

welcome you all to iit paul in this problem solving session we will cover concept based problems of aldehydes ketones and carboxylic acids as all of you know well aldehydes ketones and carboxylic acids or important class of compounds they find broad utilities in synthetic chemistry we will try to cover most of the problems with the preparation and reactions of aldehydes and ketones and carboxylic acids so let us begin with reaction of compound a with ozone followed by zinc and water produces x and y both x and y show positive iodoform test while only x shows positive tolerance and helix test identify a comma x and y from this molecular formula you can understand it is an alkene since it splits with $C_n H_{2n}$ general formula now let us look at the properties of the products both x and y show positive haloform test that means both compounds have methyl group which is bonded with a carbonyl group in addition compound x shows positive iodoform test and filling stress that means it is an aldehyde once if we know the structure of x then we can try to write the structure of y already we know that it has a methyl group which is bonded with a carbonyl group we have to add the remain three carbon atoms this will be the y from these two compounds now you can try to write the structure of olefin as is the structure of alkene before going to the next problem let us look at the mechanism of this transformation was analysis is an important transformation organic synthesis when you have the alkene which can undergo one comma three cycle addition with ozone to produce a cyclic intermediate which is not stable which undergoes retro one comma three cycle addition to produce a mixture of carbonyl and carbonyl oxide this can undergo one comma three cycle addition as this can be written you will be able to austenite once you form this one this depends upon the reaction conditions you can convert into carbonyl compound in this reaction when you use zinc in water it can reduce austenite into aldehyde in this case when you zinc in water zinc will be converted into zinc oxide and this will be reduced into aldehyde in place of zinc you can also use dimethyl sulfide which will be oxidized to dimethyl sulfoxide and you will be able to get aldehyde you can also use hydrogen peroxide when it will be converted into formic acid by oxidative cleavage so when you have alkene which can undergo one comma three cycle addition to give this intermediate which is not stable this can undergo retro one comma three cycle addition to give this carbonyl derivatives once we have this one this can under further reaction to give the volcanite that can be converted into carbonyl compound using zinc in water or dimethyl sulphide or hydrogen peroxide to produce aldehyde ketone and carboxylic acid with respect to halo form test whenever you

have

a methyl group which is bonded with a carbonyl group this can be oxidized to carboxylic

acid when you react with sodium hypo halide it will be converted into halo form and copper slick acid respect to tolerance and fillings

test tolerance reagent can be made from aqueous silver nitrate sodium hydroxide and ammonium hydroxide solution when

you mix all and you will be able to form this complex once you have this one when you react with the aldehyde and it will be oxidized to carboxylic acid

for example when you react with acetaldehyde it will be oxidized to acetic acid and silver one will be reduced to zero zero

so you

have to use two equivalent of tolerance reagent the silver one will be reduced

to zero zero this often we use to find out the presence of functional group in the molecule this is we use for the determination of already functional group

similarly we can also use fillings reagent this is made from copper sulphate solution and sodium potassium

salt of tartaric acid and you will be able to form a copper 2 complex when you

react to this copper 2 complex with aldehyde it can oxidize to carboxylic acid then copper 2 will be reduced to copper 1 as red from precipitate here also you have to use two

equivalent of copper to complex it can be converted into copper one oxide these are the common test used to find out the already functional group

now let us move to the next problem on increasing order of reactivity of the following sets of carbonyl compounds towards

a nucleophile is if you look at here there are two sets of carbonyl compounds first one involves

benzaldehyde and substituted benzaldehydes we have to find out the electrophilicity of the already functional group if you look at here

you have the methyl group at the para position here you have the nitro group as all of you know

very well methyl group can donate electron to the aromatic system it can reduce the electrophilicity

of the carbonyl group the other hand nitro group is an electron withdrawing substituent

it can pull electron from the oled group therefore if you compare the electrophilicity of the carbon

group of benzaldehyde the electrophilicity of this already is reduced because due to the

electron donating ability of the methyl group therefore one will be more electrophilic

comparing to two now let us look at benzaldehyde and four nitrobenzaldehyde this

is more electrophilic because of the electron withdrawing nature of the nitro group therefore

this will be more electrophilic in nature

so this is the order of the electrophilicity of the earlier functional group in this molecules

so when you look at the reactivity of the nucleophile as a lot of you know nucleophile will be more reactive towards the more electrophilic nature therefore the order of the reactivity of

nucleophiles toward
 this carbonyl compound will be same and this aldehyde three since is more
 electrophilic
 comparing these two will be more reactive then benzaldehyde will be more
 reactive the least
 reactive will be the four methyl benzaldehyde this is the order of the
 reactivity
 of these aldehydes towards nucleophile now let us look at these
 aliphatic carbonyl compound if you compare the electrophilicity
 of this carbonyl group with this one and you have here hydrogen
 here hydrogen has been replaced with methyl group which can give more electron
 density
 towards the carbonyl carbon therefore the electrophilicity of this carbonyl
 carbon is
 reduced comparing to this carbon of aldehyde now if you compare the
 electrophilicity of this carbonyl group with this
 one and this methoxy group is can give more electron density compared to
 methyl group therefore electrophilicity of this carbonyl is further reduced
 compared to that
 so if you see the electrophilicity of the carbonyl group it will be this order
 austral radius this
 carbon is more electrophilic comparing to this keto carbonyl group which is
 more electrically
 comparing to this carbonyl group of the ester molecule therefore the
 reactivity of the
 nucleophile towards this carbonyl compound will be as follows all really will
 be more
 reactive comparing to the keto group which is more reactive comparing the
 ester group now let us move to the next problem hydrogenation of compound a
 having
 molecular formula C_7H_5OCl using K produces l molecular formula C_7H_6O compound
 a with dimethylcadmium gives m that shows a
 positive haloform test identify a k , l and m if you look at compound a with a
 dimethyl
 cation gives m that associate phosphate haloform test that means it has a
 methyl group
 that methyl group is bonded with a carbonyl group from that easily you can find
 out the
 structure of compound a as benzyl chloride when you have a benzyl
 chloride when you react with dimethyl cadmium you will be able to form
 acetophenone you need here θ .
 5 equivalent of dimethylcadmium
 and cadmium will which will be converted into cadmium chloride is mild reagent
 it will
 not react further with this acetophenone now we can find out the structure
 of l as benzaldehyde when you do hydrogenation using palladium
 in perium sulphate it will be reduced into aldehyde this is known as cross and
 one reduction when you have the aryl or heteroaryl acid chloride you can try to
 do
 hydrogenation using palladium which is supported in barium sulphate this
 is very crucial look at the reaction pathway palladium zero undergoes
 oxidative
 addition with this acid chloride this palladium two intermediate which
 undergoes reaction with hydrogen that undergoes reductive elimination to give

aldehyde to complete the catalyst cycle if you look at here it involves a partial reduction of acid chlorate aldehyde you have to try to remember the palladium should be supported ferri sulfate then you can carry out the hydrogenation reaction to give the earlier as the product now let us look at the next example

increasing order of the acidity of the following carboxylic acids is there are two sets of carboxylic acids first one involves benzoic acid and its derivatives you look at these coposic acids as just we have seen the electrophilicity of aldehydes here benzoic acid has a methyl substituent here it has a nitro substituent at fourth position as we have seen earlier the methyl group can give electron to the aromatic system in other words it can reduce the acidity of this carboxylic acid on the other hand nitro group can pull electron from the system due to electron withdrawing nature of the nitro group therefore the acidity of this capacity acid will be higher compared to benzoic acid if you compare the acidity of benzoic acid with this four methyl benzoic acid this will be less acidic because the methyl group can give electron density to the capacity acid through aromatic ring so the order of acidity of these carboxylic acids will be as follows three will be more acidic comparing to one which will be more acidic comparing to true now let us look at the aliphatic capacity acid fluoroacetic acid chloroacetic acid and bromoacetic acid and if you see the electron withdrawing nature of floral substituent is greater compared to chloro substituent which is more comparing to bromo substituent therefore the acidity of the carboxylic acids will be in this order the fluoroacetic acid will be more acidic comparing to chloroacetic acid which will be more acidic comparing to bromoacetic acid due to the electron withdrawing nature of the halogen substituent now let us look at a series of reactions the first one involves the reaction of toluene with chromal chloride we have to find out the intermediate so when you react to toluene with chromal chloride and you will form this chromium complex this when you do hydrolysis it will be converted into aldehyde this is known as Fries reaction so aldehyde can undergo reaction with amine here you have two kind of NH_2 one is bonded with the carbonyl group another one is with nitrogen if you look at this is more nucleophilic comparing to this energy because this is bonded with this carbonyl group it can undergo addition followed by dehydration to give this compound chemoselectively this more nucleophilic NH_2 can undergo addition followed by dehydration to give this imine derivatives

and if you look at here this involves in reaction now this can undergo two comma three

sigma traffic rearrangement to give

so it can under further reaction with another

equivalent of chromal chloride to give this chromium complex once we have this one which can

undo hydrolysis to give aldehyde this all the air can be further reacted with this amine

to give these immune derivatives similarly taurine also can be reacted with acetic anhydride

the presence of chromium peroxide to give benzene diastate this can be hydrolyzed to

give benzalder as the product the next example involves

coordination of the benzene c h bond chlorine to preserve light can undergo homolytic cleavage to give chlorine radical which can undergo reaction

with benzene c h bond to give benzoyl chloride when you reflex with the water it can

convert into all together as the product see a substitution reaction when you have the chlorine radical it can react with the benzene ch bond

to give the benzyl radical which can react with another chlorine

radical to give the benzyl chloride similarly this can further react with

another radical you will be able to form the benzyl chloride once you form this one which when you react with water and reflects and you will be able

to form benzaleta as the product here the transformation of benzene to

austrophenone and benzyl it is given this can be accomplished using carbon monoxide and hydrochloric acid in

the presence of copper one chloride and anhydrous aluminum chloride this is known as gattermann coach reaction in this reaction the copper chloride

helps to form formal chloride carbon monoxide reacts with hydrochloric acid

the presence of copper one chloride to give the thermal chloride once you form this one this can

react with anhydrous aluminum chloride to give gasoline carbocation which access electrophile

which can undergo reaction with the aromatic ring through aromatic electrophilic

substitution to give benzolide as the product similarly here you can try to react with

acetyl chloride in the presence of anhydrous aluminium chloride and you will be able to form austrophenol as a product this is known as friedel crops reaction

fidel crops oscillation reaction whenever you have the acid

chloride when you try to react with lewis acid like anhydrous aluminum chloride you

will be able to form the acetylene carbocation which can undergo aromatic electrically

substitution to give ketone as a product the next example involves the transformation

of nityl to ketone and aldehyde nitel can be converted to aldehyde by two step process when you react with thin chloride the presence of hcl you will be

able to form immune intermediate thin chloride will be converted

into thin tetrachloride once you form this one this can be

converted into aldehyde by hydrolysis this is known as stevens reaction

so whenever you have a nitrile that can

be reduced to amine that immune can be hydrolyzed to aldehyde which is known as stevens

reaction in place of tin chloride you can also use diisobutyl aluminum hydride for example when you react with the nitrile you will be able to form the imine complex this when you do hydrolysis you will be able to produce the aldehyde as the product either way using tin chloride and hcl or dye ball

you can try to reduce the nitrile to amine complex that can be further hydrolyzed

to give all the air as a product on the other hand when you react with the grignard reagent here when you react with methyl magnesium bromide it can undergo addition

reaction with the nitrile group to produce this imine derivatives which when you treat with water it will be converted into ketone

so nitrile can be transformed to ketone by

reacting with rear region followed by hydrolysis on the other hand you can reduce the

nitrile to amine using dibol or tin chloride that imine can be hydrolyzed to aldehyde now let us look at this example where you have the copper like acid as well as the ester group if you look at this compound it has a chiral center the chiral center is intact the copper acid is selectively reduced

so this can be accomplished using diborane when you use a diborane it can selectively reduce

carboxylic acid without affecting the ester group we use other radiation like lithium

aluminumized it can reduce both carboxylic acid and ester here for your selective reduction of this copper like acid without

affecting the ester group you can use the diborane this can reduce the carboxylic acid to alcohol once we have this one this can be

reacted intramolecularly with ester group to give this lactone as a product this is an example for the chemoselective

reduction acid can be selectively reduced in the presence ester using diborane as a

reducing agent once you form this alcohol which can be intramolecularly cyclized to give

this lactone in the process of acid under heating the next example involves the reduction of ketone to alkane the acetophenone is reduced into ethyl benzene which has been

further oxidized to benzoic acid the benzoic acid also can be produced from bromobenzene we have to find out the suitable reagents for this transformations ketone or carbonyl compound can be

readily reduced into hydrocarbon by Clemmensen reduction using zinc amalgam in the presence of hcl that can reduce

aldehyde and ketone into hydrocarbon which is known as Clemmensen and reduction alternatively you can also reduce

the ketone into hydrocarbon using Wolff-Kishner reduction which involves reaction with hydrazine to give

hydrozone once you form the hydrozone this can be further reacted with potassium hydroxide and ethylene glycol at high temperature which can convert into hydrocarbon these two methods are used to convert

ketone to hydrocarbon once we have this ethyl benzene this can be oxidized to benzoic acid this

can be accomplished using potassium permanganate the pressure base whenever you have the benzylic ch bond those alkyl benzenes can be converted into benzoic acid irrespective of the alkyl substituent it can be methyl ethyl isopropyl

once we have the benzylic ch bond this can be converted into benzoic acid the benzoic acid also can be produced from bromobenzene it involves two step reaction first you have to react with magnesium to give grignard reagent once you form this one you can try to react with carbon dioxide which can undergo addition reaction to give the salt when you treat with proton source and you will be able to form benzoic as the product here the oxidation of alcohol to aldehyde and the carboxylic acid is shown primary alcohol can be selectively oxidized to aldehyde using pcc the structure of pcc is when you take one is to one mixture of chromium dioxide period in CS_2 they can form this salt orange color salt which is less reactive it can selectively oxidize alcohol to aldehyde this reaction can be carried out at room temperature and dichloromethane solvent it doesn't oxidize all the air to copper silica acid on the other hand when you take carbon dioxide in sulphuric acid which is known as jones reagent it will oxidize the alcohol to aldehyde the aldehyde will be further converted into carboxylic acid this because chromium dioxide is more reactive compared to the salt here the protein complex makes this chromium dioxide is less electrophilic less reactive it stops the earlier stage on the other hand when you take chromium dioxide and sulfuric acid the oil that is formed undergoes reaction to hemiacetal or acetal that further reacts with chromatrioxide to give copper slick acid the product this reaction carried out the aqueous tone so depends upon the reagent you can selectively oxidize primary alcohol to aldehyde or carboxylic acid there are several methods are available this one of the common method we use for the oxidation of alcohol to aldehyde and carboxylic acid here the reaction of aldehyde with the concentrated sodium hydroxide is shown whenever you have the aldehyde it doesn't have the alpha hydrogen atom for example this has a alpha hydrogen atom this can undergo aldol reaction on the other hand when the aldehyde doesn't have the alpha hydrogen atom like formaldehyde or benzaldehyde these aldehydes when you react with strong base like sodium hydroxide and potassium hydroxide they can undergo self oxidation and reduction to give a mixture of copper like acid and alcohol which is known as canister or reaction so in this case you have the dialdehyde which can undergo self oxidation reduction to give a mixture of compound the intra molecular reaction can produce this compound in addition to that there will be a intermolecular reaction between two different molecules which can lead to the formation of if you look at the concentration of this compound this will be higher since it is an intra molecular reaction and

this

reaction can be further converted into useful compound for example when you reflux with acid and

you will be able to form lactone as the product when you look at the reaction pathway

for example if you take benzaldehyde and you react with concentrated sodium or potassium hydroxide

you will be able to form the addition compound which can react with another aldehyde you will be able to form a mixture of aldehyde and alcohol as the product

so it undergoes self oxidation and

reduction to give you a mixture of acid and alcohol it happens when the all the air doesn't have the all by hydrogen atom if it has all the hydrogen atom the pressure of acid

or base they can undergo all null condensation we give alpha beta unsaturated carbonyl

compound both all the aldehydes and ketones they can undergo aldol condensation to give

alpha beta and such the carbonyl compounds now let us look at this

dicarboxylic acid with ammonia which can undergo whenever you

have the aromatic oxalic acid they can undergo condensation to give amide this amide when you heat further

it can undergo further reaction to give imide as the product this is an important component

so when you have

this dicarboxylic acid which is known as phthalic acid which when you react with two equivalent

ammonia you form the amide when you heat it it can undergo further reaction to give

the imide as the product now let us look at these reactions here ester is

converted to aldehyde selectively reduced partial reduction doesn't

undergo further reduction to alcohol here the ester is converted into tertiary alcohol

the partial reduction can be carried out using DIBAL just we have seen the reduction of nitrile using DIBAL

so diisobutyl aluminum

hydride can undergo reaction to give this intermediate this can be

carried out in troling solvent at negative temperature this is very important

you have to use toluene as the solvent

so this intermediate when you do work up it

will convert into all the areas of product ester can be reacted with Grignard reagent here when you react with the

excess methyl magnesium bromide two equivalent of methyl magnesium bromide it can

convert into tertiary alcohol first the Grignard reagent undergoes reaction to give ketone as a product once you form this one this can undergo over

another equivalent of methyl magnesium bromide to give the tertiary alcohol

as the product in summary we have seen problems covering ozonolysis Rosenmund Stephen Clementson and old fashioned reductions we also have seen problems

related to a thought experiment

Friedel-Crafts alkylation and regular reactions we have seen the applications of tolerance

Fillings and Jones reagents we also have seen one example for the

chemoselective reduction of copper slick acid in the process of ester using diborane we have seen two sets of compounds to determine the acidity of the carboxylic acids aromatic as well as aliphatic capacity acids in case of aromatic capacity acids the substituent the aromatic ring determine the acidity of the copper slick acids when you have the electron donating group it can reduce the acidity of the copposic acid on the other hand when you have the electron withdrawing group it can enhance the acidity of the copper slick acid similarly when you go for the aliphatic carboxylic acid the electron withdrawing nature of the substituent is crucial if you have the electron withdrawing substituent it can enhance the acidity of the capacity acid similarly it can also affect the electrophilicity of the carbonyl group we have seen two sets of compounds towards reaction with the nucleophiles i hope this lecture will be useful to you with this we conclude thank you very much you