today we are going to take up the third part of our chapter on alcohols phenols and ethers

so earlier we discussed about the alcohols and phenols where we talked about their properties their reactivities and their preparations and today we are going to take up ethers which are nothing but the dye alkyl derivatives in a way of water

so todays topic of discussion is ethers

so the ethers are nothing but if you compare it to water

so water is our h2o and if you replace one of the hydrogens by an alkyl group we say that it becomes an alcohol and if you replace both the hydrogens by either the alkyl groups or one alkyl one aryl or both the aryl groups then in such case the resultant molecules are termed as ethers

so these are the ethers which we are going to talk about today

so if it is substitution by di alkyl you call it as a dialkyl ether for example if r is equal to an ethyl group you call it as ethyl ether or a diethyl ether okay

so these are the molecules a new class of functionalities in which your hydrogen of the water has been replaced by r if you replace one of the hydrogens by aryl group it becomes an alkyl aryl ether ok

so this is an example of an alkyl aryl ether

so you can have a phenyl ethyl ether or a phenyl methyl ether which is called an anisole and if you have both these functionalities as aerial groups

so it becomes a diorile ether or a diphenyl ether if both aryls are phenyl groups

so you call it as a phenyl ether

so today we are going to understand some of the properties reactions and preparation methods for these molecules which are called ethers

so looking at the structure you can find some similarities with water

so the bond angle in case of water if you see the hoh bond angle for water is 104.

5 degrees and it has a bent structure water is a bent molecule you convert this to an alcohol replace one of the hydrogens by r and when this r is a methyl example of methanol then your bond angle changes to 108.

5

so for a methanol molecule that means we are talking about an alcohol which is again a bent molecule your bond angle is 108.

when you replace both the hydrogens by methyl and we are talking about this molecule which is a dimethyl ether then the bond angle which is the coc bond angle in this case it is equal to 111.

7 degrees

so in this case your coc bond angle when you have a dimethyl ether

so this angle is 111 degrees 0.

7 and you can see the change in the bond angles as you go from water to methanol to an ether

so if you have to talk about the dipole moment or the polarity of these molecules

so you can envision that if you have these alkyl groups ok with oxygen being more electron withdrawing in nature

so that the net inductive effect is towards oxygen these molecules tend to have a net dipole

so the molecules are polar in nature

so these ethers are polar molecules because of a net dipole moment which they possess okay some of the examples of these ethers as i was talking about

so we discussed that you know you can have something like a die ethyl ether which is in all aliphatic you can have a diphenyl ether okay which has both the phenyl groups or you have a methyl phenyl ether which is called any sole you can also have other kind of aliphatic ethers in which your alkyl groups form a cyclic ring for example this molecule in which you have a cyclic ether which is popularly called as thf it is a tetrahydrofuran which is used as a solvent in organic reaction

so you have tetrahydrofuran likewise you can have something like a tetrahydropyran ok and you can have something which is two of these ether linkages which is known as a cyclic molecule known as dioxane

so all these are examples of ethers you can also have a three membered ring with one of the oxygen and two carbon atoms and these are called oxy rains you can imagine that in this case your carbon oxygen carbon the bond angle is about 60 degree

so these molecules are highly strained systems and that is why they show high reactivity and open up ok

so what are some of the key physical properties of these molecules the physical features or the physical properties of ethers

so if you have understood that in in case of ethers your oxygen is sp3 hybridized okay and the molecules have a net dipole moment the properties let us talk about the boiling point the boiling point of these molecules is similar to that of the corresponding alkanes ok

so it is similar to corresponding alkanes the boiling point but it is lower than the alcohols then the corresponding alcohol

so if you compare alcohols and ethers then alcohols have a higher boiling point as compared to ether

so if i just make a direct comparison between n-heptane which is an aliphatic hydrocarbon and its ether analog which is again a seven membered a methyl n pentyl ether and you compare the corresponding alcohol functionality which becomes n you know a similar n hexal alcohol if you compare the boiling points of these three then your n heptane is 98 degree your ether is 100 degrees and your n hexal alcohol is 157 degrees okay

so you this again you can see that it is because of the hydrogen bonding which is happening in case of the alcohols that the boiling point is high this we discussed earlier but in case of ethers there is no intramolecular hydrogen bonding between the ether molecules and because of this the boiling points are similar to that of the corresponding alkanes ok how do they behave in terms of their solubility features

so when you talk about the solubility of the ether molecules again how is their solubility in water

so when you look at the alcohols they were highly soluble in water because of extensive hydrogen bonding in case of ethers again this lone pair of electrons on oxygen it can undergo hydrogen bonding with the water molecules which can result in its in in it getting solvated and therefore these can be miscible in water

so they have miscibility in water is you know dependent upon the type of the ether which we are using

so solubility in water for these molecules for ethers varies ok

so it varies depending upon the type of the ether

so for example for a di ethyl ether the solubility in water is very low solubility is very low and that is why it is used as a solvent for extraction of organic compounds right during the workup diethyl ether is used it is not miscible with water but another cyclic ether like a thf tetrahydrofuran this is completely water soluble

so the solubility properties vary and as we keep on increasing the chain length for the higher ethers they become less soluble in water and the lower ethers are more soluble in water

so they have a varied solubility feature why are these compounds important what are the applications what was the first application which came out from ether

so it was in 18th century or early 19th century when it was found that these ethers have been very important application to be used as an anaesthetic

so they were used as an anesthetic in medicine because they especially for the treatment of all all the tooth related disorders when they were used to cause a painless procedure during any truth operations

so now this is one of the halogenated ether which is called penthene which is a very popular anaesthetic and it is a halogenated ether which is used these days but the earlier anaesthetic which came up was the die ethyl ether

so this was a breakthrough when it was found that ethers can serve as you know important anaesthesia anesthetics in medicine ok

so looking at the applications one it is used as an anaesthetic the second application as i was telling you that since it is immiscible in water it is used as a solvent in extractions it is used as a solvent in extractions and it is also used for the preparation of grignard's reagent

so these are some of the applications of ethers in general and when we talk about diethyl ether diethyl ether is what is normally referred to as ether

so when we say ether we are talking about diethyl ether this molecule has a boiling point of 35 degrees it is highly flammable and water insoluble these are some of the properties of this which is the most widely used ethers and another key feature is that it forms explosive peroxides with oxygen it forms explosive peroxides with oxygen and that is one reason why these ethers are stored in dark colored bottles because this is a light initiated reaction

so what is the mechanism for formation of these hydro peroxides of ether

so this is a light induced reaction

so for example we talk about the diethyl ether as an example

so this is a light mediated reaction takes place by radical pathway

so if you have the die ethyl ether in the presence of light it can generate this radical which in the presence of oxygen can form this kind of a peroxy intermediate which then abstracts a hydrogen radical from the other ether molecule right resulting in the formation of the hydro peroxide of ether along with the generation of this radical which is again going back to this cycle and carrying forth all this hydroperoxide formation

so that is why ethers are stored in dark colored bottles in order to prevent the formation of these explosive hydro peroxides

so what is a method to determine you know that these hydroperoxides are getting formed in your ether bottle you open the bottle you do not know but your hydroperoxide is there

so the method of determining these hydroperoxides or peroxides in ether

so one of the test is the potassium iodide test

so what is done is that you shake the ether you take some amount of ether let say 10 ml and you shake it with the solution of potassium iodide okay you shake it with the solution of potassium iodide let us say for 10 ml it is 1 ml or 10 percent weight by volume of potassium iodide and a few drops of hcl mixed with it

so you shake it and when you shake it you will find that the iodide gets oxidized to iodine right

so you get iodine from iodide and this changes the color of the solution to yellow

so the solution turns yellow in color and this you can further confirm if you add few drops of starch to this and you will get a black violet color so this tells that the ether solution is containing some amounts of hydroperoxide another way of determining this could be by treating it with with ferrous ammonium sulphate and potassium thiocyanate solution

so you take the ether solution and shake it with a mixture of ferrous ammonium sulphate and potassium thiocyanate aqueous solution

so when you do

so the peroxide what it does is the peroxide reacts with the ferrous ions and oxidizes them to ferric ok

so this is the oxidation reaction ferrous to ferric and then these react with the thiocyanate ions which are there from potassium thiocyanate and you get this kind of the ferrous thiocyanate complex the ferric thiocyanate complex which is red in color

so this is another indication that the peroxides are present in your solution now how to remove the peroxide impurities

so the removal of the peroxides from the ethers is important in order to avoid any accidents when you are using ether as a solvent

so in order to do that

so once you have seen that it contains impurities one way is that the ether can be washed or shaken with you wash it with with ferrous irons ok you wash ether with ferrous iron solution

so the parasite solution could be solution of ferrous sulphate and what it does is it reduces peroxide

so this is one of the ways of removing the peroxide impurities or the second thing you can distill the ether from concentrated h2so4 which results in oxidation of peroxide

so it oxidizes peroxide

so these are the two ways in which we can convert the peroxides into the non harmful forms and clean clean up our ethers ok

so this was about the general properties the solubilities the boiling point and other characteristic features of ethers

so now we talk about the synthesis the methods of preparation of ethers ok

so we next go to the synthesis or the preparation of ethers

so the most popular synthetic protocol for making ethers is a name reaction which is called williamson synthesis

so williamson synthesis is a method which is used to make unsymmetrical as well as symmetrical ethers

so you are talking about two different alkyl groups or two identical alkyl groups

so this has the capacity to make both the unsymmetrical as well as symmetrical ethers ah with the help of a substitution reaction which is the sn2 reaction in this case

so what we do in williamson synthesis is you take the alkyl halide which is primarily a one degree alkyl halide and treat it with sodium alkoxide ok

so this is the sodium salt of an alcohol which is called sodium alkoxide

so when you react the alkyl halide with sodium alkoxide you get the corresponding ether along with formation of sodium halide

so in this case as i told you the limitation is that this has to be a one degree alkyl halide why

so because the reaction which is involved here is a sn2 type of reaction

so it is a sn2 substitution reaction for example you take methyl bromide and you treat it with sodium tertiary butoxide and in this case what you get is a methyl tertiary butyl ether

so there is a nucleophilic substitution of the alkoxide the alkoxide replaces the halidine so nucleophilic substitution of the halide ion by the alkoxide

so this is your leaving group

so in the same manner if you generalize it that your alkoxide ion and this is your one degree alkyl halide the nucleophile attacks the alkyl with the simultaneous loss of the leaving group and you get the ether and this is your leaving group

so in this case if we want to make unsymmetrical ethers what are our limitations

so we have suppose we want to make this molecule

so we have two choices we have two routes through which we can proceed about making these molecules one could be that we start with ethyl bromide and treat it with the sodium salt of tertiary butanol the second option could be that we start with the other halide tertiary butyl chloride and treat it with the sodium salt of ethanol in this case sodium ethoxide

so the question is which of the two is the correct approach towards making this molecule ok

so as i was explaining that in this case the approach the reaction which is going to give you the product will be this reaction and not this reaction simply for the reason that we have to understand that these alkoxides which we are using they not only act as nucleophiles ok

so they behave as nucleophiles but they also behave as strong bases which can result in a competing elimination reaction

so there is always a competing elimination reaction which will happen if your alkyl halide is not a one degree

so this if it is a one degree alkoxide elimination is very minimal or it is not there but if you have two degree and three degree alkyl halides in this case the elimination product will also be seen along with the substitution product which is the ether okay

so that is why preferably in williamson synthesis when we are doing a sn2 substitution it is the one degree alkyl halides with which the procedure is most successful all right the second method for synthesizing these ethers is an analogous method what we discussed for alcohols which was mercuration oxymercuration demercuration in this case it is called l coxy mercuration demercuration

so this is similar to what we studied earlier nothing changed for alcohols the only thing is that instead of the water molecule in this case it will be the alcohol molecule which will add up on to the alkene

so it is similar to the oxymercuration democulation in alcohols the starting product material is the same you start with an alkene and you treat it with the mercury salt which is mercuric trifluoro acetate and this is happening in presence of alcohol as one of the reagents

so what you get is this intermediate after alkoxy mercuration which when subjected to reduction with sodium borohydride gives you the corresponding alcohol after reduction of this mercury group

so the addition as was seen with case of water for making alcohols it follows markonikov's addition which means that again if you have different substituents placed on the olefin that the hydrogen is going to add to the carbon which is less substituted okay the williamson synthesis can also be applied to alkyl aryl ethers ok

so i take the alkyl aryl ethers separately just to say but the method is the same ah the williams and ether synthesis

so you take the phenol right as instead of the alkoxide you can take the sodium phenoxide

so you take this or sodium phenoxide in this particular case and you treat it

with alkyl halide
 so again you can have an alkaline solution
 so you can have aqueous naoh if you are using a phenol you use aqueous naoh right you maintain an alkaline solution and you get the corresponding alkyl aryl ether
 so these are the general conditions
 so as a representative example if you start with any halide let us say a benzyl bromide and treat it with not a preformed sodium phenoxide but a phenol in aqueous naoh you get the corresponding alkyl aryl ether right it could be this or another reagent which you can use instead of the alkyl halide with phenols it can also be methyl sulphate which in the presence of aqueous nuh again can give you this particular ether which is popularly known as anisole
 so you get any soul along with the formation of this salt it is a cheaper reagent it is cheaper reagent compared to the corresponding alkylating agent which you would have used in this case as an alkyl iodide or something
 so it is cheaper reagent than your corresponding methyl halides ok
 so in this case again just look at the reagent combination suppose you want to make this particular ether
 so you have a proper group on one side and a phenyl on the other side a propyl phenyl ether
 so how do you go about it again you have two choices two routes to think about
 so one could be that you start with propyl bromide and treat it with sodium phenoxide and the other route could be that you start with sodium propoxide and treat it with aerial bromide ok
 so again the question is that whether you want to use the sodium phenoxide or you want to use the aeryl bromide
 so this particular part does not happen in fact the reaction goes through this pathway because one can give a rational it is because of the low reactivity of these aeryl bromides towards nucleophilic substitution
 so the aryl bromides are not good substrates towards nucleophilic substitution across this is difficult and that is why we will not use this particular combination in order to carry out the we the synthesis of these kinds of ethers we move on to the other class of ether
 so so far we have talked about the cyclic uh the not the non cyclic ethers ah like your dye alkyl ethers or the aryl alkyl ethers let us see how do cyclic ethers behave in terms of their synthesis or what are the general methods for preparation of cyclic ethers which are also called epoxides
 so again depending upon the ring size of the cyclic ether if you have a three membered ring with one of the atoms oxygen this is called oxidane if you have a four membered with one of the atoms oxygen it is called oxytane
 so auxy is telling that there is an oxygen and the rest of this is telling about the chain length of the cyclic ether if it is a five membered which we just saw a few minutes ago we called it tetrahydrofuran and this is called oxolane as a general nomenclature the five membered and if it is a six membered then it is called a tetrahydropyran or this is an oxane ring and if you have a six membered with two of these ethers its a bifunctional you call it a one 4 dioxane
 so these are some of the popular cyclic ethers which we know of ok
 so one of the methods for preparing these cyclic ethers is by the air oxidation of ethylene
 so when you want to prepare a three membered auxiliary type of ring the simplest way is you carry out the aerial oxidation of ethylene or ethene in the presence of silver oxide as the catalyst at 300 degree centigrade when you get the corresponding ethylene oxide as your product ok the another method for

making the larger cyclic ethers would be by dehydration of diols

so you start with a butane diol you can start with a butane diol a 1 4 butane diol and you carry out dehydration with concentrated sulphuric acid and you get the five membered cyclic ether which is your thf along with elimination of water molecule likewise you can choose a one five pentane diol

so this is five ok one two three four five and again you with this one five pentane diol if you heat it with concentrated h2so4 high temperature 140 degree centigrade you get the six membered tetrahydro pyram along with formation of water molecules

so this is in fact a general method the dehydration of alcohols is a industrial scale method for preparation of ethers which can also work in fact for elecyclic ether

so even if you have regular acyclic alcohol you can treat it with concentrated h2so4 just simply you have to heat it when you get the corresponding ether the only difficulty with this reaction is that this is not optimized same for all types of alcohol

so for example the competing reaction always exists in this case

so if you have ethanol and you do this dehydration at 180 degrees centigrade you end up getting ethene you get the elimination product right but if you do the same reaction with ethanol at 140 degree centigrade it is then that you get the diethyl ether

so so there is a nucleophilic substitution versus elimination which are competing right

so the nucleophilic substitution is happening when the alcohol is in excess and at a lower temperature right in this case the first step is the protonation of the alcohol followed by the attack of the second alcohol molecule to form this ether but in the other case there is a competing elimination reaction if the if if the temperature is higher

so the dehydration of alcohols is also applicable for getting ethers the acyclic ethers and this normally will happen it is going to end up giving you symmetrical ethers

so this is a good method only for symmetrical ethers while williamson synthesis was able to give you unsymmetrical ethers as well ok and normally again it would be best when you have one degree alcohols here because with again 2 2 degree and 3 degree you are going to get amounts of elimination product as well which is kind of a side reaction for us and not needed okay another method for making these cyclic ethers is by the vicinal is from these vicinal halohydrins which change to epoxide

so your vicinal halohydrins which you if you recollect we did it earlier when we were talking about the alcohols that you form this kind of a hypo halos acid can form and it undergoes an addition reaction on the olefin double bond and you get this kind of a halohydrin which under alkaline conditions ok in the presence of the base can result in the formation of epoxides this we did earlier also this is one of the method for preparation of these cyclic ethers which is the vicinal halohydrin to epoxide ok

so this was all about the different methods of preparation of ethers right

so we have seen that when we have to prepare cyclic ethers acyclic ethers by and large they are two three general strategies and depending upon the nature of the ether which we want to prepare we choose the right combination of the two substrates one which is the alkoxide if you are doing williamson synthesis and second which is the alkyl halide which is generally a one degree alkyl light if we want to prevent the elimination from taking place that is a competing reaction and which lowers the yield in most of the cases

so that has to be taken care of ok

so what are the reactivities and the chemical reactions of ethers

so ethers have a very few set of reactions normally what they can undergo because the carbon oxygen bond is quite strong

so the general categories the one of the important class of reactions is the ether cleavage reactions

so we have ether cleavage reactions in which you have your ether okay which is your coc bond and you have a nucleophile which comes and attacks on this carbon okay

so you are talking about the cleavage of the co bond how can it happen

so if the nucleophile comes and attacks from the back side and you are able to force the reaction to give you this substitution product then what is the probability of this reaction to happen

so by and large we see that if directly a strong nucleophile comes and attacks ethers it is not able to carry out the cleavage of the co bond okay

so the reason is that your co bond is quite strong right and the second thing is that your leaving group which is alkoxide in this case it is a poor leaving group

so your alkoxide ion is a poor leaving group and because of these two reasons a direct cleavage of the co bond by attack of a nucleophile is very less probable ok

so just except your oxidanes right the ethers are not directly cleaved by strong nucleophile

so the only exception to this are oxy rains where directly the co bond can be cleaved because they are highly reactive species as i told you its a strained molecule the cyclic ether the oxidant is the only one which can be cleaved directly by a tag of a nucleophile but not the aliphatic ether

so for the cleavage what are our options

so in order to carry out the cleavage of the ah co bond we have to activate that ether linkage okay

so the ether linkage has to be activated

so this is the condition that has to be satisfied in order to break the ether bonds that it has to be activated

so one one of the ways would be that you make use of this cleavage by making you by using a stoichiometric amount of acid

so use stoichiometric amount of an acid which activates the oxygen

so what it does is that you have your ether and you add an acid right the first step is the protonation of the ether the proton you should ok it goes and adds on to your oxygen site and this gets protonated now after this now the next step could be the attack of the nucleophile

so one you have activated your ether now the nucleophile can come and attack either through sn1 pathway or through sn to pathway

so now the nucleophile can come and attack

so which is the pathway it is going to choose it again depends upon the nature of these alkyl groups on the ether

so if you have one degree and two degree ether carbons ok

so if your ether is comprising of the alkyl groups which are one degree and two degrees and you have a strong nucleophile

so i am talking about the conditions and you have a strong nucleophile let us say we are working with an iodide then it is the sn2 path which will operate

so sn2 operates and what will happen that your nucleophile is going to attack on which of the two carbons of the alkyl group the attack will be on the less hindered carbon as would be the typical characteristic of an sn2 reaction that the attack is on the less hindered carbon and you get a less substituted alkyl iodide and a more substituted alcohol so this is what is going to happen primarily that these are the major products if your ether is carrying the alkyl groups which are one degree and two degree

so just to represent it you have your coc linkage one side your alkyl group of the ether is a two degree alkyl group one side it is a one degree alkyl group the first step is the protonation which is activating your ether right

so you have your protonated oxygen

so now you have the choice of a one degree and a two degree alkyl group

so your iodide which is the nucleophile is going to come an attack on the carbon which is which is less hindered okay

so this goes and attacks here and you end up with the products which are the less substituted alkyl iodide ok

so your alkyl iodide is less substituted and your alcohol is the one which is more substituted it contains that alkyl part which was more substituted ok

so this is one of the conditions the second condition could be that if one of the ether carbons if one of the ether carbons is three degree ok if it is three degree now it can yield a stable carbocation ok it is capable of yielding a stable carbocation right and now once you have a carbocation from there on both your sn1 and e1 can operate

so what you will get from here if it is a 3 degree alkyl group on the ether you will get the alkyl halide which is more substituted you get a more substituted alkyl halide and you get the less substituted alcohol

so it reverses what we just saw a minute ago when it was a one degree or a two degree

so if you have a three degree alkyl halide at one place in the ether right

so the first step which is the protonation has happened already

so now it can stabilize two it can stabilize to a stable three degree carbocation

so that after that when the nucleophile attacks what you get is this alcohol which is less substituted and you get on this stable carbocation the attack of the nucleophile which gives you the alkyl halide ok

so again there are two possibilities here

so you can get the alkyl halide which is the more substituted alkyl halide or it can undergo loss of a proton that is elimination reaction which is always competing with the three degree carbocations and you can get the corresponding elimination product

so you can get both the elimination product as well as the substitution product by the sn1 pathway okay

so this is the general reactivity of the different alkyl groups in case of ethers if you have comparable ok

so if we have the rs which are comparable ok

so if you have comparably substituted carbons then you end up with a mixture of products then it is very difficult to control the product distribution

so if r and r dash are similar like 2 degrees 3 degrees they are similar in their stability orders and if you treat it with h i and you want to bring about the cleavage of the ether the co bond then in this case you will end up with a mixture of two products one will be this halide and this alcohol and the other would be this halide and this alcohol and if one of your rs is an aryl group ok what will happen if it is an aryl group and if it is an aryl group you can imagine that both sn1 and sn2 they cannot occur on the aromatic carbon sn2 cannot occur on aromatic carbon and even sn1 cannot occur on aromatic carbon you can see here that if it is this molecule phenetol ethyl phenyl ether and you try to cleave it with h i

so your first step is the protonation which gives you this protonated ether and now when your iodide comes ok so when i minus comes it cannot attack here right this is not susceptible to it is not stable carbocation or fennel and sn2 cannot occur from the rear side

so the only option which you are left with is that in this case you only end up with these two products which is a phenol and the alkyl halide

so this is about the cleavage of the acyclic ethers which is the acid catalyzed cleavage right

so now we again try to see what happens in case of oxidanes

so oxidanes also undergo acid catalyzed cleavage

so the first in a similar manner which is a acid promoted cleavage for oxidanes

so we have this oxirane again the first step is your protonation right and what you get is

so it is an unsymmetrical oxidane as you can see both the carbons are differently substituted

so you get this protonated oxidane ok

so now you have two carbons

so your c one and c two ok now the question is where is the nucleophile going to come and attack

so your nucleophile when it has to make a choice between c one and c two

so if this positive charge resides on c1 it will be stabilized much more

so this c1 carbocation will be stabilizing much more because of the two alkyl groups and therefore this positive charge since it is more stabilized on c1 the nucleophile prefers to attack c1 right and therefore the product which you get on the ring opening of this epoxide is with the c one substituted with the nucleophile and the c two bearing the hydroxyl group ok

so this is one of the aspects of the acid promoted cleavage in case of oxidants that where is the nucleophile going to open up the ring the reacting c one which we just saw it undergoes inversion of configuration it undergoes inversion of configuration which indicates that the reaction might be through sn2 mechanism that it might be going through an sn2 pathway ok

so the mechanism probably for this what is happening here is that you have your oxy rain

so you protonated it that is your first step the protonation of your oxidane right now when the nucleophile comes and attacks it attacks the more substituted carbon ok because of the significant carbocation characteristic of the carbon in this intermediate and after the reaction when it opens up then what you get is a ring the ring open product has an inversion at this carbon center ok

so your nucleophile your r dash and your r this o h this is r and this is h

so this carbon ok it shows an inversion and this carbon shows the retention of configuration as a result of the ring opening

so this is similar to something you know a cyclic intermediate the bromonium ion intermediate if you recollect it is similar to the bromonium ion intermediate in which also there is a backside attack of the nucleophile ok

so this is cyclic intermediate and the attack of the nucleophile is from rear because of which there is the inversion of configuration at this c one ok in case

so one of the cases could be that if both r and r dash are highly substituted ok

so if both r and r dash are three degree then you will have in that case a carbocation

so if you have r dash and r ok in this particular case and you get this carbocation ok now in this case if the charge is highly stabilized on this carbon then it can even open up ok

so instead of staying as a bridge cyclic intermediate it can open up to give you a open chain carbocation and if you get that carbocation species then you end up getting a racemic product mixture

so if these carbocation if this alkyl groups tend to stabilize this carbocation extremely well then this is going to open up in the first step right and before the nucleophile attacks and in that case you are going to end up with the racemic mixture of the products okay

so this is the possibility that what will happen that you it opens up and it gives you a discrete carbocation before the nucleophile attacks in your sn1 pathway okay and then you get end up with the mixture of two products one with the retention of configuration ok

so we just put this and one with the inversion of configuration where the nucleophile attacks from the same site ok

so so you get the mixture of these two products if the reaction in during the reaction this intermediate opens up okay the second which i told you which is not possible for the acyclic ethers is the nucleophile promoted cleavage which can only happen for oxy rain

so you have a nucleophile promoted cleavage which is a pure sn2 pathway ok this is a pure sn2 nucleophile promoted cleavage

so what is happening in this case is that you have your oxy rain right and a strong nucleophile can come and attack the less hindered carbon ok and this gives you this intermediate alkoxide which upon the acidic workup will give you your final product through the ring opening of the epoxide which is the alcohol

so this happens only for these systems and if you look at it observe it clear carefully you can see that on this side there is the retention of configuration while on this side since the nucleophile is attacking from the back side this carbon the configuration is inverted and if your nucleophile happens to be a grignards reagent then it can result in the formation of a new carbon carbon bond with the help of the nucleophile assisted ring cleavage of oxidanes ok

so the last example i am going to talk about the ethers is a very popular rearrangement reaction which is known as the collision rearrangement

so this is one of an important interesting rearrangement reactions of ethers and which ethers this is shown by lyle aryl ethers when they convert to ortho alyl phenols when subjected to heat

so this popularly is known as collision rearrangement

so if you have this allyl aryl ether and you heat it at about 200 degrees you get a rearranged product which is this phenol on this side and the entire lyle group comes at the ortho position and you get these ortho allyl substituted phenols right

so the question could be that if your you know ortho position is blocked then what happens

so if your ortho position is blocked with two alkyl groups lets say two methyl groups and you again subjected to the collision rearrangement then the allyl group travels to the para position it moves to the para position to give you this para substituted phenol

so this is a very interesting reaction because it allows you to get these allyl substituted phenols

so probably what is happening here is that this kind of a cyclic reaction to give you this intermediate first ok

so you have a ch two c h double bond c h two and then this moves back to give you the phenol

so we are getting we are getting these products as a result of collision rearrangement a very useful reaction ok

so i am going to stop here this is all about ethers their preparation their reactivity their cleavage reactions their physical properties

so we will stop with this and that brings us to an end of the chapter which is the alcohols phenols and ethers thank you you