PREPARATION OF ALKYNES

By-N.K.D. Sir

ALKYNES

Nomenclature of alkynes

In IUPAC system the compounds are named as alkynes in which the final – ane of the present alkane is replaced by the suffix – yne. The position of the triple bond is indicated by a number.

e.g. $CH_3C \equiv CH$ $\qquad$ $(CH_3)_2CHC \equiv CH$

Propyne $\qquad$ 3 – methyl – 1 – butyne

$$\begin{array}{l} CH_3CH_2—CH_2—\underset{\displaystyle CH_2CH_3CH_3}{\underset{|}{CH}}—C\equiv C—CH_3 \end{array}$$

4 - propyl - 2 - heptyne

When both double and triple bonds are present, hydrocarbon is named as alkenyne.

e.g. $CH_3CH = CHC \equiv CH$ $\qquad$ $HC \equiv C\,CH_2CH = CH_2$

3 – penten – 1 – yne $\qquad$ 1 – penten – 4 – yne

METHODS OF PREPARATIONS

1. Industrial source:

$$\underset{\text{Calcium Carbide}}{CaC_2} + H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Ethyne}}{HC \equiv CH}$$

The double negative carbide ion $:\overset{\ominus}{C}\equiv\overset{\ominus}{C}:$

which is strongly basic reacts with water to form acetylene

$$Mg_2C_3 + H_2O \longrightarrow Mg(OH)_2 + \underset{\text{Propyne}}{CH_3C \equiv CH}$$

$$6CH_4 + 2O_2 \xrightarrow[\text{cracking}]{1500^\circ C} 2CH \equiv CH + 2CO_2 + 10H_2$$

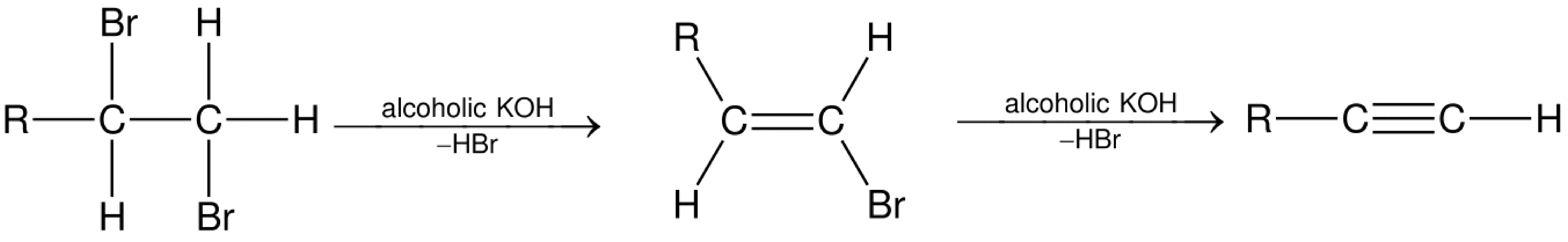
2. Kolbe's method:

Electrolysis of concentrated solution of sodium or potassium salt of maleic or fumaric acid gives acetylene at anode

$$\begin{array}{c} CHCO_2Na \\ \| \\ CHCO_2Na \end{array} \xrightarrow{+2H_2O,\text{current}} \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2CO_2 + 2NaOH + H_2$$

3. Dehydrohalogenation of 1, 2 – dihalides:

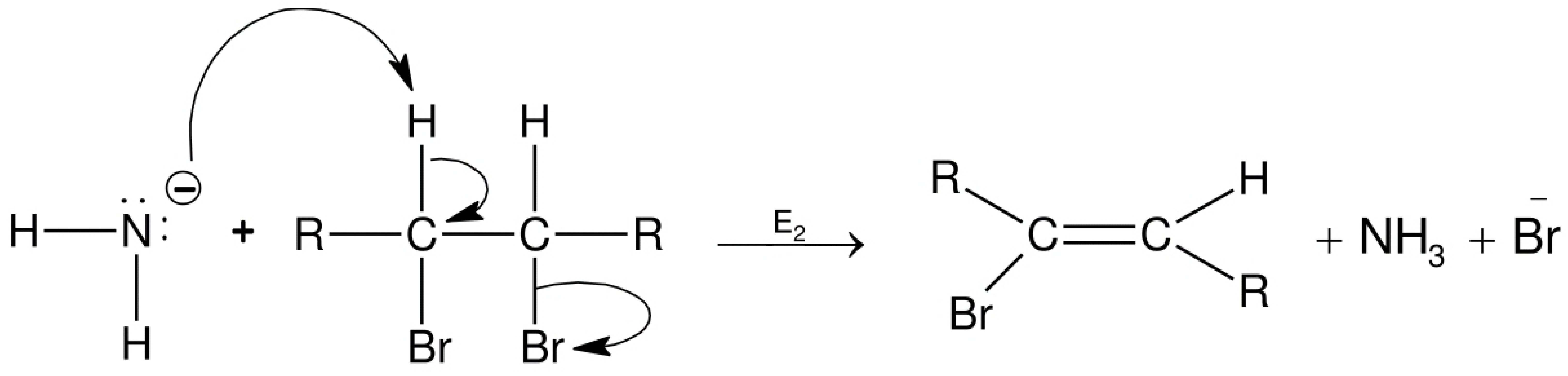
1, 2 – dihalides on treatment with alcoholic KOH gives alkynes by loss of two molecules of hydrogen halide, the intermediate being vinyl halide.



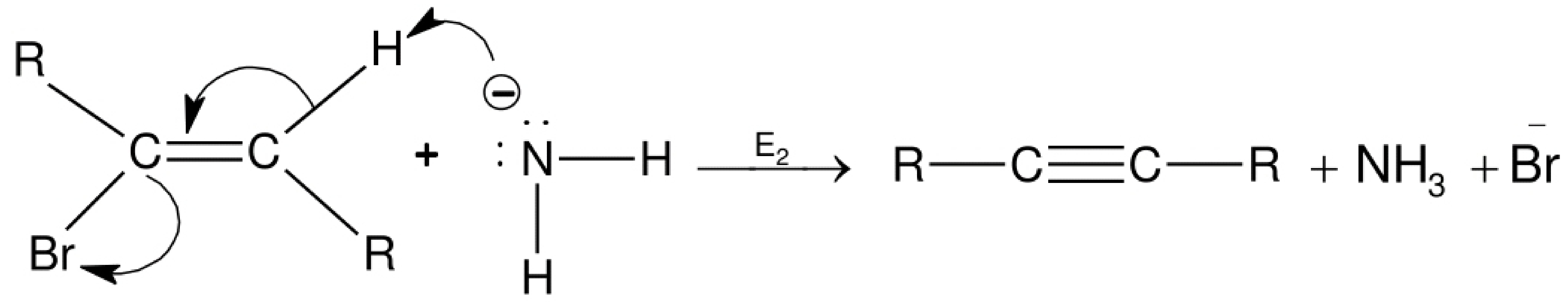
Sodamide $(NaNH_2)$ in liquid NH_3 can be used instead of alcoholic KOH.

Mechanism:

Step I:



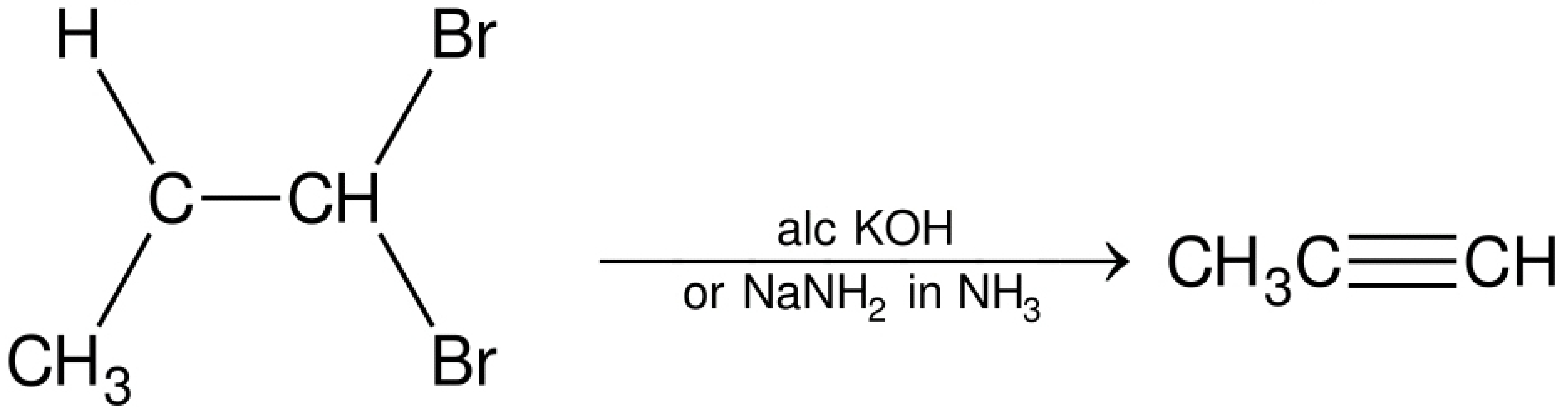
Step II:



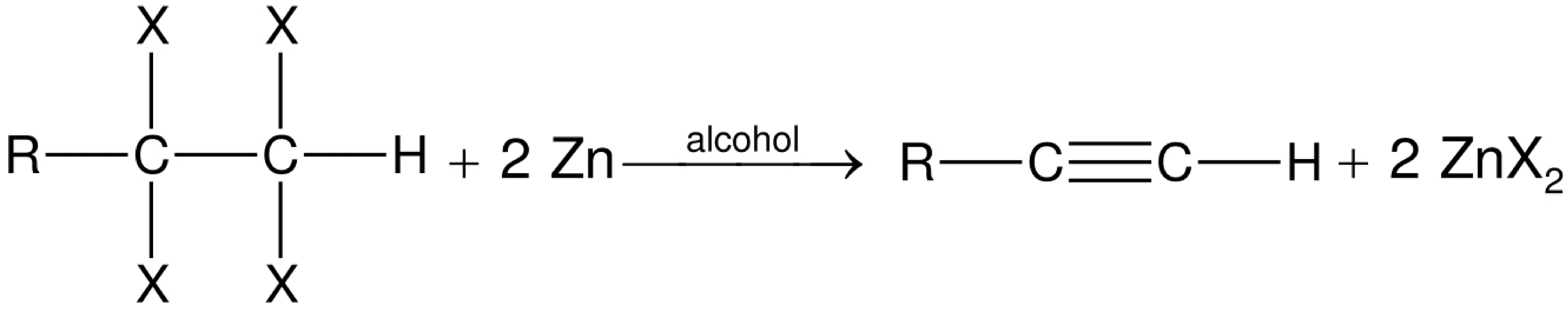
Elimination of the first molecule of HX results in the formation of vinyl halide – an alkene with halogen bonded to one of the carbons of the double bond. Strong base $\bar{N}H_2$ is taken to make the step II easier for elimination.

4. Dehydrohalogenation of 1, 1 – dihalides:

1, 1 – dihalides (geminal) with alcoholic KOH or $NaNH_2$ in NH_3 forms alkynes where intermediate is vinyl halide.



5. Dehalogenation of tetrahalides or trihalides:



$$CHX_3 + 6Ag + X_3CH \xrightarrow{\Delta} CH \equiv CH + 6AgX$$

6. **Alkylation of acetylene and terminal alkynes:**

i.e. an alkyne with $-C \equiv CH$ at the end of chain. This method is used to prepare higher alkynes.

$$HC \equiv CH + Na \xrightarrow{\text{Liquid } NH_3} HC \equiv \overset{-}{C}\overset{+}{Na} \xrightarrow{RX} HC \equiv CR$$

$$RC \equiv CH + Na \xrightarrow{\text{Liquid } NH_3} RC \equiv \overset{-}{C}\overset{+}{Na} \xrightarrow{R'X} RC \equiv CR'$$

Terminal alkyne

$$CH_3C \equiv CH \xrightarrow[\text{(ii) } CH_3CH_2I]{\text{(i) Na/liq. } NH_3} CH_3C \equiv CCH_2CH_3 \text{ (2-pentyne)}$$

Note:

RX and R′X should be 1° alkyl halides, since higher secondary and tertiary halides give mainly alkenes when they react with sodium salt of alkynes.

$$CH_3C \equiv \overset{-}{C}\overset{+}{Na} + CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3 \longrightarrow CH_3C \equiv CH + CH_3CH = CHCH_3 + NaCl$$

Alkylation can also be done by using Grignard's reagent.

$$HC \equiv CH + CH_3 - MgBr \longrightarrow CH \equiv C - Mg - Br + CH_4$$

$$HC \equiv C - Mg - Br + CH_3Br \longrightarrow CH \equiv CCH_3 + MgBr_2$$