Chem 343 – Organic Reactions
Chapter 15
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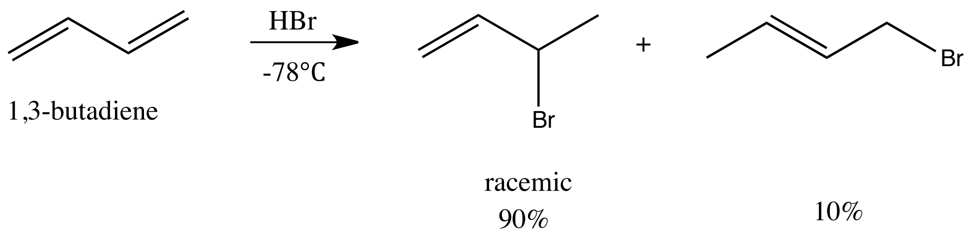
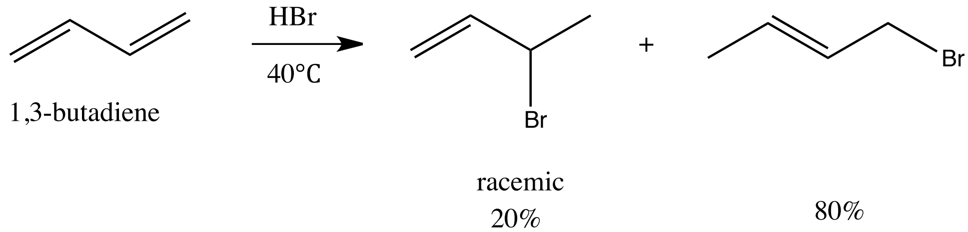
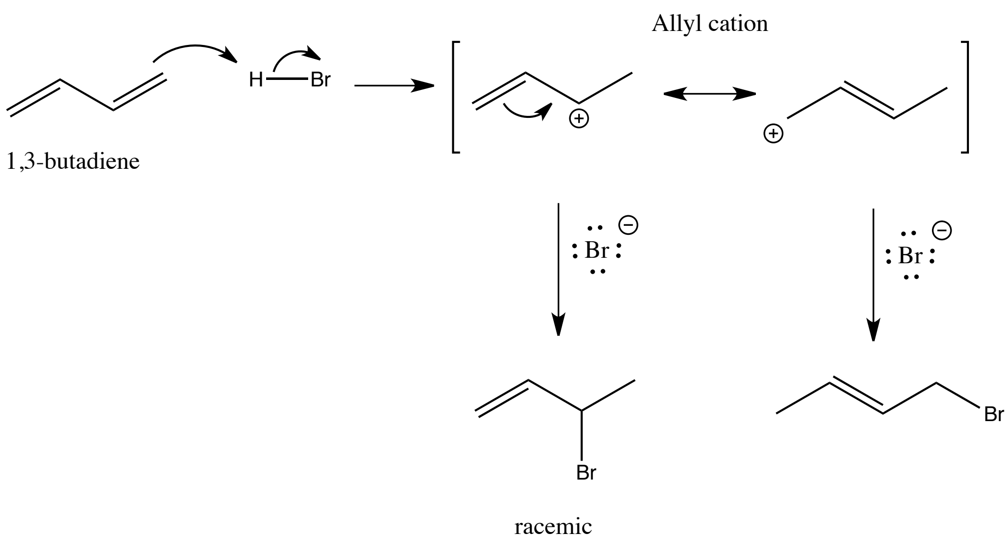
http://www.chem.wisc.edu/areas/clc (Resource page)

Dienes #1: Electrophilic Addition to 1,3-Conjugated Dienes #1



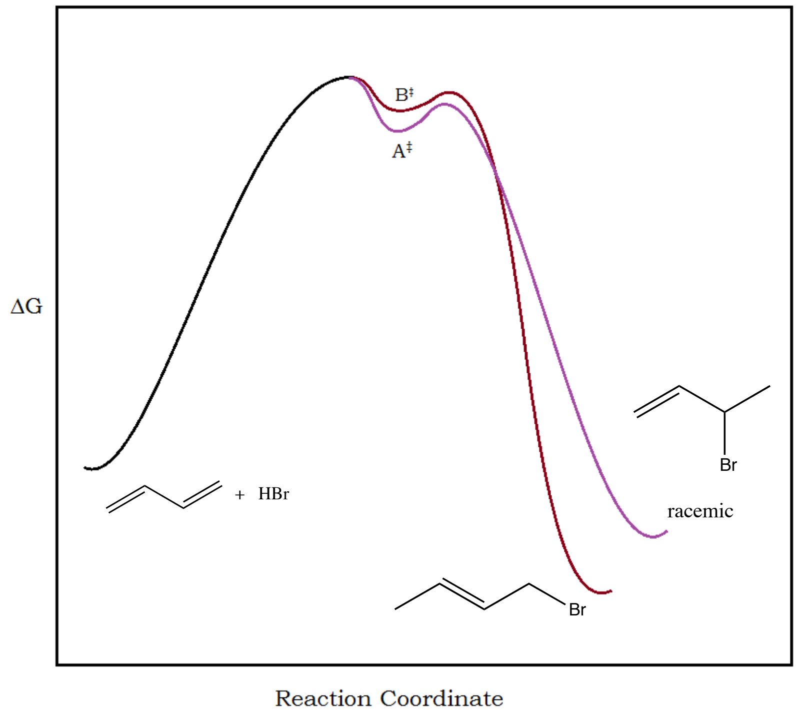


Mechanism



The reaction of an electrophile with a 1,3-conjugated diene produces an allylic cation, which is resonance stabilized (shown above). But the two allyl cations do not have the same energy. The secondary and allylic cation is more stable than a primary and allylic cation. Consequently there should be two expected products; (±)-3-bromo-1-butene and 1-bromo-2-butene. Notice that (±)-3-bromo-1-butene is the product that results from H^+ (electrophile) adding to C-1 of 1,3-butadiene and Br^- (nucleophile) adding to C-2, hence the designation 1,2-addition. Similarly, 1,4-addition produces 1-bromo-2-butene.

In cases like this reaction conditions will affect product ratio. For example, if the reaction is carried out at low temperature (kinetic control) a large fraction of molecules will have enough energy to form the lower energy secondary allylic cation, but very few molecules will have enough energy to form the higher energy primary allylic cation. Under these conditions the major product results from the reaction of the lowest energy intermediate. In this case the lowest energy intermediate produces a relatively higher energy alkene (see Zaitsev's Rule). See reaction coordinate diagram below. Note: In the diagram below A‡ represents the intermediate secondary allylic cation and B‡ represents the intermediate primary allylic cation.



On the other hand, if the conditions are such that all molecules have enough energy to form any intermediate (thermodynamic control) the initial product mixture will consist mainly of the product that results from the lowest energy intermediate, but over time the product ratio will be determined by the stability of the two products and not by their relative intermediate energies.

In summary, under kinetic control the product ratio is determined by the relative energy of the intermediates or transition states and under thermodynamic control the relative energy of the products themselves.