Symmetry, Stereochemistry and Applications
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Lecture - 34
Substitution vs Elimination Reactions

Welcome back to the course entitled Symmetry, Stereochemistry and Applications. In the last few lectures, we were discussing about the various reactions like substitution and elimination reactions.

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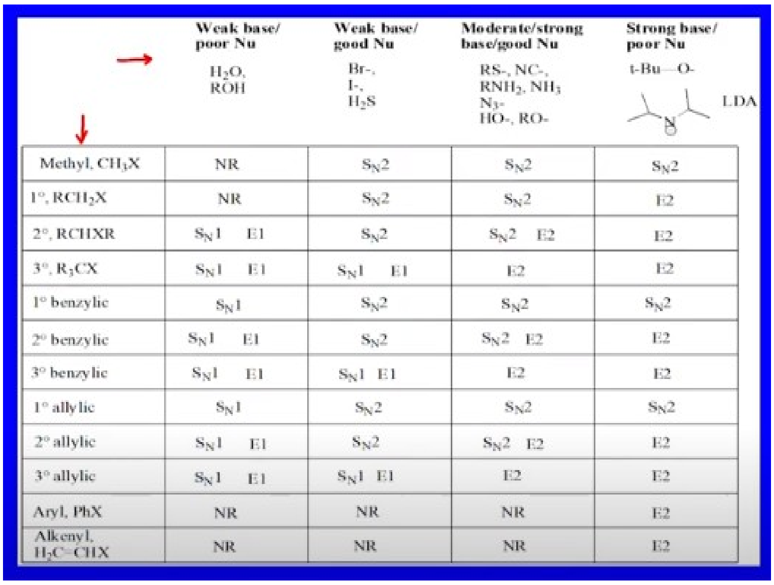

	Weak base/ poor Nu H_2O, ROH	Weak base/ good Nu Br-, I-, H_2S	Moderate/strong base/good Nu RS-, NC-, RNH_2, NH_3 N_3- HO-, RO-	Strong base/ poor Nu t-Bu—O- LDA
Methyl, CH_3X	NR	S_N2	S_N2	S_N2
1°, RCH_2X	NR	S_N2	S_N2	E2
2°, RCHXR	S_N1 E1	S_N2	S_N2 E2	E2
3°, R_3CX	S_N1 E1	S_N1 E1	E2	E2
1° benzylic	S_N1	S_N2	S_N2	S_N2
2° benzylic	S_N1 E1	S_N2	S_N2 E2	E2
3° benzylic	S_N1 E1	S_N1 E1	E2	E2
1° allylic	S_N1	S_N2	S_N2	S_N2
2° allylic	S_N1 E1	S_N2	S_N2 E2	E2
3° allylic	S_N1 E1	S_N1 E1	E2	E2
Aryl, PhX	NR	NR	NR	E2
Alkenyl, H_2C=CHX	NR	NR	NR	E2

And we have discussed about different reaction mechanisms. So in the last lecture, we concluded with this slide, where we demonstrated or where we listed the possible compounds on which the substitution and elimination reactions can be conducted with different bases and nucleophiles and what would be the most probable products and where we have a competition between SN1 and SN2 sorry SN1 and E1 or SN2 and E2.

We would now try to see these variations using a few examples. Let us try to take a few simple examples.

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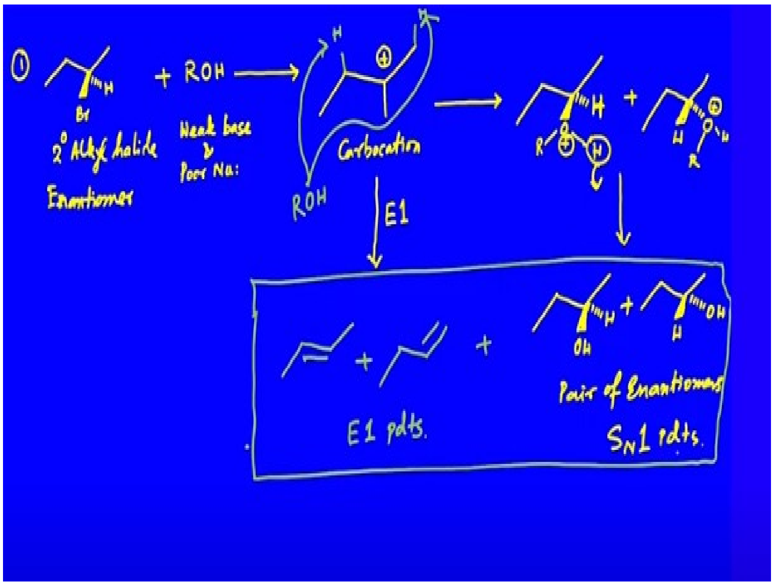

Suppose, we are using this chiral molecule which is a 2 degree alkyl halide. So if we treat this secondary alkyl halide with an alcohol what would be the product? See what we see here, this ROH is a weak base and a poor nucleophile. Therefore, in this case both SN1 and E1 products would form.

So when we have SN1 product what will happen is it will go through the formation of a carbocation at this site and then the substitution of ROH can take place from the top or the bottom of this alcohol sorry top or bottom of this carbocation resulting into these two compounds, which then on removal of this H as H+ would result into these two compounds.

So from a pure enantiomer I have got a pair of enantiomers and remember these two are SN1 products. So what has happened is from a pure chiral compound, we have ended up in a racemic mixture. The other possibility is a competing elimination reactions through the E1 mechanism from this particular carbocation. So what we have are two hydrogen atoms which are here and there.

So by a simple elimination mechanism where the ROH would either attack here or would attack there to give you these two products, which are the corresponding E1 products. So in this particular reaction, you have a possibility of getting all these four compounds, which we have highlighted here.

So although the reaction may look very simple, but, the products will be two E1 products and two SN1 products. If we make a simple change in this reaction what will happen?

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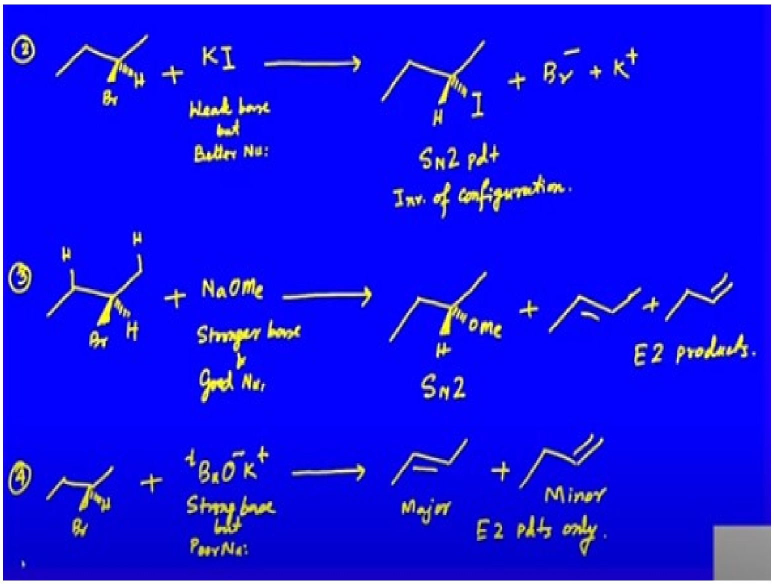

If we just take the same compound, same alkyl halide or bromide and treat this with KI, what would happen? Again this KI which is actually this iodide ion, which is a weak base but a better nuclear nucleophile, better nucleophile compared to ROH. So in this case what will happen is it will go through the SN2 mechanism and it will result into a substituted product with inversion of configuration.

So in this case there will be only one product, the corresponding SN2 product with inversion of configuration. If I take a different base or different nucleophile on the same compound, let us see what can happen? Instead of iodide if we take sodium methoxide. So here the sodium methoxide is a stronger base and a good nucleophile.

So this stronger base with a good nucleophilic capacity, what it can do is it can give you both SN2 and E2 products. So what we see here is that you have a proton there, you have a proton here. So the SN2 product would be this one. You would note that there is inversion of configuration and you should have the E2 products which are these two.

Now if we take a different base for the same substrate, potassium tert-butoxide which is a very strong base but a very poor nucleophile. Why, because this is a bulky group and hence this cannot go for any substitution reaction. So this base is a non-nucleophilic base. So by doing this reaction under a non-nucleophilic base, we would only get the E2 products, the elimination products, with this being major and the other one being minor.

So it clearly indicates that for a given substrate depending on what kind of product you need, you need to identify the correct base or correct nucleophile to get a particular product. If the choice of base or nucleophile is inappropriate, then you will end up getting undesired products. Let us take a few examples from a cyclic systems.

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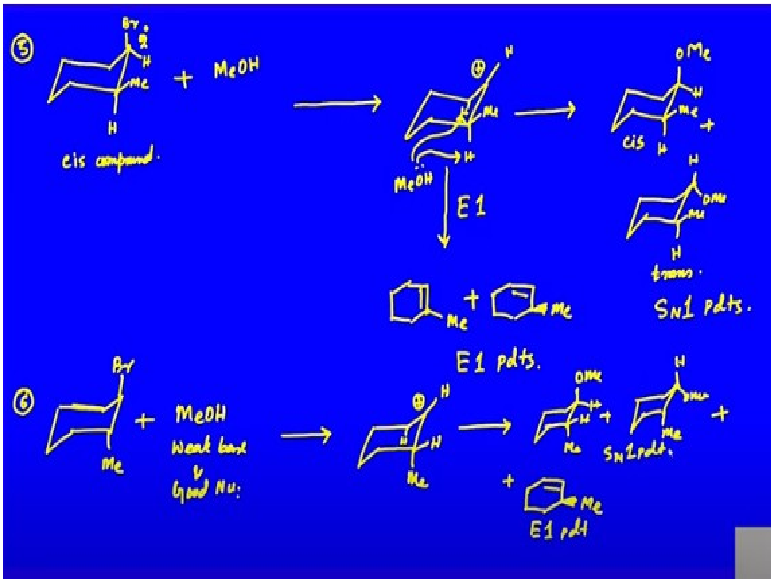

So this is a cis compound, cis 1-2-disubstituted cyclohexane. If we do the reaction with methanol, this alkyl halide is a 2 degree halide. So just like the first reaction which we discussed today we are supposed to go through the formation of carbocation. So once we form a carbocation at that site here with methyl and hydrogen down, it is possible that the methanol molecule can come from top and come from bottom of this carbocation.

And then after deprotonation it is possible to get these two products. That means, here you get a cis compound and there you get a trans compound, both are SN1 products. On the other hand you have beta hydrogen in the anti-position. So you can think of having some elimination reactions with the methanol. Whether proton abstract is abstracted from here or it is abstracted from there you end up getting two compounds which are these ones.

So these are E1 products. So under this reaction medium, you will simultaneously get two different sets of products, one set of products are SN1 products, the substitution products. The other products are the elimination products. Now if we try to see what happens if we have had started with the corresponding trans compound with the same reagent which is a weak base and a good nucleophile.

In this case what we see is that carbocation that is formed is this one. So from here, one can only get two SN1 products as before. In addition, you would get only one elimination product because this proton is not suitable for elimination. So you would only get one of the two elimination products as this. The backside elimination of this can happen only when this bond can break and that is not possible. Therefore, you only get one elimination product.

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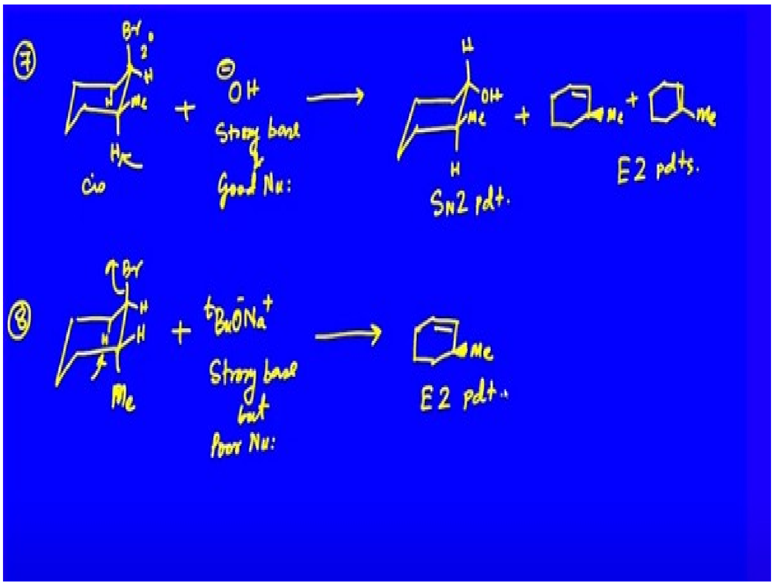

Now let us try to see what happens when we use a strong base, and a strong base which may be a poor nucleophile. We will see both the conditions. We are again taking the cis isomer. So with OH- which is a strong base and a good nucleophile what we would get is the SN2 product because now this is a stronger base than before.

So this substitution at this 2 degree alkyl site will happen through SN2 mechanism and we would get this as the SN2 product. And in addition you would get the elimination product by eliminating this proton or that proton there, which are in the axial position. Therefore, you would end up getting two elimination products which are these two.

So in reaction 8, suppose if we take the trans isomer of this particular compound with bromine and methyl group at diaxial conditions and you apply tertiary butoxide as your base. So it is a very strong base but it is a poor nucleophile because of its large bulky tertiary butyl group. So this will only give you the elimination product and here the elimination is possible only from that particular hydrogen.

So that it will take this proton and bromine will eject from there. So we will end up getting only one product which is the E2 product, right? So now again you could see that depending on the nature of the base and depending on the nature of the substrate, depending on the availability of beta hydrogen in the anti-periplanar orientation, based on the anti-periplanar availability of hydrogen at anti-periplanar position you can get a particular product compared to the other.

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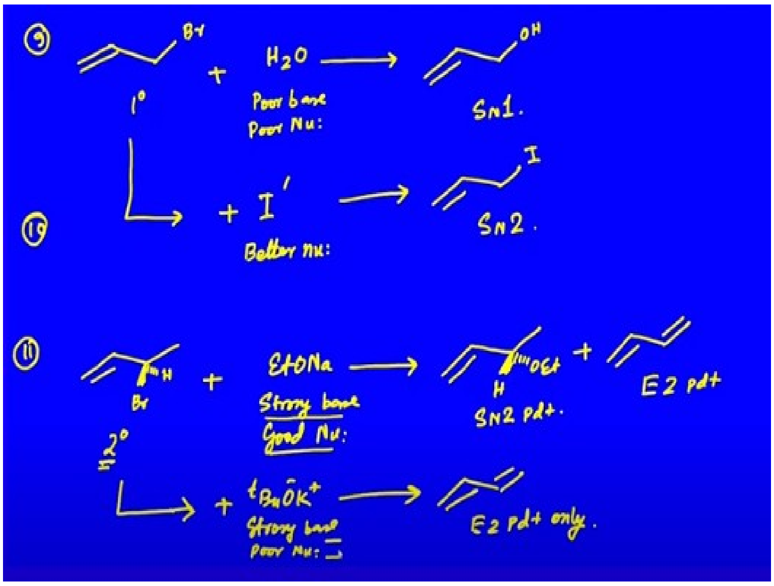

Now let us move to some other type of alkyl halides. So this is a 1 degree alkyl halide or rather called the allyl halide and what happens when we use water as a nucleophile. It is a poor base and a poor nucleophile as well. So in this case only SN1 reaction is possible and you would get this product by SN1 mechanisms.

In reaction 10, if you treat this compound with I- you would get the iodo substituted compound by SN2 mechanism because iodide is a better nucleophile. Now if we try to move to a compound where we have the allylic hydrogen, allylic bromide with a 2 degree carbon. This is a 2 degree allylic halide. So on this if we try to do sodium ethoxide, what we have, it is as strong base and also a good nucleophile.

Therefore, it will simultaneously do SN2 and E2 reactions taking place at that site. So this will be the corresponding SN2 product and this will be the corresponding E2 product. On the other hand if you take the same substrate and treat this with tertiary butoxide, potassium or sodium tertiary butoxide, this is a strong base as you have already learnt, but poor nucleophile because of large bulk.

So you will end up getting the elimination product only. So when we try to solve this type of problems we all need to look at the substrate, what kind of substrate it is, what kind of base or nucleophile it is. And then based on those you need to decide the reaction mechanism through which the product should form and then identify the correct product.

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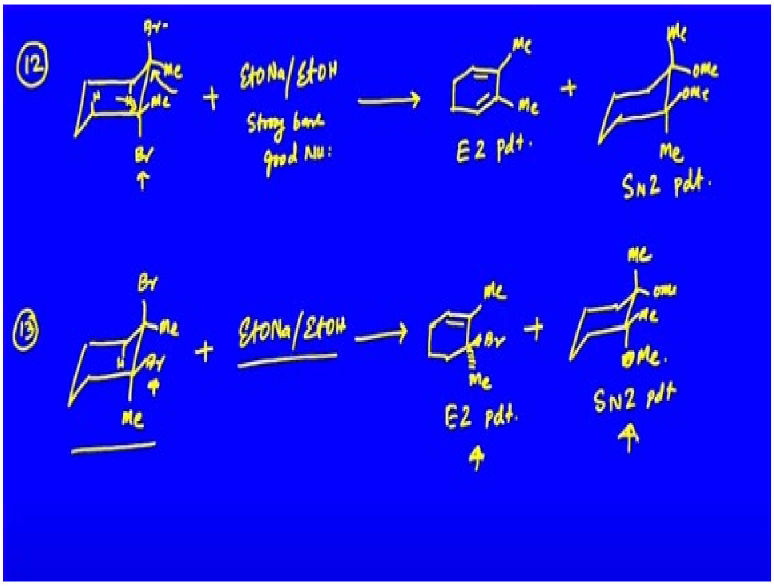

Now let us try to see what happens when you would give multiple halogens on a given compound. If we treat this dihalo dimethyl cyclohexane with sodium ethoxide in ethanol medium, what do you think should the product be? What we see here is that for this bromine we have one proton there which is in anti-periplanar arrangement.

And for that bromine we have a proton which is in the anti-periplanar arrangement and these two are easily removable with the strong base, which is also a good nucleophile. Therefore, simultaneous elimination of those two protons with the Br- ions, it would lead to the formation of this compound through elimination mechanism.

And in addition there would be SN2 reaction where the sodium ethoxide will attack from the back side on either carbon and it will give you the corresponding elimination product as this one, right? So let us see the last example for this lecture. If we had in the previous compound the bromines instead of being trans, the bromines are in cis and methyls are also in the cis orientation.

If we had used the same base and solvent combination, what would happen? So now, what we see is that for this bromine there is no hydrogen in the anti-periplanar orientation. But for this bromine we have the hydrogen which is in anti-periplanar orientation. Therefore, we would get one elimination product as this one where the other will remain as it is.

And the corresponding SN2 product will be a different one compared to the previous SN2 because now the methyls were in the cis orientation, so it will still remain as cis. And OMe groups will be in cis orientation. So this is the E2 product and that is the SN2 product. So if you can understand the nature of the base and the nature of substrate, then it will be easy for you to identify what are the possible products and then you should be able to write down the corresponding reaction mechanisms.

So with this I would like to conclude this lecture saying that please follow some textbook. Try to solve the problems that are given at the end of the textbook to be able to answer the questions that may come in your final exam. So from the next lecture, we will start something different. Thank you.