



ST. LAWRENCE HIGH SCHOOL

A JESUIT CHRISTIAN MINORITY INSTITUTION

STUDY MATERIAL FOR CHEMISTRY (CLASS-11)

TOPIC- HYDROCARBON

PREPARED BY: MR. ARNAB PAUL CHOWDHURY

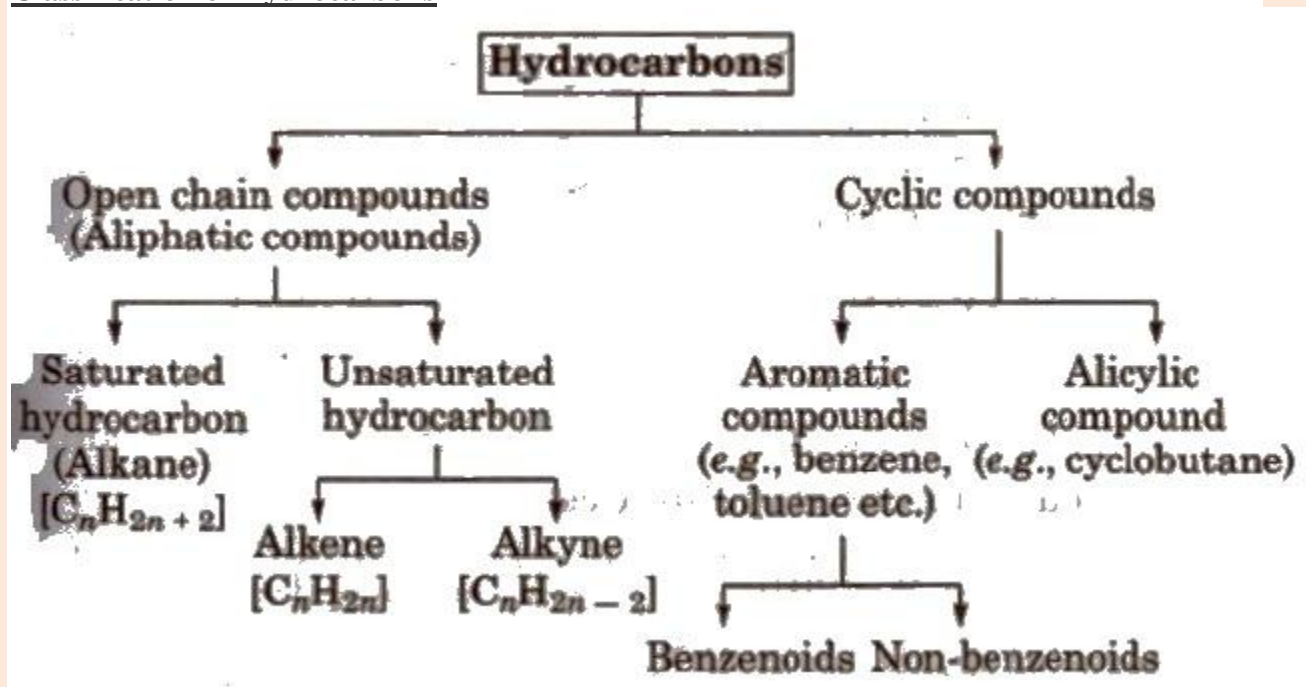
SET NUMBER-09

DATE: 18.01.2021



Hydrocarbons are the organic compounds containing carbon and hydrogen only, e.g., alkane, alkene and alkynes.

Classification of Hydrocarbons



Alkanes

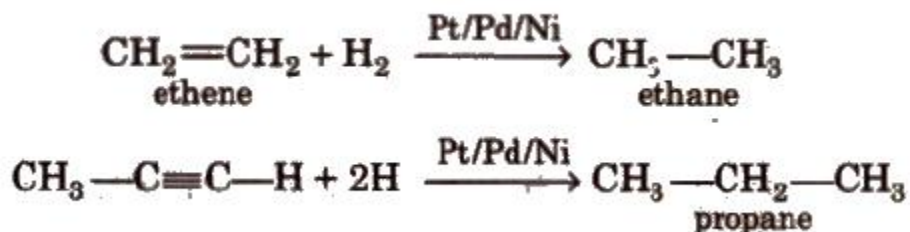
Alkanes are saturated, open chain hydrocarbons containing carbon-carbon single bonds. e.g., methane (CH₄), ethane (C₂H₆), propane (C₃H₈), etc.

These hydrocarbons are inert under normal conditions [i.e., do not react with acids, bases and other reagents]. Hence, they were earlier known as paraffins (Latin: parum-little; affinis-affinity).

Alkanes exhibit chain isomerism, position isomerism and conformational isomerism.

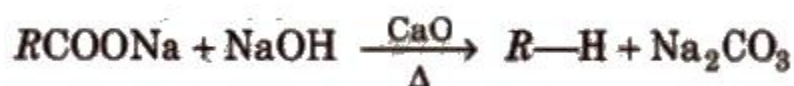
Methods of Preparation of Alkanes

i) From hydrogenation of alkenes and alkynes



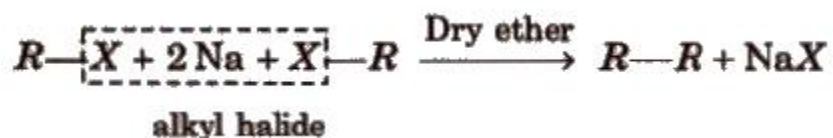
Ease of hydrogenation depends on the steric crowding across the multiple bond. More is the steric crowding, the less is the reactivity towards hydrogenation.

(ii) By sodalime Decarboxylation of sodium or potassium salts of fatty acids [decarboxylation reaction]



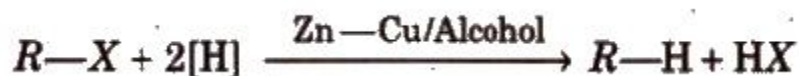
This reaction is used for descending of series as the alkane obtained has one carbon less than the parent compound. CaO is more hygroscopic than NaOH and it keeps NaOH in dry state.

(iii) By Wurtz reaction



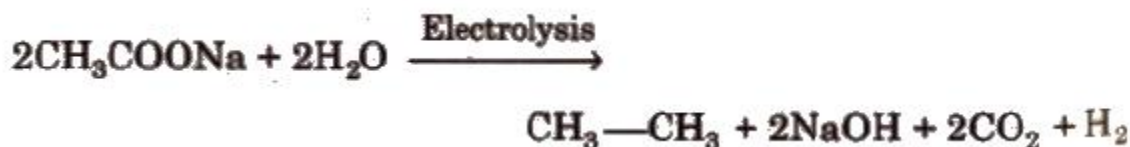
This reaction is used to increase the length of the carbon chain.

(iv) By reduction of alkyl halides



Reducing agents like Zn/HCl, HI/Red P, H₂/Pd can also be used.

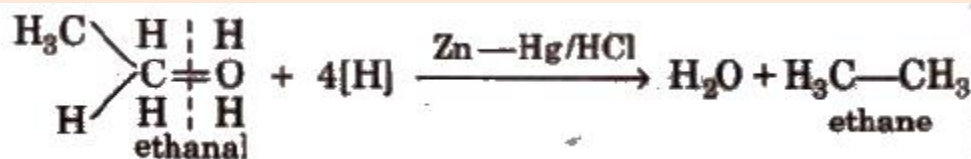
(v) By Kolbe's electrolysis



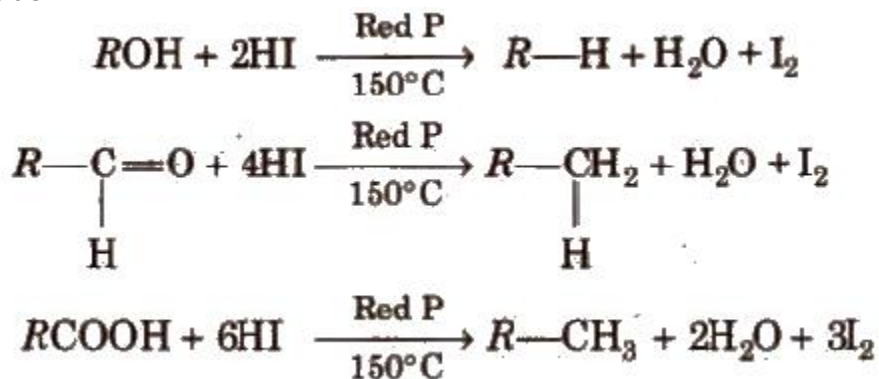
Only alkanes with even number of carbon atoms can be formed.

Alkane and CO₂ are liberated at anode while H₂ is liberated at cathode.

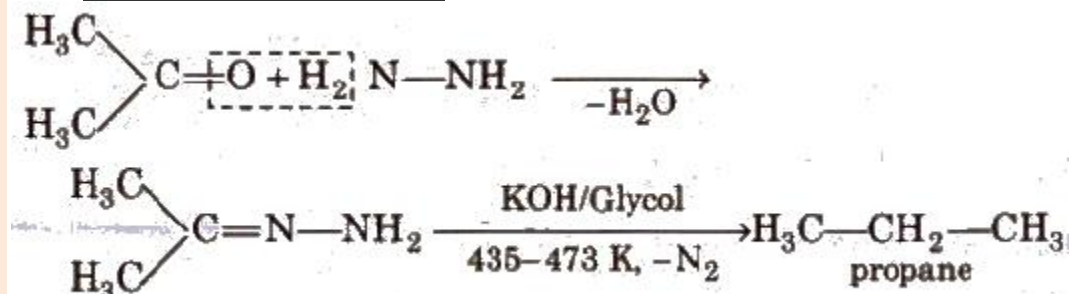
(vi) Clemmensen's reduction



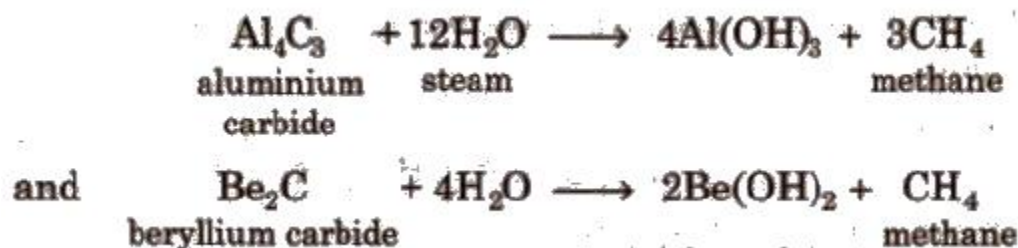
(vii) From compounds containing oxygen Alcohols, aldehydes ketones, carboxylic acids and their derivatives give alkane when treated with hot conc HI and red P in a sealed tube.



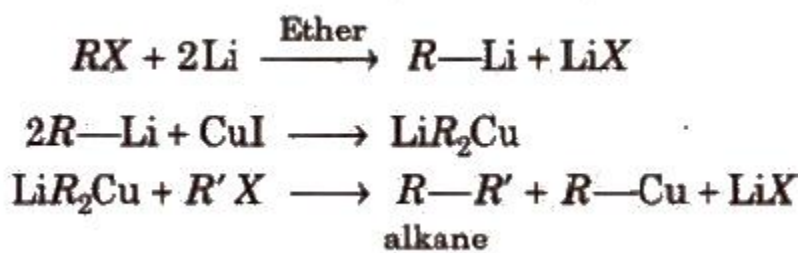
(viii) Wolff-Kishner reduction



(ix) From carbides



(x) Corey-Bouse synthesis This method can be used to prepare alkanes having odd number of carbon atoms.



Physical Properties of Alkanes:

(i) The first four members are colourless gas, next thirteen members are colourless liquids and next higher members are colourless solids.

(It can be explained on the basis of magnitude of attraction forces.)

(ii). Boiling point of alkanes decreases on branching.

BP \propto VWF (van der Waals' forces)

VWF \propto molecular mass or VAF \propto SA (surface area)

So boiling point order can be given as

n-octane > iso-octane > 2, 2, 3, 3-tetramethyl butane

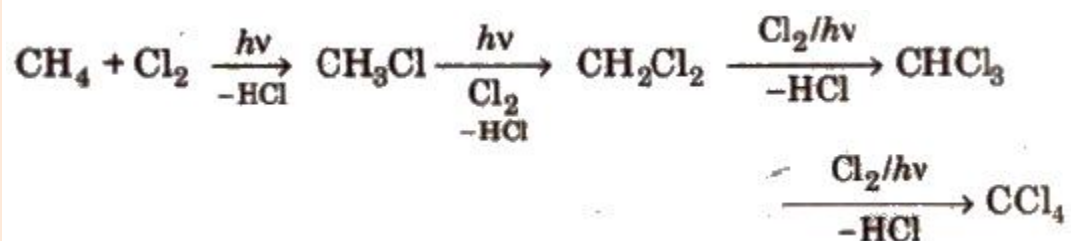
(iii). Alkanes with even number of carbon atoms have higher melting points as compared to next higher or lower alkanes with odd number of carbon atoms.

(iv). Alkanes being non-polar in nature, soluble in non-polar solvents but insoluble in polar solvent such as water.

Chemical Properties of Alkanes

(i) Halogenation of alkanes

(a) Chlorination



(b) Bromination of alkanes proceeds in the same way but not so easily.

(c) Iodination



Order of reactivity of halogens is

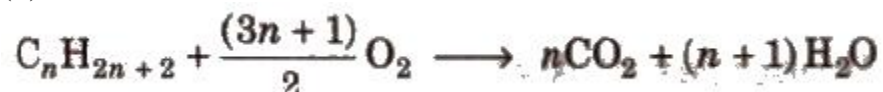


Order of reactivity of hydrogen of alkane is



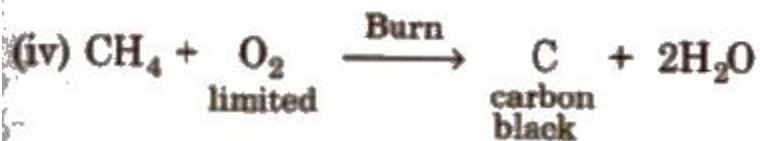
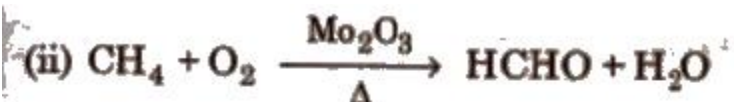
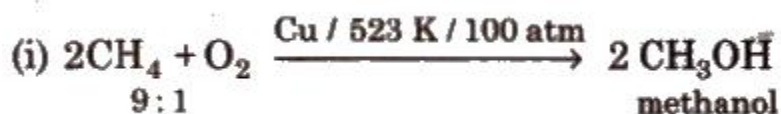
Mechanism of halogenation of alkanes is free radical in nature, i.e., the attacking reagent is a halogen free radical (X \cdot). It is a chain reaction.

(ii) Combustion

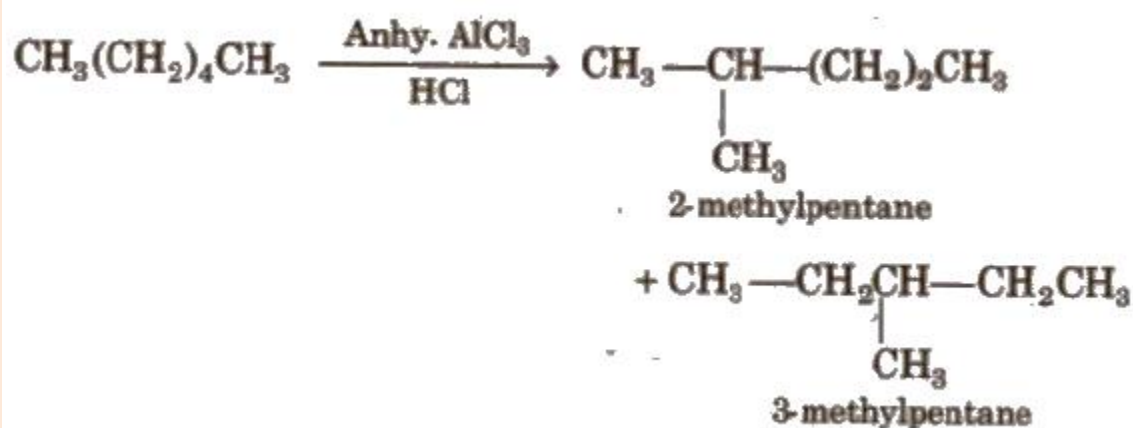


Due to the evolution of a large amount of heat during combustion, alkanes are used as fuels.

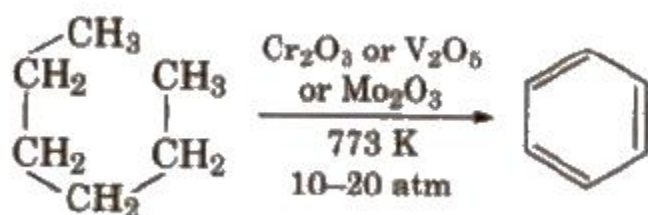
(iii) Controlled oxidation



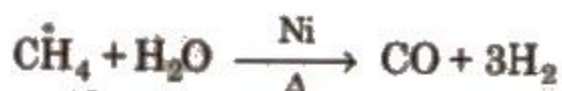
(iv) Isomerisation



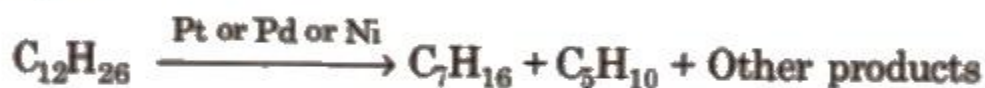
(v) Aromatisation



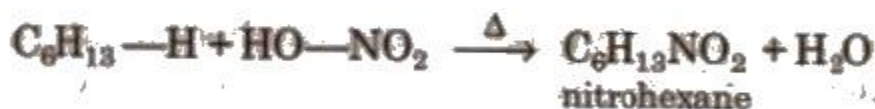
(vi) Reaction with steam



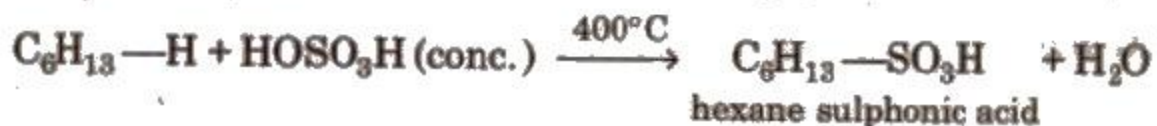
(vii) Pyrolysis



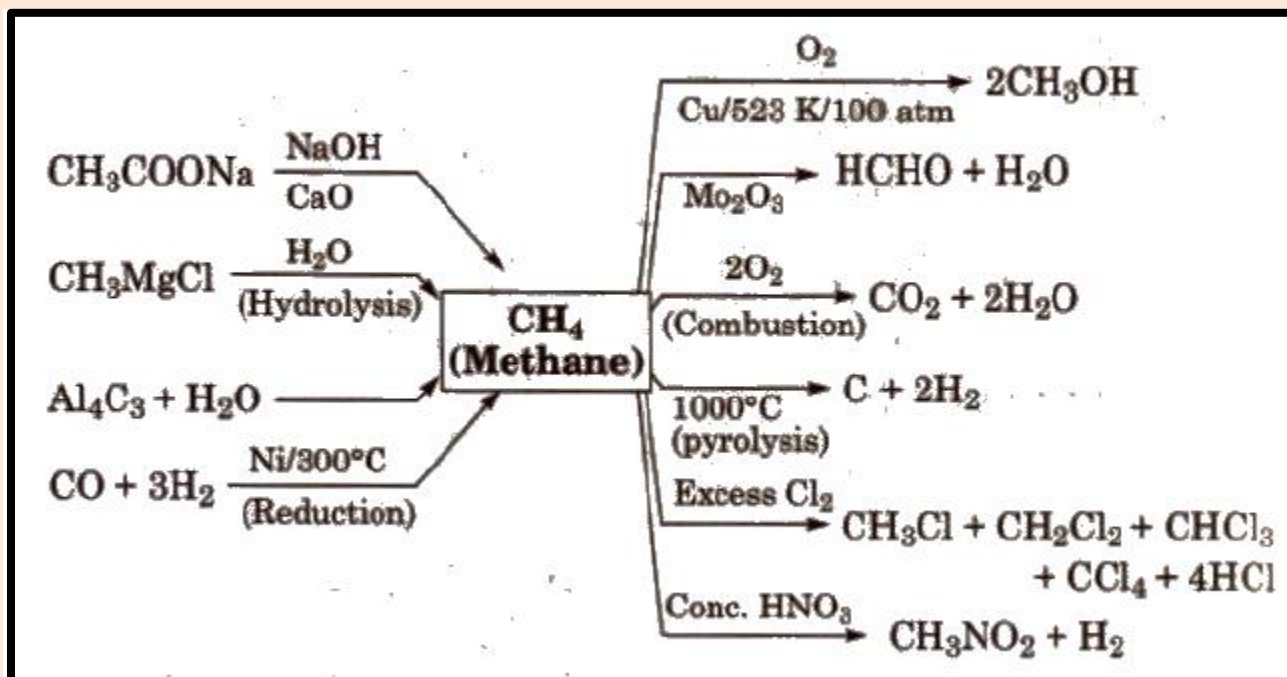
(viii) Nitration



(ix) Sulphonation

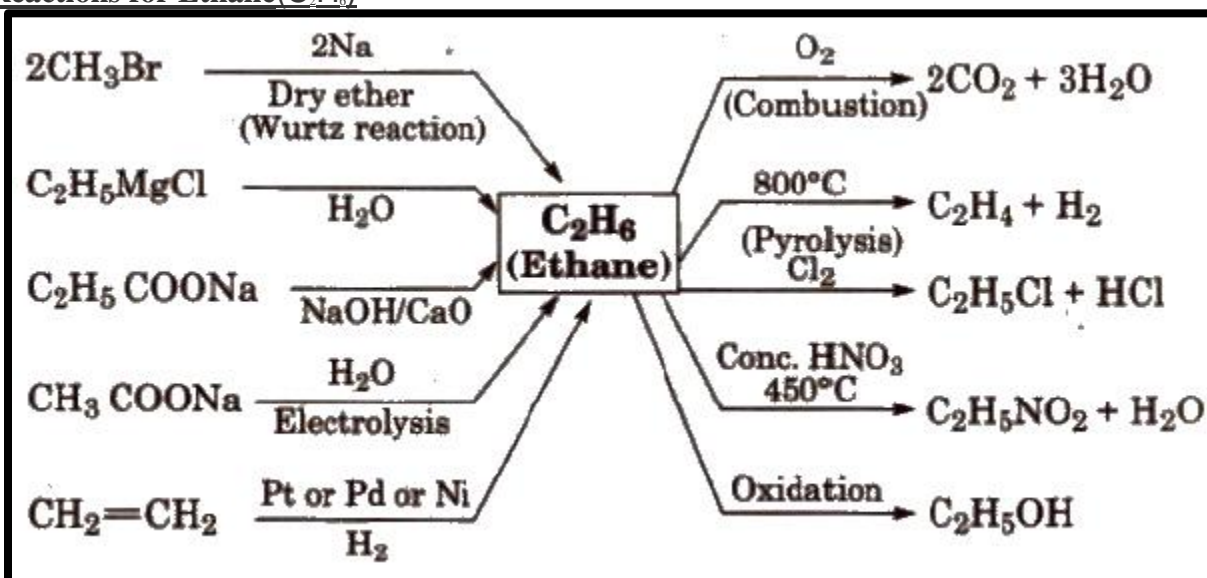


Reactions for Methane (CH_4)



(Methane cannot be prepared by Wurtz reaction, Kolbe's electrolytic process and by reduction of alkenes or alkynes).

Reactions for Ethane(C_2H_6)

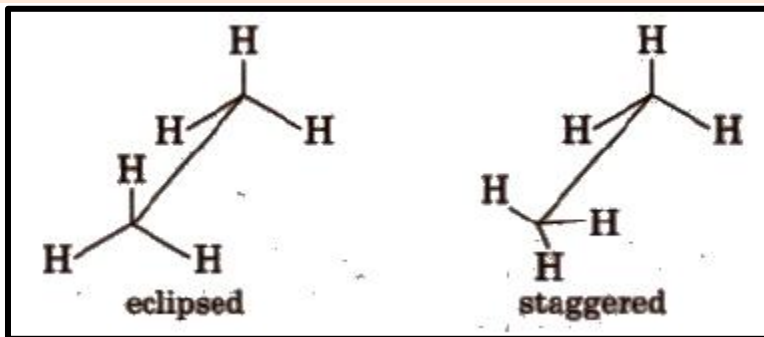


Conformations of Alkanes-

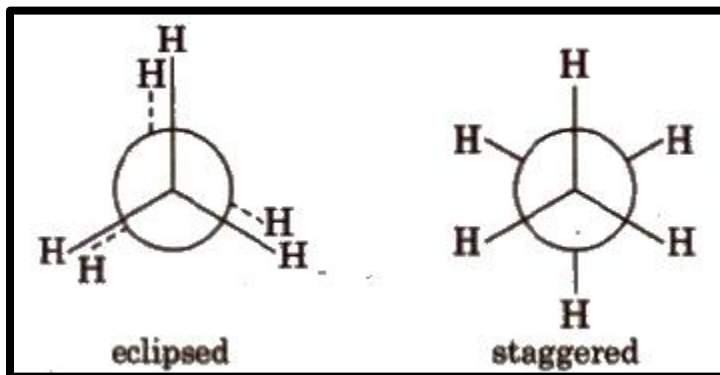
Alkanes have C-C sigma (σ) bonds and rotation about C-C single bond is allowed. This rotation results in different spatial arrangements of atoms in space which can change into one another, such spatial arrangements are called conformations or conformers or rotamers.

Conformations of ethane-

(i) Sawhorse projections



(ii) Newman projections



Intermediate conformation between eclipsed and staggered are known as skew (gauche) conformations.

Eclipsed form is least stable but staggered form is most stable due to greater distance between the bond pairs or lesser torsional strain.

The energy difference between the two extreme forms is of the order of 12.5 kJ mol⁻¹.

Alkenes

These are unsaturated non-cyclic hydrocarbons which have sp² -hybridisation with 120° bond angle.

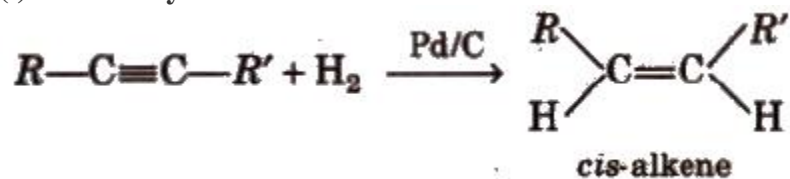
Alkenes are also called olefins [oil-forming] which indicates their high reactive nature.

Alkenes have general formula C_n H_{2n}, where n = 2,3,4 ...

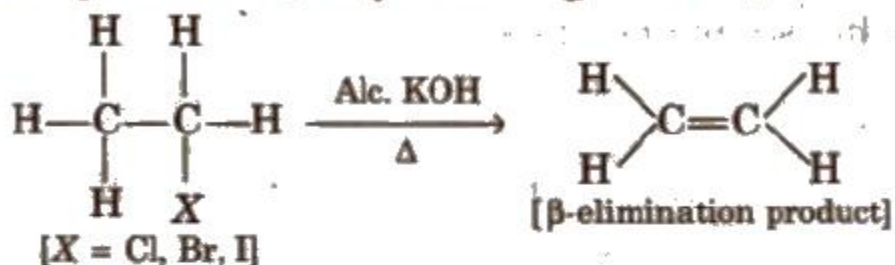
C₂H₄ (ethene), C₃H₆ (propene), etc.

Methods of Preparation of Alkenes

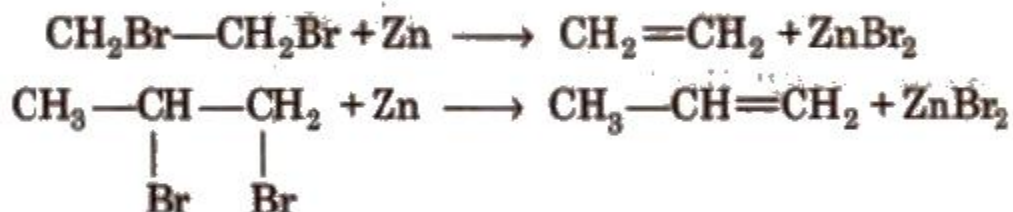
(i) From alkynes



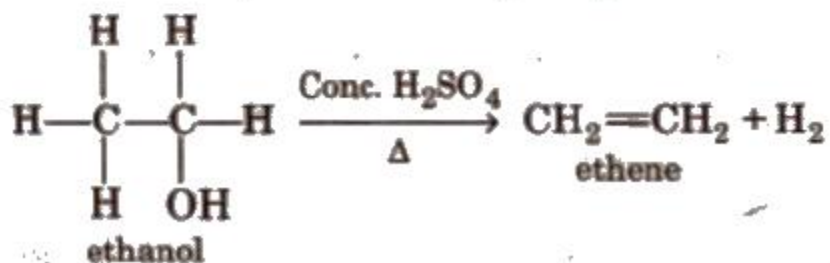
(ii) From alkyl halide [dehydrohalogenation]



(iii) From vicinal dihalides



(iv) From alcohols by acidic dehydrogenation



Physical Properties of Alkenes

Alkene as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature.

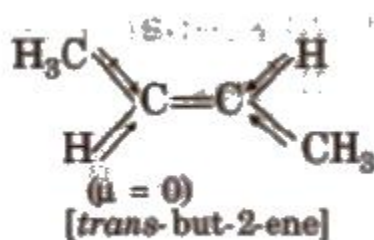
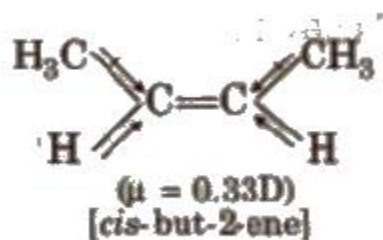
C₁ to C₃ are gases, the next fourteen are liquids and the higher members are solids. Alkenes show a regular increase in boiling point with increase in size.

Isomerism in Alkenes

Alkene show both structural isomerism and geometrical isomerism.

Structural isomerism exhibited by alkenes are chain isomerism and position isomerism.

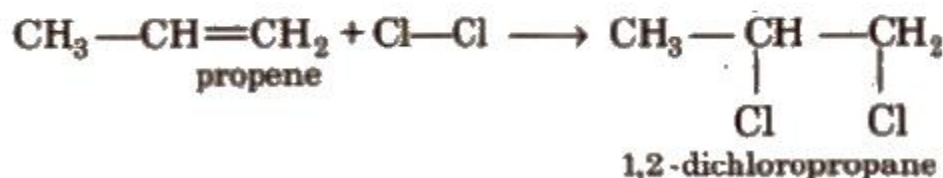
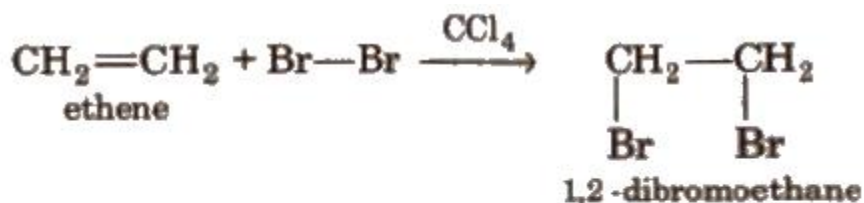
Alkenes also exhibit stereoisomerism as geometrical (cis-trans) isomerism.



Isomerism in Alkenes

Chemical Properties of Alkenes

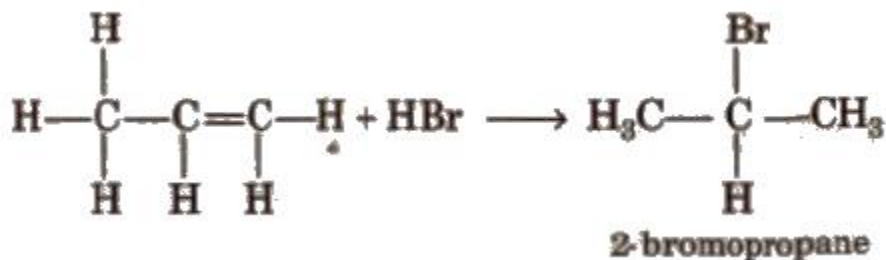
(i) Addition of halogens



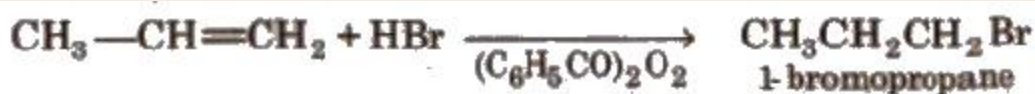
(ii) Addition of hydrogen halides HCl, HBr, HI add up to alkenes to form alkyl halides as per their reactivity order

HI > HBr > HCl

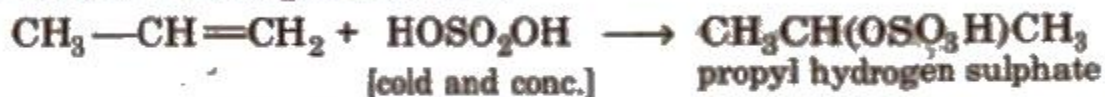
Addition reaction of HBr to unsymmetrical alkenes (Markownikoff's rule) According to Markownikoff's rule, the negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atom.



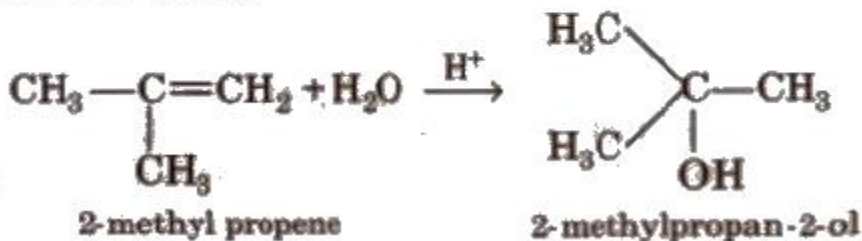
Anti-Markownikoff addition or peroxide effect or Kharasch effect In the presence of organic peroxide, addition of only HBr molecule on unsymmetrical alkene takes place contrary to the Markownikoff's rule.



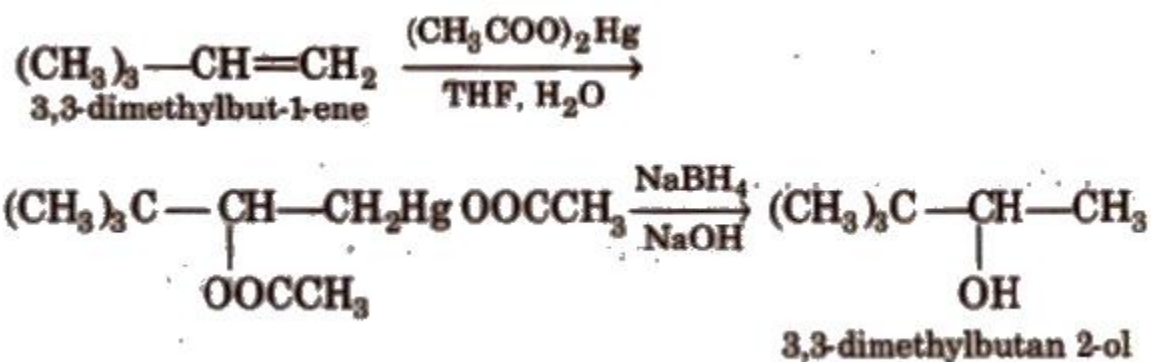
(iii) Addition of sulphuric acid



(iv) Addition of water



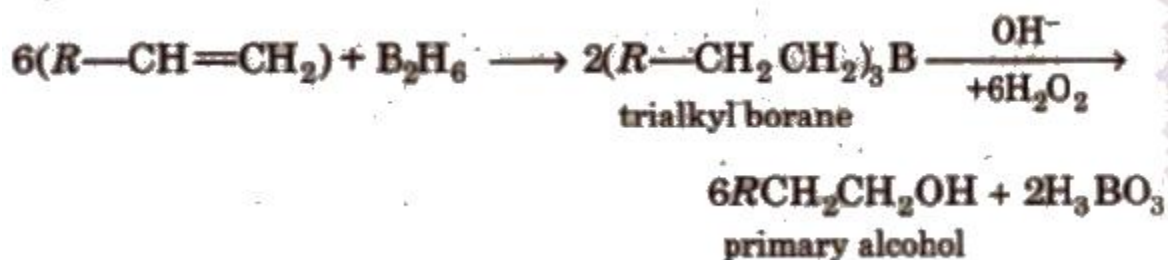
(v) Oxymercuration-demercuration This reaction is an example of hydration of alkene according to Markownikoffs rule.



It is an anti-addition reaction.

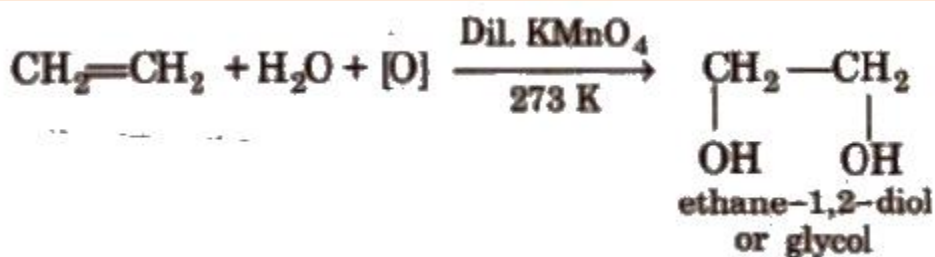
It is better than catalytic hydration by dil. H_2SO_4 , as it avoids rearrangement.

(vi) Hydroboration oxidation

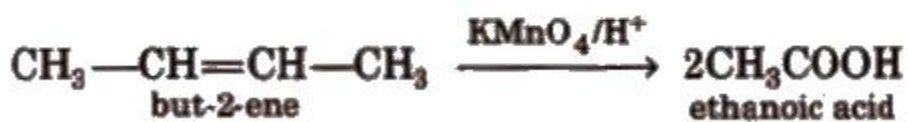
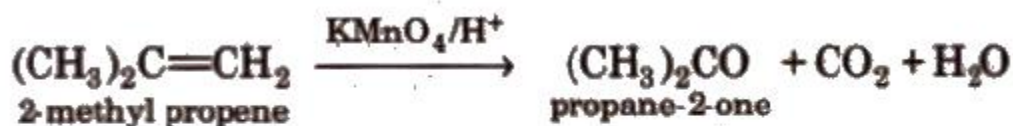


This reaction involved syn-addition of reagent.

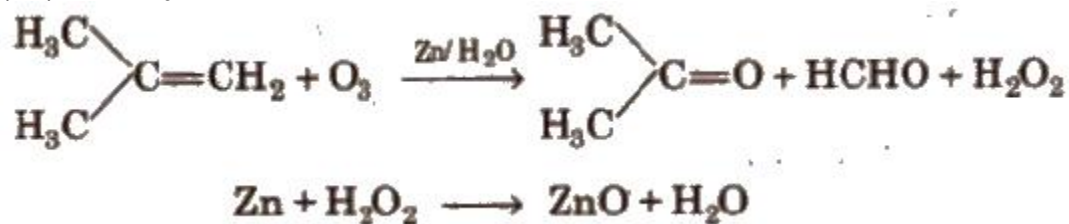
(vii) Oxidation Alkenes decolourise cold dilute aqueous solution of potassium permanganate (Baeyer's reagent). It is used as a test for unsaturation.



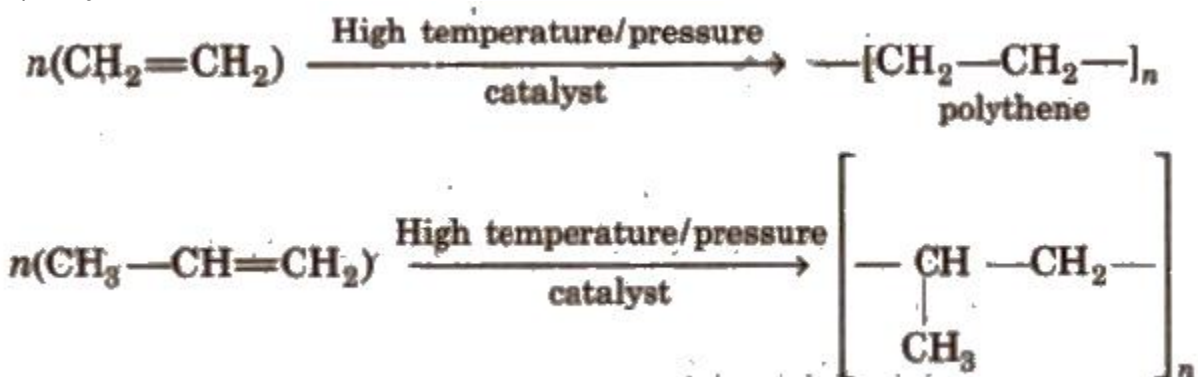
Acidic KMnO_4 or acidic $\text{K}_2\text{Cr}_2\text{O}_7$ oxidise alkenes to ketones and/or acids depending upon the nature of alkene and the experimental conditions.



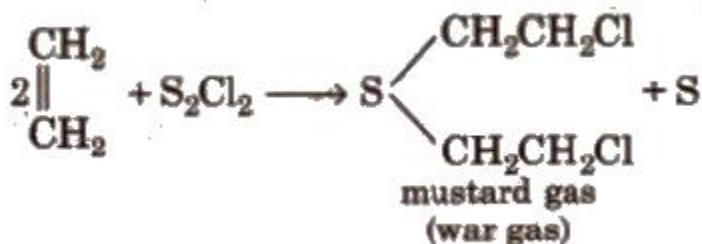
(viii) Ozonolysis



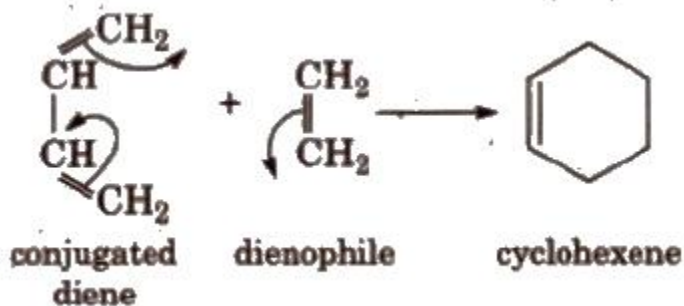
(ix) Polymerisation



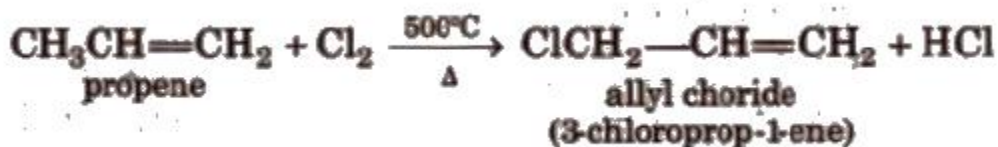
(x) Reaction with sulphurmonochloride



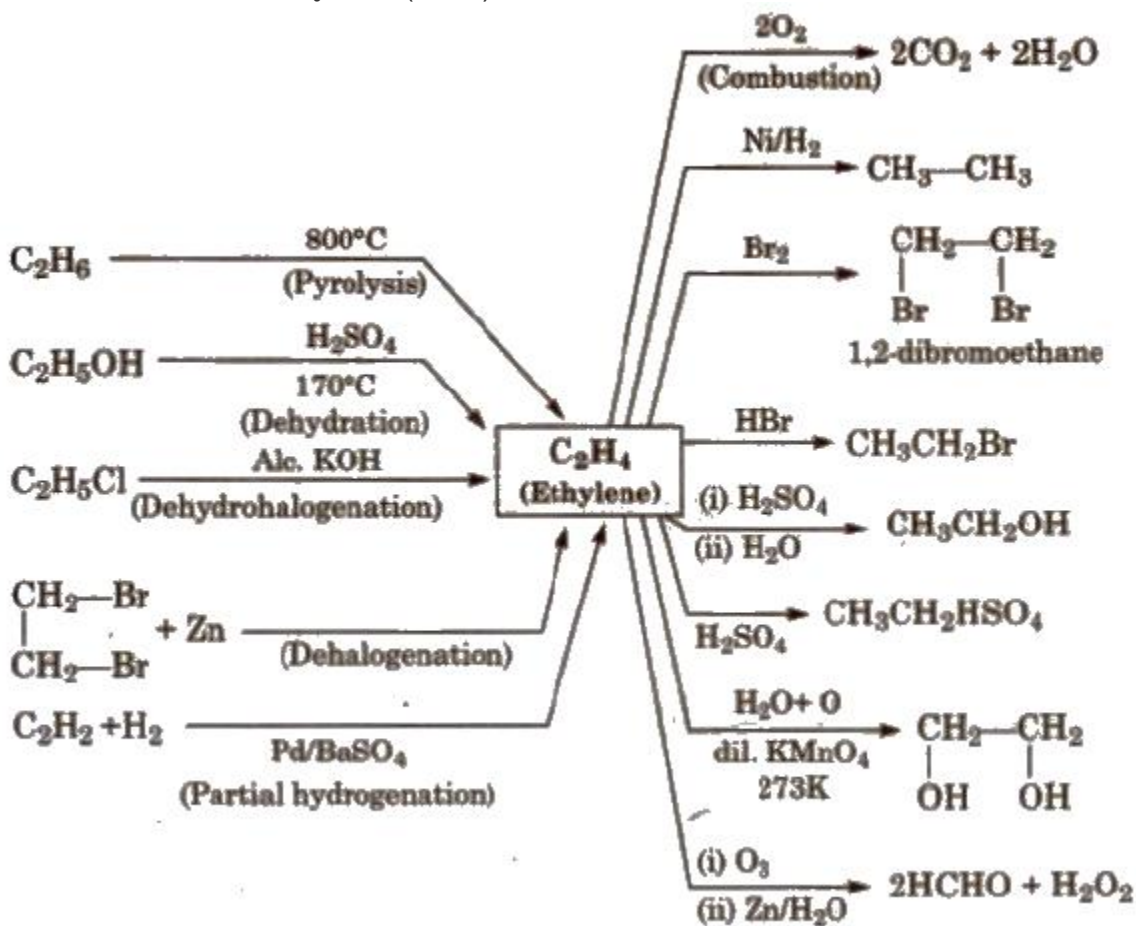
(xii) Diels-Alder reaction



(xiii) Substitution reactions These occur at very high temperature at allylic position

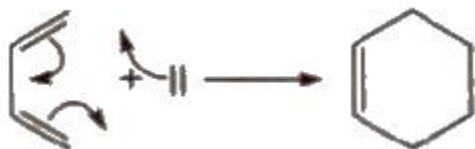


Reactions for Ethene [Ethylene] (C_2H_4)



Conjugated dienes

Dienes having alternate single (-) and double bonds (=) are called conjugated alkenes. These give Diels, Alder reaction.



Alkynes

These are unsaturated hydrocarbons with general formula C_nH_{2n-2} e.g., C_2H_2 (ethyne), C_3H_4 (propyne)

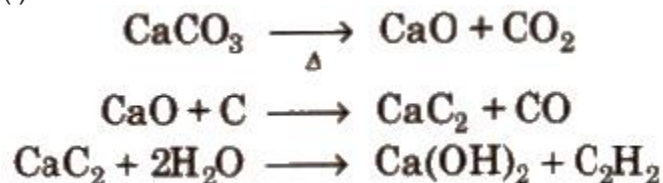
Alkynes also exhibit electrophilic addition reaction but less reactive than alkenes because the dissociation of π -electron cloud requires more energy.

In alkynes, position of triple bond is determined by ozone (O_3).

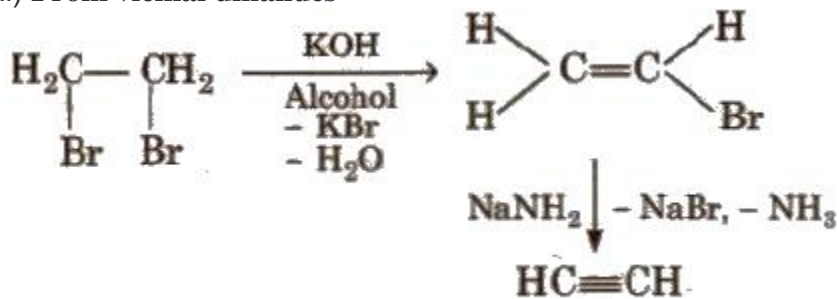
$H-C \equiv C-H$ contains 3σ and 2π - bonds and bond length is 120 pm. In acetylene. $H-C \equiv C$ bond angle is 180° .

Methods of Preparation of Alkynes

(i) From calcium carbide



(ii) From vicinal dihalides



(iii) From tetrahalides



Physical Properties of Alkynes

1. The first two members are gases next eight members ($C_5 - C_{12}$) are liquids and higher members are solids.
2. They are all colourless and odourless with the exception of acetylene which has slightly garlic odour due to the presence of PH_3 and H_2S as impurities.

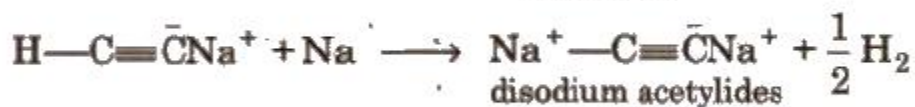
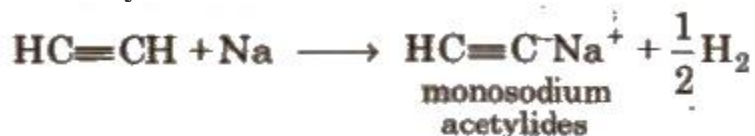
3. Alkynes are insoluble in water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.

4. Melting point, boiling point and density increase with increase in molar mass.

Chemical Properties of Alkynes

Alkynes show electrophilic as well as nucleophilic addition reactions.

(i) Acidic character of alkyne

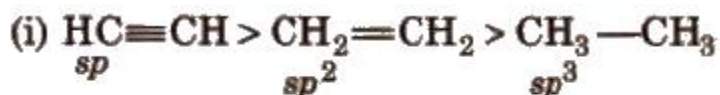


These reactions are not shown by alkenes, alkanes and non-terminal alkynes, hence used for distinction between alkane, alkene and alkyne.

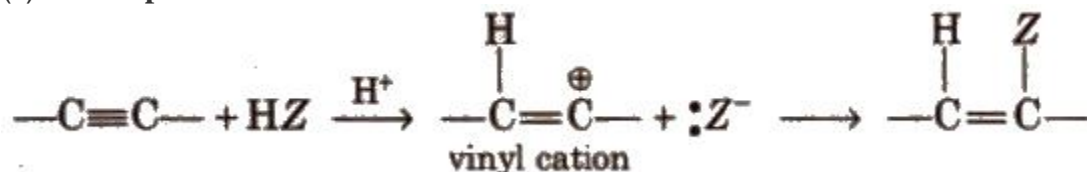
Acetylenic hydrogens are acidic in nature due to 50% s-character in sp-hybridised orbitals.

Acidity of alkynes is lesser than water.

Acidic behaviour order

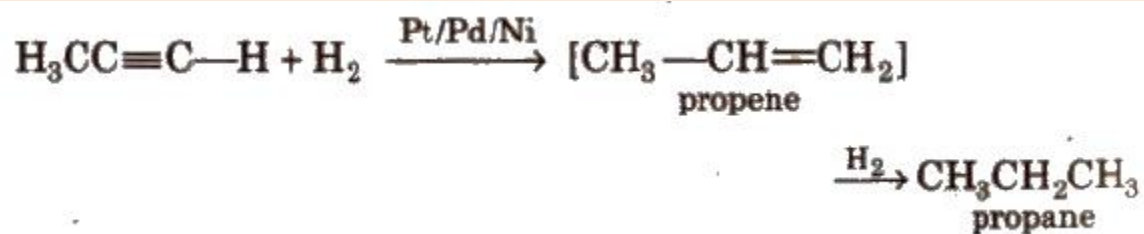


(ii) Electrophilic addition reactions

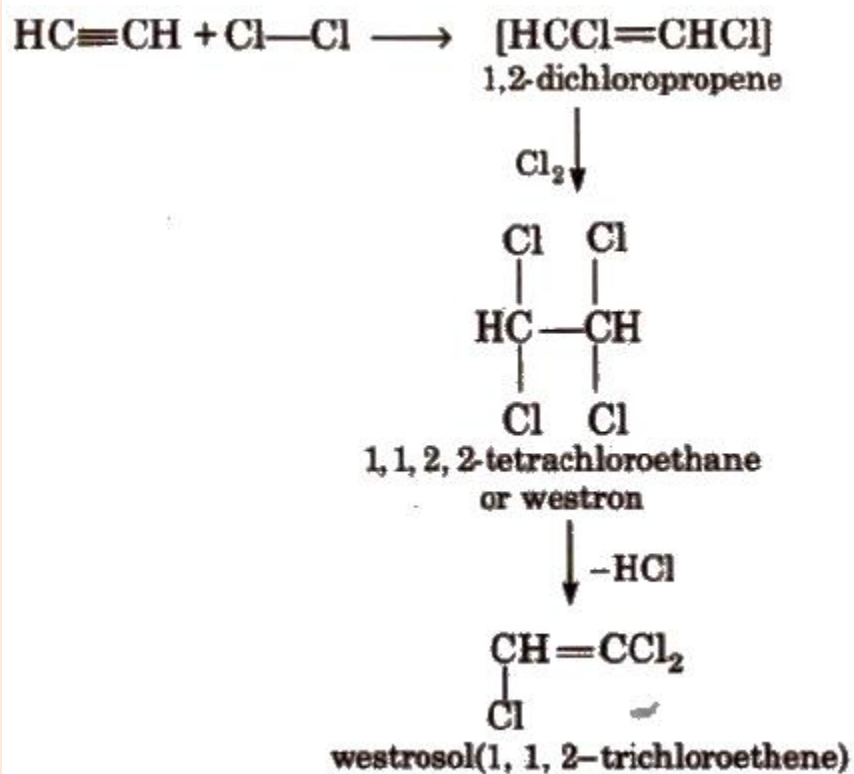


The addition product formed depends upon the stability of vinylic cation. Addition on unsymmetrical alkynes takes place according to Markovnikov's rule.

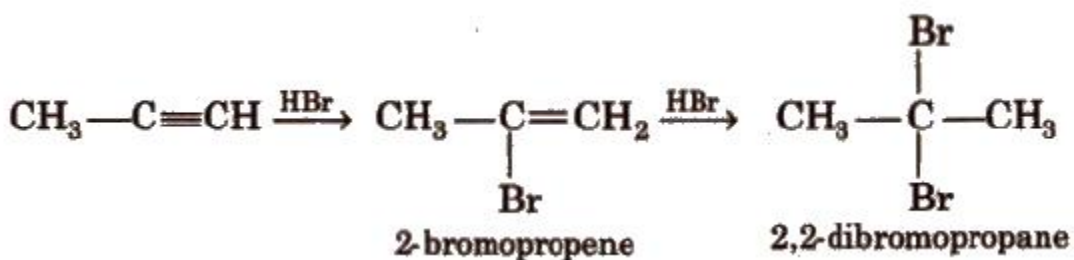
(a) Addition of dihydrogen



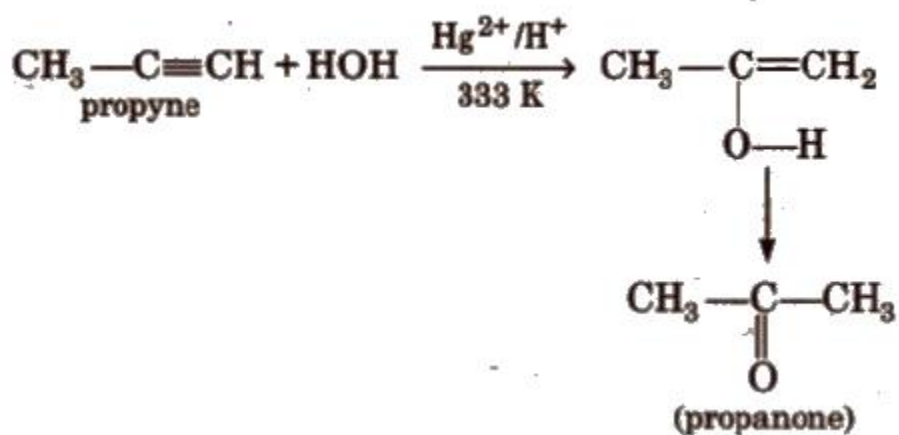
(b) Addition of halogens



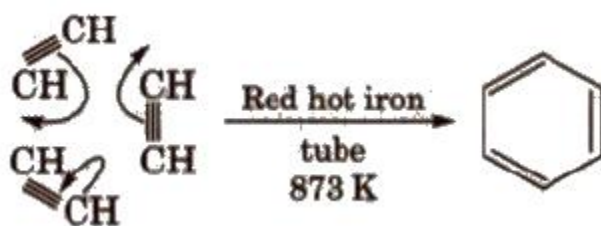
(c) Addition of hydrogen halides



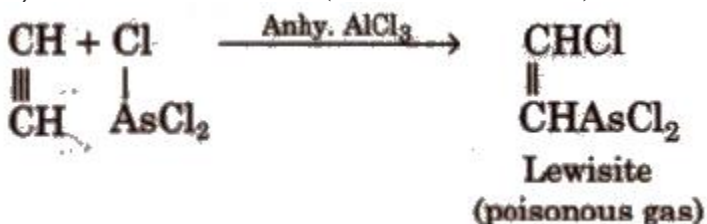
(d) Addition of water



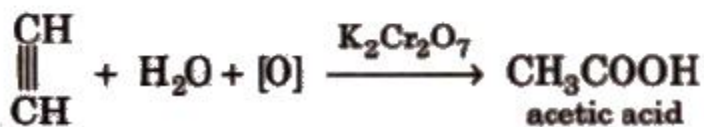
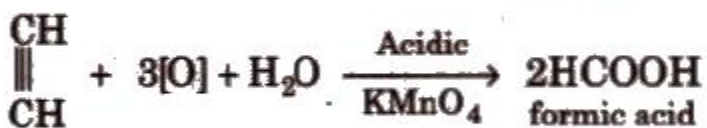
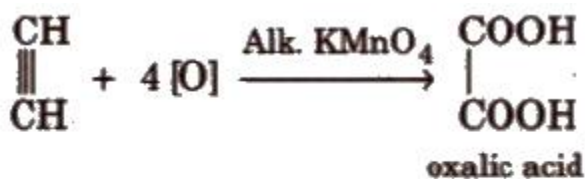
(iii) Cyclic polymerisation



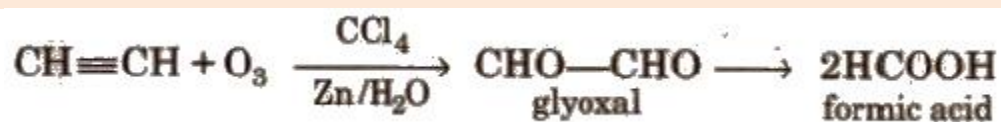
(iv) Reaction with AsCl₃ (arsenic trichloride)



(v) Oxidation

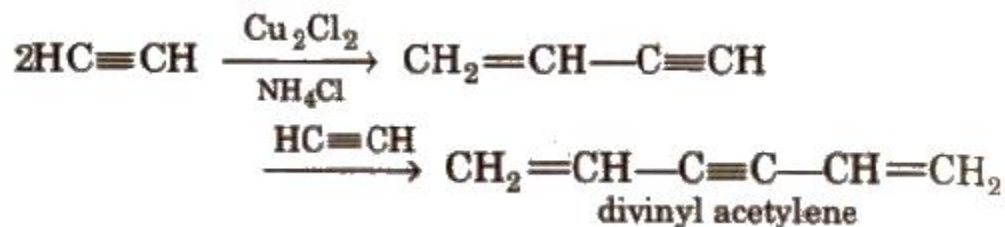


Ozonolysis

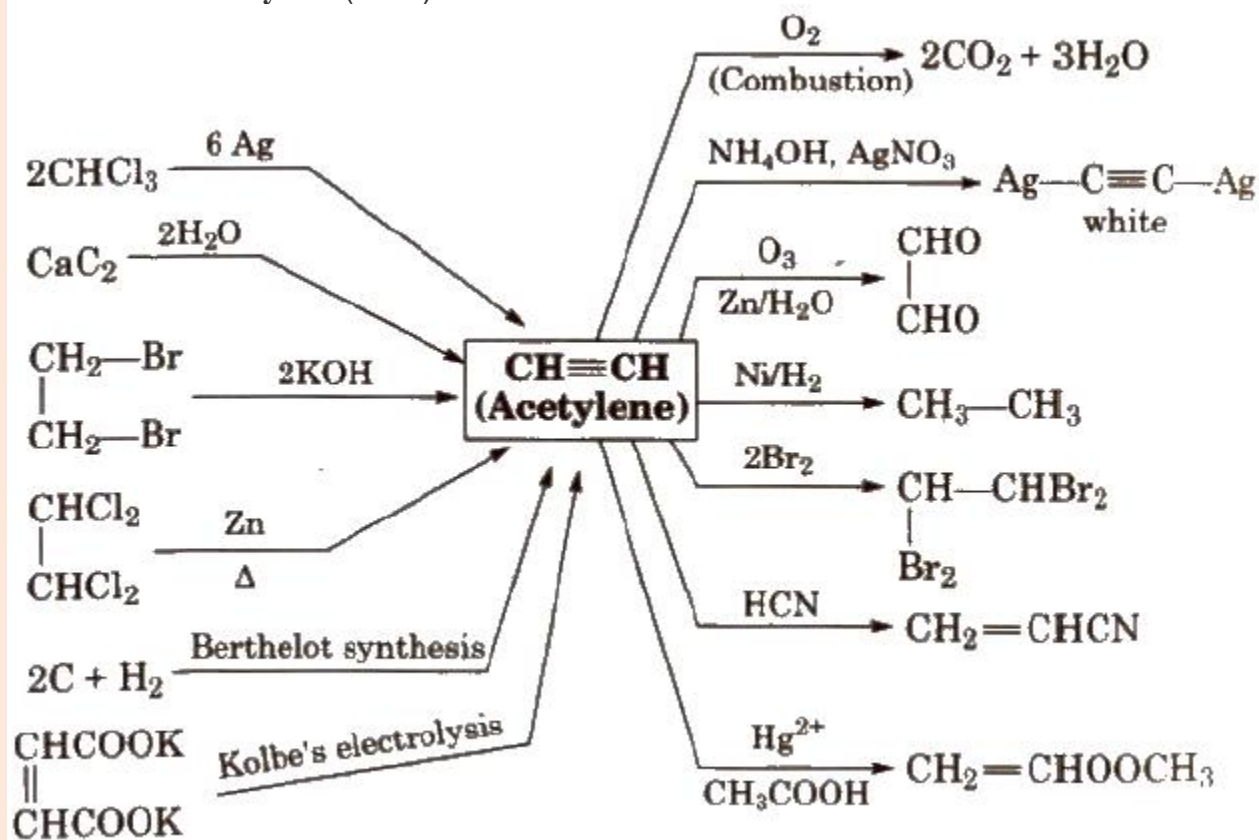


Higher alkynes give diketones which are further oxidised to carboxylic acid.

(vi) Linear polymerization



Reactions for Acetylene (C_2H_2)



PREPARED BY: MR. ARNAB PAUL CHOWHDRY