

Heterocyclic Chemistry
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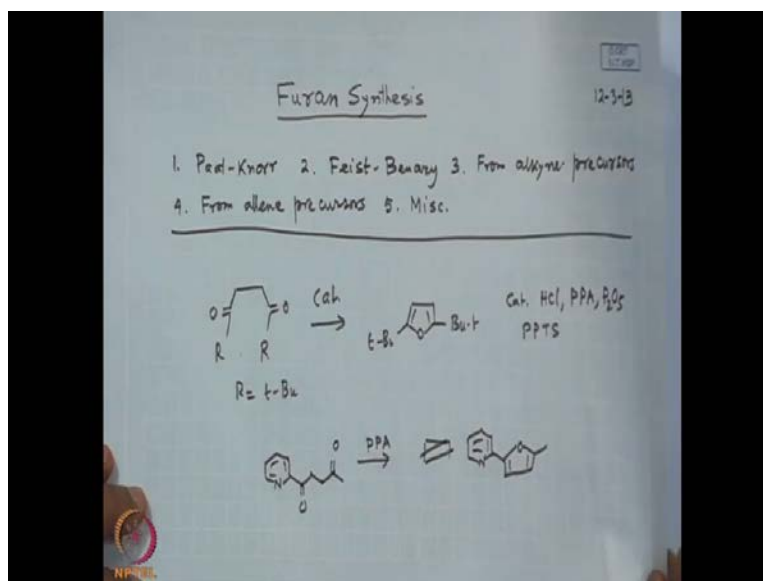
Lecture - 34
Furan Synthesis

Good morning, today topic is furan synthesis, so to be here with I think you have to justify why furan synthesis would be learned. Obviously, there are important of the furan nuclear and where they are found they are found in quietly few in classical products furan steroids bedidins. Then cuinods like furo cumariants many of you know soraline, soraline is a drug use for soraisis this is kind of a skin disease skin disease they are also contest furan. So, likewise there are quite a few pharmaceuticals which also content furan nucleus, many of you probably know one of the means furan semi tide, other one is very widely used commercialized medicine call ranitidine.

How many of you know have you heard of ranitidine it is a drug used as an antiracist, so that means furan nucleus, furan nucleus will have medical usefulness. Then of course synthetic usefulness for making other national products for containing furan in addition, many of you know furan is one of the list aromatic nucleus hetero cyclic nuclei, so hetero cyclic nucleus. So, it can be used for the synthesis of other hetero cycles, so consequently this synthesis of the furan nucleus is very important one of the classical ways to get to the furan nucleus is to convert.

Let us say existing furan nucleus into for example you have for fural, so you can converted to groom for fural. We are not talking about those kinds of reactions of the furan to furan, what today we will be talking about only the how to construct the ring of course convenient with the placement of the different subsequence at the right positions. So, that means our discussion today would be limited to the only construction of the, they are furan nucleus as usual you will go to literature you will gretastary find plenty of furan.

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So, what I will do today actually what have done in fact I have group all this synthesis into five categories one of them of course all of you know the first one is the Paal Knorr. The second one Feist Benary, Feist Benary, Feist Benary synthesis and third one I will not name it, but what I will say from alkyne precursor, alkynes precursor, alkyne precursors.

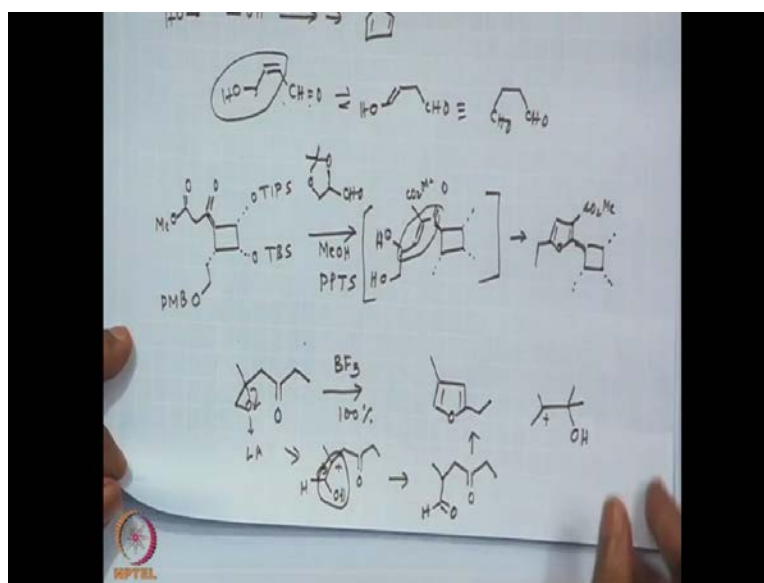
The fourth one likewise say basically methods from allene precursors which are basically equivalent to the isomeration or cycliation and the last category what could be the last category last category could be miscellaneous. Miscellaneous I will have to quite a few depending on the time we will talk about those and deliberately of have omit that is a famous class call, intermolecular heating reaction all of us know double bond can be created by heating reaction.

So, if you have intra molecular person also you can have a cyclic compound, so I will just skip them and very quickly all of you probably know flame what is the first one first one requires it is like 1, 4 dicitone that is, it that is what have to remember. In this case let us say for example if R is trisary butail, so you will get the corresponding furan derivative with trisary butail as starting material, sorry as the end product. Now, also you have to know catalyst, here what was the catalyst, the common, so you have to mind it to the catalyst it cannot have a very strong catalyst.

So, you have to have mild catalyst and you have 2 acidic catalysts you can do H C L, you can use P P A you can use P P phosphorus pentoxide, you can also use P P T S, P P T S is padinium paratonate sulphanets. So, you have these are all most of them are mild and H C L it conjugate made and you will be write molerative reason being first know fural nucleus also susceptible and undergo depravation and ends from acetic media. So, this is a, now I will just give you one more example to a clarify points, here let us say you have you have a di acetone again.

Now, if I treat this should be able to predict the reaction product what would be the reaction product if you look at it have a 1, 4 di carbonate functionality. At the same time you have an aromatic nucleus that is paradine nucleus, so when if you know you know 1, 2, 3, 4, 1, 2, 3, 4, 5, 6, so then a possibility of intra molecule, intra molecular predict of reactions. So, but so can you think of that means that is a competition between intra molecular predict of reactions and the Paal Knorr synthesis, so which one do you think would be the favored one in most cases. In these case of course all of us know paradine is a nucleus with lesser nuclei felicity because of the presence in nitrogen of, so obviously the product at would be found, here is one derived from Paal Knorr synthesis, so likewise let me go to a few variants of this.

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For example, how do how do a convert this diol into furan if you just basically do the oxidation number counting, you find that it requires oxidation. It requires oxidation that

means just again a partial oxidation would give rise to this aldehyde and if you have a kind of and isomeration for example isomeration. So, what you will see it is a nothing but it is again equivalent to corresponding 1, 3 di acetone, sorry 1, 4 di acetone, so that means what you require is aldehyde have to then have 2 acetone groups. Corresponding hydroxide would be perfectly all right if you have double bond, then automatically it goes to this our product is here.

But, so in this case this has been done with potassium dichloroacetate and of course because as the neutral probably properties like you have eventually probably because this conversion usually today is used. So, see it is rarely compared phenomena as because you have one more example this is little complex the molecule has several cyclo butane and it has several silicon producing group. Silicon producing group all has a of us know tips isomer profile T B S is trisary butile then also know that P M B para methoxy benzyle.

Then this has the other substituent is bit acetone ester kind of you predicting thing a substitute, now if you after that you can add it to be aldehyde to the C H E and I did I obtain from user as that I and cordoned form. When it the mechanize P P T S uses of the four as usual to be is the P P T S, now you see this is such a complex molecule, now what is what is the possible product what is the possible furan product. So, you have to very first thing find out the possible mode of reaction what is the possible mode of reaction, in the presence of in the presence of P P T S.

So, I will not write the whole structure that means these are all intact these there are any intact, so furan this portion also is remaining in fact. Now, you can tell me what the possible reaction of legal condition, one of the finest is called in first reactions of aldehyde acetones, this anoline condensation. So, what you will get you will get anoline kind of the condensation would be aldehyde, then you have once you have this is the aldehyde carbon. Then what you have 2 more carbon and then in the presence of methanol and all of us know this acetranate breaks, so you have 2 O H, O H groups here, so this is the intermediate actually it is not isolated.

Then you guess then you must have found the resemblance with previous example what the previous example was, you see previous example wise if you partially oxidize this one acetone. If you own alpha bated unsaturated aldehyde, so what you see here you see

a alpha beta unsaturated aldehyde and then you may be forceful. The fourth position of the alpha, beta, gamma, beta the gamma position is having a hydroxyl group, so it is strongly reasonable this unit here and this unit here. So, this will actually that means 1, 2, 3, 4, 5, so this will form a conjugated system that means product will be I will just not write the full structure you can make out the structure would be this is very recent article recent article.

So, rest of the things is as usual as before and all you could not the producing groups are surviving in this condition this. So, that means that these are all different factor kinds of variants because you will know a lot of things chemistry of carbonyl compound this thing, that thing, we can just figure out how to modify the existing methods. But, basic principle is that it has to have 1, 4 di acetone system or in this corresponding isomers or something which can be readily converted to the 1, 4 di acetones. Now, let me give you one more example which happens to be very interesting as far as the yield is called, suppose you have an acetone of this kind.

Then an epoxide in this case beta and gamma epoxide, gamma epoxy acetone told and this could be a very simple undergraduate problem you take BF₃. Then what you have get is 100 percent conversion into a product, 100 percent conversion into a product anybody can quickly tell me what is the structure of the product of course the topic today is furan synthesis. So, without looking at I can simply this furan, this furan, so what next, so there are two possibilities whenever you come across in the alkyl. If you own for the hiddenites, you think about the alkaline conversion like for if you want the epoxy side and then presence all of us told.

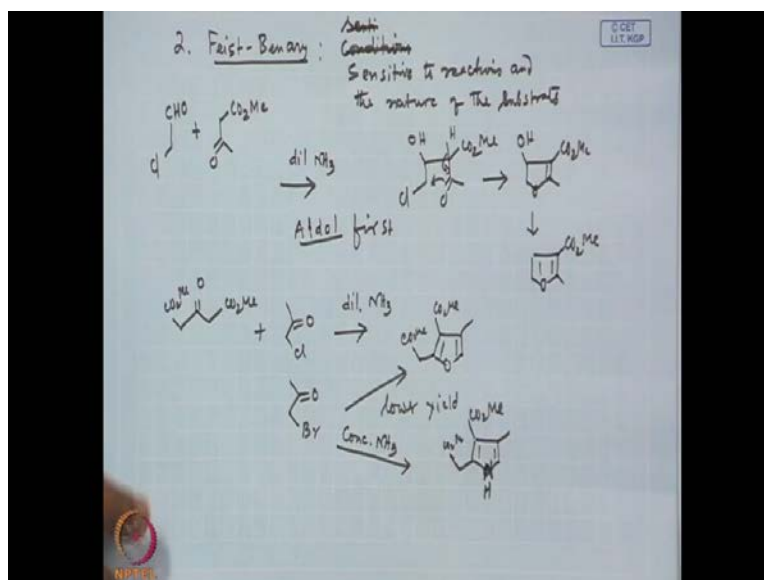
So, valley stabilizing is has you they predict sensitive so it can undergo name of the, so in case of as you frequency say if you have least acid have up a slow and because of these. Since, even induction say this will undergo you want to say that is say and you will have a carbonate and pear and it is the side and what next once for the carbonate what is the next possibility. See, basically in organic chemistry you have to identify these structural features that is important and which one is faster and which one is slower that is enough.

You can have it is and some one other say which one is that is enough they are faster and you say comitrix and then up to goes which one is right given by the thermal analysis, what did the next. If you have a negotiate structure features what is the next possible reaction by them and, so I will remind you, will remind you structural feature I can see it

is a carbonium and containing alkaline hydroxical group. What I am seeing such a, such a, such an intermediate I am talking about only this portion, only this portion where have you seen I am talking about a system like this.

So, I think we, where if I write this probably all of you know very quickly remember see the same thing, basically you have to identify say that is it that means this hydrogen. Now, it will migrate eventually what you will be getting, you will be getting acetone here, now all of you know that what it is the structure this is, this that is it. So, you want it you get is essentially 1, 4 diacetone and then of course you can make out what could be structure this is, now this aldehyde here. So, in one position you will have this ethyl and 3 positions will happen you have the methyl group structure go to the next one.

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Next is the Feist Benary, Feist Benary, so again in a Feist is approved even for a very the type of biotic acid when diol carbon is when developed is that is called cyclo profene 1 to diol carbonate 1 to like to open for the furan synthesis.

But, here is known for the furan synthesis and what you have to know, you have to know the starting materials, so these has to know what we will see product to the bottom is basically if all asitrate something to do is in allition. What is that you have to know addition, what you have to know, you have to another starting nature other starting, nature synthesis is alpha and allowed aldehyde. So, data is I should say and mechanize

should say alpha whole route reasonably and failure and you go on a, you see when reaction is go side conductive and sensitive condition reaction.

Condition that means very sensitive to sensitive to reaction conditions and the nature of the substrates nature of the substrates and we will give you examples here. But, what have to know the reaction mechanisms and what I say is acetone say of and the and normal condition and mean space is yes that is could be a normal simple I mean have harmonia. When say leaslasia and the lesia and diol monia, it slowly diol mania may for, then justify the diol monia means is synthesis for the synthesis for one of base to a cabbage S M. So, otherwise it is basically a sodium hydroxide on base, now next thing that is important, here in these reactions is to see there are two possibilities.

One it can undergo alkaline consideration and it can displace the alpha halogen compounds between two, which one is more feasible. Especially, when you have an aldehyde it is more likely that the all diol condensation would be taking first, so that means these reaction aldol is taking for us aldol first, this is first guidelines you have to do. If you do so, then what you will be getting you will be getting once again this O H, here the estered methyl and this is then of course next thing that one thing as the can that guess that immolate would now displace.

Now, this fluorine and eventually we are evaluated in hydroxyl fluorine to hydroxyl fluorine and this is methaline to, and then you of course of the final area armondation. It would may be in a progressing you thought and admiration of will be a alchodine, first we can thought up to this is we can achieving federation over in lesson those of the offering. So, this is important I mean this important is, that idea is first because of two reasons a chloride not reactive I died sub roommates. So, lesser reactive of the, so that that is why the despite less first and of course and which of the reactive chloro acetones, alpha chloro attitudes, alpha tone acetones also.

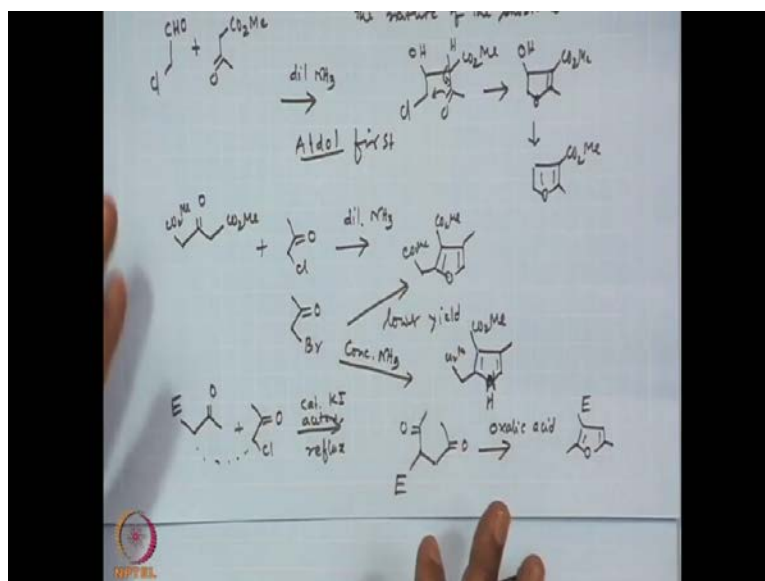
This means we have similar pattern and its chloro digit is not a good telegrams, so it will have very similar actions like we shall be have would be to one reaction. Then it is just a scatted form as it this is one of them I just explained it, as it I told late like me as it told later and is alpha chloro action. If you doing may be this is very important what I said that reaction is to be delicate to be reaction condition, we have to mention here digit dilute ammonia. Dilute ammonia and product for you get as usual it will first then these

and then we have this compound waster, here and then one more extras that, so that is more extras.

So, just like a particular phase the again ideal will first and then choric, now there are so many things are to be learned, we should have for example corresponding gloom. This also would proceed, but that is to be, he is appreciate to give the right etude and it will be could low, and these being of course there is you know that. Now, there is a competition between this all combinations and discuss the above corresponding glooming and you can say C a, C a strangely I think I do not know how anybody can be give me the right.

If you take a really concentrated ammonia is ammonia is with spend and smell ammonia what is the product there also have done there we shall be in last only. Here, what is the product also gives and also say pyrroll x as we said, we did, we did it this spiral, sorry, so that is why I am telling this the basic spites binary is very sensitive reaction.

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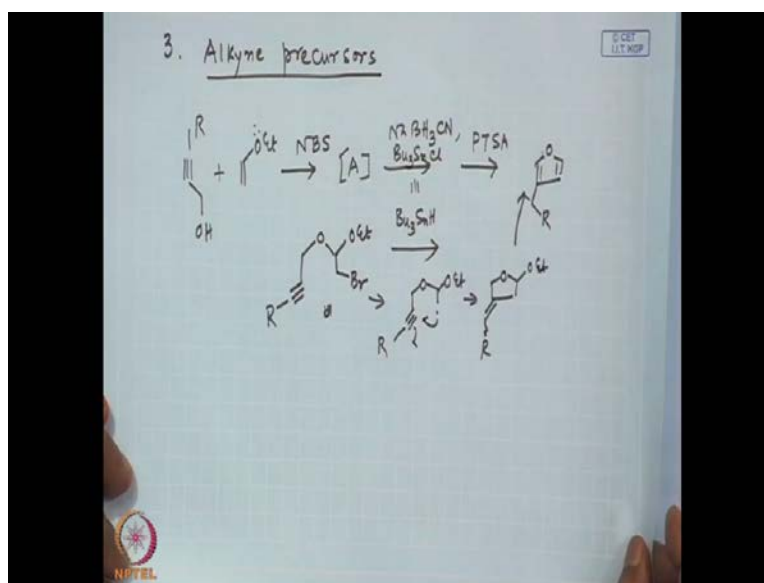


Now, I want to say that in also sensitive to the nature of soft tricks, so if you quit if you just take for example I think for simplicity say that E as an ester. Then once again alpha floro ascot 1 acetone and calculating amount of potassium iodine then acetone and every flux reflects, so what can you guess what is the product is C amicus. Now, you can change about 2 as spite kind of this product, by changing the reaction conditions all of us know if you have calculating amount of some iodine it to fluoride displace in better equation.

So, you get actually acetone, so once you have acetone, so that would displace the hydrogen what will we get, we will be get this one this is. So, you get actually acetone, so once you have acetone, so that would displace the hydrogen what will we get we will be get this one, this is one, this and then this one, then this and is to right. So, that middle carbon would displace the chlorine all a in indirectly actually I want to substitute 1, 2, 3, 4, so you have a one for it tone and if you heat oxalic acid it oxalic acid. So, we will be getting in one for again substitute fluorine, here position, so we have to substitute by an easter, so that would that mean, so this is a quite aptitude a pole on aptitude.

So, since there is easter one there is so difficult, so that can be, you know have fluoride by changing substitute, now also the mode of a different kinds of substitutes. Here, also you have different kinds of substitute we, but changing the reactions mentions you can also get the different kinds of the products.

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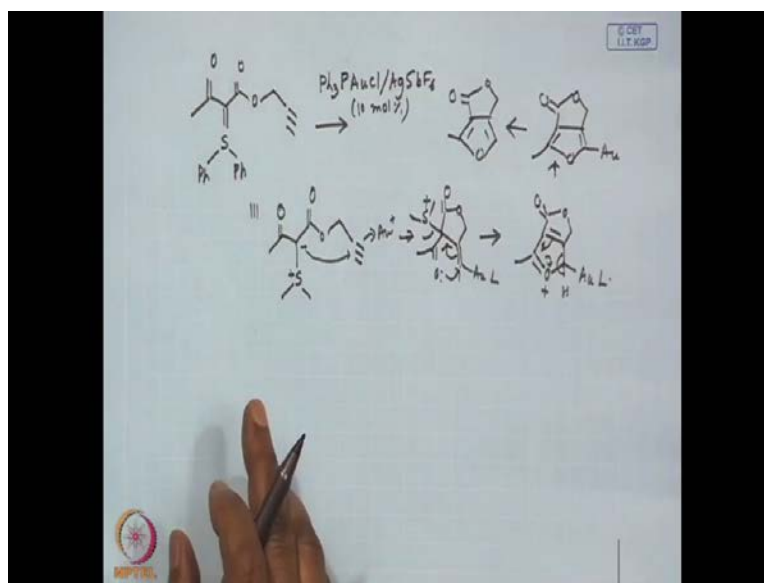
Next thing that is third on a starting from alkyne features alkyne when I am talking about developed, but the Indian scientist as Bangalore from Shri Krishna and say from alkyne precursors what is done we as taking a crocodile alcohol. If it the reaction self it is simple go except 1 chemical then that finials Lithuania is also reducing bilabul, then what is done we has to N B S. So, I occurring T product here and this is then reacted to is a sodium, saino buro hydrate, sodium saino buro hydrate and trial B, trial C, trial B 12 hydrate.

Then by this all of you know the nesel of the regions and then next thing is para trolling self reaction, if it possible 3 steps, 3 steps is not a one like people as to once we previous, once as the one step. You can try and what is the expected here what is expected if we guess, and this we should above 2 predict, the structure of a structural then I think next is to quite easy to first one. What is the chloric, these persons may habitude see and this is equal adherent and ammonia, so then we see all of us because of the quite of that because carbon is more in carefully.

So, we have the gloom, this should be plus and this plus is now captured by I will call, so what next all of us know. So, this sodium hydrate and talks about and that is equaling to 2 is in coherent 2 and B tried T hydrate and all of us know to hydrate reacts is alkhed, especially bronu compound to generate the corresponding to carbon radical. So, once you have carbon radical then you can see that means the coherent to know, so this get collated in to a racial here and is this one once you have a radical goes radical syclijence and excess syclegesion.

So, this is pretty one and what will be know will be radiances then suppose these and one is not, now once you have this there of course all of us know this is having. See, here there something go, so elimination and then substitute isolizaton mutually what will be get in and the a few run. So, see substituted that this substituted is nice to have a study it only a drawback of this method is that this request little be substituted dehydrate. So, that that is only that drawback but the pretty useful could be seeing substituted even because many products are not known plenty of a natural product.

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That is one more which can be obtained from M solve for elite, this again substituted ester in this case, now we other substituted is discipline this one. So, in this previous case it was also the propargyl alcohol, but that was an ester, but in this case which is ester here and the other unique feature is feature is this is solve for elite it is solve for elite.

So, all for guide means all of us know, so this remaining carbonyl will be negative and alpha is positive, and only with a catalytic amount of triphenylphosphine or it or as chloride. So, it or as chloride incurring of a hit of an antimony, and to and this is only thing more precise, so one what you can expect a reaction what is the reaction this is a reaction. So, if you just rewind the structure is, yes this is an extract here this is minus and this is I think tried this I am not finale may be is plus. Now, what is expected the all of us know what is the next step, next is basically may the world what the having tendency to accurate the have you bought that is it.

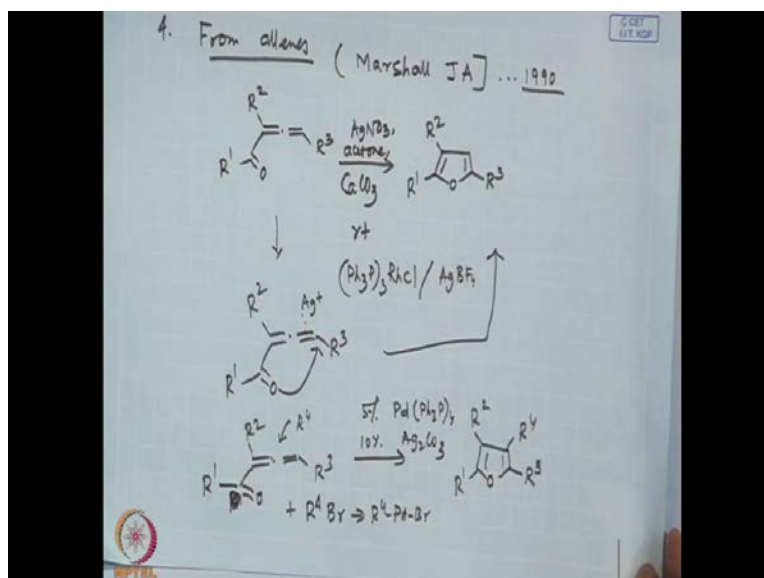
So, let me this is and what is, so this is one a like then will you have this I excess this the society is on and a this is, now this will go to work, this is we have to told. Now, this is double bond, this will bound know of reaction and if we told here then have, here what we have here is there a solve for right this is plus. Now, solve for plus, now what next 1, 2, 3, 4, 5, so we have to see really dummies have this one another go again 5, if and then there is psychology is and that this is, now will be solve for sulfide portion comes out.

Sulfide portion comes out and what you will get a, you will get is double bound one oxygen, here then this is, I normally put it I can, here this is right what next.

Then of course that is I think isomolization and isolization it will be review if we told this is, this portion as I told here and this is know is and you have. So, once you have these are enough ports and the after the workup, so what will be get it will be get a fluronox tried left one fluronic ell, left one and list case have method, good hare alpha position of that. So, as they actually if you locate it is nothing but, it is always these that one to doctorate those portion is there inside and then and this portion. If you a see here, if you hydroxide proposition alcohol, it means equaling to axons actually hydroxide al of acetate the corresponding acetate.

If you just have hydroxide, if you marquis sulfide that gives as told and in the place of or in what you had sulfide. So, throughout rest of the example we will see all the scarified necessary Q lent and, basically alpha corer acetone etc and, so I think, I think full stop here. Next cause is wistfully, I am speaking on the because of the time limit, so what will they do time limit I just give you or two more example from the alkynes portions, sorry allene subs tide.

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This is the next one, fourth one allenes and, so reaction here plus and allene, subtitle allene, substrate of this kind allene. This kind which is basically those of that any kinds and I should mention could that this is the section, due to is 12, 1 and Gems Marshal, any

would one part. If you have one right substrate one part you can get a tress of the muted furan without mass difficulty and the reaction quite generally action and the reaction of the condition surprising. This is very mild, what did you do, so any common chemical though we reaction is this award in round in 1990, so only kind of figure out, you have to basically catalyst, what could be catalyst.

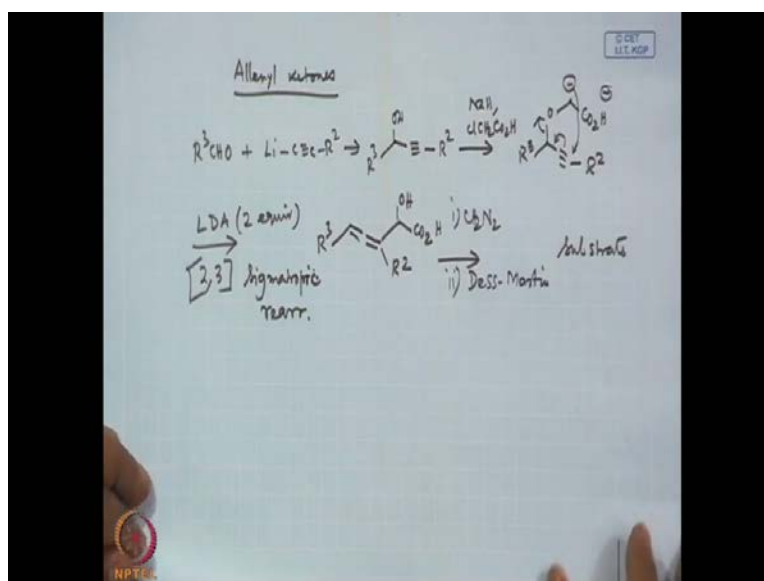
See, basically assign a chemistry one kind quickly come up with the suggestion as be very look for the catalyst go to the too predictable. Basically we need to activate either the carbonic area or the area aquatic body, in this case any allene, the allene essentially for and essential body. So, in this example we used this gold, in this case this is chipmaker gold is silver, so he used to silver nitrate. So, it is solved acetone and one of the chips at bests I have for then no even cheaper, so organic basis cheaper than that, very large calcium carbonic if felt sorry. So, in this case we will good, we will see more example, the sample people have used to also can be used one are even the more expanse sheet, four smaller also can be used.

But, 9 of course, mechanistically one can thing about that between the 2 double bond P allene one each them is close to the carbonic. So, the remote carbon would be activated, now he suite for small the 4 from the always the oxygen is sold, this we have should now are with other all. With this the bond, the option this is something unique especially chemistry I have many more example we will see the clime sold for reason for favorite and when we can go on right thing is on. Here, ask righting this method in the mechanism clear, so you have also and you thing actually and it will clear, now the same reaction, the same reaction if you take this subtitle to this kind three and they are two.

Now, use of 5 percent caladium persists past inceladium and 10 more percent silver bi carbonate silver, carbonate, sorry I think I made a mistake here R sorry, this is the carbonic. Here, carbonic bold and this is R 1 and in addition in addition had the take it one more 4 substrate, that is R 4 alkyls, a 4 alkynes, so what kind guess, so if you commercial of, now lot of heat reaction and we morsel reaction. So, this all miss, no if with the will be in so far will be the 0, so peradium 0 undergo in serene here, so R 1 is it will be the converted to R 4 palladium and all first go we peradium. We know it and as addition to the double one and only the available bond is the clear which one, which one this is also alpha beta answer.

This system you can see if look at the list portion like the R 4 situation and this position R 3 step, so R 4 will all this position all R 4 under goes insulting here addition. Then the particular would be transfer to oxygen I and then same old cycle lessons can you Hens Alley word define, find substituted, take substituted furan with all kinds of the groups in deferent places, in deferent places. So, in other words we in the reaction is flue very reaction and how did that do, it the substrate though to the get to the suture renal aptitude I think I will give the only one example.

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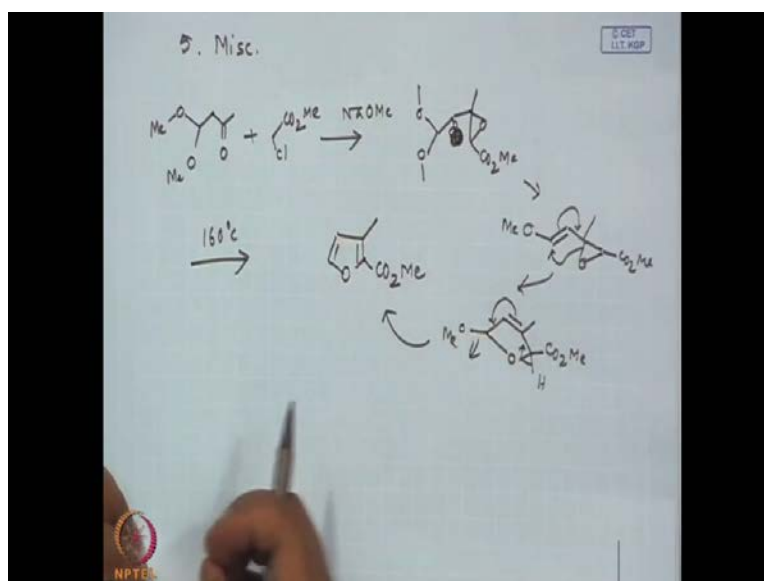
So, all in made allonyms do not kind can the made from simple starting mixture thing R 3 then corresponding lithio acetylates all of as it elites flow, all of us know just simply kind of addition reaction. Now, this reaction is sodium hydrate and flora toxic acid, I think all of us know what is happen sodium hydrate and flora oxide acid, it will undergo Williamson synthesis and Williamson synthesis.

So, have then oxygen here then this is 2 and then this is the turbo acid, now this is, so basically a slandered photo throne, this is not type of addition then this Williamson. The next thing is, this is often not used, but very, but a very versatile reaction and, so what you get here L D A is that, here in this is and what kind of this arrangement is this. So, can you guess what is L D A, of course we have because a ploric acid, here you will required more than two equivalent, more than three if you have, can you think of reaction.

Here, this is the unsound reaction after very useful reaction, can you guess anybody can guess I will write the product is just tell me the reaction what is the reaction, 2 elite, 2 phase of the re arrangement. So, this is actually as 2, 3 stigmatically C H O 3 arrangement, so what happens you forms an annaine here then another annaine here this annaine, here we have. So, if you have annaine here and annaine here this annaine might just include form type have the substitution essence and opens of these is eliminated.

So, you have this then if you put if, sorry if you use your diage methane and then an of course all kinds of oxides is in risk is these offers having used a desk methane oxide. Desk methane oxide is you get the original will be substrate and I will, if you told the one of the, so it is to one kind of make, so that means can solve proxy about all these methods. Then let us look at a few a useful, but not very general methods like say the one I will give you here.

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Then use to in my lab, if you starting material, but real this kind acetone and then for acetone to might attitude say and you can say and you have the little bonding line methane. Then you have the corresponding lime methane keytone, lie methane acetone and try to meet methane chloro acetone is the presence of a sodium is, so methoxide and because you have the, because you have method meth oxide isolation methoxide.

This is where this comes another the category of miss less miscellaneous, I think all of us know what is the next possible then accept if you say what is the possible structure. What

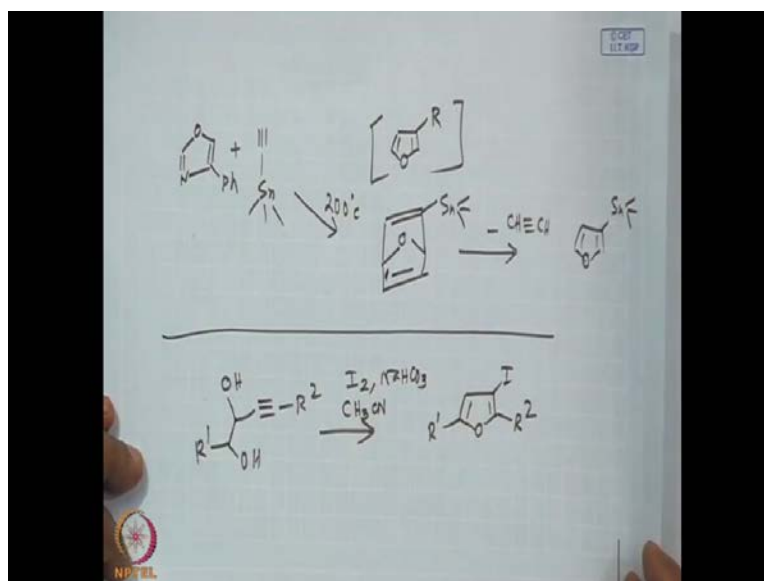
is the name of the well it also hemiashtaals the aped stable, so I can just keep them intact dargin glies of the content. So, vestal content system what you will find you will get this epoxide and this should be the C O 2 M e, yes quite expected not that great.

Now, if you heat it to remember the solver we used what you at 160 degree, you get something very unique the low high the mechanism has been described maybe in your original article I do not know. But, I have a mechanism or it that should be acceptable straightway, I get the furan, so hot what could be the mechanism what could be mechanism tell me, means we have a, we have only heat. So, that means elimination, some sort of elimination of small could be, so what is the possible elimination be loss of methanol, so loss of if you think what is the loss of methanol means.

Let us say if we want methanol goes out, so what will we getting we will be getting this kind of thing, so you know all kind of ethyl, you know ethyl? What next, I think if you remember I have been proposing one this is unique reactions 1, 3 sigma tropics, it which is not thermally allowed, but apparently it is happening you see here if you do this. So, what you will find, you will find this person then you have this estarap, here then oxygen this and you have this methoxy and double bond I mean double bond.

Now, what is you have this, then of course think of another loss of methanol and, so eventually get this port is a very unique reaction where per D g to I g equal C in 2 steps. So, you know just accept stadium meth oxide which is very deadly I will leave it stadium methanol and what can be it nice well defined furan components. So, these furan components and maybe I will, I will give you one more, one more example of is say furan synthesis and like.

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If you have to ask make a compound of this kind, yes thesis of furan is very difficult to make regime being all of us know, you readily, I will starting with this could be read, starting per furan. We get the per furan spend to sugar spend to sense just I tell one of these other one is if you say, if you take scotch or take sugar what do you get cane sugar, cane sugar, even fruit scotch.

Let us say that means access sugar prospective sugar of course, but you have you have to have one more tarmac I had, you had 2 position spent to surer gives per furan. Here, it means that two substitute the access surer should give as you if high hydroxyl methyl hale hydroxyl methyl per furan. So, what I am trying to say that getting into these getting to these high substitute furan elevate is easy two substitute is vary, but if you want to make a 3 substitute is furan is very difficult to make.

If you can come up with see like seek is to hydro mate 2 substitute cannon, his method is having a problem of use of thersabidulty in hike. If can come out with better solution that should be nice, so the most people solve this type of problem they use in indicate way of the king say if you to start with foxhole. Then this team deluges with E g time once again with T and just heat nothing else polythene that substitute is the expensive this one is not expensive we will talk about it in the next class, next class we will talk about.

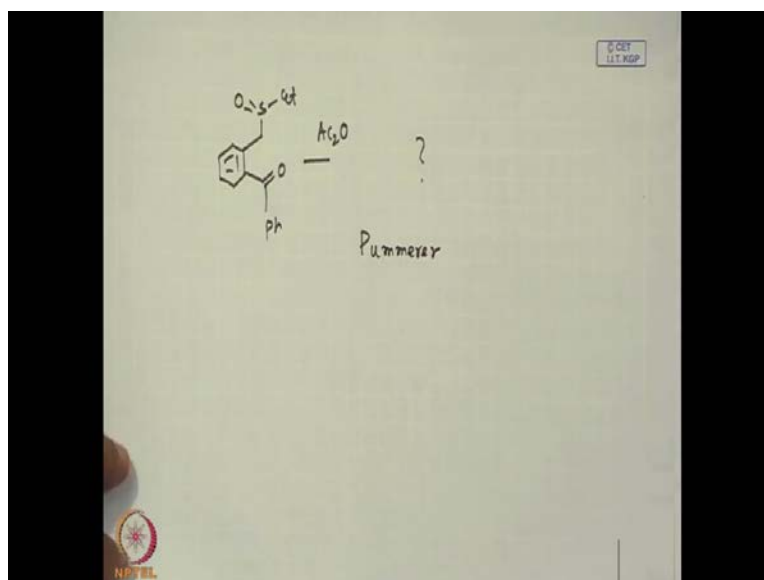
So, what is the product I think one of that it gives you double bond and next, so what would be you will get 3 substitute team debility, 3 substitute team debility. So, this is that

means say we will solve that and it could this technology and this has been used for simplifying many complex mol cans. So, maybe you can steps them there are other ways to also get to the furan compounds let see, let see that may be you can work on these one at home I will give you one more example. So, I may be miscellaneous category, let us say apparently it will looks to you very simple what offend you do not think about this kind of reaction and this one for example.

This one to see actually linear, this oxygenic squares powerful each other is far from this asexually these, but it reacts to it iodine and sodium carbonate by carbonate. Many of us know shake of the region what is the region used for closed right is standard protocol for ideal actualizations, but in this case you do not have these equalizations. But, what you getting in very rapidly you will be getting this corresponding iodine compound iodine compound apparently asexually it is quite linear kind of structure.

But, it is, so reactive this reactivity actually overnights distance eventually it gives furan debility. So, homework I think only who has submitted, homework last time homework, last week homework or go solver, yes pass to one yes, but only who many though, let us say, I will give you one more and see.

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Who can come up with this would give you the one, the one I am giving you, now is fused furan thing system, fused furan thing system, do you know the answer, I will see whether you can you can work with it and I can give you the hints. So, hints is it goes

through intermediate that much I can tell you, so in summary what you have done that means the Paal Knorr furan synthesis, even today is useful Feist Benary also useful.

Only thing that there are several variants of these methods and the next most important and these are model methods utilization of alkenes and allenes and which of this mersal furan synthesis much quite versatile. Then you have other things other miscellaneous methods, so among the miscellaneous what is the methods useful ido etherication could be one of them. Then glistening ester condensation, and what the last one is gill solder and gill solder of the iso oxozole, iso oxozoles.