By- Shailendra Shukla Sir

Unsaturated Hydrocarbons

Alkynes

Alkynes are unsaturated hydrocarbons containing carbon-carbon triple bond (C≡C). The general formula of alkenes is C_nH_{2n-2}. The first member of alkynes is acetylene or ethyne (C_2H_2).

Preparation Methods of Alkynes

(1)From Calcium carbide

On industrial scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime is obtained by heating limestone.

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

$$CaO + 3C \xrightarrow{\Delta} \underset{\text{Calcium carbide}}{CaC_2} + CO$$

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{Ethyne}}{H-C\equiv C-H} + Ca(OH)_2$$

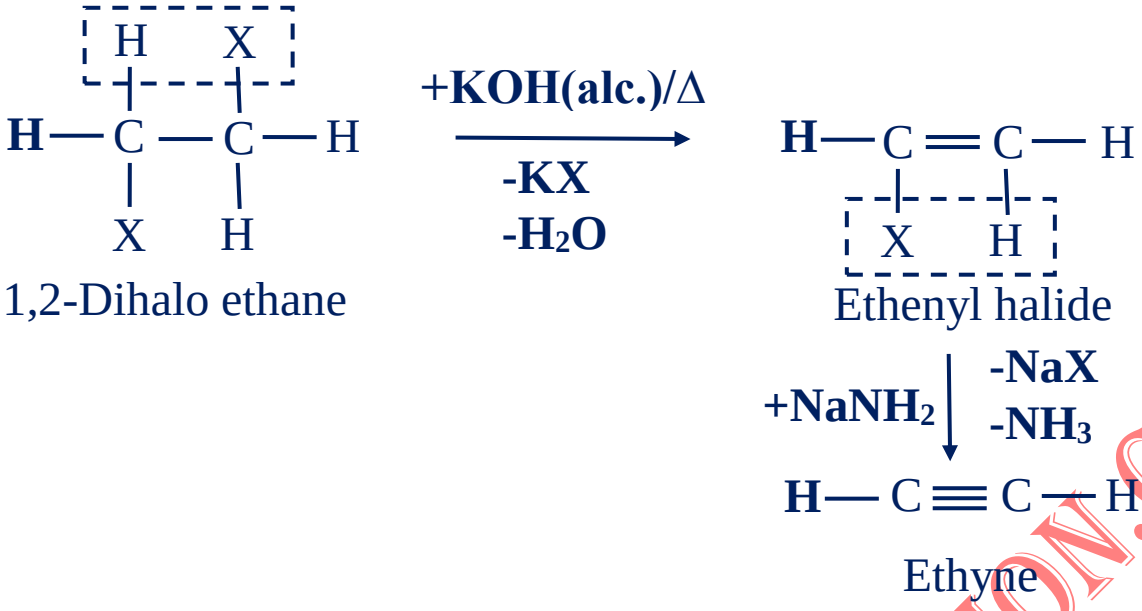
(2)From Vicinal Dihalides

Or

By Dehydrohalogenation of Vicinal Dihalides (Elimination reaction)

When vicinal dihalides are treated with alcoholic KOH, they undergo dehydrohalogenation by removal of one molecule of halogen acid to form alkenyl halides (vinyl halides), which on treatment with sodamide remove another molecule of halogen acid to form alkynes. For example, dehydrohalogenation of 1,2-dihalo ethane gives ethyne.

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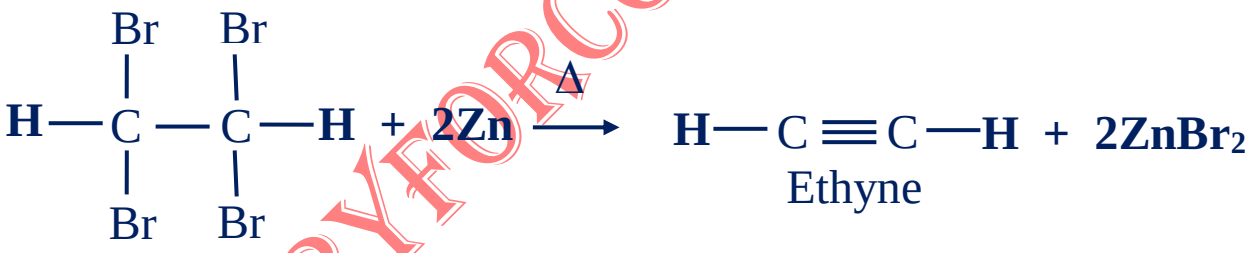
1,2-Dihalo ethane

Ethenyl halide

Ethyne

Here, after removal of one molecule of halogen acid alkenyl halides (vinyl halides) are obtained, which are highly unreactive in nature. Hence, more stronger base (sodamide) is require for removal of second molecule of halogen acid to form alkyne.

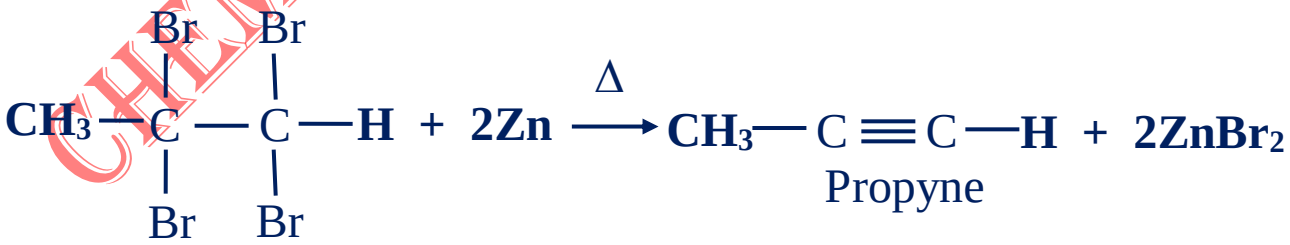
(3)By Dehalogenation of Tetrahaloethane-When 1,1,2,2-tetrahalo ethane is heated with zinc it undergoes dehalogenation to form ethyne.



1,1,2,2-tetrabromo ethane

Ethyne

Similarly, dehalogenaion of 1,1,2,2-tetrahalopropane gives propyne.



1,1,2,2-tetrabromo propane

Propyne

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Properties of Alkynes

(a)Physical Properties

(1)The first three members of alkynes are gases, the next eight are liquids and the higher members are solids.

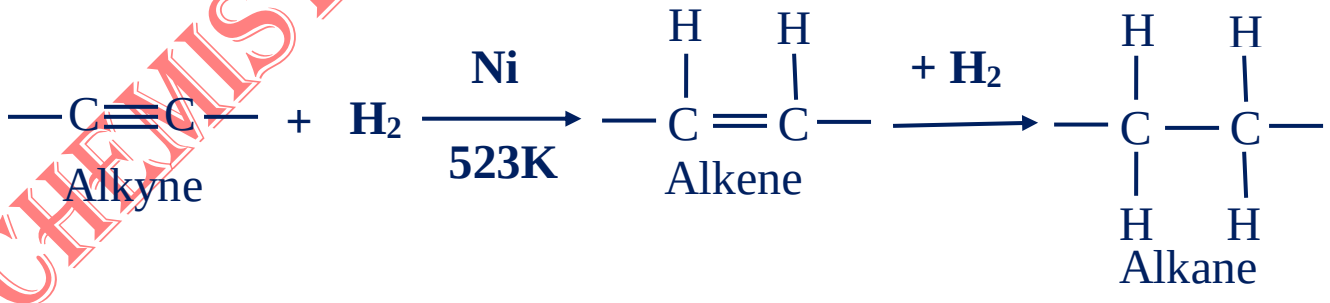
(2) All alkynes are colourless and odourless, but ethyene has its characteristic odour.
(3)Alkynes are weakly polar in nature and are lighter than water.
(4)Alkynes are immiscible (insoluble) in water, but they are fairly soluble in non- polar solvents like benzene, carbon tetrachloride, petroleum ether etc.
(5) Melting point, boiling point and density of alkynes increases regularly with increase of their molecular mass.

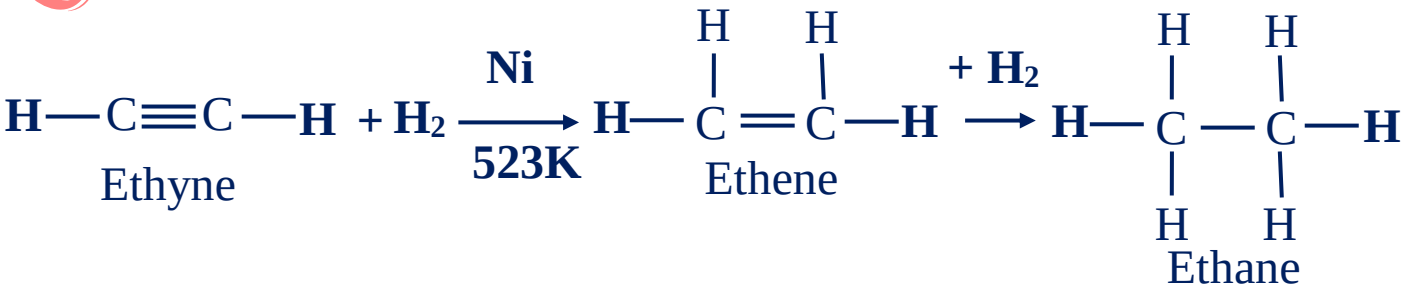
(b)Chemical Properties

Carbon-carbon triple bond (C≡C) of alkynes are the rich source of loosely held pi (π) electrons. Hence, they readily give electrophilic addition reactions in which the electrophiles add on to the carbon-carbon triple bond to form the addition products. Oxidation and ozonolysis reactions are also quite prominent in alkynes.

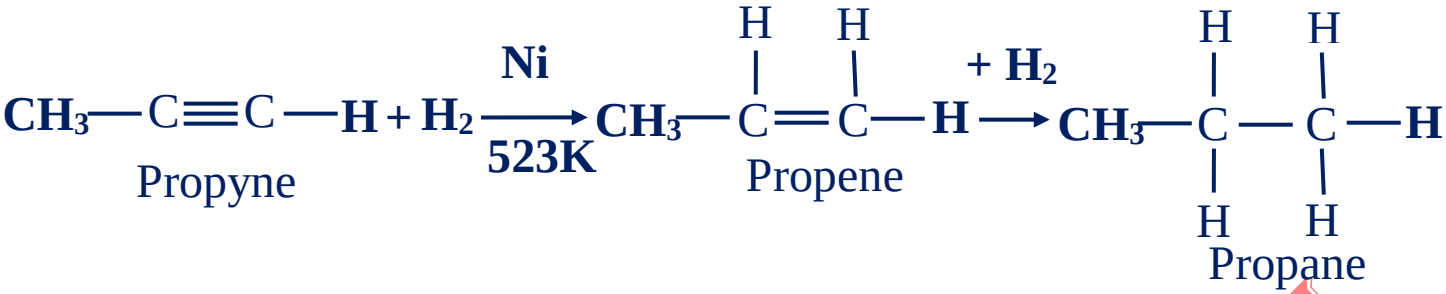
Some most common reactions of alkynes are as under-

(1)Addition of dihydrogen- Dihydrogen adds to the carbon-carbon triple bond in the presence of finely divided nickel, palladium or platinum to form alkanes. This reaction is called **hydrogenation of alkynes**. Platinum and palladium catalyze this reaction at room temperature, while, nickel catalyzes it at a relatively higher temperature (about 250^0C) and pressure.

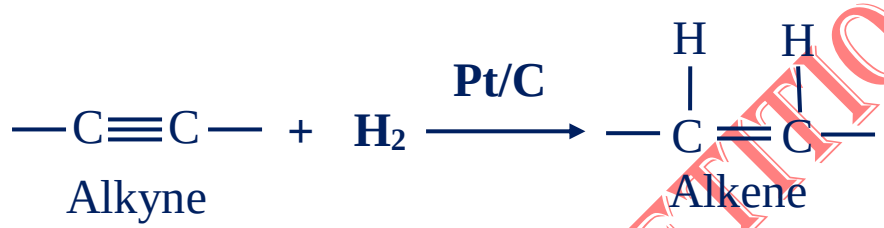


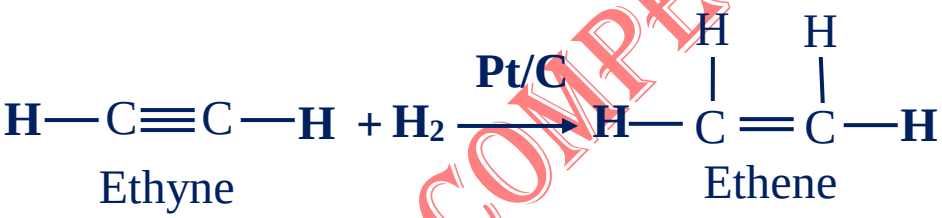


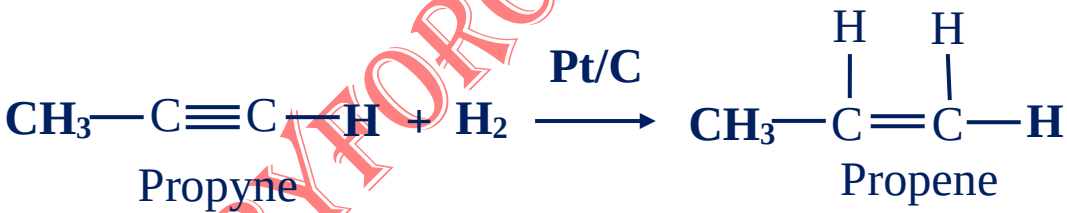
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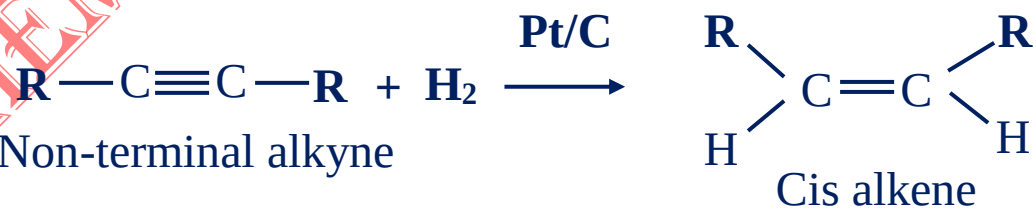
Alkynes undergo partial hydrogenation (reduction) with calculated amount of dihydrogen in the presence of palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline to give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst.

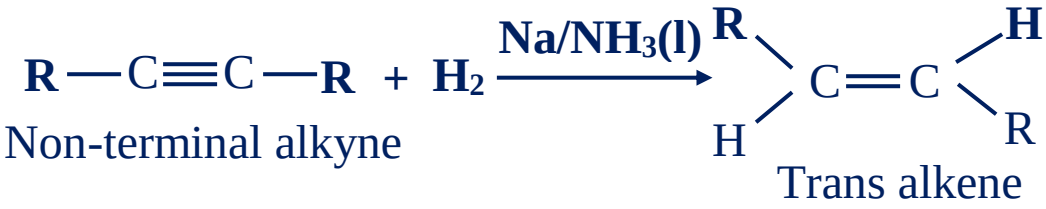






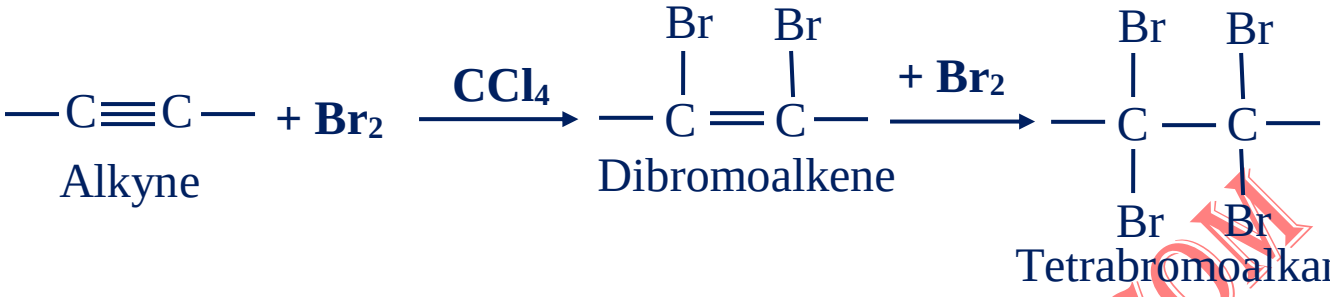
Non-terminal alkynes on partial hydrogenation (reduction) using deactivated palladised charcoal (Lindlar's catalyst) give alkenes having *cis* geometry. On the other hand, these alkynes on partial hydrogenation (reduction) using sodium in liquid ammonia or sodamide give trans alkenes.

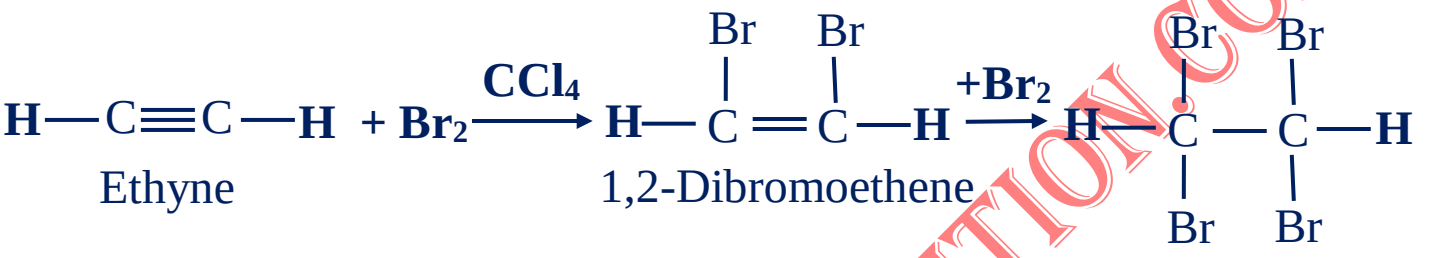




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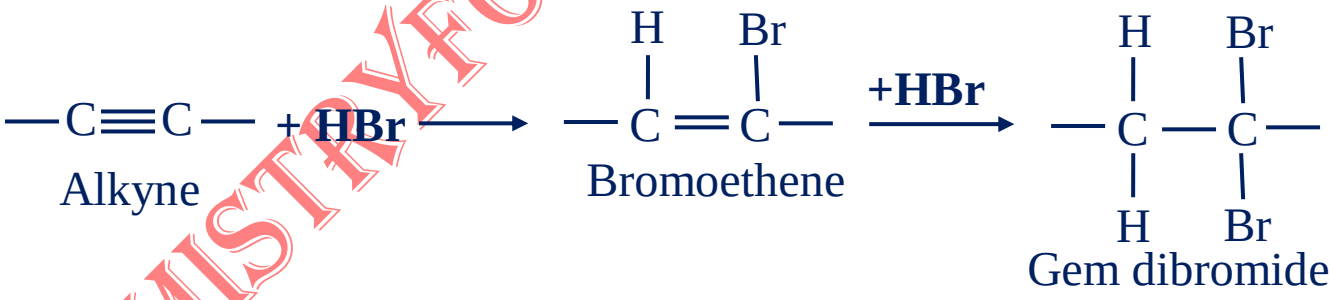
(2)Addition of Halogens-Halogens like chlorine and bromine add to the triple bond of alkynes in two step to form alkane tetrahalides.

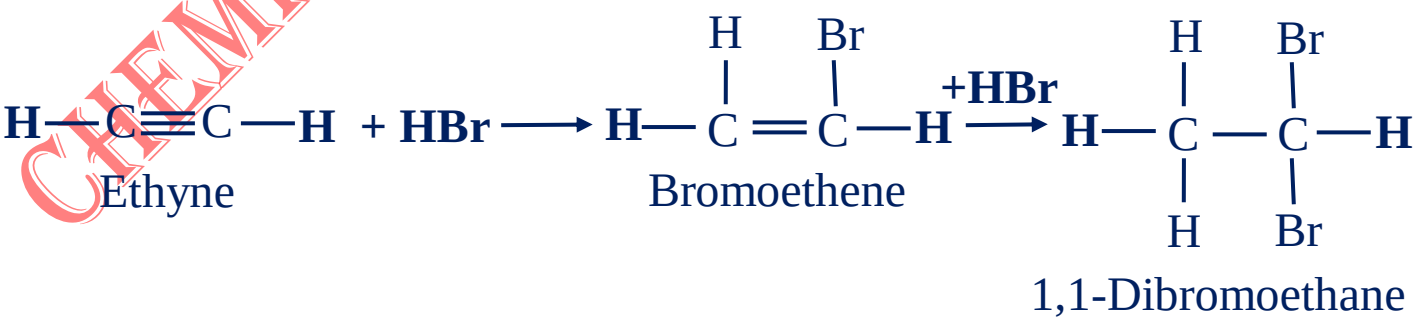




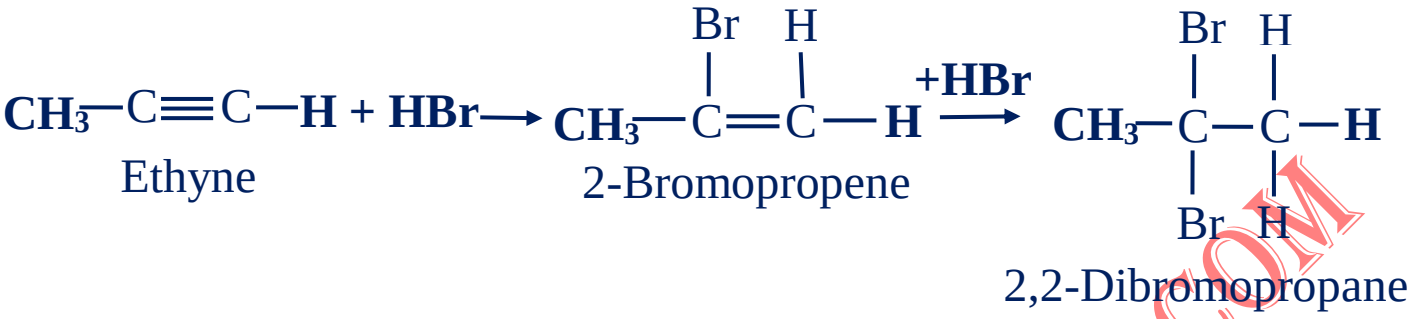
Here, reddish orange colour of bromine solution in carbon tetrachloride discharges rapidly with addition of bromine to the unsaturation site. Hence, this reaction is used as a test for unsaturation.

(3)Addition of hydrogen halides- Two molecules of hydrogen halides (HCl, HBr, HI) add to the carbon-carbon triple bond of alkynes to form gem dihalides where, both the halogen atoms get attached to same carbon atom.



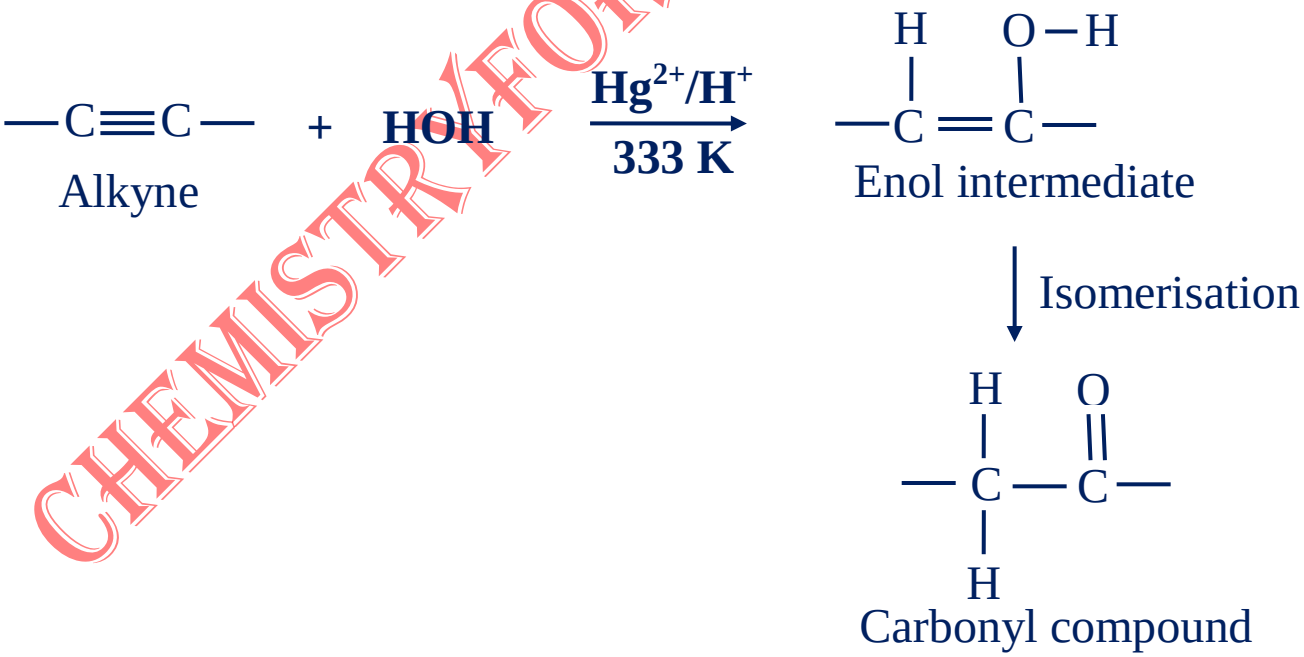


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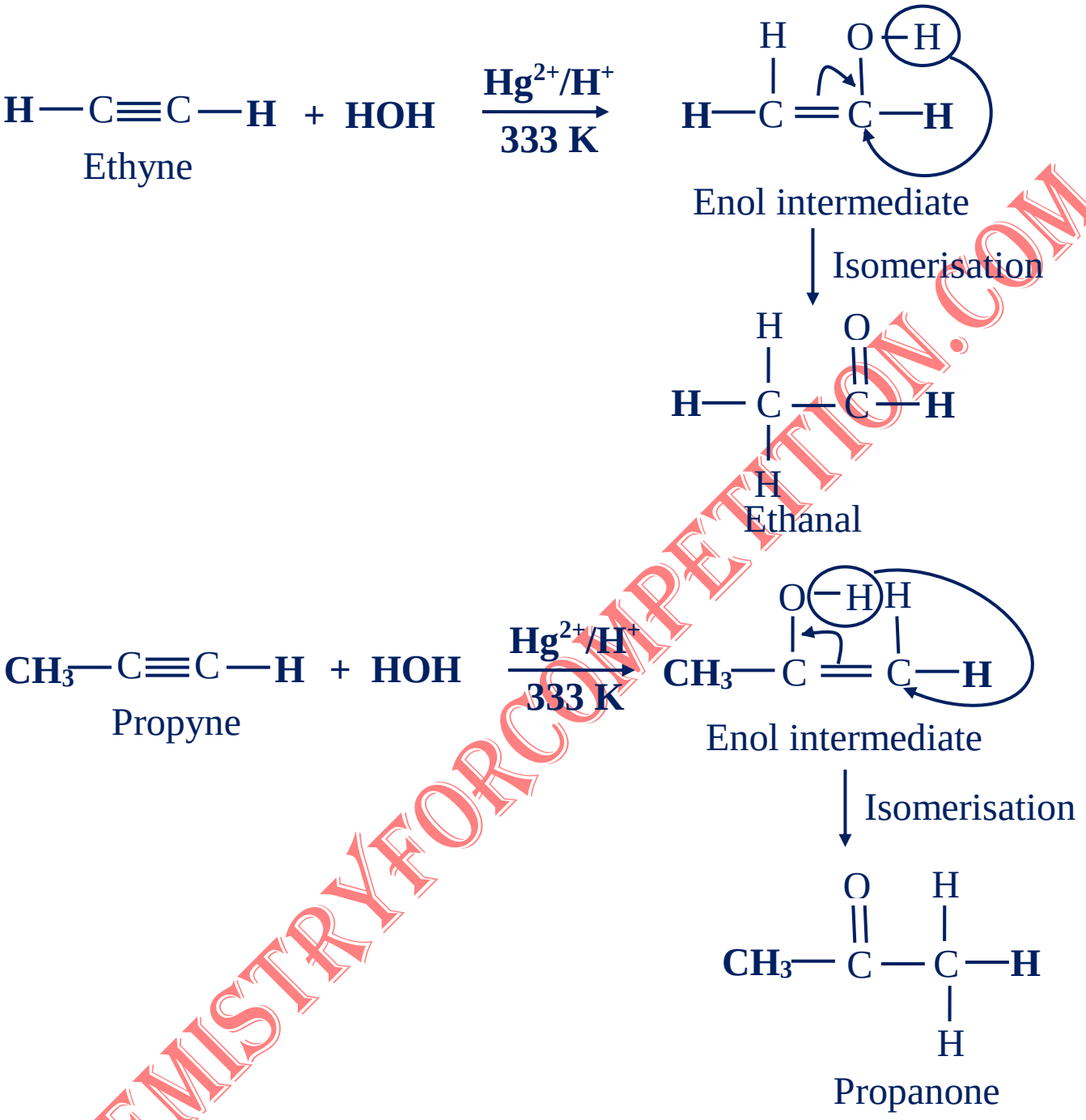
Here, in case of asymmetrical alkenes, addition occurs following Markovnikov's rule in both the steps and both the halogen atoms get attached to same carbon atom. In case of symmetrical alkenes, after addition of one molecule of halogen acid haloalkenes are obtained, where double bond is unsymmetrical. Hence, the addition of second molecule of halogen acid occurs following Markovnikov's rule and here also both the halogen atoms get attached to same carbon atom.

(4)Addition of Water-When alkynes are warmed with 40% aqueous solution of H_2SO_4 in presence of 1% aqueous solution of $HgSO_4$, a water molecule adds to the carbon-carbon triple bond to form enol intermediates which tautomerise further to form carbonyl compounds.



Here, ethyne gives aldehyde (ethanal) while, other alkynes give ketones.

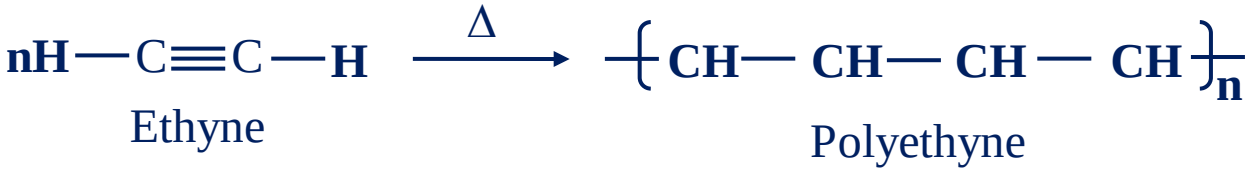
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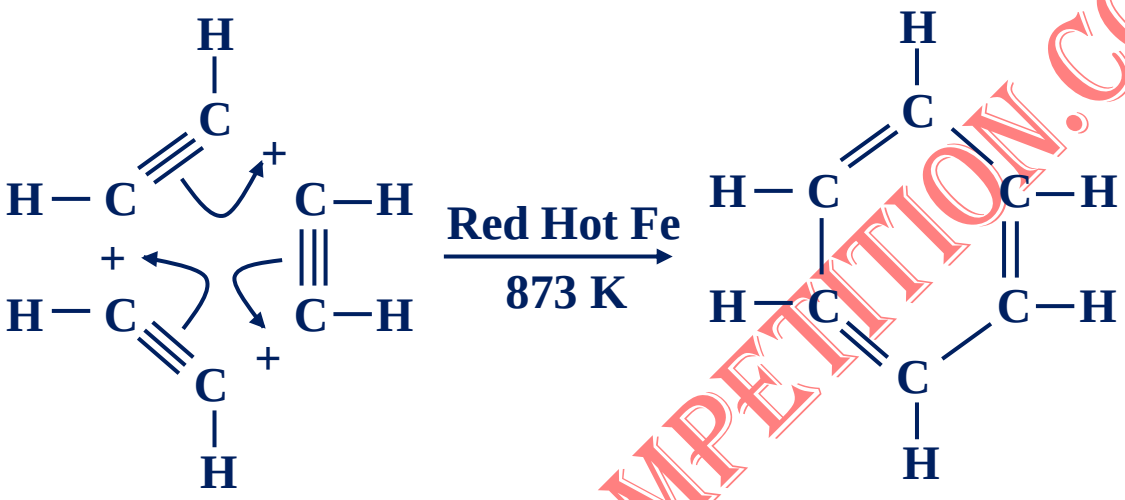
(5) Polymerisation

(a)Linear Polymerisation-Under suitable conditions ethyne undergoes linear polymerization to form polyethyne (Polyacetylene).



Polyethyne (Polyacetylene) is a high molecular weight polyene which conducts electricity in special conditions. Hence, a thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

(b) Cyclic Polymerisation- When ethyne is passed through red hot iron tube at 873K temperature, it undergoes cyclic polymerization to form benzene. This reaction is also called aromatization.



Ethyne (3 Molecules) **Benzene**

Acidic Character of Alkynes- Hydrogen atoms attached with triply bonded carbon of ethyne and terminal alkynes (1-alkynes) are weakly acidic in nature. Hence, they reacts with very strong bases such as sodium metal or sodamide ($NaNH_2$) to form sodium alkynide salts and release hydrogen gas.

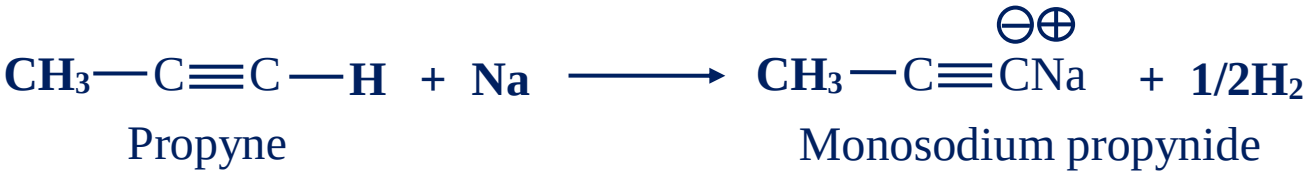


Ethyne — Monosodium ethynide or Monosodium acetylide

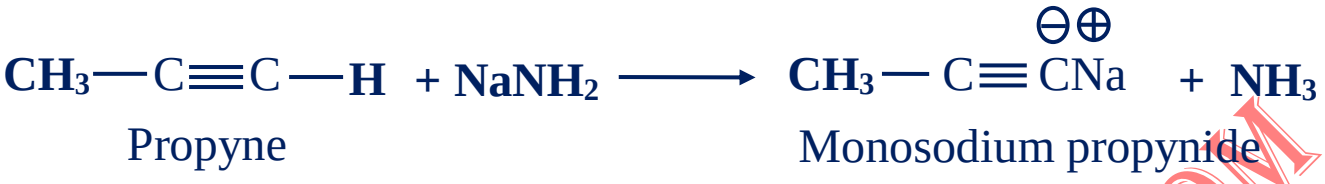


Ethyne — Disodium ethynide or Disodium acetylide

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Propyne Monosodium propynide



Propyne Monosodium propynide

Non-terminal alkynes do not contain any acidic hydrogen (hydrogen attached with triply bonded carbon atom). Hence, they do not react with sodium metal or sodamide ($NaNH_2$) to form sodium alkynide salts. For example, 2-butyne do not react with sodium metal or sodamide ($NaNH_2$) to form sodium alkynide salts.



2-Butyne

These reactions are also not given by ethene (alkenes) and ethane (alkanes). It indicates that ethyne is more acidic in nature as compared to ethene and ethane. In fact, hydrogen atoms in ethyne and 1-alkynes are attached to the *sp* hybridised carbon atoms whereas they are attached to sp^2 hybridised carbon atoms in ethene (alkenes) and sp^3 hybridised carbons in ethane (alkanes). The *sp* hybridised orbitals (having 50% s-character) of carbon atoms in ethyne molecules have highest electronegativity, hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the sp^2 hybridised orbitals of carbon in ethene (33.33% s-character) and the sp^3 hybridised orbital of carbon in ethane (25% s-character). Thus, in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane.

These reactions are used in distinction of terminal and non-terminal alkynes. It is also used in distinction of terminal alkynes with alkenes and alkanes.

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