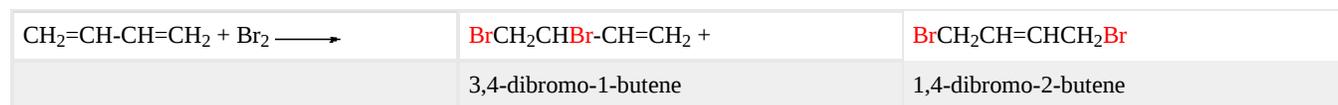


14.10: Electrophilic Addition- 1,2- Versus 1,4-Addition

Addition reactions of isolated dienes proceed more or less as expected from the behavior of simple alkenes. Thus, if one molar equivalent of 1,5-hexadiene is treated with one equivalent of bromine a mixture of 5,6-dibromo-1-hexene, 1,2,5,6-tetrabromohexane and unreacted diene is obtained, with the dibromo compound being the major product (about 50%)

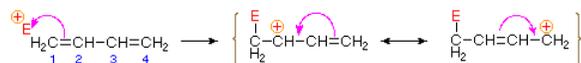
fig

Similar reactions of conjugated dienes, on the other hand, often give unexpected products. The addition of bromine to 1,3-butadiene is an example. As shown below, a roughly 50:50 mixture of 3,4-dibromo-1-butene (the expected product) and 1,4-dibromo-2-butene (chiefly the E-isomer) is obtained. The latter compound is remarkable in that the remaining double bond is found in a location where there was no double bond in the reactant. This interesting relocation requires an explanation.

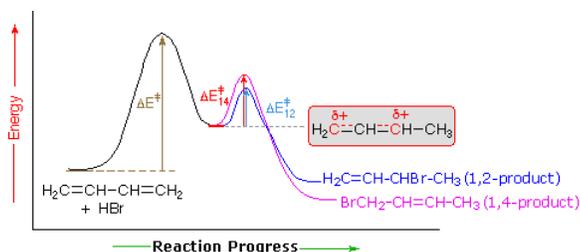


The expected addition product from reactions of this kind is the result of **1,2-addition**, i.e. bonding to the adjacent carbons of a double bond. The unexpected product comes from **1,4-addition**, i.e. bonding at the terminal carbon atoms of a conjugated diene with a shift of the remaining double bond to the 2,3-location. (These numbers refer to the four carbons of the conjugated diene and are not IUPAC nomenclature numbers.) Product compositions are often temperature dependent: at 40 °C, 85% of the product mixture in the addition reaction above is the 1,4 product, whereas at 0 °C, only about 30% is the 1,4 product.

Bonding of an electrophilic atom or group to one of the end carbon atoms of a conjugated diene (carbon #1 in the figure below) generates an allyl cation intermediate. Such cations are stabilized by charge delocalization, and it is this delocalization that accounts for the 1,4-addition product produced in such addition reactions. As shown in the diagram, the positive charge is distributed over carbons #2 and #4 so it is at these sites that the nucleophilic component bonds. Note that resonance stabilization of the allyl cation is greater than comparable stabilization of 1,3-butadiene, because charge is delocalized in the former, but created and separated in the latter.



An explanation for the temperature influence is shown in the following energy diagram for the addition of HBr to 1,3-butadiene. The initial step in which a proton bonds to carbon #1 is the **rate determining step**, as indicated by the large activation energy (light gray arrow). The second faster step is the **product determining step**, and there are two reaction paths (colored blue for 1,2-addition and magenta for 1,4-addition). The 1,2-addition has a smaller activation energy than 1,4-addition - it occurs faster than 1,4 addition, because the bromide nucleophile is closer to carbon #2 than to carbon #4. However, the 1,4-product is more stable than the 1,2-product. At low temperatures, the products are formed irreversibly and reflect the relative rates of the two competing reactions. This is termed **kinetic control**. At higher temperatures, equilibrium is established between the products, and the **thermodynamically favored** 1,4-product dominates.



When a conjugated diene is attacked by an electrophile, the resulting products are a mixture of 1,2 and 1,4 **isomers**. Kinetics and Thermodynamics control a reaction when there are two products under different reaction conditions. The Kinetic product (Product A) will be formed fast, and the Thermodynamic product (Product B) will be formed more slowly. Usually the first product formed is the more stable favored product, but in this case, the slower product formed is the more stable product; Product B.

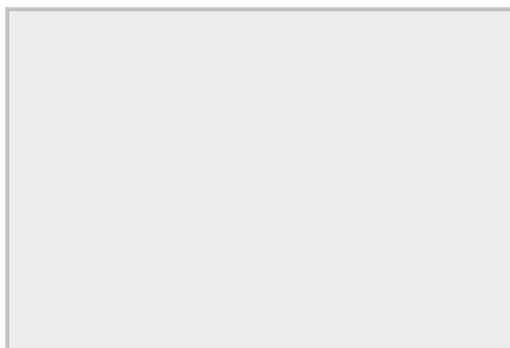
Introduction

Like nonconjugated dienes, conjugated dienes are subject to attack by electrophiles. In fact, conjugated dienes experience relatively greater kinetic reactivity when reacted with electrophiles than nonconjugated dienes do. Upon electrophilic addition, the conjugated diene forms a mixture of two products—the kinetic product and the thermodynamic product—whose ratio is determined by the conditions of reaction. A reaction yielding more thermodynamic product is under thermodynamic control, and likewise, a reaction that yields more kinetic product is under kinetic control.

Basic Reaction



Detailed Mechanism

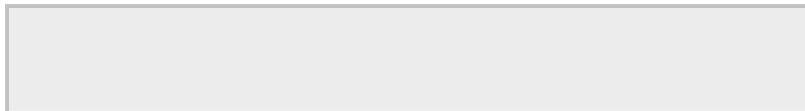


Conclusion

The reactivity of conjugated dienes (hydrocarbons that contain two double bonds) varies depending on the location of double bonds and temperature of the reaction. These reactions can produce both thermodynamic and kinetic products. Isolated double bonds provide dienes with less stability thermodynamically than conjugated dienes. However, they are more reactive kinetically in the presence of electrophiles and other reagents. This is a result of [Markovnikov addition](#) to one of the double bonds. A carbocation is formed after a double bond is opened. This carbocation has two resonance structures and addition can occur at either of the positive carbons.

Practice Problems

1. Write out the products of 1,2 addition and 1,4- addition of a) HBr and Br. b) DBr to 1,3-cyclo-hexadiene. What is unusual about the products of 1,2- and 1,4- addition of HX to unsubstituted cyclic 1,3-dienes?
2. Is the 1,2-addition product formed more rapidly at higher temperatures, even though it is the 1,4-addition product that predominates under these conditions?
3. Why is the 1,4-addition product the thermodynamically more stable product?
4. Out of the following radical cations which one is not a reasonable resonance structure?

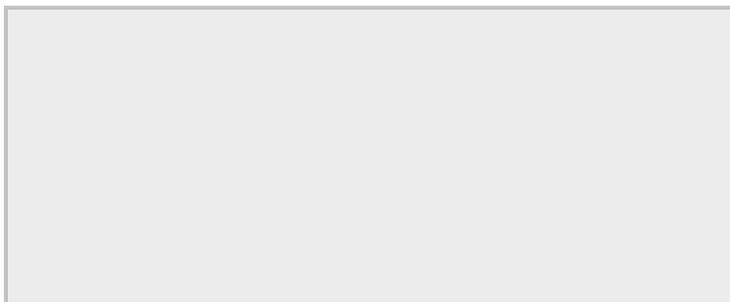


5. Addition of 1 equivalent of Bromine to 2,4-hexadiene at 0 degrees C gives 4,5-dibromo-2-hexene plus an isomer. Which of the following is that isomer:

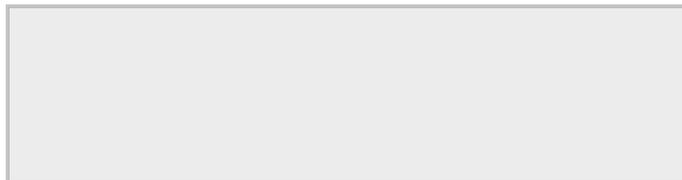
- a. 5,5-dibromo-2-hexene
- b. 2,5-dibromo-3-hexene
- c. 2,2-dibromo-3-hexene

d. 2,3-dibromo-4-hexene

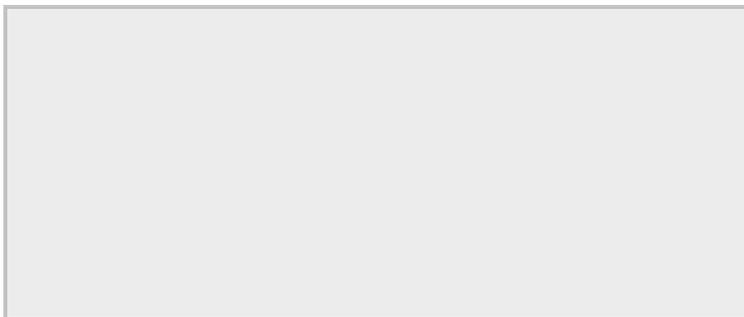
6. Which of the following will be the kinetically favored product from the depicted reaction?



7. Addition of HBr to 2,3-dimethyl-1,3-cyclohexadiene may occur in the absence or presence of peroxides. In each case two isomeric $C_8H_{13}Br$ products are obtained. Which of the following is a common product from both reactions?



8. and 9.



8. The kinetically controlled product in the above reaction is:

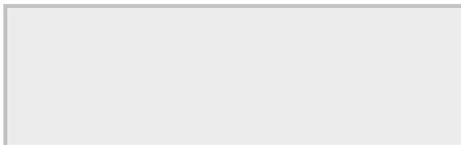
- a. 3-Chloro-1-Butene
- b. 1-Chloro-2-Butene

9. For the reaction in question 8, which one is the result of 1,4-addition?

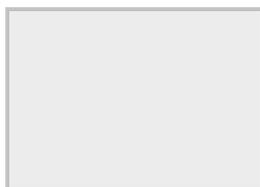
- a. 3-Chloro-1-Butene
- b. 1-Chloro-2-Butene

Answers to Problems

1. A) Same product for both modes of addition.



B) Both cis and trans isomers will form.



Addition of the HX to unsubstituted cycloalka-1,3-dienes in either 1,2- or 1,4- manner gives the same product because of symmetry.

2. Yes, the Kinetic Product will still form faster but in this case there will be enough energy to form the thermodynamic product because the thermodynamic product is still more stable.

3. The 1,4- product is more thermodynamically stable because there are two alkyl groups on each side of the double bond. This form offers stability to the overall structure.

4. All of these isomers are viable.

5. D

6. C

7. D

8. A

9. B

Contributors

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