Introductory Organic Chemistry - II
Professor Dr. Harinath Chakrapani
Indian Institute of Science Education and Research, Pune
Tutorial-5B

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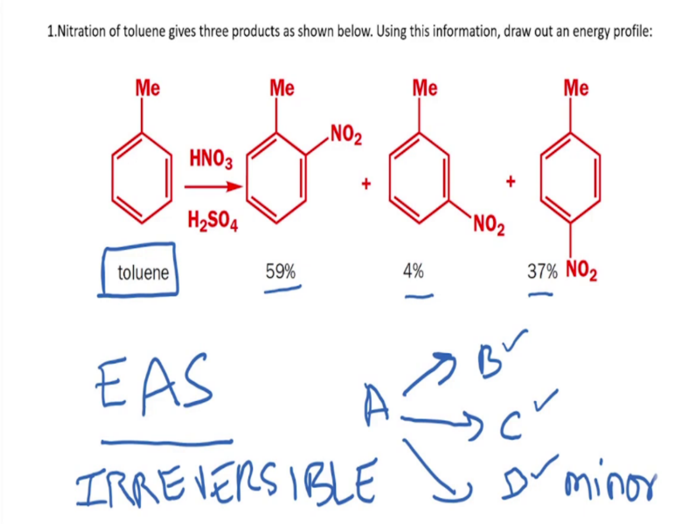
Additional Problem Set

Solutions



1.Nitration of toluene gives three products as shown below. Using this information, draw out an energy profile:

Alright, so, in this problem set, we are trying to recap many of the concepts that we have studied, I have paid particular attention to more mechanistic aspects of how things work. And in the next problem set, we will look into more of the Felkin-Ahn and associated models. So, the first question here is about the nitration of toluene. So, nitration of toluene gives us three products in 59 percent, 4 percent and 37 percent yield.

And the question here is that using this information draw out an energy profile. So, as you know, this is an example of an electrophilic aromatic substitution. So, this reaction goes through the breaking of aromaticity. Now, the important concept here to note is that, you are getting three products. So, when you have a situation where you get, A goes to maybe B, C and D. Now, the ratios of these products, of B, C and D, will depend on the rate of formation of B, rate of formation of C, and rate of formation of D.

So, if, for example, B is formed faster than C, then the yield of B would be significantly higher compared to C. And similarly, if both B and C are faster than D, then D would be called the minor product. So, this is how we understand the outcome of a reaction, therefore, looking at ratios of products formed are very useful way to understand how fast reactions go. Now, of course, in this question, or in this situation, we will make an assumption that the reaction is an irreversible reaction.

And in the case of electrophilic aromatic substitution, it would be a fair assumption to make, because if you isolate any of these products, and expose them to the same reagent HNO_3, H_2SO_4, or you just let them sit in a solvent for long enough, let us say for several days, you do not form the starting compound toluene. So, therefore, it is reasonable to say that this would be an irreversible reaction. So therefore, it makes our job easy of drawing the energy profile.

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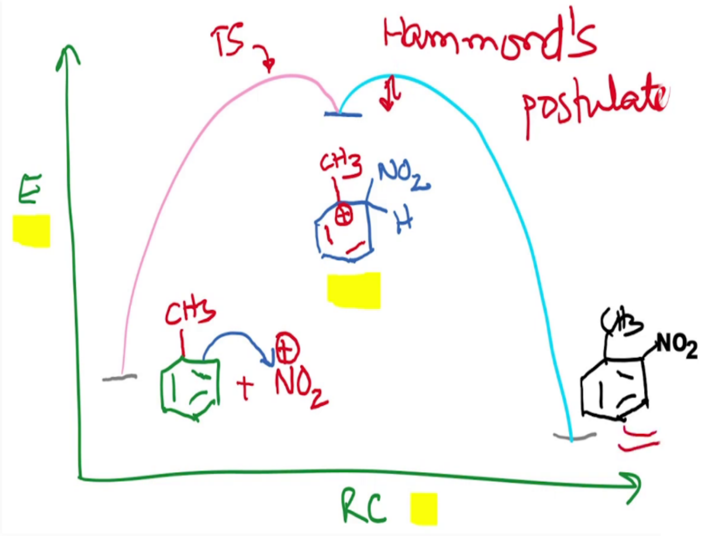

Now, in order to approach this problem, now, let us look at the energy profile for the first reaction, which is the formation of the ortho product. So important points here to note are that you have to clearly label the axis. So, you have the energy here and reaction coordinate. And so, what we know from electrophilic aromatic substitution is that there is going to be a high energy intermediate which is formed. And here comes our assumption that is Hammond postulate, which essentially allows us to understand the nature of the transition state.

So, breaking of aromaticity is going to be a highly energetically disfavored process. And so, we could assume that the combination of these two reagents is going to give you high energy intermediate. And therefore, this would be, in our energy terms, it would be a highly endothermic reaction. So, what Hammond's postulate tells us is that in a highly endothermic reaction, the stability of the transition state would resemble the product.

So therefore, this transition state here that we are looking at, is going to be closer to the product or it would be a late transition state. And this is all something that we have already looked at, I am just recapping here. Now, we cannot make any statements about stability of other compounds at this point, because we are only looking at one reaction. So let us say that this is the energy profile, and the next step you know is a relatively favorable step and it gives you the product where aromaticity is restored.

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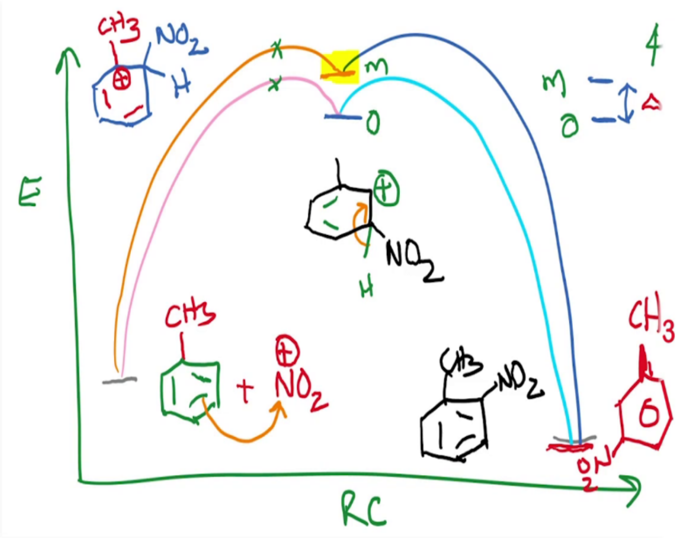

Now, if we look at this scenario, and then move on to the energy profile of the next product, which would be the meta compound. Now, what we can assume is that the starting materials are obviously the same, the product here is going to be the meta product. So let me just draw that out. So that thing is clear. Now, between these two compounds that is the ortho-nitrotoluene, and meta-nitrotoluene there is going to be some difference.

So, this difference is going to be some difference in the energy, one of them is going to be more stable than the other. But their difference in the products is not relevant in this case, because the transition state or the highest energy barrier is actually the formation of the intermediate. So, the product stability in this case is not going to be important, because the second step is not the rate-determining step, and this step is not going to be relevant in the discussion towards understanding the relative ratios.

So, therefore, whatever small differences are here are not important. Now, coming to the first step, the formation of this intermediate as shown here is going to be the key step. Now, based on the analysis that we have, for the ortho versus meta, we have already studied that the positive charge is stabilized by the methyl group, and here that positive charge does not have an opportunity to interact with the methyl group directly and so on.

So, therefore, this meta compound you can assume would have a higher energy compared to the ortho compound. So, just to be clear, this is the ortho and this is the meta. So, just to be clear, this is ortho, this is meta. So, therefore, there is going to be a small difference in the energy, or there is going to be a difference in energy between the ortho and meta products.

And according to Hammond's postulate, if there is a difference in the energy of the highly endothermic reaction of the product, then that will be reflected in the transition state. So, therefore, it is quite reasonable to propose that the transition state energies are also going to be different.

And clearly the meta has a higher barrier compared to ortho, and that is something that we see in the product ratio that is a product formation, the meta product is only four percent versus a larger amount of the ortho compound. Now, if we move on to the next example, which would be the para.

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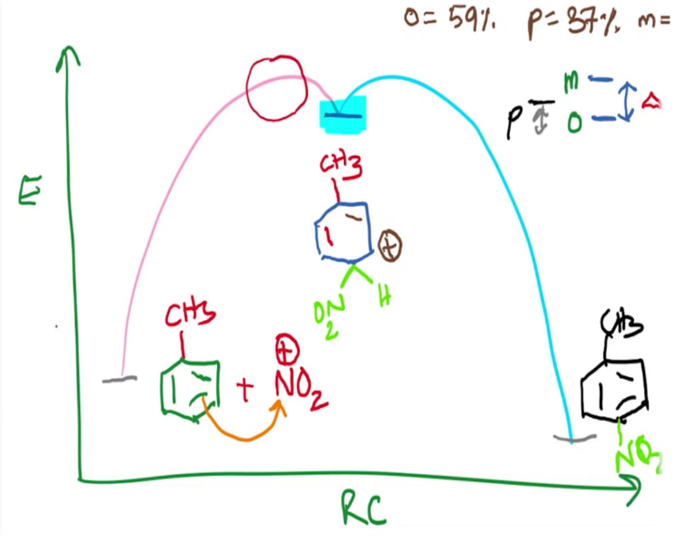

Now, again we have to sort of consider the product ratios here. So, the ortho is as we see here is 59 percent, the para is 37 percent and meta is 4 percent. So, here ortho being a higher component clearly is the most favored, followed by para, and followed by meta. So, if I have to draw an energy profile for the para, then again, as we discussed, the second step is not really important, because the barrier to the second step is significantly lower than the first step.

And if I have to compare the energy of the ortho versus meta or versus para, then in case of methyl group, the ortho substituent is relatively more stable as reflected by the percent of the product that is formed. So, if I have to lay down these energies and put them here, then the difference in energy between ortho and para will be somewhat smaller, compared to the difference between ortho and meta. So, the yield of meta is significantly lower compared to ortho and para. So, these differences in energies over here is going to account for the product distribution.

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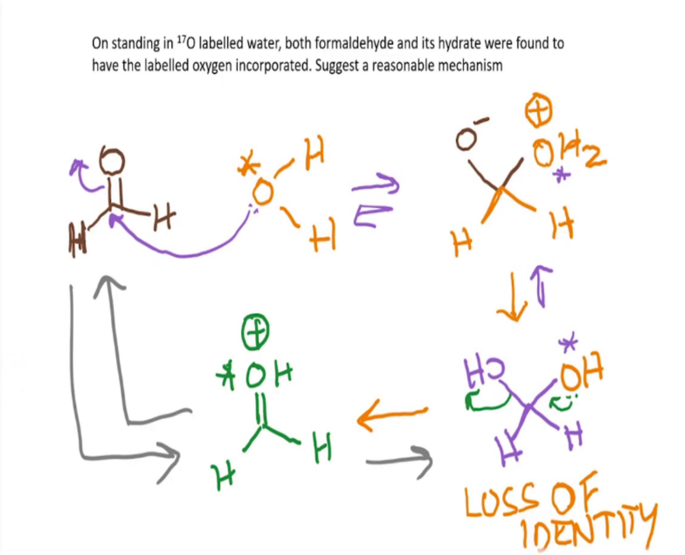

On standing in ^{17}O labelled water, both formaldehyde and its hydrate were found to have the labelled oxygen incorporated. Suggest a reasonable mechanism

Now, let us move on to the next question. So, here in this question, another interesting method to study mechanisms. So, what you do here in this type of a scenario is that you label using radioactive nuclei, you label the oxygen, or sulfur, or nitrogen whichever atom you are interested in. Sometimes you also change hydrogen to deuterium, or tritium and study the mechanism.

So, what the experiment that was done here was, you take ^{17}O labelled water, and you just add some formaldehyde. And then you measure the amount of radioactivity that is being incorporated, or amount of labeled oxygen that is incorporated. So, what we found here was that, both formaldehyde and its hydrate were found to have oxygen incorporated. So, the mechanism that we can propose here is that, we start with unlabeled formaldehyde.

And when we start with this unlabeled formaldehyde, we then react it with labeled water and once the labeled water attacks here and forms the germinal diol, which all of these will be reversible steps. And here at this point, there is no difference between this oxygen, and this oxygen that is the unlabeled oxygen versus the labeled oxygen. And so, either of them can be kicked out, if the unlabeled oxygen is kicked out, then you get a labeled formaldehyde and so on.

So, therefore, this sort of mechanism suggests, there are inference on this mechanism, is that there is a diol, there is a hydrate that is formed, and hydrate being a mixed hydrate, loses its identity. And once it loses its identity then you can have the label incorporated in actual formaldehyde as well, in the carbonyl form of formaldehyde. And so, this mechanism is, I mean, this experiment helps us understand that, this supports this mechanism.

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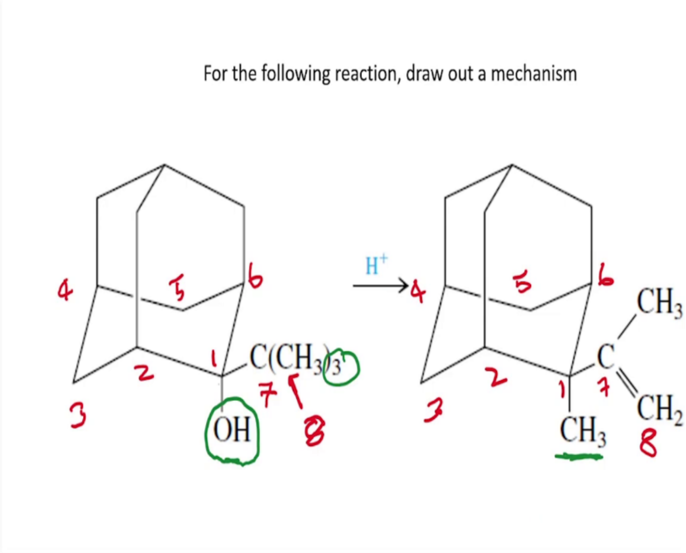

For the following reaction, draw out a mechanism

Now, let us move on to the next question. So, this question is about the formation of a carbocation and elimination reaction. So, this is something that we have looked at previously, in the previous semester. So here is your alcohol, and once it gets protonated, it will form a protonated thing, we will look at the mechanism soon. But the important thing here is that when you start out addressing such questions, the first thing you should do is to start numbering the carbons.

So, here I have numbered it in the following way. I mean, there is, of course an IUPAC way of numbering here. We are not asked to do IUPAC nomenclature. So, you can follow whatever numbering that is convenient to you, but be consistent. So here, this would be 1, 2, 3, 4, 5, 6. And this carbon here would be 7 and this carbon here would be 8.

And in the product, you see here, that carbon 1, which used to have OH, now has a methyl group. And one of these methyl groups is missing, or it has moved, and, you have a double bond between 7 and 8. So, these are the important characteristics that we need to know before we suggest a mechanism.

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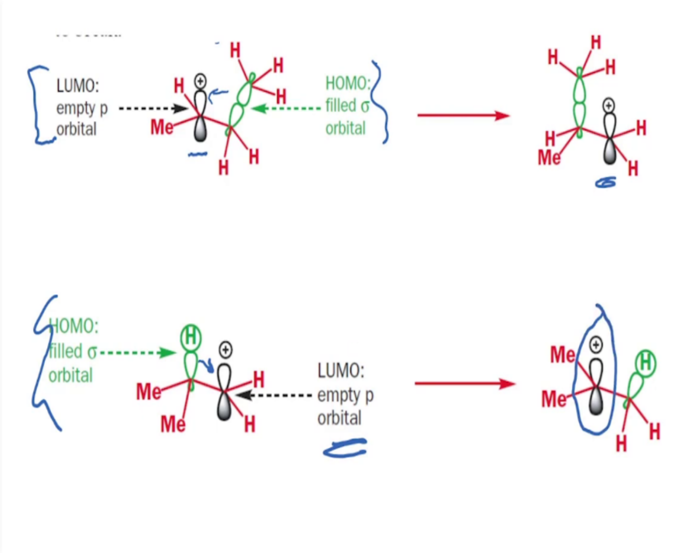

So, before we go into that, into the actual mechanism, I just want to remind you of how carbocation-based rearrangements occur or movement of groups occur. So, the way we understand this is that, a carbocation is an empty p orbital on a carbon. And this, as we discussed previously is the lowest unoccupied orbital. And it is ready or it is waiting to accept electrons from another source.

So, the source of these electrons are, in the first top case is a methyl group. And we know that the methyl group has a highest occupied molecular orbital, which is the filled sigma bond. And now once this filled sigma bond, which has two electrons starts interacting with this empty or vacant p orbital. Then, there is a transfer of electrons, and you now form a new carbocation after the migration.

So, this is one of the examples of the migration of a methyl group. Now, a similar thing happens during the migration of hydride. So, I mean, remember, there is a difference between H^+ and hydride. H^+ is not being transferred here; it is our H with a pair of electrons. So, this is the filled highest occupied molecular orbital of the carbon-hydrogen bond.

And once it interacts with this vacant p orbital, which is the LUMO. Now the hydride can shift and give you a new carbocation. So, this is how we understand the migration of groups to form different carbocations.

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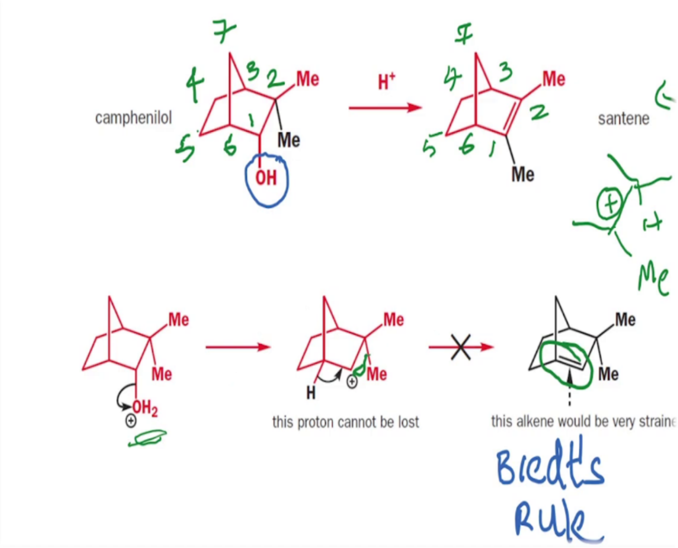

Now, when we look at the example that we are looking at, I want to remind you of a rule, which we have studied previously, which is called the Bredt's rule. So now let us look at this example before we solve the problem. So here, in this example, you start with this norbornane alcohol, so it has an OH here.

And again, we should start numbering the group so that we do not lose track. So here is 1, and I would call this as 2, 3, 4, 5, and this one is 6. So, if I follow the same numbering over here, so I start with 6, and then 4, 5, 3. And, actually, there is another carbon over here. But never mind. So now there is a 2 and there is 1. So, we would label this as 6 and we would label this as 7.

Let me just get that taken out so that we do not have any confusion. So, this would be 6 and this would be 7. So, although they are not relevant in this question, but it is useful to get the numbering correct. Now, what we see here is that this OH has gone and now there is a double bond between carbon 1 and carbon 2 and this methyl group has migrated over here. So, the mechanism that we propose in such a case is that, you have a loss of water and you generate a carbocation.

I think this is straightforward. We have studied this in E1 and S_N1 and other carbocation-based mechanisms. And now, you can envisage that this proton can be lost, and you can get a double bond. But this double bond is quite unstable, it is at the bridgehead, and it is very difficult, if not impossible, for it to assume sp^2 hybridization and 120 degrees and so on.

So therefore, the formation of this double bond is really challenging. So therefore, when a carbocation is formed, if there are other options that it can exercise, then it does that. So now you can think about the migration of this methyl group to this carbocation over here. And that generates an intermediate such as this, where you have, I am only drawing the relevant portion over here, you have the generation of a carbocation and then subsequently it loses H$^+$ to give you the product.

So, this is an example of something that we encounter very frequently that is when there is an option of doing an elimination to give you a double bond at the bridgehead, that really does not happen. So, this is something that you all need to watch out for. And instead, if there is a possibility of migration of the methyl group, it does that and it can then subsequently give you the eliminated product. Now, coming back to the question.

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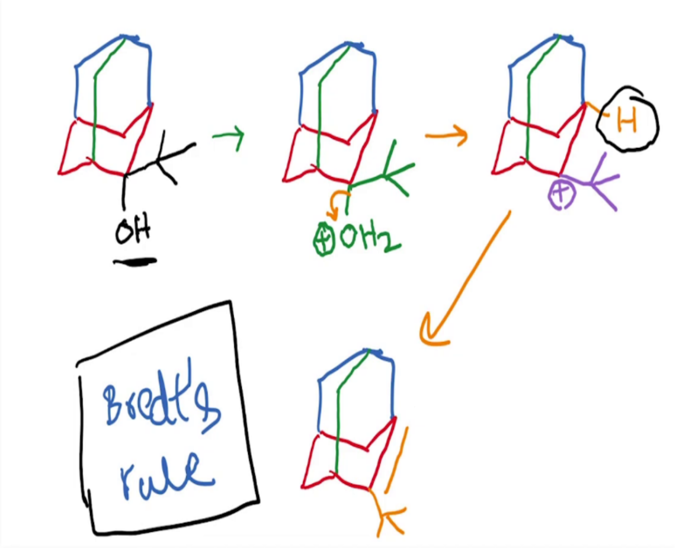

What we looking at here is a very similar situation. So, you have the OH group here which can get protonated and form OH$_2^+$ which can subsequently lose a proton to give you a carbocation. And now, you can imagine that this hydrogen here can be lost to give you the corresponding double bond, but as we discussed earlier, Bredt's rule tells us that, formation of double bond at a bridgehead is unlikely and so therefore, this kind of arrangement is not viable.

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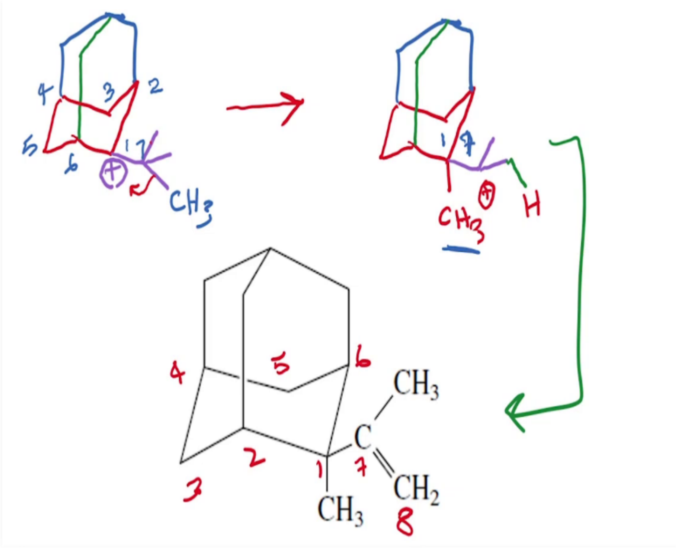

So therefore, instead, what this does is that, you can imagine that there could be a migration of this methyl group over here, and that puts this methyl in this position, I forgot to mention, but you need to number these carbons so 1, 2, 3, 4, 5, 6 and this would be carbon 7. So, in place of the carbocation at carbon 1, you now have a methyl group and the valency of carbon is satisfied and so therefore, there is no positive charge.

But instead, you form a tertiary carbocation at carbon number 7. So, which is not necessarily a bad thing to happen. You start with a tertiary carbocation and end up with another tertiary carbocation. And so it is not disfavored. And now, once this tertiary carbocation is formed, there is an opportunity for elimination to occur to give you the product.

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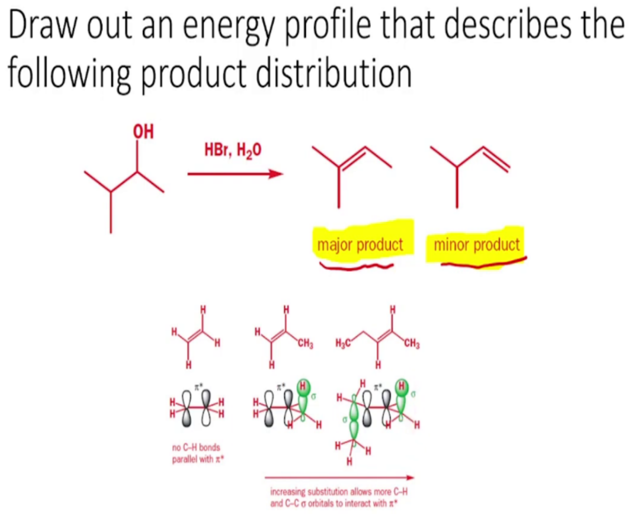

Draw out an energy profile that describes the following product distribution

Now, let us continue with the next problem. So, the question here is about somewhat related to the energy profile question, is to draw out an energy profile for this transformation. I think the mechanism of this transformation is quite clear to you, I will not spend a whole lot of time on the mechanism.

However, we need to understand that the product distribution here is a major product versus minor product. So again, coming back to the concept, if a product is the major product, then the rate of its formation is substantially higher than the rate of formation of the minor product. So, this is we are assuming that it is an irreversible reaction.

Now, what we know from our previous courses is that as you increase the substitution on the olefin then looking at the favorable interaction that we have between the olefin and the carbon-carbon bond as shown here, the interaction between the C-C sigma orbitals and the π^* orbital that stabilizes the olefin and therefore, the more substituted olefin is more stable. So, when you have a choice of forming the more substituted olefin versus the less substituted olefin the stability of the product is important, then you end up having the more substituted olefin as the product.

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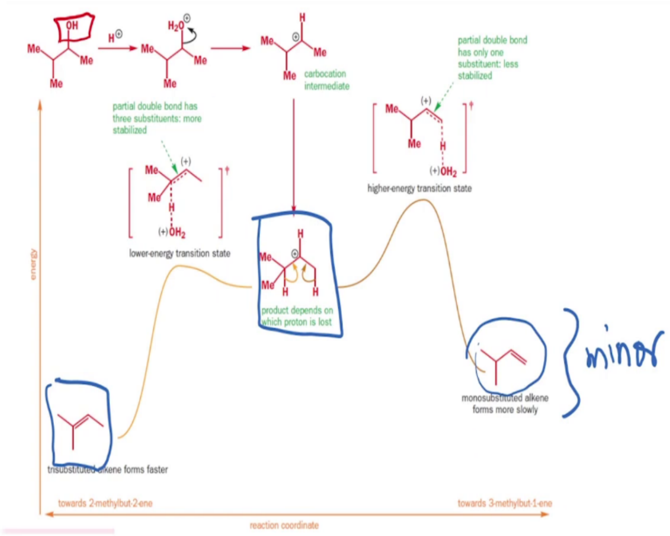

Now, let us look at the energy profile. So, here in the first step, we know that the hydroxyl group is going to get protonated and then it loses water to form this carbocation. So, this carbocation intermediate is the key intermediate as far as we are concerned. And now, if this hydride as shown here is lost, then you have some energy barrier and you form the mono substituted alkene.

And now, instead if you have the other hydride on the left, which is here, which is lost, then you form the tri-substituted alkene. And again, by invoking Hammond postulate, what we can propose is that in an exothermic reaction the transition state resembles the starting material. So here is the starting material that we are looking at which is the carbocation. And therefore, the structure of the transition state resembles the carbocation.

So, anything that stabilizes the carbocation stabilizes the transition state. So, when we look at that situation, what we find is that the positive charge is better accommodated in this in the case on the left where the more substituted alkene is formed. And, the less substituted olefin over here is not as stabilized. So, therefore, the energy profile would look something like this, where we have a higher barrier for the formation of the olefin whereas, we have a lower barrier for the formation of the more substituted olefin.

Again, I want to remind you here that the experimental details are important. And so, the experiment shows that more substituted olefin is the major product, whereas this is the minor product. So, many of the theoretical explanations that we develop are to explain the experimental results. So, consistent with this experimental result, this energy profile would show that, the formation of this less substituted olefin has a higher transition state energy.

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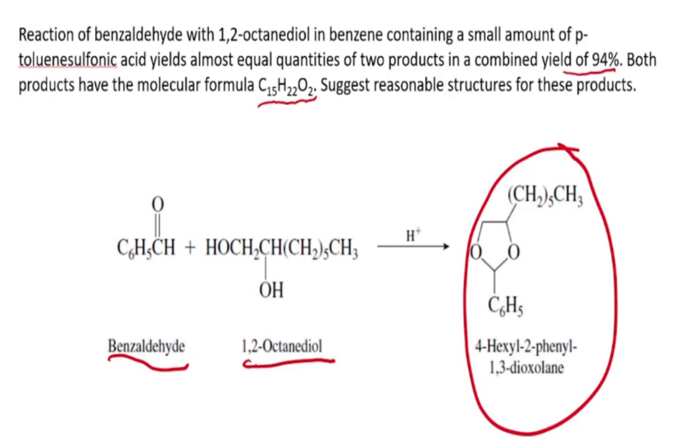

Reaction of benzaldehyde with 1,2-octanediol in benzene containing a small amount of p-toluenesulfonic acid yields almost equal quantities of two products in a combined yield of 94%. Both products have the molecular formula $C_{15}H_{22}O_2$. Suggest reasonable structures for these products.

Now, let us move on to the next question. So, here the reaction is between benzaldehyde and 1,2-Octanediol. So, benzaldehyde structure is shown here and octanediol structure is shown here. And it gives you this product. The question here is that you form not one product, but you form two products, and the combined yield of these two products is 94 percent, and they have, exactly the same molecular formula.

And so, the question is, what are the structures of these products? So, I think if you look at this question, the products that are formed are of the same molecular formula. And so, therefore, stereochemistry of the product is going to be important.

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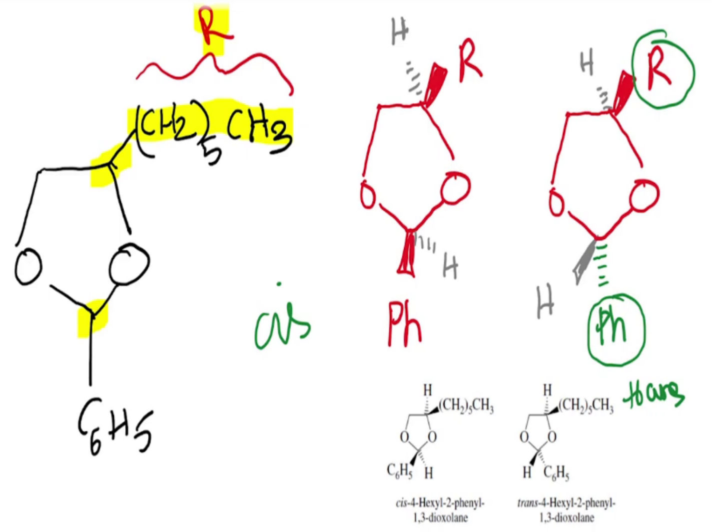

Now, if we assume that this long chain group over here is R, I mean, it is a functional group R. So, now, what we can do is, we have two situations, if I consider this carbon and this carbon, both of these carbons have stereochemistry associated with it, and so, the phenyl group can be towards us, and so, can be R group, the R group can be also towards us.

And so, that is going to be in our nomenclature, we would call this as cis, and the other situation where the phenol group is going into the plane of the board or plane of the paper, and R group remains towards us and this we would call as trans. So, based on the stereochemical analysis, we can suggest that there are two products that are formed.

So, that is one is cis and the other one is trans, I would like you to look at these structures carefully. And so therefore, I have drawn this in printed form as well, for you to look at it. And so, these two compounds are different. And they would be separable. And you can isolate the two compounds.

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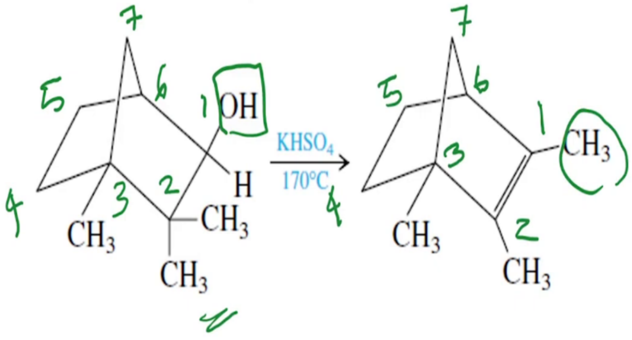
Draw out an arrow pushing mechanism for the following reaction



Let us move on to the next question. So, this is somewhat similar to the other question that we looked at. And so, it will be much easier for us to work on this question. So, the question here is draw an arrow pushing mechanism. So again here, I would urge all of you to develop a method of numbering, so let us call this as 1, 2, 3, 4, 5, and this would be 6, and this would be 7.

So, now let us follow the same nomenclature. So, we start with 7, 6, 5, 4 and carbon number 3 continues to have the methyl group and then there is 2 and there is 1. So clearly, the hydroxyl group has gone and one of the methyl groups from here has moved over here.

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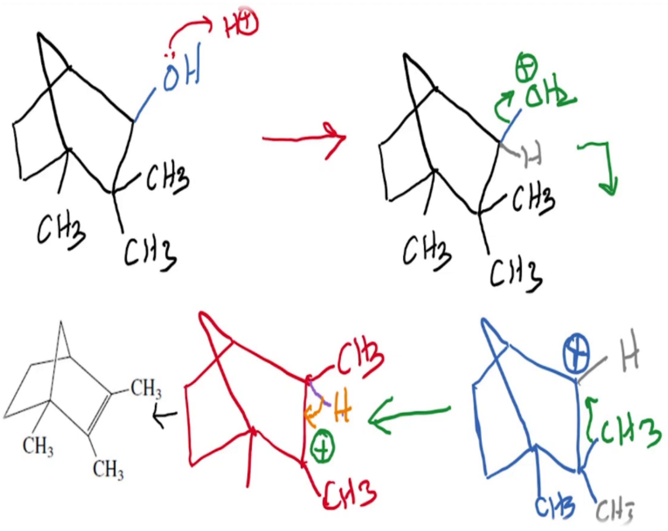

So, with this in mind, let us look at the mechanism. So, in the presence of acid, the hydroxyl group gets protonated and the formation of the carbocation and now you can propose that this methyl group migrates, we have already looked at the orbital interactions in the previous question. And so, once it moves here, it gives you a tertiary carbocation and this tertiary carbocation can then undergo elimination to give you the product.

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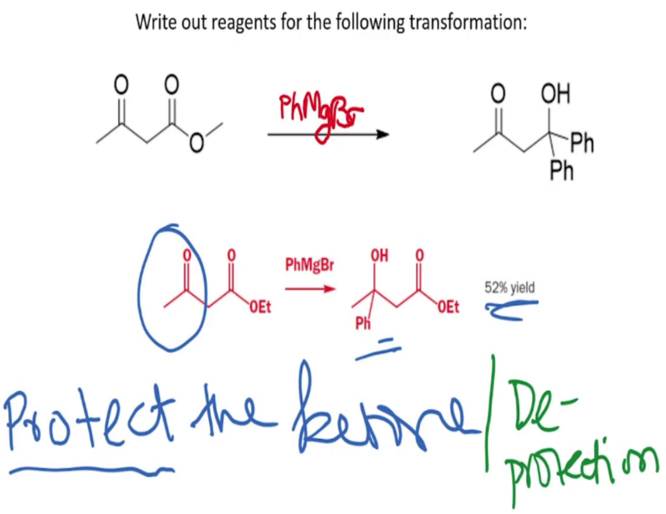
Write out reagents for the following transformation:

Now, we will move on to the next question. So here, the straightforward answer to this question would be to write that you add a phenyl magnesium bromide, which all of you have studied as Grignard reactions. And, these Grignard reactions can give you the phenyl substituted product. But in reality, when we go and do this reaction, we find that when you add phenyl magnesium bromide, you end up getting the ketone reacting and you get this product and the yield of this reaction is about 52%.

So, this is the experimental detail. So, what we need to do is we need to figure out a method by which we protect the ketone, and this word is literally to add in a functional group or to make a modification. So that you can protect it from the reagent that is being used in the step that you would like it to be used.

And so, you need to protect the carbonyl group from the phenyl magnesium bromide and then after the reaction is done, you need to do a process called as de-protection. So, this is something that is very commonly used in organic synthesis, you will learn about this in the coming semesters, but here is a good example of how you would use protection, de-protection strategy to accomplish the result that we want.

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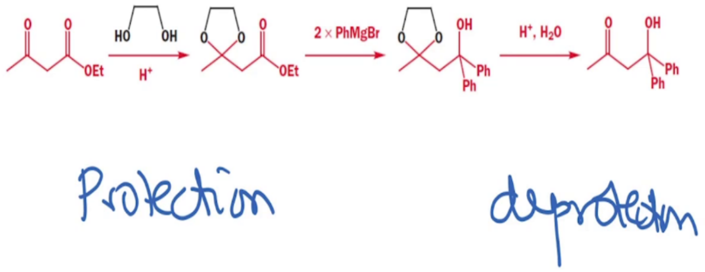

So, if you see here, the protection of this carbonyl group can be done with the 1,2-diol such as ethylene glycol. So, we already have studied this. So, if you add a source of H^+, you get this product. Esters are not reactive in this type of transformation, they do not give you the product and so, therefore, this would be a good way to protect it. Now, the question is when you add Grignard reagent, what happens?

So, when you add a Grignard reagent and, in this case, we would like to add 2 equivalents, the Grignard reagent ends up reacting with the ester because this group is now no more a ketone. So, it ends up giving you this product which is a tertiary alcohol and then subsequently if you do H^+ and H_2O, that is hydrolysis, this group, this ethylene glycol group gets hydrolyzed and gives you back the ketone.

So, this strategy is called the protection and this step is called the de-protection. So, this is very commonly used in organic synthesis, because many times we have functional groups, which are quite sensitive to the conditions under which we are going to work. And therefore, you might need to have protection de-protection kind of strategy.

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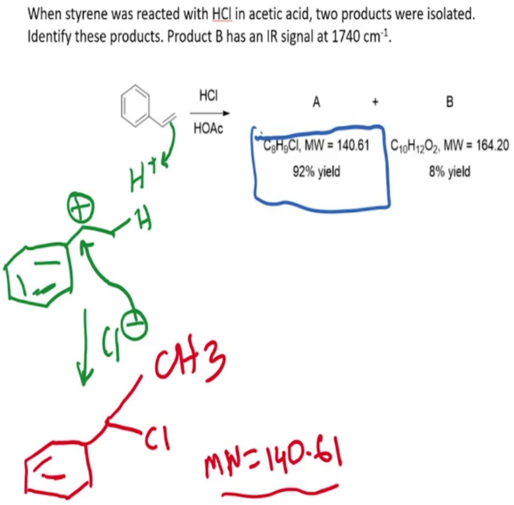

When styrene was reacted with HCl in acetic acid, two products were isolated. Identify these products. Product B has an IR signal at 1740 cm^{-1}.

Let us move to the next question. So, when Styrene is reacted with HCl, in acetic acid, two products are formed and identify these products and the clue that is given here is that product B has an IR signal at 1740 cm^{-1}. Now if you look at this product A as shown here, the product A has a chlorine in it. And since we are using HCl and HOAc, so this product is fairly straightforward for us to explain, you can go back and work out the molecular weight and so on. And it also forms a major product.

So, based on the mechanism that we or based on our prior information and knowledge that we have, we can assume that regular carbocation type mechanism is in play. And so, once it reacts with H^+ it produces a secondary carbocation, it is also a carbocation next to a benzene ring. So, it will be quite stable. And then this subsequently reacts with chloride and gives you this product. And so, if you go back and check the molecular weight it is 140.61. Now this is fairly straightforward.

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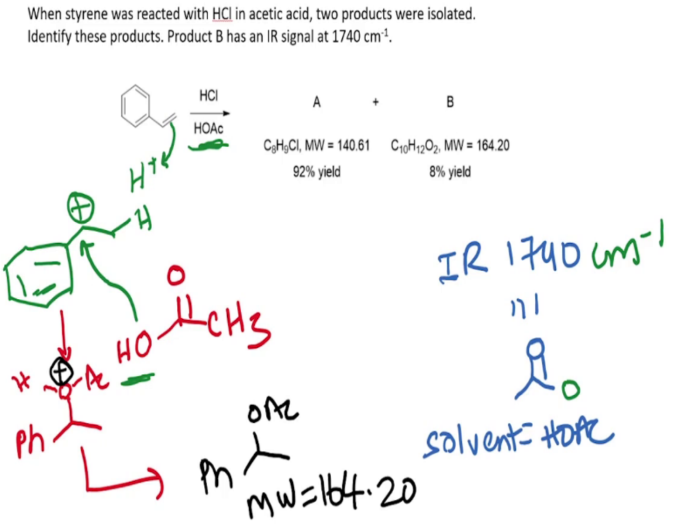
When styrene was reacted with HCl in acetic acid, two products were isolated. Identify these products. Product B has an IR signal at 1740 cm^{-1}.

Now, let us go to compound B, compound B the clue that is given us it is 1740 cm^{-1}. So, we know that 1740 cm^{-1} is a typical signal that we would see when we have a carbonyl functional group. And so that means it is either a keto or an ester or something along those lines. So, since we have acetic acid in the medium, and it is used as a solvent, the possibility of acetic acid attacking the carbocation is real.

And so, if that happens, then what you can assume is once a carbocation is formed, you would still have the chloride attack as the major product, but you could have once in a while the solvent being in the bulk can interact with a carbocation and form this kind of an intermediate where you have an oxonium ion and this is not going to be favored.

Because acetic acid is a way poor nucleophile and the product that is formed also is not substantially more stable than what we would like. So, the driving force for this reaction is not very high. And nevertheless, but once in a while this can happen because acetic acid is in a large amount, and it can give you the acetate as shown here. And this molecular weight of this molecule is 164.2 and it will also give you a signal at 1740 cm^{-1}. So therefore, this product is consistent with what we would expect.

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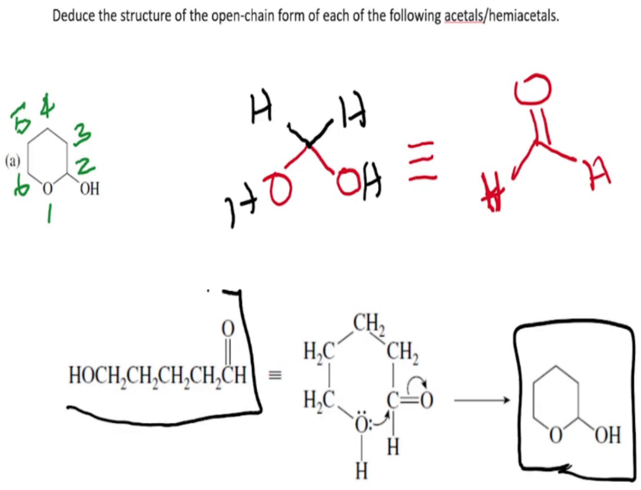

Deduce the structure of the open-chain form of each of the following acetals/hemiacetals.

Now, let us move on to the next series of questions. Here the question here is about what is the open form of acetals or hemiacetals that is shown here. So, in this question, first thing again, we should do is to number these carbons, and so, we would number this as 1, 2, 3, 4, 5, and 6. So, this is a 6-membered ring with an alcohol on it.

And so, the way we would imagine this is that if this carbon 2 is actually, an oxygen and an oxygen, so this kind of a system, where you have two oxygens is equivalent to a carbonyl. So, if you put formaldehyde in water, we have already discussed that it is going to form the diol such as this. So, and there is no oxidation or reduction step that is going on here, it is just a addition of water onto the carbonyl.

So, therefore, equivalent of a carbonyl functional group is the aldehyde or the keto. So, the way we would understand this is that, if you draw out this aldehyde with an alcohol, then if you push arrows in the following way, you would get this structure over here. So therefore, the open chain form is this.

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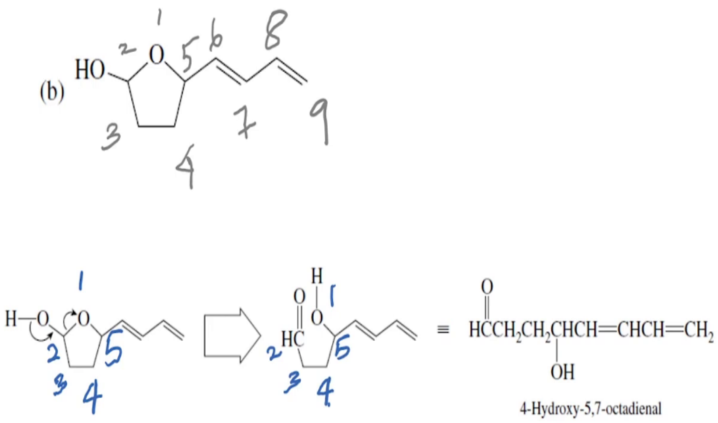
Deduce the structure of the open-chain form of each of the following acetals/hemiacetals.



4-Hydroxy-5,7-octadienal

Now, along the same lines, we can solve the next problem, I am not going to spend too much of time on this, it is just that you just need to number this in the following way 1, 2, 3, 4, 5, 6, 7, 8, 9, and you have a 5-membered ring that is being formed, and therefore the open chain compound is going to be here.

And so, we follow the same numbering as shown here. And you get the product that is formed. So, 1, 2, 3, 4, and 5. So, the oxygen here is 1, and this carbonyl is 2, this is 3, 4, and this carbon is number 5. So, if I follow this, then the open chain compound is going to be this structure as shown here on the right.

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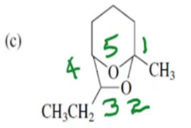
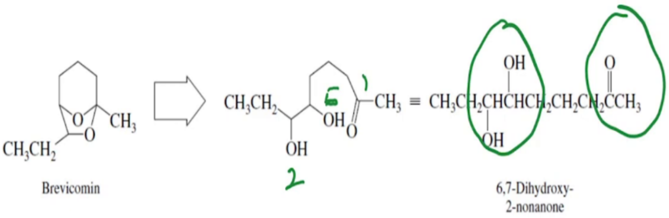


Brevicomin (sex attractant of Western pine beetle)



6,7-Dihydroxy-2-nonanone

Now, the next question is a little tricky, because it is a acetyl that is formed from a ketone and not an aldehyde. And so that is the only difference here. So again, let us just follow the same strategy that we follow which is just number it. So, the way we would number this is we start with this as 1, maybe this oxygen is 2, 3, 4, and 5, and the rest of the carbons are going to be less important.

And so, the way we will do this is that we can first imagine that if you number this again, from here, so this would be 5. And, this would be 2, and this would be 1. And so, these are the important functional groups that are here. And if you then draw out the remaining molecule, you will find that the diol is on the other chain. And it is over here and the ketone is over here. And if you form an intramolecular acetyl, you would get this product.

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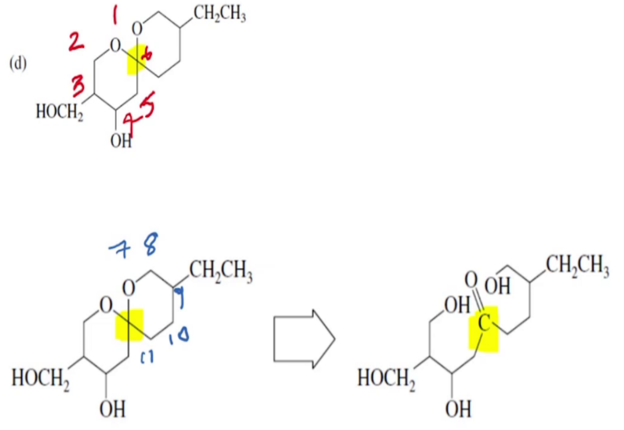

Talaromycin A

2,8-Di(hydroxymethyl)-1,3-dihydroxy-5-decanone

Now, the last question is similarly, solved in a very similar manner. Here, it is interesting, because the ketone that is actually there has diols on both sides. And if it can react an intermolecular fashion, you get this product. So again, the same strategy, we will sort of break down the bond in such a way that we would get the carbonyl and get the alcohol.

So here, this is the carbon that is going to have the carbonyl compound, which is carbon 6, which ends up here. And then you can number the remaining chain based on this and you will get the product that is formed.

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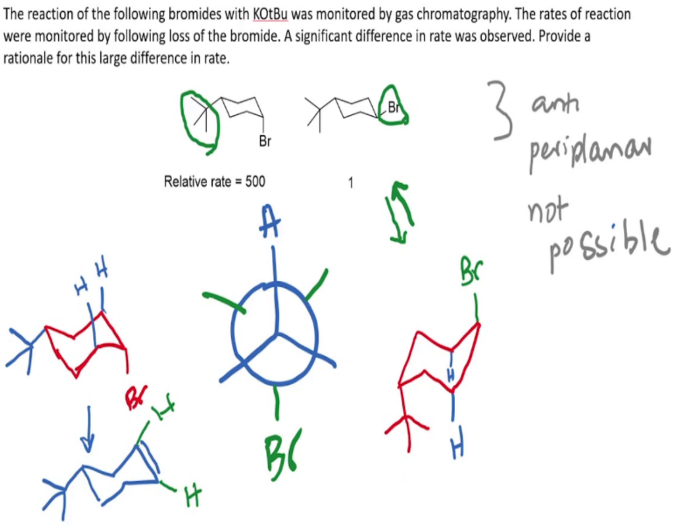

The reaction of the following bromides with KOtBu was monitored by gas chromatography. The rates of reaction were monitored by following loss of the bromide. A significant difference in rate was observed. Provide a rationale for this large difference in rate.

Relative rate = 500 1

Now, to the last question. Here the question here is that the relative rate difference is substantial, which is around 500. And so, how would you explain this result. So, we have already looked at this condition, which is the E2 condition to give you the eliminated product, which is potassium tertiary butoxide. And under these conditions, you would need an anti-periplanar transition state. And so, the Br and H have to be anti to one another.

So, if I draw the Newmann projection, it is going to look something like this. So, you have the hydrogen over here, and then the Br has to be here. And this is going to be the anti-periplanar transition state that is favored for the E2 mechanism. And so, in the first case, this anti-periplanar transition state is possible, because you have two hydrogens here which are anti to the Br and therefore the 180 degrees relationship between this can be achieved with the tertiary butyl group being in the equatorial position.

And we know that the tertiary butyl group being at equatorial position is more favored. However, in the second case, the problem that we see here is that the Br is in the equatorial position.

And therefore, if you look at the hydrogens which are next to it, it is not going to be able to achieve the 180 degrees angle. And so, this compound has to flip. So, if it does a ring flip, then you get the other isomer which is shown here. And once you do the ring flip you get the Br in the axial position and then this Br and this hydrogen are now at 180 degrees and they can be anti-periplanar and the elimination can occur.

However, there is a penalty that needs to be paid for this because the tertiary butyl group absolutely does not like to be in the axial position, which we have already studied in the previous semester. Therefore, this helps us understand why the rate of this reaction is significantly slower than the other one.