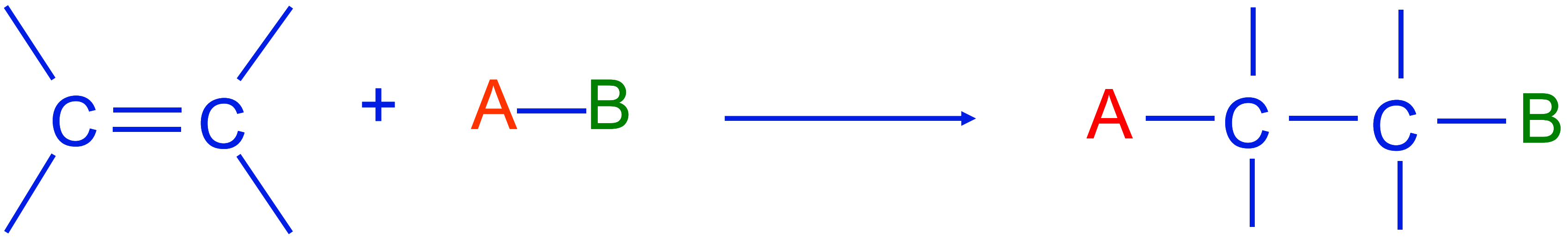
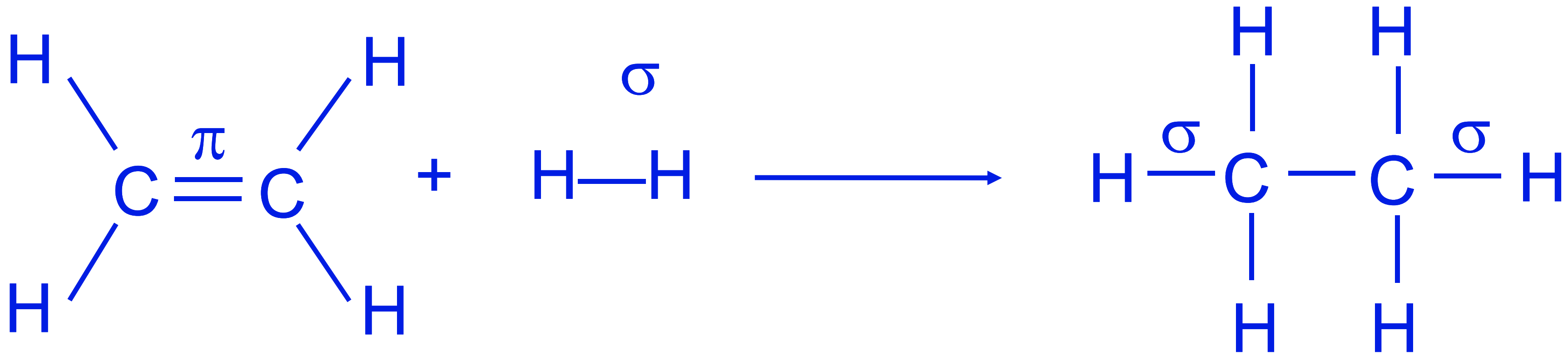
# Chapter 6
# Reactions of Alkenes: Addition Reactions

- The characteristic reaction of alkenes is addition to the double bond.

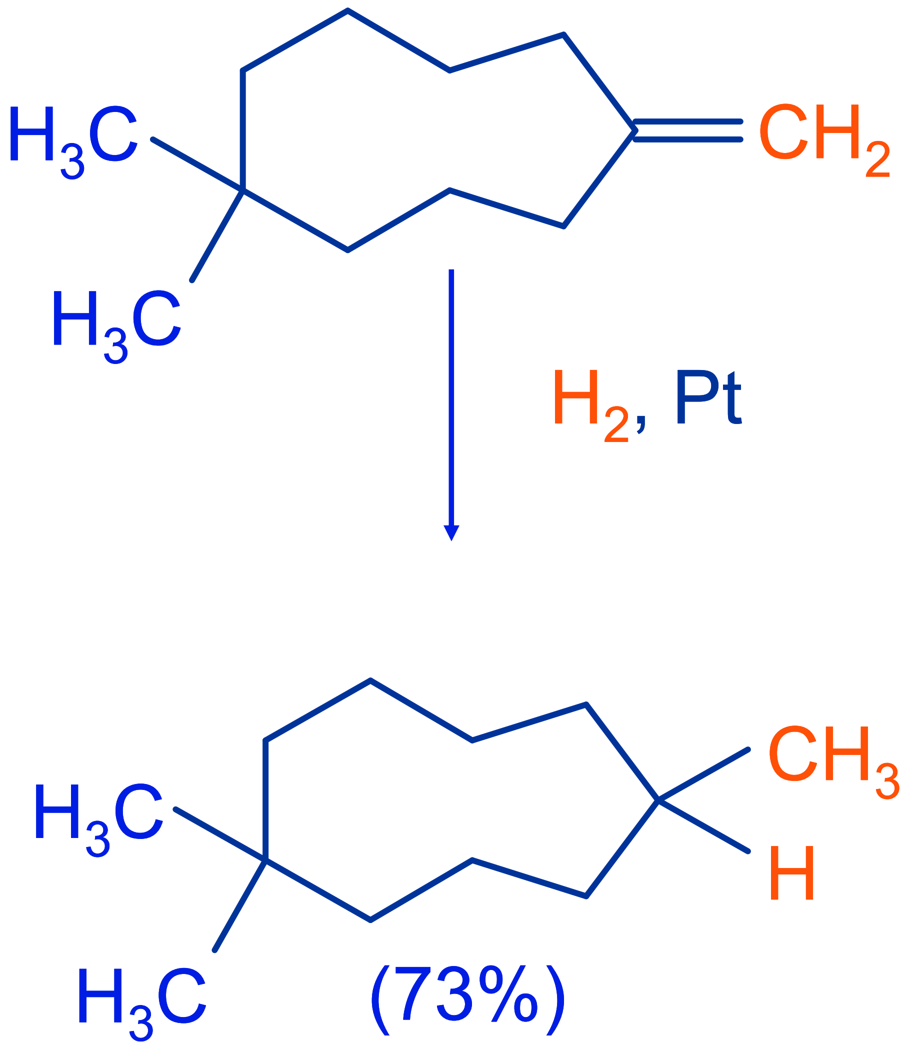


# 6.1. Hydrogenation of Alkenes
# Hydrogenation of Ethylene



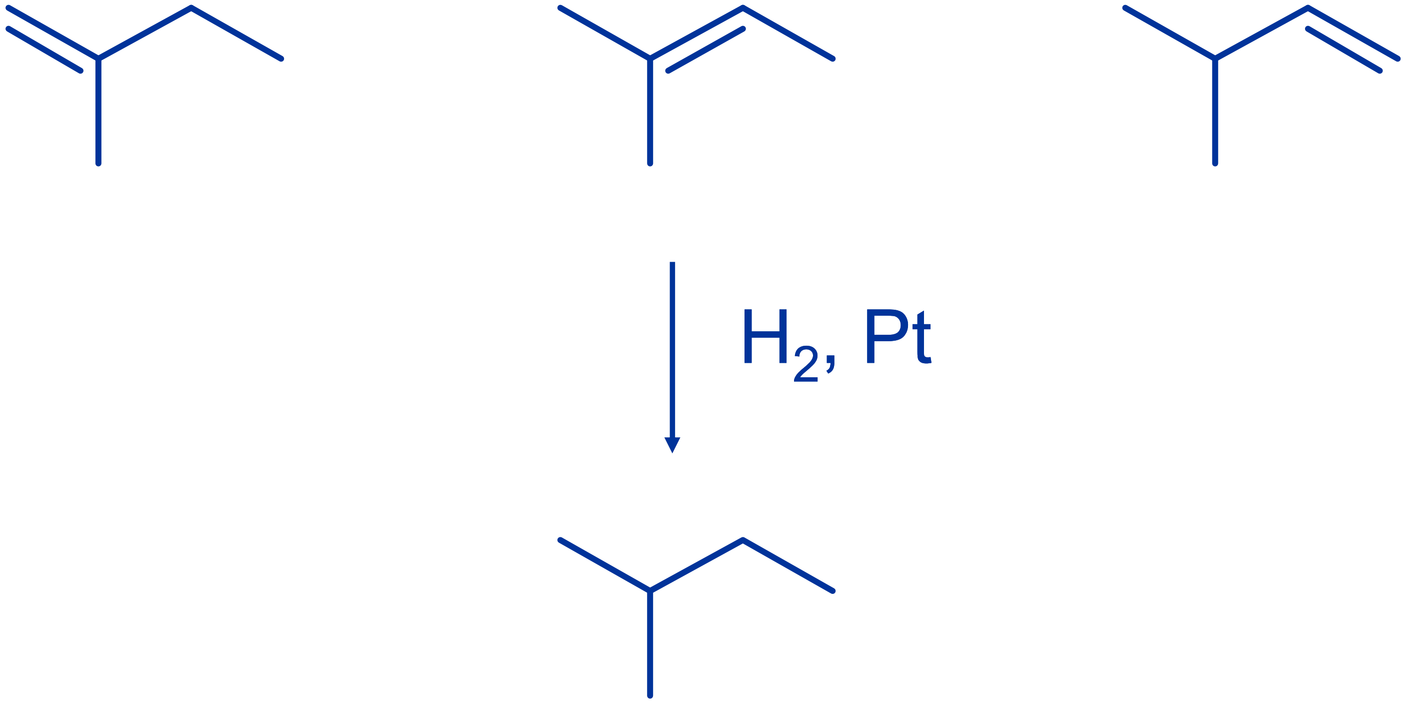
- Exothermic $\Delta H^{\circ} = -136$ kJ/mol.
- Catalyzed by finely divided Pt, Pd, Rh, Ni.
- The metals are insoluble in solvents used in this reaction: *heteregeneous reactions. Reaction occurs at the interface of the two phases.*

# Example

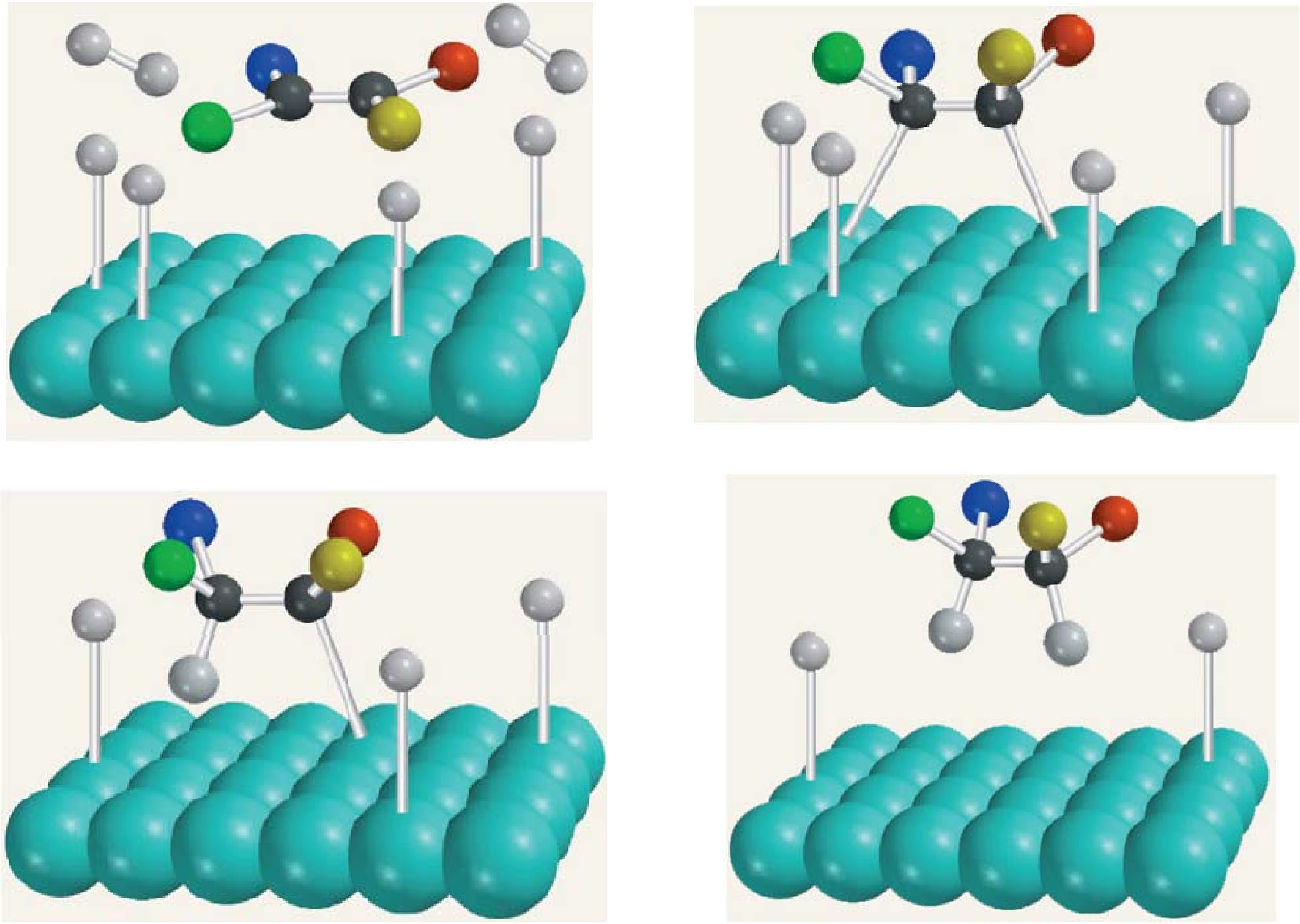


# Problem 6.1

- What three alkenes yield 2-methylbutane on catalytic hydrogenation?



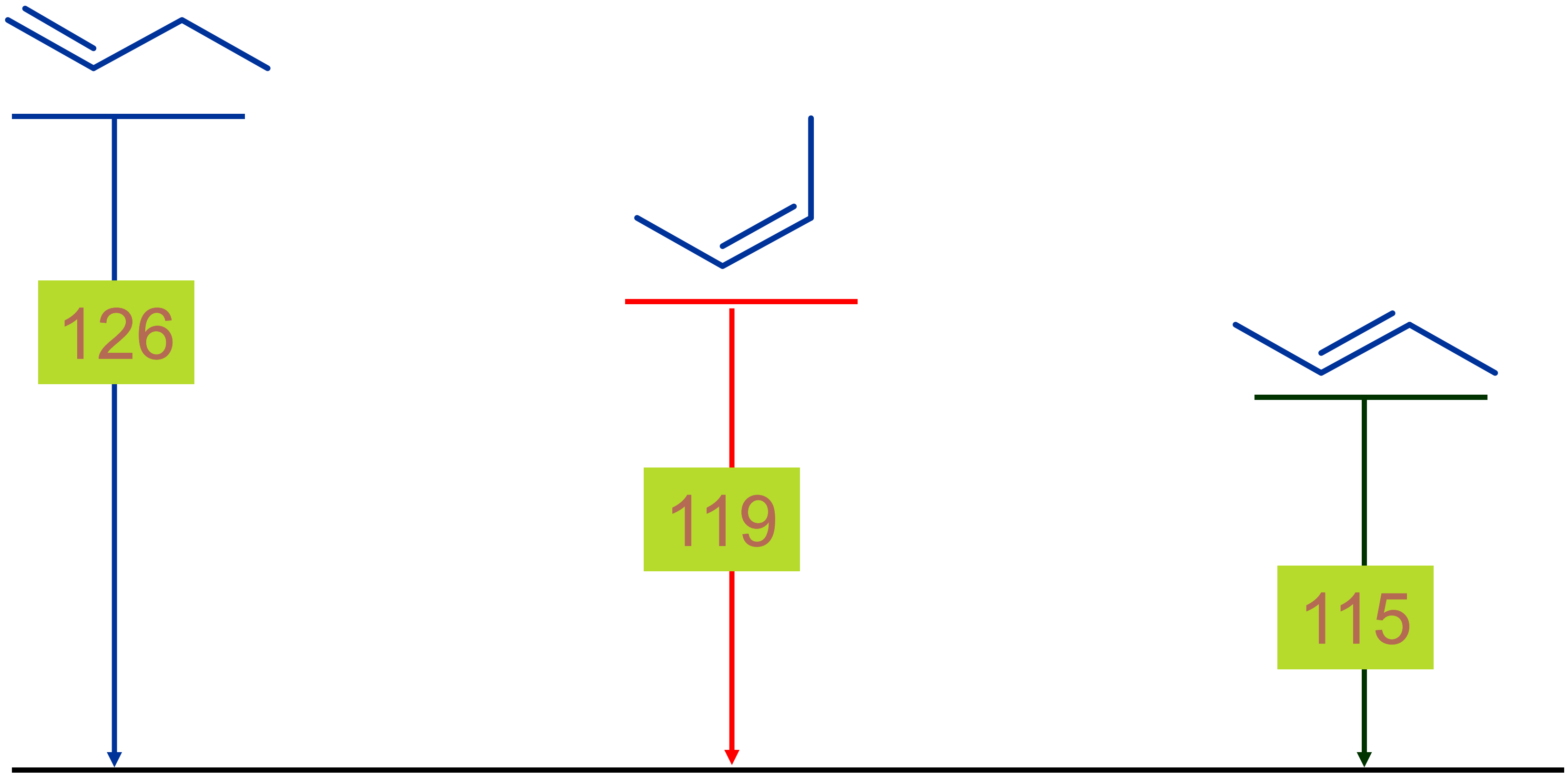
# Mechanism of Catalytic Hydrogenation: Mechanism 6.1



# 6.2. Heats of Hydrogenation

- Can be used to measure relative stability of isomeric alkenes.
- Correlation with structure is same as when heats of combustion are measured.

# Heats of Hydrogenation of Isomers



$CH_3CH_2CH_2CH_3$

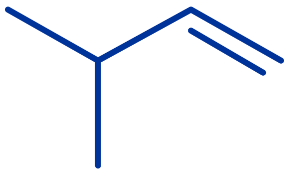
# Heats of Hydrogenation (KJ/mol)

| | |
|---|---|
| Ethylene | 136 |
| Monosubstituted | 125-126 |
| *cis*-Disubstituted | 117-119 |
| *trans*-Disubstituted | 114-115 |
| Terminally disubstituted | 116-117 |
| Trisubstituted | 112 |
| Tetrasubstituted | 110 |

# Problem 6.2

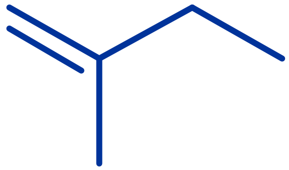
- Match each alkene of Problem 6.1 with its correct heat of hydrogenation.

126 kJ/mol

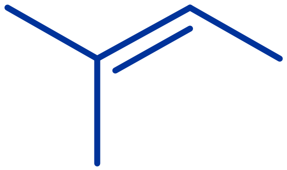


highest heat of hydrogenation; least stable isomer

118 kJ/mol



112 kJ/mol



lowest heat of hydrogenation; most stable isomer

# 6.3. Stereochemistry of Alkene Hydrogenation

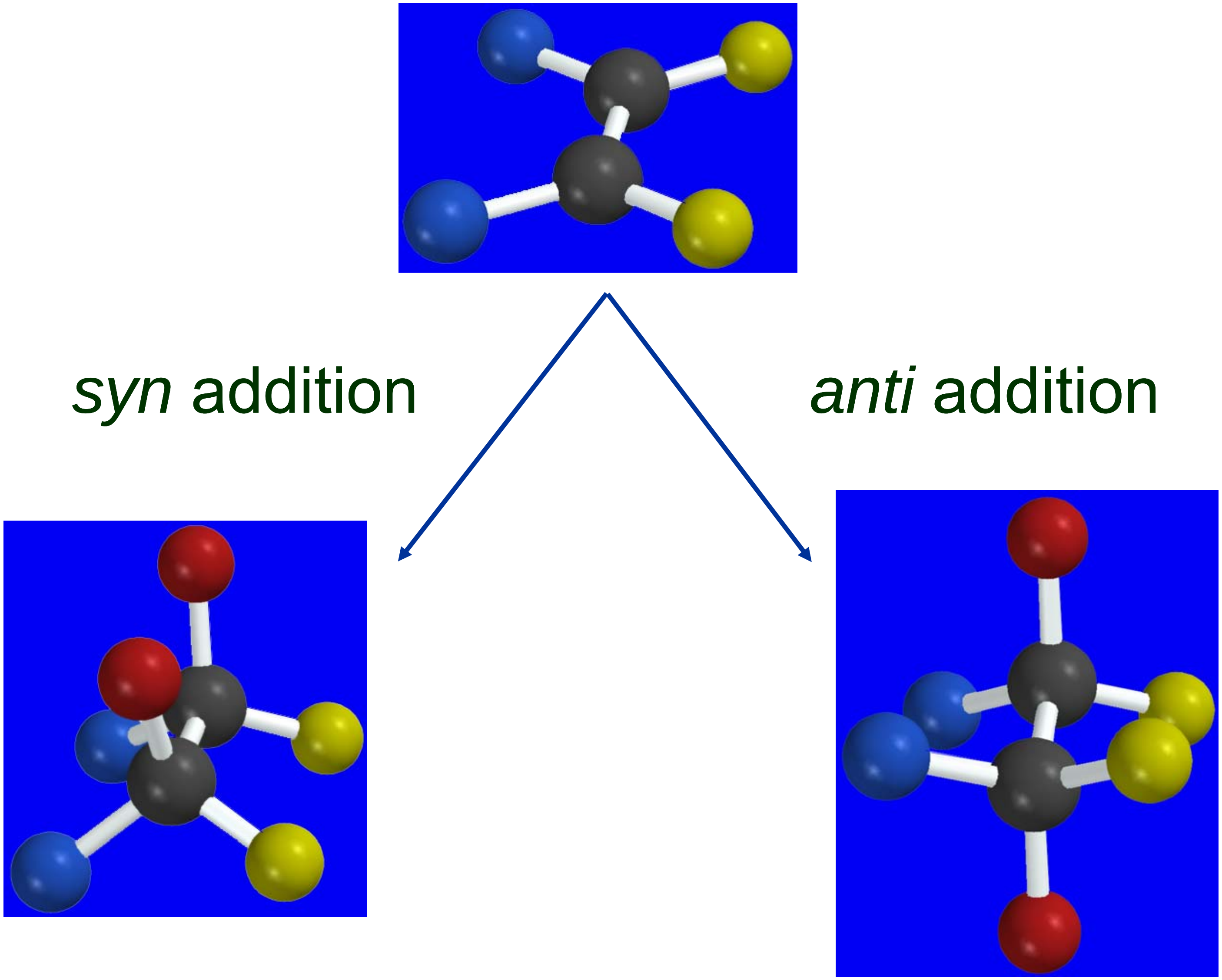
Two spatial (stereochemical) aspects of alkene hydrogenation:

(1) *Syn* addition of both H atoms to double bond.

(2) Hydrogenation is stereoselective, corresponding to addition to less crowded face of double bond.

➢ A reaction in which a single starting material can give two or more stereoisomeric products but yields one of them in greater amounts than the other (or even to the exclusion of the other) is said to be stereoselective.

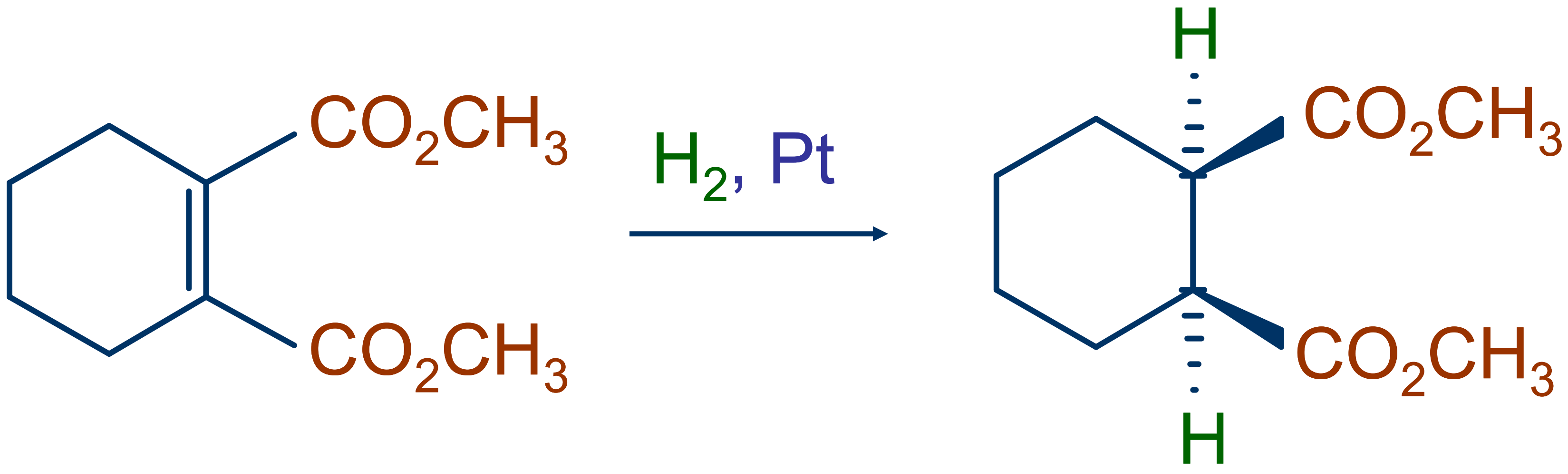
# *syn*-Additon versus *anti*-Addition



*syn* addition

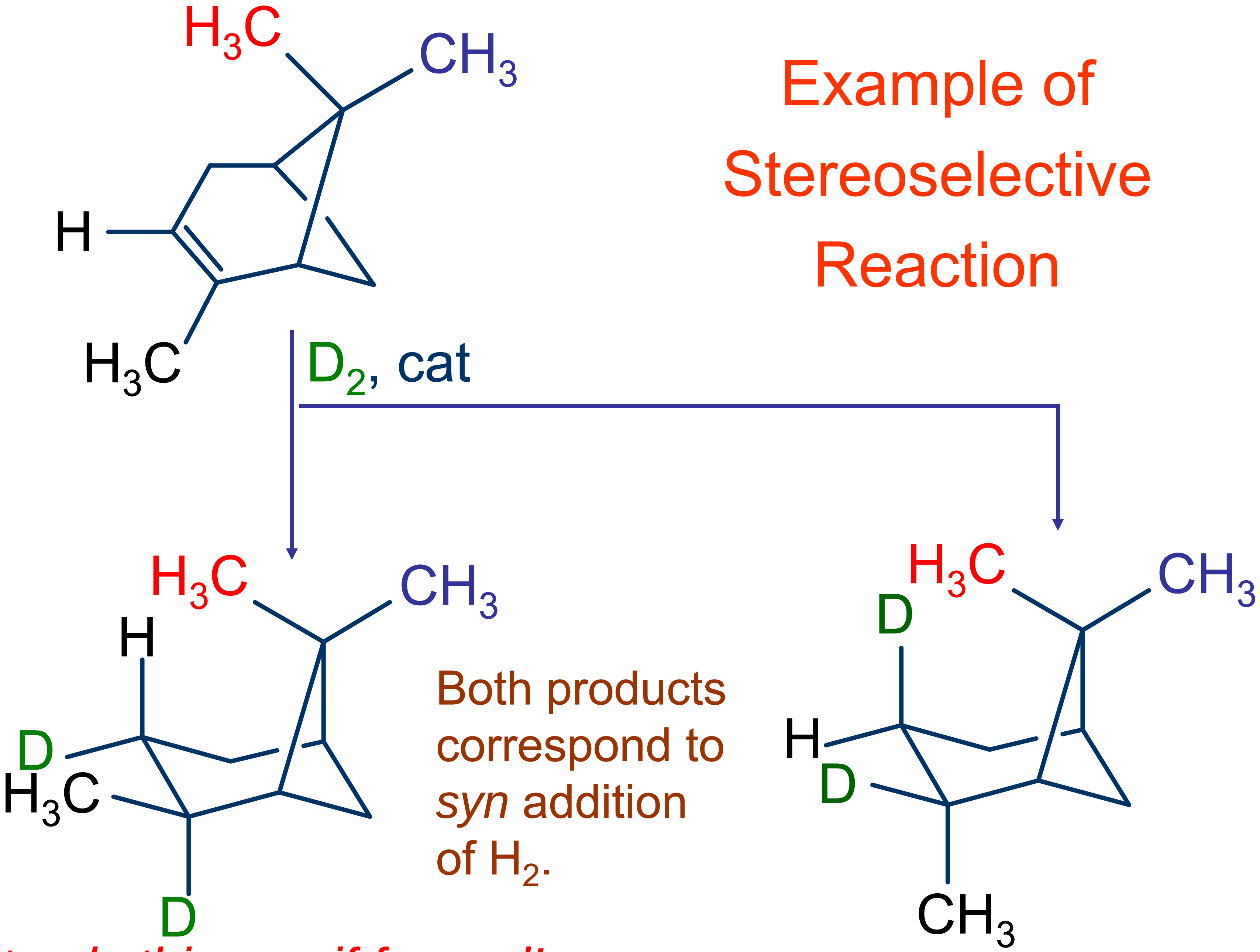
*anti* addition

# Example of *Syn* Addition



(100%)

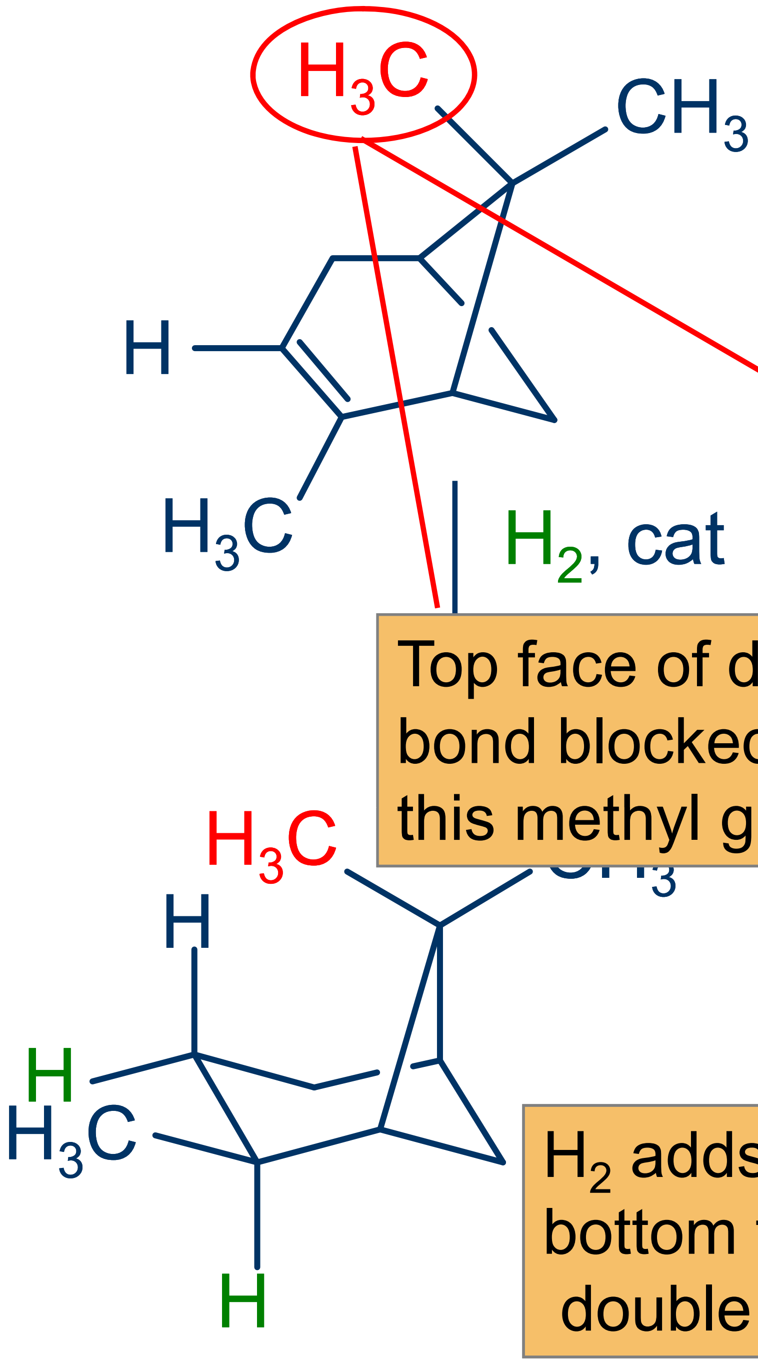
# Example of Stereoselective Reaction



Both products correspond to *syn* addition of $H_2$.

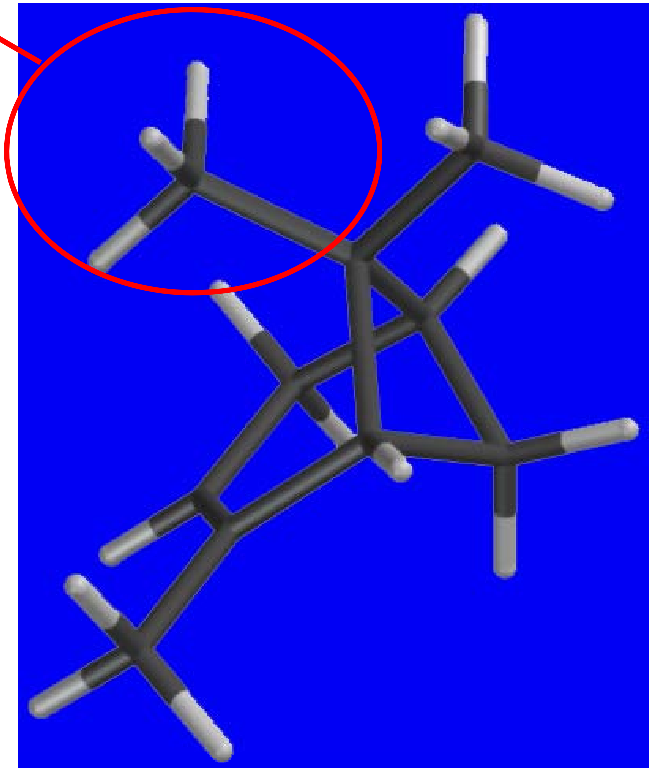
*But only this one if formed!*

# Example of Stereoselective Reaction



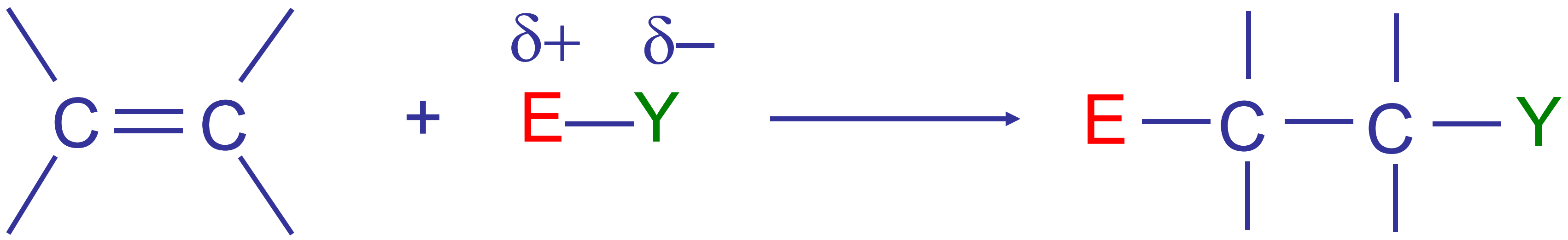
Top face of double bond blocked by this methyl group

$H_2$ adds to bottom face of double bond.

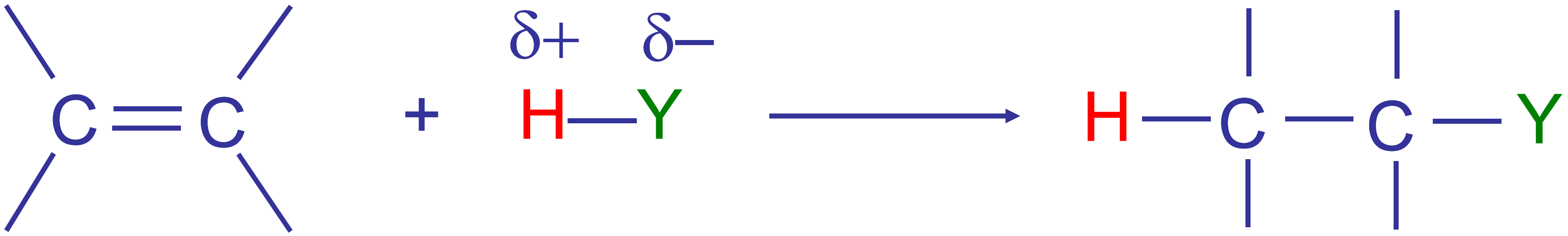


# 6.4. Electrophilic Addition of Hydrogen Halides to Alkenes

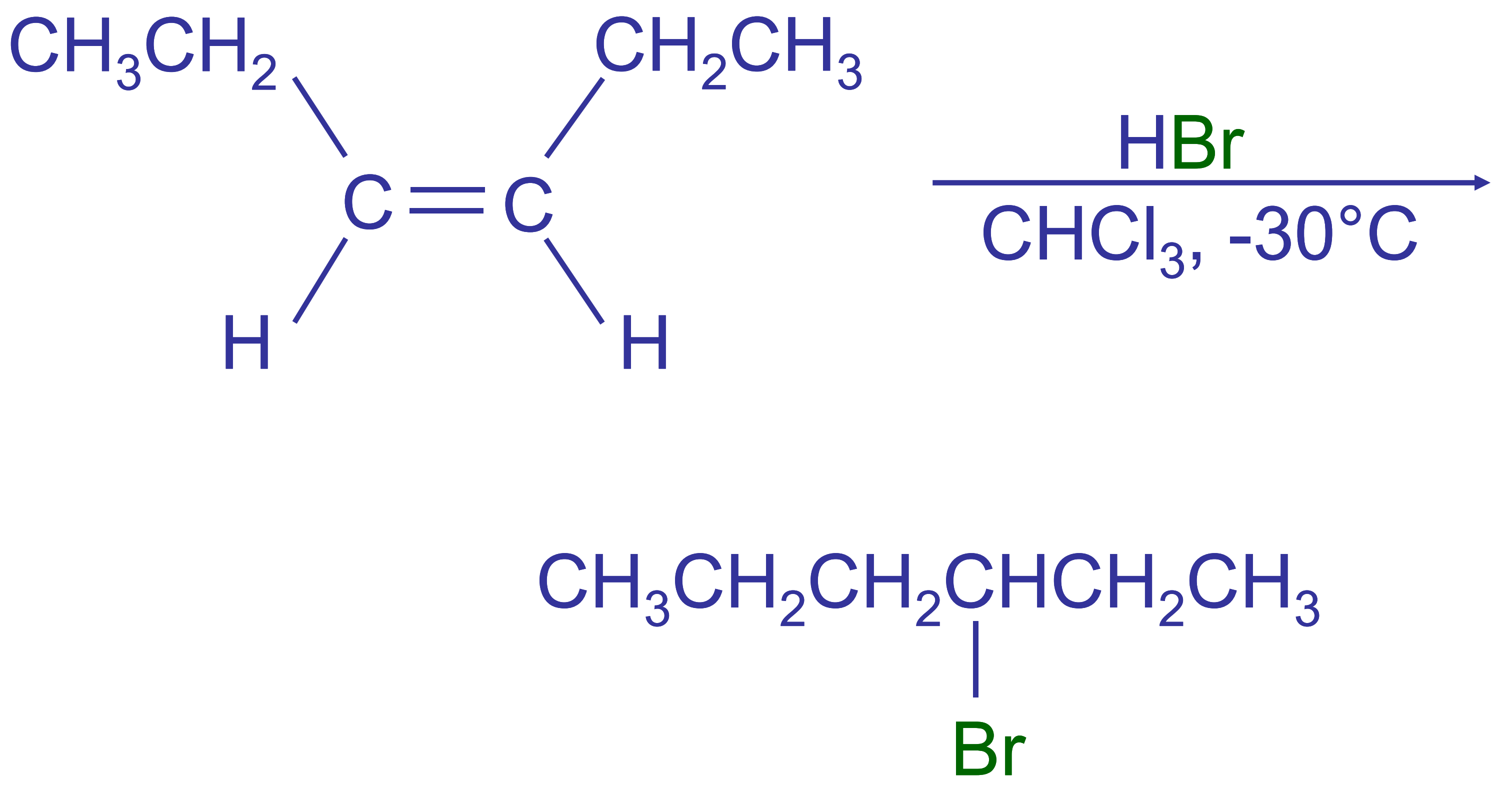
General equation for electrophilic addition



# When E$^+$ is a hydrogen halide:



# Example

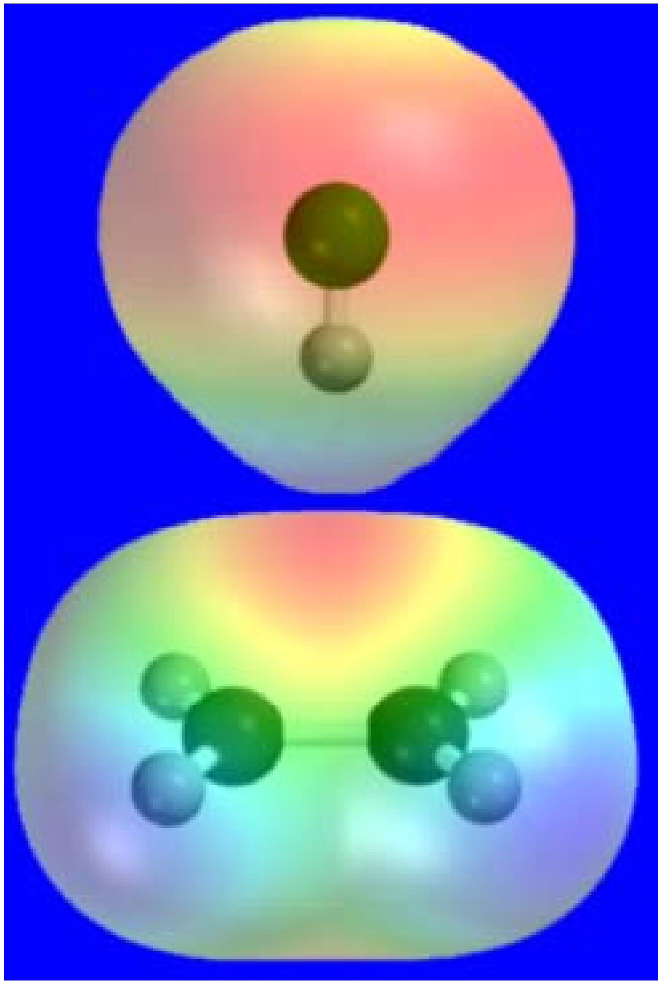


$$CH_3CH_2CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$$

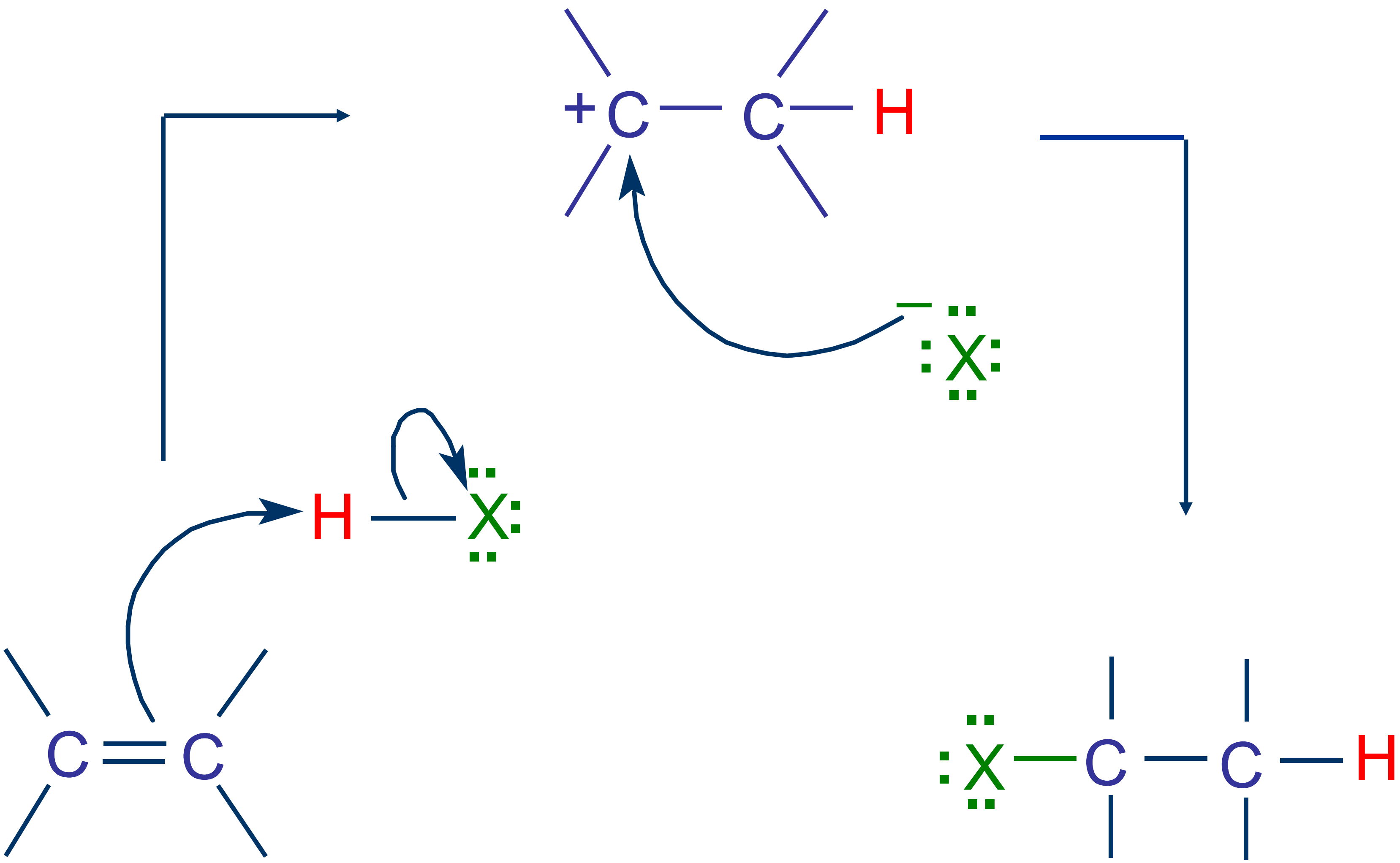
(76%)

# Mechanism

- Electrophilic addition of hydrogen halides to alkenes proceeds by rate-determining formation of a carbocation intermediate.
- Electrons flow from the π system of the alkene (electron rich) toward the positively polarized proton of the hydrogen halide.



# Mechanism



# Reactivity of Hydrogen Halide

HF << HCl < HBr < HI

least acidic

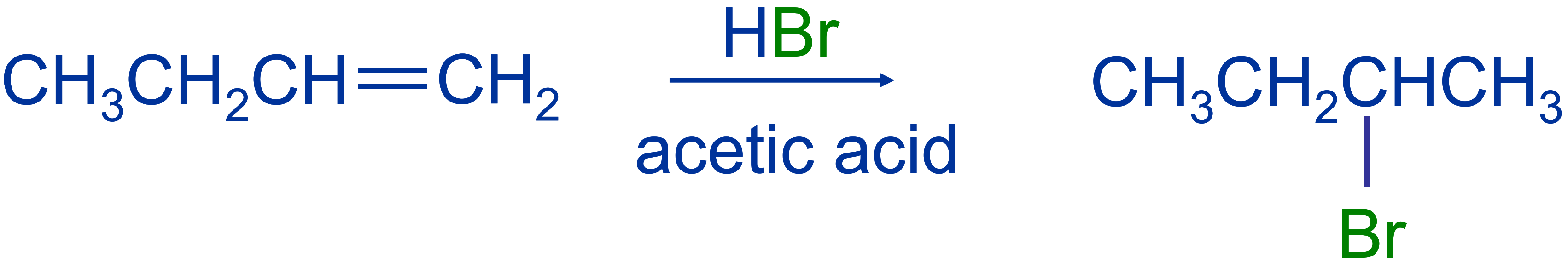
most acidic

# 6.5. Regioselectivity of Hydrogen Halide Addition: Markovnikov's Rule

- When an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogen substituents, and the halogen adds to the carbon that has the fewer hydrogen substituents.

# Markovnikov's Rule

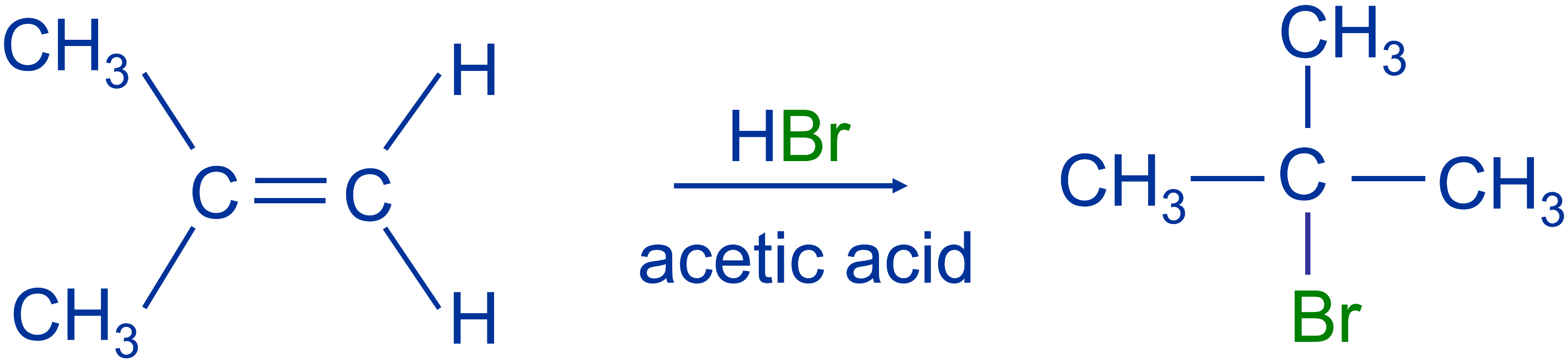
*Example 1*



$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{acetic acid}]{HBr} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{CH}}CH_3$$

(80%)

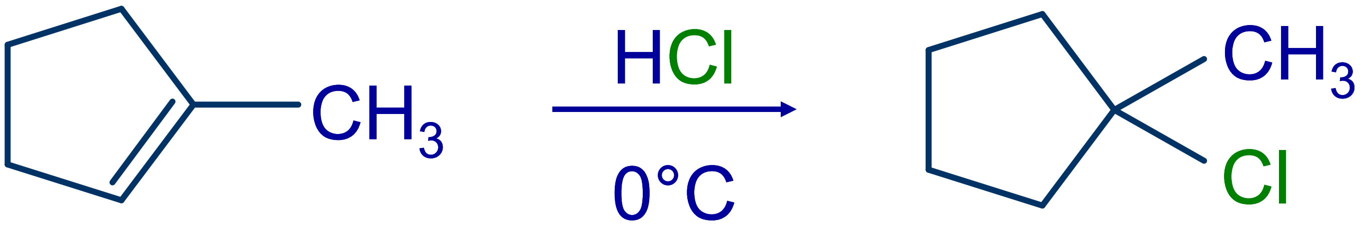
*Example 2*



(90%)

# Markovnikov's Rule

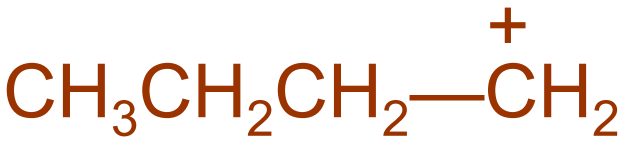
*Example 3*



(100%)

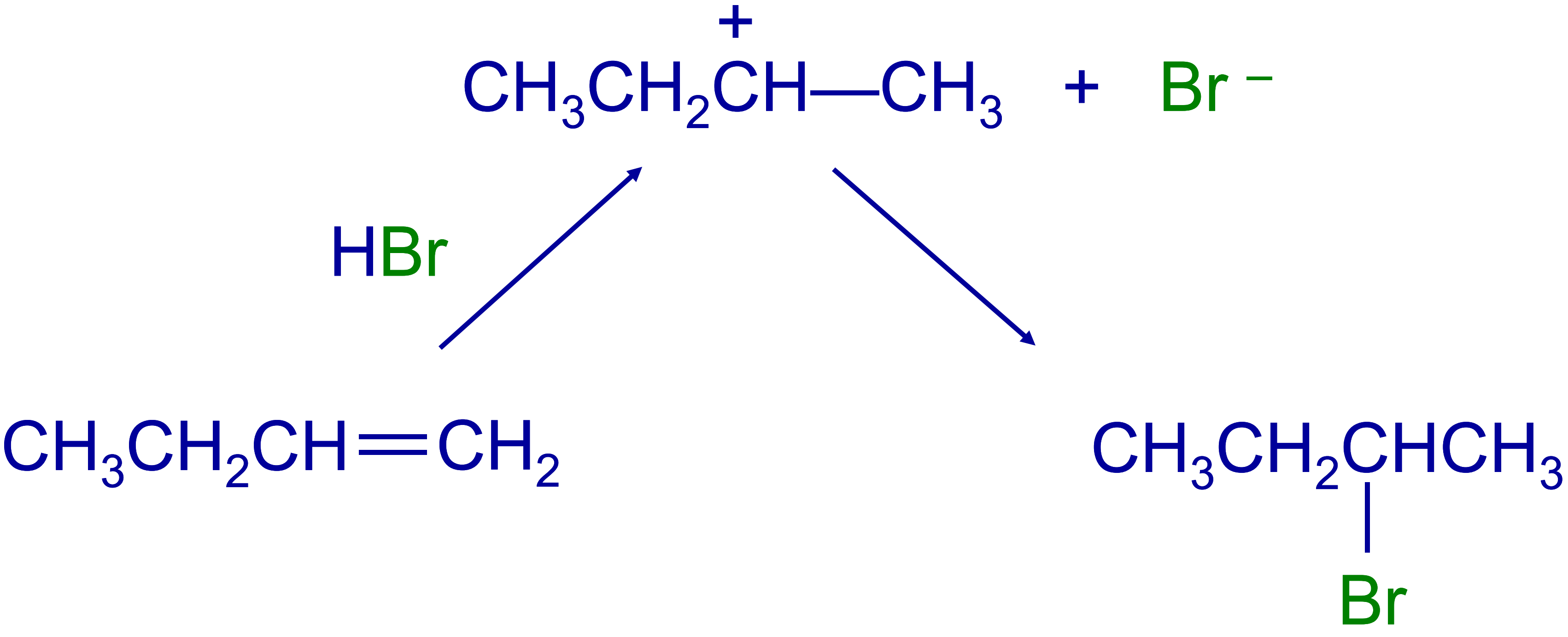
- Protonation of double bond occurs in direction that gives more stable carbocation.

# 6.6. Mechanistic Basis for Markovnikov's Rule: Example 1



$CH_3CH_2CH_2{-}\overset{+}{C}H_2$

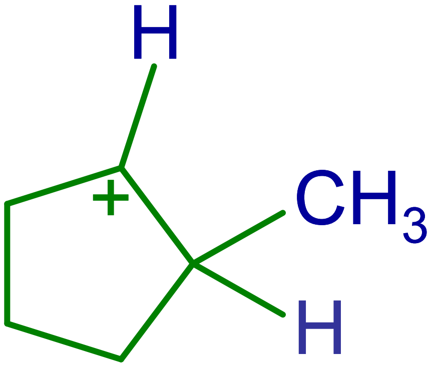
primary carbocation is less stable:  not formed

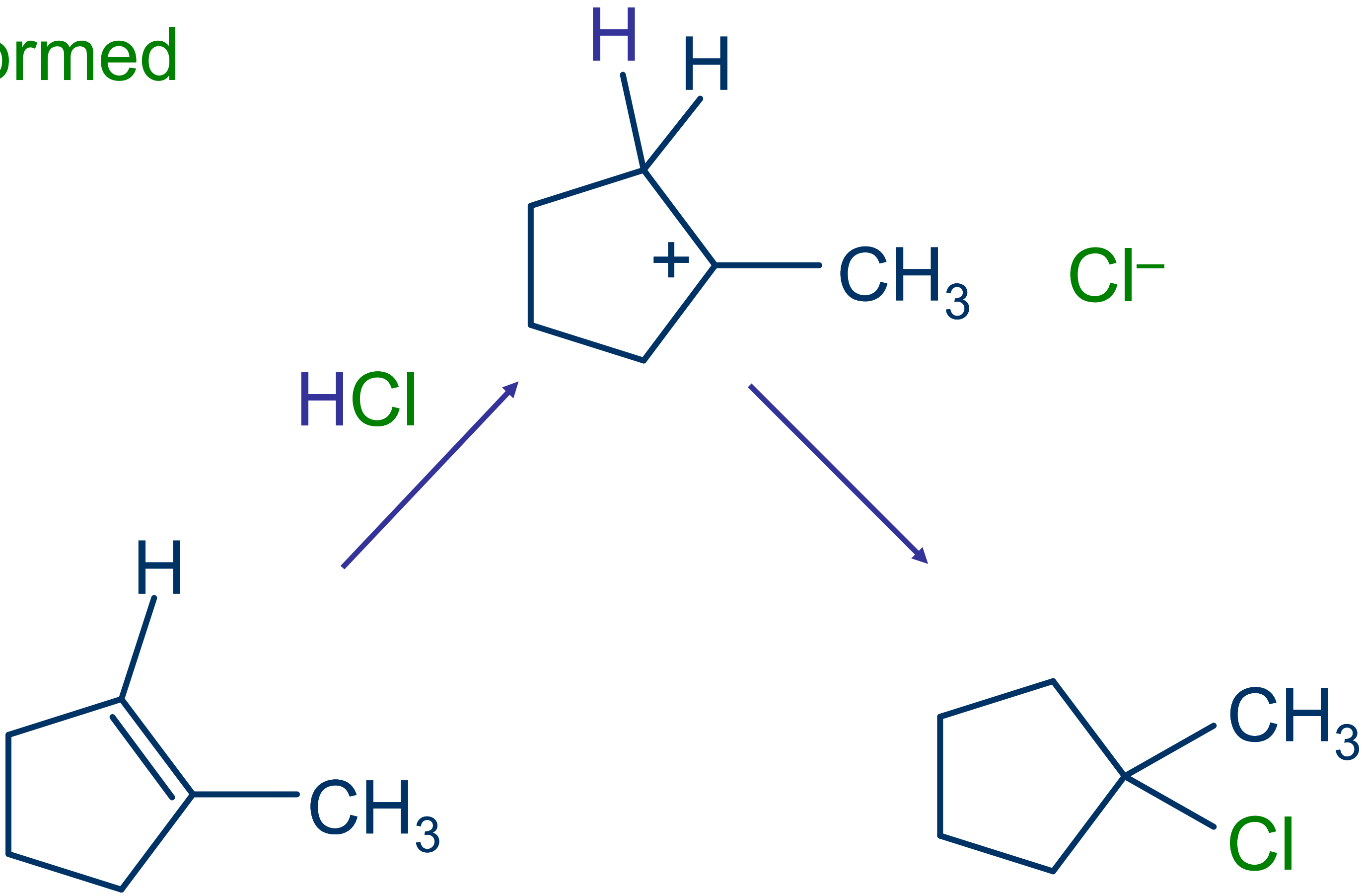


$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr} CH_3CH_2\overset{+}{C}H{-}CH_3 \;+\; Br^{-} \longrightarrow CH_3CH_2\underset{Br}{\underset{|}{C}}HCH_3$$

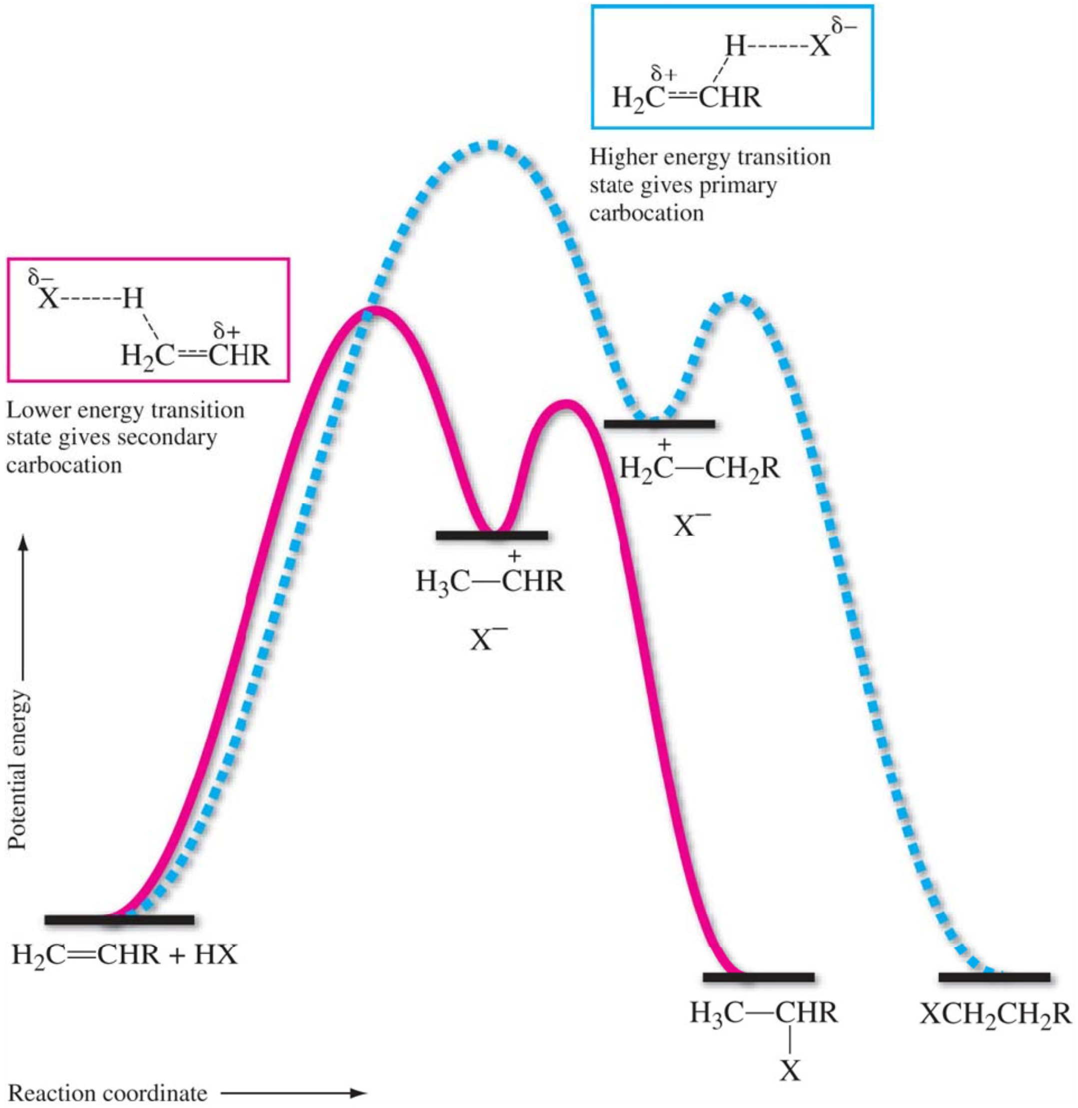
# Mechanistic Basis for Markovnikov's Rule: Example 3

secondary carbocation is less stable: not formed

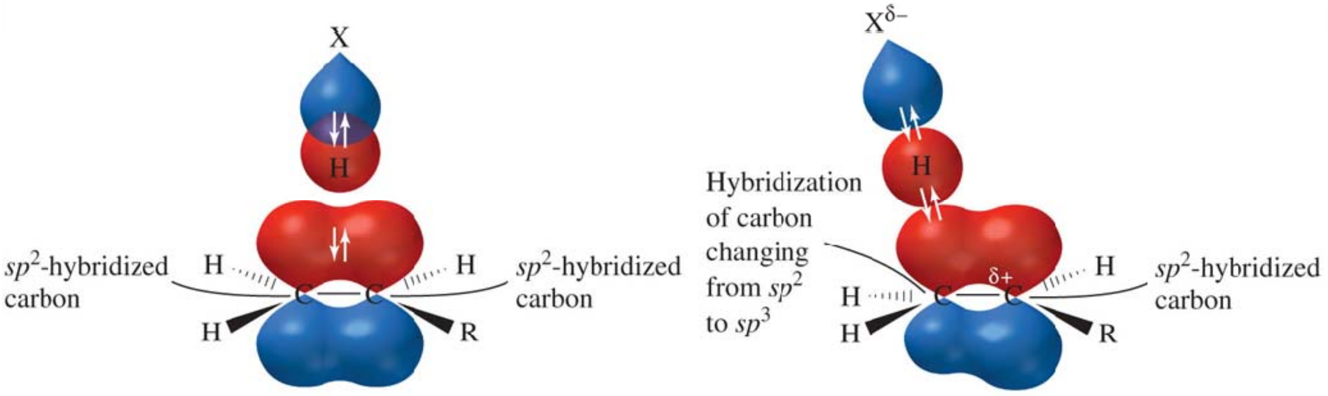




# Figure 6.4: Energy Diagrams of Markovnikov Addition and Anti-Markovnivok Addition of HX to an Alkene



# Figure 6.5: Electron Flow and Orbital Interactions



$sp^2$-hybridized carbon

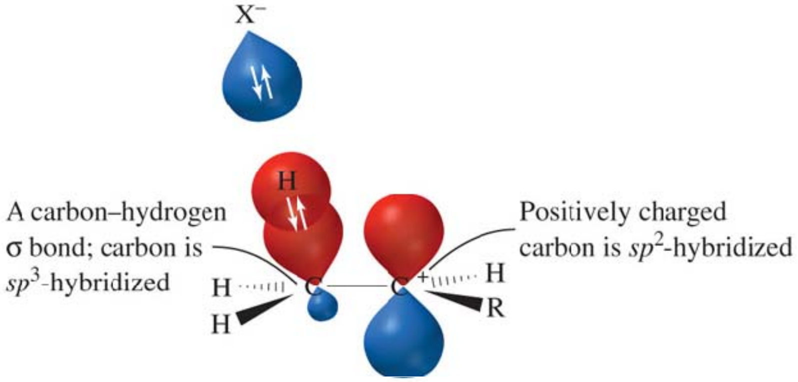
$sp^2$-hybridized carbon

Hybridization of carbon changing from $sp^2$ to $sp^3$

$sp^2$-hybridized carbon

(*a*) The hydrogen halide (HX) and the alkene ($H_2C{=}CHR$) approach each other. The electrophile is the hydrogen halide, and the site of electrophilic attack is the orbital containing the π electrons of the double bond.

(*b*) Electrons flow from the π orbital of the alkene to the hydrogen halide. The π electrons flow in the direction that generates a partial positive charge on the carbon atom that bears the electron-releasing alkyl group (R). The hydrogen–halogen bond is partially broken and a C—H σ bond is partially formed at the transition state.



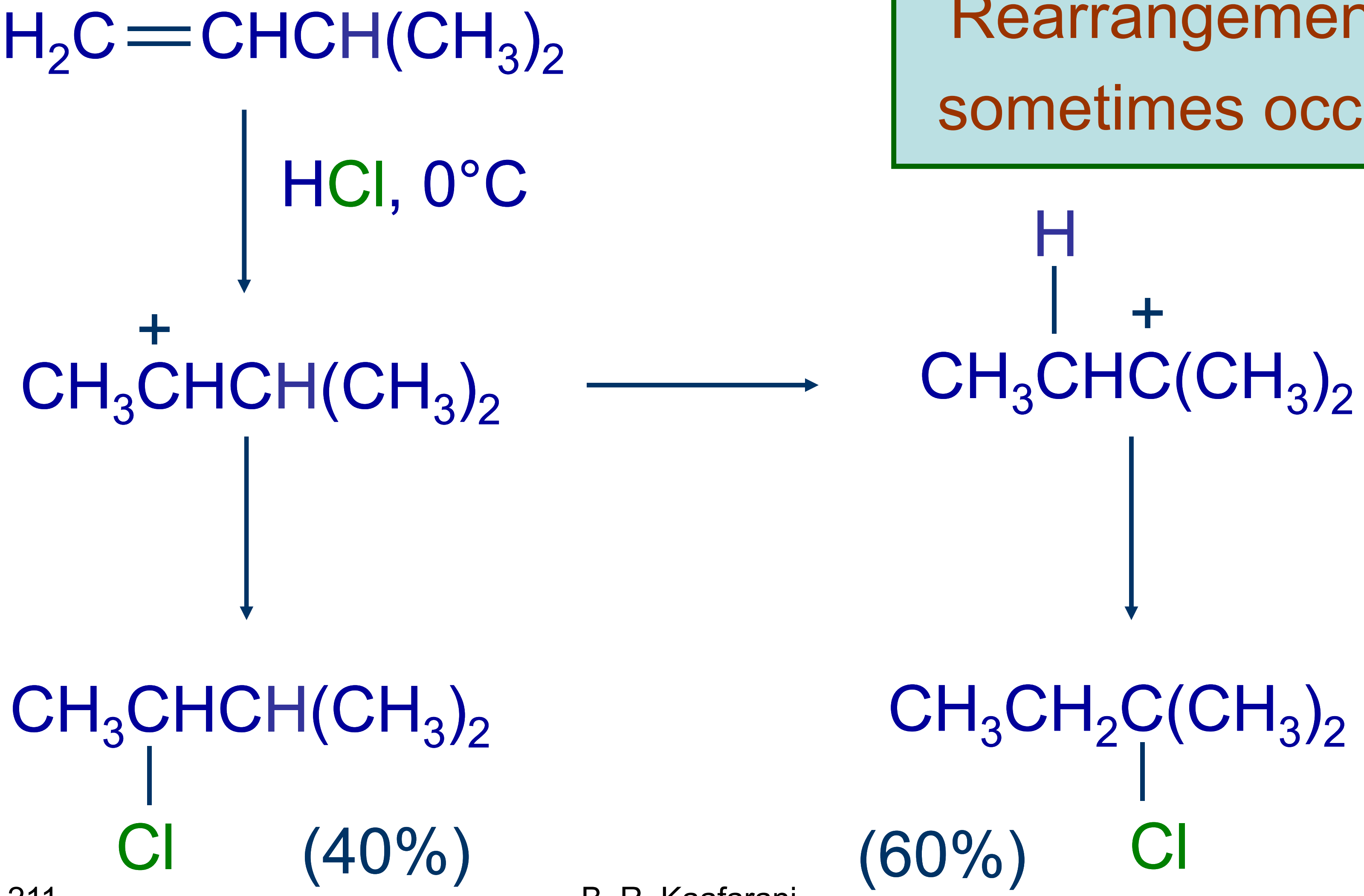
A carbon–hydrogen σ bond; carbon is $sp^3$-hybridized

Positively charged carbon is $sp^2$-hybridized

(*c*) Loss of the halide ion ($X^-$) from the hydrogen halide and C—H σ bond formation complete the formation of the more stable carbocation intermediate $CH_3\overset{+}{C}HR$.

# 6.7. Carbocation Rearrangements in Hydrogen Halide Addition to Alkenes

Rearrangements sometimes occur!



$$H_2C{=}CHCH(CH_3)_2 \xrightarrow{HCl,\ 0°C} CH_3\overset{+}{C}HCH(CH_3)_2 \longrightarrow CH_3\overset{\overset{H}{|}}{C}H\overset{+}{C}(CH_3)_2$$

$$CH_3\overset{+}{C}HCH(CH_3)_2 \longrightarrow CH_3\underset{\underset{Cl}{|}}{C}HCH(CH_3)_2 \quad (40\%)$$

$$CH_3CH\overset{+}{C}(CH_3)_2 \longrightarrow CH_3CH_2\underset{\underset{Cl}{|}}{C}(CH_3)_2 \quad (60\%)$$

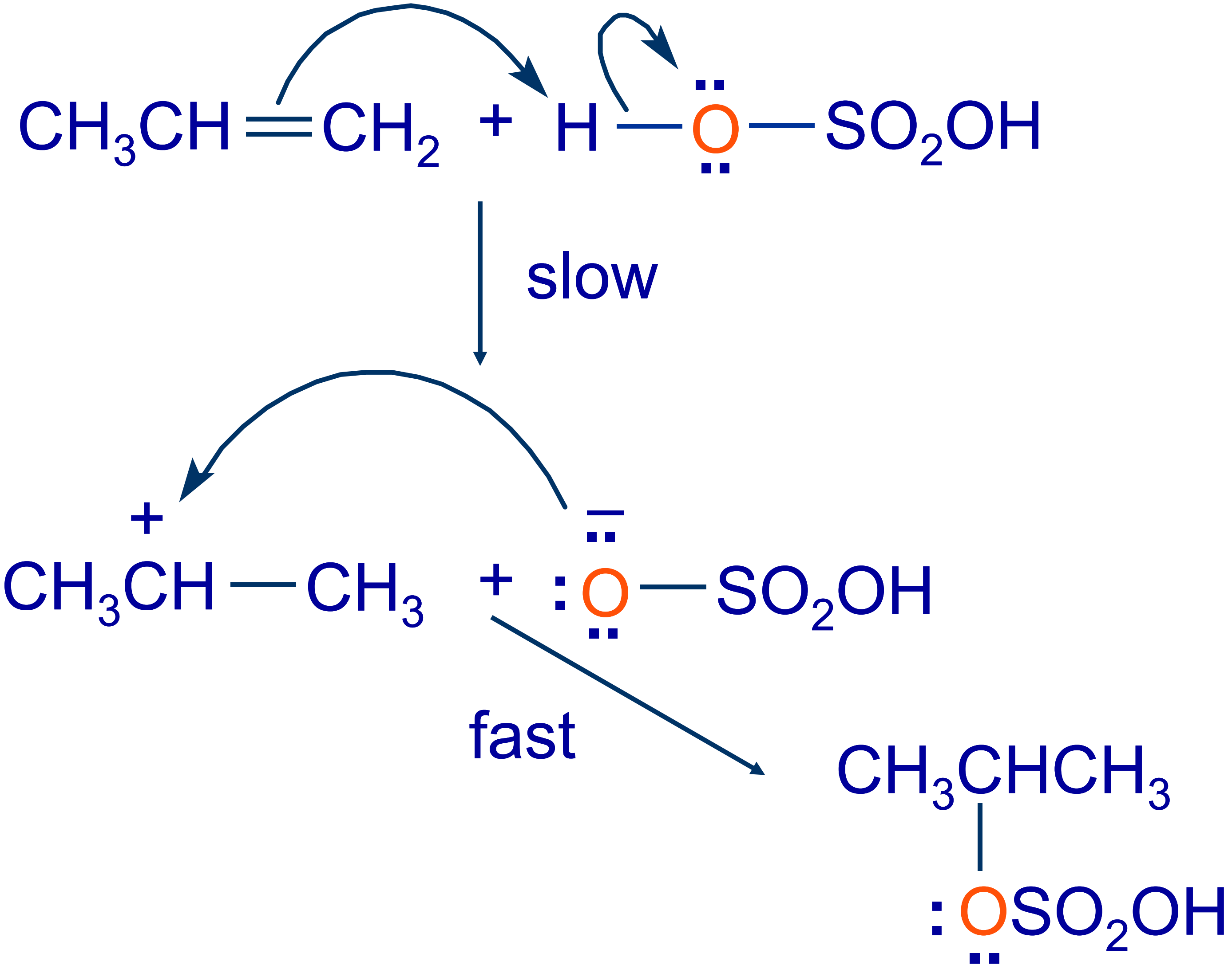
# 6.8. Addition of Sulfuric Acid ($H_2SO_4$) to Alkenes

$$CH_3CH{=}CH_2 \xrightarrow{HOSO_2OH} CH_3\underset{OSO_2OH}{\underset{|}{C}}HCH_3$$

Isopropyl hydrogen sulfate

- Follows Markovnikov's rule
- Yields an alkyl hydrogen sulfate

# Mechanism



$CH_3CH{=}CH_2 + H{-}\ddot{\underset{\cdot\cdot}{O}}{-}SO_2OH$

slow

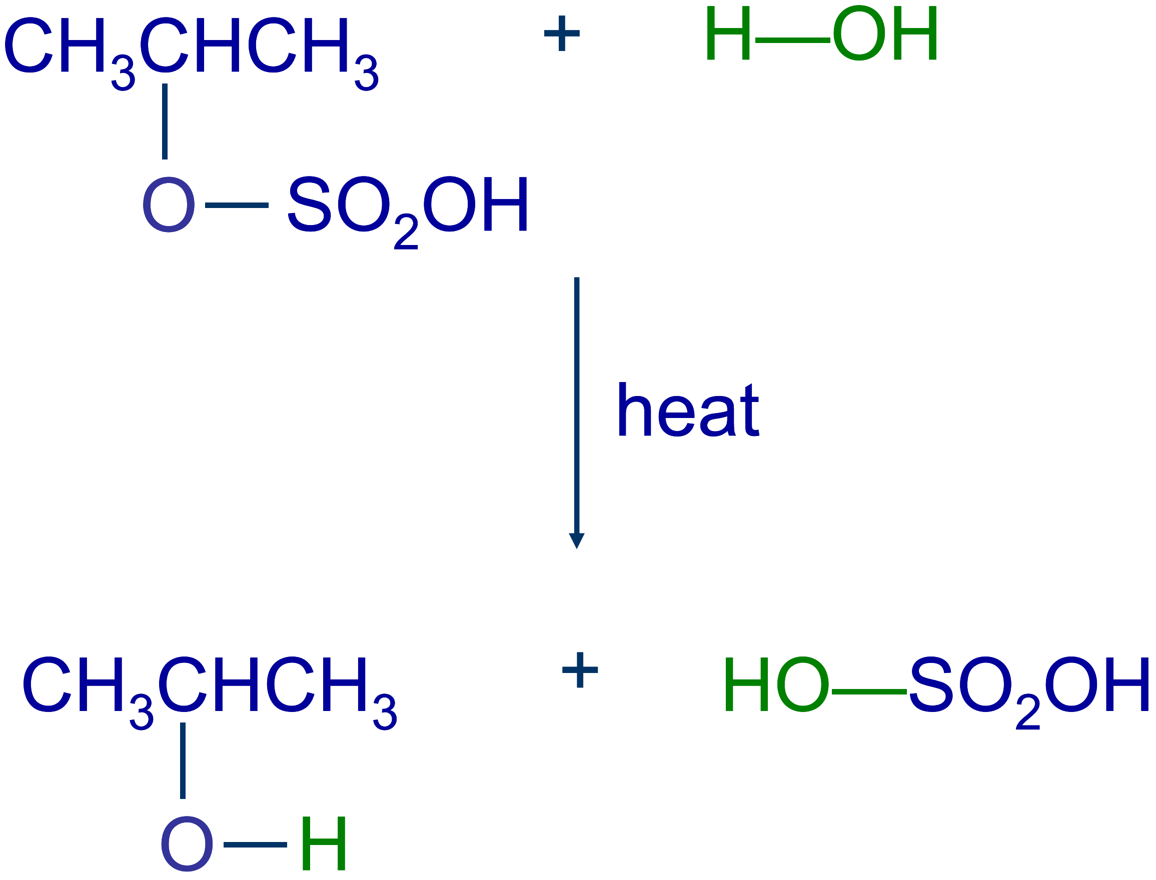
$CH_3\overset{+}{C}H{-}CH_3 + :\overset{-}{\ddot{\underset{\cdot\cdot}{O}}}{-}SO_2OH$

fast

$CH_3CHCH_3$

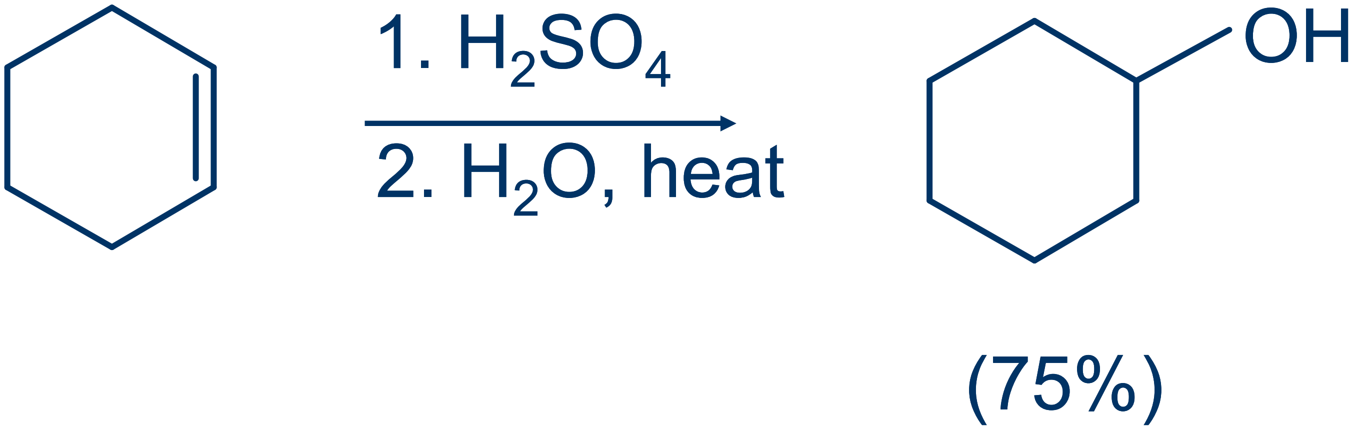
$:\underset{\cdot\cdot}{O}SO_2OH$

# Alkyl hydrogen sulfates undergo hydrolysis in hot water



$$\underset{\displaystyle \mid \atop \displaystyle O-SO_2OH}{CH_3CHCH_3} + H{-}OH \xrightarrow{\text{heat}} \underset{\displaystyle \mid \atop \displaystyle O-H}{CH_3CHCH_3} + HO{-}SO_2OH$$

# Application: Conversion of alkenes to alcohols



# But...

- Not all alkenes yield alkyl hydrogen sulfates on reaction with sulfuric acid

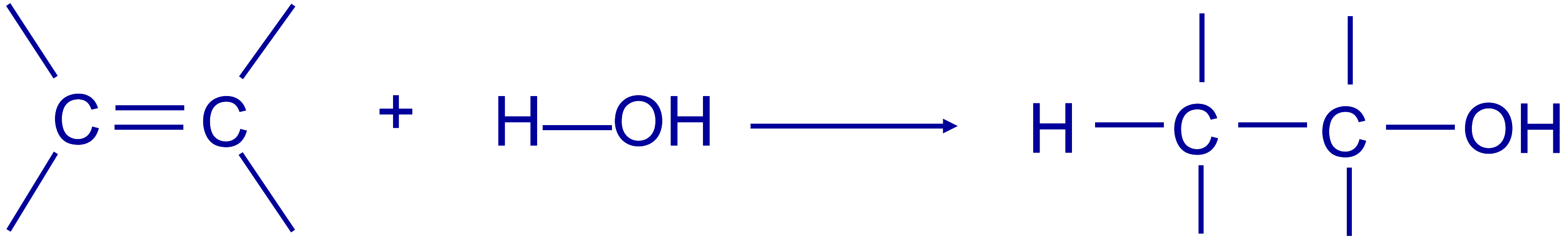
- These do:

  $H_2C{=}CH_2$, $RCH{=}CH_2$, and $RCH{=}CHR'$

- These don't:

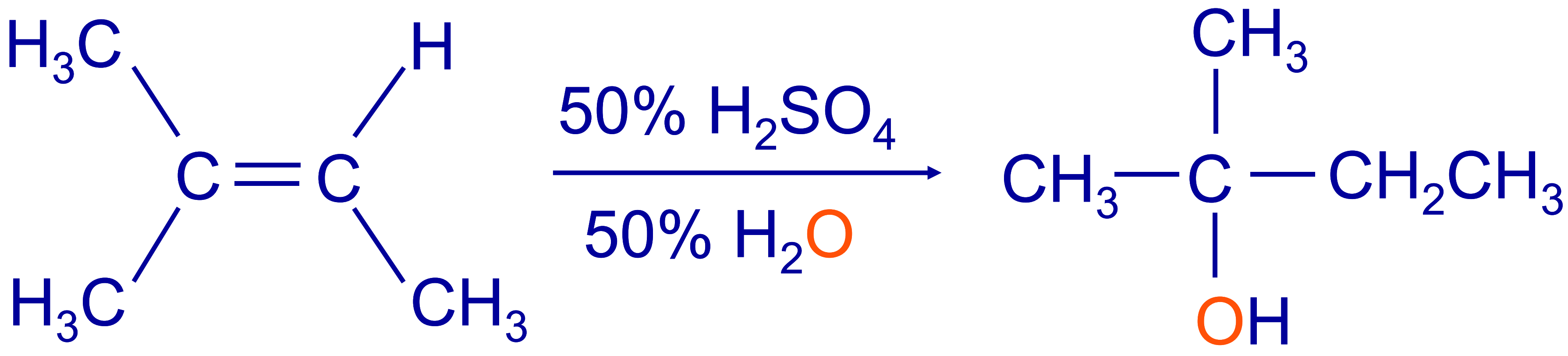
  $R_2C{=}CH_2$, $R_2C{=}CHR$, and $R_2C{=}CR_2$

# 6.9. Acid-Catalyzed Hydration of Alkenes



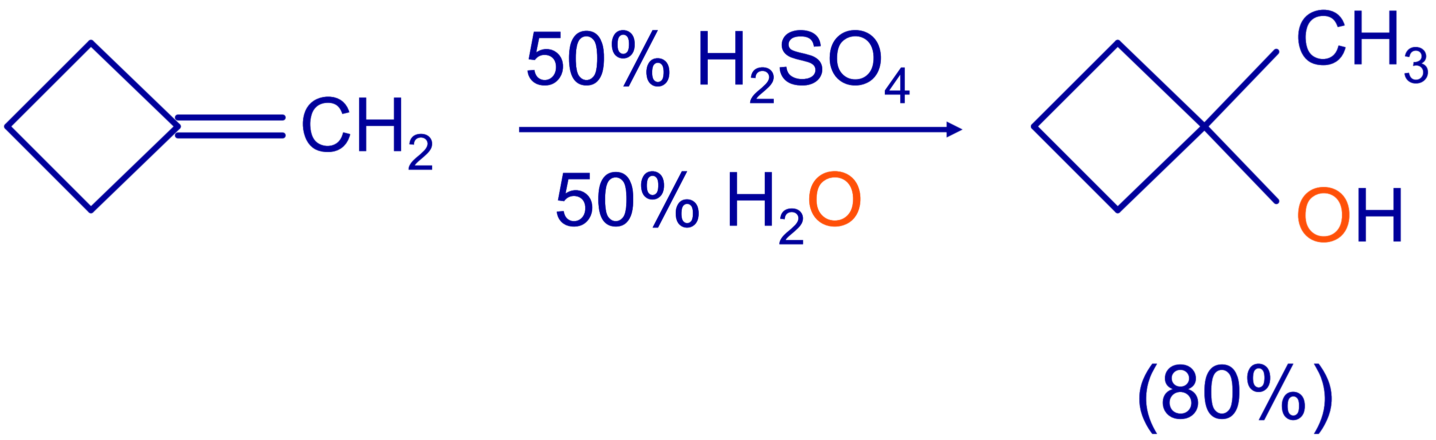
- Reaction is acid catalyzed; typical hydration medium is 50% $H_2SO_4$-50% $H_2O$.

# Follows Markovnikov's Rule



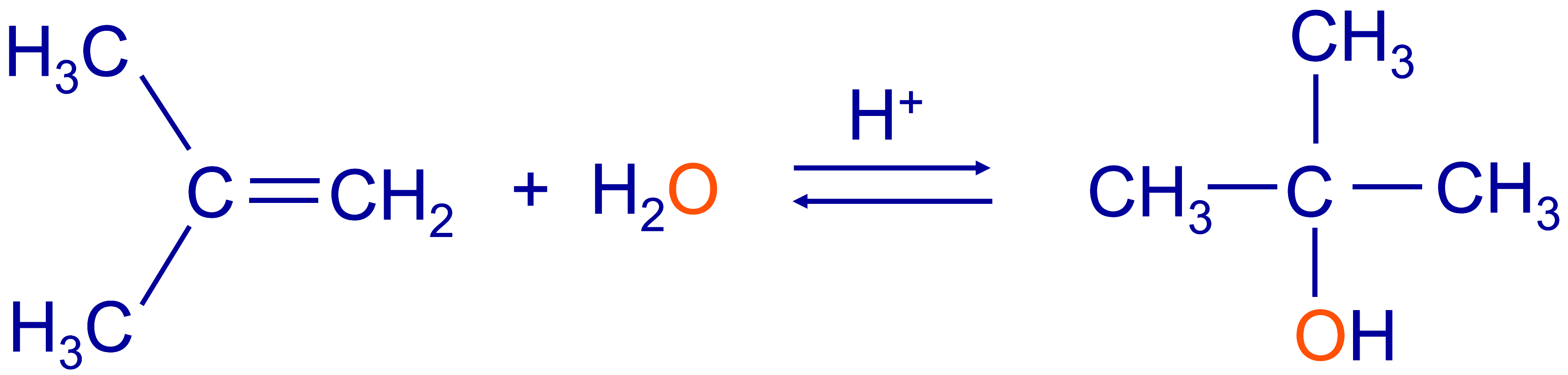
(90%)

# Follows Markovnikov's Rule



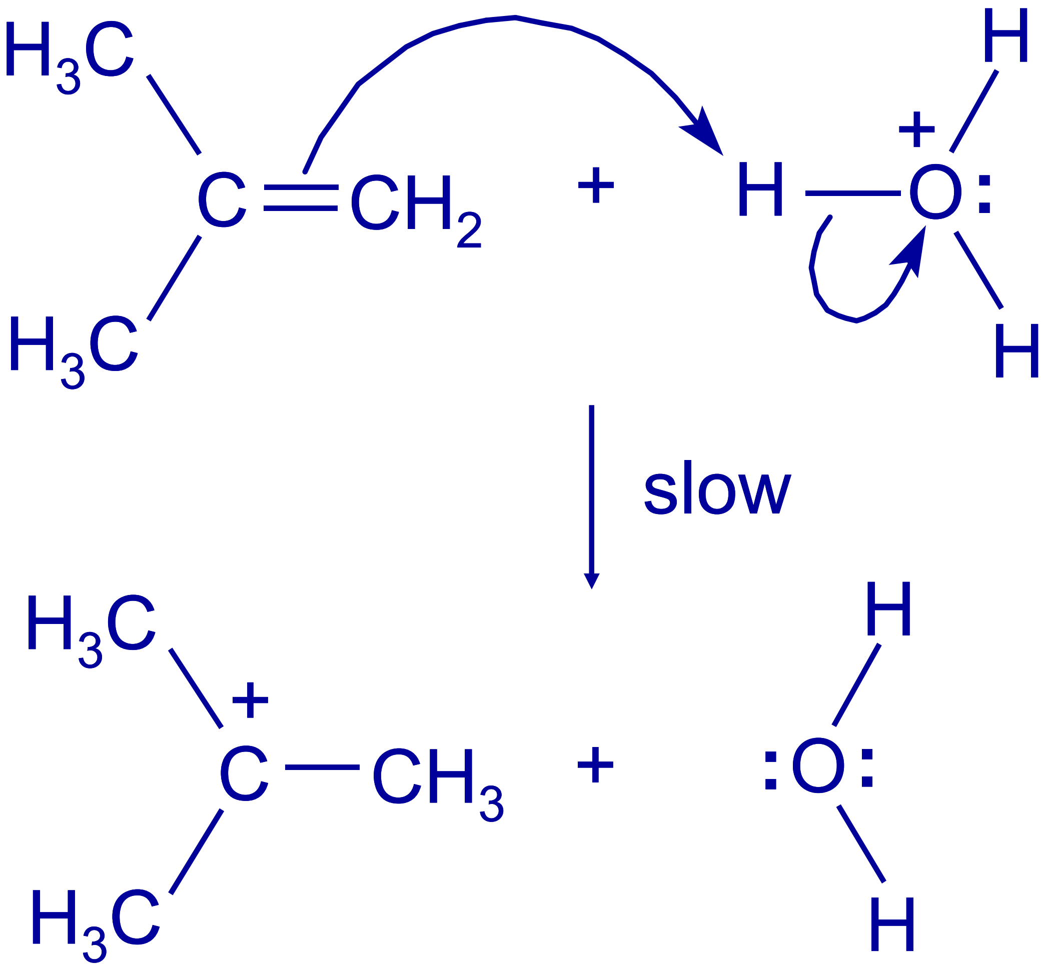
# Mechanism

- Involves a carbocation intermediate.
- Is the reverse of acid-catalyzed dehydration of alcohols to alkenes.



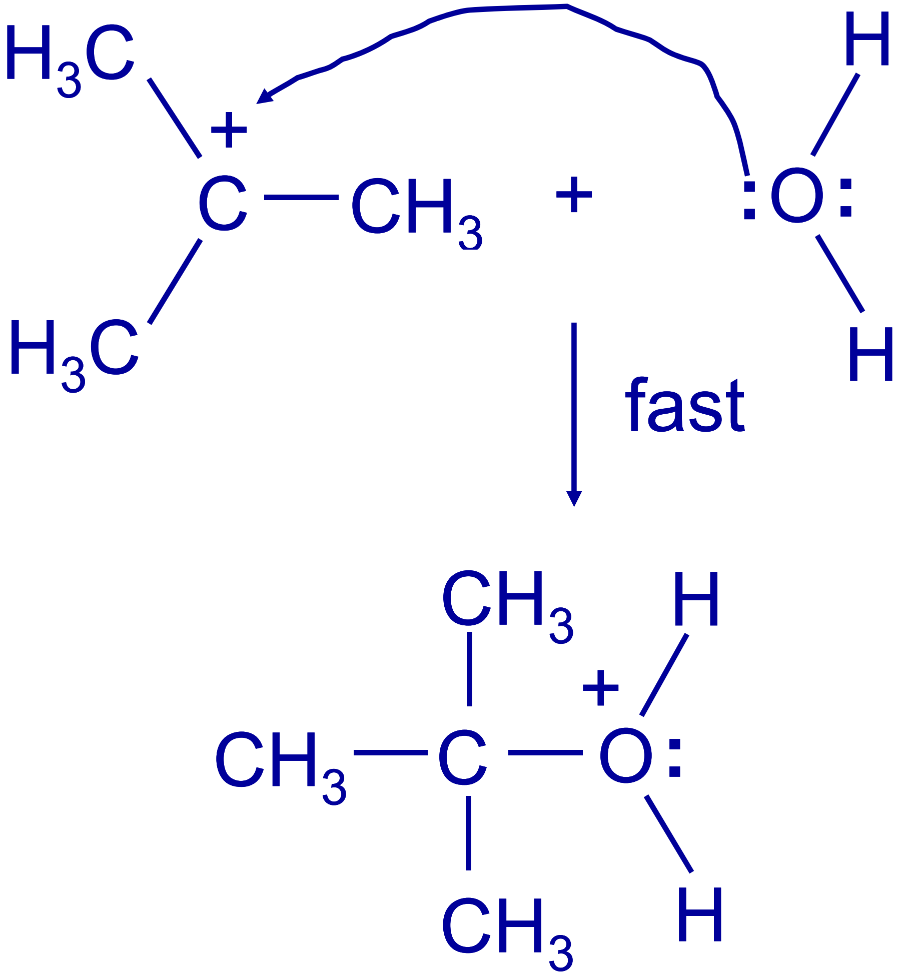
# Mechanism

Step (1): Protonation of double bond



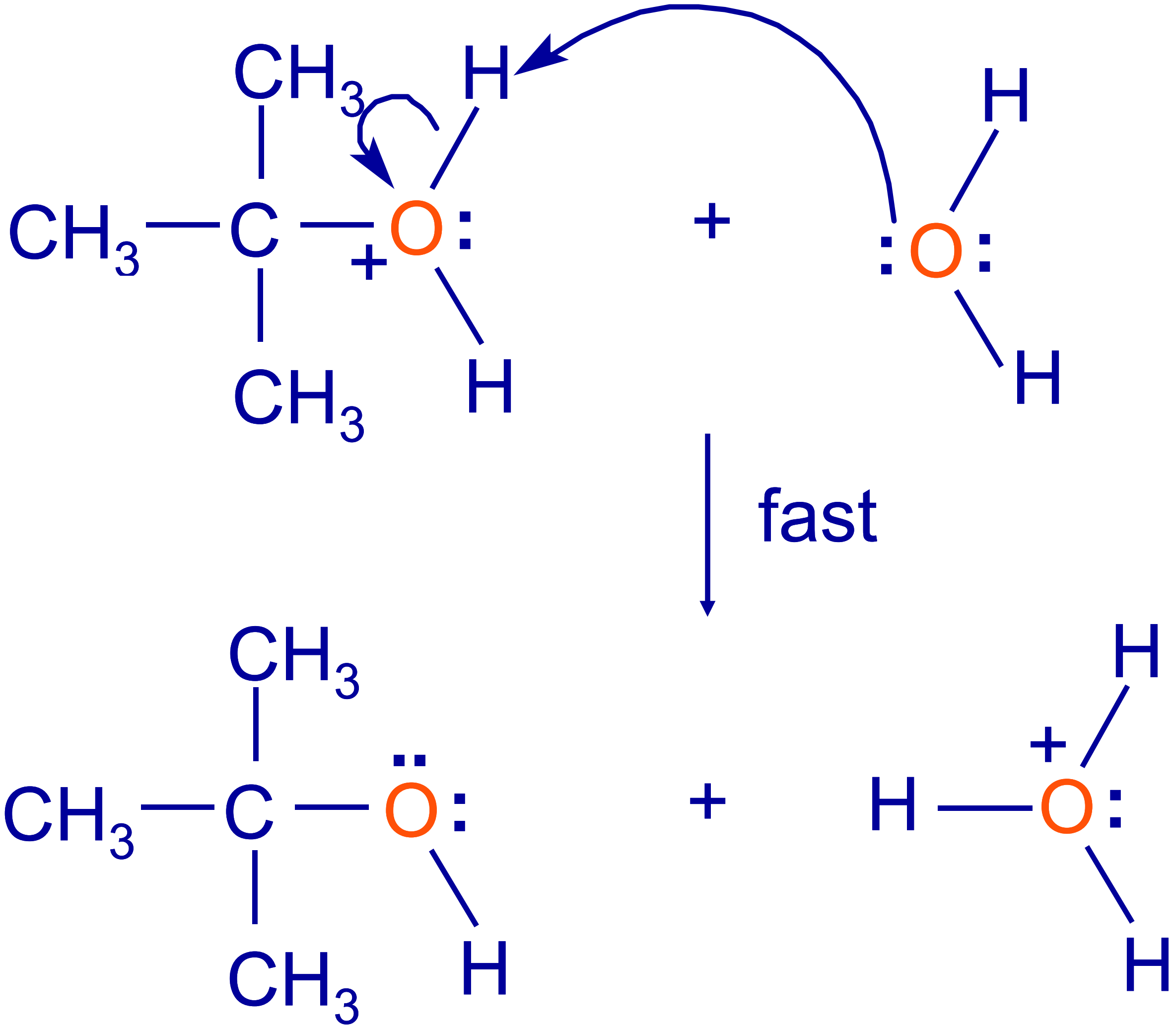
# Mechanism

## Step (2): Capture of carbocation by water



# Mechanism

## Step (3): Deprotonation of oxonium ion



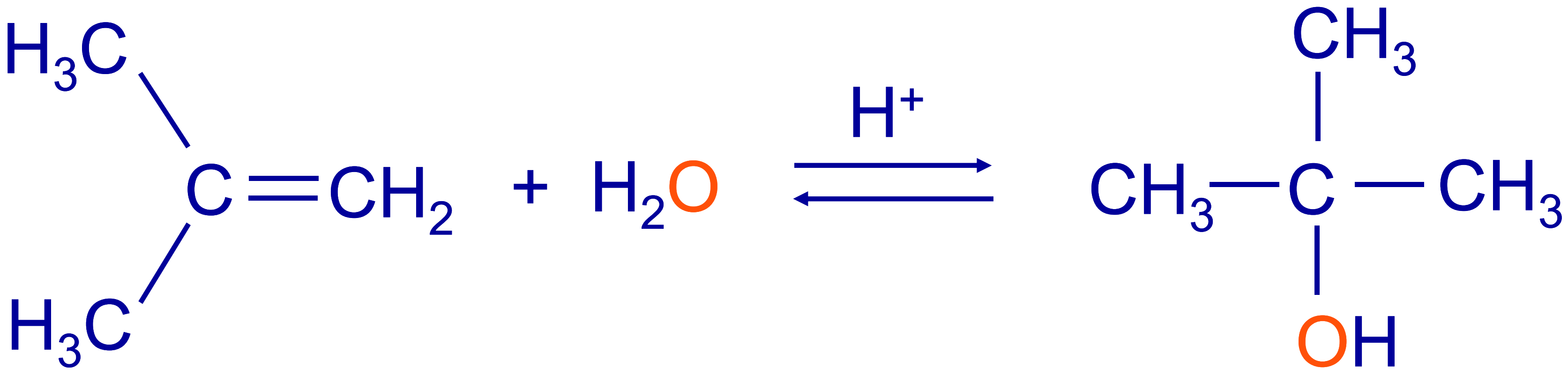
# Relative Rates

## Acid-catalyzed hydration

| | | |
|---|---|---|
| Ethylene | $CH_2{=}CH_2$ | 1.0 |
| Propene | $CH_3CH{=}CH_2$ | $1.6 \times 10^6$ |
| 2-Methylpropene | $(CH_3)_2C{=}CH_2$ | $2.5 \times 10^{11}$ |

- *The more stable the carbocation, the faster it is formed, and the faster the reaction rate.*

# Principle of Microscopic Reversibility



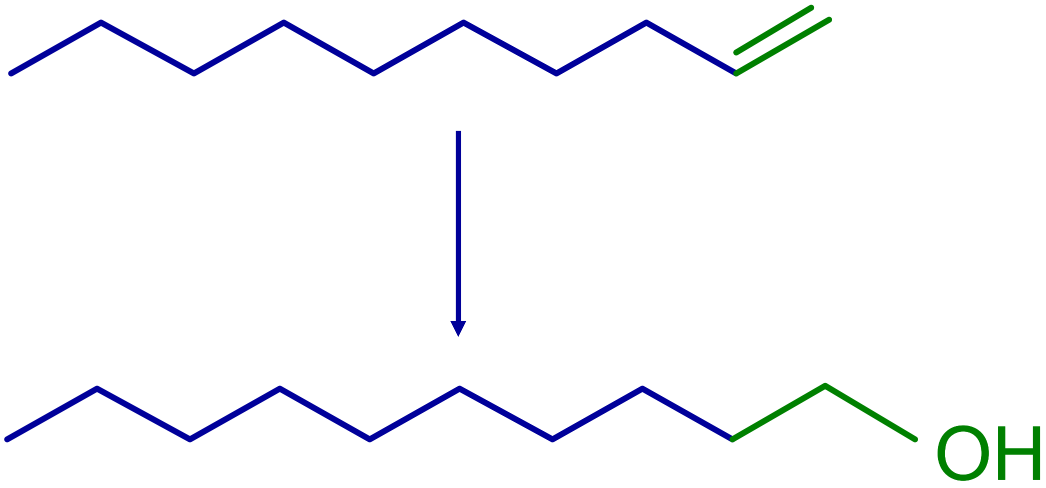
- In an equilibrium process, the same intermediates and transition states are encountered in the forward direction and the reverse, but in the opposite order.

# 6.11

# Hydroboration-Oxidation of Alkenes

# Synthesis

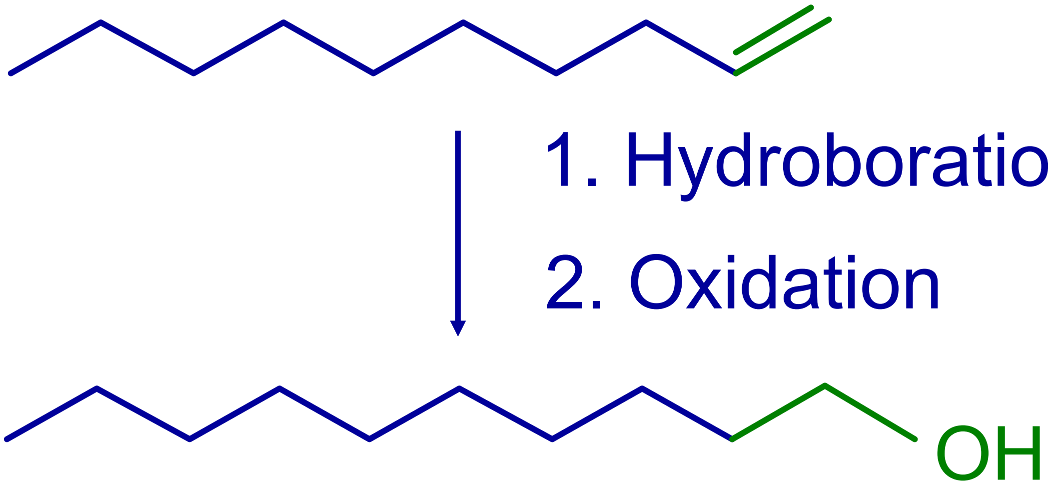
- Suppose you wanted to prepare 1-decanol from 1-decene?



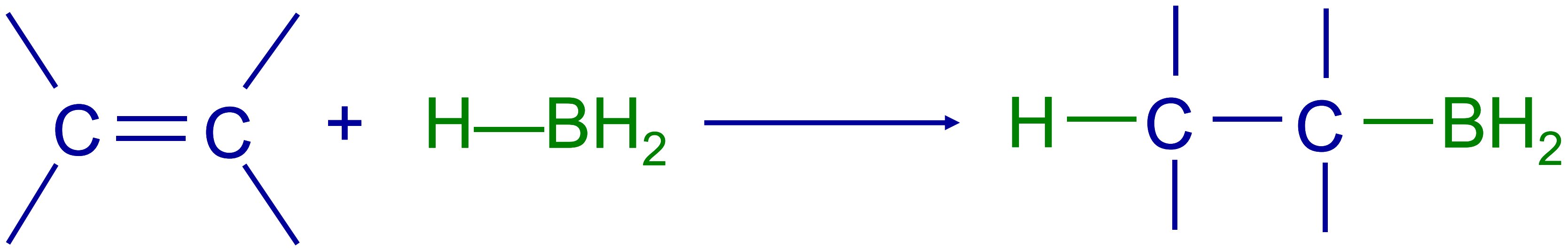
*Needed:* a method for hydration of alkenes with a regioselectivity opposite to Markovnikov's rule.

# Synthesis

- Two-step reaction sequence called hydroboration-oxidation converts alkenes to alcohols with a regiochemistry opposite to Markovnikov's rule.

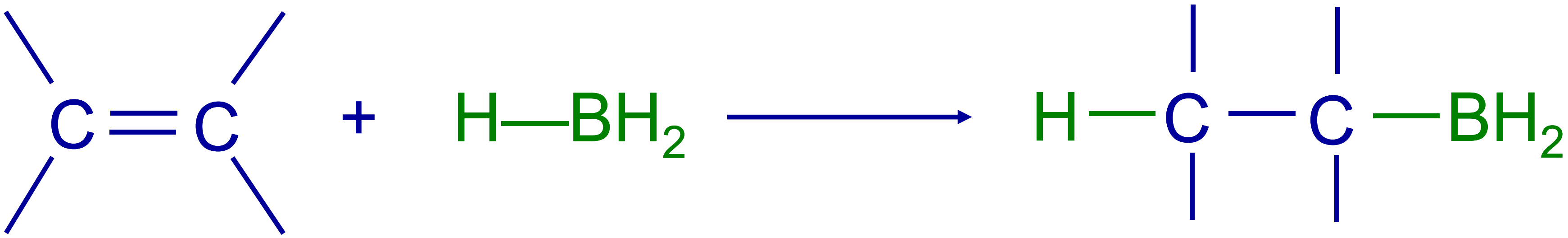


# Hydroboration Step



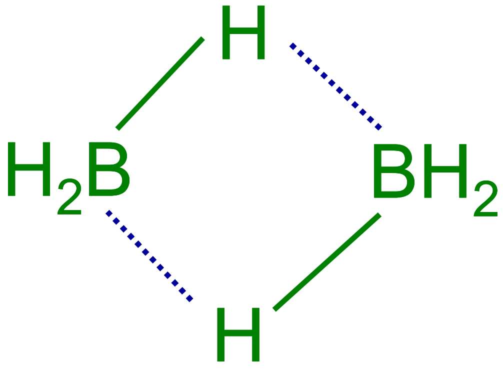
- Hydroboration can be viewed as the addition of borane ($BH_3$) to the double bond. But $BH_3$ is not the reagent actually used.

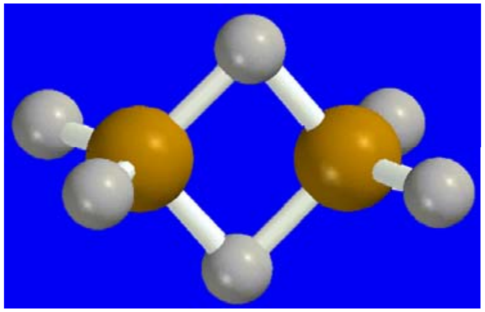
# Hydroboration Step



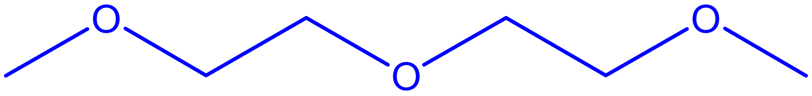
$C{=}C + H{-}BH_2 \longrightarrow H{-}C{-}C{-}BH_2$

Hydroboration reagents:



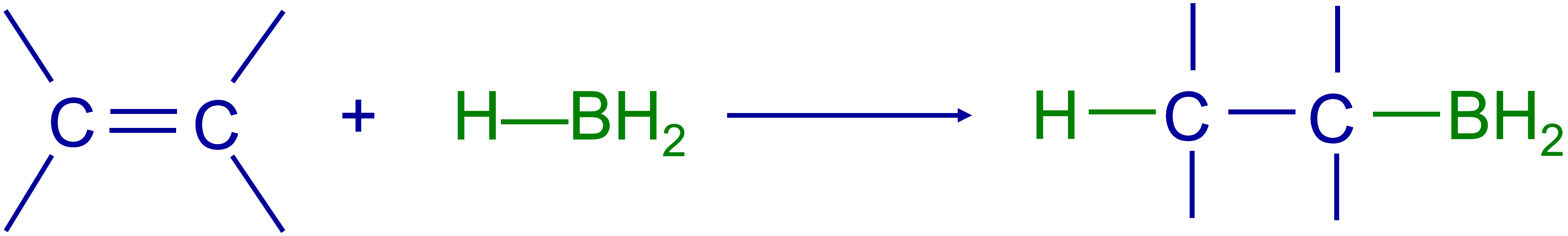


Diborane ($B_2H_6$) normally used in an ether- like solvent called "diglyme"

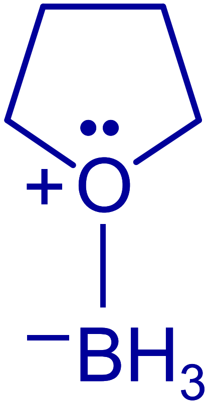


2-Methoxyethyl ether or diglyme

# Hydroboration Step

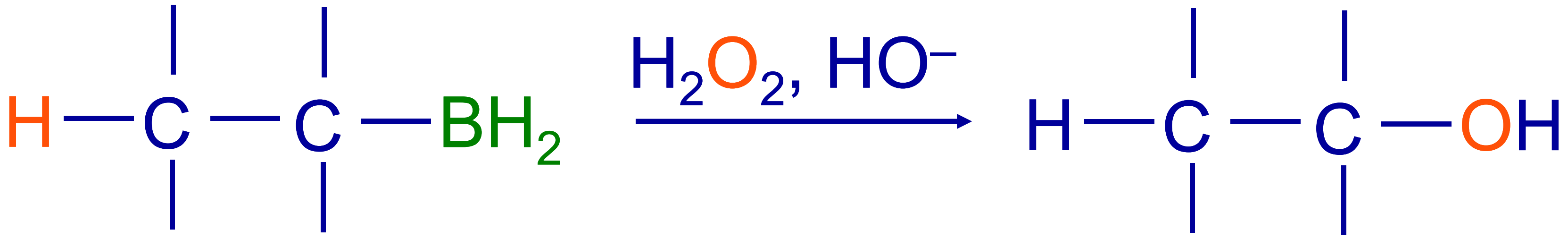


Hydroboration reagents:



Borane-tetrahydrofuran complex ($H_3B$-THF)

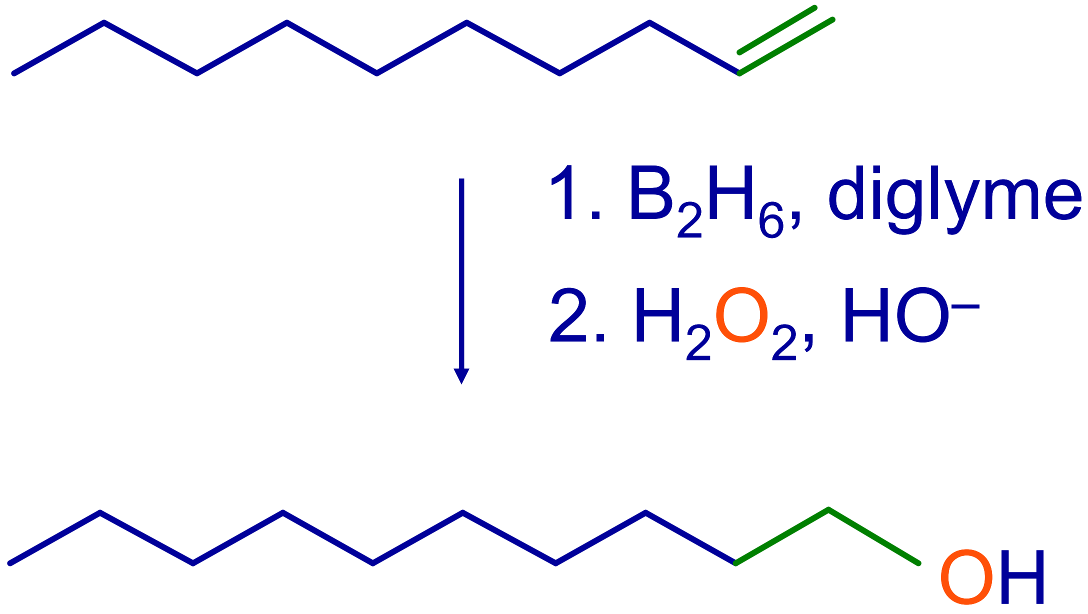
# Oxidation Step



$$\mathrm{H}-\underset{|}{\overset{|}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{BH_2} \xrightarrow{\mathrm{H_2O_2,\ HO^-}} \mathrm{H}-\underset{|}{\overset{|}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{C}}}-\mathrm{OH}$$

- Organoborane formed in the hydroboration step is oxidized with hydrogen peroxide.

# Example

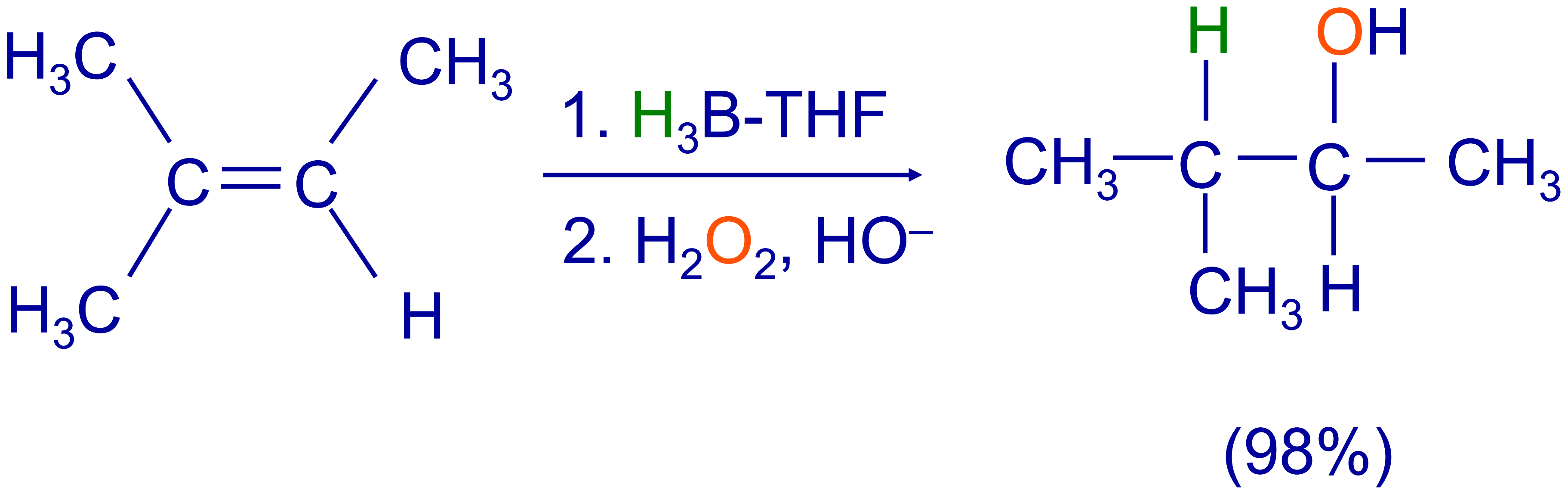


1. $B_2H_6$, diglyme

2. $H_2O_2$, $HO^-$

(93%)

# Example

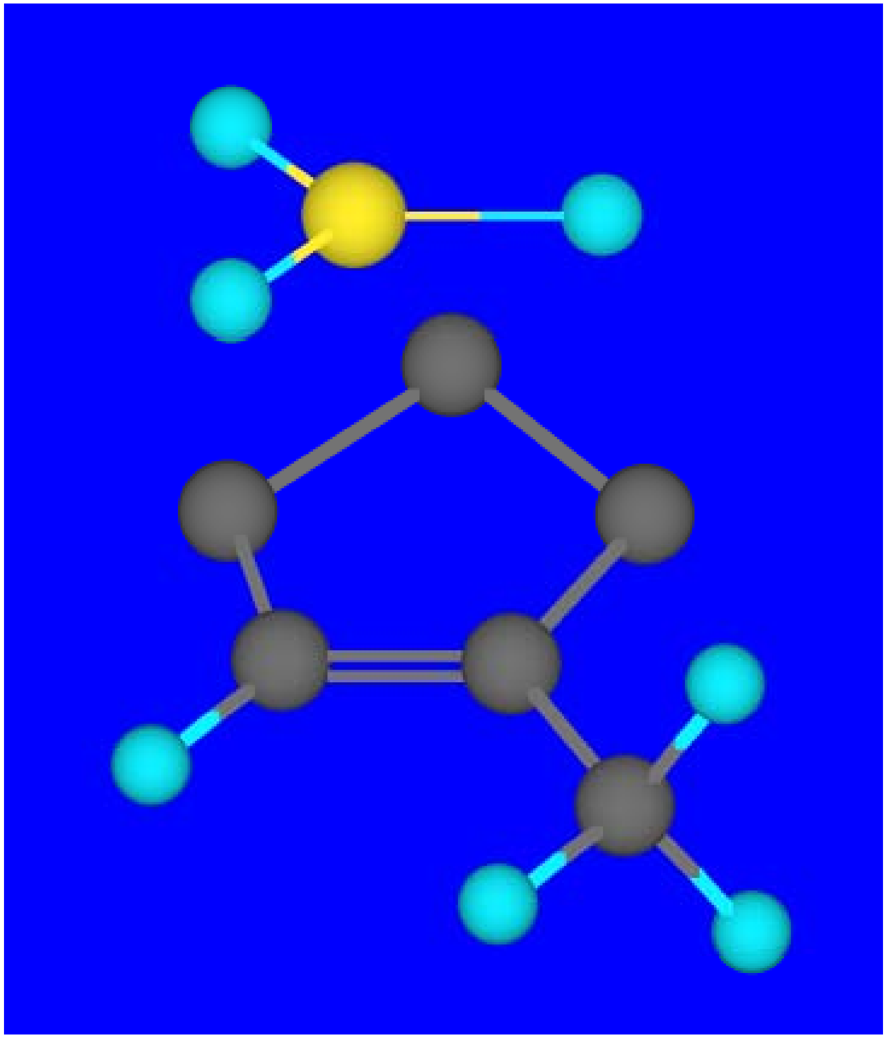


# Features of Hydroboration-Oxidation

- Hydration of alkenes.
- Regioselectivity opposite to Markovnikov's rule.
- No rearrangement.
- Stereospecific *syn* addition.

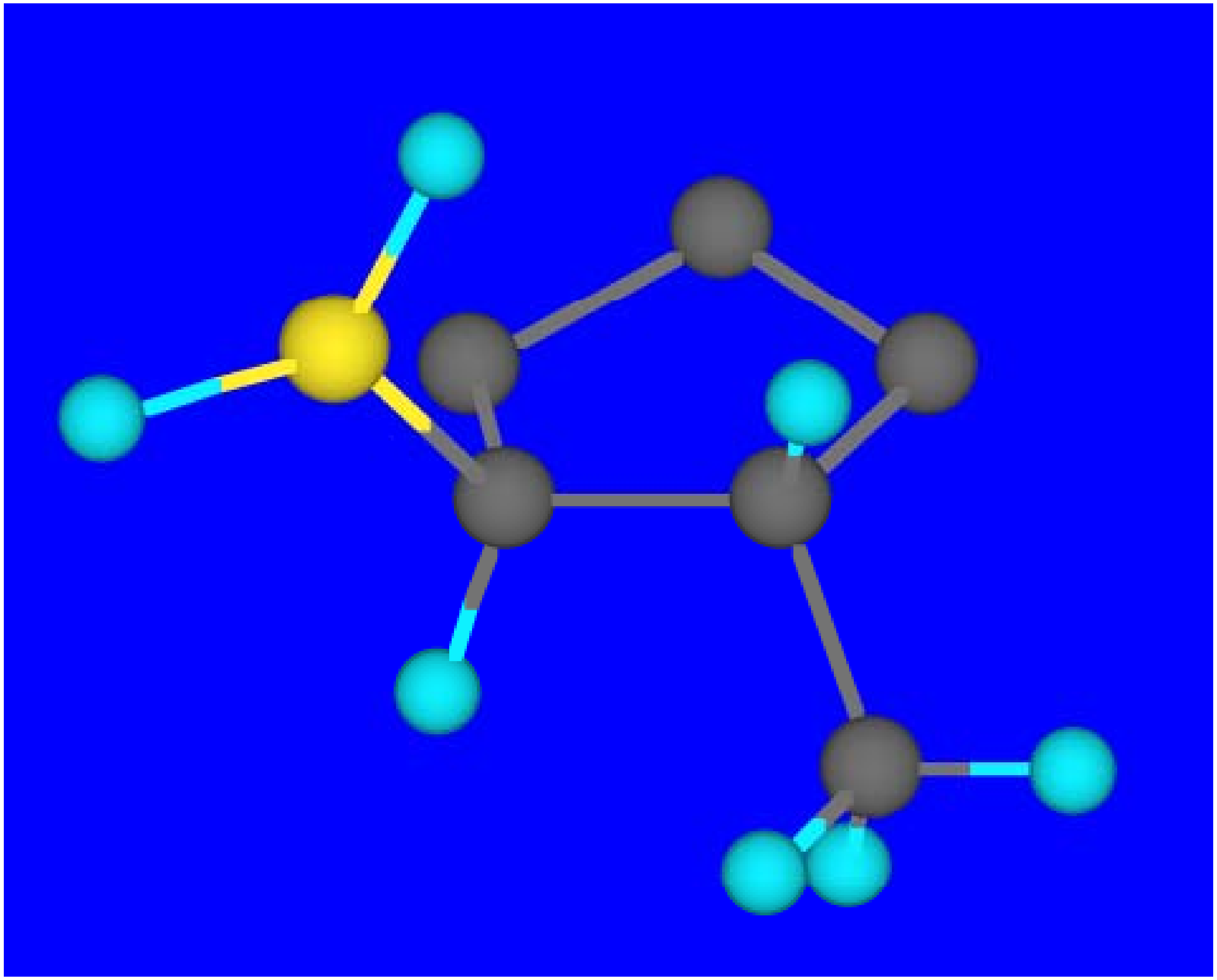
# 6.14. Stereochemistry of Hydroboration-Oxidation

1-Methylcyclopentene
+ $BH_3$



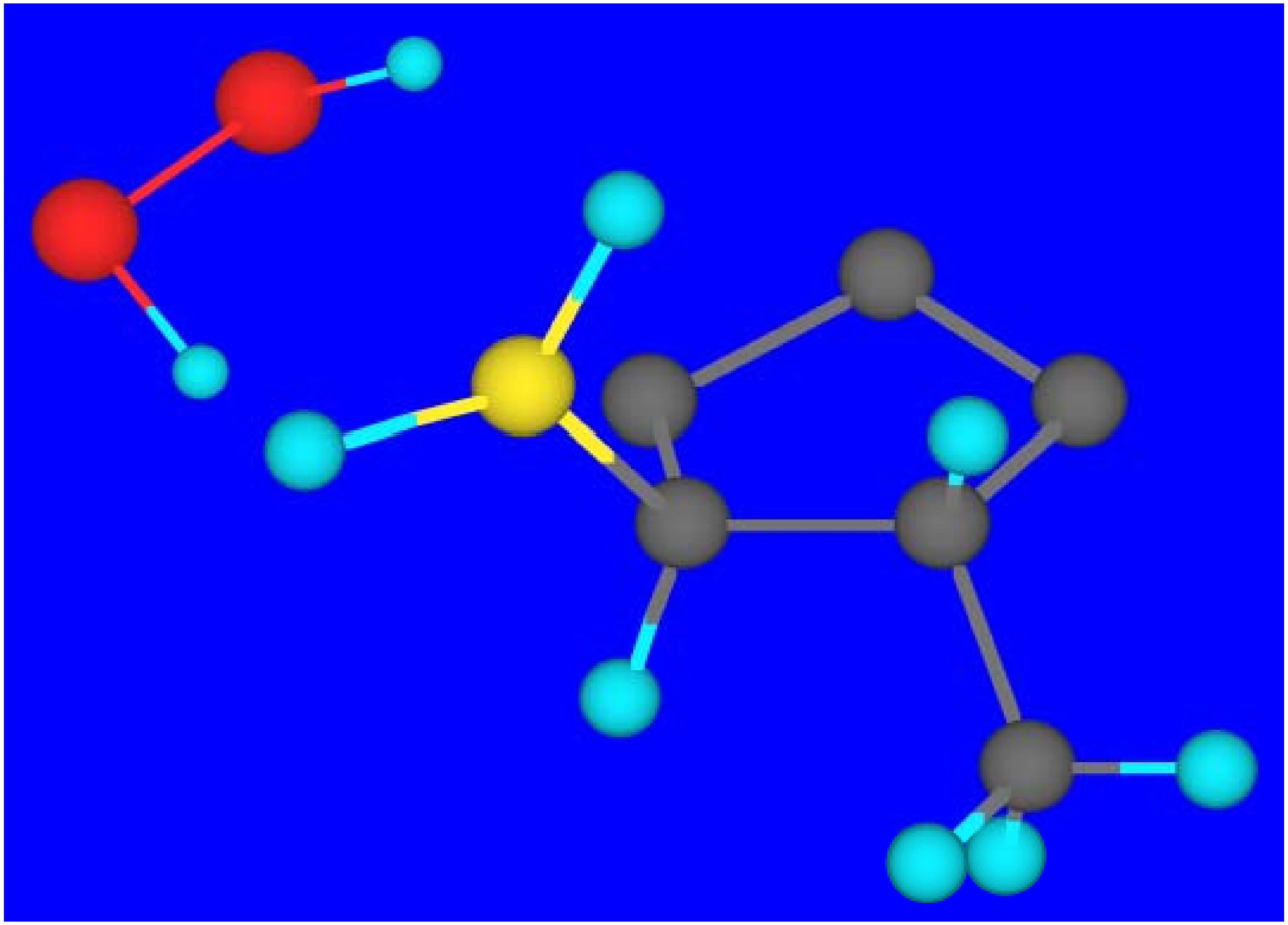
- *syn* addition of H and B to double bond.
- B adds to less substituted carbon.

# Organoborane Intermediate

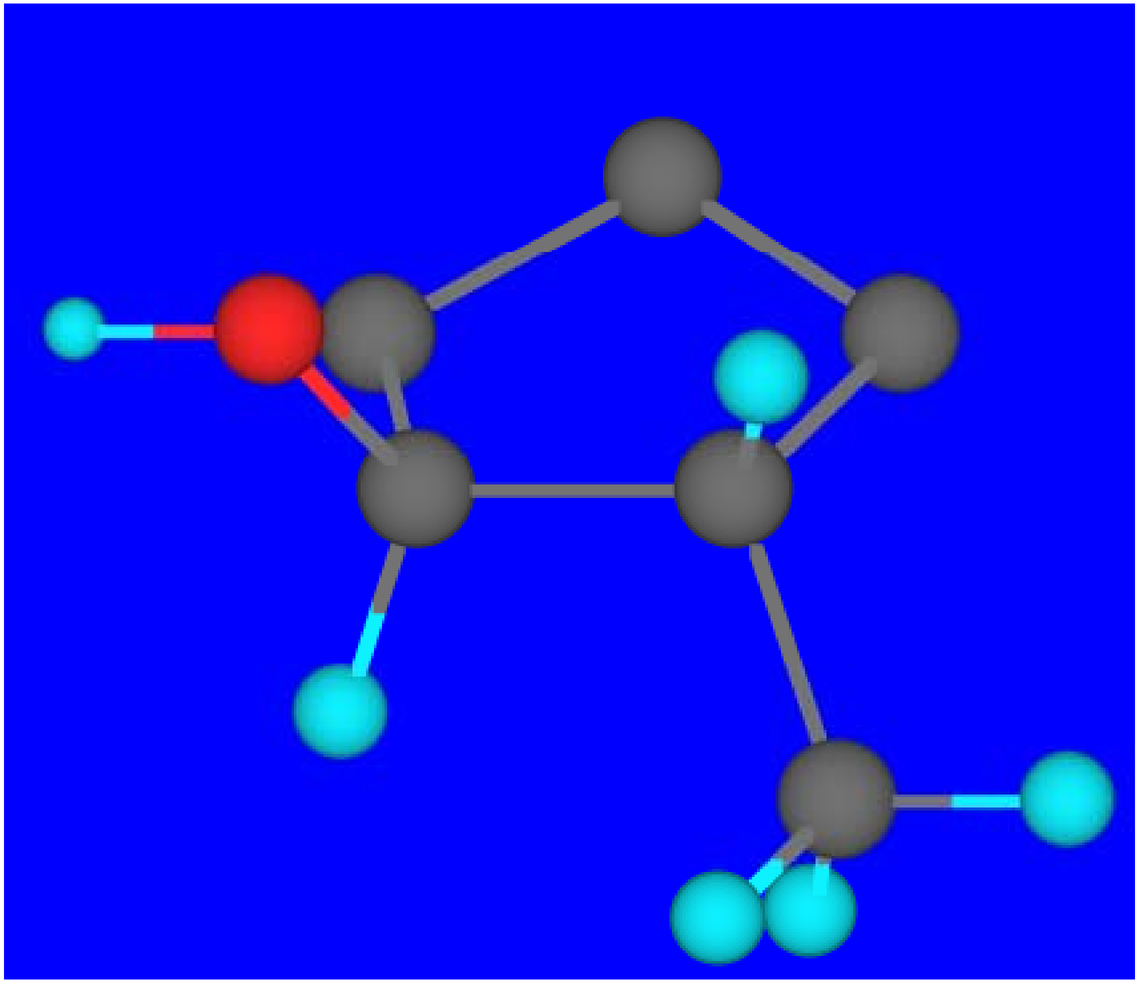


# Addition of hydrogen peroxide

OH replaces B
on same side.

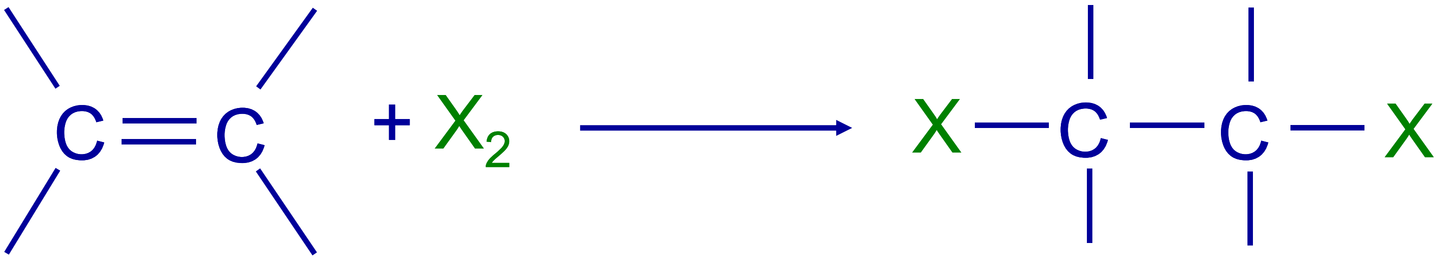


# *trans*-2-Methylcyclopentanol



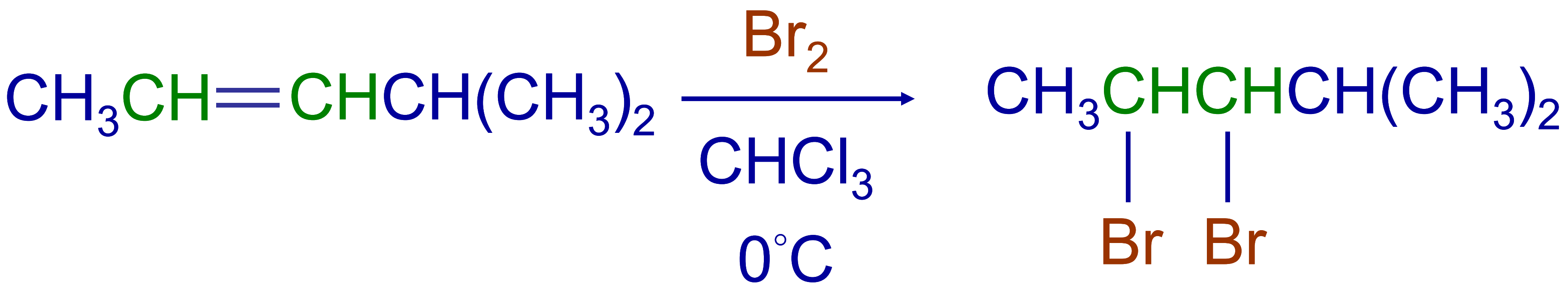
# 6.14. Addition of Halogens to Alkenes

*General features*



- Electrophilic addition to double bond.
- Forms a vicinal dihalide.

# Example



$$\mathrm{CH_3CH{=}CHCH(CH_3)_2} \xrightarrow[\substack{\mathrm{CHCl_3}\\ 0^\circ\mathrm{C}}]{\mathrm{Br_2}} \mathrm{CH_3}\underset{\mathrm{Br}}{\mathrm{CH}}\underset{\mathrm{Br}}{\mathrm{CH}}\mathrm{CH(CH_3)_2}$$

(100%)

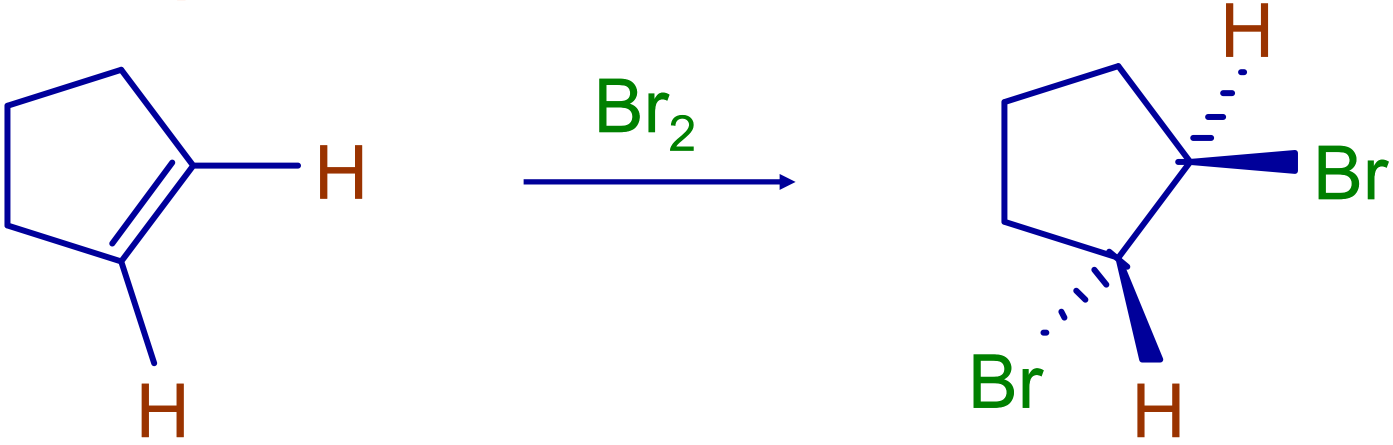
# Scope

- Limited to $Cl_2$ and $Br_2$.
- $F_2$ addition proceeds with explosive violence.
- $I_2$ addition is endothermic: vicinal diiodides dissociate to an alkene and $I_2$.

# 6.15. Stereochemistry of Halogen Addition

*anti addition*

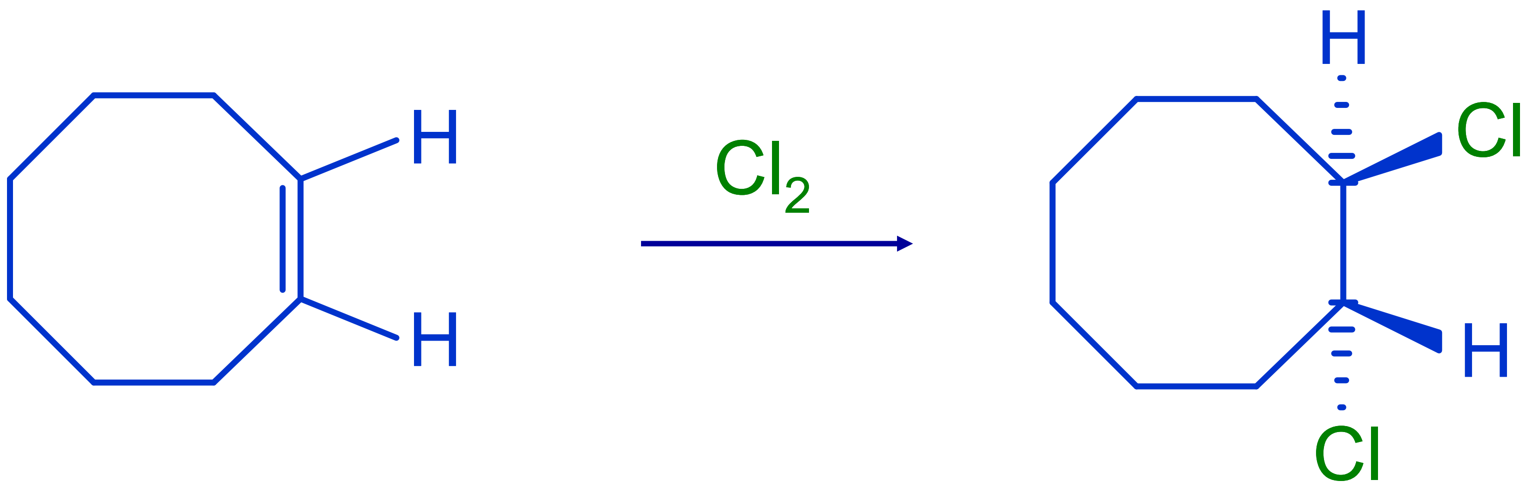
## Example



*trans*-1,2-Dibromocyclopentane

80% yield;  only product

# Example



*trans*-1,2-Dichlorocyclooctane
73% yield;  only product

# 6.16. Mechanism of Halogen Addition to Alkenes: Halonium Ions

*Mechanism is electrophilic addition*

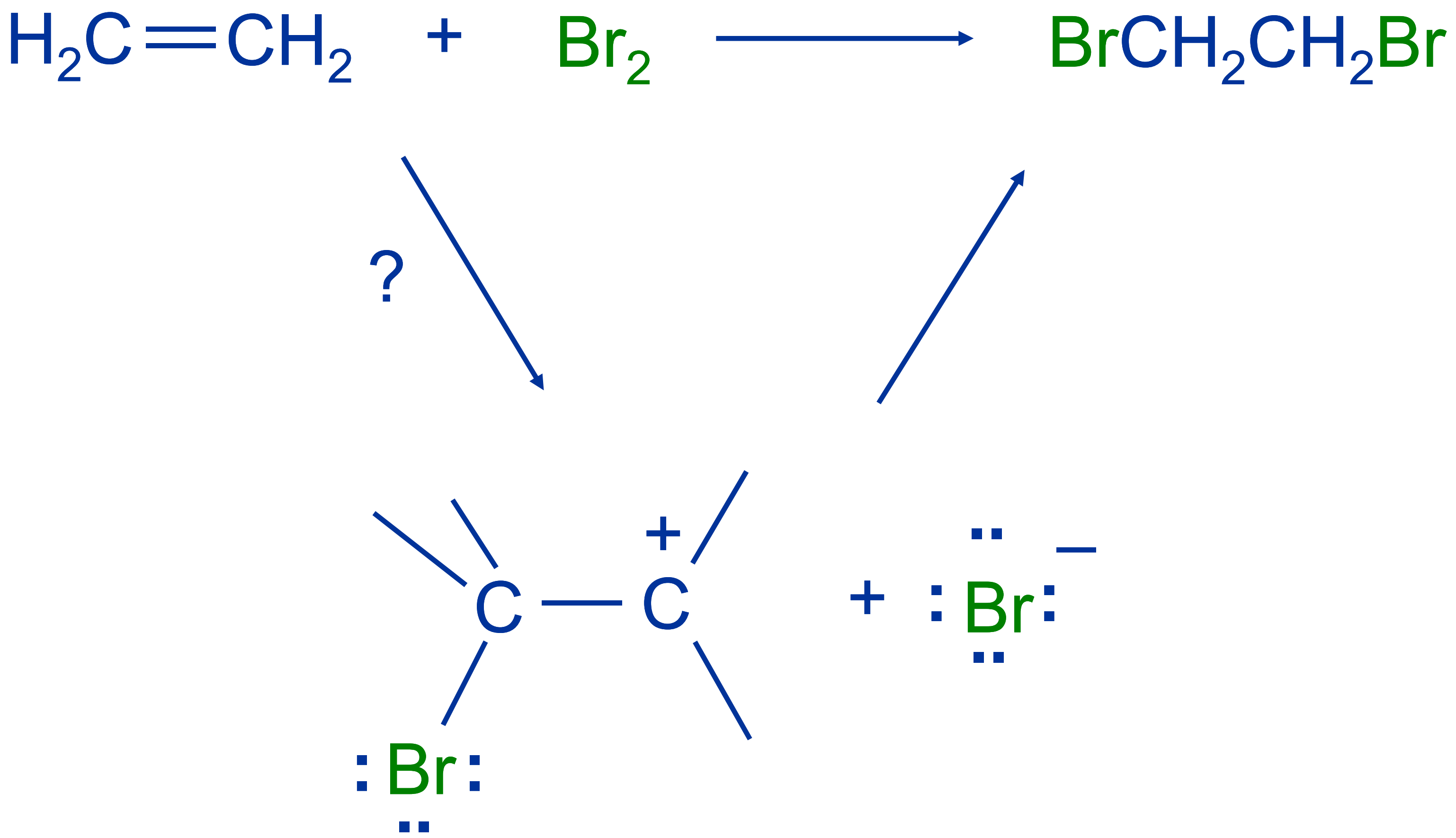
- $Br_2$ is not polar, but it is polarizable.
- Two steps:
  1. (1) Formation of bromonium ion.
  2. (2) Nucleophilic attack on bromonium ion by bromide.

# Table 6.3. Relative Rates of Bromination

| | | |
|---|---|---|
| Ethylene | $H_2C=CH_2$ | 1 |
| Propene | $CH_3CH=CH_2$ | 61 |
| 2-Methylpropene | $(CH_3)_2C=CH_2$ | 5400 |
| 2,3-Dimethyl-2-butene | $(CH_3)_2C=C(CH_3)_2$ | 920,000 |

- *More highly substituted double bonds react faster. Alkyl groups on the double bond make it more "electron rich."*

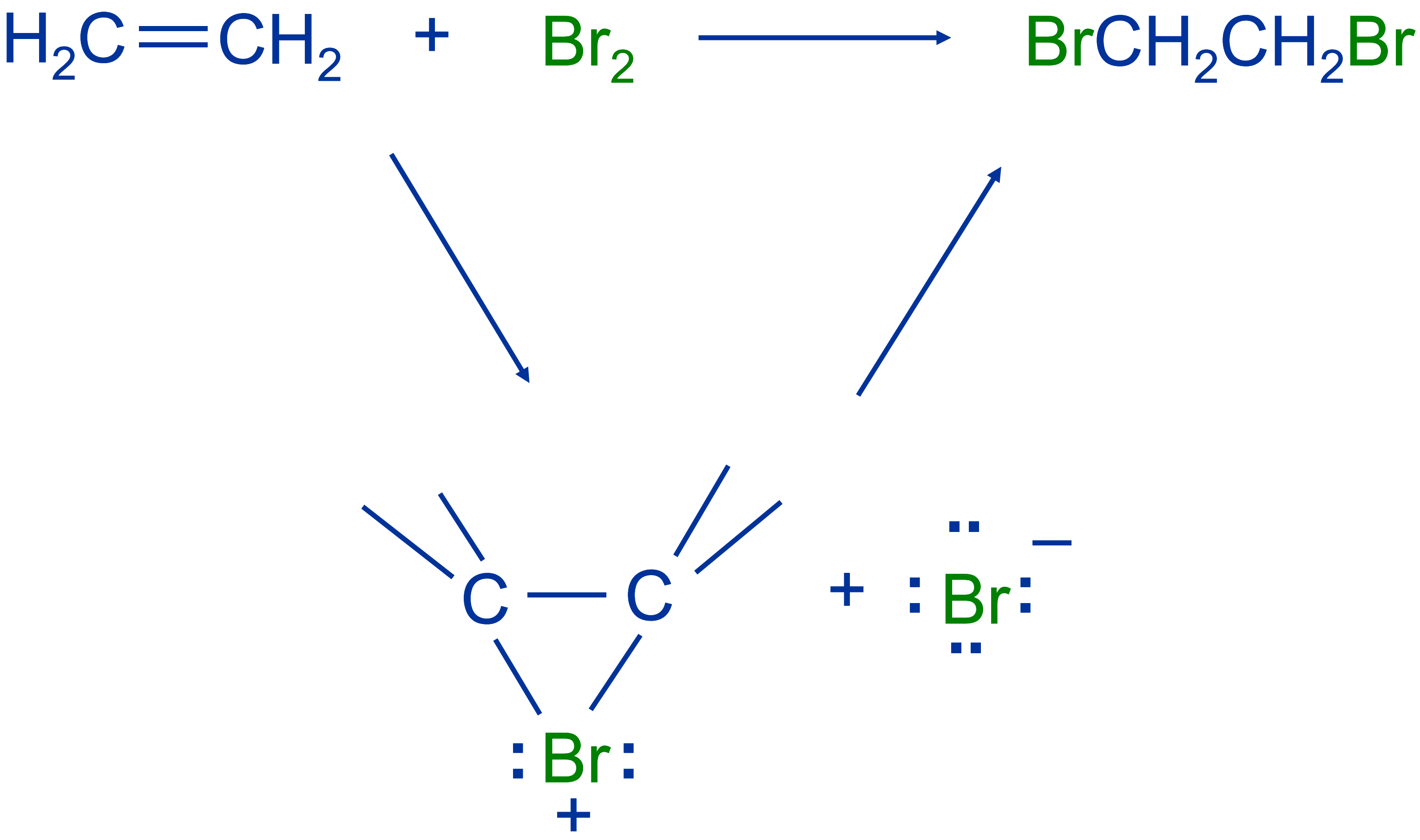
# Mechanism?



$H_2C{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$

- No obvious explanation for *anti* addition provided by this mechanism.

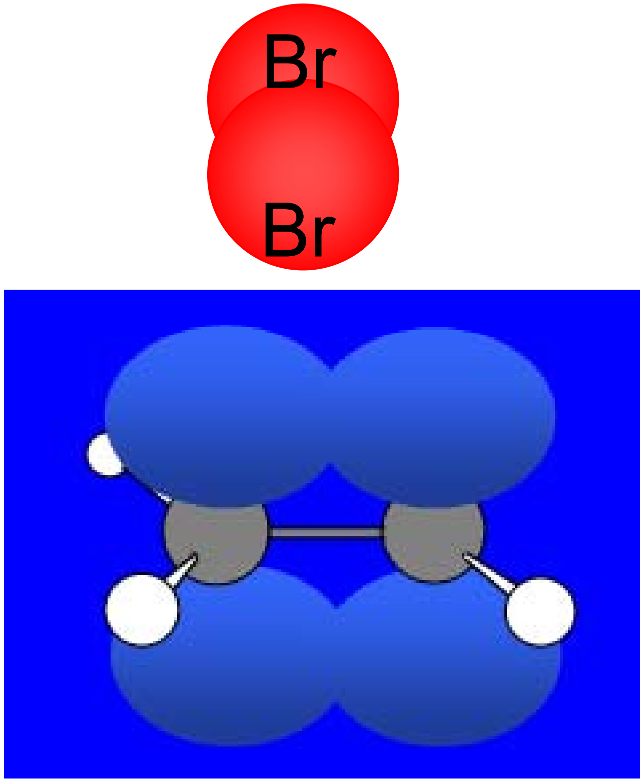
# Mechanism

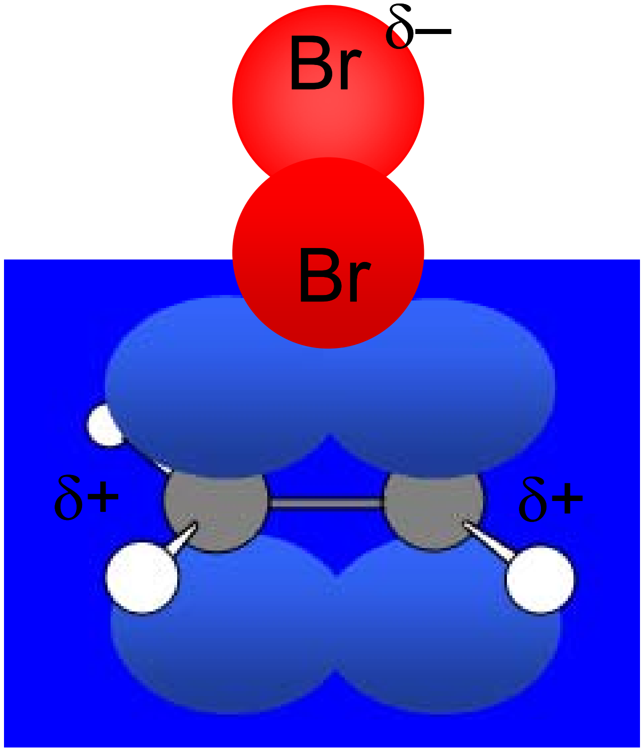


$$H_2C{=}CH_2 \; + \; Br_2 \longrightarrow BrCH_2CH_2Br$$

Cyclic bromonium ion

# Formation of Bromonium Ion



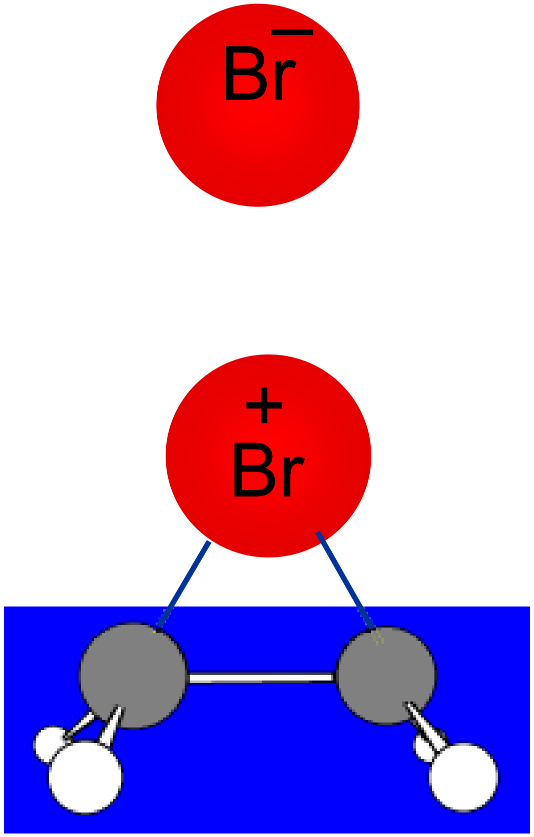


- Mutual polarization of electron distributions of $Br_2$ and alkene

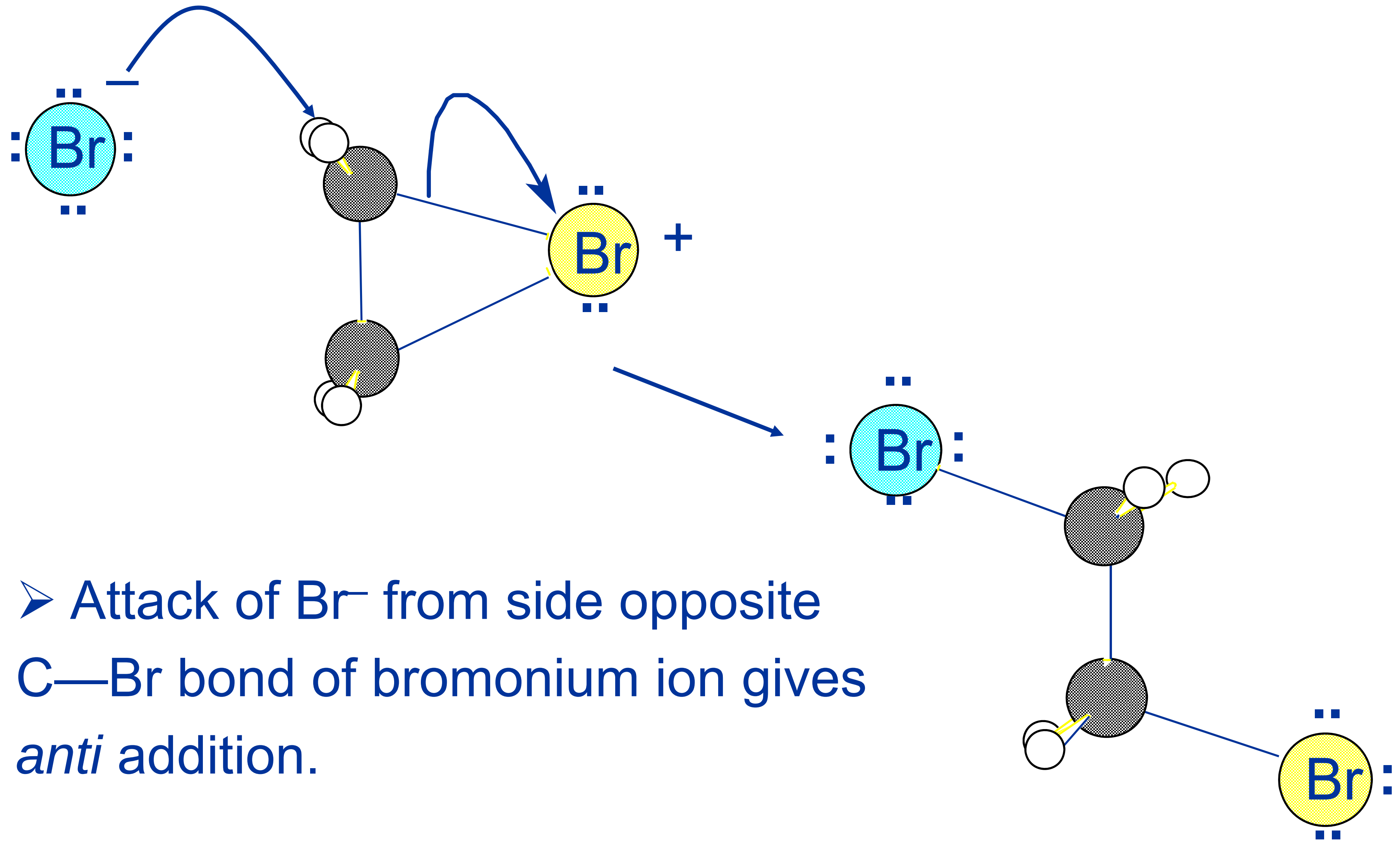
- Electrons flow from alkene toward $Br_2$

# Formation of Bromonium Ion

- π electrons of alkene displace $Br^-$ from Br.

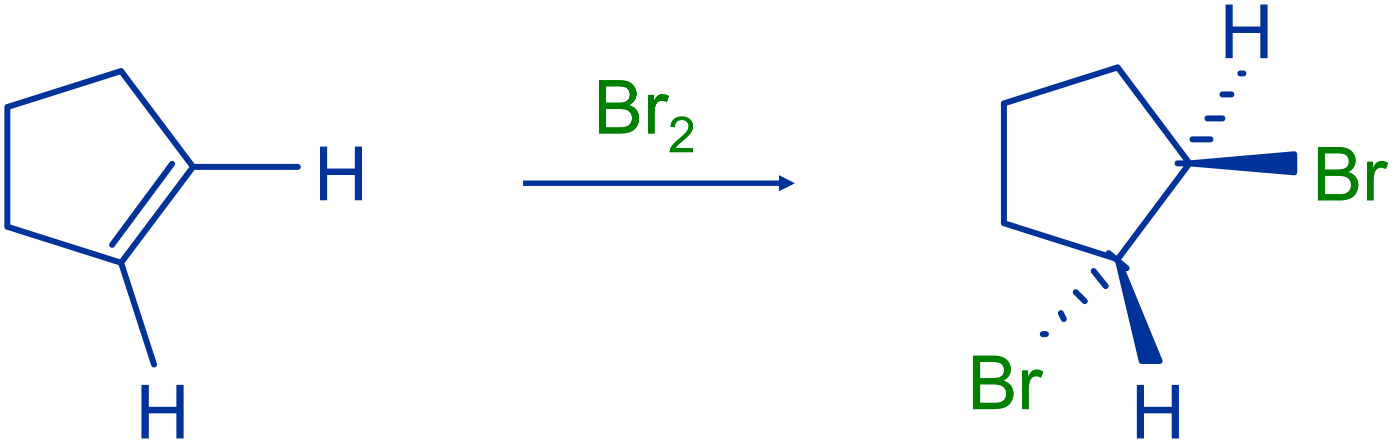


# Stereochemistry



- Attack of Br⁻ from side opposite C—Br bond of bromonium ion gives *anti* addition.

# Example

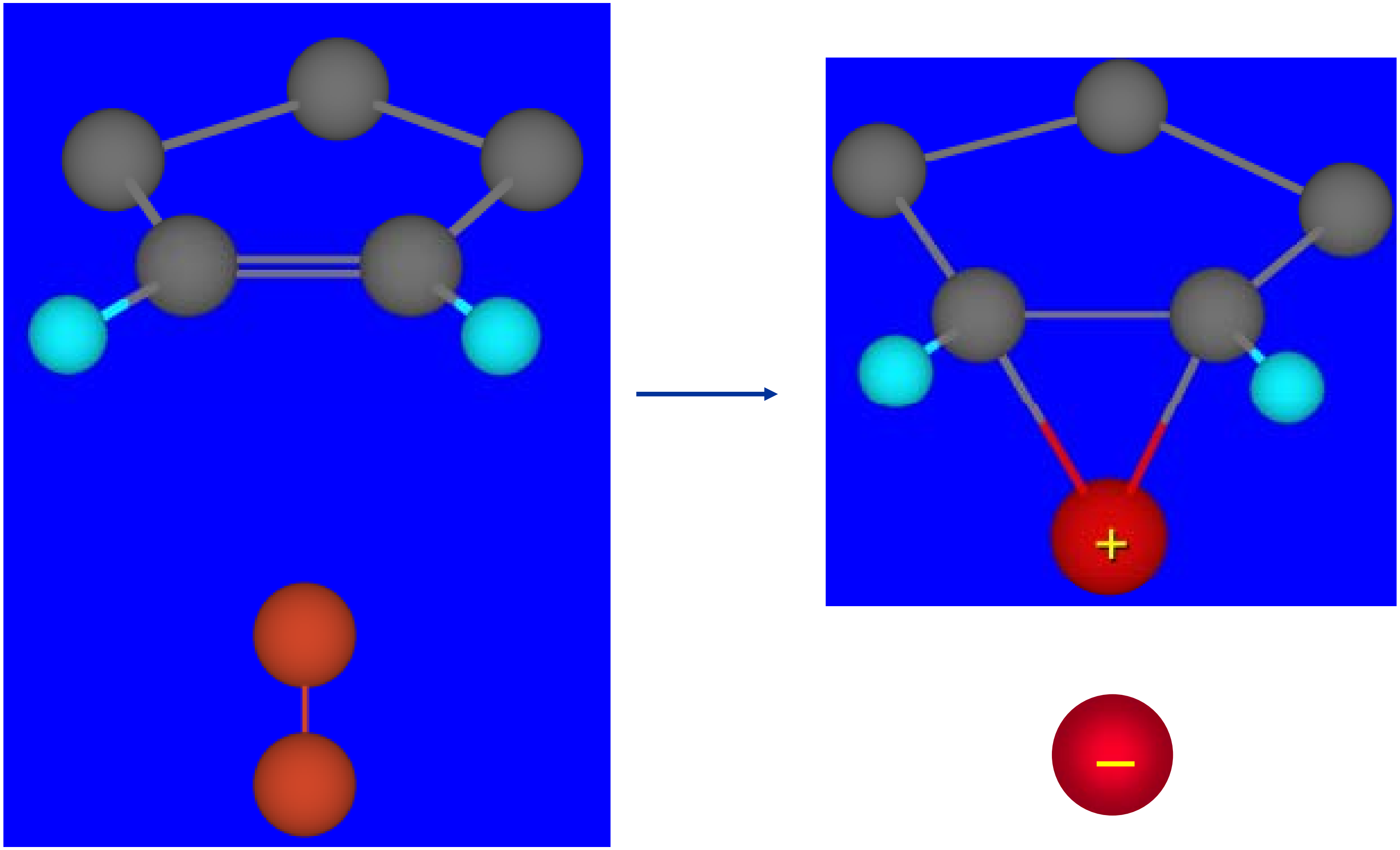


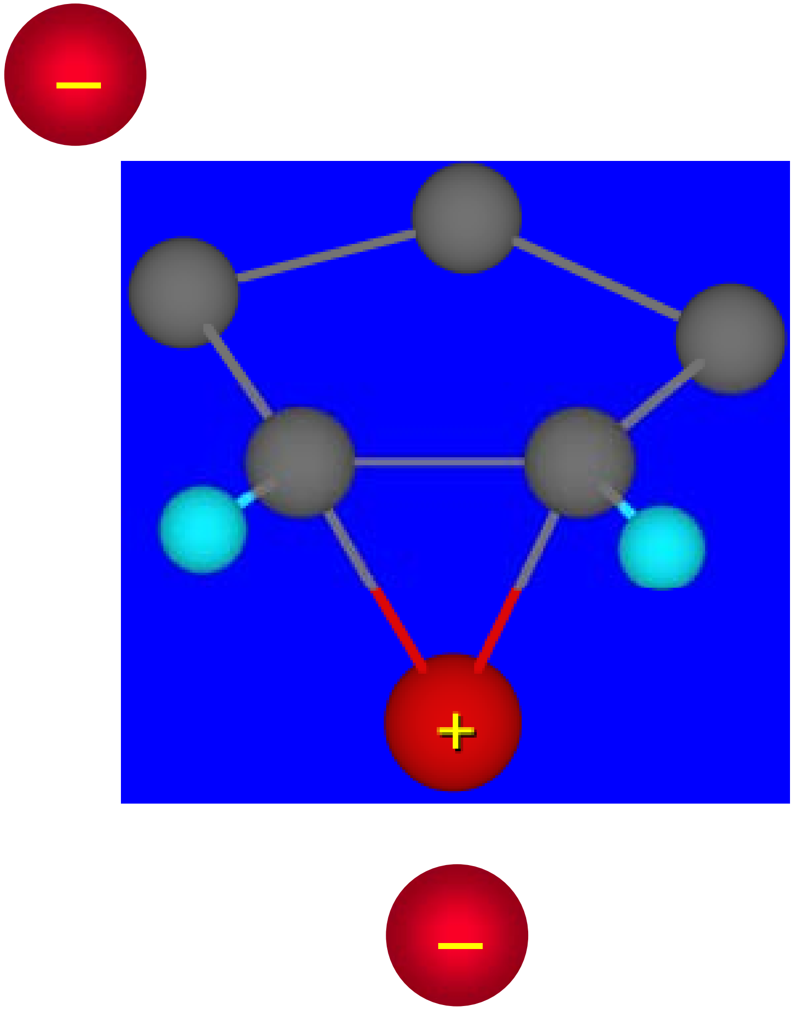
*trans*-1,2-Dibromocyclopentane

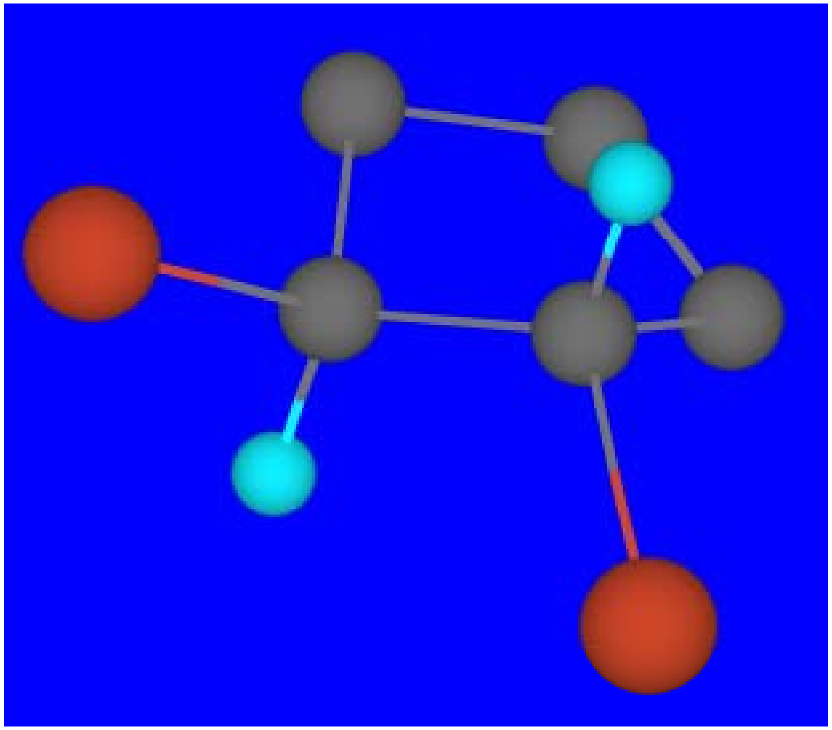
80% yield;  only product.

*Cyclopentene +$Br_2$*

*Bromonium ion*



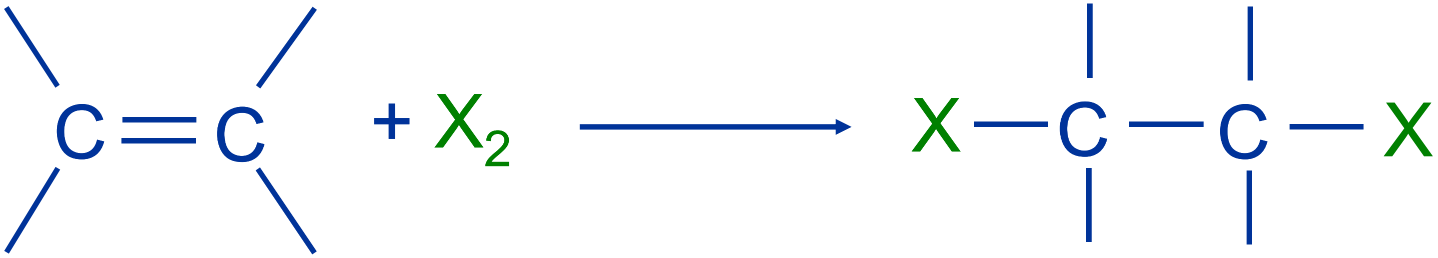




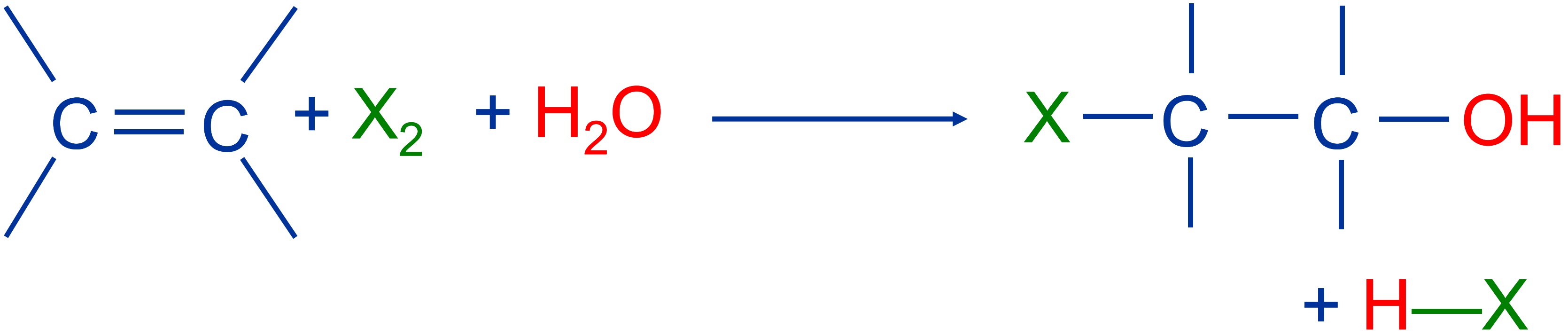
- Bromide ion attacks the bromonium ion from side opposite carbon-bromine bond.

- *trans*-Stereochemistry in vicinal dibromide

# 6.17. Conversion of Alkenes to Vicinal Halohydrins



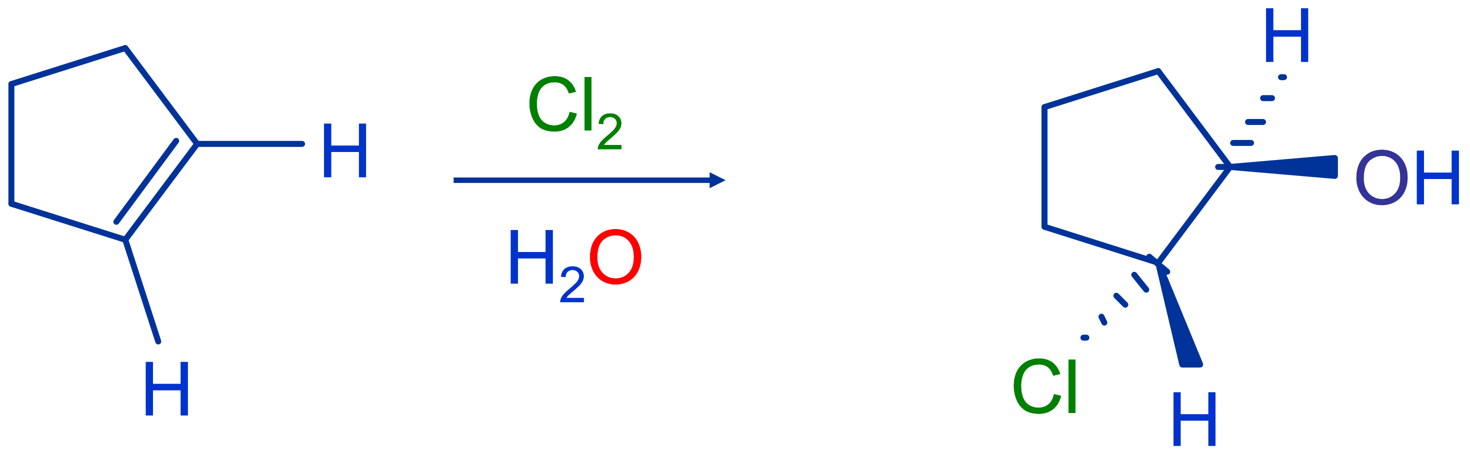
- Alkenes react with $X_2$ to form vicinal dihalides.
- Alkenes react with $X_2$ in water to give vicinal halohydrins.



# Examples

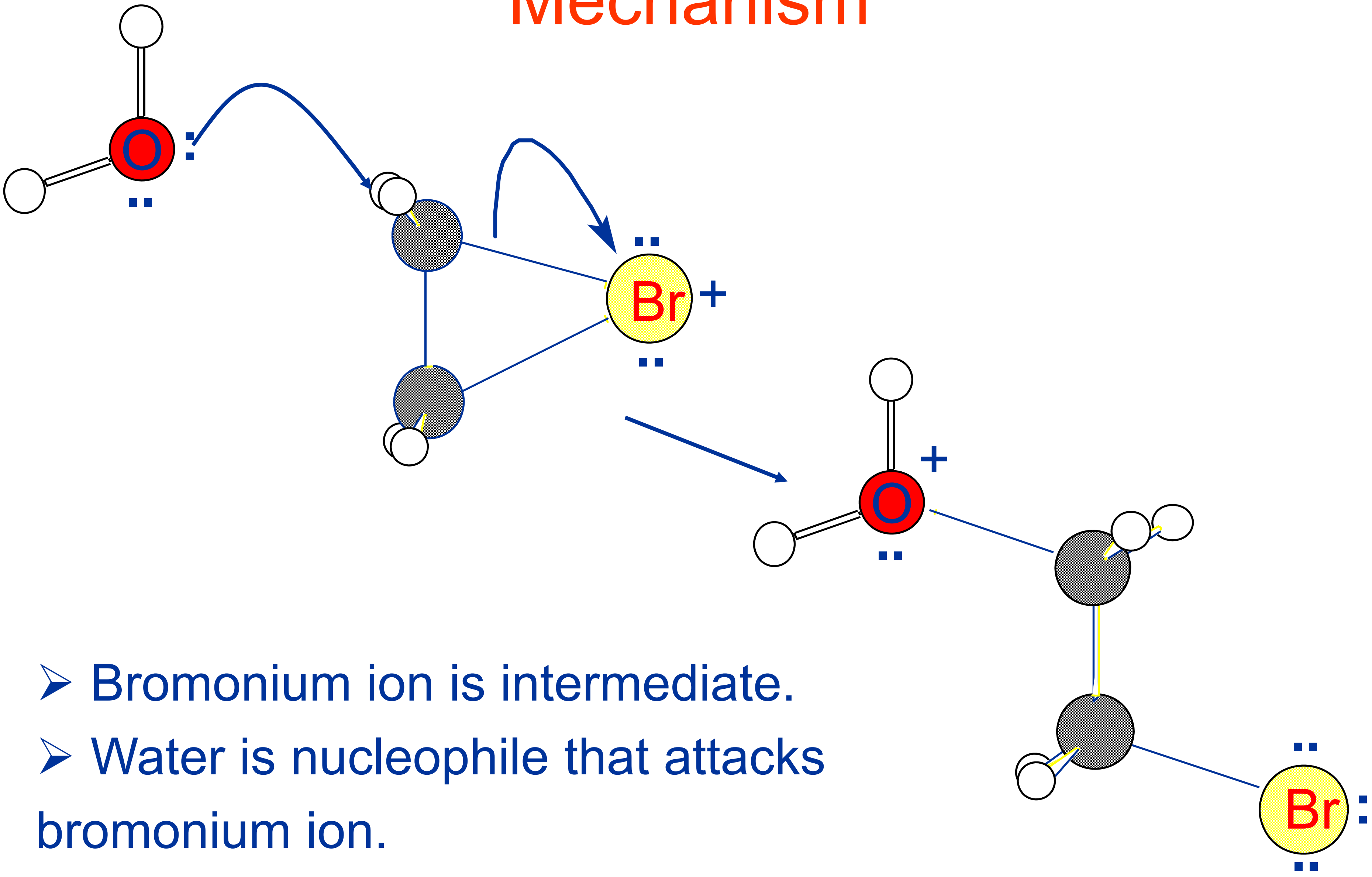
$$H_2C{=}CH_2 \;+\; Br_2 \xrightarrow{H_2O} BrCH_2CH_2OH$$

(70%)

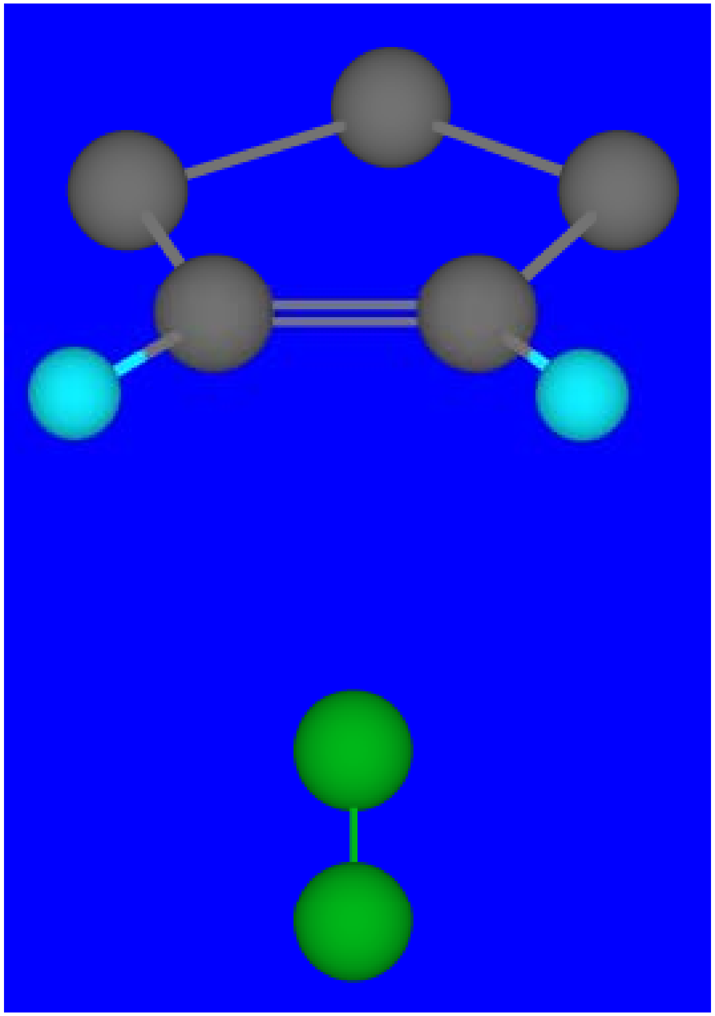


*anti* addition:  only product

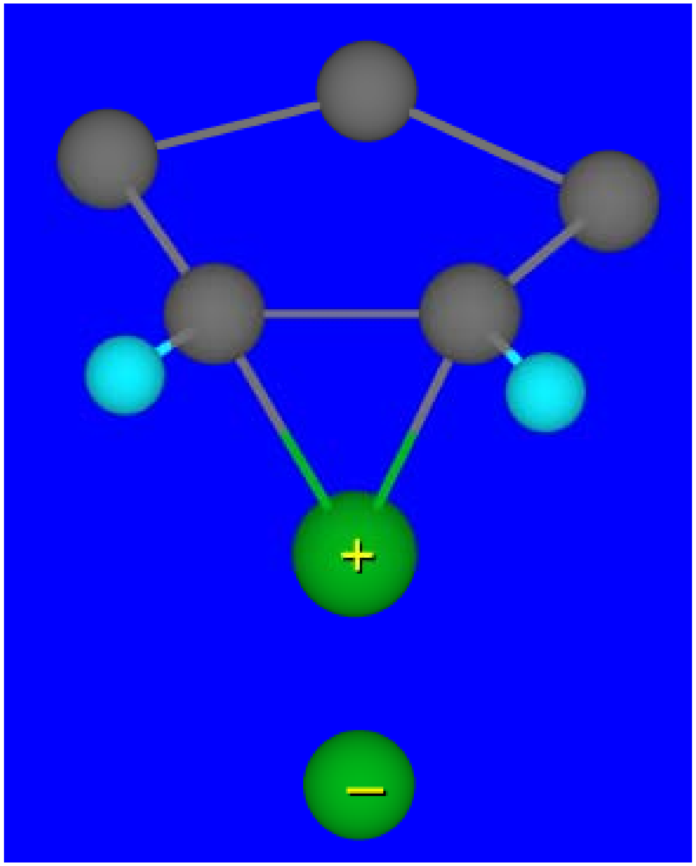
# Mechanism



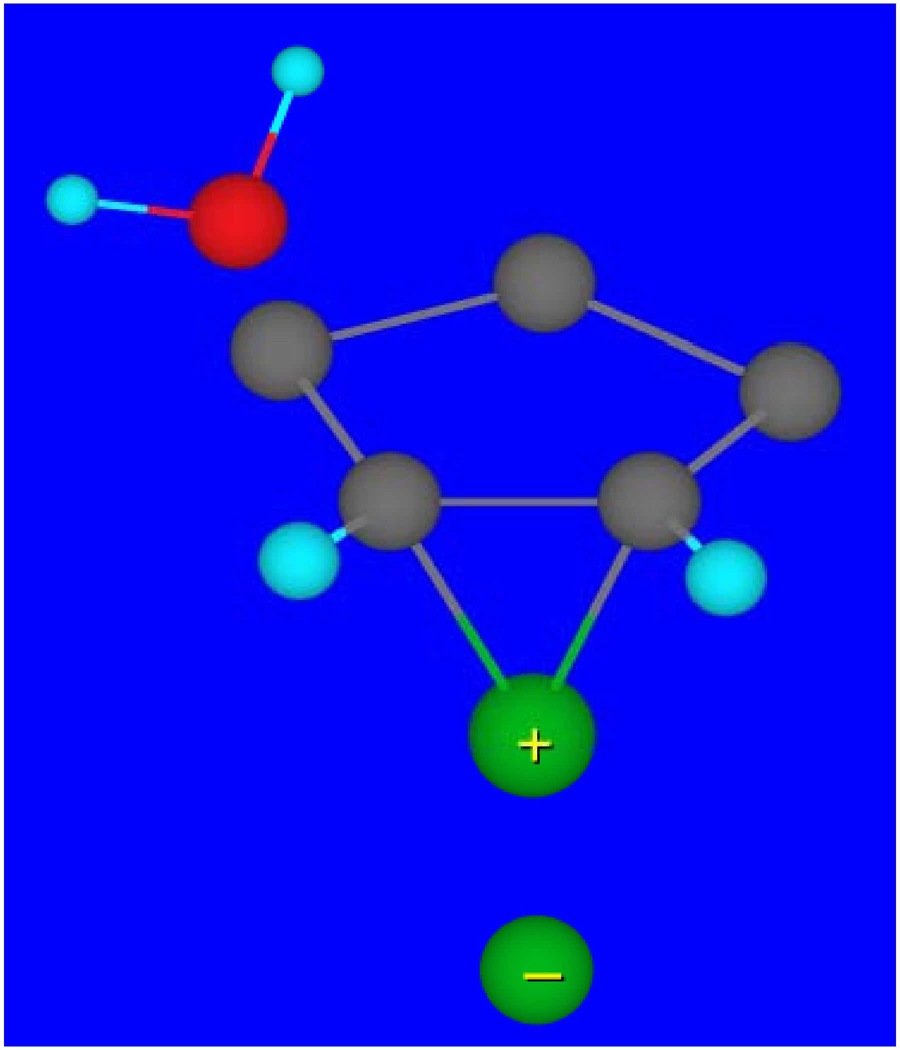
- Bromonium ion is intermediate.
- Water is nucleophile that attacks bromonium ion.

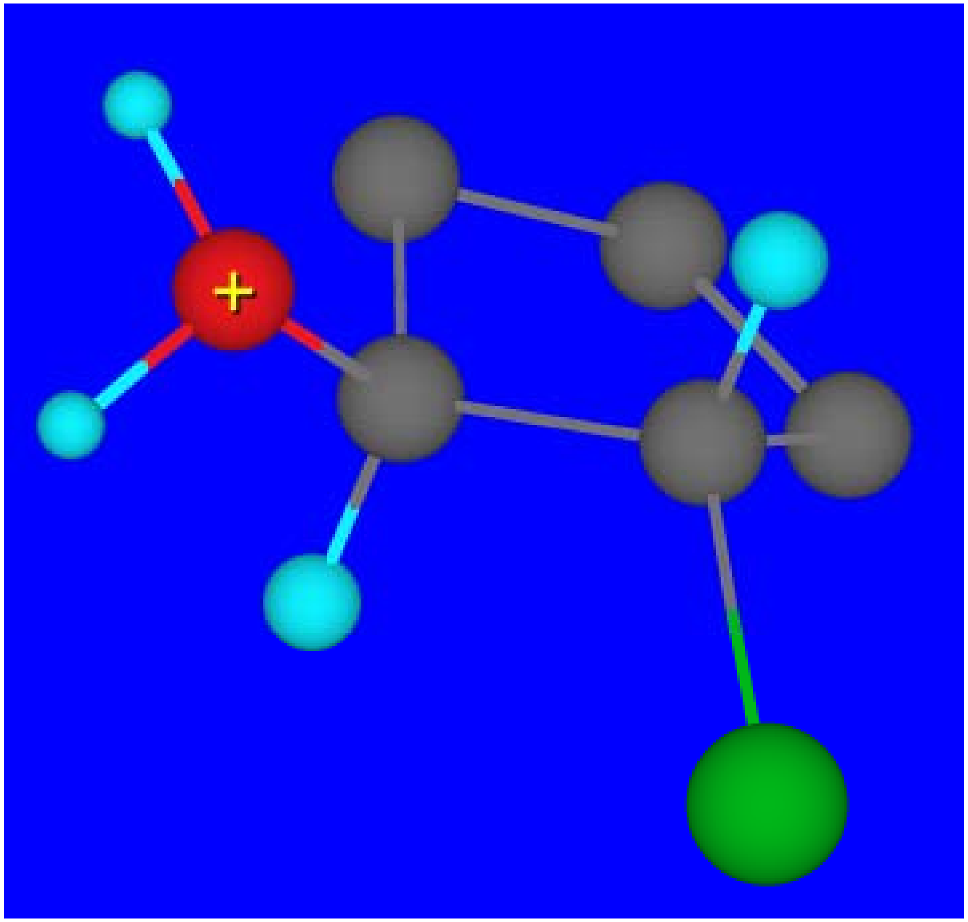


Cyclopentene + $Cl_2$



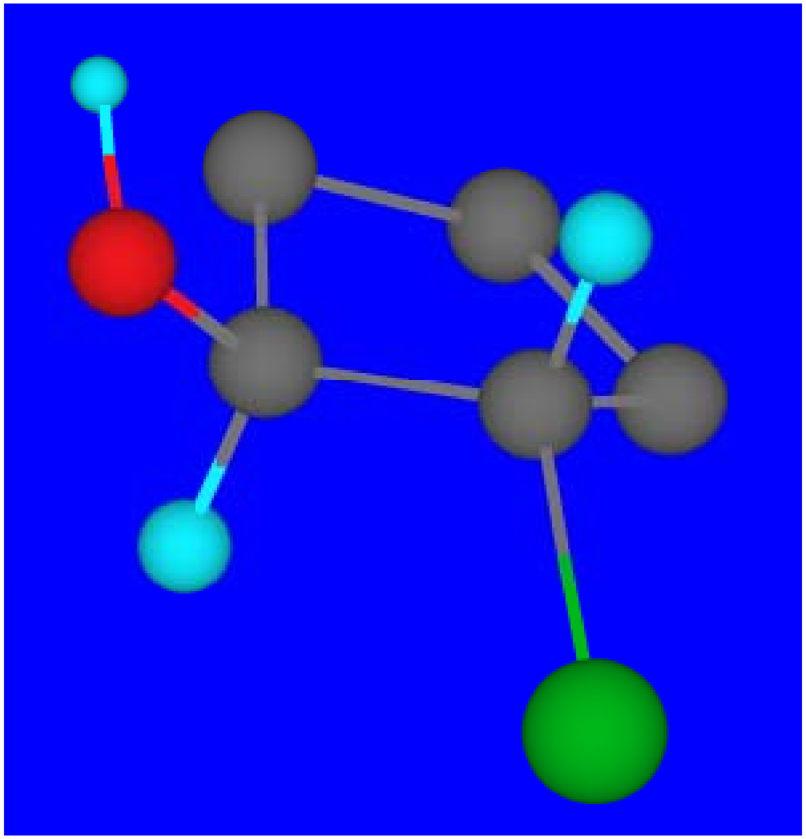
Chloronium ion





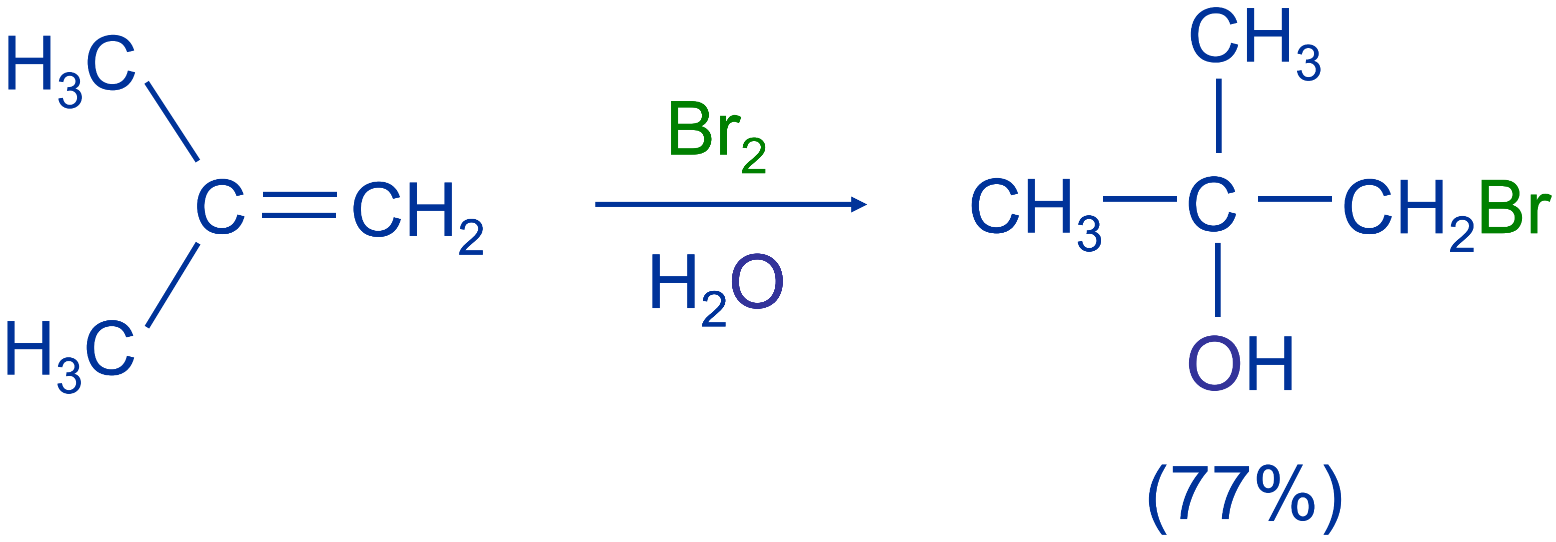
- Water attacks chloronium ion from side opposite carbon-chlorine bond.

- *trans*-Stereochemistry in oxonium ion.



*trans*-2-Chlorocyclopentanol

# Regioselectivity

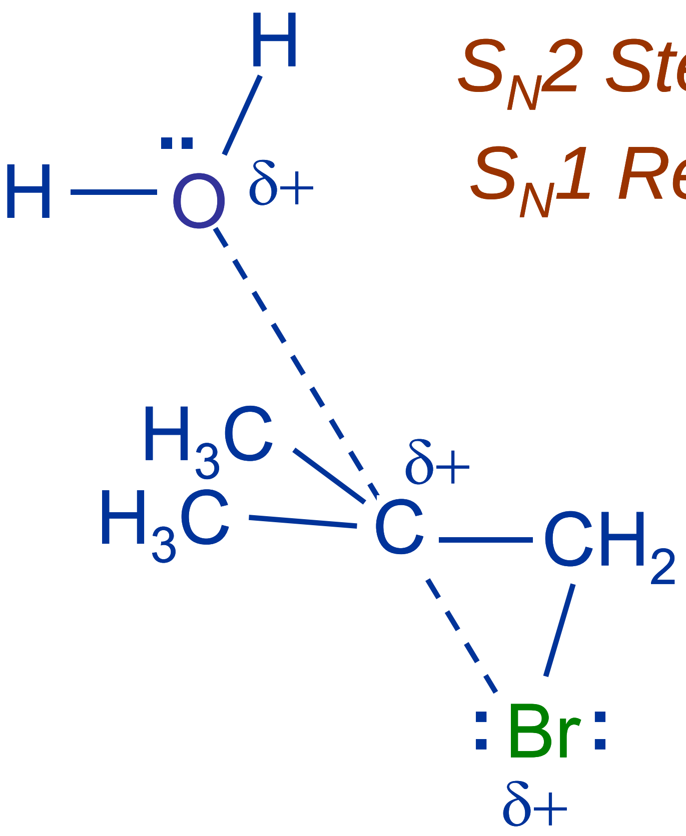


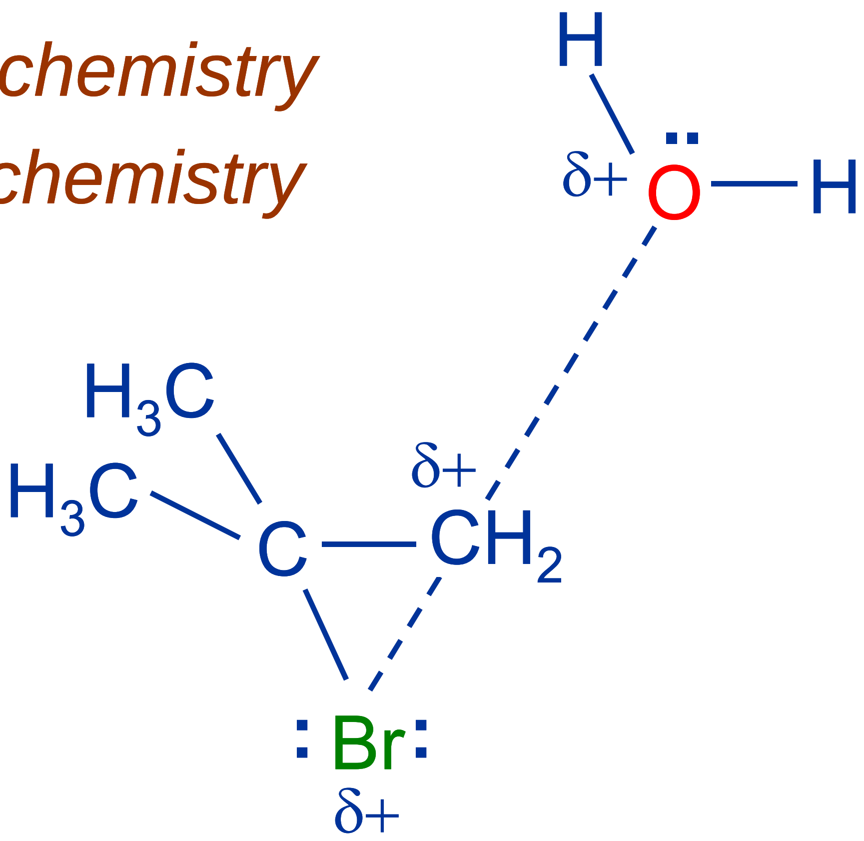
- ➢ Markovnikov's rule applied to halohydrin formation: the halogen adds to the carbon having the greater number of hydrogens.

# Explanation

*$S_N2$ Stereochemistry*

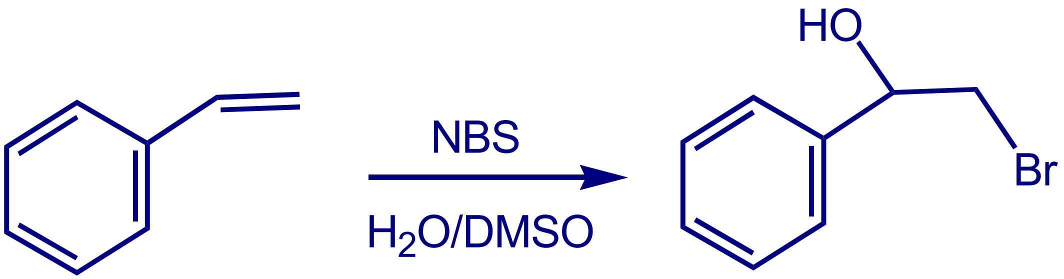
*$S_N1$ Regiochemistry*

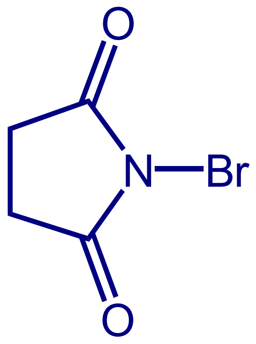




- ➢ Transition state for attack of water on bromonium ion has carbocation character; more stable transition state (left) has positive charge on more highly substituted carbon

# Few alkenes are soluble in water





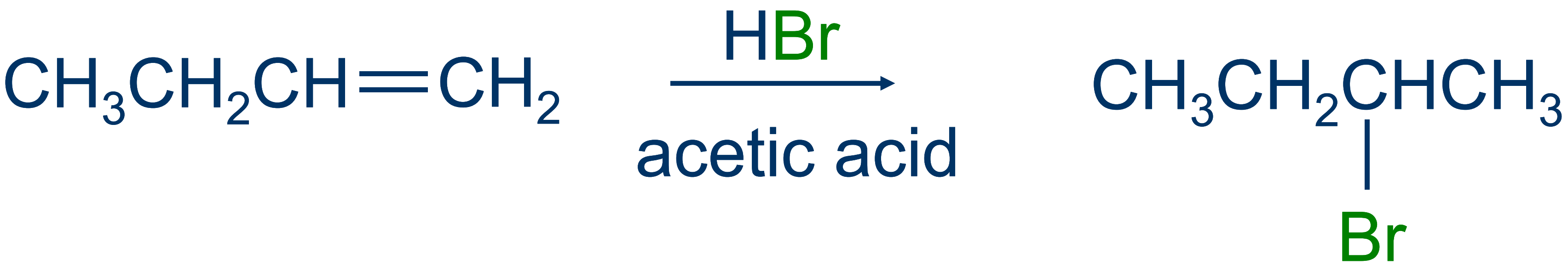
*N*-Bromosuccinimide (NBS)

- NBS is a source of $Br_2$ in low concentration: radical addition. Works for allylic susbstitution.

# 6.18. Free-radical Addition of HBr to Alkenes

The "peroxide effect"

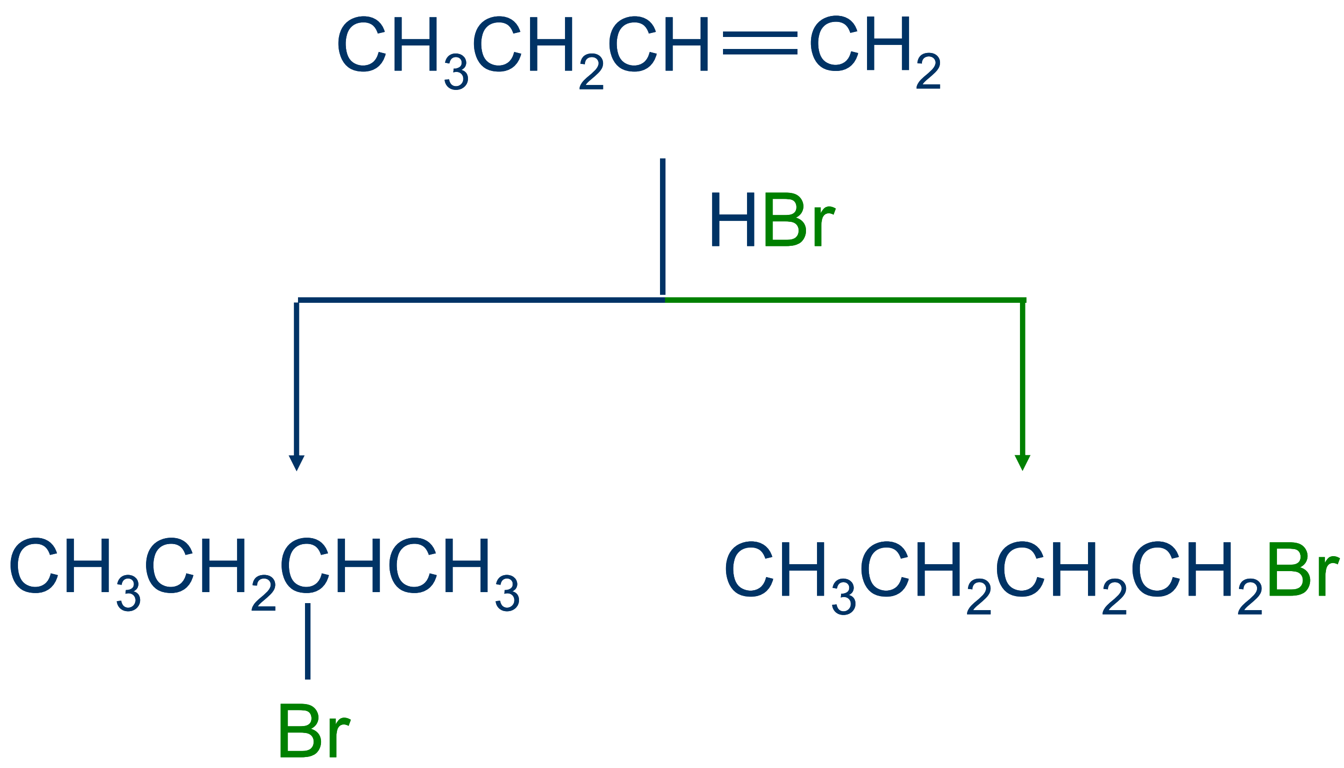
# Markovnikov's Rule



$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{acetic acid}]{HBr} CH_3CH_2\underset{\substack{|\\ Br}}{CH}CH_3$$

(90%)

# Addition of HBr to 1-Butene



$CH_3CH_2CH{=}CH_2$

HBr

$CH_3CH_2\underset{\displaystyle Br}{CH}CH_3$

only product in absence of peroxides

$CH_3CH_2CH_2CH_2Br$

only product when peroxides added to reaction mixture

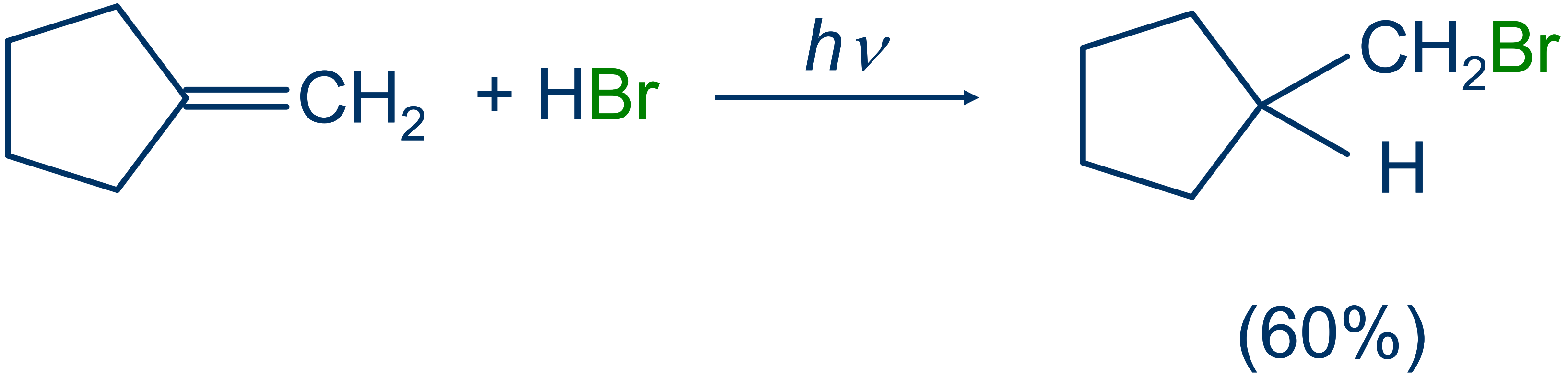
# Addition of HBr to 1-Butene

$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr} CH_3CH_2CH_2CH_2Br$$

*Addition opposite to Markovnikov's rule occurs with HBr (not HCl or HI)*

only product when peroxides added to reaction mixture

# Photochemical Addition of HBr

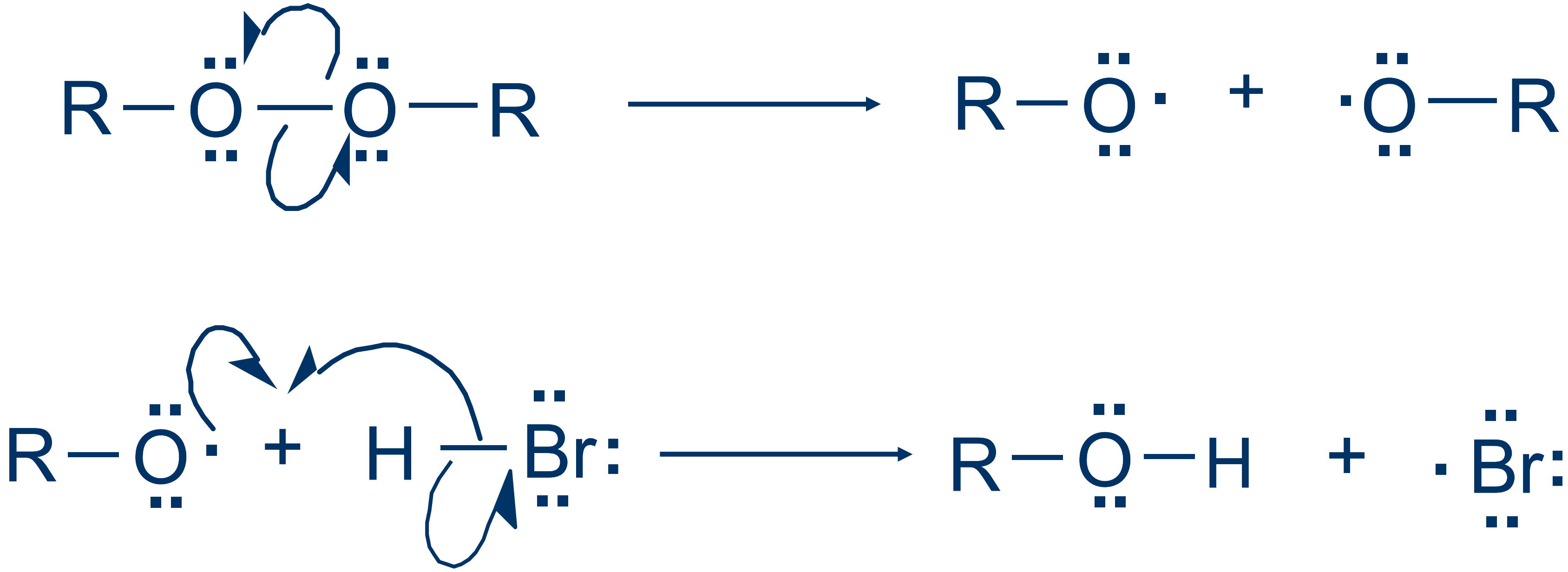


- Addition of HBr with a regiochemistry opposite to Markovnikov's rule can also occur when initiated with light with or without added peroxides.

# Mechanism

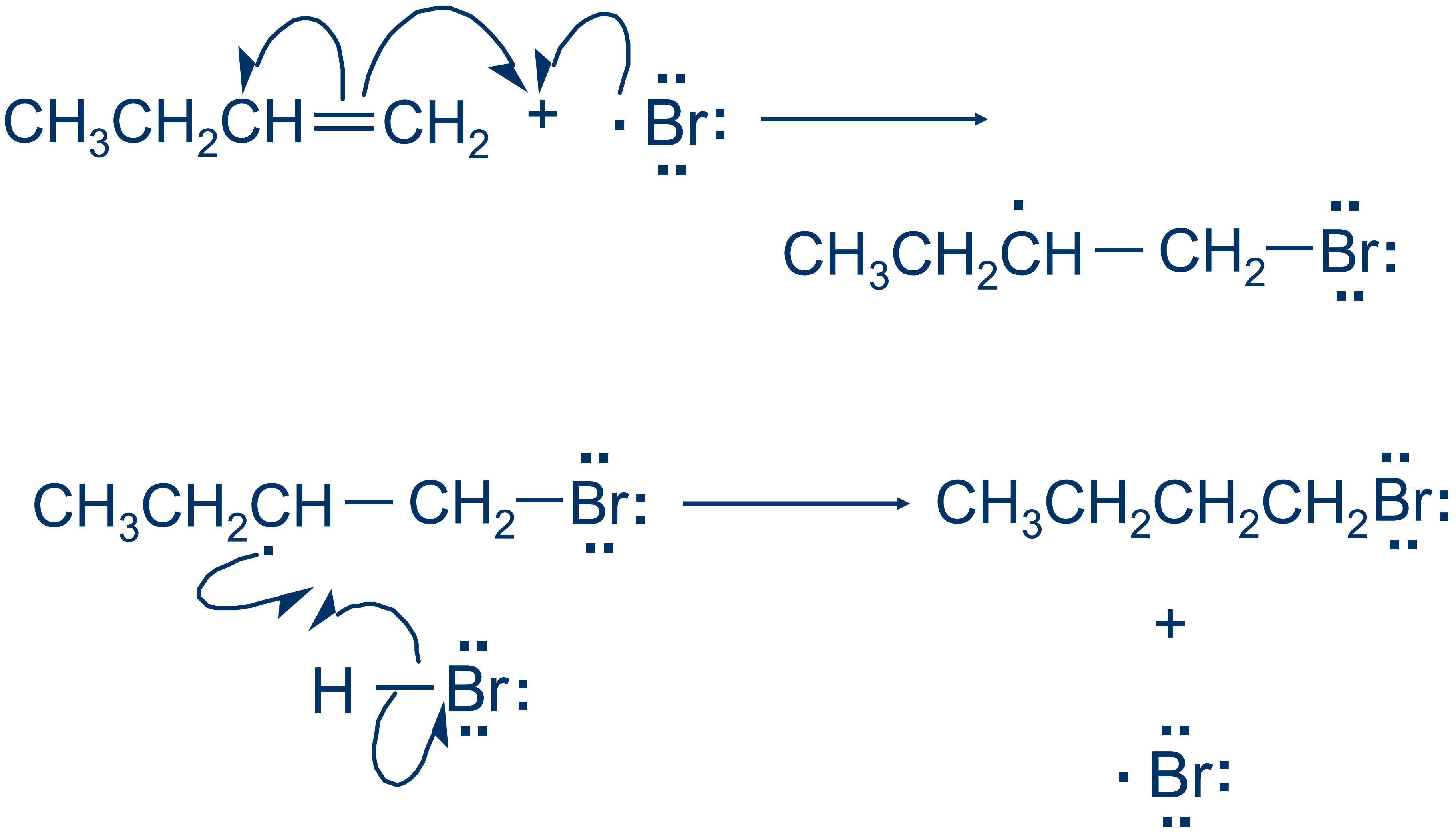
- Addition of HBr opposite to Markovnikov's rule proceeds by a free-radical chain mechanism.

*Initiation steps:*



# Mechanism

## Propagation steps:

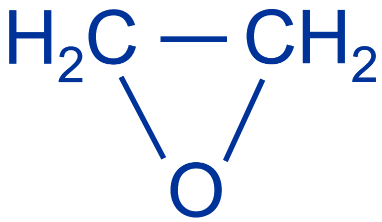


$$CH_3CH_2CH{=}CH_2 + \cdot\ddot{Br}: \longrightarrow CH_3CH_2\dot{C}H-CH_2-\ddot{Br}:$$

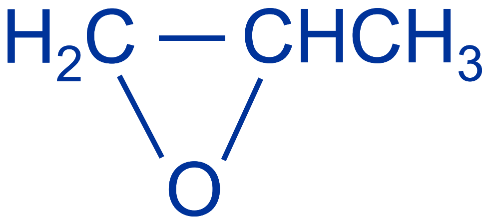
$$CH_3CH_2\underset{\cdot}{C}H-CH_2-\ddot{Br}: + H-\ddot{Br}: \longrightarrow CH_3CH_2CH_2CH_2\ddot{Br}: + \cdot\ddot{Br}:$$

# 6.19. Epoxidation of Alkenes

- Epoxides are examples of heterocyclic compounds three-membered rings that contain oxygen.



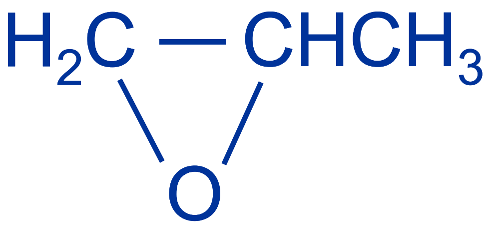
Ethylene oxide



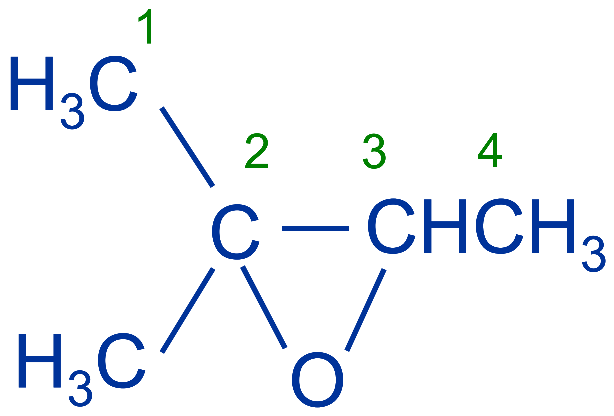
Propylene oxide

# Epoxide Nomenclature

- Substitutive nomenclature: named as epoxy-substituted alkanes.
- "epoxy" precedes name of alkane.

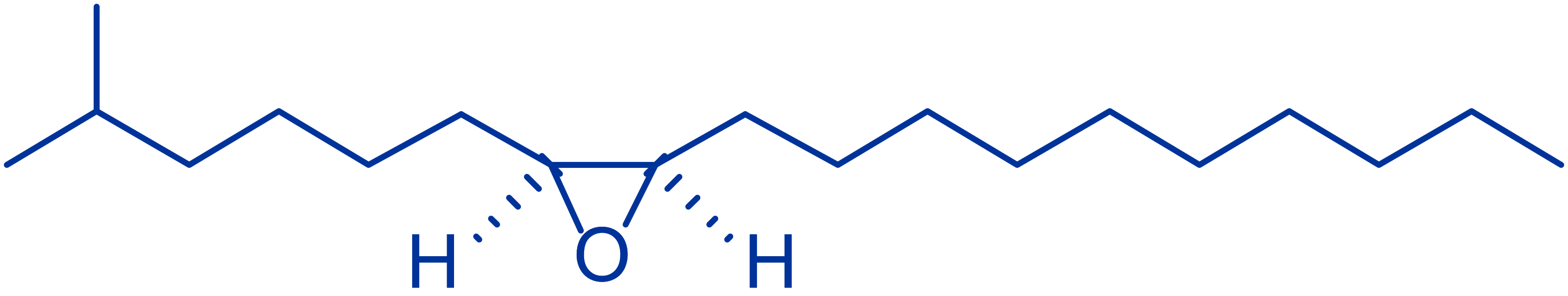


1,2-epoxypropane



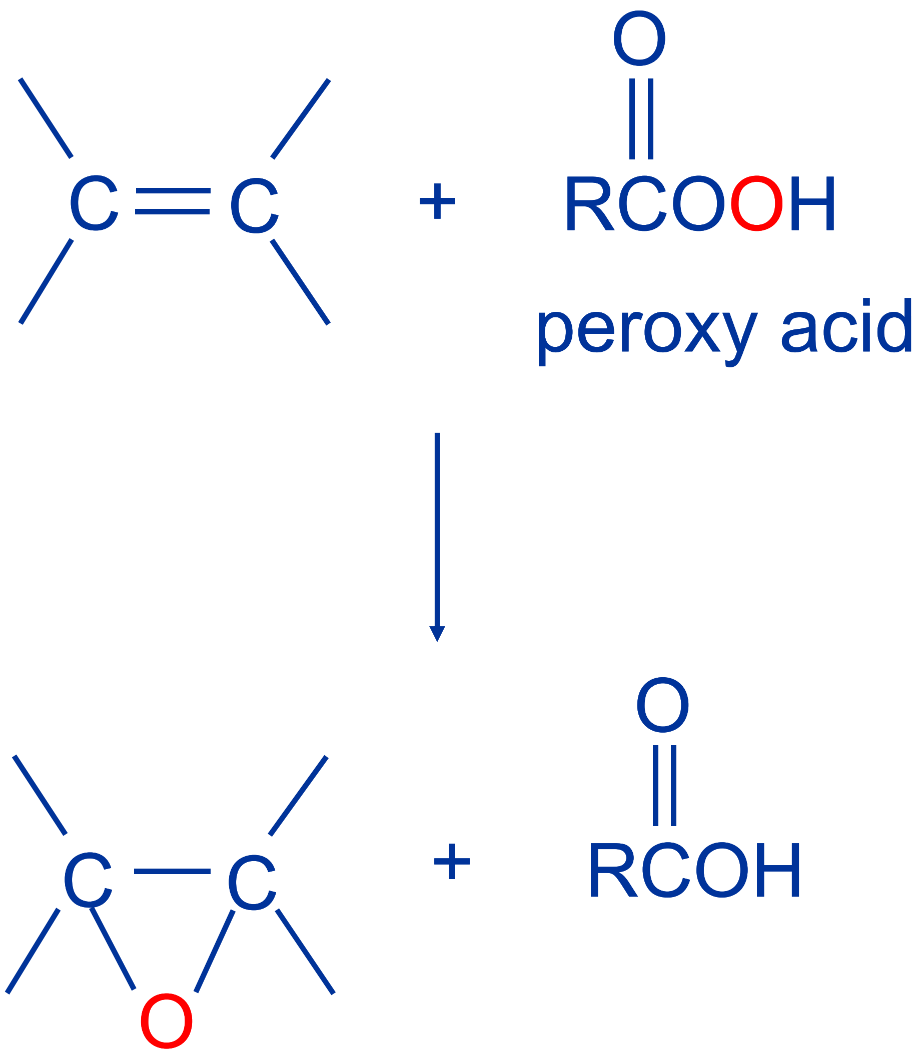
2-methyl-2,3-epoxybutane

# Problem 6.22. Give the IUPAC name, including stereochemistry, for disparlure

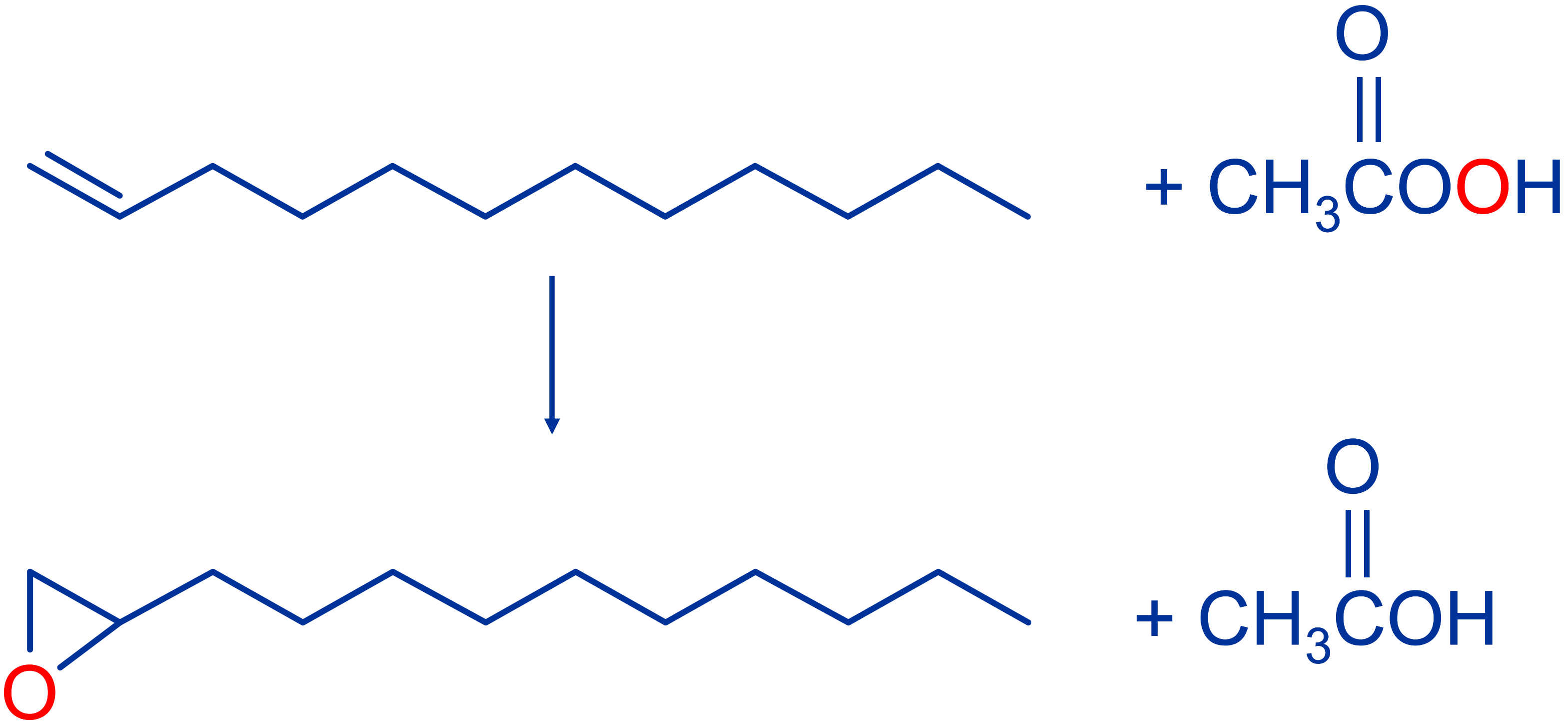


*cis*-2-Methyl-7,8-epoxyoctadecane

# Epoxidation of Alkenes



# Example

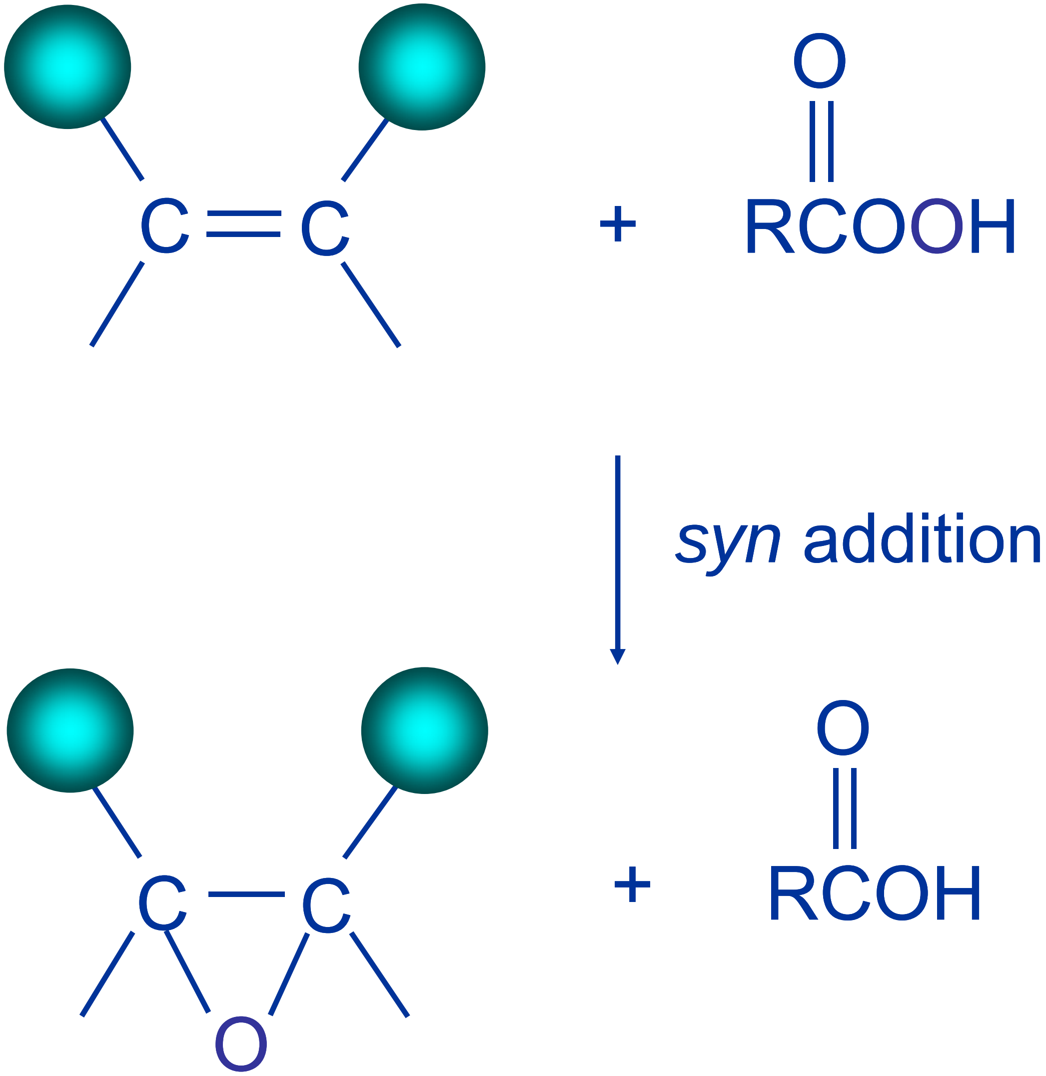


$$+\ \mathrm{CH_3\overset{\overset{\Large O}{\|}}{C}OOH}$$

$$+\ \mathrm{CH_3\overset{\overset{\Large O}{\|}}{C}OH}$$

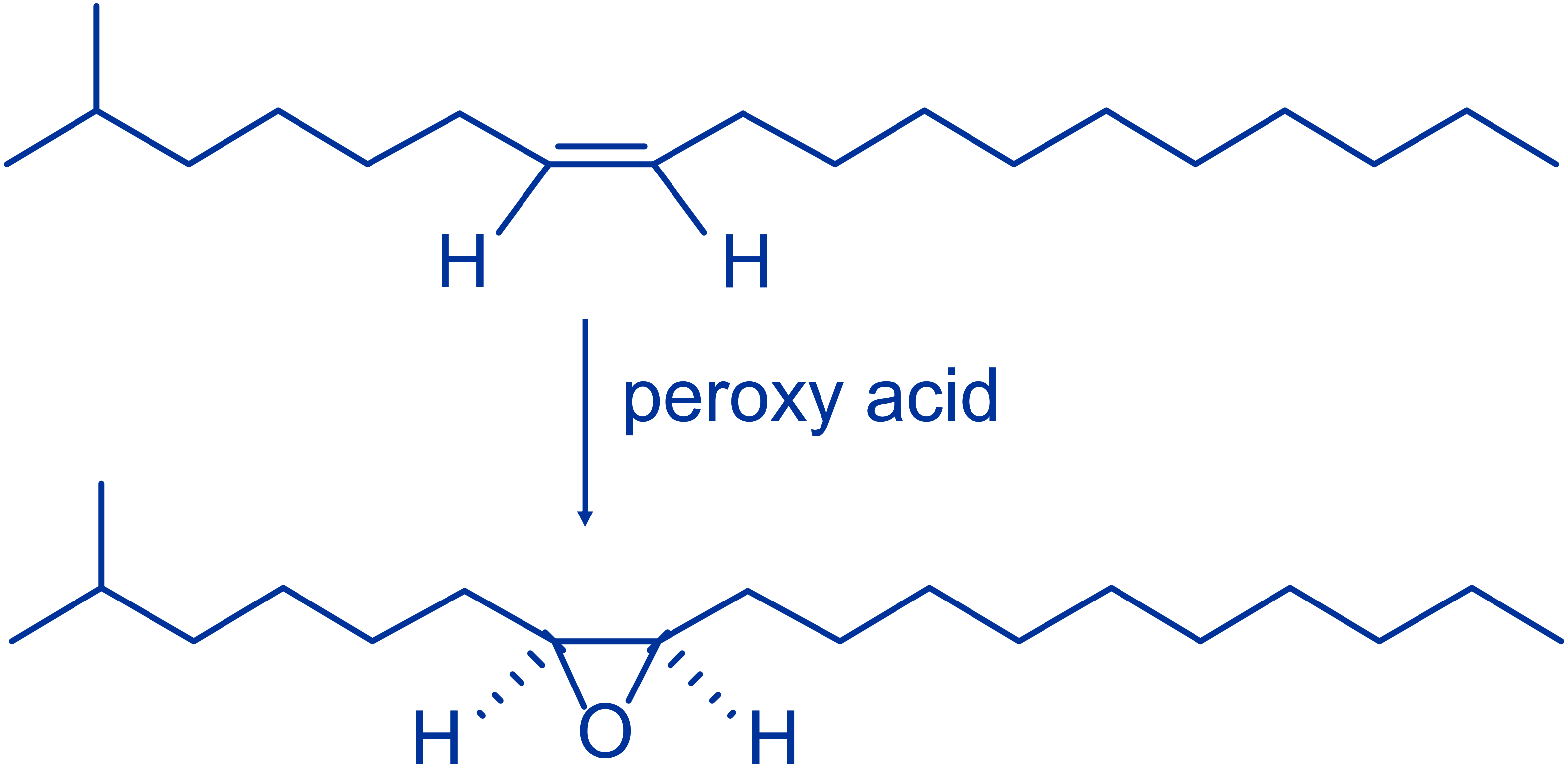
(52%)

# Stereochemistry of Epoxidation



*syn* addition

Problem 6.23. Give the structure of the alkene, including stereochemistry, that you would choose as the starting material in a preparation of synthetic disparlure.

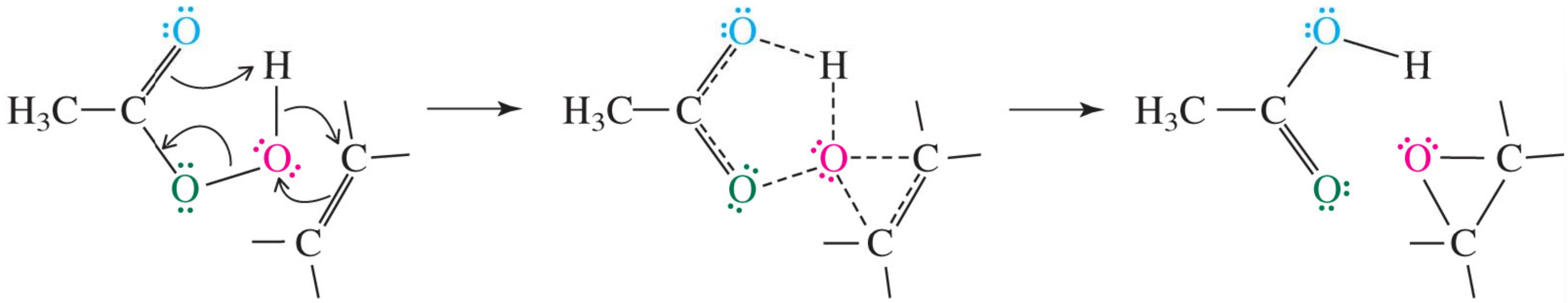


# Relative Rates of Epoxidation

| | | |
|---|---|---|
| Ethylene | $H_2C{=}CH_2$ | 1 |
| Propene | $CH_3CH{=}CH_2$ | 22 |
| 2-Methylpropene | $(CH_3)_2C{=}CH_2$ | 484 |
| 2-Methyl-2-butene | $(CH_3)_2C{=}CHCH_3$ | 6526 |

- More highly substituted double bonds react faster. Alkyl groups on the double bond make it more “electron rich.”

# Mechanism of Epoxidation



Peroxyacetic acid and alkene

Transition state for oxygen transfer from the OH group of the peroxy acid to the alkene

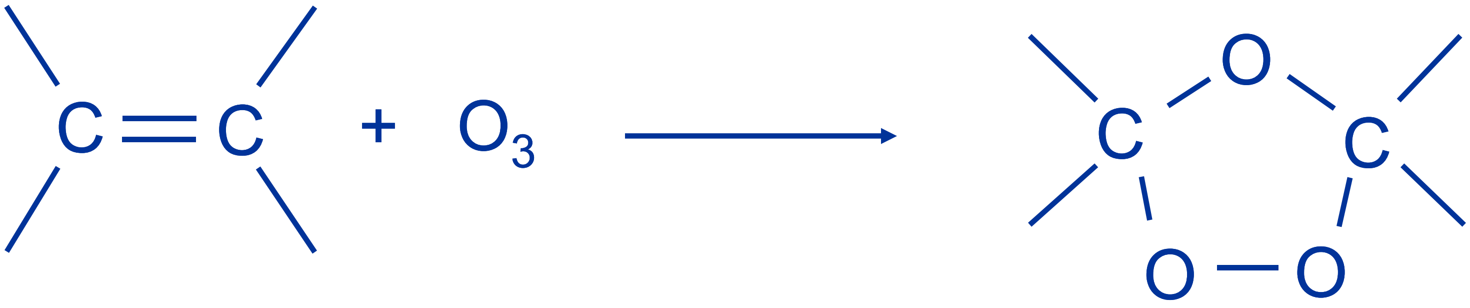
Acetic acid and epoxide

# 6.20. Ozonolysis of Alkenes

- Ozonolysis has both synthetic and analytical applications.

- Synthesis of aldehydes and ketones.

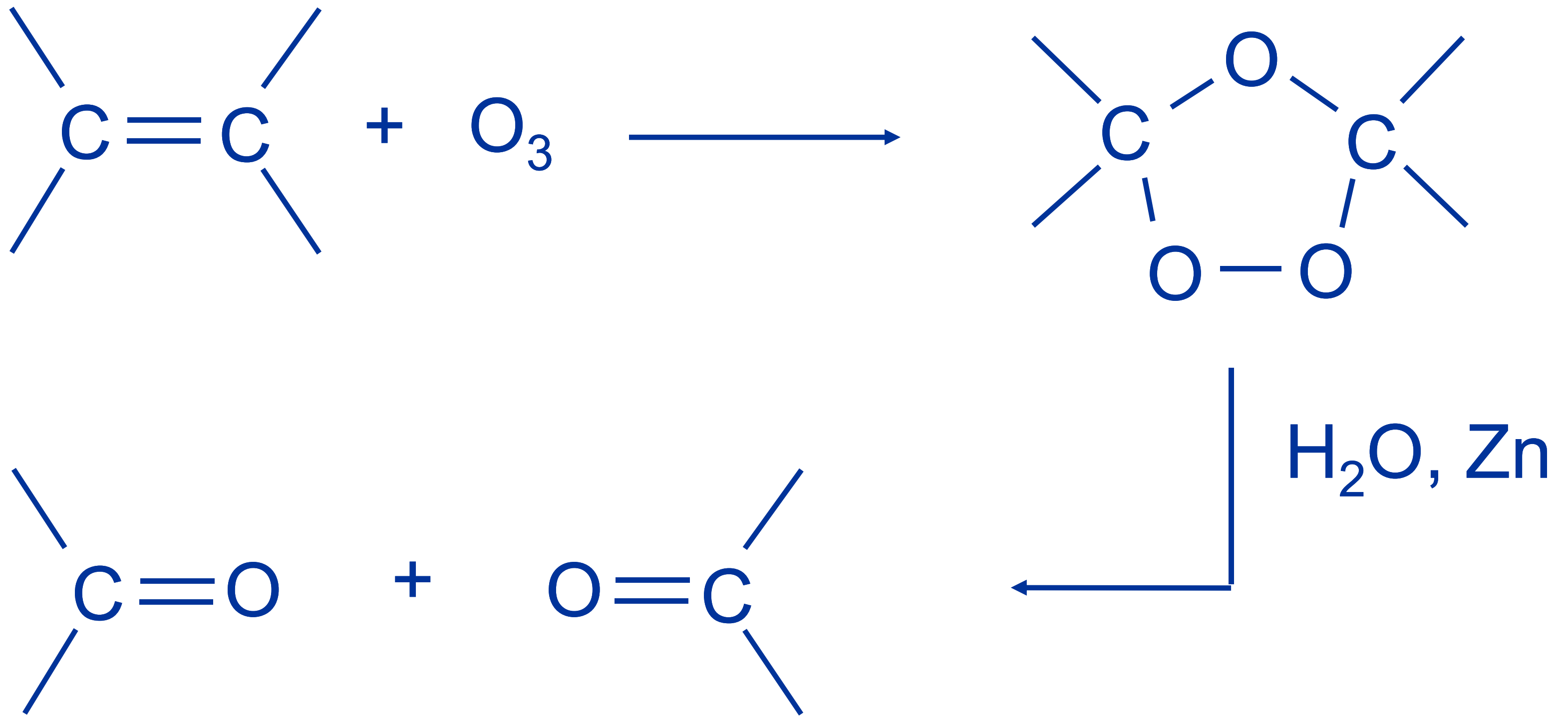
- Identification of substituents on the double bond of an alkene.



- First step is the reaction of the alkene with ozone. The product is an *ozonide.*

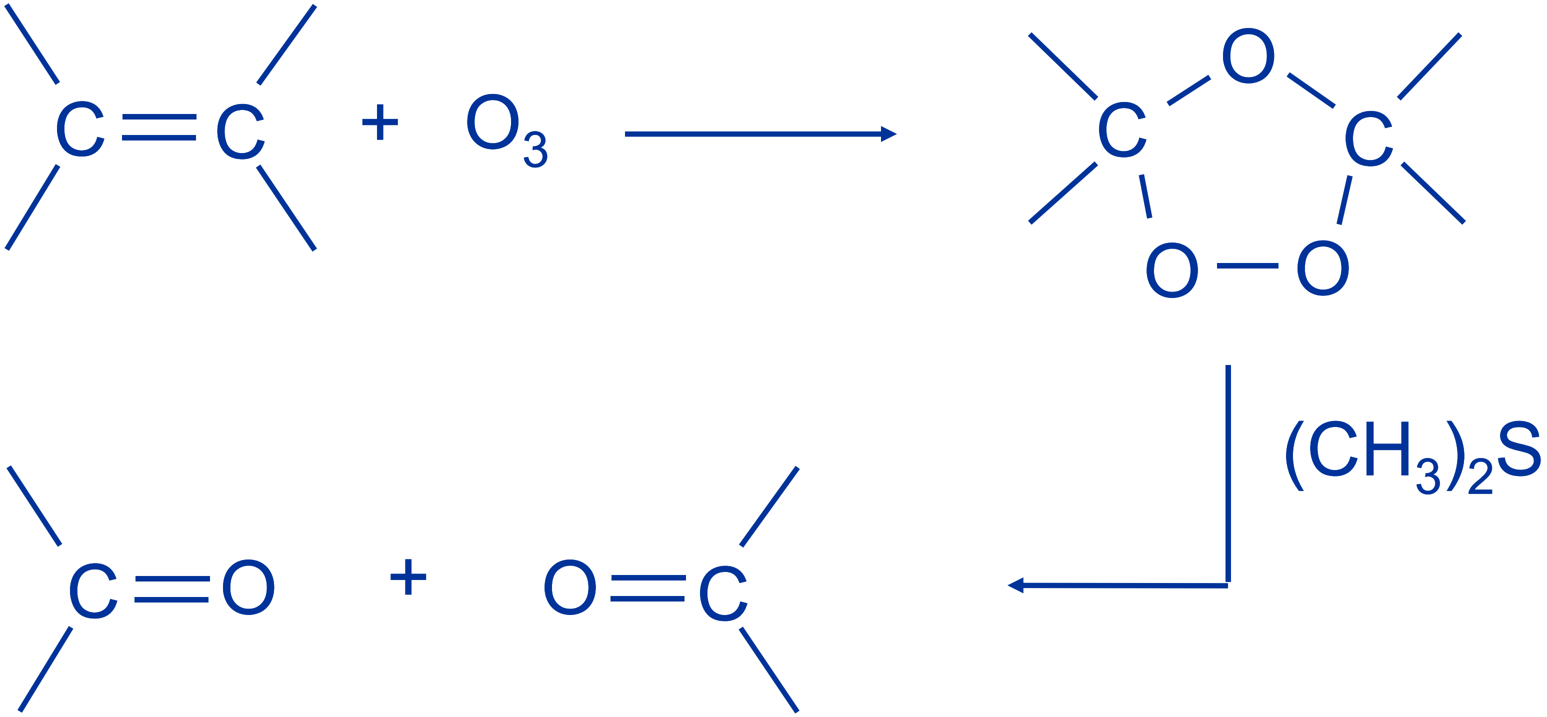
# Ozonolysis of Alkenes

- Second step is hydrolysis of the ozonide. Two aldehydes, two ketones, or an aldehyde and a ketone are formed.

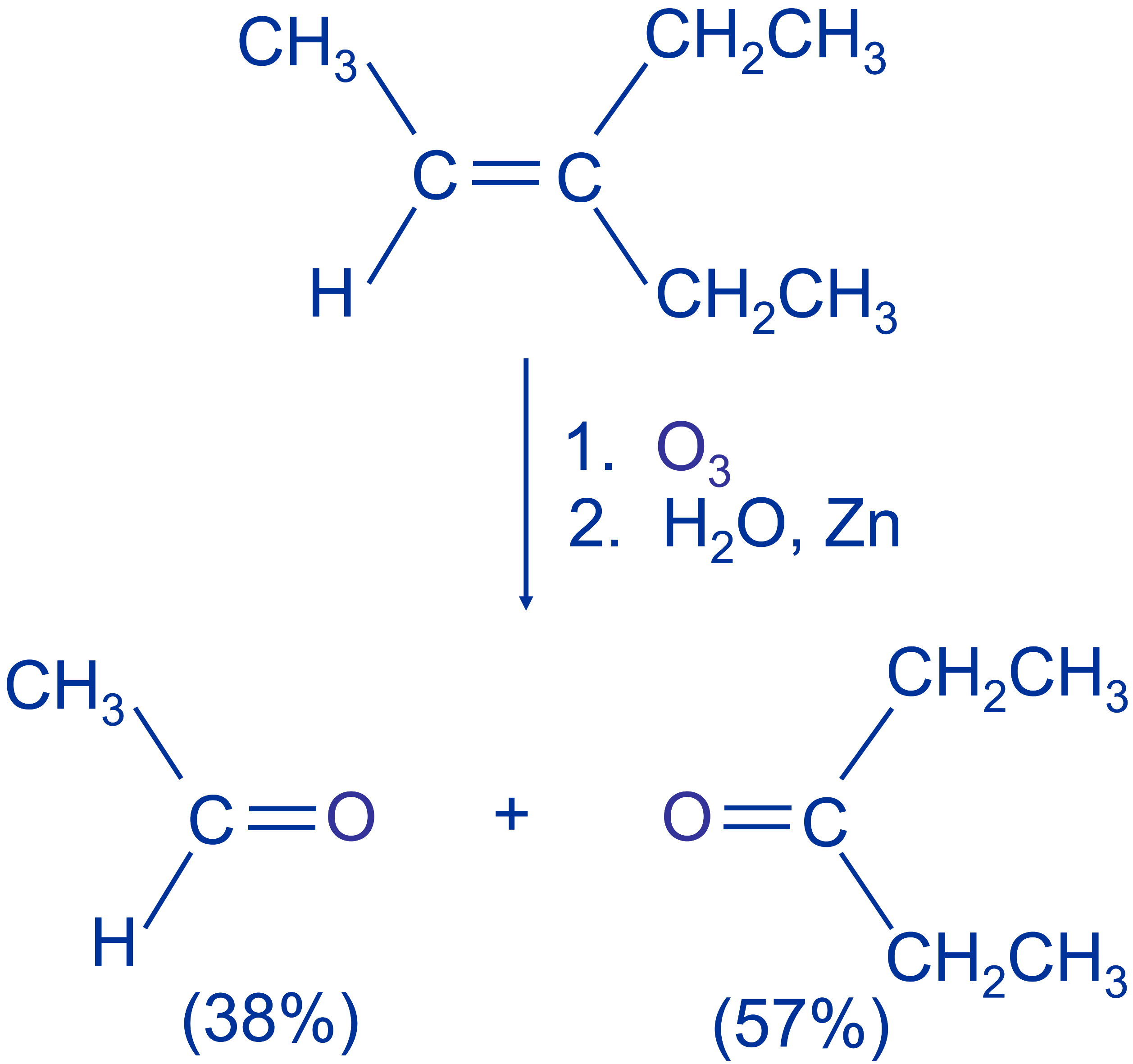


# Ozonolysis of Alkenes

- As an alternative to hydrolysis, the ozonide can be treated with dimethyl sulfide.



# Example

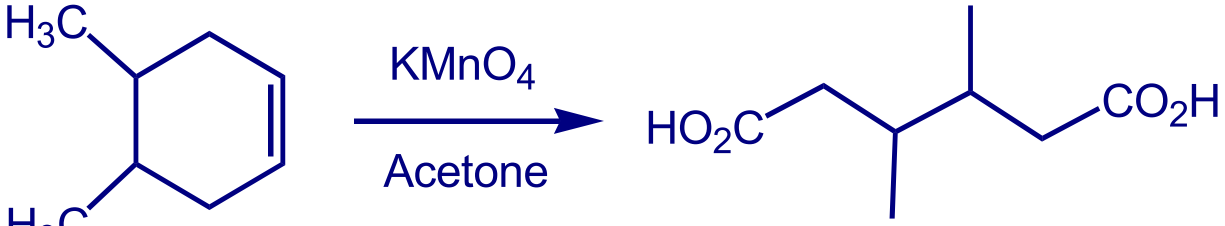


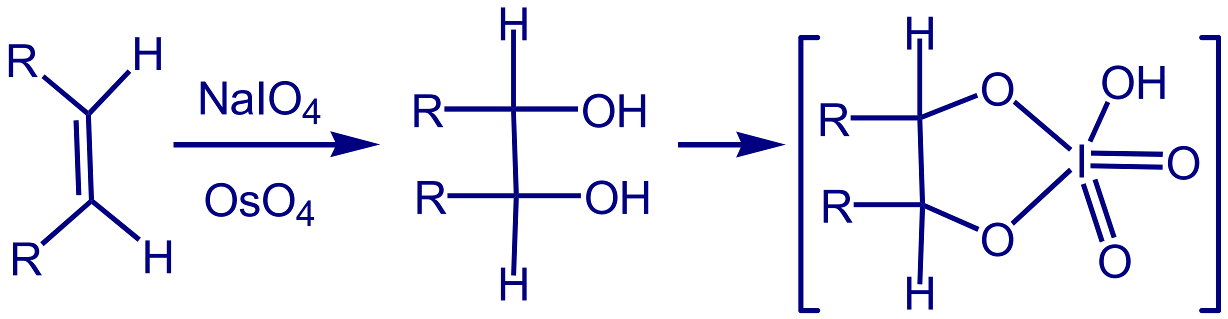
1. $O_3$
2. $H_2O$, Zn

(38%)

(57%)

# C=C bond cleavage





*Cyclic periodate intermediate*

$\longrightarrow$ 2RCHO

$KMnO_4$: Potassium permanganate

$NaIO_4$: Sodium periodate

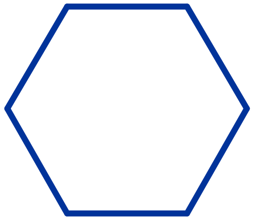
$OsO_4$: Osmium tetroxide

# Introduction to Organic Chemical Synthesis: RETROSYNTHESIS

# Prepare cyclohexane from cyclohexanol

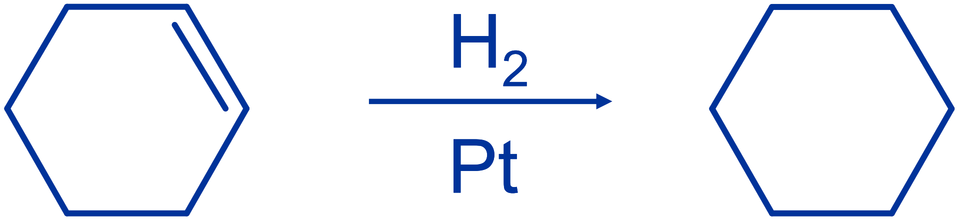
- Devise a synthetic plan:
  - Reason backward from the target molecule.
  - Always use reactions that you are sure of.

# Prepare cyclohexane from cyclohexanol



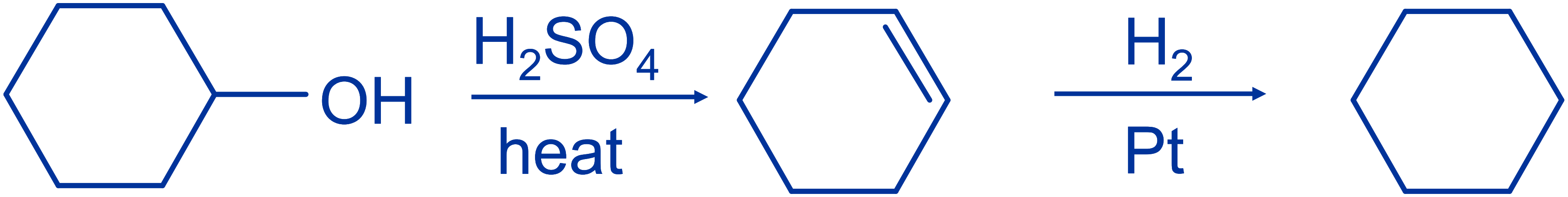
- Ask yourself the key question:
  - "Starting with anything, how can I make cyclohexane in a single step by a reaction that will work?"

# Prepare cyclohexane from cyclohexanol



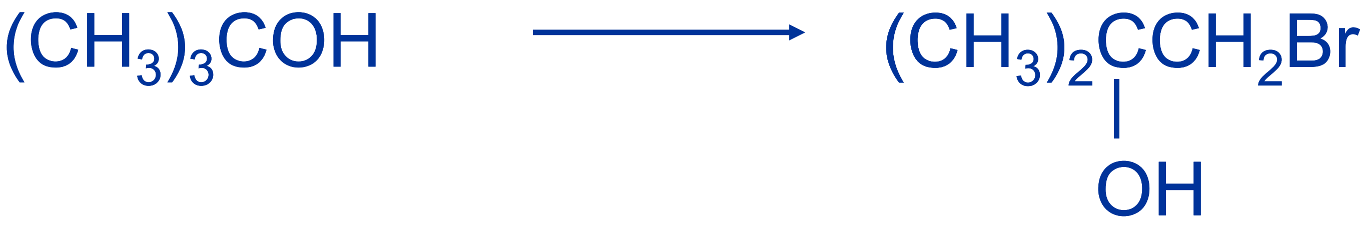
- The only reaction covered so far for preparing alkanes is catalytic hydrogenation of alkenes.
- This leads to a new question. "Starting with anything, how can I prepare cyclohexene in a single step by a reaction I am sure will work?"

# Prepare cyclohexane from cyclohexanol



- Alkenes can be prepared by dehydration of alcohols.
- The synthesis is complete.

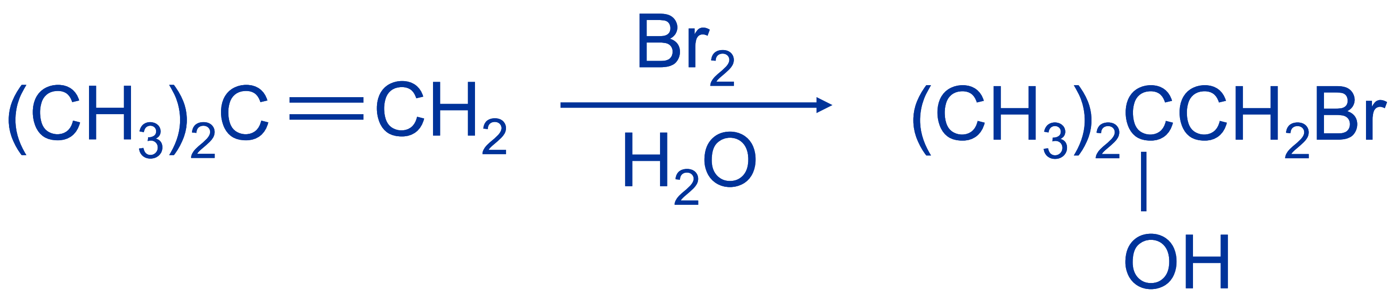
# Prepare 1-bromo-2-methyl-2-propanol from *tert*-butyl alcohol



$$(CH_3)_3COH \longrightarrow (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br$$

- "Starting with anything, how can I make the desired compound in a single step by a reaction that will work?"
- The desired compound is a vicinal bromohydrin. How are vicinal bromohydrins prepared?

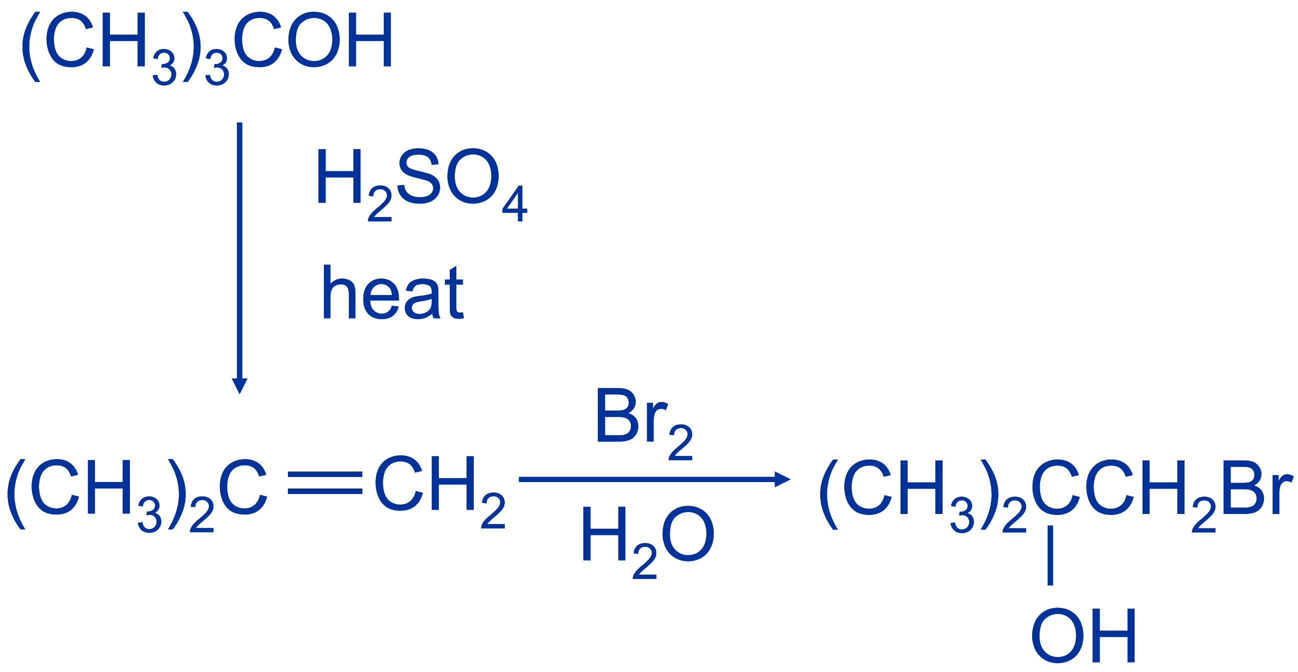
# Prepare 1-bromo-2-methyl-2-propanol from *tert*-butyl alcohol



$$(CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2C(OH)CH_2Br$$

- ➢ Vicinal bromohydrins are prepared by treatment of alkenes with $Br_2$ in water.
- ➢ How is the necessary alkene prepared?

# Prepare 1-bromo-2-methyl-2-propanol from *tert*-butyl alcohol



$$(CH_3)_3COH \xrightarrow[\text{heat}]{H_2SO_4} (CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br$$

- 2-Methylpropene is prepared from *tert*-butyl alcohol by acid-catalyzed dehydration.
- The synthesis is complete.

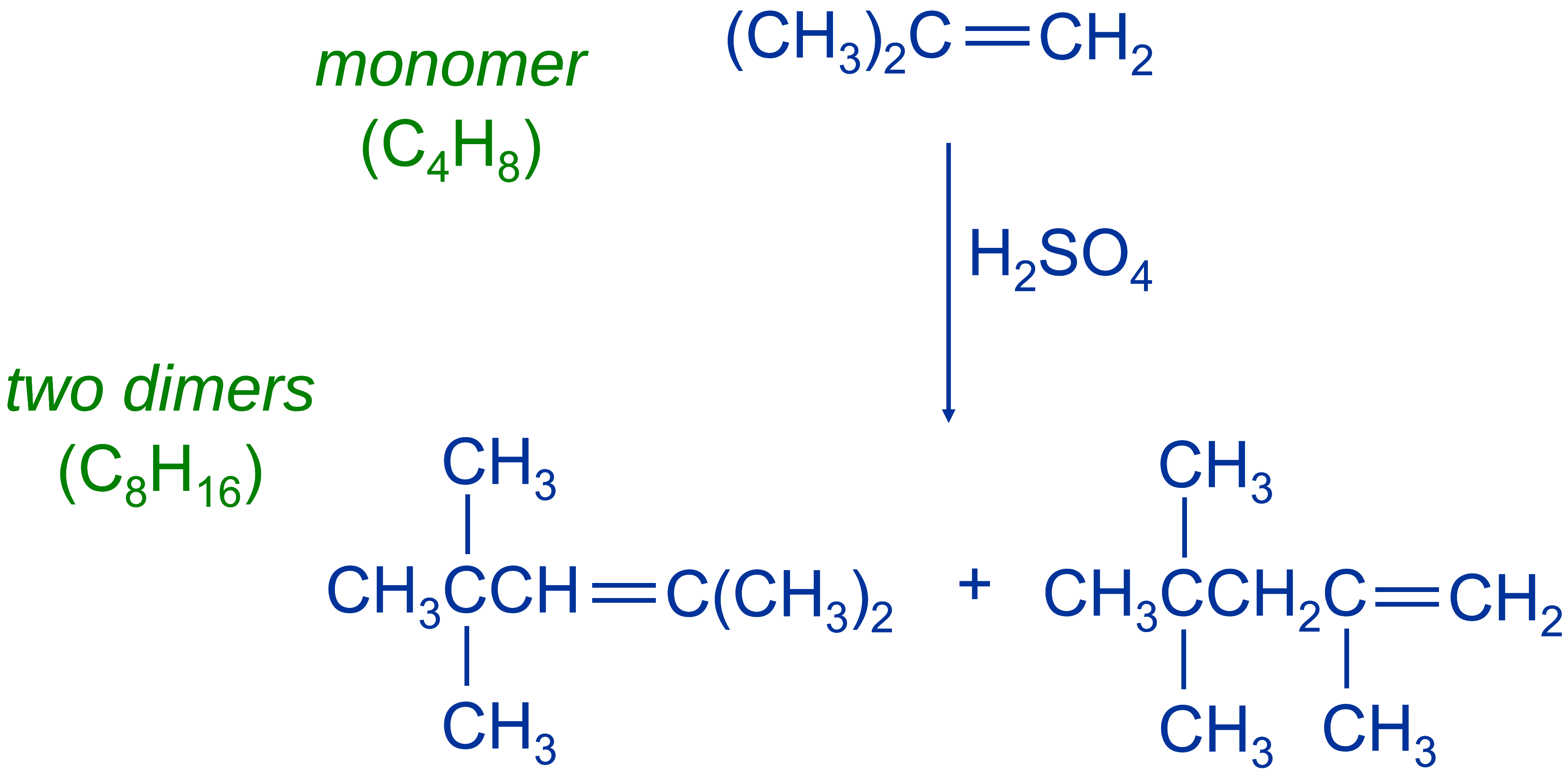
# 6.21. Reactions of Alkenes with Alkenes: Polymerization

# Polymerization of Alkenes

- Cationic polymerization
- Free-radical polymerization
- Coordination polymerization

# Dimerization

## Dimerization of 2-methylpropene



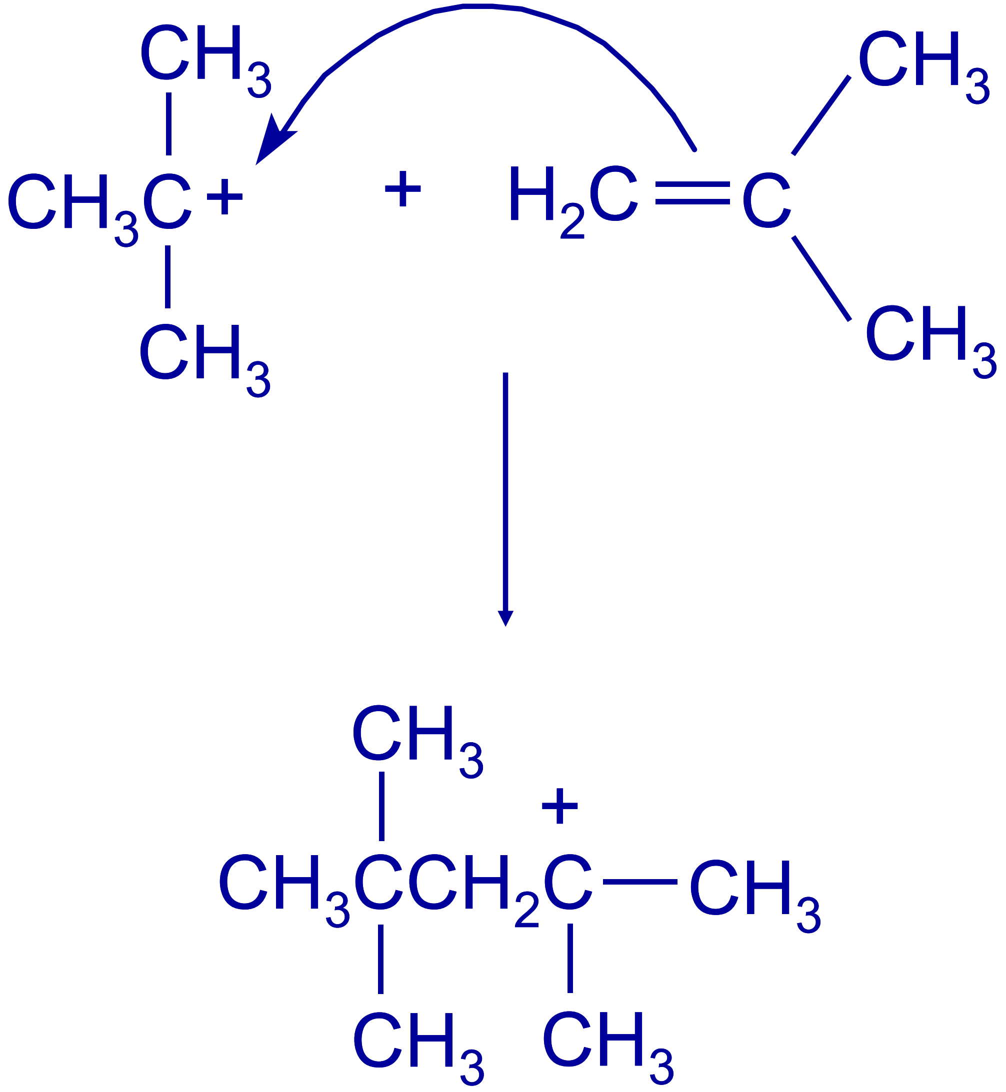
*monomer*
($C_4H_8$)

$$(CH_3)_2C=CH_2 \xrightarrow{H_2SO_4}$$

*two dimers*
($C_8H_{16}$)

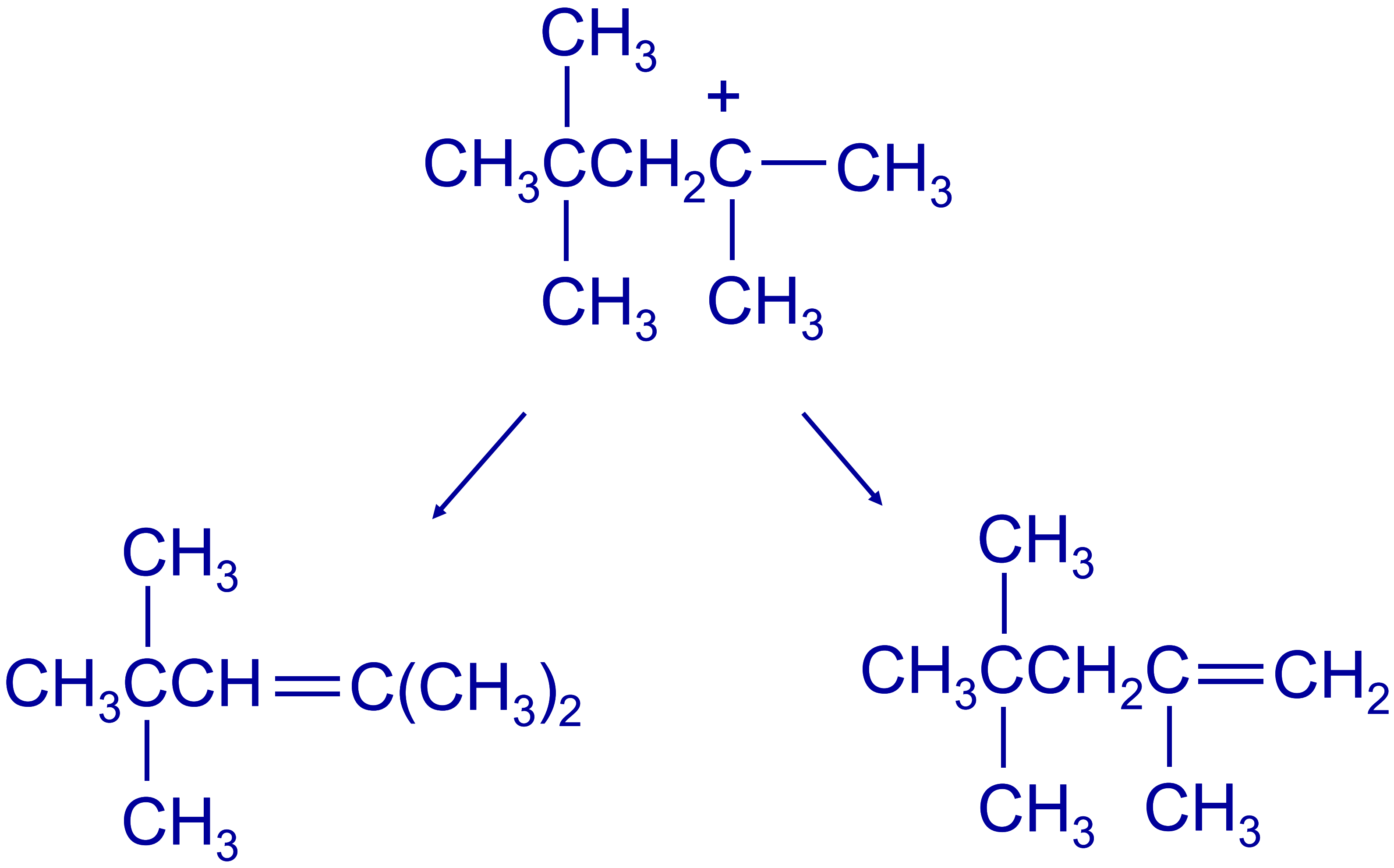
$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH=C(CH_3)_2 + CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}=CH_2$$

# Mechanism of Dimerization



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}{}^{+} \;+\; H_2C{=}C\begin{matrix}CH_3\\CH_3\end{matrix} \longrightarrow CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{+}{\underset{CH_3}{C}}{-}CH_3$$

# Mechanism of Dimerization

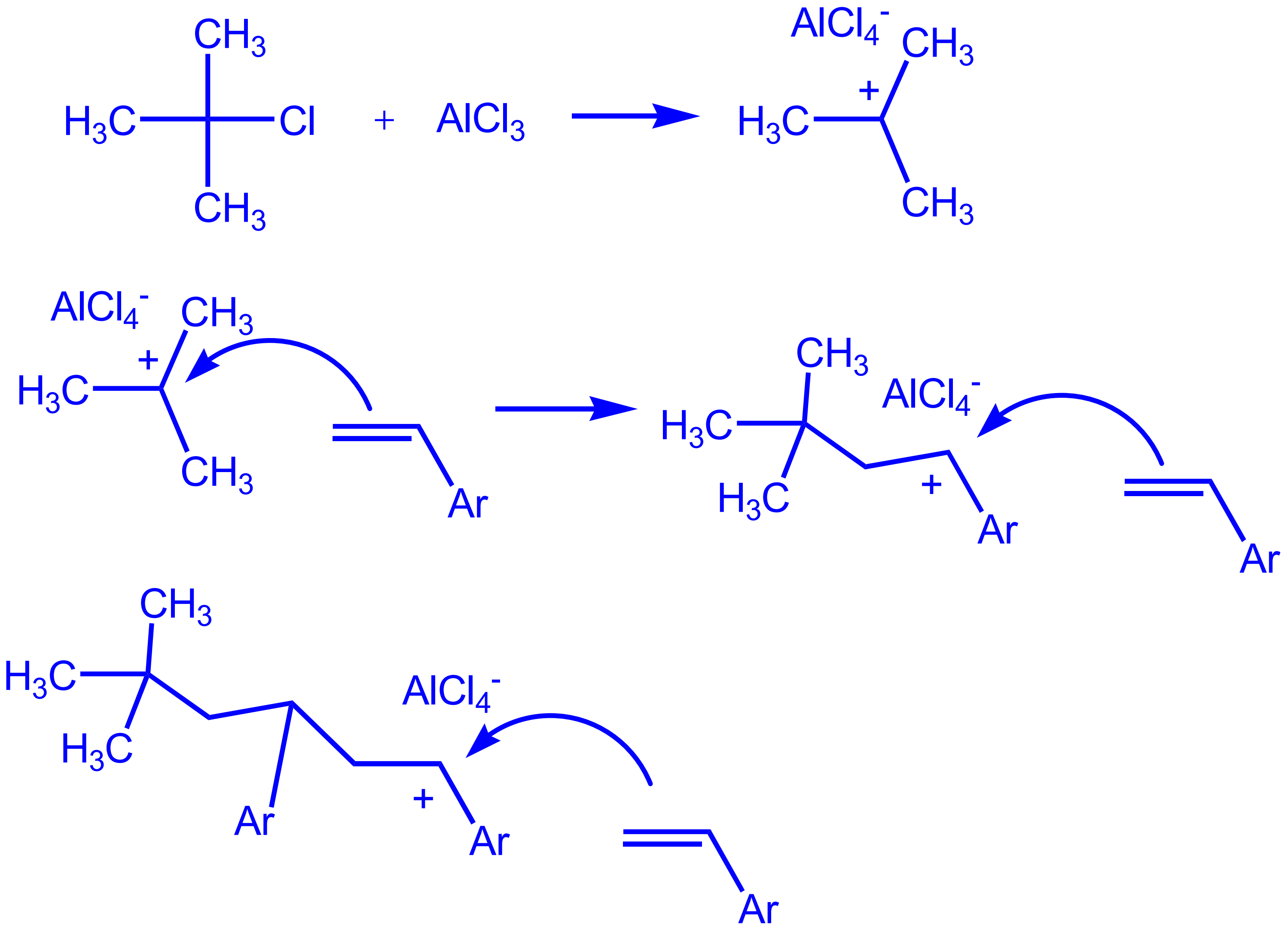


$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{+}{\underset{CH_3}{C}}-CH_3$$

$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH=C(CH_3)_2$$

$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\underset{CH_3}{C}=CH_2$$

# Cationic Polymerization



# Free-Radical Polymerization of Ethylene

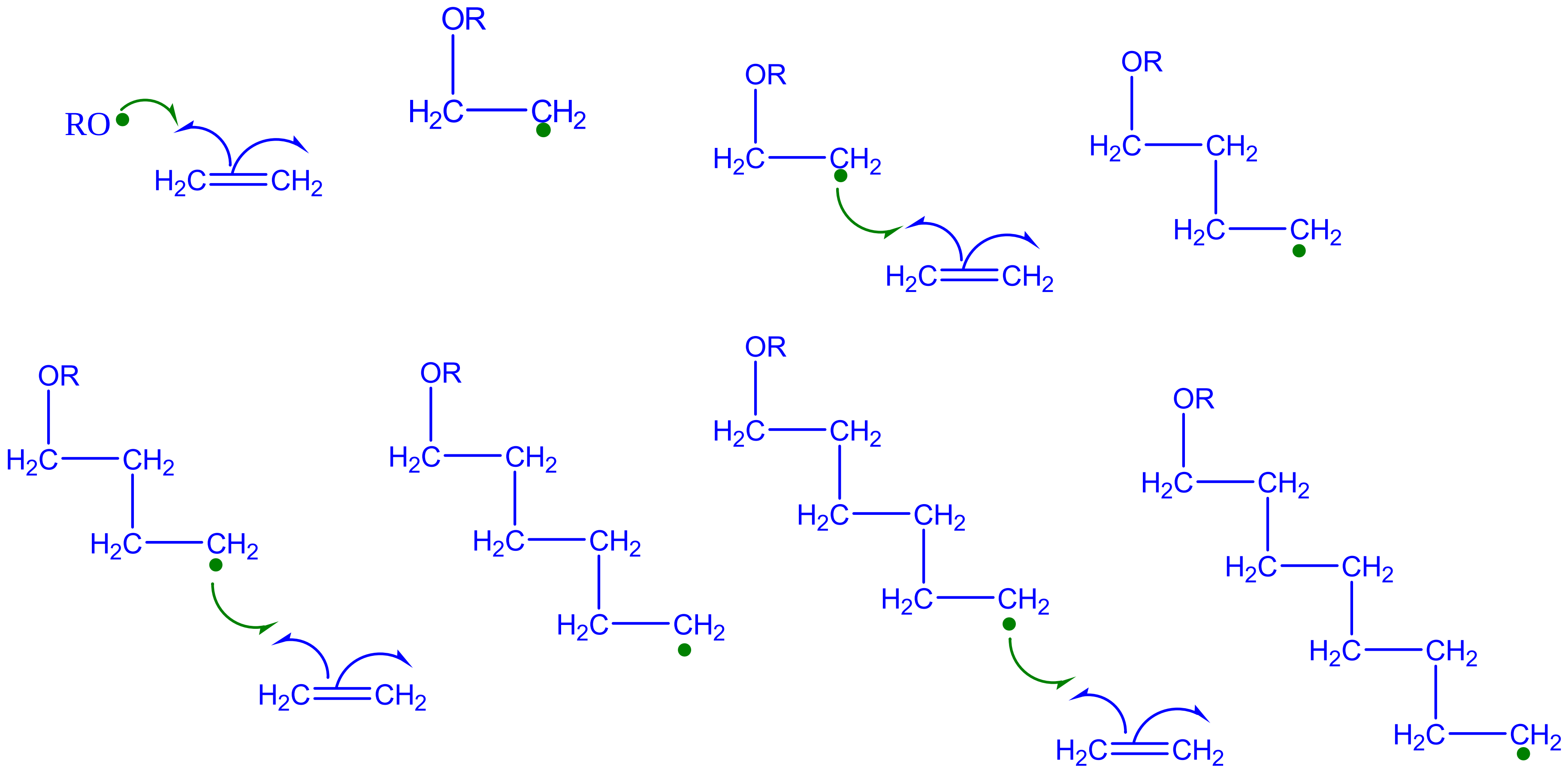
$$H_2C{=}CH_2$$

$$\begin{array}{r} 200\ ^{\circ}\mathrm{C} \\ 2000\ \mathrm{atm} \end{array} \Bigg\downarrow \begin{array}{l} O_2 \text{ or} \\ \text{peroxides} \end{array}$$

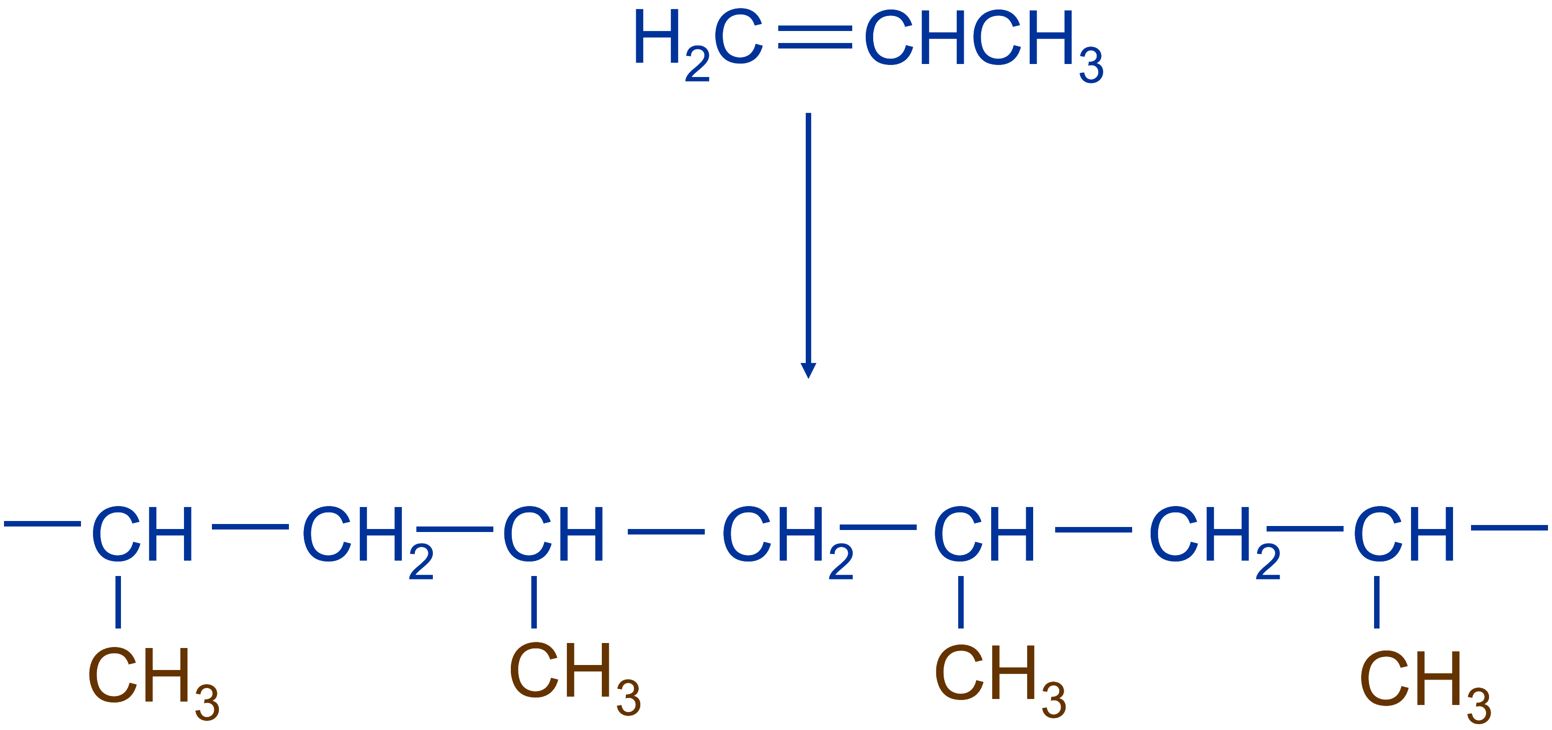
$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

polyethylene

# Mechanism



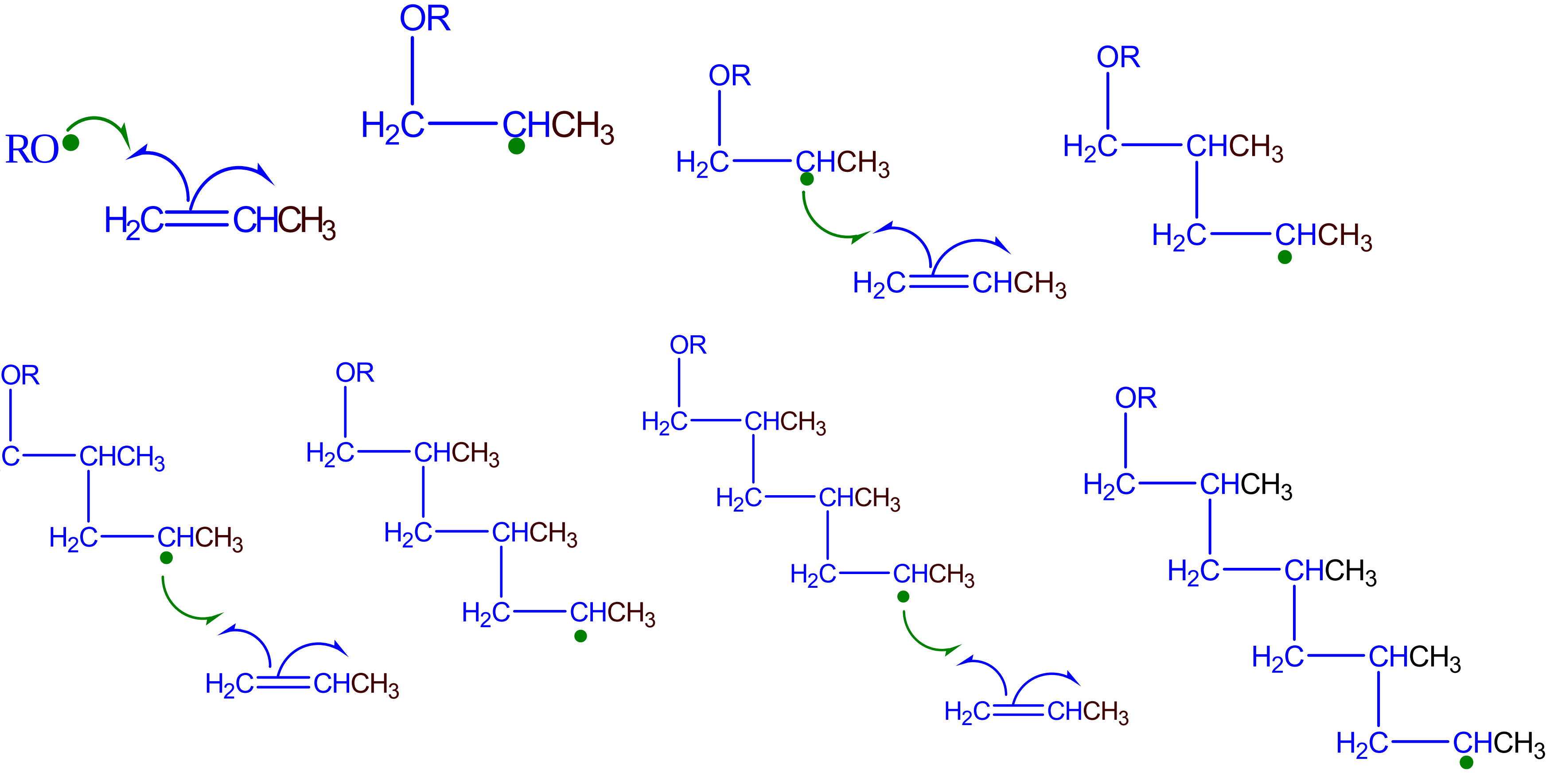
# Free-Radical Polymerization of Propene



$$H_2C{=}CHCH_3 \;\longrightarrow\; -\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-$$

polypropylene

# Mechanism



# Likewise...

$H_2C=CHCl$ → polyvinyl chloride

$H_2C=CHC_6H_5$ → polystyrene

$F_2C=CF_2$ → Teflon