Mechanism Strategies

Transcript

00:00:00:92 - 00:00:10:92
Dr.Jessie Key: Hello again, Dr. Jessie Key here. In this slide show, you'll be exploring some ways to approach understanding and remembering longer reaction mechanisms.

00:00:12:79 - 00:00:36:11
Dr.Jessie Key: You have encountered some pretty lengthy mechanisms in this unit, so I want to talk to you about some strategies you can use to keep track of it all. Trying to approach it using raw memorization of every single arrow and every intermediate structure can be overwhelming. A less taxing learning strategy called "chunking" is to think about mechanisms in terms of smaller pieces.

00:00:36:11 - 00:01:02:48
Dr.Jessie Key: Whether you realize it or not, I presented the oxygen and nitrogen nucleophilic addition mechanisms to you with some chunking already applied. Each mechanism was broken down into two smaller stages with an important intermediate for you to anchor on. In the acetal formation mechanism, it was broken into Stage 1: formation of the hemiacetal (the important intermediate).

00:01:02:48 - 00:01:28:32
Dr.Jessie Key: Stage 2: was the remainder of the mechanism, the formation of the acetal from the hemiacetal. Within each of these smaller stages, you can then remember the mechanism by the fundamental reaction step patterns which you are already familiar with! For example, in stage 1, formation of the hemiacetal, the steps are proton transfer, nucleophilic attack, and then a second proton transfer.

00:01:28:32 - 00:01:52:10
Dr.Jessie Key: For stage 2, formation of the acetal, the steps are proton transfer, loss of leaving group, nucleophilic attack, and then a final proton transfer. Another helpful strategy is to look for patterns within the reaction mechanism steps. In stage 1, formation of the hemiacetal, the steps occur in the order of proton transfer, nucleophilic attack, and proton transfer.

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Dr.Jessie Key: This stage can be thought of as a proton transfer sandwich with a nucleophilic attack filling. Looking at stage 2, formation of the acetal, its four steps are proton transfer, loss of leaving group, nucleophilic attack, and proton transfer, another proton transfer sandwich, but just with an extra filling the loss of the leaving group. So the overall mechanism is just two types of proton transfer sandwiches.

00:02:25:46 - 00:02:50:34
Dr.Jessie Key: When learning about multiple similar mechanisms, a great way to remember is to focus on the key differences between them. Let's compare the nucleophilic addition mechanism of an oxygen nucleophile to a nitrogen nucleophile. Remember with oxygen nucleophiles, the first stage is formation of the hemiacetal, which goes through a proton transfer sandwich of proton transfer, nucleophilic attack, proton transfer.

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Dr.Jessie Key: With a nitrogen nucleophile, it forms a carbinolamine intermediate by nucleophilic attack, proton transfer, proton transfer. So in terms of our analogy, nitrogen nucleophiles use an open faced proton transfer sandwich. Stage 2, formation of the acetal by an oxygen nucleophile through a 4-step proton transfer sandwich of proton transfer, loss of leaving group, nucleophilic attack, proton transfer.

00:03:19:47 - 00:03:38:93
Dr.Jessie Key: While nitrogen nucleophiles, whether forming an imine or enamine, go through a 3-step proton transfer sandwich of proton transfer, loss of leaving group, proton transfer. Proton transfers play a large role in nucleophilic addition to carbonyls. They are the bread in our mechanism sandwiches!

00:03:38:93 - 00:03:53:33
Dr.Jessie Key: I want to go over a few important points with you about proton transfers. 1. When a weaker nucleophile is used, like an oxygen nucleophile, the carbonyls protonated first to compensate by becoming a better electrophile.

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Dr.Jessie Key: 2. Avoid proton transfers that form a second positive charge in a single intermediate species. 3. Proton transfers are often used to

00:04:04:49 - 00:04:17:40
Dr.Jessie Key: help generate better neutral leaving groups. 4. Proton transfer should be done to ensure the final products do not have a formal charge.

00:04:17:40 - 00:04:24:90
Dr.Jessie Key: Hopefully, the tutorial mechanisms has given you some additional strategies for learning and applying curved arrow mechanisms!