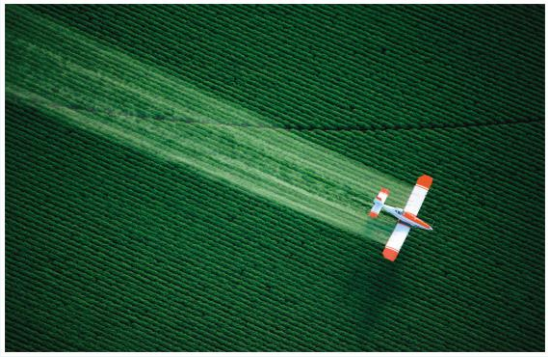
Chapter 6

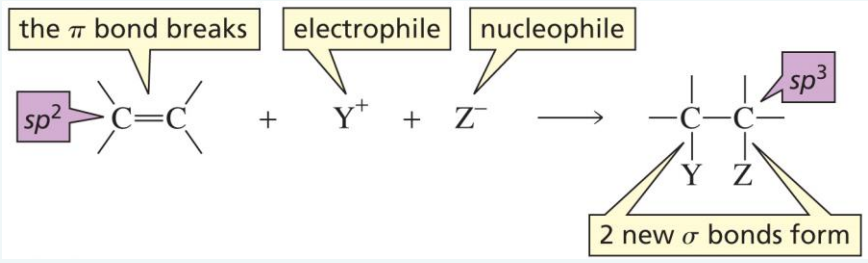


The Reactions of Alkenes and Alkynes

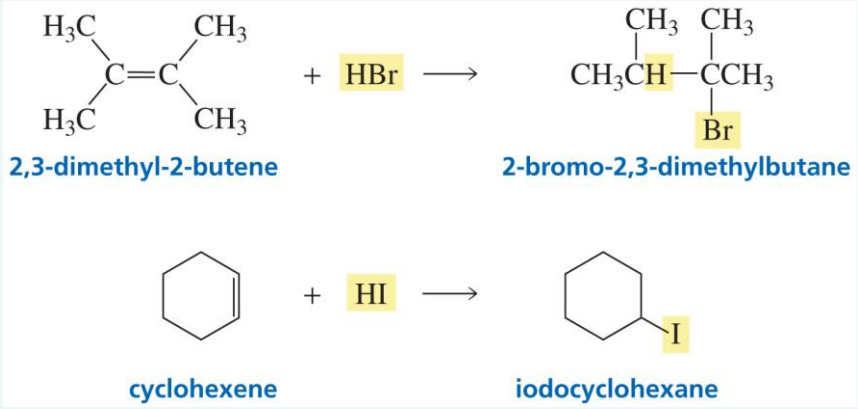
The Stereochemistry of Addition Reactions

Paula Yurkanis Bruice
University of California, Santa Barbara

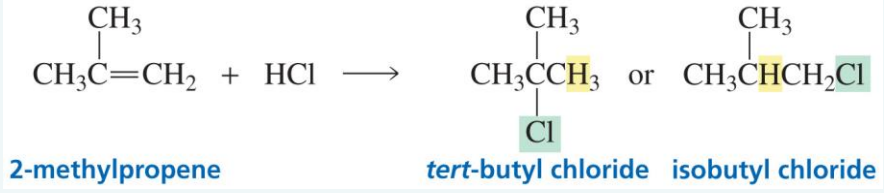
An Electrophilic Addition Reaction



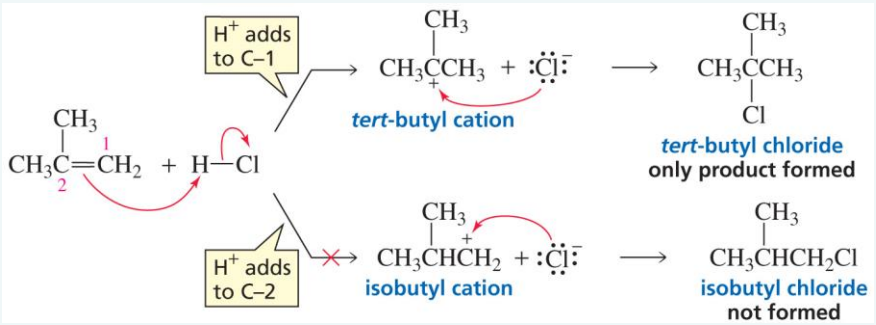
Addition of Hydrogen Halides



Which *sp*^{2} Carbon gets the H$^+$?

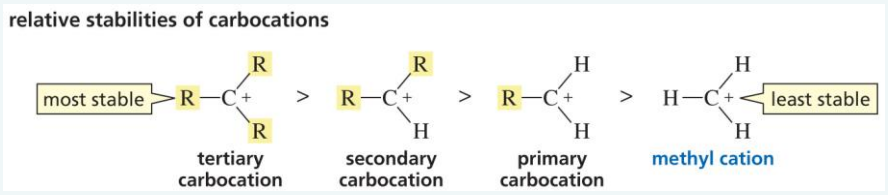


The Mechanism

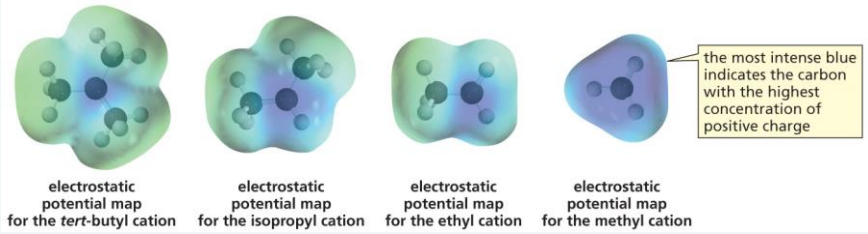


Carbocation formation is the rate-limiting step.

Relative Stabilities of Carbocations

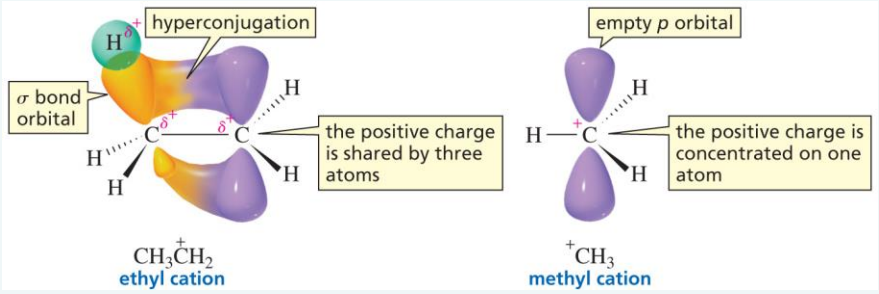


Carbocation Stability

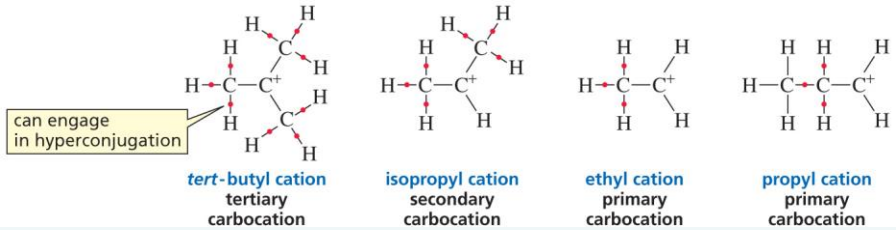


Alkyl groups decrease the concentration of positive charge on the carbon.

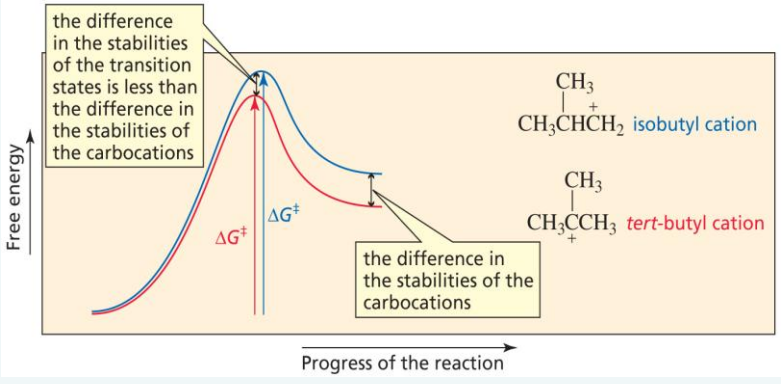
Hyperconjugation Stabilizes a Carbocation



Hyperconjugation

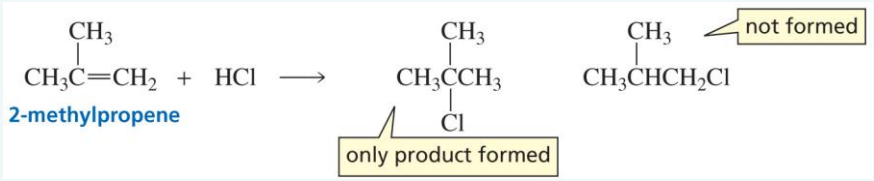


Why the difference in Rate?

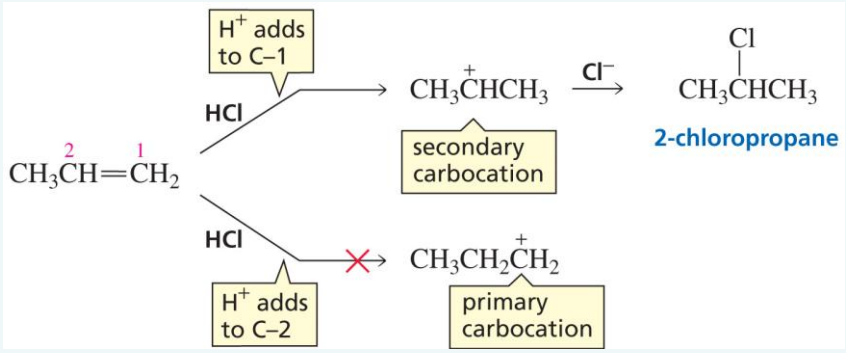


The more stable carbocation is formed more rapidly.

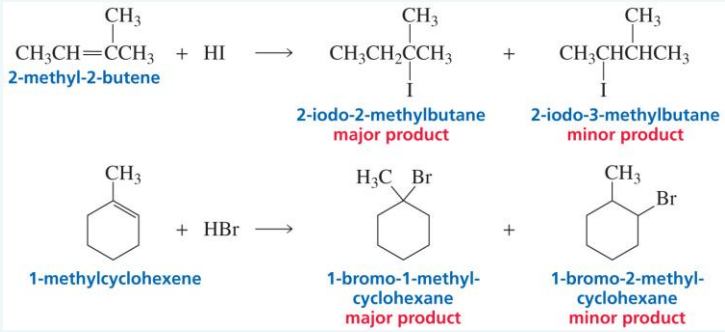
The difference in Carbocation Stability determines the Products



Electrophilic Addition Reactions are Regisoselective



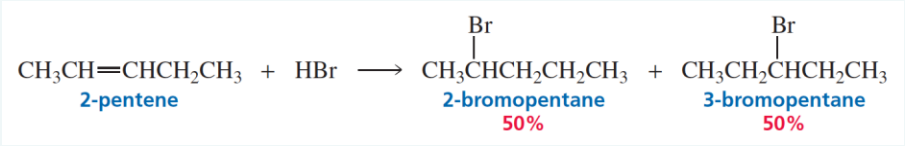
The Electrophile adds to the sp^2 Carbon bonded to the most Hydrogens

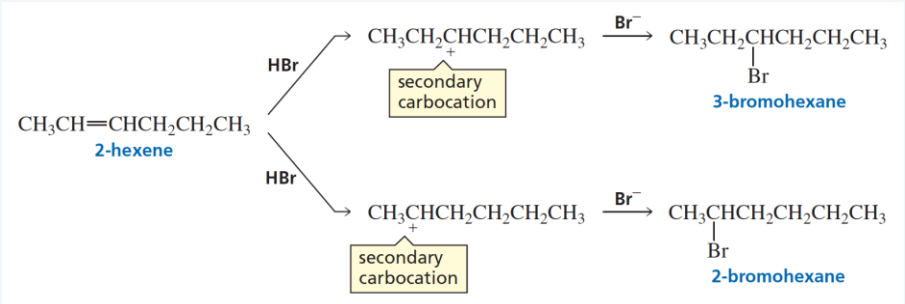


A regioselective reaction forms more of one constitutional isomer than another.

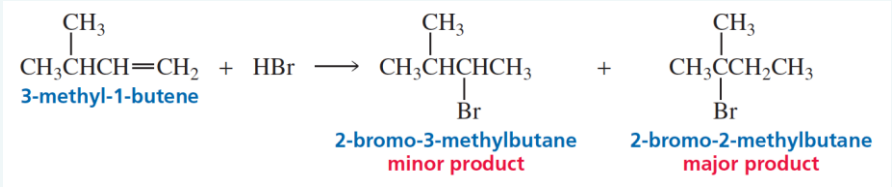
- Completely regioselective
- Highly regioselective
- Moderately regioselective

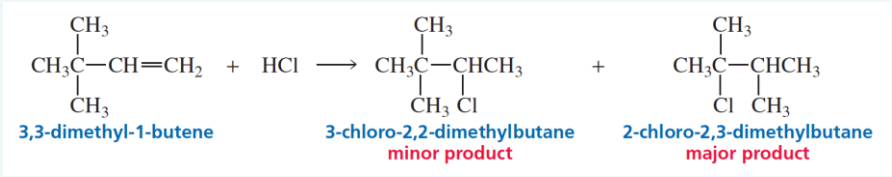
Not Regioselective



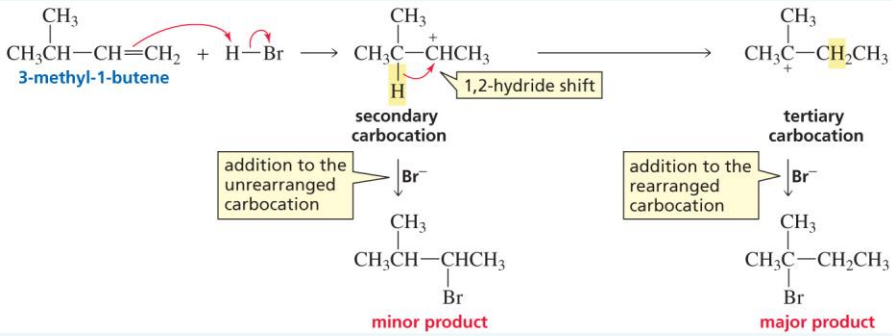


The major product is a Surprise

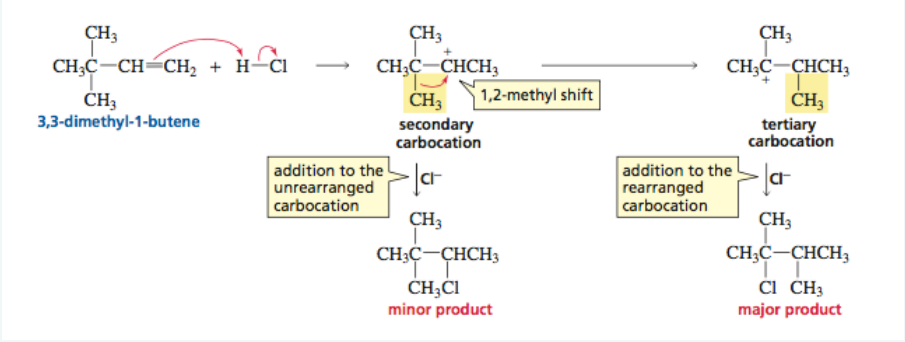




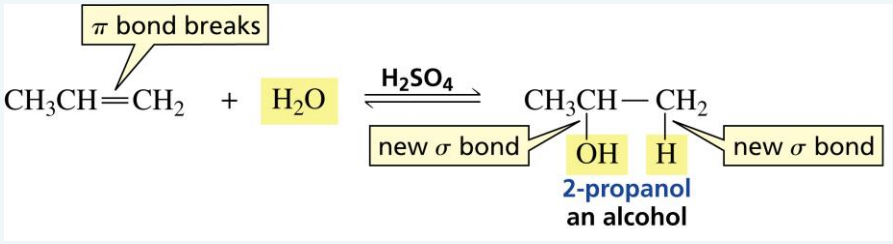
Carbocation Rearrangement (a 1,2-hydride shift)



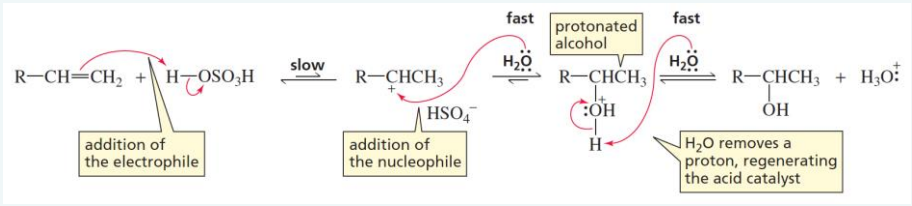
Carbocation Rearrangement (a 1,2-methyl shift)



Acid-Catalyzed Addition of Water



Mechanism for the Acid-Catalyzed Addition of Water



Regioselective vs. Stereoselective Reactions

a regioselective reaction

constitutional isomers

A ⟶ B + C

more B is formed than C

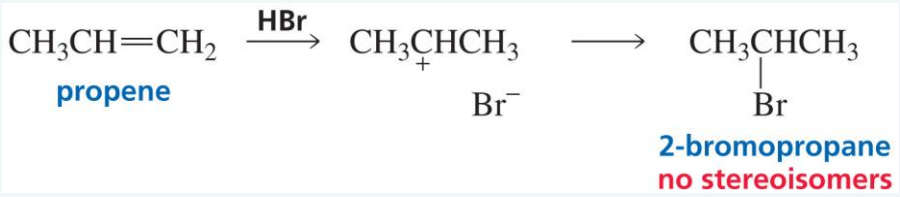
a stereoselective reaction

stereoisomers

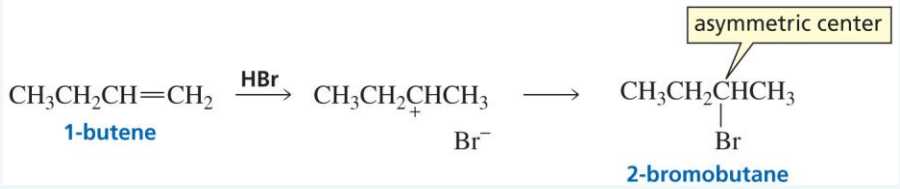
A ⟶ B + C

more B is formed than C

The Product does not have Stereoisomers

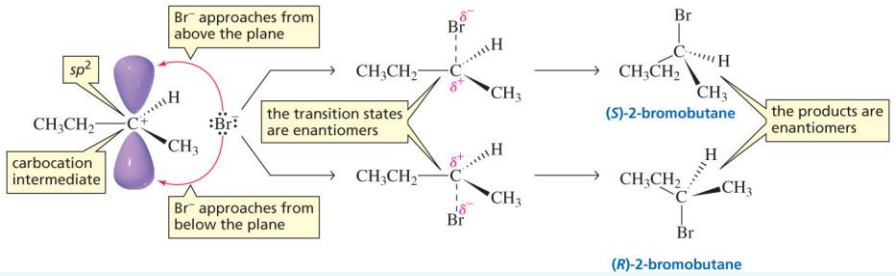


The Product is a Racemic Mixture

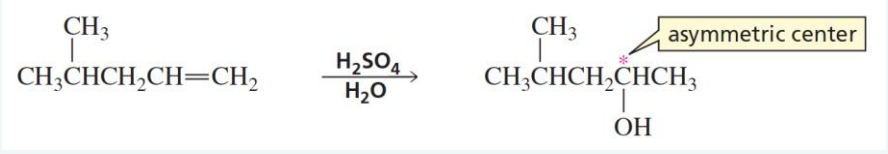


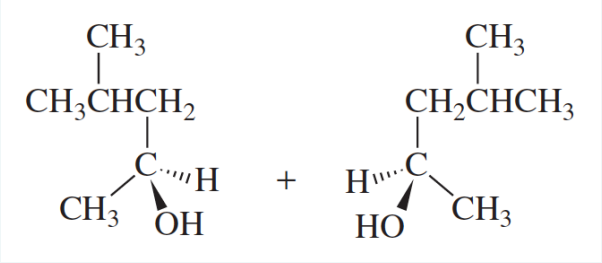
When a reactant that does not have an asymmetric center forms a product that has one asymmetric center, the product is a racemic mixture.

Formation of a Racemic Mixture

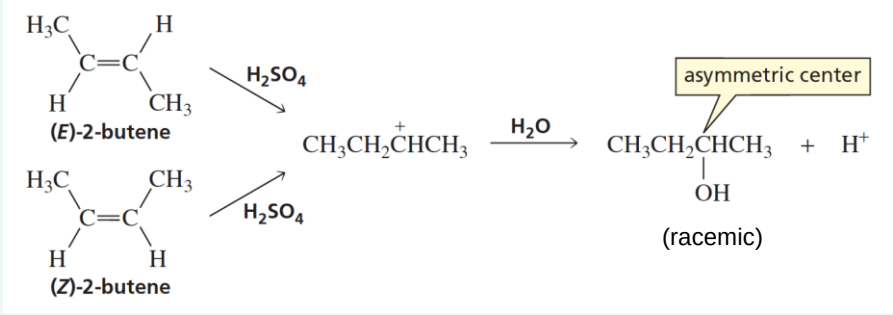


The Product is a Racemic Mixture

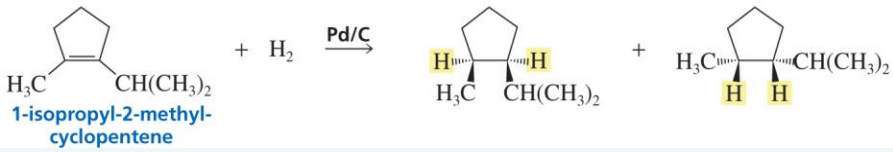




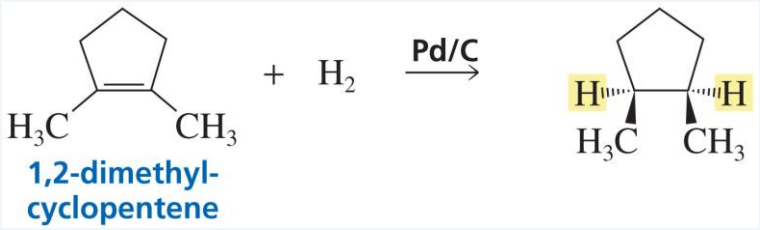
The Product is a Racemic Mixture



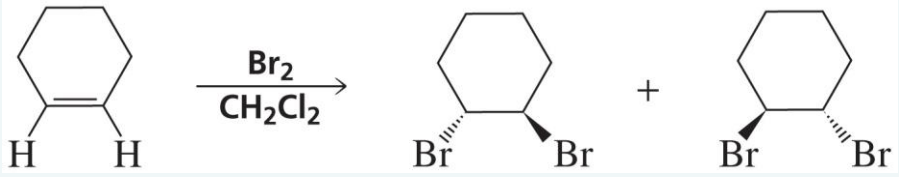
Addition of H_2 to a Cis Isomer forms only the Cis Stereoisomers



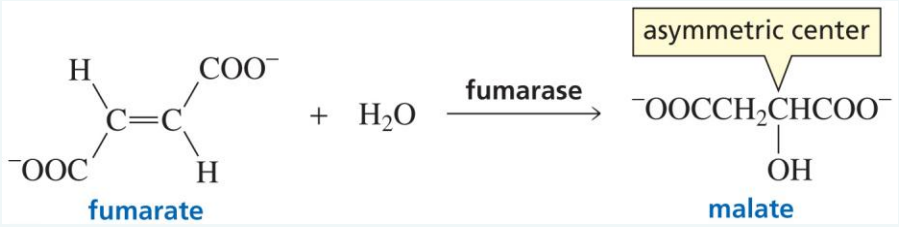
If the Substituents are the same, the Cis Stereoisomer is a Meso Compound

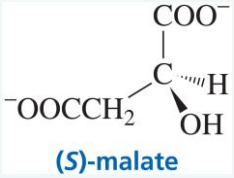


Anti Addition to a Cis Isomer forms only the Trans Stereoisomers

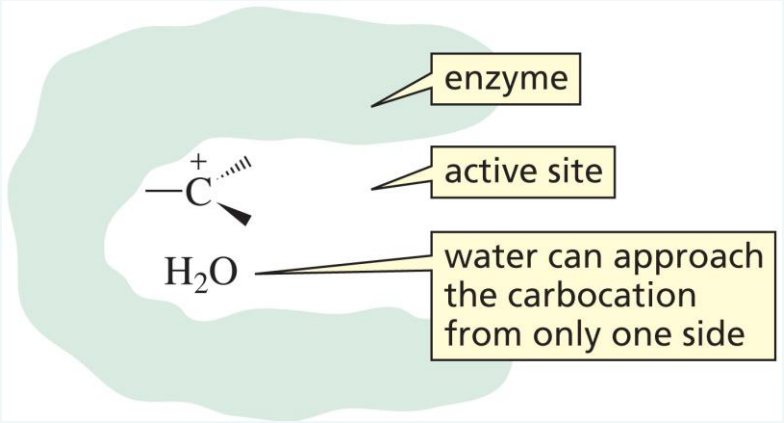


An Enzyme forms only one Stereoisomer; the Reaction is Completely Stereoselective

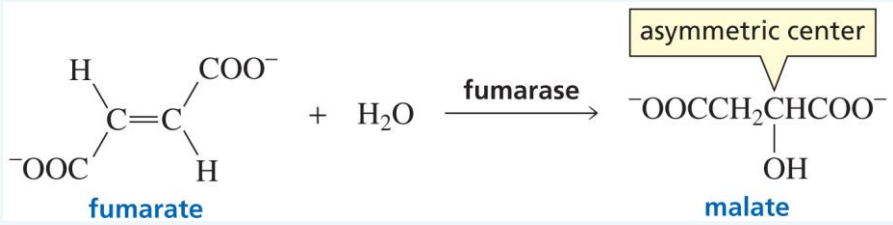


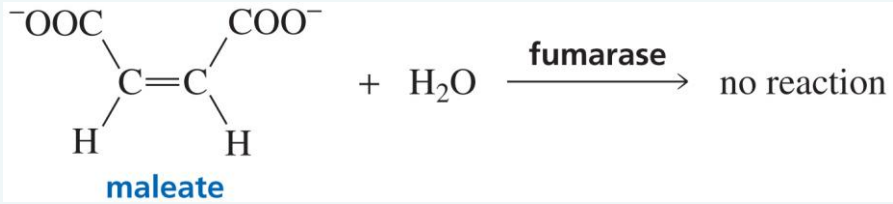


An Enzyme can block one side of the Reactant

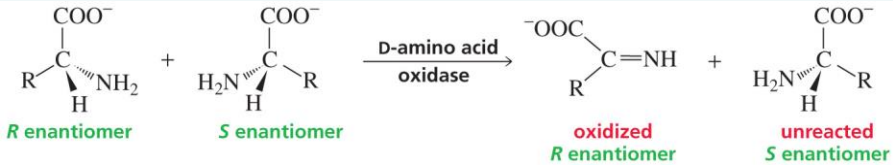


An Enzyme reacts with only one Stereoisomer





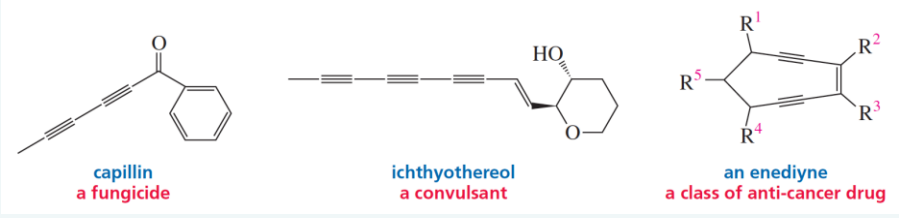
Therefore, Enantiomers can be separated using an Enzyme-Catalyzed Reaction



An Introduction to Alkynes

An alkyne is a hydrocarbon that contains a carbon–carbon triple bond.

General formula: C_nH_{2n-2} (acyclic)
C_nH_{2n-4} (cyclic)

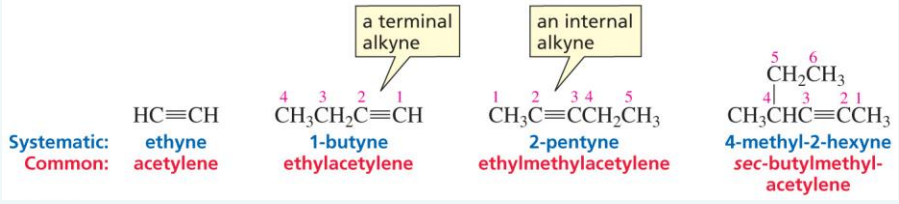


capillin
a fungicide

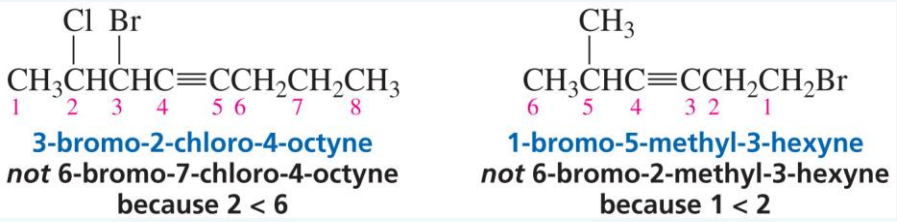
ichthyothereol
a convulsant

an enediyne
a class of anti-cancer drug

Nomenclature of Alkynes

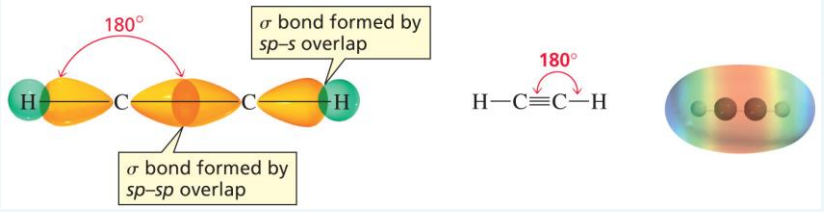


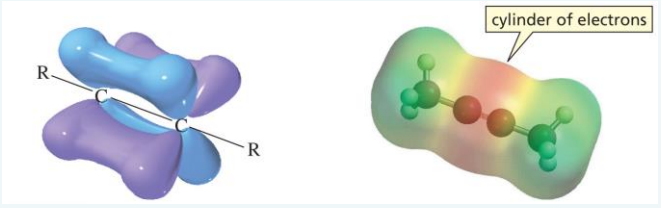
Nomenclature of Alkynes



- The "yne" suffix is assigned the lowest number.
- The substituents are assigned so the lowest number is in the name.

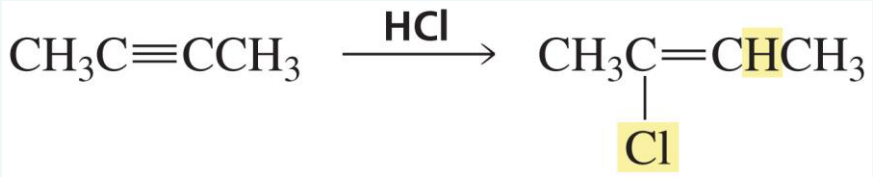
The Structure of Alkynes





The triple bond is composed of a sigma bond and two π bonds.

Alkynes (Like Alkenes) undergo Electrophilic Addition Reactions

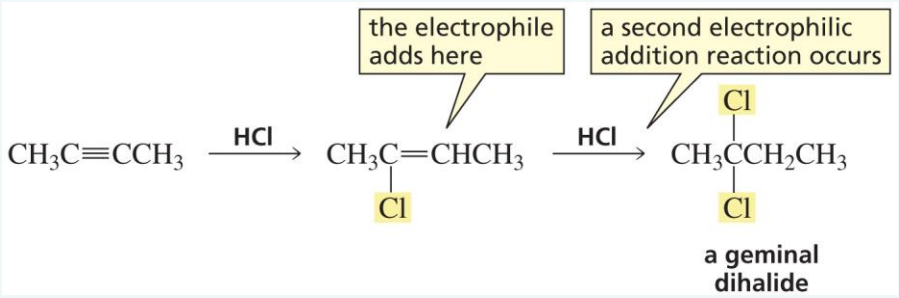


The first step is addition of an Electrophile

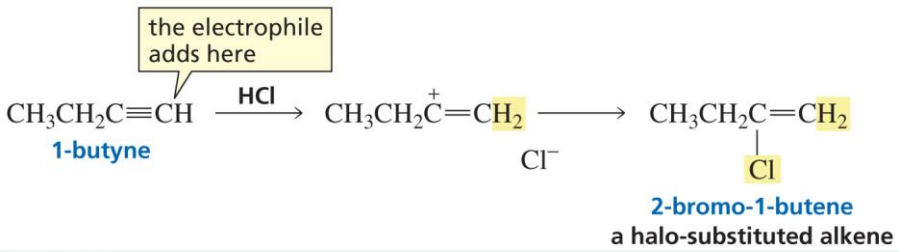
Addition of an electrophile to an alkene

Addition of an electrophile to an alkyne

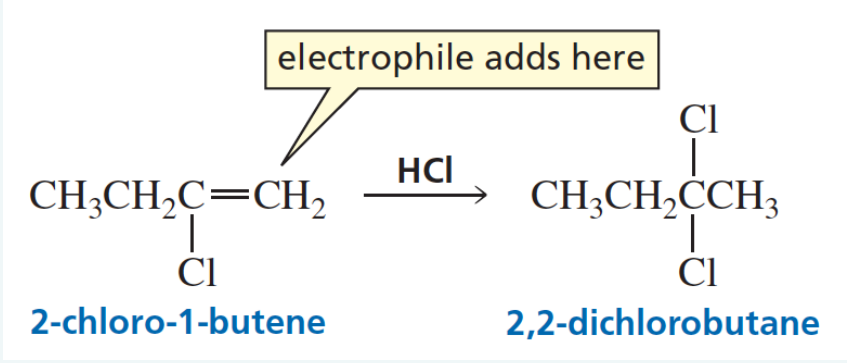
A second Addition Reaction can Occur



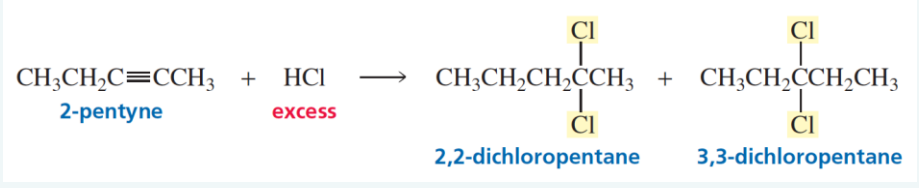
Addition to a Terminal Alkyne is Regioselective



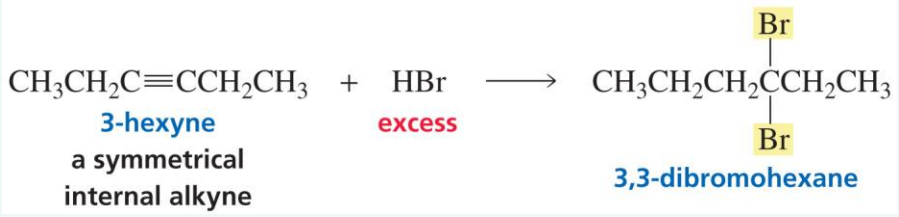
The second Electrophilic Addition reaction is also Regioselective



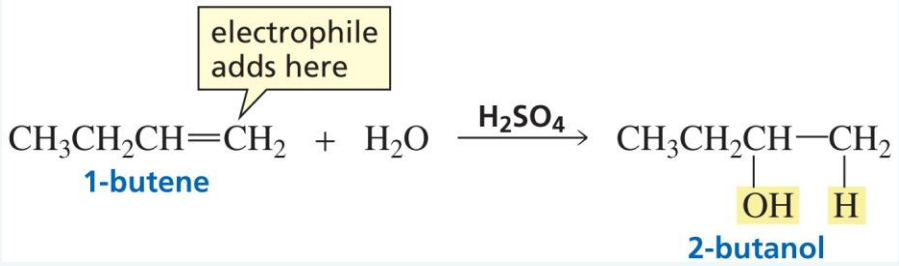
An Asymmetrical Internal Alkyne forms two Products



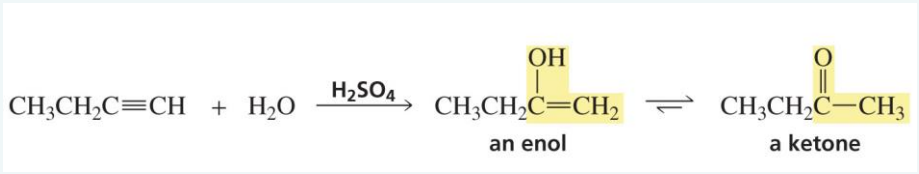
A Symmetrical Internal Alkyne forms one Product



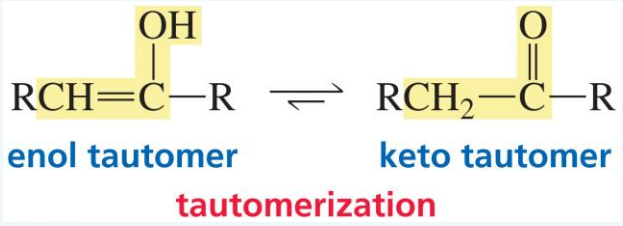
Acid-Catalyzed Addition of water to an Alkene



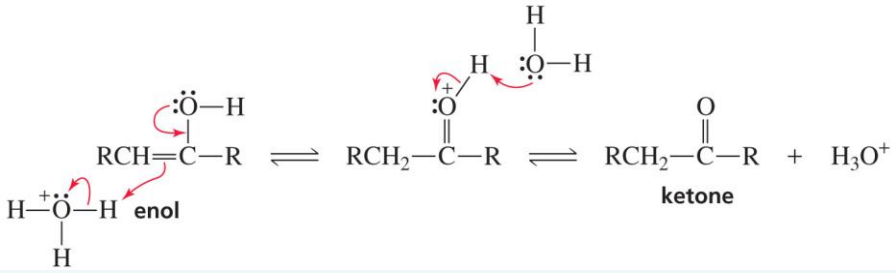
Acid-Catalyzed Addition of water to an Alkyne



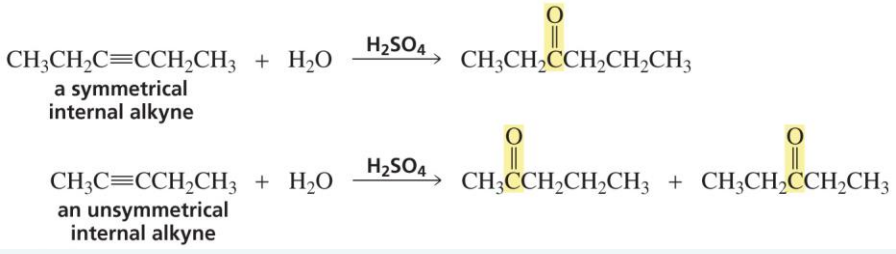
Keto–Enol Interconversion



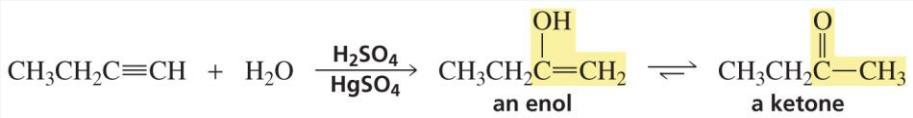
Mechanism for Acid-Catalyzed Keto–Enol Interconversion



Acid-Catalyzed Addition of Water

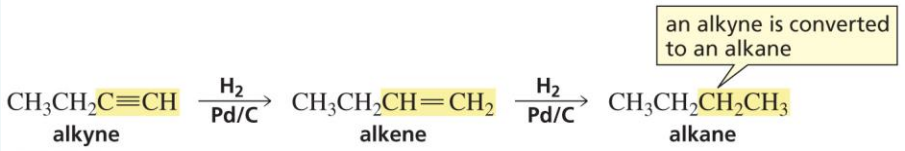


A Terminal Alkyne is less reactive than an Internal Alkyne



Because terminal alkynes are less reactive, the rate of the reaction is increased with a mercuric ion catalyst.

Addition of Hydrogen forms an Alkane

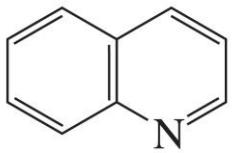


Stopping at the Alkene

Lindlar Catalyst

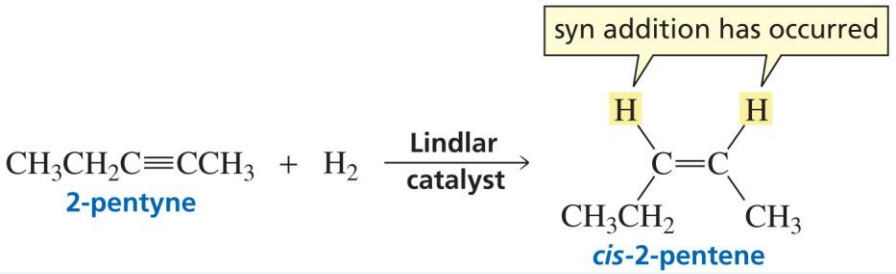
$(CH_3COO^-)_2Pb^{2+}$

lead(II) acetate

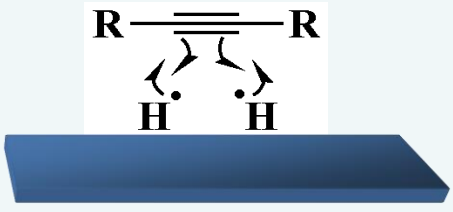


quinoline

Syn Addition



Why Cis?



The catalyst delivers the hydrogens to one side of the triple bond.