Molecular Rearrangements and Reactive Intermediates in Organic Synthesis

Prof. Santanu Panda

Department of Chemistry

Indian Institute of Technology, Kharagpur

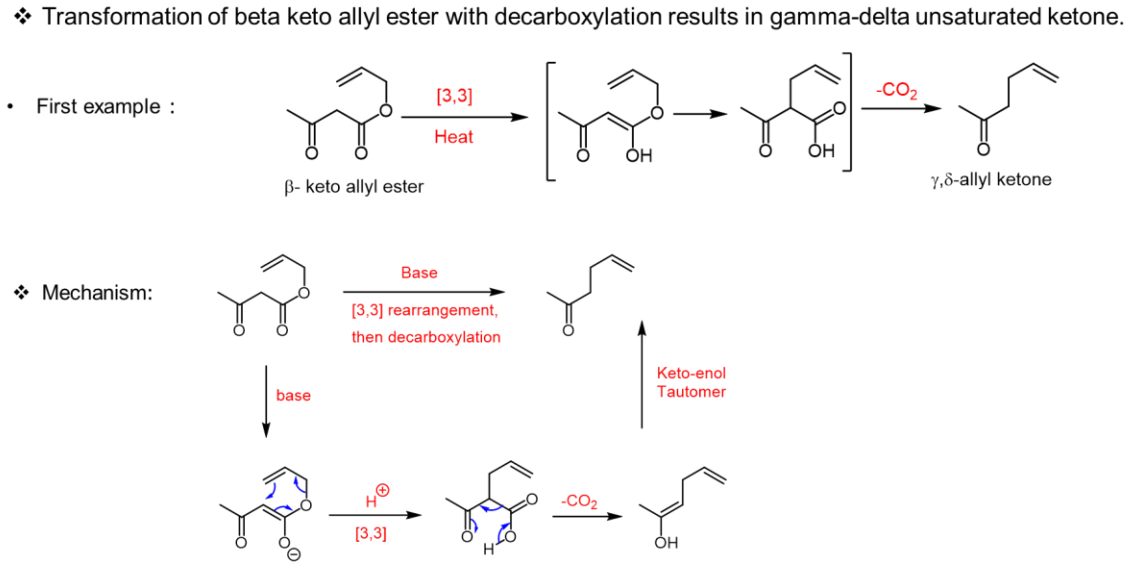
Lecture 10: Carbanion (Continued)

Welcome back to this NPTEL online certification course in the molecular rearrangement and reactive intermediates. In the last 2-3 classes, we have been trying to learn about carbanion; we have learned about carbanion formation and several different rearrangement reactions. So, in the last class, I talked about several different rearrangement reactions, but there are still some that need to be discussed in class. So, in this class, I am going to discuss some more of this rearrangement reaction. So, I am going to start talking about the Carroll rearrangement at the beginning, and then I am going to talk about the mechanism, synthetic utility, and some asymmetric versions of that. Then, I am going to talk about the [2-3] Wittig rearrangement.

Then [1,2] Wittig rearrangement, Aza-Wittig rearrangement Stevens rearrangement, and Sommelet-Hauser rearrangement. These are very important rearrangements, and you will find exam questions from them in NET GATE and JAM. So, let us start with the Carroll rearrangement. So, I was talking about the [3,3] Sigmatropic rearrangements in the last class.

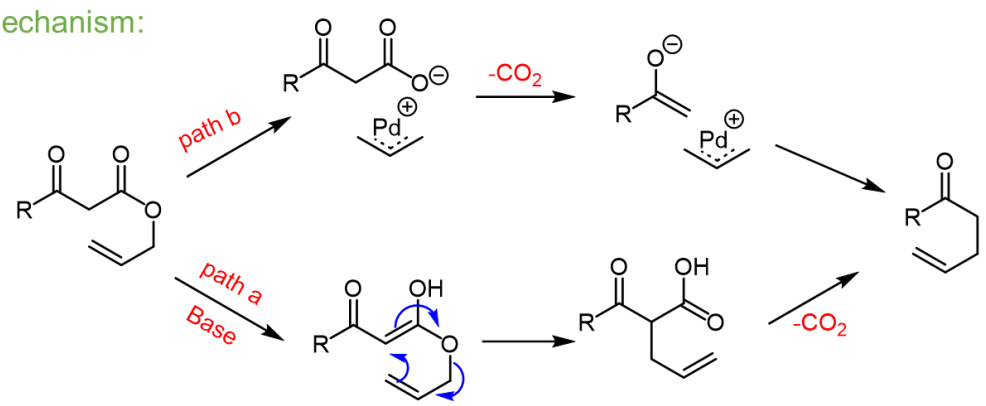
In the last two classes, I talk about different variations of it. So, there is another interesting reaction called Carroll rearrangement if you look into this transformation here. So, this is a β-keto allylic ester with decarboxylation resulting in the γ, δ-unsaturated ketone. So, what happens if you remember the normal sigmatropic rearrangement once you have started learning? That particular reaction we have learned is going to synthesize the γ, δ-unsaturated ketones. So, in this reaction also, we are seeing that the reaction is going from interesting starting material. So, you have a β- keto allylic esters here. So, this proton will be the acidic one in between these two carbonyls. Which can be abstracted to form this type of enol, and then this enol can actually now take part. So this will be a, you can give them 1, 2, and 3, and 1, 2, and 3, so it can go for [3,3] sigmatropic rearrangement. Then, after the formation of this compound, it is now a β-keto acid. So It is well known that β-keto acids are actually in the presence of heat, go for decarboxylation. So, this acid is going to get out from here, generate a minus, which can form an enol, and then it's going to get protonated. and finally convert to the corresponding unsaturated ketones. I think the

mechanism explains here clearly what I told you just now. So, I think then after the [3, 3] sigmatropic rearrangement, the decarboxylation, and then tautomerization occurs.



Here is another possibility, if you use transition metal like palladium in this particular Carroll rearrangement, what is happening here? So, the first thing I told about path A is in the presence of a base; if you use a strong base or something, in that case, path A is the one that is getting favorable, which means going from this enol and then [3, 3] sigmatropic shift and decarboxylation. but in the case of using a palladium catalyst, what is happening here? In that case, I think once you take this starting material with a palladium catalyst, then palladium catalyst can form this palladium-allyl species. You can clearly see there is an allyl acetate group here. So, now palladium can able to react with it and then form this palladium allyl species. So, there you have a 1, 3-dicarbonyl, and on one side you have this carboxylic acid group, and what is going to happen is going to take part in the decarboxylation in a reaction to generate this enolate. Now, this enolate can able to react with this allyl palladium species to form the corresponding product. So, now we are going to learn after a few slides that, as you can see, there is a palladium. So, we can bring some chiral ligands, and if you can bring some substitution here in this allyl group, that can generate a chiral center in the product. We are going to discuss that after a few slides.

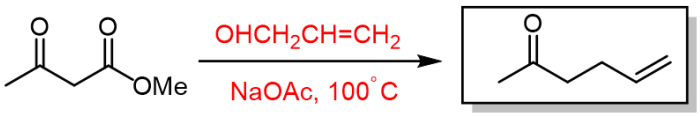
Mechanism:



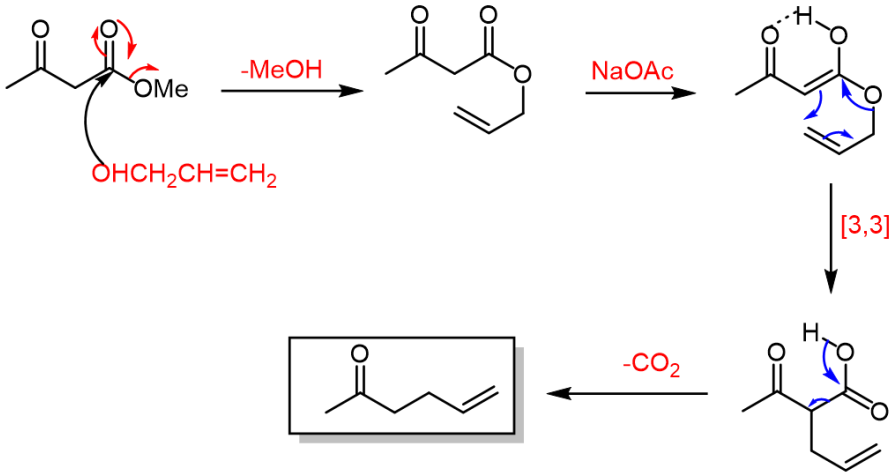
- In the presence of base and high reaction temperature reaction follows path a.
- Formation of an intermediate enol then rearranged in a Claisen rearrangement.
- Then decarboxylation.
- The final product is a gamma-delta allyl ketone.
- With palladium(0) as a catalyst, the path b follows
- Formation of an intermediate allyl cation / carboxylic acid anion organometallic complex.

Again we are explaining the formation of the starting material from so, starting from this β- keto esters. While using allylic alcohol in the presence of a base, it is going to form the starting material, which can get deprotonated. As you know, the protons between these 1,3-dicarbonyls are quite acidic, so they can easily deprotonate to this material [3,3]-sigmatropic rearrangement and decarboxylation to this corresponding product.

1.

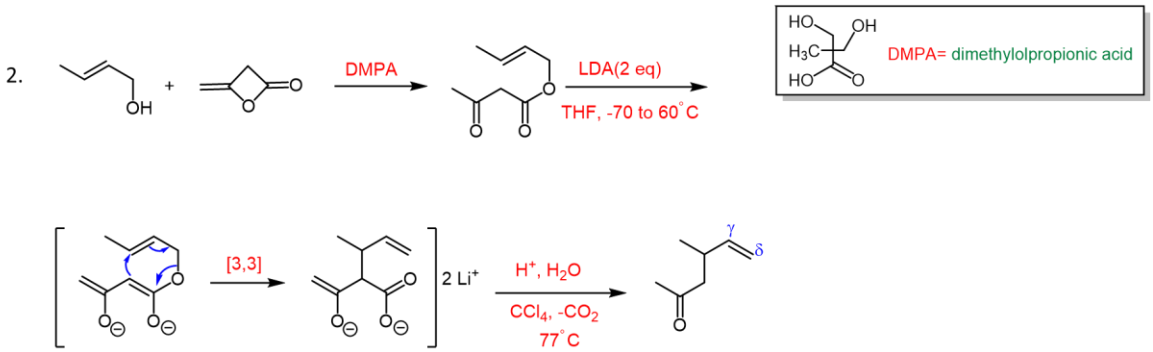


Mechanism:



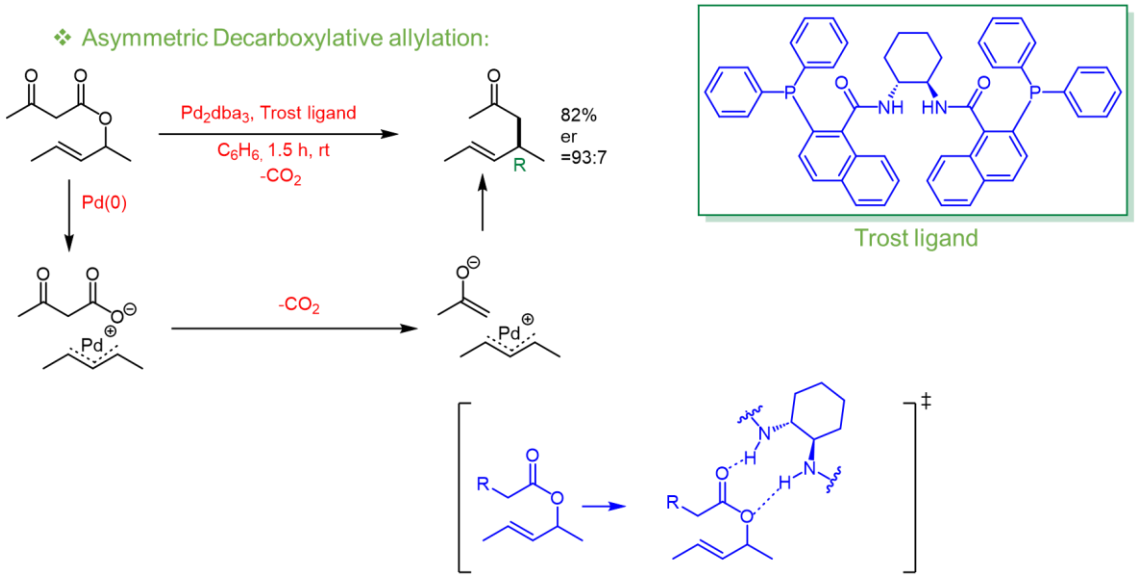
Again, here is another example of synthesizing this particular compound. So, it is an opening of this type of strain ring using allylic alcohol in the presence of acid that can achieve these compounds and, after that, treatment of LDA to deprotonate. LDA deprotonates this proton, and then after that, we can get to this corresponding enolate, which can take part in this [3,3] sigmatropic rearrangement, and then there will be protonation and then decarboxylation. So, to end up with the corresponding product. And then I'm going to talk about the asymmetric part.

2.



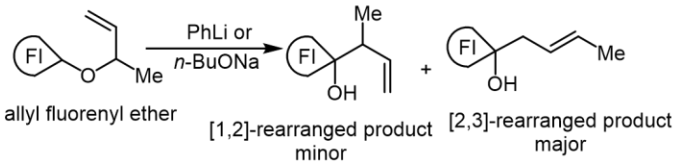
So, as I was telling that, with palladium, this was, developed using the Trost ligand. So, Barry trost has developed several ligands and several chiral ligands for asymmetric allylation reactions. So, one of these ligands is here, using this corresponding ligand, it can bind with the palladium can. So now, once the ligand is going to bind with the palladium here, what is going to happen? Now this can generate a palladium allyl species. once the nucleophile can attack to this terminal it can generate a chiral center here.

So, now you can see how cleverly they have used it because you have to generate a chiral center here. So, that means simple allylic acid will not work. So, you have to get a substituted one. on both sides. So, there is methyl substitution. So, this allylic alcohol, finally, with palladium, it can generate this palladium allyl species. Now, the decarboxylation to generate this enolate and this palladium allyl species with this chiral ligand backbone on the top of the palladium. So, now, what is happening is this can attack this terminal and then generate this corresponding chiral center here. and also, what is happening there is this product once they are forming, I think in the corresponding transition state, there will be this palladium and this chiral ligand able to block a particular phase of the allyl so that the nucleophile can approach a particular phase to generate this product with high enantioselectivity.



Now we are going to move from Carroll rearrangement, and we are going to talk about the [2,3]-Wittig rearrangement. So; this was discovered by Wittig in 1949 and later by Stevens in 1960. So, using this type of allyl Fluorenyl ether, I have drawn the structure of this part here. So, you can see this allyl fluorenyl ether in place of phenyl lithium, and if you use the sodium tertbutoxide, It is going to participate in [1,2] rearrangement products as a minor and [2,3] rearrangement product as a major. So, we are going to discuss both these [2,3] and [1,2] rearrangements. So now you can see how this type of transformation is going on. We will try to show the mechanism here. First, in the case of butyllithium, what is going to happen? You can see this is the proton, which is the most acidic proton. So this proton is getting abstracted to generate a carbanion. then the carbanion can attack to this olefin. So, this is some sort of a carbolithiation. It attacks the double bond, then pushes the arrow like that, and then cleavage of this carbon-oxygen bond. To generate this compound after protonation it is going to generate this type of homoallylic alcohol.

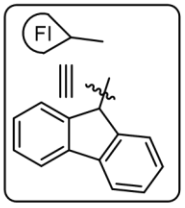
Wittig (1949) and Stevens et al. (1960):



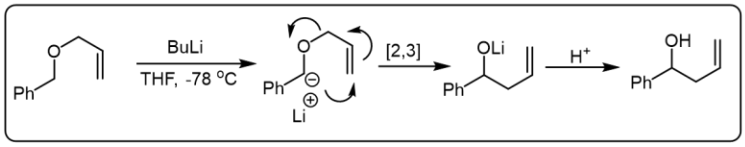
allyl fluorenyl ether

[1,2]-rearranged product
minor

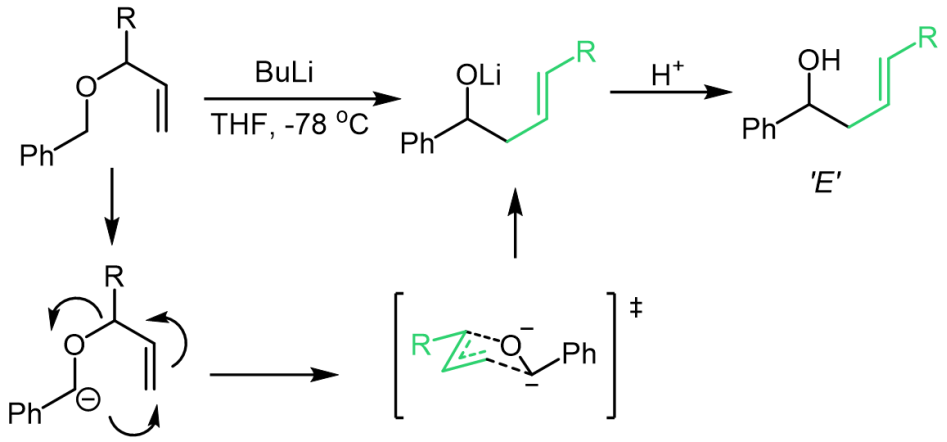
[2,3]-rearranged product
major



- Transformation of allylic ether into homo-allylic alcohol via a concerted pericyclic process.



So now we are trying to learn about transition state of this reaction. So once this attack happens, after the formation of the carbanion, once it is attacking this terminal olefin, it can go through a five-member, six-electron transition state, and it's a kind of an envelope shape. And the one of the important factor is, if you can see about this R group means this R group can be axial or equatorial position. Again the equatorial position will be less energy. So, it can able to keep in the equatorial position which can deliver this product.

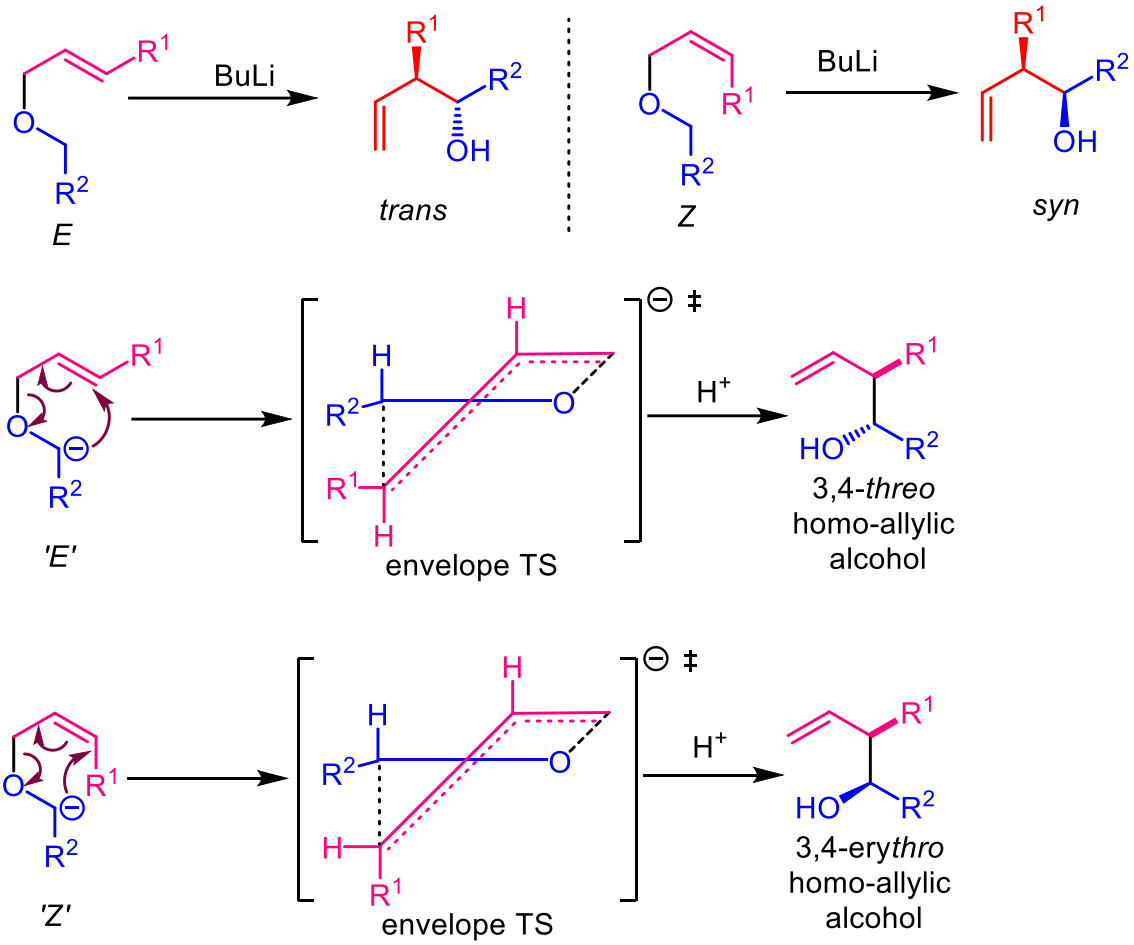


- The reaction goes through an envelope like a five-membered six electron transition state.
- R-group prefers an equatorial position resulting in the trans arrangement of the double bond.

Now, the important part is the geometry of this olefin, which ends up forming the E product. it is forming an E product because one of the reasons is that the R group is in the

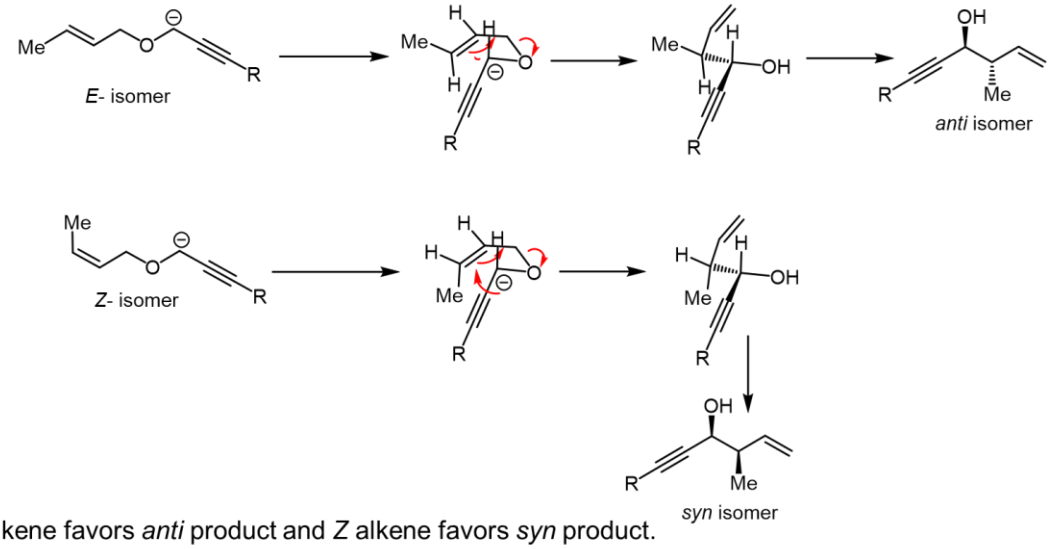
equatorial position. Now, there are examples that if you start with E versus Z. So, now, we are talking about the terminal position if you have E olefin here if you have a Z here. Now, the question comes: if you go for this [2,3] Wittig rearrangement, what will be your product? once your terminal is E, we end up getting the trans-selective product, which means this is R1 and the OH, and then if you use Z, then it will give us Z in the product.

So, now we try to understand what is happening here. So, once this is attacking this, this carbanion which is going to form first once this carbanion is attacking to this double bond and then this forms envelope transition state here one thing you have to understand, as I told you that depending on this R1 that means if it is a trans now if you try to draw a trans olefin like that. So, this is a trans, which means, this R1 will be here in this position, and once you are starting with a cis like this to make this geometry cis you can see clearly if you want to make this cis that means, you know this group will be same side this means this that means, R1 will be in this position that means, R1 is carrying you know some sort of axial position here and here some sort of equatorial position. Now, if you see if you try to compare the R 1 and then oxygen. you can see the R1 is actually here up and the OH is actually down. which is giving these three products here, or you can see the trans product now here. You can see the R1 and this oxygen both are actually on the same side, so that means that it is going to end up giving you this corresponding erythro or syn product.



So, here are some examples from the literature. So, you can see here also after the formation of this carbanion using LDA or phenyl lithium, it can take part in this [2, 3]-Wittig rearrangement, it can attack this olefin, and then it can end up forming this anti-isomer. Again, if you start with the Z-product then you end up getting to the syn isomer. I think we have already explained the transition state in the last slide.

Examples:



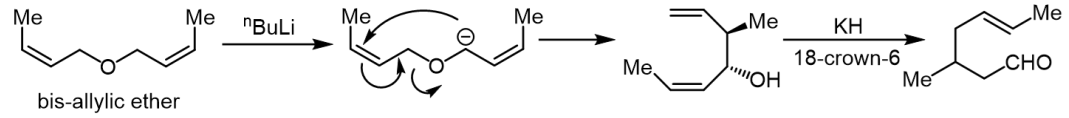
- *E* alkene favors *anti* product and *Z* alkene favors *syn* product.

Moving further, we have another system here where you can see we can also able to make a carbanion using n-butyl lithium. Now, this carbanion is going to attack this double bond here, and then it can go for this [2, 3] Wittig rearrangement to cleavage of this carbon-oxygen bond. and then which can able to generate this product. Now, the interesting part is once you generate this product, you can think about something I taught you in the previous lecture because now you can think about there will be another sigmatropic rearrangement because there is 1,2,3 and 1,2,3. So what is this rearrangement? I think I talked about oxy-cope rearrangement in the previous carbanion class. So here is what we can see: there will be a [3, 3]-sigmatropic shift, and so that is going to actually end up making this corresponding product. Again, as I mentioned, there will be this oxygen, which will finally form a double bond here.

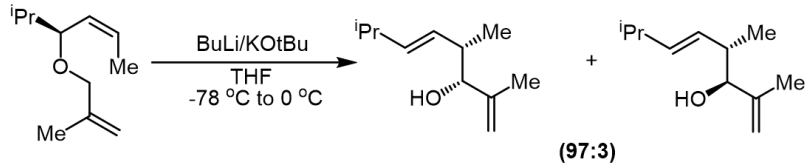
So it will convert to the aldehyde and there will be a new olefin bond going to form here. Again, I have mentioned clearly during the Oxy-cope that you have to use this KH to abstract this OH proton and then this 18-crown-6 will be useful to trap the potassium. I already explained that in the previous discussion. So, here is another example using butyllithium and potassium tert-butoxide. The first thing is an abstraction of this proton, and then it is going to attack this double bond. So, now you can see this is an allylic as well after cleavage of this carbon-oxygen bond is going to end up making this corresponding alcohol. Again, you can see that you are getting the syn product as a major product, which we have predicted if you start from a Z olefin in the terminal position.

Examples:

1.



2.



(97:3)

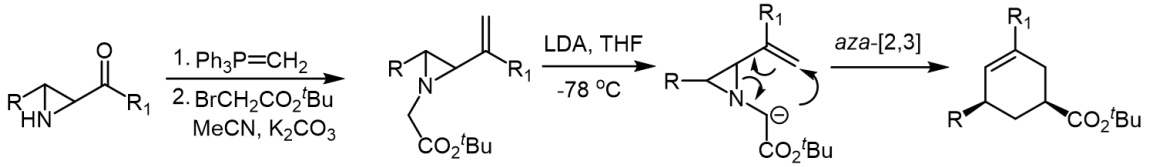
Now we are going to move to another version of the [2,3]-Wittig rearrangement called Aza-[2,3]-Wittig rearrangement. So, what is happening here? This is replaced by nitrogen. So, you can see in this reaction again the first thing is now you are generating a carbanion next to nitrogen. Of course, that proton will be a little more acidic compared to the other one, the carbon analog, and then it will take part in the very similar [2,3]-Wittig rearrangement to cleavage of this carbon-nitrogen bond, so we started with some sort of a tertiary amine you can see this is a tertiary amine here nitrogen with three different groups so after the rearrangement happens you can see we end up making this particular compound after that it will take proton to get to this compound so now it is actually from a tertiary it is becoming a secondary in this reaction one of the interesting fact is here the carbanion is generating on the nitrogen atom instead of the carbon atom which will be more favorable.

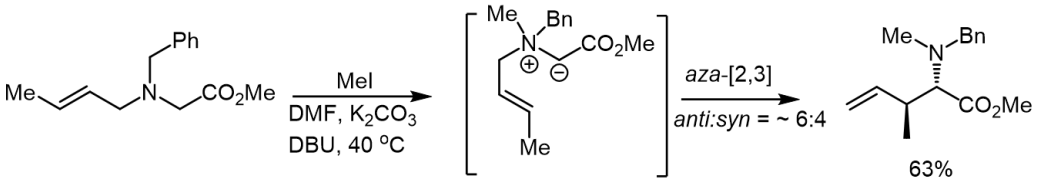
- The nitrogen analog of Wittig rearrangement is known as aza-[2,3]- Wittig rearrangement.
- Aza-[2,3]-Wittig rearrangement proceeds by a concerted six-electron, five-membered cyclic transition state of envelope geometry.
- The driving force for this reaction is transferring a formal negative charge from C to the more electronegative N-atom.

So, Here are some of the examples in this particular example. The first thing is the Wittig olefination to convert this corresponding carbon into a double bond. And then also the protection of this nitrogen group with the α-bromo ethyl esters here. So, which can form this N-CH_2COO^- tertbutyl? Now, once you treat with LDA what is going to happen? it is

going to abstract this particular proton. and now this carbon ion can attack here, and then now you can see it is going to release this strain ring, so it will allow to open this strain ring through Aza-Wittig. it can end up making now from starting from this compound, you end up making a cyclohexene. there are substitutions with an appropriate stereochemistry. So, now there is another example here, where the first thing you are using is methyl iodide with the presence of DMP and potassium carbonate. So, what is happening here, it is generating this carbanion here, and once it is generating a carbanion, it is going to attack here to this double bond to go for this Aza-Wittig reaction, and then it is open up to this corresponding product.

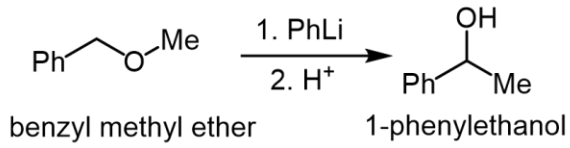
Examples:





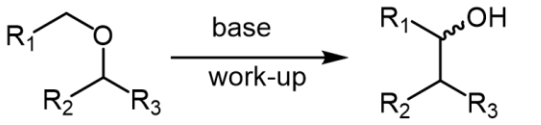
We talk about the [2,3]-Wittig rearrangement and then the Aza-Wittig rearrangement. So, now I am going to talk about another class of reaction called [1,2]-Wittig rearrangement. So, that was discovered in around 1942. So, it is a benzyl methyl ether. I think we talk about different types of ether throughout this type of rearrangement. If you remember the vinyl allyl ether for the sigmatropic rearrangement, and now we are talking about the benzyl methyl ether using phenyl lithium and H^+, it can now convert to the corresponding secondary alcohol. So, an ether is converted to a secondary alcohol in the presence of a base. Again it could be a 2 degree or 3 degree depending on the substitution.

Wittig and Löhmann (1942):



benzyl methyl ether 1-phenylethanol

- Conversion of aryl alkyl ether to corresponding secondary or tertiary alcohol in the presence of a strong base.



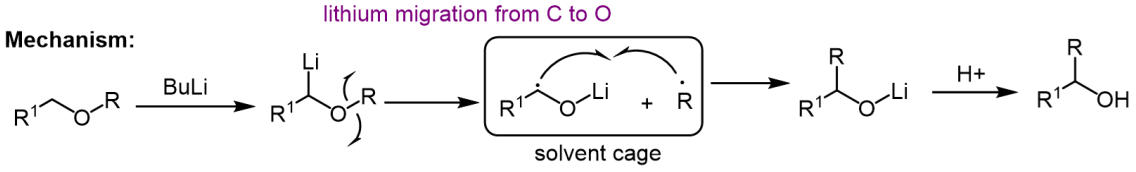
aryl alkyl ether 2° or 3° alcohol

R1 = aryl, alkenyl, alkynyl; R^{2-3} = H, alkyl.

Now we are trying to understand the mechanism because this particular reaction is a very interesting mechanism. Of course, this is a proposed mechanism, but I could not find concrete evidence for this mechanism. So, what is happening in place of butyllithium first thing is an abstraction of this proton to generate this corresponding lithium. and then what is happening? the next step is very interesting, there is a lithium migration happening here, which means this lithium is actually migrating from this carbon to this oxygen how this is happening, so we want this migration is happen here, followed by there is a generation of a radical and this particular bond is also getting flipped okay so the OR bond is getting flipped which is replacing by OLi and then the formation of a radical here and then there is R dot. Again these radicals are proposed that they are happening in a solvent case. So, they are really close in proximity. So, they can now recombine to form this corresponding OLi, which can protonated to get to the corresponding secondary alcohol.

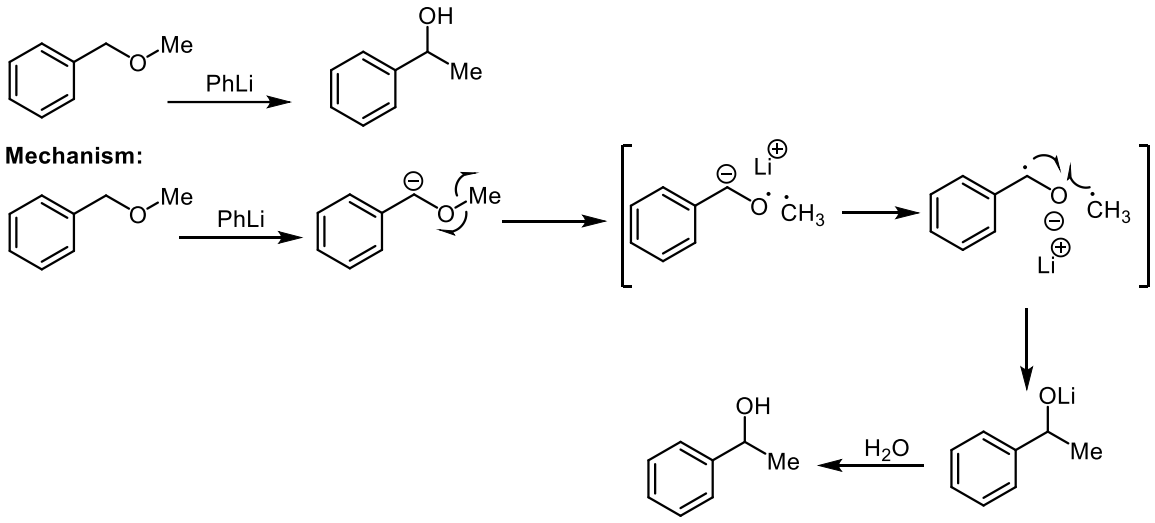
- The [1,2]-Wittig rearrangement is a carbanion rearrangement that proceeds via a radical-pair dissociation-recombination mechanism (proposed mechanism).

Mechanism:



- The R^1 substituents have to stabilize the carbanion.
- The yield is moderate due to harsh reaction conditions.

Now we try to understand that if you start with a different type of substitution or a different type of chiral center, what is going to happen? Again, we propose this mechanism here for this simple substrate that again there will be first, this proton gets abstracted to generate a carbanion, and then the reaction goes via the formation of some sort of di-radical species and then recombination of the radicals and protonation.

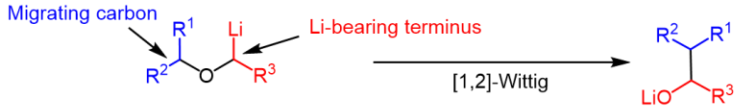


The first question arises that, we have two different terminals one is the terminal that is getting migrated or which is finally, coming and attaching with this particular center where the organolithium is and the other is the lithium-bearing terminals because what we are now going to talk about that if we bring a chiral center on the migrating carbon versus if you make a chiral lithium then what will be the product? Is it going to lose the chirality completely, or will there be some sort of retention, or there will be some sort of inversion? So, in this particular example, you can see adding from these particular compounds once they are treated with n-butyllithium, and then the corresponding alcohol gets oxidized to the carbonyl group. A 90 % retention of the configuration was observed.

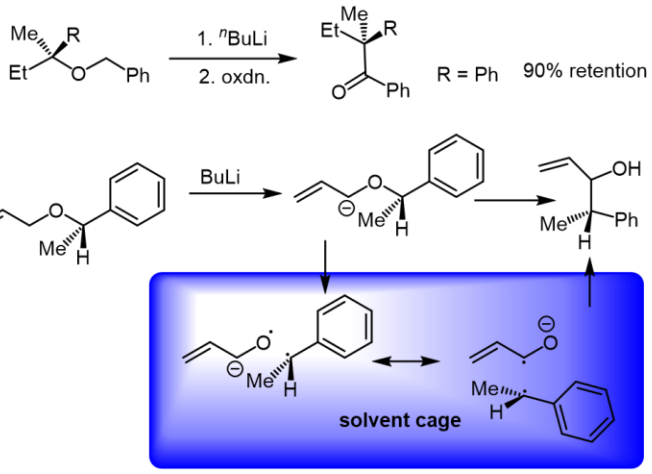
Again, what is happening first thing is abstraction of these protons are again it is next to oxygen, and this is also there is a there is a vinyl group in the next carbon. So, this will be an allyl anion. which are stabilized. Again, what is happening? after this step as you know that once you form this anion, which you can consider this anion is actually a lithium here is anion minus and lithium plus. Now, what is going to happen is there will be a cleavage of this bond, as you mentioned, and the formation of, you know, O dot and this carbon dot. So, this is again a benzylic radical will form here. And then what is going to happen? So, they are saying this is inside a solvent cage. So, they are close by, they can recombine. So, they are now there will be a lithium migration to generate a carbon radical.

Now these two radicals can recombine to form this corresponding product. So, the

important part is, as they are saying that this is happening in a solvent cage, the stereochemical information is still retained.

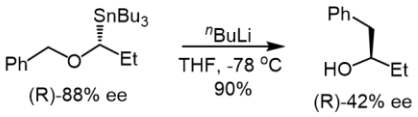


➢ **The migration occurs with retention in the configuration of the migrating carbon.**

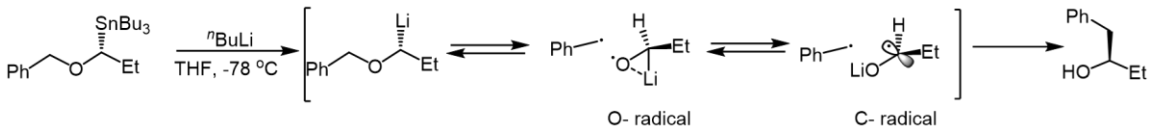


Now, the question comes as I mentioned if you start with the chiral lithium. So, with chiral lithium inversion occurs as a major product. That means if you start with chiral tin reagents this can be cleaved that carbon tin bond to generate a corresponding chiral lithium in place of n-butyl lithium, and then after that, what is happening after that again as there will be cleavage of this bond and then the formation of this benzyl radical then this will be a lithium migration formation of carbon radical and then recombination to form this product. What is happening? We only started from 88 % ee. It was found to be 42 % ee. not only that, this particular center was getting inversion, which means, what is happening? There is a 70 % inversion and 30 % retention. That is how we are getting to close to 40 % ee.

Starting from chiral lithium inversion occurs as major product

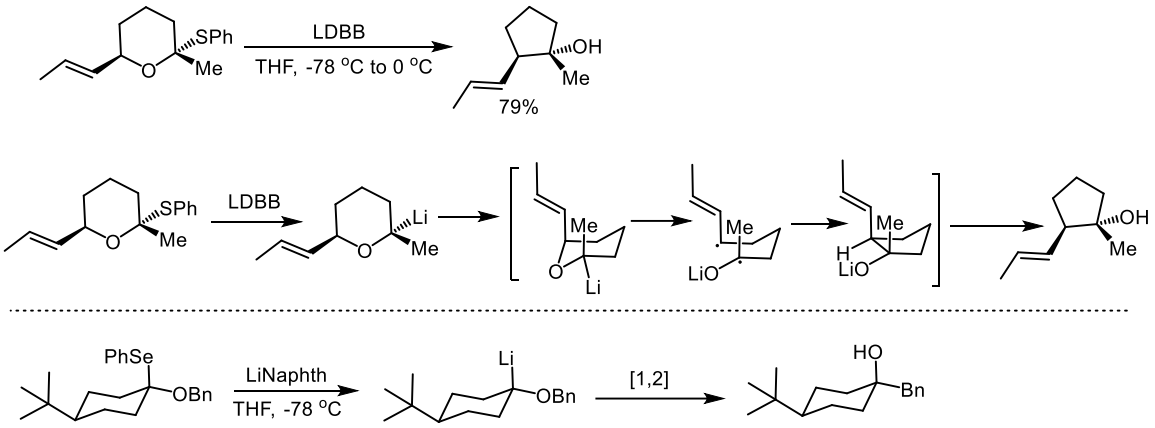


Mechanism:



Another example here, the first thing is the cleavage of this carbon-sulfur bond to generate lithium. And then what is happening? The next thing is there will be cleavage of this carbon-oxygen bond to generate this type of radical species, and then the lithium is getting

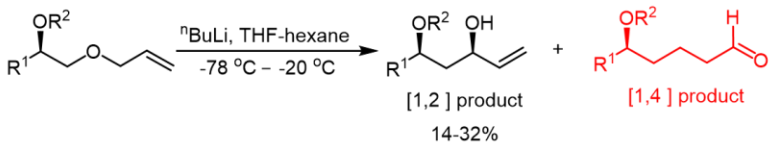
migrated to oxygen to generate this radical, which can recombine and form this product. Again, there is another example here: if you have this corresponding selenium, it can also cleave this formation of this corresponding lithium, and after that, the [1,2] Wittig rearrangement to the formation of this corresponding product. Again, you can observe the oxygen was literally here. It was equatorial, and in the end, it became axial.



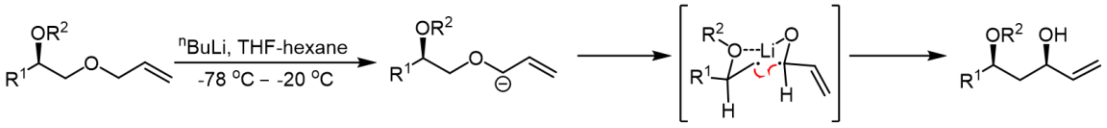
There is another example here that in this type of particular compound, actually what is happening. So, there is a chiral center next to oxygen there is one carbon gap. So, now, once it was treated with the n-butyllithium at - 78 °C, it is getting [1,2] product, not the [1,4] product.

Of course, the yields are really poor. So, I am just still trying to explain the reaction. So, the first thing is again the abstraction of this particular proton using butyllithium to generate this carbanion. The next thing is actually cleavage of this bond to generate this type of radical and then there the lithium will shift to generate this radical here.

Now these two radicals can recombine to form this product. So, starting from this product you can end up making this 1,3 dihydroxy compound. So, there is 1, 3 dihydroxy at the same time this is allylic alcohol.

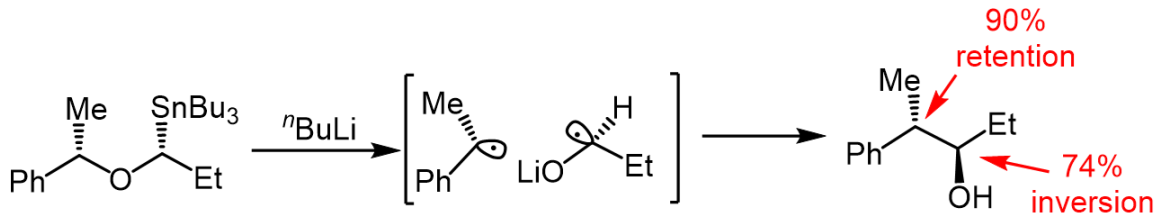


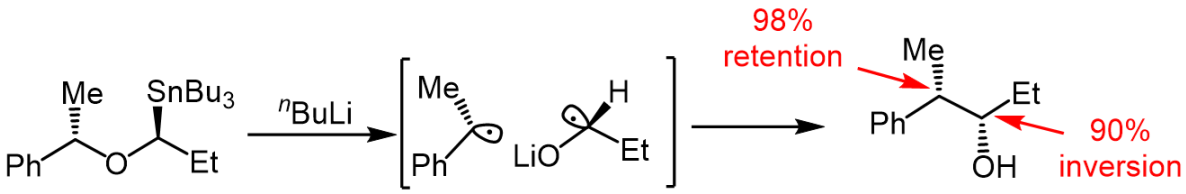
Mechanism:



- The ether oxygen coordinates with the lithium counter ion of the acrolein ketyl in the transition state.

Another example here is if you start with this reaction, which has two chiral centers. then, after the reaction of this chiral center, there will be retention, as you mentioned at the beginning; the terminus that is actually migrating will have mostly the retention, and then the other terminus will have inversion as a major. So, that is what we observe the same thing happening here I think in this case also, we are observing very similar results.

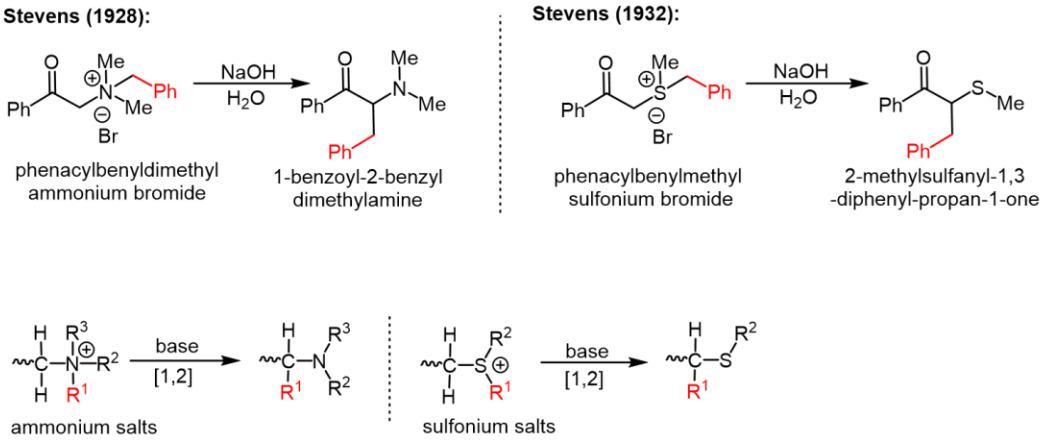




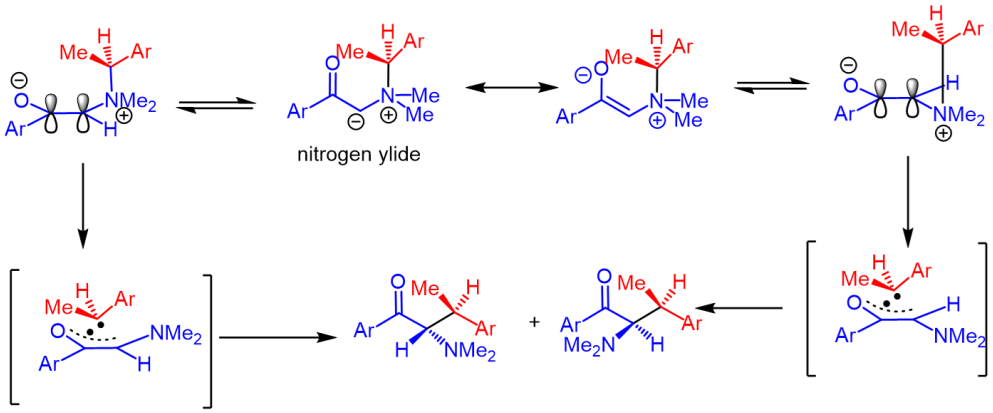
Now I am going to move forward and talk about the Stevens rearrangement, another important rearrangement reaction here, which is a base-catalyzed [1, 2] rearrangement of quaternary ammonium or sulfonium.

The first thing is making the quaternary ammonium and sulfonium, then in the presence of a base, there will be some sort of a rearrangement going to happen to get to a corresponding product. So, starting from this compound what is happening? if you see there is a phenyl $COCH_2$ in dimethyl benzylic group. So, literally, after you treat with the base, this benzylic group migrated from nitrogen to this particular carbon, and a very similar thing is happening if you have a sulfonium salt.

- Base catalyzed 1,2 rearrangement of quaternary ammonium or sulfonium salts to corresponding amines and sulfides.



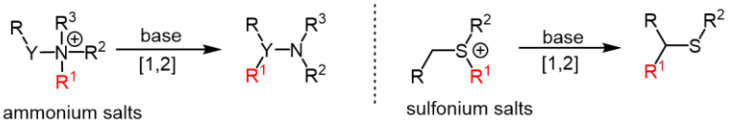
Now we try to understand the mechanism of this reaction. of course, in the presence of a base, there will be the formation of enolate of course which can now do one thing: it takes this alkyl group and then cleaves this nitrogen bond to neutralize the charge, which is going to happen. So there is also a proposal that this reaction also happens through following some sort of radical pair and then the recombination that means in this stage, what is happening? there could be radical pair formation happening to the formation of some sort of a transition state like this and then recombination of this radical pair to get to this corresponding product.

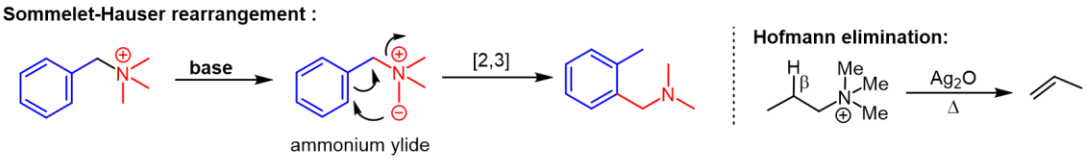


- The reaction occurs via a hemolytic cleavage followed by a radical pair recombination mechanism.

There is another issue that there is a competition between the Sommelet-Hauser rearrangement, which I am going to explain in a minute, and the Stevens rearrangement. So, now the question happens: if you have this group as a phenyl instead of alkyl, then

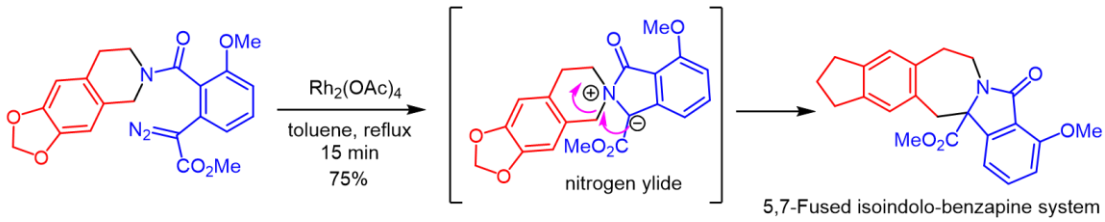
what is happening? once you abstract this proton of this CH_3^-, now instead of going for the Stevens rearrangement, it is actually attacking to this phenyl ring, So, going for [2, 3] rearrangement to get to this product so that is now getting to the Sommelet-Hauser rearrangement. or there is a possibility if you have an alkyl group with a β- hydrogen, that means then it can also go for a Hoffman elimination. So, we have to be careful that this R group cannot be a phenyl or cannot be an alkyl with a β- hydrogen.

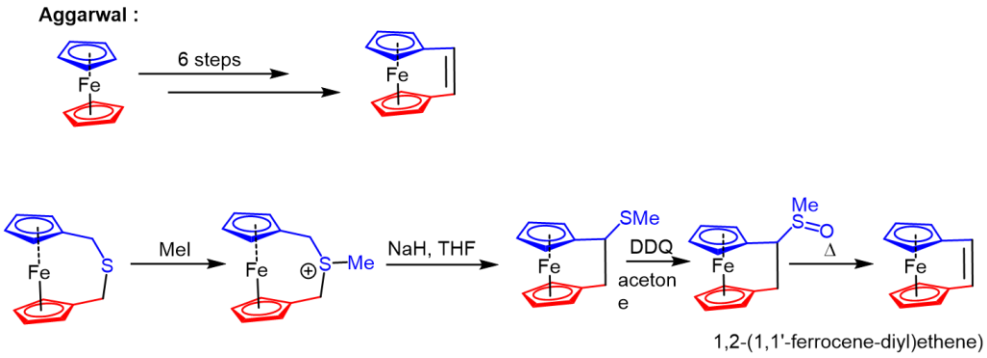




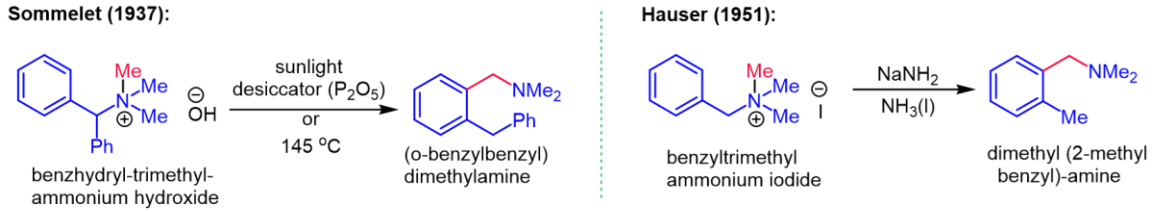
- R-group has to be able to stabilize the carbanion.
- When R is aryl or hetero aryl Sommelet-Hauser rearrangement becomes competitive.
- R^2 and R^3 groups cannot contain β-H otherwise Hoffmann elimination may take place.

Here is some example of Stevens rearrangement actually first thing you can see formation of that diazo compound in place of the rhodium, which can formation of this corresponding carbene, which can attack this nitrogen through the formation of nitrogen ylide. Then it can go for this Stevens rearrangement to cleave this carbon-nitrogen bond and then there will be a ring expansion to form this particular compounds. There is another interesting reaction with sulfur also. sulfur can be converted to SME, and then the sodium hydride can abstract the proton. It can abstract the proton, followed by there will be migration from this compound; further, the DDQ can oxidize the sulfur, and the elimination can generate this product.

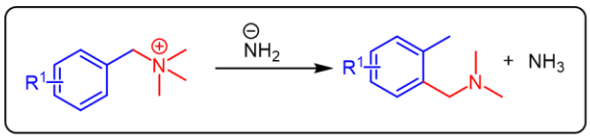




Now I'm going to talk about the Sommelet-Hauser rearrangement, which I talked about in the previous slide. Here, what is happening, as I mentioned, as soon as you have a Phenyl ring here, and it was discovered by Sommelet in 1937. So, in this compound, in place of a sunlight desiccator or 145 °C, it can form this particular product. We are going to explain, and then Hauser, in 1951, discovered a similar reactivity. So, this is a, you know [2, 3]-Wittig rearrangement of benzylic, quaternary ammonium salt via ammonium ylide. So, we are talking about some sort of a ylide. So, that means there is a negative charge next to nitrogen, which is carrying a positive charge.

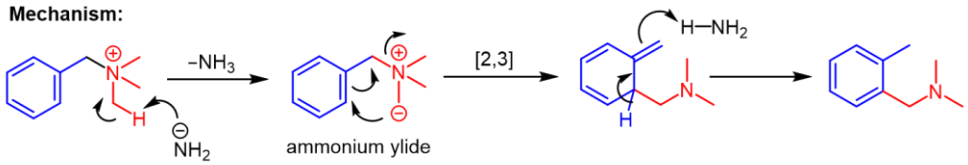


- [2,3]-Wittig rearrangement benzylic quaternary ammonium salt via ammonium ylide intermediate, which is known as Sommelet–Hauser rearrangement.



Now we are going to try to understand the mechanism of this reaction and what is happening. The first thing is an abstraction of this hydrogen. As you can see, you can use this NH_2^- to abstract it, to generate this type of carbanion species. Now, it can attack this benzene ring here, followed by the cleavage of this carbon-nitrogen bond. This hydrogen

can be abstracted to cleave this carbon-hydrogen bond to form this new bond here, and it can take the proton from ammonia to form this corresponding product. So, this is the most common reaction for producing the nitrogen ylide intermediate.



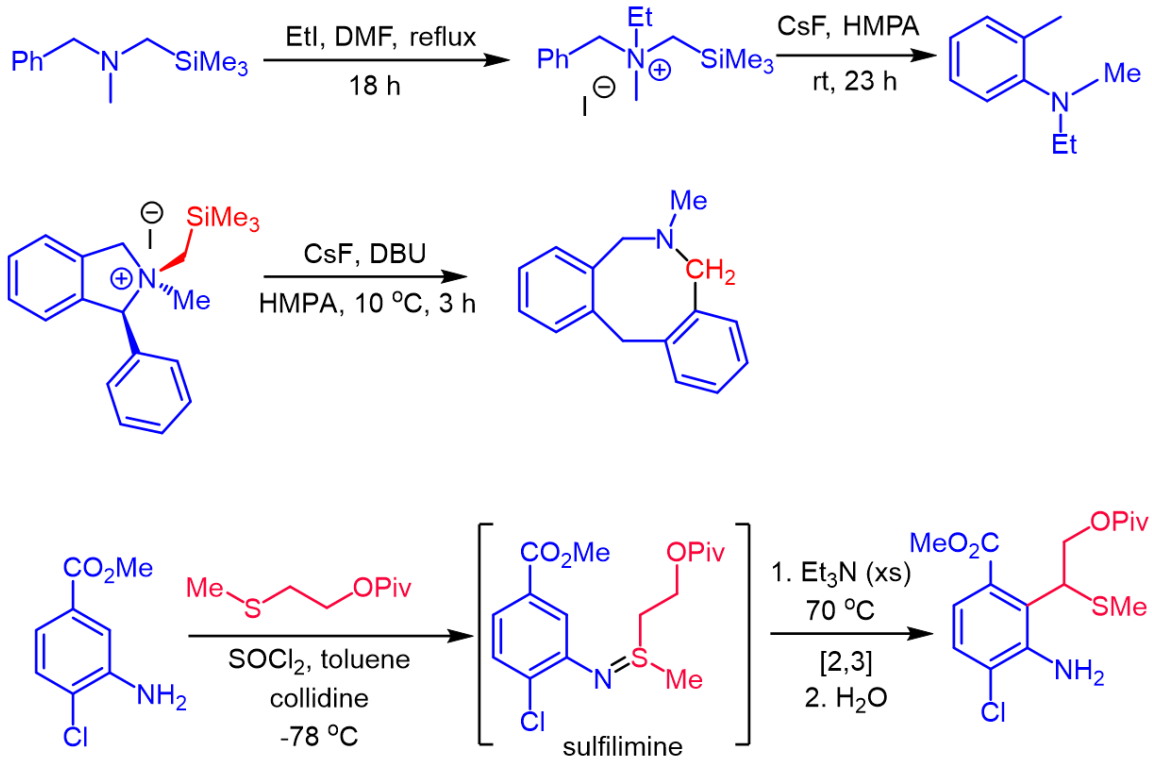
- The most common method for producing the reactive nitrogen ylide intermediate from the deprotonation of the quaternary ammonium salt is to treat it with alkali metal amides in liquid ammonia.
- Usually more stable ylide (derived from the more stable carbanion) is formed when there are two possibilities of deprotonation.
- When β-hydrogen containing N-alkyl substituents present, the Hofmann elimination may compete.

Here is some examples; of course, in place of ethyl iodide, the first thing that happens is forming this N ethyl. So, the first thing is the formation of this quaternary ammonium salt. So, now the idea is they have used the silicon. So, that means you do not have to use a stronger base to abstract the proton just by using CGM fluoride; you can cleave the carbon-silicon bond to generate an anion.

Of course, I am going to talk more about silicon chemistry about the cleavage of this carbon-silicon bond. So, the cesium fluoride actually attacks the silicon to cleave this to generate this carbanion. Now, once you have a carbanion, it is for following this [2 3] Wittig rearrangement to get to this corresponding product, which you have shown in the previous slide. Again here, there is another example. So, the first thing is in place of the cesium fluoride cleaving of the carbon-silicon bond to generate this corresponding carbanion, which can attack this phenyl ring followed by the ring expansion to this corresponding product.

You can clearly see this is the CH_2 which is going to attack here and then followed by the ring expansion and then cleavage of this bond. is another example also here, their first thing is also with starting from this compound they are making this type of sulfinimine which is participating in the [2,3] Wittig rearrangement to this corresponding product.

Examples:



In today's class, i talk about the several different anionic rearrangements i started with the carrol rearrangement, then i talked about [2,3] Wittig rearrangement Aza-Wittig rearrangement followed by, 1, 2 Wiitig, I talk about the migrating group and the chiral lithium, then what will happen, the inversion or retention, I end up with, Stevens and Sommelet-Hauser rearrangement. So, thank you for, coming to the class and please, go through the Clayden and, other textbook as I mentioned in the previous classes. And I am going to, looking forward to you in the next class.