Symmetry, Stereochemistry And Application
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Lecture No-52
Rearrangement Reactions in Organic Chemistry - Part 04

Welcome back to the course entitled symmetric stereo chemistry and applications. In this week 11 we have been discussing about a number of organic rearrangement reactions. So, in last 3 lectures we have discussed about a few rearrangement reactions and this last lecture of this week we will talk about 2 more rearrangement reactions.

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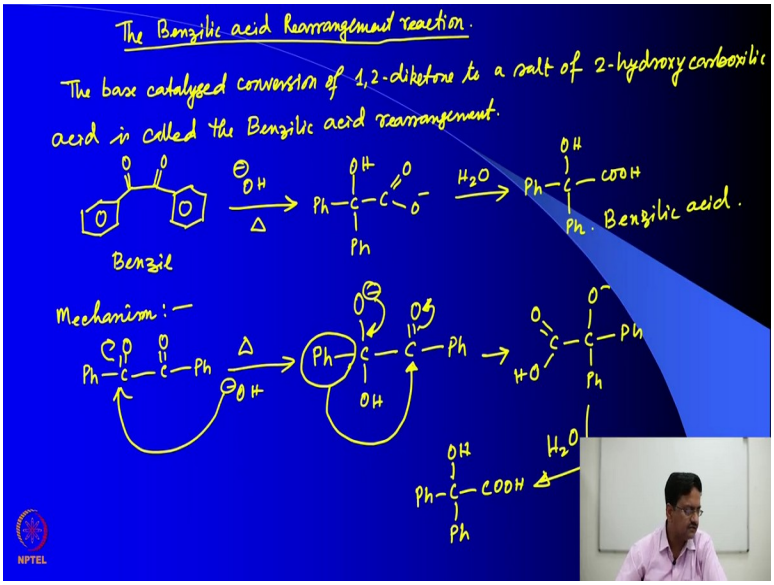

So, in this lecture the first rearrangement reaction that I would like to discuss is called the Benzylic acid rearrangement reaction, the base catalyzed conversion of 1 2 diketone to a salt of 2 hydroxy carboxylic acid is called the benzylic acid rearrangement. The name has come from the original reaction that was found on a compound called benzyl and when you do this reaction on benzyl you get an acid which is called benzylic acid. So, the name of this rearrangement reaction has come from the original compound on which this reaction was first discovered.

So, what I am trying to draw here is benzyl, when this is treated with a strong base at higher temperature what one gets is a carboxylate like this which then in by treating with water forms this alpha hydroxy carboxylic acid which is called benzylic acid. So let us see what is the

mechanism of this reaction? We start with benzyl and treat this with OH minus strong base in heating condition. So, the reaction involves the formation of the anion with the base attacking the carbonyl carbon.

And the other ketone remains as it is, then when this double bond forms back this phenyl group with its electron moves from the carbon 1 to carbon 2 in the step 2 to form the acid where this O minus is formed because of phenyl migration. And in presence of water this will take up the proton and form the desired compound benzylic acid, right. So, this reaction seems to be very simple and this is again a rearrangement reaction where the phenyl group migrates with the pair of electrons present in the bond between the phenyl group and the carbon. So, this reaction is also observed in various other similar compounds that I can show you here.

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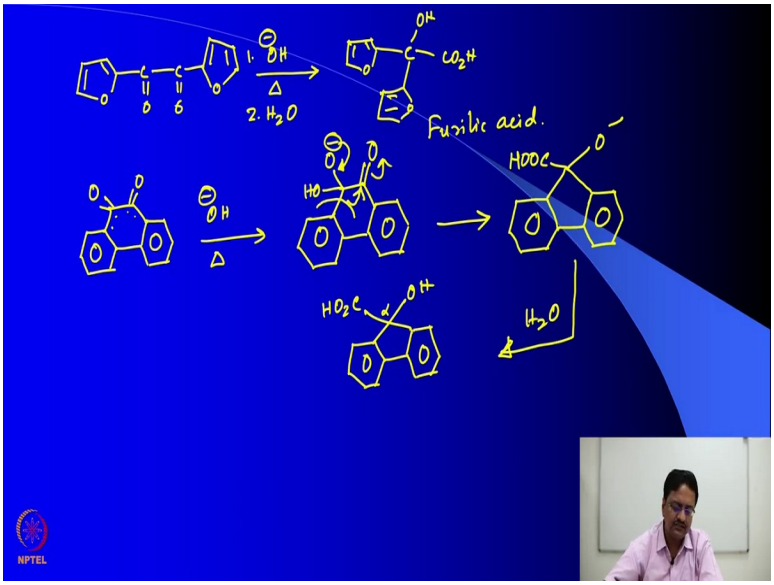

So, a similar compound is known as furayl which is this one. So, on treating furayl with base under heat followed by hydrolysis the product that you get is called the furolic acid, an interesting expansion of this can be seen in this particular reaction where we will see that how this benzalic acid rearrangement can form a product with a lesser number of carbon atoms in the chain.

So, when you treat this compound with base at high temperature it first forms this reaction intermediate and then the rearrangement takes place such that this bond breaks and migrates to

the adjacent carbon atom to give you the ring shortened product which was initially a six membered ring if you remember here this was a six membered ring. Now we have a five membered ring there with a O minus and COOH present here.

So, this compound then on hydrolysis gives you the corresponding product of benzyl to benzylic acid kind of rearrangement reaction. And the ring sizes are now reduced and have the CO2H and OH which is alpha hydroxyl carboxylic acid. So, this is another example of benzyl benzylic acid type of rearrangement in organic synthesis.

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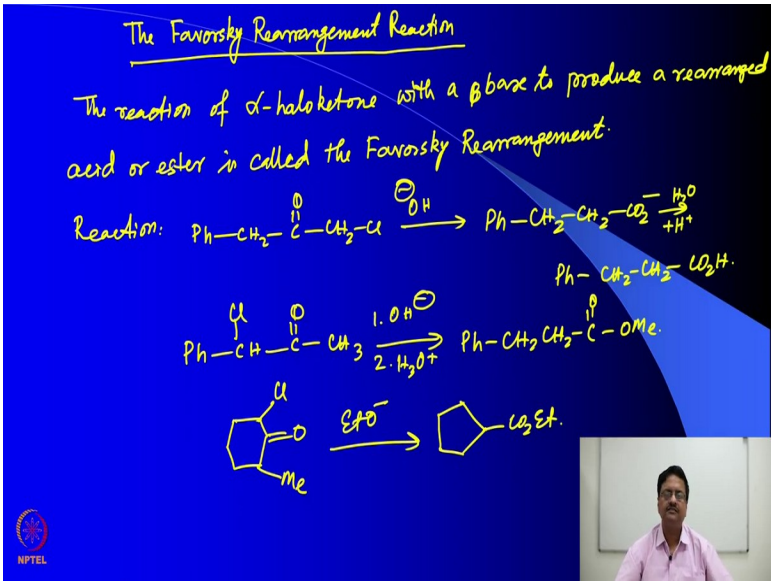

So, the last rearrangement reaction that we would like to discuss is the Favorsky rearrangement reaction. Here the reaction of alpha halo ketone with a base to produce a rearranged acid or ester is called the Favorsky rearrangement. So, the simple reaction is this one, you start with PhCH2COCH2Cl in the presence of a base you get a product like this. So, you have 2 minus on hydrolysis or on adding H plus you get the corresponding acid as your product.

Similarly if you have started with PhCHClCOCH3 you treat first this with OH minus and then do hydrolysis in acidic medium you get PhCH2CH2COOMe as your product or if you start with a cyclic compound like this and use ethoxide as a base then your product will be this one. So, all these are happening through a particular rearrangement reaction following a mechanism which we need to learn now.

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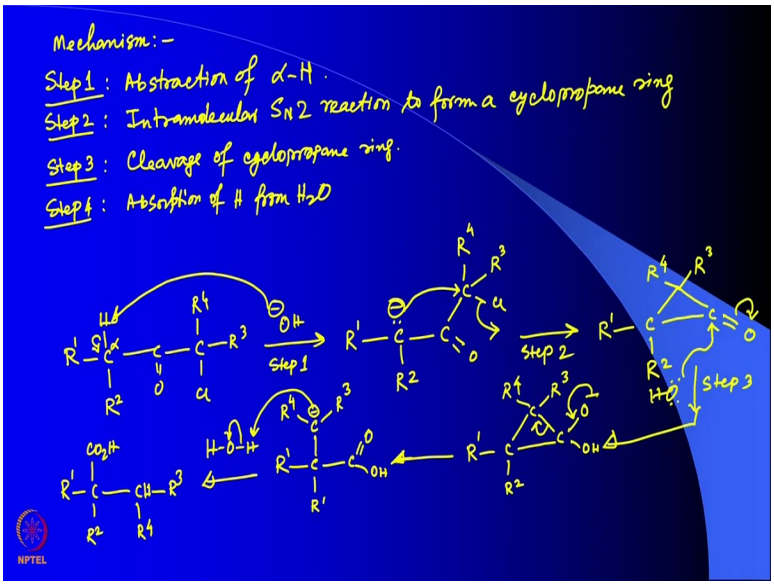

So, the mechanism of Favorsky reaction involves 4 steps step one is abstraction of alpha hydrogen. So, when we have the RCHR let us number it as one 2 then C double bond O CR3R4Cl this proton which is the alpha proton on alpha carbon is removed by the base. So, this is step one we get the corresponding anion I am writing the product in a different way. So, that we can do the next step quite easily.

Step 2 is intramolecular SN2 reaction to form a cyclopropane ring. So, this charge attacks the chlorine and chlorine is removed. So, what we get in step 2 is this cyclopropane derivative. So, step 3 is cleavage of cyclopropane ring. So, in step 3 we have base in the medium. So, it attacks the carbonyl carbon and it forms an intermediate like this then when this bond forms back this, C-C bond further breaks. So, this is continued as a step 3.

So, what has happened is in the process the groups have migrated from one carbon to another carbon. So, when you add in step 4 which is the absorption of H from water. So, the product is formed by the last step right. So, this reaction is very simple and it can be used to convert the alpha halo ketone to a corresponding acid by a simple rearrangement mechanism. So if we apply this mechanism for the cyclic compound that I had drawn in the previous slide.

If you remember in this slide we had drawn a cyclic compound here let us see how that particular compound can be formed using this reaction.

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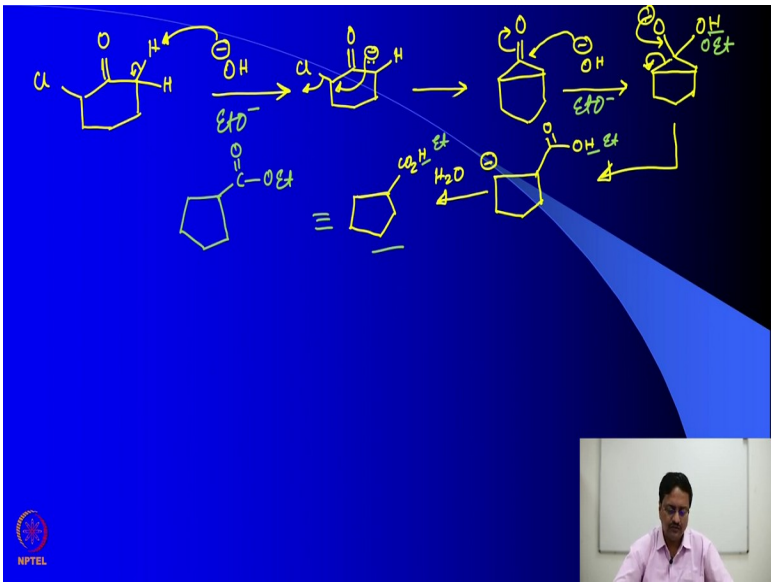

So, what I am trying to do is I am trying to use the same reaction mechanism for the formation of this 5 membered ring from a 6 membered ring compound. So you take OH minus which takes up this proton and that proton releases electron on that carbon and gets removed. Sorry I made a mistake here this both of them should be hydrogen. So, now this intra molecular SN2 reaction removes chloride and it forms a cyclopropane ring like this as you know cyclopropane rings are very much unstable.

So, then again when OH minus attacks this ionic species forms and then the bond forms again and this single bond breaks and you get a five membered ring formed with a negative charge here and double bond O and OH forming there and then you have water. So, this takes up water and gets the hydrogen on that carbon. So you get CO2H now instead of OH minus if we had used EtO minus as base and here also EtO minus as base.

Then this would have been OEt as a result this would have been Et. So, this would be Et that means we would have got a compound if you had used sodium ethoxide as base you would have got an ethyl ester if you have used sodium hydroxide as a base then you would have got the

corresponding acid as a product. So, depending on whether you use sodium hydroxide as base or sodium ethoxide as a base you get either acid or an ester in this particular reaction.

So, with this we conclude the organic chemistry part of this course I hope you have followed the course completely and we will practice these reactions and try to apply these reactions in various substrates as you may find in your textbook. So, overall in this course what we have discussed is the nomenclature of organic compounds we discussed about stereochemical aspects of it organic compounds.

We have learnt about conformation and configurations and various cyclohexane conformers etcetera and then we have understood the reaction mechanisms using stereochemistry we have understood substitution and elimination reactions and then various other organic reactions one by one in several weeks. So, in the next week we will discuss a part which is related to symmetry. But, what we have done in organic molecular symmetry is slightly different from what we will learn in the next week.

That is the last week of this course where we will talk about the crystallographic symmetry and we will see how crystallographic symmetry elements are slightly different from molecular symmetry elements and how those symmetry crystallographic symmetry should be utilized. So, this twelfth week of this course will be useful for your understanding to start learning a new subject called X-ray crystallography for which there is another NPTEL course on chemical crystallography by me.

So, if you get interested in this last week of this course the symmetry in solid state then you can opt for doing a crystallography course the molecule the chemical crystallography course that we have in NPTEL. So, we will see you next week with crystallographic symmetry and its importance and it is difference between with the molecular symmetry, thank you.