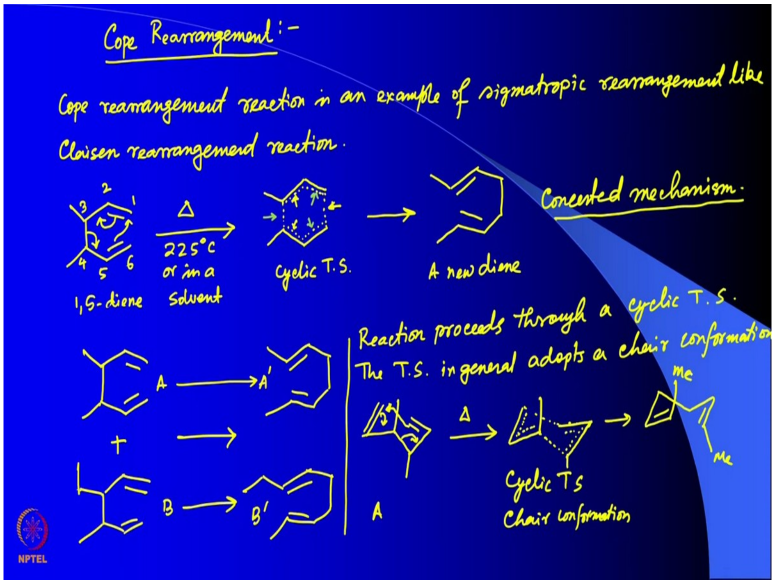
Symmetry, Stereochemistry And Application
Prof. Anghuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture No-51
Rearrangement Reactions in Organic Chemistry - Part 03

Welcome back to the course entitled symmetric stereochemistry and applications. In the 11th week we have started discussing about the various rearrangement reactions and in previous couple of classes couple of lectures we have discussed about a few important rearrangement reactions. So in the last class we were discussing about rearrangement reaction involving an ether.

(Refer Slide Time: 00:46)



Cope Rearrangement:-

Cope rearrangement reaction in an example of sigmatropic rearrangement like Claisen rearrangement reaction.

Concerted mechanism.

Reaction proceeds through a cyclic T.S.
The T.S. in general adopts a chair conformatio

So, we will discuss today now the rearrangement reaction involving a diene system. So, this rearrangement is called Cope rearrangement. In this reaction a diene compound gets converted to another diene compound by simple heating. So, this Cope rearrangement reaction is an example of sigmatropic rearrangement just like our earlier last class we discussed about the Claisen rearrangement reaction.

So, here in this reaction if you have a compound which has two double bonds at a far distance like this in a in a condition you have the double bonds in 1, 2, 3, 4, 5, 6. So, if it is suppose a one five diene this compound when heated alone at 225 degree centigrade or in a solvent this bond gets rearranged and a few bond making and bond breaking process takes place simultaneously.

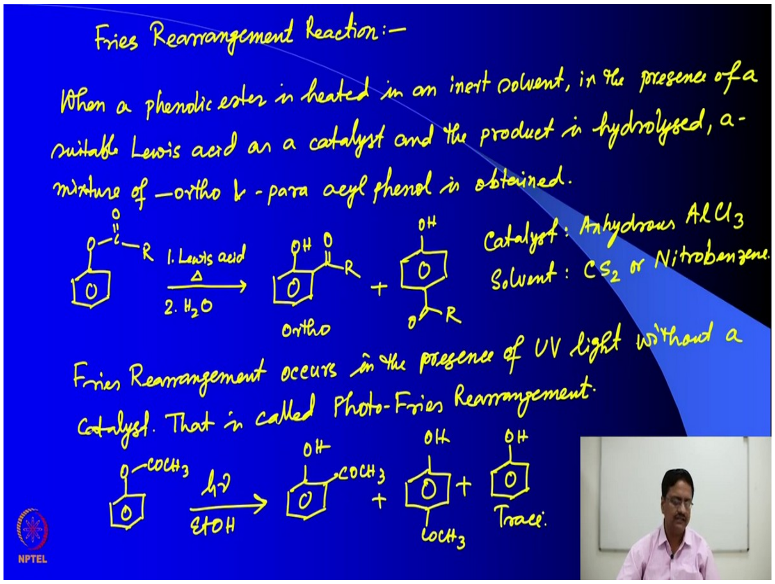
So the transition state that I am drawing here has a few dotted bonds which means either those bonds are forming or those bonds are breaking. So, this is the cyclic transition state where these bonds are forming and these bonds are breakings simultaneously. So, what should be the product? The product should be this one, a new diene after the corresponding rearrangement reaction.

This reaction also happens through concerted mechanism which means that the bond breaking and bond making processes take place together and there is no chance of any cross reacted products. So, if we take a mixture of two compounds namely these two suppose, these two compounds and heat them together from the first compound we will get this as a product from compound A we get product A prime from compound B we get product B prime and there is no question of cross reaction between A and B to give you a new product C.

So, this particular reaction proceeds through a cyclic transition state as we have already seen and the T. S. in general adopts a chair conformation. So, if I draw the diene slightly differently this is the diene molecule A drawn slightly differently. So, when the reaction takes place at elevated temperature this rearrangement takes place. So, as a result what we have is like a chair conformation of a cyclohexane.

So, the bonds which are breaking and the bonds which are in the process of making are written as dotted lines. So this is the cyclic transition state where two methyl groups are in the axial position and it is in the chair conformation. So, in the product forms you get to see this product as this. So, this is the product and the confirmation of the product is written here. So, this is how the Cope reaction can be understood through a concerted step mechanism.

(Refer Slide Time: 08:21)



Fries Rearrangement Reaction:—

When a phenolic ester is heated in an inert solvent, in the presence of a suitable Lewis acid as a catalyst and the product is hydrolysed, a-mixture of -ortho & -para acyl phenol is obtained.

Catalyst: Anhydrous $AlCl_3$
Solvent: CS_2 or Nitrobenzene.

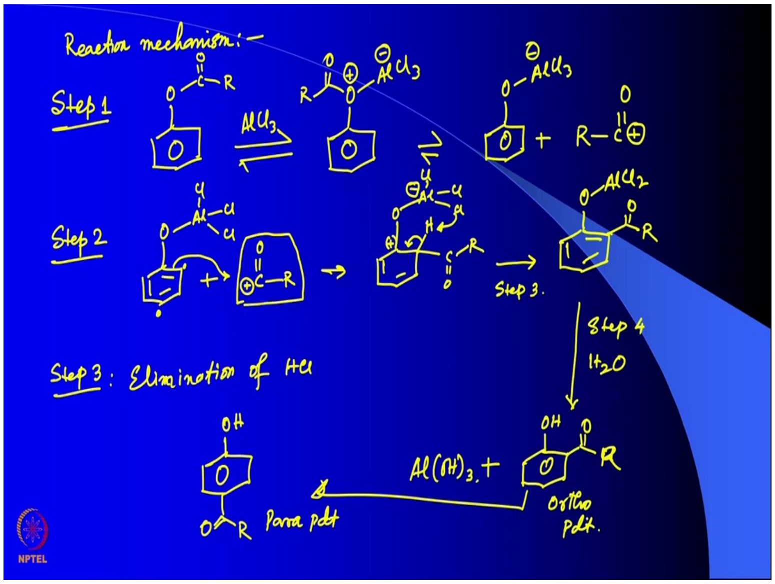
Fries Rearrangement occurs in the presence of UV light without a catalyst. That is called Photo-Fries Rearrangement.

The next reaction that we would like to discuss is the Fries rearrangement. When a phenolic ester is heated in an inert solvent in the presence of a suitable Lewis acid as a catalyst and the product is hydrolyzed a mixture of ortho and para acyl phenol is obtained. So, the reaction is like this you have a phenolic ester. We heat this in the presence of Lewis acid and number two we do hydrolysis what we get is the corresponding rearranged product with the ortho substitution ortho product and the corresponding para product as well.

So, here the catalyst is anhydrous aluminium chloride and the solvent is either carbon disulphide or nitrobenzene because these are high boiling solvents and one can heat these solvents at a higher temperature, fries rearrangement occurs in the presence of UV light without a catalyst that is called photo Fries rearrangement. So in case of photo Fries rearrangement if you have this compound use the UV light in ethanol medium.

And what we get is a mixture of products the ortho product the para product and a side product which is just the phenol. So, we should see what is the mechanism of this reaction using the Lewis acid as catalyst?

(Refer Slide Time: 13:48)

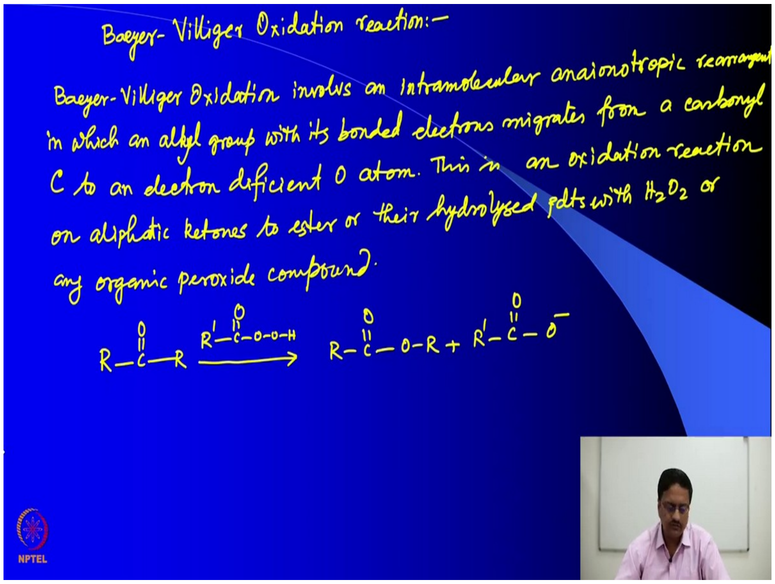


So, in this case the reaction mechanism involves the Lewis acid aluminum chloride. So in case of step one, your starting material first reacts with aluminium chloride to form, an adduct like this and then that adduct dissociates into two components like this. So, in step two, the adduct of the catalyst and the dissociated cation reacts and a further intermediate is formed which then in step three eliminates, elimination of HCl takes place in step three.

So, what happens is one of the chlorides from aluminum chloride takes up the proton and it forms the double bond here of course when this bond broke we should have a plus sign there and that plus gets further neutralized to form this product I should not write CH3, I should write it as R. So that is step three. Now in step four is a step of hydrolysis. So, on adding water to this adduct of aluminum chloride with the phenolic OH the product is released and aluminium chloride is released as aluminium hydroxide right.

So, when you see that this particular cation it can attack it can connect to the ortho position simultaneously it can connect to the para position. So, it is possible to have a second product along with this as the para substituted compound. So, this reaction does not go through a concerted step. So, that only one compound could form there is a possibility of formation of two different compounds in this reaction.

(Refer Slide Time: 18:49)



Baeyer- Villiger Oxidation reaction:-

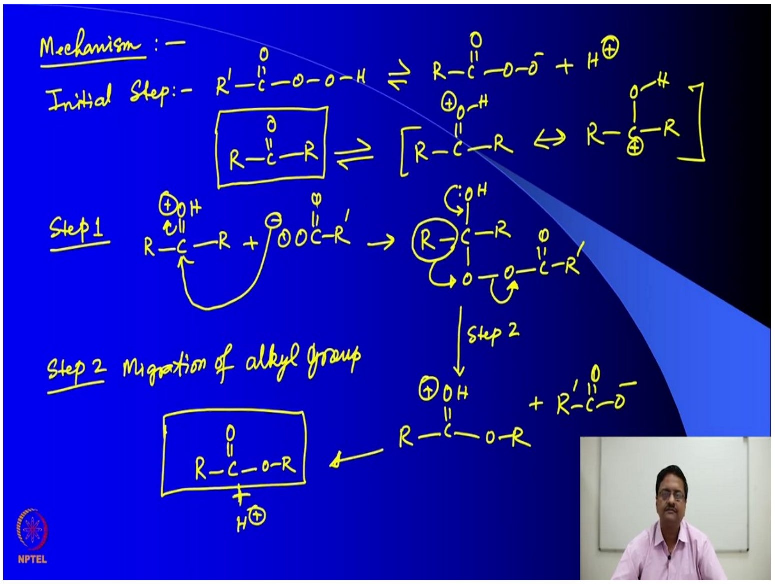
Baeyer-Villiger Oxidation involvs an intramolecular anaionotropic rearrangem
in which an alkyl group with its bonded electrons migrates from a carbonyl
C to an electron deficient O atom. This is an oxidation reaction
on aliphatic ketones to ester or their hydrolysed pdts with H_2O_2 or
any organic peroxide compound.

$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{R'-\overset{O}{\overset{\|}{C}}-O-O-H} R-\overset{O}{\overset{\|}{C}}-O-R + R'-\overset{O}{\overset{\|}{C}}-\bar{O}$$

Now let us try to see one more dif new rearrangement reaction which is called the Baeyer Villiger oxidation reaction which is also a rearrangement reaction. This Baeyer Villiger oxidation involves an intramolecular anionotropic rearrangement in which an alkyl group with its bonded electrons migrates from a carbonyl carbon to an electron deficient oxygen atom.

This is an oxidation reaction on aliphatic ketones to ester or their hydrolyzed products with hydrogen peroxide or any organic peroxide compound. So, the reaction is very simple RCOR is my starting ketone it reacts with a peroxy acid to give the RCOOR is the ester and the peroxy acid gets converted to the simple anion, the acetate anion. So, this reaction takes place through a few steps which I am going to show in the next slide.

(Refer Slide Time: 22:51)



So, the mechanism involves a few steps the initial step where the peroxy acid is dissociated to peroxy anion plus H plus and this H plus is then taken up by the corresponding ketone to form the adduct which is also resonance stabilized. So, then in step one this adduct reacts with the peroxy anion such that the anionic part attacks the electron deficient carbon and the C double bond O breaks to form this reaction intermediate.

So second step is the migration of alkyl group, so, once again if this double bond forms back this group moves from carbon to oxygen and this O-O bond that is the peroxy bond breaks. So, in step two the product is this one with the anion of the peroxy acid. So, I think somewhere we have missed the r prime which we should continue. So, that we know that this ester acid anion is from the peroxy acid.

And immediately in this reaction medium it loses that H plus and what you get is the corresponding ester with the release of H plus ion right. So, we started with a ketone and formed an ester out of that ketone which means this is a reaction where oxidation takes place and you get an oxidized product in this reaction. So, we will continue from here in the next lecture.