

returning to our discussion on carbon nitrogen bonds or nitrogen containing organic compounds one very important thing i have not yet talked about is the stereochemistry of the compound and stereochemistry plays such an important role in the biological activities that one stereoisomer is found to be medicine the other stereo isomer maybe even poison that sort of biological difference is being observed now if you look about the structure of two compounds where a carbon nitrogen bonds are being shown this is the alpha bond here also the alpha bond the substituents is the beta substituent with a ortho chloro thing this compound if i put a mirror in between these two isomer then what i see the left hand side is the mirror image of the right hand side and if i take it and fix it on the object that is the first one that is not superposing because carbonyl will be on the left hand side and in this case the carbonyl is on the right hand side so the handedness is different so this type of compounds which are non superposable mirror image relationship will be called the enantiomer so one compound having the s ketamine say plus specific rotation the other compound is r ketamine having minus specific rotation or vice versa but one is found to be anaesthetic like s ketamine and look at the biological properties of the other one that is hallucinogen so just by changing the orientation in space one compound is found to have one type of biological activity the other compound the other enantiomer is totally different so stereochemistry control stereochemistry maintaining and to know that absolute stereochemistry is very very important not only the the compound is ah whether will be biologically active or not or if active what type of biological activity it will get another important thing sometimes we ask that all the time people talk about the chirality where carbon is being present as if carbon other than carbon the chirality can not be there it is not correct but again some compounds we find where the chirality is coming from other atoms say nitrogen chirality center if i take a compound where nitrogen having the lone pair of electron tetradel the port is the lone pair of electron stain and three substituents being shown here as a cartoon pink red and green and if the other enantiomer being written again this is the mirror image of that super possible so these two are enantiomer but if we look at the nature of this compound we do not see any sort of

enantiomers getting separated out that is called amine inversion what is that how can one amine could be converted to the other amine very clearly being written this structure is  $sp^3$  hybridized detected three groups are there  $r_1$   $r_2$  or three regular tetrahedron and the fourth substituent is the lone pair of electron so this is getting converted in the transition state to an  $sp^2$  hybridized carbon so  $sp^3$  to  $sp^2$  where the p orbital keeping the electron pair and then it is reverting back either coming back to the starting material or to the other form where the nitrogen lone pair is below the plane so what is happening this is the inversion is taking place so amine inversion is it very slow or very fast very common knowledge says the inversion barrier is only 6 kilo calorie per mole for our alkyl group that is  $r_1$   $r_2$   $r_3$  that would be alkyl they can we convert it from one enantiomer to another enhancement just by putting a simple little energy at six kilo calories so they are in rapid equilibrium so what is the problem problem is you cannot catch one of this enantiomer from this rapid equilibrium thing whenever you want to get one it is getting converted to other so overall thing will be two enantiomers not being separable or resultant thing is racemic so how to convert that this is the inversion barrier is very low another very nice data is ammonia inverse 2 into  $10^{11}$  times per second unbelievable so you cannot get that ammonia substituted ammonia in the chiral form because whenever you are going to get catch 1 it is getting converted to the  $sp^2$  and then to the other form and so that is so rapid equilibrium it is very very difficult unless very low temperature and the energy barrier is being imposed then and only then you can do but there are tricks for other organic molecule having carbon nitrogen that you can do it that is inversion becomes slow when nitrogen is in a strained ring that is three membered ring in that case like ammonia or substituted ammonia that inversion will not be fast but it will be slower why because three member rings mostly sixty degree angle that biased strain as per biostrain theory will be very very strenuous so

to convert it to the  $sp^2$  hybridized form that cannot straight away go to other  $sp^3$  it will have to pass through that another  $sp^2$   $sp^3$  i mean because from  $sp^3$  to  $sp^2$  then  $sp^2$  to  $sp^3$

so these enantiomers of one two dimethyl aziridine where one carbon nitrogen bond is present and three member ring instead of carbon one nitrogen is there the nitrogen is methyl substituted carbon is also methyl substituted another is a free carbon that is having two hydrogen atom

so this type of enantiomer of one two dimethyl aziridines are three member nitrogen containing as one compound nitrogen is numbered as one

so n methyl one position one methyl and two position the next one is the another methyl so enantiomers of one two dimethyl aziridine is very much being obtained

so one way to solve this problem is making some bridge or making a small ring so that the inversion barrier is being imposed and that is why one of the enantiomer could be separated

so that is the trick to get a chiral nitrogen compound

so of course the answer i have already given nitrogen cannot achieve a one twenty degree bond angle as it is in a three member ring sixty degree dihedral angle it will be very very difficult and

so it will be remaining in the chiral form the two enantiomer can be separated

so that is a very nice trick to get the chiral nitrogen compound nitrogen atom is connected to atom which are unshear lone pair of electron like this if i put this picture in this way then what is happening a three membered ring with nitrogen that is a chlorine substitute and in this structure also this methyl methyl this is the thing this is not the chiral center because symmetry is there that is methyl this is also methyl but this is the chiral center where nitrogen having chlorine having c is me and another is the lone pair of electron and another fourth group is  $CH_2$

so all four different groups are there the fourth one is the lone pair of electron

so this is the mirror image of that and this mirror image is not super possible on that so this is a also two pairs of enantiomer which could be obtained which could be separated and which could be used for purposes

so one trick is making small ring then the nitrogen inversion could be stopped but if it is acyclic ammonia derivative very very difficult because the interconversion

is very very fast one more example is here that is strogas base where a benzene ring with carbon nitrogen carbon carbon is there its symmetrical two bench endings and there is a bridge between two nitrogen atom through a methylene group this type of bridge drink structure are very important so triggers basic also could be obtained in a chiral form because here the flipping will not be possible or in other way the interconversion of the normal to the pyramidal nitrogen will not be possible because of the strain in the molecule or bridge in the molecule which the conversion of  $sp^3$  to  $sp^2$  will be stopped another very interesting feature look this thing very carefully if we have a x y bond sometimes x is keeping the negative charge and another resonating form it is coming over here and the one of the bond getting localized or polarized to the y group so negative charge is shifting from x to y or y to x what we call this type of phenomena double headed arrow in resonance so these are two resonating structure in one case x is the nucleophile in other case y is the nucleophile it will be very clear if i if you look at this in this box there are two compounds are there one is our preferred one that is nitrile  $C \equiv N^-$  where carbon is the negative charge that is the nucleophile or  $C = N^-$  that is another pair of electron is with this carbon so that is the nitrogen is the negative charge so when a species having a negative charge not localized but delocalized sometimes with x atom sometimes with the y atom so it can bite as if with several teeth are there to the substrate which is positively charged that is  $C^+$  plus that sort of phenomena or that sort of nucleophiles are called ambident nucleophile ambident nucleophiles we know nucleophiles negatively charged or non bonded electron pair which can donate to the substrate nucleophiles which are more than one generally two or more suitable atoms through which they can attack the substrate they are attacking the substrate means they are attacking the ah positive end of the substrate so negative end should attack to the positive end and how that thing will take place and who will control that whether x will attack or the y will attack and what we call that type of species x y d localized we call it ambident nucleophile and i will show you a very nice example where you can control the attack either by carbon or by nitrogen by changing the environment or putting some catalyst look at this rbr treated with silver cyanide this is very much carbon nitrogen bond related

problem alkyl bromide  
treated with silver cyanide you get a slow process any alkyl bromide methyl  
bromide ethyl bromide  
etcetera treated with silver cyanide a  $\text{C}^{\delta+}$  will form it will form silver  
bromide which  
precipitates out we know the silver nitrate is a good reagent that sort of  
thing will take  
place silver nitrile is silver is monovalent and at the same time the  $\text{C}^{\delta+}$  will  
get  
polarized to  $\text{R}^{\delta+}$  and  $\text{C}^{\delta-}$  fine and this reaction follows very fast  
pathway to  
get  $\text{R}^{\delta+}$   $\text{C}^{\delta-}$  look at this  $\text{C}^{\delta-}$  is being written in the third bracket but the  
product being  
shown that it is  $\text{R}^{\delta+}$   $\text{C}^{\delta-}$  that means the  $\text{R}^{\delta+}$  getting attacked  
by the  $\text{C}^{\delta-}$  through the  
nitrogen not to the carbon that means nitrogen is the attacking species  
whereas just simple change  
the same alkyl bromide when treated with sodium cyanide nation what we see we  
get  $\text{RCN}$   
so this type  
of thing is called nitrile this type of thing is called isonitrile  
so totally two different type of  
mechanism is taking place in this case when we are using silver cyanide we are  
getting one type of  
product which follows substitution nucleophilic unimolecular reaction which is  
being written here  
very clearly as  $\text{S}_{\text{N}}1$  type and in the second case it undergoes a we have  
discussed about the  
substitution nucleophilic bimolecular reaction that is a transition state no  
intermediate gets  
involved  
so it gets  $\text{R}^{\delta+}$   $\text{C}^{\delta-}$  coming in this fashion  
so  $\text{C}^{\delta-}$  is the because whenever cyanide  
is being produced  $\text{C}^{\delta-}$  is the negative end and that carbon attacks to this  $\text{R}^{\delta+}$  and  
you get  $\text{RCN}$   
so there is no question of any isomerization or any stepwise process here it  
is a transition  
state mediated process we know a reaction which goes through transition step  
only is  $\text{S}_{\text{N}}2$  type a  
reaction which goes through an intermediate that means first transition state  
then intermediate  
then second transition state then to the product we call it an  $\text{S}_{\text{N}}1$  type  
so why silver is doing  
that sodium cannot answer is silver plus promotes the formation of  $\text{R}^{\delta+}$  by  
the formation of  
a  $\text{AgX}$  because that rate of reaction is very fast silver reacts with  $\text{X}$  very  
quickly and that  
generate the  $\text{R}^{\delta+}$  whereas sodium cannot do that  
so nucleophile attacks from the site in which it  
has more electronegative atom very clear answer what is that the nucleophile  
is  $\text{C}^{\delta-}$  whether  
 $\text{C}^{\delta-}$  or  $\text{N}^{\delta-}$  that will have to know answer is as silver promotes the  
formation of  
 $\text{R}^{\delta+}$  by the formation of silver halide a  $\text{AgX}$  is being formed  $\text{X}$  has been

taken care of  
 so r plus  
 is there nucleophile attack from the side in which it has more electronegative atom out of carbon and nitrogen which one is more electronegative nitrogen  
 so obviously it is not getting any chance to rearrange  
 so you get rnc is the product think very carefully silver plus promotes the formation of r plus very fast by the formation of silver halide generating the nucleophile to attack normally what is that the more electron negative side should attack first more electronegative out of carbon and nitrogen is nitrogen so nucleophile attacks from the side in which it has more electronegative atom so you get rnc by sn1 mechanism whereas sodium plus does not show such promotion for the formation of r plus because compared to silver sodium plus is very normal it does not take part the precipitation that rapidly so what it does it has a normal sn2 type reaction that is a transition state where carbon because in cyanide n a plus c n minus the negative charge is on carbon now so carbon gets directly attached to r through the transition state like this and you get rcn so very nice take one you can get rcn if you want to get rcn follow sodium cyanide if you want to get rnc follow silver's salt this has been used in number of other cases like rbr silver nitrite hgno2 slow process silver bromide then first process r o n o very very nice that is you know two acting as r o n o we took n o two plus yesterday and we found that n o two could be reacted in way ah o n o so n o two minus is this case where it is an ambident nucleophile it might attack through nitrogen it might attack through oxygen when it is an sn1 case more electronegative atom is attacking the same phenomena same logic when it is a rbr sodium nitrite or potassium nitrite k n o two case then we get a transition state and the product is being obtained as r n not r o r o n o this is r n o two totally different compound by changing the inorganic component from silver to sodium one is following sn1 mechanism another is giving sn2 type mechanism so this is a very nice role of ambident nucleophile ok ah i said about carbon nitrogen single bond carbon nitrogen double bond and very nice case of an ambident nucleophile as carbon nitrogen selectively carbon could be attacked to the substrate that r or nitrogen could be attached to the substrate r now another type of thing very much helpful because how you can convert now amide to amine by hofmann degradation reaction

i mean to a  
mine that i told you if you want to make some amine from nitrile  $R-C\equiv N$  triple  
bonding how  
can you do that basically nitrile is this and amine is  $RCH_2NH_2$  what is  
difference here  
this triple bond has been removed to single bond and two hydrogen being added  
to each carbon and  
the nitrogen atom that means two hydrogen being added to the triple bond to  
convert that  $C\equiv N$   
typical bond  $N$  to  $CH_2NH_2$  that is primary amine or one degree amine  
so that process  
will be called hydrogen addition or reduction  
so reduction of any of these functional groups  
by catalytic hydrogenation or another very good reagent is lithium aluminium  
hydride mixed hydride  
lithium hydride and aluminum hydride  $LiH_3$  and  $LiAlH_4$  together  $LiAlH_4$  that  
yields an amine this  
way if you take an oxygen oxygens are double bonded  $C=O$  group is there oximine  
so it is called oxime  
when you reduce that thing you end up with  $RCH_2NH_2$  that means amines are often  
reduced with  
sodium metal in alcohol that is another reducing agent system sodium alcohol  
potassium alcohol  
that is also being used  
so to make the amine not necessarily you will have to do simple  $S_N2$  type  
reaction you can start from a triple bonded thing follow stepwise reduction or  
one at a time both the  
bonds getting reduced  
so one way is by hydrogen or lithium aluminum hydride another way starting  
from nitrile or oxime you can make primary amine or in this case very nice  
example  $R-C(=O)NHR'$   
double prime amide you can get primary secondary or tertiary amine very nicely  
as per your desired  
as per the substituent  
so another trick or another technique to get the amine from the nitrile is  
by reduction and reducing agents are hydrogen generated in situ or lithium  
aluminium hydride  
sometimes other hydrides could also be used i said about antibiotics and the  
discovery  
of penicillin one of the very simple molecule where carbon nitrogen bond is no  
doubt  
present but again a sulfonyl group is also present these compounds are also  
found to  
have antibacterial property that was the first discovery of the antibacterial  
properties  
of certain compound in nineteen thirty six from the louis pasteur institute in  
paris a  
sulphur neelamite look at this terminology sulfonylamide sulfonyl sulphonyl  
means  $SO_2$  amide  
is  $NH_2$  and in this case there is another amine group in the four position  
sulfonylamide was found  
to be the first sulphur drug there are many use of sulphur drug not only  
antibacterial activity but  
other thing in the following years many thousands of structural variation of

sulphur nilamide were synthesized in the search of additional drugs so this is also a very nice breakthrough in the case of sulphur melamide or sulfonamide thing discovery proto alkaloids i said about some of the alkaloids another very important important alkaloid is mescaline a paid dream that is being used for treatment of coal condition caffeine caffeine is almost every day we use in tea or caffeine that has a very nice structure you can say that right handed the six member ring is peridine type but in the three position there is another nitrogen atom likewise the right hand type is a pyrrole so it is a pyrrole pyridine combined but again in the three position there is another nitrogen so one pyrrole moiety another peridine moiety somewhat different oxidation state this side is the two carbonyl group this is nothing but caffeine caffeine is obtained from tea dust caffeine is found in coffee and many other things and it has ah painkiller activities it has medicinal activities of other type and ah to certain extent it is addictive also so conicin is another alkaloids i have some more structure where the alkaloids have been classified depending on the structural features present like if i ask what type of alkaloid is this one answer should be piped in because pyridine is this when reduced form is bipyridine what type of structure is this that is pyrolytine propane is another nice compound one example i gave you quinoline is a benzo pyridine isoquinoline the nitrogen position is different in quinoline it it was one now it is in two position tetrahydroisoquinoline means one ring is fully reduced that means saturated indole that the thing i told you already indole with another indole making indigo with some substituent of the carbonyl group that is nothing but benzo pyrrole that means a benzene ring and a pyrrolynic that is the five member links are there imidazoles are the building blocks of the proteins or amino acids many compounds that is one and three position there are two nitrogen atom it is a five member ring that is imidazole and purines is one and three position exactly like this that is pyrimidine type thing and one one three that is immediate type thing so pyrimidine imidazole together is giving a very important class of compounds in the building blocks of life many material is purine so all these are nothing but carbon compounds having nitrogen or carbon nitrogen bonds are there ok these are some of the natural sources where

from you can get the alkaloids some pictures are being shown just to get the  
however the coca  
leaves or other things yeah i did not say about another very simple compound  
look at this this is  
a pyridine being attached to a pyrrole very simple nothing else but pyrrole is  
somewhat reduced by  
reduction of the pyrrole moiety what we have got we have got a new chiral  
center it was not there  
if it is pyrrole there is no chiral center the compound is not chiral but when  
you reduce it and  
you get a chiral center and you exclusively that be the hydrogen beta then  
one type of enantiomer  
if hydrogen alpha that will be another type of enantiomer  
so nicotine is a nicotine is also being  
present in all those ah beverages and many ah narcotics activity is also there  
and  
nicotine is very good as a stimulant also these are nothing but again some  
example of carbon  
nitrogen compound that is nitrogen containing organic compounds arycholine in  
methyl but  
there is a substitution in the three position with coochh3 sometimes one thing  
should come to  
your mind and most of the example what we are taking that is pyridine in the  
three position  
there is a substituent why not in the two or four position answer is very  
simple biologically  
or the biosynthetic pathway by which these compounds are being produced they  
follow  
the pyridine three carboxylic acid path that means nature is producing exactly  
in that fashion that  
is why mostly three substituted case in case of pyridine or substituted  
pyridine are the  
natural products but people can synthesize in other position as in this case  
this is the  
two position substituted protein that is called loblin lobeline could also be  
prepared by the  
similar method ok now i will show you some of the interesting reactions of the  
carbon  
nitrogen bond let us take this example if you have and c h 3 c h 2 in h 2 let  
us take this compound as a 1 degree amine one thing is there the next to the  
nitrogen the  
first carbon is called the alpha carbon the second carbon is called the beta  
carbon  
so this is a one  
degree amine because cnh2 that nh2 is three and there is a beta hydrogen being  
present in  
this molecule  
so if you treat with excess of methyl iodide what will be the product  
think you have a beta hydrogen substituted ethylamine treating with excess of  
methyl  
iodide  
so what methyl iodide will do will pick up the lone pair of electron from  
nitrogen and break the carbon iodine bond  
so as a result you get n ch3 one hydrogen getting

expelled out with the help of iodide and then in that way if you do the further methylation you end up with trimethyl alkyl ammonium iodide that means the quaternary salt  $n^+$  and  $i^-$  now one very nice discovery was done by hofmann what is that if this type of compound where a quaternary nitrogen is there counter ion may be halide that is  $br^-$  or iodide minus treated with silver oxide in presence of water you get the tri methyl alkyl ammonium hydroxide fine now this compound when heated then what will happen we mentioned that there is a beta hydrogen present in this compound then it is found that if it is heated with mild base or little bit of in water that picks up this proton that is beta hydrogen and the electron pair forming bond between carbon and hydrogen shifts towards the next carbon as a result the nitrogen which was positively charged have been thrown out of the system so what you get you get an alkene this type of reaction is known as hofmann elimination reaction what is elimination reaction when two groups leave the system at a time their relation may be alpha maybe beta may be gamma or delta for omega that type of reactions will be called elimination reaction what is the driving force here the hydrogen getting picked up by the base and the  $n^+$  plus with three bulky groups or methyl groups is the quaternary salt so that bond will be much more labile or very easy to break so that is one living group and hydrogen is the other leaving group as a process you are getting with the alkene this is an example of hopman elimination reaction cyclohexane methyl trimethyl ammonium hydroxide if you take this example and do an  $o^-$  what will happen again with respect to this  $n^+$  plus this is the alpha carbon this is the beta carbon you can take this side also no problem you get the this is this will be the gamma but when beta hydrogen is present then that will be the preferred one so what it will do it will shift over here and break that carbon nitrogen bond that will be eliminated as dimethyl amine and you get the  $c_6h_{11}$  by double bond  $ch_2$  i think you have seen this type of reaction where an alkene is being produced and then in the difference here compared to the other things what you have seen that you get the alkene mostly in the more substituted position but in this case you are getting the alkene in the less substituted position why this difference this type of products are called hofmann product and the where more substituted alkene is being produced is called the set check product and for hoffman product the  $n^+$

alkyl or cotton

result of n alkyl is very important that is why you have picked up this example over here

so this is a nice way to make the alkene in a less substituted site so this

is a hopman reaction or hopman product now in quaternary ammonium hydroxide that have two

or more non equivalent beta hydrogen look at this what do you mean by non equivalent beta hydrogen

so this example there is a beta hydrogen over here there is another beta hydrogen in this side

so what will be the product how you will be able to identify the product rule is

in quaternary ammonium hydroxide that have two or more non equivalent beta hydrogen non equivalent

beta hydrogen means this is alpha this is beta this is alpha this is also beta so this is one

type hydrogen this is another type hydrogen

so far the example i took earlier there

was only one beta hydrogen as in this case yeah here there is only one beta hydrogen so

there was straight forward no ambiguity was there but when there there are two beta hydrogen

then which one will be the major product you will have to analyze it and to find

out an answer the major product results from abstraction of the more or most acidic beta

hydrogen acidic protons will be very easy to lose because acid is a proton donor

so which proton is

more acidic that will be easy to lift the system if there were be two beta hydrogen as in this

case which one is more acidic that will leave the other one will not leave or if it leaves it

will be less in amount in this case it is very clear that  $\text{CH}_3$  that hydrogen what is happening is

more acidic whereas this more substituted  $\text{CH}_3\text{CH}_3$  is less acidic how did i say that answer is very

simple because these two methyl group donating electron to the carbon

so electron density of

this carbon is getting increased whereas here only three hydrogens are there no methyl groups

are there only one post is from other side that is they are common to that so obviously the electron

density on this carbon will be more than this one and when the electron density is more then

obviously the hydrogen will be less acidic so more acidic hydrogen will be the less substituted

one and you get the major product as this one that is why hopman product the chemistry regio means

region which region the double bond will come in that terminal one less substituted one or the

more substituted one that is with the Swedish product or the Hofmann product in Hoffmann product

again if there be two beta hydrogens which one will be selectively eliminated in the elimination

reaction answer is which one is more acidic because more acidic will be easy to leave

how to know which one is more acidic what sort of other functional group or electron donating or electron withdrawing group is present that you have to calculate and

check and steric factor also comes in the picture in the rescue and it says that this is more acidic

so you get major product as this one I will tell about another interesting feature

right you know one very nice elimination reaction when an alkyl halide say ethyl

bromide being treated with alcoholic alkali ethanolic KOH what is the product you get an elimination reaction if you treat that same alkyl halide with strong alkali what you

get the corresponding alcohol that is an  $S_N2$  type reaction

so in a beta elimination reaction

that is if we take an imine what is that nitrogen oxide look at this transparency essentially

a variation of the Hofmann elimination the Cope starts with a tertiary amine oxide

what is a tertiary amine that is all three two hydrogens and the substituents

are there there is no free hydrogen and when this is being oxidized the lone pair

of electrons of the nitrogen has picked up the two minus

so it is the nitrogen plus or minus

so this

type of compounds are called imine a tertiary imine white tertiary because this nitrogen

all the substituents are there no free hydrogen what it does because of the proximity next to

this carbon that is alpha beta this carbon this carbon having a hydrogen atom

oxygen minus will pick up this hydrogen the carbon hydrogen bond shifts over here and the

carbon nitrogen bond breaks

so it can say it is a Hofmann type reaction Hofmann type elimination

but extra thing is oxygen minus is picking up that hydrogen that acidic hydrogen and making a

almost a cyclic transition state to give a product which is nothing but an alkene and ending

dialkyl hydroxylamine this type of reaction was studied by Cope from his name it is known as Cope

reaction one new terminology you can see here syn elimination what does mean by syn elimination

the hydrogen and nitrogen whatever the groups are they are leaving the system from the same side

that is the syn means from the same side carbon's or if they leave from the opposite side one very

important thing is the two groups what it leaves are anti to each other if it is a cyclic compound it is very anti means opposite and opposite of anti is seen sin means the same

side the two groups are leaving

so that is why this terminology seen is being written over here

so another example is shown that is cyclohexyl methyl dimethylamine oxide two methyl oxide o

minus will pick up the same way the beta hydrogen and the carbon hydrogen bond electron pair

shifts over here the carbon nitrogen bond breaks and you get almost exclusively 98 percent of

methylene cyclohexane

so these are the advantage of the carbon nitrogen bond formation or carbon hydrogen bond breaking to make new compounds over there i will now take you to some of other

interesting case of the carbon nitrogen chemistry let us start with a compound where we have

a structure like this look at this structure benzene with another binding means naphthalene

in the one position there is an oxygen if that be oxygen with hydrogen that is called alphanaphthal

but other than that there is a  $\text{CH}_2\text{CHOHCH}_2\text{NHCH(CH}_3)_2$  a long carbon chain ending with a

isopropyl group

so this compound is found to have a heart stimulant or it is a very good heart stimulator very simple compound if i ask you how one can prepare this

compound because it is a carbon nitrogen compound or nitrogen containing organic compound

how to prepare answer is when you are adding look this part whenever you want to find some way out

it is better to break the molecule in such a way

so that you can make it very easily and

what you see this portion is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  two n h being replaced by n h two so c h

three c h c h three n h two being treated with some compound and i should say n h two is

the negative end

so the some other compound that means some other site where the carbon will be the positively charged this concept making carbon positive nitrogen

negative is from the knowledge from the experience and this is dependent on the latent polarity and

as i told the other day the terminology is for the synthone these are the synthone carbocation

or nitrogen anion these are the synthone

so if that be the synthol what is the synthetic

equivalent what is the starting material answer is simple epoxide is the starting

material this is a very stable compound and another answer is  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  is the second

component

so this is starting material number one this is starting material number

two if we treat them together they should undergo exclusively one type of thing  
you know this type of compound is called epoxide ethylene oxide epoxide  
so epoxide when treated  
with a nucleophile where it can attack it can attack over here and open up  
this carbon oxygen  
bond or it can do the other way around means it can attack to this carbon and  
break this  
carbon oxygen bond which way it will take place solid arrow it will take place  
the broken  
arrow it will not take place how did i know very simple answer whenever this  
type of  
reaction is nothing but a  $S_N2$  type reaction whenever a nucleophile attacks a  
substrate and  
if it is an  $S_N2$  type reaction the leaving group and the nucleophile should be  
in one  
line or  $180^\circ$  degree approach angle this is number one that could happen over  
here also this side also but during the that process you get a transition  
state where almost  
carbon is pentavalent means very much crowded  
so what the nucleophile will prefer for an  $S_N2$   
type reaction a less substituted carbon and if you look very carefully this is  
 $CH_2$  and this is  
only  $CH_2$  that means here there are two hydrogen here there is only one  
hydrogen  
so that is the  
reason the less substituted side will be attacked less substituted side will  
be attacked then you  
end up with this compound then question come how come such a big molecule you  
can prepare answer  
is not big if you break it again you end up with  $O=C-H$  two  $C=C$  double bond  $C-H$   
two from this how  
did i write again cutting the epoxide in this way taking off the oxygen then  
if i ask you  
how can you convert a  $C=C$  double bond  $C-H$  two to an epoxide your answer will  
be  
i have to get an oxygen which is positive  $O^+$  plus because  $C=C$  double bond  $C-H$   
two attacks  
an  $O^+$  plus oxygen which is positively charged what is the source for oxygen  
positively charged  
that is the reagent it may be hydrogen peroxide as simple as that peroxide  
linkage is there or  
it may be one very nice reagent is power acid power acid means a carboxylic acid  
is  
 $COOH$  a per acid peroxide linkages  $OO$  linkage will be there  $COOH$  in this case  
the two oxygen are not equivalent why because one oxygen being attached to  
carbonyl  
another oxygen being attached to hydrogen  
so this type of peroxide linkage is needed for the  
oxidation of an alkene to the epoxide and it is the  $O^+$  plus which gets picked  
up an obvious reason  
will be this oxygen will be picked up and this  $COO^-$  will be converted to the  
 $COO^-$  and  
you end up with the corresponding epoxide

so this is a very general rule that type of phenomena why selectively one oxygen of the hydrogen peroxide or metal chloro per benzoic acid or part benzoic acid or per acetic acid gets picked up the answer is this is the alpha effect nucleophile what is that terminology if two heteroatom in this case oxygen may be with sulphur or nitrogen or other thing being linked together the electron pair forming bond between them are not equally shared the one which gets the lines here is the nucleophile and one which leaves its pair is the electrophile that electrophilic oxygen will be picked up by the electron rich alkene to make it epoxide ok you can look at this and say that this is also very awkward looking molecule how to prepare that not much difficulty as i told you you should break it in such a way so that you can make it very easily i did not break it over there i just broke it over there the idea is the two component in this case will be a naphthalene derivative with a o minus over here and a c h two c h double bond c h two with a plus on that side why i did not put oxygen plus or carbon minus the answer is oxygen is more electronegative so negative charge will be more stable and carbon is more electropositive so put the positive charge on the carbon so what is the these are the synthone what is the synthetic equivalent o minus k plus you can put it and the corresponding ion you can put the bromide ion this is nothing but allyl bromide very standard compound commercially available so when allyl bromide is treated with alpha naphthol the reaction is very simple o minus will attack this carbon throw away the bromine and you get o c h two c h double bond c h two not at all difficult so a simple trick can help to get a complicated structure to be synthesized very easily by this pathway and i will tell you one more interesting feature over here that is if i write a structure like this a benzene ring with a carbonyl in h with another carbonyl and ask you what sort of compound is this one ah we have seen this type of compound that is benzene ring with two carboxylic acid group side by side that is one two dicarboxy benzene or dicarboxylic engine when that is being heated it forms an anhydride and the anhydride being treated with ammonia you get that type of imide so that is called this is again carbon nitrogen bonds are there that is called thalimide p h t h a l i m i d thalimide thalamide is very interesting compound in that sense the gabriel

thalamide

synthesis that we have studied in textbook

so it could be this hydrogen is very much acidic very much acidic with the help of a base or

mild base even you can generate the  $n^-$  and this  $n^-$  can react with many

compounds say one example i right now showed say allyl bromide it could attack over

here and can be connected to that group in  $CH_2=CH-CH_2$

so many compounds in that way could be prepared

by using the thalamide what is the advantage the advantage is this hydrogen is acidic

why because if you take off this hydrogen if you take off this hydrogen the remaining thing that is the conjugate base is nothing but this  $n^- + H^+$  plus one very general rule is which one is stronger acid sometimes you have to

answer say benzoic acid and phenol after the loss of proton from phenyl we get the phenoxide ion we can write three four resonating structure whereas for benzoic

acid after the loss of the proton the benzoit anion we can write two symmetrical resonating

structure that is very important the contribution of symmetrical resonating structures towards

resonance hybrid is maximum and because of that the proton loss will be much easier when

the stability of the conjugate base is more

so that is the reason why benzoic acid is

stronger than phenol likewise this compound will be also stronger acid the reason being

it can have a symmetrical resonating structure where the electrons are getting delocalized on

both side one this ones this carbonyl another to that carbonyl now if i at this stage if i

ask you another very simple question and of course i will give you the answer instead

of these if i write a structure this o that is sulfonyl being attached to  $n^-$  h can you guess the acidity of this proton

or strength of this compound

so far as acid strength is concerned it is unbelievable

because this proton is lost

so easily why because after losing the proton the

remaining portion that is  $SO_2$  this side  $SO_2$  that side the nitrogen atom the having the lone

pair of electron gets delocalized in number of symmetrical resonating structure more the

symmetry both the stability more symmetric resonating structure of anions how this anion is being produced by

the loss of the proton that is the conjugate base conjugate base if a

conjugate base is very stable

obviously the loss of proton will be facile and it will be unbelievable this compound is

found to have an acid strength of 12 normal like concentrated hydrochloric acid and this type

of carbon nitrogen system have been utilized because sulfonyl sulphur having d

orbital it  
can hold the electron for longer time it can be localized and it gets  
stabilized by in in the  
previous case you have two carbonyl now in this case you have  $\text{SO}_2$   $\text{SO}_2$   $\text{SO}_2$   
double bond o bond so  
that is why more symmetrical structure more time to spend the electrons over  
there and more the  
stability more the stability of the conjugate base means stronger acid and one  
important thing is  
what is the most electronegative element known your answer will be fluorine and  
if by any way we can make this type  
of compound very simple one this is doable and people have made it so two s  
o two n f we can take this fluorine this fluorine being attached at this stage  
is  
not electronegative it is almost electropositive i will tell you how if i  
bring some species  
like  $\text{O}^-$   $\text{Li}^+$  that is called enolate what happens this picks up that  
fluorine and  
breaks the fluorine nitrogen bond exactly the way it picked up the hydrogen it  
can pick up  
this protein and the remaining thing is  $\text{SO}_2$   $\text{SO}_2$   $\text{N}^-$  because this is very  
stable  
and as a process we are getting the co and f fluorine being attached  
so this type  
of reaction is called electrophilic unbelievable electrophilic chlorinating  
agent  
or electrophilic chlorination  
so electrophilic proteination is a very offshoot  
or very interesting feature which is coming from the two carbonyl thing being  
extended to  
two sulfonyl pathway  
so this is the acid strength over there ok ah i will tell give  
you some problems what you can do if you are not able to do next time i will  
give you  
the answer predict the product number one if aniline is the substrate treated  
with bromine  
and water what product will you get second problem if thalimide right now i  
wrote that one c  
o c o n minus k plus is the substrate being treated with benzyl bromide c six  
five  $\text{CH}_2\text{Br}$  what will be the product and that product is treated with koh and  
water  
heat what will be the next product third problem if i take a ketone  $\text{COCH}_3$  and  
treat  
with ammonia  $\text{NH}_3$  in presence of followed by hydrogen and nickel and under  
pressure and heat it what will be the product and  
the last one i should say is c triple bond n having these being treated with  
hydrogen nickel  
and heat what will be the product all these things i have discussed during  
this ah two three  
hours lecture of now four hours you should be able to answer if not i will  
give you the answer in  
the next lecture thank you very much and enjoy you