

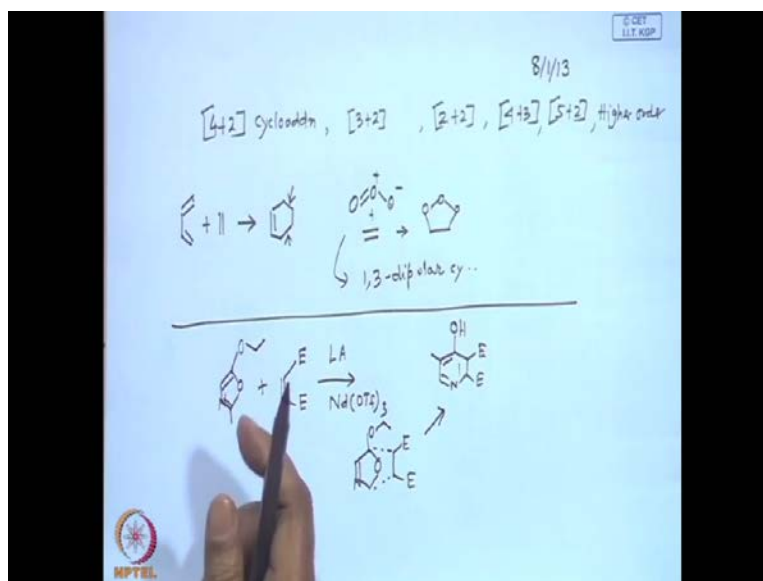
Heterocyclic Chemistry
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Lecture - 26
Cycloaddition: Revisited

Good morning. So, what you do today again what I said before, we will be talking about the cycloaddition reactions. And first few minutes may be are be about 15 minutes, we talk about the definitions, the notations. And then just repeatable revisions, what we did last time, just to clarify the definition of cycloaddition I think all of you know, what is the meaning of cycloaddition. The name employs what is the meaning cycloaddition is a chemical reaction right where 2 components add no it could be more it could be 3 also. At least 2 components add to form an adduct which is adduct are which is known as cycloadduct means all the number of the atoms of the starting materials is preserved in the product. That means there is no change in the molecular formula in going from the starting point to the end product. That means no small molecule or big molecule is being expelled or excluded from the product.

That means the total number of atoms involved in the starting materials would be same as the total number of the atoms on the product. That is number 1 number 2 definitions could be these cycloaddition reactions are those reactions in chemical term where 2 new sigma bonds are being formed at least 2 new sigma bond. There are cases where you can have 3 or 4 sigma bonds are being formed, but normally 2 sigma bonds are being formed. So, that that covers all kinds of this is cycloaddition you have come across so far and the notations are little different in many cases in synthetic chemistry that is a notation and mechanistic chemistry. There is a different notations the popular ones most of you know I think when you talk about the most popular.

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One is 4 plus 2 cycloaddition right 4 plus 2 cycloaddition reaction 4 plus 2 cycloaddition reaction and next popular 1 next popular 1 3 plus 2 cycloaddition reaction. So, you go on like this then there are of course, little less popular is 2 plus 2 then there are 4 plus 3 4 plus 3 then 5 plus 2. And then what else anything else there is there are acquired few more and so what of you do? We remember higher order cycloaddition reactions higher order cycloaddition reactions, but at the same time we have to know what these numbers mean this is important when you do the simple notation.

Actually when you talk about these notations in this class we talk about the synthetic chemistry. In synthetic chemistry these numbers actually represent the number of atoms in the reacting chains not the number of atoms of the starting material number of atoms in the reacting chain. For example, all of us know right this is the typical Diels-Alder reaction Diels-Alder reaction and the product here so erg cyclohexene.

And this is the new sigma bond and this is the new sigma bond so cyclo total number and total number of the atoms on the left hand side equal to the total number of the atoms on the right hand side. Everything is new 2 new sigma bonds are being formed cyclic compound is being formed. And this whole actually do you note the 4 1 2 3 4 5 6 that means this 4 refers refers to the number of the atoms. And, but then if you are talking about mechanism of pericyclic reactions then this 4 actually refers to the number of the pi electrons example of pi electrons. Let me give you 1 more example that would give

clarify you let us say 3 plus 2 cycloaddition reaction I think all of us know what it is ozone. And then react with the ultraviolet first it forms moleozolite and right moleozolite.

So, what is this how do you classify this reaction this reaction is classified as 3 plus 2 cycloaddition reaction 3 plus 2 cycloadditions alternatively we will talk about the alternative ones. But in this case 3 refers to the number of the atoms of the reacting chain 1 2 3. And in this case other 1 is 2 but in mechanistic chemistry or you can say when you talk about the mechanism of pericyclic reactions. This should be considered as 4 plus 2 cycloaddition reaction reason being there are 6 4 in this skeleton, you have component; you have 4 electrons in this component; you have 2 electrons that means you count the number of electrons.

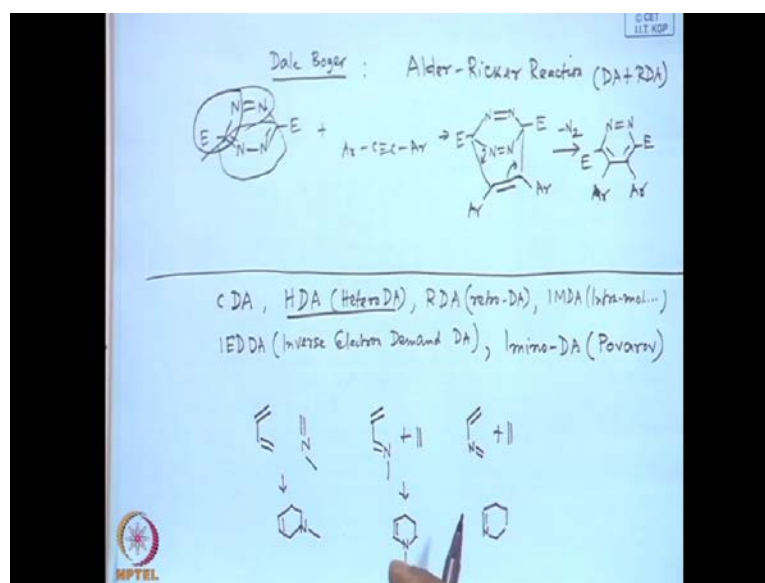
So, these are the and definitions there are some other things like this is a very next to cyclo 4 plus 2 3 plus 2 also very important. It has another name I do not know whether you know or not it has another name, what is the name 1 3 dipolar addition 1 3 dipolar cycloaddition 1 3 dipolar cycloaddition reactions just because the other thing always 2 electron component. So, in most cases this is very versatile method and so in the last class what we talked about we talked about both the reactions 4 plus 2 and 3 plus 2. So, what you do today is you have little bit associate examples of to so you the power of this reactions the nature of the product. And also you have to mentally work out some of the answers of the problems I give you here.

And then when I talk about these reaction there are two important points the first point is that heterocyclic can be used as dinophine or Dyane that is important. These are 2 ways that means you can make use of heterocycles you can build up the heterocycles of by cycloaddition reaction. That means cycloaddition reactions can be used in 2 different manner in 1 cases they can be component of the cycloaddition reaction other case result of cycloaddition reaction could be heterocycles there is you can construct them. And so if you go to my notebook previously you will just see most of the examples there you can work out. And I will just pick up only one of the examples where this heterocycles are an sorry a heterocyclic molecule has been used to construct an heterocyclic molecule. Like this one is a case in the synthesis of vitamin B6 where you will start with a compound called name oxazole good oxazole is now you have a substituted oxazole and then and if you react with this diester maleate. And my class stands for actually an ester group normally eliphered ester methyl ester.

So, then usually Lewis acid and in this case neodymium triplet so you get directly this pyridine nucleus pyridine nucleus. By the by if you have any questions you can stop me encrypt me you can ask questions it is not I does not interfere this recording here. So now, we see now you have to basically you have to try to read this equation, what is this equation you start from heterocycles 5 membered heterocyclesazole then do you sort the reaction. And mentally you have to work on the intermediate intermediate would that means pericyclic reactions. The components remains as it is without any rearrangement only a connections are being made and through the ends when the cycloaddition reaction takes place. Actually you have to concentrate on the ends not in between then you have to reorganize the electrons then rest of the things remains as it is. And then this you have this ethyl group here and then you can go on do this sort of rearrangement eventually. So, this that means this is the case often the heterocycle being used for the construction of the hetero cycle actually it.

So, dual purposes of heterocycle cycloaddition in heterocyclic chemistry so likewise there are quite interestingly. There are many examples I will just for giving you some of the ideas to how the heterocycles are used. So, what I will do? I will pick up few selected examples let us see this one is a very popular example in heterocyclic chemistry. Sometimes it is called Boger chemistry; Boger means Dale Boger a scientist in California a script research institute. He exclusively watch on tetrazine molecules tetrazine molecules when I say tetrazine molecules. You must have something in your mind, what does it mean? it means tetrazine molecule means you have 4 nitrogen's of course, and azin means when I say zole means. Basically a 5 membered ring azin means So, you have a 6 membered ring so, just I will giving you 1 example how it will works.

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And this is a molecule here and this is actually exclusively used by Dale Boger there many other who have used. And once again write e here if you mix up with and let us say triple bond. So, if you do not know in the what will happen then it is very difficult to actually make out very difficult to make out but since we know the tetrazine is a dyne is a dyne. So, what happens actually it first undergoes dual sort of reactions so dual sort of reactions. So, what you will do you first find out the ends identify the ends ends of the dyne part. So, in this case let us say the top part or the bottom part is dyne part. So, that means this end would add to the electro file sorry dyne file in this case it is this right. So, then rest remains as it is and so then reorganizes according to the haliency.

So, you get this sort of compound here and this is basically called Diel Alder adduct are flow fast to cycloaddition reaction right. So, what next actually does not stop here if you are keep on heating this reaction. The mixture eventually one can sorry nitrogen one can see there is a nice drivine force here, what is the drivine force? The drivine loss of nitrogen loss of nitrogen and so what you will find in find again now diazine product I azine product so e here and then a r and a r. So, once again this is although it is an heterocyclic compound. But you are making an heterocyclic molecule by application of the cycloaddition reaction very useful reactions. And now this has a name also this sequence has a name and some of you probably. Now, if you just again go back this sort of reaction is known as Alder Ricker reaction what it means is a basically is a combination of dual sort reaction.

And ditto realtor reaction is a combination of DA plus all of you know which obligated as RDA. So, in fact we are planning to make use of this reactions in our lab. And duty of this reaction is that tetrazine can be made very simple molecule can you guess by looking at the structure very simple molecule one of the tetrazine starting material the starting material. So, that means is a highly symmetric molecule so in organic chemistry most of you know identifying the right starting material is very important. So, that means you have to have a nice correlation with the structure with the available starting material. In fact, towards the end of the class I would summarize probably the available nitrogen sources available nitrogen is not nitric acid potassium acid etc. What we need for other things? What is the nitrogen source for the synthesis of heterocycles? Can you name any very quickly I mean you have sufficient background in heterocyclic chemistry.

Can we name 5 different nitrogen source sources who is supply nitrogen for the synthesis of heterocycles urea. One of them is urea the other 5 I require only 5 not many hydrogen I will accept ammonia accept 2 more nitro nitros compound I will take but not they have limited use. So, like these you know if you summarize if you summarize you know you will find that heterocyclic chemistry is very easy all of our teachers in science college professor A K Saini probably many of you do not know I still regard him he is still alive. And he was also a deity of our department as a faculty member and he is tutee like this only identify make a synthetic cool of nitrogen compounds from their, you pick up. And try to correlate with those cools with the final product and how synthetically. Because heterocyclic chemistry in many times many oxozoles you find very boring same thing again.

And again when it is done it is so easy and there is no stereo chemistry all the molecules are flat. But they are useful so will any case but as you go on you will just find out the kinds of nitrogen sources you need for constructing heterocycles molecule. And so coming to the answer it is nothing but glycine glycine ester if you glycine ester add nitric acid what happens. Let us say you have ethyl glycinate ethyl glycinate if you go to the back slides of my lectures. You will find the answers there ethyl glycine then treat with sodium you get the ethyl diisacitate ethyl diisacitate ethyl diisacitate ethyl diisacitate under basic conditions undergo dimerizations. So, that means let us say this portion this portion comes from the dicyanate right nitriles which one know nitrogen.

So, you get this diazole acetate and then if you dimerised them you get this compound is quite easy quite easy to make and then aromatize. So, these are the things actually you have talked about then you have solve the applications. But what we do today just little bit of the variations of diels alder reactions variations of diels alder reactions means where you talk about the regular diels alder reactions same paper try to say this is called c diels alder reactions, C D A means carbon diels alder reactions. So, then of course, there is nitrogen diels alder reactions what we call? We call H D A so H D A in this case we call hetero diels alder reactions hetero diels alder reactions. So, there are many of you like say we have already so new R D A.

So that means there are plenty of adjectives right in this case it is retro diels alder reactions any other. These are all names organic chemistry almost regularly use we call IMDA, IMDA; this is very useful reaction. I will give you more examples actually today IMDA actually intra molecule diels alder reactions. So, that means intra molecule intra molecule diels alder reactions. So, likewise there is 1 more so 1 more is there IED DA diels alder reaction what is this inverse all of you know then basically. So, these are all different kinds of reactions and that means if you have a known reactions. You want to extended today we talk about little bit of this example of this H D A. There are actually 3 different versions HDA means one of this could be that means you put hetero atom hetero atom. So, this is one of the case in this case you have plus nitrogen in the diene file there are other possibility. There are so many other possibilities let us say you have another possibility you place the double bond sorry nitrogen in the diene component.

And then of course, you chase the position you chase the position. And then you can see all kinds of course, these all of you can guess what could be the product would be cyclic on. And then with 2 new sigma bonds and electrons organized accordingly. So, like this I think all of you can write the structure so this what would be you see here in all cases all cases one product is one products are heterocycles 1 products are heterocycles. Now, question is I mean implausibly everybody write this not a big problem what you need to know which one is more feasible and which one is more likely to take place in lab that is important. And what are the problems or drawbacks in this sort of reactions, any guess? What could be the problems, that is you have been sufficiently knowledgeable about this chemistry. If you look at this is also it has this particular case this is a basically class belonging to HDA hetero diels alder.

It has a name also known as imino dislodar. I think imino dislodar means basically you guess that fixed base it is not a fixed base diels alderr it is called imino dislodar. And if you are little careful then it has also a name associated with this reaction what is this reaction call povarevac reaction. It is a Russian name of course, so pozarevac reaction. That means povarevac reaction is basically a 4 plus 2 cyclo addition reaction used or implied for construction of heterocycles heterocycles. We will have few examples we will have few examples. But before I go to the next one you have o just sit down and think about. And what are the difficulties actually if I was not knowing till my friend started doing work on these imino diels alder reaction in 1980 at Lensar polytechnic RPI.

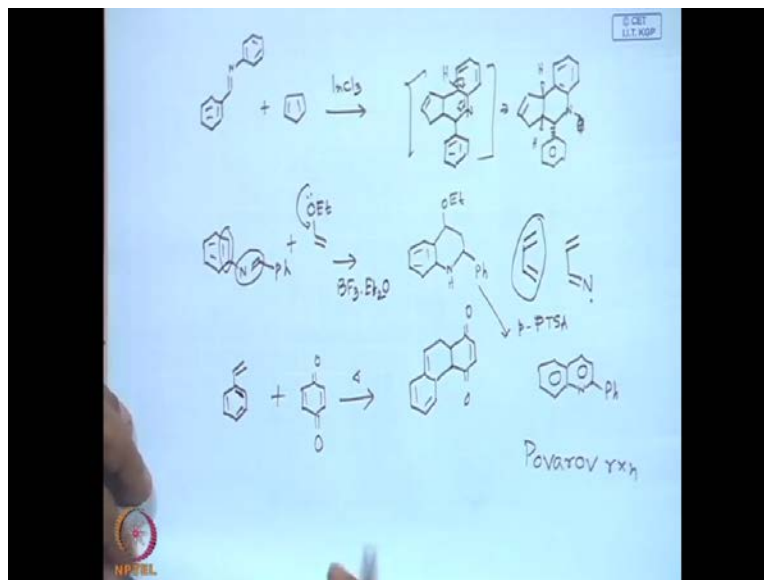
And when he started making azadynes any idea what could be the problems so many of you have been studying the biological chemistry right. In biological chemistry there are again only handful of reactions not many reactions many reactions. But one of the hottest possible reaction is what first reactions other than acid base reaction hydrogen no from where biological organic reactions bi organic reactions. Let us say this is important if you go to the, this actually we give you this concept actually gives rise to many important reactions. If you can identify if you can rank the reactions in terms of the activation energy you do not call activation energy; you do not give the numbers. But we can say this is first this is 2 this is lowest this is firs test you know that kind of thing you can do like one of the choice to look at any organic reaction is acid base.

And next one is the isolation possibility it could be one of the very first reactions actually many of you probably; you do not know fixed base formation if than water first reactions very first reactions. So this concept has given rise to many multi component reactions. So, in most of the multi component reactions you must heard actually one of the very first point is basically. And will see some of the reactions here what does it mean it mean the shift bases shift bases are not very stable. Again I ask often this question in research seminars you know many time many research scholars. You now they will say shift base as this proton here this proton here I said how did you purify he say did not purify some people without knowing you can do it.

You cannot do the chromatography on the shift base because breaks down may be starting material was very pure when pass thorough half of so fast. So, that is what you have to know that is this is basically drawback of azadiye diels alder reactions, azadiye diels alder reactions are imino solda reactions. So, you have to have sumer half idea

about you know which one is more feasible; you can write 3 different horses on the write not very popular. But again without isolation you can engage them in blisola reaction. So, like wise you know we will have little bit examples just very quickly.

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Let say you have aromatic compound now this is again shift base shift base here benzyl delhyte an alien then we took let us say cyclopentadiene. So, what can you expect out of this let us first let us say as if you do not know anything about this reactions in this case because the compounds are aromatic the shift base are falistable. And you can isolate you can just do the reaction just boil the 2 do not do anything just boil the 2 they come ou t from the reaction solid. Then if could this nothing happens but under the presence of luis acid in this case indium chloride indium chloride. So, what is expected out here is a basically lewis acid now you have to I mean independently predict what could be the outcome of this reaction? Let us say since I have been talking about diels alder reaction etc you think diels alder reaction. Suppose let us correspond the thinking to diels alder for some time.

But let us think otherwise what do you expect if the shift base is not sufficiently reactive you can expected dimerisation of the cyclopedadine because room temperature it dies. So, that means you have to have some reference that means this is a reference knowledge the cyclopedadine is sufficiently stable at room temperature but under certain time room temperature it dimerisation so that is. So, you can guess the bidobine would be falistable

so likewise you know and the product here product here basically diels alder product. So, in this case one of the double bonds one of the double bonds of this I think something is wrong here by note right one of the double bonds. That means the benzene ring this aniline part aniline part would be engaged in disola reactions. So, that means 2 and plus 2 and this 2 right.

So that means this one that shift base part and one of this double bond of this undergo reactions. And eventually that means will have a kind of double bond of here right, And but all of us know that this cannot be stable. So, it under goes isomerisations an isomerisations so what you will have? You will have a real polycyclic sorry real polycyclic and or you can say is being formed this. And as usual as usual stereo chemistry when this sort of reactions in all kinds of reactions have this stereo chemistrys have well defined well defined this is addition. And all these things and so likewise I will just give you one more example this is again a shift base if you react this c here ethyl phenyl ether ethyl phenyl ether ethyl phenyl ether.

So, what do you expect? See we have been talking about this heterocyclic chemistry etc 4 plus 2. But you have to once again you have to forget about this. And start from the very scratch if you have 2 components I mean this is talk also on symmetric chemistry class also. I talk about when reactions are when you reactions are being done or is proposed or you are supposed to predict the outcome of reactions where do you starts from. You just classify them classify them in 4 different 5 different category acid base reactions light heating reactions thermal reactions and oxidation reduction not many right. Do you remember hello all organic reactions just name a reactions outside this their category either acid catalyzed base catalyzed light heat oxidation reduction any other reactions known.

You can say isolation is a reaction but it is a thermal reaction this is a thermal reaction or it could be base catalyzed or it could be acid catalyzed. All this pericyclic reactions all pericyclic reactions are thermally allowed or photo chemically allowed so that is it. So, that means when you all not given any option here what do you expect this is a thermal reactions, but in this particular case the example is answer is b f 3 ethylate b f 3 ethylate. So, acid acid catalyze basically acid catalyzed acid catalyzed means normally if you do not have nuclofire etc. So, thermal reactions are possible disoldr and are any thermally allowed cycloadditions are possible in this case of disolder. But you have to know that

double bond of double bond of an aromatic system also can participate in the diels alder reaction, did you understand what I say? Got you did not let me just let me just give you this reference reaction then would be able to just heat it, what do you expect? This is reference reaction or what I said that although disubstituted double bonds their seated within this aromatic system. They can also come out and react with dienophiles to forms these diels alder reactions that is.

So, that means I am talking about this double bond actually this double bond belongs to the aromatic system at it is reactive as a double bond of the diene system. So, product would be so diels alder of reaction it is a product would be diels alder of reaction in such reactions are used stir steroids so this right. And then what then isolation then isolation so this just a basically an example is an example where a double bond of aromatic system is participating the diels alder reactions of diene. That means it forms a diene component that is what is happening here in this previous example what you see this double bond this double bond basically part a diene system. And in this double bond double bond together a double bond. Now, next important thing why did I choose ethyl phenyl ether I could have normal diene file normal diene file is ethyl acrylate acidline dicyclo folic acid ester so like this.

But instead of choosing those alkene nitrate but alphabetical alkene ketones instead of choosing those Michael acceptors or the diene files. I have chosen here ethyl phenyl ether guess I would say the differently little differently not specificity right. Basically that is would you have to with me see I think all of you have gone through all those who are m sc students gone through so many physical chemistry courses right. Including those who have come from Calcutta University I know they must have studied the quantum of chemistry coordinate quantum chemistry. So, just very quickly now you have to because what i am trying to say you do lot of things. But you have to screen out some of the things you have to leave something you have to gain something you have choose rightly selectly yes strictly. For example, let us say how many of you know let us see how many of you do the calculations of this 1 this 2 only 4 electron system, who will be able to calculate the homo of this and lomo of this rise hand.

I know all of you MSc students have gone through 3 or 4 quantum chemistry courses you see volucunally see what I am trying to say how do you calculate this homo energy or lomo energy of the diene. Just sit down sit down did not be stand that means those

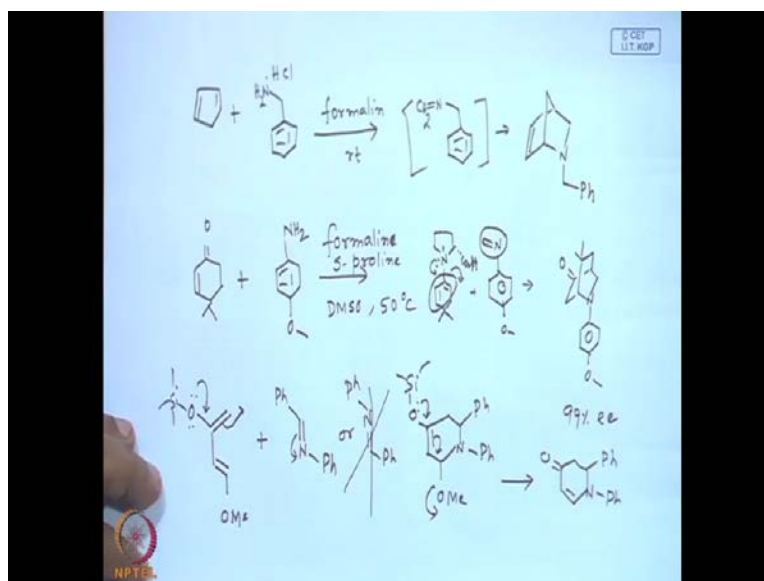
courses are useless it seems like what I am trying to say you have to know why do you study all these things. So, how much time would you take to do the calculation no how much time I said if I give you problems to? Now how much time take to complete the homo lumo calculation of this one. Now, tell me what is the bell I want a number that is what trying to say how much time would you take homo energy And lumo energy of biodyne just very quickly.

I mean you do this practice right for organic chemistry practice is little different like this when you go to this you replace CH₂ by nitrogen. Let us say just give me the answer you put the nitrogen there homo energy would increased or decreased with respect to biodyne by how much it will decrease. That is the important point you have to remember then homo energy is getting decreased. So, there means your lumo energy sorry homo energy of I mean dine file so called dine file should be increased. That means that should be balance basically the energy gap should be as minimum as possible. Then they will undergo reaction if it is decrease then that should be increased and vice versa and so you have to have a compatibility

So, but we do not talk about all these things but back in the mind just remember that it activity energy is reduced. So, that can be compensate by increasing the energy of the 2 pie electron part in this case it is the ether. And most of you probably know this benzyl ether is a electron rich system electron rich system, because of the lone pair conjugations with this pie electron so as you rightly said is an example of inverse electron tripular reaction. So, what is the product will be getting? The product will be getting and so appreciation all these things. So, what you will be getting? You will getting this one and mind it in this case what is c ethnocide on this site?

It could be on this positions also right. But once again this direction already addition to this system is due to this effect of this oxygen lone pair add to this system. So, then of course, if you just to do a little bit of synthetic manipulations normally in this case parabola in p t s a parabola in sulphonic acid you have to go then. So, what you will find it will view this reaction known as so kululine. So, this particularly reaction is known as povarov reaction this particularly reaction is known as povarov reaction till continue with this practically. This az-diels alder reactions or az-diels alder reactions are h d a hetra diels alder reactions. And let me just very quickly go to a very famous reaction in these case.

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The reacting reactants are cyclopentadiene and an imine you can say consular to be an aliphatic amine NH_2 , the corresponding salt, which is normally purified and if you react with formalin formalin. So, what just at room temperature zone at room temperature. So, what do you expect once again this is within your capability means if you just think about it. Seriously, you can tell me the right product but outcome is very interesting very interesting very simple reaction. Because you just mix them up at room temperature in water formalin means thirty percent formaldehyde and water 35 probably in water what do you expect first mum pharmacy. So, that means first you would like to see that means as I said before mum formation also require dehydration right dehydration. But it can be carried out in presence in presence of water but in present of a catalyst.

And So, what do we expect you will expect a this right now. So, obviously in this case this 1 would undergo diels alder reaction. And this would be this would be this nitrogen and this would be you can write phenyl and a double bond that is it that means cyclopentadiene is a now pole electron component and this is double. So, in this case this is basically a shift base that is what we talked about that there are 3 different bi reagents. And the reaction is very old one now gap is same way if you begin with a compound. Let us say I will just give you this is very useful ones that imines and corresponding diels alder products, because, what you end up? You will get nice heterocycles with a nitrogen of one now it bicyclic one. Now double bond can be synthetically manipulated in

different manner. So, you can play it you can do all kind of things so you get a nice cycle so payroll dinole payroll dean kind of molecules. Let me give one more interesting example where will have cyclohexanone and then again an imine again formalin.

So, what you see here the compositions are formaline. And in this case added and temperature is little high so 50 degree then something else one of the other component is s proline. So, I think all of you understand what are the things I have written the formaline is not a reactant but it is a reactant. So, what do you expect once again what I said after acid base reaction what is the first possible reactions is the formation of ammonal. See if you think about the reactions of an imine with an adelaide circuit one is very first step is formation of ammonal addition of nitrogen could be to form the alpha ammonal those are the step. So, they stay in the equilibrium with the shift basis that is one of first possible reactions in organic reactions. Now, that is what is happening here and between the two you have all components here an imine formalin. So, what you will find? You will find one of the intermediates could be this nitrogen and shift base here right.

That means you have to then look for what you have to look for something; you have to look for a dyne cyclohexazine is not a dyne right so not in all for exactly. So what you this praline will form the imine that means the other portion would be in this case this one this one sorry I think yes. So, this 1 would be this in imine inamine then now you know this now you can guess this become dyne. And this is the dynofile component this become the dyne component.

So, the eventually just if you sit down and if you work out this work out this problem at home without must problem. So, eventually what you will get you will get a again a bicyclic system and azikitone. And then you have 2 methyl groups here anything else so this is a bicyclic this dyne part would react with this and mind it in this case. Because of this nitrogen this electron flow would be towards this carbon this is important also. And this carbon would add to the imine carbon here imine carbon so that detriments region chemistry part of that region chemistry part this one.

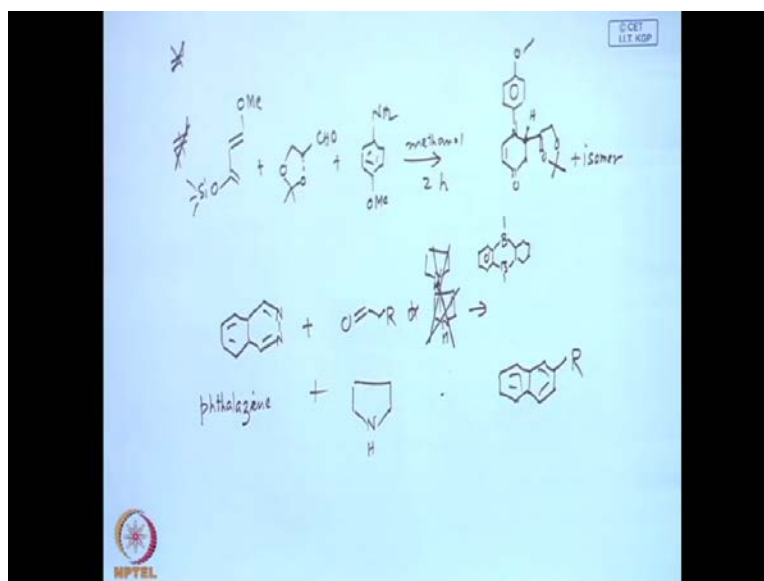
So, anything else a this is important I am writing you are writing you have to see. What are the other thing you would like to convey? What message you like to convey? This a case of oregano catalyzes and e e e is 99 percent so 99 percent. So, I mean there are other

reactions may be let us say I think would talk about one more reactions in this area. This is very interesting very chemistry many of you; this is actually is similar to kind of a dyne file called. sorry dyne call denisupski dyne. Do you remember the structure of denisupski dyne is dyne what you will see you have double bond. What are the features of the denisupski dyne? Denisupski dyne is a second position, second position is occupied by either by nitrogen or oxygen but normally it is oxygen. So, in this case you have the silicon here and this and other one is this. And you have bethox here what is the normal example you have to have a dyne file with the carbons with the carbons that is the standard example that is the standard example. But what is none that if you react with if you react with again shift base standard shift base.

So, it is easy to work with carefully stable and you can isolate and you can work with now one could have written also the different or the same thing right this. But this is not a feasible both are same though, but for the reaction with this one. This orientation is appropriate reason being you have a this oxygen this lone pair of electron directs the electrons to this carbon. And by birth of this nitrogen electro negativity these electrons are polarized towards this nitrogen. So, you get this one as a positive charge and this one as a negative charge then combine. So, eventually what you will get a reaction product where you have the silicon of here and nitrogen phenyl and phenyl.

And then you have this obithixil, what next and stilaetheres, most of you know are very again very sensitive if just 2 acids just you do the colom photography you will do little bit of acidic work and imine in ammonium chloride it will break. So, again this analyze and methanol will come out so, what you will find? You will find double bond here and see nitrogen and then phenyl and phenyl. So, what do you get yap get an heterocycle this is heterocycle heterocycle now with a payroll centre with a payroll centre. And believe me or not it took so many years to develop a new reactions on basis of this reaction. And again it is due to in this case and what they did?

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They used sorry once again they used this denisupski dyne and this aldehyde. And then corresponding imine this I will know I mean I got surprise to see that such a simple reaction published in only 2002 long ago in aglet conestipine is known since 1978. That was the first zex publication, but is an that the example I showed you before apparently it is workable right that was also known. But this reaction was do not known such a simple reaction what you do here just there do not separate them aldehyde. So, they are do not separately shift base with aldehydes and imines. Just they mix up all the 3 components together and that 2 albents like one of the chip organ methanol methanol no heating nothing at least just room temperature just room temperature.

And what you get? You get the corresponding adduct one of them of course, what you basically, what you will get is aphole perydole right 4 perydole derividi you have this one. And the, this of course, this portion and then this will have definite stereo chemistry. Here this is symmetric chemistry on the other isomal also has been formed but what you can get if you have component of this compound. And very easily you can making this simple reactions that means you have to have nice formulations. And you have could generate chemistry 2 different centers and many of you know probably this one this aldehyde easily optimable from easily optimable from where you guess very good. How do you make dimonitole and sit down sit down prediction and what you do the prediction? And then what sodium periodate.

So, that is it and the last reaction interesting reaction though I have just one more minute. So, this is a something like again this one then you take an aldehyde and then pyrrolidine I think all of you can guess pyrrolidine. So, just simply I think catalyze in this case catalyst is borane catalyst the borane catalyst here. So, basically Lewis acid Lewis acid kind of a thing these I think I made a mistake here this should be pyrrolidine. So, what do you expect better? I write separately. So, this now just like A b f 3 in this case that is not A b f 3 dibora compound and heat it. So, what do you expect expectation right that means first; this imine formation.

And actually I should have written these 2 of here. So, I think better write CH 2 that is better so first form the imine though what is the name of this molecule is a famous molecule 6 member nitrogen compound name should be piperidine. It comes from piperidine acid kinds of thing so it is known as piperazine and mind it in this case this imine not the shift base. So, you have to imine reason being when you have one nitrogen electro deficient you have to 2 nitrogens becomes more deficient. That electro deficient can be compensated by other part in this case is imine imine electron reach by virtue of nitrogen lone pair with the double bond. So, the end product here after little bit of this work, what do you will find? This is just naphthalene; this reverse way now, heterocycles are being used for synthesis of carbo cycles.