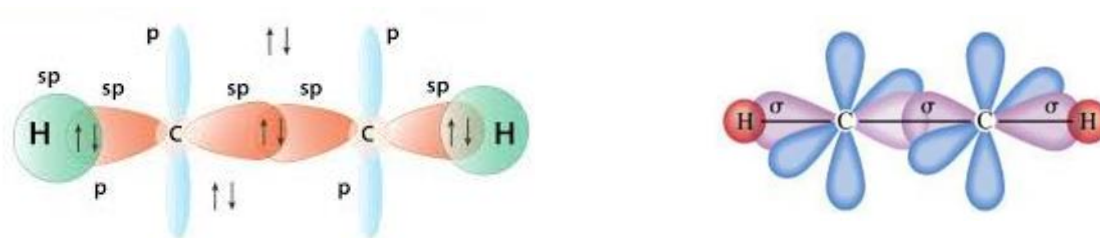


Alkynes

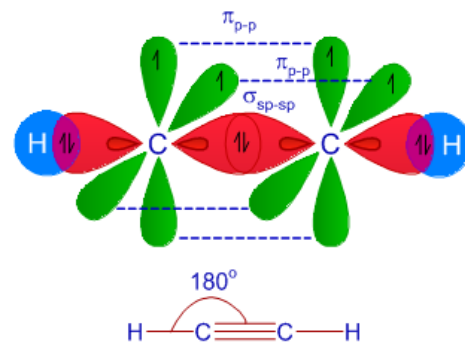
Kumud Bala

Acyclic unsaturated hydrocarbons containing a carbon-carbon triple bond are called alkynes or acetylenes. Their general formula is C_nH_{2n-2} where $n= 2, 3, 4$ etc.

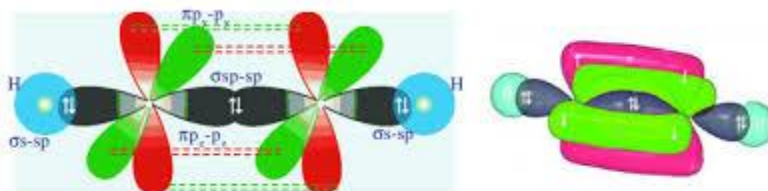
Structure of triple bond: Ethyne is the first member of alkyne series. Its structure is:



Each carbon atom of ethyne is sp -hybridized and hence has two sp -hybridized orbitals. One sp -hybridized orbitals of each carbon undergoes head on overlap with sp -hybridized orbitals of another carbon to form a sp - sp , C-C, σ -bond. The second sp -hybridized orbitals of each carbon overlaps along the internuclear axis with $1s$ -orbital of each of the two hydrogen atoms forming two sp - s , C-H, σ -bonds. Each carbon is now left with two unhybridized p -orbitals ($2p_x$ and $2p_y$) which are perpendicular to each other as well as to the plane of the carbon-carbon sigma bond. The two $2p_x$ -orbitals, one on each carbon, are parallel to each other and hence overlap sideways to form a π -bond. Similar overlap between $2p_y$ -orbitals, on each carbon, results in the formation of a second π -bond.

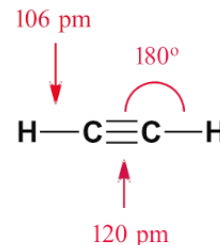


Since a p -orbital has two lobes, the electron cloud of a π -bond has two halves. If the two halves of one σ -bond (formed by overlap of $2p_x$ -orbitals) are considered to lie in the plane of the paper, then one of the two halves of the second π -bond (formed by the overlap of $2p_y$ -orbitals) would lie above the plane of the paper and the other below the plane of the paper. However, the four halves of the electron clouds of two π -bonds do not stay as such but merge together to form a single electron cloud which has cylindrical symmetry about the internuclear axis.



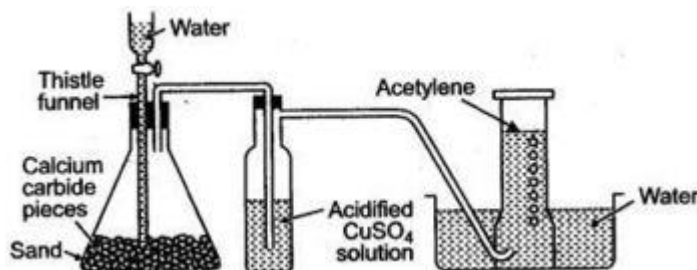
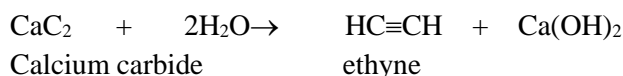
It is because of the cylindrical symmetry of the electron cloud between two carbon atoms that ethyne is a linear molecule with H-C-C bond angle of 180° .

It follows that a carbon-carbon triple bond consists of one strong σ -bond and two weak π -bonds. Total strength of carbon-carbon triple bonds in ethyne is 823 kJ/mol. It is stronger than carbon-carbon double bond of ethene (599 kJ/mol) and carbon-carbon single bond of ethane (348 kJ/mol). Further, due to smaller size of sp -orbitals (as compared to sp^2 and sp^3) and sideways overlap of p -orbitals, the carbon-carbon bond length in ethyne is shorter (120 pm) than those of $C=C$ double bond (134 pm) and $C-C$ single bond (154 pm). In spite of the presence of two π -bonds, alkynes are less reactive than alkenes towards addition reactions. Further, alkynes unlike alkenes do not exhibit geometrical isomerism due to their linear structure.



Methods of preparation of alkyne:

1. By the action of water on calcium carbide: Ethyne is prepared in the laboratory as well as on a commercial scale by the action of water on calcium carbide.



Calcium carbide needed for the purpose is manufactured by heating limestone (calcium carbonate) with Coke in an electric furnace at 2275K.

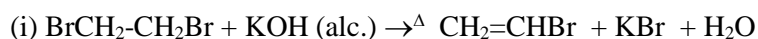
Procedure: lumps of calcium carbide are placed on a layer of sand in a conical flask fitted with dropping funnel and a delivery tube. The air present in the flask is replaced by oil gas since acetylene forms an explosive mixture with air. Water is now dropped from the dropping funnel and the acetylene gas thus formed is collected over water.

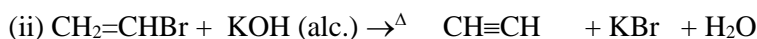
Purification: Acetylene gas prepared by the above method contains impurities of hydrogen sulphide and phosphine due to the contaminations of calcium sulphide and calcium phosphide in calcium carbide. Hydrogen sulphide is removed by bubbling the gas through an acidified solution of copper sulphate while phosphine is removed by passing the gas through a suspension of bleaching powder. Pure acetylene is finally collected over water.

2. By dehydrohalogenation of dihaloalkanes: Alkynes are prepared by dehydrohalogenation of vicinal-dihaloalkanes by heating them with an alcoholic solution of potassium hydroxide. For example,

$$\text{BrCH}_2\text{-CH}_2\text{Br} + 2\text{KOH (alc.)} \rightarrow \text{CH}\equiv\text{CH} + 2\text{KBr} + \text{H}_2\text{O}$$

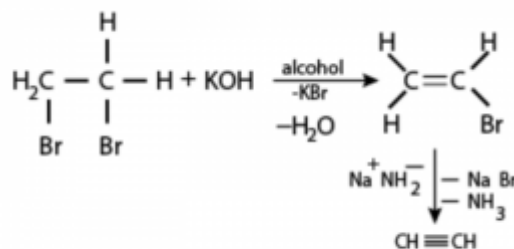
The reaction, in fact, occurs in two steps and each step involves the loss of a molecule of HBr .



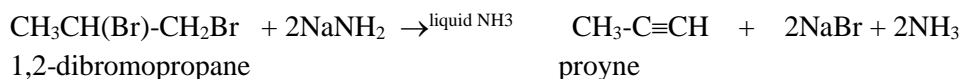
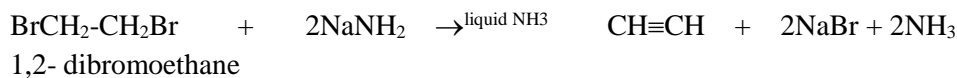


These two steps occur at different rates as explained below:

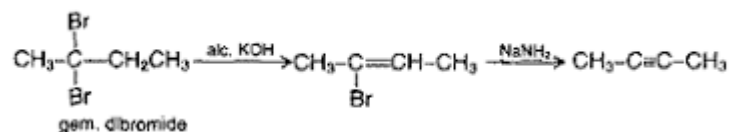
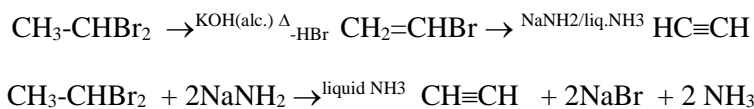
In ethylene dibromide, Br is present on a saturated carbon atom. Therefore, like alkyl halides, it is a reactive molecule. Consequently, on heating with alcoholic KOH, it readily eliminates a molecule of HBr to form vinyl bromide in good yield. In contrast, due to the presence of Br on a doubly bonded carbon atom, vinyl bromide is a highly unreactive molecule and hence on heating with alcoholic KOH, it does not easily lose a molecule of HBr to form acetylene. Thus, with alcoholic KOH, the yield of acetylene is low. Therefore, to obtain acetylene in fairly good yield from vinyl bromide, a much stronger base than alcoholic KOH such as NaNH_2 in liquid NH_3 is usually used. Thus, dehydrohalogenation of ethylene dibromide to acetylene is preferably carried out the following two stages.



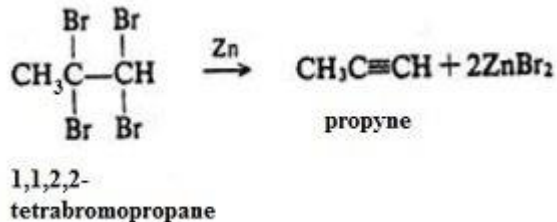
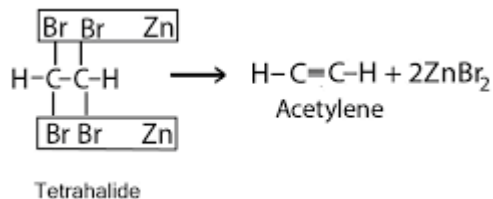
Instead of carrying out the above dehydrohalogenation in two steps, the reaction is usually carried out in one step using NaNH_2 in liquid NH_3 .



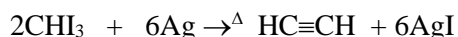
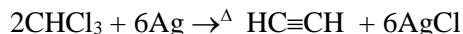
Alkyne can be prepared from gem-dihalides by the action of alcoholic KOH followed by treatment with NaNH_2 in liquid NH_3 or preferably by the action of sodamide in liquid NH_3 . For example,



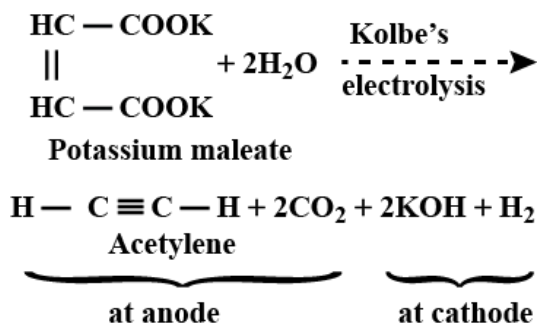
3. By dehalogenation of tetrahalides: Tetrahaloalkanes when heated with zinc dust in methanol undergo dehalogenation to yield alkene. For example,



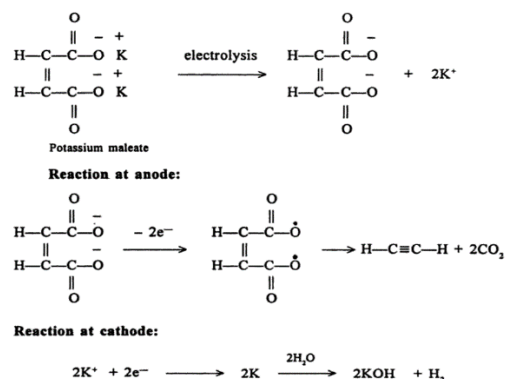
4. By dehalogenation of haloforms: Chloroform and iodoform on heating with silver powder undergo dehalogenation to form ethyne.



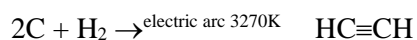
5. Kolbe's electrolytic reaction: Acetylene can be prepared by electrolysis of a concentrated solution of sodium or potassium salt of maleic acid or fumaric acid.



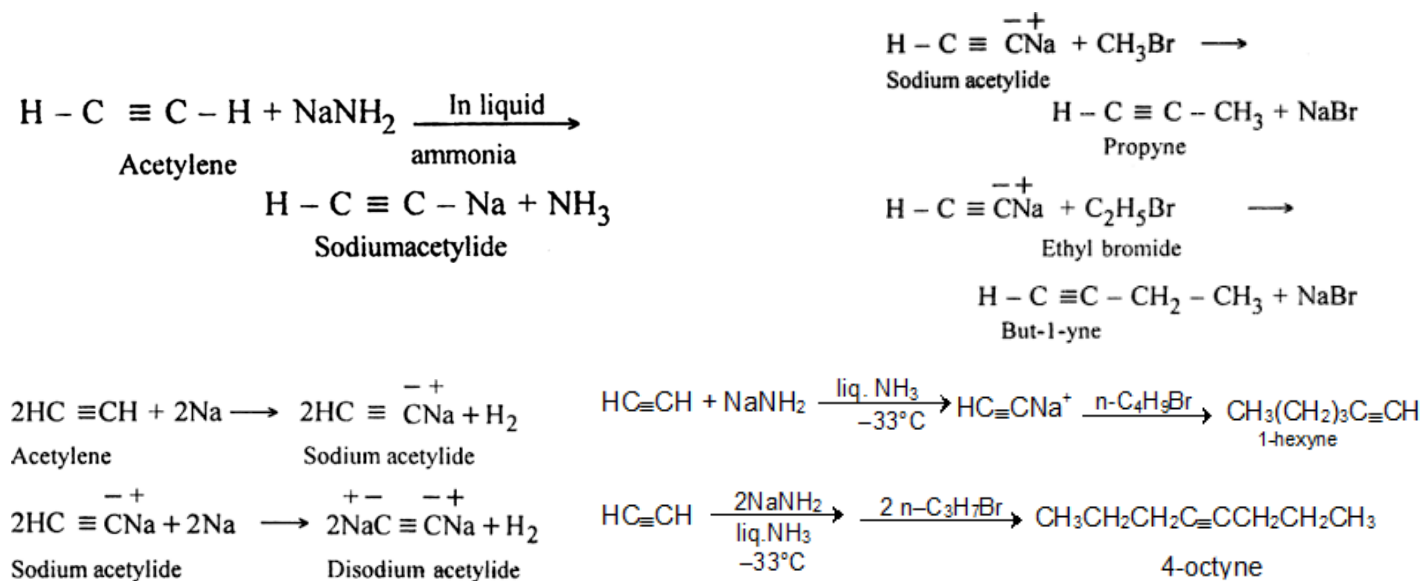
This reaction is called Kolbe's electrolytic reaction and is believed to occur by the following steps:



6. Synthesis from carbon and hydrogen: (Berthelot synthesis) Acetylene can be prepared by passing a stream of hydrogen through an electric arc struck between carbon electrodes.



7. Synthesis of higher alkynes from acetylene: Acetylene is first treated with sodium metal at 475K or with sodamide in liquid ammonia at 196K to form sodium acetylide. This upon treatment with alkyl halide gives higher alkynes. For example,



Assignment

- Acetylene gas is obtained by the electrolysis of -----
 (A) sodium fumarate (B) sodium succinate (C) sodium maleate (D) both (A) and (C)
- The IUPAC name of the compound having the formula $\text{CH} \equiv \text{C} - \text{CH} = \text{CH}_2$ is ----
 (A) 1-butyne-3-ene (B) but-1-yne-3-ene (C) 1-buten-3-yne (D) 3-buten-1-yne
- The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and alkyne. The bromoalkane and alkyne respectively are:
 (A) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C} \equiv \text{CH}$ (B) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$
 (C) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{HC} \equiv \text{CH}$ (D) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C} \equiv \text{CH}$
- When $\text{CH}_3\text{CH}_2\text{CHCl}_2$ is treated with NaNH_2 the product formed is -----
 (A) $\text{CH}_3 - \text{CH} = \text{CH}_2$ (B) $\text{CH}_3 - \text{C} \equiv \text{CH}$ (C) $\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)_2$ (D) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{NH}_2$
- Chloroform gives acetylene on treatment with ----
 (A) Li/NH_3 (B) Pt/H_2 (C) $\text{Ag}/\text{heating}$ (D) LiAlH_4
- What is the product formed when 1,1,2,2-tetrabromoethane heated with zinc dust in methanol?
 (A) acetylene (B) vinyl bromide (C) 1,1-dibromoethane (D) ethyl bromide
- Identify the compound A and B and C in the following reaction sequence: $\text{A} \xrightarrow{2\text{NaNH}_2} \text{B} \xrightarrow{2\text{CH}_3\text{I}} \text{C}$

Answers

1. (D) 2. (C) 3. (D) 4. (B) 5. (C) 6. (A) 7. (A) $\text{CH} \equiv \text{CH}$, (B) $\text{Na}^+ \text{C} \equiv \text{C}^- \text{Na}^+$ (C) $\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$