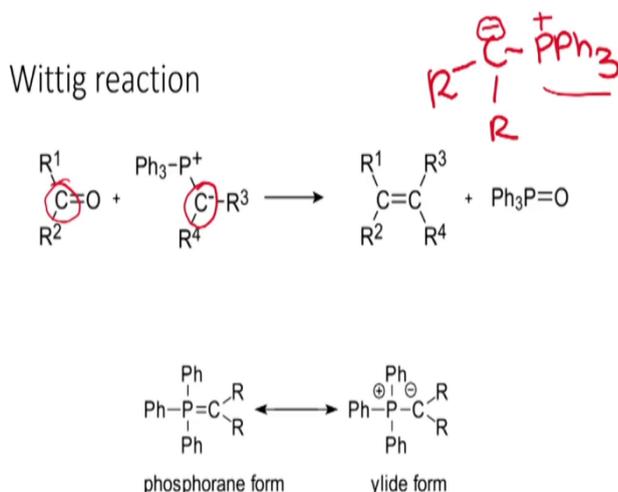


Introductory Organic Chemistry II
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Indian Institute of Science Education and Research, Pune
Module 08
Lecture 58
Named Reactions - Part 1

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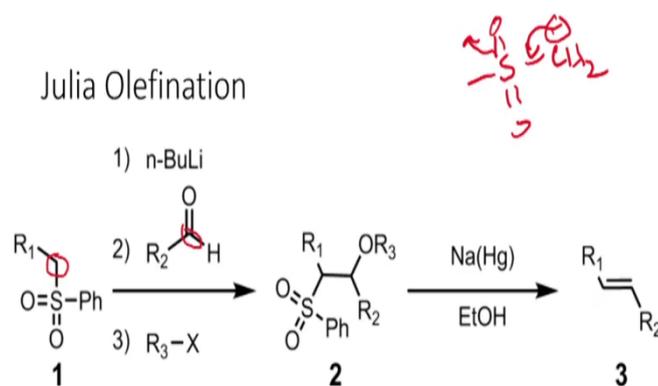
Now, let us move on to a slightly different class of reactions, which is to go to look at the Wittig reaction. So, some of you may have already studied this, the Wittig reaction is a very famous reaction for forming carbon-carbon double bonds. So, the mechanism of the Wittig reaction or the reagents are; I react a ketone here with this kind of a compound.

So, this is nothing but a carbon attached to PPh₃ and since phosphorus has four bonds, it has a positive charge. And you can deprotonate this next to this carbon and this is known as a ylide and the ylides are generated by reacting, for example, alkyl bromide with triphenylphosphine and you will get a triphenyl phosphonium type of species here and then you add a base and you get this ylide. So, this ylide is a very good nucleophile.

So, the ylide can then attack the carbonyl and give you this product. Before we go into the details of the mechanism what we need to understand here is there is a bond between this carbon and this carbon and the C double bond O is gone, there is no carbonyl as shown here. And there is now a double bond between these two carbons and the product here is

elimination reactions. And there we have proposed an anti-periplanar conformation for elimination, whereas in Wittig reaction, it is a syn-periplanar conformation.

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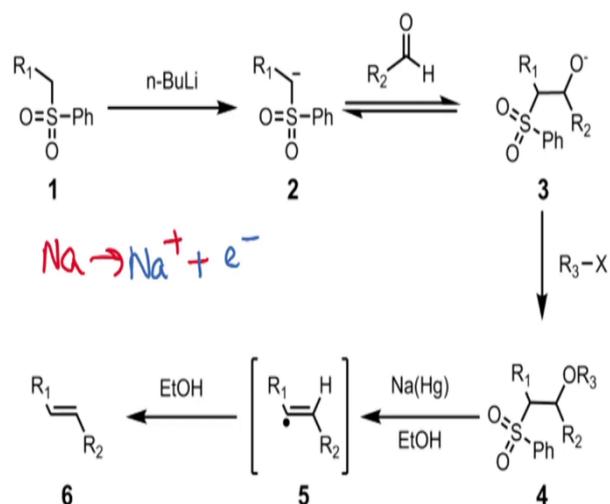
Moving on to the next Olefination reaction, this is called the Julia Olefination reaction. So, we have looked at the two categories of active methylene compounds. The first one we saw was the nitro compound. So, the alpha position to a nitro compound is quite acidic. We have also looked at Cyano compounds and Cyano also is quite electron withdrawing in nature and therefore, the alpha position to Cyano is also quite acidic.

The last compound that we are going to look at is the sulfone. So, the sulfone is also fairly electron withdrawing, because, you can imagine that this can be delocalized in the following manner. So, this alpha position to a sulfone is also quite acidic. So, therefore, if you see the reaction here, what we are doing is we are taking this compound which is the sulfone and then reacting it with n-butyl lithium followed by reaction with an aldehyde.

Now, when you see this reaction, you find that there is now a carbon-carbon bond that is formed, the carbon-carbon bond that is formed is formed between this carbon and this carbon. And this is basically a straightforward addition to a carbonyl carbon of a carbon-based nucleophile. The only difference in Julia Olefination is that there is a couple of more steps where you have the alkylation reaction that happens on this oxygen, followed by reaction with sodium amalgam and ethanol.

And these are just special conditions under which olefin can be formed. And so, we need to understand the mechanism of this process.

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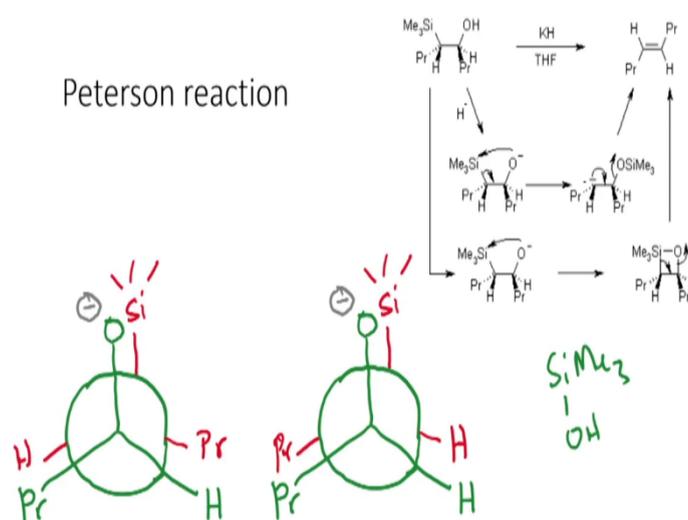
So, like I mentioned, the first reaction here is the reaction of n-butyl lithium, and you produce this enolate here, and then the enolate can attack the aldehyde and produce this kind of an intermediate. And now this O minus is actually quite a good nucleophile. So, if we react it with the alkyl halide, you produce this kind of an intermediate.

Now, we need to understand a little bit about this metal-based reaction. So, as you know, sodium can form Na⁺ and e⁻. And so, this, obviously, sodium is super reactive. And so therefore, we need to do it in a very controlled manner. So, Mercury is used. So, when you use sodium and Mercury, what happens is that it is a very good source of an electron.

So, this electron adds to this carbon-sulfur bond. And you know it results in the cleavage of this carbon-sulfur bond. And SO₂⁻ leaves, and then there is a radical that is left behind. So once this radical is left behind, you have the formation of the, it picks up in the presence of ethanol, it picks up H[•] and produces this Olefin.

So, prior to that, we actually have an elimination reaction that occurs and this elimination reaction that occurs has this R₁ and R₂ trans to one another. So, in this Julia olefination, we end up with Olefin that is produced in the following manner.

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The next reaction we are going to look at is the Peterson reaction. And in the Peterson reaction, the reagents that are used are these hydroxy silyl compounds. And the mechanism or the reagents that are used are potassium hydride and THF. And when you take this 2-silyl hydroxy aliphatic compound, you end up with an olefin at this position, that is there is a loss of SiMe₃OH.

So SiMe₃OH is actually lost, and it gives you an olefin. So, the mechanism that we propose for this reaction is as follows. So, you have a loss of OH's H⁺ that gives you this alkoxide. And now the alkoxide can react with this allyl group, we know that silicon has a very good affinity for oxygen and so when this attack happens, you can imagine that this carbon-sulfur bond is going to break and it may produce an enolate of a sort, I mean a carbanion of a sort.

And that will then subsequently undergo rearrangement or this carbanion is going to rearrange and kick out SiMe₃O⁻. Alternatively, you can also have a situation where this O minus attacks the silicon. And then much like the Wittig reaction. So, if you remember, the Wittig reaction had exactly the same kind of intermediate where you add a phosphorus instead of silicon, this can be a concerted reaction and give you this product.

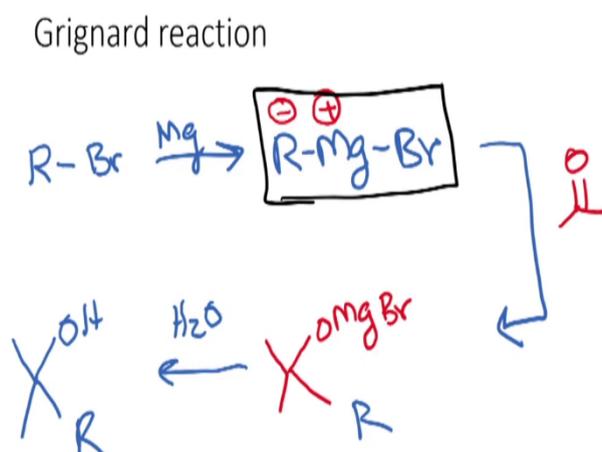
So normally, when you look at these reactions, the geometry of the product is actually going to be determined very clearly that is you do not have a mixture of products that are formed,

you normally get a single product or a majority of one product. So therefore, it is likely that the reaction happens in a more concerted fashion.

However, we need to understand the possibilities of this reaction. So, in this particular reaction, we have two conformations that can undergo elimination. So, if you see here, this oxygen and this sulfur are parallel to one another, you can have a situation where the propyl groups are actually para or actually anti to one another.

The second situation is the propyl groups are actually syn to one another. If you consider these two situations, it is likely that the energy or the barrier that one needs to cross for this reaction is going to be higher, and therefore, this is actually going to be more favored. So, you end up getting the trans product, although you have a choice of doing a trans or cis, and the trans product ends up being the major product.

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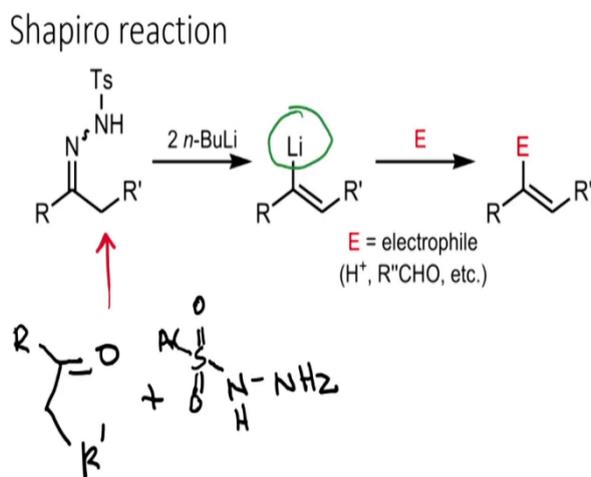


So, moving on with our named reactions, we will look at the Grignard reaction. So, the Grignard reaction is something that you guys have already learned before. So, when you react an alkyl bromide with magnesium turnings, you produce this R-Mg-Br. So, R-Mg-Br is actually can be synthesized or it is commercially available. Of course, you need to understand that it is quite explosive.

So, if you expose a little bit of water, it is going to, it is highly exothermic reaction. So, one of the things that you can do with the Grignard reagent is to react it with a ketone. And since

we are dealing a lot with carbonyl compounds in the semester, you are going to end up with this OMgBr, and then subsequently reaction of this with water is going to give you this product.

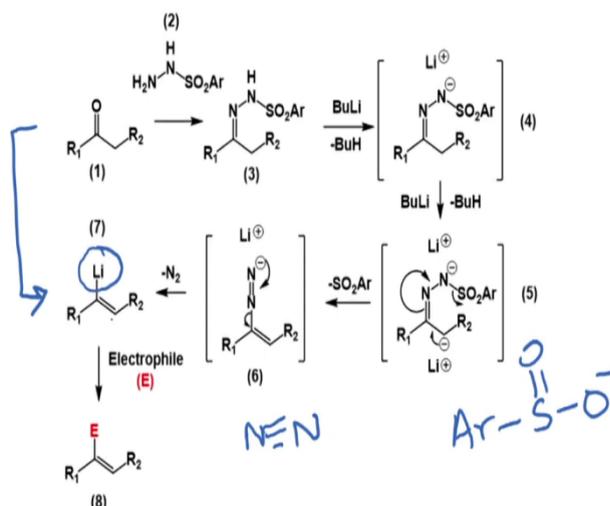
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The next name reaction that we are going to look at is the Shapiro reaction. Now, this is an interesting reaction, because this reaction involves the formation of a hydrazone, I think in chemistry practicals we have looked at functional group analysis and we find that aldehydes or ketones can actually react with 2, 4-dinitro phenyl hydrazines to give you the Hydrazone. And that is one of the ways in which we look for aldehydes or ketones.

So, the formation of this hydrazone is not a new reaction as far as we are concerned. Now, the next step is reaction with this butyl lithium. And here is where the mechanism gets interesting. We will look at it shortly. But you find here that this C double bond N is gone, and you generate this organolithium derivative, which can then react with an electrophile. And we will look at various electrophiles here, you can add a source of proton and you just get an olefin or you can react an aldehyde to give you product.

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So, the mechanism for this Shapiro reaction is as follows. So, you start with this ketone react it with Tollyhydrazine, this is SO_2 , the phenyl ring and methyl group at para position. And so, this is a hydrazine with an electron withdrawing group much like 2, 4-dinitro phenyl hydrazine. And then I am not going to go through the mechanism but you have to generated this hydrazone.

And now when you react it with butyl lithium, this NH is actually quite acidic because it is next to an electron withdrawing group which is the sulfone and so it is good to form N minus and subsequently you need to look at the arrow pushing here little carefully, you can actually produce enolate as shown here, because this alpha position is also acidic.

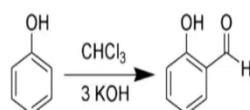
And now if you push electrons that is the enolate, the carbanion goes in and this there is a new bond formed between this nitrogen and nitrogen to give you this double bond and subsequently loss of $ArSO_2^-$, so $ArSO_2^-$ is nothing but $ArS=OO^-$. So, this is a fairly stable and a good leaving group. And you end up with an intermediate like this where there are two nitrogens with a negative charge and of course lithium ion is a counter ion.

And now if you push electrons, you can actually lose nitrogen, $N \equiv N$ and so nitrogen is lost from this molecule and you produce this lithium intermediate that we saw. And now, so, therefore, if you look at this reaction, it is the conversion of a ketone to an olefin-based organolithium compound.

These are very useful intermediates in synthesis because now you can use this and react it with ketone and react it with an aldehyde or do other reactions and you can form carbon-carbon bond forming reactions. So, the Shapiro reaction is a very useful way to convert a ketone to the corresponding lithium olefin salt which can subsequently react with electrophiles to give you the product.

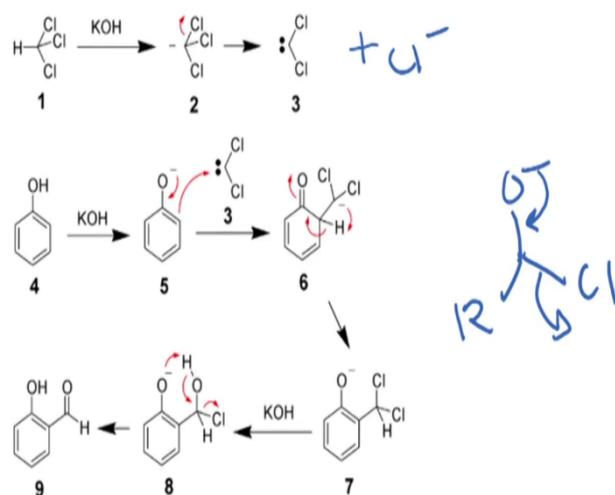
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Reimer-Tiemann reaction (via carbene intermediate)



Now the last name reaction that we want to look at is the Reimer-Tiemann reaction. So, this is something that you guys have probably seen in the past, it is no harm in revisiting it. So, you react chloroform and base with phenol and you get this product.

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So, the mechanism is as follows, chloroform is quite acidic, and you can reason this out because once the carbanion is formed, it is got three electronegative atoms next to it, so it is quite stable. And now there is an interesting reaction that happens that chloride ion leaves and leave behind a lone pair of electrons in a carbon which is known as a carbene. And now carbene is a quite a reactive group.

So, this phenolate that is produced over here, can react with this carbene and generate this kind of an intermediate with a carbanion here. And then subsequently, this aromaticity can be restored. And you get this kind of an intermediate 7, where you have CHCl_2 next to the phenol. And now you can imagine that there can be a displacement of one of the chlorides by hydroxide, this will be a $\text{S}_{\text{N}}2$ type reaction.

And once this is displaced, you have RCOCl . So, these are excellent intermediates for kicking out chloride. And so, they are not quite stable and so, they are going to just kick out chloride and form the aldehyde. So, with that, we are done with the named reactions as part of the syllabus. So, you know, some of these reactions are a little complicated, but most of them are fairly straightforward.

And as I mentioned, there is no need for you to remember the name of these reactions. It is useful to remember the name, but it is important for you to understand the mechanism of these reactions and these are very useful moving forward for various chemistry courses that you are planning to take.