



Electrophilic Addition to Dienes Mechanism

Transcript

Instructor: Jessie Key

00:00:00:00 - 00:00:13:52

Instructor: Hello again, Doctor Jessie Key here. In this video, we're going to examine electrophilic addition to a conjugated diene. Let's start with the simplest example possible, hydrohalogenation of 1,3-butadiene.

00:00:13:52 - 00:00:36:56

Instructor: Just like hydrohalogenation of an alkene from organic one, the mechanism proceeds through a two-step mechanism. Step one, proton transfer, step two, nucleophilic attack. Starting at the electron source, the pi bond between carbon one and two, we draw our arrow to the proton of HCl to form a new Sigma bond.

00:00:38:39 - 00:01:13:00

Instructor: The next arrow goes from the Sigma bond between the hydrogen and the chlorine to the chlorine atom, where it will form a new lone pair producing the anion chloride. As a result of this first proton transfer step, a carbocation intermediate is formed. Notice that protonation has occurred at the terminal carbon of the symmetrical molecule, allowing for the formation of the allylic resonance stabilized carbocation intermediate.

00:01:13:28 - 00:01:48:76

Instructor: We can generate a second resonance form by moving the pi bond between carbons three and four to form a new pi bond between carbons two and three. Protonation at one of the internal carbons, carbons two or three would produce an unstable primary carbocation that is not resonance stabilized. The resonance contributor shown on the left side features a formal positive charge at carbon number two, while the other resonance contributor shown on the right side features a formal positive charge at carbon number four.

00:01:48:88 - 00:02:30:48

Instructor: The nucleophile chloride can then perform nucleophilic attack on either resonance contributor leading to the two possible products, the 1,2 and the 1,4 adducts. The 1,2 adduct is 3-chlorobut-1-ene and the 1,4 adduct is E-2-chlorobut-2-ene. The example we just completed was symmetrical, which greatly simplified things.

00:02:30:48 - 00:02:47:60

Instructor: Let's now take a look at a more complex example, the hydrobromination of an asymmetrical conjugated diene, 1-methyl-1,3-butadiene. First, I'll number the

carbons of the conjugate diene. Note, this is not a IUPAC nomenclature numbering.

00:02:47:60 - 00:03:21:26

Instructor: It's just used to keep track during the mechanism. Since there are two different end carbons, C one and C four, we must perform the mechanism to show the outcomes of formation of the 1,2 and 1,4 adducts by protonation at both C one and C four. Starting with protonation at C one, the first arrow goes from the Pi bond between carbons one and two to extract the proton from HBR.

00:03:21:90 - 00:04:03:37

Instructor: This breaks the HBR Sigma bond, and those electrons form a new lone pair on bromine to generate the anion bromide. The resulting allylic carbocation can be represented with a second resin's structure by moving the Pi bond between carbon three and four to form a new Pi bond 2-3. Nucleophilic attack can then occur at the carbocation of either of the two resin structures, producing the 1,2 adduct here on the left and the 1,4 adduct on the right.

00:04:21:21 - 00:04:54:20

Instructor: For protonation at C four, the first arrow goes from the Pi bond between carbons three and four to attract the proton from HBR. This breaks the HBR Sigma bond and those electrons form a new lone pair on the bromine to generate the anion bromide. The resulting allylic carbocation can be represented with a second resin structure by moving the pi bond between carbon one and two to form a new pi bond between carbon two and three.

00:04:57:60 - 00:05:37:40

Instructor: Nucleophilic attack can then occur at the carbocation of either of the two resin structures, producing the 1,2 adduct here on the left and the 1,4 adduct here on the right. Therefore, with an asymmetric conjugated diene substrate like one methyl hexahydronaphthalene, we can form up to four possible products by the formation of 1,2 and 1,4 adducts at either end of the conjugated diene.