Introductory Organic Chemistry
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Lecture - 25
Alkenes - Structure, Properties & Nomenclature

Alkanes are hydrocarbons that contain only Carbon-Carbon single bonds whereas, the hydrocarbons that contain Carbon-Carbon double bonds are called as Alkenes. Earlier days, chemists noted that an oily substance was formed when Ethene, the very first alkene, the smallest alkene reacted with Chlorine. On the basis of this observation alkenes were termed as Olefins meaning oil forming. So, humans have known alkenes for a long time and now in this chapter what we are gonna do is we are going to look at the structure, the properties as well as the reactions of alkenes.

Alkenes actually play many important roles in biology. So, Ethene for example, is a plant hormone that is a compound that controls plants growth and other changes in the tissues and Ethene affects the seed germination, flower maturation, fruit ripening. You might have heard that mangoes sometimes are ripened with the help of Ethene. Many insects communicate by releasing pheromones and the chemical substances that really these species use to communicate with each other are nothing other than simple alkene molecules. So, alkenes have a huge role in biology we also use them in chemistry for various reactions and in this chapter we are gonna go over them.

So, we have learned that the general formula for alkanes that is a non-cyclical alkane is C_nH_{2n+2}. We also learned that the general molecular formula for cyclic alkane that is a cyclopropane, cyclobutane and so on is $C_nH_{2n;}$ because anytime you have a cyclic structure it reduces the number of Hydrogens by 2, right. The general molecular formula for an acyclic alkene is C_nH_{2n} because for Carbon-Carbon double bond this particular molecule has 2 fewer Hydrogen atoms in it, and, than the alkane with the same number of Carbon atoms.

So, the general formula for a cyclic alkene must be $C_nH_{2n-2,}$ right. So, we can therefore, summarize all of this in one statement that the general molecular formula for a hydrocarbon is C_nH_{2n+2} minus 2 Hydrogens for every pi bond or every ring that is there in the molecule. So, this is also called as unsaturation because alkanes contain maximum number of Carbon-

Hydrogen bonds possible that is they are saturated throughout, they are also called as saturated hydrocarbons.

In contrast alkenes or alkynes are called unsaturated hydrocarbons because they have fewer than maximum number of Carbon-Hydrogen bonds. The total number of pi bonds and rings in an alkene is called its degree of unsaturation. So, herein I am gonna give you a general formula to calculate the degree of unsaturation of any molecule, okay.

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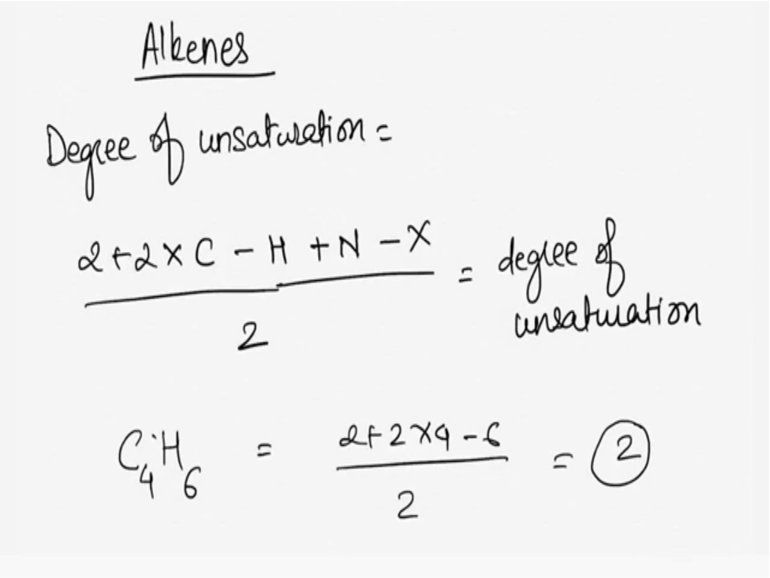

Alkenes

Degree of unsaturation =

$$\frac{2+2\times C - H + N - X}{2} = \text{degree of unsaturation}$$

$$C_4H_6 = \frac{2+2\times 4-6}{2} = \textcircled{2}$$

So, if you look at this particular formula it says,

$$\text{Degree of unsaturation} = \frac{2 + 2 * C - H + N - X}{2}$$

, will give you the degree of unsaturation for any particular compound. So, now; let’s take for example, C_4H_6, right. So, C_4H_6, I can calculate the degree of unsaturation as 2 plus 2 into number of Carbons that is 4, minus number of Hydrogens that is 6, I do not have any Nitrogens or halogens present in the molecule divided by 2. So, this one will give me,

$$\text{Degree of unsaturation} = \frac{2 + 2 * 4 - 6 + 0 - 0}{2}$$

$$\text{Degree of unsaturation} = \frac{10 - 6}{2} = 2$$

So, now, C_4H_6 has 2 degree of unsaturations meaning it could have two double bonds or it could have a double bond and a ring or it could have a triple bond, right. So, there are various isomers or constitutional isomers possible for C_4H_6. And, as we draw them you will realize that all of them are really possible isomers.

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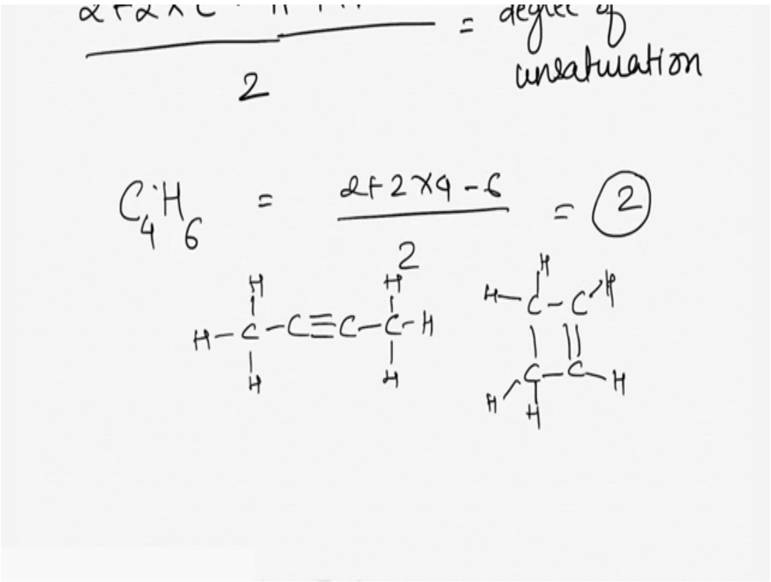

So, for example, I can have a C_4H_6 that looks like this or I can have C_4H_6 that looks like this and all of these are valid possible structures. So, it is useful to calculate the degree of unsaturation of any compound given an empirical formula to go to the molecular structure. It might help you to first calculate the degree of unsaturation and then draw the structure for that particular molecule.

In the first class we looked at the structure of Ethene that was the simplest alkene. Now, alkenes, other alkenes are gonna have similar structure to that of Ethene. Each double bonded Carbon of an alkene has 3 sp^2 orbitals that lie in the plane with an angle of 120 degrees. So, herein I have a model of Ethene with me. So, let's look at the model and, let's go back over the structure to revise what we learned in the first class.

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So, each double bonded Carbon of an alkene or in this case Ethene has 3 sp^2 orbitals that lie in the plane with the angles of 120 degrees. So, for example, this is the Carbon it's gonna have 3 sp^2 hybridized orbital one going here are coming towards me and the third one is actually in between these two. So, you can kind of imagine the third orbital that is kind of here, right. Each of these sp^2 orbitals overlap with an orbital of another atom to form a sigma bond.

So, for example, Carbon and Hydrogen are overlapping here to form the sigma bond or this Carbon-Hydrogen is overlapping to form a sigma bond. These two Carbons are in fact, overlapping to form a sigma bond as well. Thus one of the Carbon-Carbon bonds in a double bond is a sigma bond formed by the overlap of an sp^2 orbital of one Carbon with the sp^2 orbital of the other Carbon atom.

The second Carbon-Carbon bond in the double bond that is actually the pi bond is formed by the side to side overlap of remaining p orbitals of the sp^2 Carbons. So this side to side overlap happens of the p orbitals. Each of the sp^2 Carbons and the, all the atoms that are singly bonded they all lie in one plane. So, right now all of these atoms are in one single plane. In order to achieve the maximum orbital-orbital overlap the 2p orbitals must be parallel to each other. So, the strongest overlap will be when they are both parallel to each other.

So, what we have here is that 1 2 3 4 5 6 all of them are in one plane whereas, the pi bonds are kind of going above and below the plane. Because the 2p orbitals must be parallel in order to achieve the maximum overlap, the rotation about a double bond does not readily occur. So, if I try to rotate this molecule as you can imagine it is very difficult for me to rotate it along this bond I am seeing the resistance this model is offering, right.

So, you cannot really have a rotation around this bond in an alkene because the moment I rotate this, the pi bond breaks. So, if rotation were to occur the 2 p orbitals will no longer overlap and the pi bond would be broken. So, the barrier to rotation about a double bond is about 63 kilocalories per mole; if you really compare this with the barrier of rotation that we have seen for a Carbon-Carbon single bond it was just 2.9 kilocalories per mole. So, now, for double bond it is way more right, approximately 20 times more than the single bond rotation. So, a double bonded compound does not have the Carbon-Carbon bond rotating around itself because the pi bond breaks.

So, because there is an energy barrier to rotation about Carbon-Carbon double bond and alkenes such as for example, 2-Butene it can exist as two distinct forms. The Hydrogens bonded to the sp^2 Carbon can be on the same side of the double bond or on the opposite sides of the double bond. The isomers with the Hydrogen on the same side of the double bond are called as Cis-isomers and whereas, the isomer with the Hydrogen on an opposite side of the double bond are called as Trans-isomers. So, let us draw the Cis and Trans-2-Butene here to illustrate this concept.

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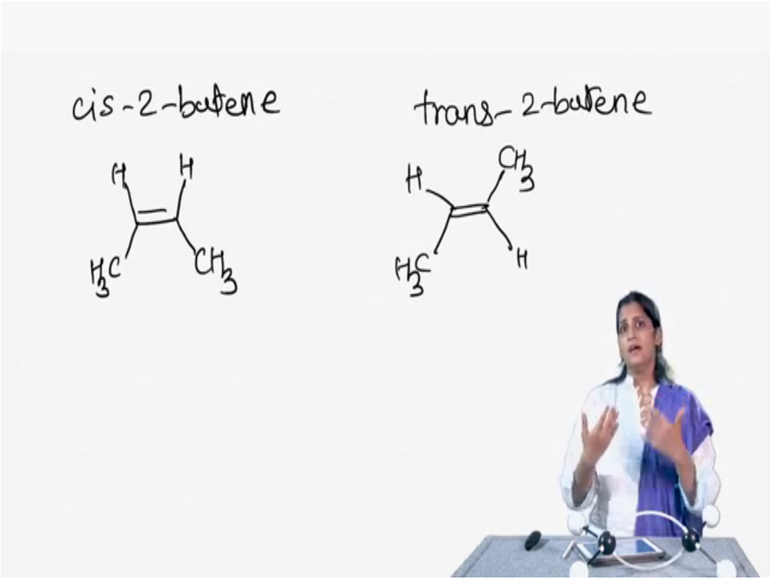

So, cis-2-Butene will have both the hydrogens on the same side of the Carbon-Carbon double bond whereas, trans-2-Buten will have the Hydrogens on the opposite sides of the double bond. So, this pair of Cis and Trans isomers is also termed as Cis-Trans isomers or geometric isomers or in fact, if you really remember the earlier chapter we said that the Cis and Trans isomers are actually diastereomers of each other, right.

In fact, we looked at some of the Cis-Trans isomers of 1 and 2 disubstituted cycloalkanes right or cyclohexanes and which basically meant that if you have a cis it means that both the substituents are on the same side and if you have trans; that means, both the substituents are on the opposite side. Cis and trans isomers have the same molecular formula, but they differ in the way their atoms are arranged in space; they are non-superimposable, non-mirror images of each other with the same molecular formula so, they are diastereomers of each other. Because we have an energy barrier to rotation around the double bond the Cis and Trans isomers cannot really interconvert.

So, except under really extreme situations or extreme conditions having energy enough to overcome the barrier and break the pi bond typically this does not happen. This means that they can be separated from each other; this means that they have very different physical properties or different chemical properties as well. More often you will see that the two isomers have very different physical properties. So, they will have different boiling points, different dipole moments and so on. We are also gonna look at some of the reactions which these two molecules do differently where in the chemical properties also differ.

So, this really fits with our definition of diastereomers is that they are non-superimposable, non-mirror images and they have different physical as well as chemical properties. In fact, one of the really cool example of cis-trans isomerism is the one with Rhodopsin. So, when Rhodopsin absorbs light a double bond interconvert between Cis and Trans forms.

So, we have Rhodopsin in our eyes and the reason why we are able to see is that there is a Cis-Trans isomerism involved when a photon that is part of light really strikes this molecule. This process plays a very important role in our vision. So, we should really thank Rhodopsin that we are able to see. In biological processes the conversion time for such reaction is much-much faster. So, for example, if I were to strike just a single photon on a Rhodopsin molecule and expect it to go from Cis to Trans conformation, it would not really happen if it was not in our eyes.

So, if it was not in vivo, if it was a bottle of Rhodopsin kept right it would never happen; so in fact, it takes more than thousand years if I were to expect any change like that with just single photon Rhodopsin changing from Cis to Trans outside of our body. But, the cool part is when the same molecule is in our eyes this isomerization happens in just a few picoseconds and we are able to see because of this isomerization. So, Cis-Trans isomers play a very important role in biology as well as in our lives as well.

Here is one more thing about Cis and Trans nomenclature. So, as long as each of the sp^2 Carbons of an alkene is bonded to only one substituent we can use the terms Cis and Trans to designate the structure of an alkene. So, if the Hydrogens are on the same side of the double bond it is Cis; if they are on the opposite side of the double bond then it is Trans. But, how would you designate the isomers of a compound that has 1-Bromo-2-chloropropenes? So, let me just write that down.

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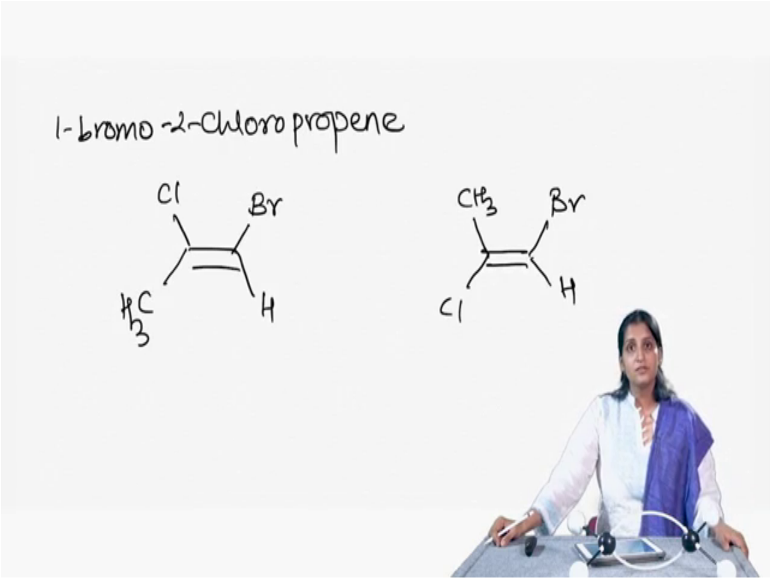

So, 1-Bromo-2-chloroproene, the way we would do is we will start with a three Carbon chain. Now, between first and second we have a double bond right. So, on one, first Carbon we want a Bromine, on the second Carbon we want a Chlorine. Now, remember that this molecule I have drawn versus this molecule here both of them are actually 1-Bromo-2-chloropropene molecules. So, it would be wrong to just name this particular molecule as 1-Bromo-2-chloropropene because I can clearly see that the two diastereomers can be written with just this name.

So, a new nomenclature or a different nomenclature had to be invented when there are four different substituents on the Carbon-Carbon double bond. So, the E and Z system of nomenclature was devised for this kind of situation. So, to name an isomer by the E and Z system, we first determine the relative priorities of the two groups bonded to one of the sp^2 carbons and then the relative properties of the two groups bonded to the other sp^2 carbons. So, what we are going to do is I am going to try to name this particular, the first molecule as E or Z.

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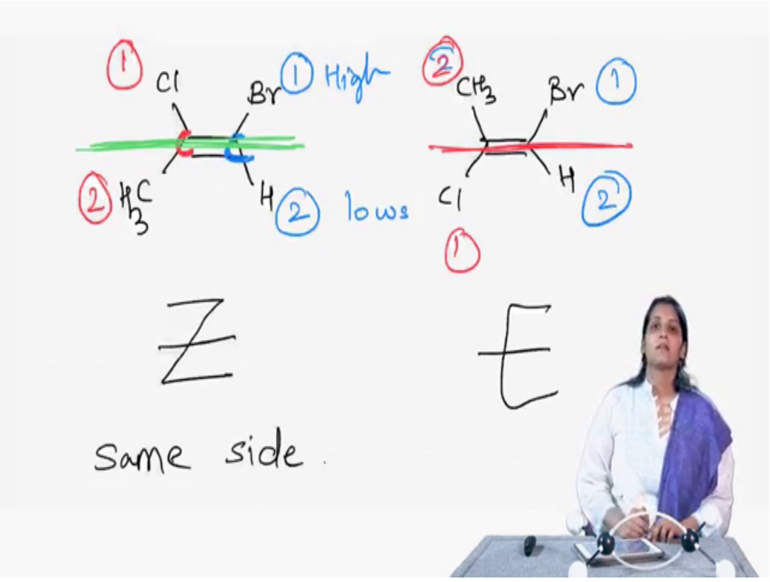

The first thing you do is you look at this particular Carbon here okay. So, I am talking about the Carbon in blue and I look at the two groups attached to it. It has a Bromine and Hydrogen. Now, the relative priority rules are the same as that of the R and S nomenclature rules that we had seen. So, the higher atomic number gets the higher priority. So, in this case Bromine will get a higher priority and Hydrogen will get a lower priority. I do the same exercise on this other side in which Chlorine will get a higher priority and this Methyl group will get a lower priority because again Chlorine has a higher atomic number than Carbon right.

Now, if I look at it along the Carbon-Carbon double bond line what I see is that both the 1's are on the same side and both the 2's are on the same side, right or you can also term it as both the highs are on one side and both the lows are on the other side. So, this particular type of compound is called as a Zee alkene or Z alkene. Now, let's do the same exercise for this other compound here Bromine gets 1, Hydrogen gets 2, Methyl gets 2 and Chlorine gets 1. So, if I see here 1 and 2 are they are on both sides of the Carbon-Carbon double bond. So, this type of alkene is called as E nomenclature.

There is quick trick to remember which one is E and which one is Z. You just imagine it in this kind of German accent that Zee is the zame zide kind of like Z is the same side that really helps me to remember that Z alkenes are the ones that have the same priority groups on the same side. So, Z is the same side that's what I remember okay. Let us take one more example of this E and Z nomenclature let's draw one compound here, okay.

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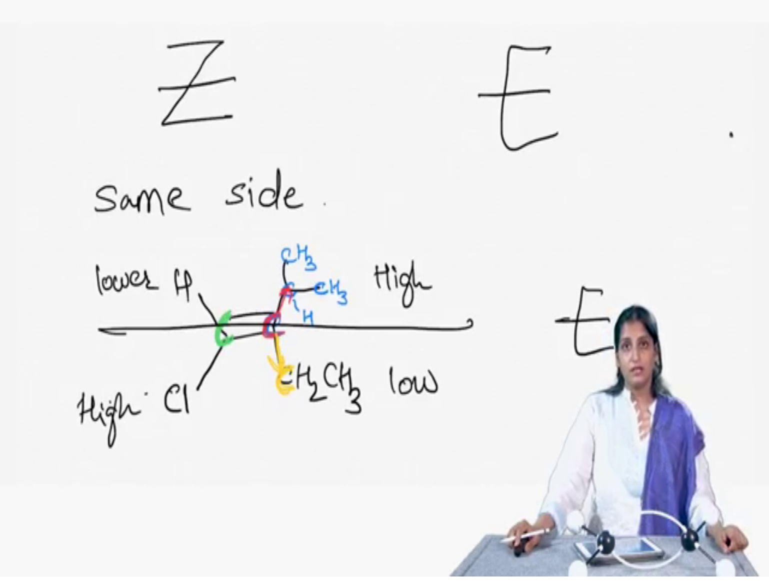

So, in order to assign the priorities here on the left hand side Carbon, that is to my left hand side, the Chlorine will get the higher priority and Hydrogen will get the lower priority; whereas this particular Carbon on the other side the CH_2CH_3 versus I have another Carbon here which is attached to two other Carbons right. So, I have an isopropyl group here. So, this particular isopropyl group will get a higher priority and CH_2CH_3 the ethyl group will get a lower priority.

Again, to go back to the rules of assigning priorities what you can imagine is that as you start walking along as you get to this particular Carbon, now you want to decide which way to go further, right. So, if I am on this particular Carbon and if I start walking this side I go to a Carbon, this particular Carbon is bonded to two other Carbons whereas if you start walking on the other side towards this yellow coloured Carbon, this Carbon is only bonded to one more Carbon. So, the top one gets the higher priority.

Now, if I really look on this side then high and low are there on one side and high and low are there on the other side. So, they are not on the same side. So, this particular molecule will be an E alkene. So, when we assign nomenclature you also want to name it as E or Z to specify the kind of double bond that is present in that alkene.

Alkenes because of their Carbon-Carbon double bonds have properties different than that of alkanes; although the melting points and boiling points are fairly similar to that of alkanes we do see some changes. So, in the case of alkenes for example, Ethene, Propene and Butene are gases at room temperature; whereas, Pentene, Hexene, Heptenes etcetera are liquids and whereas, as we go on with the larger alkene molecules like Carbon number 14 or Carbon number 15 onwards they are really solids at room temperature.

One thing to note would be that the differences in the properties of Cis and Trans alkenes. We typically see that the Cis alkenes have a lower melting point than that of the Trans alkenes. So, this is because the change in the dipole moment of the molecule and also the packing in which the compact solid is formed, it really affect the melting point of a molecule. So, the Cis and Trans pack differently when they are really packing into forming a solid. So, regarding the properties or the physical properties of alkenes you want to remember that they are very similar to that of alkanes, but there might be changes because of the cis-trans isomerism that we see in the case of alkenes.

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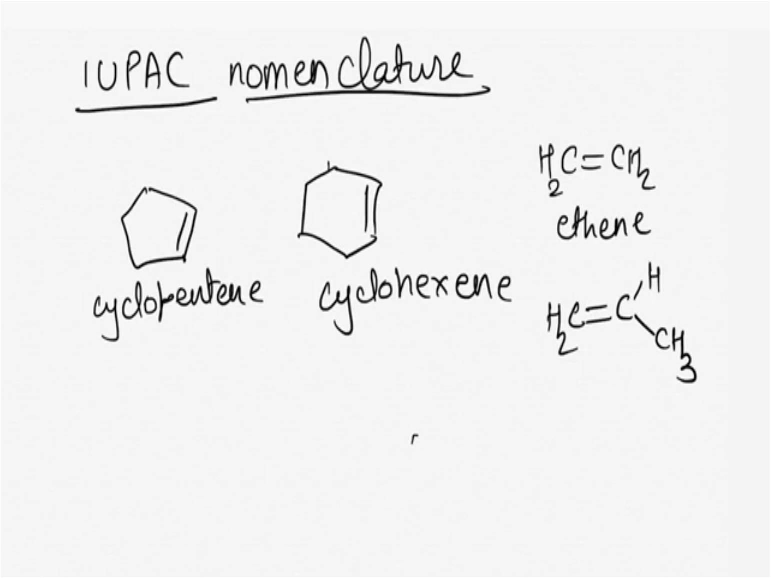

Now, we are going to go over the IUPAC nomenclature okay. So, the systematic name of an alkene is obtained by replacing ‘ane’ that is ending with an alkane with ‘ene’ that is for an alkene. So, for example, two Carbon alkene is called as Ethene and three Carbon alkene is called as Propene right; Ethene is as I said is a very important plant hormone and Propene you must have heard it is also one of the main components of gasoline right.

Ethene is also frequently called by its common name that is ethylene. In fact you also have cyclopentene wherein for example, this is the cyclopentene molecule or this is a cyclohexene molecule right. So, cyclopentene, cyclohexene right and we also talked about Ethene and similarly we also looked at Propene okay.

In order to name alkenes the rules are pretty much the same as that of naming alkanes. So, in alkanes we use to look at the longest continuous chain, here also you are going to look at the longest continuous chain containing the functional group. So, this is the difference between alkane and alkene nomenclature is that in alkene you want the Carbon-Carbon double bond to be the part of the longest continuous chain that you are going to decide.

So, what we do is, we figure out the longest continuous chain that has that alkene and we number it in the direction that gives the functional group that is the alkene suffix the lowest possible number okay. So, for example, 1-Butene signifies that the double bond is between the first and the second Carbon or 2-Hexene will signify that the double bond is between second and the third Carbon of the Hexene, right. Herein I have some examples. So, let me just take one example here.

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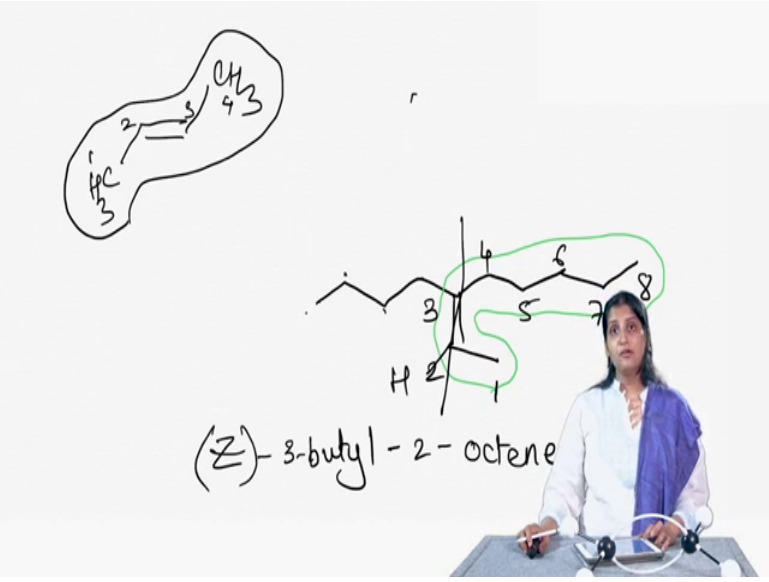

So, for example, we already looked at 2-Butene, this was trans-2-Butene. If I take the longest continuous chain it is this particular chain and 1, 2, 3, 4 right. So, we start numbering such that the double bond gets the lowest possible suffix. Now, I am going to draw one more molecule and let us now try to assign the name to this particular molecule.

So, now, if I want to name this particular Carbon compound here remember that the double bond has to be a part of the longest continuous chain. So, even though I have a longest continuous chain here which looks like this; this is not the right way to choose the longest continuous chain because the double bond lies outside of it. So, I am gonna erase this one and in fact, we are gonna choose a longest continuous chain such that it contains the double bond and this one right because that has a larger number of Carbons.

So, I have 1, 2, 3, 4, 5, 6, 7, 8 so, this is an Octene molecule. This is in fact, a 2-Octene molecule right because the double bond starts at the position 2. On the position 3 you have 1 2 3 4; so, a butyl group presents. So, this will be 3-Butyl-2-octene right, but as we said this before we are still not complete with our nomenclature because we have to specify whether it is E or Z right.

So, if I complete this molecular here with the Hydrogen I can see that the all the high priorities lie on this side of the double bond and the low priorities lie on this side of the double bond. So, what you have here is rather this is a Z alkene right. So, this is a Z-2-Butyl-2-octene molecule.

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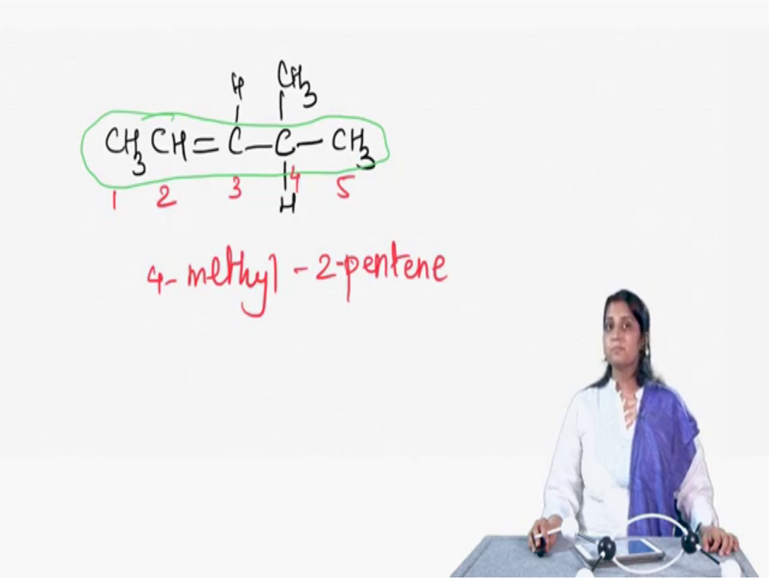

Let us take a couple of more examples. If I really look at this molecule the longest continuous chain is actually the horizontal chain. So, I will take the horizontal chain here. Now, I want to start numbering it such that the double bond gets the lowest possible number and that will be 1 2 3 right 4 and 5; on the fourth position there is a methyl group. So, this is a 4-Methyl-2-pentene okay. So, if the chain has more than one substituent then the substituents are sighted in alphabetical order just like in the case of alkanes using the same rule of alphabetizing that we have learnt earlier.

We also use the prefix as di, tri, secondary, tertiary the same thing that we learn for alkanes right; just remember that the prefixes di, tri, secondary and tertiary are ignored in alphabetizing but iso, neo and cyclo are not ignored. The appropriate number is then assign to each substituent right. So, that’s what we remember from our alkane nomenclature, now let’s try to name this particular molecule and apply the same rules.

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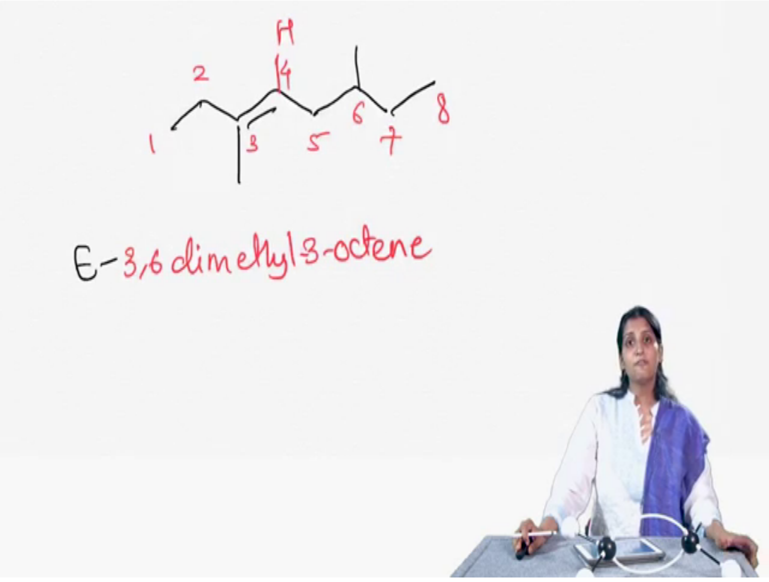

So, I have figured out the longest chain in this particular molecule it is that of an alkene; if I really see the double bond starts at position 3. So, this is a 3-octene molecule and there is a methyl group at position 3 and a methyl group at position 6 right. So, this will be 3, 6-dimethyl-3-octene.

Now, we are not done yet we also have to write down whether this is E or Z. So, there is a Hydrogen here. If I really see this, this is an E alkene and you can work this out on yourself I am not gonna go over every time figuring out how it is E or Z, but you can see that the lowest and highest priority groups are such that they are divided around Carbon-Carbon double bond. So, it is E-3, 6-dimethyl-3-octene. If the same number of alkene functional group suffix is obtained in both the directions the correct name is a name that contains the lowest substituent number.

So, for example, the 2, 5-dimethyl-4-octene is a 4-octene whereas the longest continuous chain is numbered from left to right or from right to left. So, if you number it from left to right the substituents are at positions 4 and 7, but if you number it from right to left they are at positions from 2 to 5. So, out of all of this what we choose is the 4 substituent numbers 2 is the lowest. So, the compound is named as 2, 5-dimethyl-4-octene and not 4, 7-dimethyl-4-octene.

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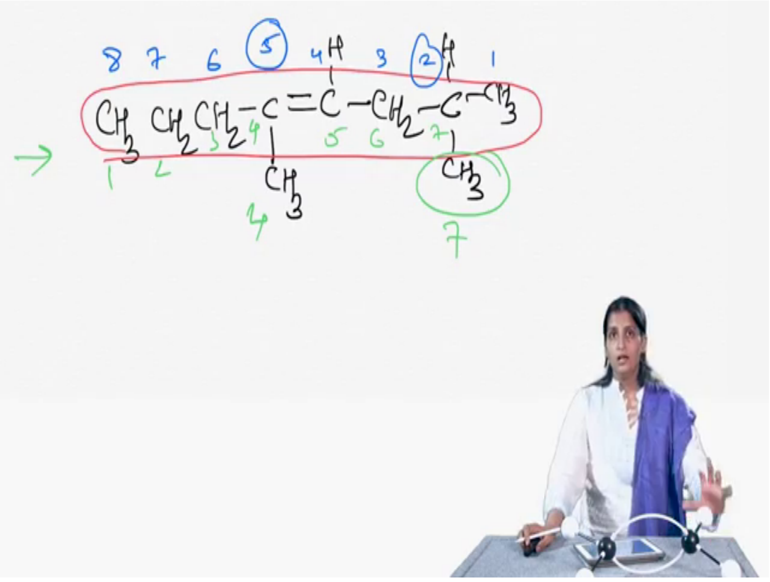

So, now let us go over this particular example. Now, there are two ways to figure out the octene chain right. It has 8 Carbon. So, it is 1, 2, 3, 4, 5, 6, 7, 8. So, I can take this red chain right and I can start numbering from either ends because from either ends the double bond gets the number 4 as the suffix, but as I said earlier that in case if from both ends the double bond comes to the same number then you need to choose a number that gives the other substituents the lowest possible number.

So, if I choose from this end I can get 1, 2, 3, 4 for the double bond, 4 for that methyl group also 5 6 7, so, on 7 you can get the methyl group. So, the methyl groups here will be on the positions 4 and 7; whereas if I start numbering from this side then I can go as 1, 2, 3, 4, 5, 6, 7, 8 right. So, the numbering in blue is actually better because it gives me a methyl group at position 2 and a methyl group at position 5. So, the methyl group at position 2 and 5 is preferred over methyl groups at position 4 and 7. So, the compound becomes 2, 5 dimethyl-4-octene and not 4, 7 dimethyl-4-octene because 2 is lower than 4 right. So, we look for the lowest possible number.

While naming cyclic alkenes the number is not needed to denote the position of the functional group because the ring is always numbered such that the double bond is in between Carbons 1 and 2. So, you start numbering from the double bond that’s the rule okay.

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So, for example, I want to name this particular cyclic alkene here. So, I start with the double bond and then I stick around the double bond. Like, let's say that the double bond here can be started by numbering from here 1, 2; that is actually wrong because I am not going in the direction of the double bond.

So, I would rather start numbering it such that I go in the direction of the double bond. So, the compound will be 1, 6-dichlorocyclohexene and not really 2, 3-dichloro cyclohexene because that does not work we have to start with the lowest possible number for the double bond and then go in the direction of the double bond in case of cyclo alkenes; okay.

So, in case of cyclone alkenes and as well as for alkenes if both the directions lead to the same number of alkene functional group suffix and the same number for one or more of the substituents then those substituents are ignored and the direction is chosen that gives the lowest number to one of the remaining substituents. So, let us look at this particular example here.

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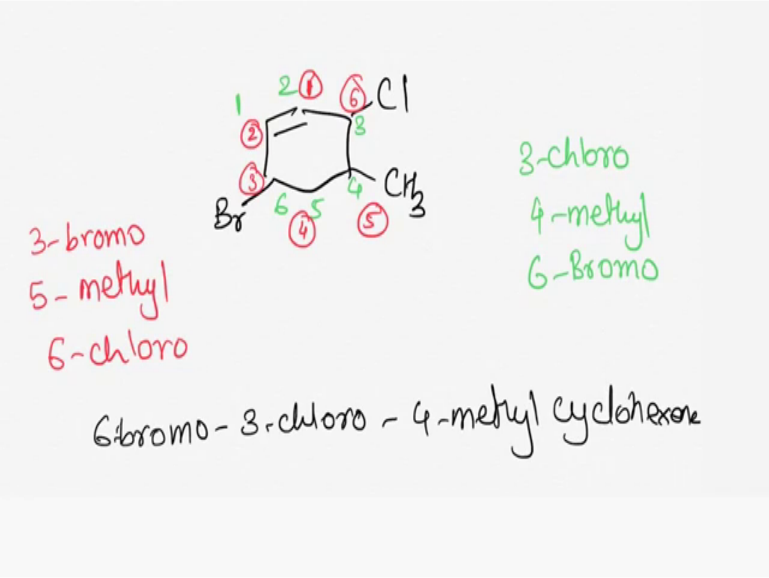

So, I have this molecule right, now I want to number it. Now, there are multiple ways to start really and I can start such that I start from here. So, this will give me 1 2 3 4 5 6 right, that's the possibility or I could start from this Carbon-Carbon double bond that is the one in the red 1 2 3 4 5 6. So, now, if I name it like the one in green I will have 3-Chloro, 4-methyl and 6-Bromo whereas if I choose the one in red I will have 3-Bromo, 5-methyl and 6-Chloro.

So, as you can see if I compare then 3, 4, 6 is a better naming scheme then 3, 5, 6 because 4 is better than 5. So, the name for this particular compound becomes when we follow alphabetical order so, this become 6-Bromo-3-chloro-4-methylcyclohexene. Now, typically when the double bond is on the first position you can write it as one cyclohexene or cyclohex-1-ene, but typically when it is at the first position you can really avoid it and it is understood that if you have not really signified the suffix for the double bond then it is at the first position, okay.

So, these are really the rules for nomenclature of alkenes very similar to that of alkanes; just a couple of more rules to remember is that a double bond being the functional group it takes a higher priority. Now, couple of other nomenclature or other terms that I want to go over one of them is called as a Vinylic Carbon.

So, Vinylic Carbon is a double bonded carbon, the carbon that is sp^2 hybridized and you know the Carbon that really forms the double bond is the Vinylic Carbon. If there was one more Carbon here that would be called as an Allylic Carbon. So, the Carbon sp^3 hybridized Carbon that is adjacent to the Vinylic Carbon is called as an Allylic Carbon.

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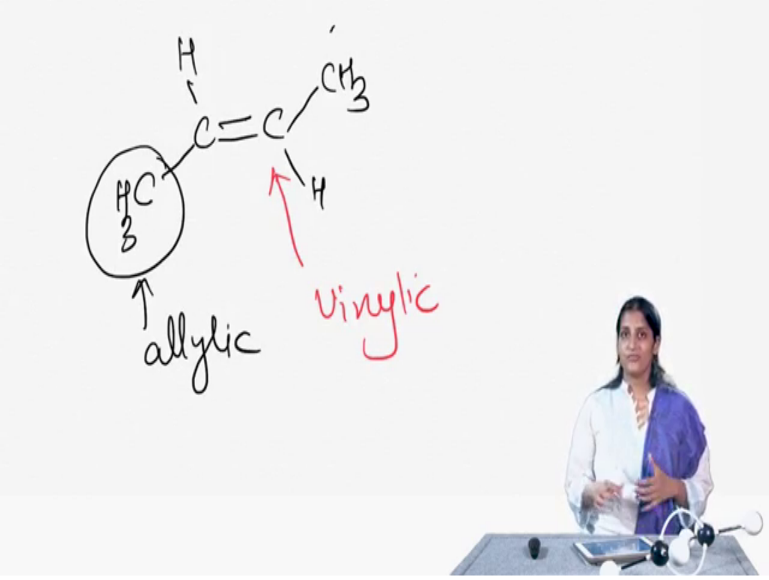

So, for example, in this molecule here, again I am taking trans-2-Butene, this is an Allylic Carbon because it is sp^3 hybridized and it is next to the Carbon-Carbon double bond; whereas, this one here is called as a Vinylic or Vinylic Carbon. So, these are just two more terminologies that will be helpful in when we are describing the reactions of alkenes and in the next class we will begin with the actual reactions of alkenes.