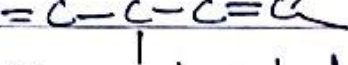
"DIENES" AND "CONJUGATED-DIENE"

Definition :— Alkenes which containing two carbon-carbon double bonds are called dienes or alkadienes. There are three types of Dienes

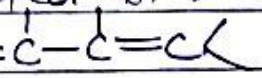
(1) Isolated or Nonconjugated Dienes
(2) Conjugated Dienes
(3) Cumulated Dienes

Isolated or Nonconjugated Dienes — when the double bonds are seperated by more than one single bond.

eg: 

Nonconjugated diene.

Conjugated Dienes — when the double bonds are seperated by one single bond, the diene is called conjugated Diene. It is most important class of dienes.

eg. 

Conjugated diene

Cumulated Dienes — when the double bonds are adjacent to each other.

eg: 

cumulated diene

Nomenclature of Dienes — Dienes are named by the IUPAC system in the same way as alkenes except that ending -adiene is used. The

positions of the double bonds are numbered to give the first carbon of each double bond a minimum number.

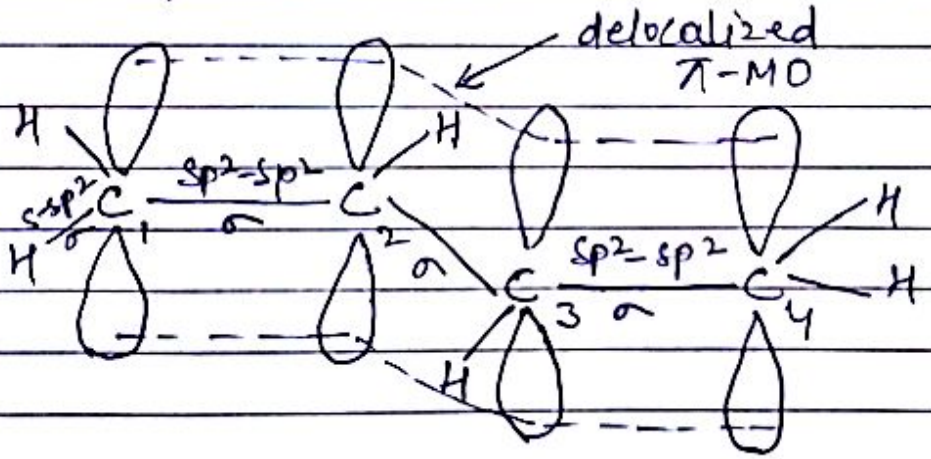
examples – $CH_2=CH-CH=CH_2$, $CH_2=CH-CH_2-CH=CH_2$

1,3-Butadiene 1,4-Pentadiene

1,3-BUTADIENE, $CH_2=CH-CH=CH_2$

This is the most important conjugated diene.

Structure – All four carbon atoms in 1,3-butadiene are sp^2 hybridized. The sp^2 hybrid orbitals overlap with each other and with s orbitals of the hydrogen atoms to form C-C and C-H σ bonds. Since the bonds result from the overlap of trigonal sp^2 orbitals, all carbons and hydrogen atoms lie in one plane.



Orbital structure of 1,3-Butadiene

In this each carbon atom possesses an unhybridized p-orbital. The p-orbitals are perpendicular to the plane of σ bonds. The p orbital on C-2 can overlap with the p orbitals on C-1 and C-3. The p-orbital can overlap with the p-orbitals on C-1 and C-3. The p-orbital on C-3 can overlap with the p-orbitals on C-2 and C-4.

Preparation – 1,3- Butadiene is prepared by the following Methods.

(1) By heating 1,4-dichlorobutane with alcoholic KOH. This is a dehydrohalogenation reaction.

$$\underset{\text{1,4-Dichlorobutane.}}{Cl\,CH_2CH_2CH_2CH_2\,Cl} + 2KOH \xrightarrow[\Delta]{\text{Alcohol}} \underset{\text{1,3-Butadiene}}{CH_2=CH-CH=CH_2} + 2KCl + 2H_2O$$

(2) By acid-catalysed dehydration of ~~1,4-butadiene~~ 1,4 butanediol.

$$\underset{\text{1,4-Butanediol}}{OH\,CH_2CH_2CH_2CH_2\,OH} \xrightarrow[\Delta]{H^+} \underset{\text{1,3-Butadiene}}{CH_2=CH-CH=CH_2} + 2H_2O$$

(3) By catalytic dehydrogenation of n-butane.

$$CH_3CH_2CH_2CH_3 \xrightarrow[600^\circ C]{Cr_2O_3/Al_2O_3} \underset{\text{1,3- Butadiene.}}{CH_2=CH-CH=CH_2}$$

Remaining part of structure – that is, all four p orbitals overlap to form a large π molecular orbital. Each pair of π electrons is thus attracted, not by two, but all four carbons.

the overlaping of p-orbitals of C-2 and C-3 in both directions, which allows the π electrons to be spread over a large area, is refered to as Delocalization. It is responsible for greater stability of 1,3-butadiene. The C-C single bonds are shorter (1.48 Å) and C-C double bonds are longer (1.37 Å) than normal isolated C-C and C=C bonds.

Propene.

Chemical Properties —

(1) **Addition of Halogen Acids** :- 1,3-Butadiene reacts with halogen acids (HBr or HCl) to give a mixture of two compounds that are 3-bromo-1-butene and 1-bromo-2-butene. there two products results from 1,2-Addition and 1,4-Addition.

$CH_2=CH-CH=CH_2 + HBr$ — 1,3-Butadiene

→ $CH_3-\underset{Br}{CH}-CH=CH_2$ — 3-Bromo-1-Butene (1,2-Addition)

→ $CH_3-CH=CH-CH_2Br$ — Bromo-2-Butene (1,4-Addition)

(2) **Addition of Halogens** :— 1,3-Butadiene reacts with halogens (Cl_2 or Br_2) in the presence of an inert solvent (CCl_4) to give a mixture of two dibromo compounds

$CH_2=CH-CH=CH_2 + Br_2$ — 1,3-Butadiene

→ $CH_2(Br)-CH(Br)-CH=CH_2$
3,4-Dibromo-1-Butene
(1,2-Addition)

→ $CH_2(Br)-CH=CH-CH_2(Br)$
1,4-Dibromo-2-Butene
(1,4-Addition)

(3) Addition of Hydrogen :— 1,3-Butadiene reacts with H_2 in the presence of a catalyst to give a mixture of 1-butene and 2-butene.

$$CH_2=CH-CH=CH_2 \xrightarrow[Pt]{H_2} CH_3CH_2CH=CH_2 + CH_3CH=CHCH_3$$

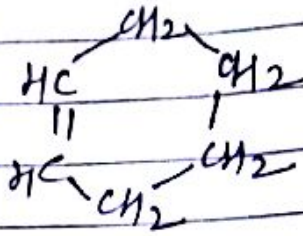
(1-Butene) (2-Butene)

(4) Polymerization :— 1,3-Butadiene polymerizes in the presence of peroxides to give polybutadiene (Buna Rubber)

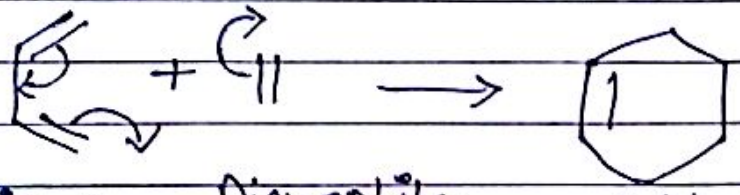
$$n\ CH_2=CH-CH=CH_2 \xrightarrow{R_2O_2} [-CH_2-CH=CH-CH_2-]_n$$

1,3-Butadiene — Polybutadiene (Buna Rubber)

(5) **Diels-Alder Reaction:**— this involves the treatment of 1,3-butadiene with an alkene or an alkyne. NO catalyst is required.

$CH_2=CH-CH=CH_2 + CH_2=CH_2 \xrightarrow{200^oC}$ 

1,3-Butadiene (Diene) + Ethylene (Dienophile) → cyclohexene (Adduct)



Diene Dienophile Adduct

The alkene or alkyne used in Diels-Alder reaction is referred to as Dienophile (diene-lover). The product of Diels-Alder reaction is called the Adduct. This reaction is widely used in the synthesis of six membered ring compounds.

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