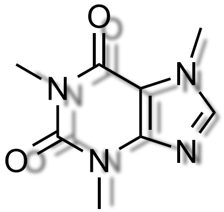


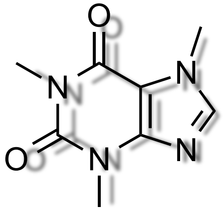
Chem 2500

Chapter 8

π Bonds as Nucleophiles

(sections 8.1-8.8)

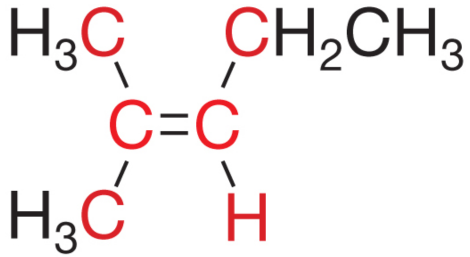
Properties of Carbon-Carbon π Bonds



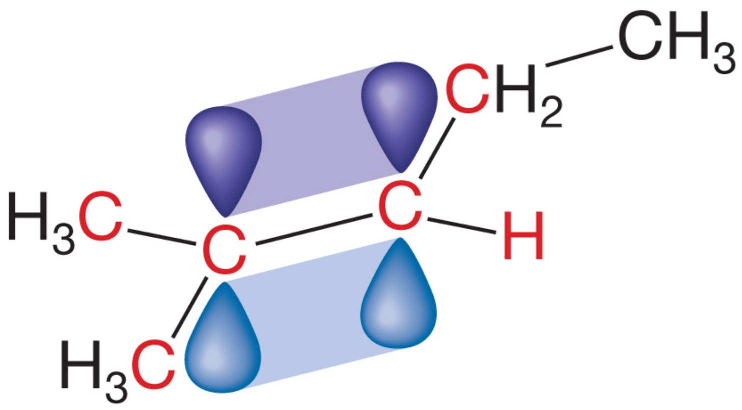
- Alkenes and alkynes are functional groups characterized by carbon-carbon double bonds and carbon-carbon triple bonds respectively.
- These groups consist of carbon atoms connected by a σ bond and one or more π bonds.
- These functional groups are good electron donors as the multiple bonds connecting the carbon atoms is an area of high electron density.
- The reactivity of these groups is derived from these π bonds, which are excellent nucleophiles.

Orbital Structure of Alkenes

- As with carbonyl groups, the two carbon atoms connected by a double bond are trigonal planar (sp^2 hybridized); the are connected together by a σ bond and a π bond.
- The 2 carbon atoms of the double bond and the 4 atoms attached to them all lie in a plane.

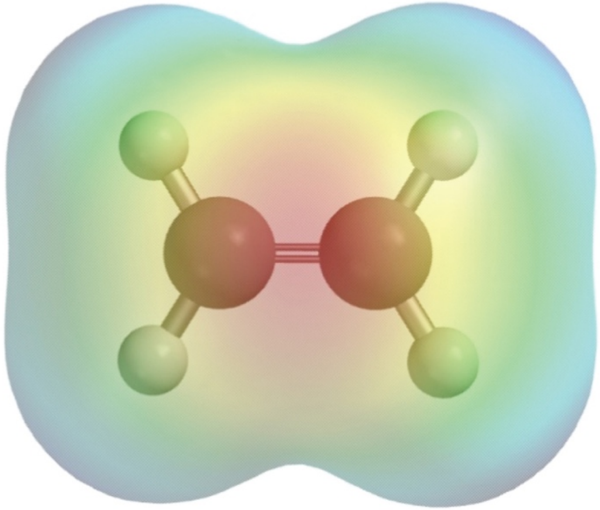


all red atoms lie in the same plane

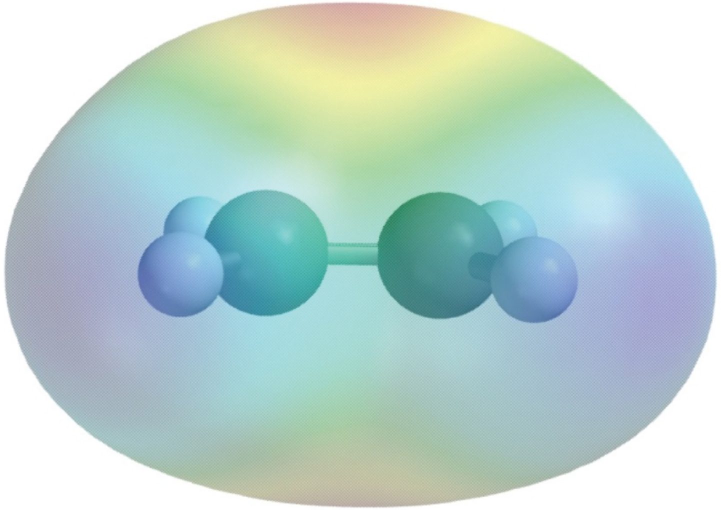


Orbital Structure of Alkenes

- The electrostatic potential map shows an area of high electron density at the centre of the carbon-carbon multiple bond.
- Alkenes are electron rich, with the π electrons found on both ‘faces’ of the group.
- Alkenes are nucleophilic and interact with electrophiles.



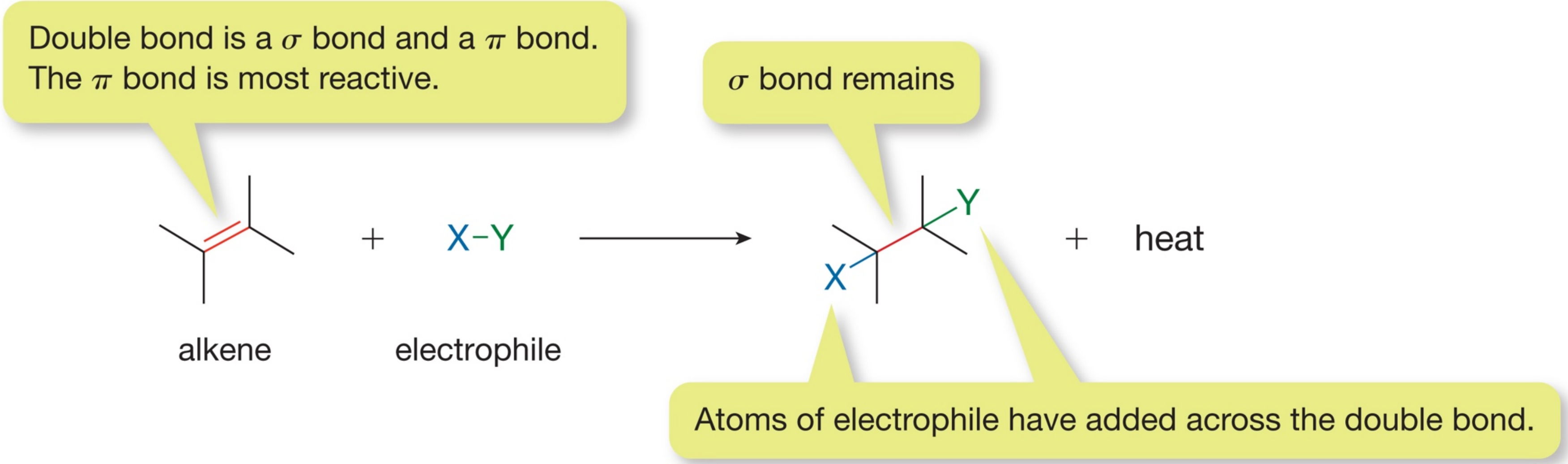
(a)



(b)

Electrophilic Addition Reactions

- The most common reaction of alkenes is the addition of atoms or groups to the carbon atoms of the double bond.
- In this reaction, the π bond is broken and 2 new σ bonds are formed; one to each carbon atom of the double bond.
- Note that only the π bond of the double bond breaks, the σ bond remains intact.



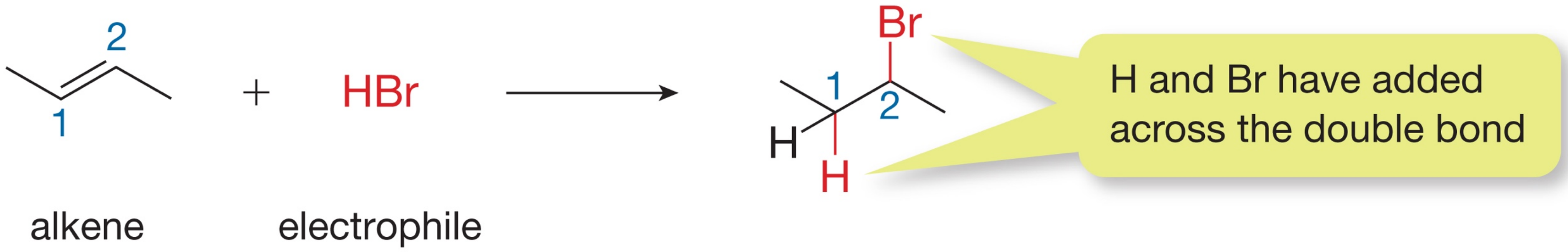
Double bond is a σ bond and a π bond. The π bond is most reactive.

σ bond remains

Atoms of electrophile have added across the double bond.

Addition of Hydrogen Halides to Alkenes

- The addition of hydrogen halides (HF, HCl, HBr, or HI) to an alkene follow this general equation:



H and Br have added across the double bond

- The electron rich alkene acts as the nucleophile and is attracted to the hydrohalogen (HBr), the electrophile.

Addition of Hydrogen Halides to Alkenes

- Because the bromine is more electronegative than hydrogen, the bond in H-Br is polarized towards bromine, making the hydrogen slightly positive. This is the electrophilic site which attracts the nucleophilic π bond of the alkene.

the π electrons are used to form a σ bond between one carbon of the alkene and the hydrogen of the electrophile

addition of hydrogen forms a carbocation

bromide leaving group

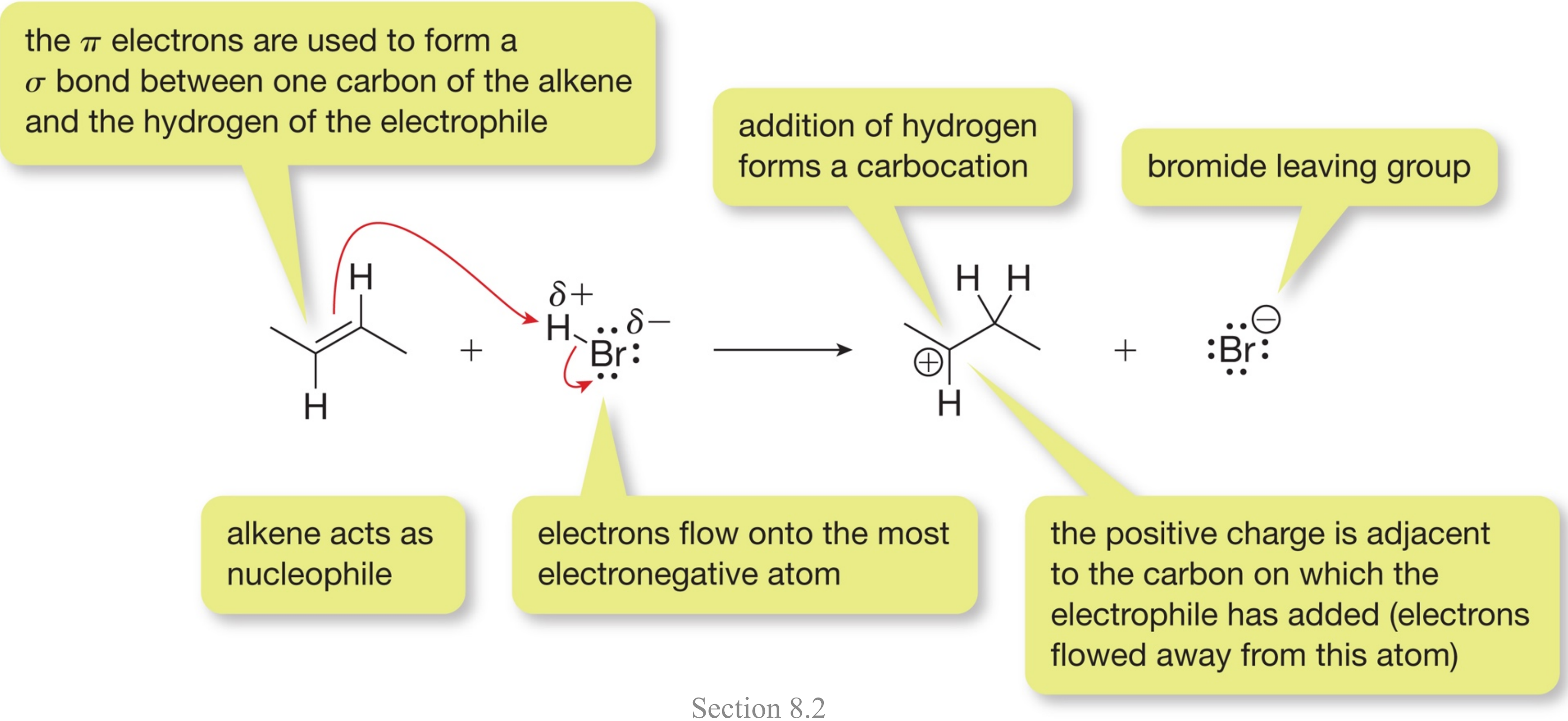
alkene acts as nucleophile

electrons flow onto the most electronegative atom

the positive charge is adjacent to the carbon on which the electrophile has added (electrons flowed away from this atom)

Addition of Hydrogen Halides to Alkenes

- This first step produces a ***carbocation***, an electron deficient carbon atom. Carbocations have high energy and are reactive species.
- Both the carbocation and bromide ion are ***reaction intermediates***; products of a reaction that are consumed in a subsequent step.



the π electrons are used to form a σ bond between one carbon of the alkene and the hydrogen of the electrophile

addition of hydrogen forms a carbocation

bromide leaving group

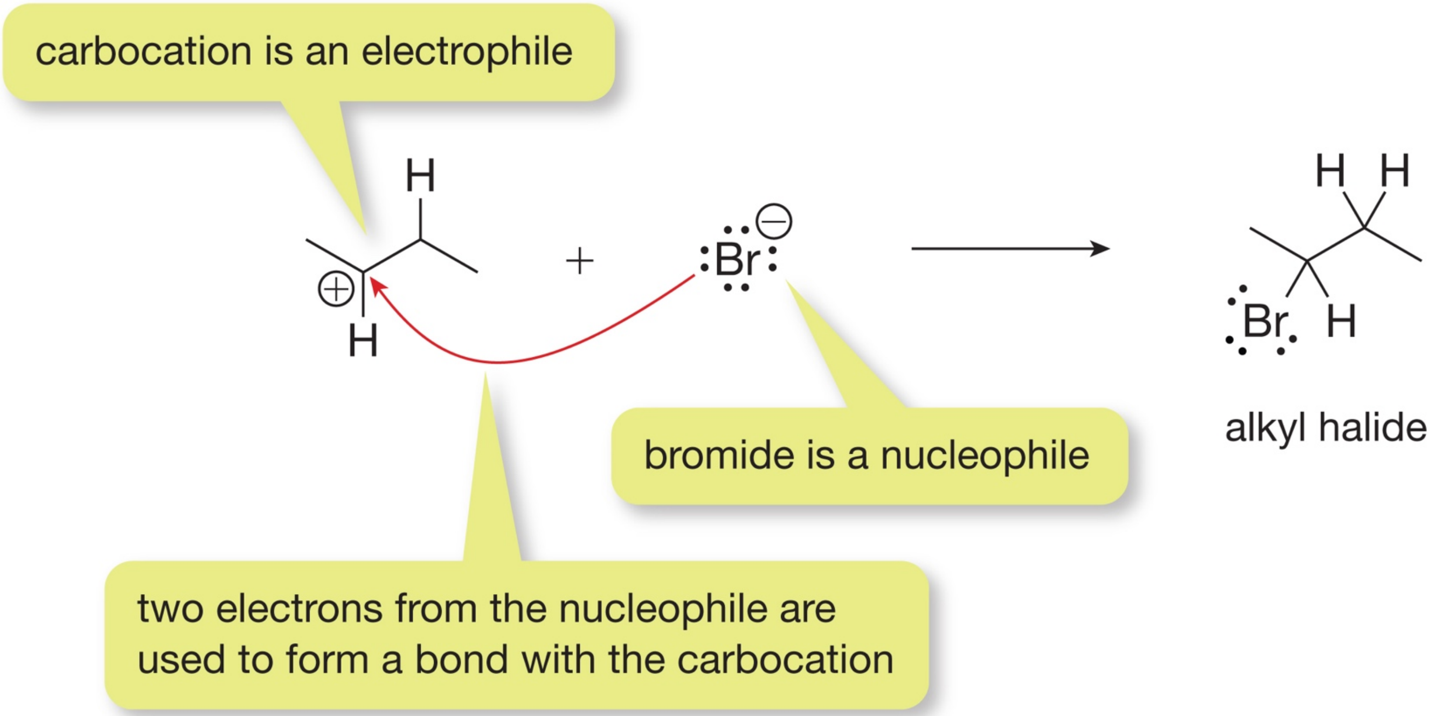
alkene acts as nucleophile

electrons flow onto the most electronegative atom

the positive charge is adjacent to the carbon on which the electrophile has added (electrons flowed away from this atom)

Addition of Hydrogen Halides to Alkenes

- The bromide intermediate has excess electrons and is a nucleophile. The carbocation is electron deficient and is an electrophile.
- In the second step of this mechanism, the nucleophilic bromide attacks the electrophilic carbocation to product a new σ bond.



carbocation is an electrophile

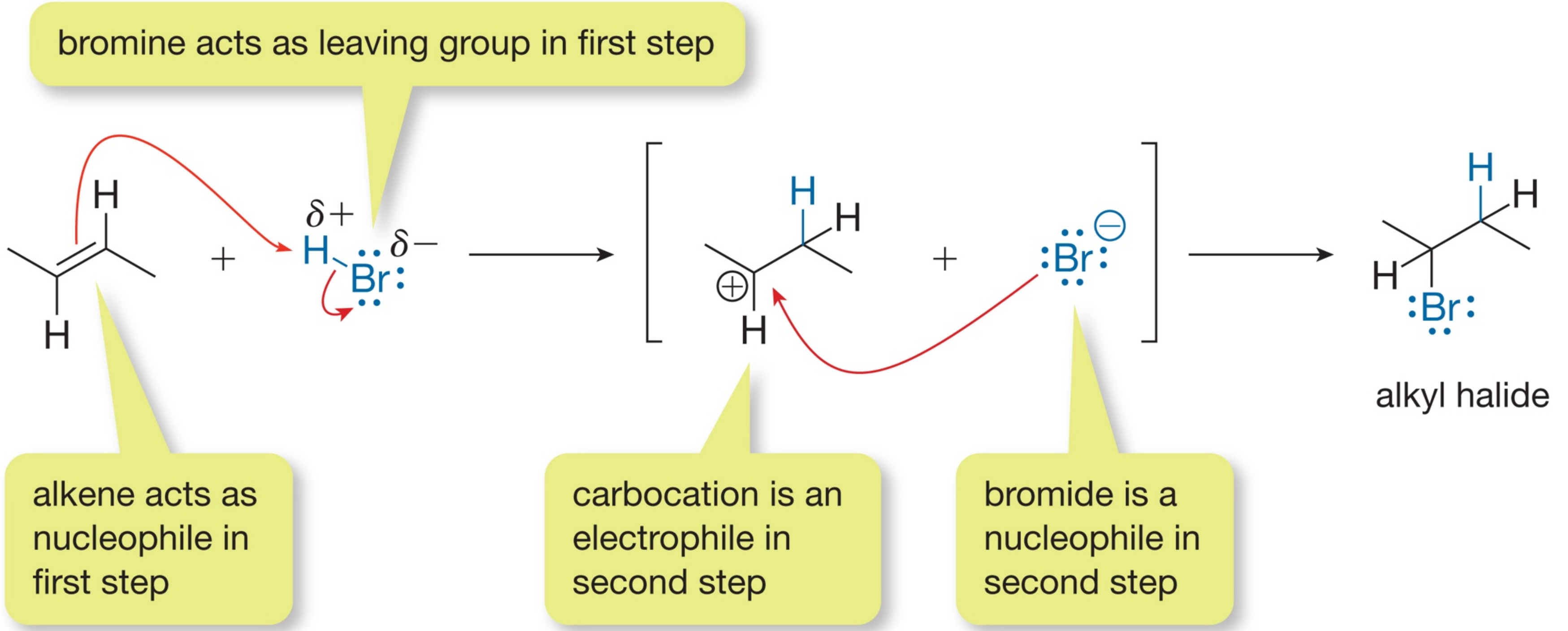
bromide is a nucleophile

alkyl halide

two electrons from the nucleophile are used to form a bond with the carbocation

Addition of Hydrogen Halides to Alkenes

- The overall result of this 2 step mechanism is to add a hydrogen atom to one end of the carbon-carbon double bond and add a bromine atom to the other
- The reaction is said to add H-Br *across the double bond*.



bromine acts as leaving group in first step

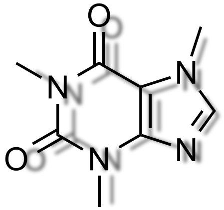
alkene acts as nucleophile in first step

carbocation is an electrophile in second step

bromide is a nucleophile in second step

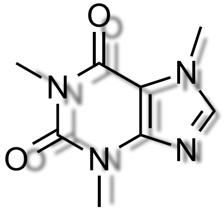
alkyl halide

Carbocation Formation and Function



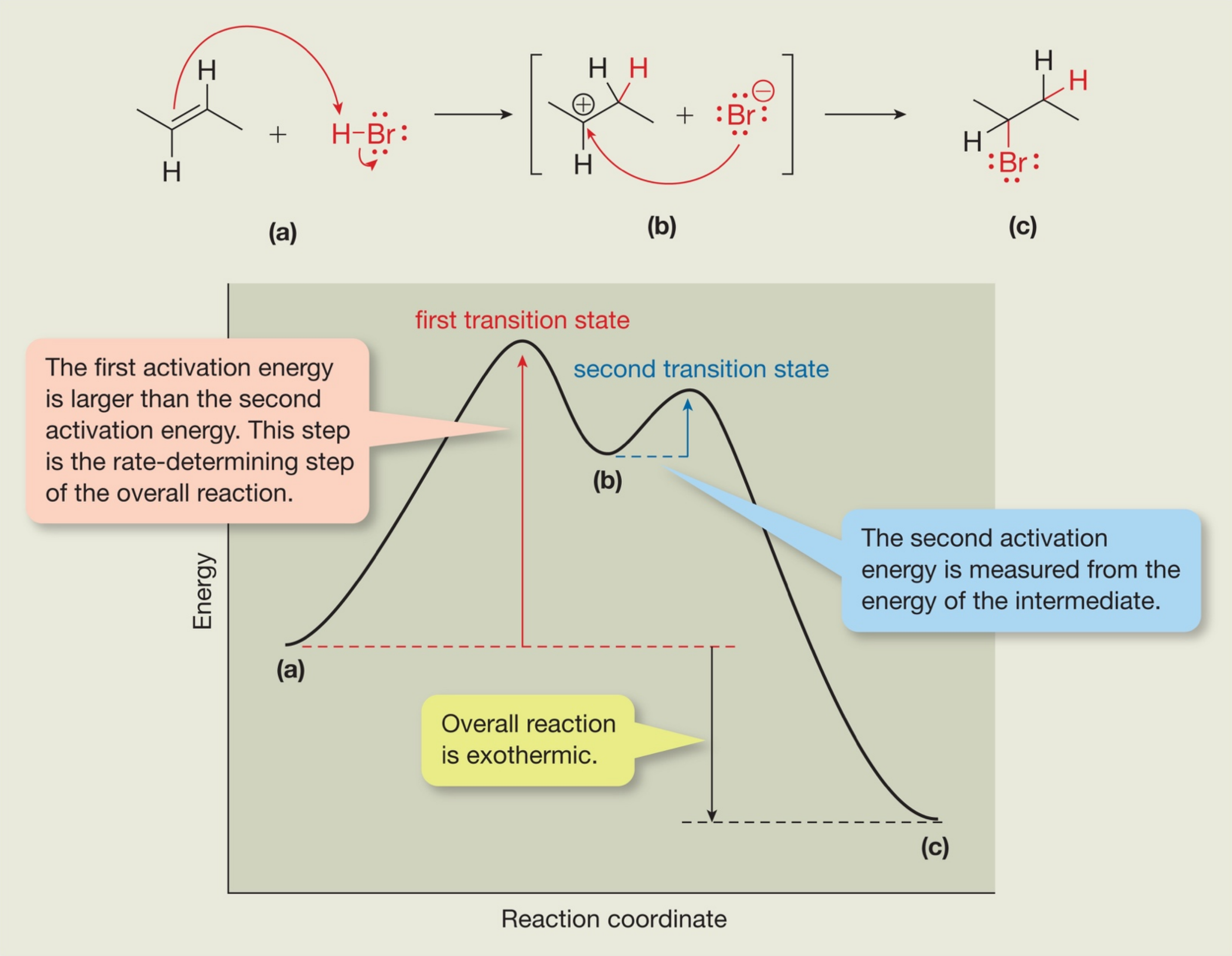
- The formation of a carbocation controls every aspect of electrophilic addition reactions.
- The rate of carbocation formation controls:
  - The reaction rate
  - The *location* to which electrophiles become attached to the alkene
  - The relative *amounts* of each product
- The nature of the carbocation can even influence the stereochemistry of the products.
- ***All of these aspects are influenced by the energy of the carbocation***.

Carbocation Formation and Function



- The ***rate-determining step*** of a chemical reaction is the step with the highest activation barrier.
- Because is it the slowest step, it controls the overall rate of the reaction.
- The rate-determining step for electrophilic addition reactions to alkenes is governed by the formation of the high-energy carbocation.

Carbocation Formation and Function

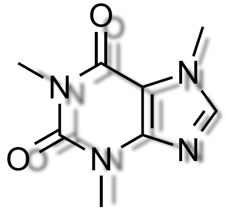


The first activation energy is larger than the second activation energy. This step is the rate-determining step of the overall reaction.

The second activation energy is measured from the energy of the intermediate.

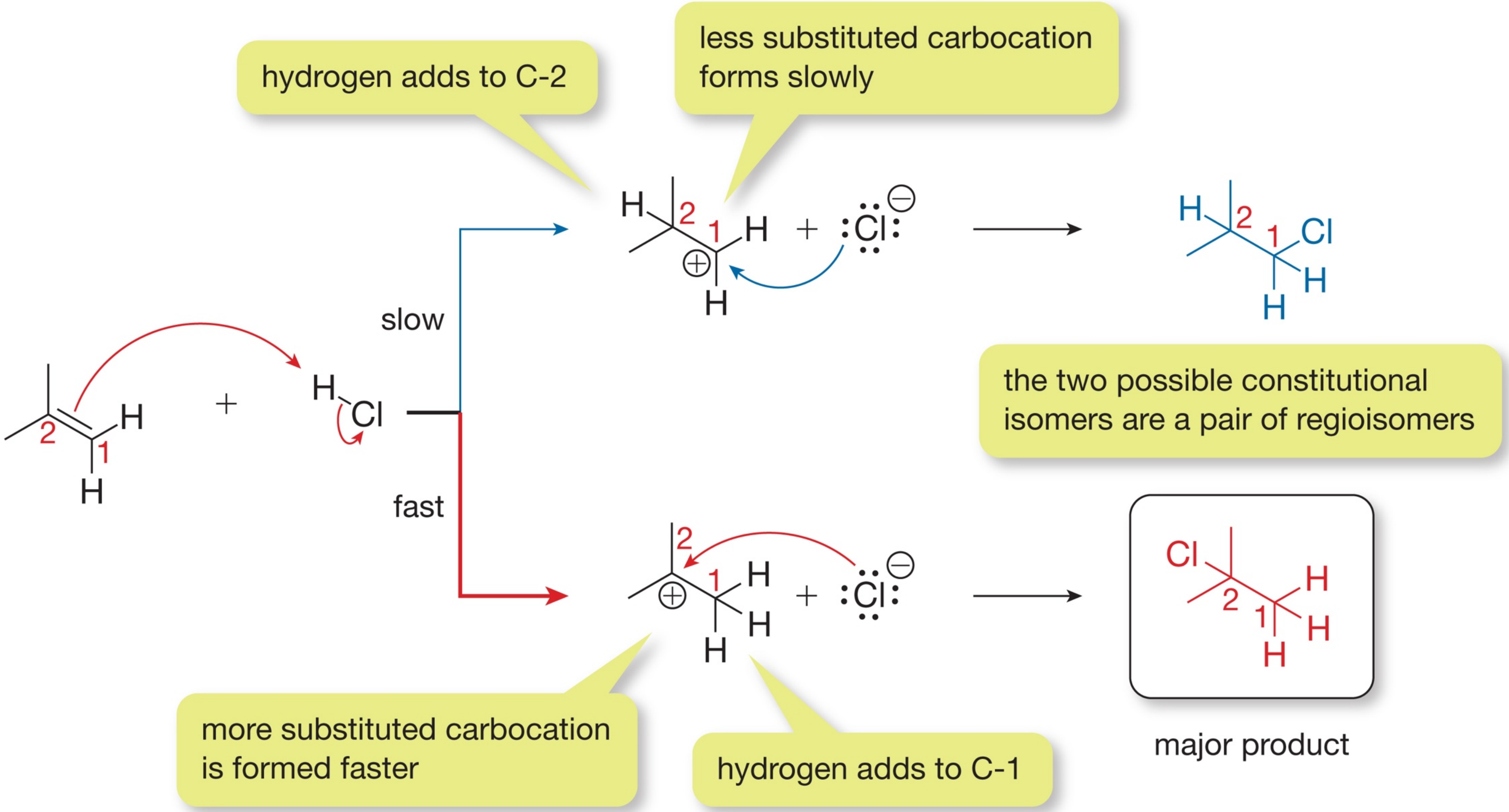
Overall reaction is exothermic.

Regioselectivity in Electrophilic Addition Reactions



- When an unsymmetrical alkene reacts with a haloacid, the hydrogen atom can bond to either carbon of the double bond. This gives 2 possible carbocation intermediates and therefore 2 different possible products.
- These products are ***regioisomers***; constitutional isomers formed when a reaction takes place at different locations of a molecule.
- The carbocation intermediate which is more stable will be formed faster.
- Reactions that produce more of one regioisomer than the other are said to be ***regioselective***

Regioselectivity in Electrophilic Addition Reactions



hydrogen adds to C-2

less substituted carbocation forms slowly

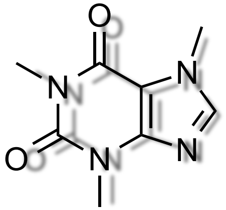
the two possible constitutional isomers are a pair of regioisomers

more substituted carbocation is formed faster

hydrogen adds to C-1

major product

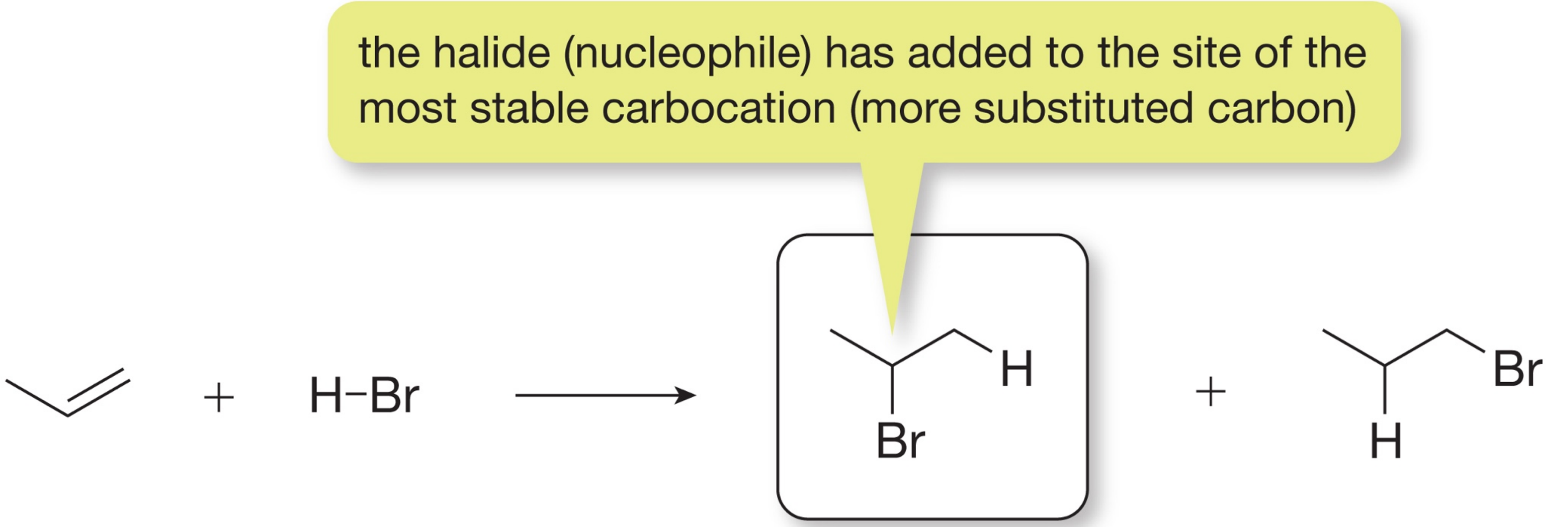
Markovnikov’s Rule



- In 1870, Russian chemist Vladimir Markovnikov observed that when an unsymmetrical alkene reacted with a halo halide, one regioisomer was produced in greater proportion than the other.
- Markovnikov described a method to predicting the regioselectivity of unsymmetrical alkenes with halo halides; he called this ***Markovnikov’s Rule***.
- The *modern interpretation* of Markovnikov’s rule is that the major product is the one formed from the most stable carbocation.

Markovnikov's Rule

- The *modern interpretation* of Markovnikov's rule is that the major product is the one formed from the most stable carbocation.



the halide (nucleophile) has added to the site of the most stable carbocation (more substituted carbon)

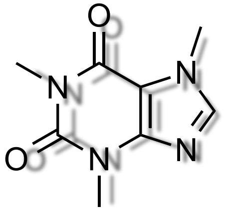
propene

2-bromopropane

1-bromopropane

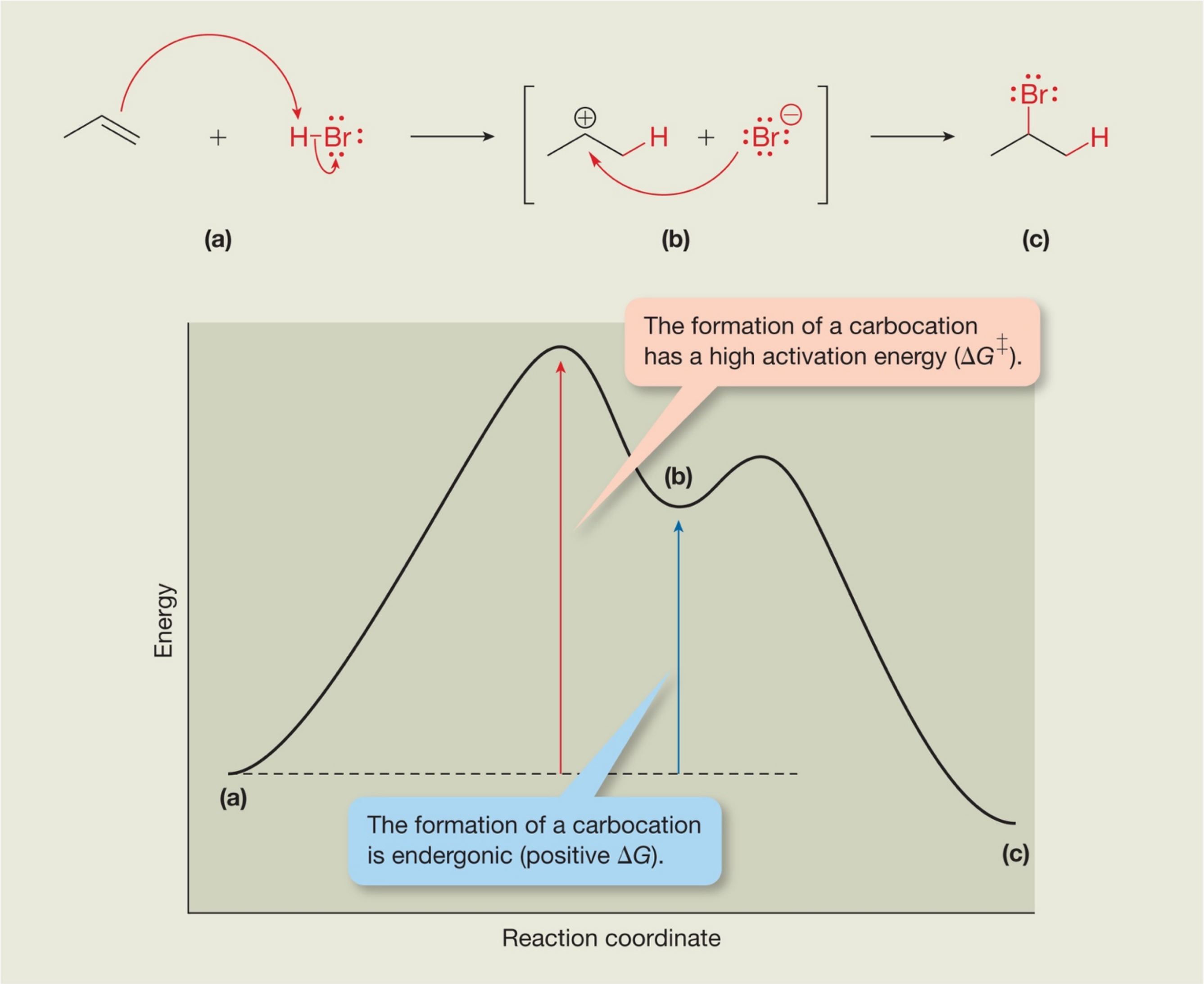
Markovnikov product

Carbocation Stability

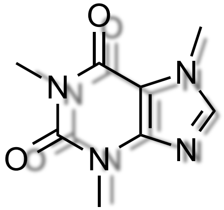


- If the regioselectivity is dictated by the carbocation formed, it is important to understand the factors which affect carbocation stability.
- Carbocations are high energy species because of the formal charge on an atom with an incomplete octet.
- Any factor which can reduce the effective positive charge on the carbocation will make it more stable.
- As a result, different carbocations form at different rates; more stable carbocations form at a much higher rate than less stable ones.

Carbocation Stability



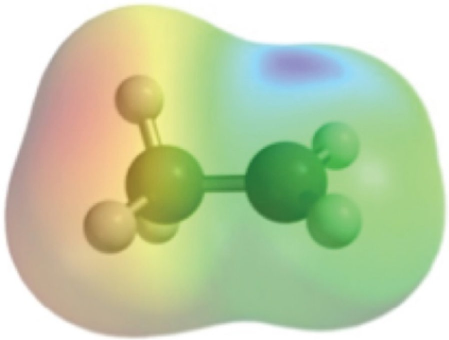
Carbocation Stability



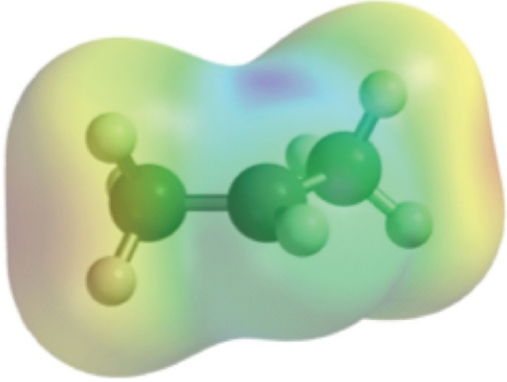
- The structural classification of a carbocation depends on the number of alkyl carbons directly bonded to the carbocation:
  - 0 alkyl carbons = methyl carbocation
  - 1 alkyl carbon = primary (1°) carbocation
  - 2 alkyl carbons = secondary (2°) carbocation
  - 3 alkyl carbons = tertiary (3°) carbocation
- Carbocations that have more alkyl groups bonded directly to them are more stable.

Carbocation Stability

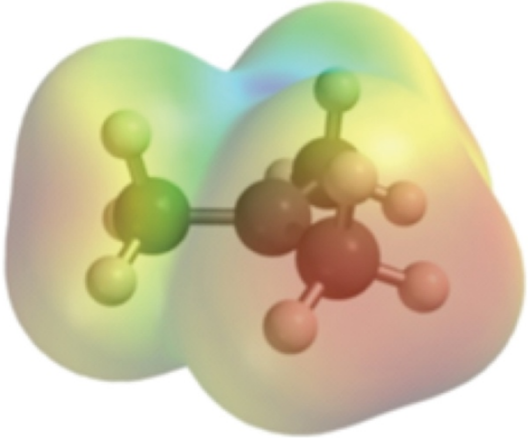
- Although carbocations have a formal charge of +1, most have an *effective* charge less than +1.
- Because alkyl groups are ***electron donating groups*** (EDGs), if directly bonded to a cationic carbon atom, they help reduce the effective positive charge on the carbocation. The more alkyl groups attached, the lower the effective charge.



primary carbocation
$(CH_3C^{\oplus}H_2)$



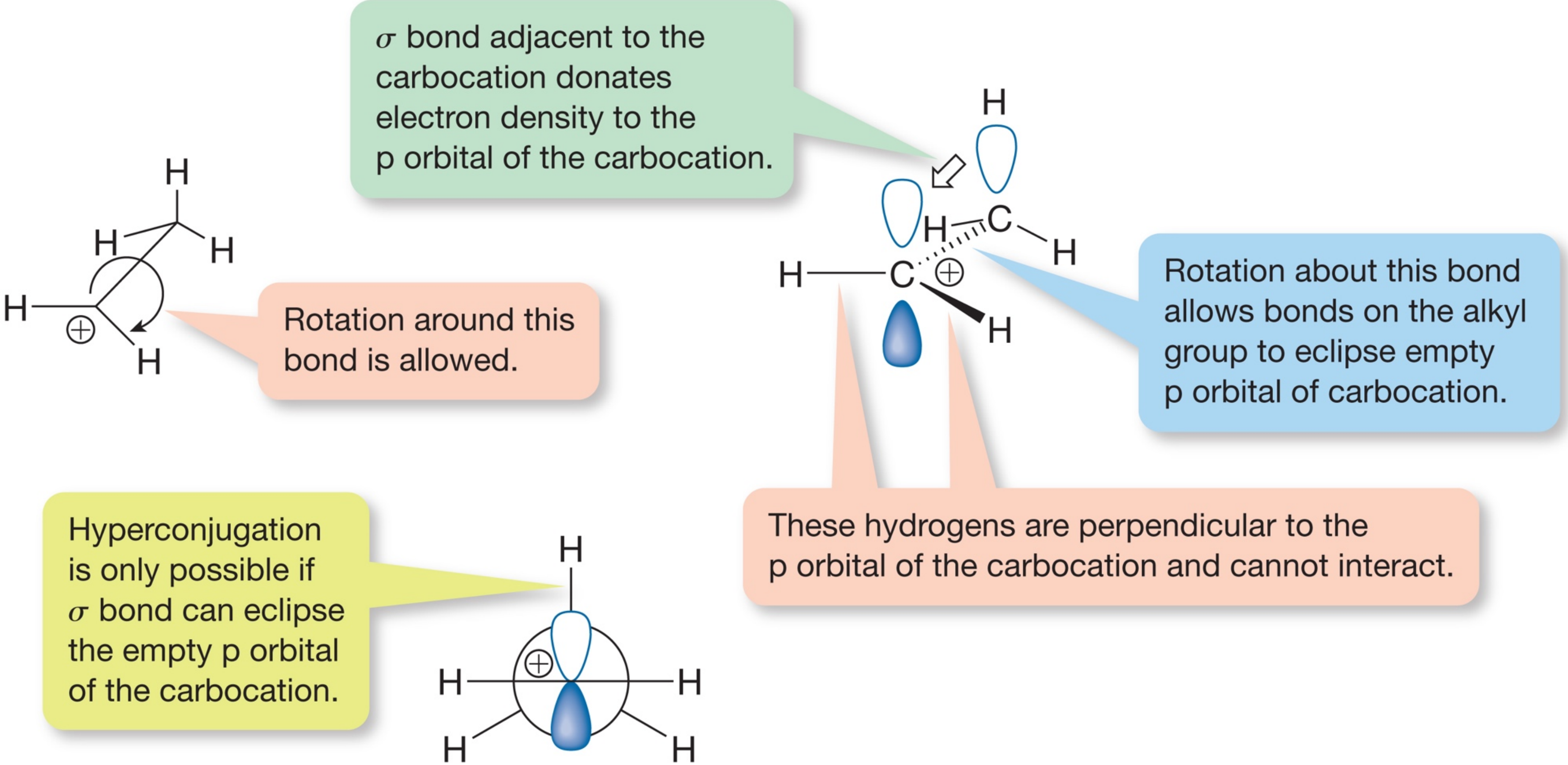
secondary carbocation
$(CH_3C^{\oplus}HCH_3)$



tertiary carbocation
$(CH_3C^{\oplus}(CH_3)CH_3)$

Carbocation Stability – Hyperconjugation

- Alkyl groups stabilize carbocations through a process called ***hyperconjugation*** – the interaction of the empty p orbital of the carbocation with the filled σ bonds on the adjacent carbon atoms.



σ bond adjacent to the carbocation donates electron density to the p orbital of the carbocation.

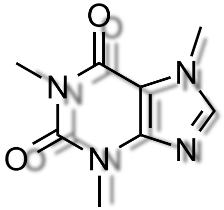
Rotation around this bond is allowed.

Rotation about this bond allows bonds on the alkyl group to eclipse empty p orbital of carbocation.

These hydrogens are perpendicular to the p orbital of the carbocation and cannot interact.

Hyperconjugation is only possible if σ bond can eclipse the empty p orbital of the carbocation.

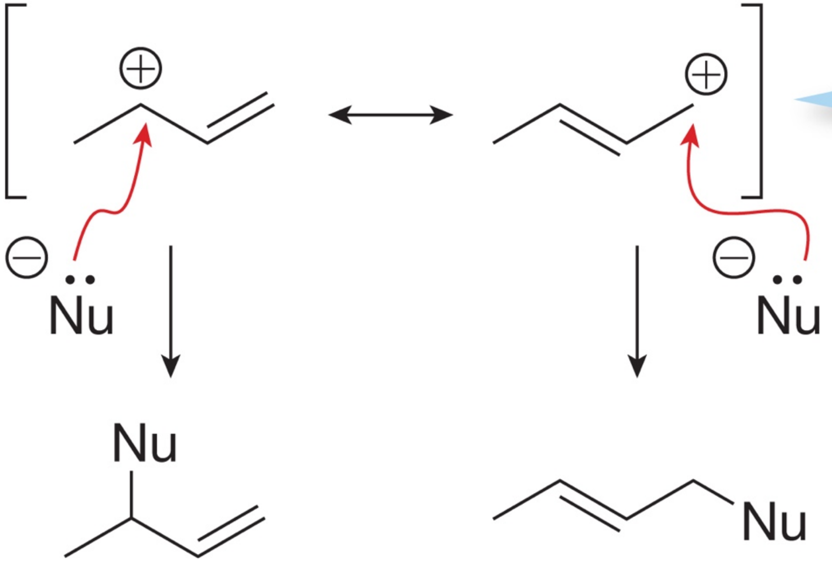
Carbocation Stability – Hyperconjugation



- When more alkyl groups are bonded to a carbocation, more hyperconjugation occurs, the effective +1 charge is reduced, and the stability of the carbocation increases.
- Therefore, the stability of carbocations can be ranked as follows:
  3° > 2° > 1° > methyl.

Carbocation Stability – Charge Delocalization

- Carbocations are also stabilized by delocalizing the charge via resonance structures. Carbocations adjacent to π bonds spread the positive charge over several atoms, increasing its stability.
- This also increases the number of sites that can react in subsequent transformations.

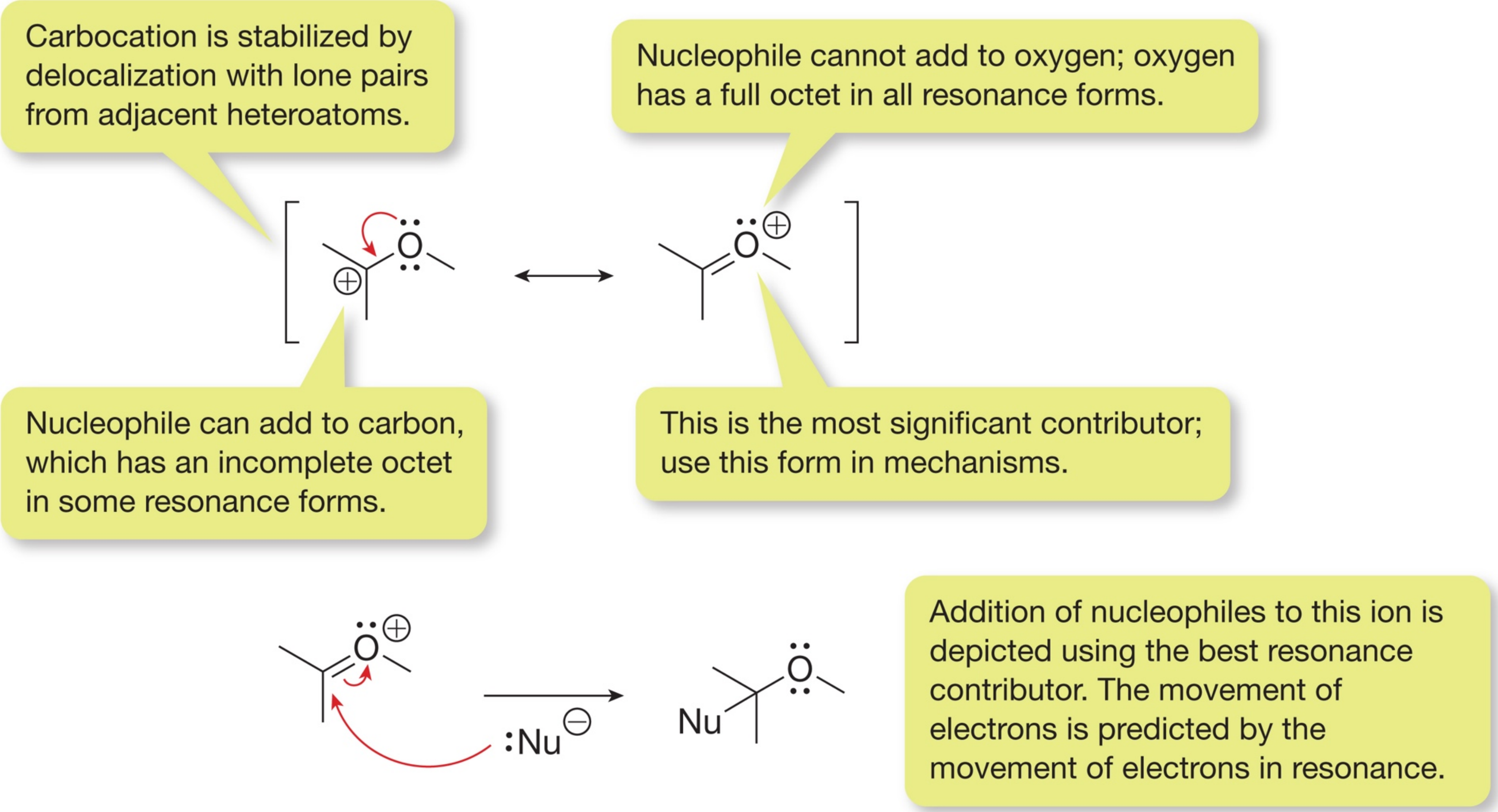


Carbocation is stabilized by delocalization with π bond.

Two reaction sites are available for nucleophiles to react with. Reaction sites can be predicted from the resonance forms.

Carbocation Stability – Charge Delocalization

- Adjacent atoms with lone pairs to can also delocalize the positive charge. This is very common with oxygen and nitrogen.



Carbocation is stabilized by delocalization with lone pairs from adjacent heteroatoms.

Nucleophile cannot add to oxygen; oxygen has a full octet in all resonance forms.

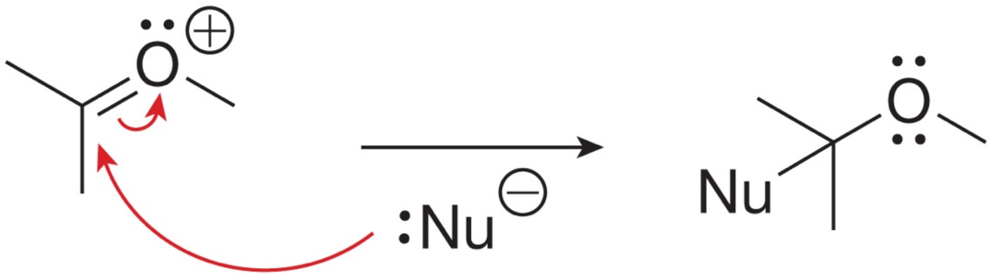
Nucleophile can add to carbon, which has an incomplete octet in some resonance forms.

This is the most significant contributor; use this form in mechanisms.

Addition of nucleophiles to this ion is depicted using the best resonance contributor. The movement of electrons is predicted by the movement of electrons in resonance.

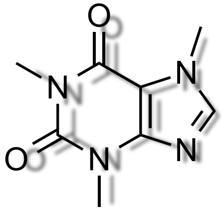
Carbocation Stability – Charge Delocalization

- Generally, charge delocalization has a greater stabilization effect than hyperconjugation.
- Therefore, reactions which proceed through charged delocalized carbocations can be exhibit a high degree of regioselectivity.



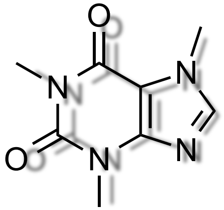
Addition of nucleophiles to this ion is depicted using the best resonance contributor. The movement of electrons is predicted by the movement of electrons in resonance.

Applying the Hammond Postulate

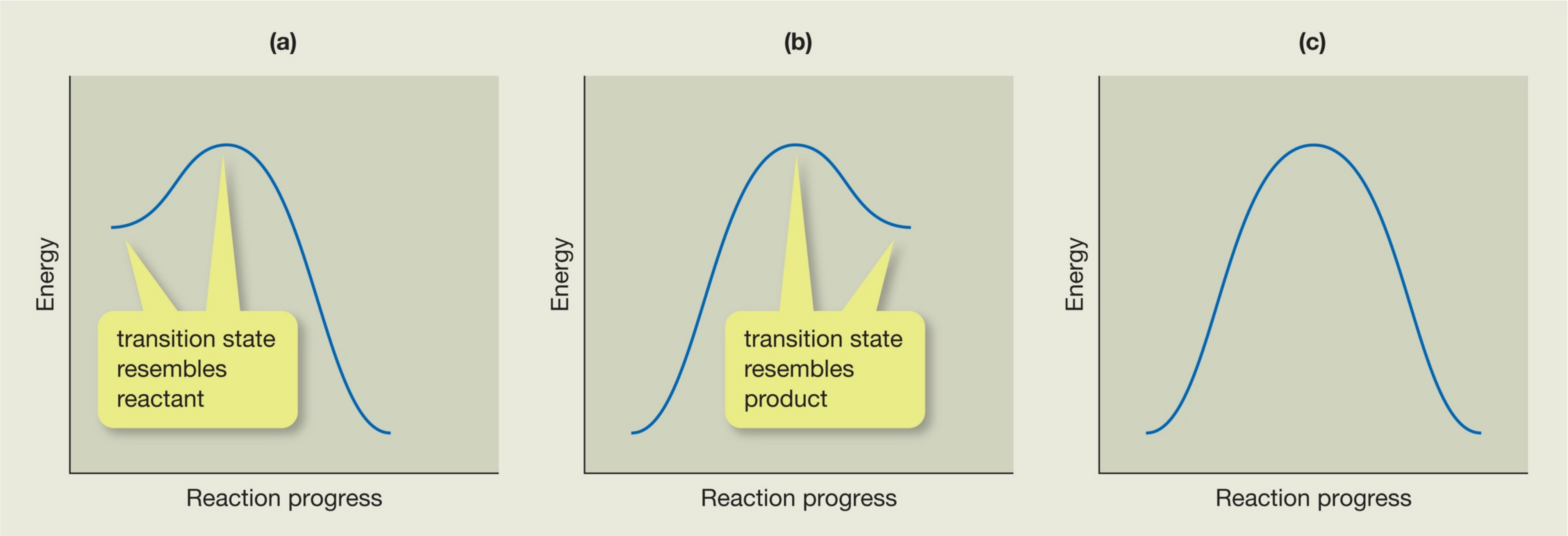


- The carbocations that forms the fastest leads to the major product of the reaction.
- The rate of formation depends on the activation energy which, in turn, depends on the energy of the transition state.
- Transition states are difficult to study because they cannot be directly observed nor isolated. Thus their energies cannot be directly measured.
- ***The Hammond Postulate*** state that the structure of the transition state resembles the species nearest to it in free energy.
- Therefore, the Hammond Postulate uses the energy of an intermediate or product to estimate the energy of nearby transition states.

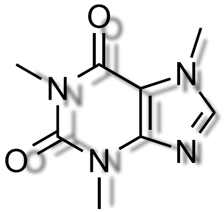
Applying the Hammond Postulate



- A transition state closer in energy to the reactants is called an ***early transition state***. A transition state closer in energy to the products is called a ***late transition state***. A transition state that is not close to either the reactants or products, resembles neither.

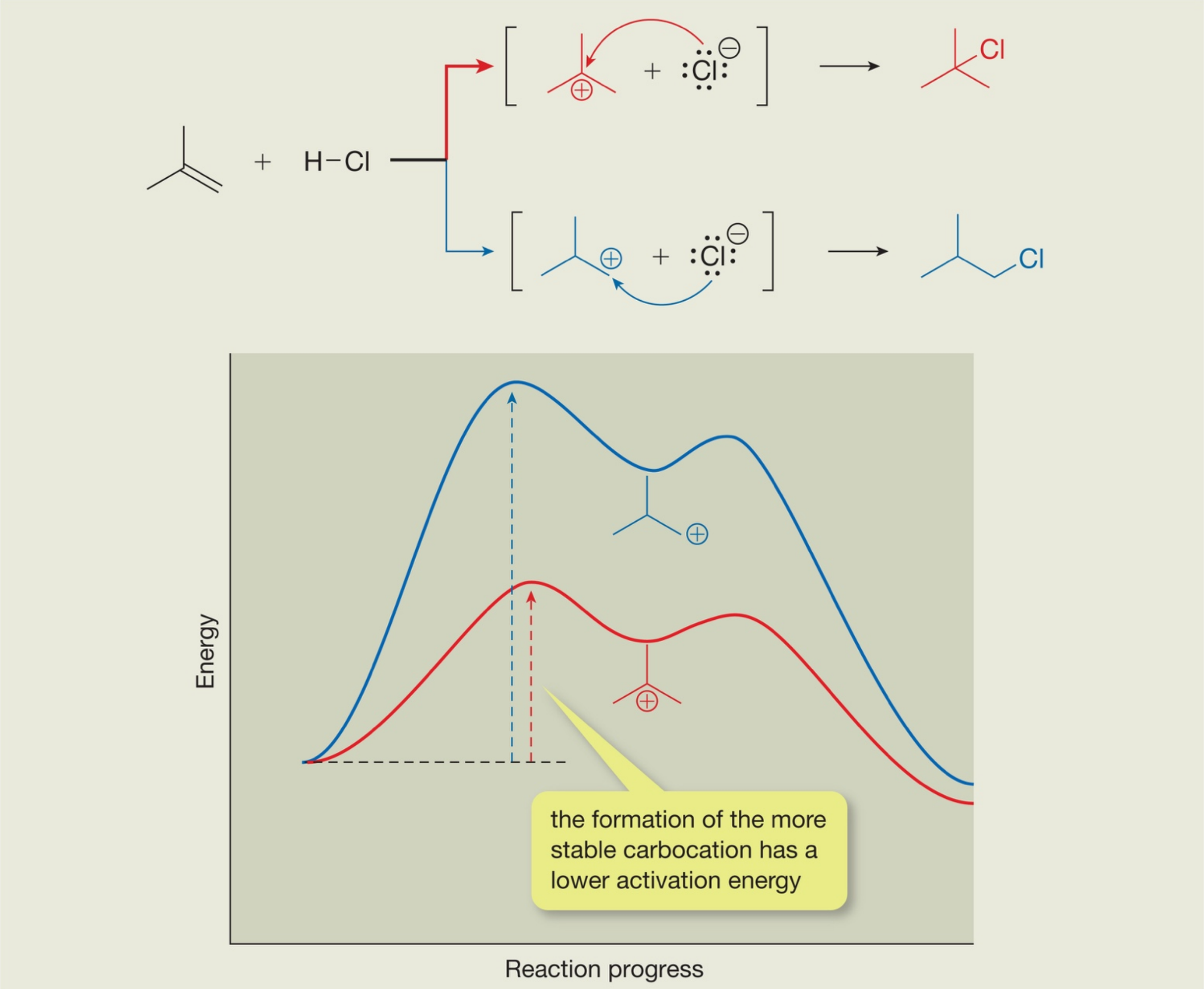


Applying the Hammond Postulate



- When π bonds act as nucleophiles, they produce carbocations as intermediates.
- The reaction coordinate diagram for these high energy intermediates indicate a late transition state.
- This means that the energy of the transition can therefore be explained by examining the structure of the carbocations that are formed as intermediates in the process.

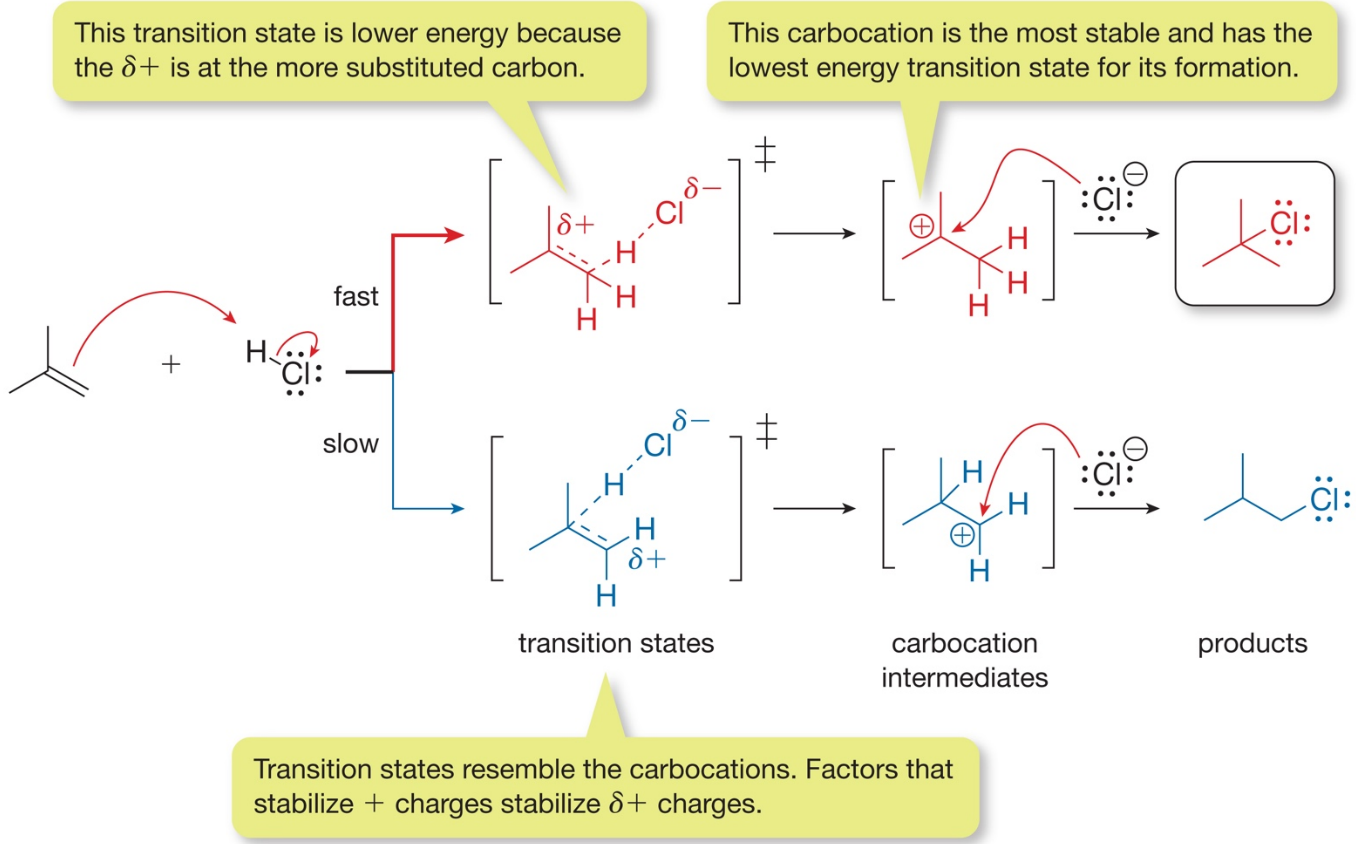
Applying the Hammond Postulate



the formation of the more stable carbocation has a lower activation energy

Applying the Hammond Postulate

- The more stable 3° carbocation has a lower activation energy and therefore forms at a faster rate, leading to the major product of the reaction (Markovnikov product).

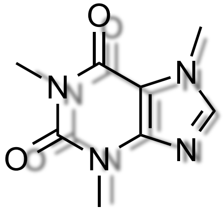


This transition state is lower energy because the δ+ is at the more substituted carbon.

This carbocation is the most stable and has the lowest energy transition state for its formation.

Transition states resemble the carbocations. Factors that stabilize + charges stabilize δ+ charges.

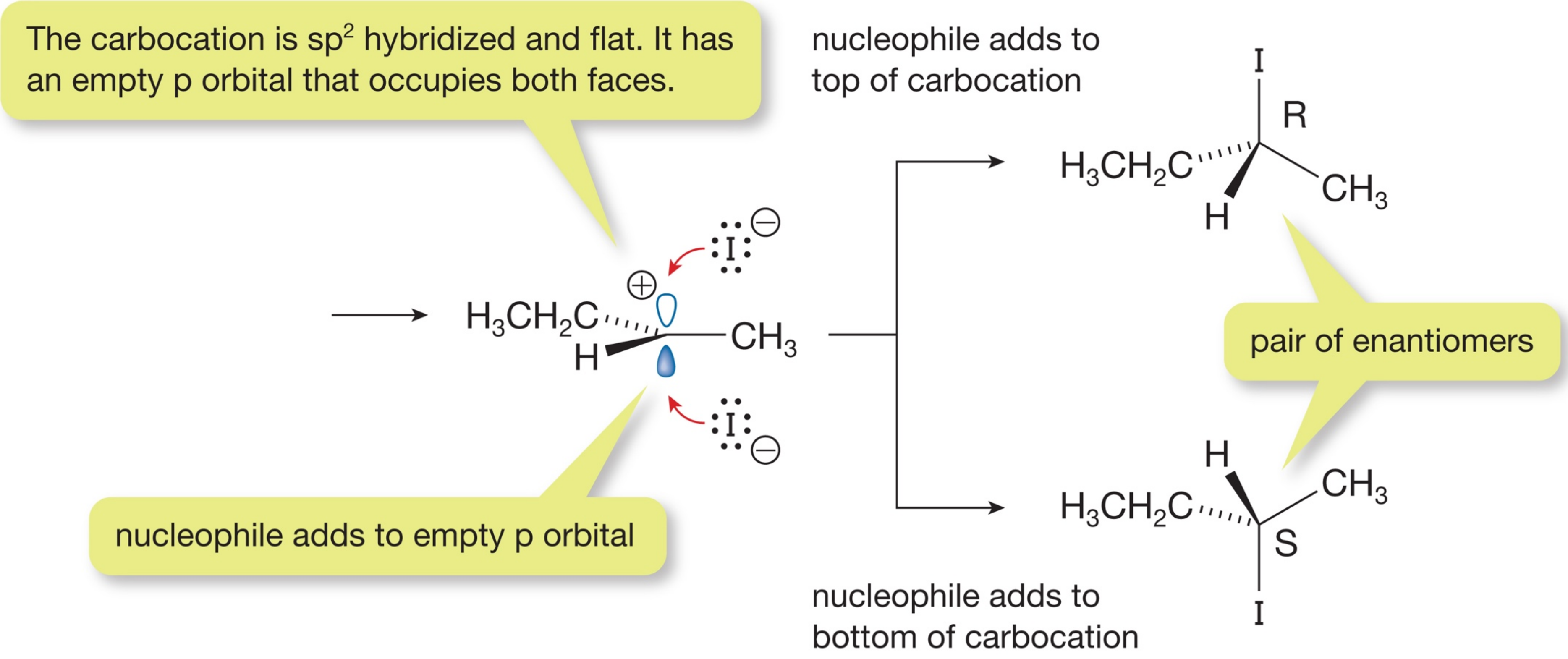
Carbocations are not Stereoselective



- The addition reaction across a π bond converts 2 sp^2 carbons into 2 sp^3 carbons. This addition may create new stereocentres which can lead to stereoisomeric products.
- Carbocations are trigonal planar and the empty orbital is perpendicular to the atoms directly attached to it.
- Nucleophiles reacting with the empty orbital can interact *with either* face of the carbocation. Attack from above will produce one stereoisomer while attack from below will produce the other stereoisomer.
- **Stereoselective** reactions are those that *favour* the formation of one stereoisomer over the another.

Carbocations are not Stereoselective

- Because the incoming nucleophile is equally likely to attack either face, this reaction is not stereoselective.
- As a result, equal quantities of the two stereoisomers is formed.



The carbocation is sp^2 hybridized and flat. It has an empty p orbital that occupies both faces.

nucleophile adds to top of carbocation

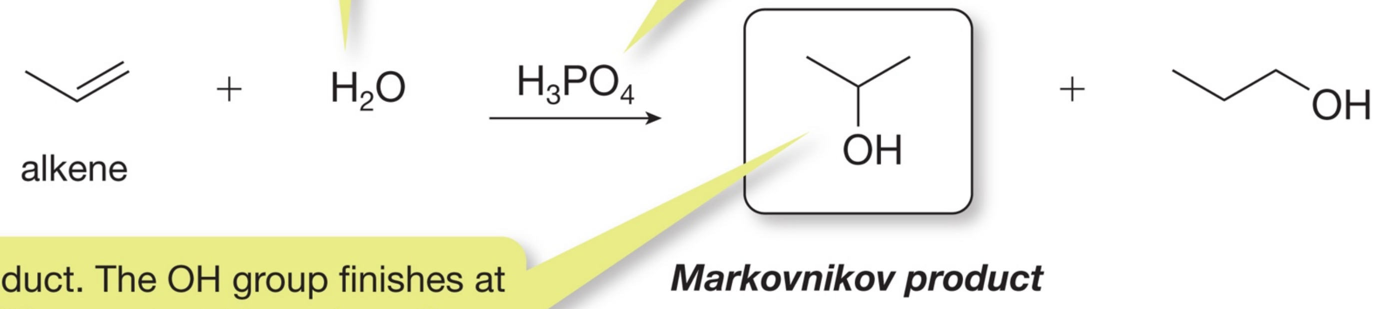
pair of enantiomers

nucleophile adds to empty p orbital

nucleophile adds to bottom of carbocation

Markovnikov Addition of Water to Alkenes.

- In the presence of a strong acid catalysis, H_3PO_4 or H_2SO_4, alkenes react with water to produce alcohols.
- This reaction is very similar to the addition of halo acids to alkenes and the major product is consistent with Markovnikov's rule; the major product arises from the most stable carbocation.



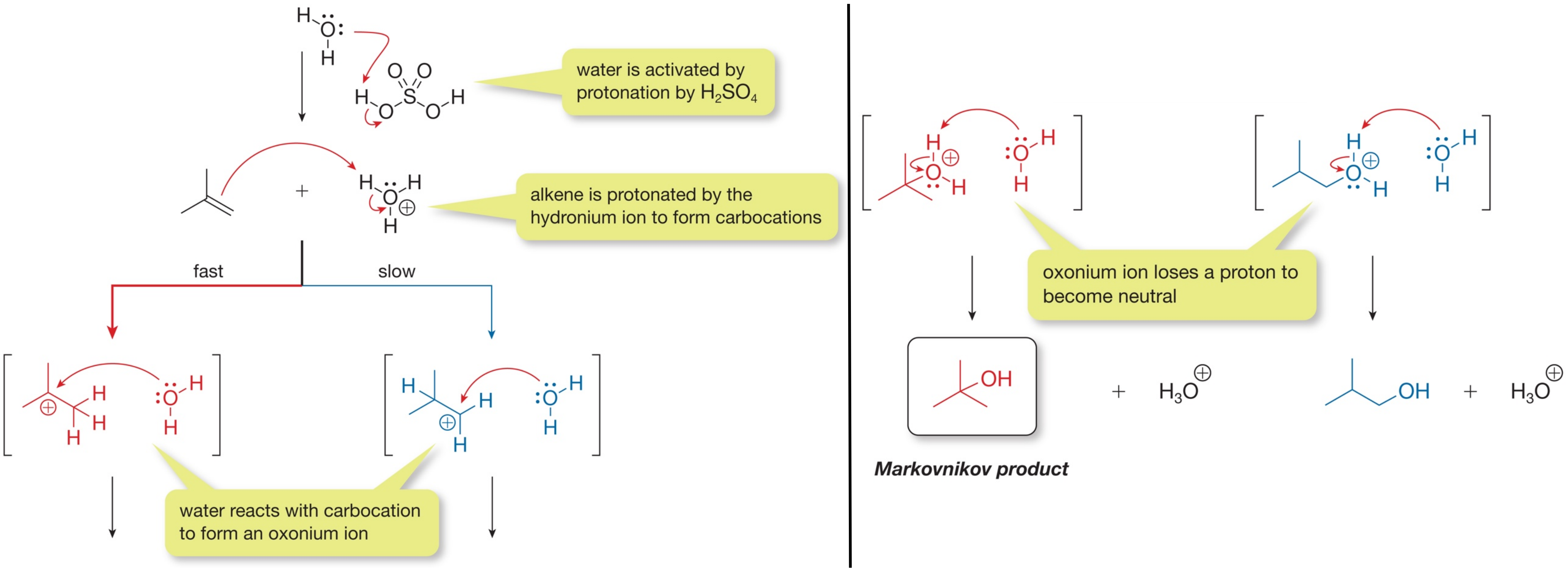
water (H–OH) adds across the double bond

strong acids are used to catalyze the reaction

Major product. The OH group finishes at the site of the most stable carbocation.

Markovnikov Addition of Water to Alkenes.

- Water is a weak acid, therefore H_3PO_4 or H_2SO_4 is needed to form hydronium ions, which are strong acids that can react with π bonds.



water is activated by protonation by H_2SO_4

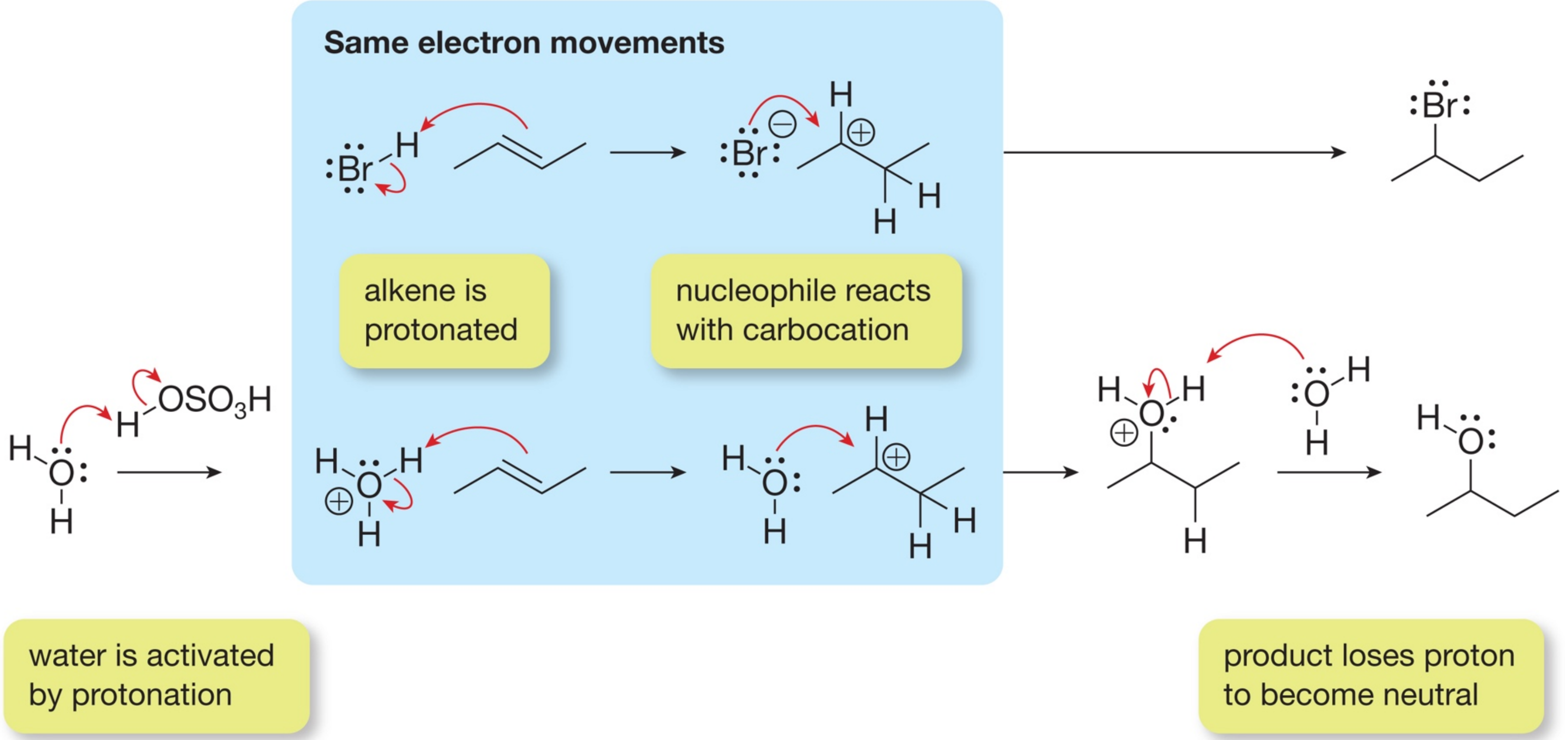
alkene is protonated by the hydronium ion to form carbocations

water reacts with carbocation to form an oxonium ion

oxonium ion loses a proton to become neutral

Markovnikov Addition of Water to Alkenes.

- A comparison of the addition reactions of H-X and H_2O to an alkene will reveal that they are mechanistically almost identical. The only difference being that the addition of water requires an initial protonation step and a final deprotonation step.



Same electron movements

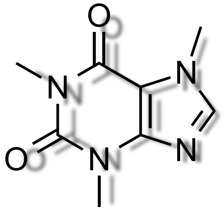
alkene is protonated

nucleophile reacts with carbocation

water is activated by protonation

product loses proton to become neutral

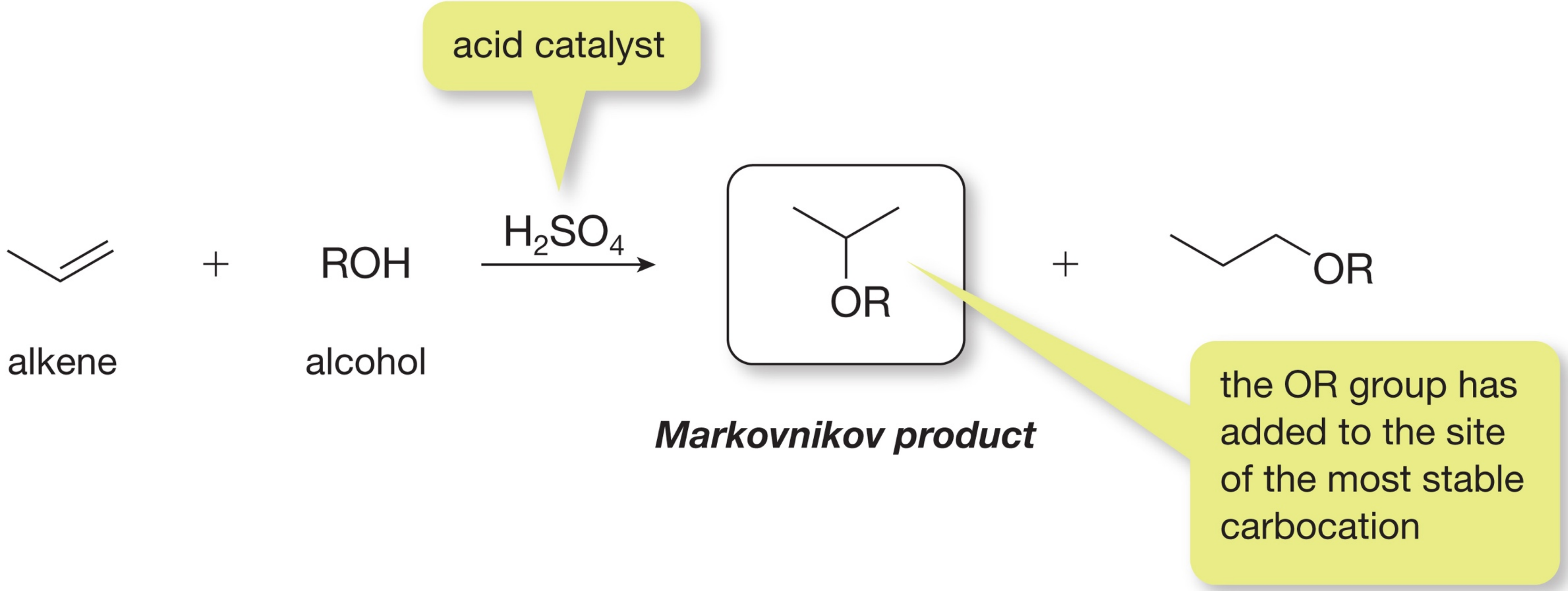
Markovnikov Addition of Alcohols to Alkenes.



- Alcohols are structurally very similar to water (R-OH vs H-OH) and therefore their reactions with many reagents are similar and, more importantly, they ***follow the same mechanism***.
- Alcohols add to alkenes to produce ***ethers***, and the reaction obeys Markonikov's rule.

Markovnikov Addition of Alcohols to Alkenes.

- Addition of alcohol:



acid catalyst

Markovnikov product

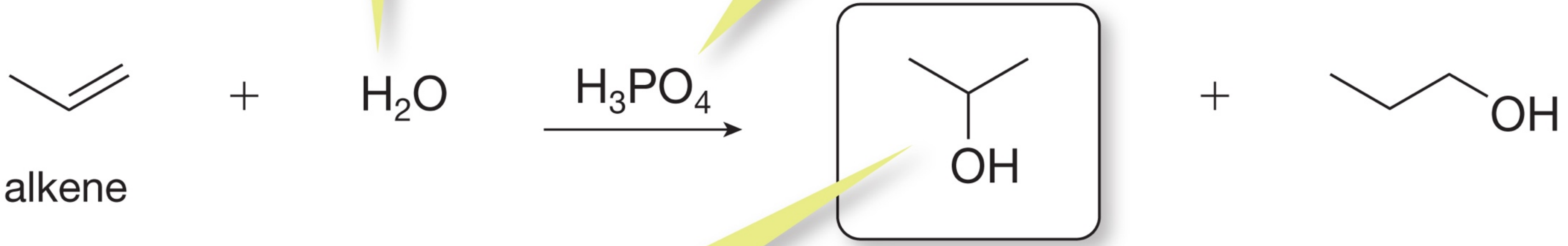
the OR group has added to the site of the most stable carbocation

Markovnikov Addition of Alcohols to Alkenes.

- Addition of water:

water (H–OH) adds across the double bond

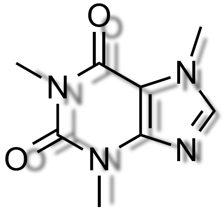
strong acids are used to catalyze the reaction



Major product. The OH group finishes at the site of the most stable carbocation.

Markovnikov product

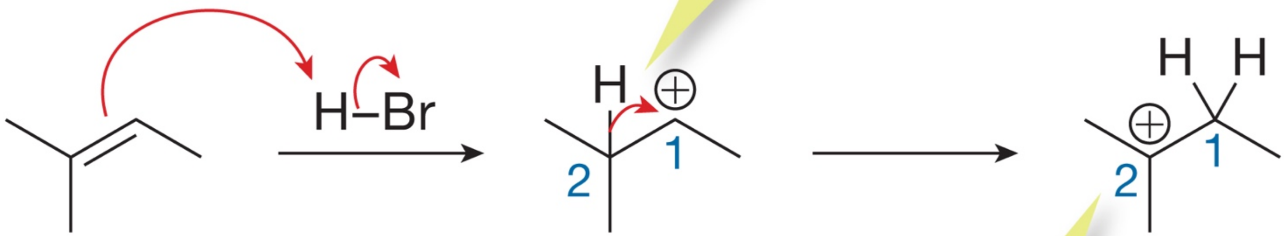
Carbocation Rearrangements



- A carbocation is a high energy intermediate that reacts quickly with nucleophiles and bases
- Carbocations can complicate reactions because they provide opportunities for potential side reactions.
- ***Carbocation rearrangements*** change the structure of the carbocation to provide a more stable intermediate.
- During a carbocation rearrangement, an atom or group adjacent to the carbocation moves with its electrons to the carbocation creating a new carbocation.

Carbocation Rearrangements

- A hydride shift occurs when a hydrogen atom adjacent to the carbocation moves, with its two electrons, to the electron deficient carbon creating a new carbocation.
- If there are no adjacent hydrides, alkyl groups, such as methyl or phenyl, can also migrate.

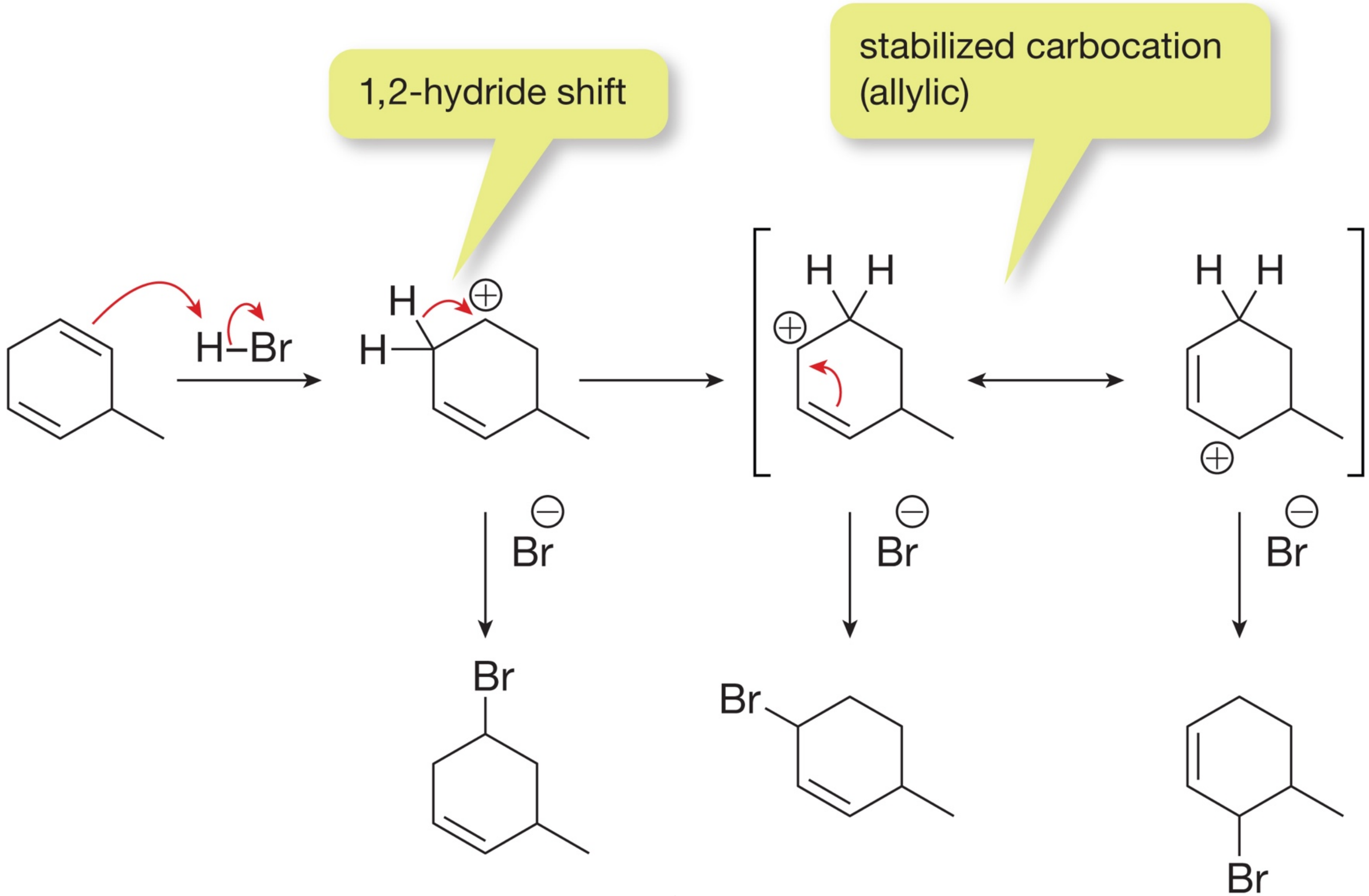


[1,2-hydride shift] hydrogen moves with a pair of electrons (CH bond) from adjacent carbon

tertiary carbocation more stable than secondary

Carbocation Rearrangements

- Rearrangements occur only when a more stable carbocation can form.

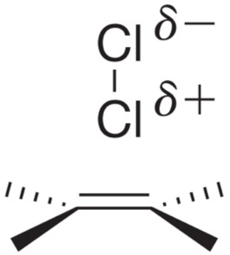


1,2-hydride shift

stabilized carbocation
(allylic)

Addition of Halogens to Double Bonds

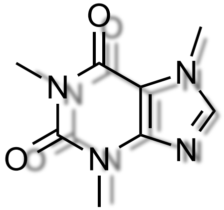
- Alkenes react very rapidly with the halogens F_2, Cl_2, Br_2 and I_2.
- When a diatomic halogen approaches a nucleophilic alkene, electron-electron repulsions between the halogen and the π bond, induce a dipole in the bond of the halogen molecule.
- This dipole makes the halogen closest to the alkene electrophilic and the other halogen atom a good leaving group.



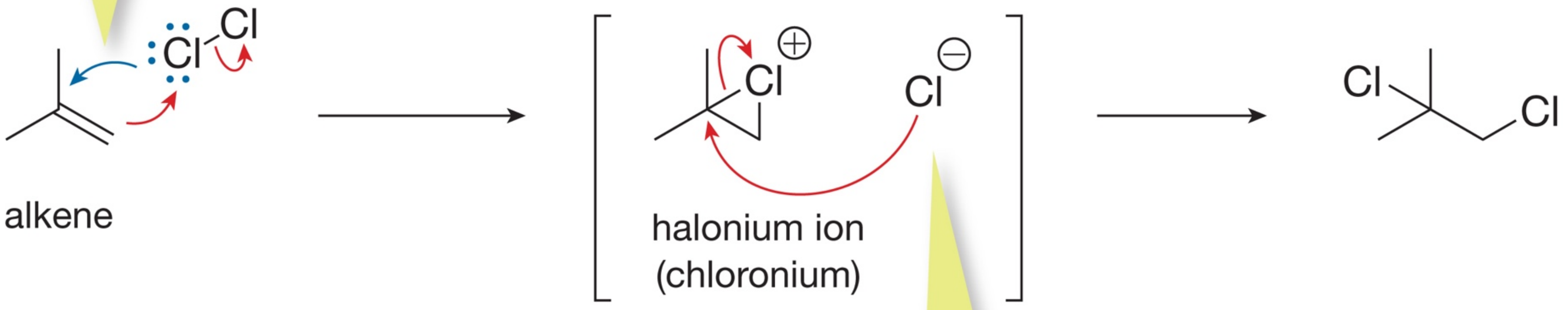
dipole induced onto Cl_2 molecule as it approaches π bond

Electron repulsion from the filled π bond forces electrons in the Cl–Cl bond onto the chlorine furthest from the π bond producing a dipole.

Addition of Halogens to Double Bonds



- When an alkene and halogen molecule react, a new bond forms between the alkene carbon and the halogen while the halogen-halogen bond breaks. Because halogens have unpaired electrons, they can make a bond with the carbocation as it forms.
- This concerted reaction produces a cyclic halonium ion.

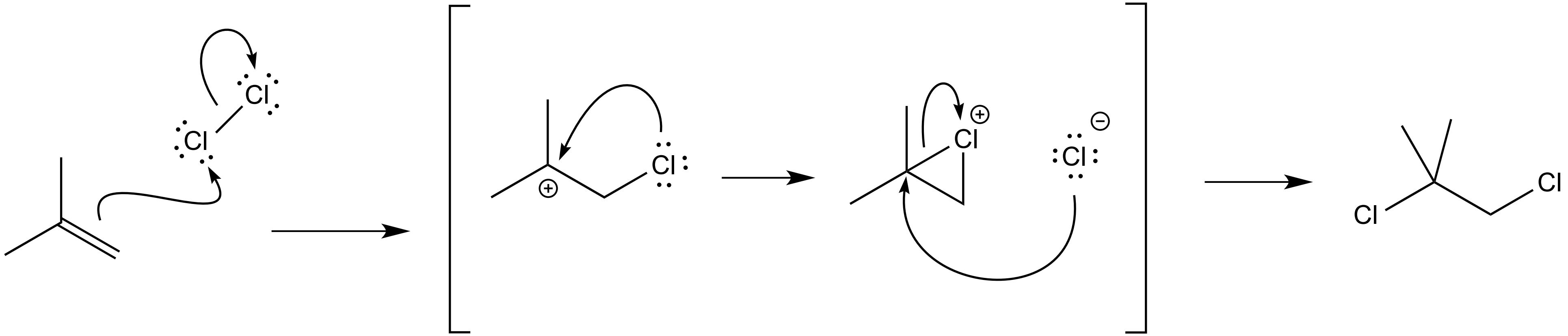


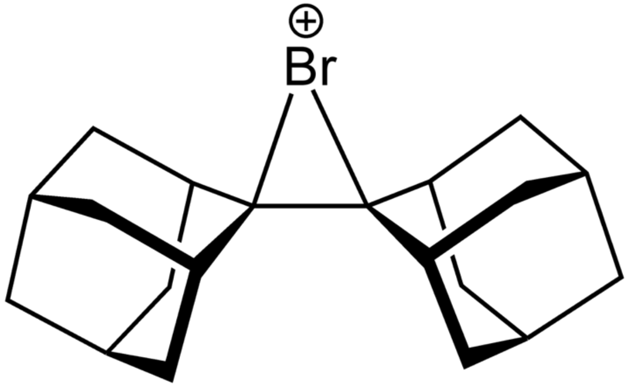
lone pair on the halogen atom forms bond to carbon

chloride is a nucleophile to open the halonium ion

Addition of Halogens to Double Bonds

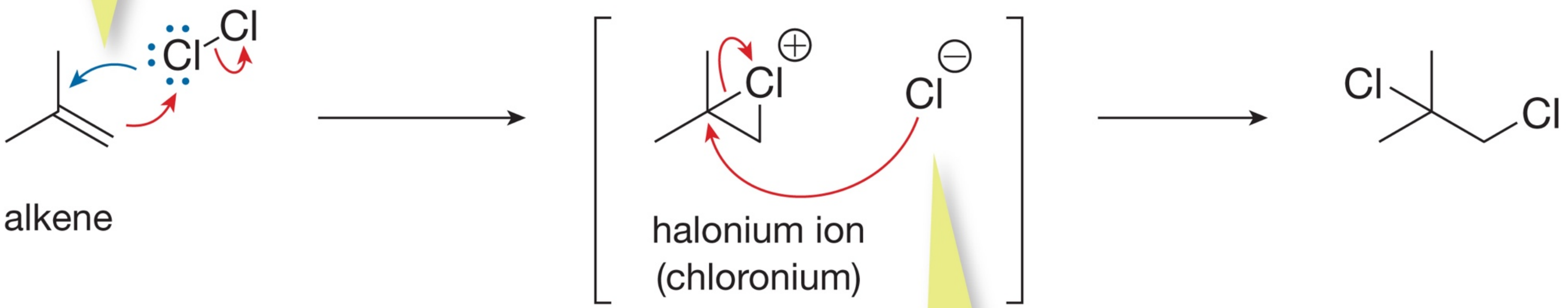
- While not mechanistically accurate, the formation of the halonium ion can be visualized in a step wise fashion:





Addition of Halogens to Double Bonds

- In the second step of the mechanism, the halide leaving group acts as a nucleophile and opens the halonium ion ring.
- The halide adds to the more substituted side of the halonium ion, the site of the best carbocation

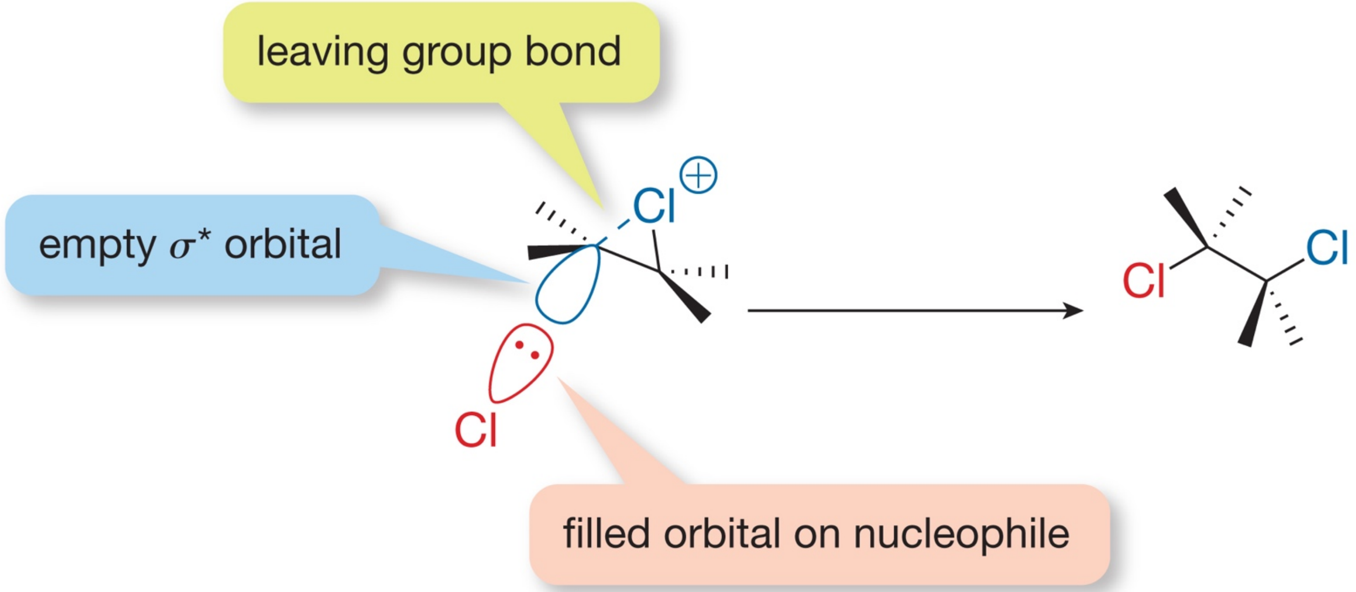


lone pair on the halogen atom forms bond to carbon

chloride is a nucleophile to open the halonium ion

Addition of Halogens to Double Bonds

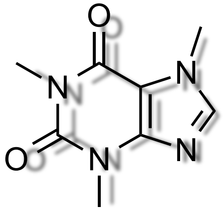
- When the halide approaches the halonium ion, it approaches the *opposite* face to that of the positive halogen. It does this because:
  - Steric hindrance between the two large halogen atoms
  - The nucleophile (halide) must overlap its filled orbital with an empty orbital on the electrophile (halonium ion). This orbital, the σ* orbital of the carbon-halogen bond is pointed toward the opposite face.


leaving group bond

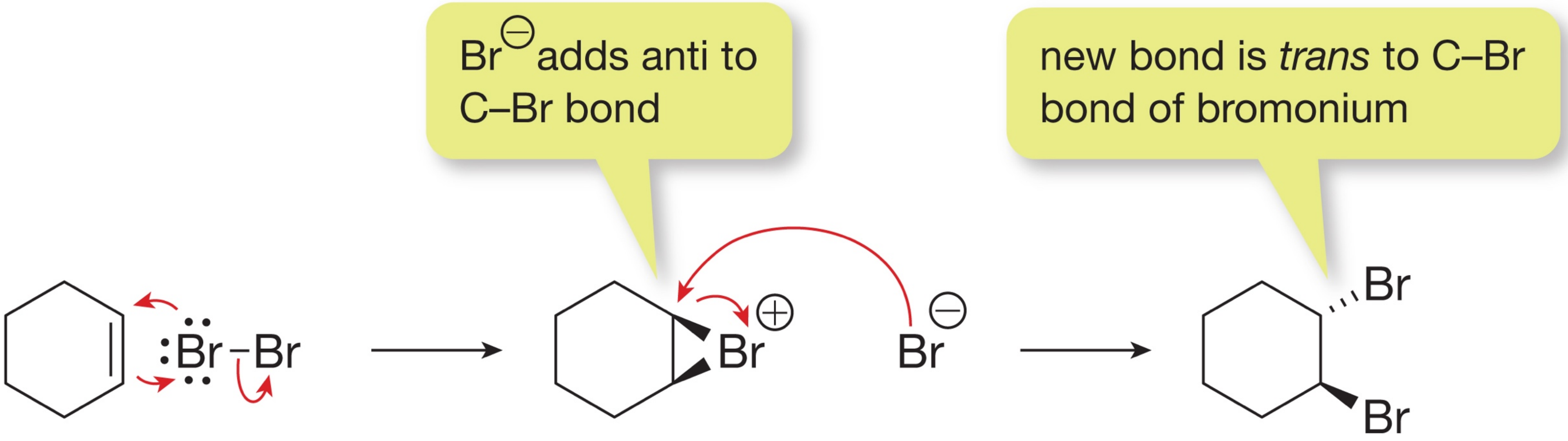
empty σ^* orbital

filled orbital on nucleophile

Addition of Halogens to Double Bonds



- The net result is ***anti-addition*** of the two halogen atoms relative to the original alkene.
- In anti-addition, the two new atoms or groups are added to opposite faces of a double bond.



Br$^{\ominus}$ adds anti to C–Br bond

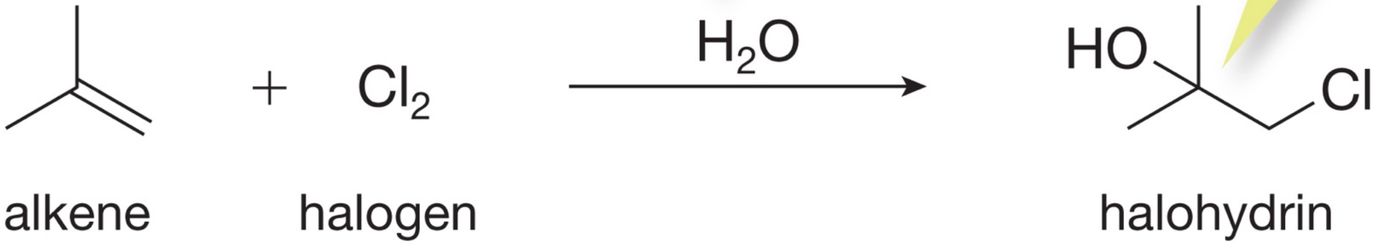
new bond is *trans* to C–Br bond of bromonium

Halohydrins

- Halonium ions can be opened with other competing nucleophiles.
- For example, halogens, in the presence of water, form halohydrins; molecules with a halogen adjacent to a hydroxyl group.
- A halonium ion still forms, but a competing nucleophile, water in this case, opens the rings.

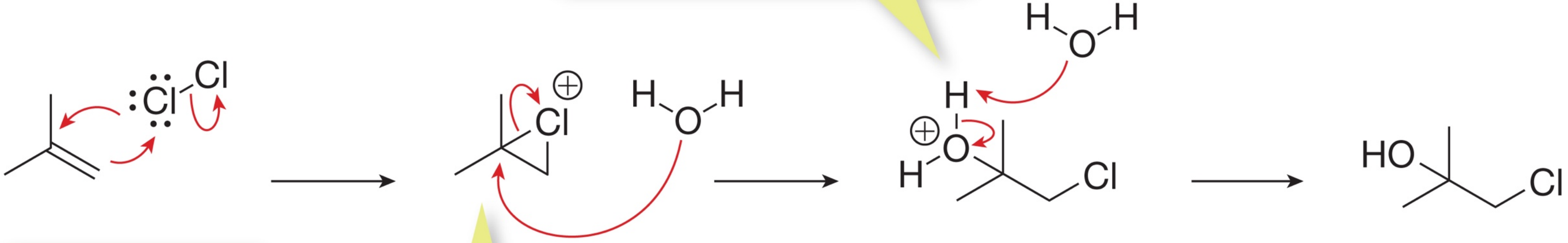
reaction done in presence of second nucleophile

the OH group has added to the site of the most stable carbocation (more substituted carbon)



Halohydrins

- Mechanistically, this is identical to the addition of a halogen to an alkene.



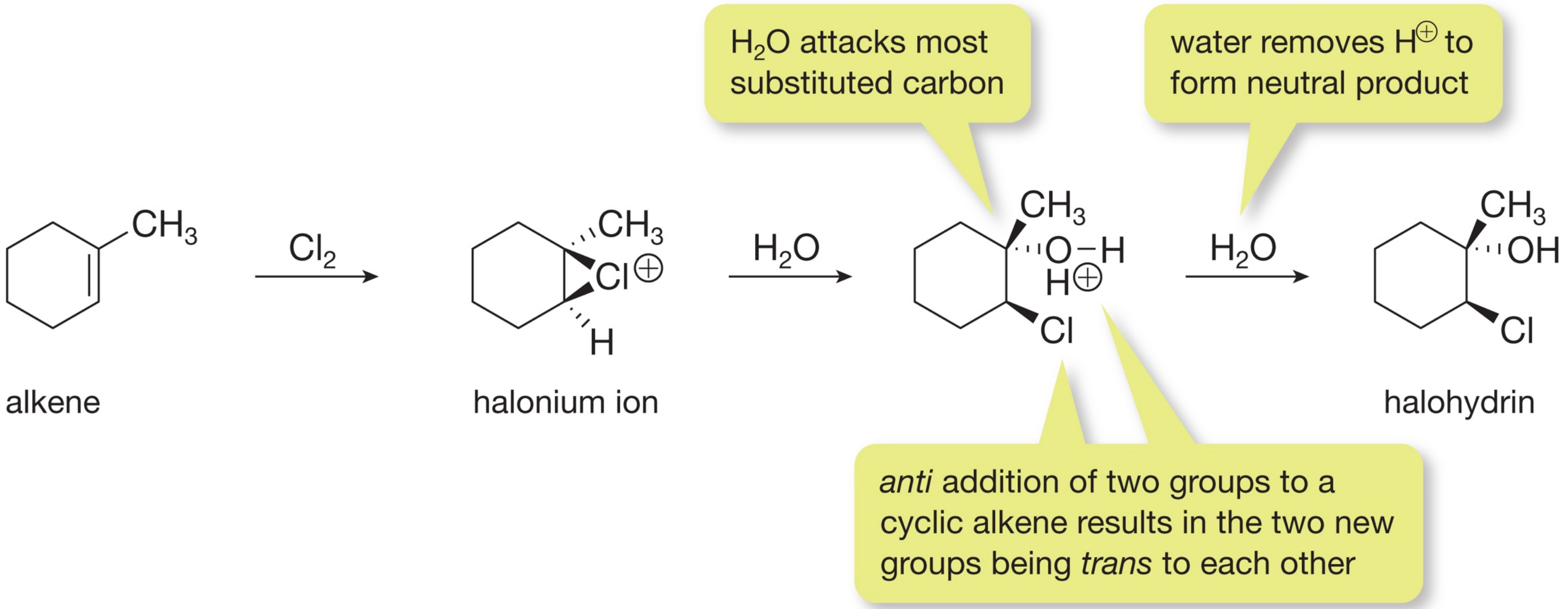
oxonium ion loses proton to become neutral

chloronium ion forms

water opens chloronium ion at location that best stabilizes carbocation (most substituted)

Halohydrins

- Halohydrin formation is also regioselective; the addition of the -Cl and -OH are exclusively trans.



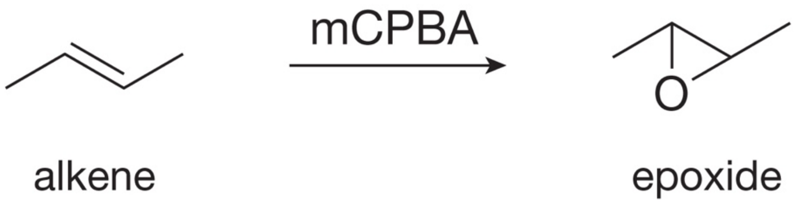
H_2O attacks most substituted carbon

water removes $H^{\oplus}$ to form neutral product

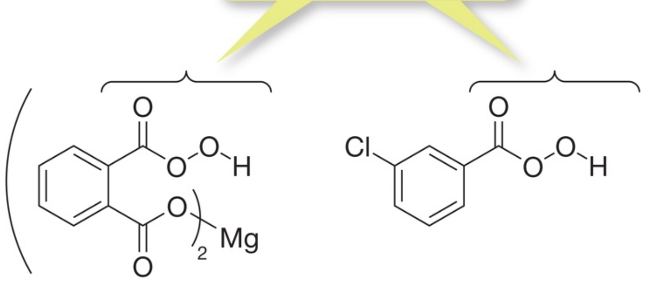
anti addition of two groups to a cyclic alkene results in the two new groups being *trans* to each other

Other Types of Electrophilic Additions

- Epoxides are 3-membered rings consisting of two carbon atoms and one oxygen atom.
- Alkenes can be converted to epoxides using peroxycarboxylic acids (RC(O)OOH).
    - Commonly used peroxyacids include monomagnesium peroxyperpthalate (MMPP) and *meta*-chloroperoxybenzoic acid (mCPBA).



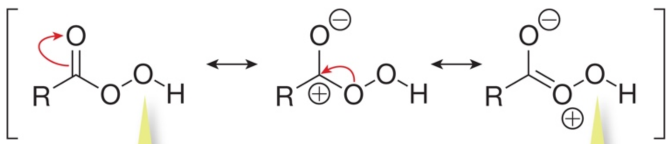
a peroxycarboxylic acid



monomagnesium peroxyperphthalate (MMPP)

m-chloroperoxybenzoic acid (mCPBA)

Resonance forms of peroxyacids

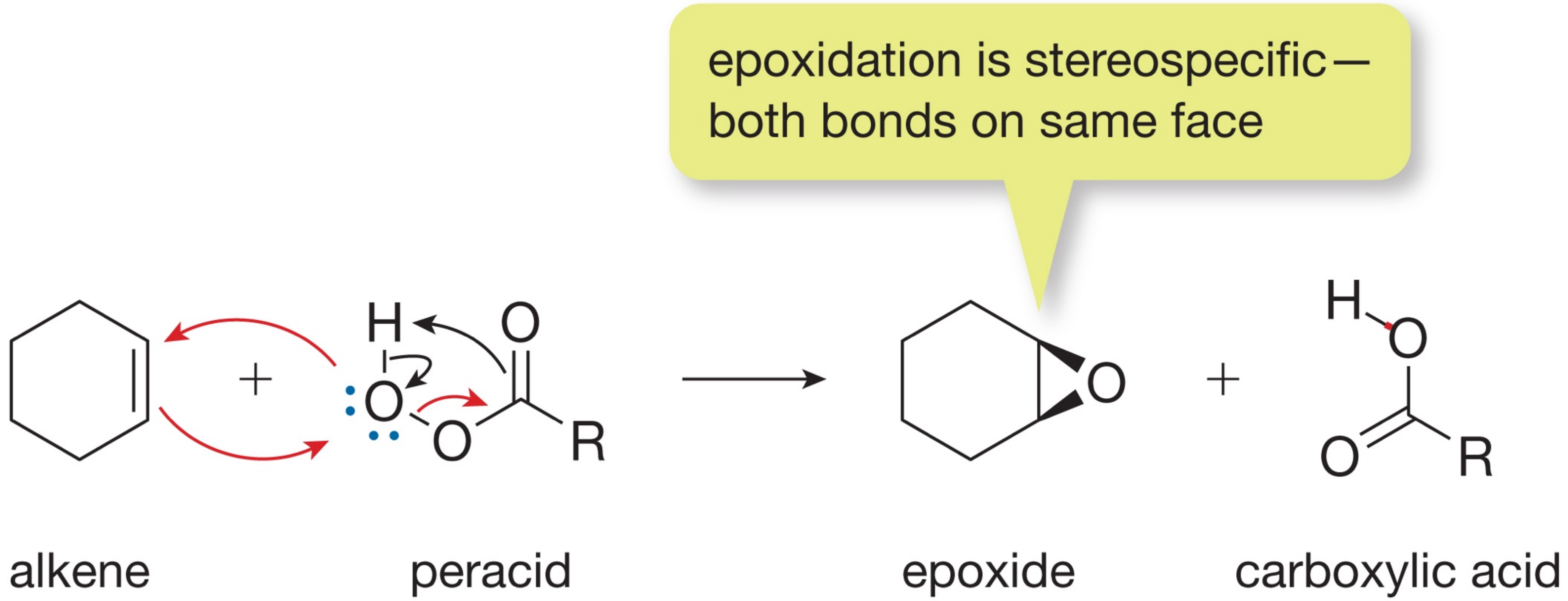


this oxygen is NOT involved in resonance

the adjacent positive charge makes this oxygen susceptible to attack by a nucleophile

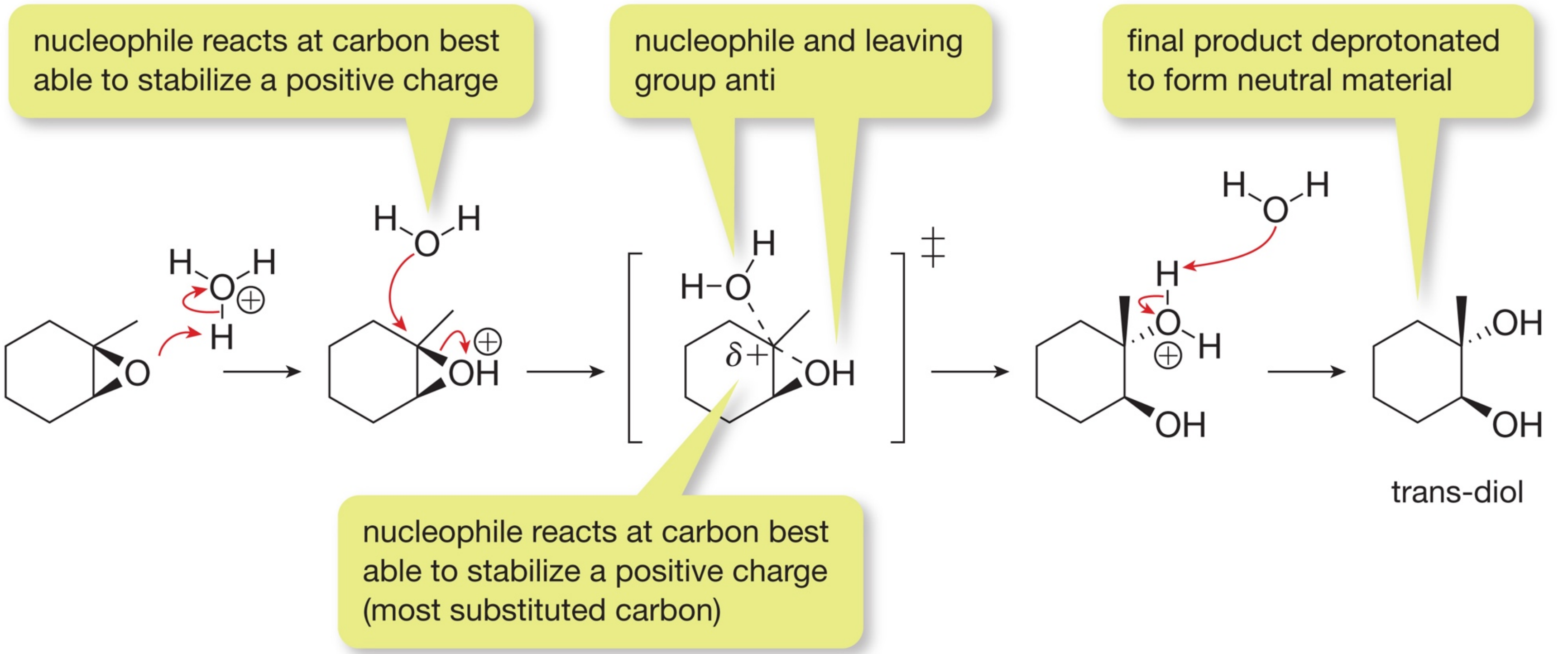
Epoxidation

- The mechanism of epoxidation follows the same pattern as that for halogenation of an alkene, but with an extra rearrangement step.
- Epoxidation is also a concerted reaction and both new carbon-oxygen bonds form on the same face of the alkene.


epoxidation is stereospecific—both bonds on same face

Epoxidation

- Just like halonium ions, nucleophiles attack epoxides exclusively by ***anti-addition***.
- The regiochemistry depends on the reaction conditions.
  - Under acidic conditions, nucleophiles attack the more substituted carbon atom.



nucleophile reacts at carbon best able to stabilize a positive charge

nucleophile and leaving group anti

final product deprotonated to form neutral material

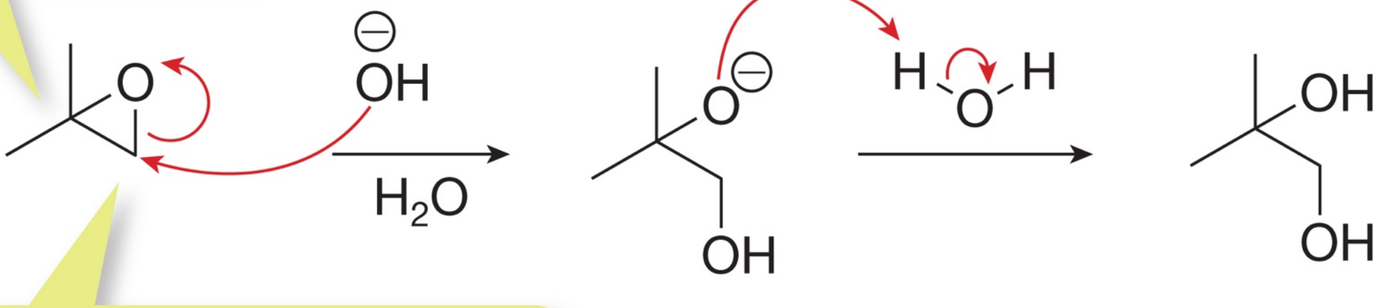
nucleophile reacts at carbon best able to stabilize a positive charge (most substituted carbon)

trans-diol

Epoxidation

- Just like halonium ions, nucleophiles attack epoxides exclusively by ***anti-addition***.
- The regiochemistry depends on the reaction conditions.
  - Under basic conditions, nucleophiles attack the least substituted carbon atom.

Base conditions:

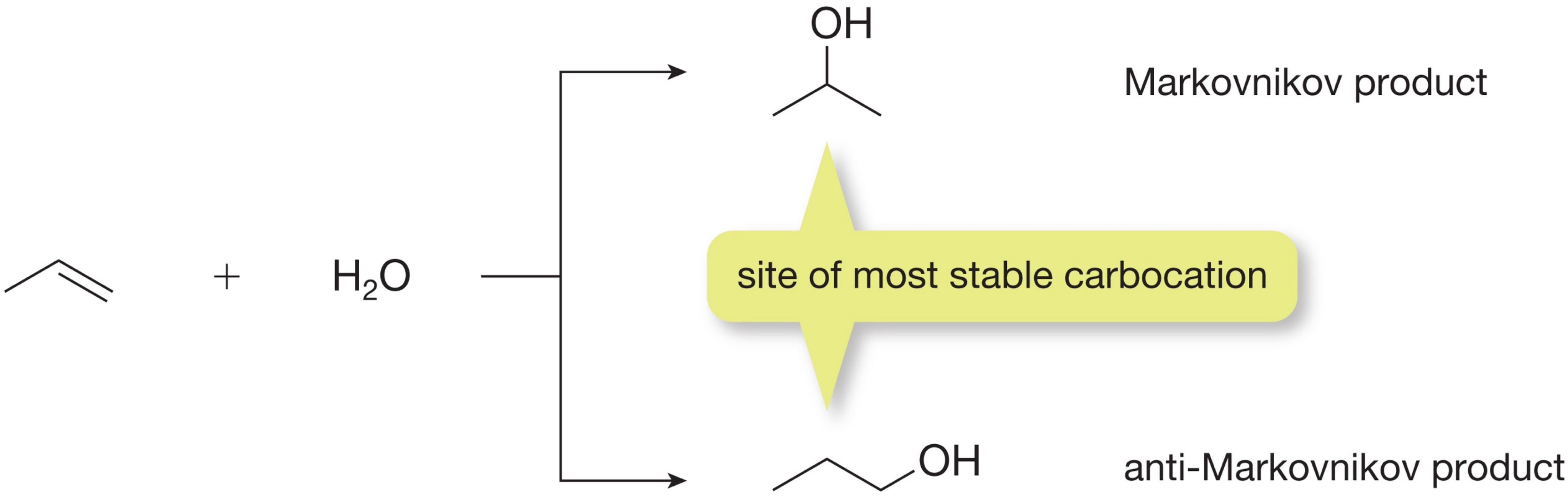


no positive charge

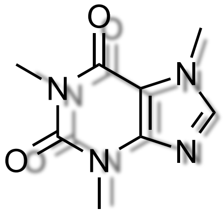
neutral rings are opened at the least substituted carbon

Hydroboration – Anti-Markonikov Addition

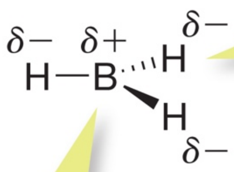
- Hydroboration allows water to be added to alkenes to give ***anti-Markovnikov products***. That is, the hydroxyl is added to the other carbon atom of the alkene.



Hydroboration – Anti-Markonikov Addition



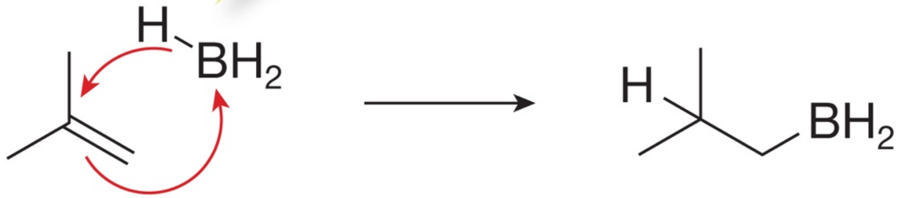
- The anti-Markovnikov addition of water is done using borane (BH_3). Because boron is electron deficient, it is an excellent electrophile.
- Hydroboration produces an alkylborane intermediate, where the H and BH_2 of borane are ***syn*** (on the same face) to each other. This is called ***syn-addition***.



Hydrogen is more electronegative than boron, so the electrons in the B–H bonds reside mostly near hydrogen. This extra electron density makes the hydrogens nucleophilic.

Boron has an incomplete octet and is very electrophilic.

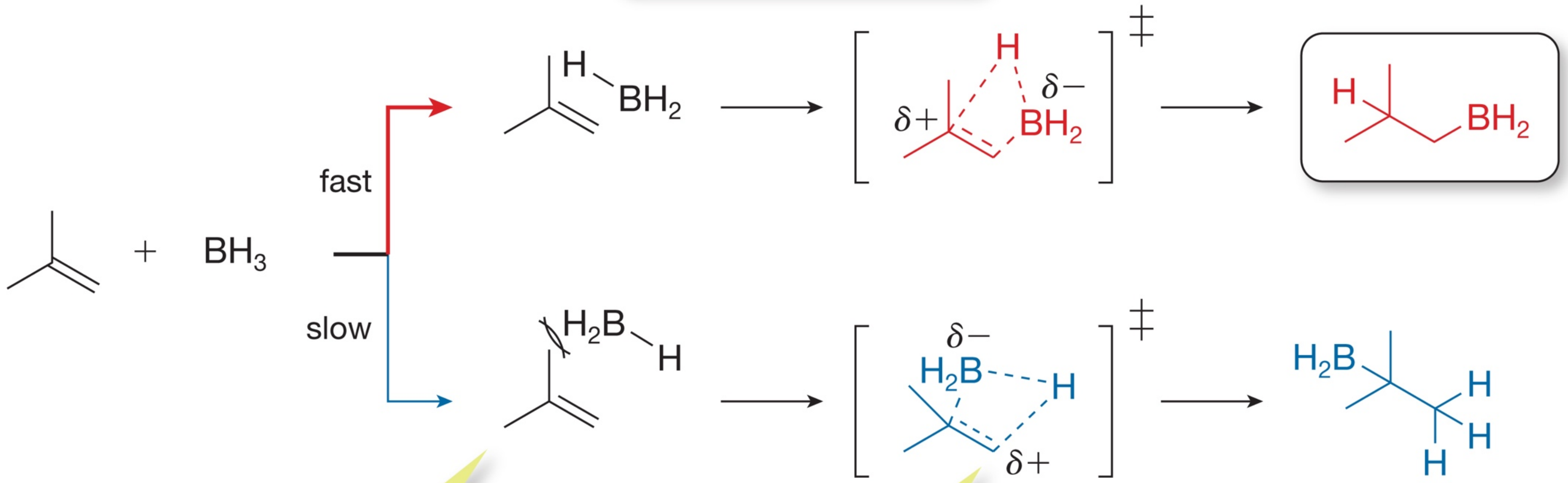
all bonds break and form in the same step



alkyl borane

Hydroboration – Anti-Markonikov Addition

- This reaction is also regioselective; the BH_2 group adds predominately to the least substituted carbon atom of the double bond.



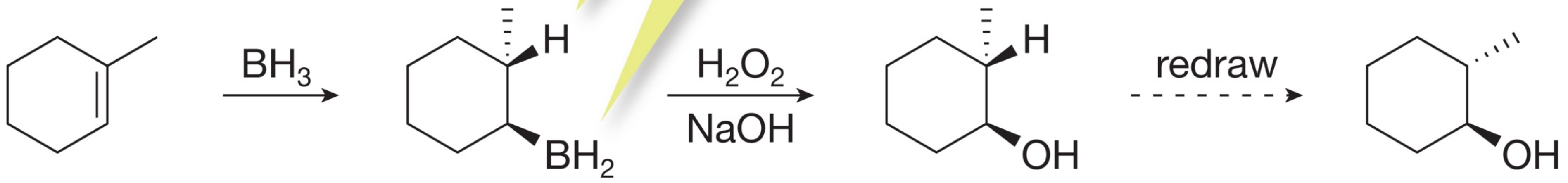
δ+ is preferred at more substituted carbon

BH_2 group is sterically hindered by the alkyl groups

C–H bond forms slowly; δ+ develops at carbon

Hydroboration – Anti-Markonikov Addition

- The second step, the alkylborane is reacted with a mixture of hydrogen peroxide (H_2O_2) and aqueous sodium hydroxide to give the product alcohol.
- The important feature is that the C-B bond is replace by a C-O bond ***with retention of configuration***. The H and BH_2 are added syn to each other.

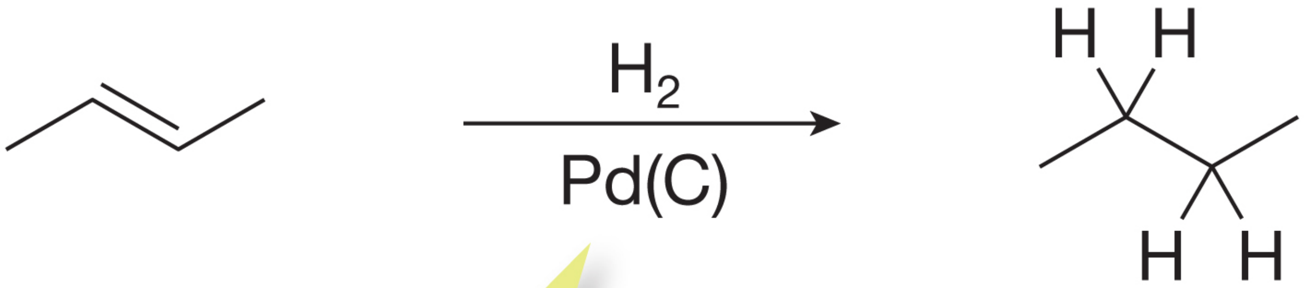


H and BH_2 have added *syn* to each other

stereocentre with BH_2 and OH groups maintains same configuration

Hydrogenation

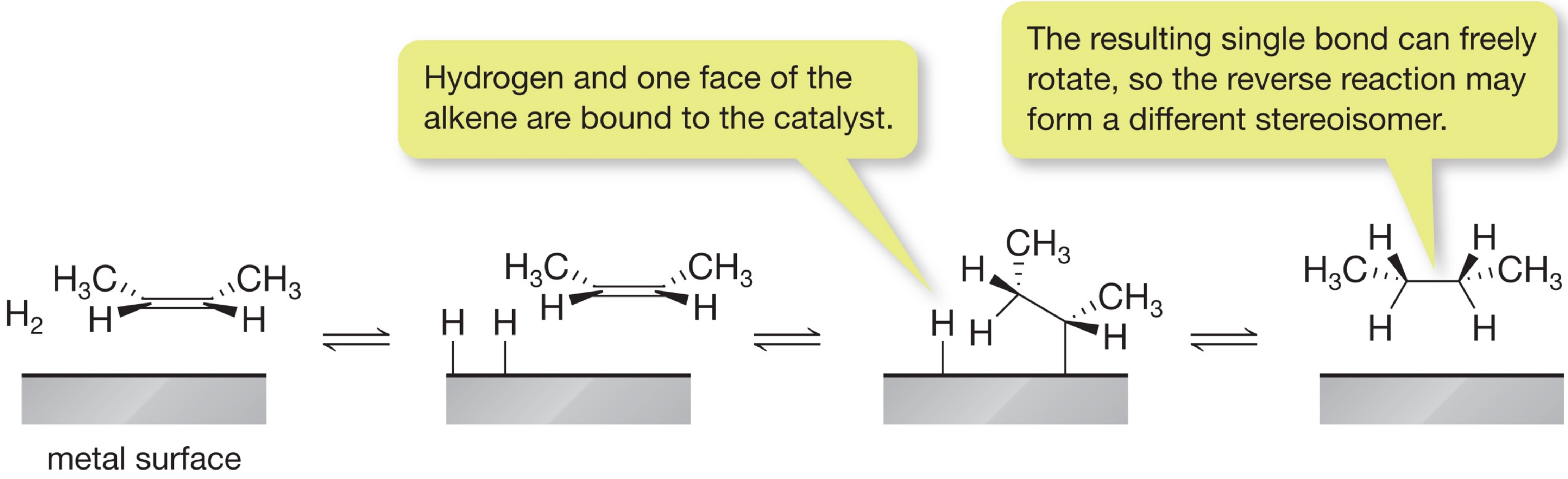
- Hydrogenation is the addition of 2 hydrogen atoms across a carbon-carbon π bond producing an alkane.
- Because H_2 is not very reactive, a catalyst is needed, typically platinum or palladium is used.



catalyst is required to add hydrogen

Hydrogenation

- The addition of the two hydrogen atoms occurs on the same face of the alkene and is therefore a ***syn addition***.

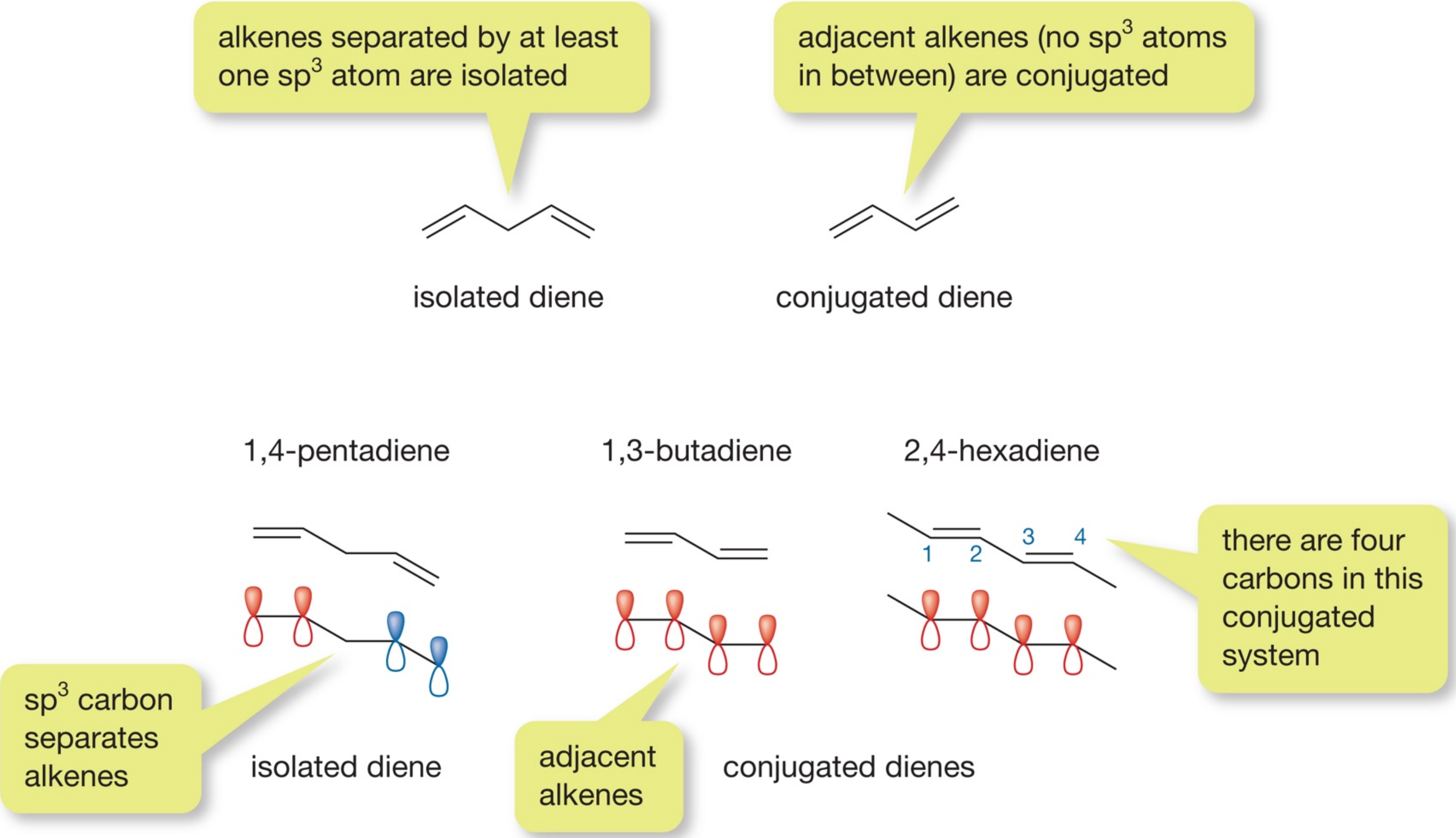


Hydrogen and one face of the alkene are bound to the catalyst.

The resulting single bond can freely rotate, so the reverse reaction may form a different stereoisomer.

Electrophilic Addition to Dienes

- Dienes are molecules containing 2 carbon-carbon double bonds.
- Dienes can either be ***isolated*** or ***conjugated:***
  - In isolated dienes, the two double bonds are separate π systems.
  - In conjugated dienes, the two double bonds are part of one continuous π system.



alkenes separated by at least one sp^3 atom are isolated

adjacent alkenes (no sp^3 atoms in between) are conjugated

there are four carbons in this conjugated system

sp^3 carbon separates alkenes

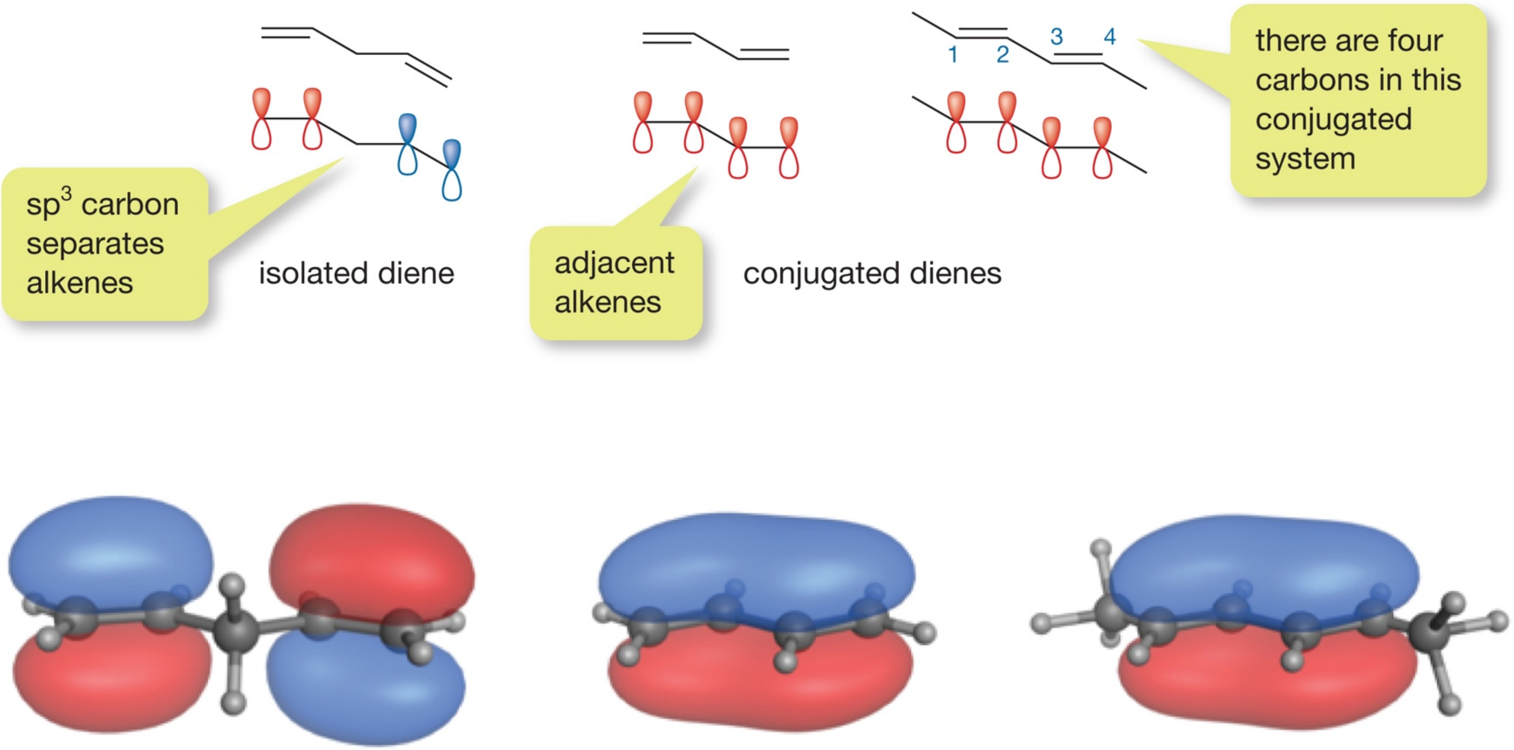
isolated diene

adjacent alkenes

conjugated dienes

Electrophilic Addition to Dienes

- The ***conjugated system*** is a region of the molecule with interacting π orbitals. The electrons in the conjugated system are delocalized over all the atoms involved.
- Only the carbon atoms involved in the interacting π bonds are part of the conjugated system.



sp^3 carbon separates alkenes

isolated diene

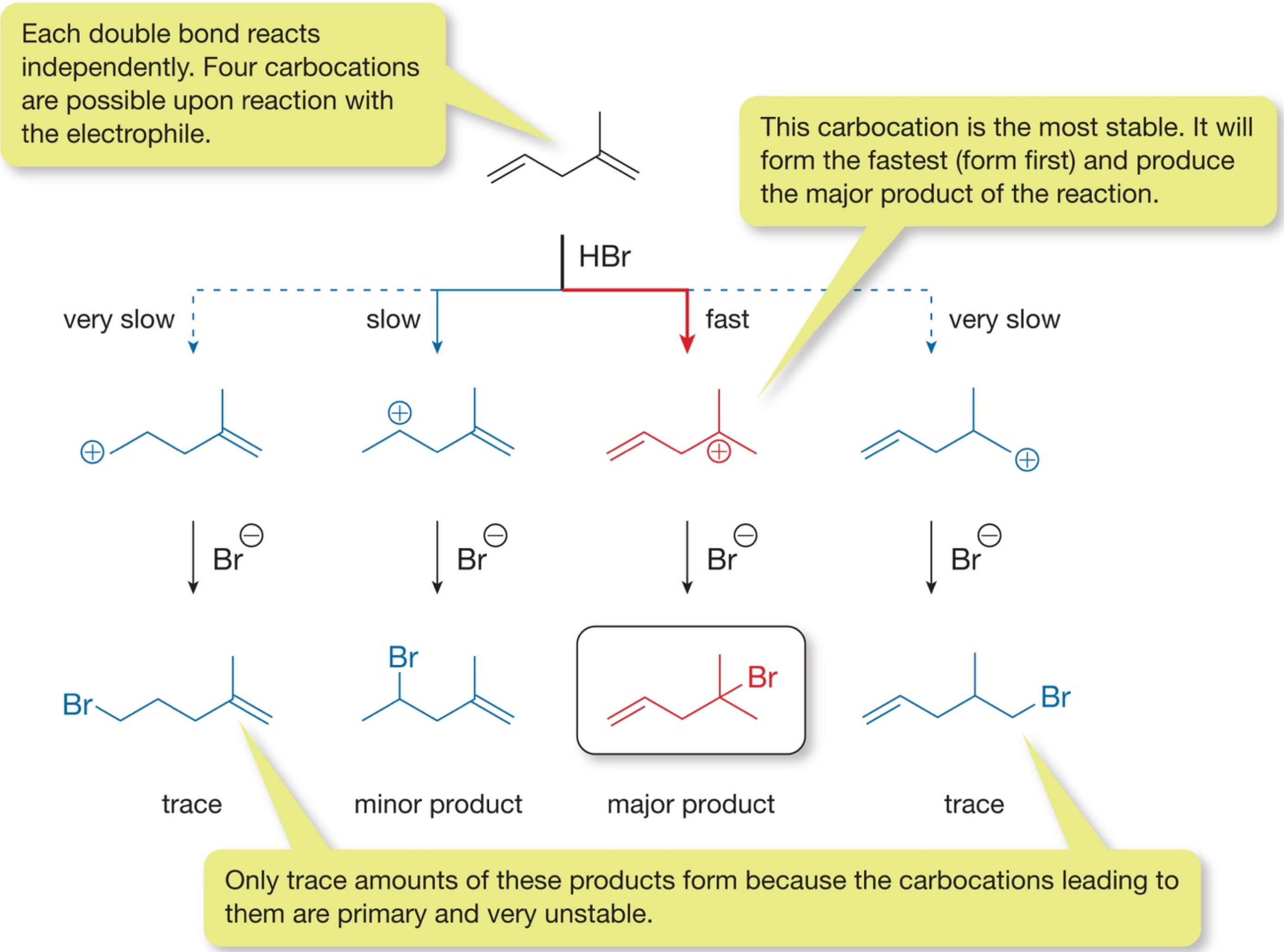
adjacent alkenes

conjugated dienes

there are four carbons in this conjugated system

Markovnikov Addition to Dienes

- For isolated dienes, because the 2 π bonds do not interact, they react independently from each other.
- Generally, the double bond that can form the most stable carbocation will react the fastest.



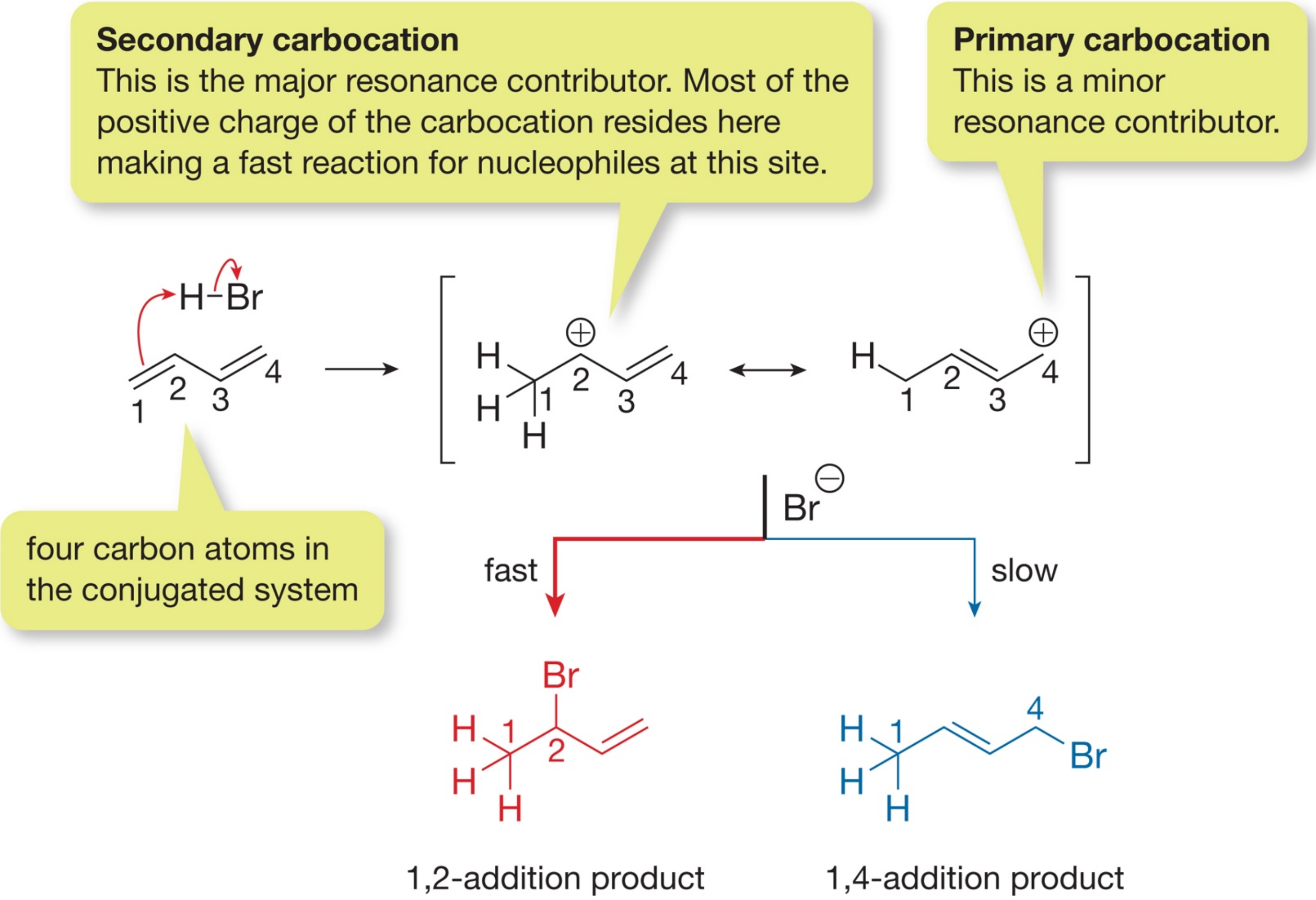
Each double bond reacts independently. Four carbocations are possible upon reaction with the electrophile.

This carbocation is the most stable. It will form the fastest (form first) and produce the major product of the reaction.

Only trace amounts of these products form because the carbocations leading to them are primary and very unstable.

Markovnikov Addition to Dienes

- For conjugated dienes, the double bonds behave like one functional group.
- The carbocation intermediate is delocalized, producing a mixture of constitutional isomers: a 1,2-addition product and a 1,4-addition product.
- The numbers refer to the carbon atoms to which the electrophile is added.

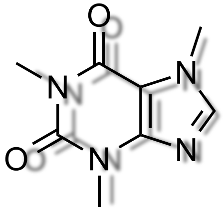


Secondary carbocation
This is the major resonance contributor. Most of the positive charge of the carbocation resides here making a fast reaction for nucleophiles at this site.

Primary carbocation
This is a minor resonance contributor.

four carbon atoms in the conjugated system

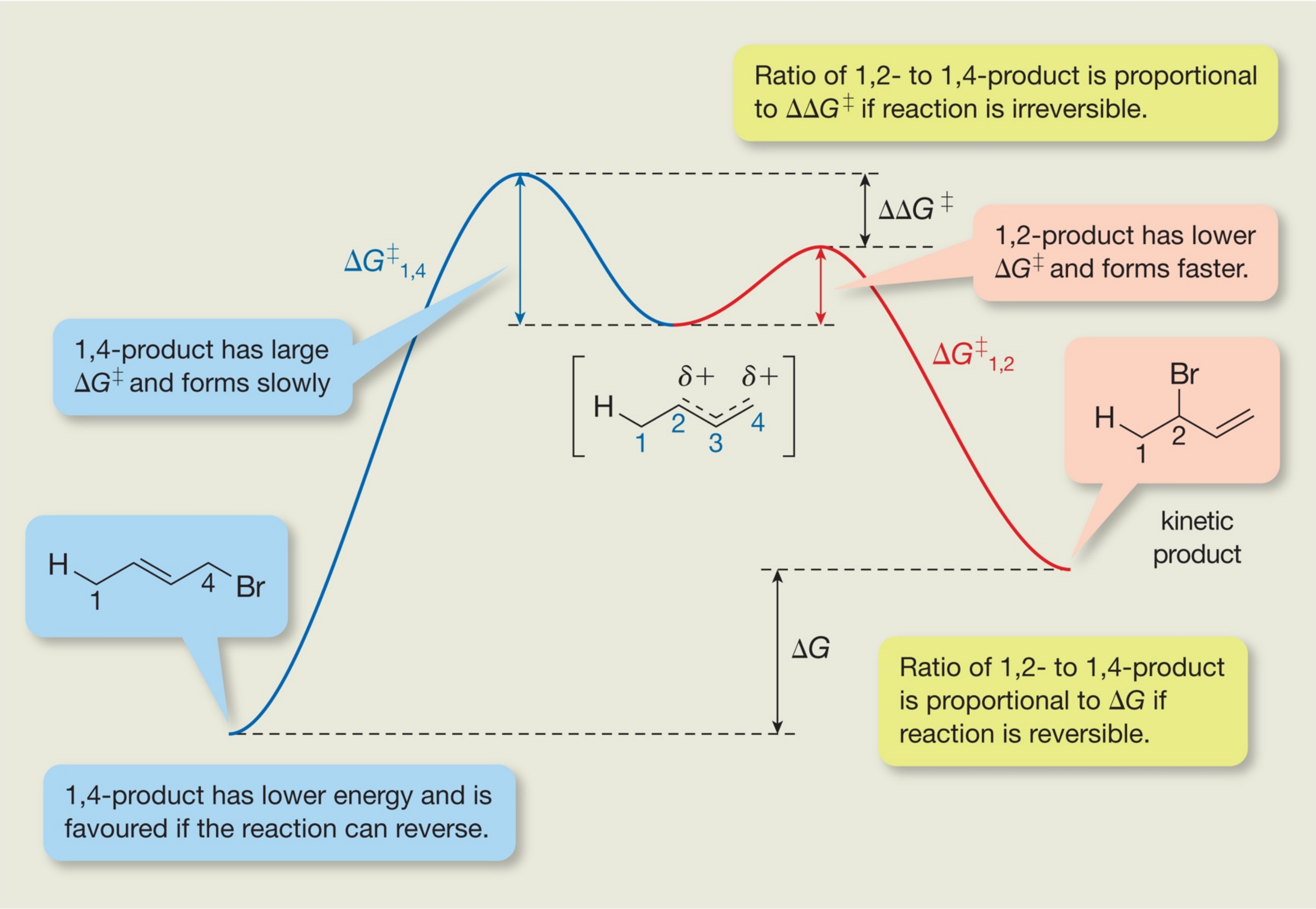
Electrophilic Addition to Dienes



- The final product distribution is controlled by two competing factors: kinetics and thermodynamics.
  - The kinetic product is the product that is formed the fastest.
  - The thermodynamic product is the product that is the most stable.
- In this reaction, the 1,2-addition product (kinetic) forms faster because it has the lowest activation energy.
- In this reaction, the 1,4-addition product (thermodynamic) forms slower because it has a higher activation energy but is the more stable product.

Electrophilic Addition to Dienes

- At low temperatures the kinetic product is the major product.
- At higher temperatures, the thermodynamic product is the major product.



Ratio of 1,2- to 1,4-product is proportional to $\Delta\Delta G^\ddagger$ if reaction is irreversible.

1,2-product has lower $\Delta G^\ddagger$ and forms faster.

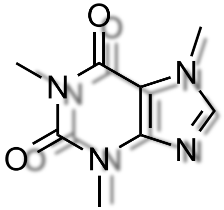
1,4-product has large $\Delta G^\ddagger$ and forms slowly

kinetic product

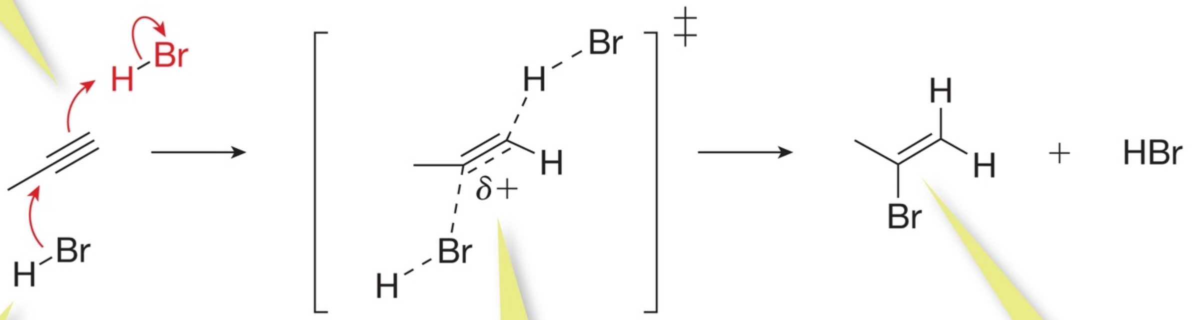
Ratio of 1,2- to 1,4-product is proportional to ΔG if reaction is reversible.

1,4-product has lower energy and is favoured if the reaction can reverse.

Electrophilic Addition to Alkynes



- An alkyne consist of one σ bond and 2 orthogonal π bonds.
- The π bonds in an alkyne react just like the π bonds in an alkene.
- Halo acids undergo Markovnikov addition to alkynes to form ***vinyl halides***, however, alkynes react so quickly that discrete carbocations are not formed.



Nucleophilic π bond removes hydrogen from a molecule of HBr.

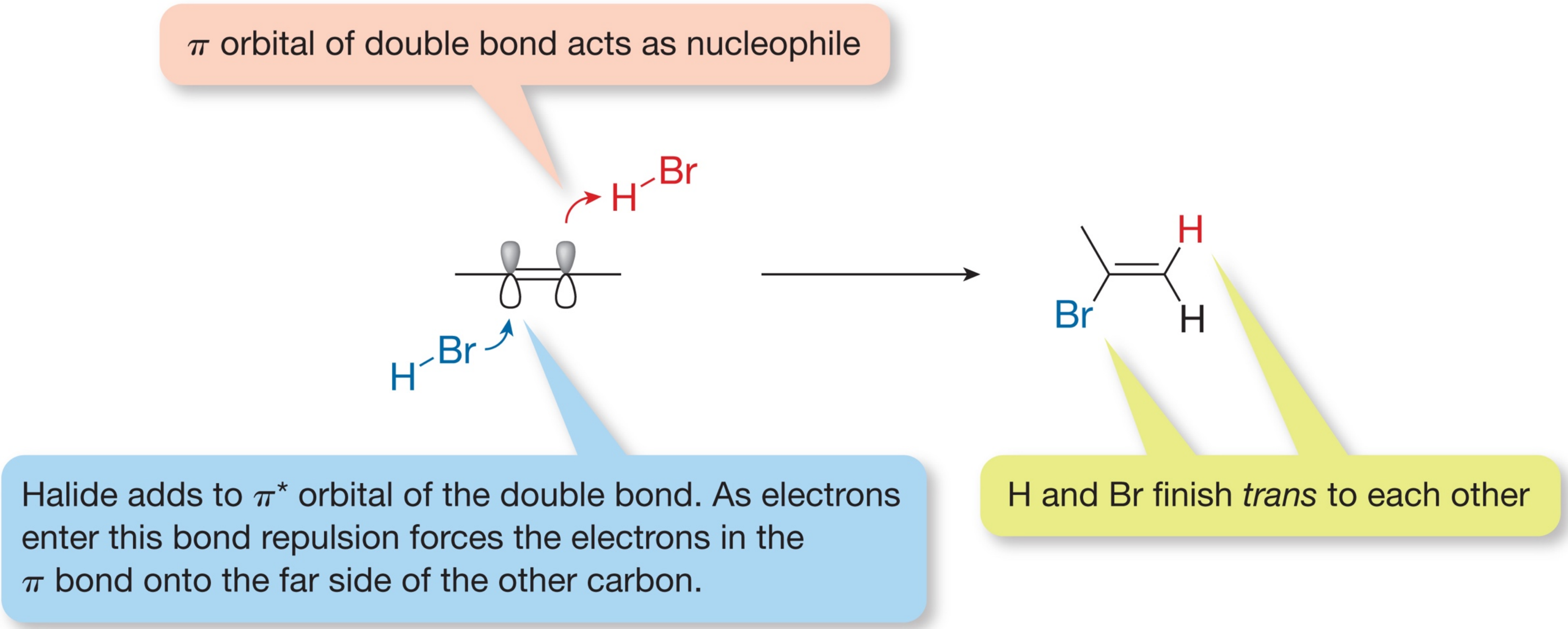
At the same time, a second molecule of HBr donates electrons to form a new carbon-halogen bond.

$\delta+$ develops and is favoured on the most substituted position.

Bromine ends up on the carbon that can best stabilize a positive charge in the transition state (most substituted position).

Electrophilic Addition to Alkynes

- Electrophiles add to alkynes in an anti fashion to give a trans isomer.



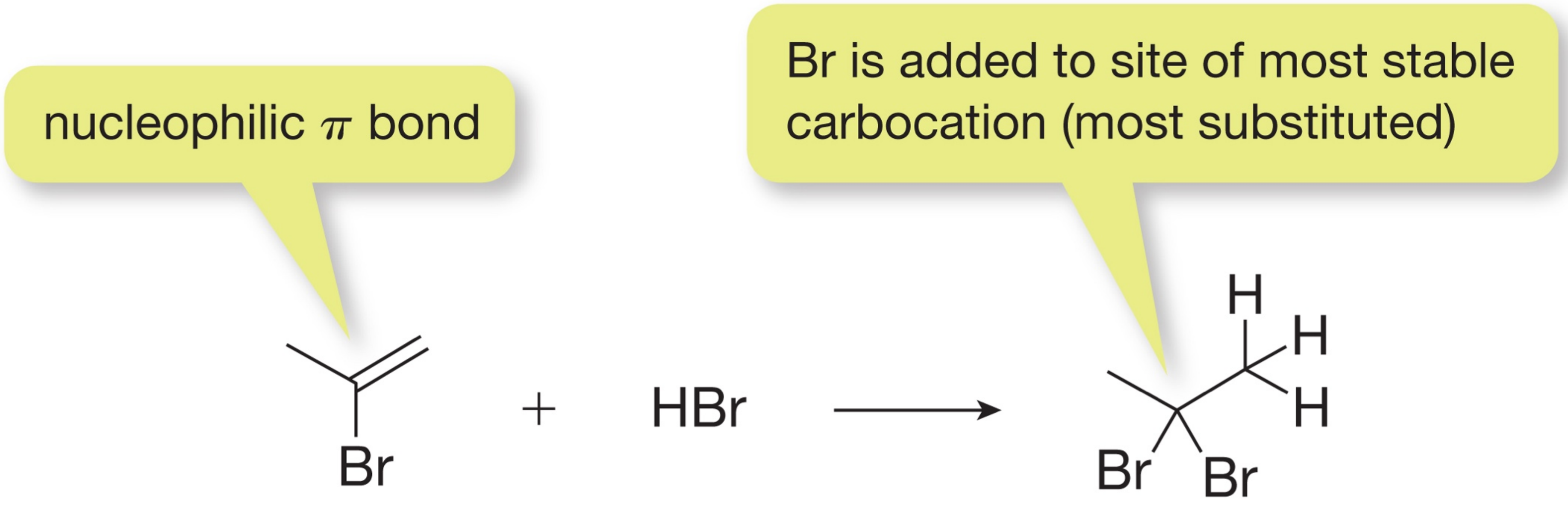
π orbital of double bond acts as nucleophile

Halide adds to π^* orbital of the double bond. As electrons enter this bond repulsion forces the electrons in the π bond onto the far side of the other carbon.

H and Br finish *trans* to each other

Electrophilic Addition to Alkynes

- Because vinyl halides contain a π bond, they can undergo a further addition reaction, giving a ***geminal halide*** product.



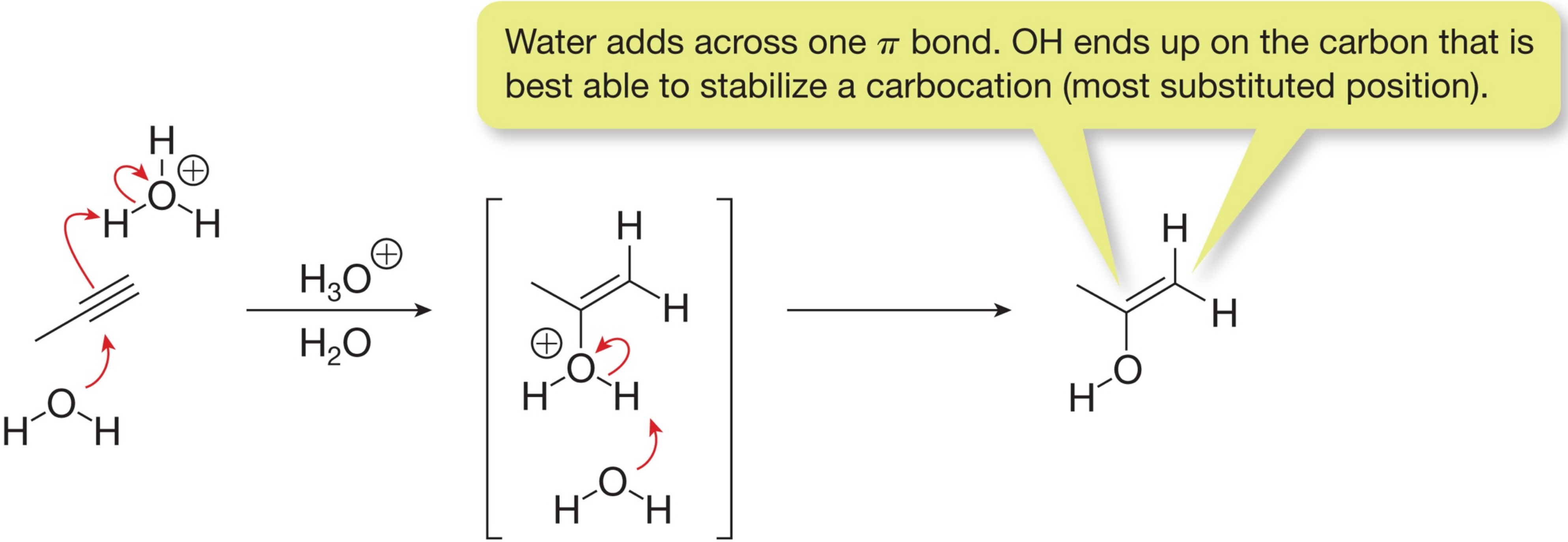
nucleophilic π bond

Br is added to site of most stable carbocation (most substituted)

geminal dihalide

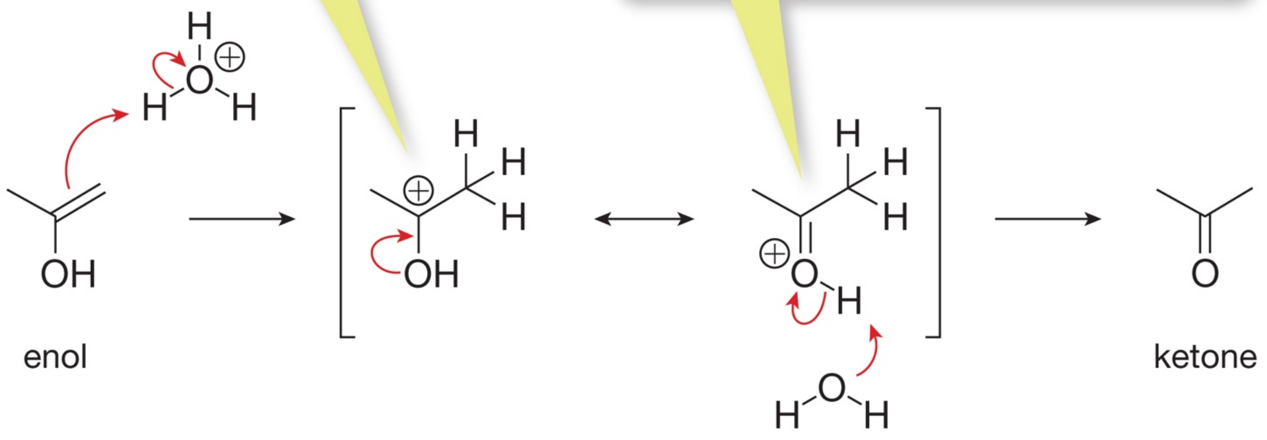
Electrophilic Addition to Alkynes

- Water can be added to alkynes to generate ***enols***. The addition of an alcohol instead of water forms an ***enol ether***.
- This reaction is also under Markovnikov control.


Water adds across one π bond. OH ends up on the carbon that is best able to stabilize a carbocation (most substituted position).

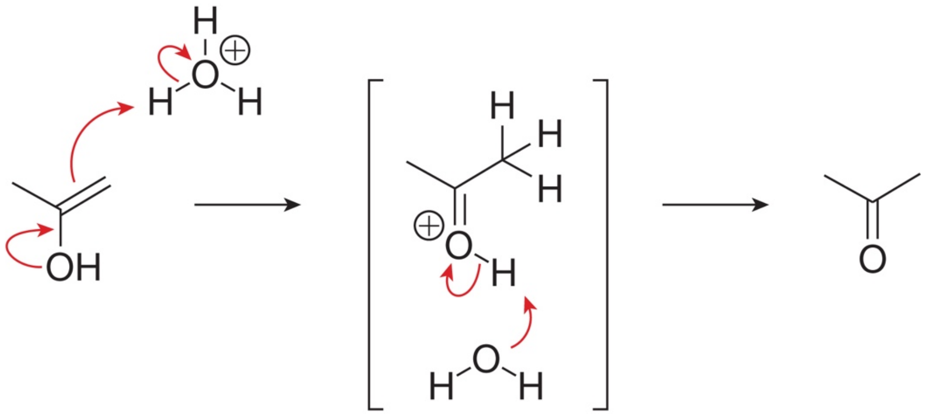
Electrophilic Addition to Alkynes

- Under acidic conditions, the enol products are quickly converted into the corresponding ketone.
- This conversion is known as a tautomerization reaction.


resonance stabilized carbocation

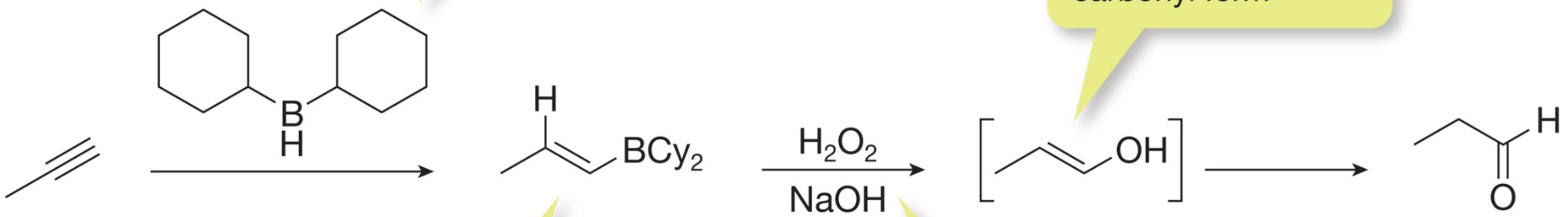
this resonance form makes the largest contribution (all atoms have octets)

Mechanism is drawn using most significant resonance form:



Electrophilic Addition to Alkynes

- The Anti-Markovnikov addition of water to alkynes can also be done using boranes. Sterically hindered boranes are used to ensure that the reaction stops after a single borane addition.
- The concerted mechanism of the addition of H and B dictate that it is a syn addition.



borane carries out anti-Markovnikov addition to one of the π bonds of the alkyne

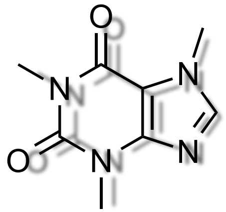
enol tautomerizes to carbonyl form

large groups on borane prevent hydroboration of second π bond

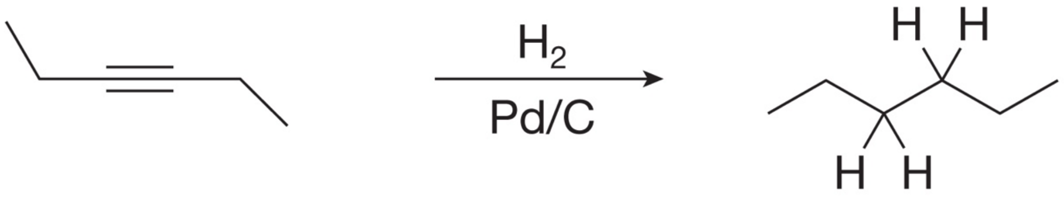
once hydroboration reaction is complete, H_2O_2 is used to introduce oxygen

aldehyde

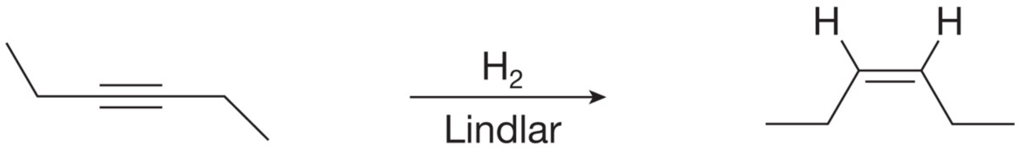
Electrophilic Addition to Alkynes



- Alkynes can also be hydrogenated, and like alkenes, a metal catalyst is required to make H_2 reactive enough to interact with the nucleophile.
- With standard metal catalyst, the alkyne is converted to the corresponding alkane.



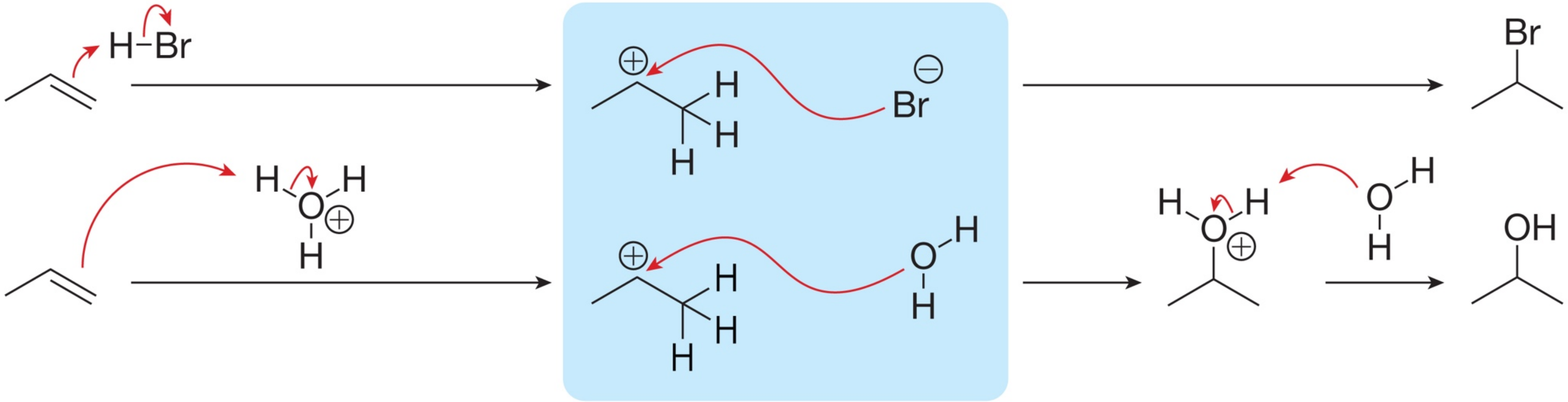
- Hydrogenation of an alkyne can be stopped at the alkene if a ***Lindlar catalyst*** is used. A Lindlar catalyst is a 'poisoned' catalyst; the metal has been deactivated such that the reaction stops at the alkene.



cis bond is formed preferentially

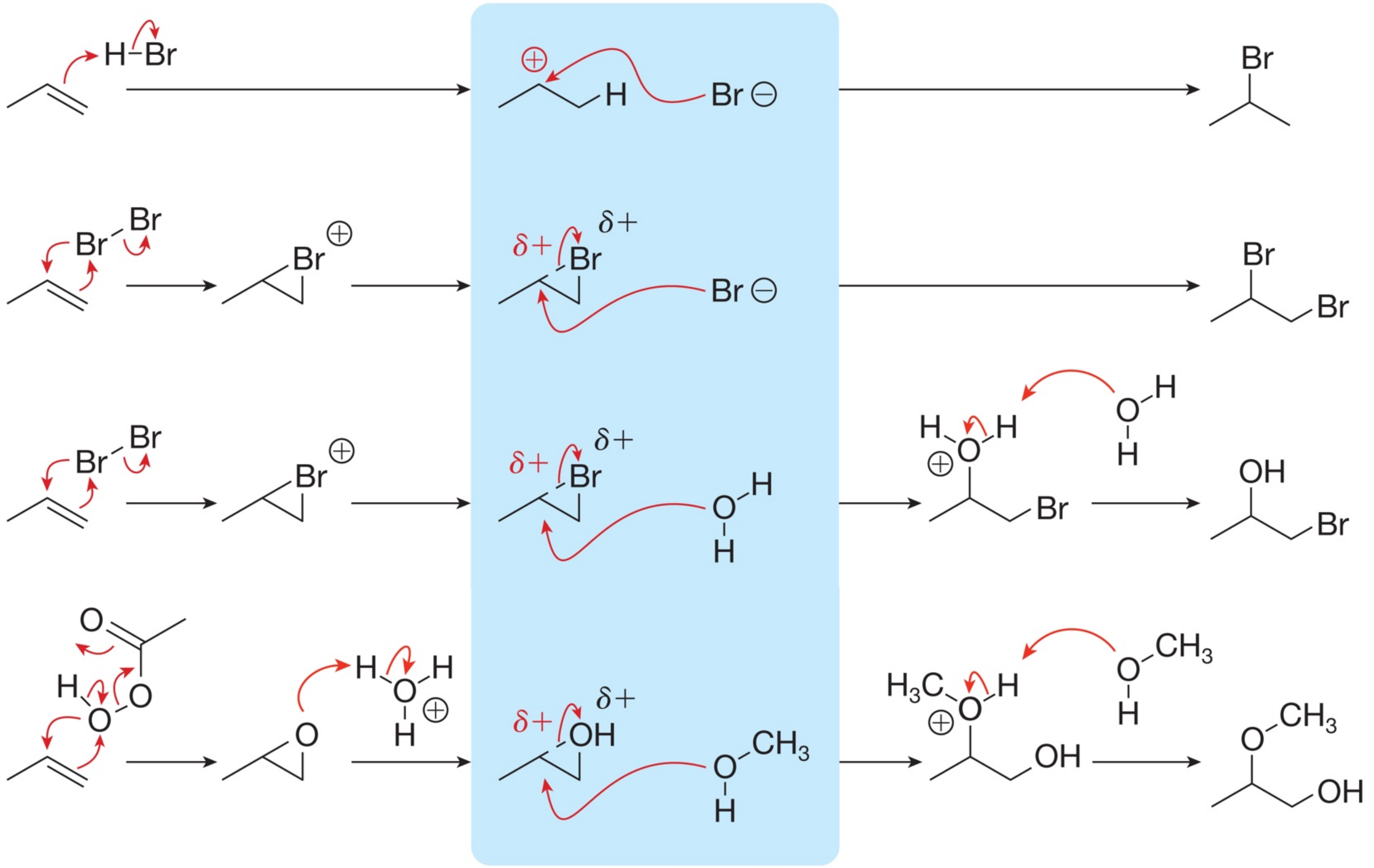
Patterns in Alkene Addition Reactions

- The additions of electrophiles to nucleophilic π bonds are systematic.
- These reactions follow patterns controlled by the stabilization of the intermediate carbocation and $\delta+$ charges.
- The major product is the one formed from the most stable carbocation (Markovnikov’s rule).



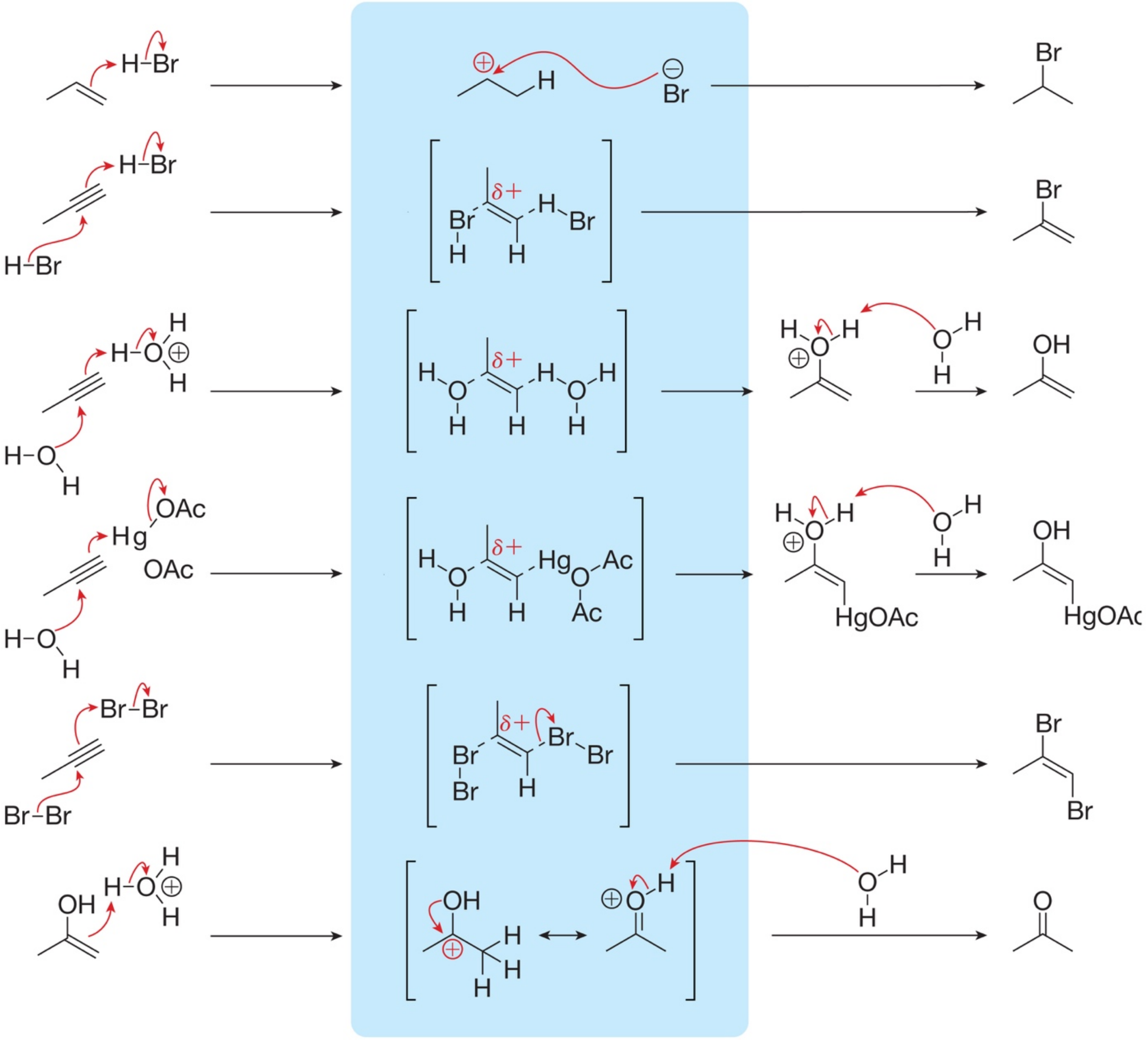
Patterns in Alkene Addition Reactions

- Some reactions proceed via cyclic intermediates, which are opened by nucleophiles.
- Nucleophiles open these ring intermediates in an anti fashion.



Patterns in Alkene Addition Reactions

- Alkynes react in similar ways but do not proceed via a full carbocation intermediate.
- Under acidic conditions, enols quickly tautomerize to the keto form.



Patterns in Alkene Addition Reactions

- Sterically hindered hydroboranes are used to add water in an Anti-Markonikov fashion.
- The overall addition of water is syn.