DIENES

Types of Dienes

Dienes are the unsaturated hydrocarbons with carbon-carbon double bonds in the molecules. These are represented by the general formula C_nH_{2n-2} which means that they are isomeric with alkynes (functional isomers). However, their properties are quite different from those of alkynes.

Depending upon the relative positions of the two double bond, dienes are classified in three types:

Isolated dienes or non-conjugated dienes: In an isolated diene, the two double bonds are separated by more than one single bond.

For example,

$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H = \overset{5}{C}H_2$
penta − 1,4 − diene

$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H(CH_3) - \overset{4}{C}H = \overset{5}{C}H_2$
3 − Methylpenta − 1,4 − diene

Conjugated dienes: In a conjugated diene, the two double bonds are present in the conjugated or alternate positions and are separated by a single bond.

$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 = \overset{4}{C}H_2$
Buta − 1,3 − diene

$\overset{1}{C}H_2 = \overset{2}{C}(CH_3) - \overset{3}{C}H = \overset{4}{C}H_2$
2 − Methylpenta − 1,3 − diene

Cumulate dienes: In this case, the two doubles in the molecules are present at adjacent positions.

For example,

$\overset{1}{C}H_2 = \overset{2}{C} = \overset{3}{C}H_2$
Buta − 1,2 − diene

$\overset{1}{C}H_2 = \overset{2}{C}(CH_3) - \overset{3}{C}H = \overset{4}{C}H_2$
Buta − 1,2 − diene

Comparison of relative stabilities of isolated and conjugated dienes

Resonance Theory: The relative stabilities of the two types dienes can also be justified on the basis of the theory of resonance. Penta-1, 3-diene (conjugated diene) is a hybrid of the following contributing structures.

$$\overset{\curvearrowleft}{CH_2}=CH-CH=CH-CH_3 \leftrightarrow \overset{\ominus}{C}H_2-\overset{\oplus}{C}H-\overset{\curvearrowleft}{CH}=CH-CH_3 \leftrightarrow \overset{\ominus}{C}H_2-CH=CH-\overset{\oplus}{C}H-CH_3$$

The delocalization of π-electron charge because of resonance decreases the energy of the molecule or increases its stability.

Penta-1, 4-diene (isolated diene) has only two contributing structures.

$$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H = \overset{5}{C}H_2 \quad \leftrightarrow \quad \overset{1\ominus}{C}H_2 - \overset{2\oplus}{C}H - \overset{3}{C}H_2 - \overset{4}{C}H = \overset{5}{C}H_2$$

(I) (II)

Since the carbon atom C_3 is not involved in any resonance, the contributing structures are less number are compared to the conjugated diene. The isolated diene is, therefore, less stable than a conjugated diene.

Stability Order

The stability order of conjugated, isolated, and cumulated dienes is determined by the degree of delocalization of pi electrons across the double bonds in these molecules.

Here's the stability order:

Conjugated diene > Isolated diene > Cumulated diene

Properties of Conjugated Dienes

The properties of the isolated dienes are similar to those of simple alkene but those of conjugated dienes are somewhat modified because of delocalization of the π-electron charge. However, they also patriate in the addition reactions. The important chemical characteristics of the conjugated dienes are briefly discussed.

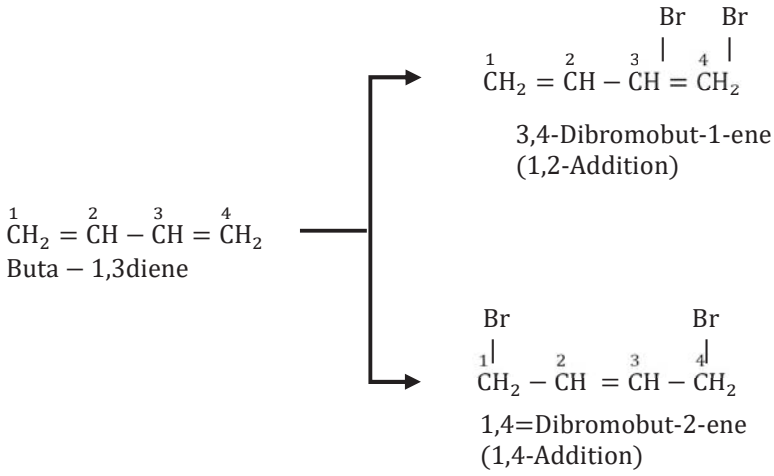
1. Addition Reaction:

Conjugated or 1, 3-dienes take part in the addition reactions which can proceed by electrophilic as well as free radical mechanism depending upon the nature of the attacking reagent and the reaction conditions.

Electrophilic Addition Reactions: The electrophilic addition is illustrated by the attack of halogen and halogen acid on Buta--1,3-diene, a conjugated diene.

Addition of halogen: If one mole of halogen attacks per mole of the diene, two types of addition products are formed. There are 1, 2 and 1, 4 addition products.

For example,



1, 2- addition is a normal addition in which one mole of halogen has been added to one of the double bonds. But 1, 4- addition is somewhat unexpected.

Mechanism: The addition is electrophilic in nature and the halogen molecule (bromine) provides the electrophilic for the attack.

$$CH_2=CH-CH=CH_2 + \overset{\delta+}{Br}-\overset{\delta-}{Br} \rightarrow CH_2=CH-\overset{\oplus}{C}H-CH_2Br + \overset{\ominus}{Br}$$

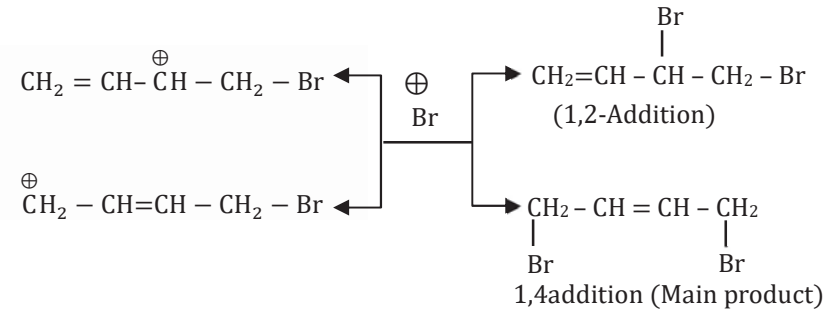
Buta-1,3-diene — Carbocation (2°)

The 2° carbocation get stablised by resonance as follows –

$$CH_2=CH-\overset{\oplus}{C}H-CH_2-Br \leftrightarrow \overset{\oplus}{C}H_2-CH=CH-CH_2-Br$$

I II

The attack of ion on carbocation (I and II)



Addition of H - X

$$CH_2{=}CH-CH{=}CH_2 \xrightarrow{HBr} ?$$

Mechanism: The addition is electrophilic in nature as H^+ ion is the electrophilic

$$CH_2 = CH - CH = CH_2 + \overset{\delta+}{H} - \overset{\delta-}{Br} \rightarrow CH_2 = CH - \overset{\oplus}{C}H - CH_3 + Br^-$$

Carbocation(2^o)

The carbocation gets resonance stablised as follows:

$$CH_2 = \underset{(I)}{CH} - \overset{\oplus}{C}H - CH_3 \rightarrow CH_2 - CH = \underset{(II)}{CH} - CH_3$$

The attack of Br^- ion on the carbocation (I) gives 1, 2-addition product whereas the attack on the carbocation (II) yields 1,4-addition product.

$$Br^- + CH_2 = CH - \overset{\oplus}{C}H - CH_3 \rightarrow \underset{\text{1, 2 – Addition product}}{CH_2 = CH - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3}$$

$$Br^- + \overset{\oplus}{C}H_2 - CH = CH - CH_3 \rightarrow \underset{\text{1, 4 – Addition product}}{CH_2 - CH = CH - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3}$$

2. Free Radical Addition Reaction:

The addition to conjugated dienes can also proceed by free radical mechanism provided it is carried in the presence of a suitable regent which can help in forming a free radical. However, the addition also yields 1, 2 and 1, 4 addition products. The free radical is illustrated by the attack of bromodichloromethane ($BrCCl_3$) on buta-1,3-diene in the presence of an organic peroxide such as benzoyl peroxide.

$$\underset{\text{Buta – 1, 3 – diene}}{\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}} + BrCCl_3 \xrightarrow[\text{Peroxide}]{\text{Benzyl}} \underset{\text{Bromotri – chloromethane}}{Cl_3\overset{4}{C}H_2\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2} + Cl_3\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_2$$

Br Br

Mechanism: The mechanism of addition is free radical in nature which is initiated by benzyol free radical. It is explained in the following steps:

Step – I Generation of free radical.

$$C_6H_5CO-O-O-COC_6H_5 \xrightarrow{\text{Homolysis}} C_6H_5-CO-\dot{O}+\dot{O}-COC_6H_5$$

$$C_6H_5-CO-\dot{O} \rightarrow \dot{C}_6H_5 + CO_2$$

$$\dot{C}_6H_5 + BrCCl_3 \rightarrow C_6H_5-Br+\dot{C}Cl_3$$

Trichloromethyl free radical

Step- II Attack of free radical on buta-1, 3-diene.

$$\dot{C}Cl_3 + CH_2=CH-CH=CH_2 \rightarrow Cl_3C-CH_2-\dot{C}H-CH=CH_2$$

Freeradical(sec o ndary)

The free radical gets resonance stablised.

$$Cl_3C-CH_2=\dot{C}H-CH=CH_2 \leftrightarrow Cl_3C-CH_2-CH=CH-\dot{C}H_2$$

Step- III Change of free radical into addition product.

The free radical takes up Ḃr from the attacking reagent to give the desired addition products.

i.e., 1, 2 and 1, 4 addition products.

$$BrCCl_3 + Cl_3C-CH_2-\dot{C}H-CH=CH_2 \rightarrow Cl_3C-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH=CH_2$$

(1, 4 – Addition Pr oduct)

$$BrCCl_3 + Cl_3C-CH_2-CH=\dot{C}H_2 \rightarrow Cl_3C-CH_2-CH=CH-\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

(1, 4 – Addition product)

3. Cyclo-Addition Reaction (Diel Alder Reaction)

Cyclo-addition reactions are one of the most important reactions of conjugated dienes. Cyclo-addition involves the combination between a conjugated diene (4π-electron system) and a compound containing a double bond (2 π -electron system) called dienophile which means a diene loving or attracting molecule. As a result, a six membered ring gets formed and the reaction is therefore known as cyclo-addition reaction. It is quite often termed as **(4 + 2) cyclo-addition reaction** because four 4 π-electron system adds to a two 2 π electron system.

The addition products are called **Diel Alder Adduct**.

For example.

Buta-1,3-diene + Ethene → Cyclohexene **(Diel Alder adduct)**

Buta-1,3-diene + Propenal (Acrolein) → 3 - cyclohexene carbaldehyde