ALKYNES

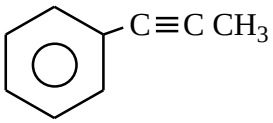
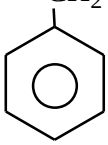
They are hydrocarbons with at least a triple bond between two carbon atoms $-C \equiv C-$

Nomenclature:

The IUPAC naming is similar to that of alkanes. The ending ***'ane'*** of the corresponding alkane is replaced by ***'yne'***.

The simplest alkyne contains two carbon atoms.

Examples include;

	Alkyne	**IUPAC name**
(i)	$HC \equiv CH$	Ethyne
(ii)	$CH_3\ C \equiv CH$	Propyne
(iii)	$CH_3\ CH_2\ C \equiv CH$	1–butyne or but–1–yne
(iv)	$CH_3C \equiv CCH_3$	2–butyne or but–2–yne
(v)	 $C \equiv C\ CH_3$	1–phenyl propyne
(vi)	$CH_2\ C \equiv CH$  etc	3–phenyl propyne

There are two types of triple bonds;

a) Terminal triple bond is one at the end of the chain. e.g. in (vi) above.

b) Internal triple bond is one in the middle of the chain. e.g. in (v) above.

Isomerism in alkynes:

Apart from ethyne and propyne, other alkynes exhibit three types of isomerism which include;

a) **Chain isomerism:**

Alkynes have the same molecular formula, same position of the functional group but the carbon chain structure is different. E.g. molecular formula C_5H_8.

→ Straight chain isomer $CH_3\ CH_2\ CH_2\ C \equiv CH$ Pent-1-yne

and

→ Branched chain isomer $CH_3CHC \equiv CH$ (with CH_3 branch) 3-methylbut-1-yne

b) **Position isomerism:**

Alkynes have the same molecular formula but different positions of the functional group on the same chain.

e.g. Molecular formula C_5H_8

→ $CH_3\ CH_2\ CH_2\ C \equiv CH$ Pent - 1 - yne (or 1 - pentyne)

→ $CH_3\ CH_2\ C \equiv\equiv C\ CH_3$ Pent - 2 - yne (or 2 - pentyne)
(same as $CH_3C \equiv\equiv CCH_2CH_3$)

c) **Functional group isomerism:**

Alkynes have same molecular formula but different functional group with dienes. Dienes are alkenes with two double bonds.
e.g. Molecular formula C_4H_6

→ $CH_3CH_2C \equiv CH$ but-1-yne (an alkyne)

→ $CH_2 = CHCH = CH_2$ 1,3-butadiene (a diene)

General Methods of Preparation

1. From dihalogen compounds:

Dihalogen compounds are refluxed with excess alcoholic potassium hydroxide. Two hydrogen halide molecules (alkyl halides) i.e. molecules of a halogen acid are eliminated.
This is an elimination reaction similar to that under preparation of alkenes from halogen compounds (alkyl halides).
Dihalogen compounds are of two types;

- Geminal dihalide in which the two halogen atoms are on the same carbon atom. i.e. RCH_2CHX_2 or RCX_2CH_3.
- Vicinal dihalides in which the two halogen atoms are on adjacent carbon atoms i.e. $RCHXCH_2X$. where X is a halogen (Cl, Br, I).

(a) From Gem dihalides

$$R\,CH_2\,CHX_2 \xrightarrow[KOH\ excess]{\text{hot ethanolic}} RC \equiv CH + 2HX$$

e.g. $$CH_3\,CH_2\,CHCl_2 \xrightarrow[\text{ethanolic KOH}]{\text{excess hot}} CH_3\,C \equiv CH + 2\,HCl$$

$$R\,CX_2\,CH_3 \xrightarrow[\text{ethanolic KOH}]{\text{excess hot}} RC \equiv CH + 2HX$$

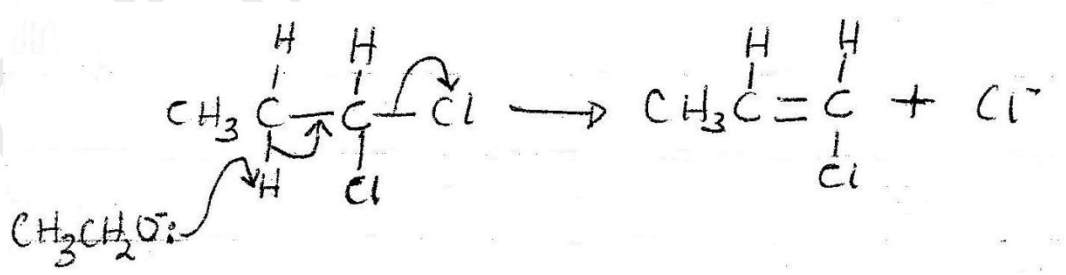
e.g. $$CH_3\,CCl_2\,CH_3 \xrightarrow[\text{ethanolic KOH}]{\text{excess hot}} CH_3\,C \equiv CH + 2\,HCl$$

Mechanism for the reaction

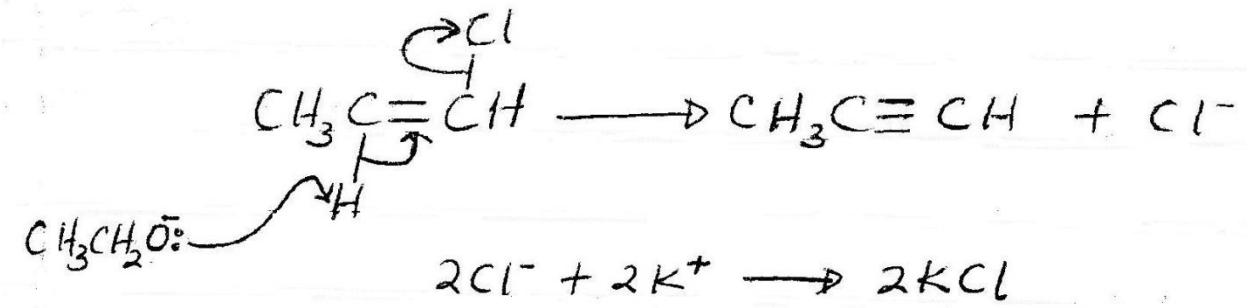
$$KOH_{(aq)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

$$CH_3\,CH_2\,OH + OH^- \longrightarrow CH_3\,CH_2O^- + H_2O$$

then;



Since the reagents are in excess, another fresh ethoxide ion (alkoxide ion) $CH_3CH_2O^-$ removes the remaining hydrogen atom to regenerate the alcohol. i.e.



(b) From vicinal dihalides

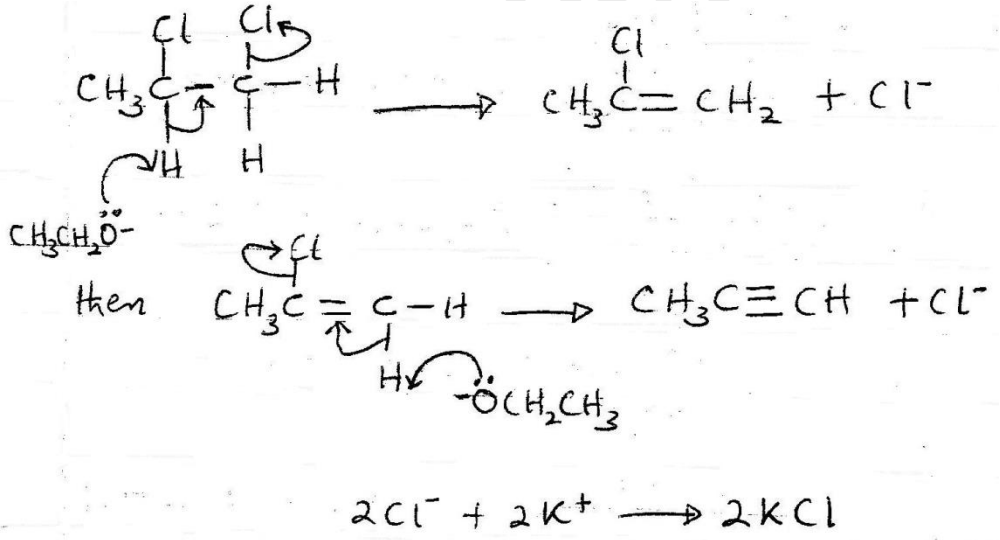
$$R\,CH\,X\,CH_2X \xrightarrow[KOH]{\text{excess hot ethanolic}} RC \equiv CH$$

$$\text{e.g } CH_3\,\underset{\displaystyle Cl}{\underset{|}{C}}H\,CH_2Cl \xrightarrow[KOH]{\text{excess hot ethanolic}} CH_3C \equiv CH$$

Mechanisms for reaction

$$KOH_{(aq)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

$$CH_3\,CH_2\,OH + OH^- \longrightarrow CH_3\,CH_2O^- + H_2O$$



2) Higher alkynes are also prepared by **reaction sodium alkynides in an inert solvent with alkyl halides.** e.g.

$$CH_3CH_2CH_2Cl + \underset{\text{(Sodium ethynide)}}{HC\equiv C^-Na^+} \longrightarrow CH_3CH_2C \equiv CH + NaCl$$

3) Other methods commonly used are specific to ethyne.

(a) Calcium oxide from calcium carbonate is heated together with coke at 2000^{o}C in an electric furnace.

$$CaO_{(s)} + 3\,C_{(s)} \xrightarrow{2000^oC} CaC_{2(s)} + CO_{(g)}$$

The calcium dicarbide formed is then hydrolysed (reacted with water). i.e.

$$CaC_{2(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)} + HC \equiv CH_{(g)}$$

The calcium dicarbide formed may alternatively be reacted with a dilute mineral acid. e.g.

$$CaC_{2(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + HC \equiv CH_{(g)}$$

(b) On an industrial scale, methane is heated at 1500°C to generate ethyne.

$$2\,CH_{4\,(g)} \xrightarrow{1500^oC} HC \equiv CH_{(g)} + 3\,H_{2(g)}$$

Reactions of Alkynes

Since alkynes have multiple bonds, their reactions are similar to those of alkenes. However here an excess of reagents is also used especially in the electrophilic addition reactions.

1) Electrophilic addition reactions

(a) Addition of halogens (Cl_2, Br_2 or I_2)

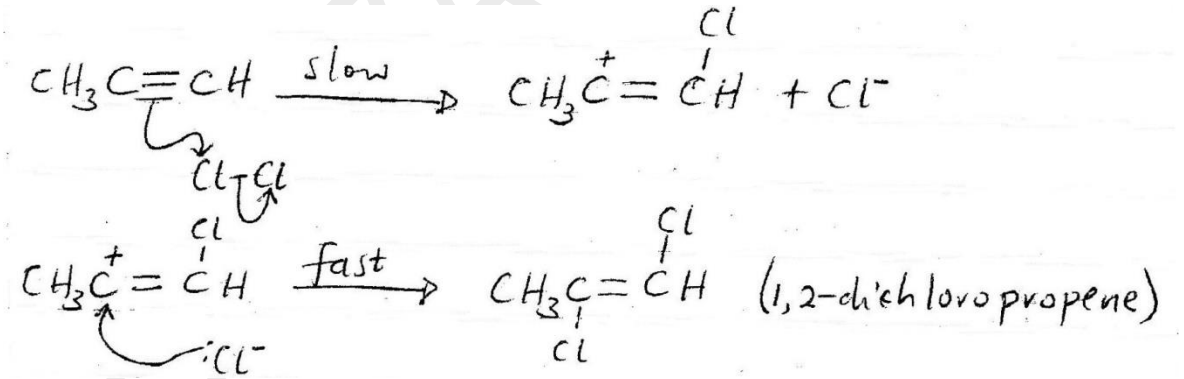
(i) Alkynes add one or two moles of halogens producing dihalides and tetrahalides respectively, in presence of an inert solvent, CCl_4.

$$RC \equiv CH + \underset{\text{excess}}{2X_2} \longrightarrow R\,CX_2\,CHX_2$$

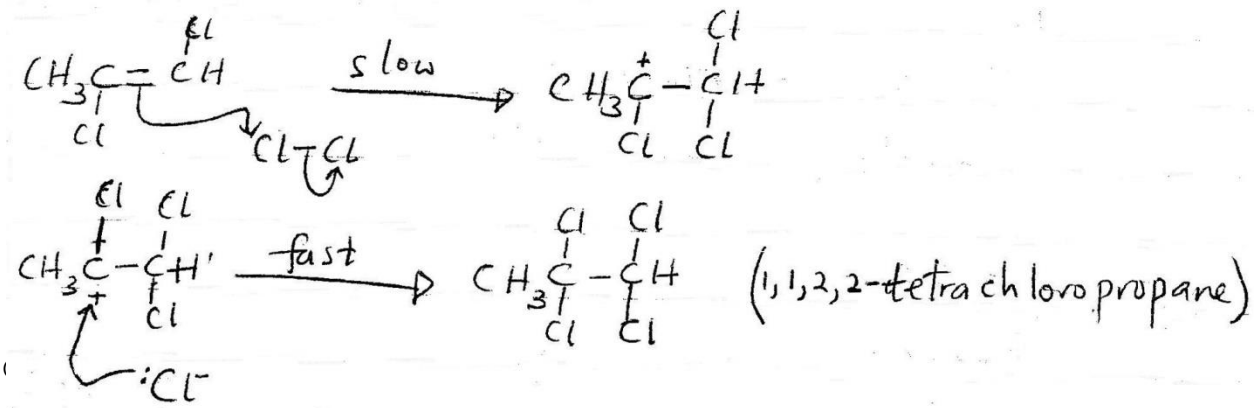
i.e. $RC \equiv CH + X_2 \xrightarrow{CCl_4} RC(X)=C(X)-H \xrightarrow[CCl_4]{X_2} RC(X)(X)-C(X)(X)-H$

e.g. $CH_3C \equiv CH + Cl_2 \longrightarrow CH_3C(Cl)=CH(Cl) \xrightarrow[CCl_4]{Cl_2} CH_3C(Cl)(Cl)-CH(Cl)(Cl)$

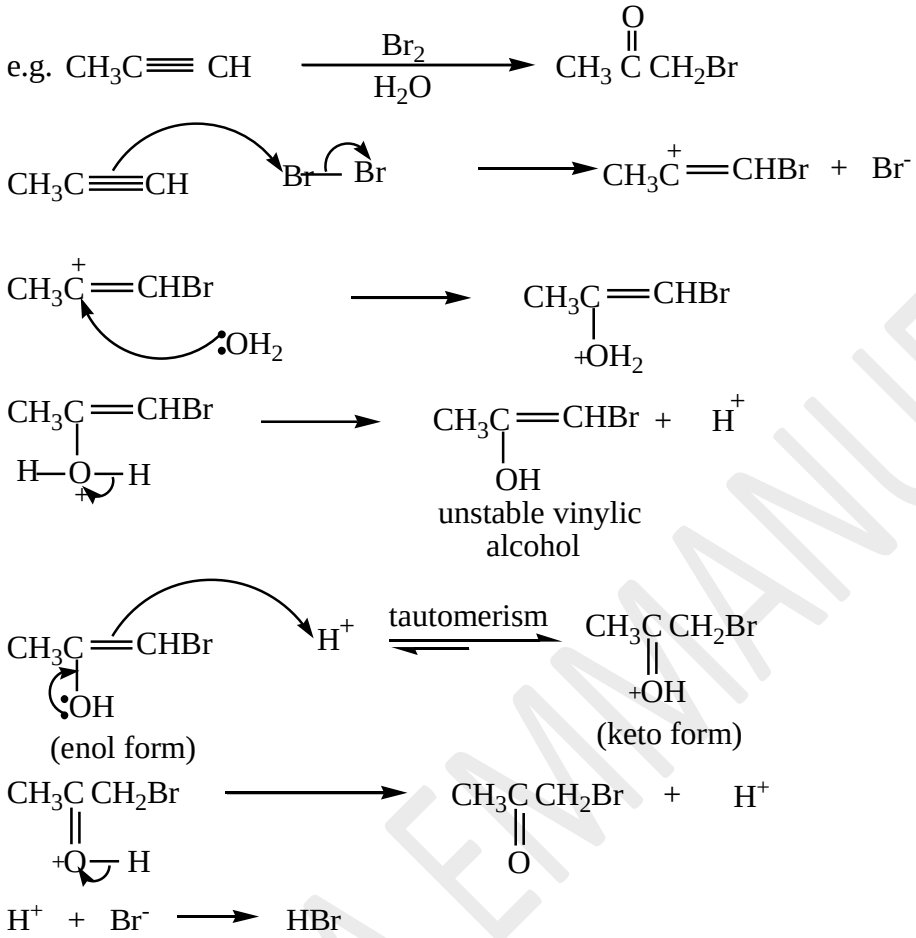
Mechanism for reaction



then another fresh molecule of Cl_2 is added since the reagent is in excess,

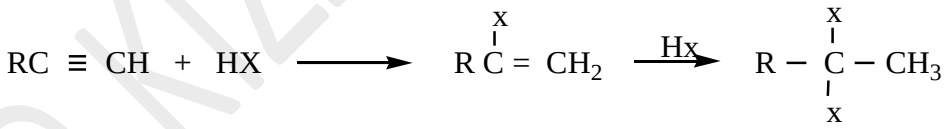


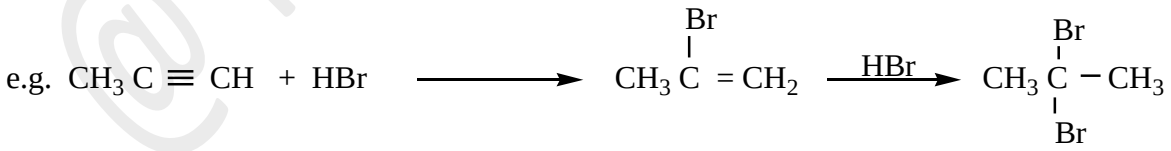
(ii) Alkynes react with halogens in presence of water to forms a halogeno carbonyl compound.



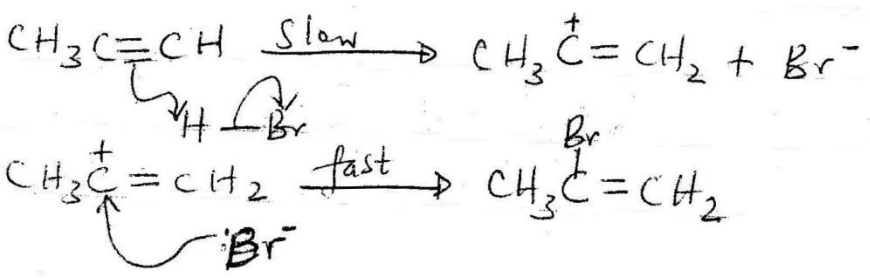
(b) Addition of halogen acids (HX)

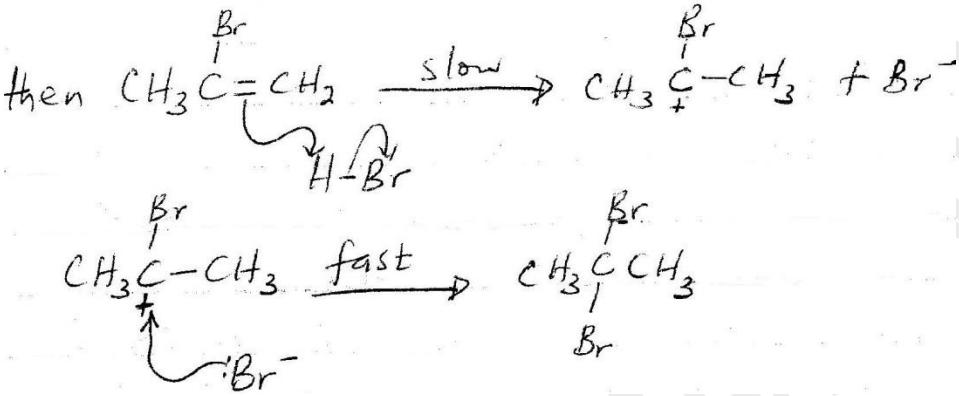
Like in addition of halogen, addition of one mole of a halogen acid produces an unsaturated compound which then adds another molecule of the halogen acid to produce a gemi – dihalide – Makwonikoff's rule is applied. i.e.





Mechanism (similar to that in alkenes)





Note: In presence of an organic peroxide, addition of hydrogen bromide only follows anti Makwonikoff's rule. e.g.

$$CH_3C \equiv CH + \underset{\text{excess}}{2\,HBr} \xrightarrow{ROOR} CH_3CH_2\overset{Br}{\overset{|}{C}}H\overset{|}{Br}$$

i.e.

$$CH_3C \equiv CH \xrightarrow[ROOR]{HBr} CH_3\overset{H}{\overset{|}{C}} = \overset{Br}{\overset{|}{C}}H \xrightarrow[ROOR]{HBr} CH_3\overset{H}{\overset{|}{C}}\overset{Br}{\overset{|}{C}}H\overset{|}{H}\overset{|}{Br}$$

Mechanism (similar to that in alkene/free radical mechanism)

2) Addition of water

Alkynes add water readily when the reaction is catalysed by strong acids and mercuric(II), Hg^{2+} ions. Aqueous solutions of sulphuric acid and mercury(II) sulphate are used.

The vinylic alcohol (contains both a double bond and a hydroxyl group adjacent to each other) produced is usually unstable and undergoes tautomerism (rearrangement from enol to keto form) producing a ketone. When ethyne is used in this reaction, ethanal, an aldehyde is formed. The rearrangement involves loss of a proton from the hydroxyl group, addition of a proton to the vicinal carbon atom and relocation of the double bond. i.e.

$$-C \equiv C- \; + \; H_2O \xrightarrow[H_2SO_4,\ 60^oC]{HgSO_4} -\overset{H}{\underset{H}{C}}-\overset{O}{C}-$$

Note: In unsymmetrical alkynes, the carbonyl carbon is formed on the carbon atom in the alkyne with preferably a larger group attached. i.e

$$\underset{\text{(Unsymmetrical alkyne)}}{R-C \equiv CH} \; + \; H_2O \xrightarrow[HgSO_4,\ 60^oC]{H_2SO_4} R\,\overset{O}{C}\,CH_3$$

$$\underset{\text{(symmetrical alkyne)}}{R\,C \equiv CR} \; + \; H_2O \xrightarrow[HgSO_4,\ 60^oC]{H_2SO_4} R\,\overset{O}{C}\,C\,H_2R$$

(same as $R\,CH_2\,\overset{O}{C}\,R$)

With ethyne, an aldehyde is formed. i.e.

$$\text{i.e.} \quad HC \equiv CH \; + \; H_2O \xrightarrow[HgSO_4,\ 60^oC]{H_2SO_4} CH_3\,CHO$$

3) Addition of hydrogen

In presence of suitable catalysts like finely divided Ni, Pt or Pd, alkynes are reduced to alkanes by hydrogen. When nickel is used, a temperature of 150^{o}c is applied but when Platinum or Palladium are used, the reaction takes place at room temperature.
(Reaction is also similar to that in alkenes).

e.g. $CH_3\,C \equiv CH + \underset{\text{excess}}{2\,H_2} \xrightarrow[150^oC]{Ni} CH_3\,CH_2\,CH_3$

i.e. $CH_3\,C \equiv CH + H_2 \xrightarrow[150^oC]{Ni} CH_3\,CH = CH_2 \xrightarrow[Ni,\,150^oC]{H_2} CH_3\,CH_2\,CH_3$

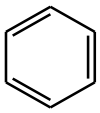
In presence of Lindlar's catalyst, the reduction with hydrogen stops with the alkene hence there is no further reduction to form an alkane.

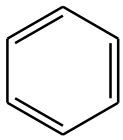
$$CH_3C{\equiv}CH + H_2 \xrightarrow{\text{Lindlar's catalyst}} CH_3CH{=}CH_2$$

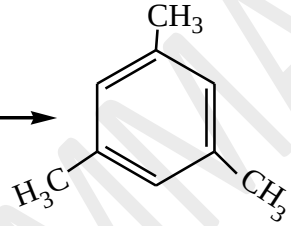
4) Polymerisation

Alkynes polymerise to give linear or cyclic products depending on the temperature and catalyst used.

These polymers formed differ from those of alkenes because they have a low molecular weight.

(a) $3\ CH \equiv CH \xrightarrow[\text{heat}]{\text{Fe}}$ 

(b) $3\ CH \equiv CH \xrightarrow[\text{heat}]{\text{Organo Nickel catalyst}}$ 

(c) $3\ CH_3C \equiv CH \xrightarrow[\text{heat}]{H_2SO_4}$ 

5) Reaction with ammoniacal solutions of;

(a) **Silver nitrate (silver nitrate in aqueous ammonia)**

When a terminal alkyne is passed through silver nitrate solution in aqueous ammonia, a white precipitate is observed of disilver dicarbide. e.g.

$$HC{\equiv}CH_{(g)} + 2\ NH_{3(aq)} + 2\ AgNO_{3(aq)} \longrightarrow AgC{\equiv}C\ Ag_{(s)} + 2\ NH_4\ NO_{3(aq)}$$

simply written as $HC{\equiv}CH_{(g)} \xrightarrow{NH_{3(aq)}\ /\ AgNO_{3(aq)}} AgC{\equiv}CAg_{(s)} + 2\ NH_4^{+}{}_{(aq)}$

Tollen's reagent may alternatively be used. It's a mixture of silver nitrate solution, aqueous sodium hydroxide and excess ammonia.

(b) **Copper(I) chloride (copper(I) chloride in aqueous ammonia)**

When a terminal alkyne is passed through Copper (I) chloride solution in aqueous ammonia a red precipitate of dicopper dicarbide is formed.

e.g. $HC{\equiv}CH_{(g)} + 2NH_{3(aq)} + Cu_2Cl_{2(aq)} \longrightarrow CuC{\equiv}CCu_{(s)} + 2\ NH_4Cl_{(aq)}$ (or 2 CuCl)

simply written as $HC{\equiv}CH_{(g)} \xrightarrow{NH_{3(aq)}\ /\ Cu_2Cl_{2(aq)}} CuC{\equiv}CCu_{(s)} + 2\ NH_4^{+}{}_{(aq)}$

Note that:

(i) This reaction gives a positive test for terminal alkynes with an acidic hydrogen (displaceable hydrogen) i.e. RC≡C-H

(ii) These two reactions are used to;

- Distinguish a terminal alkyne from an internal alkyne.
- Test for the presence of a triple bond in terminal alkynes.
- Distinguish between alkenes and alkynes. The reactions show that the hydrogen atoms in alkynes are slightly more acidic than those in alkenes.

6) Alkynes react with sodium (or sodamide) in liquid ammonia to produce sodium alkynides (salts). i.e.

$$R\,C \equiv CH \xrightarrow[\text{or } NaNH_2]{Na/\text{Liquid } NH_3} R\,C \equiv C^- Na^+$$

e.g. $CH_3C \equiv CH \xrightarrow{Na/\text{Liq } NH_3} CH_3\,C \equiv C^- Na^+$

Exercise:

How can you distinguish between;

(i) ethyne and propyne
(ii) but–1–yne and but–2–yne
(iii) but–1–yne and but–1–ene