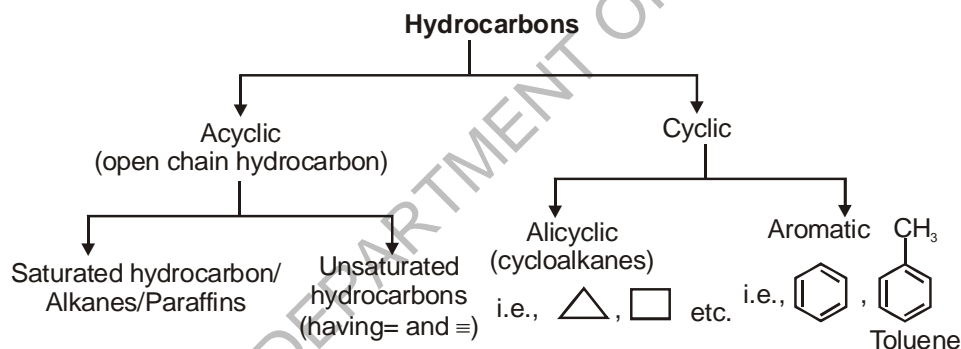


Hydrocarbons

Classification, isomerism, IUPAC nomenclature, general methods of preparation, properties and reactions. **Alkanes** - Conformations : Sawhorse and Newman projections (of ethane); Mechanism of halogenation of alkanes. **Alkenes** - Geometrical isomerism; Mechanism of electrophilic addition: addition of hydrogen, halogens, water, hydrogen halides (Markownikoff's and peroxide effect); Ozonolysis, oxidation, and polymerization. **Alkynes** - Acidic character; Addition of hydrogen, halogens, water and hydrogen halides; Polymerization. **Aromatic hydrocarbons** - Nomenclature, benzene - structure and aromaticity; Mechanism of electrophilic substitution: halogenation, nitration, Friedel – Craft's alkylation and acylation, directive influence of functional group in mono-substituted benzene.

HYDROCARBONS AND THEIR CLASSIFICATIONS

Compounds of only Carbon and Hydrogen are called hydrocarbons. They are parent organic compounds and all other organic compounds have been derived by replacing one or more H atoms from hydrocarbon.

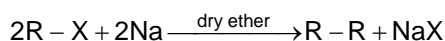


ALKANES

Methods of Preparation :

I. Reactions where number of carbon atoms are increased

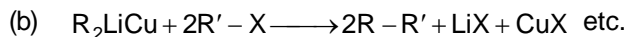
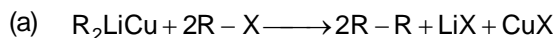
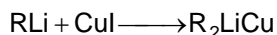
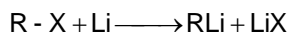
1. Wurtz Reaction



Here other metals in the finely divided state may also be used such as Cu, Ag etc.

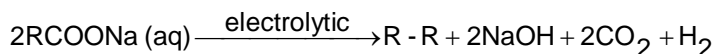
- Methane cannot be prepared by this method.
- Only symmetrical alkane can be prepared by this method in good yield.

2. Corey-House Synthesis:

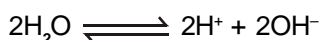
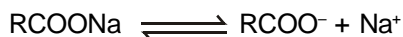


It can be used for preparing both symmetrical and unsymmetrical alkanes.

3. Kolbe's Electrolytic Decarboxylation



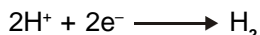
Mechanism:



Anodic Reaction



Cathodic Reaction

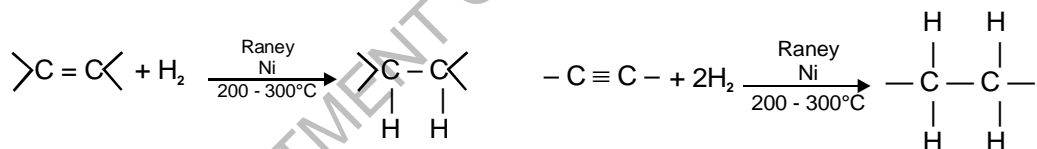


(i) Methane cannot be prepared by this method

(ii) Unsymmetrical hydrocarbon (alkane) cannot be prepared

II. Reactions where number of carbon atoms are retained

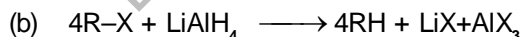
1. Sabatier - Sanderen's Reduction



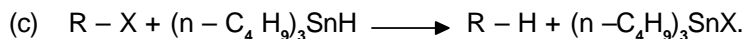
2. Reduction of Alkyl Halides



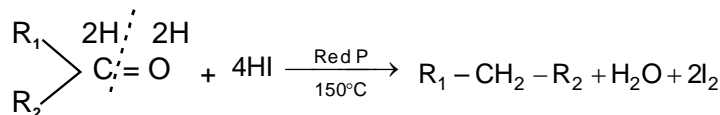
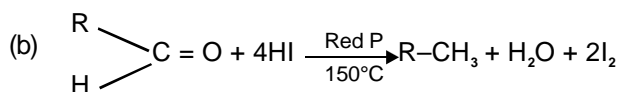
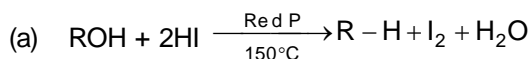
Zn - Cu and C_2H_5OH or Na and alcohol can also be used

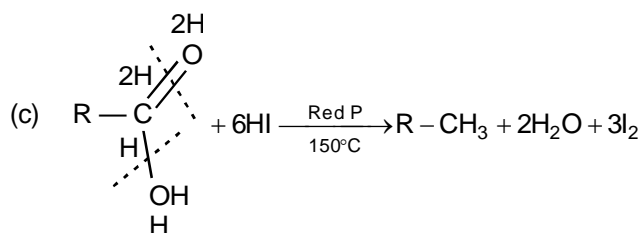


This is a nucleophilic substitution reaction with the nucleophilic H^- coming from $LiAlH_4$.

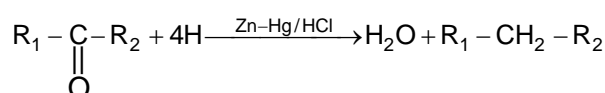
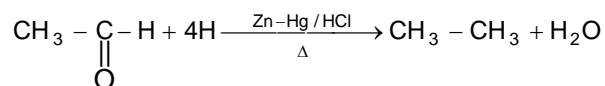


3. Reduction of Alcohols, Aldehydes, Ketones and Carboxylic Acids with HI/Red P.



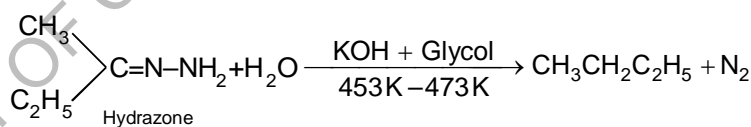
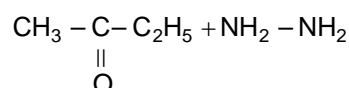
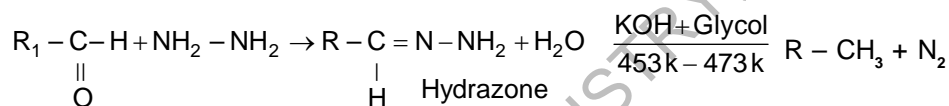


(d) Clemmensen's Reduction



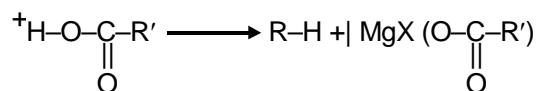
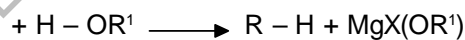
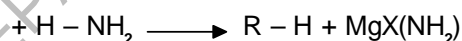
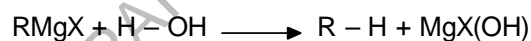
Clemmensen's reduction should not be used when the carbonyl compound has a basic end in it.

(e) Wolf-Kishner's Reduction:

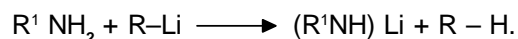


This reaction should not be used when the carbonyl compound has an acidic end in it.

4. (a) Using Grignard's Reagent

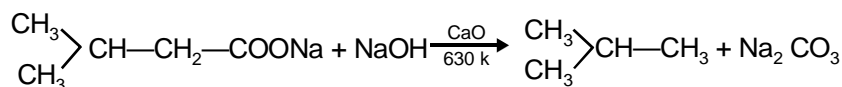
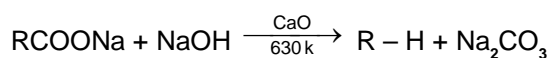


(b) Using Alkyl lithium compound



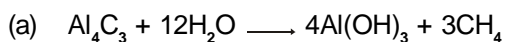
III. Reaction where number of carbon atom are decreased

Sodalime Decarboxylation

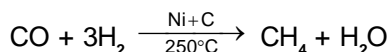


IV. Some other methods of preparation

(1) Preparation of Methane from carbides



(2) Methane from carbon monoxide



This is also called Sabatier Sanderen's reduction

Physical Properties

Boiling Point (B.P.)

B.P. increases with the increase of molecular mass. Among the isomers, straight chain alkane have higher b.p. than branched chain alkane.

Melting Point (M.P.)

The melting points do not show regular variation with increase in molecular size. The even number members have higher m.p. as compared to next alkanes with odd number of carbon atoms (ALTERATION EFFECT).

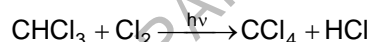
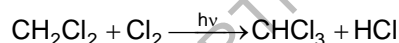
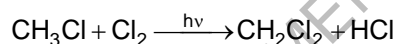
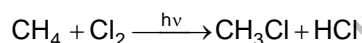
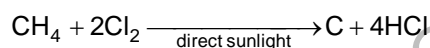
Solubility

They are soluble in non polar solvents but insoluble in polar solvents such as water.

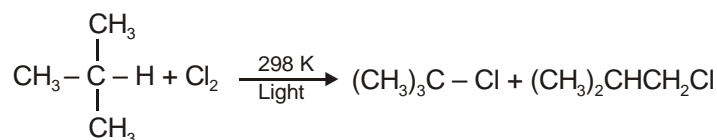
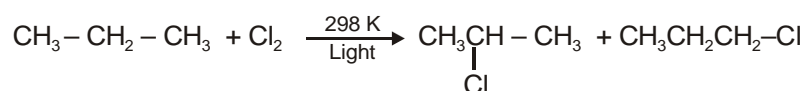
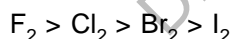
Chemical Properties

Alkanes are generally inert towards acids, bases, oxidising and reducing agents but they give following reactions:

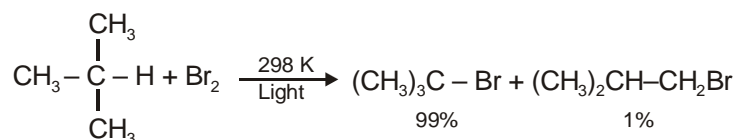
(1) **Halogenation.** Alkanes undergoes substitution reaction with halogen. Cl_2 and Br_2 only in presence of ultra violet light or high temperature (573 – 773K). But in presence of direct sunlight reaction is as



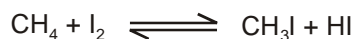
Decreasing order of reactivity of halogens towards alkanes.



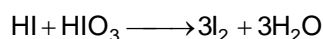
Similarly



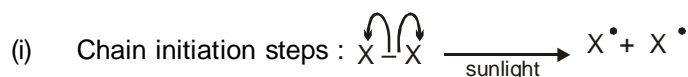
Note : The reaction with iodine is extremely slow and reversible



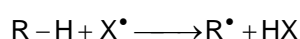
So iodination is carried out in presence of oxidising agent such as iodic acid or HNO_3 .



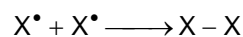
(2) **General mechanism :** Halogenation of alkanes takes place in 3 steps :



(ii) Propagation :

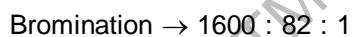
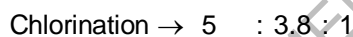


(iii) Termination



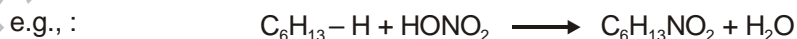
Among these three steps, propagation step is rate determining step.

The relative rates of abstraction of various types of hydrogen follow the order :

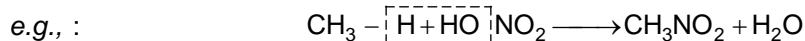


(3) **Nitration :**

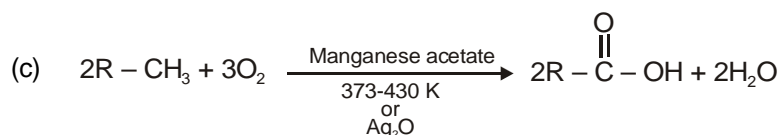
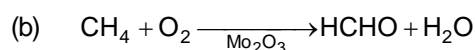
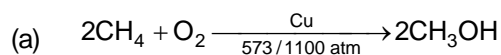
Liquid phase \longrightarrow For higher alkanes – Fuming HNO_3 , at 413 K



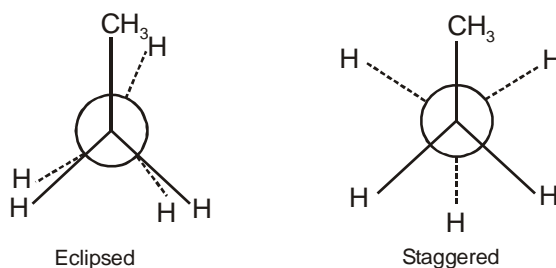
Vapour phase \longrightarrow For lower alkanes – conc. HNO_3 , at 670-750 K



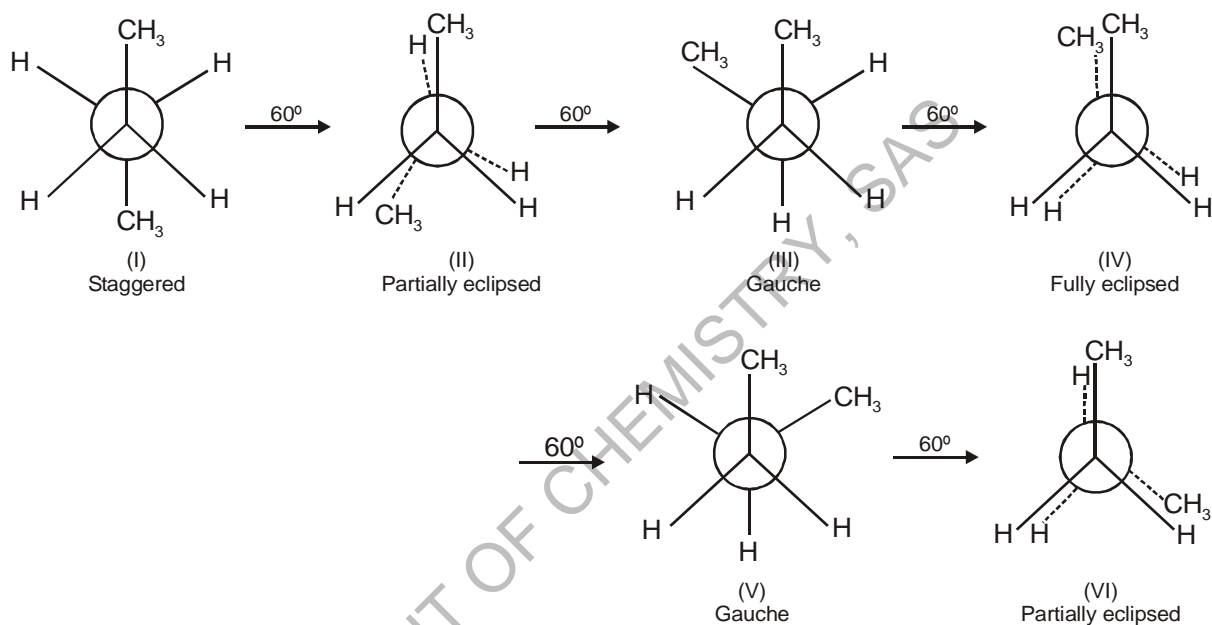
(4) **Oxidation :** Alkanes undergo oxidation under special conditions to yield a variety of products.



Conformers of propane :



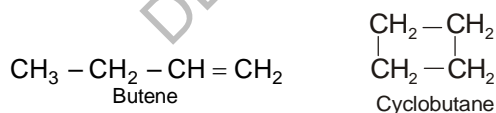
Conformers of Butane :



Stability order : I > III \approx V > II \approx VI > IV

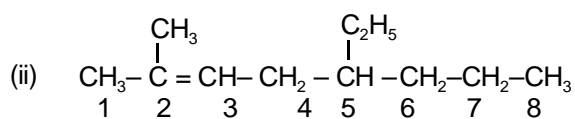
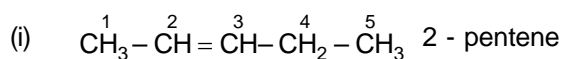
ALKENES

Alkene have the structural unit $>C=C<$. The carbon atoms carrying the unsaturation are sp^2 hybridized with the p orbital laterally overlapping to form π -bonds. They have the general formula C_nH_{2n} . They are isomeric with cycloalkanes e.g. C_4H_8



Nomenclature :

The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes. Hence few solved examples are taken.



5-Ethyl-2-methyl-2-octene

(iii) Alkene – H = Alkenyl

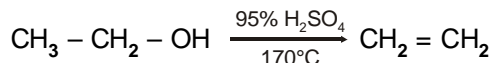
e.g., $\text{CH}_2 = \text{CH}$ – ethenyl (Vinyl group); $\text{CH}_2 = \text{CH} - \text{CH}_2$ – propenyl (Allyl group)

e.g., $\text{CH}_2 = \text{CH} - \text{Cl}$ - Vinyl chloride; $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{OH}$ Allyl alcohol

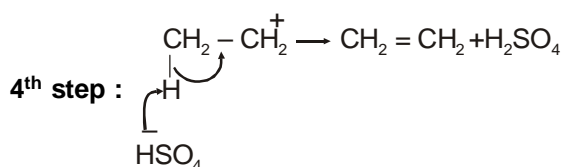
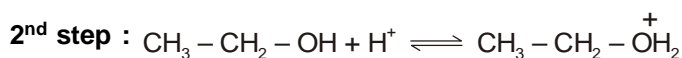
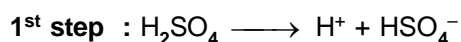
Preparations of Alkenes

From Alcohols

By heating alcohol with H_2SO_4 or H_3PO_4 at 170°C .



Mechanism :



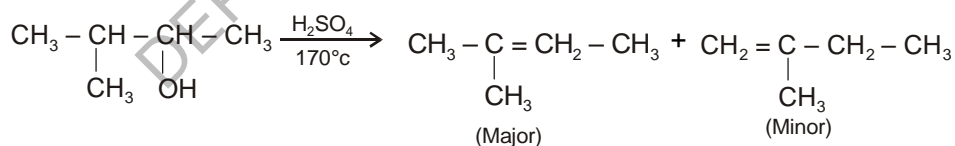
Here the 3rd step i.e. formation of carbocation is rate determining step.

The ease of dehydration of alcohols depends on the stability of carbocations formed. Hence the order of reactivity of alcohols is *ter* → *sec* → *pri* → $\text{CH}_3 - \text{OH}$ because the incipient carbonium ion stability is *ter* → *sec* → *pri* → CH_3^+ .

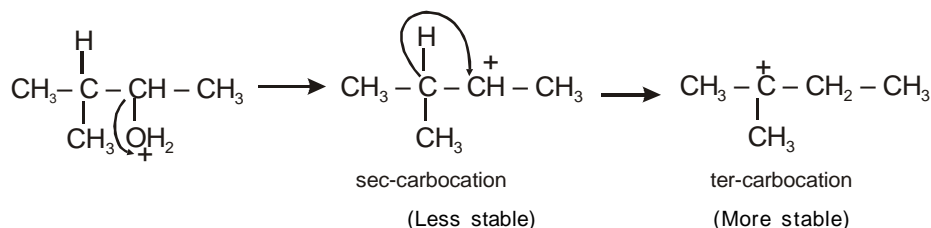
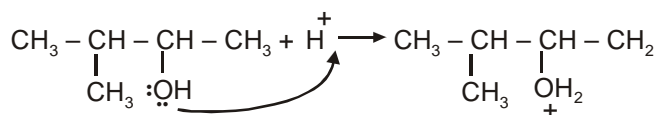
Note : Since the carbocation stability is the primary criteria so the initially formed carbocation undergoes molecular rearrangement by either to give more stable carbocation.

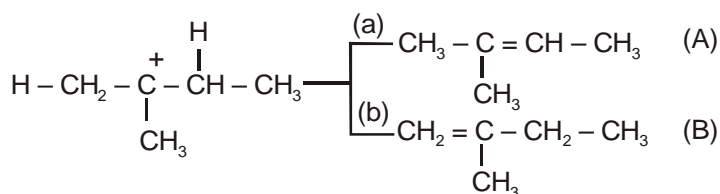
Hydride shift or

Example (Hydride shift)



Mechanism :



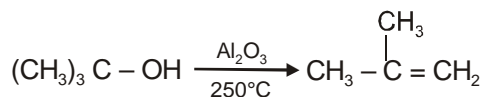
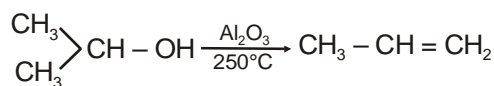
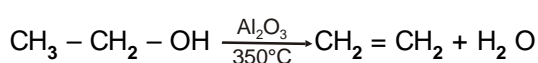


- (i) Dehydration of alcohols follow Saytzeff's rule.

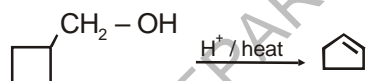
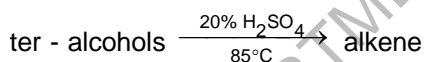
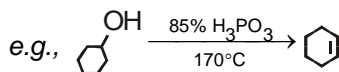
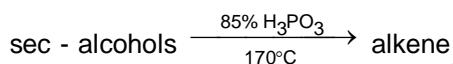
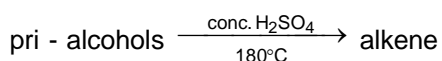
Hence (B) product is maximum.

Saytzeff's Rule: It states that "During dehydration of alcohols and dehydrohalogenation of alkyl halides the product formed is preferentially the one in which maximum number of alkyl groups are attached to the doubly bonded carbon atoms.

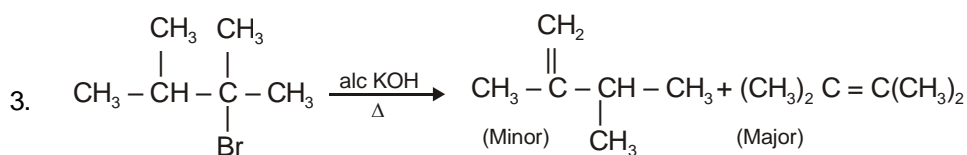
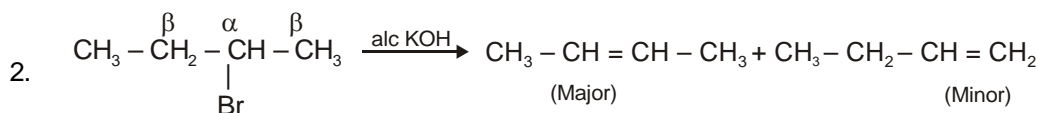
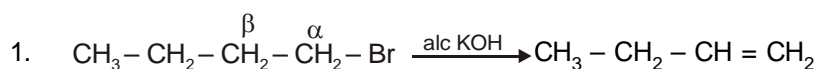
- (ii) Dehydration by passing over alumina (Lewis Acid)



The experimental conditions change with the structure of alcohols



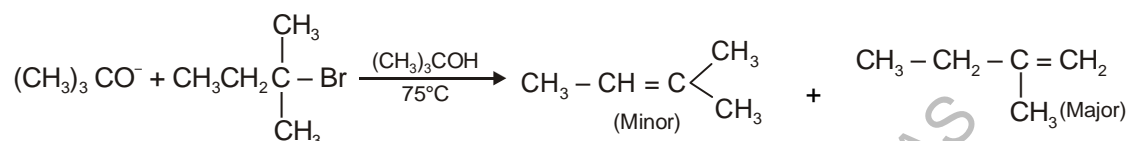
I. Dehydrohalogenation of alkyl halides



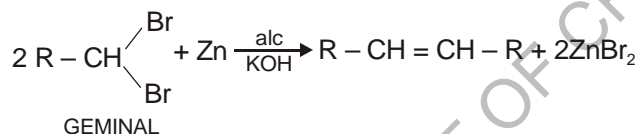
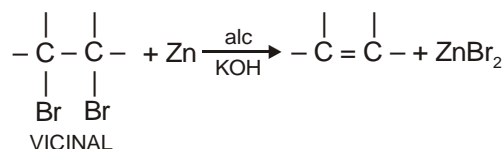
- (i) The base used may be strongly basic anions like OH^- , RO^- , $\text{C}_2\text{H}_5\text{O}^-$ ($(\text{CH}_3)_3\text{CO}^-$ etc.)
- (ii) The group leaving (*i.e.*, halogen) is a good leaving group if it is the conjugate base of a strong acid. (*i.e.*, weakly basic halide ion).
- (iii) One may also use sulphonates.
- (iv) Dehydrohalogenation of 2° and 3° alkyl halides follow Saytzeff's Rule.

II. Exception to Saytzeff's Rule (Hofmann Rule)

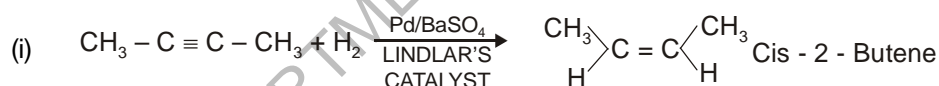
When dehydrohalogenation is carried out with potassium, tertiary butoxide there is formation of less substituted alkene.



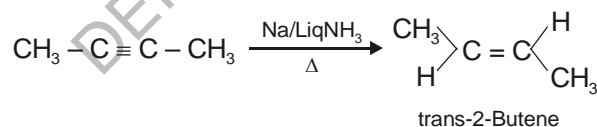
III. Dehalogenation Reactions



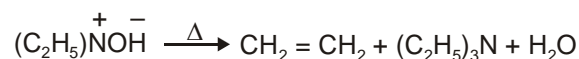
IV. By controlled hydrogenation of alkynes



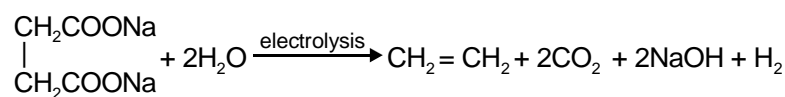
Here we may use small amounts of sulphur or quinoline also.



V. By heating Quaternary Ammonium hydroxide



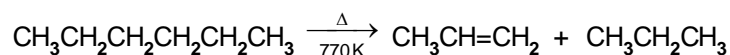
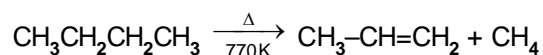
VI. Kolbe's Electrolysis



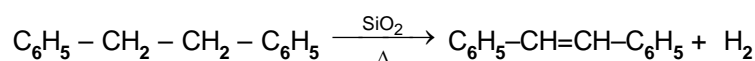
Sodium succinate

Mechanism is similar to preparation of alkanes.

VII. Pyrolysis



VIII. By heating saturated hydrocarbon with SiO_2



Physical Properties

Solubility

They are insoluble in water but soluble in organic solvents.

Boiling point

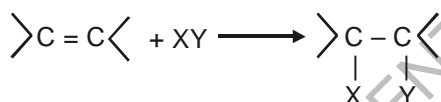
The boiling point of cis-alkenes is usually higher than corresponding trans-alkenes (More polarity).

Melting point

The melting point of trans-alkenes is usually greater than cis-alkene. (trans form is more symmetrical).

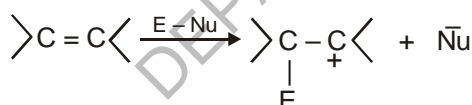
Chemical Properties

In alkenes C = C bond is made of stable σ -bond and reactive π -bond. As π -bond can easily be broken, alkenes undergo addition reactions.

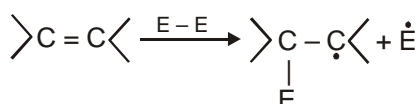


Being electron rich species they react with electrophiles in three ways.

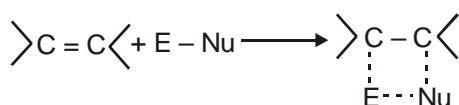
1. Ionic Mechanism



2. Free Radical Mechanism

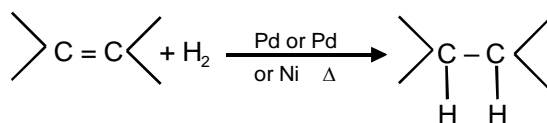


3. Transition State



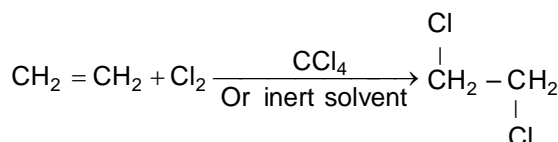
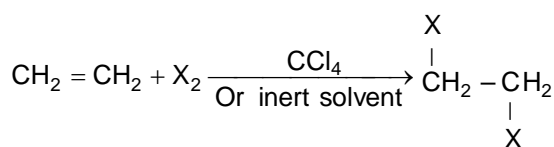
Reactions :

1. Hydrogenation :



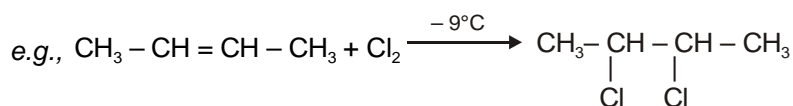
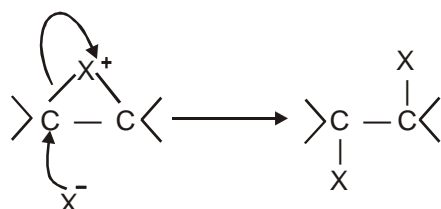
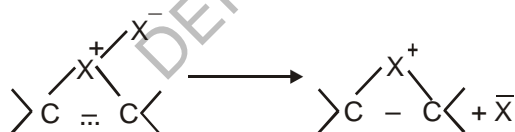
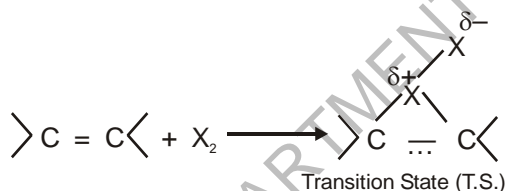
The relative rates of hydrogenation is $\text{CH}_2 = \text{CH}_2 > \text{RCH} = \text{CH}_2 > \text{R}_2\text{C} = \text{CH}_2 > \text{RCH} = \text{CHR} > \text{R}_2\text{C} = \text{CR}_2$. This is due to the fact that as number of alkyl groups increase the steric hindrance increases and thereby rate decreases.

2. Halogenation :

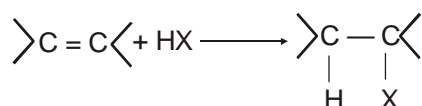


The addition always leads to the formation of trans addition product.

Mechanism :

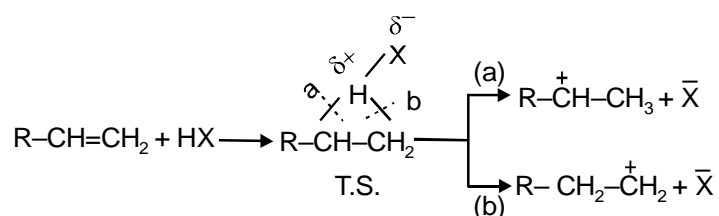


3. Addition of Halogen Acid

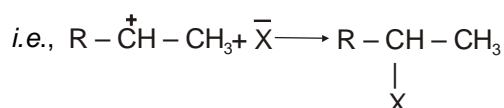


The reactivity order of halogen acid is $HI > HBr > HCl$

Mechanism :

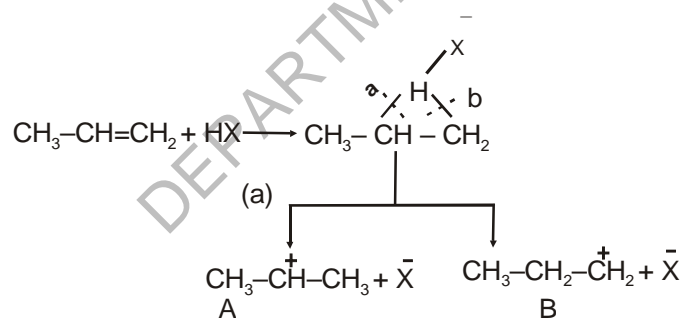


Here the transition state cleaves to form the most stable carbocation hence (a) cleavage takes place and hence, $R-\overset{+}{\text{CH}}_2-\text{CH}_3 + \bar{\text{X}}$ are formed

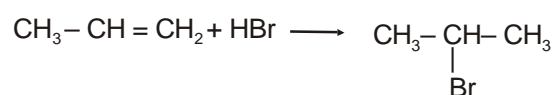
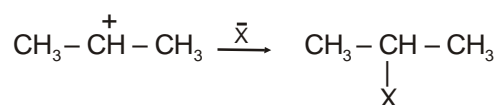


Markownikoff's Rule may therefore be applied. It states that, "During the addition of unsymmetrical reagents to unsymmetrical alkenes, the negative part of the addendum goes to carbon of double bond with least number of atoms".

Example :

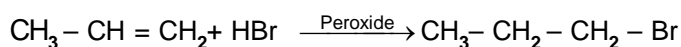


Since A is more stable than B. Hence A is formed and we get



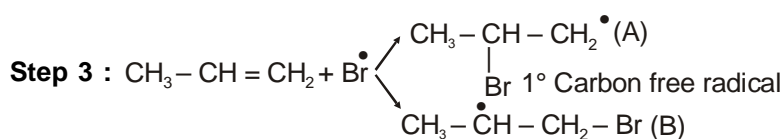
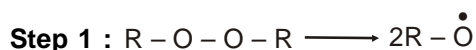
Kharasch - Mayo Effect

If the above reaction is carried out in the presence of some peroxide then addition takes place contrary to Markownikoff's Rule



Explanation

This can be explained on the basis of free radical formation



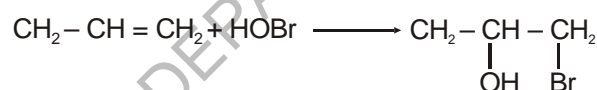
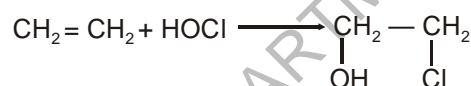
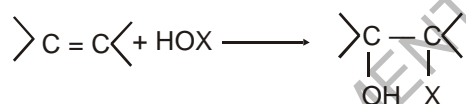
(B) is more stable than (A). 2° Carbon free radical

Hence (B) is formed.



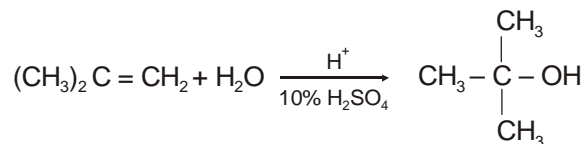
Note : Only HBr adds on by Anti Markownikoff's Rule (in presence of organic peroxide) not HCl or HI.

4. Addition of Hypohalous Acid



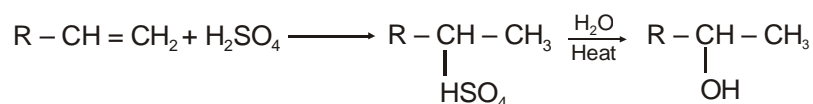
5. Addition of Water

This reaction also takes place via carbocation mechanism (Rearrangement possible).



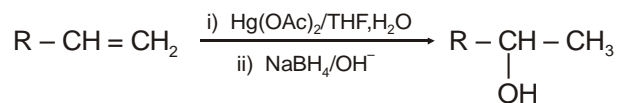
6. Addition of cold and conc. H_2SO_4

Carbocation Mechanism Followed, (Rearrangement Possible)

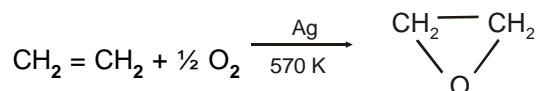


7. Oxy-Mercuration - Demercuration

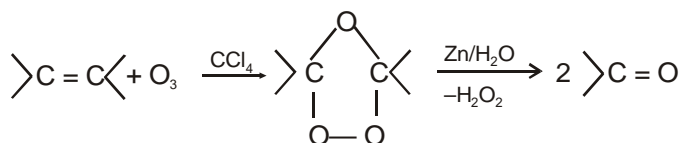
Synthesis of alcohols from alkenes is in accordance with Markownikoff's Rule (No carbocation formed)



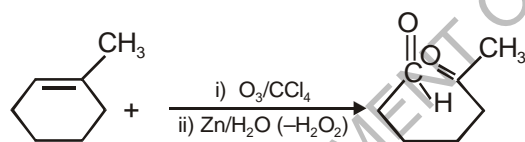
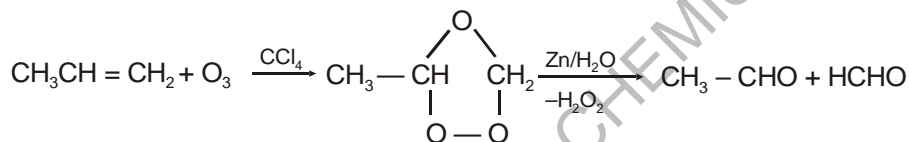
8. Addition of Oxygen:



9. Ozonolysis:

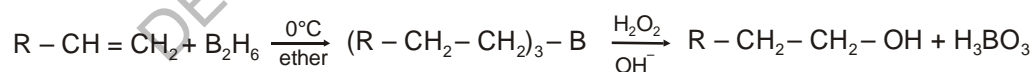


Example :



Ozonolysis helps to locate the positions of double bonds in alkene.

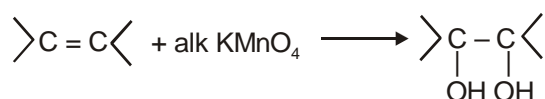
10. Hydroboration Oxidation



(Product is Antimarkownikov product.)

11. Oxidation Reactions

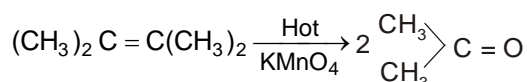
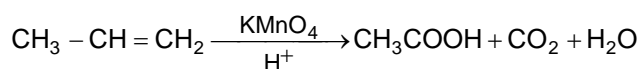
(a) Reaction with Baeyer's Reagent (Cold dilute Alkaline KMnO_4 , Hydroxylation)



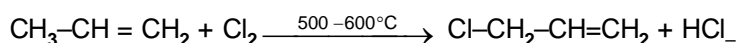
The addition is a syn addition to form vicinal dihydroxy compounds.

Note : Decolorization of Baeyer's reagent is also used as a test for unsaturation.

(b) With hot KMnO_4 or acidic KMnO_4

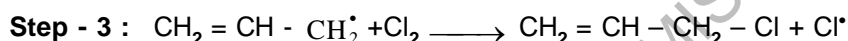
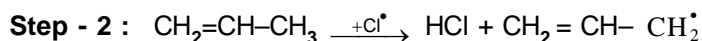
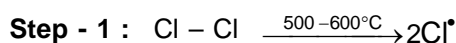


12. Substitution Reaction

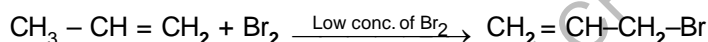


This type of reaction takes place at a carbon atom attached to double bond carbon. This is called allylic substitution.

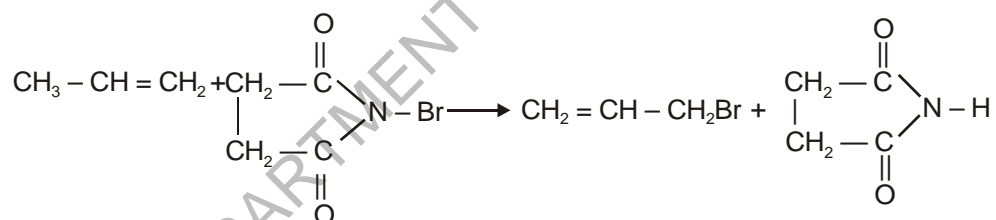
Mechanism



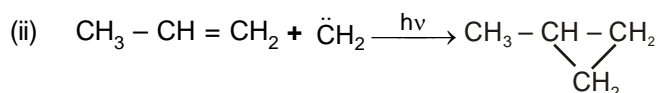
13. Wohl Zeigler Reaction



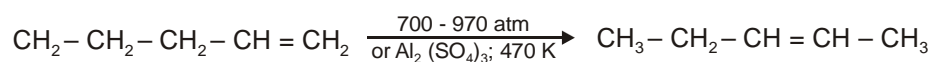
The low concentration of Br_2 is obtained from NBS



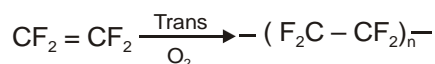
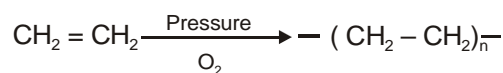
14. Addition of Carbenes



15. Isomerization :

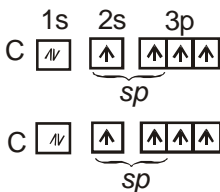
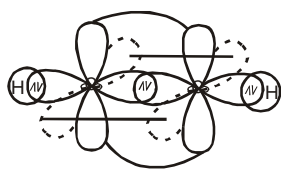


16. Polymerization :



ALKYNES

Compounds containing the structural unit $\text{C}\equiv\text{C}$ are called Alkynes. Like the double bond it is unsaturated and highly reactive towards the reagent that double bonds react with and also towards others. The simplest member of the alkyne family is acetylene, C_2H_2 . Each of the carbon atoms carrying the triple bond are sp hybridized.

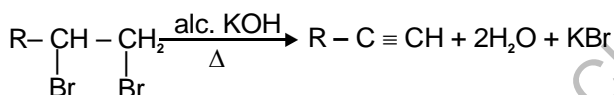
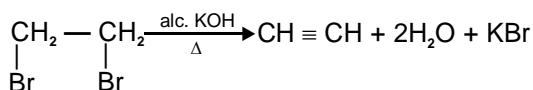


Alkynes the compounds having general formula $\text{C}_n\text{H}_{2n-2}$ where $n \geq 2$ it can be categorized by two ways.

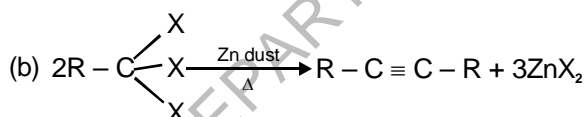
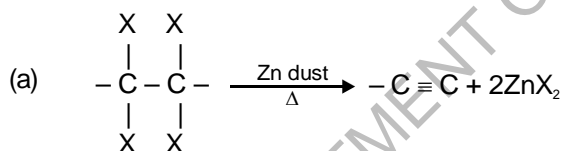
- Terminal alkynes :** Alkynes having triple bond at one end of the carbon attached to H
e.g. $\text{CH}_3-\text{C}\equiv\text{C}-\text{H}$, $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$. Terminal hydrogen is acidic in nature.
- Non-terminal alkynes :** Alkynes in which both triple bonded carbons are attached to alkyl group.

Preparation of Alkynes

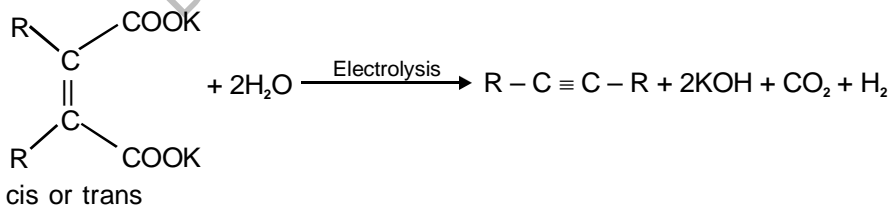
- From Dehydrohalogenation of vicinal or geminal dihalides**



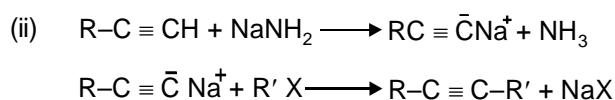
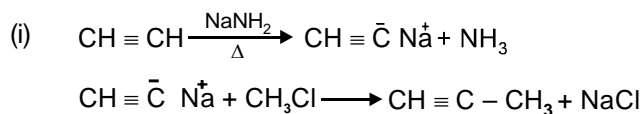
- Dehalogenation Reaction**



- Kolbe's Electrolytic Decarboxylation**



- Formation of Higher alkyne**



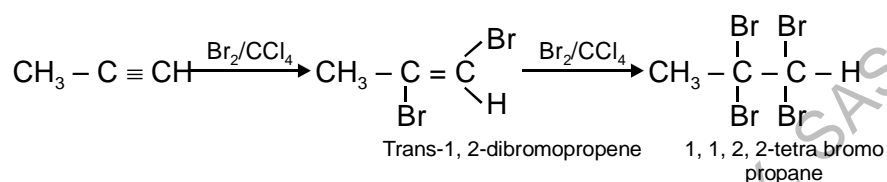
Chemical Properties

Alkynes undergo electrophilic addition generally but in the presence of salt of heavy metals which forms complexes with multiple bonds it undergo nucleophilic addition reaction.

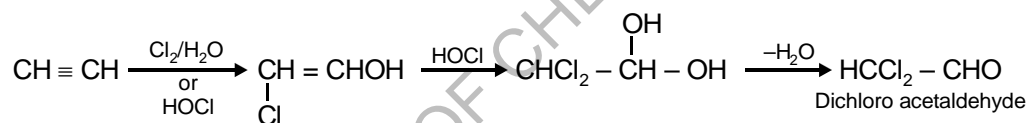
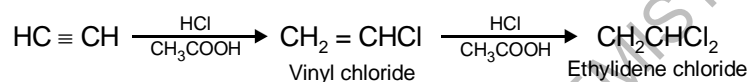
1. Addition Reaction

A. Electrophilic addition reaction :

(i) Addition of halogen



(ii) Addition of halogen acids

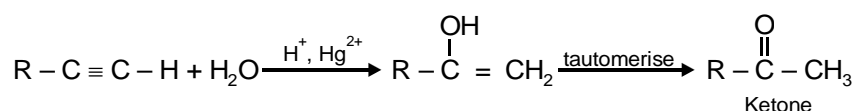
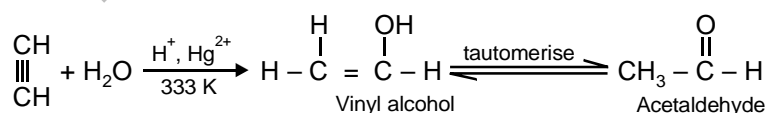


B. Nucleophilic addition reaction :

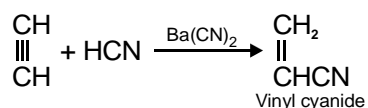
Because of greater electronegativity of sp hybridized C as compared to sp^2 hybridized carbons, Alkynes are more susceptible to nucleophilic addition reactions than alkenes. It is due to formation of some

sort of complex of heavy metal ion with π electrons like $\left[\begin{array}{c} \text{C} \equiv \text{C} \\ \diagup \quad \diagdown \\ \text{Hg}^{2+} \end{array} \right]$ and this results decrease in electron density around triply bonded carbon atoms and this can be attacked by nucleophiles.

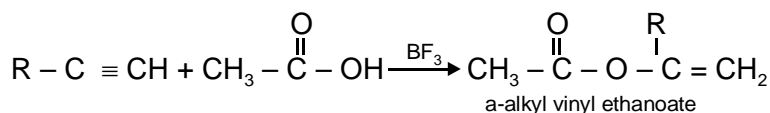
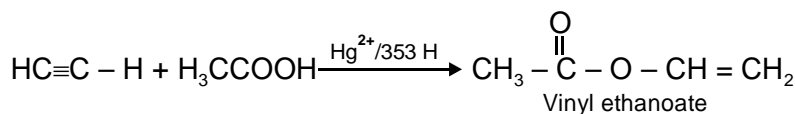
(i) Addition of H_2O or hydration of alkyne or Kucherov reaction



(ii) Addition of HCN

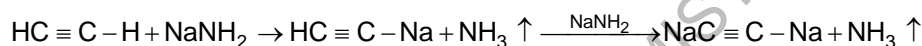
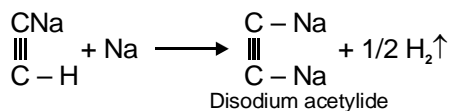
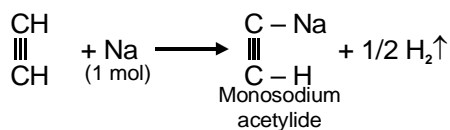


Similarly alkynes adds acids in presence of lewis acid catalyst or Hg^{2+} give vinyl ester.

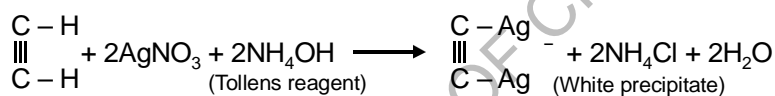


2. Reaction of Acidic H Atom

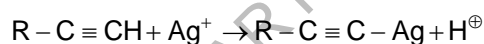
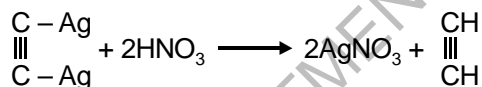
- (i) Alkynes having acidic H atom reacts with metals like Na, K, evolves H_2 gas.



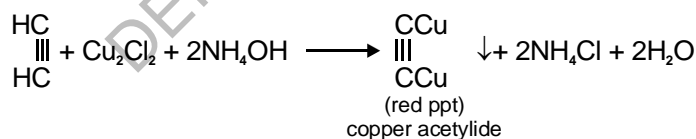
- (ii) **Reaction with Tollens reagent** : When alkyne reacts with tollens reagent (Ammonical AgNO_3 solution) it forms white precipitate of silver acetylide.



These acetylide are not decomposed by H_2O like acetylide of Na but by mineral acids like dil HNO_3 .



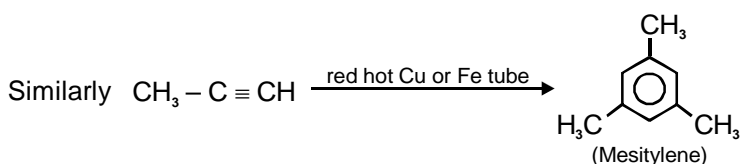
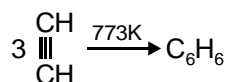
- (iii) **Reaction with Ammonical Cuprous Chloride** :

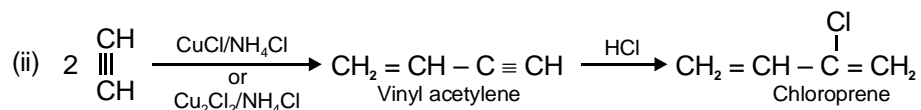


These reactions are used to distinguish terminal alkynes from other alkynes.

3. Polymerization Reaction

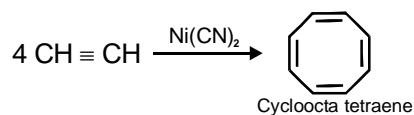
- (i) When acetylene is passed in red hot tube or retube. It converted into benzene.





Chloroprene on polymerization gives polymer called neoprene; used as artificial rubber.

(iii) Under high pressure and in presence $\text{Ni}(\text{CN})_2$ acetylene tetramerises.



4. Reaction with S_8 , N_2 , NH_3 and HCN

Acetylene reacts with S_8 , N_2 , NH_3 and HCN to form different heterocyclic compounds.

