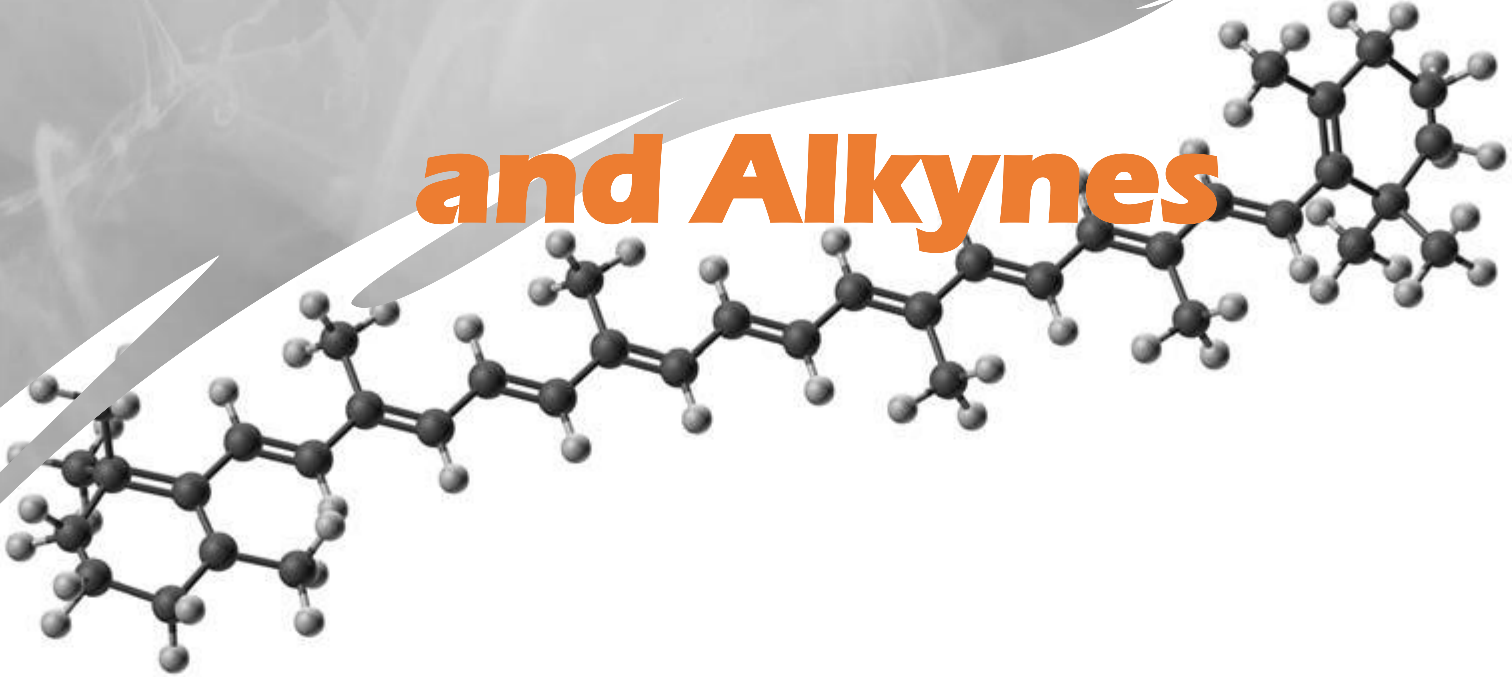
西安交通大學 化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Organic Chemistry

Chapter 5

Reactions of Alkenes and Alkynes



5.1 What Are the Characteristic Reactions of Alkenes?

5.2 What Is a Reaction Mechanism?

5.3 What Are the Mechanisms of Electrophilic Additions to Alkenes?

5.4 What Are Carbocation Rearrangements?

5.5 What Is Hydroboration–Oxidation of an Alkene?

5.6 How Can an Alkene Be Reduced to an Alkane?

5.7 How Can an Acetylide Anion Be Used to Create a New Carbon–Carbon Bond?

5.1 What Are the Characteri

The most characteristic reaction of alkenes is addition to the carbon–carbon double bond in such a way that the pi bond is broken and, in its place, sigma bonds are formed to two new atoms or groups of atoms.

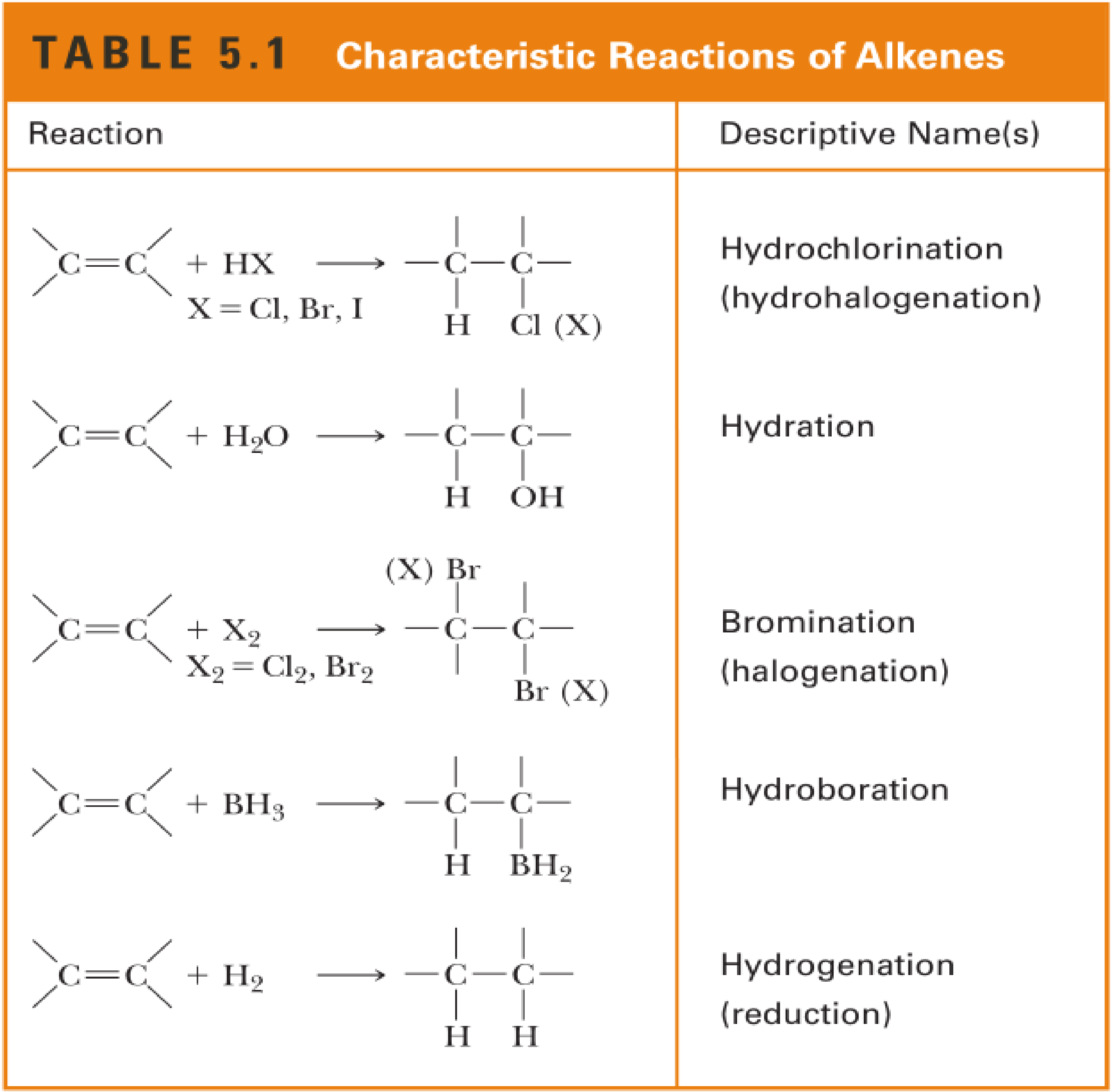


TABLE 5.1 Characteristic Reactions of Alkenes

Reaction	Descriptive Name(s)
$>C{=}C< + HX \longrightarrow -\overset{\vert}{\underset{\vert \atop H}{C}}-\overset{\vert}{\underset{\vert \atop Cl\ (X)}{C}}-$ $X = Cl, Br, I$	Hydrochlorination (hydrohalogenation)
$>C{=}C< + H_2O \longrightarrow -\overset{\vert}{\underset{\vert \atop H}{C}}-\overset{\vert}{\underset{\vert \atop OH}{C}}-$	Hydration
$>C{=}C< + X_2 \longrightarrow -\overset{(X)\ Br \atop \vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert \atop Br\ (X)}{C}}-$ $X_2 = Cl_2, Br_2$	Bromination (halogenation)
$>C{=}C< + BH_3 \longrightarrow -\overset{\vert}{\underset{\vert \atop H}{C}}-\overset{\vert}{\underset{\vert \atop BH_2}{C}}-$	Hydroboration
$>C{=}C< + H_2 \longrightarrow -\overset{\vert}{\underset{\vert \atop H}{C}}-\overset{\vert}{\underset{\vert \atop H}{C}}-$	Hydrogenation (reduction)

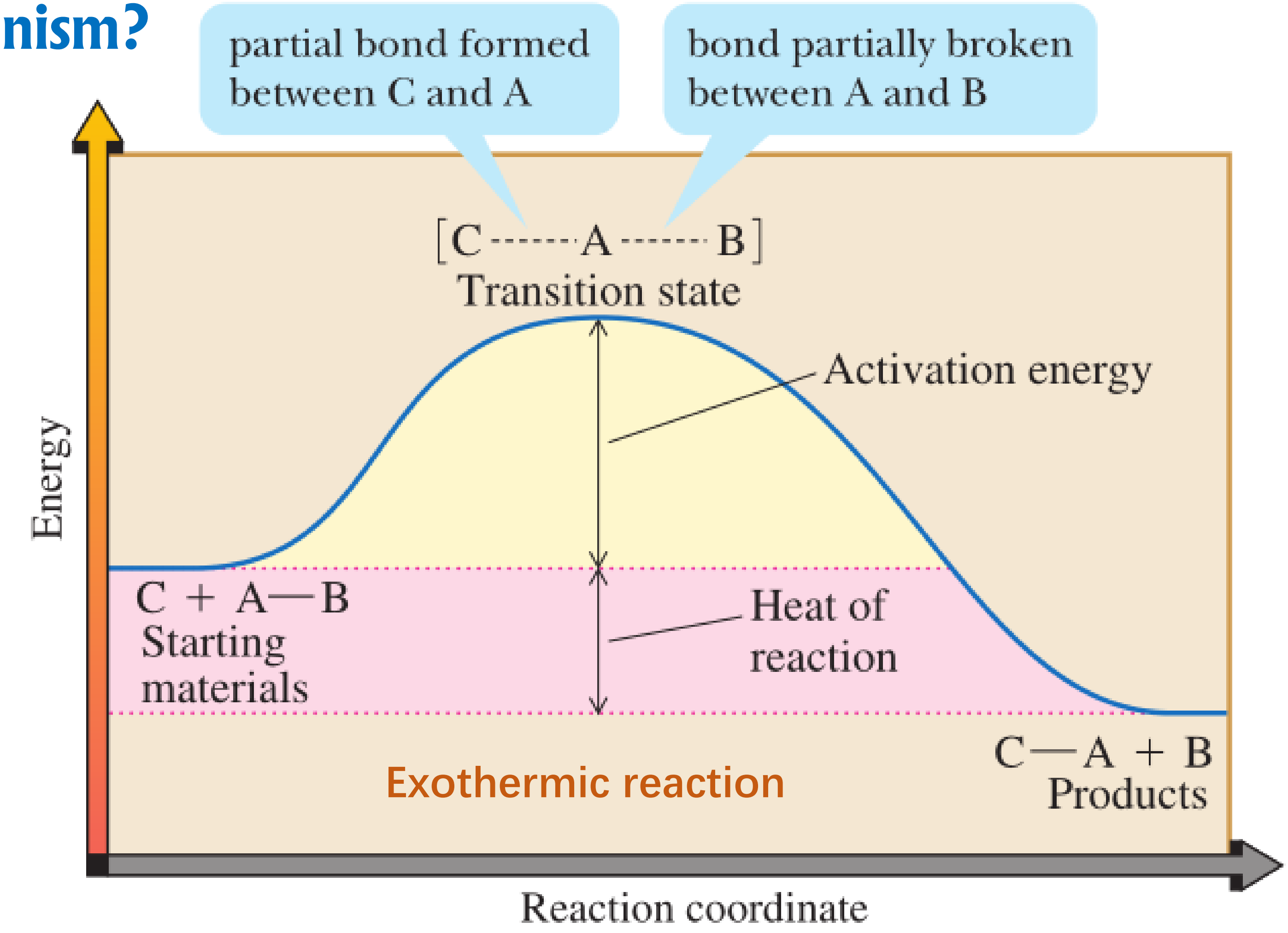
polymerization reaction

$$n\mathrm{CH_2 = CH_2} \xrightarrow{\text{initiator}} \left(\mathrm{CH_2CH_2}\right)_n$$

5.2 What Is a Reaction Mechanism?

Reaction mechanism A ste
（反应机理）

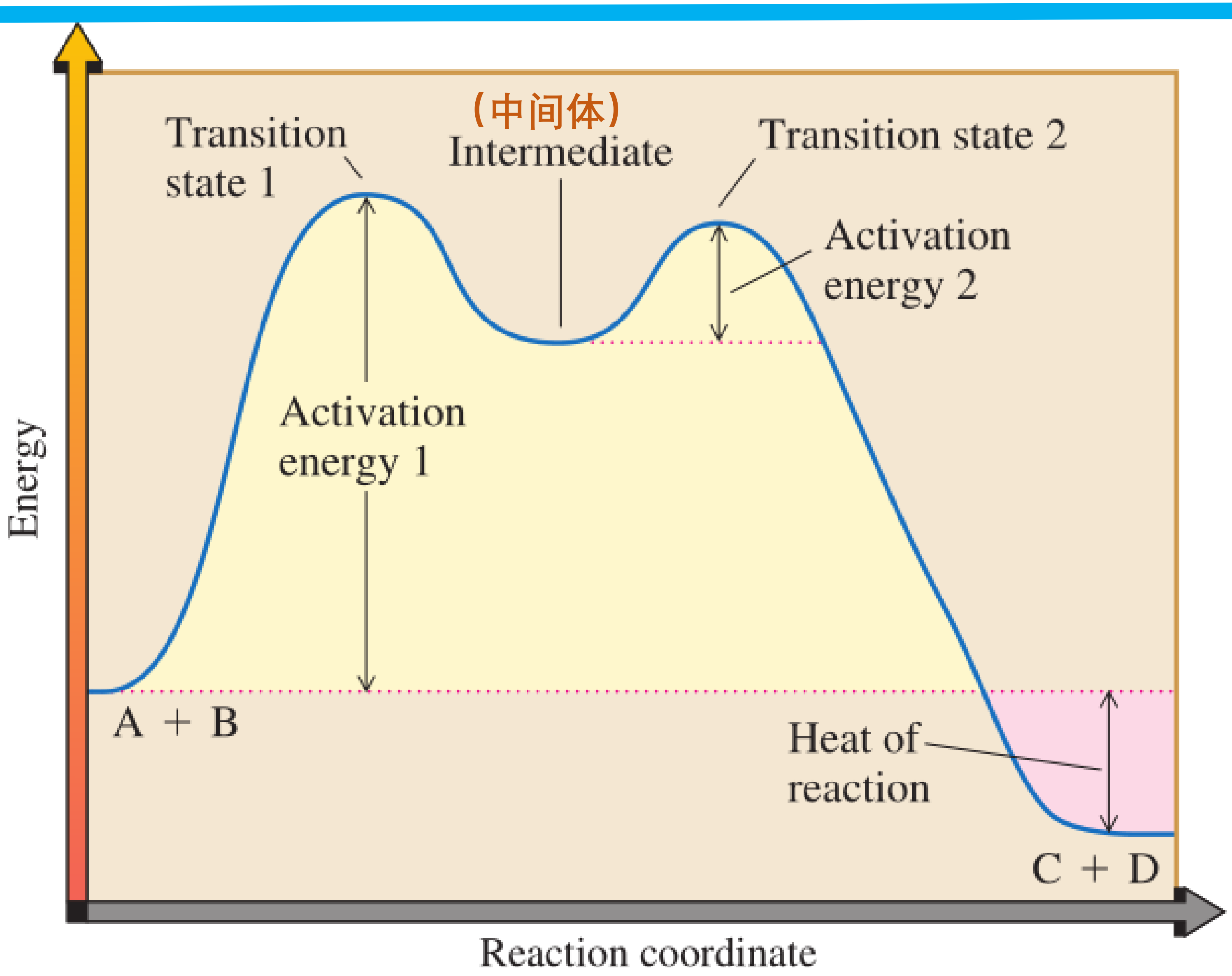
A. Energy Diagrams and Transition States



Reaction intermediate

（反应中间体）

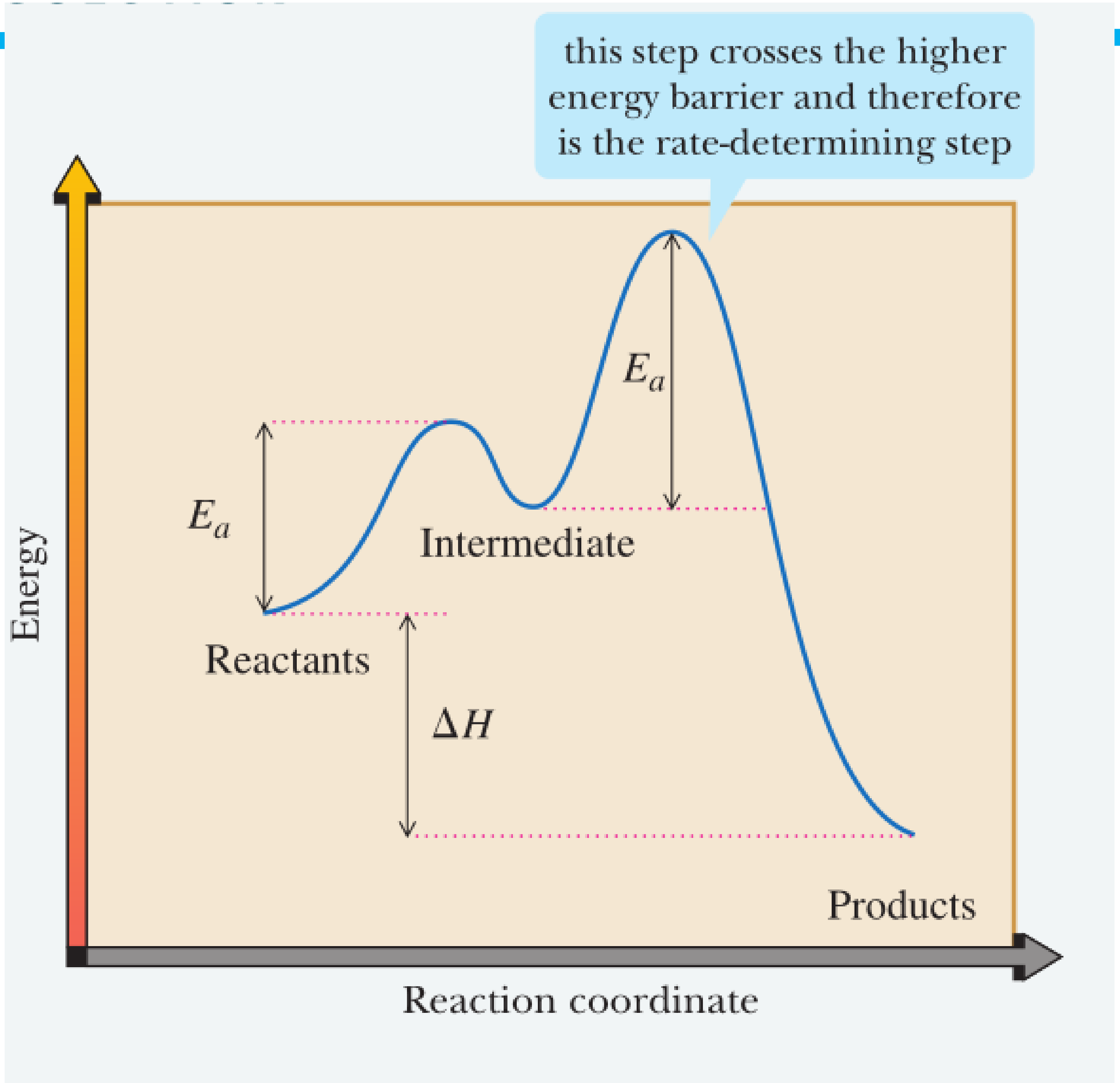
An unstable species that lies in an energy minimum between two transition states.



Rate-determining step

（速度决定步骤）

The step in a reaction sequence that crosses the highest energy barrier; the slowest step in a multistep reaction.

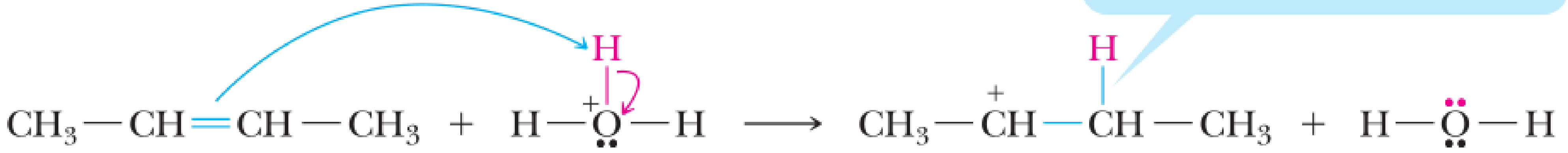


this step crosses the higher energy barrier and therefore is the rate-determining step

B. Developing a Reaction Mechanism

C. Some Common patterns in Reaction Mechanisms

Pattern 1: Add a proton



$$CH_3-CH=CH-CH_3 + H-\overset{H}{\overset{|}{\overset{+}{\underset{\cdot\cdot}{O}}}}-H \longrightarrow CH_3-\overset{+}{C}H-\overset{H}{\overset{|}{C}}H-CH_3 + H-\underset{\cdot\cdot}{\ddot{O}}-H$$

the electrons in this single bond were once part of the pi bond that abstracted the proton from hydronium

An alkene (proton acceptor or nucleophile)

Hydronium ion (proton donor or electrophile)

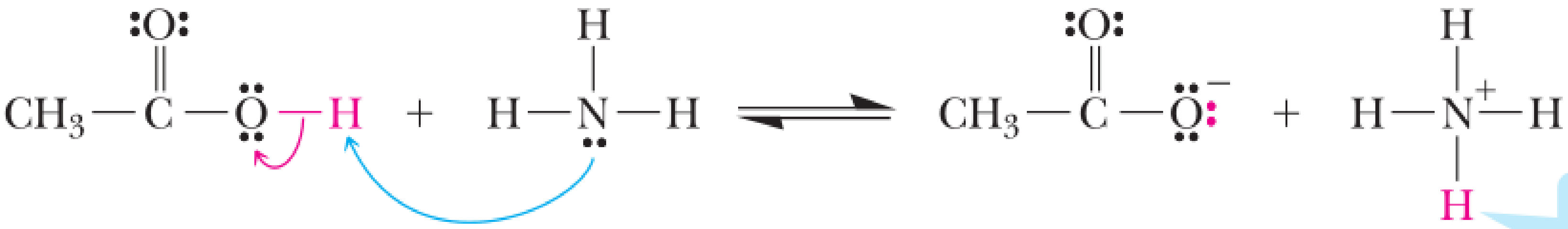
A carbocation

$$CH_3-CH=CH-CH_3 + H^+ \longrightarrow CH_3-\overset{+}{C}H-CH_2-CH_3$$

An alkene (proton acceptor or nucleophile)

A proton (proton donor or electrophile)

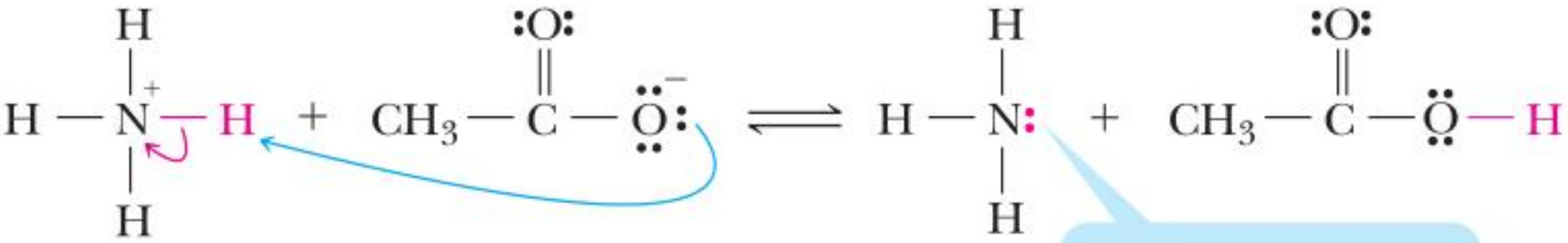
A carbocation



$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

we have **added a proton** to the nitrogen atom as a result of its nonbonded pair of electrons abstracting the proton from the acid

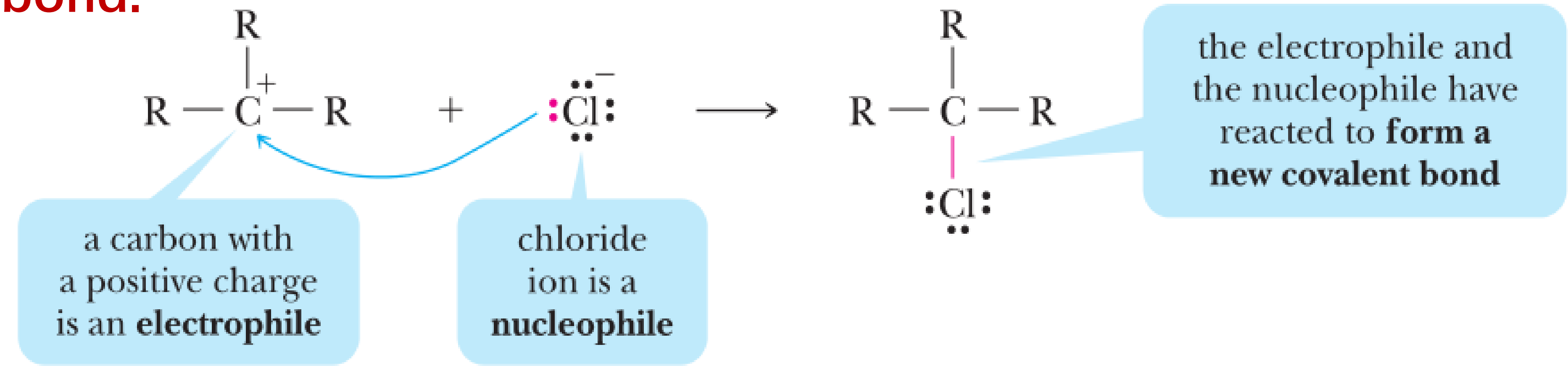
Pattern 2: Take a proton away.



$$NH_4^+ + CH_3COO^- \rightleftharpoons NH_3 + CH_3COOH$$

we have **taken a proton** away from the nitrogen atom

Pattern 3: Reaction of an electrophile and a nucleophile to form a new covalent bond.

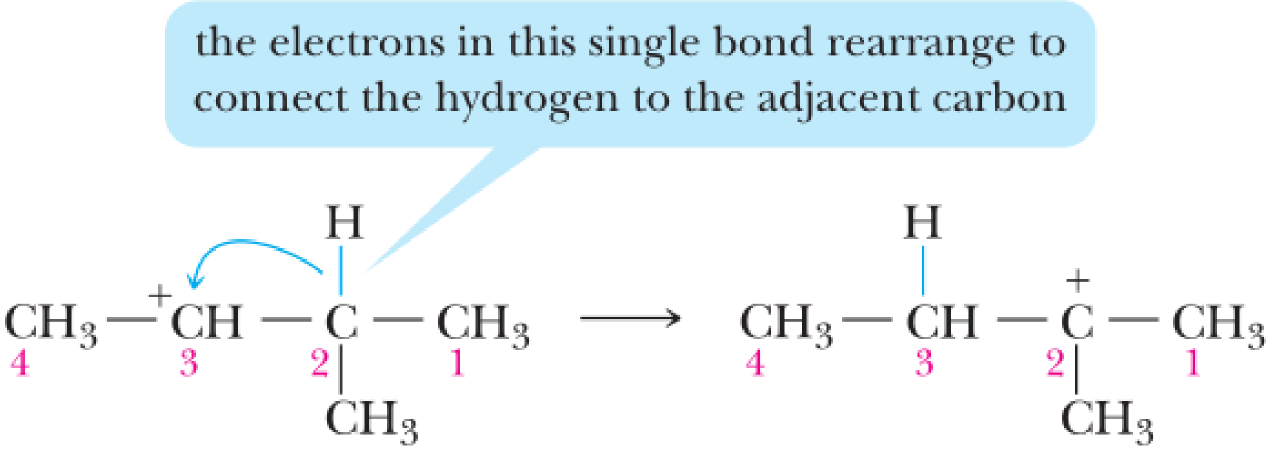


a carbon with a positive charge is an **electrophile**

chloride ion is a **nucleophile**

the electrophile and the nucleophile have reacted to **form a new covalent bond**

Pattern 4: Rearrangement of a bond.

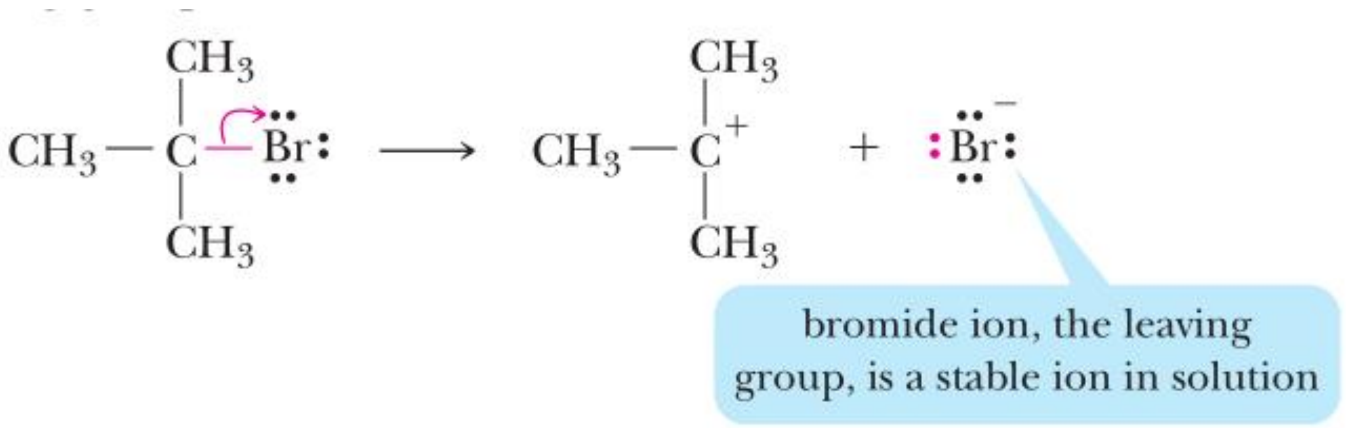


the electrons in this single bond rearrange to connect the hydrogen to the adjacent carbon

A carbocation

A more stable carbocation

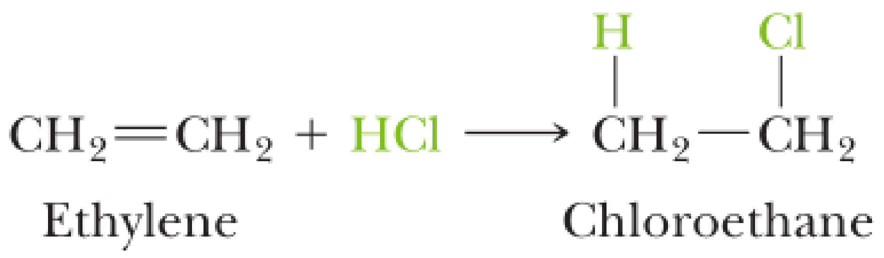
Pattern 5: Break a bond to form a stable ion or molecule.



bromide ion, the leaving group, is a stable ion in solution

5.3 What are the Mechanisms of electrophilic additions to alkenes?
（烯烃亲电加成机理）

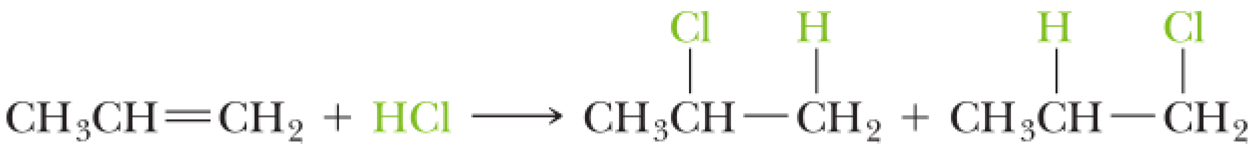
a. addition of HCl



$$CH_2{=}CH_2 + HCl \longrightarrow \underset{\displaystyle\text{H}}{\overset{}{}}\overset{\text{H}}{CH_2}-\overset{\text{Cl}}{CH_2}$$

Ethylene

Chloroethane



$$CH_3CH{=}CH_2 + HCl \longrightarrow CH_3\overset{Cl}{\overset{|}{C}H}-\overset{H}{\overset{|}{C}H_2} + CH_3\overset{H}{\overset{|}{C}H}-\overset{Cl}{\overset{|}{C}H_2}$$

Propene

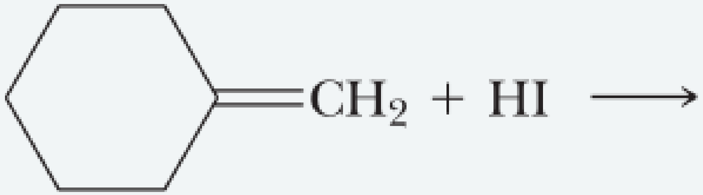
2-Chloropropane

1-Chloropropane
(not observed)

Markovnikov's rule: In the addition of HX or H_2O to an alkene, hydrogen adds to the carbon of the double bond having the greater number of hydrogens.（氢总是加在含氢多的双键碳原子上。）

(a) $CH_3CH{=}CH_2 + HI \longrightarrow$

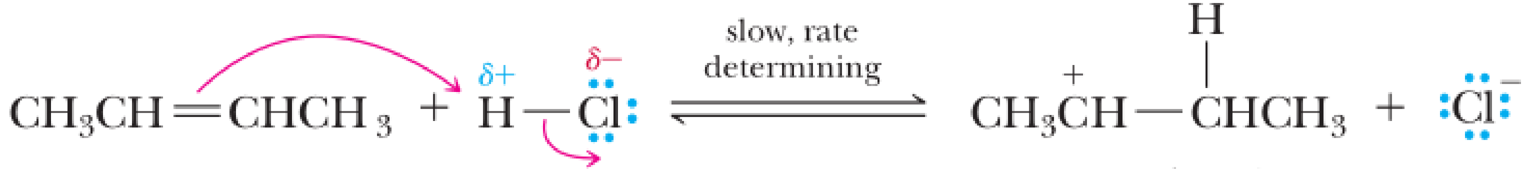
(b)



Mechanism

Electrophilic addition of hCl to 2-Butene

Step 1: Add a proton. The reaction begins with the transfer of a proton from HCl to 2-butene, as shown by the two curved arrows on the left side of Step 1:

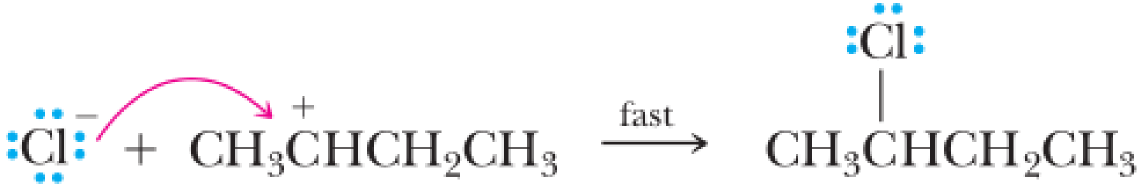


$$CH_3CH{=}CHCH_3 + \overset{\delta+}{H}-\overset{\delta-}{Cl}: \xrightleftharpoons{\text{slow, rate determining}} CH_3\overset{+}{C}H-\overset{H}{C}HCH_3 + :Cl:^-$$

(a nucleophile) (an electrophile)

sec-Butyl cation
(a 2° carbocation
intermediate)
碳正离子中间体

Step 2: Reaction of an electrophile and a nucleophile to form a new covalent bond.



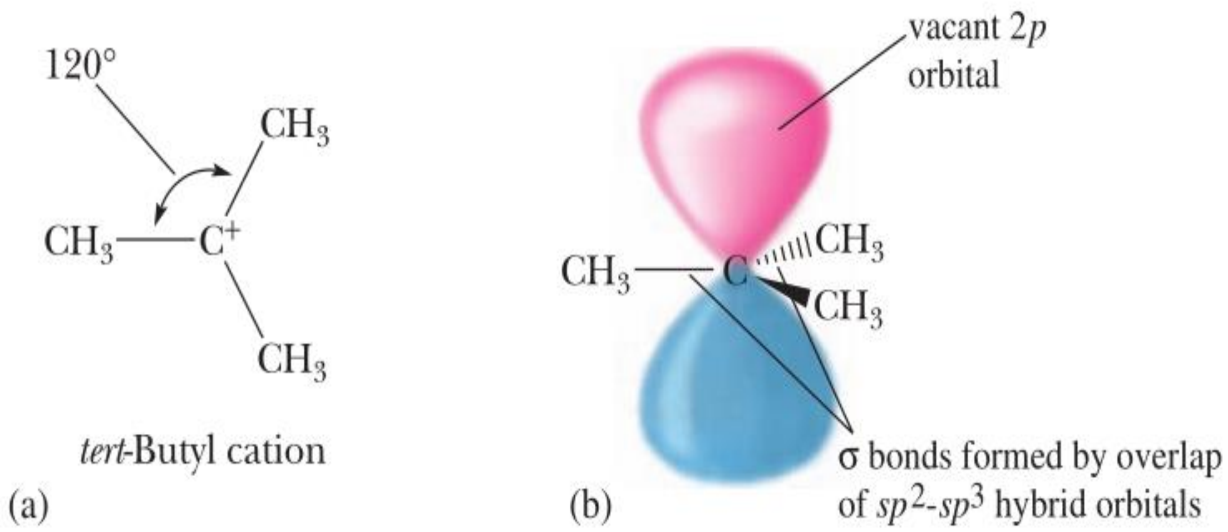
$$:Cl:^- + CH_3\overset{+}{C}HCH_2CH_3 \xrightarrow{\text{fast}} CH_3\overset{Cl}{C}HCH_2CH_3$$

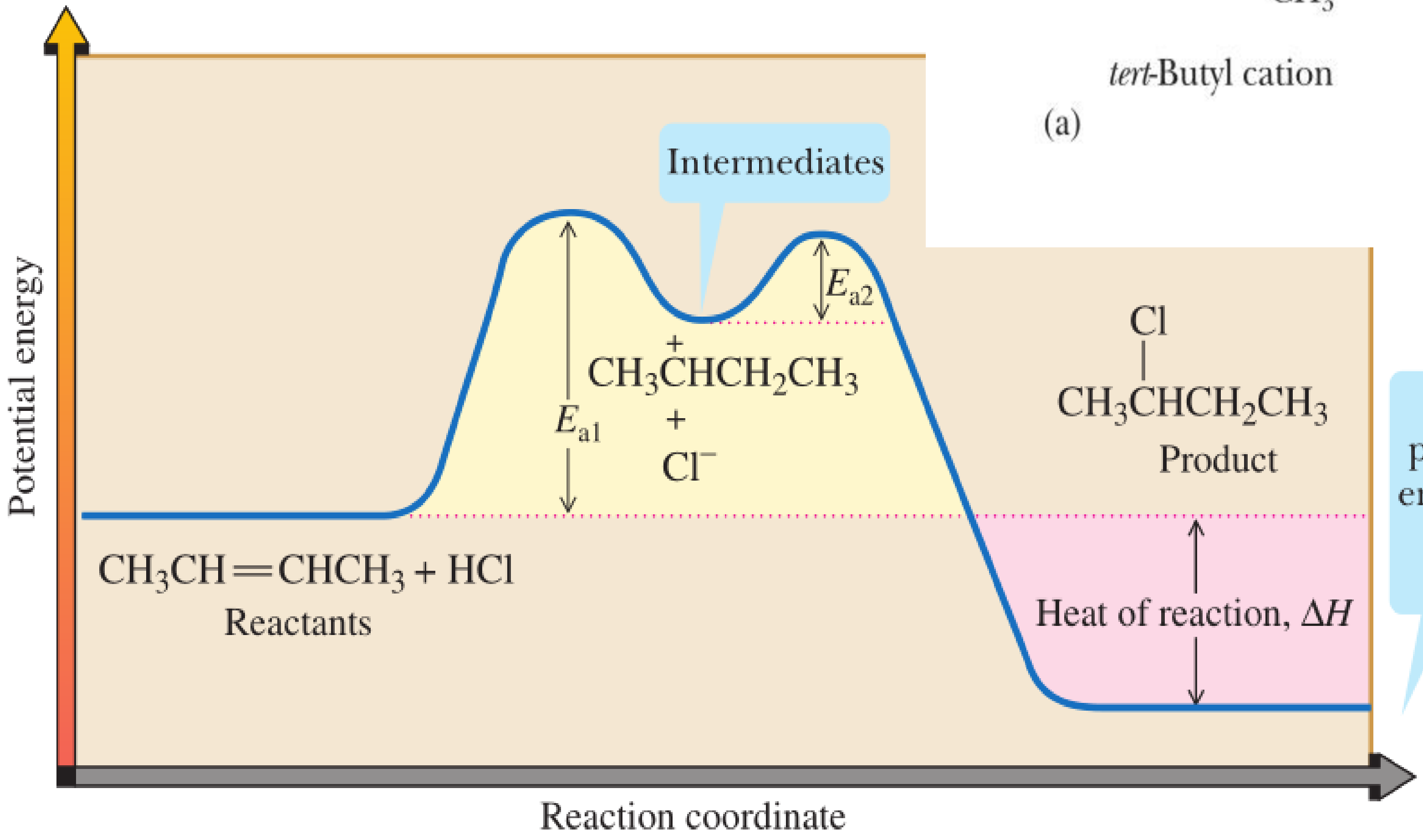
Chloride ion
(a Lewis base)
(a nucleophile)

sec-Butyl cation
(a Lewis acid)
(an electrophile)

2-Chlorobutane

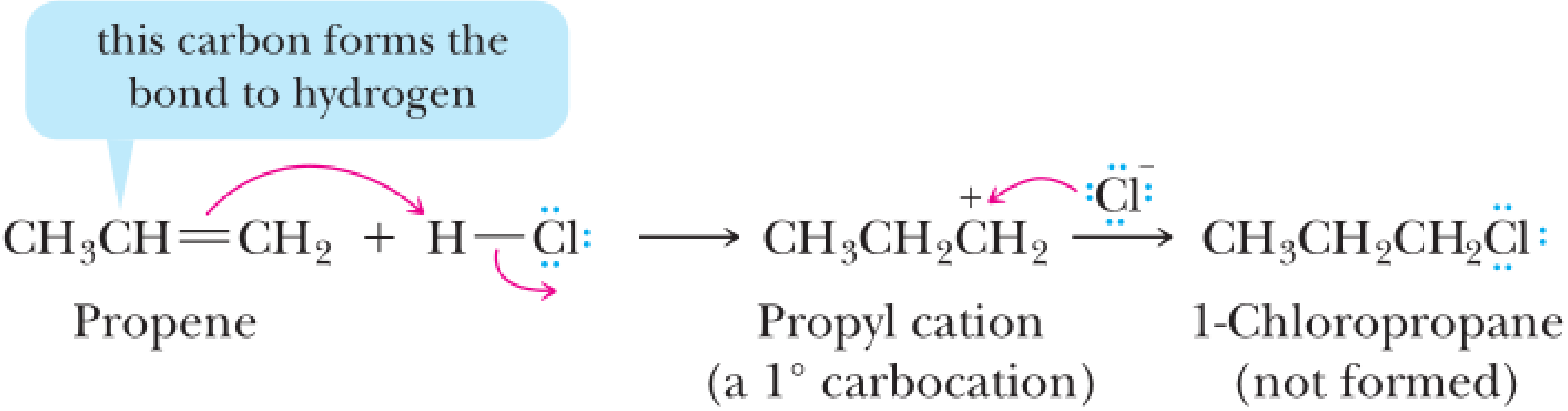
Carbocation
（碳正离子）





when the energy of the products is lower than the energy of the reactants, the reaction is overall exothermic

Relative Stabilities of Carbocations



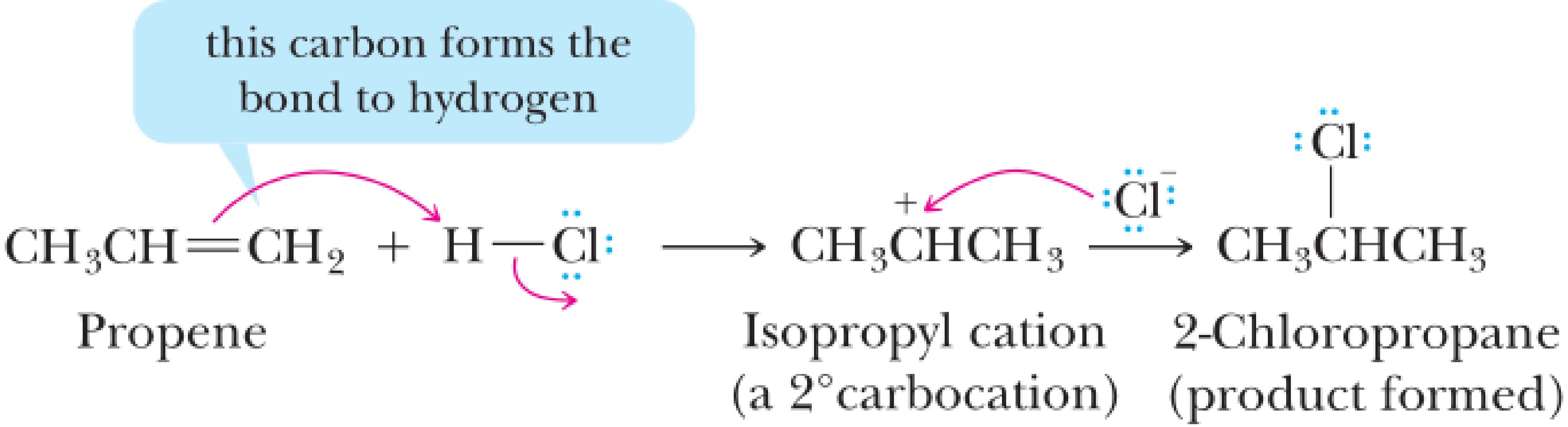
this carbon forms the bond to hydrogen

$$CH_3CH{=}CH_2 + H{-}Cl \longrightarrow CH_3CH_2\overset{+}{C}H_2 \xrightarrow{Cl^-} CH_3CH_2CH_2Cl$$

Propene

Propyl cation
(a 1° carbocation)

1-Chloropropane
(not formed)



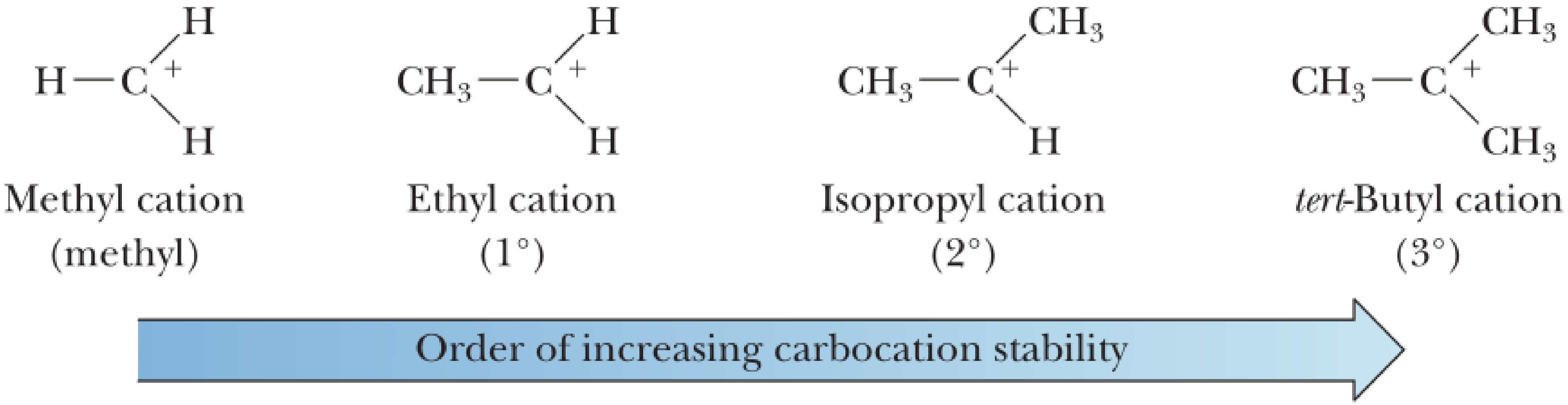
this carbon forms the bond to hydrogen

$$CH_3CH{=}CH_2 + H{-}Cl \longrightarrow CH_3\overset{+}{C}HCH_3 \xrightarrow{Cl^-} CH_3\overset{Cl}{\overset{|}{C}}HCH_3$$

Propene

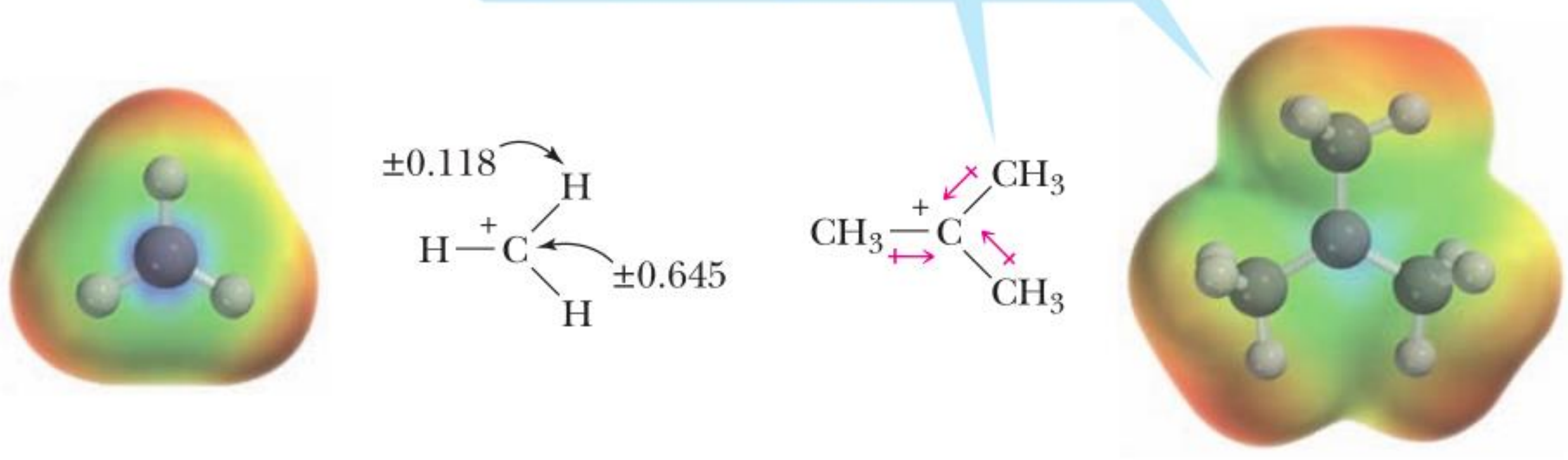
Isopropyl cation
(a 2°carbocation)

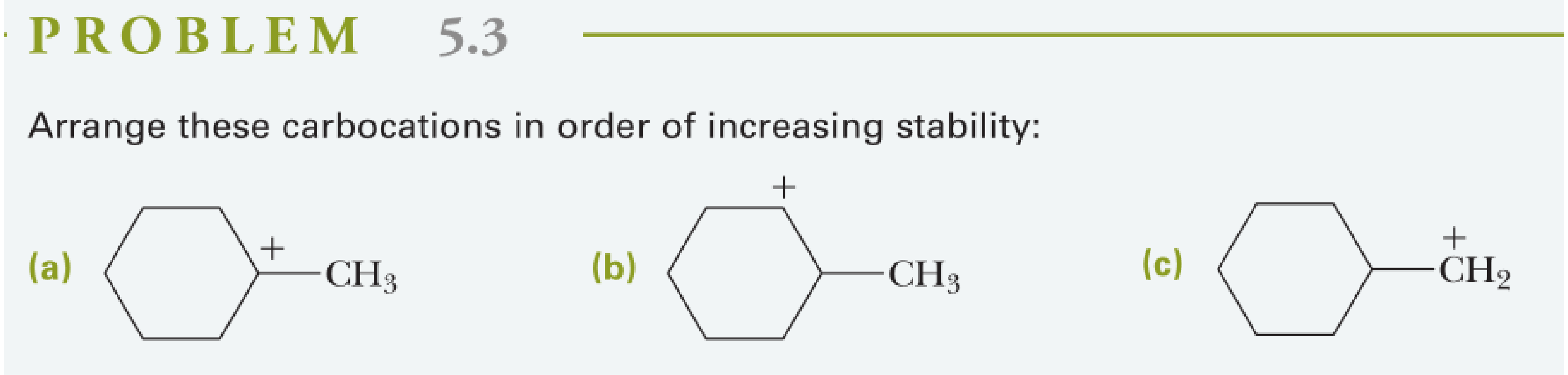
2-Chloropropane
(product formed)



WHy? How to explain?

the methyl groups donate electron density toward the carbocation carbon, thus delocalizing the positive charge





PROBLEM 5.3

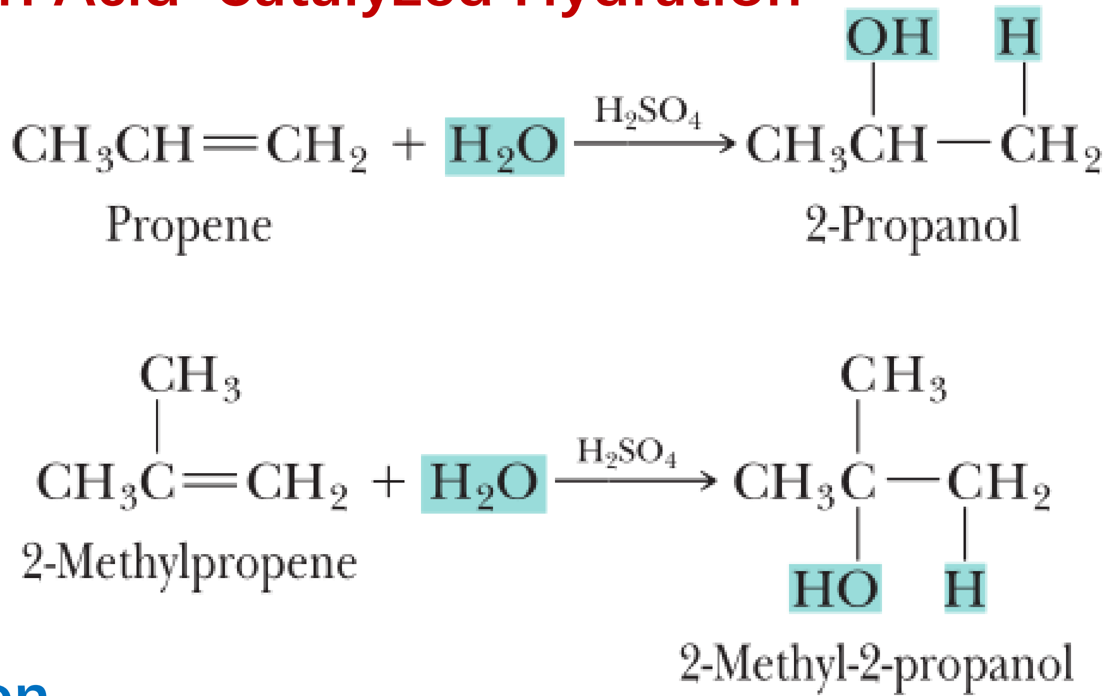
Arrange these carbocations in order of increasing stability:

(a)

(b)

(c)

B. Addition of Water: Acid-Catalyzed Hydration



$$CH_3CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{OH}{\overset{|}{C}H}-\overset{H}{\overset{|}{CH_2}}$$

Propene

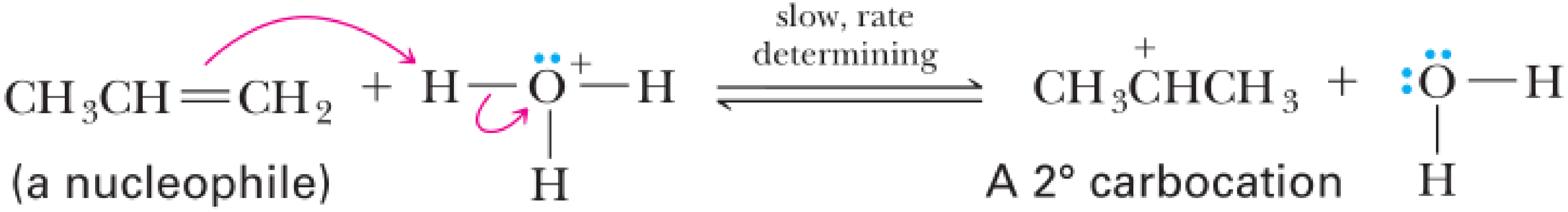
2-Propanol

$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\underset{\underset{HO}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{CH_2}$$

2-Methylpropene

2-Methyl-2-propanol

Step 1: Add a proton.



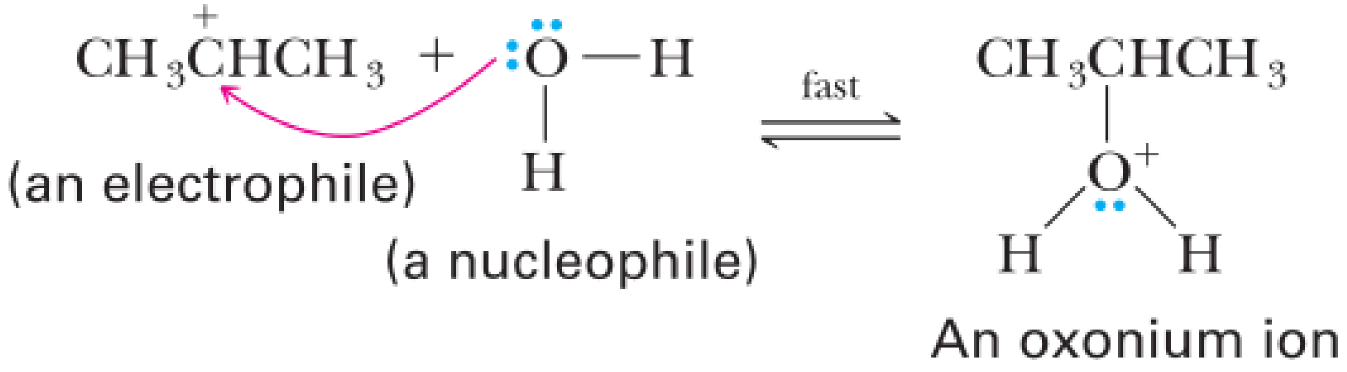
$$CH_3CH{=}CH_2 + H-\underset{\underset{H}{|}}{\overset{+}{\ddot{O}}}-H \xrightleftharpoons{\text{slow, rate determining}} CH_3\overset{+}{C}HCH_3 + :\underset{\underset{H}{|}}{\ddot{O}}-H$$

(a nucleophile)

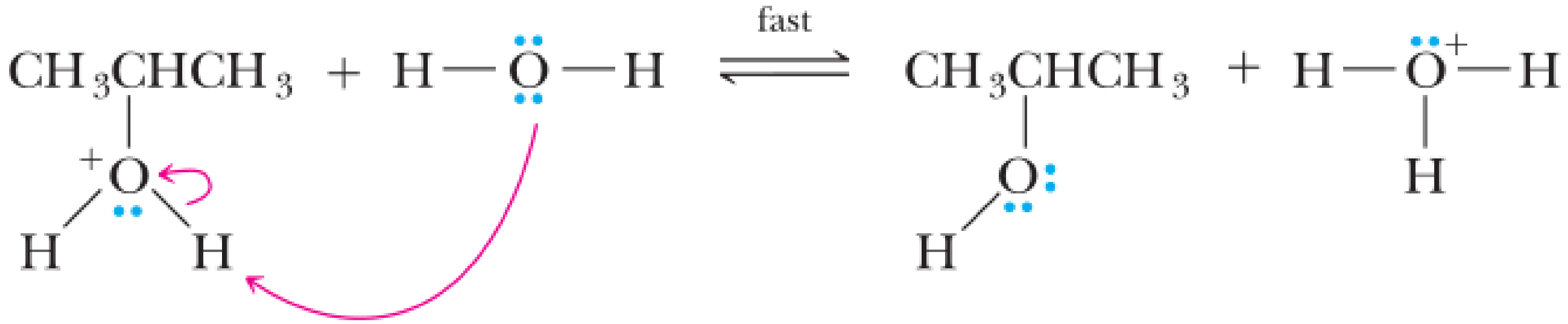
(an electrophile)

A 2° carbocation intermediate

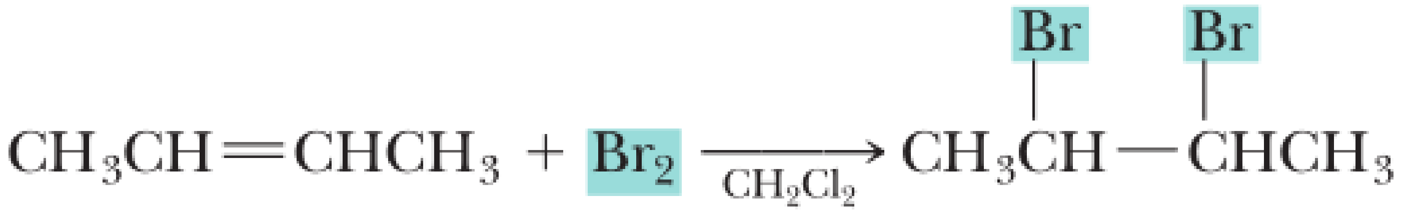
Step 2: Reaction of a nucleophile and an electrophile to form a new covalent bond.



Step 3: take a proton away.



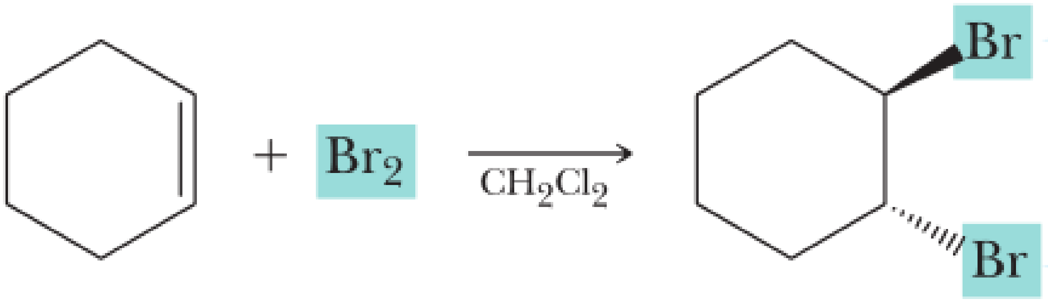
C. Addition of Bromine and Chlorine



$$CH_3CH{=}CHCH_3 + Br_2 \xrightarrow[CH_2Cl_2]{} CH_3\overset{\overset{\displaystyle Br}{|}}{C}H-\overset{\overset{\displaystyle Br}{|}}{C}HCH_3$$

2-Butene

2,3-Dibromobutane



Cyclohexene

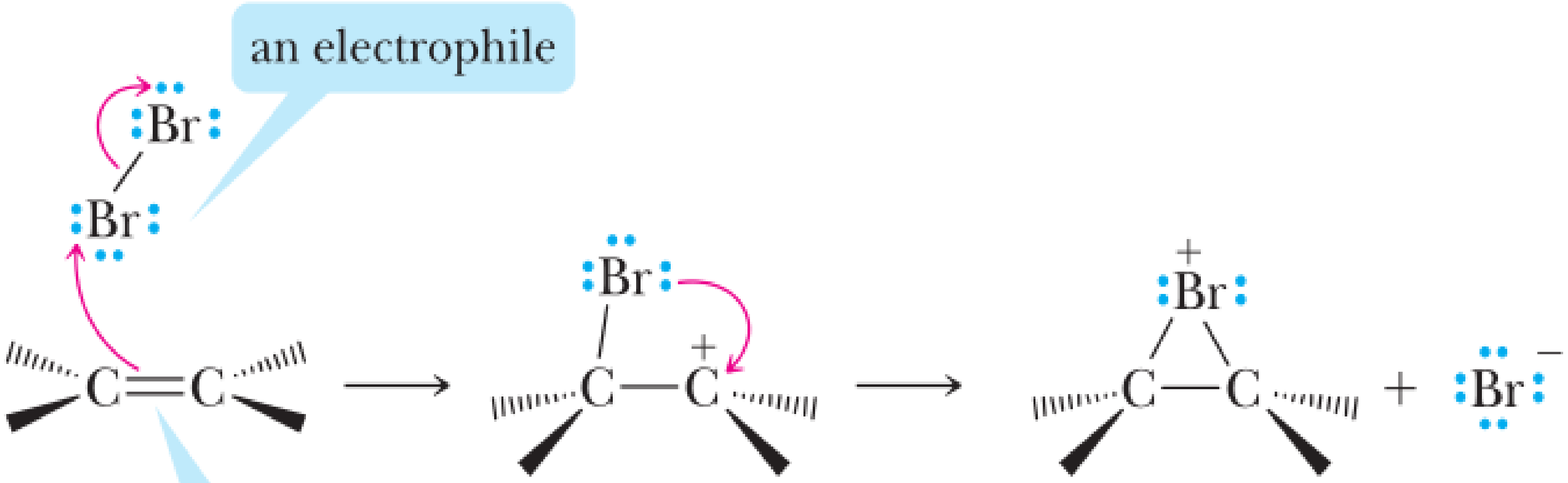
trans-1,2-Dibromocyclohexane

in anti stereoselectivity, the reactants add to opposite sides of the former C—C double bond. We know this because one Br is bonded with a solid wedge, while the other Br is bonded with a dashed wedge

Mechanism

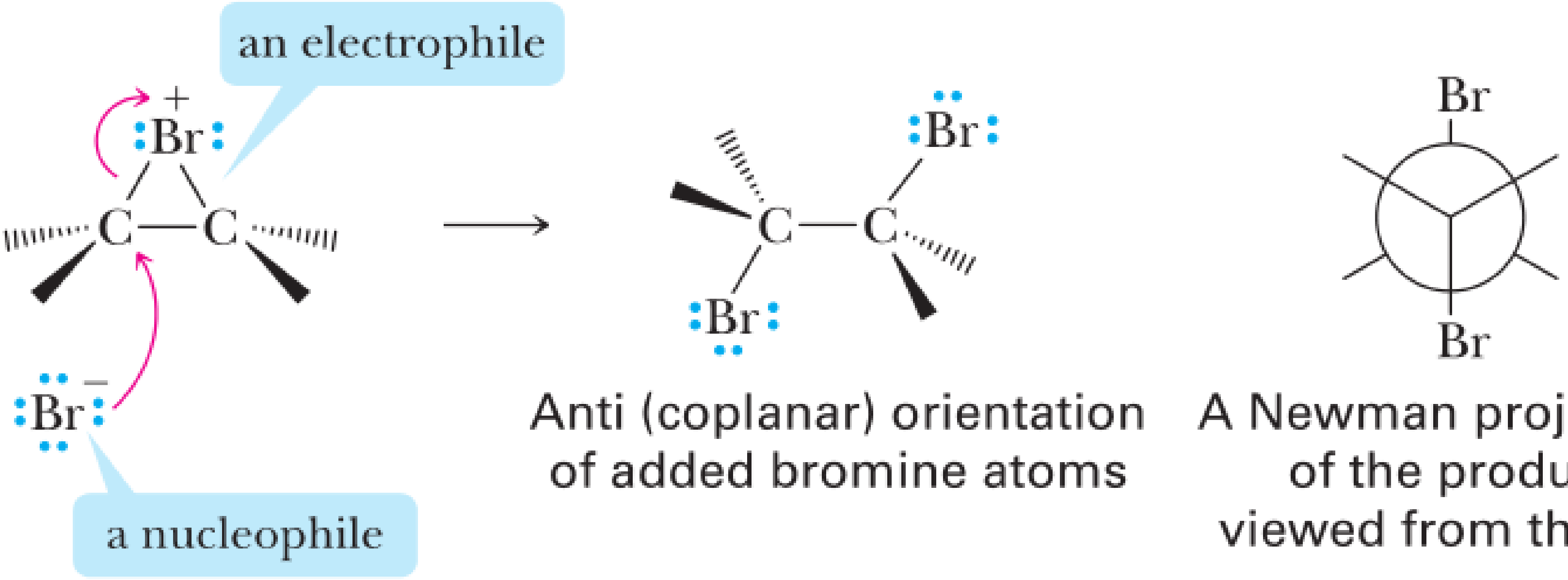
addition of Bromine with anti selectivity（溴反马式加成）

Step 1: Reaction of a nucleophile and an electrophile to form a new covalent bond.



A bridged bromonium ion intermediate

Step 2: Reaction of a nucleophile and an electrophile to form a new covalent bond



Anti (coplanar) orientation of added bromine atoms

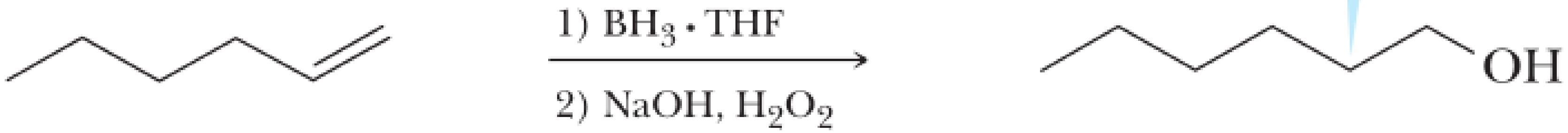
A Newman projection of the product viewed from the left

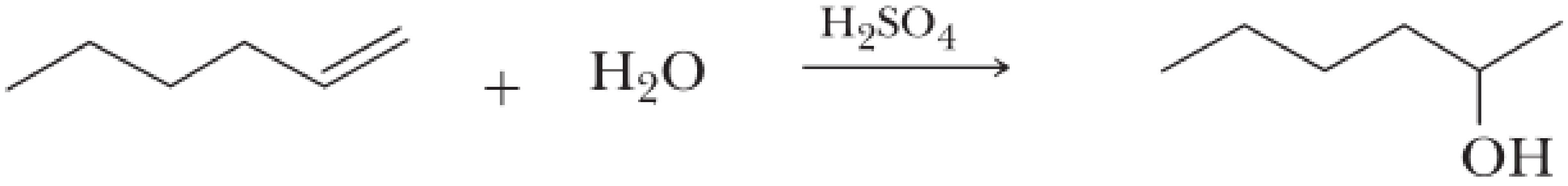
5.4 What Are Carbocation Rearrangements?(略)

5.5 What Is Hydroboration–Oxidation of an Alkene（硼氢化—氧化）?

the net result of hydroboration–oxidation is the addition of H and OH across the C—C double bond

contrary to Markovnikov's rule, the hydrogen has added to the former double-bond carbon with the fewer hydrogens

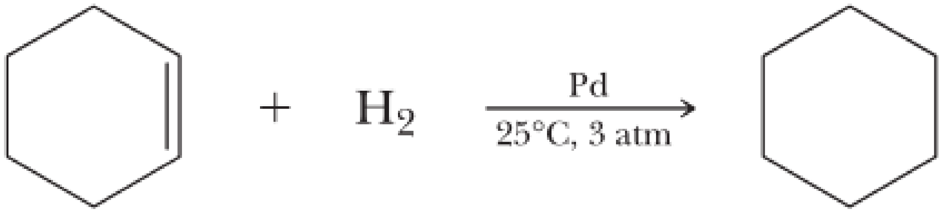




1-Hexene

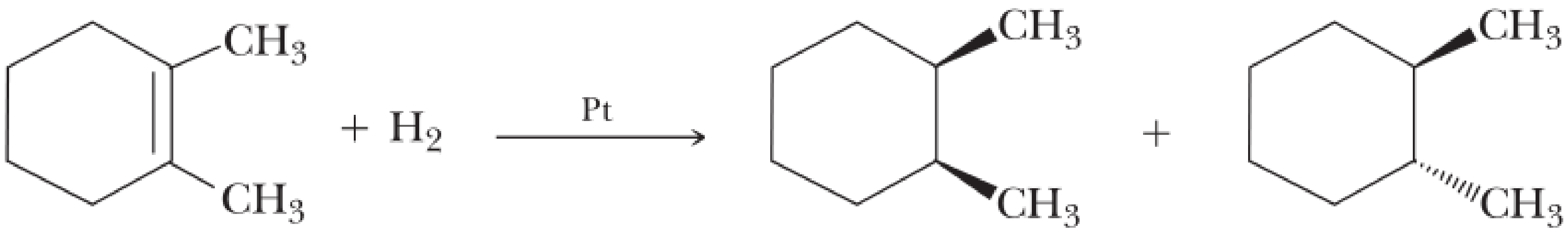
2-Hexanol

5.6 How Can an Alkene Be Reduced to an Alkane?



Cyclohexene

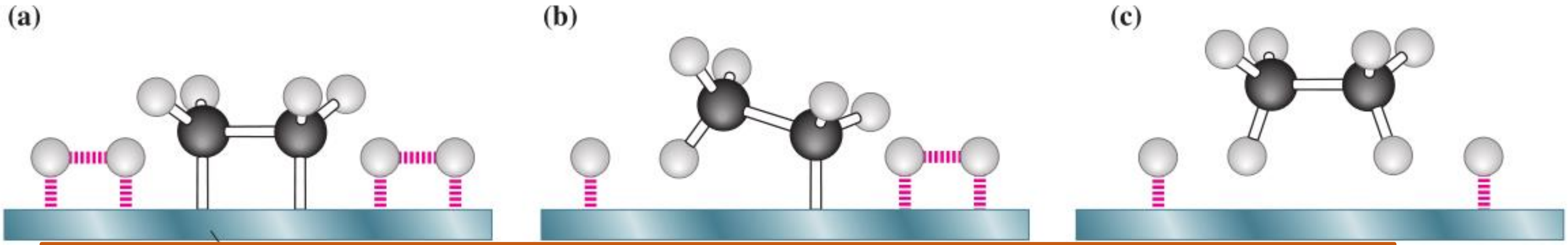
Cyclohexane



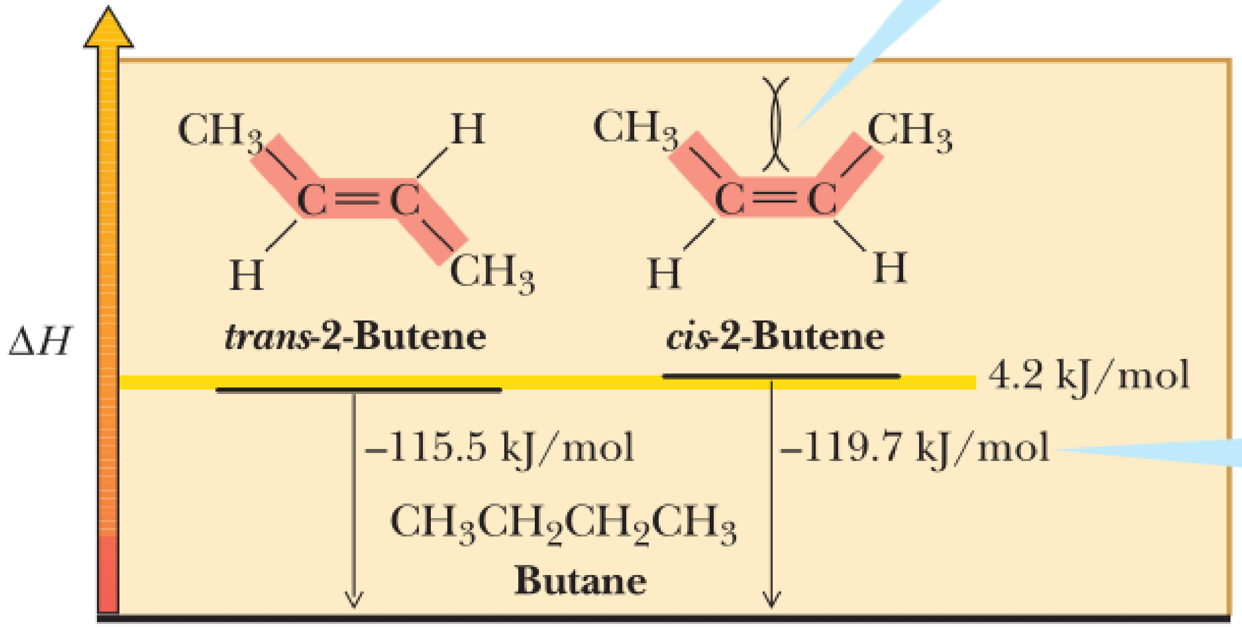
1,2-Dimethyl-cyclohexene

70% to 85% *cis*-1,2-Dimethyl-cyclohexane

30% to 15% *trans*-1,2-Dimethyl-cyclohexane

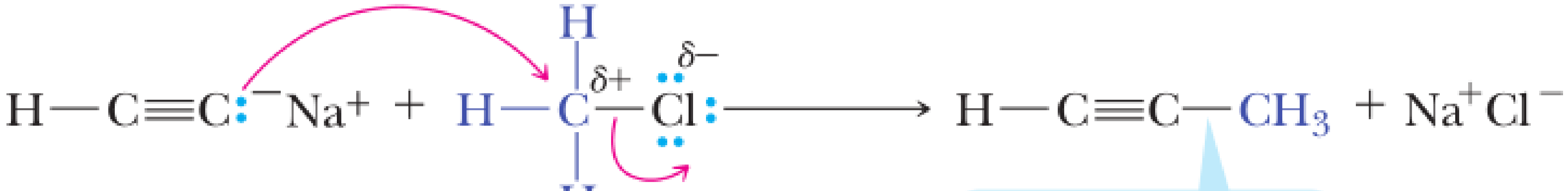


the *cis* geometry places the two alkyl groups of the alkene closer, exposing them to nonbonded interaction (steric) strain



a higher heat of hydrogenation means that more heat is released and indicates that the *cis* alkene starts at a higher energy level (the *cis* alkene is less stable than the *trans* alkene)

5.7 How Can an Acetylide Anion Be Used to Create a New Carbon–Carbon Bond（延长碳链）？



(a nucleophile) (an electrophile)

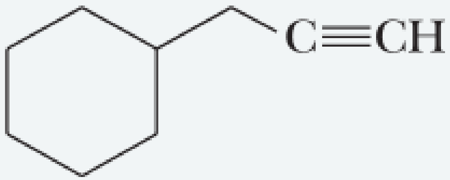
a new C—C bond is formed

$$HC{\equiv}CH \xrightarrow[\text{2) } CH_3CH_2Br]{\text{1) } NaNH_2} CH_3CH_2C{\equiv}CH \xrightarrow[\text{4) } CH_3CH_2CH_2Br]{\text{3) } NaNH_2} CH_3CH_2C{\equiv}CCH_2CH_2CH_3$$

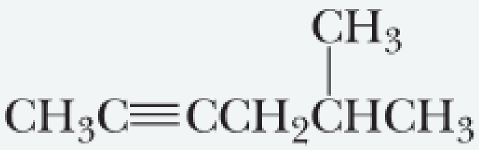
Acetylene 1-Butyne 3-Heptyne

Problem

(a)



(b)



$CH_3C{\equiv}CCH_2\overset{CH_3}{\overset{|}{C}}HCH_3$

(c) $CH_3C{\equiv}CCH_2CH_2CH_2CH_3$

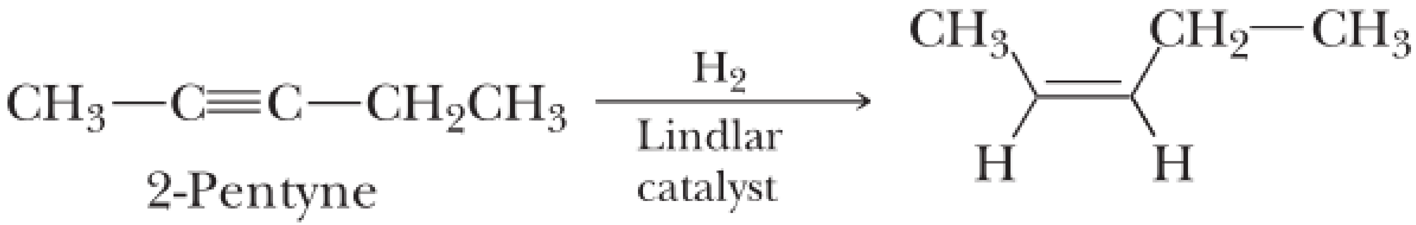
5.8 How Can Alkynes Be Reduced to Alkenes and Alkanes?

$$R-C\equiv C-H \xrightarrow{NaNH_2} R-C\equiv C\!:^-\,Na^+ \xrightarrow{R-X} R-C\equiv C-R \xrightarrow{\text{reduce}} R-C=C-R \xrightarrow{\text{various reactions}}$$

alcohols, haloalkanes,
dihaloalkanes,
alkanes, and others

$$CH_3C\equiv CCH_3 + 2H_2 \xrightarrow[3\ \text{atm}]{\text{Pd, Pt, or Ni}} CH_3CH_2CH_2CH_3$$

2-Butyne Butane



2-Pentyne

cis-2-Pentene

作 业

5. 15、5.19、5.43、