Dienes and Alkynes

(Methods of Formation and Chemical Reactions)

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Dienes

- **Definition-** The class of hydrocarbon containing two double bonds are called as **dienes**.
- General formula for dienes is C_nH_{2n-2} just like for Alkynes hence dienes are isomeric with alkynes. Dienes are classified into three types as- i) Isolated dienes ii) Conjugated dienes
- iii) Cumulative dienes
- i) Isolated Dienes- When two double bonds are separated by more than one single bond is called as **isolated diene**.
- CH_2= CH-CH_2-CH_2 (1,4 – Pentadiene)
- ii) Conjugated Dienes- When two double bonds are separated by one single bond, the dienes are called as **Conjugated dienes**.
- CH_2=CH-CH=CH_2 (1,3- butadiene)
- iii) Cumulative Dienes- When two double bonds are adjacent to with other, the dienes are called as **Cumulative dienes**.
- CH_2=C=CH_2(Propadiene)

Methods of Formation of 1,3-butadiene

1) From n-butane –

When n-butane is passed through the red hot Cr_2O_3, dehydrogenation occurs to produce 1,3- butadiene.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow[Cr_2O_3\text{(Red hot tube)}]{\text{n-butane}} CH_2{=}CH\text{-}CH{=}CH_2 + 2H_2$$

1,3- butadiene

2) From 1-butene –

When 1-butene is passed through the red hot Cr_2O_3, dehydrogenation occurs and it produces 1,3-butadiene.

$$CH_3\text{-}CH_2\text{-}CH_2{=}CH_2 \xrightarrow[Cr_2O_3\text{(Red hot tube)}]{\text{1-butene}} CH_2{=}CH\text{-}CH{=}CH_2 + H_2$$

1,3- butadiene

3) From 1,4-butandiol –

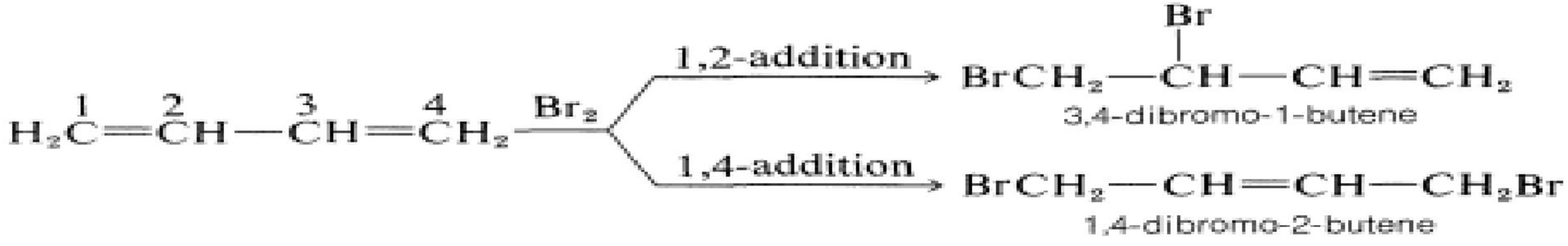
When 1,4- butandiol is reacted with conc. H_2SO_4, the dehydration of the compound takes place to produce 1,3-butadiene.

$$HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow[\text{conc. } H_2SO_4]{\text{1,4-butandiol}} CH_2{=}CH\text{-}CH{=}CH_2 + 2H_2O$$

1,3- butadiene

Chemical reactions f 1,3-butadiene

1) **Addition of Bromine -** 1,2 and 1,4- addition of bromine to 1,3-butadiene takes place to form 1,2 and 1,4 addition product.

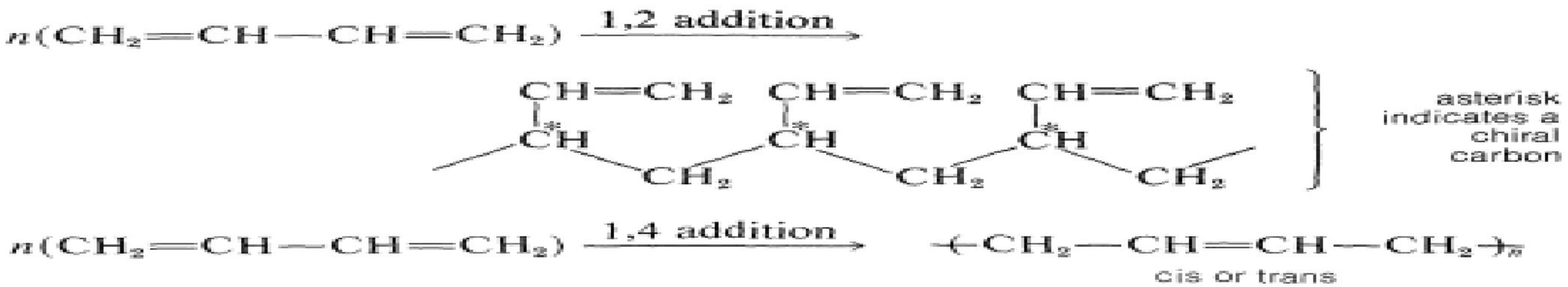


2) Addition of HBr –

CH_2=CH-CH=CH_2 + HBr -----→ CH_3CHBr-CH=CH_2 + CH_3CH=CHCH_2Br

3-bromo-1-butene 1-bromo-2-butene

3) Polymerization Reaction- on polymerization 1,3- butadiene produces 1,2 addition polymer and 1,4-addition polymer.

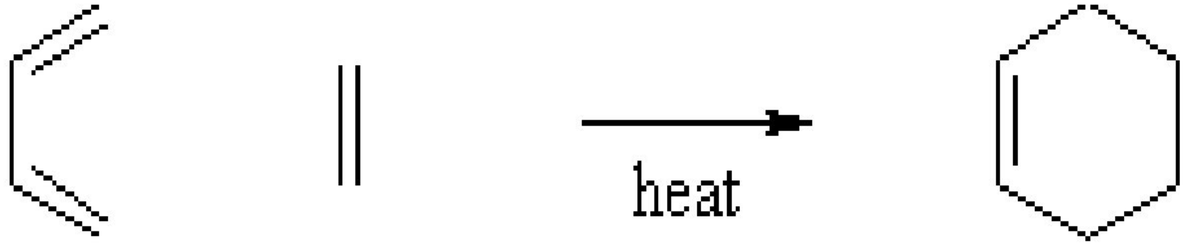


4) Reaction with Hydrogen - 1,3- butadiene reacts with hydrogen to produce 1,2 addition product, 1-butene and 1,4 addition product, 2-butene.

$CH_2=CH-CH=CH_2 + H_2 \text{-----}\rightarrow CH_3CH_2-CH=CH_2 + CH_3CH=CHCH_3$

1-butene 2-butene

5) Diel's Alder Reaction – Diel's Alder is the reaction in which diene(like 1,3-butadiene) reacts with alkene or dienophile (The unsaturated compounds like alkene, alkyne or similar compounds) to form cyclic compound. For ex, 1,3-butadiene reacts with ethene to form cyclohexene.



1,3-butadiene Ethene Cyclohexene

ALKYNES

The class of organic compounds containing carbon carbon triple bond are called as Alkynes. Alkynes have general formula C_nH_{2n-2}. Alkynes do not occur free in nature but are produced during cracking of petroleum. Commonly the members of alkyyne family are called aacetylenes. The first member of alkyne series is acetylene (H-C ≡ C-H).

Alkynes are represented as , R-C ≡ C- R

NOMENCLATURE –

Common name- According to this system first member of alkynes is named as acetylene and the higher members are regarded as derivative of acetylene.

IUPAC name- According to this system, first select longest carbon chain containing triple bond, consider its basic hydrocarbon i.e., alkane , now replace last letters **'ane'** of this alkane by **'yne' .**

Always start counting carbon atoms of carbon chain in such a way that triple bond containing carbon should acquire lowest number. Write names of remaining substituents alphabetically according to their number.

S.N.	Compound	Common name	IUPAC name
1.	CH_3-C≡ C-H	Methyl acetylene	1-propyne
2.	CH_3-C≡ C-CH_3	Dimethyl acetylene	2-butyne
3.	CH_3-CH- C ≡ CH I C H_3	Isopropyl acetylene	3- methyl -1- butyne

METHODS OF PREPARATION OF ACETYLENE

1) From Calcium Carbide –

Calcium carbide reacts with water(undergoes hydrolysis) to form acetylene.

$CaC_2 + 2HOH \dashrightarrow Ca(OH)_2 + H\text{-}C \equiv C\text{-}H$

Calcium carbide — Acetylene

2) From Vicinal dihalide –

When vicinal dihalide reacts with alc. KOH acetylene is formed.

$BrH_2C - CH_2Br + 2KOH \dashrightarrow H\text{-}C \equiv C\text{-}H + 2KBr + 2H_2O$

1,2- dibromoethane — Acetylene

CHEMICAL REACTIONS OF ACETYLENE –

1) **Hydroboration-** Acetylene reacts with diborane to form alkenyl borane which on reaction with hydrogen peroxide (H_2O_2) forms allyl alcohol which further on rearrangement finally gives acetaldehyde.

$$H\text{-}C \equiv C\text{-}H + 2BH_3 \dashrightarrow 2\ H\text{-}C(H)=C(BH_3)\text{-}H$$

$$H\text{-}C(H)=C(BH_3)\text{-}H \xrightarrow{H_2O_2} H\text{-}C(H)=C(OH)\text{-}H \xrightarrow{\text{Rearrangement}} CH_3CHO$$

Alkenyl borane — Allyl alcohol — Acetaldehyde

2) Oxidation Reaction

i) By alk. $KMnO_4$ –

On oxidation with alk. $KMnO_4$, acetylene gives oxalic acid.

H-C ≡ C-H + 4(O) ----------→ HOOC-COOH

Acetylene alk. $KMnO_4$ Oxalic acid

ii) By acidic $KMnO_4$ –

On oxidation with acidic $KMnO_4$, acetylene gives CO_2 and H_2O.

H-C ≡ C-H + 5(O) ----------→ $2CO_2\uparrow + H_2O$

Acetylene acidic $KMnO_4$

iii) By acidic $K_2Cr_2O_7$ –

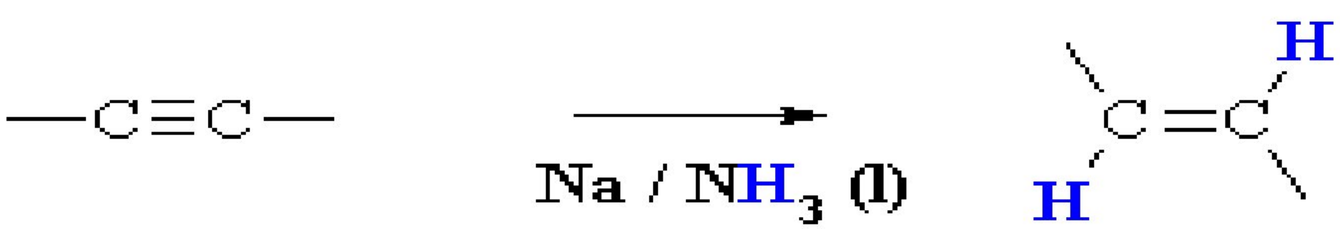
On oxidation with acidic $K_2Cr_2O_7$, acetylene gives acetic acid.

H-C ≡ C-H + (O) + H_2O ----------→ CH_3COOH

Acetylene acidic $K_2Cr_2O_7$ Acetic acid

3) Metal Ammonia Reduction of Acetylene (Reduction Reaction)-

The alkynes when reduces by Na or Li in liquid ammonia form transalkene.



Trans-alkene

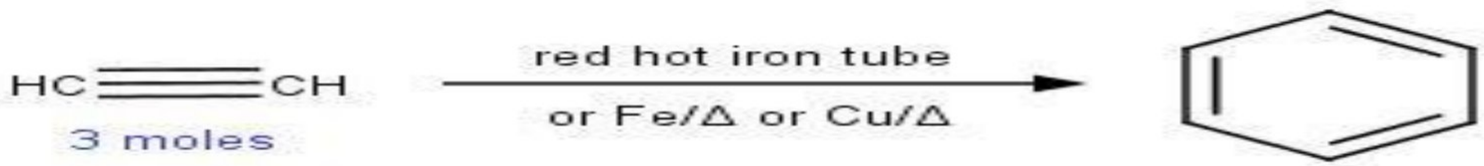
4) Polymerization Reaction –

Under suitable condition, alkynes add to one or more molecules of alkynes to form dimer, trimer or tetramer.

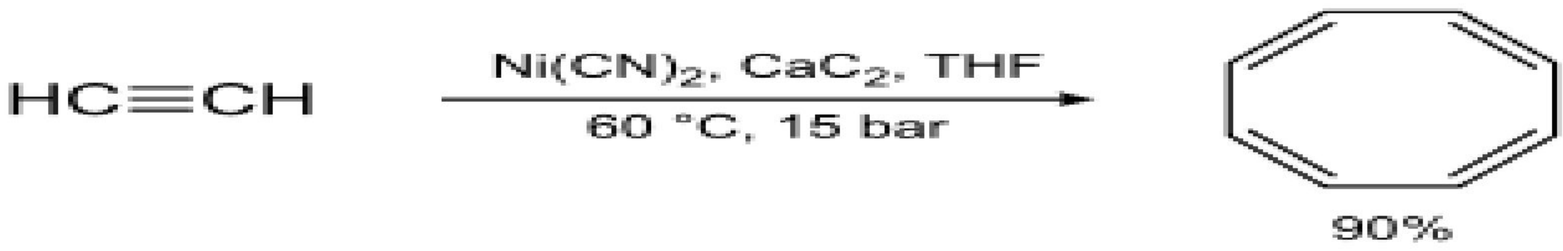
i)Dimerization-Acetylene dimerizes when passed through a solution of cuprous chloride in ammonium chloride to form a linear dimer, vinyl acetylene and divinyl acetylene.

$$H\text{-}C \equiv C\text{-}H + H\text{-}C \equiv C\text{-}H \xrightarrow[CuCl_2/\ NH_4Cl]{} \underset{\text{Vinyl acetylene}}{H\text{-}C \equiv C\text{-}CH{=}\ CH_2} \xrightarrow{} \underset{\text{Divinyl acetylene}}{H_2C{=}HC\text{-}C \equiv C\text{-}CH{=}CH_2}$$

ii) Trimerization-Three molecules of acetylene when passed through red hot tube, it trimerizes to benzene.



iii) Tetramerization- Under high pressure and in presence of nickel cyanide, acetylene polymerises to 1, 3. 5. 7- Cycloocta-tetraene.



Acetylene (4 moles) 1,2,3,4-cycloocta-tetraene

5) Oxyacetylene flame Reaction-

When acetylene is burned in presence of pure oxygen, it produces CO2 and water. During this the large amount of energy is produced. The reaction can be given as-

$2\ H\text{-}C \equiv C\text{-}H + 5\ O_2 \text{----------} \rightarrow 4CO_2 + 2H_2O + 620\ kcal$

Above reaction produces very high temperature flame which used for welding and cutting of metals. This reaction is also called as oxy-acetylene flame.

6) Acidity of Alkynes (Acetylene)-

Acetylene is different than ethylene and ethane. In acetylene, it has C ≡ C therefore the electron of C-H bonds are very close to the carbon nucleus.

$$H^{\delta+}\text{-}C^{\delta-} \equiv C^{\delta-}\text{-}H^{\delta+}$$

The Carbon atom of acetylene acquire partial -ve charge and H acquire partial + ve charge, therefore 'H' atom of acetylene can be easily removed during ionization. This property of acetylene is called as **acidic property**.

The acidic nature of acetylene can be explained by reaction with Sodium metal, which form sodium acetylide.

$H\text{-}C \equiv C\text{-}H + Na \text{----------} \rightarrow Na\text{-}C \equiv C\text{-}H \text{----------} \rightarrow Na\text{-}C \equiv C\text{-}Na$

Acetylene Sodium Sodium acetylide Disodium acetylide

7) Formation of metal Acetylide -

Acetylene undergoes reaction with metal salt in presence of ammonia, to form different metal acetylide.

i) Formation of silver acetylide –

Acetylene when passed through the solution of silver nitrate in presence of liquid ammonia, produces silver acetylide. This is also known as light metal acetylide.

$$H\text{-}C \equiv C\text{-}H + 2Ag(NH_3)_2NO_3 \xrightarrow[liq.NH_3]{} Ag\text{-}C \equiv C\text{-}Ag + 2HNO_3 + 4NH_3 \uparrow$$

Silver acetylide (white coloured)

ii) Formation of copper acetylide –

Acetylene when passed through the solution of copper chloride in liquid ammonia, it produces copper acetylide. This is also known as heavy metal acetylide.

$$H\text{-}C \equiv C\text{-}H + 2Cu(NH_3)_2Cl \xrightarrow[liq.NH_3]{} Cu\text{-}C \equiv C\text{-}Cu + 2NH_4Cl + NH_3 \uparrow$$

Copper acetylide (red coloured)