Chapter 6



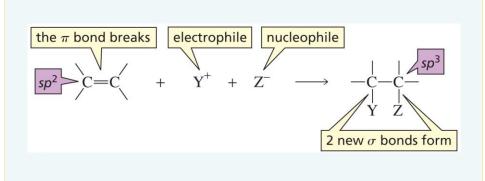
The Reactions of Alkenes and Alkynes

The Stereochemistry of Addition Reactions

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An Electrophilic Addition Reaction



Addition of Hydrogen Halides

Which sp² Carbon gets the H+?

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3\text{C} = \text{CH}_2 \ + \ \text{HCl} \ \longrightarrow \ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3\text{CC} \\ \text{H}_3 \end{array} \text{ or } \text{CH}_3\text{C} \\ \text{Cl} \\ \text{Cl} \\ \text{2-methylpropene} \end{array}$$

The Mechanism

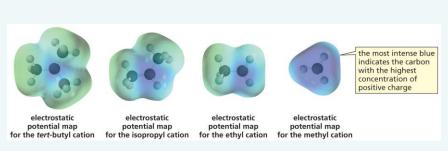
$$\begin{array}{c} \text{CH}_3 \\ \text{to C-1} \\ \text{CH}_3\text{CCH}_3 \\ \text{CH}_3\text{CCH}_3 \\ \text{CH}_3\text{CCH}_3 \\ \text{CH}_3\text{C} \\ \text{CH}_2\text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3\text{CH}_2\text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3\text{CH}_2\text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3\text{CH}_2\text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{CH}_2\text$$

Carbocation formation is the rate-limiting step.

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Relative Stabilities of Carbocations

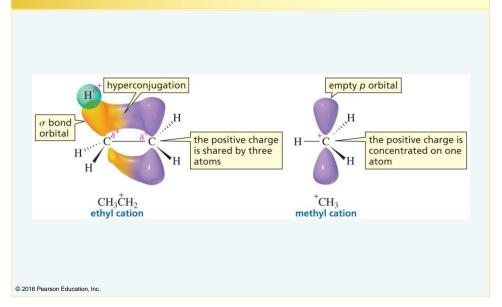
Carbocation Stability

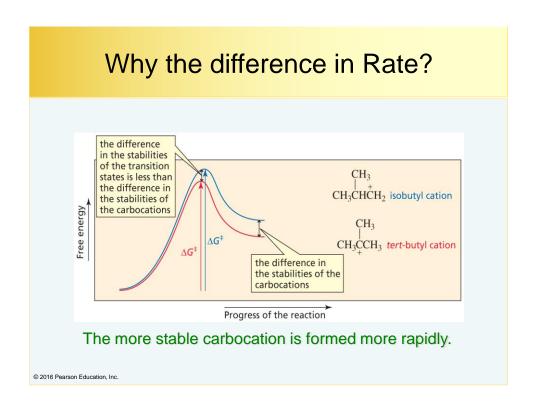


Alkyl groups decrease the concentration of positive charge on the carbon.

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Hyperconjugation Stabilizes a Carbocation

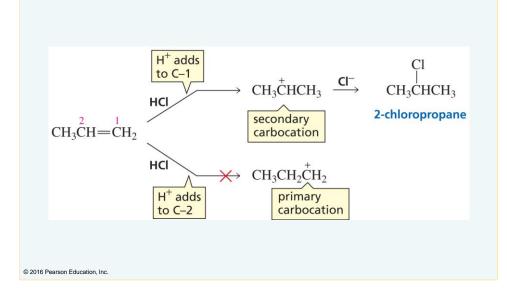




The difference in Carbocation Stability determines the Products

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \text{C} = \text{CH}_2 + \text{HCl} \longrightarrow \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \text{CCH}_3 \end{array} \\ \text{CH}_3 \text{CHCH}_2 \text{Cl} \end{array}$$

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

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Not Regioselective

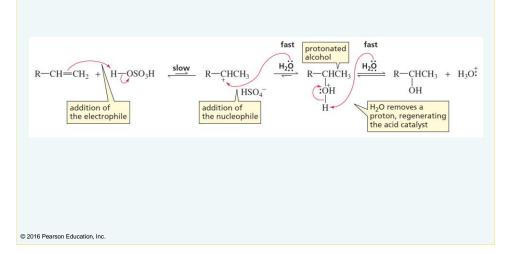
The major product is a Surprise

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 $\begin{array}{c} & & \\ &$

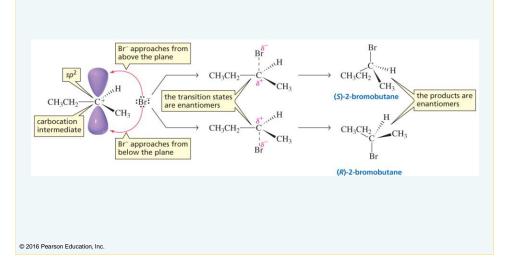
The Product does not have Stereoisomers

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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

$$\begin{array}{c} H_3C \\ C = C \\ H \\ CH_3 \\ (\emph{E})\text{-2-butene} \\ H_3C \\ C = C \\ H \\ H \\ C = C \\ H_2SO_4 \\ \end{array} \begin{array}{c} \text{asymmetric center} \\ CH_3CH_2CHCH_3 \\ OH \\ (racemic) \\ \end{array} \begin{array}{c} H_2O \\ OH \\ (racemic) \\ \end{array}$$

Addition of H₂ to a Cis Isomer forms only the Cis Stereoisomers

$$\begin{array}{c} + H_2 \\ + H_3C \\ - CH(CH_3)_2 \\ - 1-isopropyl-2-methyl-cyclopentene \\ \end{array}$$

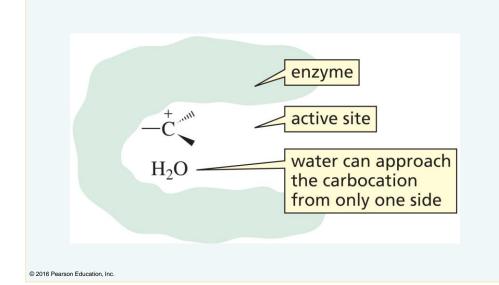
If the Substituents are the same, the Cis Stereoisomer is a Meso Compound

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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

$$\begin{array}{c} H \\ C=C \\ -OOC \\ H \\ \hline \end{array} \\ \begin{array}{c} H \\ + \\ H_2O \\ \end{array} \\ \begin{array}{c} \text{fumarase} \\ -OOCCH_2CHCOO-\\ OH \\ \text{maleate} \\ \end{array} \\ \begin{array}{c} OOC \\ COO-\\ H \\ \end{array} \\ \begin{array}{c} H \\ H_2O \\ \end{array} \\ \begin{array}{c} \text{fumarase} \\ \text{maleate} \\ \end{array} \\ \begin{array}{c} \text{no reaction} \\ \text{maleate} \\ \end{array}$$

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)

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Nomenclature of Alkynes

Nomenclature of Alkynes

Cl Br CH₃

CH₃CHCHC
$$\equiv$$
CCH₂CH₂CH₃

3-bromo-2-chloro-4-octyne not 6-bromo-7-chloro-4-octyne because 2 < 6

CH₃

CH₃

CH₃

CH₃

CH₃CHC \equiv CCH₂CH₂Br

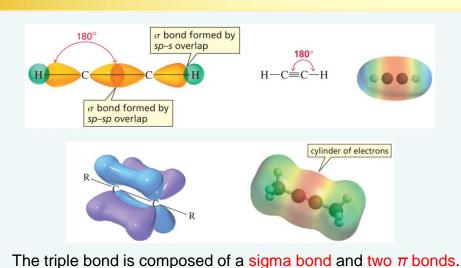
6 5 4 3 2 1

1-bromo-5-methyl-3-hexyne not 6-bromo-2-methyl-3-hexyne because 1 < 2

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

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The Structure of Alkynes



Alkynes (Like Alkenes) undergo Electrophilic Addition Reactions

$$CH_3C = CCH_3 \xrightarrow{\text{HCI}} CH_3C = CHCH_3$$

$$CI$$

The first step is addition of an Electrophile

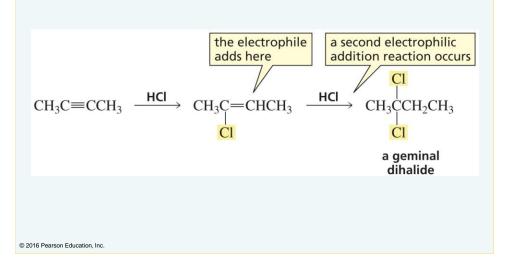


Addition of an electrophile to an alkene

Addition of an electrophile to an alkyne

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A second Addition Reaction can Occur



Addition to a Terminal Alkyne is Regioselective

the electrophile adds here

$$CH_3CH_2C \equiv CH \xrightarrow{HCl} CH_3CH_2\overset{+}{C} = CH_2 \longrightarrow CH_3CH_2C = CH_2$$

1-butyne

 Cl^-

2-bromo-1-butene a halo-substituted alkene

The second Electrophilic Addition reaction is also Regioselective

$$\begin{array}{c} \text{electrophile adds here} \\ \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 & \text{HCl} \\ \text{Cl} & \text{CH}_3\text{CH}_2\text{CCH}_3 \\ \text{2-chloro-1-butene} & \textbf{2,2-dichlorobutane} \\ \end{array}$$

An Asymmetrical Internal Alkyne forms two Products

$$CH_3CH_2C \equiv CCH_3 + HCI \longrightarrow CH_3CH_2CH_2CCH_3 + CH_3CH_2CCH_2CH_3$$

$$2\text{-pentyne} \quad \text{excess} \quad CI$$

$$2\text{,2-dichloropentane} \quad 3\text{,3-dichloropentane}$$

A Symmetrical Internal Alkyne forms one Product

Acid-Catalyzed Addition of water to an Alkene

$$\begin{array}{c} \text{electrophile} \\ \text{adds here} \\ \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 \ + \ \text{H}_2\text{O} \ & \begin{array}{c} \text{H}_2\text{SO}_4 \\ \text{OH} \end{array} \\ \text{1-butene} \end{array} \quad \begin{array}{c} \text{CH}_3\text{CH}_2\text{CH} - \text{CH}_2 \\ \text{OH} \ \text{H} \\ \text{2-butanol} \end{array}$$

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Acid-Catalyzed Addition of water to an Alkyne

$$CH_3CH_2C \equiv CH + H_2O \xrightarrow{\textbf{H_2SO_4}} CH_3CH_2C = CH_2 \implies CH_3CH_2C - CH_3$$
 an enol a ketone

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

$$CH_{3}CH_{2}C \equiv CH + H_{2}O \xrightarrow{\textbf{H}_{2}\textbf{SO}_{4}} CH_{3}CH_{2}C = CH_{2} \iff CH_{3}CH_{2}C - CH_{3}$$
an enol a ketone

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

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Addition of Hydrogen forms an Alkane

Stopping at the Alkene

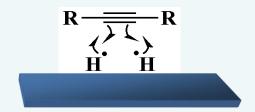
$$CH_3CH_2C \equiv CH + H_2 \xrightarrow{\text{Lindlar}} CH_3CH_2CH = CH_2$$

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Lindlar Catalyst

Syn Addition

Why Cis?



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