Organic Photochemistry and Pericyclic Reactions

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Module No. # 01

Lecture No. # 40

Application of Photochemistry

Good afternoon, so this will be our last class, so like as I said in the previous class, I will just introduce you to dyotropic rearrangement, then we will see some new application of Photochemistry, not in detail, some new application, which is right now happening in the field.

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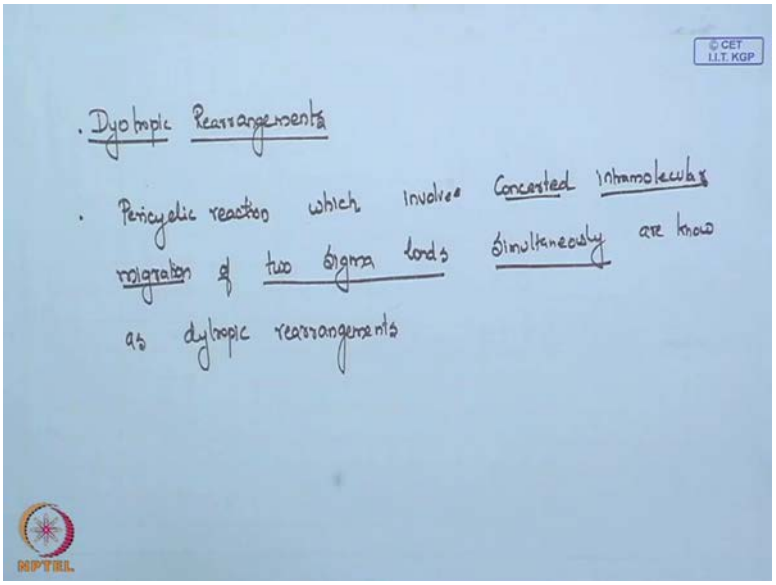

So, first will get into this dyotropic rearrangements, so what what is a dyotropic rearrangement is all about. See, pericyclic reactions, pericyclic reaction which involves pericyclic reactions which involves involve concerted intramolecular concerted intramolecular migration of two sigma bonds, very important, see it should be concerted, it should be intramolecular migration of two sigma bonds simultaneously are known as dyotropic rearrangements. So, the words is that, it should be concerted process, it should

be intramolecular migration, it should be intramolecular migration important is two sigma bonds and they should be happen in simultaneously. So, concerted process intramolecular migration of two sigma bonds happening simultaneously, this type of pericyclic reaction are called as dyotropic rearrangements. Basically dyotropic rearrangement, there are two types again it they can be classified as two types, type one in type one two migrating groups interchange the relative position that is in one case.

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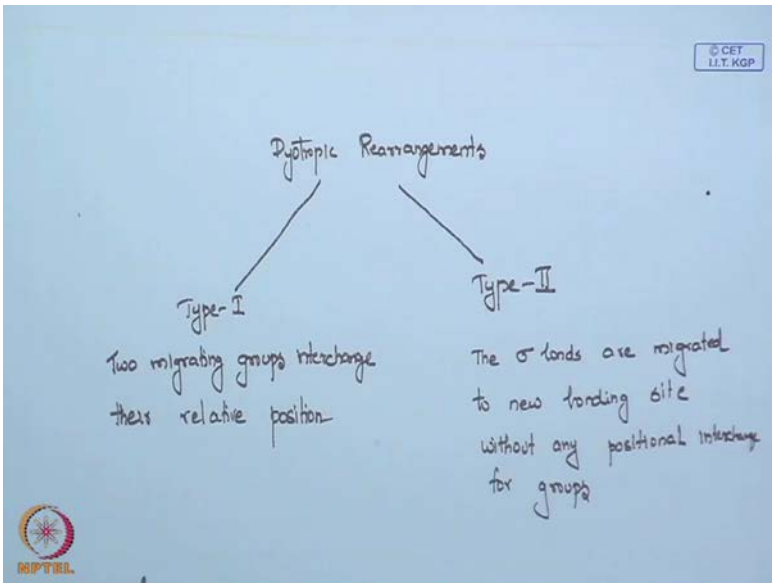

In type one you can see, I will just start of dyotropic rearrangements fine, they can be again classified into, can be called as type I and type II, type I and type II, so type I is in type I, what happens this two migrating groups, two migrating groups interchange their relative position, two migrating groups interchange their relative position they they have fall under type one of a dyotropic rearrangements.

In case of type two, it is your bond not the group, this case it is your group, in this case the sigma bond are migrated to new bonding bonding, new bonding site, but important is that without any positional interchange that is very important, any position interchange for groups see, so first what I said what I define for dyotropic rearrangement, dyotropic rearrangement should be a concerted intermolecular migration of two sigma bonds simultaneously.

Then, you that type of pericyclic reactions, so you call them as dyotropic rearrangements. In dyotropic rearrangements it is basically classified into two types like,

type I and type II. In type II it is interchange between two migrating groups, that is basically interchange of two groups which are involved in the migration. In type II it is nothing but, its sigma bond moving to the new bonding site, but important there should not be any positional interchange of groups, there should be no positional interchange of the groups, so what will do will first see type I and then will see the type II.

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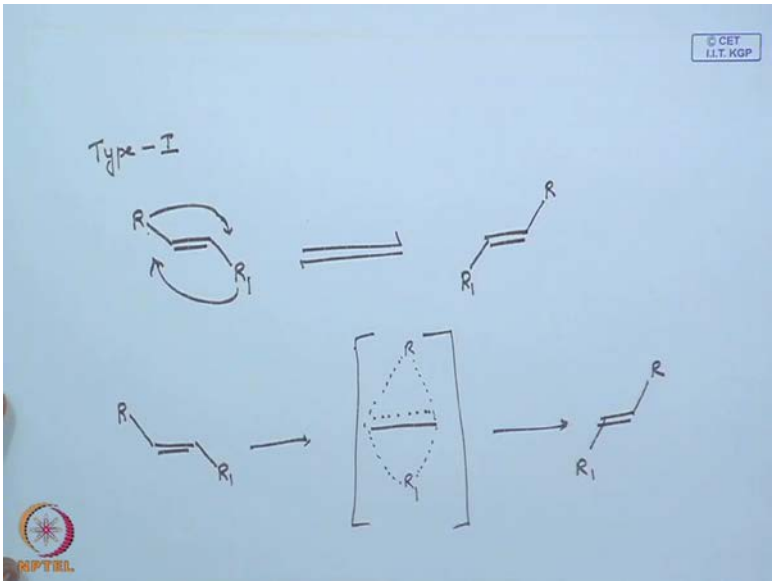

For type I its some will take an simple example of type I, see you have an alkene I call this as a R and R 1, I do a reaction on this, so what happen this is my two migrating groups, this are my migrating groups, this two migrate what type I definition is, the two migrating group should interchange each other clear, this two migrating groups and interchange each other. So, basically I get a product like R 1 and R, so you get a interchange of two groups to give you this product, so basically how to understand this, how this happens for example, if I take the same molecule R to R 1.

So, just thinking about transition state, how it can happen, I can have a transition state like this, put my R here then I have like this I can think of transition state clear, and this then I can give me change in my R to R 1, so this is your type I mechanic, type I type I dyotropic rearrangement, so type of concerted and you can see two groups they interchange their regulative position, they just interchange their regulative position clear.

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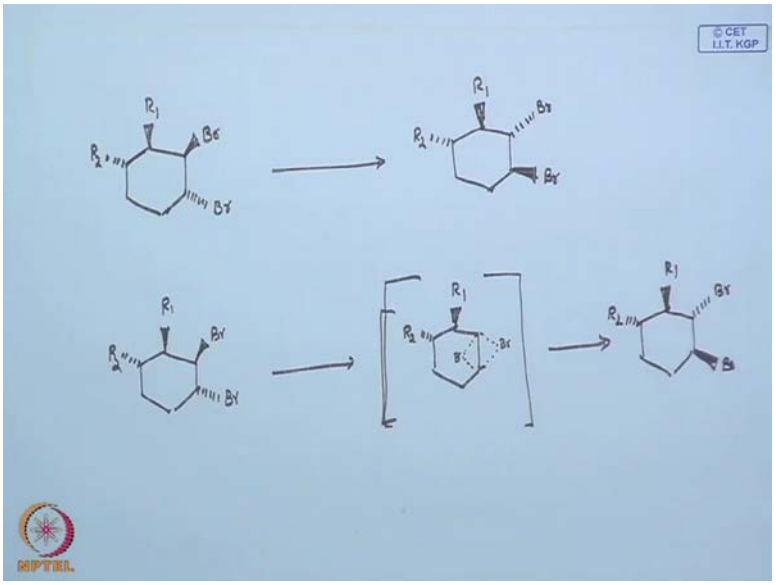

So, you see an example, very nice example, we can take a molecule and I have R 1 here, R 2 fine you have this one. I have my see this stereochemistry; I have bromine here the same bromine it has again. Now, if you take this and do the reaction, you get this product very interesting same product this is my R 1, this is going to same my, now if you see my bromine there completely interchange.

See, to fix that whether this two bromine I have keep in, I have kept this R 1 and R 2 and you see the stereochemistry of this bromine as been completely interchange, how this can saved as we write, you can write here also R 1 here R 2 then bromine, you get a transition type of state; where I can write like this two, but like this type of way in B r, B r, now they can easily interchange giving my product R 1, R 2 and we have B r fine, B r see, this you call as a type I dyotropic rearrangement any doubt with this, so this is called as type I.

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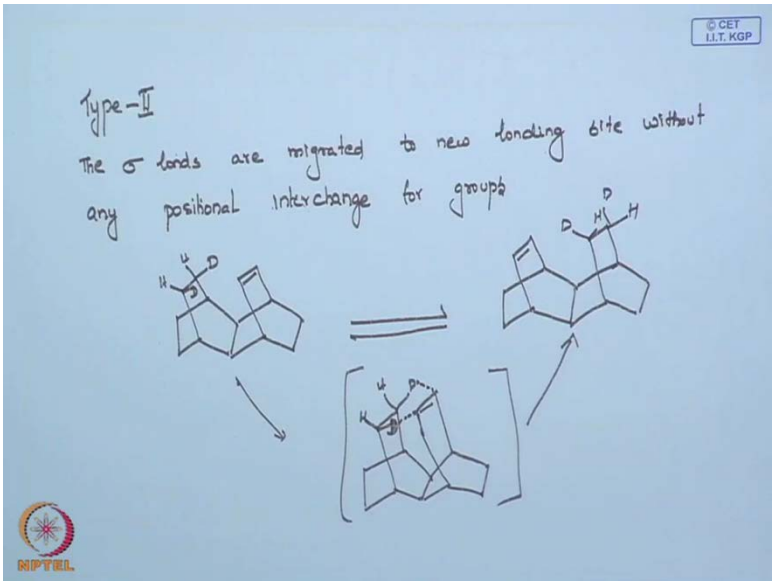

Now, will see the type II, how it works in type II, what type II defines you, what it defines? It will says that sigma bond, the sigma bond migrated to new bonding site right, new bonding site, but without any positional interchange, without any positional interchange this why I am writing this definition, because it will be helpful when you see the example, interchange for groups.

Now, will see the example I see, whether that fix with your definition, I take then this molecule (No audio from 12:26 to 12:36), I have double bond here fine, in this case I keep my hydrogen, hydrogen, but one way I keep my deuterium and I keep my deuterium here, so hydrogen I made it deuterium. Now, if you see this reaction you get product, see the product product will be not the interchange group, but the product will be more like a interchange of the sigma bond with my deuterium hydrogen there is no positional interchange in my this one, see this is the type II.

How it happens? Just just understand for the transition state can be (No audio from 13:43 to 14.08), we have now, so what happens we have a hydrogen here, right hydrogen here you have deuterium here, this double bond you have here; so this deuterium just moves across this fine, this can be a transition state, this is your deuterium it, just moves across here if they bend just to deuterium moves this direction to give you the product clear. So, this your type II of your dyotropic rearrangement, so this are the two type of your dyotropic rearrangement. So just I want to just briefly out what is dyotropic

rearrangement, and dyotropic rearrangement is a class of your pericyclic reactions, in which two sigma bonds undergoes rearrangements, intramolecularly like concerted and if the movement of your two sigma bonds should be simultaneously.

And then there are two types of dyotropic you can think about one is type I, another is type II, in type I there is a migrating group interchanges, in type II it is the sigma bond moving to the new bonding site, but without any positional interchange of the group clear. So, this is your dyotropic, so if you so that a more about your end of your pericyclic reaction.

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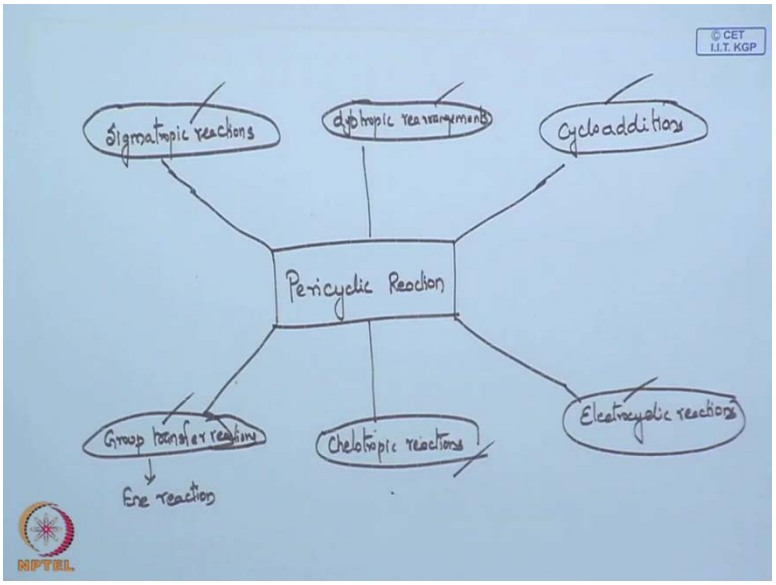

So, if you see what we have studied in pericyclic reactions, so what we have studied in pericyclic reaction, so initially we first talked about your important reaction that is your sigmatropic reaction right, we have studied about sigmatropic reactions. We studied this class, sigmatropic reaction the sigmatropic reactions we studied about different type of sigmatropic reactions like, you have studied hydrogen like, group moving then bonds, we have studied like in group moving, you are study hydrogen atom methyl's and like that and then we have study about this sigma bond movement there we have studied your cope, oxy-cope, claisen and we have studied different type of claisen rearrangements, and we have use and yes, and we have studied and we have we have start understood your stereochemistry also in detail about sigmatropic reaction.

After finishing sigma tropic reactions then we studied another important type of pericyclic reaction; that is your cycloaddition, so you have study cycloaddition reactions. We have, we are did lot of cycloaddition reactions we have in that we have particular, we have concentrating more on this are the reactions we are studied 2 plus 2 cycloaddition, 4 plus 2 cycloaddition we went p 1 4 plus 4 and we have dealt about many about your stereochemistry and all about. We we finished sigmatropic, then we study cycloaddition reaction, then we went for ene reaction, ene reactions is nothing but, it is a group transfer reaction right, then you study group transfer reaction, we study group transfer reaction nothing but, it is a ene reaction, in which we we understood the ene reaction in detail, how ene reaction works and all this things.

After studying this group transfer reaction, then we move to electro cyclic reaction, we study electro cyclic reaction, so this are the four important electro cyclic reaction we yeah, we in electro cyclic reactions, we studied the cycloaddition, cycloopening, ring opening and ring closure, con this and your stereochemistry, how they open the mode and all this things.

So, this are the four important class of reactions it as sigmatropic, cycloaddition, electro cyclic reaction, group transfer reaction, then like previous class you also discuss one more important class, how that is your chelotropic reaction reactions, so we study then chelotropic reaction in detail. After studying chelotropic reaction, today we have just given out line little bit about your dyotropic, today what we study we studying dyotropic rearrangements, this are this what we have so far under study on the on the (()) pericyclic reaction, we are study sigma tropic cycloaddition, group transfer reaction, electro cyclic reaction, chelotropic reaction and dyotropic reaction.

So, we have so the most of this are important major class of your pericyclic reactions which you have studied in detail, so that sense about about our pericyclic reactions. Now, what I am going to do, since so we have discussed about our photochemistry in the first, like in first 20 or 24, 23 lectures we have discuss about the photochemistry, where we have studied all the natures about your carbonyl chemistry and all this things; and then after later of we have discussed on our pericyclic reactions, we have finish pericyclic reaction. Now, as a last thing since the last class on the last thing what I want to do is that, I want to just introduce you to some new field and in the application of photochemistry, because that is that is how growing up in the new areas.

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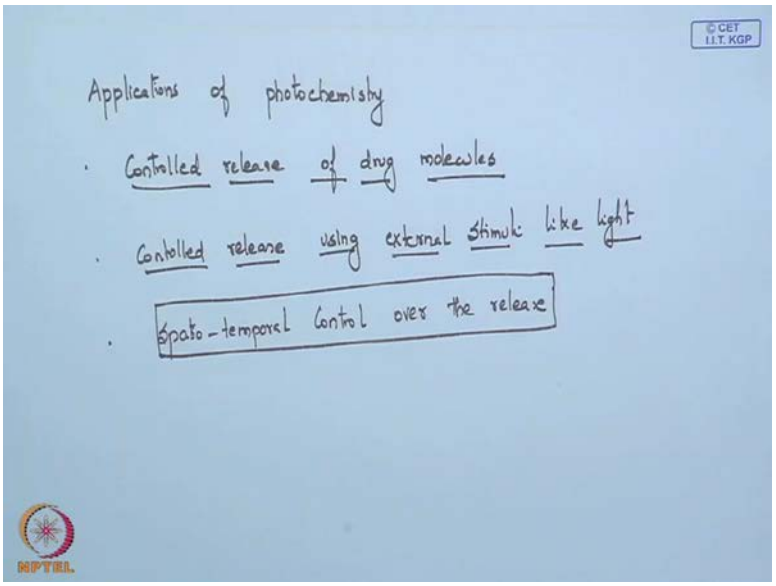

One of the important, so will concentrate the remaining the next few minutes for next half an hour we will try to concentrate on the applications of photochemistry, see the one of the hot field now days is controlled release or you can call as controlled delivery of drug molecules or even you can call them active molecules. So, that controlled release or controlled delivery of drug molecules, this is this is become a really an important field, and there are many ways you can release drugs in control fashion, the one of the best the way people do is that based on your p h.

So, you know you are system as different, once once you have system you you take a drug molecule you quoted up with some polymers, and that polymer once it goes to as p h, if it goes to as its p h then that polymol breaks out and the drugs gets released. So, that that people are doing that p h control delivery of your active molecules, then even by heat you can break the molecules, then you can deliver them. See there are many many methods like that, now like last few years using light as an external stimuli as become very interesting in the control delivery of active molecules; so release, control release using external stimuli, like light as become really interesting now a days, so why it is, so interesting what advantage its provides then your other methods, why it is become so interesting about light. See this use of external stimuli like light, you are using as an external stimuli, for example, you are taken a drug inside your body and you have some (()) cancer on your skin and by using external light, if I shine light or leaser whatever it is

and then if I can release that part alone, then it will be interesting, so that your other part is not, others are not damage only that cancer cells are damaged right.

So, that becomes so the basic advantage this provides this methods is that spatio-temporal control over the release this is what you are light gives, which is spatio-temporal control over the release; this this advantage you gets when you use light as an external what is the spatio-temporal, basically what it says that at any space given space you can release, I can I can shine in this space and get into least and other than system like that. Temporal is that you have for example, I can switch on my light, switch off, because it is an external stimuli for example, if it is p h like system you cannot switch on or switch off the system.

But, if its if you are using a light as an external once drug is released for 10 percentage or 20 percentage then you switch off the light, unlike if you want you can switch on, so you have an control like temporal control over the release state. So, that is that, is the biggest advantage you get using external stimuli, that is why people are now working usingexternal stimuli light for control release of drug molecules.

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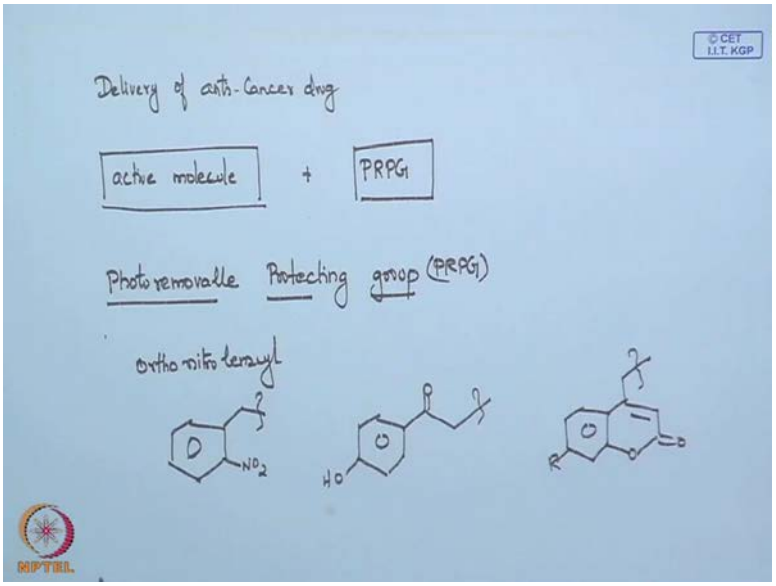

So, how they do that basically for example, you take a active molecule, active molecule in one sense I am for example, i am going to delivery anti cancer drug, delivery of anti cancer drug, so so that that anti cancer drug is my active molecule. So, there are many

many anti cancer drugs are available in the market right like, which are active basically cholera (()) (()) like, so this will be my active molecules, so that is my anti cancer drug.

Now, what I do is that, I will take another molecule which we call as photo removal protecting group, what photo removal protecting group, what is this photo removal photo removable protecting group this we call as PRPG, what is this photo removable protecting group, what it means basically we know about protecting group is right, so what we do, you you have functional group, you have two, three functional group, so you want to protect one functional group and then carry out some reaction or other functional group and make around you do acid base cleavage and removes this functional group to retain the functional other molecule right.

So, what photo remove protecting group is used is that same way, you you attach this molecule instead of using an acid or base to remove the protecting group how, you use light that is all, instead of using acid or base you can use light to remove your protecting group; then we call them as photo removal protecting groups. The n number of photo removal protecting groups, because of that n number of photo removal protecting groups are used because, if you are molecules are highly sensitive to acid or base the otherside of the functional groups, then you cannot use it right, in that case you can use photo removal protecting group, because once you shine light it is not going to affect other part of the molecule and you can cleave them.

So, it as been used in lot of organic synthesis and many photo removal protecting groups are synthesized, you can have a like ortho nitro benzyl protecting group, ortho nitro this is very commonly used benzyl, ortho nitro you can have, then you can have your active molecule here, you can ortho nitro benzyl chromo force, we have very much use. Then para hydroxyl financial compound are used, you can para hydroxyl financial people have used even you use ki marine, use even ki marine and there are many others like you can use benzyl, benzyl is well known (( )).

So, there are many photo removable protecting groups are been designed, sir you have some some are good for releasing acid, some are good for leasing pose face, calcium some can release in a high longer way length like 410, so depending upon your reaction condition your need, you can select the photo removal protecting groups. So, this are photo removal protecting group, so you take the photo removal protecting group just you

have shine light, then the photo removal protecting group comes out, releasing the molecule.

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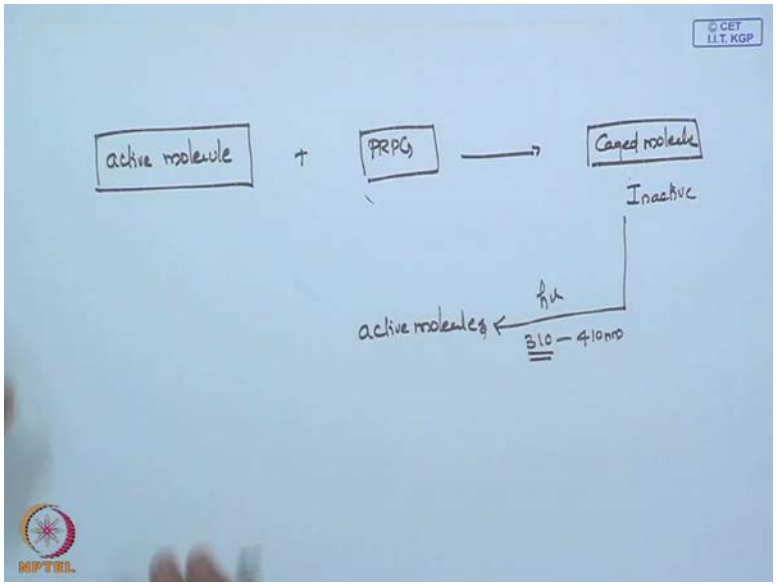

So, what you do is that you take the active molecule for example, I am taking active molecule like chlorambucil, which is my cancer drug, anti cancer drug and then I take my photo removal protecting groups, you can you can take your photo removal protecting group like ki marine, so that it can be water solvable or it can observe atlonger way does, so your cell is not affect at which can, which so there are protecting groups which can even observe at 410 hallow meter.

So, you can think you can select that type of photo removal protecting groups and the protecting groups, which it should not be after it release it should not be a talks to your system also, keeping all that point into concentration you can select your photo removal protecting groups, and several point photo removal protecting groups are even be decide now days. Now, what you do is that you add them covalently most of the case you add them as a covalent, you attach them covalently and you call them basically in photochemistry they call as caged molecules, the cage take the active drug you attach mate of photo removal protecting group then you call them as caged molecule clear.

So, the important point of this caged molecules is that, the activity of this drug will be get lost, that is basically this molecule will be inactive you should attach your protecting group in such way that for example, if you if that O H of your molecule is act is the

necessary for its activity then you attach your photo removal protecting group to the O H, so that the caged molecules becomes inactive now, after this then you shine the light externally. So, see depending upon the protecting group you can find out your gravalent it can most for 310 to you can even 410, now a days people have used 700 that is based on your 2410, 2410 observation are there right; same molecule for example, ki marine which as an observation are 350 then it 2410 it can do like 700, ki marines are known to do 2410 observation ki marines.

And this type of molecules are showed to do 2410 abstraction, that means you can use 700 nanometer, 700 nanometer you can use leaser, so you are not going to kill any, you are not going to damage the normal cells, so that becomes much more safer if you go for 2410 approach, see you cannot use 310, see if it is a system for example, your active molecule is a agro chemistry then it is fine, you you are not worry about the wavelength.

But if it is active compound like anti cancer drug you want to take it for your body, then you are worried about much about wavelength right, 310 is not safe, because that itself willcreate cancer. So, you it always safer to go above 400 nanometer and it is much more safer when you go to 700 and that can be done by your 2410 abstraction method like ki marine does, the same ki marine protecting group observes at 350 same way in 2410, the same group observes at 700 nanometer.

So, you can shine light of that wavelength and then you can release your active molecules, once you do this type of release, you can as I said you can have spatial control this part you want to release, because you going to you are going to you can other part you can close by your black cloth and just shine light on this part, so you have control over that, because it is an external stimuli then temporal control whenever you wanted you just switch on the light, whenever you do not want you switch off the light so that great advantage you get by this method.

This this based on this method, now this method as been come to delivery of anti cancer drug using this type of methods are become like venture of now new field and many many good paper are coming out of it. This recent development if you see on this type of work that is delivery of anti cancer drug by using photo removal protecting group, it is become like different like.

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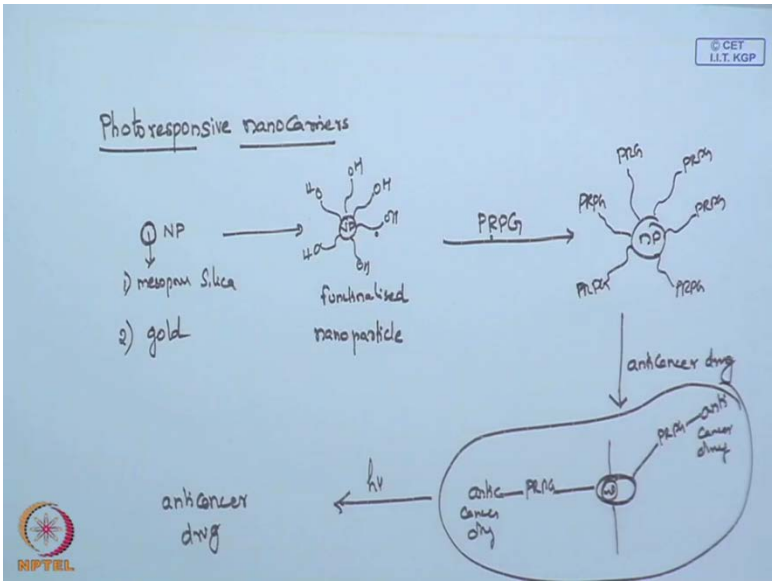

Now, it as went one step ahead and people are calling them as photoresponsive nanocarriers, see same system photoremoval protecting group slowly, now people have changed little bit and mean it as photoresponsive nanocarrier, what is that again this is going again it is a photo removal protecting group, but your photo removal protecting group is not now attach even nano articles. So, what advantage is going to be give now, see for example, like people are using mesoporous silicon, mesoporous silicon you can use nano practical like, people are using mesopore for silicon, this is your nano practical.

Then people are even using gold and you have you have several nano practical I got you can use, now you take nano of practical basically you functionalized your nano practical like in the end you try to have some groups like O H or whatever you want you functionalized this, so you have nano practical, so you will have functionalize nano practical now, functionalized nano practical. See, why I am saying this this, so far you are seen the basic of photochemistry, but you should know there like real field like real what what is happening right now in the photochemistry field, because that is very important for you.

So, you have an mesoporous silicon, they are taken nano practical what are they doing just functionalize this nano practical, now interesting part what they are doing, what we did initially we just took our photo removal protecting group and attach to your anticancer drug, but here what they are doing they taking this photo removal protecting

group then they are attaching to your nano practical. Now, what happen is you will have nano practical with again will have photo removal protecting group, so you will have system like this now and this you can construct if you want.

Once you construct like this system, now what happens this is called as photo responsive nano carrier see, you have you know there are several advantages when you are delivery a system becomes nano, because its half life time is increased it (()) becomes less and its getting into the self permeability become more right, so you have n number of advantages once a system, once you are delivery device becomes nano shape then you have lot of advantages like, the best move the best advantage (()) becomes less permeability, becomes more yeah; it you can do for differentoral administration right.

Now, what they do once you attach this photo removal protecting group, now you can attach your anti cancer drug as in the previous case right, now you have a nano practical there you have photo removal protecting group plus anti cancer drug, like this you have system like this you will have photo removal protecting group and anticancer drug, so like that you will have nano practical.

Now, if you shine light on this now it is going, now what happens this will have whole system will be nice gets into the cell, now you shine light on this and you can see your anticancer drug is released in a control fashion.

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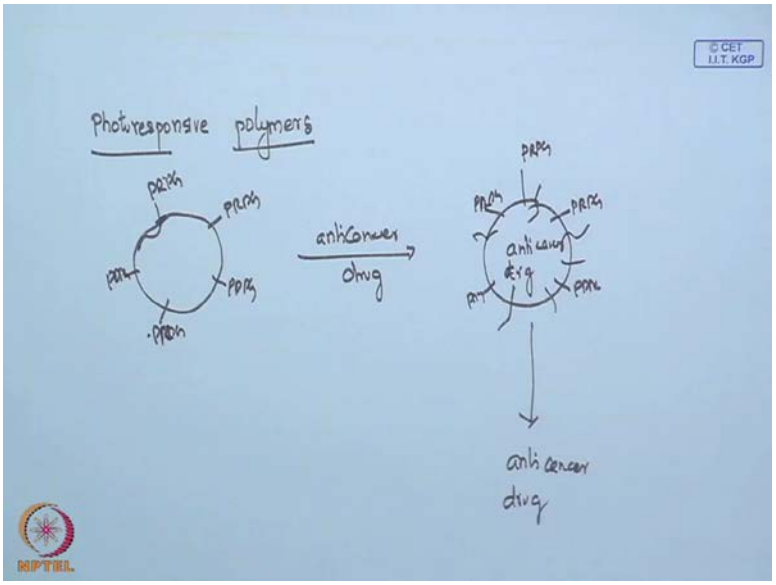

So, that is new area slowly coming up, not only on like nano practical people are even used photo responsive polymers this is photo responsive nano carrier, people are even met photo responsive polymers. You can have photo responsive polymers, because that is again have like instead of nano practical except you will have a polymers, so basically they make a polymer. This polymer in build will have photo removal protecting group, so you construct the polymer which as a photo removal protecting group, they will have photo removal protecting group in building side, now this this whole polymer this you can make it smaller, you can make (()) and (()) becomes very small.

And then you can take your anticancer drug and we can load down them, but this will be more like a physical in computation you will your anti cancer drug will be inside, it made of photoremoval protecting group, that is all, that is what I want to say. Now, what will happen, now if I shine the light since we know that photo removal protecting group it just like, so it will cleave off this will disturb giving out my anti cancer drug, so like that people have made using polymer also first initially, so control delivery of active molecules are very importantso in first case what they did is thatjust they took your photo removal protecting group attached your anti cancer drug they have showed that they can release.

And they have found two good advantages like it can have great control over the spatio and temporal this are the twothings after that what they did they took the photo removal protecting group attached your nano practical, so that it becomes a nano carrier and then you attach your anti cancer drug, then you become like photo responsive nano carriers people in in the place of nano practical people are using mesoporous silica as like gold nano practical.

So, many many of the nano practical are used now a days and then this are all about chemical in capitulation like covalently there are in capitulated, but if you want to do a physical type of uncapitulation, you can take up polymer you build up a polymer which contents photo removal protecting groupthen what happens once you have this then you make physical uncapitulation of anti cancer drug, then shine light you know that your photo removal removable observe the light.

And then you cleave of giving you anti cancer drug so this are the this is the hot field and control release of anti drug delivery, so you it is not about only anticancer drug just in I

am taken an example you can use it for any active molecules, see the same same photo removable protecting groups have been used for release of calcium irons which is, which is very important, because to study some biological process like iron channels that is were the they have been used for control release, you people have used photo removal protecting groups for release of ATP, ADP to understand what happens the biological systems. People have used to release neuron transmits to understand, what what process is happening in their cycatic neuro neruo diseases, so if you want to have it is not only aboutanticancer you have, you want to have any control release you can use photo removal protecting group.

You just you have to tied up with the active molecule and slowly sense them see now if you are for a example, if you are photo removal protecting group is fluorescent then it will be much more useful for example, you know amino acids, it is very hard for amino acids to calculate and all this things, because your non fluorescent molecules. So, if you connect amino acids with your photo removal protecting group, then you can now understand the how the amino acids gets into the cell how it interacts with the system by using your fluorescent instruments and all this things.

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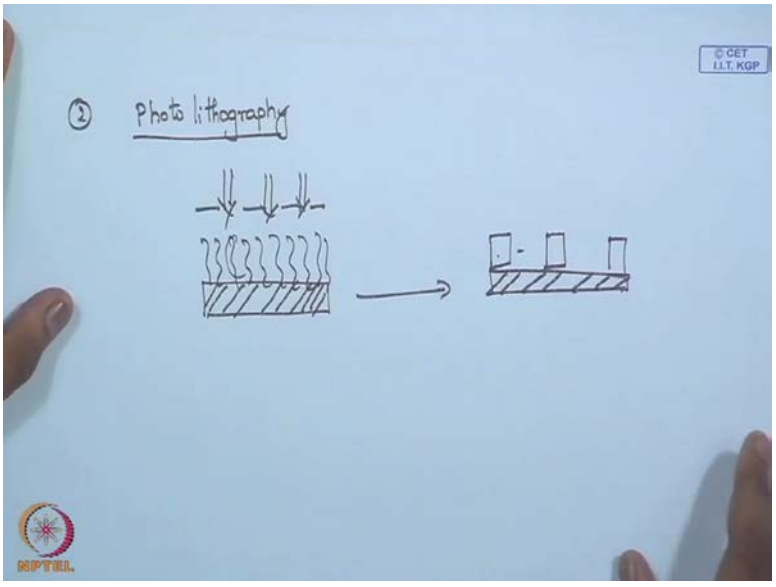

So it is it is opened up the very good area and and several several research is going on in this type of area, control delivery of molecule you see you have photo removal protecting groups. Another area which I want to highlight is second area which we will discuss is

about photo lithography you know but, photo lithography I know that you have heard about a photo lithography and it was just like a stamping process right, normally what happen is that, you take a solid support it can be silica gold, whatever silica and then you you take thiol, gold, you take thiol then you keep mask on this and shine light, wherever the light goes shine light wherever the light goes that area will be that you will have you will have gaps, you can have like this this area wherever the light goes this will go off and you can create stamping transportation, that we have study as a photo recites.

But, now what happen is that now it become much more interesting, people are started working on functional group photolithography using this, you can bring up the functional group, basically you create surfaces which can be high breath surface, like hydrophobic and hydrophilic that type of surfaces you can build.

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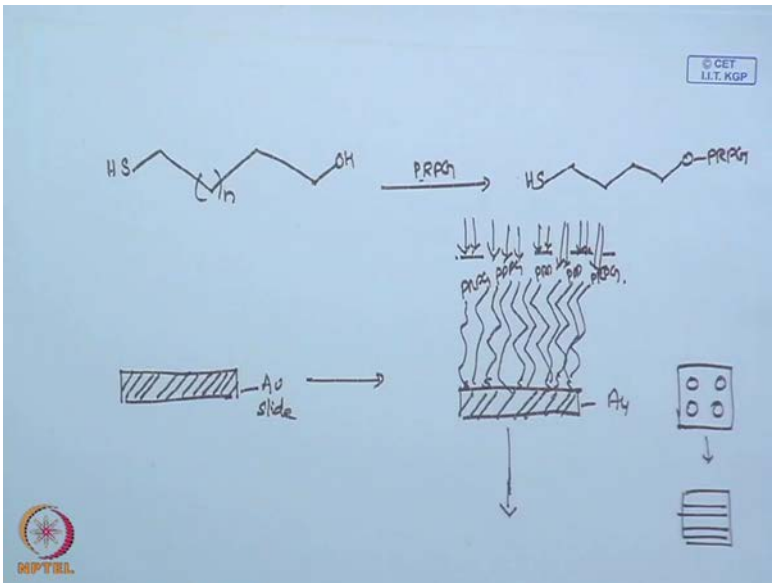


How to make them, it is nice same photoremoval protecting group using that, see for example, I take a thiol, take thiol in you have thiol like this, take your photoremoval protecting group for example, I am taking photoremoval protecting group of orthohydrobenzyl with a fluent change in it, that means its more hydrophobic, so I will be basically protecting this way my photoremoval protecting group it gets protected.

Now, you take your goals slide, you can take goal slide, now deep this goal slide into your thiol you know that once you take your goal slide and deep into your thiol thiol as your great affinity towards gold, what it forms your study that yeah it forms a self

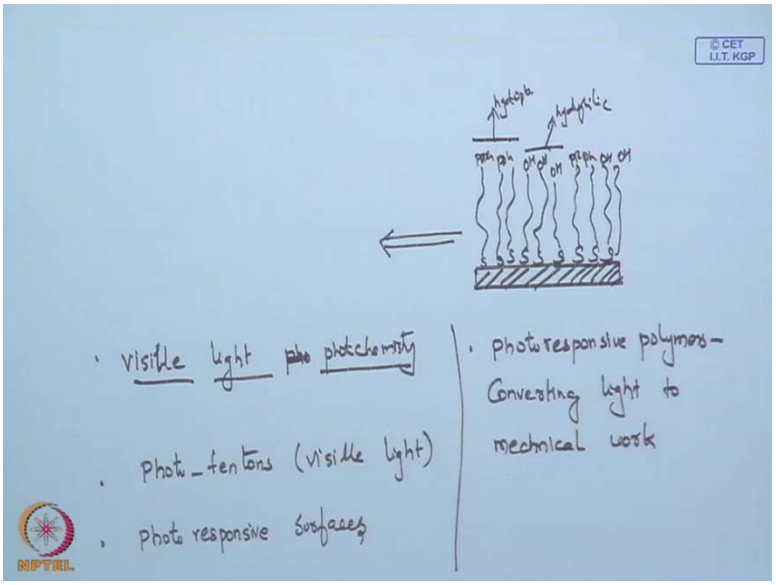
assemble monolayer. So, you have goal gold slide it forms in nice monolayers have sulfide here, photoremoval protecting group it should be nicely packed I am just since, I do not have space you will be nicely packed one this is all your photoremoval protecting group.

And it will be spaced there will be not will be whole surface will be like this will be highly packed one, relatives surface like this, now what you do see you can get mask mask of chromium mask you can get, you can have or you can make mask by yourself like you can have a holes like this in the mask or you can have a mask of parallel like this, so you can get mask of type what you want.

Then you keep this mask in the top of your stamp and then you freshly prepares stamp, see basically you are taken thiol you protected the thiol then you made a stamp on goal slide right. Once you made the stamp on goal slide what you did, you kept a mask, once you kept the mask now what you do just shine light, like like your lithography, just like your lithography, so what happens the area where there is a hole, pin holes, the light gets into that area other area it is completely masked.

So, then then what happens, once the area where the light gets in your photoremoval protecting group, once the light gets in what happens to your photoremoval protecting group, the photo removal protecting group cleaves off to give you the functional group back, what was your functional group OH right, so wherever there was a light.

(Refer Slide Time: 49:40)



So, then you will have a stamp (No audio from 49:37 to 50:05), see there will be always treated like this stamp I am drawing straight point will be treated down, now wherever the light as not fallen you will have photoremoval protecting group just like this wherever the light as fallen you will have your O H, because photoremoval protecting group goes off then you have O H see, I earlier said that I have made my photoremoval protecting group in such way that I have a fluorine in change right.

Now, my photo removal protecting group as a fluent change, so what it is so basically it will be hydrophobic and this will be hydrophilic, now I have goal surface, a surface slide so this is a hydrophobic, so I have hydrophobic surface here and this surfaceis hydrophilic. So , I can create now hydria surfaces using my lithography functional group lithography, so once you have functional, group then you can play around it you can attach your lipid molecule, you can have attach DNA or you can do whatever you want on the hydrophilic sides.

And you will have biliary system and n number of applications coming out of it, so this are now started new areas on like thing, other areas you know that another new area which as been started this visible light, visible light photochemistry, visible light light visible light photochemistry you can say using justvisible lightjust your ordinary light people have started doing chemistry that is using your ruthenium complexes. So, you can use your ruthenium complexes, ruthenium complex observes light using your ordinary CFL bulb and you can carry out all most of your reaction like some important reactions are been carried out.

In the you does not need big photo chemical apparels you can just do the reactions in visible light itself using your ruthenium complexes. So, that is also getting up in environment, if you see normally photo-fentons photo-fentons is people are working photo-fentons that is now it as become on the visible light area, what they do is that you can you can make titanium nano practical.

Then you shine light then use that, so in titanium then use that process to generate O H radical and you can degrade system, degrade pollutants, so that is also another area coming up and the final final nice area is photo responsive surfaces, you can create this is also another good area which is people are working on photo responsive surfaces, where once you shine light it will be hydrophobic, after you shine light the surface become

hydrophilic; that is another nice area coming out. The finally now, another area which people are working on is photo responsive polymers for converting light to mechanical work, that is how in new area which has been started on.

So, this are like upcoming areas in photochemistry fine, so this are some of the applications of photochemistry have which and there are many other application which you know photo dynamic trophy is another thing, but i am just touched on the new areas, so with this will end our photochemistry and pericyclic course and that is all and best of luck for you thanks.