ORGANIC CHEMISTRY

Organic Chemistry is a branch that deals with the study of compounds of carbon other than simple salts such as carbonates, Oxides and carbides. Carbon is usually combined with elements such as Hydrogen, oxygen, Halogens, Nitrogen, Sulphur and Phosphorus.

THE UNIQUE NATURE OF CARBON

- Carbon can form a vast number of different compounds. This is because of:
  - (i). the four valency electrons on carbon atom that make it possible for carbon to combine with four other atoms through covalent bonding.
  - (ii). the ability of carbon atom to combine with atoms of other non-metals e.g oxygen, hydrogen, nitrogen, sulphur, halogens and phosphorus.
  - (iii). Carbon is capable of caternating i.e form long chains with itself, some of which are straight, branched or ring.
  - (iv). the unusual strength of carbon-carbon bond which is 349kJmol^{-1}. This makes the compounds to be stable thermodynamically.
  - (v). Carbon can form multiple bonds between itself and other carbon atoms >C=C<. -C≡C - and also with atoms of other elements such as oxygen,>C=O, Sulphur,>C=S and nitrogen, – C≡N.
- Most of the bonds that carbon forms with other atoms are covalent. Example C–C, is purely covalent as the difference in electronegativity is zero, C–H is almost purely covalent as the difference in electronegativity is so small. This means that most organic compounds are non-polar.

REACTIONS OF ORGANIC COMPOUNDS

(a).**Types of organic reactions**.

The reactions of organic compounds fall under four classes as shown below.

- Substitution reactions
- Addition reactions
- Elimination reactions
- Rearrangement reactions.

All the four types of reactions may be initiated by an electrophile, nucleophile or free radical attack on the substrate.

1) Substitution reactions.

Involve the direct replacement of an atom or group of atoms by another atom or group of atoms.

Examples:

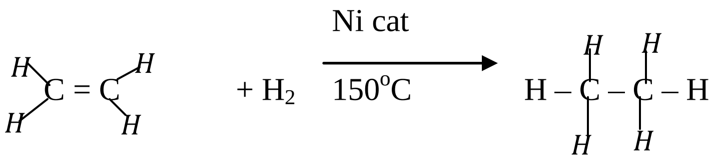
- Hydrolysis of alkylhalides with aqueous sodium hydroxide which is nucleophilic substitution reaction. $CH_3CH_2Cl + {}^-OH(aq) \quad CH_3CH_2OH + Cl^- (aq)$
- Electrophilic substitution reactions in benzene

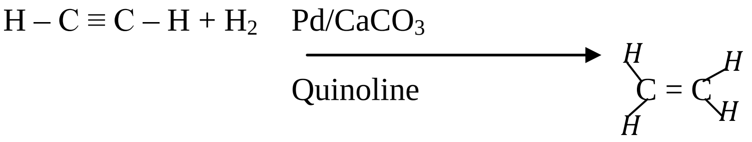
2) Addition reactions:

The attacking reagent simply adds itself across the unsaturated bond of the substrate to yield a saturated product or one in which the degree of unsaturation is reduced. Simply two molecules react of form one molecule.

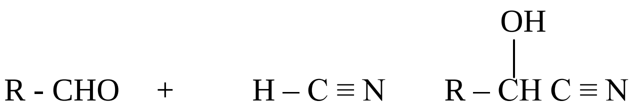
Examples:

- Electrophilic addition in alkenes and alkynes.





Nucleophilic addition reactions in carbonyl compounds



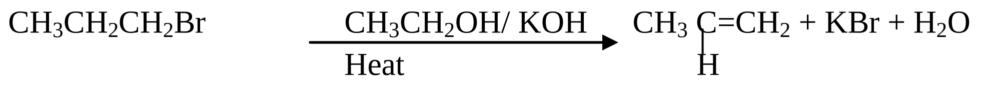
$$R - CHO \quad + \quad H-C\equiv N \quad R-\overset{OH}{\overset{|}{C}}H\ C\equiv N$$

3) Elimination reactions

This involves the removal of atoms or group of atoms in a molecule which is saturated from the adjacent carbon atoms to form multiple bonds; resulting in unsaturated molecule.

Examples:

- Dehydration of alcohols to form alkenes.
  $CH_3CH_2OH \xrightarrow[170^oC]{ConcH_2SO4} H_2C = CH_2 \quad + \quad H_2O$
- Dehydrohalogenation of alkyl halides to form alkenes and alkynes.



$$CH_3CH_2CH_2Br \xrightarrow[\text{Heat}]{CH_3CH_2OH/\ KOH} CH_3\underset{\displaystyle H}{\underset{|}{C}}{=}CH_2 + KBr + H_2O$$

4) Rearrangement.

These involve the migration of an atom or group of atoms from one site to another within the same molecule or migration of functional group from one position to another within the same molecule. Simply put one molecule reacts to give a different molecule.

Example

$CH_3CH_2CCl = CH_2 \longrightarrow CH_3CH{=}CHCH_2Cl$

(b).**Types of bond fissions**:

When organic compounds react, their bonds can split in two ways, either by Homolytic or Heterolytic bond fission.

Homolytic bond fission:

In homolytic bond fission, the bond is broken symmetrically where each of the bonded atoms take one of the electrons in the bond resulting in the formation of free radicals.

Examples $A \,\cancel{:}\, B \longrightarrow A^{\cdot} + B^{\cdot}$

Two separate free radicals

$CH_4 + Cl_2 \xrightarrow{\text{U.V light}} CH_3Cl + HCl.$

$Cl{-\!-\!-}Cl \longrightarrow \bullet Cl + \bullet Cl$

Energy is supplied, either by heat or light to break the bond and the free radical formed possess this energy and are very reactive.

The steps in free radical reaction involve initiation, propagation and termination.

A free radical is uncharged atom or molecule having unpaired valency electron and higly reactive.

Heterolytic bond fission.

In herolytic bond fission, the bond is broken unsymmetrically. Only one atom that formed the bond takes both electrons to form an anion. The rest of molecule becomes a cation.

$A{-\!-\!-}B \longrightarrow A^{+} + B^{-}$

Example

$(CH3)_3C - Cl \longrightarrow (CH3)_3C^{+} + Cl^{-}$

Carbocaton

- The ion with a positively charged carbon atom is called a carbocation.
- The ion with a negatively charged carbon atom is called carbanion

Example:

$(CH3)_3C–H \longrightarrow (CH3)_3C^- + H^+$.

Carbanion.

Carbanions are formed by removal of an atom or groups of atoms bonded to carbon without removing the bonding pair of electrons.

- The electrons will shift towards a more electronegative atom if the bonded atoms are different.
- If the bonded atoms are similar (C – C), the direction of electron movement will depend on:
  (i). Nature of other atoms or group of atoms attached to each atom.
  (ii). the conditions of the reaction i.e. solvent, temp and reactants
  (iii). Relative energy content of the excited state.

(c).Types of reagents:

- In a covalent bond between A and B, if A is more electronegative than B, the bonding electrons are closer toward A as shown $A^{\sigma +}– B^{\sigma -}$. The bond is said to be polar.
- The reagents that attack organic compounds seek out either slightly positive $\delta+$ end of the bond or slightly negative δ^- end of the bond. There are two classes of reagents.

  Nucleophilic reagents:

  A nucleophile is electron rich species and in chemical reaction will seek the nucleus (protons). It is referred to as Lewis base. Examples are:

  H_2O, ROH, ^-OH, Cl^-, Br^-, I^-, NH_3, RNH_2, CN^-

  Electrophilic reagents:

  This is an electron deficient species and in a chemical reaction, will seek an electron rich site. They can be referred to as Lewis acids.

  Examples are: H^+, NO_2, R_3C^+, RN_2^+

(d). **Reaction mechanism**:

This is the sequence of steps by which an organic reaction takes place from the start to the finish. This is worked out from the study of kinetics of the reaction.

(e). **Functional groups and homologous series**.

➢ A functional group is an atom or a group of atoms or a bond common to a series or family of organic compounds and which govern the principle chemical properties of the series.

Examples : (family series)	General formula	Functional group
Alkanes	CH_2n+2	— (bond)
Alkenes	CnH_2n	= (bond)
Alkynes	CnH_2n-2	≡ (bond)

Alcohols	CnH_2n+_1OH	-OH
Ethers	CnH_2n+_1O	-O -
Aldehydes	CH_2n+_1 CHO	H – C = O
Ketones	CO	R—C = O
Carboxylic acid	-COOH	- C = O -OH

- Homologous series is a family or class of organic compounds having the following properties:
  - (i). All members of the family can be represented by a general formula e.g. $C_nH_2n+_1$ for alkanes.
  - (ii). Each member of the series has a similar method of preparation and chemical properties.
  - (iii). As the series is ascended, a methylene group $–CH_2$ is added to each successive member.
  - (iv). As each methylene group is added, physical properties (melting point, boiling point, and density) change slightly.

(f). **Isomerism:**

This is the existence of different compounds with the **same molecular formula** but different **structural formulae**. There are various types of isomerism.

1). **Structural isomerism**:

Structural isomerism shows the sequence in which the atoms in a molecule are bonded. A structural formula can be written in full, with every bond drawn or it can be written by joining groups of atoms in sequence, provided the formula of each group is unambiguous.

$CH_3CH_2CH_2CH_3$

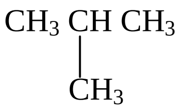
Structural isomerism is divided into three, i.e chain isomerism, position and functional isomerism.

Chain Isomerism

This is a structural isomerism where the isomers have different carbon chains, but possessing the same functional group.

Example:

$CH_3\,CH_2CH_2CH_3$ and



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

Butane

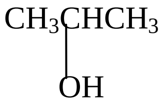
2-methylpropane

In this type of isomerism, the carbon skeleton differs.

Position isomerism:

This is a structural isomerism where the position of the functional group in the carbon skeleton differs. The isomers are chemically similar as they possess the same functional group.

Example: $CH_3CH_2CH_2OH$ and



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

Propanol

Propan-2-ol

$CH_3\,CH_2\,CH = CH_2$ and $CH_3CH= CHCH_3$

Butene But-2-ene

Functional group isomerism:

This is a structural isomerism in which the isomers have different functional groups and belong to different homologous series.

Examples:

CH_3CH_2OH and CH_3OCH_3

ethanol dimethyl ether

CH_3CH_2CHO and CH_3COCH3

aldehydes ketones

2).Stereoisomerism:

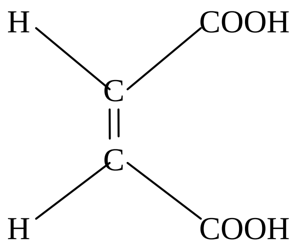
In stereoisomerism, the isomers have the same molecular formula and the same structural formula but show difference in the arrangement of bonds in space. Stereoisomerism can be; Cis – trans isomerism or optical isomerism.

Cis-trans isomerism (geometrical isomerism)

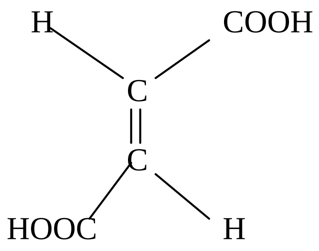
It occurs in compound in which free rotation is prevented by the presence of multiple bonds, a ring structure or steric factor.

Cis-isomer has identical or similar atoms or groups of atoms on the same side of the double bond while trans-isomer has these atoms or groups of atoms on the opposite side.

Examples:



Cis-Butenedioic acid

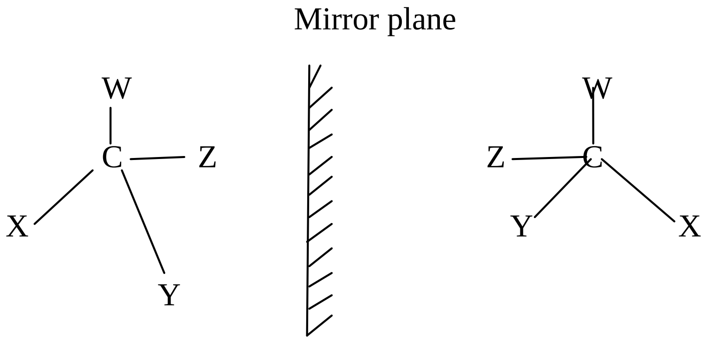


Trans-Butenedioic acid.

The physical properties and chemical properties of cis and trans isomers differ.

Optical isomerism:

If four different atoms or groups are attached to the same carbon, there are two isomers which are not super imposable on their mirror images. These isomers are called enantiomers.



Non-superimposable mirror images.

Enantiomers have identical physical constants (mpt and bpts) but may be distinguished by their ability to rotate the plane of polarized light in opposite directions. Because they exhibit this property that such isomers are said to be optically active.

NOMENCLATURE OF ORGANIC COMPOUNDS.

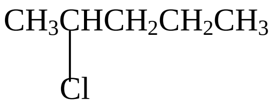
Modern systems for naming aliphatic compounds are based upon the name of alkanes. Organic compounds are named according to the International Union of Pure and Applied Chemistry (IUPAC) system where the following systematic principles are adopted.

1).The longest continuous chain of carbon atoms containing the functional group is chosen and named according to the parent alkane.

2).The carbon atoms of the chain are numbered in order to indicate the positions of any substituents in the chain. The numbers assigned are called locants to locate the position of each carbon atom in the parent chain..

3).The end of the chain from which the numbering starts is chosen so as to use the lowest values or locants.

e.g



$$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_2CH_3$$

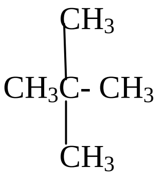
Name: 2–chloropentane **NOT** 4-chloropentane.

4).The names of substituents prefix (start before) the name of the parent alkane (suffix), these are arranged alphabetically and the positions of substitution precede the whole name followed by a dash.

A dash is used to separate a numeral from a letter and a comma is used to separate numerals.

Example:

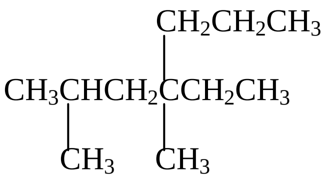
(a)



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

2,2-dimethylpropane

(b)



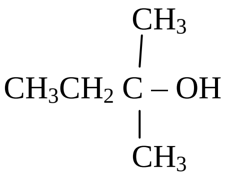
$CH_3CH(CH_3)CH_2C(CH_3)(CH_2CH_2CH_3)CH_2CH_3$

4- ethyl-2, 4-dimethylheptane.

5).When two or more substituents are identical, indicate this by use of prefix di, tri, tetra etc. as above

6).The numbers assigned to functional groups are chosen such that they take the smallest value or locant as possible. They are usually placed between the stem and the ending of the name.

Example:



$CH_3CH_2C(CH_3)_2-OH$

2 – methylbutan-2-ol

FACTORS THAT INFLUENCE A CHEMICAL REACTION IN ORGANIC COMPOUNDS.

A reaction in organic compounds may be inhibited or facilitated by:

(1).Distribution of electrons in the region of the site of reaction in the substrate i.e. electronic factor.

(2).The nature and size of atoms or groups of atoms surrounding the site of reaction i.e.steric factor.

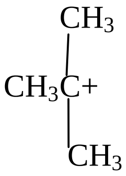
1. **Electronic factor**. This factor is looked at in three ways.

- Inductive effect (IE)

A covalent bond is usually polarized to some extent, since the atoms forming the bond have different electronegativities.

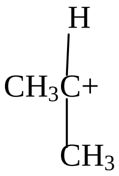
Example: -C–C–C–C—Cl

Chlorine atom is more electronegative than carbon atom hence it withdraws bond electrons closer to itself, hence it exerts a negative inductive effect (-1). In the above example, the inductive effect is transmitted along the chain although it tends to be insignificant beyond the second carbon atom. Certain groups of atoms, notably alkyl groups exert a positive inductive effect (+1) i.e are electron donating hence stabilizing the carbocation.



$(CH_3)_3C^+$

Tertiary (3°)



$(CH_3)_2CH^+$

Secondary (2°)

$CH_3CH_2C^+H_2$

Primary (1°)

Tertiary alkyl groups exert a greater positive inductive effect than secondary which in turn exert greater positive inductive effect than primary alkyl groups. This mean tertiary alkyl groups are more stable than secondary which are more stable than primary.

- Mesomeric effect (ME)

This is the shift of π electrons in multiple bonds towards the more electronegative atoms, and is similar to inductive effect in single bonds.

C—O

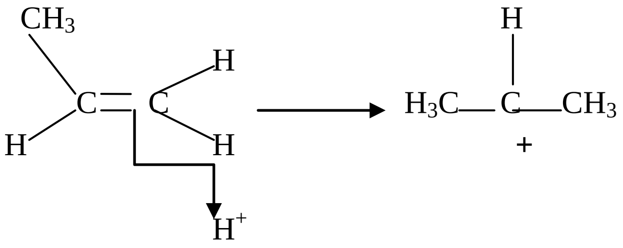
The above structure can be represented as a resonance hybrid between two canonical forms shown below.

The effect is transmitted along the chain in away similar to inductive effect. This phenomena is observed in carbonyl cpds and carboxylic acids.

- Electrometric effect.

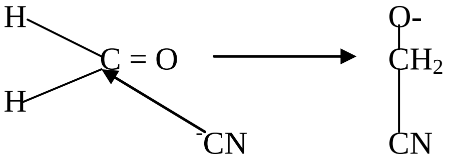
This is the temporary polarizability which occur in unsaturated systems as they are approached by the reagents. This comes into play at the demand of the attacking reagent. Example:

(1).



Occurs in reactions of alkenes

2).



This occurs in reactions of carbonyl compounds.

3).

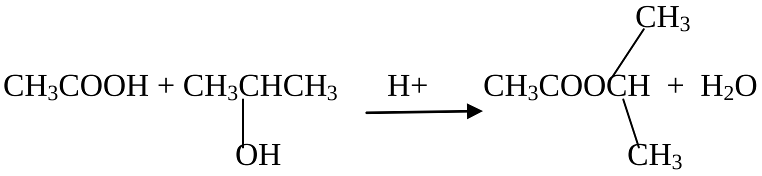
Halogens direct to 2-, and 4- positions in the benzene ring despite them being electron withdrawing.

2). **Sterric factor:**

When bulky atoms or groups of atoms are distributed around the site of reaction in an organic molecule, these atoms or group of atoms may completely prevent a reaction from occurring despite favorable electronic factors. Example: The rate of esterification of ethanoic acid with propan-2-o1 is half that with ethanol. The rate of reaction in propan-2-o1 is retarded by presence of two methyl groups on the carbon atom, compared with one on ethanol.

(i). $CH_3COOH + CH_3CH_2OH \xrightarrow{H+} CH_3COOH_2CH_3 + H_2O$

(ii).



$CH_3COOH + CH_3CH(OH)CH_3 \xrightarrow{H+} CH_3COOCH(CH_3)_2 + H_2O$

ALKANES:

Alkanes are saturated hydrocarbons and may be represented by a general formula C_nH_{2n+2}. They are normally very stable compounds and are relatively less reactive compared to unsaturated alkenes.

Sources of alkanes:

The main sources of alkanes are:

1). Natural gas: This contains mainly methane, with smaller amounts of other gases such as ethane, propane and butane

2). Petroleum: This contains a wide range of alkanes ranging from low molecular mass gases to high molecular mass waxy solids (C2- C40). The components of petroleum are separated by fractional distillation.

The fractions obtained from crude oil are:

Fraction	Boiling pt (^oC)	Length of carbon chain	Uses
Refinery gas	20	C1 – C4	Fuel, domestic heating
Light petroleum	20 – 60	C5 – C6	Solvent
Light naphtha	60 – 100	C6 – C7	Solvent
Gasoline (petrol)	40 – 205	C5 – C12	Fuel for internal combustion engines.
Kerosene (paraffin)	175 – 325	C12 – C18	Fuel for jet engines.
Gas oil	275 – 400	C18 – C25	Does not vaporize easily. Used in diesel engines. Used in industrial furnaces.
Lubricating oil	Non volatile	C20 – C34	Lubrication.
Paraffin wax	Solidifies from lubricating oil	C25 – C40	Polishing waxes. Petroleum jelly.
Bitumen	Residue	>30	Road surfacing. Roofing.

Physical properties of Alkanes.

1- The electronegativities of carbon and hydrogen are 2.5 and 2.1 respectively, therefore the C – H bond has weak dipole and attractive forces between the molecules are vanderwaals, hence lower ones are gases at room temperature, C5 – C17 are liquids, while those with large molecules are solids.

2- Branched chain alkanes have lower boiling points than unbranched chain alkanes. This is because branching reduces the strength of the attractive forces between molecules hence the branched alkanes boil off easily.

3- Liquid alkanes float on water because alkanes cannot form hydrogen bonds with water hence insoluble.

Laboratory Preparations of alkanes.

(1). From salts of carboxylic acids

(a). Alkanes can be prepared by heating a sodium salt of carboxylic acid with sodalime which is a mixture of solid sodium hydroxide and solid calcium oxide .

Example:

$$CH_3CH_2COONa \xrightarrow[\text{Heat}]{\text{NaOH (S)/CaO(S)}} CH_3CH_3 + Na_2CO_3$$

The yield of the alkane decreases with increase in the length of the carbon chain. This method also reduces the length of the carbon chain by one carbon atom.

(b). Alkanes can also be prepared by electrolysis of sodium or potassium salt of carboxylic acid (Kolbe's method). The alknane is liberated at the anode together with carbon dioxide while hydrogen gas at the cathode.

$CH_3COONa(aq) \longrightarrow CH_3COO\text{-}(aq) + Na^+(aq)$

Pt anode $2CH_3COO^-(aq) \longrightarrow CH_3CH_3(g) + CO_2(g) + 2e.$

Pt cathode $2H+(aq) + 2e \longrightarrow H_2(g)$

Suitable for preparation of symmetrical alkanes i.e R – R.

Carbon dioxide produced is removed by passing the mixture of gases through a solution of sodium hydroxide to form sodium carbonate.

$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(l)$

2). From Alkyl halides:

(a). By reduction of alkyl halides using copper-zinc couple in ethanol. The copper – zinc couple reacts with ethanol to produce nascent hydrogen required for the reduction.

$CH_3CH_2X \xrightarrow[\text{Ethanol}]{\text{Cu – Zn couple}} CH_3CH_3 + HX$, where X is Cl, Br, OR I

The carbon chain does not double or increase.

(b). By reduction of alkyl halides using lithium aluminium tetrahydride in dry ether

$4RX \xrightarrow[\text{dry ether}]{LiAlH_4} 4RH + LiAlX_4$

(c). Using sodium metal (wurtz reaction).

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

$$2CH_3CH_2X + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2CH_2CH_3 + 2NaX$$

Higher yields are obtained with alkyl halides of higher molecular mass.

3). From unsaturated hydrocarbons.

Alkenes react with hydrogen in the presence of a catalyst to form alkanes. The reaction takes place at room temperature with platinum and palladium catalysts but at 150°C with Nickel catalyst.

$$CH_3CH = CHCH_3 + H_2 \xrightarrow[150^0C]{\text{Ni Cat}} CH_3CH_2CH_2CH_3$$

Alkynes react with hydrogen in the presence of a catalyst to form alkanes with Nickel at 180°C and with platinum or palladium at room temperature.

$$CH_3C \equiv CH + H_2 \xrightarrow[180^oC]{\text{Ni Cat}} CH_3CH = CH_2 + H_2 \xrightarrow[150^oC]{\text{Ni Cat}} CH_3CH_2CH_3.$$

REACTIONS OF ALKANES

Straight chain alkanes are comparatively inert or less reactive compared to alkenes and alkynes. However, they undergo the following reactions.

1) **Cracking of alkanes**.

Cracking is a reaction in which larger saturated alkane molecule is broken down into smaller more useful alkanes (used as fuels) or alkene molecules. The petroleum industry uses pyrolysis (splitting by heat) of high molecular mass alkanes to give alkanes of small molecules. Alkanes with large molecular mass are passed over aluminium oxide mixed with silcon dioxide and heated to 450°C – 700°C.

Example:

$$2CH_3CH_2CH_3 \xrightarrow[Al_2O_3/\ SiO_2]{(450 - 700)^0C} CH_4 + CH_3CH{=}\ CH_2 + CH_2 = CH_2 + H_2\ (g)$$

2) Alkylation:

Alkylation is used to make branched chain alkanes by reaching alkanes with alkenes in the presence of a catalyst. The branched chain alkanes are used in unleaded fuels.

$$\text{Tertiary alkane + alkene} \xrightarrow[20^oC.]{\text{Conc}H_2SO_4\ \text{Cat}} \text{branched chain alkane}$$

3) Reforming:

This converts straight chain alkanes into aromatic compounds. The reaction is carried out at 500°C, 40 atmosphere pressure and a catalyst of Al_2O_3 or platinum at 10 atmospheres.

Examples: $C_6H_{14} \xrightarrow[\text{Al}_2\text{O}_3 \text{ Cat, 40Atm}]{\text{vaporized at } 500^{o}\text{C}} C_6H_6 + 4H_2\,(g)$

Hexane benzene

4) Combustion

Alkanes burn in air to give carbon dioxide and water with evolution of energy in form of heat.

$$2C_nH_{2n}+2 + 3O_2\,(g) \longrightarrow 2nCO_2\,(g) + 2(n+1)\,H_2O + \text{heat}$$

Example:

$$C_3H_8 + 5O_2\,(g) \longrightarrow 3CO_2(g) + 4H_2O(g) + \text{heat.}$$

5) Nitration

Alkanes react with concentrated nitric acid or nitrogen tetraoxide in vapour or liquid phase at high temperature of about 450°C to form nitro compounds.

$$RH + HNO_3 \xrightarrow{450^{o}C} RNO_2 + H_2O$$

6) Sulphonation

When higher alkanes are treated with fuming sulphuric acid, alkylsulphonic acids are formed.

$$RH + H_2SO_4 \qquad\qquad RSO_3H + H_2O$$

The products are strong monobasic acids whose sodium salts are used as detergents.

7) Halogenation

Alkanes react with halogens in the presence of ultra violet light. Alkanes can be chlorinated or brominated photochemically. The reaction proceeds through free radical mechanism.

Chlorination of alkanes.

Alkanes undergo clorination in the presence of ultraviolet light or at temperature of (250 – 400) °C yielding a mixture of product.

$CH_4 + Cl_2 \xrightarrow[\text{light}]{\text{u.v}}$ a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.

NB: If chlorine is in excess, that is when CH_2Cl_2, $CHCl_3$ and CCl_4 are formed.

Only CH_3Cl is formed when chlorine is limited.

Mechanism

(i). Initiation step.

$$Cl - : - Cl \xrightarrow{\text{u.v.}} {}^{\cdot}Cl + {}^{\cdot}Cl\ ,\ \Delta H = +242\text{Kmol-1}$$

(ii). Chain propagation step.

$$Cl \quad H - CH_3 \longrightarrow CH_3 + HCl \qquad \Delta H = -4\text{kJmol-1}$$

$$CH_3 \quad Cl - Cl \longrightarrow CH_3Cl + Cl;\ \Delta H = -101\text{kJmol-1.}$$

The chlorine radical and methyl radical formed are both reactive

This is the step where CH_2Cl_2, $CHCl_3$ and CCl_4 are formed if chlorine is in excess; where free radical react with neutral molecules.

i.e $Cl \quad H{-}CH_2Cl \longrightarrow CH_2Cl + HCl$

$CH_2Cl \quad Cl - Cl \longrightarrow CH_2Cl + Cl$

(iii). Chain termination step:

$Cl + Cl \longrightarrow Cl - Cl$

$CH_3 + CH_3 \longrightarrow CH_3CH_3$

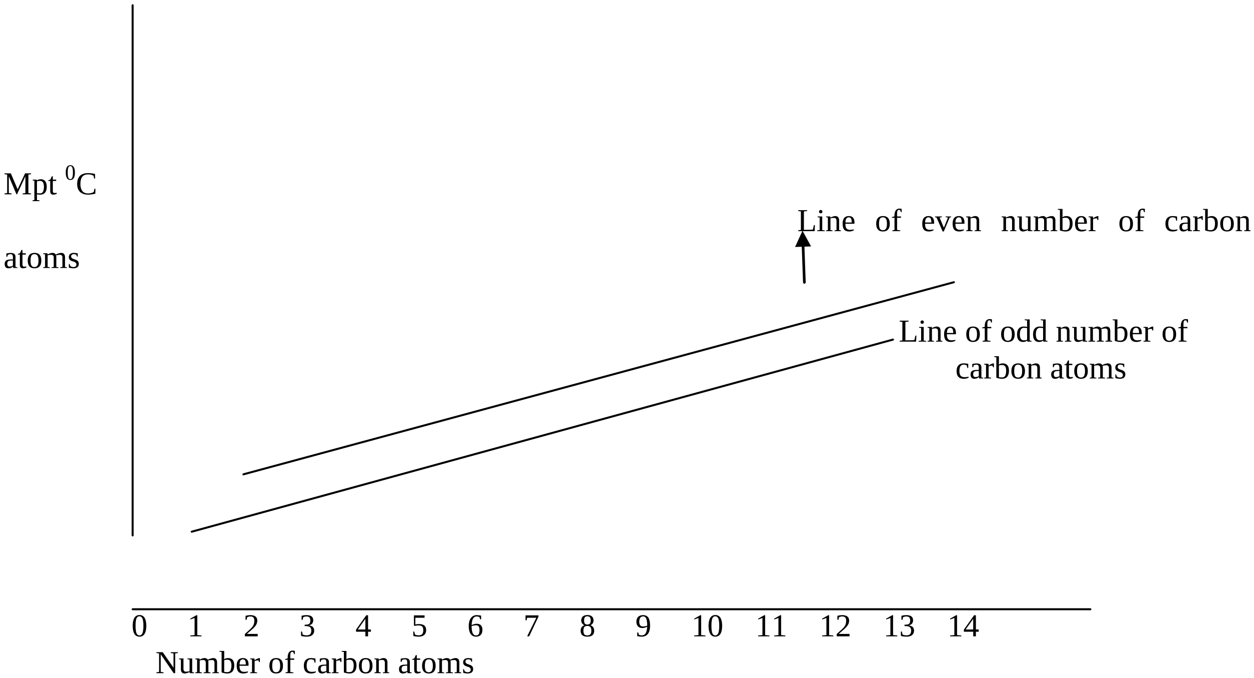
$Cl + CH_3 \longrightarrow CH_3Cl$

BOILING POINTS AND MELTING POINTS OF ALKANES.

Meltinng and boiling points increase with increase in molecular mass. Increase in molecular mass increases the strength of vanderwaals forces of attraction holding the molecules together.

- The melting points of alkanes do not fall on a smooth curve. Alkanes with even number of carbon atoms have higher melting points than those with odd number of carbon atoms. This is because the even chains pack closer together than the odd numbered carbon atoms so that the attractive forces are larger or greater in the even numbered member than in odd, hence require more energy to break them than in the odd.

Graph of melting points against number of carbon atoms of alkanes.



- Brnached chain alkanes have lower boiling points than unbranched chain alkanes. Increased branching decreases the boiling points even further. Branching of the isomer gives the molecule a more nearly spherical shape which reduces the extent of contact between the neighbouring molecules and consequently reducing the attractive forces between the molecules hence reduced boiling point.

ALKENES:

Alkenes are unsaturated hydrocarbons containing at least one double bond between two adjacent carbon atoms and are generally represented by molecular formula C_nH_{2n}. The functional group is the double bond C = C and the availability of electrons in the double bond (Pi electrons) make alkenes more reactive than alkanes.

Ethene is used in ripening of fruits such as bananas, tomatoes, citrus. It also inhibits stem growth during drought or flood.

NOMENCLATURE:

Alkenes are named as derivatives of alkanes by replacing the suffix “ane” with “ene”

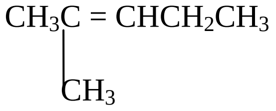
Rules:

1).The longest continuous carbon chain containing the double bond is chosen.

2).The carbon atoms are numbered starting from the side nearest the double bond so that the carbon atom carrying the double bond takes the lowest number.

3).The substituents are located by the number on the carbon atom in the longest chain carrying them.

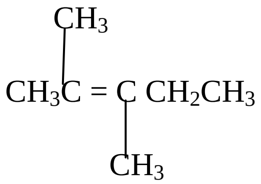
e.g (i)



$CH_3\underset{\substack{|\\CH_3}}{C} = CHCH_2CH_3$

2-methylpent-2-ene

ii)

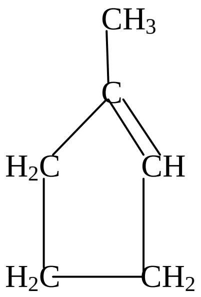


$CH_3\overset{\substack{CH_3\\|}}{C} = \underset{\substack{|\\CH_3}}{C}\,CH_2CH_3$

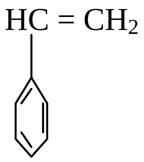
2,3-dimethylpent-2-ene.

4). The word cyclo is used for ring structures.

e.g.



1-methylcyclopent-1-ene.



phenylethene

Isomerism

Alkenes exhibit the following isomerism.

1) **Chain isomerism**

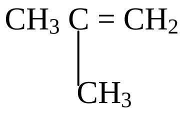
This is a structural isomerism where isomers have different carbon chains but possessing the same functional group.

Example:

(a) The molecular formula C_4H_8 can have the following chain isomers.

(i) $CH_3CH_2CH = CH_2$ Butene

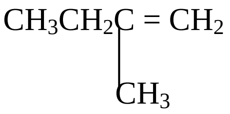
(ii).



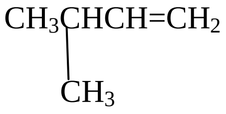
$CH_3\underset{\underset{CH_3}{|}}{C} = CH_2$ 2-methylpropene

(b).The molecular formula $C_5 H_{10}$ can have the following isomers.

$CH_3CH_2CH_2CH = CH_2$ Pentene



$CH_3CH_2\underset{\underset{CH_3}{|}}{C} = CH_2$ 2-methylbutene



$CH_3\underset{\underset{CH_3}{|}}{C}HCH=CH_2$ 3-methylbutene

2) **Position isomerism.**

This arises due to different positions taken by the double bond in the **same carbon chain.**

Examples.

The molecular formula C_4H_8 can have the following position isomers

$CH_3CH_2CH = CH_2$ butene

$CH_3CH = CHCH_3$ but-2-ene.

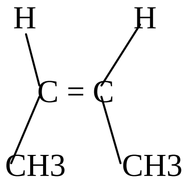
3) **Geometrical isomerism**

This arises due to **restriction of free rotation about the double bond**.

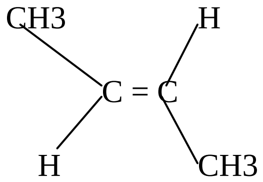
This restriction of rotation about the double bond gives rise to cis and trans isomers. In cis isomers, similar atoms are on the same plane of the double bond while in trans isomers, similar atoms are on different planes of the double bond.

Examples:

(1). But-2-ene

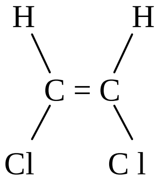


Cis – but-2-ene

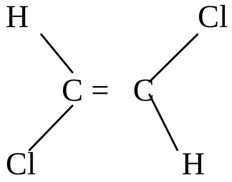


trans – but-2-ene

(2). 1,2-dichloroethene (ClHC = CHCl)



Cis – 1,2-dichloroethene



trans-1,2-dichloroethene

PREPARATION OF ALKENES

In the laboratory, alkenes are usually prepared by:

1). **Dehydration of alcohols:**

Alkenes are prepared by strongly heating an alcohol in the liquid phase with excess concentrated sulphuric acid at 170^0C for primary alcohols or using concentrated phosphoric acid. A molecule of water is lost, and the temperature depends on the nature of the alcohol.

Primary alcohols require a temperature of (170 – 180) ^oC to form alkenes. If a temperature of 140^oC is used and the alcohol is in excess, an **ether** is formed not an alkene.

Examples:

$CH_3CH_2OH \quad \underset{170^oC}{\underline{\text{Excess Conc}H_2SO_4}} \quad CH_2 = CH_2 + H_2O$

Excess

$CH_3CH_2OH \quad \underset{140^oC.}{\underline{\text{Conc}H_2SO_4}} \quad CH_3CH_2OCH_2CH_3$

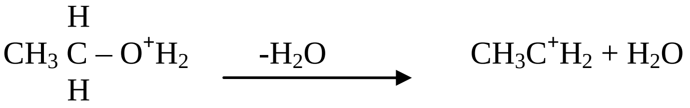
- Secondary alcohols require a temperature of 140^oC to 160^oC to form the alkene
- Tertiary alcohols require a temperature of 120^oC.

Mechanism of the reaction

(i). $CH_3CH_2OH \quad + \quad H - OSO_3H \quad CH_3CH_2O^+H_2 + {}^-OSO_3H$

Protonation of alcohol

(ii).Loss of water molecule to form a carbonium ion



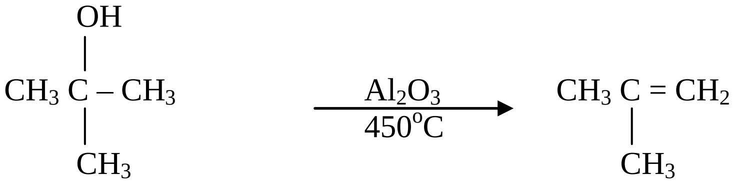
$$CH_3\overset{H}{\underset{H}{C}} - O^+H_2 \xrightarrow{-H_2O} CH_3C^+H_2 + H_2O$$

(iii). Loss of a proton to form the alkene.

$$CH_3C^+H_2 \xrightarrow{-H+} CH_2 = CH_2 + H^+$$

Alkenes are also prepared by passing alcohols in vapour phase over heated aluminium (III) oxide at a temperature of (300 – 450) ^oC.

$$CH_3CH_2OH \xrightarrow[450^oC]{Al_2O_3} H_2C = CH_2$$



$$CH_3\overset{OH}{\underset{CH_3}{C}} - CH_3 \xrightarrow[450^oC]{Al_2O_3} CH_3\underset{CH_3}{C} = CH_2$$

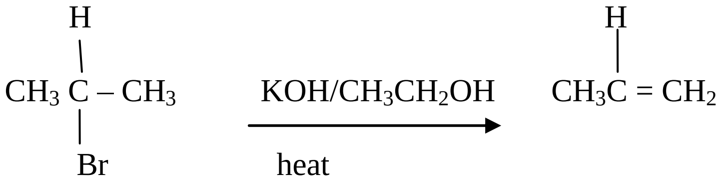
2). **Dehydrohalogenation of alkyl halides**

Alkenes are prepared from alkyl halides by heating the halide with a strong base (alcoholic potassium hydroxide). A molecule of hydrogen halide is eliminated.

Examples:

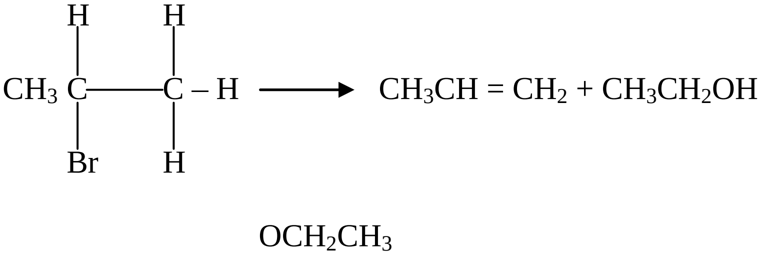
(i). $CH_3CH_2Cl \xrightarrow[\text{Heat.}]{KOH/\ CH_3CH_2OH} H_2C = CH_2 + HCl$

(ii).



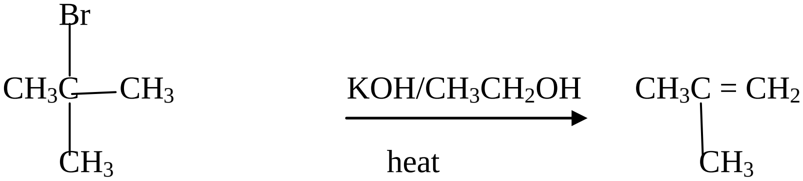
$$CH_3\overset{H}{\underset{Br}{C}} - CH_3 \xrightarrow[\text{heat}]{KOH/CH_3CH_2OH} CH_3\overset{H}{C} = CH_2$$

Mechanism for elimination bimolecular (E_2)



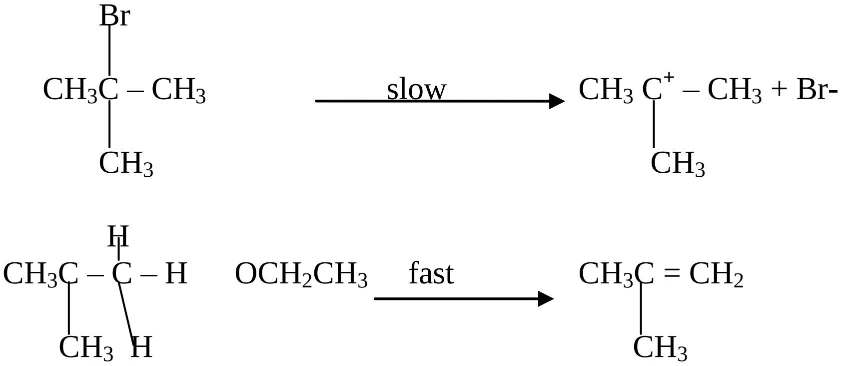
$$CH_3\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H \xrightarrow[OCH_2CH_3]{} CH_3CH=CH_2 + CH_3CH_2OH$$

(iii).



$$CH_3\underset{CH_3}{\overset{Br}{C}}-CH_3 \xrightarrow[\text{heat}]{KOH/CH_3CH_2OH} CH_3\underset{CH_3}{C}=CH_2$$

Mechanism for elimination unimolecular E1



$$CH_3\underset{CH_3}{\overset{Br}{C}}-CH_3 \xrightarrow{\text{slow}} CH_3\underset{CH_3}{C^+}-CH_3 + Br^-$$

$$CH_3\underset{CH_3}{C}-\underset{H}{\overset{H}{C}}-H \quad OCH_2CH_3 \xrightarrow{\text{fast}} CH_3\underset{CH_3}{C}=CH_2$$