

5. **By decarboxylation of carboxylic acid:** The sodium salt of carboxylic acid is strongly heated with soda lime to give alkane by elimination of CO_2 as carbonate.

$$\text{R} - \text{COONa} + \text{NaOH} \xrightarrow[\text{CaO}]{\text{Heat}} \text{RH} + \text{Na}_2\text{CO}_3$$
6. **Kolbe's electrolysis:** Sodium or potassium salts of fatty acids are electrolyzed to give higher alkanes at node.

$$2\text{CH}_3\text{COONa} + 2\text{H}_2\text{O} \longrightarrow \text{CH}_3 - \text{CH}_3 + 2\text{CO}_2 + 2\text{NaOH} + \text{H}_2$$
Methane can't be prepared by this method.
7. **By action of water on aluminium carbide or beryllium carbide:**

$$\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \longrightarrow 4\text{Al}(\text{OH})_3 + 3\text{CH}_4\uparrow$$
Aluminium carbide

$$\text{Be}_2\text{C} + 4\text{H}_2\text{O} \longrightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4\uparrow$$
Beryllium carbide

Physical Properties

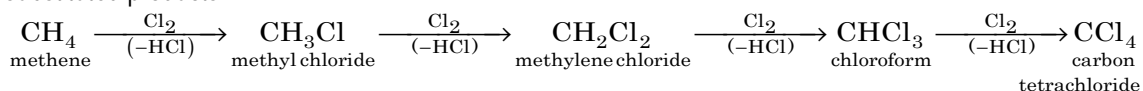
1. **State:** Due to weak forces, the alkanes upto four carbon atoms are colourless, odourless gases, the next thirteen members are colourless, odourless liquids. Alkanes from C_{18} onwards are colourless and odourless solids.
In alkenes, except ethene, all are odourless and follow some trend as alkanes. Ethene has a pleasant odour. All are colourless. Alkynes also follow the same trend as alkanes.
2. **Density:** The density of alkanes increases very slowly with the rise of molecular mass until it becomes constant at 0.8.
3. **Solubility:** They are generally insoluble in polar solvents such as water but insoluble in non-polar solvents like ether, CCl_4 , benzene etc.
4. **Boiling and melting points:** The boiling point of straight chain alkanes increase regularly with increasing number of carbon atoms. The melting points of alkanes do not follow a very smooth gradation with the increase of molecular size. Alkenes and alkynes also show a gradual increase in boiling and melting points with the increase of molecular mass in homologous series. They are less volatile than alkanes, i.e., their boiling point and melting point are higher than corresponding alkanes.

Chemical Properties

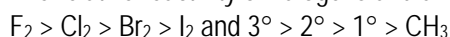
Alkanes are extremely stable and inert substance due to presence of non-polar C – C and C – H bonds. Alkanes are saturated compounds with strong sigma bonds which doesn't break under ordinary conditions. Alkanes react at high temperature by free radical mechanism.

1. **Halogenation (free radical substitution):**

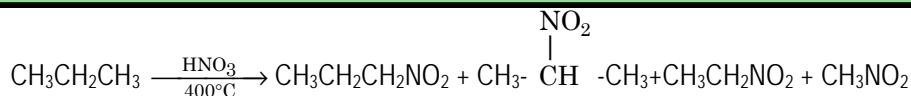
Alkanes react with halogens (Cl_2 , Br_2) in presence of light or in dark at high temperature to form corresponding substituted products.



The relative reactivity of halogens and alkanes follows this order,

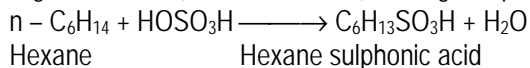


2. **Nitration:** Nitration is possible for alkanes having three or more carbon atoms. Nitration of propane yields mixture of nitro products.



3. **Sulphonation:**

Higher alkanes (hexane onwards) undergo sulphonation when treated with fuming H_2SO_4 .



4. **Oxidation or combustion:**

Alkanes burn in presence of O_2 to form CO_2 and H_2O with evolution of heat.

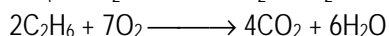
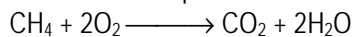


Illustration 1 : The order of reactivity of halogens towards halogenation of alkane is

(A) $\text{F}_2 > \text{Br}_2 > \text{Cl}_2$

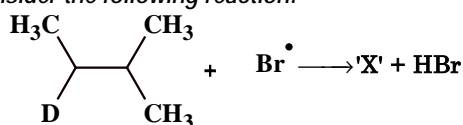
(B) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2$

(C) $\text{Cl}_2 > \text{F}_2 > \text{Br}_2$

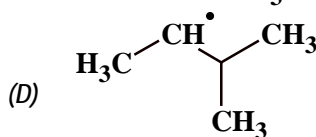
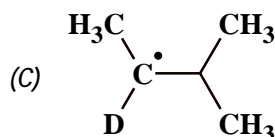
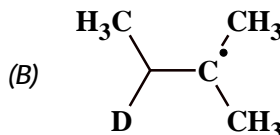
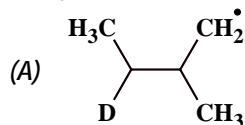
(D) $\text{Cl}_2 > \text{Br}_2 > \text{F}_2$

Solution: (B). In a group, electronegativity of the atom decreases. So, the reactivity of halogen also decreases in a group. Thus, the order of reactivity is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2$.

Illustration 2 : Consider the following reaction:



Identify the structure of the major product 'X'.



Solution: (B). Br^\bullet is less reactive and more selective and so the most stable free radical (3°) will be the major product.

Exercise 1

- (1) The compound with the highest boiling point is
 (A) *n*-hexane (B) *n*-pentane
 (C) 2,2-dimethyl propane (D) 2-methyl butane
- (2) Relative reactivity of halogens on alkanes follow the order
 (A) $F_2 > Cl_2 > Br_2 > I_2$ (B) $Cl_2 > Br_2 > I_2 > F_2$
 (C) $F_2 > I_2 > Br_2 > Cl_2$ (D) $I_2 > Br_2 > Cl_2 > F_2$
- (3) Propane is obtained from propene by which of the following method?
 (A) Wurtz reaction (B) Dehydration
 (C) Frankland reaction (D) Catalytic hydrogenation

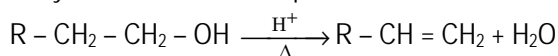
ALKENES

Alkenes are characterized by the presence of a double bond between two carbon atoms. Alkenes have the general formula C_nH_{2n} .

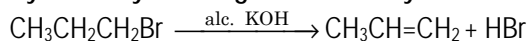
Methods of Preparation

1. By dehydration of alcohols:

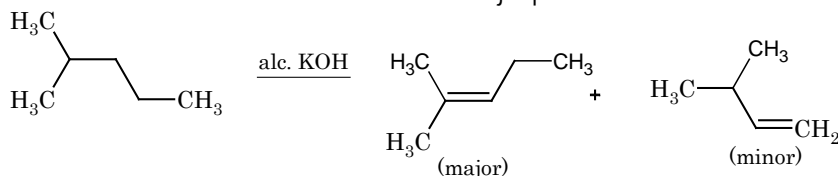
Dehydration of alcohols in presence of acids forms alkene. This is elimination reaction.



2. By the dehydrohalogenation of alkyl halides:



If dehydrogenation of alkyl halide gives two products, the major product will be according to Saytzeff's rule, i.e. the alkene which is most substituted is the major product.



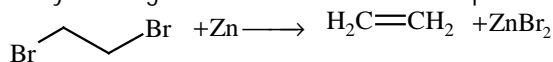
The ease of dehydrohalogenation follows the order,

Tertiary alkyl halide > secondary alkyl halide > primary alkyl halide.

Among the different halides, the order is alkyl iodide > alkyl bromide > alkyl chloride.

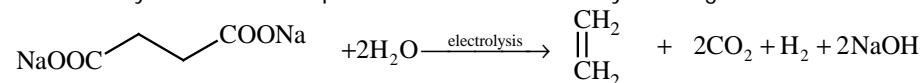
3. By the dehalogenation of vicinal dihalides:

Dehydrohalogenation of vicinal dihalides in presence of Zn dust in alcoholic solution yields pure alkene.



4. Kolbe's electrolysis method:

The electrolysis of sodium or potassium salts of dicarboxylic acid gives alkene at anode.



However, if Na/ liq NH_3 is used, *trans* alkene is formed, and in presence of Ni *cis* alkene is formed.

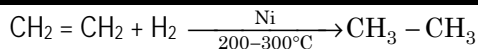
Chemical Properties

Alkenes are reactive due to the presence of double bonds. Due to presence of π bonds alkenes give electrophilic addition reaction. Alkenes also give free radical addition reaction.

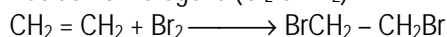
1. Addition reactions:

- (i) Addition of hydrogen (catalytic hydrogenation)

Hydrocarbons



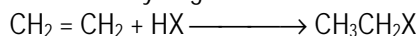
- (ii) Addition of halogens (Cl_2 or Br_2)



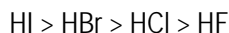
Ethylene dibromide (colourless)

Addition of bromine is used as a test for detecting the presence of a carbon-carbon double bond or triple bond.

- (iii) Addition of hydrogen halides



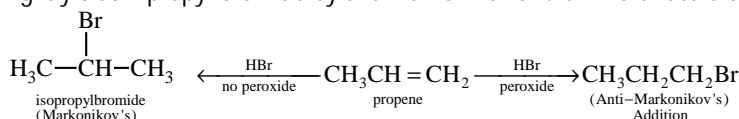
The order of reactivity among hydrogen halides is



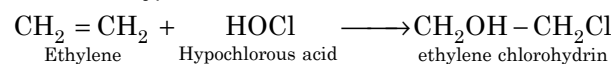
In case of unsymmetrical alkenes addition occurs according to Markonikov's rule. This reaction takes place through an ionic mechanism. Electrophilic addition to a carbon-carbon double bond involves the formation of an intermediate, i.e. more stable carbocation.

Deviation from Markonikov's rule:

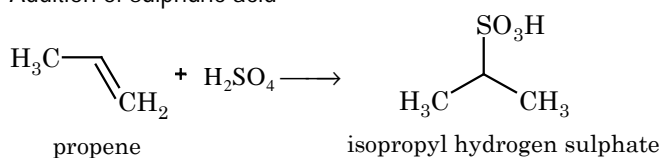
It has been observed that addition of HBr to unsymmetrical alkenes like propene in presence of air, peroxide or light yields n-propyl bromide by anti-Markonikov's rule. The effect is called peroxide effect or Kharasch effect.



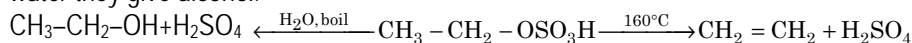
- (iv) Addition of hypochlorous acid



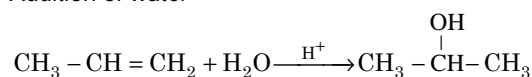
- (v) Addition of sulphuric acid



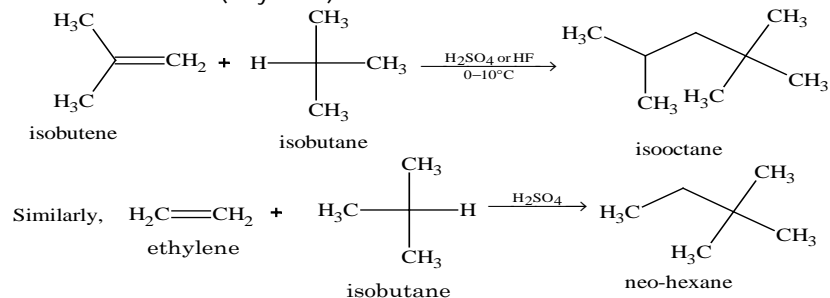
Alkyl hydrogen sulphates are water soluble, when heated at about 160°C , they give olefins. On reaction with water they give alcohol.



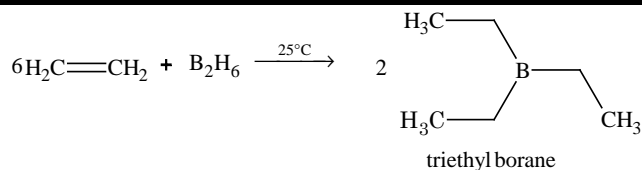
- (vi) Addition of water



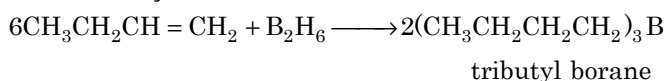
- (vii) Addition of alkanes (alkylation)



- (viii) Addition of diborane (hydroboration)

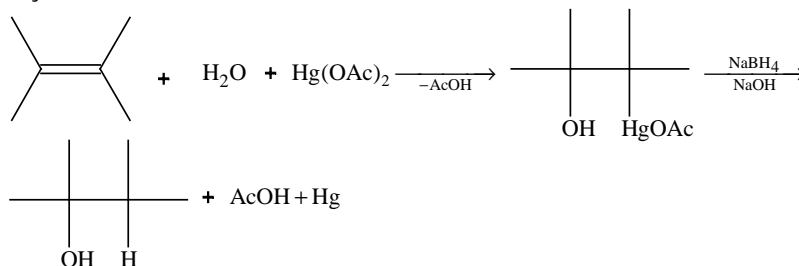


In case of unsymmetrical alkenes, addition follows the Anti Markonikov's rule.

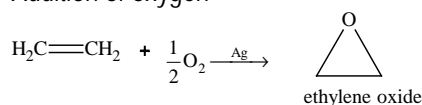


Trialkyl borane on oxidation ($\text{H}_2\text{O}_2/\text{OH}^-$) gives alcohol and on reduction (LiAlH_4) gives alkane.

(ix) Oxymercuration – demercuration

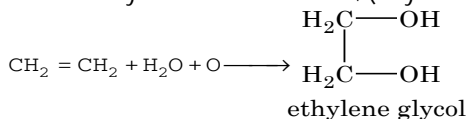


(x) Addition of oxygen

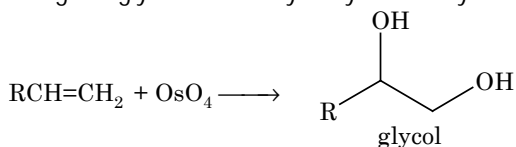


2. Oxidation:

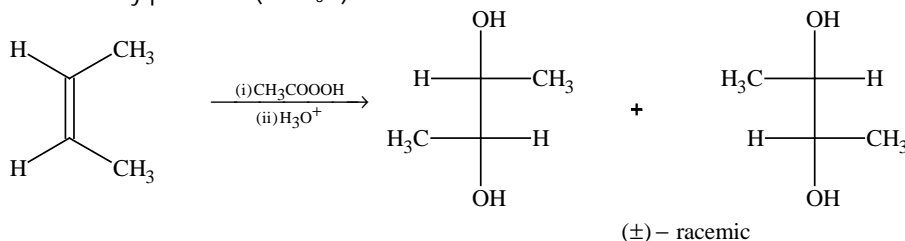
(i) Oxidation by cold alkaline KMnO_4 (Bayer's reagent)

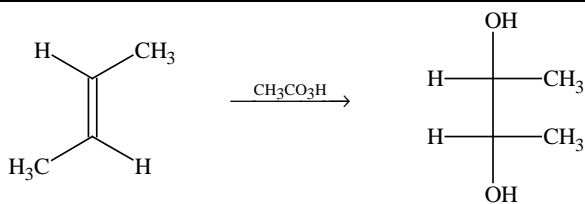


It is a test for detecting double bonds in alkene. Hydroxylation by KMnO_4 is always syn addition. The *cis* alkene on hydroxylation gives meso compound and *trans* alkene gives racemic mixture. Like Bayer's reagent OsO_4 also gives glycol and the hydroxylation is syn addition.



(ii) Oxidation by per acids (RCO_3H)

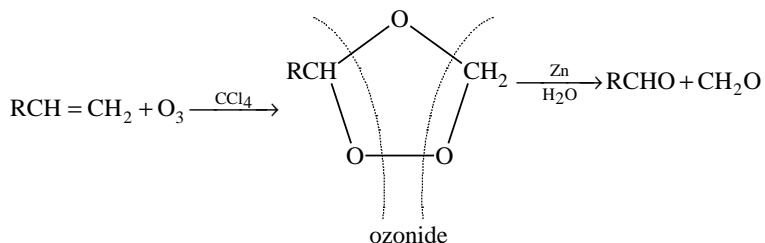




meso – compound

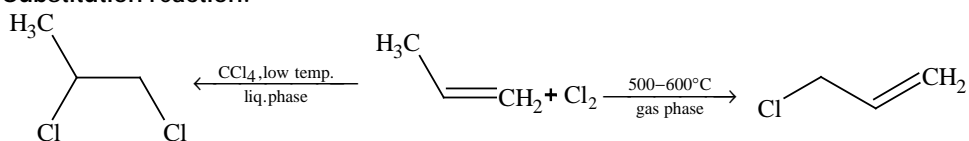
This addition occurs in *trans* manner. The *cis* alkene gives racemic mixture and *trans* alkenes give meso compound.

(iii) Ozonolysis
(a)



(iv) Oxidation by hot concentrated alkaline KMnO_4
 $\text{RCH}=\text{CH}_2 + \text{KMnO}_4 \xrightarrow{\text{(conc.)}} \text{RCOOH} + \text{CO}_2 + \text{H}_2\text{O}$

3. Substitution reaction:



However, allylic bromination (bromination at allylic carbon atom) is very easily achieved by treating the alkene having hydrogen atom at the allylic carbon atom with N-bromosuccinimide (NBS).

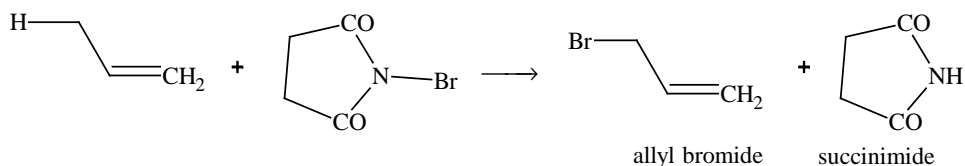
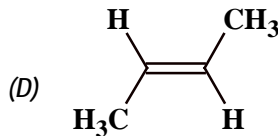
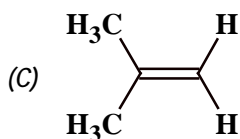
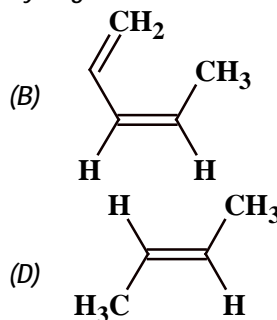
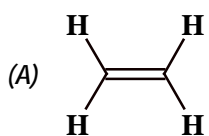


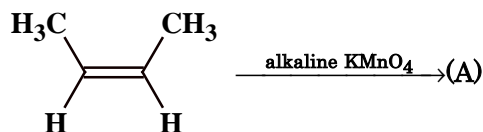
Illustration 3 : Which of the following alkene has the lowest heat of hydrogenation?



Solution:

(B). Higher the stability of alkene, lower the heat of hydrogenation.

Illustration 4 :



Which is true about this reaction?

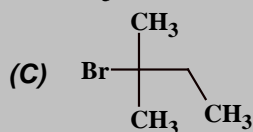
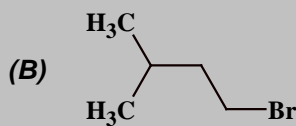
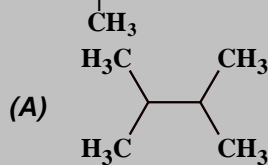
- (A) A is meso 1, 2-butan-di-ol formed by syn addition.
 (B) A is meso 1, 2-butan-di-ol formed by anti addition.
 (C) A is a racemic mixture of d and l, 1, 2-butan-di-ol formed by anti addition.
 (D) A is a racemic mixture of d and l, 1, 2-butan-di-ol formed by syn addition.

Solution: (A).

On *cis* alkene there is syn addition of two –OH groups forming meso compound.

Exercise 2

(1) $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CH} = \text{CH}_2 + \text{HBr} \longrightarrow \text{A}$ (predominant), A is



(D) None of the above

(2) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \xrightarrow[1 \text{ equiv.}]{\text{H}_2/\text{Pt}} \text{X} \xrightarrow{\text{O}_3/\text{H}_2\text{O}} \text{Y}$

X and Y are

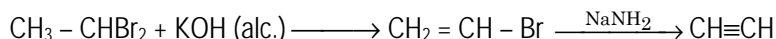
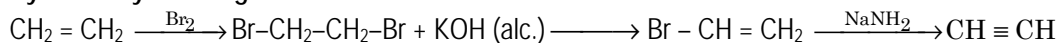
- (A) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$, ($\text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_2$)
 (B) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$, CH_3COOH (2 moles)
 (C) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$, CH_3CHO (2 moles)
 (D) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2$, ($\text{CH}_3\text{CH}_2\text{CHO} + \text{HCHO}$)
 (3) The reaction of propene with HOCl proceeds via the addition of
 (A) H^+ in the first step (B) Cl^+ in the first step
 (C) OH^- in the first step (D) Cl^+ and OH^- in a single step

ALKYNES

Alkynes are characterized by the presence of a triple bond between two carbon atoms. The general formula of alkyne is C_nH_{2n-2} .

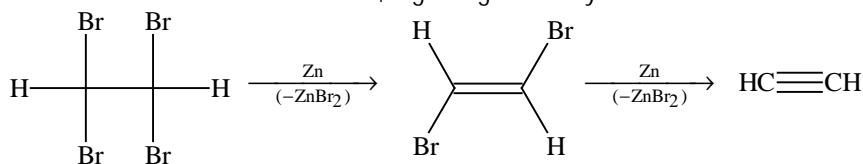
Methods of Preparation

1. **By the dehydrohalogenation of vicinal dihalides:**



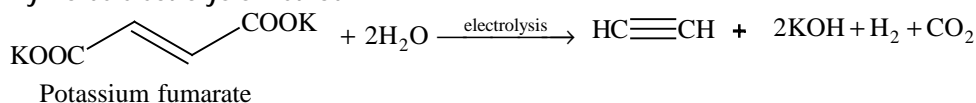
2. **By dehalogenation of vicinal tetrahalides:**

Reaction with active metals like Zn, Mg etc. gives acetylene.



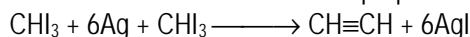
1,1,2,2 – tetrabromoethane

3. **By Kolbe electrolysis method:**



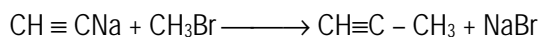
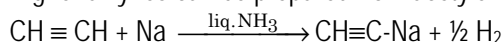
4. **By heating iodoform or chloroform with silver powder or zinc:**

This method can be used for the preparation of only acetylene.

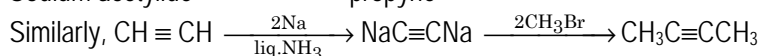


5. **From acetylene:**

Higher alkynes can be prepared from acetylene when treated with sodium metal in liquid ammonia.



Sodium acetylide propyne



Chemical Properties

Alkyne gives electrophilic addition reaction due to the presence of loosely held π electrons, but electrophilic addition reactions in alkyne are slower than that of alkenes.

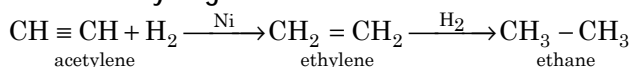
Terminal hydrogen present in alkynes is acidic in nature. Since, s electrons are closer to nucleus than p electrons, the electrons present in bond having more s character will be more closer to the nucleus. The amount of s character in various types of C – H bond are as follows

Type of C–H bond	Hybrid orbital	Percentage of s character
$\equiv C-H$	sp	50.0
$= C-H$	sp ²	33.3
$- C-H$	sp ³	25.0

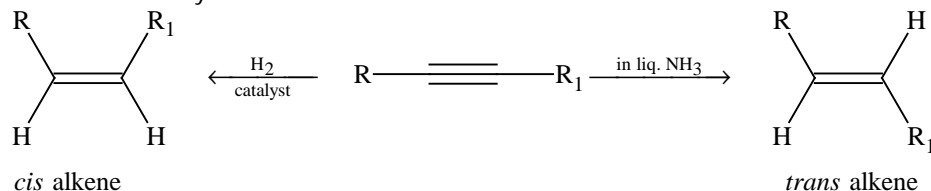
Relative acidities: $HOH \approx HOR > CH \equiv CR > \ddot{N}H_3 > CH_2 = CH_2 > CH_3 - CH_3$

Relative basicities: $\text{OH}^- \approx \text{OR}^- < \text{C}^-\equiv\text{C} - \text{R} < \text{NH}_2^- < \text{CH}^-=\text{CH}_2 < \text{CH}_2^- - \text{CH}_3$

1. Addition of hydrogen:

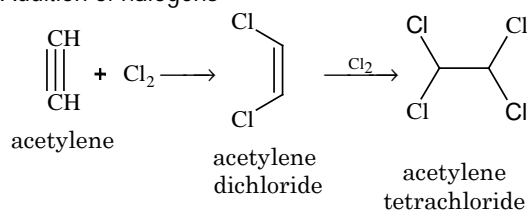


In case of alkynes where triple bond is not present at the end of the chain, on reduction gives *cis* or *trans* alkene, which depends upon the choice of reducing agent. With sodium in liquid ammonia the alkene is *trans* form and on catalytic reduction the alkene is *cis* form.



2. Electrophilic addition:

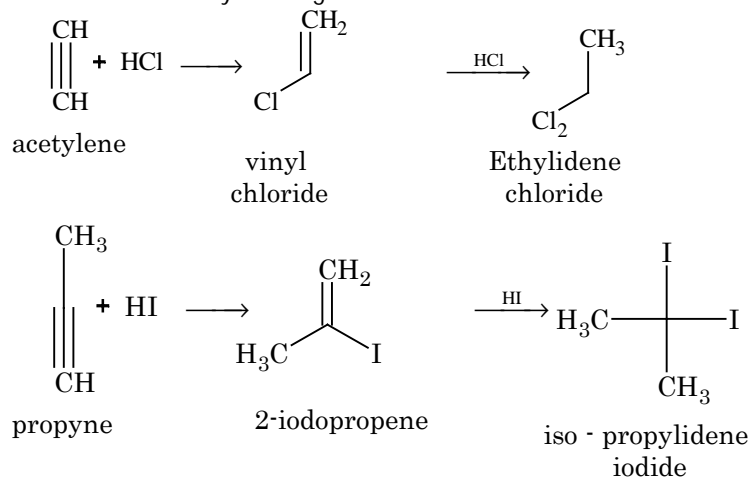
(i) Addition of halogens



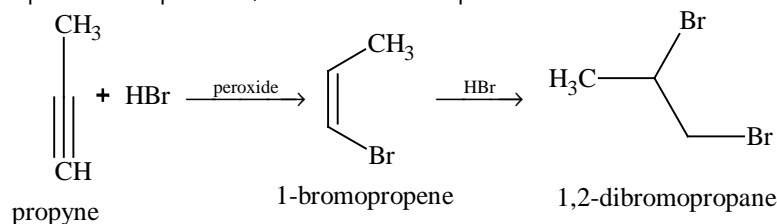
The order of reactivity of halogens is $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$

(ii) Addition of halogen acid

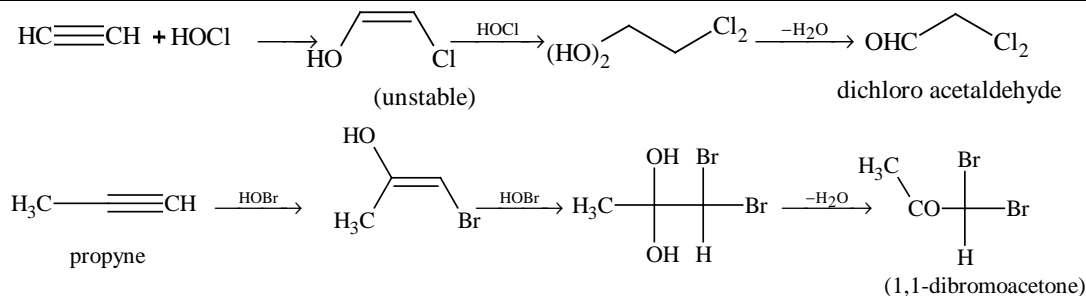
The order of reactivity of halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$.



In presence of peroxide, anti Markonikov's product is obtained.

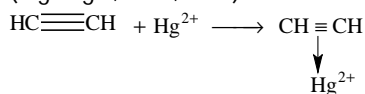


(iii) Addition of hypohalous acids

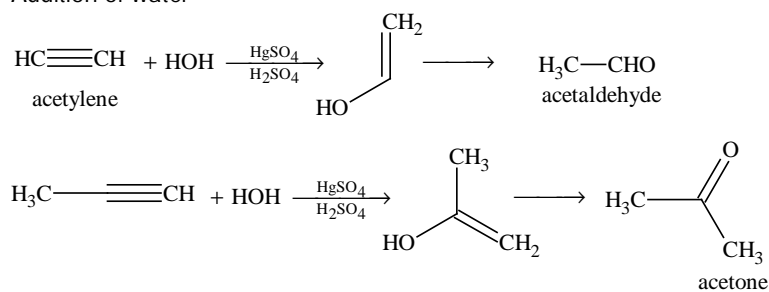


3. Nucleophilic addition reaction:

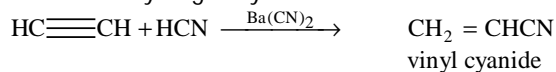
In these reactions, the addition is initiated by a nucleophile and are generally catalysed by salt of heavy metals (e.g. Hg^{2+} , Pb^{2+} , Ba^{2+}) which are found to form π compound with multiple bonds.



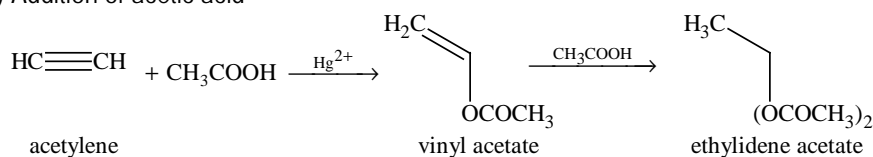
(i) Addition of water



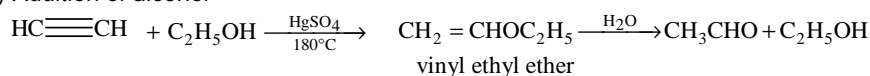
(ii) Addition of hydrogen cyanide



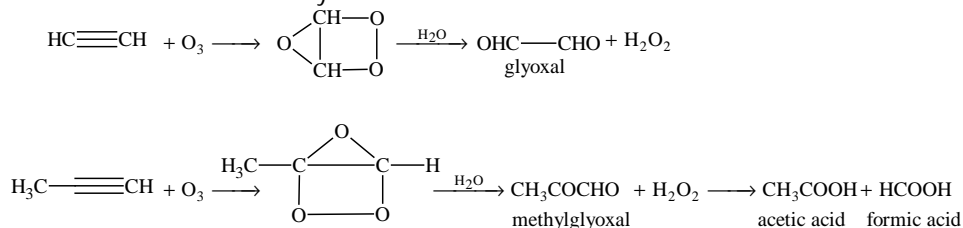
(iii) Addition of acetic acid



(iv) Addition of alcohol

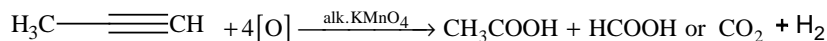
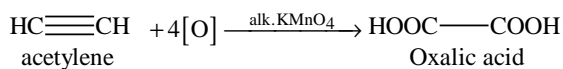


(v) Addition of ozone and ozonolysis

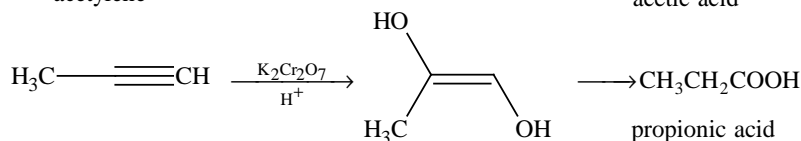
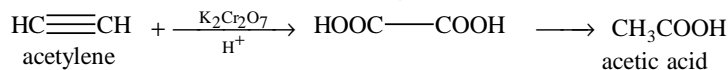


4. Oxidation:

(i) Oxidation with alkaline KMnO_4

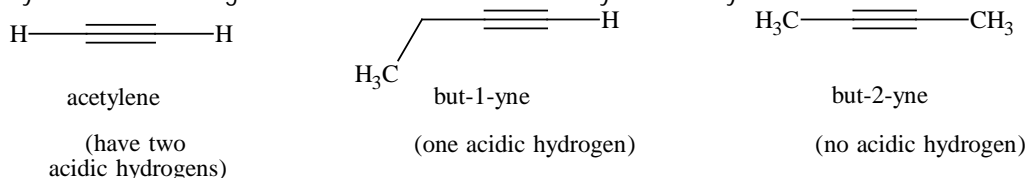


(ii) Oxidation with acidic $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4

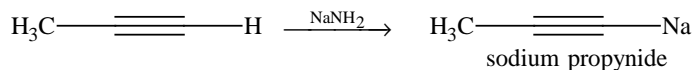
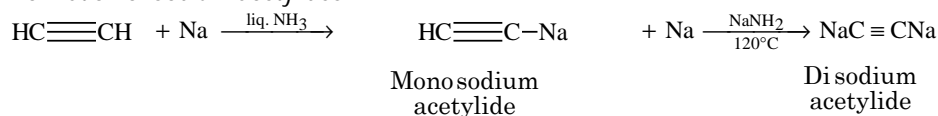


5. Formation of metallic derivatives:

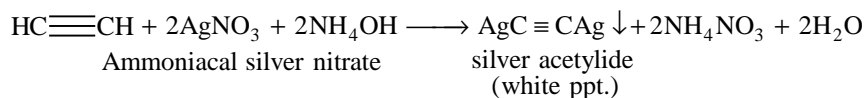
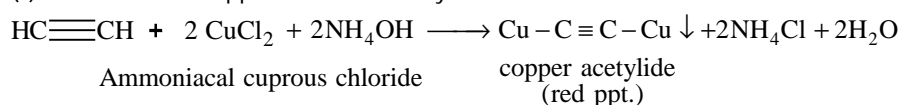
The group $-\text{C}\equiv\text{C}-\text{H}$ in alkynes is slightly acidic in nature and hence its hydrogen atom can be easily replaced by certain metals to give metallic derivatives called acetylides or alkynides.



(i) Formation of sodium acetylides

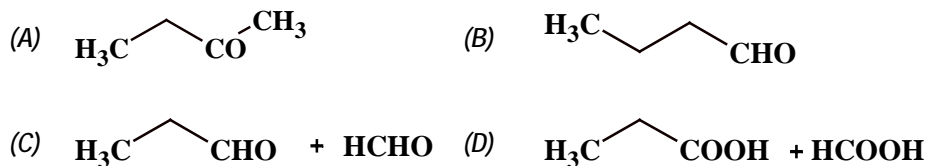


(ii) Formation of copper and silver acetylides



These reactions are used for detecting the presence of acetylinic hydrogen atom.

Illustration 4 : The products obtained via oxymercuration ($\text{HgSO}_4 + \text{H}_2\text{SO}_4$) of 1-butyne would be



Solution: (A).

