcohol

- ✓ React with Na to give bubbles of gas.
- ✓ React with carboxylic acids and acid anhydrides to give esters.

ETHERS

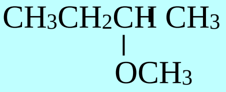
They possess the structure R-O-R^1 where R and R^1 may be aliphatic or aromatic e.g.

$CH_3CH_2OCH_2CH_3$		
Ethoxyethane	Methoxybenzene	Phenoxy benzene

Compounds in which R and R^1 are identical are described as symmetrical or simple ethers and where R and R^1 are different as unsymmetrical or mixed ethers.

NOMENCLATURE

The IUPAC system regards them as alkoxy derivatives of alkanes or of the aryl nucleus e.g.



$CH_3CH_2\underset{\underset{OCH_3}{|}}{CH}\,CH_3$ 2-methoxybutane.

CH_3OCH_3	Methoxymethane
$CH_3OCH_2CH_3$	Methoxyethane
$CH_3CH_2OCH_2CH_3$	Ethoxyethane
$C_6H_5OCH_3$	Methoxybenzene
$C_6H_5OCH_2CH_3$	Ethoxybenzene
$C_6H_5OC_6H_5$	Phenoxybenzene

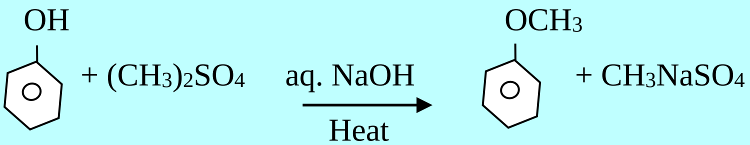
Industrial source

$$2CH_3CH_2OH \xrightleftharpoons[140^{o}C]{\text{conc. } H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

Synthetic preparations

$$RX + R^1\bar{O}Na^+ \xrightarrow{\text{reflux}} ROR^1 + NaX$$

And



Methoxybenzene

Partial Dehydration of alcohols

$$2ROH \xrightleftharpoons[140^{o}C]{\text{Conc. } H_2SO_4} ROR + H_2O$$

This method is limited only to symmetrical ethers

From Haloalkanes and dry silver (I) oxide

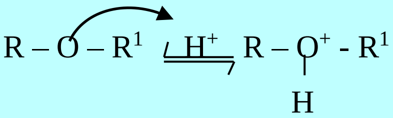
$$2RX + Ag_2O \xrightarrow{\text{warm}} ROR + 2AgX$$

This preparation is for symmetrical ethers only.

REACTIONS

Hydrolysis

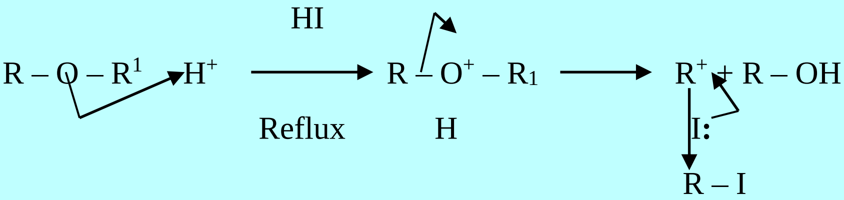
Unlike alcohols, ethers do not contain a replaceable proton and are generally unreactive compounds, not reacting with metals, strong bases or phosphorous pentahalides and not easily undergoing substitution with ionic species. However, the oxygen atom is sufficiently basic to undergo protonation in an acidic medium by the donation of a lone pair of electrons i.e.



$$R-O-R^1 \overset{H^+}{\rightleftharpoons} R-\underset{\displaystyle H}{\overset{}{O^+}}-R^1$$

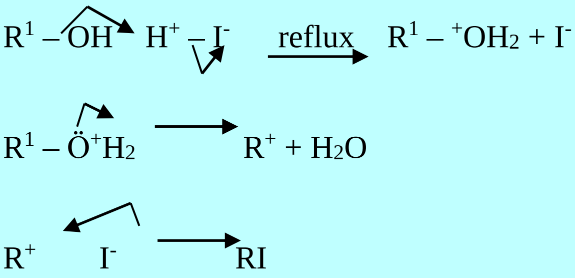
The protonated species is then susceptible to subsequent attack by a Nucleophile.

Reactions involving HX



$$R-O-R^1\ \ H^+ \xrightarrow[\text{Reflux}]{HI} R-\underset{\displaystyle H}{O^+}-R_1 \longrightarrow \underset{\begin{array}{c}\downarrow\ I:\\ R-I\end{array}}{R^+} + R-OH$$

An alcohol is formed as one of the initial products but then reacts with more hydrogen iodide to yield the iodo alkane



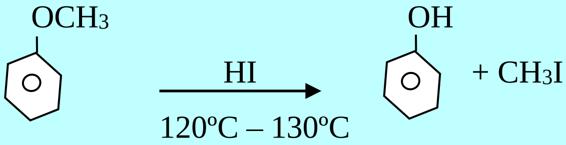
$$R^1-OH\ \ H^+-I^- \xrightarrow{\text{reflux}} R^1-{}^+OH_2 + I^-$$

$$R^1-\ddot{O}^+H_2 \longrightarrow R^+ + H_2O$$

$$R^+\ \ \ I^- \longrightarrow RI$$

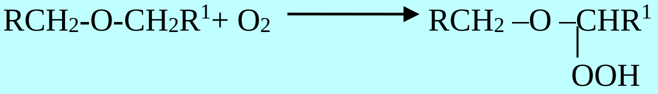
The alcohol may be isolated by employing milder conditions

e.g.



Reactivity HI > HBr > HCl

Autoxidation



$$RCH_2\text{-}O\text{-}CH_2R^1 + O_2 \longrightarrow RCH_2\,–O\,–\underset{\textstyle OOH}{\underset{|}{C}}HR^1$$

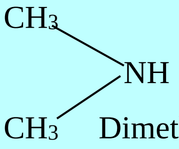
Peroxide

AMINES

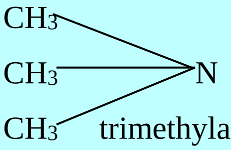
Amines are alkyl or aryl derivatives of ammonia and may be classified as primary, secondary or tertiary according to the number of alky or aryl groups attached to the nitrogen atom.

CH_3NH_2

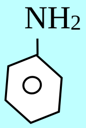
Methyl amine (1°)



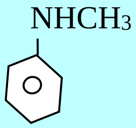
Dimethylamine (2°)



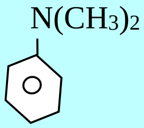
trimethylamine (3°)



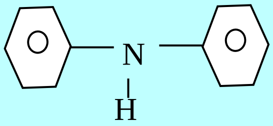
Phenyl amine (1°)



Methyl phenyl amine (2°)



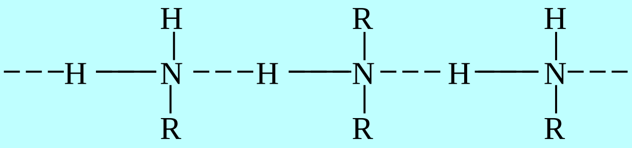
Dimethylphenylamine (3°)



Diphenylamine (2^0)

NB: Aromatic amines are compounds in which the nitrogen atom is attached directly to the aromatic ring.

They are polar compounds and their molecules, with the exception of tertiary amines, form intermolecular hydrogen bonds with each other, thus increasing their boiling points above those of less polar compounds of comparable relative molecular mass.

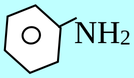


Hence the boiling point decreases in the order

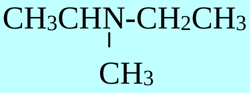
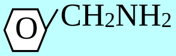
$$1^{o} \text{ amines} > 2^{o} \text{ amines} > 3^{o} \text{amines}$$

Due to the progressive decrease in intermolecular hydrogen bonding. Volatility is enhanced by branding in the carbon chain.

NB: Amines are named as amino alkanes e.g.

CH_3NH_2	Amino methane.
$CH_3NHCH_2CH_3$	Methyl amino ethane
	Amino benzene

Also can be named after the alkyl group attached to the nitrogen atom each name ending in the suffix ‘amine” e.g.

CH_3NH_2	Methyl amine
CH_3NHCH_3	Dimethyl amine
$CH_3NHCH_2CH_3$	Methyl ethylamine
 $CH_3CH\underset{\underset{\displaystyle CH_3}{\vert}}{N}-CH_2CH_3$	methyl diethyl amine
	Phenyl amine (Aniline)
	Benzyl amine

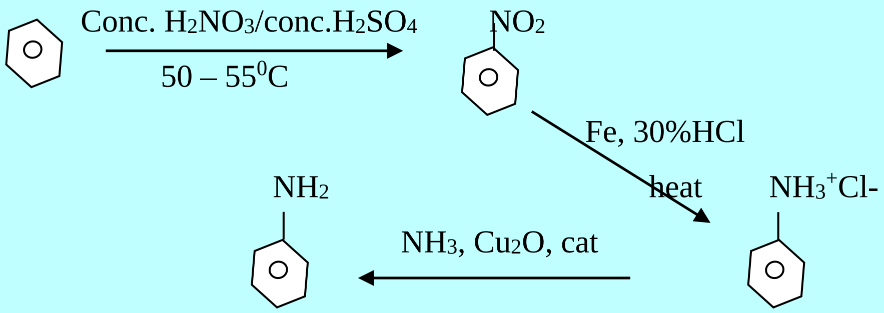
Industrial source

Methyl amines

$$\begin{tikzcd} NH_3 \arrow[r, "{CH_3OH,\ Al_2O_3 \text{ cat}}", "{\text{High pressure } 400\text{-}450^{o}C}"'] & CH_3NH_2 \arrow[r, "CH_3OH"] & (CH_3)_2NH \arrow[d, "CH_3OH"] \\ & & (CH_3)_3N \end{tikzcd}$$

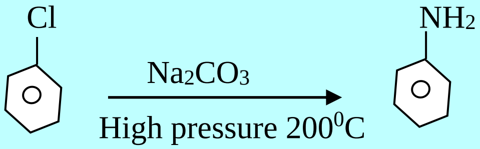
Ethyl amines are manufactured by passing ethanol, ammonia and hydrogen under pressure, over a metallic hydrogenation catalyst at 150-240ºC.

Phenyl amine (ANILINE) is manufactured from nitrobenzene which is itself prepared from the abundantly available benzene i.e.



Phenyl ammonium chloride

Aromatic amines are sometimes obtained by treating Chlorobenzene with ammonia at a high temperature and high pressure in the presence of a Copper (II) Oxide catalyst



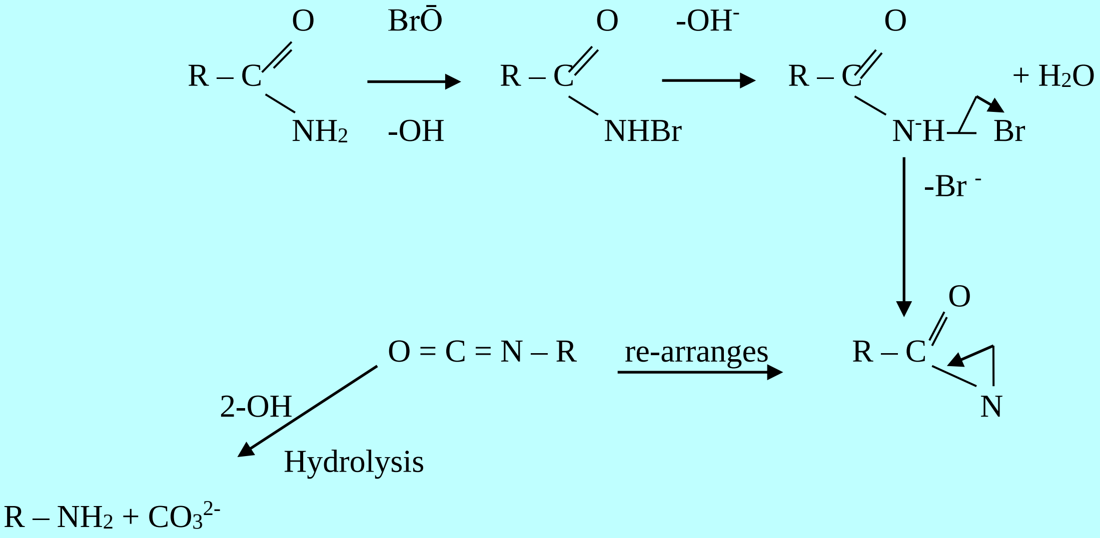
Synthetic preparations

Hofmann Degradation of amides

The amide is warmed with bromine and concentrated aqueous solution of alkali.

$$CH_3CONH_2 \xrightarrow[\text{Warm}]{Br_2\ /\ 4NaOH} CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$$

Mechanism



Reduction of Nitrites

$$RCN + \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2NH_2$$

$$HCN + \xrightarrow[\text{dry ether}]{LiAlH_4} CH_3NH_2$$

$$RCH = NOH + \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2NH_2 + H_2O$$

Or $$RCN + \xrightarrow[\text{Ethanol}]{Na} CH_3CH_2 – NH_2$$

From Haloalkanes

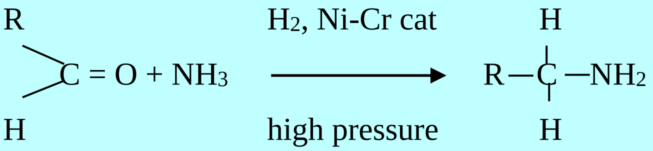
$$Rx + alc.NH_3 \xrightarrow[\text{Heat}]{\text{Sealed tube}} RNH_2 + HX$$

$$RNH_2 + RX \longrightarrow R_2NH + HX$$

$$R_2NH + RX \longrightarrow R_3N + HX$$

$$R_3N + RX \longrightarrow R_4N^+X^-$$

Reductive Amination of aldehyde and ketones

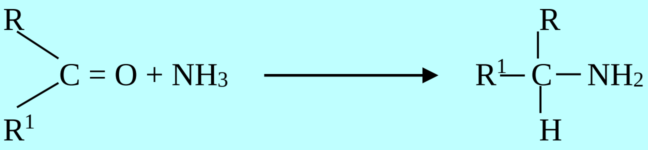


Ni-Cr cat

Nickel chromium catalyst

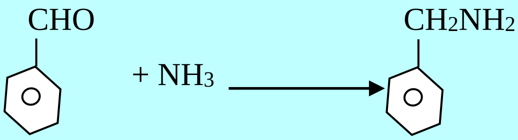
(Aldehyde)

(1^0 amine)



Ketone

(1^o amine)

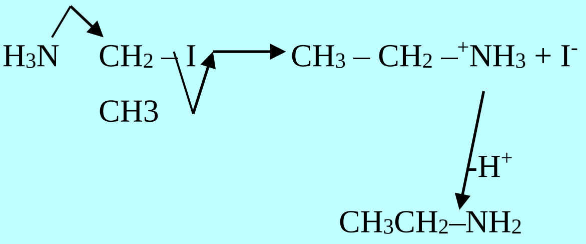


(Benzyaldehyde)

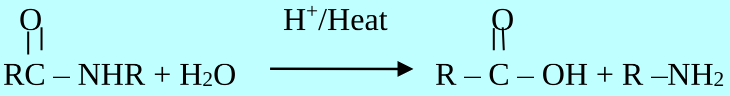
From alkyl halides

$$CH_3CH_2 - I \xrightarrow[\text{Heat}]{\text{Conc. } NH_3} CH_3CH_2 - NH_2 + HI$$

Mechanism



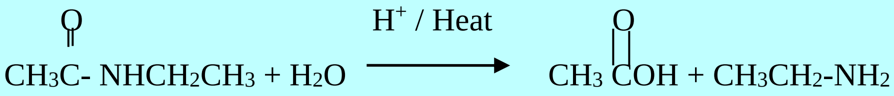
From secondary and tertiary amides



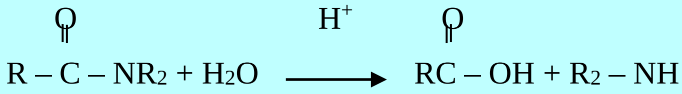
$$R\overset{O}{\overset{\|}{C}} - NHR + H_2O \xrightarrow{H^+/Heat} R - \overset{O}{\overset{\|}{C}} - OH + R - NH_2$$

Secondary Primary amine

e.g.



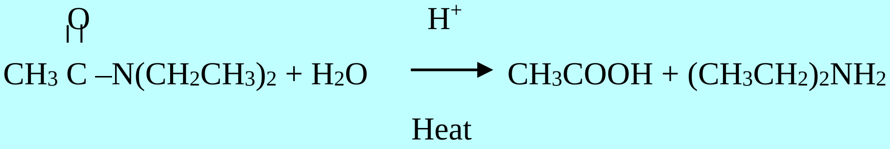
$$CH_3\overset{O}{\overset{\|}{C}}- NHCH_2CH_3 + H_2O \xrightarrow{H^+ / Heat} CH_3\overset{O}{\overset{\|}{C}}OH + CH_3CH_2-NH_2$$



$$R - \overset{O}{\overset{\|}{C}} - NR_2 + H_2O \xrightarrow[Heat]{H^+} R\overset{O}{\overset{\|}{C}} - OH + R_2 - NH$$

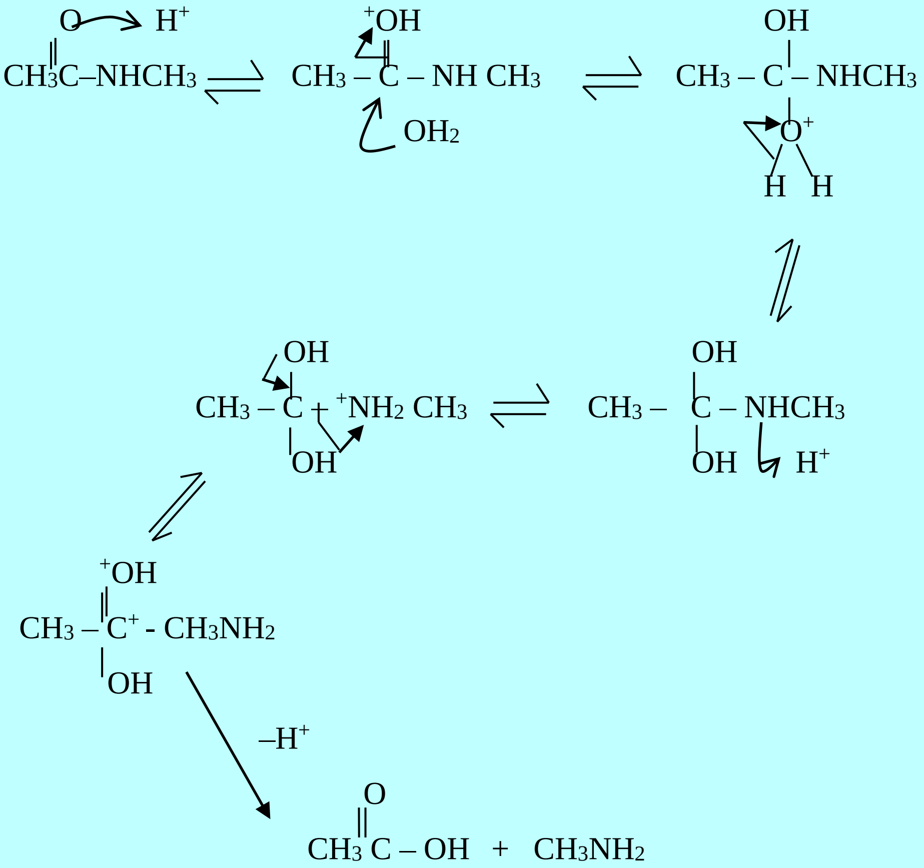
Tertiary amine Heat Secondary amine

e.g.

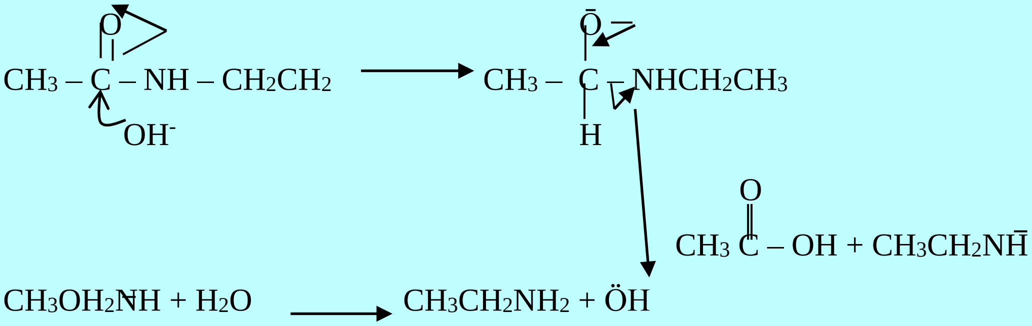


$$CH_3\overset{O}{\overset{\|}{C}} -N(CH_2CH_3)_2 + H_2O \xrightarrow[Heat]{H^+} CH_3COOH + (CH_3CH_2)_2NH_2$$

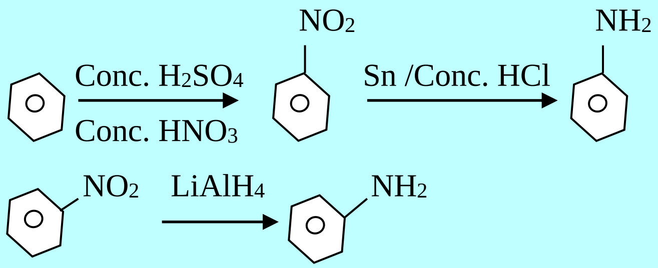
Mechanism (acid hydrolysis)



Base catalyzed



From nitro compounds



REACTIONS

Basic properties

- ✓ Amines dissolve in water to give weakly alkaline solution like ammonia the solution turns red litmus blue.

  $R\text{-}NH_2 + H_2O \rightleftharpoons R^+NH_3 + \ddot{O}H$

- ✓ The basic characters of amines are due to the presence of the non-bonded electron pair on nitrogen atom which donate electrons. Therefore, the strength of the base will depend on the availability of the non-bonded electron pair. Hence basically of amines should be in the order

Tertiary > 2º > 1º > ammonia

But the order is 2º >1º >3º >ammonia

Qn. Explain why propyl amine is a stronger base than phenyl amine.

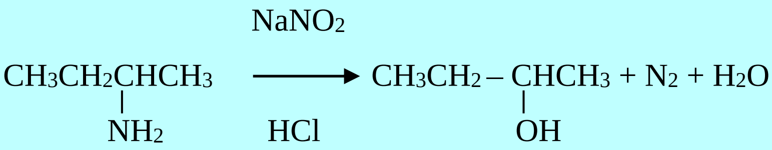
Solution

The propyl group of propyl amine releases electrons (positive inductive effect) to the nitrogen atom making the lone pair of electrons more available for proton attraction. In phenyl amine the lone pair of electrons on the nitrogen atom interacts with the decolorized electrons of the benzene ring and thus the electrons are less available for proton attraction.

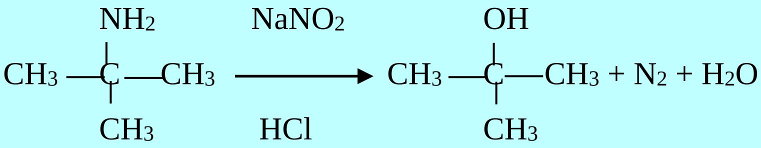
Reaction with nitrous acid

$$R - NH_2 + HNO_2 \longrightarrow R - OH + N_2 + H_2O$$

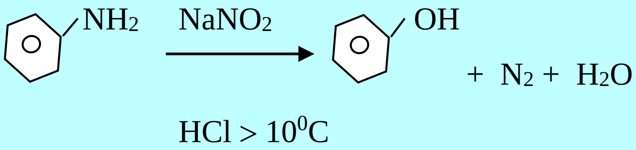
E.g. $CH_3CH_2{-}NH_2 \xrightarrow[HCl]{NaNO_2} CH_3CH_2\text{-}OH + N_2 + H_2O$

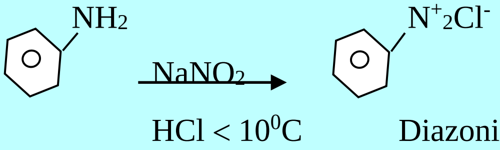


$$CH_3CH_2\underset{\substack{|\\NH_2}}{C}HCH_3 \xrightarrow[HCl]{NaNO_2} CH_3CH_2-\underset{\substack{|\\OH}}{C}HCH_3 + N_2 + H_2O$$



$$CH_3-\overset{\substack{NH_2\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3 \xrightarrow[HCl]{NaNO_2} CH_3-\overset{\substack{OH\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3 + N_2 + H_2O$$





Diazonium salt

Secondary amines react with nitrous acid to give products which are yellow oils called nitroso amines

$$R_2-NH + HNO_2 \longrightarrow R_2-N-N=O + H_2O$$

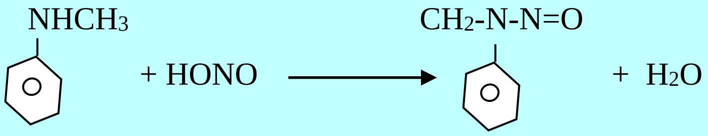
(Yellow oils)

e.g. $(CH_3CH_2)_2\,NH + HNO_2 \longrightarrow (CH_3CH_2)_2-N-N=O$

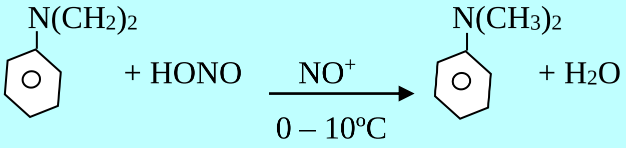
Diethyl nitroso amine

NB: Addition of phenol and Conc. H_2SO_4 to nitroso amine produces an intesice blue colour when made alkaline. This is used as a test for 2° amines.

e.g.



NB: The high reactivity of the ring enables Tertiary aromatic amines to undergo nitrosation in the 4-position (of phenol)



Reactions of Benzenediazonium salt

1. Nucleophilic substitution reaction, in which the diazonium group is liberated as nitrogen to form a carbocation (Carbonium ion) prior to attack by the nucleophile.

$$C_6H_5N^+_2 \xrightarrow[\text{Warm}]{\text{Excess dil.}H_2SO_4} C_6H_5^+ + N_2$$

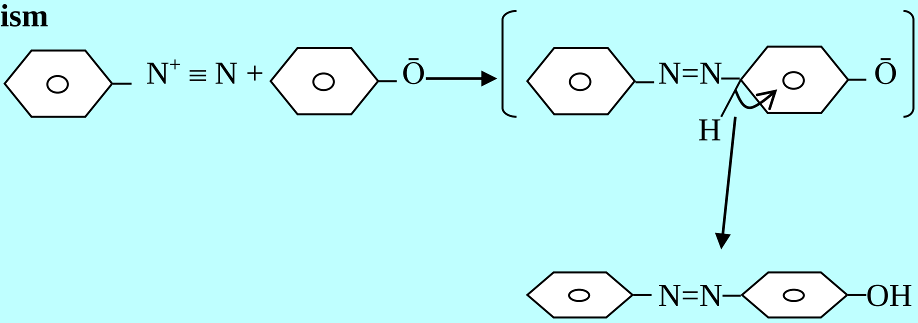
$$C_6H_5^+ \xrightarrow{H_2O} C_6H_5OH + H^+$$

NB: The presence of excess, dilute sulphuric acid prevents coupling

2. **Coupling reaction**

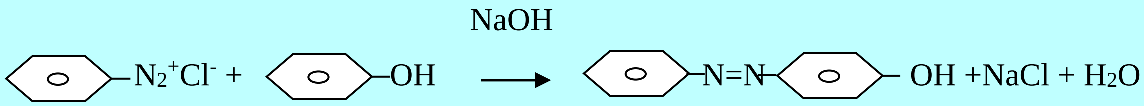
The coupling of a diazonium cation with a phenoxide or similar anion is of immense importance, especially in the synthesis of Azodyes

Mechanism

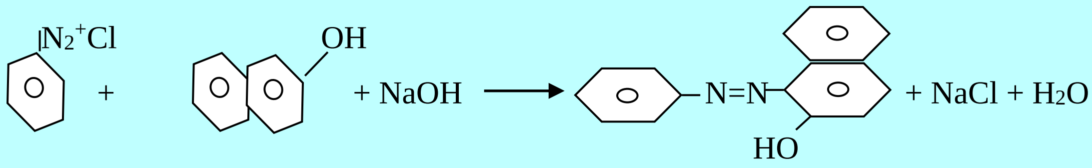


4 – Hydroxyphenyl azobenzene

(Bright yellow precipitate)

i.e. 

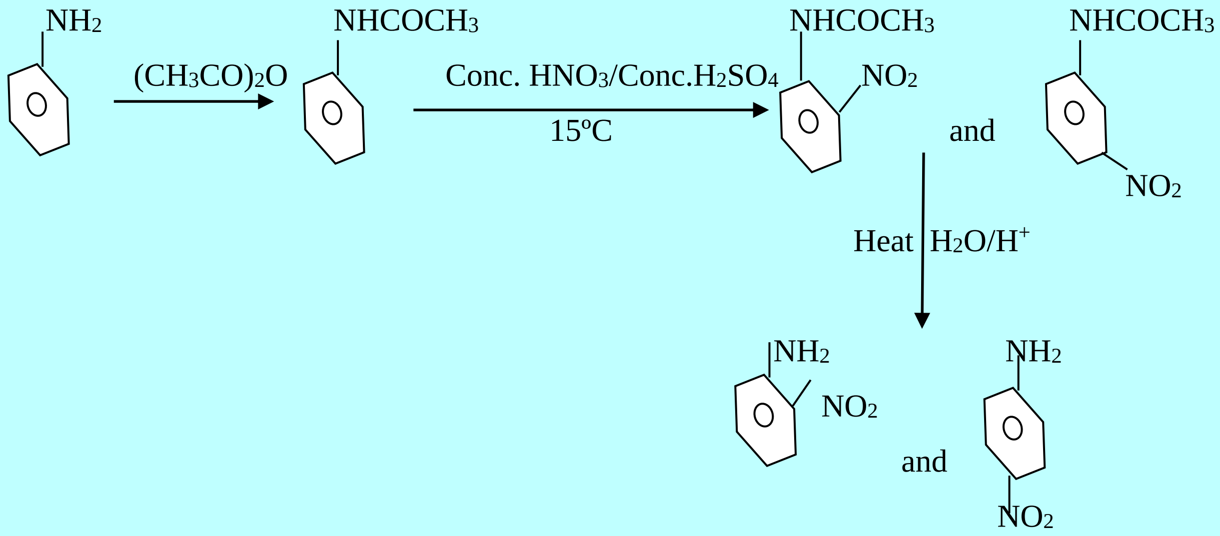
With naphthalene- 2-ol (2 naphthol), Benzenediazonium salts form bright red crystalline dyes i.e.



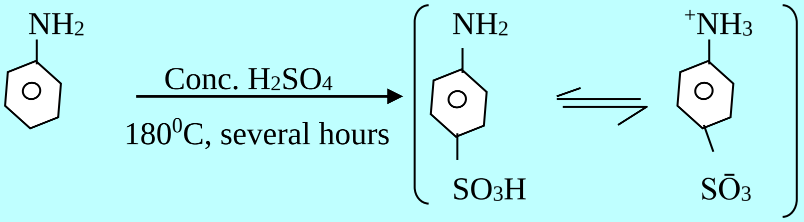
1 – Phenylazo naphthalen– 2– ol

Ring substitution

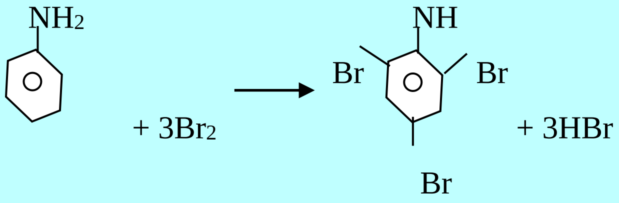
Nitration



Sulphonation

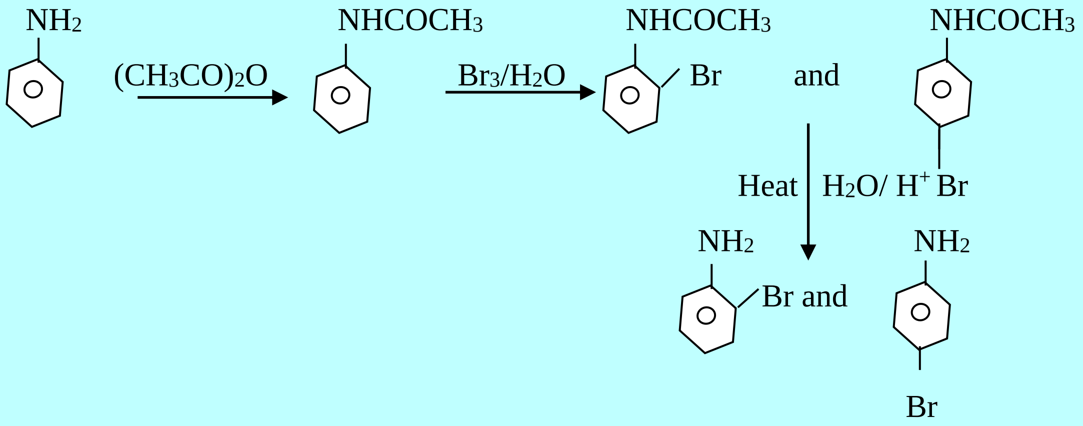


Halogenation



2, 4, 6-, Tribromo phenyl amine

and

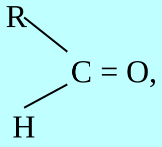


2– and 4 – Bromo phenylamine

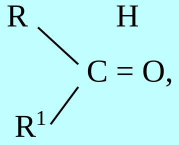
ALDEHYDES AND KETONES

Aldehydes and ketones are referred to as carbonyl compounds; they both contain the carbonyl, > C=O functional group. General formula $C_nH_{2n}O$

Aldehydes all possess a single hydrogen attached to the carbonyl carbon (–CHO)



Ketones always contain two hydro carbon groups



R and R^1 may be aliphatic or aromatic

NOMENCLATURE

Aldehydes

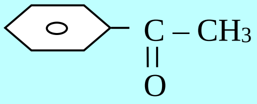
IUPAC names are obtained by dropping the ending "e" of the corresponding alkane and replacing it with suffix "al"

HCHO	Methanal (form aldehyde)
CH_3CHO	Ethanal
$C_6H_5CH_2CHO$	Phenylethanal

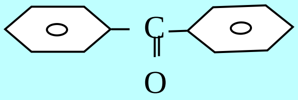
Ketones

IUPAC names are derived by taking the stem of the name of the corresponding alkane and replacing the ending "e' with the suffix "one"

CH_3COCH_3	Propanone	(Acetone)
$CH_3COCH_2CH_3$	Ethanone	



Phenylethanone



Diphenylmethanone

Industrial source

$$\left.\begin{array}{l} 2CH_3OH + O_2 \xrightarrow[560^{\circ}C\ -\ 650^{\circ}C]{\text{Ag cat}} 2HCHO + 2H_2O \\ \\ CH_3OH \xrightarrow{\text{Ag}} HCHO + H_2 \end{array}\right\} \text{By air oxidation of methanol}$$

Also large quantities of ethanal are obtained by the air oxidation of ethanol

$$2CH_3CH_2OH + O_2 \xrightarrow[\text{High temp.}]{\text{Ag}} 2CH_3CHO + 2H_2O$$

$$CH_3CH_2OH \xrightarrow{Ag} CH_3CHO + H_2$$

And also by direct dehydrogenation

$$CH_3CH_2OH \xrightarrow[300^\circ C]{\text{Finely divided Cu}} CH_3CHO + H_2$$

Also by acid hydrolysis of Ethyne

$$CH \equiv CH + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} CH_3CHO$$

Propanone (acetone) is obtained by dehydrogenating propan-2-o1 over a copper, brass or zinc oxide catalyst at 350°C– 380°C

$$(CH_3)_2\ CHOH \xrightarrow[350^\circ C\ –\ 380^\circ C]{\text{Cu, brass, or ZnO}} (CH_3)_2CO + H_2$$

Also

$$CH_2 = CH_2 + PdCl_2 + H_2O \xrightarrow[CuCl_2]{20\ –\ 60^\circ C} CH_2CHO + Pd + 2HCl$$

$$CH_3CH = CH_2 + PdCl_2 + H_2O \longrightarrow CH_3COCH_2 + Pd + 2HCl$$

Butanone is prepared similarly, but from but-1-ene.

Benzaldehyde is manufactured by chlorinating the side chain of methyl benzene to dichloromethyl benzene and then hydrolyzing

$$C_6H_5CH_3 \xrightarrow[\text{Heat}]{Cl_2} C_6H_5CHCl_2 \xrightarrow[100^0C]{H_2O} C_6H_5CHO$$

Other technique is to pass methylbenzene vapour and air over a vanadium (V) oxide catalyst heated to 350°C

$$C_6H_5CH_3 + O_2 \xrightarrow[350^\circ C]{V_2O_5} C_6H_5CHO + H_2O$$

Synthesis preparations

Oxidation of alcohols

$$CH_3CH_2OH \xrightarrow[\text{Warm}]{Cr_2O_7/H^+} CH_3CHO + H_2O$$

$$(CH_3)_2CHOH \xrightarrow[\text{Warm}]{Cr_2O_7/H+} (CH_3)_2CO + H_2O$$

NOTE: An acidified solution of manganate (VII) can be used.

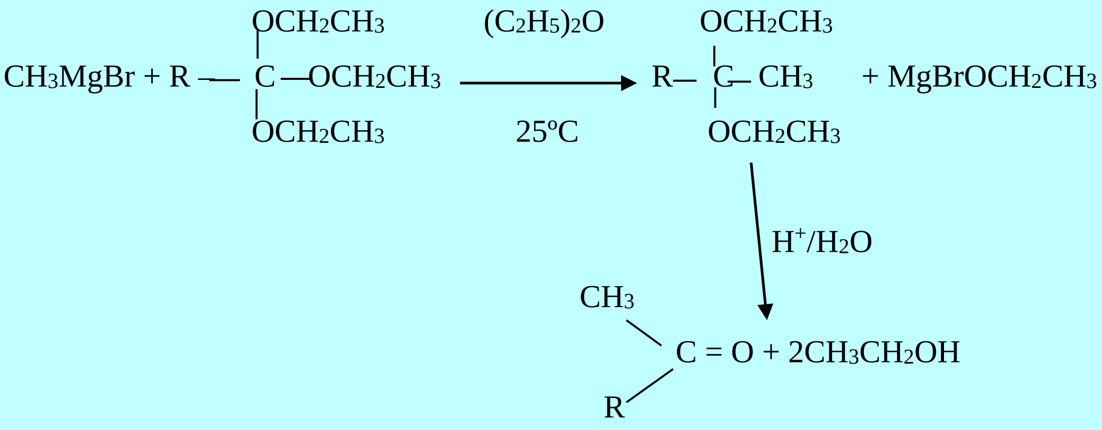
Alternatively, oxidation may be accompanied by dehydrogenation of the alcohol, using copper catalyst heated to about 300ºC.

$$CH_3CH_2OH \xrightarrow{Cu,\ 300^oC} CH_3CHO + H_2$$

$$(CH_3)_2CHOH \xrightarrow[300^oC]{Cu} (CH_3)_2CO + H_2$$

From Grignard reagents

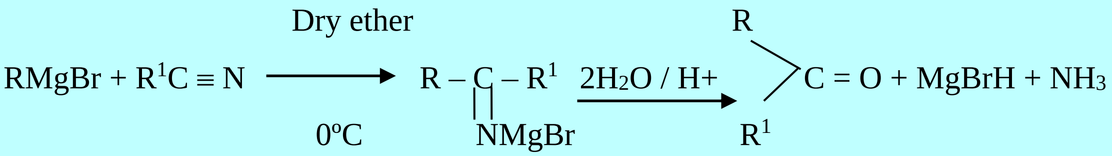
a) Using a 1,1,1-Triethoxyalkane



$$CH_3MgBr + R-\underset{OCH_2CH_3}{\overset{OCH_2CH_3}{C}}-OCH_2CH_3 \xrightarrow[25^oC]{(C_2H_5)_2O} R-\underset{OCH_2CH_3}{\overset{OCH_2CH_3}{C}}-CH_3 + MgBrOCH_2CH_3$$

$$\xrightarrow{H^+/H_2O} \begin{matrix} CH_3 \\ R \end{matrix}\!\!>C=O + 2CH_3CH_2OH$$

From alkyl and Aryl nitilles



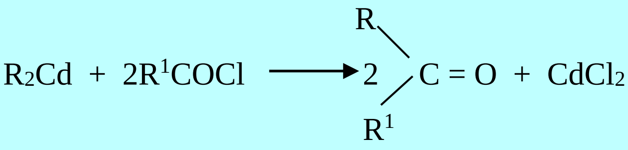
$$RMgBr + R^1C \equiv N \xrightarrow[0^oC]{\text{Dry ether}} R - \underset{\underset{NMgBr}{\|}}{C} - R^1 \xrightarrow{2H_2O / H+} \overset{R}{\underset{R^1}{>}}C = O + MgBrH + NH_3$$

(Only suitable for ketones)

From acyl chlorides

The Grignard reagent must be converted first into the less reactive di alkyl cadmium compound; otherwise the reaction proceeds to yield the tertiary alcohol

$$2RMgBr + CdCl_2 \xrightarrow[25^0C]{(C_2H_5)_2O\text{ (dry ether)}} R_2Cd + 2MgBrCl$$



$$R_2Cd + 2R^1COCl \longrightarrow 2 \overset{R}{\underset{R^1}{>}}C = O + CdCl_2$$

R and R^1 may be primary alkyl or aryl groups

Decarboxylation of calcium salts

$$(CH_3COO)_2Ca + (HCOO)_2Ca \xrightarrow[400^oC]{\text{dry distil}} 2CH_3CHO + 2CaCO_3$$

$$(CH_3COO)_2Ca \xrightarrow[400^oC]{\text{dry distil}} (CH_3)_2CO + CaCO_3$$

Decarboxylation of carboxylic acid

$$CH_3COOH + HCOOH \xrightarrow[300^oC]{MnO} CH_3CHO + H_2O + CO_2$$

$$2CH_3COOH \xrightarrow[300^oC]{MnO} (CH_3)_2CO + H_2O + CO_2$$

<u>Hydrogenation of acyl chlorides using a poisoned catalyst</u>.

A Palladium / Barium Sulphate catalyst is deactivated by addition of a poison such as quimline /sulphur to prevent further reduction to the alcohol

$$RCOCl \xrightarrow[\text{Poisoned Pd/BrSO}_4]{H_2 \text{ / Heat}} RCHO + HCl$$

Only suitable for aldehydes

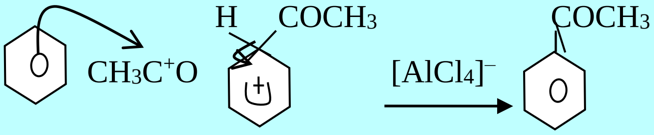
<u>Preparation of Phenylethanone</u>

Friedel – crafts Acylation

$$C_6H_6 + (CH_2CO)_2O \xrightarrow[50^oC]{AlCl_3} C_6H_5COCH_3 + CH_3COOH$$

Mechanism

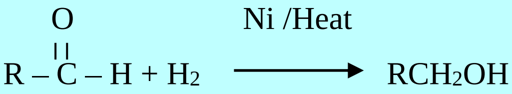
$$(CH_3CO)_2O + AlCl_3 \rightleftharpoons CH_3{}^+CO \; + \; [CH_3COO\ AlCl_3]^-$$



REACTIONS

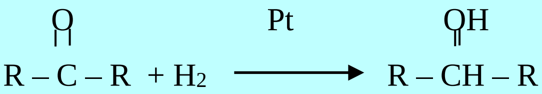
Reaction with hydrogen

Both aldehydes and ketones are reduced by hydrogen in the presence of catalyst like Ni, Pt or Pd to 1° and 2° alcohols respectively.



$$R-\overset{\overset{\displaystyle O}{||}}{C}-H + H_2 \xrightarrow{\text{Ni /Heat}} RCH_2OH$$

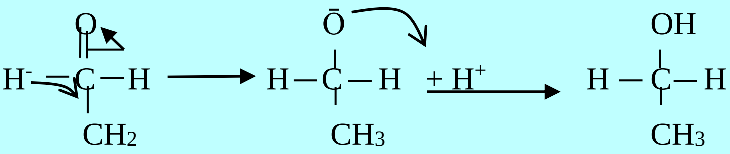
e.g.



$$R-\overset{\overset{\displaystyle O}{||}}{C}-R + H_2 \xrightarrow{\text{Pt}} R-\overset{\overset{\displaystyle OH}{|}}{CH}-R$$

The metal (Pt) aids splitting of H_2

Mechanism. $H-H \longrightarrow H^{+} + H^{-}$

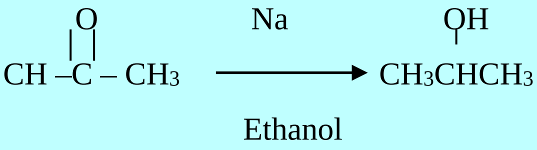


$$H^{-} - \underset{\underset{\displaystyle CH_2}{|}}{\overset{\overset{\displaystyle O}{||}}{C}} - H \longrightarrow H - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle \bar{O}}{|}}{C}} - H \xrightarrow{+ H^{+}} H - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}} - H$$

Reduction also can be affected using $LiAlH_4$ or $NaBH_4$ or Na/alcohol

I.e. $CH_3CH_2CHO \xrightarrow{LiAH_4} CH_3CH_2CH_2–OH$

And

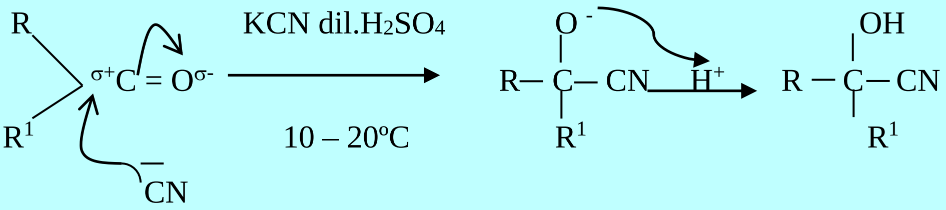


$$CH-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 \xrightarrow[\text{Ethanol}]{\text{Na}} CH_3\overset{\overset{\displaystyle OH}{|}}{C}HCH_3$$

Addition of hydrogen cyanide

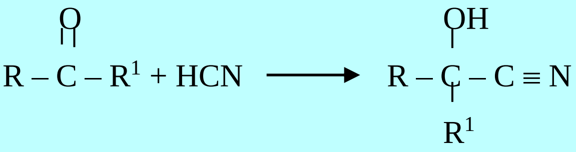
Mechanism

Aldehydes and simple ketones undergo addition of hydrogen cyanide.



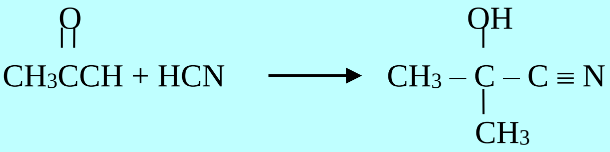
NB

Hydrogen cyanide is usually generated during the reaction by the action of dil. H_2SO_4 on alkali metal cyanide at 10-20ºC



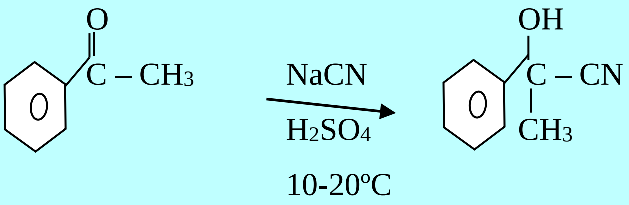
$$R - \overset{O}{\overset{\|}{C}} - R^1 + HCN \longrightarrow R - \overset{OH}{\underset{R^1}{C}} - C \equiv N$$

e.g.

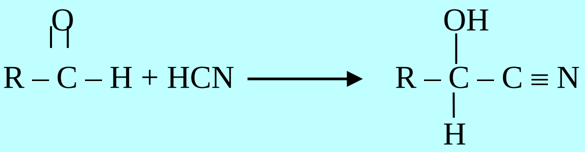


$$CH_3\overset{O}{\overset{\|}{C}}CH + HCN \longrightarrow CH_3 - \overset{OH}{\underset{CH_3}{C}} - C \equiv N$$

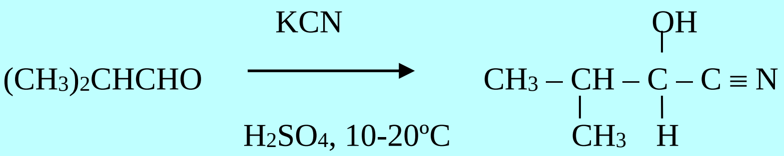
2 – Hydroxyl – 2 – methyl propanitrile



2-hydroxy -2- phenyl propanitrile



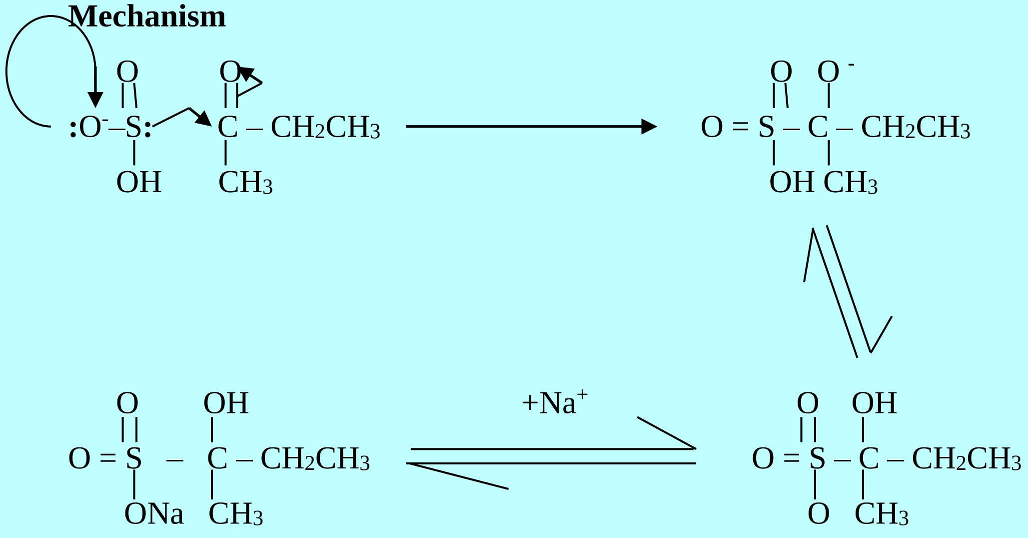
$$R - \overset{O}{\overset{\|}{C}} - H + HCN \longrightarrow R - \overset{OH}{\underset{H}{C}} - C \equiv N$$

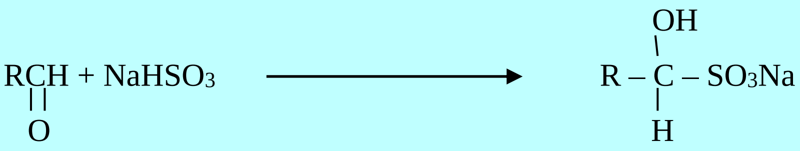


$$(CH_3)_2CHCHO \xrightarrow[H_2SO_4,\ 10\text{-}20^oC]{KCN} CH_3 - \underset{CH_3}{CH} - \overset{OH}{\underset{H}{C}} - C \equiv N$$

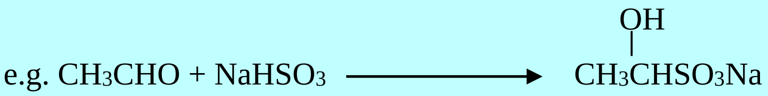
Reaction with sodium hydrogen sulphite (Sodium Bisulphite)

Mechanism

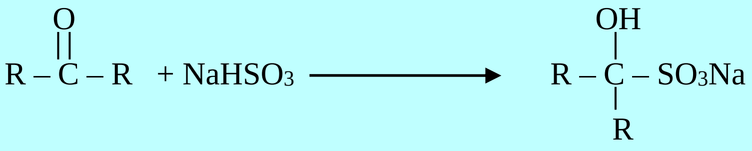




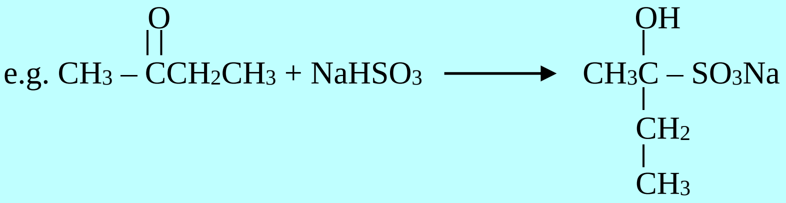
$$\mathrm{R\underset{\underset{O}{\|}}{C}H + NaHSO_3 \longrightarrow R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-SO_3Na}$$



$$\text{e.g. } \mathrm{CH_3CHO + NaHSO_3 \longrightarrow CH_3\overset{\overset{OH}{|}}{C}HSO_3Na}$$



$$\mathrm{R-\overset{\overset{O}{\|}}{C}-R + NaHSO_3 \longrightarrow R-\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{C}}-SO_3Na}$$



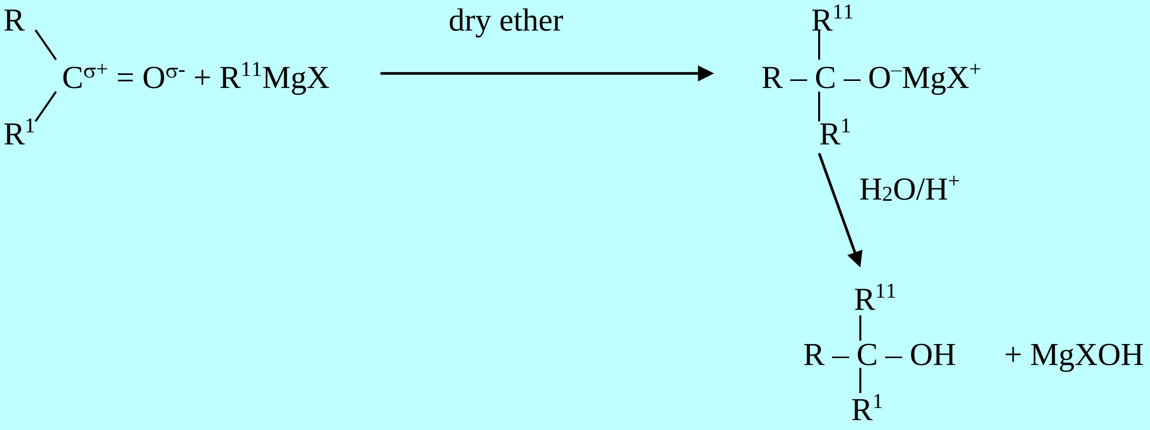
$$\text{e.g. } \mathrm{CH_3-\overset{\overset{O}{\|}}{C}CH_2CH_3 + NaHSO_3 \longrightarrow CH_3\overset{\overset{OH}{|}}{\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{C}}-SO_3Na}$$

Reaction with phosphorous pentachloride

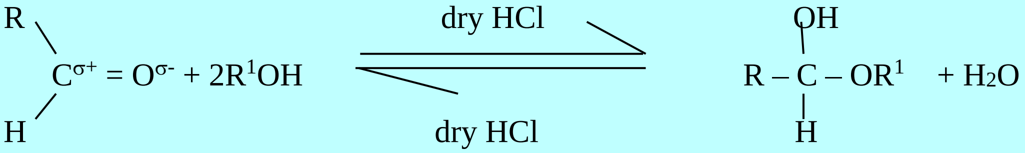
Both aldehyde and ketones react with PCl_5 to give gem dihalides

e.g. $CH_3CHO + PCl_5 \rightarrow CH_3CHCl_2 + POCl_3$

Addition of Grignard reagent

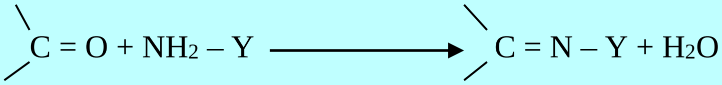


Addition of alcohol



Condensation

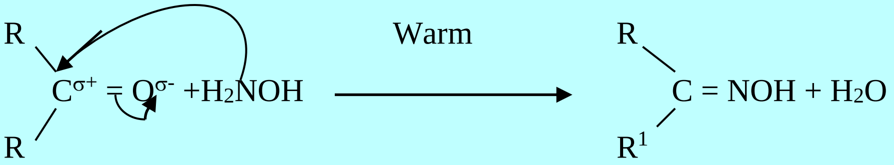
Both Aldehydes and ketones react with compounds containing $–NH_2$ with loss of water molecule.



i.e. $C = \boxed{O + H_2}N \longrightarrow C = N – Y + H_2O$

Amine group

a) With hydroxylamine NH_2OH

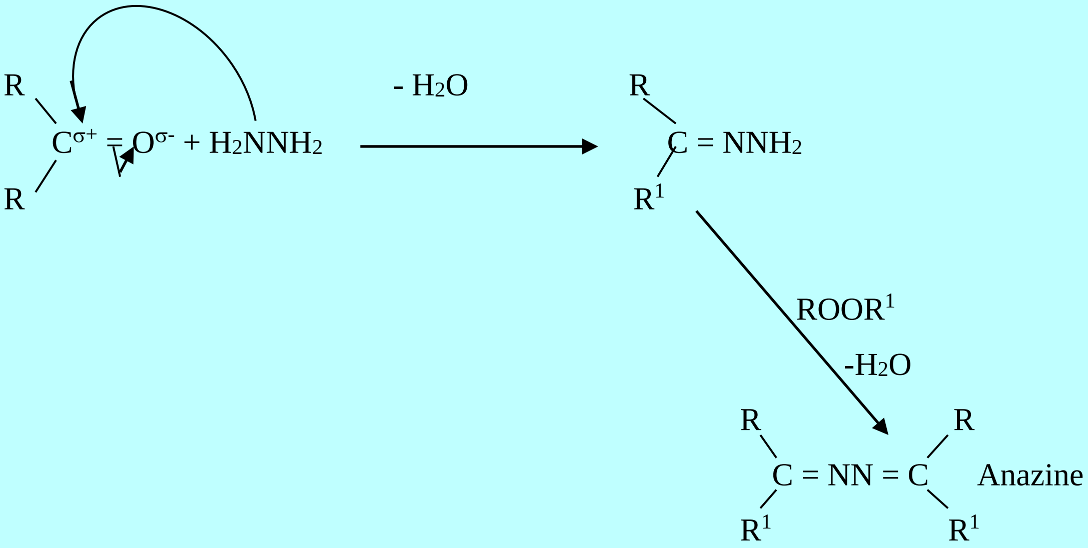


An oxime

Ethanal and propanone yield ethanal oxime and propanone oxime respectively

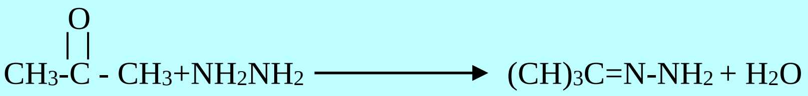
e.g. $CH_3CH_2CHO + NH_2OH \longrightarrow CH_3CH_2CHNOH + H_2O$

With hydrazine NH_2NH_2



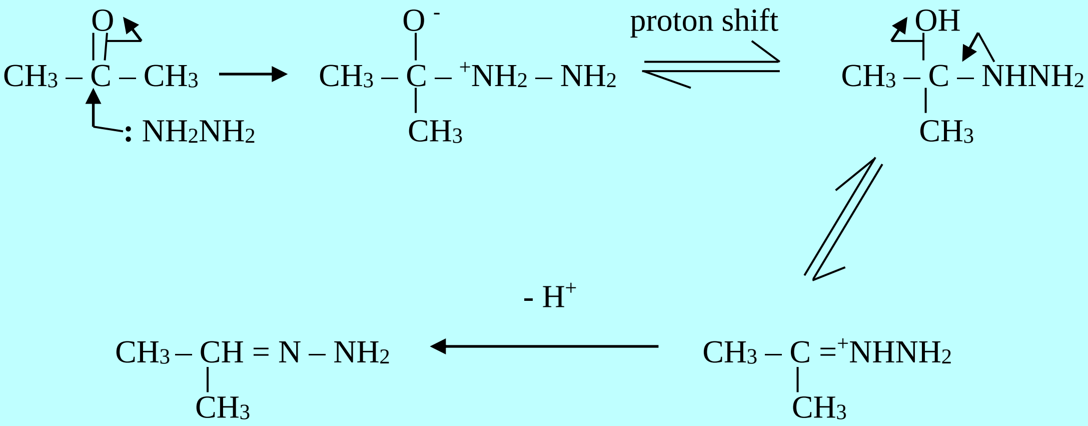
Both hydrazones and azines are crystalline solids

e.g.

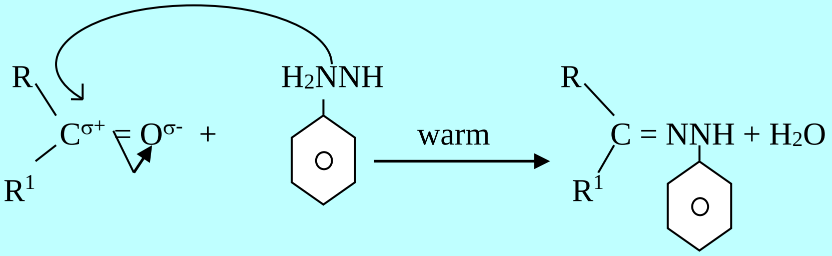


$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{ - }CH_3+NH_2NH_2 \longrightarrow (CH)_3C=N\text{-}NH_2 + H_2O$$

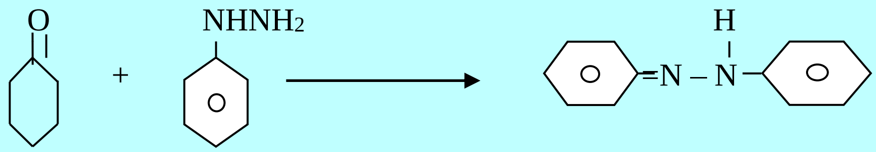
Mechanism



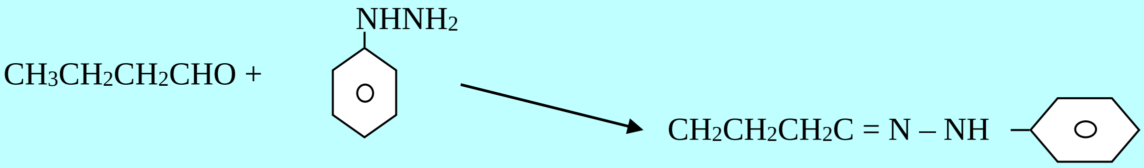
With phenyl hydrazine $C_6H_5NHNH_2$



E.g.

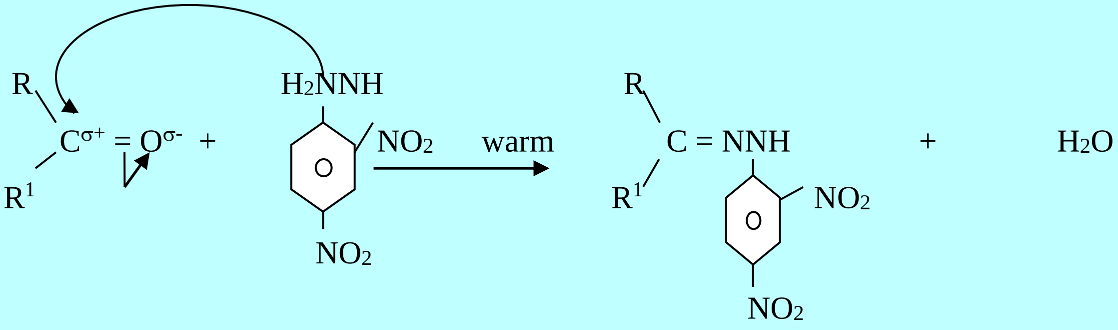


Cyclohetatone phenyl hydrazone



Butanal phenyl hydrazone

With 2, 4-dinitrophenyl hydrazine $C_6H_5(NO_2)_2NHNH_2$

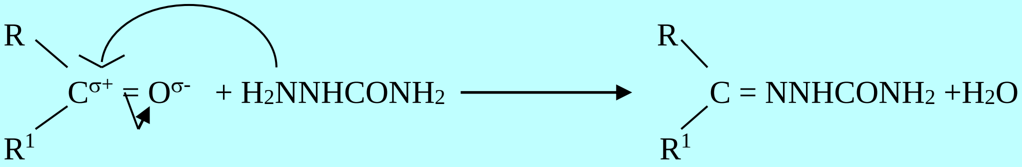


NOTE

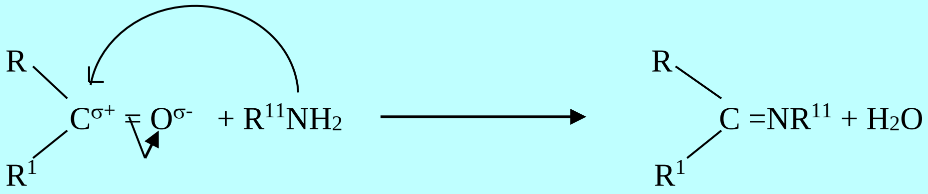
2-4-dintrophenyl hydrazine is utilized in Brady’s reagent for the detection of a carbonyl functional group.

It is moistened with methanol and then shaken with a few drops of concentrated sulphuric acid in order to convert it into the yellow sulphate. On adding the carbonyl compound, the 2-4 dinitro phenyl hydrazone crystallizes out fairly rapidly although the reaction occurs rather more slowly with ketones than with aldehydes.

With Semicarbazide $NH_2NHCONH_2$



With primary Amines (formation of Schiff Bases)



NB

Unless the carbon-nitrogen double bond is stabilized by conjugation with an aromatic nucleus, these bases tend to be unstable in aqueous solution and revert back into the starting reagents i.e. in a non-aqueous medium they polymerize i.e. stable Schiff bases can be formed between the aliphatic carbonyl compound and phenyl amine i.e.

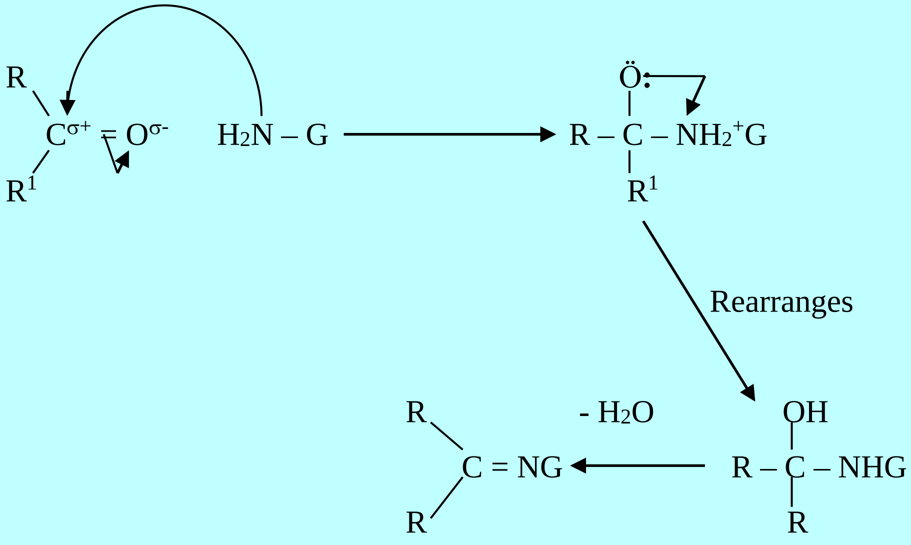
$CH_3CHO + C_6H_5NH_2 \longrightarrow$ Stable Schiff base

Benzene carbaldehyde and phenyl amine and so on

$C_6H_5CHO + C_6H_5NH_2 \longrightarrow$ Stable Schiff base

Mechanism for condensation reactions

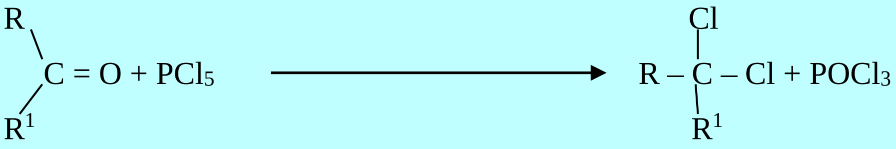
Consider an amino derivative $NH_2 - G$, where G represents the attached group.



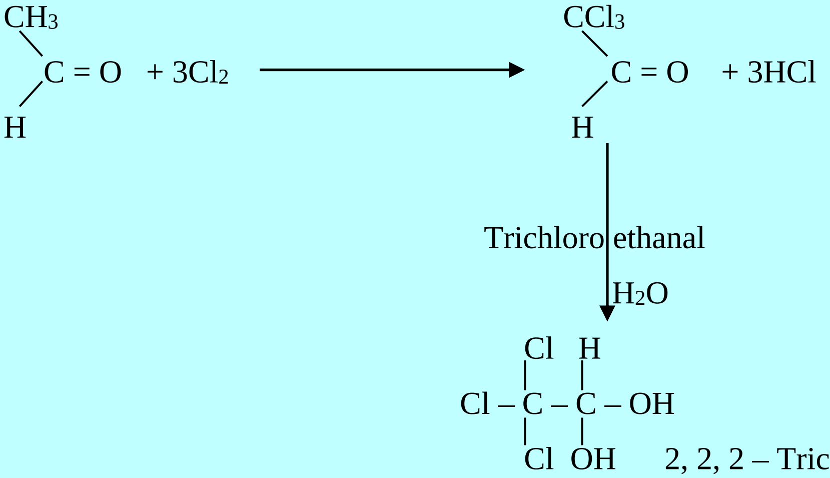
Chlorination

With phosphorus pentachloride

With anhydrous conditions, aliphatic and simple aromatic carbonyl compounds undergo replacement of the oxygen atom by two chlorines to yield the dichloro hydrocarbon

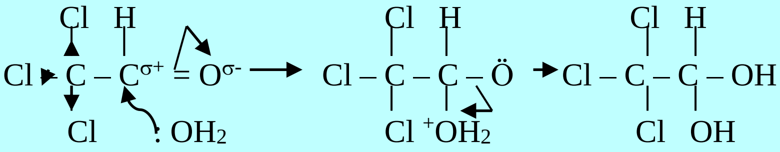


Lower dichloro alkanes are colourless liquids


Trichloro ethanal

2, 2, 2 – Trichloro ethane diol

Mechanism

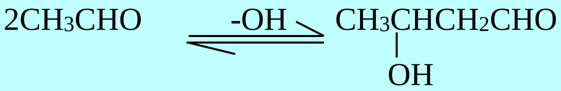


NB

Electron with drawing inductive effects of the three chlorine atoms carbonyl carbon is more positive

Under similar conditions, benzene carbaldehyde (benzaldehyde) is converted into a colourless liquid, benzene carbonyl (benzoyl) chloride C_6H_5COCl

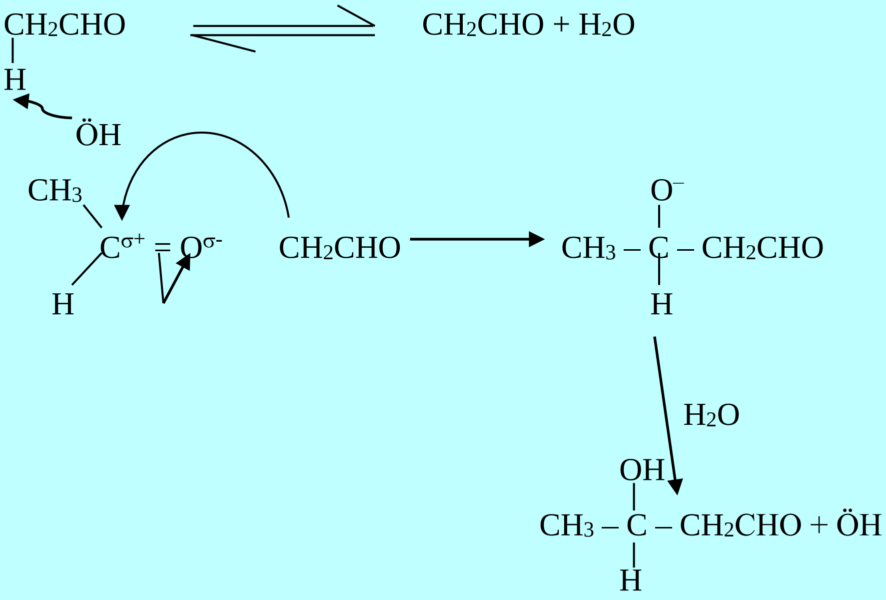
Aldol condensation



$$2CH_3CHO \underset{}{\overset{-OH}{\rightleftharpoons}} CH_3\underset{\substack{|\\OH}}{C}HCH_2CHO$$

If the concentration of hydroxide ions is too large, the reaction continues to give eventually a polymeric resin.

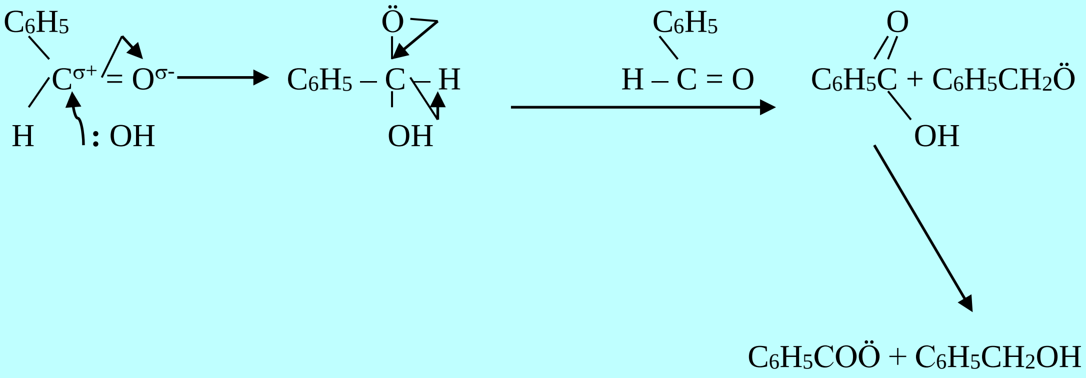
Mechanism



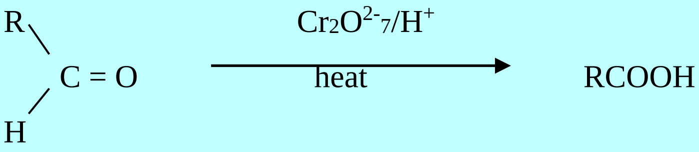
Cannizzaro reaction

This reaction is limited to aromatic and aliphatic compounds in which the carbonyl carbon is attached to a tertiary alkyl carbon atom

$2C_6H_5CHO + NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH$

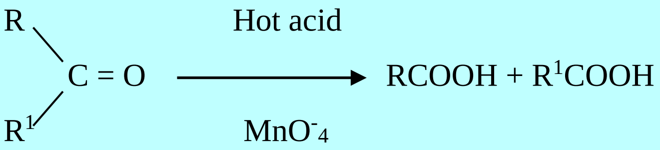


Oxidation



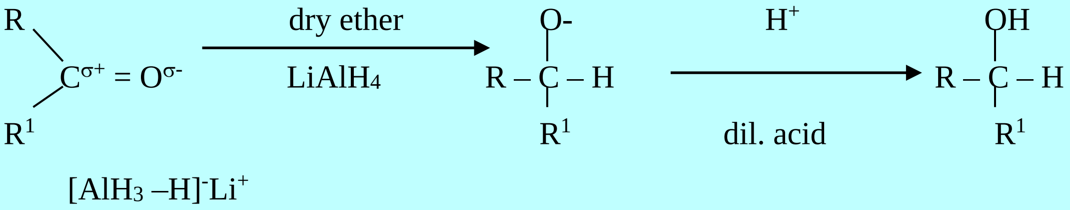
$C_6H_5CHO \xrightarrow{MnO_4/\text{Hot acid}} C_6H_5COOH$

And



Reduction

By Lithium Tetra hydridoaluminate (III)



Distinguishing between Aldehydes and Ketones

Fehling's Test

A solution of copper (I) sulphate is added to a solution of Rochelle salt, Potassium sodium 2,3-dihydroxylabutanedioate, in excess sodium hydroxide. A deep blue coloration is obtained on mixing the solution owing to the formation of complex copper (II) ions

Observation

Aliphatic aldehyde reduces the Copper (II) to the reddish-brown copper(I) oxide which is precipitated

$RCHO + 2CU^{2+} + NaOH + H_2O \xrightarrow{warm} RCOONa + CU_2O + 4H+$

Ketones and aromatic aldehydes give no reaction.

Silver mirror test

The reagent consists of a solution of Silver (I) nitrate in excess ammonia solution.

Observations

Aldehydes reduce the Ag^+ to silver which is precipitated and forms a mirror effect in the bottom part of the test-tube

Safety; residues from this reaction should never be left in the tube as explosive silver (I) oxide may form

$$RCHO + 2Ag(NH_3)_2OH \longrightarrow RCOONH_4 + \underset{\text{Silver mirror}}{2Ag} + H_2O + 3NH_3$$

NB

Ethanal reacts almost immediately but with benzene carboaldehyde (benzaldehyde) the reaction mixture requires warming

Ketones give no reaction.

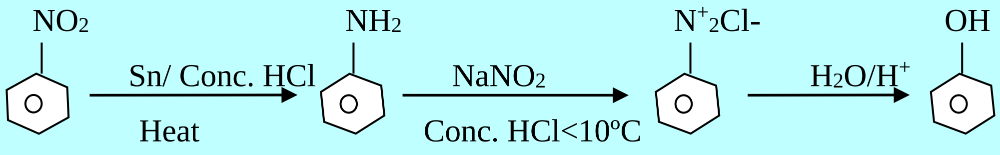
Also, Tollen's reagent (Ammonia solution is added drop wise to a solution of silver (I) nitrate in dilute aqueous sodium hydroxide until the brown precipitate just dissolves). Addition of the aldehyde brings about the formation of a silver mirror and no reaction with ketones.

NB

Ammoniacal silver (I) nitrate and Tollen's reagent are both, Unstable and should always be freshly prepared.

Qn: **Show how the following compounds can be synthesized**

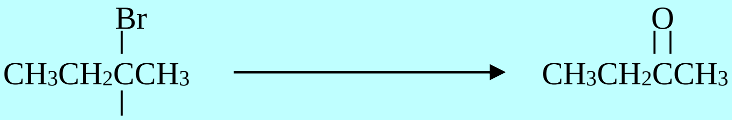
a) Phenol form nitrobenzene



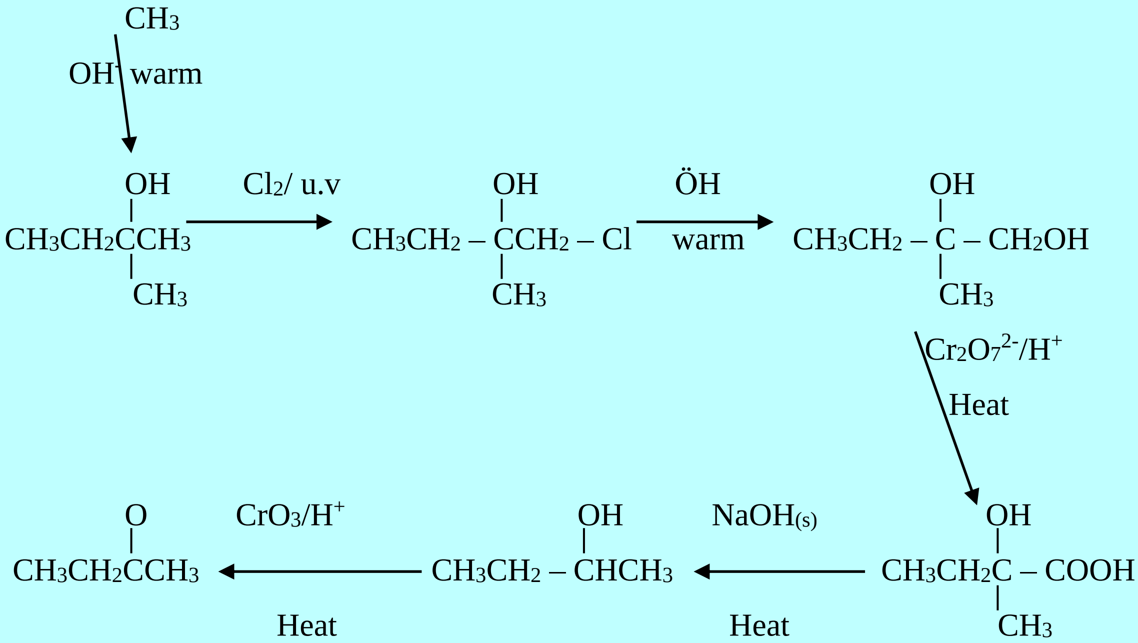
b) Propanoic acid from amino ethane.

$$CH_3CH_2 - NH_2 \xrightarrow[NaNO_2]{\text{Conc. HCl}} CH_3CH_2 - OH \xrightarrow{HCl} CH_3CH_2Cl \xrightarrow[\text{heat}]{\text{KCN/ alcohol}} CH_3CH_2CN \xrightarrow[\text{Heat}]{\text{Excess } H_2O/H^+} CH_3CH_2COOH$$

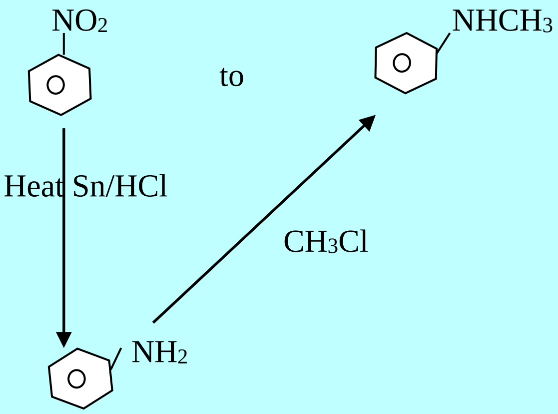
c)



$$CH_3CH_2\overset{Br}{\underset{|}{\overset{|}{C}}}CH_3 \longrightarrow CH_3CH_2\overset{O}{\overset{||}{C}}CH_3$$



d)

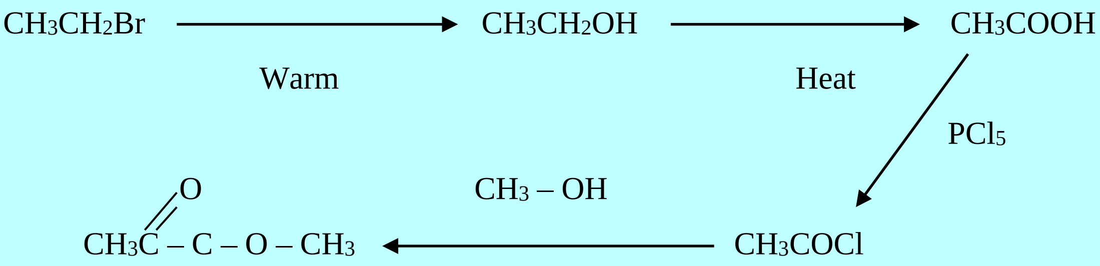


e) CH_3CH_2COOH to $CH_3CH_2 – NH_2$

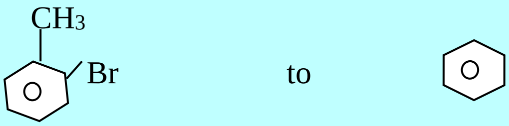
$$\begin{tikzcd}
CH_3CH_2COOH \arrow[d, "PCl_5"] & & CH_3CH_2 - NH_2 \\
CH_3CH_2COCl \arrow[rr, "Liq.\ NH_3"] & & CH_3CH_2CONH_2 \arrow[u, "Br_2/NaOH", "Heat"']
\end{tikzcd}$$

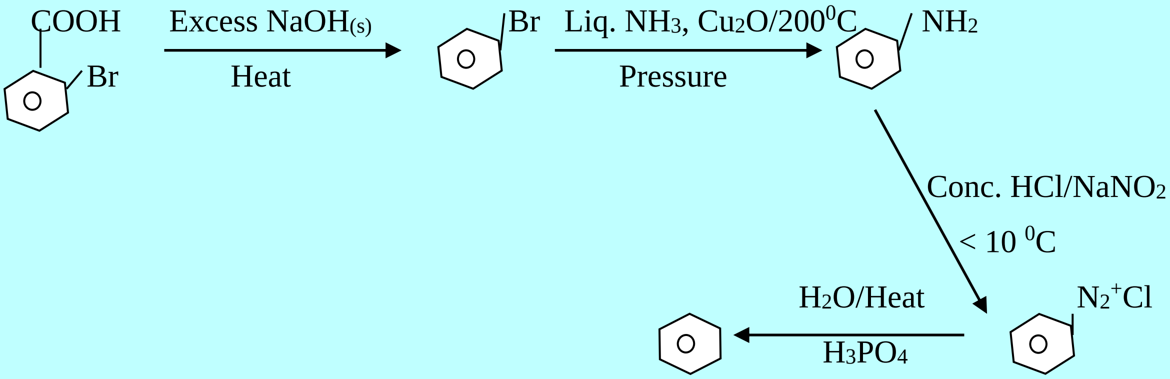
f) Methyl ethanoate from bromo ethane

ÖH $Cr_2O_7^{2-}/H^+$


CH3CH2Br
Warm
CH3CH2OH
Heat
CH3COOH
PCl5
CH3COCl
CH3 – OH
O
CH3C – C – O – CH3

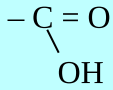
g)


CH3
Br
to


COOH
Br
Excess NaOH(s)
Heat
Br
Liq. NH3, Cu2O/200⁰C
Pressure
NH2
Conc. HCl/NaNO2
< 10 ⁰C
N2+Cl
H2O/Heat
H3PO4

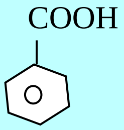
CARBOXYLIC ACIDS

Saturated aliphatic mono carboxylic acids form a homologous series of general molecular formula $C_nH_{2n+1}COOH$ the functional group is



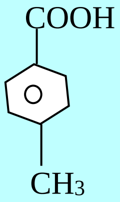
$-\underset{\setminus OH}{C}=O$

Compounds classified as aromatic carboxylic acids all contain the carboxyl group attached directly to an aromatic nucleus,



Benzene carboxylic

(Benzoic acid)



4 – methyl benzene carboxylic

Nomenclature

IUPAC names are afforded by taking the name of the appropriate alkane and replacing the ending "e" with the suffix "-oic" positions of substitution are denoted in the usual way by numbering the longest un branched chain containing the carboxyl group.

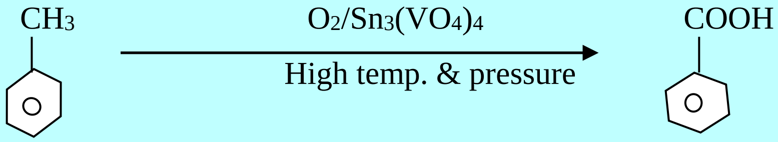
$HCOOH$	Methanoic acid
CH_3COOH	Ethanoic acid
$(CH_3)_2CHOOH$	2 - methyl propanoic acid
C_6H_5COOH	Phenyl ethanoic acid

Industrial source

Methanoic acid is manufactured by the reaction

$$CO + NaOH \xrightarrow[\text{High pressure}]{200^\circ C} HCOONa \xrightarrow{\text{dil. acid}} HCOOH$$

Benzoic acid is obtained by the air oxidation of methylbenzene using a tin (IV), Vanadate (V) catalyst



Synthetic preparations

Oxidation of primary alcohols

$$RCH_2OH \xrightarrow[\text{Excess acid}]{Cr_2O_7^{2-}\ \textbf{OR}\ MnO_4^-} RCHO \xrightarrow{\text{further oxidation}} RCOOH$$

This method is suitable for preparing aromatic as well aliphatic acids.

Grignard synthesis; Carbonation

Aliphatic acids are obtained by bubbling carbon dioxide into the Grignard reagent and then treating with dilute acid.

$$RMgBr + CO_2 \xrightarrow{\text{dry ether}} RCOOMgBr \xrightarrow[\text{Dil. Acid}]{H_2O} RCOOH + MgBrCl$$

R may be 1°, 2°, 3° or aromatic

e.g.
$$\begin{tikzcd} C_6H_5MgBr + CO_2 \arrow[r, "\text{dry ether}"] & C_6H_5COOMgBr \arrow[dr, "H_2O/H+"] & \\ & & C_6H_5COOH + MgBrCl \end{tikzcd}$$

Hydrolysis of nitriles

$$RCl + NaCN \xrightarrow{\text{aq. alcohol}} RCN + NaCl$$

$$RCN \overset{+H_2O}{\rightleftharpoons} RCONH_2 \xrightarrow{+H_2O} RCOO^{-}NH_4^{+}$$

Hydrolysis of Esters; saponification

The ester is boiled under reflux with concentrated aqueous sodium hydroxide

$$\begin{tikzcd} \underset{\text{Ester}}{RCOOR^1} + NaOH \arrow[r, phantom, "\rightleftharpoons"] & RCO\ddot{O}Na^+ + R^1OH \arrow[d, "\text{Dil.acid}"] \\ & RCOOH \end{tikzcd}$$

Cannizzaro reaction

$$\begin{tikzcd} 2C_6H_5CHO + NaOH \arrow[r] & C_6H_5C\ddot{O}Na^+ + C_6H_5CH_2OH \arrow[d, "\text{dil. acid}"] \\ & C_6H_5COOH \end{tikzcd}$$

This reaction is only undergone by aromatic aldehydes and those aliphatic ones containing no – hydrogen atoms.

Synthesis of Benzoic Acid

1. From methylbenzene (Toluene)

$$C_6H_5CH_3 \xrightarrow[\text{Heat}]{MnO_2,\ H_2SO_4} C_6H_5COOH$$

2. From chloromethyl benzene

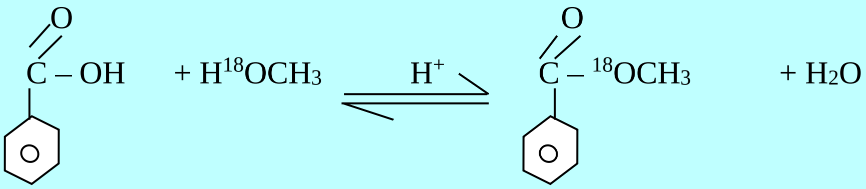
$$C_6H_5CH_2Cl \xrightarrow[\text{(2) dil. acid to precipitate}]{\text{(1) } MnO^{-}_{4}/\ddot{O}H} C_6H_5COOH$$

3. From Trichloromethyl benzene

$$C_6H_5CCl_3 \xrightarrow[\text{Fe powder, } 50^{o}C]{Ca(OH)_2} C_6H_5C(OH)_3 \xrightarrow{-\ H_2O} C_6H_5COOH$$

REACTIONS

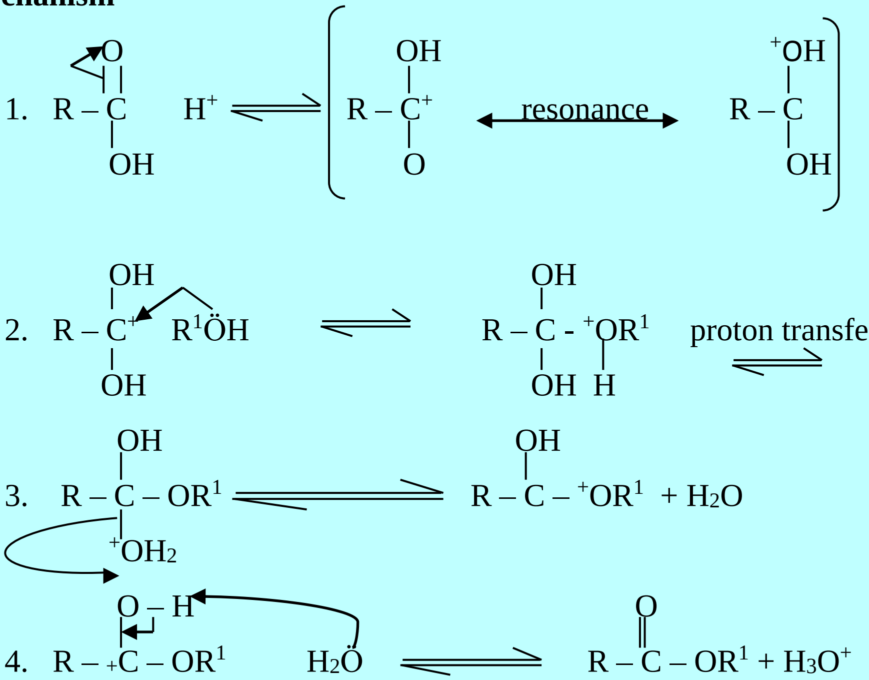
Esterification



NB

Isotopic labeling of the oxygen atom on the alcohol using ^{18}O show that primary and some secondary alcohols undergo alkoxy-hydrogen fusion i.e. mass spectrometry detects the radioactive oxygen only in the fragment prevented from the ester and not from the water.

Mechanism



The overall reaction is reversible.

Halogenation

$$RCH_2COOH \xrightarrow[\text{Warm}]{Br_2,\ PCl_3} RCHBrCOOH \xrightarrow{Br_2,\ PCl_3} RCBr_2COOH$$

$$CH_3COOH + Cl_2 \xrightarrow{UV} ClCH_2COOH + HCl$$

$$\Big\downarrow \text{NaOH}$$

$$HO-CH_2COONa$$

And $ClCH_2COOH \xrightarrow{liq.NH_3} HN-CH_2COOH + NH_4Cl$

Conversion into Acyl chlorides

Both aliphatic and aromatic carboxylic acids readily undergo replacement of a hydroxyl group on reacting with PCl_3, PCl_5 and $SOCl_2$

$$RCOOH + PCl_5 \longrightarrow \underset{\text{Acyl chloride}}{RCOCl} + POCl_3 + HCl$$

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

Reduction

$$RCOOH \xrightarrow[2)\ H_2O]{1)\ \text{dry ether}} RCH_2OH$$

Amide formation

$$RCOOH + (NH_4)_2CO_3 \longrightarrow RCOO\text{-}NH^{+}_4 + CO_2 + H_2O$$

$$RCOO^{-}NH^{+}_4 \underset{\text{Heat } 100^oC – 200^oC}{\overset{\text{Excess RCOOH}}{\rightleftharpoons}} RCONH_2 + H_2O$$

Decarboxylation of the sodium salt

1. Heating with soda lime

$$\underset{\text{(Soda lime)}}{RCOONa + NaOH} \xrightarrow{\text{fuse}} RH + Na_2CO_3$$

2. Kolbe' synthesis

$$2RCOONa + 2H_2O \xrightarrow[\text{aq. } CH_30H]{} \underbrace{R – R + CO_2}_{\text{Anode}} + \underbrace{2NaOH + H_2}_{\text{Cath}}$$

Hot symmetrical alkane

Qn. Show how the following can be obtained

FATS AND OILS

Fats and oils are one of the three major groups of foods used by humans, the word oil is used by chemists in a wide sense it includes the fats and oils to be studied in this section. Three contexts are used, namely.

- Fatty oils- obtained from plant and animal sources example palm oil, fallow and white sperm wax
- Mineral oils obtained from petroleum (crude oil), coal and shale, example lubricating oil and paraffin oil.
- Essential oils-volatile and pleasant, sometimes sharp smelling(fragrant) extracts from plants example oil of turpentine, menthol, cinnamon oil and orange-peel oil.

NOTE:

Generally, fats are considered as high melting point substances, compared with oils which have low melting points. At room temperature fats usually occur as solids and oils as liquids.

- Fats and oils such as palm oil and groundnuts oil are a mixture of esters mainly of glycerol, propane-1,2,3,-triol
- They are commonly known as glycerides or esters of glycerol and can be amino-di-or tri-esters

Uses of fats and oils

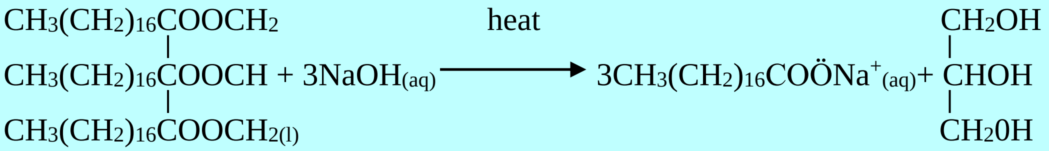
- ✓ They are used as food mainly to provide energy, when fats are stored in the body it protects animals from cold since it is a poor conductor of heat.
- ✓ Some oils such as linolein are used to treat one side of a cotton material. The dried oil produces the water proof material linoleum
- ✓ However, the two important uses of fats and oils are from their direct use as food is in the making hardened oil such as margarine, and soap.

Soap making- saponification

Saponification is the chemical process of an alcohol breaking down an alkyl alkanoate or ester to from soap. Soap is sodium or potassium salt of along chain alkanoic acid or fatty acid.

The saponification process can be represented generally for fats and oils which contain one or ester groups followed by a specific example using tristearism, a common fat in most oils and fats

Vegetable oil / + alkali ⟶ Soap + glycerol
animal fat



$$\begin{array}{llll} CH_3(CH_2)_{16}COOCH_2 & \text{heat} & & CH_2OH \\ \quad\quad\quad\quad\quad | & & & | \\ CH_3(CH_2)_{16}COOCH + 3NaOH_{(aq)} & \longrightarrow & 3CH_3(CH_2)_{16}CO\ddot{O}Na^+_{(aq)} + & CHOH \\ \quad\quad\quad\quad\quad | & & & | \\ CH_3(CH_2)_{16}COOCH_{2(l)} & & & CH_2 0H \end{array}$$

(Oil in palm oil) sodium stearate glycerol
(Sodium actadecanoate)

Fats, oils, sodium hydroxide or potassium hydroxide, brine solution and water are the main raw materials in the production of soap.

Oil and a measured quantity of alkali are mixed together in a container. The mixture is heated with steam and then boiled to mix well to form crude soap. Hot brine (saturated salt solution) is added to the product mixture to throw up the crude soap known as grained soap. This process is called salting out.

The lower aqueous layer is glycerol dissolved in salt solution and it is called lye. Glycerol is extracted from it and purified. The grained soap is then washed many times to remove remaining salt and glycerol impurity and then bleached. Repeated washing and bleaching removes undesirable colouring, smell and other impurities. After this stage, special colouring, perfume and preservatives are added and mixed with the soap.

Structure and Cleansing action of soaps

The structure of soap is made up of a

- Long chain non-polar hydrocarbon
- Ionic, polar head.

The non-polar hydrocarbon tail $CH_3(CH_2)n$ in which n is usually large is insoluble in water, but soluble in oils and grease which are organic substances. The tail end is called the hydrophobic end because it is insoluble in water.

The ionic head (-COÖNa$^+$) is soluble in water but does not dissolve in organic substance such as oil and grease. The head is called the hydrophilic end because of its ability to dissolve in water.

NOTE:

Soap cleanses by

- Wetting the material
- Emulsifying the grease or oil to which the dirt is held.

Other processes such as lathering aid the removal of the dirt

Wetting action of soap

When water is mixed with soap, it spreads and wets the cloth. Soap lowers the surface tension of water and allows the aqueous soap solution to spread, wet and cleanse dissolution removes some nearby water molecules on the surface of the droplet and weakens the hydrogen bond forces on the surface. As a result, the surface tension is lowered and the water spreads, pushing out more detergent species to take part in the cleansing action.

Cleansing action of soap

Dirt is held to a material by oil or grease. In the cleansing process the material is first wetted. The hydrocarbon tail of the soap dissolves in the grease which remains suspended in the water by the attraction of the ionic end of the soap species. The model of the sequence through which the grease holding the dirt to the material is removed. Agitation by hand or machine heating and removal of the soap solution and its latter finally removes the dirt.

POLYMERS

The simplest molecules which form the giant single molecule are known as monomers and the large molecule is called a polymer. Poly means many and mono mean one.

Polymerization is the chemical process of joining a large number of small molecules to form one giant molecule of very high molecular mass. The giant molecule product of polymerization is known as a polymer. A monomer is a simple molecule from which a polymer can be made. Some polymers found in nature are known as natural polymers. Those made artificially by man are known as synthetic or man-made polymers.

Examples of natural polymers

- Carbohydrates such as monosaccharides, disaccharides and polysaccharides
- Starch
- Proteins.

Synthetic polymers

Examples

- Plastics, plastics can be partly identified by two simple tests namely
  - ✓ Gentle heating.
  - ✓ Strong and prolonged heating.

Two groups can be identified from experiments. Some of the plastics melt and turn back to solids when cooled, they can be moulded or remoulded into other shapes. The other types of plastics do not melt on heating. They may become hard or clear on strong heating.

Examples of plastics which can be melted and reshaped are polythene, Polypropene, polyvinylchloride (PVC) and nylon.

Examples of the type which does not melt include Bakelite (phenol-methanal) and urea-methanal.

Types of plastics

- Thermoplastics are plastics which soften and melt on heating and become solid again on cooling. They have weak inter-chain forces which can be easily broken by heating.
- Thermosets or thermosetting plastics are plastics which do not melt on heating. They have strong covalent bonds, called cross –links between polymer chains which cannot be broken easily.

NOTE:

The difference between thermoplastics and thermosets arises through the arrangement and bonding in the long chains in all polymers. The chains in the thermoplastics are held together by weak vanderwaal’s forces. These weak inter-chain forces can be easily broken. When heated, the chains break loose, and slide over each other. The molten liquids can be poured into shaped containers to give different forms. Thermoset chains are bonded to each other by strong cross-link covalent bonds from one chain to others all through the polymer. These strong cross-links cannot be broken easily. Extreme heating decomposes the thermosets.

Preparation and manufacture of polymer

Two types of reactions are used to form polymers. The two differ mainly in the way the products are formed during the formation of the chains of the polymer. In one way, only one single large molecule is formed. In the other, small molecules such as water or hydrogen chloride are condensed out in addition to the large molecule of the polymer.

- **Addition polymerization**. In addition, polymerization a large number of unsaturated molecules gain to form the polymer, which is saturated. An example is polythene, the monomer is $CH_2 = CH_2$, the repeating unit is $–CH_2\text{-}CH_2\text{-}$ and its polymer is represented as $-(CH_2\text{-}CH_2)-_n$ where n is a large number. Monomers of addition polymers always contain an unsaturated bond which is the source of its reactivity.
- **Condensation polymerization**. In condensation polymerization, a large number of molecules join together by the elimination of a small molecule often, but not always

water. An example is nylon. Condensation polymers are made by joining molecules which have two reactive function groups. The functional group of different molecules react together to form a chain with the elimination of small molecules.

Poly ethene (polythene)

Simple alkenes polymerize to form a family of long-chain addition polymers which are flexible solids and may adopt many forms.

$$nCH_2=CH_2 \xrightarrow[\text{1500atm, 200ºC}]{O_2\text{ initiator}} \sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2 \sim$$

polyethene

Polytetrafluoroethene (PTFE, Teflon, Fluon)

This is obtained by the pyrolysis of chlorodifluoromathene like contain other chlorofluoro-derivatives of methane and ethane, is available refrigerant and is known as froen-22

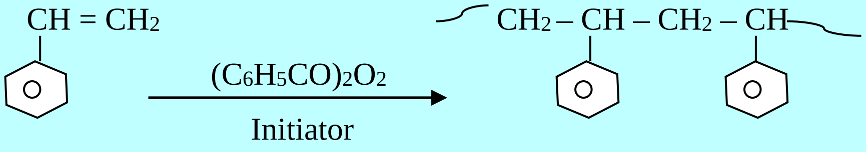
$$nCF_2=CH_2 \xrightarrow[\text{45-50atm}]{\text{peroxide initiators}} \sim CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2 \sim$$

PTFE, Teflon

Suitable for manufacturing non-stick cooking utensils and low friction bearings since it’s highly resistant to chemical and possesses an extremely low coefficient of friction.

Polyphenylethene (polystyrene)

Free-radical polymerization of phenylethene (styrene) is brought about by a dibenzene carboxyl peroxide initiator at a temperature of 85-100ºC



Polystyrene

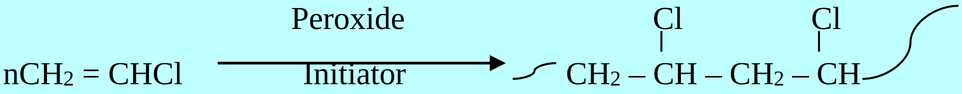
Ethenyl (vinyl) polymers

Polychloroethene (polyvinyl chloride, PVC) i.e.

$$CH \equiv CH + HCl \xrightarrow[\text{Charcoal Cat}]{\text{Hg Cl}_2} CH_2 = CHCl$$

$$120 - 180^{o}C$$

Then



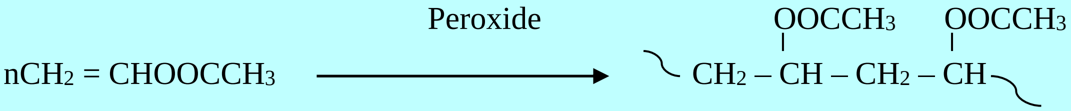
$$nCH_2 = CHCl \xrightarrow[\text{Initiator}]{\text{Peroxide}} \sim CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} \sim$$

It’s a thermosoftening plastic which can easily be moulded and it is used in the manufacture of plastic raincoats, curtains, furniture coverings, records, water piping and guttering etc

<u>Polyethenyl ethanoate (polyvinyl Acetate PVA)</u>

$$CH \equiv CH + CH_3COOH \xrightarrow[160 - 170^{o}C]{(CH_3COO)_2Zn,\ \text{Charcoal}} \underset{\text{Ethenyl ethanoete}}{CH_2 = CHOOCCH_3}$$

Free –radical polymerization can be brought about by light, peroxides etc



$$nCH_2 = CHOOCCH_3 \xrightarrow[\text{Initiator}]{\text{Peroxide}} \sim CH_2 - \overset{\overset{OOCCH_3}{|}}{CH} - CH_2 - \overset{\overset{OOCCH_3}{|}}{CH} \sim$$

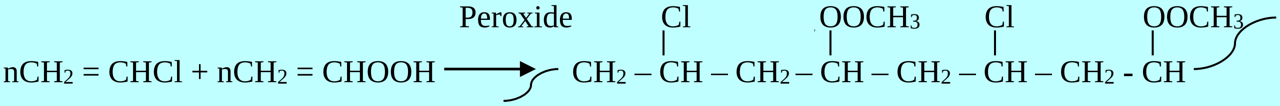
(polyvinyl acetate PVA)

It is used in sheets as the middle layer of Triplex safety glass

NB: Its uses are limited as it tends to be too soft for many practical applications

<u>Vinyon</u>

Is a copolymer of chloroethene and ethanylethanoate

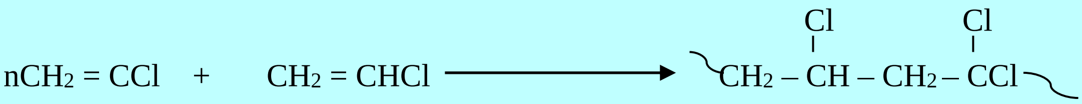


$$nCH_2 = CHCl + nCH_2 = CHOOH \xrightarrow[\text{Initiator}]{\text{Peroxide}} \sim CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \overset{\overset{OOCH_3}{|}}{CH} - CH_2 - \overset{\overset{Cl}{|}}{CH} - CH_2 - \overset{\overset{OOCH_3}{|}}{CH} \sim$$

Vinyon

Vinyon fibre exhibits the flexible properties of PVA and has the strength of PVC, although its uses are still limited owing to its comparatively low softening temperature of 65ºC

Saran



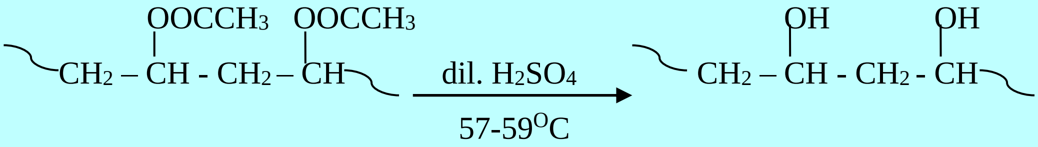
$$nCH_2 = CCl \quad + \quad CH_2 = CHCl \longrightarrow \sim CH_2 - \overset{\overset{Cl}{|}}{C}H - CH_2 - \overset{\overset{Cl}{|}}{C}Cl \sim$$

1, 1-Dichloro ethane Chloro ethene Saran

85% 15%

Polyethenol (polyvinyl/ alcohol)

Obtained by the acid hydrolysis of polyethenylethanoate

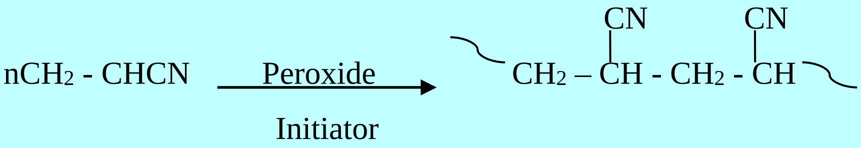


$$\sim CH_2 - \overset{\overset{OOCCH_3}{|}}{C}H - CH_2 - \overset{\overset{OOCCH_3}{|}}{C}H \sim \xrightarrow[57\text{-}59^{O}C]{dil.\ H_2SO_4} \sim CH_2 - \overset{\overset{OH}{|}}{C}H - CH_2 - \overset{\overset{OH}{|}}{C}H \sim$$

It provides a useful intermediate for preparing other polymers

Is also used in making water-soluble coatings and adhesives.

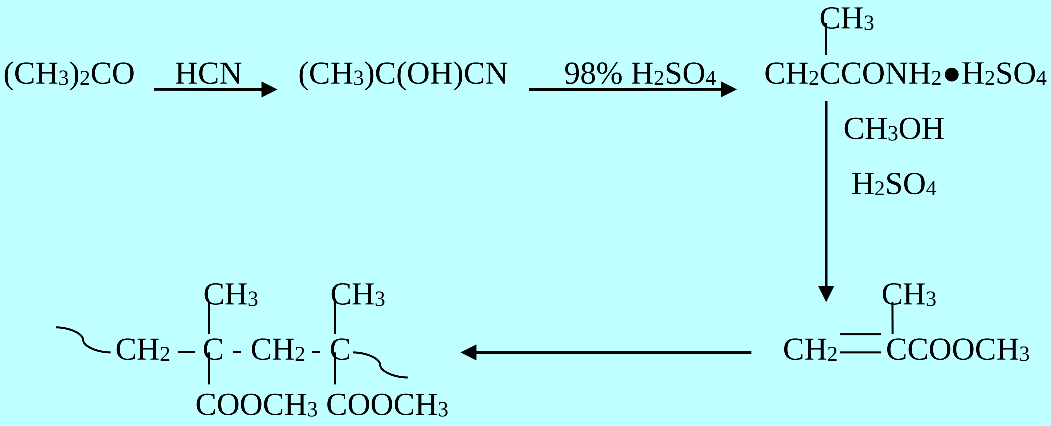
Polypropenonitrile (polyacrylonitrile, Orlon)



$$nCH_2 - CHCN \xrightarrow[Initiator]{Peroxide} \sim CH_2 - \overset{\overset{CN}{|}}{C}H - CH_2 - \overset{\overset{CN}{|}}{C}H \sim$$

Perspex (polymethyl-2-methylpropenoate)

Perspex is a strong, transparent thermoplastic which has a variety of uses although it is probably most frequently encountered as a replacement for glass. It is obtained from propanone (acetone)



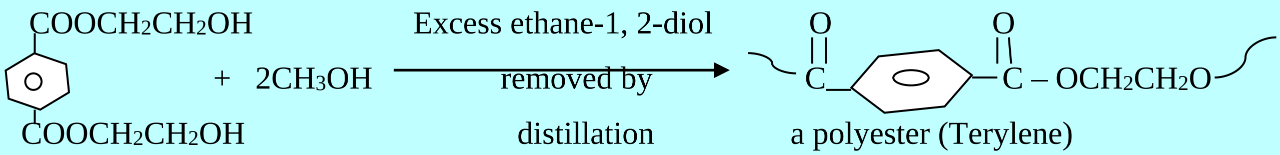
$$(CH_3)_2CO \xrightarrow{HCN} (CH_3)C(OH)CN \xrightarrow{98\%\ H_2SO_4} CH_2\overset{\overset{CH_3}{|}}{C}CONH_2{\bullet}H_2SO_4$$

$$\xrightarrow[H_2SO_4]{CH_3OH} CH_2 = \overset{\overset{CH_3}{|}}{C}COOCH_3 \longrightarrow \sim CH_2 - \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \underset{\underset{COOCH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \sim$$

(Perspex)

Condensation polymers

- **Polyesters**



a polyester (Terylene)

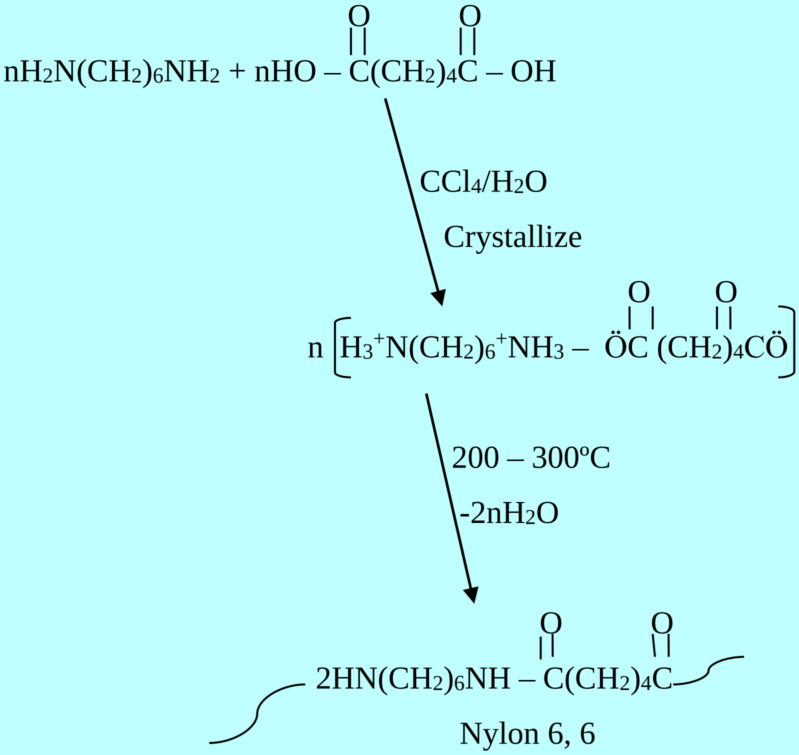
Dihdroxyethyl benzene -1, 4, - dicarboxylate

(Hydroxyethyl terephthalate)

It is used in the textile industry to make clothing materials

- **Nylon 6.6**

It is manufactured from hexane-1, 6-dioic, acid, dissolved in tetrachloromethane (carbon tetrachloride) and an aqueous solution of hexane-1, 6-diamine and used in making threads, ropes, stockings, shirts, finishing nets, toothbrushes, electrical equipment etc



$$nH_2N(CH_2)_6NH_2 + nHO - \overset{O}{\overset{||}{C}}(CH_2)_4\overset{O}{\overset{||}{C}} - OH$$

$$\xrightarrow[\text{Crystallize}]{CCl_4/H_2O}$$

$$n\left[H_3{}^{+}N(CH_2)_6{}^{+}NH_3 - \ddot{O}\overset{O}{\overset{||}{C}}(CH_2)_4\overset{O}{\overset{||}{C}}\ddot{O}\right]$$

$$\xrightarrow[-2nH_2O]{200 - 300^{\circ}C}$$

$$2HN(CH_2)_6NH - \overset{O}{\overset{||}{C}}(CH_2)_4\overset{O}{\overset{||}{C}}$$

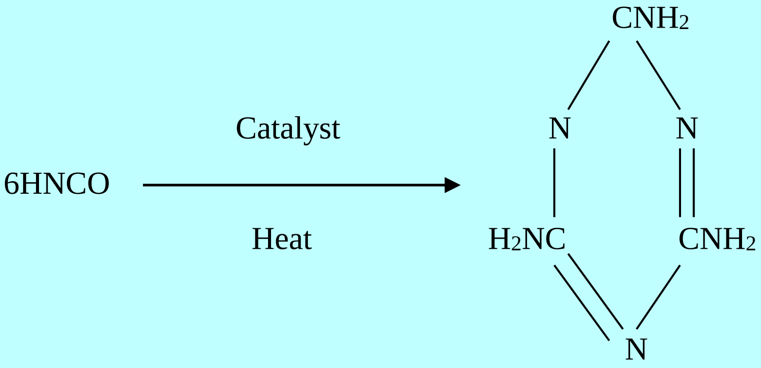
Nylon 6, 6

- **Melamine –methanal resins**

Is manufactured from urea by strong heating it to form, acid, HNCO and ammonia.

$(NH_2)C = O \xrightarrow{\text{heat}} HNCO + NH_3$

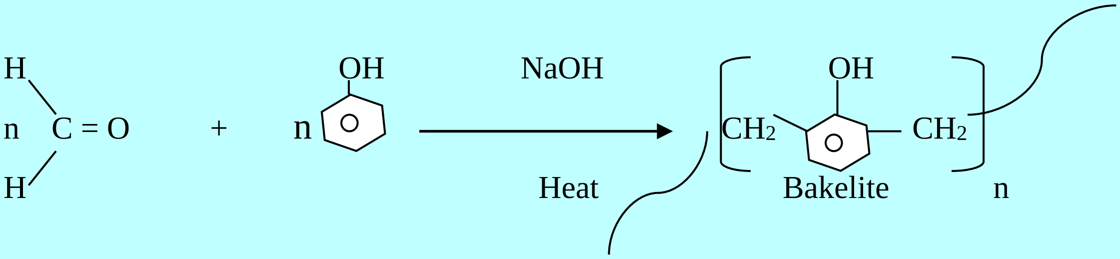
Then passing it over a heated catalyst



- **Bakelite (Phenol-methanal)**

Phenol and aqueous solution of methanol in the presence of a little sodium hydroxide is heated. The reaction goes through two stages to finally form cross-links with the elimination of water molecules.

It is used for electric switches, handles of cooking utensils, parts of cars and boats, radio, television and telephone equipment and cameras.



LET US REVISE

1. 1.86g of a compound X contains carbon, hydrogen and nitrogen only. X on combustion liberated 5.28g of carbon dioxide gas and 224cm^3 of nitrogen gas at s.t.p

a) Determine the empirical formula of X

Solution

Mass of carbon in carbondioxide = $^{12}/_{44} \times 5.28$

= 1.44g

Mass of nitrogen = $^{28}/_{22400} \times 224$

= 0.28g

Mass of hydrogen = 1.86 – (1.44 + 0.28)

= 0.14g

Elements	C	:	H	:	N
Moles of atoms	$\frac{0.144}{12}$		$\frac{0.14}{1}$		$\frac{0.28}{14}$
	0.12		0.14		0.02
Divided by smallest	$\frac{0.12}{0.02}$		$\frac{0.14}{0.02}$		$\frac{0.02}{0.02}$
	6	:	7	:	1

Empirical formula is C_6H_7N

b) When vapourised, 0.2g of X occupied 81cm^3 at 184.1^{0}C and 101.325KPa. Determine the molecular formula of X.

Solution

V_1 = 81cm^3 V_2 = ?

T_1 = 273 + 1841 T_2 = 273K

= 4571K

P_1 = 101.325KPa P_2 = 101.325Pa

$$Using\ \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{101.325 \times 81 \times 273}{457.1 \times 101.325}$$

= 48.377cm^3

But 48.377cm^3 of X contain 0.2g of X

22400cm^3 of X contain $\frac{0.2\times22400}{48.377}$

= 92.6g of X

Then $(C_6H_7N)n$ = 92.6

(16 x 12 + 1 x 7 + 1 x 14)n = 92.6

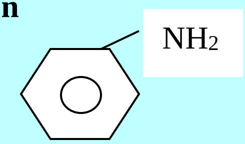
$$\frac{93n}{93} = \frac{92.6}{93}$$

n = 1

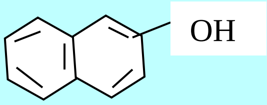
Hence molecular formula of X is C_6H_7N.

c) X burns with a sooty flame and the PH of its aqueous solution is greater than 7. Write the molecular structure of X.

Solution



d) X was reacted with sodium nitrate in the presence of hydrochloric acid at 5^{0}C and the product treated with 2-naphthol,



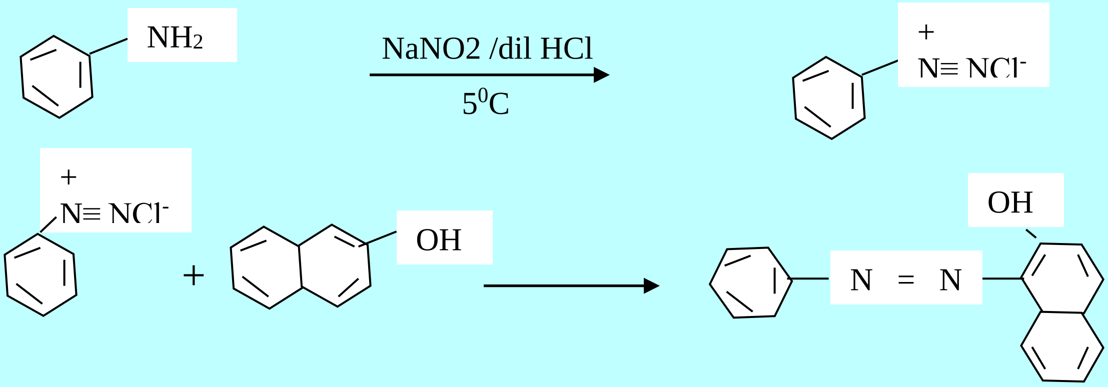
i) State what was observed

Solution

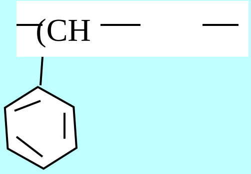
Red precipitate

ii) Write equations for the reactions that took place

Solution

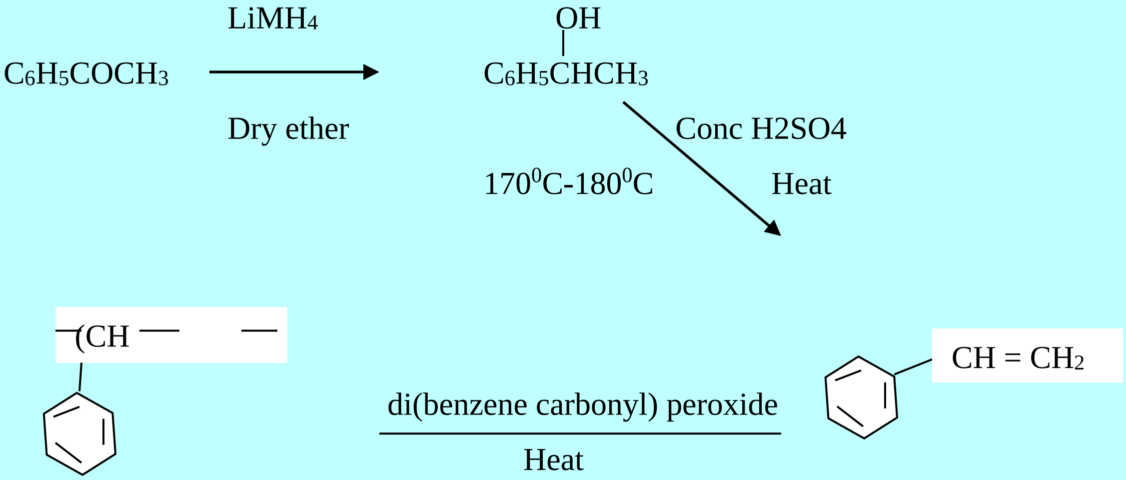


2. Write equations to show how the following compounds can be synthesized and, in each case, indicate the conditions for the reaction.

a) 

from $C_6H_5COCH_3$

Solution



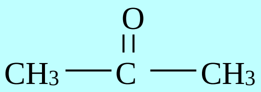
$$C_6H_5COCH_3 \xrightarrow[\text{Dry ether}]{LiMH_4} C_6H_5\overset{OH}{C}HCH_3$$

Conc H2SO4

Heat

170^0C-180^0C

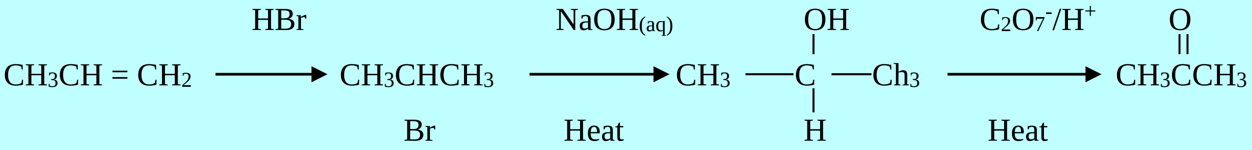
$$\xleftarrow[\text{Heat}]{\text{di(benzene carbonyl) peroxide}} CH = CH_2$$

b) 

$$CH_3 - \overset{O}{\overset{\|}{C}} - CH_3$$

from $CH_3CH = CH_2$

Solution

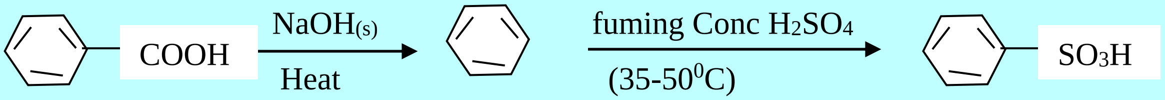


$$CH_3CH = CH_2 \xrightarrow{HBr} CH_3\underset{Br}{C}HCH_3 \xrightarrow[\text{Heat}]{NaOH_{(aq)}} CH_3 - \underset{H}{\overset{OH}{C}} - Ch_3 \xrightarrow[\text{Heat}]{C_2O_7^-/H^+} CH_3\overset{O}{\overset{\|}{C}}CH_3$$

c)

SO_3H from COOH

Solution



$$\text{COOH} \xrightarrow[\text{Heat}]{NaOH_{(s)}} \quad \xrightarrow[(35\text{-}50^0C)]{\text{fuming Conc } H_2SO_4} SO_3H$$

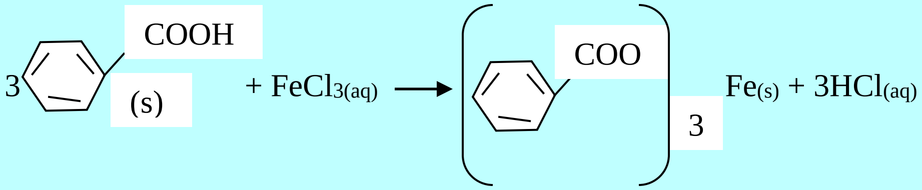
3.a) State what would be observed and, in each case, write equation for the reaction that would take place if a mixture of the following compounds were heated.

i) Benzoic acid and Iron (II) Chloride solution.

Solution

Observation: Reddish-brown precipitate

Equation:



ii) Methanoic acid and ammoniacal silver nitrate.

Solution

Observation: Silver mirror

Equation: $2Ag^{+}_{(aq)} + 2NH_{3(aq)} + HCOOH_{(aq)} \longrightarrow 2Ag_{(s)} + CO_{2(g)} + 2NH_4{}^{+}{}_{(aq)}$

b(i) Write equation and outline a mechanism for the reaction between 2 – bromo – 2 – methylpropane and sodium ethoxide.

Solution

$(CH_3)_3CBr + CH_3CH_2ON^{+}{}_{a} \longrightarrow (CH_3)_2\,C = CH_2 + CH_3CH_2OH + NaBr$

Mechanism

$(CH_3)_3CBr \rightleftharpoons (CH_3)_3\,C^{+} + Br^{-}$

$CH_2 —— C(CH_3)_2 \longrightarrow CH_2 = C(CH_3)_2 + CH_3CH_2OH$

|

H

OCH_2CH_3

ii) Write the name given to the type of mechanism you have outlined in b(i) above.

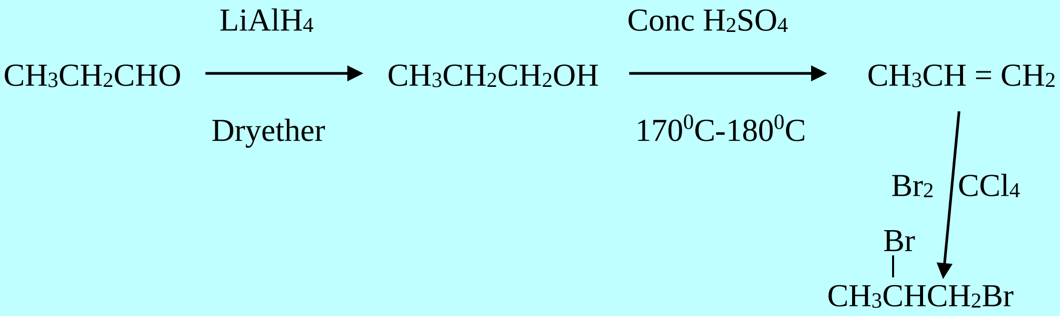
b) Solution

Elimination unimolecular

4. Write equations to show how the following conversions can be carried out in each case indicate the reagents and condition for the reactions.

a) CH_3CH_2CHO to $CH_3CHBrCH_2Br$

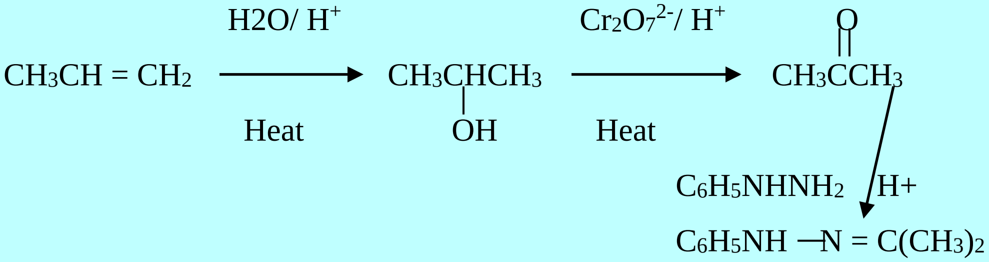
Solution



$$CH_3CH_2CHO \xrightarrow[\text{Dryether}]{LiAlH_4} CH_3CH_2CH_2OH \xrightarrow[170^0C-180^0C]{\text{Conc } H_2SO_4} CH_3CH = CH_2 \xrightarrow{Br_2\ /\ CCl_4} CH_3\overset{\overset{Br}{|}}{C}HCH_2Br$$

b) $CH_3CH = CH_2$ to $C_6H_5NH – N = C(CH_3)_2$

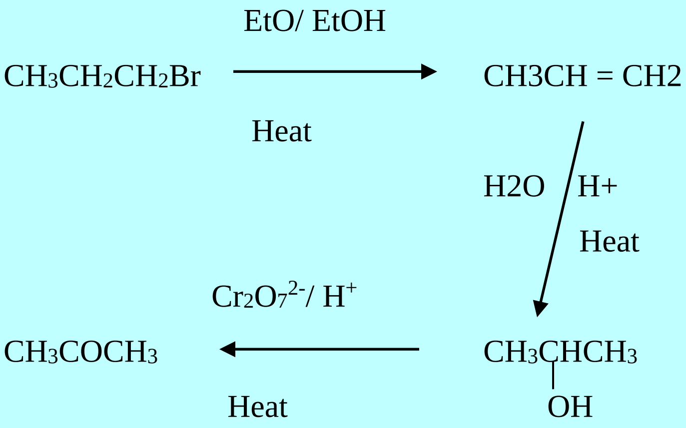
Solution



$$CH_3CH = CH_2 \xrightarrow[\text{Heat}]{H2O/\ H^+} CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[\text{Heat}]{Cr_2O_7^{2-}/\ H^+} CH_3\overset{\overset{O}{||}}{C}CH_3 \xrightarrow{C_6H_5NHNH_2\ /H+} C_6H_5NH - N = C(CH_3)_2$$

c) $CH_3CH_2CH_2Br$ to CH_3COCH_3

Solution



$$CH_3CH_2CH_2Br \xrightarrow[\text{Heat}]{EtO/\ EtOH} CH3CH = CH2 \xrightarrow[\text{Heat}]{H2O\ /H+} CH_3\underset{\underset{OH}{|}}{C}HCH_3$$

$$CH_3COCH_3 \xleftarrow[\text{Heat}]{Cr_2O_7^{2-}/\ H^+} CH_3\underset{\underset{OH}{|}}{C}HCH_3$$

5(a) Name one source of vegetable oil

Solution

Sunflower, simsim, ground nuts, soya beans, cotton seeds, shea nuts, coconut, palm oil seed, etc.

b) Describe briefly show how soap can be prepared from one of the sources of vegetable oil you have named in (a) above.

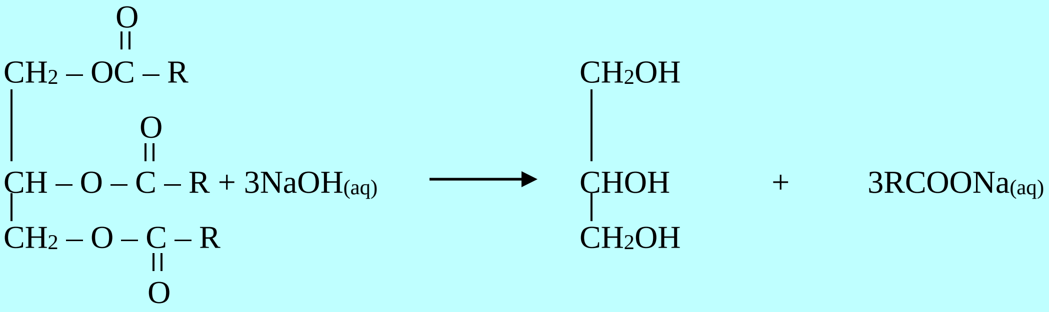
Solution

Roast/dry the seeds, crush/grind to make paster with water until oil floats on top and decant off the oil. Mix the oil with excess concentrated sodium hydroxide solution and heat/boil with constant stirring for a long time. Add concentrated sodium chloride solution to precipitate the soap.

c) Write the general equation for the;

i) formation of soap

Solution



$$\begin{array}{l} CH_2 - O\overset{O}{\overset{\|}{C}} - R \\ | \\ CH - O - \overset{O}{\overset{\|}{C}} - R + 3NaOH_{(aq)} \\ | \\ CH_2 - O - \underset{O}{\underset{\|}{C}} - R \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOONa_{(aq)}$$

ii) reaction between hard water and soap.

Solution

$2RCOONa^{+}_{(aq)} + Ca2^{+}_{(aq)}$ $(RCOO)_2Ca_{(s)} + 2Na^{+}_{(aq)}$

d) A sample of soap was prepared from 9.5g of a vegetable oil containing the ester of hexadecanoic acid ($C_{15}H_{31}COOH$). Calculate the mass of soap formed.

Solution

RMM of ester = (12x15) + (1x31) + (12x1) + (16x2) + (1x1)

= 806

Moles of ester = $^{9.5}/_{806} = 1.179 \times 10^{-2}$

But

1 mole of ester produces 3 moles of soap

50 moles of soap = 3 x 1.179 x 10^{-2}

= 3.537 x 10^{-2}

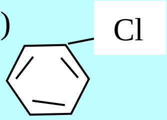
RMM of soap $C_{15}H_{31}COONa$ = 278

Then 1 mole of soap contain 278g of soap

$3.537\text{x}10^{-2}$ moles of soap contain $\frac{278\times3.537\times10^{-2}}{1}$

$= 9.839$

6. Name one reagent that can be used to distinguish between each of the following pairs of compounds. In each cases state what is observed if each member of the pair is treated with the reagent.

a)


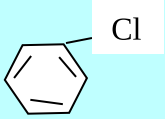
and $CH_3CH_2CH_2Cl$

Solution

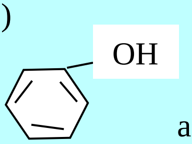
Reagent: Hot sodium hydroxide solution followed by silver nitrate solution.

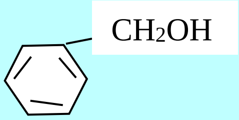
Observation:

$CH_3CH_2CH_2Cl$ ———— White precipitate



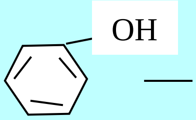
——— No observable change

b)


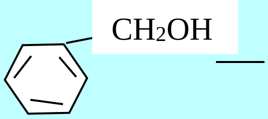
and


Solution

Reagent: Neutral Iron (II) chloride solution

Observation:


——Violet/purple colouration



—— No observable change

c) $CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$

Solution

Reagent: Iodine solution and sodium hydroxide solution

Observation:

$CH_3COCH_2CH_2CH_3$ – yellow precipitate

$CH_3CH_2COCH_2CH_3$ – No observable change

d) $CH_3CH_2CH_2NH_2$ and $CH_3NHCH_2CH_3$

Solution

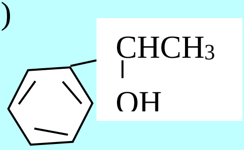
Reagent: Sodium nitrate and cold concentrated hydrochloric acid.

Observations

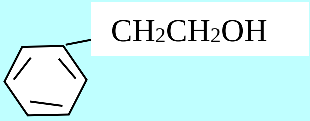
$CH_3CH_2CH_2NH_2$ - gives bubbles of a colourless gas and a colourless solution

$CH_3NHCH_2CH_3$ – gives a yellow oil

e)



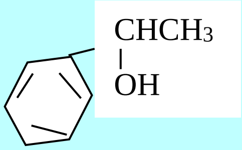
and



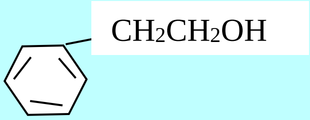
Solution

Reagent: Anhydrous Zinc chloride and concentrated hydrochloric acid

Observation:



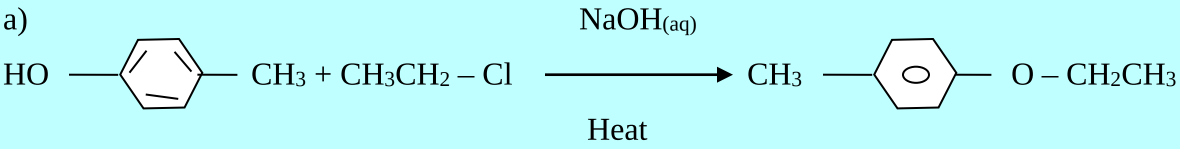
- Gives cloudy solution within 5-10 minutes



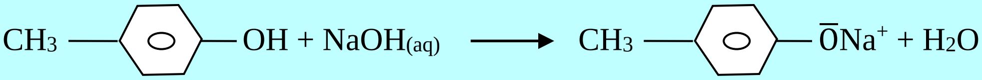
- Cloudy solution not formed at room temperature but on heating it forms

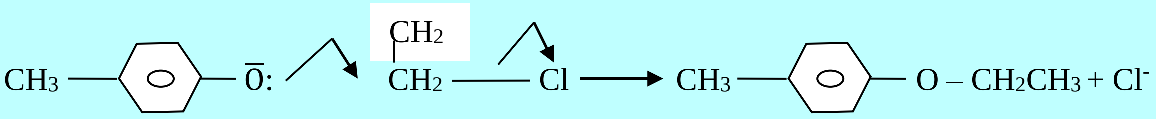
7. Complete the following equations and in each case write the accepted mechanism for the reaction.

a)

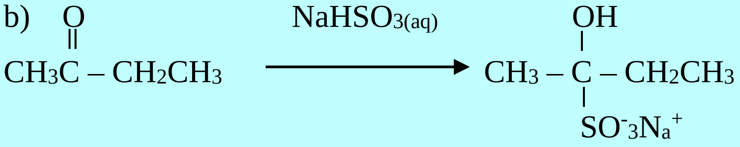


Solution



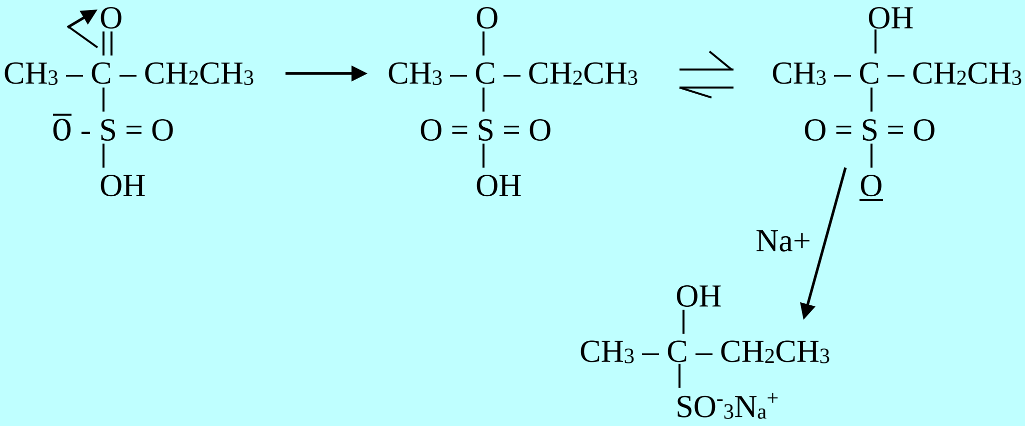


b)



$$CH_3\overset{O}{\overset{\|}{C}}-CH_2CH_3 \xrightarrow{NaHSO_{3(aq)}} CH_3-\underset{SO^-_3Na^+}{\overset{OH}{C}}-CH_2CH_3$$

Solution



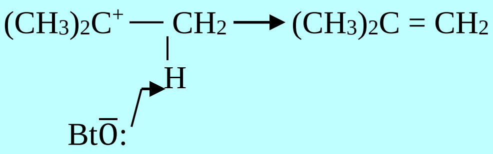
$$CH_3-\underset{\bar{O}-S=O,\ OH}{\overset{O}{\overset{\|}{C}}}-CH_2CH_3 \longrightarrow CH_3-\underset{O=S=O,\ OH}{\overset{O}{C}}-CH_2CH_3 \rightleftharpoons CH_3-\underset{O=S=O,\ \underline{O}}{\overset{OH}{C}}-CH_2CH_3 \xrightarrow{Na+} CH_3-\underset{SO^-_3Na^+}{\overset{OH}{C}}-CH_2CH_3$$

b) EtŌ / EtOH

$$(CH_3)_3C-I \xrightarrow[\text{Heat}]{} (CH_3)_2C=CH_2$$

Solution

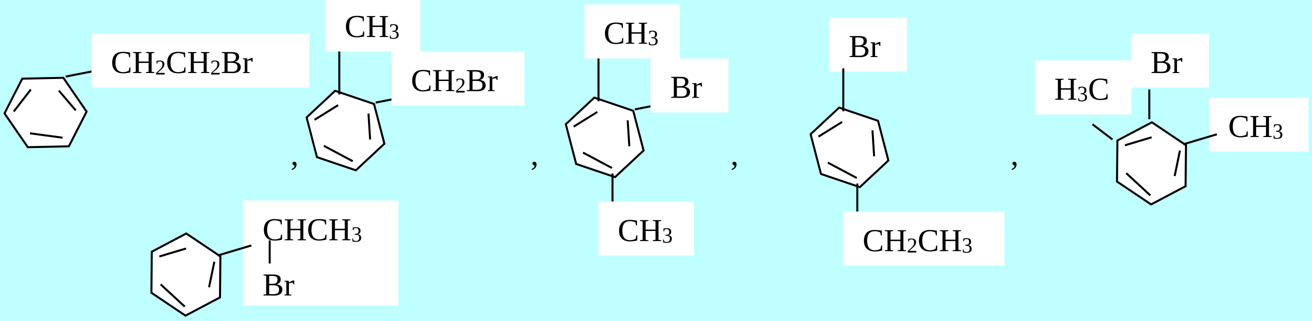
$$(CH_3)_3C-I \rightleftharpoons CH_3-C^+(CH_3)_2 + I^-$$



$$(CH_3)_2C^+-\underset{H}{CH_2} \longrightarrow (CH_3)_2C=CH_2$$

8(a) A compound X C_8H_9Br burns with a sooty flame write all the possible structural formulae of X.

Solution

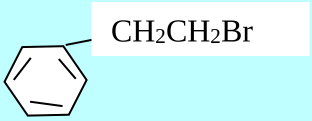


b) When X was heated under reflux with aqueous sodium hydroxide solution, a compound Q, C_8H_9Br was formed.

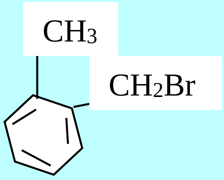
i) Identify X and Q

Solution

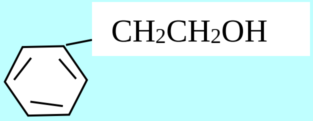
X – is



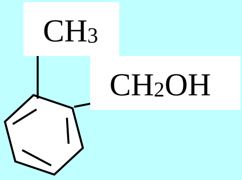
or



Q – is

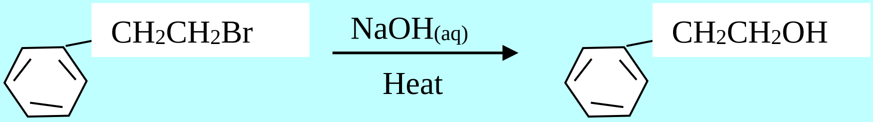


or



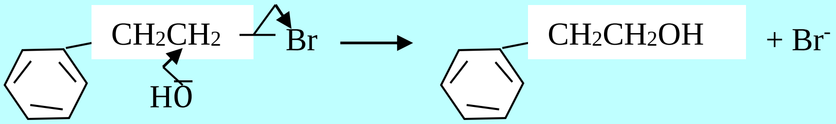
ii) Write an equation and indicate a mechanism for the reaction leading to the formation of Q from X.

Solution



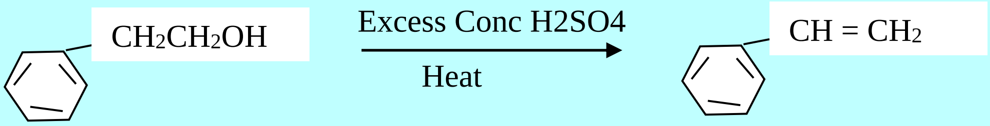
Mechanism

$$NaOH_{(aq)} \rightleftharpoons Na^{+}_{(aq)} + \overline{O}H(aq)$$



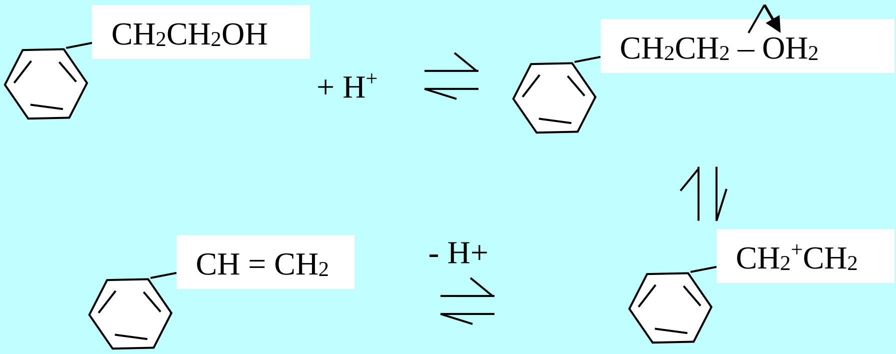
c. Q was converted in a one-step reaction to an alkene. Write equation and outline a mechanism for the reaction.

Solution



Mechanism

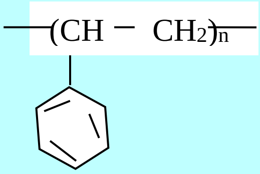
$H_2SO_{4(aq)} \rightleftharpoons H^+ + \bar{O}SO_3H$



d. The Alkene in (c) above was polymerized.

i) Write the structural formulae of the polymer

Solution



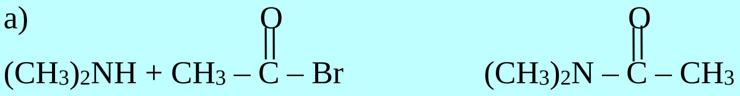
ii) State the type of polymerization involved

Solution

Addition polymerization.

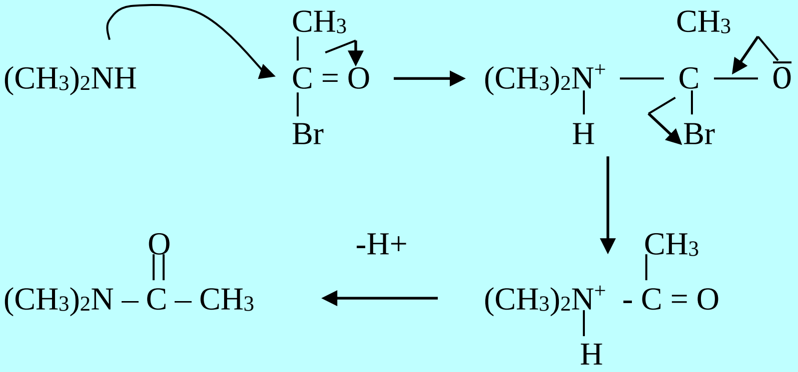
9. Complete the following equations and in each case outline the accepted mechanism for the reaction.

a)

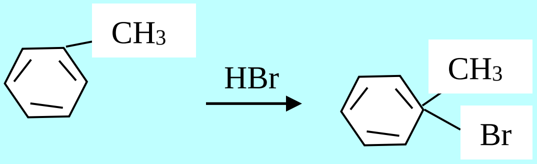


$(CH_3)_2NH + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Br \qquad (CH_3)_2N-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

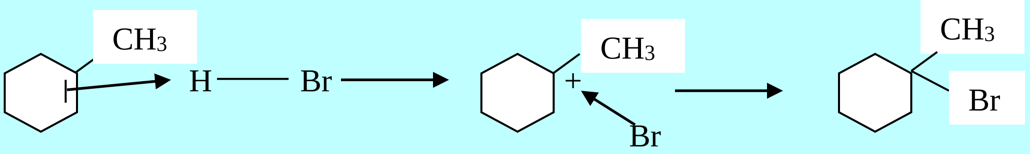
Solution



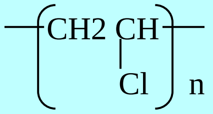
b)



Solution



10(a) State the conditions for the formation of polyvinyl chloride.



$-\!\left(CH_2 \; \underset{\underset{\displaystyle Cl}{|}}{CH} \right)_n\!-$

Solution

- Heat/ High temperature/ or 100^0C
- Peroxide or Hydrogen peroxide, Dibenzoyl peroxide
- High pressure

b) The osmotic pressure of a solution containing $4.00gdm^{-3}$ of polyvinyl chloride in dioxin is 65Pa at 20^0C. Calculate the number of monomers in polyvinyl chloride.

Solution

$V_1 = 1000cm^3 (ldm^3)$ $V_2 = ?$

$P_1 = 65Pa$ $P_2 = 1.0 \times 10^5Pa$

$T_1 = 20 + 273 = 293k$ $T_1 = 273k$

$$Using\ \frac{P_2V_2}{T_2} = \frac{P_1V_1}{T_1}$$

$$V_2 = \frac{1 \times 65 \times 273}{293 \times 1.01 \times 10^5}$$

$= 60.56314 \times 10^{-5}dm^3$

Now

$60.56314 \times 10^{-5}dm^3$ of polyvinyl chloride contain 4g of polyvinyl chloride

$22.4dm^3$ of polyvinyl chloride contain $\frac{22.4 \times 4}{60.56314 \times 10^{-5}}$

$= 1.4794477 \times 10^{-5}$

$= 147944.77g$

So

Molar mass of monomer ($CH_2 = CHCl$) = (12x2) + 3 + 35.5

= 62.5

Therefore $\frac{62.5n}{62.5} = \frac{147944.77}{62.5}$

$n = 2367.1$

Hence $n \approx 2367$

c) State one use of polyvinyl chloride

Solution

Making pipes, films, records, insulators for cables rain coats, etc

Self-check

1.a) Ethyne was bubbled through an ammoniacal silver nitrate

Solution

i) State what was observed

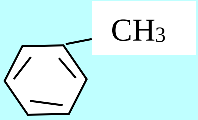
ii) Write equation of reaction that occurs in (a)(i) above.

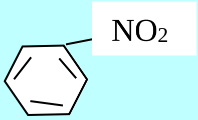
b) Give a reaction scheme to show how the following conversions can be effected in each case indicate the reagents required and the conditions of reaction.

i) ethanol to ethyne

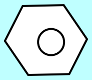
ii) ethyne to ethanomide

iii) $CH_3CH_2CH_2OH$ to $CH_3CH_2NH_2$

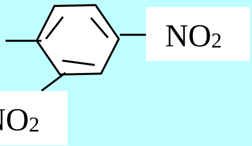
iv) 

to 

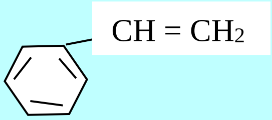
2. Complete the following equations and in each case suggest the mechanism of reaction.

a)  + $CH_3CH_2Cl \xrightarrow{AlCl_3}$

b) $CH_3COCH_3 + NaHSO_3 \longrightarrow$

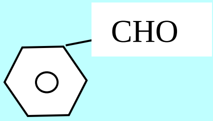
c) $CH_3CH_2CHO + H_2N - NH -$ 

$\xrightarrow{H^+}$

d) 

$\xrightarrow[H_2O]{Br_2}$

e) $(CH_3)_3C - OH \xrightarrow[\text{Heat}]{\text{Conc } H_3PO_4}$

f) 

$^-OA_{(aq)}$

3(a) Compound M contains 61% by mass of carbon, 15.3% by mass of hydrogen, the rest being nitrogen. Calculate;

i) The empirical formula of M

ii) The molecular formula of M (Vapour density of M is 29.5)

b) M reacts with nitrous acid forming gas N and a compound O. O reacts with acidified potassium dichromate (VI) solution on warming forming compound P, which reacts with iodine and potassium hydroxide solution forming a yellow precipitate.

i) Identify the compounds O, P and M and the gas N.

ii) Write an equation leading to the formation of the yellow precipitate.

iii) Write an equation and outline a mechanism for the reaction between P and phenylhydrazine in the presence of dilute sulphoric acid.

c) Write equations to show how the following conversion can be effected. Indicate reagents and conditions for the reaction.

(i) P to propan – l – ol

(ii) propene to P

4. When 0.10g of an organic compound X containing carbon, hydrogen and oxygen only was subjected to combustion, it gave 0.227g of carbon dioxide and 0.0929g of water. 0.368g of X when vaporized at 37^0C and 760mmHg it occupied a volume of $161.4cm^3$

a(i) Calculate the empirical formula of X.

(ii) Deduce the molecular formula of X

b) Determine the structural formulae and their IUPAC names of all the possible Isomes of X.

c) X reacts with hydroxyl amine in acidic medium but does not react with ammoniacal silver nitrate solution. Identify X.

d) Write equations to show how;

i) X can be synthesized from ethanol

ii) X can be converted to ethanoic acid

e) Write equation for the reaction between X and dilute sodium hydroxide solution at room temperature.

5.a) Describe the reactions of amines with nitrous acid. Write equations for the reactions and state the observations.

b) 0.354g of a compound X containing carbon, hydrogen and nitrogen gave 0.981g of carbondioxide, and 0.233g of water when burnt in excess air. The same mass of X gave $41.5cm^3$ of nitrogen at 0^0C and 760mmHg calculate the empirical formula of X.

c) When X was steam distilled at 98^0C and 760mmHg, the distillate was found to contain 72.1% of water. If the vapour pressure of water at 98^0C is 707mmHg.

i) Calculate the relative molecular mass of X.

ii) Determine molecular formula of X.

d) Write equations to show how X can be;

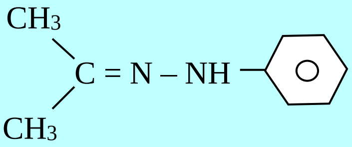
i) prepared from benzene

ii) converted to benzoic acid

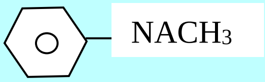
6(a) Define the term catenation

i) Why does carbon have such a high-profile ability to catenate?

b) Write equation to show how the following compounds can be synthesized.

i) 

from propene

ii) 

from benzene

iii) $CH_3CO_2CH_3$ from bromoethane

iv) $CH_3CA_2C \equiv CH$ from ethanol

v) $(CH_3)_2C = NOH$ from propene

7. Write short notes on the following;

a) Elimination uni -molecular reaction

b) Sulphonation reaction

c) Nitration reaction

-END-