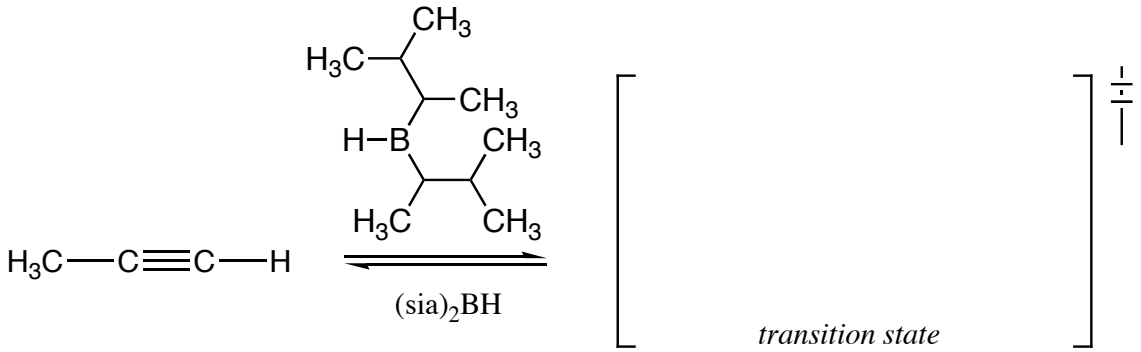
Terminal Alkyne Hydroboration



2. H_2O_2 / $HO^{\ominus}$

(Chemist opens flask and adds new reagent)

Keto-enol tautomerization

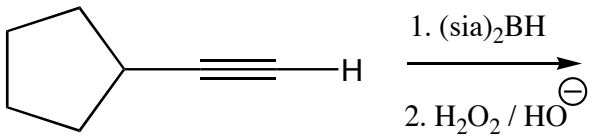
Products

Summary:

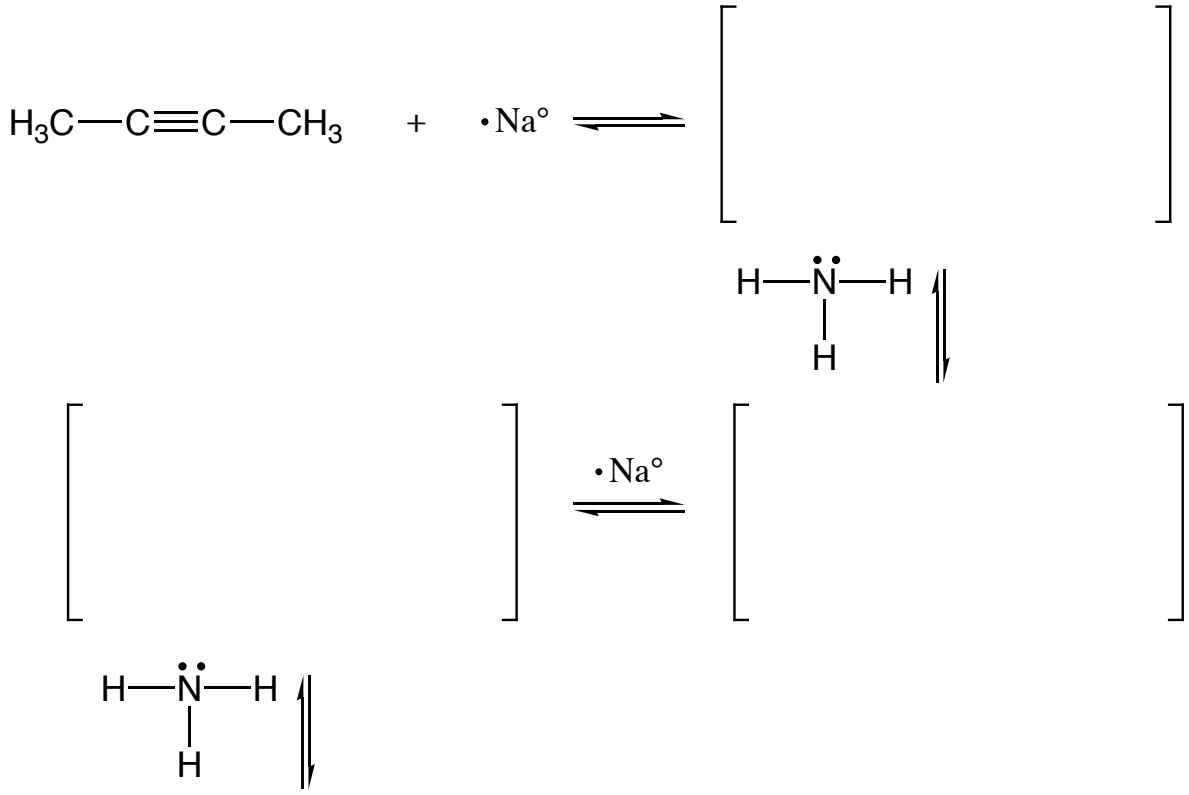
Regiochemistry:

Stereochemistry:

Example:



Reduction of Alkynes Using Sodium and Ammonia



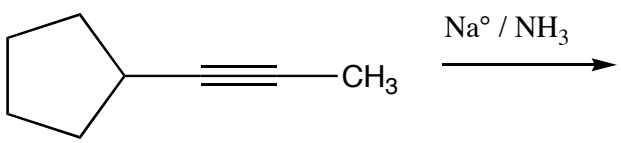
Products

Summary:

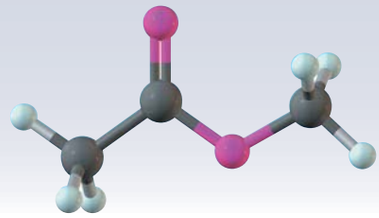
Regiochemistry:

Stereochemistry:

Example:



Appendix 3 Bond Dissociation Enthalpies



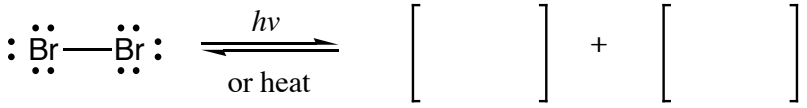
Bond dissociation enthalpy (BDE) is defined as the amount of energy required to break a bond homolytically into two radicals in the gas phase at 25°C.

$$A—B \rightarrow A\cdot + B\cdot \qquad \Delta H^0 \text{ [kJ (kcal)/mol]}$$

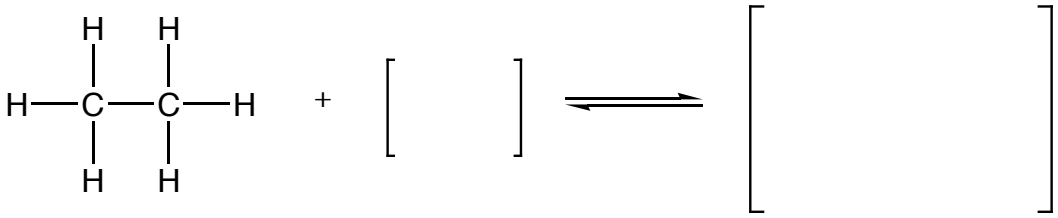
Bond	ΔH^0	Bond	ΔH^0	Bond	ΔH^0
H—H bonds		**C—C multiple bonds**		**C—Br bonds**	
H—H	435 (104)	CH_2═CH_2	727 (174)	CH_3—Br	301 (72)
D—D	444 (106)	HC≡CH	966 (231)	C_2H_5—Br	301 (72)
				$(CH_3)_2CH$—Br	309 (74)
X—X bonds		**C—H bonds**		$(CH_3)_3C$—Br	305 (73)
F—F	159 (38)	CH_3—H	439 (105)	CH_2═$CHCH_2$—Br	247 (59)
Cl—Cl	247 (59)	C_2H_5—H	422 (101)	C_6H_5—Br	351 (84)
Br—Br	192 (46)	$(CH_3)_2CH$—H	414 (99)	$C_6H_5CH_2$—Br	263 (63)
I—I	151 (36)	$(CH_3)_3C$—H	405 (97)		
		CH_2═CH—H	464 (111)	**C—I bonds**	
H—X bonds		CH_2═$CHCH_2$—H	372 (89)	CH_3—I	242 (58)
H—F	568 (136)	C_6H_5—H	472 (113)	C_2H_5—I	238 (57)
H—Cl	431 (103)	$C_6H_5CH_2$—H	376 (90)	$(CH_3)_2CH$—I	238 (57)
H—Br	368 (88)	HC≡C—H	556 (133)	$(CH_3)_3C$—I	234 (56)
H—I	297 (71)			CH_2═$CHCH_2$—I	192 (46)
		C—F bonds		C_6H_5—I	280 (67)
O—H bonds		CH_3—F	481 (115)	$C_6H_5CH_2$—I	213 (51)
HO—H	497 (119)	C_2H_5—F	472 (113)		
CH_3O—H	439 (105)	$(CH_3)_2CH$—F	464 (111)	**C—N single bonds**	
C_6H_5O—H	376 (90)	C_6H_5—F	531 (127)	CH_3—NH_2	355 (85)
				C_6H_5—NH_2	435 (104)
O—O bonds		**C—Cl bonds**			
HO—OH	213 (51)	CH_3—Cl	351 (84)	**C—O single bonds**	
CH_3O—OCH_3	159 (38)	C_2H_5—Cl	355 (85)	CH_3—OH	385 (92)
$(CH_3)_3CO$—$OC(CH_3)_3$	159 (38)	$(CH_3)_2CH$—Cl	355 (85)	C_6H_5—OH	468 (112)
		$(CH_3)_3$ C—Cl	355 (85)		
C—C single bonds		CH_2═$CHCH_2$—Cl	288 (69)		
CH_3—CH_3	376 (90)	C_6H_5—Cl	405 (97)		
C_2H_5—CH_3	372 (89)	$C_6H_5CH_2$—Cl	309 (74)		
CH_2═CH—CH_3	422 (101)				
CH_2═$CHCH_2$—CH_3	322 (77)				
C_6H_5—CH_3	435 (104)				
$C_6H_5CH_2$—CH_3	326 (78)				

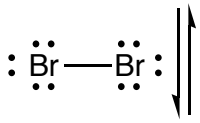
Alkane Free Radical Halogenation

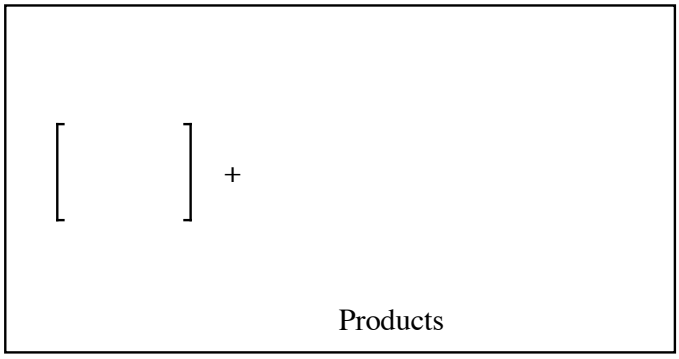
Initiation



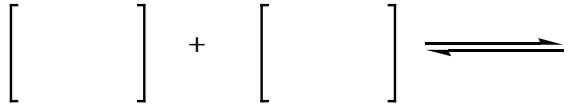
Propagation

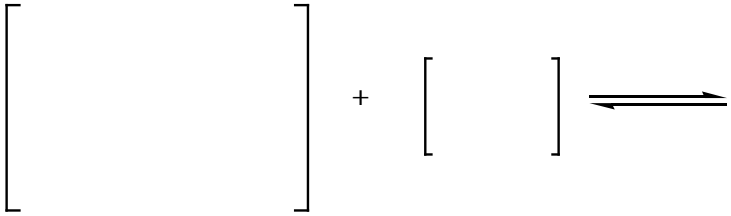


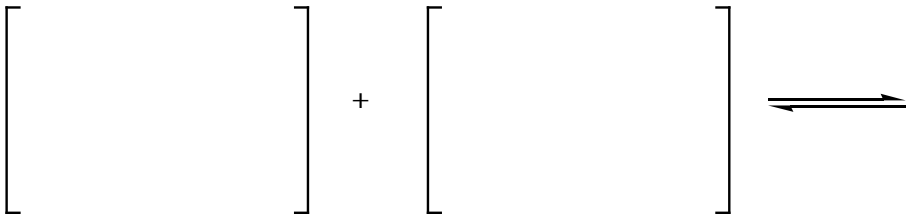




Termination







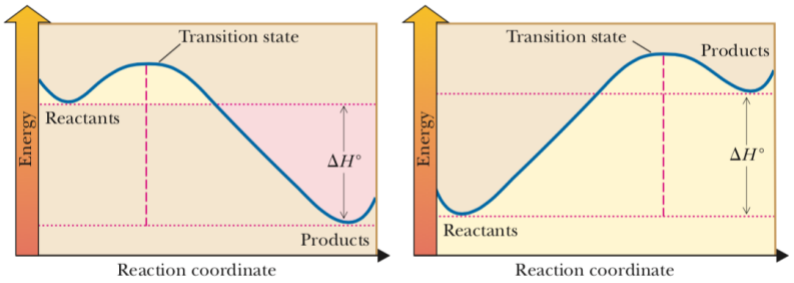
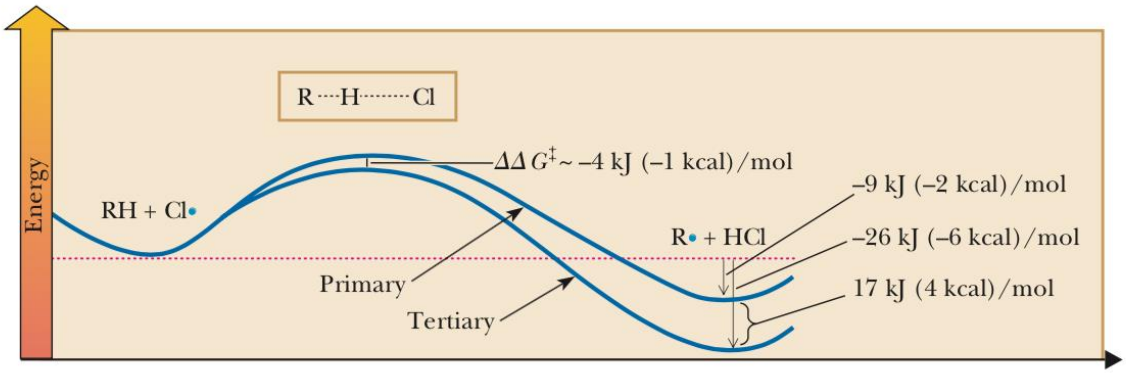
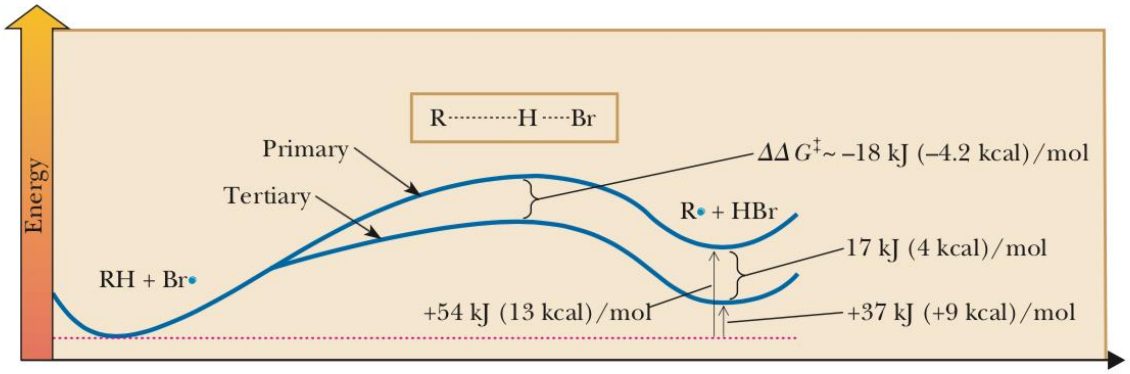


Figure 8.2
Hammond's postulate. Energy diagrams for two one-step reactions. In the exothermic reaction, the transition state occurs early, and its structure resembles that of the reactants. In the endothermic reaction, the transition state occurs late, and its structure resembles that of the products.



(a) Chlorination

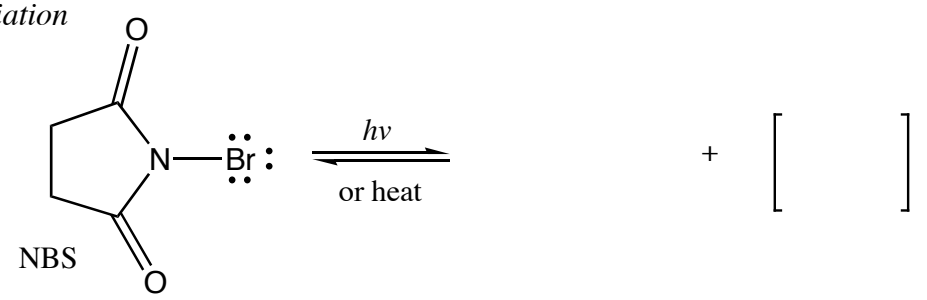


(b) Bromination

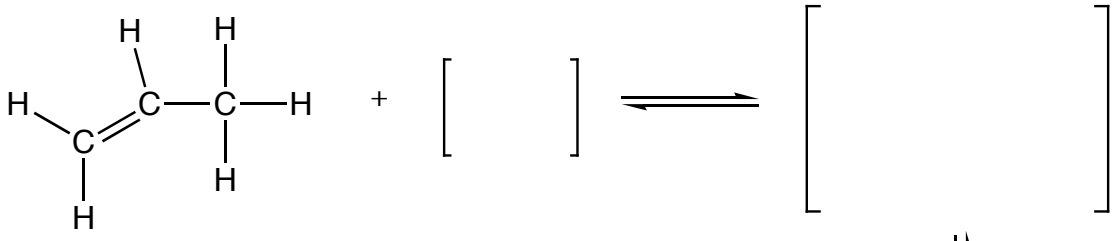
Figure 8.3
Transition states and energetics for hydrogen abstraction in the radical chlorination and bromination of 2-methylpropane (isobutane). The product is the intermediate radical, R·.

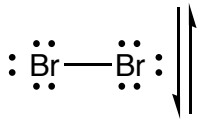
Allylic Halogenation

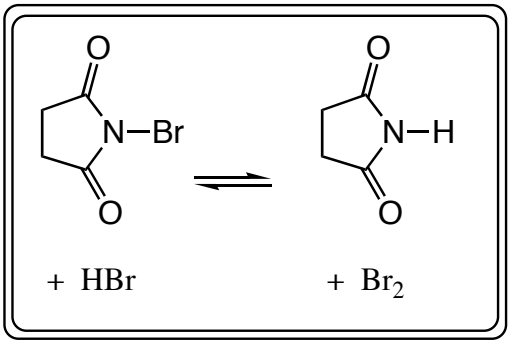
Initiation

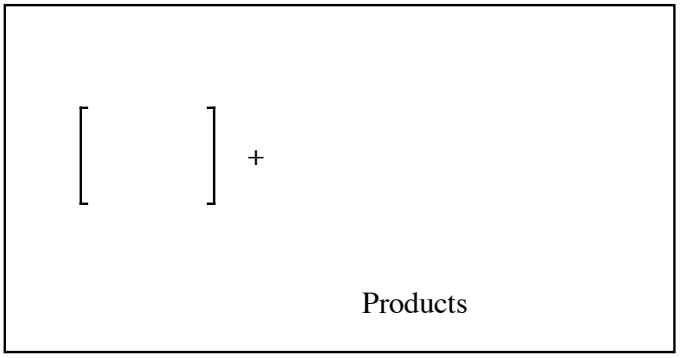


Propagation

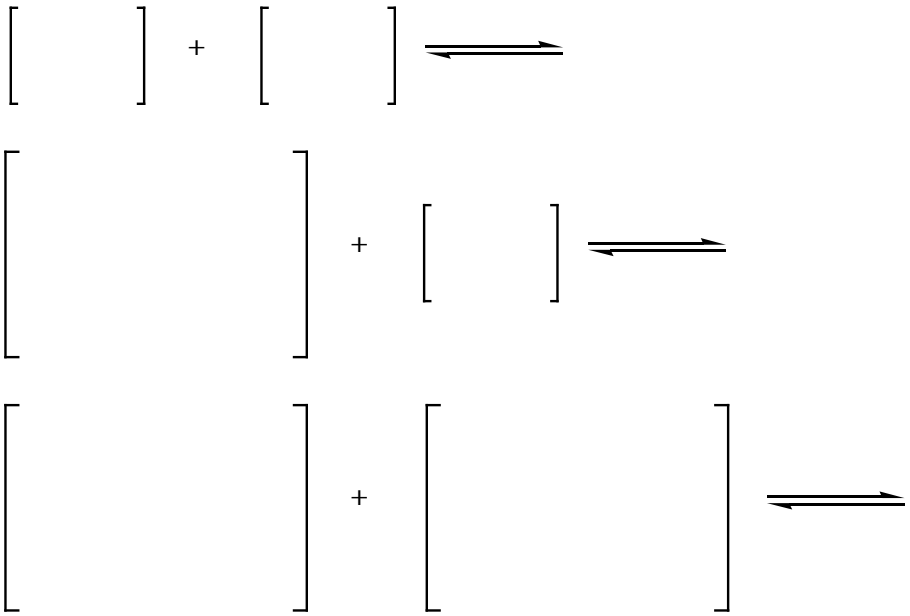






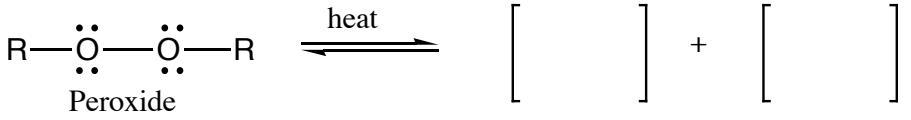


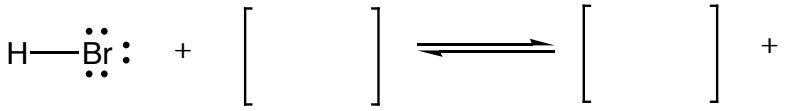
Termination



Non-Markovnikov Addition of HBr to an Alkene

Initiation





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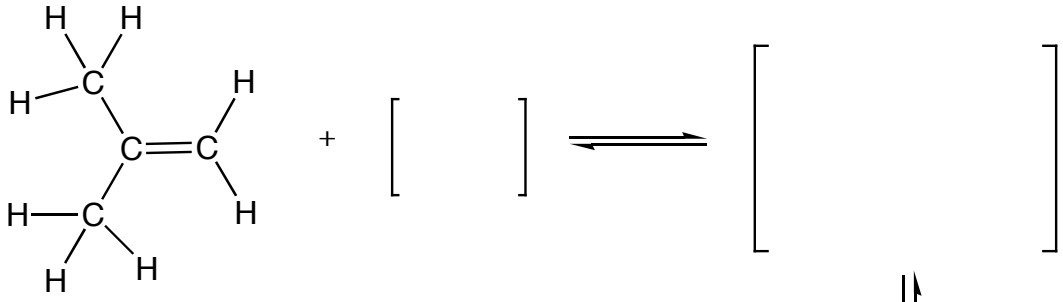

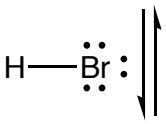

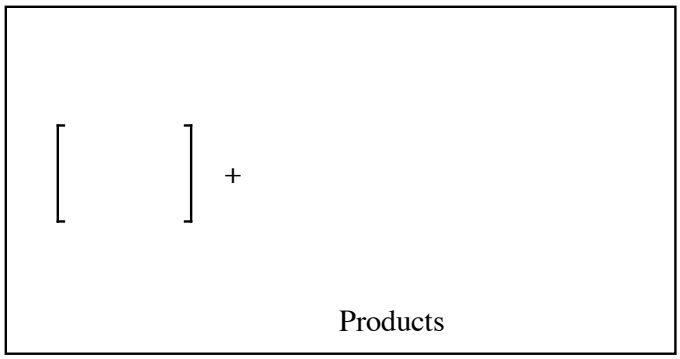

Termination