so myself terming from department of chemistry iit guwahati i welcome you all to iit paul program in this class we will study about part two aromatic hydrocarbons the part one we have seen the structure and bonding aromaticity resonant and stability and preparation of benzene and the derivatives and the physical properties

So in this class we will study about the chemical properties of benzene and their derivatives

So benzene can undergo substitution addition and oxidation reactions and generally simple benzene can undergo electrophilic aromatic substitution here this is called electrophilic substation or electrophilic aromatic substitution reactions and and vigorous conditions this not common and certain conditions vigorous conditions benzene also can undergo addition reaction and oxidation reactions and mainly the aromatic electrophilic substitution is very popular to transform benzene to substituted benzenes let us look at first the electrophilic substitution reaction and this we are going to look at it today nitration sulfonation halogenation alkylation acylation

So these all reactions involved take place via electrophilic substitution reactions and they involve common uh reaction pathway first the electrophile is produced in the reactions once the electrophile is generated the benzene is a nucleophilic enough reacts now the electrophile and generates a this intermediate it forms this called sigma complex generate this carbonium and intermediate once you form this intermediate they write in different way and some time they write like this

So this this first you form this intermediates once you form this intermediate

So so base can remove this rho turn then you restore the aromaticity

So it involves two steps and first you form this intermediate sigma complex or the intermediate once you form this one then it can convert into the aromatic compound what basically happens and the hydrogen atom which present in this carbon has been replaced substituted by electrophile therefore you say called substitution reactions since it involves electrophile it is called electrophilic substitution reaction and when you talk about the rate of these two reactions this is slow this is fast it involves two steps this reaction was this reaction takes place if you compare the rate of the reaction this is a slow step this is a first step this is a common mechanism involved the all electrophilic substitution reactions aromatic electrophilic substitution reactions now let us go one by one nitration say acid base reaction and for example when you react benzene with the nitric acid the presence of sulfuric acid the nitration takes place to give nitro benzene and this water is byproduct let me draw the mechanism of this reaction b in this the voyage group undergoes protonation and where the sulfuric acid as its acid and this axis of base it is a in a equilibrium reaction acid base reaction you generate this intermediate ah make this o h is a good living group and step two is also an equilibrium reaction this is a formation of nitronium ion plus water

So this electrophile once form the ah nitronium ion which can undergo a reaction with your benzene a you form this ah intermediate and once you form this one and now this can in step four deprotonation using base can give the nitro benzene you need less catalytic amount of sulfuric acid in this reaction it acts as a base deprotonation of this species can regenerate the aromatic ring aromaticity of this compound and you end up with the product it involves as you can see here it involves four steps say acid base reaction first step and this access here acid this axis acid base and it makes protonation of this o h group hydroxy of a nitric acid makes a good living group um that can generate the nitronium ion which is electrophile in this reaction once you form this one and this benzene in nucleophile it can undergo a reaction with the electrophile you form this intermediate once you form the intermediate and the base can remove this proton and to give the aromatic nitro compound the next reaction is sulfonation do

So in this reaction one molecule of sulfuric acid acts as a base another axis acid

So this molecule can take this proton to form the electrophile once we have this form this one this can push this one you generate the electrophile plus

So this is written this is a electrophile in this reaction and you have generate water as by product once you form the electrophile as just we have seen the case of nitration it can react with benzene and you can make the sigma complex then whatever the intermediate where the hydrogen can be removed this can act as a base this one can remove the proton then you can get the sulfonated compound the byproduct is going to be water the mechanism will be similar in both cases and the case of nitration sulfuric acid is actually catalyst in other words it's actually acid and the the nitric acid pick up the proton from the um sulfuric acid and forms convert into water and no two plus electrophile that undergoes reaction the case of sulfonation and one of the sulfuric acid one acts as a acid another one acts as a base you generate the electrophile then which undergoes reaction with your benzene and sulfonation takes place the next example is halogenation

So benzene can be converted into for example two chlorobenzene when we react with c l two in the presence of lewis acid like anhydrous aluminum chloride or fecl3 it can be converted into chlorobenzene and the byproduct will be hcl because it has two atoms one of one of the chlorine goes to here another chlorine goes here you generate hcl and regarding the mechanism this also involves two steps and the cl2 this is a lewis acid and it can react with aluminum to form cl plus electrophile and alcl4 you form this first the formation of the electrophile takes place once it forms as just we have seen it can react with your benzene do you have this intermediate once you form this one this can react with this can pick up the proton you get this how the halogenation takes place you can use anhydrous aluminium chloride or fecl3 and

So on the next example is alkylation and oscillation reactions for example when you react chloro methane with benzene the presence of aluminum chloride it can be converted into methyl benzene and hcl just as we have seen just now the case of chlorination instead of one chlorine now we have the methyl group and this is the electrophile in this case and the substitution takes place you can make alkyl benzene and similarly when you have chloroethane you can convert into ethyl benzene however when you go for larger alkyl halides chloropropane and we will have problem there and in this case when you react usually the isopropyl benzene is obtained as a product this is because you ah first the aluminum chloride reacts with this one you form the alkyl carbocation right in this case the electrophile is this one

So these are the electrophiles in this reactions first the chloromethane is converted into this methyl carbocation and which is the electrophile undergoes substitution reaction and in this case if we form this primary carbocation once again that undergoes reaction but in this case what happens as soon as you form and this propyl carbocation primary carbocation which undergoes rearrangement to more stable secondary carbocation before it undergoes substitution reaction once you form this one this is the electrophile in this reaction this undergoes reaction it gives the product

So it is they have some limitation in the case of little trough this is called peril craft alkylation and then when simple like chloromethane chloro ethane is fine when you go for larger alkyl halides there is a problem will end up with mixture of compounds mainly this this is called cumin in this case and the isoprop benzene forms as a major compound this because how it happens and as soon as you form the carbocation which undergoes rearrangement and this is the actual electrophile in this then the substitution reaction takes place and not necessary you should use alkyl halide for the alkylation reactions you can also use alkanes for example if you have benzene propane and it can undergo radially alkylation the presence of acids such as phosphoric acid to give isopropyl benzene and at the beginning we have seen during the alkene reactivity of alkenes towards acids in this case what happens this alkene reacts with acid form profile carbocation and this acts as a electrophile in this case

So depends upon the reaction and conditions and you can in the case of alkyl halide you have to use aluminum lewis acid like aluminum chloride and

So in case you can also use alkene as a source to make alkyl benzene is also electrophilic alkylation reaction next oscillation ah just we have seen alkylation using aluminum chloride and if instead of alkyl halide if you use acyl halide for example acetyl chloride it can undergo substitution reaction with the benzene to give a stophenone and the acetyl chloride can react with benzene to give astrophenone and the presence of anhydrides aluminium chloride and here what happens first as we have seen earlier acetyl chloride reacts with aluminum chloride to give acyl carbocation and this acts as a electrophile the substitution reaction takes place once undergoes first benzene reacts you generate the sigma complex as we have seen then this can remove the proton and do you generate in this case hcl as a byproduct if you use austral quality get astrophenol astrophenol we use another other kabbas like for example benzyl chloride you will get the benzophenone in the case

So it is very very useful reaction and is very useful reaction to make ketones next addition reaction and the vigorous conditions benzene can be converted into cyclohexane by reduction using nickel catalyst in this case the hydrogen undergoes addition to the benzene and you need three molecule of hydrogen to give cycloaction this is an example for addition reaction under vigorous conditions takes place benzene also can be reacted with chlorine the price of light to give hexachloro cyclohexane

So in this case what happens is addition reaction and the chlorine the pressure of light undergoes homolysis to generate cl radical this cl radical reacts with the benzene to form this radical intermediate this radical intermediate this is called initiation step just we have seen the beginning of the reaction with alkanes the chlorine can under homolysis to generate chlorine radical that radical can undergo addition reaction with this benzene to form this radical secondary radical intermediate this is called propagation step this is a chain initiation provocation once you form this radical this radical can react with a c l dot to give this dihalo derivatives this again can react with the radical and go on like this and you form this hexachloro cyclohexane this is once the radical the substrate is consumed then the two radical can combine together c l dot the reaction can be stopped this is a radical process and this is we use as insecticide

So these two are an examples for addition reactions these reactions as you can see here takes place under vigorous conditions right when we saw the electrophilic substitution reactions they are very reactive you have to do under milder conditions and easy to handle but this one you have to do on high pressure hydrogenation reactions similarly then you have to irradiate under light uv light and then you generally form the radical reaction then once form the radical which undergoes reaction you get the hexa chloro cyclohexane the next is oxidation of benzene benzene can be completely oxidized to carbon dioxide plus water

So benzene also can be oxidized to partially to malik and hydride when you react benzene in the pressure vanadium and oxide partially what you do you generate and four molecule of water or carbon carbon dioxide these are examples for oxidation reactions this is a partial oxidation and this is ox complete oxidation of benzene to carbon dioxide and water

So far we have seen the chemical properties of benzene if it is a simple benzene it can be readily converted into substituted benzene using electrophilic substitution reactions where we have seen nitration sulfonation halogenation alkylation and oscillation then we have seen addition reactions which are not popular however at a high pressure and catalytic conditions aromatic hydrocarbons can be reduced to alkanes we have seen example the transformation of benzene to alkane using nickel catalyst under hydrogen pressure then we have seen one example for free radical addition of halogen chlorine to benzene to form hexachlorocyclohexane then we have seen example for oxidation reactions two examples we have seen one is complete oxidation computation that's called and oxidation of benzene to carbon dioxide and water then another one we have seen partial oxidation benzene through malik and hydride using meridian pentoxide this reaction is carried out around of 450 degree celsius and where you generate carbon dioxide water as by product ah these reactions are carried out and of course as you can see here under excess oxygen pressure and simple mono substitution reactions fine in the case of electrically substitution reaction on the other hand if the benzene has substituent already

So let us see the effect of substituent in the aromatic electrophilic substitution reactions for example if the substrate already has substituent like electron withdrawing group let us take this example nitrobenzene

So the the structure of nitrobenzene is hybrid of the following resonance structures do do if you look at the rational structures you can find and the electron density at the ortho and para carbon atoms less comparing to the metacarbon atom therefore whenever you do the electrically substitution reaction with the benzene ring that contains electron with the drawing group here n o t is electron with the drawing group the electrophile undergoes substitution at carbon at meta position not ortho and para position because as you can see here the electron density if you write the resonance structures of this nitro benzene you can see here the electron density at the ortho and para position is less comparing to the meta position therefore and for example if you do the nitration this system

So you will end up with metro nitro benzene as a product in comparing to the ortho and para nitro uh dinoto intervention because the electron density are these carbon atoms less when you have the electron with the dry group not only nitro group when you have the cyano cf3 aldehyde ester and

So these all are electron with the drawing group they can take electron from the benzene ring and

So make the arthron paraposition less electron density comparing to the meta position therefore the substitution selectively takes place meta position this is called meta directing group now let us take one more example that contain electron donating group for example benzene that contain amide functional group this is electron donating group whether methoxy hydroxy or amine which contain that amide functionality this or electron donating group and in this case and this lone pair of nitrogen can delocalize to form the following structures to do if you look at these structures as you can see here in this case the electron density is more at the ortho and para position you can see here the orthocarbon has more electron density and para carbon also therefore whenever you have this kind of substituent the benzene ring if you do the electrophilic substitution with these substrates and selectively the electrophile undergoes reaction at ortho and the para position to give a mixture of compounds most of the times and usually the reaction doesn't take place and meta position this because you have more electron density at the ortho and para position

So this is called ortho and para directing group whether when you have o h group or methoxy group or alkyl group or amide for example these are called ortho and vera directing group because as you can see here this is the structure this the amide the structure of the resonance structure of the following hybrid of the following resonance structures as you can see here once if you have the substituent the electron density at the ortho and para position higher than meta position therefore selectively the electrical substitution takes place at ortho and para position comparing to meta positions and similarly when you have the oh group methoxy and methyl and any you will get similar kind of results let me take one example and if you do the nitration of this substrate just we have seen the nitration of nitrobenzene and when you do the nitration of this substrate and you will get a mixture of compound on the other hand just we have seen if you do the nitration with the nitro benzene

So we will end up with meta nitro benzene

So these reactions clearly suggest that and it depends upon the substituent present whether electron donating group usually the electrophile undergoes substitution reaction at ortho or paraposition on the other hand if you have electron with the drawing group the substitution selectively takes place in meta position this is because just we have seen when you write the resonance structures you can find out the electron density different in this carbon atoms when you have the electron donating group and the ortho and para carbon atoms have more electron density compared to the meta therefore the electrophile undergoes substitution at earth on parapositions on the other hand when you have the electron with the drawing group and the meta carbon has more electron density comparing to ortho and para therefore the electrical substitution takes place at meta position in summary in the part 2 we have seen the chemical properties of aromatic substrates we have seen different types of electrically substitution reactions we have seen nitration sulfonation chlorination then we have seen alkylation oscillation reactions then we have seen two examples for addition reactions and these addition reactions are carried out under vigorous conditions and one example is hydrogenation of benzene to alkene you see nickel catalyst the other example what we have seen is addition of free radical to benzene to produce hexachlorocyclohex we use as insecticide these two are addition reactions then we have seen oxidation reactions that also depends upon the reaction conditions and you can completely oxidize benzene to carbon dioxide or you can also partially oxidize benzene to molecular height at this one of the example similarly you can also oxidize benzene to aldehydes clay axle using ozone and zinc reduction process and this called partial oxidation and then we have seen um the effect of directing group present in the benzene ring and if simple benzene and selectively one of the hydrogen is replaced by substitution reaction on the other hand if substituted benzene and the substituent present can dictate the position of the substitution that the nature of the substitution reactions for example if you have the electron withdrawing group usually and the electrophilic substitution will take place at third carbon atom that is called meta substitution the other hand if your benzene has electron donating group and the substitution takes place either at carbon 2 or 4 or mixture both and this is called ortho and para substitution reactions with this we conclude thank you very much you