ALKYNE

- C_nH_{2n-2}

PREPARATION (Ethyne)

1. Industrial method :- (Carbide Method)

$$CaO + C \xrightarrow{2000^\circ C} CaC_2 \xrightarrow{H_2O} CH \equiv CH \quad Ca(OH)_2$$

2. From CH_4 (Ethyne)

$$2\,CH_4 \xrightarrow[1500^\circ C]{\text{Pyrolysis}} CH \equiv CH + 3H_2$$

3. Dehydrohalogination of dihalide :-

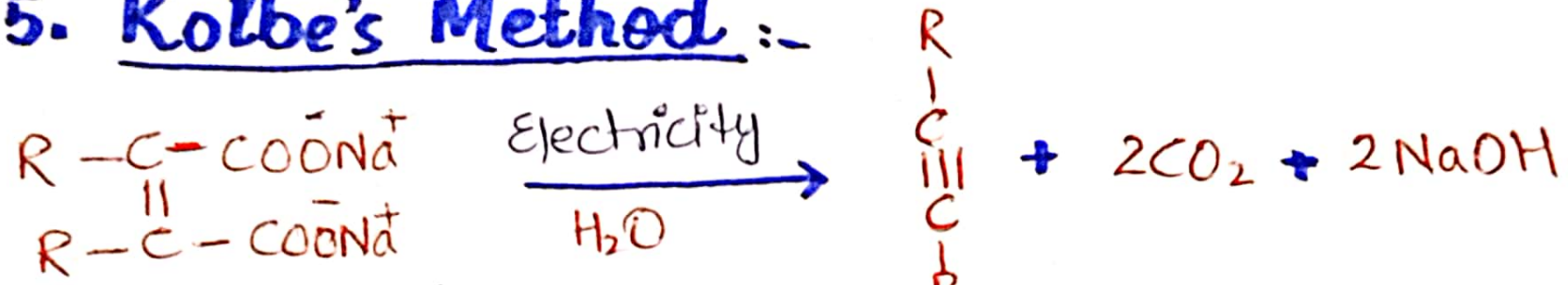
$$R-\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-R \xrightarrow[150^\circ C]{\text{alc. KOH (2 moles)}} R-C \equiv C-R$$

- $NaNH_2$ can be used as strong base in liq. NH_3 at $-33^\circ C$ or mineral oil at $160^\circ C$

4. From tetrahalide :-

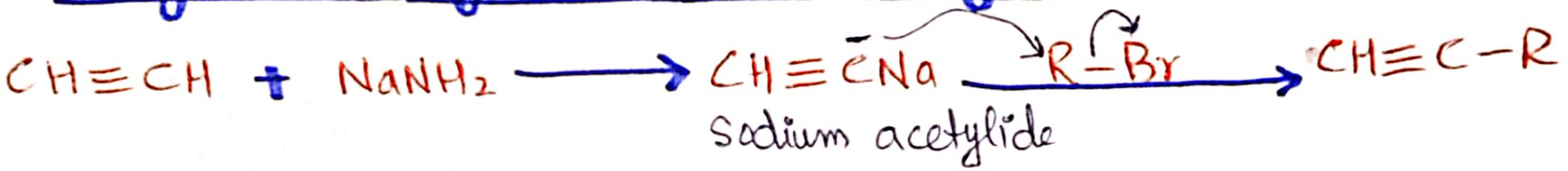
$$R-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-R \xrightarrow{Zn/CCl_4} R-C \equiv C-R.$$

5. Kolbe's Method :-



Sodium salt of maleic acid.

6. Alkylation of terminal alkyne :-



Physical Properties :-

- Acelylene has garlic like smell, other are colouless and odourless.
- Gases ($C_2 - C_4$), Liquid ($C_5 - C_{12}$), Solid ($> C_{12}$)
- M.P°, B.P°, density increase with mol. wt.
- Insoluble in water, soluble in non-polar solvents.

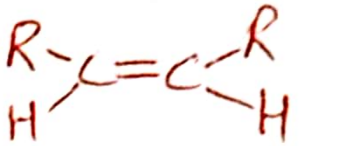
REACTIONS

Alkyne less reactive than alkene.

	Reagent	Condition	Product
1. Hydrogenation	$\begin{matrix}CR\\ \|\|\\ CR\end{matrix} + H_2$	Pt, Pd or Ni	RCH_2-CH_2R
	$CR\equiv CR + H_2$	Lindlar's catalyst ($Pd(BaSO_4)$ Quinoline)	cis-alkene
		Na in liq. NH_3, $-33^\circ C$	trans-alkene
2. Halogenation:-	$CR\equiv CR + Br_2$	CCl_4, $25^\circ C$	$RCBr_2-CBr_2R$
3. Addition of Halogen Acid:- (HBr or HCl)	$CR\equiv CH + HBr$	$HgBr_2$	$RCBr_2-CH_3$ Markonikov's addition
	$CR\equiv CH + HBr$	H_2O_2	RCH_2-CHBr_2 (Anti-markonikov)
	$CH\equiv CH + CH_3COOH$	$Zn(OAc)_2$, $180-200^\circ C$	$CH_2=CH-OCOCH_3$
	$CH\equiv CH + HCN$	$CuCl, NH_4Cl$	$CH_2=CH-CN$

	Reagents	Conditions	Products
	$CH\equiv CH + HCl$	$HgCl_2$ or $CuCl$	$CH_2=CH-Cl$
4- Hydration :- Oximercuration demercuration. * only acetylene forms aldehyde, other alkynes form ketone. used for industrial Preparation of acetaldehyde ($CH_3\overset{O}{\overset{\|}{C}}-H$)	$R-C\equiv CH + H_2O$	$HgSO_4$ / $Hg(OAc)_2$	Vinyl alcohol $\rightleftharpoons$ Acetaldehyde
5- Oxidation :- • Alkaline $KMnO_4$ leads To cleavage of bond to form oxidative product	$CR\equiv CR$	O_3 or neutral $KMnO_4$	$R\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$ 1,2-dicarbonyl compound. $\xrightarrow{H_2O_2}$ $RCOOH + RCOOH$
• CrO_3/CH_3COOH a weak oxidizing agent	, oxidizes double bond, leaving triple bond intact		
6- Combustion :-	$2CH\equiv CH + 5O_2$		$4CO_2 + 2H_2O +$ heat

7. Hydroboration :-

	Reagent	Condition	Product
Hydroboration-Pyrolysis.	$RC\equiv CR + B_2H_6$	$\xrightarrow[CH_3COOH]{0^\circ C}$	 Cis-alkene.
Hydroboration-oxidation.	$RC\equiv CH + B_2H_6$ terminal alkene.	then H_2O_2, OH^-	RCH_2CHO Aldehyde.

8. Addition of NH_3 & HCN :-

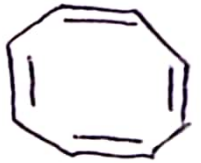
$CH\equiv CH + NH_3$	$\xrightarrow[300^\circ C]{Al_2O_3}$	CH_3-CN Acetonitrile
$CH\equiv CH + HCN$	$\xrightarrow[heat]{Cu_2Cl_2 / NH_4Cl}$	$CH_2=CH-CN$

9. Polymerization :-

$R-C\equiv CH$	$\xrightarrow[Pyridine, 60^\circ C]{CuCl, O_2}$	$R-C\equiv C-C\equiv C-R$ Diyne.
$CH\equiv CH + CH\equiv CH$	$\xrightarrow[HCl]{CuCl, NH_4Cl}$	$CH_2=CH-C\equiv CH$ Vinylacetylene.

Vinylacetylene $\xrightarrow{Conc.\ HCl}$ $CH_2=CH-\underset{Cl}{C}=CH_2$ Chloroprene

Chloroprene $\rightarrow$ Neoprene (Synthetic Rubber)

	Reagent	Condition	Product
	$3\,CR{\equiv}CH$	Red-hot glass tube (500-700°C)	Benzene and its derivatives
	$4\,CH{\equiv}CH$	$Ni(CN)_2$, 70°C; inert solvent, 20 atm	Cyclooctatetraene 
10. Formation of metal acetylide. Acetylenic Hydrogen is acidic.	(only terminal alkynes) $RC{\equiv}CH + NaNH_2$	liq. NH_3	$RC{\equiv}CH$. $H_2O\uparrow$ $RC{\equiv}C^-Na^+$ Powerful Nucleophile
	$RC{\equiv}CH + AgNO_3$	NH_4OH	$RC{\equiv}CAg$ (white ppt.)
	$RC{\equiv}CH + Cu_2Cl_2$	NH_4OH	$RC{\equiv}CCu$ (Reddish brown ppt.)

- Ag and Cu salts of acetylene give back alkyne on acid hydrolysis. —— used for separation of terminal alkynes from internal alkynes.

Uses of Acetylene :-

- used in oxy acetylene torch for welding and cutting metal.
- Preparation of alcohols, acetic acids and acetaldehyde.
- Preparation of polymers like PVC, PVA, neoprene rubber.
- Preparation of acetylene tetrachloride — solvent.
- Ripening of fruit.