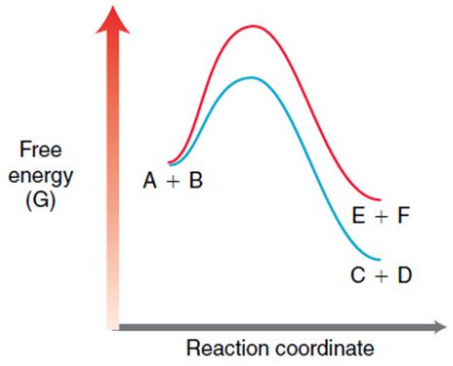
Practice Questions

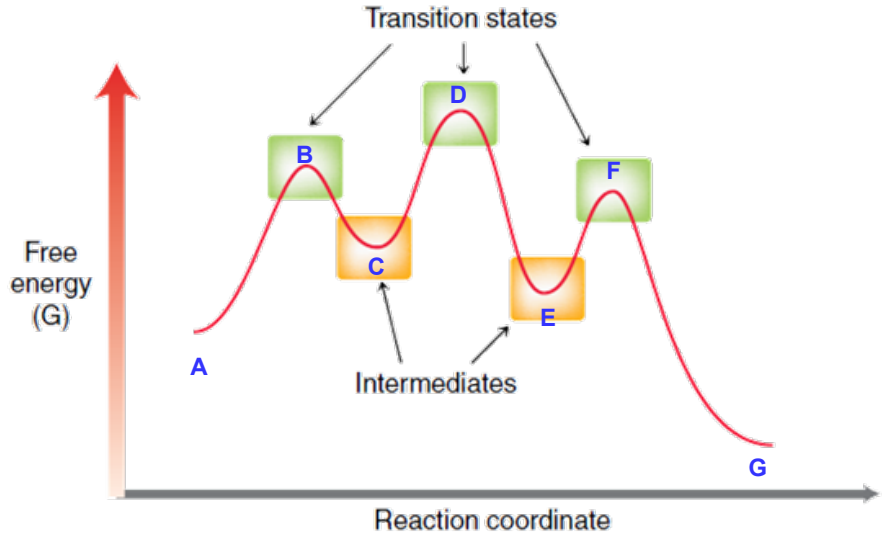
Energy Diagrams

Kinetics vs. Thermodynamics

- Which products are thermodynamically favored ?
- Which products are kinetically favored ?

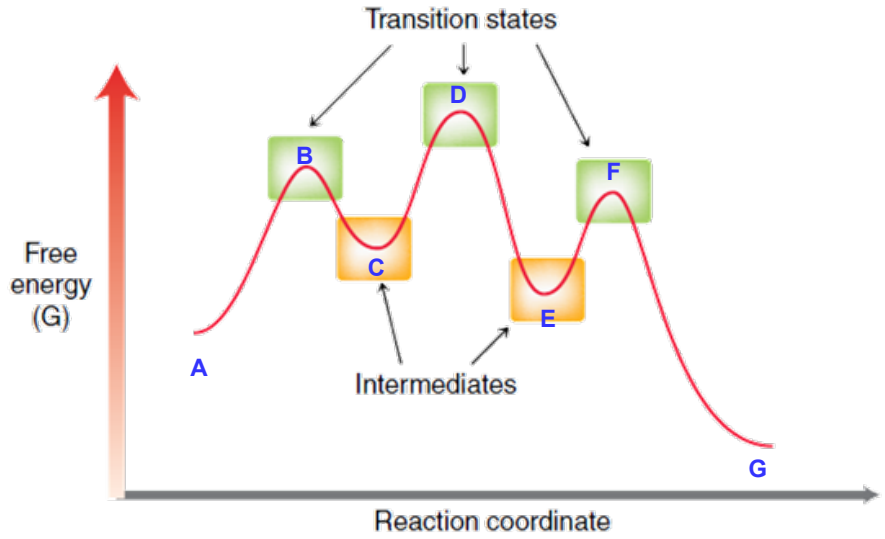


Practice Questions



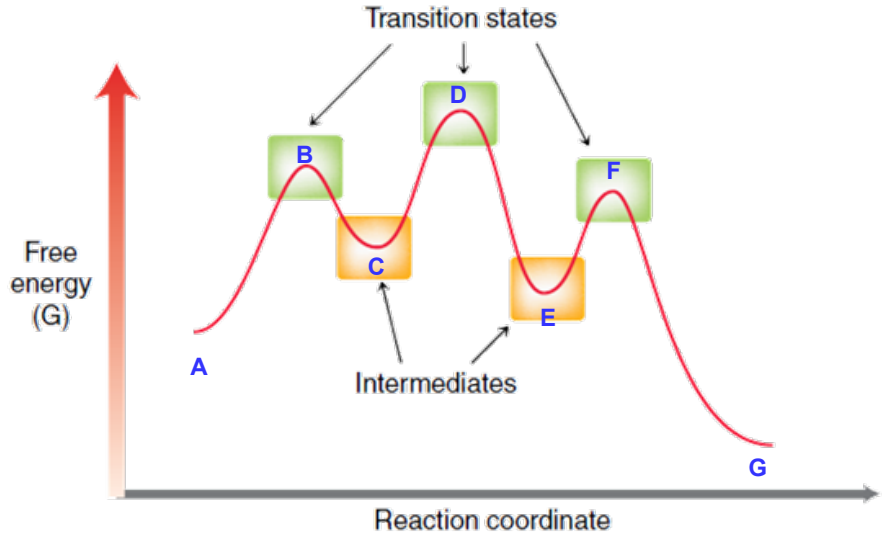
- **How many steps are there in this reaction?**

Practice Questions



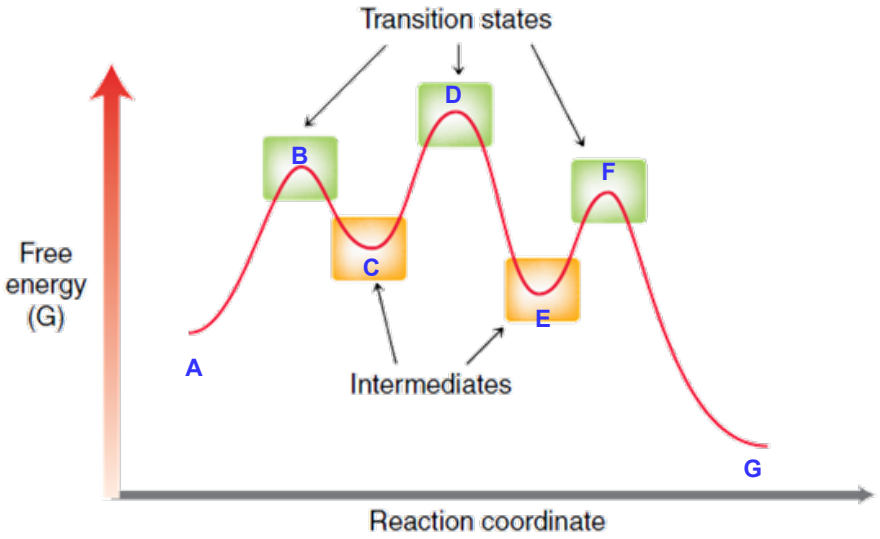
- **What is the highest-energy transitions state?**

Practice Questions



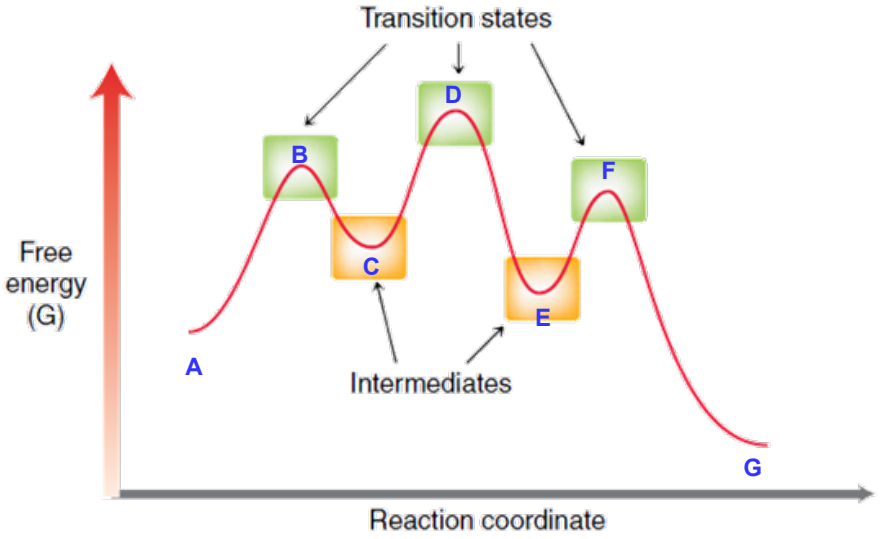
- **What is the highest-energy intermediate?**

Practice Questions



- **Is this reaction exergonic or endergonic?**

Practice Questions



- **Which steps determines the reaction's rate?**

CHEM 109A
Organic Chemistry

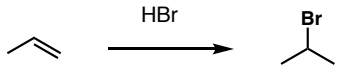
https://labs.chem.ucsb.edu/zakarian/armen/courses.html

Chapter 6

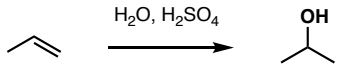
1. The Reactions of Alkenes
2. The Stereochemistry of Addition Reactions

summary of reactions

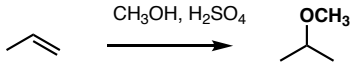
electrophilic addition; H — element



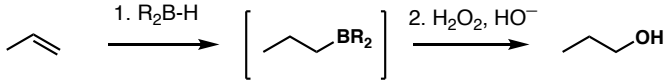
addition of **H — X**



addition of H_2O



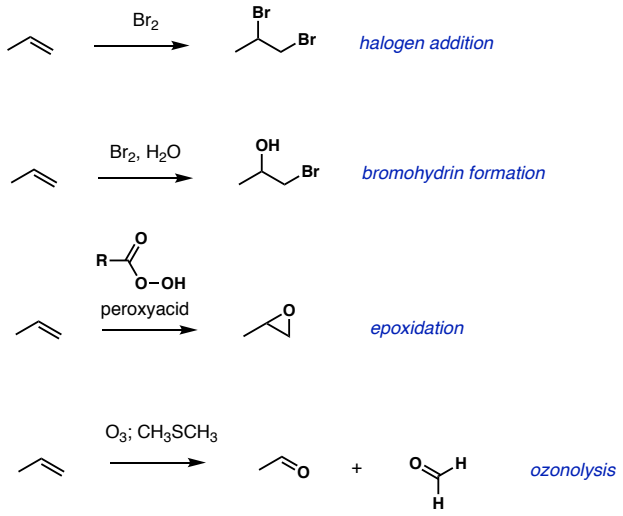
addition of ROH



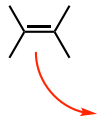
hydroboration/ oxidation

summary of reactions

electrophilic addition; element—element

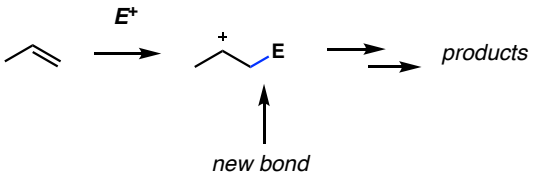


summary of mechanisms



E^+ or $E^{\delta+}$

E = *electrophiles*

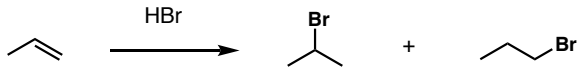


many form reactive intermediates in the first step: **carbocations**

now, are these *nucleophiles* or *electrophiles*?

summary of reaction selectivity

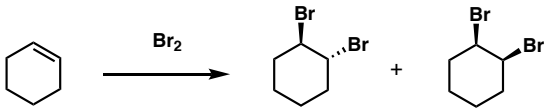
1. ***regioselectivity***



which is the major product?

---

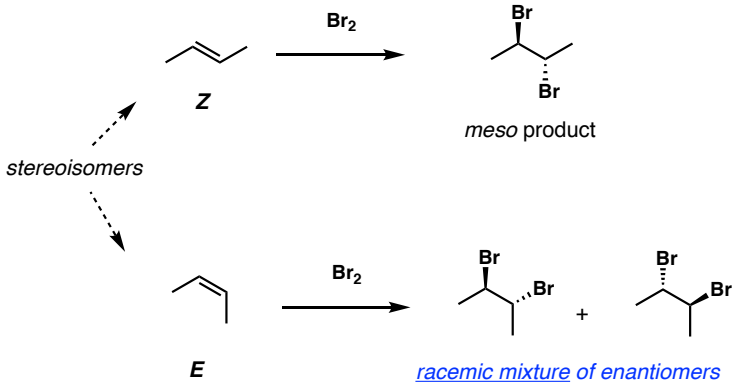
2. ***stereoselectivity***



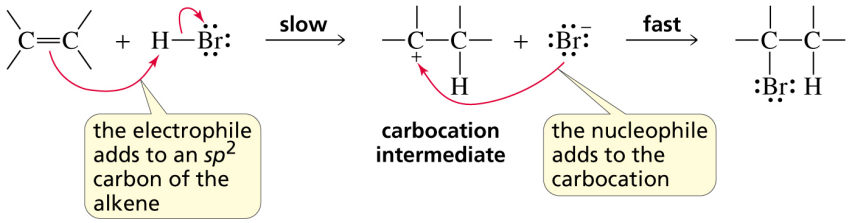
which is the major product?

summary of reaction selectivity

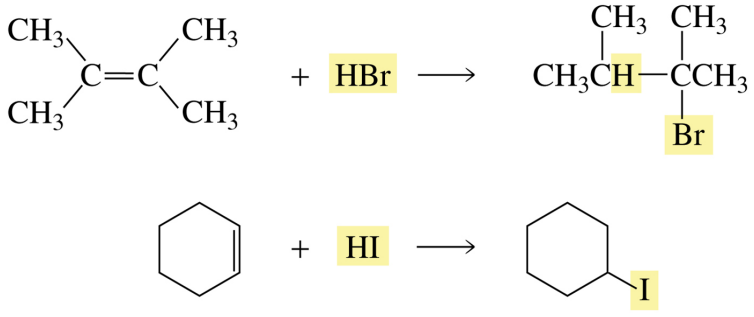
3. ***stereospecificity***



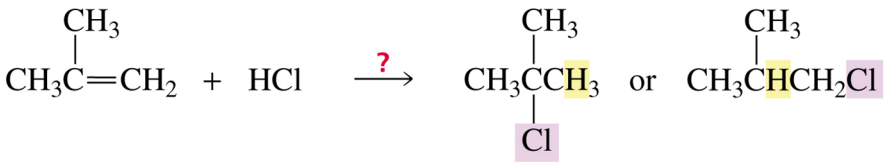
The Mechanism of an Electrophilic Addition Reaction



Addition of Hydrogen Halides



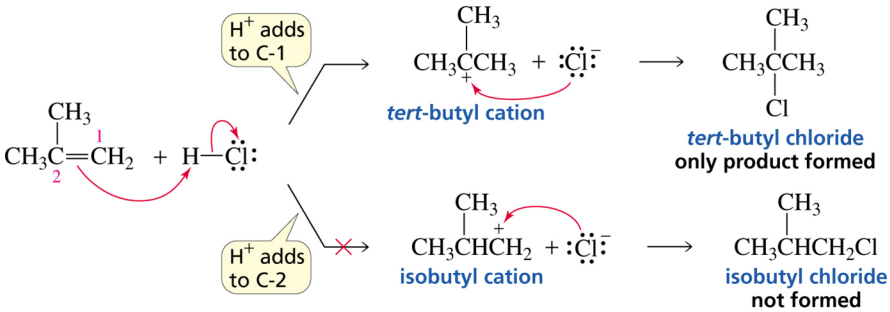
Which sp^2 Carbon Gets the H^+?



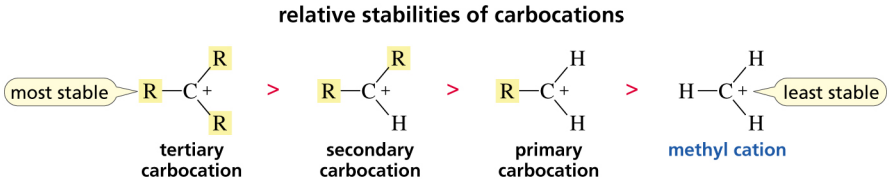
tert-butyl chloride isobutyl chloride

The Mechanism

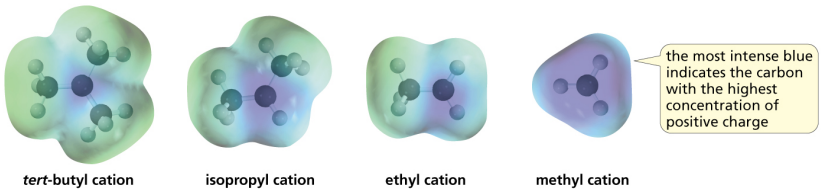
Formation of the carbocation is the rate-limiting step.



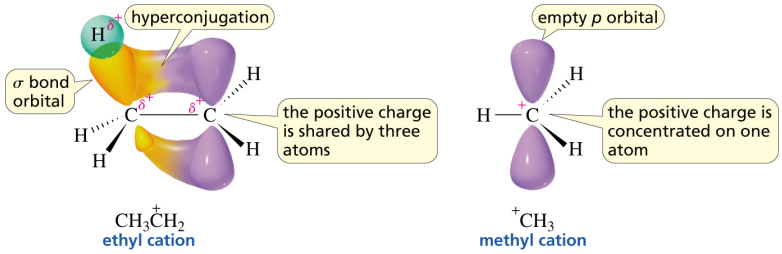
Relative Stabilities of Carbocations

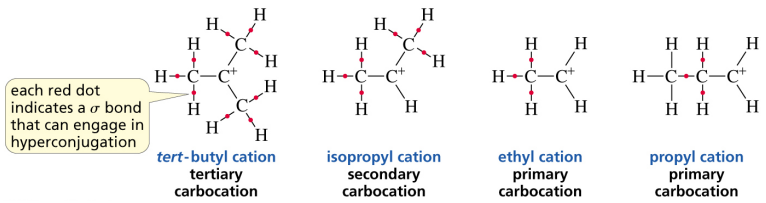


Alkyl groups decrease the concentration of positive charge on the carbon.



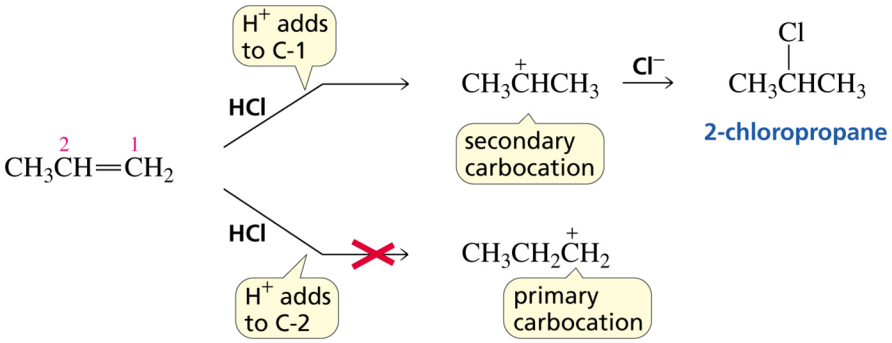
Hyperconjugation





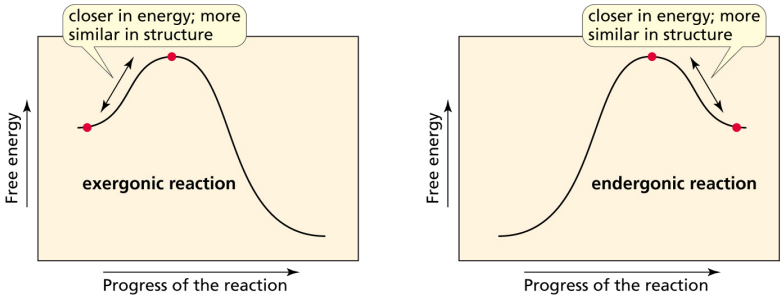
Why the Difference in Rate?

The more stable carbocation is formed more rapidly.



The Hammond Postulate

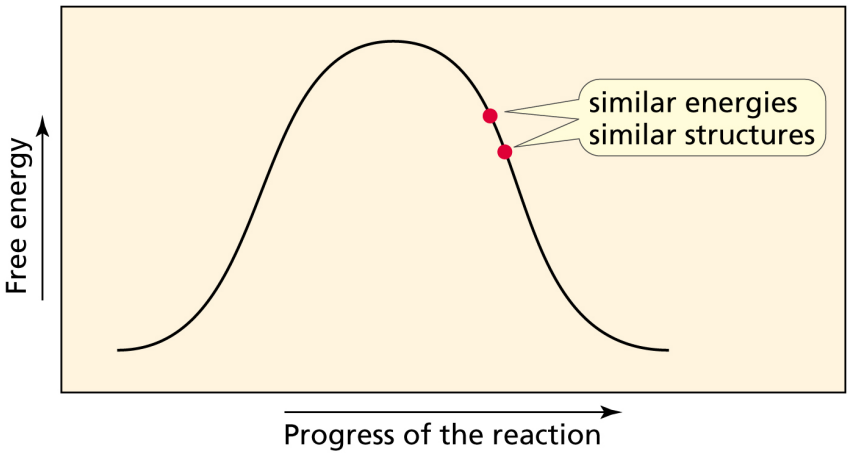
The transition state resembles what it is closer to in energy.



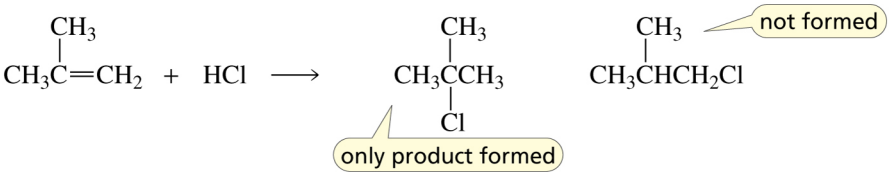
exergonic reaction: The transition state resembles the reactants.

endergonic reaction: The transition state resembles the products.

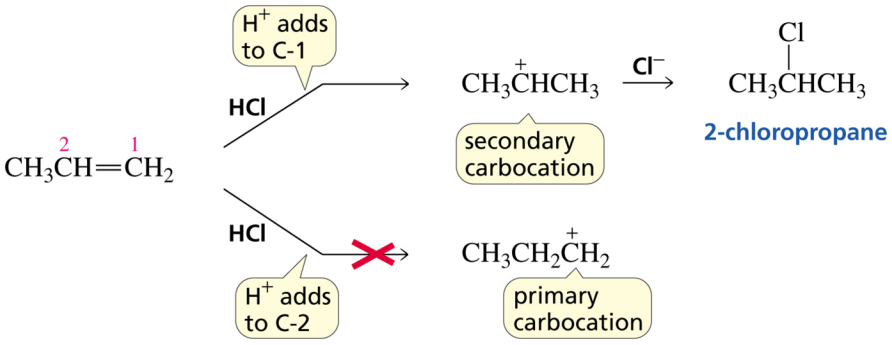
Similar Energies = Similar Structures



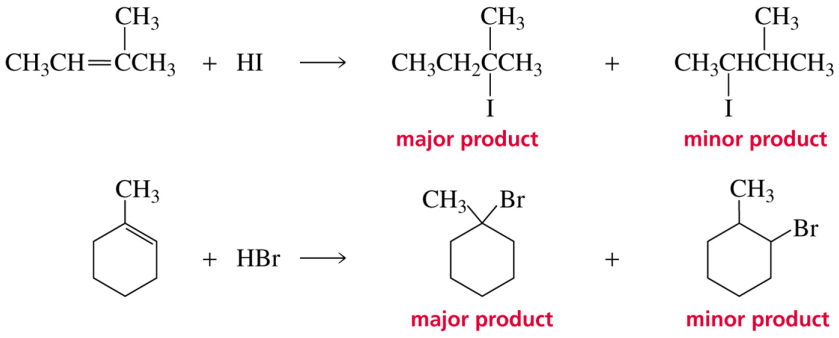
The Relative Rates of Carbocation Formation Determine the Relative Amounts of Products



What Product Is Formed?



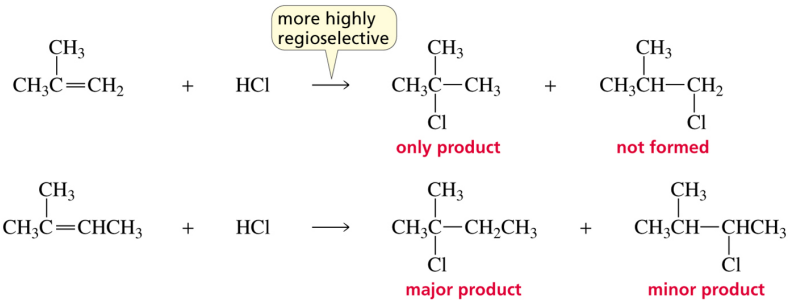
The Electrophile Adds to the sp^2 Carbon Bonded to the Most Hydrogens



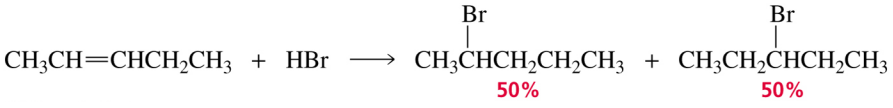
Regioselective Reaction

A regioselective reaction is a reaction that forms more of one constitutional isomer than of another.

The reaction can be: moderately regioselective
highly regioselective
completely regioselective



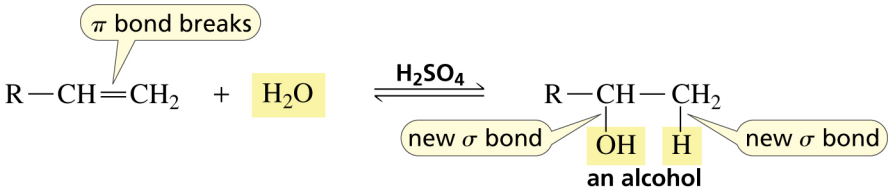
Not Regioselective



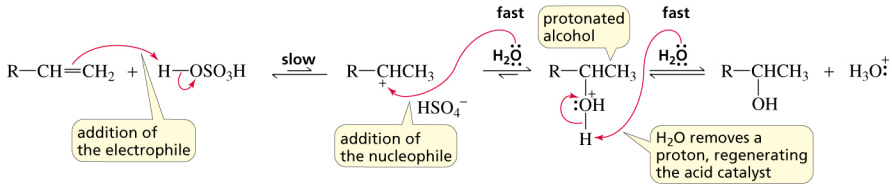
Acid-Catalyzed Addition of Water

$$CH_3CH{=}CH_2 \quad + \quad H_2O \quad \longrightarrow \quad \text{no reaction}$$

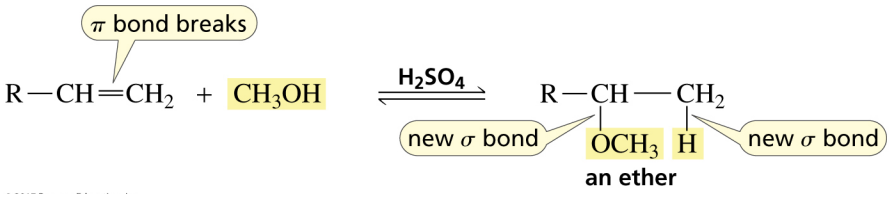
A reaction takes place if an acid is added.



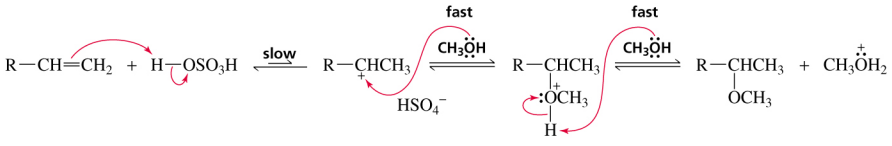
Mechanism for the Acid-Catalyzed Addition of Water



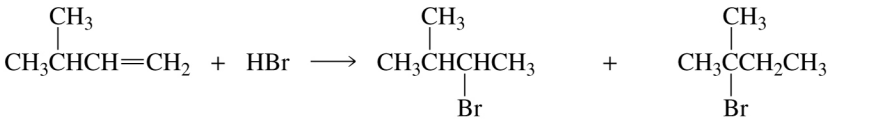
Acid-Catalyzed Addition of an Alcohol



Mechanism for the Acid-Catalyzed Addition of an Alcohol



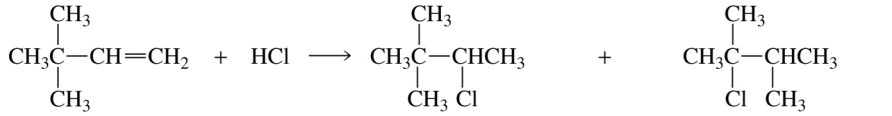
The Major Product is a Surprise



2-bromo-3-methylbutane
minor product

2-bromo-2-methylbutane
major product

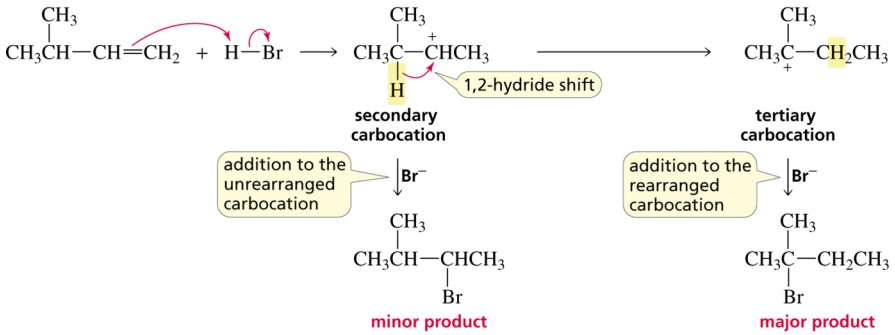
The Major Product is a Surprise



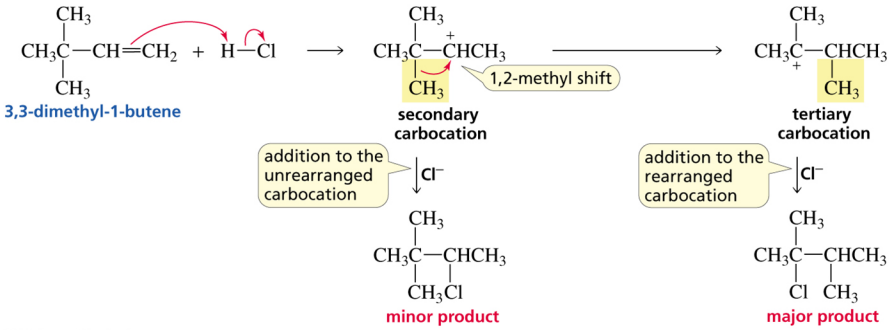
3-chloro-2,2-dimethylbutane
minor product

2-chloro-2,3-dimethylbutane
major product

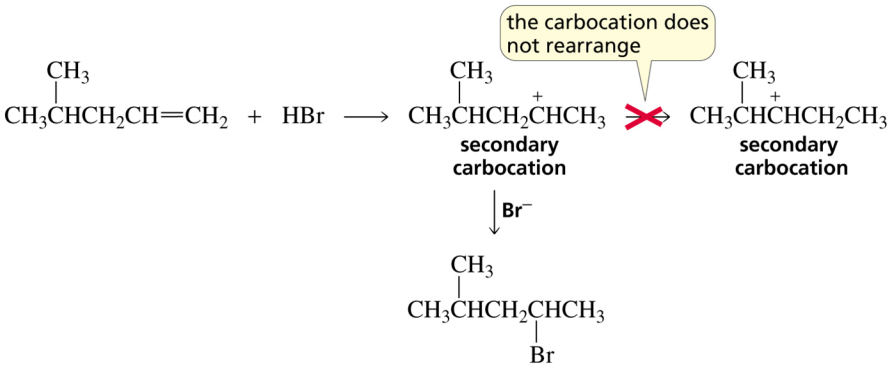
A Carbocation Rearrangement (a 1,2-hydride shift)



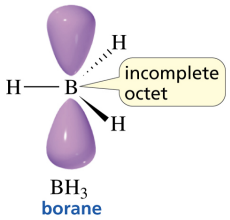
A Carbocation Rearrangement (a 1,2-methyl shift)

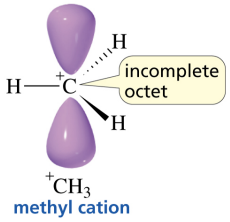


The Carbocation Does Not Rearrange (No Improvement in Carbocation Stability)



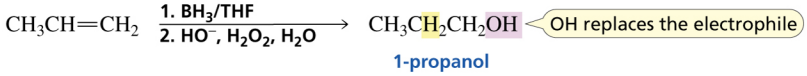
BH_3 is an Electrophile





Hydroboration–Oxidation

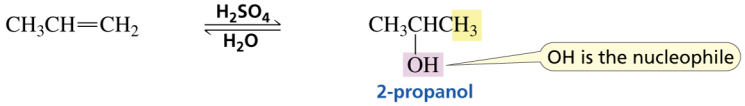
hydroboration-oxidation



1-propanol

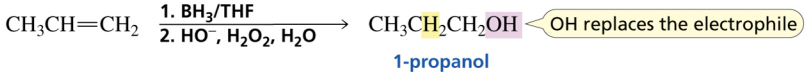
The Electrophile Adds to the *sp*^{2} Carbon Bonded to the Most Hydrogens

acid-catalyzed addition of water



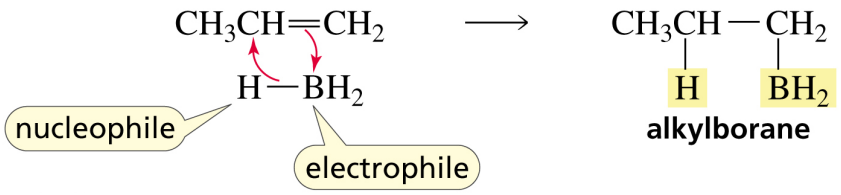
2-propanol

hydroboration-oxidation



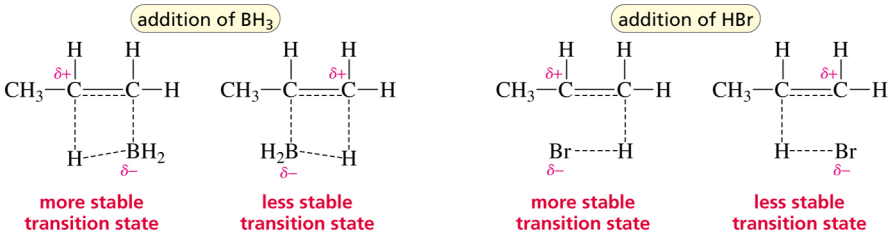
1-propanol

Mechanism for Hydroboration

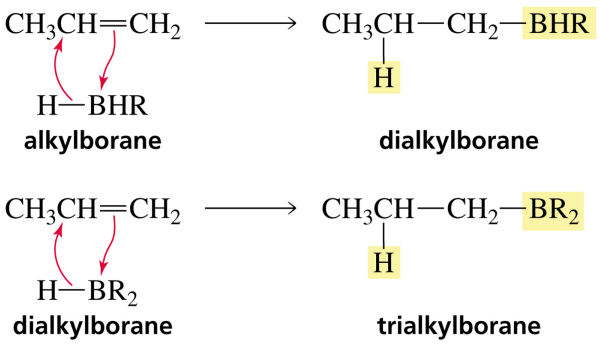


Addition of BH_3 and Addition of HBr Follow the Same Rule

The electrophile adds to the *sp*² carbon bonded to the most hydrogens.

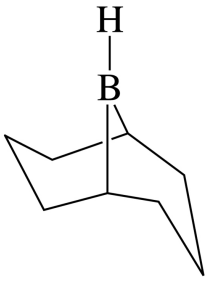


BH_3 Has Three Potential Hydride Ions, so a Dialkylborane and a Trialkyleborane Can Be Formed



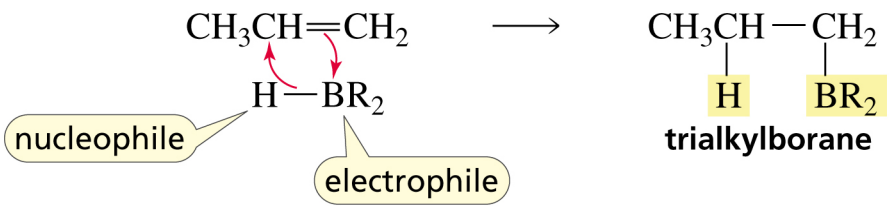
Only One Hydride Ion is Needed for Hydroboration

Because of its bulky R groups, R_2BH has a stronger preference for the less substituted sp^2 carbon.



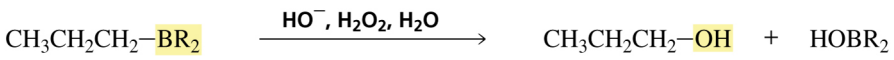
9-BBN
9-borabicyclo[3.3.1]nonane
R_2BH

The Mechanism is the Same



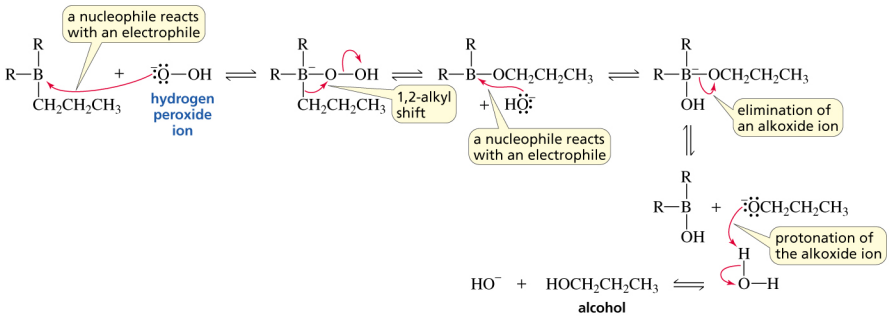
Hydroboration is Followed by Oxidation

In the oxidation reaction, OH replaces BR_2

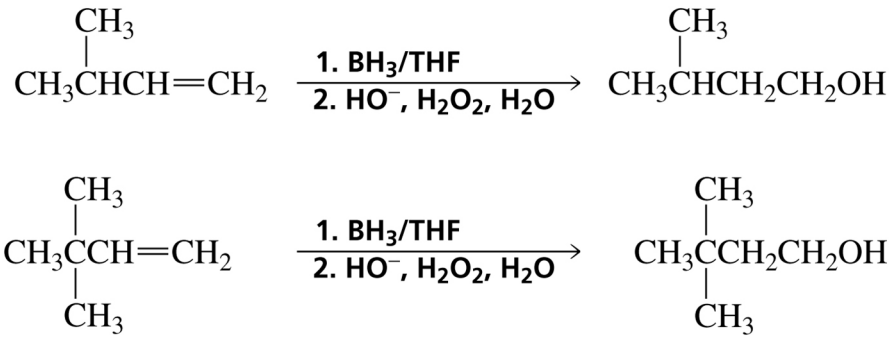


It is an oxidation reaction because the number of C-O bonds increases.

Mechanism for the Oxidation Reaction

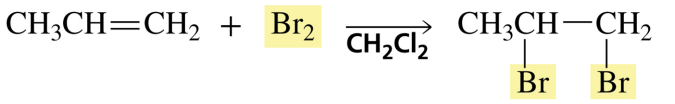


No Carbocation Rearrangement

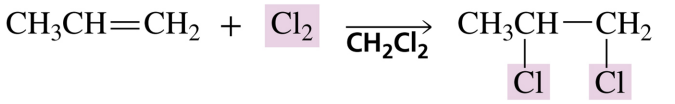


A carbocation is not formed, so a carbocation rearrangement cannot occur.

Addition of Br_2 or Cl_2

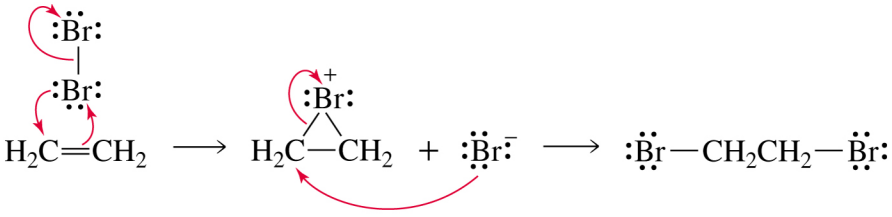


vicinal dibromide



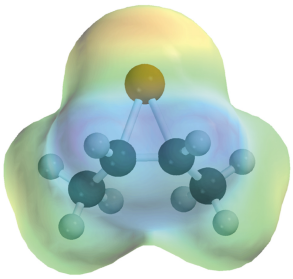
vicinal dichloride

The Mechanism for the Addition of a Halogen



cyclic bromonium ion

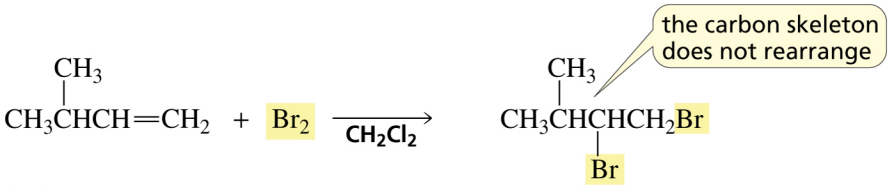
A Cyclic Bromonium Ion Intermediate



cyclic bromonium ion

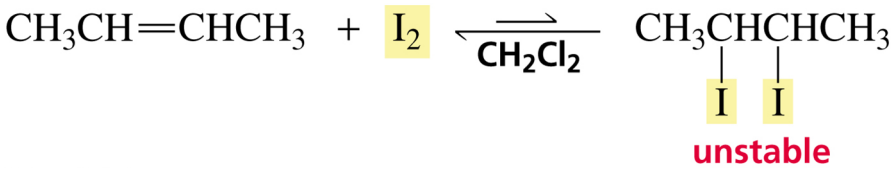
The carbons atoms connected to the oxygen atom are the most electrophilic atoms.

No Carbocation Rearrangement



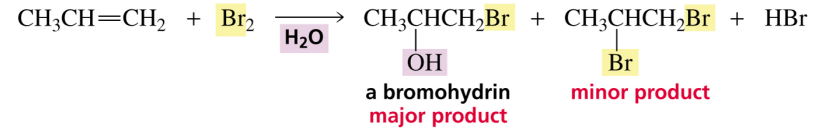
A carbocation is not formed, so a carbocation rearrangement cannot occur.

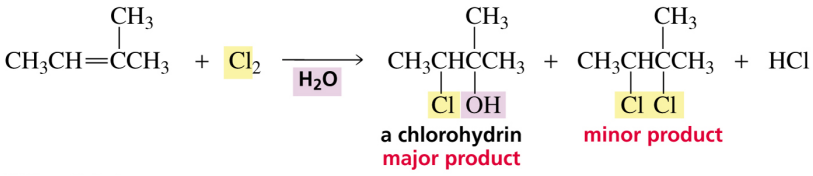
Alkenes Do Not Add I_2



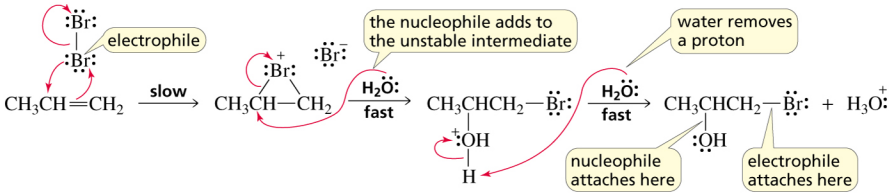
unstable

Formation of Halohydrins



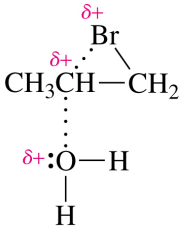


Mechanism for Halohydrin Formation

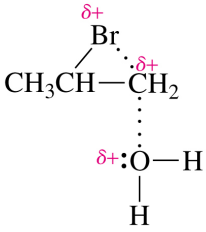


Why Does It Follow the Same Rule?

The electrophile adds to the *sp*^{2} carbon bonded to the most hydrogens.

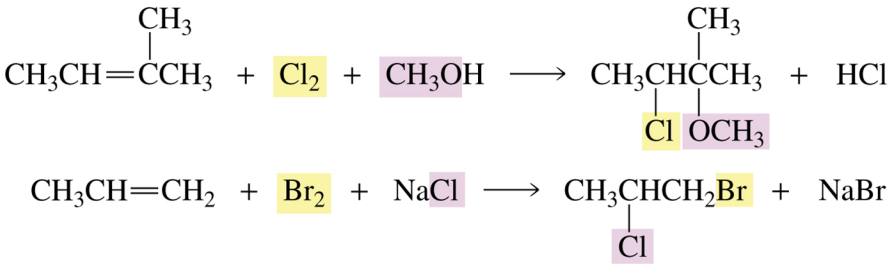


more stable transition state

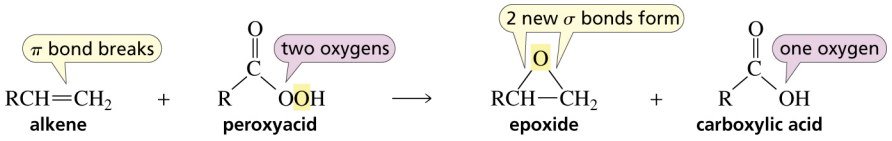


less stable transition state

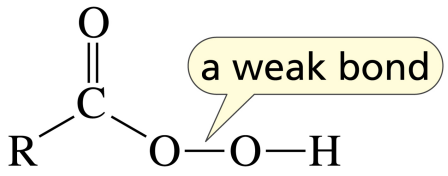
More Reactions



Addition of a Peroxyacid

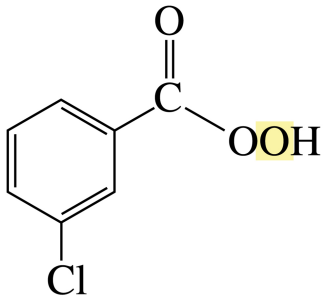


An Oxygen–Oxygen Single Bond is a Weak Bond



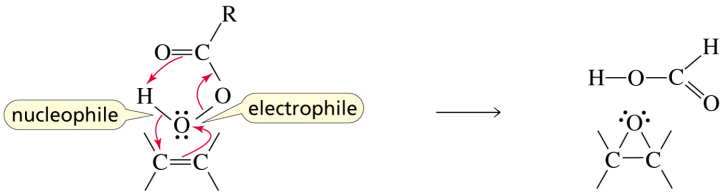
peroxyacid

MCPBA is a Commonly Used Peroxyacid

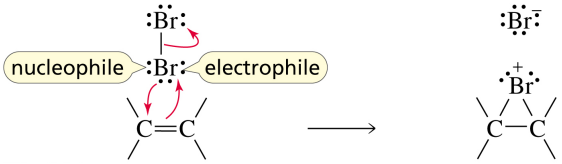


MCPBA

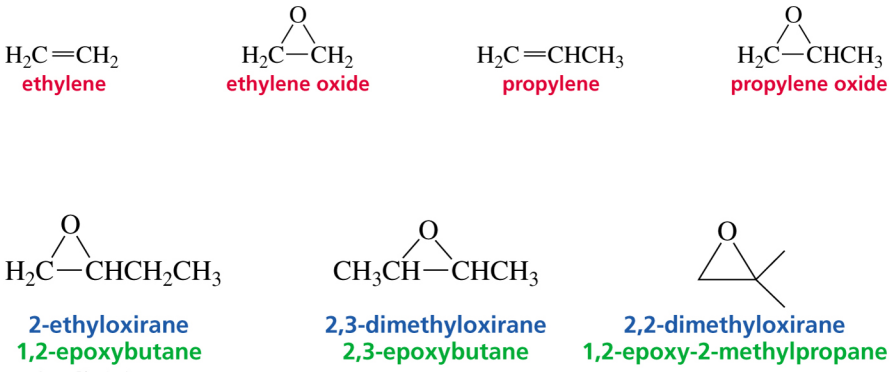
Mechanism for Epoxidation



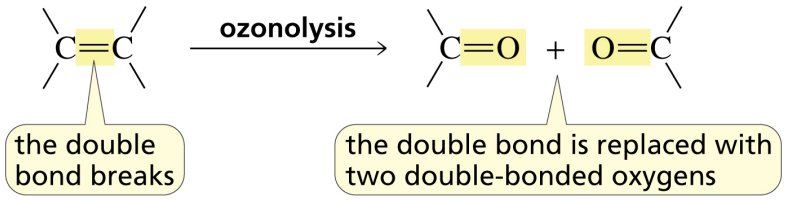
The mechanism is similar to that for the addition of Br_2.



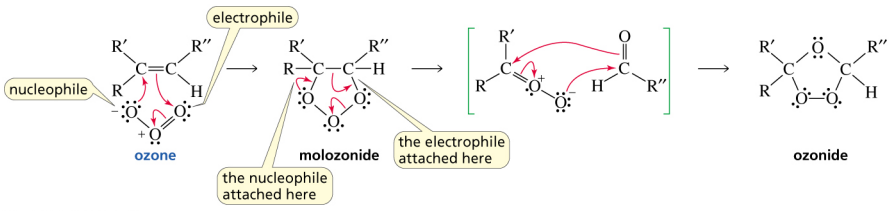
Nomenclature of Epoxides



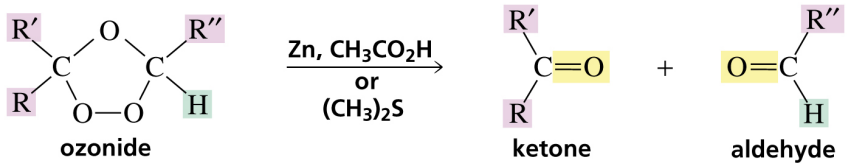
Ozonolysis



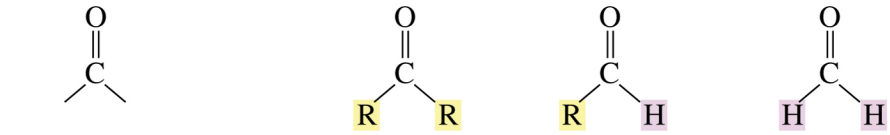
Mechanism for Ozonide Formation



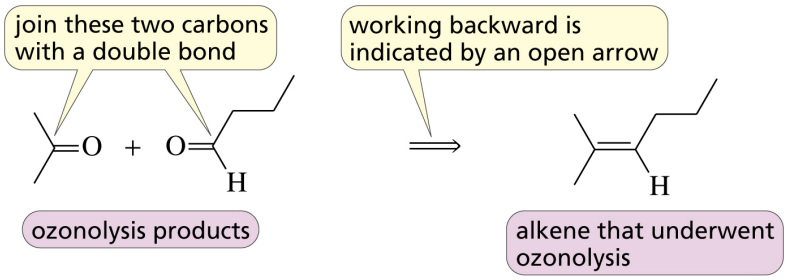
The Ozonide is Converted to Ketones and/or Aldehydes



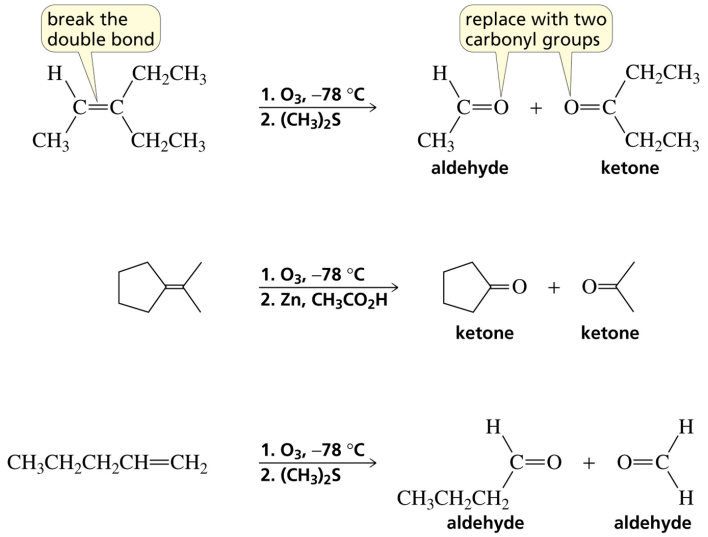
Ketones and Aldehydes



What Alkene Formed the Ozonolysis Products?

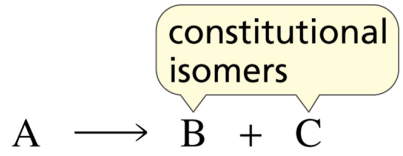


Ozonolysis



A Regioselective Reaction

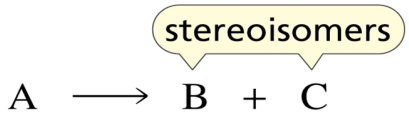
a regioselective reaction



more B is formed than C

A Stereoselective Reaction

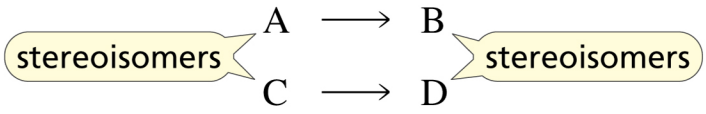
a stereoselective reaction



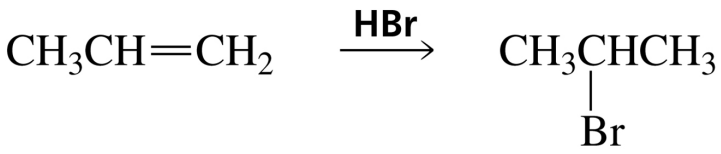
more B is formed than C

A Stereospecific Reaction

stereospecific reactions

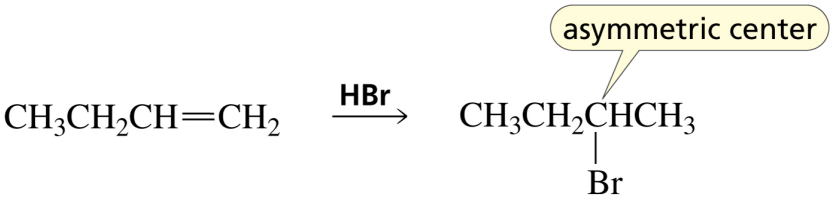


The Product Does Not Have Stereoisomers

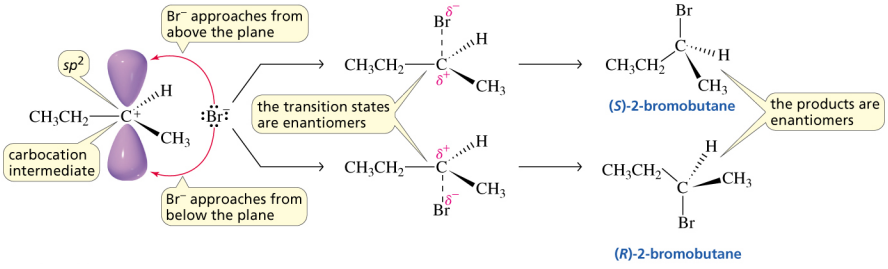


no stereoisomers

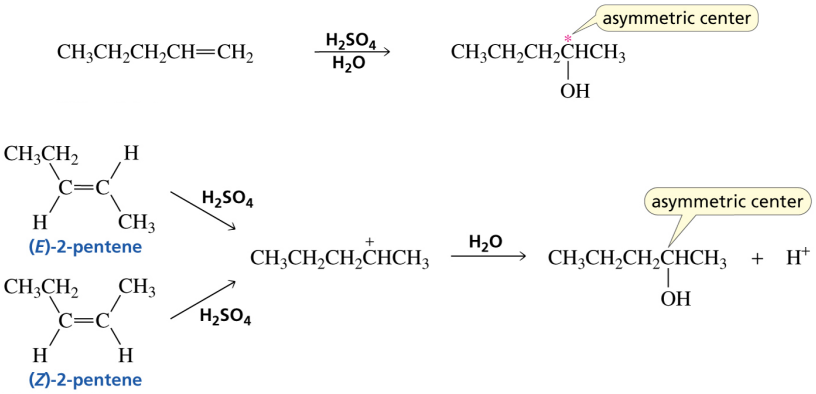
The Product is a Racemic Mixture



Why a Racemic Mixture is Formed

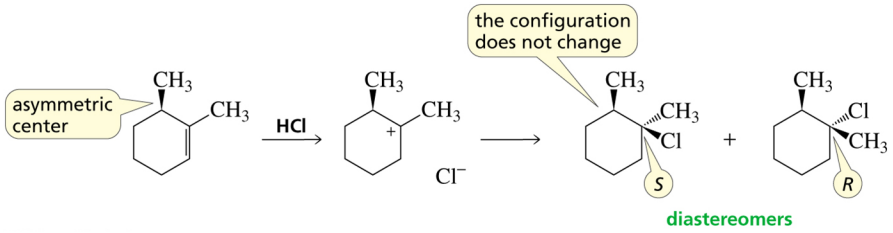


Forming a Racemic Mixture



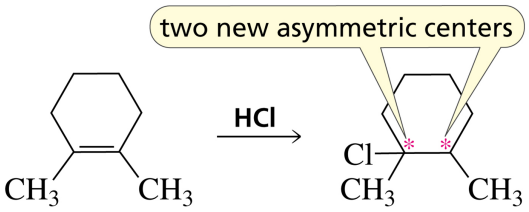
If the reactant does not have an asymmetric center
and the reaction forms a product with an asymmetric center,
the product will be a racemic mixture.

Forming a Second Asymmetric Center



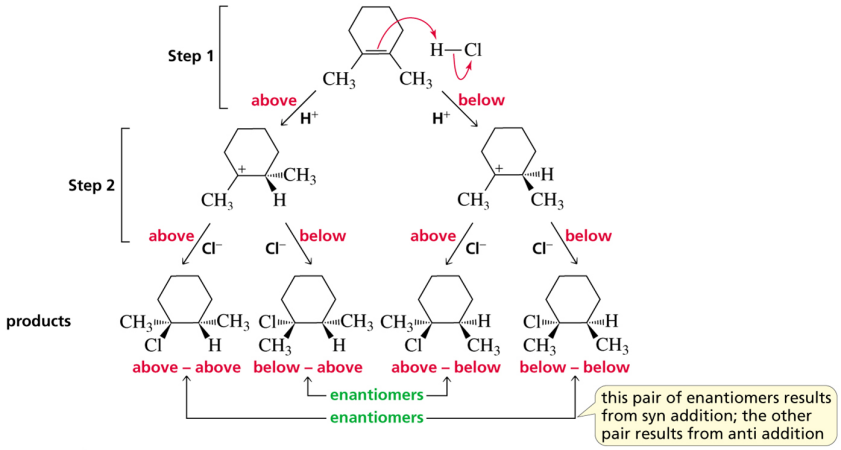
If the reactant has an asymmetric center
and the reaction forms a product with a new asymmetric center,
the product will be a pair of diastereomers.

Reactions That Form Two Asymmetric Centers



The stereoisomers obtained as products depend on the mechanism of the reaction.

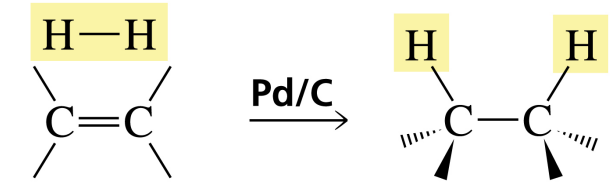
Four Stereoisomers are Obtained if the Reaction Forms a Carbocation Intermediate



syn and anti additions

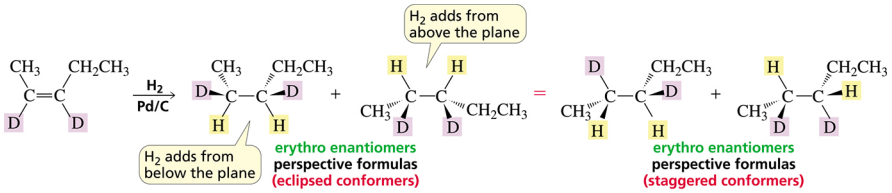
The Stereochemistry of Hydrogen Addition

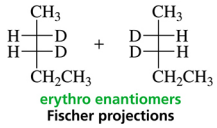
only syn addition



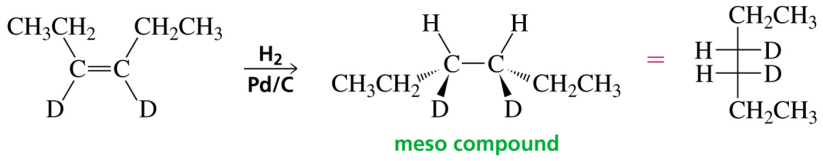
addition of H_2 is a syn addition

Syn Addition to a Cis Isomer Forms Only the Erythro Stereoisomers



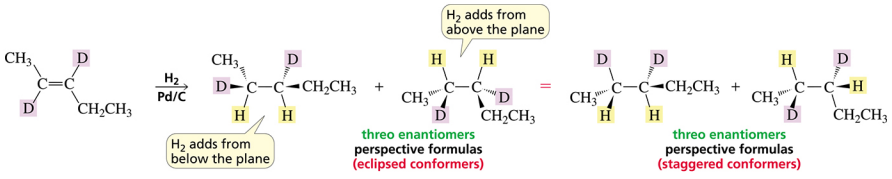


If the Substituents are the Same, the Erythro Stereoisomer is a Meso Compound



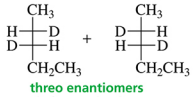
meso compound

Syn Addition to a Trans Isomer Forms Only the Threo Stereoisomers



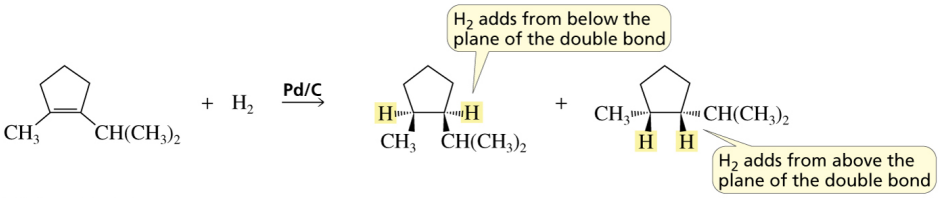
threo enantiomers
perspective formulas
(eclipsed conformers)

threo enantiomers
perspective formulas
(staggered conformers)

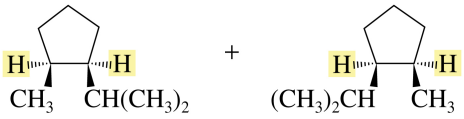


threo enantiomers
Fischer projections

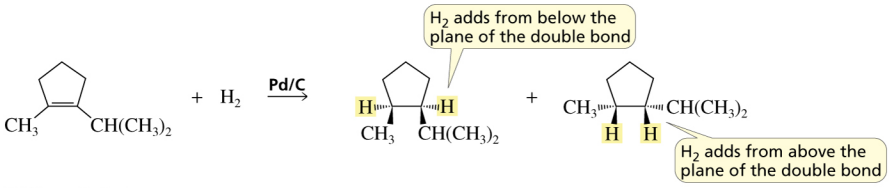
Syn Addition to a Cis Isomer Forms Only the Cis Stereoisomers



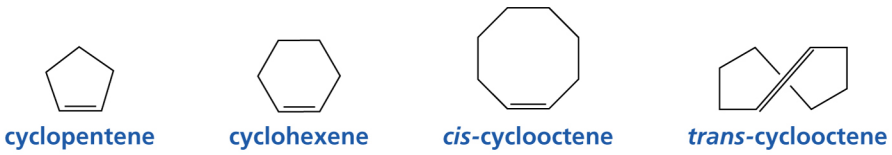
The products can also be written as mirror images.



If the Substituents are the Same, The Cis Stereoisomer is a Meso Compound



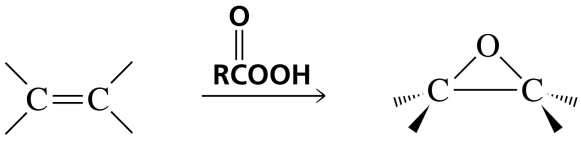
Cyclic Alkenes are Cis, Unless They Have at Least Eight Ring Atoms



cyclopentene cyclohexene *cis*-cyclooctene *trans*-cyclooctene

The Stereochemistry of Peroxyacid Addition

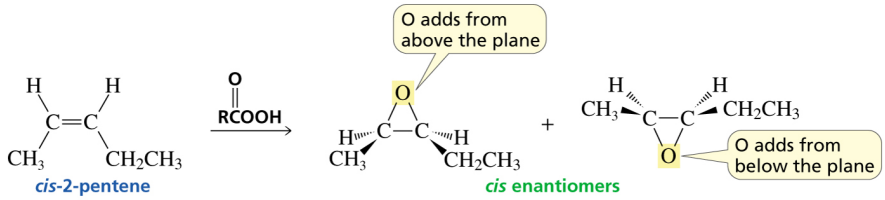
only syn addition



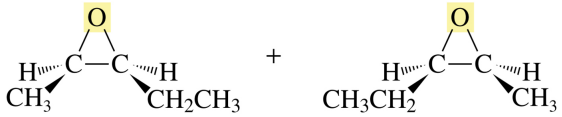
an alkene an epoxide

addition of peroxyacid is a syn addition

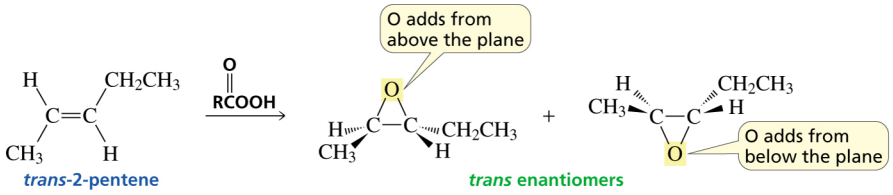
Syn Addition to a Cis Isomer Forms Only the Cis Enantiomers



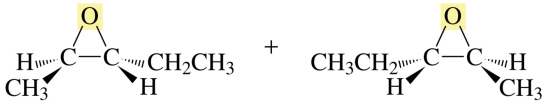
The products can also be written as mirror images.



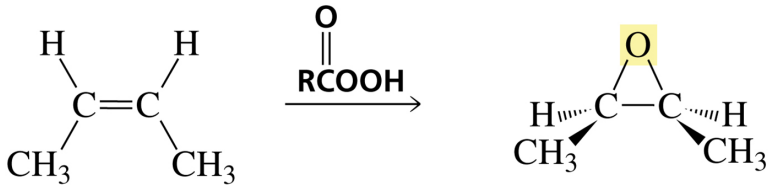
Syn Addition to a Trans Isomer Forms Only the Trans Enantiomers



The products can also be written as mirror images.



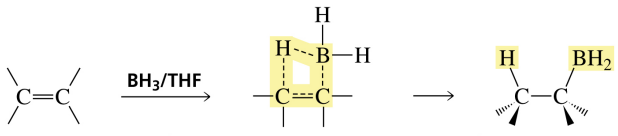
If the Substituents are the Same, the Cis Stereoisomer is a Meso Compound



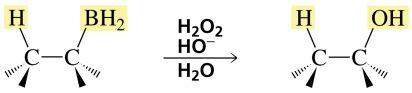
cis-2-butene

The Stereochemistry of Hydroboration–Oxidation

only syn addition



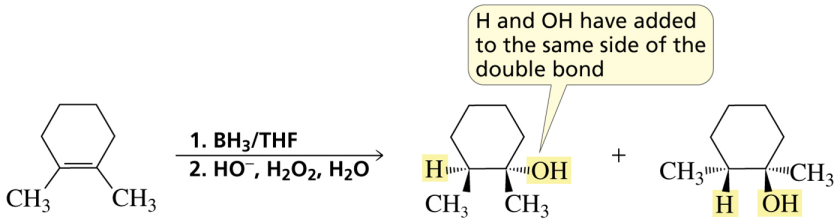
addition of borane is a syn addition



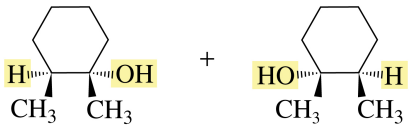
an alkyl borane an alcohol

hydroboration–oxidation is overall a syn addition of water

The H and OH Add to the Same Side of the Ring

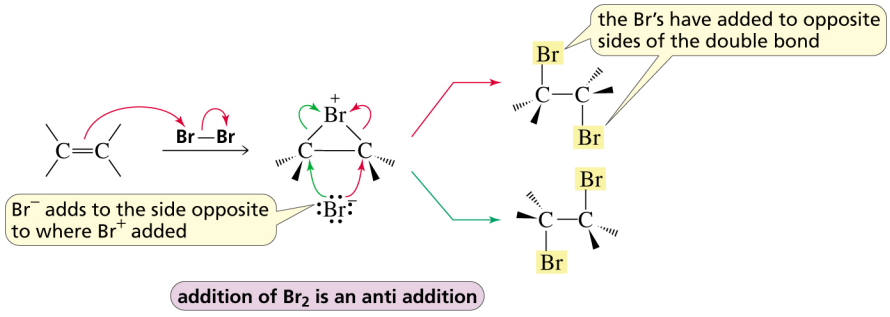


The products can also be written as mirror images.

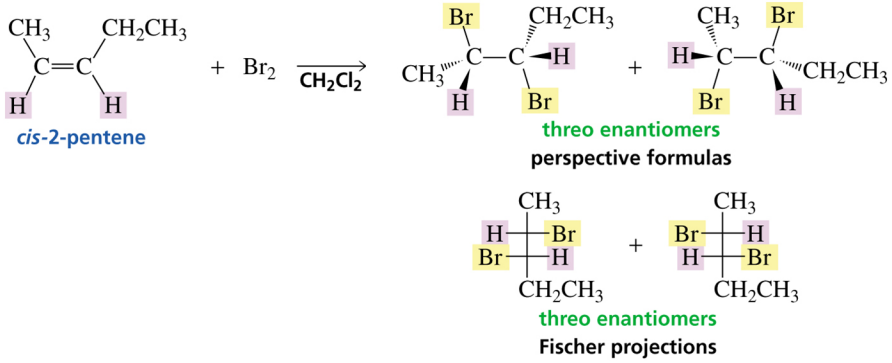


Stereochemistry of Reactions That Form a Cyclic Bromonium (or Chloronium) Ion Intermediate

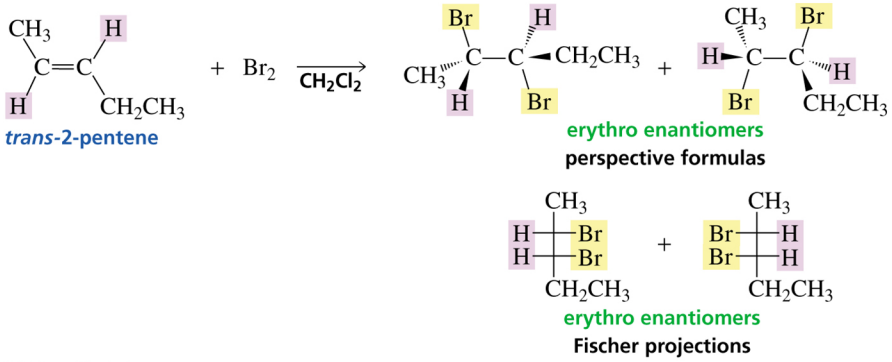
only anti addition



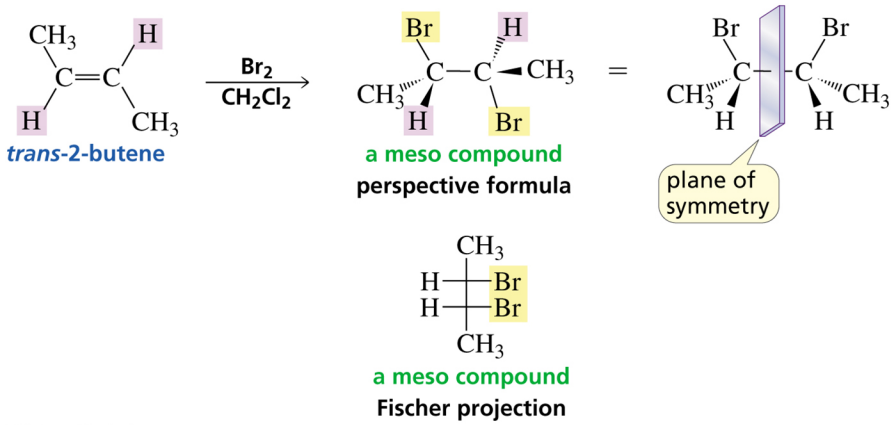
Anti Addition to a Cis Isomer Forms Only the Threo Stereoisomers



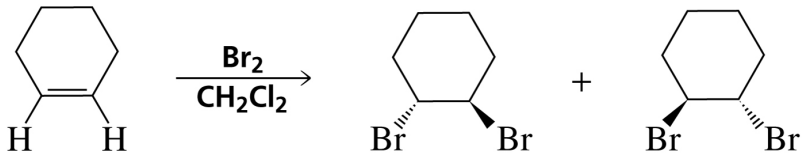
Anti Addition to a Trans Isomer Forms Only the Erythro Stereoisomers



If the Substituents are the Same, the Erythro Stereoisomer is a Meso Compound



Anti Addition to a Cis Isomer Forms Only the Trans Stereoisomers



CIS-SYN-(ERYTHRO or CIS)

You can change two terms but not one.

CIS-ANTI-(THREO or TRANS) OK

TRANS-ANTI-(ERYTHRO or CIS) OK

CIS-ANTI-(ERYTHRO or CIS) not OK

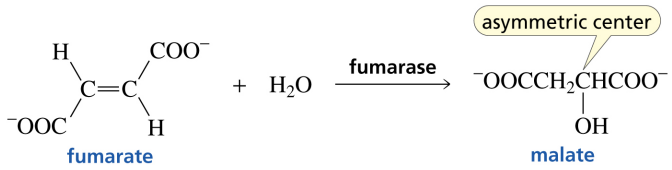
Table 6.1 Stereochemistry of Alkene Addition Reactions

Reaction	Type of addition	Stereoisomers formed
Addition reactions that create one asymmetric center in the product		If the reactant does not have an asymmetric center, then a racemic mixture is formed.
		If the reactant has an asymmetric center, then unequal amounts of a pair of diastereomers are formed.
Addition reactions that create two asymmetric centers in the product		
Addition of reagents that form a carbocation intermediate	syn and anti	Four stereoisomers are formed; the cis and trans isomers each form the same products.
Addition of H_2	syn	cis → erythro or cis enantiomers*
Addition of a peroxyacid	syn	trans → threo or trans enantiomers
Addition of BH_3 or BHR_2	syn	
Addition of Br_2, $Br_2 + H_2O$, Br_2 + ROH (any reaction that forms a cyclic bromonium or chloronium ion intermediate)	anti	cis → threo or trans enantiomers trans → erythro or cis enantiomers*

*An acyclic compound forms the erythro enantiomers; a cyclic compound forms the cis enantiomers. If the two asymmetric centers have the same substituents, a meso compound will be formed instead of the pair of erythro or cis enantiomers.

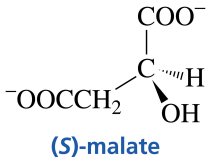
© 2017 Pearson Education, Inc.

An Enzyme Forms Only One Stereoisomer

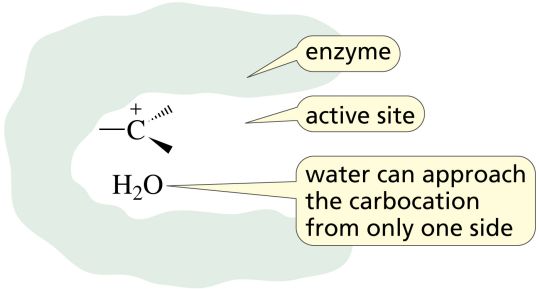


Enzyme-catalyzed reactions are completely stereoselective.

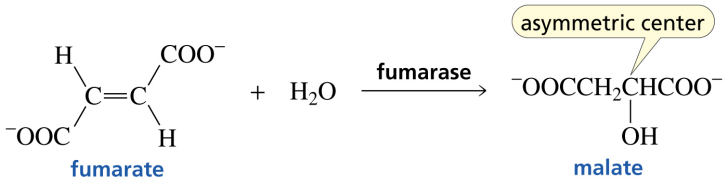
Only the *S* stereoisomer is formed.

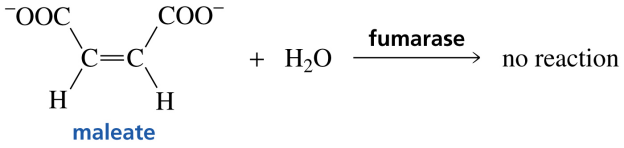


An Enzyme Can Block One Side of the Reactant



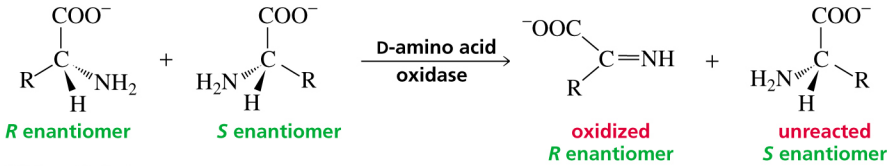
An Enzyme Catalyzes the Reaction of Only One Stereoisomer





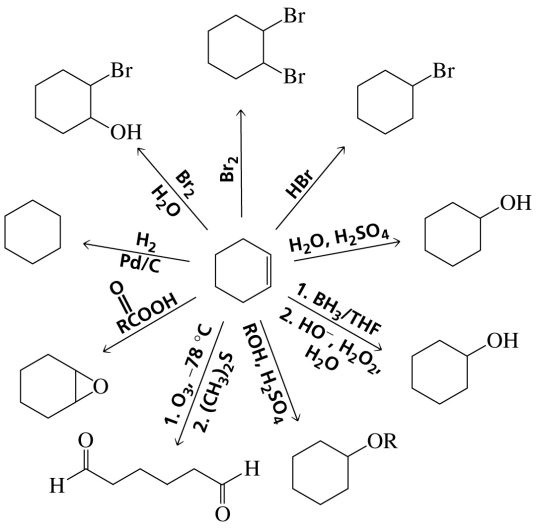
Enzyme-catalyzed reactions are stereospecific.

The Stereospecificity of an Enzyme-Catalyzed Reaction Allows Enantiomers to be Separated



When A Reacts, B is Synthesized

$$\mathbf{A} \longrightarrow \mathbf{B}$$

A reacts;
B is synthesized

Compounds That Can Be Formed From an Alkene