ALKYNE

1. GENERAL INTRODUCTION

(a) These are the acyclic hydrocarbons which contains carbon-carbon triple bond are called alkyne.

(b) Hybridisation state of triply bonded carbon in alkyne is sp or also called as diagonal hybridisation.

(c) Geometry of carbon is linear in alkynes.

(d) Bond angle in alkyne is 180°.

(e) Their general formula is C_nH_{2n-2}

(f) C–C triple bond length is 1.20 Å.

(g) C–H bond length is 1.08 Å.

(h) C–C triple bond energy is 190 kcal./mol.

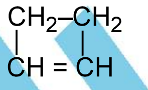
(i) C–H bond energy is 102.38 kcal./mol.

(j) Alkyne shows chain, position and functional isomerism. They are functional isomer with cycloalkene and alkadiene.

(i) C_1 – C_4 compound do not show chain isomerism.

(ii) Functional isomer of C_4H_6

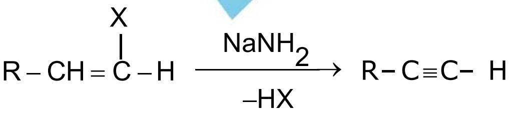
eg

$CH_3-CH_2-C\equiv CH$ 1 - Butyne	$CH_3-CH=C=CH_2$ 1,2 -Butadiene
$CH_2=CH-CH=CH_2$ 1,3-Butadiene	 Cyclobutene

2. METHODS OF PREPARATION

2.1 From Gem Dihalides (Dehydrohalogenation):

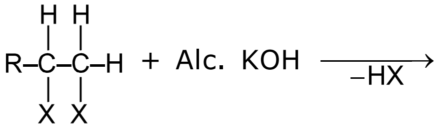
$$R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-H + \text{alc. KOH.} \xrightarrow[-HX]{}$$



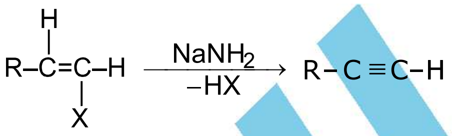
$$R-CH=\overset{X}{C}-H \xrightarrow[-HX]{NaNH_2} R-C\equiv C-H$$

Note : Alc.KOH is not used for elimination in second step because in this case elimination takes place from doubly bonded carbon atom which is stable due to resonance so strong base $NaNH_2$ is used for elimination of HX.

2.2 From Vicinal Dihalides (Dehydrohalogenation) :



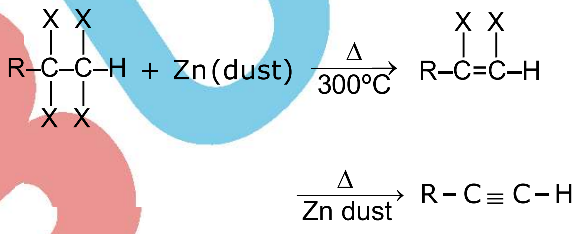
$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H + \text{Alc. KOH} \xrightarrow[-HX]{}$$



$$R-\overset{H}{C}=\underset{X}{C}-H \xrightarrow[-HX]{NaNH_2} R-C\equiv C-H$$

Note : In the above reaction if the reactant secondary butylene chloride is taken then the products are 2-butyne, 1, 2-butadiene and 1, 3- butadiene in which 2-butyne is the chief product.

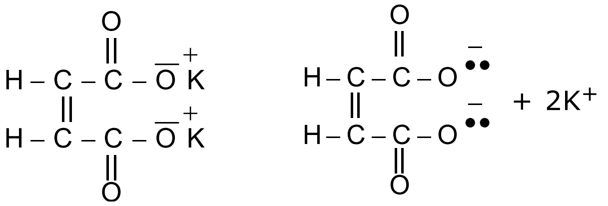
2.3 From Tetrahaloalkanes (Dehalogenation)



$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H + Zn(dust) \xrightarrow[300^\circ C]{\Delta} R-\overset{X}{C}=\overset{X}{C}-H \xrightarrow[\text{Zn dust}]{\Delta} R-C\equiv C-H$$

In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

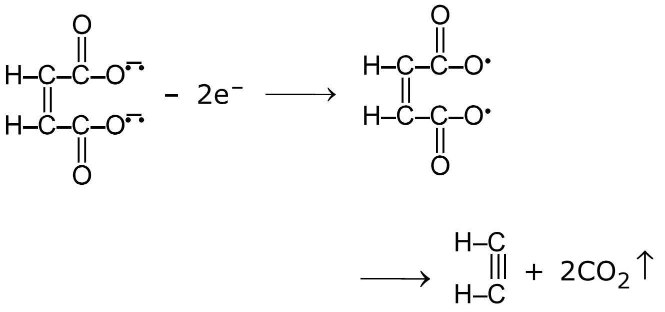
2.4 From Kolbe's Synthesis :



$$\begin{array}{l} H-C-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{K} \\ \quad\ \| \\ H-C-\underset{O}{\underset{\|}{C}}-\bar{O}\overset{+}{K} \end{array} \qquad \begin{array}{l} H-C-\overset{O}{\overset{\|}{C}}-O^- \\ \quad\ \| \\ H-C-\underset{O}{\underset{\|}{C}}-O^- \end{array} + 2K^+$$

Potassium Malaete

At Anode :



$$\begin{array}{l} H-C-\overset{O}{\overset{\|}{C}}-O^- \\ \quad\ \| \\ H-C-\underset{O}{\underset{\|}{C}}-O^- \end{array} - 2e^- \longrightarrow \begin{array}{l} H-C-\overset{O}{\overset{\|}{C}}-O^\bullet \\ \quad\ \| \\ H-C-\underset{O}{\underset{\|}{C}}-O^\bullet \end{array} \longrightarrow \begin{array}{l} H-C \\ \quad ||| \\ H-C \end{array} + 2CO_2\uparrow$$

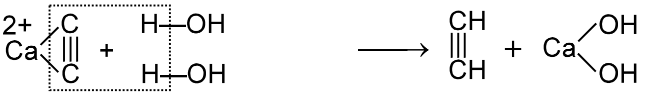
At Cathode :

$$2K^+ + 2e^- \longrightarrow 2K^{\bullet}$$

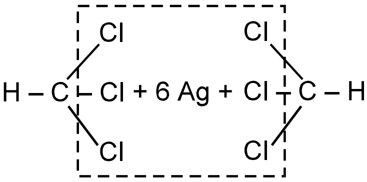
$$2K^{\bullet} + 2H_2O \longrightarrow 2KOH + H_2\uparrow$$

2.5 Laboratory method of preparation of Acetylene :

(a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.



(b) It can also be prepared from $CHCl_3$ with Ag dust.



$$\xrightarrow[-AgCl]{} H-C\equiv C-H$$

2.6 From Alkynes : (To form higher Alkynes)

2.6.1 With Na : When acetylene or 1- alkyne react with Na in presence of liq. NH_3 then an intermediate compound sodium acetylide or sodium alkynide is formed which gives higher alkyne with alkyl halide.

$$2H-C\equiv C-H + 2\ Na \xrightarrow[-H_2]{liq.NH_3} 2H-C\equiv\overset{-}{C}\overset{+}{Na}$$

$$\xrightarrow{X-R} H-C\equiv C-R$$

$$2R-C\equiv C-H + 2Na \xrightarrow[-H_2]{liq.NH_3} 2R-C\equiv\overset{-}{C}\overset{+}{Na}$$

$$\xrightarrow{X-R'} R-C\equiv C-R'$$

2.6.2 With GR : When acetyline or 1- alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.

$$H-C\equiv CH + R-Mg\text{-}X \xrightarrow[-RH]{} H\equiv C-MgX$$

acetylene

$$\xrightarrow[-MgX_2]{XR} H-C\equiv C-R$$

$$R-C\equiv C-H + R-Mg-X \xrightarrow[-RH]{}$$

$$R-C\equiv C-MgX \xrightarrow{R'-X} R-C\equiv C-R'$$

3. PHYSICAL PROPERTIES

(a) Alkynes are colourless, odourless and tasteless.

(b) Lower alkynes are partially soluble in H_2O. (It is due to its polarisibility).

(c) Higher alkynes are insoluble in water due to more % of covalent character.

(d) Completely soluble in organic solvents.

(e) Melting point and boiling point increases with molecular mass and decreases with number of branches.

(f) Upto C_4 alkynes are gaseous.C_5-C_{11} are liquid, C_{12} & above are solids.

(g) Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene (AsH_3) & Phosphine (PH_3).

(h) Acetylene & 1- alkyne are acidic in nature. It is due to greater electronegativity of sp hybridised 'C'.

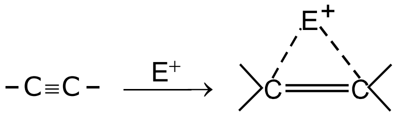
(i) Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very stronger as $^-NH_2$ or $^-CH_3$ etc.

4. CHEMICAL PROPERTIES

Like alkene, alkyne also shows electrophilic addition reaction but alkynes are less reactive towards electrophilic addition than alkene.

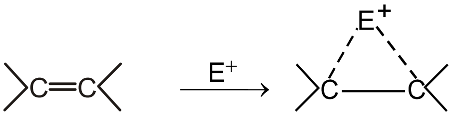
Of course alkyne is more reactive towards hydrogenations as it is expected due to greater unsaturacy. Lower reactivity of alkyne towards electophilic addition probably caused by greter activation energy due to less stable intermediate

(i)



Less stable due to shorter –C=C– bond

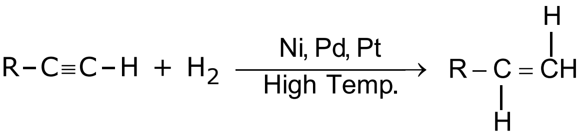
(ii)



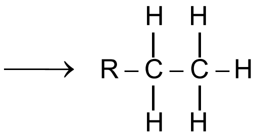
More stable due to longer $>C-C<$

5. CHEMICAL REACTIONS

5.1 With Hydrogen :



$$R-C\equiv C-H + H_2 \xrightarrow[\text{High Temp.}]{\text{Ni, Pd, Pt}} R-\underset{H}{C}=\overset{H}{C}H$$



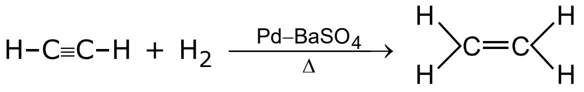
$\longrightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$

The above reaction is called as **Sabatier Senderson's reaction**.

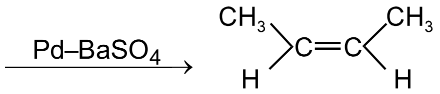
5.1.1 Hydrogenation in the presence of lindelar's Catalyst :

Addition up to alkene takes place in cis manner.

(i)



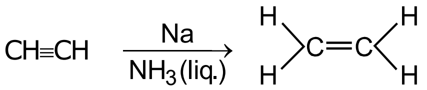
(ii) $CH_3-C\equiv C-CH_3 + H_2$



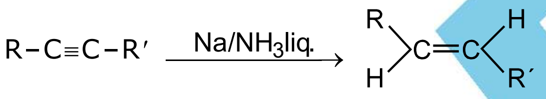
5.1.2 Hydrogenation by Na + NH_3 (liq.) :

Addition upto alkene takes place in trans manner

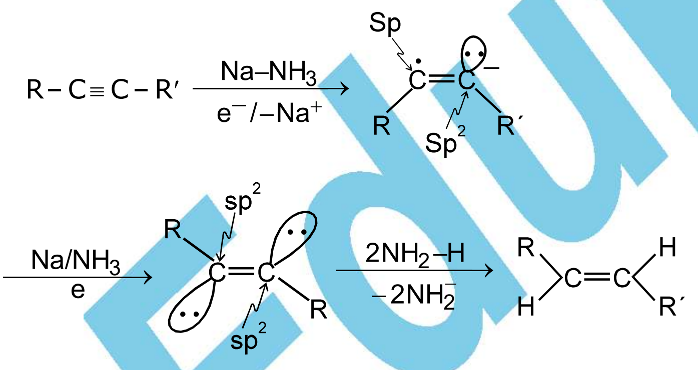
(i)



(ii)



Mechanism :

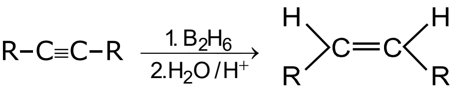


5.1.3 Hydrogenation by $LiAlH_4$:-

Addition upto alkene takes place in trans manner by $LiAlH_4$ also.

5.1.4 Reduction with the help of B_2H_6 :

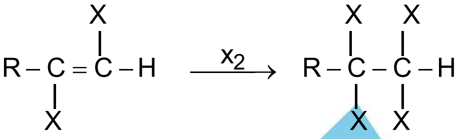
Alkyne is first reacted with B_2H_6 and is follwed by acidic hydrolysis, cis alkene is obtained.



5.2 Halogenation :

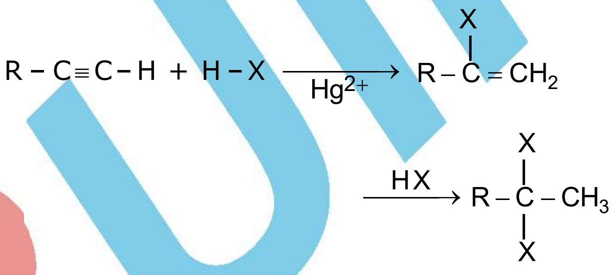
In presence of Lewis acid as a catalyst alkyne form tetrahaloderivative with halogen.

$$R-C\equiv C-H + X-X \xrightarrow[X\,=\,F,Cl,Br]{FeX_3}$$



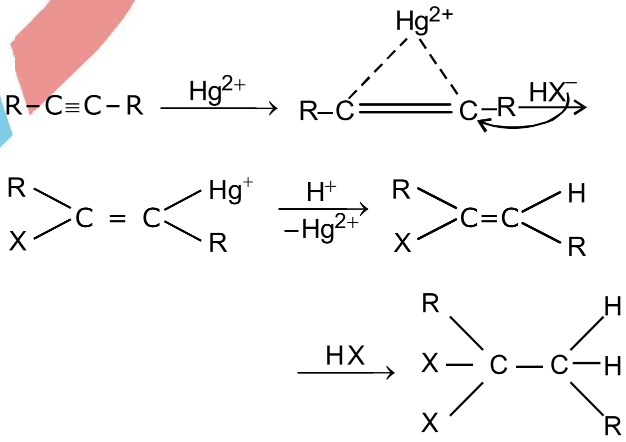
5.3 Reaction with HX/Hydrohalogenation:

Alkyne form gem dihalide with HX because reaction follows markownikoff's Ist and IInd rule both.

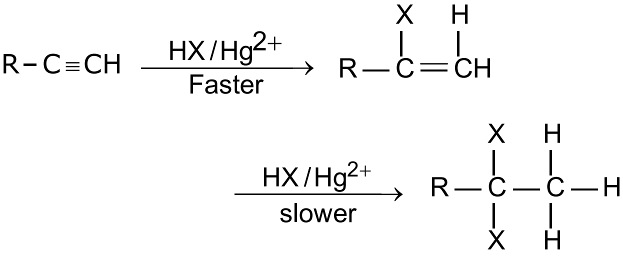


gem dihalide

Mechanism : The reaction takes place in the presence of Hg^{2+} ion.

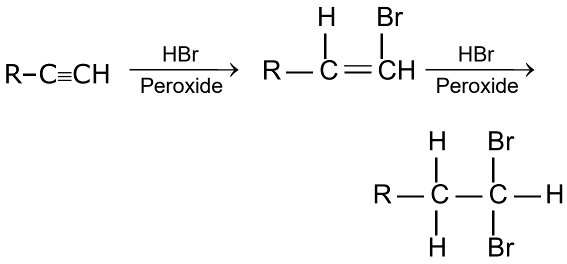


Note :- (i) First step is faster than the second step among addition of two HX on alkyne.



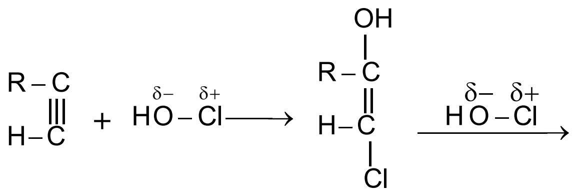
Slower rate of addition of 2nd molecule is caused by lower electron cloud density on C = C, due to – I effect of 'Cl'.

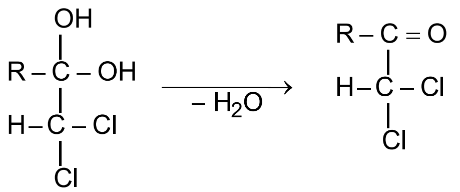
(ii) peroxide give same effect as in alkene



5.4 Reaction with Hypochlorous acid or Chlorine water :

Hypochlorous acid is broken into $O^{\ominus}H^{\oplus}$ Cl& ions & give addb. according to markonicoff's rule.

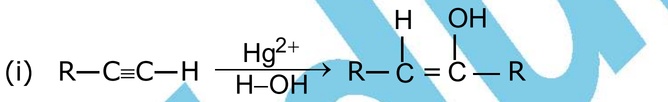




unstable

5.5 Hydration :

Addition of water takes place in the presence of Hg^{2+} ($HgSO_4$ + H_2SO_4)



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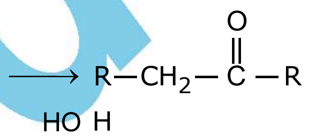

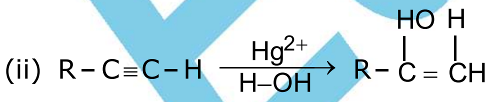

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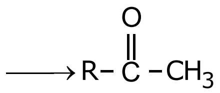
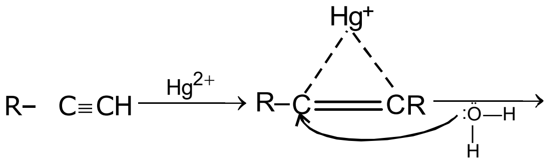
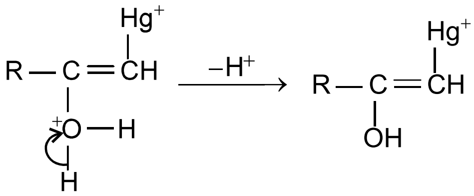
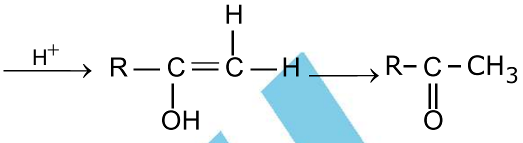


Mechanism :

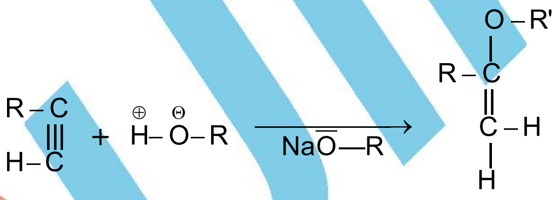




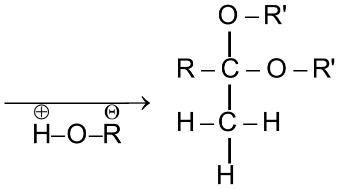


unstable

5.6 Addition of alcohol



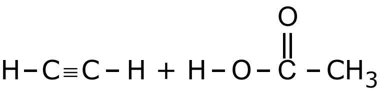
olefinic ether

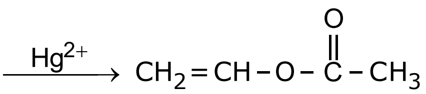


acetal / ketal

5.7 Addition of carboxylic acid :

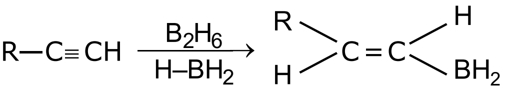
In the presence of Hg^{2+} unioxylation of carboxylic acid takes place.



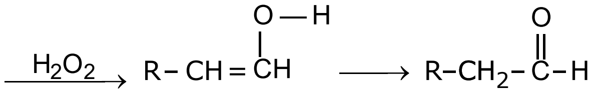


5.8 Hydroboration :

Carboxyl compound is obtained by hydroboration followed by treatment with



syn addition



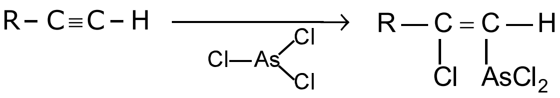
5.9 Addition of HCN :

Addition takes place in the presence of CuCl

$$H-C\equiv C-H + H-CN \xrightarrow[770^\circ]{CuCl} CH_2=CH-C\equiv N$$

5.10 Addition of $AsCl_3$:

Lewisite is obtained

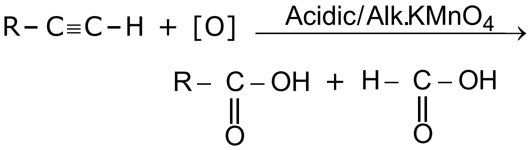


$$R-C\equiv C-H \xrightarrow[Cl-As\langle^{Cl}_{Cl}]{} R-\underset{Cl}{\underset{|}{C}}=\underset{AsCl_2}{\underset{|}{C}}-H$$

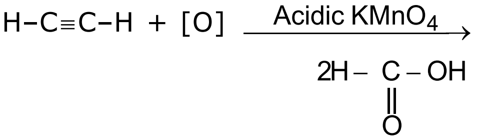
Lewisite

5.11 Oxidation :

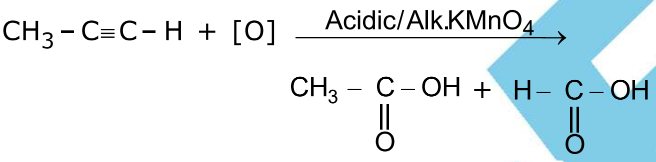
5.11.1 With acidic or alkaline $KMnO_4$ alkyne break into two parts from triply bonded carbon and every part forms respective acid.



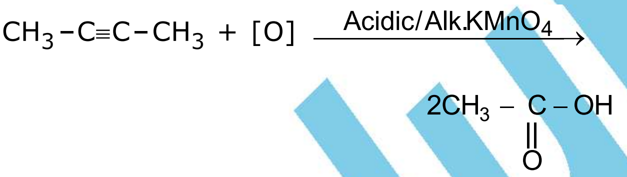
$$R-C\equiv C-H + [O] \xrightarrow{Acidic/Alk.KMnO_4} R-\underset{\underset{O}{\|}}{C}-OH + H-\underset{\underset{O}{\|}}{C}-OH$$



$$H-C\equiv C-H + [O] \xrightarrow{Acidic\ KMnO_4} 2H-\underset{\underset{O}{\|}}{C}-OH$$



$$CH_3-C\equiv C-H + [O] \xrightarrow{Acidic/Alk.KMnO_4} CH_3-\underset{\underset{O}{\|}}{C}-OH + H-\underset{\underset{O}{\|}}{C}-OH$$

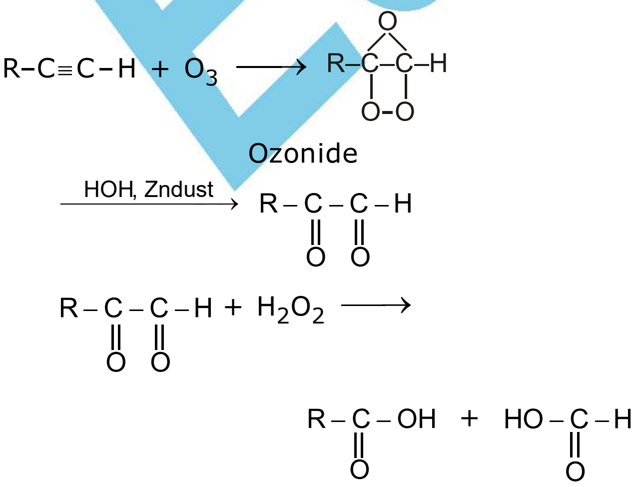


$$CH_3-C\equiv C-CH_3 + [O] \xrightarrow{Acidic/Alk.KMnO_4} 2CH_3-\underset{\underset{O}{\|}}{C}-OH$$

Exception : Acetylene forms oxalic acid with alkaline $KMnO_4$ exceptionally.

$$H-C\equiv C-H + [O] \xrightarrow{Alk.KMnO_4} \begin{array}{l}COOH\\|\\COOH\end{array}$$

5.11.2 Oxidation with Ozone:



$$R-C\equiv C-H + O_3 \longrightarrow \text{Ozonide} \xrightarrow{HOH,\ Zndust} R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H$$

$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H + H_2O_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH + HO-\underset{\underset{O}{\|}}{C}-H$$

5.12 Acidic nature of 1- Alkyne or Acetylene

In 1- alkyne or acetylene, the H which is linked with sp hybridised carbon is called as acidic or active H. It can easily be substituted by metal or alkaline species. Hence 1- alkyne or acetylene are acidic in nature. eg.

5.12.1 Reaction with Na :

$$2R-C\equiv C-H + Na \xrightarrow[-H_2]{Liq.NH_3} 2R-C\equiv C^{\ominus}Na^{\oplus}$$

sodium alkynide

OR

$$2R-C\equiv C-H + NaNH_2 \xrightarrow[-NH_3]{} 2R-C\equiv C^{\ominus}Na^{\oplus}$$

$$H-C\equiv C-H + Na \longrightarrow Na^{\oplus}C^{\ominus}\equiv C^{\ominus}Na^{\oplus}$$

disodium acetylide

Note : Where this alkynide is treat with alkyl halide higher alkyne is obtained.

$R-C\equiv CNa + X-R' \longrightarrow R-C\equiv C-R' + NaX$

$Na-C\equiv CNa + 2R'-X \rightarrow R'C\equiv C-R' + 2NaX$

5.12.2 Reaction with Ammonical Silver Nitrate solution : (Tollen's Reagent)

$$2R-C\equiv C-H + AgNO_3 + NH_4OH \xrightarrow[-H_2O]{} 2R-C\equiv C^{\ominus}Ag^{\oplus}$$

silver alkynide (white ppt)

$$H-C\equiv C-H + AgNO_3 + NH_4OH \xrightarrow[-H_2O]{} Ag^{\oplus}C^{\ominus}\equiv C^{\ominus}Ag^{\oplus}$$

silver acetylide (white ppt)

5.12.3 Reaction with Ammoniacal Cuprous Chloride solution :

$$2R-C\equiv C-H + Cu_2Cl_2 + NH_4OH \xrightarrow[-2HCl]{} 2R-C\equiv C^{\ominus}Cu^{\oplus}$$

cuprous alkynide (red ppt.)

$$H-C\equiv C-H + Cu_2Cl_2 + NH_4OH \xrightarrow[-2\,HCl]{} Cu^{\oplus}C^{\ominus} \equiv C^{\ominus}Cu^{\oplus}$$

dicuprous acetylide (red ppt.)

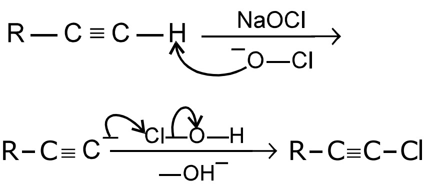
5.12.4 Reaction with NaOCl :

Acidic hydrogen is substituted by 'Cl'

(i) $H-C\equiv C-H \xrightarrow{NaOCl} Cl-C\equiv C-Cl$

(ii) $R-C\equiv C-H \xrightarrow{NaOCl} R-C\equiv C-Cl$

Mechanism :



$$R-C\equiv C-H \xrightarrow{NaOCl} R-C\equiv C^{-} \xrightarrow[-OH^-]{Cl-O-H} R-C\equiv C-Cl$$

Note : These (5.12.2) and (5.12.3) both reactions are used in the test of terminal alkynyl hydrogen. These ppt or metal acetylide or alkynide are insoluble in solution and in dry condication explode, therefore they are destroyed with HNO_3 before dryness (they form same compound again)

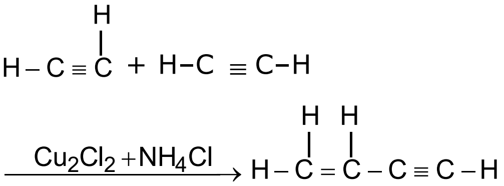
5.13 Polymerisation Reactions : Alkyne mainly shows addition polymerisation reactions.

5.13.1 Dimerisation and Cyclysation

(a) Dimerisation :

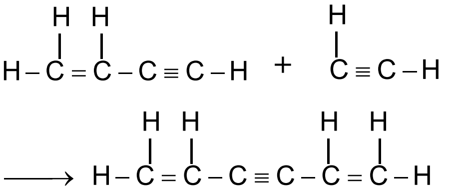
Two mole acetylene reacts with Cu_2Cl_2 & NH_4Cl and forms vinyl acetylene.

Note : If acetylene would be in excess then product would be divinyl acetylene and the reaction is called *trimerisation.*



$$H-C\equiv \overset{H}{\overset{|}{C}} + H-C\equiv C-H \xrightarrow{Cu_2Cl_2+NH_4Cl} H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-H$$

vinyl acetylene or butenyne

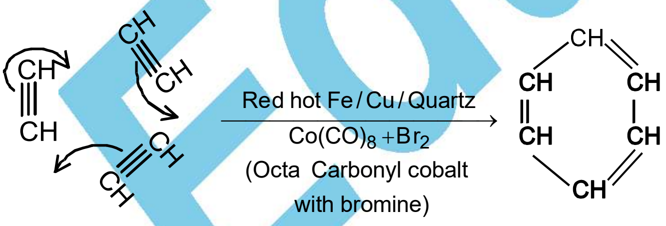


$$H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-H + \overset{H}{\overset{|}{C}}\equiv C-H \longrightarrow H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-C\equiv C-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H$$

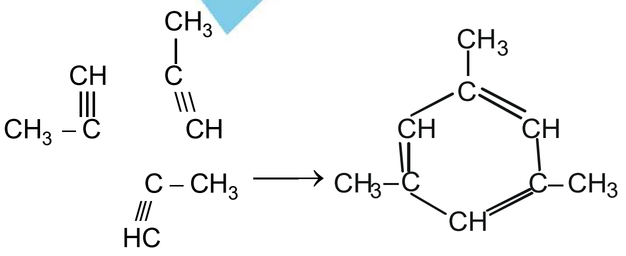
divinyl acetylene

(b) Trimerisation :

If three mole of acetylene is passed into red hot iron or Cu or quartz tube, then a cyclic trimer is formed which is called benzene.



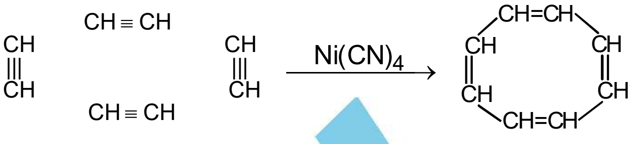
benzene



mesitylene (having 3-1°, 3-2° & 3-3° carbons)

Important : Mesitylene can also be obtained from acetone by condensation polymerisation.

(c) Tetramerisation : According to the name four moles of acetylene are heated with nickel tetra cyanide, then acetylene forms a cyclic tetramer cyclo octa tetraene.



cyclooctatetraene (Nonaromatic)

5.13.2 Coupling:-

(a) Alkyne form respective cuprous alkynide with ammonical cuprous chloride solution. When cuprous alkynide is reacted with pottasium ferri cyanide $[K_3Fe(CN)_6]$ they converted into conjugated diyne.

$$R-C\equiv CH + Cu(NH_3)_2Cl \longrightarrow \underset{\text{cuprous alkynide}}{R-C\equiv C.Cu}$$

$$2R-C\equiv C.Cu \xrightarrow[\Delta]{O_2} \underset{\text{diyne}}{R-C\equiv C-C\equiv C-R}$$

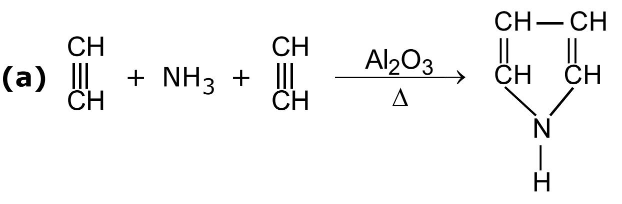
(b) Coupling is also done easily by 1-alkyne in the presence of Cu_2Cl_2 (cuprous compound) and amine (ie. pyridine + air) cuprous alkynide is formed (this coupling is known as oxidative coupling or glaser coupling)

$$2R-C\equiv CH + \frac{1}{2}O_2 \xrightarrow{Cu_2Cl_2/NH_3} R-C\equiv C-C\equiv C-R + H_2O$$

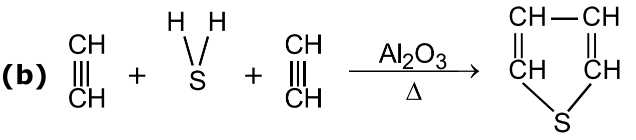
$$2CH_3-C\equiv CH + ½O_2 \xrightarrow{Cu_2Cl_2/NH_3} CH_3-C\equiv C-C\equiv C-CH_3 + H_2O$$

2,4-Hexadiyne.

5.14 Formation of heterocyclic compounds :



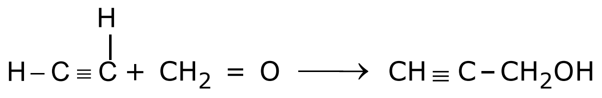
Pyrrole



Thiophene

5.15 Reaction with Formaldehyde

1– Alkyne in the presence of copper react with methanal to form alkynol.



$$H-C\equiv \overset{H}{C} + CH_2 = O \longrightarrow CH\equiv C-CH_2OH$$

prop-2-yne-1-ol

Note : Acetylene react with two mole of HCHO (methanal) to give 2–butyne–1,4–diol. This reaction is used in the formation of 1,3 butadine. Which is used in the formation of buna rubber.

5.16 Isomerisation :–

(a) When 1-alkyne is treated with alcoholic KOH 2-alkyne is formed.

$$R-CH_2-C\equiv CH \xrightarrow[\Delta]{\text{Alco.KOH}} R-C\equiv C-CH_3$$

1 – alkyne 2 – alkyne

(b) When 2-alkyne is treated with sodamide then it is converted into 1-alkyne.

$$CH_3-C\equiv C-CH_3 \xrightarrow[-NH_3]{NaNH_2}$$

$$CH_3-CH_2-C\equiv CNa \xrightarrow[-NaOH]{+H_2O} CH_3-CH_2-C\equiv CH$$

6. IMPORTANT – POINTS

(1) Alkyne with conc. H_2SO_4, alkyledene hydrogen sulphate is formed.

(2) Alkyne with dil. H_2SO_4 and Hg^{+2}, carbonyl compound is formed.

(3) With hypohalous acid dihalo carbonyls is formed. With ethyne dihalo aldehyde & with other alkynes dihalo ketones are formed.

(4) With aqueous solution of sodium hypochlorite (NaOCl) acidic hydrogen of 1-alkyne is substituted by Cl (subtitution reaction)

(5) Product formed by reaction of 1-alkyne and dialkyl borane, when treated with (H_2O_2 / NaOH) (oxidation)– carbonyl compound is formed. When treated with $3CH_3COOH$ - alkene is formed.

(6) Alkyne form bicyclo compound with diazomethane in the presence of sunlight.

(7) Alkyne with organic acid alkylidine acetate is formed in the presence of Hg^{2+} ion.

(8) Ethyne is used in oxy-acetylene flame (2800-3200ºC) for cutting and welding of metal.

(9) Ethyne is used in carbide lamps for lightning (is a illuminating agent in hawker's lamp)

(10) When hydrogen is passed in atmosphere of electric arc between. carbon electrode, a mixture of H_2 & ethyne is formed (Berthelot Method).

(11) Mixture of ethyne and nitrogen in electric spark converted into HCN .

(12) Ethyne burns with sooty flame due to presence of high % of carbon.

(13) Acetylene is used in artificial ripening of fruits.

SOLVED PROBLEMS

Ex.1 ***The triple bonded carbon atoms –***

(a) Are sp hybridised

(b) Are sp^3 hybridised

(c) Forms three sigma bonds and one pi bond

(d) Forms two pi bonds and two sigma bonds

The correct answer is –

(A) a, c (B) a, d (C) a, b (D) b, d

Ans. (B)

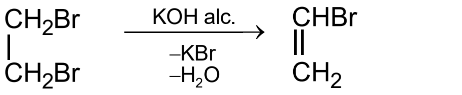
Sol. H – C ≡ C – H each carbon is sp hybridised & forms 2π & 2σ bonds.

Ex.3 ***Ethylene dibromide on treating with alcoholic KOH gives –***

(A) C_2H_6 (B) CH_4 (C) C_2H_4 (D) C_2H_2

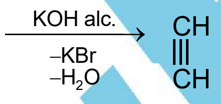
Ans. (D)

Sol. Alkynes can be prepared by dehydrohalogenation of alkyl dihalides



$$\begin{matrix}CH_2Br\\ |\\ CH_2Br\end{matrix} \xrightarrow[-KBr,\ -H_2O]{KOH\ alc.} \begin{matrix}CHBr\\ ||\\ CH_2\end{matrix}$$

Ethylene dibromide Vinylbromide



$$\xrightarrow[-KBr,\ -H_2O]{KOH\ alc.} \begin{matrix}CH\\ |||\\ CH\end{matrix}$$

Acetylene

Vinyl bromide being less reactive and thus to get better yield a stronger base $NaNH_2$ is used in second step.

Ex.4 ***Reaction***

$CH_3CH_2Br + A \rightarrow CH_3CH_2–C≡C–CH_2– CH_3$

here the compound. A will be –

(A) $CH_3\ COOAg$ (B) CH = CNa

(C) NaC = CNa (D) C_2H_5ONa

Ans. (C)

Sol. $CH_3–CH_2–$ $–C≡C–$ $–CH_2–CH_3$

$\longrightarrow CH_3–CH_2–C≡C–CH_2–CH_3$

Ex.5 ***Acetylene can be prepared from –***

(A) Potassium fumarate

(B) Calcium carbide

(C) Ethylene bromide

(D) All ***Ans. (D)***

Sol. These are methods of preparation of C_2H_2. Potassium fumerate on electrolysis, CaC_2 on hydrolysis and ethylene bromide on elimination gives acetylene.

Ex.6 ***Which of the following acid is dibasic –***

(A) $CH_3–CH =CH–CH_3$ (B) $(CH_3)_2C=CH_2$

(C) $CH_3 – C ≡ CH$ (D) CH≡CH

Ans. (D)

Sol. Acetylene contains two active hydrogen atoms.

Ex.7 ***Order of acidity of H_2O, NH_3 and acetylene is –***

(A) NH_3 > CH ≡ CH > H_2O

(B) H_2O > NH_3 > HC ≡ CH

(C) H_2O > HC ≡ CH > NH_3

(D) NH_3 > H_2O > HC ≡ CH ***Ans. (C)***

Sol. The order of acidity of H_2O, NH_3 and acetylene depends upon the relative basicity of OH^-, NH_2^- and $HC ≡ C^-$ the decreasing nature of basic character is $NH_2^- > HC≡ C^- > OH^-$, hence the decreasing order of acidity is H_2O > HC ≡ CH > NH_3.

Ex.8 ***Alkynes can be reduced to alkenes by hydrogenation in presence of –***

(A) Raney Ni (B) Anhy. $AlCl_3$

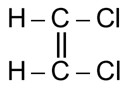
(C) Pd (D) Lindlar's catalyst

Ans. (D)

Sol. $CH ≡ CH \xrightarrow[Catalyst]{Lindlar} CH_2 = CH_2$. Lindlar catalyst prevents further reduction of ethene to ethane.

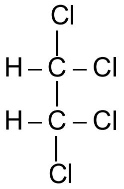
Ex.9 ***Westrosol has the following formula –***

(A)



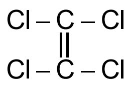
$$\begin{matrix}H–C–Cl\\ ||\\ H–C–Cl\end{matrix}$$

(B)



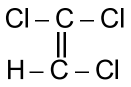
$$\begin{matrix}Cl\\ |\\ H–C–Cl\\ |\\ H–C–Cl\\ |\\ Cl\end{matrix}$$

(C)



$$\begin{matrix}Cl–C–Cl\\ ||\\ Cl–C–Cl\end{matrix}$$

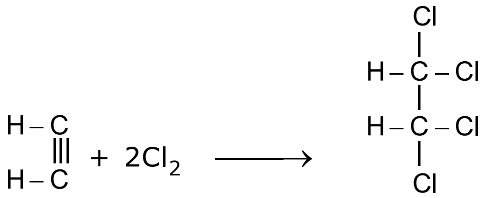
(D)



$$\begin{matrix}Cl–C–Cl\\ ||\\ H–C–Cl\end{matrix}$$

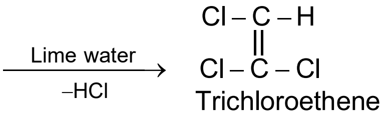
Ans.(D)

Sol. Acetylene adds up two molecules of chlorine to give tertachloroethane, known as westron industrially. This on dehydrochlorination of westron with lime water gives trichloro ethene, commerically called westrosol



$$\begin{matrix}H–C\\ |||\\ H–C\end{matrix} + 2Cl_2 \longrightarrow \begin{matrix}Cl\\ |\\ H–C–Cl\\ |\\ H–C–Cl\\ |\\ Cl\end{matrix}$$

Westron



$$\xrightarrow[-HCl]{\text{Lime water}} \begin{matrix} Cl-C-H \\ \| \\ Cl-C-Cl \end{matrix}$$

Trichloroethene
(Westrosol)

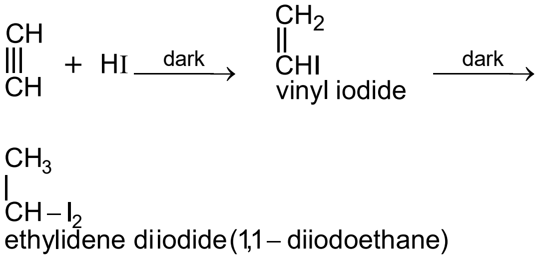
Ex.10 *Acetylene on treating with HI gives –*

(A) 1, 1-Diiodoethane (B) Ethylene

(C) Iodoethane (D) Ethane

Ans. (A)

Sol. Acetylene on treating with HI gives 1,1-diiodoethane



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + HI \xrightarrow{\text{dark}} \begin{matrix}CH_2\\ \|\\ CHI\end{matrix} \xrightarrow{\text{dark}} \begin{matrix}CH_3\\ |\\ CH-I_2\end{matrix}$$

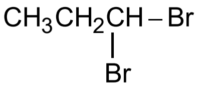
vinyl iodide

ethylidene diiodide (1,1 – diiodoethane)

The reactivity of halogen acids is HI > HBr > HCl

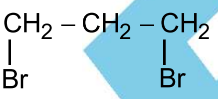
Ex.11 *The product formed by the addition of HBr to propyne in the presence of H_2O_2 is –*

(A)



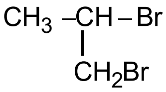
$CH_3CH_2\underset{\substack{|\\Br}}{CH}-Br$

(B)



$\underset{\substack{|\\Br}}{CH_2}-CH_2-\underset{\substack{|\\Br}}{CH_2}$

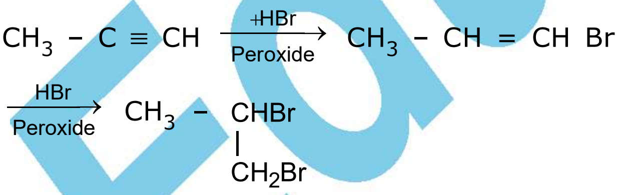
(C)



$CH_3-\underset{\substack{|\\CH_2Br}}{CH}-Br$

(D) All above Ans. (C)

Sol. The product formed by the addition of HBr to propyne in the presence of H_2O_2 is $CH_3CH(Br)CH_2Br$. The addition is contrary to Markownikoff's rule.



$$CH_3 - C \equiv CH \xrightarrow[\text{Peroxide}]{+HBr} CH_3 - CH = CH\ Br \xrightarrow[\text{Peroxide}]{HBr} CH_3 - \underset{\substack{|\\CH_2Br}}{CHBr}$$

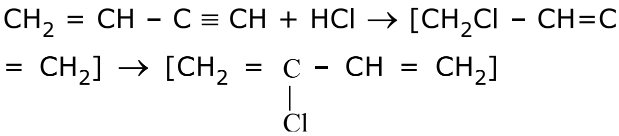
Ex.12 *On passing vinyl acetylene into conc. HCl in the presence of cuprous and ammonium chlorides, the following is produced-*

(A) Neoprene (B) Isoprene

(C) Chloroprene (D) None of these

Ans. (C)

Sol. On passing vinyl acetylene into conc. HCl acid in the presence of cuprous and ammounium chlorides. There is a great deal of evidences that chloroprene is formed and the reaction proceeds by 1,4 addition followed by rearrangement under the influence of the catalyst.



$$CH_2 = CH - C \equiv CH + HCl \rightarrow [CH_2Cl - CH=C = CH_2] \rightarrow [CH_2 = \underset{\substack{|\\Cl}}{C} - CH = CH_2]$$

Chloroprene (2-chlorobuta-1, 3-diene)

Ex.13 *The compounds A and B in the sequence*

$CH\equiv CH + H_2O \xrightarrow[60°C]{H_2SO_4, HgSO_4} A \xrightarrow{[O]} B$ ***are ?***

(A) Acetone and acetic acid respectively

(B) Acetaldehyde and acetic acid respectively

(C) Acetaldehyde and ethyl alcohol respectively

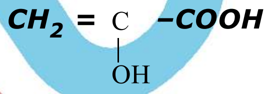
(D Acetone and acetaldehyde respectively

Ans. (B)

Sol. $CH\equiv CH + H_2O \xrightarrow[60°C]{H_2SO_4, HgSO_4} CH_3CHO \xrightarrow{[O]} CH_3COOH$

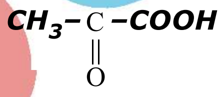
Ex.14 ***$CH \equiv C-COOH \xrightarrow{HgSO_4/H_2SO_4}$ product(A),A is-***

(A)



$CH_2 = \underset{\substack{|\\OH}}{C} - COOH$

(B)

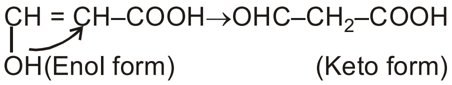


$CH_3-\underset{\substack{\|\\O}}{C}-COOH$

(C) $OHC-CH_2-COOH$

(D) $OH-CH=CH-COOH$ ***Ans. (C)***

Sol. $CH\equiv C-COOH \xrightarrow{H^+-OH^-}$



$\underset{\substack{|\\OH}}{CH} = CH-COOH \rightarrow OHC-CH_2-COOH$

(Enol form) (Keto form)

Ex.15 *When acetylene is passed into methanol at 160-200ºC in the presence of a small amount of potassium methoxide and under pressure, the following is formed –*

(A) Polyvinyl alcohol

(B) Divinyl ether

(C) Dimethyl ether

(D) Methyl vinyl ether ***Ans. (D)***

Sol. When acetylene is passed into methanol at 160-200ºC in the presence of a small amount (1-2%) of potassium methoxide and under pressure just high enough to prevent boiling, methyl vinyl ether is formed.

The mechanism is believed to involve nucleophillic attack in the first step.

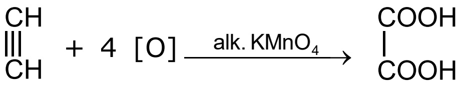
$HC \equiv CH + CH_3\ O^- \rightarrow C^-H = CH\ OCH_3$

$\xrightarrow{CH_3OH} CH_2 = CH_2O\ CH_3 + CH_3O^-$

Methyl vinyl ether

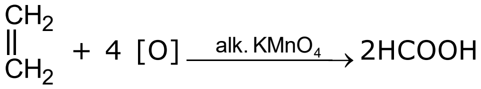
Ex.18 ***Acetylene and ethylene react with alk $KMnO_4$ to give –***
(A) Oxalic acid and formic acid
(B) Acetic acid and ethylene glycol
(C) Ethyl alcohol and ethylene glycol
(D) None ***Ans. (A)***

Sol. Acetylene and ethylene react with alk. $KMnO_4$ to give oxalic acid and formic acid respectively.



$$\underset{CH}{\overset{CH}{|||}} + 4\,[O] \xrightarrow{alk.\,KMnO_4} \underset{COOH}{\overset{COOH}{|}}$$

acetylene oxalic acid



$$\underset{CH_2}{\overset{CH_2}{||}} + 4\,[O] \xrightarrow{alk.\,KMnO_4} 2HCOOH$$

ethylene formic acid

Ex.19 ***Acetic acid is the only product of ozonolysis of***
(A) 1- Butyne
(B) Dimethyl acetylene
(C) Ethyl acetylene
(D) 2- Butene ***Ans. (B)***

Sol. Acetic acid is the only product of ozonolysis of dimethyl acetylene.
$CH_3 - C \equiv C - CH_3 + O_3 \rightarrow$

Ex.20 ***Acetylenic hydrocarbons are acidic because–***
(A) Sigma electron density of C — H bond in acetylene is nearer a carbon which has 50% s-character
(B) Acetylene has only one hydrogen atom at each carbon atom
(C) Acetylene contains least number of hydrogen atoms among the possible
(D) Acetylene belongs to the class of alkynes with formula $C_n H_{2n-2}$
Ans. (A)

Sol. The acidic character of H is,
F—H > O—H > ≡ C—H > N—H; H atom attached on F, O, N and triply bonded carbon is acidic.

Ex.21 ***The basic character of OH^-, NH_2^-, C_2H^- is:***

(A) $C_2H^- > NH_2^- > OH^-$

(B) $C_2H^- > OH^- > NH_2^-$

(C) $NH_2^- > C_2H^- > OH^-$

(D) $OH^- > C_2H^- > NH_2^-$ ***Ans. (C)***

Sol. The acidic nature is $H_2O > C_2H_2 > NH_3$; Thus conjugate base order will be
$OH^- < C_2H^- < NH_2^-$

Ex.22 ***Which is the most suitable reagent among the following to distinguish compound (c) from the rest of the compounds :***
(a) $CH_3C \equiv CCH_3$
(b) $CH_3CH_2 - CH_2CH_3$
(c) $CH_3CH_2C \equiv CH$ ***(d)*** $CH_3CH = CH_2$
(A) Br_2 in CCl_4
(B) Br_2 in CH_3COOH
(C) Alkaline $KMnO_4$
(D)Tollen's reagent ***Ans. (D)***

Sol. Terminal alkynes (≡C–H) give white precipitate with Tollen's reagent (ammoniacal $AgNO_3$)

Ex.23 ***Acetylene gives –***
(A) White ppt with $AgNO_3$ and red ppt with Cu_2Cl_2
(B) White ppt with Cu_2Cl_2 and red ppt with $AgNO_3$
(C) White ppt with both
(D) Red ppt with both ***Ans. (A)***

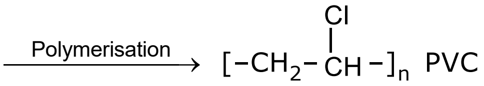
Sol. CAg ≡ CAg is white and CuC ≡ CCu is red.

Ex.24 ***How can we distinguish between butyne-1 and butyne-2 –***
(A) By alkaline $KMnO_4$
(B) By Br_2 water
(C) By ammoniacal cuprous chloride
(D) By Benedict reagent ***Ans. (C)***

Sol. Only terminal alkyne give red ppt. with ammoniacal cuprous chloride sol.

Ex.25 ***Starting compound for P.V.C. preparation is–***
(A) Ethylene ***(B) Acetylene***
(C) Ethane ***(D) None*** ***Ans. (B)***

Sol. $HC \equiv CH \xrightarrow{HCl} CH_2 = CH{-}Cl$



$$\xrightarrow{Polymerisation} [-CH_2-\overset{Cl}{\overset{|}{CH}}-]_n \text{ PVC}$$

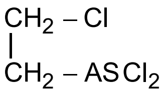
(poly vinyl chloride)

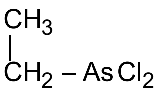
Ex.26 ***Acetylene trimerises to give benzene. The reaction occurs in the presence of –***
(A) Iron
(B) Silica
(C) $(C_6H_5)_3\,P + Ni(CO)_4$
(D) $Cr_2O_3 + P_2O_5$ ***Ans. (C)***

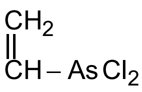
Sol. When ethyne is passed through a red hot iron tube, benzene is formed. This reaction was first discovered in 1870. When this reaction is carried out in the presence of nickel carbonyl and triphenyl phosphene in benzene solution. 90% yield is obtained.

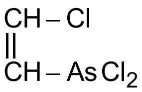
$\xrightarrow[\text{benzene}]{}$ or

Ex.27 Lewisite has the following structure –

(A)

$\begin{matrix} CH_2 - Cl \\ | \\ CH_2 - AsCl_2 \end{matrix}$

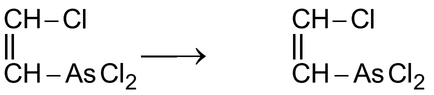
(B)

$\begin{matrix} CH_3 \\ | \\ CH_2 - AsCl_2 \end{matrix}$

(C)

$\begin{matrix} CH_2 \\ \| \\ CH - AsCl_2 \end{matrix}$

(D)

$\begin{matrix} CH - Cl \\ \| \\ CH - AsCl_2 \end{matrix}$

Ans. (D)

Sol. Lewisite has the structure Cl–CH=CH–$AsCl_2$. Arsenous chloride adds on acetylene to form lewisite which is used as a poisonous war gas.


$\begin{matrix} CH - Cl \\ \| \\ CH - AsCl_2 \end{matrix} \longrightarrow \begin{matrix} CH - Cl \\ \| \\ CH - AsCl_2 \end{matrix}$

Lewisite

(β–Chlorovinyl dichloro arsene)

Ex.28 Ethylene and acetylene may be distinguished by using –

(A) Tollen's reagent
(B) Baeyer's reagent
(C) Schiff's reagent
(D) Bromine water ***Ans. (A)***

Sol. Acetylene reacts with tollen's reagent to form a white precipitate of silver acetylide

Ex.29 Acetylene reacts with CO and H_2O to form acrylic acid in the presence of the following–

(A) Hg^{+2} + H_2SO_4 **(B) Ni**
(C) BF_3 + HgO **(D) Pd + $BaSO_4$**

Ans. (B)

Sol. Acetylene reacts with CO and water in the presence of Nickel Catalyst to give acrylic acid, $Ni(CO)_4$ is probably formed as an intermediate species which catalyses the reaction


$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + CO + \begin{matrix} H \\ | \\ OH \end{matrix} \xrightarrow{Ni} \begin{matrix} CH_2 \\ \| \\ CH - COOH \end{matrix}$

Ex.30 Which of the following compound can be prepared from acetylene by carbonylation?

(A) CH_3 – ***$COOC_2H_5$***
(B) CH_2 = CH – COOH
(C) CH_3 – CH_2 – COOH
(D) CH_3 – CH_2 – $COOCH_3$ ***Ans. (B)***

Sol. The compound which can be prepared from acetylene by carbonylation is CH_2 = CH – COOH

$$H - C \equiv C - H + CO + H_2O \xrightarrow[Ni(CO)_4]{BF_3}$$

acetylene

$$CH_2 = CH - COOH$$

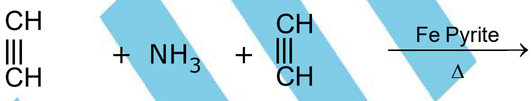
acrylic acid

Ex.31 HC ≡ CH on treatment with NH_3 in the presence of Fe-pyrite produces the following products.

(A) Pyridine ***(B) Ethyl amine***
(C) Methyl amine ***(D) Pyrolle***

Ans. (D)

Sol. HC ≡ CH on treatment with NH_3 in the presence of Fe-pyrite produces Pyrolle.


$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + NH_3 + \begin{matrix} CH \\ ||| \\ CH \end{matrix} \xrightarrow[\Delta]{\text{Fe Pyrite}}$

Actylene

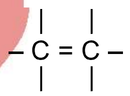
Pyrolle (Pyrolle is a hetrocyclic compound)

Ex.32 Of the following the compound that will most readily react with gaseous Br_2 is –

(A) C_3H_6 ***(B) C_4H_{10}***
(C) C_2H_2 ***(D) C_6H_6*** ***Ans. (A)***

Sol.

$\overset{|}{-C} = \overset{|}{C} -$ is more reactive than – C ≡ C –

and

$-\underset{|}{\overset{|}{C}} = \underset{|}{\overset{|}{C}} -$

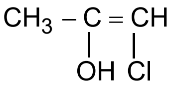
Ex.33 Acetylene reacts with HCN in the presence of $Ba(CN)_2$ to yield:

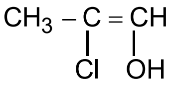
(A) Vinyl cyanide
(B) 1,1- dicyanoethane
(C) 1,2-dicyanoethene
(D) None ***Ans. (A)***

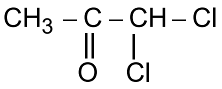
Sol. CH≡ CH + HCN $\xrightarrow{Ba(CN)_2}$ CH_2 = CH (CN)

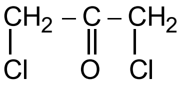
Vinyl Cyanide

Ex.34 The addition of HOCl to CH_3–C ≡CH in the presence of mineral acids produces.

(A)

$CH_3 - \underset{OH}{\underset{|}{C}} = \underset{Cl}{\underset{|}{CH}}$

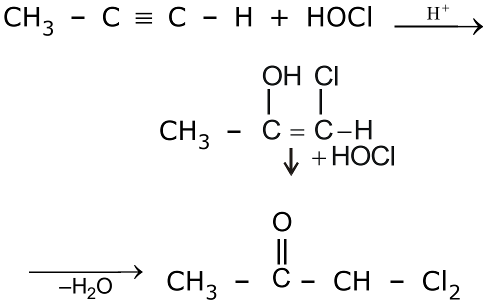
(B)

$CH_3 - \underset{Cl}{\underset{|}{C}} = \underset{OH}{\underset{|}{CH}}$

(C)

$CH_3 - \underset{O}{\underset{\|}{C}} - \underset{Cl}{\underset{|}{CH}} - Cl$

(D)

$\underset{Cl}{\underset{|}{CH_2}} - \underset{O}{\underset{\|}{C}} - \underset{Cl}{\underset{|}{CH_2}}$

Ans. (C)

Sol. The addition of hypochlorous acid (HOCl) on propyne in the presence of mineral acids produce dichloro ketones.



$$CH_3 - C \equiv C - H + HOCl \xrightarrow{H^+} CH_3 - \overset{OH}{\overset{|}{C}} = \overset{Cl}{\overset{|}{C}} - H \xrightarrow{+HOCl} \xrightarrow{-H_2O} CH_3 - \overset{O}{\overset{||}{C}} - CH - Cl_2$$

1,1 dichloropropanone

Ex.35 When 2-butyne reacts with sodamide in an inert solvent in the presence of dilute HCl, the product formed is:

(A) n-Butane **(B) 2-Butene**

(C) 1-Butyne **(D) 1-Propyne**

Ans. (C)

Sol. When 2-butyne is heated with $NaNH_2$ in an inert solvent, the sodium derivative of but-1-yne which is converted into but-1-yne by the action of dil HCl.

$$CH_3 - C \equiv C - CH_3 + NaNH_2 \xrightarrow{\text{Paraffin}}$$

$$NH_3 + CH_3CH_2C \equiv CNa \xrightarrow{\text{dil. HCl}} CH_3CH_2C \equiv CH$$

1-butyne