

Hydrocarbon

A compound of carbon and hydrogen is known as hydrocarbon.

• Saturated Hydrocarbon

A hydrocarbon is said to be saturated if it contains only C—C single bonds.

For example: Ethane $\text{CH}_3\text{—CH}_3$

• Unsaturated Hydrocarbon

A hydrocarbon is said to be unsaturated if it contains $\text{C} = \text{C}$ or $\text{C} \equiv \text{C}$ multiple bonds.

Example: ethene $\text{CH}_2 = \text{CH}_2$

ethyne $\text{HC} \equiv \text{CH}$

• Aromatic Hydrocarbon

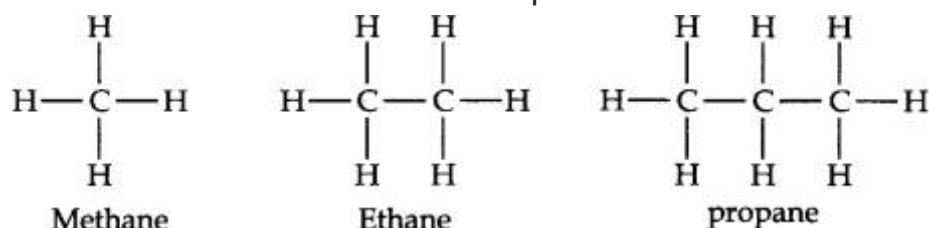
Benzene and its derivatives are called aromatic compounds.

Alkanes

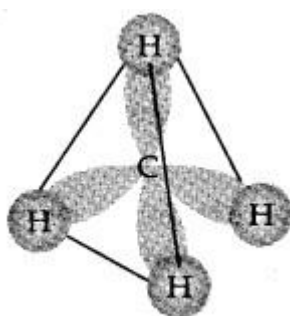
Alkanes are the simplest organic compounds made of carbon and hydrogen only.

They have the general formula $\text{C}_n\text{H}_{2n+2}$ (where $n = 1, 2, 3,$ etc.)

The carbon atoms in their molecules are bonded to each other by single covalent bonds. Since the carbon skeleton of alkanes is fully saturated with hydrogens, they are also called saturated hydrocarbons. Alkanes contain strong C—C and C—H bonds. Therefore, this class of hydrocarbons are relatively chemically inert. Hence they are sometimes referred to as paraffins (Latin parum affinis = little affinity). First three members of this class can be represented as



Structure:



Structure of methane

In methane carbon forms single bonds with four hydrogen atoms. All H—C—H bond angles are of 109.5° . Methane has a tetrahedral structure. C—C and C—H bonds are

formed by head-on overlapping of sp^3 hybrid orbitals of carbon and $1s$ orbitals of hydrogen atoms.

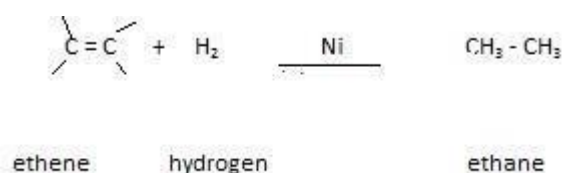
Preparation of alkanes

1. Naturally, they are synthesised by decomposition of plants and waste matter.
2. In laboratory: They are prepared from :

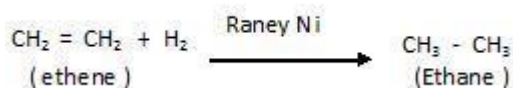
- From unsaturated hydrocarbons
- From alkyl halides
- By reduction of alkyl halides
- By use of Grignard reagent
- From carboxylic acids

(a) **From unsaturated Hydrocarbons**:-The method involved is by hydrogenation that is addition of H_2 . It is also called as reduction reaction.

The general reaction involved:



A special reaction occurs where we use Raney Ni which is actually activated nickel (alloy of 50 % Ni, 50 % Al). But the reaction is assigned a special name that is **Sabatier Sanderson Reduction**. The reaction is given below:

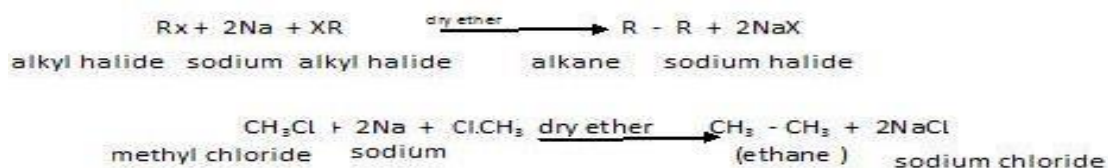


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(b) From Alkyl halides (RX)

The methods that can be used for preparing alkanes by using alkyl halides are:

- Wurtz reaction
- Reduction of alkyl halide
- By use of Grignard reagent
- **Wurtz reaction**: in this two molecules of alkyl halide react with sodium in presence of dry ether as shown below:



Please note the dry ether is used so as to keep sodium dry so that it does not catch fire in moist conditions.

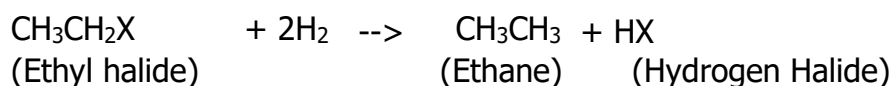
Limitation of this reaction: is that we need to take same alkyl halides otherwise we get mixtures of alkanes and due to almost same boiling points etc, they are difficult to separate. Another limitation of this is that by this method we can prepare alkanes only with even number of Carbon atoms.

(c) **Reduction of alkyl halides:** - It can be done by using various Reducing agents like:

- With Zn and HCl

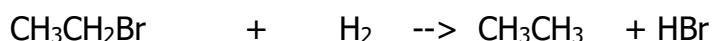
In this the Zn and HCl both react and produce nascent Hydrogen to carry out reduction.

(Zn/HCl)

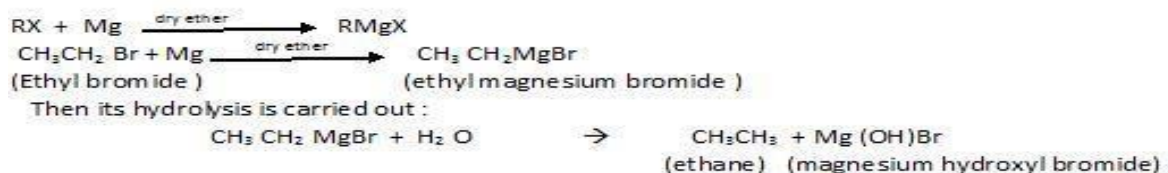


- Pt or Pd can be used as reducing agent

(Pt/Pd)

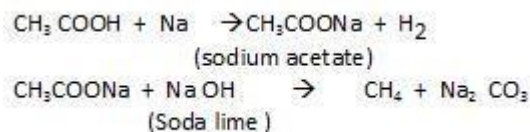


(d) By use of Grignard reagent (RMgX)



(d) From Carboxylic acids (RCOOH)

- **By Decarboxylation:** It is removal of CO_2 In this first carboxylic acid, is made to react with sodium metal then followed by its reaction with sodium hydroxide to get the desired alkane.



- **Kolbe's electrolysis Reaction:** In this electric current is passed through metal carboxylic salt



Physical Properties of alkanes

1. **Polarity of alkanes:** Alkanes are non-polar in nature because of same electro negatives of carbon atoms.
2. **Existence:** The force of attraction present in them is Vander wall forces due to which the lower members i.e. C_1 to C_4 exist as gases, $\text{C}_5 - \text{C}_7$ as liquid and higher ones are solid.
3. **Boiling point:** - Because of non-polar character they have low boiling point. The boiling points increase with increase in the number of carbon atoms due to increase in Vander wall forces of attraction. However, with increase in branching the surface area decreases and hence, Vander wall force decreases and hence the boiling point decreases.

For example: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ butane has more boiling point than 2 methyl propane

(d) **Melting Point:** - It not only depends on mass but also on structure of hydrocarbon.

- So, alkane with odd number of carbon atom has low melting point
- Alkane with even number of carbon atoms have high melting point
- Because they have symmetrical structure, so they fit better in lattice due to this their

Melting point is high.

For example: Pentane has low melting point than hexane because hexane has symmetrical structure.

(e) **Solubility:** We know Hydrocarbons are non-polar and we also know like dissolve like

So they are not soluble in H_2O but soluble in organic solvents like ether CCl_4 ,

Chemical properties of alkanes

We know that saturated Hydrocarbons are quite less reactive and undergo reaction with difficulty therefore they are called paraffin's.

The reactions shown by them are given below:

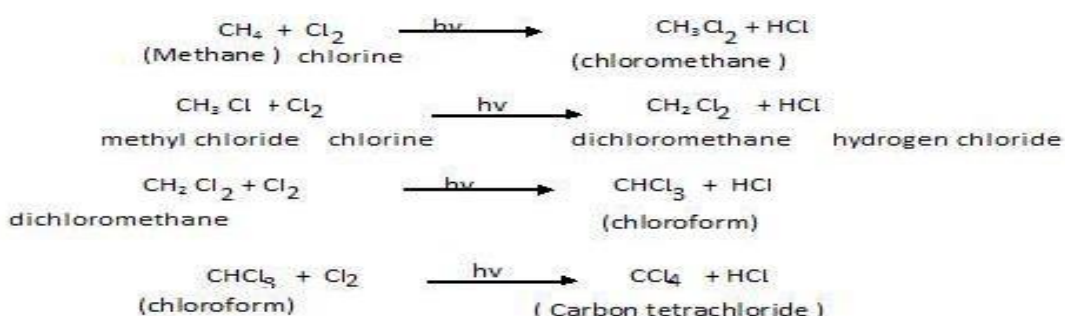
- **1st Substitution reaction:** In this one or more Hydrogen's are replaced by other atoms.

For example

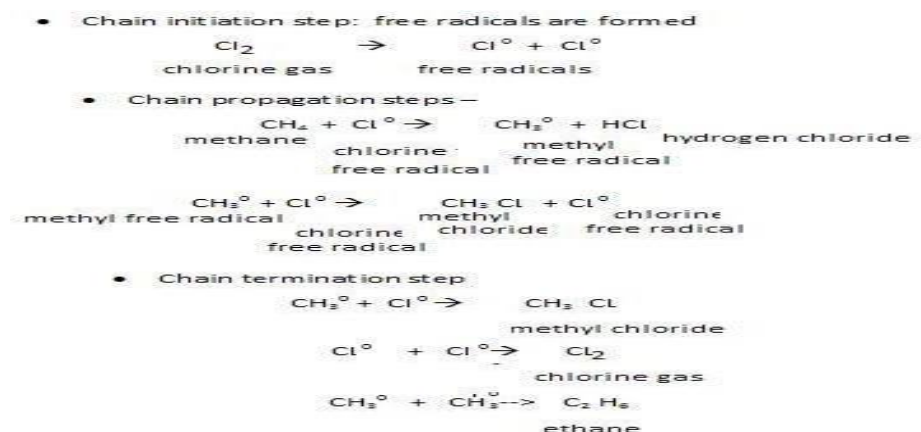
- **Halogenations**– In it the Substitution By halogen X (Cl, F, Br, I) occur
Order of reactivity: $F > Cl > Br > I$

Out of them chlorine shows this reaction to an efficient level.

Chlorination of methane: This reaction occurs in normal light



It involves Free radical mechanism as shown below:



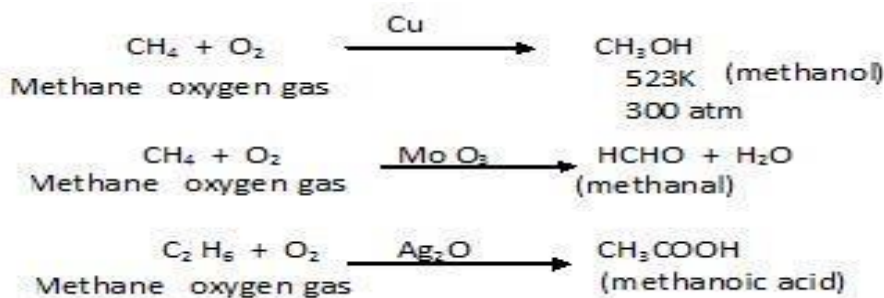
- **2nd Oxidation Reaction:** it is the Reaction with oxygen
This reaction may be may be uncontrolled or controlled oxidation. If it is combustion reaction than the products are always CO₂, H₂O, heat and light.
- If it is Complete combustion : then also the products are CO₂, H₂O, heat and light

$$\text{CH}_4 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Heat}$$
- Incomplete combustion or oxidation :



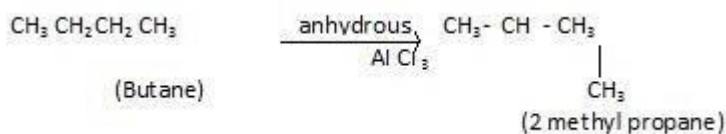
This CO makes the surface black and called Carbon black or soot.

- **Controlled oxidation** - occur in presence of catalyst and on the basis of catalyst the products are formed. Like in presence of Copper alcohol is formed, in presence of molybdenum oxide – aldehyde is formed and in presence of silver oxide – carboxylic acid is formed.

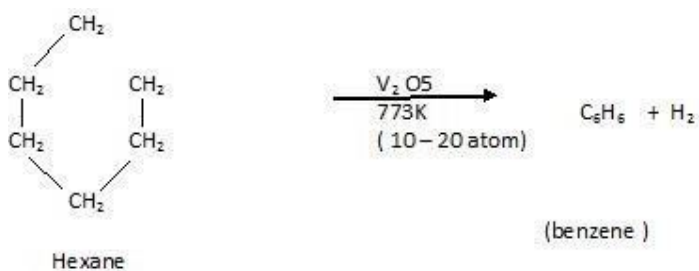


○ 3rd Isomerisation

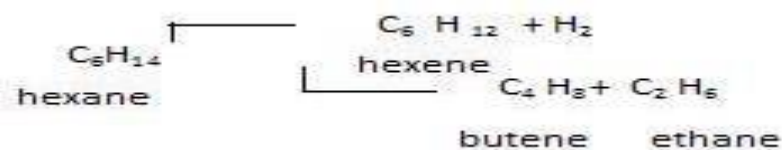
If we subject alkanes to (anhydrous) Aluminium chloride then isomer of alkane is formed.



- **4th Aromatization Reaction:** In this an Aromatic compounds are found are called (Cyclization)



- **5th Thermal decomposition or pyrolysis:** In this breakdown of bigger alkane into lower alkanes occur and is called as thermal cracking.



Conformational Isomerism

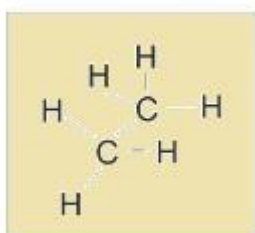
It arises due to free rotation around C – C bond. We can define it as:

Definition: The different arrangement of atoms in space which can be obtained due to rotation about

C – C bond are called Conformation. It is not totally free but there is energy barrier of 120kJ/mol that has to be overcome. This is called torsion strain that exist between two forms.

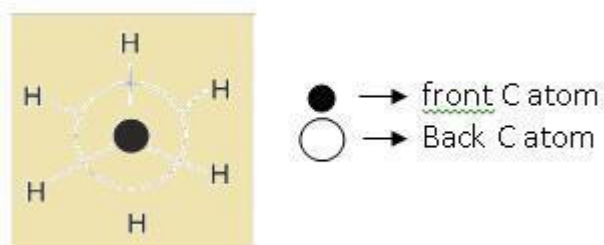
Conformations of ethane: There are two projections.

- Sawhorse projection: In this H and C are bonded to each other and is represented in form of lines.



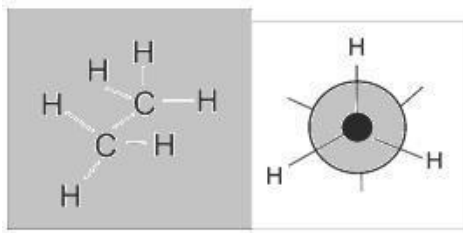
(Sawhorse)

- Newman projection: In this carbon is represented by drawing circles and hydrogen are represented by drawing lines as shown.

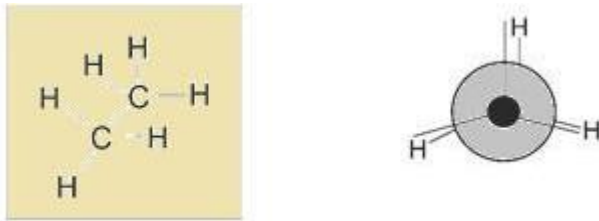


The two form of new man projection are: **eclipsed and staggered**

- Staggered: In this hydrogen are far apart from each other

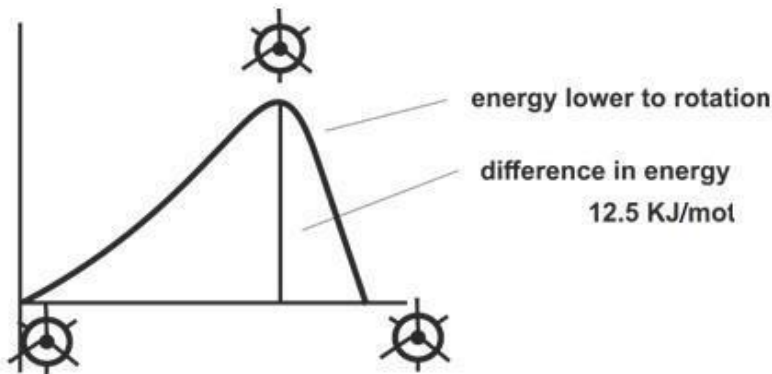


- Eclipsed: this hydrogen are just at back of each other



When staggered is rotated by 60° we get eclipsed form .In this: 60° -torsional angle .Torsional angle is angle by which one form is rotated to get the other form.

Torsional strain: It is the repulsive force that acts and give differnt stability of different forms .



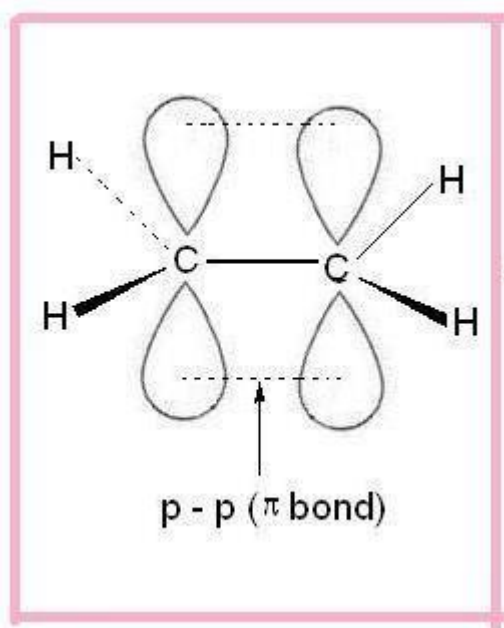
The difference in their energy is given above and this is easily overcome and they keep inter converting.

Alkenes

They are the hydrocarbons with $C = C$ (double bond) with one σ bond and other π bond.

- Their General formula $C_n H_{2n}$
- They are oil like - called olefins.
- They are reactive due to π bond and common reaction they undergo in **addition Reaction**.

- The lowest member of alkenes is ethene (C₂H₄).
- The structure of alkene is:



ISOMERISM: There are two types of isomerism.

- Structural isomerism
- Stereoisomerism

Stereoisomerism

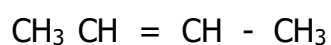
Geometrical Isomerism - The spatial arrangement of atoms is going to be different in it.

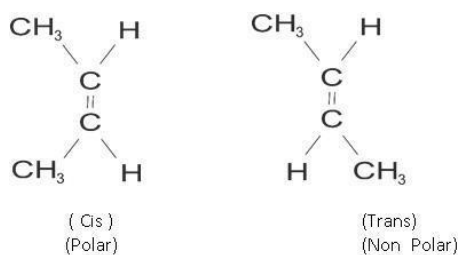
It is caused due to restricted rotation about C = C bond .

Condition Required to show this geometrical isomerism :

1. Presence of double
2. Both atom attached to C should be different.

Example: but-2 ene





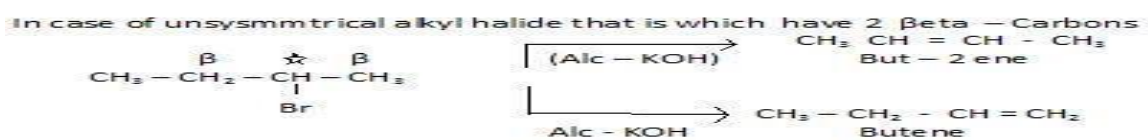
The cis and trans have some chemical properties but different physical properties as arrangement of atoms is different. Like cis is more polar than trans.

Please note

- Because of different polarities the Cis have higher values of boiling point than Trans.
- Trans will have higher melting point whereas Cis will have lower melting point.
- Trans has symmetrical structure and will fit better in crystal lattice.
- Stability of trans isomer is more than Cis as Cis itself suffer steric hindrance .

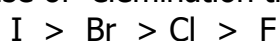
Preparation of Alkenes

1. **From alkyl halides: (RX)** by the process of dehydrohalogenation, it is also called Beta elimination .



In this case it has two beta carbons so, we make use of special rule that is Saytzeff's rule.

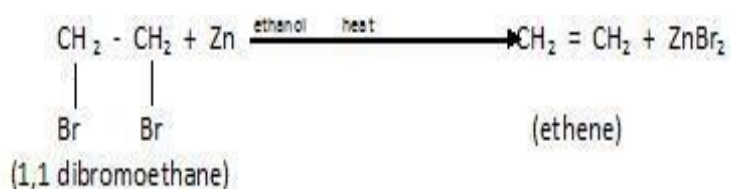
Saytzeff's rule: In case of reacting alcoholic KOH with unsymmetrical halide , that alkene is preferred which is maximum alkylated. So , in above example But - 2 - ene is preferred . If we see ease of elimination the order is :



The better the leaving group more easily the reaction occurs .The reactivity of alkanes towards this reaction is : tertiary > secondary > primary

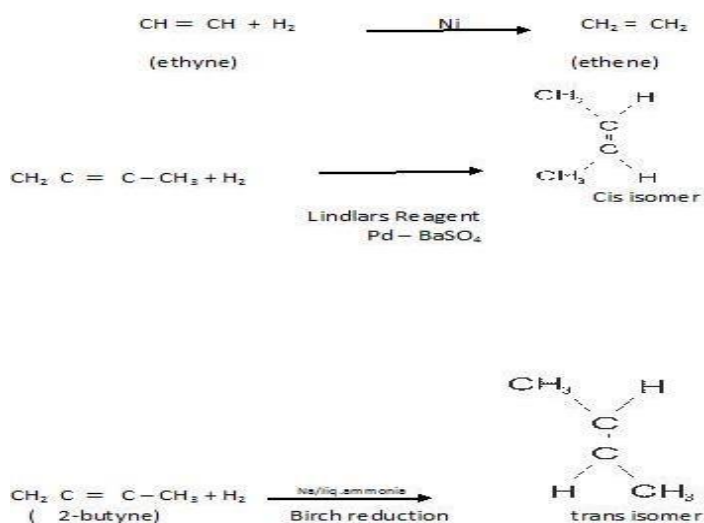
2. From dihalogen derivatives

Let us take an example of Vicinal dihalide that is :



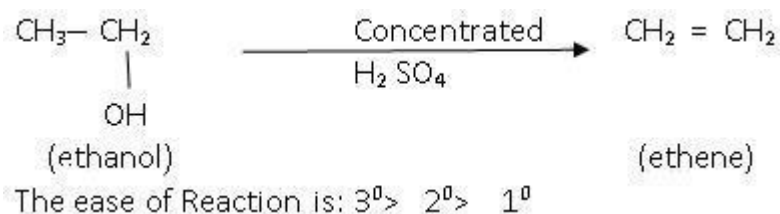
In this renewal of halogen is taking place therefore the process is called dehalogenation .

3. **From alkynes :** by the process hydrogenation. The reaction involved is given below:

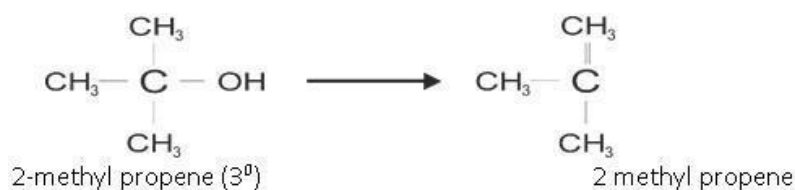


4. From Alcohols :

It is prepared by Dehydration Reaction of alcohols.



The ease of Reaction is: $3^\circ > 2^\circ > 1^\circ$
 Another example is:



Physical Properties Of alkenes

1. **Existence:** Lower members are colourless (Ethene is with sweet smell and other alkenes are odourless).
2. **Melting Point:** - Alkenes have higher melting point than alkanes because π e⁻ cloud will be more polarized. If we compare melting point of Cis and Trans then, Trans possess high melting point than Cis because Trans have symmetrical structure so, they fit better in lattice.
3. **Boiling Point:** They show regular graduation.
 - With increase in Carbon atoms, Vander wall force increases so, boiling point also increases.
 - Boiling point decreases with increase in branching. As surface area reduces vander wall force decreases, therefore boiling point also decrease.
 - Out of cis and trans, trans has low boiling point and cis possess high boiling point due to polarity.
5. **Solubility:** - Alkenes have greater solubility than alkanes.
 - Solubility increase with increase in C atoms.
 - Lower members are sparingly soluble but soluble in organic solvents like Benzene, ether, Carbon tetra chloride etc.

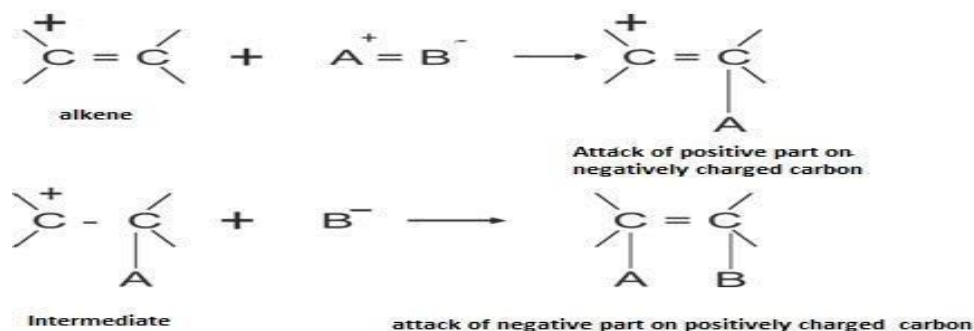
Chemical properties of alkenes

It shows mainly two types of reactions:

- Electrophilic addition reaction :
- Oxidation reaction

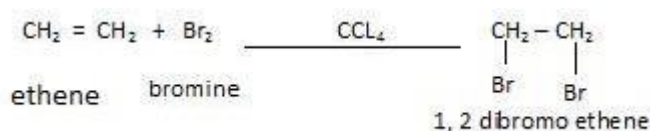
1. Electrophilic addition reactions

The basic mechanism involved in it is shown below:

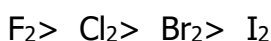


The more the ease of reaction, more stable is the intermediates i.e. carbocation.

o Addition of halogen

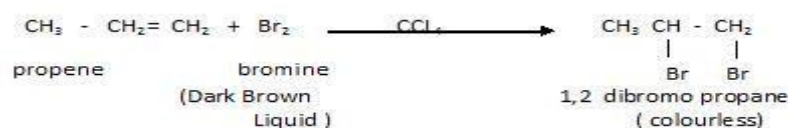


Order of reactivity of halogens towards this reaction is:



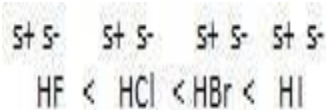
- o In case of addition of fluorine, the reaction occurs so violently that it leads to explosion, as it is an exothermic reaction.
- o In case of addition of iodine, the reaction take place under special conditions as the reaction is reversible.
- o This reaction is also considered as a test for un-saturation (alkenes and alkynes): bromine water test. This test is given below.

(Test for un-saturation)

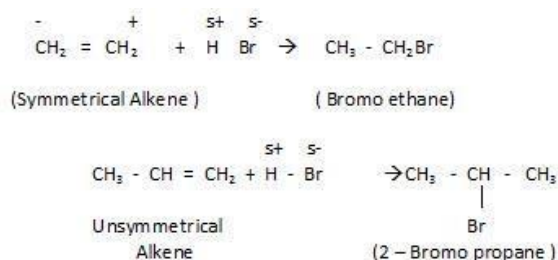


o Addition of halogen acids (HX)

The order of reactivity towards this reaction is:

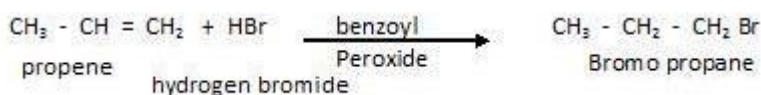


- The HI has weak bond because of incomparable size, that is the reason its reactivity is high towards this reaction.

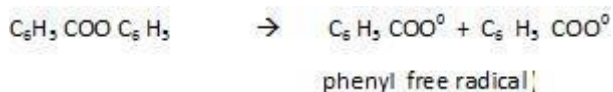


In case of unsymmetrical alkenes, Markovnikov's rule is followed.

- **Markovnikov's rule:** According to this, addition of any group in unsymmetrical alkene, the negative part of the reagent will attach itself to the Carbon atom carrying lesser number of Hydrogen and Hydrogen goes to the Carbon with maximum number of hydrogen.
- But if Reaction occurs in presence of peroxide like benzoyl peroxide, The rule that is followed is Anti-Markovnikov's Rule or Kharasch effect (and this valid only for HBr) .
- **Anti Markonikovs Rule :** According to it the negative part attaches to the carbon atom with maximum number of hydrogen and positive part attaches to the carbon atom with lesser hydrogen .

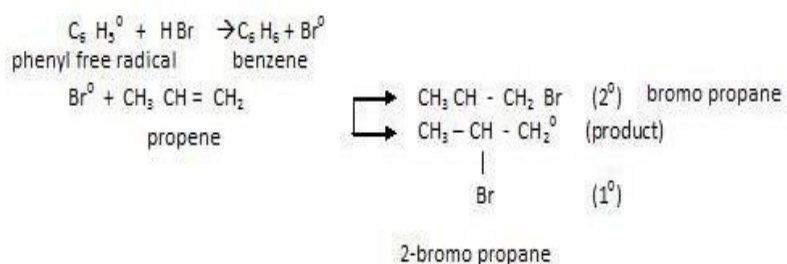


- Mechanism involved is free radical mechanism as shown below :
- Chain initiation step:



This radical is unstable therefore it decomposes to form C_6H_5^* (Phenyl free radical) and CO_2 .

- Chain Propagation step:

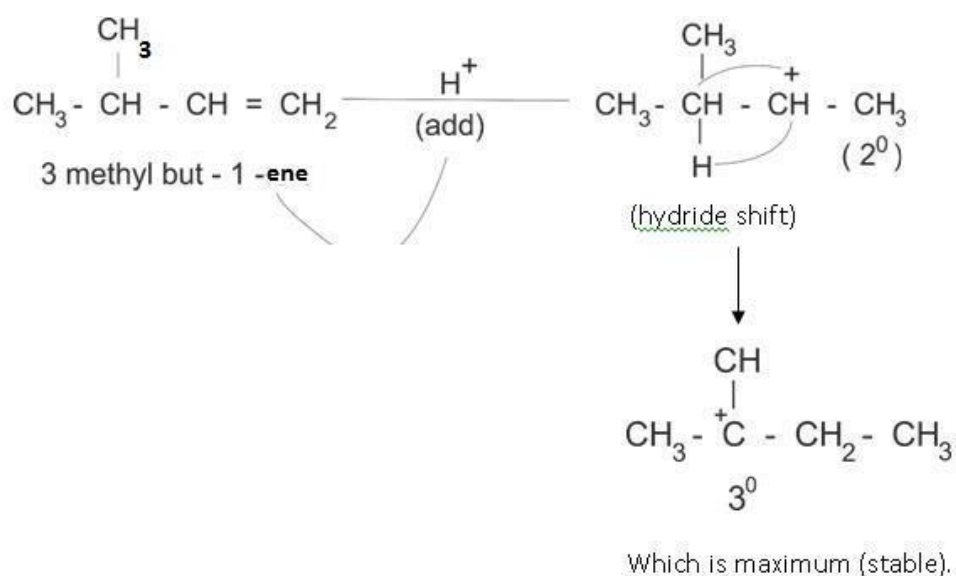


We know 2° free radical more stable therefore, the preferred product is going to be that which helps in yielding 2° free radical.

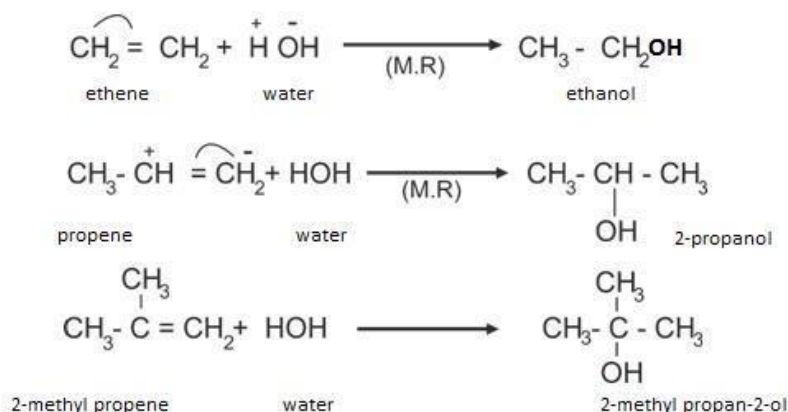
Please note:

- Markonikov's Rule is for all attacking agents.
- Anti-Markonikov's Rule is only for HBr (due to thermodynamic reasons).

Rearrangement of Carbocation – Hydride shift



(d) Addition of H₂O



2. Oxidation Reactions

The oxidation can occur in different ways:

Combustion

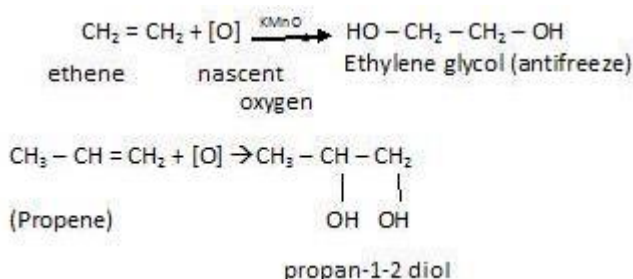
Complete oxidation: In this CO_2 , H_2O , heat and light is produced

Incomplete combustion: In this CO , H_2O and heat and light are given out.

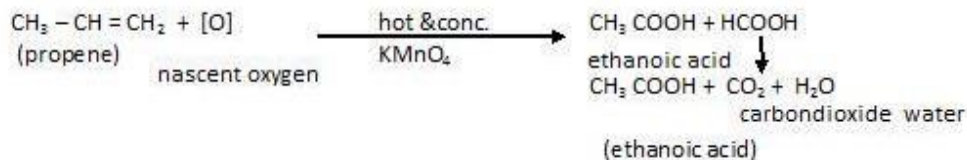
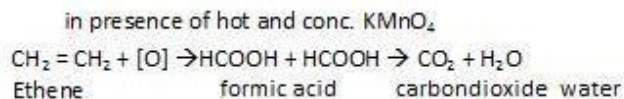
Controlled oxidation: It occurs in different ways:

- Oxidation with (cold & dilute) KMnO_4 : Whenever oxidation of alkenes occurs in presence of strong oxidising agent like potassium permanganate. In it hydroxylation occurs and as a result alcohols (diols) are formed.

For example:

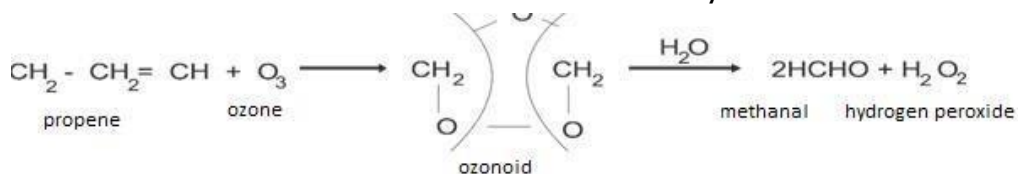


- Oxidation with hot and concentrated KMnO_4 : When alkenes react with hot and concentrated potassium permanganate, the cleavage occur across double bond :
- For example:



Please note: If there is no Hydrogen atom with carbon connected by double bond than ketone is formed and If there is H with carbon, then carboxylic acid is formed.

- Oxidation with ozone: It is also called as ozono- lyses.



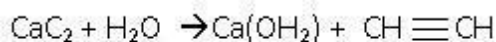
Alkynes

In this triple bond is present between carbon atoms (C C bond).The hybridisation is sp and the general formula involved is $\text{C}_n\text{H}_{2n-2}$.

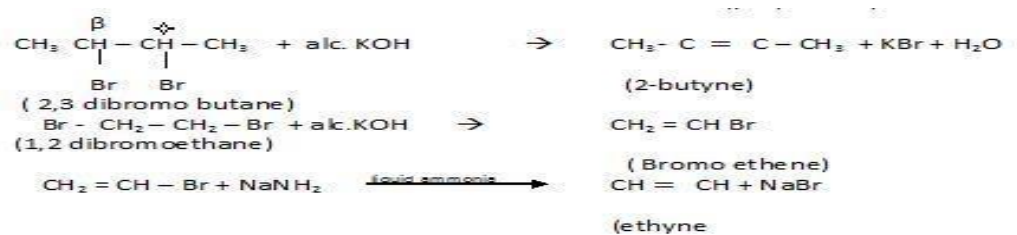
- The lowest member of alkynes is: simplest compound that is $\text{CH} \equiv \text{CH}$ (ethyne).
- The common name of it is acetylene.
- It has high Bond dissociation energy, as there is triple bond present therefore the energy is high of the order 823 KJ/mol.
- Due to this reason the acetylene is mixed with O_2 and the flame is used for welding purpose.

Preparation of Alkynes

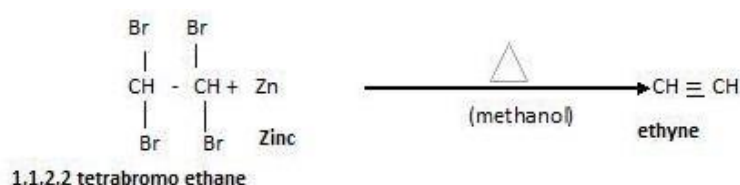
1. Laboratory preparation –It is prepared in by action of H_2O on Calcium carbide i.e. CaC_2



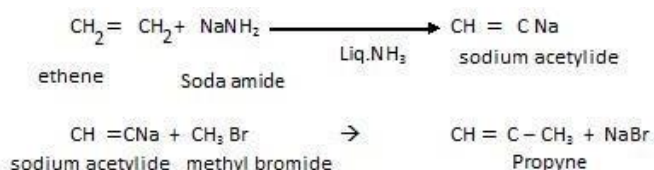
2. By dehydrodogenation of vicinal dihalide



3By action of Zinc on Tetra halogen derivatives



3. **We can prepare higher alkyne from acetylene:** This is also called up-gradation reaction.



Physical properties of alkynes

1. **Existence:** Acetylene, propyne, butyne are gases and other with carbon 4 to 12 are liquids, more than 12 are solids.

C₄ - C₁₂ liquids

> C₁₂ solids.

- They all have no smell, except garlic like smell of acetylene.

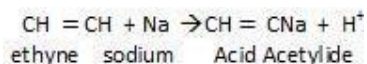
2. **Solubility:** They are weakly polar in nature and not soluble in H₂O but soluble in organic solvents.

3. **Melting point and boiling point:** Because of triple bond they have higher melting point and boiling point.

- With increase in number of carbon atoms the boiling point increases.
- With increase in branching the boiling point decreases.

Chemical properties of alkynes

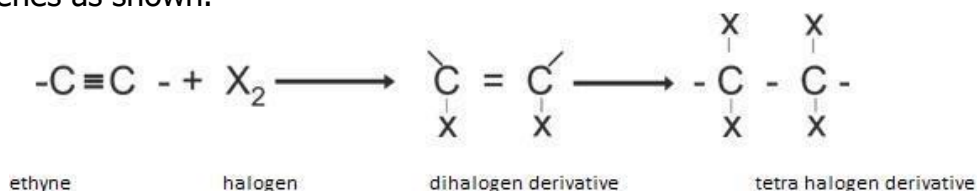
1. **Acidic Character** – This is shown by replacement of one of the hydrogen atom by metal atom.



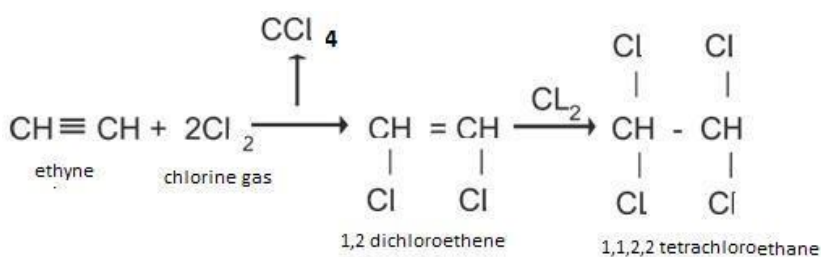
Alkynes are acidic because of sp hybridisation of Carbon atom. The "s" character in case of alkynes is 50%. Due to more "s" character, electrons in sp hybrid orbitals are held more tightly by nucleus and are quite electronegative. As a result, the H – C bond get more displaced towards carbon atom and proton is easily released. Due to this, the bond easily breaks and the Hydrogen is easily released.

Application: By this we can upgrade number of carbon atoms in alkynes.

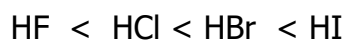
2. **Addition reaction:** The basic general reaction involved in addition is similar to that of alkenes as shown.



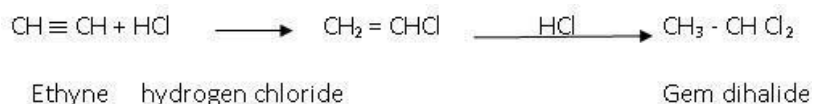
- o Addition of halogens

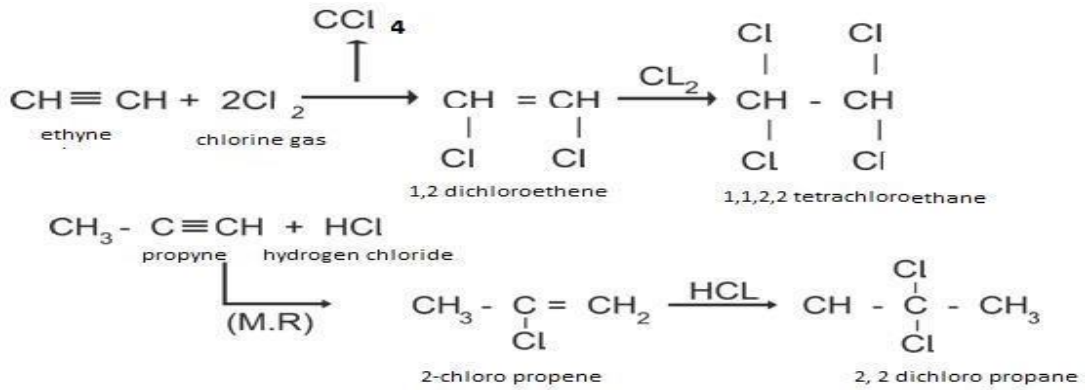


- o Addition of halogen acids (hydro halogenations Reaction) : The order of reactivity of this reaction is:



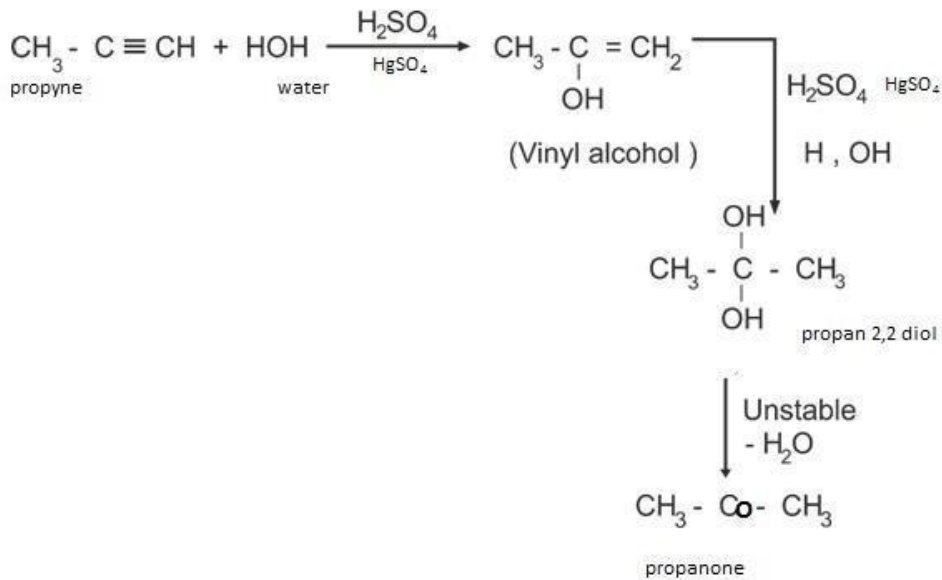
The reaction involved is:



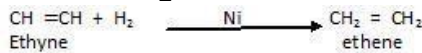


Anti-markoniov's rule is followed in case of addition of HBr:

○ **Addition of H₂O (hydration Reaction)**

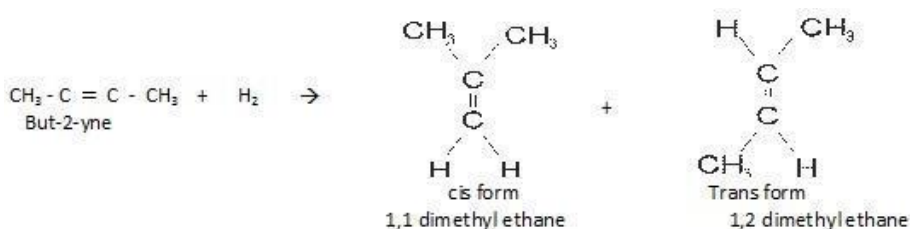


○ **Addition of H₂**



Please note:

When we use lindlar catalyst that is Pd/BaSO₄ we get Cis form and whenever we use catalyst that is Na in liquid NH₃, then it is called birch reduction and we get trans form as shown below :

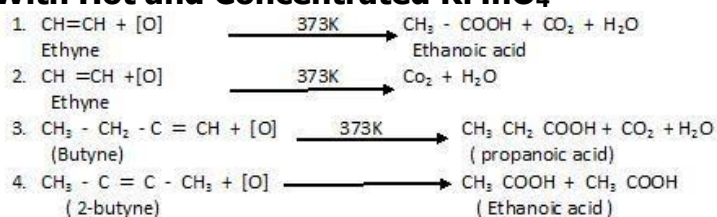


2. Oxidation of alkynes

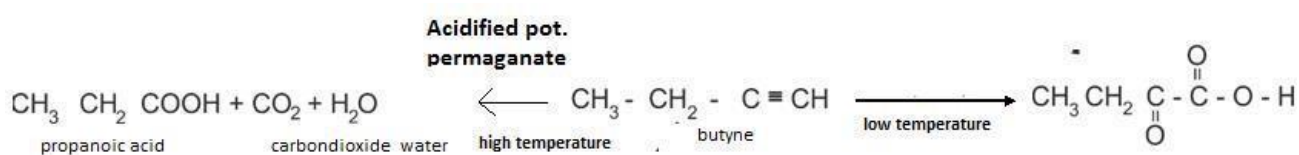
The oxidation is carried out with:

- Cold and dilute alkaline potassium permanganate
- Hot and concentrated potassium permanganate
- With ozone

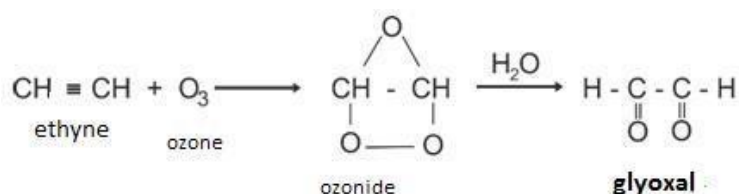
With Hot and Concentrated KMnO_4



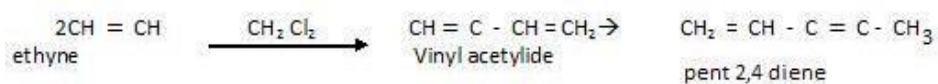
- Please note that if we carryout oxidation of butyne with acidic potassium permanganate under low and high temperature we get different products as shown below:



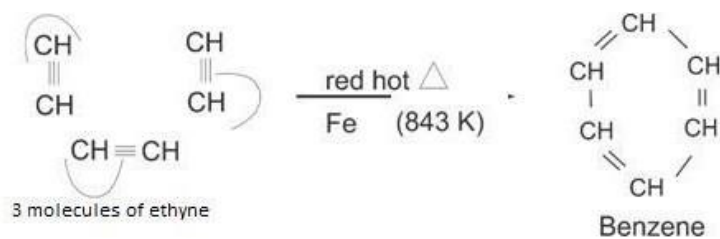
With Ozone



3. Polymerisation



o Cyclic Polymerisation



Note-The above content has been absolutely prepared from home