Introductory Organic Chemistry
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Lecture - 14
Chirality and Stereochemistry
Part - 1

So, today we are going to talk about Chirality and before we early go ahead and learn what chirality is we are going to hear a story. This is a story of a chemist name Frances Kelsey, she was a chemist in FDA in the United States of America and a drug was launched in around 1950's to 1960's in the European market by the name of thalidomide. The drug was used to reduce morning sickness or nausea in the pregnant women and was being popular in the European countries as well as Canada.

And the drug company also wanted to sell the drug in the US and they were forcing kind of trying to pressurize Frances Kelsey to give the FDA approval. So, they were trying to get her to approve that the drug was safe for pregnant women.

However, despite of all the pressure she refused to except that the drug was safe and she kept denying their requests saying that more information was needed to claim the drug to be safe and very soon she was proven right. Reports soon started coming in from Europe and Canada of babies being born with lots of birth defects and without limbs. Some of them missed some body parts and turns out the thalidomide that the mothers took during their pregnancy was responsible for causing these birth defects in more than 10,000 babies.

So, what really happened, how can the drug molecule turn out to be kind of a poison for these babies? Turns out the thalidomide exists as two different molecules which are 2 different enantiomers. So, we will look at what enantiomers are, but before that if you look at this molecule closely here.

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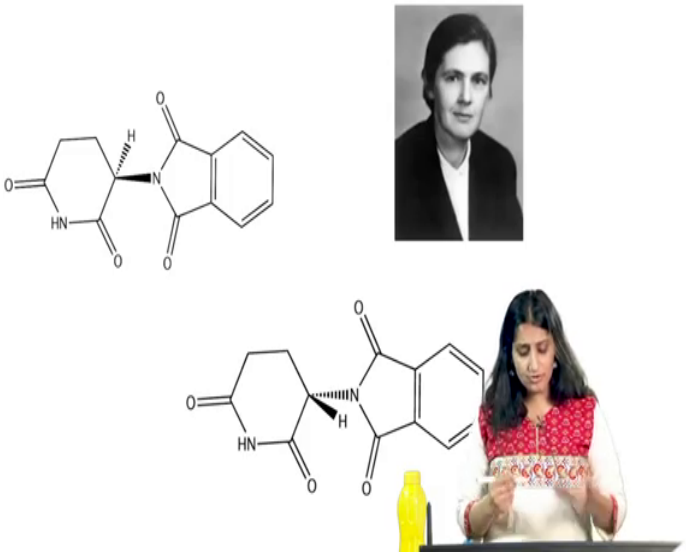

If you look at this particular carbon, now that carbon has 4 different attachments. It has a hydrogen, it has a nitrogen attach to it and if you look at on these two sides of the ring, have different attachments to it. So, you can imagine that this particular carbon can form these 4 bonds such that they can be arrange differently in 3 dimensional space.

So, you can imagine that in one case you have the nitrogen coming towards you which is what we have drawn or you can also draw it such that, the nitrogen can go away from you. So, this is what the 2 molecules really can look like. In fact, these two molecules are called as enantiomers of each other because if you really see they, both of them, are mirror images of each other and they are non superimposable mirror image.

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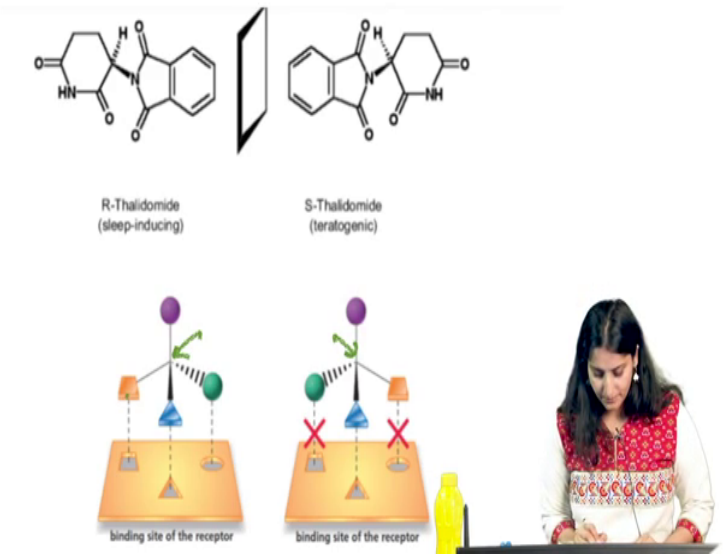

So, here I have drawn the R - thalidomide which has the mirror image of S – thalidomide. Now, what happens is that the drug binds to receptors in our body, whenever we take a drug our body is going to have some receptors that bind to it. As you can imagine one of the molecule binds to the receptors. So, for example, the R thalidomide will bind to the receptors whereas, the S will not bind. And, what was happening is that the S-thalidomide was actually targeting some other receptors in the body resulting in the birth defects that were happening in babies.

So, when doctors prescribed thalidomide they were not aware that thalidomide was existing as a mixture of 2 compounds that resulted into two different results, as you can see the R was the right drug and S was the poison for the babies. Frances Kelsey won the President's award for stopping the sale of Thalidomide in the US. So, for her sheer determination of not approving or not succumbing to the pressure that was put by the drug companies, she actually won the President's award and her work was applauded worldwide.

So, as you can see in this particular figure you can see that I have a pair of enantiomers which are mirror images of each other; as you can see this is the chiral carbon in each case. Their mirror images, they have 4 different attachments and if I look at a binding site of a receptor you can see that as I try to fit one, such that all of them match; I cannot do the same thing for the other. If you can see in these two cases there is no matching, right? So, as you can imagine enantiomers cannot bind to the same drug receptors if the receptor itself has chirality or the receptor itself has some asymmetry that requires a particular enantiomer to bind to it.

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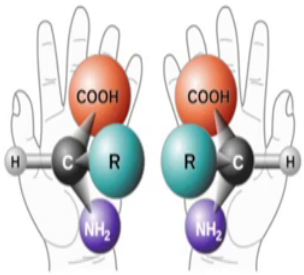

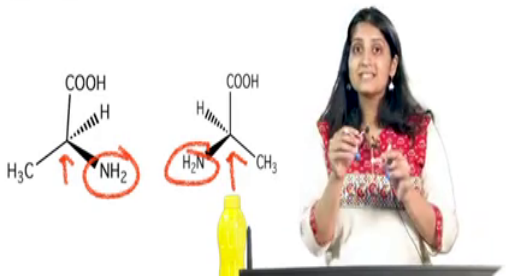

This incidence caused a global awareness on the properties of molecules called as chirality. So, now, let us look at what is chirality. So, here I have a molecule, here, it's Alanine or in fact, it is one of the amino acids. Now if you notice here we have a chiral carbon and if you see that carbon has 4 different attachments, the dash is something that we say goes away from us and the wedge comes towards you. So, in this case the NH_2 groups are coming towards me and the hydrogens are going away.

One of the things I want to point out about these chiral carbons, sometimes you will also see them refer to as stereocenters. Now something about this stereocenters; remember, carbon, a tetrahedral carbon is a stereo center if it has 4 different attachments to it. So, here I have for example, this is one of the chiral centers and it has 4 different attachments: a blue, green, red and a white sphere. If I look at its mirror imagine, which is, let me just create a mirror image. this is the mirror image, right?

If I want these two molecules to superimpose on each other there is no way, I can do that. So, anytime I try to combine such that 2 of the colors overlap. So, let's now overlap the white and the green. So, these two are overlapping, but as you can see as I overlap the white and the green, the blue and the reds don't match. On the other hand, if I try to really overlap the blue or the red, the white and green won't match. So, there is no way for if I have chiral center or a pair of enantiomers really I cannot superimpose them such that they directly superimpose on top of each other such that all 4 groups match with each other.

One of the things I want to point out is that if you have less than 4 different attachments. So, here for example, in this molecule I have the central red carbon has 3 different attachments. So, you have a blue, a black and 2 of the white spheres. So, this particular carbon is not a chiral carbon, because it has 3 different attachments and if I look at its mirror image. So, this is a mirror image or its enantiomer if you want to call it, but I can easily superimpose them such that all the colors kind of coincide with each other. So, you can see that the blue and the black match as well as the 2 whites match.

So, if I want to have a pair of enantiomers they should be non-superimposable and they should be mirror images of each other, such that you cannot lift one of these mirror image put it on the other and cause a perfect superimposition. So, now let us look at what are these chiral carbons or what are the chiral centers, so as I said sometimes we also call them as stereo centers. So, one of the ways for a molecule to be chiral is to have a stereo center, a stereo center is an atom or a group of atoms sometimes that can potentially cause a molecule to be chiral.

Now, stereo centers can give rise to chirality. So, please remember what I am saying here I am saying they can give rise to chirality, they are not only condition that is necessary to give rise to chirality and in fact, in the next class we are going to look at some of the examples wherein there is a stereo center, but the molecule is not chiral or a molecule is chiral, but does not have really a tetrahedral carbon.

So, stereo centers can give rise to chirality. We just looked at enantiomers and enantiomers are a pair of stereoisomers. So, I also want to talk about one more term here; we looked at constitutional isomers which were of the same molecule that they have the same molecular formula, but different structural formula. Then we also looked at conformational isomers which can be interconverted into each other through a rotation of single bond.

Now, here we are looking at one more set of isomers these are stereoisomers and stereoisomers cannot be interconverted into each other through a set of rotations. For example, here I have a pair of enantiomers right the same pair that we looked at and I cannot interconvert this to this through a simple bond rotation. If I really have to interconvert this into this what I will have to do is, I will have to break a bond and reattach a bond too, in order to go from one of the enantiomers to the other. So, you cannot interconvert enantiomers just like that from one to another, you will have to break and make a new bond.

So, stereoisomers are the same constitutional isomers, but they differ in the way they are arranged in a 3 D space. So, their molecular formula, molecular weight is exactly the same, but they differ in the way they are arranged in the 3 D space around the atom.

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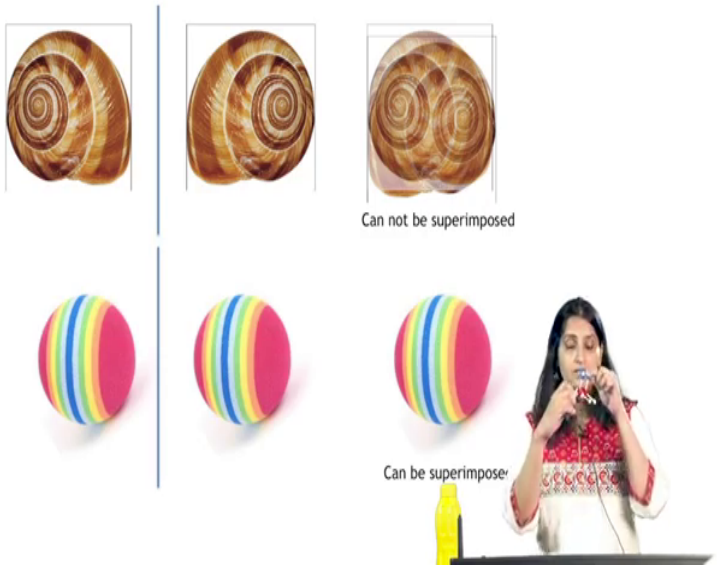

So, as we said having a stereo center does not make a molecule chiral; chirality also needs lack of symmetry. As you can imagine a symmetric object has a plane of symmetry in it. So, for example, here I have a pair of spectacles in, they do have a plane of symmetry such that one part of the object matches with the other part of the object, right? Such that this particular object itself is symmetrical or for that matter this water bottle is symmetrical such that you can have a plane of symmetry that goes through the water bottle and in fact, the object is symmetrical, you will see that it is not a chiral object.

On the other hand, if I look at my keys here, right as you can see this particular key does not have plane of symmetry I cannot create a plane such that the 2 parts exactly match with each other. So, it is possible for this particular key to have an enantiomer which is its mirror image and which is non superimposable. If you look around you will find many objects that are non-superimposable mirror images, one of them are your pair of hands. So, my two hands are non-superimposable mirror images of each other. So, I have to lift one place and then put it on this as you can see I cannot create a superimposition, perfect superimposition, for my two hands.

So, as we saw that symmetric objects have a plane of symmetry and they can be superimposed on to each other. In fact, if you remember these, this molecule it has a plane of symmetry, right? If you draw a line here you can see that this half of the molecule is the same as the other half of the molecule so, they can be easily superimposed, right? So, the molecules that have a plane of symmetry can be easily superimposed whereas, the ones that don't have the plane of symmetry it is very difficult to create the superimposition. And this property of asymmetric objects to give rise to the fact that they cannot be superimposed really gives rise to chirality.

Okay, so now, let us look at how to name these molecules because if we have two separate set of molecules, we need to be able to identify them and we need to able to name them. So, now, we are going to look at the Cahn-Ingold and Prelog's rules in order to name enantiomers.

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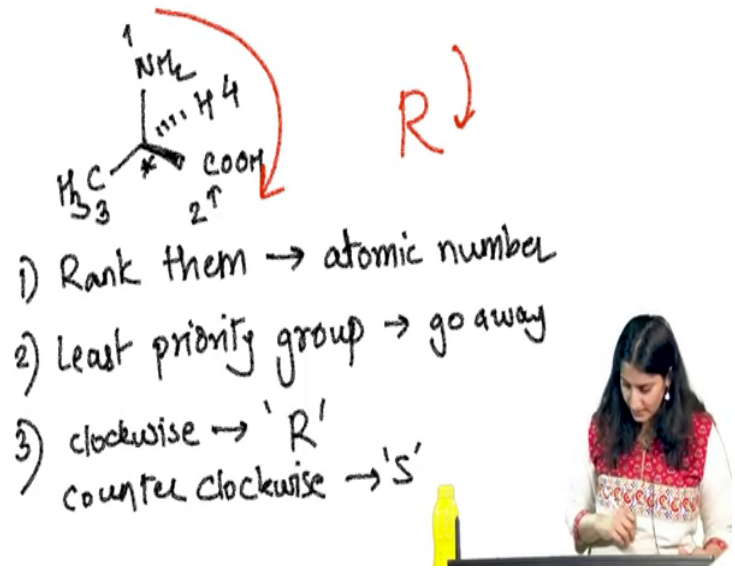

So, let's start with R-Alanine. So, this is one of the molecules right and I want to now name it. Now the rules go like this, the first rule is that we first locate the chiral carbon. So, this, in this case it is very easy this is the chiral center. You will see that many a times it is represented with an asterisks. So, here in you can see that the asymmetric center is attached to a nitrogen, a carbon, a carbon and a hydrogen. After this, what we are going to do is, we are going to number them such that we are going to number them based on the atomic number. So, the highest atomic number gets the first priority and the lowest atomic number gets the

last priority. So, we are going to number them. So, we are going to rather rank them, not number them, so rank them accordingly, according to their atomic number, right?

So, in this case for example, Nitrogen has the atomic number 7 so that will be the first priority, now I have two carbons, right and in any case both the carbons have the same atomic number. So, I cannot differentiate so, what I do next is I look at the next attachment. So, for example, this carbon here is attach to an oxygen, oxygen and a hydrogen, right? So, this particular carbon has a double bond to one of the oxygen and a single bond to other oxygen whereas, this other carbon here has just a attachment to three other hydrogens. So, then this particular carbon gets the second priority and then this the other carbon, the methyl carbon, gets the third priority; hydrogen as you can imagine will get the fourth priority.

Now, once you have ranked all the attachments to a chiral carbon what you are going to do is, we are going to arrange these or look at the molecules such that the least priority group goes away, okay. So, this is one of the key steps. So, the least priority group should go away from you. As you can see the dashed representation means the hydrogen is already going away from you and then what we do is, we look at how the other three groups are going. So, for example, in this case if this is the hydrogen, I make it go away from you and then you look at how these priorities are either are they clockwise or they are counter clockwise.

If they are clockwise; if they go clockwise then in fact, you are going to ;have them; have to call them R which stands for Rectus and if they are counter clockwise then they will be called as S for Sinister. Now, one quick way let's figure out whether first of all this alanine is R or S as you can imagine in this case we have labeled our priorities. So, this is moving in this particular fashion so, this is going clockwise so, this is R.

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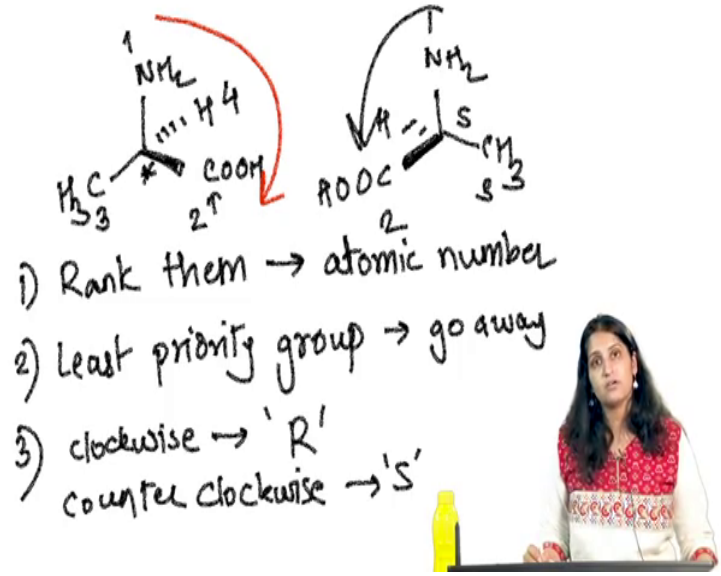

If I look at its mirror image. So, let me draw its mirror image here. So, again 1 2 3, if I look at the mirror image then it goes in the opposite direction, right? So, it rotates in the opposite direction and that will be the S stereoisomer, okay. One good quick way to remember what is R and what is S, sometimes people tend to forget what is clockwise and counter clockwise.

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So, here is a quick way to remember when I write R my hand moves in the clockwise direction first and when I write S my hand moves in the anti clockwise direction first. So, this is a very quick way to remember what is R and what is S. Okay, so, I am also going to show one or 2 more tricks to really identify, how, whether a stereo center is R or S. So, let us go forward and let us look at some of the tricks.

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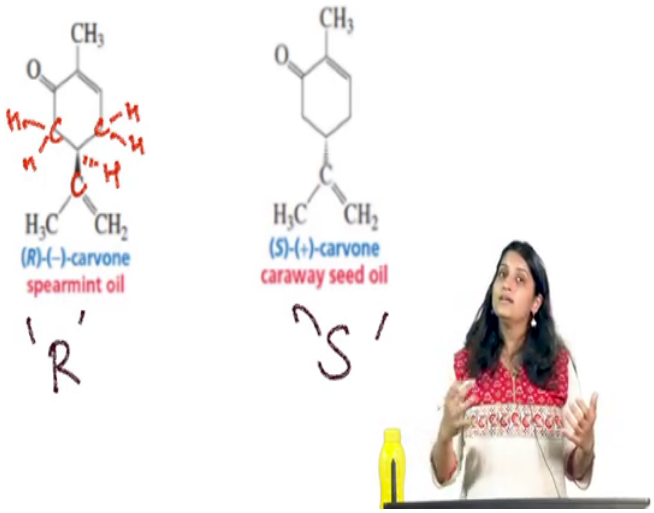

The next example I want to solve here is this particular molecule which is carvone, now they have already solved it, but let me go over the example again. Now carvone is actually a natural product and carvone is found in spearmint oil and it is also found, its enantiomer for that matter is found in the caraway seed oil.

So, now let us try to solve whether this is really R or S, let us try to verify. Now in this case remember they don't draw the hydrogen. So, in this case we do have a hydrogen that is going away from us and the carbon is coming towards you. So, now, let us try to arrange them on the basis of priority.

If I really look this carbon is attached to three carbons and a hydrogen, right? Let us also draw the attachments to these carbons so, that we can make it very very evident here. Now, in between these 3 carbons which one should really get a higher priority and for that what I am going to do is, I am going to draw the molecule again.

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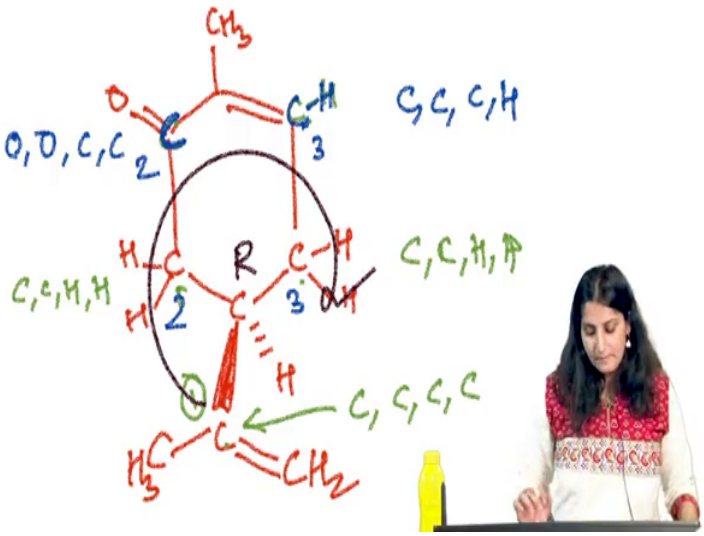

So, now, let us try to rank the attachments to this particular carbon, as you can see you have 3 carbons, the first carbon here has 2 attachments carbon, carbon, hydrogen, hydrogen. This carbon also here has attachment such as C, C, H, H this carbon here for example, has attachments C, C, C, C. So, that is a carbon that is attached to all 4 carbons. So, between in the first try when we look at C, C, C, C versus C, C, H, H this one clearly win so, this win will get the first priority.

Now, to determine the priority order between the second and the third carbon; now let us look at it again. Now we have C, C, H, H. If you are ever stuck at a point where in the attachments look exactly the same what you do is you proceed forward. So, you can kind of imagine like you are walking on the road at any point if you come to a point where you see all the 4 attachments are same, what you do is you further walk along one of the attachments and see if you find a point of difference, okay.

So, here in what I have is this particular carbon versus this carbon; if I look at the attachments here, this particular carbon here; I has the attachments oxygen; it is again attached to an oxygen so, O, O, C, C. So, whenever there is a double bond you write that bond twice because it is making 2 bonds with that right. So, it is this particular carbon has attachments of O, O, C and C whereas, in the other case you have the attachments of C, C, C and H. Now between oxygen and carbon, oxygen wins so, this one will get a second priority, this one will get a third priority. So, likewise this will be 2 this will be 3.

Now, what is our next rule? We have to orient the molecule such that the least priority group goes away from us and in this case you have the hydrogen going away from you indeed. So, in this case the molecule is showing you an R orientation so this is in fact, R- Carvone. So, that is right; and whereas, its mirror image which is present in the caraway seed oil is S-enantiomer.

So in fact, you much have smelled these two molecules one of them is the spearmint which is a very minty smell whereas, the other one is caraway seed oil, now caraway seed oil in Indian context we call it as the saunf, right? And you will remember that these two actually smell very differently. Now one question to ask is if they are really very similar to each other the same molecular formula why do they smell differently is because your nose has receptors that bind particularly to the one and not to the other and in the case of caraway seed oil you have different receptors binding. So, what happens is our receptors are chiral so, we smell differently, okay.

So, now let us look at a couple of other examples and as I said I am going to show a couple of tricks to get to the answer very quickly while naming R and S.

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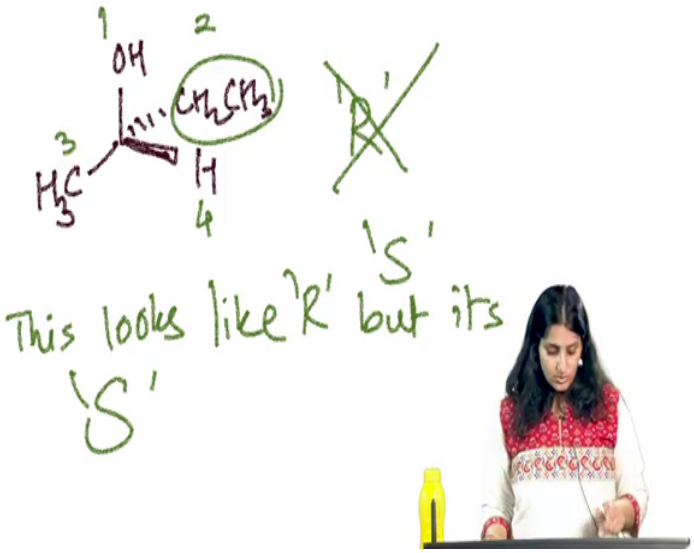

Here in let us draw one molecule I have this particular molecule here, now this is 2- butanol, okay. So, what we are going to do is, we are going to label it such that it is R or S. Now it is very easy to figure out the priority order in this case oxygen gets the first one, then this CH_2CH_3 group will get the second one and then this group will get the third one and the

fourth hydrogen as you can see is coming towards you. Now, whenever you have a molecule in which the least priority group is coming towards you of course, you can try to imagine it from the other side such that you can think that the hydrogen is going away how would the molecule appear to me and then try to figure out the answer.

But, one of the quick ways to come up with the answer is you solve the problem imagining that the hydrogen is going away from you. So, in this case this looks like R right, but in fact, I have violated one of the rules and the hydrogen is coming towards me so, it is not R and it is S. So, whenever I see a least priority group coming towards me what I think is this looks like R, but it is S or vice versa. If you get an answer of S then the real stereo center is really R, okay. So, whenever the least priority group is coming towards you just switch the answer; that's what the trick is.

Now, let us go to the next one, now let us look at the scenario when the least priority group is in the plane of the paper. This is going to be a little tricky because when it is in the plane of the paper it becomes difficult to imagine such that the least priority group goes away from you, right?

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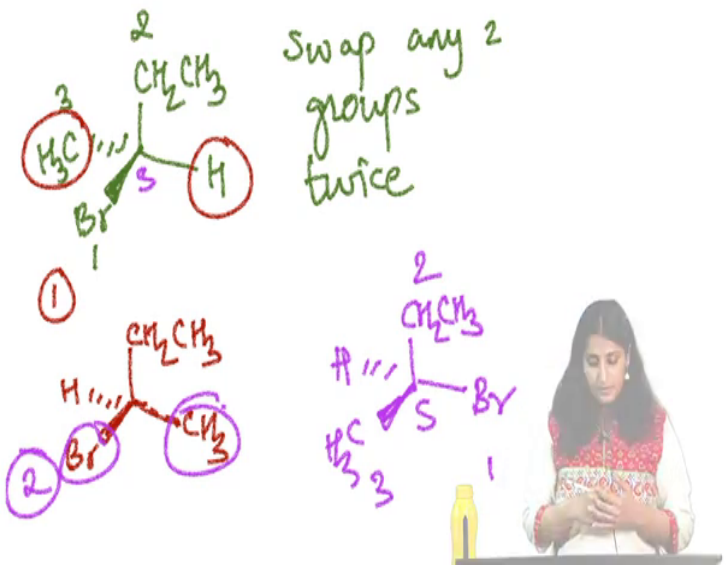

So, now I am going to draw a molecule here right. So, this is 2-bromobutane; now let us try to figure out whether this is R or S. As you can see the hydrogen is in the plane of the paper. Now, again what you do is you prioritize; so this is 1; bromine gets the first priority, the ethyl group gets the second, the methyl group gets the third so, we are good to that part. Now in

order to get the hydrogen such that it goes away from me what I am going to do is, I am going to swap any 2 groups twice. Okay, so this is important. Swap any 2 groups twice, okay.

I am going to first swap; so, in my first swap I am going to swap hydrogen and methyl such that the hydrogen goes away which is what I really want. That is my first swap and now that the hydrogen is away from me I can figure out the configuration, but remembered we have to swap twice. So, right now if I get the answer the answer will be wrong. So, what I am going to do is, I am going to swap it again such that I am going to let's say swap between bromine and methyl so, that is my second swap. So, what do I find; I will make methyl come here and hydrogen going away from you; CH_2CH_3 and then bromine.

Now, solve this particular molecule using our regular rules. So, 1 2 3 it moves like S and this is S. So, since the stereo center after two swaps is S, the stereo center in the original one has to be S, okay. So, as you can imagine whenever you have the least priority group in the plane of the paper the trick is to swap any two groups twice it would be great if you can get the least priority group going away from you so, that you can easily solve that question.

So, there are many chiral molecules in nature and one of the reasons chirality is so important to us is that most of the natural products or derivatized drugs or medicines are chiral in nature and when they, when we take them as medicines most of the receptors in our body; drug receptors, enzyme receptor, bindings sites are all chiral in nature. So, chirality is very important study in order to come up with, say for drugs or say for medicines for that matter.

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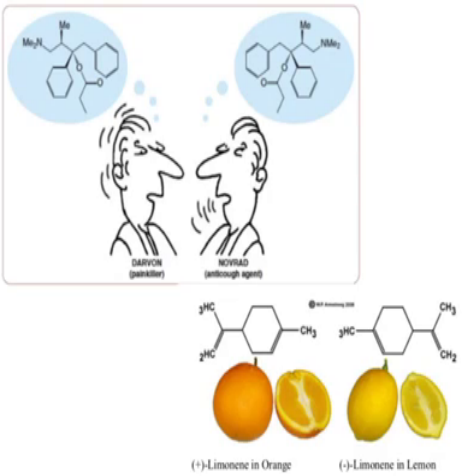

Now, here I have some of the examples of the chiral molecules that we find in nature, one of them is actually something called as Darvon so, this is one of the drugs that is used as a painkiller and in fact, it is mirror image called as Novrad; so, Darvon's mirror image is Novrad is actually used as an anti cough agent. So, two different enantiomers are used as medicines, but in a different way, right? So, or you can really see here I have (+)- Limonene, right.

So, if you really see this particular carbon here is the chiral carbon, right and these; this carbon gives rise to the chirality in limonene and limonene is really present either in oranges or in lemons and the reason why you smell these two things different is that because each of these have a different enantiomer present in them in majority.

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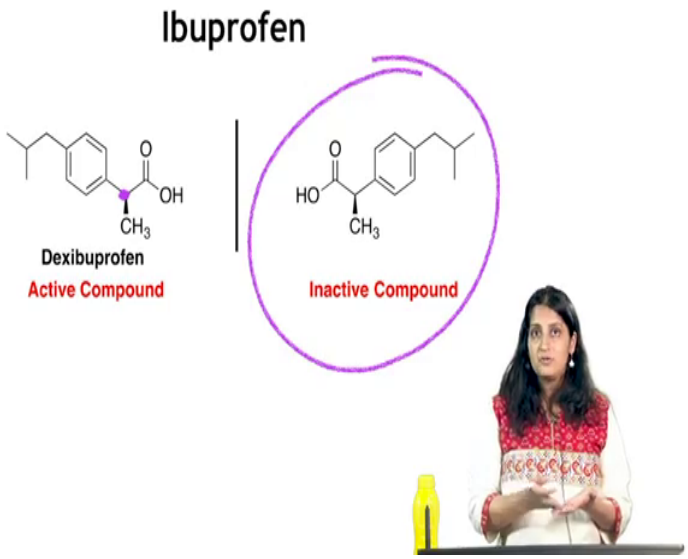

Here is one more example so, all of us must have taken Ibuprofen as a pain reliever or for fever sometimes in our lives and unless you are really allergic to Ibuprofen, but if you really look at the molecule of Ibuprofen what you will see is that it has a chiral center again and only one of them is actually active; in the sense only one of them will really act as a medicine for the pain relief. So, the Dexibuprofen is actually the pain reliever or really the active molecule whereas, if you look at its enantiomer, this one here, it's not really active and it's going to really not do anything.

So, when drug companies have to sell their drugs into the market they first have to go through thorough checks and in the case of Ibuprofen what happens is that it is sold as a mixture of

two enantiomers, one of them is active the other one simply does not do anything to or does not cause any harmful effects. In the case of thalidomide, if you remember, Thalidomide was not safe because the other enantiomers caused adverse effects. In the case of Ibuprofen, the other enantiomer does not really do much, in fact, our body has an enzyme that converts this Ibuprofen the inactive form to the active form. So, we do have racemases which racemize the Ibuprofen in order to convert the inactive to the active form.

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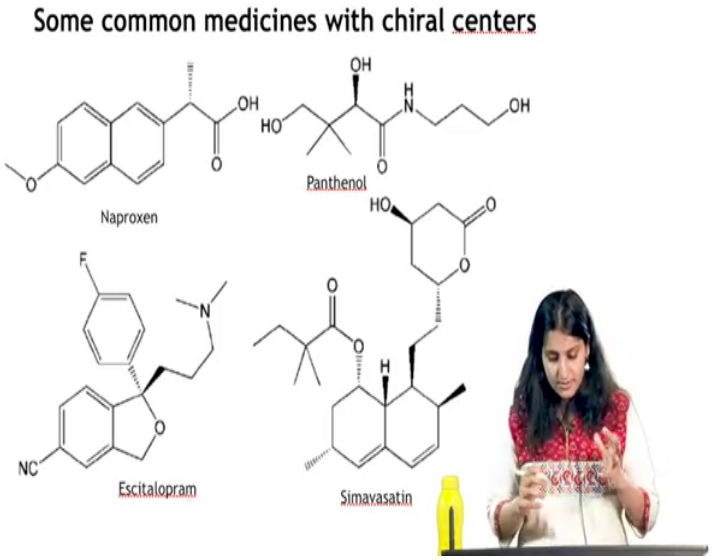

Herein I have some more common medicines with the chiral centers. Try to look at all the drugs that are there in the market, try to look at where the chiral center is and name them as R or S. So, for example, you can very well take this slide and try to figure out whether each of the centers in each of these drug molecules is R or S; try to name them. So, Naproxen here is used to reduce swelling or is used as a pain reliever, Panthenol is actually pro-vitamin B5. So, you must have heard the ads for pro-vitamin B5 and that is really going to act as the pro-vitamin drug. Then you also have the Escitalopram this one here is used to treat anxiety or depression, fourth one here Simavasatin is actually used to treat the patients with heart diseases.

So, as you can see most of the drug molecules in the market today are chiral in nature. In fact, I am going to say some of the other names that you must have heard which are really chiral in nature. So, cholesterol, cocaine, morphine, then you have sucrose, glucose, most of the sugars, most of the amino acids are all chiral in nature. Progesterone, estrogen all of these

molecules are going to have some, one or the other chiral center in their structure and that's why the study of chirality or the study of the properties of molecules to orient their attachments differently in a 3 D space is so important.

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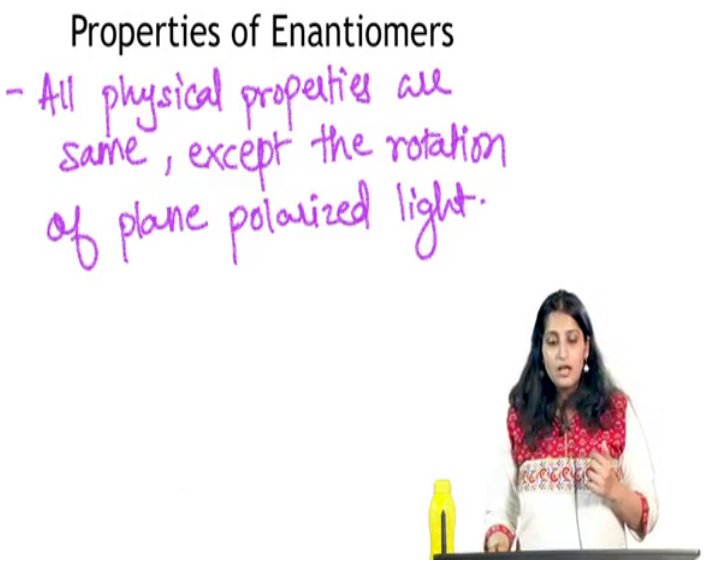

So, now let us think about the properties of these enantiomers. So, we have looked at set of molecules that are mirror images of each other, that are non-superimposable, but what are their properties? One of the key point to note here is that they are pretty much the same except their arrangement in 3 D space. So, enantiomers have the same physical property so, they have the same melting point, the same boiling point, solubility refractive index pretty much all other properties that you can think about; the properties are going to be very similar; all the physical properties are going to be very similar for the two enantiomers; in fact, they are quite the same.

However, the enantiomers differ in only one property and that is the degree to which they rotate the plane polarized light, okay. So, I am going to write here that pretty much all physical properties are same except the rotation of plane polarized light, okay. If I take a pure R enantiomer of a compound that will rotate this particular plane polarized light in one direction whereas, the pure S enantiomer of the same compound will rotate the plane polarized light to the other direction and if I really take a mixture of these two then kind of, or rather an equal mixture then I would not see any rotation of the plane polarized light.

The instrument which helps me really determine this rotation is called as a polarimeter. So, now, let us look at polarimeter and what polarimeter does is this particular diagram.

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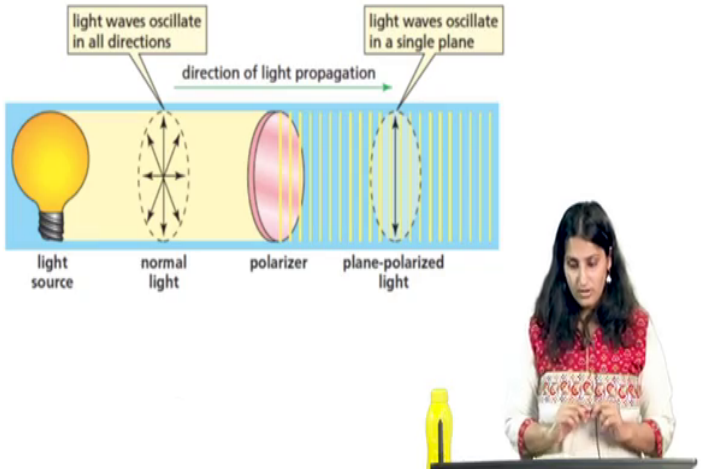

So, there is a light source and as you know that light travels in all directions. So, light waves are going to oscillate in all directions and you have the normal light and then you have something called as a polarizer. So, this polarizer is going to give you the light waves that are oscillating in only one direction. So, it polarizes light and you only have the light waves going in one direction.

Now, these light waves what they does, is they pass these light waves that are going in one single plane through the sample and as these light waves passed through the sample what is going to happen the sample, because the molecules have some kind of handedness, the sample then rotates this plane polarized light such that it either rotates it towards one direction or the other, okay. So, the polarized light will then rotate after it passes through the sample chamber and the analyzer will then detect whether the light has rotated counter clockwise or clockwise such that you have a detector.

Now, using this instrument what we can really figure out for any pure enantiomer is it is specific rotation. So, what we are going to now see is, what is specific rotation.

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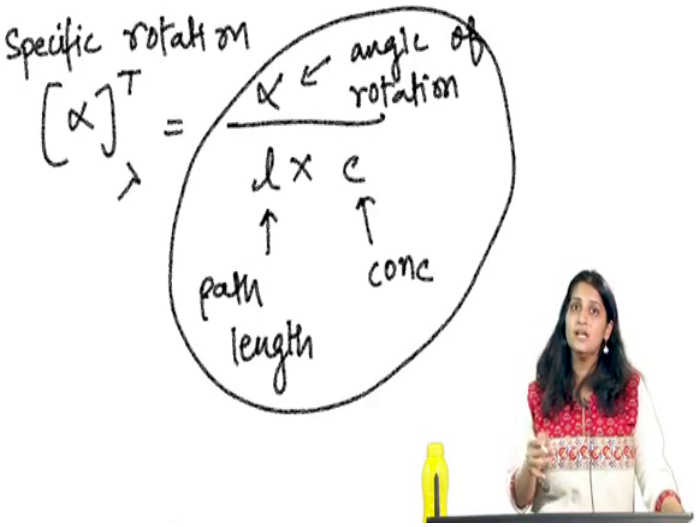

So, specific rotation alpha at a particular wavelength and at a particular temperature is equal to observed rotation over length of the samples l into the concentration in grams of the substance in 1 ml of the solution so, this is my concentration. So, let's say that I have a sample what is the concentration of the sample? l is the path length. So, the path length traversed by the light such that before it comes out of the sample and alpha here is the angle of rotation that I measure in degrees and whereas, alpha at a particular wavelength or the specific rotation is going to be thus given by,

$$[\alpha]^T_\lambda = \frac{\alpha}{l \times c}$$

So, polarimetry is an important technique in fine chemicals or pharmaceutical industries to assess the identity and purity or the quality of the compounds. So, let's say that I want to market a particular medicine, particular drug molecule. I would have to prove that it is very pure such that the impurities cannot lead to any side effects. Now, in order to show the purity one of the ways to do it is of course, the purity of the molecule itself, but we also have to prove that the molecule is not existing as a pair of enantiomers and whether I have a pure enantiomer you have to test it using polarimetry and show to it that the plane polarize light is only rotated in a single direction.

So, polarimetry is specifically used for the measurement of optical rotation of chiral compounds which can be used to distinguish the identity of two enantiomers, whether I have R or S can be determined using polarimetry, but remember polarimetry is just telling me is

that whether the light is getting rotated towards the right hand side so, it is also called as dextrorotatory or l which is the laevorotatory. So, when I take a sample put it in the polarimeter all I get to know is whether it is dextrorotatory or laevorotatory. I want to mention that this is nothing to do with R or S; d or l notation do not correlate with R or S meaning, d does not mean R and l does not mean S, okay. I can have a compound where in the R enantiomer rotates the plane polarized light towards right whereas, for some other compound I can have the S enantiomer rotates the light towards the right hand side. So, please do not correlate these two, okay.

What is true is that if I have a particular enantiomer and if it rotates the plane of plane polarized light towards one direction, then its counterpart which is the other enantiomer will rotate the plane polarized light towards the other direction and that is all. So, I do not get to know whether the molecule is R or S using a polarimeter, I just get to know whether it rotates the plane polarized towards right or left. Then how do people find out what is R and what is S? So, given molecule how do we come to know whether the particular compound exists as R or S. The technique used for that is actually crystallography so, you have to make a crystal structure of the particular compound, subject it to the crystallographic analysis and crystallographic analysis will tell you whether the molecule is R or S.

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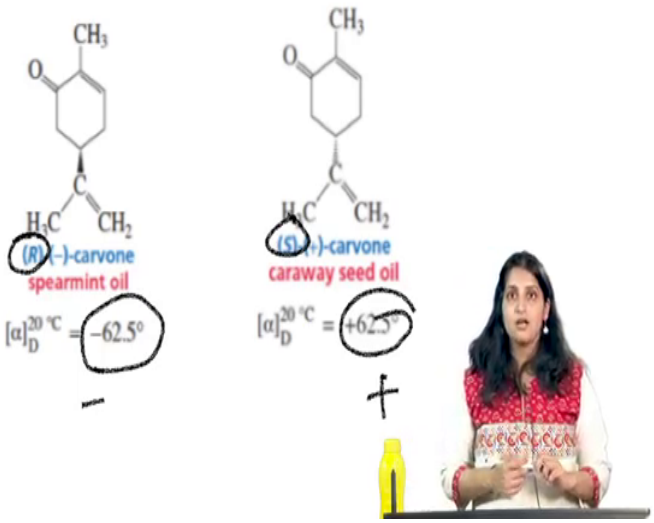

In fact, if you look at the two enantiomers here is something I want to point out is that let's say that the R-Carvone here rotates the alpha at 20 degrees is minus 62.5, meaning it rotate

towards one side. Its counterpart which is the S enantiomer will rotate it exactly in the same degrees, same number of degrees, just in the other direction. So, this one is negative whereas, this one rotates it in the positive direction.

So, now in this chapter we looked at what chirality is, we looked at what enantiomers are, how to name them or how to label them. In the next chapter we are going to dive further into chirality and look at what happens when you have more than one chiral center for example. So, till then what you can do is, you can look around and figure out which objects are chiral, whether they have a plane of symmetry, whether they don't have a plane of symmetry and what really gives rise to their chirality, till that time.