Electrophilic Addition to Dienes Mechanism

Transcript

00:00:00:00 - 00:00:07:46
Dr.Jessie Key: Hello again, Dr. Jessie Key here. In this video, we're going to examine electrophilic addition to a conjugated diene.

00:00:07:46 - 00:00:23:68
Dr.Jessie Key: Let's start with the simplest example possible, hydrohalogenation of buta-1,3-diene. Just like hydrohalogenation of an alkene from Organic I, the mechanism proceeds through a two-step mechanism. Step 1: proton transfer.

00:00:23:68 - 00:00:48:43
Dr.Jessie Key: Step 2: nucleophilic attack. Starting at the electron source, the pi bond between carbon 1 and 2, we draw our arrow to the proton of H-Cl to form a new sigma bond. 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.

00:00:53:40 - 00:01:22:92
Dr.Jessie Key: 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. We can generate a second resonance form by moving the pi bond between carbons 3 and 4 to form a new pi bond between carbons 2 and 3.

00:01:25:76 - 00:02:00:12
Dr.Jessie Key: Protonation at one of the internal carbons, carbons 2 or 3 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 2, while the other resonance contributor shown on the right side features a formal positive charge at carbon number 4. 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.

00:02:15:56 - 00:02:41:06
Dr.Jessie Key: The 1,2 adducts is 3-chlorobut-1-ene and the 1,4- adduct is (E)1-chlorobut-2-ene. The example we just completed was symmetrical, which greatly simplified things.

Let's now take a look at a more complex example, the hydrobromination of an asymmetrical conjugated diene, 1-methylhexahydronapthalene.

00:02:41:06 - 00:03:21:26
Dr.Jessie Key: First, I'll number the carbons of the conjugate diene, note, this is not IUPAC nomenclature numbering, it's just used to keep track during the mechanism. Since there are two different end carbons, C1 and C4, we must perform the mechanism to show the outcomes of formation of 1,2- and 1,4-adducts by protonation at both C1 and C4. Starting with protonation at C1, The first arrow goes from the pi bond between carbons 1 and 2 to extract the proton from H-Br.

00:03:21:90 - 00:04:03:37
Dr.Jessie Key: This breaks the H-Br 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 resonance structure by moving the pi bond between carbon 4 and 4 to form a new pi bond between 2 and 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 ,4-adduct on the right.

00:04:21:21 - 00:04:54:20
Dr.Jessie Key: For protonation at C4, the first arrow goes from the pi bond between carbons 3 and 4 to abstract the proton from H-Br. This breaks the H-Br 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 resonance structure by moving the pi bon between carbon 1 and 2 to form a new pi bond between carbon 2 and 3.

00:04:57:60 - 00:05:37:40
Dr.Jessie Key: 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 1-methylhexahydronapthalene, 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.