First lecture

Organic chemistry

Organic chemistry is the scientific study of the structure, properties, composition, reactions, and synthesis of organic compounds that by definition contain carbon ,

It is a specific discipline within the subject of chemistry.

Organic compounds are molecules composed of carbon and hydrogen, and may contain any number of other elements.

Many organic compounds contain nitrogen, oxygen, halogens, and more rarely phosphorus or sulphur.

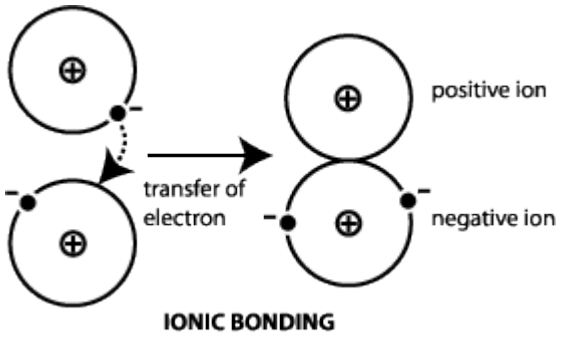
chemical bond

A chemical bond is a lasting attraction between atoms, ions or molecules that enables the formation of chemical compounds. The bond may result from the electrostatic force of attraction between oppositely charged ions as in ionic bonds or through the sharing of electrons as in covalent bonds. The strength of chemical bonds varies considerably; there are "strong bonds" or "primary bonds" such as covalent, ionic and metallic bonds, and "weak bonds" or "secondary bonds" such as dipole–dipole interactions, and hydrogen bonding.

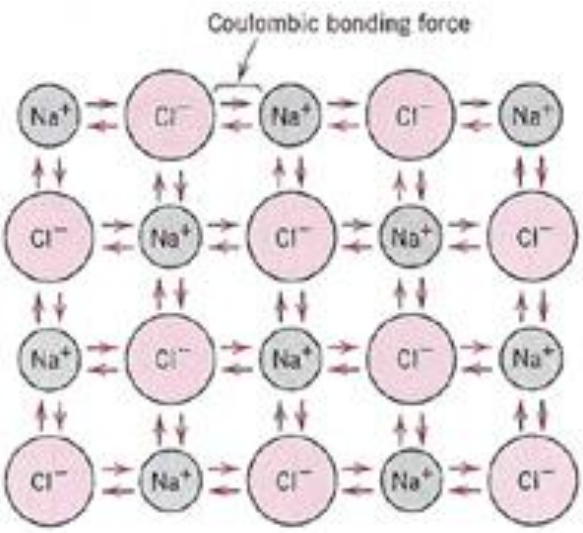
The main types of chemical bond

1- Ionic bonding

An ionic bond is formed when valence electrons are transferred from one atom to the other to complete the outer electron shell.

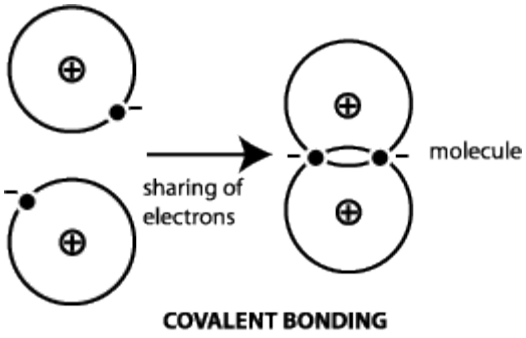


Example: A typical ironically bonded material is NaCl (Salt):

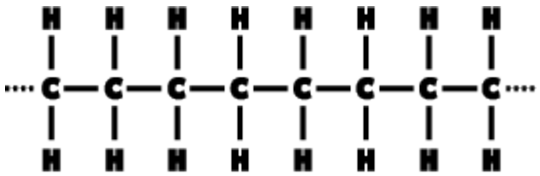


2 - Covalent bonding

A covalent bond is formed when the valence electrons from one atom are shared between two or more particular atoms.



Example: Many compounds have covalent bonding, such as polymers. Nylon rope is an example of a material that is made up of polymers. Polymer structures typically are long chains of covalently bonded carbon and hydrogen atoms in various arrangements.

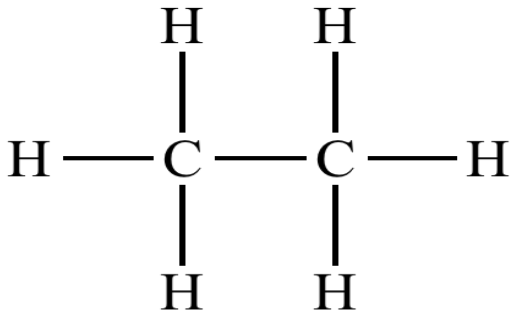


Number of covalent bond between carbon atoms

1- Single bond

Two atoms share one pair of electrons

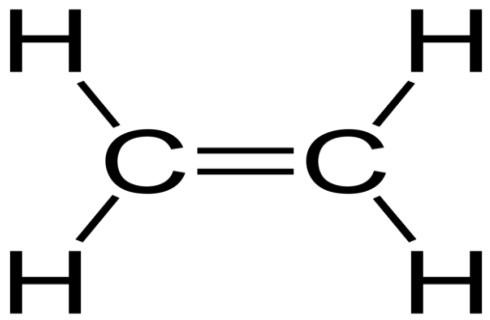
Example : ethane



2 – Double bond

Two atoms share two pair of electrons

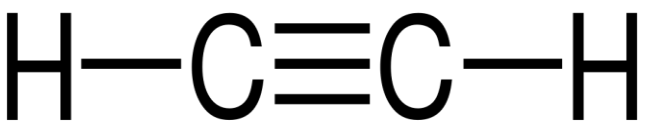
Example : ethene



3 – Triple bond

Two atoms share three pair of electrons

Example : acetylene



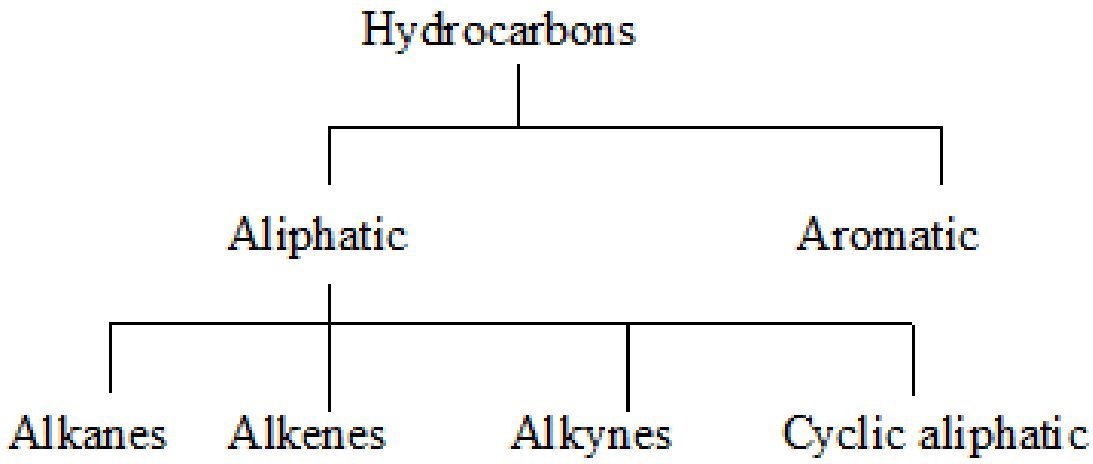
Hydrocarbons

Hydrocarbons are organic compounds contain only two elements, hydrogen and carbon, and hence are known as hydrocarbons. On the basis of structure, hydrocarbons

classification of hydrocarbons

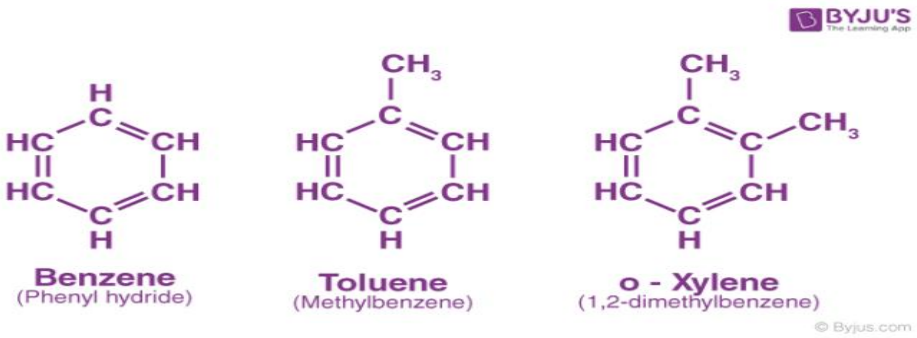
are divided into two main classes, aliphatic and aromatic. Aliphatic hydrocarbons are

further divided into families: alkanes, alkenes, alkynes, and their cyclic analogy (cycloalkanes, etc.).



Aromatic hydrocarbons: are aromatic organic compounds containing solely carbon and hydrogen atoms. The configuration of six carbon atoms in aromatic compounds is called a "benzene ring.

Example :



aliphatic hydrocarbon is an organic compound containing hydrogen and carbon atoms that are usually linked together in chains that divided in two types :

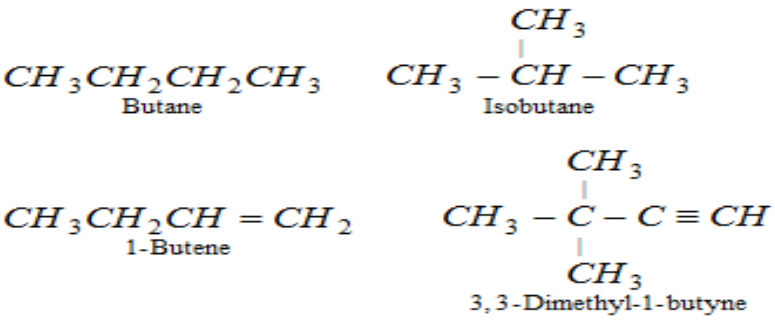
1- Open chain : it is a chain of aliphatic hydrocarbon which has linear formula of carbon atoms without closed bonds.

Open chain Aliphatic compounds may be saturated or unsaturated.

Saturated hydrocarbon contains mainly of alkanes which are open chain hydrocarbons containing carbon-carbon single bond.

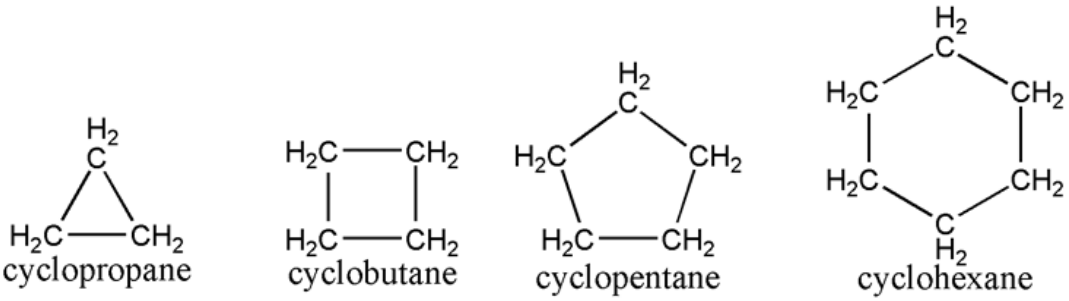
Hydrocarbon molecules with at least one double bond are called unsaturated meaning that more hydrogen atoms cane be added to these molecules.

Example



2- Cyclic : it is a type of aliphatic hydrocarbon which has cyclic bond in its formula.

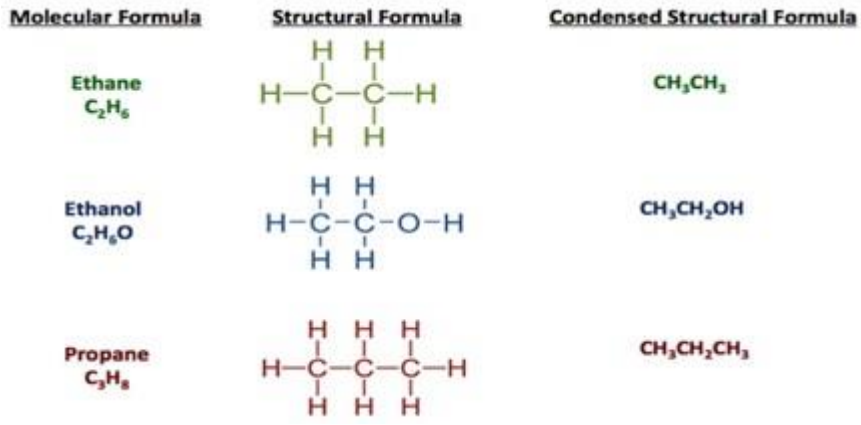
Example



molecular formula and structural formula

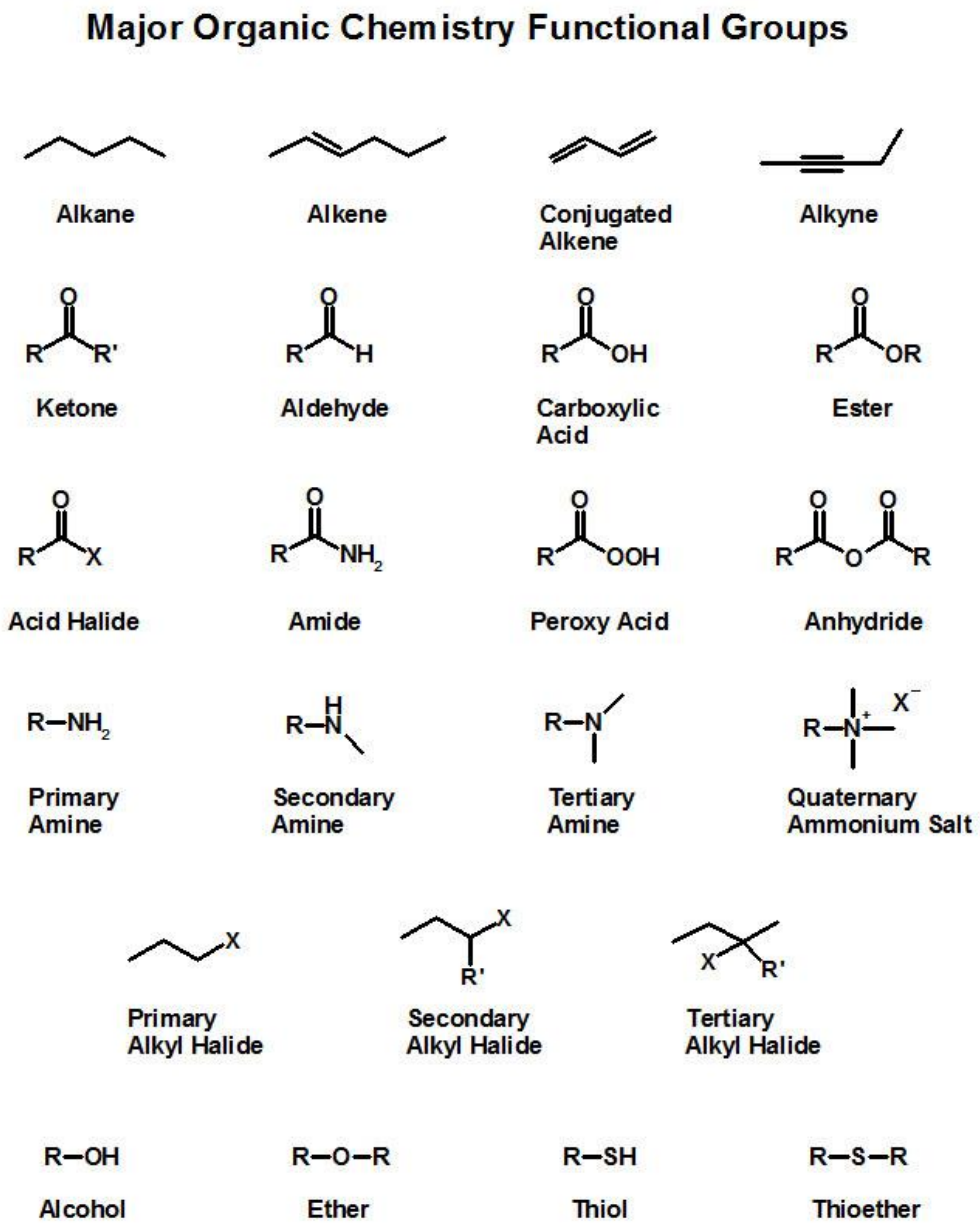
Molecular formula definition is - a chemical formula that gives the total number of atoms of each element in each molecule of a substance.

Structural formulas identify the location of chemical bonds between the atoms of a molecule. A structural formula consists of symbols for the atoms connected by short lines that represent chemical bonds—one, two, or three lines standing for single, double, or triple bonds, respectively.



Functional group

Functional group: A group of atoms whose bonding is the same from molecule to molecule. A functional group has similar behavior regardless of the molecule that contains it, so molecules with identical functional groups tend to have similar chemical and physical properties. In addition, functional groups with similar structures tend to impart similar chemical and physical properties to the molecules which contain them.



Physical Properties of Alkanes

1- Alkanes molecules are nonpolar or very weak polar .

2- Stronger intermolecular forces are there

3- Except the very small alkanes , the boiling point rises to 20 to 30 degrees for each carbon that is added to the chain .

4- The first four alkanes are gases the next 13 alkanes (C5-C18) are liquids , and those contining 18 or more carbon atoms are solids .

5- A branched chain isomer has a lower boiling point than a stright chain isomes and the more numerous the branches ,the lower boiling point .

6- The alkanes are soluble in nonpolar solevents such as benzene , ether , chloroform and are insoluble in water and other highly polar solvents .

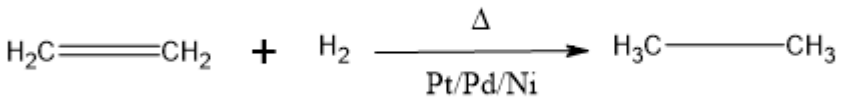
7- All alkanes are less dense from water.

Preparation of Alkanes

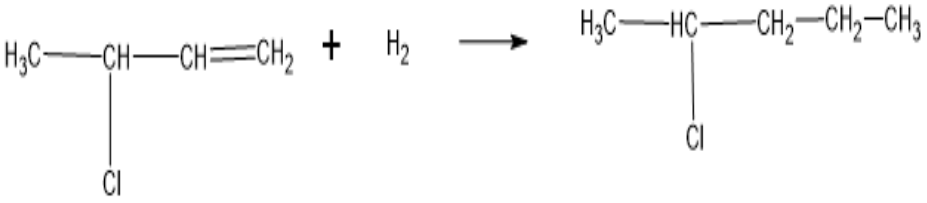
1- Hydrogenation of alkenes

Hydrogenation is the most useful method for preparing alkanes. It is the addition of H2 to a multiple bond.

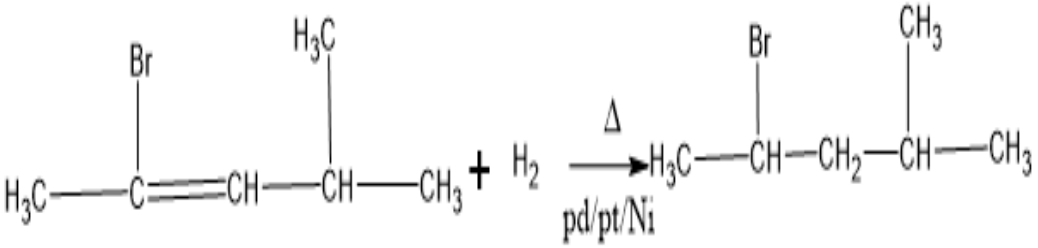
With catalysts Pt , Ni , Pd and heat



Ethane **ethane**

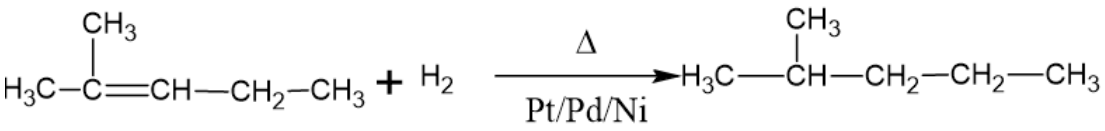


2-chloro-butene **2-chloro-butane**



2-bromo-4-methyl-2-penten **2-bromo-2-4methyl-pentane**

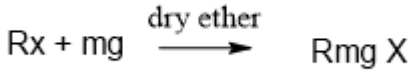
Example : prepare 2-methyl pentane from elkene ?



2- Reduction of alkyl halides

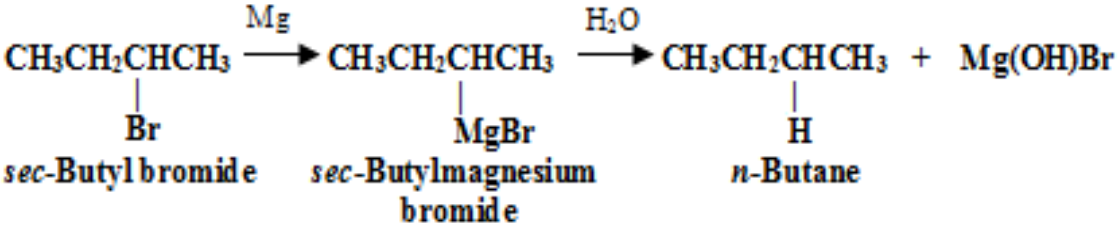
(a) Hydrolysis of Grignard reagent

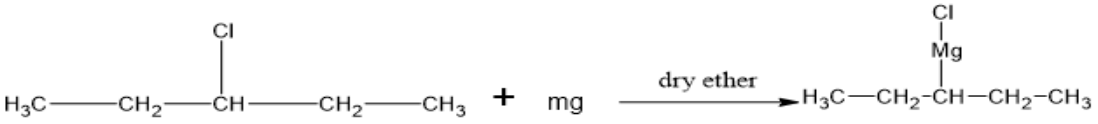
When a solution of an alkyl halide in dry ethyl ether, is allowed to stand over turnings of metallic magnesium, the resulting solution is known as a Grignard reagent. The reaction with water gives an alkane.



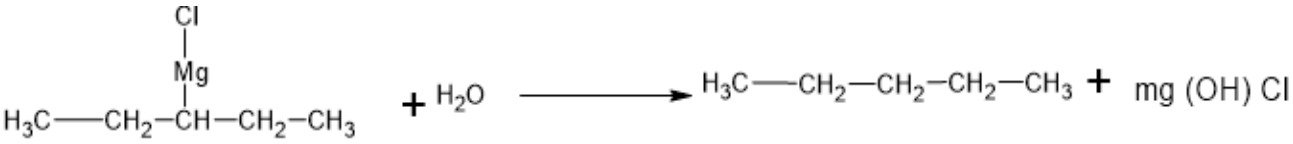
Where RH :Alkane , RmgX :Grignard Reagent

Examples :





3-chloro-pentane Grignard Reagent



Pentane

(b) Reduction by metal and acid

R—X + metal/acid → RH

active metals = Sn, Zn, Fe, etc.

acid = HCl, etc. (H^+)

$CH_3CH_2\underset{Cl}{C}HCH_3 + Sn/HCl \rightarrow CH_3CH_2CH_2CH_3 + SnCl_2$

2-chloro-butane — *n*-butane

$CH_3CH_2\overset{Br}{\underset{CH_3}{C}}CH_3 + Zn/H^+ \rightarrow CH_3CH\overset{CH_3}{}CH_3 + ZnBr_2$

2-bromo -2methyl -propane — 2-methyl propane

(c) Using $LiAlH_4$ as a reducing

$4RX + LiAlH_4 \longrightarrow 4RH + LiX + AlX_3$

Example

$4\ CH_3\ CH_3CH_2Cl + LiAlH4 \longrightarrow CH_3CH_2CH_3 + LiCl + AlCl_3$

Reactions of Alkanes

Alkanes are generally not considered to be very reactive substance. However, under suitable conditions they are do react.

1- **Halogenation**

halogenation is a chemical reaction that involves the addition of one or more halogens (Cl,Br,I,F) to a compound or material. The pathway and stoichiometry of halogenation depends on the structural features and functional groups of the organic substrate, as well as on the specific halogen.

$$CH_4 + Br_2 \xrightarrow{Heat\ /\ light} CH_3Br + HBr$$

$$CH_3CH_3 + Cl_2 \xrightarrow{Heat\ /\ light} CH_3CH_2Cl + HCl$$

2- Oxidation (Combustion)

Combustion is the complete oxidation of organic compound into carbon dioxide and water molecules in presence of oxygen gas whereas oxidation is the addition of oxygen in a compound or addition with an element.

Although alkanes are resistant to attack by oxidizing agents generally, they all undergo combustion in air or oxygen, the products of complete oxidation being carbon dioxide and water.

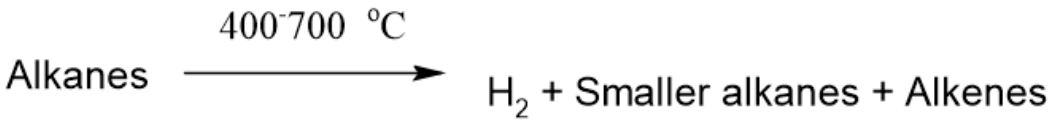
$$C_nH_{2n+2} + \text{excess } O_2 \xrightarrow{\text{flame}} nCO_2 + (n+1)\,H_2O$$

$$CH_4 + 2O_2 \xrightarrow{\text{flame}} CO_2 + 2H_2O$$

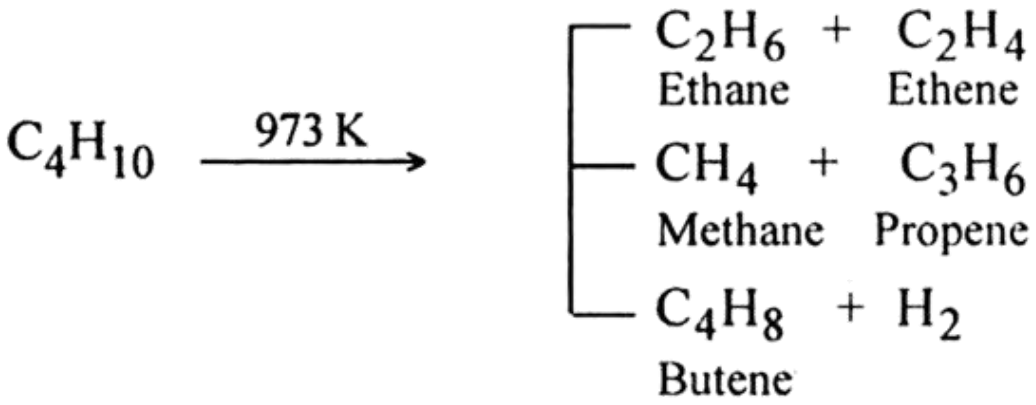
$$C_5H_{12} + 8O_2 \xrightarrow{\text{flame}} 5CO_2 + 6H_2O$$

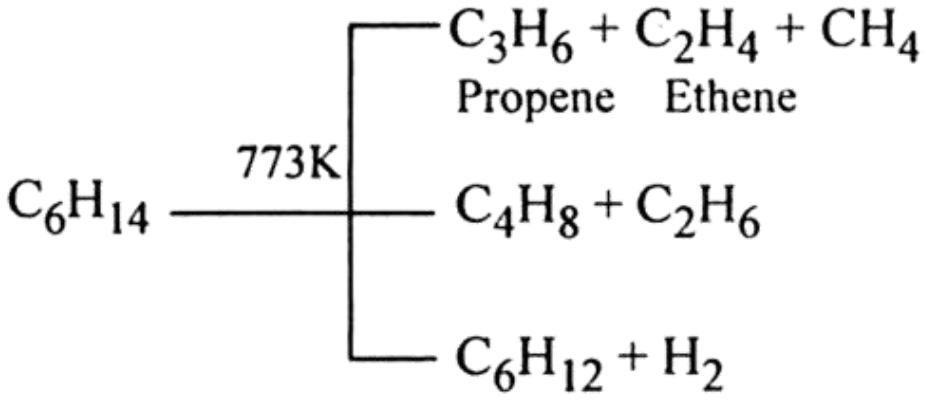
Cracking (pyrolysis)

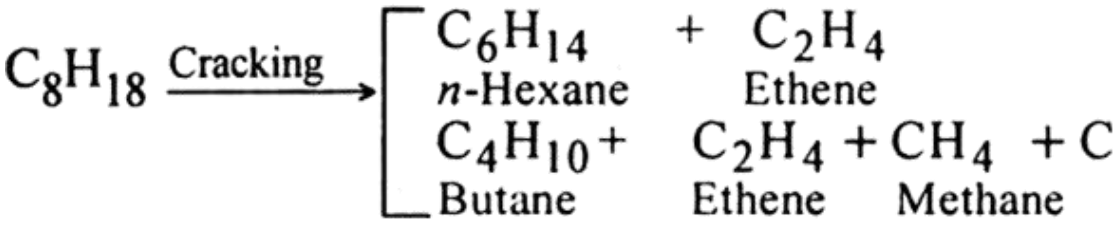
the process by which heavy hydrocarbon molecules are broken up into lighter molecules by means of heat.



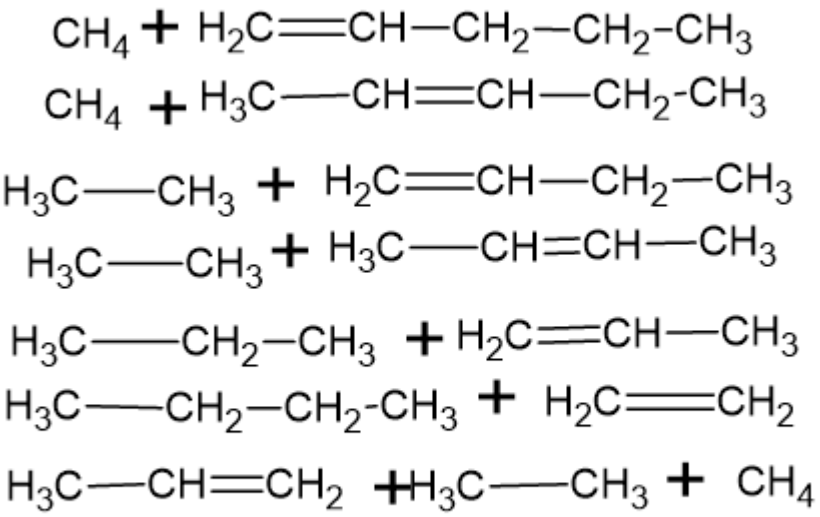
Examples



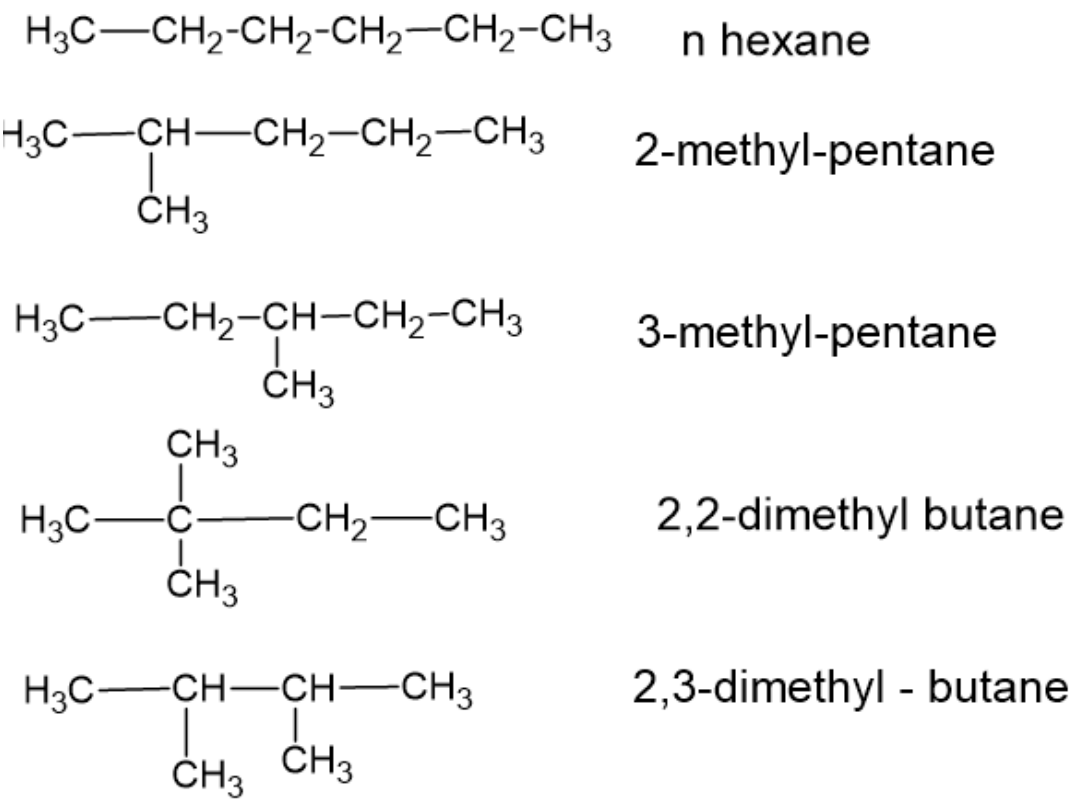




Q/ Give a productions of Hexane cracking (straight only) ?



Q/ Give the possible structures for this formula C_6H_{14} and name it?



Alkenes

Alkenes are a homologous series of hydrocarbons that contain a carbon-carbon double bond. The number of hydrogen atoms in an alkene is double the number of carbon atoms, so they have the general formula C_nH_{2n} .

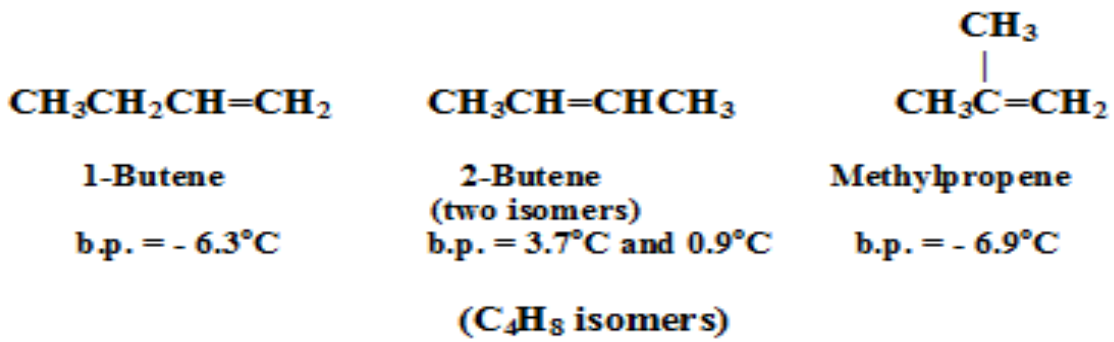
The carbon-carbon double bond is unsaturated and hence highly reactive toward a wide variety of reagents.

The first nine member of the alkenes:

General formula	Structure	Name
C_2H_4	$CH_2 = CH_2$	Ethene
C_3H_6	$CH_2 = CHCH_3$	Propene
C_4H_8	$CH_2 = CHCH_2CH_3$	1-Butene
C_5H_{10}	$CH_2 = CH(CH_2)_2CH_3$	1-Pentene
C_6H_{12}	$CH_2 = CH(CH_2)_3CH_3$	1-Hexene
C_7H_{14}	$CH_2 = CH(CH_2)_4CH_3$	1-Heptene
C_8H_{16}	$CH_2 = CH(CH_2)_5CH_3$	1-Octene
C_9H_{18}	$CH_2 = CH(CH_2)_6CH_3$	1-Nonene
$C_{10}H_{20}$	$CH_2 = CH(CH_2)_7CH_3$	1-Decene

Isomerism in Alkenes

Isomeric compounds are also possible in the alkenes. For the molecular formula C4H8, there are three different ways of organizing the four carbon atoms and the double bond :



Naming of alkenes

Common names are seldom used except for three simple alkene; ethylene,

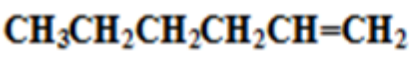
propylene, and isobutylene. Most alkene are named by IUPAC system.

1- The longest continuous chain of carbon atoms containing the double bond serves as the parent compound.

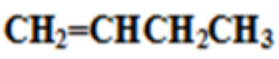
2- The ending –ane of the corresponding alkane hydrocarbon name is replaced by the ending –ene.

3- The position of the double bond is indicated by the lower number of the numbers of the carbon atoms to which it is attached. The number that represents this position is placed before the parent compound name. Alkyl groups attached to the parent compound are designated as is done for the alkane.

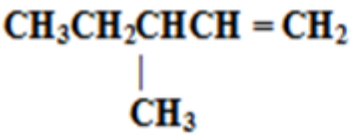
4- If a geometric isomer is designated, the name begins with cis- or trans-.



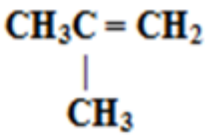
1- Hexene



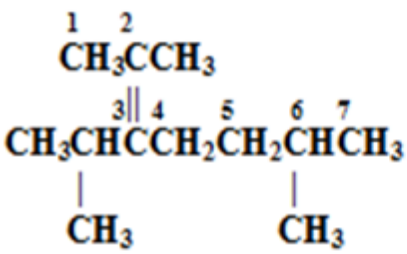
1-Butene



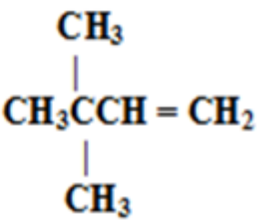
3-Methyl-1-pentene



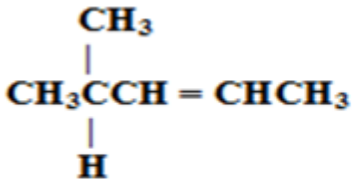
2-Methylpropene



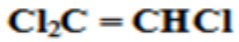
3-Isopropyl-2,6-dimethyl-2-heptene



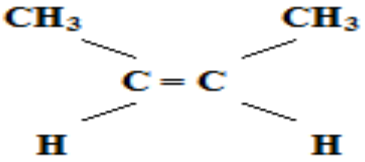
3,3-Dimethyl-1-butene



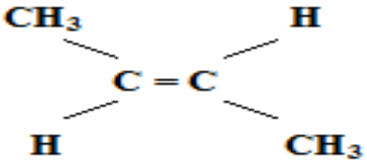
4-Methyl-2-pentene



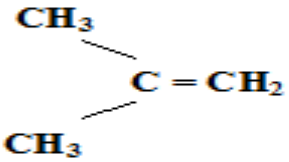
Trichloroethene



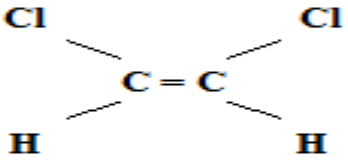
cis-2-Butene



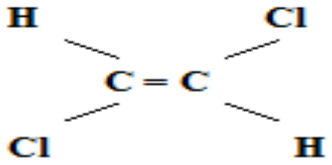
trans-2-Butene



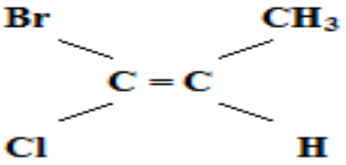
2-Methylpropene



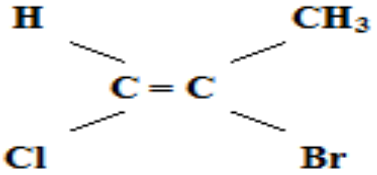
cis-1,2-Dichloroethene



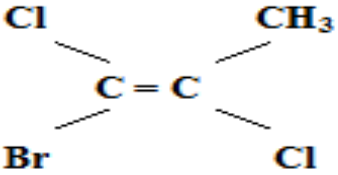
trans-1,2-Dichloroethene



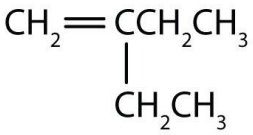
1-Bromo-1-chloropropene



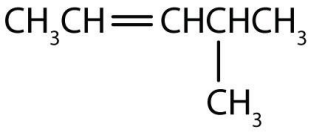
2-Bromo-1-chloropropene



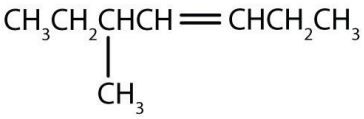
1-Bromo-1,2-dichloropropene



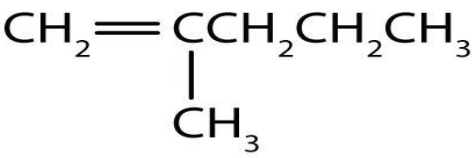
2-ethyl-1-butene



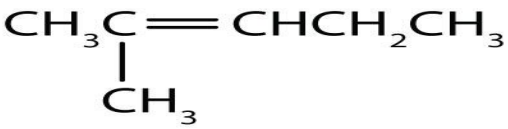
4-methyl-2-pentene



5-methyl-3-heptene

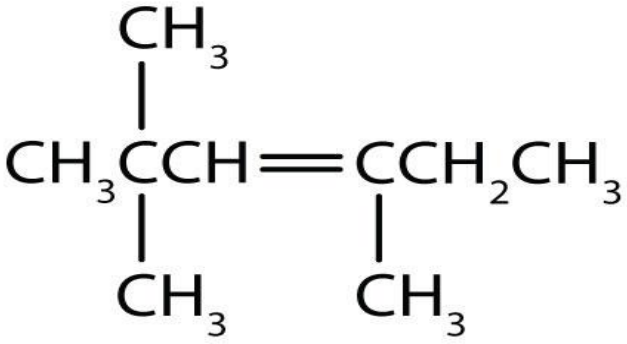


2-methyl-1-pentene

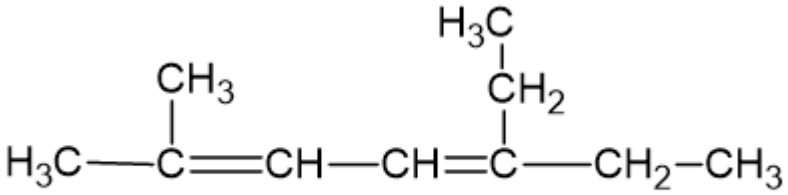


2-methyl-2-pentene

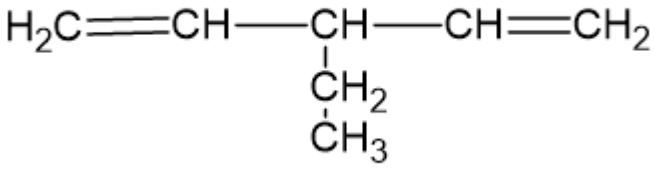
2,5 di methyl hexene



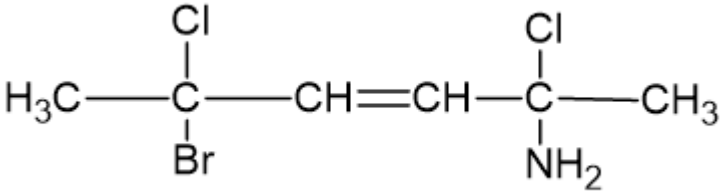
2,2,4 tri methyl – 3- hexene



5-ethyl-2-methyl-2,4-heptadiene



2-chloro-3-ethyl-1,4-pentadiene

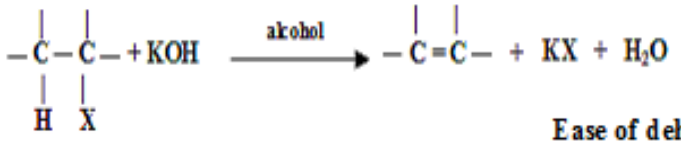


2-amino-5-bromo-2,5-dichloro – 3- hexene

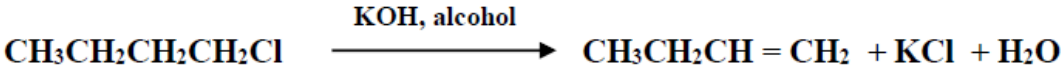
Preparation of Alkenes

1- Dehydrohalogenation of alkyl halides

Dehydrohalogenation involves loss of the halogen atom and of hydrogen atom from a carbon adjacent to the one losing the halogen (1,2-elimination).



Ease of dehydrohalogenation of alkyl halides $3^\circ > 2^\circ > 1^\circ$

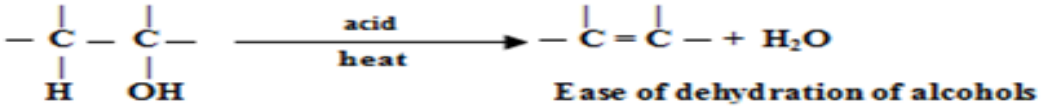


***n*-Butyl chloride** **1-Butene**

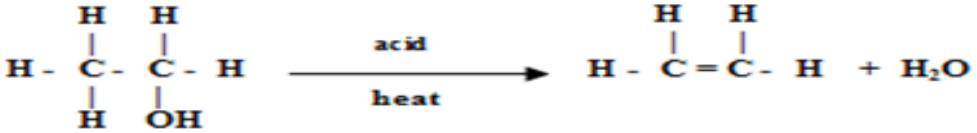
Example : prepare 2-hexene by using KOH ?

2- Dehydration of alcohols

In the dehydration of alcohols, the H and OH are lost from adjacent carbons (1,2- elimination). An acid catalyst is necessary and application of heat.

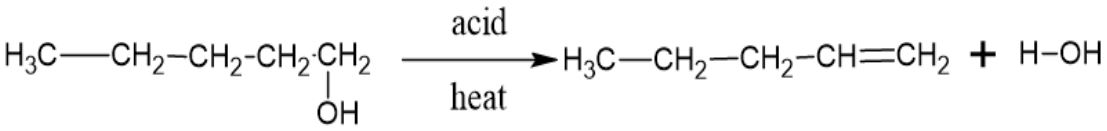


Ease of dehydration of alcohols
$3^\circ > 2^\circ > 1^\circ$



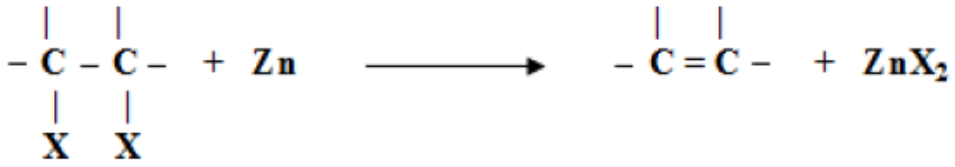
Ethyl alcohol **Ethylene**

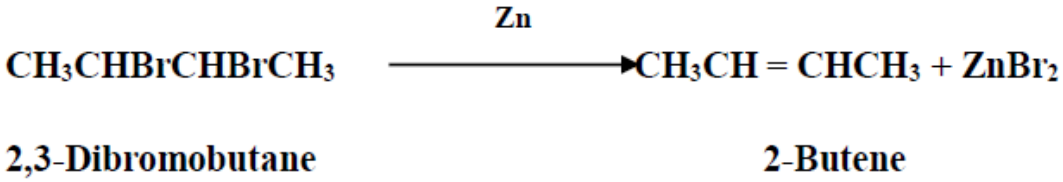
Example : prepare 1- pentene from alcohol ?



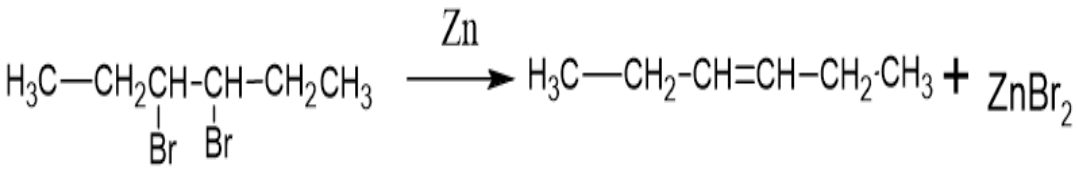
3- Dehalogenation of vicinal dihalides

Alkenes can be prepared by elimination of two halide atoms from a vicinal (neighbouring) dihalides.



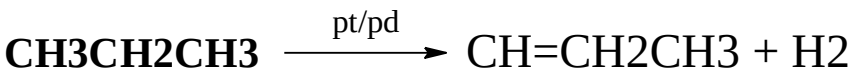


Example : prepare 3-hexene by 3- Dehalogenation of vicinal dihalides?



4- Cracking of petroleum hydrocarbons .

This method usually for commercial alkenes with pd,pt as a catalyst



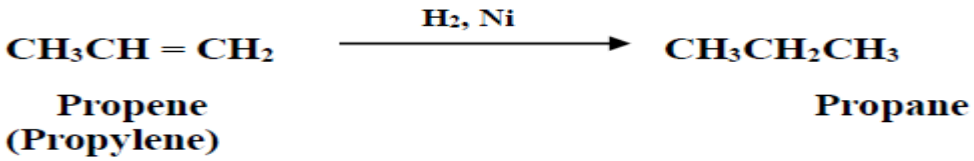
Reactions of alkenes

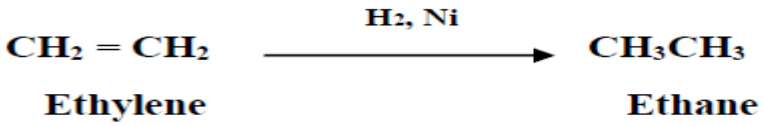
The presence of the carbon-carbon double bond confers very considerable

chemical activity on the alkenes and consequently they react with a much wider variety of reagents than do the alkanes. The π-bond component of the double bond is weaker than the σ-bond component and the π-electrons are more easily accessible to attacking reagents.

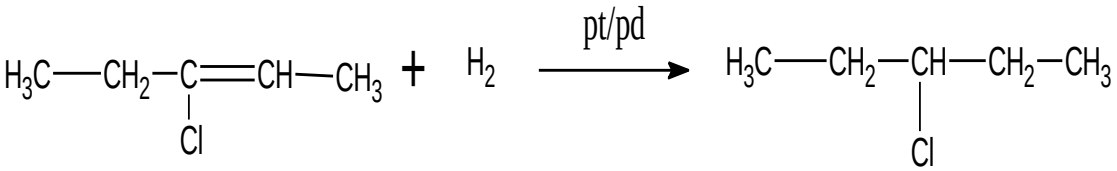
1- Addition of hydrogen

When an alkene is mixed with hydrogen, there is no appreciable reaction, but in the presence of certain metal catalysts such as nickel, platinum or palladium, a fairly rapid reaction occurs leading to the uptake of hydrogen.



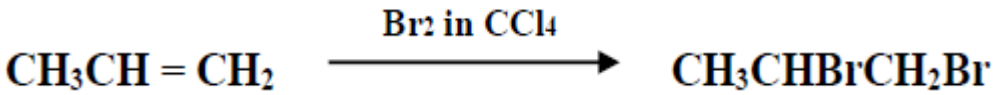


Example : give a productions of 3-chloro-2-pentene hydrogenation ?

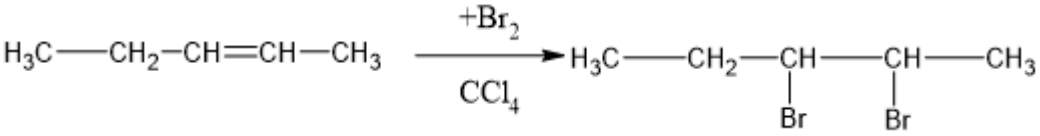


2- Addition of halogen

Chlorine and bromine react readily with alkenes, in the liquid or vapour states, to form dihalogeno addition products, the two halogen atoms are attached to adjacent carbons. Iodine generally fails to react.



Example : complete this reaction :



3- Addition of hydrogen halides

The reaction of alkyl halide with alkenes is subjected to Markovnikov's rule

Markovnikov's rule

The rule states that with the addition of HX other polar reagent to an unsymmetrical alkene, the acid hydrogen (H) or electropositive part gets attached to the carbon with more hydrogen substituents, and the halide (X) group gets attached to the carbon with more alkyl substituents. in which the rule is stated that the X component is added to the carbon with the fewest hydrogen atoms while the hydrogen atom is added to the carbon with the greatest number of hydrogen atoms.

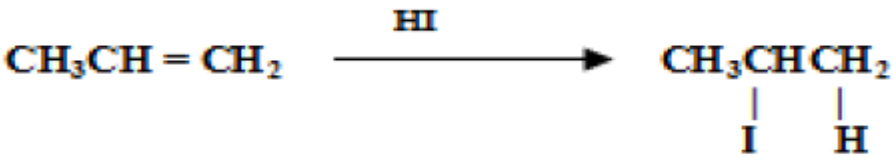
Symmetrical alkenes have the same number of hydrogen atoms on both sides of the double bond...

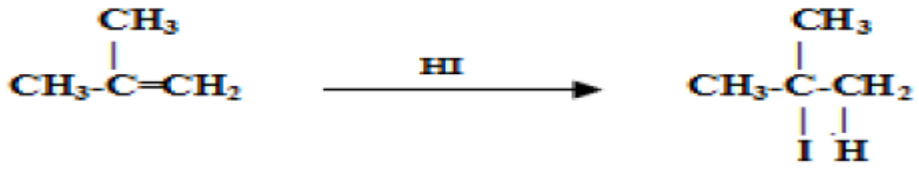
ethene... CH2=CH2

Unsymmetrical alkenes have different number of hydrogen atoms on each side of double bond .

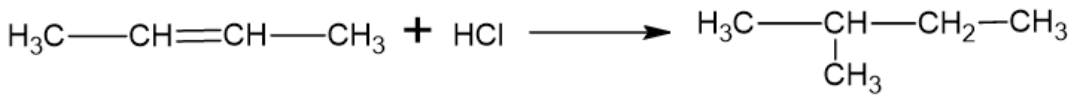
but-1-ene.... CH3 =CH-CH2-CH3

Examples of Unsymmetrical alkenes reaction with HX





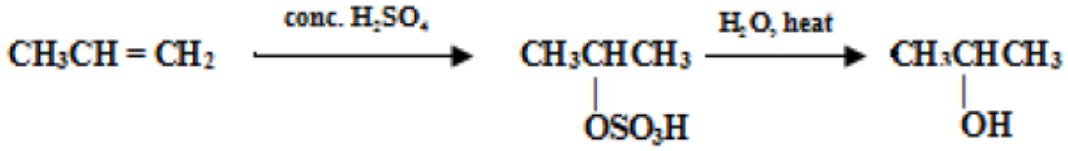
Examples of symmetrical alkene reaction with HX

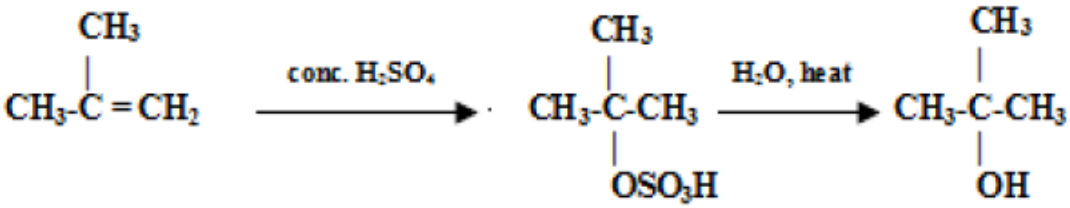


4- Addition of sulphuric acid

Alkenes are slowly absorbed when they are bubbled through, or shaken with, cold concentrated sulphuric acid. The reaction involves the addition of H and HSO4 groups across the double bond, to form alkyl hydrogen sulphates, which is on dilution with water and heating yield alcohol.

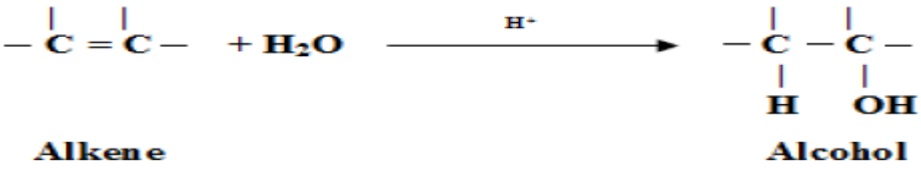
Examples



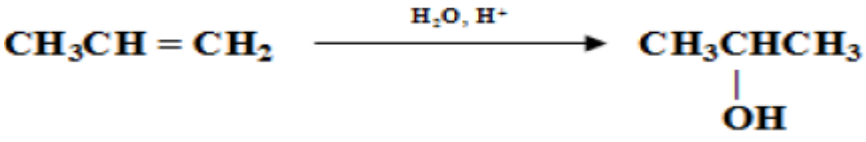


5- Addition of water. Hydration

Alkenes are also reacting with water, and this reaction is carried out in a dilute acid medium. The reaction follows Markovnikov's rule.

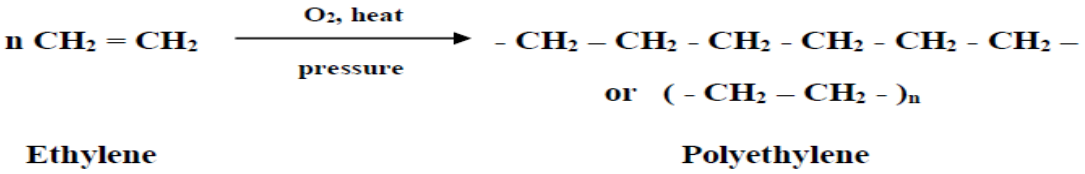


Example



6- Polymerization

In the presence of a certain catalyst, alkene molecule can add on to each other in a head-to-tail fashion to form long-chain molecules of a very high relative molecular mass.



Physical properties of alkenes

1-Physical state

Ethene, Propene, and Butene exists as colorless gases. Members of the 5 or more carbons such as Pentene, Hexene, and Heptene are liquid, and members of the 15 carbons or more are solids.

2-Density

Alkenes are lighter than water and are insoluble in water due to their non-polar characteristics. Alkenes are only soluble in nonpolar solvents.

3-Solubility

Alkenes are virtually insoluble in water, but dissolve in organic solvents. The reasons for this are exactly the same as for the alkanes.

4-Boiling Points

The boiling point of each alkene is very similar to that of the alkane with the same number of carbon atoms. Ethene, propene and the various butenes are gases at room temperature. All the rest that you are likely to come across are liquids. Boiling points of alkenes depends on more molecular mass (chain length). The more intermolecular mass is added, the higher the boiling point. Intermolecular forces of alkenes gets stronger with increase in the size of the molecules.

5- Alkenes are non-polar, and they are both immiscible in water and less dense than water. In addition, they do not conduct electricity.

Fifth lecture

Alkynes

Molecules of alkyne series of hydrocarbon are characterized by having two adjacent carbon atoms joined to one another by a triple bond. The carbon-carbon triple bond is unsaturated and highly reactive toward the reagents that double bonds react with.

The general formula is CnH2n-2.

$HC \equiv CH$	Ethyne (acetylene)
$HC \equiv CCH_3$	Propyne
$HC \equiv CCH_2CH_3$	1-Butyne
$HC \equiv C(CH_2)_2CH_3$	1-Pentyne
$HC \equiv C(CH_2)_3CH_3$	1-Hexyne
$HC \equiv C(CH_2)_4CH_3$	1-Heptyne
$HC \equiv C(CH_2)_5CH_3$	1-Octyne
$HC \equiv C(CH_2)_6CH_3$	1-Nonyne
$HC \equiv C(CH_2)_7CH_3$	1-Decyne

Physical Properties of Alkynes

Being compounds of low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ether, benzene, and carbon tetrachloride. They are less dense than water. Their boiling points show the usual increase with increasing

carbon number, and the usual effects of chain branching; they are very nearly the same as the boiling points of alkanes and alkenes with the same carbon skeletons .

Naming of alkynes

1- Find the longest carbon chain that includes both carbons of the triple bond.

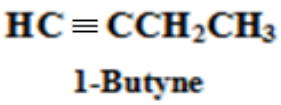
2- Number the longest chain starting at the end closest to the triple bond.

3- After numbering the longest chain with the lowest number assigned to the alkyne, label each of the substituents at its corresponding carbon. While writing out the name of the molecule, arrange the substituents in alphabetical order. If there are more than one of the same substituent use the prefixes di, tri, and tetra for two, three, and four substituents respectively. These prefixes are not taken into account in the alphabetical order.

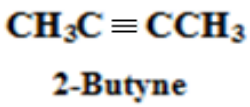
4- When there are two triple bonds in the molecule, find the longest carbon chain including both the triple bonds. Number the longest chain starting at the end closest to the triple bond that appears first.

The suffix that would be used to name this molecule would be –diyne.

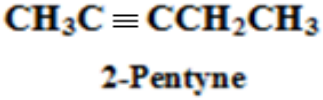
5- A molecule that contains both double and triple bonds is called an alkenyne. The chain can be numbered starting with the end closest to the functional group that appears first.



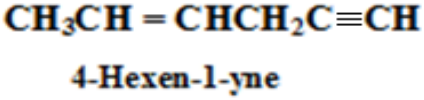
1-Butyne



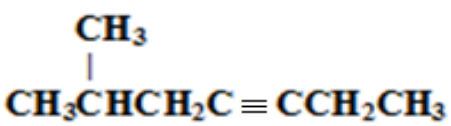
2-Butyne



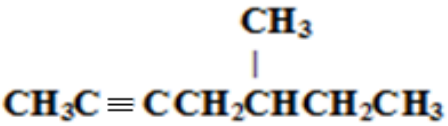
2-Pentyne



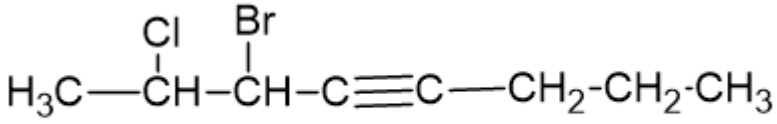
4-Hexen-1-yne



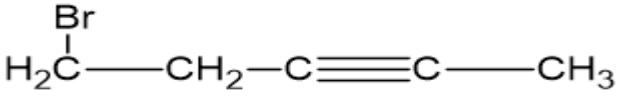
6-Methyl-3-heptyne



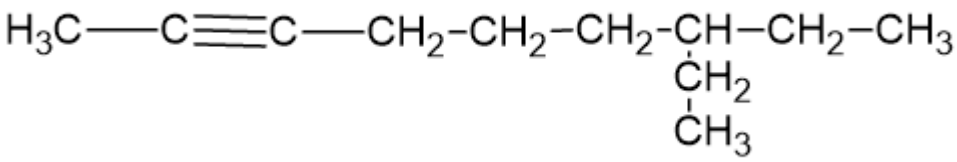
5-Methyl-2-heptyne



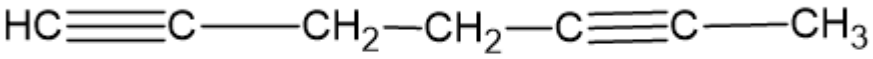
3-bromo-2-chloro-4-octyne



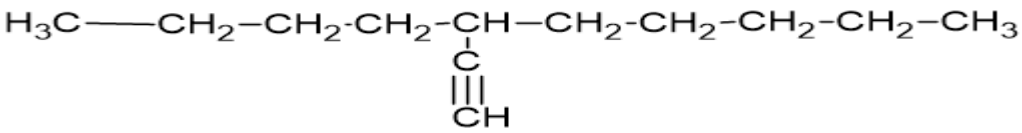
5-bromo-2-pentyne



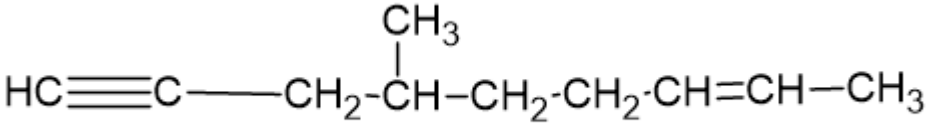
6-ethyl-2-nonyne



1,5-hepta di yne



3-butyl-1-octyne



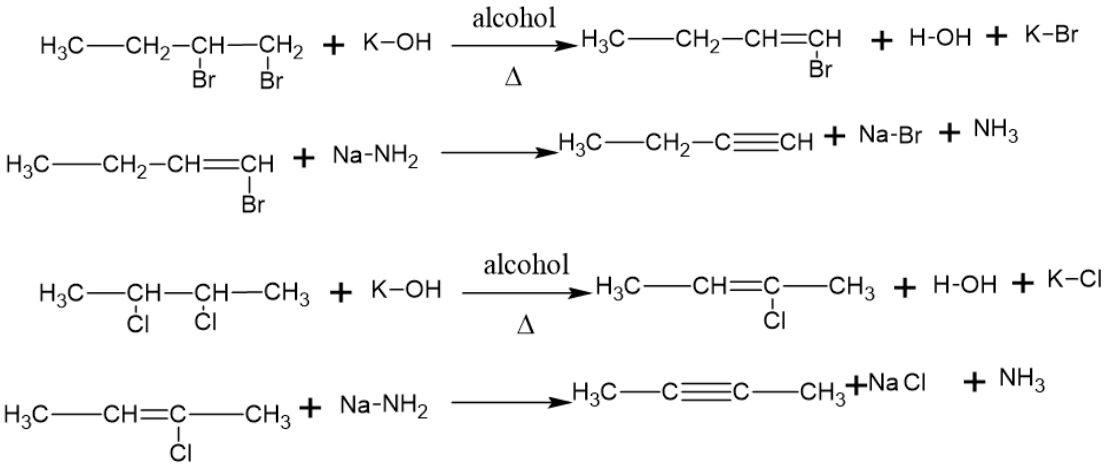
4-methyl-7-nonen-1-yne

Preparation of Alkynes

1- De hydrogenation of vicinal di halides

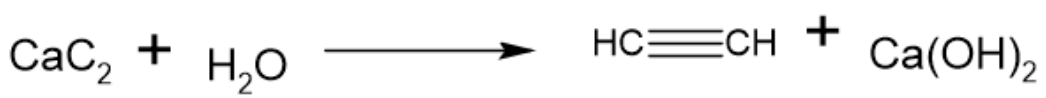
vicinal di halides : compounds that have halogens on adjacent carbons, are prepared by the reaction between a halogen and an alkene.

Examples



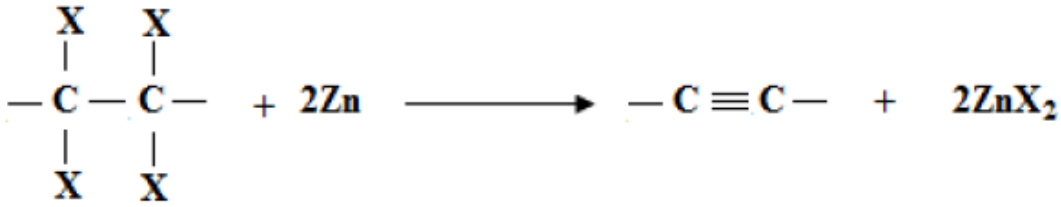
2- Reduction of calcium carbid with H_2O

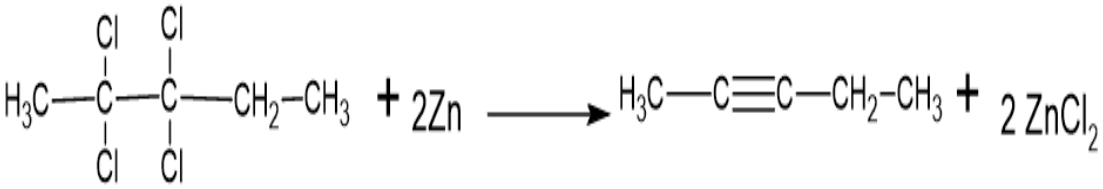
This method is only used for acetylene preparation

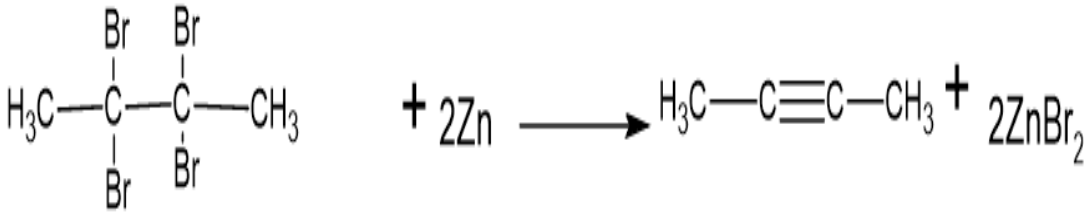


3- De halogenation of tetra halides

Alkynes can be prepared by de halogenation of tetra halides.



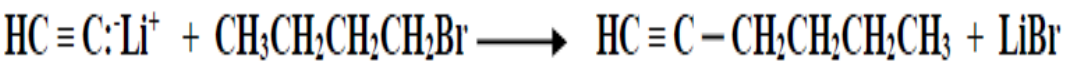


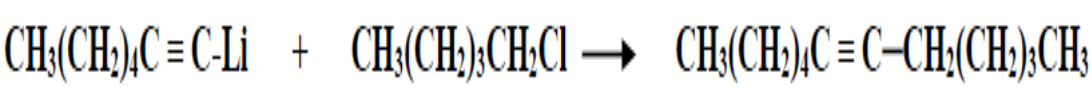


4- Reaction of metal acetylides with alkyl halides

Lithium or sodium acetylides can react with primary alkyl halides. The alkyl group becomes attached to the triply bonded carbon, and a new, larger alkyne has been generated.

Examples





Reactions of alkynes

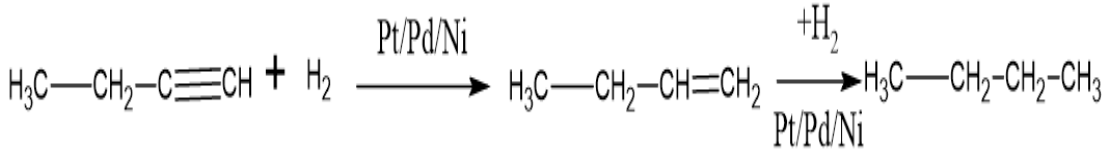
The carbon-carbon triple bond –C≡C– consists of one σ-bond , so it is not

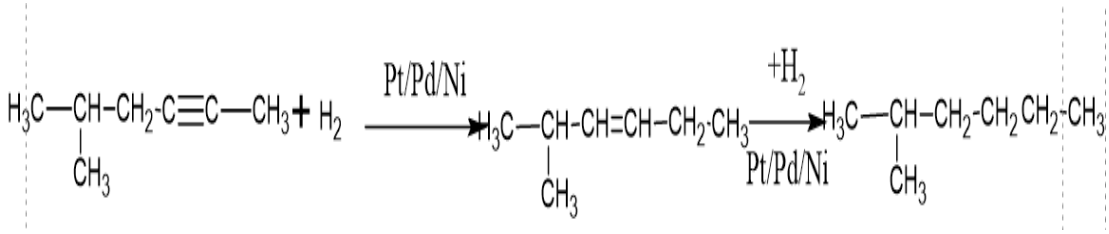
surprising that addition reactions are a characteristic feature of this functional group.

Despite its high formal unsaturation, the triple bond dose not usually

react so vigorously as a carbon-carbon double bond, as in alkenes, and it is therefore sometimes possible to stop the addition reaction after the uptake of 1 mol of reactant, rather than 2 mol which would be possible in principle.

1- Addition of hydrogen





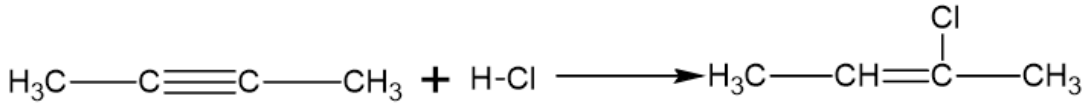
2- Addition halogen acid

The addition according to markonikov rule such as alkenes about symmetrical and un symmetrical alkynes .

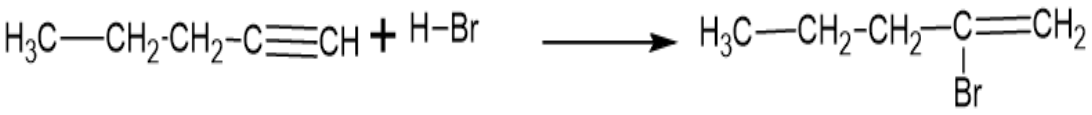
Symmetrical alkynes have the same number of hydrogen atoms on both sides of the triple bond...

Unsymmetrical alkynes have different number of hydrogen atoms on each side of triple bond .

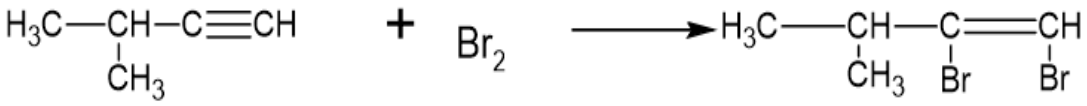
Example of addition to Symmetrical alkynes

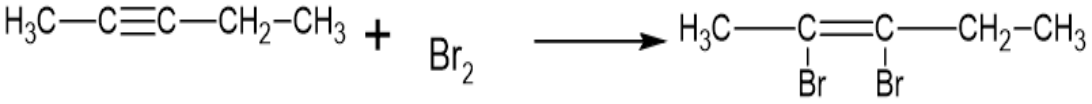


Example of addition to un Symmetrical alkynes

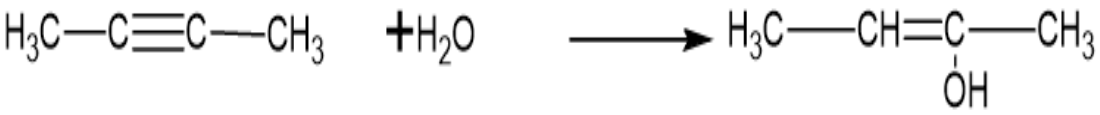


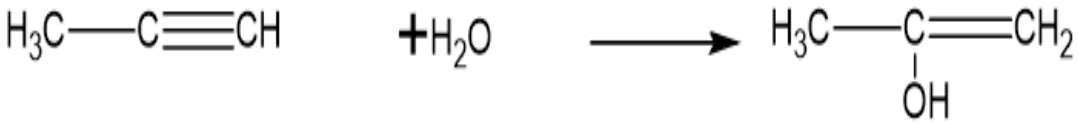
3- Addition of halogens





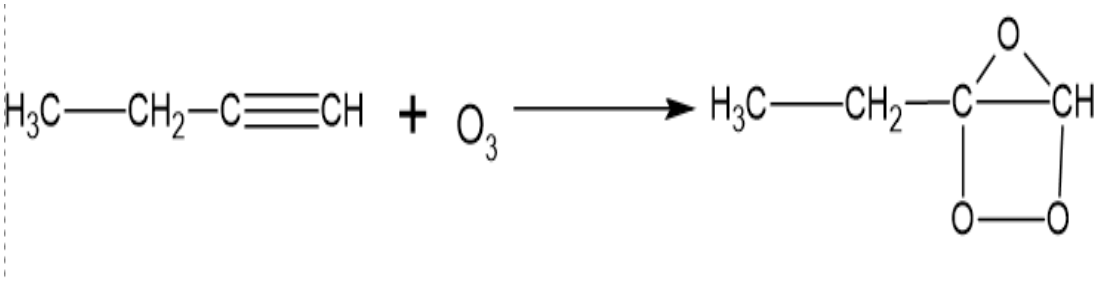
4-Hydration





5- Ozonolysis

Is an organic reaction where the unsaturated bonds of alkenes, alkynes, compounds are cleaved with ozone.

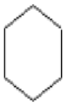


Cycloalkanes

the cycloalkanes are the monocyclic saturated hydrocarbons. In other words, a cycloalkane consists only of hydrogen and carbon atoms arranged in a structure containing a single ring (possibly with side chains), and all of the carbon-carbon bonds are single. Cycloalkanes are named analogously to their normal alkane counterparts of the same carbon count: cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc.

one ring have the chemical formula CnH2n.

The cycloalkanes without side chains are classified as small (cyclopropane and cyclobutane), common (cyclopentane, cyclohexane, and cycloheptane), medium (cyclooctane through cyclotridecane), and large (all the rest)

Cycloalkane	Molecular Formula	Basic Structure
Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	
Cycloheptane	C_7H_{14}	
Cyclooctane	C_8H_{16}	
Cyclononane	C_9H_{18}	
Cyclodecane	$C_{10}H_{20}$	

Naming of cycloalkanes

1-Determine the cycloalkane to use as the parent chain. The parent chain is the one with the highest number of carbon atoms. If there are two cycloalkanes, use the cycloalkane with the higher number of carbons as the parent chain.

2-If there is an alkyl straight chain that has a greater number of carbons than the cycloalkane, then the alkyl chain must be used as the primary parent chain. Cycloalkane acting as a substituent to an alkyl chain has an ending "-yl" and, therefore, must be named as a cycloalkyl.

3-Determine any functional groups or other alkyl groups.

4-Number the carbons of the cycloalkane so that the carbons with functional groups or alkyl groups have the lowest possible number. A carbon with multiple substituents should have a lower number than a carbon with only one substituent or functional group. One way to make sure that the lowest number possible is assigned is to number the carbons so that when the numbers corresponding to the substituents are added, their sum is the lowest possible.

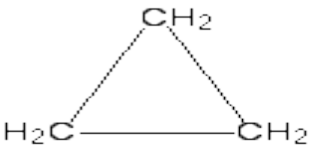
5-When naming the cycloalkane, the substituents and functional groups must be placed in alphabetical order.

6- Indicate the carbon number with the functional group with the highest priority according to alphabetical order. A dash"-" must be placed between the numbers and the name of the substituent. After the carbon number and the dash, the name of the substituent can follow. When there is only one substituent on the parent chain, indicating the number of the carbon atoms with the substituent is not necessary

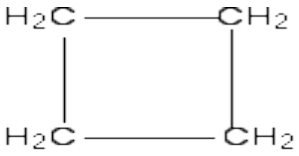
7-If there is more than one of the same functional group on one carbon, write the number of the carbon two, three, or four times, depending on how many of the same functional group is present on that carbon. The numbers must be separated by commas, and the name of the functional group that follows must be separated by a dash. When there are two of the same functional group, the name must have the prefix "di". When there are three of the same functional group, the name must have the

prefix "tri". When there are four of the same functional group, the name must have the prefix "tetra". However, these prefixes cannot be used when determining the alphabetical priorities.

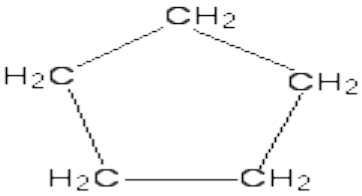
8-After all the functional groups and substituents have been mentioned with their corresponding numbers, the name of the cycloalkane can follow.



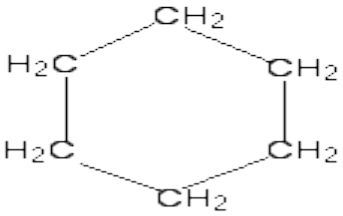
cydopropane



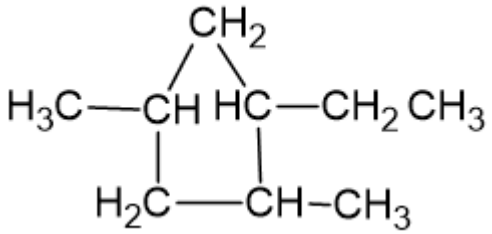
cydobutane



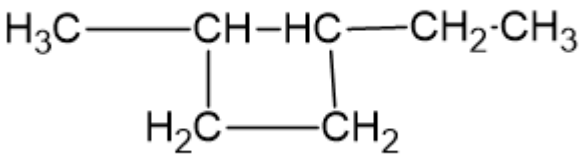
cydopentane



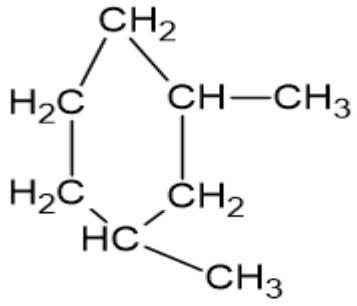
cydohexane



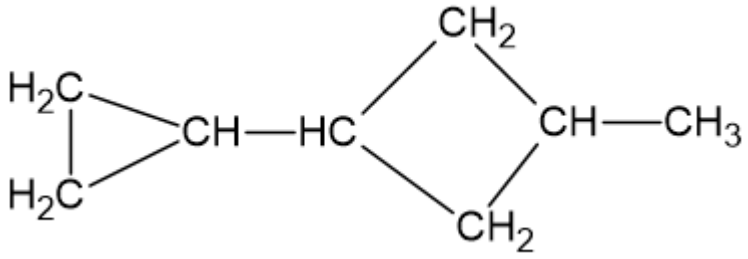
1-ethyl-2,4-dimethyl-cyclopentane



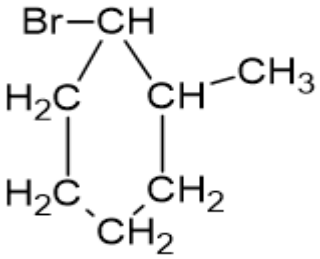
1-ethyl-2-methyl-cyclobutane



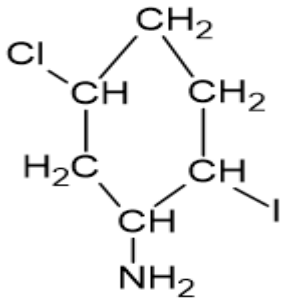
1,3-dimethyl-cyclohexane



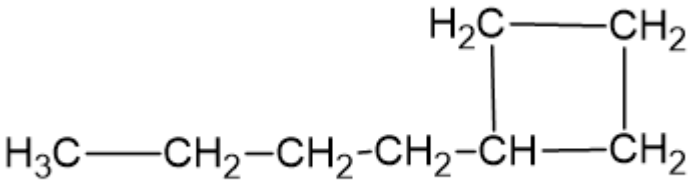
1-cyclopropyl-3-methyl-cyclobutane



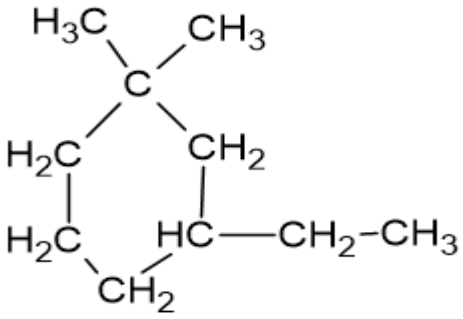
1-bromo-2-methyl-cyclohexane



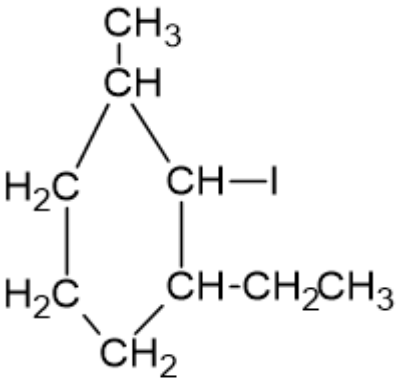
1-amino-5-chloro-2-iodo-cyclohexane



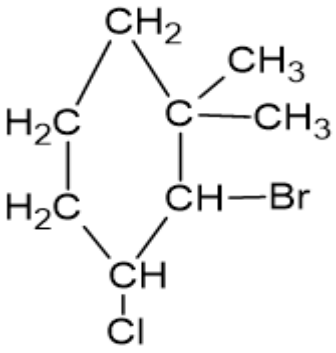
Butylcyclobutane



1-ethyl-3,3-dimethyl-cyclohexane



1-ethyl-2-iodo-3-methyl-cyclohexane



1-bromo-2-chloro-6,6-dimethylcyclohexane

physical properties of cycloalkanes

Similar to alkanes, cycloalkanes are covalent, non-polar molecules, therefore when bonding they use Van der Waals forces. Due to this type of bonding, the smaller cycloalkanes such as cyclopropane and cyclobutane are gases and the rest are liquids and solids.

As the number of carbon atoms in the molecule increase, the Van der Waals forces are stronger and therefore will have higher melting and boiling points. In fact, cycloalkanes have higher boiling points, melting points and densities than linear alkanes.

Also, cycloalkane VDW forces are stronger than alkanes as the ring shape allows for greater area of contact and they are more reactive.

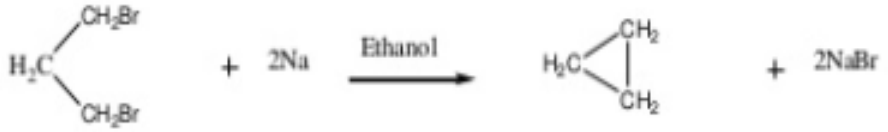
Cycloalkanes are less dense than water and have low solubility, and lower cycloalkanes are especially flammable in oxygen.

Also, cycloalkanes are considered saturated molecules due to single alkane bonds.

Preparation of cycloalkanes

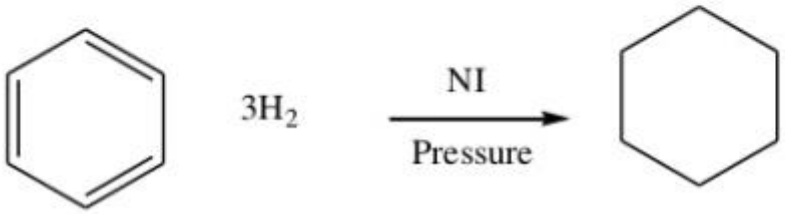
1. From Dihalogen Compounds: Suitable dihalogen compounds on treatment with sodium or zinc give corresponding cycloalkanes.

- **From Dihalogen Compounds**



2-

From Aromatic Compounds: Benzene may be catalytically hydrogenated at elevated temperature and pressure to yield cyclohexane.



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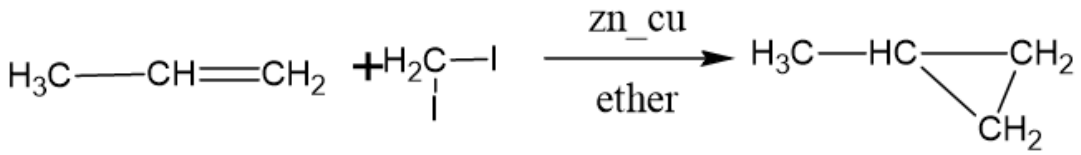
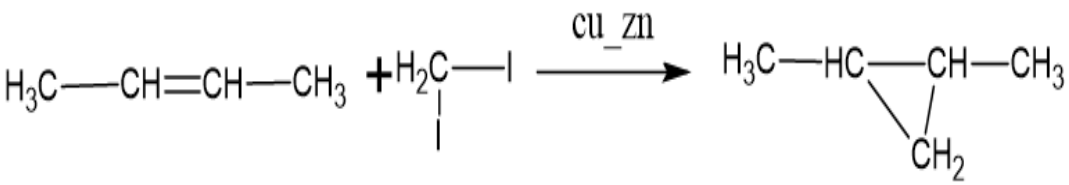
3- By Simmons-Smith reaction

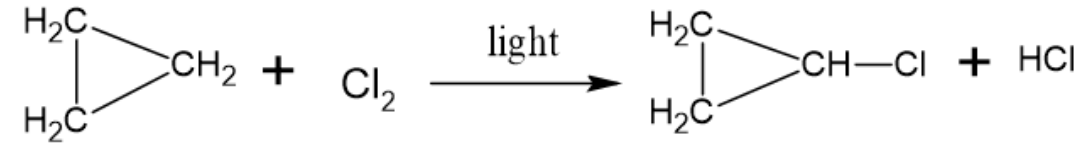
Simmons-Smith reaction is an asymmetric reaction in which a carbenoid adds to an alkene or alkyne to form a cyclopropane. It is an essential reaction involving an organozinc reagent. The reaction is typically conducted using diiodomethane in combination with metallic zinc and copper (Zn(Cu)).

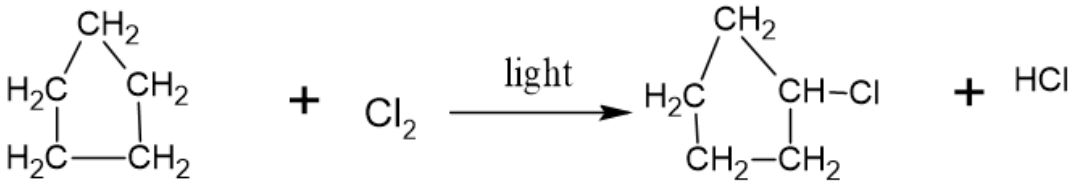




Reactions of cycloalkanes

1- Halogenation

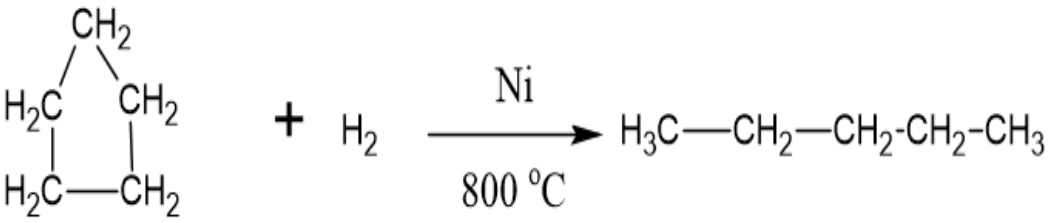


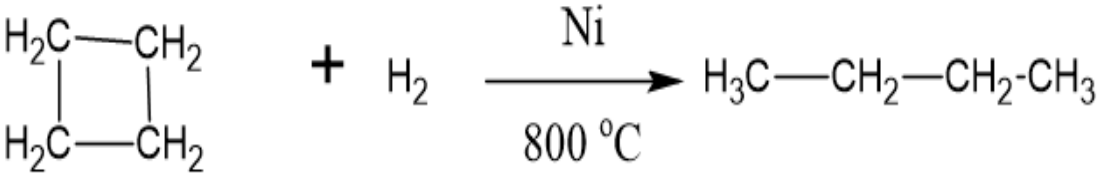


2- Combustion

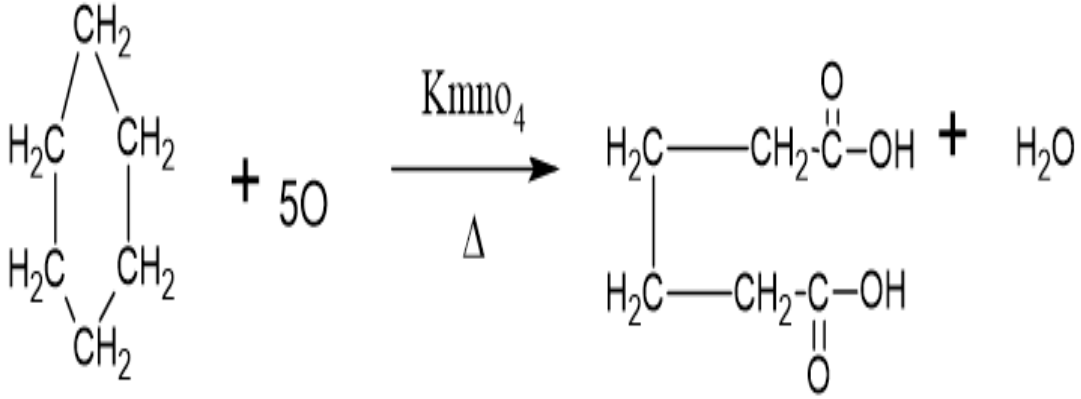
Different products can be produced depending on starting material combustion conditions but generally the product will be aldehydes.

3- Hydrogenation





4- Oxidation of cycloalkanes by hot alkene kmno4



Alcohols

All alcohols contain the hydroxyl group (-OH) attached to a saturated carbon. These have the general formula R-OH, where R is an alkyl or substituted alkyl group.

The group may be primary, secondary, or tertiary; it may be open chain or cyclic; it may contain a halogen atom, an aromatic ring, or additional hydroxyl group.

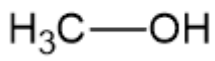
The -OH group is the functional group, determines the properties characteristic of this family. Variations in structure of the R group may affect the rate at which the alcohol undergoes certain reactions, and even, in a few cases, may affect the kind of reaction.

Compound in which the hydroxyl group is attached directly to an aromatic ring are not alcohols; they are phenols.

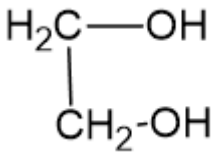
Classification of alcohols

Alcohols classified in three types

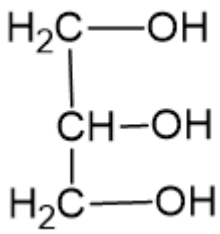
1- Monohydric : which containing one of hydroxyl group (OH) like



2-Dihydric : which containing two of hydroxyl group (OH) like

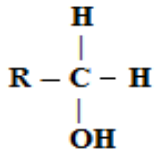


3-Trihydric :which containing three of hydroxyl group (OH) like

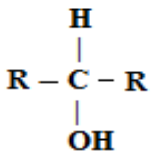


Mono alcohols other than methanol, are classified as, primary, secondary, or tertiary, depending on the number of carbons bonded to the carbon atom bearing the –OH group.

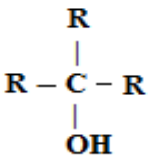
If one carbon is bonded to this carbon atom, the alcohol is primary, if two carbons are bonded, it is secondary, and if three carbons are bonded, it is tertiary.



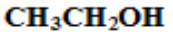
Primary (1°)



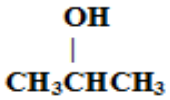
Secondary (2°)



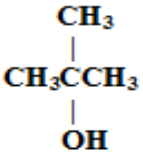
Tertiary (3°)



Ethanol (1°)



2-Propanol (2°)



2-Methyl-2-propanol (3°)

Naming of alcohols

Among the simple alcohols the common names are very commonly used. To write these names, simply put the name of its alkyl group and follow it by the word alcohol.

For example; CH3OH methyl alcohol.

The IUPAC rules for naming the alcohols are very similar to those for naming alkanes, and the following principle are followed:

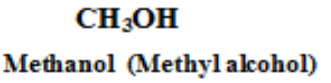
1- The longest carbon chain that contains the hydroxyl group is considered the parent

compound.

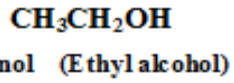
2- The –e ending of the name of this carbon chain is replaced by –ol.

3- The location of the hydroxyl and any other groups are shown by the smallest

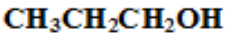
possible numbers, with the position of the hydroxyl group having the highest priority.



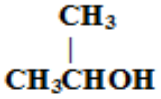
Methanol (Methyl alcohol)



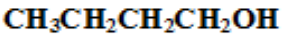
Ethanol (Ethyl alcohol)



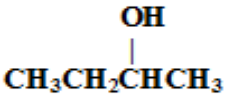
1-Propanol



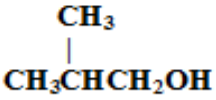
2-Propanol (Isopropyl alcohol)



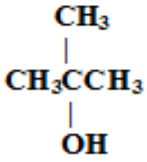
1- Butanol



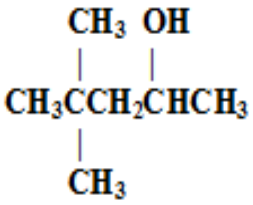
2-Butanol (*sec*-Butyl alcohol)



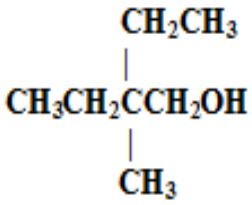
2-Methyl-1-propanol
(Isobutyl alcohol)



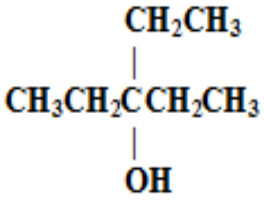
2-Methyl-2-propanol
(*tert*-Butyl alcohol)



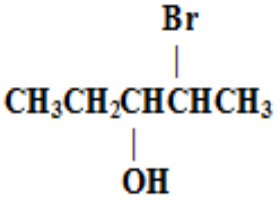
4,4-Dimethyl-2-pentanol



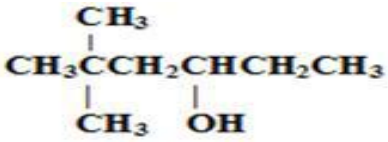
2-Ethyl-2-methyl-1-butanol



3-Ethyl-3-pentanol

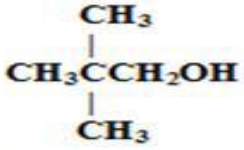


2-Bromo-3-pentanol

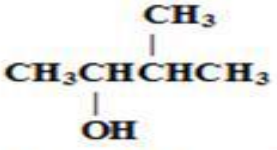


5,5-Dimethyl-3-hexanol

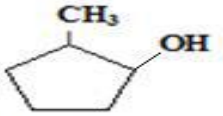
2-Chloroethanol



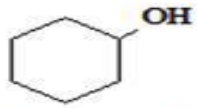
2,2-Dimethyl-1-propanol



3-Methyl-2-butanol



2-Methylcyclopentanol

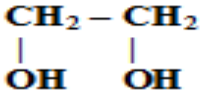


Cyclohexanol

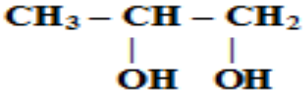
(Benzyl alcohol)

(*p*-Nitrobenzyl alcohol)

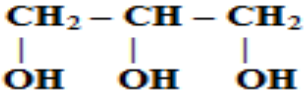
In the IUPAC system, a compound containing two hydroxyl groups is named as a diol, one containing three hydroxyl groups is named as a triol, and so on.



1,2-Ethanediol
(Ethylene glycol)

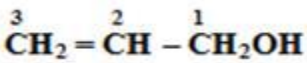


1,2-Propanediol
(Propylene glycol)

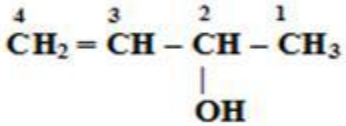


1,2,3-Propanetriol
(Glycerol, Glycerin)

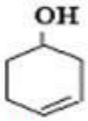
An alcohol containing a double bond is named as an alkenol, with number to indicate the position of the double bond and the hydroxyl group.



2-Propen-1-ol



3-Buten-2-ol



4-Cyclohexenol

Physical Properties of Alcohols

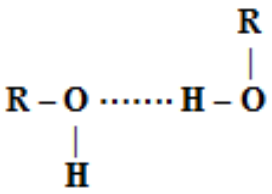
Alcohol molecules are polar, because the –OH group is highly polar. To show this, only compare boiling of ethane for example (formula weight 30 , b.p. –89), with methyl alcohol (formula weight 32 , b.p. 65).

Force of attraction between alcohol molecules obviously must be greater than between molecules of alkanes. Hydrogen bonding accounts for this.

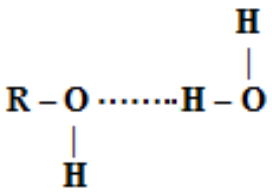
The presence of an alcohol group sharply increases the tendency to dissolve in water.

Methane, for example, is insoluble in water, but methyl alcohol is completely soluble,

because of the hydrogen bonding with water as illustrated:



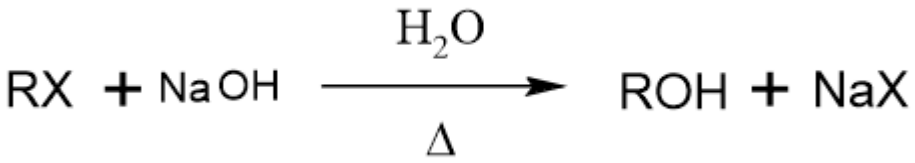
Intermolecular bonding

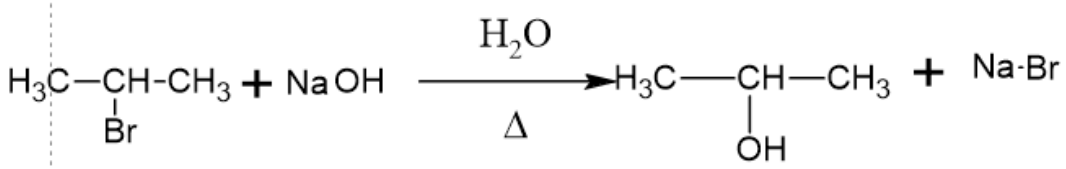


Hydrogen bonding with water

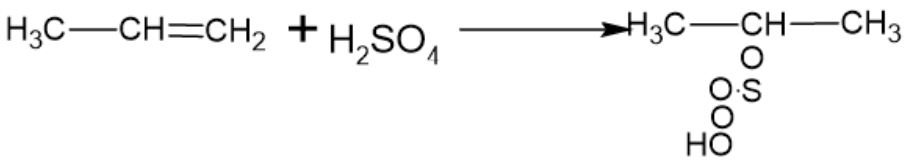
Preparation of alcohols

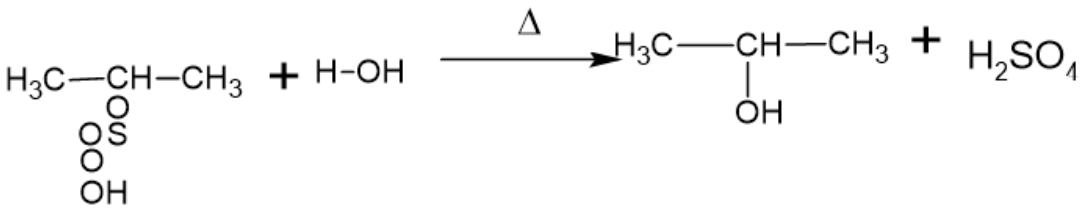
1- Hydrolysis of alkyl halides (with strong base)



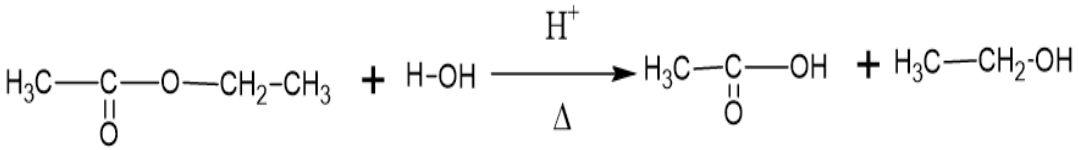


2- Hydration of alkenes (with strong acid)



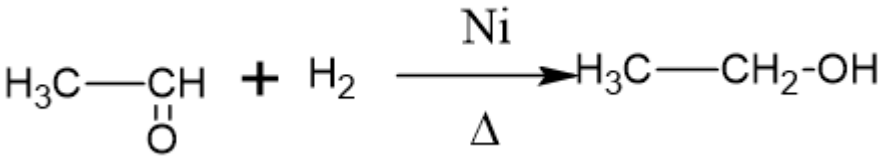


3- Hydrolysis of ester

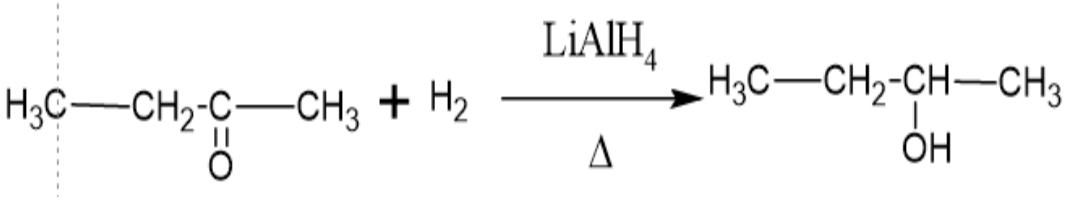


4- Reduction of aldehydes and ketones

Aldehydes for preparing primary alcohol

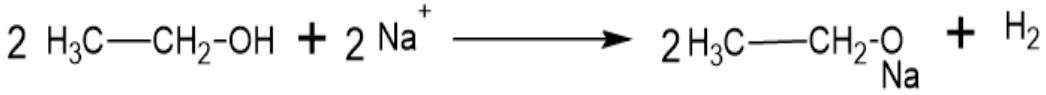


Ketones for preparing secondary



Reactions of alcohols

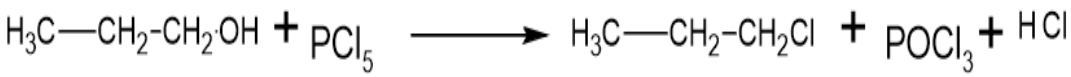
1- Reaction with active metal



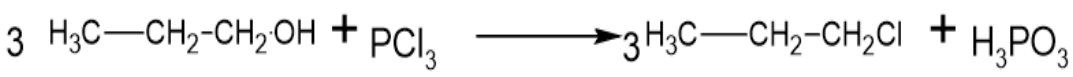
Sodium Alkoxide

2- Reaction with phosphorus

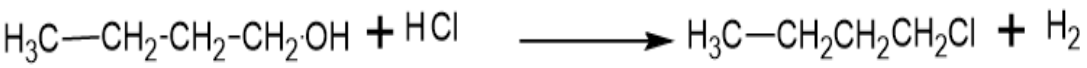
1 – With PCl_5



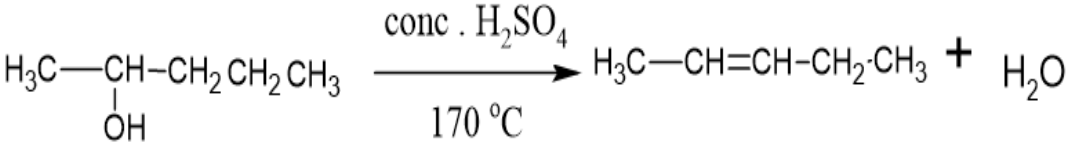
2 – With PCl_3



3- Reaction with hydrogen halides

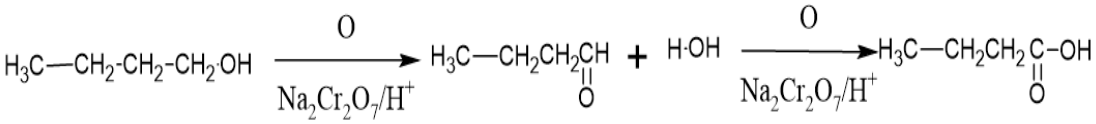


4- Dehydration of alcohol

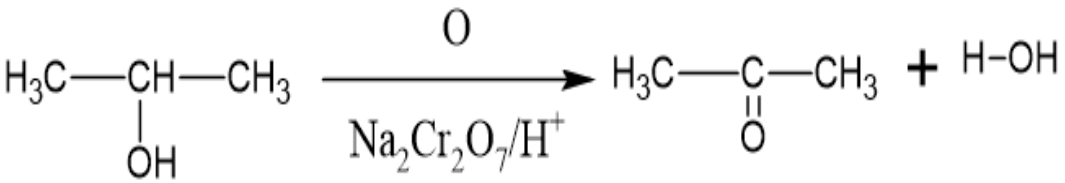


5- Oxidation of alcohols

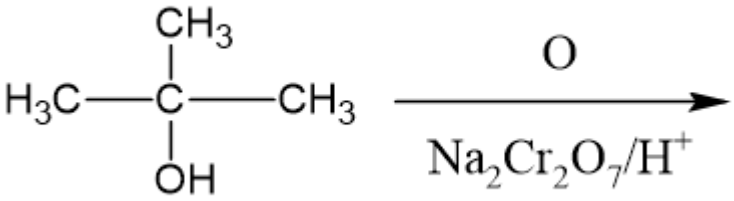
A- Oxidation of primary alcohol



B- Oxidation of secondary alcohol



C-Oxidation of tertiary alcohol



No reaction

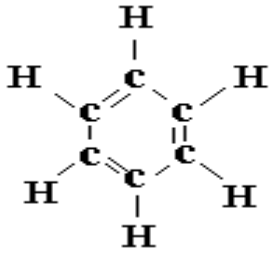
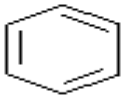
Aromatic compounds

Hydrocarbons containing one or more benzene rings called aromatic hydrocarbons.

The word aromatic was derived from (aroma) which describes the odour of these compounds. While aliphatic means fatty, and include open-chain compounds and those cyclic compounds that resemble them.

Benzene, the parent compound of this large family of organic substances, has the general formula CnH2n-6.

Benzene molecule contain three of double bond change in position continuously.


Nomenclature of Benzene Derivatives

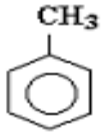
Substituted benzenes are named in a systematic manner by combining the

substituent name with the word benzene. If more than one substituent is present, the location of the second group must be indicated relative to the first. Some substituted benzenes have special names like toluene, aniline, phenol and so on.

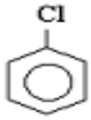
The IUPAC system retains certain common names for several of the simpler mono substituted alkyl benzene.

Derivatives of benzene can be calssified according to substituted benzene as:

1 – mono substituted benzene which contain benzene molecule attatched with one branch such as :

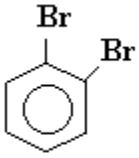


Methylebenzene (Toluene)



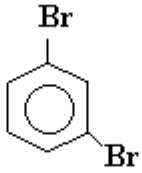
Chlorobenzene

2- di substituted benzene which contain benzene molecule attached with two branches such as :



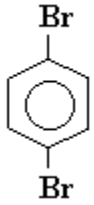
1,2- di bromo benzene

(Ortho benzene)



1,3- di bromo benzene

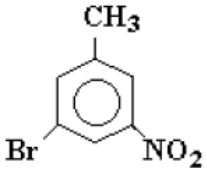
(Meta benzene)



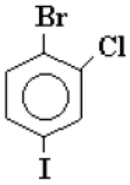
1,4- di bromo benzene

(Para benzene)

3- Poly substituted benzene which contain benzene molecule attached with three or more branches such as :

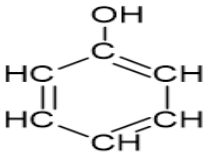


5-Bromo-3-nitrotoluene

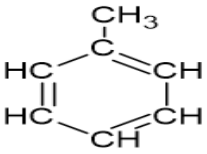


2-Chloro-4-iodobromobenzene

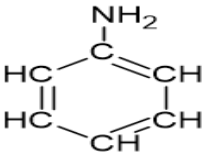
Examples of naming



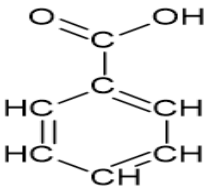
Phenol



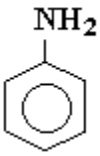
Toluene



Aniline

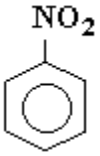


Benzoic acid

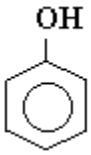


Amino benzene

(Aniline)

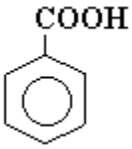


Nitrobenzene



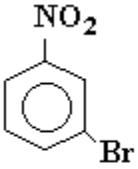
Hydroxy benzene

(Phenol)



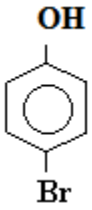
Benzene carboxylic acid

(Benzoic acid)

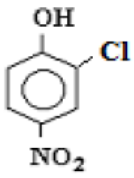


3-Bromo-1-nitrobenzene

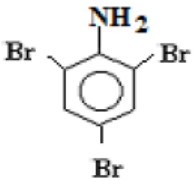
(m-Bromonitrobenzene)



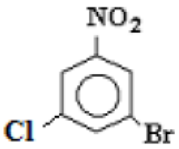
(p-Bromophenol)



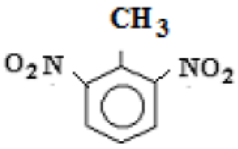
2-Chloro-4-nitrophenol



2,4,6-Tribromoaniline



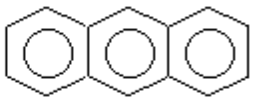
3-Bromo-5-chloronitrobenzene



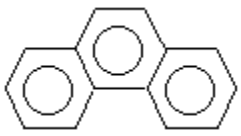
2,6-Dinitrotoluene

Poly Aromatic Hydrocarbons

Naphthalene



Anthracene



Phenanthrene

Naphthacene

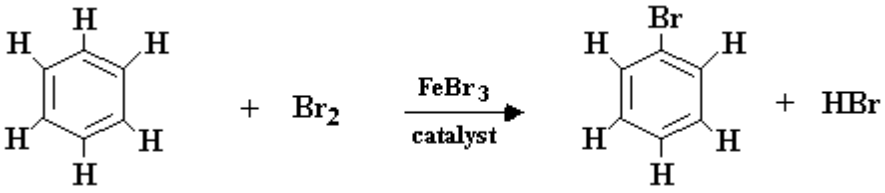
Properties of Benzene

Benzene is a colourless , flammable liquid obtained chiefly from coal tar. Although it has the same empirical formula as a acetylene (CH) and a high degree of unsaturation (three C=C bonds), it is much less reactive than either ethylene and acetylene.

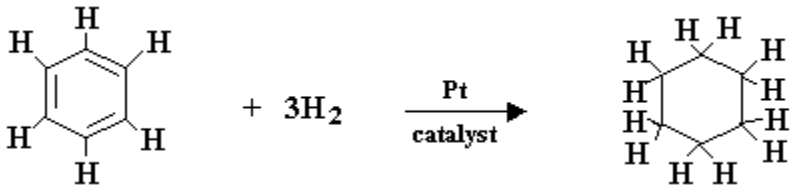
The stability of benzene is the result of electron delocalization; the electrons in the three pairs circulate around the entire ring.

Having this much room, which the six electrons can move, the benzene molecule strongly resists any chemical event that might disrupt this closed circuit of electrons.

Benzene undergoes substitution rather than addition reactions. Substitution reaction is the replacement of an atom or a group of atoms in a compound by another atom or another group of atoms.



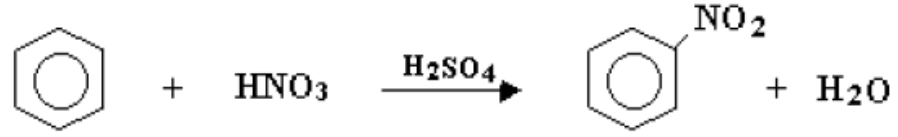
Addition reaction like hydrogenation, very difficult to happen, only with higher temperature and pressure than in the alkanes.



Reactions of benzene

1- Nitration

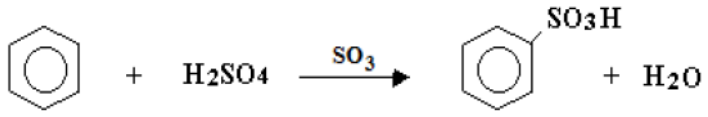
The substitution of one or more nitro group into the benzene ring is effected by the use of a special nitrating mixture of concentrated nitric and sulphuric acid.



Benzene **Nitric acid** **Nitrobenzene**

2- Sulfonation

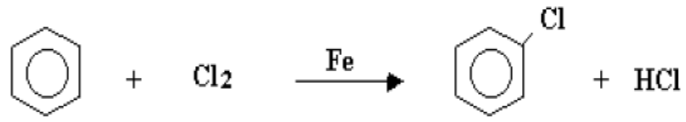
Under the same conditions of nitration, benzene is unattacked by concentrated sulphuric acid, but if it is heated under reflux for about 6 h with the concentrated acid, sulphonation takes place.



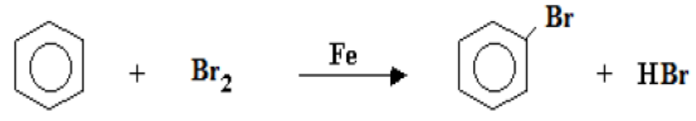
Benzene **Sulfuric acid** **Benzenesulfonic acid**

3- Halogenation

Benzene reacts with halogens in the presence of certain catalyst, such as iron or iron (III) or aluminum chloride, substituted compound being formed.



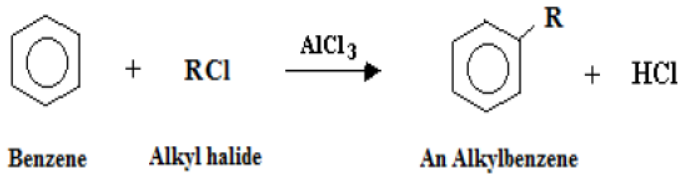
Benzene **Chlorobenzene**



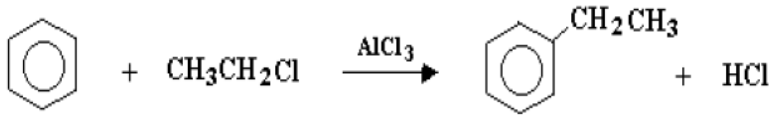
Benzene **Bromobenzene**

4- Friedel-Crafts alkylation

Benzene reacts exothermically with alkyl halides, in the presence of powdered, anhydrous aluminum chloride. Hydrogen halide evolved. This type of reaction is called Friedel-Crafts reaction.



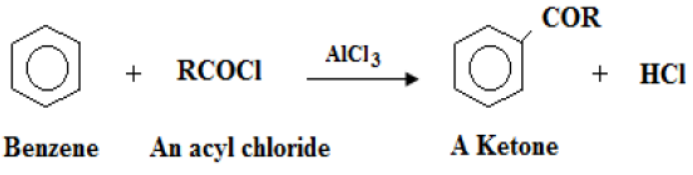
Benzene Alkyl halide An Alkylbenzene



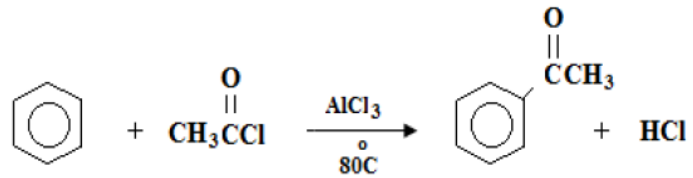
Benzene Ethyl chloride Ethylbenzene

5- Friedel-Crafts acylation

An acyl group RCO-, becomes attached to the aromatic ring, thus forming a ketone; the process is called **acylation**.



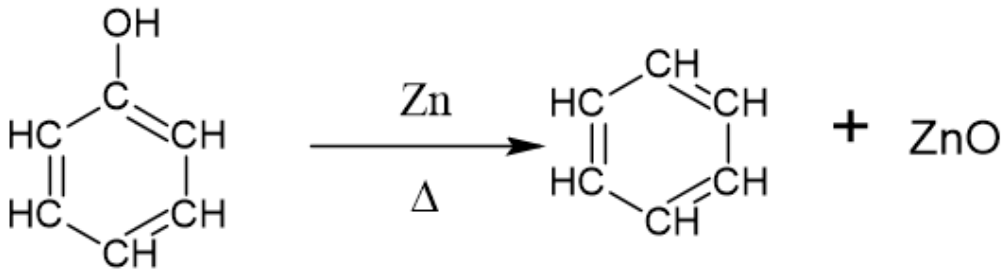
Benzene An acyl chloride A Ketone



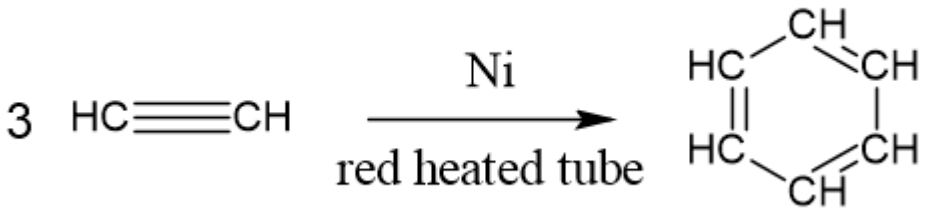
Benzene Actyl chloride Acetophenone

Preparation of aromatic compounds

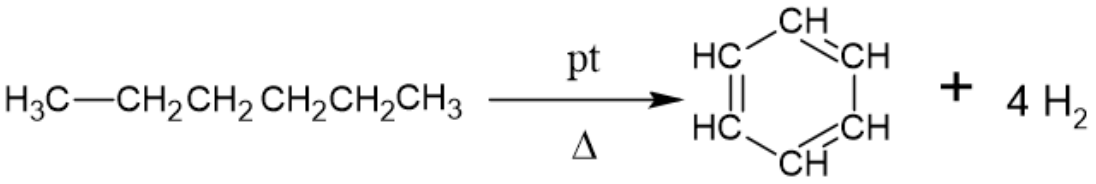
1- Reduction of benzene



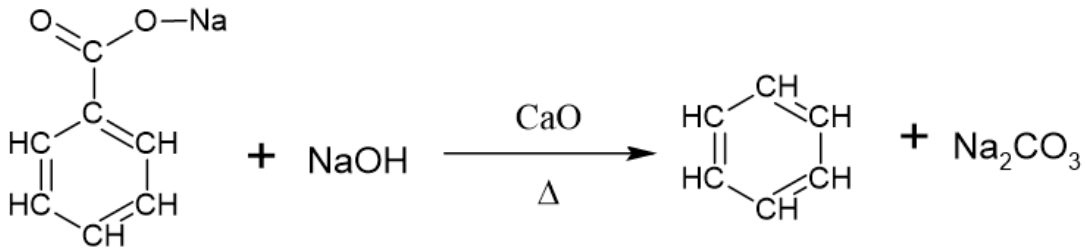
2-By passing ethyne (acetelene) through red heated tube



3- From n-hexane

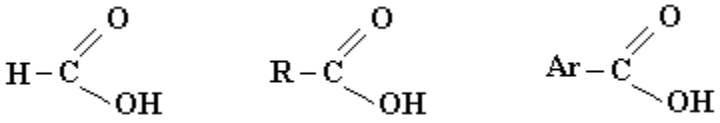


4- React sodium salt of benzoic acid with NaOH



Carboxylic acids

Carboxylic acids are organic compounds that show appreciable acidity. These compounds contain carboxyl group.



The carboxyl group can be attached to hydrogen (HCOOH), or an alkyl group (RCOOH).

HCOOH

Methanoic acid
(Formic acid)

CH_3COOH

Ethanoic acid
(Acetic acid)

CH_3-CH-COOH
|
Br

2-Bromopropanoic acid
(α-Bromopropionic acid)

Naming of Carboxylic acids

Aliphatic carboxylic acids have been known for along time, and as a result have common names that refer to their sources rather than to their chemical structures.

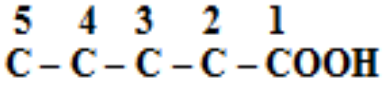
Formic acid, for example, adds the sting to the bite of an ant (Latin: formica, ant); butyric acid gives rancid butter its typical smell (Latin: butyrum, butter); and caproic, caprylic, and capric acids are all found in goat fat.

Table of Carboxylic Acids

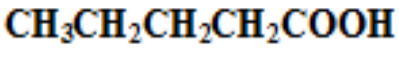
Name	Formula	Origin of name
(Formaic acid) Methanoic	$HCOOH$	L.formica, ant
(Acetic acid) Ethanoic	CH_3COOH	L. acetum, vinger
(Propionic acid) Propanoic	CH_3CH_2COOH	Gr. Proto, first pion, fat
(Butyric acid) Butanoic	$CH_3(CH_2)_2COOH$	L. butyrum, butter
(Valeric acid) Pentanoic	$CH_3(CH_2)_3COOH$	L. valere, to be strong (valerian)
(Caproic acid) Hexanoic	$CH_3(CH_2)_4COOH$	L. caper, goat
(Caprylic acid) Heptanoic	$CH_3(CH_2)_5COOH$	L. caper, goat
(Capric acid) Decanoic	$CH_3(CH_2)_8COOH$	L. caper, goat
(Lauric acid) Dodecanoic	$CH_3(CH_2)_{10}COOH$	Laurel
(Myristic acid) Tetradecanoic	$CH_3(CH_2)_{12}COOH$	Myristica, nutmeg
(Palmitic acid) Hexadecanoic	$CH_3(CH_2)_{14}COOH$	Palm oil
(Stearic acid) Octadecanoic	$CH_3(CH_2)_{16}COOH$	Gr. Stear, tallow

The IUPAC names follow the usual pattern. The longest chain carrying the carboxyl group is considered the parent structure, and is named by replacing the –e of the corresponding alkane with –oic acid.

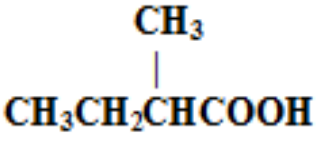
The position of the substituent is indicated by a number.



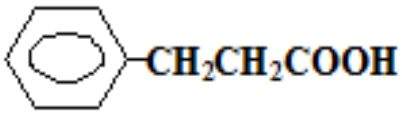
Used in IUPAC names



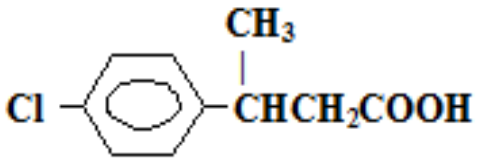
Pentanoic acid



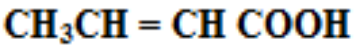
2-Methylbutanoic acid



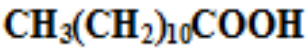
3-Phenylpropanoic acid



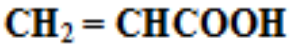
3-(*p*-Chlorophenyl)butanoic acid



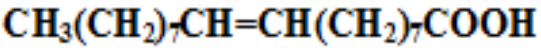
2-Butenoic acid



Dodecanoic acid
(Lauric acid)

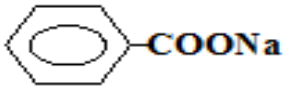


Propenoic acid
(Acrylic acid)

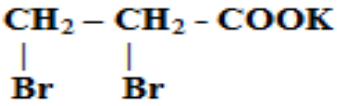


cis-9-Octadecenoic acid
(Oleic acid)

The name of a salt of a carboxylic acid consists of the name of the cation (sodium, potassium, ammonium, etc.) followed by the name of the acid with the ending –ic acid changed to –ate.



Sodium benzoate



Potassium 2,3-dibromopropionate
(Potassium α,β-dibromopropionate)

$(CH_3COO)_2Ca$

Calcium acetate

$HCOONH_4$

Ammonium formate

Physical Properties of Carboxylic Acids

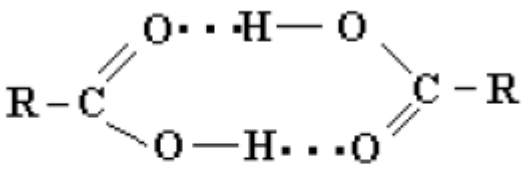
Both parts of a carboxyl group, the carbonyl and the hydroxyl, are polar groups, and can form hydrogen bonds with each other and with other kind of molecules.

The aliphatic acids therefore show very much the same solubility behavior as the alcohols.

Water solubility undoubtedly arises from hydrogen bonding between the carboxylic acid and water.

Carboxylic acids have higher boiling points than alcohols of comparable molecular weight.

These high boiling points are due to the fact that a pair of carboxylic acid molecules is held together not by one but by two hydrogen bonds.

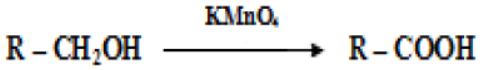


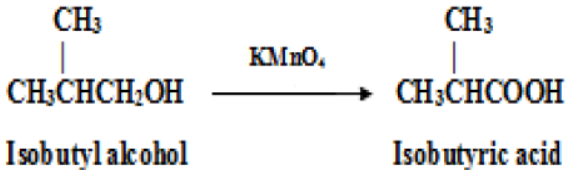
Intermolecular hydrogen bonding

Preparation of Carboxylic Acids

1- Oxidation of primary alcohols

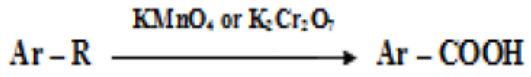
The oxidation of an alcohol involves the loss of one or more hydrogens (α-hydrogen) from the carbon bearing –OH group. If the alcohol is primary and loses both hydrogen atoms, the product is a carboxylic acid.

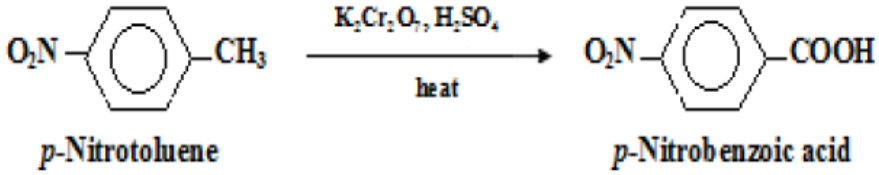


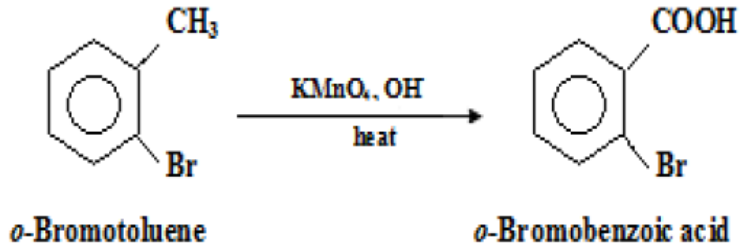


2- Oxidation of alkylbenzenes

One of the most useful methods of preparing an aromatic carboxylic acid involves oxidation of the proper alkylbenzene.

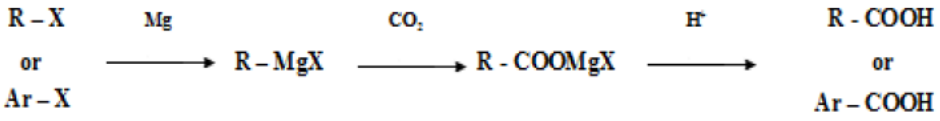


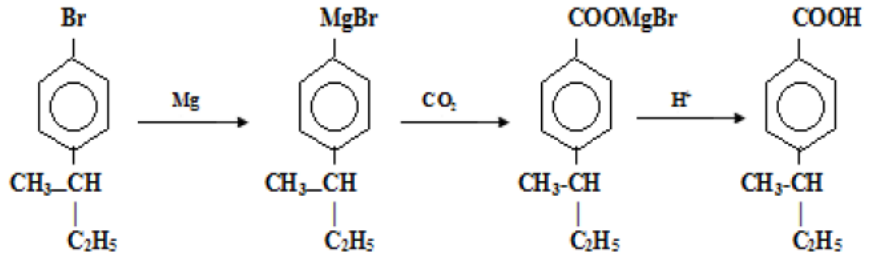




3- Carbonation of Grignard reagents

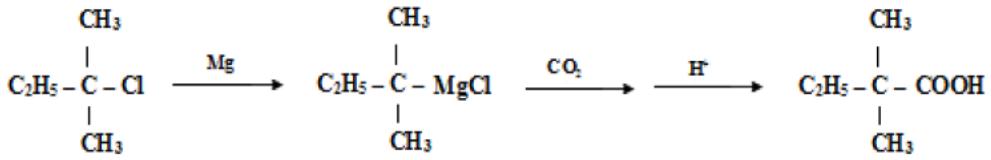
The Grignard synthesis of a carboxylic acid is carried out by bubbling gaseous CO_2 into the ether solution of the Grignard reagent, or by pouring the Grignard reagent on crushed dry ice (solid CO_2).





p-Bromo-*sec*-butylbenzene

p-*sec*-Butylbenzoic acid



tert-Pentyl chloride

2,2-Dimethylbutanoic acid
(Ethyldimethylacetic acid)

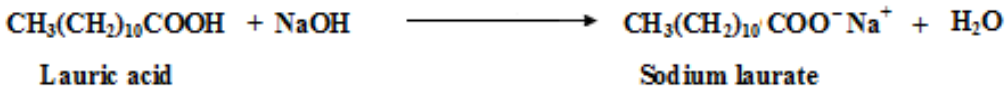
Reactions of Carboxylic Acids

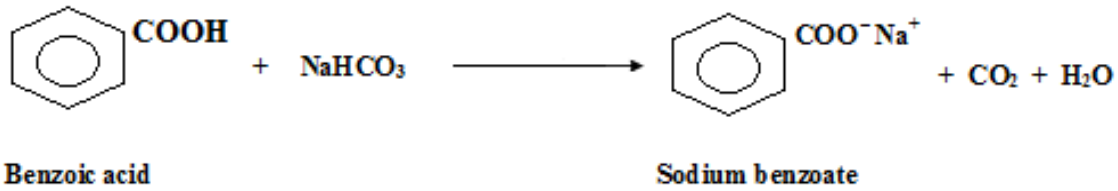
Although the carboxyl group apparently contains a carbonyl group linked to a hydroxyl group, carboxylic acids rarely display properties of either ketones or alcohols. Carboxylic acids are weak acids, but they can react smoothly and quickly at room temperature with strong bases like NaOH.

1- Acidity. Salt formation

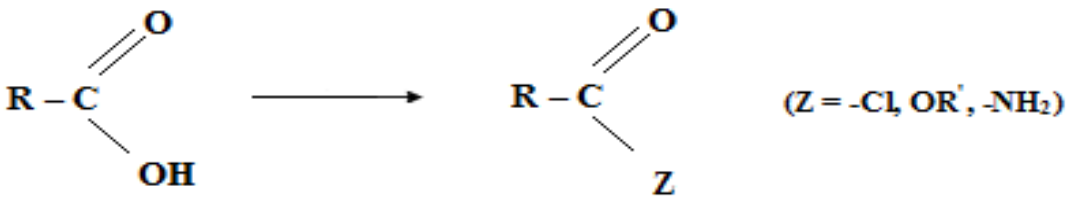
Although carboxylic acids are weak acids by comparison with mineral acids, the soluble carboxylic acids form distinctly acidic solution in water, unlike alcohols.

Carboxylic acids react quickly with NaOH, KOH, and other strong bases to form water-soluble salts and water.



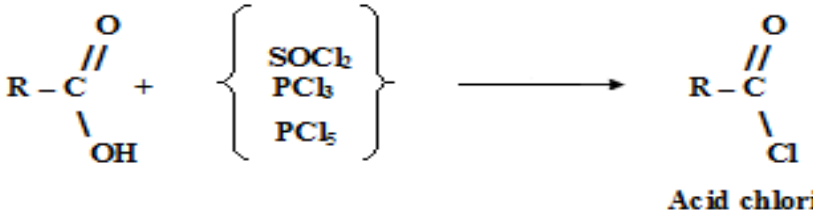


2- Conversion into functional derivatives

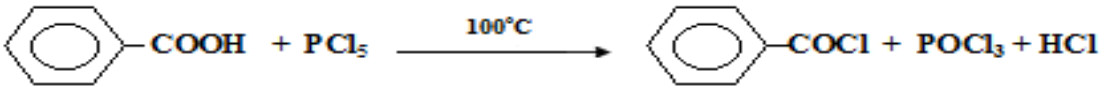


(a) Conversion into acid chlorides

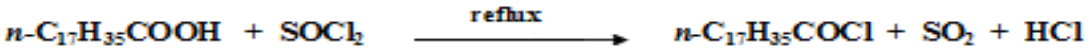
Treatment of a carboxylic acid, usually dissolved in a dry solvent to moderate the reaction, with phosphorus pentachloride, phosphorus trichloride or sulphur dichloride oxide (thionyl chloride), yields an acid chloride.



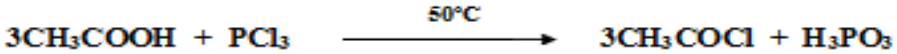
Acid chloride



Benzoic acid — Benzoyl chloride



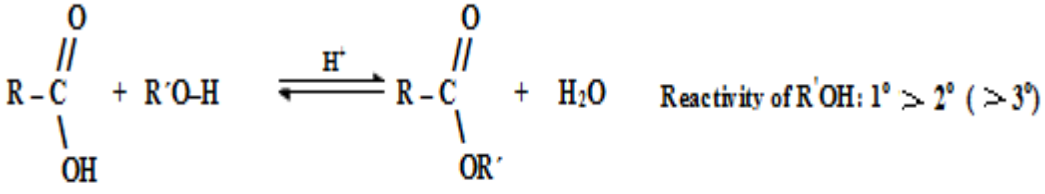
Stearic acid — Thionyl chloride — Stearoyl chloride



Acetic acid — Acetyl chloride

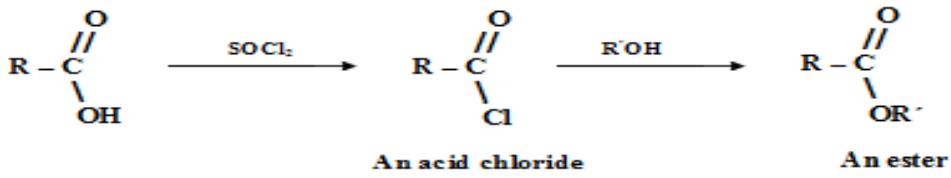
(b) Conversion into esters

Carboxylic acids react with alcohols to form neutral compounds called esters.



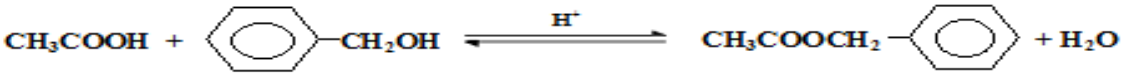
An ester

Reactivity of R′OH: 1° > 2° (> 3°)

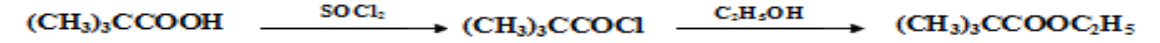


An acid chloride

An ester



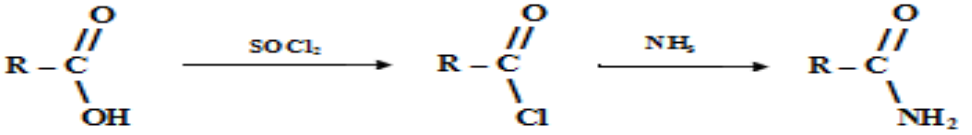
Acetic acid Benzyl alcohol Benzyl acetate



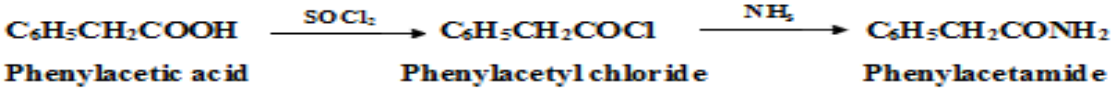
Trimethylacetic acid Ethyl trimethylacetate

(c) Conversion into amides

Carboxylic acids can be converted to amides by reaction with thionyl chloride then ammonia.



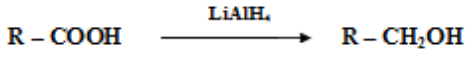
An acid chloride An amide



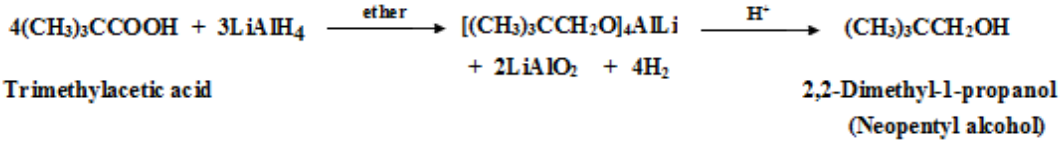
Phenylacetic acid Phenylacetyl chloride Phenylacetamide

3- Reduction

Carboxylic acids are readily reduced by lithium tetrahydridoaluminate LiAlH4 to primary alcohols.

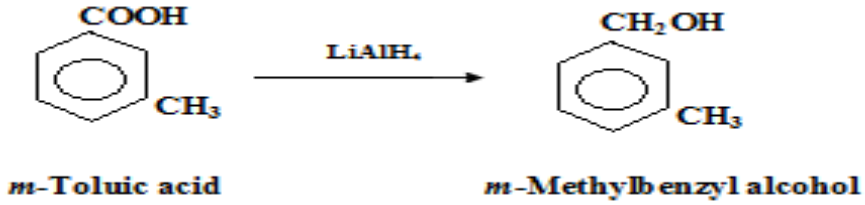


1° Alcohol



Trimethylacetic acid

2,2-Dimethyl-1-propanol (Neopentyl alcohol)



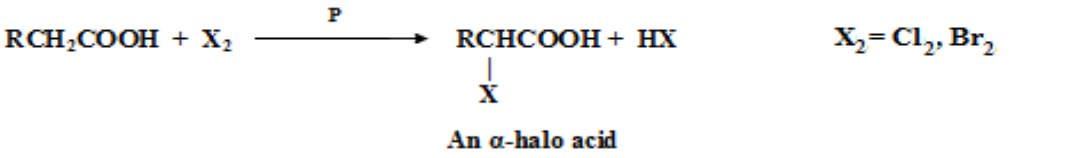
m-Toluic acid *m*-Methylbenzyl alcohol

4- Substitution in alkyl or aryl group

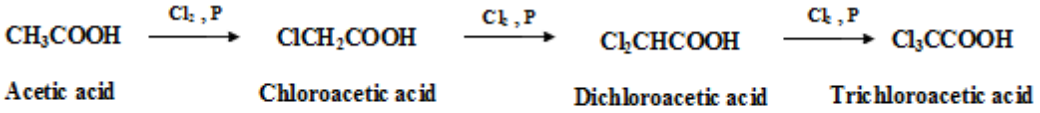
(a) Alpha-halogenation of aliphatic acids. Hell-Volhard-Zelinsky reaction

In the presence of a small amount of phosphorus, hydrogen atom bonded to the carbon atom adjacent to a carboxyl group can be substituted by chlorine or bromine.

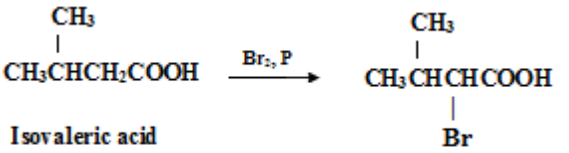
The reaction yield compound in which α-hydrogen has been replaced by halogen.



An α-halo acid



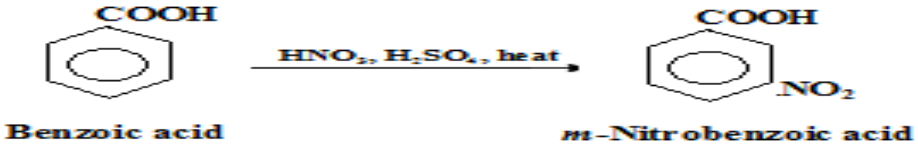
Acetic acid Chloroacetic acid Dichloroacetic acid Trichloroacetic acid



Isovaleric acid α-Bromoisovaleric acid

(b) Ring substitution in aromatic acid

Groups like NO2, can be substituted on the ring of the aromatic acids. It is meta electrophilic substitution.



Benzoic acid *m*-Nitrobenzoic acid