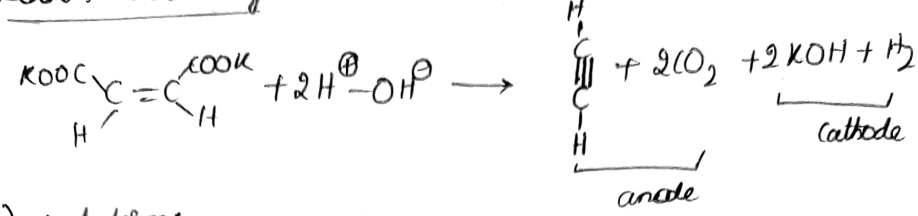
Alkynes

→ G.F – C_nH_{2n-2}, sp – 180° (linear), C–C – 1.20Å, C–H – 1.06Å

atleast 5 C to exhibit isomerism, less reactive than alkenes.

(I) Preparation

i) Kolbe's electrolysis:



ii) iodoform:

$2CHI_3 + 6Ag \longrightarrow H-C\equiv C-H + 6AgI$

iii) Carbides:

$CaC_2 \xrightarrow{\text{hydrolysis}} H-C\equiv C-H + Ca(OH)_2$

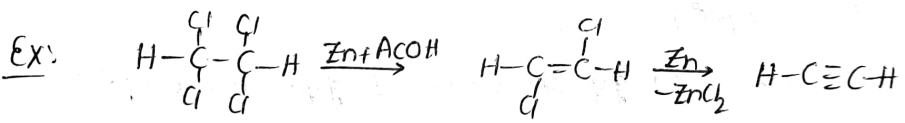
$Mg_2C_3 \xrightarrow{\text{hydrolysis}} CH_3-C\equiv C-H + 2Mg(OH)_2$

iv) Dehalogenation: removal of only X_2

a) Zn + CH_3COOH c) Ag in C_2H_5OH e) Aq. KOH

b) Mg in C_2H_5OH d) NaI in acetone

Ex:



v) Dehydrohalogenation: removal of H_2O & X_2

@ alc. KOH (or) NaOH

ⓑ Solid KOH — if strong base used it undergoes E_2 elimination

ⓒ $NaNH_2$

from gem, vicinal dihalide we can get alkynes.

higher alkynes using acetylides ($CH\equiv C^{\ominus}$)

acetylide is possible if terminal alkyne only

$H-C\equiv C-H \xrightarrow{2NaNH_2} Na^{\oplus}C^{\ominus}\equiv C^{\ominus}Na^{\oplus}$ $\quad H_2O > CH\equiv CH$ (acidic character)

vi) with Grignard reagent

$CH_3-C\equiv C-H \xrightarrow{CH_3MgBr} CH_3-C\equiv CMgBr \xrightarrow{C_2H_5I} CH_3-C\equiv C-C_2H_5 + MgI_2$

vi) with carbonyl compounds:

$$CH_3-C\equiv C-H \xrightarrow[\text{ii) } CH_3CHO \text{ ; iii) } H_3O^{\oplus}]{\text{i) } NaNH_2} CH_3-C\equiv C-\underset{}{\overset{OH}{C}}H-CH_3$$

vii) with 1°-R-X

$$H-C\equiv C-H \xrightarrow[R-X]{NaNH_2} R-C\equiv C-R$$

if 2°, 3° R-X used E_2 elimination.

with NH_3 ($NaNH_2$) effervescence is observed.

$$H-C\equiv C-H \xrightarrow[\text{ii) } CH_3-\underset{Cl}{C}H-CH_3]{\text{i) } NaNH_2} H-C\equiv C-Na + CH_3-\underset{Cl}{C}H-CH_3 \rightarrow H-C\equiv C-H + CH_2=CH-CH_3$$

$$Ag-C\equiv C-Ag + 2HCl \longrightarrow H-C\equiv C-H + 2AgCl$$

(Acetylene)

viii) Berthelot synthesis:

$$2C + H_2 \xrightarrow[3270K]{\text{electric arc}} C_2H_2$$

ix) Fritsch Buttenberg Wiechel rearrangement:

$$\underset{Ph}{\overset{Ph}{}}\!>C=C<\underset{H}{\overset{Br}{}} \xrightarrow[-C_2H_5OH]{C_2H_5O^{\ominus}} Ph-C\equiv C-Ph$$

(II) Physical Properties:

→ alkynes upto 4C are gases, C_5-C_{12} are liquids, above C_{12} solids.

→ only acetylene have garlic odour due to impurities like PH_3 & H_2S

(III) Chemical Properties:

i) addⁿ of H_2

$$H-C\equiv C-H + H_2 \xrightarrow{Pt/Pd/Ni} CH_2=CH_2 \xrightarrow{H_2} C_2H_6$$ (Sabatier - Senderens reduction)

$$\underset{H}{\overset{R}{}}\!>C=C<\underset{R}{\overset{H}{}} \xleftarrow[\text{liq } NH_3]{H_2/Na \text{ in}} R-C\equiv C-R \xrightarrow[\text{quinoline}]{H_2/Pd-BaSO_4} \underset{H}{\overset{R}{}}\!>C=C<\underset{H}{\overset{R}{}}$$

ii) $E^{\oplus}$ addⁿ

$$H-C\equiv C-H + Cl_2 \xrightarrow{SbCl_5} H-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-H$$ (westron) solvent)

$$CH_3-C\equiv C-H + Br_2 \xrightarrow{CCl_4} CH_3-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-H$$

Red-brown   colourless

→ Addⁿ of halogen acids (HX)

Order of reactivity – HI > HBr > HCl > HF (M·R)

$$H-C\equiv C-H \xrightarrow{H-Cl} CH_2=CHCl \xrightarrow[M.R]{HCl} CH_3-CHCl_2$$

→ Addⁿ of hypohalous acid or halohydrin formation:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \quad (M\cdot R)$$

$$H-C\equiv C-H \xrightarrow{HOCl} H-\underset{OH}{\overset{OH}{C}}-\underset{Cl}{\overset{Cl}{C}}-H \xrightarrow[-H_2O]{\Delta} H-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{Cl}{C}}-H$$

→ with $AsCl_3$

$$H-C\equiv C-H + AsCl_3 \longrightarrow H-\overset{Cl}{\overset{|}{C}}=CHAsCl_2$$ (or) Lewinite

$Nu^{\ominus}$ addⁿ rxns

→ Alkynes undergo nucleophilic addⁿ in presence of heavy metal ions (Ex: Ba^{2+}, Hg^{2+}, Cu^{+}, Cu^{2+}, Ni^{2+}, etc)

i) Hydration (1% 4 Hg SO_4 + 30% H_2SO_4 / Δ) – M·R

$$H-C\equiv C-H \xrightarrow{Hg^{2+}} CH_3-\overset{H}{\overset{|}{C}}=O$$

for internal $CH_3-C\equiv C-CH_3$ (O, H_2 (or) H_2, O)

for external $HC\equiv C-H$ (O, H_2 only)

ii) with HCN

$$H-C\equiv C-H \xrightarrow{HCN} H-\underset{H}{\overset{|}{C}}=\overset{CN}{\overset{|}{C}}-H$$

vinyl cyanide (or) acrylonitrile

iii) with CH_3COOH

$$H-C\equiv C-H \xrightarrow{CH_3COOH} CH_2=CH-O-\overset{O}{\overset{\|}{C}}-CH_3$$

vinyl acetate

iv) with alcohol

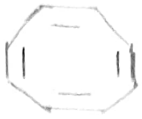
$$H-C\equiv C-H + C_2H_5OH \xrightarrow[\Delta]{HgSO_4} CH_2=\underset{H}{\overset{OH}{C}}-O-C_2H_5 \xrightarrow[-C_2H_5OH]{} CH_2=\overset{OH}{\overset{|}{C}}-H \rightleftharpoons CH_3CHO \quad (T\cdot M)$$

v) with HBO

$$CH_3-CH_2-C\equiv C-H \xrightarrow[ii)\,H_2O_2/OH^{\ominus}]{i)\,BH_3/THF} CH_3-CH_2-CH=\overset{OH}{\overset{|}{C}}-H \underset{T\cdot M}{\rightleftharpoons} CH_3-CH_2-CH_2-CHO$$

→ Polymerisation:

$3CH \equiv CH \xrightarrow{Fe/\Delta} C_6H_6$

$4CH \equiv CH \xrightarrow[\Delta]{Ni(CN)_4}$ 

Linear

$2\,H-C\equiv C-H \xrightarrow[CuCl_2]{NH_4Cl,} CH_2=CH-C\equiv CH$

$H-C\equiv C-H$

$CH_2=CH-C\equiv C-CH=CH_2$

NOTE:	Alkane	Alkene	Alkyne	
			Terminal	Internal
① Br_2 test	X	✓	✓	✓
② Bayer's test	X	✓	✓	✓
③ Tollen's test	X	X	✓	X
④ Ammonical copper-(I) chloride	X	X	✓	X

→ Oxidation with SeO_2

$H-C\equiv C-H \xrightarrow{SeO_2} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$ (or) $\begin{matrix}CHO\\CHO\end{matrix}$

→ Bayer's reagent (cold, dil, alkaline $KMnO_4$) without $C=C$ cleavage

$\equiv C-R \xrightarrow{B.R} -\overset{O}{\overset{\|}{C}}-R$

$\equiv C-H \xrightarrow{B.R} -COOH$

hot, alk; acidified $KMnO_4$

$\equiv C-R \xrightarrow[\Delta]{KMnO_4/H^{\oplus}} R-COOH$

$\equiv C-H \xrightarrow[\Delta]{KMnO_4/H^{\oplus}} H-\overset{\beta}{C}-OH \longrightarrow CO_2+H_2O$

→ Preparation of heterocyclic compounds.

$2CH \equiv CH + S \xrightarrow[\text{metal tube}]{\text{Red hot}}$ 

$2CH \equiv CH + NH_3 \xrightarrow{\text{II}}$  pyrrole

$2CH \equiv CH + HCN \xrightarrow{\text{II}}$  pyridine

$CH \equiv CH + CH_2N_2 \xrightarrow{\text{II}}$  pyrazole

→ **Isomerisation**: shifting of internal or terminal alkynes.

$$CH_3-C\equiv C-CH_3 \xrightarrow{NaNH_2} H_3C-CH_2-C\equiv C-H \xrightarrow{alc.KOH} CH_3-C\equiv C-CH_3$$

→ **Propargylic halogenation**:

$H-C\equiv C-CH_2-$

↓ propargylic carbon. It reacts with NBS, SO_2Cl_2, Me_3COCl, Cl_2

$$H-C\equiv C-CH_3 \xrightarrow{NBS} H-C\equiv C-CH_2-Br$$

→ with Sia_2BH

$$CH_3-C\equiv C-H \xrightarrow[ii)\ H_2O_2/OH^{\ominus}]{i)\ Sia_2BH} H_3C-HC=C(OH)-H \xrightleftharpoons{T.M} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$$

→ with chromic acid ($K_2Cr_2O_7 + H_2SO_4$)

$$CH\equiv CH + H_2O + [O] \longrightarrow CH_3COOH$$