Molecular Rearrangements and Reactive Intermediates in Organic Synthesis

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Lecture 57: Tutorial 2

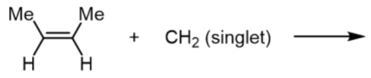
Welcome back to this NPTEL online certification course in molecular rearrangement and reactive intermediates. In the previous class, I started talking about some of the previous year questions for the carbocation and the carbanion part. And in the today's class I want to talk about some of the previous year question covering the carbene and nitrene. Again these questions I am discussing because this can help you to prepare for this competitive exams. So, let us start with the previous year questions. So, first question is I think you have if you have cover my lecture notes then you must have seen this type of reactivity of carbene.

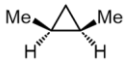
So, if you have a singlet carbene here I think you should put two dot here just to show this is a carbene. So, we are talking about a reaction of a singlet carbene and an olefin. So, what you have learned that if you have a singlet carbene then the reaction is with the olefin is stereospecific. So, that means, if you remember the structure of carbene let me draw one more time for you.

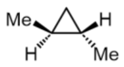
If these are the 2 H and then you can think about having an empty p orbital and also and then one sp^2 hybrid orbital. If you remember that structure of it and then if you think about the olefin you can think about olefin if this is a methyl, methyl and they are cis. Now you can think about olefin both side they are a single electron they are forming bond and they are opposite spin. If these are opposite spin and there you can see the carbene which is also singlet. Now this now this bond formation going to take place in a very concerted manner.

So, in a concerted manner because you can see this is up they can this can take the down one and the down one it can take the up. So, it can form a concerted reaction will take place. So, as the concentrated reaction taking place it is going to form the product where you can see both the methyl will be same side. So, this will be the product and if you remember and if you do the reaction with the triplet then you end up getting a mixture of both the product. You get a mixture of A and B, but here you will get only A.

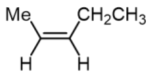
Previous year questions

Q.1) 

(a) 

(b) 

(c) 50:50 mixture of above two compounds

(d) 

Correct answer: (a)

Now the next question from starting from this cyclopentene you treat with A you get to this corresponding you got a cyclopropyl ring here and you have a dibromide. And then you to the $AgNO_3$ and H_2O and this is end up forming B. So, first thing is if you think about the first reaction just in the previous slide I shown you the generation of the reaction of carbene with a olefin to form a cyclopropane. So, it is clearly indicating that A will have some sort of a reagent which can because this is a reaction which is going through the $:CBr_2$. So, if you want to generate that carbene what will be the reagent of choice.

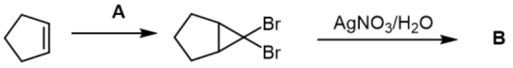
So, we have learned about the reaction called α-elimination. If you remember from $CHBr_3$ if you treat with KO^tBu, we have already discussed that these type of things, when I have teaching you guys carbene. So, please if you forgot this go back to that notes. End up forming $-CBr_3$ then there will be α-elimination, -Br that is going to generate the corresponding carbene. So, now the reagent of choice so the A will be $CHBr_3$ with KO^tBu.

Now if you look into in in all this option there is 2 option, option C and option D where you see the the A is same. Now let us look into what will be your B. So, once you form this dibromide what is going to happen you treat with corresponding Ag. So, now if you treat with Ag, what is going to happen here? If you remember Ag will try to form bond with the Br and it is going to slowly going to cleave the C-Br bond and end up giving you. It will form some sort of a carbocation here, now that will allow opening of the cyclopropane ring.

So, the 5 member going to expand to a 6 member with a + here and you already have H_2O in the medium. So, that can attack here to get to the corresponding product. So, you will have a Br here and you have a OH. So that will be your product B. So, now if you look into this options, your option C have this product or option D.

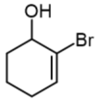
In case of option D, the Br is in the wrong place. So, C is the correct answer.

Q. 2)

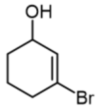


NET June 2012

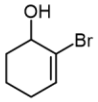
(a) **A** = CH_2Br_2 and KO^{t}Bu, **B** =



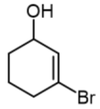
(b) **A** = CH_2Br_2 and KO^{t}Bu, **B** =



(c) **A** = $CHBr_3$ and KO^{t}Bu, **B** =



(d) **A** = $CHBr_3$ and KO^{t}Bu, **B** =



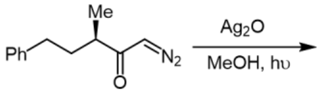
Correct answer: (c)

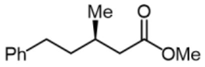
Let us move to the next problem. So, in this problem what you know what we are going to see that here you can see α-keto diazo compound. If you have this α-keto diazo compound and if you are treating with Ag_2O, remember the reaction I teach you which I cover in again during the carbene chemistry.

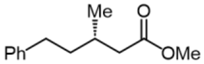
So, this is a reaction called Wolff rearrangement if you remember, so let us try to learn what is happening here if you remember in the Wolf rerrangement we end up formation of ketene. So once you know, you can think this thing as we can draw in other resonance structure you can draw them. So, now, you can think about from here in place of Ag_2O in light what is happening, it is converting to the corresponding ketene. So, it is forming this ketene here. And now once is forming the ketene now you have the MeOH here.

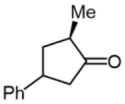
So, the MeOH will be attacking on the ketene, it is going to come back and then finally, this can able to take a H which can take a H from MeOH to get to the final product. If you remember this reaction, so this is the important step formation of the ketene and then the ketene. The methanol can attack to that C then this can able to form the corresponding ester and the -charge here which can be take a H from MeOH. So now the important thing is in this reaction the stereochemistry is not getting affected because all the reaction is happening here the ketene formation is not affecting the stereochemistry. That means if you look into all this product which is given in the option you have to find first what is the right product.

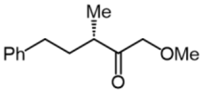
The option A and B looks the product looks same but only thing is the stereochemistry. So as the stereochemistry there should not be any change going to be happened that is why the option A will be the correct option here. Again if you forgot I will ask you to go back to the carbene chemistry lectures and go through the Wolff rearrangement.

Q.3)  **NET Dec 2012**

(a) 

(b) 

(c) 

(d) 

Correct answer: (a)

So, the next question formation of ketone 2 from diazo ketone 1 involves. So, they are saying that this is your 1, this is your 2 using PhCOOAg and heat.

Now the question they are asking what is the formation of ketone involves what type of generation of a carbene and 2,3 sigmatobic rearrangement, generation of carbene and electrocyclic ring closing reactions. Or it is going through generation of ketene and [2+2] cycloaddition or generation of ketene and 3,3 sigmatropic rearrangement. So, there are four option. So, let us try to find out what is the mechanism for this conversion. Again if you see that this is again α-keto diazo compound, α-keto diazo ketones, it is a diazo ketone.

So, now if you have this diazo ketone let us see what is going to happen. So, there is a 5 member and a 3 member ring here and then there is a double bond here, there is a methyl group here C=O and N_2. So, again I think if you see that the reaction condition the the role of Ag is not very much clear, but one of the important role could be the activating of the corresponding carbonyl group. So, that can allow you to the generation of the ketene. So, once you use Ag and heat that can allow you generation of the corresponding ketene.

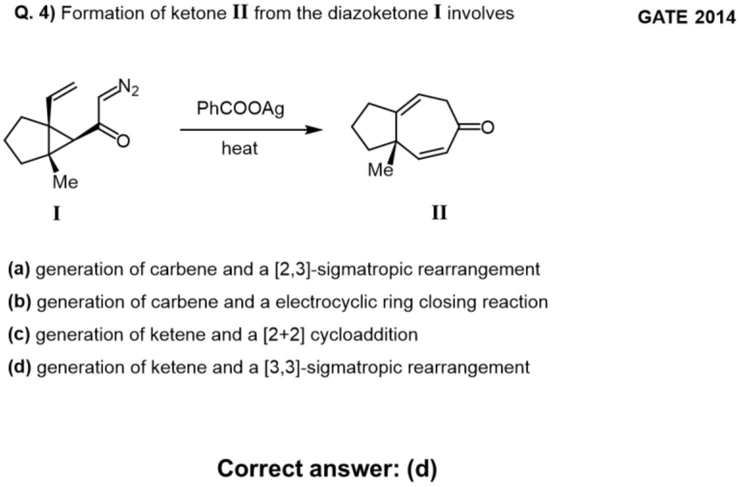
So, let us first draw that. So you will be generating a ketene here. So, now once you have generated the ketene now what is the next thing going to happen? Now if you see here in this particular compound you can think about from here this is 1,2,3 as well as here also this is 1,2 ,3. So, now you can think about a [3,3] sigmatropic shift where this can attack here this, bond can come back here this cyclopropane ring can break. If that is happening that can take you all the way.

So, now, what is happening here, ring expansion is happening. So, you initially and there is a double bond going to form here and then there will be a carbonyl group. There is a methyl here which was there from the beginning and then there is a double bond here.

So, you can see this 1 between this 1 and 1 this 2 bond there is a formation of a double bond. So, now, if you give them the name.

So, that suppose this is the terminal position. Here you are forming the double bond. So, here this was the originally this is the position which is the 3. This is the position of 2, there is the position of 1 and then on the other side also this is the 3, this is the 2 and this is the 1. So, what happen is actually expanded to form this 7member ring here.

So, from this the cyclopropane and then from this ketene the cyclopropane rupture, happen of the cyclopropane this C-C bond which allow the ring expansion through a [3,3] sigmatropic unit. So, now if you try to see the options then we are clearly seeing that is a generation of ketene is the important things and then the [3,3] sigmatropic rearrangement is the another important thing. This is not going via [2+2] cycloaddition. So, the answer D is the correct answer.


Q. 4) Formation of ketone **II** from the diazoketone **I** involves **GATE 2014**

(a) generation of carbene and a [2,3]-sigmatropic rearrangement
(b) generation of carbene and a electrocyclic ring closing reaction
(c) generation of ketene and a [2+2] cycloaddition
(d) generation of ketene and a [3,3]-sigmatropic rearrangement

Correct answer: (d)

Again the product of the following reaction gives 6 line in ^{13}C NMR spectrum with peaks at 175, 52, 50, 46, 37, 33 ppm.

So, you can see clearly from the structure of the compound is. Again you can see this is very similarly the diazo ketone compounds and once you have a diazo ketone and under light just now we have seen. So, these are the I think the Wolff rearrangement comes in a several times in different exam. So, I try to cover some of these problems also here. So, you can see in this question also this is a question about the Wolff rearrangement.

And again what is going to happen once you use light under the methanol condition, diazo ketone is going to convert to. So, there will be a. So, first if you going to write them like this you can also think about writing like this. At the beginning like as O- and so, they will participate under light to formation of corresponding ketene. So, that can allow you to form the corresponding ketene here.

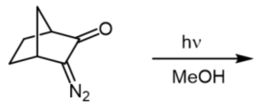
Now, once it is going to form the corresponding, so you can see these are the H here and then there will be a methanol here is going to attack, then it is going to come back. - and COMe which can take a H from the methanol to get to the corresponding product. So what is going to happen here, you end of a ring contraction going to happen through the formation of the corresponding ketene. And then from there once you have a ketene then you have a nucleophile methanol in the reaction and which going to form the corresponding ester. So, now if you try to see the corresponding ^{13}C NMR what we can see there is a 175 peaks which are indicate this is the ester or amide or something which is not a ketone.

So, you can see this in this compound the ester can come at that 175 and now if you count how many different type of C are there. We can see there are the 5 peaks for the different C and you can see there is one there will be 1, there will be 2 and there will be 3, 4 and 5. So, there will be 5 different type of C peaks we can able to see.

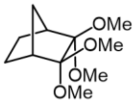
Because you can see in these cases you have a peak from the ester that is 1 then you have this terminal which will be 2 and then you have this particular C which will be 3.

But these are the C which are symmetric because you can see these 2 so if you count total, it will be 5 so the answer c is the correct answer.

Q. 5) The product of the following reaction gave **6** line ^{13}C NMR spectrum with peaks at δ 175, 52, 50, 46, 37, 33 ppm. The structure of the product is **GATE 2014**



(a)



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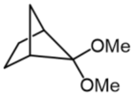

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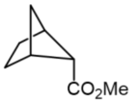
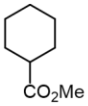


(d)



Correct answer: (c)

Again now we have learned this type of reactions here. So, now, if you treat with $CHCl_3$ and aqueous NaOH. So, this can generate the corresponding $:CCl_2$ and that $:CCl_2$ will form cyclopropane with this electron rich double bond. So that can end up forming with 2 methyl group here and you have a base in the medium that can allow you. So, it can happen like these where or it can happen the Cl- can come back and take the H either way either from these or from these from the top one.

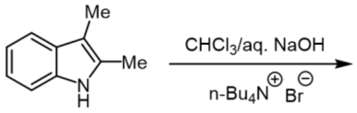
So, this will open the cyclopropane ring and also it is going to expand. So, you can think about formation of this bond at the same time you can able to eliminate this Cl or you can do in the 2 steps. If you do in a single step then this can take you all the way keeping the Cl here and we will have a methyl here and here.

It will take you all the way to the quinoline. So, starting from indoles, it will take you all the way to quinoline where you will have a Cl in this position and you will have a Me in the C_2 and C_4 position.

So, now look into the different type of option given here. If you see among all the option the first you know of course, in these cases the first thing is what will be the I think it might be that they have given 2 different answer here. It means they are asking that what will the what type of carbene going to form and what will be the product. Now, you can see the answer C and answer D. So, both have very same product what the last product are same, but in the C and D one thing was different.

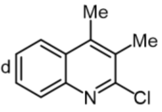
What is the difference? In one case, it is saying :CHCl, another case is :CCl2. So, you clearly understand :CCl2 will be the corresponding carbene then only you can able to get to this corresponding product. So, option D will be the correct option.

Q. 6)

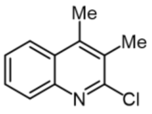


NET Dec 2013

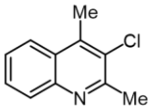
(a) :CHCl and



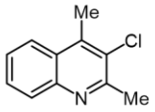
(b) :CCl_2 and



(c) :CHCl and



(d) :CCl_2 and



Correct answer: (d)

So, moving further the another very important reaction and also it comes in the Simmons-Smith reaction comes several times in the exam CH_2I_2 and Zn-Cu. So, if you use that if you remember that this is going to form corresponding cyclopropane through the formation of the corresponding Zn carbenoid.

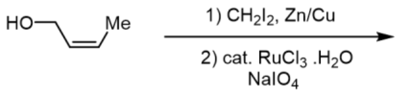
Again this is we discussed several problems the mechanism everything was you can going to find in the carbene chapter. I am going to tell you one more time what is going to happen. So, first thing is if you look on this olefin it is a Z-olefin and if you remember it the reaction using ah the Zn carbenoid these are going to generate a singlet carbene. So, this is going to be stereospecific with the olefin. So, that means the cyclopropane which is going to form here.

So, first if you remember let me just brush try to tell you again what is happening here once you use this Zn-Cu it is going to form this CH_2I_2 and Zn going to insert. So, this is called the corresponding carbenoid . So, this corresponding carbenoid can react with an olefin can try to write some sort of mechanism where the I is getting out and this is getting in. So, this is a concerted reaction again. So, that is why it is stereospecific and now if you look into that the stereospecific product that means both of this group the CH_2OH and the methyl will be same side.

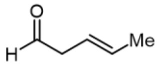
So, if you look into the different option and then what you have given let us see the next part. After them they given that the $RuCl_3.H_2O$, $NaIO_4$. If you remember this is a very good oxidizing agent which can convert the alcohol to all the way to the corresponding acid. So, now if now we have to look into not alcohol we are looking into the corresponding acid.

Now, if you go to the different option in the option C and D has the acid, but here in case of option D, the acid and the Me is in the same side. So, this will be the correct option.

Q. 7) The major product formed in the following reaction is **NET June 2016**



(a)



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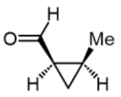
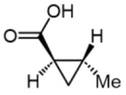
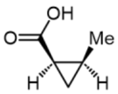


(c)



(d)



Correct answer: (d)

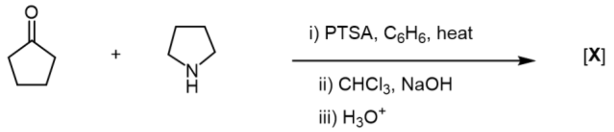
The next problem again, it is you can see it is a cyclopentanone and you have this pyrrolidine and you treat with PTSA C_6H_6 and heat. So, if you treat them what is going to happen here, first it is going to form and then you are treating with $CHCl_3$, NaOH. Again if you see $CHCl_3$, NaOH then you always think about generation of $:CCl_2$ and then it is treating with H_3O+.

So, let us try to figure out what is happening here. We know if you have a 2^o amine & carbonyl compound in place of acid what is going to happen $-H_2O$. So, it is going to form a corresponding iminium. Now you can also you can also in equilibrium and try to form a enamine. So, now, once it is forming the corresponding enamine if you have seen in case of indoles. So, now, you once you have this :CCl2 that can form the corresponding cyclopropane.

And now once you have the cyclopropane what you are going to see there that there will be some sort of a ring rupturing. Because if you look into all the different type of products here what we are seeing here some of the product you have cyclopentadiene and in one cases you have a cyclohexane. So, once you have formed this bond we remember that in case of indoles the N came into the picture. Here also you will going to see that this N lone pair going to give electron density here that is going to expand this ring going to get rid of the Cl.

So, let us try to draw what we are trying to get here. So, we now the ring got expanded and also what is happening here you are forming a double bond here and in the next C you are forming a iminium back and then you have a Cl here. So, if you give H_3O+ to this, this can allow the hydrolysis, the H_2O can attack here and this will allow hydrolysis of the corresponding. And then after the attacking there will be OH and there will be the N going to get protonated going to get out and going to form the corresponding carbonyl compound. So, again you can see only one option out of this has ring expansion the option D is the going to be the correct option here.

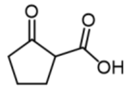
Q. 8) In the following reaction sequence



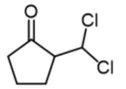
GATE 2011

the major product [**X**] is

(a)



(b)



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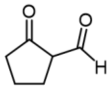

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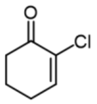


Correct answer: (d)

So, this is another important question you will see in the several year, these type of the question come when they ask you to use two different reagents.

Both cases you are going to form cyclopropane, but they have different reactivity. So, this is another important question you will see in the several year, these type of the question come when they ask you to use two different reagents. Both cases you are going to form cyclopropane, but they have different reactivity. So, let us start what is happening here. So, in one cases we are saying that if you use a reagent A you are forming cyclopropane.

So, if I give them a number 1 and number 2 ring then in case of the reagent A the cyclopropane formation happening in the allylic alcohol. So, this is the allylic alcohol getting cyclopropanated, not only that it is the cyclopropane formation happening on the same side of the OH. And if you go to the B now the cyclopropane formation happening in the ring number 1 and here the double bond forming corresponding cyclopropane. And that is also happening on the other side of the methyl if the methyl is up, cyclopropane happening from the bottom side. So, if you remember one thing, I think, I taught you that if you have this type of allylic alcohol.

I think this was also taught when I think in case of the mCPBA epoxidation same for the Simmons–Smith the cyclopropanation. Every case is what you find out that if you have a OH group which act as a directing group. Then if you use Zn -Cu and CH_2I_2 you will end up forming a cyclopropane on the same side of the OH. And I clearly explain you that O is going to form a chelate with the Zn because once the cyclopropane formation happening. If you have a double bond here and if this is forming the corresponding cyclopropane then we always write this is goes via a transition state where you have a CH_2 here.

And then there is a I here and then there is a corresponding ZnI_2. So, we talk about that the Simmons–Smith reaction always goes where this butterfly like transition state. So, the reaction happening in a concerted manner. So, here also you can see that once you have this alcohol that can coordinate with the Zn. So, you can see if you have an alcohol somewhere in your starting material, this can coordinate and direct the cyclopropanation in the same phase. You can see a picture is given here the corresponding that the transition state for this reaction you can see once you try to draw them in the half chair you have this double bond.

And you have this OH here which is coordinating with the Zn, this allowing the cyclopropanation happening from the same phase. So, that means, we can understand this product if you want to form then you have to use the Simmons–Smith reagent. So, that means, if you go to option number A and option number B then either option A or option B is correct because both cases we can find this is the reagent which is given. Now, go to the reagent B what is going to be the reagent B here. So, now we are talking about a cyclopropane formation happening which is α,β-unsaturated carbonyl compound.

So, if you remember we talk about a S ylide chemistry and there also I talk about that if you have a S ylide. Either it could be a sulfonium or it could be a sulfoxonium if you remember I talk about both of this. And if you have this type of ylide and if you have this sulfonium and then once you treat with NaH or a base BuLi, you can able to generate the corresponding ylide. So, I cover this in the S chemistry when I cover the organosulphur chemistry. And also I talk about that and if you treat with them to a corresponding cyclohexenone or α, β-unsaturated carbonyl compound these are always going to take part in the attacking here.

Again there are two different things I taught you that one it can attack here or it can attack to the carbonyl compound.

If we attack to the carbonyl compound, it is going to form the epoxide. If it is going to attack here, it is going to form the. And then you can see the chances of attacking for these type of reagents, there are more tendency to attack to the 1,2 versus the 1,4. But if you see in this particular cases where they want us to get to this product.

Then you have only this option that you have to use this as a reagent to get to the corresponding product and you have two other option you can. So, let me just tell you again. So, first cases, we understand. So, we understand the first part, I think right.

Let us let me just clarify this again one more time. So, we have understood that the you have to use the corresponding Zn-Cu here to get to this product. We got the right. Now, if you want to come back and understand what is the reason of what we need here to get to this compound. You can see, there is a α, β-unsaturated carbonyl compound here. So, if you want α, β-unsaturated carbonyl compound to cyclopropane, there is a reagent which you I cover in the S chemistry that is either you can use this.

There is two different reagents in the one could be a sulfonium salt or it could be a sulfoxonium. And also I mention that in these two reagent if you give a base then what you are going to form? You are going to end up forming the corresponding ylide. And I clearly mention you guys that there is a different of the reactivity between these because this ylide is a stabilized ylide. In case of sulfoxonium for this one, this is a stabilized one, here there is no stabilizing group.

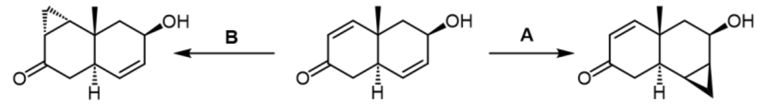
So, that is why this is this CH_2- is more hard compared to here. So, this can go for a 1,2 addition that means, if you take a α, β-unsaturated carbon. So, let us give this is your 1 and or this is a 1' this is a 2'. Now, if you take this 1' reagent and take with a α, β-unsaturated carbonyl compound what is going to happen? The corresponding sulfonium ylide going to attack to the corresponding carbonyl compound from O-, it is going to come back you can go through the notes in details going to form the corresponding epoxide.

But as soon as you use the stabilized one the sulfoxonium, this is going to go for a 1,4-addition and once there is a 1,4-addition, O-CH_2SOMe^+.

It is going to come back and going to form the corresponding cyclopropane. And then again you can see the the attacking is happening from the bottom side to avoid the steric with the Me group. Let us move to the. So, then the answer is going to be the B. Here you can see, we have to use a stabilized ylide, not a unstabilized one.

Again in this question what we are seeing that what will be the product here again you are using a Simmons–Smith reagent, but this is a allylic compound.

Q. 9)



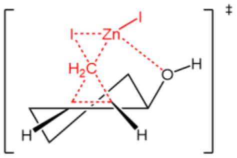
NET June 2012

(a) **A** = CH_2I_2, Zn-Cu; **B** = $Me_3S^+I^-$, NaH

(b) **A** = CH_2I_2, Zn-Cu; **B** = $Me_3S^+(O)I^-$, NaH

(c) **A** = $Me_3S^+I^-$, NaH; **B** = $Me_3S^+(O)I^-$, NaH

(d) **A** = $Me_3S^+(O)I^-$, NaH; **B** = CH_2I_2, Zn-Cu



Correct answer: (b)

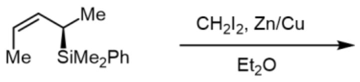
So, now if you try to draw this type of allylic compound, you have to understand that suppose you have the double bond here. So, what we are trying to draw here. We are trying to draw an olefin. And we have to understand there to avoid allylic strain, you always want the H to be eclipsing the olefin not the bigger group.

So, you want to put the H here. So, that can eclipse with the olefin and you want to put the larger group here up that means, you want to put the Si here. Si is already in the up here. So, you can show the stereochemistry and you have a Me here. So, here now you can see here if Si is here up and then now H is here. Now, if you want to see the Simmons–Smith reacts in the reagent to approach, it can approach the top phase or the bottom phase.

But in the top phase, it can have a steric & with this $SiMe_2Ph$ that is why the reaction going to happen through the bottom phase. So, now it is going to form the corresponding cyclopropane. So, it is going to form the cyclopropane from the other phase. Now, if you see the example given here, they are also in showing.

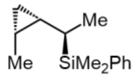
So, these are the two cases it is showing, it is going to coming from the bottom phase. But here it is showing, this will be trans, that is not the correct thing, you already started with a Z olefin. So, your product will be again, both of this group will be in the same side. So, the option A will be the correct option.

Q. 10)



GATE 2021

(a)



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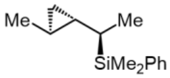

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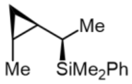

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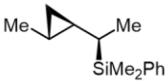


Correct answer: (a)

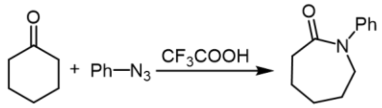
In this reaction what is going to happen if you take this Ph-N_3 and the cyclohexanone with CF_3COOH, you end up forming this product.

So, they are given the product. Now the appropriate intermediate involved in this reaction is. What will be the intermediate from there you can get to the product? You can about the Smith reaction which I cover, I think when I was talking about the nitrene part, I covered this. So, now, what is going to happen here, again when I was covering, I think similar type of reaction was covered. When I was giving the lecture on that nitrene part and if you remember I was using some Lewis acid like $TiCl_4$, but once you have a CF_3COOH that can protonate this. Now, if you try to write the azide like this, you try to write them like instead of forming this bond here.

If I can write them like + and -, then this can attack here to the carbonyl. If you want a ring expansion, you have to attack here. So, this will be OH and Ph-N_2+. This can allow the O lone pair can allow it to come back here and in expansion get rid of N_2. This can allow you to formation of this 7 member ring where you have a N-Ph here.

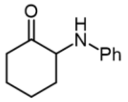
So now if you want to go through this what will be your corresponding intermediate. Now if you search from A, B, C and D you can see clearly D is the one intermediate from there the reaction is going to the product.

Q. 11) Consider the following reaction:



Correct answer: (d)

The appropriate intermediate involved in this reaction is

(a)


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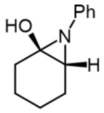

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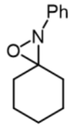

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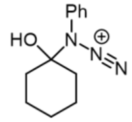


So this is a another questions here using you are using this azide source with this carboxylic acid and you are using a in t-BuOH and you are getting the product B. So let us try to draw what is this what is happening here.

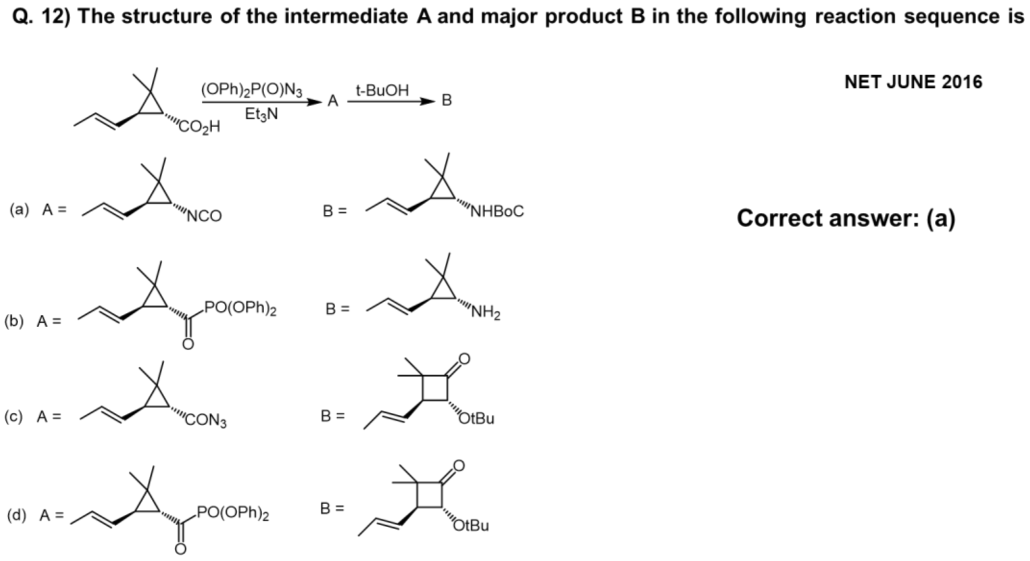
So of course, there is no change in the cyclopropane. So, the change what is happening in this COOH. Now, you have this other compound. So, you have this $(OPh)_2P(O)N_3$. Again very similar reactivity, we are going to see here, it is a -.

So, this can attack to the corresponding. So, you can think about there is a N_2 here. So, this O- can attack in the P, this can come back and this will go back and this can able to flip this bond. So, I am not writing the entire things. So, here what you are seeing the OH, you have OPO and then N- and N_2+. So, you can see what is going to happen, this OH is going to come back and this become a kind of a leaving group. So, this can get out from here, this will generate from there will be generating some sort of a acyl azide and if you remember acyl azide means this is ready for the Curtius rearrangement.

So, this is ready. So, if you remember, this is going to come back from the corresponding O- and then it is going to come back and going to form the corresponding isocyanate. So, let me just write down O- N. So, this is going to come back, this can migrate here get it up N_2 and forming the O=C=N and you will have the corresponding cyclopropane. So, let me now draw the cyclopropane, this isocyanate going to form.

You are treating with the t-BuOH so that can attack to the corresponding CO. This is going to come back and so and then it can able to form a N-. So, that means what we are finding out, the same stereochemistry will be written here, the acid stereochemistry will just only going to convert to corresponding NH. So, in the product what is going to be B. B going to be a structure like this where the cyclopropane stereochemistry will be retained. Whatever the substitution was here, will not be affecting here because they are not taking part in the reaction.

Only thing is, this is going to convert to NH with COO-t-Bu. So, this is called a BOC. So, it is going to convert to product B which is the NH-BOC and the starting material and there will be another intermediate going to be the A which is the corresponding isocyanate. So, it will form isocyanate and then it will go to form the corresponding amine.



Q. 12) The structure of the intermediate A and major product B in the following reaction sequence is

NET JUNE 2016

(a) A =

B =

(b) A =

B =

(c) A =

B =

(d) A =

B =

Correct answer: (a)

Again I think in this part I bring so many problems from the nitrene and carbene chemistry.

Please practice more and more problems for the exam. Again thank you so much for the coming to the class. I am going to see you in the next tutorial. Thank you.