Introductory Organic Chemistry
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Lecture - 12
Tutorial – 02

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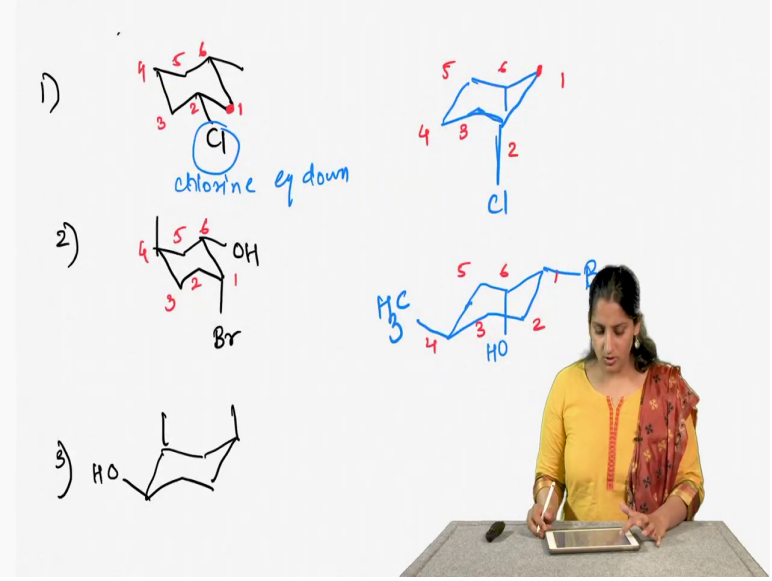

Welcome, to the tutorial for alkanes. Now for the first question it talks about drawing a chair flip, right. So, we are going to go over the step by step approach to draw the correct chair flip. Let us look at the first problem here, what we have is a molecule cyclohexane molecule and first thing to do is to draw the correct chair flip skeleton.

Then, the next step I do is to really number the carbons of the first cyclohexane. So, this is 1, 2, 3, 4, 5, 6 and you can really begin the numbering from any side, it does not matter, any carbon, does not matter, but just make sure that you keep the same numbering or the same direction of numbering in the flip as well.

So, now when this molecule has to flip, I know that the leg of one chair becomes the head of the other chairs; those are the two carbons. So, I should start numbering my other carbon here in the same manner 4, 5 and 6; these are the numbers on the flip chair. I see that carbon number 2 here is going equatorial down, right.

Carbon number 2 here is going, the chlorine is going equatorial down. We know that when the chair flips, it flip such that axial changes to equatorial and equatorial changes to axial, but down still remains down. So, on carbon number 2 of the flip chair it is going to go as axial down right so, equatorial down will go to axial down. If we look at carbon number 6, carbon number 6 has an equatorial down group again and in this case also it will move to axial down as the methyl group. So, that is the flip for our chair.

Now, let us look at the next problem. In the next problem what we have is a molecule that has bromine, OH and methyl group attached to it. Again we follow the same strategy, first thing always number your carbon. I am going to start numbering from here 1, 2, 3, 4, 5, 6, again when you do the chair flip it becomes 1, 2, 3, 4, 5 and 6; those are the groups. OH is going equatorial down and when it flips on the sixth carbon it needs to go now axial down, right.

So, OH here will go axial down. Carbon number 1 has bromine and bromine is going axial down, so, on carbon number 1 it's gonna go as equatorial down. Again one thing to remember and it's a good thing to remember, is that the head carbon of any chair, the axial group is going to be pointing up always, right. So, the corresponding groups then get aligned like carbon number 1, 3 and 5 will have their axial groups going up and carbon number 2, 4 and 6 will have their axial group going down. That's something good thing to remember when you are doing chair flips.

Carbon number 4 here has an axial up group. So, in this case the compound is gonna go equatorial up as the methyl. So, that becomes the chair flip for this molecule; let's go ahead and solve the next one, now for this one we have again the first thing to do is to draw the skeleton, okay.

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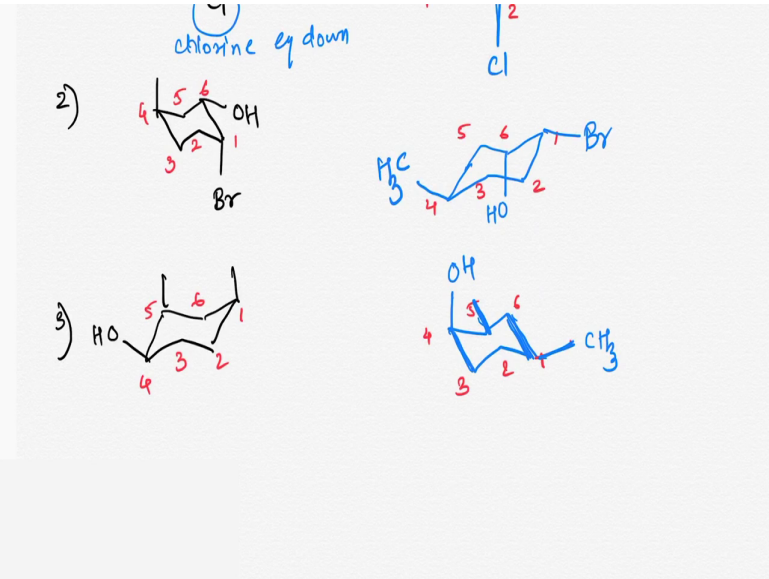

It is very important right that you draw the bonds going in the right direction right, because the bonds are representing the 3D geometry. So, it's important that we follow the right direction.

Again figure out your first carbon and label it the same way on either chairs, right. Carbon number 1 has a methyl group that is going axially up. So, in this case it will have a methyl group that will also go equatorially up. Remember that when the chair flips axial shifts to equatorial, equatorial shifts to axial, but down still remains down up still remains up. On carbon number 4, I have an equatorial up OH; so, on carbon number 4 here it will go as axial up OH.

On carbon number 5, I have an axial up methyl group so, it is gonna go as equatorial up methyl group and it is important that we follow the direction right. So, for example, this methyl group that we have just drawn is parallel to the two lines on the cyclohexane chair right. So, that is how it should be. Okay.

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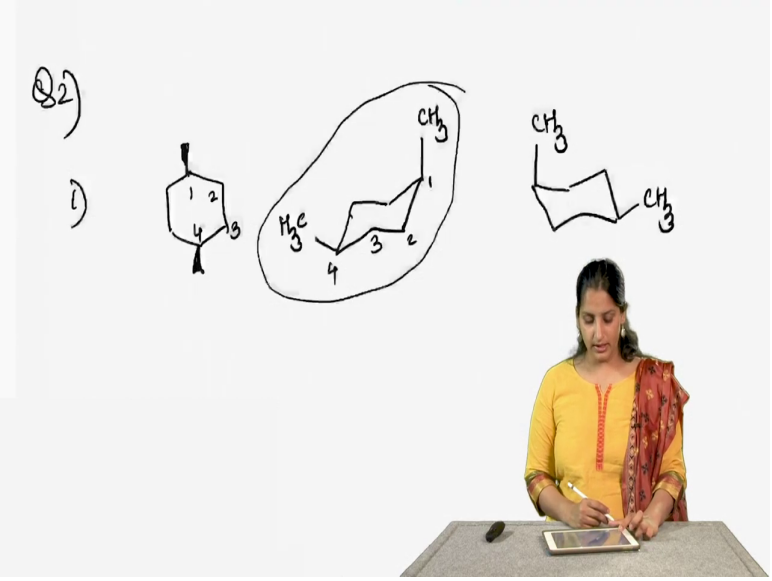

Now, the question number 2 gets a little tougher what it asks you is that, it wants you to draw the most stable chair conformation of the following dash and wedge structure. So, the first step we need to do is we need to first convert the dash and wedge structure to the corresponding chair structure. So, let's look at the first one, now in this case you have a cyclohexane that has two methyl groups going in the same direction that is coming towards you.

Let us number are initial cyclohexane so, I have substituents on 1 and 4 positions. Carbon number 1 has a methyl going up, so I am going to draw a methyl going up here, and I have carbon number 4 also with the methyl going up okay. So, this becomes the chair of the corresponding dash and wedge structure. But is this is the most stable chair? What we do is we draw the chair flip and we figure out if it is really the most stable chair.

So, if I have to draw a chair flip, I know that carbon number 1 will shift to equatorial and carbon number 4 will shift to axial, right. If you really see both of them have equal stabilities because one group is axial and one group is equatorial and both of the groups are methyl. So, really difficult to predict which one is which rather both of them are going to have equal stability. So, you can really draw either one of these as your answers, right.

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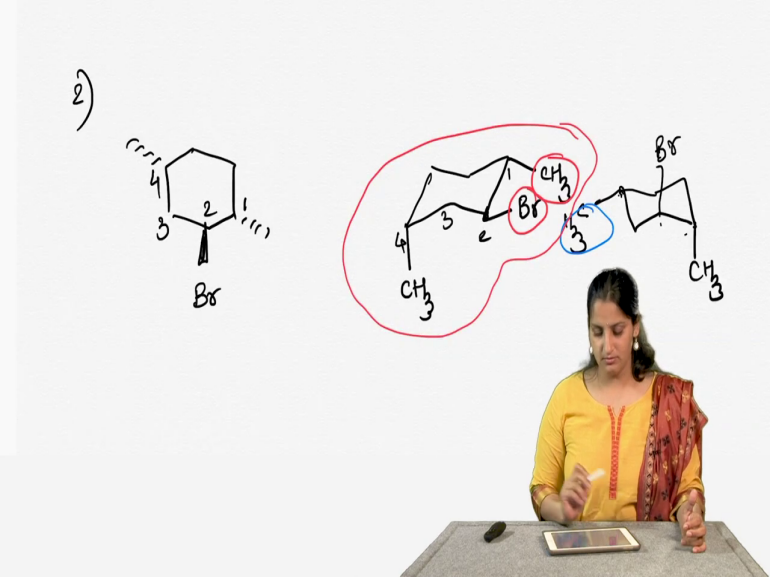

Let's go to the next one, the next one we are going to do the same thing we are going to start numbering; we will start numbering it from here 1, 2, 3, 4 and on our chair I am going to draw the same numbering. Now on carbon number 1 the methyl group is going down, the group that goes down on carbon number 1 is the equatorial down group.

Remember because the head always points high the group that goes up is axial group on carbon number 1. So, the down group is equatorial group. On carbon number 2, the group that goes up here is bromine. Again, look at this particular carbon here the group that goes up on this carbon is the equatorial up group that will be the bromine the other group goes axial down, right. And on carbon number 4; 1 2 3 and 4 the group that goes down is a methyl group; now on carbon number 4, the group, the position that goes down is actually axial down so, that will be the conformation. If I do a chair flip of this, methyl will go axial down here, bromine, 1 2, bromine will go axial up and this methyl will go equatorial down.

If I see this first chair has a bromine and a methyl equatorial where as the second chair has 1 methyl groups equatorial. Now bromine if we really look at the A value the size is quite big right. So, this particular the first one is gonna be the correct answer, let's go to the next one.

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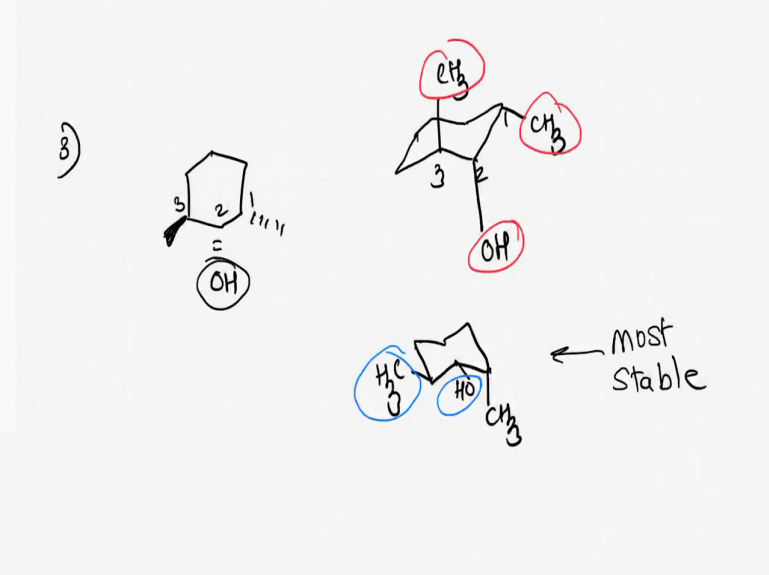

The next one we are going to do the same thing first draw the chair, number are carbons 1, 2, 3 and the first one is going down; the methyl group is going down on carbon number 1. So, here the down group on the first carbon is an equatorial group so, it goes down.

The OH is going down in carbon number 2 here, the down group on carbon number 2 is an axial group. So, it goes down here and the methyl is going up and the methyl will go up here, okay. So, we have drawn the correct representation, but we don't know if it is most stable or not. So, let's draw the chair flip, what I have here is, this becomes my carbon number 1 methyl will go down, OH will go equatorial down and the other methyl will go equatorial up.

If I see this, there is a methyl equatorial, there is a methyl axial and there is an OH axial whereas in this case you have a methyl equatorial and an OH equatorial which really favours it, right. So, in this case this will be the most stable conformer, okay.

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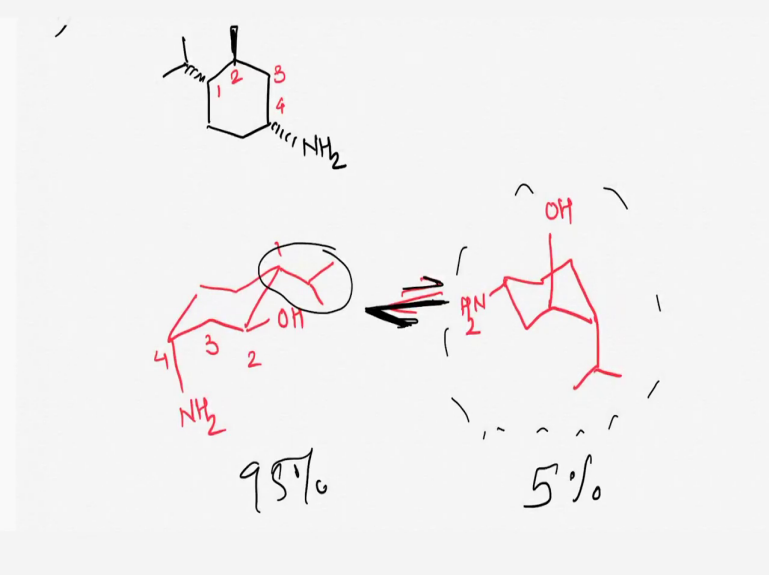

So, for the next one it is asking you to first convert this corresponding dash and wedge structure to the chair structure and then it is asking you to draw the chair flip, and later it wants you to find out what is the Keq for the flip right.

So, let us go step by step, let's first draw the corresponding chair. If I draw the chair for this one, then I have an isopropyl group going down on carbon number 1, OH is going up on carbon number 2 and on carbon number 4, NH_2 is going down so, NH_2 is here. When this chair flips right what do we have? The flip will look like this, okay. So, this is how the flip looks like. Now my first job is to figure out whether this is gonna be an equilibrium happening as these two chairs are flipping with respect to each other.

Remember that in this case we have an isopropyl group that is going equatorial. So, it is going to be much more preferred it is a very bulky group it is going to be much more preferred in the equatorial position and so, this equilibrium is rather shifted towards one side such that more often if I click a picture of the molecules. I will see more number of molecules in the first conformation that is the left hand side conformation than the right hand side conformation, okay. But our job is to calculate the percentage of molecules that exist in the least stable conformation. So, how many molecules are really in this particular conformation that is the question. In order to do that we need to look at the $\Delta G°$ values for going from axial to equatorial.

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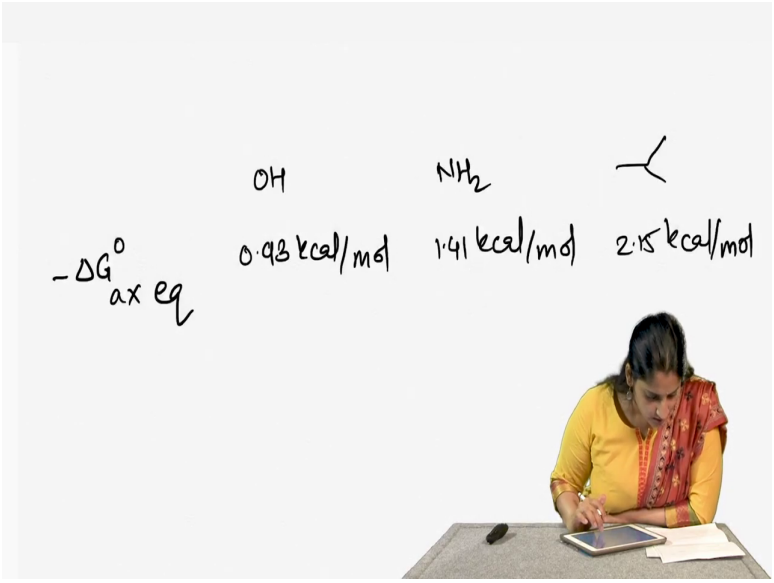

So, if I look at the table that is given, the minus ΔG° value going from axial to equatorial for the OH is 0.93 kilo calories per mole and NH_2 is 1.41 kilo calories per mole and the isopropyl group is 2.15 kilo calories per mole right. Okay, now we know that as this flip is happening, it's a, not all groups are going from axial to equatorial in fact, the isopropyl group is going from equatorial to axial, we know that the OH is going from equatorial to axial, but NH_2 is going from axial to equatorial. So, what we are going to do now is, we are going to sum it up because ΔG values can be additive in the sense we can add all of these values to really figure out the ΔG value for the total flip.

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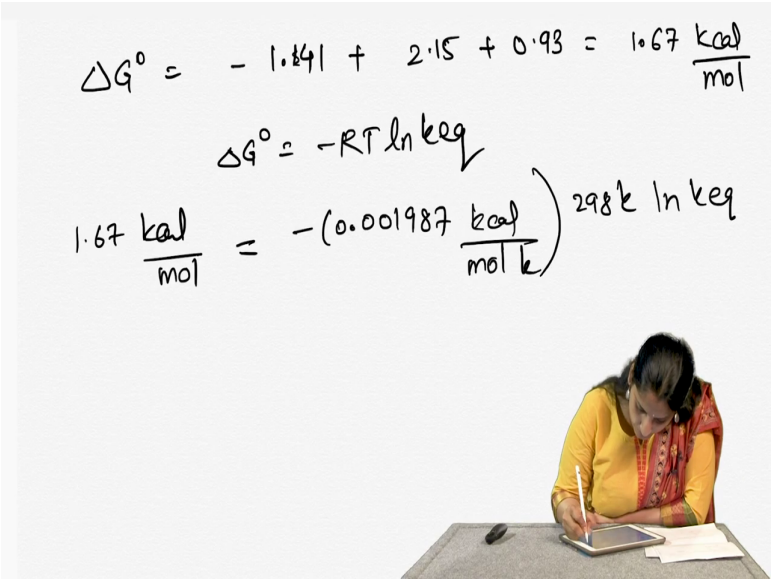

So, if I do the ΔG° calculation,

$\Delta G^\circ = -1.41 + 2.15 + 0.93$ (minus 1.41 because NH_2 is going from axial to equatorial)

So, the total ΔG value for this flip is

$\Delta G^\circ = 1.67$ kcal mol^{-1}

Now, we apply the equation, $\Delta G^\circ = -RT \ln K_{eq}$ and figure out the value of Keq. So, here in if I substitute all the values,

1.67 kcal mol^{-1} = - 0.001987 kcal mol^{-1} K^{-1} **X** 298 K **X** ln Keq

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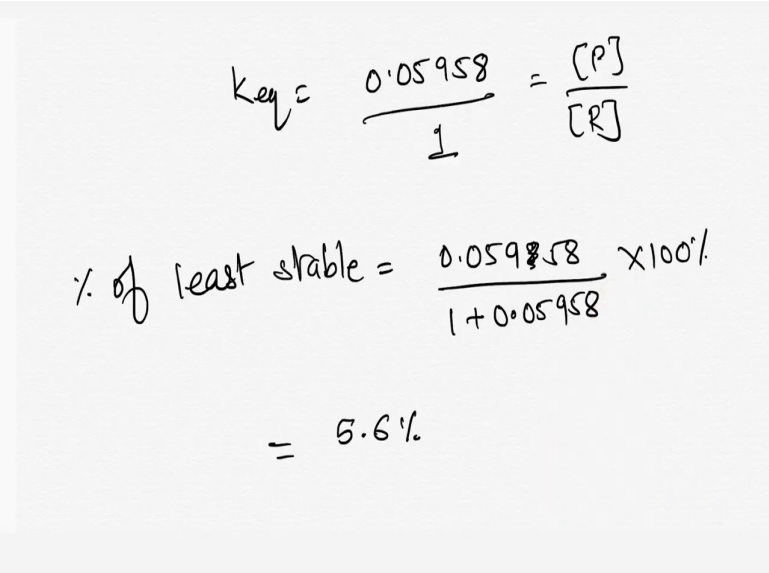

So, if I figure out the value of Keq, it comes out to be 0.05958, right.

Keq = 0.05958

But we also know that Keq is nothing but concentration of products over concentration of reactants, right and this is let's say that this is divided by 1, then if the concentrations of the products is 0.05958, the corresponding reactants have a concentration of 1, right. So, when we look at the percentage of the least stable chair, right, because our least stable chair is actually our product chair. So, that becomes

% of least stable chair = $\frac{0.05958}{(1 + 0.05958)} \times 100\%$

that is because we take the component divided by total, total is 1 plus 0.05958. So, the answer comes out to be around,

% of least stable chair = 5.6 %

So, if I really look at this chair flip, 95 percent of the molecule around are going to be in the first conformation whereas, only 5 percent of the molecules will be in the second conformation. So, you can imagine that just to put that isopropyl group in the equatorial position, what the molecule wants to do is it wants to be in the first conformation rather than the second one.