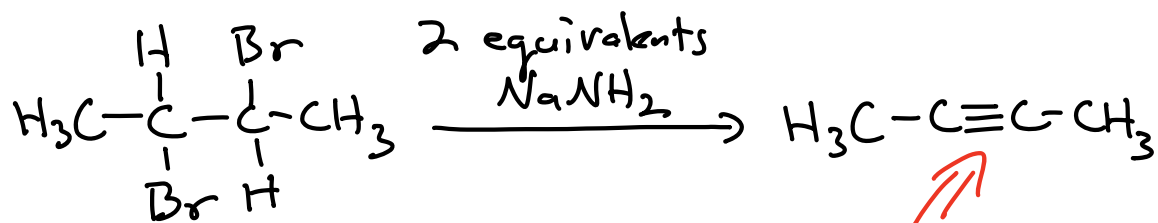




c) Conversion of a vicinal dihalide into an alkyne

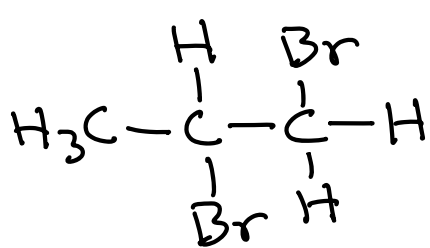


vicinal dihalide

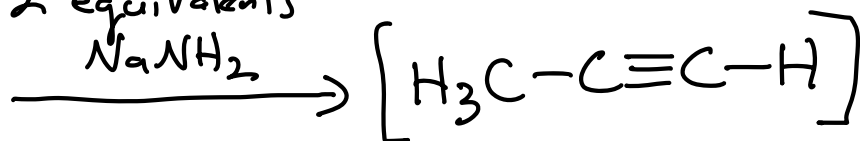
Not this alkyne is NOT terminal (No  $\equiv\text{C}-\text{H}$ )



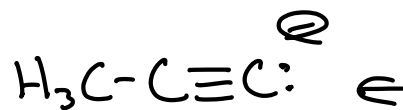
Time capsule  $\rightarrow$  This is a double E2



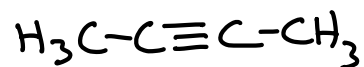
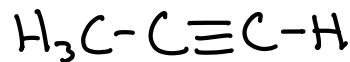
2 equivalents  
 $\text{NaNH}_2$



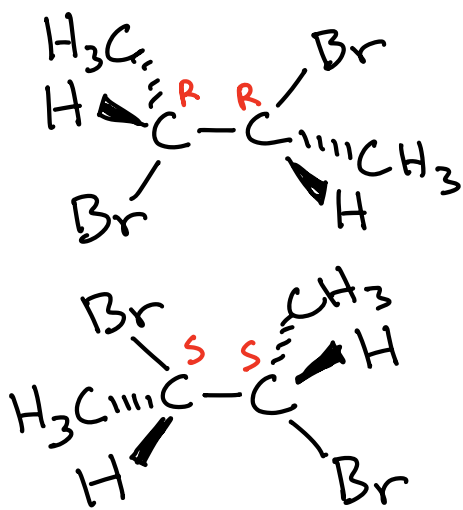
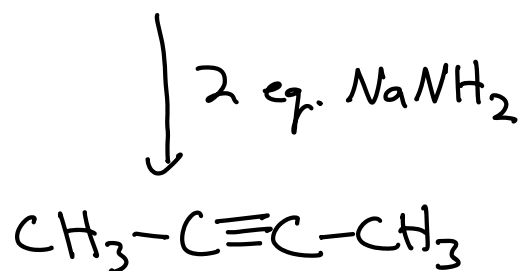
↓ 1 equivalent  
 $\text{NaNH}_2$



↓ 2.  $\text{HCl}/\text{H}_2\text{O}$   
mild

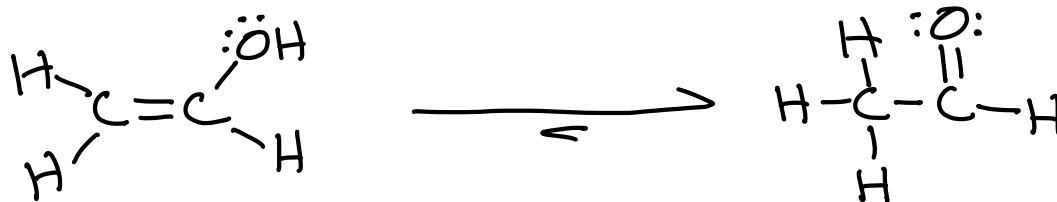


# Big Deal



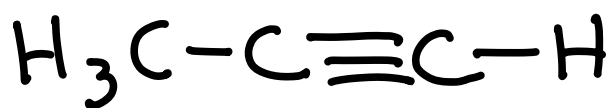
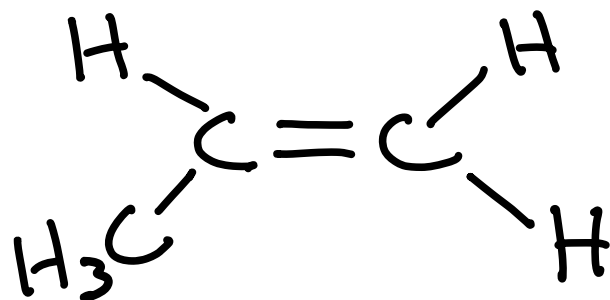
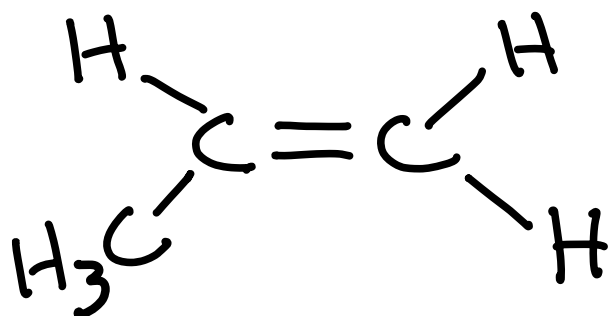
Racemic

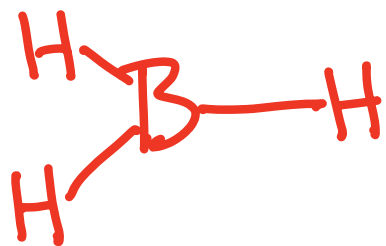
# New Concept



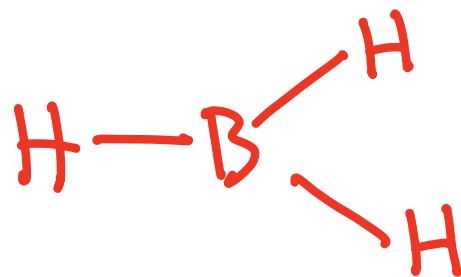


© 2012 Lone Star Outdoor News Photo by David J. Sams, LSON

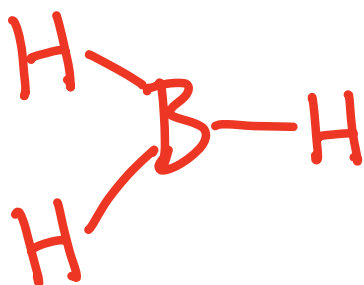




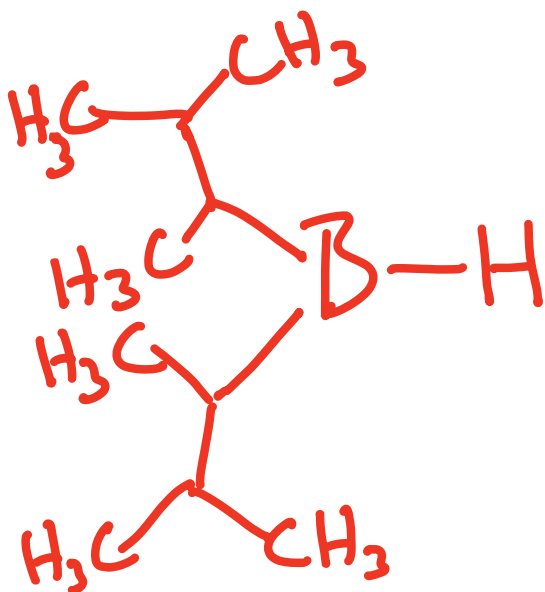
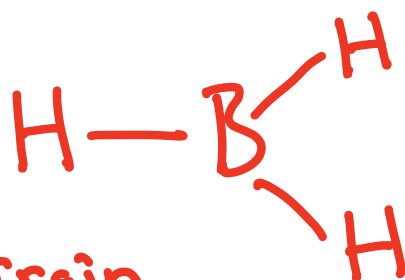
Steric Strain



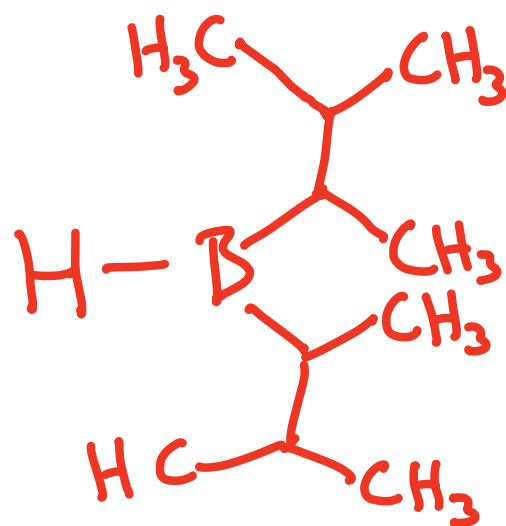
Much less Steric Strain



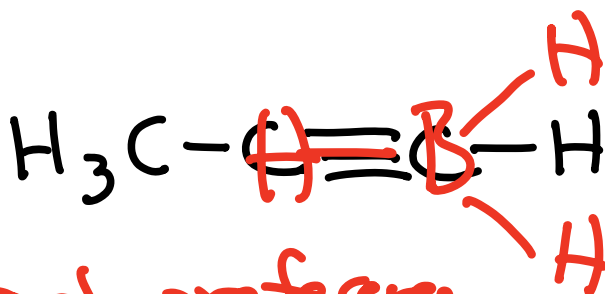
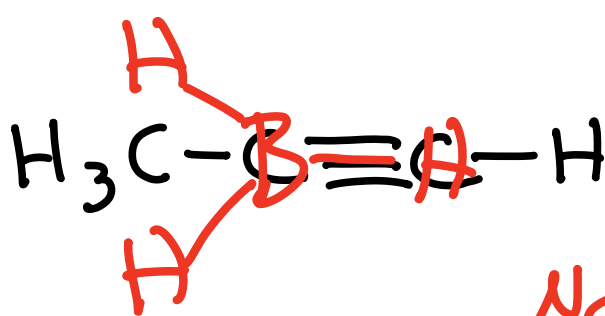
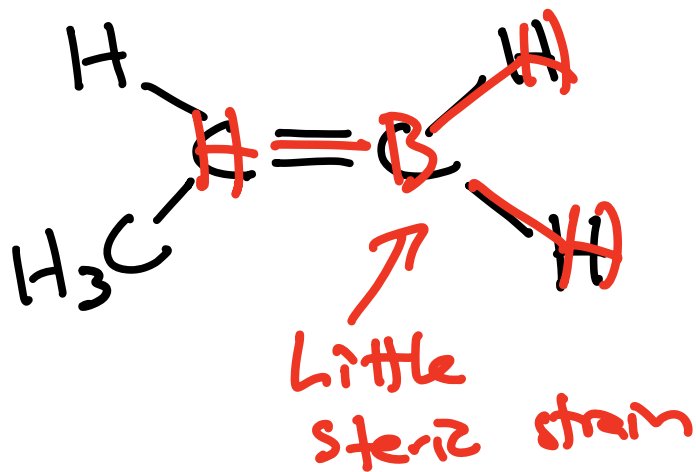
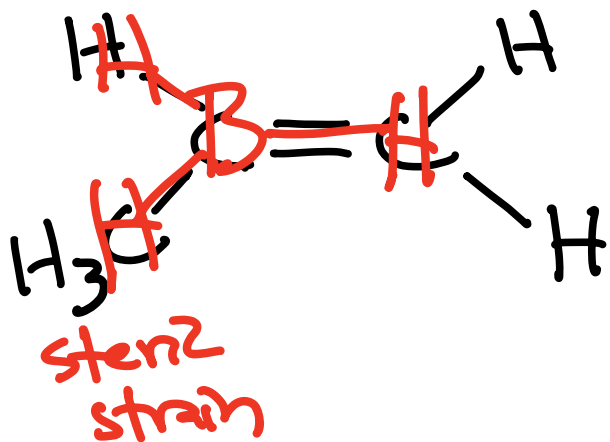
No steric strain  
No real preference



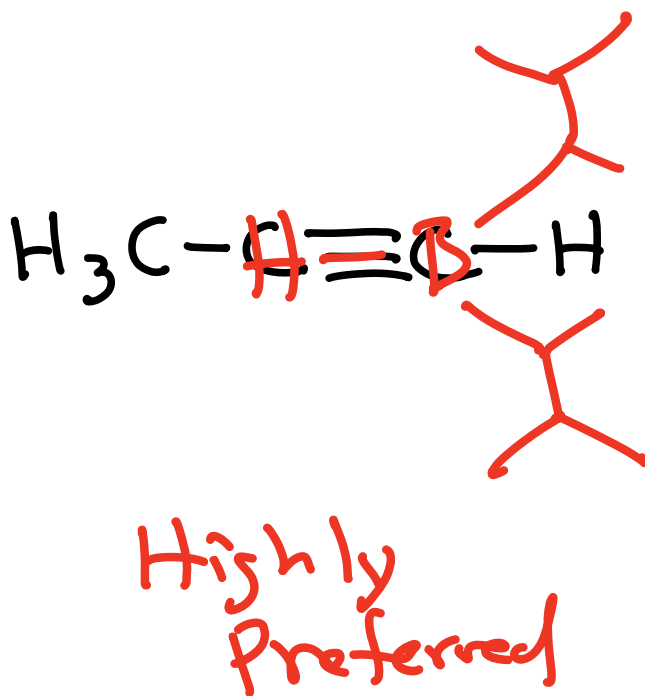
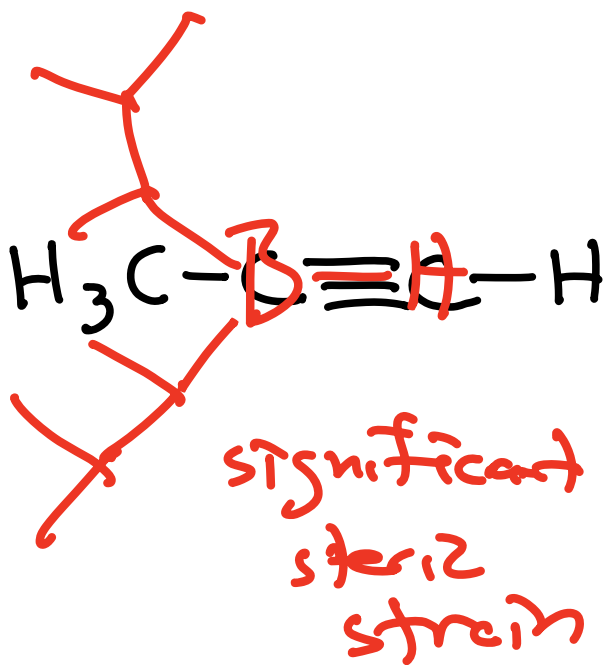
Significant Steric Strain



Highly Preferred

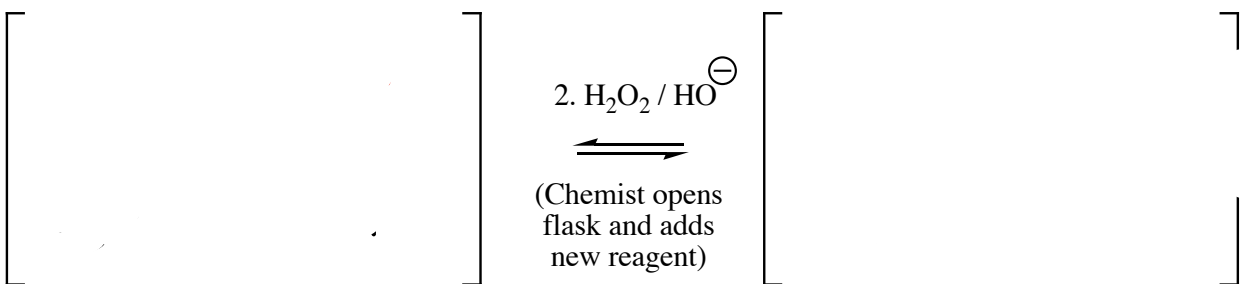
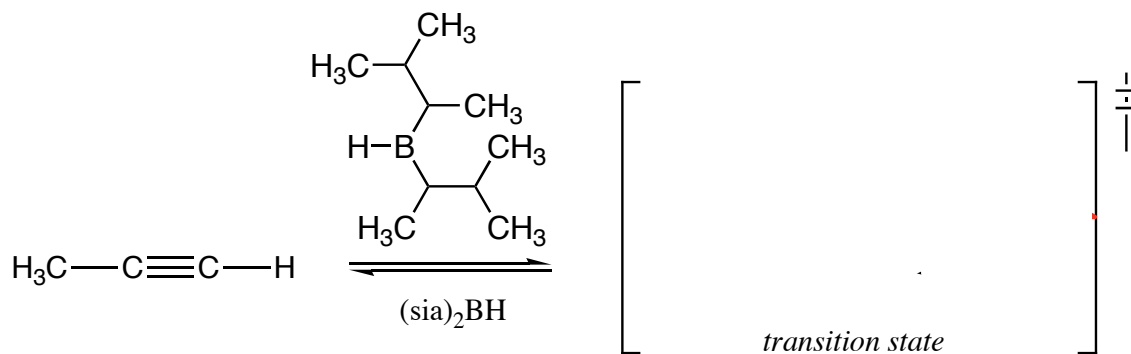


No real preference

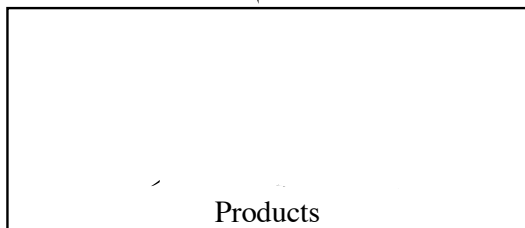




## Terminal Alkyne Hydroboration



Keto-enol  
tautomerization  $\rightleftharpoons$

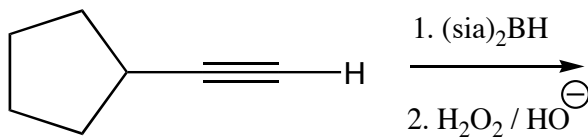


Summary:

Regiochemistry:

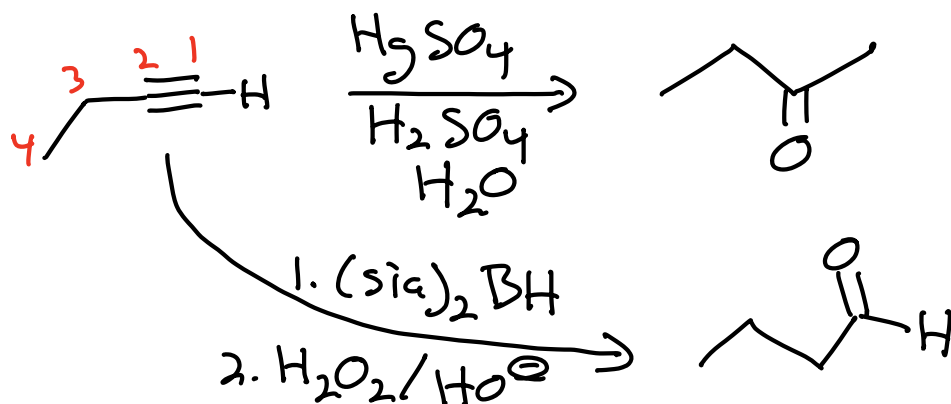
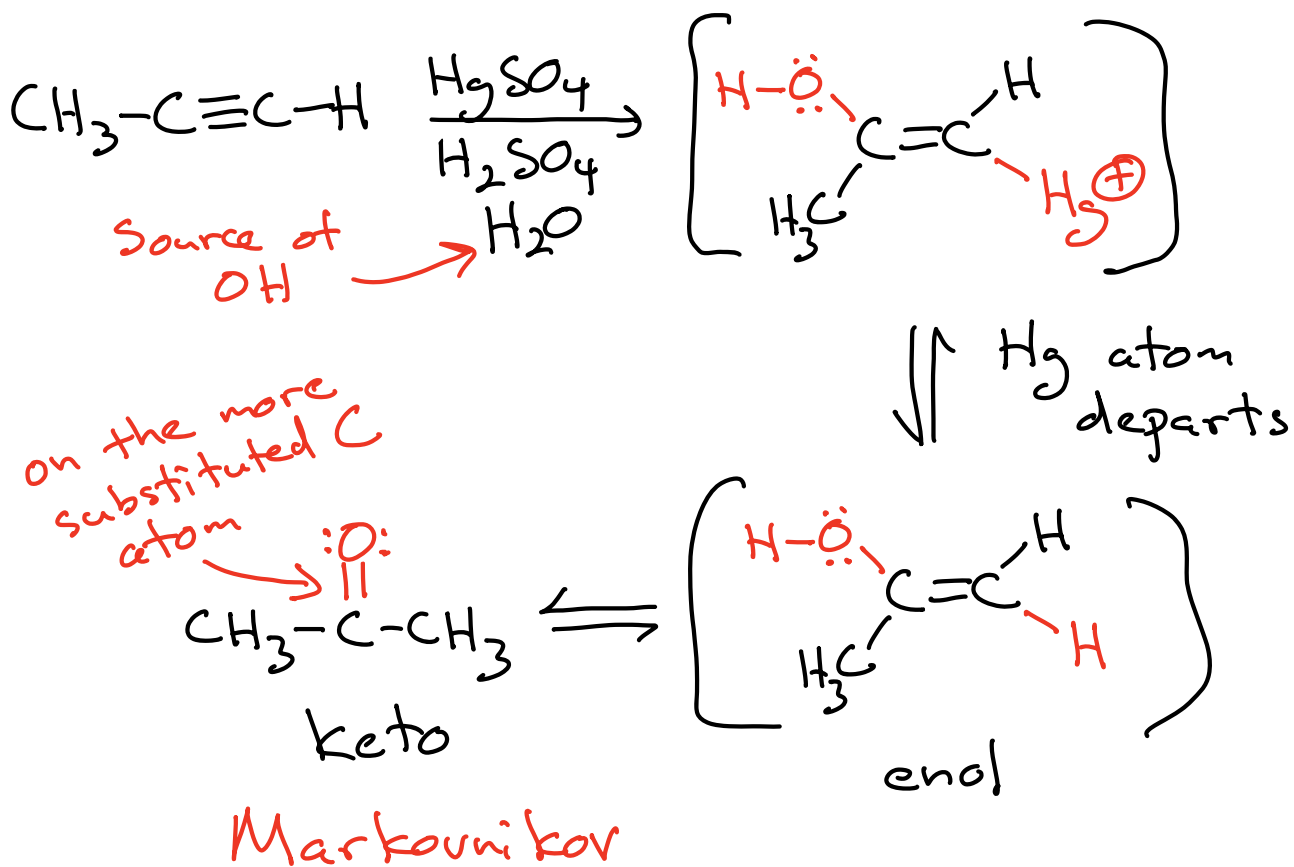
Stereochemistry:

Example:



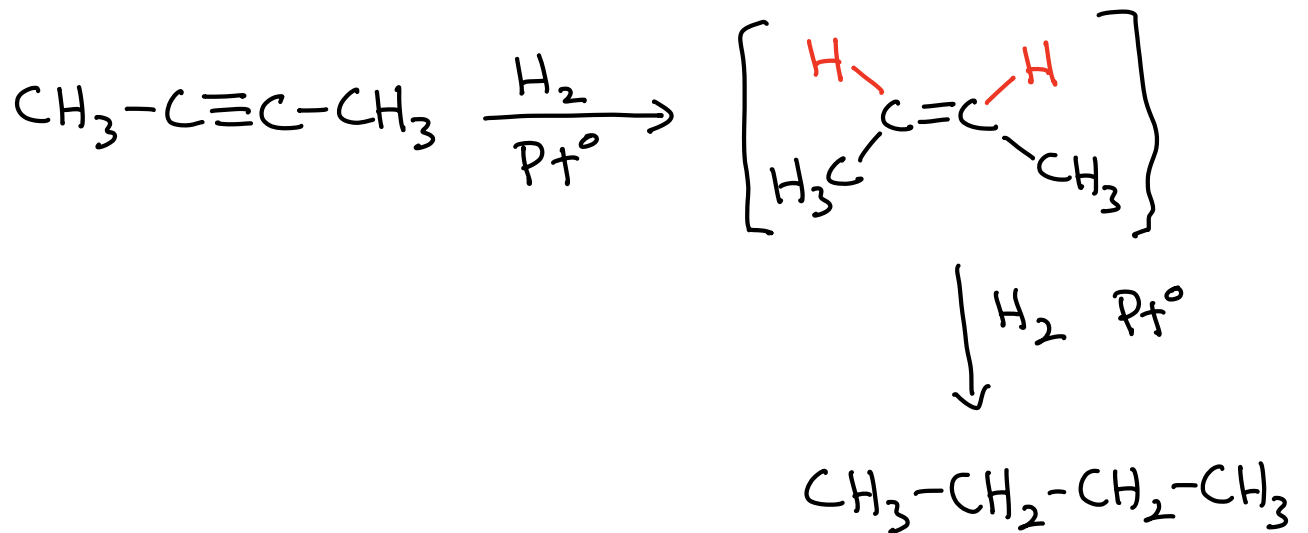


# Hydration of an alkyne using $\text{HgSO}_4, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$

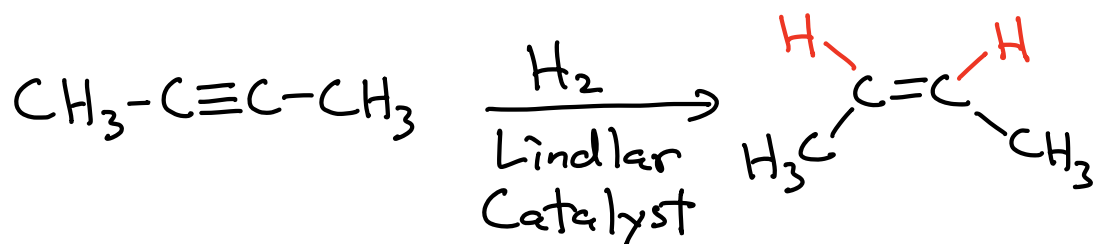


# Reduction of Alkynes

## 1) Hydrogenation



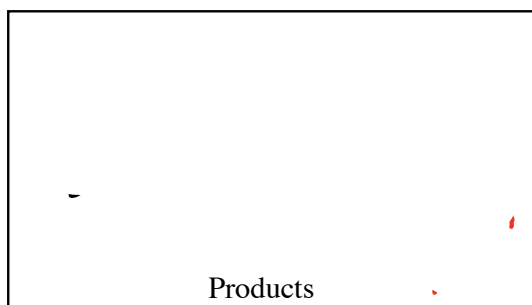
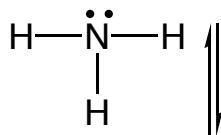
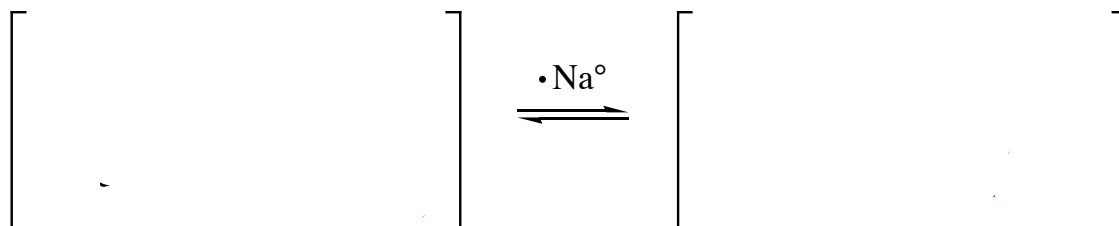
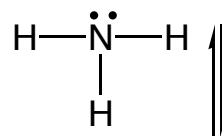
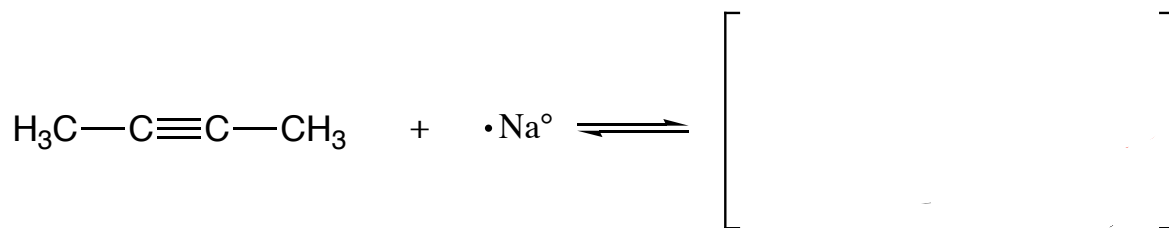
Lindlar Catalyst  $\rightarrow$







## *Reduction of Alkynes Using Sodium and Ammonia*

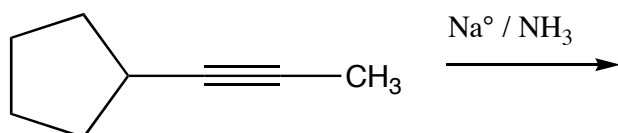


Summary:

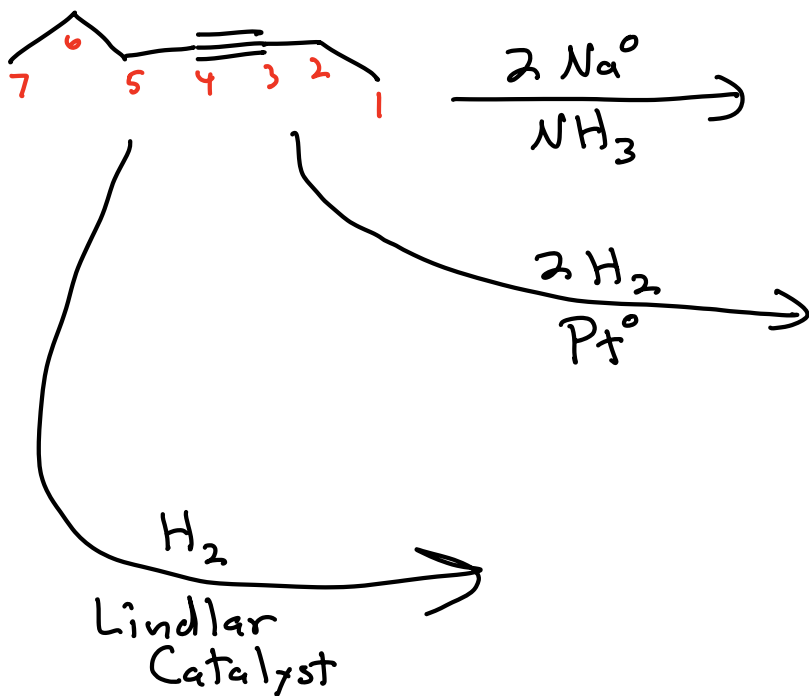
Regiochemistry:

Stereochemistry:

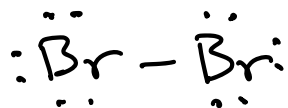
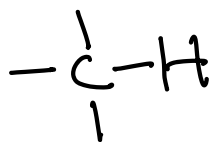
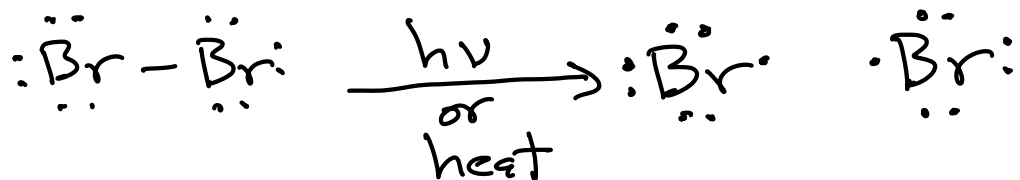
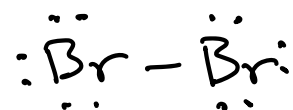
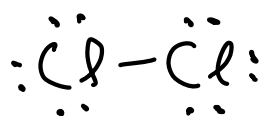
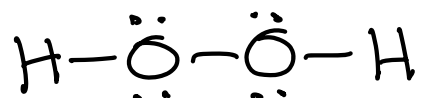
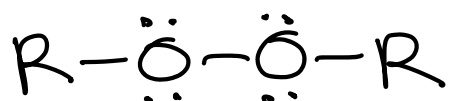
Example:



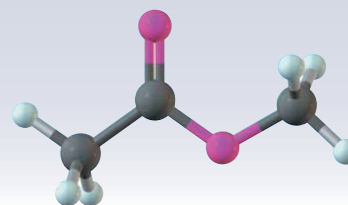
Reductions of alkynes  $\rightarrow$  3 choices







# Appendix 3 Bond Dissociation Enthalpies



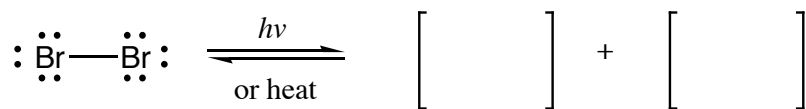
Bond dissociation enthalpy (BDE) is defined as the amount of energy required to break a bond homolytically into two radicals in the gas phase at 25°C.



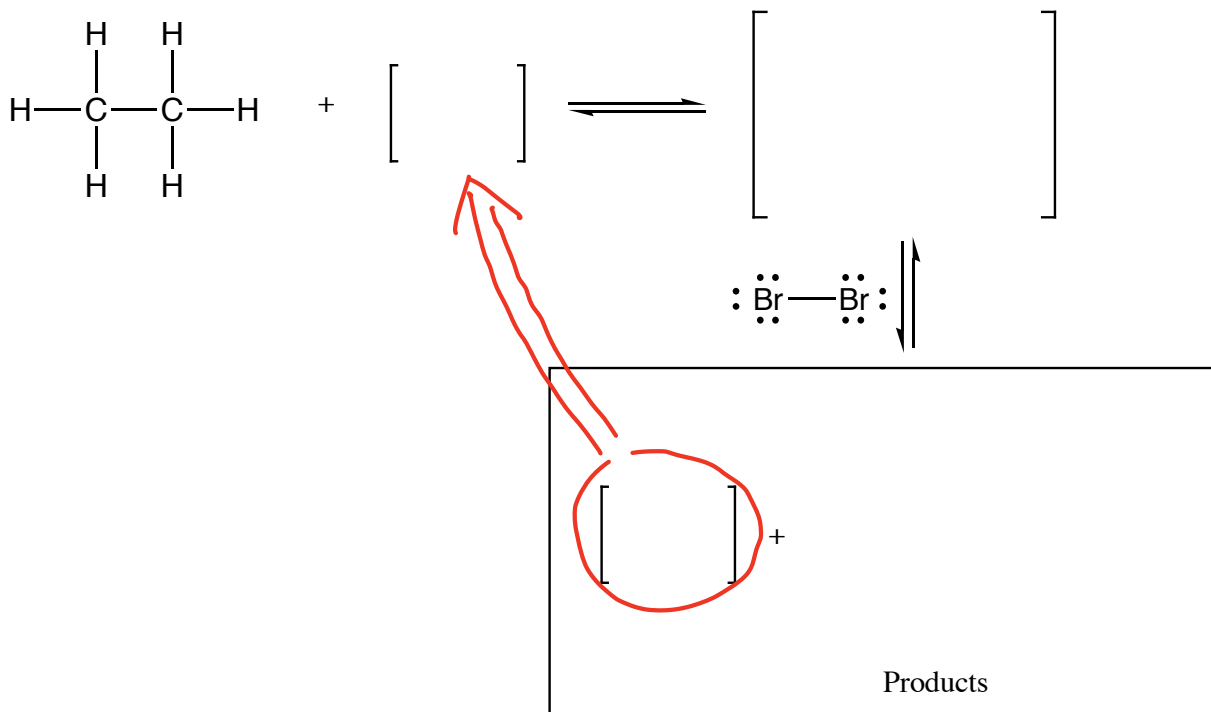
Bond	$\Delta H^0$	Bond	$\Delta H^0$	Bond	$\Delta H^0$
<b>H—H bonds</b>		<b>C—C multiple bonds</b>		<b>C—Br bonds</b>	
H—H	435 (104)	CH <sub>2</sub> =CH <sub>2</sub>	727 (174)	CH <sub>3</sub> —Br	301 (72)
D—D	444 (106)	HC≡CH	966 (231)	C <sub>2</sub> H <sub>5</sub> —Br	301 (72)
<b>X—X bonds</b>		<b>C—H bonds</b>		(CH <sub>3</sub> ) <sub>2</sub> CH—Br	309 (74)
F—F	159 (38)	CH <sub>3</sub> —H	439 (105)	(CH <sub>3</sub> ) <sub>3</sub> C—Br	305 (73)
Cl—Cl	247 (59)	C <sub>2</sub> H <sub>5</sub> —H	422 (101)	CH <sub>2</sub> =CHCH <sub>2</sub> —Br	247 (59)
Br—Br	192 (46)	(CH <sub>3</sub> ) <sub>2</sub> CH—H	414 (99)	C <sub>6</sub> H <sub>5</sub> —Br	351 (84)
I—I	151 (36)	(CH <sub>3</sub> ) <sub>3</sub> C—H	405 (97)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —Br	263 (63)
<b>H—X bonds</b>		CH <sub>2</sub> =CH—H	464 (111)	<b>C—I bonds</b>	
H—F	568 (136)	CH <sub>2</sub> =CHCH <sub>2</sub> —H	372 (89)	CH <sub>3</sub> —I	242 (58)
H—Cl	431 (103)	C <sub>6</sub> H <sub>5</sub> —H	472 (113)	C <sub>2</sub> H <sub>5</sub> —I	238 (57)
H—Br	368 (88)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —H	376 (90)	(CH <sub>3</sub> ) <sub>2</sub> CH—I	238 (57)
H—I	297 (71)	HC≡C—H	556 (133)	(CH <sub>3</sub> ) <sub>3</sub> C—I	234 (56)
<b>O—H bonds</b>		<b>C—F bonds</b>		CH <sub>2</sub> =CHCH <sub>2</sub> —I	192 (46)
HO—H	497 (119)	CH <sub>3</sub> —F	481 (115)	C <sub>6</sub> H <sub>5</sub> —I	280 (67)
CH <sub>3</sub> O—H	439 (105)	C <sub>2</sub> H <sub>5</sub> —F	472 (113)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —I	213 (51)
C <sub>6</sub> H <sub>5</sub> O—H	376 (90)	(CH <sub>3</sub> ) <sub>2</sub> CH—F	464 (111)	<b>C—N single bonds</b>	
<b>O—O bonds</b>		C <sub>6</sub> H <sub>5</sub> —F	531 (127)	CH <sub>3</sub> —NH <sub>2</sub>	355 (85)
HO—OH	213 (51)	<b>C—Cl bonds</b>		C <sub>6</sub> H <sub>5</sub> —NH <sub>2</sub>	435 (104)
CH <sub>3</sub> O—OCH <sub>3</sub>	159 (38)	CH <sub>3</sub> —Cl	351 (84)	<b>C—O single bonds</b>	
(CH <sub>3</sub> ) <sub>3</sub> CO—OC(CH <sub>3</sub> ) <sub>3</sub>	159 (38)	C <sub>2</sub> H <sub>5</sub> —Cl	355 (85)	CH <sub>3</sub> —OH	385 (92)
<b>C—C single bonds</b>		(CH <sub>3</sub> ) <sub>2</sub> CH—Cl	355 (85)	C <sub>6</sub> H <sub>5</sub> —OH	468 (112)
CH <sub>3</sub> —CH <sub>3</sub>	376 (90)	(CH <sub>3</sub> ) <sub>3</sub> C—Cl	355 (85)		
C <sub>2</sub> H <sub>5</sub> —CH <sub>3</sub>	372 (89)	CH <sub>2</sub> =CHCH <sub>2</sub> —Cl	288 (69)		
CH <sub>2</sub> =CH—CH <sub>3</sub>	422 (101)	C <sub>6</sub> H <sub>5</sub> —Cl	405 (97)		
CH <sub>2</sub> =CHCH <sub>2</sub> —CH <sub>3</sub>	322 (77)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —Cl	309 (74)		
C <sub>6</sub> H <sub>5</sub> —CH <sub>3</sub>	435 (104)				
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —CH <sub>3</sub>	326 (78)				

## Alkane Free Radical Halogenation

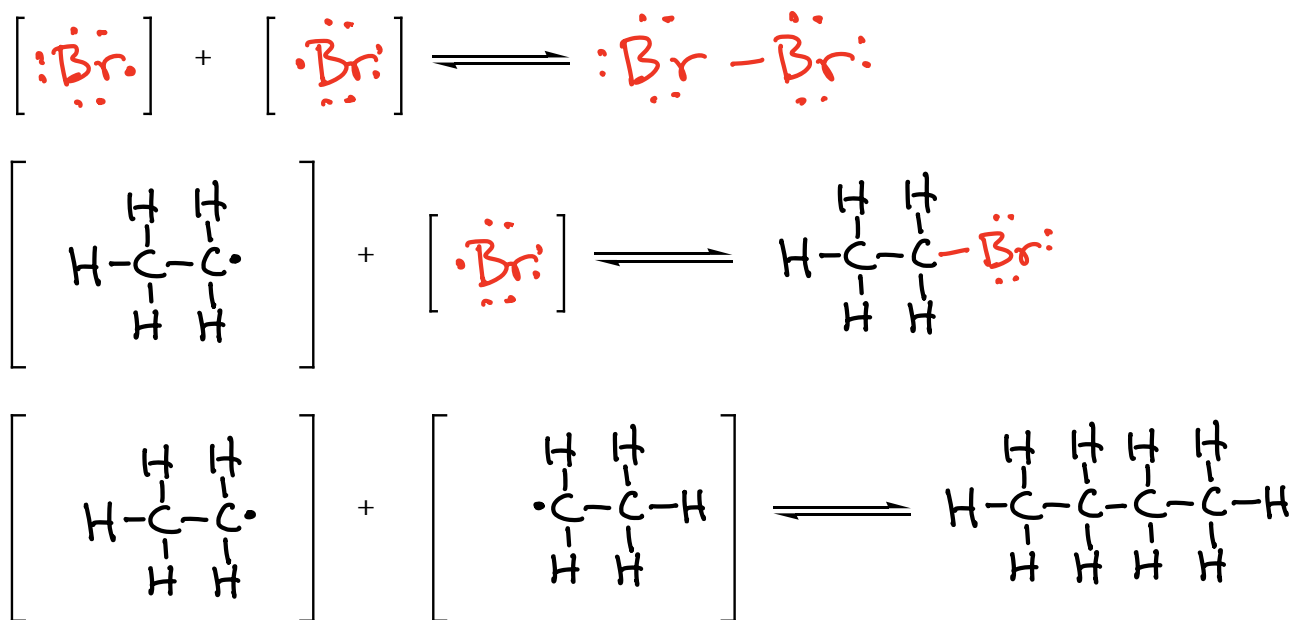
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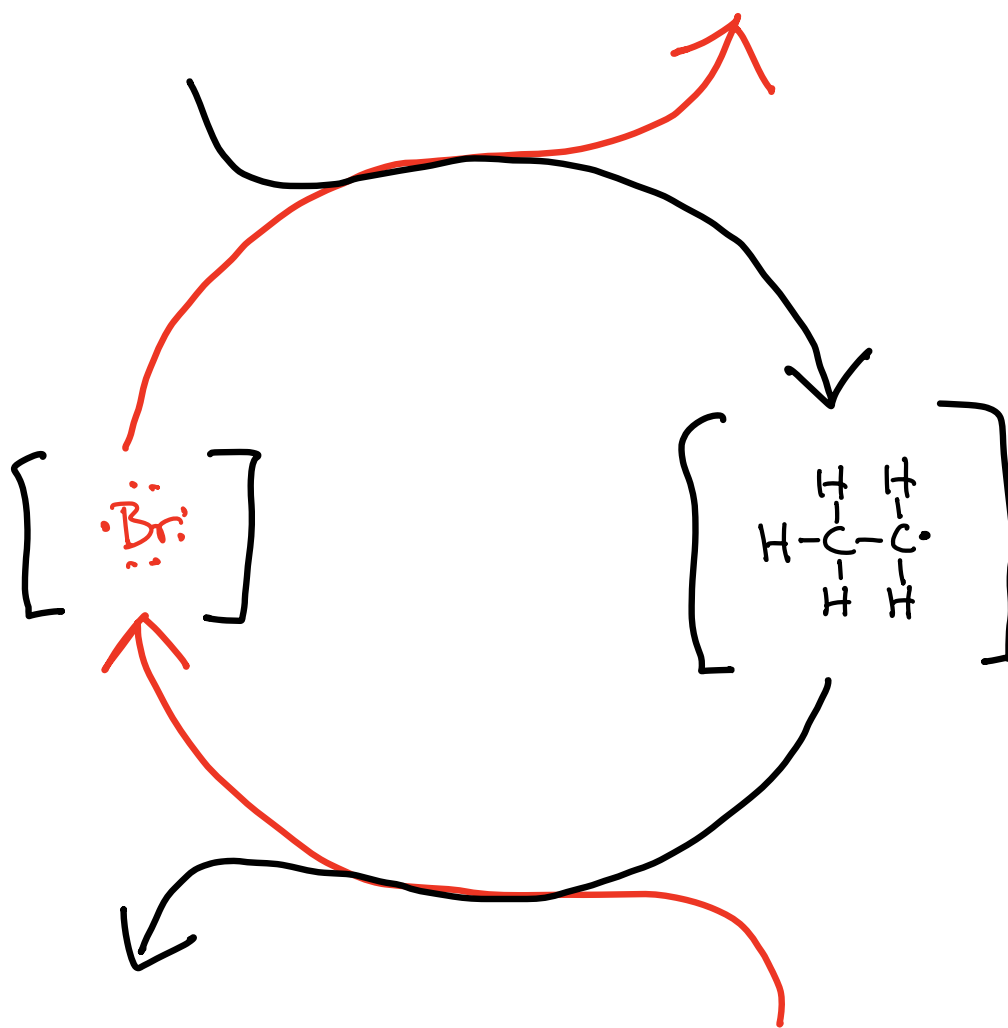
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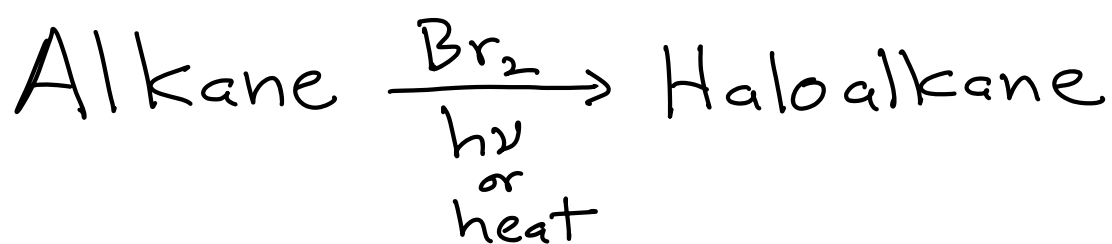
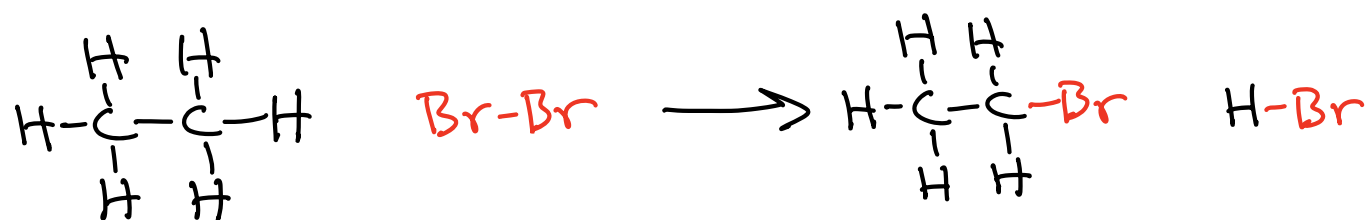


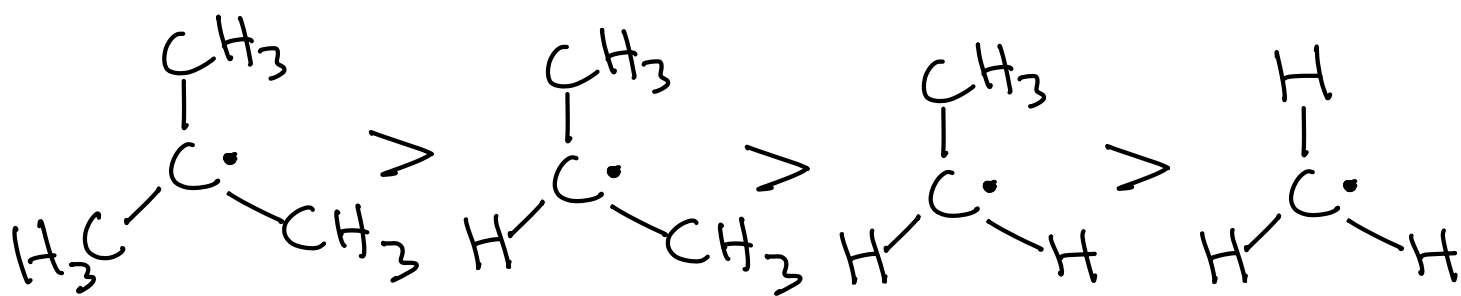
### Termination



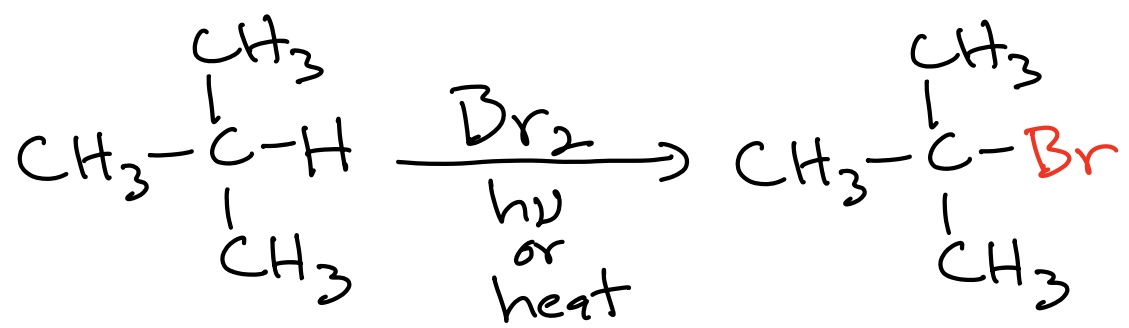
# Propagation Process Diagram

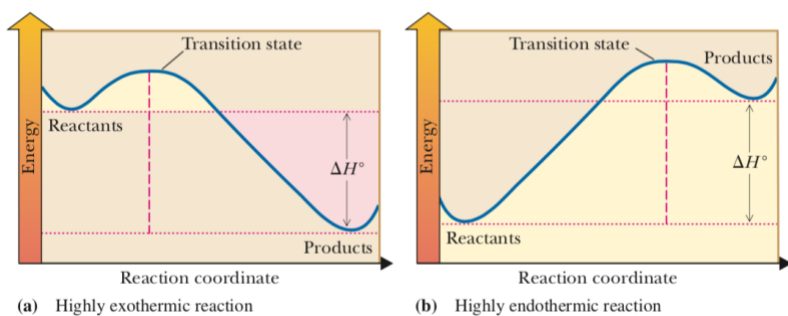




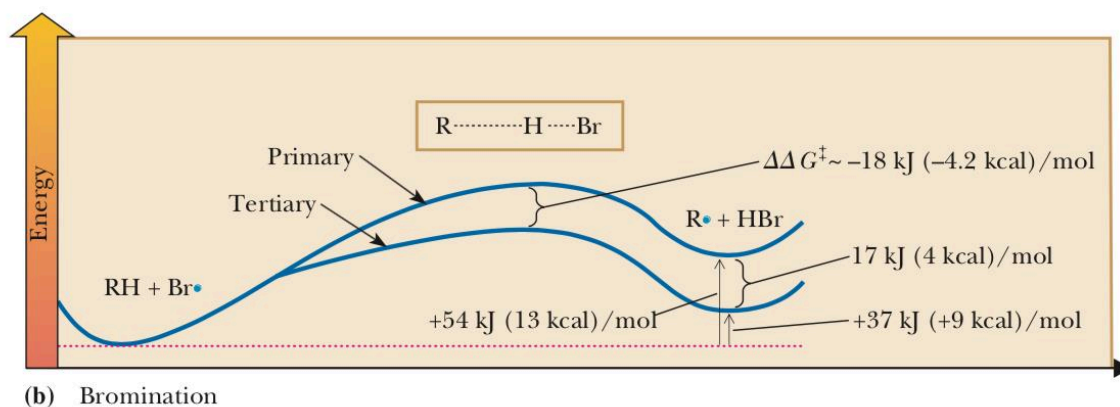
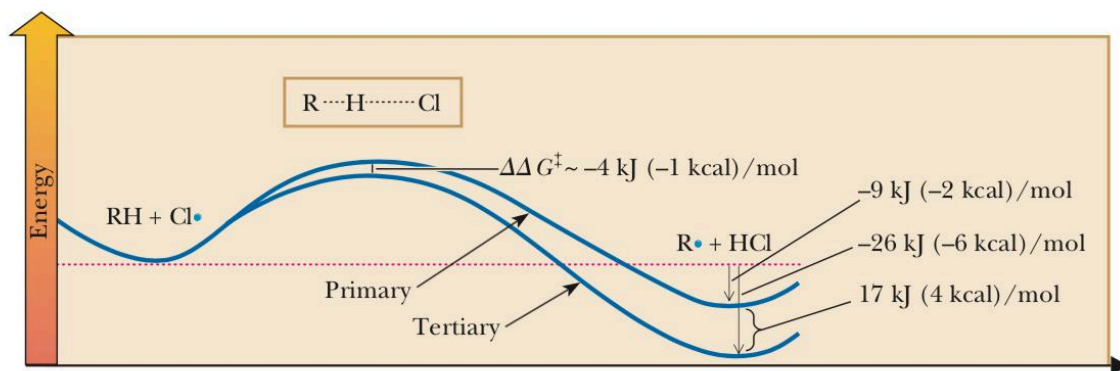


← Radical Stability





**Figure 8.2**  
Hammond's postulate. Energy diagrams for two one-step reactions. In the exothermic reaction, the transition state occurs early, and its structure resembles that of the reactants. In the endothermic reaction, the transition state occurs late, and its structure resembles that of the products.

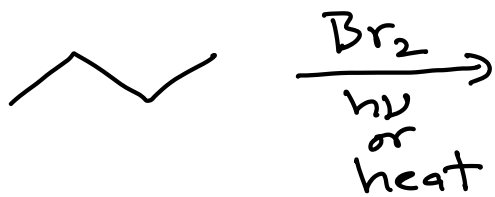
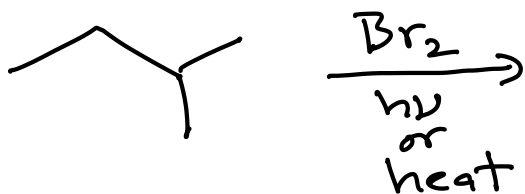
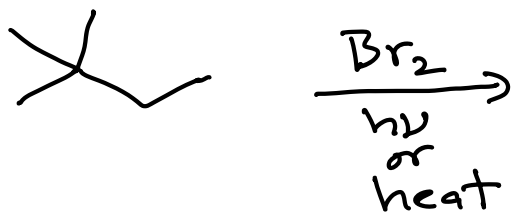


**Figure 8.3**

Transition states and energetics for hydrogen abstraction in the radical chlorination and bromination of 2-methylpropane (isobutane). The product is the intermediate radical, R•.



# Examples



**Organic Chemistry is the study of carbon-containing molecules.**

**This class has two points.**

***The first point of the class is to understand the organic chemistry of living systems. We will teach you how to think about and understand the most amazing things on the planet!!***

Water is essential for life, you will learn why water has such special properties.

8/28/24

You will learn the secret structural reason proteins, the most important molecular machines in our bodies, can support the chemistry of life.

9/11/24

You will learn why when you take Advil for pain, exactly half of what you take works, and the other half does nothing.

9/25/24

You will learn how toothpaste works.

10/7/24

You will learn how a single chlorofluorocarbon refrigerant molecule released into the atmosphere can destroy many, many ozone molecules, leading to an enlargement of the ozone hole.

You will learn how medicines like Benadryl, Seldane, and Lipitor work.

You will learn how Naloxone is an antidote for an opioid overdose.

You will learn why Magic Johnson is still alive, decades after contracting HIV.

You will learn how MRI scans work.

***The second point of organic chemistry is the synthesis of complex molecules from simpler ones by making and breaking specific bonds.***

You will learn how to understand movies of reaction mechanisms like alkene hydration.

10/9/24

You will learn reactions that once begun, will continue reacting such that each product molecule created starts a new reaction until all the starting material is used up.

You will learn reactions that can make antifreeze from vodka.

You will learn a reaction that can make nail polish remover from rubbing alcohol.

You will learn how to look at a molecule and accurately predict which atoms will react to make new bonds, and which bonds will break during reactions.

You will learn how to analyze a complex molecule's structure so that you can predict ways to make it via multiple reactions starting with less complex starting molecules.

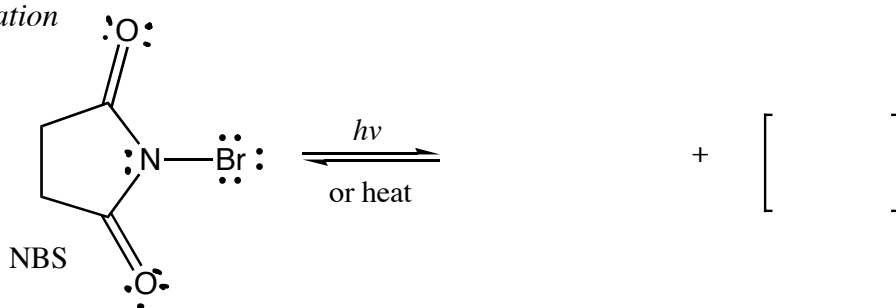


# Allylic Halogenation

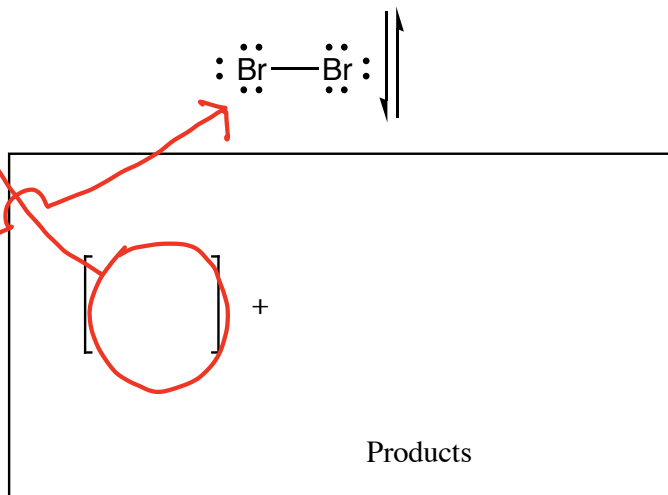
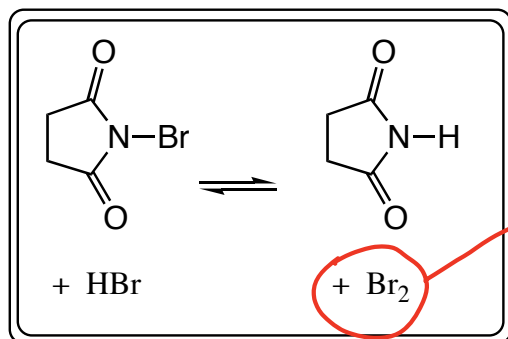
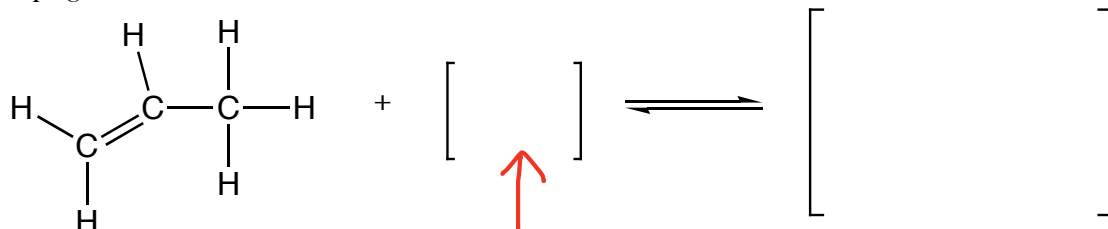


## Allylic Halogenation

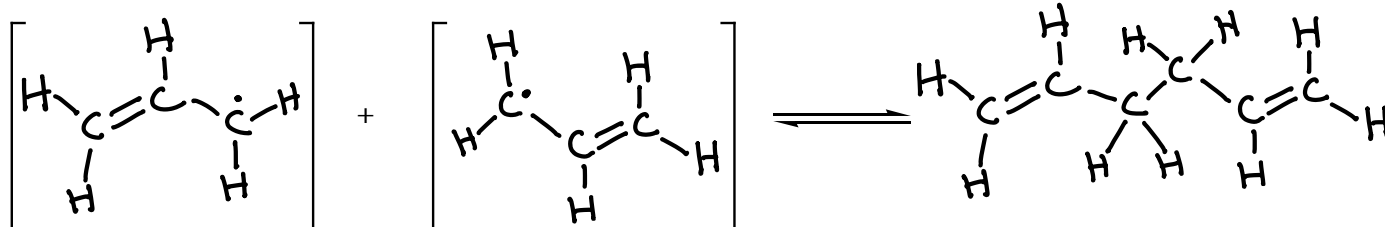
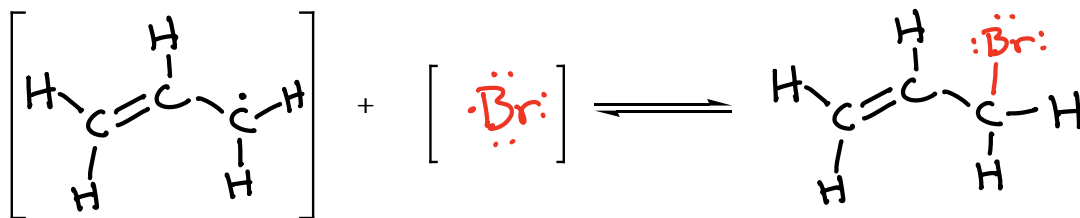
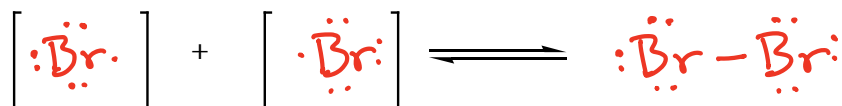
Initiation



Propagation



Termination



Big Change —



When analyzing allylic halogenation reactions (NBS and  $h\nu$ )

1. Consider all possible allylic radicals that can be formed.
2. Analyze all contributing structures for all of the allylic radicals.
3. Add a Br atom at the site of the unpaired electron for all contributing structures for all of the allylic radicals.
4. From all of the possible products, the predominant product is the one **THAT IS THE MOST STABLE ALKENE** – the most substituted alkene – alkyl groups stabilize alkenes – *trans* over *cis*.
5. Note: It is OK if the product you choose derives from an allylic radical contributing structure that is a minor contributor. **FOR THIS REACTION WE ONLY CARE ABOUT THE RELATIVE STABILITIES OF THE PRODUCT ALKENES.**

