Symmetry, Stereochemistry and Applications

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Lecture - 35
Addition Reactions to Alkenes and Alkynes - Part 01

Welcome back to the course entitled Symmetry, Stereochemistry and Applications. In the last week, we were discussing about substitution and elimination reactions. And we have discussed a few examples on substitution and elimination reactions in the last class.

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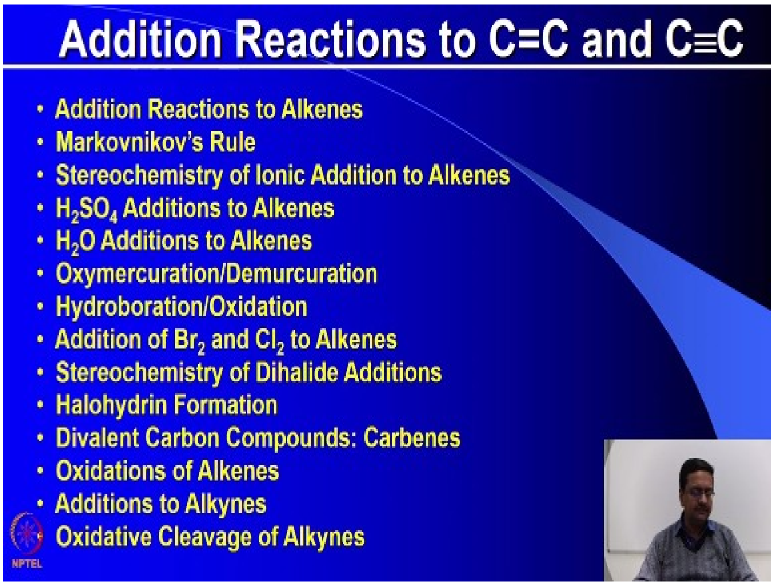

Addition Reactions to C=C and C≡C

- Addition Reactions to Alkenes
- Markovnikov's Rule
- Stereochemistry of Ionic Addition to Alkenes
- H_2SO_4 Additions to Alkenes
- H_2O Additions to Alkenes
- Oxymercuration/Demurcuration
- Hydroboration/Oxidation
- Addition of Br_2 and Cl_2 to Alkenes
- Stereochemistry of Dihalide Additions
- Halohydrin Formation
- Divalent Carbon Compounds: Carbenes
- Oxidations of Alkenes
- Additions to Alkynes
- Oxidative Cleavage of Alkynes

So today, we are going to start in this new week discussion on the addition reactions to carbon-carbon double bond and C-C triple bonds. So in this week, we will discuss about these following reactions. We will talk about the addition reactions to alkenes, Markovnikov's rule, stereochemistry of ionic additions to alkene, sulphuric acid addition to alkene, water addition, oxymercuration and demurcuration.

Hydroboration/oxidation, addition of bromine and chlorine to alkenes, stereochemistry of dihalide additions, halohydrin formation. Then we talk about the divalent carbon compounds that those are called carbenes and then additions to alkenes, additions to alkynes, oxidative cleavage of alkynes. And then we will discuss about various oxidation and reduction procedures that are generally done in the organic chemistry laboratories.

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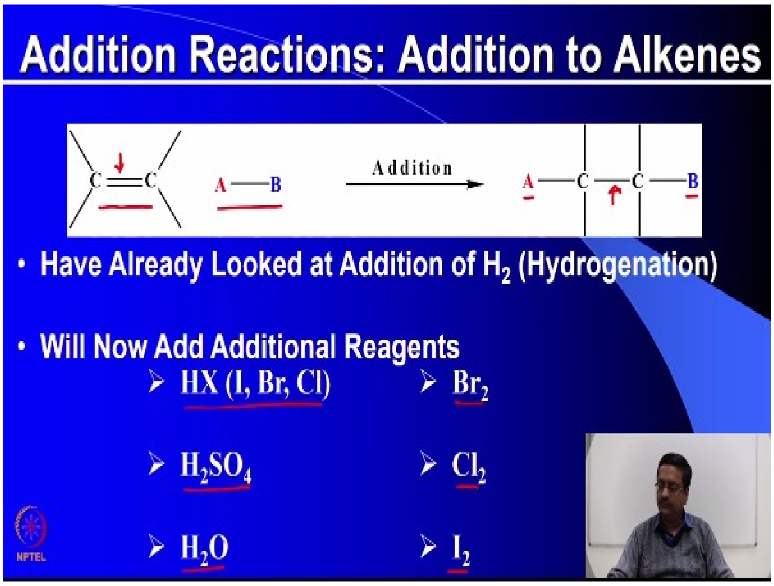

Addition Reactions: Addition to Alkenes

- Have Already Looked at Addition of H_2 (Hydrogenation)
- Will Now Add Additional Reagents
  - HX (I, Br, Cl)
  - Br_2
  - H_2SO_4
  - Cl_2
  - H_2O
  - I_2

So to start with when we think of addition reactions, that means, we are talking about saturation of a unsaturated carbon compound. So for example, if we have a C=C double bond as this one here, and if you want to add a substrate, which is A-B, maybe unsymmetrical or symmetrical, then this A and B gets added and the double bond is converted to a single bond. So it is very similar to the addition of hydrogen.

You may have learnt in your 10 + 2 how the hydrogen is added to a C=C double bond. So we will now discuss the reaction mechanisms of addition of unsymmetrical substrates to a C=C double bond. So we will discuss the addition of various HX, halogens, sulphuric acid and water in a systematic manner.

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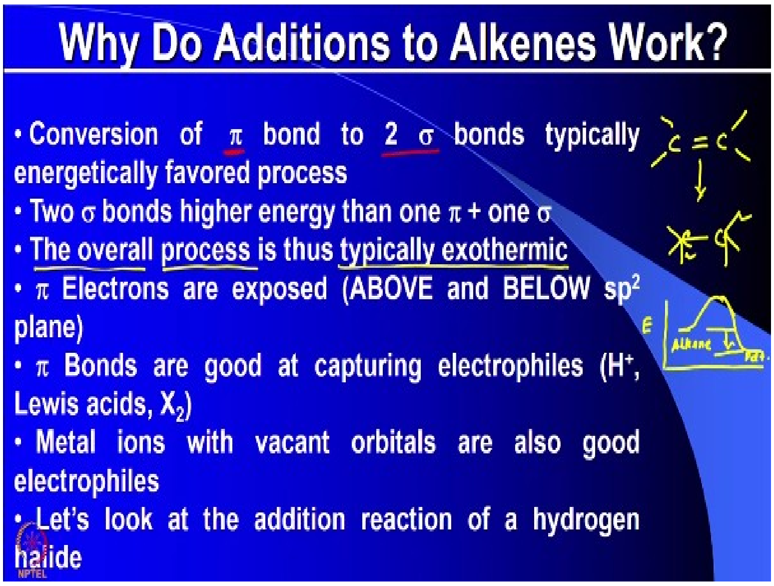

Why Do Additions to Alkenes Work?

- Conversion of π bond to 2 σ bonds typically energetically favored process
- Two σ bonds higher energy than one π + one σ
- The overall process is thus typically exothermic
- π Electrons are exposed (ABOVE and BELOW sp^2 plane)
- π Bonds are good at capturing electrophiles (H^+, Lewis acids, X_2)
- Metal ions with vacant orbitals are also good electrophiles
- Let's look at the addition reaction of a hydrogen halide

So why do these addition reactions work? How does this reaction proceed? So in this addition reaction, you see that we convert one pi bond to two sigma bonds. You had a C C double bond and from that, we have converted it into a C C single bond. So what has happened is we removed one pi bond and created two sigma bonds. And normally this process is energetically favored.

The two sigma bonds are higher energy than one pi and one sigma bond. So as a result, in general the overall process is typically exothermic. What do we mean? If we draw the energy profile diagram of this reaction, if we have this alkene at this level, it goes through a transition state and the product is generally more stable. The additional product has more stability than alkene.

And therefore, it releases this amount of heat which is a phenomena of exothermic process. So pi electrons are exposed above and below the sp2 hybridized carbon atoms. And this pi bonds are good for capturing electrophiles like H+ ions, Lewis acid and halogens. Even the metal ions with vacant d orbitals are also good electrophiles which can form bond with these pi electrons. So let us look at the addition reactions of some hydrogen halides.

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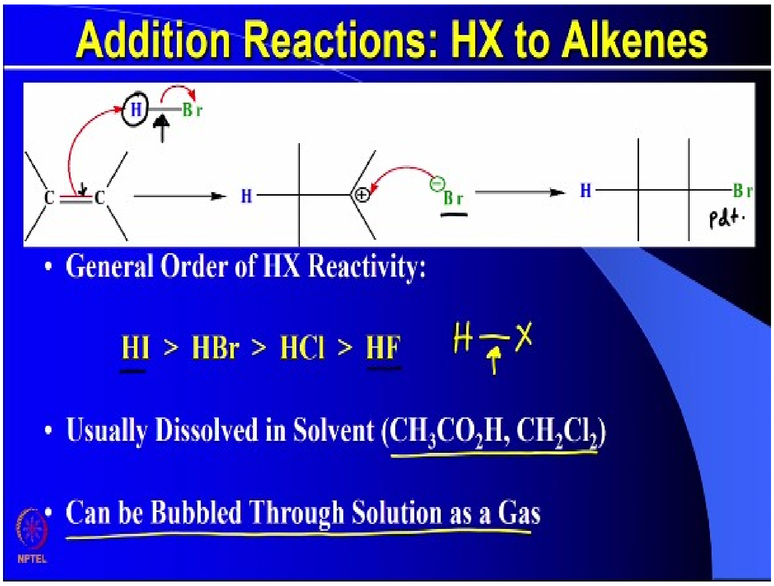

Addition Reactions: HX to Alkenes

- General Order of HX Reactivity:

  HI > HBr > HCl > HF   H—X

- Usually Dissolved in Solvent (CH_3CO_2H, CH_2Cl_2)
- Can be Bubbled Through Solution as a Gas

So when you try to add a hydrogen halide to alkene what happens is the first process first step is the step of breaking of this pi bond. So the pi bond is broken and the electron is donated to the H+ and it forms this carbocation and Br- is released. And then in the solution when we have Br-, this Br- gets attached to the carbocation site and forms the addition product.

So this particular reaction has a general trend of reactivity, with HI being most reactive and HF being the least reactive. This reactivity order depends on the bond strength of H-X. Higher the strength of this bond lower is the possibility of reactivity because in this first step, the bond breaking of H-X takes place. So this sigma bond is first broken and the proton is added to one of the carbon atoms and bromine is released as Br-.

Usually we do this reaction dissolved in some solvents. Sometimes, it is possible that the H-X is bubbled through a solution of alkene in a solution.

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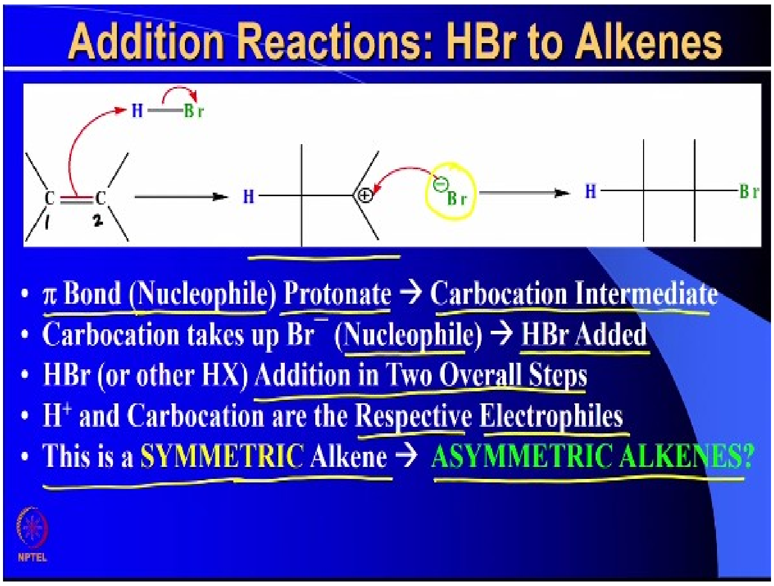

Addition Reactions: HBr to Alkenes

- π Bond (Nucleophile) Protonate → Carbocation Intermediate
- Carbocation takes up Br^- (Nucleophile) → HBr Added
- HBr (or other HX) Addition in Two Overall Steps
- H^+ and Carbocation are the Respective Electrophiles
- This is a SYMMETRIC Alkene → ASYMMETRIC ALKENES?

So when we try to understand the addition of HBr what we see is that the pi bond which is the nucleophile, it first gets protonated and forms the carbocation as intermediate, as you can see here this is the carbocation intermediate. Then this carbocation takes up the Br-, which is the nucleophile. So HBr gets added and this addition happens in overall two steps. H+ and carbocation are respective electrophiles.

And this is a symmetric alkene where these additional reaction we have discussed. So in case of symmetric alkene it does not matter whether the first carbon or on the second carbon H+ gets added. But this becomes important when the alkene is asymmetric. That means, the two carbon atoms C1 and C2 have different substitutions.

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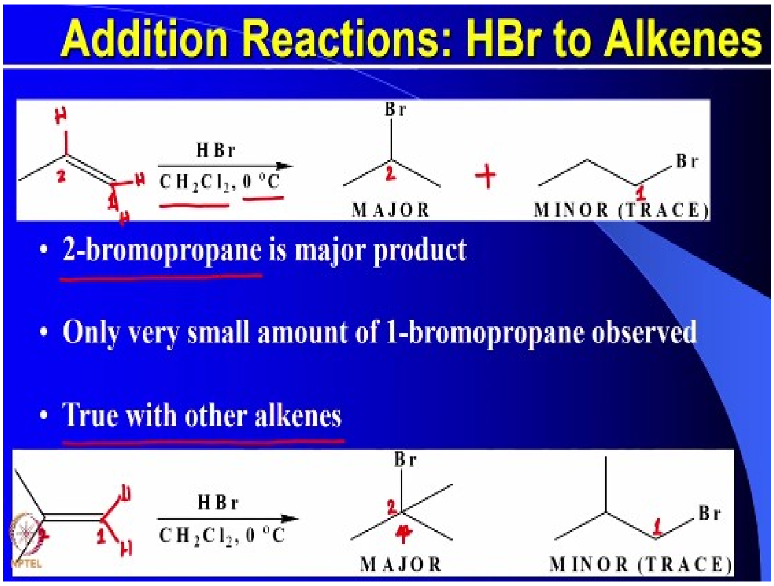

Addition Reactions: HBr to Alkenes

- 2-bromopropane is major product
- Only very small amount of 1-bromopropane observed
- True with other alkenes

Let us see what happens in those cases where the alkene is not symmetric or asymmetric. So in this case what you can see is here, carbon 1 and carbon 2 are different. Carbon 1 has two hydrogens and carbon 2 has one hydrogen. If you do HBr addition to this alkene using dichloromethane as solvent at zero degree centigrade, we get two products with very much different percentages.

Bromine added to carbon 2 is the major product and bromine added to carbon 1 is a minor or trace product. So 2-bromopropane is observed as the major product in this reaction. And this is true with other alkenes as well. So here if you have two carbon atoms connected to carbon number 2 and two hydrogens attached to the carbon number 1, addition to the carbon number 2 with bromine is the major product.

And addition of bromine to the carbon number 1 is minor or trace product. How does this happen?

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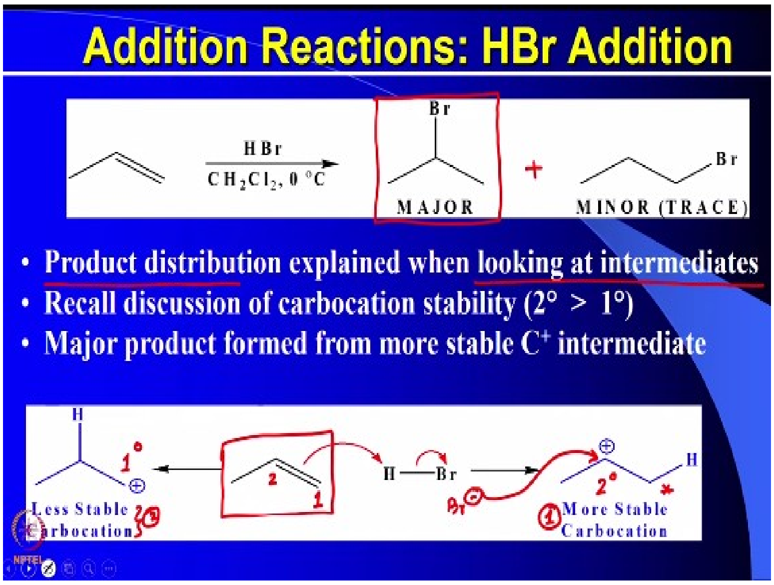

Addition Reactions: HBr Addition

- Product distribution explained when looking at intermediates
- Recall discussion of carbocation stability (2° > 1°)
- Major product formed from more stable C^+ intermediate

What is the reaction mechanism in this case? So this reaction goes through the formation of carbocation which we have already discussed. So the product distribution is explained by looking at the reaction intermediates. So if you have this compound, you try to add H+. So if H+ is added to carbon number 1, you get this carbocation. If H+ is added to carbon number 2, you get a different carbocation.

Now if you compare the stability of these two carbocations 1 and 2, what you see is that this carbocation 1 is a 2 degree carbocation while this carbocation 2 is 1 degree carbocation. And we have already learnt in our previous week's lecture that 2 degree carbocations are more stable compared to 1 degree carbocation. Therefore, this 2 degree carbocation is more stable and hence, this forms much more amount.

As a result, when the bromine is added, Br- is added it is added to carbon number 2 and not on carbon number 1. And therefore, you always receive this compound as major product and the other one as minor or trace product.

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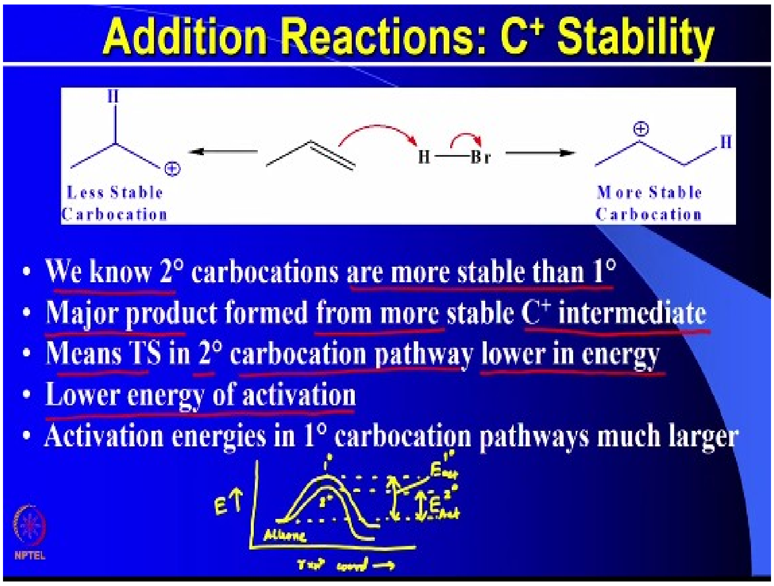

Addition Reactions: C⁺ Stability

- We know 2° carbocations are more stable than 1°
- Major product formed from more stable C⁺ intermediate
- Means TS in 2° carbocation pathway lower in energy
- Lower energy of activation
- Activation energies in 1° carbocation pathways much larger

So what we have learned is that the 2 degree carbocations are more stable than 1 degree. So the major product formed from the most stable carbocation as the intermediate and hence, the transition state for 2 degree carbocation pathway is lower in energy and hence, it has a lower energy of activation then that is why this reaction is favored to form the major product as 2 bromo product.

So what we are trying to make out here is that when you draw the reaction coordinate with energy in y axis and reaction coordinate in x axis, suppose this is your alkene. If it goes through the 2 degree carbocation pathway, it forms the product here. If this goes through the 1 degree carbocation pathway, it is the product here.

So the Eact for the carbocation pathway 1 is more compared to the Eact for the pathway with carbocation of 2 degree. Therefore, the product which forms through the carbocation formation of 2 degree carbocation is more stable and it forms in more quantity. Therefore, you get a large difference in the amount of two different addition products.

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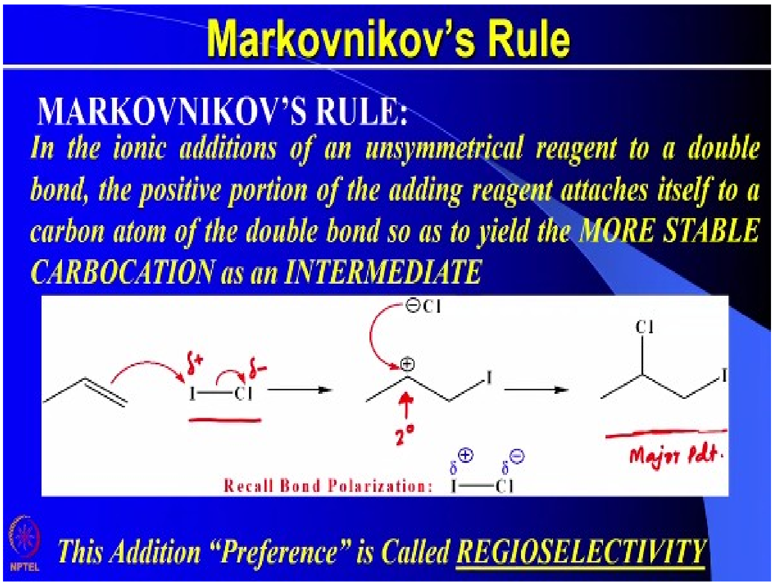

Markovnikov's Rule

MARKOVNIKOV'S RULE:

In the ionic additions of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield the MORE STABLE CARBOCATION as an INTERMEDIATE

Recall Bond Polarization: $\overset{\delta\oplus}{I}—\overset{\delta\ominus}{Cl}$

This Addition "Preference" is Called REGIOSELECTIVITY

And this particular observation that this part goes through a carbocation pathway leads to a rule called the Markovnikov's rule. So what does this rule state? It states that in the ionic additions of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield the more stable carbocation as an intermediate.

So this statement clearly is dependent on the stability of carbocation. So for example, if we are trying to add I-Cl, we clearly know that I is delta positive and Cl is delta negative in this particular compound. So the positive part of this adding reagent attaches to the double bond in such a way to generate a more stable carbocation which is a 2 degree carbocation.

And then this 2 degree carbocation takes up the Cl- and it forms this compound as the major product. This preferential addition of unsymmetrical reagent to this alkene is called regioselectivity, which we will discuss in detail in the next week's lectures.

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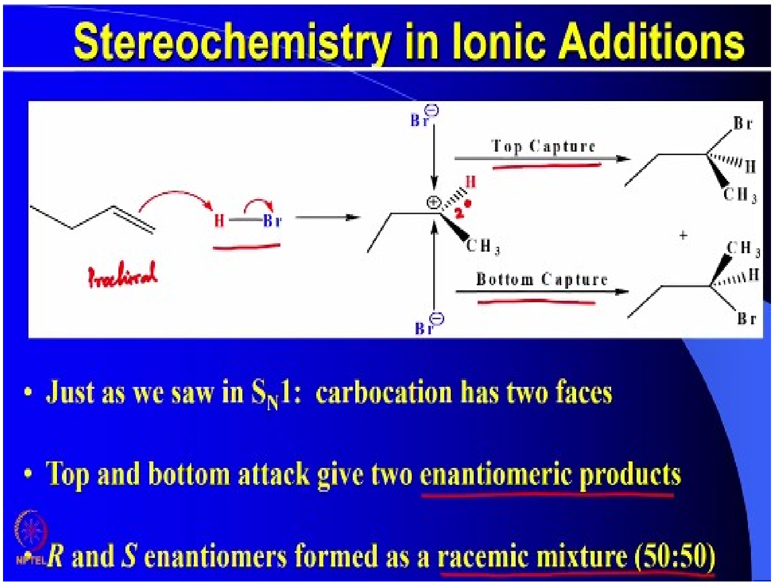

Stereochemistry in Ionic Additions

- Just as we saw in S_N1: carbocation has two faces
- Top and bottom attack give two enantiomeric products
- *R* and *S* enantiomers formed as a racemic mixture (50:50)

So when we try to see what happens when we have a compound which is a prochiral molecule. When we try to add HBr to such a prochiral molecule, the first addition of hydrogen generates 2 degree carbocation. And this 2 degree carbocation is a planar molecule and as a result, this planar molecule can take up from a bromine from the top and bromine from the bottom.

So if bromine comes from top the two bonds which are on the plane is pointing downwards. And if the bromine adds from the bottom, then the bonds which are on the plane points upwards. So this top capture of bromine and bottom capture of bromine results into two different compounds, which are essentially a pair of enantiomers. So in this reaction, using a prochiral compound, we could generate a pair of chiral molecules which are pair of enantiomers.

And needless to say that these two faces of the carbocation are equally populated, equally accessible to the bromine atom or bromide ion. And hence, it gives rise to a racemic mixture of these two compounds which are enantiomers. So we end up getting a racemic mixture of a chiral compound.

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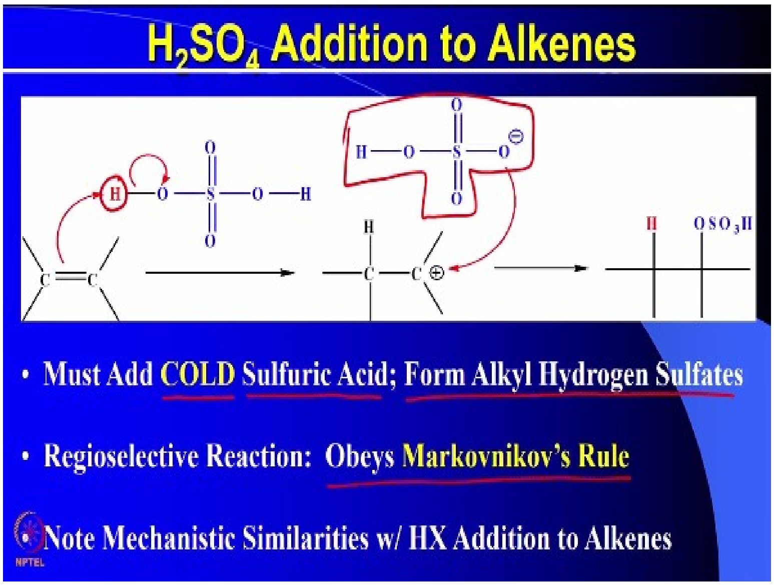

H_2SO_4 Addition to Alkenes

- Must Add COLD Sulfuric Acid; Form Alkyl Hydrogen Sulfates
- Regioselective Reaction: Obeys Markovnikov's Rule
- Note Mechanistic Similarities w/ HX Addition to Alkenes

Now let us see what happens when we try to add sulphuric acid to alkenes. We must add cold dilute sulfuric acid to form this alkyl hydrogen sulfate. So when you add the sulfuric acid, the double bond takes the proton and bisulfate anion is released which in turn then gets bonded to the carbocation and forms this bisulfate addition product. So this is again, the mechanism is similar to the mechanism of HX addition. And it also obeys the Markovnikov's addition rule.

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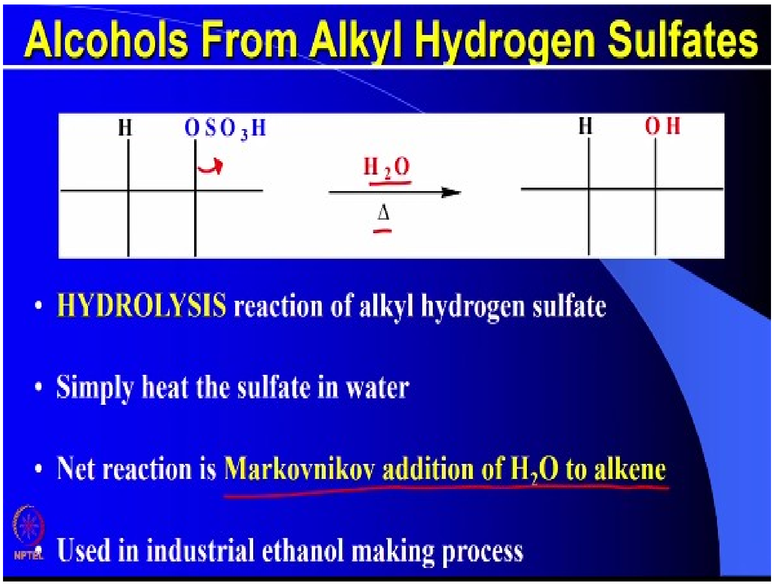

Alcohols From Alkyl Hydrogen Sulfates

- HYDROLYSIS reaction of alkyl hydrogen sulfate
- Simply heat the sulfate in water
- Net reaction is Markovnikov addition of H_2O to alkene
- Used in industrial ethanol making process

But then what happens is this bisulfate gets hydrolyzed in presence of water, when the solution is heated mildly and HSO4- is released and water gets added. So again the net reaction is the addition of water to alkene and it forms an alcohol. So this reaction is generally used in industrial process of ethanol making.

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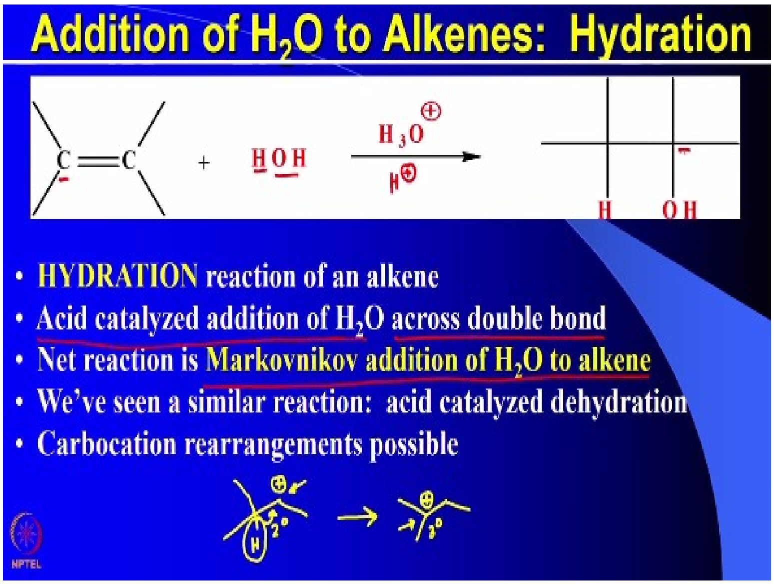

Addition of H_2O to Alkenes: Hydration

- HYDRATION reaction of an alkene
- Acid catalyzed addition of H_2O across double bond
- Net reaction is Markovnikov addition of H_2O to alkene
- We've seen a similar reaction: acid catalyzed dehydration
- Carbocation rearrangements possible

So when you try to add water to alkene, which is called the hydration reaction, it is generally acid catalyzed addition of water across a double bond and net reaction is Markovnikov addition of water to these alkene and you can see that one proton gets added to one of the carbon atoms, the OH group gets added to the other carbon atom and it is in the presence of H+, which is maybe dilute sulphuric acid.

And, in this particular type of type of reactions, it is possible to have a rearrangement of carbocation if possible, because if there is a possibility of hydride shift or a methyl shift, then the hydride orbital shift may happen and you may end up getting a more stable carbocation from a 2 degree carbocation.

For example in this case, if this hydride is shifted from here to this side, then we would get a carbocation formation at this point where it is a 3 degree carbocation and you might end up seeing a product where the OH is not connected to this carbon, rather OH gets connected to the 3 degree carboxyl and forms a new product.

So when you encounter such a situation you need to look at whether there is possibility of any hydride or methyl shift which may result into a more stable carbocation. And hence, you will see a different product that is being formed.

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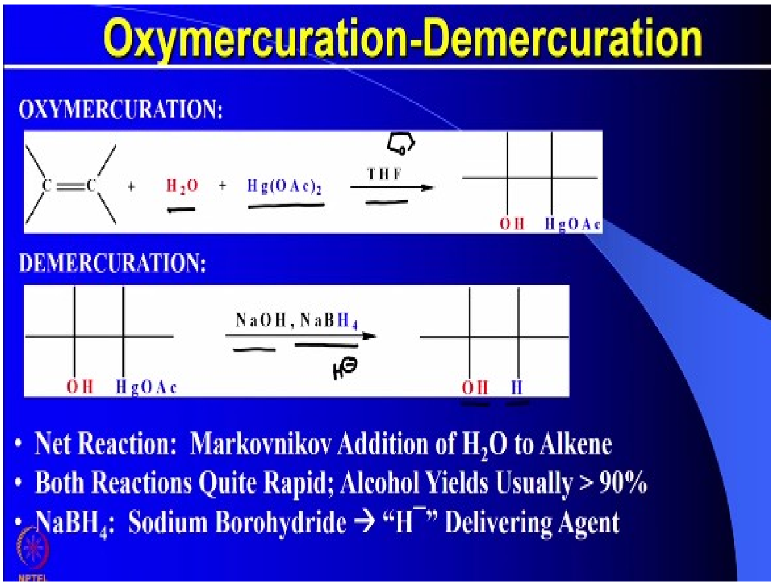

Oxymercuration-Demercuration

OXYMERCURATION:

DEMERCURATION:

- Net Reaction: Markovnikov Addition of H_2O to Alkene
- Both Reactions Quite Rapid; Alcohol Yields Usually > 90%
- $NaBH_4$: Sodium Borohydride → "H^-" Delivering Agent

Now let us see a different reaction called the oxymercuration and demercuration reactions on alkene. So when you treat an alkene compound, a double bonded molecule in the presence of water and mercury acetate in THF solvent, THF is tetrahydrofuran, which is used as a very common solvent.

The first step of this reaction follows Markovnikov addition rule and the OH and HgOAc are added across the double bond and in case of demercuration reaction in sodium hydroxide and NaBH4 sodium borohydride which is a reducing agent and also a supplier of hydride ion, you can get the H-OH addition, that is addition of water to alkene and both the reactions are quite rapid and its yield is nearly 90%.

Sodium borohydride acts as a hydride delivering agent and this also happens through the Markovnikov process.

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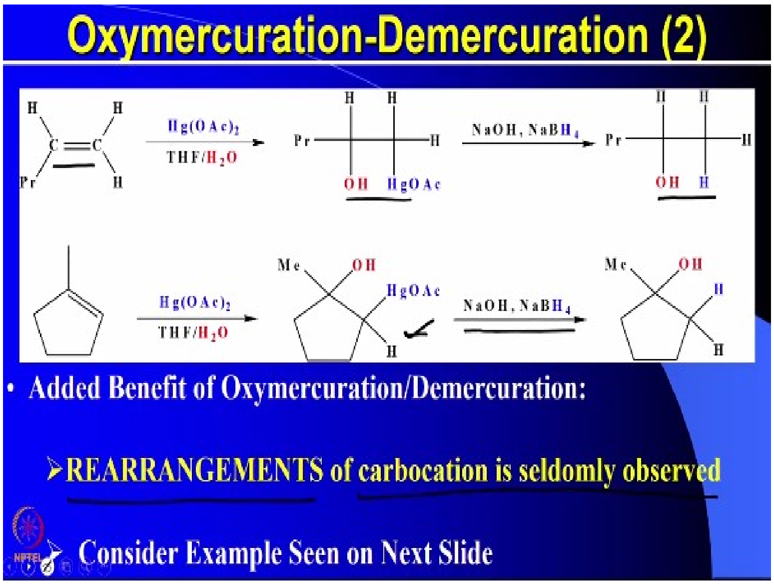

Oxymercuration-Demercuration (2)

- Added Benefit of Oxymercuration/Demercuration:
  - REARRANGEMENTS of carbocation is seldomly observed
  - Consider Example Seen on Next Slide

So if you have the unsymmetrical alkene, this goes through the Markovnikov addition process and forms a product which is a Markovnikov addition product of water. This type of reaction can be done on cyclic alkenes as well. So in case of cyclic alkene you get the intermediate like this, as we see here. And then on reacting with sodium hydroxide, sodium borohydride you get the water addition product.

But what you see here very important is that rearrangement of carbocation is not observed in most of the cases. So why does it happen? Let us see in the next slide.

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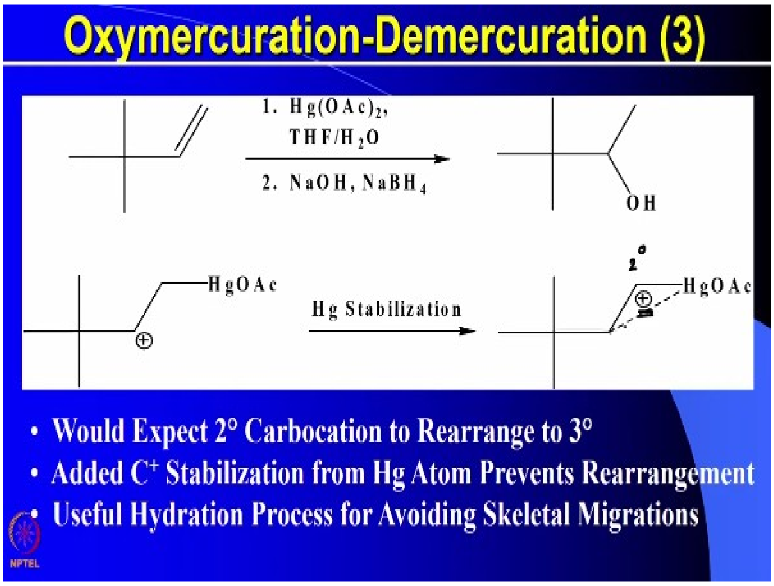

Oxymercuration-Demercuration (3)

- Would Expect 2° Carbocation to Rearrange to 3°
- Added C⁺ Stabilization from Hg Atom Prevents Rearrangement
- Useful Hydration Process for Avoiding Skeletal Migrations

This oxymercuration-demercuration process goes through the formation of a carbocation where the mercury is bonded to two carbon atoms simultaneously because of its very large size. And this 2 degree carbocation is not possibly to go for any rearrangement to go for a 3 degree carbocation because this mercury forms a partial single bond with both the carbon atoms and it does not allow for the formation of or shift of hydride and forming more stable carbocation.

Therefore, in this particular mechanism, you do not get a variety of product, rather you get only one product.

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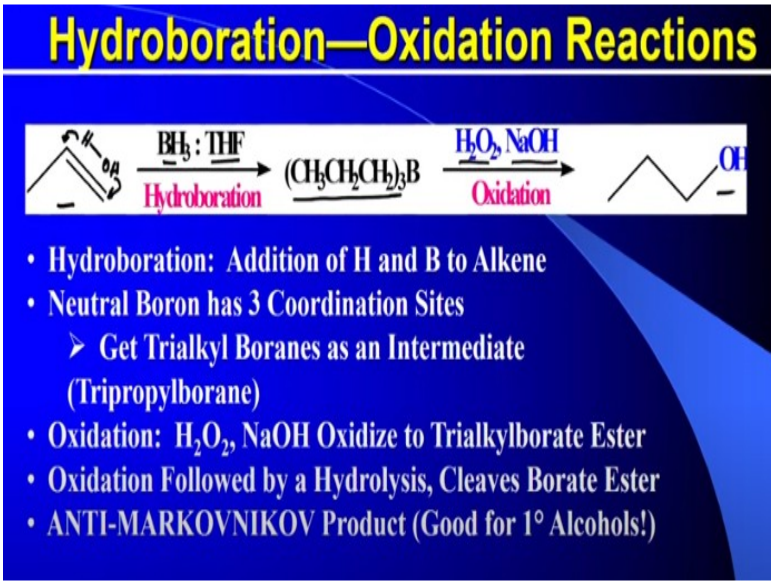

Hydroboration—Oxidation Reactions

$\xrightarrow[\text{Hydroboration}]{BH_3 : THF} (CH_3CH_2CH_2)_3B \xrightarrow[\text{Oxidation}]{H_2O_2, NaOH}$

- Hydroboration: Addition of H and B to Alkene
- Neutral Boron has 3 Coordination Sites
  - ➢ Get Trialkyl Boranes as an Intermediate (Tripropylborane)
- Oxidation: H_2O_2, NaOH Oxidize to Trialkylborate Ester
- Oxidation Followed by a Hydrolysis, Cleaves Borate Ester
- ANTI-MARKOVNIKOV Product (Good for 1° Alcohols!)

If we do the same reaction with a slightly different reagent we try to add water, but we add this water using hydroboration-oxidation mechanism. So if you treat this alkene with BH3 THF medium, first it forms this boron compound trialkyl borane and then the trialkyl borane is hydrolyzed by H2O/NaOH are oxidized to form this compound which you see that is an anti-Markovnikov product.

So in this process water is added across this double bond in this way. H gets added here and OH gets added here compared to all the previous cases where H and OH were getting added in the opposite direction.

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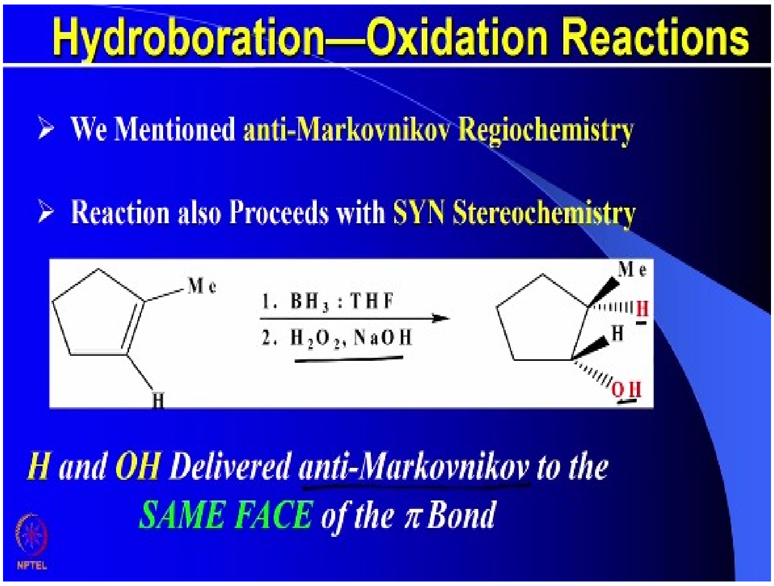

Hydroboration—Oxidation Reactions

- We Mentioned anti-Markovnikov Regiochemistry
- Reaction also Proceeds with SYN Stereochemistry

H and OH Delivered anti-Markovnikov to the SAME FACE of the π Bond

So here what we see is called the anti-Markovnikov regioselectivity or regiochemistry. And these reaction also proceeds through SYN stereochemistry. So if you had a double bond as one here, the first step is borohydride addition, BH3 addition in THF and then oxidation by H2O2, what we see here is that H and OH are delivered from the same side of the double bond.

So it is either delivered both from bottom or both are delivered from top and hence, this mechanism is called a SYN addition and this addition follows anti-Markovnikov product or anti-Markovnikov mechanism.

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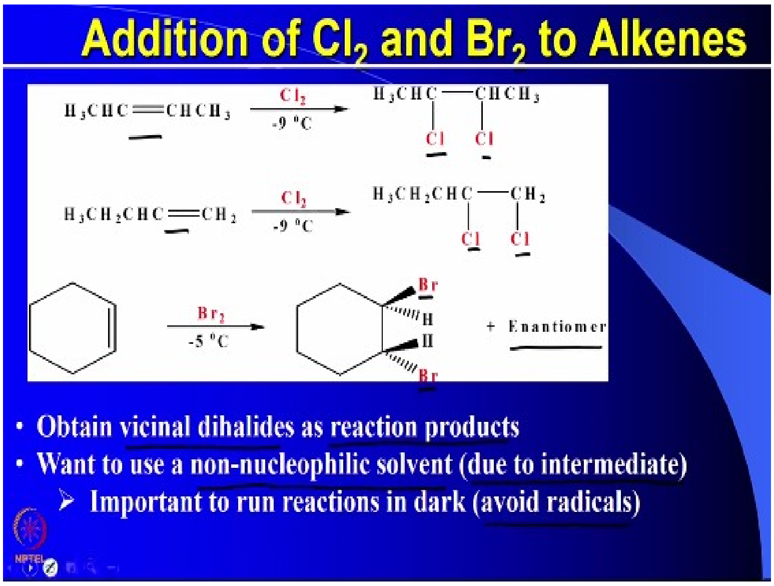

Addition of Cl_2 and Br_2 to Alkenes

- Obtain vicinal dihalides as reaction products
- Want to use a non-nucleophilic solvent (due to intermediate)
  - Important to run reactions in dark (avoid radicals)

So when you try to add chlorine or bromine to alkene, it is very easy. You can bubble chlorine or bromine through a solution or a solution of bromine or chlorine in CCl4 can be added to a double bonded compound and we get dichloride or dibromide. If we add bromine to a cyclic compound, it is very easy to see that the addition of bromine can take place from top and bottom.

But what we see is that the addition of two bromine atoms are in anti-position and the corresponding other enantiomer is also formed. So in this reactions, we get we vicinal dihalide as reaction product. We want to use a non-nucleophilic solvent due to the intermediate that is formed which we will see in the next slide. And it is important to run the reaction in the dark to avoid formation of active radicals.

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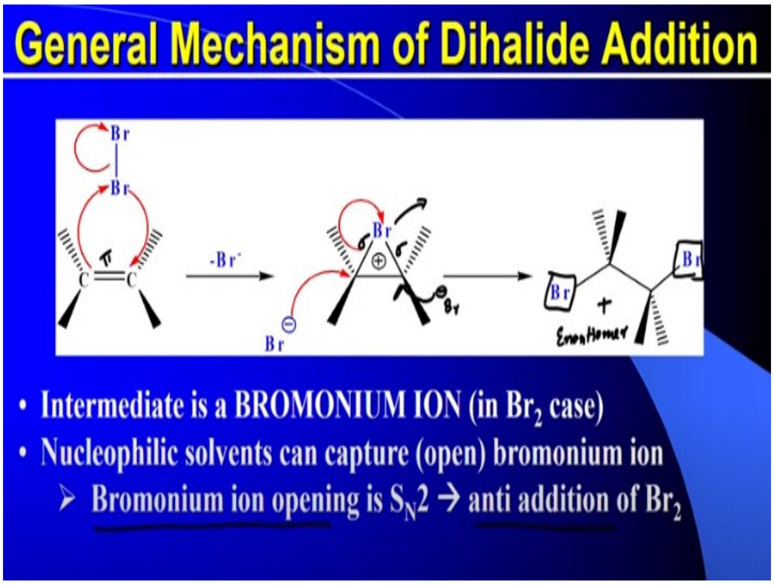

General Mechanism of Dihalide Addition

- Intermediate is a BROMONIUM ION (in Br_2 case)
- Nucleophilic solvents can capture (open) bromonium ion
    - Bromonium ion opening is S_N2 → anti addition of Br_2

So the mechanism of this reaction is interesting. When you add bromine to a double bond, the first thing that happens is breaking of this pi bond and formation of two sigma bonds with bromine making a positive charge at the center. And this is called the bromonium ion. And then this Br- can attack the either carbon from two sides to give this product plus the corresponding enantiomer.

And this addition makes it anti-addition. So if bromine comes from the bottom, this bromine goes up. So you get two bromine atoms bundle across the C-C single bond, they are in anti-position.

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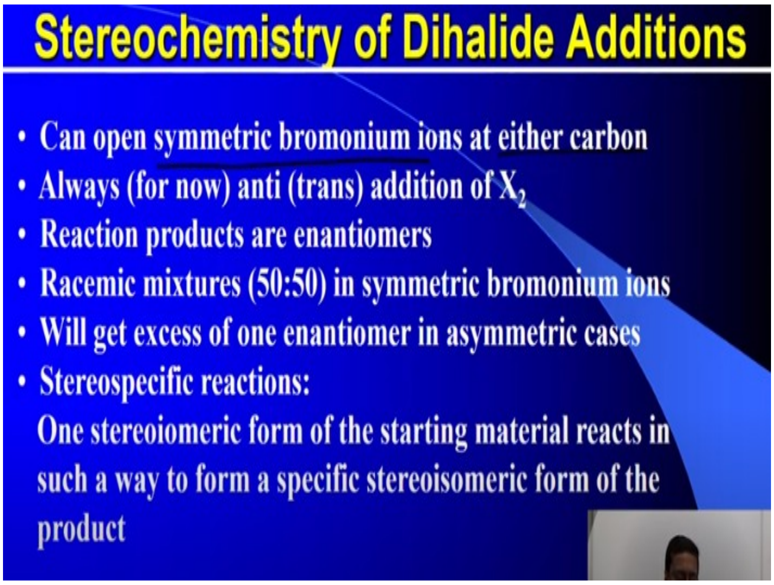

Stereochemistry of Dihalide Additions

- Can open symmetric bromonium ions at either carbon
- Always (for now) anti (trans) addition of X_2
- Reaction products are enantiomers
- Racemic mixtures (50:50) in symmetric bromonium ions
- Will get excess of one enantiomer in asymmetric cases
- Stereospecific reactions:
  One stereoiomeric form of the starting material reacts in such a way to form a specific stereoisomeric form of the product

So in case of dihalide addition, it can open symmetric bromonium ions at either side. Always anti or trans addition of halogen takes place. Reaction products are enantiomers, but there is no specificity for this reaction. So it is always you get a racemic mixture in case of symmetric bromonium ions. You will get excess of one enantiomeric product in asymmetric cases.

And this is a stereospecific reaction where one stereoisomeric form of the starting material reacts in such a way to form a specific stereoisomeric form of the product. So we will discuss about stereospecificity also in the next week. So from here we will continue in the next class.