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# Hydrocarbon1 ( Alkane, Alkene, Alkyne ) Handwritten Notes



( NEET Organic  
Chemistry )



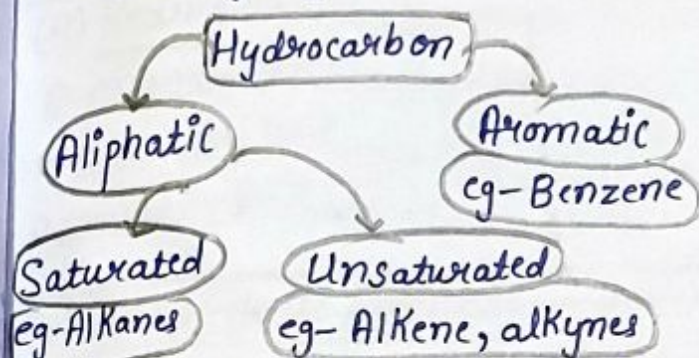
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# HYDROCARBONS..

## Introduction..

- Hydrocarbons are compounds of carbon and Hydrogen.

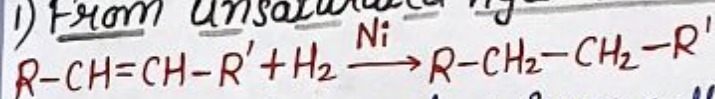


## Alkanes...

- General formula =  $C_n H_{2n+2}$ .
- All H-C-H bond angles in alkanes are  $109.5^\circ$ .
- Isomerism
- Alkanes show chain isomerism.
- Methane, ethane and propane do not exhibit structural isomerism.
- Isomerism is exhibited by alkanes which contain minimum 4 carbons.
- examples →  $C_4 H_{10}$  butane has two isomers
- a) n-butane =  $CH_3-CH_2-CH_2-CH_3$
- b) Isobutane =  $CH_3-\underset{\substack{| \\ CH_3}}{CH}-CH_3$

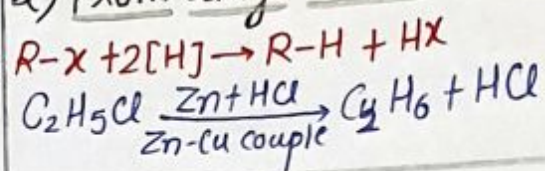
## # Preparations of Alkanes.

### i) From unsaturated hydrocarbons.



- Other catalyst used platinum, palladium, nickel or  $PtO_2$  form alkanes.
- Platinum and palladium can catalyse the reaction at room temperature but Nickel as a catalyst requires higher temperature and pressure.

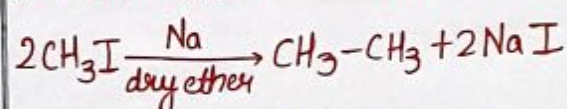
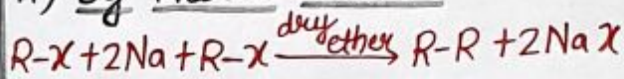
### 2) From alkyl halides Reduction



### Key note

- $LiAlH_4$  can reduce only  $1^\circ$  and  $2^\circ$  alkyl halides. But  $3^\circ R-X$  gives elimination product as the major product.
- $NaBH_4$  reduces  $2^\circ$  and  $3^\circ R-X$  only.
- TPH (Triphenyl tin hydride),  $Ph_3SnH$  can reduce  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  alkyl halides.

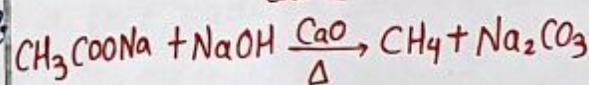
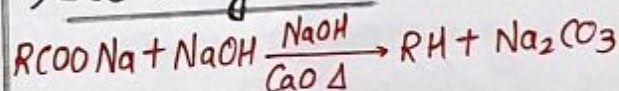
### ii) By Wurtz Reaction



- This method is used in preparation of alkanes containing even no. of carbons.
- Methane cannot be prepared by this method.
- Tertiary alkyl halides cannot be converted into alkanes by this method becoz they convert into alkenes due to elimination.

### 3) From Carboxylic Acids.

#### i) Decarboxylation



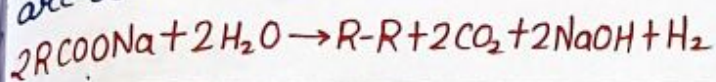
Alkane obtained by this method has one carbon less than the parent acid.

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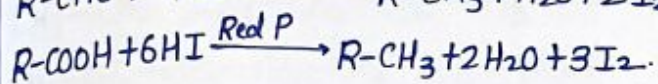
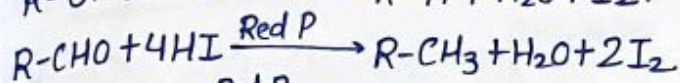
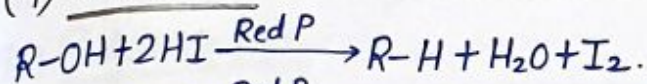


## ii) Kolbe's Electrolytic Method.

- Alkanes with even number of carbon are obtained at anode.

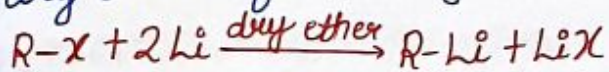


## (4) Reduction

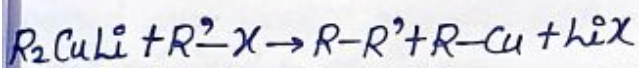
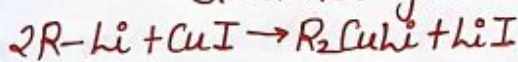


## (5) Corey-House Synthesis

- Alkyl halides reacts with lithium in dry ether to form alkyl lithium.



This alkyl lithium reacts with CuI to give dialkyl lithium cuprate known as Gilman reagent.



The alkyl group of dialkyl lithium cuprate may be methyl, primary, secondary or tertiary.

## Properties

### # Physical properties

- Molecules possess only weak Vander waals forces of attraction and as molecular weight increases forces of attraction increases.

At 298 K →

- $C_1 - C_4$  are gases
- $C_5 - C_{17}$  are liquids
- Above  $C_{17}$  are solids.

### # Boiling point →

- In alkane, boiling point increases with increase in the molecular weight due to increase in the Van der waals forces.
- In chain isomers, the isomer with more branches has low boiling point.

example - Among isomers of pentane, order of boiling point is:

Pentane > isopentane > neopentane

### # Melting Point →

- Alkanes with even number of 'C' atoms have more melting points than their preceding and succeeding odd 'C' alkanes because alkanes with even number of carbon atoms pack closely which permits greater intermolecular attractions.

### # Solubility →

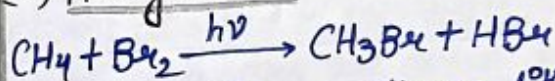
- Alkanes are lighter than water. These are insoluble in water and are hydrophobic in nature.
- But these are soluble in organic solvents and their solubility decreases with increase in their molecular weight.

### # Chemical properties

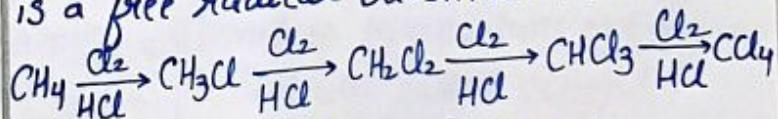
- Alkanes are extremely stable and inert. These are inactive towards acids, bases, oxidising and reducing agents.
- Under suitable conditions, alkanes undergo substitution reactions.

#### 1.) Substitution Reactions →

##### (i) Halogenation.

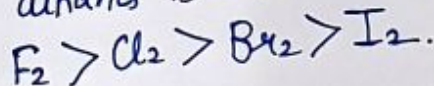


- The reaction of alkanes like methane with halogens in presence of sunlight is a free radical substitution reaction.



during halogenation, mixture of halogen derivatives are formed.

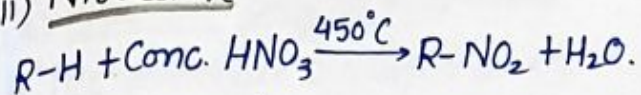
- Order of reactivity of halogen with alkanes is →



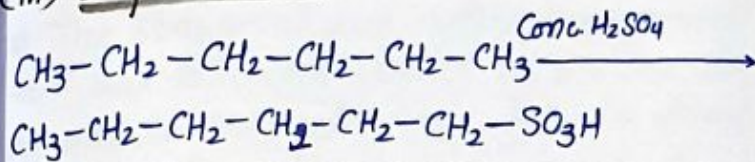


- Order of reactivity of hydrogen in alkane with halogen is:  
 $3^\circ\text{H} > 2^\circ\text{H} > 1^\circ\text{H}$

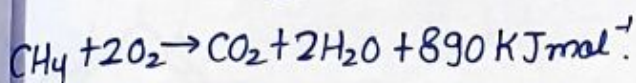
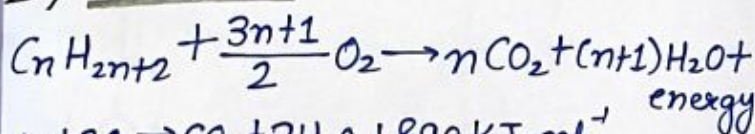
## (ii) Nitration



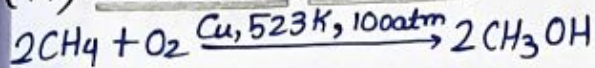
## (iii) Sulphonation



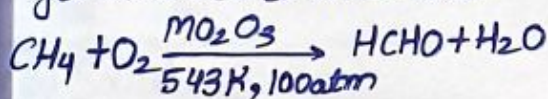
## 2.) Combustion



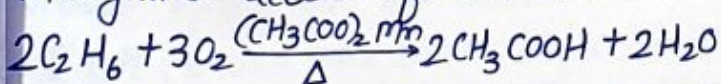
## (iv) Controlled Oxidation



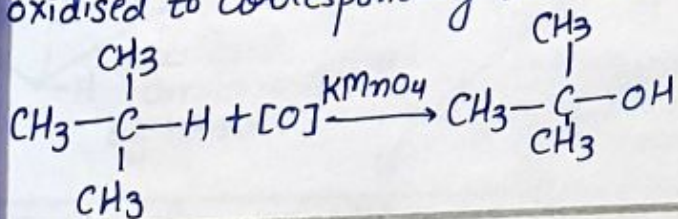
- A mix. of methane and oxygen when passed over heated molybdenum oxide, get oxidized to methanal.



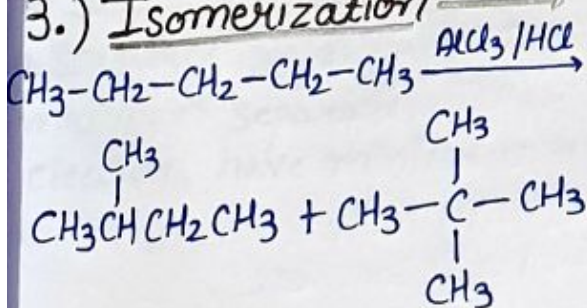
- Ethane when oxidised in presence of manganese acetate forms acetic acid.



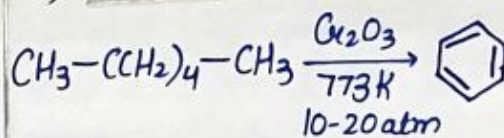
- Normal alkanes are resistant to the attack of oxidising agents (eg- $\text{KMnO}_4$ ). But alkanes of the type  $\text{R}_3\text{-CH}$  are, However, attacked by  $\text{KMnO}_4$  and are oxidised to corresponding alcohols.



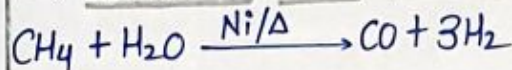
## 3.) Isomerization



## 4.) Aromatisation or Catalytic Reforming



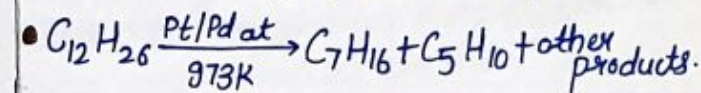
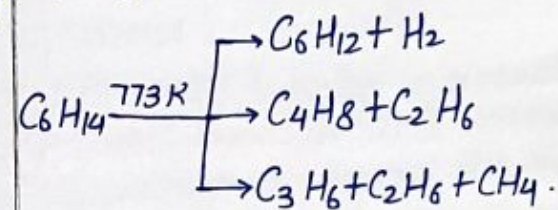
## 5.) Reaction with Steam



## 6.) Pyrolysis

- Decomposition of higher alkanes into smaller fragments on strong heating in the absence of air is called pyrolysis or cracking.

Pyrolysis is a free radical reaction.



- Lower hydrocarbon exist in gaseous state while higher hydrocarbon exist in liquid and solid state.

## # Conformational Isomers

- The rotation about carbon-carbon single bond is not completely free.

### :- Conformations of Ethane are.

- The conformations in which hydrogen atoms attached to two carbons are far apart each other are called **staggered conformation**.

- The conformations in which hydrogen atoms attached to two carbons are as close as possible are called **eclipsed conformation**.

- In all conformations, bond angles and Bond length remain the same.



°- Rotation about C-C bond in ethane is possible because of cylindrical symmetry of sigma bond between C-C bond.

### (a) Newman projections →

- The molecule is viewed at the C-C bond head on.
- The staggered and eclipsed conformations are inter convertible by the rotation of one carbon with respect to the other around the  $\sigma$  bond that connects them.

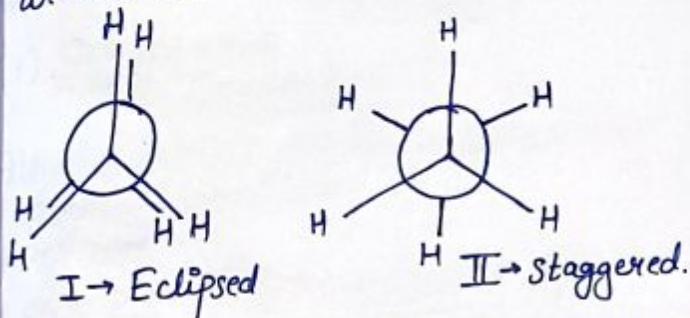
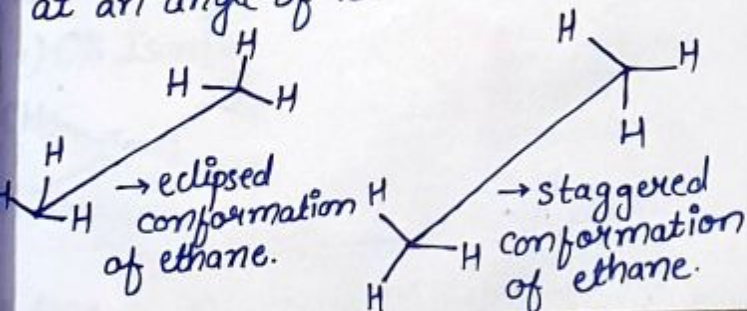


fig - Newman's projections of Ethane.

Eclipsed form (I) dihedral angle =  $0^\circ$   
Staggered form (II) dihedral angle =  $180^\circ$

### (b) Sawhorse projections →

- In this projection, the molecule is viewed along the molecular axis.
- Each carbon has three lines attached to it which indicate the groups attached to it and these three lines are inclined at an angle of  $120^\circ$ .



### # Relative stability of Conformations

- Staggered conformation bonds are at maximum separation. Thus, bonded electrons have minimum repulsion.

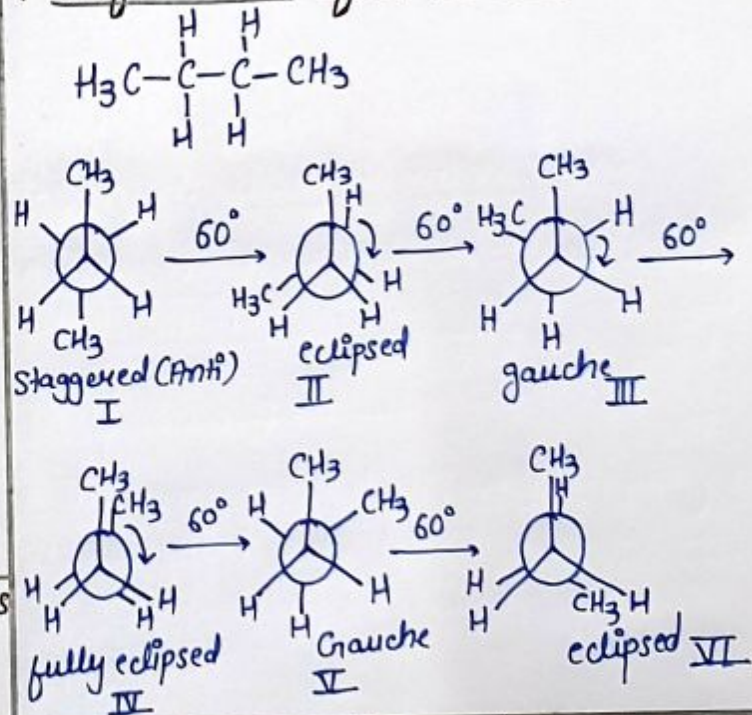
• But in eclipsed conformation, bonds are close and repulsions are maximum thus it is less stable. In eclipsed conformation, the destabilisation is due to torsional strain.

• Of all conformations of ethane, the staggered form has the least torsional strain and the eclipsed form has maximum torsional strain.

### # Relative Stabilities of the Conformations of Ethane →

- Difference in energy content between the eclipsed and staggered form is  $12 \text{ kJ mol}^{-1}$ .
- This small barrier to rotation is called **Torsional Barrier**. This energy is not large enough to prevent the rotation. Thus, the conformers keep on changing from one form to another. The eclipsed conformation is least stable whereas the staggered conformation is more stable.

### # Conformation of n-Butane



### # Relative Stability of the conformation of n-Butane →

Anti > Gauche > eclipsed > fully eclipsed.



# Alkenes...

• General formula =  $C_n H_{2n}$

## # Structure of double bond.

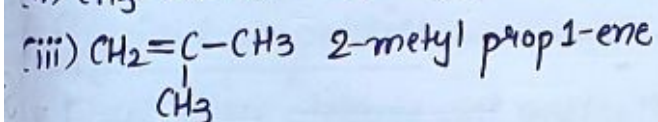
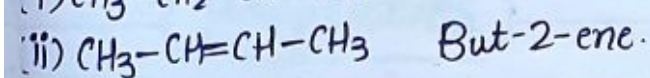
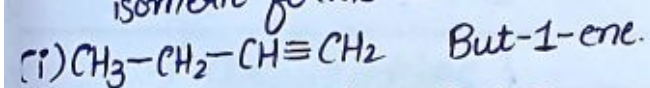
•  $\pi$  bond contains loosely bonded electrons. These electrons attract electrophiles and thus the characteristic reactions of alkenes are electrophilic addition rxn.

## # Isomerism — Alkenes show both structural and stereo isomerism.

### (1) Structural Isomerism

Alkenes exhibit chain, positional and functional isomerism.

• example — Butene exists in three isomeric forms as →

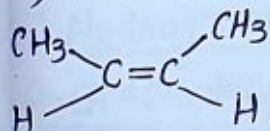


### (2) Geometrical Isomers

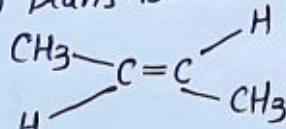
- Alkenes exhibit geometrical isomerism.
- Geometrical isomerism arises due to restricted rotation of  $C=C$ .

Two types of geometrical isomers:—

1) Cis Isomer.



2) Trans-isomer.



‘But-2-ene’

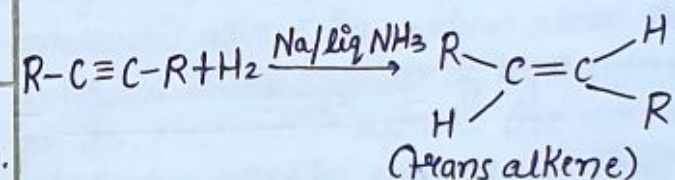
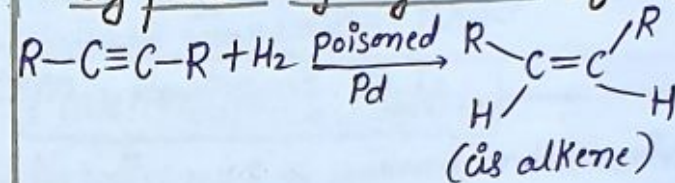
- Due to difference in configuration, cis and trans isomers differ in physical properties like melting points, boiling point, dipole moment etc...

## # Difference between cis and trans-isomers →

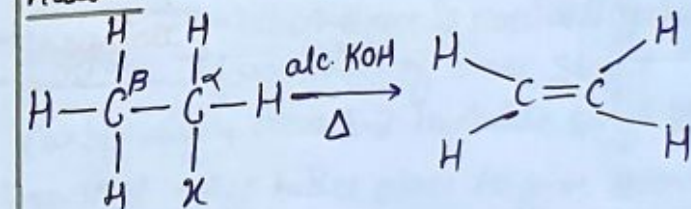
- Melting point of trans isomer is greater than cis-isomer due to symmetrical packing of trans compound.
- Boiling point of cis-isomer is greater than trans-isomer because cis-isomer has higher polarity.
- Cis form of alkene is more polar than trans alkene.
- In solids, trans isomer has higher melting point than cis isomer.
- Trans isomer is more stable than cis-isomer.

## Preparation

### 1.) By partial hydrogenation of alkyne



### 2.) By dehydrohalogenation of alkyl halides



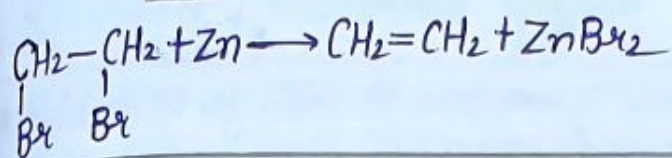
(X = Cl, Br, I)

**Key Note** → Order of ease of dehydrohalogenation of  $R-X$ :  $3^\circ > 2^\circ > 1^\circ$ .

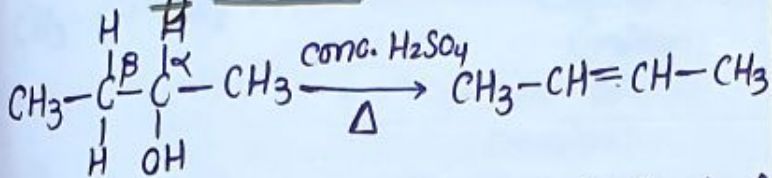
- Reactivity order of  $R-X$ :  $R-I > R-Br > R-Cl$ .
- More stable alkene is formed as major product.



### 3.) By Dehalogenation of vicinal dihalides $\longrightarrow$

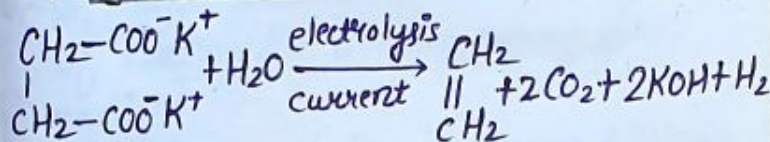


### 4.) By acid catalysed dehydration of alcohols. $\longrightarrow$



- Ease of dehydration of alcohol =  $3^\circ > 2^\circ > 1^\circ$ .
- More stable alkene is formed as major product.

### 5.) By Kolbe's Electrolytic synthesis.



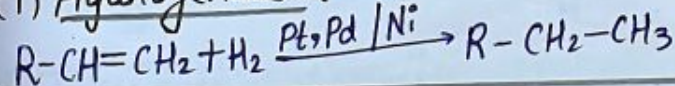
## Properties

### # Physical properties

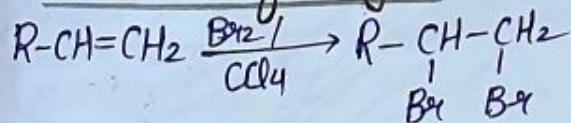
- First three alkenes are gases, next fourteen alkenes are liquid and higher alkenes are solids.
- Melting point and boiling point increases with the increase in molecular weight.

### # Chemical Properties

#### (1) Hydrogenation $\longrightarrow$



#### (2) Addition of Halogens $\longrightarrow$



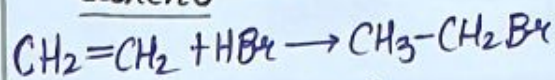
1,2-dibromoethane

Reddish brown orange colour of  $\text{Br}_2$  in  $\text{CCl}_4$  is discharged.

### (3) Addition of hydrogen Halide $\longrightarrow$

- Alkenes add up a molecule of hydrogen halide to form alkyl halide.

#### (i) Addition of $\text{HBr}$ to symmetrical alkene $\longrightarrow$

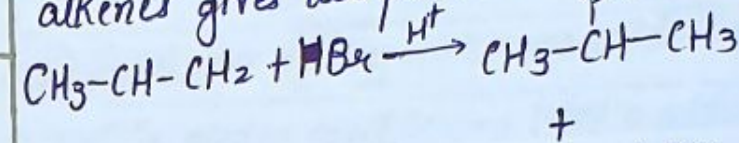


#### • Order of Reactivity $\longrightarrow$

$\text{HI}, \text{HBr}, \text{HCl}, \text{HF}$

#### (ii) Addition of $\text{HBr}$ to unsymmetrical alkenes $\longrightarrow$

Addition of alkenes to unsymmetrical alkenes gives two products.  $\text{Br}$



This electrophile addition reaction follows Markovnikov's rule.

### Markovnikov's Rule...

Negative part of addendum (attacking molecule) attack the carbon atom that contains lesser number of hydrogen atoms or the electrophile attacks the carbon of double bond in such a way that more stable carbocation is formed as intermediate.

#### Key Note

When there is possibility of formation of more stable carbocation, then 1-2 hydride shift or methyl shift takes place to give more stable product.

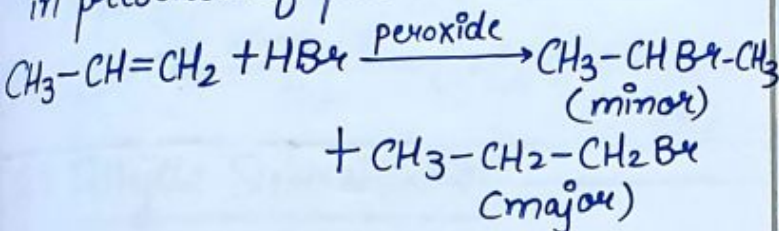


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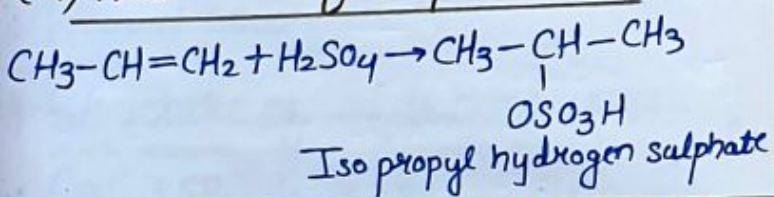
## Anti Markonikov's addition / Kharasch / Peroxide effect

- Addition of  $\text{HBr}$  to unsymmetrical alkene follows anti Markonikov's rule in presence of peroxide.



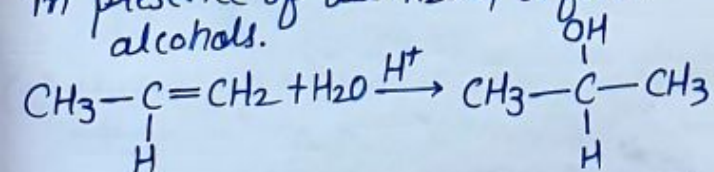
- Secondary free radical is more stable than primary free radical.
- Order of stability of free radicals is:  $3^\circ > 2^\circ > 1^\circ$ .
- So, major product is obtained by attack of electrophile on secondary free radical.
- peroxide effect is not observed in case of addition of  $\text{HF}$ ,  $\text{HCl}$  and  $\text{HI}$ .

### (4) Addition of Sulphuric Acid.



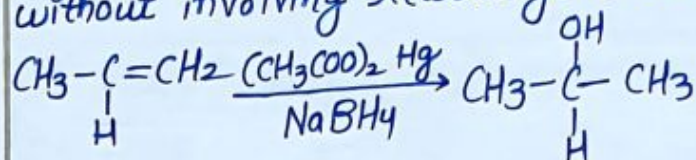
### (5) Addition of water : Hydration.

- (a) By Alkenes add a molecule of water in presence of dil.  $\text{H}_2\text{SO}_4$  to form alcohols.



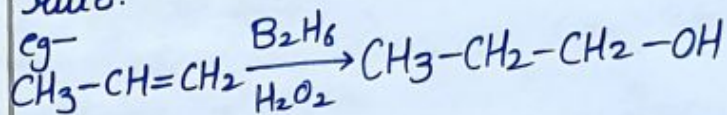
### (b) Oxymercuration-demercuration

- Product is alcohol obtained by adding water according to Markonikov rule without involving rearrangements.



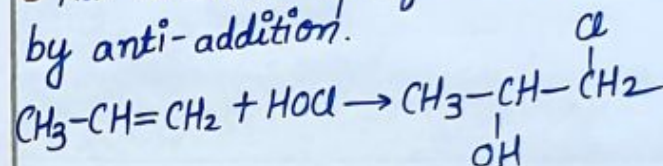
### (c) Hydroboration-Oxidation

- product is alcohol obtained by adding water according to Anti Markonikov rule.



### (6) Addition of hypochlorous acid

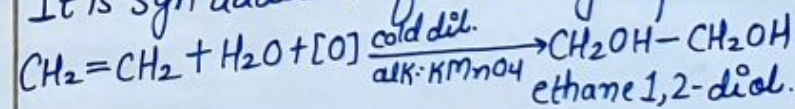
- $\text{R}_x^{\text{n}}$  is stereo specific and  $\text{HOCl}$  is added by anti-addition.



### (7) Oxidation

#### (i) Oxidation by Bayer's reagent.

Bayer's reagent is cold dilute aqueous sol.<sup>n</sup> of  $\text{KMnO}_4$ . Alkenes are oxidised by Bayer's reagent to corresponding diols. It is syn addition of two  $\text{OH}$  groups.



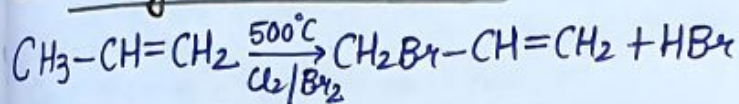
Alkenes decolourise  $\text{KMnO}_4$ . Hence above rx.<sup>n</sup> is used to test unsaturation.



## (ii) Oxidation by Acidic potassium Dichromate. $\rightarrow$

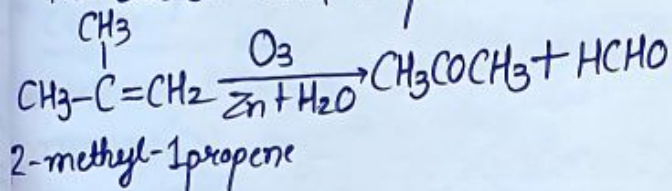
- In this oxidation reaction,  
=CH<sub>2</sub> part get oxidized to CO<sub>2</sub> + H<sub>2</sub>O  
=CHR part get oxidized to RCOOH.  
=CR<sub>2</sub> part get oxidized to RCOR.  
 $(CH_3)_2C=CH_2 \xrightarrow[(O)]{KMnO_4/H^+} (CH_3)_2C=O + CO_2 + H_2O$

## (8) Allylic Substitution



## ... Ozonolysis ...

To detect the position of unsaturation  
i.e. double and triple bond.



## Alkynes

- General formula = C<sub>n</sub>H<sub>2n-2</sub>

## # Structure of Triple Bond

C $\equiv$ C, sp, 180°, 2 $\pi$  and 1 $\sigma$  bond.

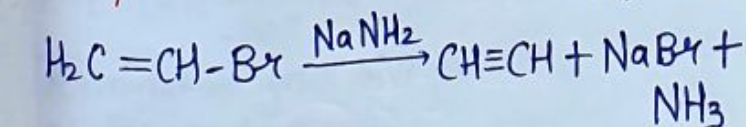
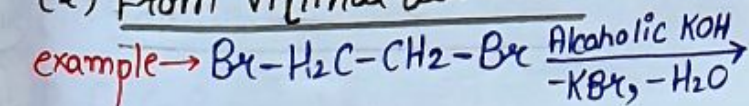
No. of linear atoms in alkynes = No. of sp carbons = 2

## Preparations..

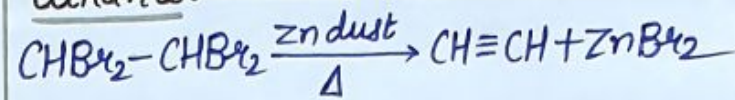
### (1) Hydrolysis: From Calcium Carbide (Industrial method)

- $CaC_2 + H_2O \xrightarrow{\text{hydrolysis}} H-C\equiv C-H + Ca(OH)_2$
- $Mg_2C_3 + 4H_2O \rightarrow CH_3-C\equiv CH + 2Mg(OH)_2$

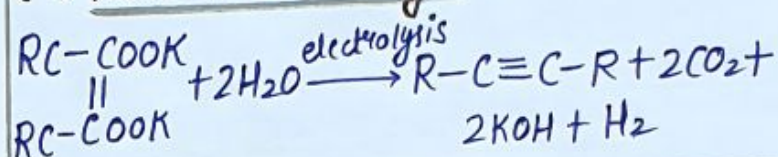
### (2) From Vicinal dihalides.



## (3) Dehalogenation - From tetra halo alkanes.



## (4) Kolbe's Electrolysis.



## properties..

### # physical properties $\rightarrow$

- Melting points and boiling points of alkynes are higher than those of corresponding alkanes and alkenes because alkynes have linear structure due to which molecules are more closely packed.

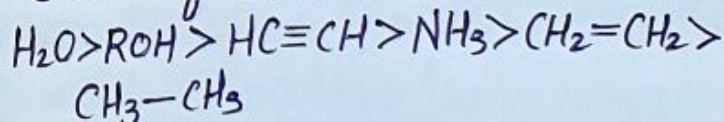
### # Chemical properties $\rightarrow$

- Alkynes are less reactive than alkenes towards electrophilic addition reaction because the electrons in alkynes are more tightly held than alkenes.

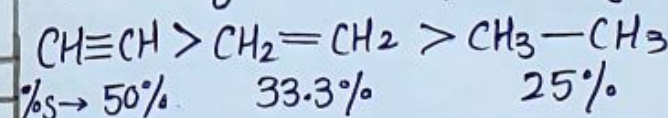
### (i) Acidic nature of alkyne. $\rightarrow$

- Hydrogens attached to sp carbons are acidic in nature. As the % of s-character in hybrid orbitals ~~for~~ increases, acidic nature increases.

- Order of acidic nature:



- Order of acidic nature in hydrocarbon:



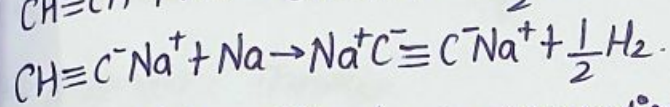
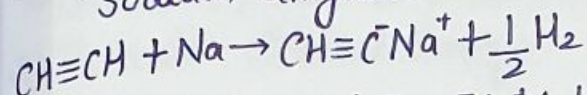
%s  $\rightarrow$  50%      33.3%      25%

# NEET SLAYER

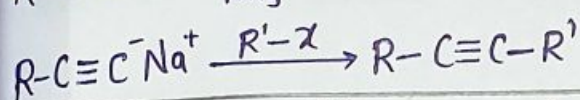
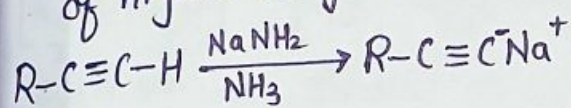


## (2) Reaction with sodium in liquid ammonia.

- Terminal alkynes react with sodium in liquid ammonia or sodamide to form sodium alkynide.

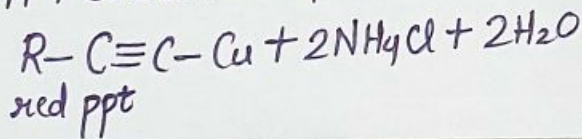


- This rxn is utilized for preparation of higher alkynes.



## (3) Reaction with ammoniacal cuprous chloride

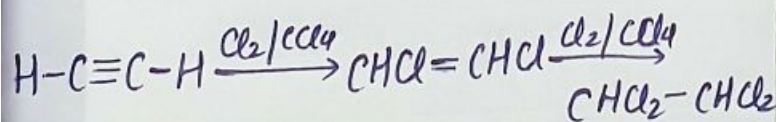
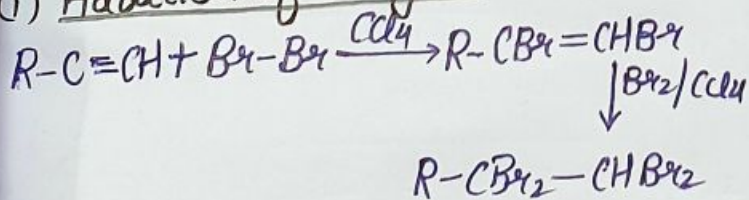
- When acetylene is passed through ammoniacal cuprous chloride soln, a red precipitate of copper acetylide is formed.



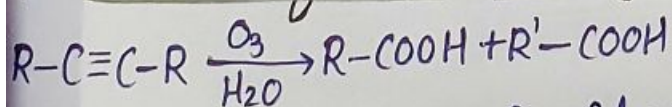
## (4) Addition Reactions

- Alkynes undergo both electrophilic and nucleophilic addition reactions.

### (i) Addition of halogens.



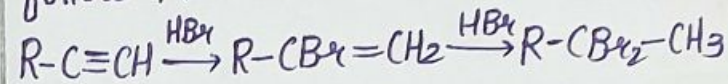
### (ii) Addition of Ozone: Ozonolysis.



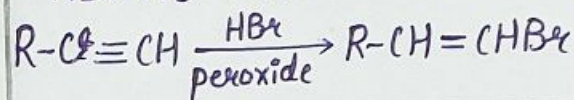
Terminal alkynes give formic acid as one of the product which is further oxidised to  $\text{CO}_2$ .

## (iii) Addition of hydrogen halides

- Both additions are regioselective and follow Markonikov's rule.



- Order of reactivity of  $\text{HX}$  is  $\text{HI} > \text{HBr} > \text{HCl}$ .

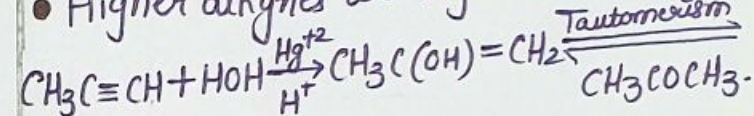


## (iv) Addition of water (Hydration) - Nucleophilic addition reactions.

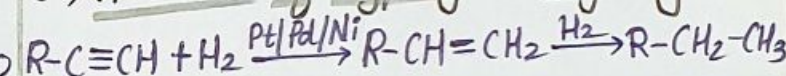
- Alkynes add water in presence of dil  $\text{H}_2\text{SO}_4$  and  $\text{Hg}^{+2}$  ions to form carbonyl compounds.

- Acetylene is hydrated to acetaldehyde.

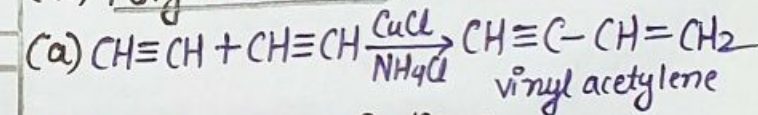
- Higher alkynes are hydrated to ketones.



## (v) Addition of hydrogen: Hydrogenation

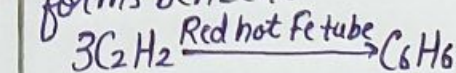


## (vi) Polymerisation



### (b) Cyclic polymerisation: Trimerisation.

- Acetylene when passed through red hot iron tube at 873 K undergoes cyclic polymerisation forms benzene.



## (5) Isomerisation

- Alc. KOH shifts terminal  $\text{C}\equiv\text{C}$  to internal  $\text{C}\equiv\text{C}$  alkyne.

- $\text{NaNH}_2$  shifts internal  $\text{C}\equiv\text{C}$  to terminal  $\text{C}\equiv\text{C}$ .

