hello everyone in the last class you were introduced to glycols and we discussed that what are the different methods of preparation of glycols and what are the different kinds of reactions they undergo in which we saw that the reactions of glycols are similar to those of the monohydrate alcohols continuing with that series today's class we are going to do some more reactions of glycols which are typical of glycols and then ah we are going to continue on from there to phenols

so let us start from where we stopped in the last class talking about the reactions of glycols and in this category today we are going to learn about the oxidation reaction of glycols

so if you recollect we did the oxidation of alcohols the monohydric and today we are going to learn about that of glycols ok

so first case i am going to discuss is with acidified kmno4

so acidified kmno4 is one reagent which is used to oxidize glycols and the product which we get through the oxidation of glycols with acidified kmno4 is either an acid and or could be a ketone

so if you start with a one degree and a two degree alcohol combination in a glycol you end up with an acid and if you start with a three degree o h you get a ketone

so in the acidified chemino 4 oxidation of glycols this is what happens you treat the glycol with kmno4 acidified and you end up with two moles of formic acid with the fission taking place between this carbon-carbon bond

so there is this fission or cleavage of the carbon carbon bond between the two carbons containing the hydroxyl groups take place ok

so carbon carbon bond cleavage takes place this is what happens

so this is a case when both of them are primary in nature if you start with a one which is a secondary alcohol and a primary alcohol

so in this case you will get the corresponding carboxylic acid depending upon the r group and you get one mole of formic acid

so again the fission or the cleavage takes place between the carbon carbon bond here if you start with a tertiary alcohol and a secondary alcohol you end up with a ketone and the acid

so as we say that with 3 degree alcohols we get the ketones and with the 1 degree and 2 degree we get the acid

so this is the oxidation of the glycols with kmno4 acidified another reagent which is used for their oxidation is per iodic acid

so what happens when they are treated with periodic acid which is represented by hio4 or instead of periodic acid we can also use sodium per iodate

so instead of this you can also use sodium per iodate both the cases the oxidation proceeds in the same manner

so with periodic oxidation if you start with the glycol and you treat it with hio4 or naio4 as was happening with kmno4 the cleavage of the bond occurs at this position but instead of the acid as you were getting previously you end up with the mixture of the aldehyde

so in this case since it is symmetrical you get two moles of formaldehyde along with formation of water and the per iodic acid is reduced to iodic acid or if you start with sodium per iodate it also gives you the reduced form naio3

so essentially with periodic acid what we are getting is that your plus seven oxidation state is changing to plus 5 oxidation state of iodine when it forms the iodic acid and the products which are obtained are as you can see from this you get aldehydes and or ketones

so here again if you start with a one degree and a two degree alcohol you get an aldehyde and if you start with the three degree alcohol you get the ketone

so this is what a periodic oxidation of glycol is we take few more examples we see a combination of a 2 degree and a 1 degree treat it with periodic acid and you can guess that as a result of the cleavage here the product is going to be this aldehyde along with the formaldehyde and water and one mole of hio3

so you can see that one mole of hio4 is used when you have one glycolic unit okay when the fission is taking place between one carbon-carbon bond pair if you start with a tertiary and a primary alcohol combination treat it with h i o four and as we said if you have a three degree alcohol then you would expect it once it cleaves it is going to furnish a ketone along with formaldehyde the rest of the byproducts being the same if you start with both three degree alcohols you were introduced last time when you have a diol with both the carbons as tertiary this is called a pinecol and when you treat a pineapple with hio4 you get two molecules of the ketone along with hio3 and water

so the importance of this reaction lies in the carbohydrate chemistry okay

so this reaction is very important it is used in carbohydrate chemistry for elucidating the structure of the sugars

so carbohydrates contain many hydroxyl group it's a polyhydroxyl containing compound

so to find out what is the number of the hydroxyl groups present and what is the kind of the positioning they have with them with each other we use this periodic acid oxidation ok

so let us see some typical examples of periodic oxidation ok

so we will do this together this is your starting substrate ok you subject it to hio4 oxidation what do we expect there is one fission possible here another possible here

so this would require two moles of hio4 and the terminal carbons bearing the hydroxyl get oxidized to aldehyde and the middle one it gets oxidized fully to the acid

so this is what happens with the per iodate oxidation that if you have all the carbons in the middle which bear the hydroxyl functionality get oxidized all the way to acid and that is why it is used in the structural elucidation of sugars

so if you have further elongated chain you have a four carbon system

so you would expect three of these carbon carbon linkages to cleave for which you will require three moles of hio4 and the product would be from the terminal you would get the formaldehyde there are two internal middle carbons containing the o h functionality

so you get two moles of formic acid here and one mole of formaldehyde from the other terminal carbon atom

so this is what happens in case of sugars if you have a terminal formyl group this molecule ok

so again we are looking at two carbon bond cleavage treat it with two moles of hio4 now the terminal formyl group is going to oxidize to formic acid and the internal one is also going to oxidize to formic acid and this terminal ch2oh yields formaldehyde

so if any aldehyde or ketone is present adjacent to the o to the o h carbon bearing o h it also gets oxidized look at this example if you have this ketone following the same rationale treat it with two moles of hio4 and you get formaldehyde another formaldehyde and the internal ketone carbonyl is oxidized to co2

so this is what happens if you have a ketone or an aldehyde it gives you a co2 or a formic acid if any carboxylic group an ester group or a methoxy group for that matter is present next to the carbon bearing the hydroxyl functionality

so if you have to carry out the periodic oxidation of this this reaction does not happen

so these compounds are not oxidized by hio4 likewise if you have a methylene functionality which is coming in between the two hydroxy carbons this again is immune to periodic acid oxidation and you do not see a product in this case as well another important thing which has to be noted here is that for periodic oxidation it is the cis glycols we are taking into consideration the stereochemistry as well with cis glycols these are oxidized by hio4 but if you start with trans glycols these are not oxidized by h i o four

so which means that if you start with this cis one two diol ok we are talking about cis cis1 to diol in a cyclic system or in a acyclic system

so these can be cleaved ok to give you with periodic acid to give you the corresponding oxidized product but if you

so these are ok but if you start with the trans isomer for whatever reason if this stereochemistry is fixed here if you start with the trans isomer then these are not oxidized

so the question is why why does that happen that it is only giving you the oxidation with the cis stereochemistry

so if you just look at the way this oxidation takes place you start with a cis glycol okay let me just redraw this if you start with a cis glycol okay and you treat it with periodic acid

so the first step is that there is this attack of this lone pair of electrons on iodine and you get an intermediate and then there is a subsequent attack by the other hydroxyl oxygen lone pairs and you further get this cyclic intermediate which is followed by loss of this water molecule to generate this cyclic ester ok

so you get this per iodate ester as the intermediate and it is then the decomposition of this per ioda tester ok it is this decomposition of the per iodate ester which is considered actually to be the rate determining step in case of simple glycols and it is this periodic oxidation which gives you finally your two carbonyls along with the formation of hi three

so this is considered to be the rate determining step when we are dealing with simple glycols however if you are dealing with pinecols ok

so in case of pineal coals where you have two tertiary carbons tertiary dietary diol in this case it is because of the steric hindrance offered by these alkyl groups that the ray determining step in fact is the formation of the cyclic intermediate okay it is the formation of cyclic intermediate which is the ray determining step when you are starting with pineal coals and subjecting them to hio for oxidation

so you start with the pinecole treated with hio4 this formation of this cyclic intermediate and this is actually the ray determining slow step and then the decomposition of this to the corresponding aldehyde ketone is the faster step another variance in this oxidation the third one is if you do this with lead tetra acetate

so we discussed with acidified kmno4 then with per iodic acid and then with let tetra acetate oxidation with lead tetra acetate is actually complementary to periodic acid oxidation

so what do we mean by that

so you take lead tetra acetate in acetic acid oxidation of glycols with let tetra acetate becomes important for the glycols which have low solubility in water ok

so glycols which have low solubility in aqueous medium will be more favorable to be oxidized by a lat tetra acetate oxidation

so this is complementary to periodic acid oxidation why because in periodic oxidation it was an aqueous medium which was being used for the reaction but in case of lead tetra acetate oxidation of diols the reaction is carried out in organic solvent like benzene tolvin dichloromethane tetrahydrofuran etc and in this case it is both the syn and the anti glycols that means both the cis as well as the trans one two diols can oxidize the reaction with cis however is much faster versus are more reactive as compared to trans but both reactions do take place as in this case we get both the open chain as well as cyclic intermediates being formed okay which allows both the cis and transforms to react

so let us look at one of the examples of let tetra acetate oxidation of the glycols and the products it yields you treat this glycol with lead tetra acetate glacial acetic acid as was happening with periodic acid you get this carbon-carbon cleavage giving you two molecules of formaldehyde and lead tetra acetate is reduced to the diacetate along with formation of two molecules of acetic acid which are released if you start with this diol and same thing let it recitate you get this product mixture which is a ketone and an aldehyde

so three degrees again giving a ketone one degree is giving you an aldehyde as was happening with h i o four and if you start with a pinecol as we saw earlier also with h i o 4 you get the same products which is the ketone in this case think about the mechanism here again what is it that is happening during the reaction mechanistically that is giving you this product

so you are starting with the diol you are treating it with lead tetra acetate the first step as you would anticipate is the attack of this hydroxyl onto lead and the replacement of one of the acetates by the glycolic o h

so it leads to the formation of this intermediate right and this does not stop here there is loss of another molecule of acetic acid as we saw in the final equation two molecules of acetic acid are being lost

so another molecule of acetic acid is lost and we get now the cyclic intermediate which undergoes decomposition as was happening previously also with the iodate ester and you end up with the mixture of your carbonyl compounds and generation of lead dye acetate this mechanism explains why cis diols would react fast and give you these oxidation products what happens in case of trans diols that once you generate this intermediate in the first step ok you generate this intermediate now in case of trans diols there is a possibility that the acetate loses in this manner and still you are able to get the complementary product with this carbon-carbon bond fission which was not possible in case of hio4 and still you end up with the same product mixture however the yield or the rate of the reaction for trans is less than that of says cis are more reactive cis 1 2 diols are more reactive then the trans one to diols because of the formation of this cyclic intermediate which makes the reaction more facile

so this is about the oxidation reaction of glycols with the different reagents acidified kmno4 hio4 and let tetra acetate another reaction of the glycols which is very important and popular and i refer to in the last class also is the pinnacle pinecolon rearrangement

so you already are familiar with the word pine coal now that it is a diol in which the two hydroxyls are on the two tertiary carbons but how is it synthesized ok

so there is a very special way of making these pinnacles starting from ketones

so you start with the ketone and treat it with a metal like a magnesium or aluminum a metal which is less reactive than sodium or you can use even the amalgam and in this first step there is a single electron transfer from the metal to the carbonyl ok

so from the metal to the carbonyl there is a single electron transfer which results in the formation of this radical anion

so you get an anion radical which again reacts with another molecule of ketone to give you another anion radical and then these two anion radicals they dimerize they to dimerize in the absence of any proton donor and when they

dimerize they give you this molecule which is magnesium pinecolate which then undergoes acidification to yield the desired pinnacle
so this is a method through which the pinnacles are prepared starting from ketones and then what we are learning now is how do these pinnacles undergo rearrangement to give what we call as ketones which are pinnacleones
so pinnacle pinnacleone rearrangement is essentially the rearrangement of a pinnacle which we now know is a one two diol a tertiary one two tertiary diol
so a pineacol is converted to a ketone and what is the reagent the reagent is concentrated h2so4 or anhydrous zinc chloride
so the reaction takes place in concentrated h2so4 and anhydrous zinc chloride to convert a pineal coal to a pineal colon and this is what it looks like
so you start with this pinecole and you treat it with concentrated h2so4 it undergoes elimination of a water molecule and in the process what you get is this ketone in which there is a migration of an alkyl group from carbon 1 to carbon 2.

so the reaction this is called a rearrangement
so whenever we talk about rearrangement it it implies that it involves a migration of something
so there is a migration of alkyl group to convert up in a coal to this ketone which is called a pinecolon now in this case your r could be anything it could be a methyl
so it could be tetramethyl it could be a tetra phenyl
so if you have this then it is your symmetrical pinnacle you can also have different r's
so you your r could be h methyl phenyl or a mixture of these
so the migratory aptitude
so the question is which r is going to migrate
so the migratory aptitude for between these different functional groups follows the order hydrogen followed by the aryl followed by alkyl and in the alkyl again the more electron donating the alkyl the better is the migratory aptitude of that
so this is very interesting reaction of diols in which there is a rearrangement to give a ketone let us briefly analyze what is happening through this reaction
so what is the mechanism of this reaction which is carried out in the presence of concentrated h2so4
so you are starting with your diol diet tertiary diol and you are treating it with the acid ok you are subjecting it to acidic conditions ok
so the first step one would expect is the protonation of the pinnacle
so this is the first thing that one would anticipate is happening that your hydroxyl gets protonated
so there is this protonation of the pinnacle and this is a reversible reaction ok
so this is plus this is minus this is a reversible reaction the first step being the protonation of pinecone reversible step the next is the loss of water molecule ok to give you a carbocation
so there is a loss of water molecule and it results in formation of carbocation this is the second step which also involves the migration of the alkyl group simultaneously
so but i will show them one by one what is happening
so this step is the loss of water and formation or generation of this carbocation and this is followed or is happening complementarily that this alkyl group here is migrating towards this carbon which is bearing a positive charge
so that you get this kind of a cyclic intermediate

so this step is the rearrangement or the migration of the alkyl group but the question is why would the alkyl group migrate

so you are going from a tertiary to a tertiary carbon ok its already a tertiary carbonyl mine but still there is a migration from a 3 degree to a 3 degree taking place

so why is it at all happening

so this is where cons your concept of neighboring group participation that the alkyl group migration on this carbon is actually what facilitates the elimination of this water molecule ok

so this is the concept of neighboring group that this when it migrates on this carbon it pushes this h2o out and this facilitation is what is responsible for the migration otherwise there should be no reason why a tertiary carbon carbonium ion is changing to another tertiary carbonium ion if if there was no such kind of a stabilization being provided

so once you get this intermediate through the migration of the alkyl group

so the other tertiary carbon is what bears the positive charge now

so there is basically shift of the positive charge from one tertiary carbon to another because of migration of the alkyl group which is actually a neighboring group assisting the elimination of the leaving group here and this then undergoes loss of a proton ok

so if we just show it like this this undergoes a loss of proton to give the pinecolon ok and this resonating structure stabilizes and drives the alkyl migration ok

so the important thing about this reaction if you notice that the first step was reversible it involves an intermediate formation of a carbonium ion and the migration of the r group

so the r group should be located trans to the leaving group

so the migrating r group should be trans to the leaving hydroxyl group and both the migration of r and the loss of water they take place simultaneously and this is what is actually driving the reaction forward let us also worry a little about the migratory aptitude which we discussed that this is a migratory aptitude but what is it that our series which we gave that the migratory aptitude of hydrogen is the maximum followed by aryl followed by alkyl

so this migratory aptitude depends upon a few things which the reaction considers before favoring a particular migratory group over the other

so the first is the nature of the group itself ok

so it is the nature of the migrating group preferentially the electron rich group migrates

so the group has to migrate towards a positively charged carbon right

so it is a electron deficient site which is where it is migrating therefore the group has to be electron rich to have an impact in the reaction and for it to migrate

so for example in this if can be illustrated by this that if you have this particular pinnacle under the acidic conditions

so both the carbons are equivalent

so anywhere you can create the carbonium ion it would not make a difference

so if this is your substrate and in the first step you created this carbonium ion

so the next step is now between these two the aryl and the paramethoxy phenyl between the phenyl and the paramethoxyphenyl which group is going to migrate

so when we say electron rich group migrate

so between the two it is the methoxy substituted benzene which is more electron rich therefore this is the one which migrates and you get this carbocation preferentially yielding the corresponding ketone pineal colon as the major product

so the migration of this one takes place over the phenyl because this is more electron rich as compared to phenyl

so this is how we this is

so whatever we are claiming is through what we have seen through the products

so we found that this is the major product and this is what made us believe not one reaction but many reactions which have been carried out and similar analysis has been found in all of them which makes us make a general statement that it is the electron rich substituent which migrates in preference to the other if both have a choice of migrating the second thing on which the migratory aptitude depends is the stability of the carbocation

so we are talking about the intermediate carbocation and its stability

so let us look here you have this pinnacle okay and the first step you treat with h2so4 and you are generating a carbocation

so now between these two tertiary carbons there are two possibilities of generating the carbocation one could be

so if i number the carbons as one and two

so it could either be on carbon one or carbon two if it happens on carbon two this is what you get and if it happens on carbon 1 the generation of the carbocation if it happens on carbon 1 this is what you get ok

so you can get ideally two carbocations a and b

so the question is based on the stability the one which is more stable is the one which will be preferentially formed

so when you look at structure a and structure b in structure b the positive charge is on the carbon which is attached to two phenyl groups and therefore this is there is more of a charge delocalization on the two benzene rings and this will be formed preferentially

so if this is formed preferentially the product from the pinnacle pinnacle on rearrangement of this is going to yield you the major product from b as the intermediate which will then involve migration of the methyl group and formation of this pinecolone

so this is formed as the major product because b is the more stable carbocation and therefore this will be formed in preference to the other yielding you this product as the major product okay the third parameter which decides the migratory aptitude is the stability of the cyclic intermediate

so we said that during the migration a cyclic intermediate three membered is getting formed

so depending upon the stability the reaction draws its thermodynamics accordingly that which is the one is going to form over the other

so for this if you look at this pinnacle in which both sides it can form a carbocation

so there is no question of any difference between the two carbons

so either carbons if it forms it is going to be identical carbocation

so we are done away with that first thing now the question is between the phenyl and the methyl which is the one that migrates

so we are talking about one the electron rich group migrates right but between the two whichever migrates what is going to be the effect on the nature of the intermediate cyclic intermediate which is going to get generated

so if the phenyl group migrates what is going to happen is

so this is the carbon the any of these two will migrate on this carbon

so when it migrates on this carbon the fennel migrates this is the intermediate which you get and if the methyl group migrates ok if this one migrates this is the intermediate which you get now if you compare these two intermediates 1 and 2 you see that 1 is more stable as compared to 2 because again it is a resonance stabilized structure the positive charge is over a phenyl ring

so it has more resonance stabilized structure therefore the phenyl group migration is preferred over the alkyl group migration

so this is from where we draw the rational that ph gets preference over an alkyl group migration ok

so based upon this logic which we have just discussed let us take a few examples and see what are the products which are going to arise from this pinnacle pinnacleon rearrangement

so let us take some examples to validate what we have just said

so in this case you are having two different tertiary carbons ok and each of the tertiary carbons is capable of giving you a carbocation

so the question is which is the major product if you consider all the three factors then you will find that the major product which should form should be this ketone

so between this and this which is the most stable carbocation which is going to be generated is the one which is having two phenyl rings

so if the positive charge is being generated here then the methyl group will migrate on to this carbon okay and therefore it is going to result in this ketone if you have instead of this this pinnacle again we have discussed already now both the cases it is identical carbocation which will be formed

so now depends upon the migratory aptitude which depends upon the stability of the cyclic intermediate

so in this case a phenyl migration would be preferred over a methyl migration and therefore the product which we expect to be the major product will be through a phenyl group migration ok try solving this one

so i can just write in this case that here a phenyl group is the one which migrates and in this case the carbocation is getting generated on carbon one ok

so this forms the carbocation

so that the methyl migration takes place and you get a ketone on carbon two okay in case number three again it is not a symmetrical system

so you have the probability of generating two different carbocations

so we think that the carbon one which beers the phenyl group is the one which is going to form the carbocation

so if it forms the carbocation then there is going to be a migration of either the methyl or the hydrogen and we have seen that the migratory aptitude of hydrogen is the maximum

so this hydride migrates and the product which you get will be this ok lets see few more examples

so the product should be through this hydride migration ok if you are having this is slightly different if you start instead of the pinnacle you start with this as your starting material

so it is not a diol but it is capable of generating the same carbonium ion which you were getting from the pinnacle when you treat this with nitrous acid

so when you treat this with nitrous acid what is going to happen this is going to get removed and you get a carbonium ion being generated on this carbon

so the question is that between carbon 1 and carbon 2 you already have fixed the position of carbonium ion generation which is carbon 2 and now depends of these 2 aryl groups which is the one which migrates it is the paramethoxy or the metamethoxy benzene which migrates in this case

so one would imagine that the paramethoxy is the one which is going to be more electron rich and therefore this is the one which migrates and gives you the product which is through a paramethoxy phenyl migration carbon 2 and on carbon 1 you get this ketone with the metamethoxy phenyl drink ok another example treat it with a gno3 ok you are going to generate carbocation again on this carbon 2

so the product is going to be again there is going to be a choice between a methyl group and an ethyl group migration and ethyl being more electron rich is the one which is going to migrate leaving you with this acyl unit and
so you have ah this carbon it i just redraw this
so this is a methyl and the carbon with two hydrogens and the ethyl group migration ok another example if you take an example of a cyclic diol now this is interesting just look at it carefully that if you take a cyclic diol like this right again this is a pinnacle both are tertiary right what i can do for your convenience i just number this 1 2 3 4 five and six
so between carbon one and carbon six the first thing is which is the one which is going to form a carbocation when it is treated with under acidic conditions
so we could say that you know if the carbocation forms at carbon 6 it is part of a six membered ring it is going to be more stable as compared to when it is forming in a five membered system
so if it generates at carbon 6 now the next thing would be this a migration of this carbon carbon bond ok
so this carbon carbon bond will migrate at this position which is the carbon 6 to give you the spirocyclic ring system in which the two rings are connected through this common carbon and this carbon one is the one which gets converted to carbonyl
so if i number it again this is your carbon six okay this is the carbon one which was bearing the hydroxyl two 3 4 and this carbon 5 now gets connected to carbon 6 by the c c bond migration on to this position
so you get the ring expansion product these are spiro compounds
so what is happening is a ring expansion of five membered is changing into a six membered ring ok
so this is an example where your pinacol pinacolone rearrangement is giving you a ring expanded product ok let us take another example if you have a combination of a four membered and a five membered system okay in this case again there is a choice whether the carbocation is generated on the 5 member or the 4 member 5 in this case being more stable
so the carbon carbon bond migration is going to take place from the 4 membered system
so that there is a ring expansion and in this case you will get two fused five membered rings and this is the spiral compound which you will get similarly if you have two five membered diols with a difference in the methyl group substitution ok
so here again one of them is going to undergo a ring expansion to give you a six membered ketone
so in this case again the carbocation is generated on this carbon and this migrates and forms the six membered with the carbonyl functionality if you have a combination of two six membered one is a methyl substituted and you subject it to the same conditions of pinacol pinnacle colon rearrangement
so in this case between the two this is the one which forms the carbocation this ring
so you have ring one and ring two ok
so ring two forms the carbocation and ring one carbon carbon migrates to give you a seven membered ring ok
so you get this 6 and 7 membered ring this is the product which you expect another example if you have this die also there is one hydroxyl on this cyclic five membered and another on this chain
so if i just number them for your convenience four five
so you treat it with concentrated h2so4 same conditions the product which you expect please try to do it yourself what is going to happen which is the one

which is going to be more stable six or one carbonyl mine

so at which position it is going to be more stable at six right because of the two phenyl group

so once it forms at six then there is going to be a migration from of the cc bond from the ring

so that it again leads to a ring expansion product with this bearing the carbonyl functionality

so if you just see what has happened this is your carbon bearing the o h and now a keto and this is the carbon 6 bearing the two phenyls in 2 3 four and five

so you can see that it apparently is a very simple reaction but it results in very interesting products as a result of the ring expansion in case of cyclic diols another example in case of a monocyclic diol if you start with this okay and you subject it to the same condition

so as you would expect you know the first step will be the protonation followed by loss of a water molecule

so that you are going to have a carbonium ion something like this right now again there are two possibilities one could be that there is this hydride migration ok this one migrates right

so if it is through a hydride migration or there is a carbon carbon

so this is this can be root one this could be root two if there is a carbon carbon bond migration

so what are the two products which you expect

so if the hydrogen goes here right

so this is going to move and you will in this case expect a cyclohexenone right as the product but if there is a carbon-carbon bond migration

so what what is happening in this case in this case instead of the ring expansion it is giving you a ring contraction product

so you get this as your major product

so this is a ring contraction

so far the examples we studied were offering expanded products this is a ring contraction product which apparently is the major product which is formed from this reaction

so that means hydride migration is not the preferred pathway it is the carbon carbon migration of this bond which is the preferred rule

so what could be the reason for this to happen

so if you just look at the mechanism

so the first thing is we have to know about the stereochemistry of this diol okay it could either be a cis or a trans

so if you are starting with a mixture of a cis or a trans let us say in the chair conformation how it would look like if you start with the trans isomer a trans one two diol it means this is what it would look like your trans 1 2 cyclohexane diol this is the diagonal and this would exist in the ring flipped form also which i will just write could be the other form that is the dye equatorial

so both are trans isomers the diagonal or the die equatorial now in this case if the first step let us say is the protonation ok what will happen first of all in the case of the dye eggshell

so for the diagonal we saw that for any alkyl group or the hydride to migrate the h and oh should be anti to each other

so they have to be anti periplana ok they have to be anti periplanar for this to migrate and the migration to take place but in this case the h and o h in no case they can be anti to each other therefore in in this particular diagonal no reaction is possible in the case of die equatorial once this gets protonated ok now the next step is that when it is protonated this leaves okay and the leaving

group and the neighboring group have to be anti-periplanar
so this carbon carbon is what is anti-periplanar to the leaving group and therefore what happens is that you get a carbon-carbon bond migration which is actually acting as the neighboring group in this case and giving you only one product which is the ring contraction product
so the cc is anti-periplanar to the leaving group and you get only one product when you start with the trans isomer from the die equatorial conformation if you take the complementary cis isomer you start with the cis isomer of this diol in which the two hydroxyls are actually equatorial with respect to each other
so now your leaving group okay once it is protonated
so your leaving group let us say and your neighboring group have to be anti-periplanar
so if it happens from this carbon then it is this carbon carbon which is going to migrate if it happens from here then it is this hydride which is going to migrate okay
so in this case you have these two options either you have this combination or you have this combination
so that in case of this cis isomer from a hydride migration okay if this hydride migrates then you get the cyclohexanone and if the carbon carbon bond migrates then again you get this aldehyde therefore since the aldehyde is coming from two different pathways and if you sum up all the contributions then this this product which predominates when we carry out the acid catalyzed migratory behavior of this cyclic diode all right
so in the next class we are going to start with phenols and we will see what are the similarities and differences phenols have with respect to the alcohols
so till then you revise your alcohols and gear up for the phenols for the next class thank you you