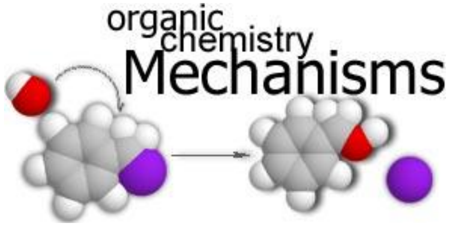
CHEM 344

ORGANIC REACTION MECHANISM

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE



PRE-REQUISITES COURSE; CHEM 241

CREDIT HOURS; 2 (2+0+0)

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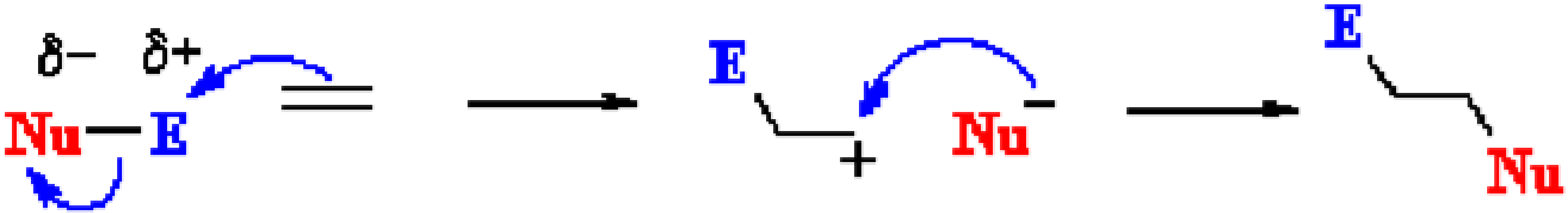
Addition to Carbon–Carbon Double bond

Electrophilic Addition Reactions

ELECTROPHILIC ADDITION REACTION

- *Electrophilic addition reactions* are an important class of reactions that allow the interconversion of C=C and C≡C into a range of important functional groups. .
- Conceptually, addition is the reverse of elimination
- What does the term "electrophilic addition" imply ?

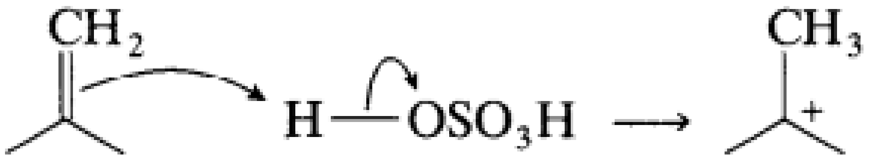
  *A **electrophile, E$^+$** , is an electron poor species that will react with an electron rich species (C=C)*
  An addition implies that two systems combine to a single entity.



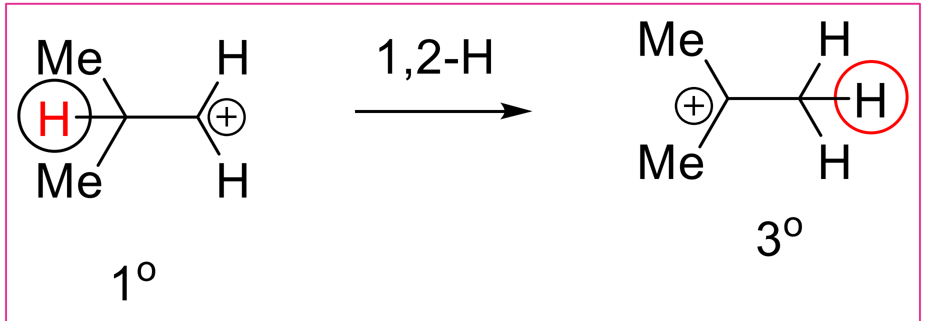
- **Electrophilic addition reaction involves two major steps:**
  (1) Addition of the electrophile to the nucleophilic π bond to give **carbocation intermediate**,
  (2) Reaction of the carbocation with a nucleophile.
- Simultaneous formation of the two σ bonds

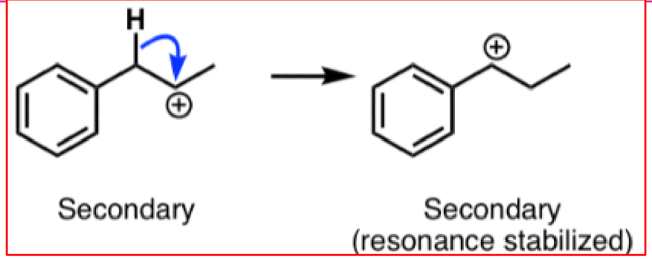
FORMATION AND STABILITY OF CARBOCATION

- *Protonation of an olefin*; Intermediate cations are often produced by addition of a proton or a Lewis acid to a π bond.

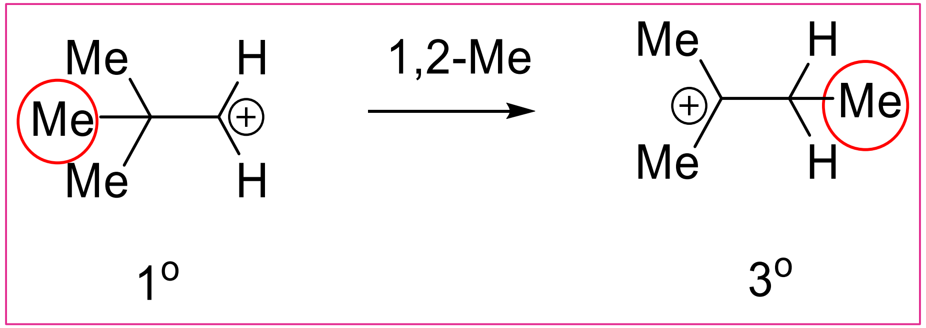


- *Carbocation rearranges to another carbocation of equal or greater stability*.
  - 1,2-Hydride Shift



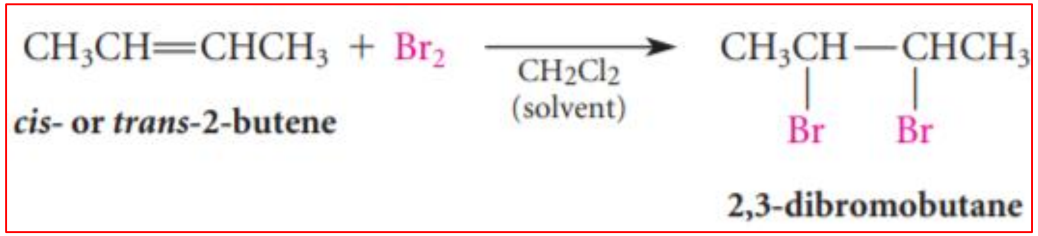


  - 1,2-methyl shift

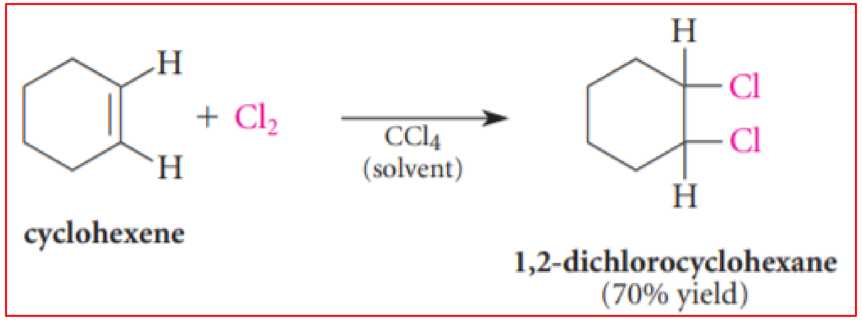


HALOGENATION OF ALKENES

A) ADDITION OF CHLORINE AND BROMINE



$$CH_3CH{=}CHCH_3 + Br_2 \xrightarrow[CH_2Cl_2\ \text{(solvent)}]{} CH_3\underset{Br}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH}}CH_3$$

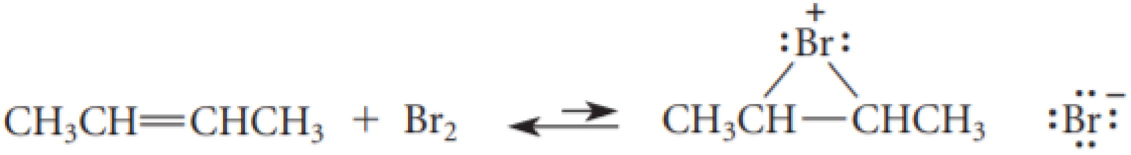


- The products of these reactions are ***vicinal dihalides*** *"compounds with halogens on adjacent carbons"*.
  - **Bromine and chlorine** are the two halogens used mostly in halogen addition.
  - **Fluorine** is so reactive that it not only adds to the double bond but also rapidly replaces all the hydrogens with fluorines, often with considerable violence.
  - **Diiodides** are unstable and decompose to the corresponding alkenes and I_2.
  - These reaction run at *low temperature*, and *Dark* (Avoid Radicals).
  - Inert solvents such as methylene chloride (CH_2Cl_2) or carbon tetrachloride (CCl_4) are used as these solvents dissolve both halogens and alkenes.
  - In fact, this discharge of color is a useful qualitative test for alkenes.

A) ADDITION OF CHLORINE AND BROMINE

MECHANISM

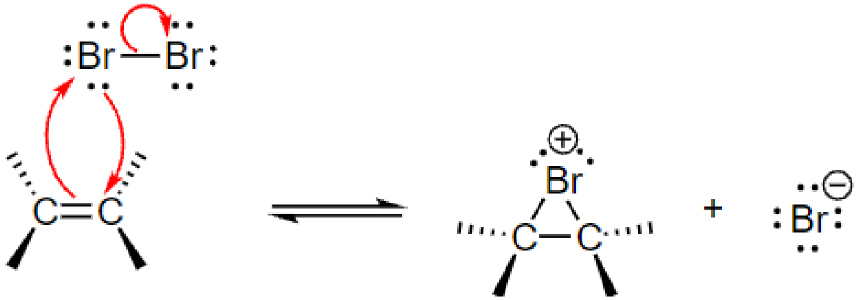
- Addition of bromine to alkene involves a *reactive intermediate called a* ***bromonium ion***.
- **Carbocations** are not actual intermediates in most halogen additions.



a bromonium ion

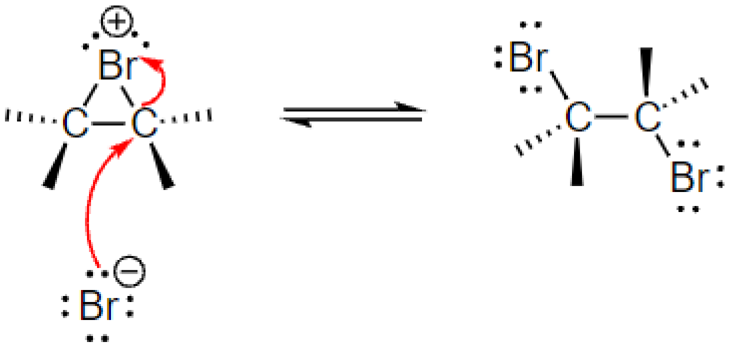
- **Step 1,**

  Heterolytic cleavage of polarized Br-Br bond occurs and Br with the positive charge forms a cyclic intermediate “bromonium ion” with the two carbons from the alkene.



- **Step 2,**

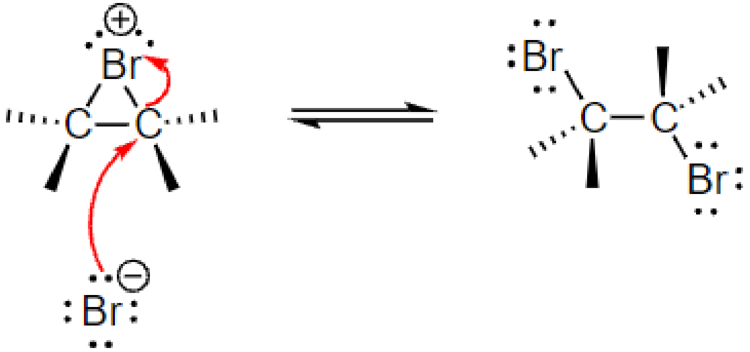
  Bromide anion attacks either carbon of the bridged bromonium ion from the back side of the ring.



A) ADDITION OF CHLORINE AND BROMINE

MECHANISM

- *The ring opening up with the two halogens on opposite sides as each other.*
- ***Anti stereochemistry**;*
  - *The two bromine atoms come from opposite faces of the double bond.*
  - *The product is that the bromines add on **trans** to each other.*
- *The halide ion can attack any carbon from the opposite side of the ring it creates a mixture of steric products.*
- *Optically inactive starting material produce optically inactive achiral products; **a racemic mixture**.*

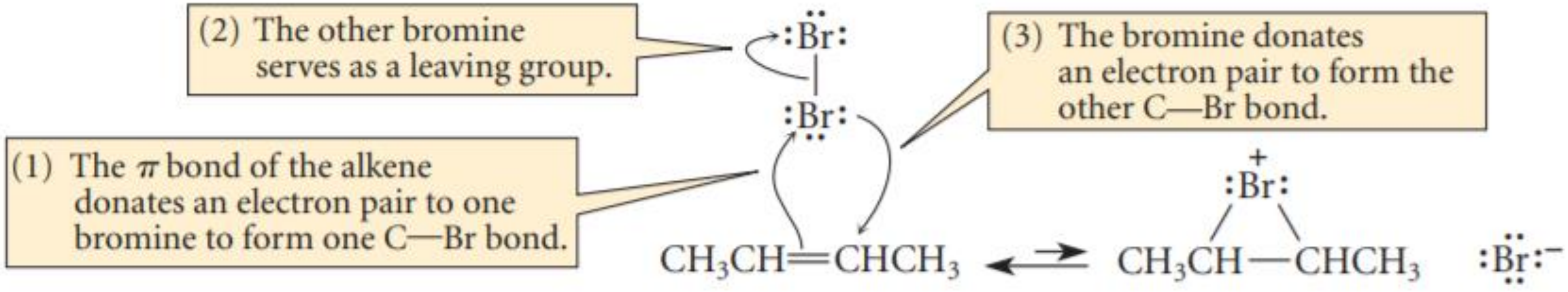


A) ADDITION OF CHLORINE AND BROMINE

EXAMPLE 1

- **Step 1,**

  The electrons of the π-bond are donated to one of the bromines, the other bromine acts as a leaving group, and a carbocation is formed.



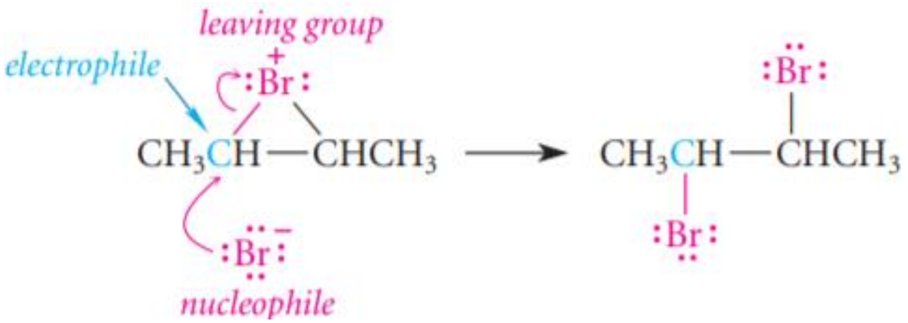
(2) The other bromine serves as a leaving group.

(1) The π bond of the alkene donates an electron pair to one bromine to form one C—Br bond.

(3) The bromine donates an electron pair to form the other C—Br bond.

- **Step 2,**

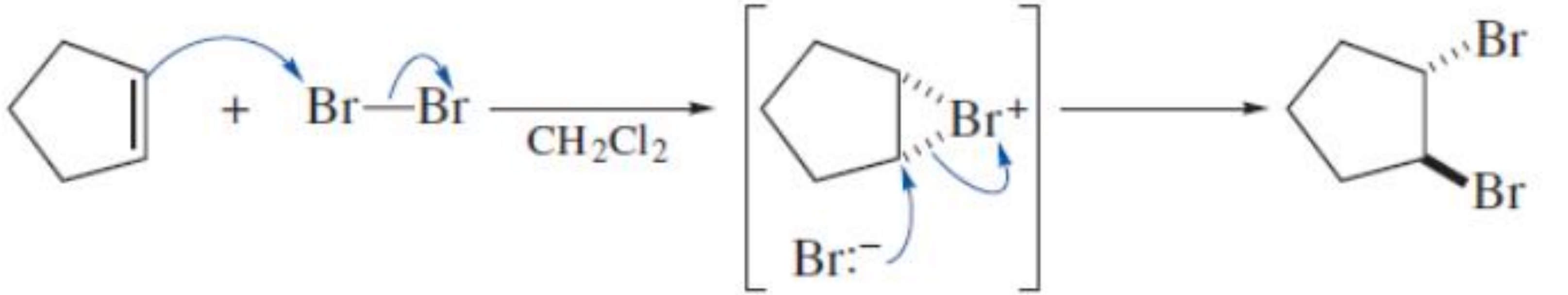
  The carbocation undergoes a Lewis acid–base association reaction with the neighboring bromine. (intramolecular (internal) Lewis acid–base association reaction)



A) ADDITION OF CHLORINE AND BROMINE

EXAMPLE 2

- The reaction of bromine with cyclopentene is stereospecific and proceeds by *anti addition*.



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Cyclopentene
(*colorless*)

Bromine
(*red-brown*)

A cyclic bromonium ion

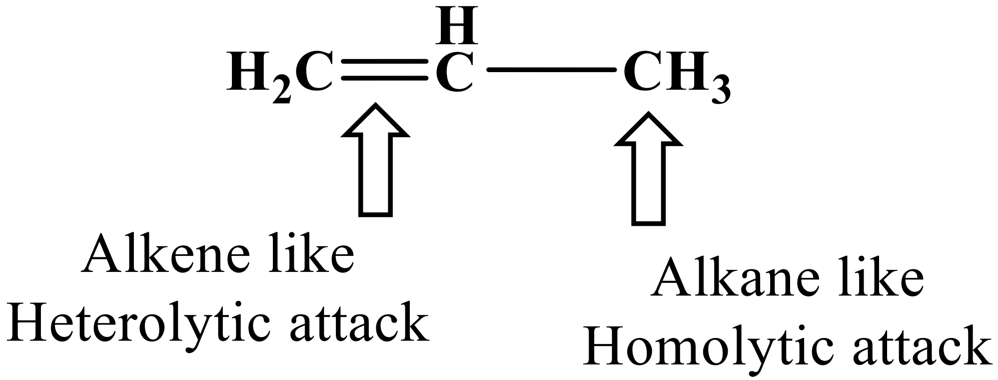
trans-1,2-
Dibromocyclopentene
(*colorless*)

A) ADDITION OF CHLORINE AND BROMINE

SUMMARY

- Overall transformation : C=C to X-C-C-X.
- Reagent: normally the halogen (e.g. Br_2) in an inert solvent like methylene chloride, CH_2Cl_2.
- Regioselectivity: not relevant since both new bonds are the same, C-X.
- Reaction proceeds *via* cyclic halonium ion.
- Stereoselectivity: anti since the two C-X bonds form in separate steps one from X_2 the other X^-.

ELECTROPHILIC ADDITION *vs.* FREE- RADICAL SUBSTITUTION



$H_2C{=}CH{-}CH_3$

Alkene like
Heterolytic attack

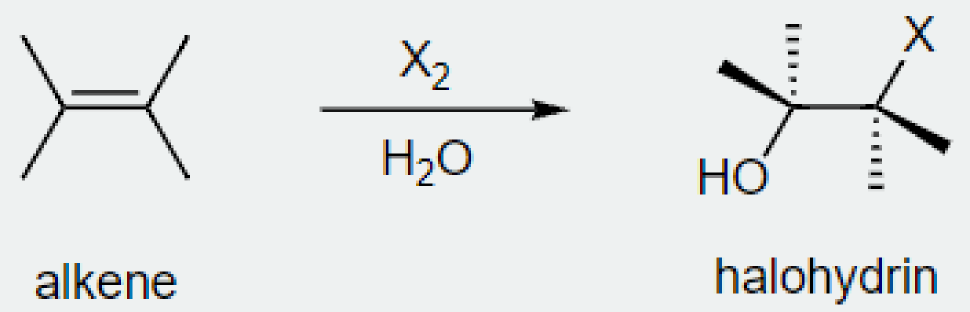
Alkane like
Homolytic attack

- The propylene molecule has two sites where the halogen can attack, the double bond and the methyl group.
  - **Alkanes** undergo **substitution** by halogen at *high temperatures* and generally in the *gas phase conditions* favor to form free radicals.
  - **Alkenes** undergo **addition** of halogen at *low temperatures* and generally in *liquid phase conditions* favor to form heterolytic reactions.

$$H_2C{=}CH{-}CH_3 + Cl_2 \xrightarrow[\text{gas phase}]{600\ ^{\circ}C} H_2C{=}CH{-}CH_2Cl + HCl$$

B) HALOHYDRIN FORMATION

- The addition of hypohalous acid (HO-X) such as *hypobromous acid, HO-Br*, or *hypochlorous acid, HO-Cl* to an alkene to give a 1,2-halo alcohol, called *a halohydrin*.
- Bromohydrin and chlorohydrin are examples of halohydrins (where X = Br or Cl).

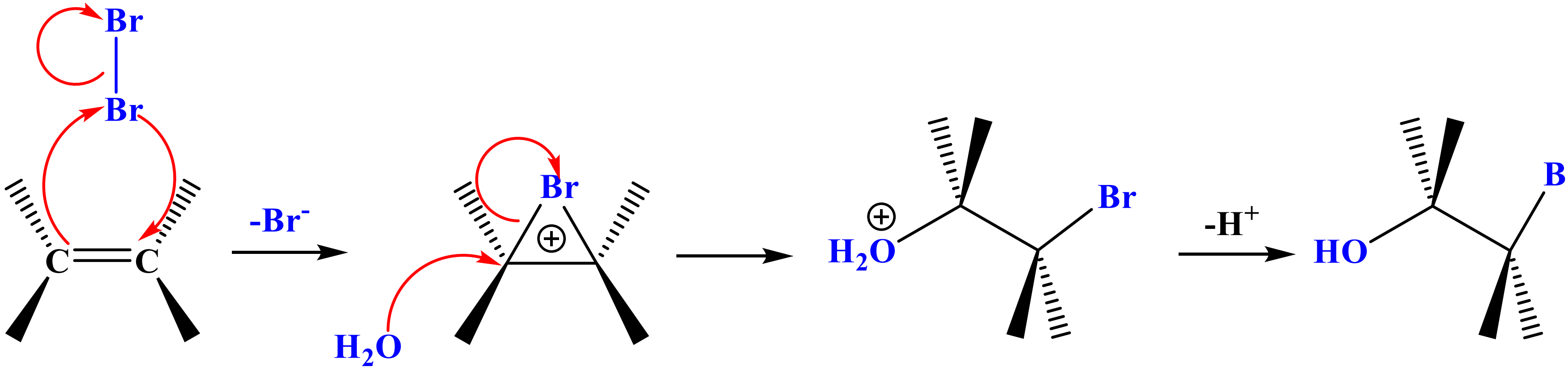


B) HALOHYDRIN FORMATION

MECHANISM

1) Reaction of the alkene with Br_2 yields a *bromonium ion intermediate*.
2) Water acts as a nucleophile, using a lone pair of electrons to open the bromonium ion ring and form a bond to carbon .

   Since oxygen donates its electrons in this step, it now has the positive charge.
3) Loss of a proton from oxygen then gives H_3O^+ and the neutral bromohydrin addition product.

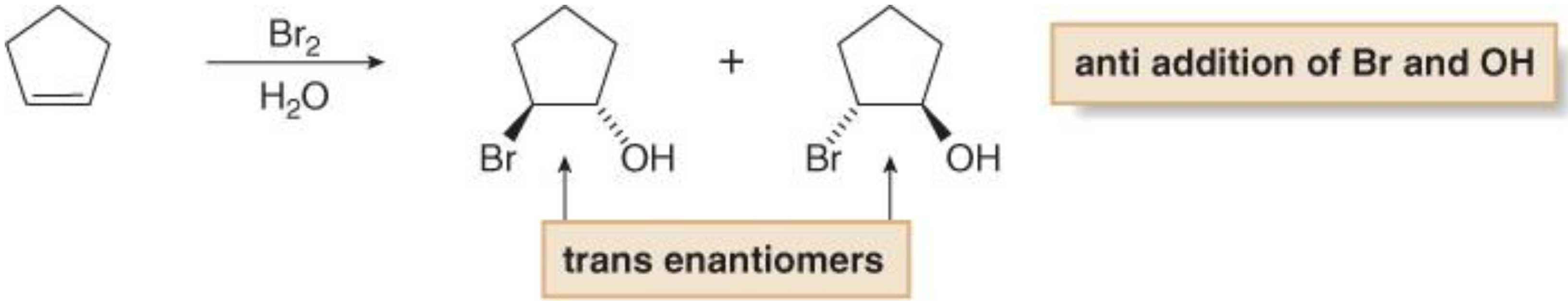


Nucleophilic Solvents (H_2O) can open Bromonium ion

B) HALOHYDRIN FORMATION

EXAMPLES

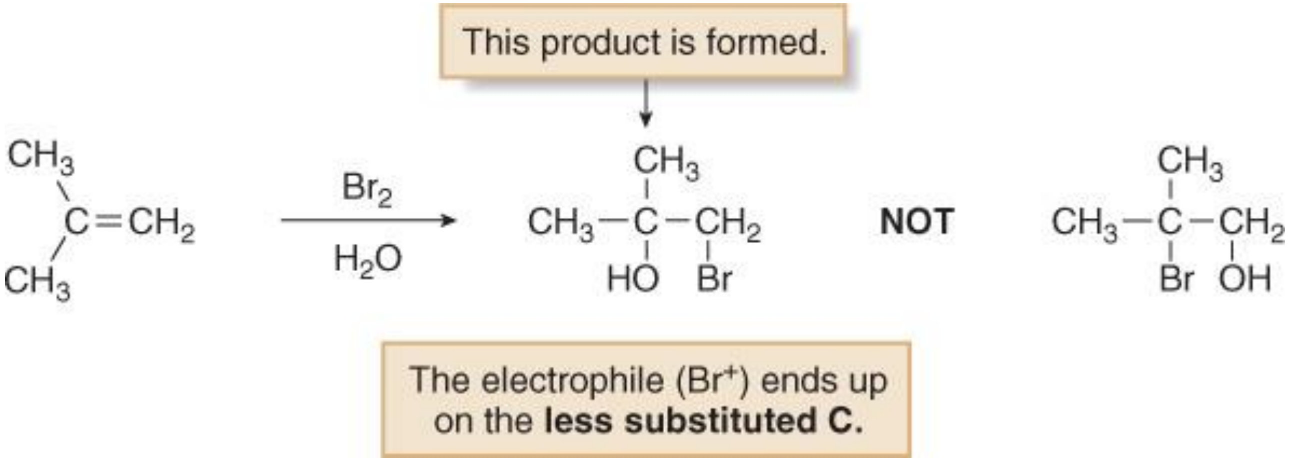
- Symmetric alkene; anti addition of Br and OH



anti addition of Br and OH

trans enantiomers

- Unsymmetric alkene; *The* ***reaction is highly Regioselective.***
- The reaction of water with the bromonium ion can give two possible products.



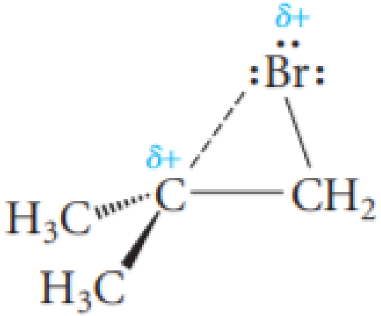
This product is formed.

The electrophile (Br^+) ends up on the **less substituted C.**

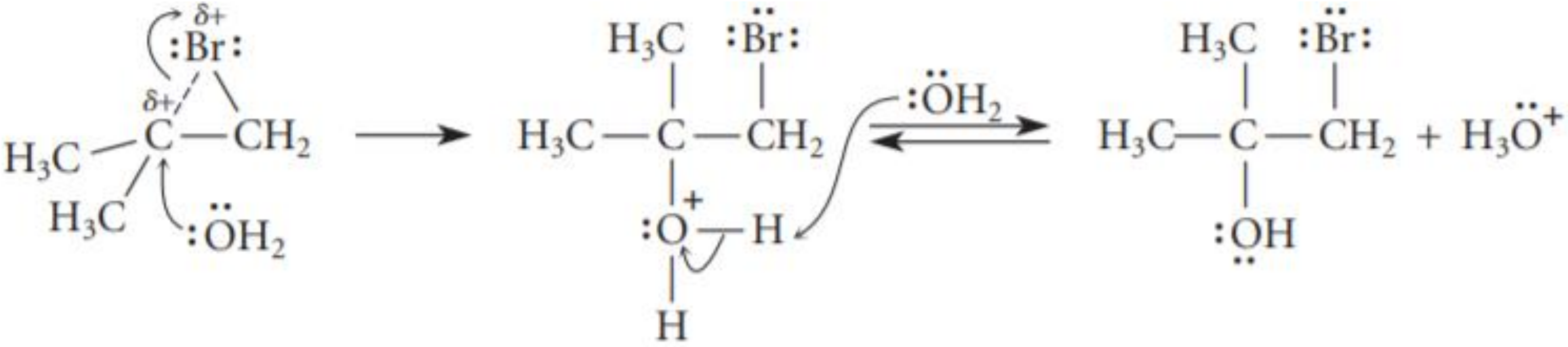
B) HALOHYDRIN FORMATION

EXAMPLES

- The **bond between this carbon and the bromine** is *so long and weak* that this species is essentially a carbocation containing a weak carbon–bromine interaction.



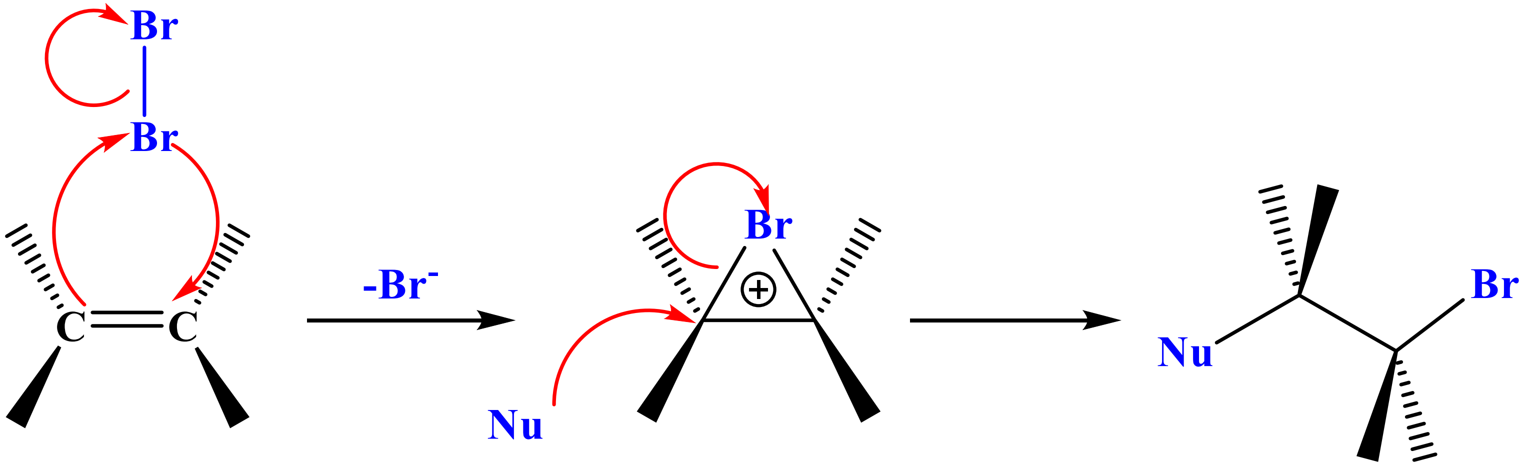
- Water reacts with the bromonium ion at the *tertiary* carbon, and the weaker bond to the leaving group is broken, to give the observed regioselectivity.



B) HALOHYDRIN FORMATION

MECHANISM

- Water is available at a higher concentration than the bromine ion,
- Water is also a better nucleophile than the bromine ion.
- The better a nucleophile, the more likely it is to attack.

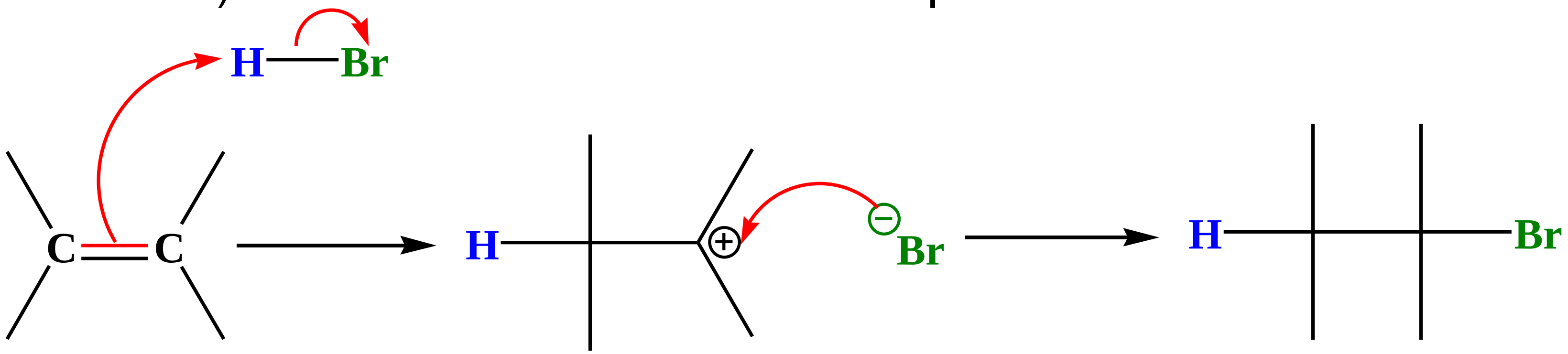


Nu= $\bar{C}N$-, $\bar{N}H_2$-, $\bar{O}CH_3$, etc....

Electrophile Moiety	Nucleophile Moiety
H	Cl
H	Br
H	I
H	OSO_3H
H	$\overset{\oplus}{OH_2}$
Cl	Cl
Br	Br
Cl	OH
Br	OH

ADDITION OF HX TO ALKENE

- All of the halides (HI > HBr > HCl > HF) can participate in this reaction with different rates due to *the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s*.
- This reaction works well with HBr and HCl.
- HI can also but used by reacting potassium iodide (KI) with phosphoric acid (H_3PO_4).
- Overall reaction;
  - The π-bond of the alkene is broken to form two single, σ-bonds.
  - π Bond (Nucleophile) Protonate → Carbocation Intermediate.
  - Carbocation Captured by Br^- (Nucleophile) → HBr Added.
  - HBr (or other HX) Addition in Two Overall Steps.



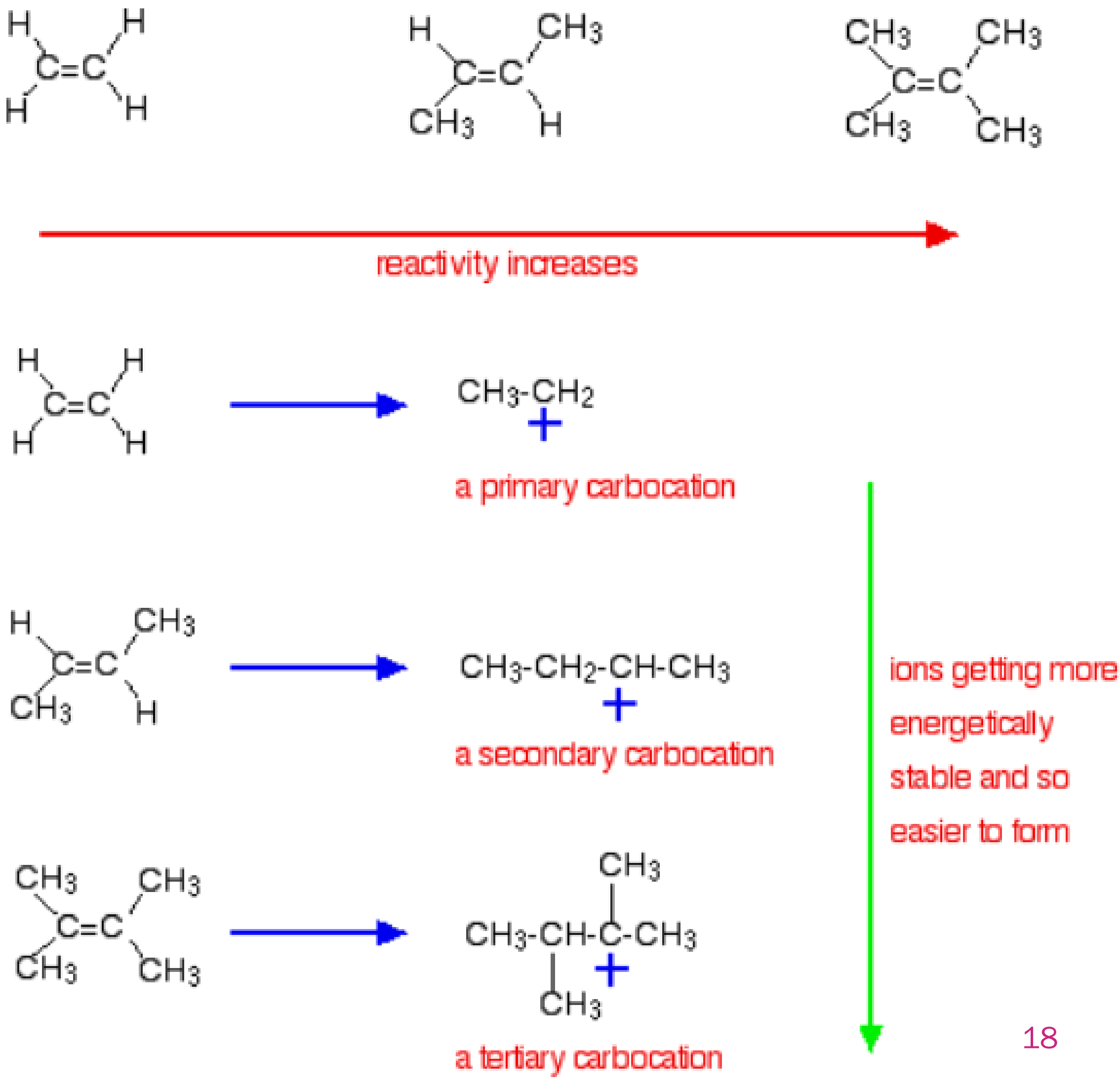
ADDITION OF HX TO ALKENE

REACTION RATES

Variation of rates when you change the alkene

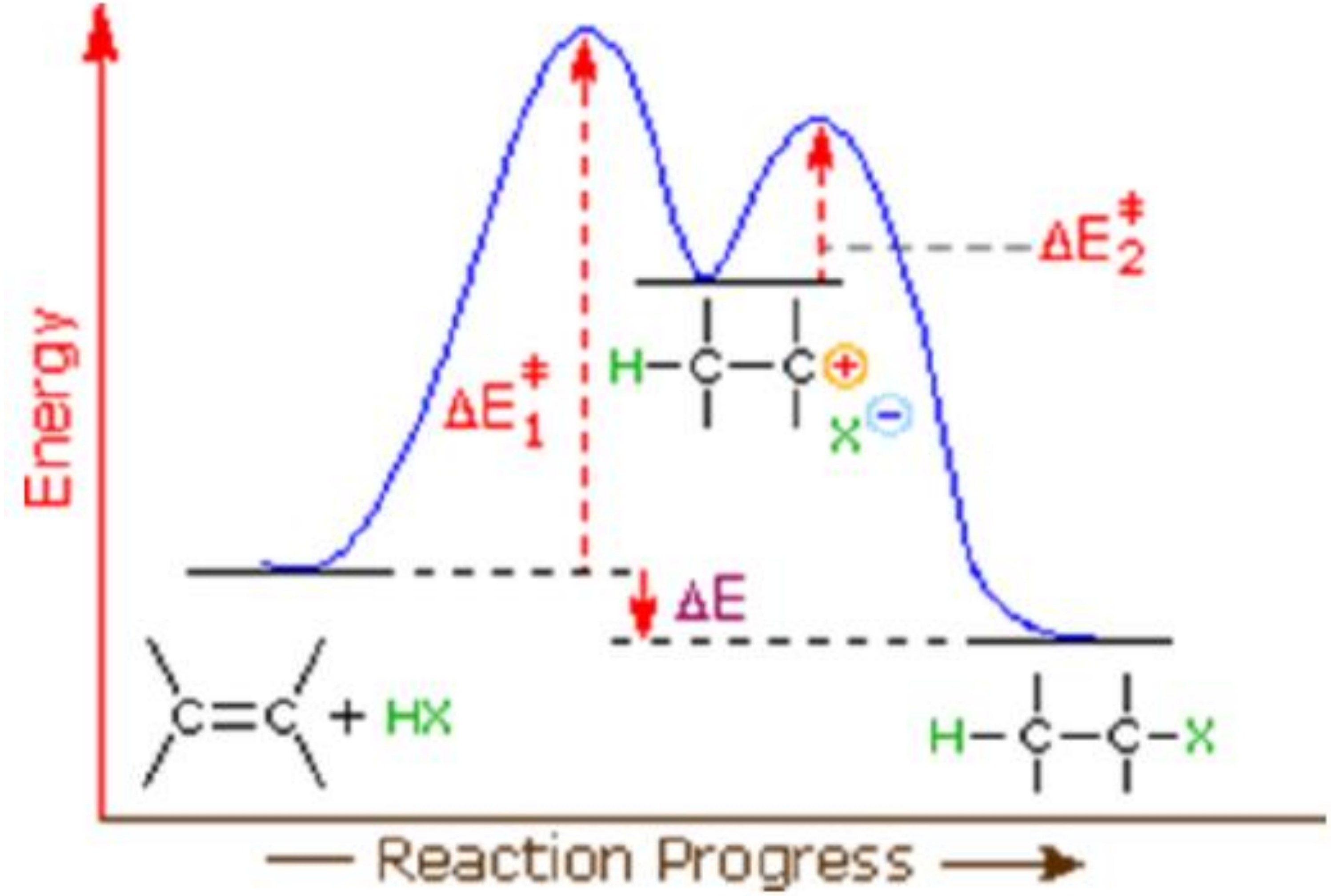
- The more important reason, is the stability of the intermediate ion formed during the reaction.
- Two-step electrophilic addition mechanism
- The *first step* of the mechanism is the *rate-determining step*.
- This electrophilic addition is a *second order reaction*.

Rate = k[Alkene][HX]



ADDITION OF HX TO ALKENE

REACTION ENERGY DIAGRAM



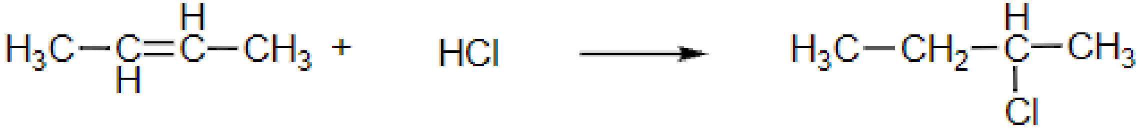
ADDITION OF HX TO ALKENE

ADDITION TO SYMMETRICAL ALKENES

- With ethene and hydrogen chloride, you get chloroethane.

$$H_2C{=}CH_2 \quad + \quad HCl \longrightarrow H_3C{-}CH_2Cl$$

- With but-2-ene you get 2-chlorobutane:



$$H_3C{-}\underset{H}{C}{=}\overset{H}{C}{-}CH_3 + HCl \longrightarrow H_3C{-}CH_2{-}\underset{Cl}{\overset{H}{C}}{-}CH_3$$

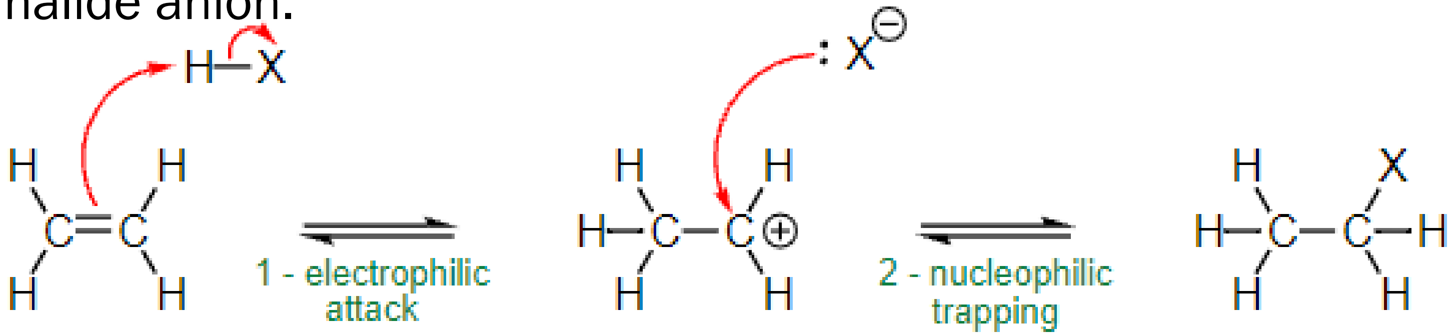
Mechanism

Step 1) Electrophilic Attack

The 2 π electrons from the double bond attack the H (electrophile) in the HX makes one of the carbons become an electron deficient "carbocation intermediate (sp^2 hybridized carbon) ".

Step 2: Nucleophilic attack by halide anion

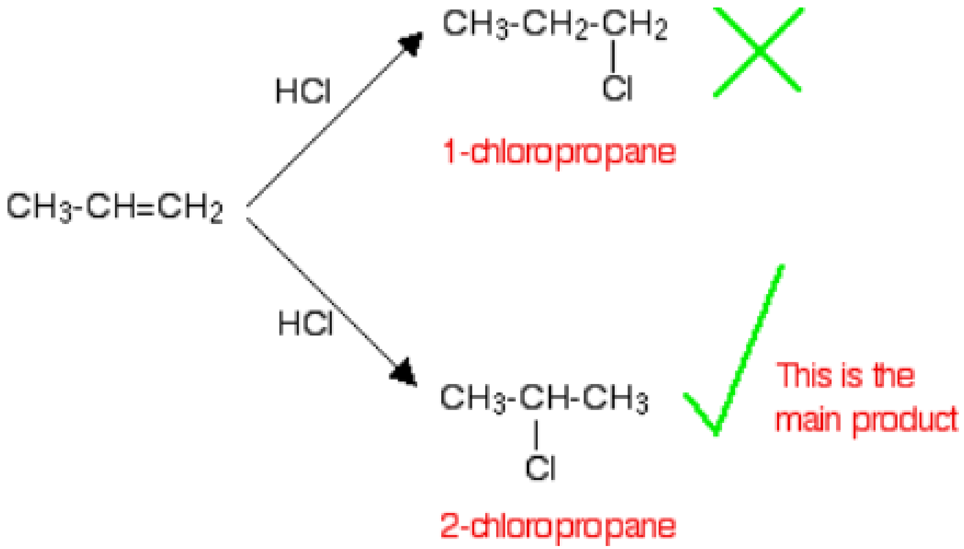
The formed carbocation now can act as an electrophile and accept an electron pair from the nucleophilic halide anion.



ADDITION OF HX TO ALKENE

ADDITION TO UNSYMMETRICAL ALKENES

Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule



- If HCl adds to an unsymmetrical alkene like propene; there are two possible ways it could add.
- However, in practice, there is only one major product according to **Markovnikov's Rule;**

  “When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.”

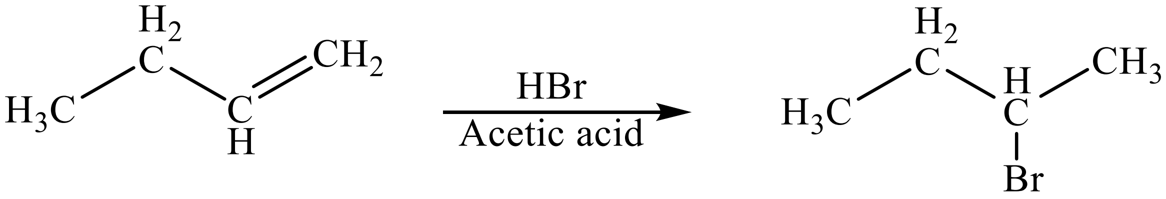
ADDITION OF HX TO ALKENE

REGIOSELECTIVITY OF HX ADDITION:

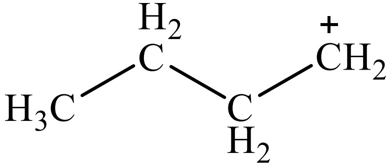
Markovnikov's Rule

Mechanism for Markovnikov's Rule; *Stability of Carbocation*

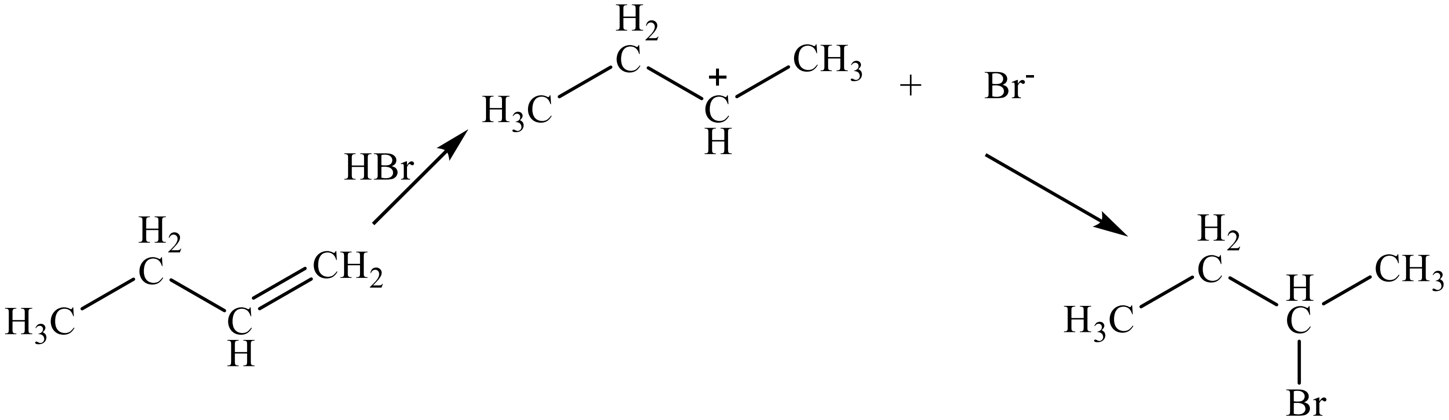
Protonation of double bond occurs in direction that gives the more stable of two possible carbocations.



1-Butene



Primary carbocation is less stable: not formed

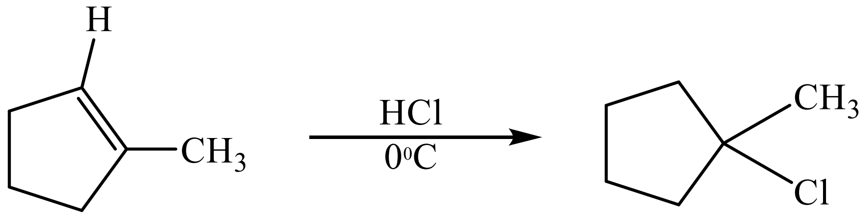


REGIOSELECTIVITY OF HX ADDITION: ADDITION OF HX TO ALKENE

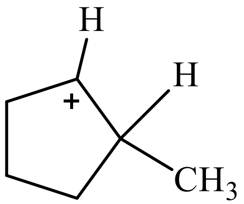
Markovnikov's Rule

Mechanism for Markovnikov's Rule; *Stability of Carbocation*

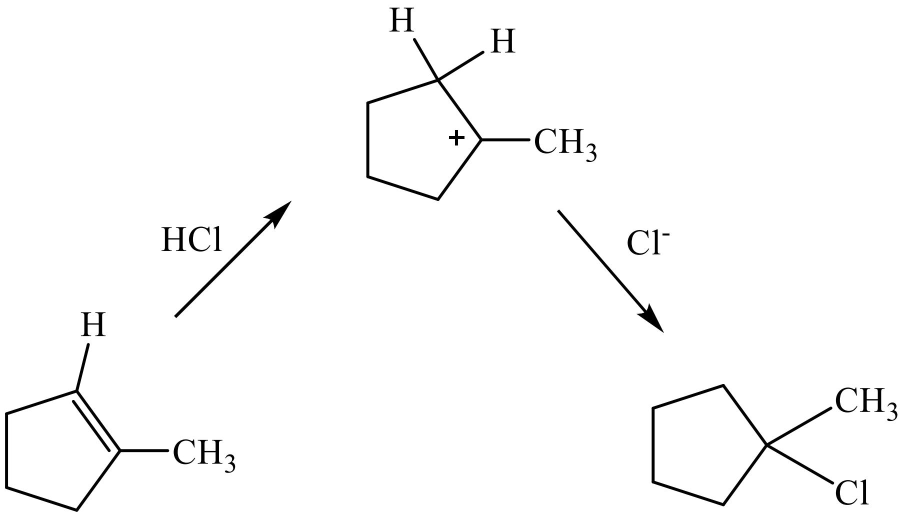
Protonation of double bond occurs in direction that gives the more stable of two possible carbocations.



1-Methylcyclopentene



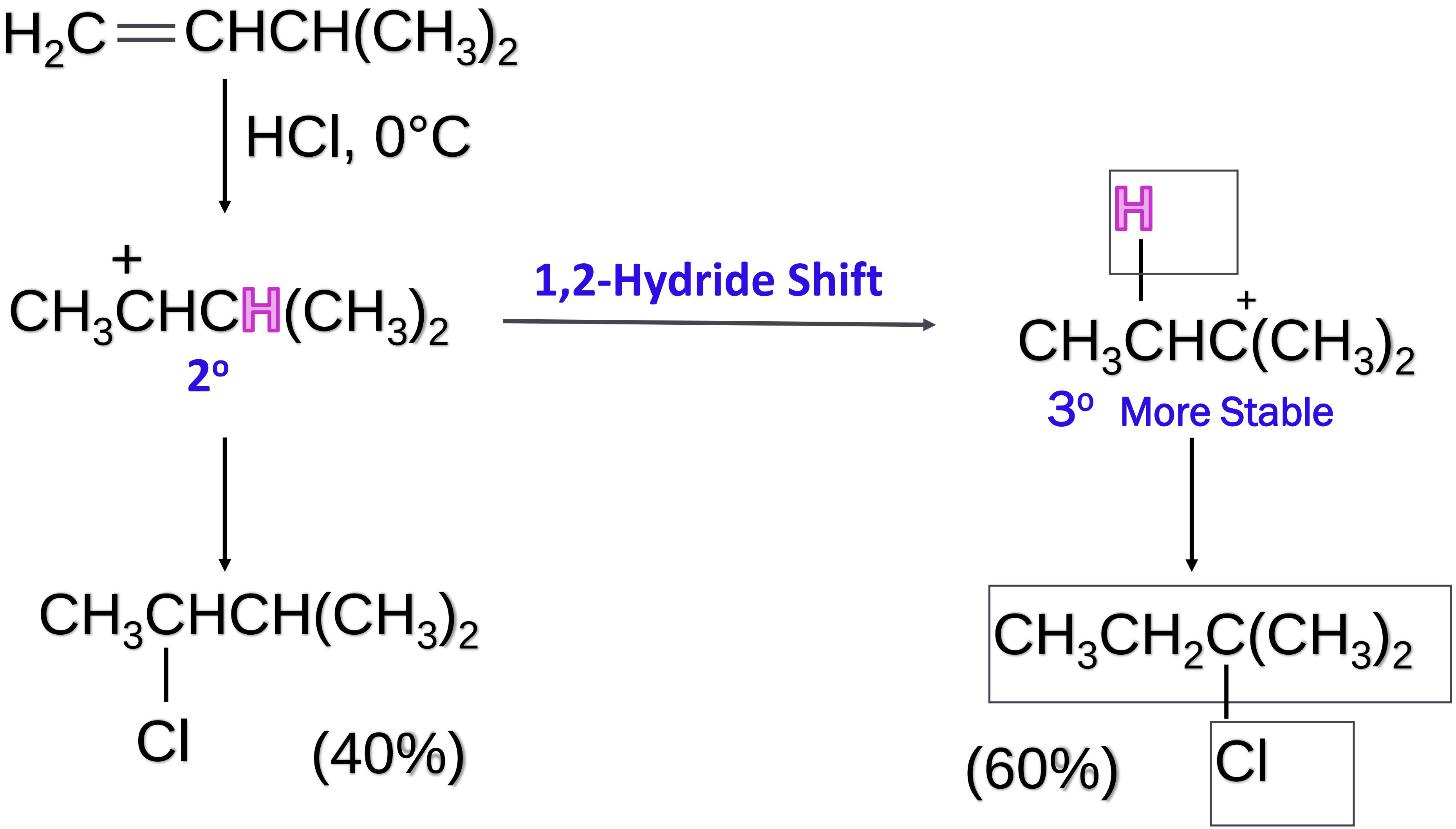
Secondary carbocation is less stable: not formed



REGIOSELECTIVITY OF HX ADDITION: ADDITION OF HX TO ALKENE

Markovnikov's Rule

Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes



$H_2C{=}CHCH(CH_3)_2$

HCl, 0°C

$CH_3\overset{+}{C}HCH(CH_3)_2$

2°

1,2-Hydride Shift

$CH_3\overset{H}{C}H\overset{+}{C}(CH_3)_2$

3° More Stable

$CH_3\underset{Cl}{C}HCH(CH_3)_2$ (40%)

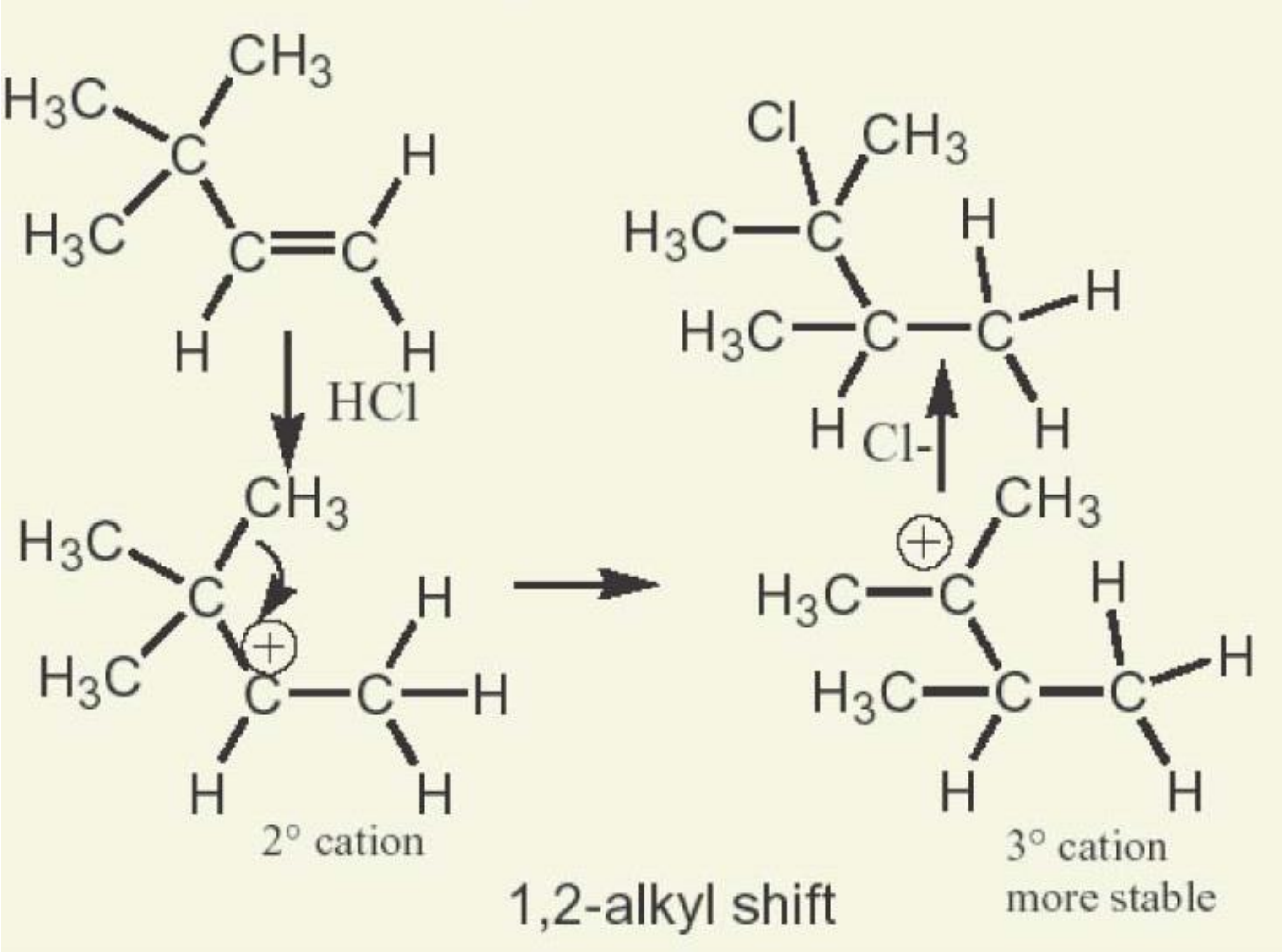
$CH_3CH_2\underset{Cl}{C}(CH_3)_2$ (60%)

REGIOSELECTIVITY OF HX ADDITION: ADDITION OF HX TO ALKENE

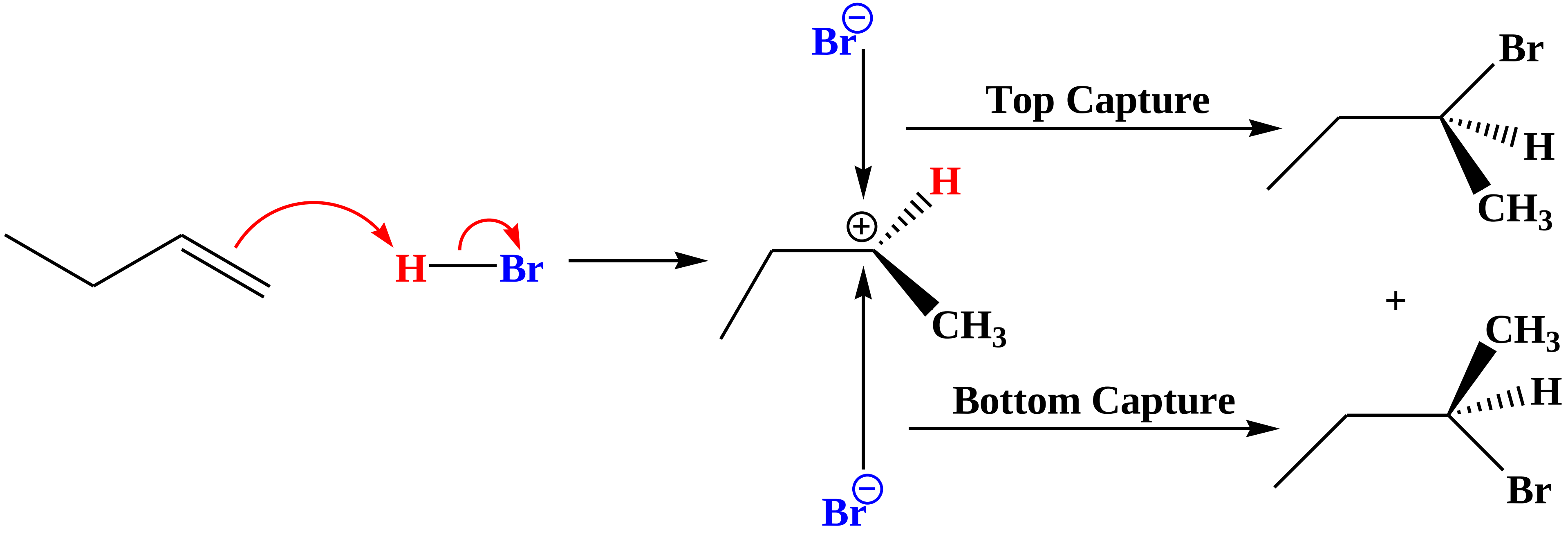
Markovnikov's Rule

Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes

1,2- Methyl Shift



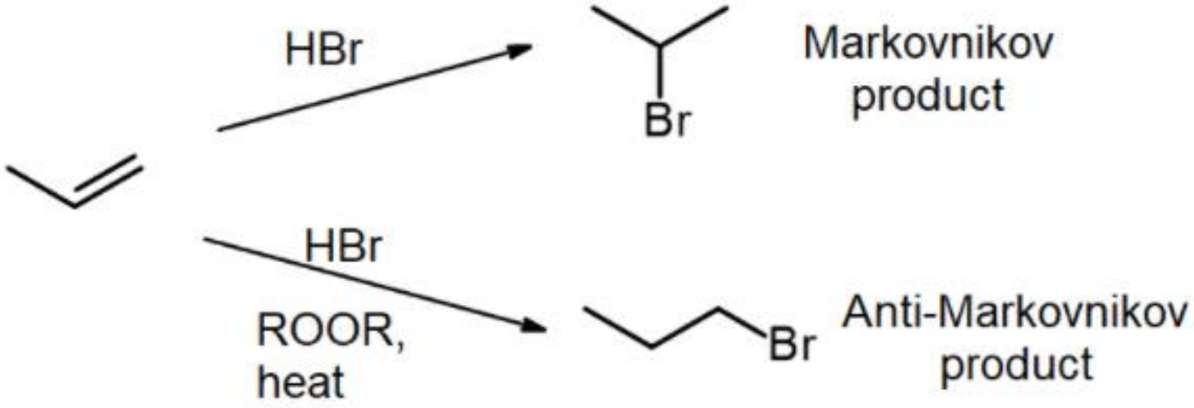
STEREOCHEMISTRY IN IONIC ADDITIONS



- Just as We Saw in S_N1: C^+ Has TWO FACES
- Top and Bottom Attack Give Two Stereochemical Products
- *R* and *S* Enantiomers Formed as a Racemic Mixture (50:50)

ANTI-MARKOVNIKOV HBR ADDITION:

“Free Radical Addition”

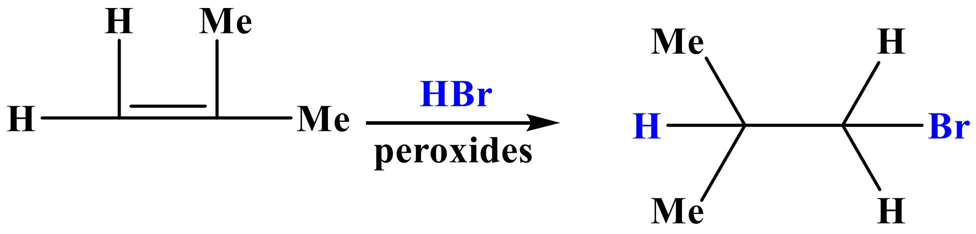


- HBr adds to an unsymmetrical alkene to form an alkyl halide forming “Markovnikov product”
- When HBr heated in the presence of a dialkyl peroxide (often written as ROOR), a radical mechanism takes over forming “anti-Markovnikov product”- due to the so-called “***peroxide effect***”.

ADDITION OF HX TO ALKENE

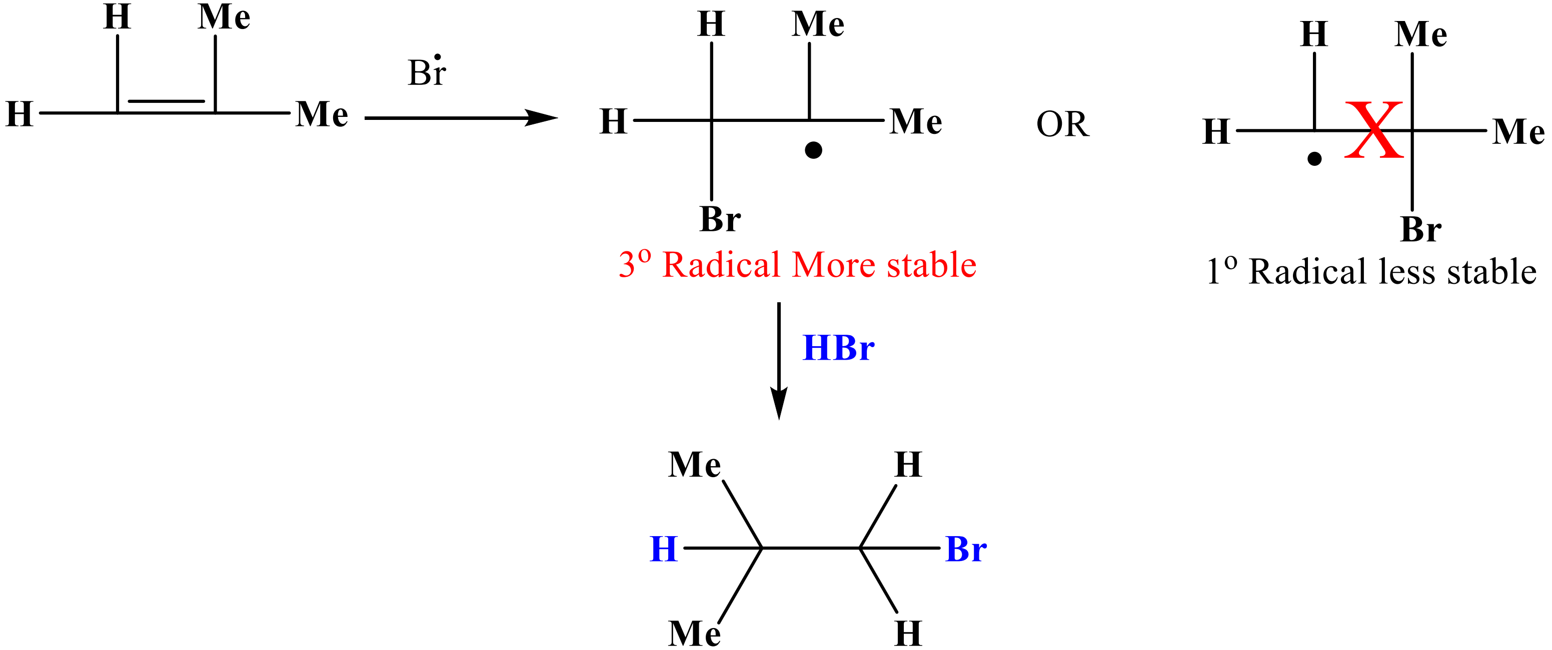
ANTI-MARKOVNIKOV HBR ADDITION:

“Free Radical Addition”



Mechanism

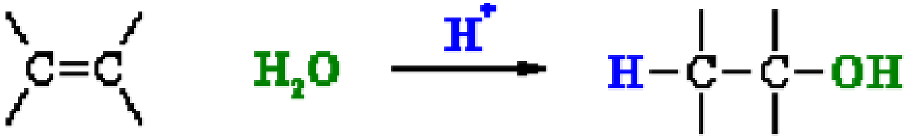
$$\text{Peroxide} \longrightarrow \text{Rad}^{\bullet} \xrightarrow{\text{HBr}} \text{Rad-H} + \text{Br}^{\bullet}$$



ADDITION OF H_2O TO ALKENE

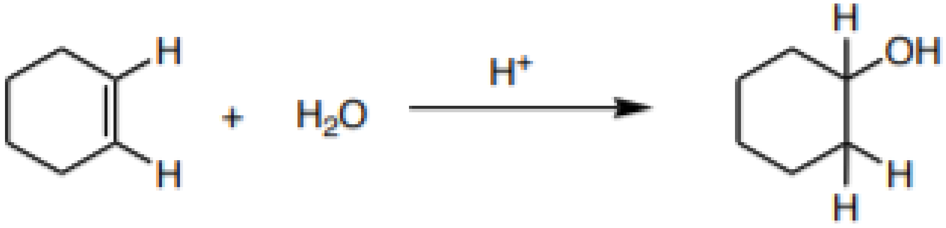
HYDRATION OF ALKENES

- Addition of water (H-OH) across a double bond to give an alcohol

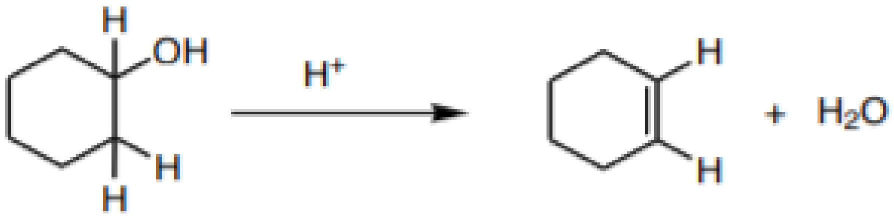


$$C=C \quad H_2O \xrightarrow{H^+} H-C-C-OH$$

1) Acid catalyzed hydration- Markovnikov addition of H-OH



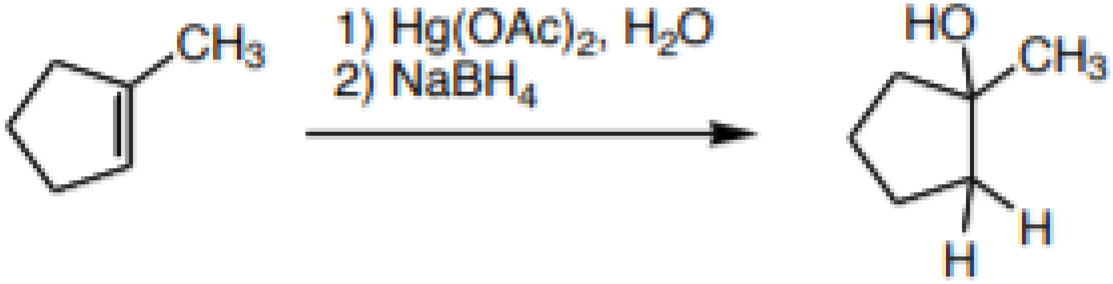
- Acid catalysts are used in high temperature industrial processes: ethylene is converted to ethanol
- Carbocation Rearrangements.
- Similar Reaction: Acid Catalyzed Dehydration



ADDITION OF H_2O TO ALKENE

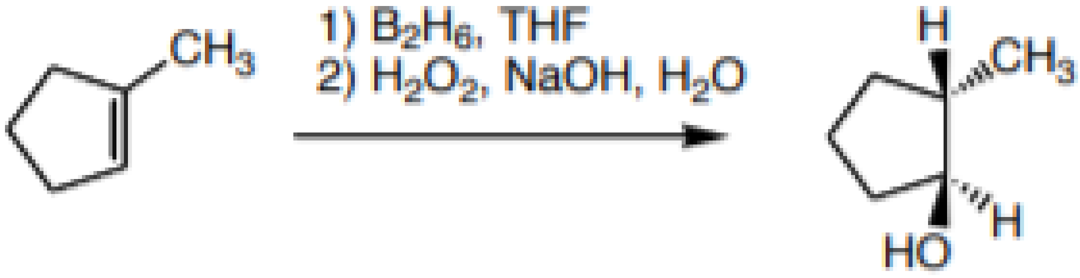
HYDRATION OF ALKENES

2) **Oxymercuration-** Markovnikov addition H-OH



- No Carbocation Rearrangements.

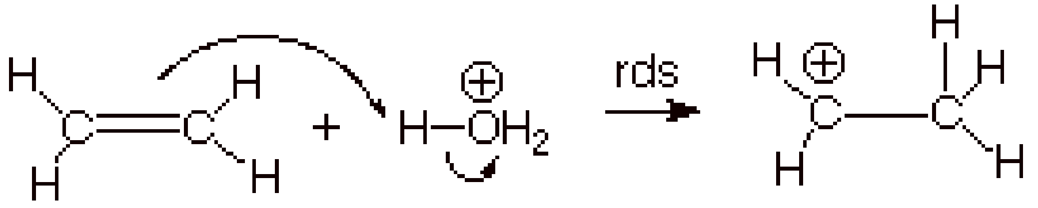
3) **Hydroboration-** Anti-Markovnikov addition of H-OH, Syn addition of H-OH



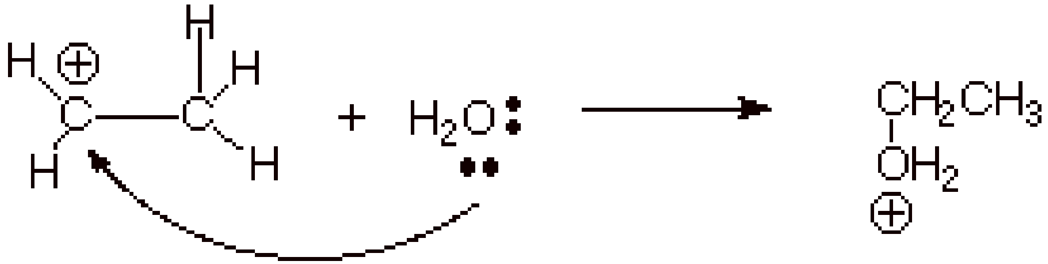
ACID CATALYZED HYDRATION; Mechanism

- **Step 1:**
  An acid/base reaction; Protonation of the alkene to generate the more stable carbocation.

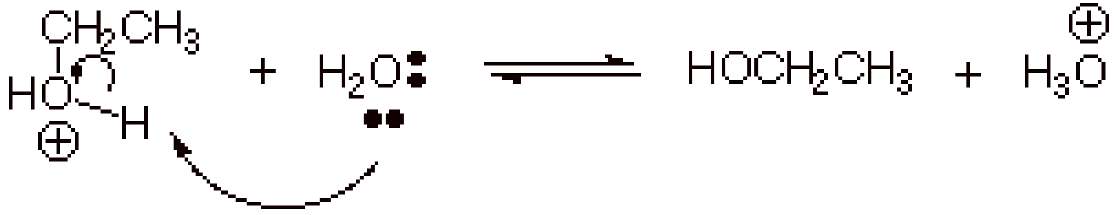
  The π electrons act pairs as a Lewis base.



- **Step 2:**
  Attack of the nucleophilic (H_2O) on the electrophilic carbocation creates an oxonium ion.

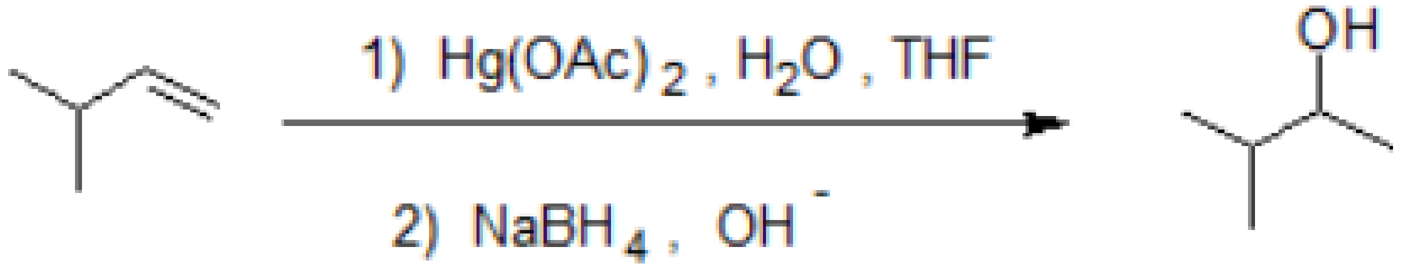


- **Step 3:**
  An acid/base reaction; Deprotonation by a base generates the alcohol and regenerates the acid catalyst



OXYMERCURATION-DEMERCURATION

- **Addition of water** follows *Markovnikov's rule* with *no rearrangement* for the carbon carbocation due to the formation of cyclic intermediate

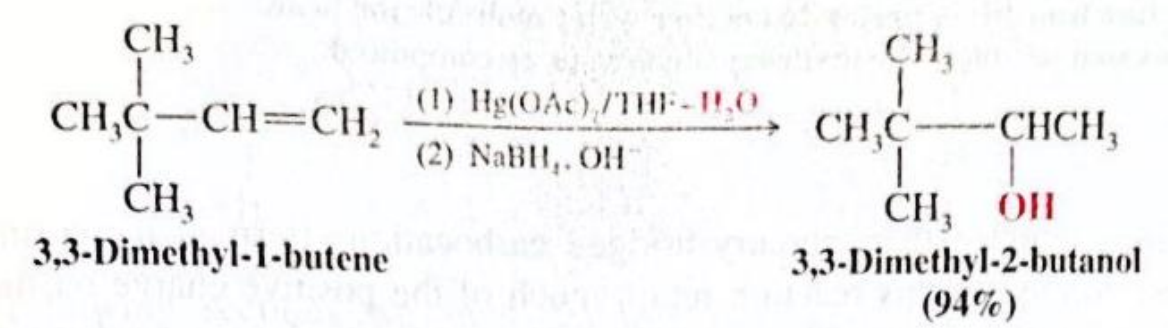


- Net Reaction: Markovnikov Addition of H_2O to Alkene.
- Both Reactions Quite Rapid; Alcohol Yields Usually > 90%
- Strong acids are not required
- Carbocation rearrangements are avoided because no discreet carbocation intermediate forms.

HYDRATION OF ALKENES

OXYMERCURATION-DEMERCURATION; Mechanism

OXYMERCURATION



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow[(2)\ NaBH_4,\ OH^-]{(1)\ Hg(OAc)_2/THF-H_2O} CH_3\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}CH_3$$

3,3-Dimethyl-1-butene

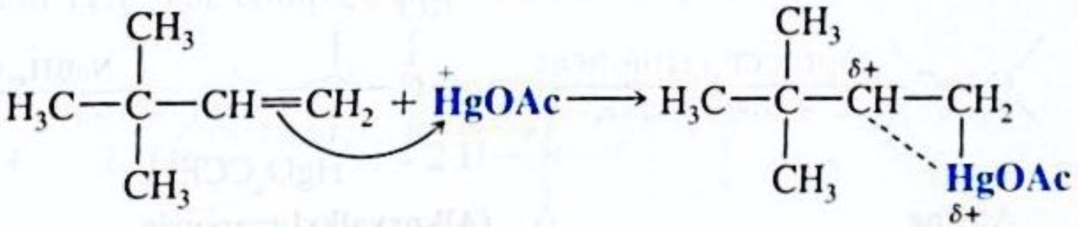
3,3-Dimethyl-2-butanol (94%)

Step 1

$$Hg(OAc)_2 \rightleftharpoons \overset{+}{Hg}OAc + OAc^-$$

Mercuric acetate dissociates to form a $\overset{+}{Hg}OAc$ cation and an acetate anion.

Step 2



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 + \overset{+}{Hg}OAc \longrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\delta+}{CH}-\underset{\underset{\delta+}{HgOAc}}{CH_2}$$

3,3-Dimethyl-1-butene

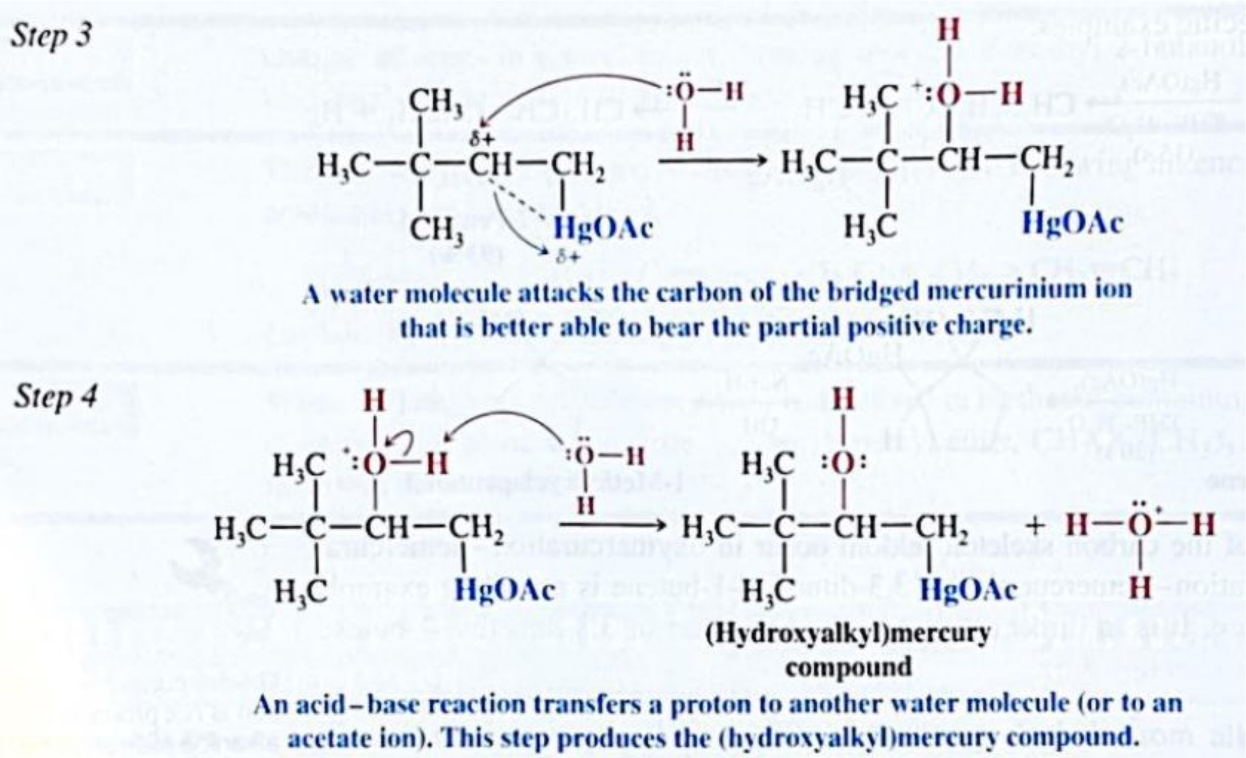
Mercury-bridged carbocation

The alkene donates a pair of electrons to the electrophilic $HgOAc^+$ cation to form a mercury-bridged carbocation. In this carbocation, the positive charge is shared between the 2° (more substituted) carbon atom and the mercury atom. The charge on the carbon atom is

HYDRATION OF ALKENES

OXYMERCURATION-DEMERCURATION; Mechanism

OXYMERCURATION


Step 3

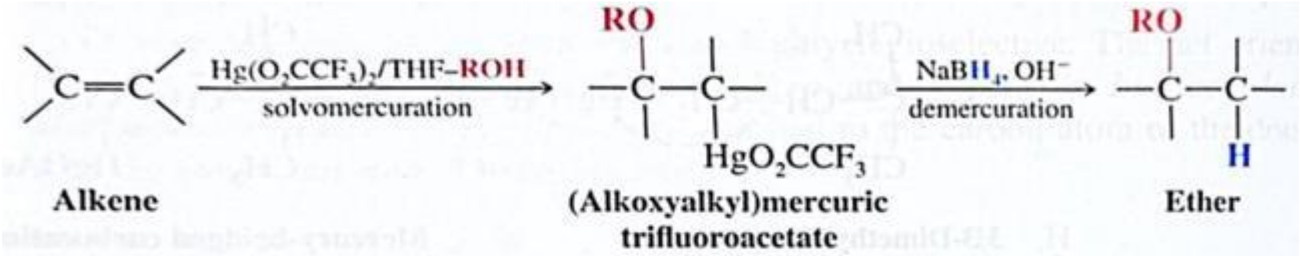
A water molecule attacks the carbon of the bridged mercurinium ion that is better able to bear the partial positive charge.

Step 4

(Hydroxyalkyl)mercury compound

An acid–base reaction transfers a proton to another water molecule (or to an acetate ion). This step produces the (hydroxyalkyl)mercury compound.

DEMERCURATION

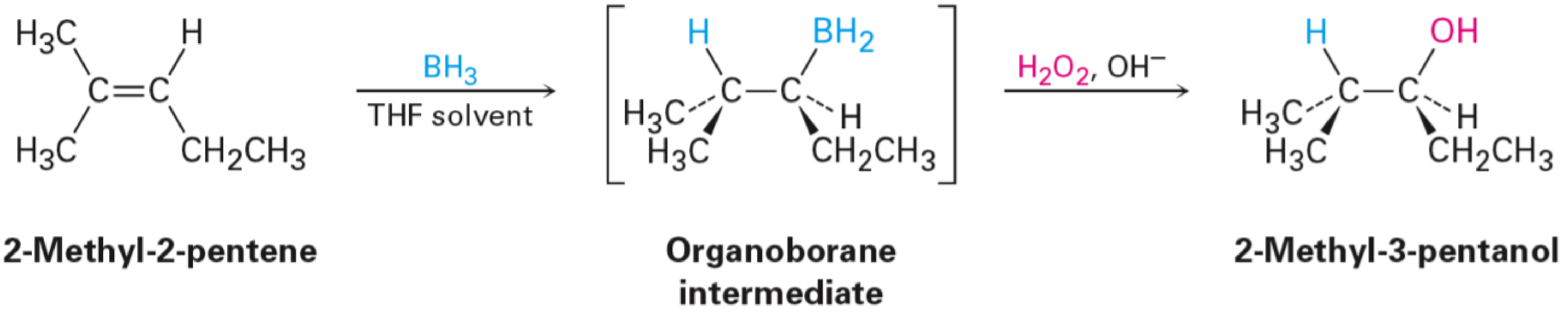


Alkene

(Alkoxyalkyl)mercuric trifluoroacetate

Ether

HYDROBORATION-OXIDATION

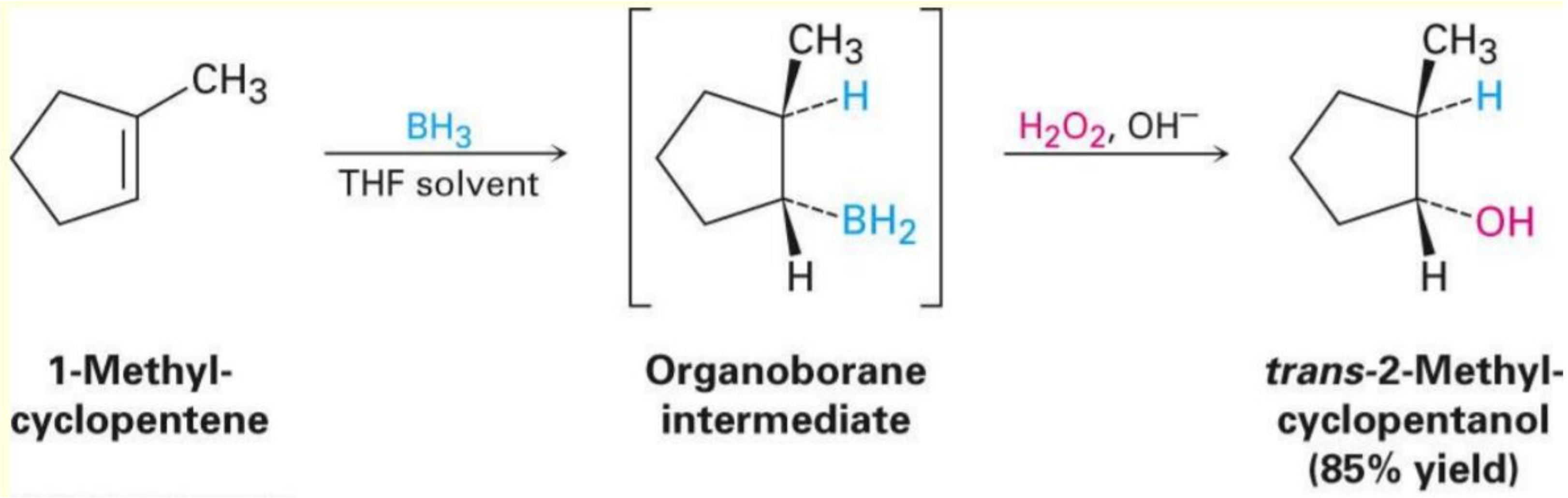


- The reaction proceeds in an Anti-Markovnikov manner; (Good for 1° Alcohols)
- In the alkene double bond;
  - Hydrogen (from BH_3 or BHR_2) attaches to the more substituted carbon.
  - Boron attaches to the least substituted carbon.
- This process does not require any activation by a catalyst.
- Oxidation: H_2O_2, NaOH Oxidize to Trialkylborate Ester.

HYDROBORATION-OXIDATION

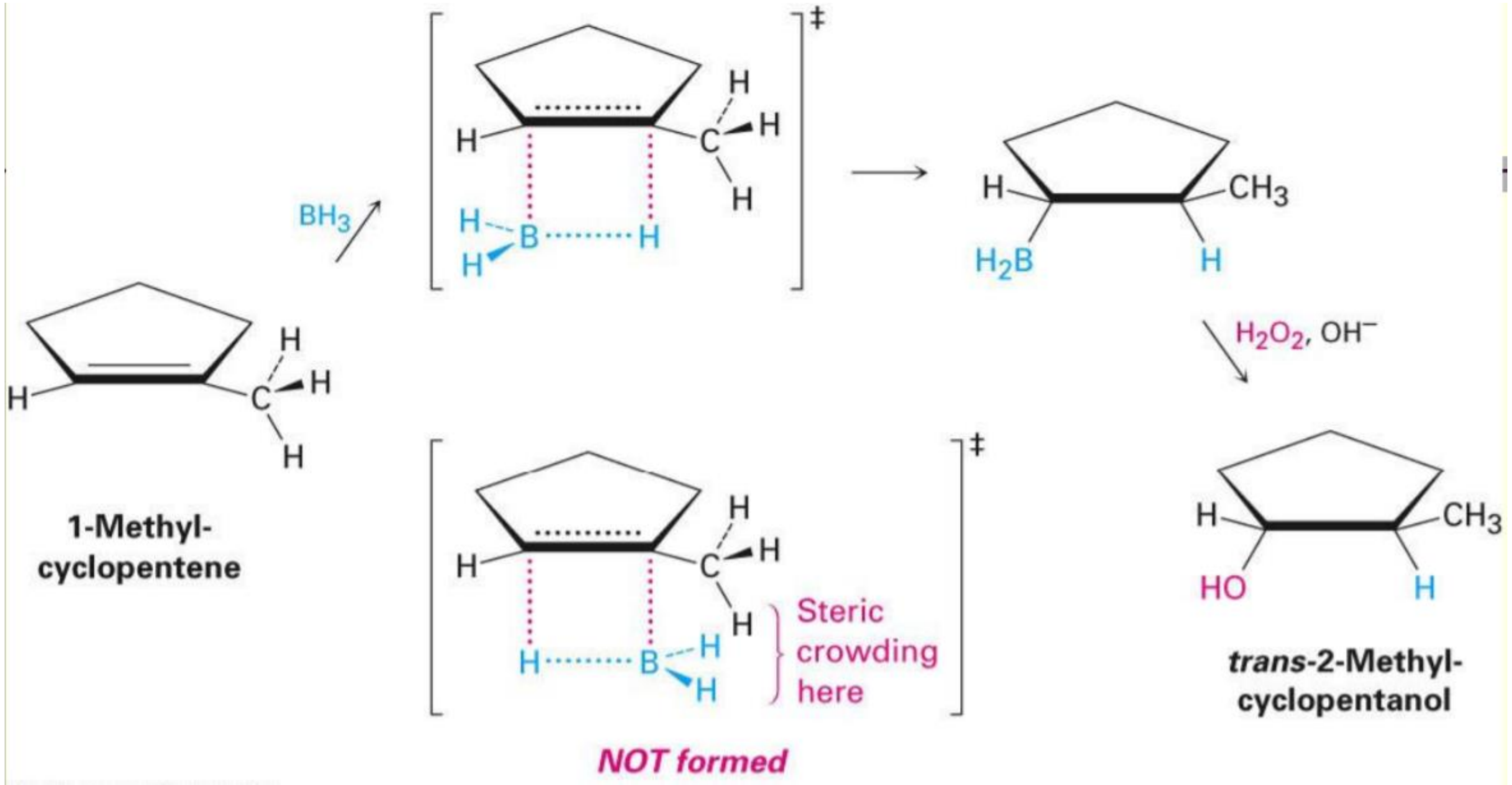
- Regiochemistry is opposite to Markovnikov orientation

  OH is added to carbon with most H's
- H and OH add with *syn stereochemistry*, to the same face of the alkene (opposite of anti addition),
- STEREOSPECIFIC



HYDROBORATION-OXIDATION

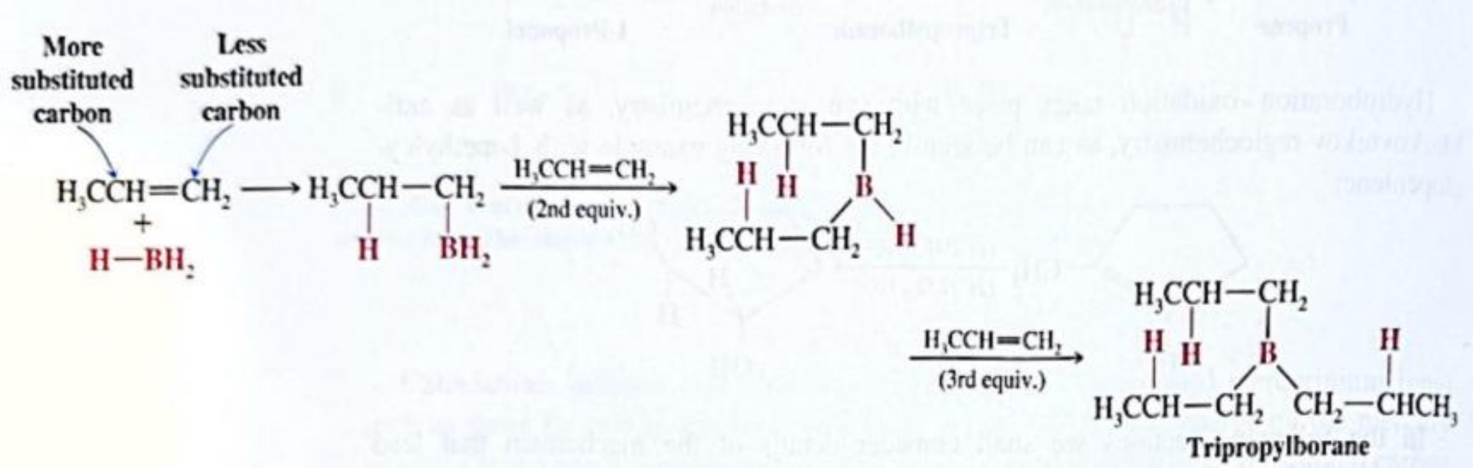
- Borane (BH_3) is electron deficient and is a *Lewis acid* and Alkene is *Lewis base*
- Transition state involves anionic development on B
- The components of BH_3 are added across C=C
- More stable carbocation is also consistent with steric preferences



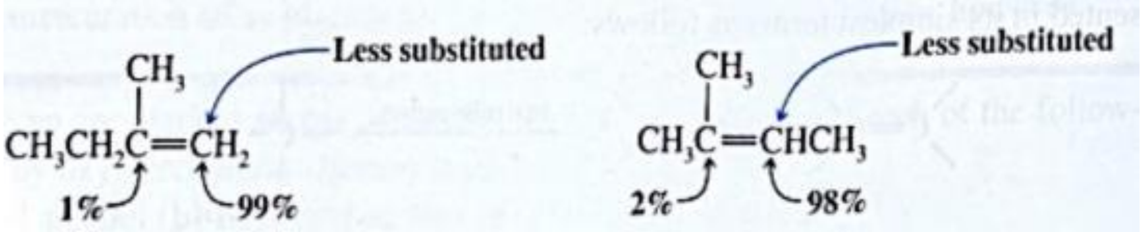
HYDROBORATION-OXIDATION; Mechanism

- Step 1: Hydroboration of alkene

In this first step the addition of the borane to the alkene is initiated and proceeds as a concerted reaction because bond breaking and bond formation occurs at the same time.

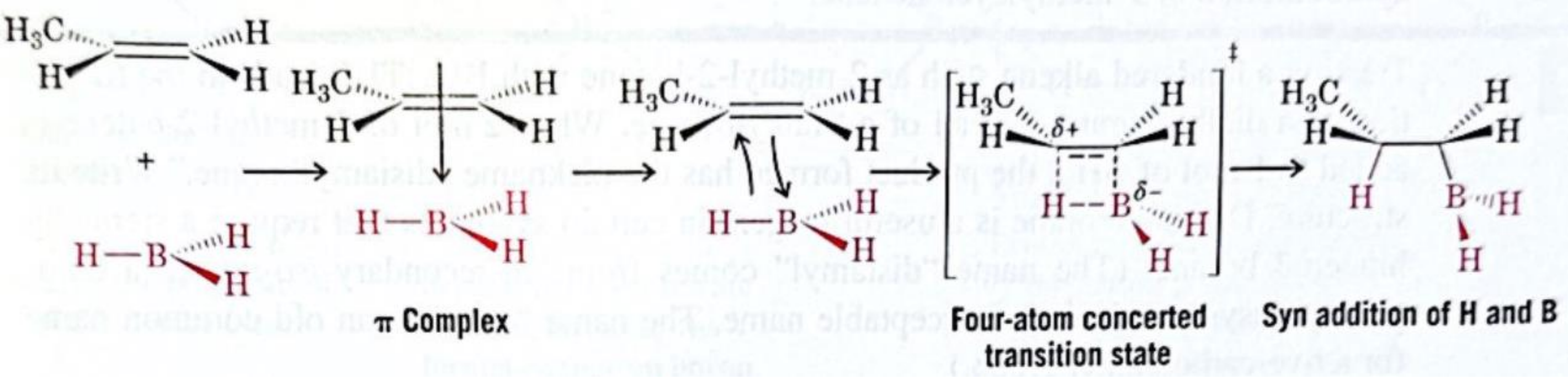


- The boron atom becomes attached to the less substituted carbon atom of the double bond.



HYDROBORATION-OXIDATION; Mechanism

- Both electronic and steric factors account for the anti-markovinkov orientation of the addition.



π Complex

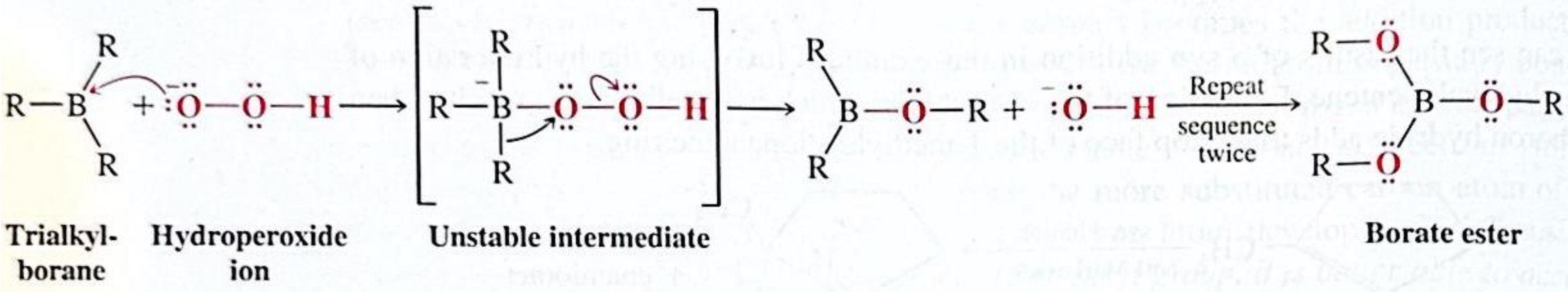
Four-atom concerted transition state

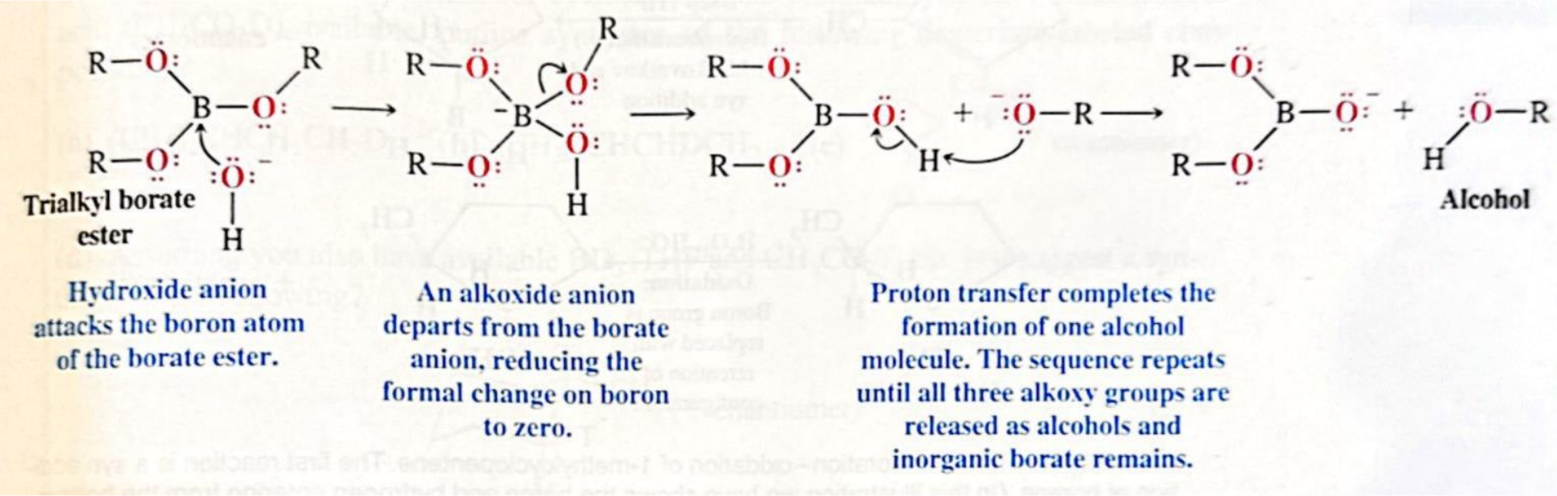
Syn addition of H and B

- Step 2: Oxidation and hydrolysis of trialkylborane

$$R_3B \xrightarrow[\text{(oxidation and hydrolysis)}]{H_2O_2\text{, aq. NaOH, 25°C}} 3\,R{-}OH + B(ONa)_3$$

HYDROBORATION-OXIDATION; Mechanism





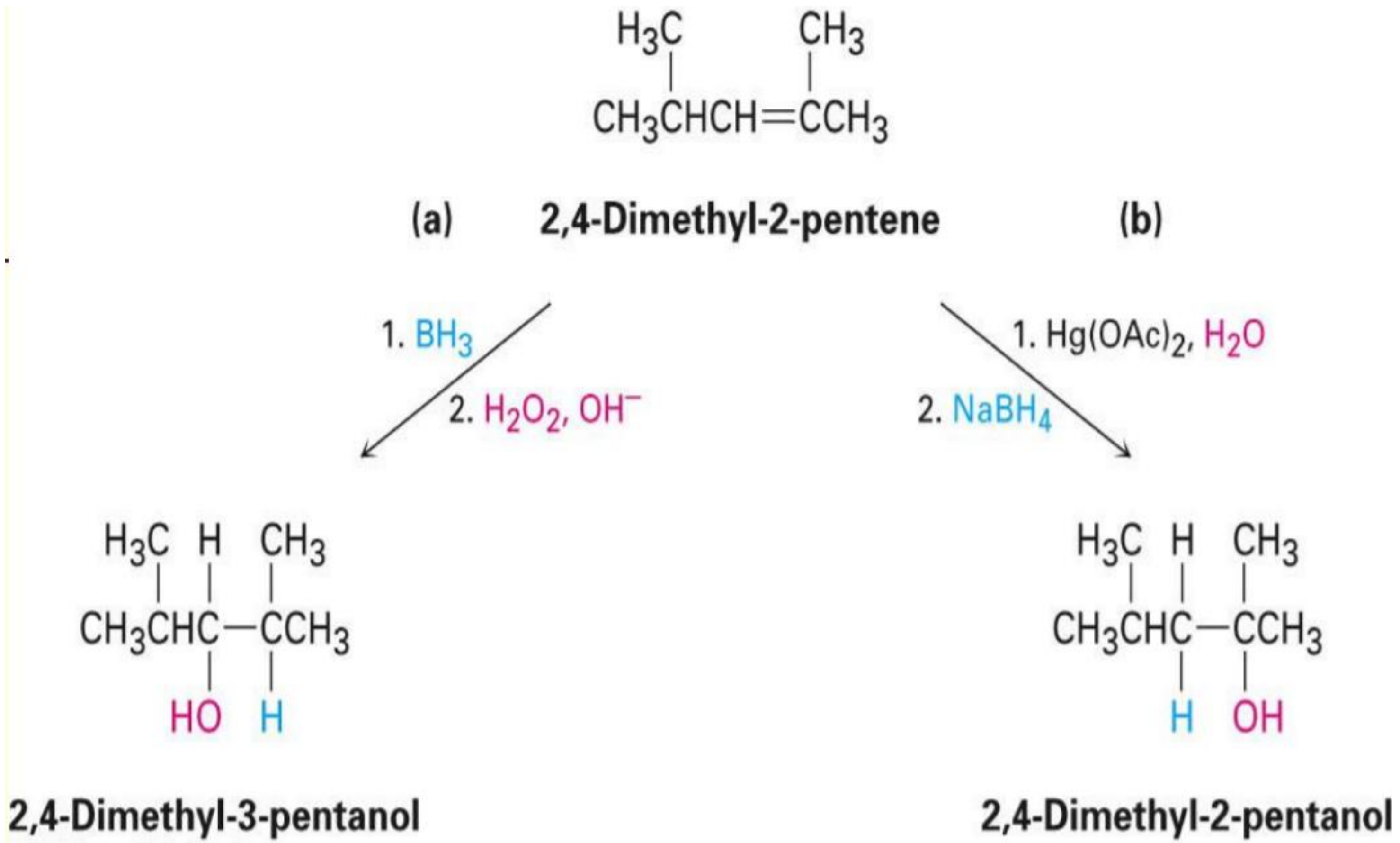
Hydroxide anion attacks the boron atom of the borate ester.

An alkoxide anion departs from the borate anion, reducing the formal change on boron to zero.

Proton transfer completes the formation of one alcohol molecule. The sequence repeats until all three alkoxy groups are released as alcohols and inorganic borate remains.

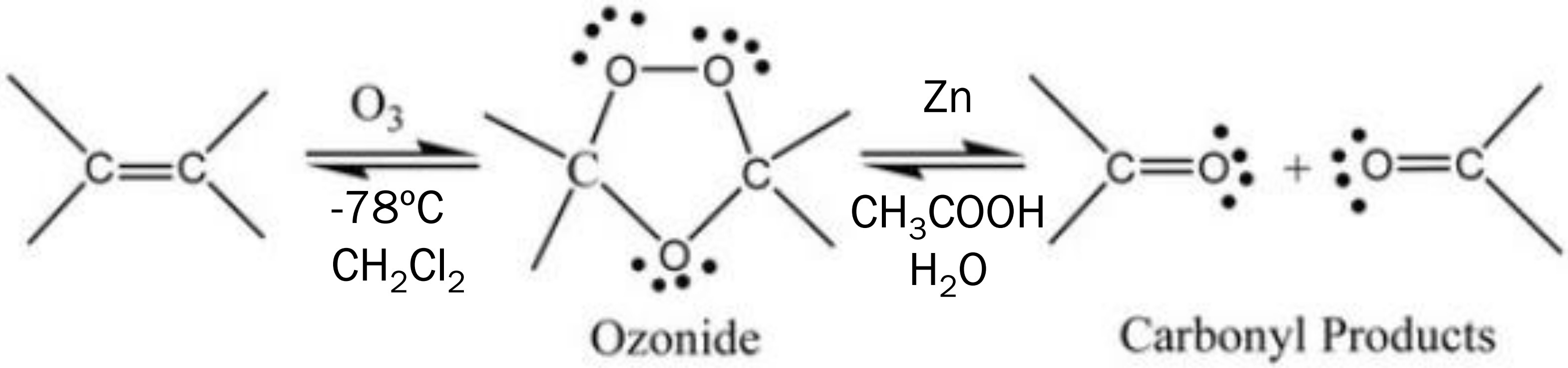
HYDROBORATION-OXIDATION & OXYMERCURATION

- Hydroboration/oxidation occurs with *syn stereochemistry* and gives the *anti Markovnikov addition* product
- Oxymercuration gives the *Markovnikov* product .



OZONOLYSIS: ALKENE CLEAVAGE

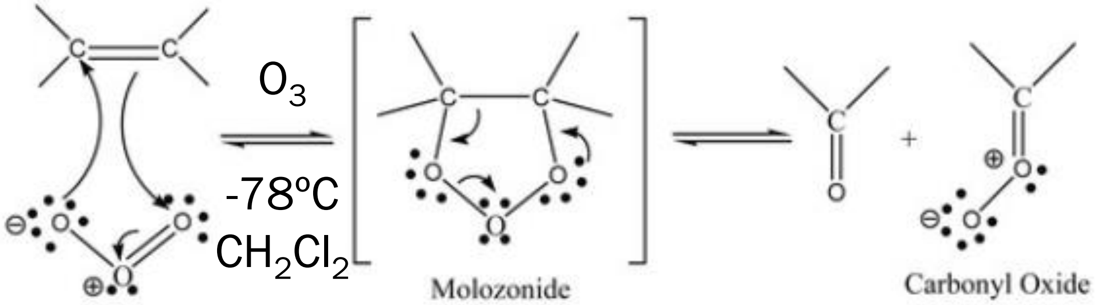
- **Ozonolysis** is a method of oxidative cleaving alkenes using ozone (O_3).
- The process allows for *carbon-carbon double bonds* to be replaced by *double bonds with oxygen*.
- This reaction is often used to identify the structure of unknown alkenes by breaking them down into smaller, more easily identifiable pieces.



MECHANISM

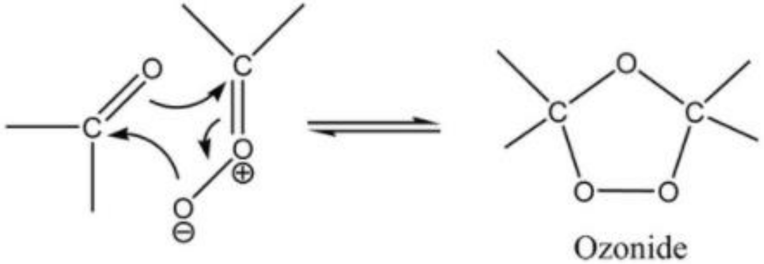
- **Step 1:**

  Initial electrophilic addition of ozone to the Carbon-Carbon double bond forming the unstable *molozonide intermediate*, which breaks apart to form a carbonyl and a carbonyl oxide molecule.



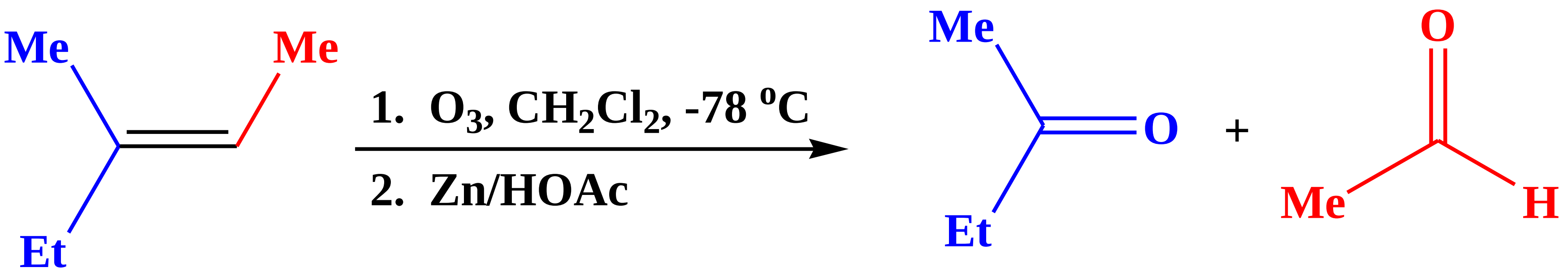
- **Step 2:**

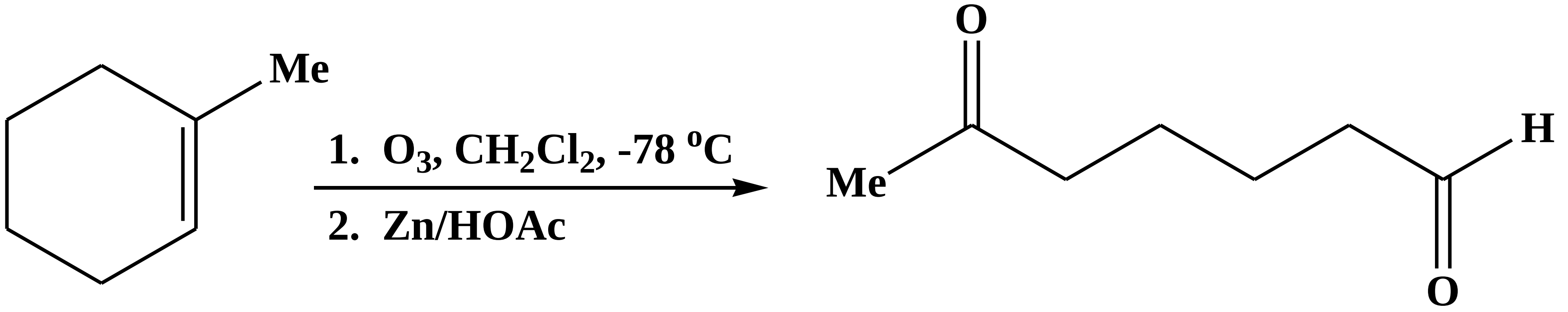
  The carbonyl and the carbonyl oxide rearranges and reforms to create the stable ozonide intermediate.



A reductive workup could be performed to convert the ozonide molecule into the desired carbonyl products.

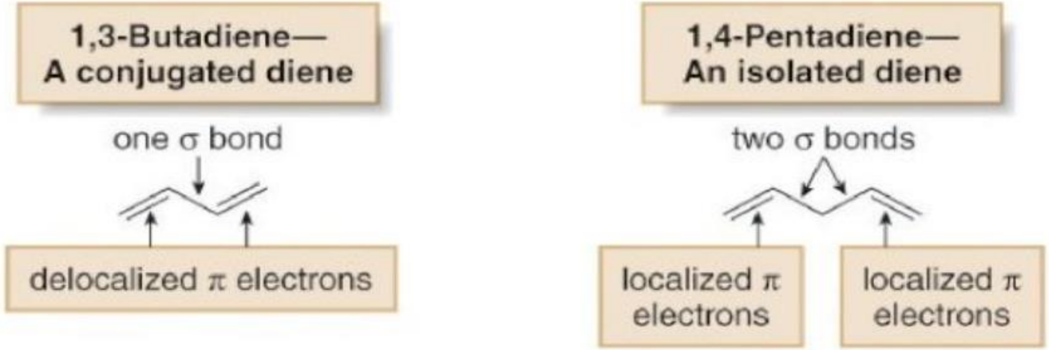
EXAMPLES


Me
Me
Et
1. O_3, CH_2Cl_2, -78 °C
2. Zn/HOAc
Me
O
Et
+
O
Me
H


Me
1. O_3, CH_2Cl_2, -78 °C
2. Zn/HOAc
O
Me
H
O

CONJUGATED DIENES

- Compounds have more than one double bond.
- If they are separated by only one single bond they are *conjugated*.
- The *conjugated diene* 1,3-butadiene has properties that are very different from those of the *nonconjugated diene*, 1,5-pentadiene



1,3-Butadiene—A conjugated diene

one σ bond

delocalized π electrons

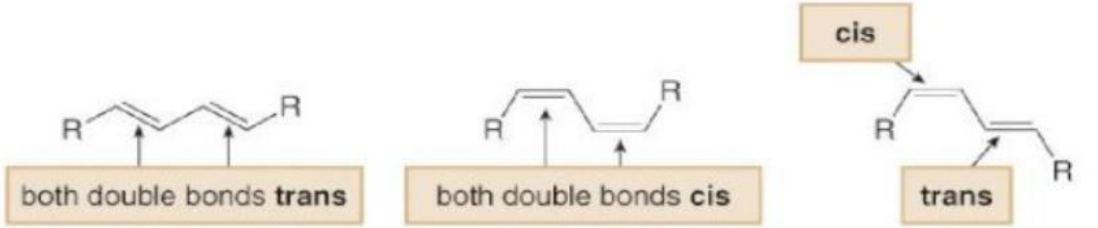
1,4-Pentadiene—An isolated diene

two σ bonds

localized π electrons

localized π electrons

- Three **stereoisomers** are possible for 1,3-dienes with alkyl groups bonded to each end carbon of the diene.



both double bonds **trans**

trans, trans-1,3-diene
or
(*E,E*)-1,3-diene

both double bonds **cis**

cis, cis-1,3-diene
or
(*Z,Z*)-1,3-diene

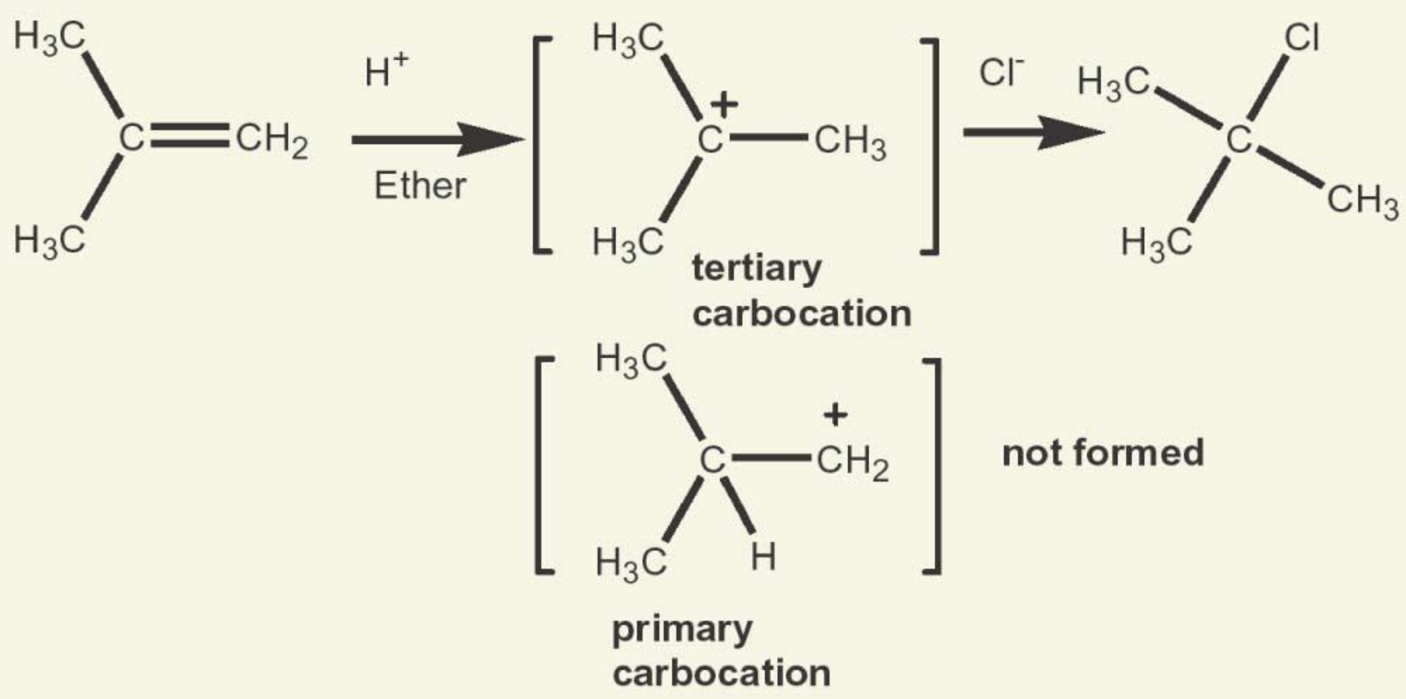
cis

trans

cis, trans-1,3-diene
or
(*Z,E*)-1,3-diene

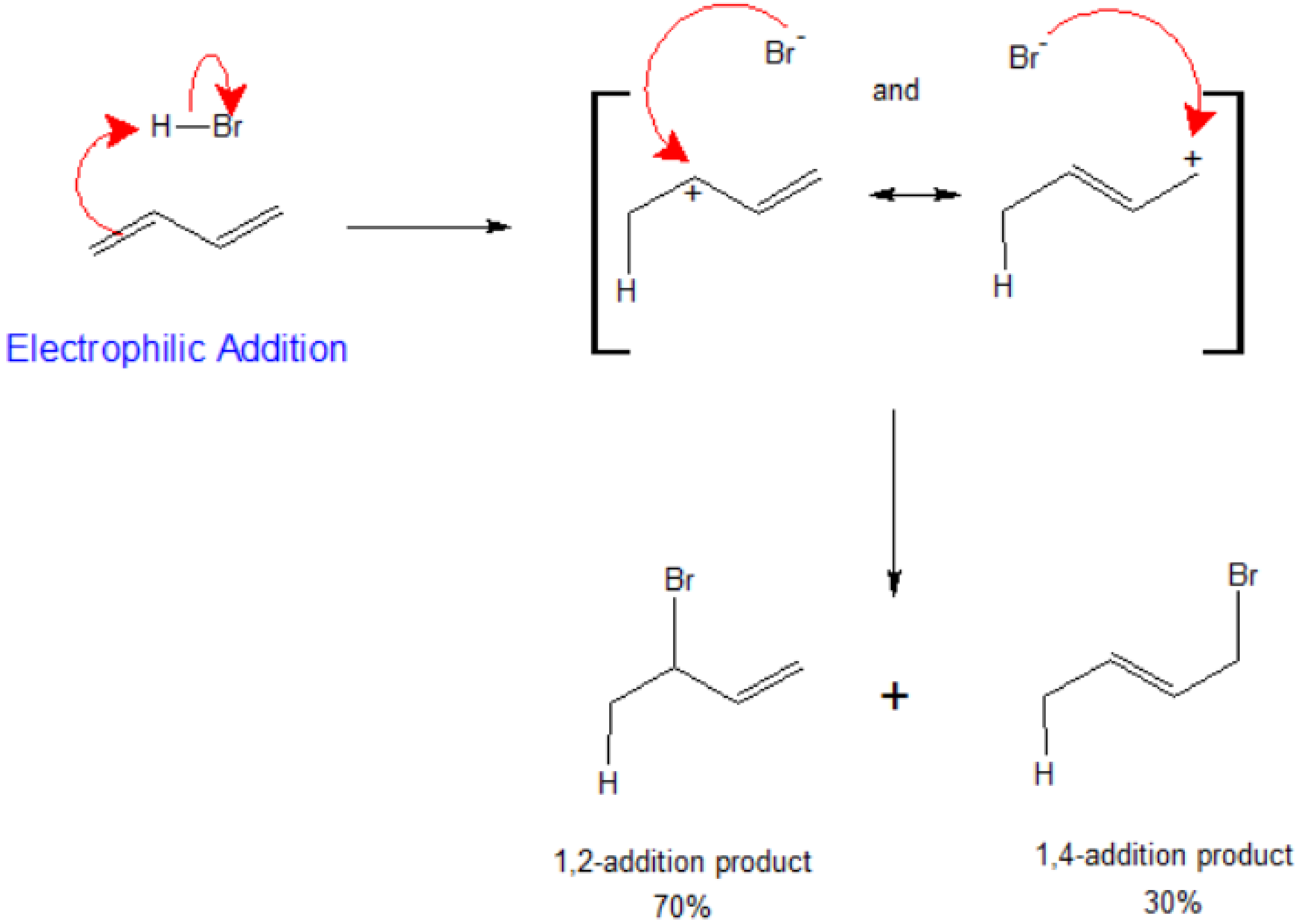
ALLYLIC CARBOCATIONS

- The allyl carbocation is another example of conjugated system.
- Conjugation stabilizes the allyl carbocation and making it more stable than a normal primary carbocation.
- With conjugated dienes the allylic carbocation intermediately generated has different resonance forms.



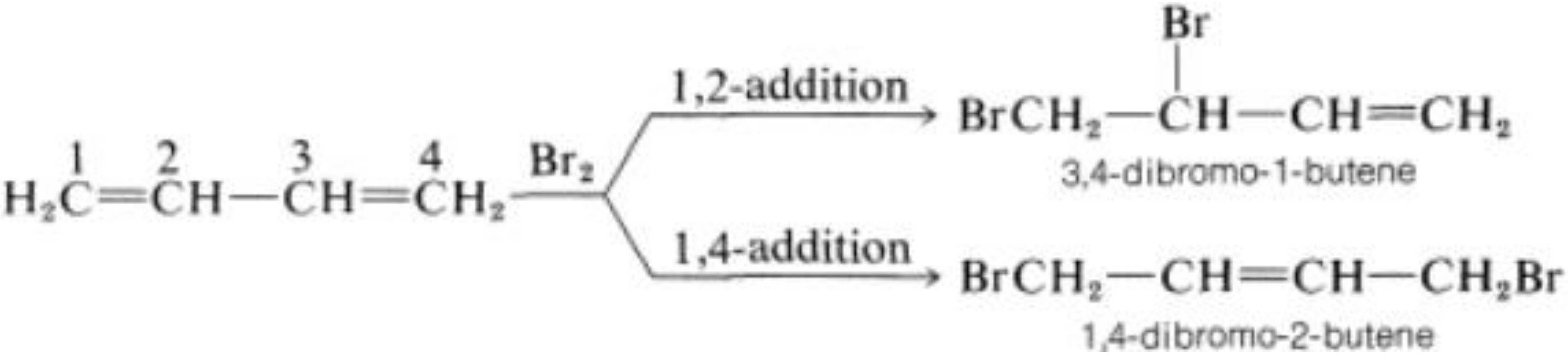
EXAMPLE

Addition of HBr to 1,3-butadiene: 1,2-addition & 1,4-addition



EXAMPLE

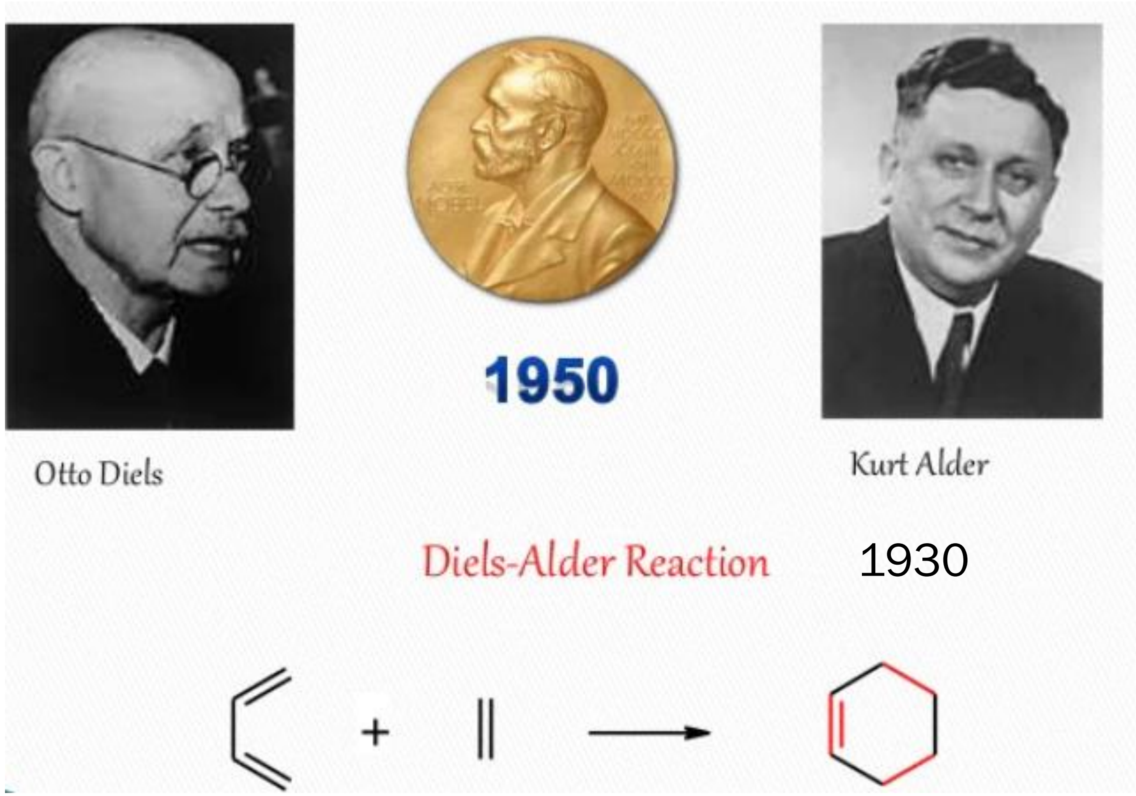
Addition of Br_2 to 1,3-butadiene:



- The 1,2-addition product is favored because its secondary allylic carbocation intermediate is more stable

CYCLOADDITION TO CONJUGATED DIENES: THE DIELS–ALDER REACTION

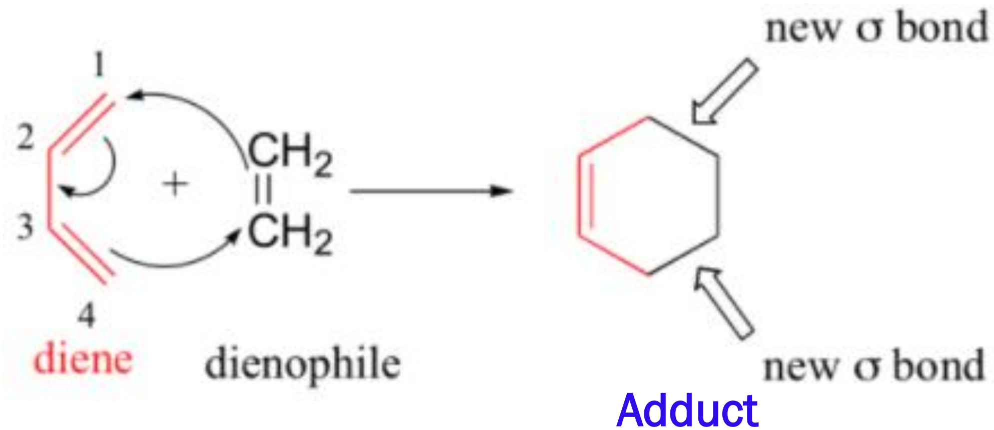
- **Polyenes** (including dienes) can undergo a variety of **pericyclic reactions** “*the π-electrons rearrange to form new bonds*”.
- In a **cycloaddition**, one π-system is “added across” another π-system (often on a different molecule), creating a ring.



CYCLOADDITION TO CONJUGATED DIENES: THE DIELS–ALDER REACTION

- **Diels-Alder reaction** is one of the most important pericyclic reaction and is a type of cycloaddition.
  - **This is a [4+2] cycloaddition;**

    meaning that one reactant contributes 4 π–electrons while the other contributes 2 π–electrons.
  - A Diels-Alder reaction must involve a **diene** and **dienophile** "*alkene (or alkyne)*".
  - A Diels-Alder adduct (addition product) contains formation of *cyclohexene ring* by addition of the dienophile to the diene.



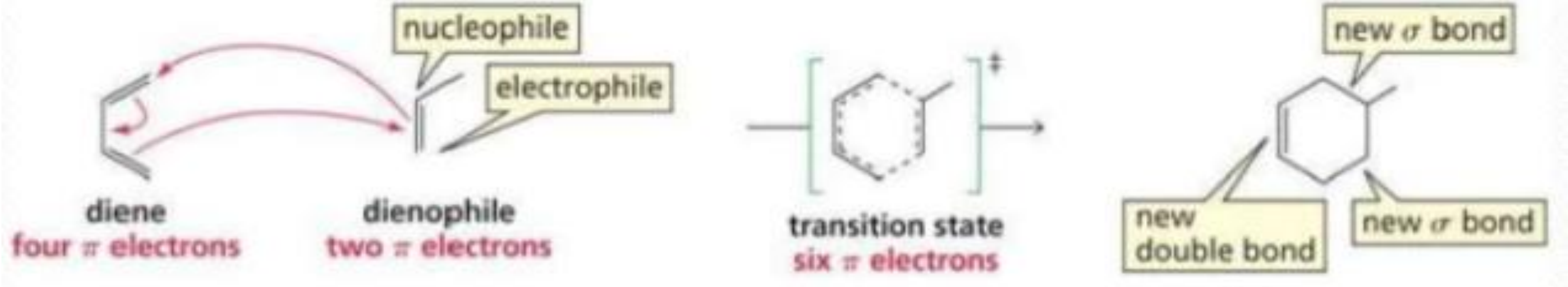
Adduct

- The formation of the ring involves *no intermediate* (concerted formation of two bonds)
- Two π-bonds are converted to two sigma-bonds.
- Six-membered ring is formed

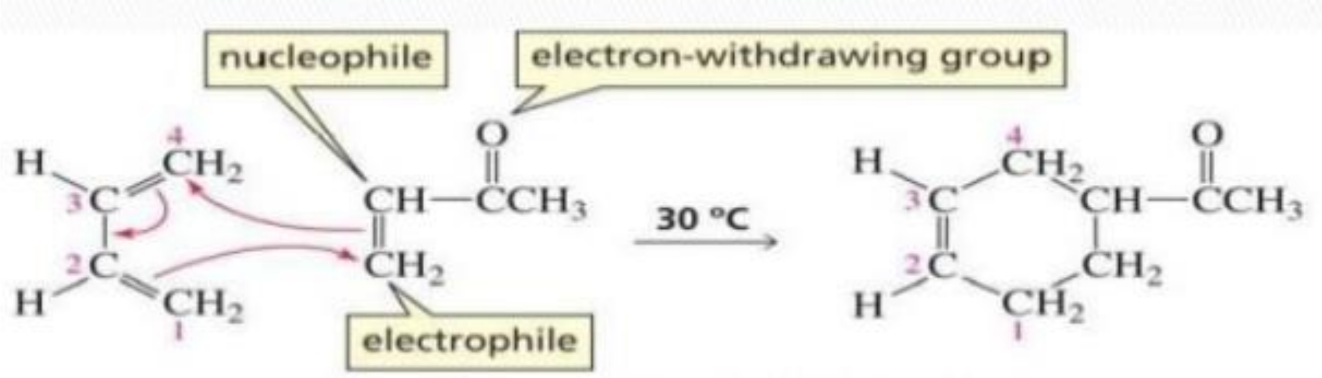
CYCLOADDITION TO CONJUGATED DIENES: THE DIELS–ALDER REACTION

MECHANISM

- A conjugated diene reacts with a double-bonded dienophile.



- Dienes are electron-rich; dienophiles are electron poor.

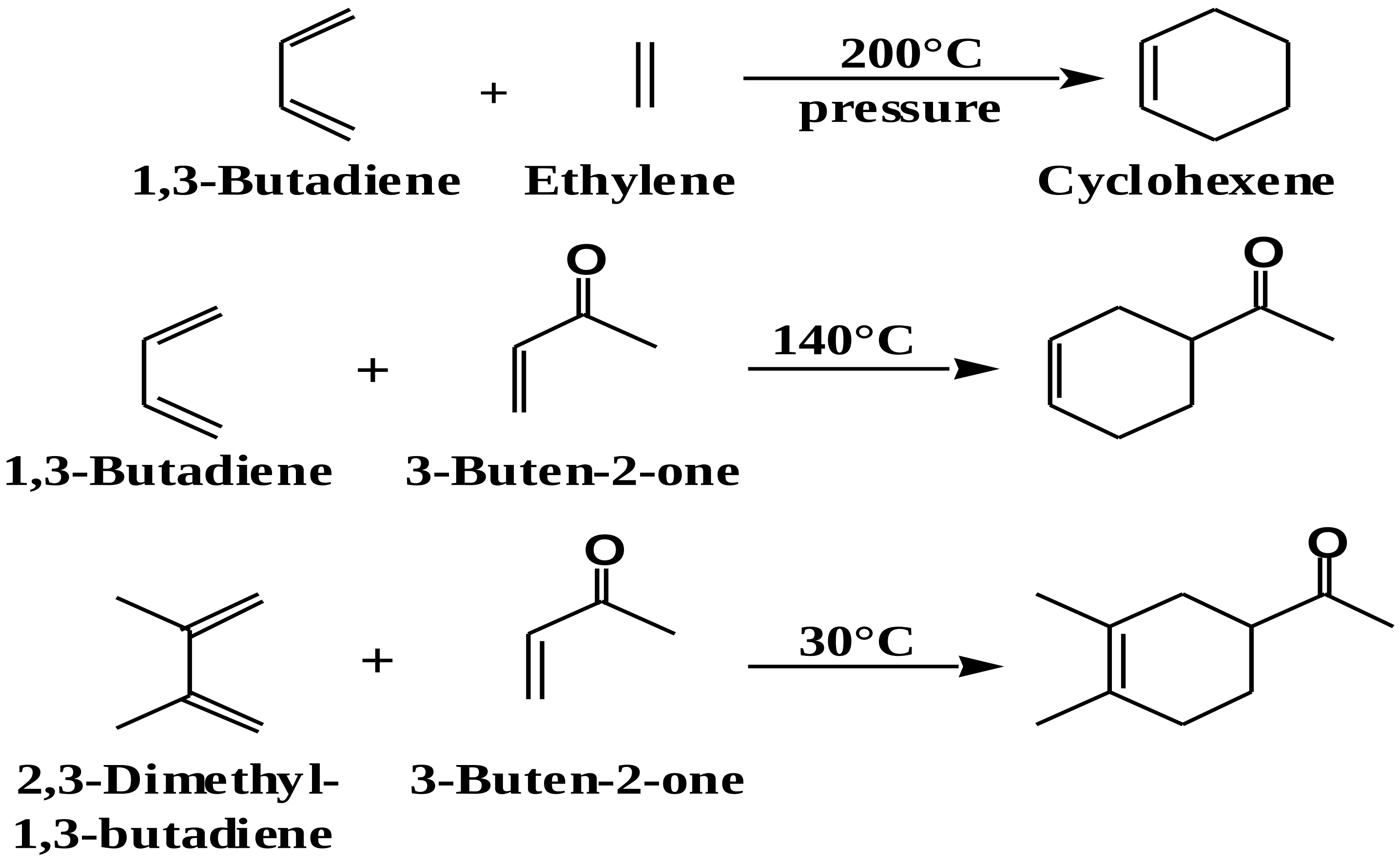


$$CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \longleftrightarrow \overset{+}{C}H_2{-}CH{=}\overset{\overset{\displaystyle O^-}{|}}{C}CH_3$$

resonance contributors of the dienophile

CYCLOADDITION TO CONJUGATED DIENES: THE DIELS–ALDER REACTION

MECHANISM



- Reaction is facilitated by a combination of electron-withdrawing substituents on one reactant and electron-releasing substituents on the other.