Alkynes

These are unsaturated hydrocarbons with general formula C_nH_{2n-2} e.g. C_2H_2 (ethyne), C_3H_4 (propyne).

Structure

H—C≡C—H contains 3 σ and 2π-bonds and bond length is 120 pm. In acetylene, H—C—C bond angle is 180°. In alkynes, position of triple bond is determined by ozone (O_3). In alkynes show position chain functional and ring **chain isomerism.**

Methods of Preparation of Alkynes

(i) From calcium carbide

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + C \longrightarrow CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

(ii) From *vicinal* dihalides

$$H_2C(Br)-CH_2(Br) \xrightarrow[\text{Alcohol}]{\text{KOH}} \underset{\text{– KBr, – } H_2O}{H_2C=CHBr} \xrightarrow[\text{– NaBr, – } NH_3]{NaNH_2} HC\equiv CH$$

(iii) From tetrahalides

$$Br_2CH-CHBr_2 + 2Zn \xrightarrow[\Delta]{CH_3OH} H-C\equiv C-H + 2ZnBr_2$$

Physical Properties of Alkynes

(i) The first two members are gases, next eight members (C_5—C_{12}) are liquids and higher members are solids.

(ii) They are all colourless and odourless with the exception of acetylene which has slightly garlic odour due to the presence of PH_3 and H_2S as impurities.

(iii) Alkynes are insoluble in water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.

(iv) Melting point, boiling point and density increase with increase in molar mass.

Chemical Properties of Alkynes

Alkynes also exhibit electrophilic addition reaction but less reactive than alkenes because the dissociation of π-electron cloud requires more energy. Alkynes show electrophilic as well as nucleophilic addition reactions.

(i) Acidic character of alkyne

$$HC\equiv CH + Na \longrightarrow \underset{\text{Monosodium acetylide}}{HC\equiv C^-Na^+} + \frac{1}{2}H_2$$

$$H-C\equiv C^-Na^+ + Na \longrightarrow \underset{\text{Disodium acetylide}}{Na^+-C\equiv C^-Na^+} + \frac{1}{2}H_2$$

$$CH_3-C\equiv C-H + NaNH_2 \longrightarrow \underset{\text{Sodium propynide}}{CH_3-C\equiv C^-Na^+} + NH_3$$

These reactions are not shown by alkenes, alkanes and non-terminal alkynes, hence used for distinction between alkane, alkene and alkyne. Acetylenic hydrogens are acidic in nature due to 50% s-character in *sp*-hybridised orbitals.

Acidity of alkynes is lesser than water.

Acidic behaviour order

(a) $\underset{sp}{HC\equiv CH} > \underset{sp^2}{CH_2=CH_2} > \underset{sp^3}{CH_3-CH_3}$

(b) $HC\equiv CH > CH_3-C\equiv CH >> CH_3-C\equiv C-CH_3$

(ii) Electrophilic addition reactions

$$-C\equiv C- + HZ \xrightarrow{H^+} \underset{\text{vinyl cation}}{-\overset{H}{\overset{|}{C}}=\overset{\oplus}{C}-} + :Z^- \longrightarrow -\overset{H}{\overset{|}{C}}=\overset{Z}{\overset{|}{C}}-$$

The addition product formed depends upon the stability of vinylic cation. Addition on unsymmetrical alkynes takes place according to Markownikoff 's rule.

Few addition reactions are as follows :

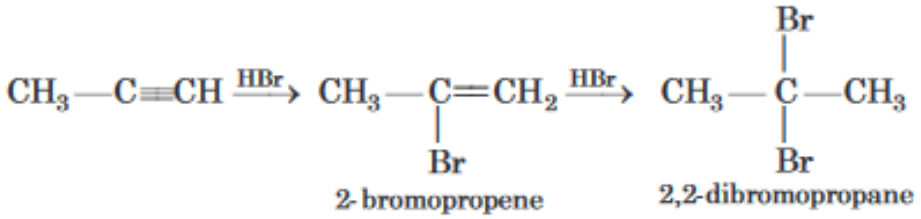
(a) Addition of dihydrogen

$$\underset{\text{propyne}}{H_3CC\equiv C-H} + H_2 \xrightarrow{Pt/Pd/Ni} \underset{\text{propene}}{[CH_3-CH=CH_2]} \xrightarrow{H_2} \underset{\text{propane}}{CH_3CH_2CH_3}$$

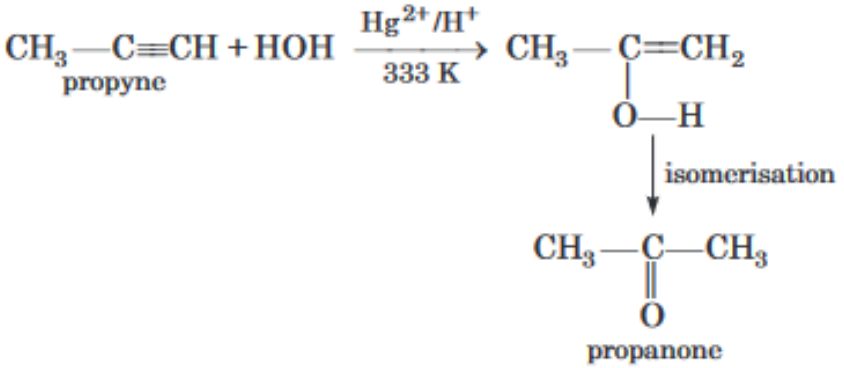
(b) Addition of halogens

$$HC\equiv CH + Cl-Cl \longrightarrow \underset{\text{1,2-dichloropropene}}{[ClHC=CHCl]} \xrightarrow{Cl_2} \underset{\substack{\text{1,1,2,2-tetrachloroethane}\\ \text{or westron}}}{\begin{matrix} Cl & Cl \\ | & | \\ HC & -CH \\ | & | \\ Cl & Cl \end{matrix}} \xrightarrow{-HCl} \underset{\text{westrosol(1, 1, 2–trichloroethene)}}{\begin{matrix} CH=CCl_2 \\ | \\ Cl \end{matrix}}$$

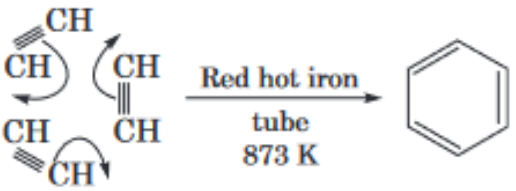
(c) Addition of hydrogen halides



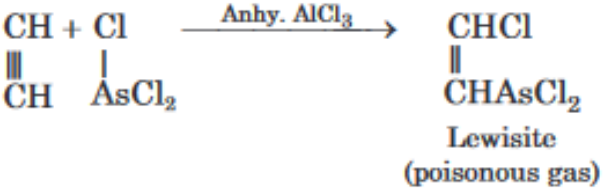
(d) Addition of water



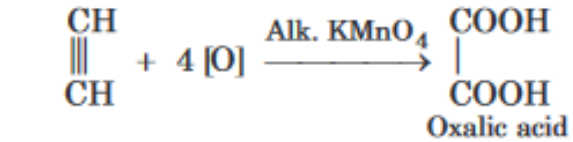
(iii) Cyclic polymerisation

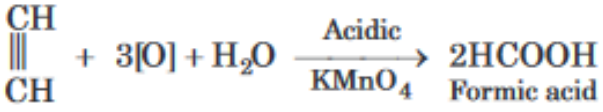


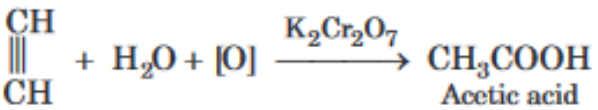
(iv) Reaction with $AsCl_3$ (arsenic trichloride)



(v) Oxidation







(vi) Ozonolysis

$$CH{\equiv}CH + O_3 \xrightarrow[Zn/H_2O]{CCl_4} \underset{\text{glyoxal}}{CHO{-}CHO} \longrightarrow \underset{\text{formic acid}}{2HCOOH}$$

Higher alkynes give diketones which are further oxidised to carboxylic acid.

(vii) Linear polymerisation

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

$$\xrightarrow{HC{\equiv}CH} \underset{\text{divinyl acetylene}}{CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2}$$

Reactions for Acetylene (C_2H_2)