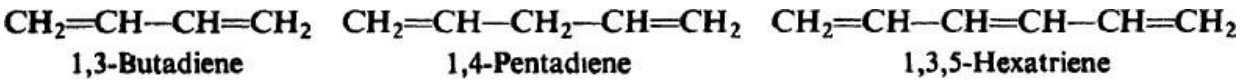
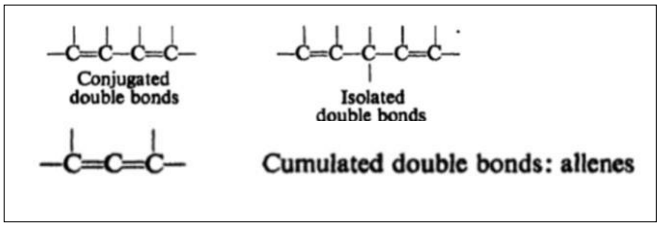
Conjugated dienes

- A diene is a hydrocarbon chain that has two double bonds that may or may not be adjacent to each other. The arrangements of these double bonds can have varying effects on the compounds reactivityand stability.
- Diene is used, with two numbers to indicate the positions of the two double bonds. This system is easily extended to compounds containing any number of double bonds.

Examples

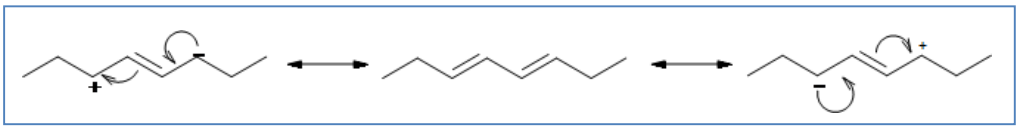


- Dienes are divided into two important classes according to the arrangement of the double bonds.
  1. Double bonds that alternate with single bonds are said to be **conjugated;**
  2. Double bonds that are separated by more than one single bond are said to be **isolated.**
  3. Contain **cumulated** double bonds; these compounds are known as **allenes.**



Stability of conjugated diene

- Conjugated dienes are more stable than non-conjugated dienes (both isolated and cumulated) due to factors such as delocalization of charge through resonance and hybridization energy.
- This can also explain why allylic radicals are much more stable than secondary or even tertiary carbocations. This is all due to the positioning of the pi orbitals and ability for overlap to occur to strengthen the single bond between the two double bonds.
- The resonance structure shown below gives a good understanding of how the charge is delocalized across the four carbons in this conjugated diene. This delocalization of charges stabilizes the conjugated diene:

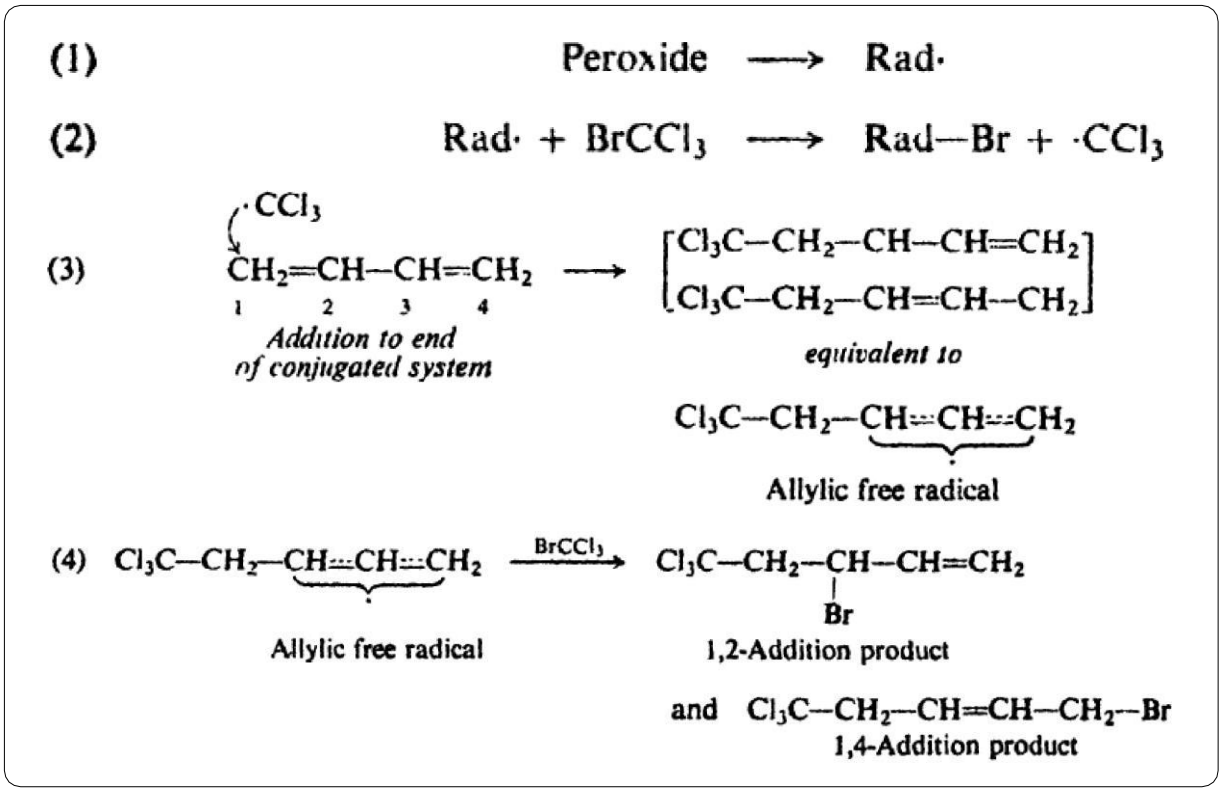


Free-radical addition to conjugated dienes

- In free-radical addition, conjugated dienes show two special features:
- They undergo 1, 4-addition as well as 1, 2-addition, and they are much more reactive than

ordinaryalkenes.

- Addition of $BrCCl_3$ to 1, 3-butadiene in the presence of a peroxide.
- The peroxide decomposes **(step 1)** to yield a free radical, which abstracts bromine from $BrCCl_3$**(step 2)** to generate a $\cdot CCl_3$ radical.
- The $\cdot CCl_3$ free radical thus formed ads to the butadiene **(step 3).**
- Addition to one of the ends of the conjugated system is the preferred reaction, since this yields a resonance-stabilized allyl free radical.
- The allyl free radical then abstracts bromine from a molecule of $BrCCl_3$**(step 4**) to complete the addition, and in doing so forms a new $\cdot CCl_3$ radical which can carry on the chain. In step (4) bromine can become attached to either C-2 or C-4 to yield either the 1, 2- or 1, 4-product.

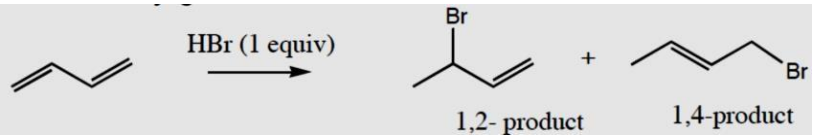


Electrophilic addition reaction

- With conjugated dienes, electrophilic addition of one equivalent of HBrgives two products;

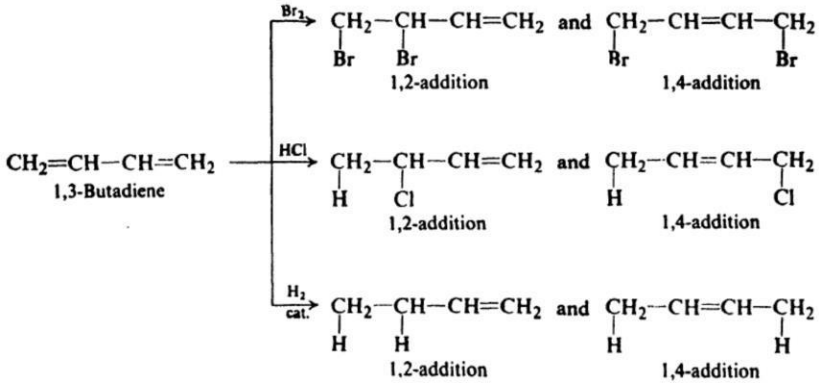
1. 1,2-product from Markovnikov addition
2. 1,4-product from conjugate

additionFor example-



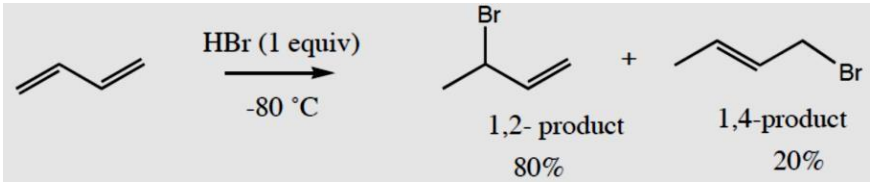
- Addition of HX to a conjugated diene forms 1,2- and 1,4-products because of the resonancestabilized allylic carbocation intermediate.

- When **1, 3-butadiene** is treated with bromine under similar conditions, there is obtained not only theexpected 3,4-dibromo-l-butene, but also l,4-dibromo-2- butene.
- Treatment with HCl yields not only 3-chloro-l-butene, but also l-chloro-2-butene.
- Hydrogenation yields not only 1-butene but also 2-butene,

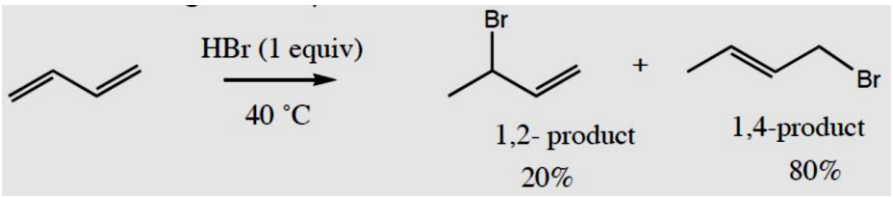


Kinetic versus thermodynamic products

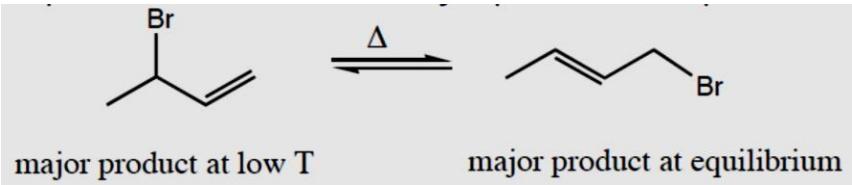
- The amount of 1,2- and 1,4-addition products formed in electrophilic addition reactions ofconjugated dienes depends greatly on the reactionconditions:
- At low temperatures, the major product is formed by 1,2-addition. Thekinetic product is formedfaster and predominates at low temperature:



- At higher temperatures, the major product is formed by 1,4-addition. Themore slowly formedthermodynamic product is more stable andpredominates at higher temperatures.



- In fact, when a mixture containing mainly the 1,2-product is heated, the1-4-addition productbecomes 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)

(i) DIELS ALDER REACTION

- Addition of a conjugated diene to an unsaturated molecule to give six membered ring compound is known as **Diels alder reaction**.

- Example-