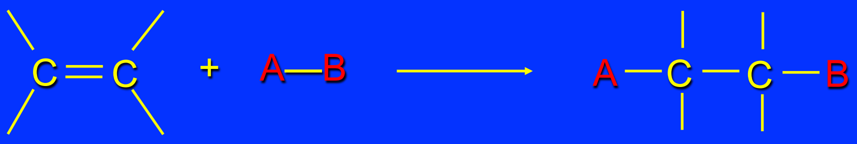
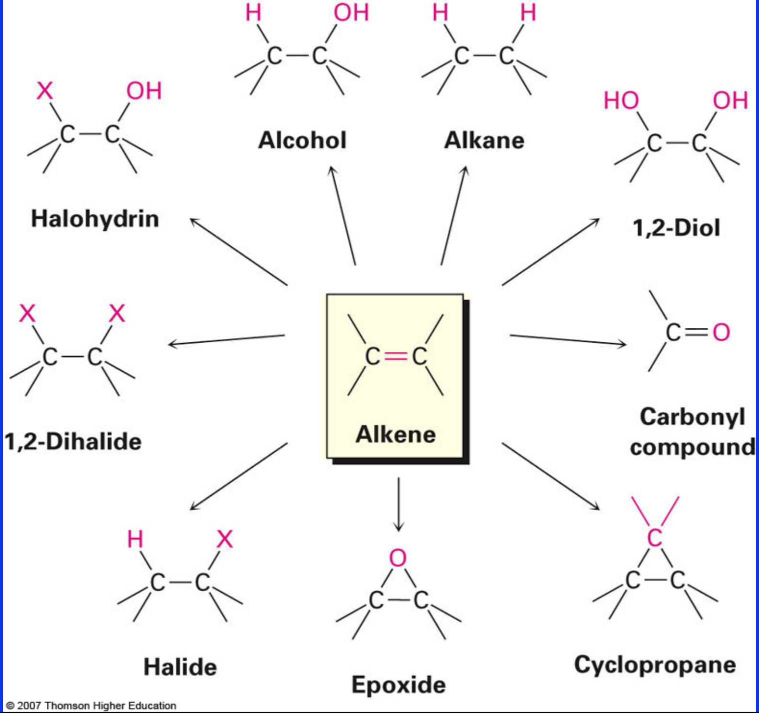
Chapter 6

Reactions of Alkenes: Addition Reactions

Reactions of Alkenes

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





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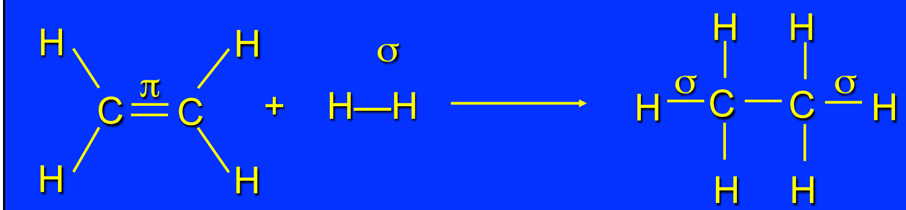
Hydrogenation of Alkenes

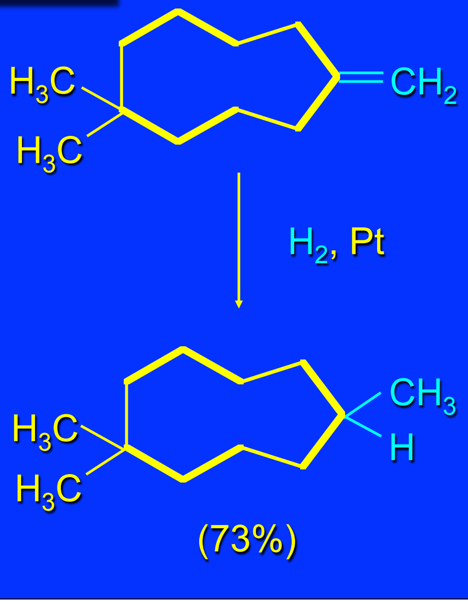
Hydrogenation of ethylene



exothermic ΔH° = –136 kJ/mol

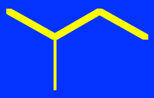
catalyzed by finely divided Pt, Pd, Rh, Ni

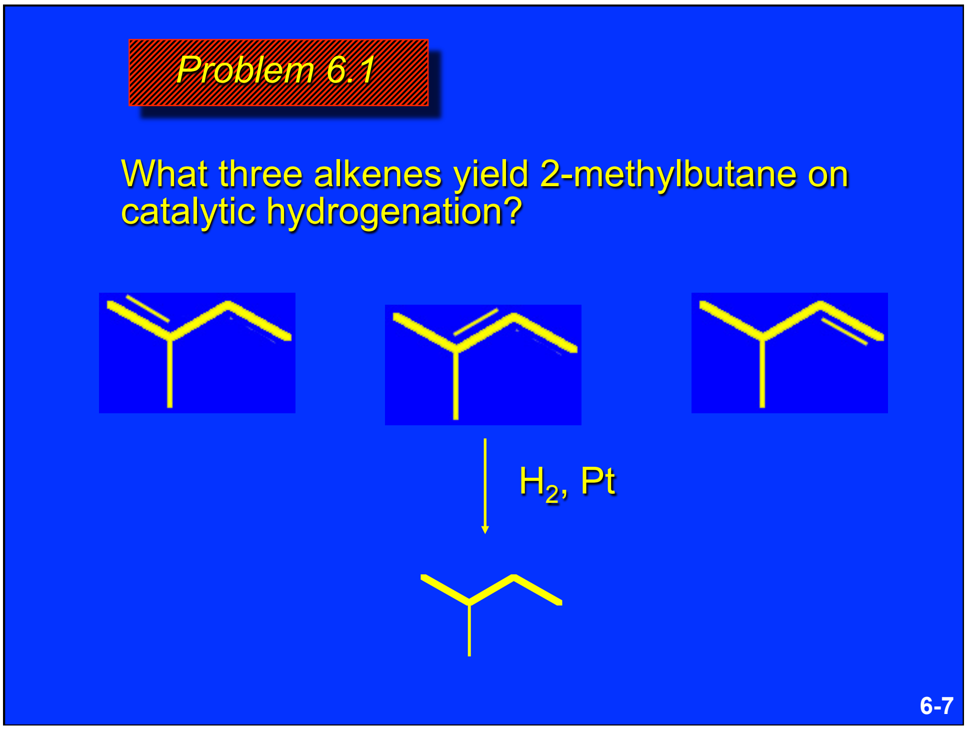
Example



Problem 6.1

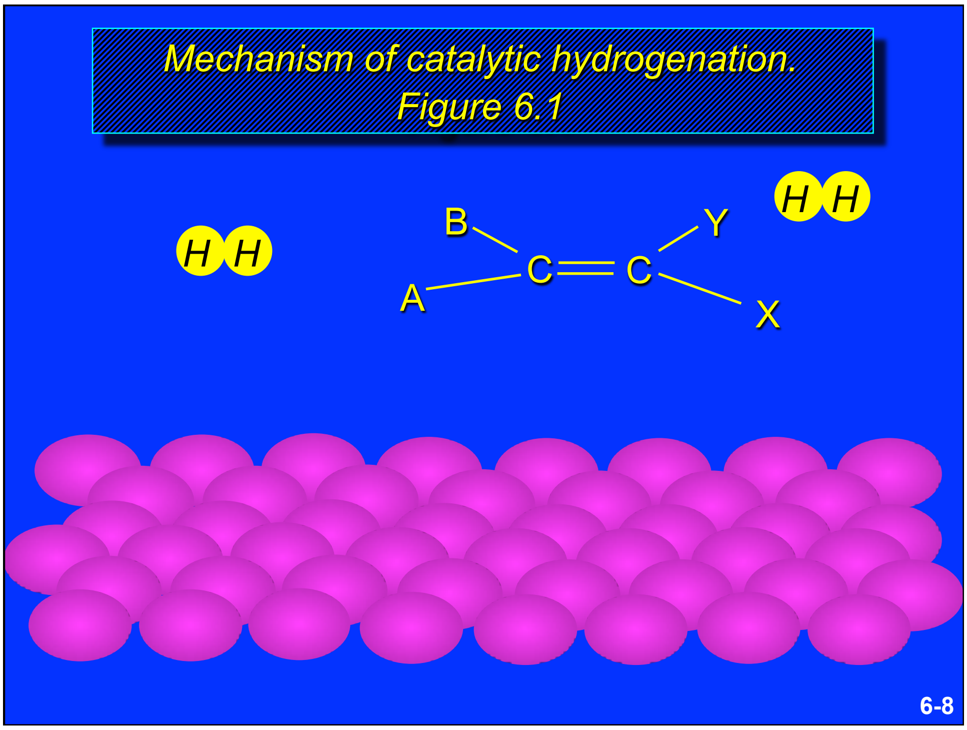
What three alkenes yield 2-methylbutane on catalytic hydrogenation?





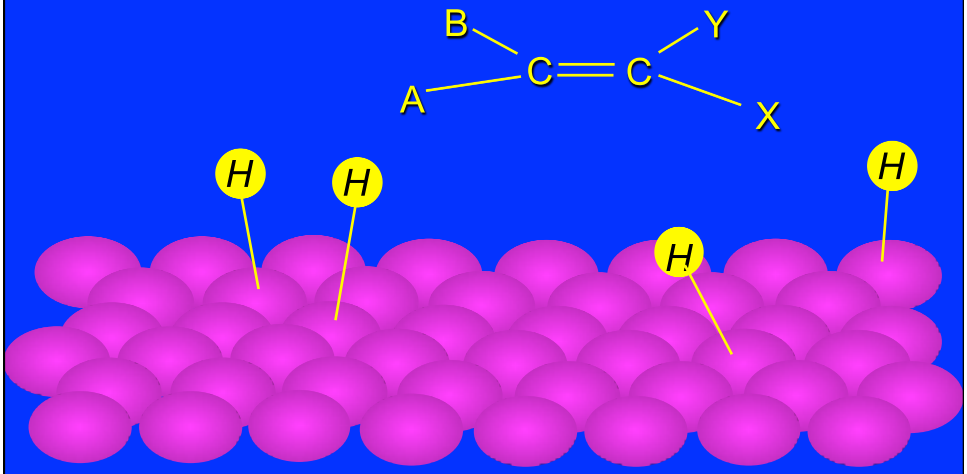
Problem 6.1

What three alkenes yield 2-methylbutane on catalytic hydrogenation?

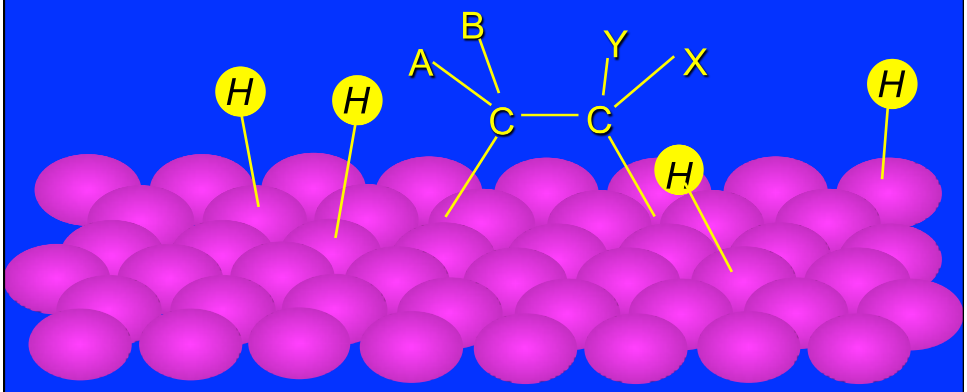


Mechanism of catalytic hydrogenation. Figure 6.1

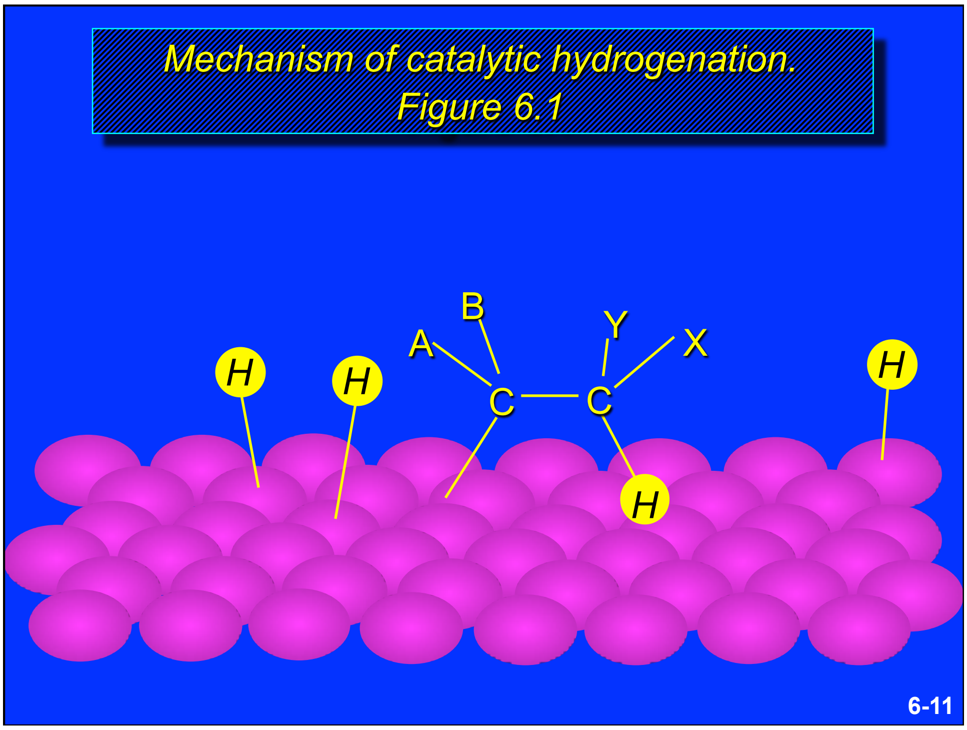
Mechanism of catalytic hydrogenation. Figure 6.1



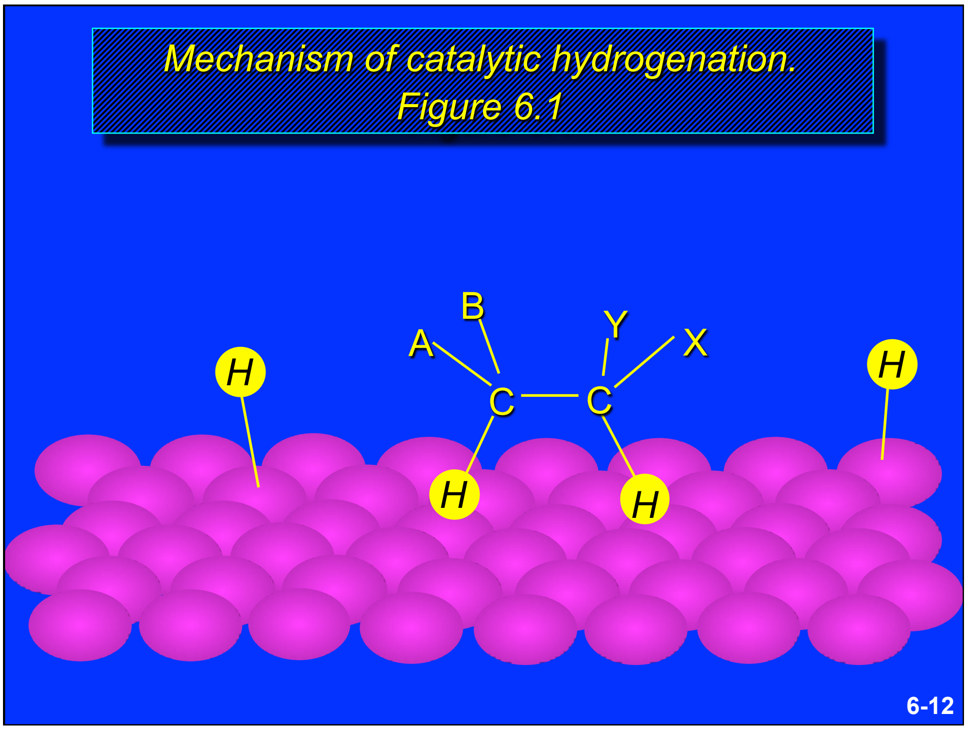
Mechanism of catalytic hydrogenation. Figure 6.1



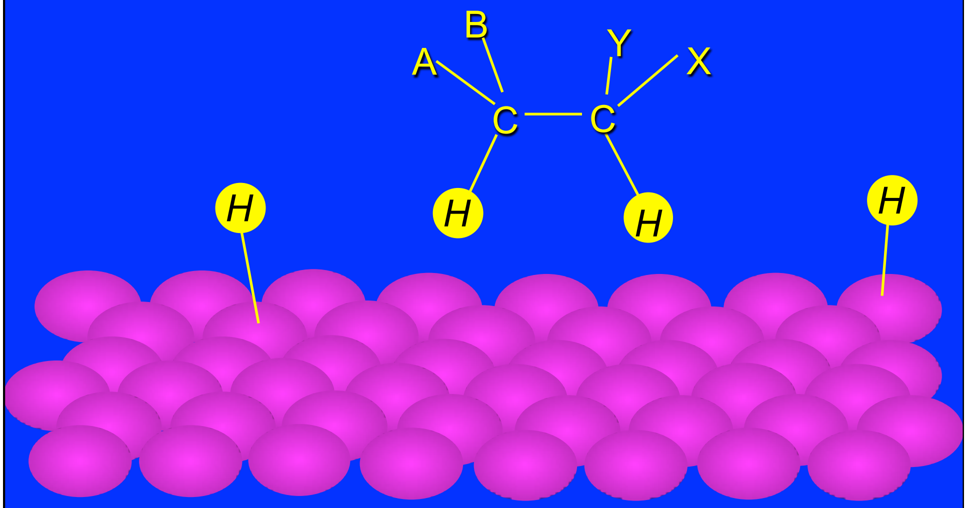
Mechanism of catalytic hydrogenation.
Figure 6.1



Mechanism of catalytic hydrogenation.
Figure 6.1



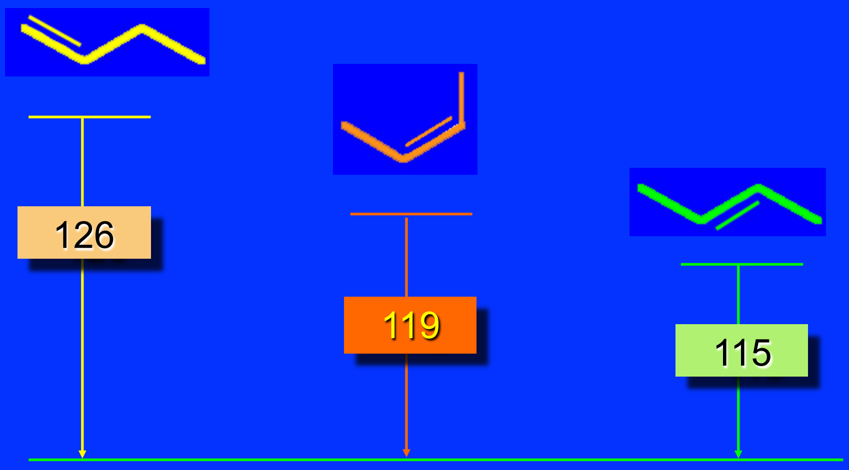
Mechanism of catalytic hydrogenation. Figure 6.1



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



$CH_3CH_2CH_2CH_3$

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

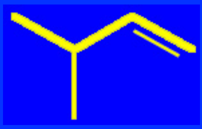
118 kJ/mol

112 kJ/mol

Problem 6.2

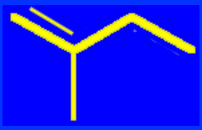
Match each alkene of Problem 6.1 with its correct heat of hydrogenation.

126 kJ/mol

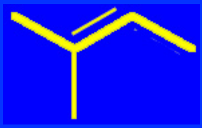


highest heat of hydrogenation; least stable isomer

118 kJ/mol



112 kJ/mol



lowest heat of hydrogenation; most stable isomer

Stereochemistry of Alkene Hydrogenation

Two spatial (stereochemical) aspects of alkene hydrogenation:

- syn addition of both H atoms to double bond
- hydrogenation is stereoselective, corresponding to addition to less crowded face of double bond

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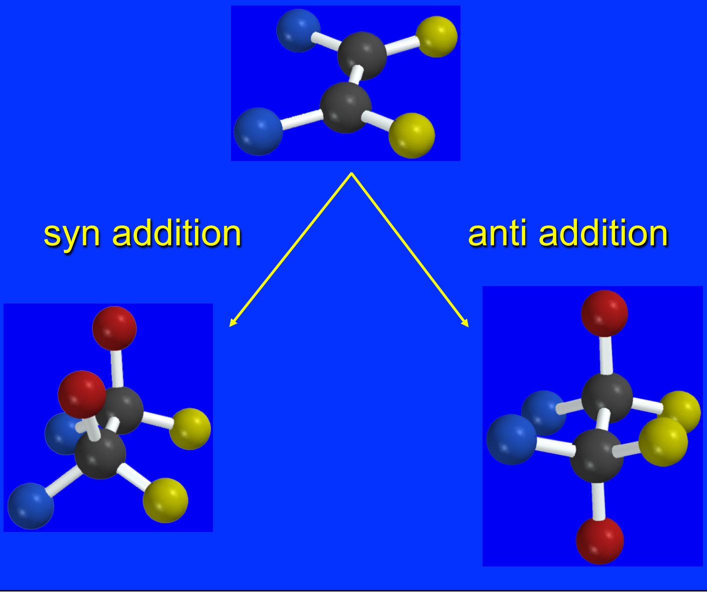
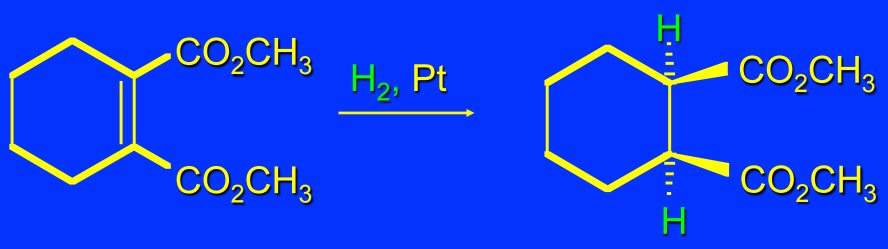
syn-*Addition versus* anti-*Addition*



syn addition

anti addition

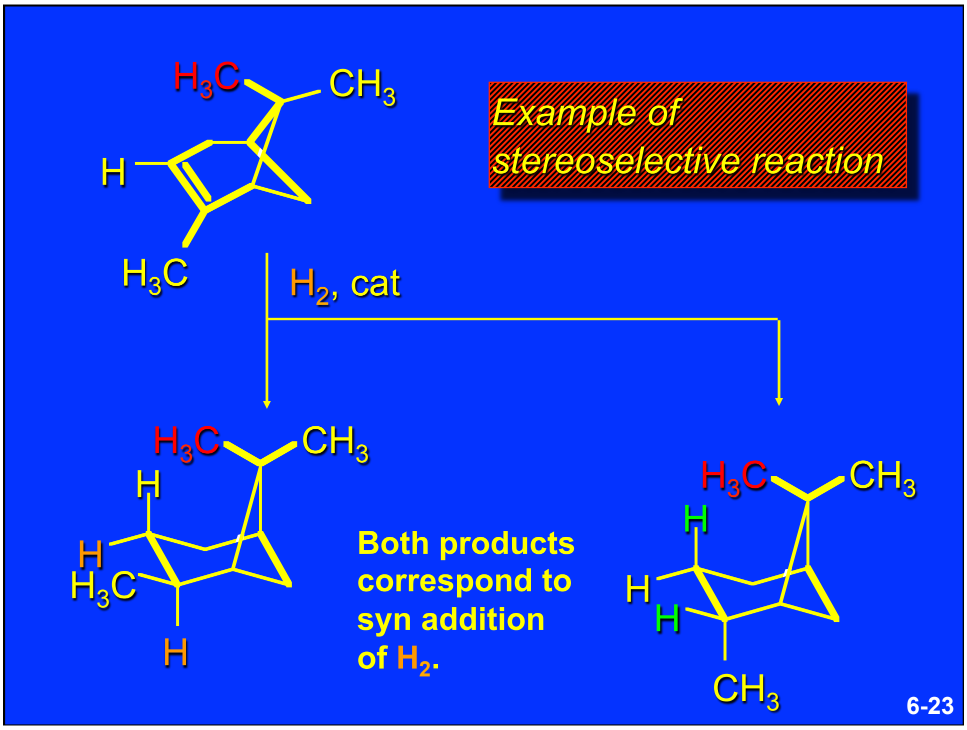
Example of syn-Addition



(100%)

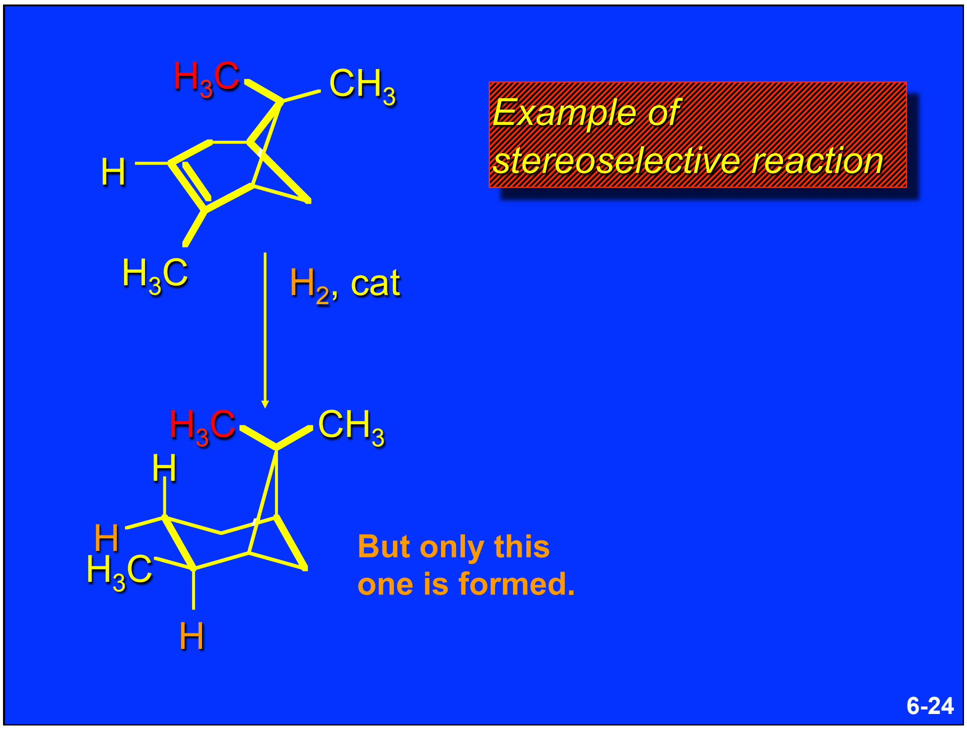
Stereoselectivity

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**.



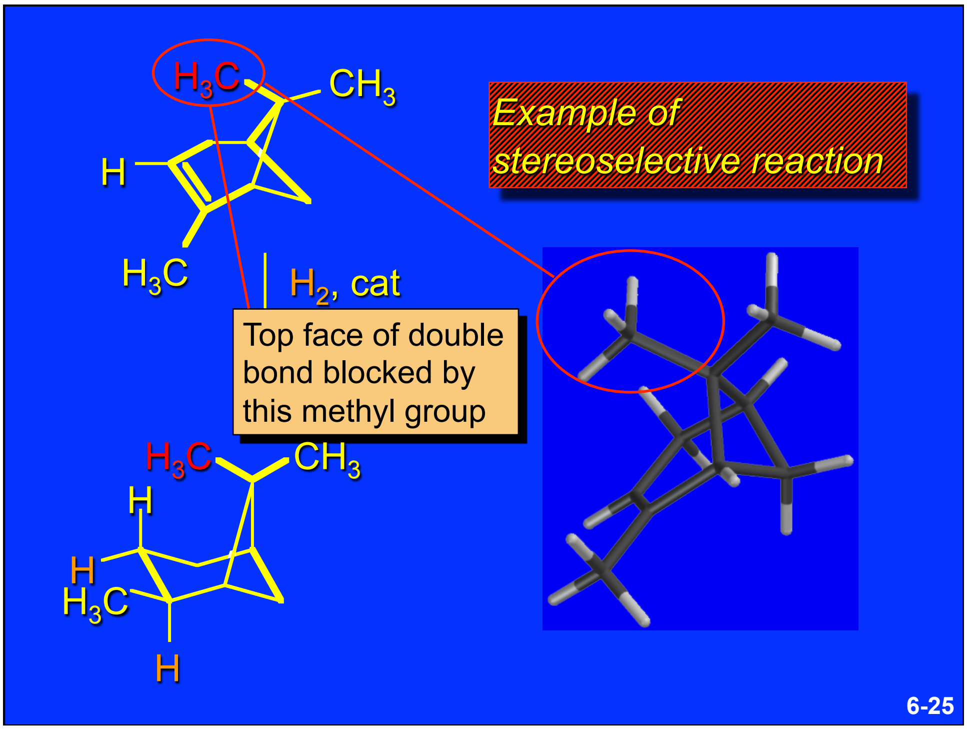
Example of stereoselective reaction

Both products correspond to syn addition of H_2.



Example of stereoselective reaction

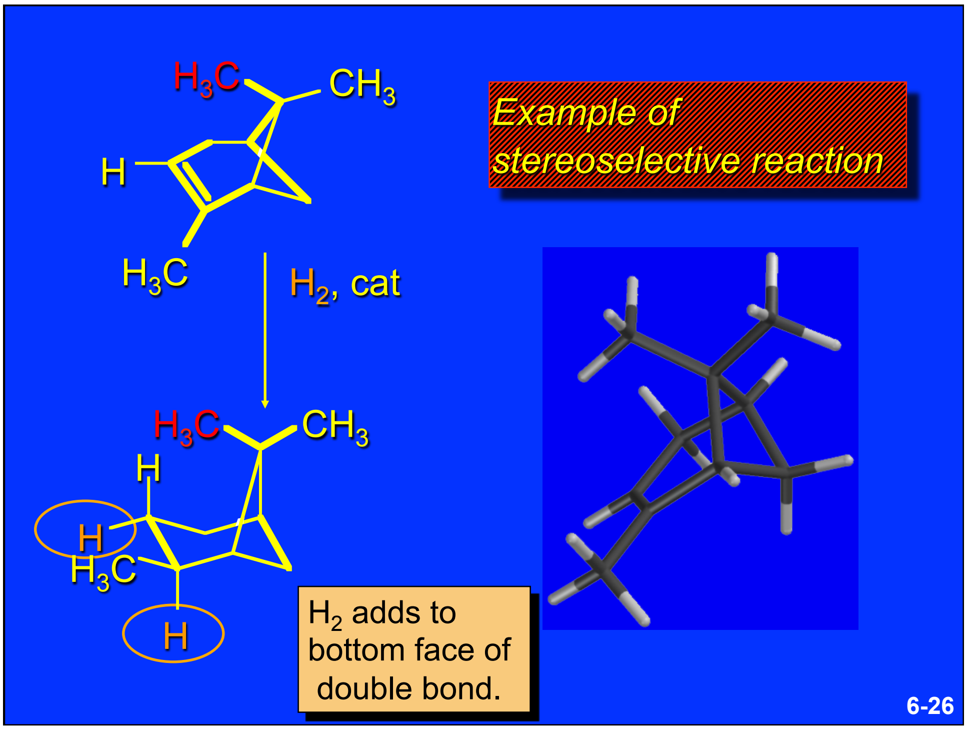
But only this one is formed.



Example of stereoselective reaction

H_2, cat

Top face of double bond blocked by this methyl group

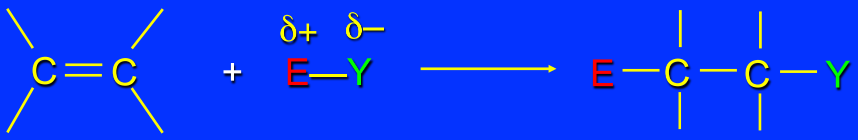


Example of stereoselective reaction

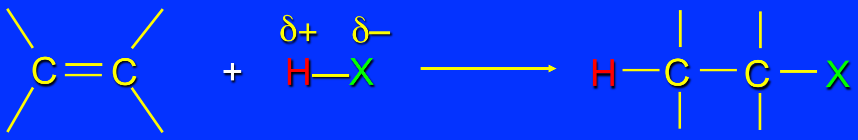
H_2, cat

H_2 adds to bottom face of double bond.

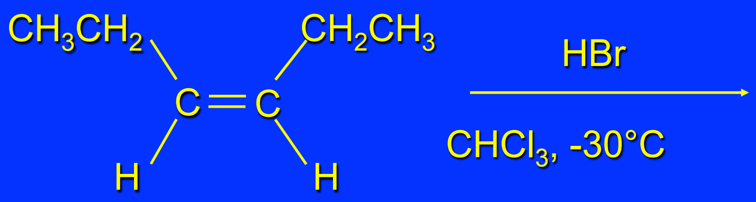
Electrophilic Addition of Hydrogen Halides to Alkenes

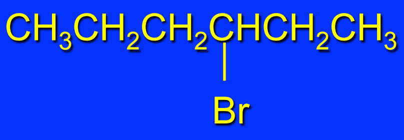


When EY is a hydrogen halide



Example





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

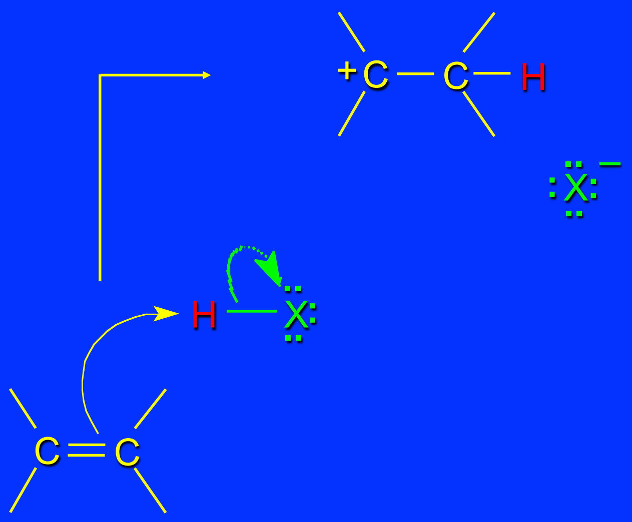
(76%)

Mechanism

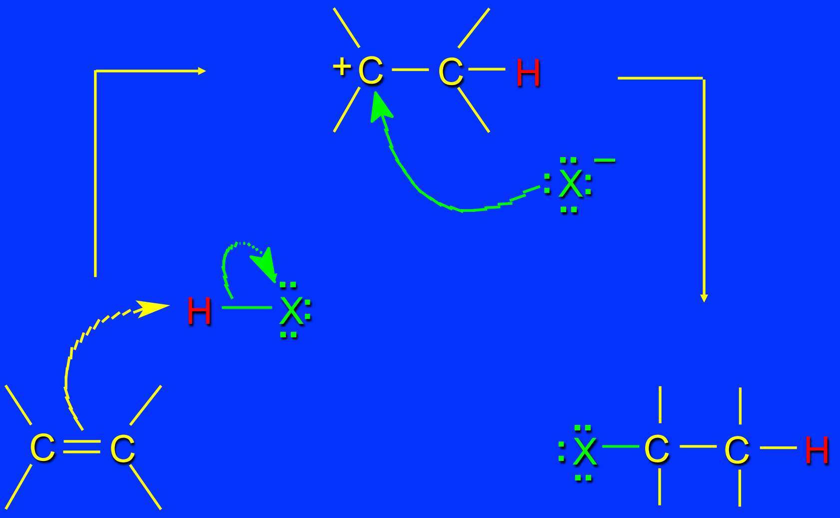
Electrophilic addition of hydrogen halides to alkenes proceeds by rate-determining formation of a carbocation intermediate.

Electrons flow from the π system of the alkene (electron rich) toward the positively polarized proton of the hydrogen halide.

Mechanism



Mechanism

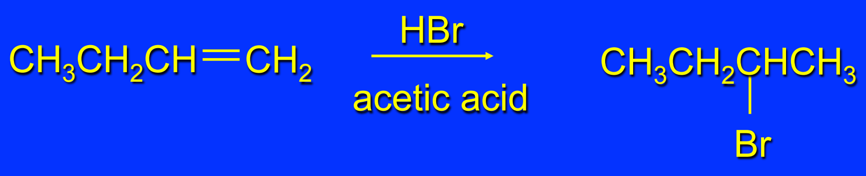


Regioselectivity of Hydrogen Halide Addition:

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

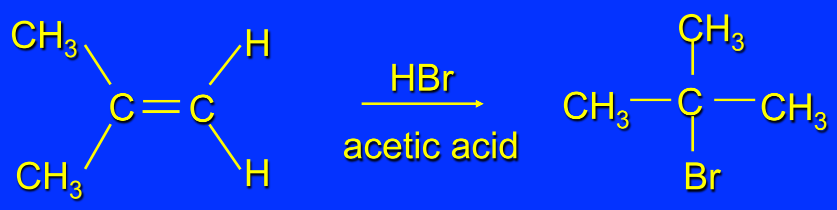


$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{acetic acid}]{HBr} CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$

(80%)

Example 1

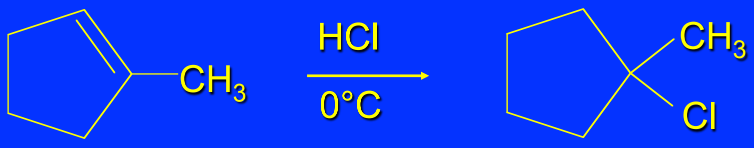
Markovnikov's Rule



(90%)

Example 2

Markovnikov's Rule



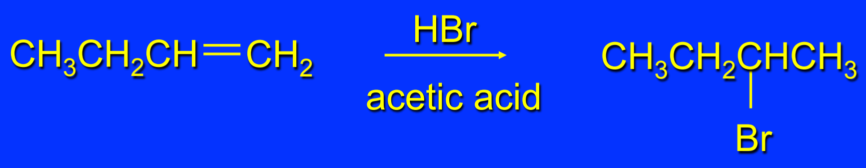
(100%)

Example 3

Mechanistic Basis for Markovnikov's Rule

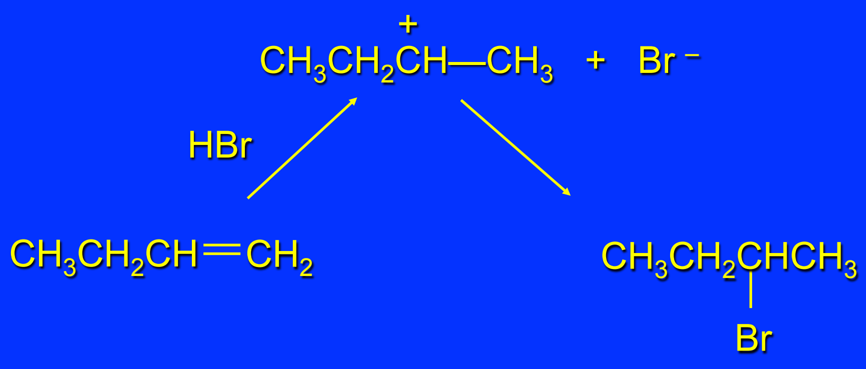
Protonation of double bond occurs in direction that gives more stable of two possible carbocations.

Mechanistic Basis for Markovnikov's Rule: Example 1



$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{acetic acid}]{HBr} CH_3CH_2\underset{\substack{|\\ Br}}{C}HCH_3$$

Mechanistic Basis for Markovnikov's Rule: Example 1

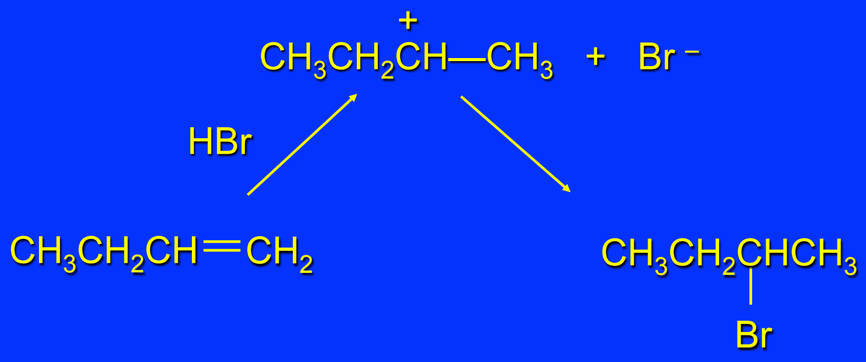


$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr} CH_3CH_2\overset{+}{C}H{-}CH_3 + Br^{-} \longrightarrow CH_3CH_2\underset{\substack{|\\ Br}}{C}HCH_3$$

Mechanistic Basis for Markovnikov's Rule: Example 1

$CH_3CH_2CH_2\text{—}\overset{+}{C}H_2$

primary carbocation is less stable: not formed

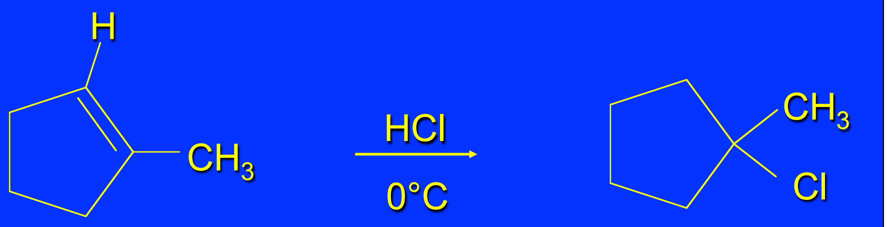


$CH_3CH_2\overset{+}{C}H\text{—}CH_3 + Br^-$

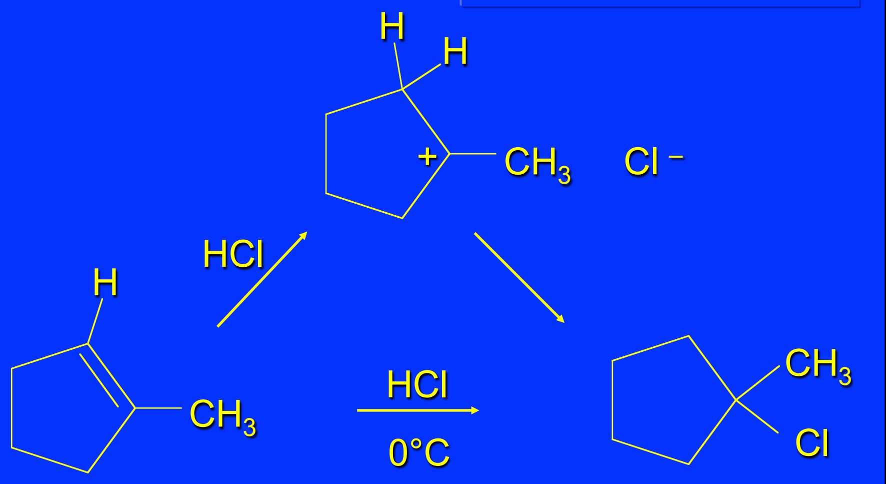
$CH_3CH_2CH{=}CH_2$

$CH_3CH_2CHCH_3$ with Br on C-2

Mechanistic Basis for Markovnikov's Rule: Example 3

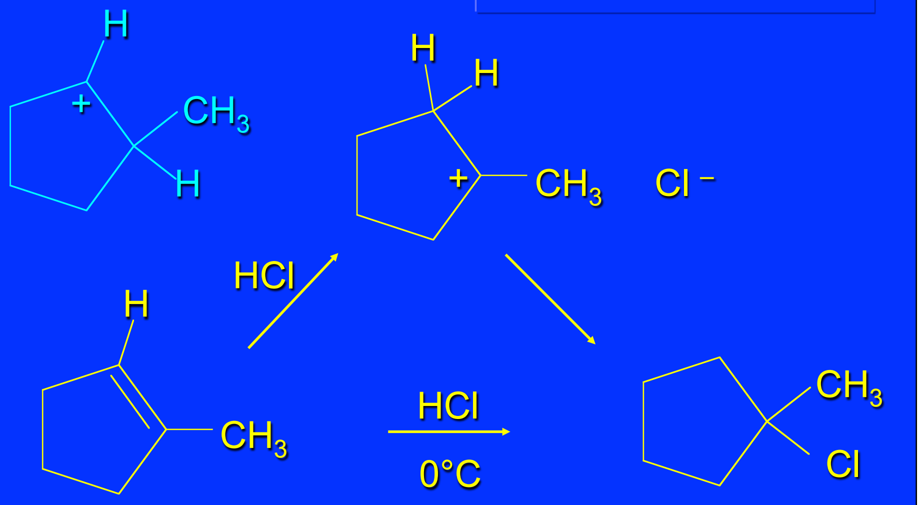


Mechanistic Basis for Markovnikov's Rule: Example 3

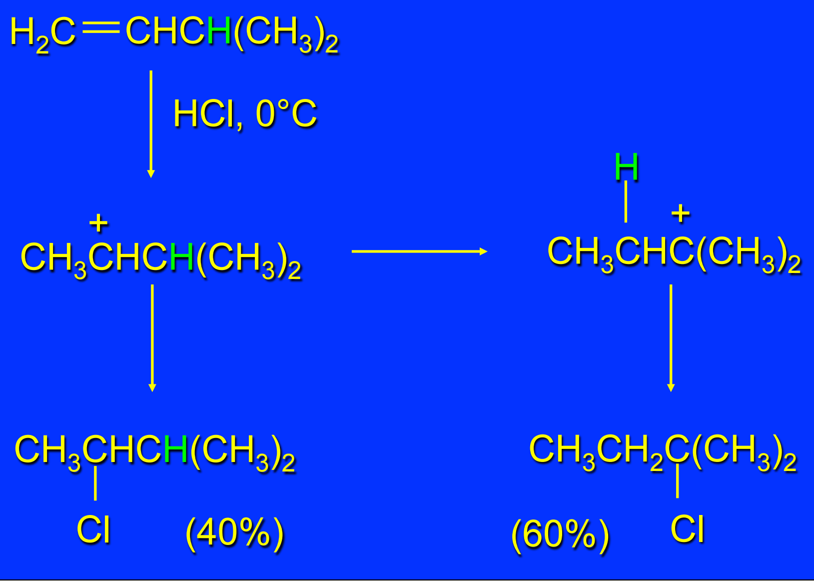


Mechanistic Basis for Markovnikov's Rule: Example 3

secondary carbocation is less stable: not formed



Carbocation rearrangements sometimes occur



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

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

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

Free-radical Addition of HBr to Alkenes

The "peroxide effect"

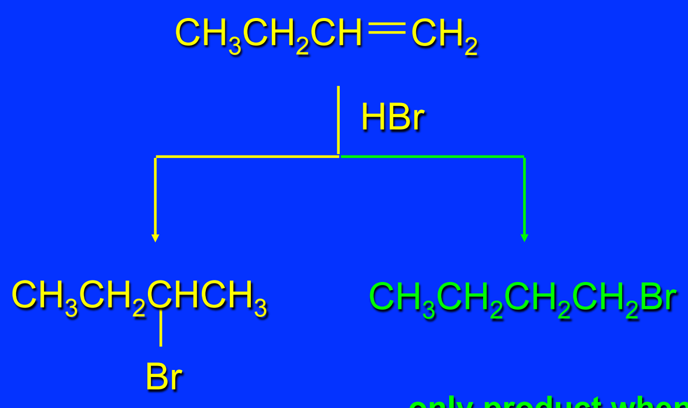
Markovnikov's Rule

$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{acetic acid}]{\text{HBr}} CH_3CH_2\underset{Br}{C}HCH_3$$

(80%)

Example 1

Addition of HBr to 1-Butene



$CH_3CH_2CH{=}CH_2$

HBr

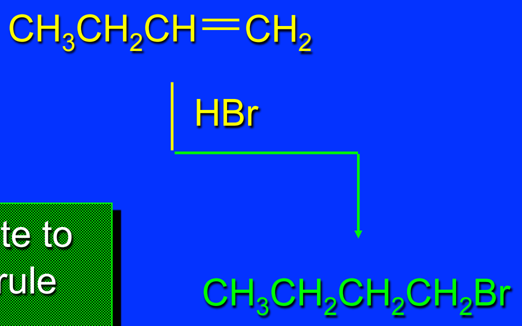
$\underset{\textstyle Br}{CH_3CH_2\overset{}{C}HCH_3}$

$CH_3CH_2CH_2CH_2Br$

only product in absence of peroxides

only product when peroxides added to reaction mixture

Addition of HBr to 1-Butene



$CH_3CH_2CH{=}CH_2$

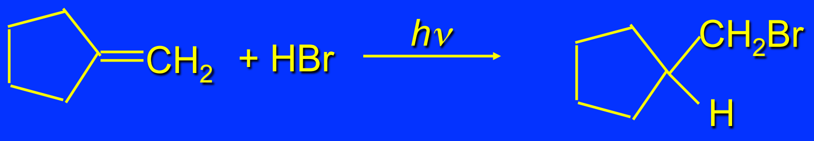
HBr

$CH_3CH_2CH_2CH_2Br$

addition opposite to Markovnikov's rule

occurs with HBr (not HCl or HI)

only product when peroxides added to reaction mixture



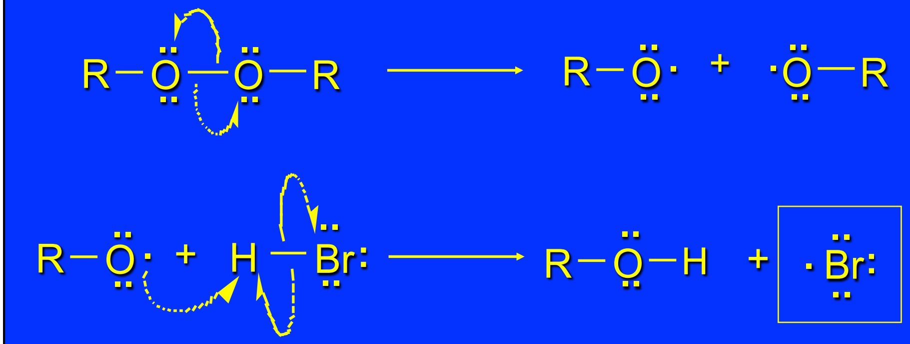
(60%)

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

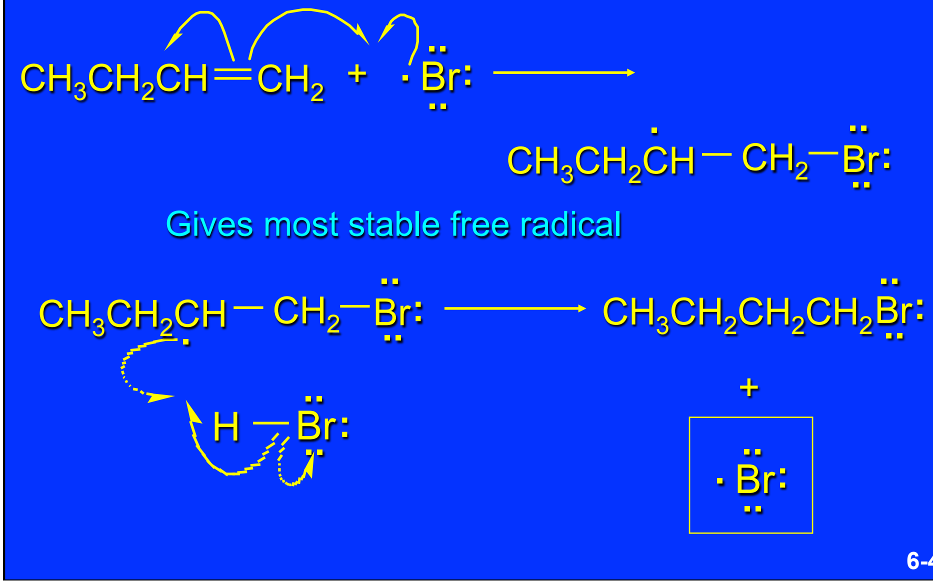
Mechanism

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

Initiation steps:



Propagation steps:

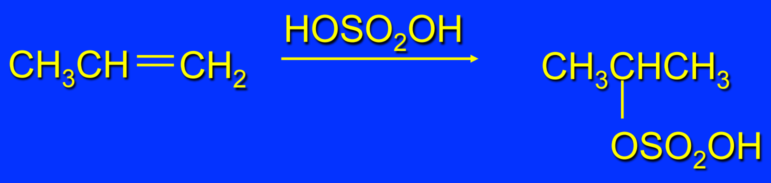


$$CH_3CH_2CH{=}CH_2 + \cdot\ddot{\underset{..}{Br}}: \longrightarrow CH_3CH_2\dot{C}H-CH_2-\ddot{\underset{..}{Br}}:$$

Gives most stable free radical

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

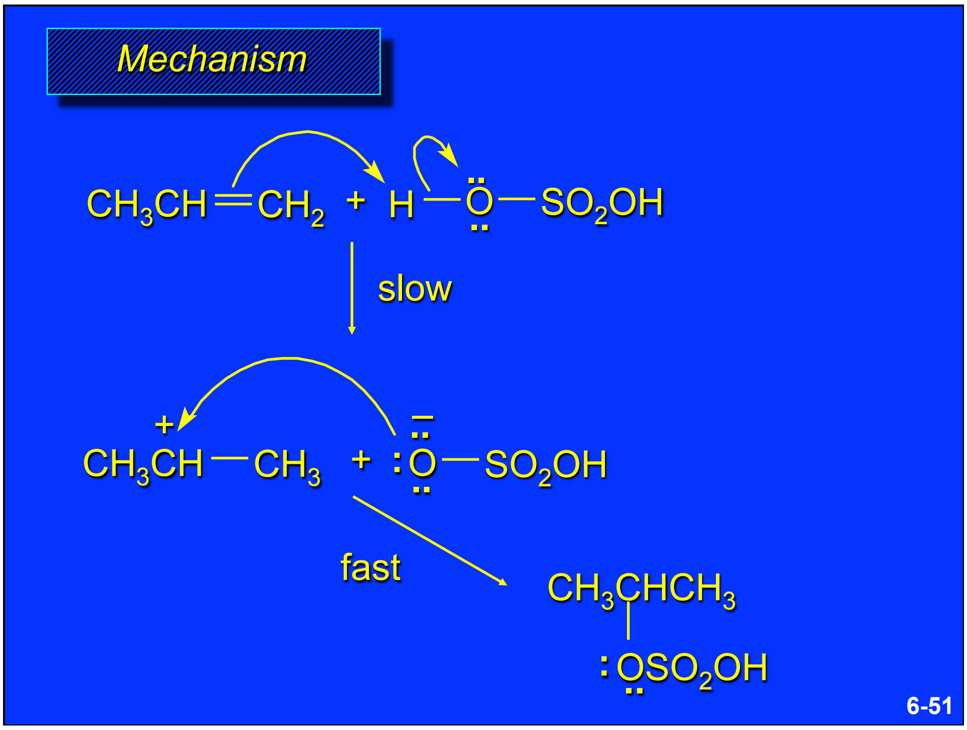
Addition of Sulfuric Acid (H_2SO_4) to Alkenes



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

Isopropyl
hydrogen sulfate

follows Markovnikov's rule:
yields an alkyl hydrogen sulfate



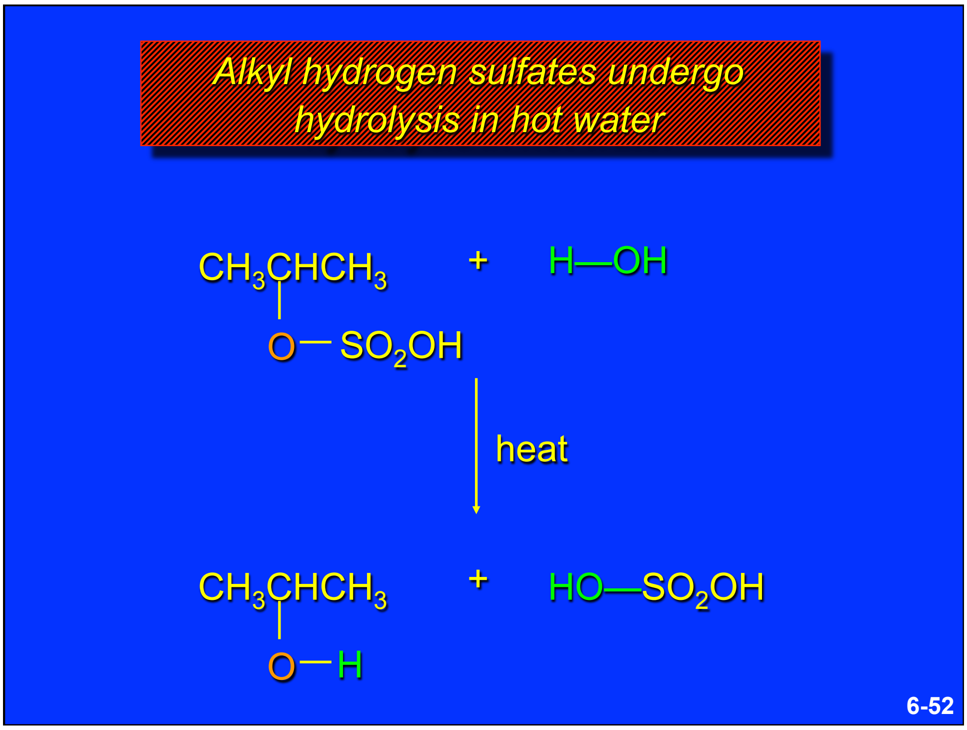
Mechanism

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

$$\Big\downarrow \text{slow}$$

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

$$\xrightarrow{\text{fast}} CH_3\underset{|\atop :\ddot{O}SO_2OH}{C}HCH_3$$



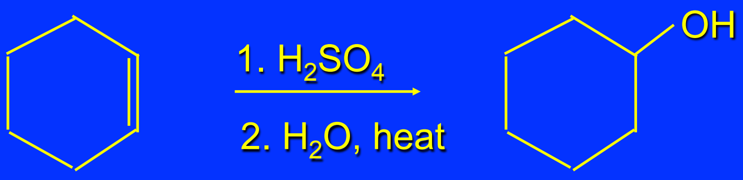
Alkyl hydrogen sulfates undergo hydrolysis in hot water

$$CH_3\underset{|\atop O-SO_2OH}{C}HCH_3 \quad + \quad H{-}OH$$

$$\Big\downarrow \text{heat}$$

$$CH_3\underset{|\atop O-H}{C}HCH_3 \quad + \quad HO{-}SO_2OH$$

Application: Coversion of alkenes to alcohols



$\xrightarrow[\text{2. } H_2O\text{, heat}]{\text{1. } H_2SO_4}$

(75%)

But...

not all alkenes yield alkyl hydrogen sulfates on reaction with sulfuric acid (concentrated).

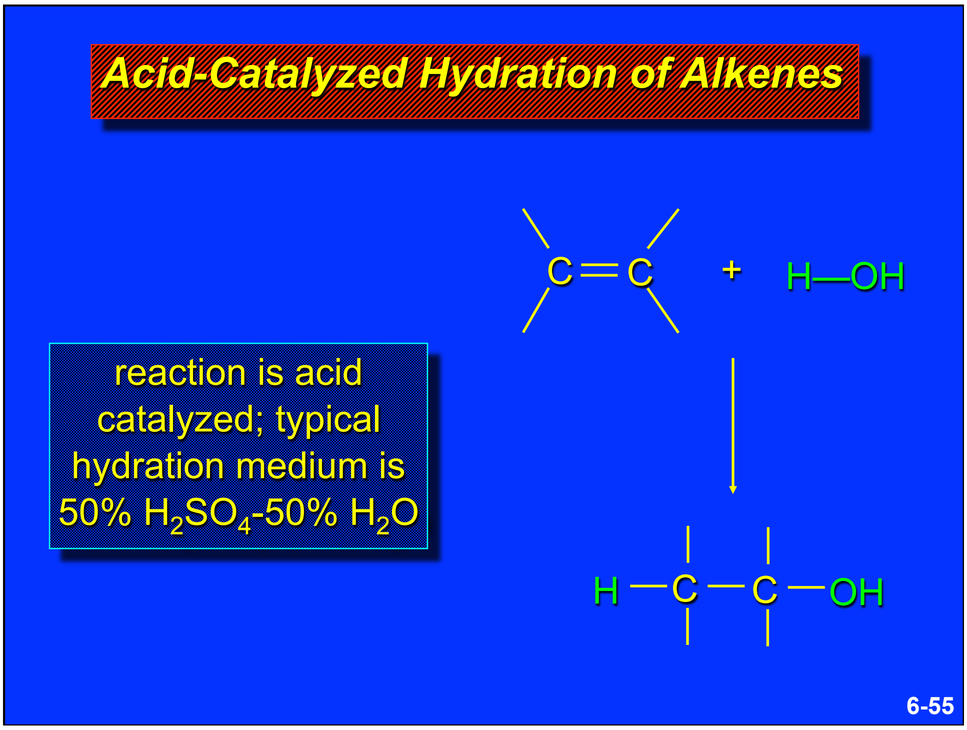
these do:

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

these don't:

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

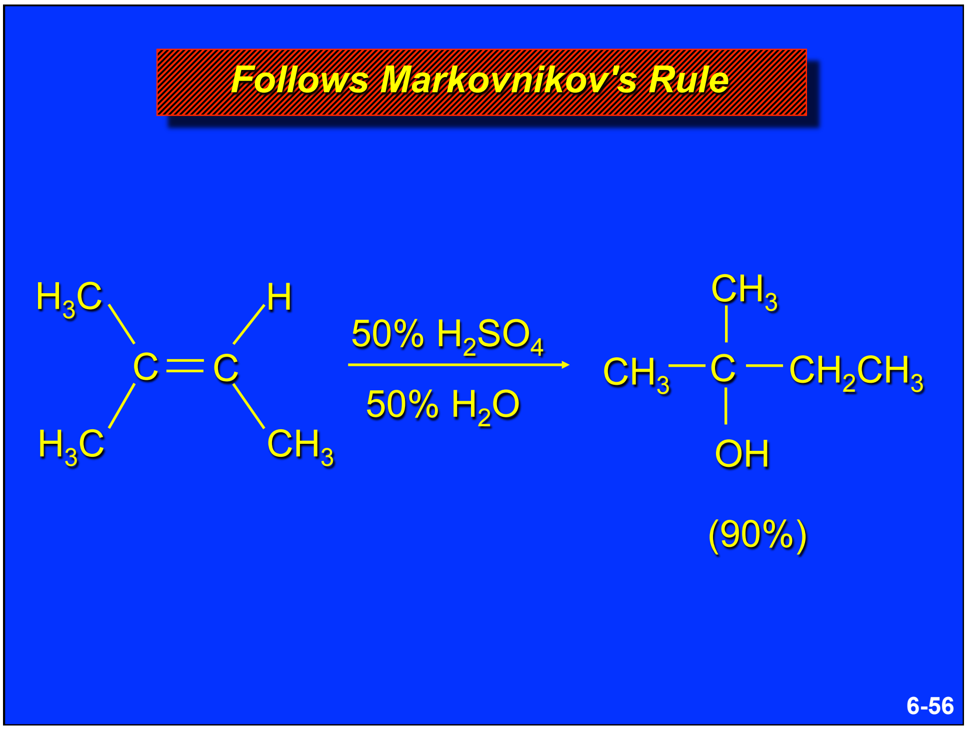
(These form polymers, sec 6.21)



Acid-Catalyzed Hydration of Alkenes

reaction is acid catalyzed; typical hydration medium is 50% H_2SO_4-50% H_2O

$$\text{C}{=}\text{C} + \text{H—OH} \longrightarrow \text{H—C—C—OH}$$

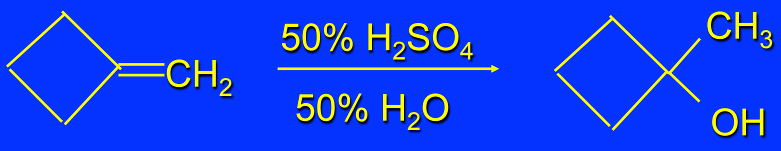


Follows Markovnikov's Rule

$$(H_3C)_2C{=}C(H)CH_3 \xrightarrow[50\%\ H_2O]{50\%\ H_2SO_4} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{-}CH_2CH_3$$

(90%)

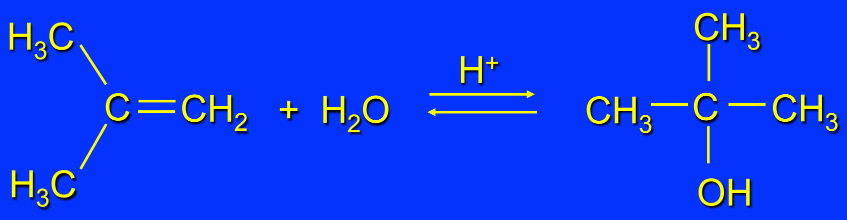
Follows Markovnikov's Rule



(80%)

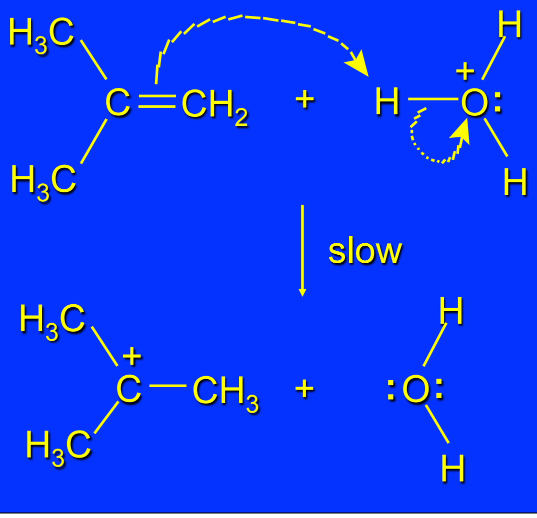
Mechanism

involves a carbocation intermediate and is the reverse of acid-catalyzed dehydration of alcohols to alkenes



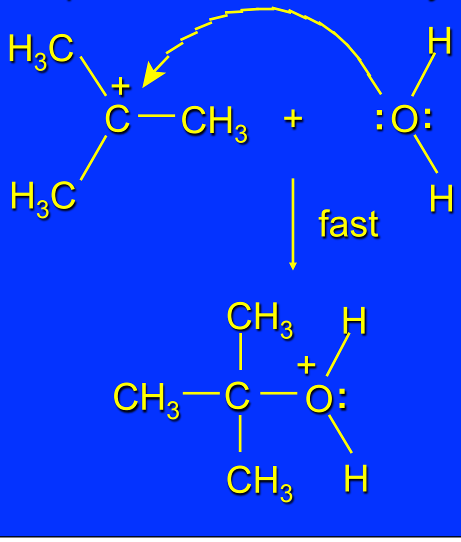
Mechanism

Step (1) Protonation of double bond



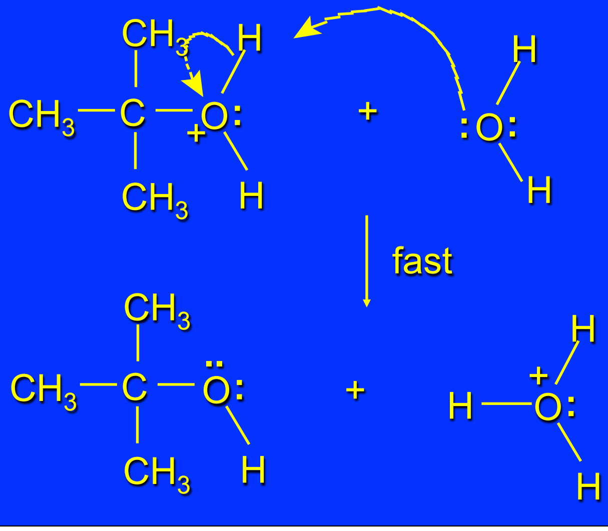
Mechanism

Step (2) Capture of carbocation by water



Mechanism

Step (3) Deprotonation of oxonium ion



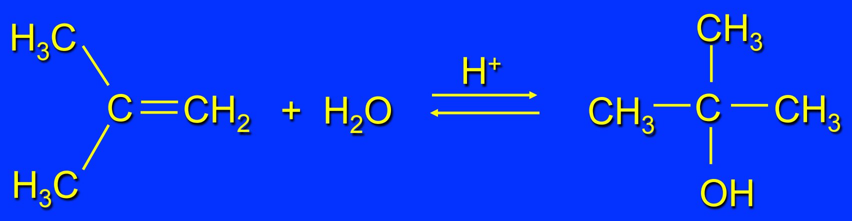
Relative Rates

Acid-catalyzed hydration

ethylene	$CH_2{=}CH_2$	1.0
propene	$CH_3CH{=}CH_2$	1.6×10^6
2-methylpropene	$(CH_3)_2C{=}CH_2$	2.5×10^{11}

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

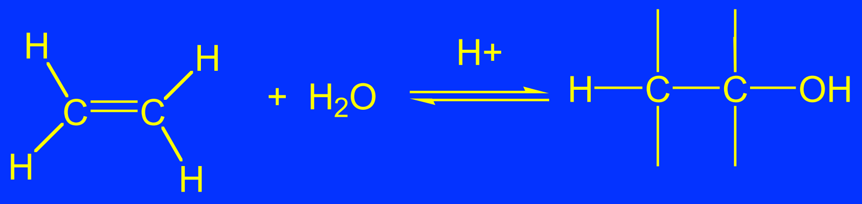
Principle of microscopic reversibility



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

Thermodynamics of Addition-Elimination Equilibria

Hydration-Dehydration Equilibrium



How do we control the position of the equilibrium and maximize the product?

Le Chatelier’ s Principle

A system at equilibrium adjusts so to minimize any stress applies to it.

For the hydration-dehydration equilibria, **the key stress is water.**

Adding water pushes the equilibrium toward more product (alcohol).

Removing water pushes the equilibrium toward more reactant (alkene).

Le Chatelier’ s Principle

At constant temperature and pressure a reaction proceeds in a direction which is spontaneous or decreases free energy (G).

The sign of G is always positive, but ΔG can be positive or negative.

$$\Delta G = G_{products} - G_{reactants}$$

Spontaneous when $\Delta G < 0$

Le Chatelier's Principle

For a reversible reaction:

$$aA + bB \leftrightarrow cC + dD$$

The relationship between ΔG and ΔG^o is:

$$\Delta G = \Delta G^o + RT \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

R = 8.314 J/(mol·K) and T is the temperature in K

Le Chatelier's Principle

At equilibrium, $\Delta G = 0$ and the following becomes true:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Substituting K_{eq} into the previous equation gives:

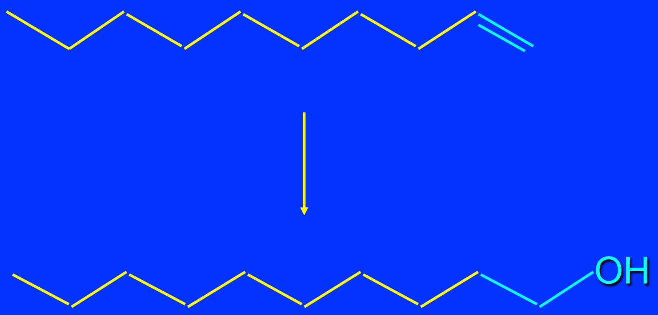
$$\Delta G^o = - RT \ln K_{eq}$$

Reactions for ΔG^o positive are endergonic and for

ΔG^o negative are exergonic.

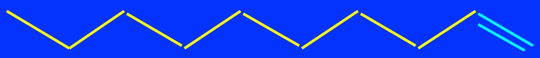
Hydroboration-Oxidation of Alkenes

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

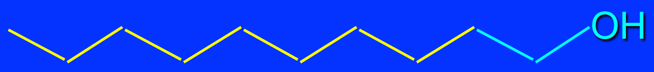


Synthesis

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

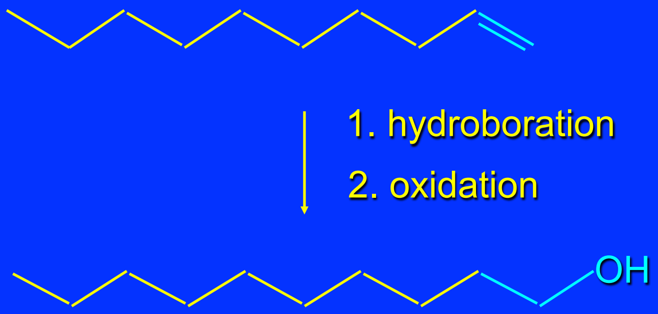


Needed: a method for hydration of alkenes with a regioselectivity opposite to Markovnikov's rule.



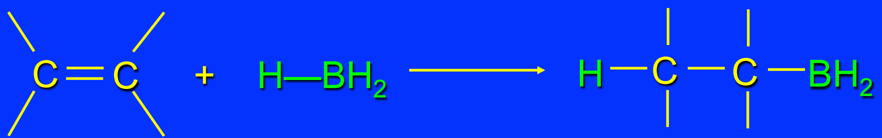
Synthesis

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



1. hydroboration
2. oxidation

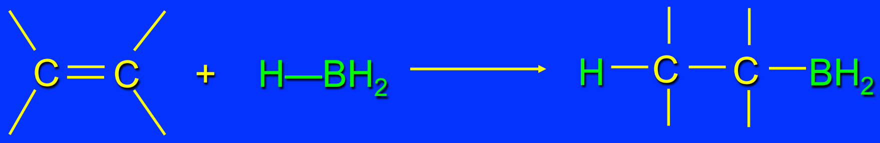
Hydroboration step



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

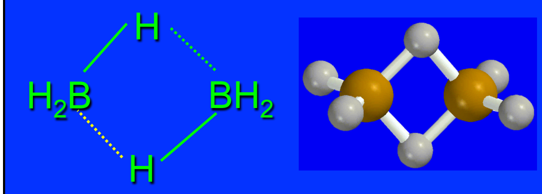
Hydroboration can be viewed as the addition of borane (BH_3) to the double bond. But BH_3 is not the reagent actually used.

Hydroboration step



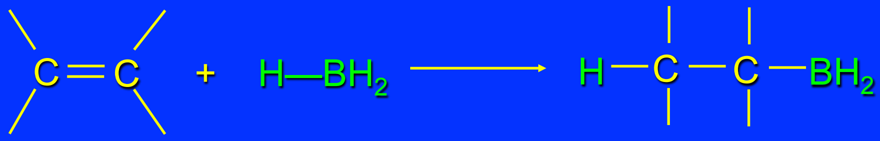
$$C{=}C \; + \; H{-}BH_2 \longrightarrow H{-}C{-}C{-}BH_2$$

Hydroboration reagents:



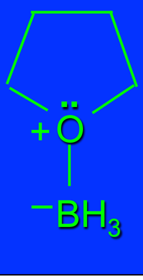
Diborane (B_2H_6) normally used in an ether- like solvent called "diglyme"

Hydroboration step



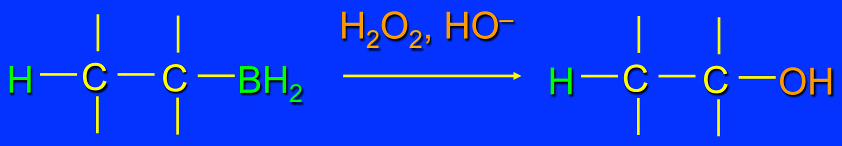
$$C{=}C \; + \; H{-}BH_2 \longrightarrow H{-}C{-}C{-}BH_2$$

Hydroboration reagents:



Borane-tetrahydrofuran complex (H_3B-THF)

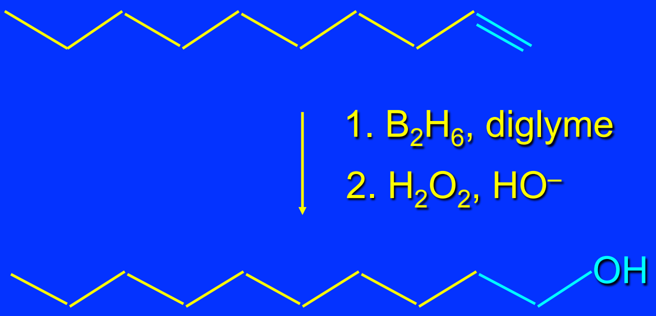
Oxidation step



$$H-C-C-BH_2 \xrightarrow{H_2O_2,\ HO^-} H-C-C-OH$$

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

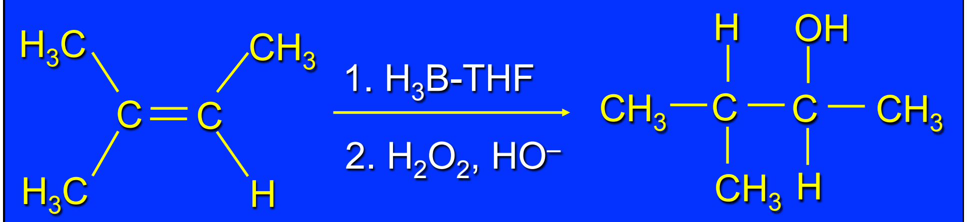
Example



1. B_2H_6, diglyme
2. H_2O_2, HO^-

(93%)

Example

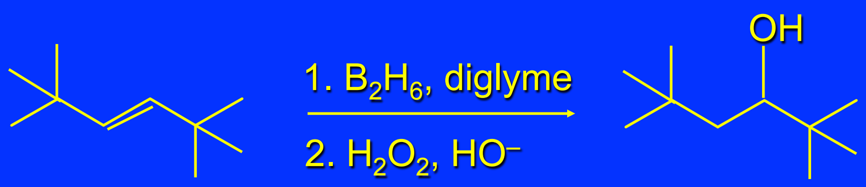


1. H_3B-THF

2. H_2O_2, HO^-

(98%)

Example



1. B_2H_6, diglyme

2. H_2O_2, HO^-

(82%)

(no rearrangement)

Features and Stereochemistry of Hydroboration-Oxidation

- hydration of alkenes
- regioselectivity opposite to Markovnikov's rule
- no rearrangement
- stereospecific *syn* addition

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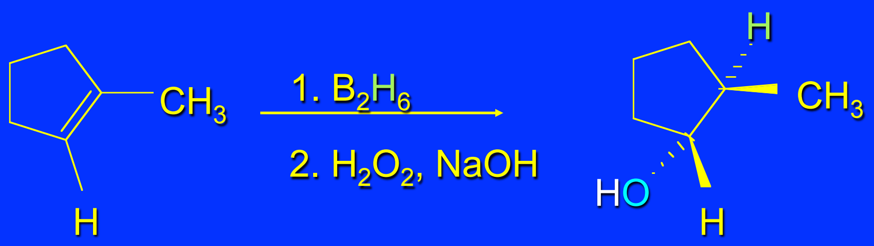
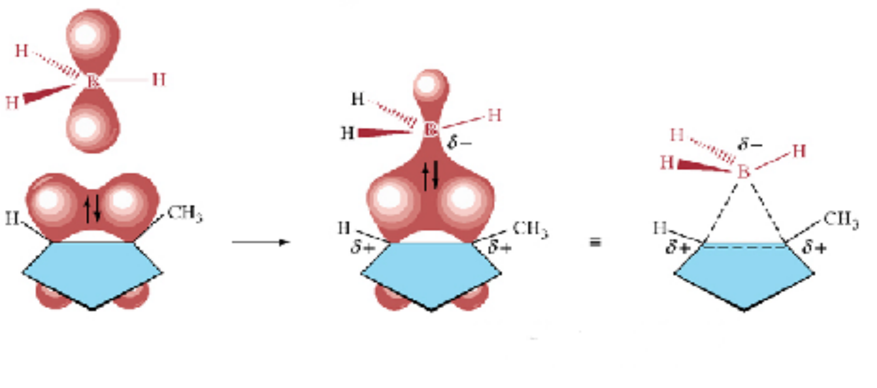
syn-Addition

- H and OH attach to the same face of double bond



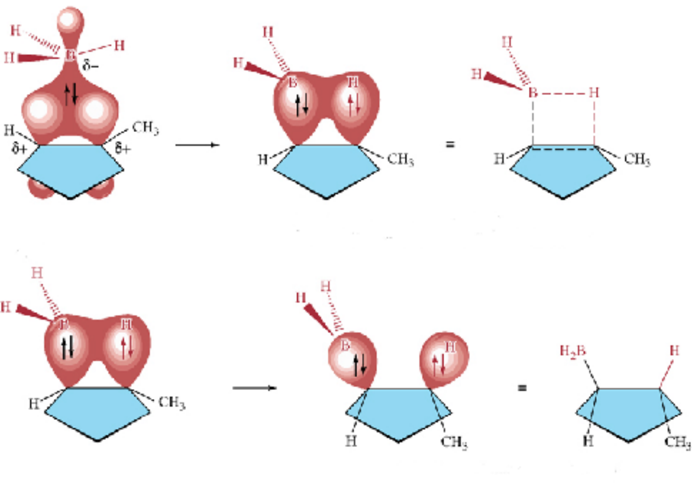
only product is *trans*-2-methylcyclopentanol (86%) yield

Mechanism of Hydroboration-oxidation



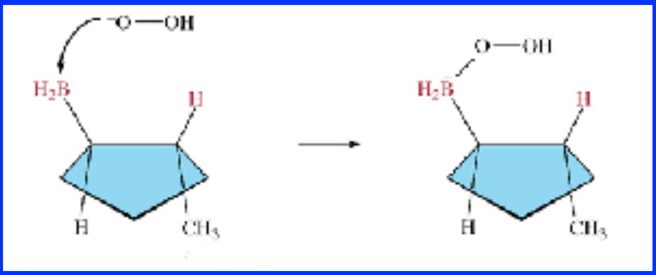
π electrons from alkene flow into 2p orbital of boron

Hydroboration-oxidation



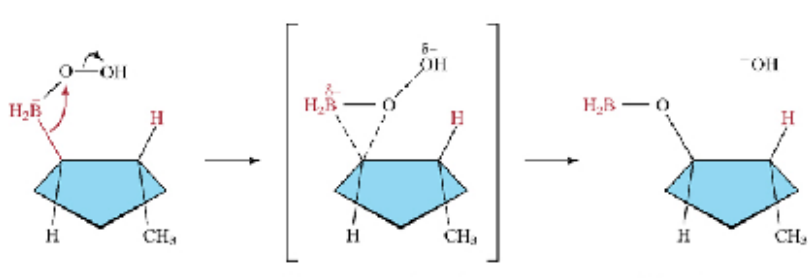
H atom with 2 electrons migrates to C with greatest (+) charge (most highly substituted). Syn add.

Hydroboration-oxidation



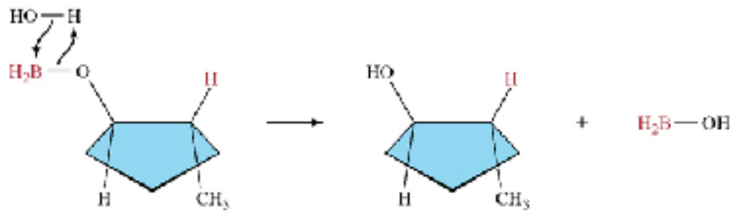
Anion of hydrogen peroxide attacks boron

Hydroboration-oxidation



Carbon with pair of electrons migrates to oxygen, displacing hydroxide. Oxygen on same side as boron

Hydroboration-oxidation



Hydrolysis cleaves boron-oxygen bond resulting in anti-Markovnikov addition

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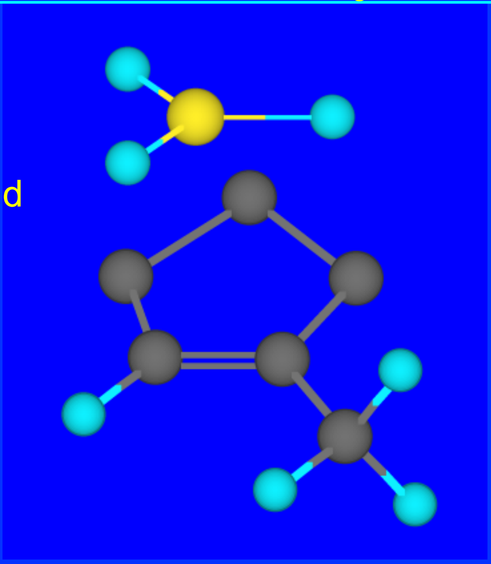
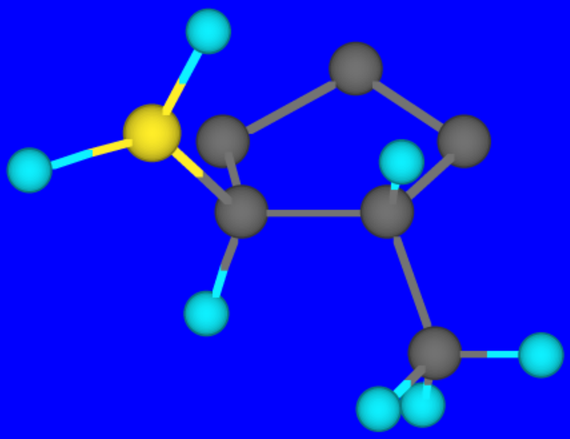
1-Methylcyclopentene + BH_3

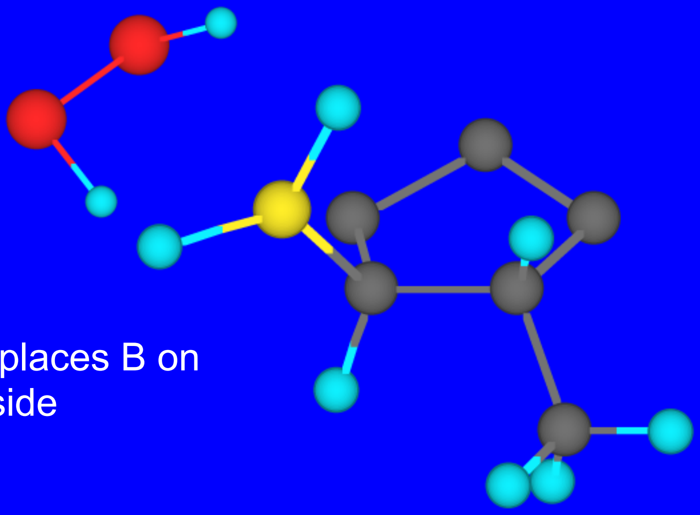
- syn addition of H and B to double bond
- B adds to less substituted carbon



Organoborane intermediate

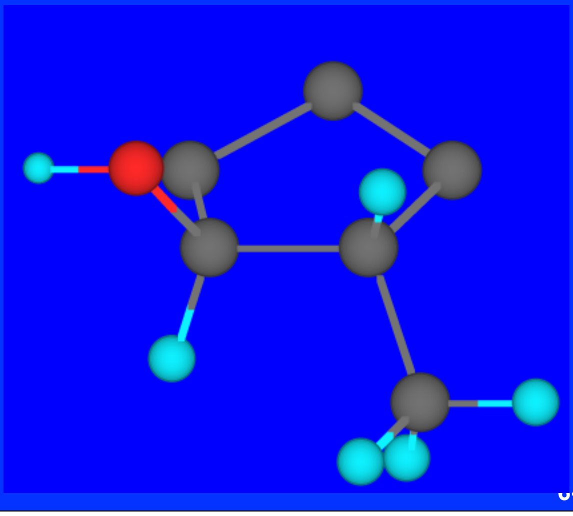


Add hydrogen peroxide

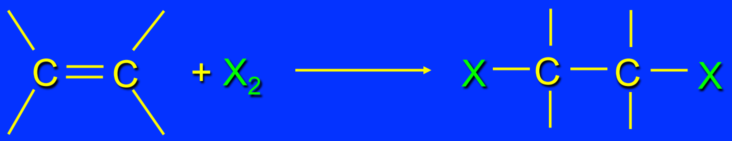


- OH replaces B on same side

trans-2-Methylcyclopentanol

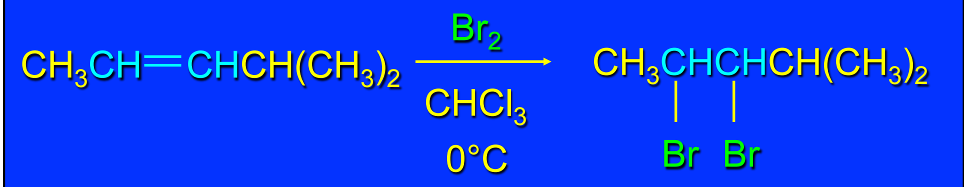


Addition of Halogens to Alkenes



electrophilic addition to double bond forms a dihalide

Example



$$CH_3CH{=}CHCH(CH_3)_2 \xrightarrow[\substack{CHCl_3 \\ 0°C}]{Br_2} CH_3\underset{\displaystyle Br}{\underset{|}{C}H}\underset{\displaystyle Br}{\underset{|}{C}H}CH(CH_3)_2$$

(100%)

Scope

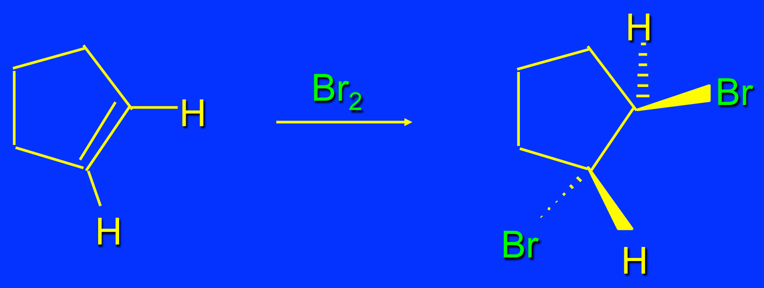
Limited to Cl_2 and Br_2

F_2 addition proceeds with explosive violence

I_2 addition is endothermic:

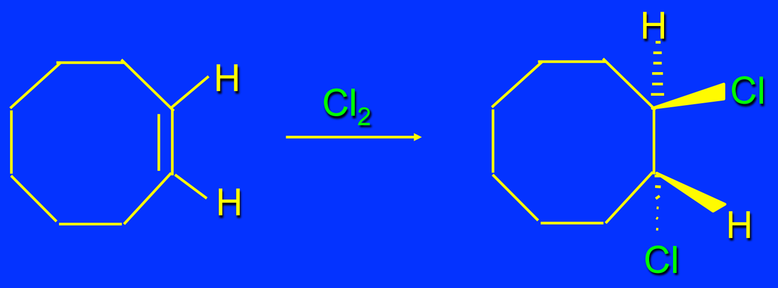
vicinal diiodides dissociate to an alkene and I_2

Stereochemistry of Halogen Addition: ***Anti*-Addition**



trans-1,2-Dibromocyclopentane
80% yield; only product

Example



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

Relative Rates

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 of Halogen Addition to Alkenes: Halonium Ions

Mechanism is electrophilic addition

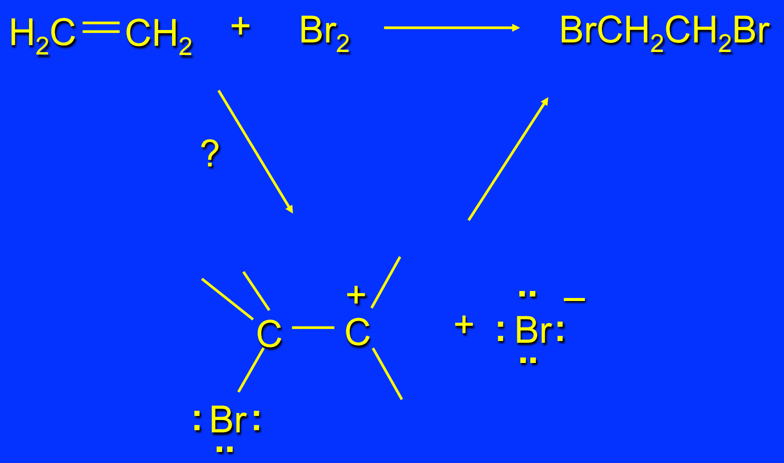
Br_2 is not polar, but it is polarizable

two steps involved

(1) formation of bromonium ion

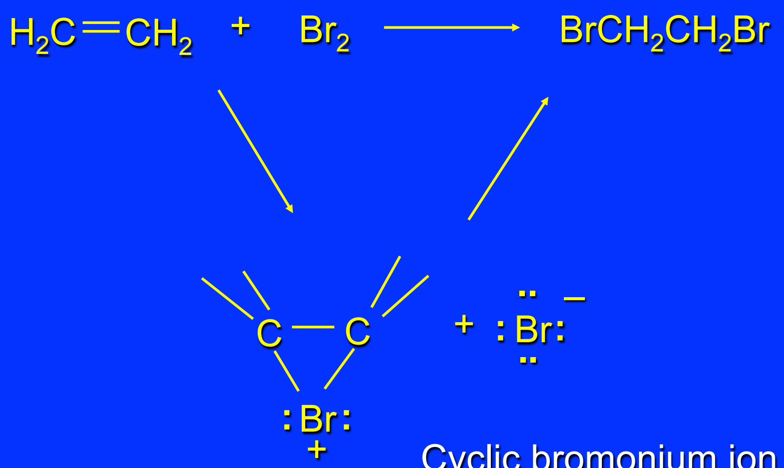
(2) nucleophilic attack on bromonium ion by bromide

Mechanism?

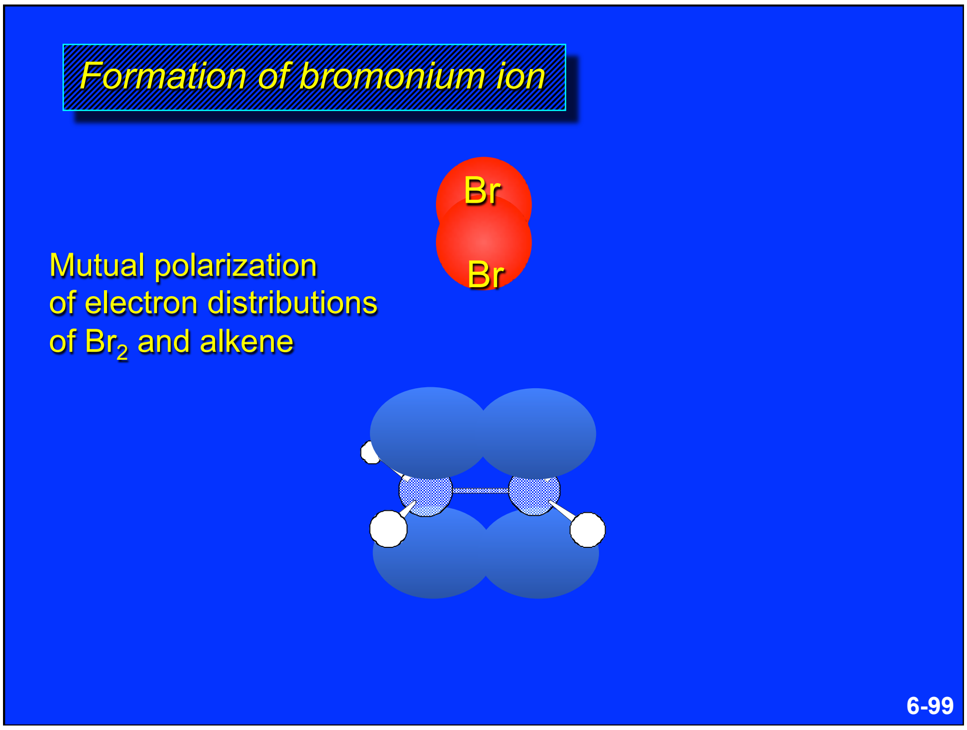

$H_2C{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$

No obvious explanation for anti addition provided by this mechanism.

Mechanism

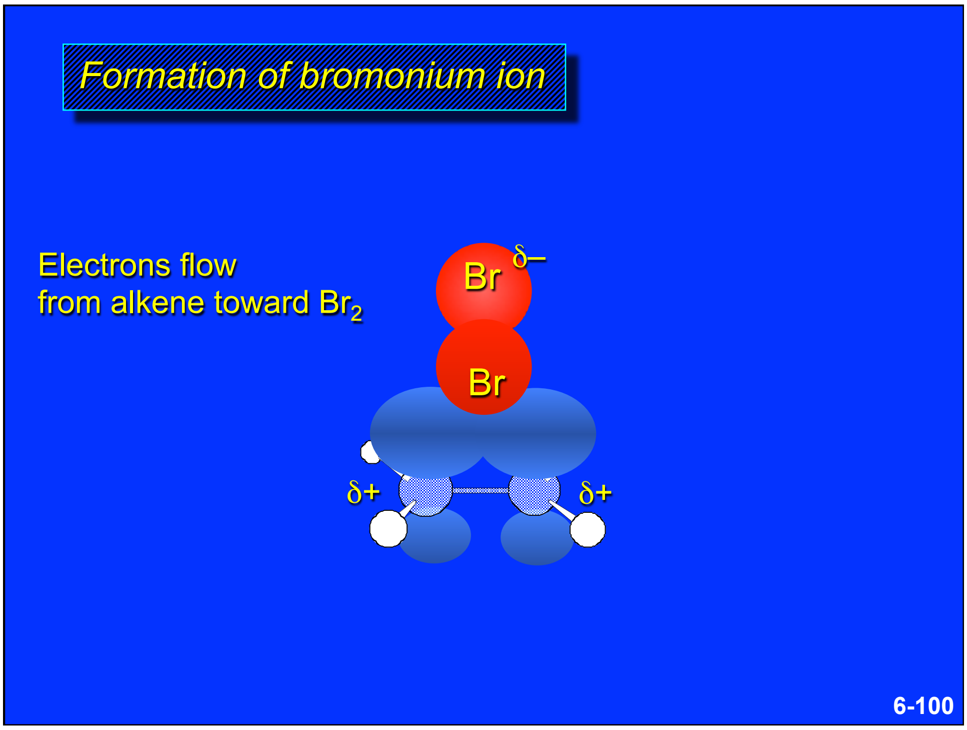

$H_2C{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$

Cyclic bromonium ion



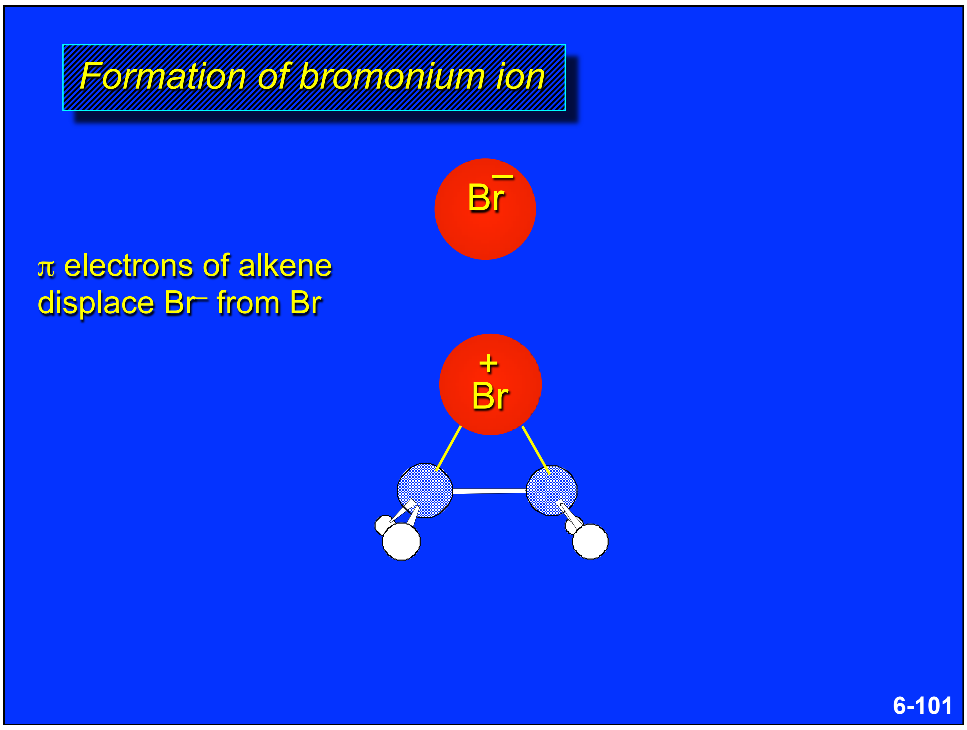
Formation of bromonium ion

Mutual polarization
of electron distributions
of Br_2 and alkene



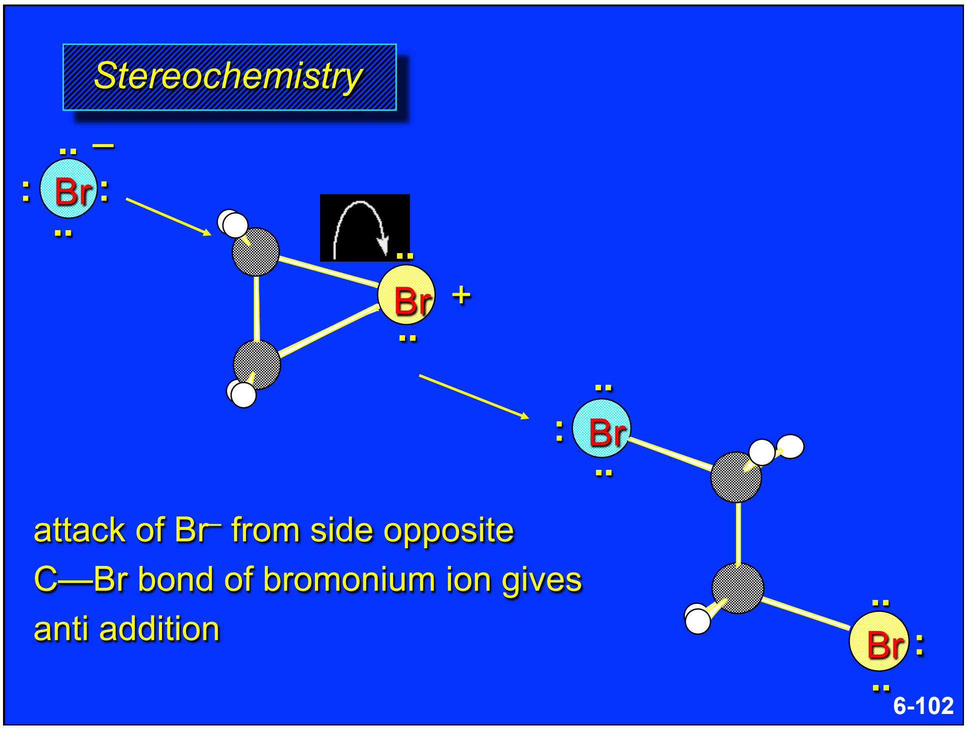
Formation of bromonium ion

Electrons flow
from alkene toward Br_2



Formation of bromonium ion

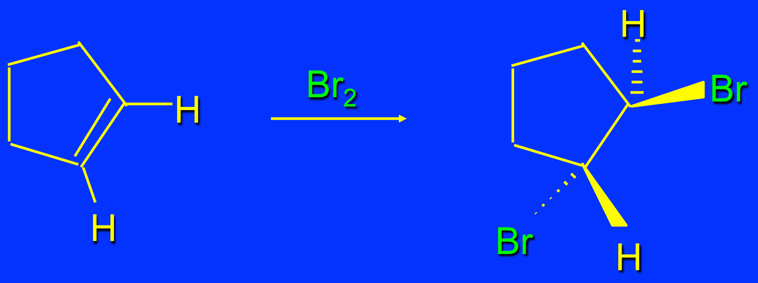
π electrons of alkene
displace Br^- from Br



Stereochemistry

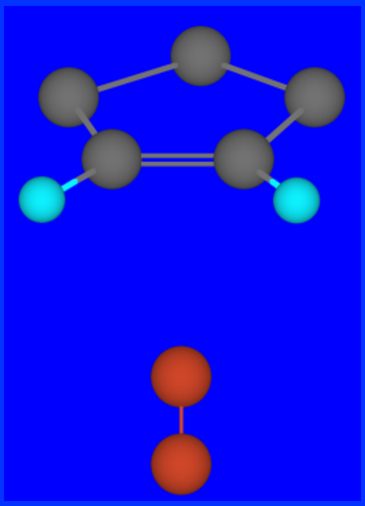
attack of Br^- from side opposite
C—Br bond of bromonium ion gives
anti addition

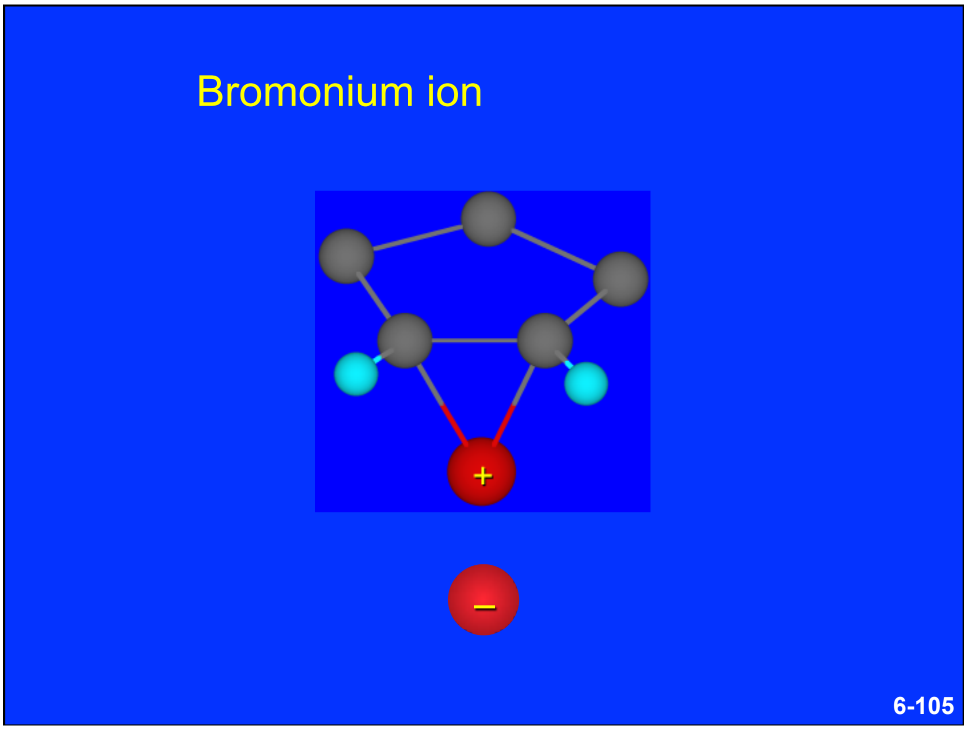
Example



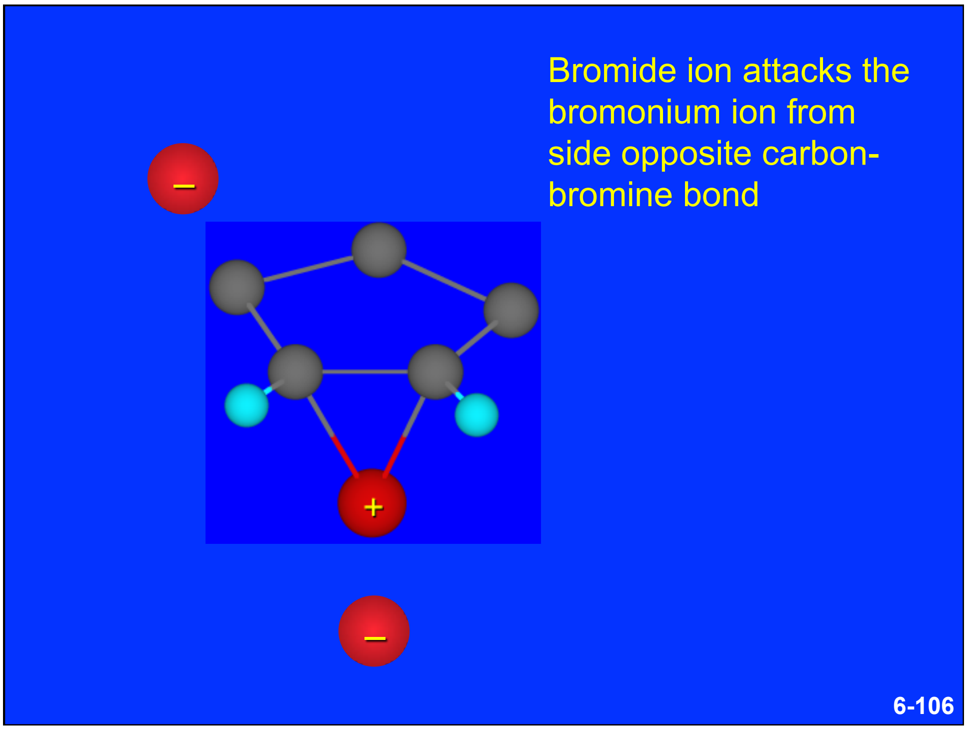
trans-1,2-Dibromocyclopentane
80% yield; only product

Cyclopentene
$+Br_2$

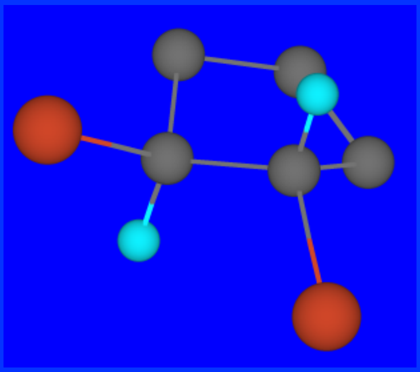




Bromonium ion



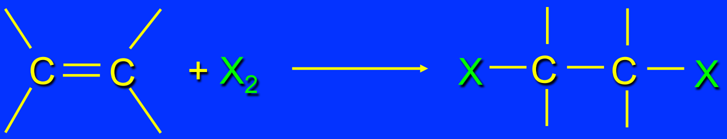
Bromide ion attacks the bromonium ion from side opposite carbon-bromine bond



trans-Stereochemistry in
vicinal dibromide

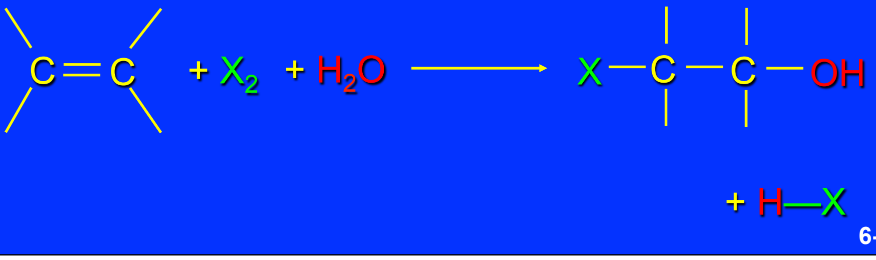
Conversion of Alkenes to Vicinal Halohydrins

alkenes react with X_2 to form vicinal dihalides



$$C{=}C + X_2 \longrightarrow X{-}C{-}C{-}X$$

alkenes react with X_2 in water to give vicinal halohydrins

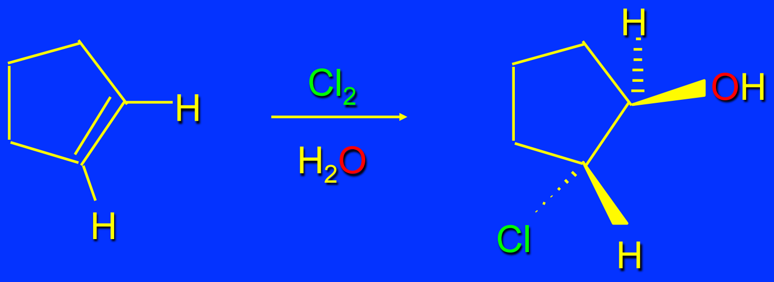


$$C{=}C + X_2 + H_2O \longrightarrow X{-}C{-}C{-}OH + H{-}X$$

Examples

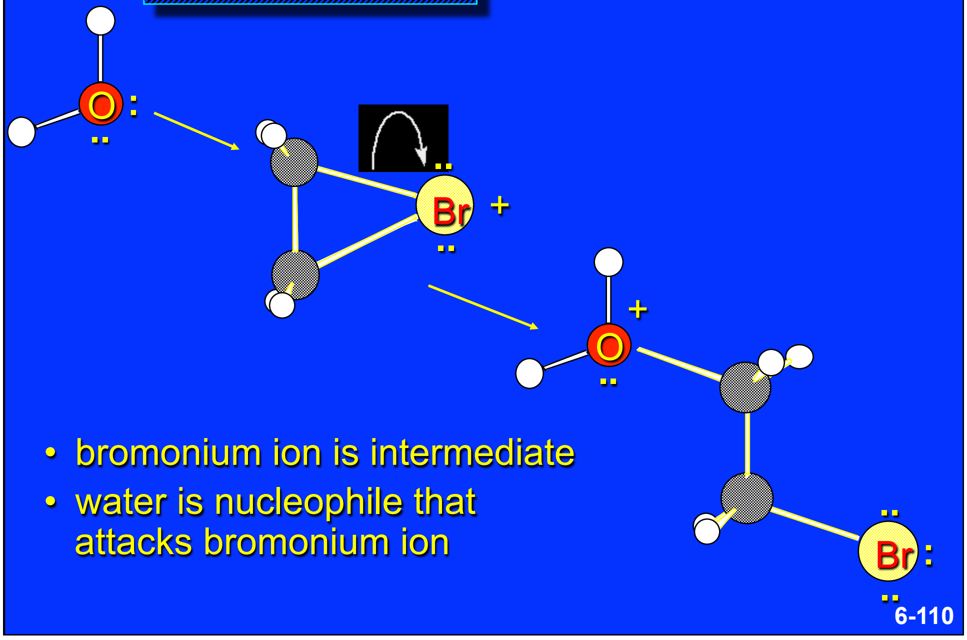
$$H_2C{=}CH_2 \quad + \quad Br_2 \xrightarrow{H_2O} BrCH_2CH_2OH$$

(70%)

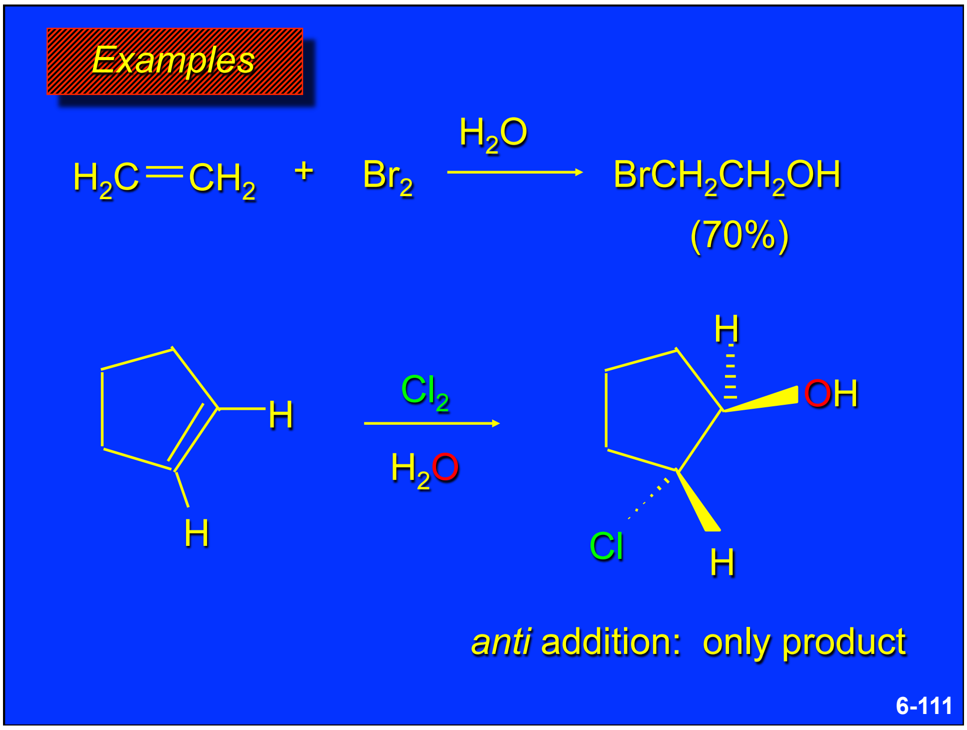


anti addition: only product

Mechanism



- bromonium ion is intermediate
- water is nucleophile that attacks bromonium ion

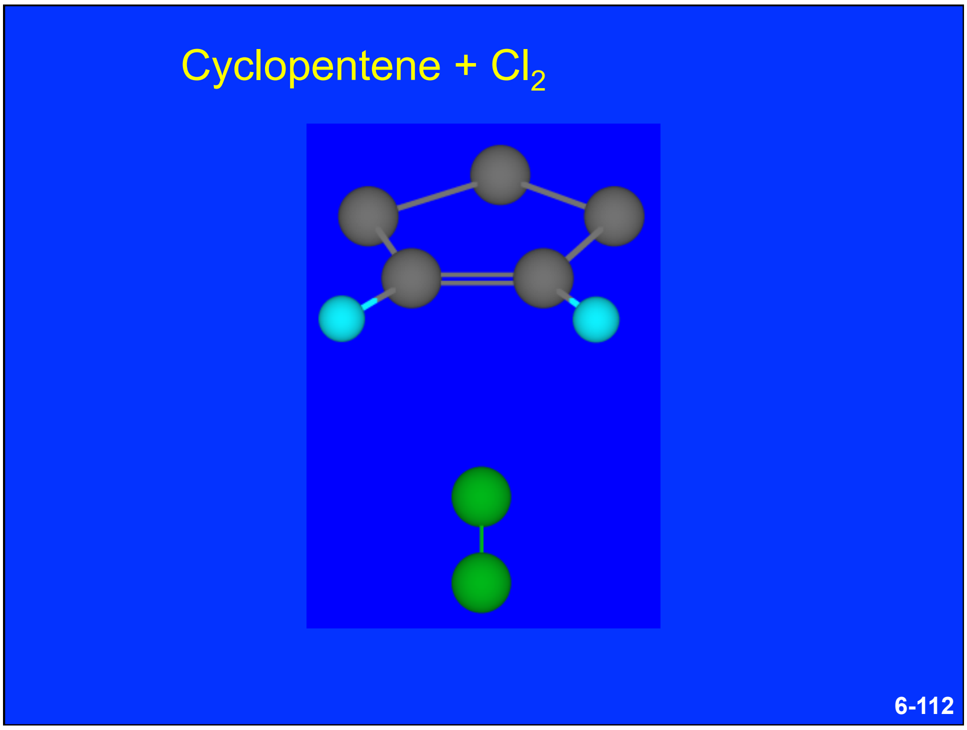


Examples

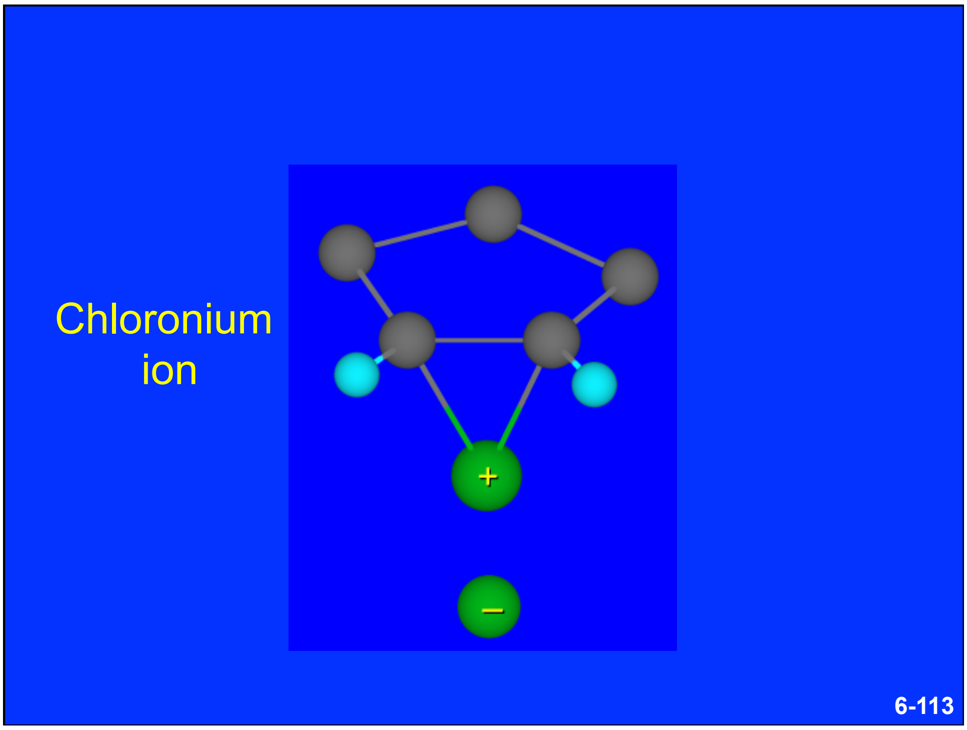
$$H_2C{=}CH_2 \quad + \quad Br_2 \xrightarrow{H_2O} BrCH_2CH_2OH$$

(70%)

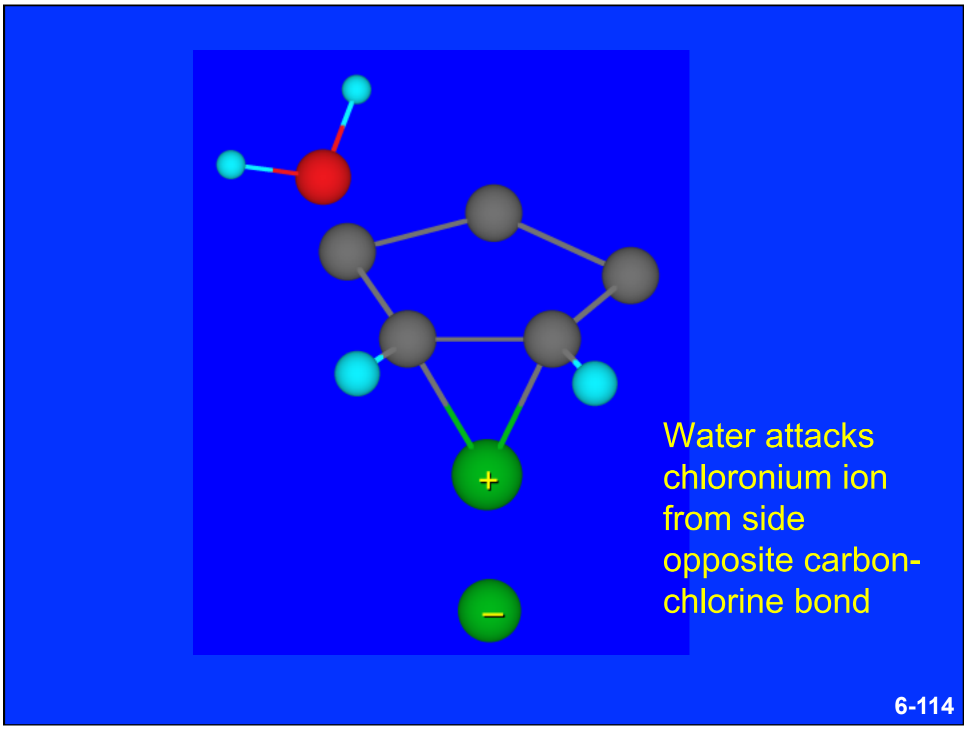
anti addition: only product



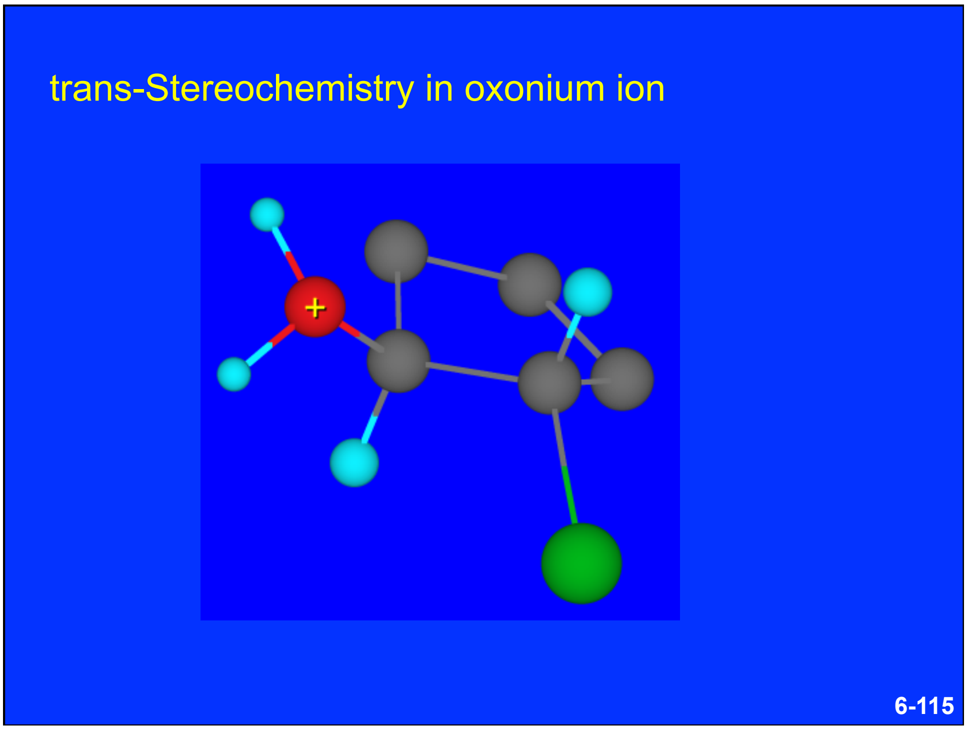
Cyclopentene + Cl_2



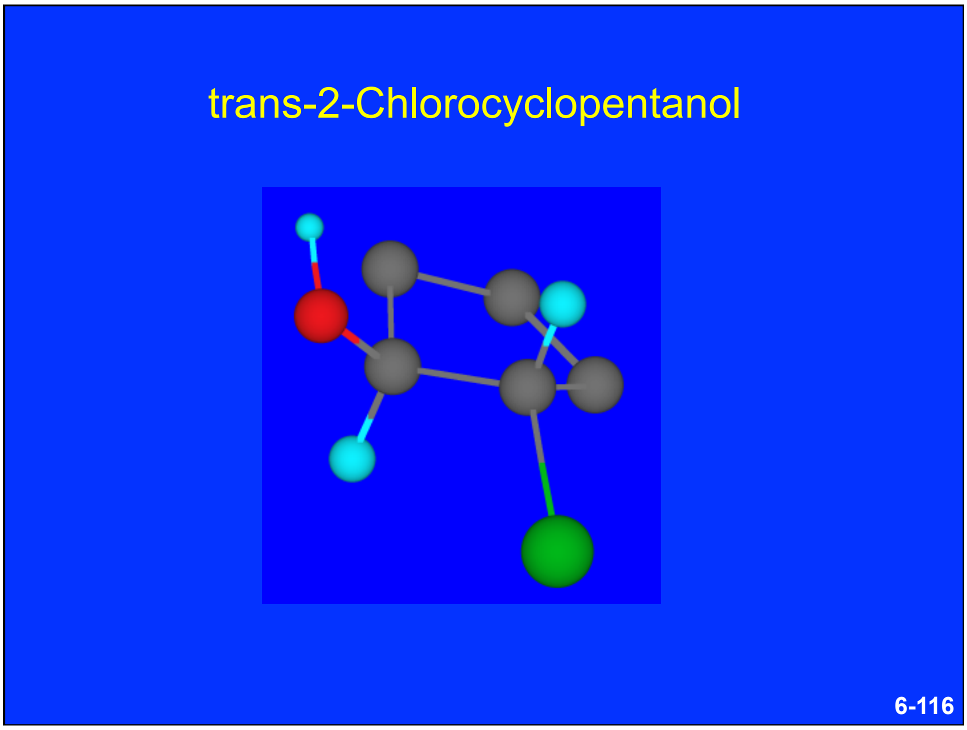
Chloronium ion



Water attacks chloronium ion from side opposite carbon-chlorine bond

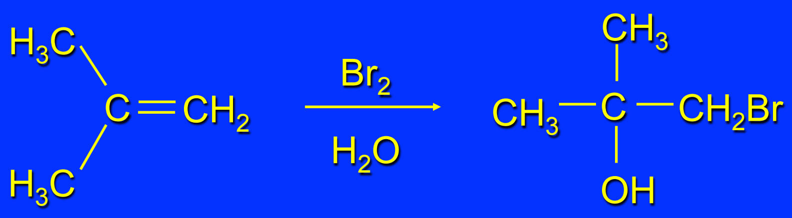


trans-Stereochemistry in oxonium ion



trans-2-Chlorocyclopentanol

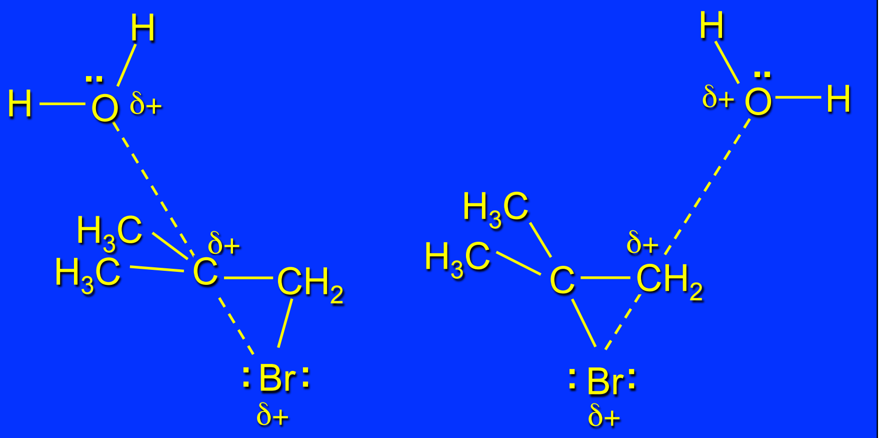
Regioselectivity



(77%)

Markovnikov's rule applies to halohydrin formation: the halogen adds to the carbon having the greater number of hydrogens and OH adds to carbon having fewer number of hydrogens.

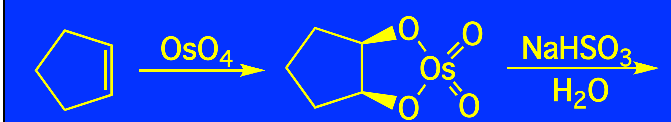
Explanation



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

Oxidation of Alkenes: Glycol Formation

- Osmium tetroxide (OsO_4) is an oxidizing agent that converts an alkene to a **glycol** - a compound with two hydroxyl groups (-OH) on adjacent carbon atoms



A cyclic osmate

cis-1,2-Cyclopentanediol
(a *cis* glycol)

- The oxidation of an alkene by OsO_4 is **stereoselective** and proceeds with **syn-stereoselectivity:**
  - addition of -OH groups on the same side of the carbon-carbon double bond

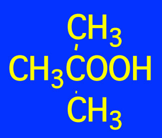
---

Oxidation of Alkenes: Glycol Formation

- **Syn-addition** is due to the formation of the five-membered cyclic osmate intermediate that fuses *cis* to the original alkene
- OsO_4 is *very* expensive and *highly* toxic
- Used in catalytic amounts with stoichiometric amount of another oxidizing agent to reoxidize its reduced form and thus recycle the catalyst.

HOOH

Hydrogen peroxide



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}OOH$$

tert-Butyl hydroperoxide
(*t*-BuOOH)

Oxidation of Alkenes: Glycol Formation

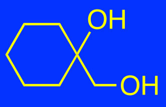
- Draw the product formed by treating each alkene with aqueous OsO_4/H_2O_2.

  a) 1-Methylcyclopentene b) *cis*-2-Pentene

- What alkene when treated with OsO_4/ROOH, gives each glycol?

a)

b)

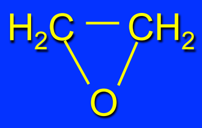


Epoxidation of Alkenes

Epoxides

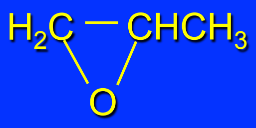
- are examples of heterocyclic compounds
- three-membered rings that contain oxygen

ethylene oxide



H_2C-CH_2 (with O bridging)

propylene oxide



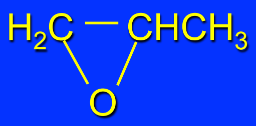
$H_2C-CHCH_3$ (with O bridging)

Epoxide Nomenclature

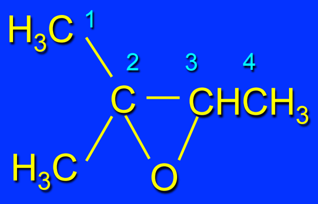
Substitutive nomenclature:

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

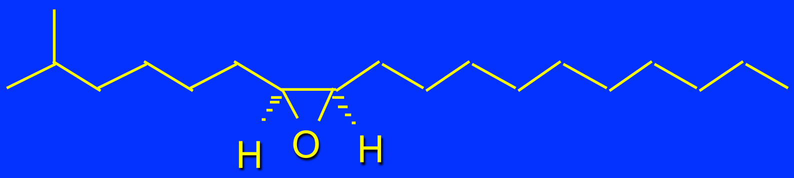
1,2-epoxypropane



2-methyl-2,3-epoxybutane

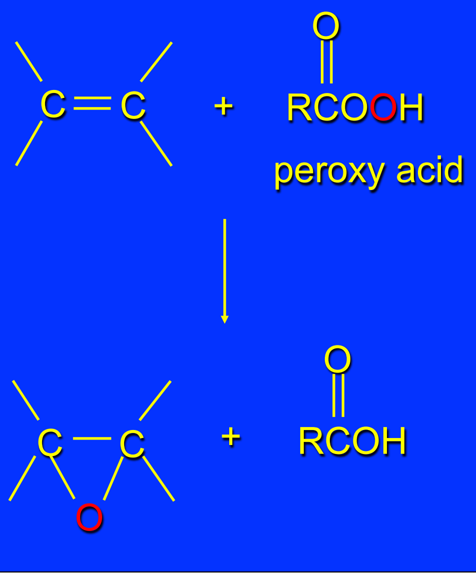


Problem 6.17 Give the IUPAC name, including stereochemistry, for disparlure.

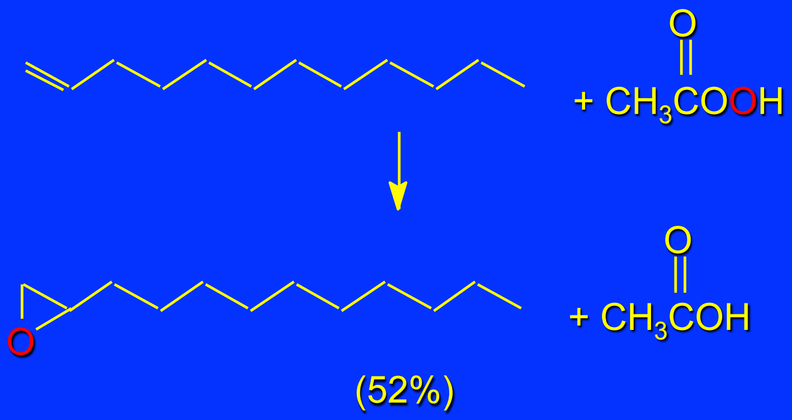


cis-2-Methyl-7,8-epoxyoctadecane

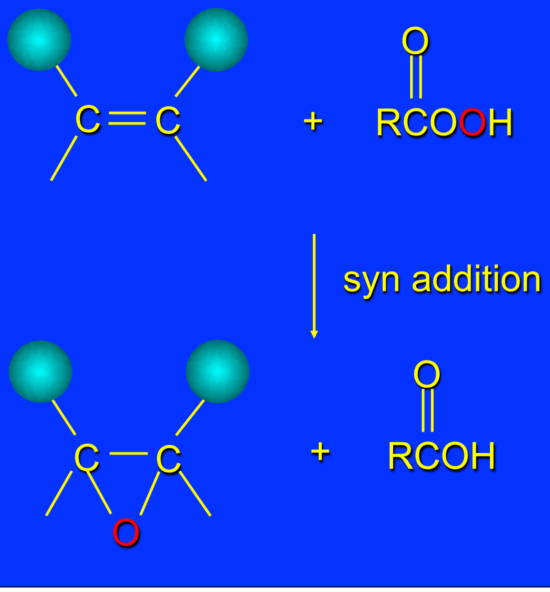
Epoxidation of Alkenes



Example



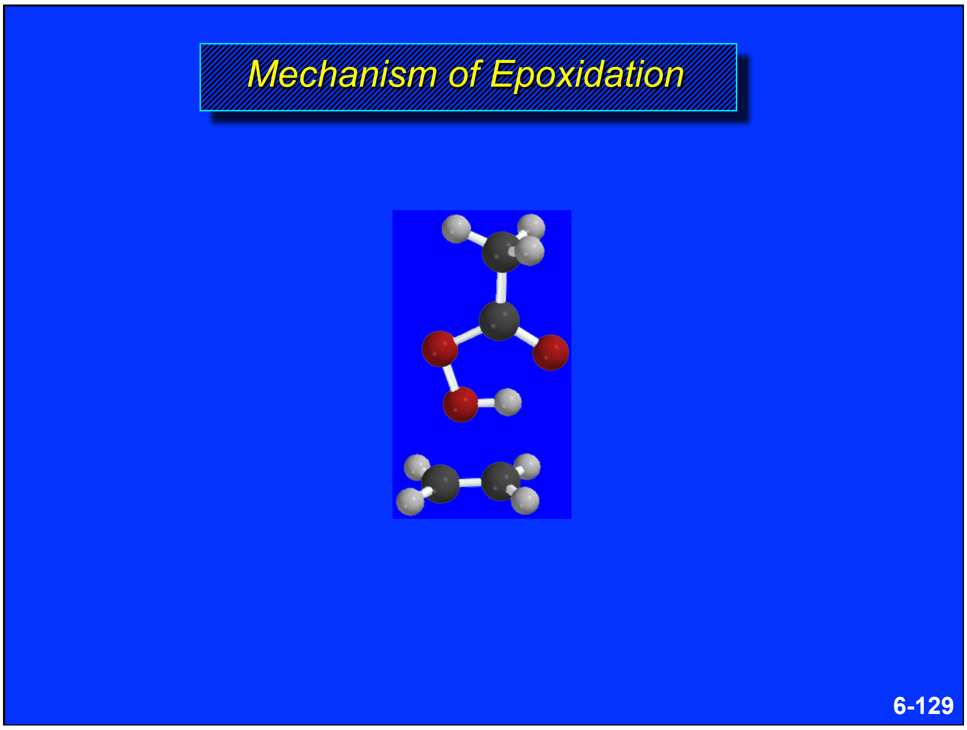
Epoxidation of Alkenes



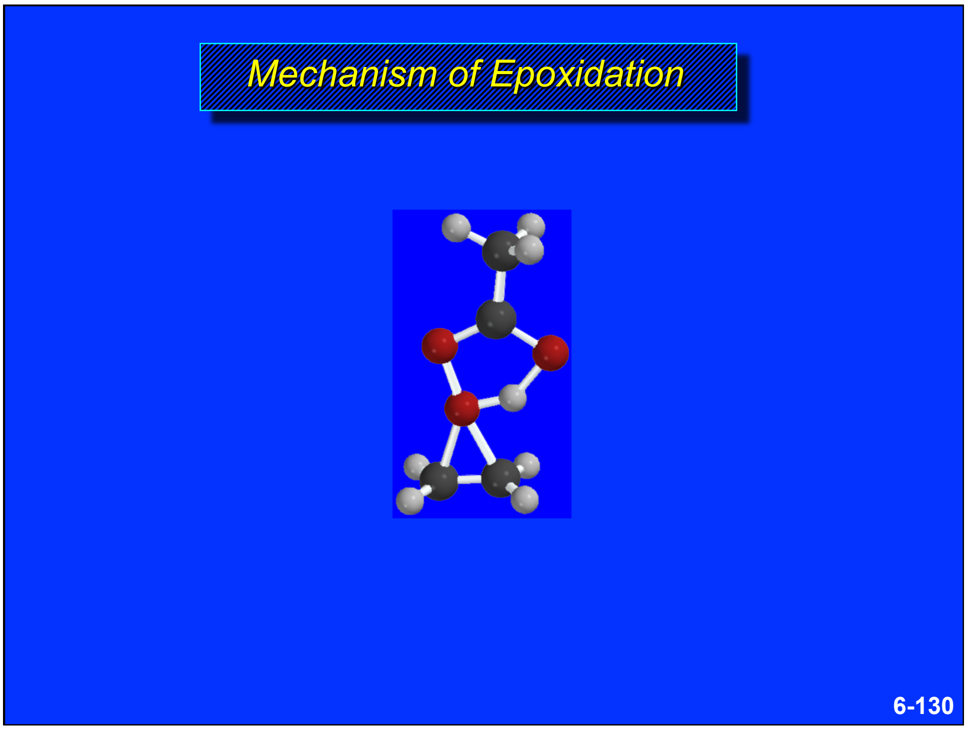
Relative Rates of Epoxidation

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."

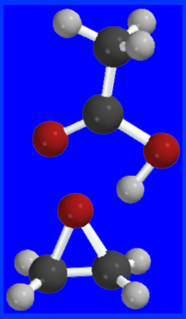


Mechanism of Epoxidation



Mechanism of Epoxidation

Mechanism of Epoxidation



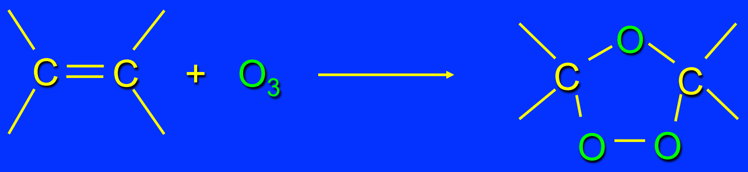
Ozonolysis of Alkenes

Ozonolyis has both synthetic and analytical applications.

- synthesis of aldehydes and ketones
- identification of substituents on the double bond of an alkene

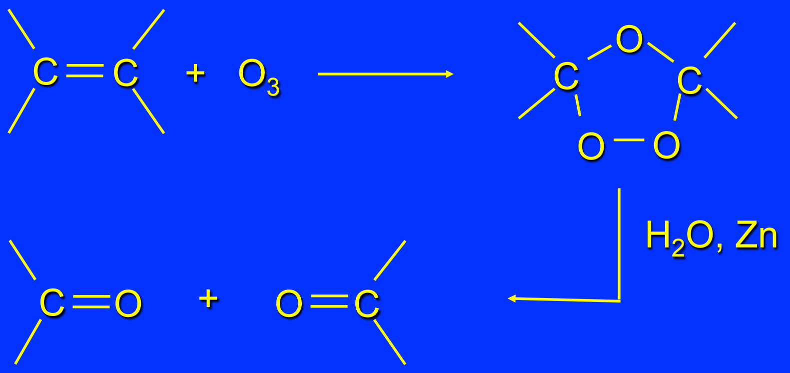
Ozonolysis of Alkenes

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



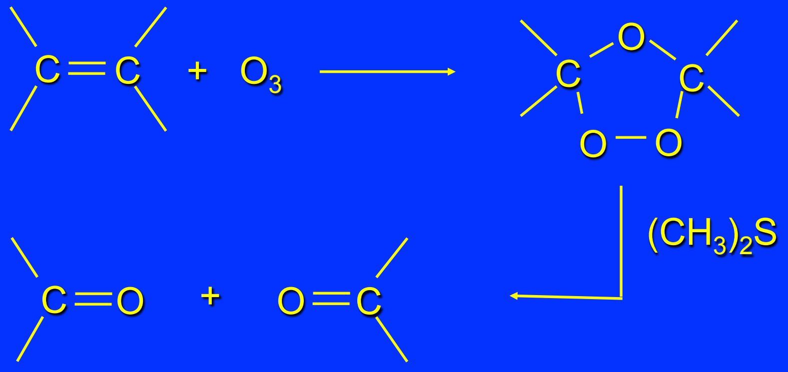
Ozonolysis of Alkenes

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

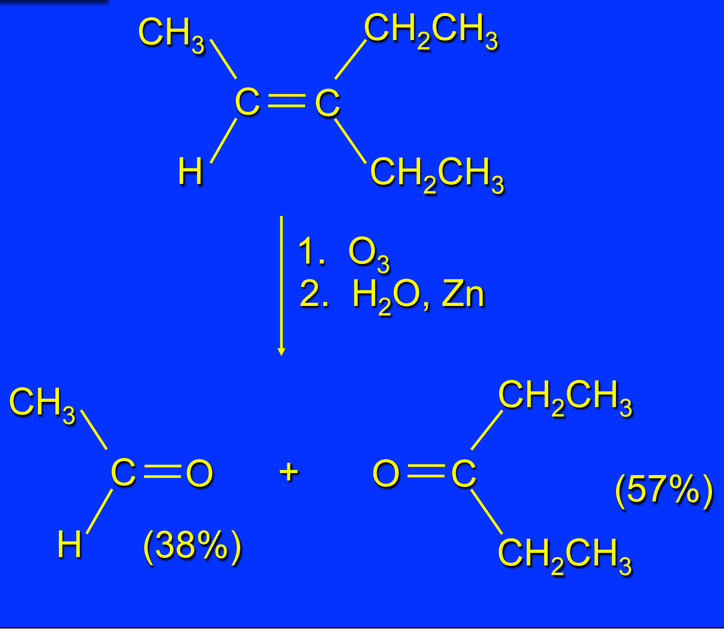


Ozonolysis of Alkenes

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

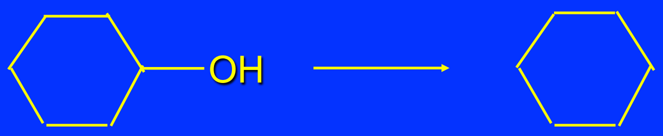


Example



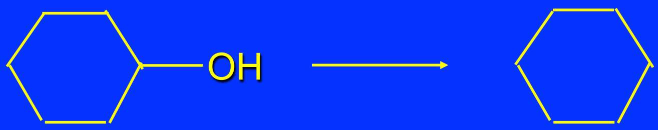
Introduction to Organic Chemical Synthesis

Prepare cyclohexane from cyclohexanol



devise a synthetic plan
  - reason backward from the target molecule
  - always use reactions that you are sure will work

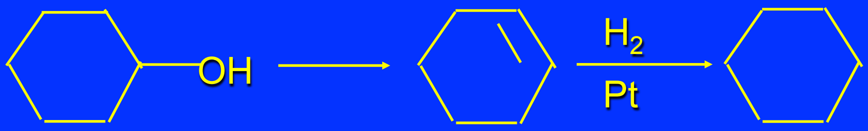
Prepare cyclohexane from cyclohexanol



ask yourself the key question

> "Starting with anything, how can I make cyclohexane in a single step by a reaction I am sure will work?"

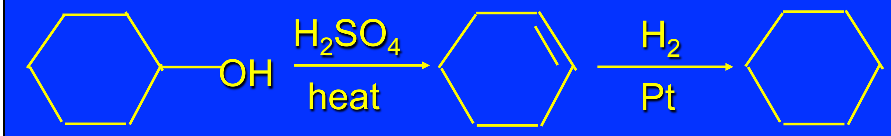
Prepare cyclohexane from cyclohexanol



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?"

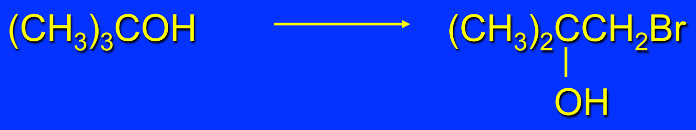
Prepare cyclohexane from cyclohexanol



Alkenes can be prepared by dehydration of alcohols.

The synthesis is complete.

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



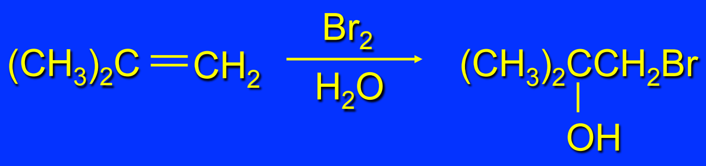
$$(CH_3)_3COH \longrightarrow (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br$$

"Starting with anything, how can I make the desired compound in a single step by a reaction I am sure 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

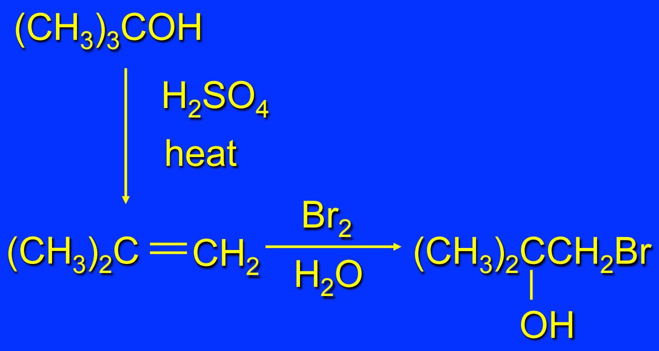


$$(CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br$$

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



$$\begin{array}{l} (CH_3)_3COH \\ \big\downarrow \; H_2SO_4,\ \text{heat} \\ (CH_3)_2C{=}CH_2 \xrightarrow[H_2O]{Br_2} (CH_3)_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2Br \end{array}$$

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

The synthesis is complete.

Reaction of Alkenes with Alkenes: Polymerization

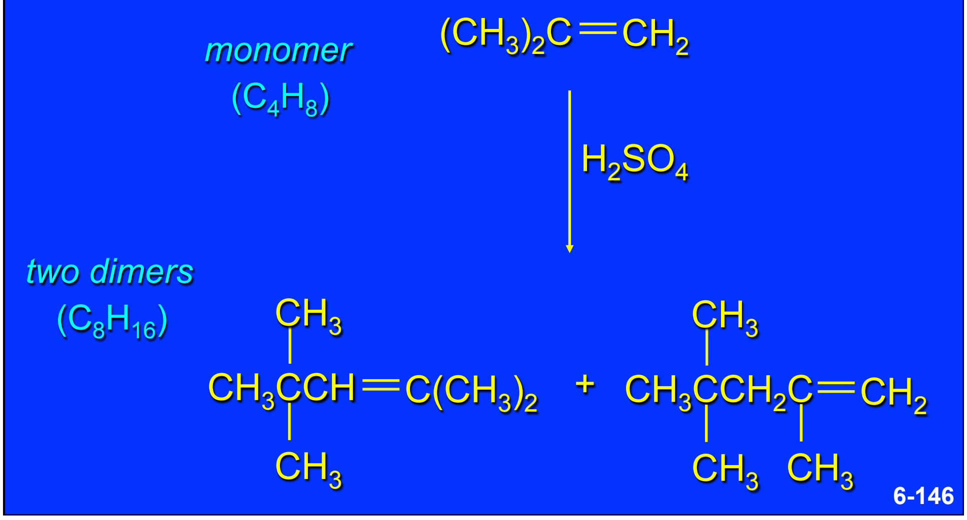
cationic polymerization

free-radical polymerization

coordination polymerization

Cationic Polymerization

Dimerization of 2-methylpropene



monomer

(C_4H_8)

$(CH_3)_2C{=}CH_2$

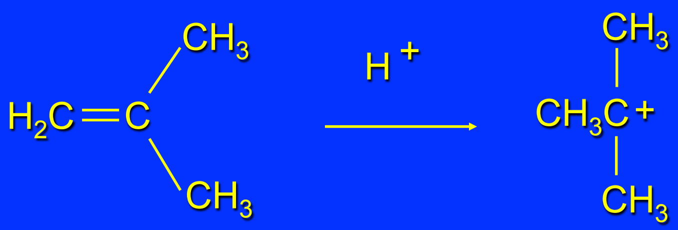
$$\xrightarrow{H_2SO_4}$$

two dimers

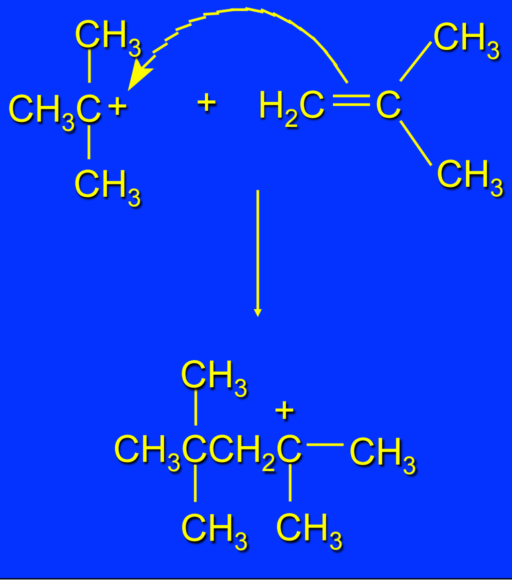
(C_8H_{16})

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

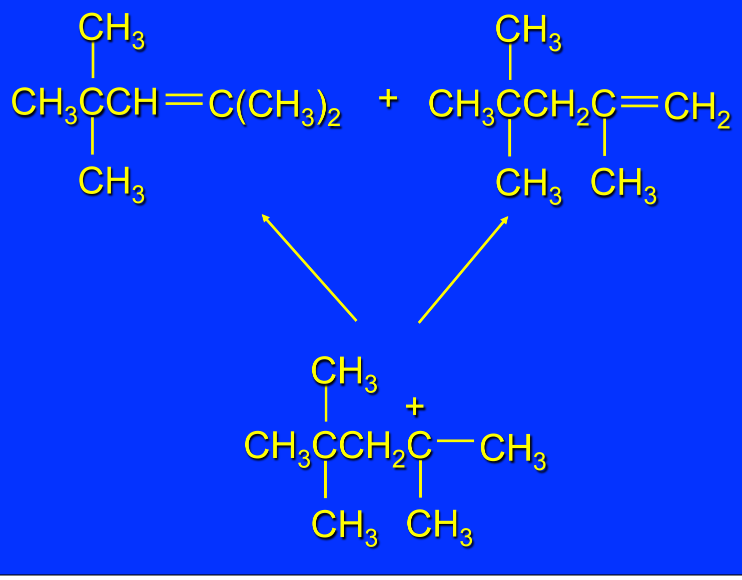
Mechanism of Cationic Polymerization



Mechanism of Cationic Polymerization



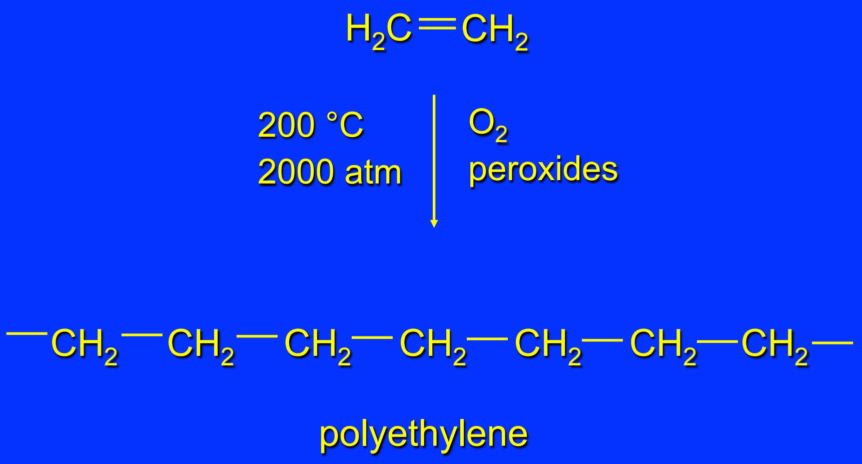
Mechanism of Cationic Polymerization



$$CH_3C(CH_3)_2CH{=}C(CH_3)_2 \quad + \quad CH_3C(CH_3)_2CH_2C(CH_3){=}CH_2$$

$$CH_3C(CH_3)_2CH_2\overset{+}{C}(CH_3){-}CH_3$$

Free-Radical Polymerization of Ethylene

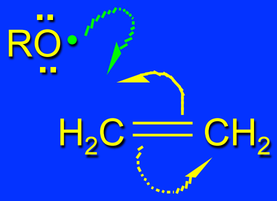


$$H_2C{=}CH_2 \xrightarrow[\text{2000 atm}]{\text{200 °C}} \text{(}O_2\text{, peroxides)}$$

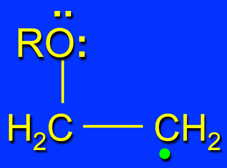
$$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

polyethylene

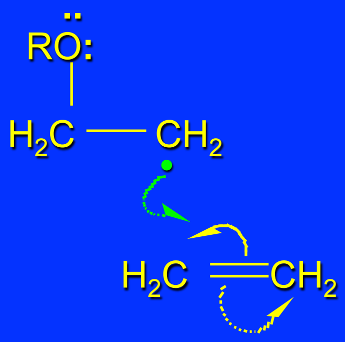
Mechanism



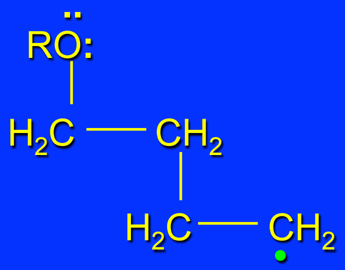
Mechanism



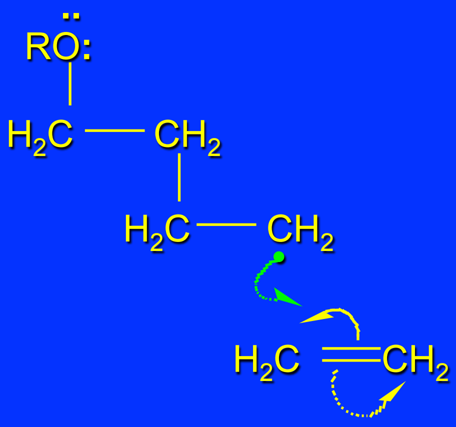
Mechanism



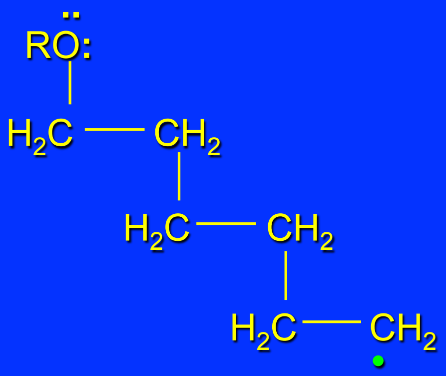
Mechanism



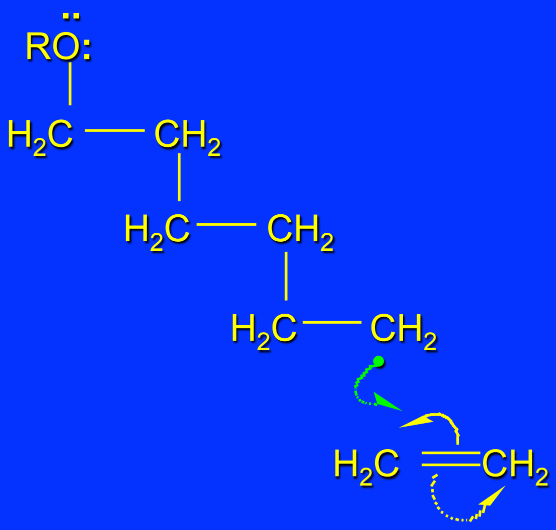
Mechanism



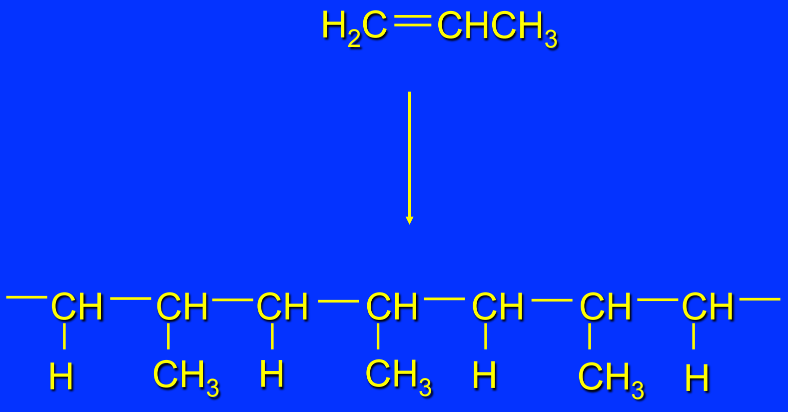
Mechanism



Mechanism



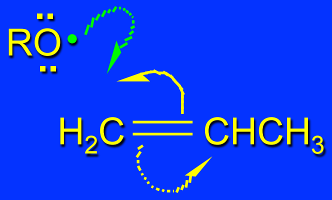
Free-Radical Polymerization of Propene



$$H_2C{=}CHCH_3 \longrightarrow -\underset{H}{CH}-\underset{CH_3}{CH}-\underset{H}{CH}-\underset{CH_3}{CH}-\underset{H}{CH}-\underset{CH_3}{CH}-\underset{H}{CH}-$$

polypropylene

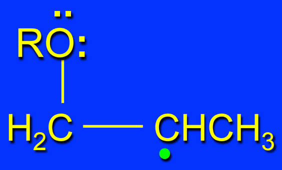
Mechanism



$R\ddot{\underset{\cdot\cdot}{O}}\cdot$

$H_2C{=}CHCH_3$

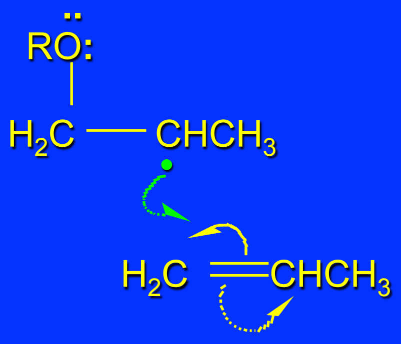
Mechanism



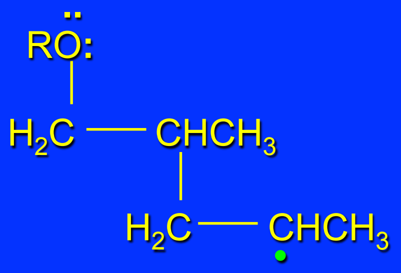
$R\ddot{O}{:}$

$H_2C{-}\dot{C}HCH_3$

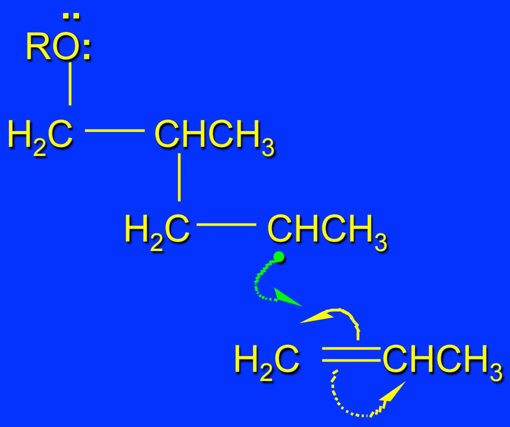
Mechanism



Mechanism



Mechanism



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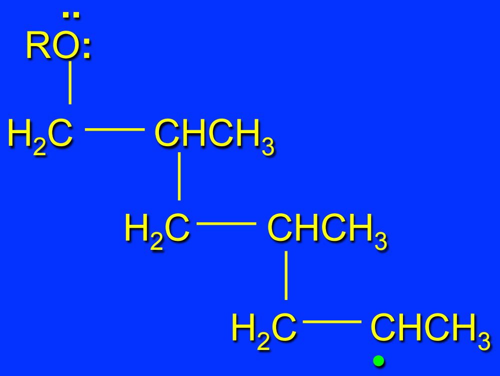

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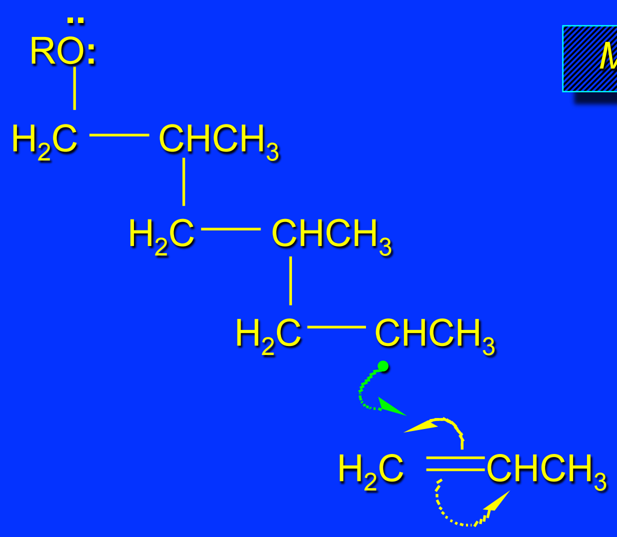

$H_2C{=}CHCl$ → polyvinyl chloride

$H_2C{=}CHC_6H_5$ → polystyrene

$F_2C{=}CF_2$ → Teflon

Coordination Polymerization

An alternative polymerization technique that employs novel transition metal catalysts.

The Ziegler route to polyethylene is even more important because it occurs at modest temperatures and pressures and produces *high density polyethylene* which has properties superior to the low density material produced by free-radical polymerization.

End of Chapter 6