Molecular Rearrangements and Reactive Intermediates in Organic Synthesis

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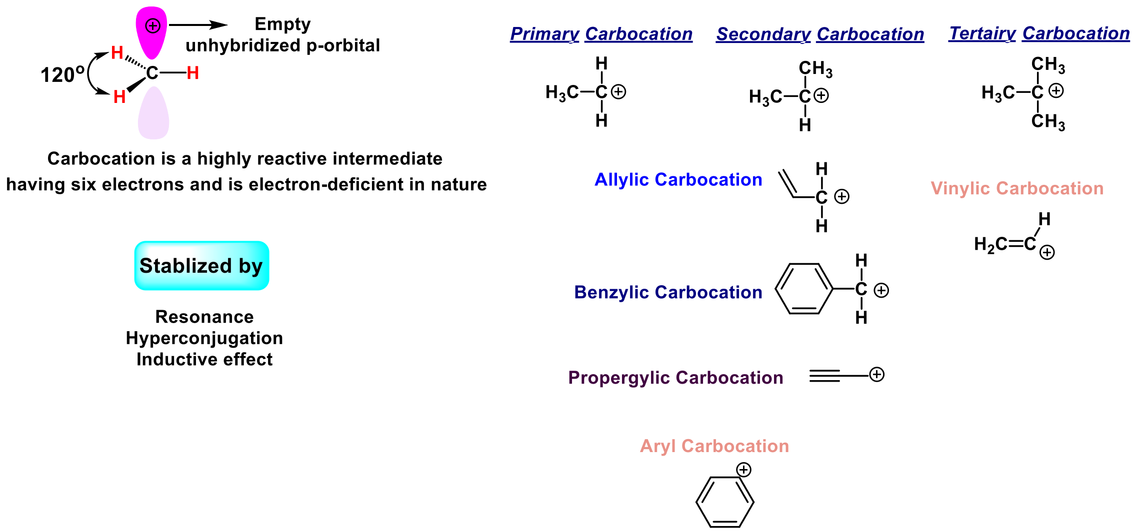
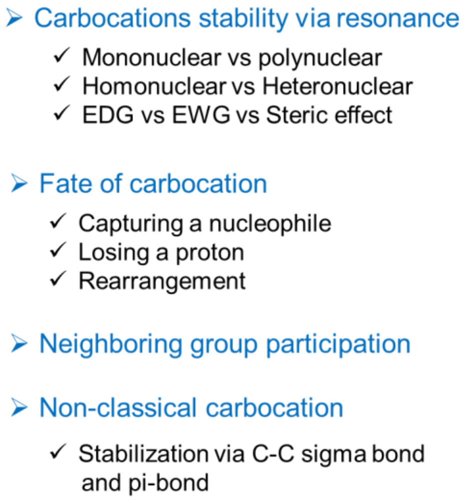
Lecture 02: Carbocation

Welcome you guys, welcome back to the class of the rearrangement and the reactive intermediates. So, I am still going to continue the carbocation, which I started in the last class. So, I started talking about the carbocation in the last class about what are the different types of carbocation and I taught about primary, secondary, and then tertiary and allylic carbocations. I also taught about the benzylic carbocations and then also I spent some time about talking their stability. So, if you compare them like allylic vs. tertiary vs. secondary vs. benzylic, I have gone through their different type of effects including inductive effect, hyperconjugation, resonance effect.



But there are still some different classes of carbocations and some of the effects which I have not covered in the last class. Today's class I am going to start again with the resonance effect and then also try to talk about the stability first, and then we are going to capture the fate of the carbocation. That means, once you have formed a carbocation, what is the fate of the carbocation? Is it going to go for elimination or it will go for a nucleophilic substitution or it will go for some sort of rearrangement? So, I am going to talk about them and then I am going to start with the neighboring group participation. So, as I am going to start talking about the stability of carbocation, one of the other ways to stabilize a carbocation through a neighboring group participation via a σ-bond electron density or through a lone pair or through a π-bond electron density.



- ➢ Carbocations stability via resonance
  - ✓ Mononuclear vs polynuclear
  - ✓ Homonuclear vs Heteronuclear
  - ✓ EDG vs EWG vs Steric effect
- ➢ Fate of carbocation
  - ✓ Capturing a nucleophile
  - ✓ Losing a proton
  - ✓ Rearrangement
- ➢ Neighboring group participation
- ➢ Non-classical carbocation
  - ✓ Stabilization via C-C sigma bond and pi-bond

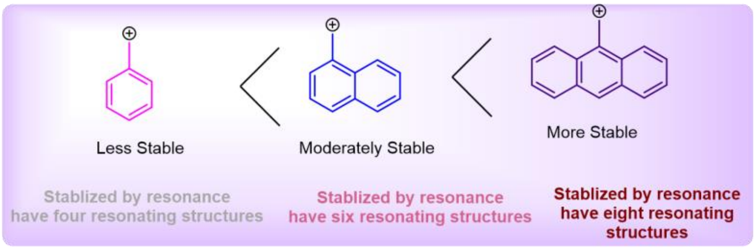
And then I am going to introduce you to the non-classical carbocation. So, last class I already talked about non-classical carbocation. I talked about the carbonium ion, but again I think in this class towards the end I am going to bring some examples to tell you where we have to really empathize about the non-classical carbocation. So, I am going to start with where I left off in the last class. If I have a benzylic, the question comes that if you bring substitution here into the aromatic ring, suppose you bring something like an electron donating or withdrawing group or if you bring another aromatic ring here like naphthyl versus a phenyl or if you have a something like anthracenyl. So, you have two actually aromatic ring in the both side of the phenyl ring. Now, if you compare them which one of them will be more stable?

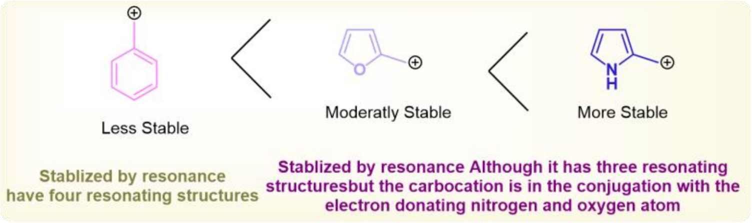
Although they look all of them as benzylic, but the last one the one here will be the more stable. Because if you start drawing the number the resonance structure you will end up getting 6 resonating structures. And then once you move to anthracene, you will end up getting 8 resonating structures. So, as the number of resonating structures is getting increased going from phenyl to naphthyl to anthracenyl we are seeing the stability of this corresponding benzylic carbocation will be also increased. So, that can be explained through this resonance effect. Now, the other thing is what will happen if you compare benzylic versus something which has like from comes from a furan. So, it is an alpha carbon where there is a furan group attached or there is a pyrrole attached here.

So, now if you compare them which carbocation will be more stable? We start talking about the resonance in the last class. So, we know for the phenyl group how to draw the resonance structure but what will happen if you have this furan? Because, once you have a furan your oxygen has a lone pair. So, this lone pair will try to make a resonance structure. And now you can see that once you are going from a carbon to a oxygen to a nitrogen which can also give very similarly the pyrrole can also get stabilized.

So, the lone pair can also get stabilized this carbocationic charge. So, once you go for this type of stabilization what is going to happen now as that in nitrogen having a lone pair and nitrogen is less electronegative compared to oxygen. So, the tendency of nitrogen to go for resonance to stabilize the carbocation will be more compared to the oxygen compared to the carbocation. That is why the carbocation here which is next to the pyrrole will be more stable compared to the furan one compared to the benzene ring.

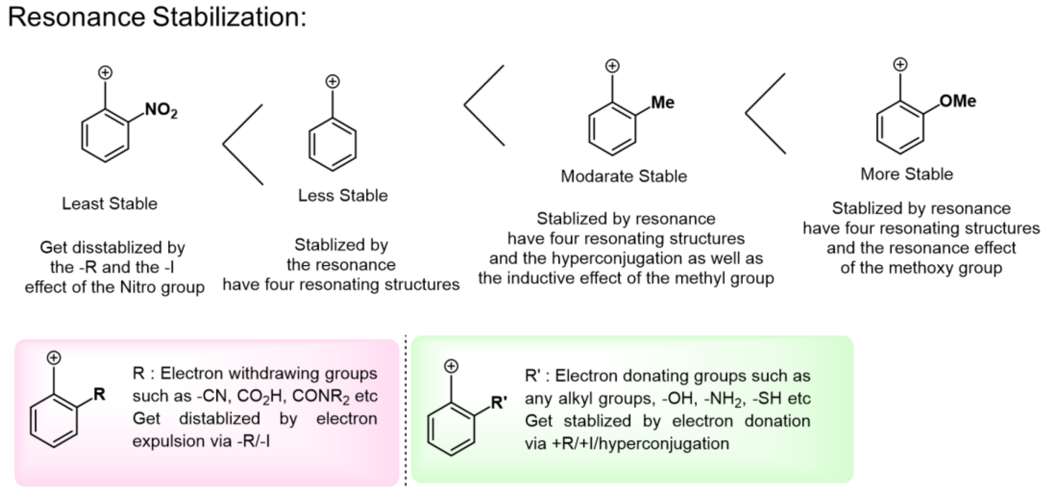
Resonance Stabilization:





So, now we will move for some other examples where if you keep the benzene ring fix and bring the substitution. So, I told you at the beginning that if you bring substitution there are two different types of substitution you can classify them. One is, you can have a substitution which is electron donating and you can have a substitution which is electron withdrawing. Now, depending on the electron donation, you can able to stabilize a carbocation. Now, if you put a electron withdrawing group, your carbocation is already electron deficient. Now, if you bring an electron-withdrawing group into the benzene, what is going to happen? It will destabilize the carbocation even more. So, that is actually happening in the first example that what we are showing here that once you bring a nitro group there, we are actually the normal benzylic carbocation will be more stable compared to that, but as soon as you try to bring something which is electron-donating like you have a methyl group here or you bring something like methoxy group which can also stabilize that carbocation through resonance. So, you can see that those types of electron-donating groups can stabilize the carbocation through resonance. So, we have listed some of the examples like -OH, -NH_2, and -SH. So, all the different types of groups which can donate electrons to stabilize the corresponding carbocation.

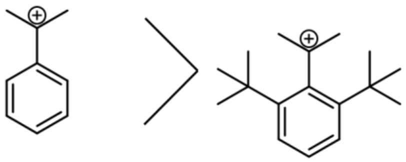
So, those types of groups can even stabilize the carbocation more and they will be more stabilized compared to the. So, here you can see the one with the methoxy will be more stabilized compared to just a normal benzylic one. Again, I think this is a very simple concept we can explain through the resonance very easily.



And now moving forward we can talk about that that if there is a some sort of a steric hindrance in the 2 and the 6 position that means, there is a carbocation here we can see here this is a benzylic and there is another also there is a benzylic, but only difference between these two that we put two bulky group in the 2 and 6 positions that means, the both the 2 and 6 positions have a very bulky group that actually going to make some role here. So, we have learnt that to stabilize a benzylic carbocation we have to rely on this resonance structure.

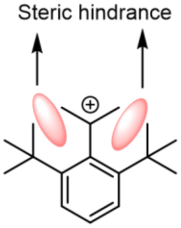
We have already shown that there will be resonance structure which can draw like that here. So, now if you can clearly understand that once you try to draw the resonance structure with two bulky groups that will not going to allow you to bring the planarity because as soon as this structure becomes planar through the resonance those two groups cannot allow them to come into planarity. So, because of presence of those two bulky groups, that particular carbocation cannot get stabilized. So, that is why this particular carbocation formation will be very less compared to the benzylic one ok. That is why you have to remember that if you put two bigger groups with isopropyl or tert-butyl like that in this two ortho position of the phenyl ring, then the formation of the benzyl carbocation will be get hindered. So, there will be in a very less chance for that.

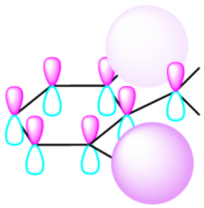
Steric Destabilization:



Get stablized by
the resonance and
by six hyperconjugation

Although
it get stablized by the resonance and
by six hyperconjugation
but the resonance does not occur properly
due o the steric of the two isopropyl group





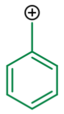
Now, I am going to talk about another very important effect which is the stability of the carbocation. So, we are talking about cyclopropyl methyl carbocation. The cyclopropyl methyl carbocation is a very interesting class of carbocation. Because, we always think till now that benzylic will be the more stable carbocation, but now you come to know that the cyclopropyl methyl carbocations are even more stable compared to the benzylic carbocation.

So, now the question comes why, that is happening? Now, if you think about the cyclopropyl ring, the first thing we learnt in the organic chemistry that the cyclopropyl ring has a ring strain. So, this is, one of the first important concepts that we have a ring strain in the cyclopropyl ring. The cyclopropyl ring cannot fit into sp^3 hybridization with such a small bond angle. So, because of these, the bonds which are supposed to be in the axis is no more in the axis.

So, it forms banana bonds. So, because of the formation of this bond, what is happening here So, these bonds are not any more in the axis, they are literally kind of behaving like so that so this electron density of this sigma bond now can be transferred here to stabilize the carbocation. So, there is two things happening one is this sigma bond the conjugations which I told right now another is the ring strain. So, both the factor you know allowing you so now you can able to draw the different different resonance structure like that. where you can show them we can draw this after you break this one you make a carbonation here or you make a carbocation here. what is happening because of these two reasons this electron density can be transferred here via sigma bond conjugation and sigma bond hyperconjugation to stabilize this carbocation and there is a large driving force for this ring strain. So, that allows you to stabilize this carbocation more compared to a normal benzylic carbocation. We try to show a very similar thing here in this diagram, where we are trying to show you that this electron density sigma over electron density can allow you to give electron density to the empty p-orbital to stabilize it.

Cyclopropyl methyl carbocation is stable due to the σ-bond conjugation

benzylic carbocation

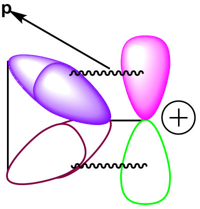


vs

cyclopropyl methyl carbocation

More Stable

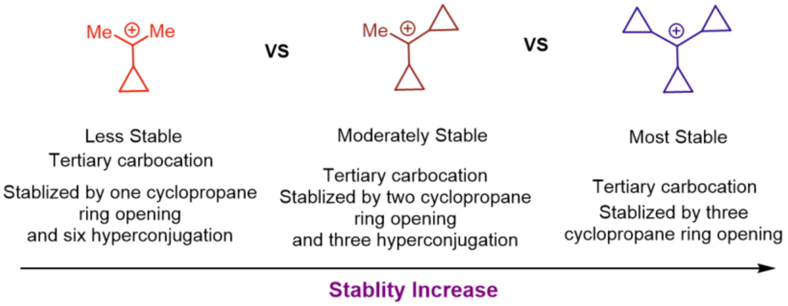
Stablized by cyclopropane ring opening
Strained ring opening is the driving force



Stablization by the bend σ-bond
of the cyclopropane ring
as well as ring strain releasing

Let’s try to bring a greater number of cyclopropyl. So, here what we have we have a scenario where we are increasing the number of cyclopropyls. So, this is a tertiary carbocation we have this. So, what we are trying to compare here is that once you have a methyl group, we know that the methyl group has three hyperconjugations each methyl group, but now if you replace one methyl group with a cyclopropane what is going to happen your stability going to increase enormously compared to the starting one. So, if you bring three cyclopropane it will be the most stable one. So, I told you in the previous slide that this effect of cyclopropane because cyclopropane wants this ring strain to be released and secondly, they have this you know banana bond which is perfectly ready for giving the sigma bond hyperconjugation to stabilize the the carbocation. So, that is why this will be more stable compared to this and this will be more stable compared to this. So, if you compare this hyperconjugation of the methyl group versus cyclopropyl then cyclopropyl will be the winner here.

Cyclopropylic stabilization:



Less Stable
Tertiary carbocation
Stablized by one cyclopropane ring opening and six hyperconjugation

Moderately Stable
Tertiary carbocation
Stablized by two cyclopropane ring opening and three hyperconjugation

Most Stable
Tertiary carbocation
Stablized by three cyclopropane ring opening

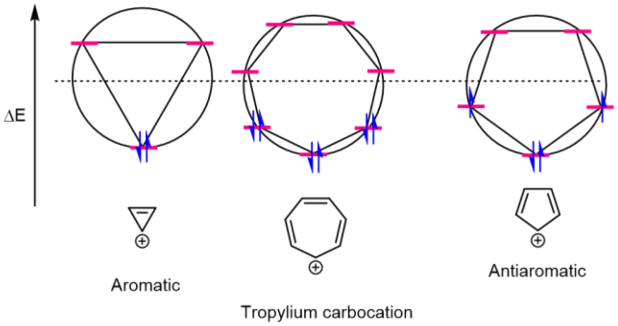
Stablity Increase

So, moving forward we are going to talk about aromaticity. I think you all know the definition of aromatic compounds. So, I do not have to tell you a couple of important things in the definition we mentioned the planar fully conjugated monocyclic system with 4n+2 pie electron has to have a closed shell of electrons, and all in the bonding orbitals the electron has to be in the bonding orbitals are exceptionally And if you see the example I am going to bring here you can see there are different types of carbocation I brought here. So, if you see that this carbocation here is aromatic and the next one we already learned about this propylene carbocation is also aromatic, but the other one is anti-aromatic here. Because you can clearly see this one is not following the definition of an aromaticity ok. So, that is why what is going to happen is these two are getting aromatic and these two are anti-aromatic.

Hückel's rule: **Planar, fully conjugated, monocyclic systems with (4n + 2) π electrons have a closed shell of electrons all in bonding orbitals and are exceptionally stable. Such systems are said to be aromatic.**

Analogous systems with 4n π electrons are described as anti-aromatic

Hückel's Molecular Orbital Theory:



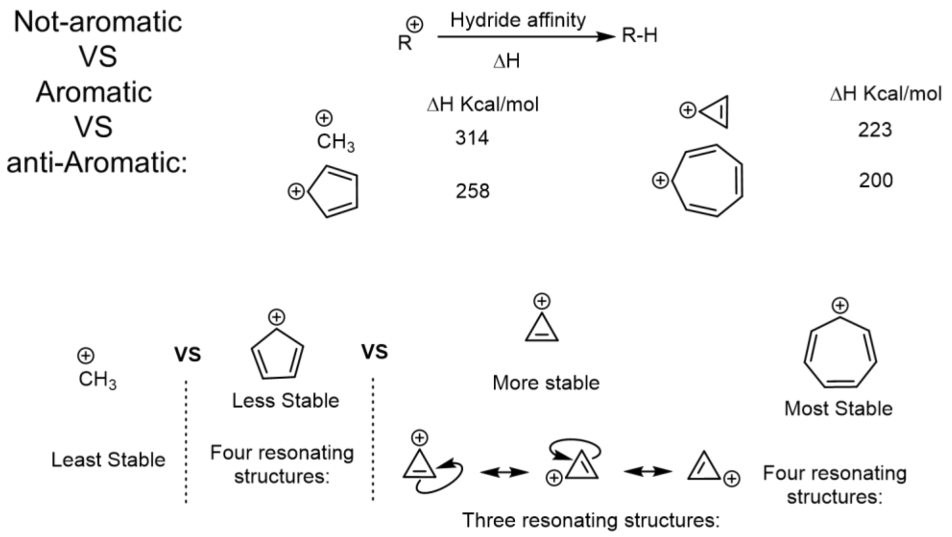
Aromatic

Tropylium carbocation

Antiaromatic

Now, what is that important to carbocation stability? You can clearly see that from the hydride affinity values. So, if you compare the hydride affinity of methyl versus cyclopentadienyl cation versus this tropolium versus this cation you can see that this is only 200, this is 223, this is 258. So, you can see there if you try to compare them first let us try to compare them one after another, we can compare first this one and this one let us try to compare between these two aromatics.

So, they both are aromatic, but if you compare them then which one of them will be more stable? If you compare them the tropolium will be more stable because of what is happening because the tropolium will get the four resonance structures compared to this one ok. And now if you see, these two are even more stable compared to this one, ok. Because one of the reasons I mentioned in the last slide, although these are aromatic compounds, but this is an anti-aromatic compound. Because of that reason, this compound will be, this carbocation will be, less stable compared to this one and this one. So, actually, I am planning to share all the different hydride affinity values. So, I am going to share that in the weekly assignment. So, you can able to practice more of this during that time.

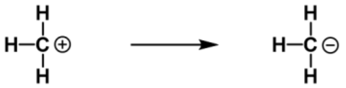


So, now I am going to move further and I am going to talk about the fates of carbocation. So, we have learned first what are the different methods of formation of carbocation. We have learned about different types of carbocation stability.

We have learned about alpha to the cyclopropyl carbocation. We have learned benzylic, and allylic. you know we have learned about the vinylic carbocations and now we are thinking that if a carbocation is forming here, we know carbocation has 6 electrons with a carbon center and what is going to happen it always has a tendency to go back to 8 electrons to fill the octet. So, what it will be going to do it will have 3 different things it can either capture a nucleophile. If it captures a nucleophile having 2 electrons then it can get to the octet, it can also loss a proton to form a π-bond, which we are going to learn we have already learned during the E1 elimination, and then the other important thing is the rearrangement.

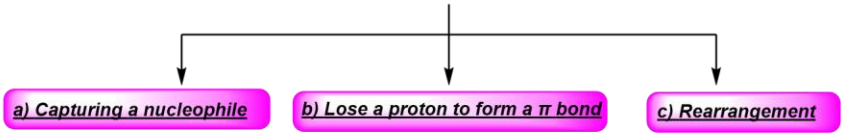
After the formation of carbocation, it rearranges to form a different carbocation which will be either or I think it has to be more stable. So, let us talk about that.

Generally, carbocations are unstable due to their open octets and positive charges.
Hence strongly influenced by filling the octet of the carbon bearing the positive charge



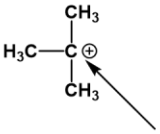
6 e- with the carbon center   8 e- with the carbon center

Therefore to gain the stability, the carbocation generally follow three pathways:



So, the first thing is if you capture a nucleophile as I said once you have a carbocation it is a 6 electrons species. So, it will look for a 2 electrons species like a nucleophile like here we are talking about F^- which can react with this CH_3^+ to form this once it will form that now your carbon has an octet. So, that means, the carbocation has a tendency to react with these two electrons pieces to form this octet. So, that is the first thing.

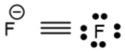
a) Capturing a nucleophile:



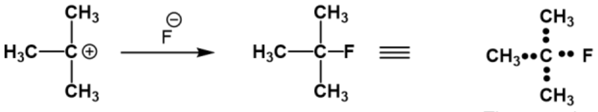
Looking for a anaionic species which can provide two electrons to fill the octet

electrophilic center

6 e- with the carbon center
hence extremely urged to fill the octet

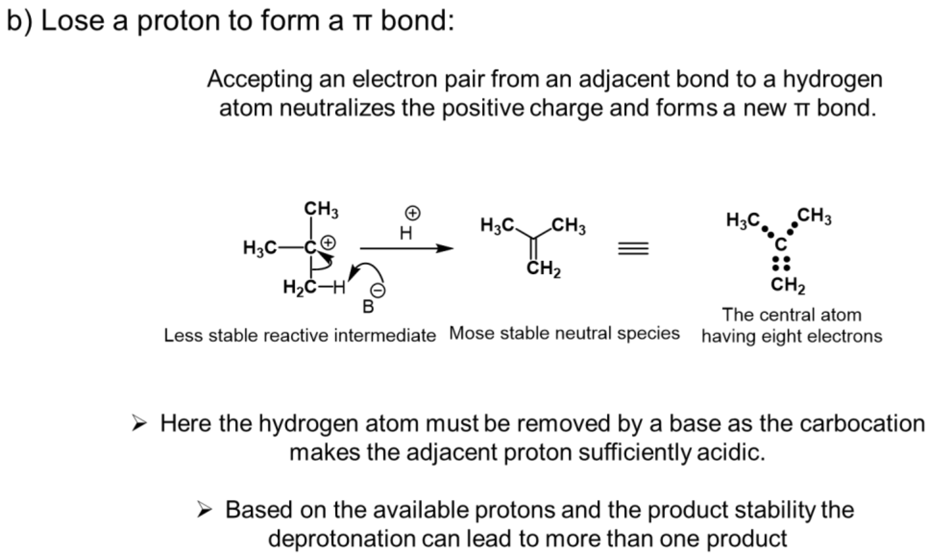


Anionic species (Nucleophile)



Less stable reactive intermediate   Mose stable neutral species   The central atom having eight electrons

The second thing is that it can lose a proton which is very similar to, I think we talked about the E1 at the beginning, we talked about the E1 elimination. So, this is going to happen if it is possible to abstract a C-H group here this C-H then it can able to what is going to happen? Now, it actually going to abstract this and form this bond here and form this. So, it goes for an E1 elimination. So, that is already studied before then the other possibility is the rearrangement.



b) Lose a proton to form a π bond:

Accepting an electron pair from an adjacent bond to a hydrogen atom neutralizes the positive charge and forms a new π bond.

Less stable reactive intermediate

Mose stable neutral species

The central atom having eight electrons

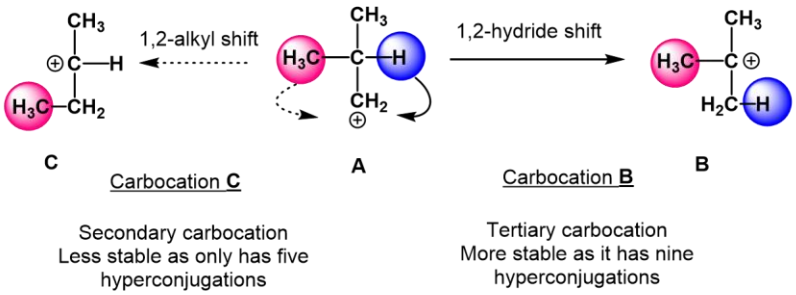
- Here the hydrogen atom must be removed by a base as the carbocation makes the adjacent proton sufficiently acidic.
- Based on the available protons and the product stability the deprotonation can lead to more than one product

Can it go for a rearrangement? Now, what we are talking about here is that if we generate a carbocation here, a neopentyl carbocation here. Now, after that what is the possibility? It can either go for a hydrogen shift from here to here. So, we call it 1,2-hydride shift or it can go for a 1,2-alkyl shift that means, this methyl group here can also able to migrate to neutralize the positive charge now we first we understand the hydride shift. What will happen if you go for a hydride shift if you go for hydride shift, we generate a tertiary carbocation here, you can see we generate a tertiary carbocation here now once you go for a 1,2-alkyl shift, we generate a secondary carbocation here. So, there is a difference between the stability the tertiary carbocations are more stable than secondary which I explained before. So, that's why you will see the hydride shift will be here there will be more chance for this you know hydride shift to generate this tertiary carbocation.

Now we are going to talk about other sorts of rearrangement where although there is the carbocation which is tertiary but there is something else happening here. So there is a driving force for ring opening. Suppose you have you know this particular carbocation here. where you have a cyclobutane ring and you are forming a carbocation to the next carbon and there is a carbocation here. So, now, there are you know two possibilities that can happen it can either this hydride can be moved here to generate this more stable tertiary carbocation or it can go for a 1,2 alkyl shift here.

So, that means, this ring can get expanded. So, there is a chance of you know ring expansion versus a hydride shift. Now what is going to happen? Again, as the ring has a huge strain if you see again this is instead of 108 degrees you have only 90 degrees in case of cyclobutane. that means this ring has a strain. So, it will try to escape from the ring strain which means, ring expansion will be the major driving force for this 1,2-alkyl shift for the formation of this F compared to the E. So, it is not always that you will go for the carbocation stability, you have to find out what are the things happening here. Despite the formation of a secondary cation, the driving force for the ring opening to release the strain will be the winner here.

c) Rearrangement:



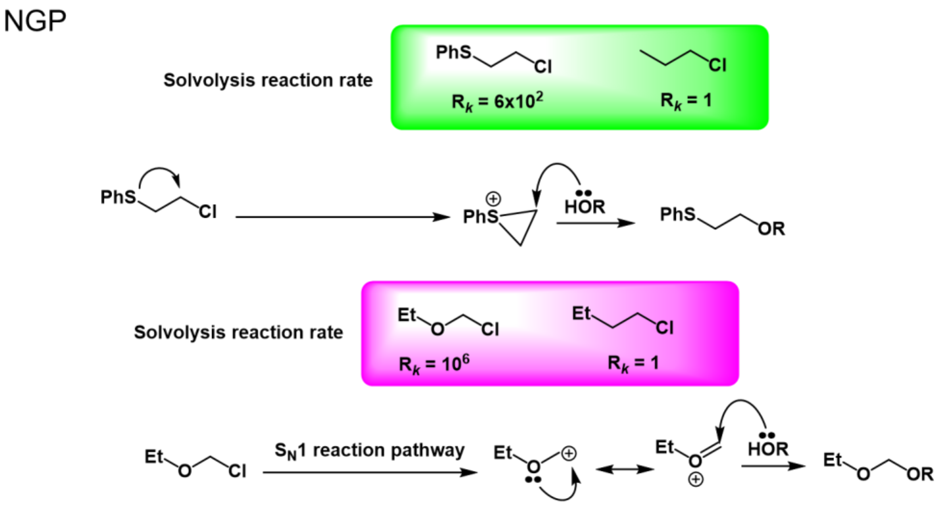
Now, we are going to talk about the neighboring group effect which is another topic. In the neighboring group effect what we have seen that there is also the formation of some sort of a carbocations. So, here you are going to see that in the first example what we are trying to show here we also call this neighboring group of it Anchimeric assistance. So, now, if you try to compare the reaction rate here for this you know solvolysis, we find out that this one is $6x10^2$ times higher compared to this butylchloride.

So, just replacing here by carbon with sulfur we saw there is so much increase in the reaction rate. So, what is happening here? So, first, what is happening this sulfur as a lone pair is going to attack to the back side of this C-Cl bond to eliminate this chlorine here to form this particular sulfur with a positive charge species. Once you form a positive charge species with the 3-member ring there is lot of strain here. Now, to release the strain the nucleophile can easily attack here to form this product. Because, of this sulfur attacking and formation of this particular strain compound now nucleophiles can easily attack and form to the product.

Now, another example of the S_N1 reaction I am going to talk about this one here. Here you can see what will be the difference if in this position where you have carbon versus oxygen here. What difference is going to make here. Because if you try to compare the S_N1 reaction rate, it is found out that this is going to react 10^6 times faster compared to this. So, again we found out there is this neighboring group effect.

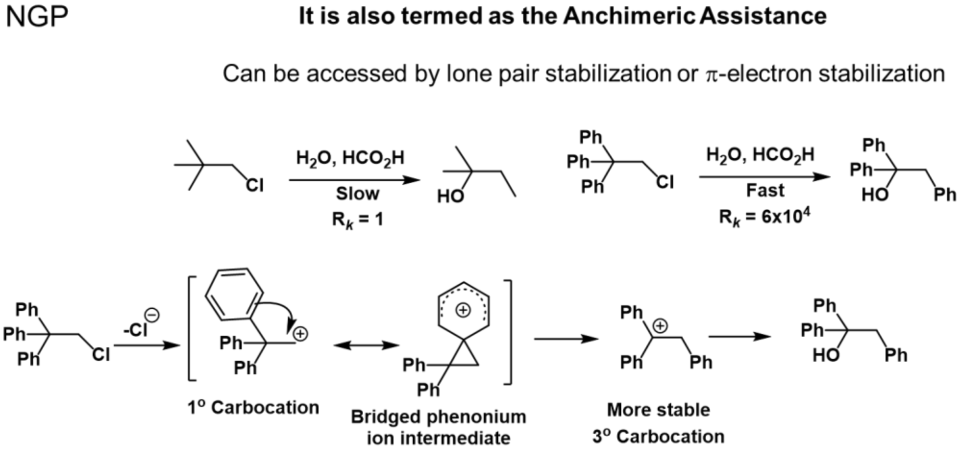
What is happening here the first step of the S_N1 reaction was going to be the dissociation of this carbon, the C-Cl bond, to the formation of this carbocation. Now, you have learned that what particularly for if you have a primary carbocation formation happening, then that S_N1 reaction will be much slower. But you have oxygen here that can stabilize the corresponding positive charge. I have already mentioned during the resonance effect that if you have a group that has a lone pair that can able to donate the lone pair then that can stabilize the positive charge that will allow the nucleophile to easily attack here and form a product.

So, in one case we have learned that the lone pair can attack from this and in another case the oxygen can give the lone pair to stabilize this, stabilize this corresponding carbocation.



So, moving forward we have another example here where we can see there is a neopentyl chloride here and so we are talking about the hydrolysis of this what is going to happen. Now, if you think about that there is a primary carbon here again if you try to put acid for an SN^1 reaction they are not a very good substrate for S_N1 reaction. So, what is going to happen the reaction will be slow. But as soon as you replace these three methyls with three phenyls, the reaction is fast.

How much fast is 6 x10^4. So, now despite being a primary carbocation formation going to happen, the reaction is fast. Why it is happening? Because once the carbocation formation is happening you have some extra stabilization is happening here. That means now this phenyl ring electron density going to this pie electron density going to come and stabilize this carbocation from some sort of a bridge phenonium intermediates. So, because of this pie electron donation from this phenyl ring this particular carbocation going to get stabilized. So, that will allow the formation of this more stable 3-degree carbocation because this phenyl group going to get migrated now this is a really stable carbocation now it can go for S_N1 to go for this particular product. So, replacing this you know methyl group with a phenyl group we can see a real acceleration of the S_N1 rate.

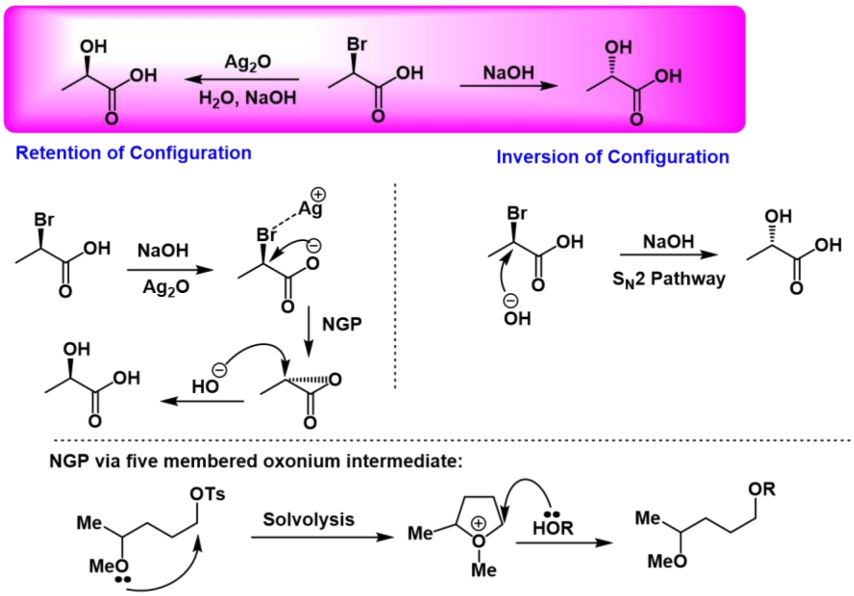


So, moving further we can learn that there are other very good examples where we can see in one case we can see retention of configuration and the other cases we can see the inversion of configuration. That means, what is happening here we are showing here that in this example, once you treat with silver oxide, H_2O, and NaOH, we can find that there is a bromine was replaced by OH and there is a retention of configuration. But once you simply use NaOH, we found there is an inversion of configuration very similar to a simple S_N2 reaction. As these compounds are alpha to the carboxylic acid this particular carbon is going to be attacked for S_N2 is a very good S_N2 substrate.

So, you can see in the S_N2 pathway there will be an inversion, but what happens once you put silver there Once you put silver there now silver is trying to form a bond with the bromine. Once it forms a bond with the bromine this C-Br bond gets weaker. Now, there is an Anchimeric assistance or the oxygen lone pair participating in the NGP to go for a first there are S_N1 reactions here to get rid of the bromine and now there will be a second S_N1 here to open up the ring. So, that is why as there are two inversions happening first inversion happening here second inversion happening here. So, two inversions can give you retention that is why what is going to happen is you end up going to retention in this particular case.

Also NGP can be happening here if you have a methoxy group here it can also participate in the NGP first through this lone pair as I showed you before with the sulfur and then it can be also open up to form this compound. So, again the hydrolysis rate will be much faster if you have this internal group that can give you the lone pair to open up the ring.

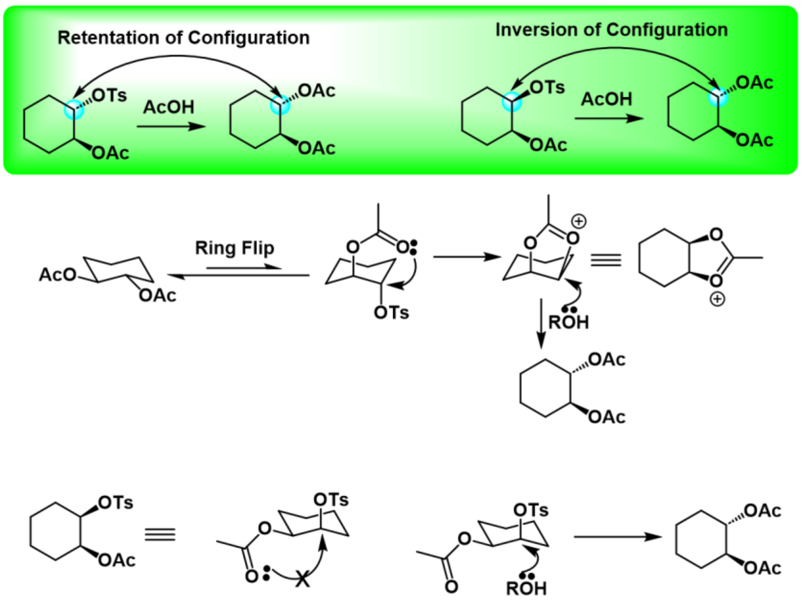
NGP



And now there is another example if you have this particular case here you have an -OTS and you have an -OAC group here. So, this is a case of cyclohexyl where you have a substitution in the 1,2 positions. Now if you have this you know the -OTS group here what you can see here with acetic acid once I go for the acetolysis we end up here the retention and here we end up seeing the once you go for this one here, we go for the inversion.

So, what is happening here in the first case? If you see here 1,2 substitution, they both can be equatorial because they are trans or they can be diaxial. In this diaxial scenario, the oxygen lone pair can able to push the electron density to the σ*-orbital able to form this. And now, once you form this carbocation intermediate here, there is a charge on the oxygen, so the alcohol now can attack from here. So, it can attack from here and give it to the corresponding product. So, you know, what is happening here? Again, two inversions are happening. First, S_N2 is happening from here, there is a second S_N2 happening here. So, both inversion gives you the retention and the other cases as it cannot happen from this particular configuration is not allow that is why simply there is a S_N2 going to happen which going to give you inversion.

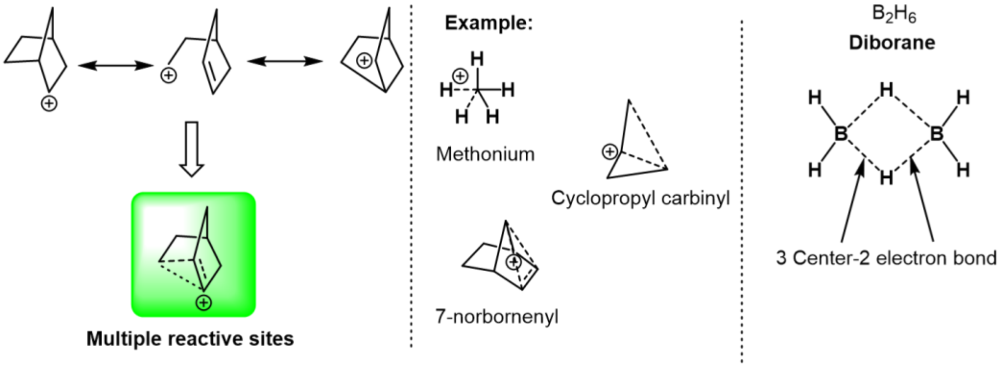
NGP



So, moving further we are going to talk about the non-classical carbocation I told you about. So, again in the non-classical carbocation, I am going to show you some examples where this positive charge will be stabilized by the σ-bond or the π-bond, or a strained cyclopropyl ring. So, there will be fully charged delocalization across the participating field and empty orbitals and we are going to see that all the atoms involved bear a charge and electrophilic characters. So, I already talked about the methonium at the beginning which is CH_5^+ and then there are some examples like cyclopropyl carbinyl or the seven norbornenyl systems.

I am going to explain through some examples and again I think we all know about the diborane structure which also forms through these 3c-2e bond which we are going to see different types of in norbonenyl systems and different types of carbonyl systems. We are going to observe the formation of this 3c-2e bonds.

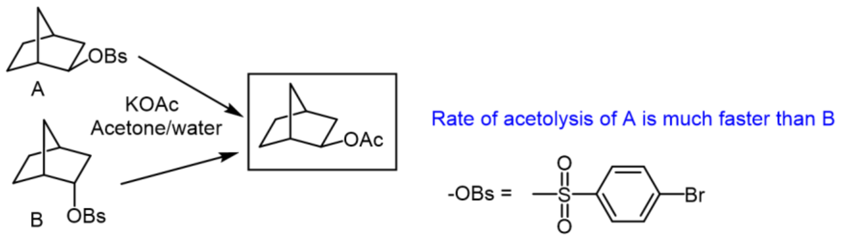
- Full charge delocalization across participating filled/empty orbitals
  - All atoms involved bear charge and electrophilic character



So, let us try to learn about non-classical carbocation through some of the examples we have. So, what is happening? If you try to compare the hydrolysis rate here compared to **A** versus **B**. So, what is going to happen here is that the rate of acetylysis of **A** is much faster than **B**. So, what is happening here is why the rate of **A** is much faster now you can see that this sigma bond of this carbon and this oxygen has a sigma star orbital here.

So, we call it a σ*-orbital. Now this σ-electron of this carbon-carbon bond here can give electron density to this σ*-orbital which allows breakage of this carbon-oxygen bond. So, you can see in a minute you know what is happening here.

non-classical carbocation: cations that receive stabilization via NGP of adjacent C–C σ-bond and π-bond

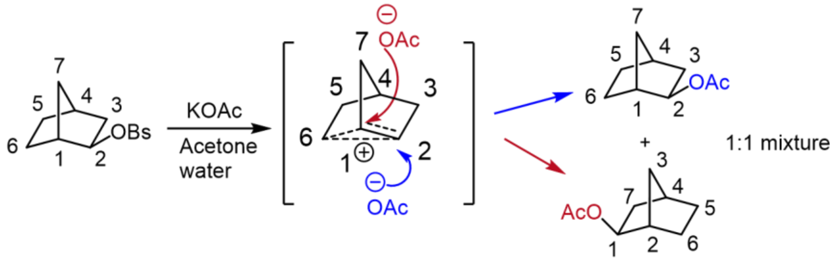


So, this σbond is giving electron density to the σ*-orbital here and that will allow the breakage of this bond which allows to generate of this type of carbocationic species here. So, this is a very interesting type of carbocationic species because now if you try to write a carbocation you can see the charges now you have to write a carbocation character at the beginning you are going to write here.

Now, you can write the carbocation. So, that means we can write this particular thing instead of writing carbocation character in this different position we try to write like that where it is actually a 3c-2e bond going to form. So, this is actually going through a non-classical carbocation. So, now what is going to happen your -OAC can have a possibility to attack from this C-2 position. or it can attack from this C-1 position here.

So, this is the number one carbon. So, it can attack through the one or it can attack through the two. So, that way it can give a one-to-one mixture of this you know these two compounds. So, if it attacks through the two it will form this, if we attack through the one it can form this ok. So, this data kind of clearly reflects that it is going through the formation of some sort of a non-classical carbocations.

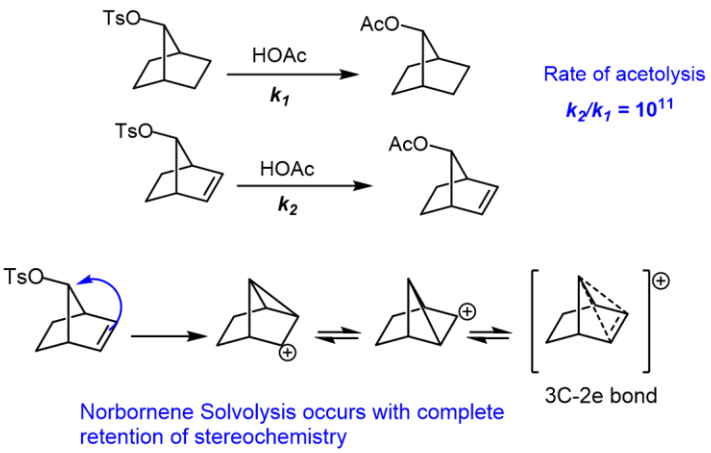
non-classical carbocation: cations that receive stabilization via NGP of adjacent C–C σ-bond and π-bond



There is more data to explain this that if you try to do the NGP through an adjacent carbon-carbon pie bond, that means you have an example here. We are again trying to do an acetolysis of this -OTs group here. Now, if you try to compare the acetolysis between these two compounds, so the only difference is here you have an extra pie bond, which is not there. And there is a rate difference of 10^{11} between this one and this one. So, this is going much faster compared to this. What is happening here? Now, because there is a π-bond here, now this π-bond also can participate in this. So, this π-bond can give electron density to this again to this σ*-orbital here.

So, if it is going to give electron density here that will allow you because of this bond, and that will allow the formation of this carbocation. Now, you can able to shift here again can form another carbocation here we can write finally, it cannot be from here,we can write finally, like a 3c-2e bond. So, again this type of norbornene solvolysis, and also one of the important things here also the reaction is happening with complete retention of stereochemistry. That means, because it is forming through this type of carbocation, now there is it is going to end up making only one particular product. It is not that we are going to end up getting a mixture or we can get some product where the -OAC will be forming here, no that is not happening.

Because, once you go for this particular type of carbocation now the nucleophile can attack here only on one side to form this type of exclusively with the retention of stereochemistry.



non-classical carbocation: stabilization gained via NGP of adjacent C–C π-bond

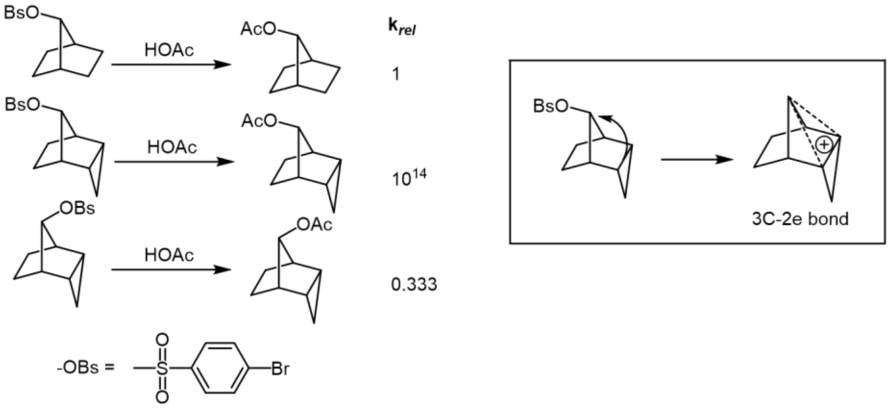
Rate of acetolysis

$k_2/k_1 = 10^{11}$

Norbornene Solvolysis occurs with complete retention of stereochemistry

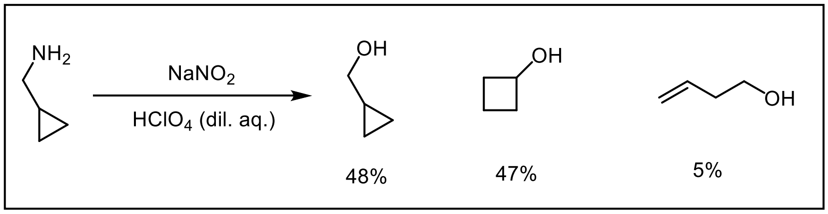
And moving further we have other examples where we have learned first with the σ-bond, we have learned through the pie bond now there is a case of cyclopropyl. If this cyclopropyl group is here it can able to give electron density to the σ*-orbital, then you can see this has a 10^{14} reaction rate compared to here which you do not have this cyclopropyl group. Or if you put the cyclopropyl group not in the particular position if you put it in a different place then the rate is also not higher.

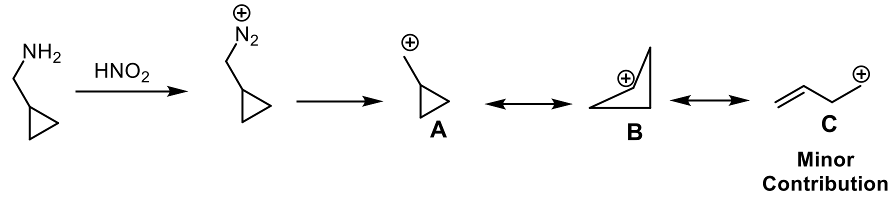
That means the cyclopropyl group has to orient in such a way that this sigma bond electron density can be given to the sigmaster orbital. that will allow the formation of this reaction higher we can see where this is going through these 3c-2e bonds here because of this giving sigma electron density so this is another example of this non-classical carbocation.



non-classical carbocation: stabilization gained via NGP of adjacent cyclopropyl C-C σ-bond

And then the final example here if we start with this type of cyclopropyl $\text{-CH}^2\text{-NH}^2$ compound with $NaNO_2$ what is going to happen not only we get this product we also got his product with you know cyclobutyl and we were finally, also able to get this one. So, how this is happening? The first thing is the formation of this N_2^+, then the breakage of this bond formation of this carbocationic charge, there is a ring expansion happening here, going through some sort of a carbocationic species which is a non classical carbocationic species. So, this can able to give you this particular product here this can able to give to this product and now once you open up you can able to form this particular carbocation which can give you this particular product which is a minor compound.





So, in this class, we have learned about stability, we have learned about the electron-withdrawing group, and the donating group and we have also learned about how nucleophiles and electrophiles which are important during the fate of the carbocations, where the nucleophile can attack and then we have also learned about the non-classical carbocations and we are going to see you guys in the next class.