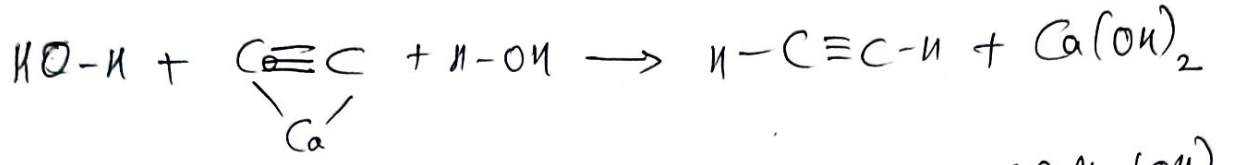
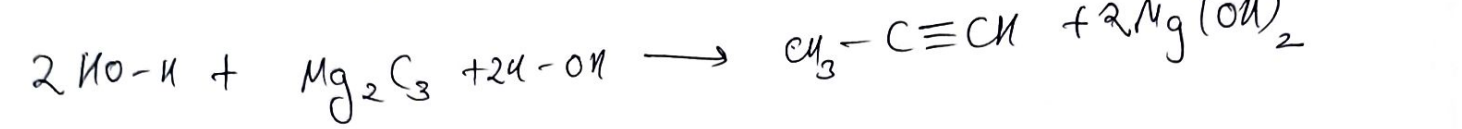
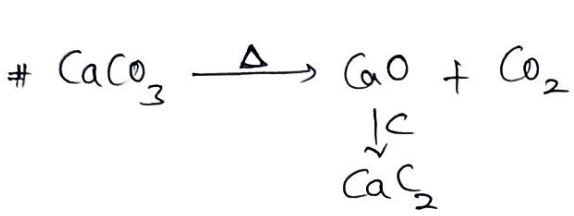
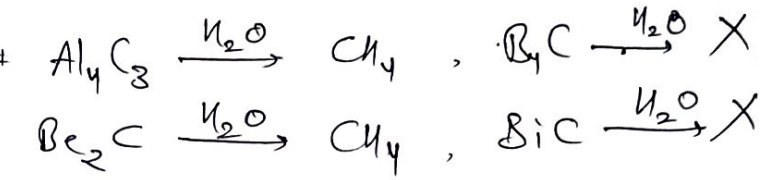
Alkynes : MOP

① By the action of water on calcium carbide [Wohler's reaction]



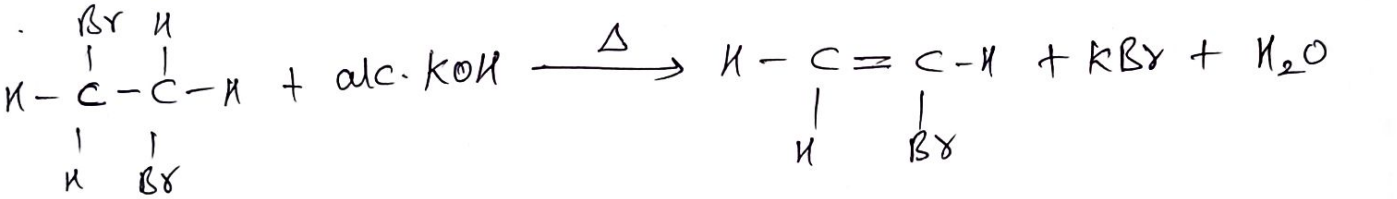


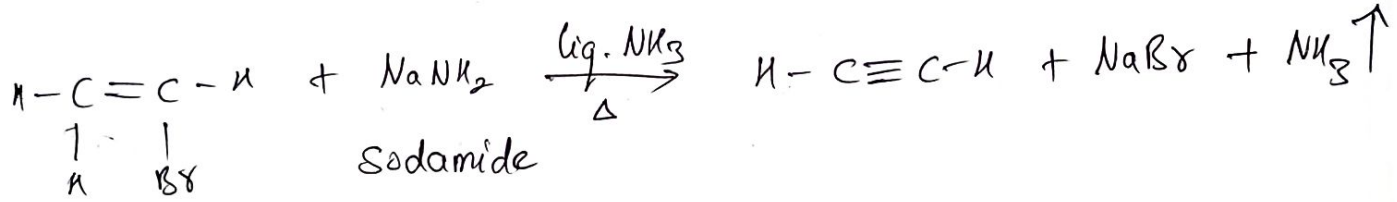




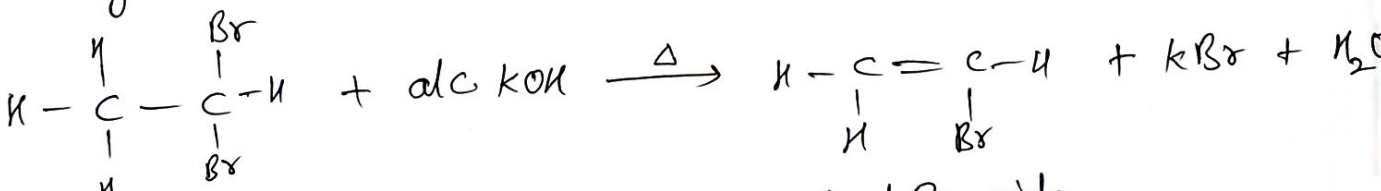
② By dehydrohalogenation of vicinal or geminal dihalides:

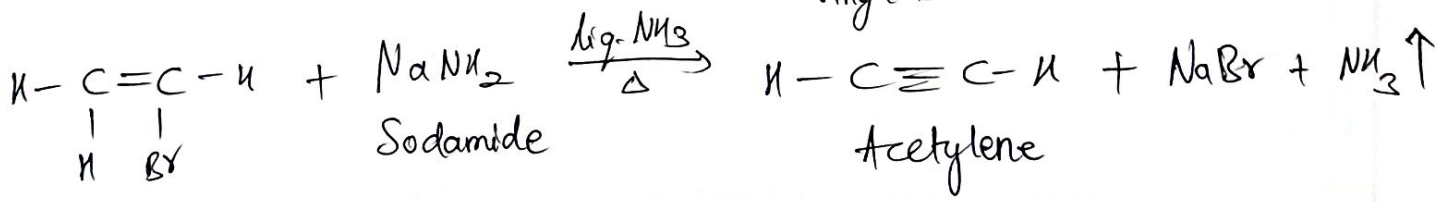
a)





b) from geminial dihalides:





Double Dehydrobalogenation:

$$Br-CH_2-CH_2-Br + 2NaNH_2 \xrightarrow[\Delta]{liq.\ NH_3} H-C\equiv C-H + 2NaBr + 2NH_3$$

$$CH_3-\underset{\underset{Br}{|}}{CH}-Br + 2NaNH_2 \xrightarrow[\Delta]{liq.\ NH_3} CH_3\equiv CH + 2NaBr + 2NH_3$$

(3) Be dehalogenation of tetrahalogen derivates of alkanes:

$$H-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-H + 2Zn \xrightarrow[\Delta]{methanol} H-C\equiv C-H + 2ZnBr_2$$

(4) Be electrolysis of aqueous solution of Potassium fumarate / Potassium meleate (Kolbe's electrolysis reaction):

$$\begin{array}{l} CH\ COOK \\ \| \\ CH\ COOK \end{array} + 2H_2O \xrightarrow{electrolysis} \begin{array}{l} CH \\ \| \\ CH \end{array} + 2CO_2 + H_2 + 2KOH$$

(5) By dehalogenation of haloform: Haloforms (chloroform, Bromoform & iodoform) on heating with silver powder undergo dehalogenation to give acetylene.

$$CHCl_3 + 6Ag + CHCl_3 \xrightarrow{\Delta} HC\equiv CH + 6AgCl$$

⑤ Synthesis from Carbon & Hydrogen (Berthelot's synthesis):

$$2C + H_2 \xrightarrow[3270K]{\text{electric arc}} HC \equiv CH$$

⑥ Synthesis of higher Alkyne:

i) Lower alkyne + Grignard Reagent $\xrightarrow{\text{dry ether}}$ Alkane $\xrightarrow[\text{dry ether}]{R''-X}$ Higher alkyne

Eg. $CH_3-C\equiv CH + CH_3MgBr \xrightarrow[\text{ether}]{\text{dry}} CH_4 + Mg(C\equiv C-CH_3)Br \xrightarrow[\text{dry ether}]{CH_3-Br}$

$$CH_3-C\equiv C-CH_3 + MgBr_2$$

$$R-C\equiv CH + R'MgX \xrightarrow[\text{ether}]{\text{dry}} R'H + Mg(C\equiv C-R)X \xrightarrow[\text{dry ether}]{R''-X} R-C\equiv C-R'' + MgX_2$$

ii) $R-C\equiv C-H \xrightarrow{NaNH_2 / liq\ NH_3} R-C\equiv C^{\ominus}Na^{\oplus} \xrightarrow[-NaX]{R'-X} R-C\equiv C-R'$

Terminal Alkyne

CHEMICAL properties:

Alkynes are acidic in Nature.

$$R-C\equiv CH \longrightarrow R-C\equiv C^{\ominus} + H^{\oplus}$$

(sp^1) (stable)

a) Rxn with $Na / liq\ NH_3$, Δ

$$R-C\equiv C-H \xrightarrow[\Delta]{Na / liq\ NH_3} R-C\equiv C^{-}Na^{+} + \frac{1}{2}H_2\uparrow$$

$$H-C\equiv C-H \xrightarrow[(excess),\ \Delta]{Na / liq\ NH_3} Na^{+}-C\equiv C^{-}Na^{+} + \frac{1}{2}H_2$$

c) Rxn with $NaNH_2$

$$R-C\equiv C^{-}-H^{+} + Na^{+}NH_2^{-} \longrightarrow R-C\equiv C^{-}Na^{+} + NH_3\uparrow$$

$$H-C\equiv C-H + \underset{\text{(excess)}}{NaNH_2} \longrightarrow Na^{+}C\equiv C^{-}Na^{+} + 2NH_3\uparrow$$

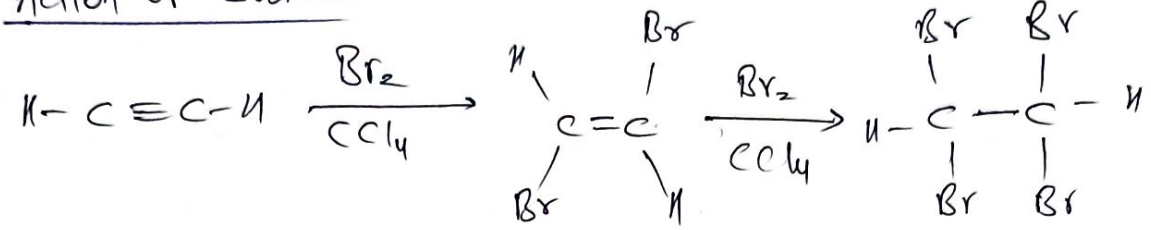
Chemical Reaction of Alkynes:

1) Addition Reaction

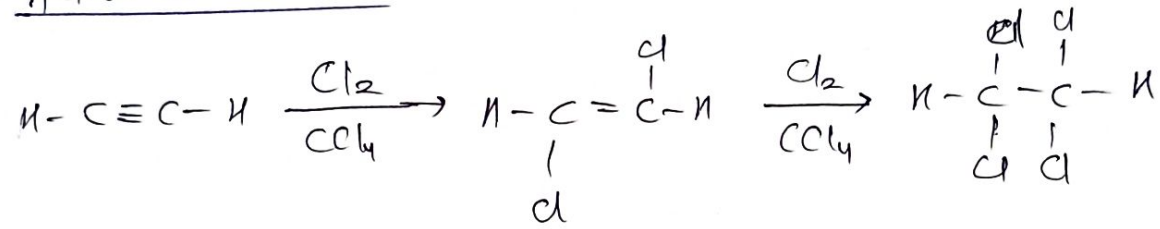
a) Hydrogenation ✓

b) Addition of Halogens:

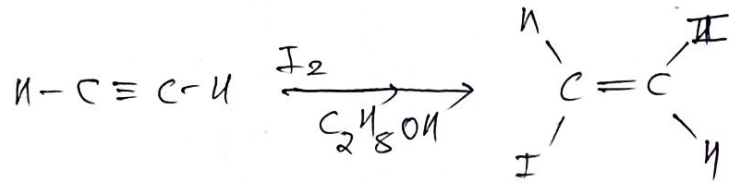
i) Action of Bromine:



ii) Action of chlorine:



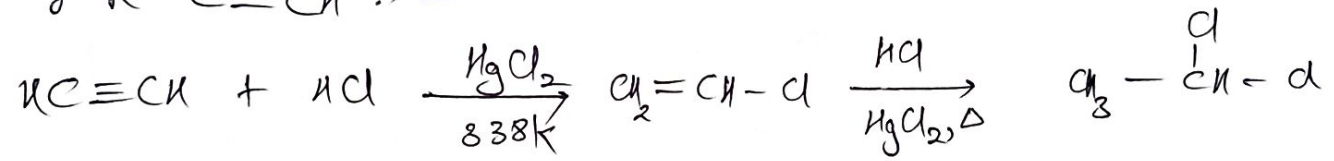
iii) Action of Iodine:



Note: $Cl_2 > Br_2 > I_2$

2) Addition of Halogen acids (HCl, HBr, HI)

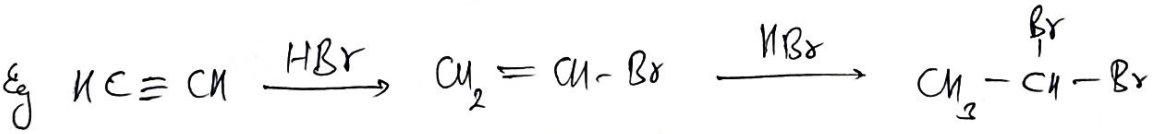
~~R-C≡CH~~ 1) Addition of HCl:



2) Action of HBr:

Unsymmetrical alkyne → Markonikov's Rule

$H_2O_2 + HBr \rightarrow$ Anti-Markonikov's Rule



Vinyl Bromide

g. $CH_3-C\equiv CH \xrightarrow{HBr} CH_3-\overset{Br}{C}=CH_2 \xrightarrow{HBr} CH_3-\overset{Br}{\underset{Br}{C}}-CH_3$

h $CH_3-C\equiv CH \xrightarrow[H_2O_2]{HBr} CH_3-HC=CH-Br \xrightarrow[H_2O_2]{HBr} CH_3-CH_2-CH_2-Br$

3) Action of HCl :

$H-C\equiv C-H \xrightarrow{HI} CH_2=CH-I \xrightarrow{HI} CH_3-\overset{I}{CH}-I$

Reactivity: $HI > HBr > HCl > HF$

4) Addition of water

$H-C\equiv C-H$ + $H-OH \xrightarrow[1\%\ HgSO_4,\ \Delta]{40\%\ H_2SO_4\ (dil)} CH_2=CH-OH \overset{tauto}{\rightleftharpoons} CH_3-CHO$

Acetylene — vinyl alcohol (enol form) — ethanal (keto form)

In unsymmetrical & terminal alkynes, Markownikoff's Rule is observed for addition.

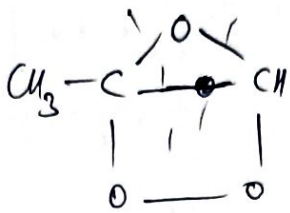
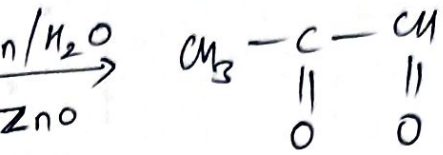
In unsymmetrical & non-terminal alkynes, a mixture of two isomeric ketones is obtained (with methyl ketone as predominant product if possible).

5) Addition of Hydrogen cyanide (HCN) :

$HC\equiv CH + HCN \xrightarrow{Ba(CN)_2} CH_2=CH-CN$

Vinyl cyanide

Ozonolysis

$CH_3-C\equiv CH \xrightarrow[196-200K]{O_3/CH_2Cl_2}$  $\xrightarrow[-ZnO]{Zn/H_2O}$ 

Propyne ozonide

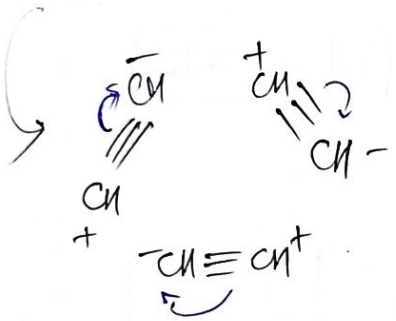
2-oxo propanal

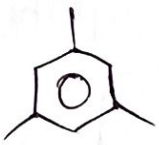
(iii) Polymerization Rxn

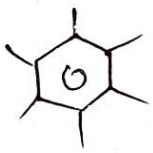
(1) Coupling Rxn of $HC\equiv CH$

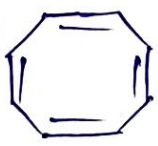
Cyclic polymerization:

$3\,CH\equiv CH \xrightarrow[\text{trimerization}]{\text{red hot iron tube, } 873K}$ 



eg $3\,CH_3-C\equiv CH \xrightarrow{\text{Red Hot Tube, } 873K}$ 

eg $3\,CH_3-C\equiv C-CH_3 \xrightarrow{\text{Red Hot Tube, } 873K}$ 

(2) $4\,CH\equiv CH \xrightarrow[DMF,\ High.P]{Ni(CN)_2}$  (Non aromatic) 

Tube like stru.

③ Linear coupling

$$2CH \equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2 = CH - C \equiv CH$$

Vinyl acetylene

$CH \equiv CH$ ⟷ $H - C \equiv CH$

④ oxidative coupling

$$2R - C \equiv C - Cu \xrightarrow{O_2} R - C \equiv C - C \equiv C - R$$

$R - C \equiv C - [Cu + O_2 + Cu] - C \equiv C - R$

Test of Terminal alkyne

1) Tollen's Test

$$R - C \equiv C - H \xrightarrow[NH_4OH]{AgNO_3} R - C \equiv C^- Ag^+$$

white ppt

2) Cuprous chloride test:

$$R - C \equiv C - H \xrightarrow[NH_4OH]{Cu_2Cl_2} R - C \equiv C - Cu$$

Red ppt