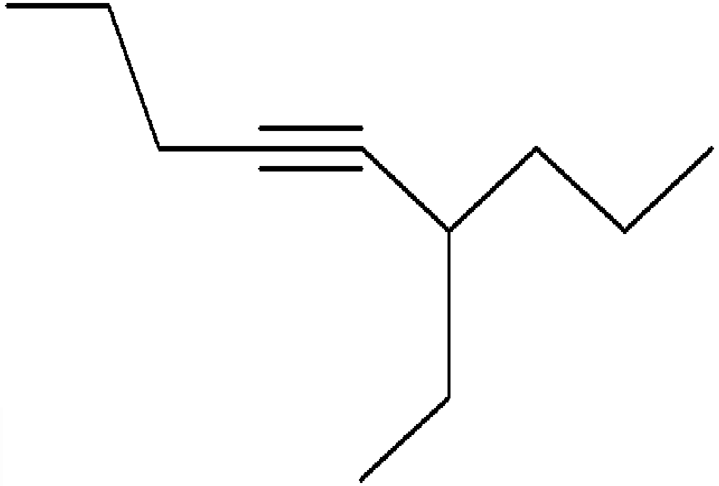
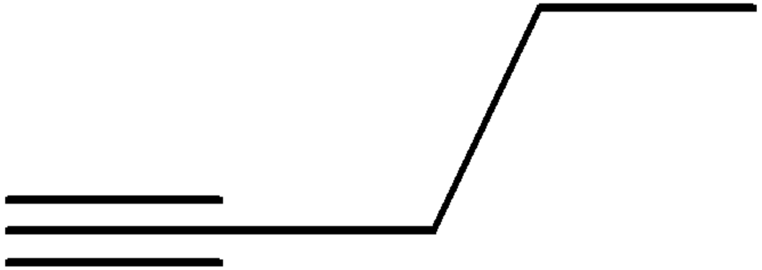
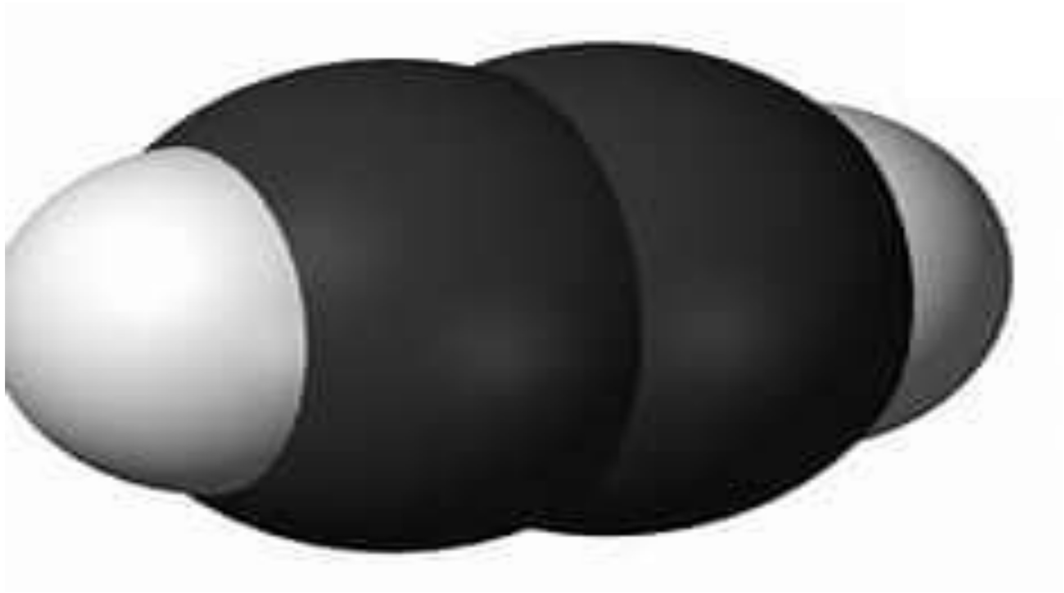
Alkynes



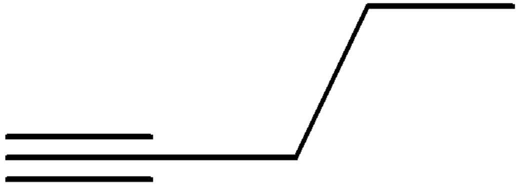


$H-C\equiv C-H$

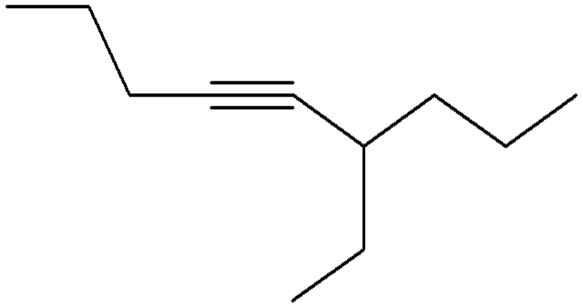


Alkynes

- Contain triple bond between two C atoms
- Gen Formula C_nH_{2n-2} where n = 2, 3, 4 & so on
- Nomenclature
- Common system
- Derivatives of Acetylene
- IUPAC System
- Add word –yne to the word root



1-Pentyne or Pent-1-yne



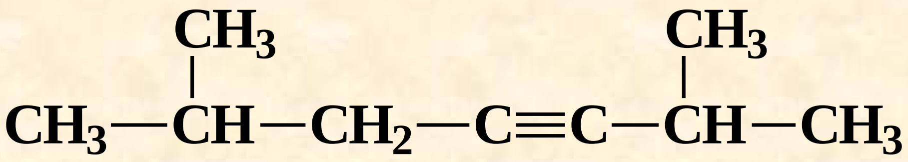
6-Ethylnon-4-yne

$$CH_3{-}C{\equiv}CH$$

IUPAC : Propyne
Common : Methyl acetylene

$$CH_3{-}C{\equiv}C{-}CH_2{-}CH_2{-}Br$$

5-Bromo-2-pentyne
Not 1-Bromo-3-pentyne



$$CH_3{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_2{-}C{\equiv}C{-}\overset{\overset{CH_3}{|}}{CH}{-}CH_3$$

IUPAC :2,6-Dimethyl-3-heptyne
Common :Isobutylisopropylacetylene

Alkynes

❑ Nomenclature contd…

C_4H_6	$CH_3CH_2{-}C\equiv CH$	Ethylacetylene *or* α-Crotonylene	1-Butyne
	$CH_3{-}C\equiv C{-}CH_3$	1, 2-Dimethylacetylene *or* β-Crotonylene	2-Butyne

$$\overset{5}{C}H_3{-}\overset{4}{C}H{=}\overset{3}{C}H{-}\overset{2}{C}\equiv\overset{1}{C}H$$

Pent-3-en-1-yne

$$\overset{6}{C}H\equiv\overset{5}{C}{-}\overset{4}{C}H_2{-}\overset{3}{C}H_2{-}\overset{2}{C}H{=}\overset{1}{C}H_2$$

Hex-1-en-5-yne

❑ Alkynyl groups…

$CH\equiv C{-}$

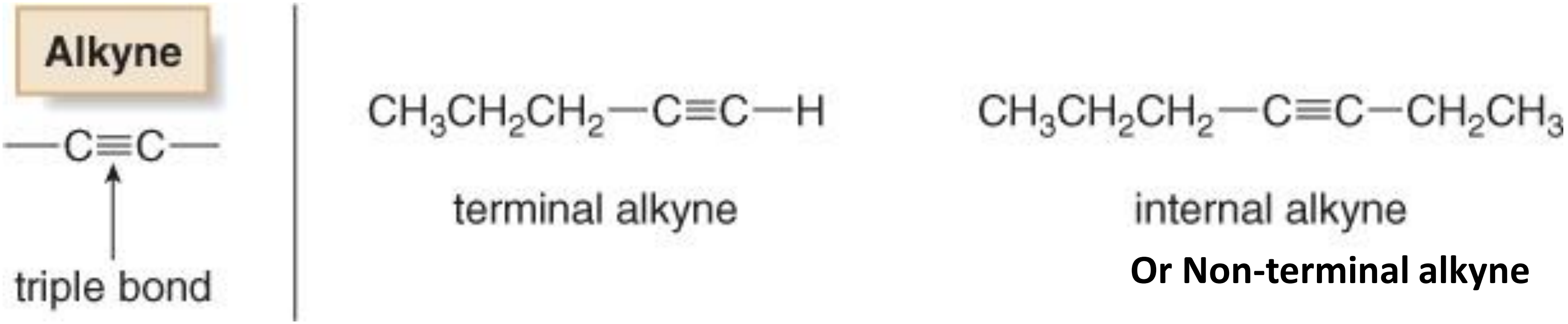
Ethynyl

$CH_3{-}C\equiv C{-}$

1-Propynyl

Alkynes

❑ Terminal & Non-terminal alkynes



Or Non-terminal alkyne

Methods of formation of Alkynes

1. By the action of water on calcium carbide

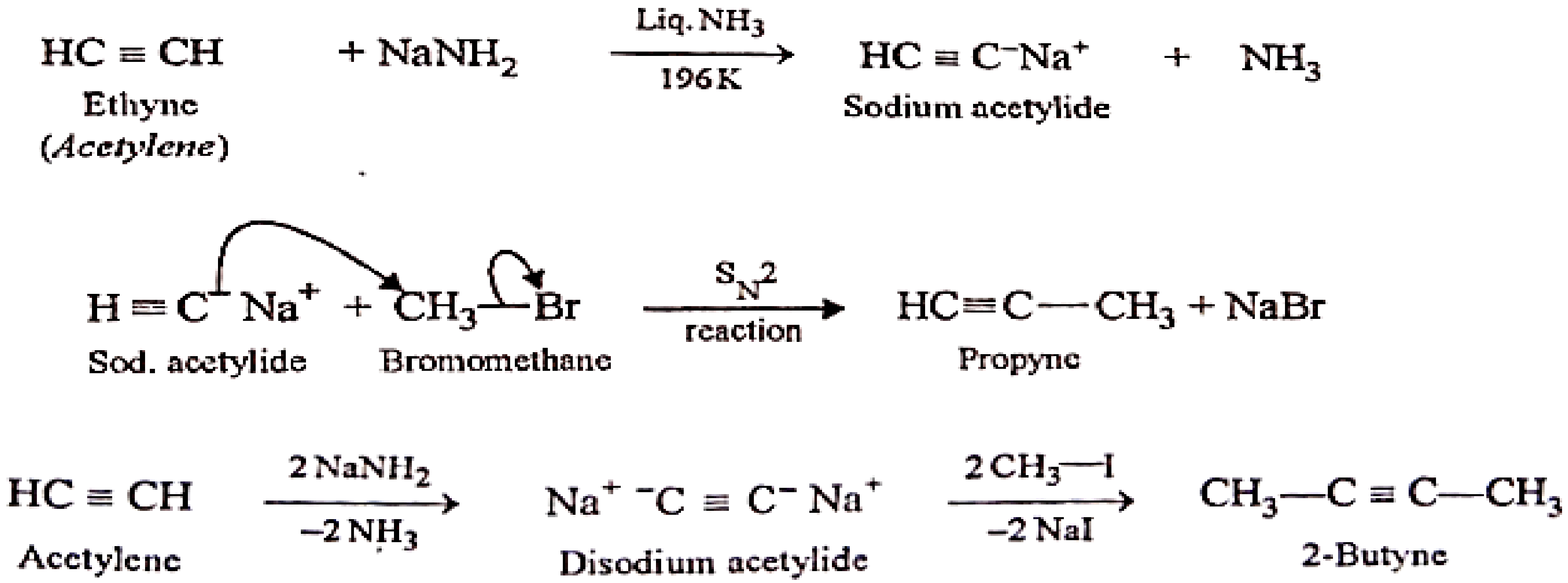
- **Ethyne (acetylene) is prepared in the laboratory as well as on a commercial scale by the action of water on calcium carbide.**

$$\underset{\text{Calcium carbide}}{CaC_2} + 2\,H_2O \longrightarrow \underset{\substack{\text{Ethyne}\\(\textit{Acetylene})}}{HC \equiv CH} + Ca(OH)_2$$

Methods of formation of Alkynes

Synthesis of higher alkynes from acetylene.

- Acetylene is first treated with sodium metal at 475 K or with sodamide in liquid ammonia at 196 K to form sodium acetylide. This upon treatment with primary alkyl halides undergoes SN^2 reaction to give higher alkynes. For example



$$\underset{\text{Ethyne (Acetylene)}}{HC \equiv CH} + NaNH_2 \xrightarrow[196\,K]{Liq.\,NH_3} \underset{\text{Sodium acetylide}}{HC \equiv C^-Na^+} + NH_3$$

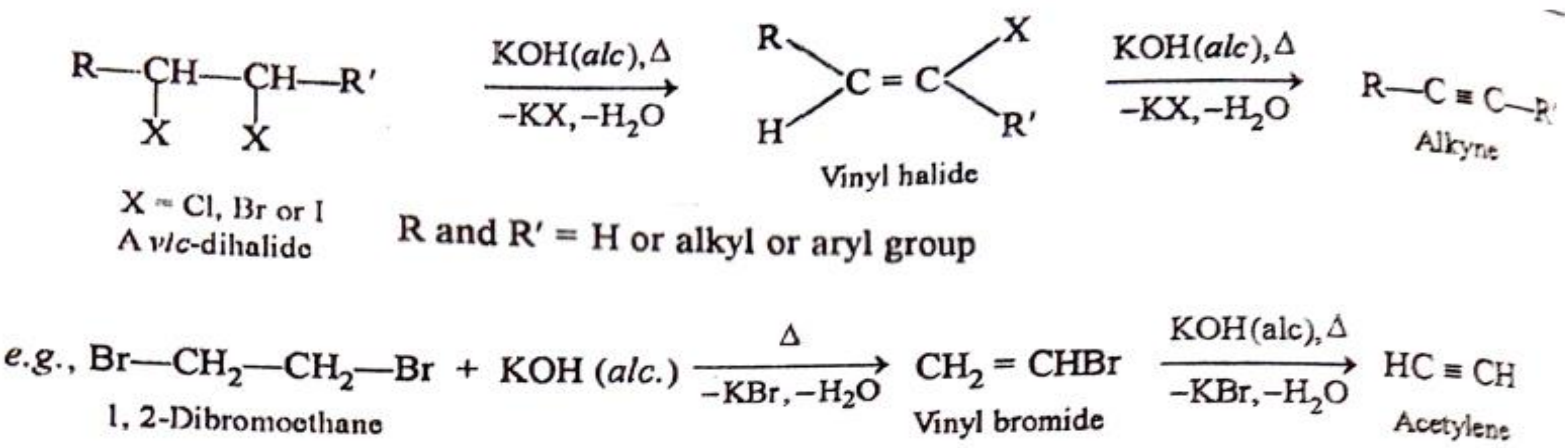
$$\underset{\text{Sod. acetylide}}{H \equiv C^- Na^+} + \underset{\text{Bromomethane}}{CH_3-Br} \xrightarrow[\text{reaction}]{S_N2} \underset{\text{Propyne}}{HC \equiv C-CH_3} + NaBr$$

$$\underset{\text{Acetylene}}{HC \equiv CH} \xrightarrow[-2\,NH_3]{2\,NaNH_2} \underset{\text{Disodium acetylide}}{Na^+ \, ^-C \equiv C^- \, Na^+} \xrightarrow[-2\,NaI]{2\,CH_3-I} \underset{\text{2-Butyne}}{CH_3-C \equiv C-CH_3}$$

Methods of formation of Alkynes

2. By Dehydrohalogenation of vicinal dihalides

- Reaction occurs in two stages



$$R-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-R' \xrightarrow[-KX,-H_2O]{KOH(alc),\Delta} \begin{matrix} R \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} X \\ R' \end{matrix} \xrightarrow[-KX,-H_2O]{KOH(alc),\Delta} R-C\equiv C-R'$$

X = Cl, Br or I
A *vic*-dihalide

Vinyl halide

Alkyne

R and R′ = H or alkyl or aryl group

$$e.g., \; Br-CH_2-CH_2-Br + KOH\,(alc.) \xrightarrow[-KBr,-H_2O]{\Delta} CH_2=CHBr \xrightarrow[-KBr,-H_2O]{KOH(alc),\Delta} HC\equiv CH$$

1, 2-Dibromoethane

Vinyl bromide

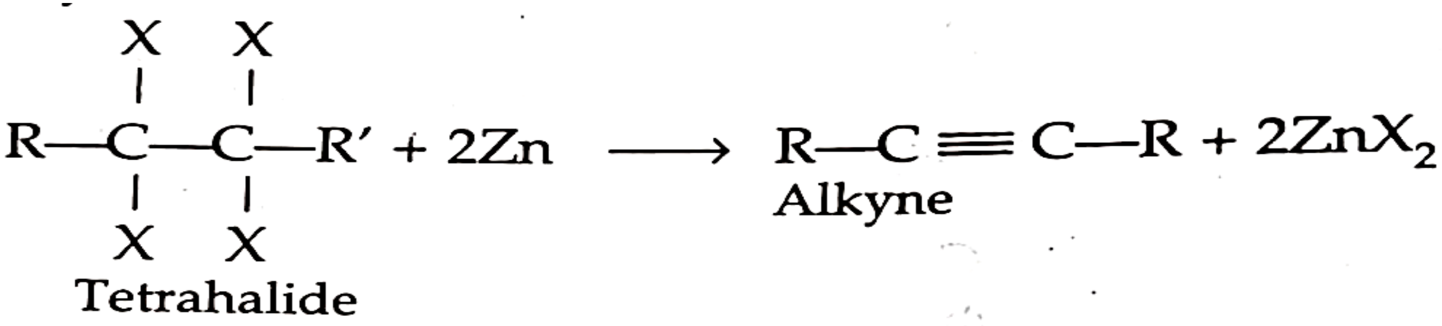
Acetylene

- **Sometimes stronger base $NaNH_2$ is needed to carry out the second stage of the reaction**

Methods of formation of Alkynes

3. By dehalogenation of tetrahalides

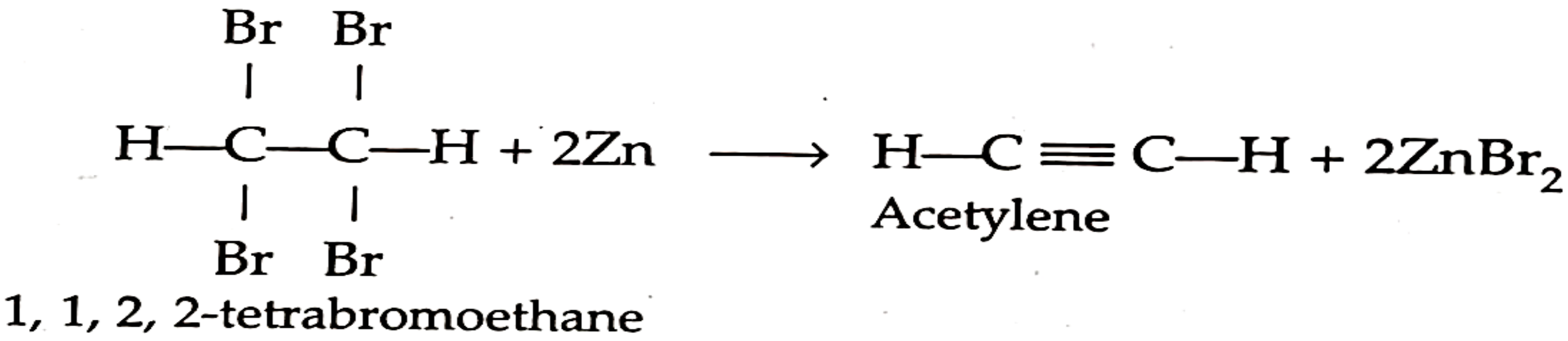
- By heating with Zinc dust



$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-R' + 2Zn \longrightarrow R-C\equiv C-R + 2ZnX_2$$

Tetrahalide

Alkyne



$$H-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H + 2Zn \longrightarrow H-C\equiv C-H + 2ZnBr_2$$

1, 1, 2, 2-tetrabromoethane

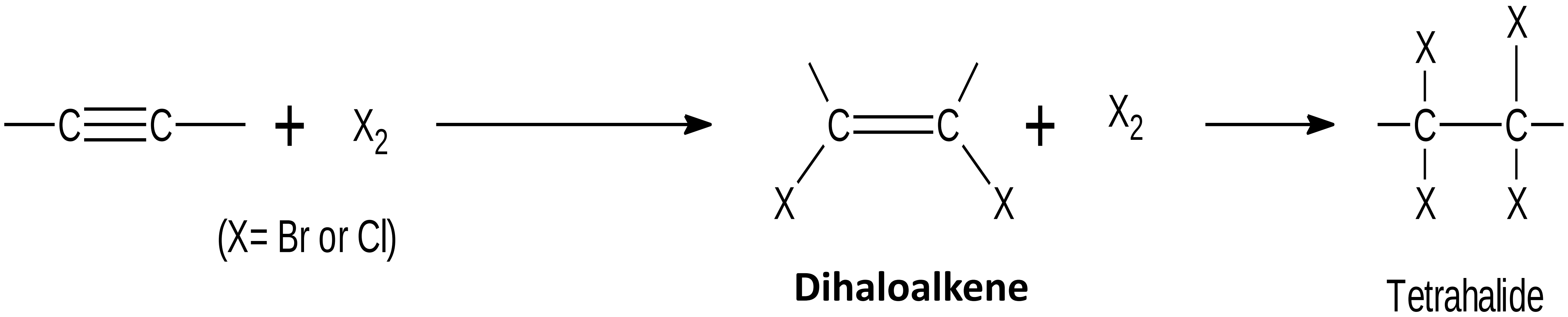
Acetylene

Chemical Properties

- Highly reactive due to the presence of two pi bonds
- Undergo addition, oxidation, and polymerization reactions

1. Addition of Bromine & other halogens.

- Two halogen molecules add across two pi bonds

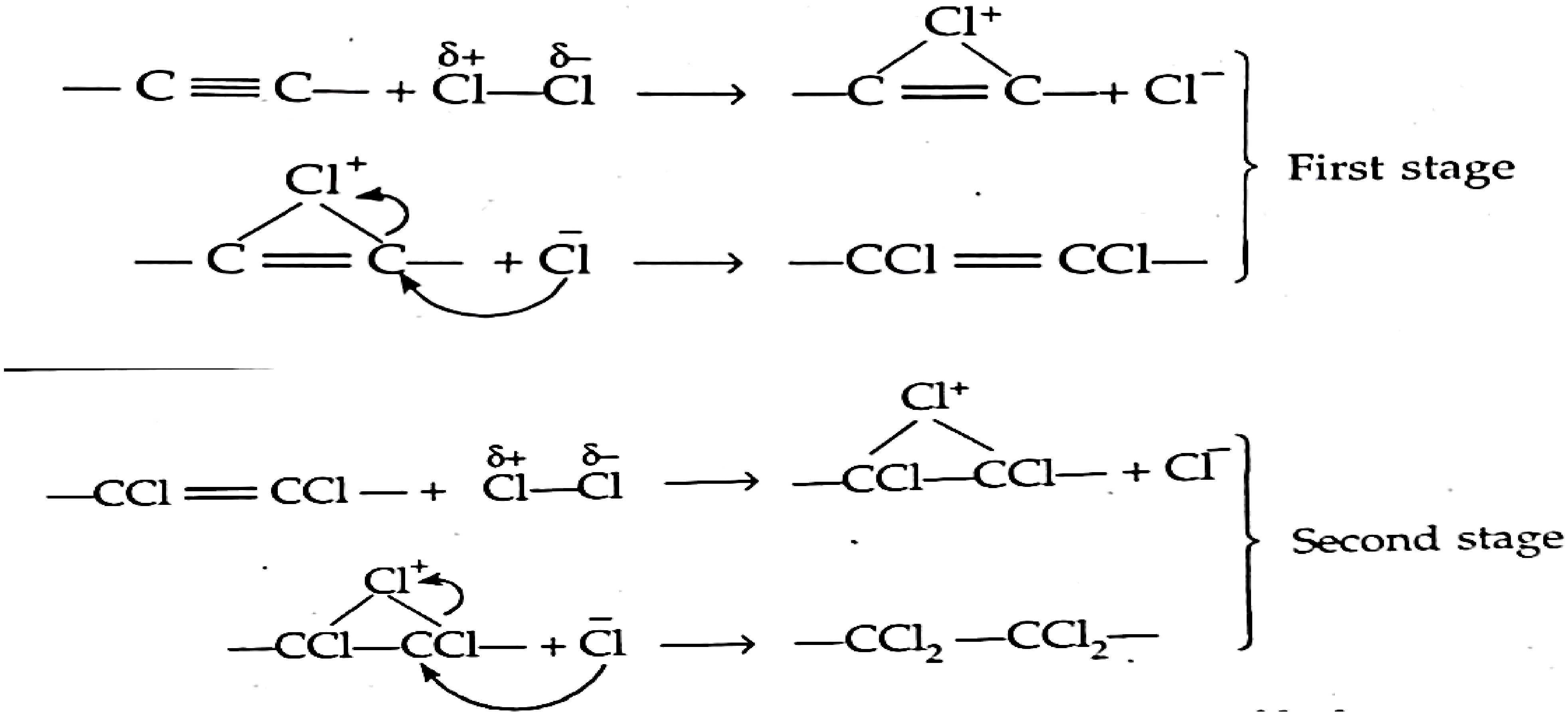


- When Bromine adds across pi bonds, its brown color is discharged
- This reaction can be used as a test for the presence of multiple bonds in a compound

Chemical Properties

❖ Mechanism of addition

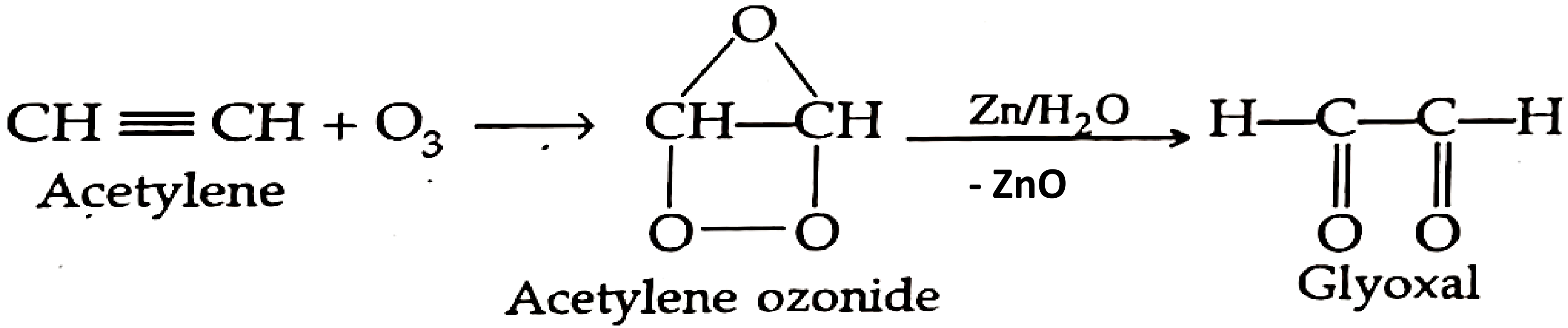
- Addition takes place through the formation of cyclic halonium ion in two stages & addition occurs in trans or anti manner

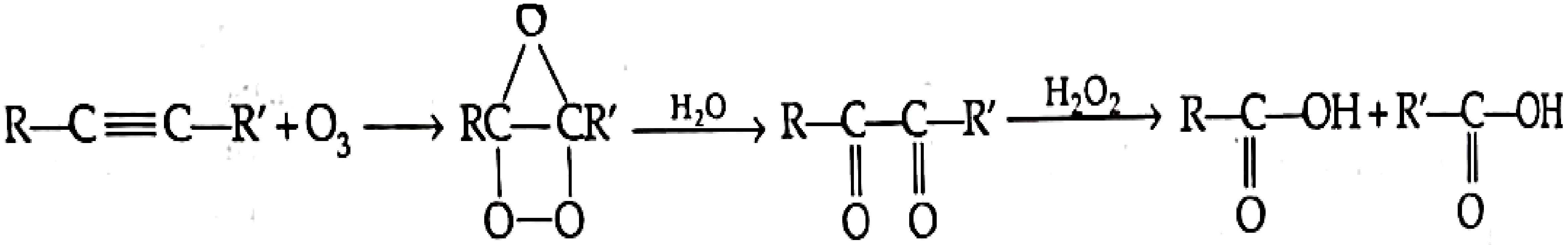


Chemical Properties

2. Ozonolysis

- **Dicarbonyl compounds are formed**

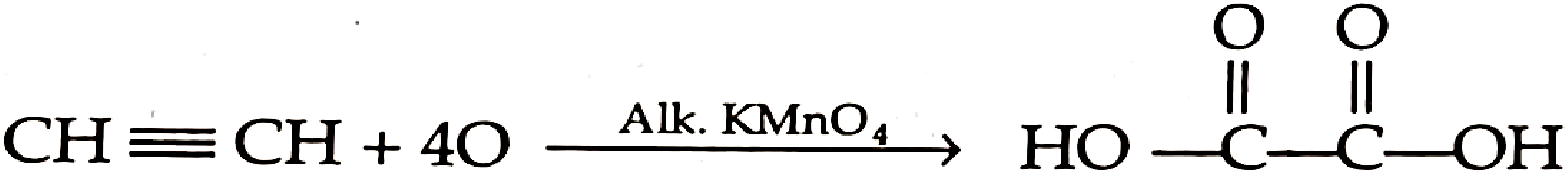




Chemical Properties

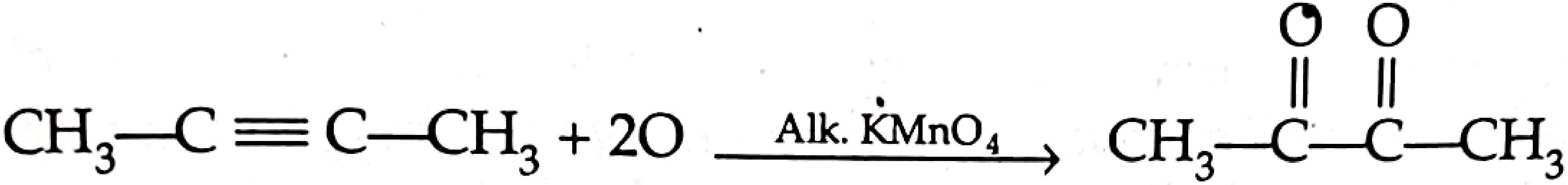
3. Oxidation with potassium permanganate

- At room temperature



$$CH\equiv CH + 4O \xrightarrow{\text{Alk. KMnO}_4} HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$$

Oxalic acid



$$CH_3-C\equiv C-CH_3 + 2O \xrightarrow{\text{Alk. KMnO}_4} CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$$

2-Butyne

2, 3-Butanedione

Chemical Properties

3. Oxidation with potassium permanganate contd….

❖ At high temperature

$$CH_3{-}CH_2{-}C \equiv CH + 4O \xrightarrow[373-383\text{ K}]{\text{Alk. }KMnO_4} CH_3{-}CH_2{-}COOH + CO_2$$

1-Butyne Propanoic acid

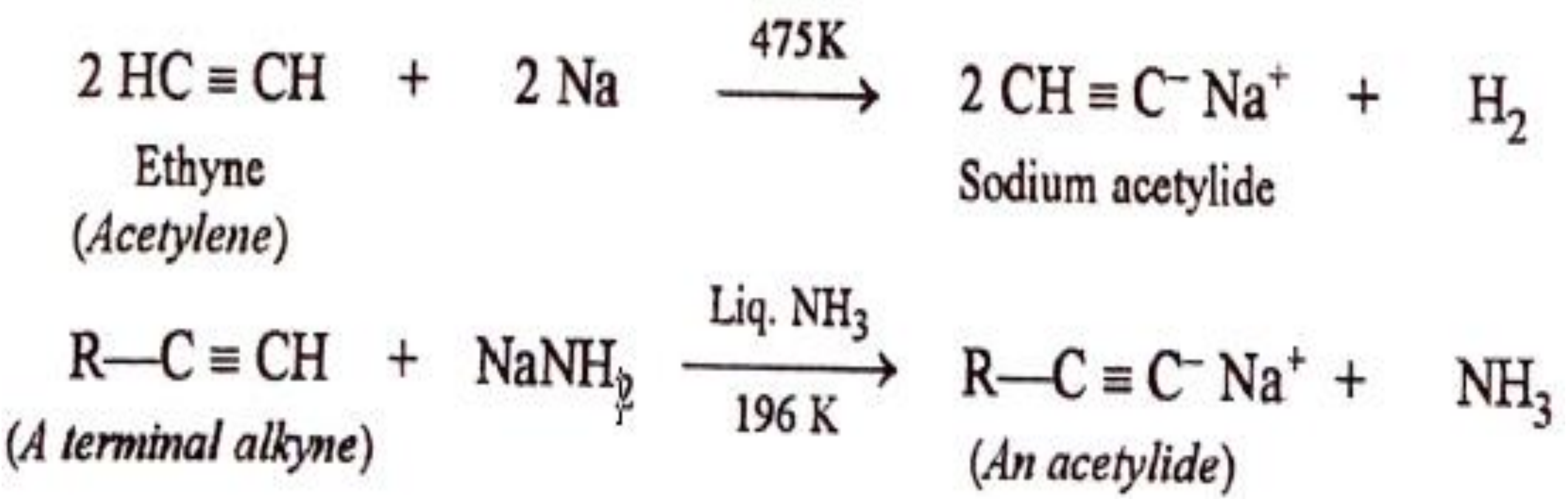
$$CH_3{-}C \equiv C{-}CH_3 + 4O \xrightarrow[373-383]{\text{Alk. }KMnO_4} 2\,CH_3\,COOH$$

- When alk. $KMnO_4$ reacts with alkynes, its pink color is discharged
- Discharge of pink color is used as a test for unsaturation
- This test is known as Baeyer’s Test

Chemical Properties

4. Formation of alkali metal acetylides.

- **Ethyne and other terminal alkynes (or 1-alkynes) react with strong bases such as sodium metal at 475 K or sodamide in liquid ammonia at 196 K to form sodium acetylides with the evolution of H_2 or NH_3 gas**



$$2\,HC \equiv CH + 2\,Na \xrightarrow{475K} 2\,CH \equiv C^- Na^+ + H_2$$

$$R{-}C \equiv CH + NaNH_2 \xrightarrow[196\ K]{Liq.\ NH_3} R{-}C \equiv C^- Na^+ + NH_3$$

Chemical Properties

5. Formation of heavy metal acetylides.

- **With Tollens reagent(Ammonical silver nitrate solution)**

$$\underset{\text{Ethyne}}{HC\equiv CH} + \underset{\text{Tollens' reagent}}{2\,[Ag(NH_3)_2]^+\,OH^-} \longrightarrow \underset{\substack{\text{Silver acetylide}\\ \textit{(White ppt.)}}}{AgC\equiv CAg} + 2\,H_2O + 4\,NH_3$$

$$\underset{\textit{(Terminal alkyne)}}{R{-}C\equiv CH} + \underset{\text{Tollens' reagent}}{[Ag(NH_3)_2]^+\,OH^-} \longrightarrow \underset{\substack{\text{Silver alkynide}\\ \textit{(White ppt.)}}}{R{-}C\equiv C{-}Ag} + H_2O + 2\,NH_3$$

- **This reaction can be used to distinguish terminal alkynes from non-terminal alkynes or other hydrocarbons**

Chemical Properties

5. Formation of heavy metal acetylides contd….

❖ With Ammonical cuprous chloride solution

$$HC \equiv CH + 2\,[Cu(NH_3)_2]^+\,OH^- \longrightarrow CuC \equiv CCu + 2\,H_2O + 4\,NH_3$$

Ethyne — Copper acetylide *(Red ppt.)*

$$R{-}C \equiv CH + [Cu(NH_3)_2]^+\,OH^- \longrightarrow R{-}C \equiv C{-}Cu + H_2O + 2\,NH_3$$

(Terminal alkyne) — Copper alkynide *(Red ppt.)*

- ➢ This Reaction can also be used to distinguish terminal alkynes from non-terminal alkynes or other hydrocarbons

Chemical Properties

- **Formation of acetylides is due to the acidic nature of terminal alkynes**

$$H\text{-}C\equiv C\text{-}H \rightarrow H\text{-}C\equiv \overset{-}{C}: \quad + \quad H^+$$

Acetylene Acetylide anion

- **Causes of Acidity**

1. **Hybridization**

- C bearing triple bond is SP hybridized so it has more s character due to which it is more electronegative and hence can release H^+ ion

2. **Stability of alkynyde ion**

- SP carbon being more electronegative can accommodate the negative charge better

Chemical Properties

- **Alkynes are less reactive than alkenes towards electrophilic addition reactions. Why?**

Two reasons

1. Hybridization

- **In alkynes C is sp hybridized. SP hybrid carbon is more electronegative. So electron pairs of triple bonds are less available for attack.**

2. Cylindrical pi electron cloud

- **Two p orbitals on each carbon atom overlap to form a cylindrical pi electron cloud in which the pi electrons are more delocalized. So the pi electrons are less available for attack.**

Questions

1. How will you justify the following

i. Alkynes undergo both electrophilic and nucleophilic addition reactions

ii. Terminal alkynes are acidic in character whereas internal alkynes are not

iii. Alkynes are less reactive than alkenes toward electrophilic addition reactions

2. What happens when ……

i. Ethyne reacts with ammonical silver nitrate solution

ii. Propyne is treated with ozone followed by reductive hydrolysis