hello everyone in the last class we started phenols and we saw what are the different ways in which phenols can be prepared either at an industrial level or on a lab scale preparation from there we talked about the physical properties of phenols and saw that how they are different from alcohols and moved on to studying the reactions of phenols which were essentially discussed in two ways either on the basis of the reactions of the nucleus the phenolic ring or the hydroxyl group and we saw what are the similarities and differences the phenolic o h has with the hydroxyl of an alcohol we discussed variety of reactions on the nucleus where we saw that the nucleus is activated by virtue of the hydroxy group which activates the ortho and para positions and that is why when we have to carry out reactions like an electrophilic substitution reaction of a phenol it is a much more active substrate as compared to an unsubstituted benzene and then we also saw that how different reactions like a halogenation sulfonation and nitration yields a mixture of ortho and para products and this mixture can be selectively generated

so instead of the mixture we can selectively get one isomer one rigid isomer depending upon the conditions we choose for the reaction that means the reaction can either be kinetically driven or thermodynamically driven which yields us a particular regio isomer today we are going to continue on with this reactions of phenols and we are going to learn one important reaction which is called the reamer demon reaction

so we are continuing on with the reactions of phenols on the nucleus and in this the first reaction for today is the riema temer reaction and in fact this is the third of its kind when we are talking about the reaction

so in this an important reaction is the reamer demon reaction based on the name of these two chemists

so it is a name reaction as you can easily guess the reaction is important because it gives us an access to formylated phenol

so the reaction enables us to carry out an ortho formylation of phenols

so a formyl group can be introduced on a phenolic ring with the help of this reaction

so essentially what the reaction involves is that you take the phenol take it in a biphasic solvent system

so the biphasic solvent system comprises of chloroform and an aqueous solution of sodium hydroxide

so you take naoh aquas and when you do this reaction you usually have to take three equivalents of the alkali when you heat all these constituents at about 70 degrees followed by an acidic workup you end up with two products both formylated and one is ortho hydroxy benzaldehyde which is the major product which we also call as ortho celliceldehyde and the minor product is the para isomer which you obtain along with formation of nacl and water

so this reaction is important because it is giving us an access to the aldehyde substrate on the phenolic ring it does not require anhydrous condition

so reemertimer reaction the importance is that the reaction does not require anhydrous conditions for carrying out this formylation ok let us take few more examples to see the kind of products which we obtain if we have another reagent instead of chloroform like a ccl4

so you start with a phenol in the same manner treated with carbon tetrachloride in the presence of aqueous alkaline solution followed by acidic workup the product which you get in this case is not the aldehyde but it is the carboxy derivative the corresponding acid which you get as the major product

so in this case you get ortho hydroxy benzoic acid or salicylic acid as the major product when you carry out the reaction of phenols with carbon tetrachloride instead of chloroform so you end up with a mixture again of the ortho and the para isomer the ortho being the major and the para being the minor let us take another example if you already start with a subpara substituted phenol like a para cresol and you subject it to riemertemer reaction conditions since it is already para substituted

so you would expect the formylation to go at the ortho position but along with this an unusual product is seen in this case which is this keto form along with these two substituents at ideally the para position

so this is an unusual compound with the para substituted phenol which we see if you take the ortho substituted phenol for that matter in this case the product which you see since it is already ortho substituted

so the product mono substituted this side

so what you get is the para formylation and you get this sweet smelling compound which is called vanillin let us look at the mechanism of what is happening in the reaction what is happening and how chloroform is the reagent and it is giving you a formal unit

so what is happening let us look at the mechanism

so the first step is that chloroform under alkaline conditions in the presence of the base it gives you it abstracts the proton of chloroform and gives you a carbon ion

so it gives you this trichloro carbonyl which again loses a chloride iron to give you this intermediate which is called the dichloro carbene

so in this reaction it is this dichloro carbene which is the active intermediate and the reactive species which is carrying out the formylation

so once this dichloro carbene is formed it is it has electrophilic character the next target would be that it would look up for any nucleophilic site

so what we have in the reaction is the phenol in aqueous alkali it easily would form the sodium phenoxide iron and in fact it would exist in the form of this phenoxide ion and the dichloro carbene which is electrophilic

so when it happens to exist in the form of the sodium phenoxide it in fact increases the nucleophilicity at the ortho position

so the nucleophilicity at the ortho position of a phenoxide is much more as compared to phenol

so this activated ortho site attacks the carbene which is electrophilic carbene and what you get as an intermediate is this moiety which under aqueous conditions picks up the proton

so all these are the transient species which are being generated and the next key step would be the aromatization

so the keto changing to trying to change to the enolic form

so what we get is back the phenoxide ion with the ortho position substituted with chcl2 okay

so in this case there is loss of this proton and the next step is the hydrolysis

so once you generate this c h c l two ok i will write it again once you generate this intermediate here

so the two chlorines on this carbon right which are electron withdrawing in nature ok they make this carbon partially positive and under alkaline conditions chloride is lost and replaced by the hydroxide the substitution takes place twice one more hydroxide unit adds up

so what you get is right and the last step is removal of a water molecule to give you the ortho formile substituted phenoxide which under acidic workup gives you the corresponding ortho formylated phenol

so this is the most plausible mechanism for the riemertemer reaction resulting in the ortho formylation so since you can see that the ortho position is activated and even the para position is activated right both are nucleophilic sites

so the reaction also gives us the para formilated product but as a minor isomer okay let us see the unusual case when the reaction was being carried out with the para substituted phenol that is the cresol what was happening

so you have the phenoxide ion of paracrisol and you treat it with dichloro carbene okay same thing at the ortho site the reaction occurs the usual way just what we saw few minutes back you get this intermediate with the methyl substituent at the para position and we also see that the other intermediate is possible in which the ccl2 attacks the para position

so you get this another intermediate

so you get two of them and the next step from here would be the ortho substituted would work the same way as we saw above that in the request conditions this is going to pick up the proton followed by aromatization to give you the phenoxide ion and this is subsequently subjected to the alkaline hydrolysis and further to the acid catalyzed workup and it gives you the ortho for my product in the other case when you are getting this intermediate being also generated during the reaction and you carry out under aqueous conditions when this reaction what is going to form is this right now for the reaction to take place for the next step there has to be a hydrogen here a proton which has to be lost for it to aromatize but since no proton is present at the para position

so the reaction stops here and you get this as the product

so there is no hydrogen which is available for the reaction to proceed the usual way right and therefore it stops here and does not aromatize giving you this as the side product okay let us see what happens with carbon tetrachloride when we start with okay with ccl4 we said that we are getting the corresponding acid and not the formylated compound ok

so what is happening with ccl4 again phenol is forming the phenoxide ok

so this is your nucleophilic site which is created now the chlorines which are minus i electron withdrawing create this delta positive charge on the carbon which is now the electrophilic center and is attacked by the nucleophilic ortho site to give you this intermediate which rapidly loses the chloride ion and results in the formation of this which again quickly aromatizes as was seen with addition of dichloro carbene it aromatizes and it gives you this compound which further undergoes hydrolysis under alkaline conditions to give you this intermediate which rapidly would lose a molecule of water this is followed by acidic workup and the salt is converted to phenol along with formation of the or the installation of this carboxyl group at the ortho position ok

so this is how we see that when we have a carbon tetrachloride we end up with the acid and not the formal group and this acid again is important because we can subject this asset to esterification ok

so if we treat this with alcohol acid catalyzed conditions what we get is this molecule carry out the esterification we get this molecule which is called methyl salicylate or oil of winter green ok

so this particular compound has medicinal properties and it is used as a relaxant for muscular pain okay

so this is one way in which we can further derivatize this salicylic acid into methyl salicylate the ester derivative and we can also carry out its acetylation with acetic anhydride when we carry out the acetylation of this compound the phenolic o h is the one which will get acetylated to give you this acetyl salicylic acid which is nothing but the pain reliever known by the name aspirin

so the salicylic acid is an important precursor for these two medicinally active compounds and can be synthesized through the riema demon root by using carbon tetrachloride as the reagent ok we move on to the next reaction which again furnishes the carboxyl group on a phenol and this reaction is known as the coal based reaction

so right now it is essentially some of the name reactions which we are dealing with the coal based reaction or the coal schmitt reaction what the reaction involves is you take the phenol and you heat this phenol which exists in the form of phenoxide ion

so you take the phenol under alkaline conditions right and you treat it with carbon dioxide gas ok at a high temperature and under pressure

so of the order of 100 atmosphere when you heat it and this followed by acidic workup the product which you get is what you just got above by the reemertemo reaction that is the salicylic acid you get this product also through the coal base schmidt reaction when you carry out this at 120 to 140 degrees centigrade you get this ortho isomer and if the same thing is carried out at a temperature greater than 140 degrees centigrade okay you get the para isomer you get the para hydroxy benzoic acid as your main product

so essentially what you can say is that the reaction involves heating of your sodium phenoxide which will essentially exist under alkaline condition phenol will exist in this form and you treat it with co2 120 to 140 degrees or greater than 140 degrees what you get is the para isomer and in this case you get the ortho isomer and what is happening is that again this is an activated ortho site because it is existing in the form of the phenoxide ion

so it is reactive ok

so it is the nucleophilic site and the carbon dioxide it acts as a weak electrophile ok this is a weak electrophile and you are having a strong more reactive nucleophile towards the electrophilic substitution reaction

so essentially the reaction is an electrophilic substitution reaction if you look at the mechanism it involves under alkaline conditions you know now by now that the phenol will exist in the form of an oxide ion and your carbon dioxide is the electrophile in this particular case

so as would be expected it would engage in a electrophilic substitution reaction with the phenoxide ion and this would lead to a quick tautomerization to give you the keto form changes to your enol form and i am writing straight away the o h here and what you get is this molecule right

so this is in the form of its sodium salt and then when you do an acid workup what you get is the salicylic acid

so this is the reaction of phenols with carbon dioxide called the coles reaction again used for the synthesis of ortho carboxy phenols or salicylic acid in this case let us look at another type of reaction

so phenols as we know are activated species and they are quite prone to oxidation

so already the hydroxyl group bearing the lone pair of electrons make the species highly susceptible to oxidative conditions

so they have high electron density and because of this they easily get oxidized even in air they will get oxidized on long keeping and they develop a pink color ok they give a pink color even when you keep it in air it will undergo aerial oxidation

so what is happening with the phenols which are reactive chromophore susceptible to oxidation

so in the presence of oxygen and light phenols get oxidized to q nons ok and what you get is this kind of a molecule which is called para benzocunon and the para benzoquinone again in the presence of more phenol which is there available it forms this kind of a hydrogen bonded compound which is responsible actually for giving pink color to phenols on long keeping and this compound is known as phenocunon

so this is the molecule which is pink in color and the pink color which develops in phenol is because of the formation of this molecule phenols can also get oxidized by other reagents like the regular reagents which we studied earlier the chromium based jones reagent with the jones reagent phenols get oxidized to the corresponding para benzoquenone okay if you oxidize it with silver oxide it gets oxidized to the corresponding orthoisomer ortho benzoquinone and then there are other oxidants also the stronger ones the potassium permanganate the dichromates which also carry out the oxidation of phenols and give you the corresponding qnons with different kind of substitutions

so either ortho pera or mixture another oxidant which is used for phenols oxidation is potassium per sulfate which in the presence of koh under alkaline conditions gives you this molecule which is called qnol

so the conversion of this phenol into qnol

so you are taking essentially reacting it with alkaline potassium per sulfate and this reaction is known as elbs per sulphate oxidation conversion of phenol into qnol elves per sulphate oxidation okay another name reaction for phenols is the gattermann's aldehyde synthesis

so so far you have seen that riema temer was one method to get the ortho formilated phenols this is another method to get the formylated phenols and it is known as gatterman's aldehyde synthesis in this what you start with is a phenol you take the phenol and treat it with a mixture of hcl and hcn and the conditions are anhydrous in this case

so that is why i told you in the riema temer the good thing was that you do not need anhydrous condition

so you have to use anhydrous alcl3 and it gives you an intermediate amine which eventually on the aqueous workup will give you treatment with water it gives you selicealdehyde the ortho formylated phenol

so if you look at the role of hcl and hcn they are essentially the providers of the formyl group

so hcl and hcn together gives an intermediate amine which is a chloroamine and the phenol now this is not under alkaline condition

so the phenol is existing in the form of phenol ok this phenol on reaction with the amine the chloroamine the ortho position anyways is activated in a phenol

so it undergoes this substitution in the presence of the levis acid substitution and you get this intermediate a mean attached at the ortho position and this immediately aromatizes to give you the ortho imean substituted phenol which on hydrolysis gives you the corresponding formyl related phenol

so this is the gatterman's aldehyde synthesis again for synthesizing the formylated phenols at the ortho position ok another reaction very important reaction of phenols is the coupling reaction with dizonium salt it is a very interesting reaction because you end up seeing a dense coloured product which is like a dye and the dye we call is the azodian

so aryla means essentially they form the dizonium salt

so the dizonium salt of arylamines through the sandmares reaction

so you get the aryl dizonium chloride and this is treated with because the reaction is under alkaline condition

so your phenol is existing in the form of phenoxide

so when the dizonium salt is treated with the phenoxide ion what happens is this kind of a coupling reaction takes place under alkaline conditions chloride ion is lost from the dizonium and what you get is n double bond n

so you get this intermediate and this intermediate again as one would expect would like to aromatize to give the corresponding phenoxide here which on acidic

workup will give you the colored compound which we call as the azure die
so this is a colored compound and this is pera hydroxy azo benzene
so you get these azo dyes which are coloured compounds and they in fact are kind of a way to see that the amine is a primary a rhylamine and it forms the dizonium after diazetization and then it couples with the phenols different kinds of phenols form different types of dyes right and you get this molecules ok the next reaction of phenols is called a thaline reaction thaline reaction is essentially a condensation reaction
so a condensation means the species the substrates are reacting with the release of small molecules
so what are the substrates involved as the name says thaline reaction and it is a reaction of phenols
so one substrate is a phenol which we take two moles and we treat it with phthalic anhydride anhydride of phthalic acid and the phthalic anhydride is taken one mole these two are treated with in presence of a levis acid or even concentrated sulphuric acid and they undergo condensation that means they are undergoing loss of a molecule which is water in this case and the product which you get is called phenophthalene which is a colorless compound but it is an important acid base indicator is it is an acid base indicator it is colorless in acidic conditions and turns to pink under alkaline condition
so whenever we carry out titrations the acid base titrations we can use phenophthalene as an indicator
so the reaction involves two molecules of phenols
so we have two phenols and they react with one molecule of phthalic anhydride
so your phthalic anhydride is this in the presence of zinc chloride or aluminum chloride anhydrous
so the reaction is essentially the condensation with the loss of water molecules
so one is this para hydrogen para to the hydroxyl another para to the hydroxyl and the oxygen
so this is lost during condensation and the product which you get is this molecule which is called phenophthalene
so in alkaline conditions this gets it converts in the form of an oxide ion and then this opens up and it gives you the pink color
so this is a reaction of synthesizing phenolphthalein starting from phenols another reaction for phenol is the lieberman's nitroso reaction this reaction in fact is used to test phenols it is a test for phenols because it is a reaction which can be monitored through visual changes
so it gives you different colors as it proceeds
so what happens during the reaction is you start with the phenol if the molecule is a phenol if the compound in hand is a phenol you treat it with nano2 sulphuric acid when you treat the phenol with sodium nitrite and concentrated sulphuric acid you see the development of a transient brownish red colour a transient brownish red color which soon changes to a blue green color and if you dilute this solution with water
so on dilution with water the blue green changes to a permanent red color and now to this red colored solution if you add the base naoh it restores the original blue green color
so these are the different color changes the reaction undergoes starting from this transient color to a blue green color to a red color and back to a blue green color as you dilute it or you you treat it with alkali
so what is happening what are the different colors due to and what are the species involved
so if you look at this reaction and what it is going through you treat the

phenol with nano2h2so4 which is essentially the nitrous acid and we have done this before that it leads to the nitro station the electrophilic substitution of phenol you get the para nitroso phenol the para nitrosophenol can be written in the form of its isomer which is an oxyme a monoxime it is a monoxime of para benzoquinone

so what happens is that once phenol is converted to nitroso which is existing in the form of this monoxide and it sees another molecule of phenol it forms this intermediate which is the brown red the initial brown red color which we see it forms this intermediate because the reaction is in the presence of concentrated h2so4

so in the presence of sulphuric acid this brown red intermediate it changes to the next one that is the blue green color

so what happens that it gets protonated in the presence of sulfuric acid and it forms this kind of a molecule which is the one which gives its the blue green color

so the initial blue green color and the brown red color they develop and now the next is that when you dilute the solution

so you treat it with water on dilution what you get is the same molecule which you were getting earlier showing red brown color this is the red color

so you get this molecule which is the endophenol and this on treatment again with aqueous naoh gives you this molecule which is which is blue in color and its also endophenol existing in the phenoxide ion form

so you get this change from red to blue and which is a marker that the molecule is a phenol

so this is actually a color test for identification of phenols which is used in the lab another reaction of phenols is the use of phenols in the synthesis of resins

so we have synthesis of the popular phenol formaldehyde resins which is commonly known by the name bakelite

so the synthesis of phenol formaldehyde resin it is again a name reaction the leader menacing reaction for the synthesis of bakelite and the raw materials involved here are again you take phenol you treat it with formaldehyde these are the two components of the resin

so you have phenol formaldehyde both are in excess ok you take excess of the two and in alkaline or acidic conditions okay they yield you big light

so first of all before forming bakelite they form some compounds which are the methylol derivative

so you form the monomethylol phenol right when one mole of this reacts with one mole of formaldehyde and then when this undergoes reaction with another mole of formaldehyde you get the dimethylol phenol and these mixture of these molecules when they are further subjected to high temperature and pressure they result in the formation of bakelite

so this is what the synthesis involves that you start with the phenol treat it with formaldehyde in the presence of alkaline or acidic conditions

so depending upon the conditions we choose we get different types of resins ok if you choose alkaline or acidic conditions you get different resins but the reaction is possible under both conditions you can get the methylol monomethyloid derivative

so c h two o h can either occupy the ortho position or it can occupy the para position

so you end up with a mixture of the ortho and para monomethyl oil derivatives and when they react with another molecule of formaldehyde

so it gives you the dimethylol derivatives ok

so now it could either be both ortho

so you get a 2 6 dimethylol or it could be ortho para you would get a 2 4 dimethylol

so you get a 2 6 or a 2 4 dimethylol derivatives and now when these are heated you get bakelite which is a polymer or resin which involves different types of cross linking depending upon the monomers which are formed during the reaction and the stoichiometry in which they are generated

so you get a complex network the structure of bakelite would again depend as i was saying that it would depend upon the ratio of the monomers the mono and dye which are generated initial step and the conditions which are being used the acid or the base for the generation of these monomers and what you get will be something like this

so it is a cross linked polymer ok

so you get this kind of extensive cross linking which will depend upon the nature of the monomer

so you get a cross linked resin ok

so this was about the use of phenols in making phenol formaldehyde resins another reaction important reaction which is actually not a reaction but a rearrangement reaction is called fry's rearrangement

so fry's rearrangement is an important reaction of phenols in which the sl group migrates to the ortho and para position

so what are we talking about

so if you recollect when we talked about the acceleration of phenol

so you start with the phenol okay this phenol essentially behaves as a bident nucleophile it is a bidentate nucleophile if you subject it to a friedel crafts acceleration there are two possibilities it can either undergo a c acylation or it can undergo o acceleration

so depending upon the conditions you choose if you carry out the acceleration let us say with acetyl chloride in the presence of alcl3 you get c acylation which is a thermodynamic controlled product and you carry out the reaction with acid chloride you get the oscillation product which is a kinetically controlled product

so essentially what is happening that in friedel crafts assilation of phenols when you carried out an oscillation and converted the phenol into this ester the phenolic ester ok this is phenyl acetate converted this to phenolic ester in the presence of alcl3 ok in the presence of alcl3 as the catalyst this ester can undergo a rearrangement to give you this product which is hydroxy aromatic ketone

so you get this para hydroxy acetophenone

so when you carry out this reaction with alcl3 as the catalyst it involves migration of this sl group at the para position when the reaction is carried out at 25 degree centigrade

so you get these hydroxy aromatic ketone and if you take this para hydroxy acetophenone or the hydroxyketone at the para position and you further subject it to alcl3 catalytic treatment at a high temperature 160 degrees centigrade in that case the product changes to the more stable ortho isomer you get the more stable ortho isomer which is a thermodynamic product

so what we are seeing here is that this phrys rearrangement can give us selectivity in terms of the ortho or the para isomer

so the para isomer is a kinetic product at low temperature is generated and if the same is heated it converts into the more stable thermodynamically stable ortho isomer and if we start from phenyl acetate and directly subject it to alcl3 treatment at 160 degrees centigrade it gives us the more stable ortho isomer in those conditions

so if you carry out the reaction at any temperature in between the two you can will end up with a mixture of ortho and para products and the ortho and para mixture if you get then they need to be separated with the help of steam distillation

so steam distillation because the ortho isomer will be volatile

so if you see that in case of ortho isomer if you just look at the structure it would be an intramolecular hydrogen bonding which is stabilizing the ortho isomer and therefore it will not undergo intermolecular hydrogen bonding which keeps it as a volatile liquid and it can be separated from the corresponding para isomer with the help of steam distillation

so it has its its volatility with steam is what helps us to separate the two isomers if you have this molecule

so if you have this molecule and you treat it with alcl3 again at 25 degrees centigrade low temperature kinetic control you expect to get the para isomer exclusively and if you do this at 165 degrees centigrade you get the thermodynamic product the ortho isomer exclusively and if you again treat this with a l c l three at a high temperature the para isomer changes to ortho and in between 25 and 165 we get a mixture of ortho and para products

so this is what the rearrangement involves that there is a migration of this sl group from oxygen to carbon which could be ortho or para under different conditions

so what is happening and what is the role of a l c l three in this case

so when you start with your ester the role of alcl3 is that it forms a complex with the starting material and activates its

so essentially its role is to activate the starting ester ok

so it forms a complex with the ester and activates it ok

so if i show it like this this is a positive charge right and then

so it forms this activated complex which undergoes dissociation it dissociates and when it dissociates it gives you this intermediate right

so this dissociates to give you this intermediate which subsequently furnishes this sl group right which can again be written in the other resonant form

so you get this species and now what happens that what is left out there is this oxygen alcl3 right and what phenol does it is activated phenol now ok

so it attacks your carbon with this positive charge ok

so it will attack here

so if i have to just show this is going to attack this carbon and what you get is this intermediate which would undergo aromatization to give this product which is still the activated olcl3 linkage which on hydrolysis gives you this ortho acylated phenol

so this is the proposed mechanism for fry's rearrangement with the help of alcl3 as an activator of the starting material and the product

so with this we come to an end of the discussion on phenols what we have covered is quite extensive and next time we are going to start the remaining part of this module which is ethers

so till then bye you