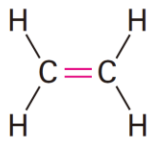
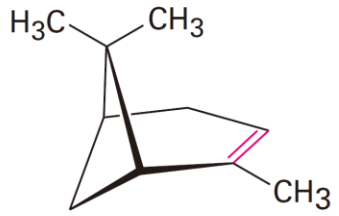
7 烯烃：结构与反应

烯烃在自然界中普遍存在

An **alkene**, sometimes called an *olefin,* is a hydrocarbon that contains a carbon–carbon double bond. Alkenes occur abundantly in nature. Ethylene, for instance, is a plant hormone that induces ripening in fruit, and α-pinene is the major component of turpentine. Life itself would be impossible without such alkenes as β-carotene, a compound that contains 11 double bonds. An orange pigment responsible for the color of carrots, β-carotene is an important dietary source of vitamin A and is thought to offer some protection against certain types of cancer.

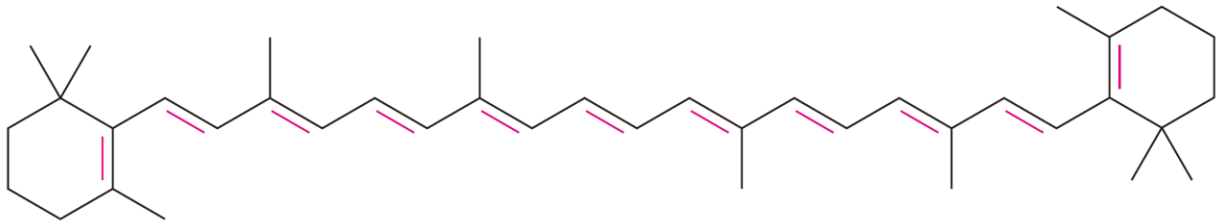


Ethylene



α-Pinene

苹烯，松节油的主要成分



β-Carotene
(orange pigment and vitamin A precursor)

beta-胡萝卜素

7.1 烯烃的工业制备及应用

- 每年数以亿吨级的乙烯和丙烯等被生产出来，用于制造聚乙烯、聚丙烯、乙二醇、乙酸等初级化工原料。

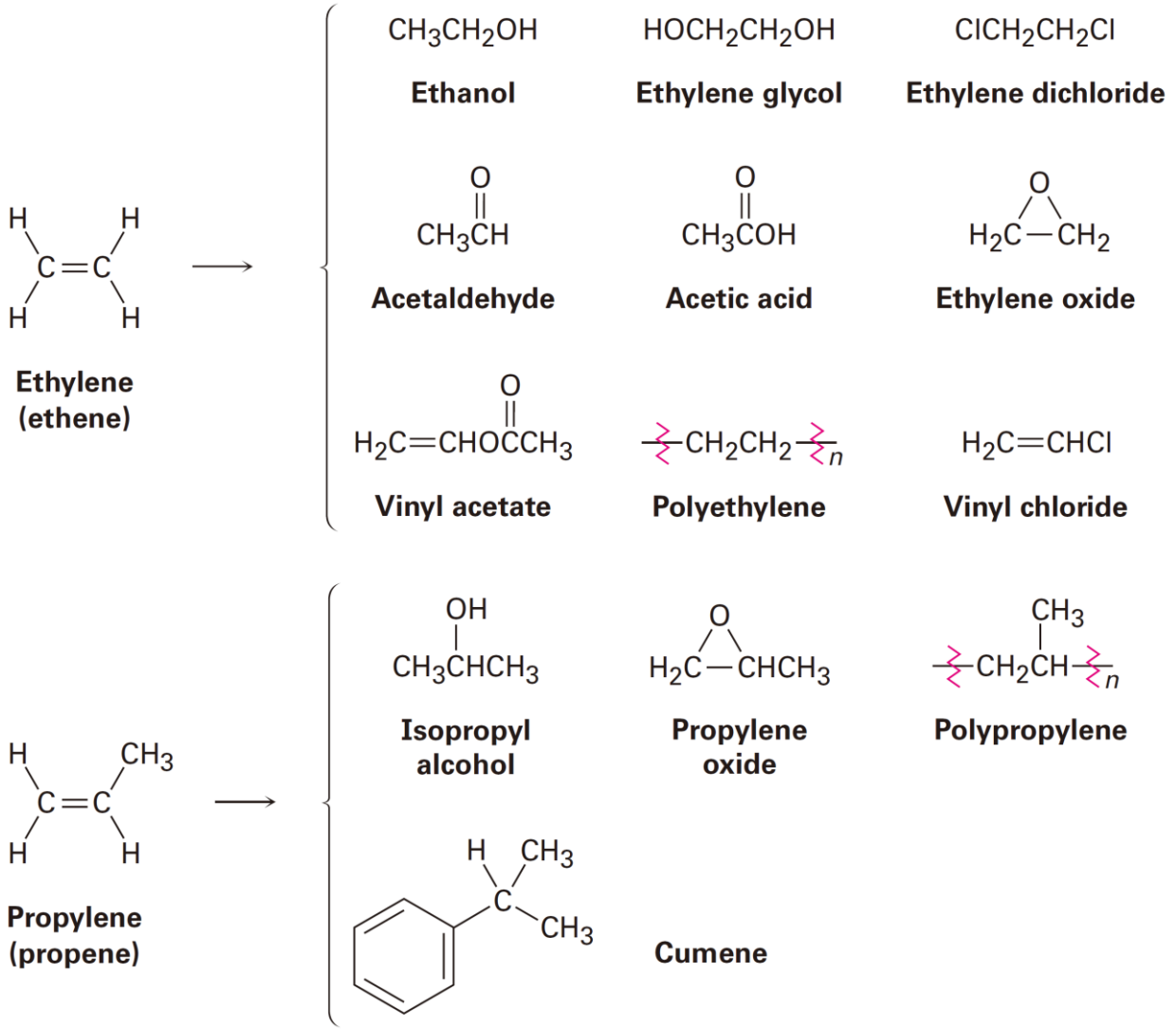


Figure 7.1 Compounds derived industrially from ethylene and propylene.

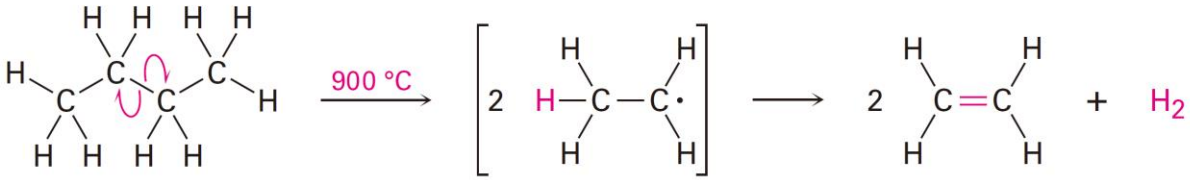
7.1 烯烃的工业制备及应用

- 烷烃的蒸汽裂化制备烯烃(steam cracking)

$$CH_3(CH_2)_nCH_3 \quad [n = 0\text{–}6]$$

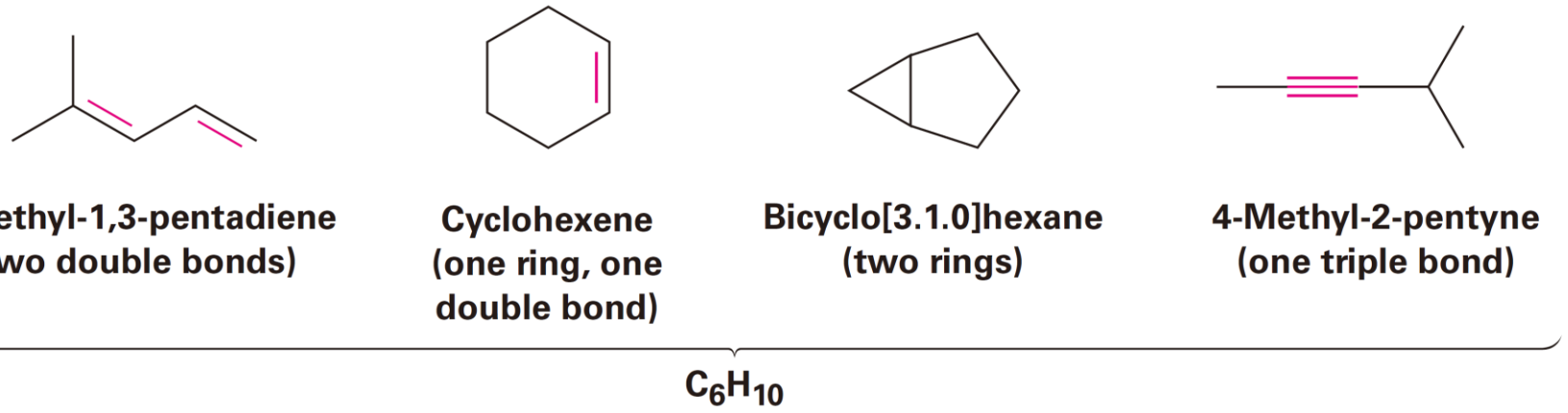
$$\xrightarrow[\text{steam}]{850\text{–}900\ ^\circ C}$$

$$H_2 + H_2C{=}CH_2 + CH_3CH{=}CH_2 + CH_3CH_2CH{=}CH_2$$



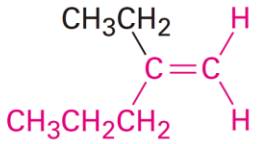
7.2 不饱和度

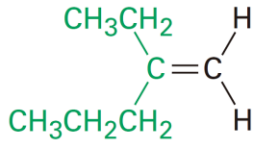
- 不饱和度，又称缺氢指数，是有机物分子不饱和程度的量化标志。
- 计算方法： 每个环、π键各将不饱和度增加1 单键对不饱和度不产生影响，因此烷烃的不饱和度是0。 一个双键贡献一个不饱和度。 一个叁键贡献两个不饱和度。



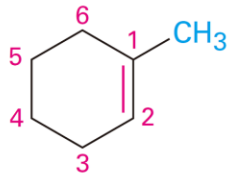
7.3 烯烃的命名

1. 找到母链

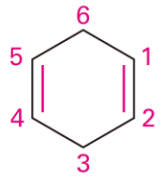




Named as a *pentene* *NOT* as a hexene, since the double bond is not contained in the six-carbon chain

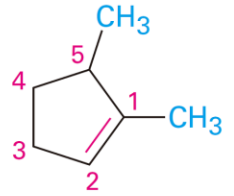


1-Methylcyclohexene



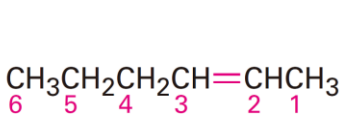
1,4-Cyclohexadiene

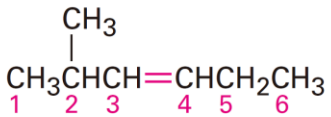
(New: Cyclohexa-1,4-diene)



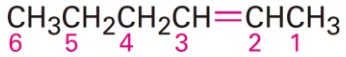
1,5-Dimethylcyclopentene

2. 编号

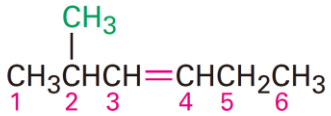




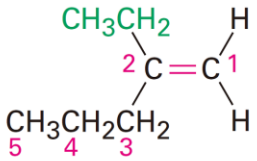
3. 命名



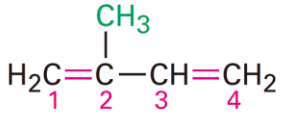
2-Hexene



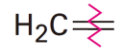
2-Methyl-3-hexene



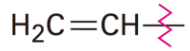
2-Ethyl-1-pentene



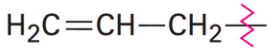
2-Methyl-1,3-butadiene



A methylene group



A vinyl group



An allyl group

Table 7.1 Common Names of Some Alkenes

Compound	Systematic name	Common name
$H_2C{=}CH_2$	Ethene	Ethylene
$CH_3CH{=}CH_2$	Propene	Propylene
$CH_3C(CH_3){=}CH_2$	2-Methylpropene	Isobutylene
$H_2C{=}C(CH_3){-}CH{=}CH_2$	2-Methyl-1,3-butadiene	Isoprene

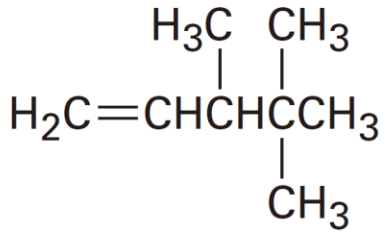
7.3 烯烃的命名

- 课堂练习

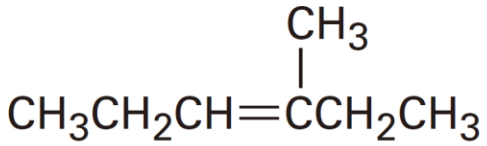
Problem 7.4

Give IUPAC names for the following compounds:

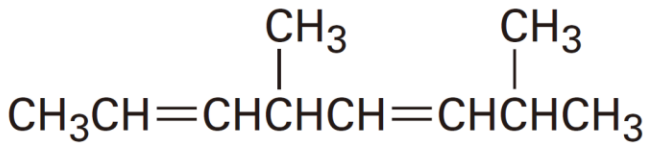
(a)



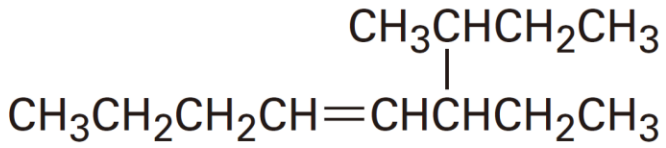
(b)



(c)



(d)



Problem 7.5

Draw structures corresponding to the following IUPAC names:

(a) 2-Methyl-1,5-hexadiene

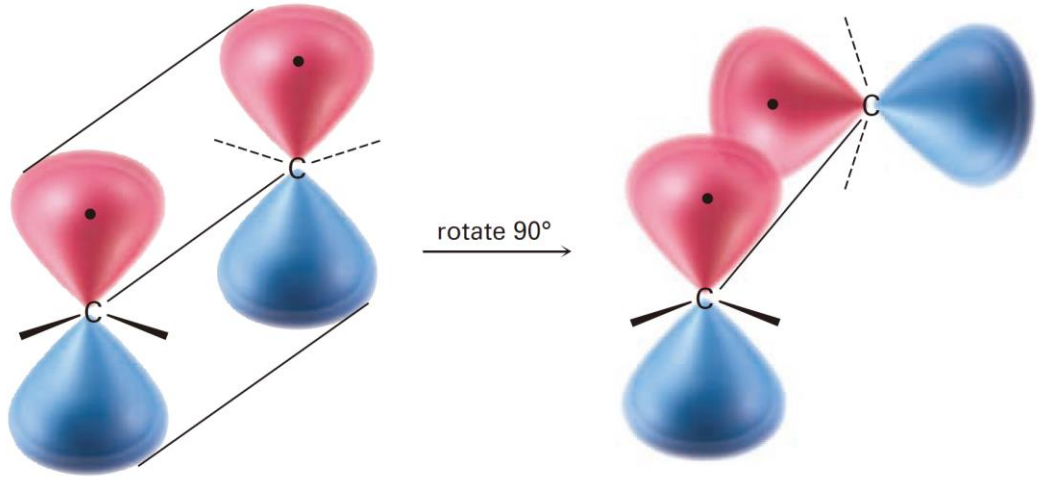
(b) 3-Ethyl-2,2-dimethyl-3-heptene

(c) 2,3,3-Trimethyl-1,4,6-octatriene

(d) 3,4-Diisopropyl-2,5-dimethyl-3-hexene

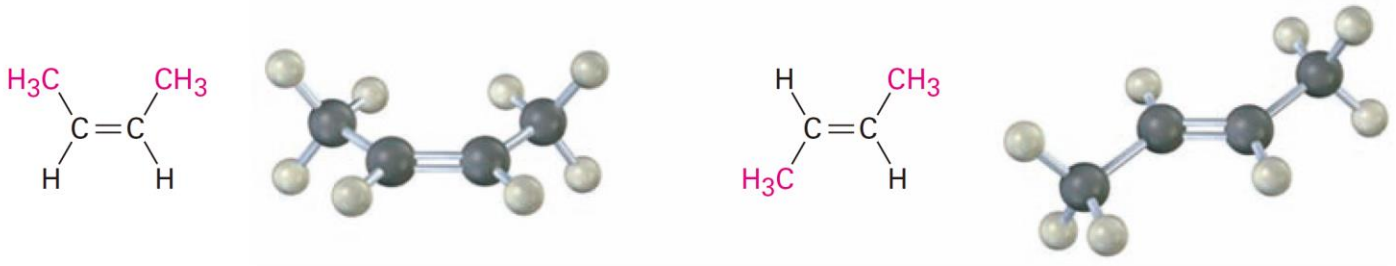
7.4 烯烃的顺反异构

- 顺反异构是指化合物分子中由于具有自由旋转的限制因素，使各个基团在空间的排列方式不同而出现的非对映异构现象。



π bond
(*p* orbitals are parallel)

Broken π bond after rotation
(*p* orbitals are perpendicular)



***cis*-2-Butene**

***trans*-2-Butene**

7.4 烯烃的顺反异构

- 课堂练习

Problem 7.9

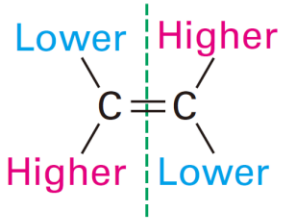
Which of the following compounds can exist as pairs of cis–trans isomers? Draw each cis–trans pair, and indicate the geometry of each isomer.

(a) $CH_3CH{=}CH_2$ **(b)** $(CH_3)_2C{=}CHCH_3$

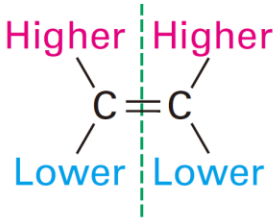
(c) $CH_3CH_2CH{=}CHCH_3$ **(d)** $(CH_3)_2C{=}C(CH_3)CH_2CH_3$

(e) $ClCH{=}CHCl$ **(f)** $BrCH{=}CHCl$

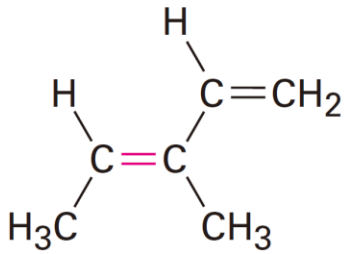
7.5 烯烃的E/Z构型判断



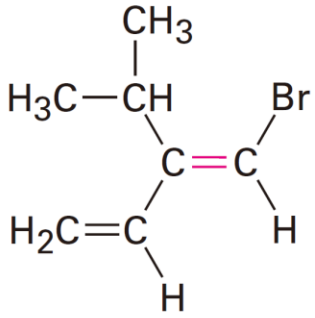
E double bond
(Higher-ranked groups
are on opposite sides.)



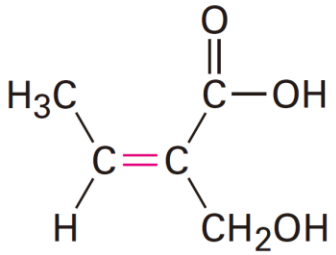
Z double bond
(Higher-ranked groups
are on the same side.)



(*E*)-3-Methyl-1,3-pentadiene



(*E*)-1-Bromo-2-isopropyl-1,3-butadiene



(*Z*)-2-Hydroxymethyl-2-butenoic acid

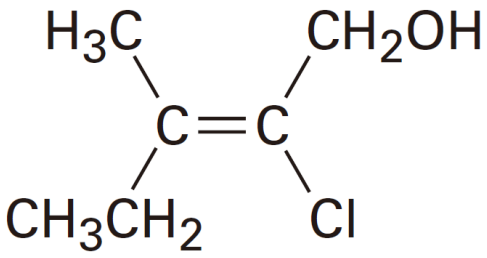
7.5 烯烃的E/Z构型判断

- 课堂练习

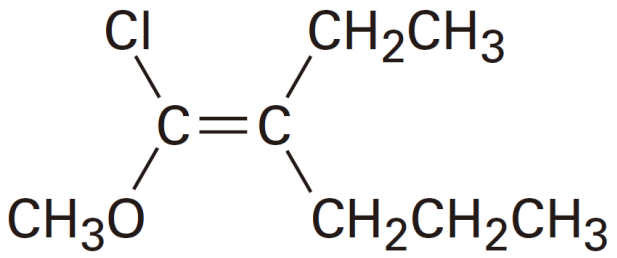
Problem 7.13

Assign *E* or *Z* configuration to the following alkenes:

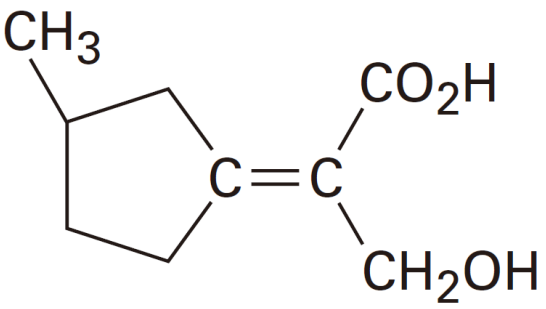
(a)



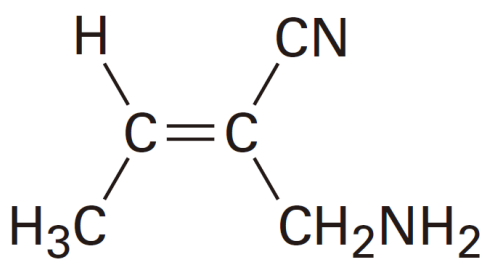
(b)



(c)

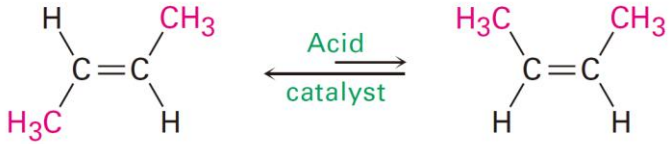


(d)

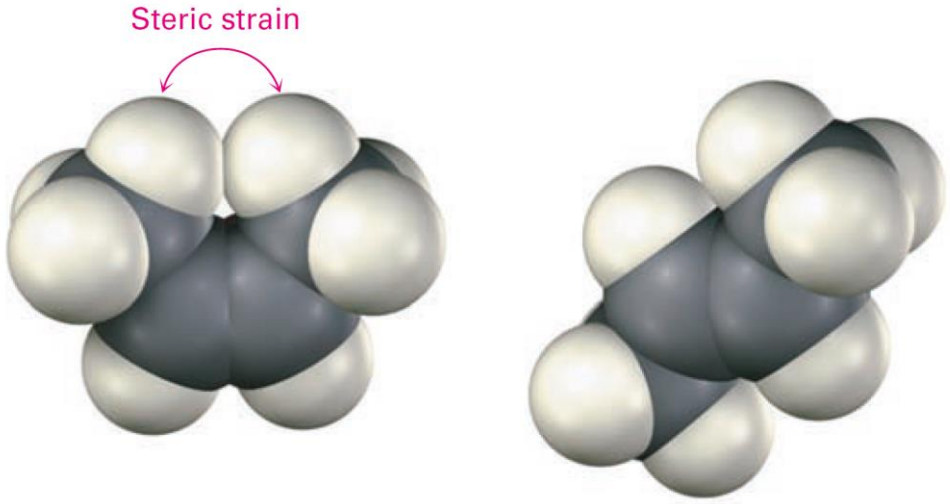


7.6 烯烃的稳定性

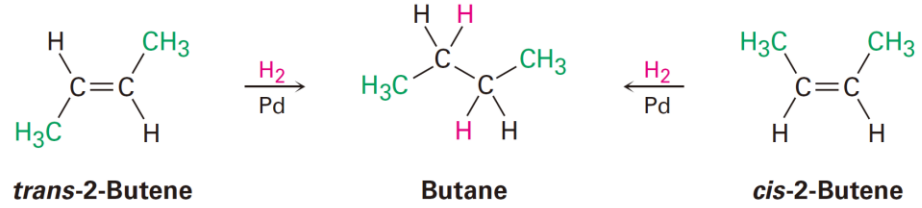
- 由于空间位阻，反式烯烃比顺式烯烃稳定。
- 如何量度稳定性：氢化热



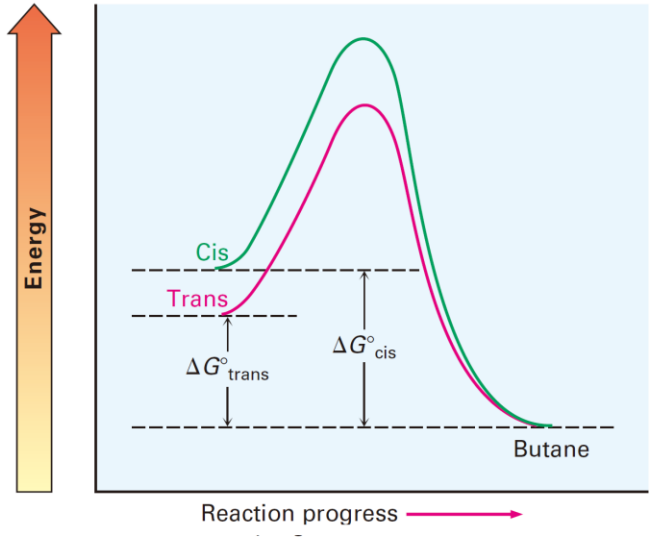
Trans (76%)　　Cis (24%)



cis-2-Butene　　*trans*-2-Butene



trans-2-Butene　　Butane　　*cis*-2-Butene

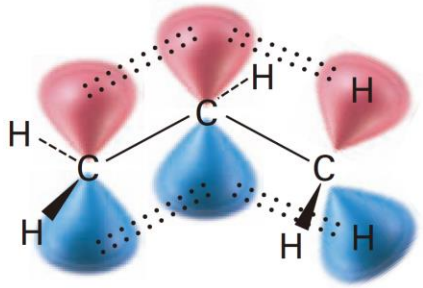


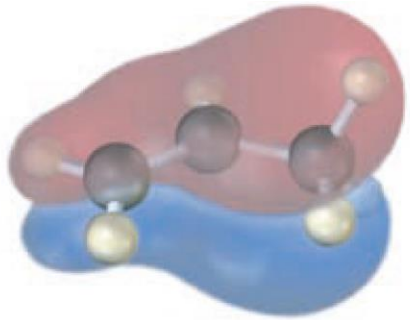
Cis isomer
$\Delta H°_{hydrog} = -120$ kJ/mol

Trans isomer
$\Delta H°_{hydrog} = -116$ kJ/mol

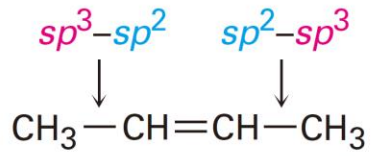
7.6 烯烃的稳定性

- 影响稳定性的另一个因素是p-π共轭

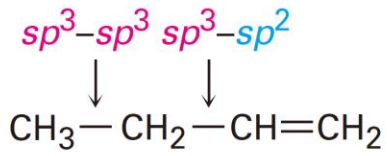




A second factor that contributes to alkene stability involves bond strengths. A bond between an sp^2 carbon and an sp^3 carbon is somewhat stronger than a bond between two sp^3 carbons. Thus, in comparing 1-butene and 2-butene, the monosubstituted isomer has one sp^3–sp^3 bond and one sp^3–sp^2 bond, while the disubstituted isomer has two sp^3–sp^2 bonds. More highly substituted alkenes always have a higher ratio of sp^3–sp^2 bonds to sp^3–sp^3 bonds than less highly substituted alkenes and are therefore more stable.



2-Butene
(more stable)



1-Butene
(less stable)

7.6 烯烃的稳定性

- 稳定性顺序

Tetrasubstituted > Trisubstituted > Disubstituted > Monosubstituted

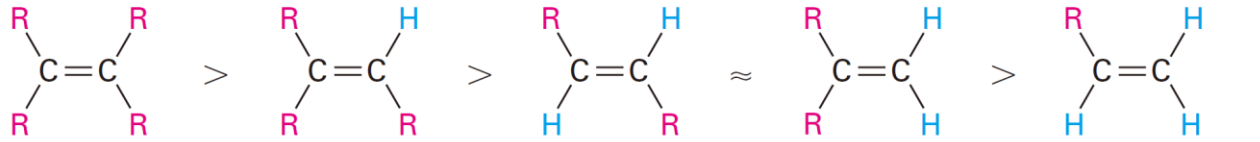


Table 7.2 Heats of Hydrogenation of Some Alkenes

Substitution	Alkene	ΔH°_{hydrog} (kJ/mol)	ΔH°_{hydrog} (kcal/mol)
Ethylene	$H_2C{=}CH_2$	−137	−32.8
Monosubstituted	$CH_3CH{=}CH_2$	−126	−30.1
Disubstituted	$CH_3CH{=}CHCH_3$ (cis)	−120	−28.6
	$CH_3CH{=}CHCH_3$ (trans)	−116	−27.6
	$(CH_3)_2C{=}CH_2$	−119	−28.4
Trisubstituted	$(CH_3)_2C{=}CHCH_3$	−113	−26.9
Tetrasubstituted	$(CH_3)_2C{=}C(CH_3)_2$	−111	−26.6

7.6 烯烃的稳定性

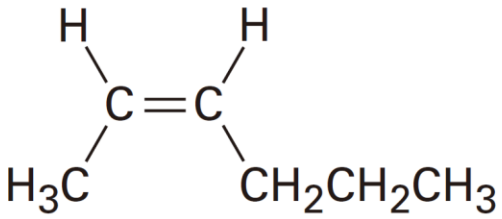
- 课堂练习

Problem 7.15

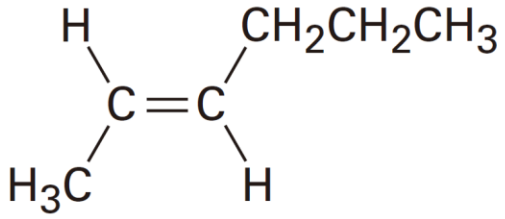
Name the following alkenes, and tell which compound in each pair is more stable:

(a) $H_2C{=}CHCH_2CH_3$ or $H_2C{=}C(CH_3)CH_3$

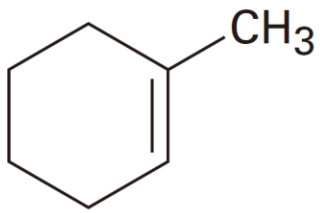
(b)



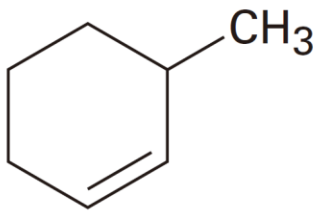
or



(c)



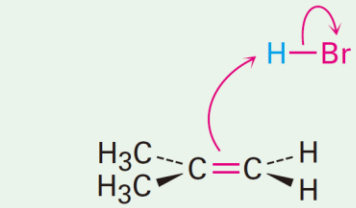
or



7.7 烯烃的亲电加成反应

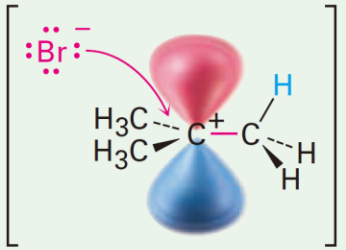
1 A hydrogen atom on the electrophile HBr is attacked by π electrons from the nucleophilic double bond, forming a new C–H bond. This leaves the other carbon atom with a + charge and a vacant *p* orbital. Simultaneously, two electrons from the H–Br bond move onto bromine, giving bromide anion.

2 Bromide ion donates an electron pair to the positively charged carbon atom, forming a C–Br bond and yielding the neutral addition product.



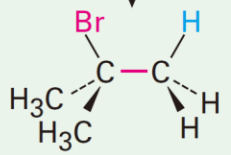
2-Methylpropene

1



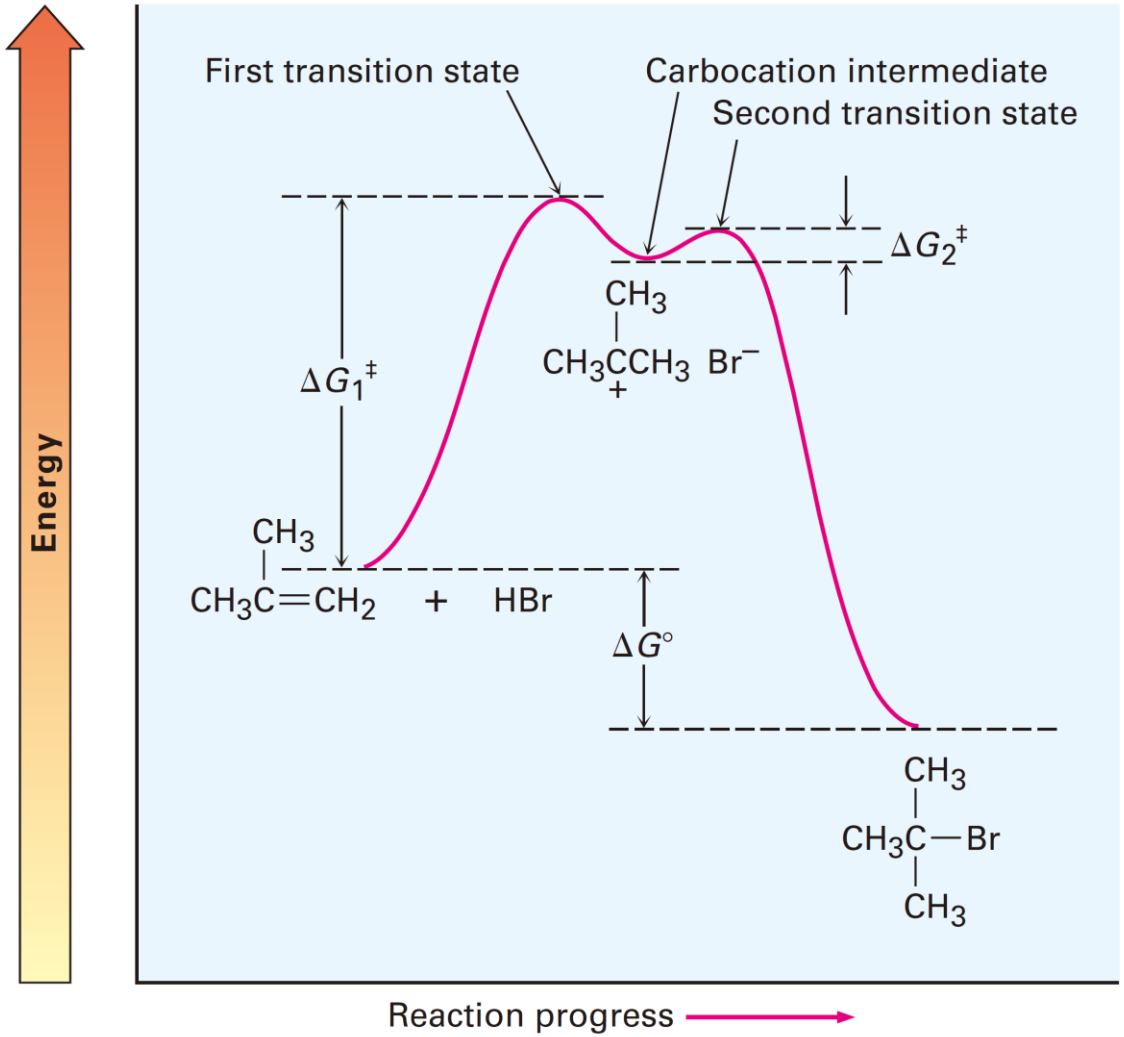
Carbocation intermediate

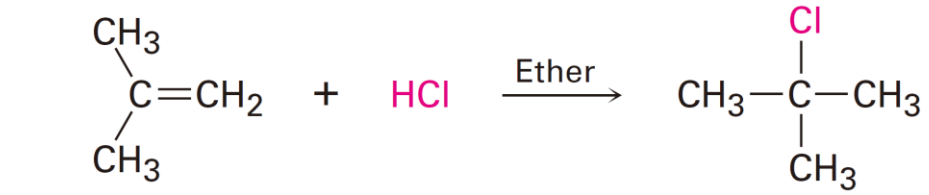
2



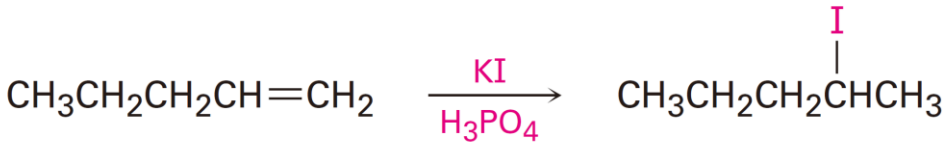
2-Bromo-2-methylpropane

7.7 烯烃的亲电加成反应

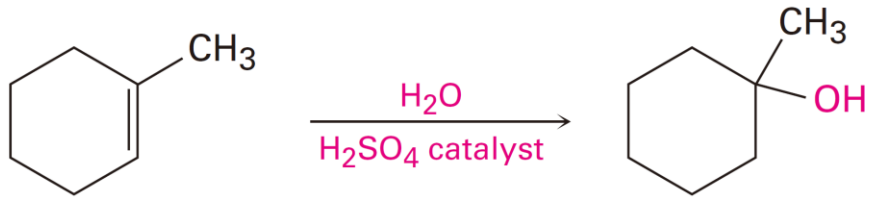




2-Methylpropene **2-Chloro-2-methylpropane (94%)**



1-Pentene **(HI)** **2-Iodopentane**

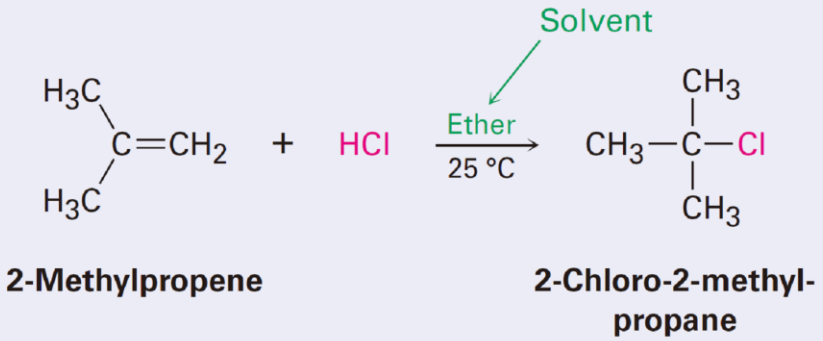


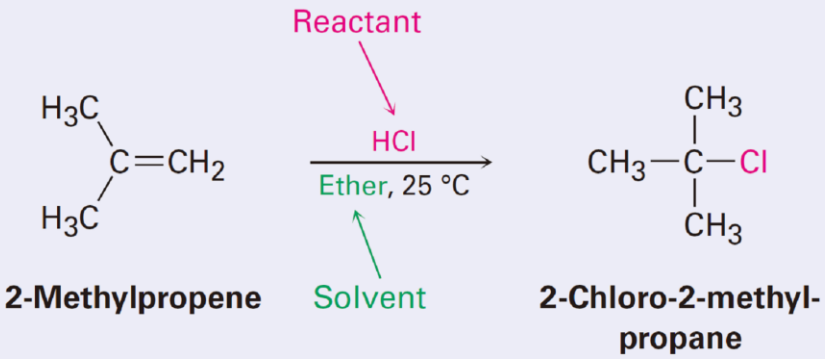
1-Methylcyclohexene **1-Methylcyclohexanol**

7.7 烯烃的亲电加成反应

- 规范书写化学方程式

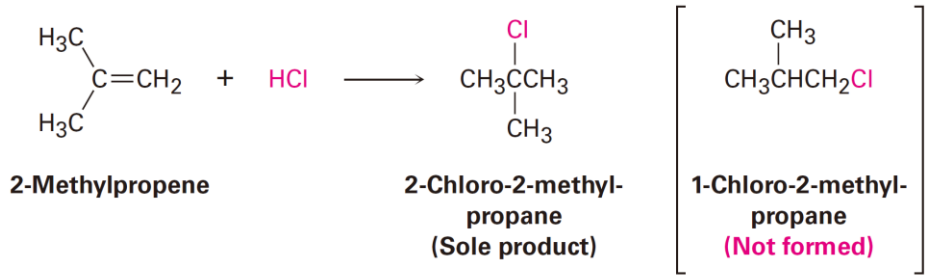
Writing Organic Reactions





7.8 加成方向：马氏规则

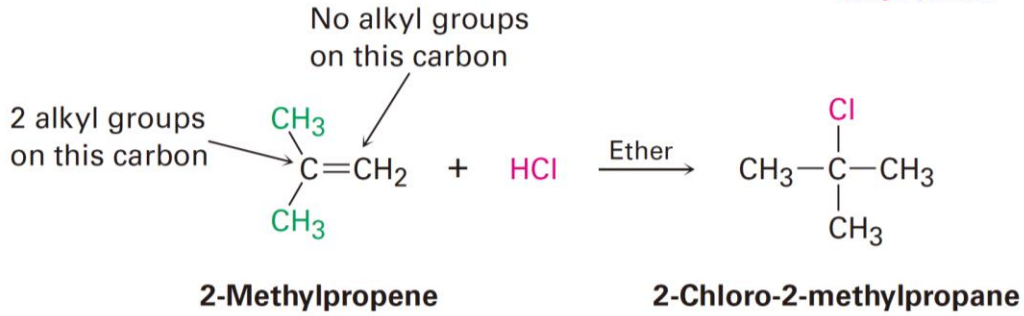
- 马尔科夫尼科夫规则，又称马氏规则，是有机化学中区域选择性经验规则，其内容即：当发生亲电加成反应时，亲电试剂中的正电基团总是加在连氢最多的碳原子上，而负电基团则会加在连氢最少的碳原子上。

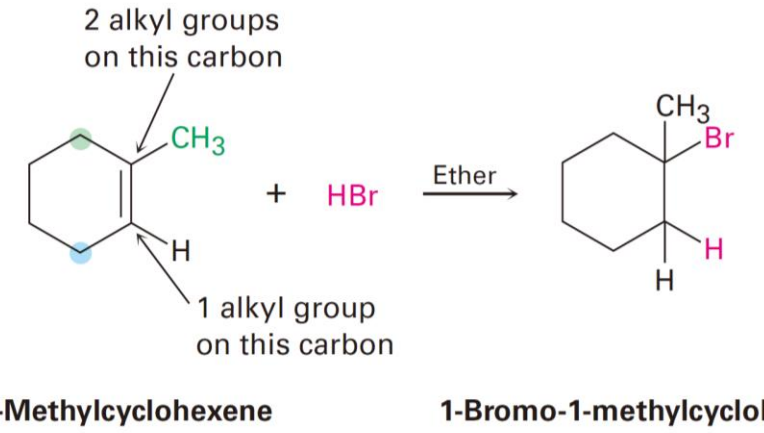


Markovnikov's rule

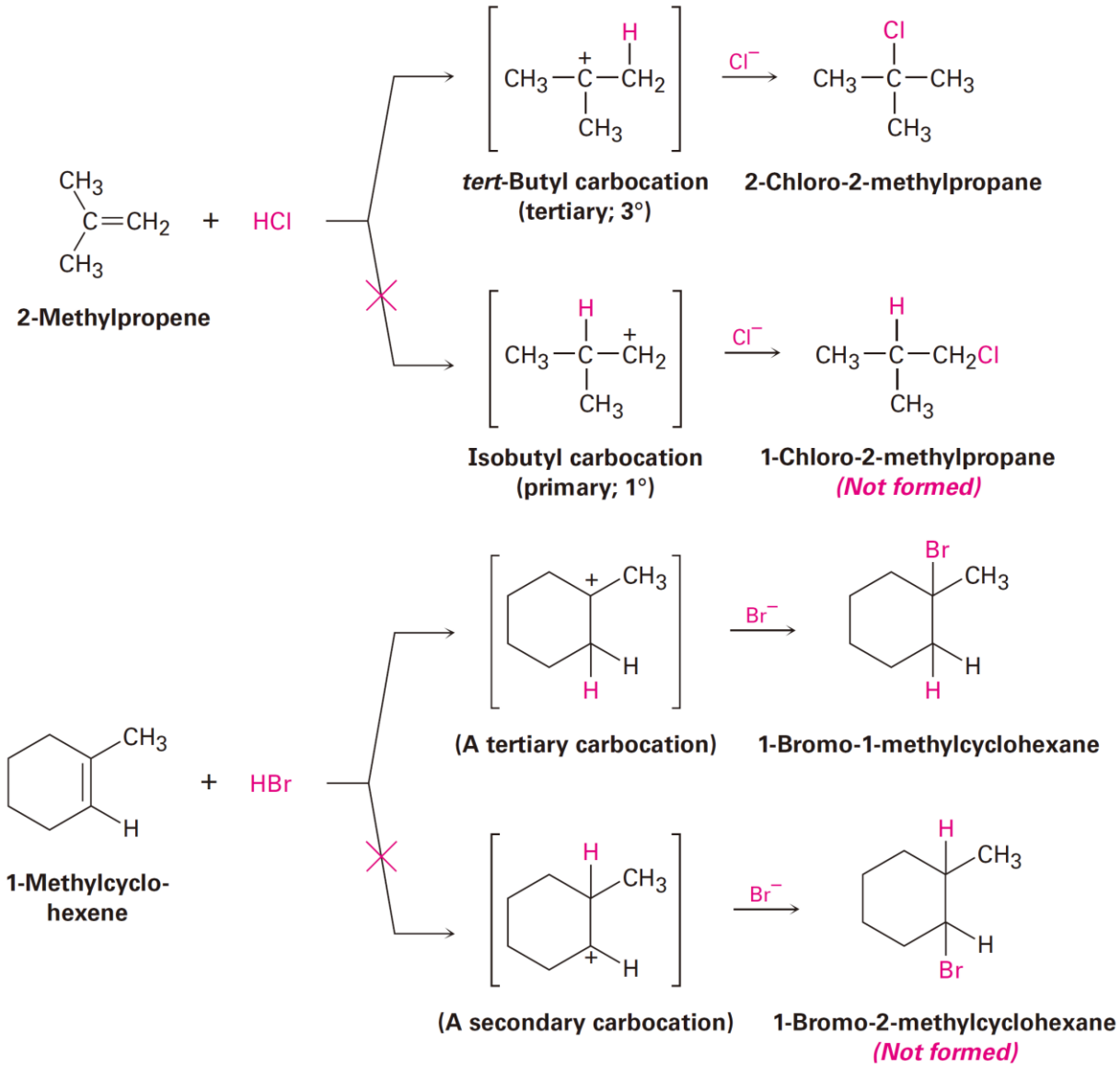
In the addition of HX to an alkene, the H attaches to the carbon with fewer alkyl substituents and the X attaches to the carbon with more alkyl substituents.

氢多加氢





7.8 加成方向：马氏规则


2-Methylpropene
HCl
tert-Butyl carbocation
(tertiary; 3°)
2-Chloro-2-methylpropane
Isobutyl carbocation
(primary; 1°)
1-Chloro-2-methylpropane
(Not formed)
1-Methylcyclo-
hexene
HBr
(A tertiary carbocation)
1-Bromo-1-methylcyclohexane
(A secondary carbocation)
1-Bromo-2-methylcyclohexane
(Not formed)

7.8 加成方向：马氏规则

- 课堂练习

Problem 7.16

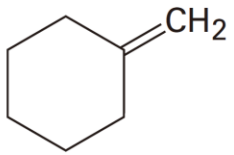
Predict the products of the following reactions:

(a)  $\xrightarrow{HCl}$?

(b) $CH_3CH_3C{=}CHCH_2CH_3 \xrightarrow{HBr}$?

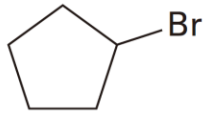
(c) $CH_3CH_3CHCH_2CH{=}CH_2 \xrightarrow[H_2SO_4]{H_2O}$?

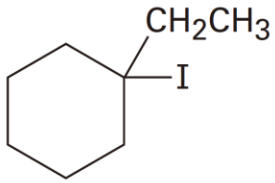
(Addition of H_2O occurs.)

(d)  $\xrightarrow{HBr}$?

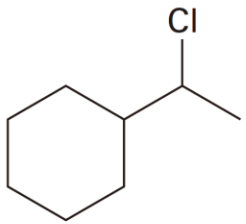
Problem 7.17

What alkenes would you start with to prepare the following products?

(a) 

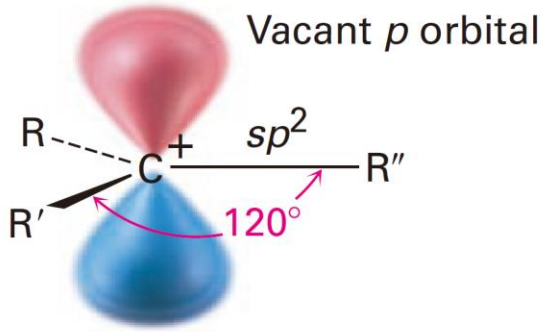
(b) 

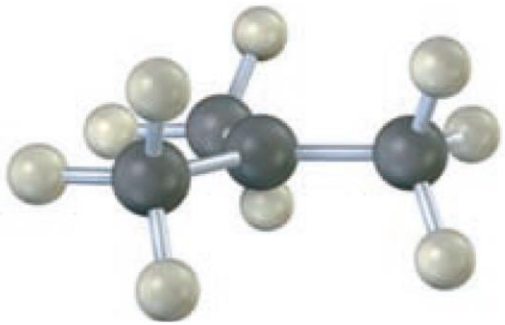
(c) $CH_3CH_2CHCH_2CH_2CH_3$ (Br)

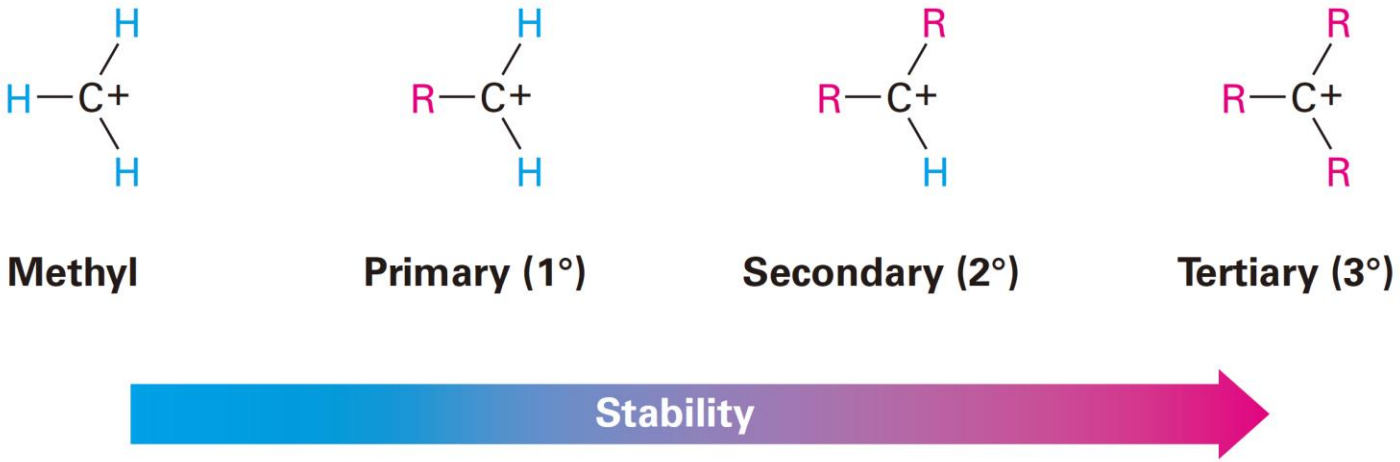
(d) 

7.9 碳正离子的稳定性

- 超共轭效应在有机化学中是指一个σ键里的电子和一个临近的半满或全空的非键p轨域或反键的π轨域或全满的π轨域之间的相互作用，该相互作用能够使整个体系变得更稳定。







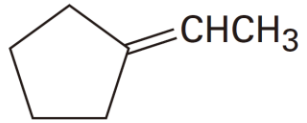
7.9 碳正离子的稳定性

- 课堂练习

Problem 7.18

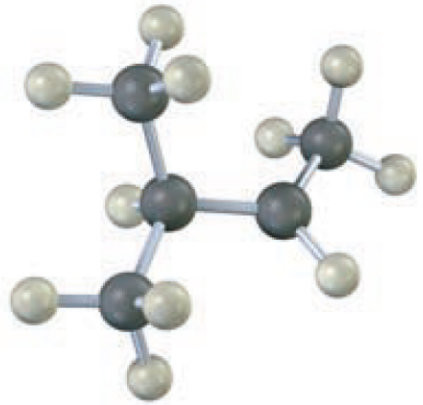
Show the structures of the carbocation intermediates you would expect in the following reactions:

(a) $CH_3CH_2C(CH_3)=CHCHCH_3$ $\xrightarrow{HBr}$?

(b)  $\xrightarrow{HI}$?

Problem 7.19

Draw a skeletal structure of the following carbocation. Identify it as primary, secondary, or tertiary, and identify the hydrogen atoms that have the proper orientation for hyper-conjugation in the conformation shown.



7.10 哈蒙德假说

- 哈蒙德假说(Hammond's Postulate)是有机化学中根据过渡态理论而产生的假说。
- 内容：如果化学反应中过渡态和反应物(或生成物)能量近似则结构近似，即中间态和反应物与产物中能量较高（较不稳定）的一个结构近似。

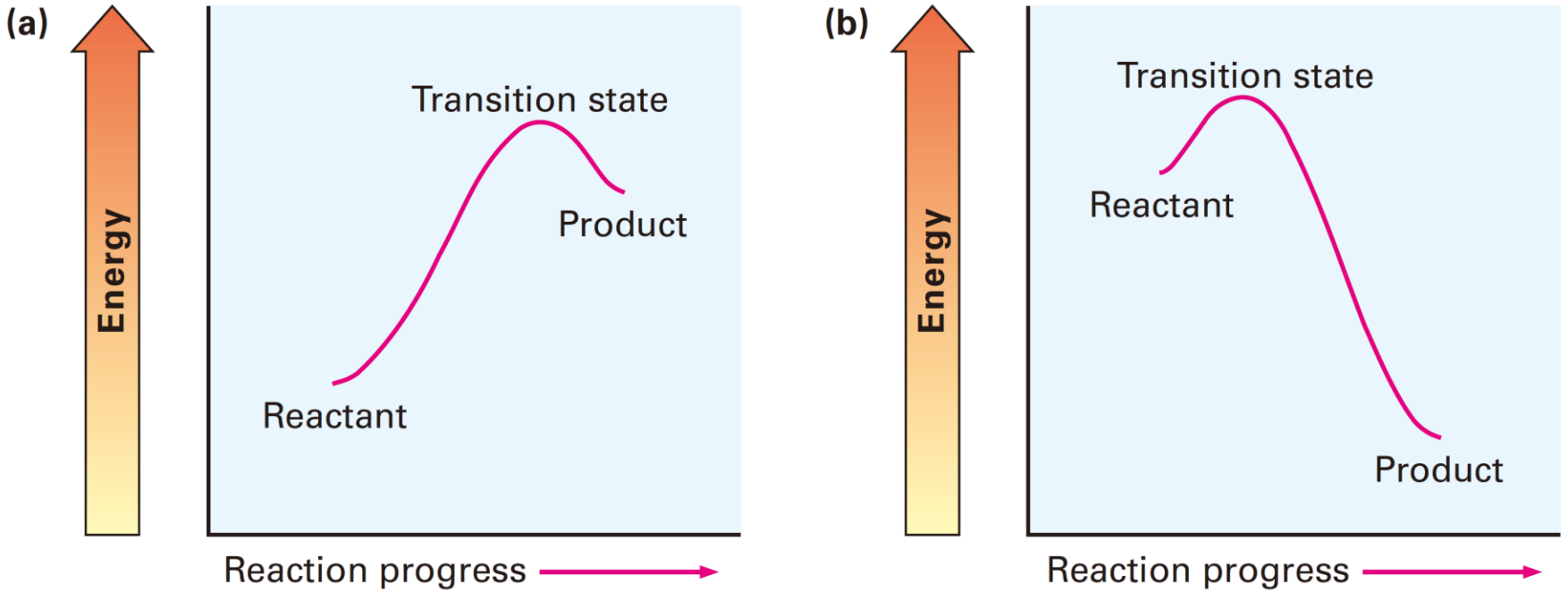
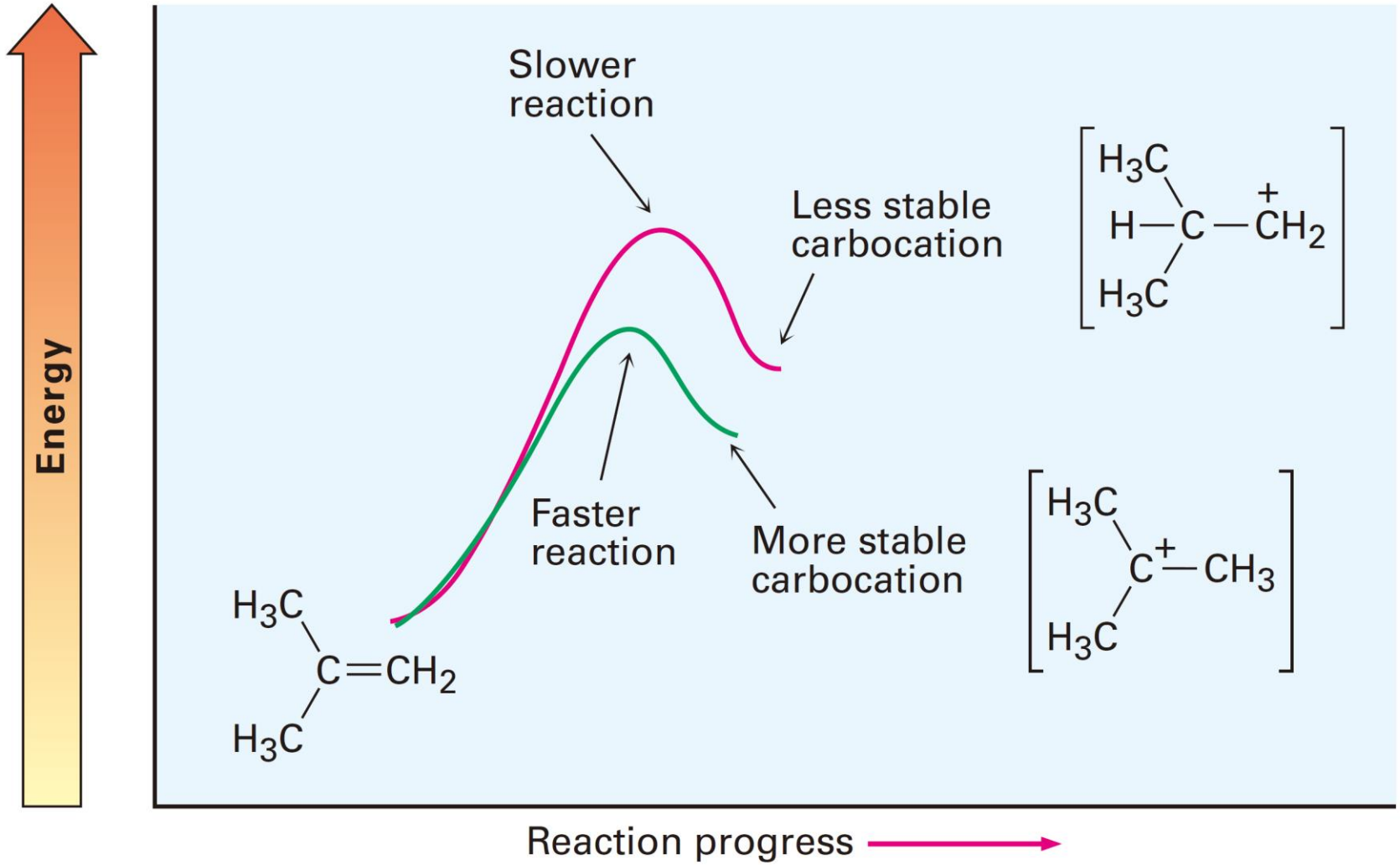


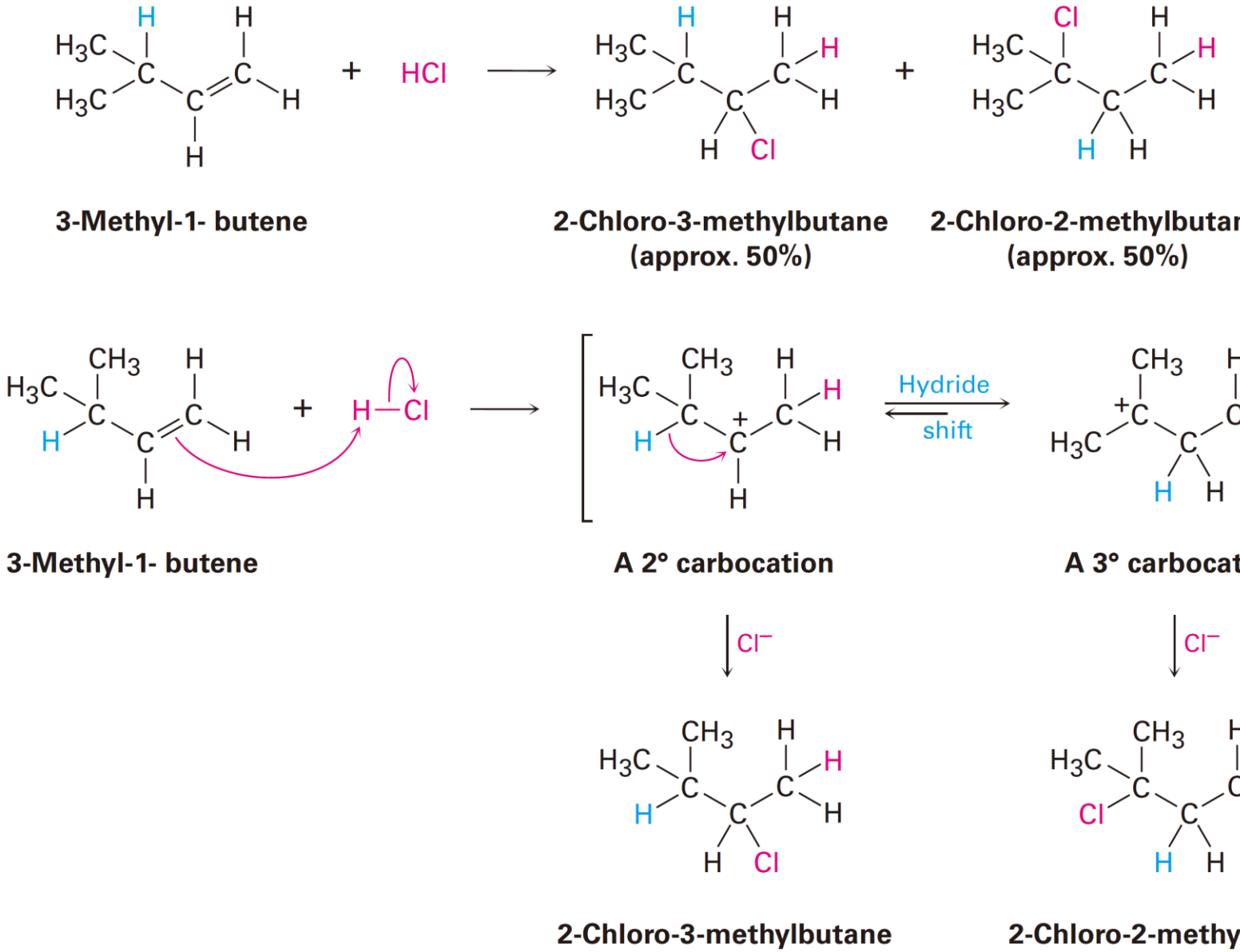
Figure 7.14 Energy diagrams for endergonic and exergonic steps. **(a)** In an endergonic step, the energy levels of transition state and *product* are closer. **(b)** In an exergonic step, the energy levels of transition state and *reactant* are closer.

7.10 哈蒙德假说

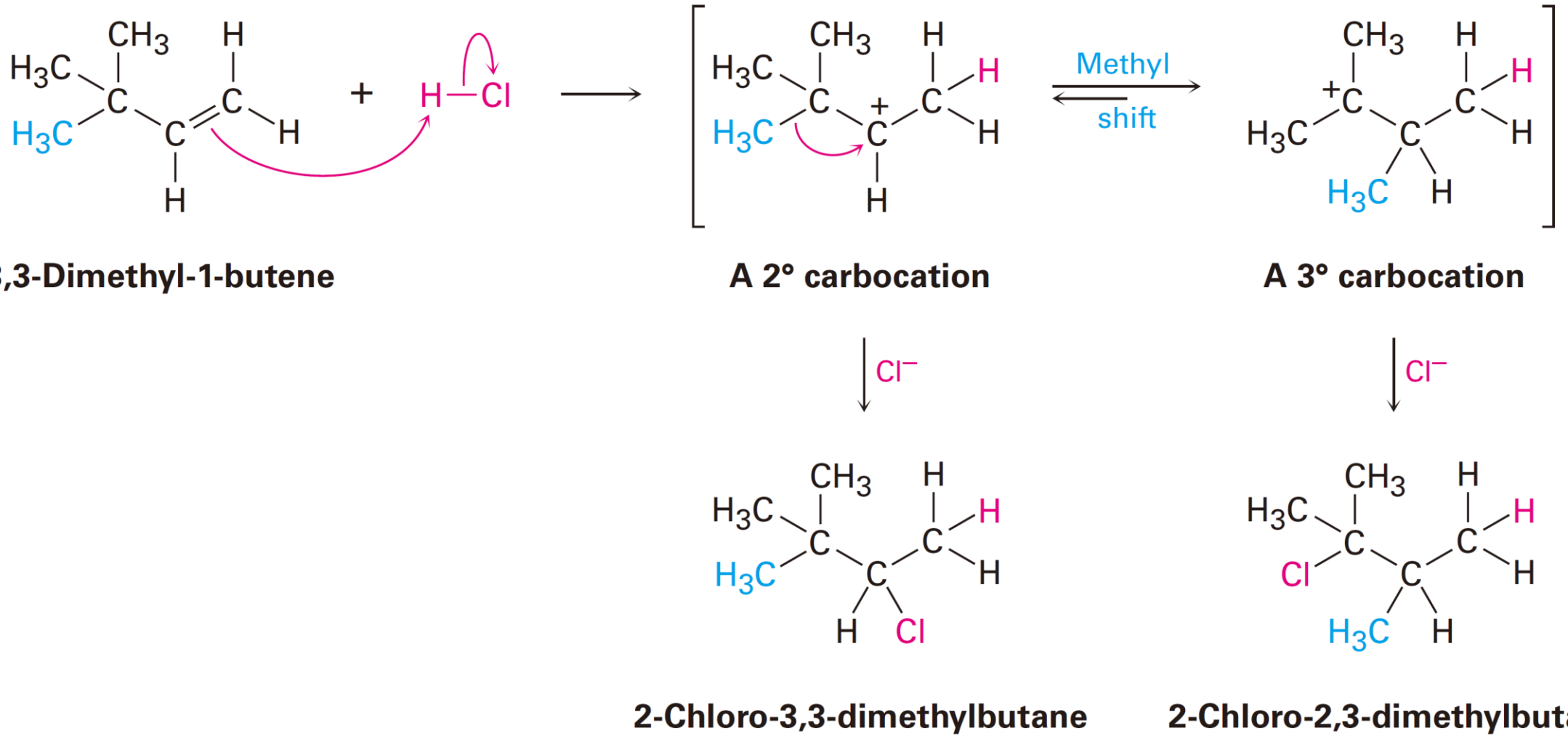
- 哈蒙德假说的应用



7.11 碳正离子重排


3-Methyl-1- butene
HCl
2-Chloro-3-methylbutane
(approx. 50%)
2-Chloro-2-methylbutane
(approx. 50%)
3-Methyl-1- butene
A 2° carbocation
Hydride
shift
A 3° carbocation
Cl⁻
Cl⁻
2-Chloro-3-methylbutane
2-Chloro-2-methylbutane

7.11 碳正离子重排

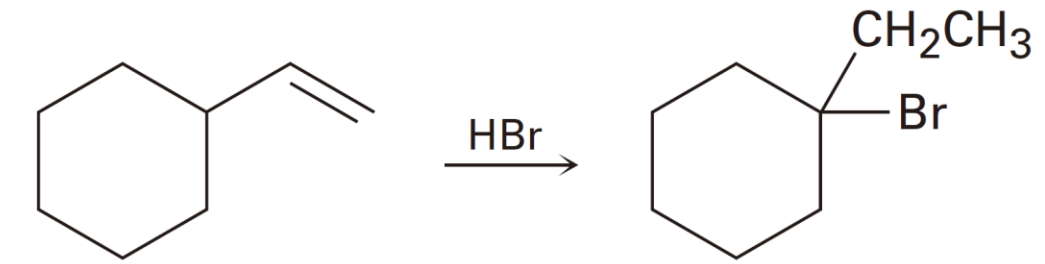

CH3
H
H3C
C
C
H3C
C
H
H
+
H—Cl
Methyl
shift
+
Cl−
Cl−
Cl
3,3-Dimethyl-1-butene
A 2° carbocation
A 3° carbocation
2-Chloro-3,3-dimethylbutane
2-Chloro-2,3-dimethylbutane

7.11 碳正离子重排

- 课堂练习

Problem 7.21

On treatment with HBr, vinylcyclohexane undergoes addition and rearrangement to yield 1-bromo-1-ethylcyclohexane. Using curved arrows, propose a mechanism to account for this result.



Vinylcyclohexane **1-Bromo-1-ethylcyclohexane**

作业

- 7.50, 7.54, 7.55, 7.56, 7.62, 7.64