

hello everyone i am dr ramirez ramopaniker i am an associate professor at the department of chemistry in indian institute of technology kanpur

so in the last three lectures that i had given i was talking about the chemistry of halo alkenes and haloaromatics

so today i would continue to do that

so this as you already know is from the unit 10 of the ncert textbook for chemistry for class 12 students and what is left out of this unit to be discussed is about the reactions of haloaromatics

so haloaromatics as you know are compounds where halogen atom is attached to an aromatic compound

so in the last class we had discussed about the reactions of haloalkanes and i also made it a point to mention that the reactivity pattern of halo alkenes are quite different from that of haloalkanes

so we would look at the reactions of haloalkanes today in the reactions of halo alkanes one of the most interesting and most useful reaction was the nucleophilic substitution reaction we said that if we have a halogen atom attached to an alkyl group the halogen atom can be replaced by a number of different functional groups by using various nucleophiles

so that is supposed to be that was supposed to be and that we have mentioned is actually the most useful reaction and one of the best to make various derivatives of hydrocarbons but now once we come to haloaromatics quite interestingly all the nucleophilic substitution reactions at first seem to be a possibility these reactions do not work well

so unlike alkyl halides aryl halides are extremely slow and extremely sluggish when it comes to reaction with nucleophiles

so there are various reasons for this

so we would look at the reasons one by one

so if you would have a look at the screen here you would find that one of the factors is a resonance effect

so as you can see whenever we have a halogen atom attached to an aromatic ring the halogen atom that i have shown here is chlorobenzene

so chlorine has lone pairs of electrons

so these lone pairs of electrons because the carbon-chlorine bond can rotate these lone pairs of electrons would come parallel to the electron cloud that is present in an aromatic ring

so you know that an aromatic ring is stabilized by electron clouds on either side of it

so similarly when a chlorine atom comes has this lone pairs of electrons they can come in parallel with the electron clouds present on

an aromatic ring and start to interact with these electron clouds
so they can have bonding interactions which we normally say as resonance structures that can be formed from this or
the effect is called as resonance effect
so this representation show you how we would be able to draw them in simple chemical terms and show how a bonding interaction can happen between
the lone pairs on chlorine and the aromatic ring
so this is what we mean by resonance effect
so you
can see that the lone pair of the chlorine atom is donated to the chlorine carbon bond effectively
forming a double bonded compound
so that means we have a chlorine carbon double bond but now that chlorine has given its electrons to form this bond it receives a positive charge
but however when the double bond is formed one of the double bonds in the ring within the
aromatic compound also migrates to the adjacent carbon giving a negatively charged species
so from
a neutral structure we have a structure that is charged with positive charge on chlorine atom and
negative charge on one of the carbon atoms now the negative charge does not stay on that particular
carbon atom it continues to move through the aromatic ring
so you would find that the negative charge then goes and forms a new double bond while an existing double bond is now moved on to one
of the carbon atoms to give you a new negatively charged carbon atom now this negatively charged
then moves across the ring and forms a new double bond and negative charge is localized on another
carbon atom
so all these structures are returned with the arrows that correspond to resonant
structures that means none of these structures really do exist the actual structure is a mixture
of all the structures that we have drawn here
so out of the four structures we have three of them have a positively charged chlorine atom and all such compounds to have a carbon chlorine
double bond to
so therefore this double bond character between carbon and chlorine makes it difficult to cleave the carbon chloride bond so in effect the carbon chlorine bond has become
shorter it has a double bond and character
so it is much stronger than a single carbon chlorine bond and one interesting thing to note is that whenever we were writing halo alkenes we always
said that the carbon which is attached to the chlorine atom receives a slight positive charge
but whereas in the structures that we have now you would find that chlorine is

having a positive charge it is because we have a double bond that is generated on chlorine at the expense of a lone pair of electrons that was present in chlorine so it has a double bond between carbon and chlorine

so a partial double bond between carbon and chlorine that results in lesser reactivity

of this molecule that means it is difficult to substitute that particular chlorine from the

carbon atom now going ahead a second reason for this is the difference in hybridization of

carbon atom in $C-X$ bond

so I have two structures here one of them is an aryl halide a haloarene and another one is an alkyl halide

so if you look at the carbon that has bonded to the halogen atom in a haloarene it is an sp^2 hybridized carbon atom

so what do we exactly

mean by an sp^2 hybridized carbon atom is that the amount of s character on the orbital that is

being used by carbon or the atomic orbital that is used by carbon is more

so whenever we increase the

s character in an orbital the orbital becomes more electronegative because s is the inner shell

so therefore you would find that the increased percentage of s or s character in the orbital

makes this particular orbital more electronegative or in other words the carbon that is bonded to

X in an aryl halide is more electronegative than the carbon that is bonded to a halogen atom

in a haloalkene

so therefore because the carbon is now more electronegative it does not allow the

bond to be polarized as much as it is polarized in a haloalkane or in other words the electron

that you find between carbon and halogen is not moved too much towards chlorine

so the extent of

polarization is less the bond therefore happens to be shorter

so if you compare a chloroalkene

and chloroarene generally it is found that the chloroarene has a shorter carbon chlorine

bond in comparison with the chloroalkene

so this shorter bond also means that it is

stronger and this also can be attributed to the fact that the carbon chloride bond

has a double bond character which we saw before

so because of these factors it

becomes difficult to cleave this bond

so that is the whole point

so if you want to do a

substitution with the nucleophile we would like to break the carbon chlorine bond

so that becomes

difficult now then we can also think about the other mechanism that was a possibility for haloalkynes which was S_N1 substitution reactions where we have to assume that the halogen leaves from the molecule and gives the positive charge to the carbon atom to which it is attached this is difficult because the bond is not polarized and even if we assume that under forcing conditions we were to force an S_N1 reaction on a haloalkane you would find that the positive charge now has to reorganize an orbital which is sp^2 hybridized so carbon uses a sp^2 hybridized orbital to form the carbon chlorine bond now when the chlorine leaves with its electrons the sp^2 orbital is now empty or it or therefore the carbon receives a positive charge and that orbital so the problem with having that positive charge is all the aromatic ring is electron rich if this is my plan is to be supposed as the aromatic ring you would find that the electron clouds are on either side of this so you have electron clouds on top and bottom of the aromatic ring now the orbital that has the positive charge also lies along the plane of this so it is in one plane so whenever we generate a positive charge is generated on the aromatic ring that particular orbital is in the plane of the aromatic ring and therefore that empty orbital cannot be supported by the electron clouds on either side because this is actually in the node between the two components of the electron cloud that is available on aromatic ring so this cannot be resonant stabilized so that is the trouble we have so therefore this aryl cation are extremely unstable so there are two reasons one of them the empty orbital is known as p_z orbital which is more electronegative so the carbon starts to feel more positive charge and the second reason is that this particular positive charge or the absence of electrons cannot be supported by the electron cloud that is present in the aromatic ring because it a kind of falls in the nodes of this electron cloud the node of this electron cloud so that makes an S_N1 mechanism practically impossible for haloalkane so we have seen that the S_N2 reaction required that we cleave the carbon halogen bond when the nucleophile approaches and the S_N1 reaction requires that it cleaves even before so both these are not possible and there is also

another reason why S_N2 reactions are not possible because aromatic rings are electron rich they have the aromatic electron cloud a nucleophile is also electron rich so when two electron rich species have to come together for a reaction to happen you normally find that there is a large amount of repulsion between the electron rich species and that results in the reaction being slower so these factors these four factors that it is I have discussed now there is resonance the difference in hybridization instability of aryl cations and finally the repulsion between a nucleophile and an aromatic ring so all these factors contribute together and make nucleophilic substitution reactions of aromatic compounds extremely difficult it does not mean that we cannot carry out these reactions we can of course do these reactions but some of these reactions would require extremely hard conditions ah in comparison with what was required for the reactions of halo alkenes so I have an example here so these are reactions of chloro arranged with hydroxide ions so hydroxide ion is a nucleophile so let us take the first example that is given this given here so if you take chlorobenzene and treat it with sodium hydroxide then the condition that is required is 623 kelvin so it is approximately 300 and it is 350 degree celsius and 300 atmosphere so the reaction requires extremely high pressure and very high temperature only then the nucleophilic substitution does happen so the nucleophilic substitution of a chlorine with the hydroxide anion is possible provided we will give extremely harsh conditions including very high temperature and very high pressure now you can see that there are two steps to the reaction one is where you treat it with sodium hydroxide at the temperature and pressure that you mentioned and in the second step is the same molecule is treated with an acid so H^+ here is required because under basic condition the phenol that is formed would be phenoxide anion because phenol is acidic so in the presence of sodium hydroxide after the first step the product you get will be a sodium salt of phenol so you have to neutralize it that is why we have H^+ as a second step okay now in the second reaction what you are seeing is this we have the same substrate but we have added an ortho on para position to the chlorine so when we add an energy to the para position that this is a mono substituted chlorobenzene or a chloro nitrobenzene

so in this particular case we have this nitro group present and then there is a dramatic difference in the conditions that are required earlier we needed a much higher temperature and very high pressure here the pressure factor has been removed so this reaction happens at atmospheric pressure and at not so high temperature so 443 kelvin approximately 175 degree celsius so the reaction would happen at a slightly lower temperature than what is what was earlier required and it gives us the product after a protonation using an acid ok now in the third example we have added one more nitro group and we see that the trend continues so when as we keep on increasing the number of nitro groups in aromatic ring the reaction conditions become milder and milder so under this condition you need less than 100 degree celsius for the reaction to be carried out and there is no requirement of higher pressure so we get the product which is a dinitro phenol as the product in this case tri nitrochlorobenzene so here there are three nitro groups on position on the two ortho position and the para position so if you would like to name it other ways we can say that this is two four and six positions of the chlorobenzene we have nitro substitutions but now you would find that the condition is extremely simple and this reaction works almost like the reactions of alkyl halides here all you need to do is take water and warm the reaction mixture so we do not even need sodium hydroxide where an h minus nucleophile has to react instead water with its lone pairs will be able to do a nucleophilic substitution reaction on this substrate and give us this product which is picric acid this particular product is called picric acid now so so what we have seen is that a chloroalkyl chloroarrange are sluggish they do not give you nuclear fluid substitution reactions you have to really force the conditions but as we keep on adding a group such as nitro so nitro specifically here because nitro is an electron withdrawing group so what we are actually doing to the substrates here by increasing the number of nitro groups is to make the aromatic ring electron deficient so an aromatic ring was eight layer electron rich so once you put a nitro group the nitro group is ela pulls the electron towards itself so therefore the aromatic ring slowly starts to become electron

deficient and that would make the approach of the nucleophile to the aromatic ring easier and also the aromatic ring would be able to handle a negative charge so we would look at the mechanism soon and then we will find how this reaction works so ah so in this page you can see the mechanism of this particular reaction so what i have first here is the para nitrochlorobenzene so or pyrochloro-nitrobenzenous it has to be called so you would find that in the in the parasubstituted compound the reaction follows a very interesting path it is not like sn1 or sn2 reactions the o h minus starts to attack on the carbon atom that is attached to chlorine and then we get an intermediate where there is a carbon atom that is attached both to chlorine and to the hydroxide group now the double bond that was present with that carbon atom has moved on to the adjacent carbon with the forming a negatively charged carbon there so there is a carbon ion formed and we have a carbon that is tetrahedral that is attached to four different groups ok and now what happens the negative charge is then delocalized throughout the ring um similar to the resonance structures that we drew earlier so the negative charge moves on and then a new double bond is formed and then now we have the negative the carbon ion on the carbon that is attached to nitro group and then it moves further and the carbonyl reaches here and finally when the double bond is reinstated the chlorine atom can come out as a chloride ion so effectively if you look at the structure on extreme left and the structure on extreme structures on extreme right you see that this is a nucleophilic substitution reaction the chlorine atom has been replaced by the hydroxy by the hydroxide ion but however there are these intermediates and these intermediates are called as meisenheimer complexes so these intermediates that are written here are called as meisenheimer complexes um so these are compounds where we have a nucleophile added onto an aromatic ring by giving a negative charge on the aromatic ring now ah the our aromatic ring in this case is substituted we have substituted it with a nitro group so you also see the nitro group is electron withdrawing and in at least one of the structures one of the three structures that i have written in square brackets here you can see that the negative

is on the carbon atom that is attached to the nitro group
so that means this negative charge
also can be delocalized on to the nitro group
so therefore the nitro group which is
electron withdrawing will be able to pull the electrons towards itself and
stabilize
the mesoheimer complex
so mesoheimer complex is formed a nucleophile adds on to an aromatic ring
to a halo aryl and forms a negatively charged species along with the
tetrahedral carbon atom
and now the such species are stabilized whenever there are electron
withdrawing groups present on
the carbon atoms where the negative charge starts to appear
so there are three structures
that represent the mesoheimer complex and in one of them the negative
charge is on
the carbon atom that is attached to nitro group
so that makes this reaction happen now the first
step of the reaction where the H^- has to come and start forming the
tetrahedral carbon
atom this is the slower step in the reaction it is reasonable because now we
are talking about
breaking the aromaticity of the aromatic ring so here we had an aromatic ring
very much intact
now once we start forming this tetrahedral carbon atom here the aromaticity of
the molecule
is lost
so this is there for a very slow process but after once this has happened the
elimination
of chloride as an anion is extremely fast
so the last step that means breaking the breakdown of the
mesoheimer complex into the products is faster
so the first step is lower whereas the second
step is faster
so that is how this reaction works now i have the same mechanism for a ortho
nitro
derivative
so that means i have orthochloride nitrobenzene
so now in this particular structure
you would particular compound you find that it is you will find that it is the
exact same things
that are happening the OH^- attacks it forms a tetrahedral carbon atom
the negative charge is
now already on the carbon atom that is attached to nitro
so very good
so the negative charge can
be delocalized onto the nitro group and stabilized now the resonance
structures continue
to form that means the negative charge continues to move through through the
aromatic ring and we can again draw three mesoheimer complex structures all
of them in
resonance
so effectively the negative charge is sented through the five carbon atoms
that are

present uh in in this complex and only one of the carbon atom is tetrahedron structure
so one way of drawing meson hammer complexes that you would find being used by people is to draw the structure like this with the negative charge and then a chloride voice and at nitro at whichever position you would like to put it either ortho or para so there is this negative charge that is delocalized through this part of the molecule and we have a tetrahedral carbon there so this is how normally a meson hammer complex is represented with a single structure otherwise we will have to draw all the three structures to represent it correctly now here again the first step is elimination of this so in these two structures these two examples that i have drawn i have the nitro group on ortho and para positions and in both the meson hammer complexes those are formed you find that the negative charge is on a carbon atom that is near to the nitro that is attached to the nitro group so in the second case it is on carbon number two and in the first case it is on carbon number four so these structures are something that we need to remember because those are the ones which make this reaction first now i would go on and see what happens when the nitro group is on meta position so that means when we have metachloronitrobenzene here again though h minus can come and attack here so we know h minus attacks we generate a negative charge like just like in the other cases we do have the meson hammer complex and now the negative charge forms a new double bond and the negative charge the negative charge moves through the ring by forming a new double bond and moving the electron moving the pair of electrons through the aromatic ring we get the second structure and finally the third now in this sequence of reaction in the in this series of meson hammer complex structures that we have drawn you would find that the negative charge is never on the carbon atom that is attached to the nitro group so in this it is not on the carbon that is attached to nitro group here again it is not the case and not even in this so therefore although nitro group is something that can withdraw electrons it can stabilize the negative charge better if the negative charge comes on the carbon atom to which the nitro group is attached now if none of the structures the negative charge comes to the carbon atom to which nitro group is attached then the negative charge is

not stabilized so
therefore a substitution of an electron with a growing group such as the nitro group on meta position does not make this reaction faster once again we saw that chlorobenzene reacts very slowly to nucleophilic substitution reactions we saw that if increase the number of nitro groups on ortho and para positions the rate of the reaction increases the condition required to carry out the reaction becomes milder and milder however if the nitro group is present on a meta position this does not happen so in short we would be able to say that the rate of these reactions are enhanced only if the electron withdrawing group such as the nitro group is present on ortho and para positions and if they are present on meta positions then the reactions do not happen faster ok so that is about nucleophilic substitution reactions of halo arrange so so you would already realize that it is a tough reaction to do so people not normally go for that but however aromatic rings because of its electron cloud because of its rich electronic species those are present the aromatic ring itself they tend to give you another reaction which the which alkyl halides cannot give and those are electrophilic substitution reactions you have already learned them probably while you are learning aromatic compounds so electrophilic substitution reactions do happen in halo arranged now what does a halogen atom do to an aromatic ring so we are now going to discuss about halo arranged that means these are aromatic rings that are attached to a halogen atom so let us see what can a halogen do to an aromatic ring so halogen atom by itself is something that will pull electrons out because the carbon chlorine bond the carbon halogen bond the halogen pulls electrons so they are slightly deactivating so they tend to deactivate the aromatic ring by deactivation of an aromatic ring we mean that an aromatic ring loses its electron density to a substituent so the substituent is something that pulls electrons slightly from the aromatic ring and make the aromatic ring feel less electron rich so halogens do that but however aromatic halogen atoms also have this lone pair so these these are structures we already drew once so these long pairs of electrons in halogen atoms can be delocalized onto the rings to get this structure

so it can go with the negative charge on ortho position para position and on the other ortho position and in such structures

we have this carbon halogen double bond so this is something we saw and the halogen gets a positive charge too

so so there are two things now one of them is the halogen atom pulls electrons

from the aromatic ring because it is an electron negative atom

so therefore the aromatic ring is

now electron deficient at the same time although it makes the aromatic bring electron deficient

whatever electron density is available on the aromatic ring it is enhanced on ortho and para

positions because in these resonance structures you can see that there are negative charges which

are on ah in structure one and three you will find that the negative charges are on ortho position

to the halogen atom and in structure two which i am showing you now the negative charge is on the carbon atom 4.

so therefore these structures are favor substitutions on these positions so effector

and electrophile

so once again electrophiles are those species which have a positive charge or those which are electron deficient and are looking for an electron rich species to react with

so when an electrophile approaches a halo arrane it sees that the alloying is not

so easily reacting but however if it has to react it would try to react through ortho

and para positions of of the halogen atom it is because those are the ones that have

negative charges in the resonance structures

so here i have these structures representing

an ortho attack and an and a para attack that means attack at an ortho position and at a para position

so simply drawing we would be able to draw that the double bond present in the aromatic

ring would migrate to react with the electrophile which is shown as e and a positive which is

shown as c having a positive charge then a new bond is formed of course this carbon atom has

a hydrogen atom

so we say that this carbon is now a tetrahedral and the positive charge resides on the carbon atom that has chlorine now the presence of a positive charge adjacent

to chlorine atom is not good because chlorine is electronegative

so it does not want the positive charge there

so therefore the ring that is why we say the ring is deactivated but however

once the positive charge comes there the lone pairs can stabilize the positive charge so that also helps in the ortho attack so if the attack has to happen it can happen in ortho similarly if the attack has to happen in para position we have a new carbon lone pair bond where is the electrophile and that carbon now is tetrahedral and if you draw two arrows as I have shown here you will be able to see that the positive charge is now on the carbon that is attached to chlorine and chlorine will be able to stabilize the positive charge using its lone pair so these are the reasons why ortho and para positions substitutions at ortho and para positions can be stabilized by halogen whereas if the substitution was at meta position the positive charge will not come on to the carbon having chlorine and therefore a resonant stabilization will not be possible so you may you can draw those structures yourself and feel for it okay so now let us look at some of the most useful electrophilic substitution reactions of halogen uh halo arranged so the first reaction is halogenation itself so that means if we have a halogen we can add more halogen atoms to that so this is a reaction we have learnt while we are talking about the preparative methods for halo arranged so you can take a halogen treat it with another halogen with halogen molecule either chlorine or bromine in the presence of anhydrous $FeCl_3$ or Fe itself so which would form a PCl_3 which acts as a Lewis acid and $FeCl_3$ would then react with chlorine forming what will be $FeCl_4^-$ plus Cl^+ positive so the Cl^+ positive that is formed would be the electrophile so if you look at the reactions that of that electrophile that I mentioned earlier where the electrophile is shown as shown in red colour here that electrophile is Cl^+ plus now Cl^+ the electrophile thus formed would then react on ortho and para positions as expected and normally you would also find that the substitution on para position is more favorite it is just because two substitutions on ortho position that means one two substitutions on aromatic ring as in this case we can see here one two dichlorobenzene so when you have substitutions on adjacent carbon atoms on an aromatic ring there would be some steric hindrance because if you look at this double bond this double bond is now as if it is a cis double bond with

both the chlorine atoms are on same side
so it is like a double bond having c substitution so
they are very close
so there would be some sort of repulsion between them
so normally you would
find that the para substitutions are favored in an electrophilic substitution
reaction so
halogenation gives you two products a mixture of ortho and para substituted
compound one for
dichlorobenzene and one two dichlorobenzene or ah
so out of these two dichlorobenzenes one
which has the substitutions on one and fourth position that is the para
positions will be
the one that is formed as the major product okay
so the second reaction we will talk about
is nitration reaction
so nitration reaction is by which we put a nitro group on to the
aromatic ring and normally depending on the electron richness of the aromatic
compound
that is subjected to nitration we can use various reagents
so in this case you see that we use a
reagent that is hno₃ nitric acid and sulfuric acid a mixture of nitric acid
and sulfuric acid
is sometimes called as a nitrating mixture so this particular mixture will be
able to nitrate a
molecule because under these conditions hno₃ gets protonated and we would
generate an electrophile
which is no₂⁺
so this is the electrophile that is reacting and this electrophile can then
go
on to ortho position or para position forming two different mono nitro
compounds
so one chloride
four nitro benzene and one chloride two nitro benzene
so these are the two compounds that
we would get and if you have to say which is the major compound because the
major compound
is the one where substitution is at the fourth position we have already seen
why
so so this
this is also a useful reaction of halo arrange now the third reaction is
sulfonation
so in
sulfonation what we add is an so₃h group
so it is called sulfonic acid group
so ah if you take
a haloarane and treat with concentrated h₂so₄
so concentrate h₂so₄ there again what happens is
the one h two software molecule will protonate another h two software
molecules and a water
molecule leaves and effectively we get an electrophile which can be written
like this so
s o three h is the electrophile in this cases
so then so₃h would react with the hyalurine

both in ortho and para positions we would get two products that is four chloro benzene

sulfonic acid and two chlorobenzene sulfonic acid and out of these two structures you already know

that the four chlorobenzene sulfonic acid would be the major product and two chlorobenzene

sulfonic acid would be the minor compound ok um

so the next reaction that we will

discuss is Friedel-Crafts alkylation you already learned Friedel-Crafts alkylation of

aromatic compounds

so in this what is required is a haloalkane

so we take a haloalkane and treat

it with anhydrous $AlCl_3$ aluminum chloride where aluminum chloride acts as a Lewis acid and breaks

the carbon-chlorine bond

so effectively what we would have is something that can be represented as CH_3^+ positive especially if the alkyl halide used is methyl chloride then we do not really

make a CH_3^+ positive but we would have something that is partially bonded to chlorine and having a

lot of positive charge on CH_3

so this again then gets bonded to aluminum

so this is how we get we

polarize this molecule and negative charge starts to develop on chlorine

so we have an electrophile

that is now an alkyl cation a carbocation and that electrophile would react with the haloalkane on

ortho and para position and giving us one chloro-methyl benzene and one chloride two methyl benzene

the two substituted product the ortho substituted product is the minor product this reaction has

an interesting fact that once we add an alkyl group onto a benzene ring onto an aromatic

ring the alkyl group makes the benzene ring more electron rich

so there is only one problem

with this reaction normally when we carry out this reaction the products that are formed in the

reaction are more electron rich are more activated than the starting materials themselves

so they

might start giving you multiple alkylation so the reaction may not stop at forming one CH_3

we might end up getting additional CH_3 groups on aromatic ring

so this is one of the

problems with Friedel-Crafts alkylation because the product always is more reactive than the starting

material

so so that is something that we need to keep in our mind whenever we want to do a Friedel-Crafts

alkylation there are other problems with the reaction too which you might learn if you

take up chemistry in a high in the higher class ok now Friedel-Crafts acylation is another reaction

where instead of an alkyl halide we use an acyl halide
so these are acid chlorides
so what i
have here is acetyl chloride
so we can call it the spherical cross acid dilation in this
particular example
so if you take acetyl halide this also has a carbon chlorine bond and we use
the same catalyst
so the catalyst we use we use this anhydrous aluminum chloride now what
would
aluminum chloride do aluminum chloride would break the bond here and then we
get CH_3CO^+ as
the electrophile
so you would find that CH_3CO^+ with the positive charge on carbon which would
also be shared with oxygen this is a relatively stable electrophile um quite
unlike metal cation
so this acyl cation would now be able to act as an electrophile and react with
aromatic ring giving
us two products um two mono substituted products one where the substitution is
in fourth position
another one where the substitution is in second position of course the major
product is one where
the substitution is in the fourth or para position now unlike alkylation
reactions acylation
reactions are would stop at mono substitution because the cell group because
the product
that is formed in this case is a ketone and once you have a CH_3CO attached to
benzene it is
called acetophenone you will learn that while you study ketones
so these compounds are more
deactivated than halo arranged by themselves so because an acetyl group and a
cell group normally
deactivates the aromatic ring
so therefore the action would stop at one step
so in that way they
would give you better control over an alkylation reaction in both the cases
aluminum chloride
is the lewis acid that is most commonly used there is only one one issue
normally in fredericks
alkylation reaction you would only need to use one equivalent of aluminum
chloride as the lewis
acid whereas in this you would only require to use aluminium chloride and
catalytic amount
because there is a catalyst that will continue to activate methyl chloride or
the haloalkane that is
used but whereas whenever we you do acceleration reactions the product has a
keto group which
coordinates with aluminum chloride
so therefore in these reactions the amount of catalyst used
is more
so you would have to use at least one equivalent of the catalyst for this
reaction to
go well ok
so that is about the electrophilic substitution reactions of aromatic

compounds now

we would go ahead with the third kind of reaction that is reaction with metals

so this is probably

one reaction where haloalkanes exactly match haloalkynes

so the reactivity pattern is not

largely different because you know in these reactions the haloalkane is reacting with

the metal and metals are substantially more electron electropositive than carbon itself

so they have similar pattern of reacting between haloalkanes alkynes and haloalkenes

so one of the

reactions called as the words phytic reaction in this reaction we can take a haloalkene and a

haloalkene and treat with sodium and get these compounds which are cross coupled products where

an alkyl group is now attached to an aryl

so we get an aryl compound also an alkyl aryl compound sometimes called as alkyl aryl compounds

so this can be prepared once there is a cross coupling of course there are troubles with this reaction as you can see we could assume that two aryl groups can combine

and give you a hydrocarbon give you an alkyl aryl given alkene similarly two aromatic

compounds can combine together give you two are aromatic rings linked with each other

through a single bond

so that is possible and that reaction is called as fitting reaction

so in

phytic reaction what happens is two haloalkenes react together in the presence of sodium and two

molecules of sodium halide comes out and then we get a compound where two aromatic rings

are linked together through a single bond these kind of compounds are called by aryls and in

this particular example we have two phenyl rings which are linked together and this is called a

biphenyl

so we can prepare by phenyl by using this reaction but it is you would normally feel

that the synthetic utility is not much because we are using metallic sodium for this reaction

so metallic sodium is very reactive and it would normally catch fire if you are not careful and

so on it reacts violently with water moisture

so therefore the moisture in the air is sufficient

to give you a very explosive reaction

so therefore this is practically not used much but we have

to realize that this is a theoretical possibility this is something that we can do while studying

the reactions of alkyl halides with metals you have studied wurtz reaction

so wurtz reaction was

when an alkyl halide is treated with sodium to get a dialkyl compound dialkyl hydrocarbon now once

you do and once you do the same reaction with halo arranged we call it fitting so that is why this reaction where its actually a mixture of phytic reaction and woods reaction so that is called woods fatigue reaction so the name would make sense to you if you start looking at this compound so this is pretty much about the reactions of halo arranged so now we have discussed all the three kinds of reactions that haloarines can give you so the reactions of halo arrange are electrophilic substitution reactions which are probably the most useful nucleophilic substitutional reactions through myosenheimer complexes not so much useful but it does happen and finally the reaction with metals where there is a met where we can do this cross do this coupling reactions either feeding reaction or wood sweating reaction so in the last part of this chapter what this chapter what we would discuss is about some poly halogen compounds that are most commonly found and most commonly used so the first member so these are poly halogen compounds that means these are compounds where at least two halogen atoms are attached to the carbon atom so the simplest member is that that you would come across is dichloromethane so dichloromethane is a liquid so if you take it at room temperature it has a boiling point around 40 degrees so it is a liquid but volatile liquid so if you keep it it just vanishes and it is normally used as a solvent in organic chemistry labs wherever people use it it is as a solvent in industry it can be used as a pain remover because most of the pains are organic compounds and because dichloromethane is a solvent for organic compounds it can be used to remove those and because it is volatile it vaporizes faster so it can also be used as a propellant in eros also now however it is not a nice compound to meddle around with because it harms if you inhale and see it has a low boiling point so if you keep a bottle of dichotomy then open in this room after some time you would have dichloromethane fumes in the room and it hams the human central nervous system so therefore it is not good if you are subjected to this compound and one other thing is that whenever we use them in labs if it happens to fall on your body and the hand especially and this part of the skin that is more sensitive like between your fingers for example and between the nails and so on you would immediately start start to feel an extremely burning sensation so dichloromethane has this

problem

so it probably

absorbs through the skin too

so ah if it touches your skin on especially on sensitive skin

it would start to give you a very burning sensation

so these are things that we should be

careful when we deal with dichloromethane but however its applications are

so good it is a very

good solvent that it is still being continuously used especially in organic chemistry laboratories

now the next compound is trichloromethane which you would all know more as a chloroform now

chloroform again is a solvent it is a very good solvent for fats all sorts of fats can be

dissolved in it is used as a solvent for alkalites alkaloids

so like you know alkaloids are compounds

that contain nitrogen atoms

so these are natural products which are available in nature

so whenever

we would like to extract them from natural sources

so imagine that there is a biologically active

compound present in a plant material and if you would like to extract it

chloroform is one of the

solvents that you can use to extract out alkaloids it also dissolves iodine bromine and

so on now it

is also used for the product production of rion refrigerant free on r22

so r22 is the compound

that is attached to ch

so the compound has it is a fluoro

so freons are all we will talk about them

preons are all compounds that have fluorine and chlorine attached to the same carbon atom now if

if you take methane add two fluorine one chlorine and one hydrogen then that compound is called as

r twenty two

so this is made from ah chloroform

so that is one of its ah application it has an anaesthetic effect

so if you inhale it ah you would feel dizzy

so it has an anaesthetic effect

so just like dichloromethane it is harmful

so you we cannot inhale it too much if inhale them in

smaller amounts will start to feel dc

so it has an anaesthetic effect and what is more damaging

is if we get continuously if we inhale a lot of it it can damage our liver and kidney

so because

in the liver chloroform starts to get processed so liver takes care of all these bad compounds that

get into your body

so it will start to process chloroform and start to generate phosgene in in liver and all these byproducts that are formed they can also ham your kidney

so chloroform

is not something that we should be inhaling it is also oxidized by air in the presence of light
so if there is light present
so you know this carbon chlorine bonds can break because they we have seen that before that carbon chlorine bonds are weak so sometimes they get broken if energy is provided in the form of light
so if there is oxygen and air present then chloroform would break down into a compound that is called phosgene
so it would show the structure of phosgene here
so chloroform would break break down into phosgene and phosgene is an extremely toxic compound
so if you inhale toxic uh phosgene death is a sure thing if you if we inhale them in larger amounts so chloroform itself is harmful but phosgene is toxic by its just not harmful it is toxic but it has a nice smell it has a smell that is similar to the fruit sapota if you know chikku that is called in hindi
so this ah this has a very pleasant smell but it is an extremely toxic compound
so we should be very careful while handling chloroform
so therefore chloroform is not normally kept in a bottle half filled because if you take a bottle and fill chloroform to the half the remaining half is air
so now if this is subjected to this is exposed to light then phosgene generates and phosgene is a gas so therefore whoever opens the bottle would actually get exposed to phosphine
so therefore normally chloroform is always kept in dark colored bottles and as much as possible we fill it to the top
so that there is no air present to react with chlorophyll now the third compound i will talk about is triiodo methane
so this is similar to chloroform the chlorine is replaced with iodine
so it is CHI_3 iodo form was earlier used as a source of iodine
so an iodine is known to have a very good effect because it can kill a lot of microorganisms
so it is used for healing wounds
and
so on
so it was used as an antiseptic the reason why it was being used even without knowing
people used to apply iodo form and hydrophane when exposed when exposed generates iodine
so it was actually iodine that was acting as the antiseptic
so when later on on realizing that it is just iodine that is doing it now ah iodo form is replaced with other compounds but earlier it was used as an antiseptic now the next compound we will talk about is tetrachloromethane CCl_4 or carbon tetrachloride carbon attached to four

chlorine atoms this is uh
used for the preparation of a lot of refrigerants and because it can be used
for making freon that
i have already talked to you about and they can also be used as propellants it
has a boiling
point of around 75
so it can be used also and it it gives you vapors now the problem with
carbon
tetrachloride is it is not advisable to use them not even as much as
chloroform or dichloromethane
because it is known to cause damage to nerve cells and it can also cause liver
cancer in humans so
it might cause depending on the level of exposure it may cause liver cancer
so therefore carbon
tetrachloride we have to be extremely careful with and another problem is
carbon tetrachloride if it
is released into the atmosphere it just moves up and reaches to the top and
interacts with the
ozone layer and then it depletes the ozone layer through a free radical
reaction where the
carbon chlorine bond breaks and the radical formed ah would start to react
with the ozone thereby
depleting ozone and thus causing problem okay now um
so we saw for we have been saying
that chloroform and carbon tetrachloride can be used for making freons
so this freons are as i
have told you once they are compounds that are linked to fluorine and chlorine
so they can
also be called as chlorofluorocarbon compounds
so these are compounds where a carbon atom is
attached to chlorine and fluorine and may be additional carbon carbon bonds
they are stable
these compounds are extremely stable they are unreactive they do not normally
react they are
non corrosive they do not cause any corrosion by themselves and they are gases
but they can
easily be liquefied because they are higher the high density gases
so they can be liquefied
by applying pressure now freon 12 or CCl_2F_2 is one of the most used in
industries and it is
prepared by you from carbon tetrachloride using swartz reaction
so swartz reaction is something we
learned the length and whenever we have to make a fluoroalkyne we take a
chloro alkane or a bromo
alkene and treat with silver silver fluoride or cobalt fluoride and
so on certain metal fluorides
which would then precipitate a metal chloride or a metal bromide and form this
carbon fluorine
bonds
so the swartz reaction is used for making freons from compounds that have
carbon chlorine
bonds now they again are used as aerosol propellant propellants refrigerants and
for air conditions
and

so on freons just like ah carbon tetrachloride are one of the major causes of the depletion of ozone layer because freons would again move up the atmosphere reach where the ozone layer is and then in those zone once it reaches there it would start to react with ozone through free radical that are generated from these freons and therefore ah deplete the ozone layer which would result in ultraviolet radiations coming through the atmosphere into earth and would affect all the living organisms because we cannot be exposed to ultraviolet radiations

so this is one

of the disadvantages of using freon

so no matter how we carefully we use crayons at some point of time they are going to be released into the atmosphere and finally they are going to result in the depletion of phoson layer

so this is something and that we should take care and try to avoid the use of friends with other refrigerants refrigerants for example where the use of these

harmful chemicals can be avoided the last compound last poly halogen compound that i would talk

about is probably the most talked about talked about among all the poly halogen commons this is ddt

so the structure of ddt is given here so you can see the structure of tdt in this slide so

this has a trichloromethyl group and there is a ch there is another carbon

so this is trichloroethane

and the second carbon atom is attached to two benzene rings which are substituted with chlorine atom

so ah one of the ways of naming it is p p prime that means para para prime di chlorophenyl

trichloroetane

so we have ah chlorophenyl groups two of them

so that is we say dichlorophenyl and

then trichloroethane

so this this part of the molecule is trichloroital part

so this is ddt so

ddt was known for a long time but in the 1930s it there was a scientist called paul hermann muller

who found out that this particular compound has can kill a lot of insect it can kill a number of arthropods

so suddenly this started to be used as an insecticide it was started to be used as a pesticide in agriculture in households people started to use this and

so on and this discovery was

so important at that point because there were various diseases that were spreading through the human population by way of insects

so it included diseases like malaria which is spread by mosquito

so that is one of the examples
so in order to prevent the
spread of these diseases these diseases people started to use ddt in larger
amounts and started
spreading them
so it was at that time such a find it was such a useful compound that mueller
got
nobel prize in 1948 for finding the biological finding the application of ddt
so it was talked
about
so much and its use was
so much that people started to use it but there was a problem
associated with ddt the ddt once it goes into the environment it does not get
disintegrated so
therefore what happens is once it is sprayed in a field in an agricultural
field or something
it just gets washed down into the water bodies and every fish and other
animals that are
living in the water body would start to consume ah compounds or constitu would
get affected
by ddd or they will go into the body of these animals from water and after
sometime these fish
will be consumed by bigger animals such as beds for example and then ddt gets
into the body
of birds
so a bed will be consuming very large number of fishes and because ddt does
not get
out of the body or does not get disintegrated therefore the amount of ddt
present in the animal
gets increased over a period of time and this results in various problems
so for beds one of the
big issues was that the egg shells of many beds including eagles pelicans and
so on
so they
started to become extremely weaker and crumbled and therefore the eggs were
never hatching
so this
resulted in a lot of issues and by 1960s people started to realize that use of
ddt has to be
avoided somehow
so there was a big protest against the production and use of tdt therefore by
1972
dd2 ddt was banned from agricultural applications in u.
s and in 1973 the government approved that
this decision is good and from 1973 onwards u.
s in the united states of america did it is not
being used however they continued to produce it until 1986 they were producing
ddt and selling it
to other countries and countries including india are still using ddt and right
now india is
the only country that produces dtt
so even china has stopped producing it now but india
still produces ddt the harmful effects of ddt are known but still it is sad
thing that we are

using it because it is an effective insecticide so any other replacement of ddt with other compounds are expensive

so that is one of the reasons why ddt is continuing to be used but this is something that has to be avoided if possible

so so

so in short whenever we talk about poly halogen compound gdt is something that we cannot ignore

so so that is a poly halogen compound

that had a lot of application which people start stop to apply and now we are we have to

reach a phase where we stop using ddt completely

so this is all about this particular unit

so in

this unit we have discussed the reactions of halo alkynes and halo alkenes arranged in detail and you would

know that the various topics that we covered

so we started off this unit by discussing about some

very much biologically active compounds that fall into this category at that time itself i have told

you that poly halogen compounds are harmful

so we have now seen some of the examples and you know

despite having certain applications they are still harmful

so they can they have to be used

with care then we went ahead and we discussed about the classifications of halo alkanes and

halo alkenes the simplest classification was as mono halogenated or poly halogenated compounds and

so on then we discussed about the methods

of preparing them alkyl halides or haloalkanes are prepared largely from the alcohols by using either hcl or you can use phosphorus trihalides or

phosphorus oxychloride

and the best method to make chlorides chloroalkynes from alkyl halides is by using tiny

chloride

so because the byproducts that was formed are gaseous halo alkenes are prepared mostly

by using electrophilic aromatic substitution and also by way of sandman reaction which

we have seen while most of the synthesis of these compounds would rely on the synthesis of

chlorinated and brominated compounds fluorinated and iodinated compounds

so fluoro or fluoro and

iodo organo compounds are generally prepared by doing halogen exchange then we went ahead and

talked about the properties of these molecules their physical properties they generally have

higher boiling points than their hydrocarbons they are dense most of the poly halogenated

compounds are denser than water however their solubility in water is very less so

these are the main points that we discussed then ah coming to the chemical properties or

reactivities of alkyl halides alkyl halides have three major reactions the

most important
one is nucleophilic substitution reactions then the second one is elimination
reactions
of halo alkenes which gives you alkenes and finally the reaction of halo
alkanes with metals
where grignard reagent was one of the very useful reagent that we could
prepare by making a carbon
magnesium bond
so we talked about that and you in later units you would see that grignard
reagent
is used in organic synthesis for making very many number of compounds and in
the reactions of
halo arranged which we discussed today we said that nucleophilic substitution
reactions
are possible but under harsh conditions but electrophilic substitution
reactions of halo
arrange are the most commonly discussed one allorance do not have an
elimination reaction
in general because an elimination would require that you put a triple bond in
an aromatic ring
so halo arrange do not give you elimination reaction except for under very
special conditions
and they also do react with metals where but most of the reactions that they
can also form grignard reagents with metal when they are treated with
magnesium
but we mostly discussed the fitting reaction and word fatigue reaction in this
and finally
we talked about poly halogen compounds and we discussed a number of their
applications but
we emphasized on the fact that poly halogenated compounds cannot be used in
larger amounts and
as much as possible their application has to be replaced with certain other
compounds because
they might continue to be in the environment and cause harm to the living
organisms
so that
is the end of this unit thank you very much you