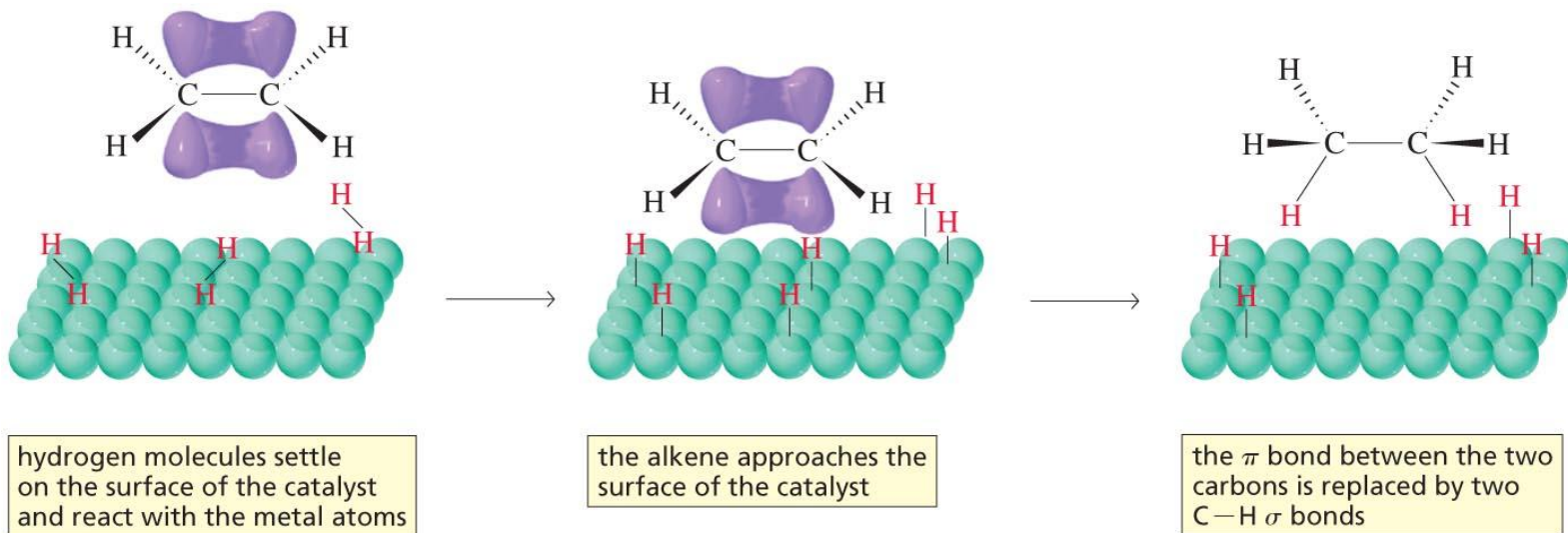


Organic Chemistry

2th Edition

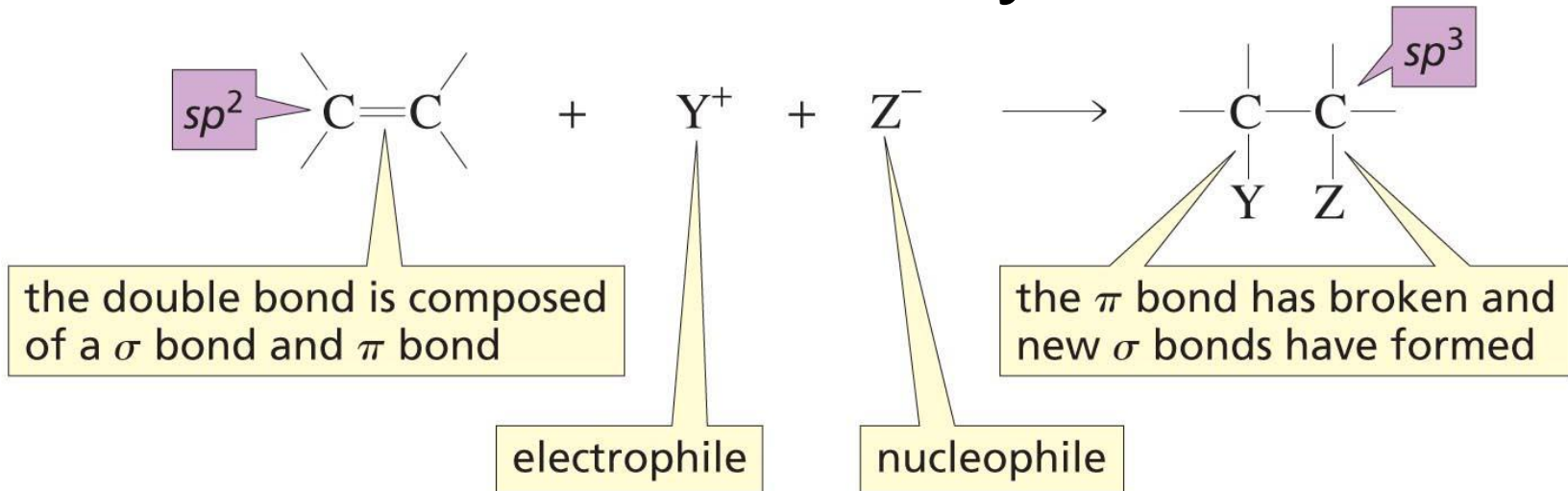
Paula Yurkanis Bruice

Chapter 5 The Reactions of Alkenes



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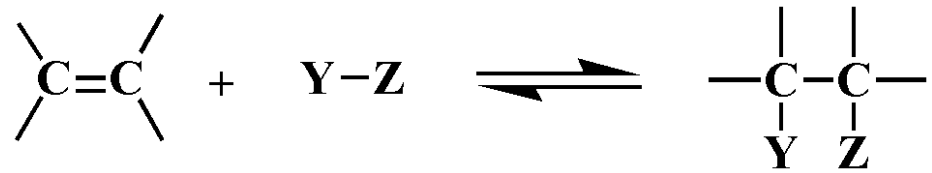
Electrophilic Addition of Alkenes: Reaction and Synthesis



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**Y-Z: H-Cl, H-Br, H-I,
Cl-Cl, & Br-Br**

**Reaction of an alkene is
an addition reaction.**



Electron-rich atoms or molecules (nucleophiles) are attracted to electron-deficient atoms or molecules (electrophiles):



these are nucleophiles because they have a pair of electrons to share

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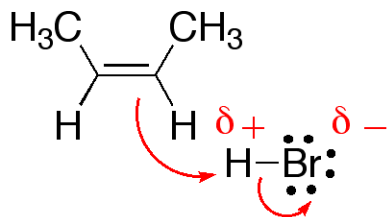


these are electrophiles because they can accept a pair of electrons

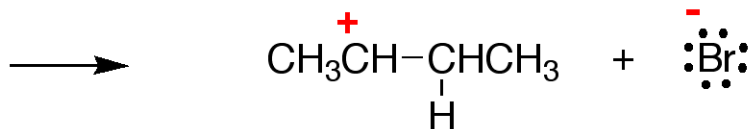
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Your First Reaction: Addition of HBr to an Alkene

Nucleophile



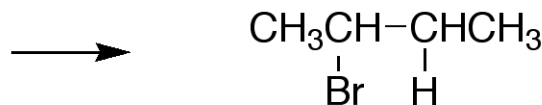
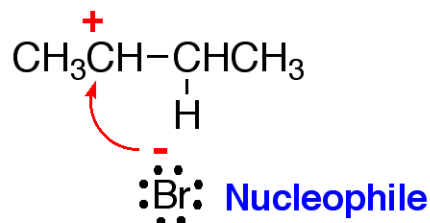
Electrophile



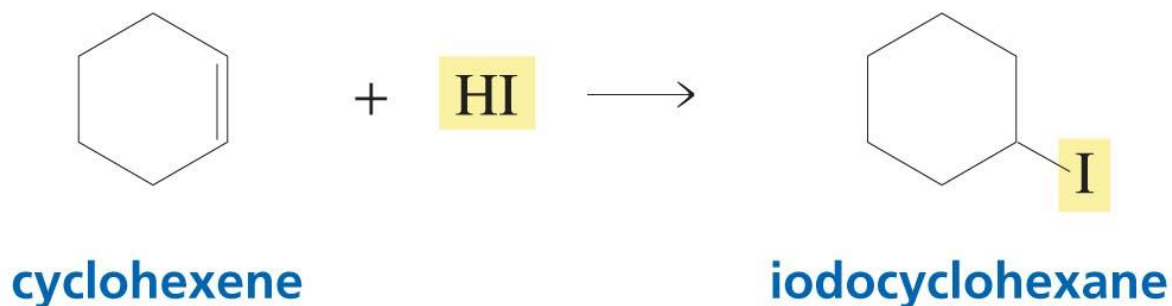
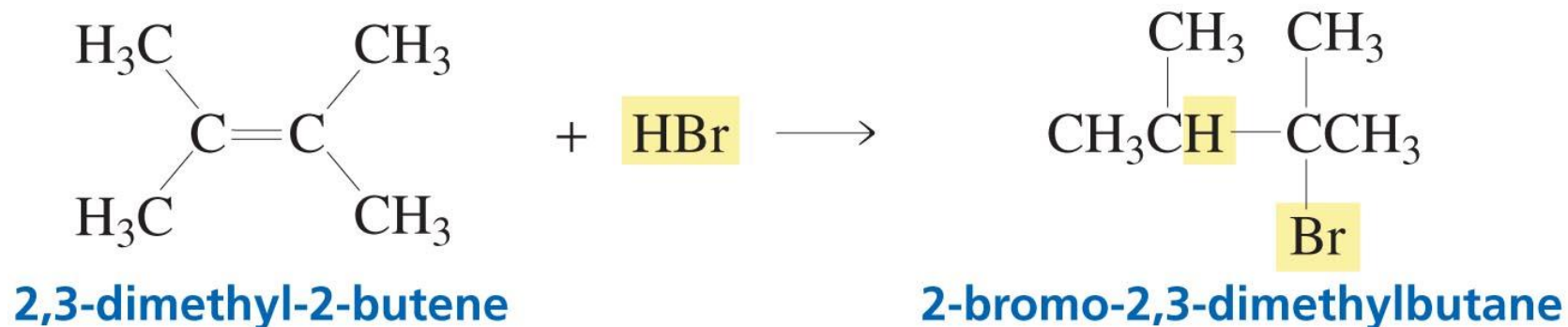
1st Step: Addition of a proton to the alkene. The proton is the electrophile.

2nd Step: Bromide traps the carbocation. Bromide is the nucleophile.

Electrophile

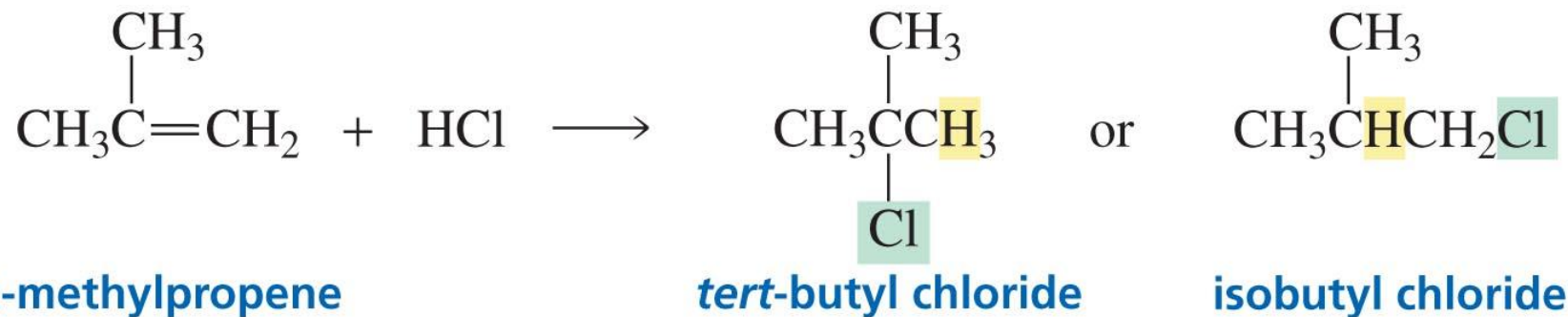


Addition of Hydrogen Halides



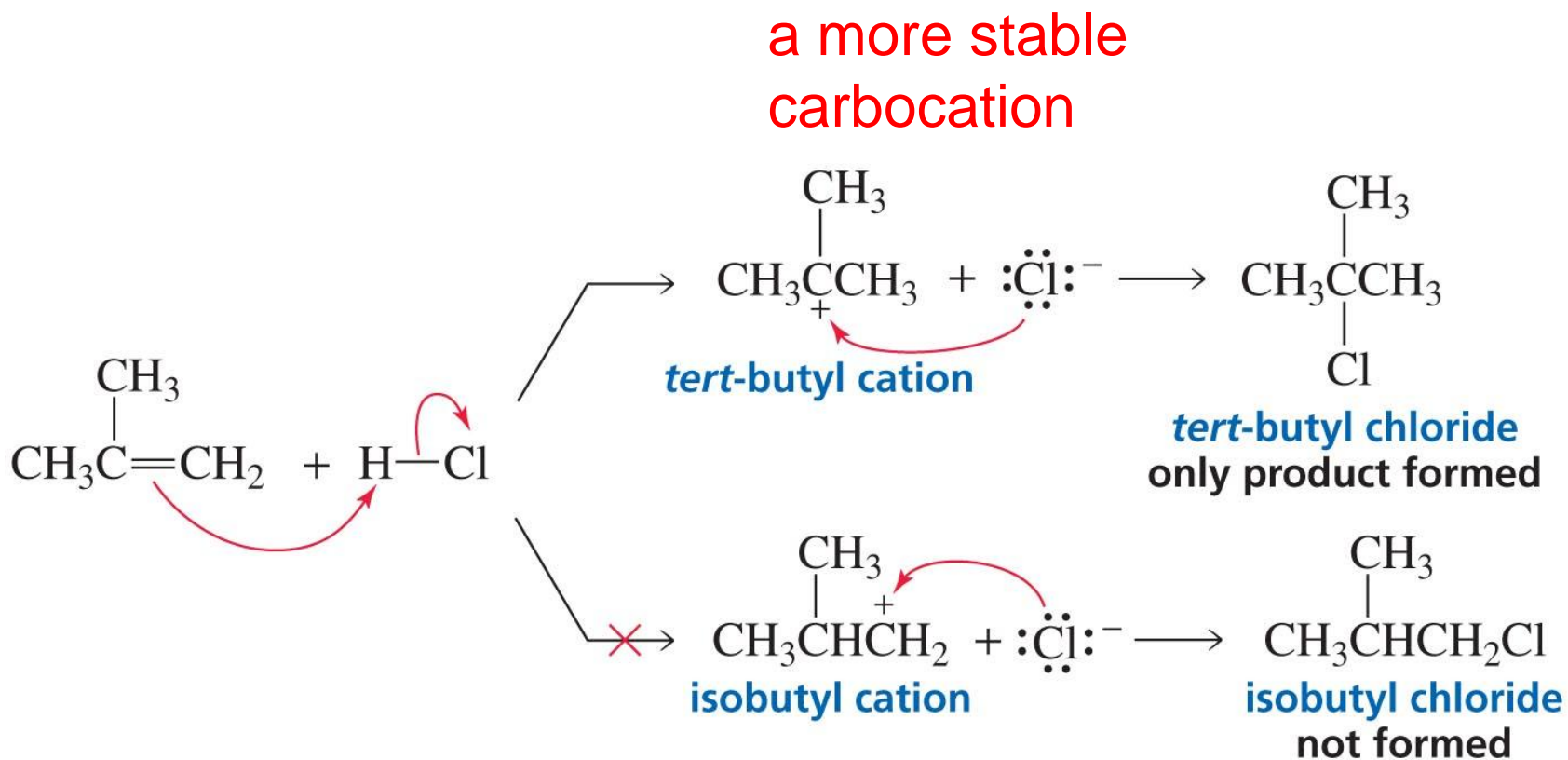
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What is the product?



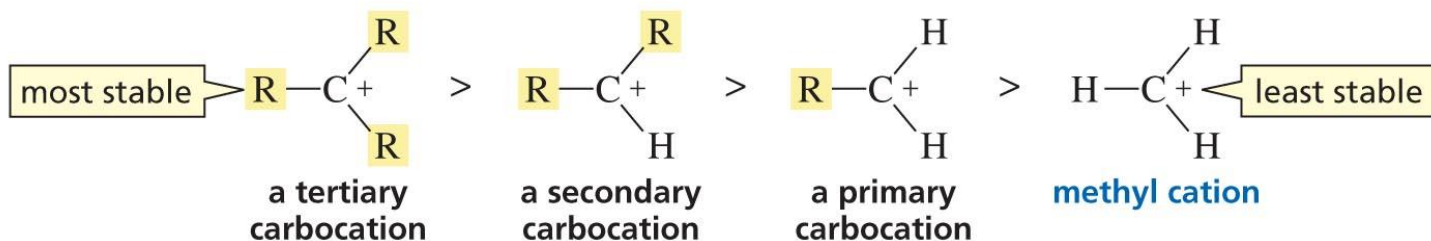
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Carbocation Formation Is the Rate-Limiting Step

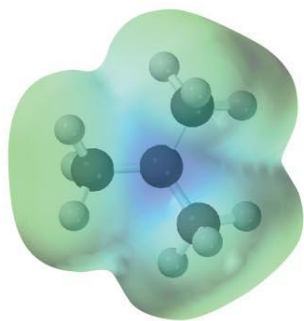


Carbocation Stabilities

relative stabilities of carbocations

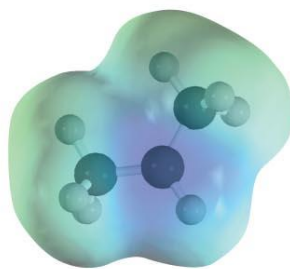


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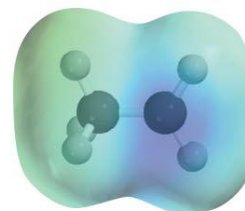


electrostatic potential map for the *tert*-butyl cation

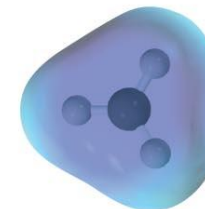
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electrostatic potential map for the isopropyl cation



electrostatic potential map for the ethyl cation

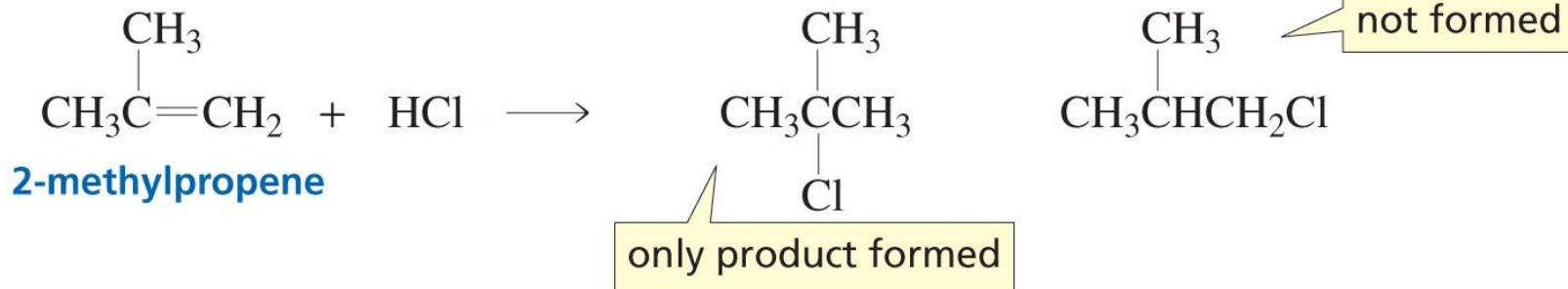


electrostatic potential map for the methyl cation

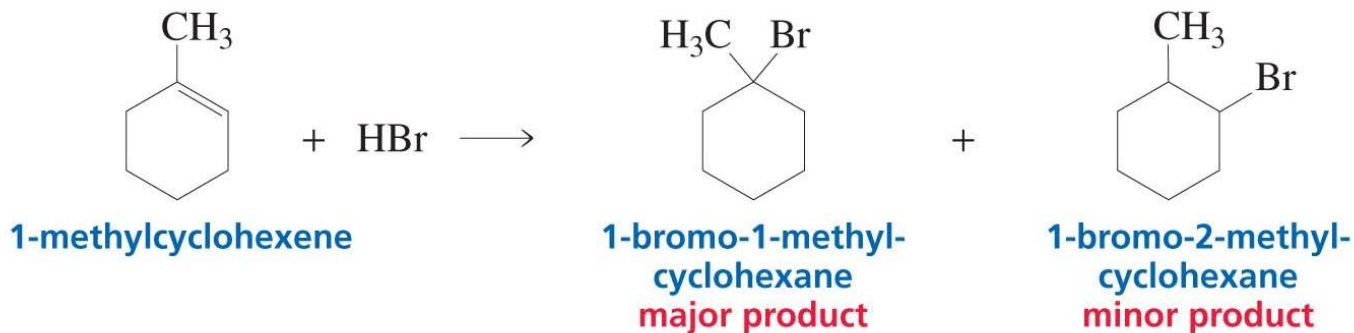
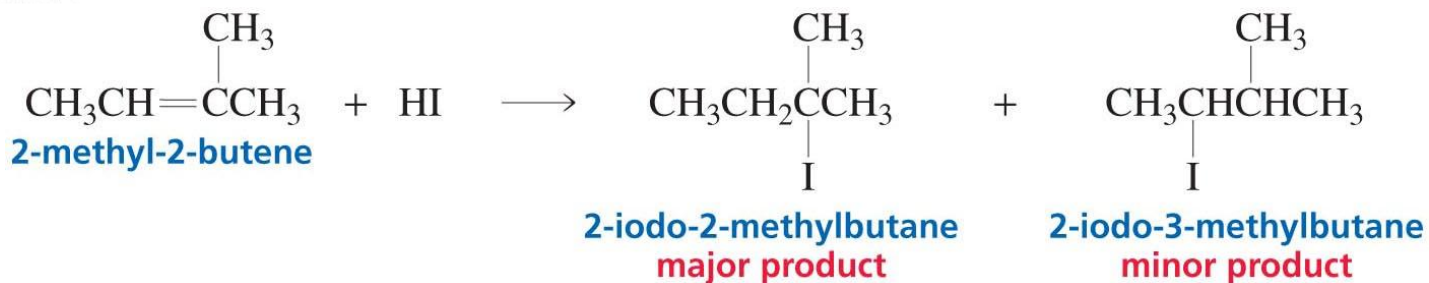
Alkyl groups decrease the concentration of positive charge in the carbocation

Markovnikov's Rule

The electrophile adds to the sp^2 carbon that is bonded to the greater number of hydrogens:



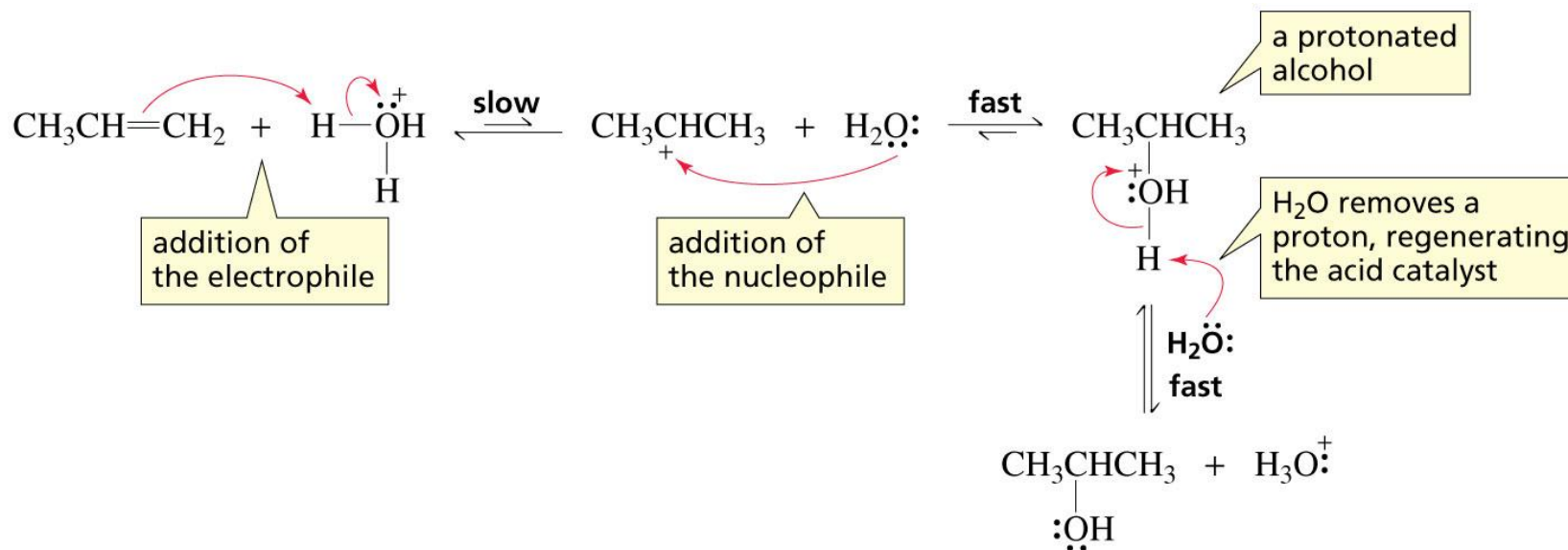
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Addition of Water to Alkene



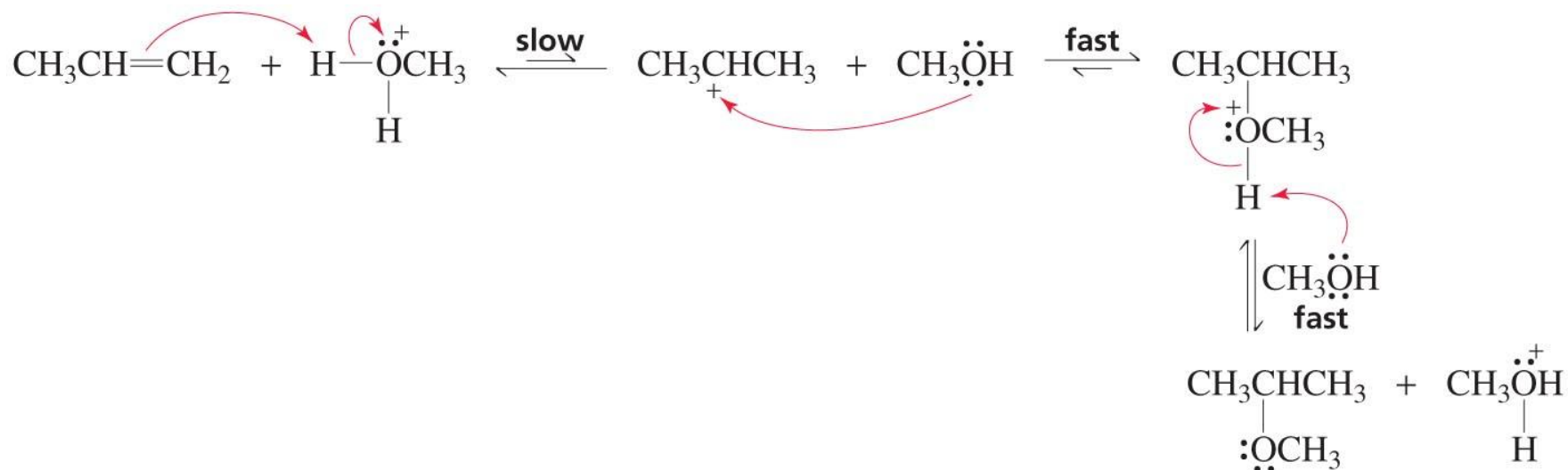
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What is the electrophile?

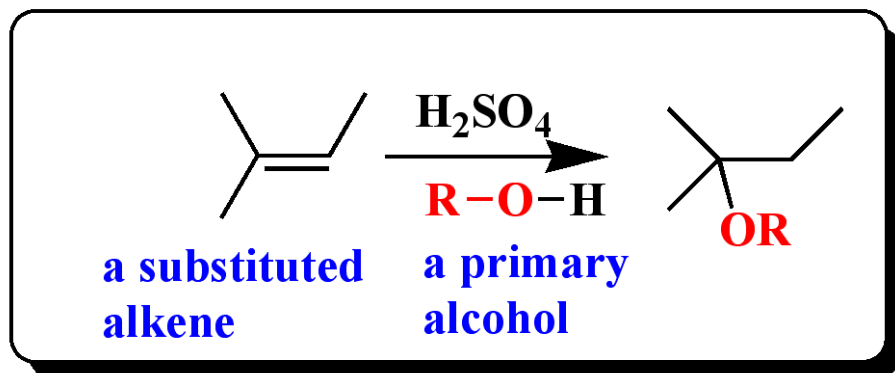
What nucleophile is present in the greatest concentration?

Acid Catalyzed Addition of Alcohol

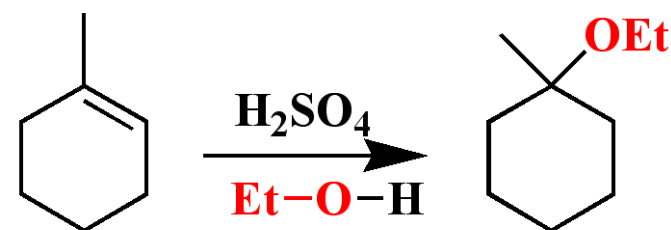
Mechanism:



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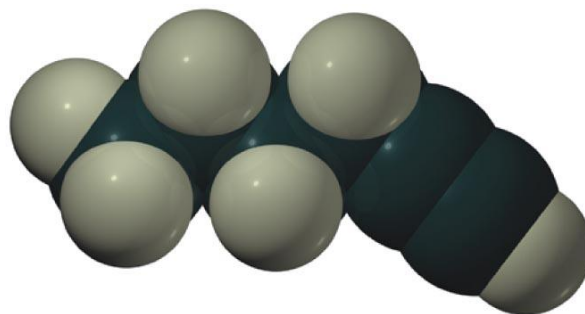


Example

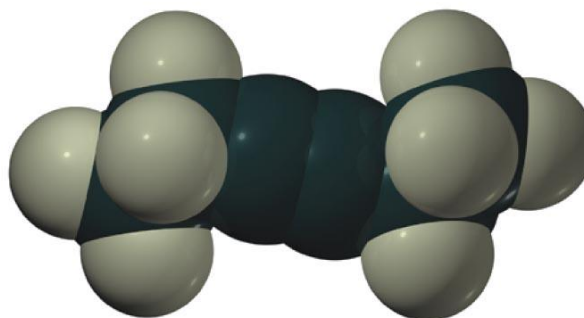


An alkyne is a hydrocarbon that contains a carbon–carbon triple bond

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

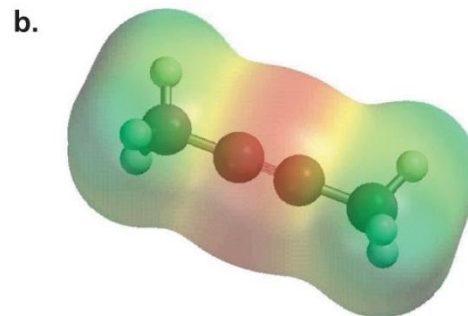
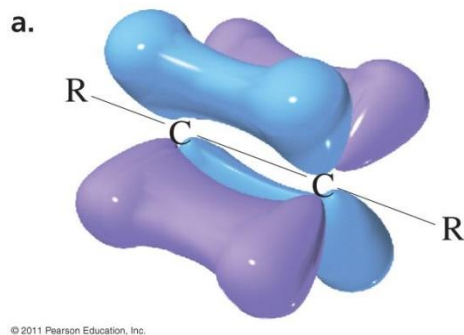
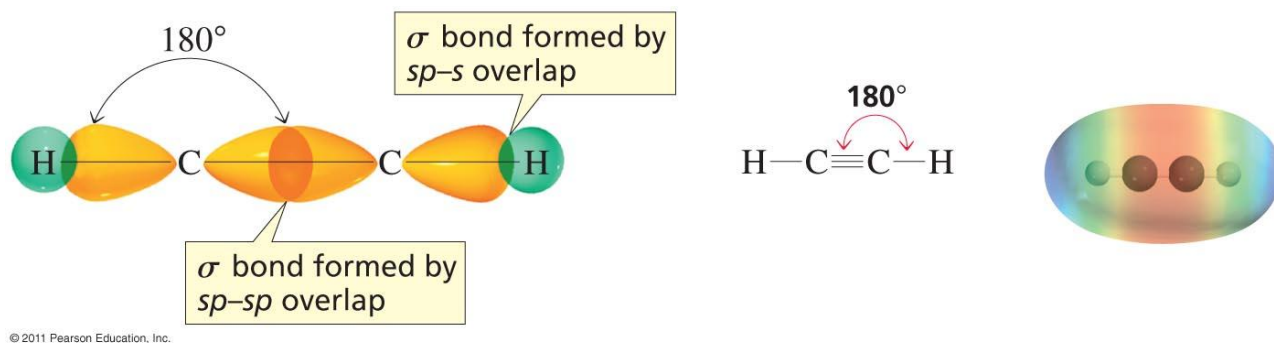


1-hexyne
a terminal alkyne



3-hexyne
an internal alkyne

The Structure of Alkynes



A triple bond is composed of a σ bond and two π bonds

Nomenclature

In common nomenclature, alkynes are named as substituted acetylenes:

Systematic: ethyne
Common: acetylene



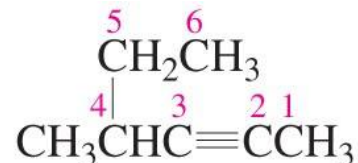
Systematic: 1-butyne
Common: ethylacetylene
a terminal alkyne



Systematic: 2-pentyne
Common: ethylmethylacetylene
an internal alkyne



Systematic: 4-methyl-2-hexyne
Common: sec-butylmethylacetylene

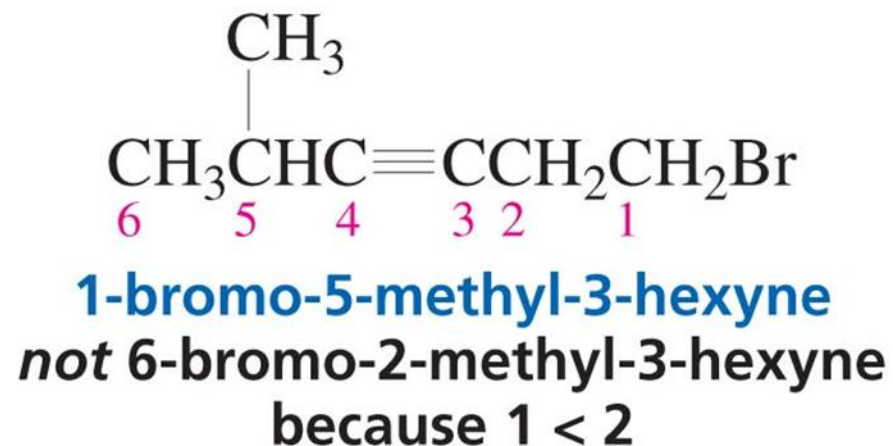


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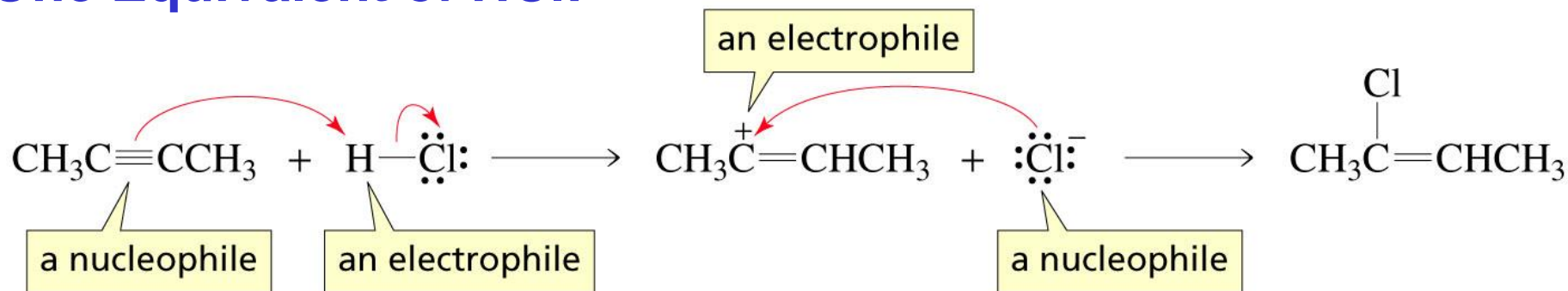
3-bromo-2-chloro-4-octyne
not 6-bromo-7-chloro-4-octyne
because $2 < 6$

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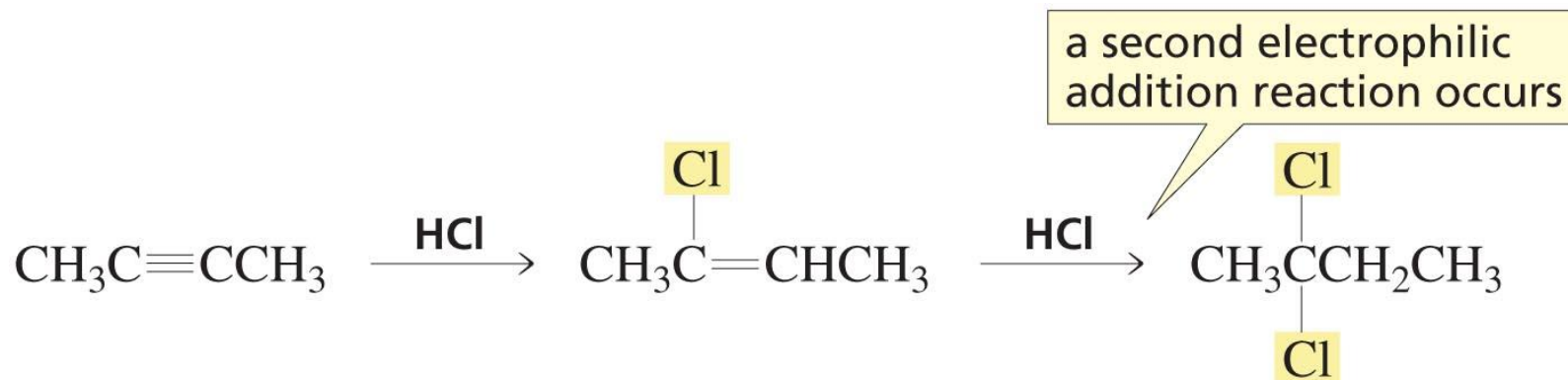
Electrophilic Addition of Hydrogen Halides to Alkynes

One Equivalent of HCl:



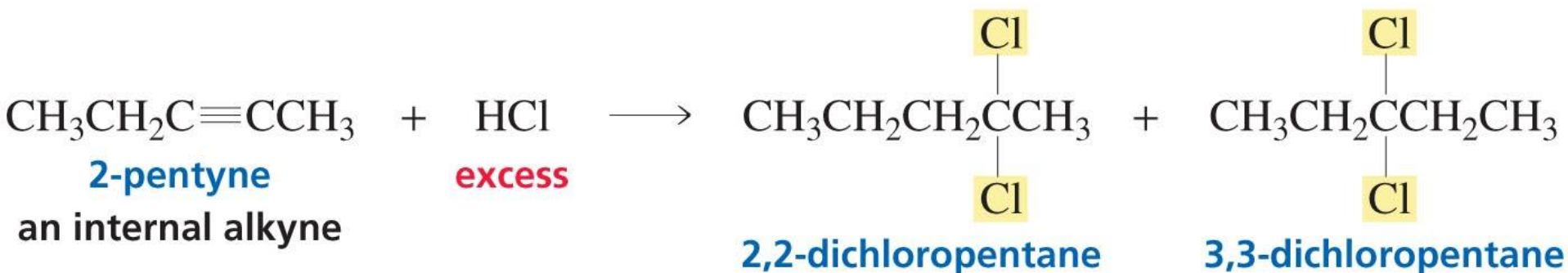
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Excess HCl:

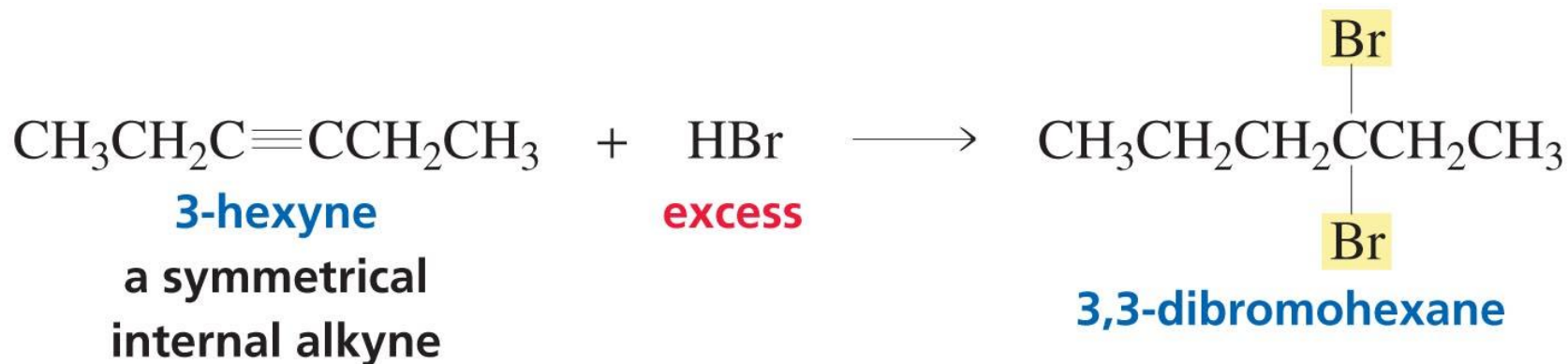


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The initial addition of the proton can occur with equal ease to either of the *sp* carbons and the *geminal* regioisomer always results:

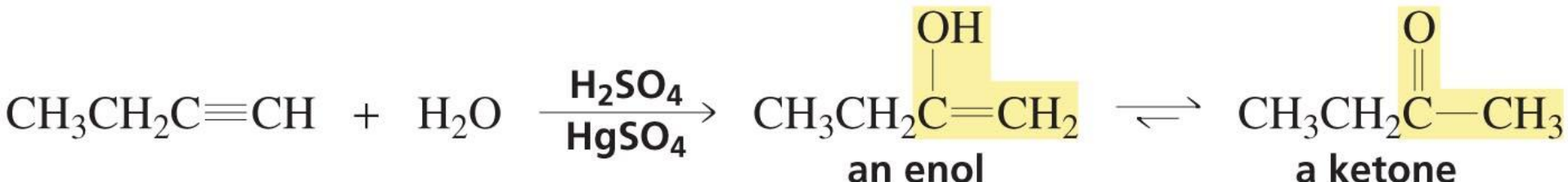


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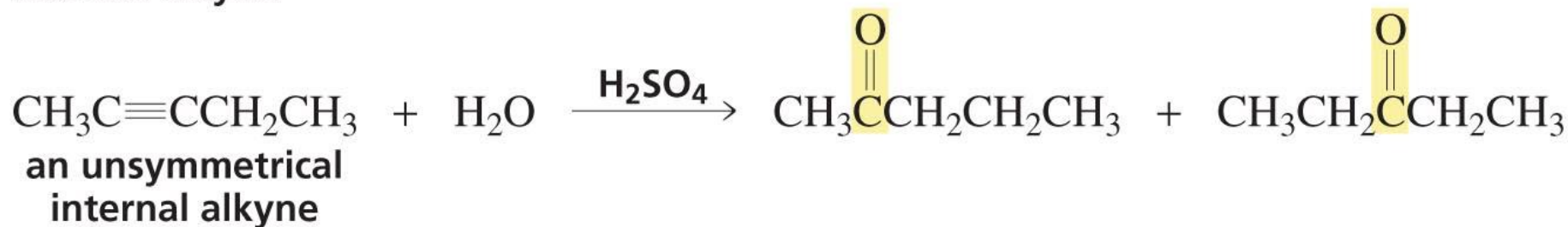
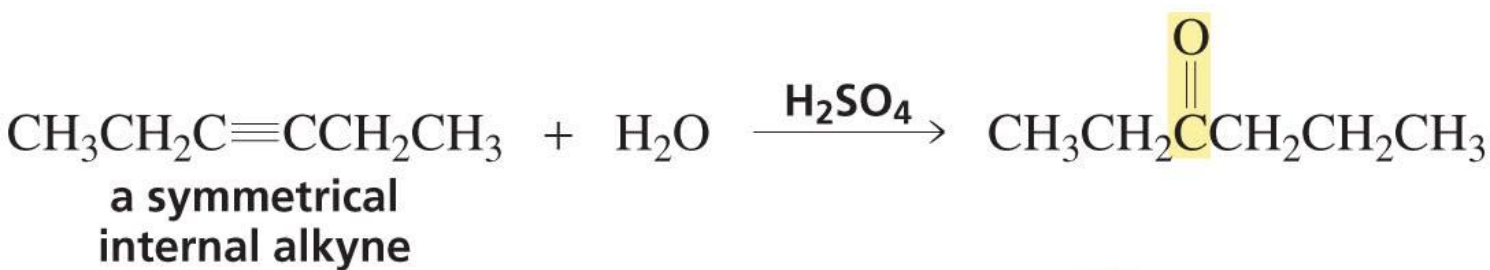


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Addition of Water to an Alkyne



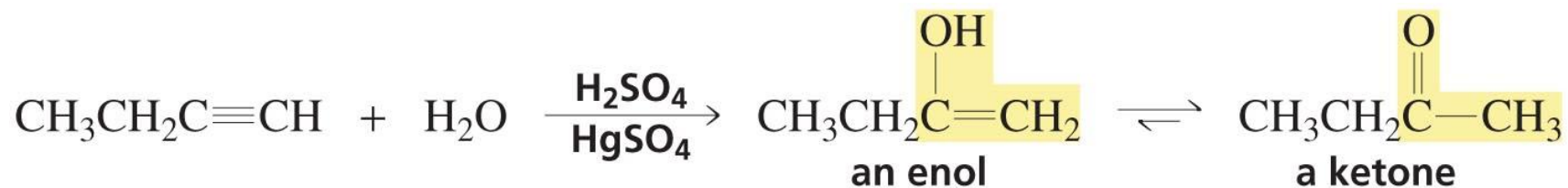
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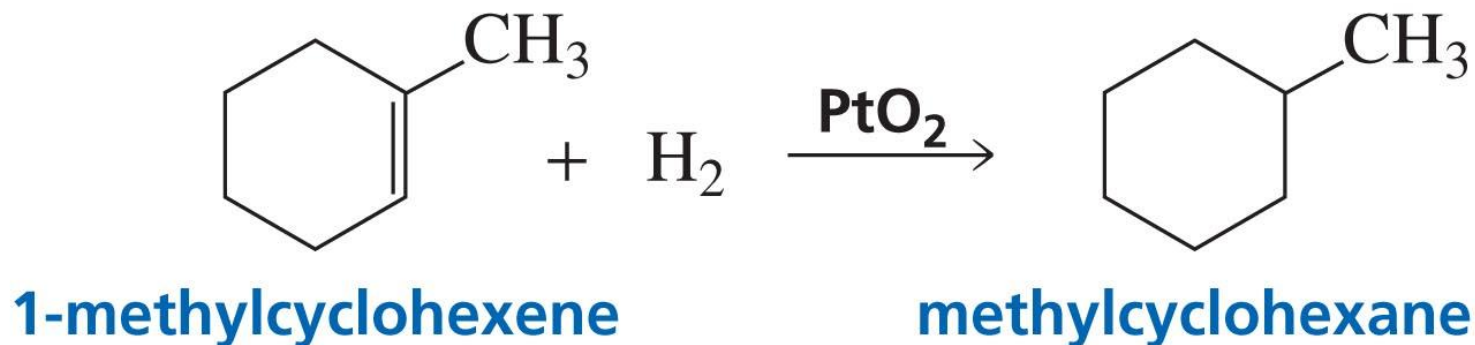
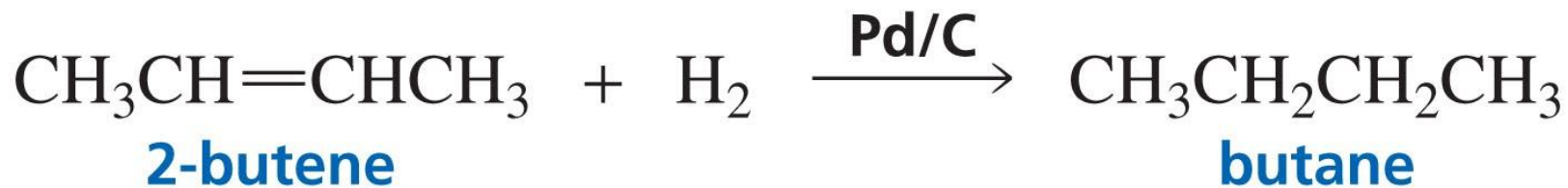
One method of synthesizing ketones.

Hg^{2+} is added to increase the rate of water addition to terminal alkynes:



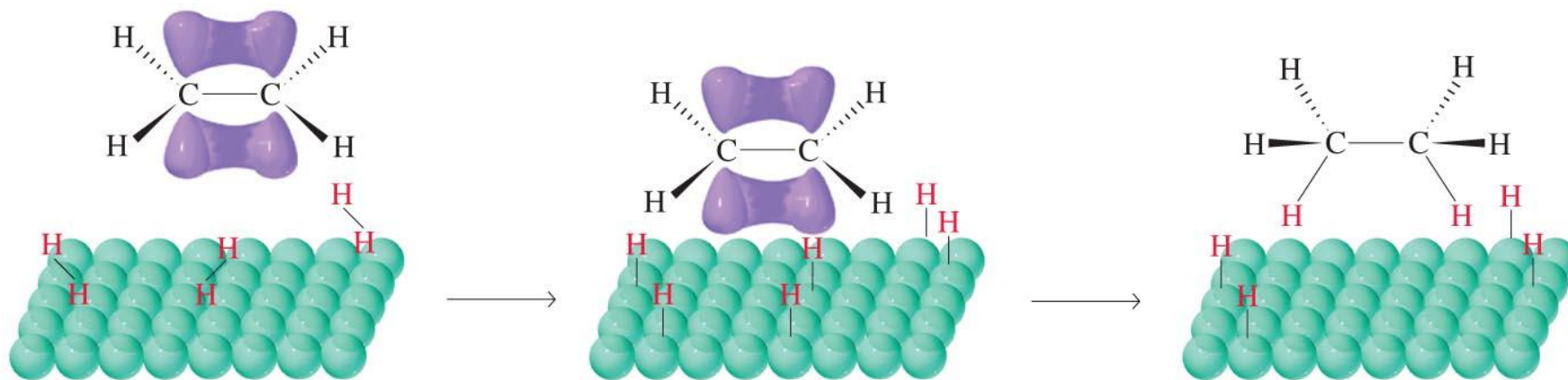
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Addition of Hydrogen to Alkenes



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Catalytic Hydrogenation of an Alkene

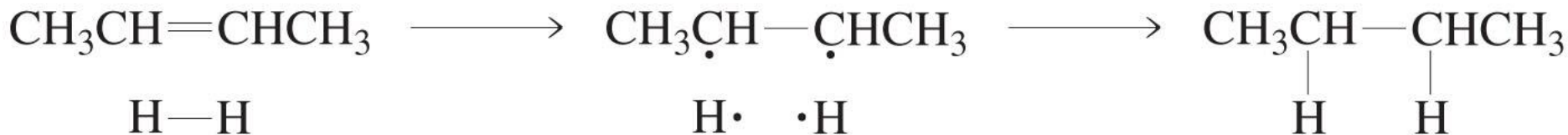


hydrogen molecules settle on the surface of the catalyst and react with the metal atoms

the alkene approaches the surface of the catalyst

the π bond between the two carbons is replaced by two C—H σ bonds

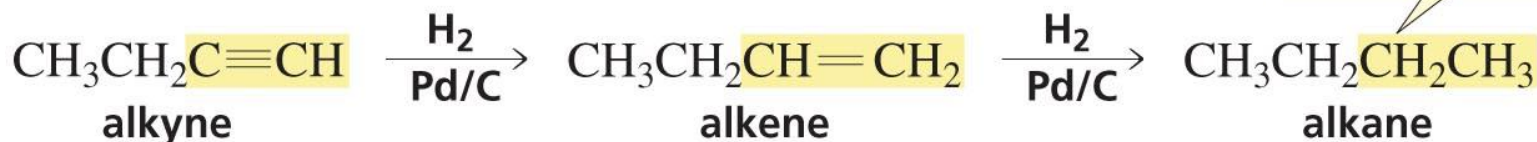
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Addition of Hydrogen Formation of Cis Alkene

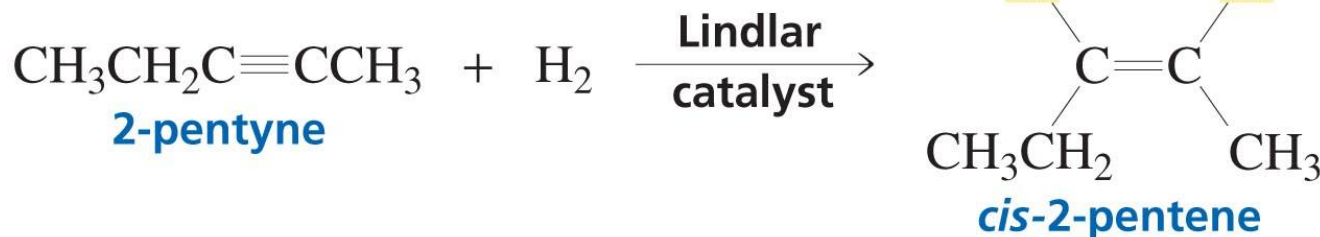
Catalytic reduction of an alkyne affords an alkane without buildup of the alkene intermediate:



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an alkyne is converted to an alkane

Use a “poisoned” catalyst developed by Lindlar to obtain the alkene:



syn addition has occurred

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