ALKADIENES Section - 5

Alkadienes are isomers of alkynes and cycloalkenes. These are classified in three categories.

Hydrocarbons containing cumulated double bonds are called allenes or cumulated dienes.

 $CH_2 = C = CH_2$

Propadiene C₃H₄

 $CH_2 = C = CH - CH_3$

Butadiene C_4H_6

(b) Those dienes which have an alternate system of double and single bonds are called conjugated dienes.

 $CH_2 = CH - CH = CH_2$

1, 3 Butadiene

$$CH_2 = C - CH = CH_2$$

$$CH_3$$

2-Methyl-1, 3-Butadiene



1, 3-Cyclohexadiene

(c) In case, when one or more sp³ hybridised carbon atoms come in between the double bonds in dienes, then they are called isolated dienes.

 $CH_2 = CH - CH_2 - CH = CH_2$

1, 4-Pentadiene

Note: Conjugated dienes are most stable among dienes. They are stabilised due to resonance.

Preparation of Conjugated dienes:

1. From isolated dihalides

$$\begin{array}{c} \operatorname{CH_2} - \operatorname{CH_2} - \operatorname{CH_2} - \operatorname{CH_2} & \xrightarrow{\operatorname{NaNH_2}} & \operatorname{CH_2} = \operatorname{CH} - \operatorname{CH} = \operatorname{CH_2} \\ | & | & | \\ \operatorname{Cl} & \operatorname{Cl} & \text{1, 3-Butadiene} \\ \end{array}$$

$$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 & \xrightarrow{\text{NaNH}_2} & \text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH}_2 + \text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2 \\ & \text{Cl} & \text{Cl} & \text{1, 3-Pentadiene (Major)} & \text{1, 4-Pentadiene (Minor)} \\ \end{array}$$

2. From isolated diols:

$$\begin{array}{cccc} CH_3-CH-CH_2-CH_2 & \xrightarrow{H_2SO_4} & CH_2=CH-CH=CH_2 & + CH_3-CH=C=CH_2 \\ OH & OH & 1, 3-Butadiene (Major) & 1, 2-Butadiene (Minor) \end{array}$$

Reactions of Conjugated Dienes:

For the discussion of reactions of conjugated dienes we shall take 1, 3-Butadiene as an example.

- 1. Electrophillic Addition:
 - 1, 3-Butadiene when reacts with HCl show unusual behaviour to give mixture of two products:
 - 3-Chloro-1-butene (1, 2-addition product) and 1-Chloro-2-butene (1, 4-addition product)
 - (a) The formation of 1, 4-addition product is interesting.

$$CH_2 = CH - CH = CH_2 \xrightarrow{HCl} CH_3 - CH - CH = CH_2 + CH_3 - CH = CH - CH_2Cl$$

$$Cl$$

$$(1, 2-addition)$$

$$(1, 4-addition)$$

Note: Usually 1, 4-addition product is major.

(b) Addition of HBr to 1, 3-Butadiene takes place differently at different temperature to give 1, 2-addition and 1, 4-addition products as follows:

$$CH_2 = CH - CH = CH_2 + HBr \longrightarrow$$

(i) At -80° C (Low temperature):

$$CH_3 - CH - CH = CH_2 + CH_3 - CH = CH - CH_2Br$$

Br

(1, 2-addition)(80%) (1, 4-addition) (20%)

(ii) A 40°C (Near room temperature and above):

$$CH_3 - CH - CH = CH_2 + CH_3 - CH = CH - CH_2Br$$
Br
(1, 2 - addition)(20%) (1, 4 - addition) (80%)

Note: At high temperatures, in case of HBr, 1, 2-addition product rearranges to give 1, 4-addition product.

(c) Addition of Br₂ to 1, 3—Butadiene also gives a mixture of 1, 2-addition and 1, 4-addition products.

(i)
$$CH_2 = CH - CH = CH_2 \xrightarrow{Br_2 \\ -15^{\circ}C} \xrightarrow{CH_2 - CH - CH} = CH_2 + CH_2 - CH = CH - CH_2Br$$
 Br
 Br
 Br
 Br
 Br
 $(1, 3 - Butadiene)$
 $(1, 2 - addition) (54%)$
 $(1, 4 - addition) (46%)$

(ii) $CH_2 = CH - CH = CH_2 \xrightarrow{Br_2} 1$, 4-addition is major

Hydrocarbons Vidyamandir Classes

2. Free radical addition:

In presence of peroxides, both 1, 2-addition product and 1, 4-addition products are formed. Consider addition of BrCCl₃ in presence of peroxide.

$$CH_2 = CH - CH = CH_2 + BrCCl_3 \longrightarrow Cl_3C - CH_2 - CH - CH = CH_2 + Cl_3C - CH_2 - CH = CH - CH_2Br$$

$$Br$$

$$(1, 2 - addition)$$

$$(1, 4 - addition)$$

Note: Temperature dependency of products is similar to that of HBr addition. Also refer to Diel - Alder reactions (dienes with alkenes) in cycloalkenes.

3. Reduction:

Catalytic hydrogenation of conjugated dienes in presence of H_2 /Li gives a mixture of 1, 2-addition and 1, 4-addition product with the 1,4-addition products being major.

$$CH_2 = CH - CH = CH_2 \xrightarrow{H_2/Li} \begin{array}{c} H & H & H \\ | & | & | \\ CH_2 - CH - CH = CH_2 & + CH_2 - CH = CH - CH_2 \\ \end{array}$$

$$But - 1 - ene \ (Minor) \qquad But - 2 - ene \ (Major)$$

However, the chemical reduction of 1, 3-Butadiene with sodium in alcohol gives mainly the 1, 4-addition product, i.e., But-2-ene.

$$CH_2 = CH - CH = CH_2 \xrightarrow{Na/alcohol} CH_3 - CH = CH - CH_3$$

1, 3-Butadiene But-2-ene

Under these conditions the isolated double bonds are not reduced. This suggests that dienes are much more reactive than simple alkenes.

4. Polymerization:

$$\begin{array}{c} \text{n}\left(\text{CH}_{2}=\text{CH}-\text{CH}=\text{CH}_{2}\right) \xrightarrow{\quad \text{Peroxides} \quad } \left(-\text{CH}_{2}-\text{CH}=\text{CH}-\text{CH}_{2}-\right)_{\text{n}} \\ \text{Buta-1, 3-diene} \end{array}$$

Since each repeating unit in polybutadiene contains a double bond, it may have either *cis* or *trans*-configuration. Actually the polybutadiene polymer obtained by free-radical polymerisation has *trans*-configuration.

$$n\begin{pmatrix} CH_{3} & Peroxides \\ CH_{2} = C-CH = CH_{2} \\ 2-Methylbuta-1, 3-diene \\ (Isoprene) & Major Product \\ (Gutta Percha) \\ \end{pmatrix} n\begin{pmatrix} Cl & Cl \\ CH_{2} = C-CH = CH_{2} \\ 2-Chlorobuta-1, 3-diene \\ (Chloroprene) & Polychloroprene \\ (Chloroprene) & (Neoprene) \end{pmatrix}$$

Neoprene is an important substitute for natural rubber and is superior to natural rubber in being more resistant to oil, gasoline and other organic solvents.

Illustration - 9 Isomers A, B, C, and E have a common molecular formula C_4H_6 . Identify A, B, C..... as per given instructions.

- (a) A reacts with RMgBr to give a hydrocarbon.
- (b) B reacts with Br_2 to give a mixture of two products.
- (c) C, an alicyclic compound, when oxidised by hot acidic $KMnO_4$, gives a dicarboxylic acid whose sodium salt on electrolysis gives an alkene, D. Also identify D.
- (d) E is an alicyclic compound which is oxidized by hot $KMnO_4$ to give 3-Oxo-1-butanoic acid.

SOLUTION:

C₄H₆: can be alkyne, or alkadiene, or cycloalkene.

(a) A should be a terminal alkyne as it reacts with Grignard reagent.

(A)
$$CH_3CH_2C \equiv CH^{\delta+} \xrightarrow{R MgBr} RH + CH_3CH_2C \equiv C - MgBr$$

(b) B should be a conjugated diene as it gives a mixture of products.

$$\begin{array}{c} \text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \xrightarrow{\text{Br}_2} & \text{CH}_2 - \text{CH} - \text{CH} = \text{CH}_2 + \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \\ & | & | & | & | \\ & \text{Br} & \text{Br} & \text{Br} & \text{Br} \\ & & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\$$

(c)
$$(C)$$
 (C) (C)

D is clearly ethene as it is the only alkene formed by Kolbe's electrolysis.

(d)
$$(O)$$
 COOH

Me

(a chain isomer of cyclobutene)

(E) (O)

(3-Oxo-1-butanoic acid)

Illustration - 10 *Give the products.*

(a)
$$H$$
 O (b) O O_3 O_3 O_4 O_3 O_4 O_5 O_5 O_7 O_8 $O_$

SOLUTION:

Note that aldehyde group is oxidised to acidic group.

Hydrocarbons Vidyamandir Classes

(b)
$$O_3$$
 O_3 O_3 O_4 O_5 O_5 O_5 O_7 O_8 O_8

IN-CHAPTER EXERCISE-E

1. Identify the products A, B, C, \ldots

(i)
$$CH_2 = CH - CH = CH_2 + CH_2 = CH - CH_2Cl \longrightarrow A$$

(ii)
$$CH_2 = C = CHCH_3 \xrightarrow{O_3} B$$

(iii) 1, 4-Cyclohexadiene
$$\xrightarrow{KMnO_4, hot}$$
 C

$$\frac{H_2}{\text{Lindlar's catalyst}} \to E$$

2. An organic compound $E(C_5H_8)$ on hydrogenation gives compound $F(C_5H_{12})$. Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E and F.

Choose the correct alternative. Only One Choice is Correct. However, questions marked * may have More than One Correct option :

- 3. (i) In allene (C_3H_4) , the type(s) of hybridisation of the carbon atom is(are):
 - (A) $sp \ and \ sp^3$
- (B) $sp \ and \ sp^2$
- (C) Only sp^3
- (D) sp^2 and sp^3

- *(ii) 2, 3-Pentadiene, $CH_3CH = C = CHCH_3$ is:
 - (A) A planar substance

(B) A conjugated diene

(C) An allene

- (D) A substance capable of cis-trans isomerism
- (iii) Hydrogenation of cyclohexene releases 120 kJ/mol of heat. Which of the following most likely represents the observed heat of hydrogenation of 1, 3-cyclohexadiene?
 - (A) 232 kJ/mol
- (B) $247 \, kJ/mol$
- (C) $240 \, kJ/mol$
- (D) 120 kJ/mol

- (iv) Which statement best describes the structure of allene molecule, $H_2C = C = CH_2$?
 - (A) The C-atoms form an angle of 120° and the H-atoms lie in the same plane as the C-atoms
 - (B) The C-atoms form an angle of 120° and the H-atoms lie in a plane perpendicular to that of the C-atoms
 - (C) The C-atoms form an angle of 180° and the four H-atoms lie in the same plane
 - (D) The C-atoms form angle of 180° and the two CH₂ groups are perpendicular to one another
- (v) What is the product of 1, 4-addition in the reaction shown?

(vi) What hydrocarbon reacts with the compound shown (on heating) to give the indicated product?

$$\bigcup_{O}^{O} \longrightarrow H_{3}C \longrightarrow \bigcup_{O}^{O} C$$

(A) 2-Methyl-1-butene

(B) 2-Methyl-2-butene

(C) 2-Methyl-1, 3-butadiene

- (D) 1, 3-Pentadiene
- 4. What two compounds of molecular formula $C_{11}H_{20}$ give 2, 2, 6, 6-tetramethylheptane on catalytic hydrogenation over platinum?
- **5.** Write structural formulas for all the:
 - (i) Conjugated dienes

(ii) Isolated dienes

(iii) Cumulated dienes

That gives 2, 4-dimethylpentane on catalytic hydrogenation.

6. A monomer of polymer on ozonolysis gives two moles of CH₂O and one mole of CH₃COCHO. Write the structure of monomer and write all 'cis' configuration of polymer chain.