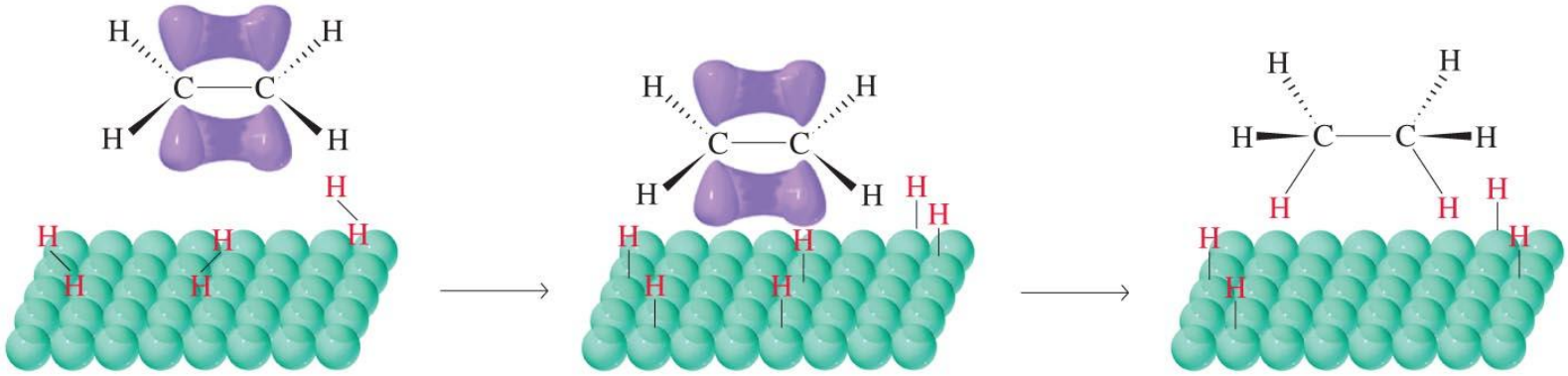
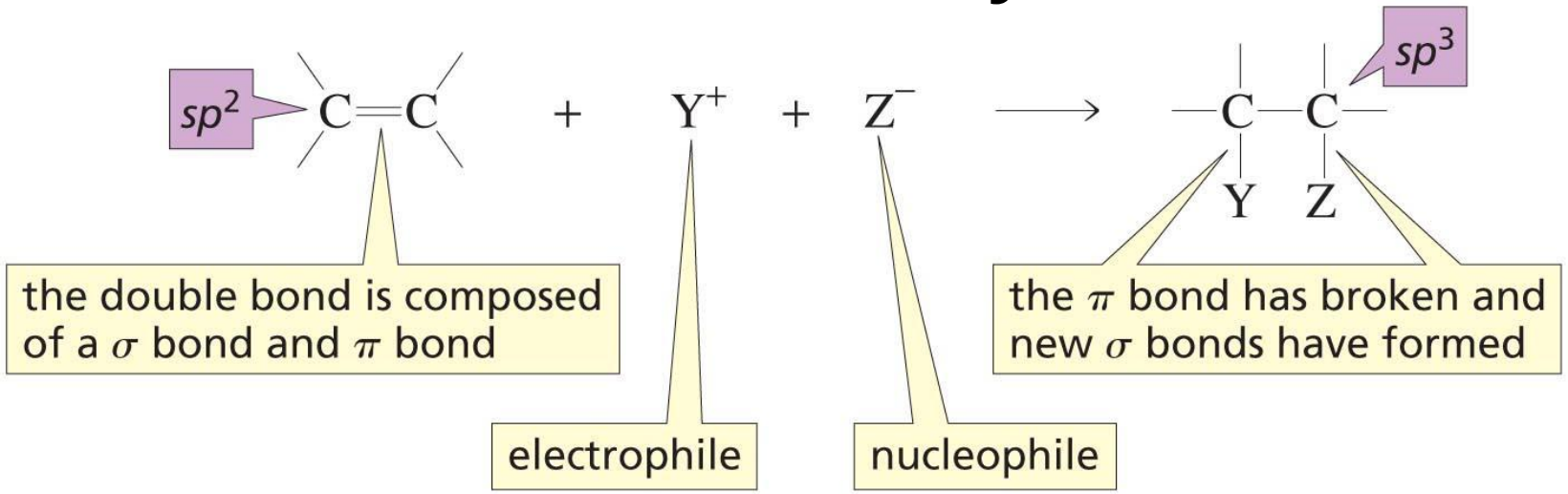
Organic Chemistry
2th Edition
Paula Yurkanis Bruice

Chapter 5
The Reactions of Alkenes

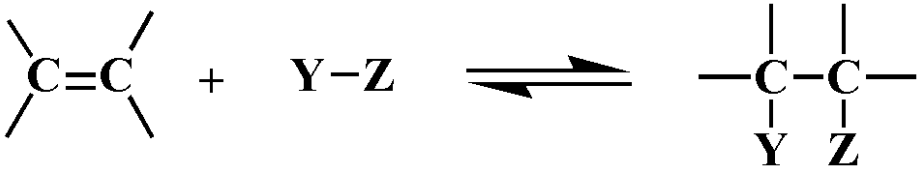


Electrophilic Addition of Alkenes: Reaction and Synthesis

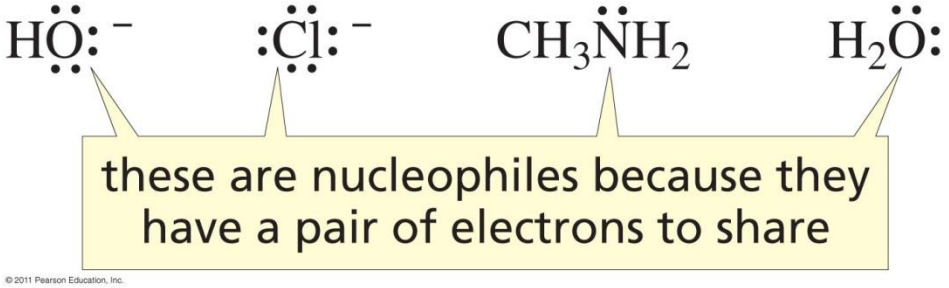


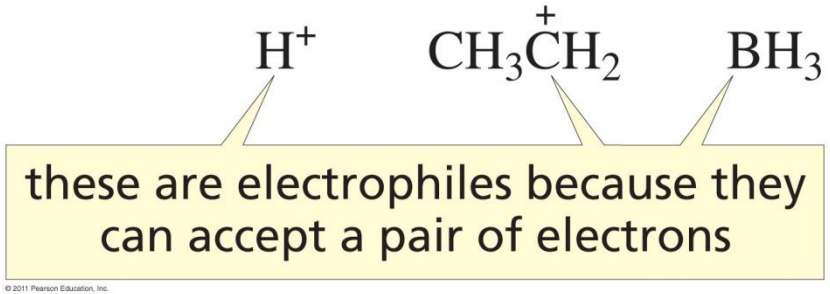
Y-Z: H-Cl, H-Br, H-I, Cl-Cl, & Br-Br

Reaction of an alkene is an addition reaction.

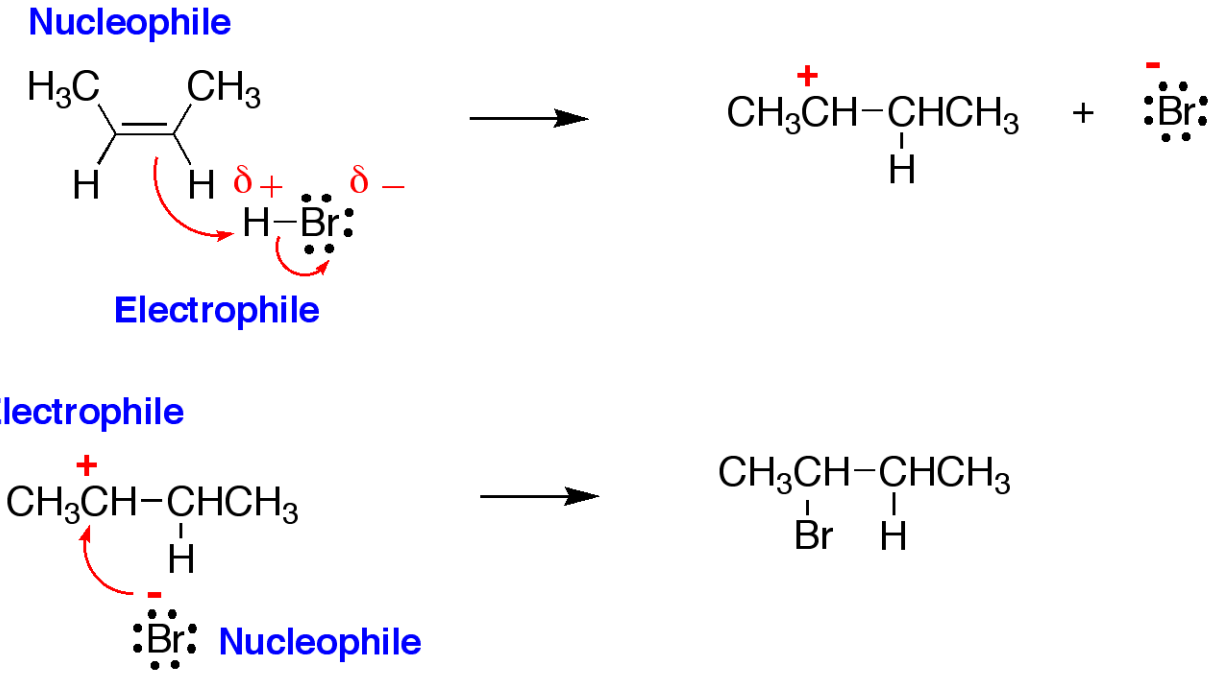


Electron-rich atoms or molecules (nucleophiles) are attracted to electron-deficient atoms or molecules (electrophiles):





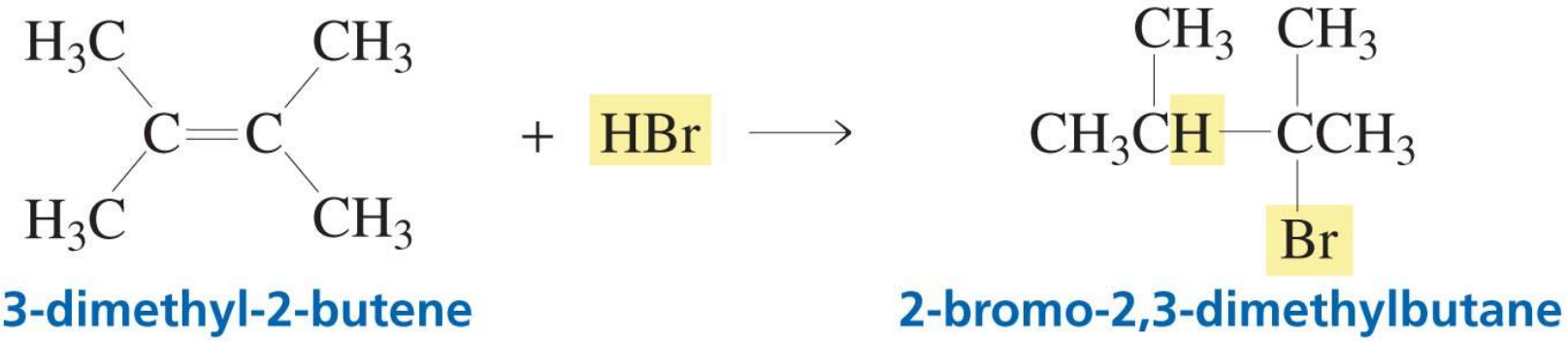
Your First Reaction: Addition of HBr to an Alkene



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

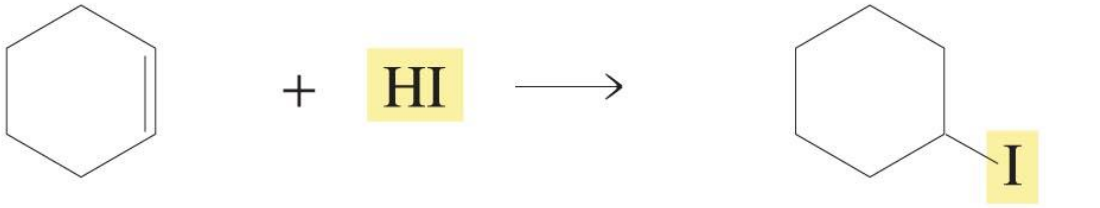
2nd Step: Bromide traps the carbocation. Bromide is the nucleophile.

Addition of Hydrogen Halides



2,3-dimethyl-2-butene

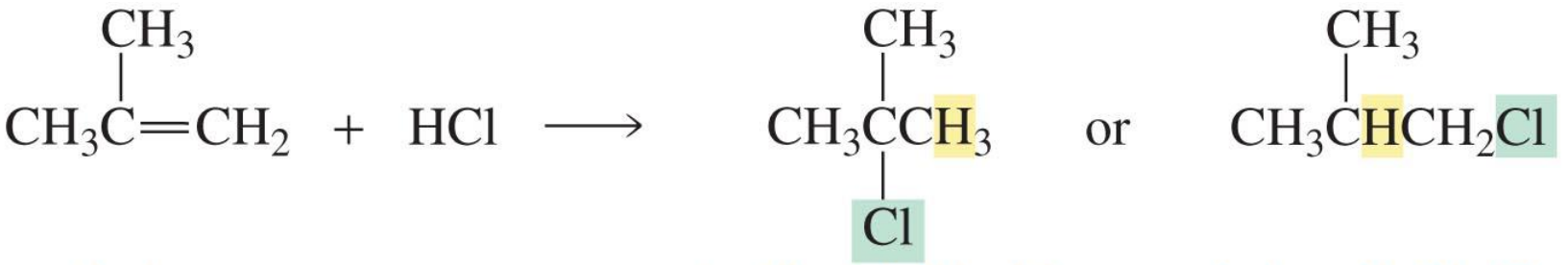
2-bromo-2,3-dimethylbutane



cyclohexene

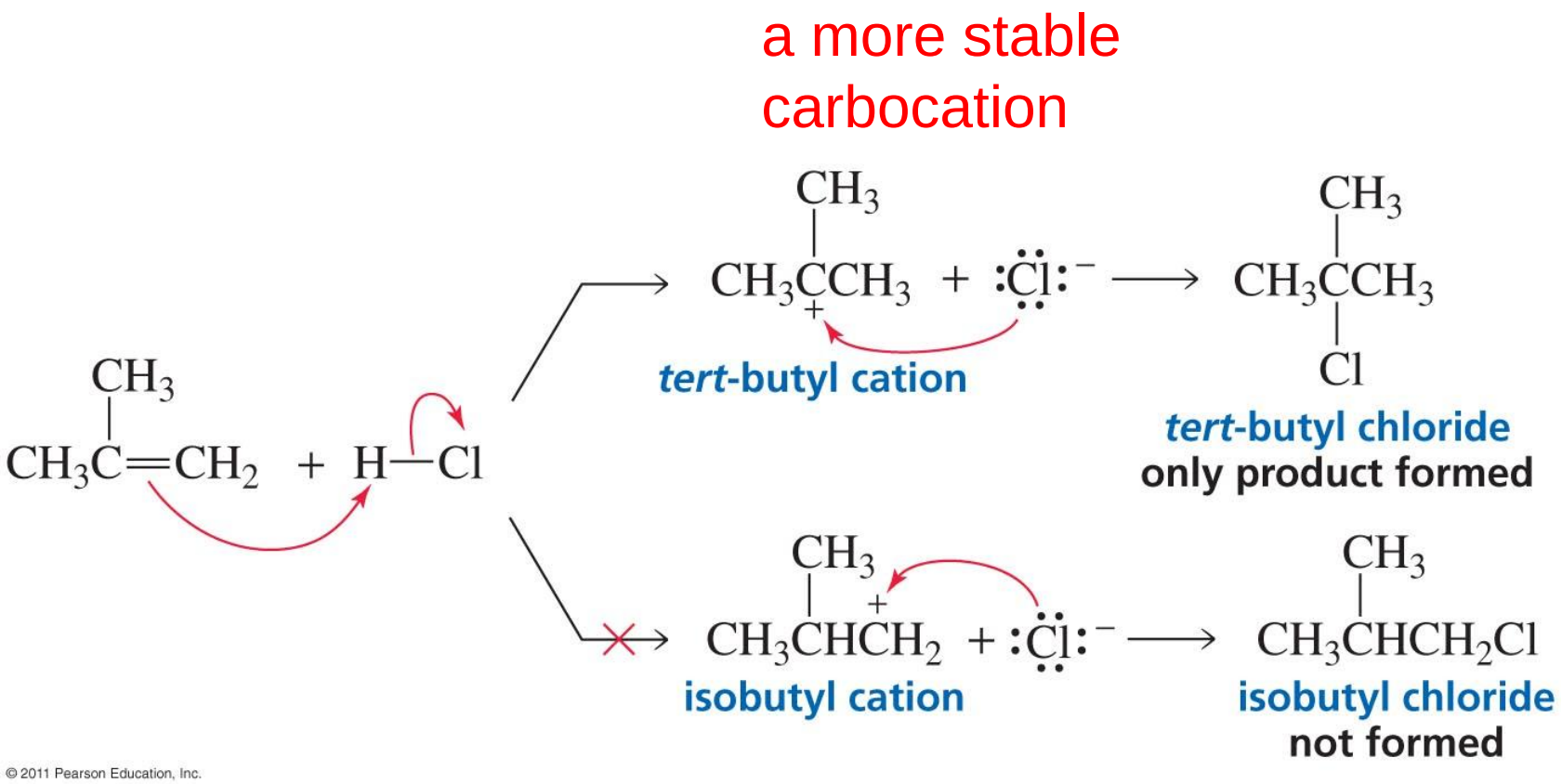
iodocyclohexane

What is the product?

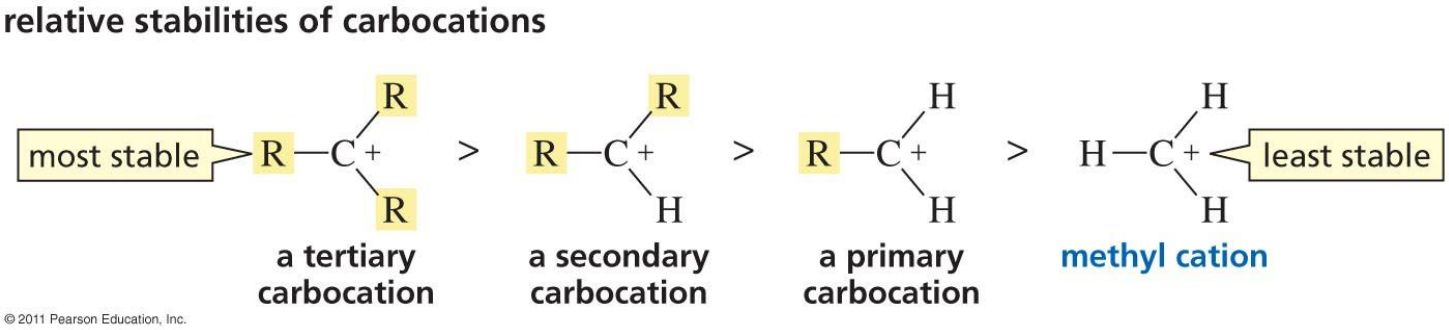


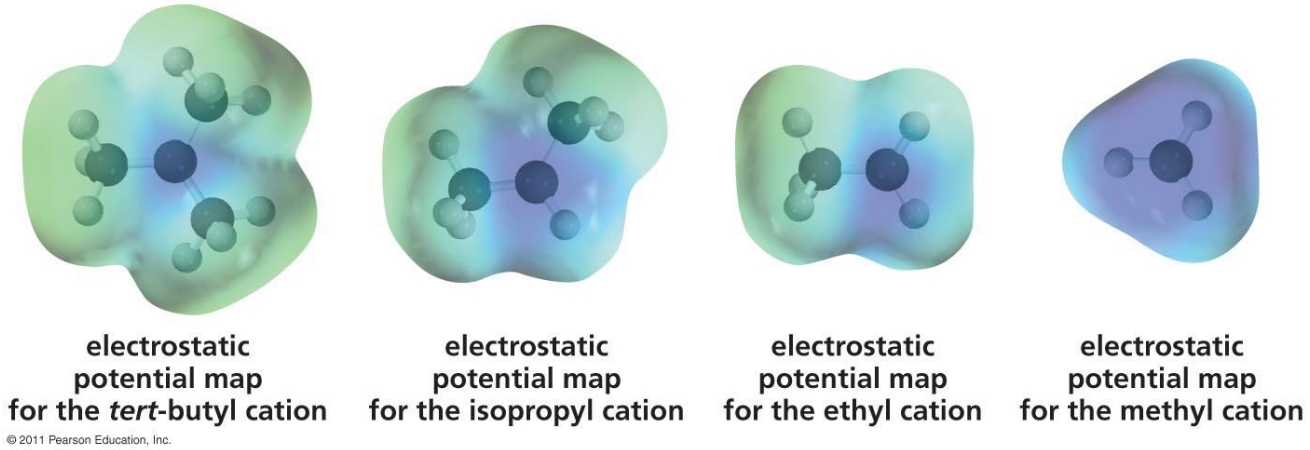
2-methylpropene **tert-butyl chloride** **isobutyl chloride**

Carbocation Formation Is the Rate-Limiting Step



Carbocation Stabilities

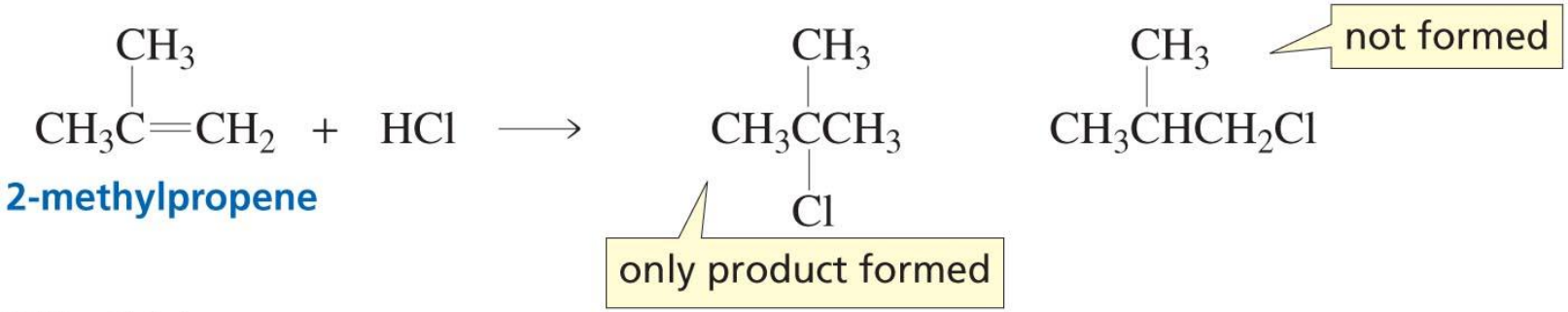


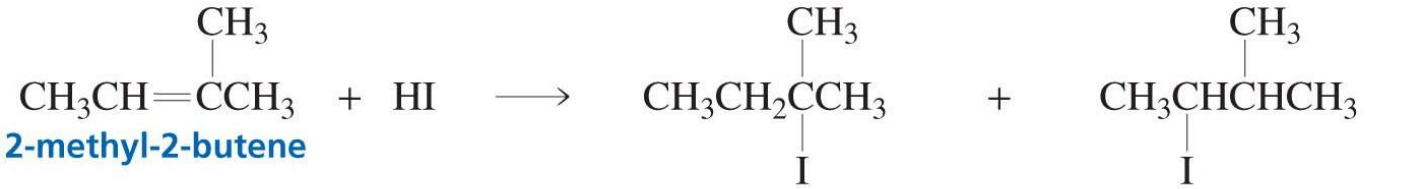


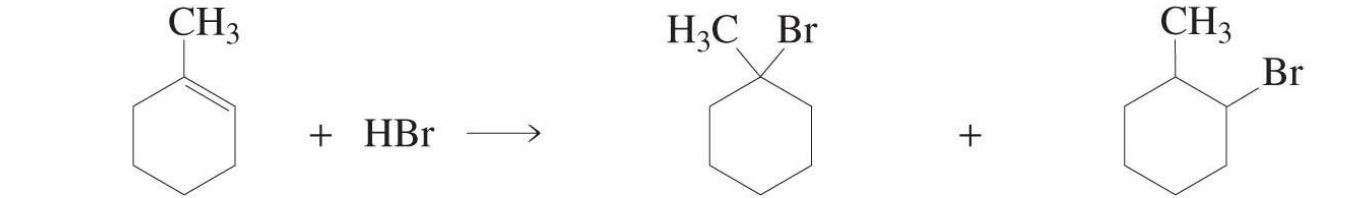
Alkyl groups decrease the concentration of positive charge in the carbocation

Markovnikov's Rule

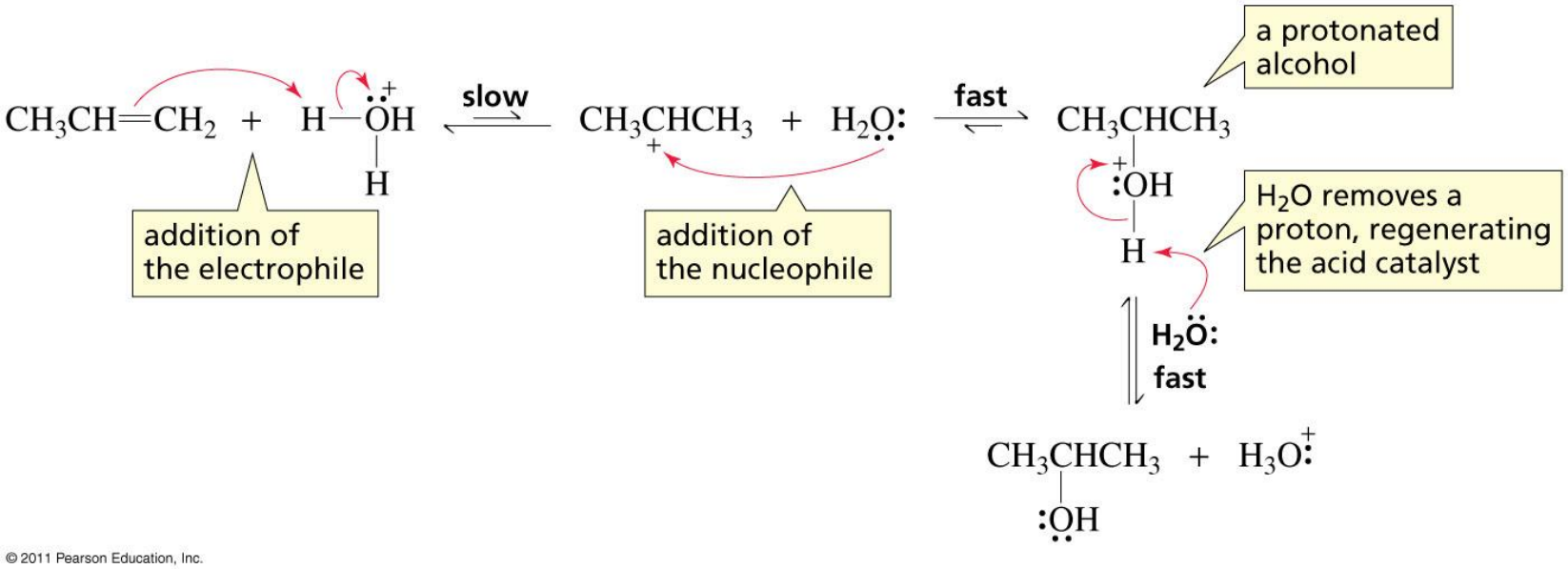
The electrophile adds to the sp^2 carbon that is bonded to the greater number of hydrogens:







Addition of Water to Alkene

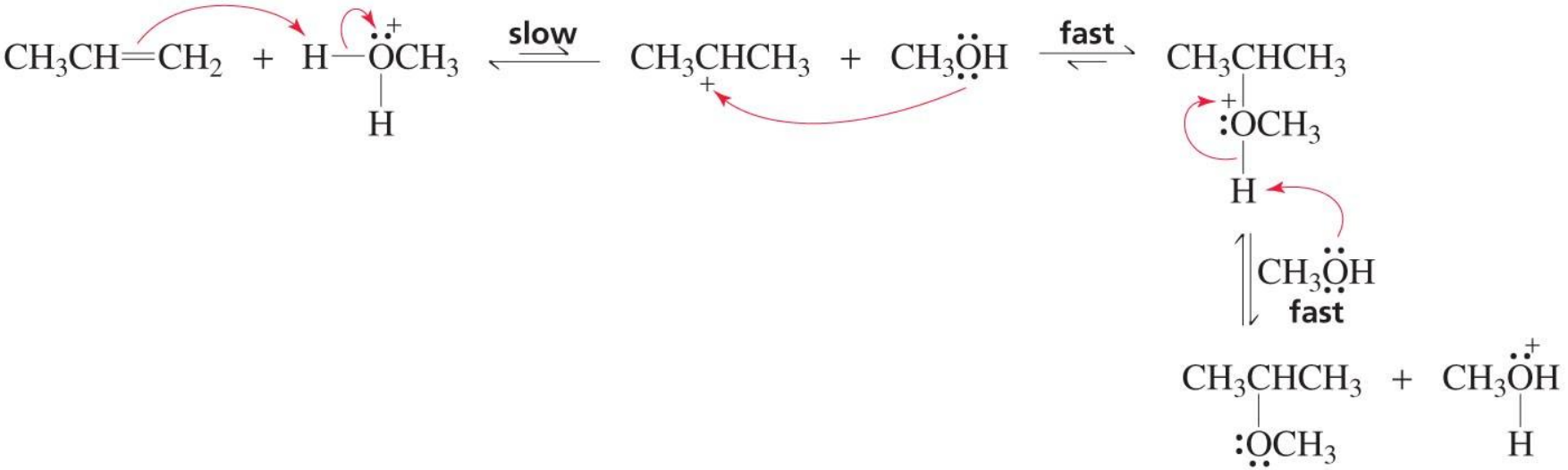


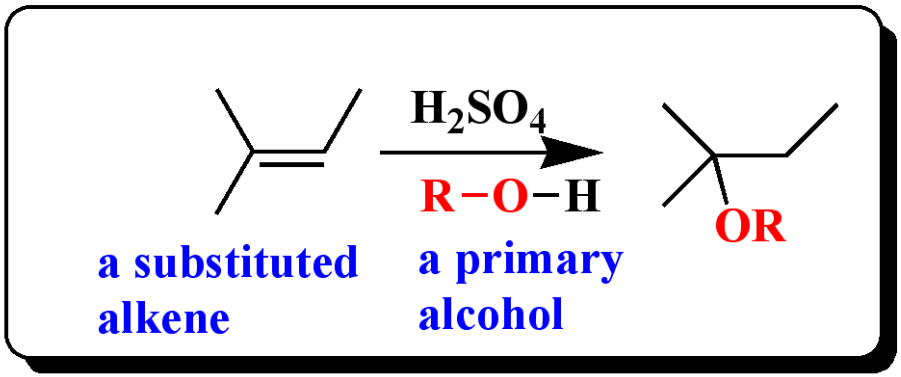
What is the electrophile?

What nucleophile is present in the greatest concentration?

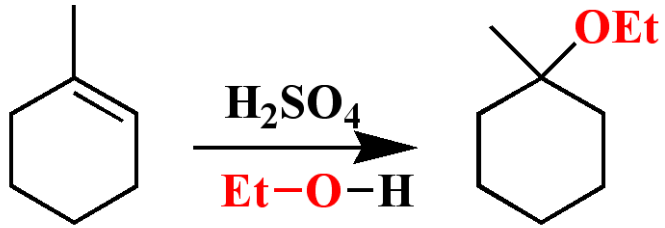
Acid Catalyzed Addition of Alcohol

Mechanism:



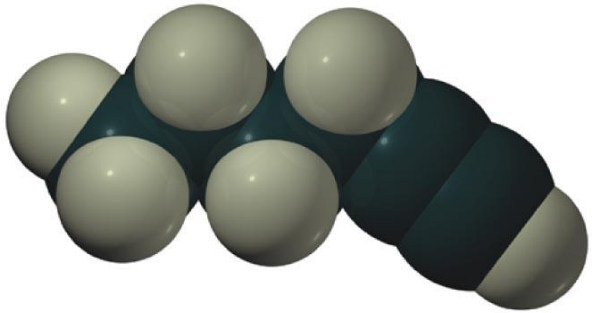


Example

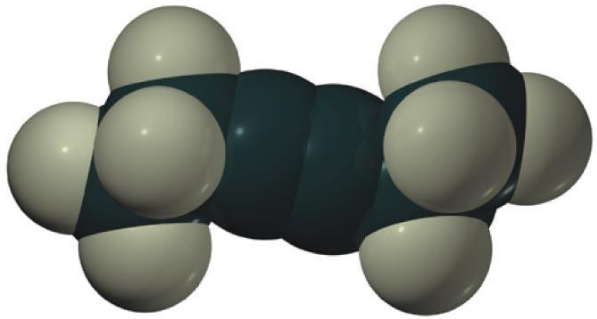


An alkyne is a hydrocarbon that contains a carbon–carbon triple bond

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



1-hexyne
a terminal alkyne



3-hexyne
an internal alkyne

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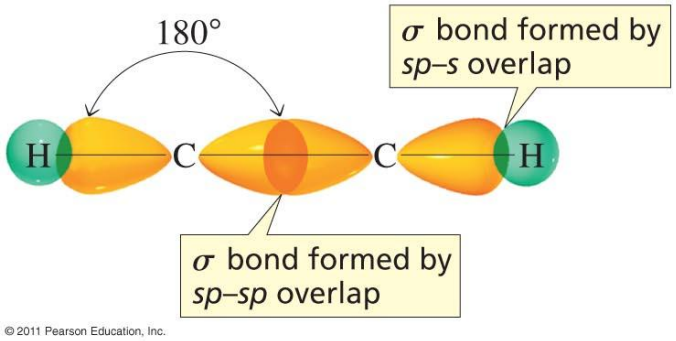
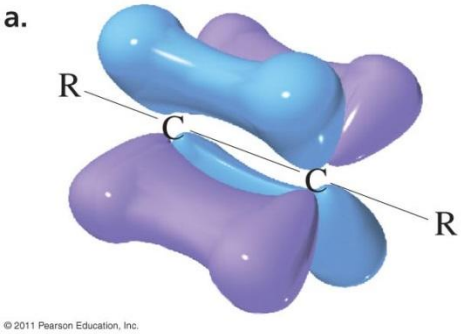
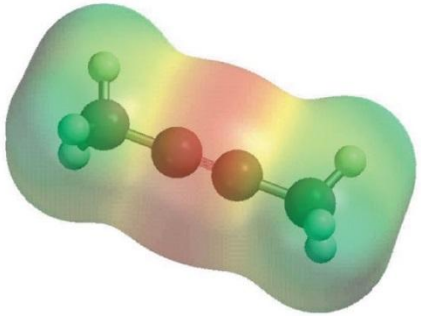
The Structure of Alkynes



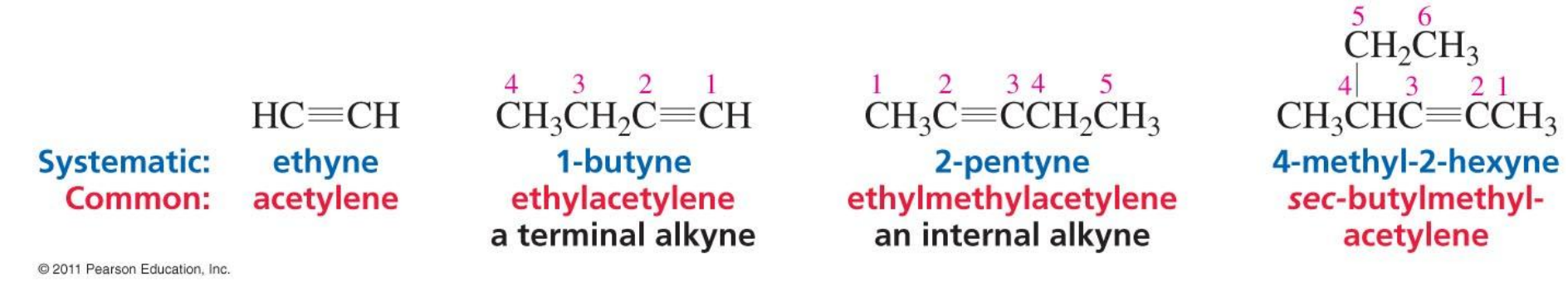




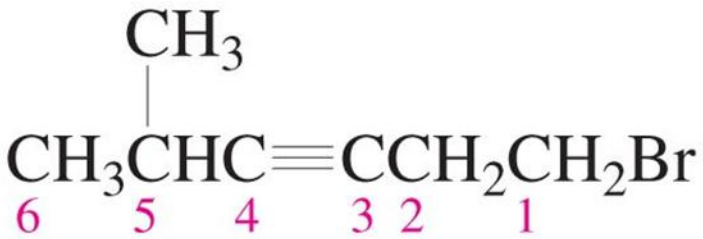
A triple bond is composed of a σ bond and two π bonds

Nomenclature

In common nomenclature, alkynes are named as substituted acetylenes:



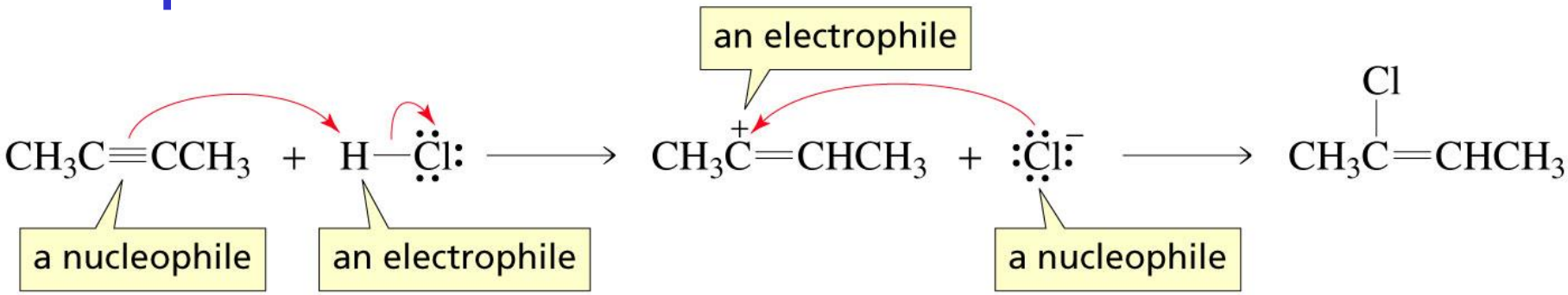
3-bromo-2-chloro-4-octyne
not **6-bromo-7-chloro-4-octyne**
because 2 < 6



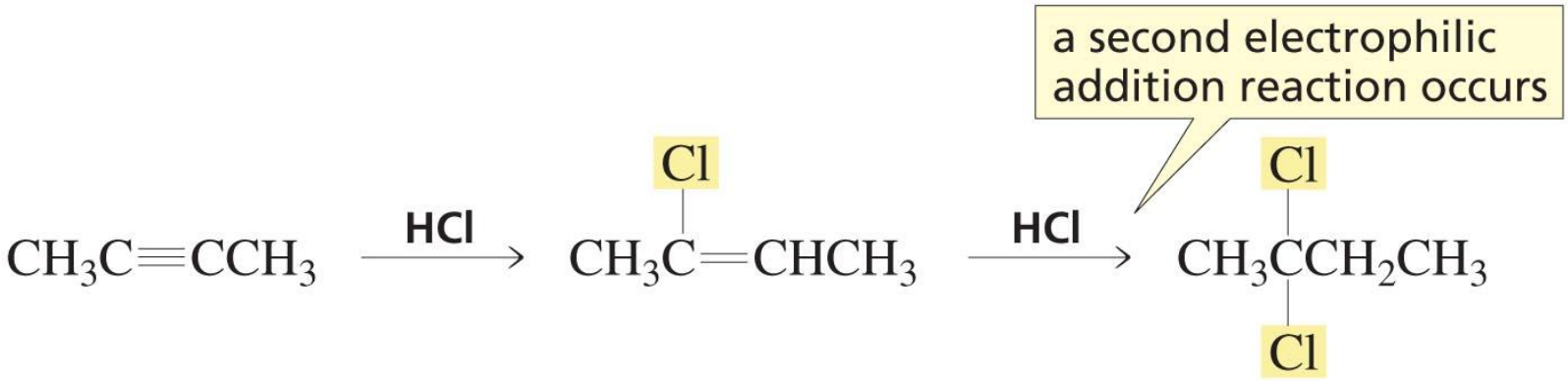
1-bromo-5-methyl-3-hexyne
not **6-bromo-2-methyl-3-hexyne**
because 1 < 2

Electrophilic Addition of Hydrogen Halides to Alkynes

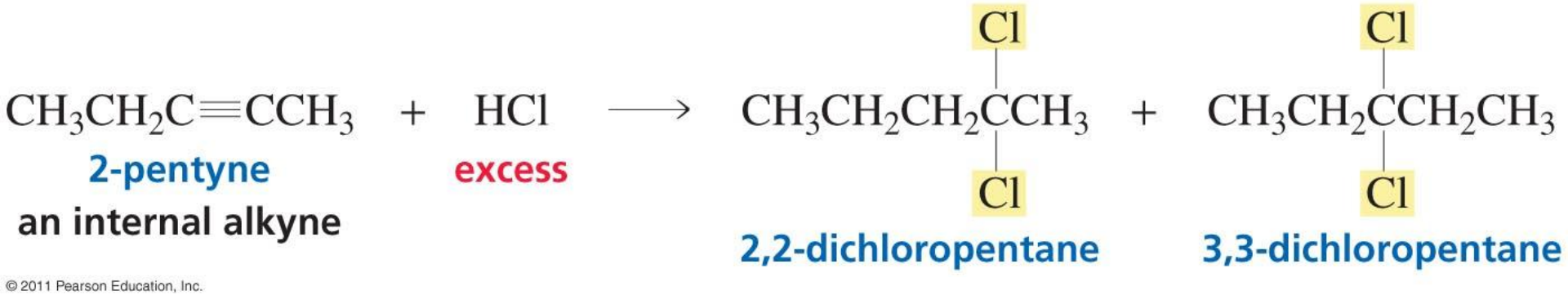
One Equivalent of HCl:

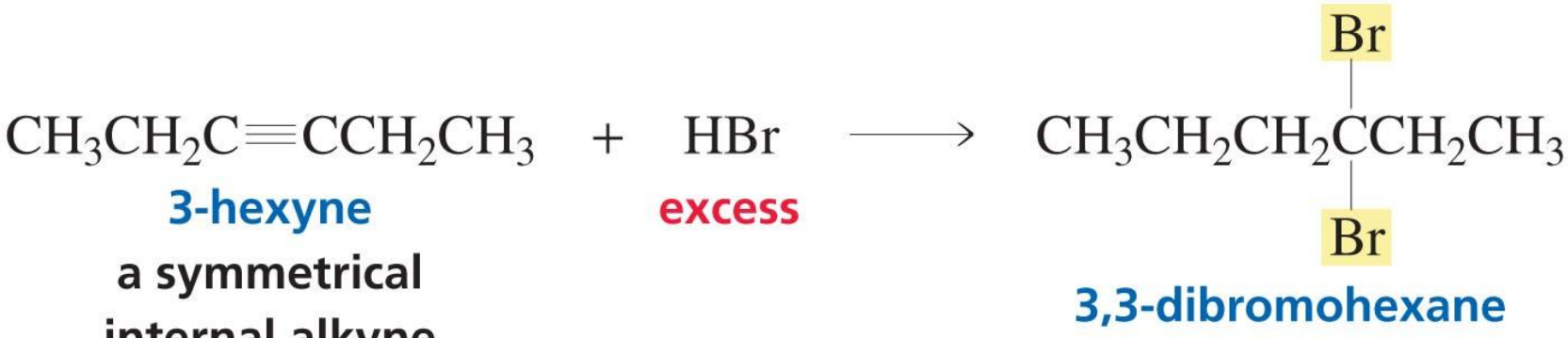


Excess HCl:

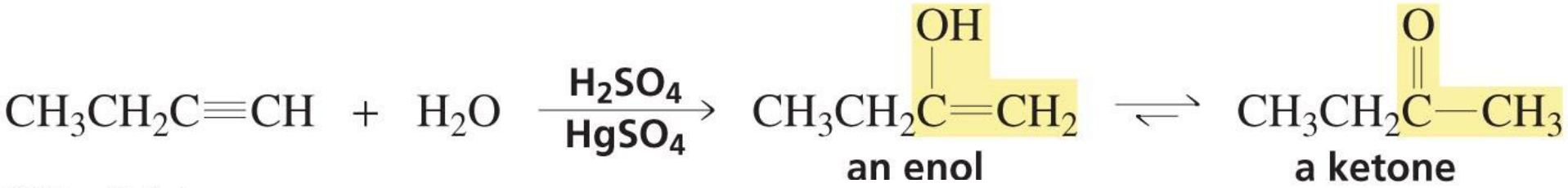


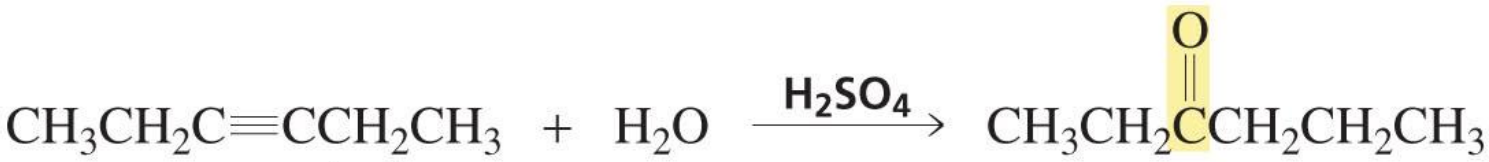
The initial addition of the proton can occur with equal ease to either of the *sp* carbons and the *geminal* regioisomer always results:

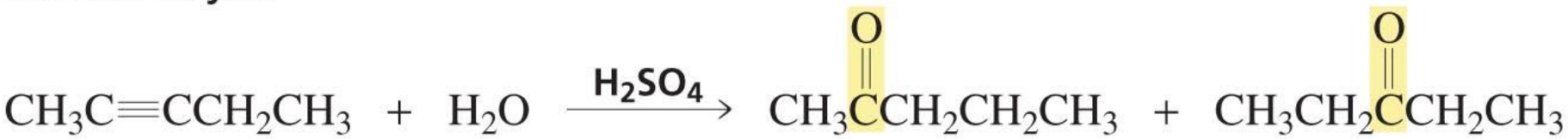




Addition of Water to an Alkyne

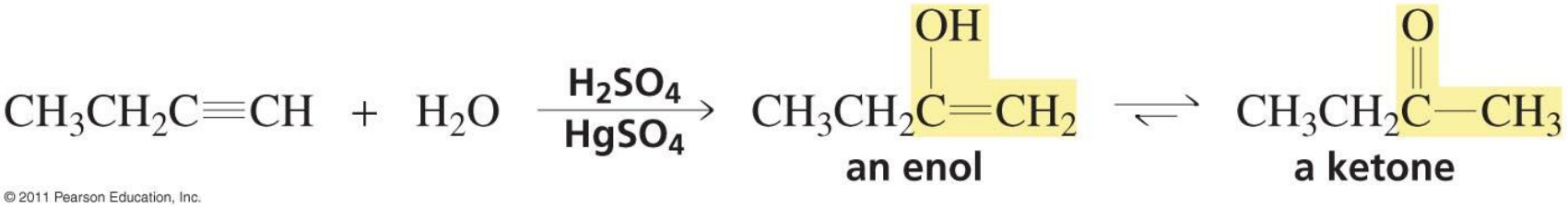




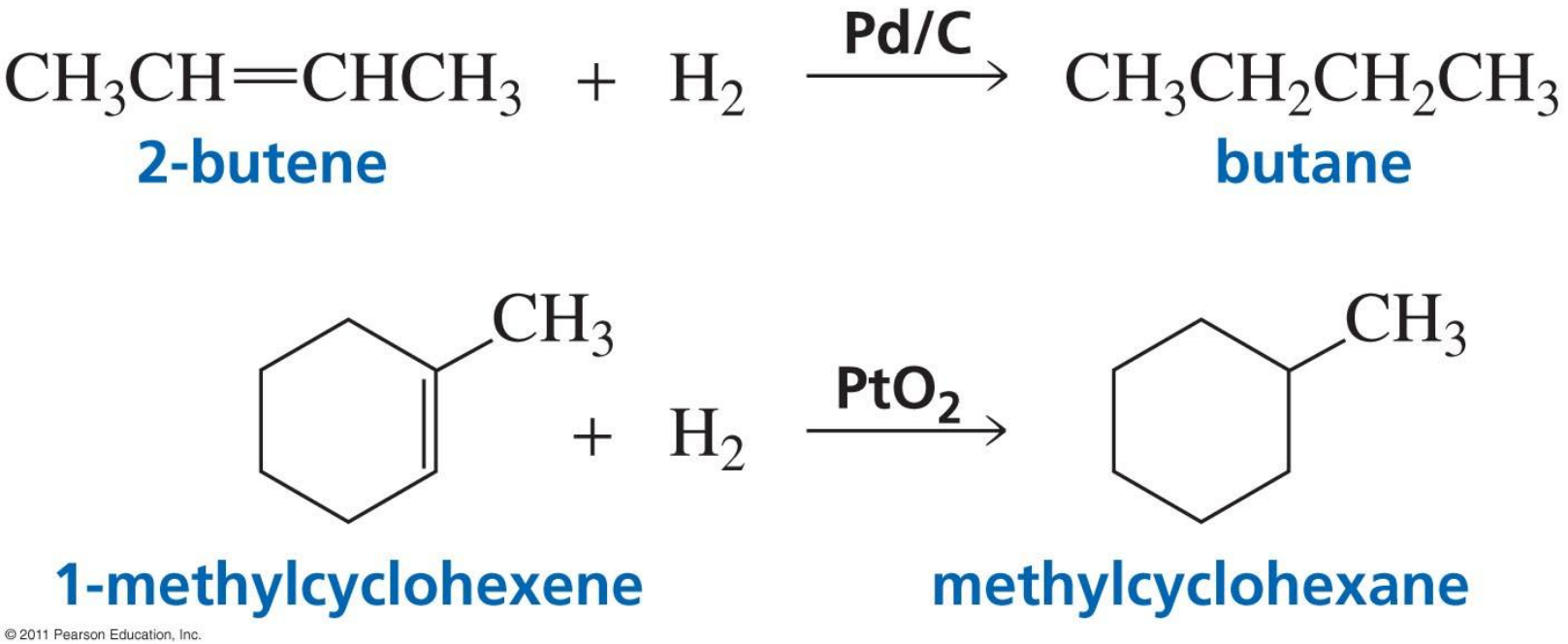


One method of synthesizing ketones.

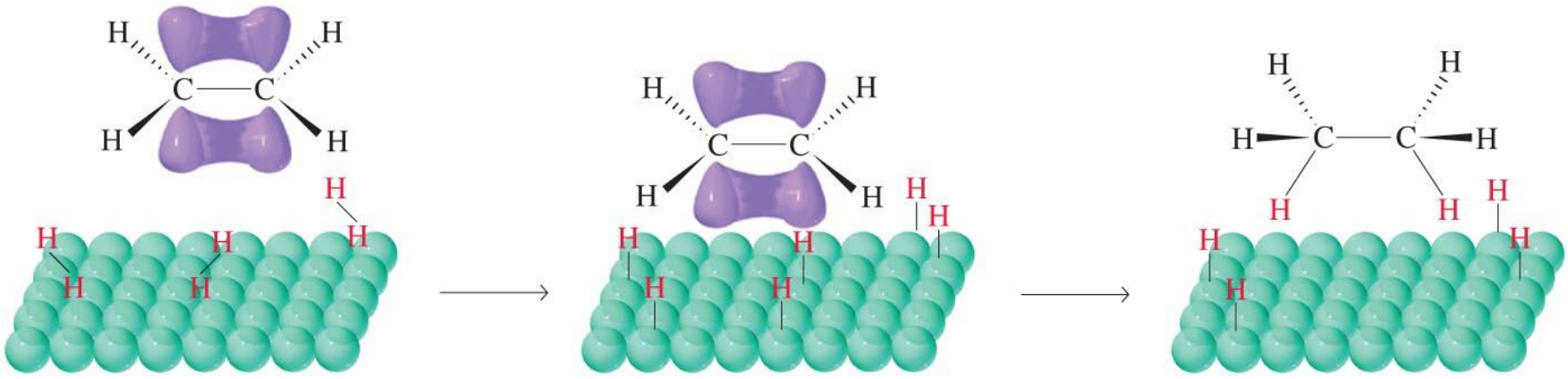
Hg^{2+} is added to increase the rate of water addition to terminal alkynes:

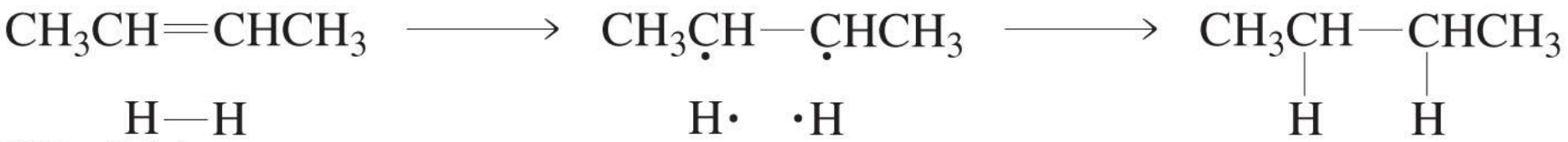


Addition of Hydrogen to Alkenes



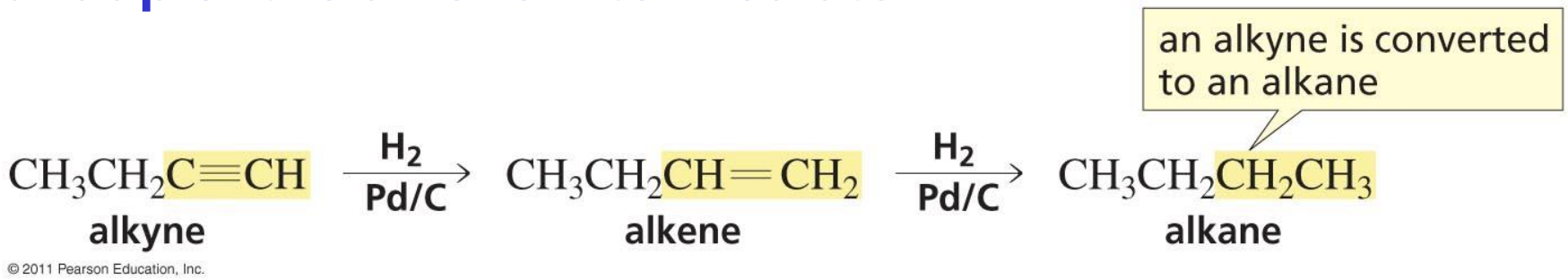
Catalytic Hydrogenation of an Alkene





Addition of Hydrogen Formation of Cis Alkene

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



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