جامعة شط العرب
الكلية التقنية الهندسية
قسم هندسة تقنيات الوقود والطاقة

Organic Chemistry

By
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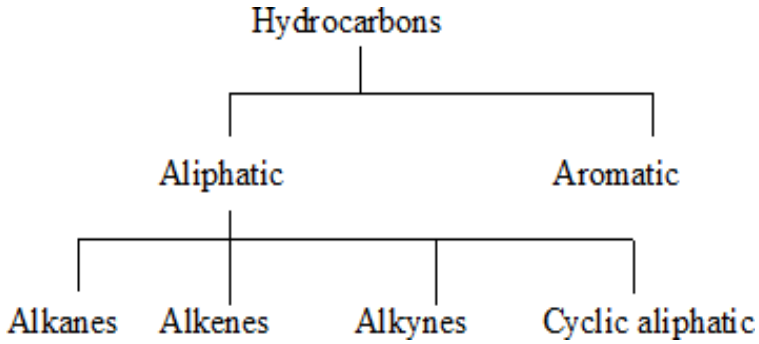
M.Sc. C. B. Chemistry

Lecture - 1 (Alkanes)

2025 A. D. **1446 A. H.**

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.

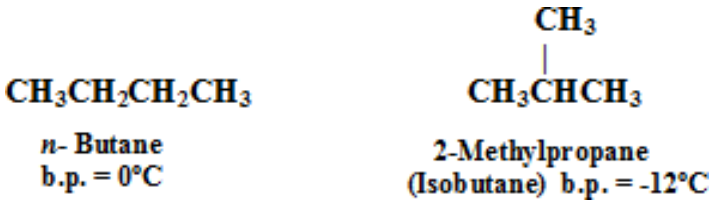
Table 1.1 The first ten member of the alkanes

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

1.1 Isomerism in Alkanes

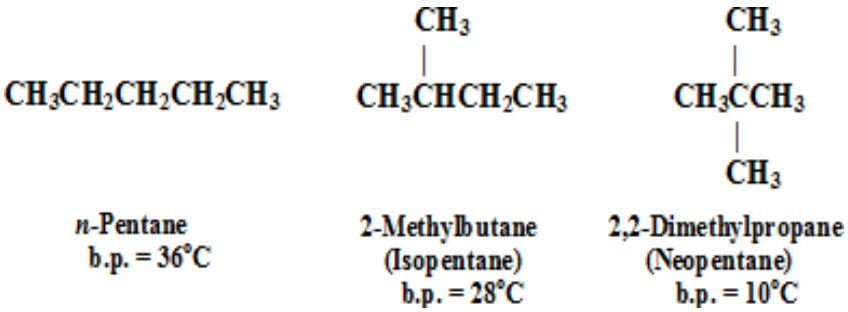
Compounds that have the same molecular formula but different structural formulas were defined as isomers. Isomeric compounds are not possible in the alkanes series until we reach the molecular formula C_4H_{10}. There are two arrangements for the formula C_4H_{10}, and two isomers are known as shown:



(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:

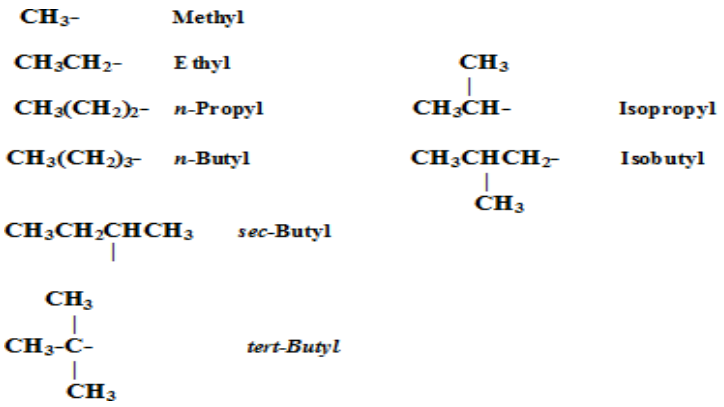


(C_5H_{12} isomers)

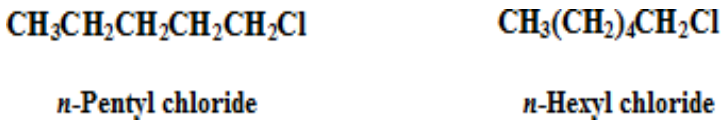
The difference in the structure is due to different arrangements of the carbon atoms.

1.2 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} .



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.



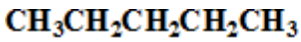
The prefix *iso*- is used to designate any alkyl group (of six carbons or fewer) that has a single one-carbon branch on the next-to-last carbon of a chain and has the point of attachment at the opposite end of the chain.

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

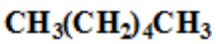
1.3 Nomenclature

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:

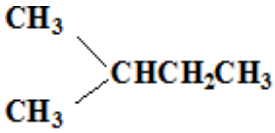


n-Pentane

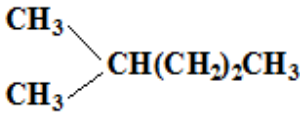


n-Hexane

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:



Isopentane



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.

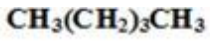
To specify which carbon atom of the parent chain holds a branch, number the parent chain from whichever end of its chain reaches the first branch with the lower number.

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

5- 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.

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

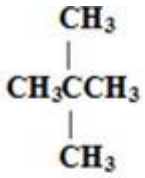
If two different chains of equal length are present, choose the one with the larger number of branch points as the parent.



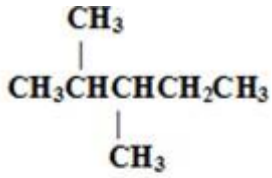
Pentane
(*n*-Pentane)

2-Methylpentane
(Isohexane)

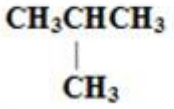
(Isopentane)



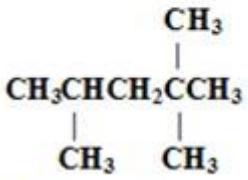
Dimethylpropane
(Neopentane)



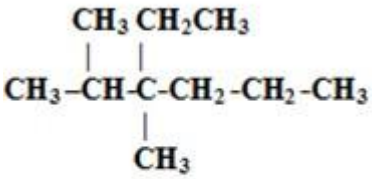
2,3-Dimethylpentane



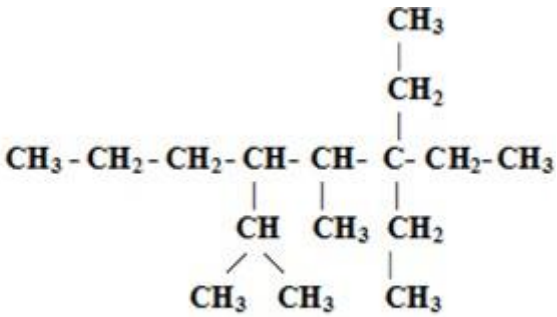
Methylpropane
(Isobutane)



2,2,4-Trimethylpentane



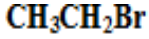
3-Ethyl-2,3-dimethylhexane



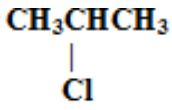
3,3-Diethyl-5-isopropyl-4-methyloctane

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.

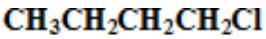
Chloromethane
(Methyl chloride)



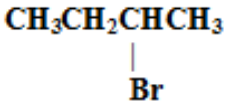
Bromoethane
(Ethyl bromide)



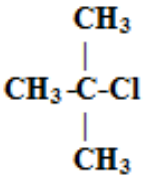
2-Chloropropane
(Isopropyl chloride)



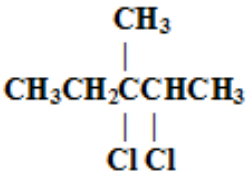
1-Chlorobutane
(Butyl chloride)



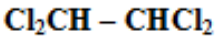
2-Bromobutane



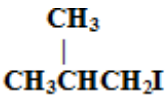
2-Chloro-2-methylpropane



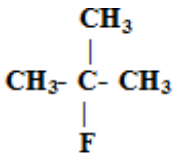
2,3-Dichloro-3-methylpentane



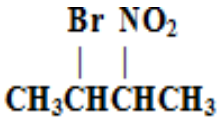
1,1,2,2-Tetrachloroethane



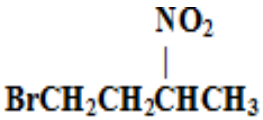
1-Iodo-2-methylpropane



2-Fluro-2-methylpropane



2-Bromo-3-nitrobutane



1-Bromo-3-nitrobutane

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

1.2 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.

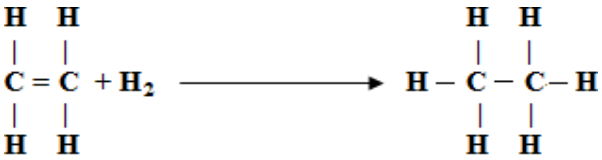
1.4 Preparation of Alkanes

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**



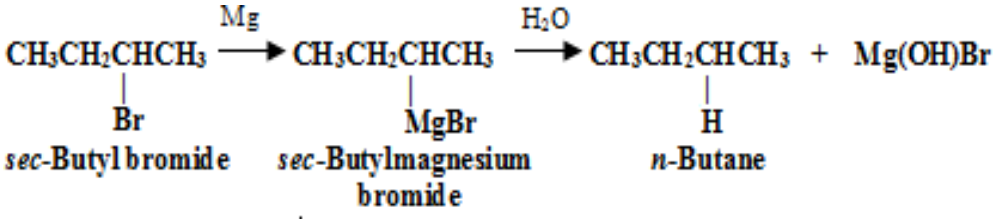
Ethylene **Ethane**

2- Reduction of alkyl halides

(a) Hydrolysis of Grignard reagent

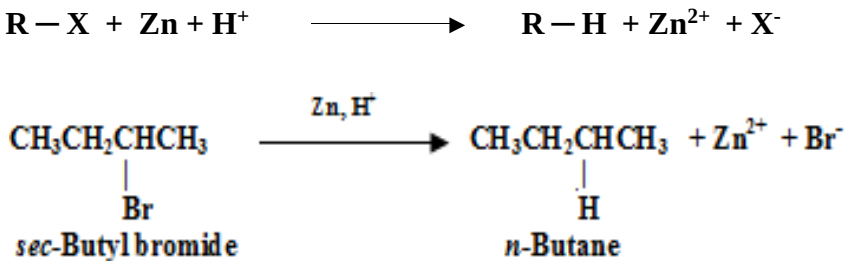
When a solution of an alkyl halide in dry ethyl ether, is allowed to stand over turnings of metallic magnesium, the resulting solution is known as a Grignard reagent. The reaction with water gives an alkane.

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

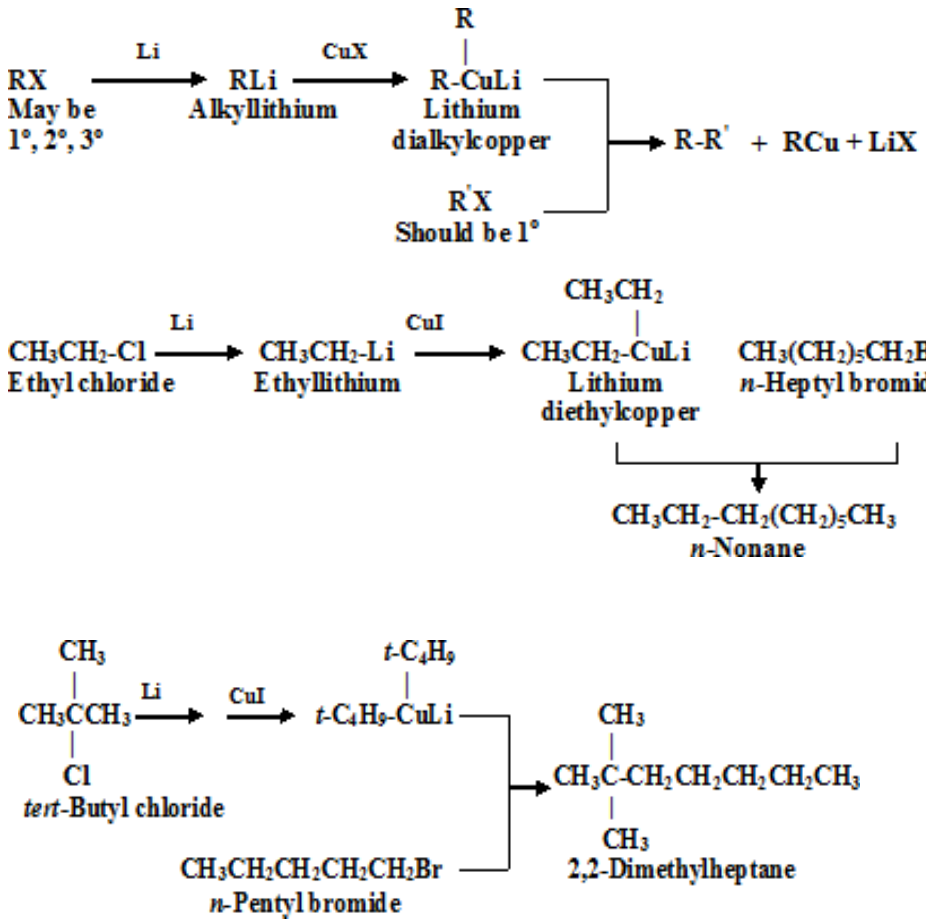


(b) Reduction by metal and acid

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.



3- Coupling of alkyl halides with organometallic compounds

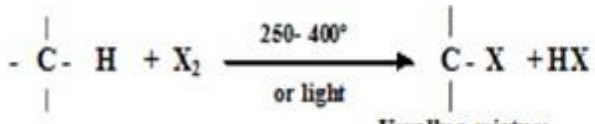


1.3 Reactions of Alkanes

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

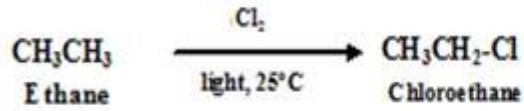
1- Halogenation

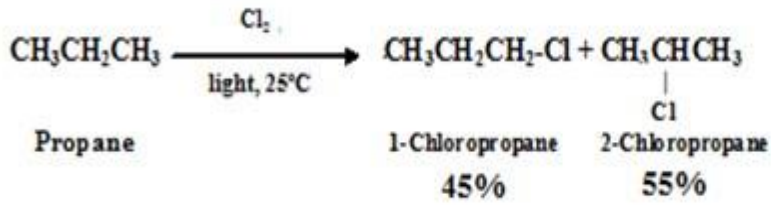
Alkanes react with the halogens (except iodine) to form substitution products.

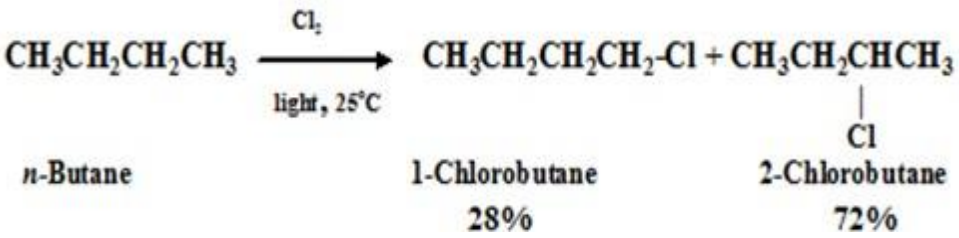


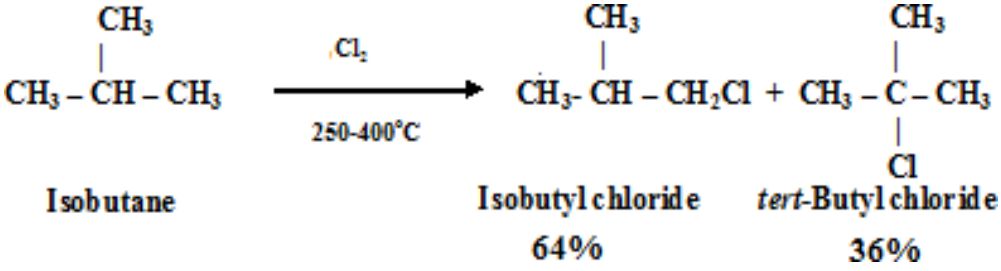
Reactivity X_2: $Cl_2 > Br_2$

H_2: $3° > 2° > 1° > 2°\ CH_3\text{-}H$



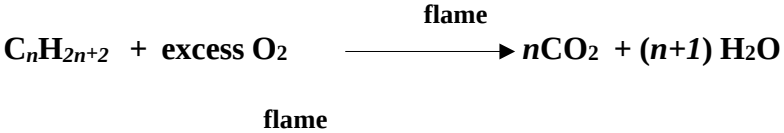






2- Oxidation (Combustion)

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} + excess O_2 → nCO_2 + $(n+1)\ H_2O$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

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

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Lecture - 2 (Alkenes)

2025 A. D. **1446 A. H.**

2. 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.

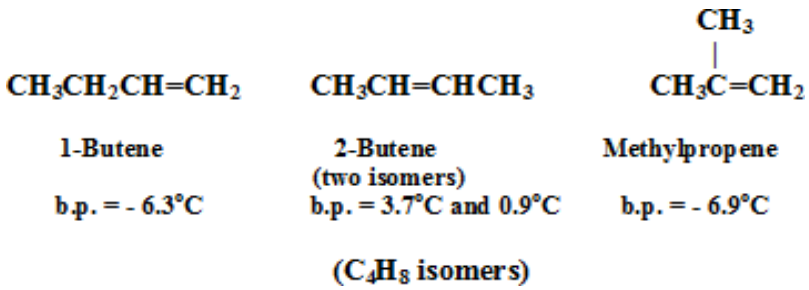
The general formula of alkenes is $\mathbf{C_nH_{2n}}$, where *n* is the number of carbon atoms. The first nine members of this series are listed in Table 2.1.

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

2.1 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:



2.2 Nomenclature

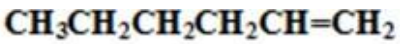
Common names are seldom used except for three simple alkene; ethylene, propylene, and isobutylene. Most alkene are named by IUPAC system.

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

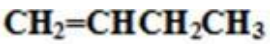
2- The ending ***–ane*** of the corresponding alkane hydrocarbon name is replaced by the ending ***–ene***.

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.

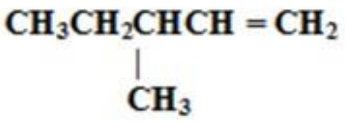
4- If a geometric isomer is designated, the name begins with *cis*- or *trans*-.



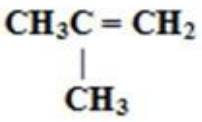
1- Hexene



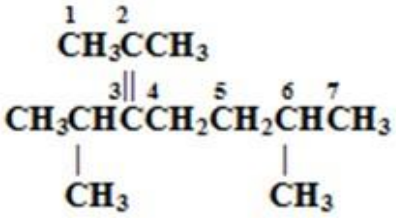
1-Butene



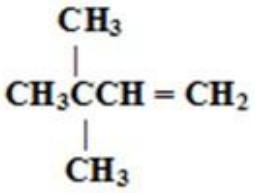
3-Methyl-1-pentene



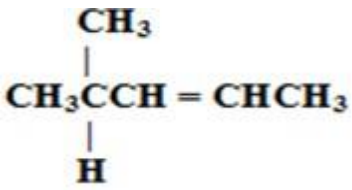
2-Methylpropene



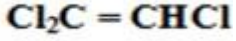
3-Isopropyl-2,6-dimethyl-2-heptene



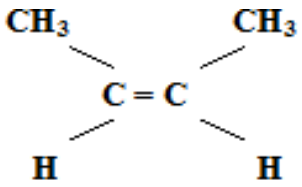
3,3-Dimethyl-1-butene



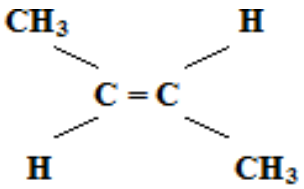
4-Methyl-2-pentene



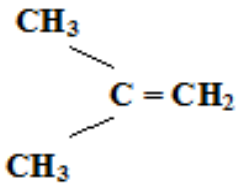
Trichloroethene



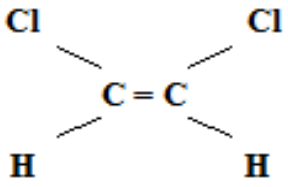
cis-2-Butene



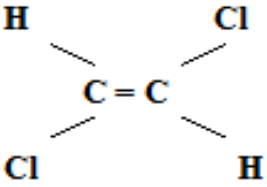
trans-2-Butene



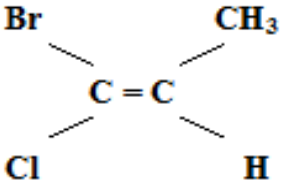
2-Methylpropene



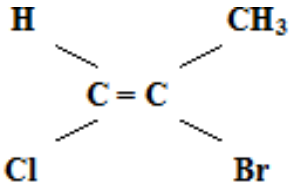
cis-1,2-Dichloroethene



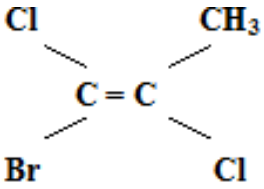
trans-1,2-Dichloroethene



1-Bromo-1-chloropropene



2-Bromo-1-chloropropene



1-Bromo-1,2-dichloropropene

2.3 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.

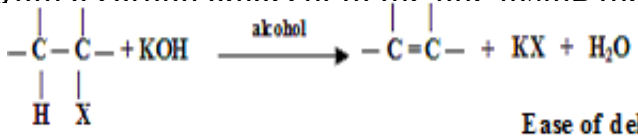
They are less dense than water. The boiling point riseswith increasing carbon number; as with alkane, branching lowers the boiling point.

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.

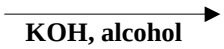
2.4 Preparation of Alkenes

1- Dehydrohalogenation of alkyl halides

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

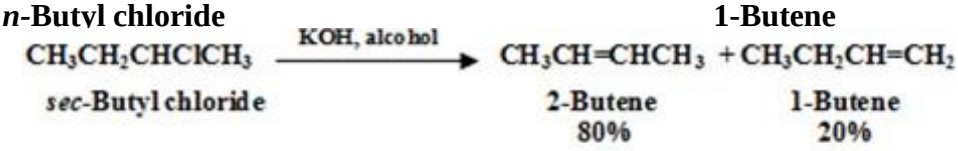


Ease of dehydrohalogenation 3° > 2° > 1°
of alkyl halides



$CH_3CH_2CH_2CH_2Cl$ → $CH_3CH_2CH = CH_2 + KCl + H_2O$

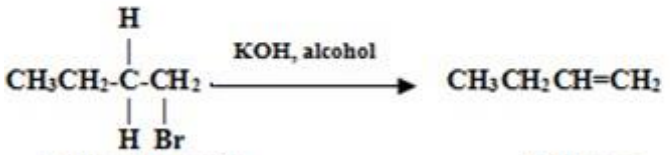
***n*-Butyl chloride** → **1-Butene**



sec-Butyl chloride

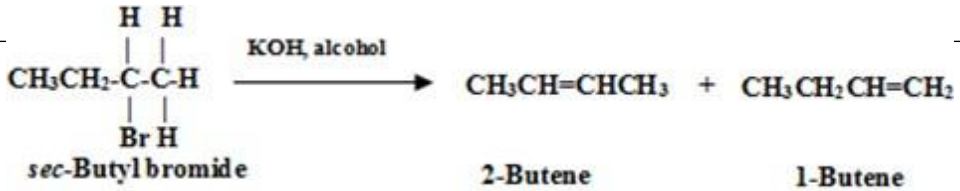
2-Butene 80%

1-Butene 20%



n-Butyl bromide

1-Butene
Only product

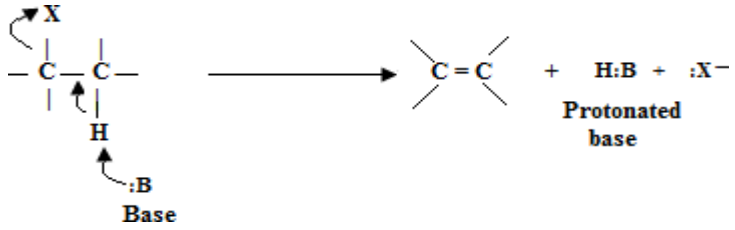


sec-Butyl bromide

2-Butene 81%

1-Butene 19%

***Mechanism*:**

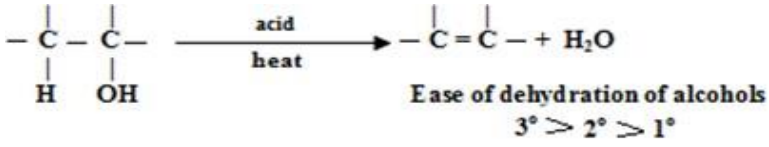


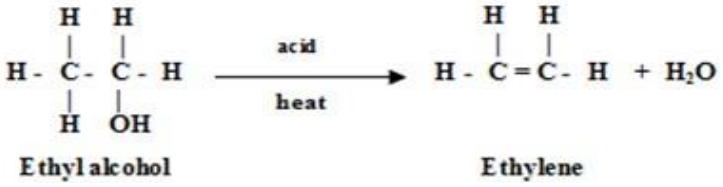
The base **:**B can be neutral or negatively charged: for example, H_2O or OH^-. The conjugate acid H:B will then be positively charged or neutral: for example, H_3O^+ or H_2O.

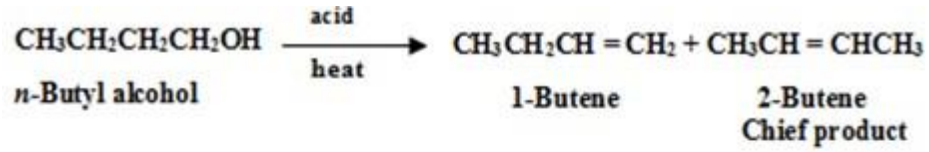
Halogen leaves the molecule as halide ion, and hence must take its electron pair along. Hydrogen is abstracted by the base as a proton, and hence must leave its electron pair behind; it is this electron pair that is available to form the π bond between the carbon atoms.

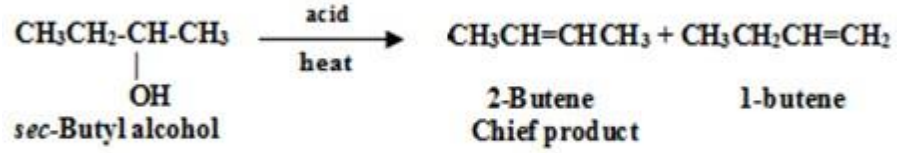
2- Dehydration of alcohols

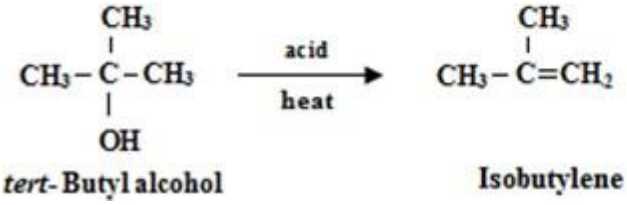
In the dehydration of alcohols, the H and OH are lost from adjacent carbons (*1,2-elimination*). An acid catalyst is necessary and application of heat.



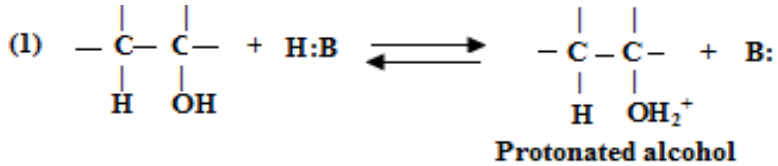


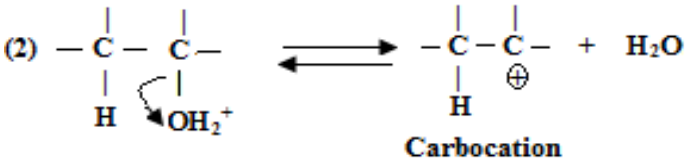


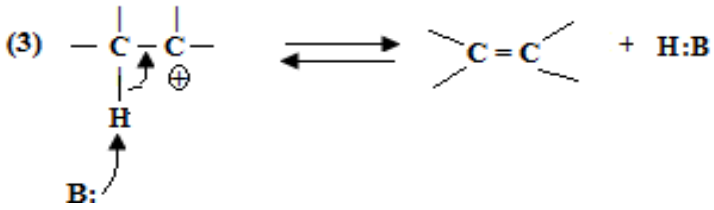




***Mechanism*:**



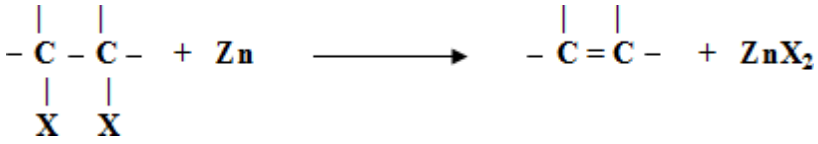




For secondary and tertiary alcohols the above mechanism is generally accepted. Step (1) is a fast acid-base reaction between the alcohol and the catalyzing acid which gives the protonated alcohol and the conjugate base of the acid. In step (2) the protonated alcohol undergoes heterolysis to form the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

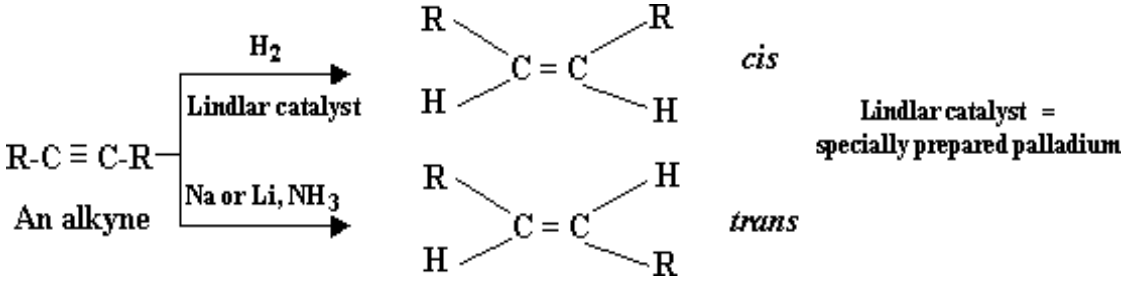


$$CH_3CHBrCHBrCH_3 \xrightarrow{Zn} CH_3CH = CHCH_3 + ZnBr_2$$

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.



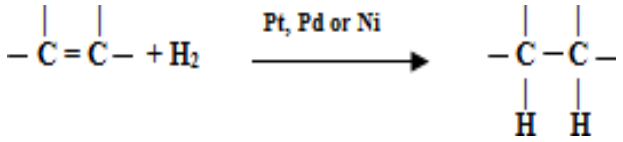
2.5 Reactions of alkenes

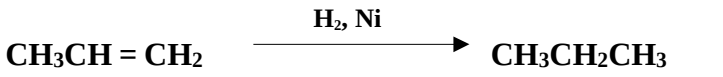
The presence of the carbon-carbon double bond confers very considerable chemical activity on the alkenes and consequently they react with a much wider variety of reagents than do the alkanes. The π-bond component of the double bond is weaker than the σ-bond component and the π-electrons are more easily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

(Addition Reactions)

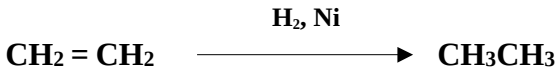
1- Addition of hydrogen

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.





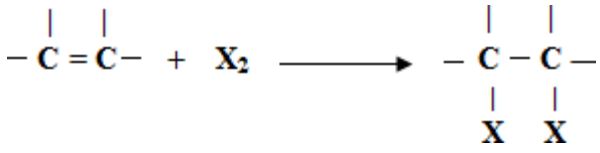
Propene (Propylene) **Propane**



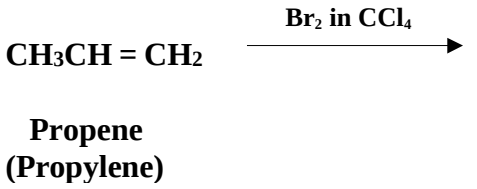
Ethylene **Ethane**

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.



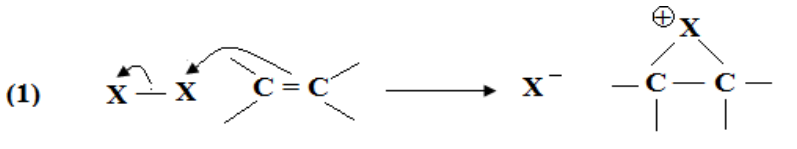
$X_2 = Cl_2, Br_2$



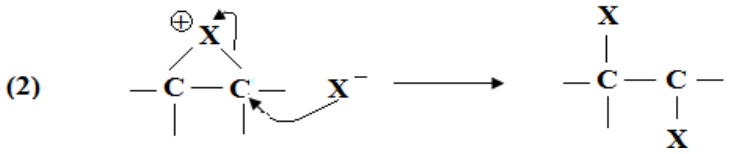
Propene (Propylene)

1,2-Dibromopropane (Propylene bromide)

Mechanism:



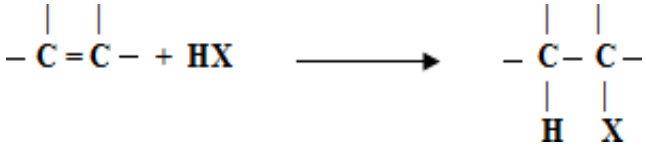
A halonium ion



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.

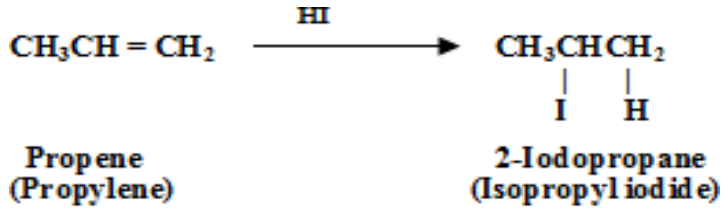
3- Addition of hydrogen halides

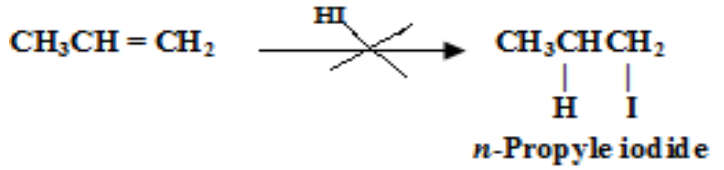
Alkenes react, usually on heating, with hydrogen halides (either gaseous or in concentrated solution) to form an addition product.

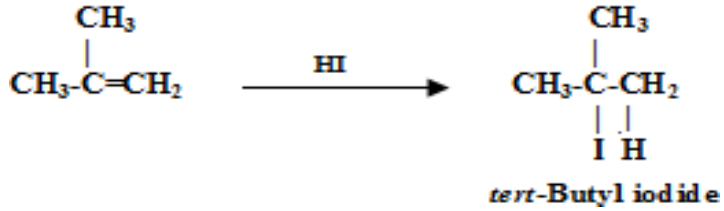


HX = HCl, HBr, HI

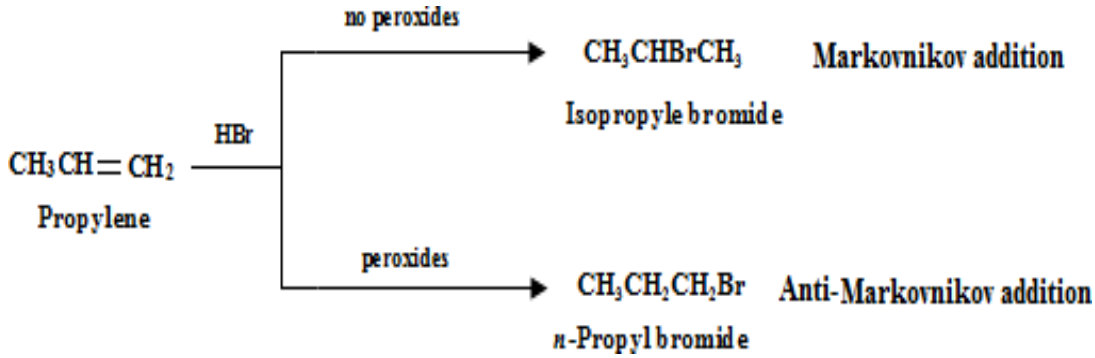
The hydrogen attaches itself to the carbon that already holds the greater number of hydrogens. This statement is called ***Markovnikov's rule***.





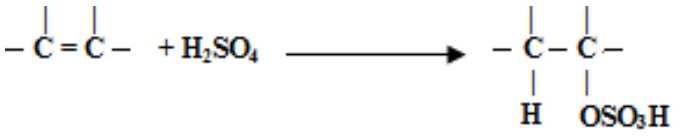


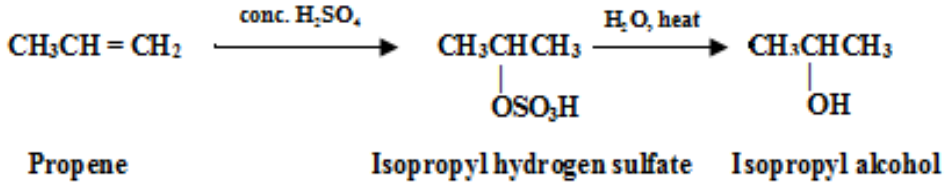
If the reaction takes place in the absence of peroxide, the addition of HBr, to alkenes follows Markovnikov's rule. On the other hand, if the reaction takes place in the presence of peroxide, HBr adds to alkenes in the reverse direction.

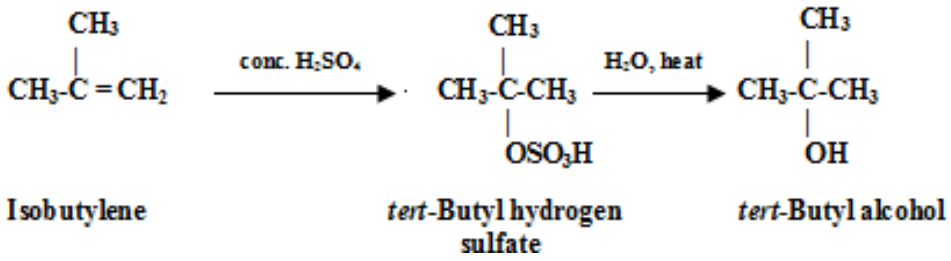


4- Addition of sulfuric acid

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.

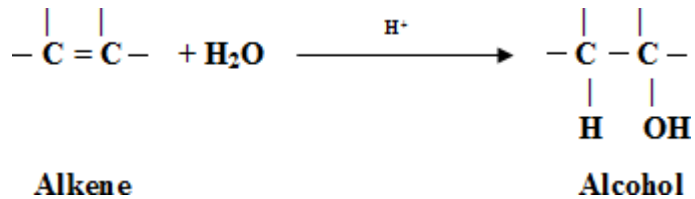


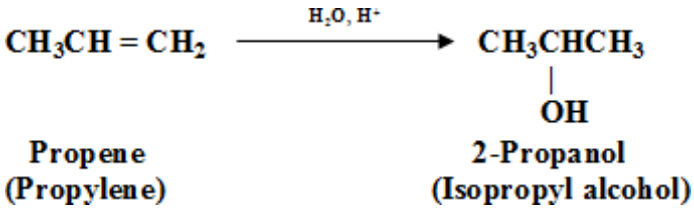




5- Addition of water. Hydration

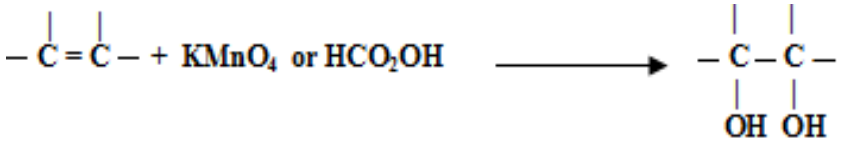
Alkenes are also reacting with water, and this reaction is carried out in a dilute acid medium. The reaction follows Markovnikov's rule.

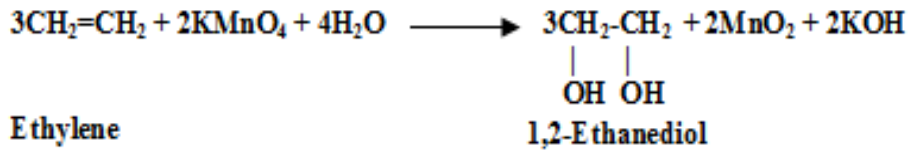


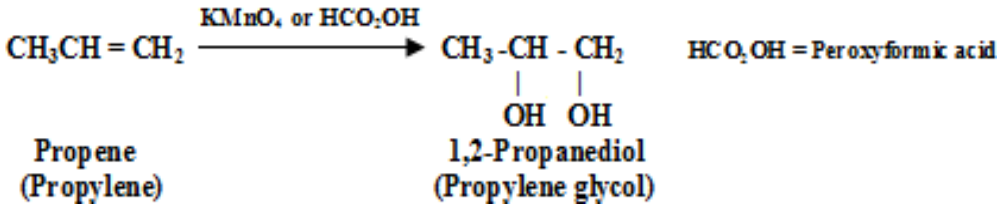


6- Hydroxylation – glycol formation

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.

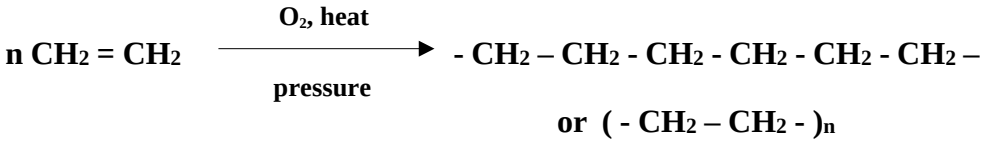






7- Polymerization

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.

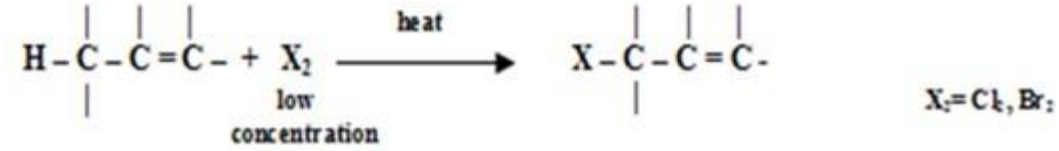


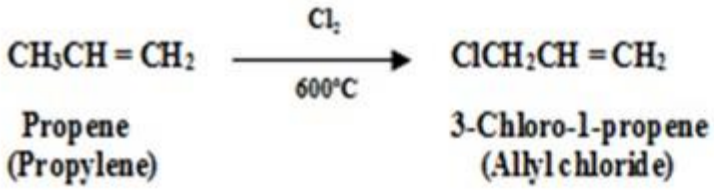
Ethylene **Polyethylene**

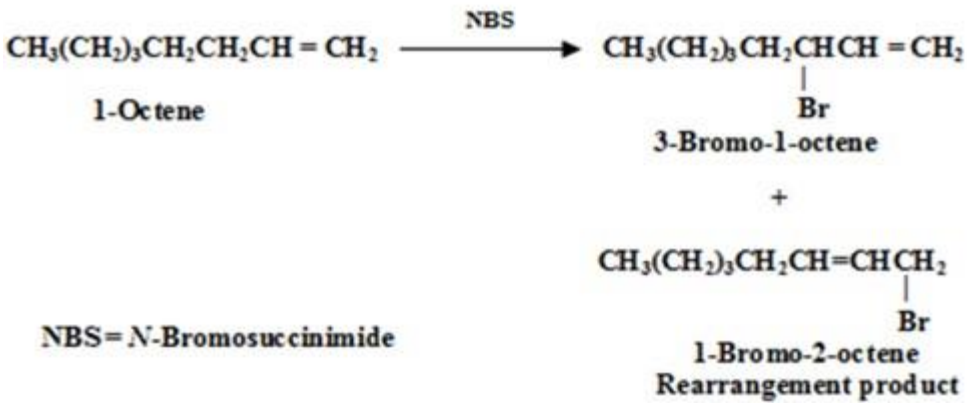
(Substitution Reactions)

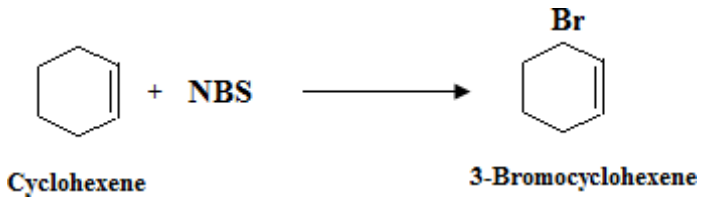
Halogenation. Allylic substitution

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





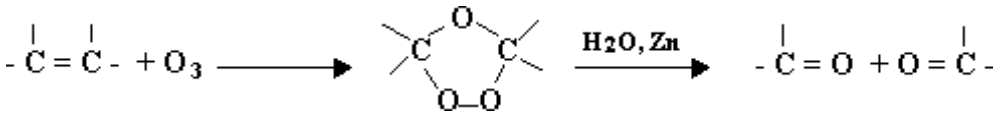




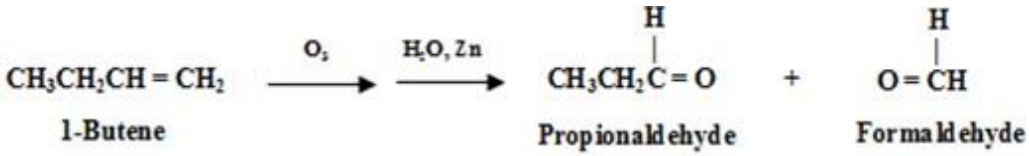
(Cleavage Reactions)

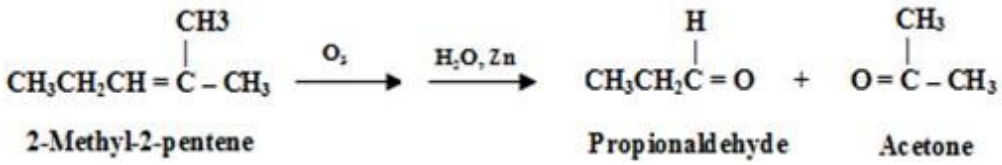
Ozonolysis

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**





جامعة شط العرب
الكلية التقنية الهندسية
قسم هندسة تقنيات الوقود والطاقة

Organic Chemistry

By
Murtadha Firas Alkinani
M.Sc. C. B. Chemistry

Lecture - 3 (Alkynes)

2025 A. D. **1446 A. H.**

3. 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

3.1 Nomenclature

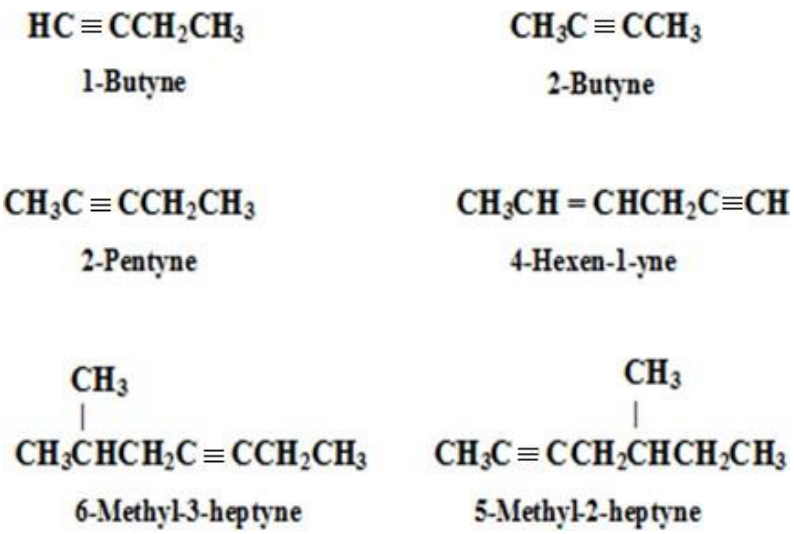
The alkynes are named according to two systems. In one, they are considered to be derived from acetylene by replacement of one or both hydrogen atoms by alkyl group.

$H - C \equiv C - C_2H_5$ **(Ethylacetylene) 1-Butyne**

$CH_3 - C \equiv C - CH_3$ (**Dimethylacetylene) 2-Butyne**

$CH_3 - C \equiv C - CH(CH_3)_2$ (**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**.



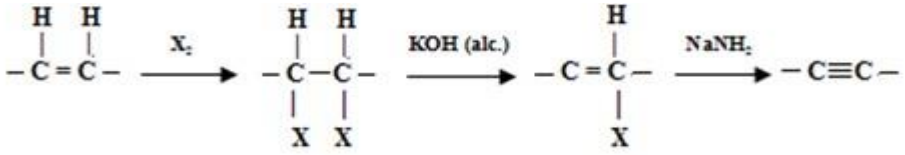
3.2 Physical Properties of Alkynes

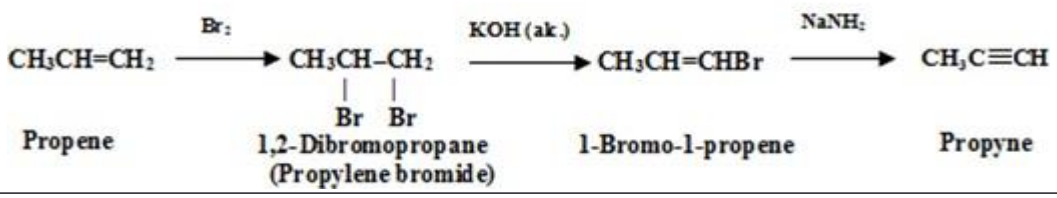
Being compounds of low polarity, the alkynes have physical properties that are essentially the same as those of the alkanes and alkenes. They are insoluble in water but quite soluble in the usual organic solvents of low polarity: ether, benzene, and carbon tetrachloride. They are less dense than water.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

3.3 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.





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.

$$-C\equiv C-H \xrightarrow{LiNH_2} -C\equiv C:^-Li^+ + RX \longrightarrow -C\equiv C-R + LiX$$

R must be 1°

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

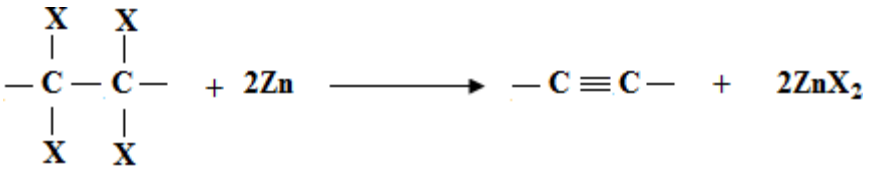
Lithium acetylide **_n_-Butyl bromide** **1-Hexyne (_n_-Butylacetylene)**

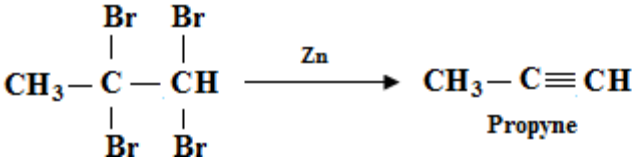
$$CH_3(CH_2)_4C\equiv C\text{-}Li + CH_3(CH_2)_3CH_2Cl \longrightarrow CH_3(CH_2)_4C\equiv C-CH_2(CH_2)_3CH_3$$

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

3- Dehalogenation of tetrahalides

Alkynes can be prepared by dehalogenation of tetrahalides.





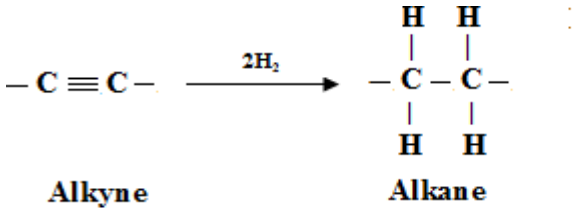
3.4 Reactions of Alkynes

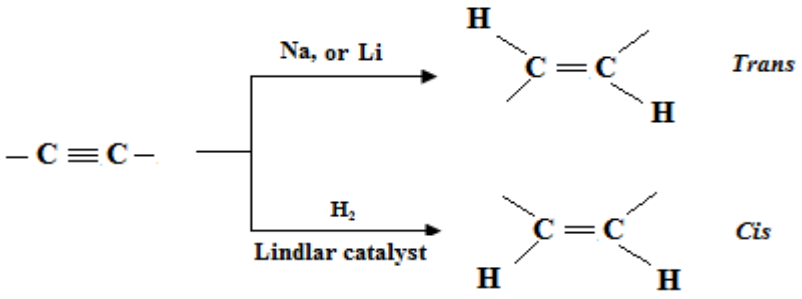
The carbon-carbon triple bond –C≡C– consists of one σ-bond and two weaker π-bonds, so it is not surprising that addition reactions are a characteristic feature of this functional group. Despite its high formal unsaturation, the triple bond dose not usually react so vigorously as a carbon-carbon double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

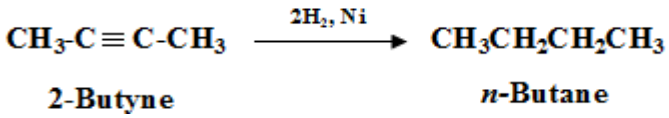
(Addition Reactions)

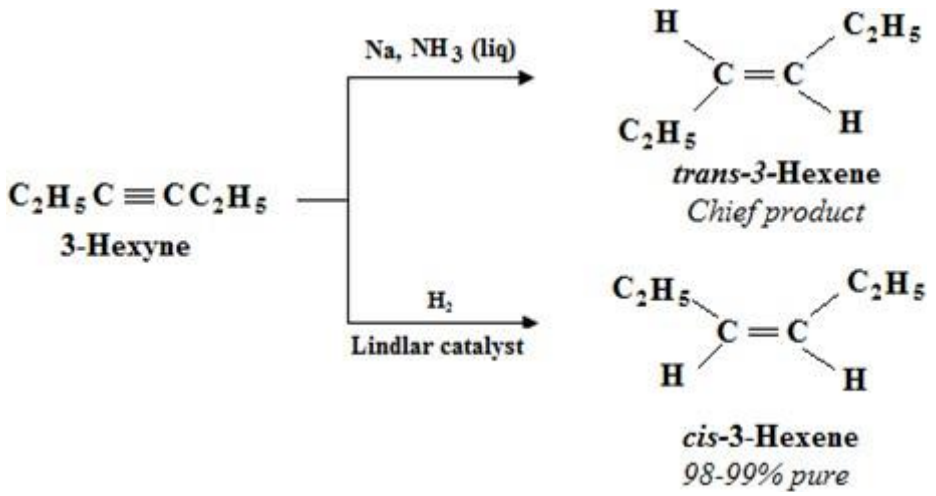
1- Addition of hydrogen

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.



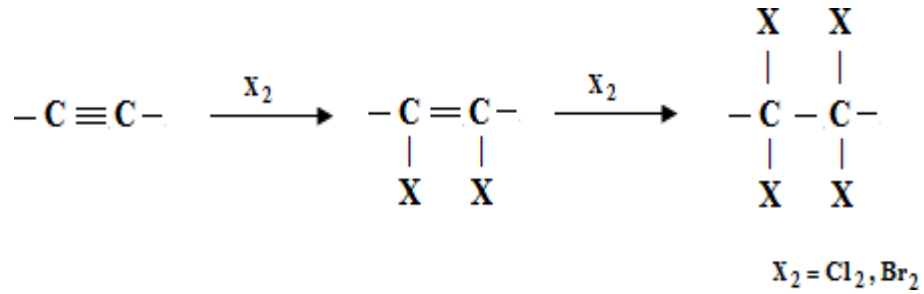


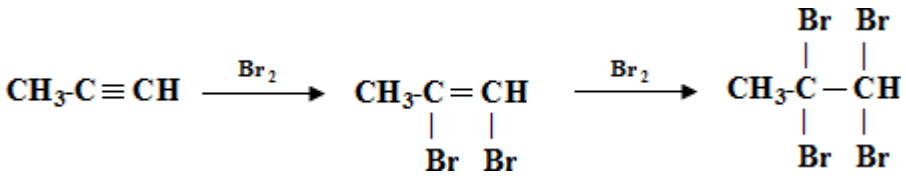




2- Addition of halogen

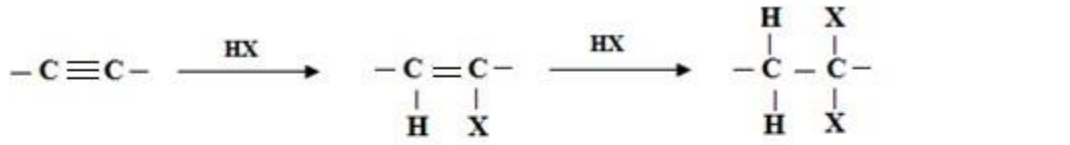
Alkynes can react with chlorine and bromine to yield tetrahaloalkanes. A dihaloalkene is an intermediate.



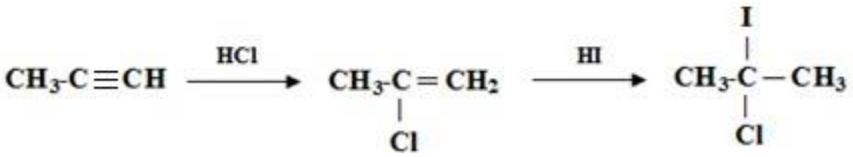


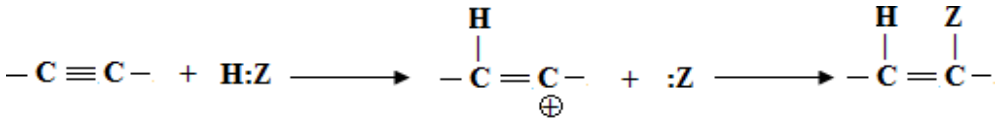
3- Addition of hydrogen halides

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*.



HX = HCl, HBr, HI

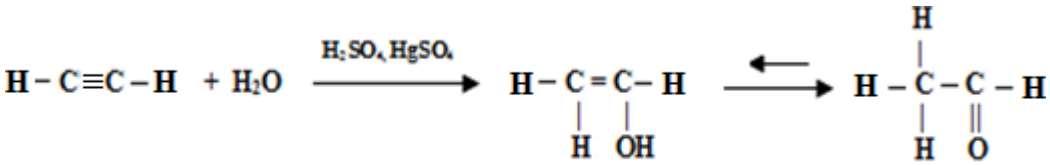




A vinylic cation

4- Addition of water (hydration)

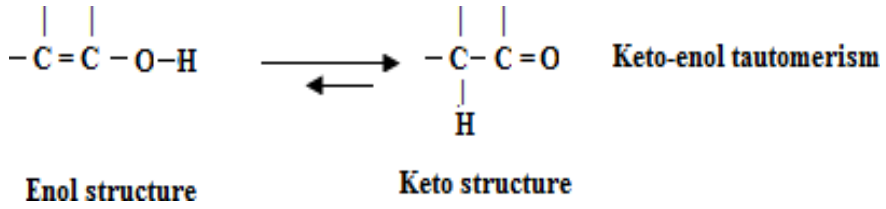
In the presence of dilute sulphuric acid and a mercury(II) sulphate catalyst at about 60°C, water adds across a triple bond and alkyne is said to be hydrated.

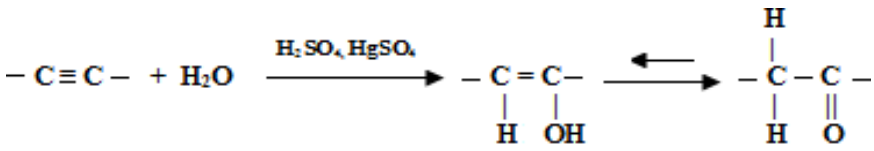


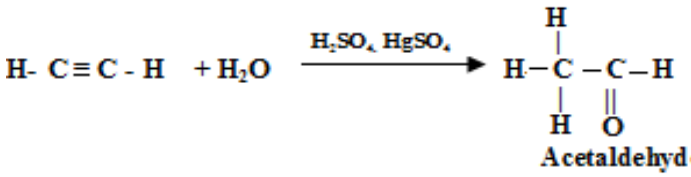
Acetylene | Vinyl alcohol | Acetaldehyde

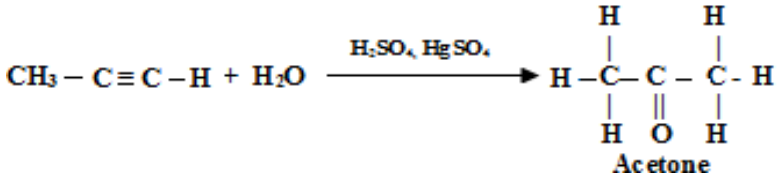
If hydration of acetylene followed the same pattern as hydration of alkenes, we would expect addition of H- and –OH to the triple bond to yield *vinyl alcohol*. But all attempts to prepare vinyl alcohol result, like hydration of acetylene, in the formation of acetaldehyde.

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.

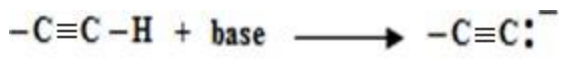






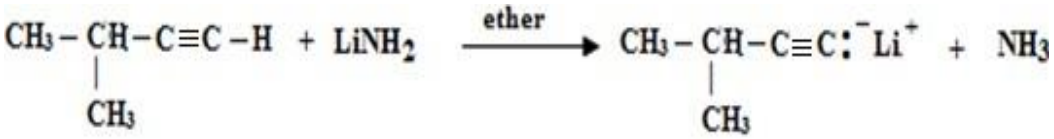


(Reaction as Acid)



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.



Lithium isopropylacetylide

Lithium methyacetylide

Ethynylmagnesium bromide