Organic Chemistry I

University of Anbar /College of Engineering
Chem. & Petrochemical Eng. Department
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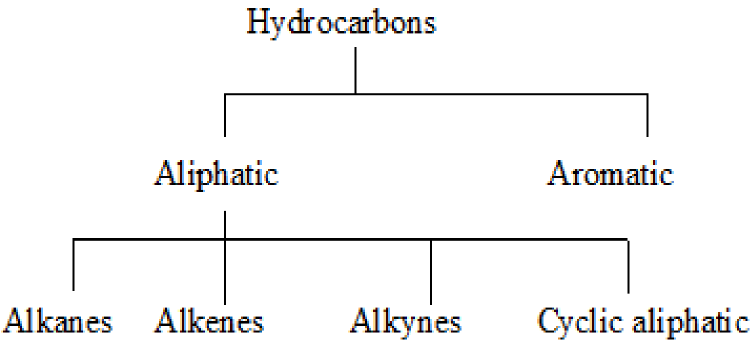
Lecture - 1

Alkanes

1.1 Introduction

Hydrocarbons are organic compounds contain only two elements, hydrogen and carbon, and hence are known as hydrocarbons. On the basis of structure, hydrocarbons are divided into two main classes, aliphatic and aromatic. Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic analogs (cycloalkanes, etc.).



The simplest member of the alkane family and one of the simplest of all organic compounds is methane, CH_4.

The atoms of the alkane hydrocarbons are joined to one another only through single bonds. The carbon-carbon single bond is of low reactivity. The general formula is $\mathbf{C_nH_{2n+2}}$, where n is the number of carbon atoms. For example, if the molecule contains three carbon atoms, $n = 3$ and $(2n + 2) = 8$, the formula is C_3H_8. If the molecule contains ten carbon atoms, $n = 10$ and $(2n + 2) = 22$, the formula is $C_{10}H_{22}$. Each member of the alkanes series differ from the preceding and the succeeding members by CH_2 atoms, and each carbon atom of an alkane molecule is covalently bonded to for other atoms. The first ten members of this series are listed in Table 1.1.

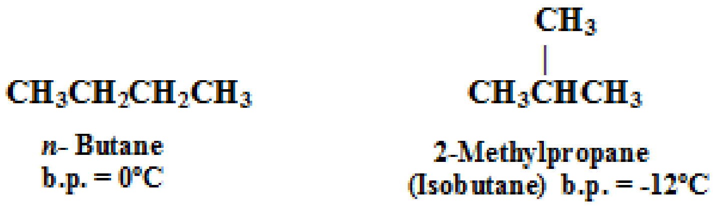
Table 1.1 The first ten member of the alkanes

General formula	Structure	Name
CH_4	CH_4	Methane
C_2H_6	CH_3CH_3	Ethane
C_3H_8	$CH_3CH_2CH_3$	Propane
C_4H_{10}	$CH_3(CH_2)_2CH_3$	Butane
C_5H_{12}	$CH_3(CH_2)_3CH_3$	Pentane
C_6H_{14}	$CH_3(CH_2)_4CH_3$	Hexane
C_7H_{16}	$CH_3(CH_2)_5CH_3$	Heptane

C_8H_{18}	$CH_3(CH_2)_6CH_3$	Octane
C_9H_{20}	$CH_3(CH_2)_7CH_3$	Nonane
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	Decane

1.2 Isomerism in Alkanes

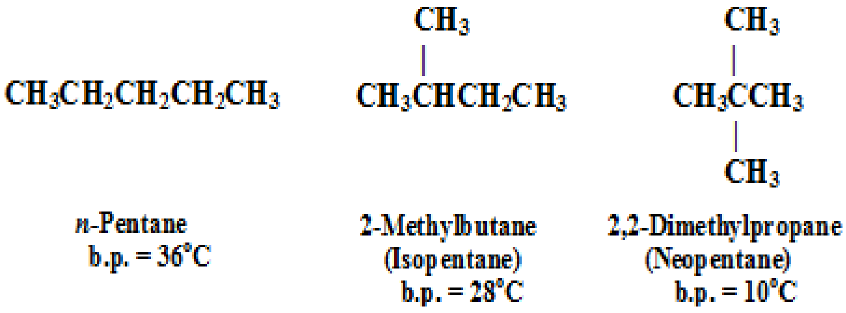
Compounds that have the same molecular formula but different structural formulas were defined as isomers. Isomeric compounds are not possible in the alkanes series until we reach the molecular formula C_4H_{10}. There are two arrangements for the formula C_4H_{10}, and two isomers are known as shown:



(C_4H_{10} isomers)

They differ both chemically and physically from one another. Experimentally, they can be identified by differences in their melting points, boiling points, densities, solubilities and some other features.

For the formula C_5H_{12}, three isomers have been found, as shown:



(C_5H_{12} isomers)

The difference in the structure is due to different arrangements of the carbon atoms.

1.3 Alkyl Groups

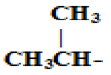
Any branch consisting of only carbon and hydrogen and only single bond is called **alkyl group**. The general formula for an alkyl group is C_nH_{2n+1} , since it contains one less hydrogen than the parent alkane, C_nH_{2n+2} .

CH_3- **Methyl**

CH_3CH_2- **Ethyl**

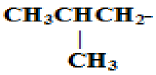
$CH_3(CH_2)_2$- ***n*-Propyl**

$CH_3(CH_2)_3$- ***n*-Butyl**



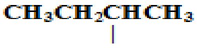
$$\overset{\displaystyle CH_3}{\overset{|}{CH_3CH}}-$$

Isopropyl



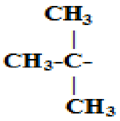
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2-$$

Isobutyl



$$CH_3CH_2\underset{|}{CH}CH_3$$

***sec*-Butyl**



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

***tert*-Butyl**

However large the group concerned, the prefix *n*- is used to designate any alkyl group in which all carbons form a single continuous chain and in which the point of attachment is the very end carbon.

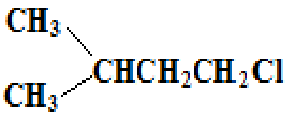
$CH_3CH_2CH_2CH_2CH_2Cl$

_n_-Pentyl chloride

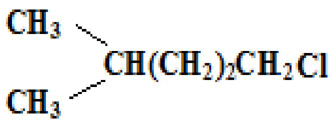
$CH_3(CH_2)_4CH_2Cl$

_n_-Hexyl chloride

The prefix *iso*- is used to designate any alkyl group (of six carbons or fewer) that has a single one-carbon branch on the next-to-last carbon of a chain and has the point of attachment at the opposite end of the chain.



Isopentyl chloride



Isohexyl chloride

If the branching occurs at any other position, or if the point of attachment is at any other position, this name does not apply.

1.4 Nomenclature

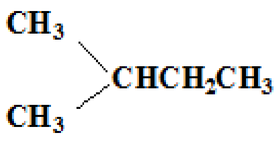
Common names:

The prefixes *n*-, *iso*-,and *neo*- are adequate to differentiate the various butanes and pentanes, but beyond this point an impracticable number of prefixes would be required. However, the prefix *n*- has been retained for any alkane, no matter how large, in which all carbon form a continuous chain with no branching:

$$CH_3CH_2CH_2CH_2CH_3 \qquad\qquad CH_3(CH_2)_4CH_3$$

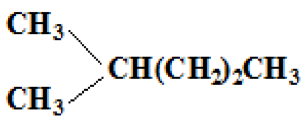
***n*-Pentane** **n-Hexane**

An *isoalkane* is a compound of six carbons or fewer in which all carbons except one from a continuous chain and that one carbon is attached to the next-to-end carbon:



$$\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\rangle CHCH_2CH_3$$

Isopentane



$$\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\rangle CH(CH_2)_2CH_3$$

Isohexane

In naming any other of the higher alkanes, we make use of the IUPAC system.

IUPAC system:

Essentially the rules of the IUPAC system (International Union of Pure and Applied Chemistry) are:

1- Use the ending **(*–ane*)** for all alkanes.

2- Attach a prefix to this, to specify the number of carbon atoms in the longest continuous chain in the molecule. The prefixes through C-10 are:

Meth-	1C	Hex-	6C
Eth-	2C	Hept-	7C
Prop-	3C	Oct-	8C
But-	4C	Non-	9C
Pent-	5C	Dec-	10C

3- Pick the longest continuous chain in a branched chain alkane as the basis for the name.

4- To specify which carbon atom of the parent chain holds a branch, number the parent chain from whichever end of its chain reaches the first branch with the lower number.

5- Determine the correct name for each branch or any other group or atom such as a halogen atom.

6- If the same group occurs more than ones as a side chain, indicate this by the prefix di-, tri-, tetra-, etc., to show how many of these groups are, and indicate by various numbers the positions of each group.

7- If there are several different groups attached to the parent chain, name them in alphabetical order.

If two different chains of equal length are present, choose the one with the larger number of branch points as the parent.

$CH_3(CH_2)_3CH_3$

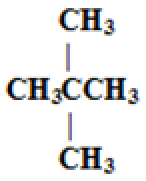
Pentane
(*n*-Pentane)

$$\begin{matrix} CH_3 & \\ & CH(CH_2)_2CH_3 \\ CH_3 & \end{matrix}$$

2-Methylpentane
(Isohexane)

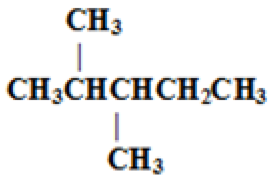
$$\begin{matrix} CH_3 & \\ & CHCH_2CH_3 \\ CH_3 & \end{matrix}$$

(Isopentane)



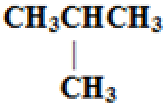
$$\mathrm{CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3}$$

Dimethylpropane
(Neopentane)



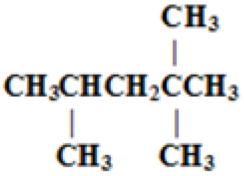
$$\mathrm{CH_3\overset{\displaystyle CH_3}{CH}\underset{\displaystyle CH_3}{CH}CH_2CH_3}$$

2,3-Dimethylpentane



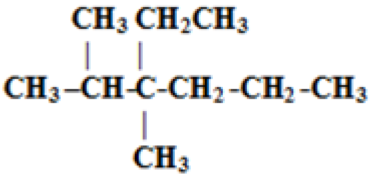
$$\mathrm{CH_3\underset{\displaystyle CH_3}{CH}CH_3}$$

Methylpropane
(Isobutane)



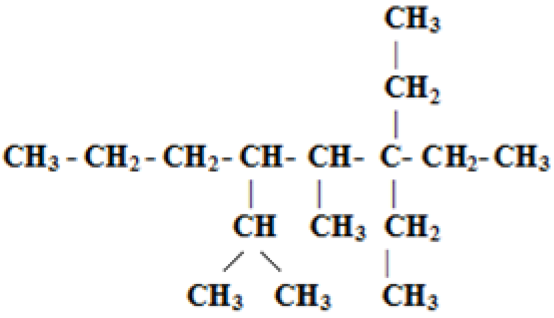
$$\mathrm{CH_3\underset{\displaystyle CH_3}{CH}CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_3}$$

2,2,4-Trimethylpentane



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{CH}{-}\overset{\displaystyle CH_2CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}CH_2{-}CH_3}$$

3-Ethyl-2,3-dimethylhexane



$$\mathrm{CH_3 - CH_2 - CH_2 - \underset{\displaystyle \begin{array}{c} CH \\ \diagup \ \diagdown \\ CH_3 \quad CH_3 \end{array}}{CH} - \underset{\displaystyle CH_3}{CH} - \overset{\displaystyle \begin{array}{c} CH_3 \\ | \\ CH_2 \end{array}}{\underset{\displaystyle \begin{array}{c} CH_2 \\ | \\ CH_3 \end{array}}{C}} - CH_2 - CH_3}$$

3,3-Diethyl-5-isopropyl-4-methyloctane

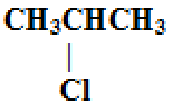
The alkyl halides which appear so often in the alkane chemistry are named *haloalkanes*; that is, halogen is simply treated as a side chain. We first name the alkane as though no halogen were present, and then add *fluoro, chloro, bromo,* or *iodo*, together with any needed number and prefixes.

CH_3Cl

Chloromethane
(Methyl chloride)

CH_3CH_2Br

Bromoethane
(Ethyl bromide)

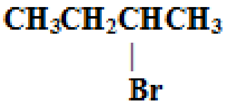


$CH_3\underset{\underset{Cl}{|}}{CH}CH_3$

2-Chloropropane
(Isopropyl chloride)

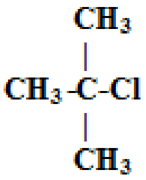
$CH_3CH_2CH_2CH_2Cl$

1-Chlorobutane
(Butyl chloride)



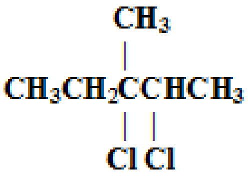
$CH_3CH_2\underset{\underset{Br}{|}}{CH}CH_3$

2-Bromobutane



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

2-Chloro-2-methylpropane

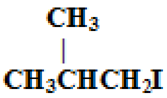


$CH_3CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}\underset{\underset{Cl}{|}}{CH}CH_3$

2,3-Dichloro-3-methylpentane

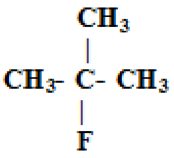
$Cl_2CH-CHCl_2$

1,1,2,2-Tetrachloroethane



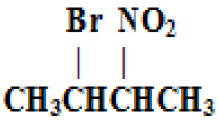
$CH_3\overset{\overset{CH_3}{|}}{CH}CH_2I$

1-Iodo-2-methylpropane



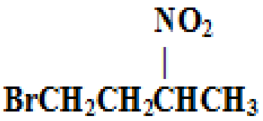
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{F}{|}}{C}}-CH_3$

2-Fluro-2-methylpropane



$CH_3\overset{\overset{Br}{|}}{CH}\overset{\overset{NO_2}{|}}{CH}CH_3$

2-Bromo-3-nitrobutane



$BrCH_2CH_2\overset{\overset{NO_2}{|}}{CH}CH_3$

1-Bromo-3-nitrobutane

The names shown beneath the structural formulas are systematic names. Those shown in parentheses are common names.

1.5 Physical Properties of Alkanes

The alkane molecule is held together entirely by covalent bonds, which either join two atoms of the same kind and hence are non-polar, or join atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non-polar or very weakly polar. The forces holding non-polar molecules are limited to van der Waals forces, they are weak and of very short range. They act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Within a family, therefore, we would expect that the larger the molecule and hence the larger its surface area the stronger the intermolecular forces.

The boiling points and the melting points of the alkanes rise as the number of the carbons increases. That is because boiling and melting require overcoming the intermolecular forces of liquid and a solid; the boiling point and melting points rise because these intermolecular forces increase as the molecules get larger.

The branching, lower the boiling points because with branching the shape of the molecule tends to approach that of a sphere; and as this happens the surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature.

In agreement with the rule of thumb, "like dissolves like", alkanes are soluble in non-polar solvents such as benzene, ether, and chloroform, and are insoluble in water and other highly polar solvents. Considered themselves as a solvent, the liquid alkanes dissolves compounds of low polarity and do not dissolve compounds of high polarity.

The relative density increases with size of the alkanes, and all alkanes are less dense than water. In general, to be denser than water a compound must contain a heavy atom like Br or I, or several atoms like Cl.

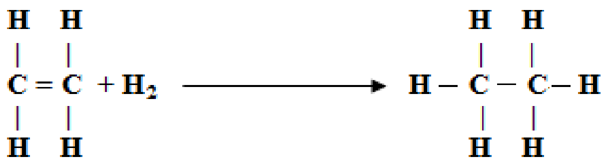
1.6 Preparation of Alkanes

1- Hydrogenation of alkenes

Hydrogenation is the most useful method for preparing alkanes. It is the addition of H_2 to a multiple bond.

$$C_nH_{2n} \xrightarrow{H_2+Pt,Pd \text{ or } Ni} C_nH_{2n+2}$$

Alkene **Alkane**



$$\begin{array}{cc} H & H \\ | & | \\ C & = C \\ | & | \\ H & H \end{array} + H_2 \longrightarrow H - \begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} - \begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} - H$$

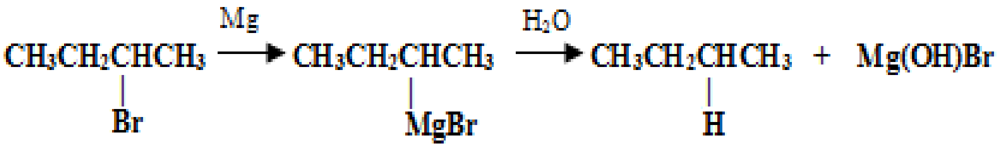
Ethylene **Ethane**

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.

$$R-X + Mg \xrightarrow{H_2O} \underset{\text{Grignard Reagent}}{R-MgX} \longrightarrow R-H + Mg(OH)X$$



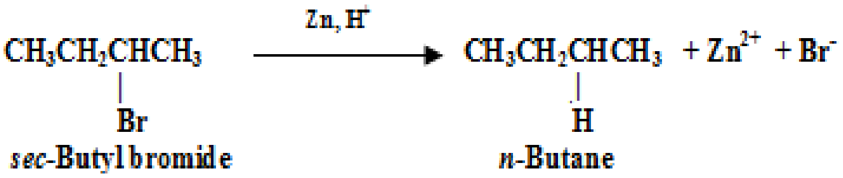
$$\underset{\displaystyle Br}{\underset{|}{CH_3CH_2CHCH_3}} \xrightarrow{Mg} \underset{\displaystyle MgBr}{\underset{|}{CH_3CH_2CHCH_3}} \xrightarrow{H_2O} \underset{\displaystyle H}{\underset{|}{CH_3CH_2CHCH_3}} + Mg(OH)Br$$

sec-Butyl bromide *sec*-Butylmagnesium bromide *n*-Butane

(b) Reduction by metal and acid

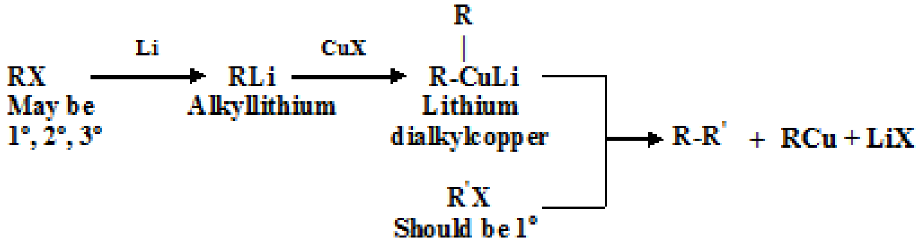
Reduction of an alkyl halide with metal and acid, involves the replacement of a halogen atom by a hydrogen atom. The product is an alkane.

$$R-X + Zn + H^+ \longrightarrow R-H + Zn^{2+} + X^-$$

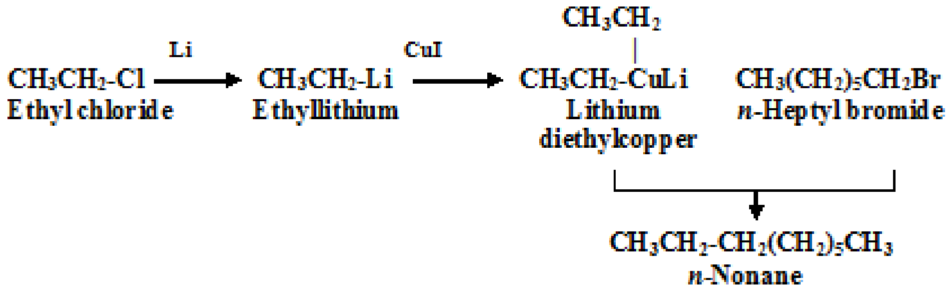


$$\underset{\textit{sec}\text{-Butyl bromide}}{\underset{\underset{Br}{|}}{CH_3CH_2CHCH_3}} \xrightarrow{Zn,\ H^+} \underset{\textit{n}\text{-Butane}}{\underset{\underset{H}{|}}{CH_3CH_2CHCH_3}} + Zn^{2+} + Br^-$$

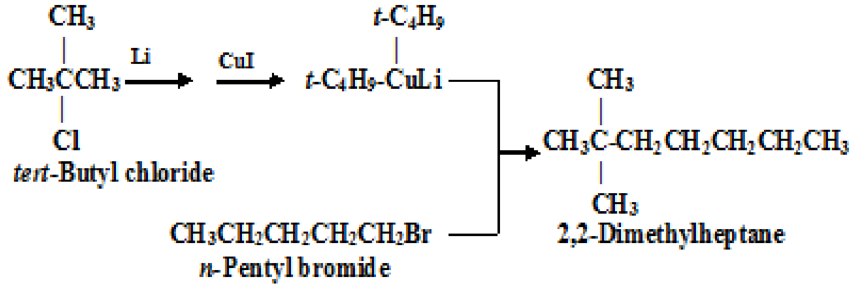
3- Coupling of alkyl halides with organometallic compounds



$$\underset{\substack{\text{May be}\\ 1°,\ 2°,\ 3°}}{RX} \xrightarrow{Li} \underset{\text{Alkyllithium}}{RLi} \xrightarrow{CuX} \underset{\substack{\text{Lithium}\\ \text{dialkylcopper}}}{\overset{\overset{R}{|}}{R\text{-}CuLi}} + \underset{\text{Should be }1°}{R'X} \longrightarrow R\text{-}R' + RCu + LiX$$



$$\underset{\text{Ethyl chloride}}{CH_3CH_2\text{-}Cl} \xrightarrow{Li} \underset{\text{Ethyllithium}}{CH_3CH_2\text{-}Li} \xrightarrow{CuI} \underset{\substack{\text{Lithium}\\ \text{diethylcopper}}}{\overset{\overset{CH_3CH_2}{|}}{CH_3CH_2\text{-}CuLi}} + \underset{\textit{n}\text{-Heptyl bromide}}{CH_3(CH_2)_5CH_2Br} \longrightarrow \underset{\textit{n}\text{-Nonane}}{CH_3CH_2\text{-}CH_2(CH_2)_5CH_3}$$



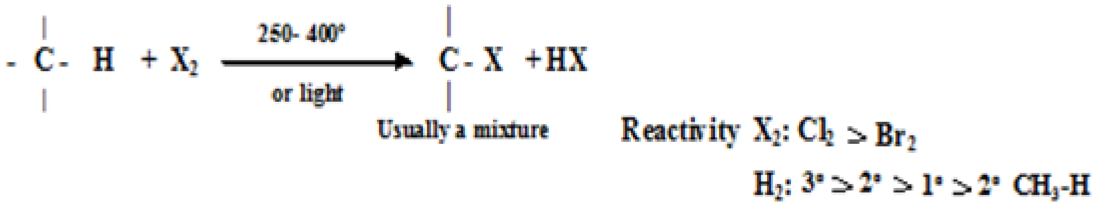
$$\underset{\textit{tert}\text{-Butyl chloride}}{\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{CH_3CCH_3}}} \xrightarrow{Li} \xrightarrow{CuI} \overset{\overset{t\text{-}C_4H_9}{|}}{t\text{-}C_4H_9\text{-}CuLi} + \underset{\textit{n}\text{-Pentyl bromide}}{CH_3CH_2CH_2CH_2CH_2Br} \longrightarrow \underset{\text{2,2-Dimethylheptane}}{\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH_3C\text{-}CH_2CH_2CH_2CH_2CH_3}}}}$$

1.7 Reactions of Alkanes

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

1- Halogenation

Alkanes react with the halogens (except iodine) to form substitution products.



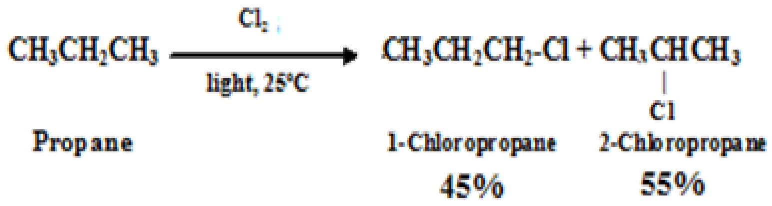
$$-\overset{|}{\underset{|}{C}}-H + X_2 \xrightarrow[\text{or light}]{250\text{-}400^\circ} \overset{|}{\underset{|}{C}}-X + HX$$

Usually a mixture

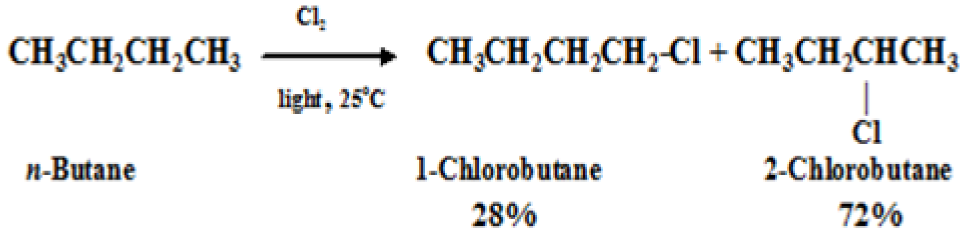
Reactivity X_2: $Cl_2 > Br_2$

H_2: $3^\circ > 2^\circ > 1^\circ > 2^\circ$ CH_3-H

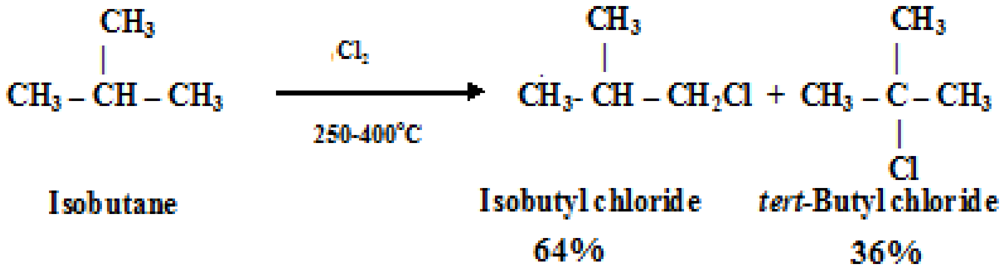
$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[\text{light, }25^\circ C]{Cl_2} \underset{\text{Chloroethane}}{CH_3CH_2\text{-}Cl}$$



$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{light, }25^\circ C]{Cl_2} \underset{\substack{\text{1-Chloropropane}\\45\%}}{CH_3CH_2CH_2\text{-}Cl} + \underset{\substack{\text{2-Chloropropane}\\55\%}}{CH_3\underset{\underset{Cl}{|}}{C}HCH_3}$$



$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light, }25^\circ C]{Cl_2} \underset{\substack{\text{1-Chlorobutane}\\28\%}}{CH_3CH_2CH_2CH_2\text{-}Cl} + \underset{\substack{\text{2-Chlorobutane}\\72\%}}{CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3}$$



$$\underset{\text{Isobutane}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3} \xrightarrow[250\text{-}400^\circ C]{Cl_2} \underset{\substack{\text{Isobutyl chloride}\\64\%}}{CH_3\text{-}\overset{\overset{CH_3}{|}}{C}H-CH_2Cl} + \underset{\substack{tert\text{-Butyl chloride}\\36\%}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3}$$

2- Oxidation (Combustion)

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.

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

flame

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

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

Organic Chemistry I

University of Anbar /College of Engineering
Chem. & Petrochemical Eng. Department
1st Year 2019 - 2020

Dr.Hamad K. Abdul Kadir

Assistant Prof. In Chemistey

Lecture - 2

Alkenes

2.1 Introduction

Molecules of the alkene (also called olefins) series of hydrocarbons are characterized by having two adjacent carbon atoms joined to one another by a double bond. The carbon-carbon double bond is unsaturated and hence highly reactive toward a wide variety of reagents.

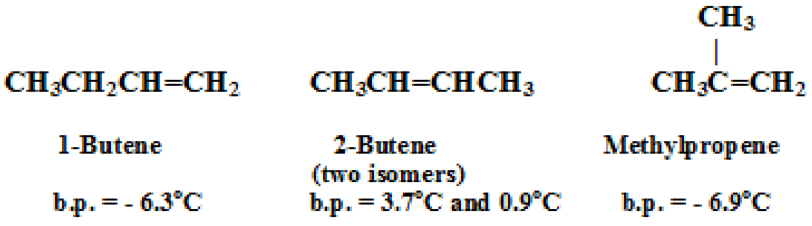
The general formula of alkenes is $\mathbf{C_nH_{2n}}$, where n is the number of carbon atoms. The first nine members of this series are listed in Table 2.1.

Table 2.1 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

2.2 Isomerism in Alkenes

Isomeric compounds are also possible in the alkenes. For the molecular formula C_4H_8, there are three different ways of organizing the four carbon atoms and the double bond:



$CH_3CH_2CH{=}CH_2$ — **1-Butene**, b.p. = - 6.3°C

$CH_3CH{=}CHCH_3$ — **2-Butene** (two isomers), b.p. = 3.7°C and 0.9°C

$CH_3\overset{\overset{\large CH_3}{|}}{C}{=}CH_2$ — **Methylpropene**, b.p. = - 6.9°C

(C_4H_8 isomers)

2.3 Nomenclature

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.

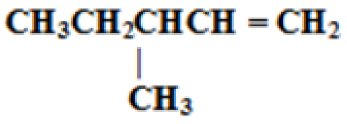
4- If a geometric isomer is designated, the name begins with *cis*- or *trans*-.

$CH_3CH_2CH_2CH_2CH=CH_2$

1- Hexene

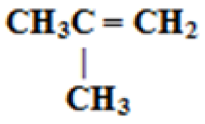
$CH_2=CHCH_2CH_3$

1-Butene



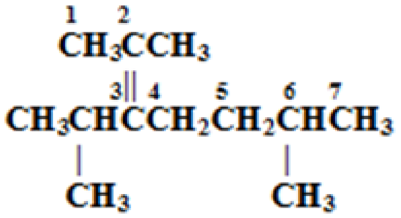
$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}CH=CH_2$

3-Methyl-1-pentene



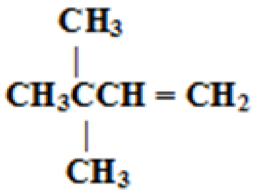
$CH_3\underset{\underset{CH_3}{|}}{C}=CH_2$

2-Methylpropene



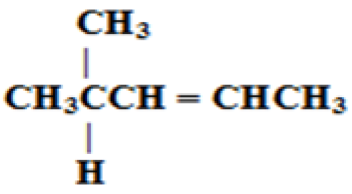
$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{\overset{1\ \ 2}{CH_3CCH_3}}{3\|\ 4}}{C}\overset{5}{C}H_2\overset{6}{C}H_2\underset{\underset{CH_3}{|}}{\overset{}{CH}}\overset{7}{C}H_3$

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



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

3,3-Dimethyl-1-butene

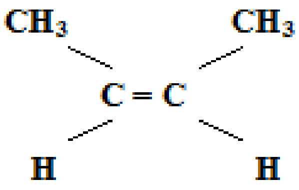


$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}CH=CHCH_3$

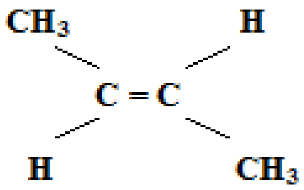
4-Methyl-2-pentene

$Cl_2C=CHCl$

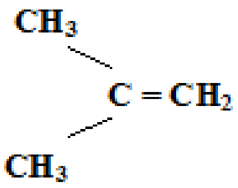
Trichloroethene



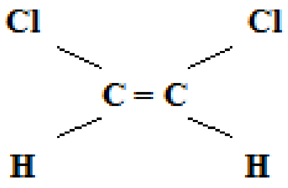
cis-2-Butene



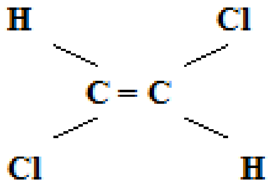
trans-2-Butene



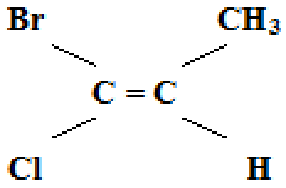
2-Methylpropene



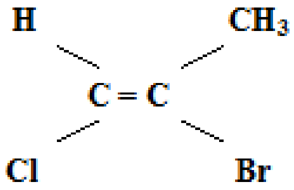
cis-1,2-Dichloroethene



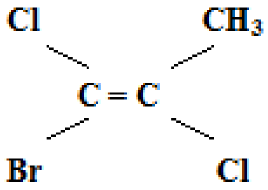
trans-1,2-Dichloroethene



1-Bromo-1-chloropropene



2-Bromo-1-chloropropene



1-Bromo-1,2-dichloropropene

2.4 Physical Properties of Alkenes

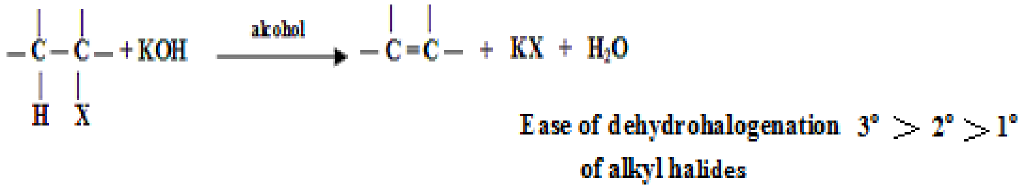
The alkenes possess physical properties that are essentially the same as those of the alkanes. They are insoluble in water, but quite soluble in non-polar solvents like benzene, ether, and chloroform. They are less dense than water. The boiling point rises with increasing carbon number; as with alkane, branching lowers the boiling point.

Like alkanes, alkenes are at most only weakly polar. Since the loosely held π electrons of the double bond are easily pulled or pushed, dipole moments are larger than for alkanes.

2.5 *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*).



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- + KOH \xrightarrow{\text{alcohol}} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

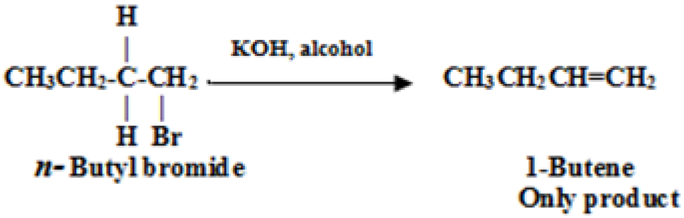
Ease of dehydrohalogenation $3° > 2° > 1°$
of alkyl halides

$$CH_3CH_2CH_2CH_2Cl \xrightarrow{\text{KOH, alcohol}} CH_3CH_2CH=CH_2 + KCl + H_2O$$

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

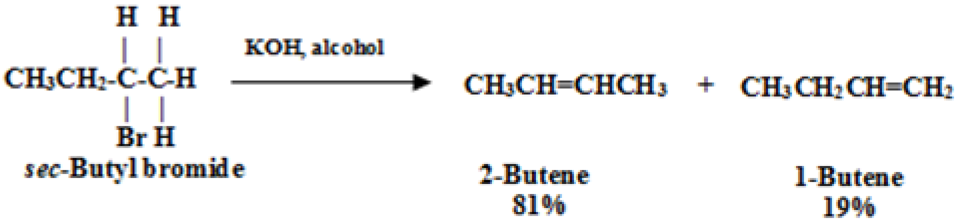
$$CH_3CH_2CHClCH_3 \xrightarrow{\text{KOH, alcohol}} CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$$

***sec*-Butyl chloride** **2-Butene 80%** **1-Butene 20%**



$$CH_3CH_2\text{-}\underset{H}{\overset{H}{C}}\text{-}\underset{Br}{CH_2} \xrightarrow{\text{KOH, alcohol}} CH_3CH_2CH=CH_2$$

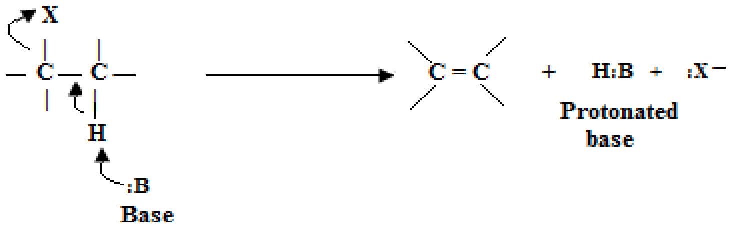
***n*-Butyl bromide** **1-Butene**
Only product



$$CH_3CH_2\text{-}\underset{Br}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}H \xrightarrow{\text{KOH, alcohol}} CH_3CH=CHCH_3 + CH_3CH_2CH=CH_2$$

***sec*-Butyl bromide** **2-Butene 81%** **1-Butene 19%**

***Mechanism*:**

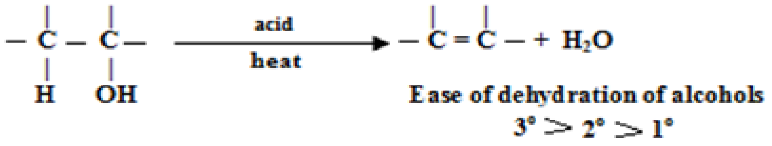


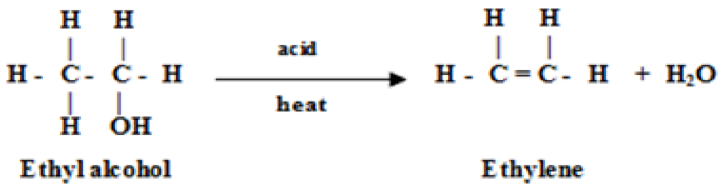
The base **:**B can be neutral or negatively charged: for example, H_2O or OH^-. The conjugate acid H:B will then be positively charged or neutral: for example, H_3O^+ or H_2O.

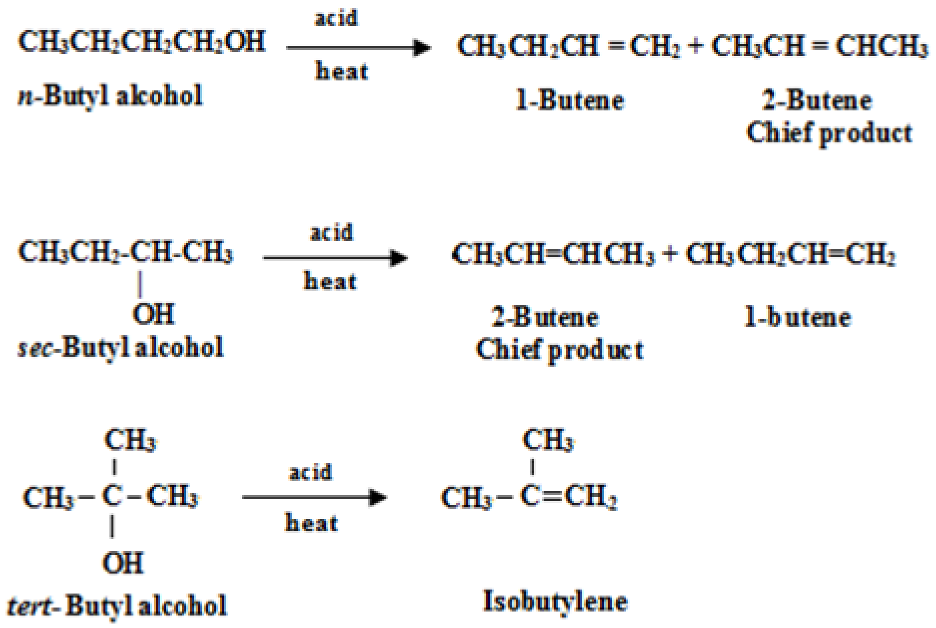
Halogen leaves the molecule as halide ion, and hence must take its electron pair along. Hydrogen is abstracted by the base as a proton, and hence must leave its electron pair behind; it is this electron pair that is available to form the π bond between the carbon atoms.

2- Dehydration of alcohols

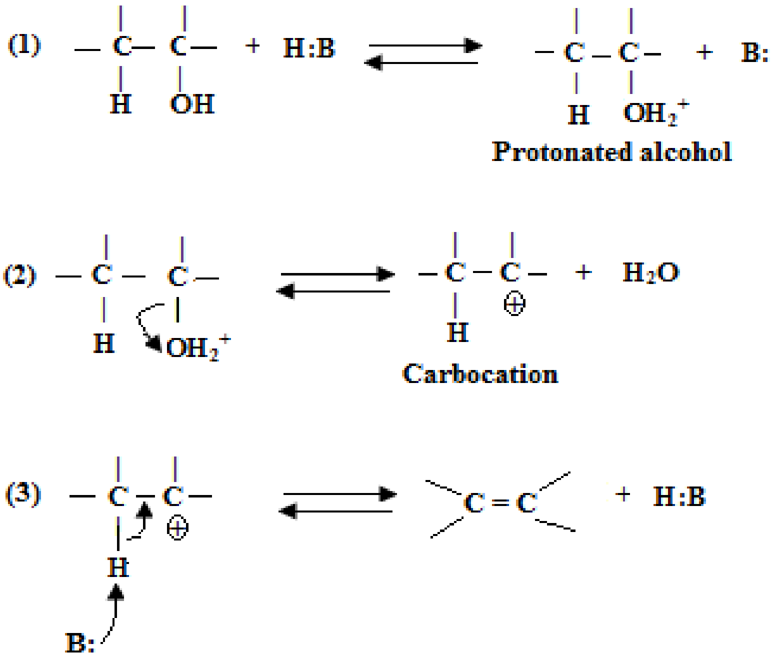
In the dehydration of alcohols, the H and OH are lost from adjacent carbons (*1,2-elimination*). An acid catalyst is necessary and application of heat.







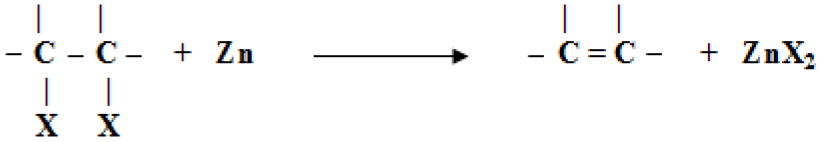
***Mechanism*:**



For secondary and tertiary alcohols the above mechanism is generally accepted. Step (1) is a fast acid-base reaction between the alcohol and the catalyzing acid which gives the protonated alcohol and the conjugate base of the acid. In step (2) the protonated alcohol undergoes heterolysis to form the carbocation and water. In step (3) the carbocation losses a proton to the base to yield alkene.

3- Dehalogenation of vicinal dihalides

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



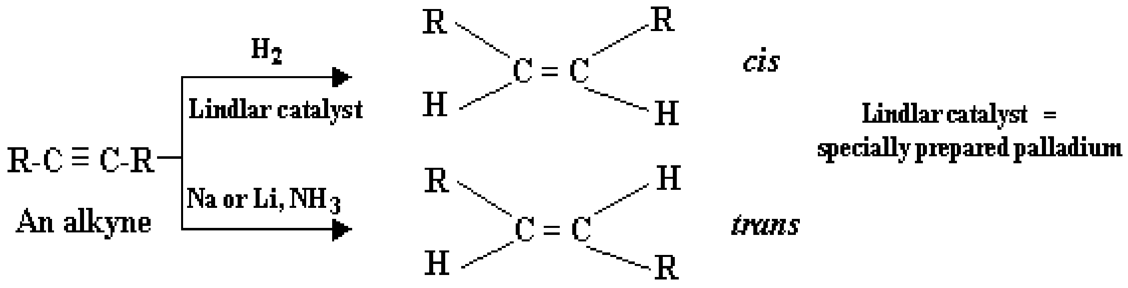
$$-\underset{X}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{|}{C}}}- \; + \; Zn \longrightarrow -\overset{|}{C}=\overset{|}{C}- \; + \; ZnX_2$$

$$CH_3CHBrCHBrCH_3 \xrightarrow{Zn} CH_3CH = CHCH_3 + ZnBr_2$$

2,3-Dibromobutane **2-Butene**

4- Reduction of alkynes

Trans alkene can be obtained by reduction of alkynes with sodium or lithium in liquid ammonia. Cis alkene is obtained by hydrogenation of alkynes with a specially prepared palladium called Lindlar catalyst.



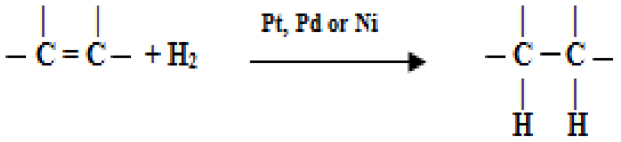
2.6 *Reactions of alkenes*

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.

(Addition Reactions)

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.



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

$$CH_3CH=CH_2 \xrightarrow{H_2,\ Ni} CH_3CH_2CH_3$$

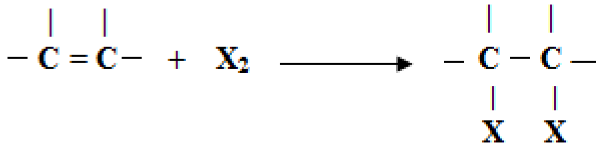
Propene (Propylene) — **Propane**

$$CH_2=CH_2 \xrightarrow{H_2,\ Ni} CH_3CH_3$$

Ethylene — **Ethane**

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.



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

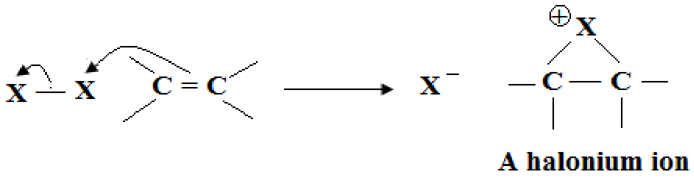
$X_2 = Cl_2, Br_2$

$$CH_3CH=CH_2 \xrightarrow{Br_2 \text{ in } CCl_4} CH_3CHBrCH_2Br$$

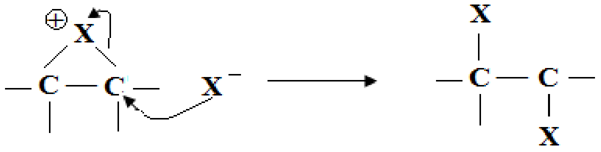
Propene (Propylene) **1,2-Dibromopropane (Propylene bromide)**

Mechanism:

(1)



(2)



In step (1) a halogen is transferred, without a pair of electrons, from a halogen molecule to the carbon-carbon double bond; there is formed a halide ion and organic cation. In step (2) this cation reacts with a halide ion to yield the addition product.

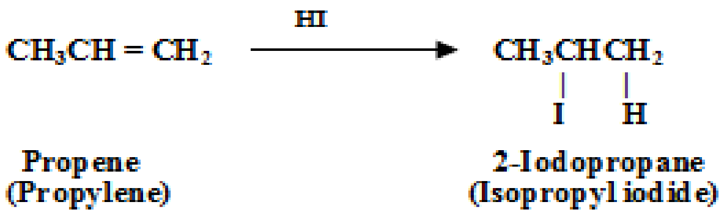
3- Addition of hydrogen halides

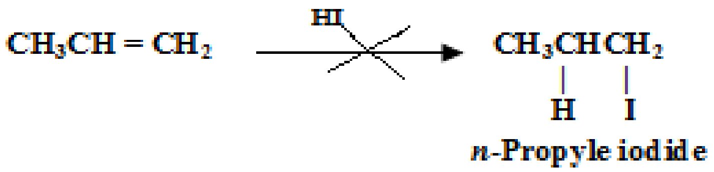
Alkenes react, usually on heating, with hydrogen halides (either gaseous or in concentrated solution) to form an addition product.

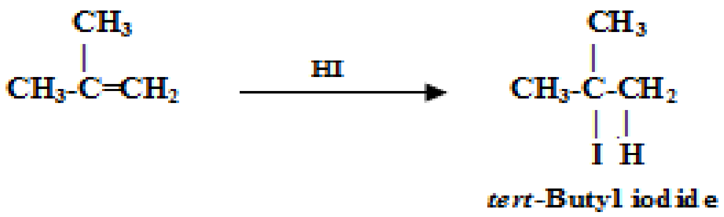
$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-$$

HX = HCl, HBr, HI

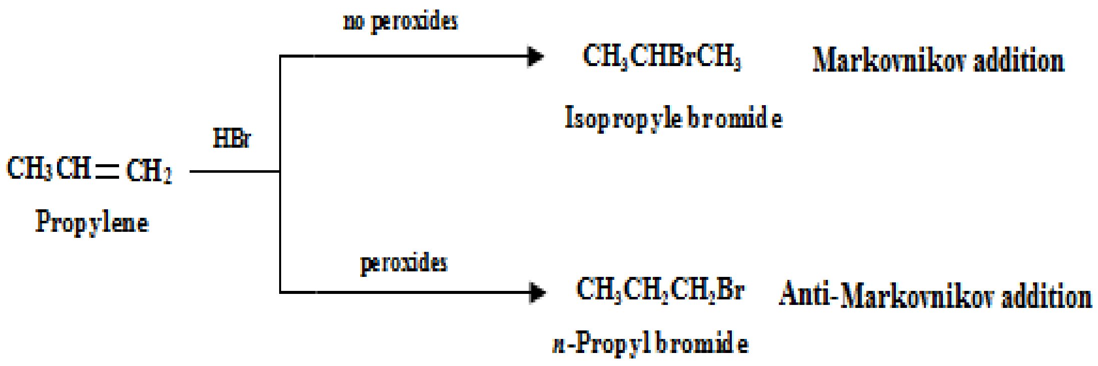
The hydrogen attaches itself to the carbon that already holds the greater number of hydrogens. This statement is called ***Markovnikov's rule***.





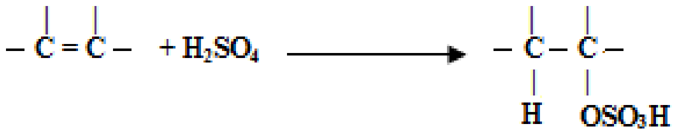


If the reaction takes place in the absence of peroxide, the addition of HBr, to alkenes follows Markovnikov's rule. On the other hand, if the reaction takes place in the presence of peroxide, HBr adds to alkenes in the reverse direction.

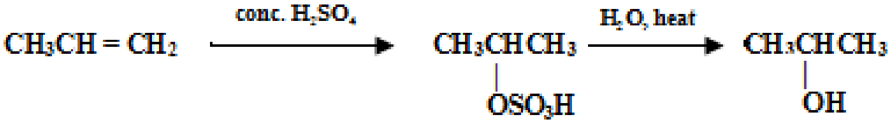


4- Addition of sulfuric acid

Alkenes are slowly absorbed when they are bubbled through, or shaken with, cold concentrated sulphuric acid. The reaction involves the addition of H and HSO_4 groups across the double bond, to form alkyl hydrogen sulfates, which is on dilution with water and heating yield alcohol.

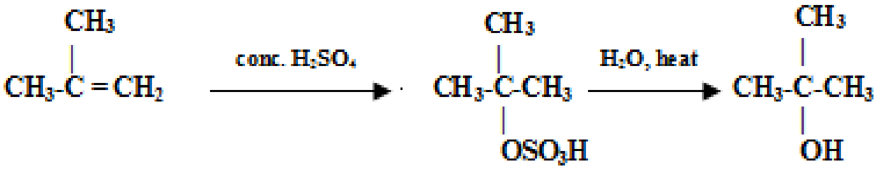


$$-\overset{|}{C}=\overset{|}{C}- \; + H_2SO_4 \longrightarrow -\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{OSO_3H}{|}}{\overset{|}{C}}-$$



$$CH_3CH=CH_2 \xrightarrow{\text{conc. } H_2SO_4} CH_3\underset{\underset{OSO_3H}{|}}{CH}CH_3 \xrightarrow{H_2O\text{, heat}} CH_3\underset{\underset{OH}{|}}{CH}CH_3$$

Propene | Isopropyl hydrogen sulfate | Isopropyl alcohol

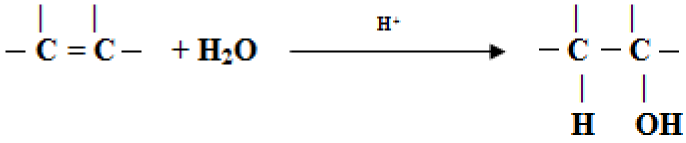


$$CH_3\text{-}\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{\text{conc. } H_2SO_4} CH_3\text{-}\underset{\underset{OSO_3H}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3 \xrightarrow{H_2O\text{, heat}} CH_3\text{-}\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH_3$$

Isobutylene | *tert*-Butyl hydrogen sulfate | *tert*-Butyl alcohol

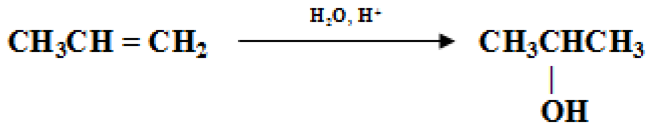
5- Addition of water. Hydration

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



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

Alkene | Alcohol

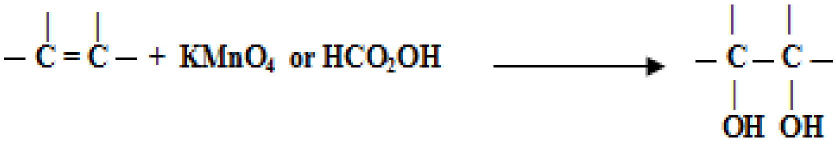


$$CH_3CH=CH_2 \xrightarrow{H_2O,\ H^+} \underset{\displaystyle OH}{CH_3\overset{}{C}HCH_3}$$

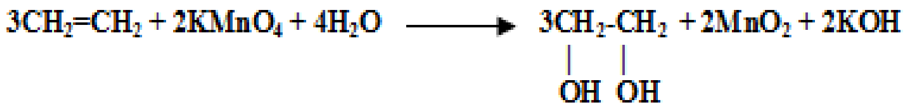
Propene (Propylene) → 2-Propanol (Isopropyl alcohol)

6- Hydroxylation – glycol formation

Alkanes are highly resistant to chemical oxidizing agents under normal conditions. In contrast, alkenes are quite sensitive to oxidation by several oxidizing agent. If an alkene is shaken with a few drops of a dilute acidified solution of $KMnO_4$, the purple solution is rapidly decolorized. The alkene is oxidized to an addition product, in which two hydroxyl groups have been added across the carbon-carbon double bond; the product is a di-alcohol or diol.

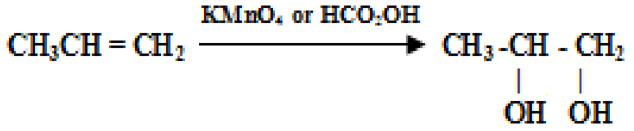


$$-\overset{|}{C}=\overset{|}{C}- + KMnO_4 \text{ or } HCO_2OH \longrightarrow -\underset{\underset{\displaystyle OH}{|}}{\overset{|}{C}}-\underset{\underset{\displaystyle OH}{|}}{\overset{|}{C}}-$$



$$3CH_2{=}CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{\underset{\displaystyle OH}{|}}{CH_2}\text{-}\underset{\underset{\displaystyle OH}{|}}{CH_2} + 2MnO_2 + 2KOH$$

Ethylene → 1,2-Ethanediol



$$CH_3CH=CH_2 \xrightarrow{KMnO_4 \text{ or } HCO_2OH} CH_3\text{-}\underset{\underset{\displaystyle OH}{|}}{CH}\text{-}\underset{\underset{\displaystyle OH}{|}}{CH_2}$$

HCO_2OH = Peroxyformic acid

Propene (Propylene) → 1,2-Propanediol (Propylene glycol)

7- 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.

$$n\,CH_2=CH_2 \xrightarrow[\text{pressure}]{O_2,\ \text{heat}} -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

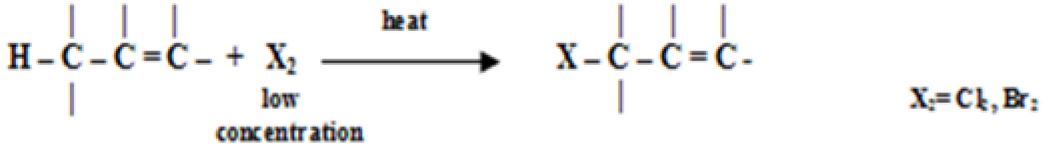
$$\text{or}\quad (-CH_2-CH_2-)_n$$

Ethylene **Polyethylene**

(Substitution Reactions)

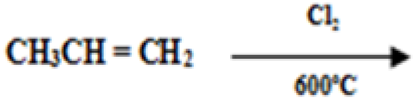
Halogenation. Allylic substitution

Alkenes react with halogens, substitution reaction. The reaction carried out as follow:



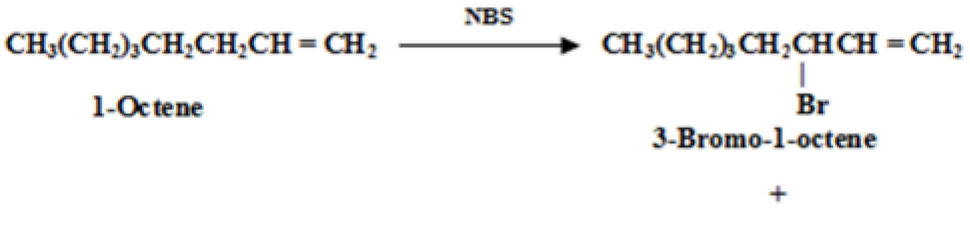
$$H-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}- + X_2 \xrightarrow[\text{low concentration}]{\text{heat}} X-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{C}-$$

$X_2 = Cl_2, Br_2$



$$CH_3CH=CH_2 \xrightarrow[600°C]{Cl_2} ClCH_2CH=CH_2$$

Propene (Propylene) → 3-Chloro-1-propene (Allyl chloride)



$$CH_3(CH_2)_3CH_2CH_2CH=CH_2 \xrightarrow{NBS} CH_3(CH_2)_3CH_2\underset{\underset{Br}{|}}{CH}CH=CH_2$$

1-Octene → 3-Bromo-1-octene

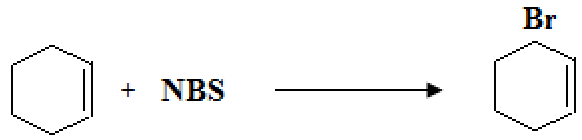
+

$$CH_3(CH_2)_3CH_2CH=CH\underset{\underset{Br}{|}}{CH_2}$$

1-Bromo-2-octene

Rearrangement product

NBS = *N*-Bromosuccinimide



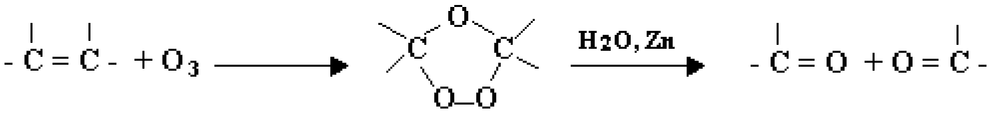
Cyclohexene

3-Bromocyclohexene

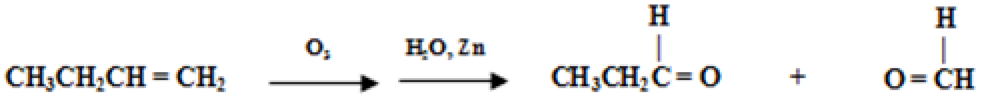
(Cleavage Reactions)

Ozonolysis

O_3 (ozone) is produced by passage of an electric discharge through oxygen O_2. If the mixture of gases is bubbled through a solution of an alkene at low temperature, an unstable product known as an ozonide is formed. Ozonides are unstable and are readily hydrolysed to form aldehydes or ketones.



Ozone **Ozonide** **Aldehydes and ketones**

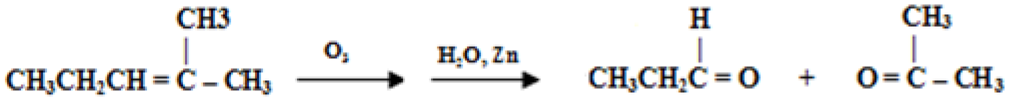


$$CH_3CH_2CH=CH_2 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn} CH_3CH_2\overset{H}{\overset{|}{C}}=O + O=\overset{H}{\overset{|}{C}}H$$

1-Butene

Propionaldehyde

Formaldehyde



$$CH_3CH_2CH=\overset{\mathrm{CH3}}{\overset{|}{C}}-CH_3 \xrightarrow{O_3} \xrightarrow{H_2O,\ Zn} CH_3CH_2\overset{H}{\overset{|}{C}}=O + O=\overset{CH_3}{\overset{|}{C}}-CH_3$$

2-Methyl-2-pentene

Propionaldehyde

Acetone

Organic Chemistry I

University of Anbar /College of Engineering
Chem. & Petrochemical Eng. Department
1st Year   2019 - 2020

Dr.Hamad K. Abdul Kadir

Assistant Prof. In Chemistey

Lecture - 3

Alkynes

3.1 Introduction

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 $\mathbf{C_nH_{2n-2}}$.

$HC \equiv CH$	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

3.2 Nomenclature

The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl group.

$\mathbf{H - C \equiv C - C_2H_5}$	**(Ethylacetylene) 1-Butyne**
$\mathbf{CH_3 - C \equiv C - CH_3}$	**(Dimethylacetylene) 2-Butyne**
$\mathbf{CH_3 - C \equiv C - CH(CH_3)_2}$	**(Isopropylmethylacetylene) 4-Methyl-2-pentyne**

For more complicated alkyne the IUPAC names are used. The rules are exactly as for the alkenes, except that the ending **-yne** is used in place of **–ene**.

$HC{\equiv}CCH_2CH_3$

1-Butyne

$CH_3C{\equiv}CCH_3$

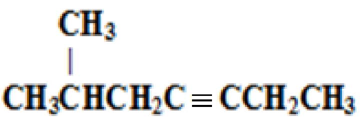
2-Butyne

$CH_3C{\equiv}CCH_2CH_3$

2-Pentyne

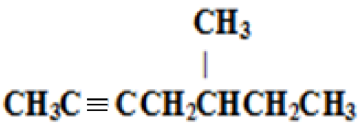
$CH_3CH{=}CHCH_2C{\equiv}CH$

4-Hexen-1-yne



$$\overset{CH_3}{\overset{|}{CH_3CH}}CH_2C{\equiv}CCH_2CH_3$$

6-Methyl-3-heptyne



$$CH_3C{\equiv}CCH_2\overset{CH_3}{\overset{|}{CH}}CH_2CH_3$$

5-Methyl-2-heptyne

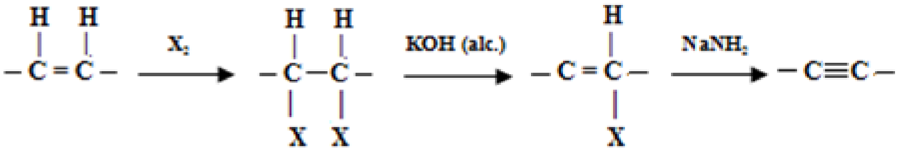
3.3 *Physical Properties of Alkynes*

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.

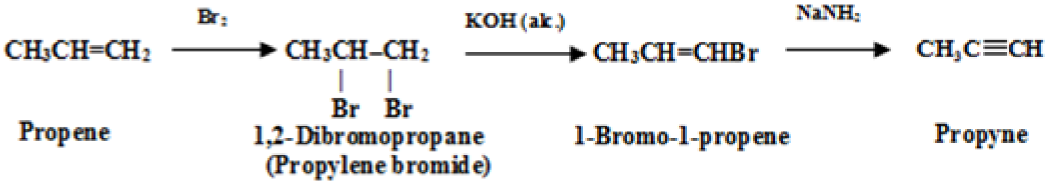
3.4 *Preparation of Alkynes*

1- Dehydrohalogenation of alkyl halides

A carbon-carbon triple bond is formed in the same way as a double bond: elimination of atoms or groups from two adjacent carbons.



$$-\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}- \xrightarrow{X_2} -\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}- \xrightarrow{\text{KOH (alc.)}} -C{=}\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}- \xrightarrow{NaNH_2} -C{\equiv}C-$$



$$CH_3CH{=}CH_2 \xrightarrow{Br_2} CH_3\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow{\text{KOH (alc.)}} CH_3CH{=}CHBr \xrightarrow{NaNH_2} CH_3C{\equiv}CH$$

2- 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.

$$-C\equiv C-H \xrightarrow{LiNH_2} -C\equiv C{:}^{-}Li^{+} + \underset{\text{R must be }1^{o}}{RX} \longrightarrow -C\equiv C-R + LiX$$

$$HC\equiv C{:}^{-}Li^{+} + CH_3CH_2CH_2CH_2Br \longrightarrow HC\equiv C-CH_2CH_2CH_2CH_3 + LiBr$$

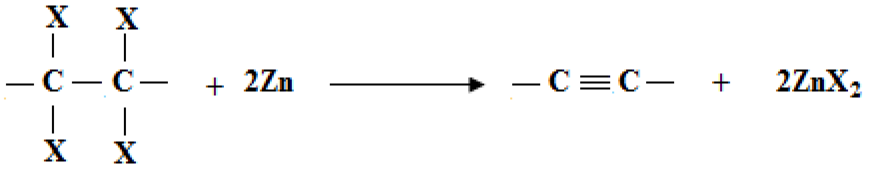
Lithium acetylide *n*-Butyl bromide **1-Hexyne**
(*n*-Butylacetylene)

$$CH_3(CH_2)_4C\equiv C\text{-}Li + CH_3(CH_2)_3CH_2Cl \longrightarrow CH_3(CH_2)_4C\equiv C-CH_2(CH_2)_3CH_3$$

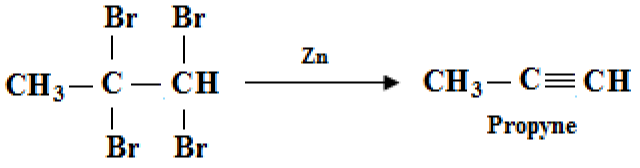
Lithium *n*-pentylacetylide **_n_-Pentyl chloride** **6-Dodecyne**

3- Dehalogenation of tetrahalides

Alkynes can be prepared by dehalogenation of tetrahalides.



$$-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}- + 2Zn \longrightarrow -C\equiv C- + 2ZnX_2$$



$$CH_3-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}H \xrightarrow{Zn} CH_3-C\equiv CH$$

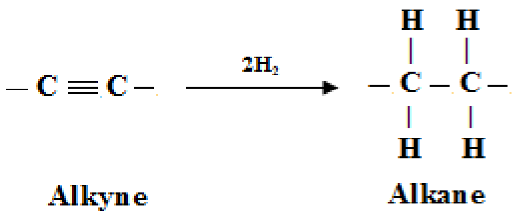
3.5 Reactions of Alkynes

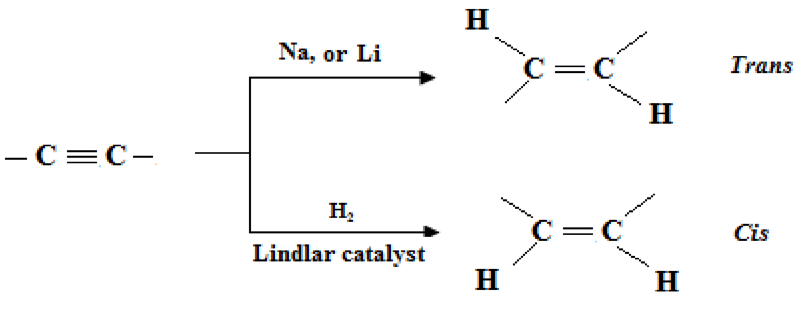
The carbon-carbon triple bond –C≡C– consists of one σ-bond and two weaker π-bonds, so it is not surprising that addition reactions are a characteristic feature of this functional group. Despite its high formal unsaturation, the triple bond dose not usually react so vigorously as a carbon-carbon double 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.

(Addition Reactions)

1- Addition of hydrogen

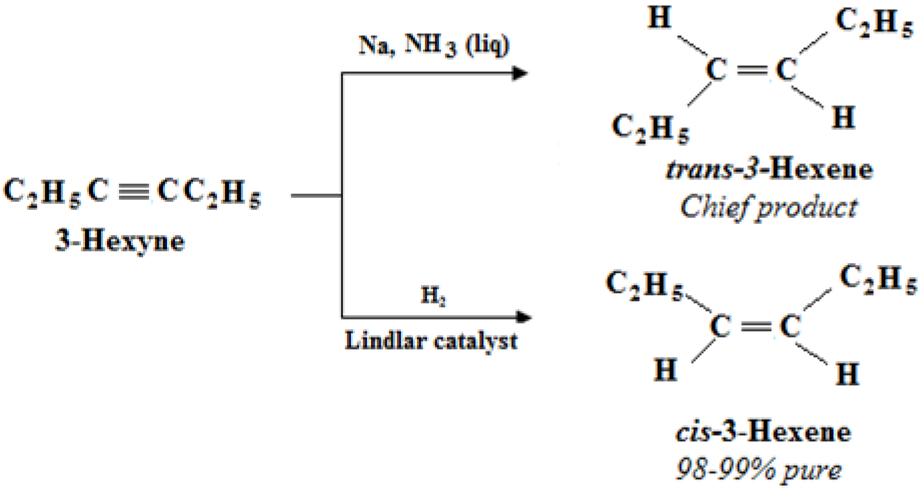
As would be expected, alkynes can be hydrogenated catalytically, taking up 2 mol of hydrogen per mol of alkyne to form the corresponding saturated molecule. Careful control of the hydrogenation can stop the reaction at the alkene stage.





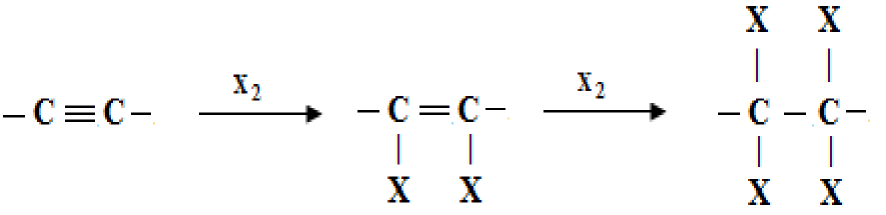
$$CH_3\text{-}C\equiv C\text{-}CH_3 \xrightarrow{2H_2,\ Ni} CH_3CH_2CH_2CH_3$$

2-Butyne **n-Butane**



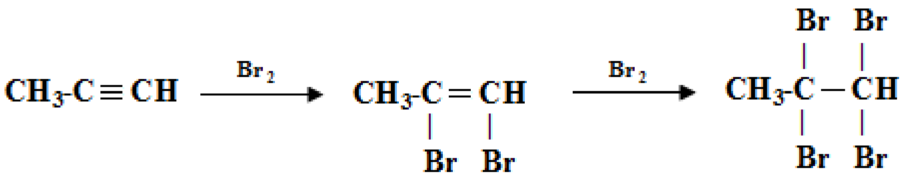
2- Addition of halogen

Alkynes can react with chlorine and bromine to yield tetrahaloalkanes. A dihaloalkene is an intermediate.



$$-C\equiv C- \xrightarrow{X_2} -\underset{X}{\underset{|}{C}}=\underset{X}{\underset{|}{C}}- \xrightarrow{X_2} -\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-$$

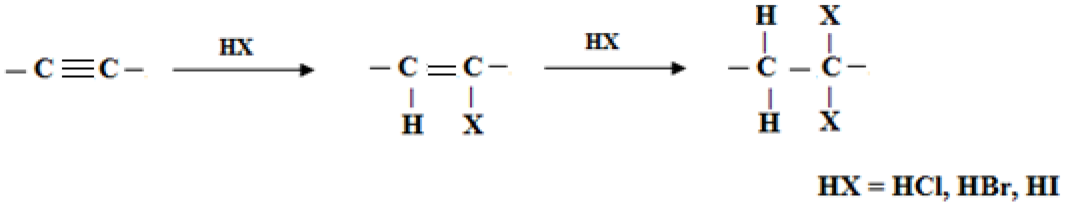
$X_2 = Cl_2, Br_2$

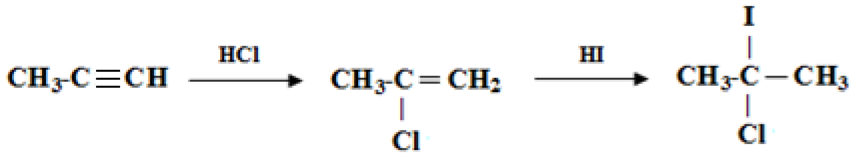


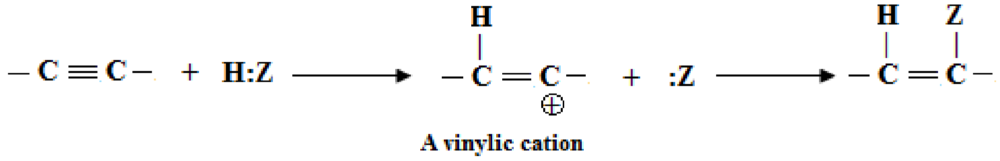
$$CH_3\text{-}C\equiv CH \xrightarrow{Br_2} CH_3\text{-}\underset{Br}{\underset{|}{C}}=\underset{Br}{\underset{|}{CH}} \xrightarrow{Br_2} CH_3\text{-}\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-\overset{Br}{\overset{|}{\underset{Br}{\underset{|}{CH}}}}$$

3- Addition of hydrogen halides

Alkynes also react with hydrogen halides to form alkyl halides. Addition of acids like hydrogen halides is electrophilic addition, and it appears to follow the same mechanism with alkynes as with alkenes: via an intermediate carbocation. The difference is that here the intermediate is a *vinylic cation*.

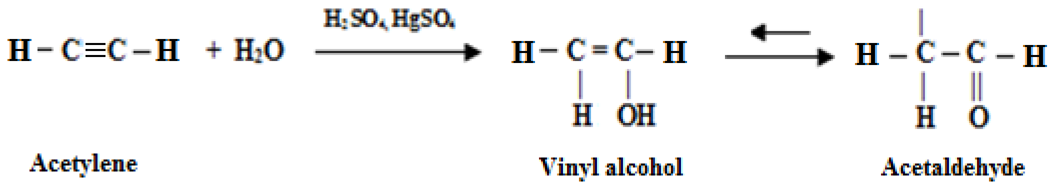






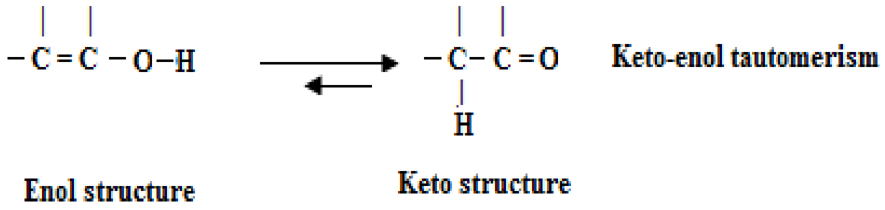
4- Addition of water (hydration)

In the presence of dilute sulphuric acid and a mercury(II) sulphate catalyst at about 60°C, water adds across a triple bond and alkyne is said to be hydrated.

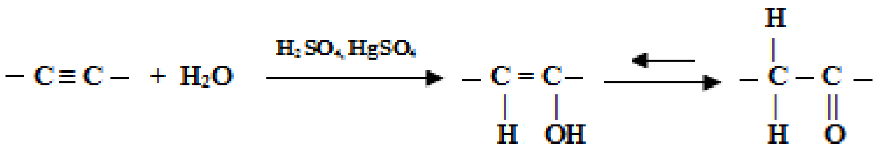


If hydration of acetylene followed the same pattern as hydration of alkenes, we would expect addition of H- and –OH to the triple bond to yield *vinyl alcohol*. But all attempts to prepare vinyl alcohol result, like hydration of acetylene, in the formation of acetaldehyde.

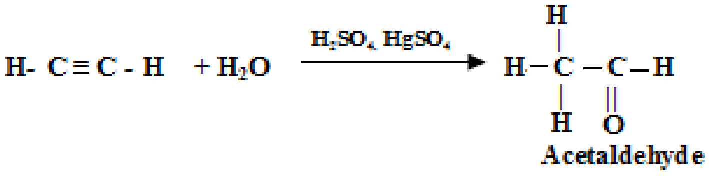
A structure with –OH attached to doubly bonded carbon is called **enol** (*-ene* for the carbon-carbon double bond, *-ol* for *alcohol*). It is almost always true that when we try to make a compound with the enol structure, we obtain instead a compound with **keto**structure (one that contains a C=O group). There is an equilibrium between the two structures, but it generally lies very much in favor of the keto form.



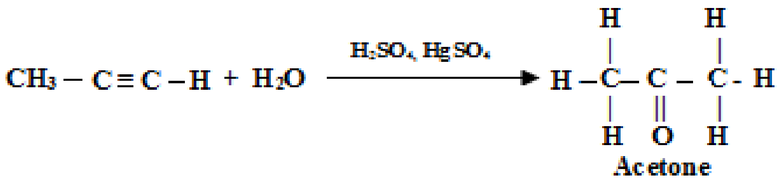
$$-\overset{|}{C}=\overset{|}{C}-O-H \rightleftharpoons -\underset{H}{\overset{|}{\underset{|}{C}}}-\overset{|}{C}=O$$



$$-C\equiv C- + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} -\underset{H}{\underset{|}{C}}=\underset{OH}{\underset{|}{C}}- \rightleftharpoons -\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-$$



$$H-C\equiv C-H + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-H$$



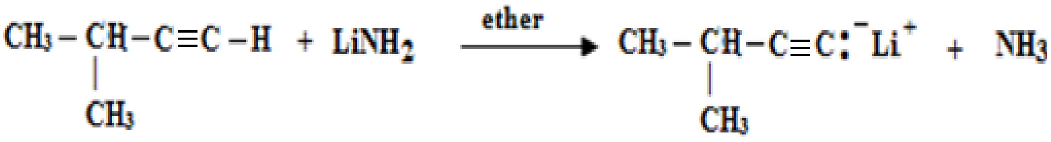
$$CH_3-C\equiv C-H + H_2O \xrightarrow{H_2SO_4,\ HgSO_4} H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$$

(Reaction as Acid)

$$-C{\equiv}C-H + \text{base} \longrightarrow -C{\equiv}C\!:^-$$

Formation of metal acetylides

Hydrogen attached to triply bonded carbon, as in acetylene or any alkyne with the triple bond at the end of the chain (RC≡C-H), shows appreciable acidity. So when a terminal triple bond is treated with an alkylmagnesium halide or an alkyllithium, the alkane is displaced from its salt, and the metal acetylide is obtained.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C{\equiv}C-H + LiNH_2 \xrightarrow{\text{ether}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C{\equiv}C\!:^-Li^+ + NH_3$$

Lithium isopropylacetylide

$$CH_3-C{\equiv}C-H + n\text{-BuLi} \longrightarrow CH_3C{\equiv}C^-Li^+ + n\text{-BuH}$$

Lithium methyacetylide

$$HC{\equiv}CH + C_2H_5MgBr \longrightarrow HC{\equiv}CMgBr + C_2H_6$$

Ethynylmagnesium bromide

Organic Chemistry I

University of Anbar /College of Engineering
Chem. & Petrochemical Eng. Department
1st Year   2019 - 2020

Dr.Hamad K. Abdul Kadir

Assistant Prof. In Chemistey

Lecture-4

Alcohols

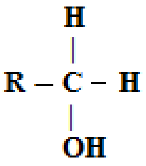
4.1 Introduction

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 double bond, 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.

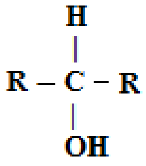
4.2 Classification of alcohols

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.



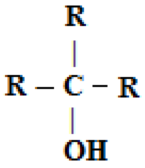
$$\begin{array}{c} H \\ | \\ R-C-H \\ | \\ OH \end{array}$$

Primary (1°)



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

Secondary (2°)

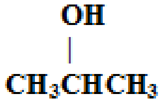


$$\begin{array}{c} R \\ | \\ R-C-R \\ | \\ OH \end{array}$$

Tertiary (3°)

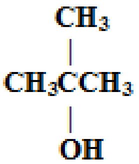
CH_3CH_2OH

Ethanol (1°)



$$\begin{array}{c} OH \\ | \\ CH_3CHCH_3 \end{array}$$

2-Propanol (2°)



$$\begin{array}{c} CH_3 \\ | \\ CH_3CCH_3 \\ | \\ OH \end{array}$$

2-Methyl-2-propanol (3°)

4.3 Nomenclature

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; CH_3OH 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.

CH_3OH

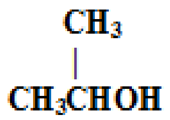
Methanol (Methyl alcohol)

CH_3CH_2OH

Ethanol (Ethyl alcohol)

$CH_3CH_2CH_2OH$

1-Propanol

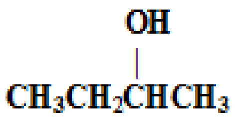


$CH_3\overset{\overset{CH_3}{|}}{C}HOH$

2-Propanol (Isopropyl alcohol)

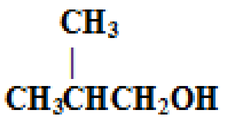
$CH_3CH_2CH_2CH_2OH$

1- Butanol



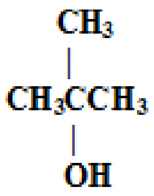
$CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_3$

2-Butanol (*sec*-Butyl alcohol)



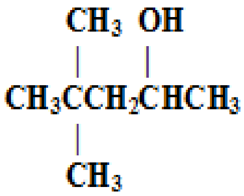
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2OH$

2-Methyl-1-propanol
(Isobutyl alcohol)



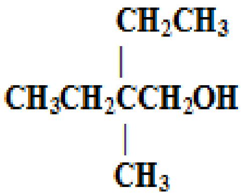
$CH_3\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_3$

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



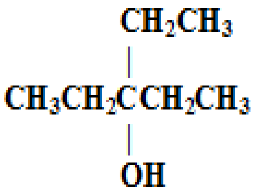
$CH_3\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}CH_2\overset{\substack{OH\\|}}{C}HCH_3$

4,4-Dimethyl-2-pentanol



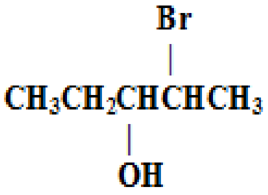
$CH_3CH_2\underset{\substack{|\\CH_3}}{\overset{\substack{CH_2CH_3\\|}}{C}}CH_2OH$

2-Ethyl-2-methyl-1-butanol



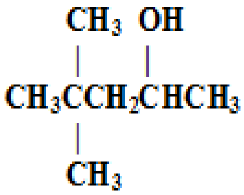
$CH_3CH_2\underset{\substack{|\\OH}}{\overset{\substack{CH_2CH_3\\|}}{C}}CH_2CH_3$

3-Ethyl-3-pentanol



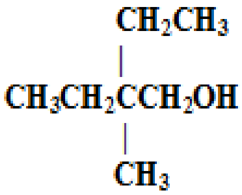
$CH_3CH_2\underset{\substack{|\\OH}}{C}H\overset{\substack{Br\\|}}{C}HCH_3$

2-Bromo-3-pentanol



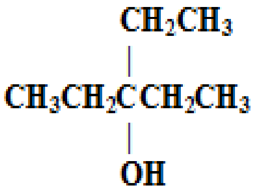
$CH_3\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}CH_2\overset{\substack{OH\\|}}{C}HCH_3$

4,4-Dimethyl-2-pentanol



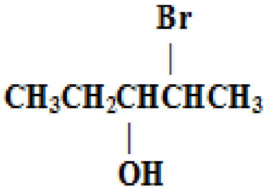
$CH_3CH_2\underset{\substack{|\\CH_3}}{\overset{\substack{CH_2CH_3\\|}}{C}}CH_2OH$

2-Ethyl-2-methyl-1-butanol



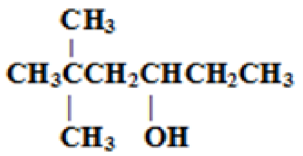
$CH_3CH_2\underset{\substack{|\\OH}}{\overset{\substack{CH_2CH_3\\|}}{C}}CH_2CH_3$

3-Ethyl-3-pentanol



$CH_3CH_2\underset{\substack{|\\OH}}{C}H\overset{\substack{Br\\|}}{C}HCH_3$

2-Bromo-3-pentanol

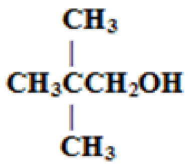


$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2\underset{\displaystyle OH}{CH}CH_2CH_3$$

5,5-Dimethyl-3-hexanol

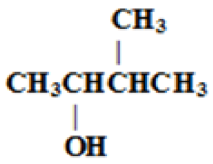
$ClCH_2CH_2OH$

2-Chloroethanol



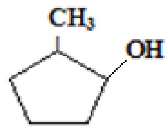
$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}CH_2OH$$

2,2-Dimethyl-1-propanol

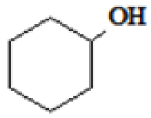


$$CH_3\underset{\displaystyle OH}{CH}\overset{\displaystyle CH_3}{CH}CH_3$$

3-Methyl-2-butanol

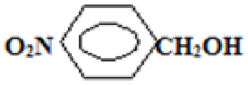


2-Methylcyclopentanol



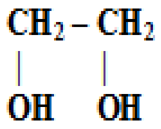
Cyclohexanol

(Benzyl alcohol)



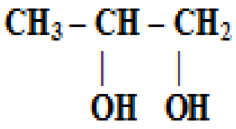
(*p*-Nitrobenzyl alcohol)

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.



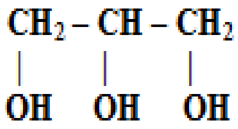
$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle OH}{CH_2}$$

1,2-Ethanediol
(Ethylene glycol)



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

1,2-Propanediol
(Propylene glycol)



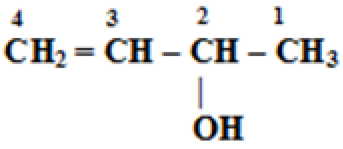
$$\underset{\displaystyle OH}{CH_2}-\underset{\displaystyle OH}{CH}-\underset{\displaystyle OH}{CH_2}$$

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.

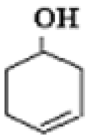
$\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2OH$

2-Propen-1-ol



$\overset{4}{C}H_2=\overset{3}{C}H-\underset{\displaystyle OH}{\overset{2}{C}H}-\overset{1}{C}H_3$

3-Buten-2-ol



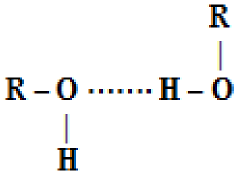
4-Cyclohexenol

4.4 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).

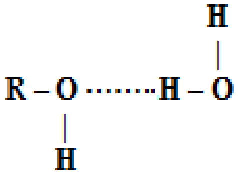
Force of attraction between alcohol molecules obviously must be greater than between molecules of alkanes. Hydrogen bonding accounts for this.

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:



$R-\underset{\displaystyle H}{O}\cdots\cdots H-\overset{\displaystyle R}{O}$

Intermolecular bonding



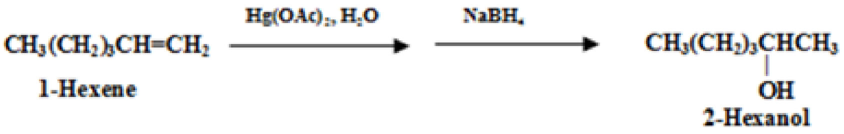
$R-\underset{\displaystyle H}{O}\cdots\cdots H-\overset{\displaystyle H}{O}$

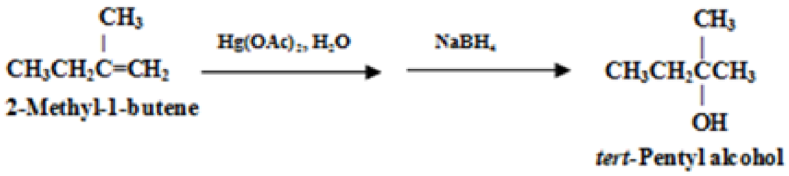
Hydrogen bonding with water

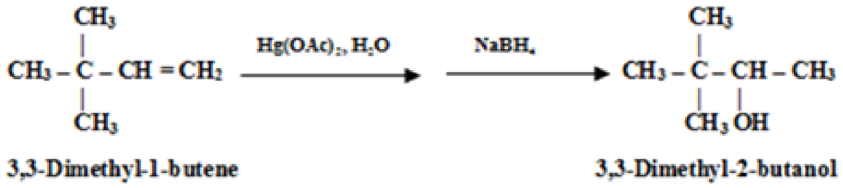
4.5 Preparation of Alcohols

1- Oxymercuration – demercuration

Alkenes react with mercuric acetate in the presence of water to give hydroxymercurial compounds which on reduction yield alcohols.

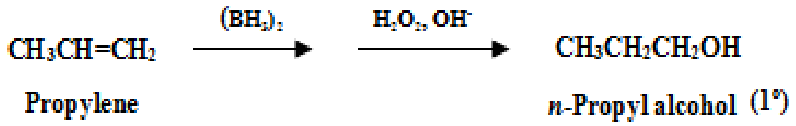




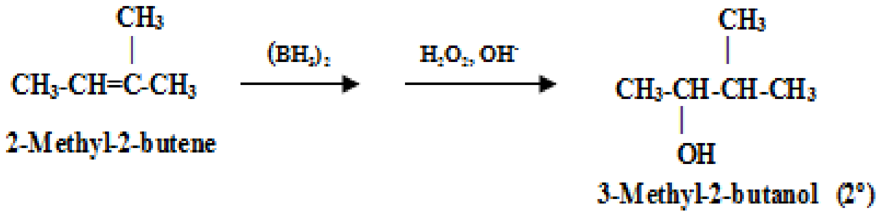


2-Hydroboration - oxidation

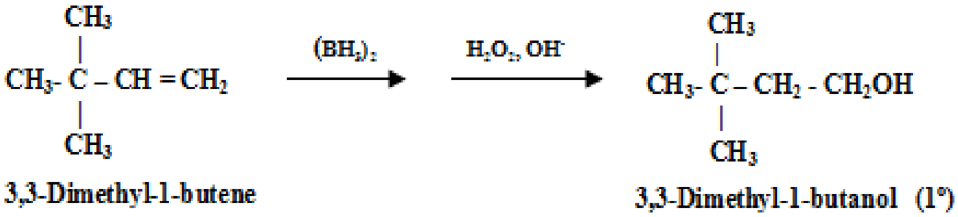
With the reagent diborane, $(BH_3)_2$, alkene undergo hydroboration to yield alkylboranes, which on oxidation give alcohols. Hydroboration involves addition of BH_3 to the double bond, with hydrogen becoming attached to one doubly bonded carbon, and boron to the other. The alkylborane can then undergo oxidation, in which the boron is replaced by -OH.



$$CH_3CH{=}CH_2 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3CH_2CH_2OH$$



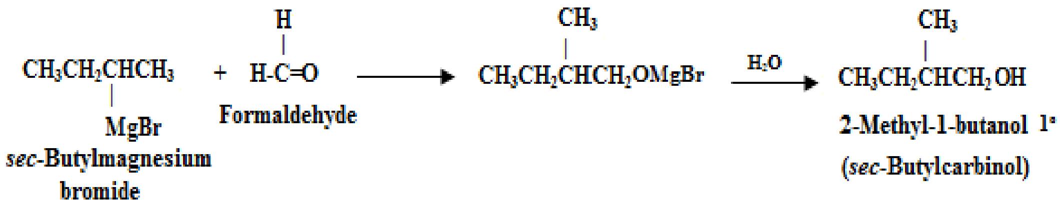
$$CH_3\text{-}CH{=}\overset{CH_3}{\overset{|}{C}}\text{-}CH_3 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_3$$



$$CH_3\text{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH=CH_2 \xrightarrow{(BH_3)_2} \xrightarrow{H_2O_2,\ OH^-} CH_3\text{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2\text{-}CH_2OH$$

3- Grignard reaction

One of the most important uses of the Grignard reagent lies in its reaction with aldehydes and ketones. The product is the magnesium salt of the weakly acidic alcohol and is easily converted into alcohol itself by the addition of the stronger acid, water.



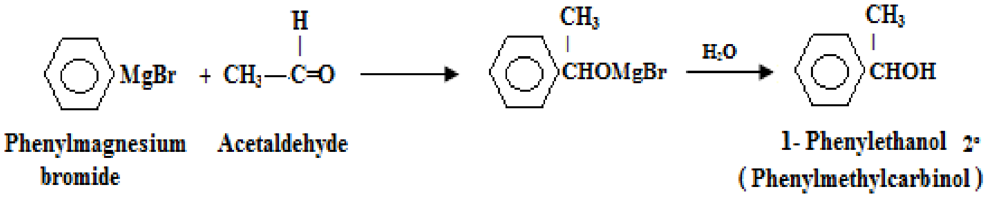
$$CH_3CH_2\underset{\substack{|\\ MgBr}}{CH}CH_3 + H\text{-}\overset{\substack{H\\ |}}{C}{=}O \longrightarrow CH_3CH_2\overset{\substack{CH_3\\ |}}{C}HCH_2OMgBr \xrightarrow{H_2O} CH_3CH_2\overset{\substack{CH_3\\ |}}{C}HCH_2OH$$

sec-Butylmagnesium bromide

Formaldehyde

2-Methyl-1-butanol 1°

(*sec*-Butylcarbinol)

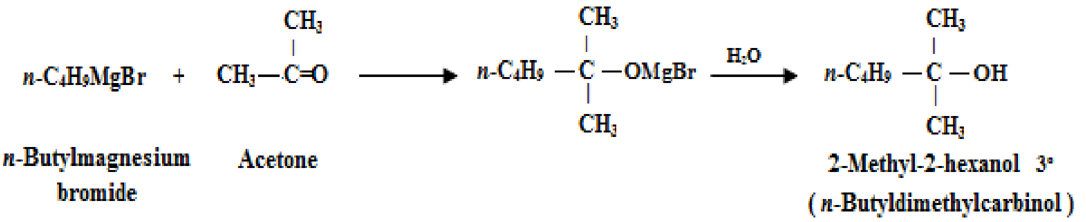


Phenylmagnesium bromide

Acetaldehyde

1- Phenylethanol 2°

(Phenylmethylcarbinol)



$$n\text{-}C_4H_9MgBr + CH_3\text{—}\overset{\substack{CH_3\\ |}}{C}{=}O \longrightarrow n\text{-}C_4H_9\text{—}\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}\text{—}OMgBr \xrightarrow{H_2O} n\text{-}C_4H_9\text{—}\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{C}}\text{—}OH$$

n-Butylmagnesium bromide

Acetone

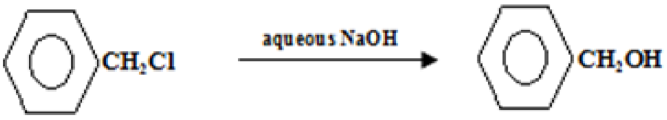
2-Methyl-2-hexanol 3°

(*n*-Butyldimethylcarbinol)

4- Hydrolysis of alkyl halides

Alcohols can be prepared by the hydrolysis of alkyl halides.

$$R\text{-}X + OH^- \text{ (or } H_2O) \longrightarrow R\text{-}OH + X^- \text{ (or } HX)$$

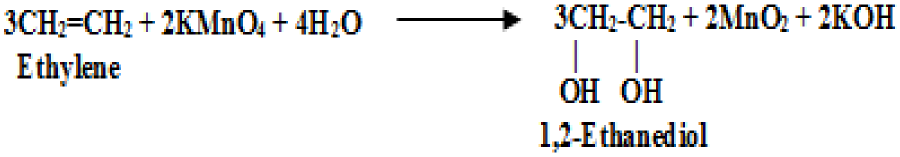


Benzyl chloride

Benzyl alcohol

5- Hydroxylation of alkenes

Certain oxidizing agents convert alkenes into 1,2-diols:dihydroxy alcohols containing the two –OH groups on adjacent carbons. (They are also known as *glycols*).



$$3CH_2{=}CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{OH}{\underset{|}{C}H_2}-\underset{OH}{\underset{|}{C}H_2} + 2MnO_2 + 2KOH$$

Organic Chemistry

College of Engineering / University of Anbar
Dept. of Chem. & Petrochem.Eng.
1st Year / 2019 -2020
Lecture-5

Ethers

By

Assist. Prof. Dr. Hamad K. Abdul Kadir

Introduction 9.1

Compounds in whose molecules two organic groups are joined to the same oxygen atom are called ethers:

R-O-R or Ar-O-R or Ar-O-Ar

9.2 Nomenclature

The common names of simple ethers are made by naming the groups attached to oxygen and follow these names by word ether.

CH_3OCH_3

Dimethyl ether

$C_2H_5OC_2H_5$

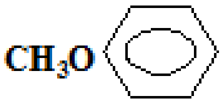
Diethyl ether

$CH_3OC_2H_5$

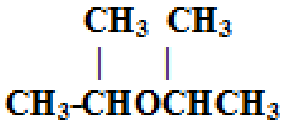
Ethyl methyl ether

$CH_3CH_2CH_2OCH_2CH_2CH_3$

Dipropyl ether

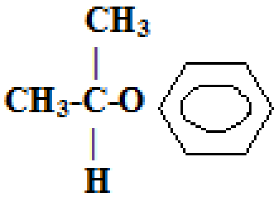


Methyl phenyl ether



$$CH_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{C}HO\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$$

Diisopropyl ether



Isopropyl phenyl ether

$CH_3CH_2CH_2OCH(CH_3)_2$

Isopropyl *n*-propyl ether

In the IUPAC system, ethers are named by selecting the longest carbon chain as the parent alkane and naming the .**–OR** group attached to it as alkoxy group

OCH_3 methoxy-

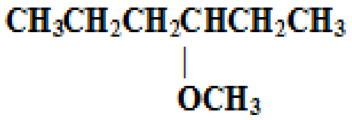
.OCH_2CH_3 ethoxy …….etc-

$CH_3OCH_2CH_2CH_3$

1-Methoxypropane

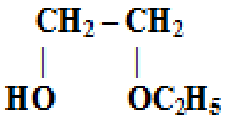
$CH_3CH_2CH_2CH_2OCH_2CH_3$

1-Ethoxybutane



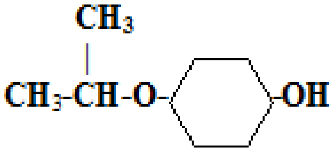
$$\underset{OCH_3}{CH_3CH_2CH_2\underset{|}{C}HCH_2CH_3}$$

3-Methoxyhexane

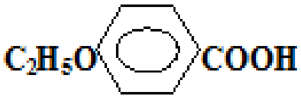


$$\underset{HO}{\overset{CH_2}{|}} - \underset{OC_2H_5}{\overset{CH_2}{|}}$$

2-Ethoxyethanol



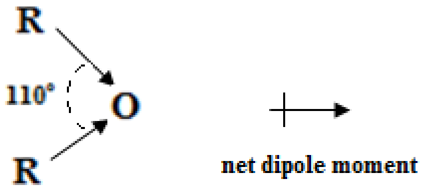
4-Isopropoxycyclohexanol



p-Ethoxybenzoic acid

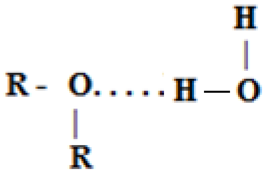
Physical Properties of Ethers 9.3

Since the C-O-C bond angle is not 180°, the dipole moment of the two C-O bonds do not cancel each other; .consequently, ethers possess a small net dipole moment



This weak polarity does not appreciably affect the boiling point of the ethers, which are about the same as those of alkanes having comparable molecular weights, and much lower than those of isomeric alcohols. The hydrogen bonding that holds alcohol molecules strongly together is not possible for ethers, since they contain hydrogen bonded only to carbon.

On the other hand, ethers show solubility in water comparable to that of the alcohols, both diethyl ether and *n*-butyl alcohol, for example, being soluble to the extent of about 8 g per 100 g water. We attributed the water solubility of the lower alcohols to hydrogen bonding between water molecules and alcohol molecules; the .water solubility of ether arises in the same way



Hydrogen bonding with water

Preparation of Ethers 9.4

Williamson synthesis -1

In the Williamson synthesis an alkyl halide (or substituted alkyl halide) is allowed to react with a sodium .alkoxide or sodium phenoxide

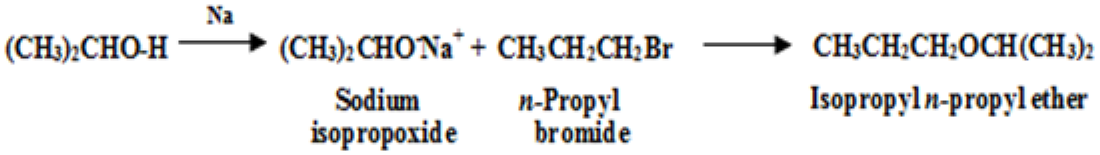
sodium alkoxide

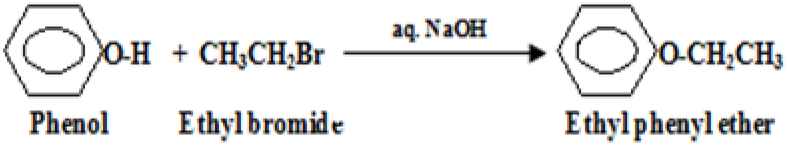
$R'O^-Na^+$ $\qquad$ $R\text{-}OR'$

$RX + \text{ or } \longrightarrow \text{ or}$

ArO^-Na^+ $\qquad$ $R\text{-}OAr$

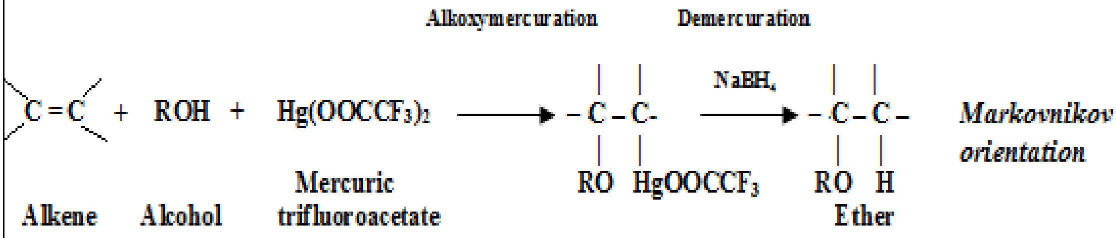
sodium phenoxide

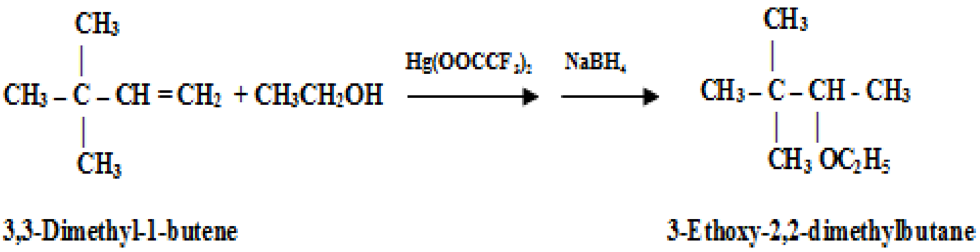




Alkoxymercuration – demercuration -2

Alkenes react with mercuric trifluoroacetate in the presence of an alcohol to give alkoxymercurial compounds .which on reduction yield ether





Reactions of Ethers 9.5

Ethers are comparatively unreactive compounds. The ether C–O –C linkage is quite stable toward bases, oxidizing agents, and reducing agents. In so far as the ether linkage itself is concerned, ethers undergo just one kind of reactions, cleavage by acids. It takes place only under quite vigorous conditions.

Cleavage by acids

A more widely used method of cleaving ethers, .involves reacting with HX

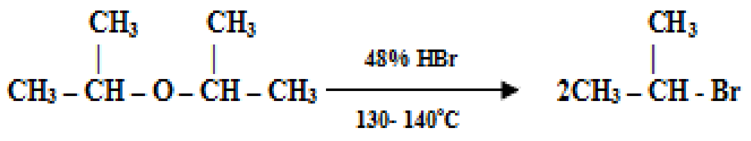
$$R-O-R' + HX \longrightarrow R-X + R'-OH \xrightarrow{HX} R'-X$$

$$Ar-O-R + HX \longrightarrow R-X + Ar-OH$$

$$\text{Reactivity of HX: } HI > HBr > HCl$$

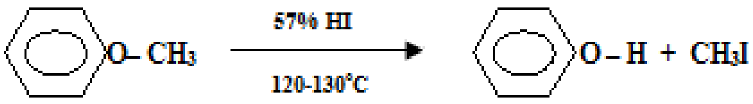
Cleavage takes place only under quite vigorous conditions: concentrated acids (usually HI or HBr) and high .temperatures

A dialkyl ether yields initially an alkyl halide and an alcohol; the alcohol may react further to form a second .mole of halide



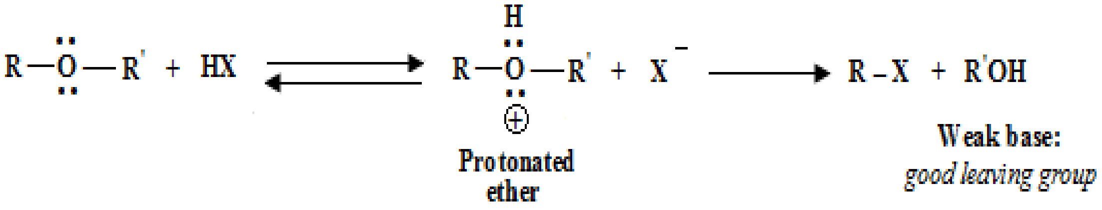
$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}H}-O-\overset{CH_3}{\overset{|}{C}}H-CH_3 \xrightarrow[130\text{-}140^\circ C]{48\%\ HBr} 2CH_3-\overset{CH_3}{\overset{|}{C}}H-Br$$

Diisopropyl ether Isopropyl bromide



Anisol Phenol Methyl iodide

Cleavage involves nucleophilic attack by halide ion on this protonated ether, with displacement of the weakly basic .alcohol molecule



Organic Chemistry I

University of Anbar /College of
Engineering Chem. & Petrochemical Eng.
Department 1st Year 2019 - 2020

Dr.Hamad K. Abdul Kadir
Assistant Prof. In Chemistey

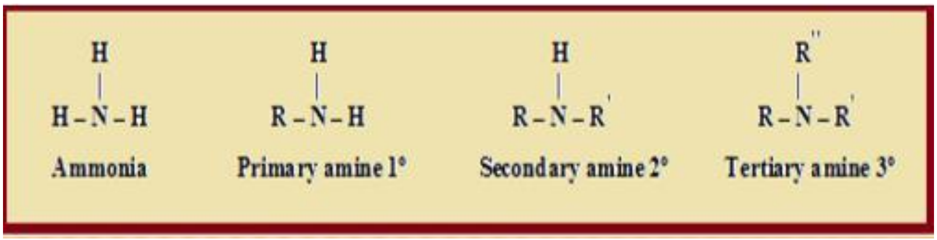
Lecture-6

Amines

12.1 Introduction

The amines are basic, proton-accepting compounds. One, two or three hydrogen atoms on a molecule of ammonia can be replaced by hydrocarbon group, and the resulting compounds are amines.

Amines are classified as primary, secondary, or tertiary, according to the number of groups attached to the nitrogen atom.

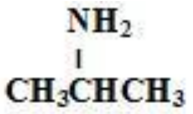


$$\begin{array}{cccc} \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{R''} \\ | & | & | & | \\ \mathrm{H-N-H} & \mathrm{R-N-H} & \mathrm{R-N-R'} & \mathrm{R-N-R'} \end{array}$$

Ammonia | Primary amine 1° | Secondary amine 2° | Tertiary amine 3°

12.2 Nomenclature

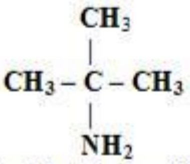
Systematic names for aliphatic amines are derived just as they are for alcohols. The suffix –e of the parent alkane is dropped and is replaced by –amine.



$$\begin{array}{c} \mathrm{NH_2} \\ | \\ \mathrm{CH_3CHCH_3} \end{array}$$

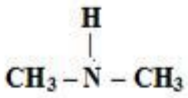
2-Propanamine

Common names for most aliphatic amines are derived by naming the alkyl group or groups attached to nitrogen, and following these by the word **–amine**. More complicated ones are often named by prefixing **amino-** (or *N*-methylamino-, *N*,*N*-dimetylamino-, etc.) to the name of the parent chain.



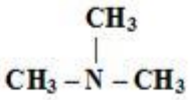
$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3-C-CH_3} \\ | \\ \mathrm{NH_2} \end{array}$$

***tert*-Butylamine (1°)**



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{CH_3-N-CH_3} \end{array}$$

Dimethylamine (2°)



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3-N-CH_3} \end{array}$$

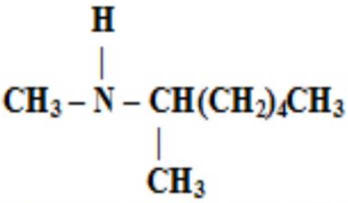
Trimethylamine (3°)

$H_2NCH_2CH_2CH_2COOH$

γ-Aminobutyric acid (1°)

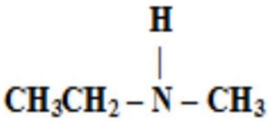
$H_2NCH_2CH_2OH$

2-Aminoethanol (1°)
(Ethanolamine)



$CH_3-N(H)-CH(CH_3)(CH_2)_4CH_3$

2-(*N*-Methylamino)heptane (2°)

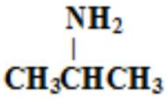


$CH_3CH_2-N(H)-CH_3$

Ethylmethylamine (2°)

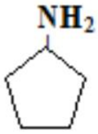
$CH_3CH_2CH_2NHCH_3$

Methylpropylamine (2°)

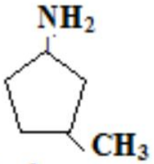


$CH_3CH(NH_2)CH_3$

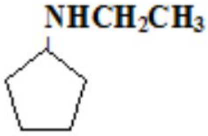
Isopropylamine (1°)



Cyclopentaneamine (1°)

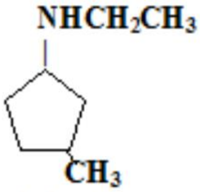


3-Methylcyclopentaneamine (1°)



N-Ethylcyclopentaneamine

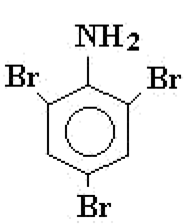
(2°)



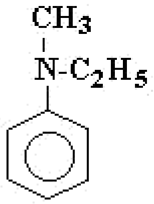
N-Ethyl-3-methylcyclopentaneamine

(2°)

IUPAC nomenclature retains the common name aniline for $C_6H_5NH_2$. Its simple derivatives are named using the prefixes -*o*,-*m*, and –*p*, or numbers to locate substituents. An aminotoluene is given the special name of *toluidine*.

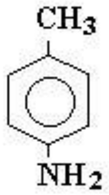


(2,4,6-Tribromoaniline) (1°)

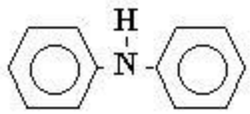


(*N*-Ethyl-*N*-methylaniline) (3°)

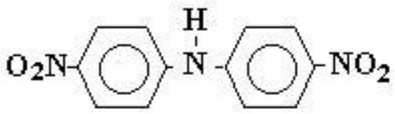
(*p*-Nitroso-*N,N*-dimethylaniline) (3°)



(*p*-Toluidine) (1°)



Diphenylamine (2°)



4,4-Dinitrodiphenylamine (2°)

Salts of amines are generally named by replacing **–amine** by **-ammonium** (or **–aniline** by **–anilinium**), and adding the name of the anion (chloride, nitrate, sulfate, etc.). For example:

$(C_2H_5NH_3^+)_2SO_4^{2-}$	$(CH_3)_3NH^+NO_3^-$	$C_6H_5NH_3^+Cl^-$
Ethylammonium sulfate	**Trimethylammonium nitrate**	**Anilinium chloride**

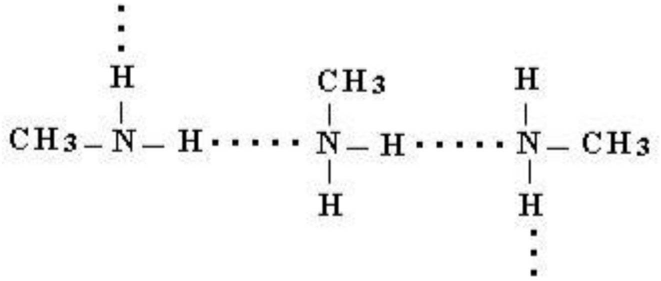
12.3 Physical Properties of Amines

Amines are moderately polar. For this reason the low formula weight amines are readily soluble in water due to the formation of hydrogen bonds with water. They have higher boiling points than non-polar compounds of the same molecular weight, because of the formation of intermolecular hydrogen bonds, except for tertiary amines.

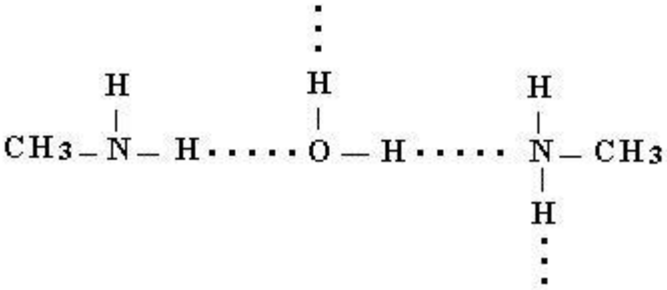
Amines are soluble in less polar solvents like ether, alcohol, benzene, etc. The methylamines and ethylamines smell very much like ammonia; the higher alkylamines have decidedly fishy odors.

Aromatic amines are generally very toxic; they are readily absorbed through the skin, often with fatal results.

Aromatic amines are very easily oxidized by air, and although most are colorless when pure, they are often encountered discolored by oxidation products.



(Intermolecular H bonds)



(H bonds with water)

12.4 Preparation of Amines

1- Reduction of nitro compounds

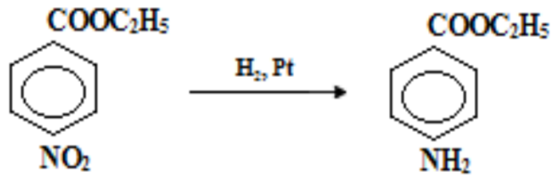
Nitro compounds can be reduced in two general ways: (a) by catalytic hydrogenation using molecular hydrogen, or (b) by chemical reduction, usually by a metal and acid.

Hydrogenation of a nitro compound to an amine takes place smoothly when a solution of nitro compound in alcohol is shaken with finely divided nickel or platinum under hydrogen gas.

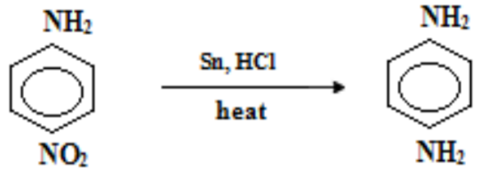
$$\begin{matrix} Ar-NO_2 \\ \text{or} \\ R-NO_2 \end{matrix} \xrightarrow{\text{metal, } H^+ \text{ or } H_2\text{, catalyst}} \begin{matrix} Ar-NH_2 \\ \text{or} \\ R-NH_2 \end{matrix}$$

Chiefly for aromatic amines

Nitrocompound **1° Amine**



Ethyl *p*-nitrobenzoate **Ethyl *p*-aminobenzoate**



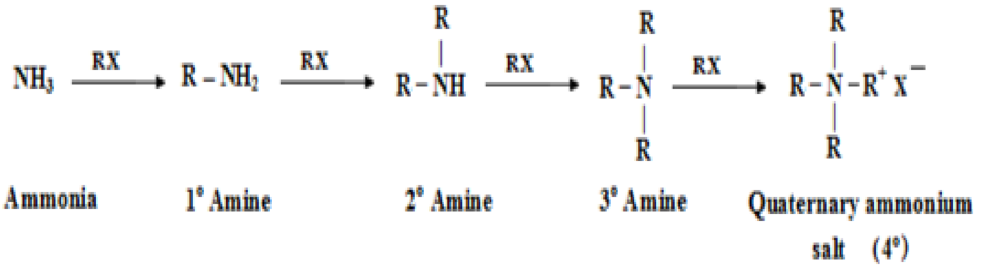
***p*-Nitroaniline** ***p*-Phenylenediamine**

$$CH_3CH_2CH_2NO_2 \xrightarrow{\text{Fe, HCl}} CH_3CH_2CH_2NH_2$$

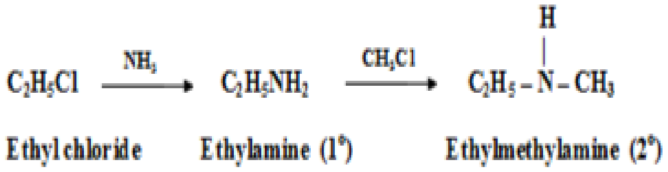
1-Nitropropane ***n*-Propylamine**

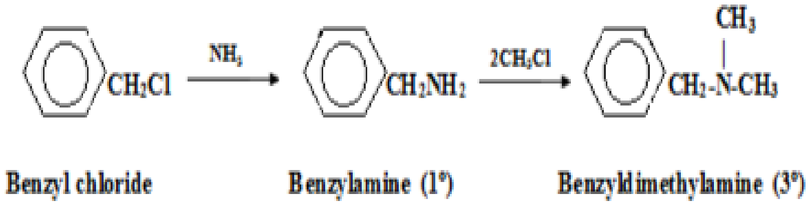
2- Reaction of halides with ammonia or amines

Many organic halogen compounds are converted into amines by treatment with aqueous or alcoholic solution of ammonia.



RX must be alkyl, or aryl with electrons-withdrawing substituents





Organic Chemistry

University of Anbar /College of Engineering
Chem. & Petrochemical Eng. Department
1st Year 2019 - 2020

Dr.Hamad K. Abdul Kadir

Assistant Prof. In Chemistey

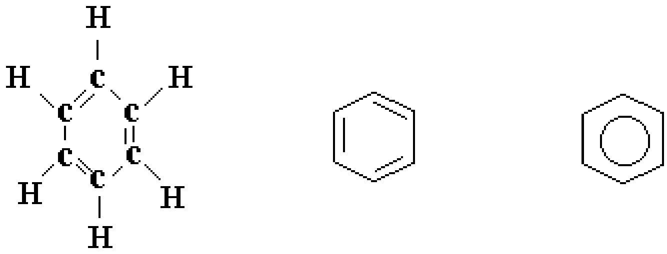
Lectures 7 & 8

Aromatic Hydrocarbons

9.1 Introduction

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.

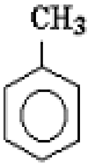
Benzene, the parent compound of this large family of organic substances, has the general formula $\mathbf{C_nH_{2n-6}}$.



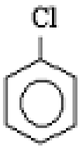
Kekulé structure

9.2 Nomenclature of Benzene Derivatives

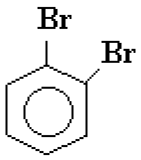
Substituted benzenes are named in a systematic manner by combining the substituent name with the word benzene. If more than one substituent is present, the location of the second group must be indicated relative to the first. Some substituted benzenes have special names like toluene, aniline, phenol and so on. We can use the abbreviation *o-* , *m-* and *p-* to indicate the position of the substituent. The IUPAC system retains certain common names for several of the simpler mono substituted alkyl benzene.

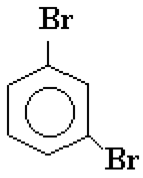


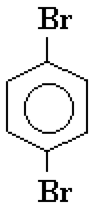
Methylebenzene
(Toluene)



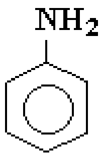
Chlorobenzene

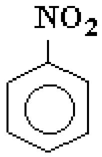




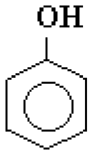


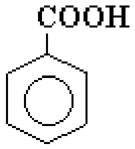
1,2-Dibromobenzene 1,3-Dibromobenzene 1,4-
Dibromobenzene
(*o*-Dibromobenzene) (*m*-Dibromobenzene) *(p*-
Dibromobenzene)



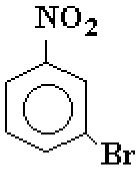


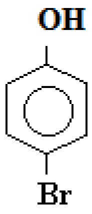
Aminobenzene Nitrobenzene
(Aniline)



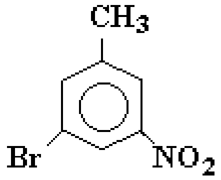


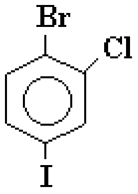
Hydroxybenzene Benzenecarboxylic
acid
(Phenol) (Benzoic acid)



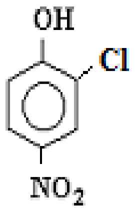


3-Bromonitrobenzen (*p*-
Bromophenol)
(*m*-Bromonitrobenzene)

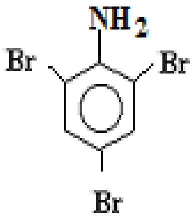




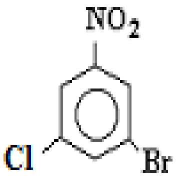
5-Bromo-3-nitrotoluene 2-Chloro-4-
iodobromobenzene



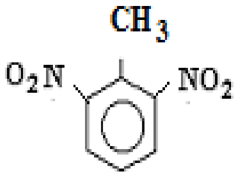
2-Chloro-4-nitrophenol



2,4,6-Tribromoaniline



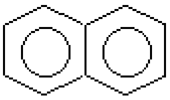
3-Bromo-5-chloronitrobenzene



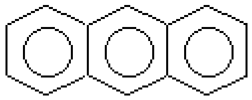
2,6-Dinitrotoluene

9.3 Polynuclear Aromatic Hydrocarbons

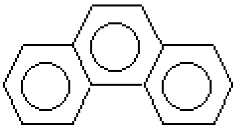
Two aromatic rings that share a pair of carbon atoms are said to be *fused*. The simplest and most important of these fused-ring hydrocarbon is *naphthalene* $C_{10}H_8$.



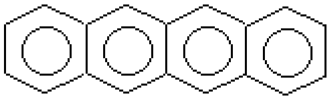
Naphthalene



Anthracene

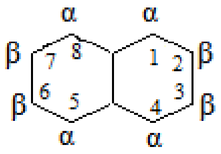


Phenanthrene

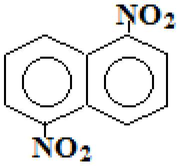


Naphthacene

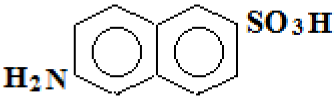
Positions in the naphthalene ring system are designated as shown:



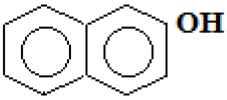
Two isomeric monosubstituted naphthalene are differentiated by the prefixes 1- and 2-, or α- and β-. The arrangement of groups in more highly substituted naphthalenes is indicated by numbers:



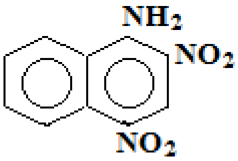
1,5-Dinitronaphthalene



6-Amino-2-naphthalenesulfonic acid



2-Naphthol
β-Naphthol

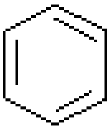


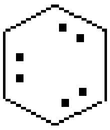
2,4-Dinitro-1-naphthylamine

9.4 Properties of Benzene

Benzene is a colorless, 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.

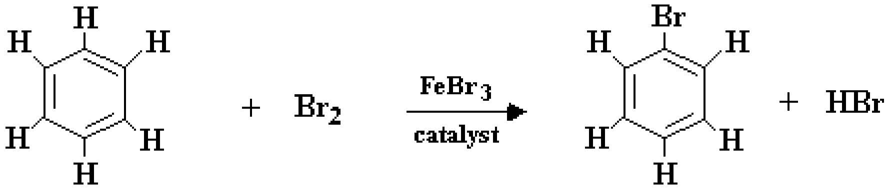
The stability of benzene is the result of electron delocalization; the electrons in the three pairs (pi e^-) circulate around the entire ring.



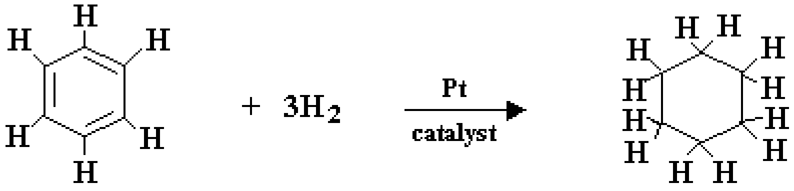


Having this much room, which the six electrons can move, the benzene molecule strongly resists any chemical event that might disrupt this closed circuit of electrons.

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.

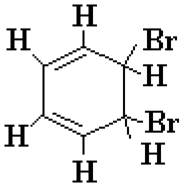


Addition reaction like hydrogenation, very difficult to happen, only with higher temperature and pressure than in the alkanes.



Benzene **Cyclohexane**

Note that if the reaction was addition, electron delocalization would be destroyed in the product:



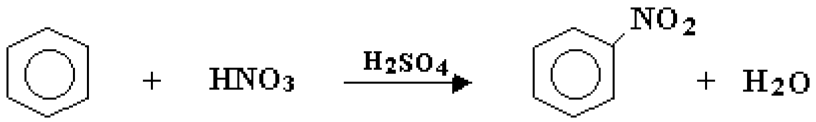
The molecule would not exhibit the usual aromatic characteristic of chemical unreactivity.

9.5 Reactions of Benzene

The particularly characteristic delocalized system of π-electrons within the benzene molecule means that benzene is not easily attacked by acids, alkalis or oxidizing agents, unlike other unsaturated compounds such as alkenes. Like alkenes, however, it does undergo some addition reactions, although substitution reactions are much more characteristic of benzene's chemical behavior.

1- Nitration

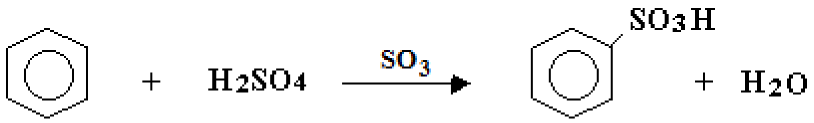
The substitution of one or more nitro group into the benzene ring is effected by the use of a special nitrating mixture of concentrated nitric and sulphuric acid.



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

2- Sulfonation

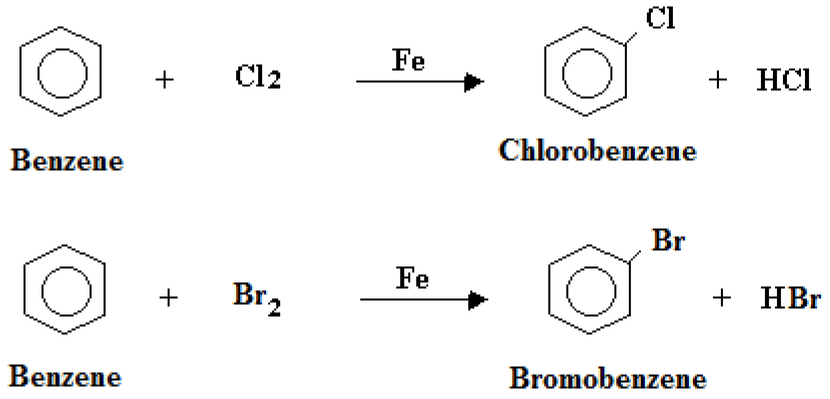
Under the same conditions of nitration, benzene is unattacked by concentrated sulphuric acid, but if it is heated under reflux for about 6 h with the concentrated acid, sulphonation takes place.



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

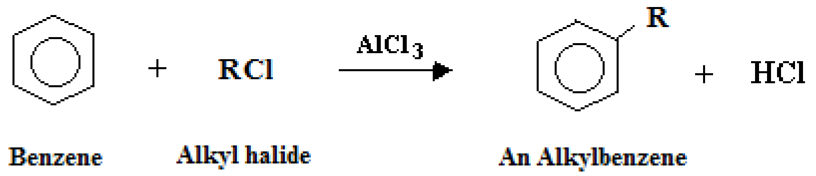
3- Halogenation

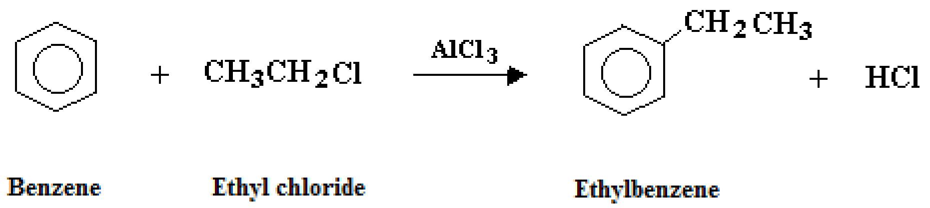
Benzene reacts with halogens in the presence of certain catalyst, such as iron or iron (III) or aluminum chloride, substituted compound being formed.



4- Friedel-Crafts alkylation

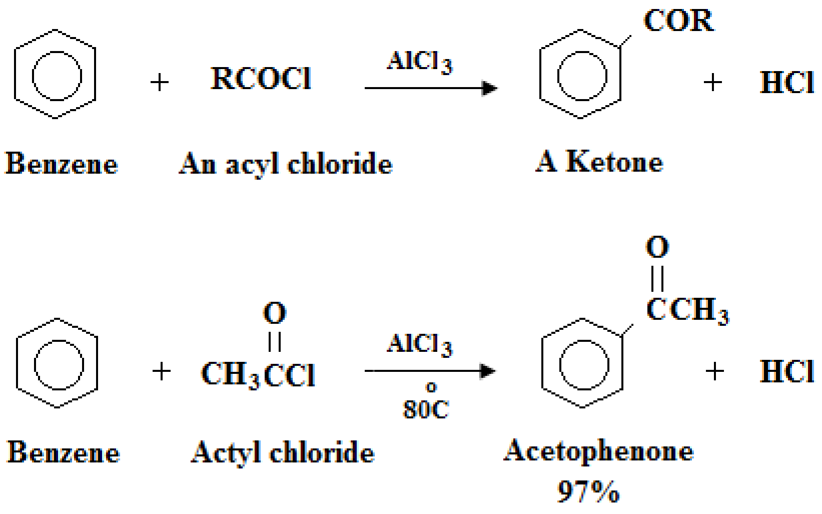
Benzene reacts exothermically with alkyl halides, in the presence of powdered, anhydrous aluminum chloride. Hydrogen halide evolved. This type of reaction is called Friedel-Crafts reaction.





5- Friedel-Crafts acylation

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



9.6 Electrophilic Aromatic Substitution

We have already seen that the characteristic reaction of benzene involve substitution, in which the resonance-stabilized ring system is preserved.

Above and below the plane of the benzene ring is a cloud of π electrons. Because of resonance, these π electrons are more involved in the holding together carbon nuclei than are the π electrons of a carbon-carbon double bond. Still, in comparison with σ electrons, these π electrons are loosely held and are available to a reagent that is seeking electrons.

It is not surprising that in its typical reactions the benzene ring serves as a source of electrons, that is, as a base. The compounds with which it reacts are deficient in electrons, that is, are electrophilic reagent or acids. Just as the typical reactions of the alkenes are electrophilic addition reactions, so the typical reactions of the benzene ring are electrophilic substitution reactions.

These reactions are characteristic not only of benzene itself, but of the benzene ring wherever it is found, and, indeed, of many aromatic rings, benzenoid and non-benzenoid.

Electrophilic aromatic substitution includes a wide variety of reactions: nitration, halogenation, sulfonation, and Friedel-Crafts reactions, undergo by nearly all aromatic rings;reactions like nitrosation and diazo coupling, undergone only by rings of high reactivity.

1- Nitration

Ar = *aryl*, any aromatic group with attachment directly to ring carbon

$$\mathrm{ArH + HONO_2 \xrightarrow{H_2SO_4} ArNO_2 + H_2O}$$

A nitro compound

2-Sulfonation

$$\mathrm{ArH + HOSO_3H \xrightarrow{SO_3} ArSO_3H + H_2O}$$

A sulfonic acid

3- Halogenation

$$\mathrm{ArH + Cl_2 \xrightarrow{Fe} ArCl + HCl}$$

An aryl chloride

$$\mathrm{ArH + Br_2 \xrightarrow{Fe} ArBr + HBr}$$

An aryl bromide

4- Friedel-Crafts alkylation

$$\mathrm{ArH + RCl \xrightarrow{AlCl_3} ArR + HCl}$$

An alkylbenzene

5- Friedel-Crafts acylation

$$\mathrm{ArH + RCOCl \xrightarrow{AlCl_3} ArCOR + HCl}$$

An acyl chloride **A ketone**

6- Protonation

$$\mathrm{ArSO_3H + H^+ \xrightarrow{H_2O} Ar\text{-}H + H_2SO_4}$$ **Desulfonation**

$$\mathrm{ArH + D^+ \longrightarrow ArD + H^+}$$ **Hydrogen exchange**

7- Nitrosation

$$\mathrm{ArH + HONO \longrightarrow Ar\text{-}N{=}O + H_2O}$$ **Only for highly reactive ArH**

A nitroso compound

8- Diazo coupling

$$\mathrm{ArH + Ar'N_2^+X^- \longrightarrow Ar\text{-}N{=}NAr' + HX}$$ **Only for highly reactive ArH**

A diazonium salt **An azo compound**