Dienes.

These are hydrocarbon with two carbon-carbon double bonds. Dienes are of three types

(1) **Conjugated dienes**: Double bonds are separated by one single bond.

Ex: $CH_2 = CH - CH = CH_2$ (1, 3-butadiene)

(2) **Cumulative dienes**: Double bonds are adjacent to each other.

Ex: $CH_2 = C = CH_2$ Propadiene [allene]

(3) **Isolated or Non-conjugated**: Double bonds are separated by more than one single bond.

Ex: $CH_2 = CH - CH_2 - CH = CH_2$ (1, 4 pentadiene)

The general formula is C_nH_{2n-2}. The predominant member of this class is 1, 3-butadiene.

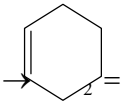
(1) **Method of preparation**

(i) **From acetylene**: $2HC \equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} \underset{\text{Vinyl acetylene}}{HC \equiv C - CH = CH_2} \xrightarrow[Pd/BaSO_4]{H_2} \underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH = CH_2}$

(ii) **From 1, 4-dichlorobutane**: $\underset{\text{1,4 -Dichlorobu tane}}{CH_2Cl\,CH_2CH_2\,CH_2Cl} \xrightarrow{Alc.KOH} \underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH = CH_2}$

(iii) **From 1,4-butanediol**: $\underset{\text{1, 4-Butanediol}}{CH_2OH\,CH_2CH_2\,CH_2OH} \xrightarrow[\text{heat}]{H_2SO_4} \underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH = CH_2}$

(iv) **Frombutane**: $\underset{\text{n-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[600^oC]{\text{Catalyst}} \underset{\text{1, 3-Butadiene}}{CH_2 = CH - CH = CH_2}$ (Cr_2O_3 used as catalyst.)

(v) **From cyclohexene**:  $\underset{\text{1, 3-Butadiene}}{= CH - CH = CH_2} + \underset{\text{Ethene}}{CH_2 = CH_2}$

(2) **Physical property:** 1, 3-butadiene is a gas.

(3) **Chemical properties**

(i) **Addition of halogens:**

$\underset{\text{1, 3-Butadiene}}{CH_2 = CHCH = CH_2} + Br_2 \xrightarrow{CCl_4}$

- $CH_2BrCHBrCH=CH_2$ — *3,4-Dibromo-1-butene (1, 2-Addition) predominates (62%) in non-ionising solvent (hexane)*
- $CH_2BrCH=CH.CH_2Br$ — 1,4-Dibromo-2-butene (1, 4-Addition) predominates (70%) in an ionising solvent (acetic acid)

Mechanism

Step I: The halogen molecule (Br_2) undergoes heterolytic fission.

$$Br_2 \longrightarrow \underset{\text{Bromonium ion}}{Br^+} + : \underset{\text{Bromide ion}}{Br^-}$$

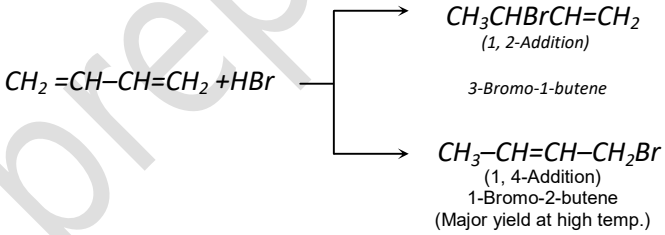
Step II: The bromonium ion attacks the double bond to give a resonance stabilized carbonium ion.

$$Br^+ + CH_2 = CH - CH = CH_2 \longrightarrow \begin{matrix} BrCH_2 - \overset{+}{C}H - CH = CH_2 (A) \\ \updownarrow \\ BrCH_2 - CH = CH - \overset{+}{C}H_2 (B) \end{matrix}$$

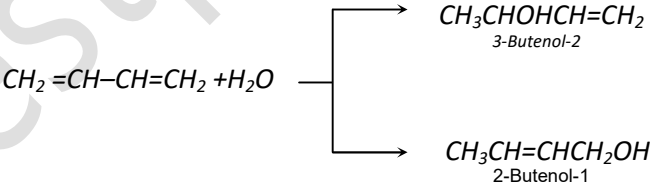
Step III: The bromide ion combines with (A) to form 3, 4-dibromo-1-butene (1, 2-addition). It combines with (B) to form 1, 4-dibromo-2-butene (1, 4-addition).

$Br - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH = CH_2$ 1, 2-product; $Br - CH_2 - CH = CH - CH_2 - Br$ 1, 4-product

(ii) **Addition of halogen acids**:

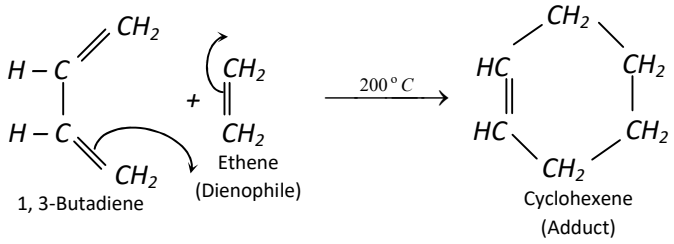


(iii) **Addition of water**:



(iv) **Polymerization:** $\underset{\text{1, 3-Butadiene}}{nCH_2 = CHCH = CH_2} \xrightarrow{\text{Peroxide}} [-\underset{\text{Buna rubber}}{CH_2CH = CHCH_2} -]_n$

Diels-alder reaction:

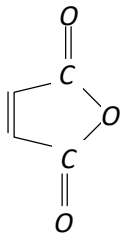
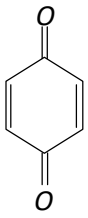
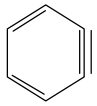


Note: Diene is known as Diene and alkene or alkyne is known as Dienophile.

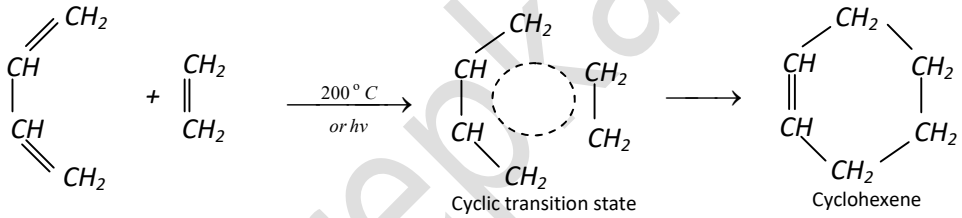
If product is cyclohexene then dienophile is alkene or alkene derivative.

If product is 1, 4-cyclohexadiene then dienophile is alkyne or alkyne derivative.

Dienophiles of the reaction may be one of the following,

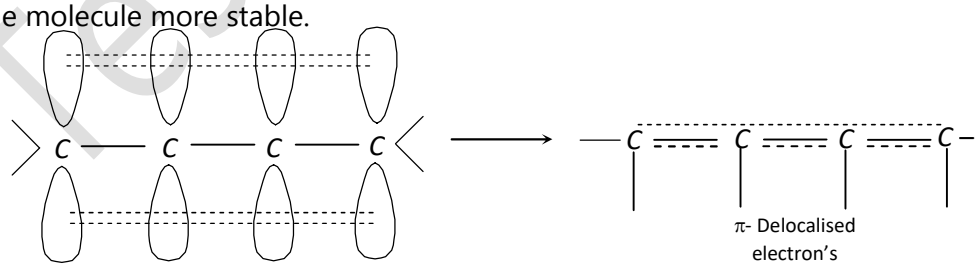
Alkenes; Alkynes; $CH_2 = C = CH_2$;  ;  ; 

Mechanism (FMO)



Stability of conjugated dienes: It explained on the basis of delocalization of electron cloud between carbon atoms.

The four π electrons of 1, 3-butadiene are delocalized over all the four atoms. This delocalization of the π electrons makes the molecule more stable.



(v) **Ozonolysis**: $CH_2 = CHCH = CH_2 + 2O_3 \xrightarrow{Zn/H_2O} 2HCHO + OHCCHO$