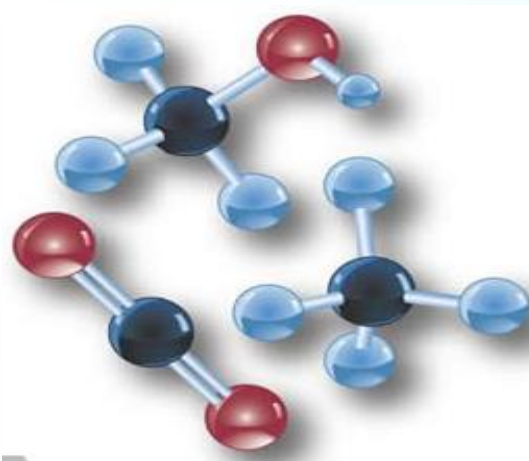


Organic Chemistry





Chapter 5

Organic Compounds

—Alkene



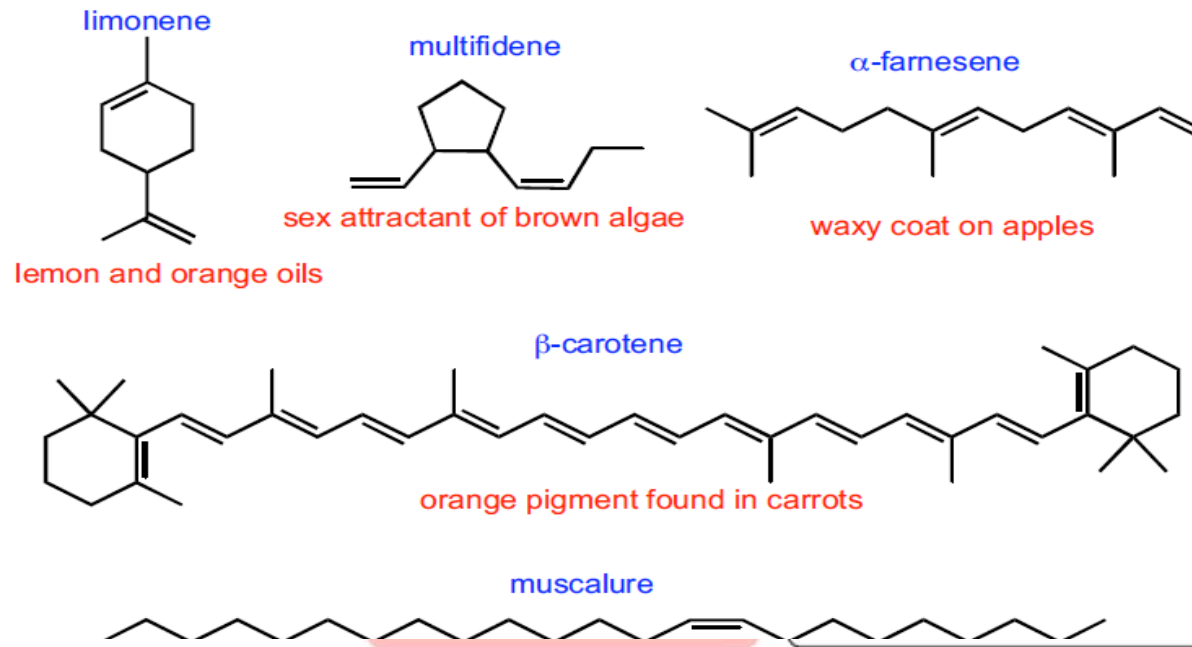
Outline:

- 1. What are the structures and shapes of alkenes?**
- 2. How do we name alkenes?**
- 3. What are the characteristic reactions of alkenes?**
- 4. What are the mechanisms of electrophilic additions to alkenes?**
- 5. How can an alkene be reduced to an alkane?**

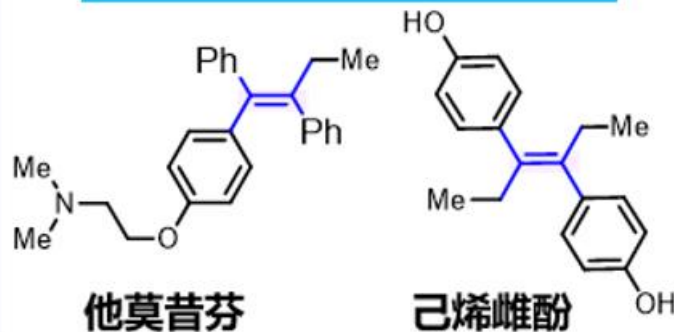


1. What are the structures and shapes of alkenes?

含有碳碳重键($C=C$ 或 $C\equiv C$)的开链烃称为不饱和烃。



全取代烯烃药物分子

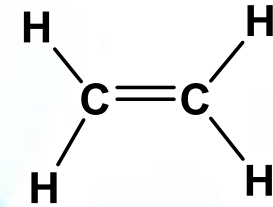
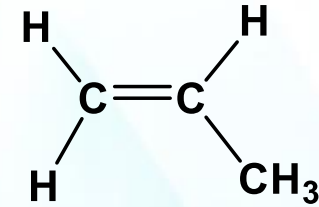


视觉循环的本质——烯烃光异构行为

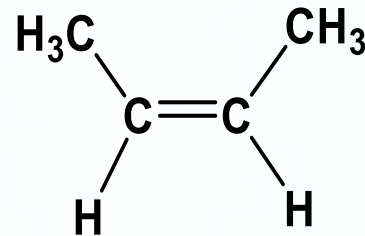


All alkenes with just one double bond fit the **general formula C_nH_{2n}** in which n is the number of carbons in the chain.

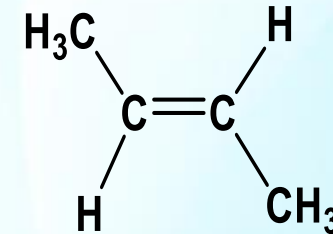
Ethene	C_2H_4	$CH_2=CH_2$
Propene	C_3H_6	$CH_2=CHCH_3$
1-Butene	C_4H_8	$CH_2=CHCH_2CH_3$
2-Butene	C_4H_8	$CH_3CH=CHCH_3$



Cis-trans isomerism



cis-Butene



trans-Butene

(1) Calculating the Degrees of Unsaturation



Degrees of unsaturation = number of rings and/or multiple bonds



1 degree of unsaturation = 1 rings or 1 double bond

2 degree of unsaturation = 2 double bonds, 2 rings,

1 ring + 1 double bond, or 1 triple bond

Example: C_6H_{10} (fully saturated would be C_6H_{14})

$14 \text{ H} - 10 \text{ H} = 4$ hydrogen atoms = 2 H_2 (pairs of hydrogen atoms)

= 2 degrees of unsaturation

If molecular formula contains:

1) Halogen (F, Cl, Br, I)-**add number** of halogens to number of **hydrogen atoms**

$\text{C}_4\text{H}_6\text{Br}_2$ is equivalent to C_4H_8 , degrees of unsaturation =1

2) Oxygen---**ignore it!**

$\text{C}_5\text{H}_8\text{O}$ is equivalent to C_5H_8 , degrees of unsaturation =2

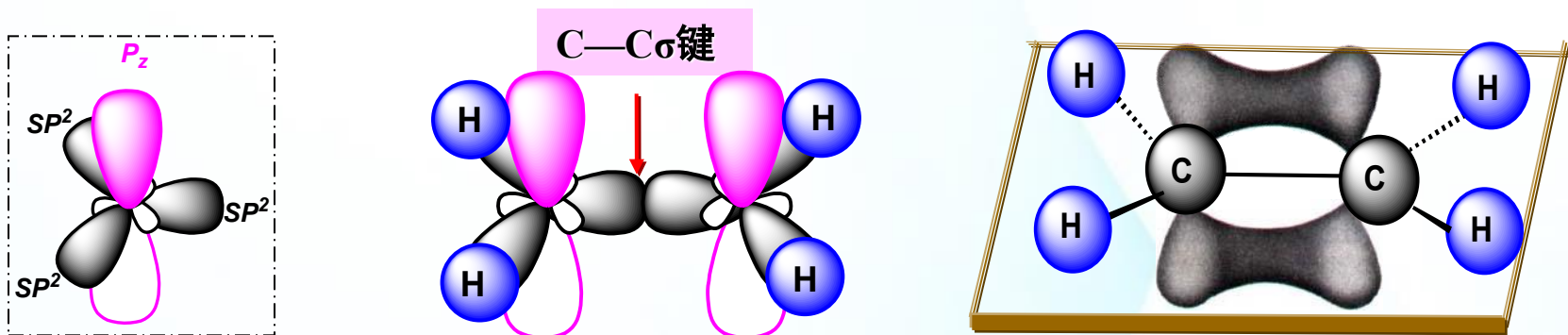
3) Nitrogen---**subtract number** of nitrogen atoms from number of **hydrogen atoms**

$\text{C}_5\text{H}_9\text{N}$ is equivalent to C_5H_8 , degrees of unsaturation =2



(2) Structure

C_2H_4 中，C采取 sp^2 杂化，形成三个等同的 sp^2 杂化轨道：



π 键的不可旋转性：打开 π 键约需要 268kJ/mol 能量，因而室温下无法旋转，由此产生**顺反异构体**。





① π 键电子云流动性大, 受核束缚小, 易极化。

② π 键键能小, 不如 σ 键牢固。

碳碳双键键能为611KJ/mol,

碳碳单键键能为347JK/mol,

π 键键能为 $611-347=264\text{K/mol}$

$\therefore$ π 键易断裂、易发生化学反应。

问题: 根据烯烃的结构,它应具有怎样的化学性质?

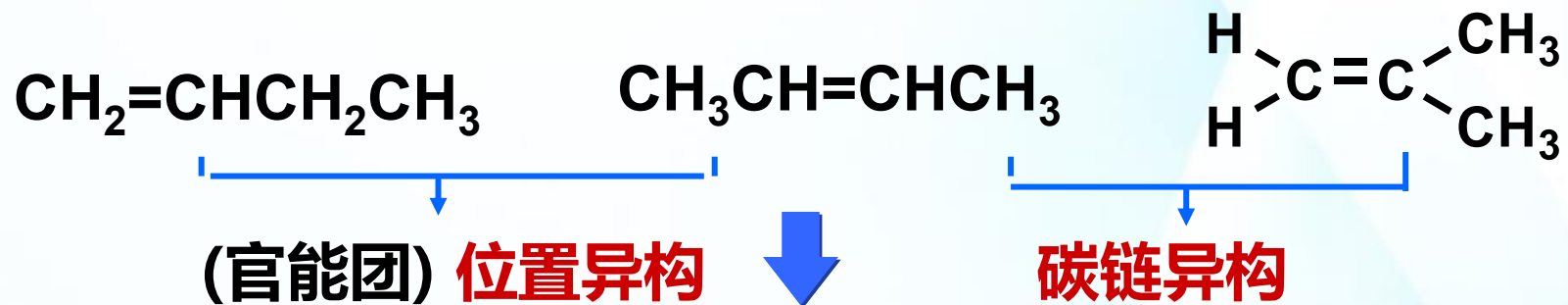
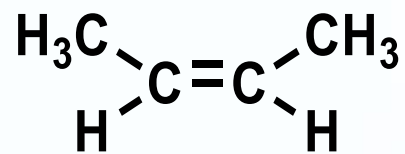
③ π 键不能自由旋转

顺反异构?



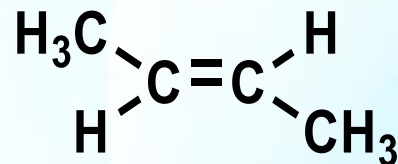
Bond rotation round a C=C bond is not possible and isomers are possible depending on the substituents present.

烯烃异构 { 碳链异构
官能团位置异构 (双键位置不同引起的)
顺反异构 } 构造异构



顺-2-丁烯

mp. -106°C , b.p 1°C



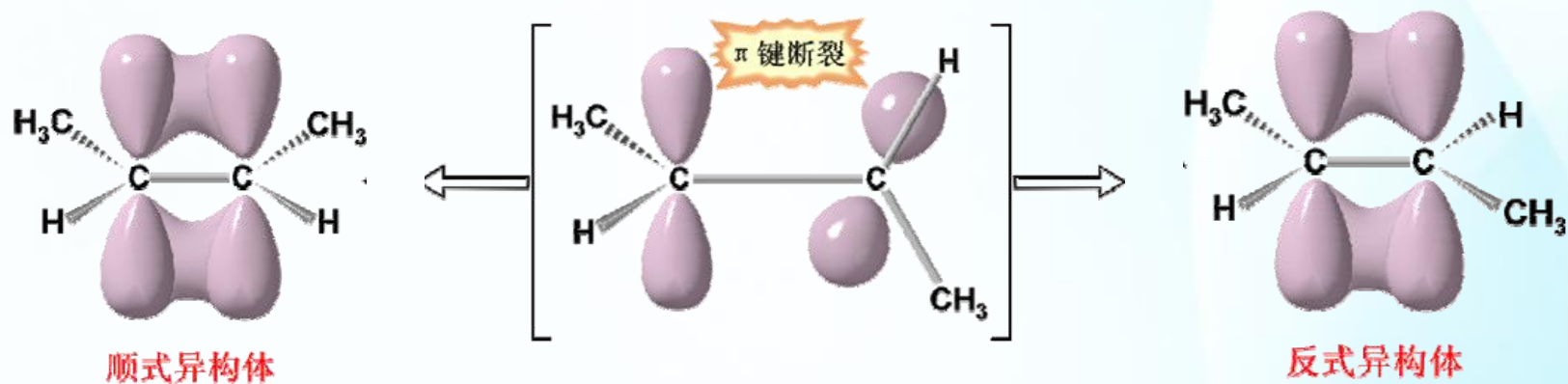
反-2-丁烯

mp. -139°C , b.p 4°C



立体异构

- 由于**双键不能自由旋转**，当双键的两个碳原子各连接不同的原子或基团时，可能产生不同的异构体。

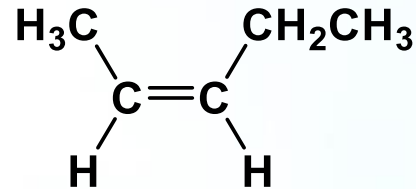


戊烯：6种异构体



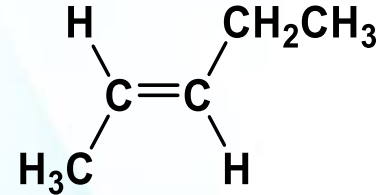
戊-1-烯

Pent-1-ene



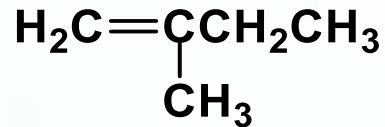
顺-戊-2-烯

cis-pent-2-ene



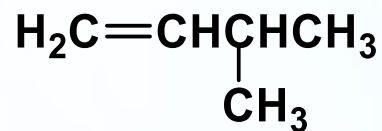
反-戊-2-烯

trans-pent-2-ene



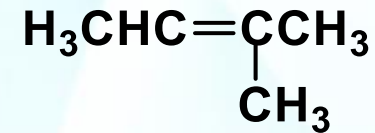
2-甲基丁-1-烯

2-methylbut-1-ene



3-甲基丁-1-烯

3-methylbut-1-ene



2-甲基丁-2-烯

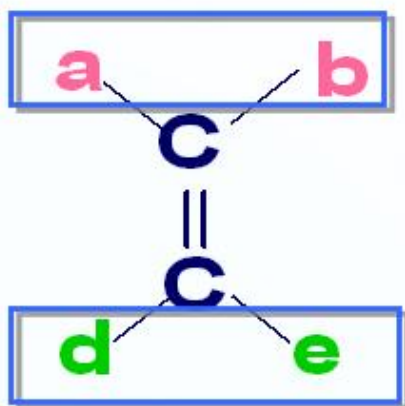
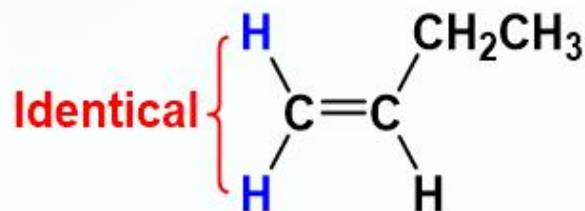
2-methylbut-2-ene

Stereoisomers: *cis*-Butene and *trans*-butene have the same constitution but differ in the arrangement of their atoms in space, isomers as such are classified as stereoisomers, and the term *cis* and *trans* specify the configuration of the double bond.



形成顺反异构的条件:

- ①分子中有限制碳碳 σ 键旋转的因素（碳碳双键或碳环）；
- ②每个双键碳原子必须连接两个不同的原子或原子团。



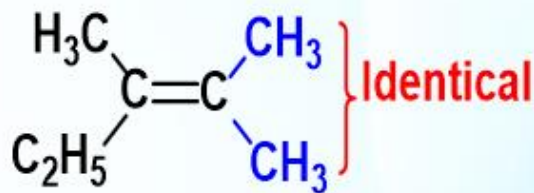
无顺反异构

● $a=b$ 或 $d=e$ 无顺反异构

● $a \neq b$ 且 $d \neq e$ 有顺反异构

✓ $a=d$ 或 $b=e$ 为顺式构型

✓ $a=e$ 或 $b=d$ 为反式构型



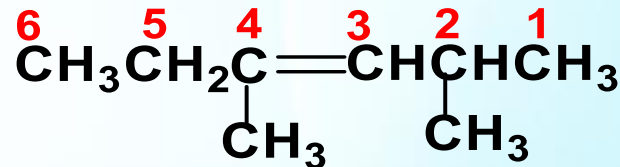
无顺反异构



- ① 要选择含有C=C的最长碳链为主链;
- ② 编号从最距离双键最近的一端开始, 并用阿拉伯数字表示双键的位置;
- ① The longest continuous chain that includes the double bond forms the base name of the alkene;
- ② The chain is numbered in the direction that gives the doubly bonded carbons their lower numbers.



Hex-2-ene

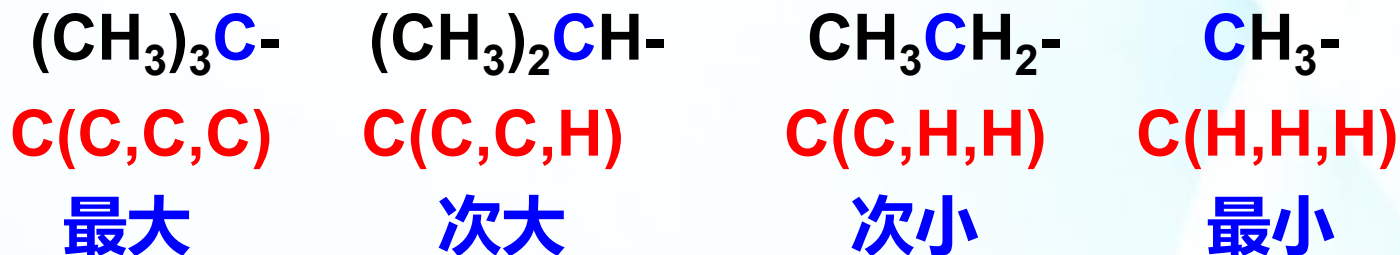


2,4-Dimethylhex-3-ene

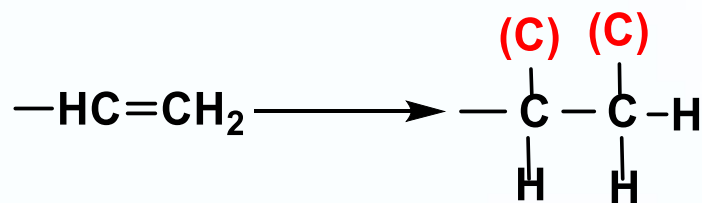
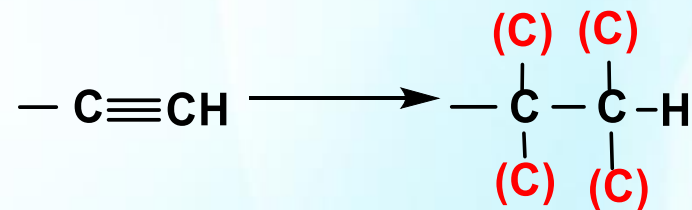


②若几个取代基中与主链相连的原子相同时，则比较与该原子相连的后面的原子，依次外推，直到比较出为止。

如： $-\text{CH}_2\text{CH}_3 > -\text{CH}_3$ $-\text{CH}_2\text{Cl} > -\text{CH}_2\text{F}$ $-\text{CH}_2\text{OCH}_3 > -\text{CH}_2\text{OH}$



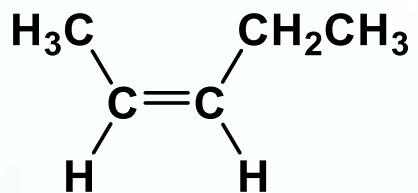
③若取代基中的一个原子以双键或三键与其他原子相连时，则把它看作与该原子二次或三次相连。



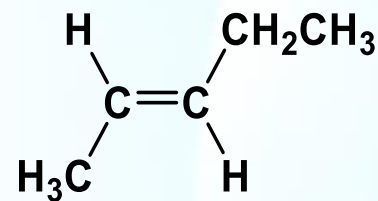
系统命名法

顺式：双键碳原子上**两个相同的原子或基团**处于双键同侧

反式：双键碳原子上**两个相同的原子或基团**处于双键反侧



顺-戊-2-烯
cis-pent-2-ene



反-戊-2-烯
trans-pent-2-ene

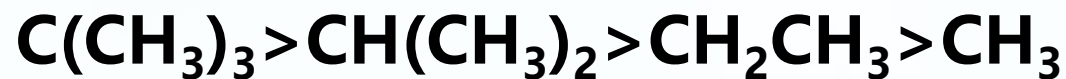
③ Z、E 标记法

次序规则

- 原子序数越大越优先，同位素原子按质量大小排，孤电子对最小



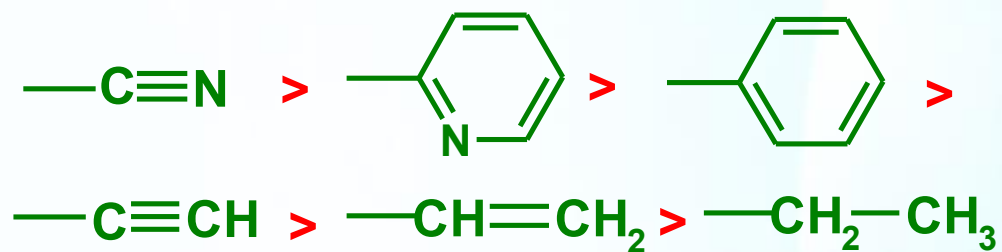
- 若与双键直接相连的原子的原子序数相同，则从此原子起向外比较，依次类推，直到解决优先次序



③ Z、E 标记法

次序规则

➤ 不饱和键中，三键拆成三个单键，双键拆成两个单键

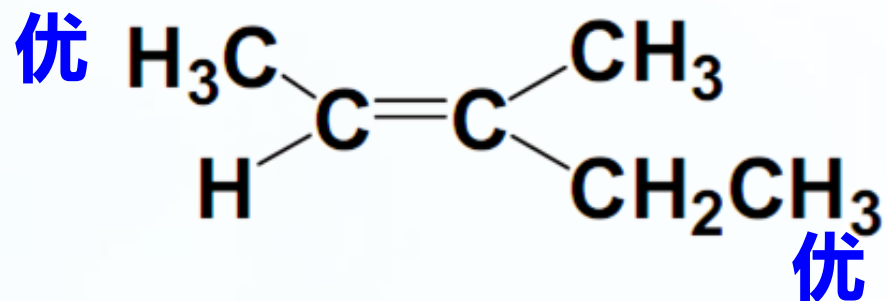


系统命名法

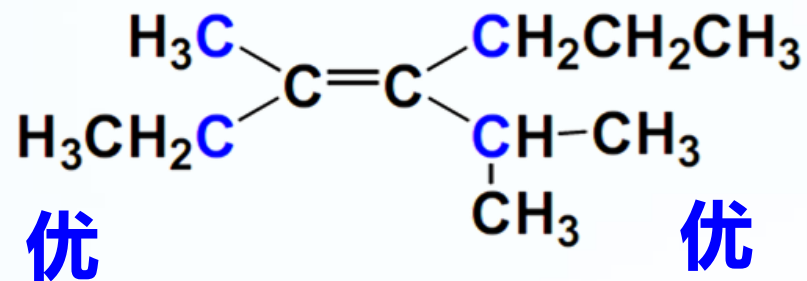
③ Z、E 标记法

E式：双键碳原子上两个较优基团或原子处于双键**异侧**。

Z式：双键碳原子上两个较优基团或原子处于双键**同侧**。

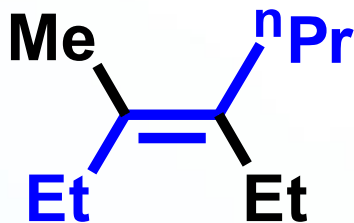


(E)-3-甲基戊-2-烯

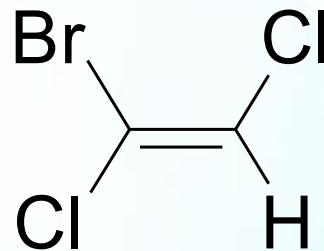


(Z)-3-甲基-4-异丙基庚-3-烯

➤ Z式不一定是顺式；E式不一定是反式



顺-3-甲基-4-乙基-3-庚烯
(E)-3-甲基-4-乙基-3-庚烯

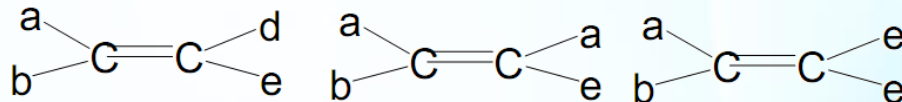


反-1,2-二氯-1-溴乙烯
(Z)-1,2-二氯-1-溴乙烯

产生顺反异构的条件

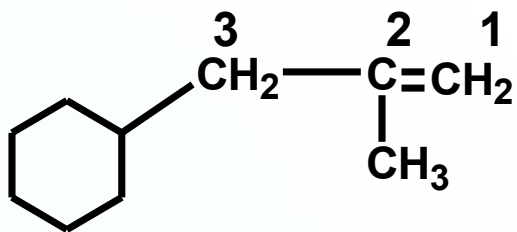
- 分子中有限制旋转的因素存在
- 每个不能自由旋转的碳原子上必须连有两个不同的原子或基团

顺反异构的类型



- 双键化合物的顺反异构
- 脂环化合物的顺反异构

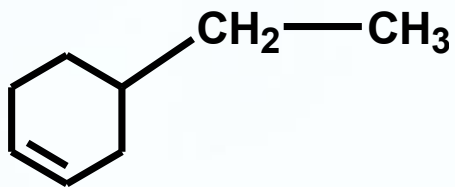
烯烃命名实例



双键在链上，链为母体，环为取代基
双键在环上，以环为母体，称环某烯

2-甲基-3-环己基-1-丙烯

2-methyl-3-cyclohexylprop-1-ene



4-乙基环己烯

4-ethylcyclohex-1-ene

万能命名公式：(E/Z)-取代基1-取代基2-碳链词干-双键位置-ene



一、主链选定规则

- **核心原则**：必须选取**包含C=C双键的最长碳链**作为母体主链，不含双键的碳链一律不作为主链
- **等长链取舍**：两条等长链均含双键时，优先选择**取代基数量更多**的碳链
- **环烯烃**：直接以碳环为母体，双键为命名核心，不额外开链



二、碳链编号规则（最关键，扣分高频点）

- **编号起点**：从**距离双键最近**的一端开始编号，核心目标是让**双键碳原子编号最小**
- **单烯烃标注**：只标记双键两端**编号更小**的碳原子位置
- **环烯烃强制规则**：双键两端碳原子**必须编为1号、2号**，后续再让取代基编号尽可能小
- **优先级**：双键编号优先于所有取代基编号，不可颠倒顺序



三、母体标准格式（严禁老式写法）

- **单烯烃**：碳数词干-双键位置-ene ☒ 例：pent-2-ene（禁止老式2-pentene）
- **多烯烃**：碳数词干-双键1位置,双键2位置-diene/triene ☒ 例：buta-1,3-diene
- **环烯烃**：cyclo-碳数词干-双键位置-ene ☒ 例：cyclohex-1-ene（不可省略双键位置）



四、取代基命名规则

- 取代基后缀统一加：-yl (甲基methyl、乙基ethyl、环己基cyclohexyl、卤原子同烷基)
- 书写顺序：严格按照英文字母顺序排列，忽略di-、tri-等重复前缀和位置数字
- 相同取代基：加di- (二)、tri- (三)，标注全部对应位置
- 书写格式：位置-取代基-位置-取代基-母体，全程用短杠连接



五、几何异构规范 (现代IUPAC首选)

- 正式命名优先使用E/Z构型，cis/trans仅为俗称，正式考试、论文禁止使用
- 书写格式：(构型)-母体名称，括号右侧必须加短杠
- (Z)-：双键两侧较优基团处于同侧；(E)-：双键两侧较优基团处于异侧



◆ 反面：格式规范+易错提醒+标准示例

💡 一、标点符号铁律（零失误要求）

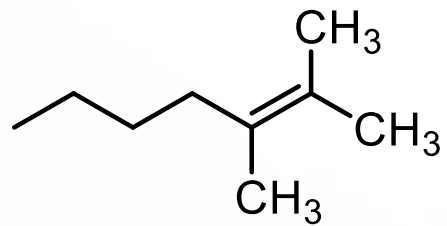
- 数字与英文单词之间：必须加短杠 (-) → 2-methyl ✓, 2methyl ✗
- 多个不同取代基之间：短杠分隔 → 3-cyclohexyl-2-methyl ✓
- E/Z括号后：强制加短杠 → (Z)-pent-2-ene ✓
- 多个位置数字之间：逗号分隔，无空格 → 1,3-diene ✓

💡 二、高频易错避坑提醒

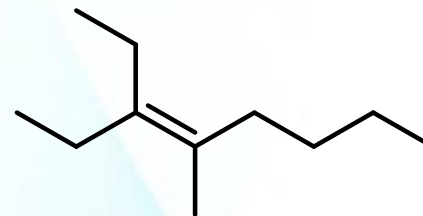
- 禁止老式错位写法：2-butene ✗, 规范写法but-2-ene ✓
- 环烯烃严禁省略双键位置：4-ethylcyclohexene ✗, 规范写法4-ethylcyclohex-1-ene ✓
- 取代基顺序：字母序≠碳链长短，cyclohexyl 排在 methyl 之前
- 多烯烃：词干末尾加a（如buta-、penta-），单烯烃不加

💡 三、标准示例合集（直接套用）

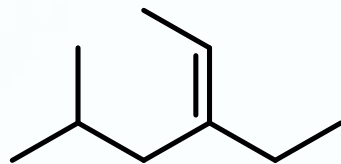
- 2-甲基丁-1-烯 → 2-methylbut-1-ene
- 顺-戊-2-烯（标准Z型）→ (Z)-pent-2-ene
- 2-甲基-3-环己基丙-1-烯 → 3-cyclohexyl-2-methylprop-1-ene
- 4-乙基环己烯 → 4-ethylcyclohex-1-ene
- 1,3-丁二烯 → buta-1,3-diene



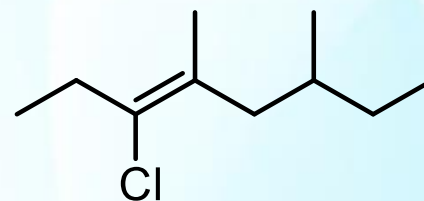
2,3-dimethylhept-2-ene



3-ethyl-4-methyloct-3-ene



(Z)-3-ethyl-5-methylhex-2-ene

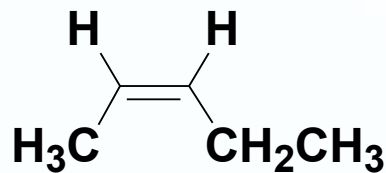


(Z)-3-chloro-4,6-dimethyloct-3-ene



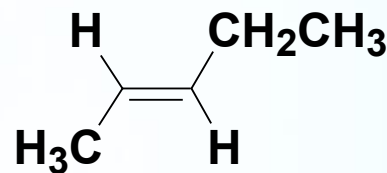
2.1.3 烯烃的物理性质

- 常温常压下，烯烃的沸点、熔点与烷烃相似。
- 末端烯烃（ α -烯烃）的沸点比双键在碳链中间的低。



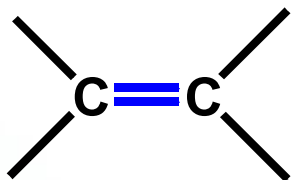
沸 点 36.9°C

熔 点 -151.4 °C

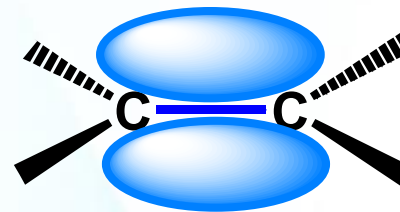


36.6°C

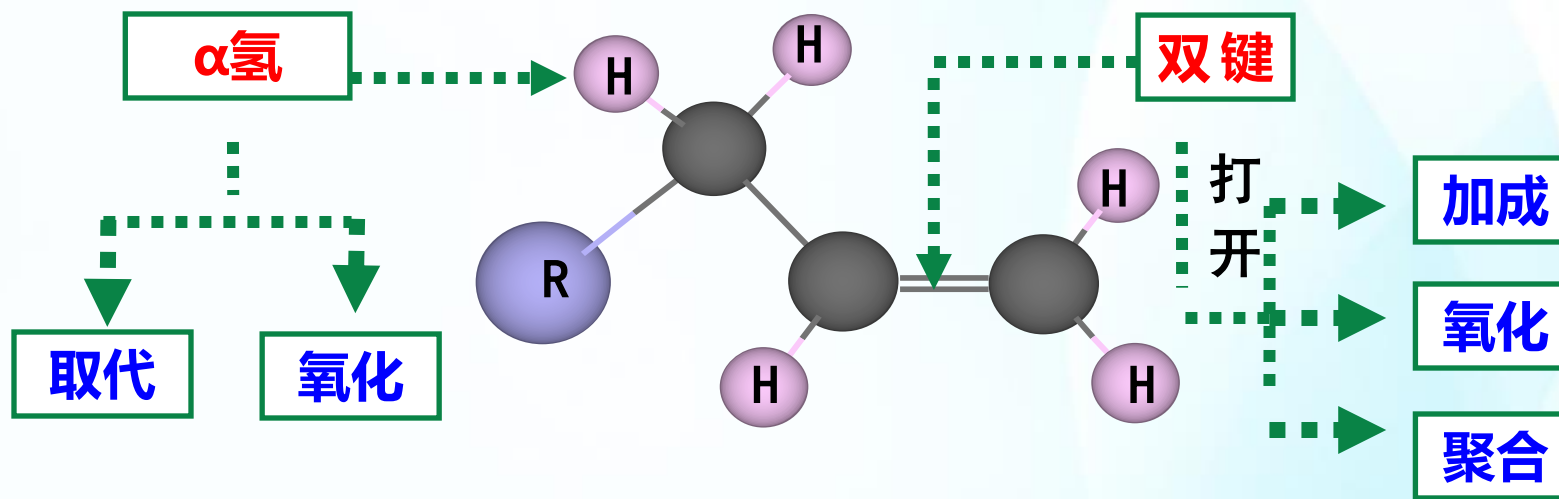
- 136°C



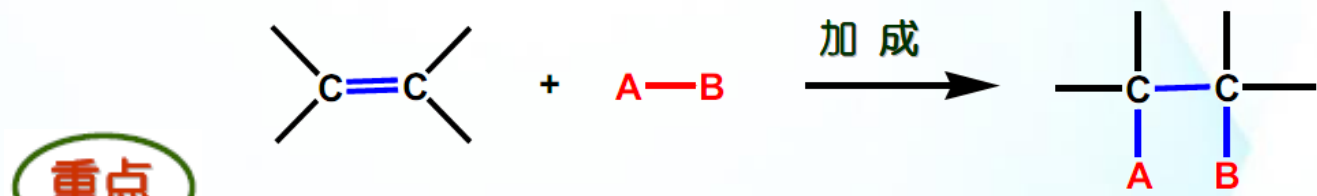
σ 键 -347 kJ / mol
 π 键 -263 kJ / mol



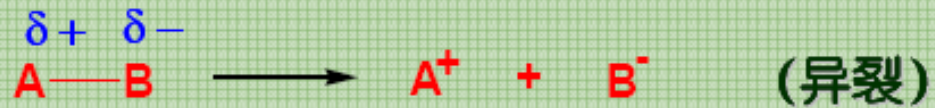
π 电子易参与反应，是电
子供体，有亲核性。



烯烃加成的三种主要的类型



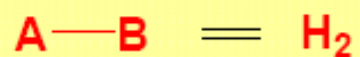
➤ 亲电加成



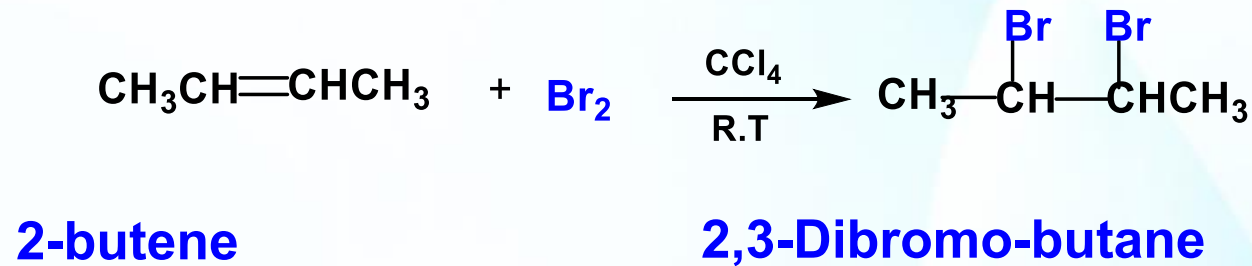
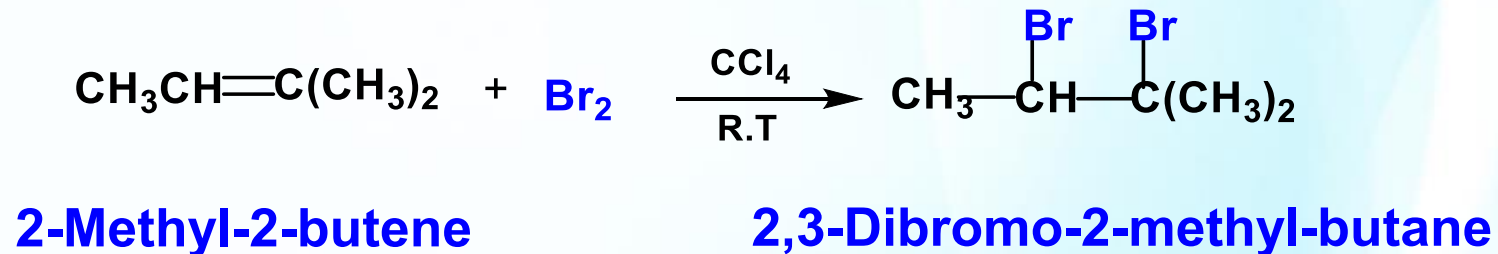
➤ 自由基加成



➤ 催化加氢



A. Halogen Addition





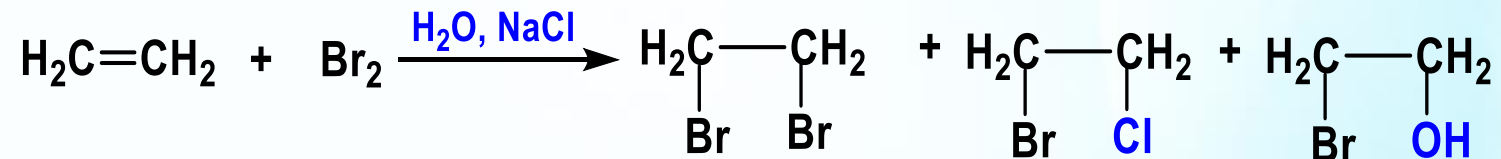
1. 不同的取代乙烯与溴加成的相对反应速率:

$\text{H}_2\text{C}=\text{CHBr}$	$\text{H}_2\text{C}=\text{CH}_2$	$\text{H}_2\text{C}=\text{CHCH}_3$	$\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$	$\text{H}_3\text{CHC}=\text{C}(\text{CH}_3)_2$
0.04	1.0	2.03	5.53	10.4

←
双键上电子云密度减小,
亲电加成反应速率减小
-Br是吸电子基!

→
烷基取代增多, 双键上电子云密度增大,
亲电加成反应速率增大
-CH₃是给电子基!

2. 当体系中存在氯化钠时, 则反应产物为混合物:

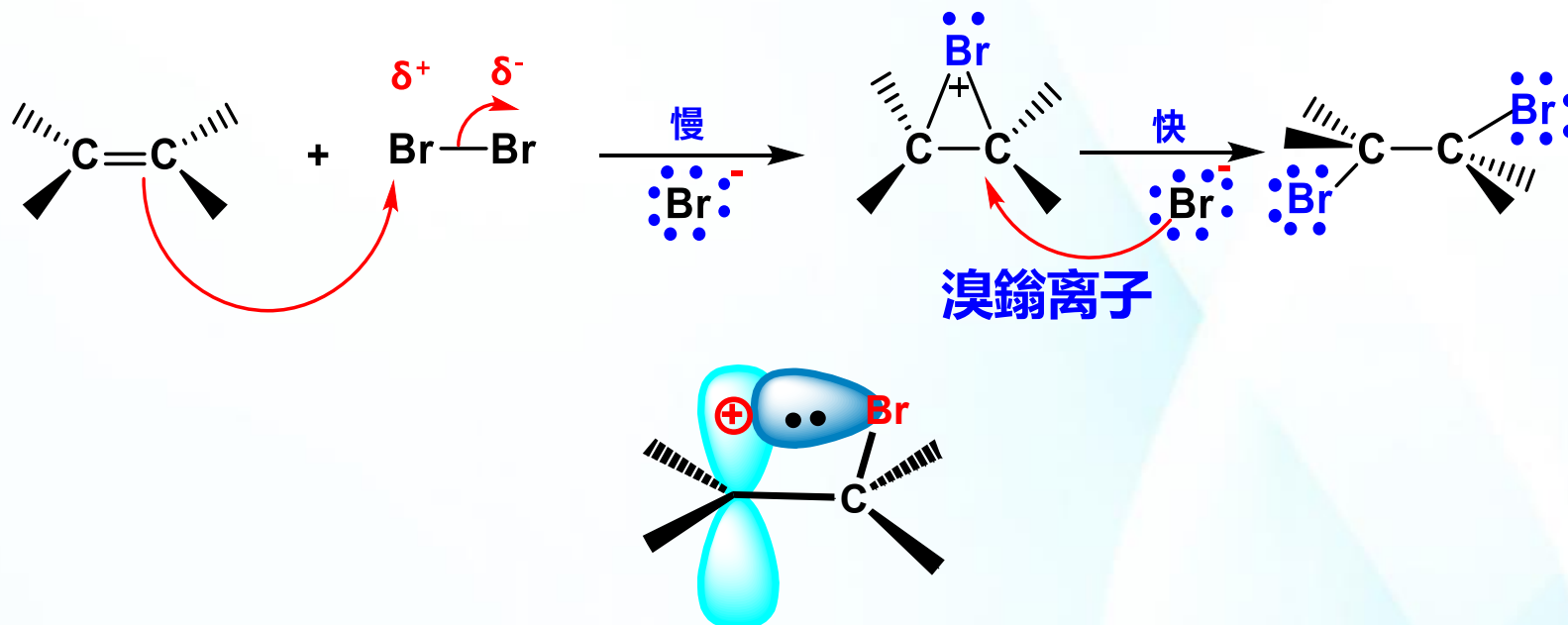


无 $\text{ClCH}_2\text{CH}_2\text{OH}$ 生成! Why?



◆ Mechanism:

反应是分步进行的:



The carbocation intermediate can be **stabilized** by neighboring alkyl groups and the bromine atom.

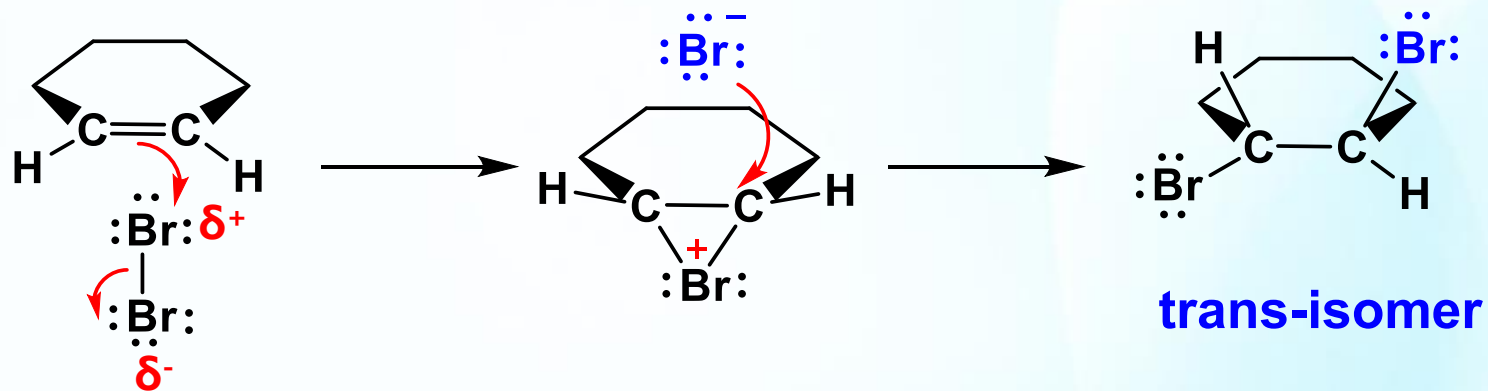
第一步是亲电反应的**速控步骤**;

反式加成。

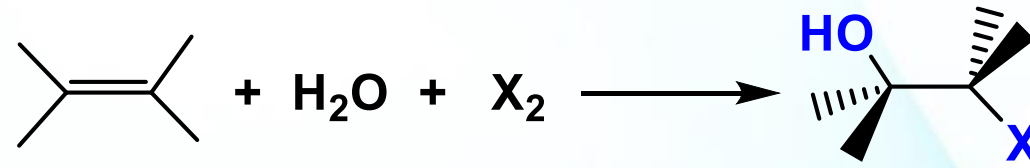
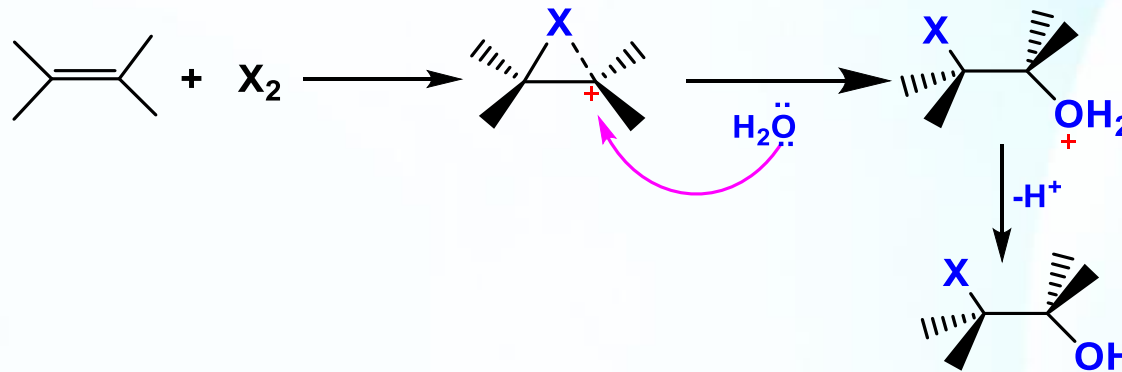
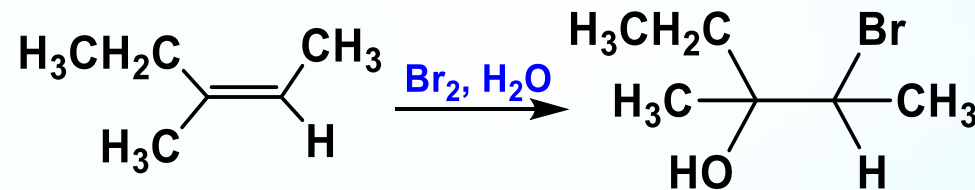
Evidence for the existence of the bromonium ion is provided from the observation that bromine adds to cyclic alkenes in an **anti-stereochemistry**.

In other words, each bromine adds to **opposite faces** of the alkene to produce only the **trans isomer**.

None of the cis isomer is formed.



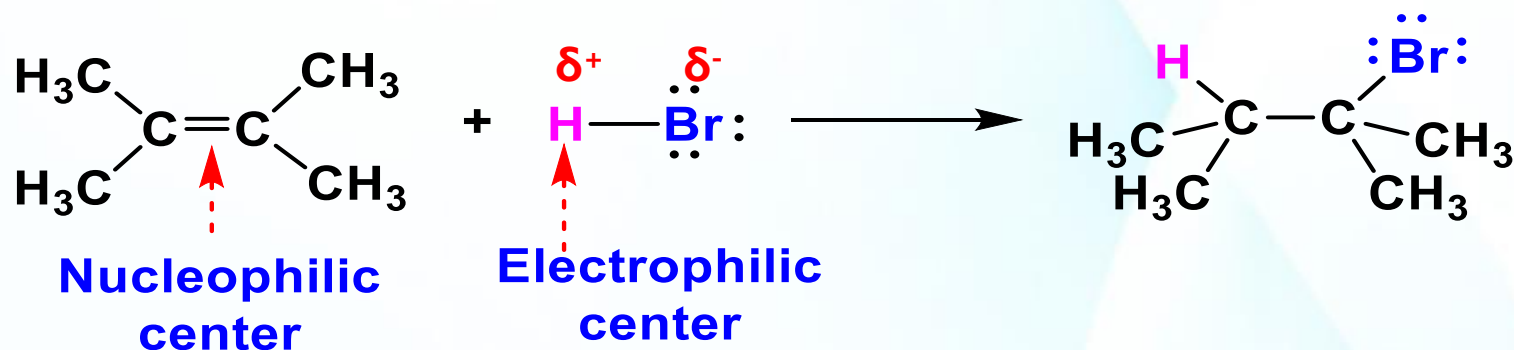
If water is used as a solvent, the hydroxyl group is attached to the more substituted carbon.





B. Addition of Hydrogen Halides

Hydrogen bromide has a polar H-Br bond and so the **hydrogen is an electrophilic center** and **the bromine is a nucleophilic center**.

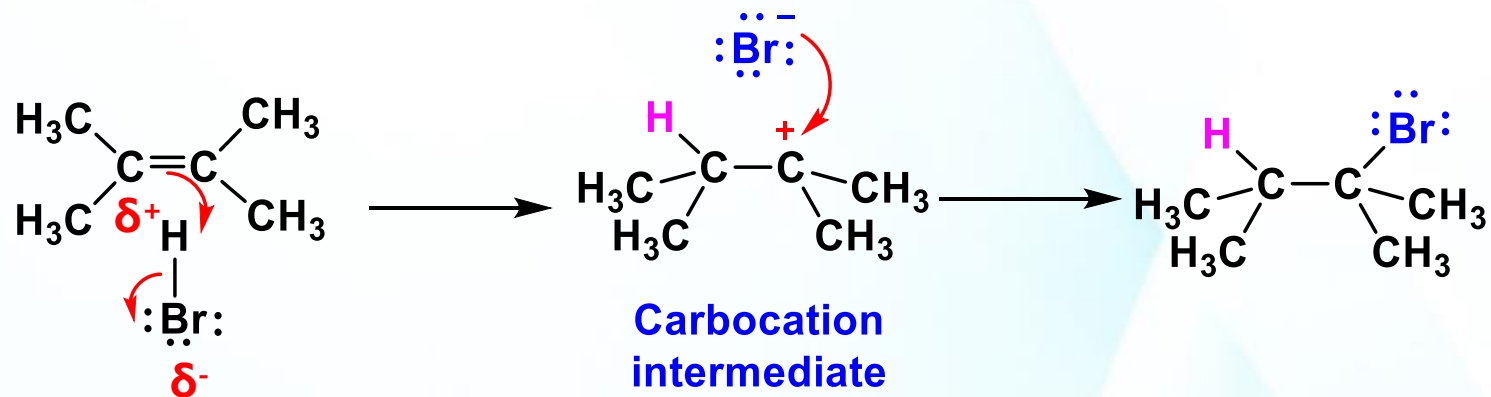


However, halogen atoms are extremely **weak nucleophilic centers** and so this molecule is more likely to react as an electrophile through its **electrophilic hydrogen**.



◆ Mechanism:

The mechanism of electrophilic addition is a two stage process which goes through a **carbocation intermediate**.

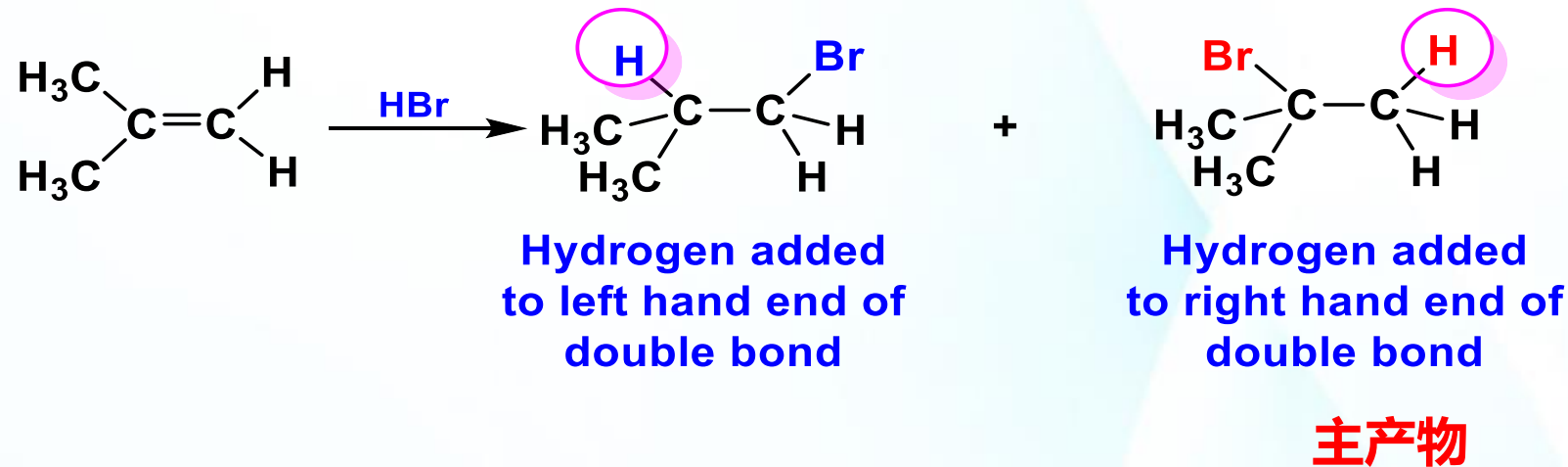


This is known as a carbocation since the positive charge is on a carbon atom.

This structure is known as a reaction intermediate.

It is a reactive species and will not survive very long with the bromide ion in the vicinity.

The addition of a hydrogen halide to an **unsymmetrical alkene** can result in two different products.



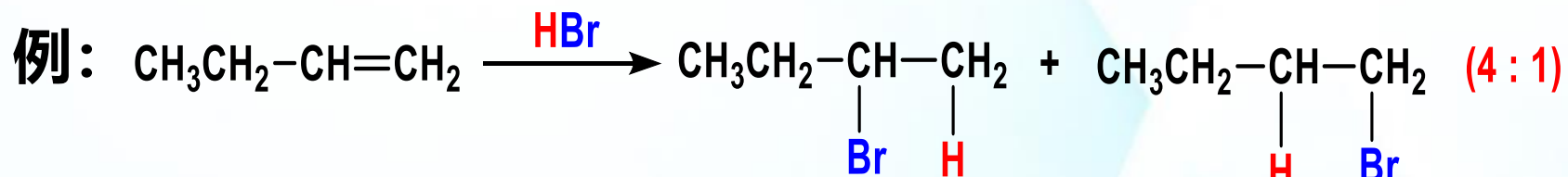
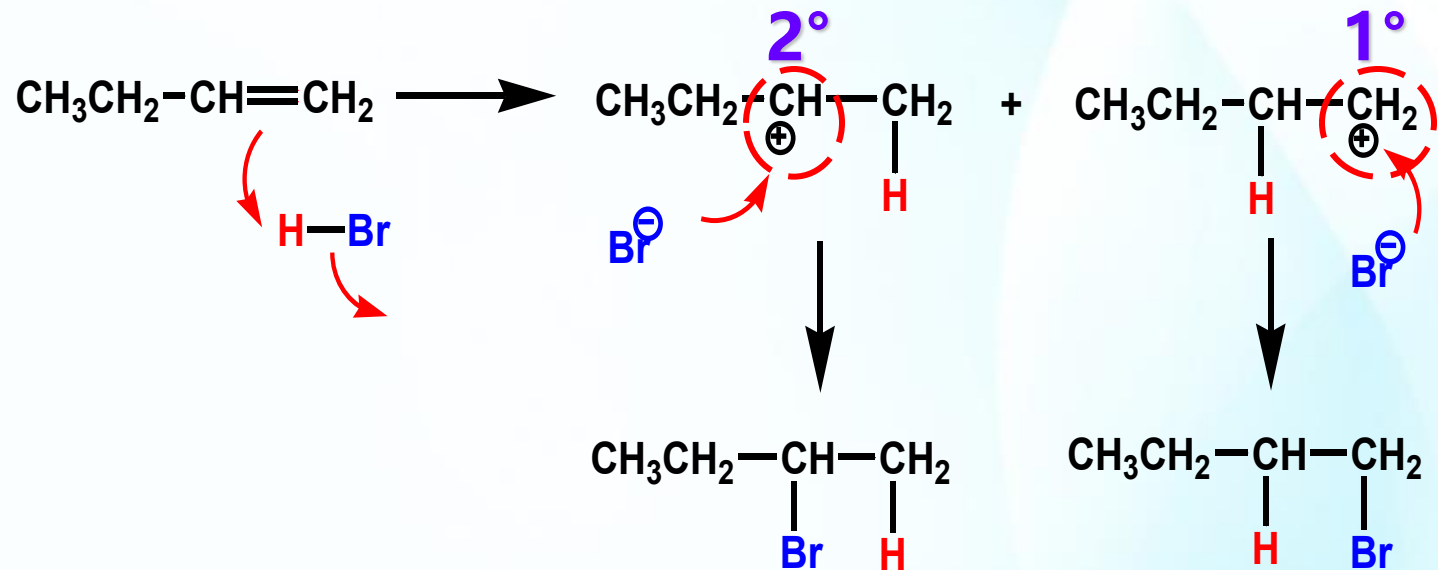
This produces the **more substituted alkyl halide**.

Markovnikov's rule: 不对称不饱和烃进行加成反应时，试剂中带正电的部分主要加到含氢较多的不饱和碳原子上。

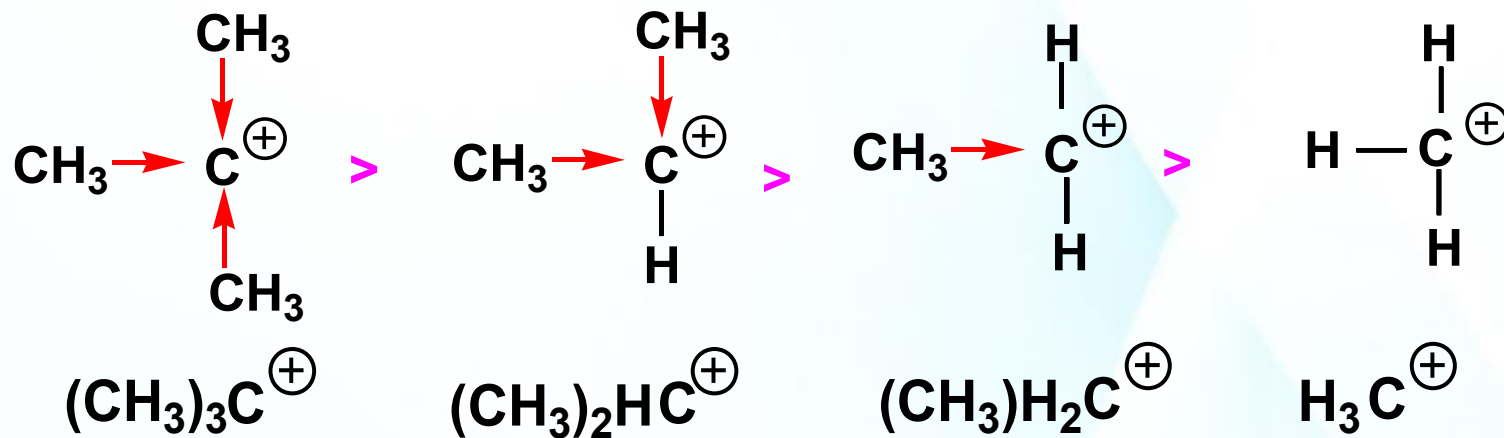


为什么烯烃和炔烃加卤化氢时遵循马氏规则？

由反应中间体正碳离子的稳定性所决定的。



Carbocations are stabilized by induction, hyperconjugation, or delocalization.



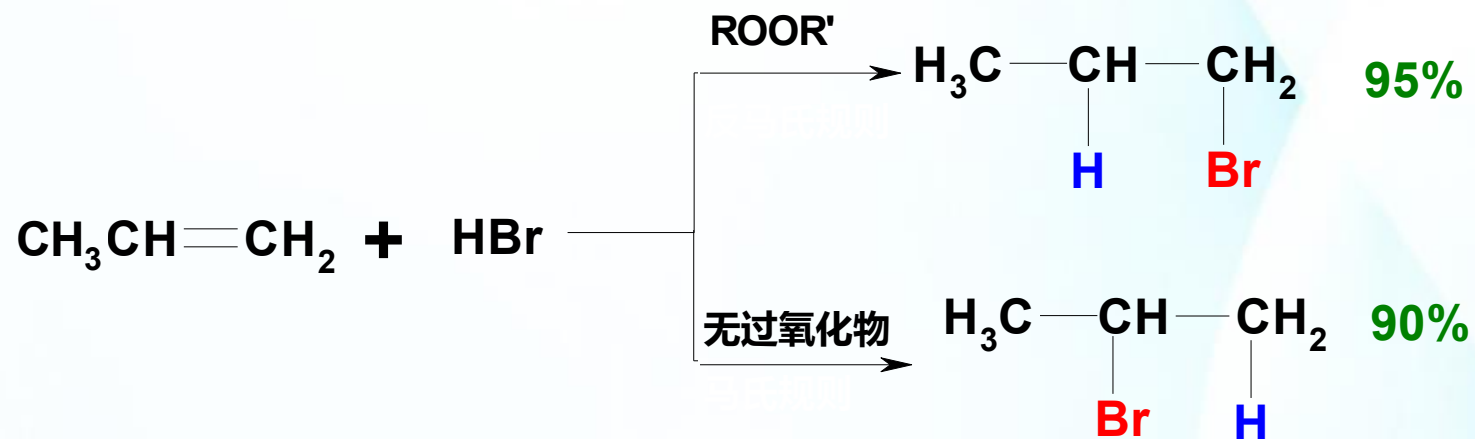
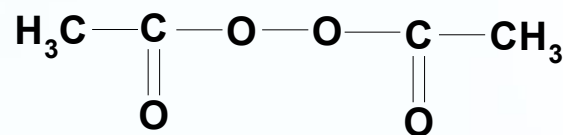
即: $3^\circ \text{C}^{\oplus} > 2^\circ \text{C}^{\oplus} > 1^\circ \text{C}^{\oplus} > \text{H}_3\text{C}^{\oplus}$

Alkyl groups can donate electrons toward a neighboring positive center and this helps to stabilize the ion. The more alkyl groups attached, the greater the stabilizing effect.

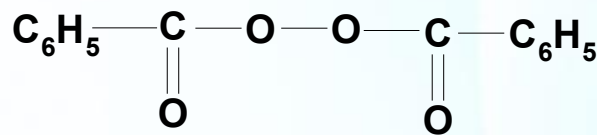


烯烃的自由基加成

在过氧化物存在下，氢原子加在含氢少的碳原子上。注意：只有HBr有此反应



过氧化乙酰

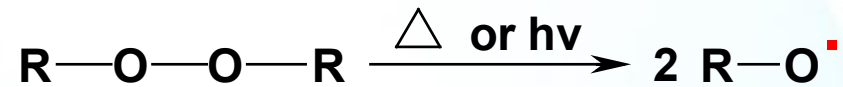
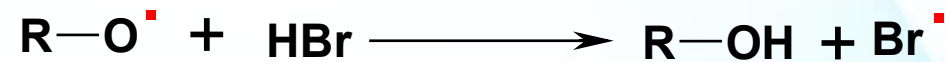


过氧化苯甲酰

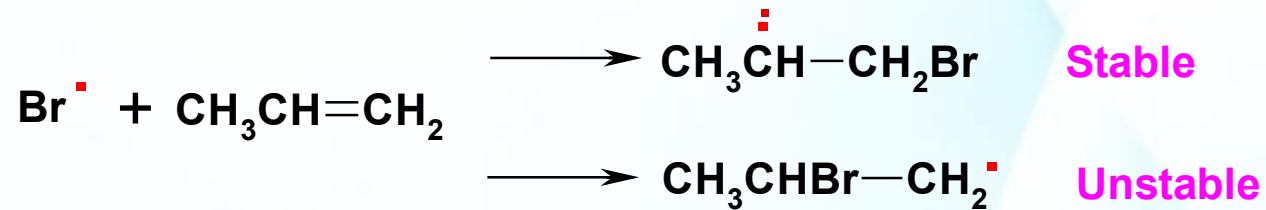
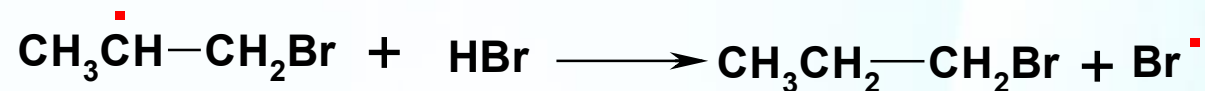
烯烃的自由基加成

反应机理

链引发



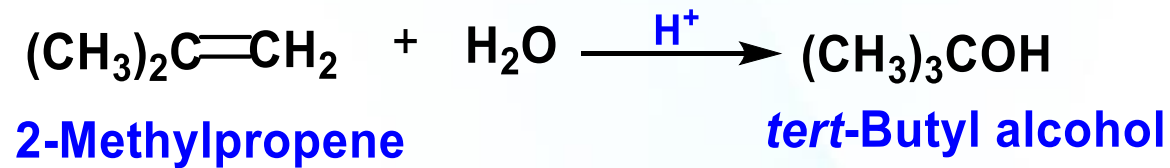
链增长



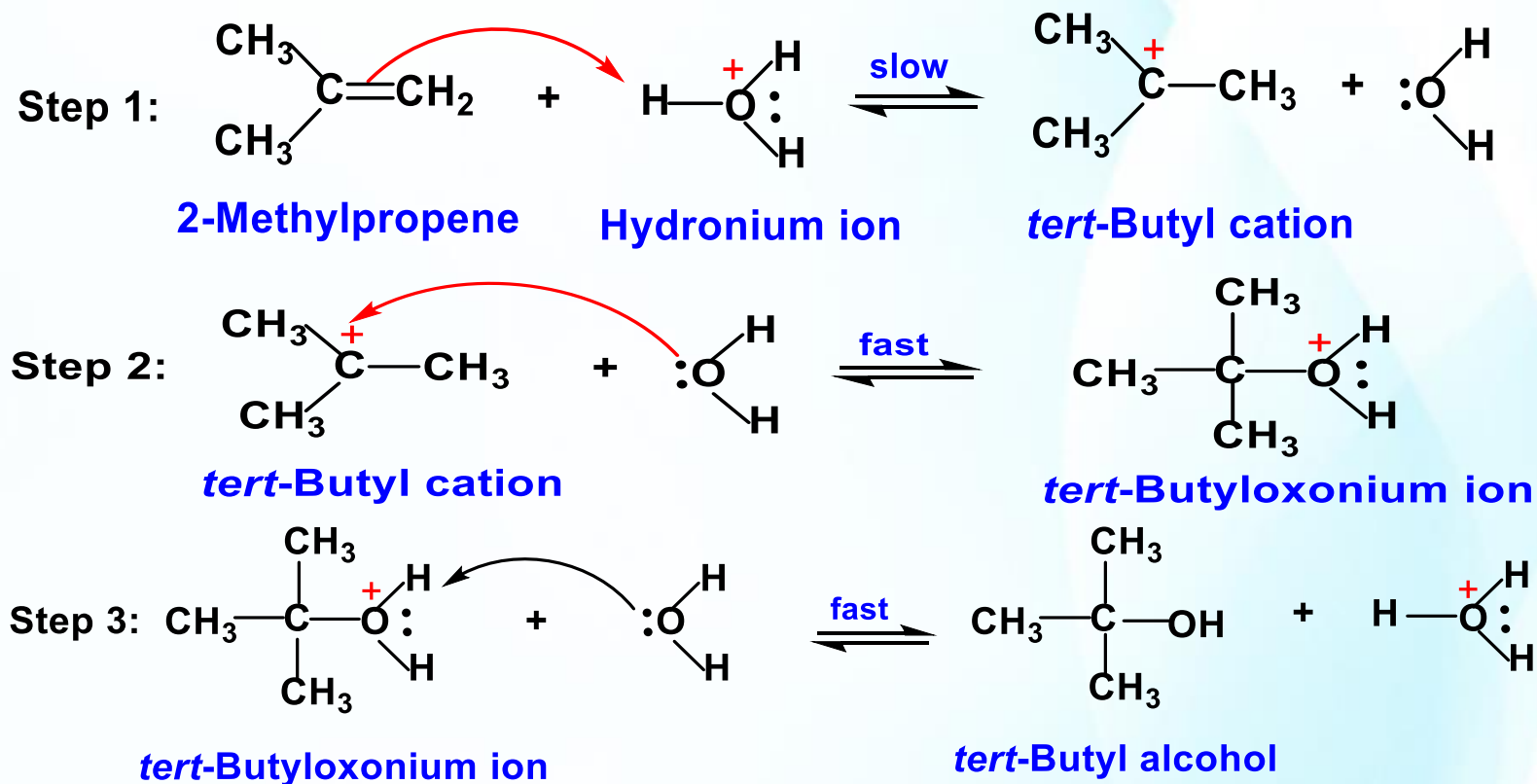
自由基的稳定性与正碳离子的顺序相同，即也是 $3^\circ > 2^\circ > 1^\circ$ ，因而双键自由基加HBr的产物是**反马氏规律**的



C. Acid-Catalyzed Hydration of Alkenes



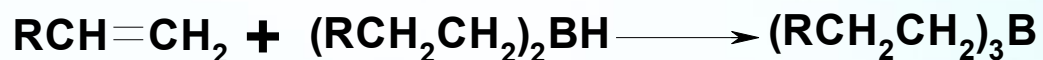
◆ Mechanism:



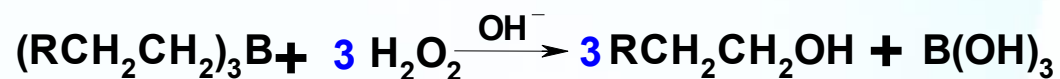
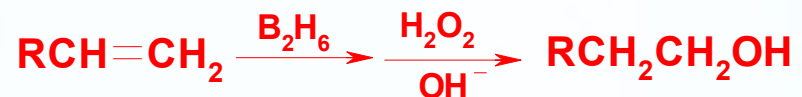


烯烃的硼氢化-氧化反应

硼氢化：硼原子加到含氢较多的碳原子上

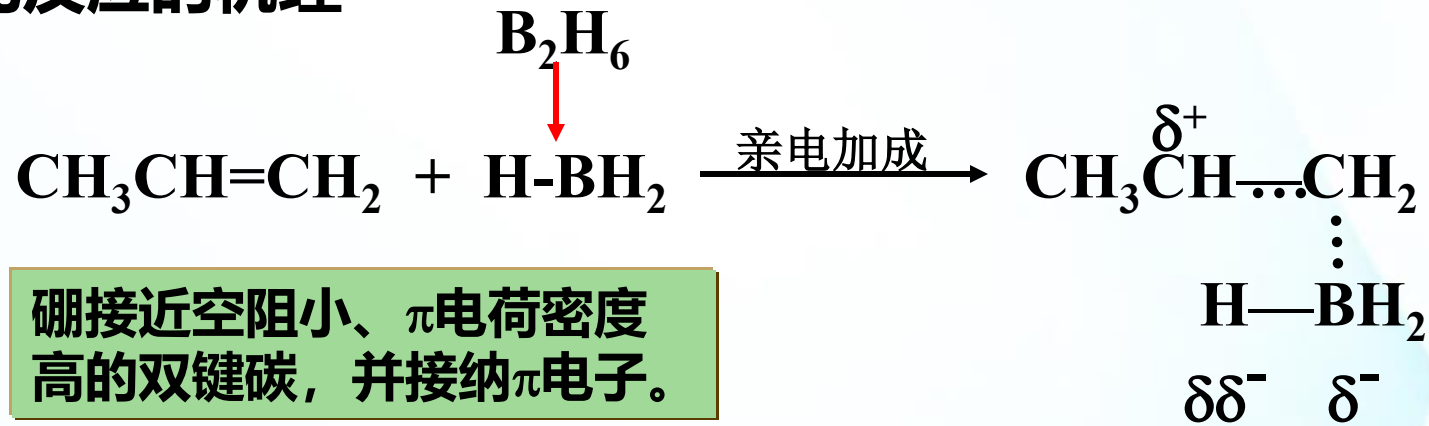


烷基硼氧化



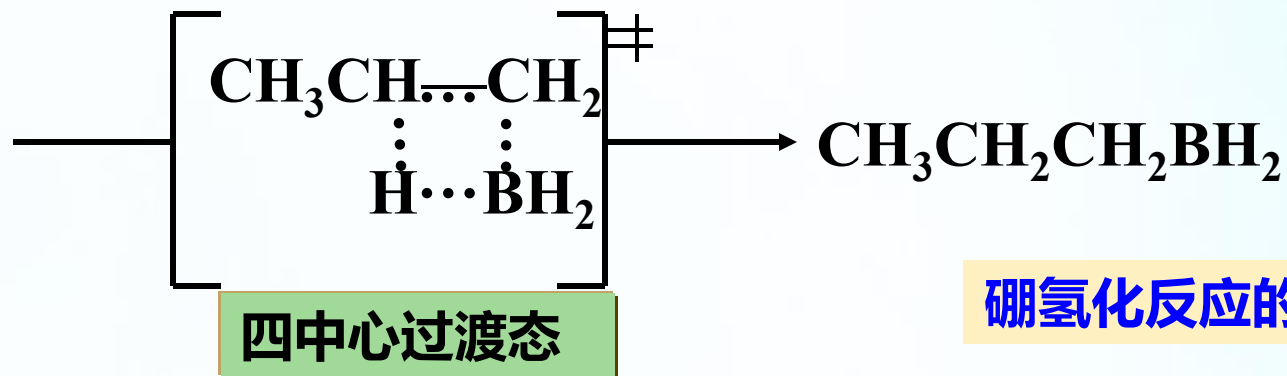
α -烯烃经硼氢化-氧化反应均得到伯醇，顺式加成反马氏规则

硼氢化反应的机理



硼接近空阻小、 π 电荷密度高的双键碳，并接纳 π 电子。

负氢与正碳互相吸引。



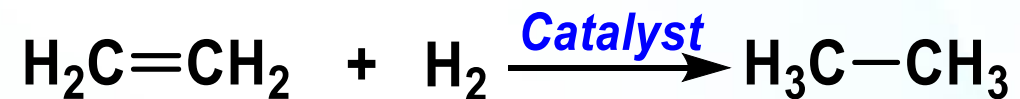
硼氢化反应的特点

- *1 立体化学：顺型加成（烯烃构型不会改变）
- *2 区域选择性—反马氏规则。
- *3 因为是一步反应，反应只经过一个环状过渡态，所以不会有重排产物产生。

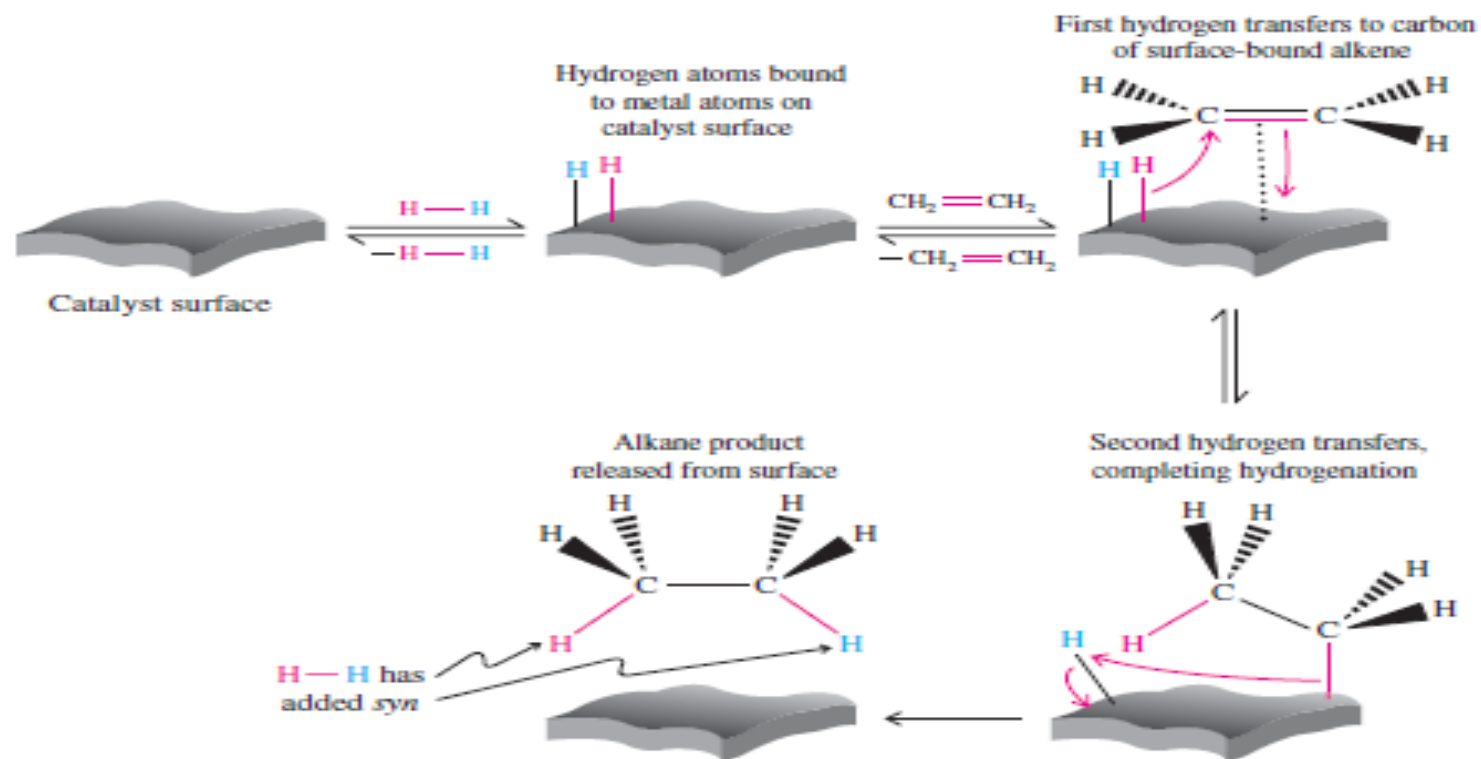


(2) Reduction and Oxidation of Alkenes

A. Reduction (Alkenes to alkanes)



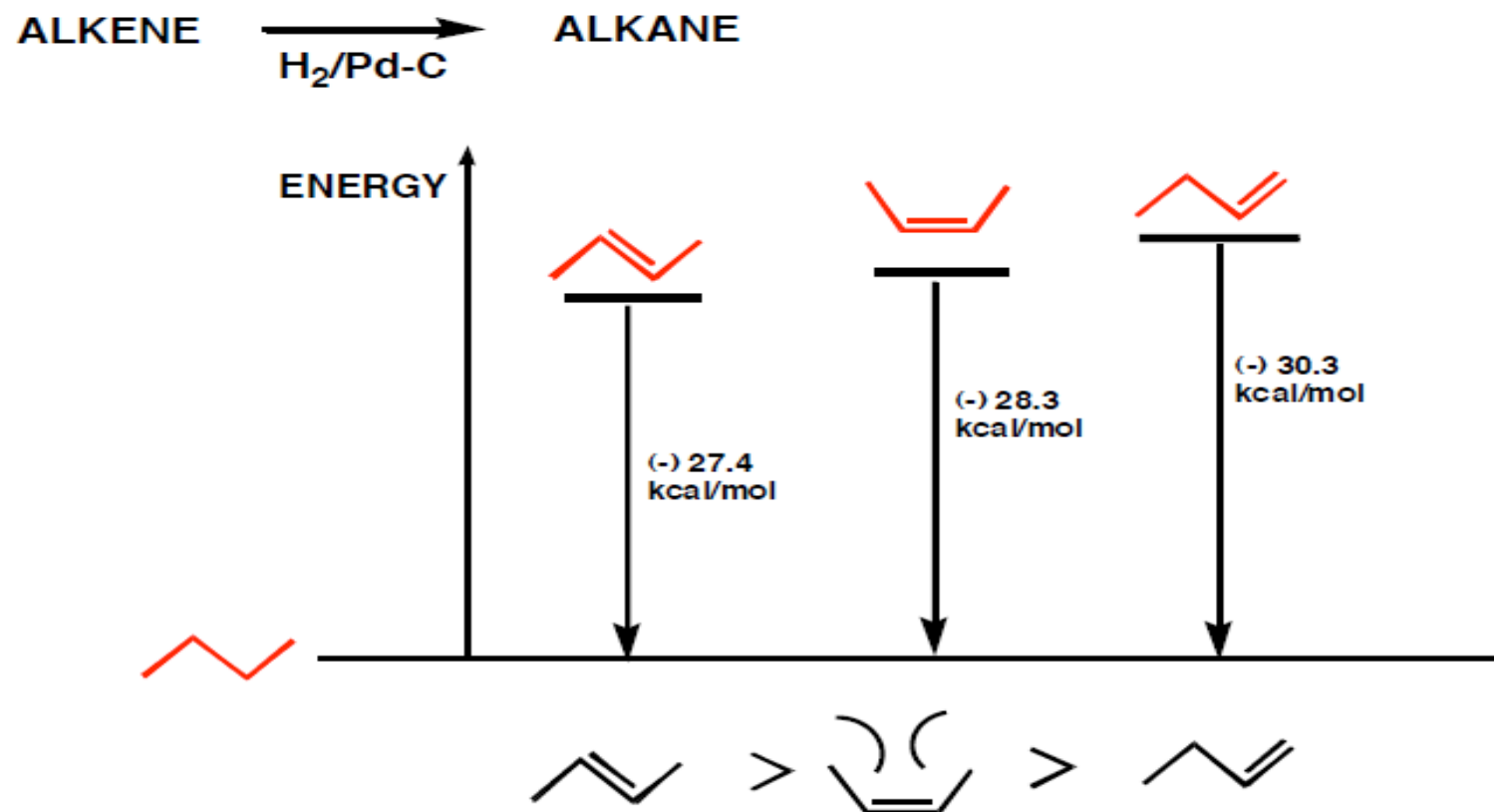
(*Catalyst*: Pt, Pd, Ni等)





氢化热——1mol不饱和烃氢化时所放出的能量。

Heat evolved upon catalytic hydrogenation (ΔH°)
A MEASURE OF ALKENE STABILITY



The greater the substitution, the lower is the heat of hydrogenation.



The heat of hydrogenation of a *trans*-alkene is lower than that the isomeric *cis*-alkene.

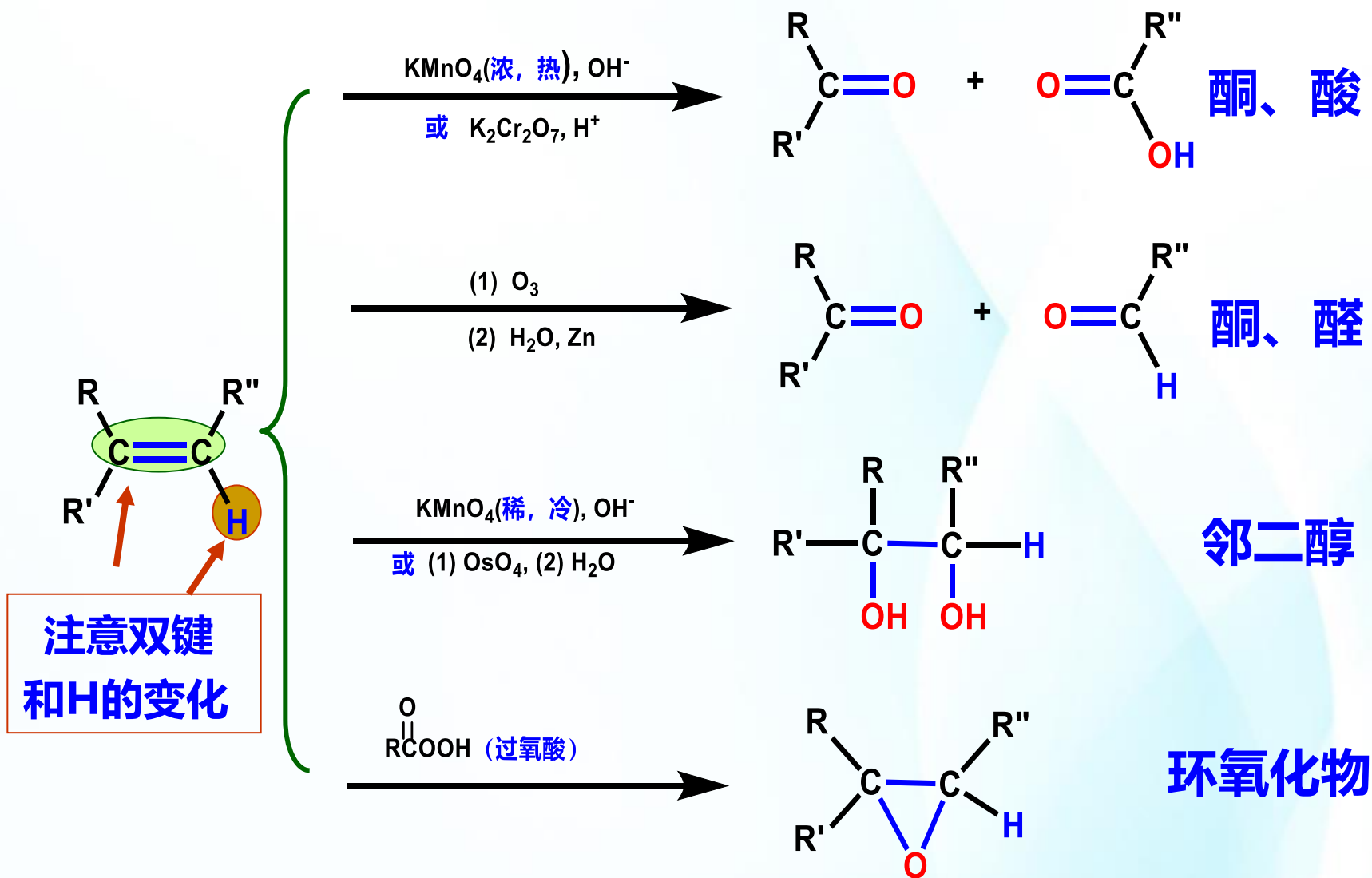


氢化热越高，不饱和烃稳定性越差。

The more substituents which are present on an alkene, the more stable the alkene is.

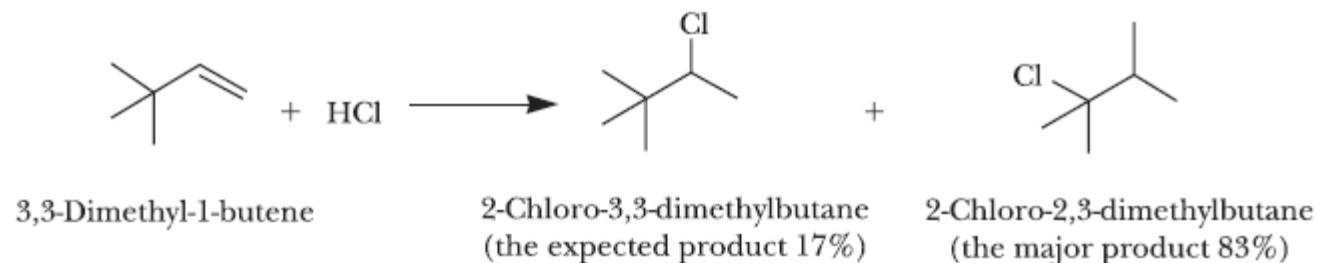


B. Oxidation

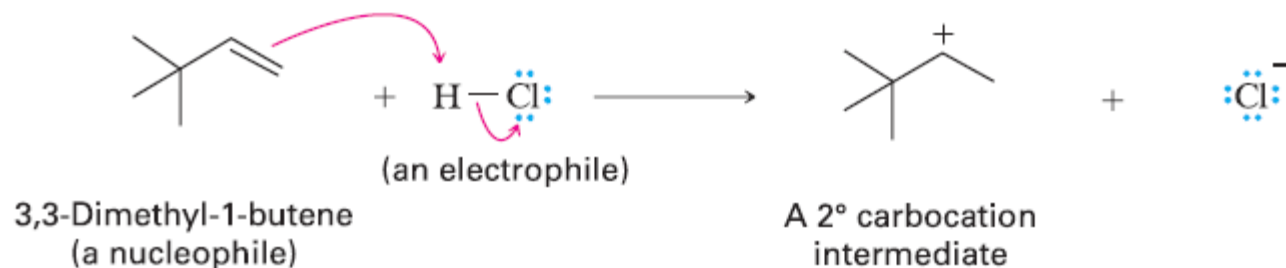




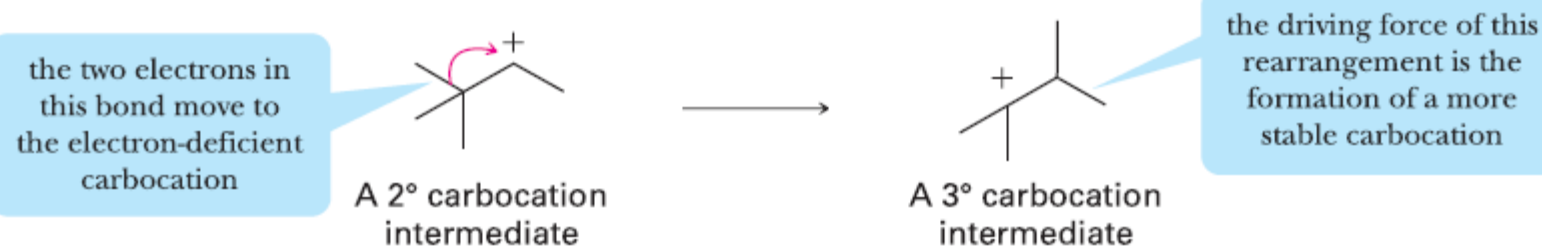
1. 烯烃的结构 (π 键和异构) ;
2. 烯烃的命名 (IUPAC命名、顺/反命名、Z/E命名) ;
3. 烯烃的化学性质
 - 亲电加成反应
 - 催化氢化反应
 - 氧化反应



STEP 1: Add a proton. Proton transfer from the HCl (an electrophile) to the alkene (a nucleophile) gives a 2° carbocation intermediate.

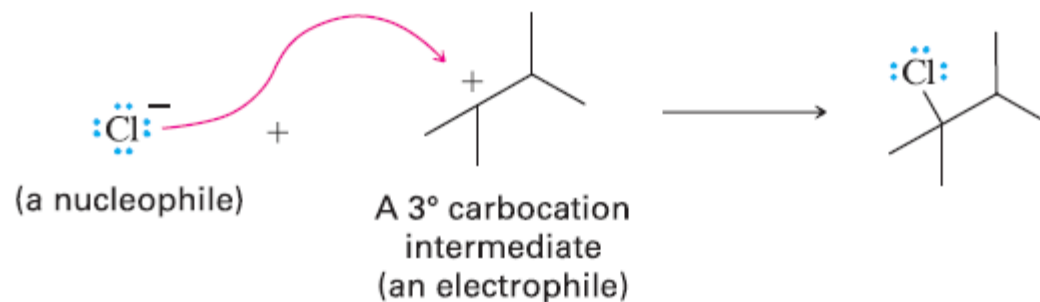


STEP 2: Rearrangement of a bond. Migration of a methyl group with its bonding electrons from an adjacent carbon gives a more stable 3° carbocation intermediate. The major movement is that of the bonding electron pair with the methyl group following.



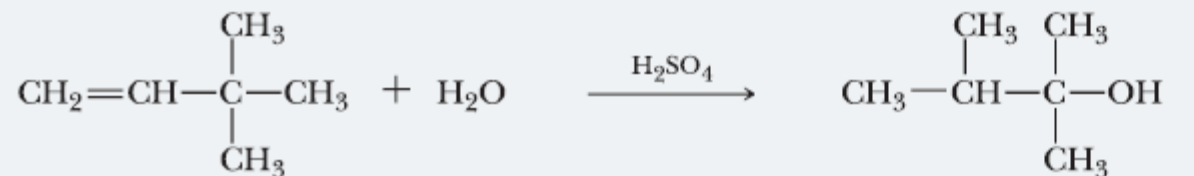


STEP 3: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the 3° carbocation intermediate (an electrophile and a Lewis acid) with chloride ion (a nucleophile and a Lewis base) gives the rearranged product.



PROBLEM 5.8

The acid-catalyzed hydration of 3,3-dimethyl-1-butene gives 2,3-dimethyl-2-butanol as the major product. Propose a mechanism for the formation of this alcohol.

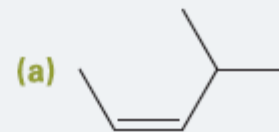
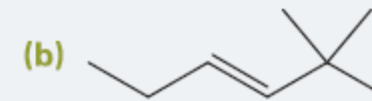


3,3-Dimethyl-1-butene

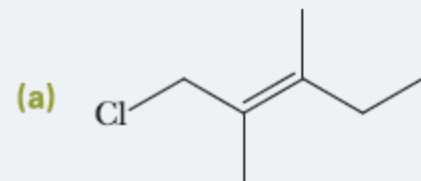
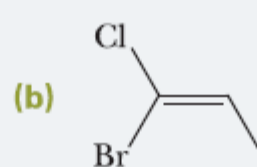
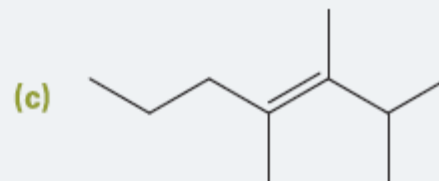
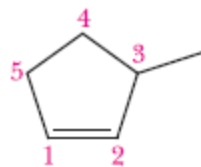
2,3-Dimethyl-2-butanol



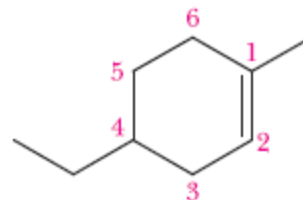
Name each alkene, and, using the *cis-trans* system, specify its configuration:



Name each alkene and specify its configuration by the E,Z system:



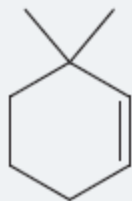
3-Methylcyclopentene
(not 5-methylcyclopentene)



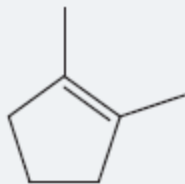
4-Ethyl-1-methylcyclohexene
(not 5-ethyl-2-methylcyclohexene)



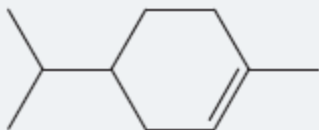
(a)



(b)



(c)



- (a) 3,3-Dimethylcyclohexene
- (b) 1,2-Dimethylcyclopentene
- (c) 4-Isopropyl-1-methylcyclohexene

4.15 Draw a structural formula for each compound: (See Examples 4.1, 4.5)

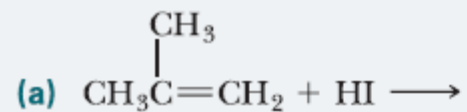
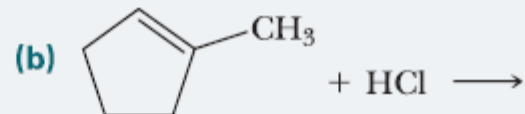
- (a) *trans*-2-Methyl-3-hexene
- (b) 2-Methyl-3-hexyne
- (c) 2-Methyl-1-butene
- (d) 3-Ethyl-3-methyl-1-pentyne
- (e) 2,3-Dimethyl-2-butene
- (f) *cis*-2-Pentene
- (g) (*Z*)-1-Chloropropene
- (h) 3-Methylcyclohexene

4.16 Draw a structural formula for each compound: (See Examples 4.1, 4.5)

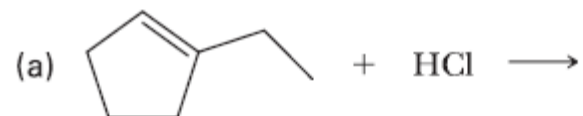
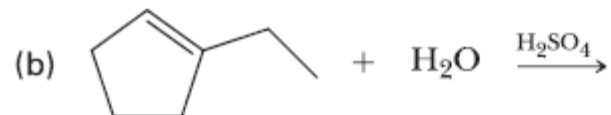
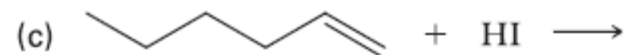
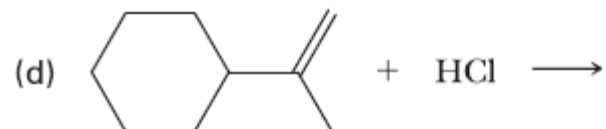
- (a) 1-Isopropyl-4-methylcyclohexene
- (b) (6*E*)-2,6-Dimethyl-2,6-octadiene
- (c) *trans*-1,2-Diisopropylcyclopropane
- (d) 2-Methyl-3-hexyne
- (e) 2-Chloropropene
- (f) Tetrachloroethylene



Name and draw a structural formula for the major product of each alkene addition reaction:

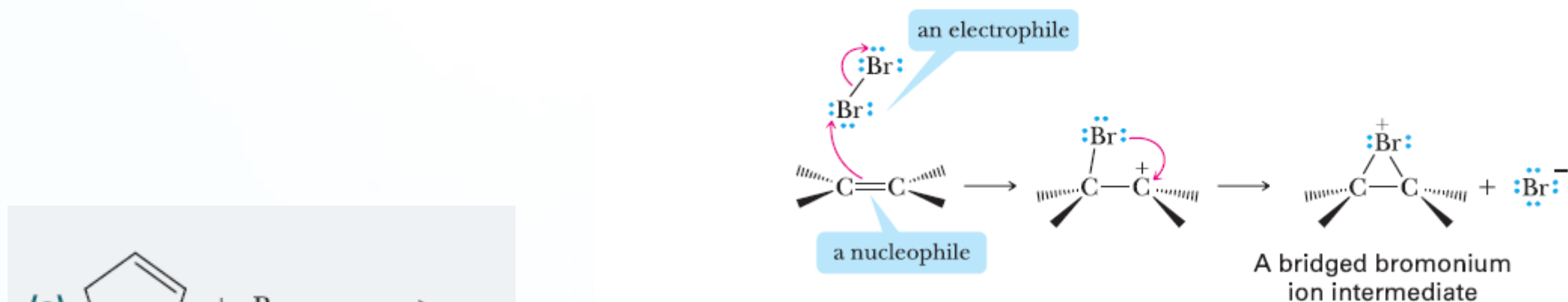


5.19 Complete these equations by predicting the major product formed in each reaction: (See Examples 5.2, 5.5)

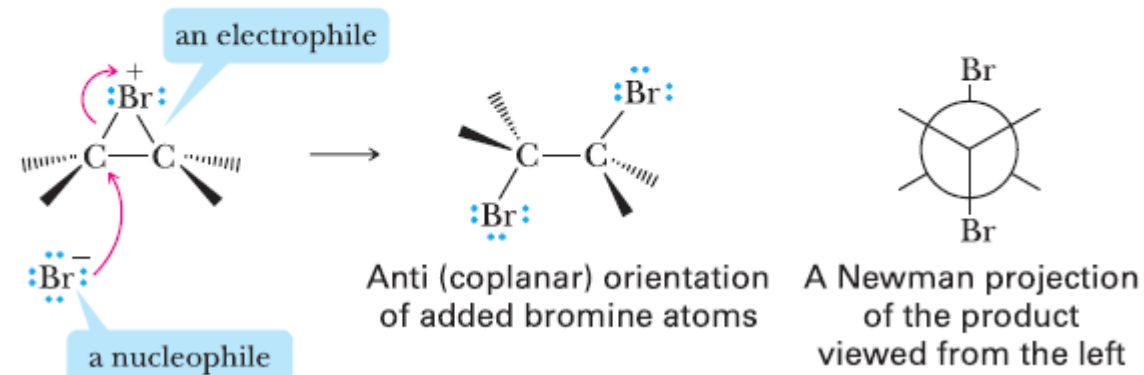




STEP 1: Reaction of a nucleophile and an electrophile to form a new covalent bond. Reaction of the pi electrons of the carbon-carbon double bond (a nucleophile) with bromine (an electrophile) forms a bridged bromonium ion intermediate in which bromine bears a positive formal charge:



STEP 2: Reaction of a nucleophile and an electrophile to form a new covalent bond. A bromide ion (a nucleophile and a Lewis base) attacks carbon (an electrophile and a Lewis acid) from the side opposite the bridged bromonium ion, opening the three-membered ring:





也许有一天, 不知不觉, 你将渐渐活出写满答案的人生!