

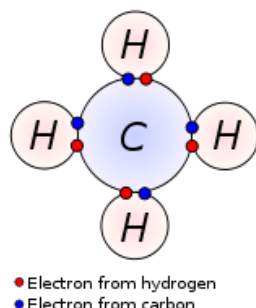
**Organic chemistry:** is a branch of chemistry that studies the structure, properties and reactions of organic compounds, which contain carbon in covalent bonding.

### ***Chemical Bonding:***

Chemical compounds are formed by the joining of two or more atoms. A stable compound occurs when the total energy of the combination has lower energy than the separated atoms. The bound state implies a net attractive force between the atoms ... a chemical bond. The two extreme cases of chemical bonds are:

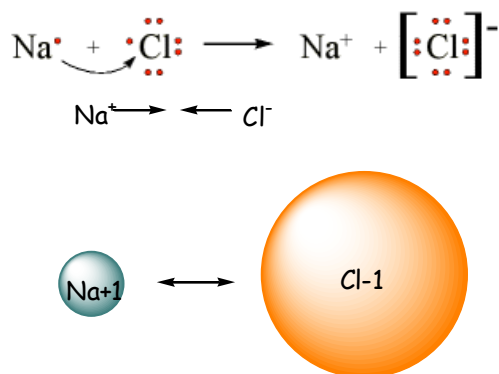
### ***Covalent bonds:***

Covalent bonds are formed by the sharing of a pair of electrons between atoms with little or no differences in electronegativity.



### ***Ionic bonds:***

Ionic bond is formed by the completely transfer of electrons from one atom to another. In the process of either losing or gaining negatively charged electrons, the reacting atoms form ions. The oppositely charged ions are attracted to each other by electrostatic forces, which are the basis of the ionic bond. For example, reaction of sodium with chlorine.



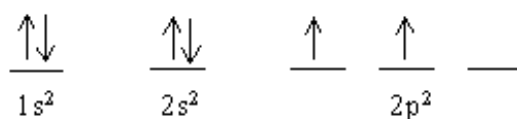
### ***Hybridization of carbon:***

The element, carbon, is one of the most versatile elements on the periodic table in terms of the number of compounds it may form. It may form virtually an infinite number of compounds. This is largely due to the types of bonds it can form and the number of different elements it can join in bonding. Carbon may form single, double, and triple bonds. The hybridization of carbon involved in each of these bonds will be investigated in this section.

From the ground state electron configuration, carbon has four valence electrons, two in the 2s subshell and two in the 2p subshell. The 1s electrons are not available for bonding.

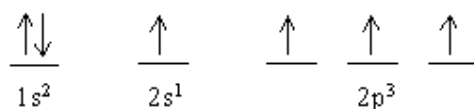
If carbon were to hybridize from this ground state carbon will form an excited state by promoting one of its 2s electrons into its empty 2p orbital and hybridize from the excited state. By forming this excited state, carbon will be able to form four bonds. The excited state configuration is shown below:

Since both the 2s and the 2p subshells are half-filled, the excited state is relatively stable.

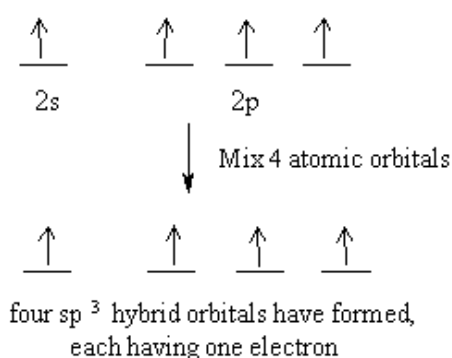


If carbon were to hybridize from this ground state carbon will form an excited state by promoting one of its 2s electrons into its empty 2p orbital and hybridize

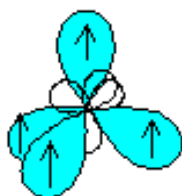
from the excited state. By forming this excited state, carbon will be able to form four bonds. The excited state configuration is shown below:



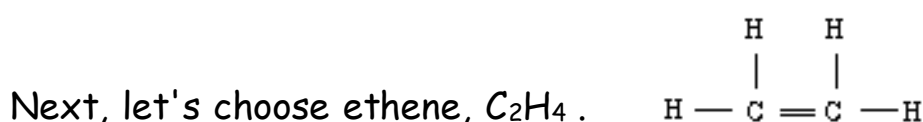
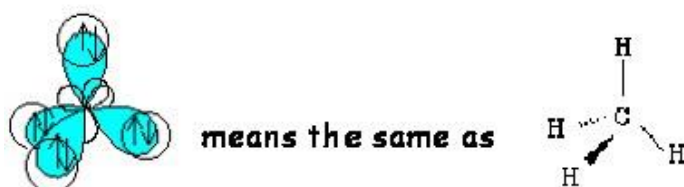
Since both the 2s and the 2p subshells are half-filled, the excited state is relatively stable. The number of hybrid orbitals formed equals the number of atomic orbitals mixed the description of the atomic orbitals mixed is equivalent to the hybridization of the carbon atom. For example, we choose methane, CH<sub>4</sub>, the atomic orbitals of excited state carbon found in the valence shell:



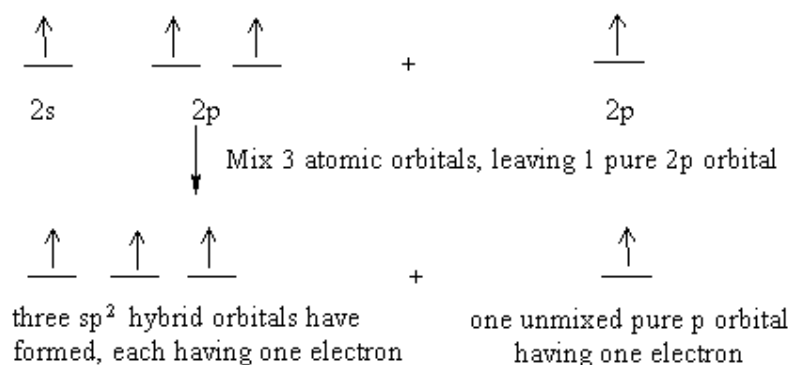
The four sp<sup>3</sup> hybrid orbitals will arrange themselves in three dimensional space to get as far apart as possible (to minimize repulsion). The geometry that achieves this is tetrahedral geometry, where any bond angle is 109.5°.



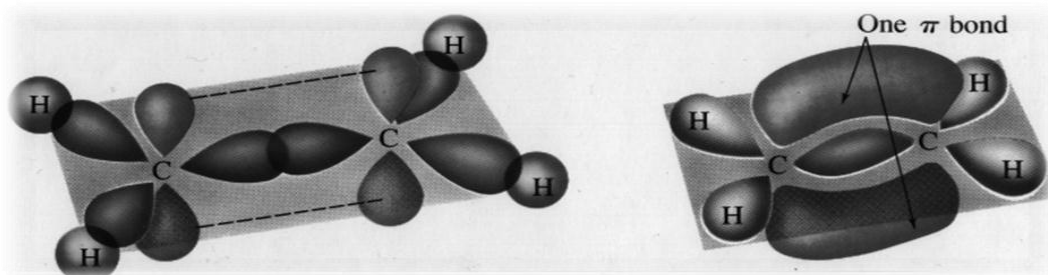
Each hybrid orbital contains 1 electron. A hydrogen 1s orbital will come in and overlap with the hybrid orbital to form a sigma bond (head-on overlap), as shown below:



The (s) orbital and two of the (p) orbitals for each carbon have been mixed, thus the hybridization for each carbon is  $sp^2$ .



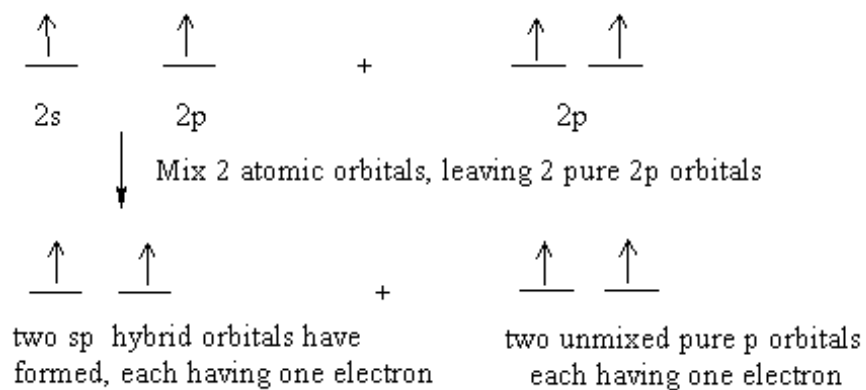
The three  $sp^2$  hybrid orbitals will arrange themselves in three dimensional space to get as far apart as possible. The geometry that achieves this is trigonal planar geometry, where the bond angle between the hybrid orbitals is  $120^\circ$ . The unmixed pure p orbital will be perpendicular to this plane. Keep in mind, each carbon atom is  $sp^2$ , and trigonal planar.



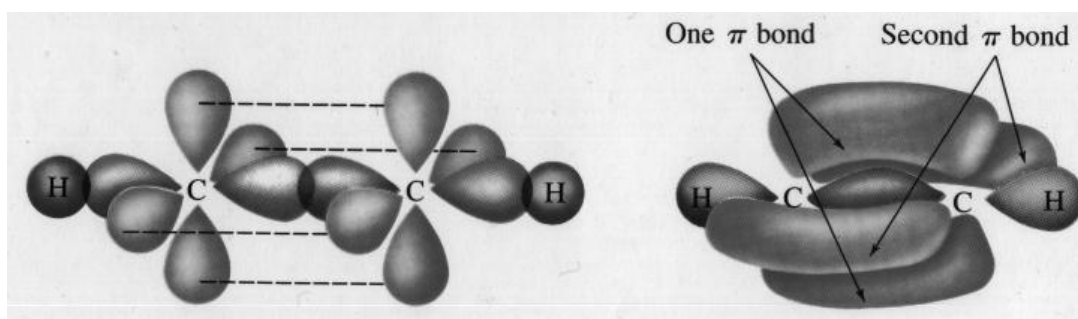
Finally, let's look at acetylene,  $C_2H_2$ . First, draw the Lewis structure:



The Lewis structure shows two groups around each carbon atom. This means two hybrid orbitals have formed. To form two hybrid orbitals, two atomic orbitals have been mixed.



The two sp hybrid orbitals arrange themselves in three dimensional space to get as far apart as possible. The geometry which achieves is linear geometry with a bond angle of 180°. The two pure (p) orbitals which were not mixed are perpendicular to each other.



## ***ALKANES (PARAFFINES):***

ALKANES : saturated compounds they have a single and strong covalent bonds general formula is (  $C_nH_{2n+2}$  ) the hybrid is  $SP^3$ .

<b>Methane</b>	<b>CH<sub>4</sub></b>	<b>C<sub>1</sub></b>
<b>Ethane</b>	<b>CH<sub>3</sub>CH<sub>3</sub></b>	<b>C<sub>2</sub></b>
<b>Propane</b>	<b>CH<sub>3</sub> CH<sub>2</sub> CH<sub>3</sub></b>	<b>C<sub>3</sub></b>
<b>Butane</b>	<b>CH<sub>3</sub> (CH<sub>2</sub>)<sub>2</sub> CH<sub>3</sub></b>	<b>C<sub>4</sub></b>
<b>Pentane</b>	<b>CH<sub>3</sub> (CH<sub>2</sub>)<sub>3</sub> CH<sub>3</sub></b>	<b>C<sub>5</sub></b>
<b>Hexane</b>	<b>CH<sub>3</sub> (CH<sub>2</sub>)<sub>4</sub> CH<sub>3</sub></b>	<b>C<sub>6</sub></b>
<b>Heptane</b>	<b>CH<sub>3</sub> (CH<sub>2</sub>)<sub>5</sub> CH<sub>3</sub></b>	<b>C<sub>7</sub></b>
<b>Octane</b>	<b>CH<sub>3</sub> (CH<sub>2</sub>)<sub>6</sub> CH<sub>3</sub></b>	<b>C<sub>8</sub></b>
<b>Nonane</b>	<b>CH<sub>3</sub> (CH<sub>2</sub>)<sub>7</sub> CH<sub>3</sub></b>	<b>C<sub>9</sub></b>
<b>Decan</b>	<b>CH<sub>3</sub> (CH<sub>2</sub>)<sub>8</sub> CH<sub>3</sub></b>	<b>C<sub>10</sub></b>

Iso butane (CH<sub>3</sub>)<sub>2</sub>CH CH<sub>3</sub>

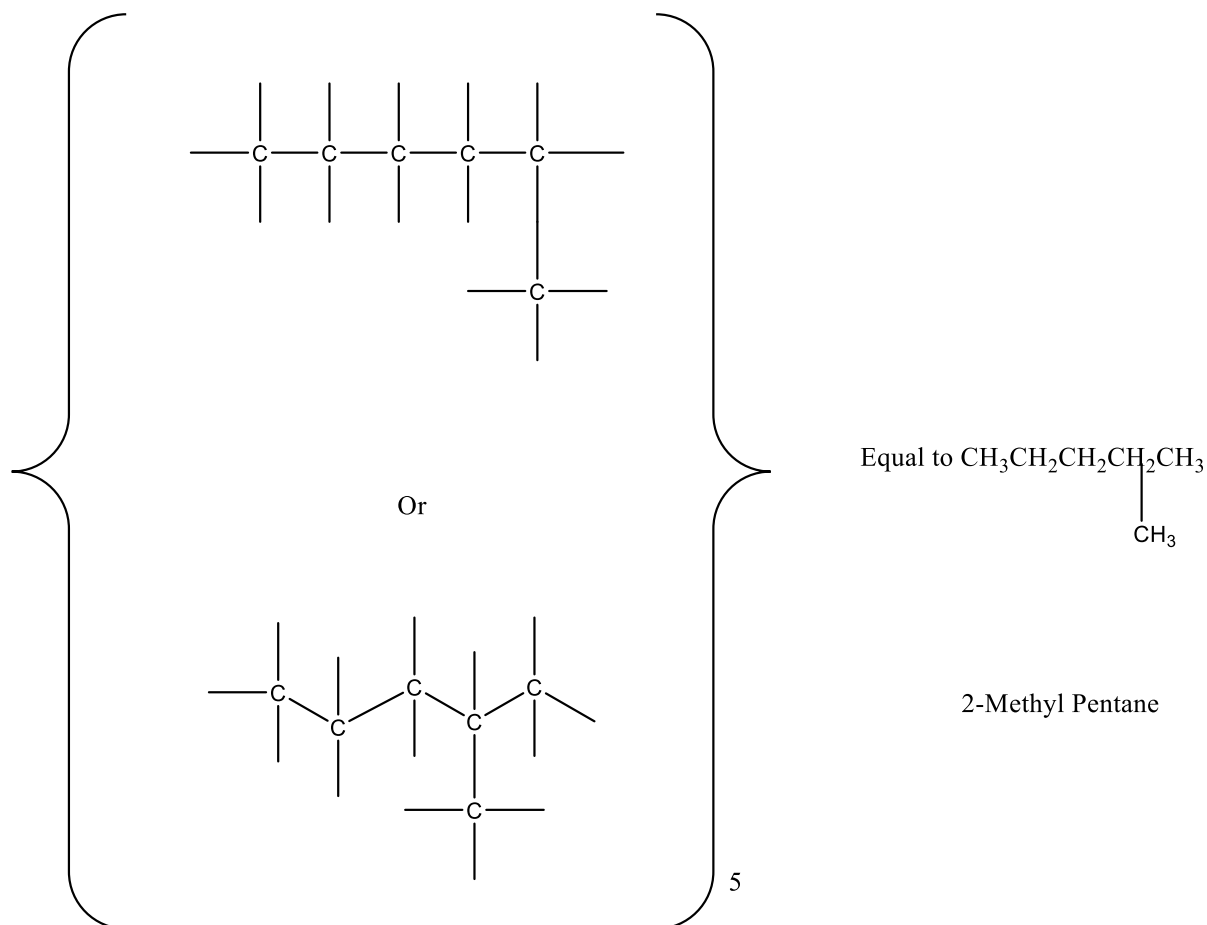
Iso pentane (CH<sub>3</sub>)<sub>2</sub>CH CH<sub>2</sub> CH<sub>3</sub>

Neo pentane (CH<sub>3</sub>)<sub>4</sub>C

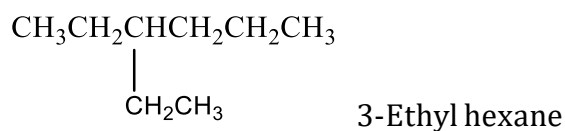
## ***IUPAC NAME OF ALKANES:***

### **The rules of IUPAC system are:**

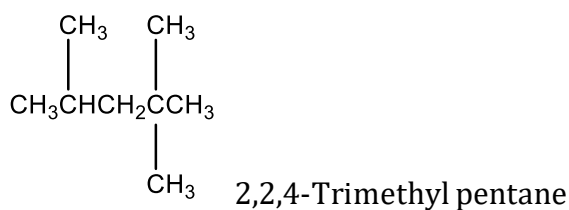
1. Select the longest chain and numbering the chain start whichever end result in the use of the lowest numbers:



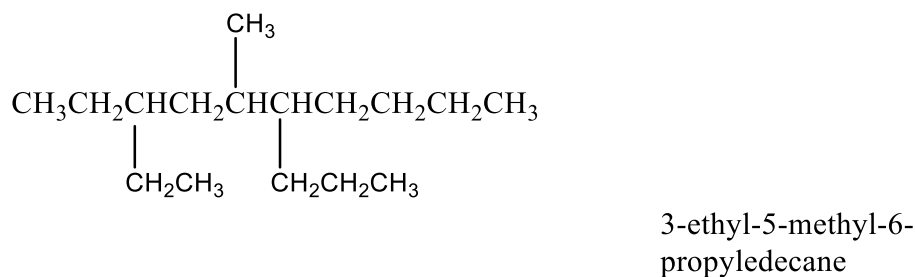
2. Write the number of the branch Carbone and (-), the name of group then alkane ( alk + ane ):



3. If the same alkyl group or any element attached we use the : tetra, tri , di prefixes :

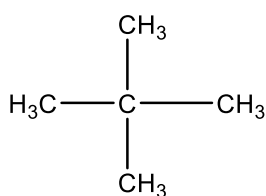


4. If there are several different alkyl group attached to the chain name them in alphabetical order:

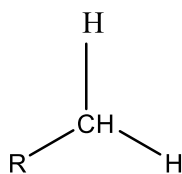


### ***COMMON NAME OF ALKANES:***

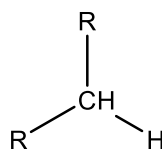
We use the prefixes n- , iso, neo:



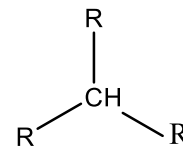
Neo pentane



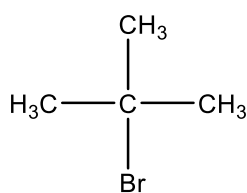
Pry.



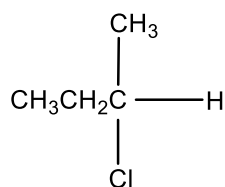
Sec.



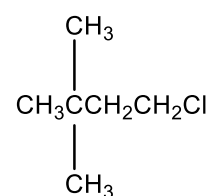
Ter.



Ter. Butylbromide



Secbutylchloride



Neohexylchloride



## ***PROPERTIES OF ALKANES:***

The boiling point rises 20 to 30 degree for each Carbone that is added to the chain. The density increase with size of the alkanes but alkanes are less dense of water, the normal alkanes are have more boiling point than the corresponding isomers.

n- Butane has a boiling point 0 c

iso- Butane has a boiling point -12 c

ISOMERS: two or more compounds have the same molecular weight but they differ in physical and chemical properties because they are differed in formulation.

Alkane is saturated and nonpolar compounds.

**C1 – C5 GASES**

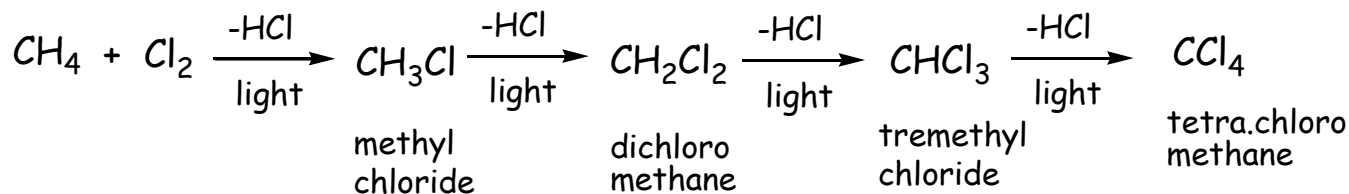
**C5 – C17 LIQUIDS**

**C17 > SOLIDS**

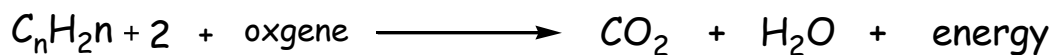
In agreement with rule of thamb ((like dissolves like)) alkanes soluble in nonpolare solvents such as , benzene , ethers.....ect and insoluble in water and other highly polar solvents.



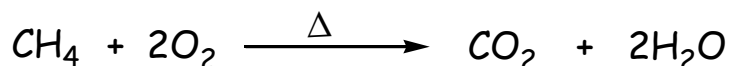




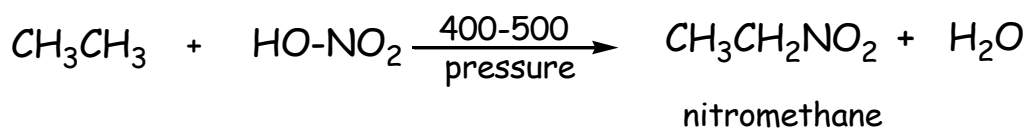
## 2. COMBUSTION:



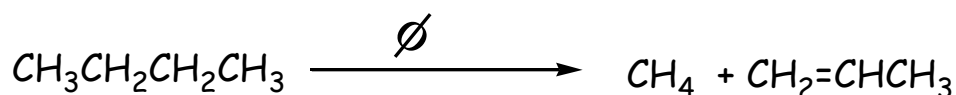
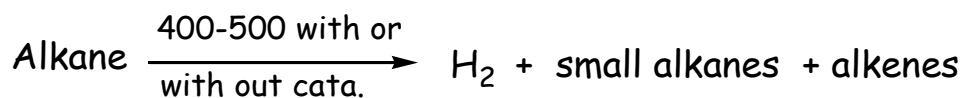
$$\Delta H = 848 \text{ kJ/mol}$$



## 3. NITRATION OF ALKANE: (substituted of $\text{NO}_2$ )



## 4. CRACKING:



## USES:

Propane and Butane mixed = home gas

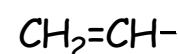
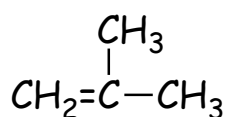
2,2,4 -Tri methyl Pentane = increase the Octane number.

## ALKENES (( OLFINES ))

### ALKENES:

Unsaturated compounds contain double bond , general formula is (  $C_nH_{2n}$  ) the hybrid of unsaturated Carbon is  $SP^2$ .

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



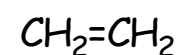
Iso butene ( $C_4H_8$ )

Allyl group ( $C_3H_5-$ )

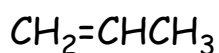
Vinyl group ( $C_2H_3-$ )

### AUPIC NAME OF ALKENES:

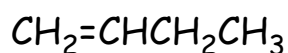
1. Select the longest chain that contain the double bond and numbering from the double bond side , each name is derived by changing the ending -ane of corresponding alkane name to -ene.



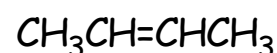
Ethene



Propene



1-Butene



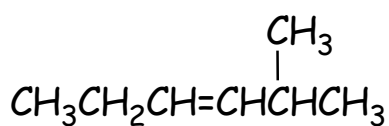
2-Butene

2. Indicate by a number the position of the double bond in the chain and (-) then name of alkene ( alk+ene )

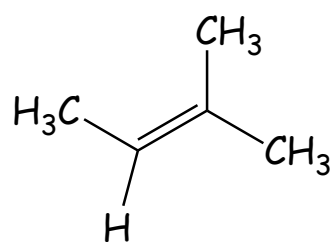


2-Hexene

3. If the double bond in the mid of compound , numbering from branch.

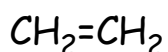


2-Methyl-3-hexene

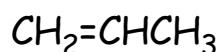


2-Methyl-2-butene

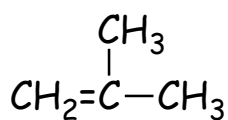
### COMMON NAME OF ALKENE :



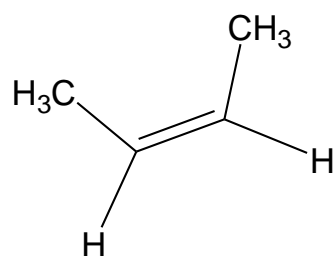
Ethylene



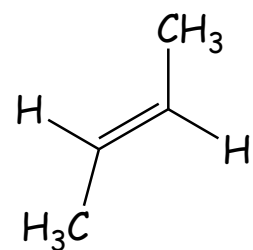
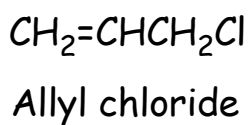
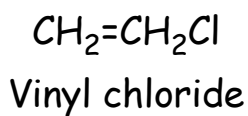
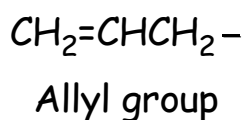
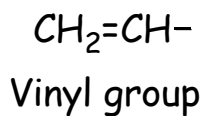
Propylene



Iso butene



cis-2-butene

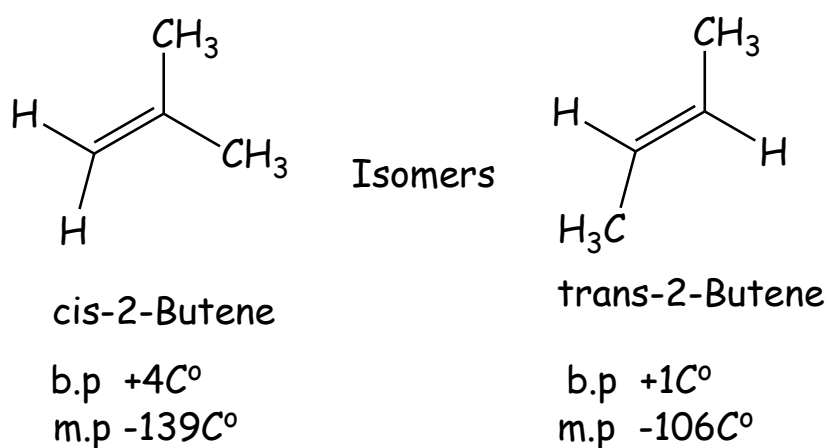


trans-2-Butene

## PROPERTIES:

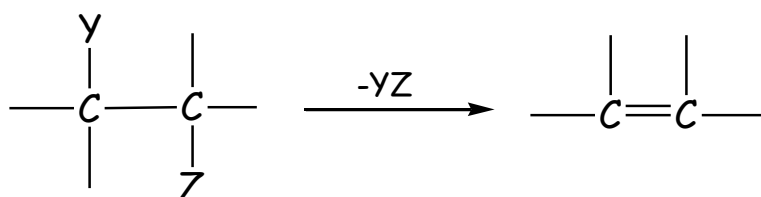
They are insoluble in water but quite soluble in non polar solvents like benzene , ether .

They are less dense than water the boiling point rises with increasing carbon number. Alkene weakly polar.

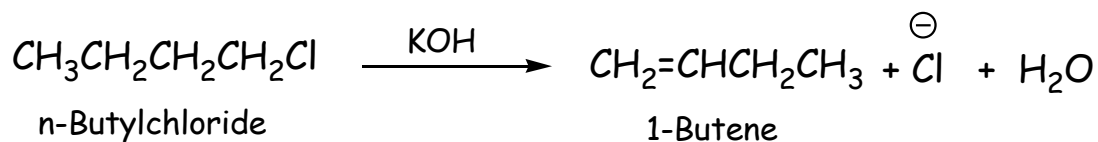
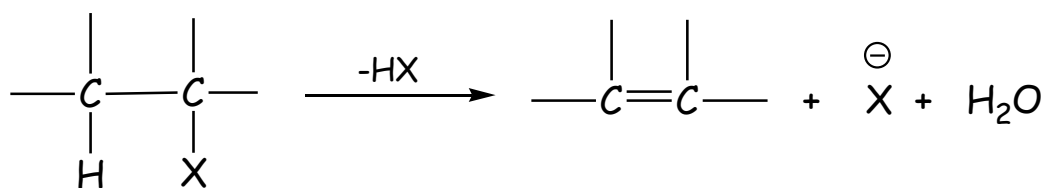


## PREPARATION OF ALKENE:

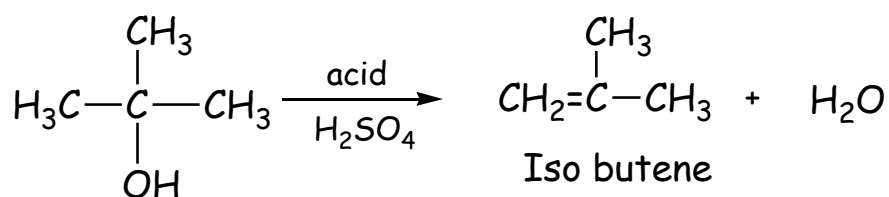
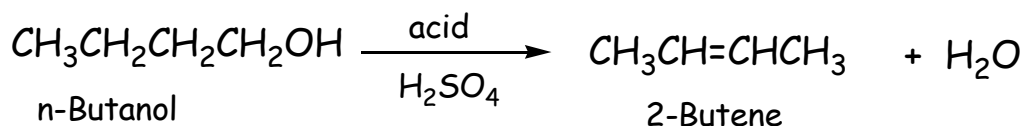
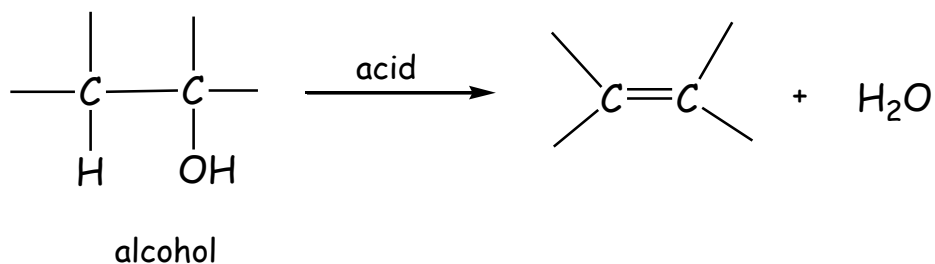
Preparation of alkene result from elimination of groups from two nearby carbon atoms.



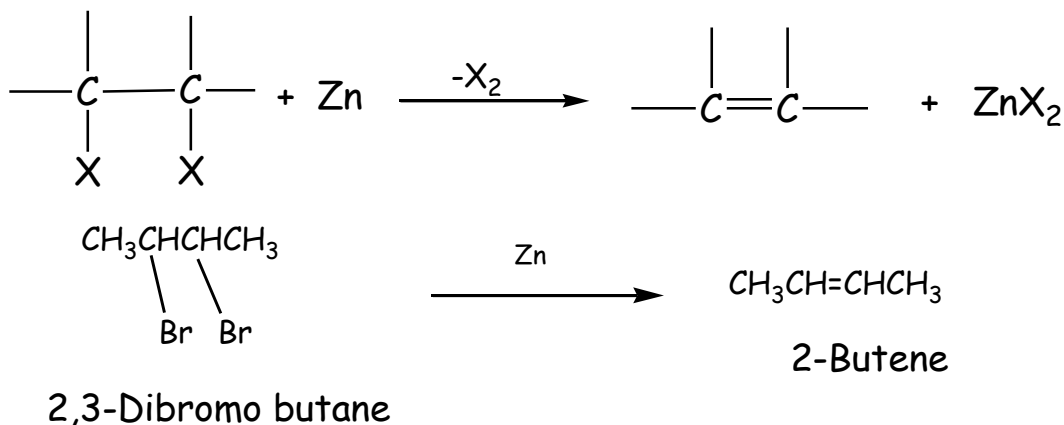
### 1. Dehydrohalogenation of alkyl halides ( elimination of HX).



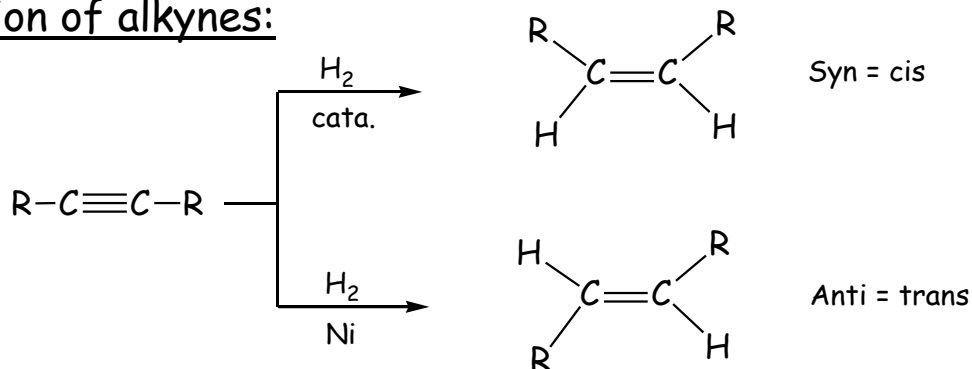
## 2. Dehydration of alcohols (elimination of H<sub>2</sub>O):



## 3. Dehydrogenation of vicinal dihalides:



## 4. Reduction of alkynes:

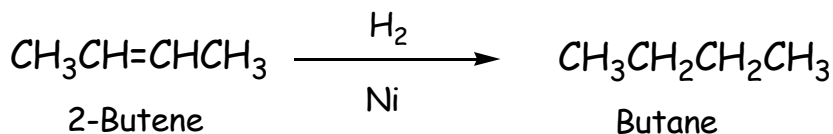
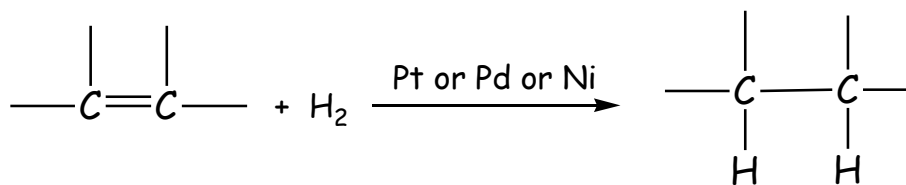




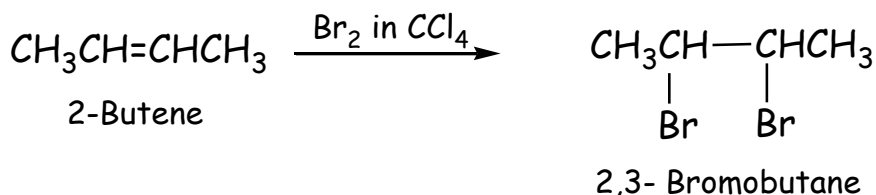
## REACTION OF ALKENE:

### a) Addition reactions:

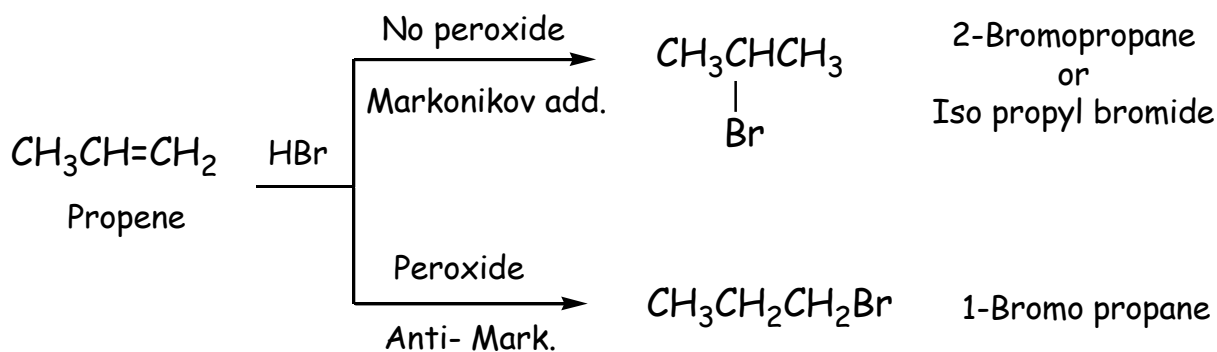
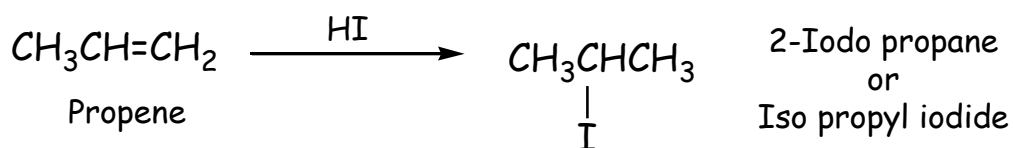
#### 1. Addition of hydrogen. (catalytic hydrogenation)



#### 2. Addition of halogens. (halogenations by addition)

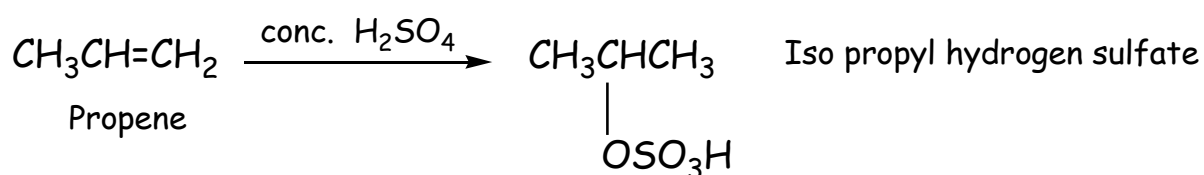
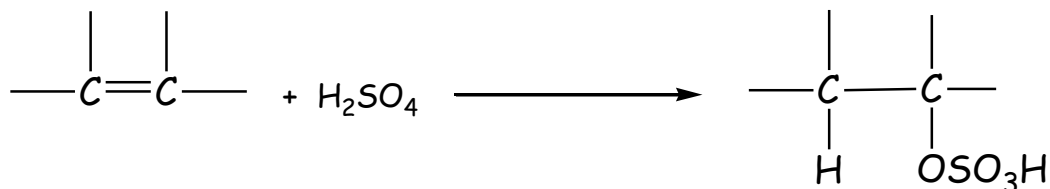


#### 3. Addition of hydrogen halides:

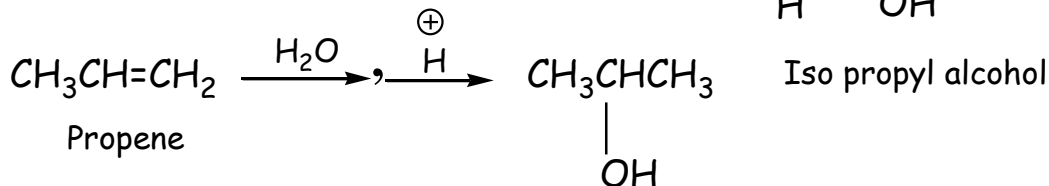
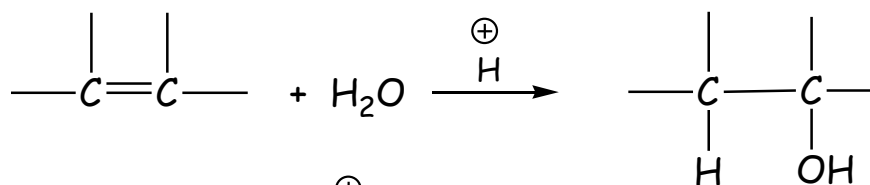


**Markovnikov's rule:** For addition of hydrogen halides (HX) to unsymmetrically substituted alkenes, the H atom adds to the C with the most H atoms already present.

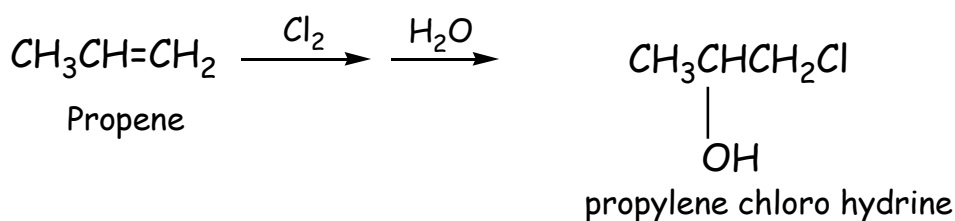
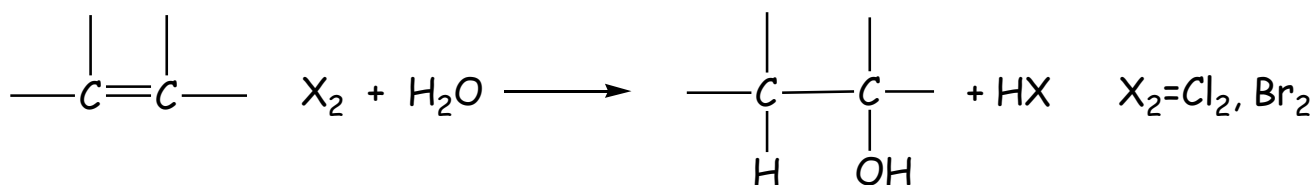
4. Addition of sulfuric acid:



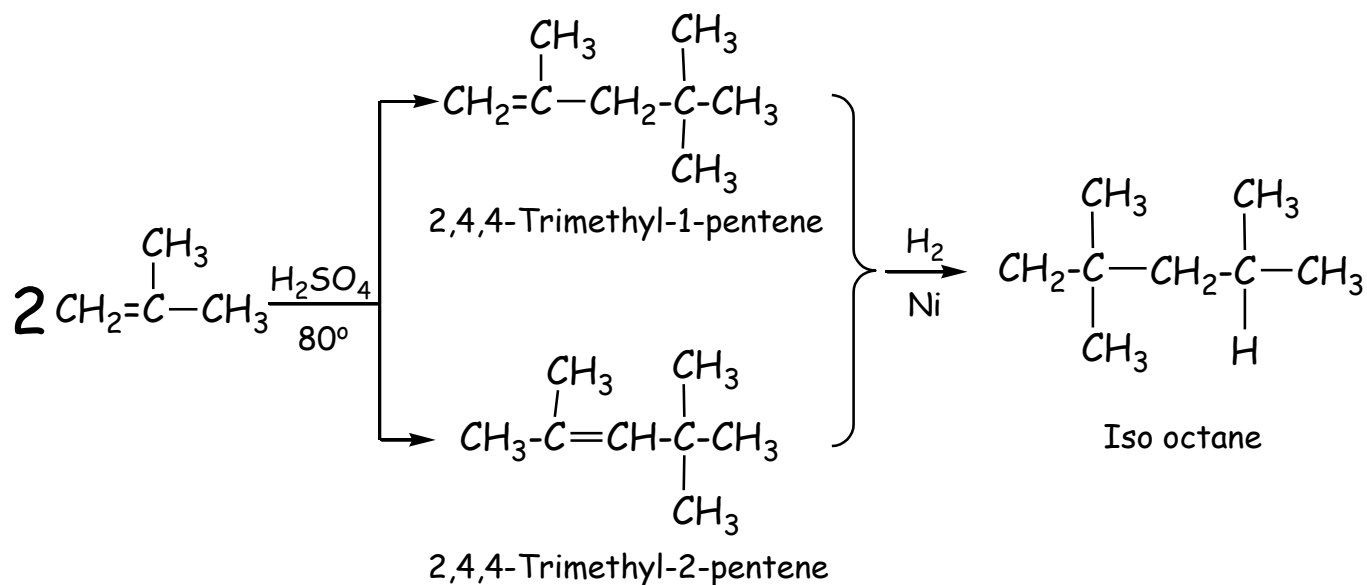
5. Addition of water (hydration).



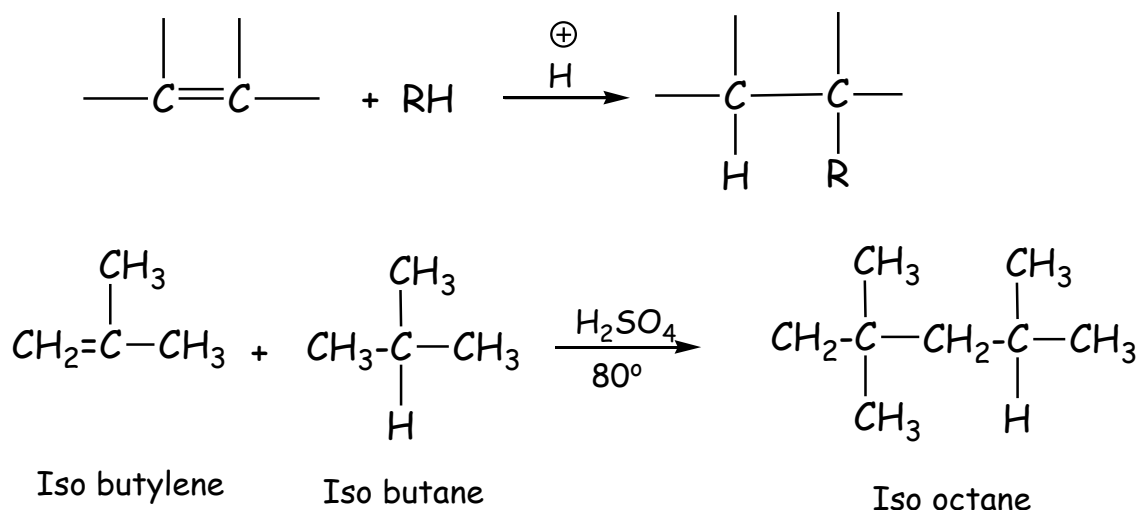
6. Halohydrin formation. (addition of X<sub>2</sub> and H<sub>2</sub>O)



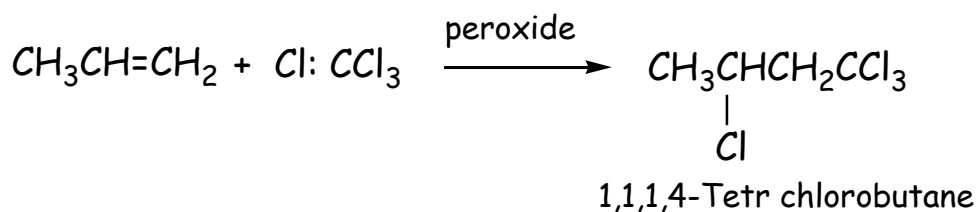
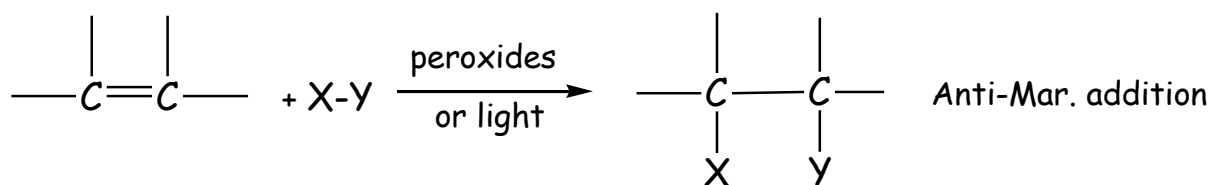
## 7. Dimerization of alkene:



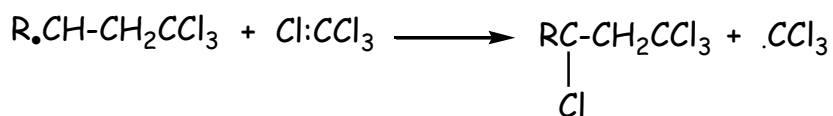
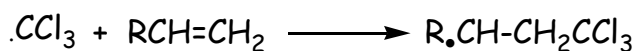
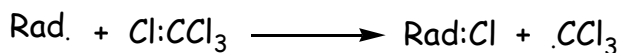
## 8. Alkylation:



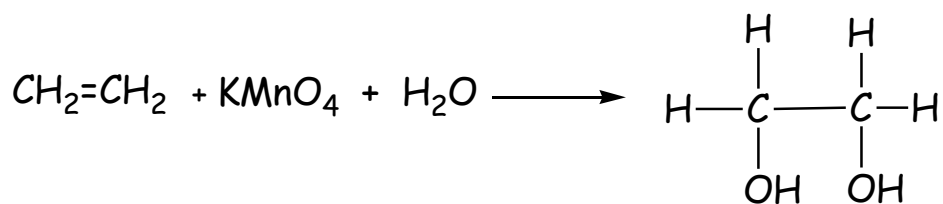
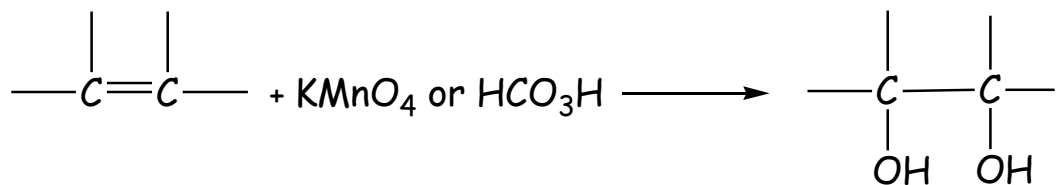
## 9. Addition of free radicals:



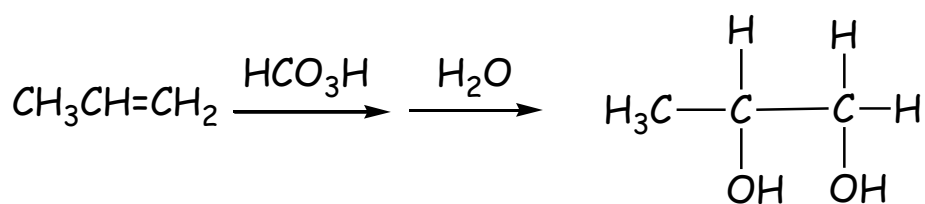
peroxide  $\longrightarrow$  Rad.



## 10. Hydroxylation. (Glycol formation)

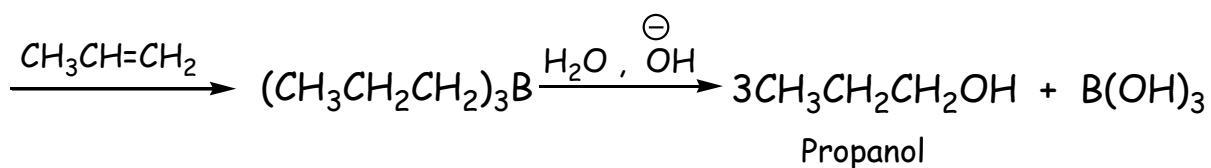
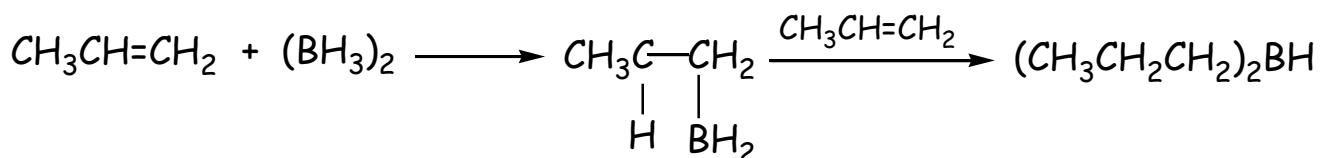


Ethylene glycol (1,2-ethane diol)

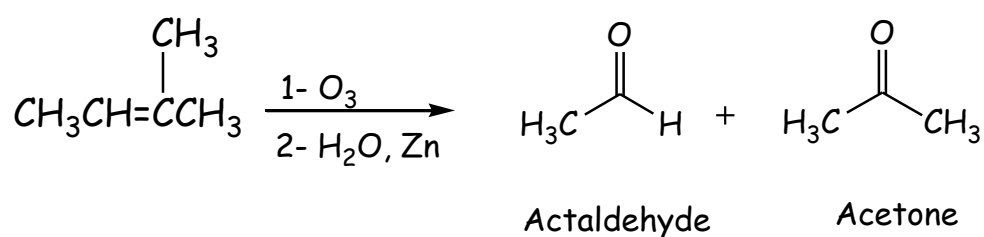
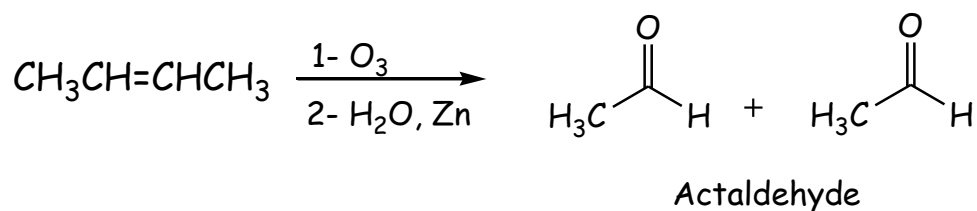
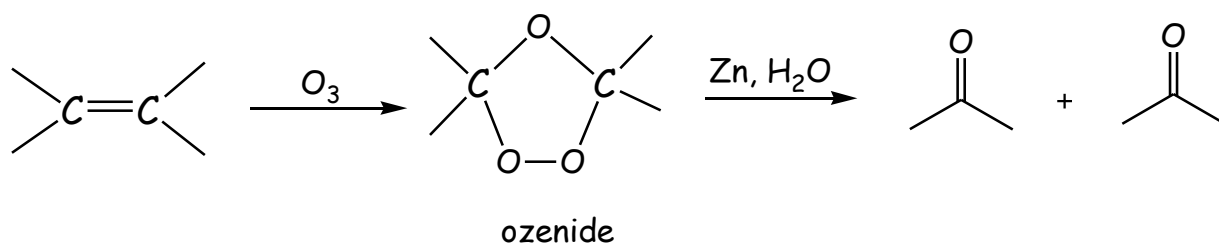


propylene glycol

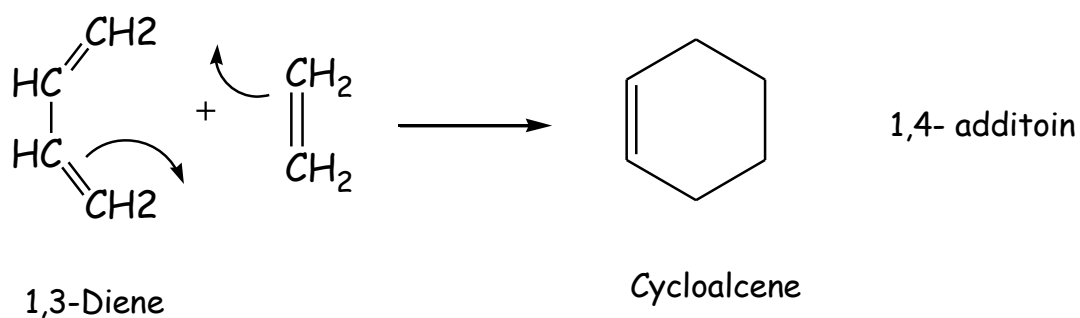
## 11. Hydroboration. (oxidation to form alcohol)



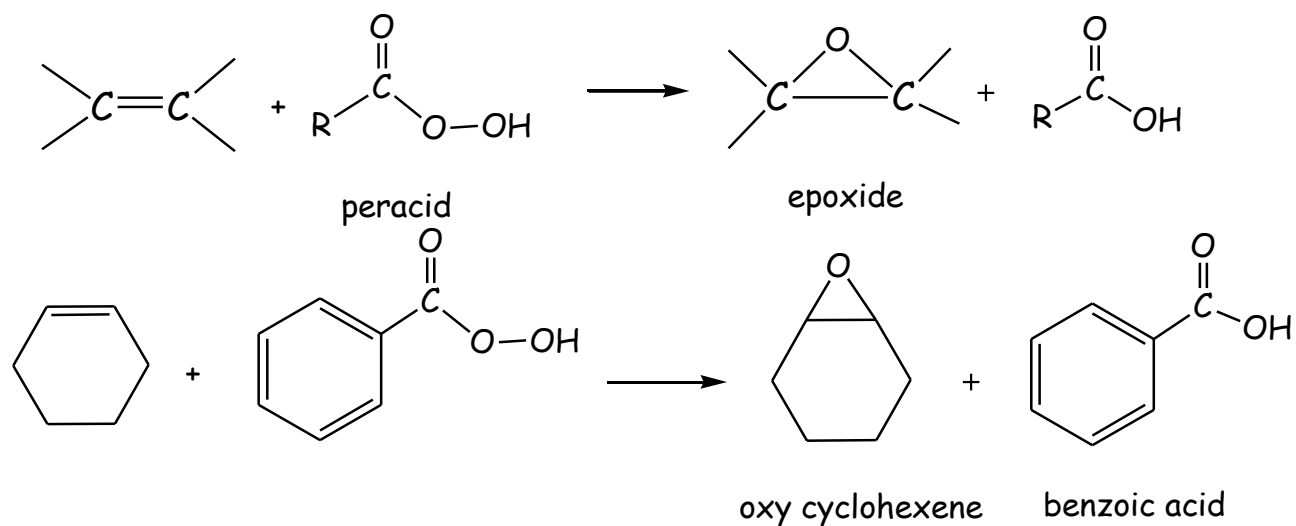
## 12. Oxidation with Ozone:



## 13. Diels-Alder reaction:

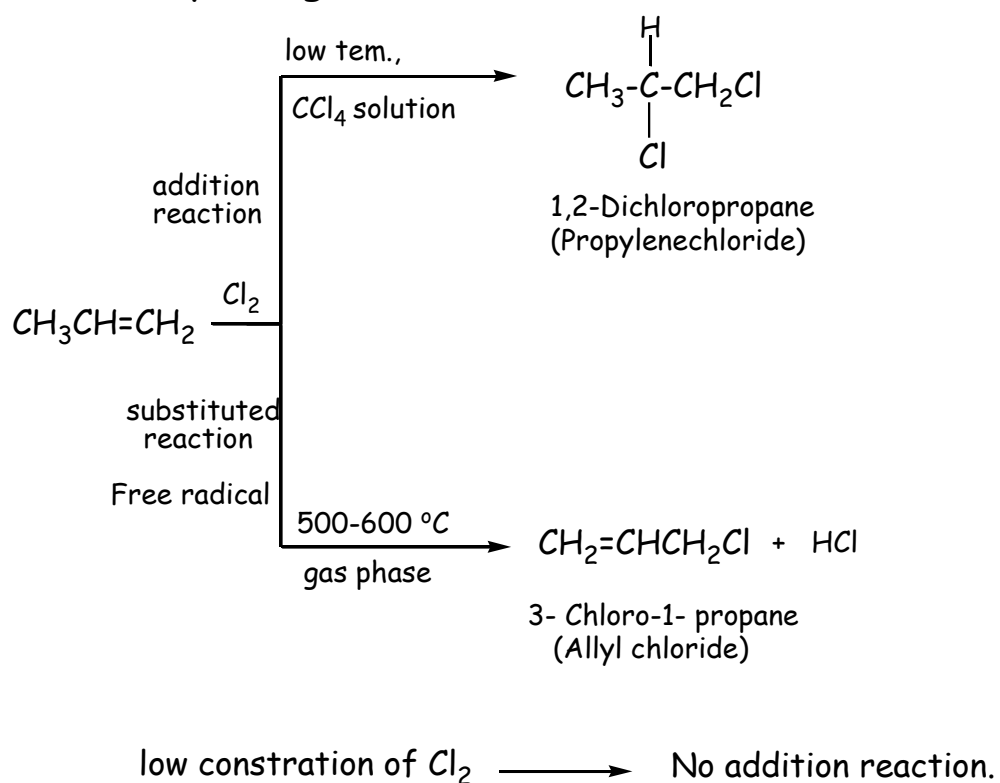


## 14. Oxidation with peracids:



## B) SUBSTITUTION REACTION:

### 1- Substitution by halogen:



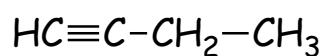
## ALKYNES (ACETYLENES):

ALKYNES : unsaturated compounds contain triple bond general formula is  $(C_nH_{2n-2})$ . The hybrid of carbon is  $(SP)$

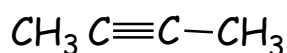
ACETYLENE	$HC\equiv CH$
PROPYNE	$HC\equiv C-CH_3$
1-BUTYNE	$HC\equiv C-CH_2-CH_3$
1-PENTYNE	$HC\equiv C-(CH_2)_2-CH_3$
1-HEXYNE	$HC\equiv C-(CH_2)_3-CH_3$
1-HEPTYNE	$HC\equiv C-(CH_2)_4-CH_3$
1-OCTYNE	$HC\equiv C-(CH_2)_5-CH_3$
1-NONYNE	$HC\equiv C-(CH_2)_6-CH_3$
1-DECAYNE	$HC\equiv C-(CH_2)_7-CH_3$
2-BUTYNE	$CH_3C\equiv C-CH_3$
2-PENTYNE	$CH_3C\equiv CCH_2CH_3$
3,3-DIMETHYL - 1-BUTYNE	$HC\equiv C-C(CH_3)_3$

### NOMENCLATURE :

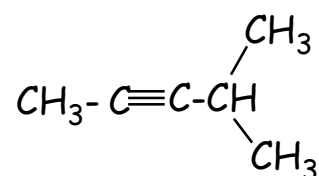
The alkynes are named according to two systems by replacement of one or both hydrogen atoms by alkyl groups.



Ethyl acetylene  
(1-Butyne)



Dimethylthyl acetylene  
(2-Butyne)



Methyl iso propyl acetylene  
(4-Methyl-2-pentyne)

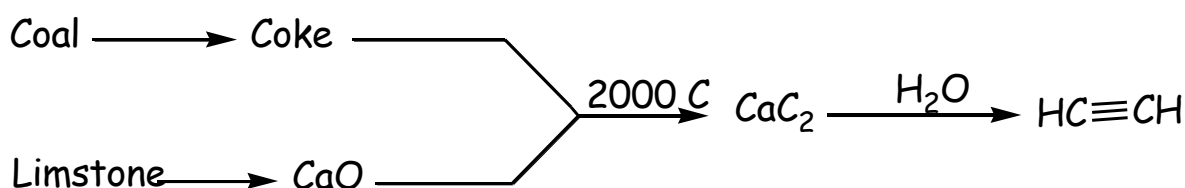
PROPERTIES : they have same properties of ALKANE and ALKENE but some of them contain acid hydrogen.

Acidic Acetylene	Non- acidic acetylene
1. Triple bond in the head of compound therefore contain acidic H.	1. Triple bond in the mid of compound therefore not contain acidic H.
2. React by substitution reaction and gave Acetylide	2. Not react by substitution reaction and not gave Acetylide
3. Contain two fractional groups triple bond and acidic H.	3. Contain one fractional group only triple bond.

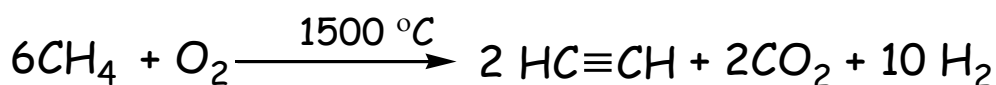
### INDUSTRIAL SOURCE:

1. We can preparation acetylene from Calesuim carbide ( $\text{CaC}_2$ )

By reaction with ( $\text{H}_2\text{O}$ )



2. Oxidation of methane ( from petrol ).

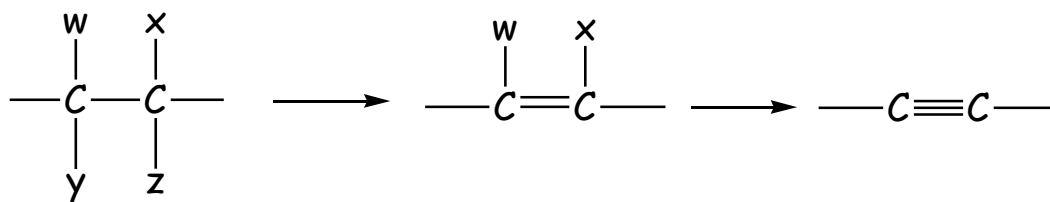


### PREPARATION OF ALKYNES :

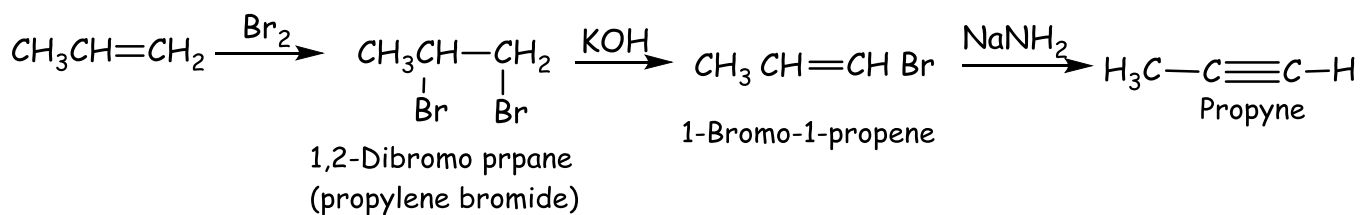
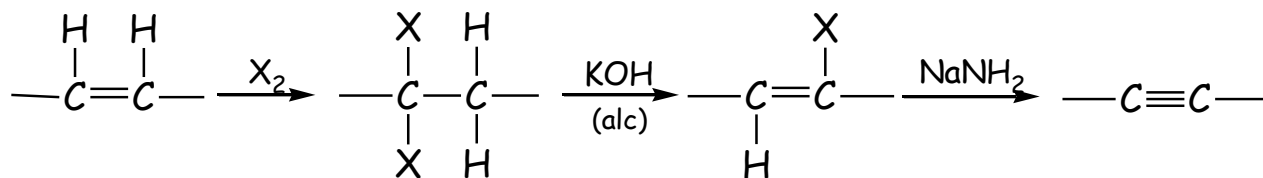
Carbon-Carbon triple bond is formed in the same way as double bond:

Elimination of atoms group from vicinal carbons. The groups eliminated and the reagents used are essentially the same as in the preparation of ALKENE .



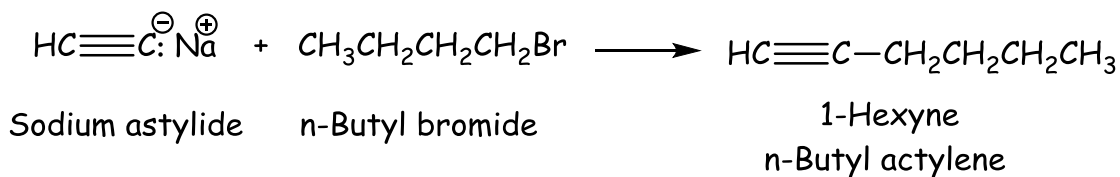
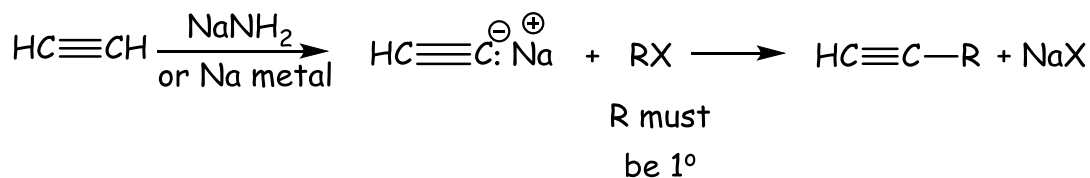


### 1. Dehydrohalogenation of alkyl dihalides.

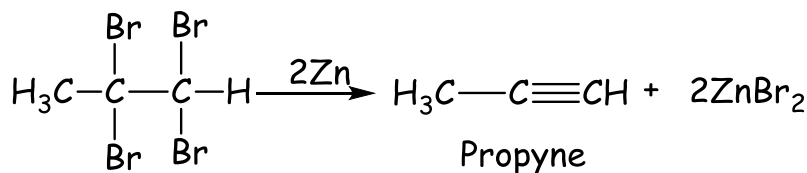
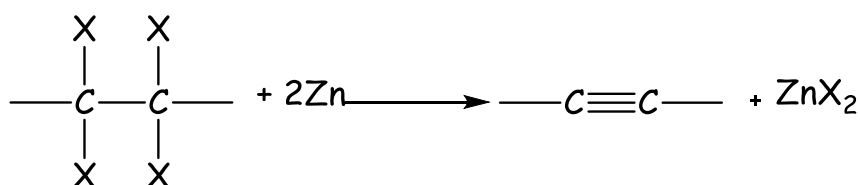


### 2. Reaction of Sodium acetylides with primary alkyl halides:

(substitution reaction)



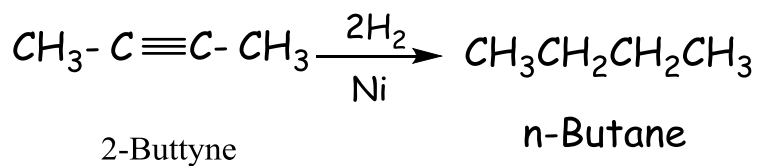
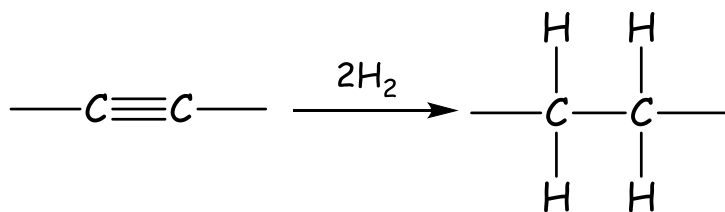
### 3. Dehalogenation of tetra halides:



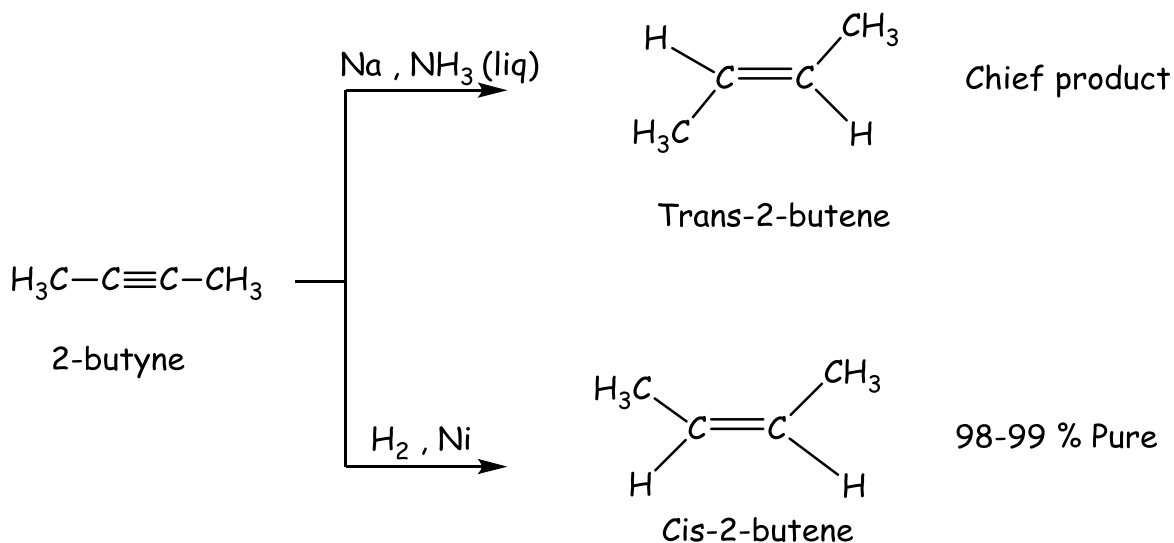
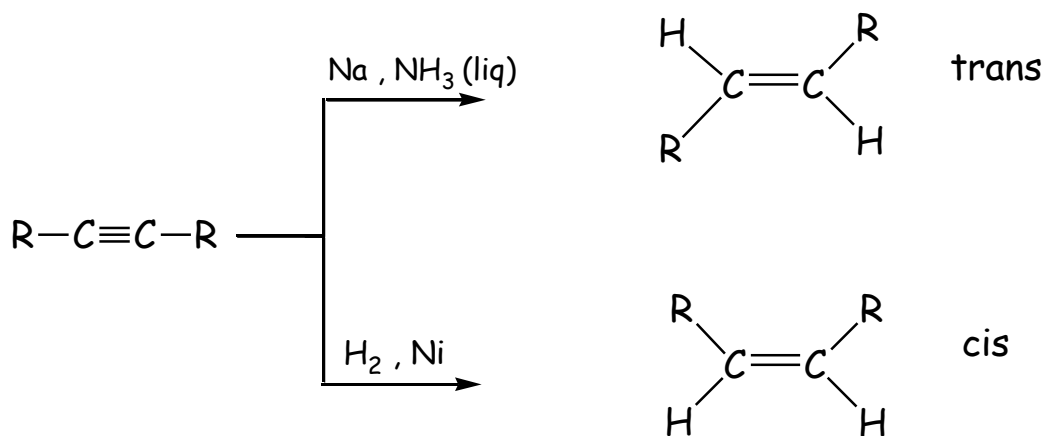
## REACTIONS OF ALKYNES:

Addition reaction:

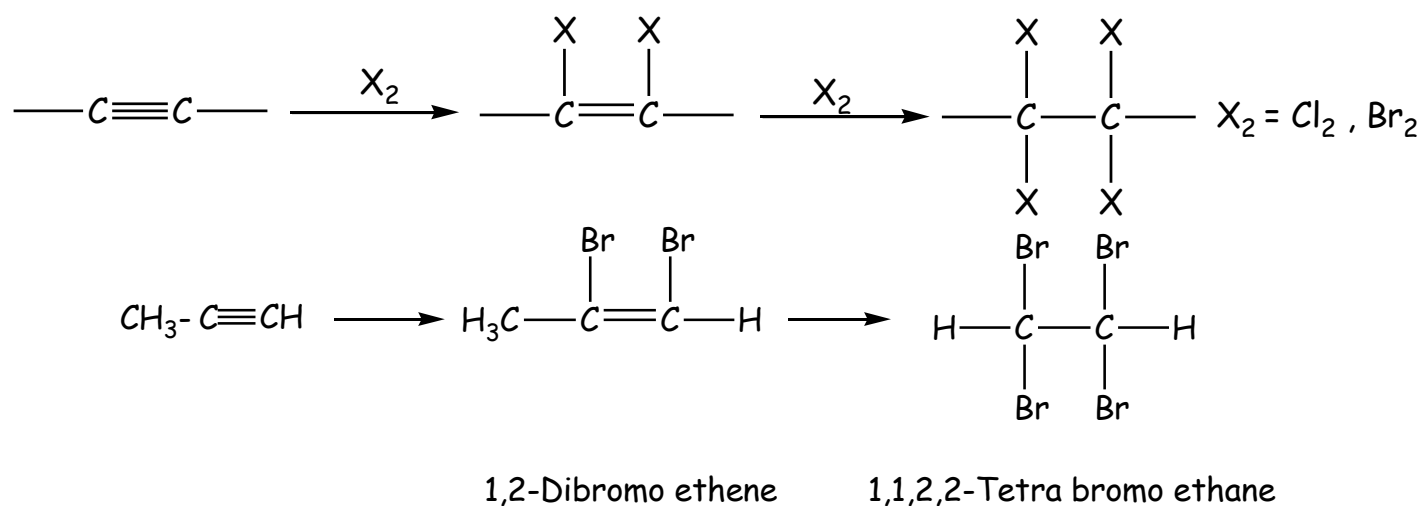
### 1. Addition of hydrogen:



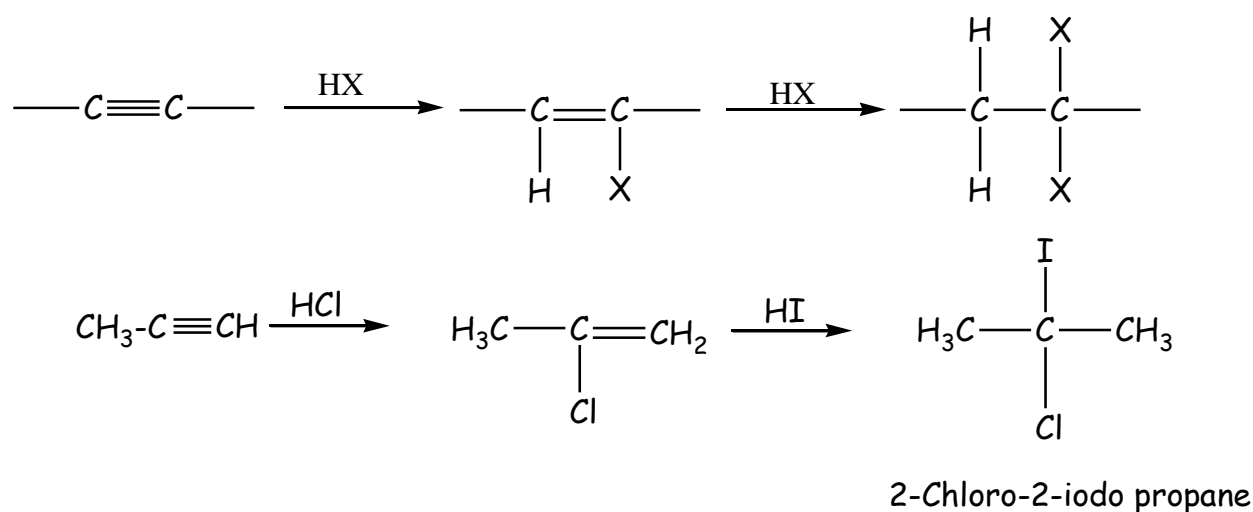
### 2. Addition of hydrogen include two products:



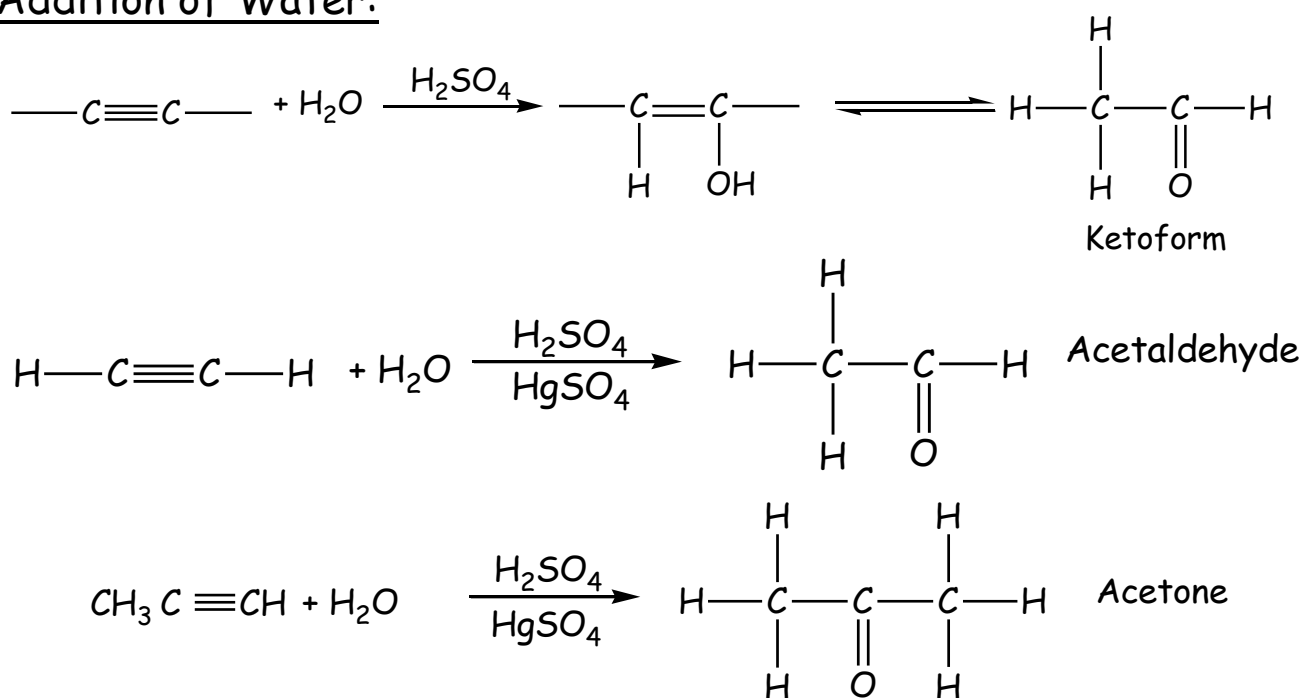
### 3. Addition of halogens:



### 4. Addition of hydrogen halides:



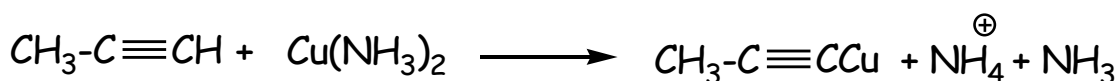
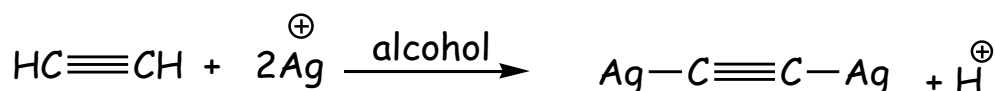
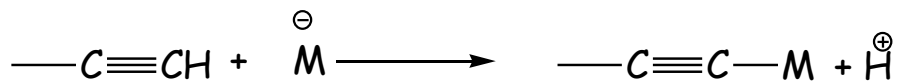
### 5. Addition of Water:



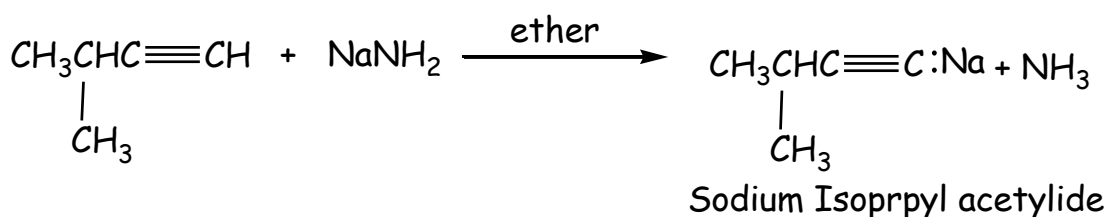
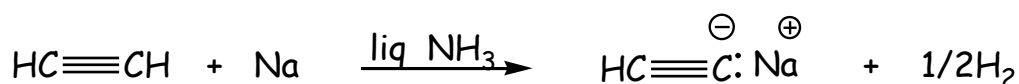
Reaction as acid:



6. Formation of heavy metal acetylides:

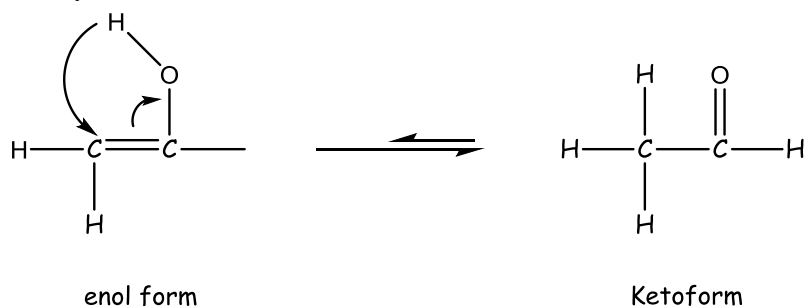


7. Formation of alkali metal acetylides:



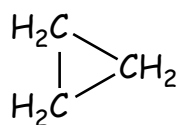
### TAUTAMERISM:

Compounds whose structures differ in arrangement of atoms, but which exist in easy and rapid equilibrium are called "Tautomerism" involves structures that differ in the point of attachment of hydrogen as in keto-enol.

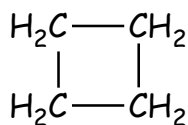


## ALICYCLIC HYDROCARBONS

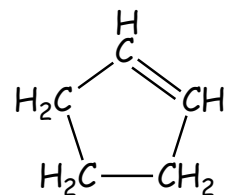
The carbon atoms are arranged to form rings, the cyclic aliphatic hydrocarbons are named by prefixing cyclo- to the name of the ring :



Cyclopropane



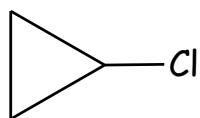
Cyclobutane



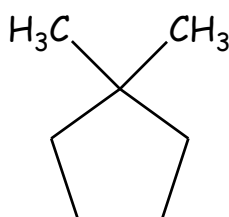
Cyclopentene

Substituent on the ring-alkyl groups, halogens. Are named and their position are indicated by numbers we do all in such away

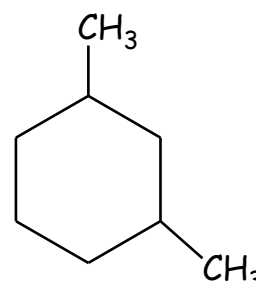
As to give the lowest combination of numbers.



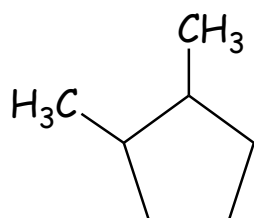
Chloro cyclopropane



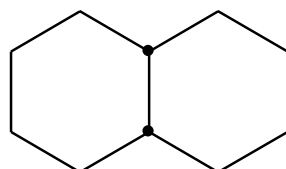
1,1-Dimethyl Pentane



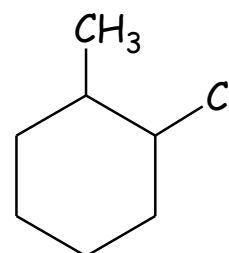
1,3-Dimethyl cyclohexane





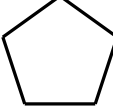
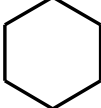
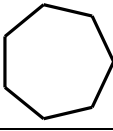
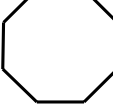
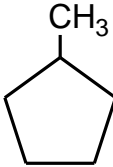
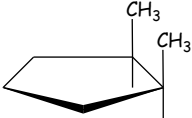
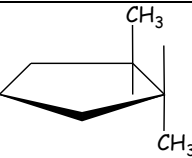

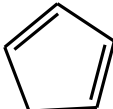
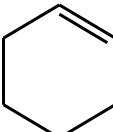
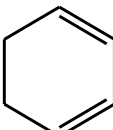
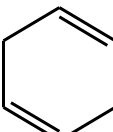
1,2-Dimethyl cyclo Pentane



Decalene

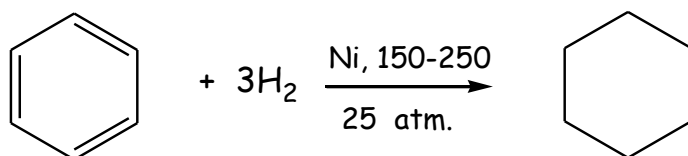


2-Chloro-1-methyl cyclo hexane

Name	M.P °C	Structures
Cyclo propane	-127	
Cyclo butane	-80	
Cyclo pentane	-44	
Cyclo hexane	6.5	
Cyclo heptane	-12	
Cyclo octane	14	
Methyl Cyclo pentane		
Cis-1,2-dimethyl Cyclo pentane		
Trans-1,2-dimethyl Cyclo pentane		
Cyclo pentene		
1,3-Cyclo pentadiene .		
Cyclo hexane		
1,3-Cyclo hexadiene		
1,4-Cyclo hexadiene		

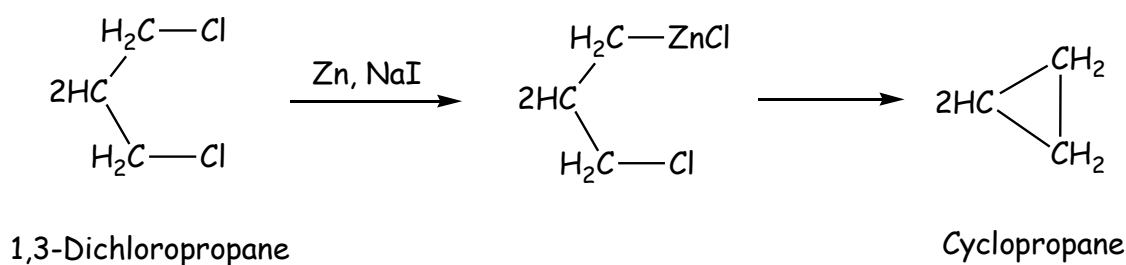
## PREPARATION OF CYCLIC COMPOUNDS.

Industrial source: by hydrogenation of aromatic compounds :



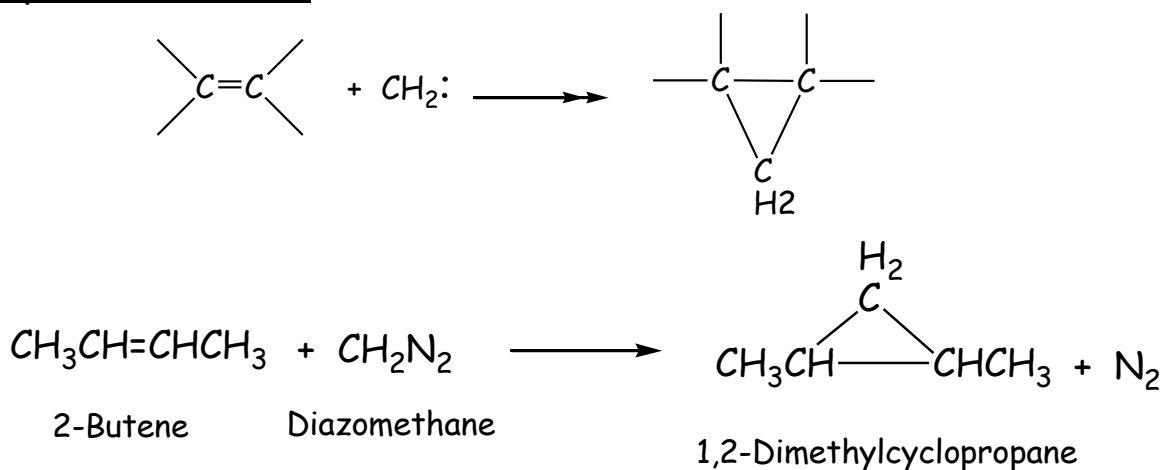
Laboratory preparation:

1. Cyclization: dihalide can bring about coupling between two alkyl groups (that are part of the same molecule)

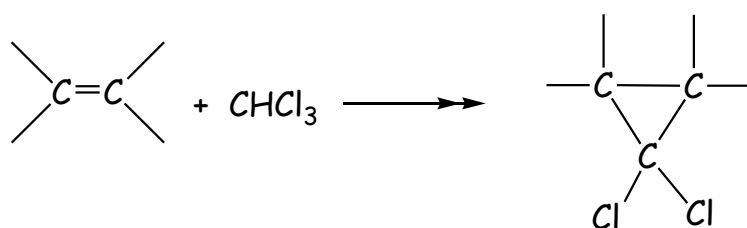


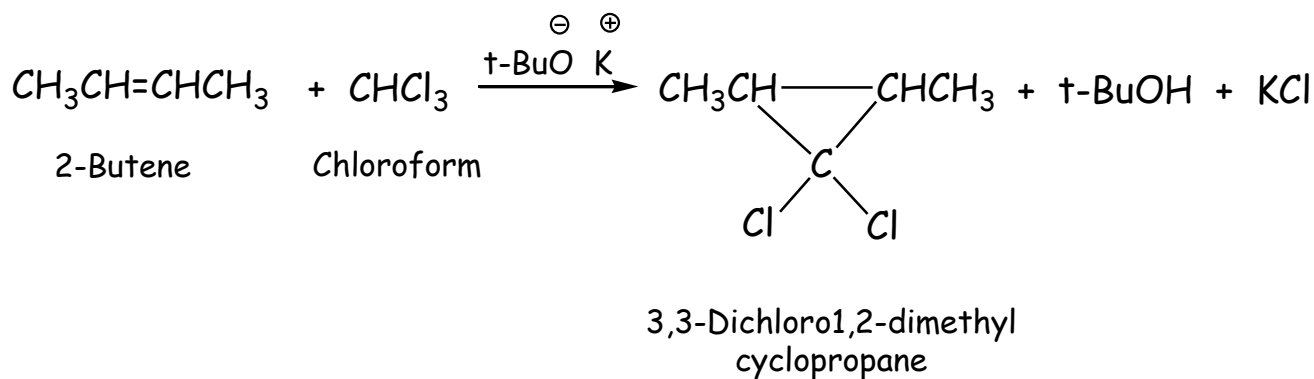
2. Cycloaddition: (by carbenes and methylene)

a. Methylene addition:



b. Carbenes addition: (substituted carbenes)

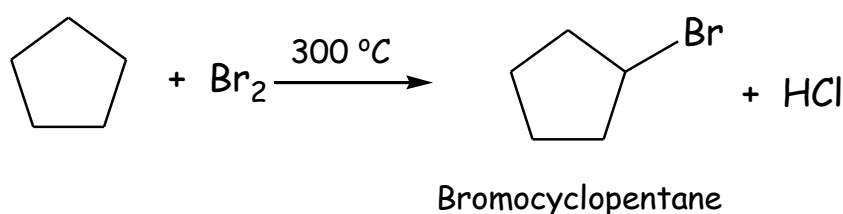
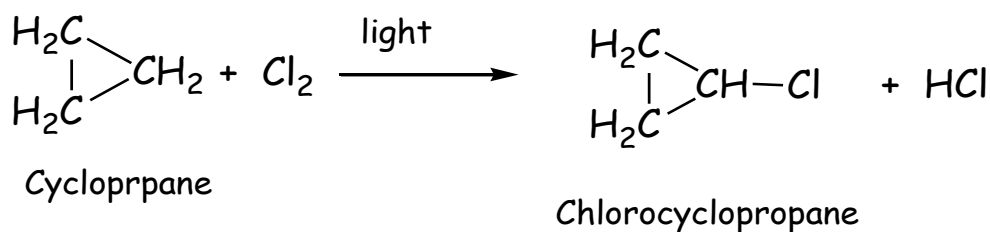




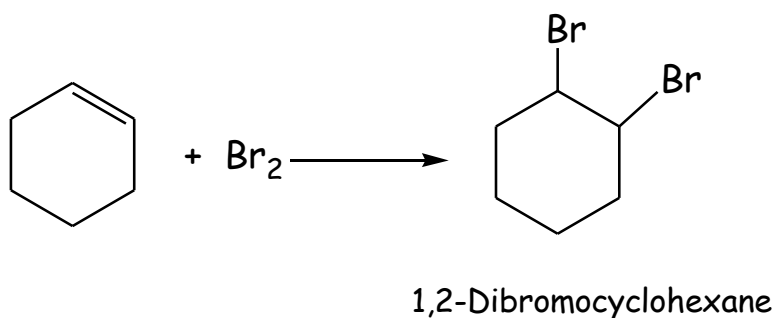
## REACTIONS:

Alicyclic hydrocarbons undergo the same reactions as their open chain analogs.

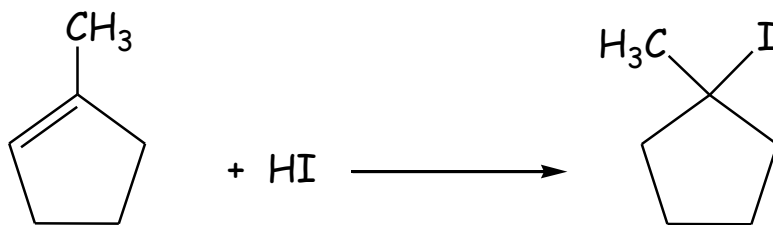
Cycloalkane undergo chiefly free radical substitution



Cycloalkane undergo chiefly addition reactions:

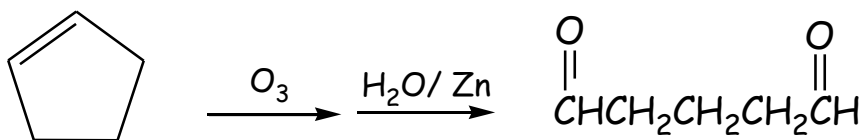






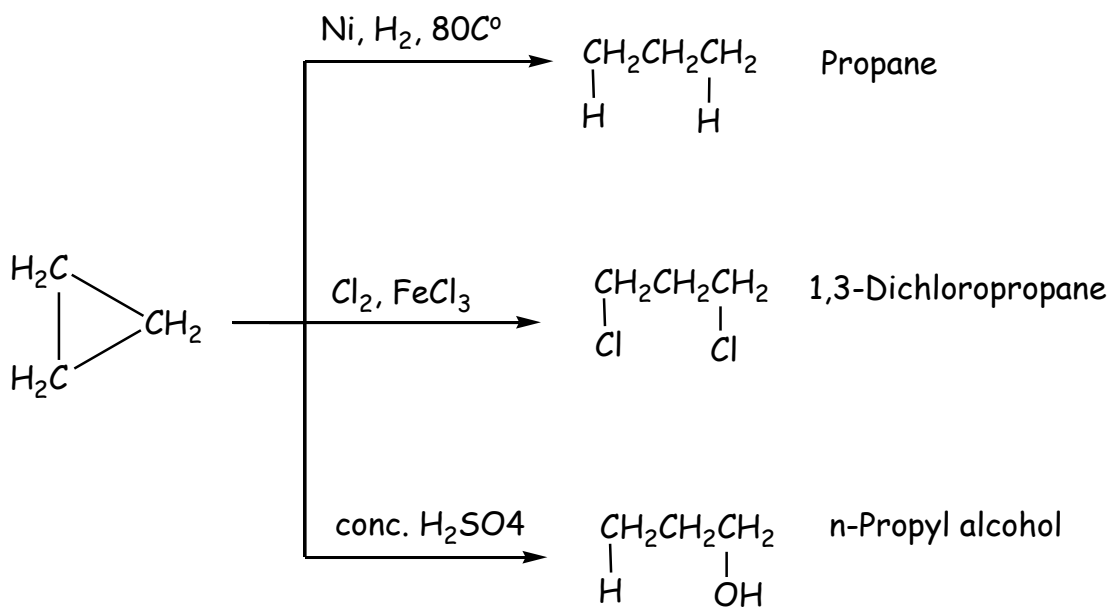
Methylcyclopentene

1-Iodo-1-methylcyclopentane



Cyclopentene

Adialdehyde



## (Aromatic compounds)

Aromatic character. The Huckel ( $4n + 2$ ) rule:-

What properties do all aromatic compounds have in common ?

From the practical standpoint:

1. Aromatic compounds have a high degree of unsaturation.
2. Aromatic compounds are resistant to addition reactions.
3. Aromatic compounds undergo electrophilic substitution.

From theoretical standpoint:

1. Aromatic compounds must have a cyclic clouds of delocalized ( $\pi$ ) electrons above and below the plane of the molecule.

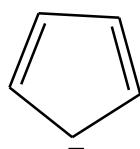
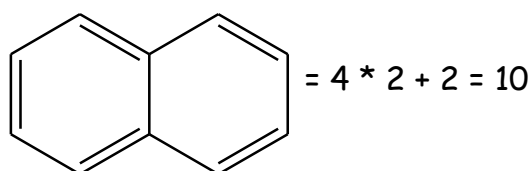
2. The ( $\pi$ ) clouds must contain of ( $4n+2$ )  $\pi$  electrons.

$n = 0, 1, 2, 3, \dots$  ect. And there must be a particular number of  $\pi$  electrons.

2, 6, 10,  $\dots$  ect.

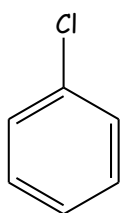
Benzene has six  $\pi$  electrons.

$$4 * 1 + 2 = 6 \pi \text{ electrons.}$$

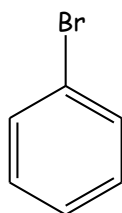


Nomenclature of benzene derivatives :-

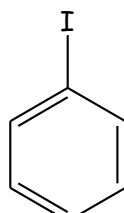
We simply prefix the name of substituent group to the word - benzene, as for example chlorobenzene and bromobenzene.



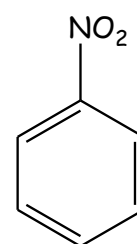
Chlorobenzene



Bromobenzene

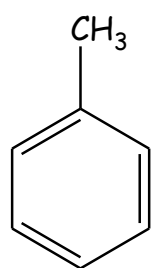


Iodobenzene

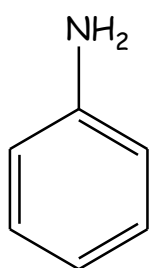


Nitrobenzene

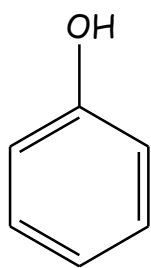
Other derivatives have special names, for example ethyl benzene is always known as toluene, aminobenzene as aniline, hydroxybenzene as phenol.



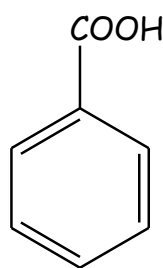
Toluenen



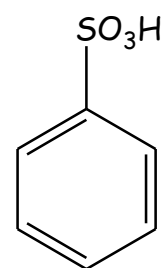
Aniline



Phenol

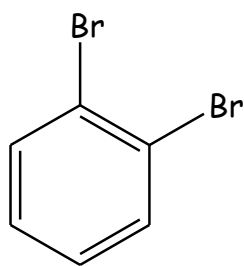


Benzoic acid

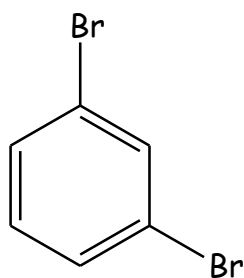


benzene sulfonic acid

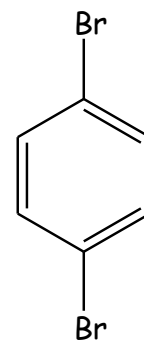
The three possible isomers of a disubstituted benzene are differentiated by the use of the name ortho, meta and para. Abbreviated as o-, m- and p-.



*o*-Dibromobenzene

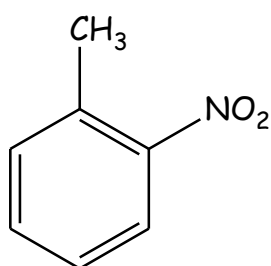


*m*-Dibromobenzene

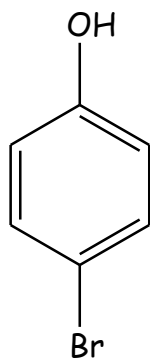


*p*-Dibromobenzene

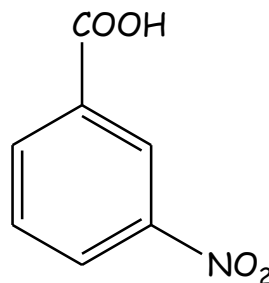
If two groups are different, gives a special name to molecula and named the compound as a derivative of the special compound as, for example nitrotoluene, bromophenol .... ect.



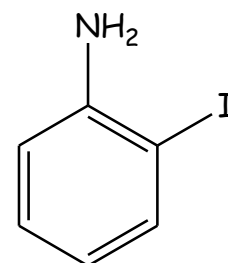
*o*-Nitrotoluene



*p*-Bromophenol

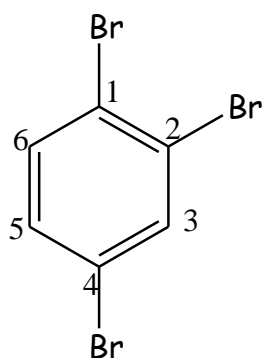


*m*-Nitrobenzoic acid

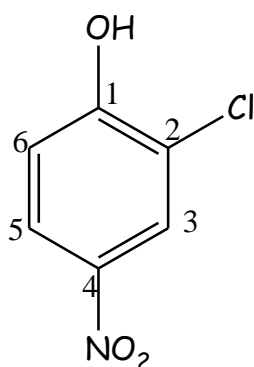


*o*-Iodoaniline

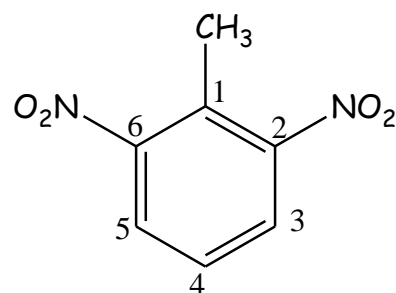
If more than two groups are attached to the benzene ring, numbers are used to indicate their relative positions, for example :



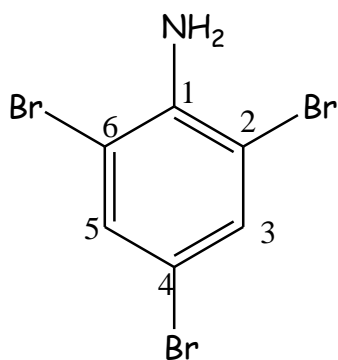
1,2,4-Tri bromobenzene



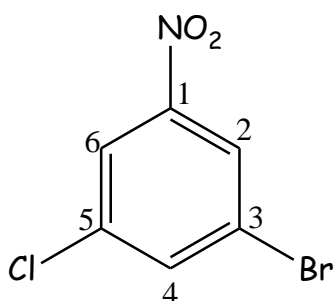
2-Chloro-4-nitrophenol



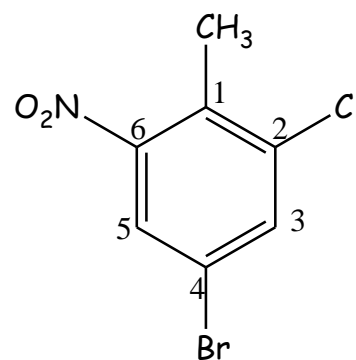
2,6-Dinitro toluene



2,4,6-Tribromo aniline

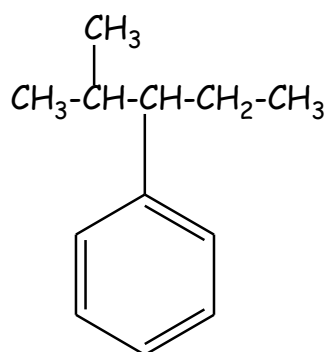


3-Bromo-5-chloronitrophenol

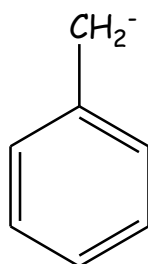


2-Chloro-4-bromo-6-nitro toluene

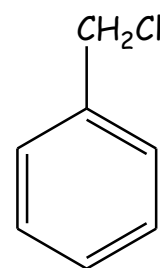
If benzene attached with aliphatic chain (contain four carbon atoms or more) the benzene ring name phenyl:



2-Methyl-3-phenyl pentane

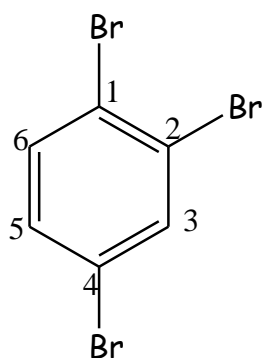


Benzyl group

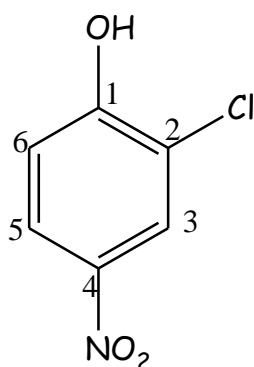


Benzyl chloride

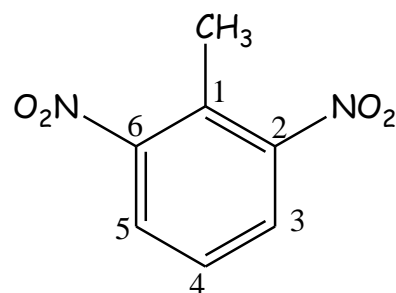
If more than two groups are attached to the benzene ring, numbers are used to indicate their relative positions, for example :



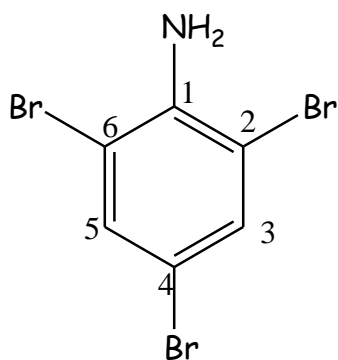
1,2,4-Tri bromobenzene



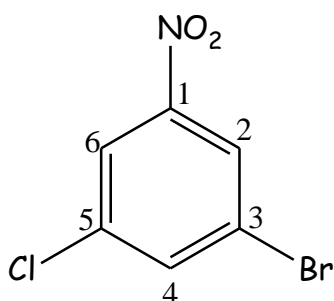
2-Chloro-4-nitrophenol



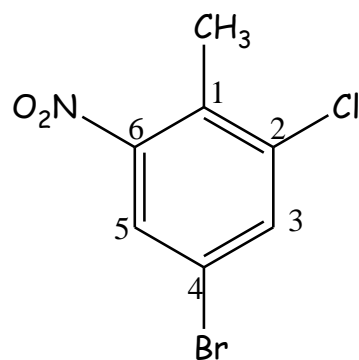
2,6-Dinitro toluene



2,4,6-Tribromo aniline

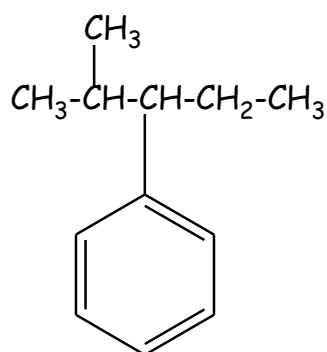


3-Bromo-5-chloronitrophenol

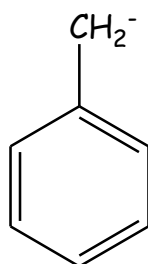


2-Chloro-4-bromo-6-nitro toluene

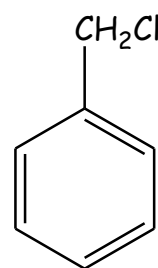
If benzene attached with aliphatic chain (contain four carbon atoms or more) the benzene ring name phenyl:



2-Methyl-3-phenyl pentane



Benzyl group



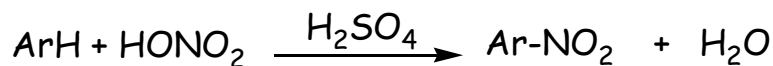
Benzyl chloride

## Reactions of Aromatic compounds:

### a) Electrophilic aromatic substitution:-

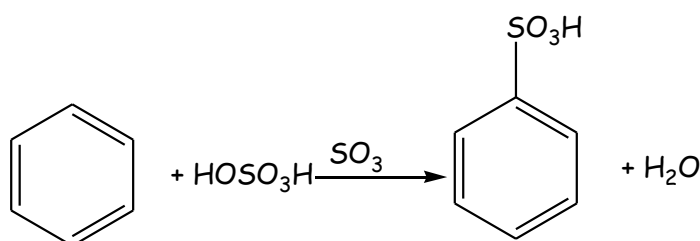
The characteristic reactions of benzene involve substitution in while the resonance stabilized ring system reactions are :-

#### 1. Nitration:-



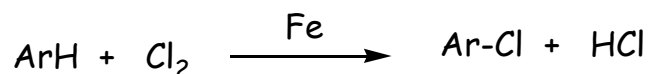
A nitro compound

#### 2. Sulfonation:-

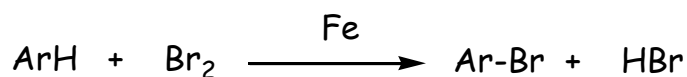


A Sulfonic acid

#### 3. Halogenation:-

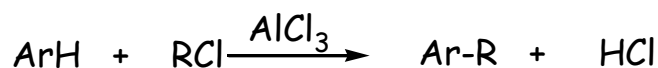


An anylchloride



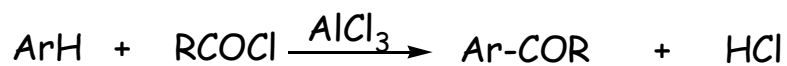
#### 4. Friedel-Craft's reactions:-

##### a. Alkylation:-



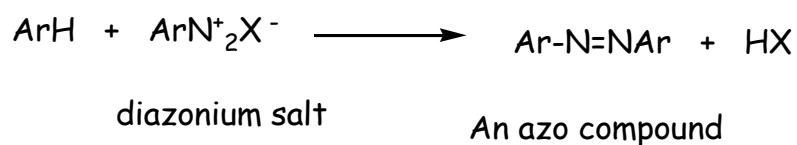
Alkyl benzene

##### b. Acylation :-



Keton

## 5. Diazo coupling:-

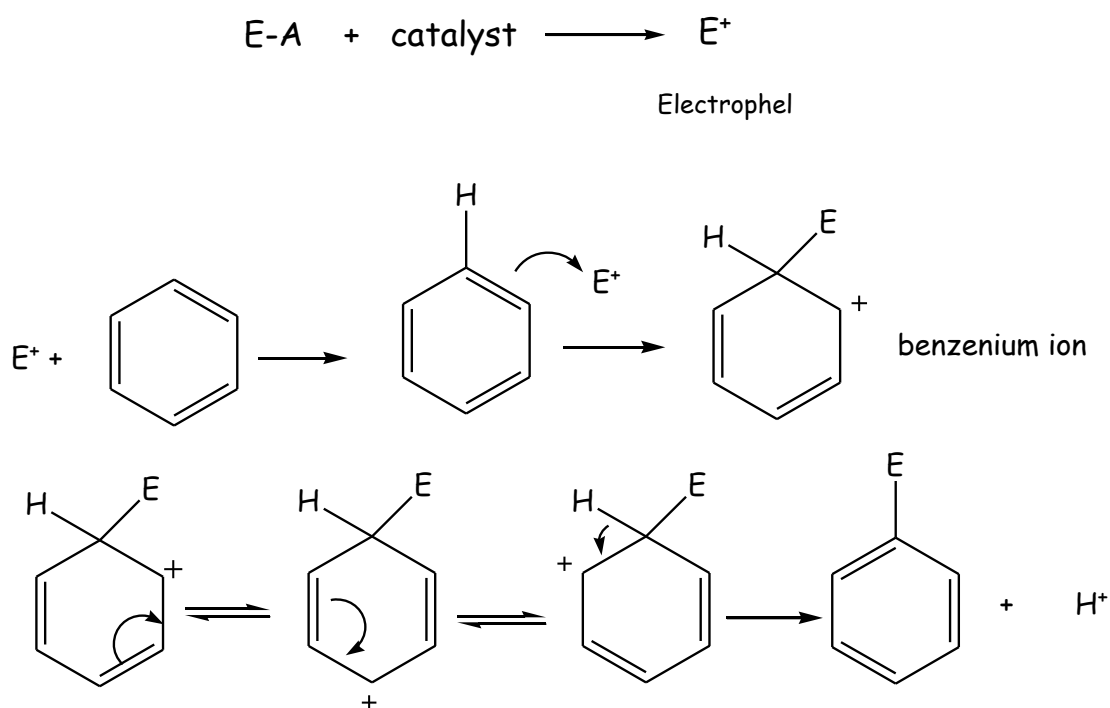


There are two questions:-

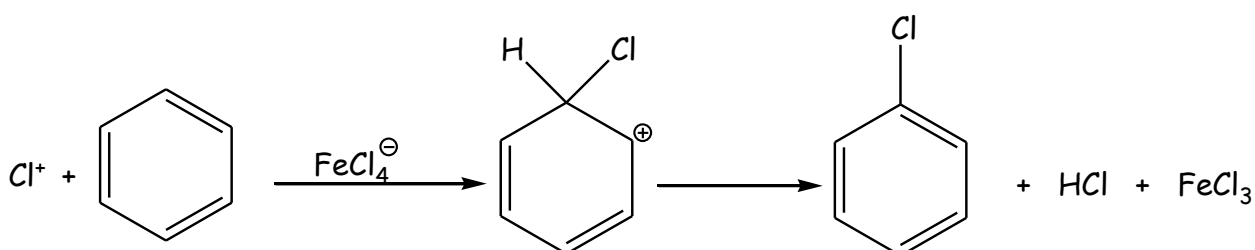
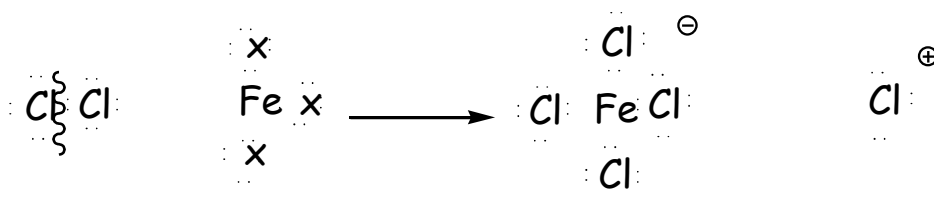
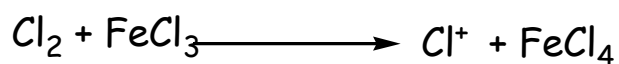
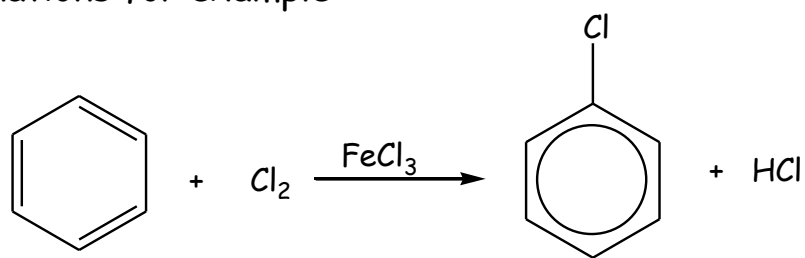
A. Why we used these reagents ?

B. What is the mechanism which these reaction take place ?

1. Above and below the plane of the benzene ring there is cloud of  $\pi$  electrons.
2. These  $\pi$  electrons loosely held and are available to a reagent that is seeking electrons.
3. Benzene ring serves as a source of electrons, that is as a base.
4. The compounds with which it react are deficient in electrons, that is are electrophilic reagents or acid.

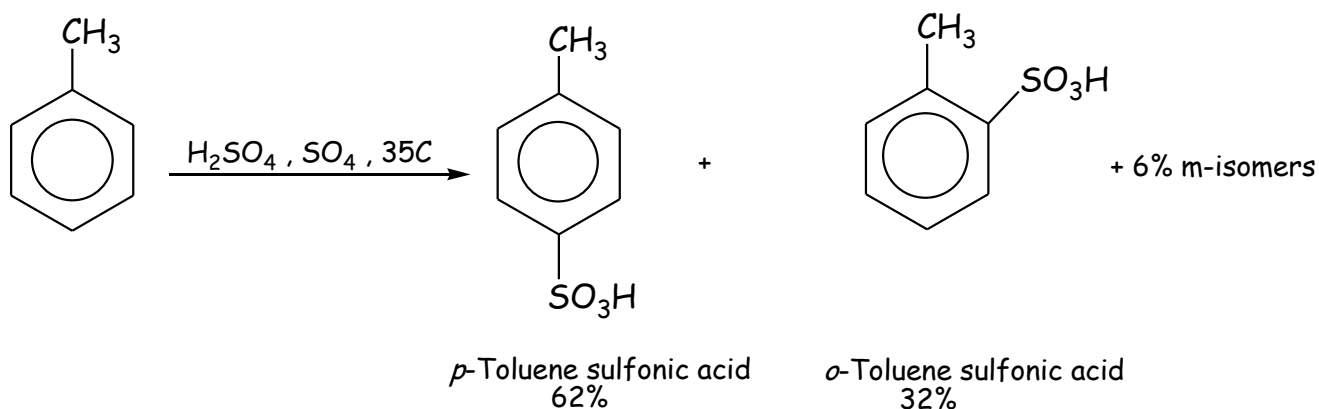


We take halogenations for example :-



### Effect of substituent groups :-

Like benzene, toluene undergoes electrophilic aromatic substitution. There are three possible monosulfonation products this reaction yields amounts of only two of them: the ortho and para isomers.





Benzene reacts completely within 20 to 30 minutes, where toluene is found to react within only a minutes or two.

On the other hand, Nitrobenzene, to take a different example, has been found to undergo substitution more than benzene, and to yield chiefly the meta isomers.

The groups that makes the ring more reactive than benzene is called an activating groups, a group that make a ring less reactive than benzene is called deactivating groups.

### Effect of groups on Electrophilic aromatic Substitution.

Activating: ortho and para directors	Deactivating: Meta directors
strongly, activating -NH <sub>2</sub> (-NHR, -NR <sub>2</sub> ) -OH	-NO <sub>2</sub> - <sup>+</sup> N(CH <sub>3</sub> ) <sub>3</sub> -CN -COOH(-COOR) -SO <sub>3</sub> H -CHO , -COR
Moderately activating -OCH <sub>3</sub> (-OC <sub>2</sub> H <sub>5</sub> ,ect.) -NHCOCH <sub>3</sub>	Deactivating: ortho and para directors
Weakly activating -C <sub>6</sub> H <sub>5</sub> phenyl -CH <sub>3</sub> (-C <sub>2</sub> H <sub>3</sub> )	-F , -CL , -Br , -I

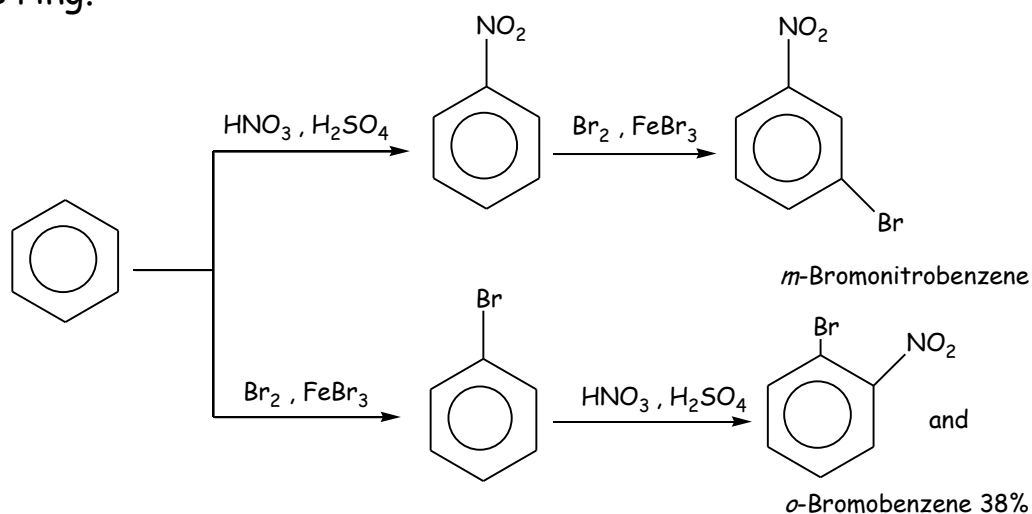
B) There is often little substitution between two groups that are meta to each other.



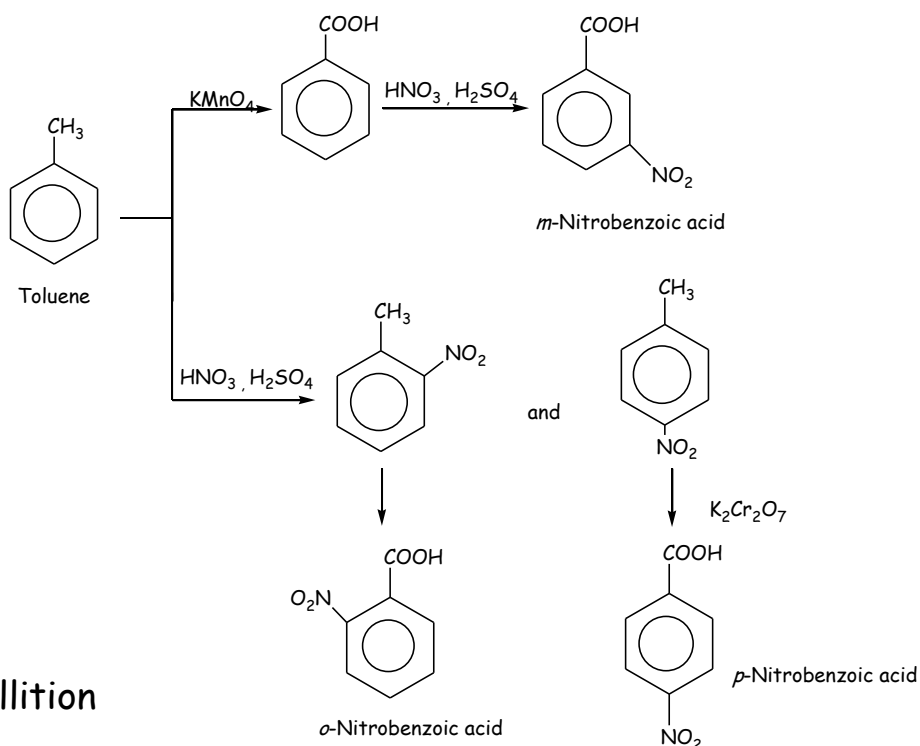
## Orientation and synthesis:

In the laboratory synthesis we should avoid use of a reaction that produce a mixture.

1. We must consider the order in which we introduce these various substituent into the ring.



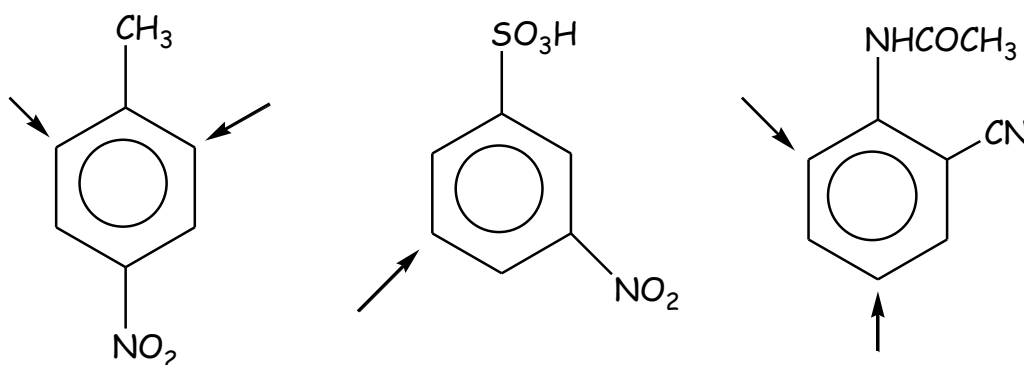
2. If our synthesis involves conversion of one group into another, we must consider the properties for this conversion.



We can separate *o*- and *p*- by distillation

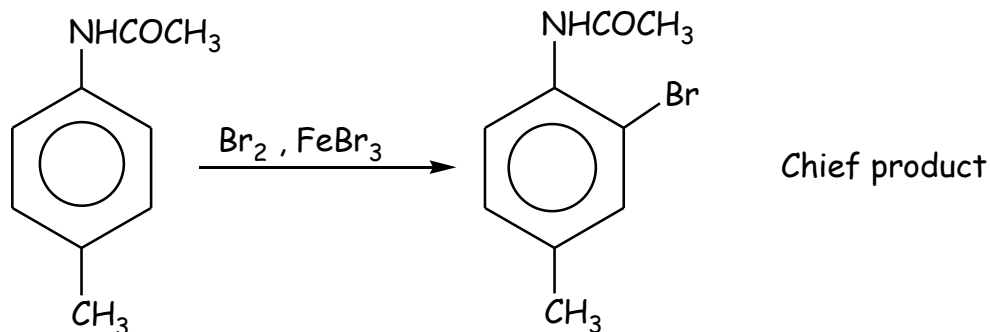
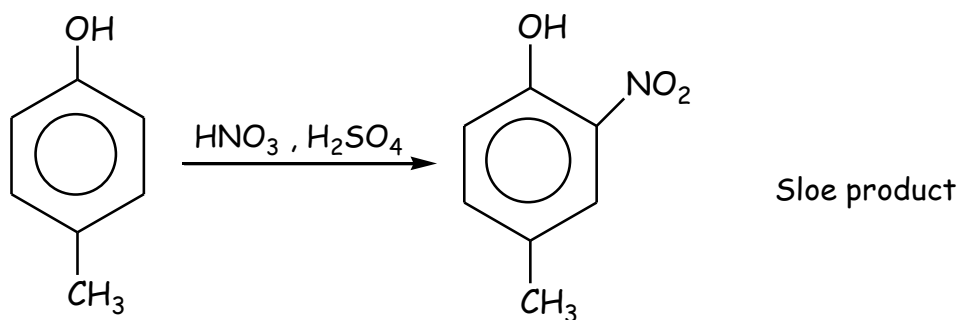
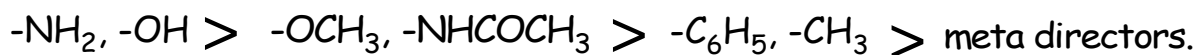
## Orientation in disubstituted benzene:

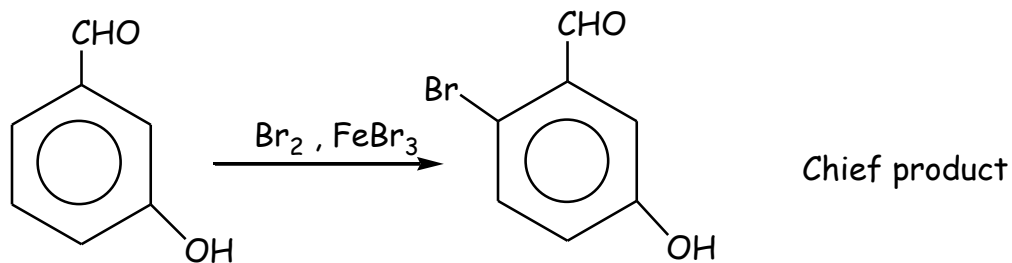
1. If the two substitutions may be located so that the directive influence of one reinforces that of the other. For example.



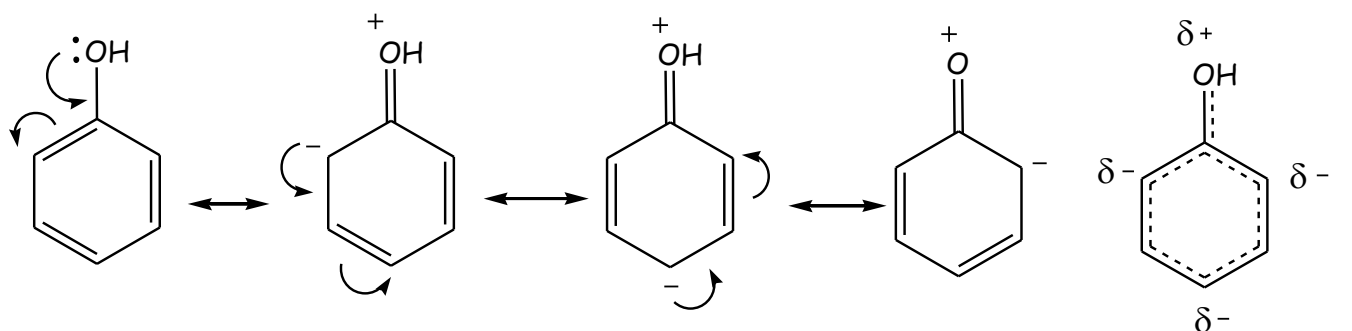
2. When the directive effect of one group opposes that of the other it's still possible in certain cases to make prediction in accordance with the following generalization.

a. Strongly activating group generally win out over deactivating or weakly activating groups. The difference in directive power in the sequence:-





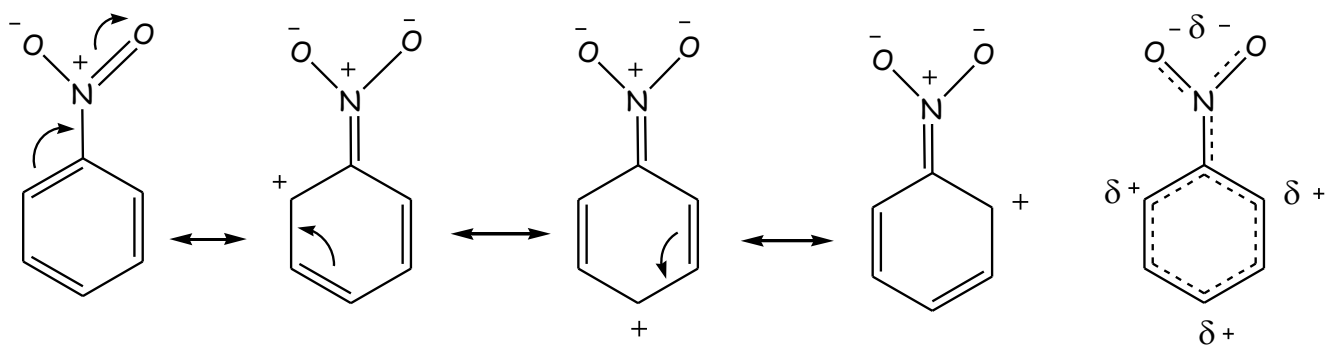
Activating groups ortho & para directors:



Activating group

Resonance hybrid

Except the methyl and aryl groups, have a pair electrons in which they covalent with ring in a resonance. Deactivating groups are pull the electrons from the benzene ring and make it poor in electrons.

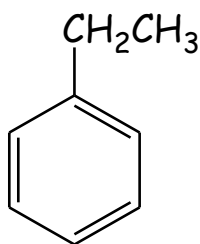


Deactivating groups

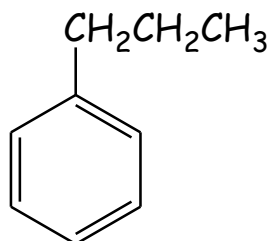
Resonance hybrid

## Aromatic- Aliphatic Compounds (Arenes):-

Benzene ring will undergo electrophilic substitution reactions and the side chain undergo free radical substitution reactions.



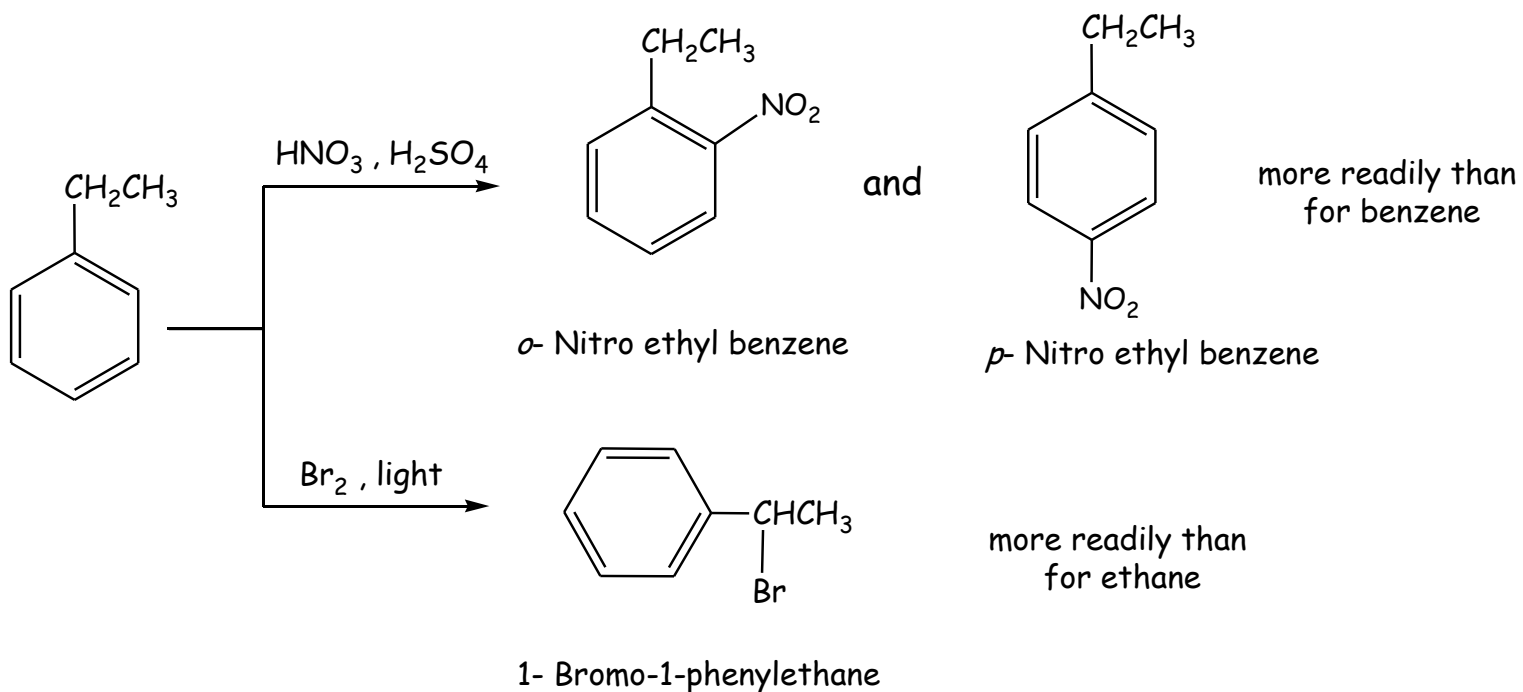
Ethyl benzene



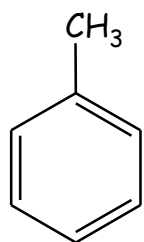
Propyl benzene

The alkyl group will effect of the aromatic properties of the ring and the ring will effect of the aliphatic properties of the side chain.

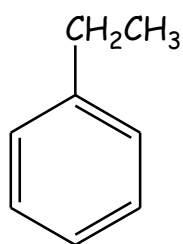
For example:



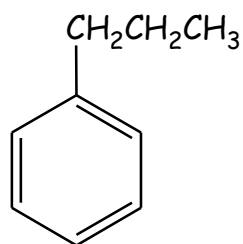
# Structure and nomenclature:



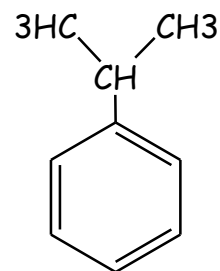
Toluene  
Methyl benzene



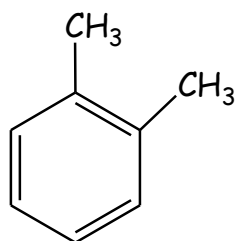
Ethyl benzene



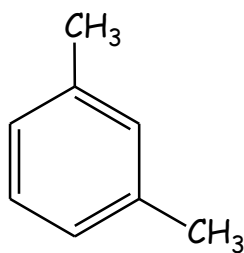
Propyl benzene



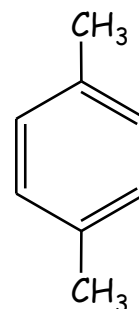
Isopropyl benzene



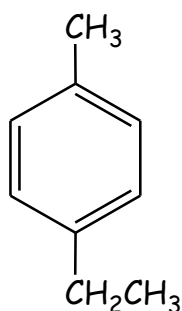
*o*-Xylene



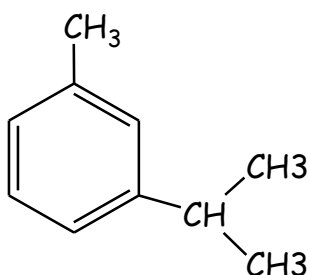
*m*-Xylene



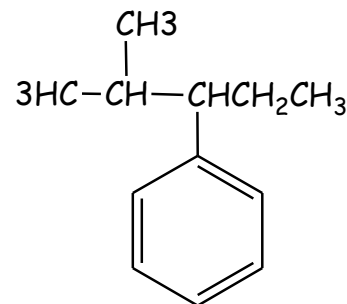
*p*-Xylene



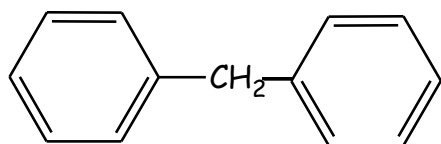
*p*-Ethyl toluene



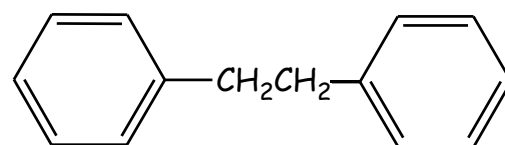
*m*-Isopropyl toluene



2-Methyl-3-phenylpentane

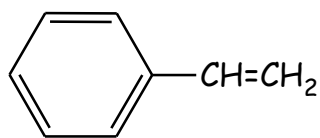


Diphenyl methane

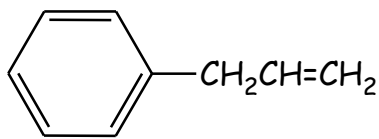


1,2-Diphenyl Ethane

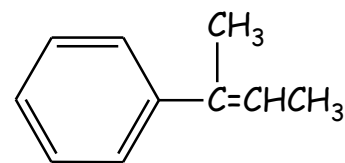
## Alkenyl benzene:



Styrene  
Vinyl benzene  
Phenyl ethylene

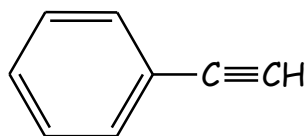


Allyl benzene  
3-Phenyl propane

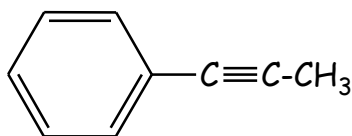


2-Phenyl butane

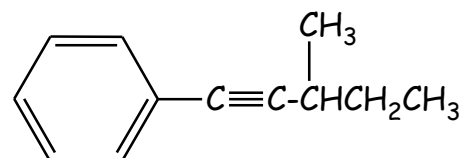
## Alkynyl benzene:



Phenyl acetylene



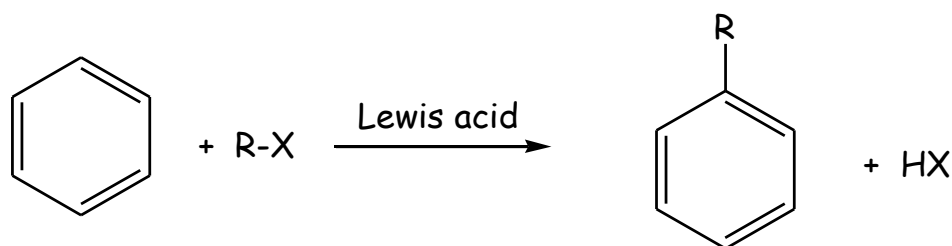
Phenyl ethyl acetylene



3-Methyl-1-Phenyl pentyne

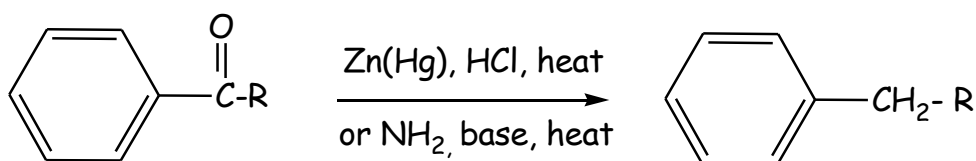
## Preparation of alkylbenzene:

1- Attachment of alkyl groups: (Friedel-Crafts alkylation)

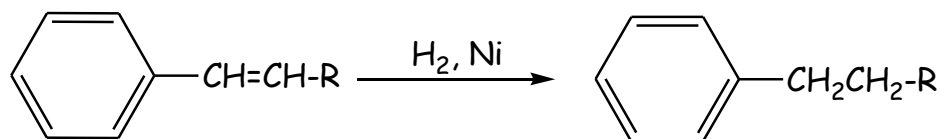


Lewis acid:  $\text{AlCl}_3$ ,  $\text{BF}_3$ , HF

2-Conversion of side chain: Clemmensen or Wolff Kishner reaction

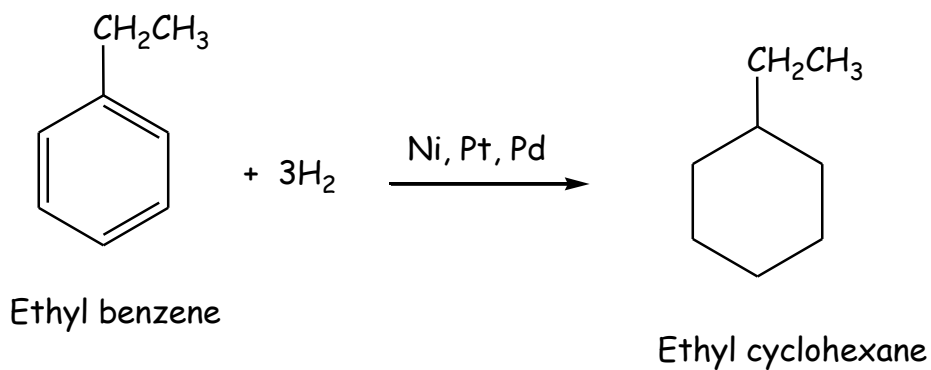


3-Hydrogenation of alkyl benzene:

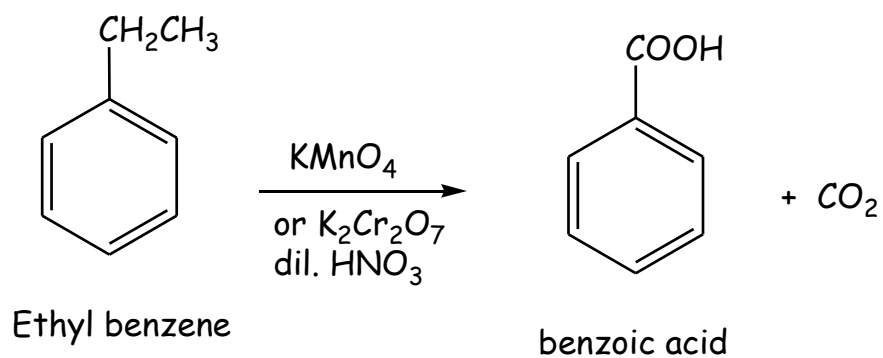


## Reactions of alkyl benzene:

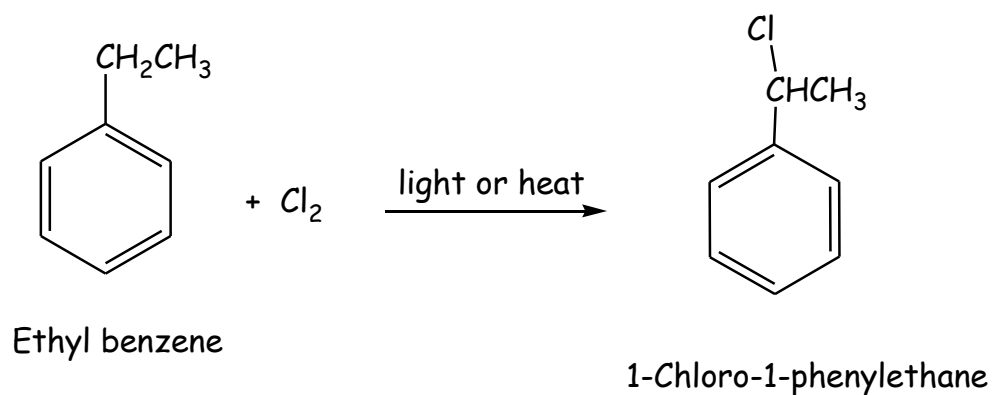
### 1- Hydrogenation



### 2-Oxidation:



### 3-Halogenation of side chain:





#### 4- Substitution in the ring , electrophilic aromatic substitution:

