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Wittig Reactions

Transcript

00:00:00:48 - 00:00:13:24
Dr.Jessie Key: Hello, again, Dr. Jessie Key here. In this slideshow, you will be exploring a very important carbon-carbon bond forming reaction that can be performed with aldehydes and ketones, known as the Wittig reaction.

00:00:15:08 - 00:00:49:47
Dr.Jessie Key: The Wittig reaction is named after German chemist George Wittig and yes, you're hearing me pronounce that name correctly, "Vi-Tig" with a 'vee' sound instead of how it is written with a "W". Wittig won the Nobel Prize in chemistry in 1979 for his work with boron and phosphorus containing compounds, and the Wittig reaction is the most famous example of this. The Wittig reaction uses a regent known as a phosphorane ylide, pronounced "ill-id", to convert an aldehyde or ketone into an alkene.

00:00:49:47 - 00:01:21:39
Dr.Jessie Key: The term ylide refers to any neutrally charged molecule where there is a negatively charged atom bonded to a positively charged heteroatom. The phosphorane ylide, also referred to more loosely as the "wittig reagent", has a negatively charged carbon bonded to the positively charged phosphorus in its more representative resonance form. However, another resonance form can be written by moving the lone pair electrons from the carbon to form a pi bond between the carbon and the phosphorous.

00:01:21:39 - 00:01:39:57
Dr.Jessie Key: At first glance, this neutral uncharged resonance form should seem more significant. However, it is not a major contributor due to poor carbon-phosphorous p orbital overlap. The 2p orbital of the carbon is significantly smaller than the 3p orbital of the phosphorous.

00:01:40:53 - 00:02:10:05
Dr.Jessie Key: To generate the Wittig reagent, an alkyl halide is reacted by SN2 with a triphenyl phosphine nucleophile to form a phosphonium salt intermediate. The phosphonium salt is then deprotonated by the strong base butyl lithium to give the phorphorane ylide Wittig reagent. The Wittig reaction mechanism has been widely debated but is now accepted to occur by a two-step process.

00:02:10:05 - 00:02:41:79
Dr.Jessie Key: In the first step, a two plus two [2+2] cycloaddition occurs between the carbonyl and phosphorane ylide to generate an oxaphosphetane intermediate. We can show this with curved arrow notation by drawing an arrow from the lone pair of the nucleophilic ylide carbon to the electrophilic carbonyl carbon and a second arrow from the carbonyl pi bond to the ylide phosphorous. The second step is a fragmentation, where the 4-membered ring of the oxaphosphetane breaks apart to give the alkene product and triphenylphosphine oxide byproduct.

00:02:41:79 - 00:03:06:09
Dr.Jessie Key: The curved arrow notation for this has an arrow starting at the carbon-oxygen single bond going to form a new phosphorous oxygen pi bond. A second arrow goes from the phosphorous carbon bond to form a new carbon-carbon pi bond. Overall, you can think of the Wittig reaction as a way to stick together two molecular segments via a carbon-carbon double bond.

00:03:06:09 - 00:03:30:61
Dr.Jessie Key: We can join together an aldehyde or ketone with an alkyl halide (via a phosphorane ylide) almost like sticking together two pieces of lego- making a larger, more complex structure. Practice problem. What starting materials could be used to generate 2-methyl-1-phenylprop-1-ene by a Wittig reaction?

00:03:30:61 - 00:03:54:65
Dr.Jessie Key: Stop the presentation and apply what you've learned to determine what carbonyl and alkyl halide could be used to generate this product. To solve this problem, you need to cut the alkene and make one piece the carbonyl and the other piece the alkyl halide. In the case of this problem, there are actually two correct answers.

00:03:54:65 - 00:04:24:71
Dr.Jessie Key: Shown on the left side of the slide, we could use benzaldehyde as the carbonyl component and 2-bromopropane as the alkyl halide. Alternatively, shown on the right, we could use benzylbromide as the alkyl halide and propan-2-one (or acetone) as the carbonyl. You've just learned about the Wittig reaction, a very important reaction which is used often in synthetic strategies to make more complex molecules by joining aldehyde or ketone fragments with alkyl halides fragments.