Course on Stereochemistry
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Module 4
Lecture No 14
Conformations and Confermers

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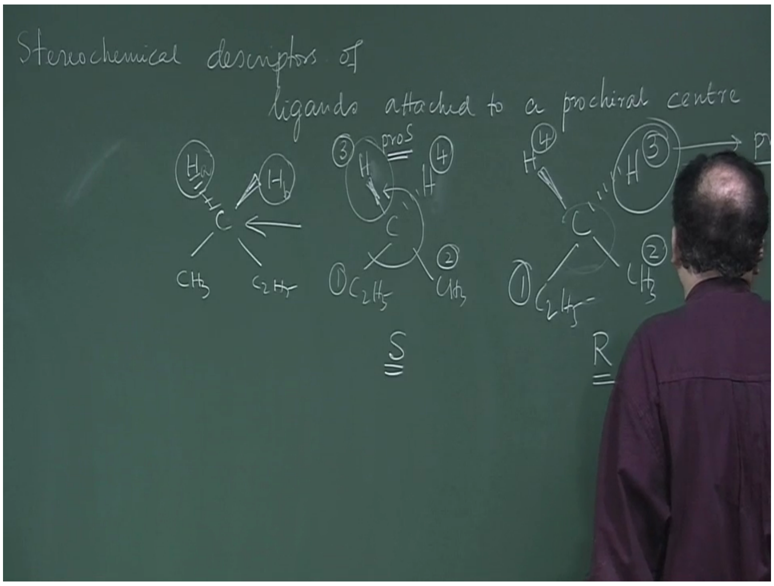

Okay welcome back last time we ended up with saying the concept of prochiral centre that prochiral centre is can be of various types but one type is that if a carbon is there where ligands are different like a methyl and C2H5 and then it is attached to supposed to hydrogens then there this carbon become a prochiral center again I repeat because one transformation that means if I replace one of these hydrogens by another group which is different from these 2, then it becomes a chiral centre, so one transformation can convert it into a chiral center.

Now exchanging these hydrogen leads to one form, exchanging these hydrogen leads to another form, that is why yesterday we have seen that these 2 hydrogens are called enantiotopic hydrogens, but these 2 hydrogens now we have to give some names, we can always say we cannot just say this is the beta hydrogen, this is the alpha hydrogen because this alpha beta depends on how you write it, I can always turn it down and suppose this is Ha and Hb and Hb now looks beta but if I rotate the molecule write it in another fashion like C2H5 on the side and CH3 on this side, then Hb becomes alpha and Ha become beta.

So they can constantly change the way you write it depends on that but the descriptor should be independent of that, it does not matter how you write it but if I assign a descriptor for this hydrogens, not the alpha beta because alpha beta keeps on changing. A descriptor like RS then I can name or tell which hydrogen and talking about, okay. Now the way to do the assignment of stereochemical descriptor to this hydrogen, suppose in this case two hydrogens they are enantiotopic, is that what you do that, if you want to know what is the configuration of these hydrogens or what this not configuration, what is the stereochemical descriptor for this hydrogen.

Then what you do you assign priority sequence of all the groups but when it comes to the because these 2 should have the same priority because they are the same atoms but as you are trying to figure out what is this hydrogen? So you give a higher priority to this hydrogen over the other hydrogen which were not considering. So when I assign priority of the ligands attached to this carbon, this is C2 H5 so that will obviously be 1, this will obviously be 2, now since I am trying to figure out, what is the stereochemical descriptor for this hydrogen, so why I assign this as 3 and this as 4. Now I will look at the absolute configuration what I am getting? So I am getting see I do not have to converted in to Fischer projection or any other thing, this is simple because this hydrogen is alpha, so I am looking it away from the 4th group, so whatever I will see that is the configuration of the system.

So this becomes S, now if that be the case then this hydrogen will be called a pro S hydrogen. For assigning a stereochemical description of the hydrogen, this hydrogen, then what we will do the priority sequence will change, we have to give higher priority to this hydrogen over the other hydrogen because we are considering this hydrogen now. So this remains still 1 that remains that remains 2 only change is this will be 3 because you not considering this one and this will become the 4th priority. So now you see what is the... You have to be now careful because your H 4, the 4th group is now towards you, okay. So whatever you see we have to do you have to reverse that in order to assign the configuration.

So what we are seeing this is 1, 2, 3 so it is going in an antique clock wise but actually it is cow clockwise when seen from the backside that means away from the 4th group. So this hydrogen… so this configuration is now R, so if that be the case, then you call this hydrogen as pro R, So pro R pro S is the descriptor that is given to the ligands attached to a prochiral center. Remember it should… it is not always hydrogen it can be any other group.

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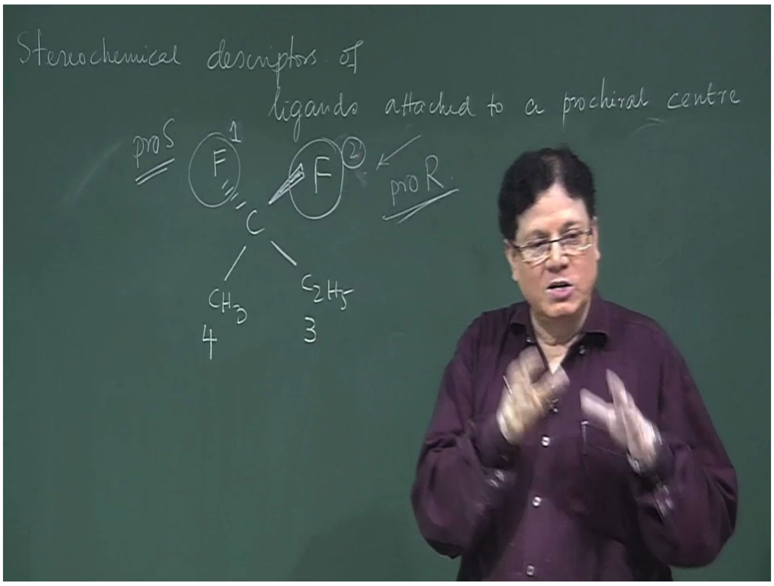

I give you another example suppose I want to figure out which one is pro R and which one is pro S in this system. See this is a fluorine another fluorine and this is a methyl and this is the ethyl, almost similar compound but the hydrogens are replaced by fluorine. So if I want to know, what is the pro which one is the pro R fluorine, which one is the pro S fluorine? What we have to do? We have to again assign priority but remember the one which we are considering 1st amongst these enantiotopic groups, that will be given higher priority over the other, so amongst these this with methyl, ethyl and fluorine which one comes 1st?

Fluorine has higher atomic number, so this fluorine because I am considering this fluorine first, so this will be 1, that will be 2, this will be 3 and that will be 4, okay. So now we have to now you need some you need some three-dimensional vision to check whether is R or S. Now again I tell you, you can converted into Fischer projection and do it that is one way or if you are very good in in figuring out from the wedge formula, you can do that.

So for the sake of time I do it, I look it from the side because I should look from the opposite side of the 4, so if I look from this side this is 1 so 1st this is one then it goes to 2 and then comes back to 3 so the direction as clockwise, okay. So if the direction as clockwise, so 1 then it goes down so 1 then it goes down and then comes back to the (())(7:30). So it is clockwise so that will be pro R, okay. In the same way you can do the configuration of this the stereochemical descriptor of this other fluorine and in that case this will be 1, when you considered this fluorine this will be one and that will be 2 and again you have to look from the side but you should not look from this site. What happens 1st you have fluorine down one group down then you come up to the top fluorine 2 then you go to the ethyl, so it is going in an anticlockwise fashion, so that will be your pro S, okay.

I think this is clear so basically the same groups have to be considered given priority but the group that you are considering that should precede over the group you are not considering in terms of priority sequence. So that is the concept of stereochemical descriptor for ligands attached to a prochiral center, okay. This is important because there are many reactions specially the reactions happening in the body where the enzymes which are the natural catalyst, so they can pick up one of these hydrogens the pro R they can distinguish between these hydrogens and they will pick up either the pro R hydrogen or the pro S hydrogen while doing the reactions, suppose it is oxidation of hydrogen then they can pick up they can discriminate between these 2 hydrogens and so enzymes can discriminate between the pro R and the pro S hydrogen and the way to describe is to use this concept, okay.

So that takes care of the stereochemical descriptor of stereogenic centers, then the ligands and then the spaces and so more or less that takes care of that part. Now we will go into another concept which is with molecules which are flexible in nature, molecules which are not rigid where there is continuous moment. See all molecules there is continuous vibration rotation that is going there little bit, not rotations sometimes they are restricted sometimes they are restricted like if you lower the temperature all these vibrations and rotations will be restricted because you are not supplying the energy to vibrate or to rotate, okay.

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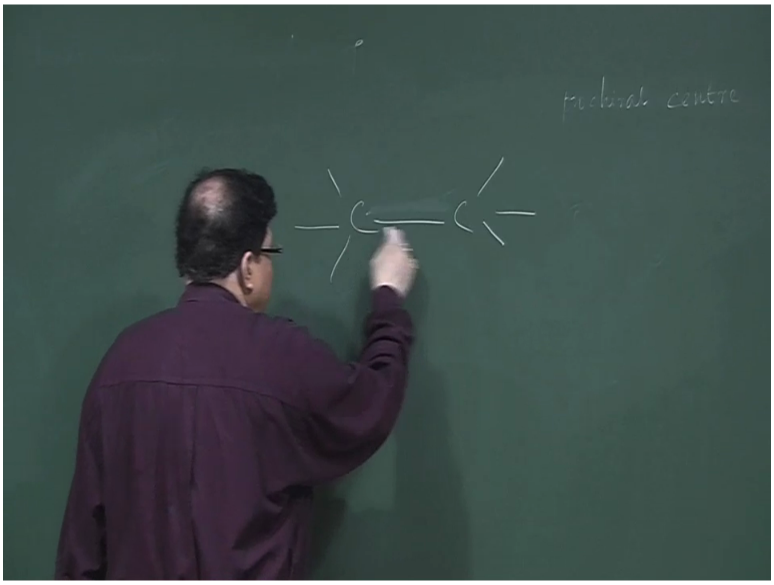

Some molecules the rotation is not allowed even at room temperature, there are some molecules. Like in case of a double 11 compound you cannot actually rotate the two ends, one carbon keeping one carbon fixed you cannot rotate the other carbon because that will break the pi bond that is there, so the rotation is not possible. So that is called restricted rotation, but if you have a single bond a carbon carbon single bond, then you have 3 ligands on both side, okay and these carbon carbon are attached to each other then because it is a single bond, so now there is a possibility of rotation between the carbons.

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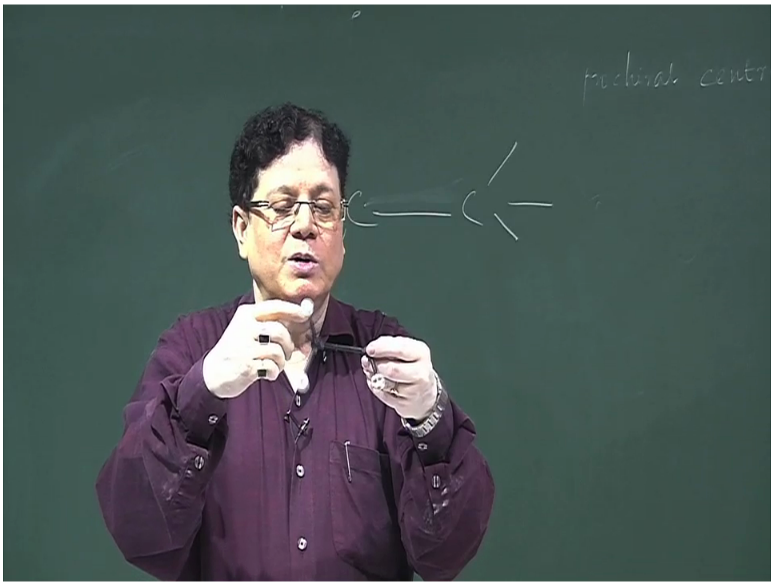

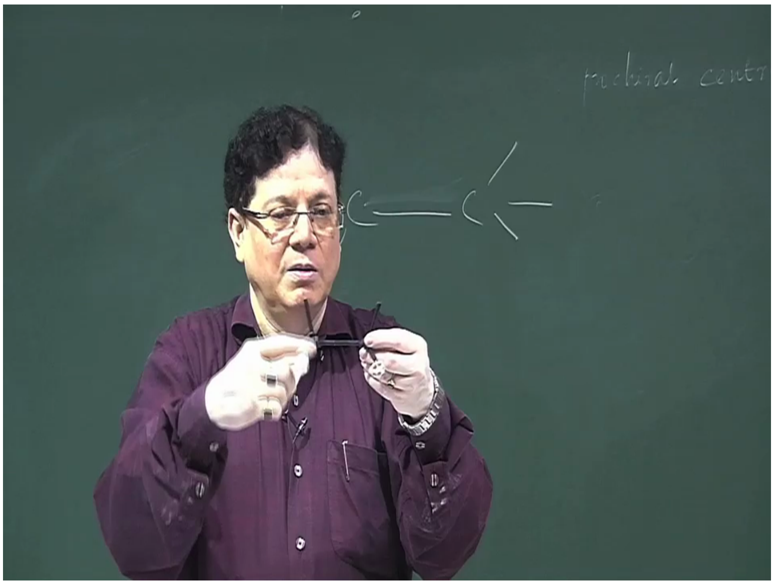

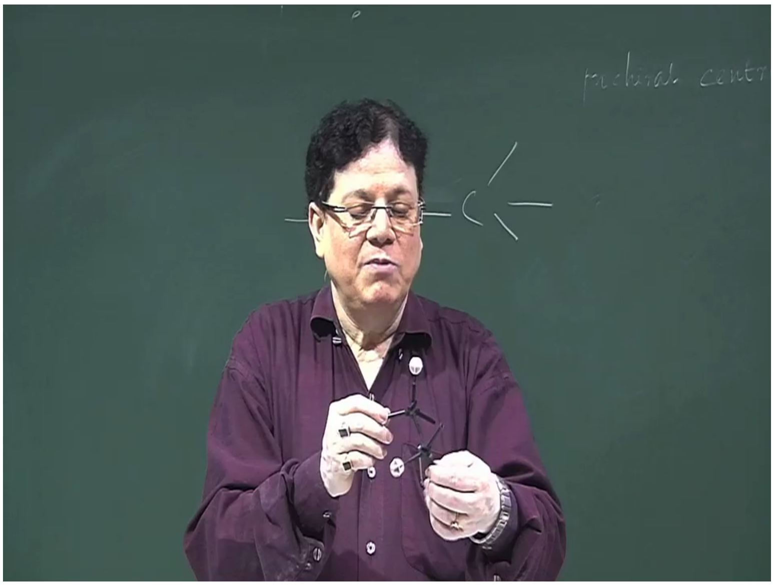
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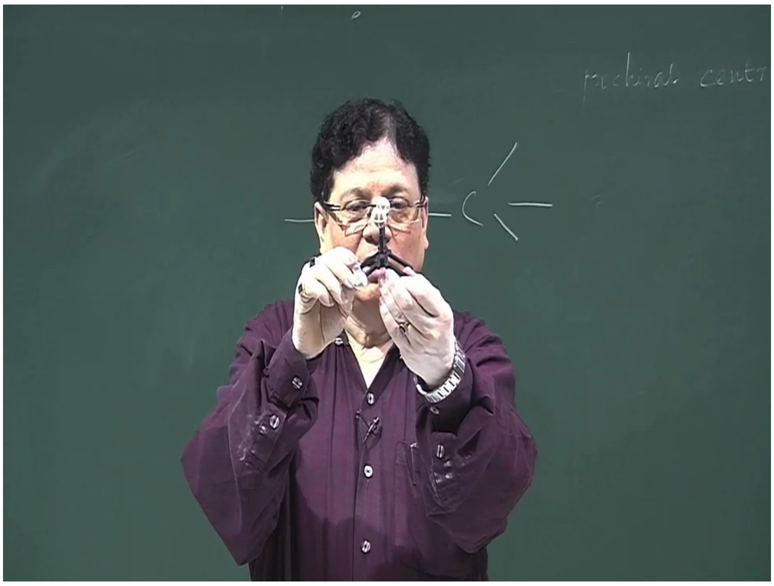
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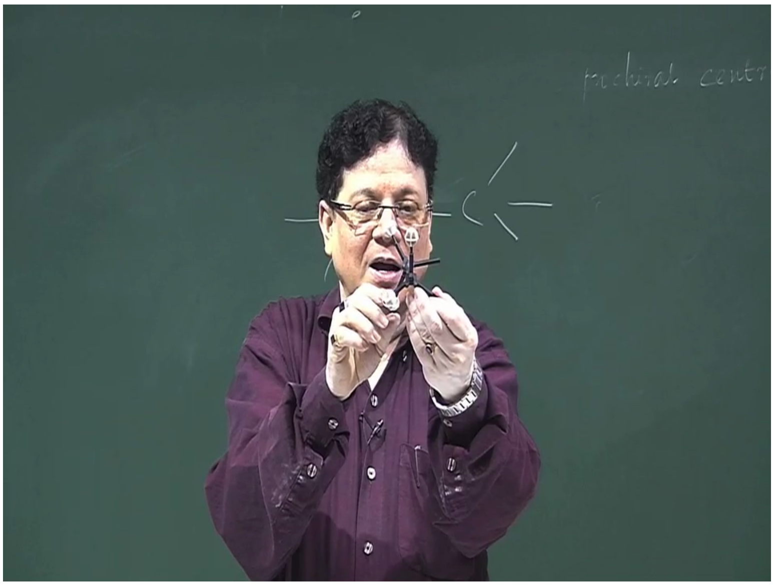
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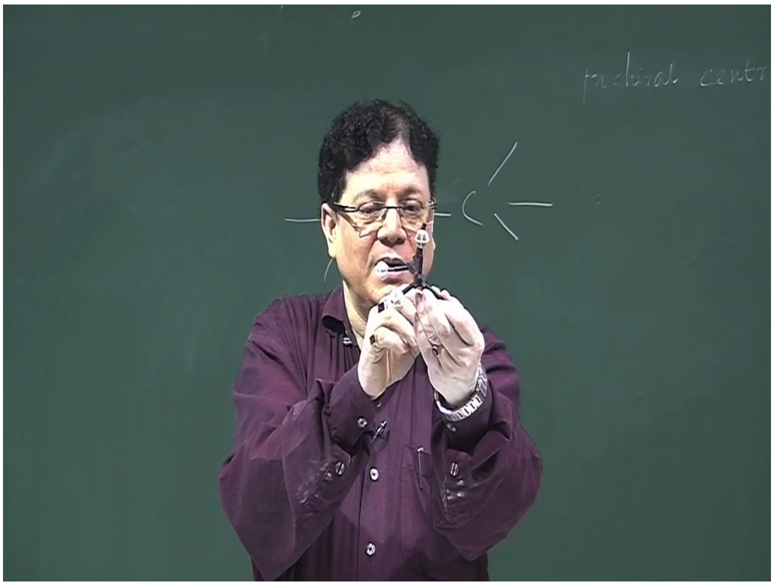
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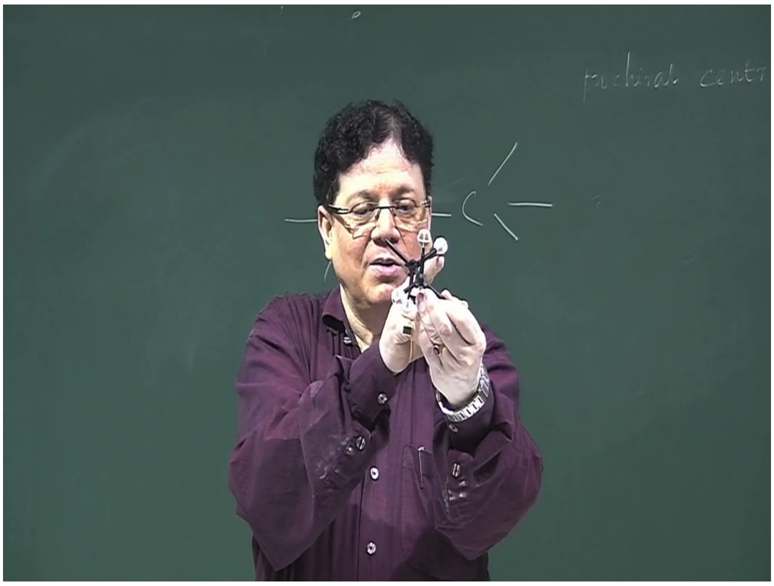
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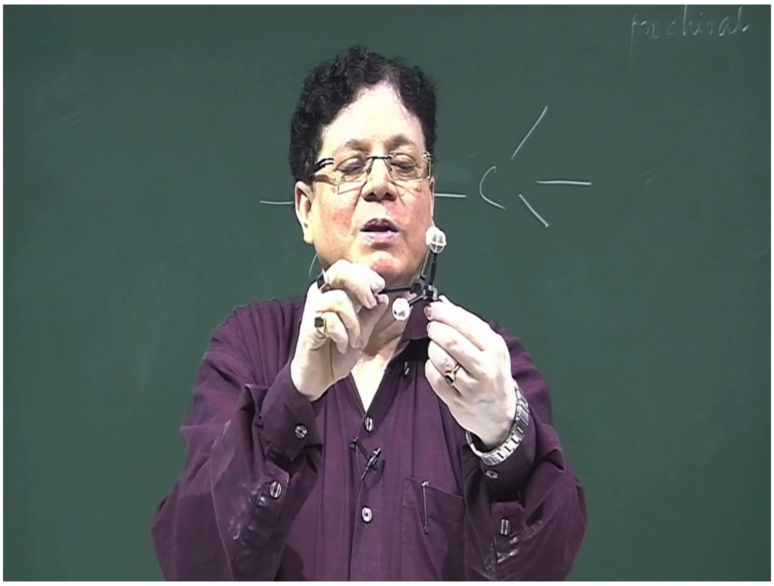
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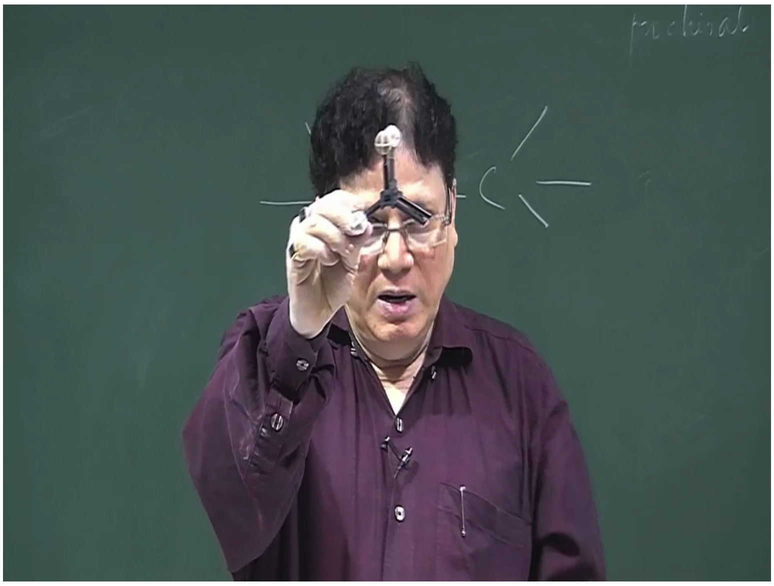
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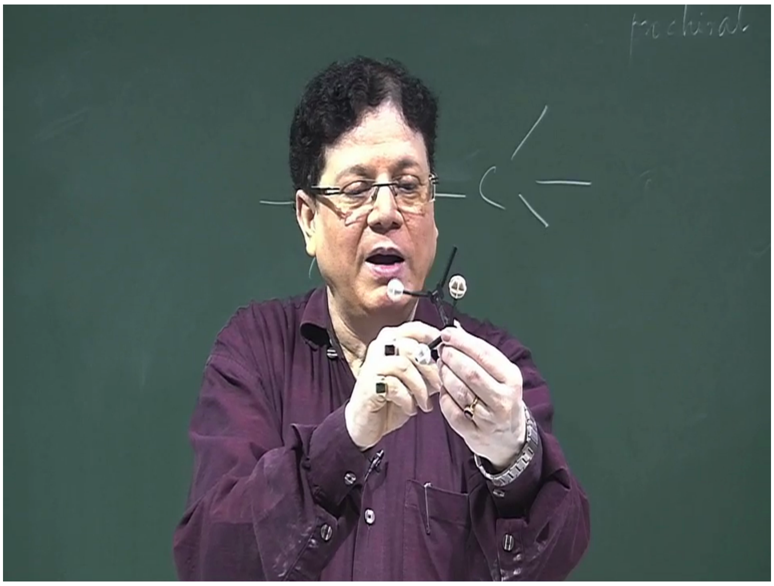
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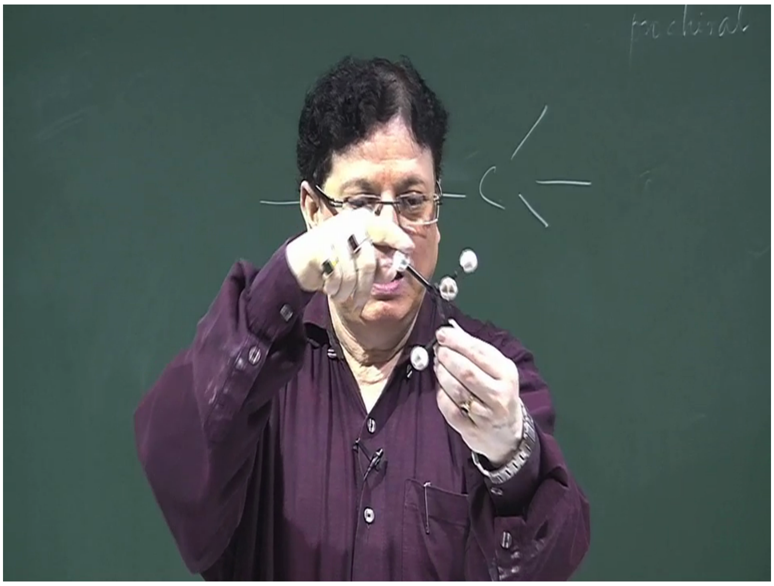
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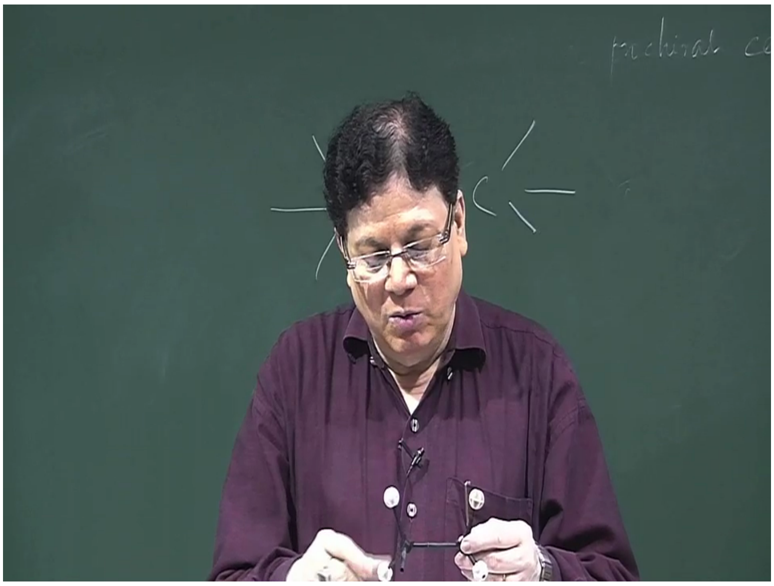
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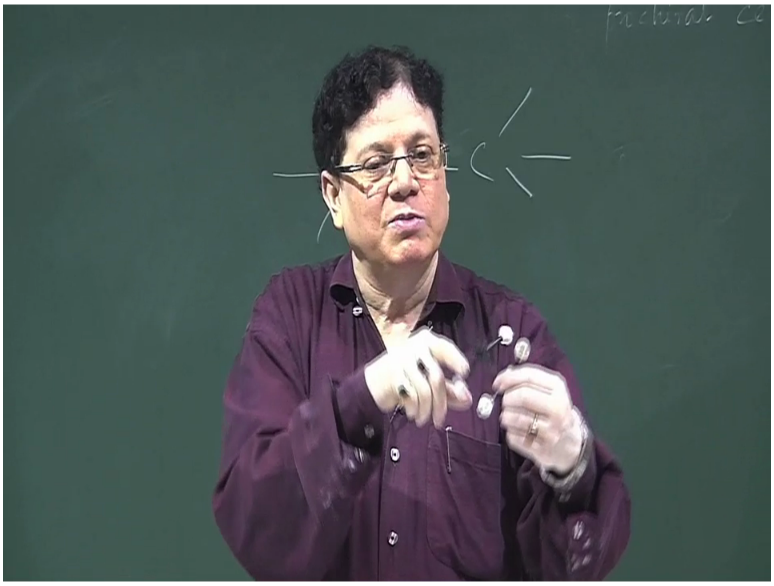

Like suppose I have this molecule, this is the carbon carbon bond, these are attached to 3 ligands and now see there is no problem as such you can rotate this carbon freely but how free is this rotation that will depend on the relationship between these ligands with the relationship between these ligands, what is the geometrical relationship? So in terms of this relationship is described in terms of what are called dihedral angles, dihedral angles are basically angles between planes, so when I talk about dihedral angles, so if I talk about these 2 right atoms the dihedral angles between these between this CH and this CH is actually containing this CC bond so basically one plane continuing this CC and CH and the other plain continuing this CC and CH.

So that is what is the dihedral angles, so when I rotate what is changing is the dihedral angle, suppose this I call the dihedral angle 0, then now as I rotate I keep changing the dihedral angle, dihedral angle is increasing, it comes to 120 and then this is 180, remember am considering only these 2 atoms and then from 180 it goes to 240 and finally it comes to the back and 360, the complete who rotation, okay. So it rotates, the question is while this while doing this rotation as I said the dihedral angle between these substituents dihedral angle means again I repeat, that is actually the, the plane containing these atoms, but for simplicity we just look at this white bonds and we see that CH bond and then that CH bond, what is the angle between these 2? Okay, that we for simplicity we call that as the dihedral angle sometimes it is also called torsional angle, angle of torsion, okay.

So as I rotate it, we see that in one case as I rotate it first of all I have infinite number of possible air animents in space infinite number, where the dihedral angles varies from 0 to 360 degree, okay so I have infinite number of possible geometries. Now what are these called, these are called conformations, okay.

So conformations are basically in molecules which are allowed free rotation and so the number of infinite number of geometric arrangements that you get while rotating while rotating a carbon carbon say a carbon carbon single bond you are rotating, so that is the conformations okay. What about the energy profile that when you do these rotations, when you get all these conformations, do they have same energy or not? Or do they differ in energy?

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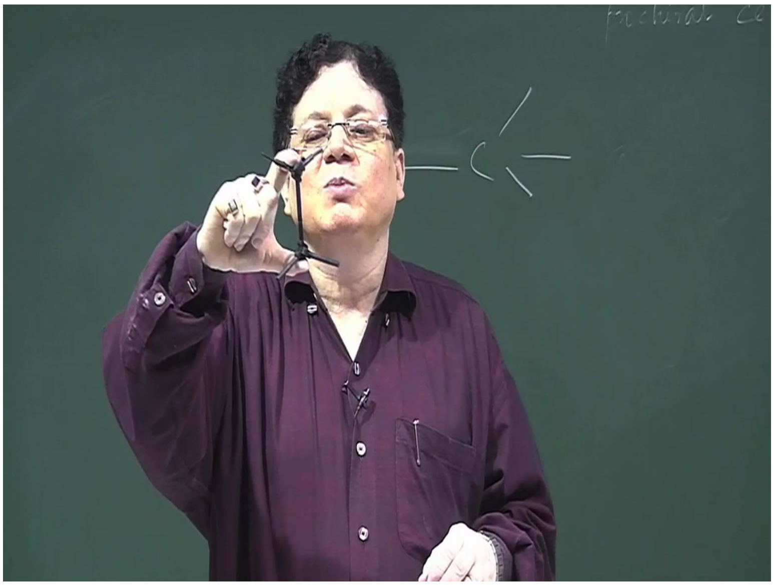

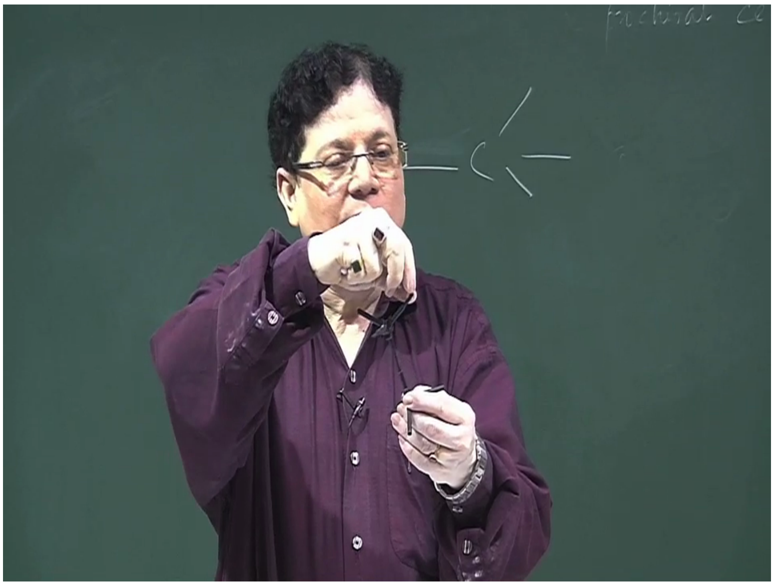

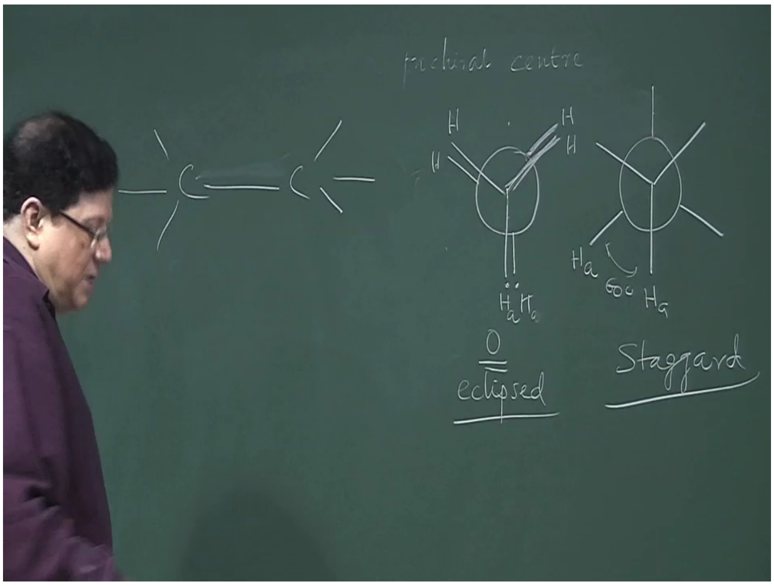

So what happens people have actually found, take the most simple the simplest of all system that is the ethane because remember it actually happens around CC bond rotation, so we are not talking about methane, methane cannot have that conformations, okay. It starts from ethane where there is a carbon carbon bond and that bond has to be single bond, double bond you cannot rotate.

So suppose this is the ethane and you have as I said you have infinite number of conformations possible depending on the dihedral angle between the adjacent bonds but out of these people have identified 2 extreme conformations. One in case it looks like so we are drawing the Newman projections formula because that is the best way to describe confirmation and analysis. See you have been one case you have this, you have this the molecular look like this that means there is suppose that means the dihedral angle here is 0, if I just considered these 2.

Suppose these are hydrogen all are hydrogen, actually all are hydrogen and ethane, but we have to fix somehow we call this as Ha and Ha. So we are talking about the dihedral angle between CHa, C1Ha and C2Ha the dihedral angle and so we identified 2 extreme ones, one is where all the bonds are eclipsing each other as I see it eclipsing each other and the other one where are bonds are not eclipsing each other, that are these bonds are in between the other bonds. So earlier this is eclipsing that one, now what happens this bond has suppose moved here suppose this is the Ha, so this is the Ha, so you have mutated this one and brought it here and so you have to come you are come that means you are rotating the other ones also, so other ones are also rotating, okay. So these are the 2 extreme conformations that you get, in between there are different types of dihedral angles, okay.

Here the dihedral angle is here is 60 degree in this confirmation here it is 0, okay now this form is actually called Staggard and this one is what is called the Eclipsed form. Obviously staggered form will be more stable than the eclipsed form, in case of ethane, we start with ethane the stability the stability difference between the staggered and the eclipse varies from that substituent to subsequent. If it is ethane then because of this electronic repulsion between the CH and CH which are eclipsing each other, this is more this is having more energy than the staggered form, how much more it is about calculated which has been determined, it is about 3.3 kcal per mole okay.

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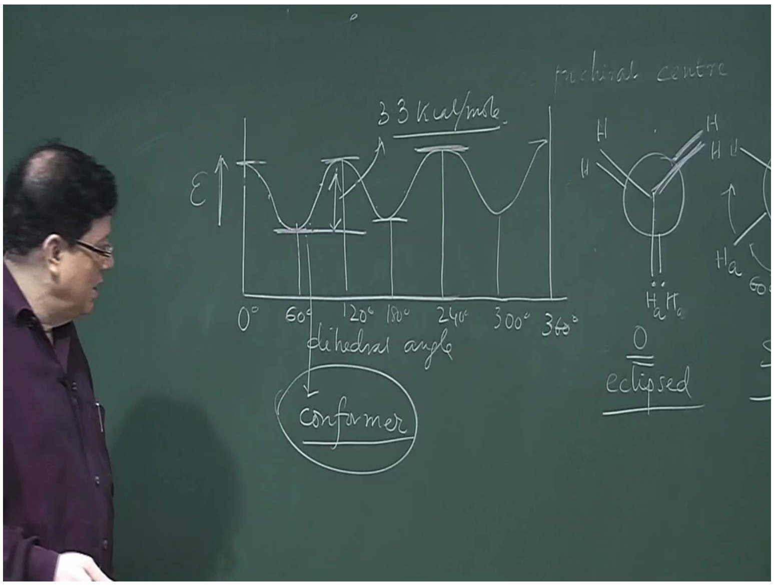

So when we draw an energy versus dihedral angle, suppose we start from this one this form okay this eclipsed form, so here the dihedral angle is 0 degree, dihedral angle versus energy, so what will happen to the energy, the eclipse form has the highest energy so you start from here then as you move the hydrogen so energy slowly decreases because the repulsion that repulsion slowly decreases, so now ultimately it at, it is, it attains a minimum but then after if you further move it, then this Ha is now slowly becoming closer to the this CH bond.

So the energy starts increasing again, so what will happen this will take up take up like this, so this is after 60 degree rotation, this is after 120, 120 means you again you again get these 2 hydrogens eclipsing each other, then you have a 180 degree rotation, then you have 240 rotation then you have a 300 degree and finally a 360 comeback to the eclipsed form, oaky. So this is the energy profile diagram of ethane or we call the confirmation analysis, confirmation analysis which means that which means say whatever things means how the reactivity depends on the confirmation, how the energy varies with the confirmation, so this is the variation of energy with dihedral angle.

By the way this is also called torsional angle. Now this, so you see there is a maxima so its alternates between a maxima and the minima, this maximum points are the eclipsed form the minima points are the staggered form, okay. Every point in this diagram, every point in this diagram represents a confirmation with a particular dihedral angle, okay. However the molecule will prefer to exist in this form because that has a minima 1st of all, that has got lower energy than the eclipsed form and the difference in energy as I said is about 3.3 kcal per mole and 3.3 kcal per mole okay.

So more than 99% of the molecule will exist in the staggered form but that does not prohibit the molecules from undergoing free rotation. See one staggered form going to the other staggered form going to the other staggered form and as you raise the temperature that moment will be more rapid the inter-conversion will be more rapid but here also introduce again I repeat every point in this graph represents a confirmation, however the confirmation which lie in the energy minima in the in the minima energy minima or the minima in the energy profile diagram that is called conformer, so we have a special conformer, so conformer is are the ones which lie in the energy minima and but the conformations are all every point in this diagram represents a confirmation, okay but the conformer are the one which lie in the minima.

So eclipse form is not conformer because it lies in the maximum nor the ones where which lies in this dots here, they are not conformer, they conformer is only the ones which are lying in the energy minima at this point, so that you must understand the difference between conformations and conformer, so the…now come back to the, we have just introduced this concept, conformations are the infinite number of arrangements special arrangements that you get while you by rotation around a rotation around a single bond not for a diatomic molecule.

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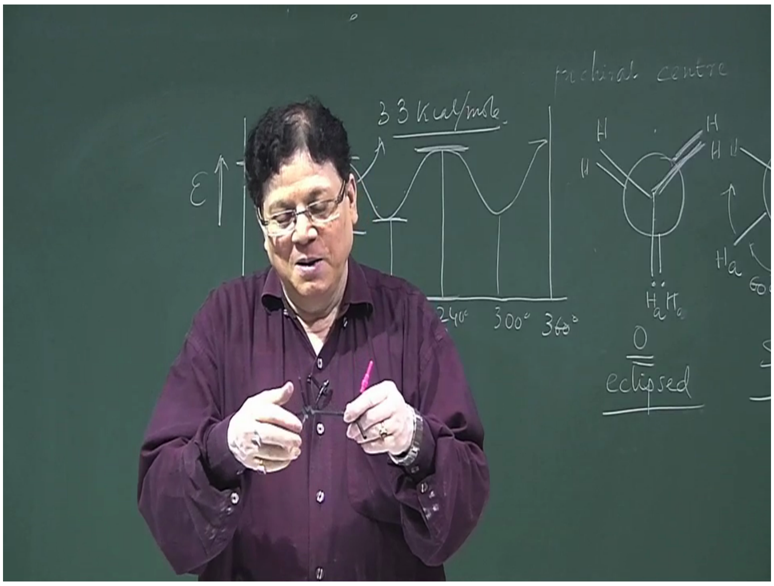

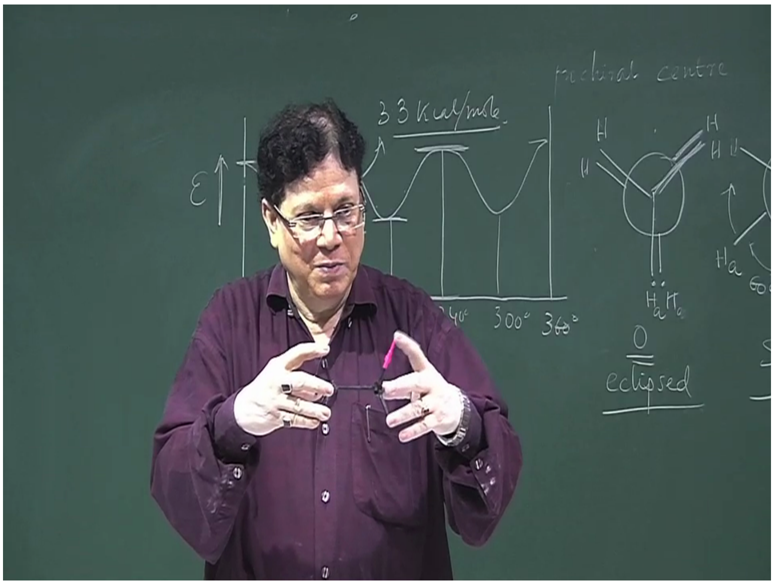

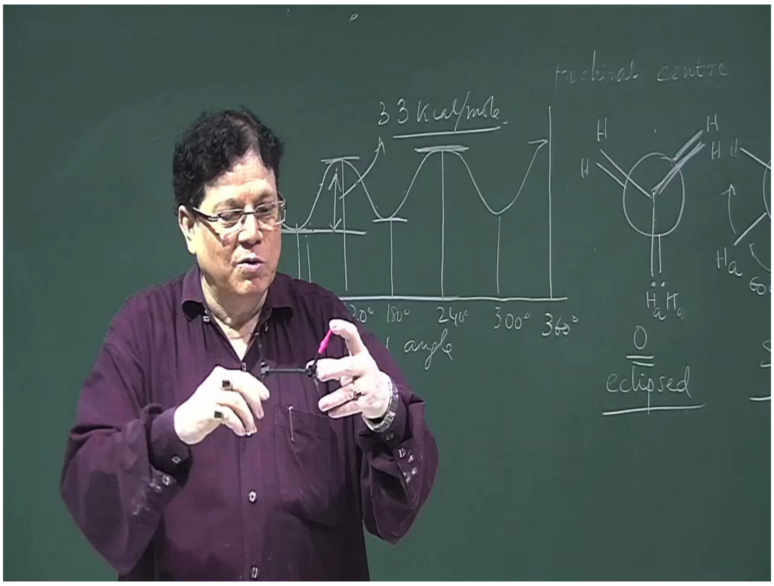

Remember if it is only a diatomic molecule that means suppose it is chlorine, this is chlorine. So if you rotates nothing happens unless these are attached to ligands that means it has to be more than monorelent okay these atoms, but let us concentrate on carbon, carbon has 3 extra groups apart from this carbon carbon bond, so by rotation around this carbon carbon and you get in finite number of arrangements in space, so these infinite number of arrangements are called conformations. Now these confirmation will lie when energy they have not the same energy, as you rotate the energy keeps on changing and the confirmation which lie in the minimum in the energy profile diagram they are called the conformer. Why they are called conformer?

Because this is the one which is mostly present in the system, although it rotates but at a certain point of time if you want to see by spectroscopic means, which one is present most, then you will find that this is present more than 99%, okay. So that is the so all conformations are not confermers but all confermers are also conformations. So this fact will become clearer when we go to the higher system like N-butane I think that will be covering the next lecture, okay. Thank you.