

1. Electrophilic Addition to Conjugated Dienes (Section 20.2) The ratio of 1,2- to 1,4-addition products depends on whether the reaction is under kinetic control or thermodynamic control. When a conjugated diene reacts with HBr, initial protonation of one of the double bonds gives a resonance-stabilized allylic cation; reaction of bromide with one of the carbons of this intermediate bearing the partial positive charge gives the 1,2-addition product, and reaction at the other gives the 1,4-addition product.

$$CH_2 = CHCH = CH_2 + HBr \longrightarrow CH_3CHCH = CH_2 + CH_3CH = CHCH_2Br$$

$$Products at -78°C \text{ (kinetic control):} 90\% 10\%$$

$$Products at 40°C \text{ (thermodynamic control):} 15\% 85\%$$

2. The Diels-Alder Reaction: A Pericyclic Reaction (Section 20.5) A Diels-Alder reaction takes place in a single step, without intermediates, and involves a redistribution of six π electrons in a cyclic transition state. The configuration of the diene and dienophile is preserved. Formation of the endo adduct is favored.

Please note that in certain editions of the textbook the Diels Alder Reaction is covered in Chapter 24.

Halogenætion

B

Halogenætion

B

H

B

H

B

H

Product

Product