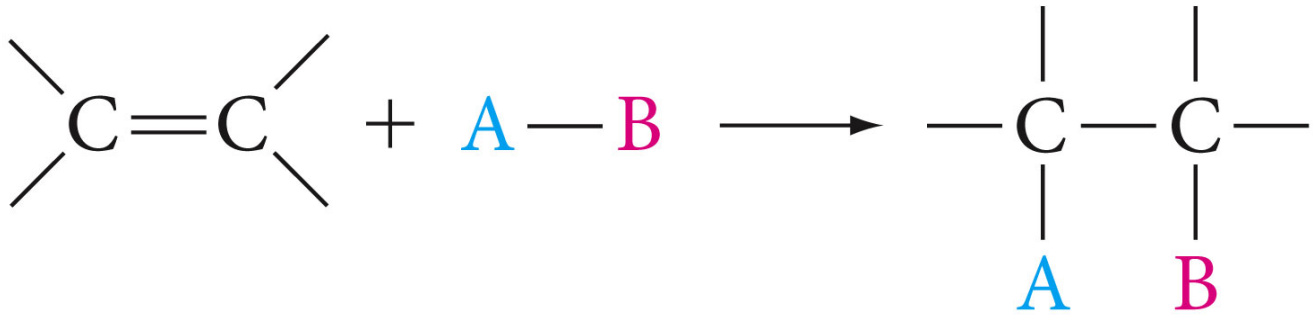
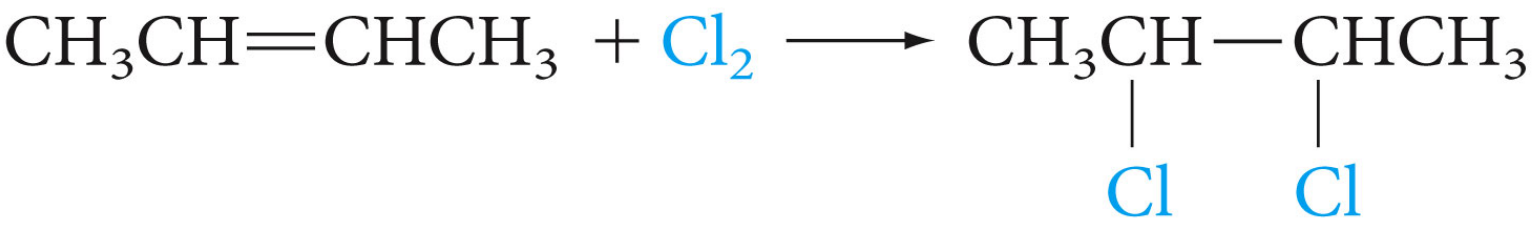
Addition Reactions

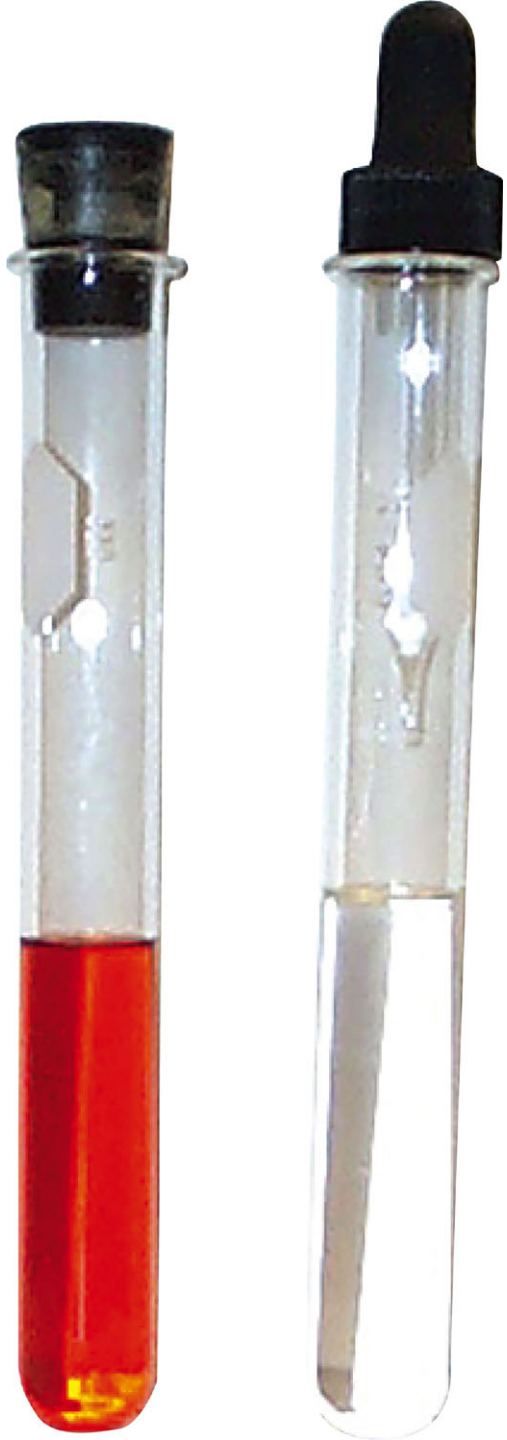


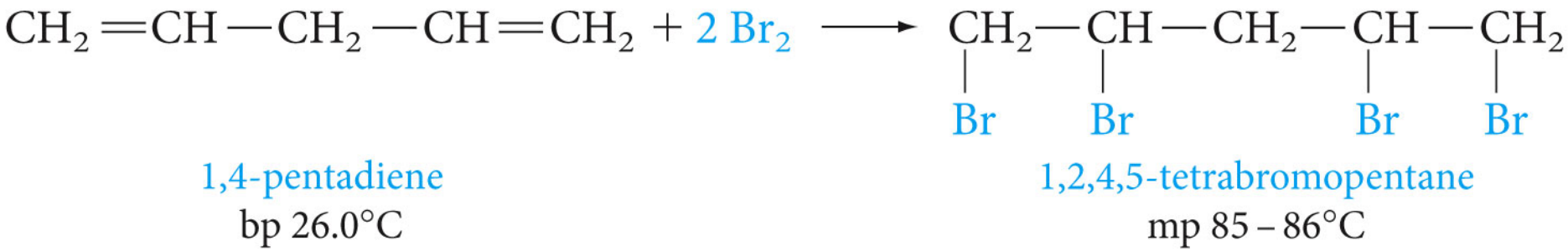
Addition of halogens X_2



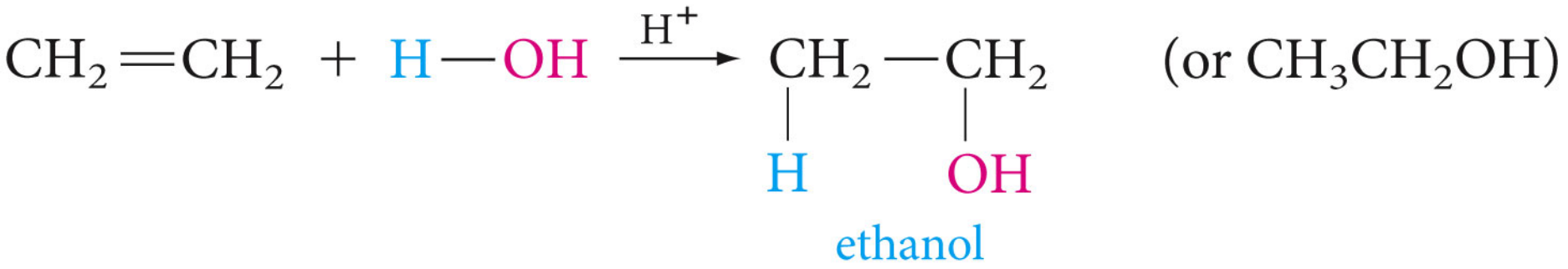
2-butene
bp 1–4°C

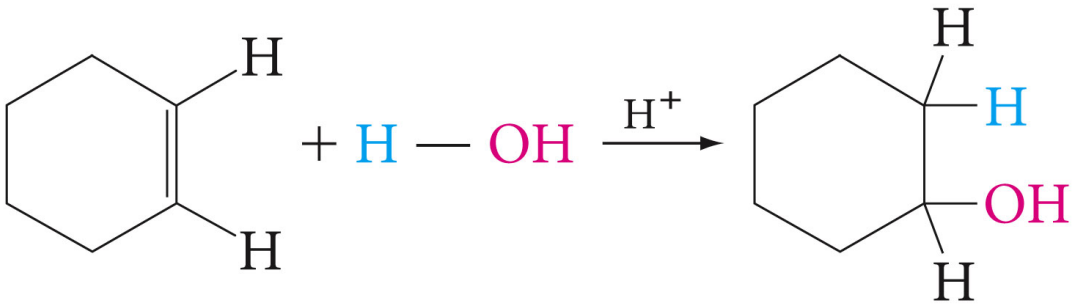
2,3-dichlorobutane
bp 117–119°C





Addition of Water (Hydration)

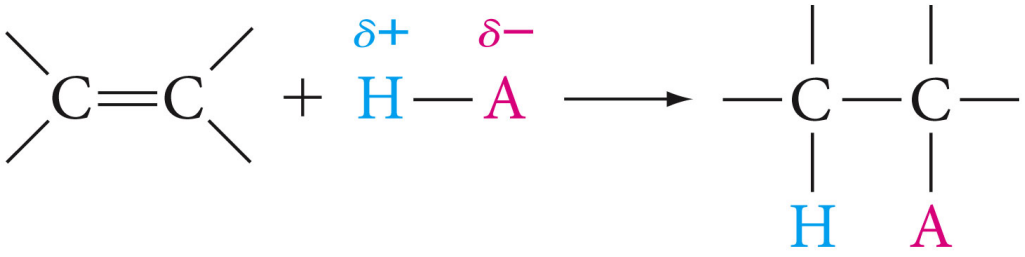




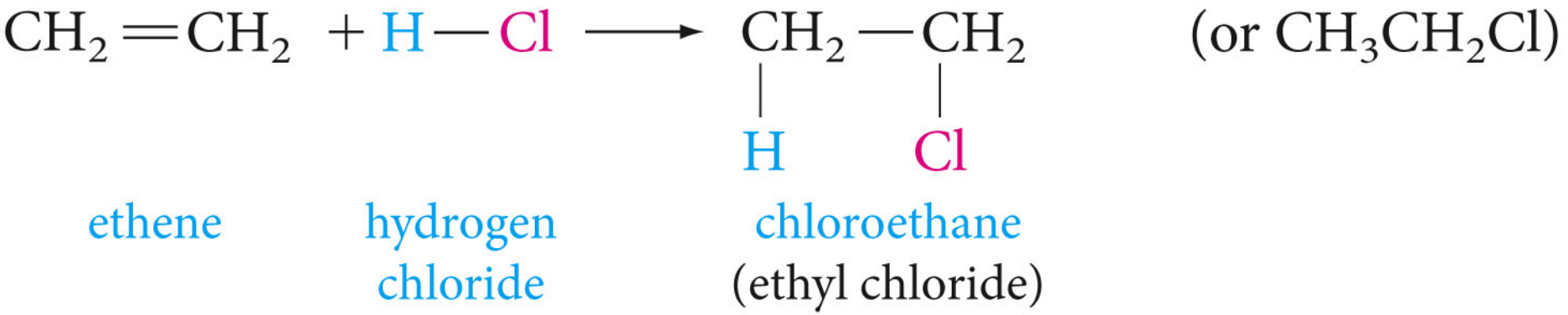
cyclohexene
bp 83.0°C

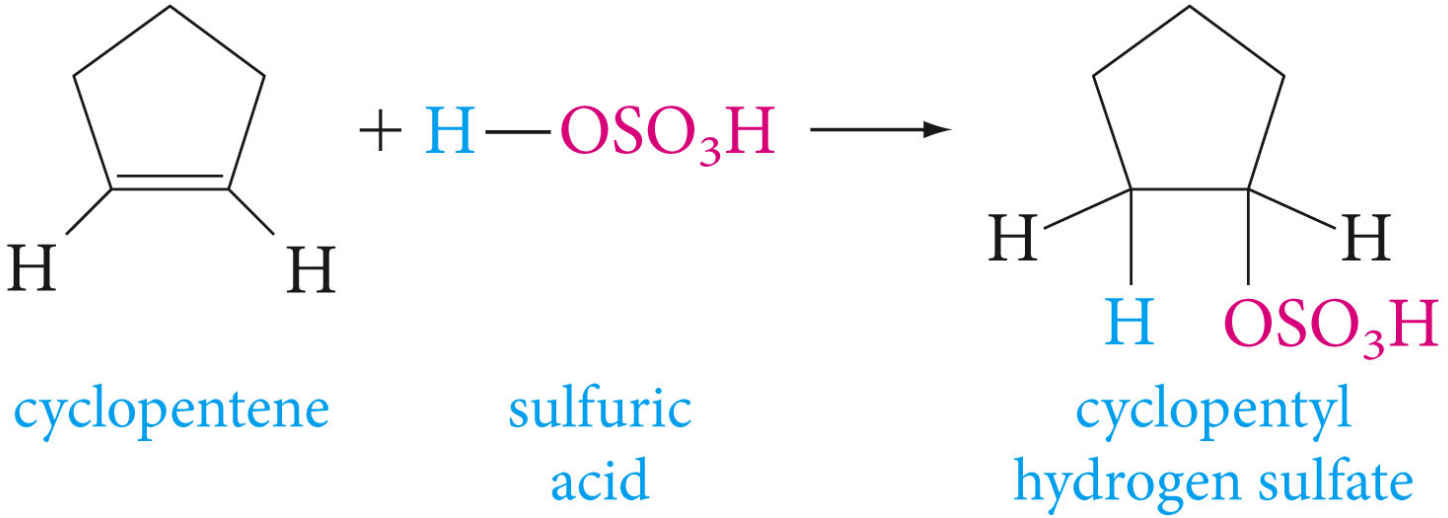
cyclohexanol
bp 161.1°C

Addition of Acids



Acids that add this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I) and sulfuric acid (H-OSO_3H)





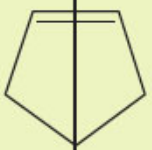
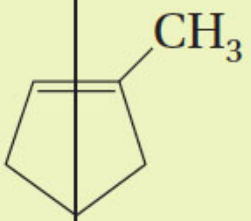
Write the equation for each of the following reactions

a) 2-butene + HCl

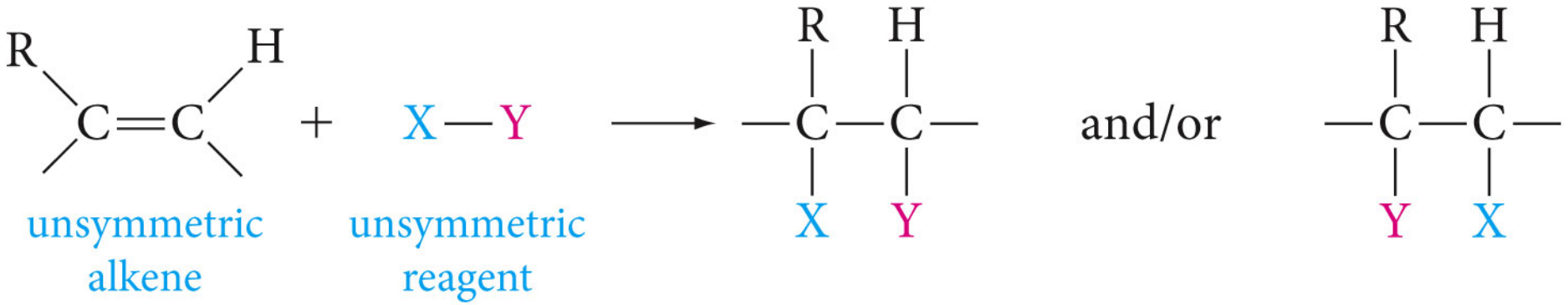
b) 3-Hexene + HI

c) 4-methylcyclopentene + HBr

Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

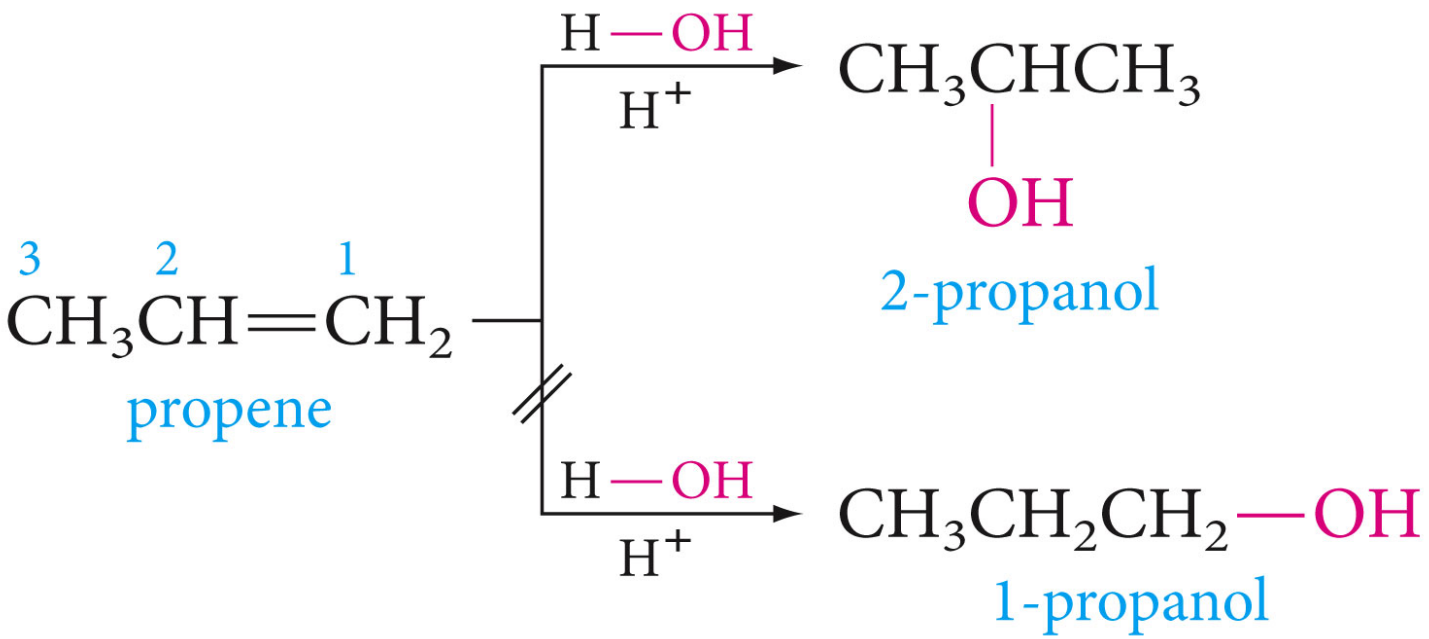
	Symmetric	Unsymmetric
Reagents	Br—Br Cl—Cl H—H	H—Br H—OH H—OSO_3H
Alkenes	$CH_2=CH_2$	$CH_3CH=CH_2$
		
	mirror plane	not a mirror plane

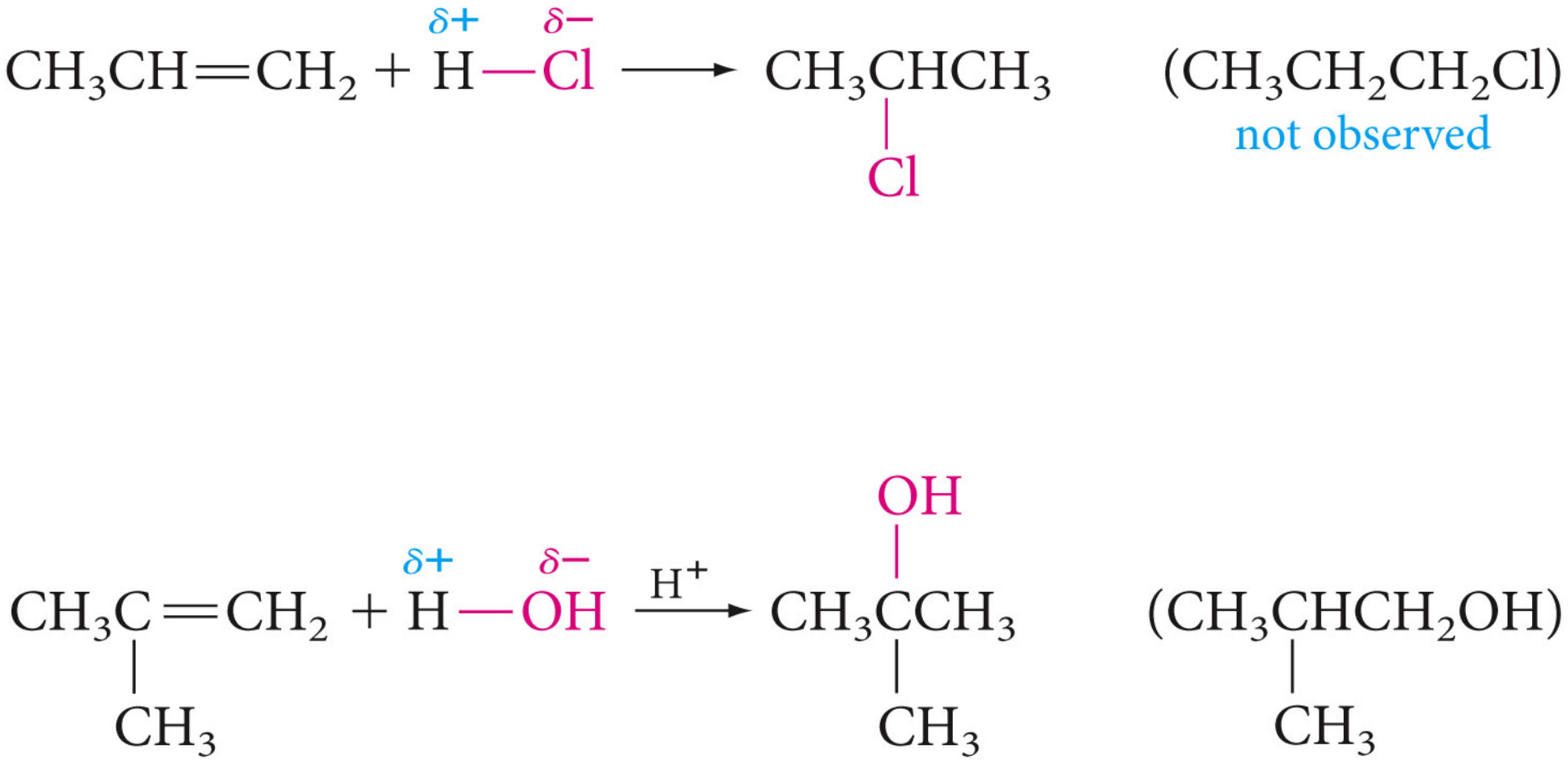
Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule

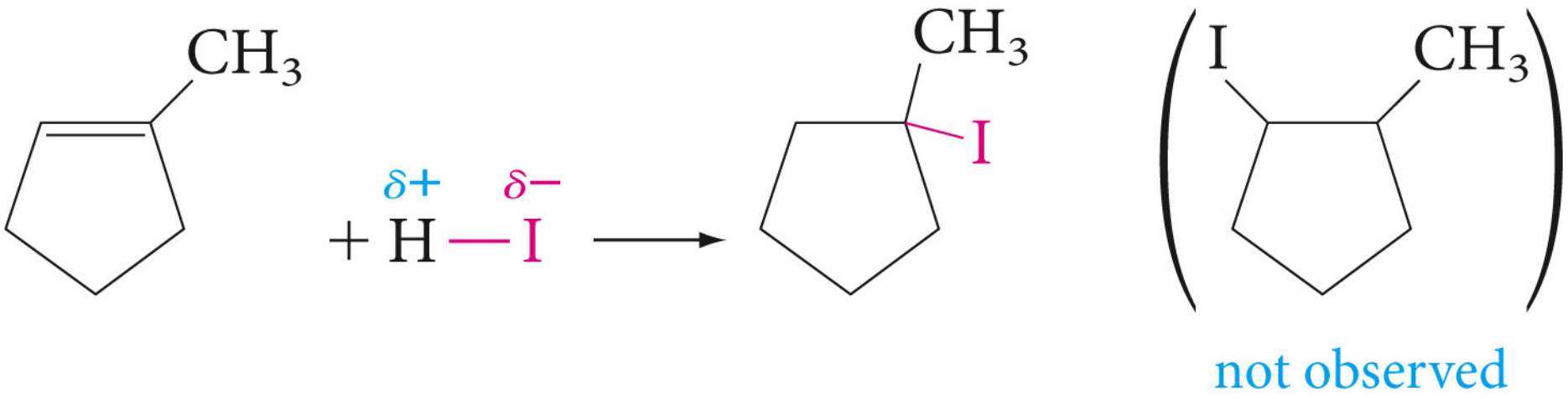


unsymmetric alkene

unsymmetric reagent

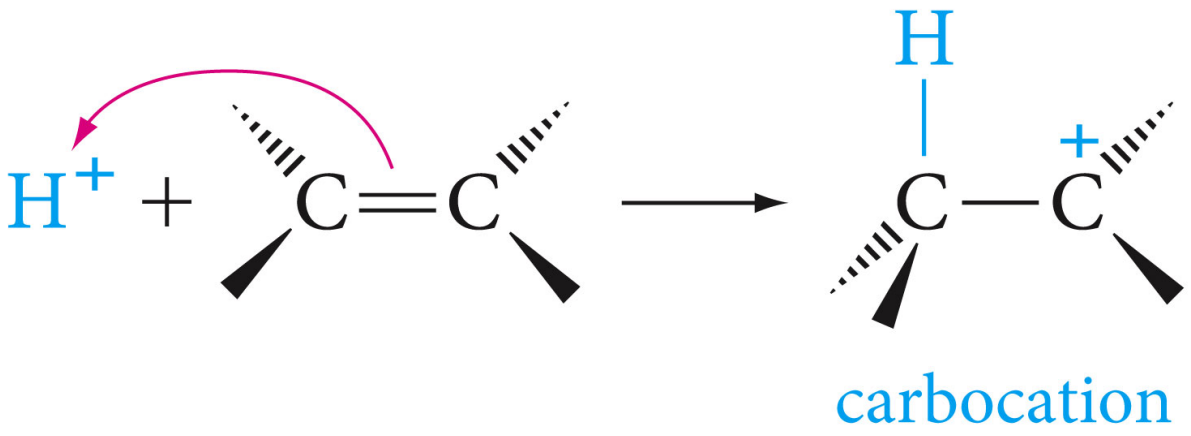

H—OH
H+
CH3CHCH3
OH
2-propanol
3 2 1
CH3CH=CH2
propene
H—OH
H+
CH3CH2CH2—OH
1-propanol

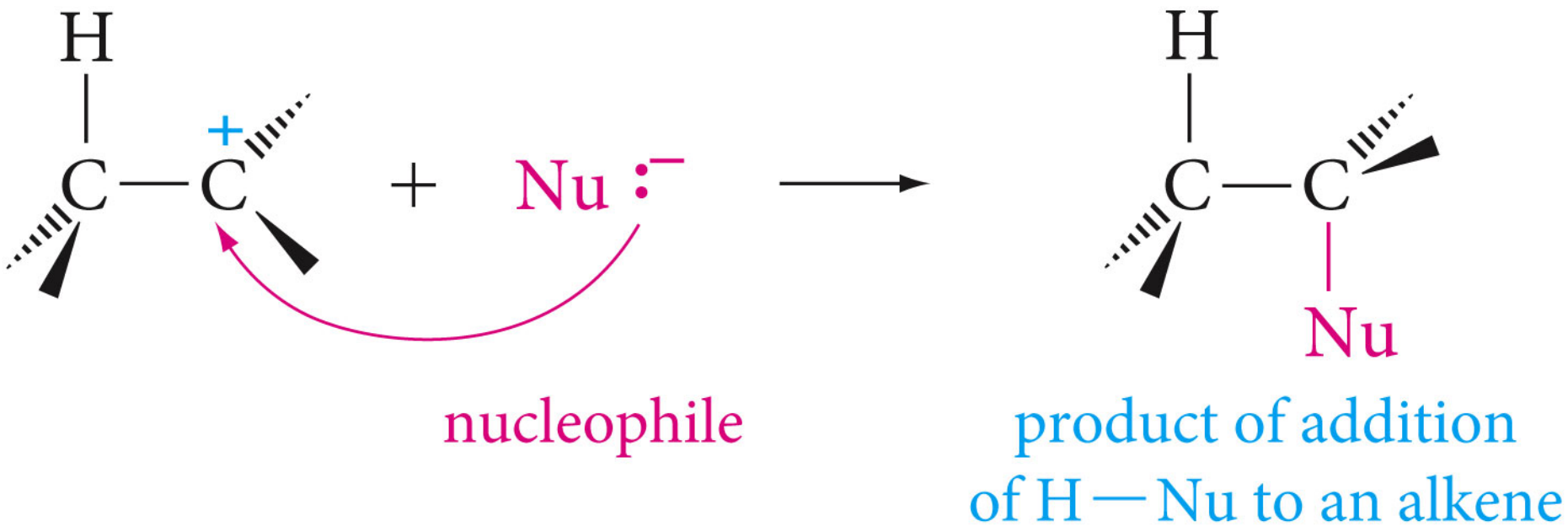

δ+ δ−
CH3CH=CH2 + H—Cl
CH3CHCH3
Cl
(CH3CH2CH2Cl)
not observed
δ+ δ−
CH3C=CH2 + H—OH
H+
OH
CH3CCH3
CH3
CH3
(CH3CHCH2OH)
CH3
not observed

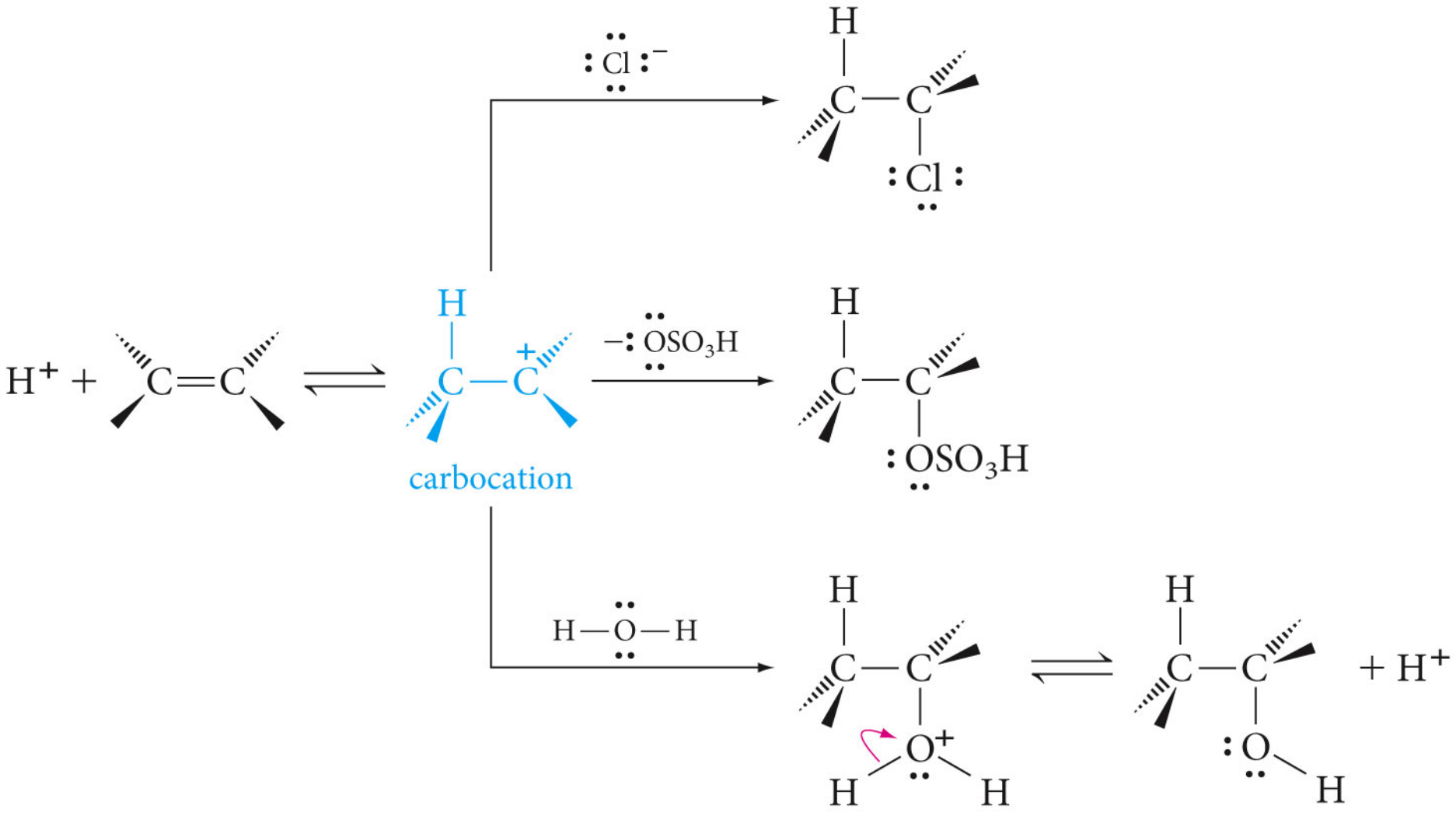


not observed

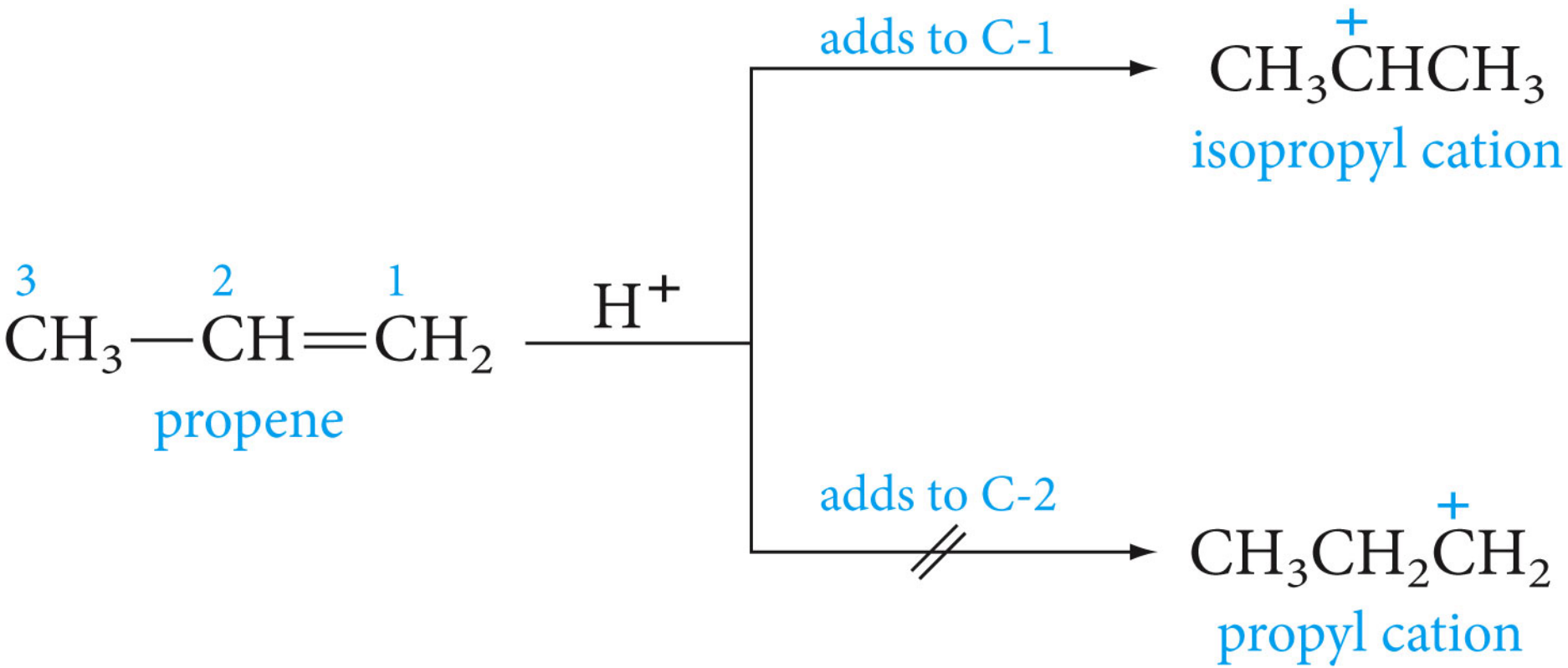
Mechanism of Electrophilic Addition to Alkenes

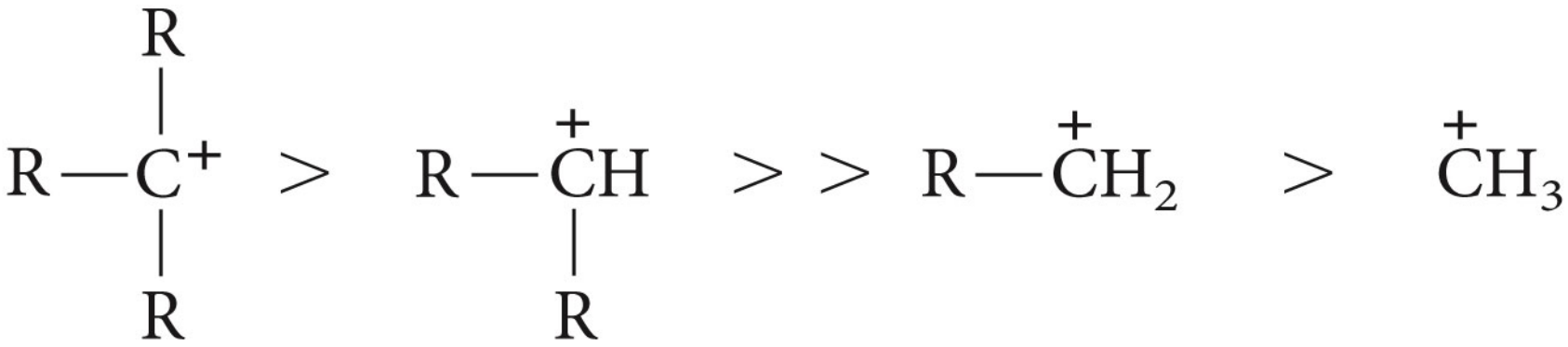



H
C
C
+
+
Nu :⁻
H
C
C
Nu
nucleophile
product of addition
of H—Nu to an alkene

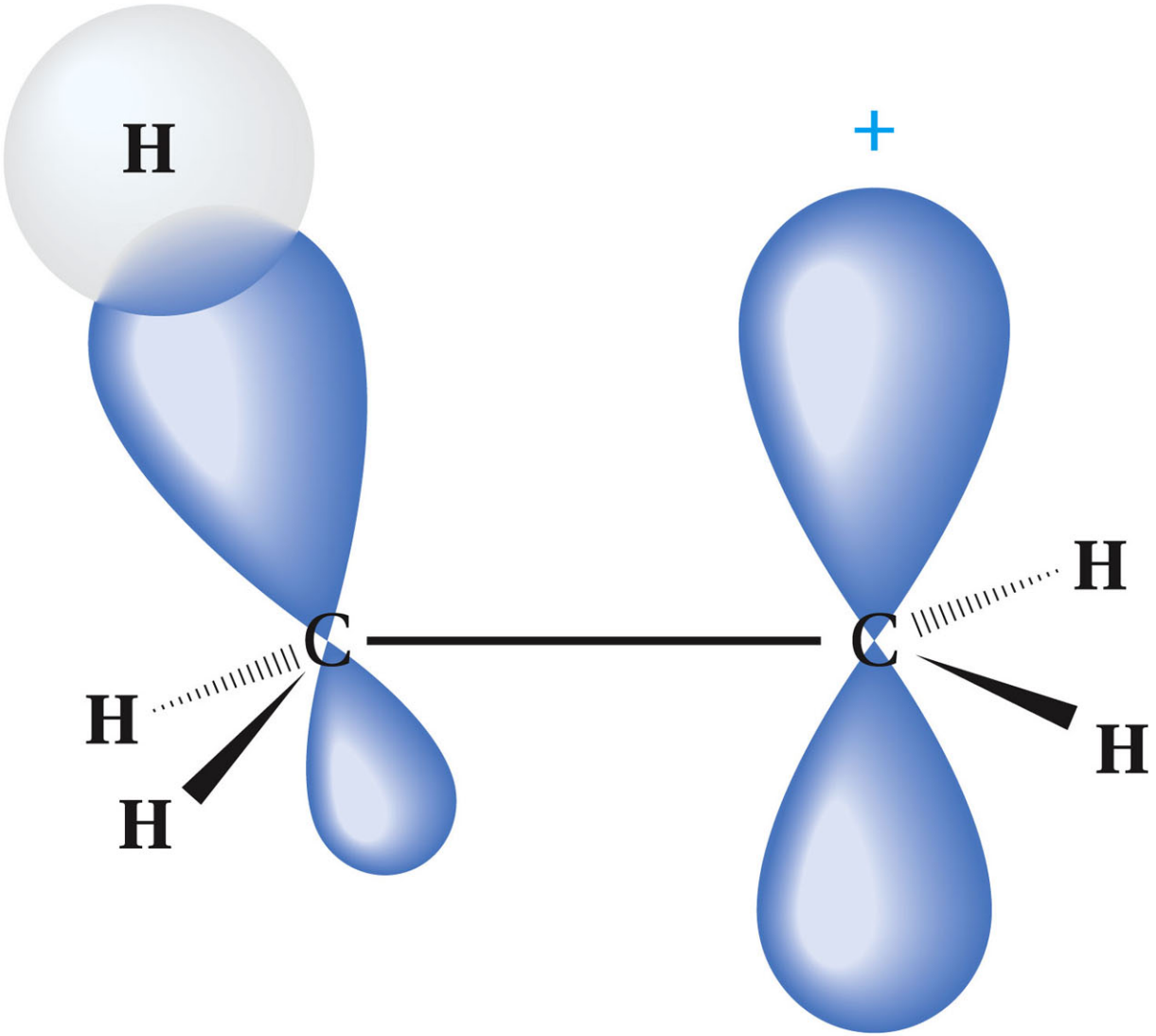

carbocation
+ H+

Markovnokov's Rule Explained

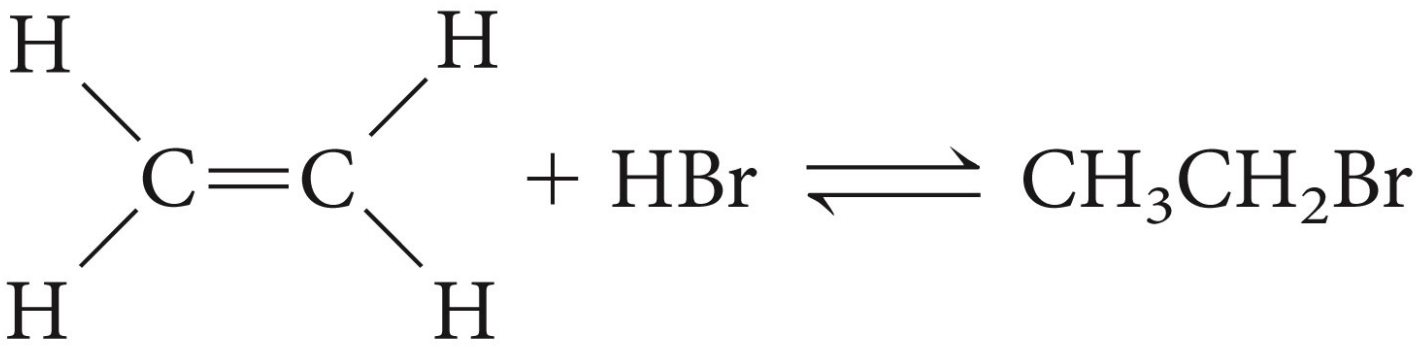


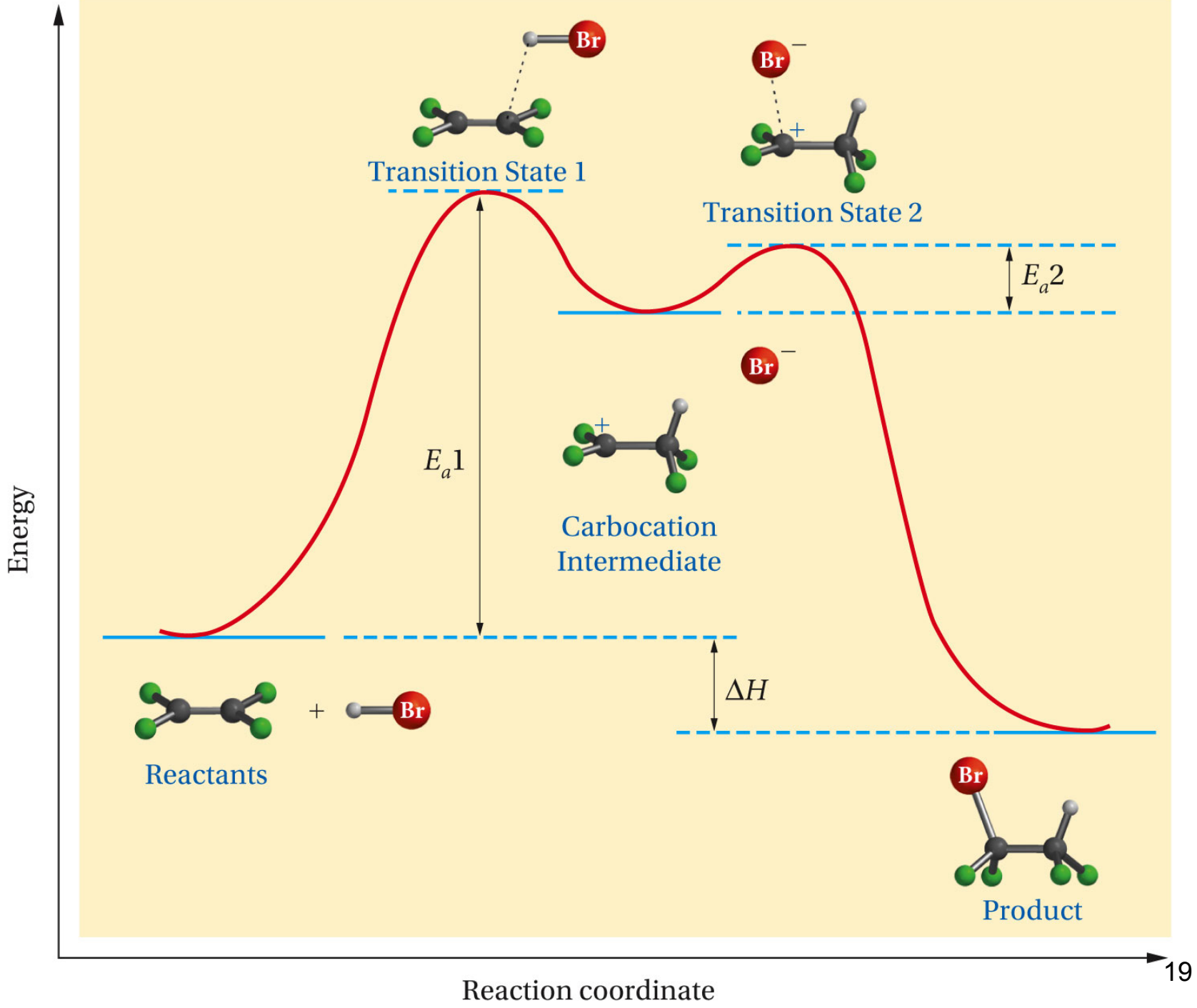

R
R—C+
R
>
R—CH
R
>>
R—CH2
>
CH3
tertiary (3°)
secondary (2°)
primary (1°)
methyl (unique)
most stable
least stable

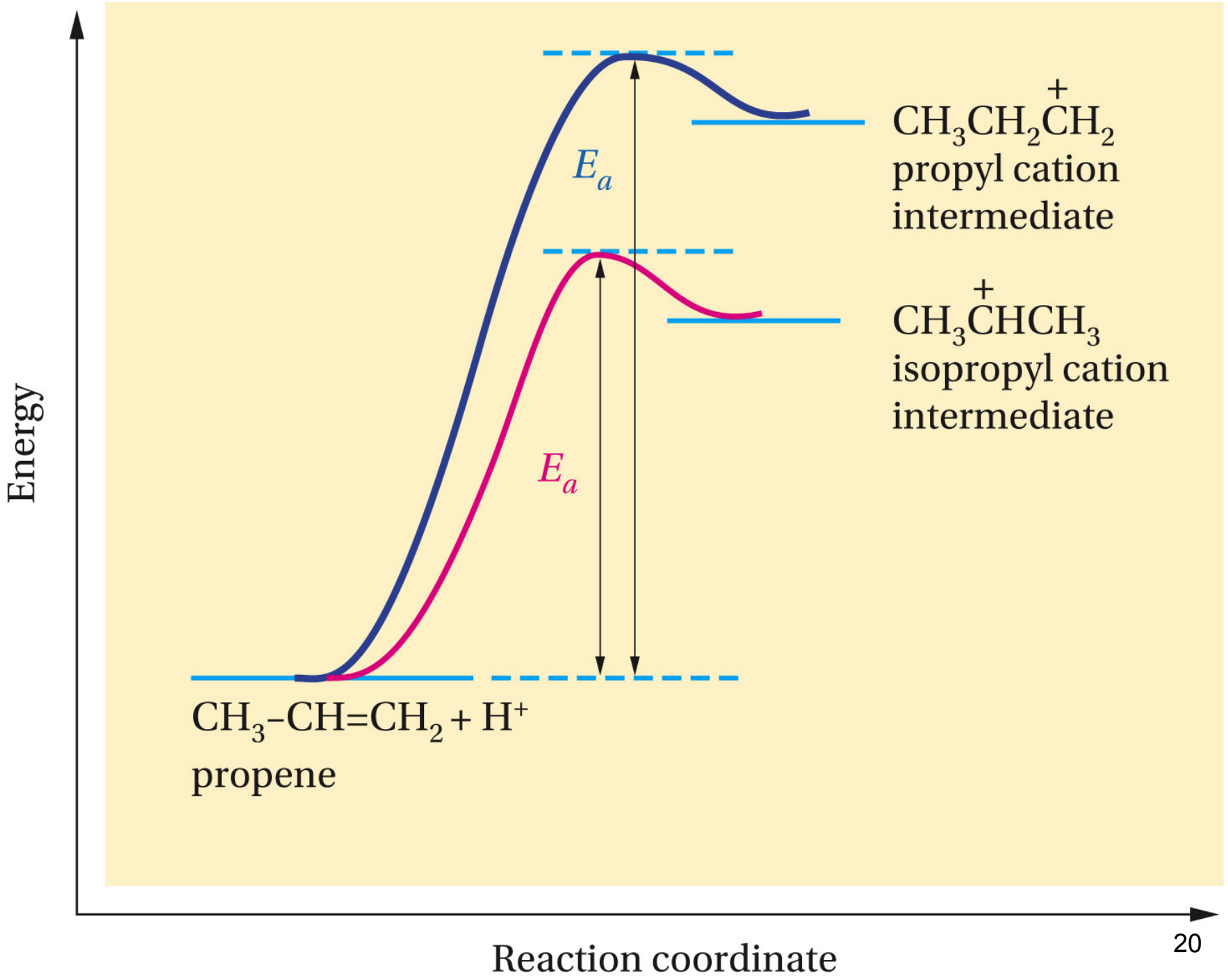
C-H σ-*p* overlap

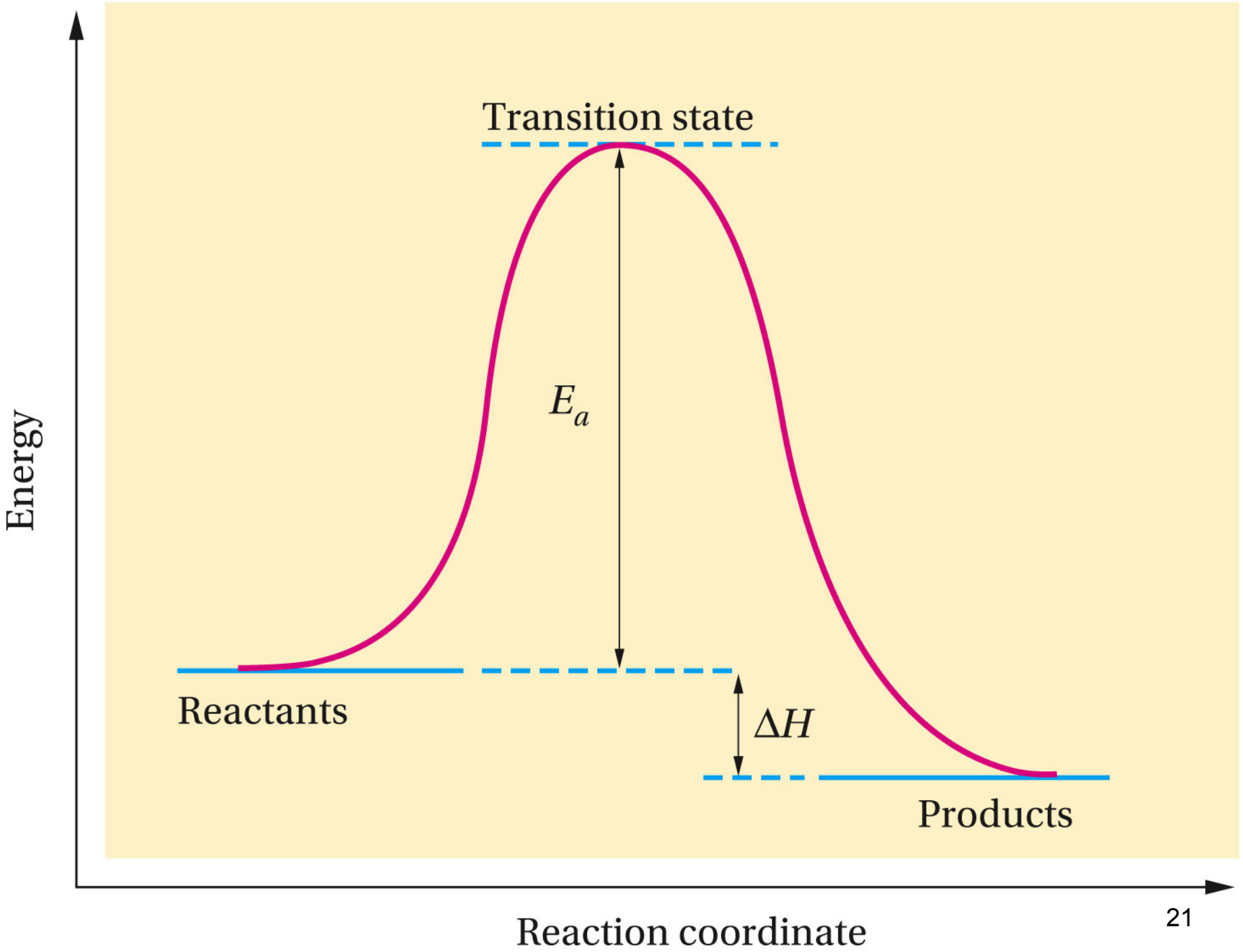


Reaction Equilibrium

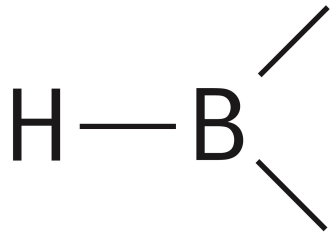


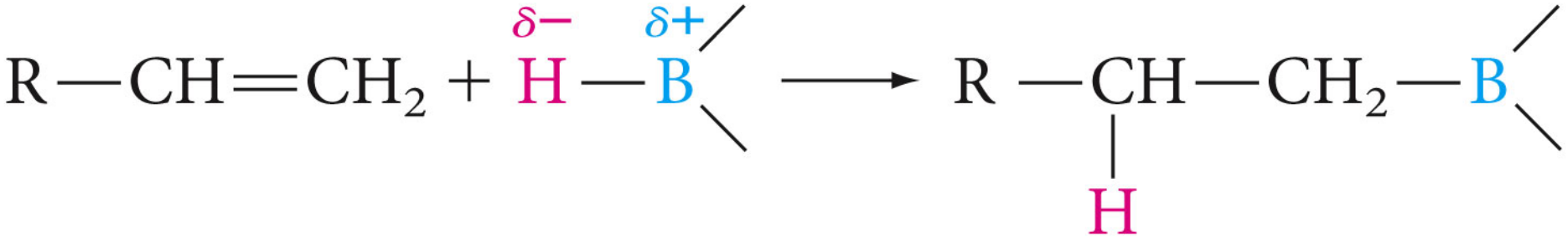

Energy
Br
Transition State 1
Br
Transition State 2
E_a2
Br
E_a1
Carbocation
Intermediate
ΔH
Reactants
+
Br
Br
Product
Reaction coordinate

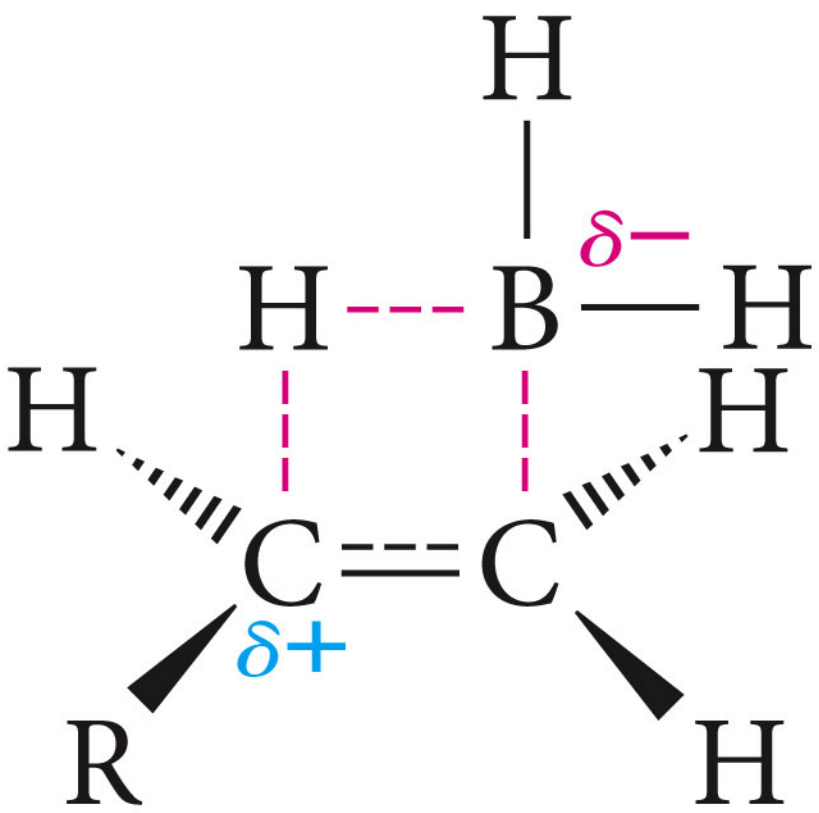

Energy
E_a
E_a
$CH_3CH_2\overset{+}{C}H_2$
propyl cation
intermediate
$CH_3\overset{+}{C}HCH_3$
isopropyl cation
intermediate
$CH_3–CH=CH_2 + H^+$
propene
Reaction coordinate


Transition state
E_a
Reactants
ΔH
Products
Energy
Reaction coordinate

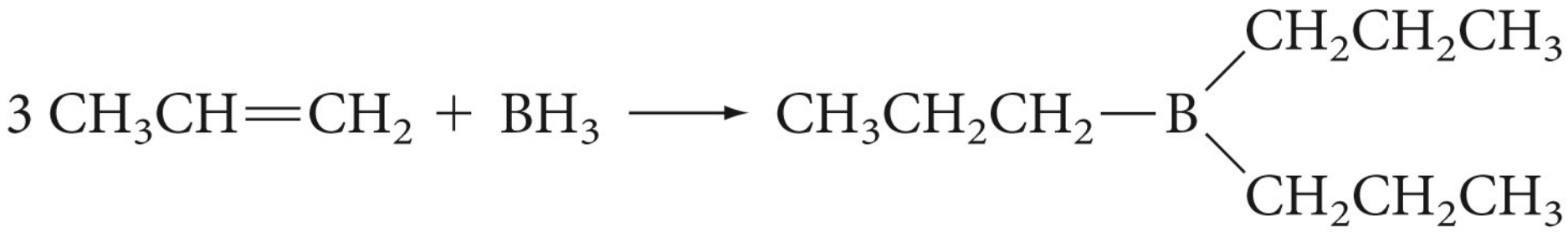
Hydroboration of Alkenes



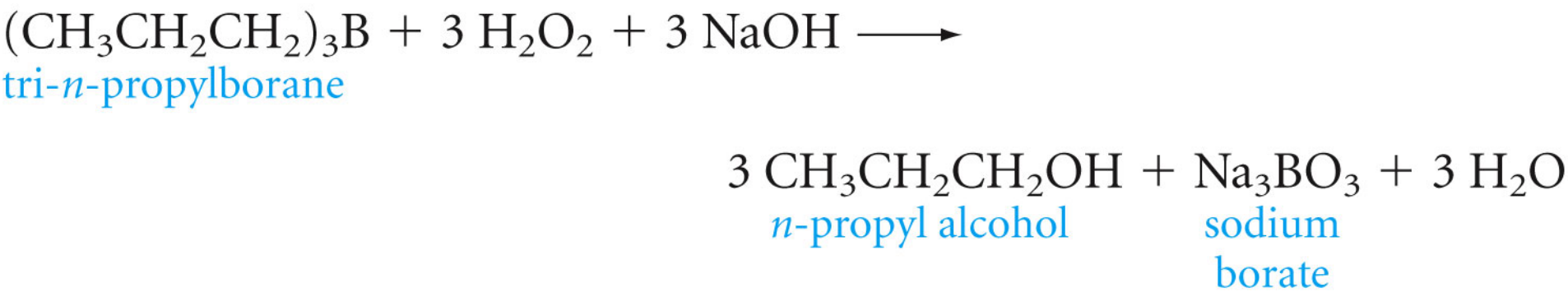




transition state
for hydroboration

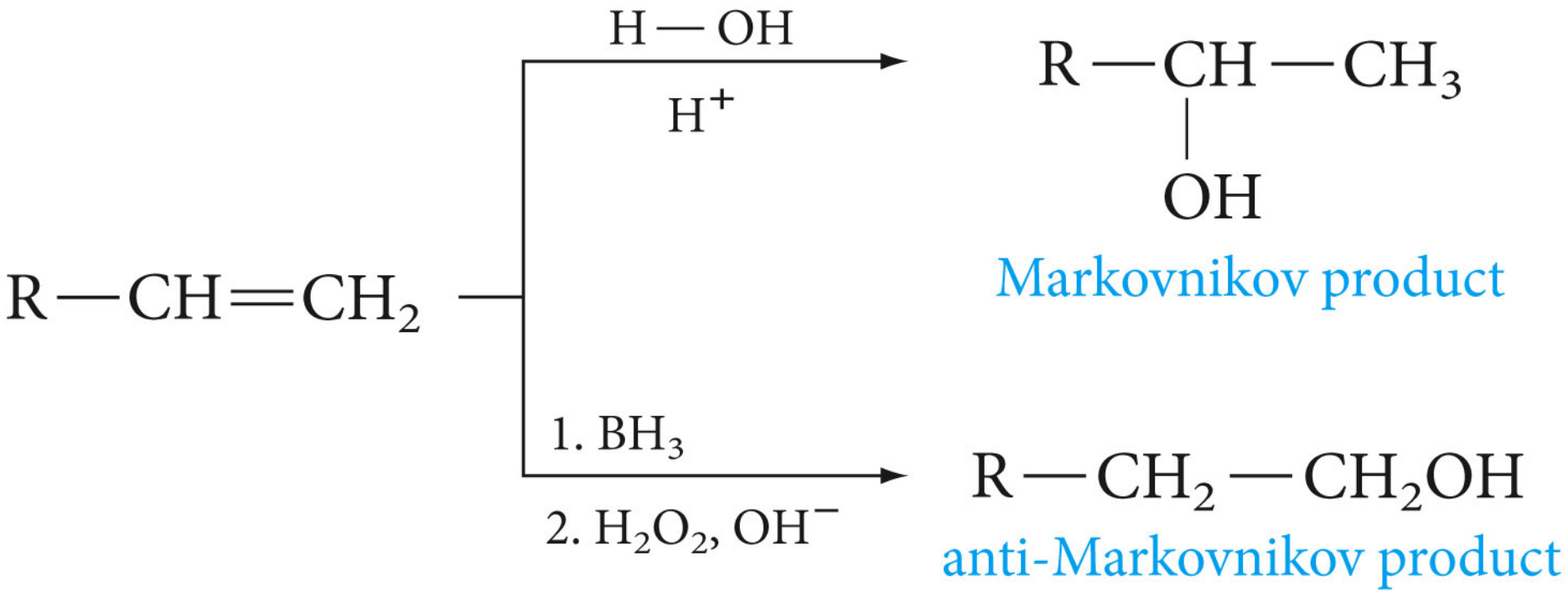


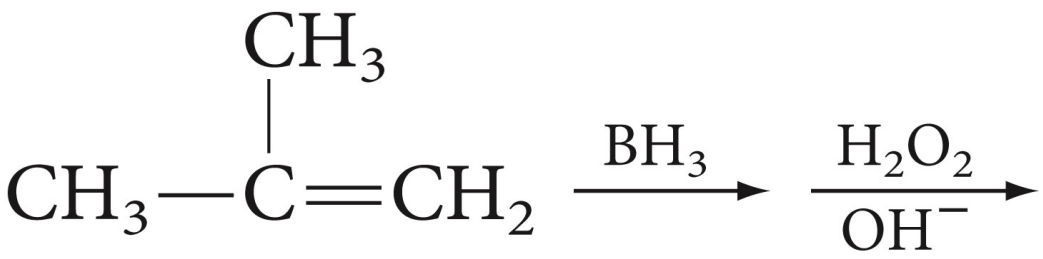
propene borane tri-*n*-propylborane

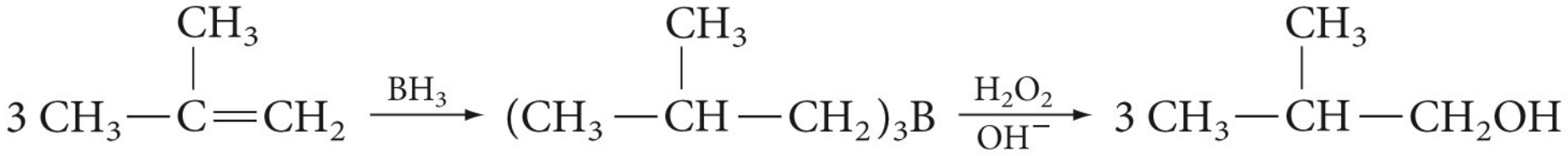


tri-*n*-propylborane

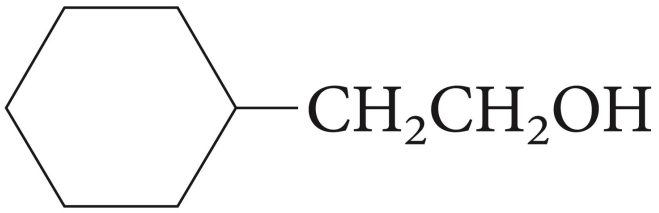
n-propyl alcohol sodium borate


H — OH
H+
R — CH — CH3
OH
Markovnikov product
R — CH=CH2
1. BH3
2. H2O2, OH−
R — CH2 — CH2OH
anti-Markovnikov product

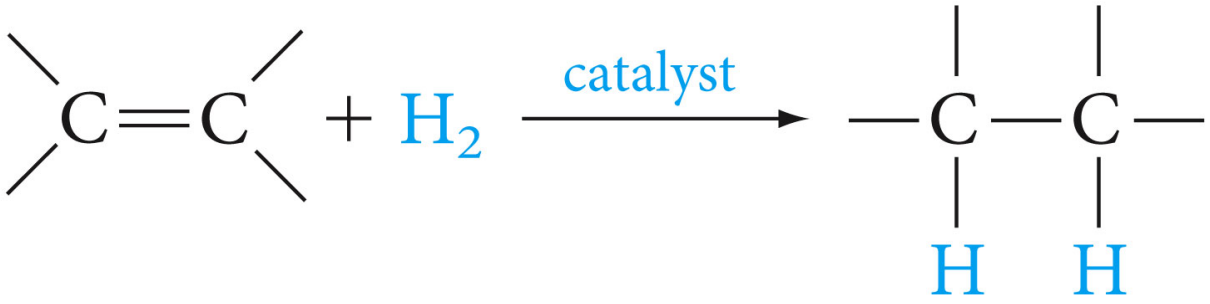

CH3
CH3—C=CH2
BH3
H2O2
OH−

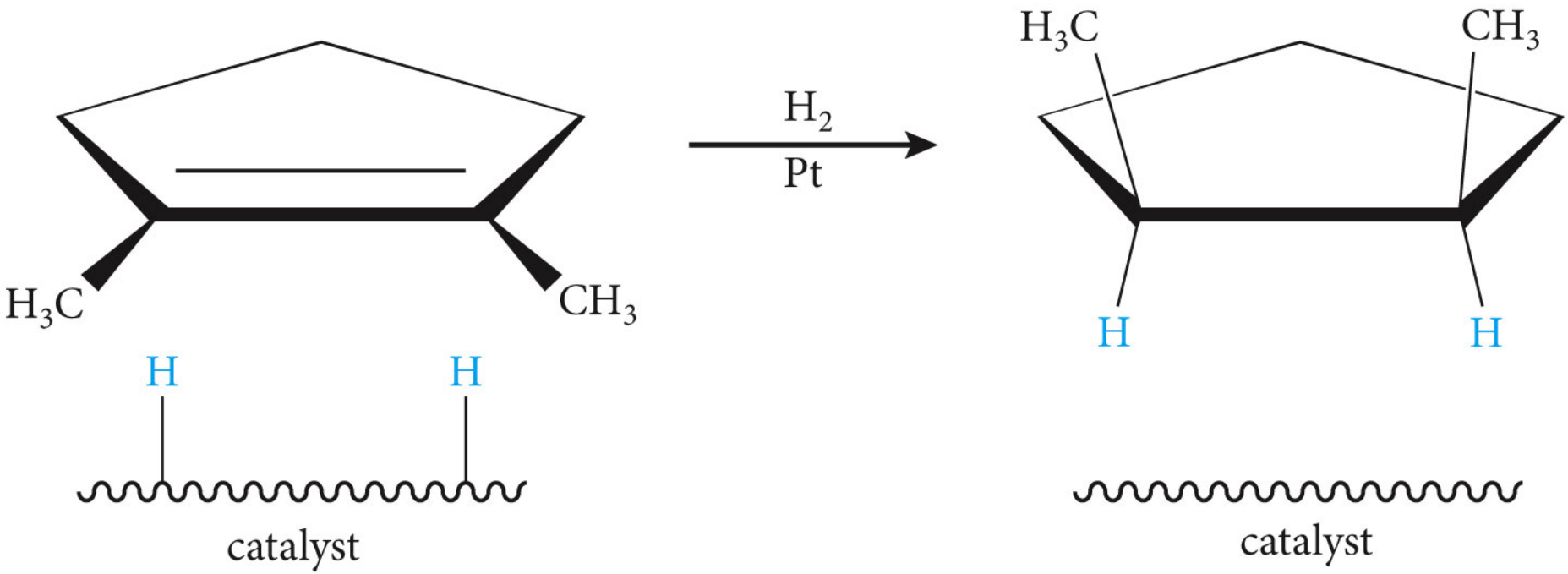

CH3
3 CH3—C=CH2
BH3
(CH3—CH—CH2)3B
H2O2
OH−
3 CH3—CH—CH2OH

What alkene is needed to obtain he alcohol below via hydroboration-oxidation sequence, what product would this alkene give with acid-catalyzed hydration.



Addition of Hydrogen




H3C
CH3
H
H
catalyst
H2
Pt
H3C
CH3
H
H
catalyst