

hello everyone in the last lecture we discussed the oxidation and rearrangement reactions of glycols with this

we conclude the alcohol portion of this chapter and today we are going to continue with another

topic from this module that is phenols okay so our today's topic for discussion is phenols and

the general structure the chemical structure which represents phenols is given

like this phenols are essentially a hydroxylated benzene ok

so it is a hydroxy

benzene it is also known as carboxylic acid phenols are also known as carboxylic acids if you

look at this structure of phenol the hydroxy is attached directly to this sp² carbon

which is a part of the benzene ring if i rewrite this structure in another manner for the same phenol this is the structure of cyclohexa-2,4-diene-1-one

so this essentially represents the keto form of the phenol

so this can change to the enolic form which is actually the phenolic form in this case

so this is the keto form and this is the enol form of this molecule and this is what we call as the

keto enol tautomerism

so the keto enol tautomerism exists in case of phenols and the enolic form that is the phenol in this case is the major contributor and the keto form

contributes in a minor way that is why if you look at this equilibrium it is more towards

the enolic form and less towards the keto form the stability of the enolic form can be understood

in terms of the aromaticity acquired as a result of enolization

so this aromatic ring is what

is the driving force for the enolic form to predominate okay

so this is the thing which exists

because in this case there is only the carbonyl one carbonyl which is giving you more stability

over a carbon carbon double bond right but in the case of a phenol it is the aromatization

which is a driving force ok let us look at some of these examples of phenolic compounds if you

have a simple phenol substituted with a methyl group at the ortho meta or para position which i

can represent like this it becomes a ortho methyl a metamethyl or a para methylphenol and these

methylated phenols are called chrysol

so the methyl substituted phenol is called chrysol and

if you see this is isomeric with this molecule which is nothing but your benzyl alcohol

so chrysol are isomeric with benzyl alcohol but this is not a phenol a benzyl alcohol is an aromatic alcohol right this is an alcohol this is not a phenol it's an

aromatic aryl ring containing alcohol but a phenol is o h is directly connected to the

benzene ring

so the two have significantly different properties ok likewise there can be other aromatic alcohols and if you have to name these aromatic alcohols so you would take

this as the preference one two three

so you say that this is a three phenyl propanol but these are aromatic alcohols they are different from phenols the most important application of phenols

is found in the phenol formaldehyde resins ok the phenols are important precursors to

these polymers and there is where it finds its principal use let us see some of the

methods of preparation of these molecules

so the preparation of phenols can be carried out on an industrial scale and at lab scale let us see some of the methods for

the industrial preparation of phenols

so to get the bulk amount of phenol on the industrial level one of the methods which is used is from the coal tar distillation

so it is a natural source the coal tar and when we carry out the distillation of the coal tar we get different fractions from the fractional

distillation you get the light oil the middle oil and the heavy oil fractions from the cold are

distillation and it is the middle oil fraction which comprises of mixture of phenols and

naphthalene ok

so it is this middle oil which is then subjected middle oil fraction is subjected

to subsequent treatment from which pure phenol can be isolated

so this is on the industrial scale for isolation of phenol and the boiling point of pure phenol lies in the range 180 to

182 degrees celsius another method on an industrial level for the preparation of phenols

is from chlorobenzene starting from chlorobenzene phenol is prepared by a process which is known

as douce process ok it is popularly called the douce process and in this what is done is that

chlorobenzene is treated with aqueous solution of sodium hydroxide at a high temperature and

under pressure okay

so it is treated at a high temperature and pressure and under these conditions it results into formation of sodium phenoxide which on acidic workup gives us the

corresponding phenol

so this is called the douce process and in this the formation of the phenol is believed to occur via a benzyne mechanism

so i am sure you must have studied the benzyne mechanism the elimination addition pathway

so that is the intermediate involved in the substitution

of the chloro group by the hydroxy group because it is kind of a nucleophilic substitution reaction

and we know that aryl chlorides or aryl halides for that matter are not very easily susceptible to substitution nucleophilic therefore since we find this to happen the mechanism has been proposed to go by a benzyne intermediate another method for the industrial preparation of phenol is starting from cumene cumene is also known as isopropyl benzene so we start from isopropyl benzene or cumene and treat it with air so under oxidative conditions it yields an intermediate which is a cumene hydro peroxide so you get this as the intermediate which is cumene hydro peroxide this is your starting cumene you subject it to aerial oxidation you get this intermediate and this on treatment with acid results in the formation of phenol along with generation of a ketone which is nothing else but acetone so you get the phenol and you get acetone as the byproduct from the cumene oxidation so from in going from the hydroperoxide to phenol we believe what is happening is that there is a migration of this phenyl group so this reaction it involves the migration of this phenyl group to give you this intermediate so you get this intermediate the phenyl group migrates towards the oxygen you get this intermediate with this carbon bearing a positive charge and then you get this intermediate in which you have two leaving groups on an sp^3 carbon so this leaves ok and from here this is what you get the phenol and formation of acetone so this reaction is a commercially successful process of making phenols ok so this is a commercially most successful method of making phenols starting from cumene and cumene can be easily prepared from benzene treatment with propene so you can easily get cumene so this is an acid catalyzed reaction ok you get the cumene and cumene on aerial oxidation gives us the phenol and acetone ok these are some of the industrial methods for the synthesis of phenols let us see what are the lab scale preparations the lab scale preparation of phenols so in this there are again several methods the first one i am going to discuss is starting from sulfonic acid from sulfonic acid as the precursor this is actually called the alkali fusion of sulfonate so you have alkali fusion of sulfonates so in the presence of the alkali what happens that you have your sulfonic acid in the presence of alkali you get the sodium salt of sulfonate ok so this is your starting precursor your sodium aryl sulfonate and this is subjected to fusion with the alkali

ok

so you treat it with NaOH aqueous conditions at 300 degree centigrade so this is the fusion step where you get sodium phenoxide along with formation of Na_2SO_3 and this then upon acidic workup gives us the phenol ok

so in

this case you get the phenol and your aryl can be anything you could have a phenyl you could have a substituted phenyl ok a tall vial any of these groups so

this is a method a lab scale method for preparation of phenols starting from sulfonic

acids as the substrate the next method is by hydrolysis of diazonium salts

so it is starting from diazonium salts and carrying out its hydrolysis in aqueous acidic solution

so you have a diazonium salt you subject it to acidic hydrolysis at a certain temperature

so the reaction involves

heating and you get the phenol along with the liberation of N_2 and H^+ and the diazoniums we

know are easy to obtain starting from the aryl amines and the aliphatic amines again you have

studied that you can always prepare starting from benzene subjecting it to electrophilic

substitution nitration in this case you get the nitro substituted benzene reduce it with tin

HCl you get the aniline and the aliphatic amine can be subjected to diazotization with NaNO_2/HCl

at low temperature when you get the diazo compound which can then be subjected to this hydrolysis

acidic hydrolysis under heat and you get the phenol and nitrogen in HCl so this is essentially

a very straightforward method starting from the diazonium salt hydrolysis another

method is from Grignard's reagent you take the Grignard's reagent in the presence of air treat them with oxygen and

this is followed by again a dilute acid hydrolysis

so what happens overall you start with the aryl Grignard reagent phenyl magnesium halide in the presence of oxygen it forms this organomagnesium

which upon acidic hydrolysis acidic workup gives you the phenol and this magnesium salt

so these are some of the methods for the lab scale preparation of phenols let us now look

at some of the physical properties of phenols

so when you see a phenol there is a hydroxyl which is attached to this carbon which is sp^2 hybridized and part of the aromatic ring if you look at the

physical state these are usually colorless liquids or they are low melting solids

so if you look at a phenol for that

matter simple phenol unsubstituted it is a solid with a melting point 43 degrees

centigrade it's a low melting solid but it has a high boiling point of 182

degree centigrade and the high boiling point you can imagine can be attributed to the hydrogen bonding property of this molecule which we discussed earlier the other thing they possess is a typical carbolic odor because of this hydrogen bonding ability of the phenols it is also possible to solubilize them in water

so they are moderately soluble in water because you have two parts you have the hydroxyl which is solubilizing it but you also have this bulky aerial group which is hydrophobic and that is why they are moderately soluble in water and therefore they are also soluble in organic solvents just the way the amines are highly susceptible to oxidation the lone pair of electrons on oxygen it also makes them a good candidate to get oxidized so the phenols get oxidized easily and if you keep them over a period of time some color develops in these phenols ok

so these are prone to oxidation just like amines so these are some of the typical physical properties of phenols let us now look into some of the reactions which they undergo and at the same time let us compare them with what we have learnt earlier with respect to the alcohol

so i am going to divide the reactions into two categories one as we did for the alcohols earlier one is due to the o h group and the other now in this case is going to be due to the aryl nucleus

so unlike the alkyl part here you are dealing with the aryl so what are the reactions typical of the aryl nucleus and due to o h group and because of the hydroxyl again you can have two types a those reactions which resemble alcohols

so you know that this was happening with alcohols also and b those which do not resemble alcohols ok so let us take each of them one by one

i start with the reactions due to o h group and in here i take those in which the phenols have a resemblance to alcohols let us look some of those reactions in which first a hydrogen is replaced when a hydrogen is replaced in an alcohol the first thing if you remember we saw was the reaction with a sodium metal so the way alcohols were reacting with sodium metal phenols are also capable of reacting with the sodium metal it is because of the acidity of this phenolic o h and it gives you the sodium phenoxide along with the elimination of the hydrogen gas

so the reaction is similar to what was seen for alcohols ok the other reaction which is similar to alcohols is the acylation reaction

so you treat the alcohols with acid chloride acetic anhydride and you

get the corresponding esters right
so you take acetyl chloride treat
it with phenol ok and what you get is this ester which is phenyl acetate we will
discuss later that this phenyl acetate
is susceptible to a rearrangement reaction okay which is called a phry's
rearrangement
where this sl group is going to get lost from this position and going to be a
part
of the aryl ring okay
so this ester right in the presence if this reaction is carried out
further in the presence of any lewis asset this is going to migrate to a ortho
or a para
position in the benzene ring okay
so that happens under the influence of a lewis acid but otherwise
if you carry out the pyridine assisted acylation of the phenol you end up with
a phenyl ester ok so
in this case all your esters will be phenyl esters ok another reaction is
benzoylation similar
to alcohols in this you treat it with benzoyl chloride in aqueous nuh ok and
this reaction
is popularly known as shorten bomban reaction
so you start with your benzoyl chloride treat
the phenol in the presence of aqueous sodium hydroxide you just shake these
and you immediately see the formation of this ester which is phenyl benzoate
along with nacl water and this is called the
shortened bombing reaction okay phenols can also be treated with benzene
sulfonyl
chloride and in this case we get what we call as the tosylates and tosyl group
is a very good
leaving group as you might have come across in the nucleophilic substitution
reactions
so to prepare
these tosylates this is what you do you start with benzene sulfonyl chloride
and you treat this with
phenol it gives you the sulfonyl ester
so you get $\text{C}_6\text{H}_5\text{SO}_2\text{OC}_6\text{H}_5$ and these
compounds are called tosylates it is a phenyl benzene sulfonate ok the same
thing which
was happening with alcohols it can happen with phenols also when
you treat them with alkyl halides in alkaline conditions and this reaction is
what
is popularly known as the william suns synthesis okay
so the reaction involves the formation of alkyl aryl ethers
so its a very popular reaction
for making alkyl aryl ethers you start with the phenol which under alkaline
condition
exist in the form of sodium phenoxide and you treat this with an alkyl halide
ok if
you treat us with methyl chloride in aqueous nuh it undergoes the nucleophilic
substitution
reaction to give you the alkyl aryl ether which this one is called any sole
so this is
essentially a nucleophilic substitution reaction for the preparation of the
alkyl aryl ethers

the interesting thing in this reaction is that when you have to prepare the alkyl aryl ether so there can be two combinations for preparing the same alkyl aryl ether the question is what do we do which alkyl halide do we start with and which phenoxide should we start with for example ok i will take one example for this suppose we have to make this molecule which is phenyl propyl ether there can be two routes or two combinations of reagents which can be used to arrive at this molecule in one case you can start with this alkyl halide and the sodium phenoxide the other could be that you start with this sodium alkoxide and treat it with you treat this with the aryl halide so two routes are possible to arrive at this product so the question is which is the combination of substrates that one will choose over the other so i put a tick here that this reaction is feasible but this reaction is not feasible now you think why because it involves a nucleophilic substitution so when we have to carry out a nucleophilic substitution on an aryl halide it is not very easy okay so the aryl halides have a low reactivity towards a nucleophilic substitution reaction therefore we will not choose an aryl halide as one of the reacting species instead we will choose the corresponding phenoxide and take the alkyl bromide to form this alkyl aryl ether ok let us look at now few of those reactions resembling alcohols in which the hydroxyl group is replaced so far we were talking about cases in which the hydrogen of the phenol was replaced when the hydroxyl is replaced there is one example the reaction with PCl_5 ok so in this case you take the phenol you treat it with PCl_5 when we are taking the alcohol we were getting the corresponding alkyl halide in this case however the reactivity of a phenol O-H to get replaced by the chlorine is not so facile ok why because we know that a nucleophilic substitution on the aryl ring is very slow okay so this will not work so easily however if we make this substituted with electron withdrawing groups okay like a two four di nitro phenol and then we carry out the reaction with PCl_5 then in this case we can get the corresponding chloro derivative along with the formation of these molecules so for this we have to have an electron withdrawing substituent which activates this carbon and makes it more susceptible towards the nucleophilic substitution reaction okay so this is the similarity and the difference with respect to alcohols with which it will happen very fast likewise reaction with ammonia so in this you take the alcohol the

phenol and
you heat it at about 250 degrees centigrade in the presence of anhydrous zinc chloride
so this is the reaction with
another nucleophile that is the ammonia and you take the phenol you have to react this with ammonia this is done
at about 250 degree centigrade in the presence of anhydrous zinc chloride to give you
these aryl amines as the product so however the o h substitution is more facile
in alcohols as compared to that in phenols ok let us look at the other category of reactions
in which phenols do not resemble alcohols let us see those reactions in which the phenols do
not resemble alcohols and the first in this list is the reaction with ferric chloride solution so
the action of ferric chloride solution
so this reaction is actually taken as a test for identification of phenol
so it is a qualitative color test for identification of phenols this tells us if the o h group is attached to the aryl core ok
so the reactions in which phenols do not resemble alcohols is by virtue of the fact that o h group is attached to the aryl core and
this is what makes them different from alcohol so the action of ferric chloride solution on alcohol
on the phenol gives you a violet green purple red color
so there is an appearance of all these different types of colors depending upon the type of phenol you are using
and this happens due to the formation of ferric complexes of ferric chloride with phenol
so the ferric chloride solution gives a positive test or it gives a color change a ferric chloride solution is orange in color yellowish orange
so it will change to all these different colors if it sees any of these enols or phenols and enols and phenols give a positive ferric chloride test
so this is what is not given by alcohol
so you can distinguish that the hydroxyl containing compound is an alcohol or a phenol another reaction in which they are different is the reaction with zinc dust you heat the phenol with zinc dust ok you heat it and what you get is the reduced form of the phenol you get arenese as the product ok
so the phenols on treatment with zinc dust are reduced to adenes okay another difference between them is based upon the acidic nature of phenols ok
so the acidic nature of phenols the acidity of phenols is not the same as that of alcohol
so if i have to draw a comparison a carboxylic acid being most acidic and an alcohol being least acidic in between comes the phenol ok

so the acidity of phenol lies between the carboxylic acid and the alcohol but a phenol is about 1 million times more acidic than alcohols ok it is one million times more acidic than alcohols but still it is a weak acid

so because of the acidic nature of phenols what are the different things it does which are not given by an alcohol one it turns a blue litmus red ok second it dissolves in alkali it dissolves in alkali completely because you get the corresponding sodium phenoxide so it dissolves in alkali the other thing is which is similar to an alcohol but different from a carboxylic acid is that it does not give no effervescence with sodium bicarbonate solution okay it is not acidic enough to release carbon dioxide on treatment with sodium bicarbonate

so if we look at the acidity of phenol in aqueous solution it is weakly acidic and can give you this phenoxide ion ok

so this is a weak acid and this is a strong base and this is a very stable base at the same time

so if you look at the structure of the phenol and the phenoxide ion

so we know that a phenol can exist in all these resonance stabilized structures with the charge accumulating at the ortho and para positions ok and if you look at the phenoxide ion in this case the charge is in fact much more concentrated ok and the phenoxide ion is stabilized again by resonance

so it is stable because it is stabilized by all these resonating structures it is stabilized by resonance and that is why it has this ability to lose the proton because the corresponding phenoxide anion which is produced is resonant stabilized

so the pka of the phenols in water at 25 degrees centigrade a simple phenol it is eight nine ok let us compare some of the p k values of the differently substituted phenols

so as to get an idea of how the acidity varies according to the electronic influence

so if you have phenol or two methoxy or two methylphenol which we say is a orthochrysol or a three methyl phenol or a four methylphenol

so i am talking about orthochrysol metachrysol and parachrysol okay if you have a two chlorophenol a three chlorophenol a four chlorophenol or two nitrophenol a three nitrophenol or four nitrophenol or if you have di substituted a two four dinitro phenol or a tri substituted two four six nitro phenol

which has the common name picric acid

so the acidity is comparable to an acid

so it gets

the name picric acid and compare it to cyclohexanol

so the p k values of these different

phenols and cyclohexanol is of the order nine point eight nine with two methyl

phenol

it increases ok

so a lower p k shows it is more acidic here it is increasing because the methyl group it increases the electron density on the ring and therefore the acidity of the

o h bond decreases with a three methyl

so when you change the substitution from two to three

so at the meta position it is less influencing and the p k is therefore lower little lower

than the ortho substituted isomer

so it is ten point zero one with para it is similar to ortho

10.

17 with the two chlorophenol now the chloro applying its minus i effect ok the

inductive effect the acidity increases and the pka reduces to eight point one with

three three chloro the inductive is lower little less because it is away and therefore

it is and there is the mesomeric effect okay as well which is operating in case of this chloro

it is eight point eight zero with four chloro ok the pka is further low it is

nine point two zero two nitrophenol very strong electron withdrawing it is the minus

m effect which makes it most acidic more than that of the simple phenol and the p k becomes

7.

17 with 3 nitro the minus m is not operative it is a minus i you have 8.

28 with the 4 nitro

derivative it is similar to the ortho 7.

15 with dinitro substitution it becomes more acidic

3.

96 and that is why we saw that in this case the substitution was happening with pcl5 with

the 246 nitro it becomes 0.

38 and compare it to a cyclic alcohol the cyclohexanol which is 18.

so this is a rough estimate of the pka values and the effect of different electronic

substituents at different positions on the aerial ring of the phenol and the relative influence it

has on the acidity behavior of these molecules ok all right

so this was about the reactions

with respect to the hydroxyl group now we move on to the second aspect of the phenol reactions that is the reactions of the nucleus what happens from the nucleus perspective

so in this the first example i am taking is hydrogenation reaction

hydrogenation is

you are reacting the phenol with hydrogen in the presence of a catalyst a nickel

catalyst in this case and you heat it right and you get the reduced product and the reduction of the aromatic core is what is taking place and you get cycloalkanols this is what you get

so you start with the phenol treat it with hydrogen three moles of hydrogen will be required for complete reduction of all the three

bonds of the aromatic ring in the presence of nickel as the catalyst and you get the reduced product your cyclohexanol the more important reactions of the nucleus are the electrophilic substitution reactions the electrophilic substitution reactions are the reactions in which the electrophile comes and attacks onto the benzene ring or the arene ring and this you must have studied when you do did the aromatic hydrocarbons the reactions on a benzene ring ok so the different types of electrophilic substitutions you know are halogenation nitration sulfonation friedel crafts reaction all these are also possible on a phenol but they have a different reactivity pattern which follows for the phenols so what happens is that your hydroxyl group it activates the benzene ring and because it activates the benzene ring the relative reactivity of the phenolic aryl core towards the electrophilic substitution is much more as compared to the unsubstituted one which is a simple benzene so let us see one by one what happens with in with the different electrophilic substitution reactions halogenation as the first one so one thing which we know that because of the hydroxyl group our ring is activated okay so the o h is an activating group and as we just saw it activates the ortho and para position so the ortho and para positions are electron rich right because of the hydroxyl group activation there is a more charge at the ortho and para position the negative charge by virtue of which the electrophile will prefer to attack at these sites so in halogenation reaction you start with a phenol and let us take examples of a bromination reaction you treat it with bromine ok now i take two conditions you treat it with bromine water is the one condition if you do so you get not a mono substituted or a disubstituted but you get a tri-substituted tri bromo substituted phenol ok you get a tri bromo substituted phenol if you treat it with bromine water if you treat this with bromine in a non polar solvent like a cs₂ or acetic acid at low temperature at 0 degrees centigrade you are able to control the reactivity the electrophilicity of bromine so the electrophilic reactivity of bromine is reduced when we carry this out in a non polar solvent and at low temperature and under such conditions we end up with a mixture of mono substituted ortho and para products with the para bromophenol being the major product so this is the major when we carry out the bromination at 0 degree centigrade with carbon disulphide as the solvent so as is

expected because the nucleus is highly activated because of the hydroxyl group which has given

its electrons at the ortho and para position the reaction yields a mixture of the ortho

and para substituted products and this bromine reagent what we are using source of bromine

generation we call this a bromate bromide method

so your bromine water okay what you are using comes from a mixture

of we can use a mixture of potassium bromate plus potassium bromide

so it

is a bromate bromide method all right another example of electrophilic substitution is sulfonation what is happening in sulfonation reaction compare it to the

sulfonation of benzene ok ok one more thing i would like to point out in bromination is you just

notice that under the conditions of bromination the lewis acid has not been used is not required

for bromination

so you remember that with benzene ring we were making use of lewis acids to activate

the conditions and helps in the generation of the electrophile ok

so it increases the

reactivity of the electrophilic substitution but with phenols this is not required ok

sulfonation you start with the phenol you treat it with concentrated

H_2SO_4 the temperature is ranging in the range 15 to 25 degree

centigrade the product which you get is the ortho sulfonated phenol ok you get the ortho

substituted phenol and if the same reaction with concentrated H_2SO_4 is carried out at

100 degrees centigrade we get the product which is a para substituted phenol

so in this case we get the para isomer and if you heat the ortho isomer at 100 degree centigrade it gets converted to the para isomer and if you

carry out this reaction with concentrated H_2SO_4 at any temperature in the range 320 degree

centigrade you end up with a mixture of ortho and para

so this three different conditions tell

us that what is happening is that when the reaction is carried out at low temperature we

are getting one product the ortho substituted which is a kinetic product

so we are talking

about the kinetic versus thermodynamic stability of substitution in this case when we carry it

out at higher temperature we are getting the more stable the thermodynamically more stable

product

so we say it is a thermodynamically controlled reaction

so we get a thermodynamic

product and if we heat it ok at high temperature

so sulfonic acid is a very bulky group it is

a bulky group and it will not like to stay at the ortho position next to hydroxy and

therefore it will migrate it will prefer to stay at the para position at a high temperature because that is not the most thermodynamically favorable position for the stay of the sulphuric acid it is a bulky group so that is why a parasubstituted product is thermodynamically favorable and the ortho one forms as a kinetic product at low temperature ok

another reaction in this is the nitration reaction you start with phenol you treat it with dilute nitric acid 25 percent nitric acid temperature is 25 degree centigrade you get ortho nitro phenol ok and you get paranitrophenol so you get a mixture of ortho and para isomers with the ortho being the major and para being minor the same thing if you carry out instead of dilute nitric acid you use concentrated nitric acid you get not a mono substituted but a tri nitro substituted phenol which is called picric acid but the thing is the yield in this case is still not good so you saw that the yield here also the percentage conversion it's a 30 to 40 percent yield and a 10 percent yield so yields are poor in case of nitration ok so nitration results in poor yield of products and this happens because of oxidation of the starting material as a side reaction so the starting phenol gets oxidized as i told you it is quite prone to oxidation so under the in the presence of nitric acid it undergoes oxidation and it gives you more of the oxidative side products and less of the desired nitro derivative so a better method to execute this reaction and get the nitro derivative is that you first sulfonate it you treat it with sulphuric acid and we just saw that when you do this in any of these temperature ranges you end up with a mixture of ortho and para sulfonic acid but the yield in this case is good okay it is not at least getting oxidized the core is not getting oxidized so when you get the mixture of this ortho and para now you subject it to nitration ok you treat this with concentrated hno₃ and when you subject it to nitration here you get 246 trinitrophenol that is the picric acid so here you get this in good yield so you first converted into the sulfonic acid derivative and the sulfonic acid its a good leaving group ok so it facilitates the reaction ok and the second thing is that because it is present it deactivates the benzene prevents it from oxidation ok it deactivates the benzene nucleus and prevents its oxidation which was happening because of this o h group right

so it prevents the oxidation by deactivating the benzene nucleus of the phenol

and then it is easily replaced by NO_2

so this method for making picric acid is better in terms of the yield as compared to a direct nitration ok another reaction which involves

an electrophilic substitution is the Friedel-Crafts reaction it's a Friedel-Crafts

alkylation which I am going to discuss today which involves the treatment of the phenol with alkyl halide in the presence of a Lewis acid to give alkyl phenols

so you take the phenol okay treat it with alkyl halide in the presence of the Lewis acid you end up with a mixture of

ortho and para alkylated phenols if you start with the phenol and treat it with a bulky

alkyl halide like a tertiary butyl chloride this is a case which selectively gives only the para substituted product

so in this case the alkylation happens only at the para position unlike the other case it is by virtue of this you say virtue or it is

because of the steric hindrance offered by the tertiary butyl group ok another reaction I am

going to take in this electrophilic substitution is the nitro station reaction

so in the nitro

station what is happening you replace the H by NO₂ ok

so your electrophile is NO⁺ and

you know that NO⁺ is a weak electrophile yet it undergoes a reaction onto phenol so

your reaction involves treatment of the phenol with nitrous acid

so you take the phenol

treated with nitrous acid at low temperature and it undergoes a nitro station

so the ortho position

is blocked here it undergoes nitro station at the para position and the nitrous acid can be

generated we know from the corresponding nitrite salt in the presence of the acid

so this is how

you generate nitrous acid and this nitrous acid is capable of carrying out the nitrosation of the

phenol and this is one of the examples where an electrophile like a nitrosyl ion can be added it

can be substituted the phenol can give us the nitrosylated phenols okay

so I stop here with the electrophilic

substitution reactions there are still many more reactions of phenols which we have to discuss

but I will stop here and next class will take up another very important reaction of phenols

that is the Reimer-Tiemann reaction but till then you can just go through all this and revise

and gear up for the next class thank you you