Chapter-III

Alkanes, Alkenes & Alkynes

Presented by

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A] Alkanes :

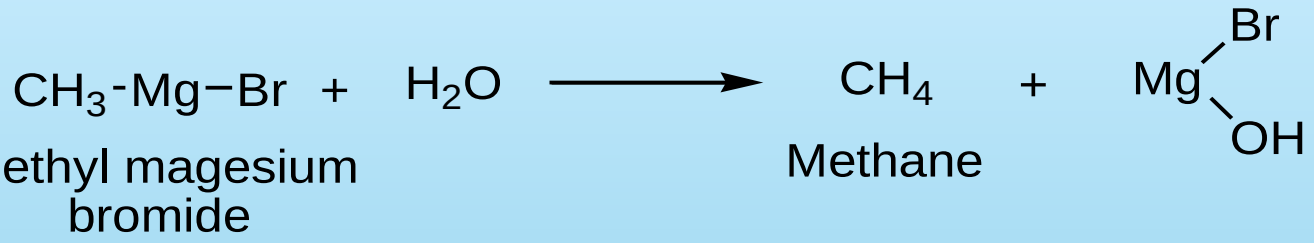
- Saturated hydrocarbons containing carbon-carbon single bonds are called as alkanes.
- The general molecular formula of alkane is C_nH_{2n+2}. They are also called as paraffins.
- Where, n = No. of carbon atoms.
- Ex. CH_4, CH_3-CH_3
- Methane Ethane

Prepration methods of Alkane

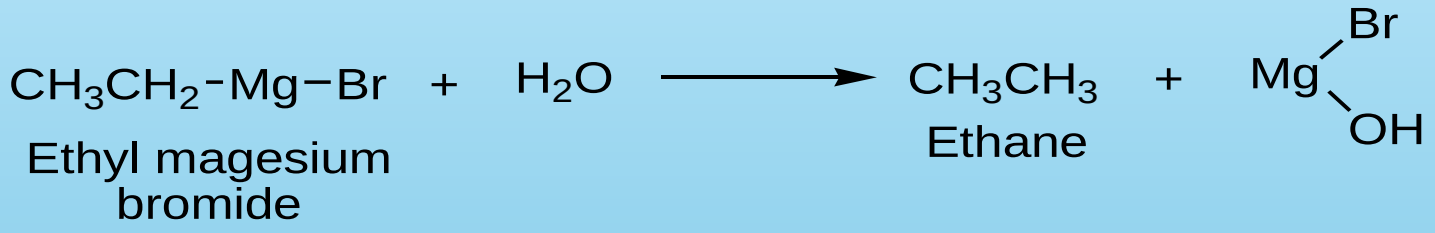
a] Hydrolysis of Grignard's reagent :

- Grignards reagent (Alkyl magnesium halide) on hydrolysis with water gives corresponding alkanes.

Ex. i)

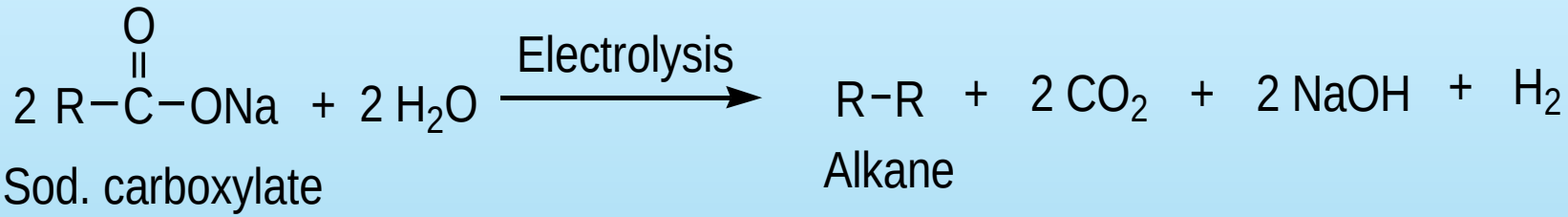


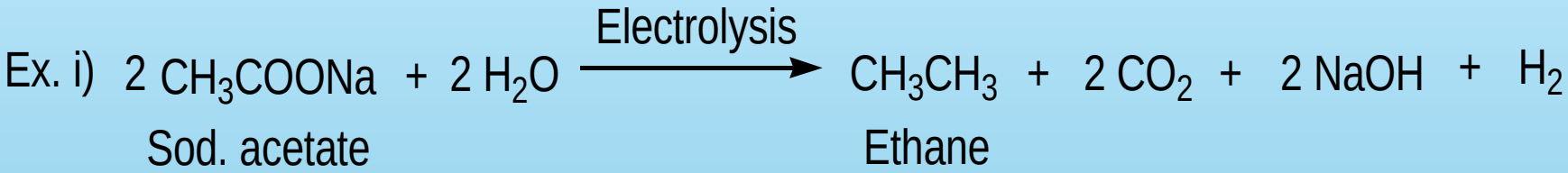
Ex. ii)



b] Kolbes synthesis :

- Electrolysis of concentrated solution of sodium or potassium salt of carboxylic acids gives corresponding alkanes.
- This method is particularly suitable for preparation of symmetrical alkanes.





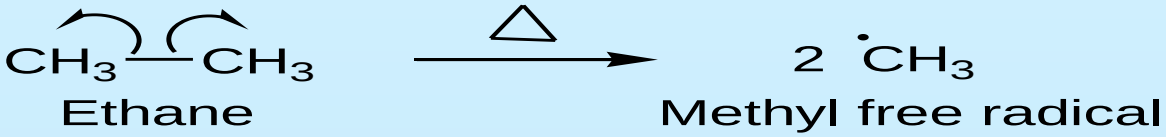
Chemical reactions of Alkanes

a] Pyrrolysis

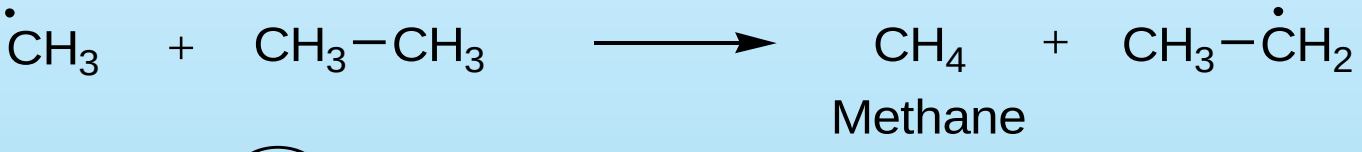
- The decomposition of compound by heat is called pyrolysis.
- When alkanes are heated to high temperature (500-800^{0}C) in absence of air gives mixture of smaller alkanes, alkenes and hydrogen.
- Ex. When ethane is heated at 500^{0}C in absence of air gives mixture of methane, ethylene and hydrogen.

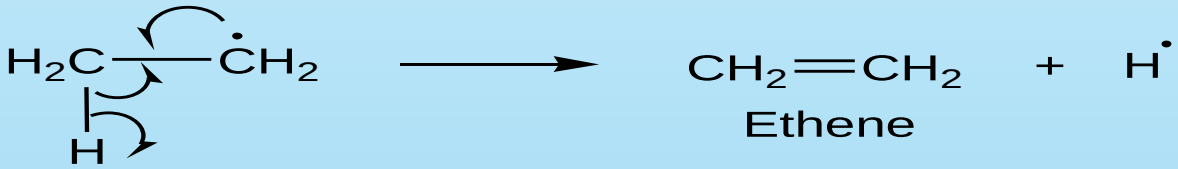
$$\underset{\text{Ethane}}{CH_3—CH_3} \xrightarrow[\text{Absence of air}]{500^0C} \underset{\text{Methane}}{CH_4} + \underset{\text{Ethene}}{CH_2=CH_2} + H_2$$

- Mechanism : Mechanism of this reaction as follows.
- **i) Chain initiation step :**
- Ethane molecule on decompose to give methyl free radical.

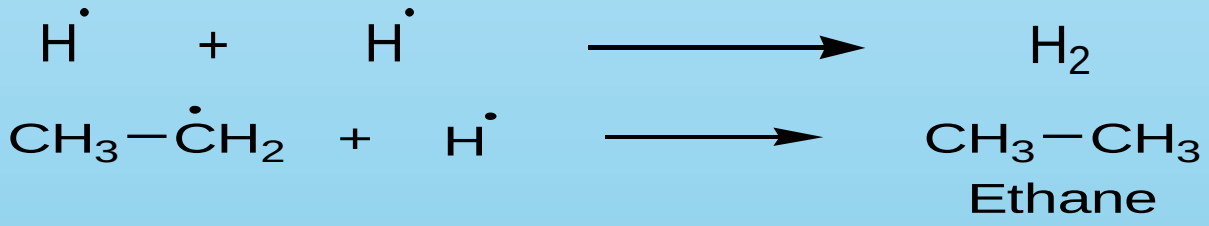


- **ii) Chain propogation step :**
- Methyl free radical attack on ethane to form methane and ethane



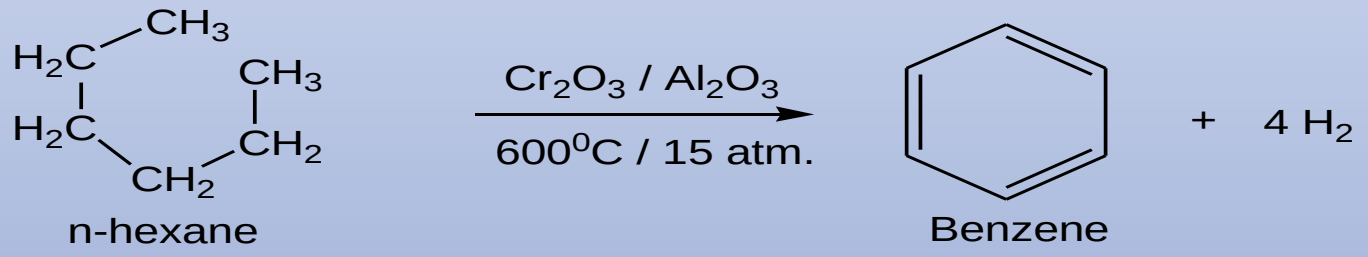


- **iii) Chain termination step :**
- Unreacted free radicals reacted with each other to give H_2 molecule and ethane.



b] Aromatization

- Higher alkanes (6 to 10 carbon atoms) are converted into benzene or its homologous at high temp. in presence of catalyst is known as aromatization.
- Ex. When n-hexane is passed over Cr_2O_3 & Al_2O_3 catalyst at 600^0C, 15 atm. pressure to give benzene.



B) Alkenes

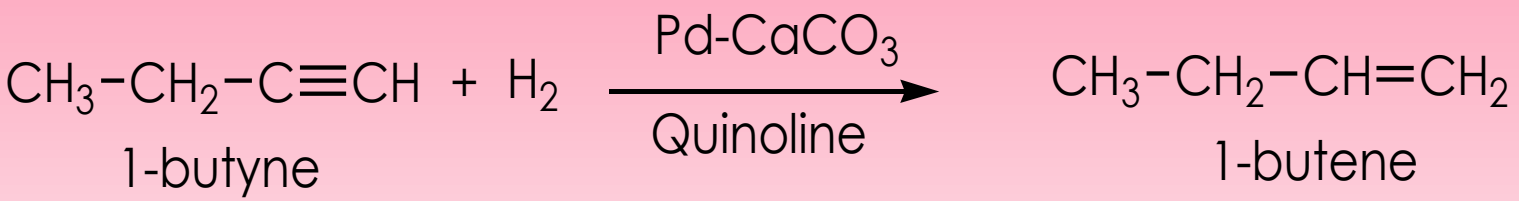
Alkenes are unsaturated hydrocarbons containing one carbon carbon double bond in their molecule.

- The general molecular formula of alkene is C_nH_{2n}
- Where, n = no. of carbon atoms.

Preparation methods :

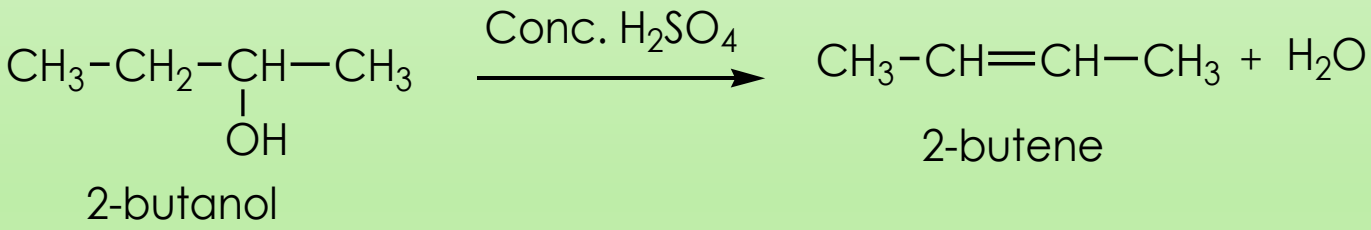
a) 1-butene from 1-butyne :

Reduction of 1-butyne using $Pd/CaCO_3$, quinoline (Lindlar's catalyst) gives 1-butene.



b) 2-butene from 2-butanol :

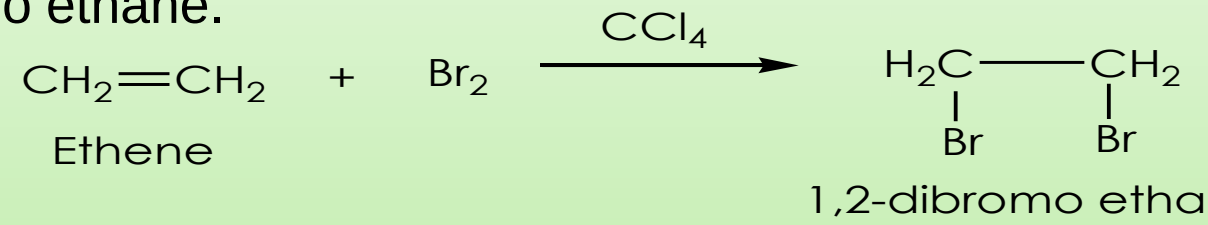
Acid catalyzed dehydration of 2-butanol with conc. H_2SO_4 gives 2-butene.



Chemical reactions of Alkenes :

a) Electrophilic addition of Br_2 to ethene :

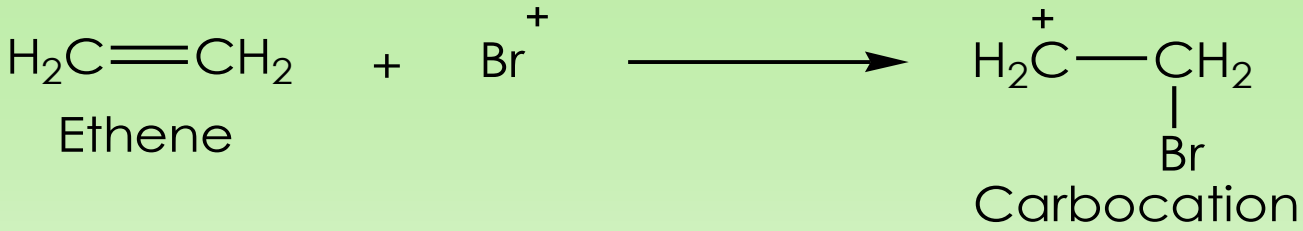
Addition of Br_2 to ethene in the presence of CCl_4 solvent gives 1,2-dibromo ethane.



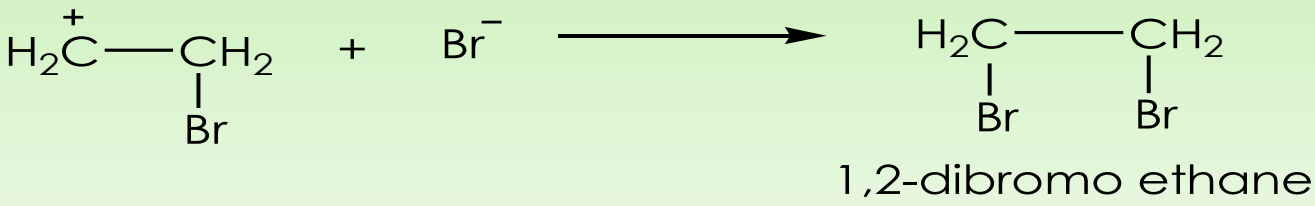
Mechanism: Mechanism of this reaction as follows.

Step-I : Formation of electrophile.

Step-II : Electrophilic attack of Br^+ on ethene gives carbocation .

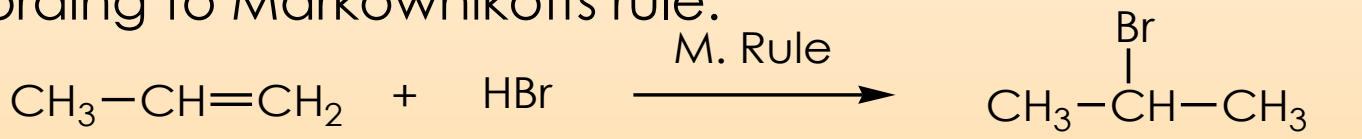


Step-III : Attack of bromide ion to form 1,2-dibromoethane.



b) Electrophilic addition of HBr to propene :

Addition of HBr to propene in gives 2-bromo propane according to Markownikoffs rule.

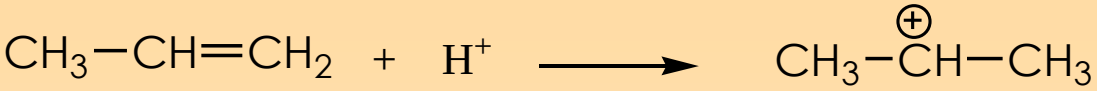


Propene — 2-bromo propane

Mechanism : Mechanism of this reaction as follows.

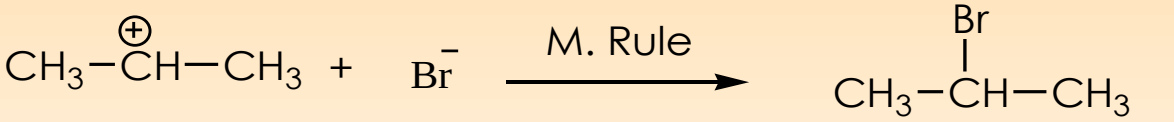
Step-1 : Formation of Electrophile

Step-2 : Attack of Electrophile H^+ to propene



Propene — Carbocation

Step-3 : Formation of 2-bromo propane.



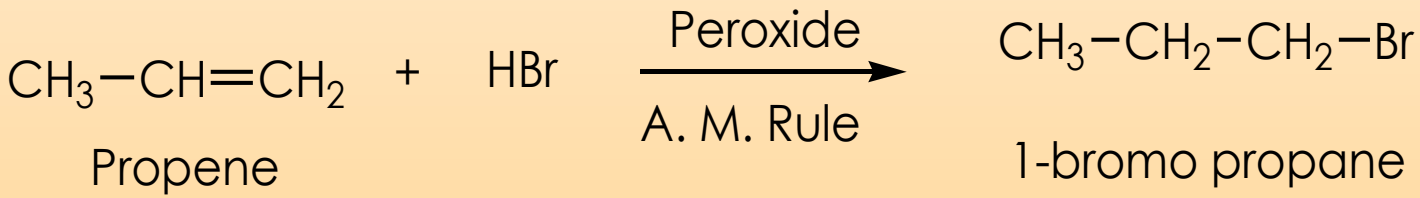
2-bromo propane

Markownikoffs Rule :

- When an unsymmetrical reagent adds to an unsymmetrical alkene, then the negative part of reagent adds to that carbon of carbon-carbon double bond which carries less number of hydrogen atoms.

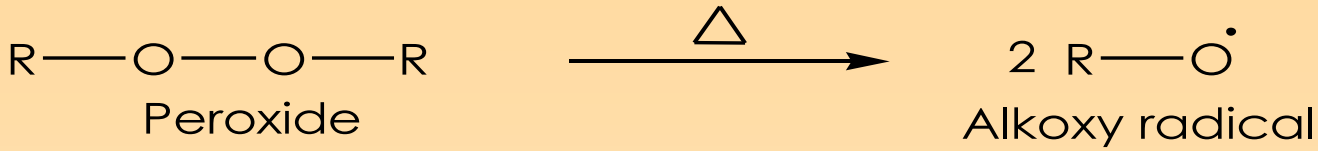
c) Free radical addition of HBr to propene :

Addition of HBr to propene in the presence of peroxide gives 1-bromo propane according to Antimarkownikoffs rule.



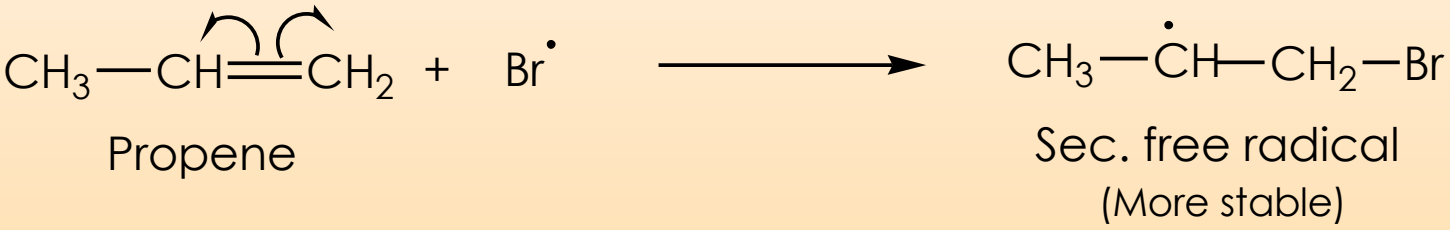
Mechanism : Mechanism of this reaction as follows.

Step-1 : Dissociation of peroxide to give alkoxy free radicals.

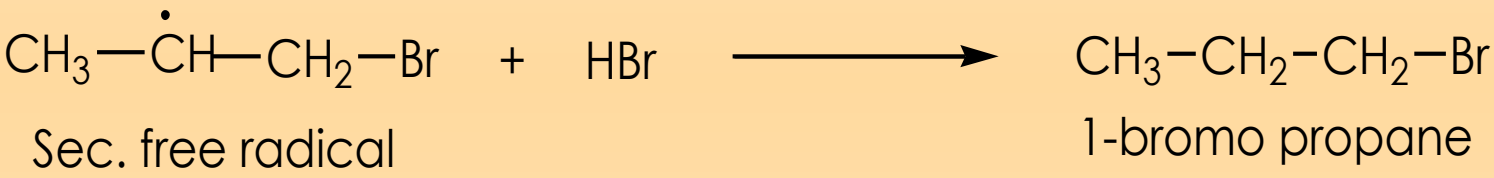


Step-2 : Alkoxy radicals combines with HBr to form bromine free radical.

Step-3 : Attack of bromine free radical to propene to form stable sec. free radical.



Step-4 : Sec. free radical attack on HBr molecule to form 1-bromo propane according to anti-markownikoffs rule.



Antimarkownikoffs Rule/ Peroxide effect/ Kharasch effect :

When an unsymmetrical reagent adds to an unsymmetrical alkene, then the negative part of reagent adds to that carbon of carbon-carbon double bond which carries more number of hydrogen atoms. This effect is also called as Peroxide effect or Kharasch effect.

C] Alkynes :

- "Unsaturated hydrocarbons containing one carbon carbon triple bond is called as alkyne "
- General molecular formula of alkyne is C_nH_{2n-2}

  Where, n - No. of carbon atoms.

  Ex. CH≡CH Acetylene (ethyne)
- **Preparation methods of Acetylene (ethyne) :**
- **a) From Iodoform :**
- When two molecules of Iodoform on heating with silver metal gives acetylene.

$$\underset{\text{Iodoform}}{CHI_3} + 6\,Ag + CHI_3 \xrightarrow{\Delta} \underset{\text{Acetylene}}{CH{\equiv}CH} + 6\,AgI$$

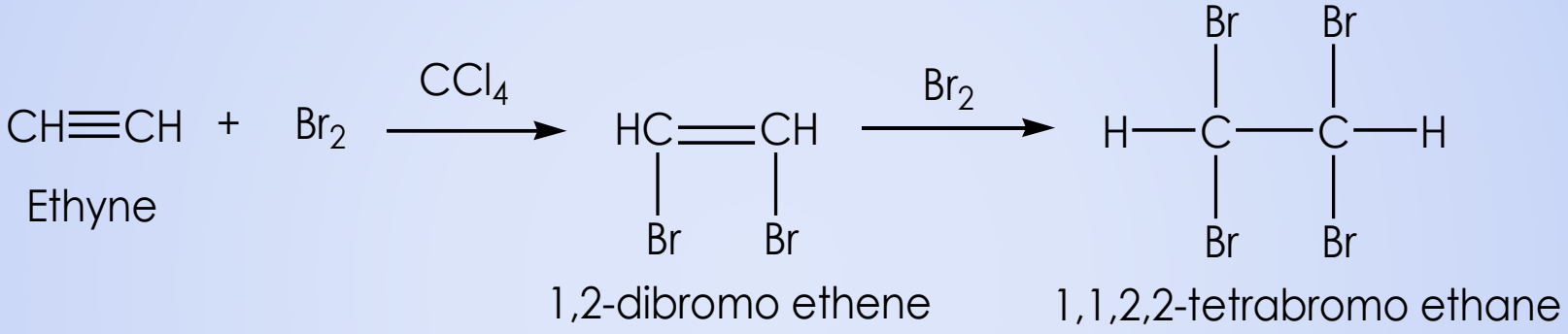
- **b) From Calcium carbide (CaC_2) :**
- Hydrolysis of calcium carbide with water gives acetylene.

$$\underset{\text{Calcium carbide}}{CaC_2} + H_2O \longrightarrow \underset{\text{Acetylene}}{CH{\equiv}CH} + Ca(OH_2)$$

Chemical reactions of Ethyne (Acetylene)

- **a) Electrophilic addition of Br_2 to Ethyne :**

  Addition of one Br_2 molecule on Ethyne in presence of CCl_4 solvent gives 1,2-dibromo ethene. Which on again react with second molecule of Br_2 gives 1,1,2,2-tetrabromo ethane.



- **Mechanism :** Mechanism of this reaction as follows.
- **Step-I :** Formation of Electrophile Br^+

$$Br_2 \rightarrow \underset{\text{Electrophile}}{Br^+} + Br^-$$

- **Step-II** : Attack of Electrophile Br^+ on ethyne

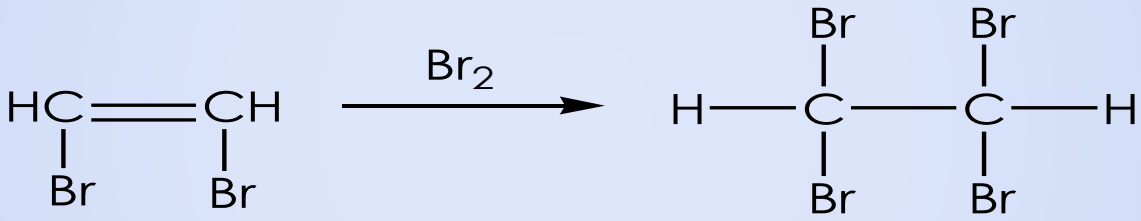
$$\underset{\text{Ethyne}}{CH{\equiv}CH} + Br^+ \rightarrow \underset{\text{Carbocation}}{{}^+CH{=}CH\text{-}Br}$$

- **Step-III** : Formation of 1,2-dibromo ethene

$$^{+}CH{=}CH{-}Br \; + \; Br^{-} \; \rightarrow \; Br{-}CH{=}CH{-}Br$$

1,2-dibromo ethene

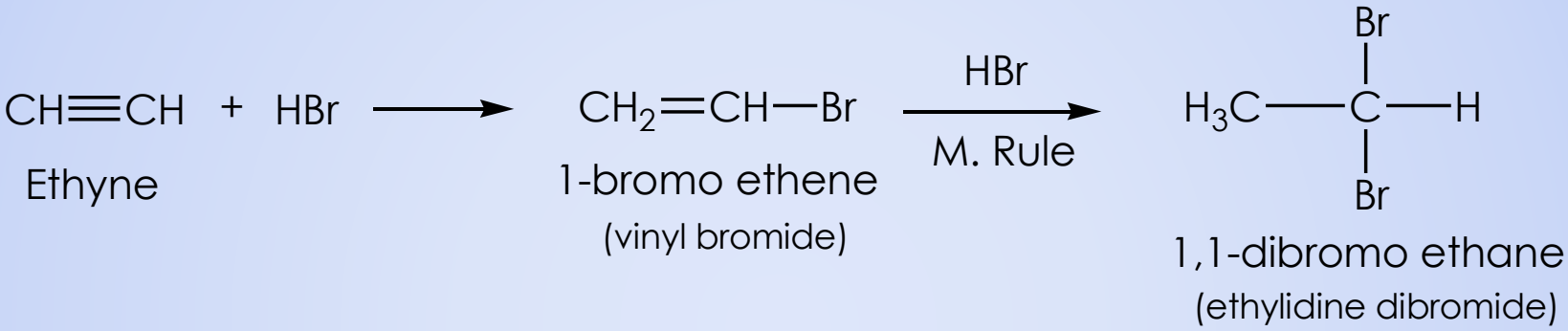
- **Step-IV** : Similarly, second molecule of Br_2 added on 1,2-dibromo ethene to form 1,1,2,2-tetrabromo ethane



1,2-dibromo ethene 1,1,2,2-tetrabromo ethane

b) Electrophilic addition of HBr to Ethyne

Ethyne react with one molecule of HBr gives vinyl bromide (1-bromo ethene). Which on again react with second molecule of HBr gives 1,1-dibromo ethane according to M. Rule.



- **Mechanism :** Mechanism of this reaction as follows.

  Step-I : Dissociation of HBr molecule

  $$HBr \longrightarrow \underset{\text{Electrophile}}{H^+} + Br^-$$

  Step-II : Attack of electrophile H^+ on ethyne to form carbocation

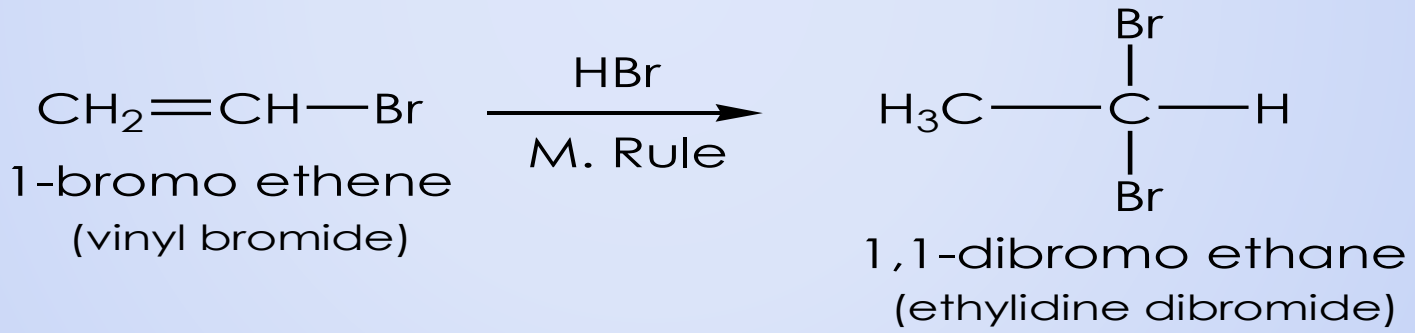
  $$CH{\equiv}CH + H^+ \longrightarrow \underset{\text{Carbocation}}{{}^+CH{=}CH_2}$$

Step-III : Nucleophilic attack of Br^- on carbocation to form of vinyl bromide

$$^{+}CH{=}CH_2 \quad + \quad Br^- \longrightarrow \quad CH_2{=}CH\text{-}Br$$

Vinyl bromide

Step-IV : Similarly, second molecule of HBr added on vinyl bromide to form 1,1-dibromo ethane



- Thank You ……