

welcome to iit paal program we will continue the chapter aldehydes ketones and carboxylic acid today first we will talk about the structure of the carbonyl group

so as you can see that carbon is two s two p two hybridized and in carbonyl group carbon is sp^2 hybridized

so in sp^2 hybridization as you can see in the ground state there are two s electron and two p electrons and in the excited states one electron

jumps from s orbital to p orbital and after that hybridization occurs

so each s p two orbital gets one electron and an hybridized p orbital gets one electron

so this s p two orbitals form sigma bonds

whereas the unhybridized p orbitals makes the pi bonds and this pi bonds happens with the oxygen

atom with the p orbital of the oxygen atom where also one electron resides and eventually the

oxygen atom also is sp^2 hybridize

so all these three sigma bonds stay in the one plane and that's why these atoms attach to the carbon atom also are coplanar and this geometry is called

trigonal planar and the pi electron cloud resides above and below the plane

so now we will

discuss about the polarity of the carbonyl group

so in carbonyl group since oxygen is electronegative then carbon there is a delta minus in the oxygen atom and delta plus charge in the carbon atom

so what happens this is done since there is an excess of electrons this oxygen atom is nucleophilic center and it can act as a lewis base and this carbon atom is electrophilic

center and can act as a lewis acid center also there is a dipolar resonance structure

which explains that carbonyl high polarity which explains the high polarity of the carbonyl group now we will talk general procedure for the synthesis of aldehydes and ketones

so do

so first one is the oxidation of alcohols and this oxidation has been extensively discussed in unit 11.

so here the primary alcohols on oxidation gives aldehydes and secondary alcohols and there are variety of reagents which act as oxidizing agents for this kind of oxidation pcc pyridinium chlorochromate and chromium

trioxide in mineral acid or medium acid this is selective reagent for oxidation of alcohol to aldehydes

so that further oxidation

of aldehyde does not happen the second procedure is the dehydrogenation of alcohols

so this is an industrial method and suitable for volatile alcohols and in this process the alcohols are passed

through the silver or copper catalyst

so another important method is the from hydrocarbons and the first method is

the ozonolysis this also has been discussed in unit 13

so in origin analysis what happens an alkene on reductive after treatment with ozone and a

reductive workup gives two carbonyl compounds here you can get depending on the substituents either two aldehydes or two ketones are mixture of aldehydes and ketones do another method is the from alkalines

so here here in alkyne if it is acetylene acetylene only gives acetylene but any other alkyne terminal alkyne or internal alkyne whatever it will give the ketone this also has been discussed i think unit 13 class 12.

so we will discuss some special preparation special preparation of aldehydes and first we will discuss from acyl chloride do this is the name reaction which is Rosenmund reaction and it has been discovered in nineteen eighteen

so here this acid chloride is used which is selectively reduced to aldehyde here barium sulphate is very important because it has a low surface area it reduces the activity of palladium also for do for some reactive acid chloride to reduce

further the activity of palladium some poisons like quinoline quinoline etcetera are used nitriles are very important starting material for the synthesis of aldehyde and ketones we will first discuss the synthesis of aldehydes

so here mild reduction happens with essential to an acyl the iminium ion is formed and which hydrolyzed on hydrolysis gives aldehyde this is the name reaction this

is called Stephen reaction another procedure from nitriles is there the full name of divergent is diisobutyl aluminum hydride and the structure is

so two isobutyl group are attached to the aluminum and there is only single hydrogen

so that's

why it is milder than lithium aluminum hydride but it is stronger than sodium borohydride what will happen if you put one equivalent of divergent to nitriles

so this imine is formed and this on hydrolysis gives the aldehydes this is an important synthesis

because if you have alpha beta unsaturated nitriles this also selectively gives the aldehydes there is no reduction of the double bond esters can also be used for the reduction

using divergent and that also gives aldehydes but under special condition what is the special

condition one equivalent divergent you have to use and toluene is the giant the solvent of choice here because if you use at room temperature then you will get some alcohol

so what happens if you add one equivalent divergent this intermediate forms only one hydride

delivery takes place and this is stable at low temperature and on hydrolysis this compound do

so only on hydrolysis only the aldehyde it forms

because if you excess hydride then this or will come out and then you will get the alcohol

so we will discuss now special preparation of aromatic aldehydes

so methyl benzene can be oxidized to aromatic hydrides and this can be done by two ways first one do um chromium dioxide and acidic canadian mixture

so the first one will discuss first oxidation with chromos chloride

so here what happens if you put methyl benzene like toluene here in presence of carbon

disulphide you get benzaldehyde and what is the mechanism

so this is called in reaction

first step may be in reaction

so in reaction like this the

double bond forms here and then this one and then a c l minus can come there are two possibilities either again

this sequence happens that is the in and two three sigma tropic with another chromoscoride and

then you can get this compound and this on hydrolysis give you earlier

alternatively we can think

that the a c l minus can depotenate this and you can get directly earlier

so either possibility may happen

so chromium dioxide acidic and iodide also a good reagent for the oxidation of methyl benzene to benzene derivatives and the intermediate are believed to be similar like similar like chromoscolide reaction that this

intermediate is formed which on hydrolysis gives aldehyde

so chromium trioxide

in acetic acid in acidic aniodide chromial acetate this forms and this is the active reagent

which reacts and may be similar mechanism like in reaction and rearrangement like previous reaction this happens the second procedure is the to

so here also methyl benzenes are used and chlorine in presence of light benzyl

chloride this is formed and this one hydrolysis the benzyl lead so this is very important this is side chain chlorination if you put chlorine and

any other

lewis acid then the chlorination will happen in the chain

so for selective chlorination

on the methyl group you have to put this uv light and

so that the radical

method the coordination will happen benzenes can also be used for the

synthesis of aromatic androids and there are various methods we

will discuss mainly two methods first one is the gattermann coach

so what is that which in this carbon monoxide and acell is used another method we will

discuss little bit which is called bilsmeier hack here p o c l three d m

so for benzene it is understood

that you have to bring one more carbon atom and this single carbon unit

like pure c 3 or the dmf that takes part in this kind of reaction

so first we

will discuss gatterman koch reaction and here you have to put some catalyst also anhydrous and cl3

so this is friedel cup type reaction and this

is i as i told you previous slide that lewis acid has been used if you want to functionalize

the benzene ring

so here this catalyst helps in the fetal caviar

so what is the mechanism of this

reaction

so carbon monoxide can be drawn like this and then
so this is the active reagent that is generated
from PCl_3 and HCl from carbon monoxide and this then does the fiddle cup
reaction

so fiddle
cup reaction mechanism is that this kind of and then minus h plus will give you
the product next we will discuss vilsmer hack reaction and here the reagents are
 POCl_3 and DMF

so if you mix pure PCl_3 and DMF this species forms and this is the active
reagent which takes parts
in the fiddle cup reaction

so do

so first this have forms and
then iminium ion generated and iminium ion on hydrolysis gives a dent

so we will discuss special preparation of ketones

so first one from nitriles or from acid
chlorides of course also from acid chloride

so earlier we have seen acid chloride can be
synthesized it can be used for the synthesis of aldehydes

so here we will see that acid
chloride will be used for the synthesis of ketones and here like gignet
reagent generally used and with cadmium chloride

so cadmium r two

r two cadmium is the active species here

so what happens first step is the

two r m g x this is gigner reagent b and then acid chlorides do

so this r two cadmium then reacts with

the acid chloride and r2 cadmium is milder than gigna reagent

so that it stays in the ketone otherwise

otherwise tertiary alcohol if you treat it as it chloride with gigna reagent
you get tertiary alcohol and earlier i told that nitriles can
be used also for the synthesis of ketones

so we will discuss now and here always you need another r another
group like r here also nitro

so you have to bring another group like r and that can

be ignored and it can get the ketones and this is here ketamine

so earlier

aldemine was formed now it is ketamine

so ketamine is formed and ketamine

on hydrolysis gives ketones and last one we will discuss that is from benzene

so from benzene we have

previously seen synthesis of earlier its benzaldehydes or aromatic
aldehydes now we will see synthesis of ketones

so for the synthesis of ketones you can

do fiddle cave reaction with acid chloride it can be aliphatic acid chloride or
or aromatic acid chloride and in presence of catalyst
anidas aluminum chloride you get the ketone

so this is friedel craft reactions

so this is a powerful reaction to get different aromatic compounds and now we
will conclude here the synthesis part you