

BP 202T - PHARMACEUTICAL ORGANIC CHEMISTRY - I

UNIT: 2 ALKANES, ALKENE & CONJUGATED DIENES

CLASS: 8

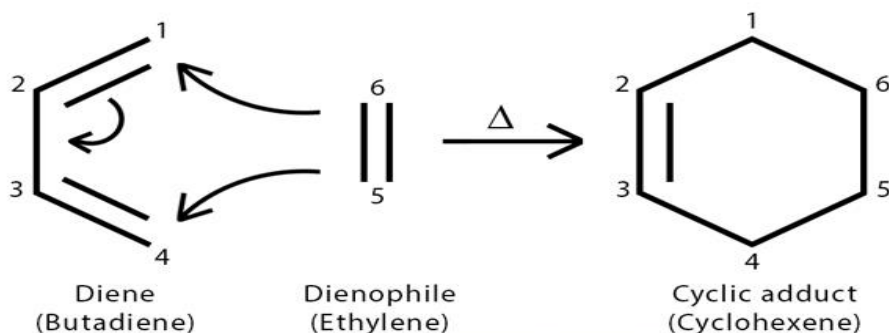
**TOPIC: DIEL'S ALDER REACTION & ELECTROPHILIC ADDITION
REACTION OF CONJUGATED DIENES****DIEL'S ALDER REACTION**

The Diels-Alder reaction is an important organic chemical reaction where the reactants include a substituted alkene and a conjugated diene. This substituted alkene is commonly referred to as a dienophile. This reaction gives rise to a substituted derivative of cyclohexene. The **Diels-Alder reaction is a very good example of pericyclic reactions which proceed via concerted mechanisms** (i.e. all bond breakage and bond formation occurs in a single step).

This reaction was discovered by the **German chemists Otto Diels and Kurt Alder in the year 1928**, for which they received the Nobel Prize in Chemistry in the year 1950. The Diels-Alder reaction can be used to form six-membered rings since there is a simultaneous construction of two **new carbon-carbon bonds**.

Mechanism of Diels-Alder Reaction

1. Electrons from the dienophile attack carbon (C) 1 on the diene resulting in a single bond between C1 and C6.
2. Electrons from the double bond between C1 and C2 relocates to between C2 and C3.
3. Double bond between C3 and C4 are broken and the electrons form a single bond between C4 and C5 to form the product.
4. All processes take place in a single step.

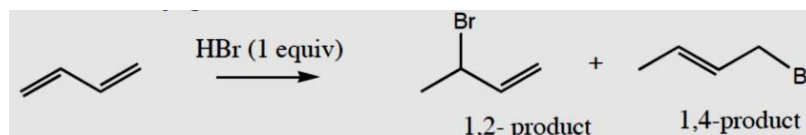


ELECTROPHILIC ADDITION REACTION OF CONJUGATED DIENES

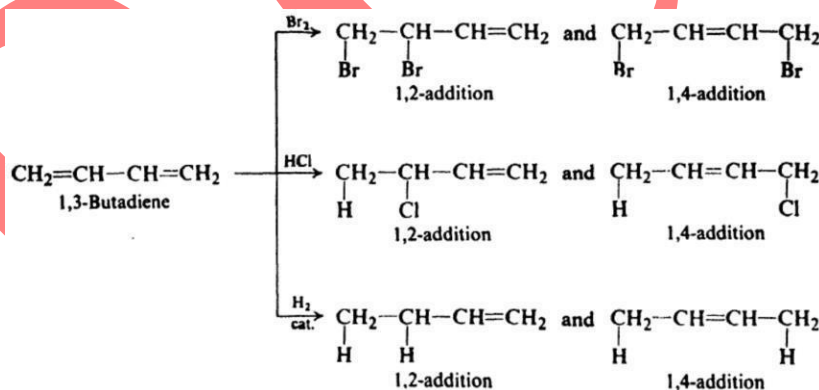
With conjugated dienes, electrophilic addition of one equivalent of HBr gives two products;

- 1,2- Product from Markovnikov addition
- 1,4- Product from conjugate addition

For example:

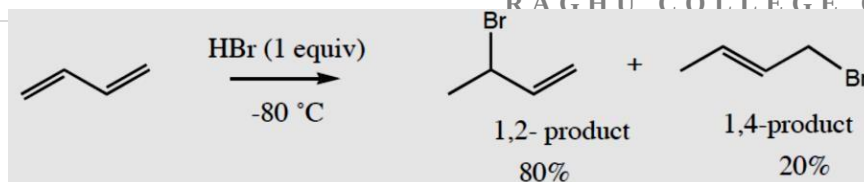


- Addition of HX to a conjugated diene forms 1,2- and 1,4-products because of the resonance stabilized allylic carbocation intermediate.
- When 1,3-butadiene is treated with bromine under similar conditions, there is obtained not only the expected 3,4-dibromo-1-butene, but also 1,4-dibromo-2-butene.
- Treatment with HCl yields not only 3-chloro-1-butene, but also 1-chloro-2-butene.
- Hydrogenation yields not only 1-butene but also 2-butene,

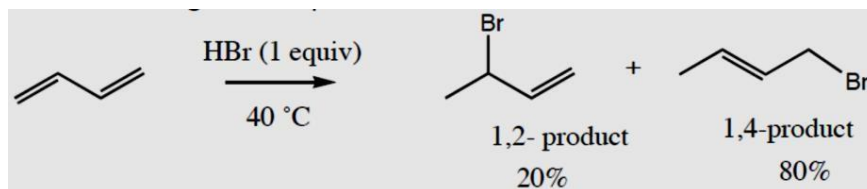


KINETIC VERSUS THERMODYNAMIC PRODUCTS

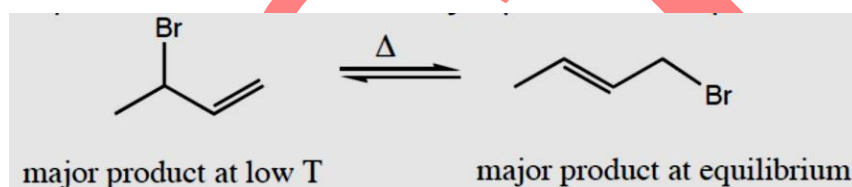
- The amount of 1,2- and 1,4-addition products formed in electrophilic addition reactions of conjugated dienes depends greatly on the reaction conditions:
- At low temperatures, the major product is formed by 1,2-addition. The kinetic product is formed faster and predominates at low temperature:



- At higher temperatures, the major product is formed by 1,4-addition. The more slowly formed thermodynamic product is more stable and predominates at higher temperatures.



- In fact, when a mixture containing mainly the 1,2-product is heated, the 1,4-addition product becomes the major product at equilibrium:



- Why is the 1,4-addition product the more stable (thermodynamic) product?
- Because more substituted alkenes are more stable (Remember, increasing alkyl substitution stabilizes an alkene by an electron-donating inductive effect).

5 MARKS QUESTIONS

- Explain the mechanism of Diel's Alder reaction with an example
- Explain electrophilic addition reaction of conjugated dienes with mechanism