

hi i am professor j k ray of iit kharagpur
for last four lectures i delivered on nitrogen containing organic compounds
and today i am
delivering the last of this five lecture series where some more interesting
features of nitrogen
containing organic compounds will be discussed yesterday or that fourth
lecture i said about a
very interesting type of nucleophilic substitution reaction that is again
being shown here when RBr
means alkyl bromide is treated with silver cyanide we get RNC and when RBr is
treated with sodium
cyanide we get RCN that means in the first case it is the nitrogen acting as a
nucleophile
in the second example it is the carbon of nitrile is acting as a nucleophile
why this
difference that is being written over here and also i explain that capability
of silver plus to
precipitate silver halide is much much better than sodium plus to precipitate
sodium halide so
that helps the more electronegative nitrogen to attack in the first case and
which follows
a mechanism $\text{S}_{\text{N}}1$ and in the second case it is a straight forward no
precipitation of like
the previous one
so it is a two stage process it is a substitution nucleophilic bimolecular
rather one transition state process i will tell little bit about the $\text{S}_{\text{N}}1$ and
 $\text{S}_{\text{N}}2$ reactions
now
so in the second case the transition state for $\text{S}_{\text{N}}2$ reaction look very
carefully that $\text{S}_{\text{N}}2$
is written S capital in subscript and 2 in the same size as that of S
not S_{N}^2
some people write as S_{N}^2 no that is wrong
so it is the abbreviation of substitution
nucleophilic bimolecular $\text{S}_{\text{N}}2$ what it does a nucleophile with the pair of
electron or
the negative charge attacks the substrate and the leaving group that is X and
the
nucleophile enters from the opposite side so leaving group and the nucleophile
making an angle
of hundred and eighty degree
so this type of thing is called back side attack
so what happens the
inversion of configuration is taking place you can see X is on the right hand
side in the substrate
and Y is on the left hand side of the substrate
so this sort of thing is called if the compound
is chiral the plus will be converted to minus and the minus will be converted
to plus
so this is
the $\text{S}_{\text{N}}2$ type reaction and this inversion is called walden inversion or walden
inversion
so inversion
of configuration is a very important phenomena what are nucleophiles

nucleophiles are electronic species which reacts with electron poor species of course electron rich will not prefer electron rich there will be repulsion so it will prefer the electron deficient species what are the nucleophilic substitution one nucleophile replaces another the nucleophile which is being replaced is called the leaving group and the nucleophile which is entering is called the entering nucleophile it occurs when an electron rich species that is the nucleophile reacts with an electron electrophilic saturated carbon atom is attached two times is written to an electro negative group that is very important which we call the leaving group so leaving group is one sense is also when it is living is a nucleophilic type and nucleophile will be much more stronger than the leaving group one so far as the electron density or negativity is concerned nucleophile adds first and leaving group go later does it happen so nucleophile being added so we can see a pentavalent carbon species like this and then the living group leaves and nucleophile enters another possibility is leaving group goes first and nucleophile comes later that means out of these four substituents on the carbon that is the substrate x is leaving first making the carbon as carbocation and then the nucleophile attacks so this is one type of reaction nucleophile attacks and leaving group goes simultaneously that is a very important feature y minus is attacking x minus is leaving this is a concerted or simultaneous process so these are the three possibilities over there what we see we do not see any example where nucleophile adds first and leaving group goes later we see some example where leaving group goes first and nucleophile comes later through the formation of carbocation and this mechanism is called substitution nucleophilic unimolecular abbreviated as S_N1 type now nucleophile attacks and leaving group goes simultaneously that is a concerted process should be classified as S_N2 so i have in brief said about S_N1 and S_N2 type reaction in connection with the carbon nitrogen nucleophile where carbon is attacking in one case nitrogen is attacking in the other case in nitrile two types of discrete mechanisms are there one is a S_N1 already explained substitution nucleophilic unimolecular not first order r_x slow r plus x minus then y minus first r_y so rate will depend only on the slow step that is the concentration of r_x it is the

molecularity is one not the order and S_N2 type is a stands for substitution in
 for nucleophilic two for bimolecular where it is a concerted process the
 concentration of both the nucleophile and the substrate is very important in predicting the
 reaction rate so rate depends on the concentration of both r_x and the y minus
 so S_N2 hydrolysis of bromo methane in aqueous base proceed according to the rate $k [C_2H_5Br] [OH^-]$ let
 us take an example is it so how it happens that C_2H_5Br when treated with OH^- it forms a transition state like this and then it gives a
 product what is happening the bromine has left which has entered both alkyl bromide and weight
 are participating in the rate limiting that is slowest step of the reaction that is why the both
 the substrate and the nucleophiles concentration has been considered in the rate determining
 step we know if there be a multi step reaction the slowest step is the great determining step as it is
 only one step reaction only one transition state so it will go from substrate to the product through the formation of
 an activated complex that is called the transition state which minus becomes partially attached to
 carbon before bromine minus is fully detached so one detached another attach and that happens
 simultaneously energy necessary for breaking carbon bromine bond where from it is coming it
 is supplied by that produced in forming the $C-O$ bond so one bond is broken another bond is made so
 energy being compensated or energy being utilized in that way quantum mechanical calculation
 shows that an approach by OH^- along the line of centers of the carbon bromine bond is
 of the lowest energy that is a very important feature for S_N2 type reaction nucleophile attacks
 by molecular process that depends on both the molecularity of the substrate and the nucleophile
 and the sp^3 hybridized carbon changes in that way nucleophile attacks from behind the carbon
 chlorine bond this is where the sigma star anti bonding orbital of the carbon chlorine bond
 is situated this is a very important picture carbon chlorine bond having two lobes one the
 filled one that is carbon chlorine with the two electrons staying over there but there is
 a tiny lobe on the opposite side that is called anti-bonding lobe with very clearly shown over
 here so this is the anti anti-bonding lobe this is the bonding lobe so bond formation takes
 place from the anti-bonding side and breaking takes place from the bonding side and it is
 some sort of oriented in this fashion

so this is called transient state energy maximum where the carbon is apparently shown as sp² hybridized rate depends on both the molecularity of both concentration of our health halogen in this case and nucleophile and ultimately nucleophile enters from the opposite side of the leaving group and inversion of configuration takes place inversion of configuration is a very characteristic of asymptote type reaction and racemization is a very characteristic of S_N1 type reaction this is the difference what are the reactive intermediates if i take this energy profile diagram where energy being plot with the reaction coordinate reaction coordinate means any many features like time temperature bond distance being a plot so a plus b gives right to a transition state then it comes to a little bit energy minima called intermediate then another transition state and give the product d plus c if this be the energy profile diagram then this c point will be called the reactive intermediate that means it is an intermediate but it is it is also reactive which will combine with the nucleophile to give the second transition state and then the product rate will depend on k_a energy minima is the reactive intermediates thing and we know a plus b when going to this transition state that will be ΔG plus the first one and $\Delta G'$ in the second case is little bit less compared to the first one and the energy difference between the starting material and the product is ΔG zero see S_N1 and U1 reaction mechanism are more or less similar and the radical chain reactions also are of same type now this will be very clear to explain the fact of the bonding orbital say methyl chloride as i showed as i gave you the first example so bonding orbital is this one and this is the antibonding orbital of x so each one have a bonding side and an antibonding side anti-bonding side is smaller inside orbital coefficient because there is no electron but bonding one bigger inside and this is in one phase this is in the opposite phase that is why it is made little bit darker and this is white so when the nucleophile comes the bigger one will overlap with the bigger one or the black will overlap with this black or vital and then what will happen the tiny one on the other side also overlap with the tiny one of the x then what happens field orbital of nucleophile and empty orbital of carbon a halogen bond that is the sigma star orbital there are two orbitals one is

sigma another sigma
star that then it produces a transition state like this where nucleophile is
going and leaving
group is still attached you get a apparently pentavalent type of transition
state
so new sigma
bond being formed old sigma bond being broken and p orbitals of the carbon
atom being shown
in that way and ultimately the substrate has changed to the product when the
reaction is
over nucleophile has enter from the opposite side of the living group
so this is a very good
orbital picture of the sn2 type reaction this is also very clear when which
minus attack the carbon
bromine born bromine is little bigger it is being shown with colour things
carbon bromine s p three
hybridized methyl bromide which minus is attacking again from the tiny side
the overlap is taking
place o is being attached bromine steel attached
so this is the transition state then you get the
product where the inversion of configuration has taken place bromide has left
in normal structure
it is written over here which minus attacking the methyl bromide from the
opposite side of the
bromine inversion of configuration is taking place bromide minus is left out
that is a leaving group
and methyl bromide is now converted to methanol important point in this case
to remember that
inversion of configuration does not mean are going to ace or vice versa some
people have a
concept that always r will be changed to s or s will be changed to r that
happens in maximum
cases but r and s is the abbreviation of rectus and sinister that is absolute
stereochemistries
notation but that is the thing scientist saying that these are the priority
rule you have to
apply
so based on r will not be changed to s s will not be changed to r but one
thing is for
sure inversion of configuration means if the pol from the polarimeter the data
of the substrate
is plus optical active compound substrate the product will be the minus or
vice versa so
that means inversion of configuration means it is an sn2 type reaction and if
it is an
sn1 type reaction there will be racimization ok it is like inversion of an
umbrella in
a storm this is the thing happen this is the cartoon picture umbrella was this
way it has
been converted inverted in the other side
so it is called a balden inversion this is a good example
let us taken chiral carbon all four substituents are there this is in plane
bond this is also in
plane bond that is thiodide iodide is the leaving group c six h thirteen is

one substituent methyl
 second substituent hydrogen third substituent the
 compound is found to have a specific rotation of this
 be plus something now these three groups are being shown in different types of
 bond as I said the normal line means in plane bond broken line means below the plane bond that is
 called alpha bond and thick line means above the plane bond that is beta bond
 so this is the absolute stereochemistry of the starting material when we are treating with iodide because already I is
 here just to differentiate this isotopic iodide is being taken what will happen that will
 act as a nucleophile that will attack to this carbon from the opposite side of I I prime will enter
 or I star will enter and I prime will leave and what will happen as a result the inversion of
 configuration is taking place what is the proof if I put it in the polarimeter we will see
 the I plus has been changed to the specific rotation has changed from plus to minus that is the
 thing I said R normally changes to S S normally changes to R but there are some examples where R
 remaining are S remaining is but plus will always change to minus or minus will always change to plus if
 it is an S_N2 type reaction
 so inversion of configuration means notation that is plus minus two minus or
 minus two plus not necessarily R two S or S two R rate of racemization twice the
 rate of inversion or incorporation
 so reaction profile of S_N2 will be very straightforward initial state transition state final state
 so this is the free energy diagram and very clearly it is energy profile diagram very clearly shown the
 transition state only one transition state and a concerted process for S_N1 the hydrolysis of
 tertiary butyl chloride by base proceed according to the rate where k₁ is t BuCl concentration or
 independent of [OH⁻] minus that means in this case the nucleophile is OH⁻ but its con-
 centration has nothing to do with the rate determining step why because in tertiary butyl chloride it
 is the sp³ hybridized carbon and with the attached with the chlorine chlorine is leaving
 and that will live fast why because three methyl group is quite bulky and moreover it pushes
 electron to the this carbon helping this carbon to release the chlorine very easily and as a result it
 gets converted to the carbocation means positive charge planar though it is shown in this way it
 is planar so what is happening sp³ hybridized thing has changing to sp² hybridized thing
 so this is the slow step and this should be a rate determining step and next what happens H

minus is the nucleophile that will come that might come or attack this carbocation from right hand side and from left hand side with equal ease because it is the flat molecule the attack from top or attack from bottom is of equal rate as a result there will be the plus and minus will be of equal amount and if i mix plus and minus together the resultant thing will be plus minus we call it a racemic that means it is zero rotation in the polarimeter zero rotation in the polarimeter happens in number of other cases if it is not a chiral compound then or if it is a meso compound and third case is of course it is a racemic compound so in S_N1 the racemic mixture will be formed halides undergoes slow ionization to yield the ion pair R^+ plus and Cl^- minus followed by fast attack by H^- minus or solvent or nucleophile to give the substrate the energy necessary to effect always this energy balance is important the energy necessary to affect the initial ionization is largely recovered from the energy evolved through solvation of the resultant ion pair so this is happening in S_N1 type reaction what are the factors which affect the rates of S_N1 and S_N2 reaction the structure of the substrate we found that a methyl halide undergoing S_N2 tertiary butyl halide undergoing S_N1 then what happens the in between substrate concentration and reactivity of nucleophiles are also very important especially for a centro type thing for bimolecular reaction only the effect of solvent is also a determining factor some protic solvents a maprotic solvent that also changes their reaction rate tremendously the nature of living group called nuclear fuse because what type of living group is there is it easy to leave or it is difficult to remove that is also very important factor because the bond strength is the important factor over there and stereo chemical implication of the mechanism as i told you already the inversion of configuration S_N2 racimization is S_N1 say with as i told you the first case methyl bromide without looking at that as carbon being attached to three tiny hydrogen this should be attacked from the opposite side of the carbon bromine bond very easily so it will undergo very facilitation too and the last example where the tertiary butyl bromide is there that is just the opposite effect the attack of the nucleophile from the opposite side of the bromine is very much difficult because of the steric factor and electronic factor

so what it will do it will first release the bromine as bromide minus and it will be converted to carbocation and then it will react with the alcohol and or which minus whatever the nucleophile is to give the product what will happen to ethyl bromide and so isopropyl bromide in the this type of cases ready hydrolysis takes place methyl bromide and tertiary butyl bromide i have explained why more resistance in case of ethyl bromide and isopropyl bromide why look at the data $r \times y$ minus $r y x$ minus and if we follow the reaction mechanism very cleanly we will find that s_n2 rate will be maximum for methyl halide look at the data six into ten to the power three and s_n1 rate is found to be zero point zero zero two almost negligible and the last case where the s_n2 reaction is very slow that is zero point zero zero zero zero five again you can neglect it and the s_n1 rate is four into ten to the power six i explained why and in between thing you see more s_n2 in the ethyl case less s_n1 in the ethyl case and in the isopropyl case it is a 50 50.

both s_n1 and s_n2 mechanism is being operated so in a nucleophilic substitution reaction both when carbon and nitrogen are the nucleophile and using the metal ion we did that by dented or i should say that ambident nucleophilic thing but that reaction follows in one case s_n2 in other case s_n1 and silver is doing a miracle in the first place and sodium is not doing that but it is following a step forward as in one type reaction so now it is clear what are s_n1 and s_n2 type reaction for s_n2 methyl greater than primary greater than secondary very very greater than tertiary which is unreactive position two and for s_n1 just the reverse order tertiary very very greater than secondary secondary greater than primary primary greater than methyl so this order being followed in s_n2 type and s_n1 type reaction i believe this is a ah very good way to explain the substitution nucleophilic bi-molecular or substitution nucleophilic unimolecular reaction now returning back to that carbon nitrogen bonds and its capability i will take up some more example i did at the beginning that how can you introduce a how can you produce a carbon nitrogen bond from a simple benzene ring the answer was by nitration of benzene by mixed acid it is written here when a r h not only benzene or substituted benzene naphthalene etcetera nitration is being done in a mixed acid that is m

a nitric acid and sulfuric acid together what sulfuric acid does it takes off the water from nitric acid generating NO_2 plus and so NO_2 enters and hydrogen leaves so it is an electrophilic substitution reaction you end up with a RN_2^+ and reduction of that a RN_2^+ will give you the amine at i mean and it is a simple case if a r is c six h five it is aniline so aniline may be prepared by reduction of nitrobenzene the overall synthetic sequence begins with nitration of the starting array and then the reduction the reaction may be done in number of ways the dissolving metal reduction of nitrobenzene to aniline these reactions use metals such as iron zinc and tin and typically are carried out at reflux in hydrochloric acid solution sometimes with added acetic acid because acetic acid is a very nice thing it is a not only acidic compound but also it is a good solvent to dissolve both inorganic and the organic part together so a good solvent and acidic in nature so sometimes acetic acid helps to dissolve the aromatic compounds and also it is an acid so pip iron and 30 percent hcl and heat will convert nitrobenzene to the anilinium chloride and anilinium chloride to aniline this is the salt and base being formed by the treatment of H^- in water so i said about the because aniline is a very nice material in that sense from here you can make lot of compounds i gave the list yesterday by digitization and followed by sandmeyer reaction lot of functionality could be introduced over there another example where the nitration of toluene has taken place which gives a mixture of ortho and para let us take the para is being separated it should be sterically more preferred so para nitro toluene when reduced with tin and hydrochloric acid it will form the corresponding ammonium salt like the previous case treatment with H^- and water will give the paratoluidin sometimes catalytic hydrogenation is also good i will give you a very nice example anilines may also be prepared by catalyzed reaction of preform hydrogen with nitro aromatic look at this paranitro ethyl benzoate this side in the fourth position there is a carboxylic esters your to eat ethyl ester ethyl paranite of benzoate if we reduce with hydrogen in impact platinum catalyst in ethanol as the

solvent what will be the product will have to think very carefully there are two groups one is nitro another is carbonyl which one will be reduced selectively that means whose reduction potential is more obviously nitro will be much easier to be reduced and if we use sufficient amount or high pressure then definitely carbonyl will also be reduced to the alcohol but under normal condition it is selectively the nitro group will be reduced to amine keeping the carbonyl intact so this is when two functional groups are there one selectively could be reduced basically the nitro group whose reduction potential is very easy to achieve but hydrogen and platinum could be converted to the amine so this is another way to make carbon nitrogen bond through the nitration followed by reduction that reduction even keeping the other groups which are also reducible intact reductive amines are also very important way to make the carbon nitrogen bond look at this we are starting from simple carbonyl compound aldehydes and ketones can be converted into amines by catalytic or chemical reduction in the presence of ammonia because if you reduce an aldehyde or ketone will get the corresponding alcohol or ketone will give secondary alcohol aldehyde primary alcohol but if we do that reduction in presence of ammonia then what happens you see hydrogen reduction is being done in presence of ammonia we end up with RCH_2NH_2 what is that a primary amine one degree amine R_2NH is there if we do that thing in presence of not ammonia but R_2NH_2 then what we get we get R_2CHNH_2 what is that this is the secondary amine two degree amine and in the third case R_3N and H are three that means we are starting with the substituted amine then we see no hydrogen directly being attached to nitrogen so it is a 3 degree amine or tertiary amine this comparison can alternatively be viewed as reductive alkylation a loop this way starting from ketone through the help of amine we are getting some compound where reduction of the carbon oxygen double bond has taken place of course oxygen has been removed so we can call this process as reductive alkylation so alkylation is taking place in the nitrogen side and reduction of the bond double bond is also taking place so another terminology is reductive alkylation by the help of amine or ammonia and treating with aldehyde or ketone in presence of corresponding reducing agent what is the mechanism of this

reaction we will try to understand because whenever a nucleophile is there an electrophile will be preferred by the nucleophile a mechanism for reductive amination is addition of the amine to the carbonyl you see carbonyl carbon will be positive why because the carbon oxygen double bond will be pulled towards the oxygen atom more so oxygen will be the negative nature this carbon will be positively charged so $\text{H}_2\text{N}-\text{R}$ double prime that is a non bonded electron pair on nitrogen that lone pair will be acting as a nucleophile to attack the carbonyl from the opposite side see when we are talking about primary amine one degree amine or ammonium you will get as a result O^- will pick up the proton from here as O^- and remaining thing is NHR one hydrogen being taken by the O^- and R and R' remaining intact so this type of compounds are similar to hemiacetal it is in this case we should call it hemiamino because it is $\text{C}=\text{N}$ not $\text{C}=\text{O}$ but in $\text{C}=\text{O}$ one H nature then loss of water is taking place how because this hydrogen and this which leaves so there is a this type of things is called a beta elimination reaction this hydrogen leaves the nitrogen hydrogen bond shifted to make a double bond over here and which at the same time leaves so two groups leaves at the same time which are beta to each other is called beta elimination or E2 elimination and we end up with an imine now this if this reduction is carried out with hydrogen and nickel or very nicely agent normally not use that is sodium cyanoborohydride NaBH_3CN sodium cyanoborohydride very selective reducing agent so what it does the reduction of this carbon nitrogen double bond will take place again it is a carbon nitrogen compound and it will get NHR double prime and H that means the hydrogen being added over here the second hydrogen is being added to this nitrogen so two hydrogen atoms being attached in this way so this is whether it is primary one degree or secondary two degree mean you get this sort of thing and if it is a two degree i mean how the reaction is taking place the similar mechanism in this case the nucleophilicity of this nitrogen will be better than this one because there are two alkyl groups in this case one alkyl group but some static factors also come into play so what it will happen it will attack the carbonyl carbon then you get a hemiamino exactly in this fashion now the dehydration will take place not through the loss

of proton because there is no proton over here but it nitrogen having the non bonded electron pair
so it comes over here to make the nitrogen carbon double bond and weight being thrown out
so it will be water loss and $R-C-R'$ will be there and remaining thing is $N-R$ double prime or $N-R$ triple prime and after the reduction what we get we end up with the tertiary amine
so this is the way how the what is the mechanism of the reduction is taking place there some examples are being shown the actual example say benzaldehyde with the starting material instead of arbitrarily any ldi dot ketone did with ammonia with hydrogen and nickel under pressure and heat it what will be the product now you can write straight away following this mechanism NH_3 the lone pair nitrogen attacking over here going $C=O$ is getting polarized to O^- and then this proton is getting picked up by that O^- to make $O-H$ then elimination is taking place followed by reduction of the double bond
so you get carbon nitrogen double bond is reduced you get $C-H$ and H_2 see one step with the help of ammonia hydrogen and a little bit pressure and catalyst you get benzyl i mean so benzaldehyde to benzyl have been if somebody asked how to make it this is the very nice way to make it amination of aldehyde or alkylation of ammonia whatever way you call it say let us take another example two pentanone treated with ammonia in presence of sodium borohydride or sodium cyanoborohydride same thing will happen you get the NH_2 being attached in place of the carbonyl you get two pentane amine why because one two three four five longest hydrocarbon chain it is pentane the minimum sub numbering to the substituent
so it will be two amino or two amino pentane or which is called two pentane amine if cyclohexanone is the starting material and dimethylamine is the base or nucleophile sodium cyanoborohydride is the reagent you end up with a compound like this N,N dimethyl cyclohexane amine
so what we have shown the different types of substrate under condition which follows that amine or ammonia primary secondary or tertiary you can end up with the substrate through from the carbonyl to the carbon nitrogen bond
so this is a very nice way to make carbon nitrogen one one way i said electrophilic substitution in the aromatic system that is nitration followed by reduction and put lot of functional growth even for aliphatic and aromatic both the cases this method is in that way is much

better straight

away from putting two reagents you can get an aldehyde or ketone converted to the corresponding

carbon nitrogen that is CH_2NH_2 type things some more examples are being shown here cyclohexanone from ammonia and hydrogen you can get this amine right now we explain can you do it in other way obviously answer is

we know a very nice reagent we have studied the Beckmann type rearrangement where an oxime getting involved

so how to prepare an oxime from a carbonyl compound to it with hydroxylamine in presence of acid you get a double bonded $\text{N}=\text{O}$

so carbon nitrogen double bond is being produced with weight which could be removed very easily do a sodium ethanol what sodium ethanol will generate

hydrogen this and hydrogen that will convert this $\text{N}=\text{O}$ to $\text{N}-\text{H}$ the double bond will be reduced

and O and H will leave the system making the compound cyclohexylamine

so cyclohexane known to

cyclohexane amine could be done in two ways either ammonia hydrogen nickel or hydroxylamine making it

oxime followed by sodium ethanol now take another nice example two phenyl ethanol nitrile $\text{C}\equiv\text{N}$

$\text{C}\equiv\text{N}$ triple bonding that is triple bonded compound we want to reduce the triple bond to single

bond what should we do we will have to do lot of or sufficient amount of reducing agent that is

hydrogen and nickel at 140°C it is found not only that $\text{C}\equiv\text{N}$ bonding is getting reduced

through the double bond to the single bond that is $\text{CH}_2\text{CH}_2\text{NH}_2$

so it is now a primary or one degree

amine to phenyl ethane ethan amine if it is not an carbonyl compound not and triple bonded compound

or carbon nitrogen triple bonded compound or nitrile if it is a simple chloride C

$\text{O}-\text{C}-\text{Cl}$ acid chloride benzoyl chloride how can you convert this to this $\text{H}_2\text{N}-\text{CH}_2$ obviously you need in that case some amine let us take ethylamine is the reagent

so amine will react with this COCl this lone pair of electron and nitrogen will attack to this carbon $\text{C}-\text{O}$ bond will take place it will be backfired

followed by the loss of chlorine

so chlorine will be eliminated as HCl

so remaining thing is $\text{CO}-\text{NH}_2$

CH_2-CH_3 where the other hydrogen has gone it has picked up the chloride ion to make HCl now this

one when reduced with lithium aluminium hydride in ether very good reducing agent mixed hydride in

water what you get the CO in the similar fashion getting reduced to the CH_2 because it is the

hydrogen addition hydrogen addition is reduction oxygen removal is also reduction

so $\text{C}-\text{H}_2-\text{N}-\text{H}-\text{C}$

two h five is the final product

so this is the way one starting material or one substrate to another substrate we can play with the functional group inter conversions through the knowledge of carbon

nitrogen bond formation carbon nitrogen bond reduction or carbon nitrogen ah triple bond to

single bond or carbon oxygen double bond to carbon nitrogen single bond

so all these things are

being explained with this transparency over here i showed you all these things so

now i will end up with one example ah yesterday that suppose you want to make this is the thing i did not say earlier you want to make an compound which is nr a five member nitrogen containing heterocyclic compound where carbon nitrogen bond

is there

so you can say ah you have seen this type of compound it is nothing but a pyrrole derivative

only difference is instead of n h i have put in r that means alkylate piro if i ask you how can

you prepare this type of compound your answer will be very simple i told you that break the

molecule into simpler component and then you can find out way to make it if we write a things

like this c o c o r let us take r over here what is this compound say r is c h

three c h three c o c h two c h two c o c h three

so this compound can undergo keto in

old type protomerism very easily because it has an alpha carbon atom and any hydrogen being attached

to alpha carbon atom can help to get it enolized this is one second point is if i treat with some

amine or let me put it in this way r n h two now this amine the lone pair of electron can

attack the carbonyl compound to the carbon atom then the electron pair forming the bond

between carbon and oxygen will be shifted towards the oxygen atom and what you see

then in this way we get a very nice thing that o minus has take is being formed and n h h that is a and r is there now the nitrogen is teta

valence

so it should be a positively charged

so this is simple the attack of the

alkyl amine to the carbonyl compound you can say why did i take on the left hand

carbonyl because it is symmetrical if i take the righton it will get the similar compound

no change

so o minus will pick up this hydrogen the electron pair between nitrogen and hydrogen

will shift on nitrogen

so it will be nothing but cor is intact in one end the other side is o h

and this is n h r now there is no charge that has been satisfied and one r is already there

now what will happen very interesting thing this hydrogen and this o h will

leave the system
at a time and it will be eliminated very easily at the same time at the same
time what it can
do the nitrogen lone pair can also attack the carbonyl compound
intramolecularly this is much
energy preferred reaction
so i am jumping a step over here and as a result i can show you that
you end up with ok let me write down no problem r in h if i keep it intact
then there is a new bond
being formed between this nitrogen and the carbon
so what is the thing one two three four five now
if i write that thing that anti elimination has taken place
so the structure of this compound
will be converted to this nitrogen is there r is being attached there is a
double bond in this
side and this side is r and i can put an o h and exactly in a similar fashion
another two
hydrogens are there the anti one will prefer to be eliminated to end up with a
nitrogen r double
bond double bond r and there was an r over here
so you are able to make pyrrole starting from very
simple acyclic compound a diketone in that way i will end up today's thing with
one more nice
case or nice example if the problem is like this a heterocyclic nitrogen
containing compound
and if somebody ask you how can you convert a five member to a six member
compound these
are very known compound this is a pyrrole and this is pyridine as i explained
the other day
pyrrole is acidic in nature pyridine is basic in nature those are all carbon
nitrogen containing
compound and i can say that it is doable what is the difference between this
and that there is one
carbon more in that case and how to add one carbon and then play with that
substituent you
know one reaction i will tell you that if you recapitulate that reaction it
will be very
clear that if you convert the p role to n minus that means the proton of the
pyrrole being
picked up by the base let me put a base like sodium ethoxide we know sodium
ethoxide gets
polarized to o t minus and n a plus
so oet minus will pick up this proton make the nitrogen minus
with the lone pair of electron and the counter ion will be the sodium ion
so pyrrole salt is
being produced with the help of sodium ethoxide and i need one carbon
so how to get one carbon
and that answer is very simple that is the sodium ethoxide itself can help
so in presence
of a very interesting compound called chloroform and aesthetic but interesting
thing is carbon
chlorine bond three carbon chlorine bonds are there and one carbon hydrogen
so if you
treat with sodium methoxide the same reagent what will happen this has done

with the pyrrole this acid base sort of thing but it can do a very nice reaction over here that this negative charge can pick up this proton and then the bond between carbon and hydrogen can shift over carbon now the carbon will be pentavalent it will have to lose one carbon chlorine bond and that will happen and then ultimately what is remaining we get C-Cl and a non-bonded electron pair on this carbon what we call this type of species look at very nice I think definitely we are calling this type of species as carbene a divalent carbon but if I ask what type of nature this carbene possesses is it electrophilic or nucleophilic then you get confused that there is a non-bonded electron pair so it might act as a carbene yes carbene can act as a nucleophile under different conditions but in this particular case if we count the number of electrons around this carbon two pairs of bonded that is two plus two four with two chlorine atoms and the non-bonded electron pair whose spin normally is being opposite this is called the singlet carbon so total number of electrons around the carbon including the non-bonded electron pair is six so its octet is not fulfilled so obviously it will be electrophile or electrophilic so carbon is a very interesting species in that sense it has an unpaired electron but it is mostly under the normal condition is electrophilic in nature and you have studied one reaction for sure you know if I take phenol and treat with chloroform and alkaline CHCl_3 the alkali may be sodium hydroxide or sodium ethoxide what will be the product you know this reaction from memory or from other thing you can say that will end up with ortho hydroxy benzaldehyde and a mixture of para hydroxy benzaldehyde that means this aldehyde group is coming in the ortho and para position because the phenolic hydroxyl group is ortho para orienting and where from this CHO is coming through the formation of this carbene which is an electrophile because electrophilic substitution reaction is facile in case of $\text{C}_6\text{H}_5\text{OH}$ in phenol it is getting activating the ortho and para position so same sort of thing will happen over here but in case of pyrrole what will happen the lone pair of electron now will add to the carbon having the two chlorine group attached so this sort of addition species will be formed and then this lone pair shifts over here and this bond breaks and one of the carbon

chlorine bonds leaves the system as a result what you get you end up with a three chloro period in very nice way
so i have given one synthetic method for pyridine through pyrrole or i have also ah suggested that one five member nitrogen containing heterocyclic compound could be converted to the six member nitrogen containing heterocyclic compound by this way
so in brief carbon nitrogen bond formation carbon nitrogen single double triple all those bonds playing with that bond like nitrile taking the carbon as a nucleophile nitrogen as the nucleophile to get very interesting molecules amides then as i told at the beginning that carbon nitrogen bonds are very much present in living system and almost everyday life we need our life is made up of this carbon nitrogen bonds in many ways
so i believe this five lecture series will help you to understand or to get the gist that without this carbon nitrogen bond people cannot exist because all this amino acid the peptide proteins alkaloids many medicinally important compounds are antibiotics are coming from this carbon nitrogen bond
so beta lactam thank you very much you