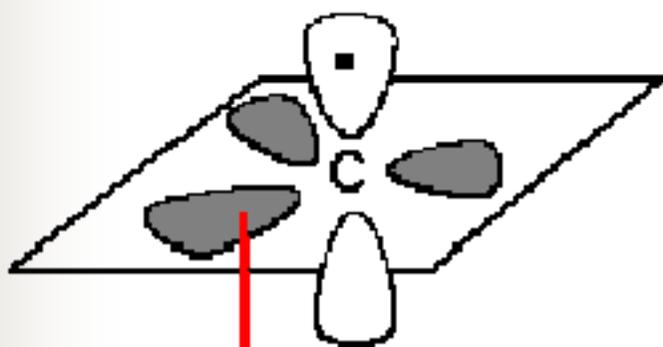
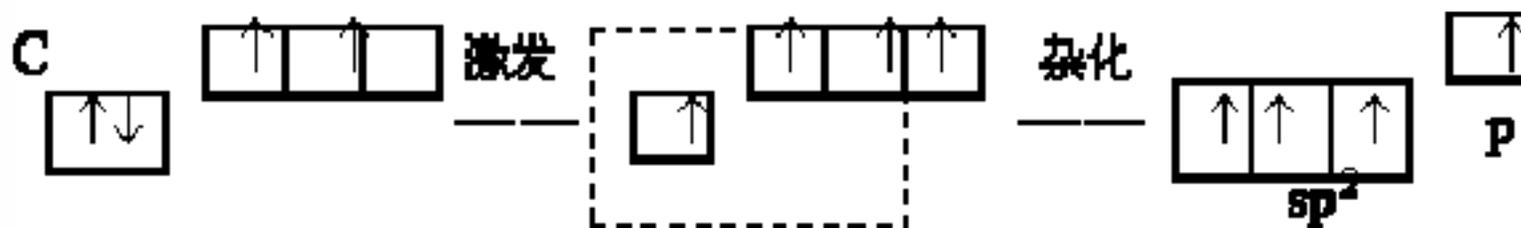


§ 4 烯 炔



§ 4.1 烯烃的结构

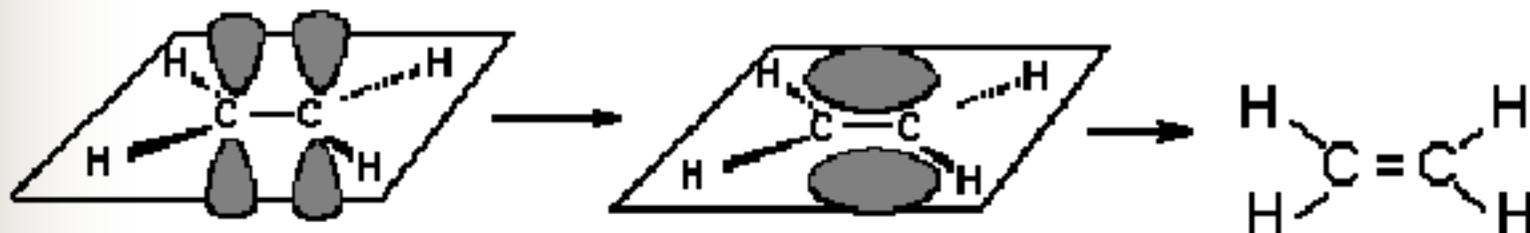
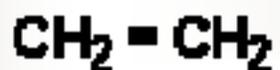
■ 1. 双键 ($C=C$) 的结构



sp^2 键角 120° , p 轨道
垂直于平面



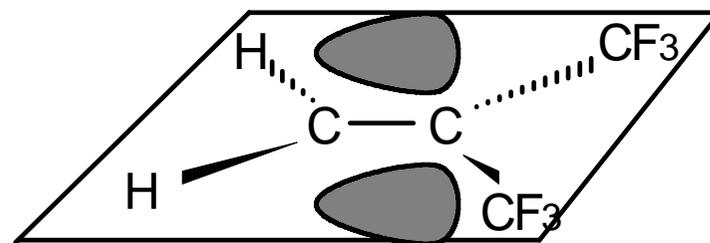
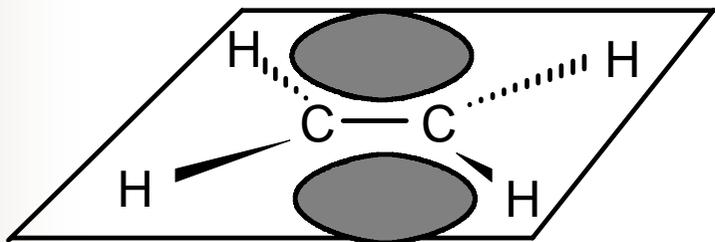
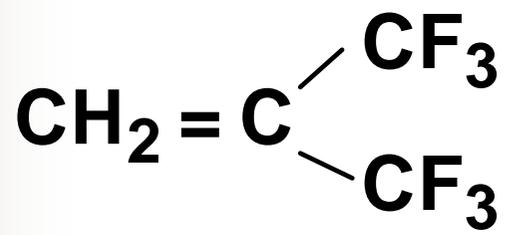
sp^2 杂化轨道
中 s 成分比 sp^3
中的 s 成分大,
因此,电负性
 $sp^2 > sp^3$



sp^2 头碰头重叠 \rightarrow σ 键
p 肩并肩重叠 \rightarrow π 键

π 键特点:

- π 键不能独立存在; 与 σ 键共存;
- π 键不能旋转; 产生几何异构;
- π 键富含电子; 易与缺电子试剂反应;
- π 键受原子核控制弱; 易被极化。

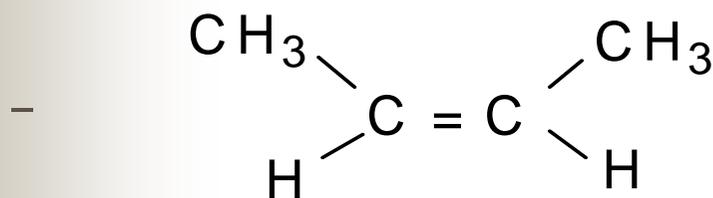


$-\text{CF}_3$ 为吸电子基团

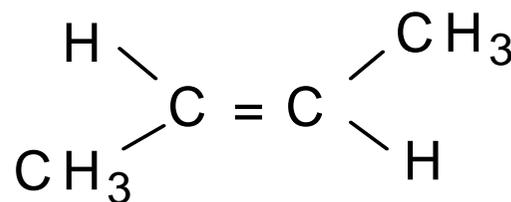
2. 几何异构

A. 产生条件

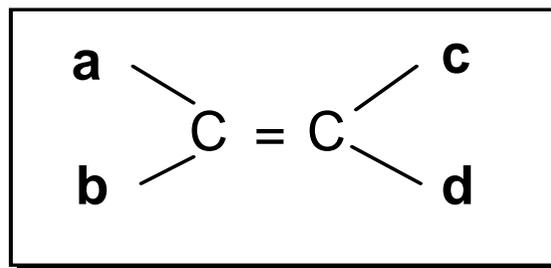
- a. 分子中有阻碍旋转的因素
- b. 被阻碍旋转的碳原子上连有不同基团



cis



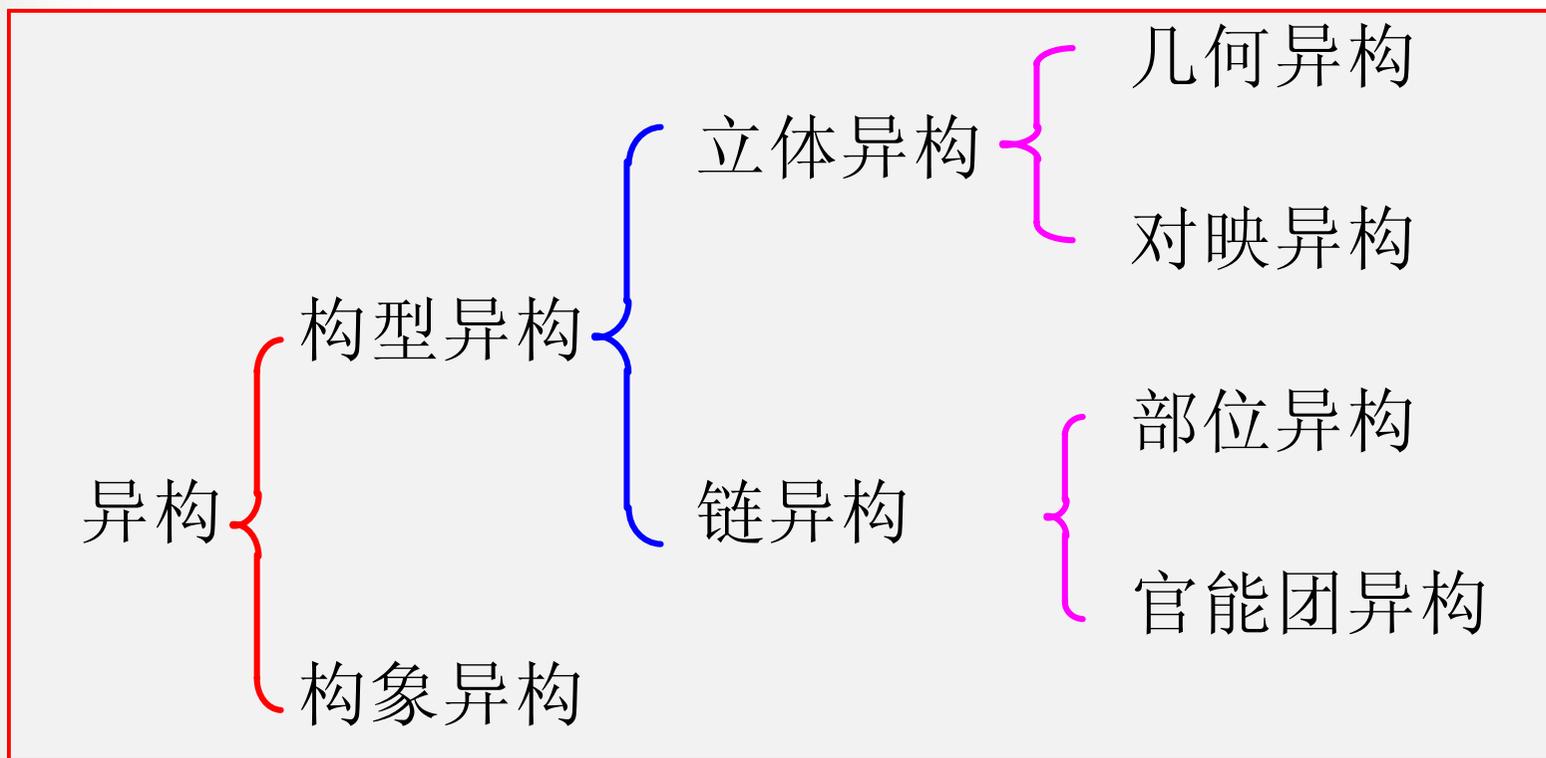
trans



◆ 产生顺反异构的条件:

$$\mathbf{a \neq b; \quad c \neq d}$$

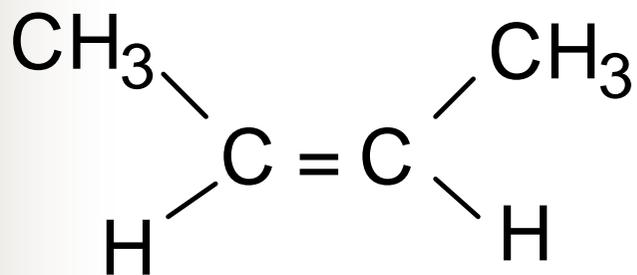
总结 —— 异构体的分类



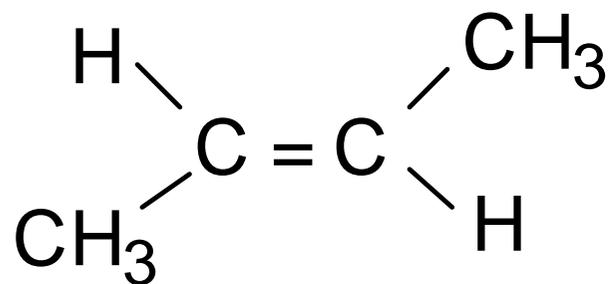
8. 几何异构的标识

a. 顺反命名法

- 相同基团在同侧时称为顺(cis);
- 在异侧时称为反(trans);



顺-2-丁烯

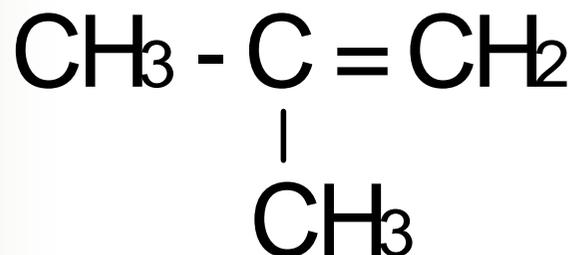


反-2-丁烯

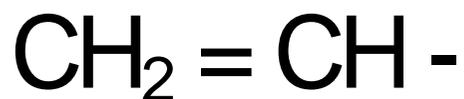
C1的两个基团与C2的两个基团相同时，常使用该命名法。

§ 4.2 烯烃的命名

■ 1. 习惯命名法



异丁烯



乙烯基



丙烯基



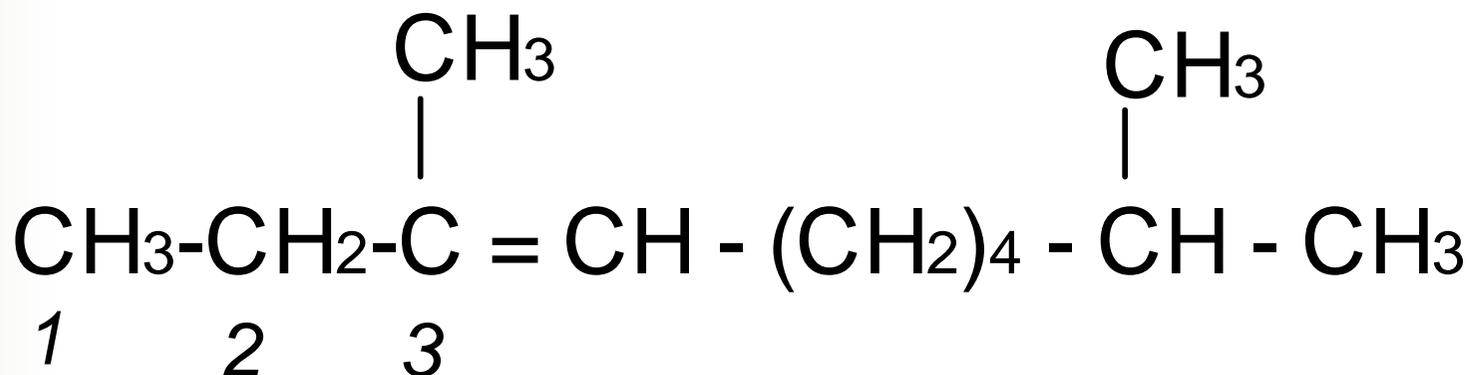
烯丙基



亚甲基

2. 系统命名法

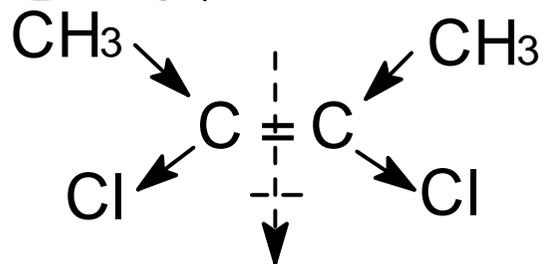
- 选含双键的最长碳链为主链；
- 从双键最近处编号；
- 双键位置写在母体化合物命名前加‘-’；
取代基写在更前面；
- 如有几何异构，在最前面用Z, E标识。



3,9 - 二甲基 - 3 - 癸烯

§ 4.3 物理性质

与烷烃类似，但Z与E的物理性质不同

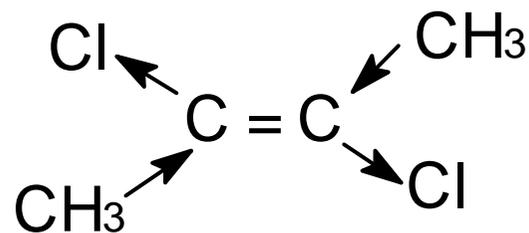


b.p. 60 °C

m.p. -80 °C

$\mu=1.85\text{D}$

(Z)-2,3-二氯-2-丁烯



b.p. 48 °C

m.p. -50 °C

$\mu=0\text{D}$

(E)-2,3-二氯-2-丁烯

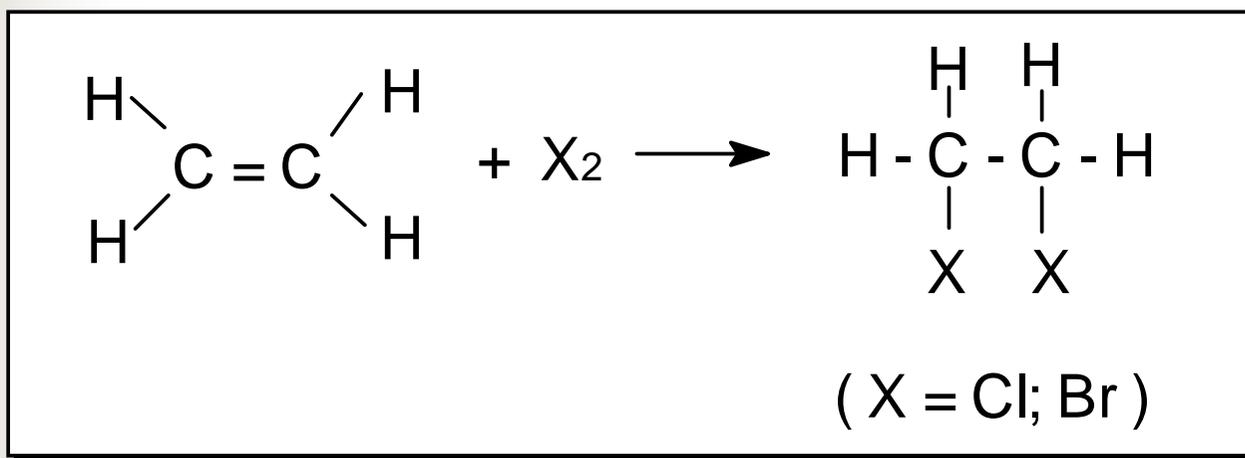
总结：沸点与极性有关，极性大(偶极矩大)，沸点高；

熔点与晶格能(对称性)有关，对称性好，熔点高

对称性： 对称中心 > 对称面

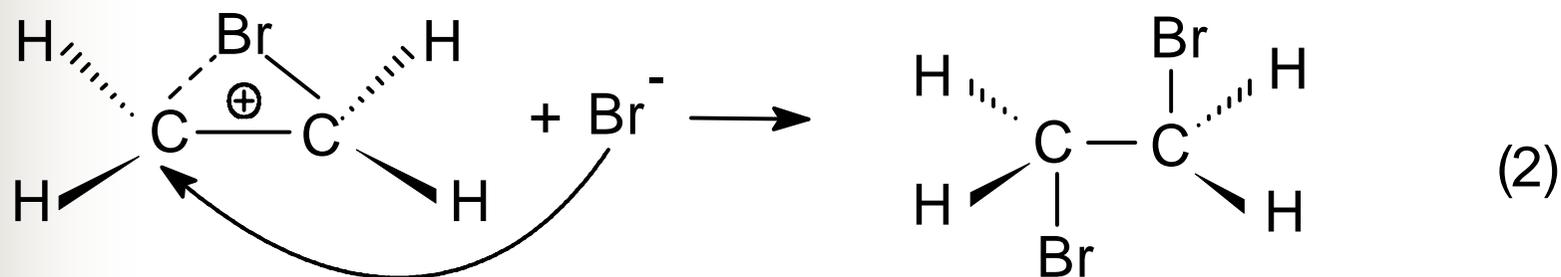
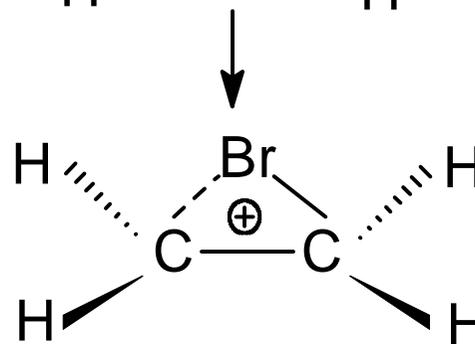
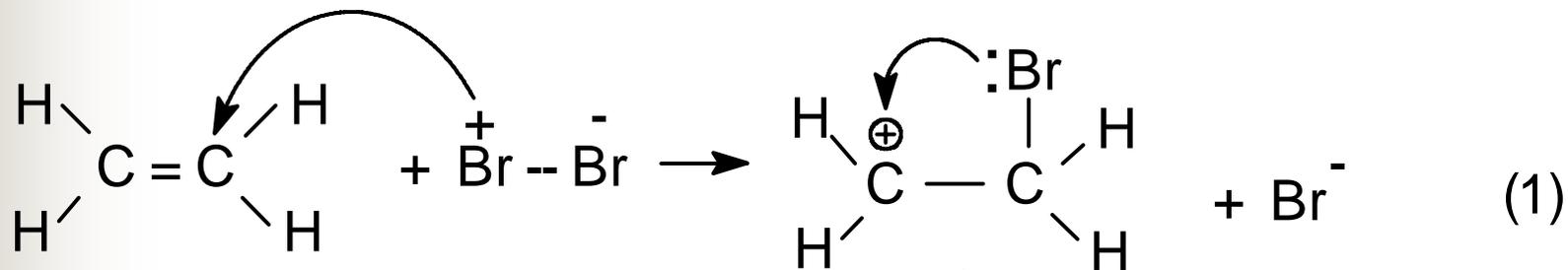
§ 4.4 化学性质 I —— 亲电加成

1. 与卤素反应 —— 立体选择

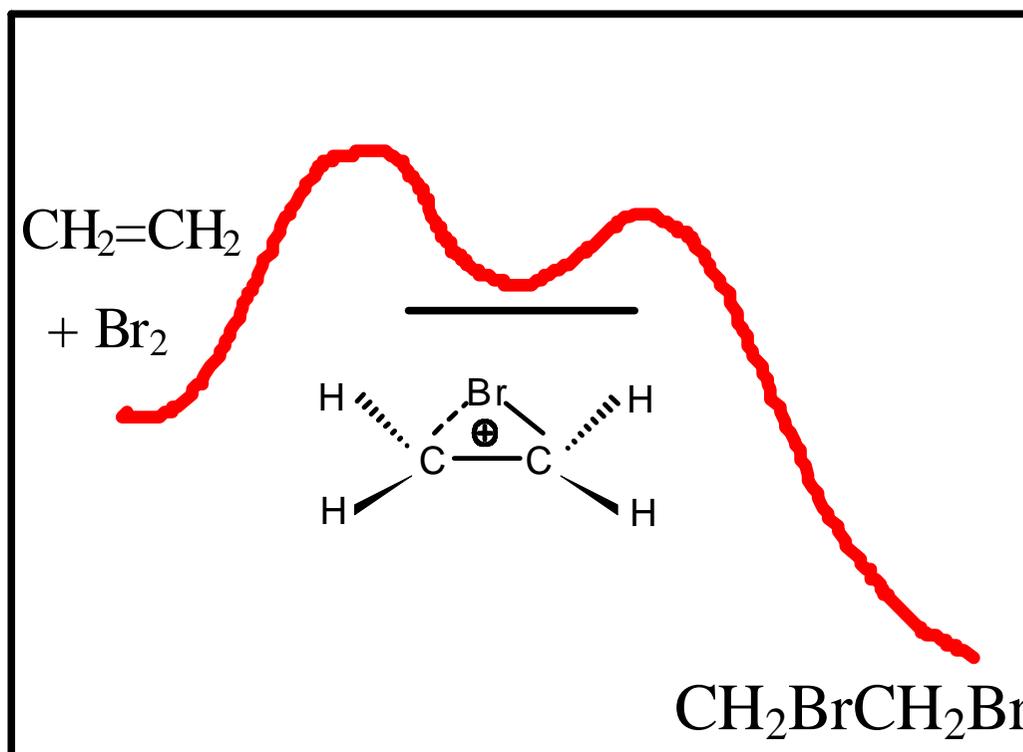


- A. 特点:
- a. 可以在室温下进行，
Br₂ 退色，鉴定 C=C 双键；
 - b. 合成邻二卤代烷的方法。

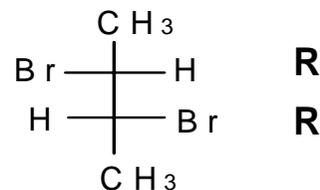
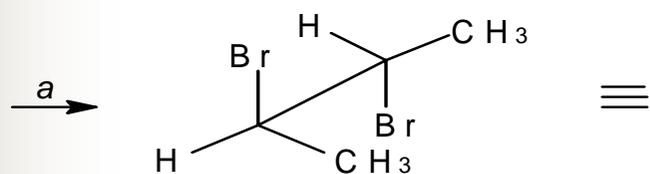
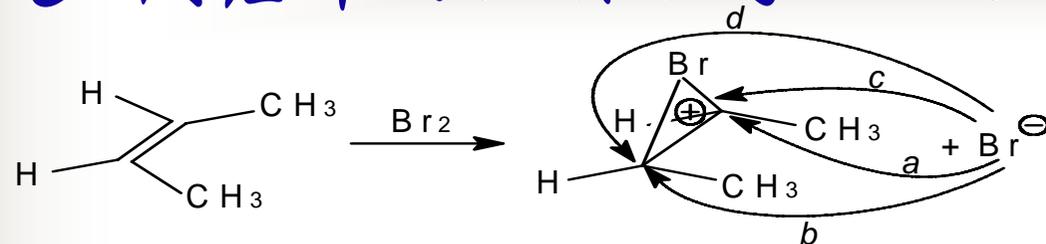
8. 反应机理——正碳离子机理



- 总结： a. 经历三员环状溴翁离子，
Cl不易形成翁离子
b. 反式共平面加成
c. 能量

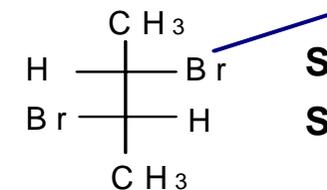
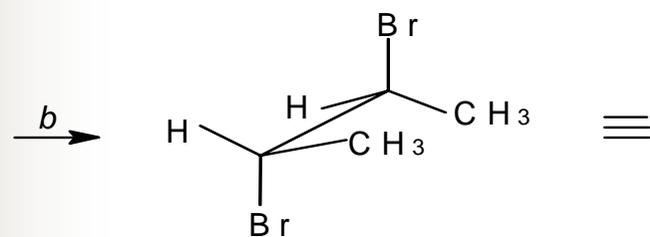


C. 反应中的立体化学——立体选择性



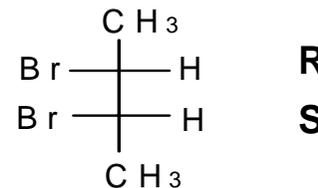
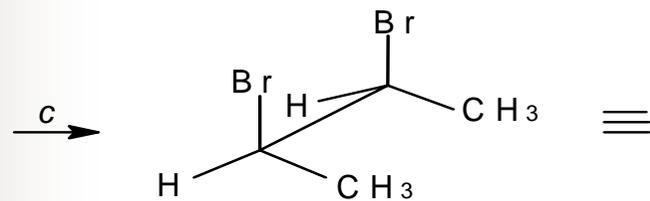
R
R

对映体
(反式加成)
> 99%



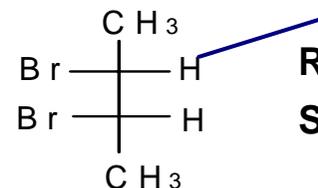
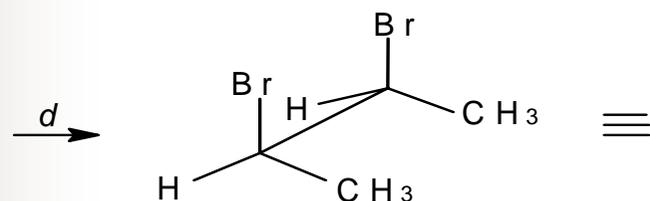
S
S

两个溴原子在
对侧称为
苏式



R
S

同一物质
(顺式加成)
< 1%

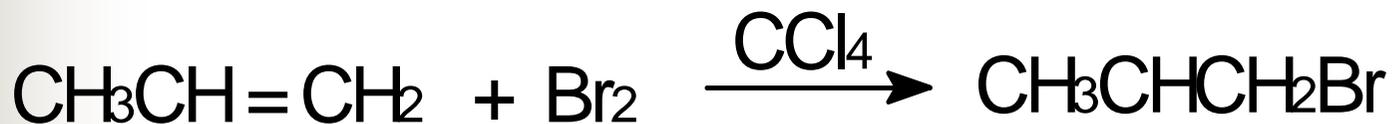
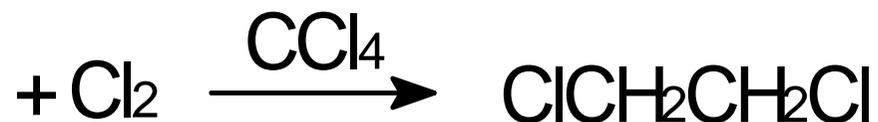


R
S

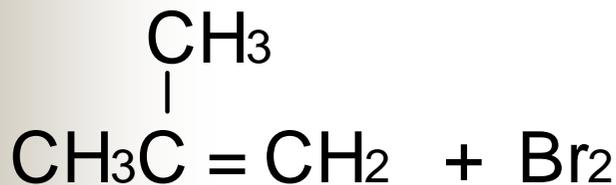
两个溴原子在
同侧称为
赤式

- 立体选择性反应：
- 一定构型的反应物经反应后生成一种优势构型的产物（包括对映体）
- 说明反应中几种可能的立体过程中有一种是优势的。
- 卤素加成立体化学：
- 反式共平面加成

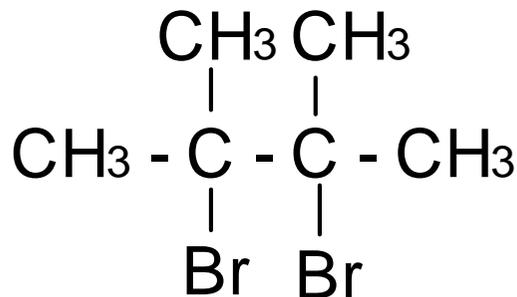
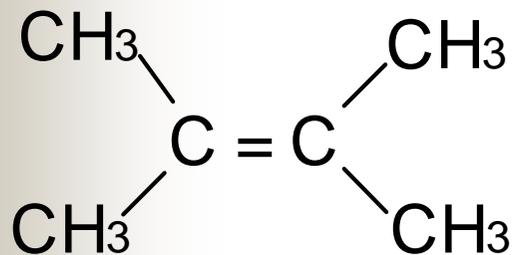
D. 反应实例



80%



94%



100%

■ 烯烃活性:

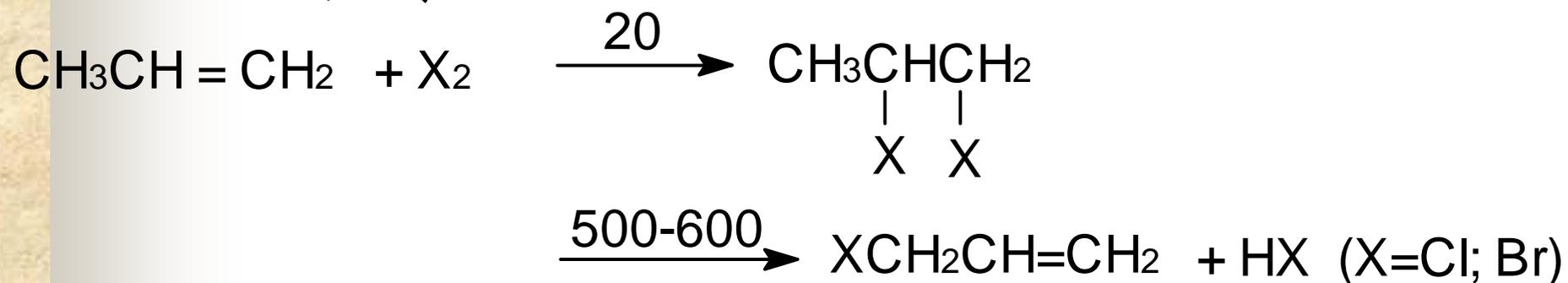
■ 烷基及推电子基团取代多的烯烃活性高

■ $R_2C=CR_2 > R_2C=CHR > RHC=CHR >$

$RCH=CH_2 > CH_2=CH_2 > CH_2=CHCl$

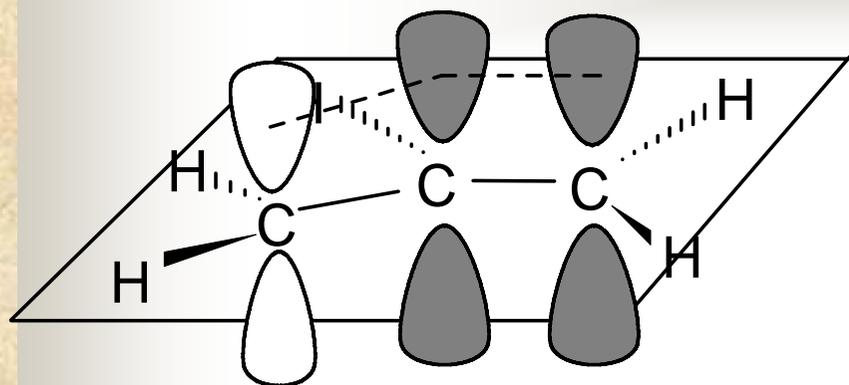
E. 烯丙位溴代——自由基机理

a. 反应事实

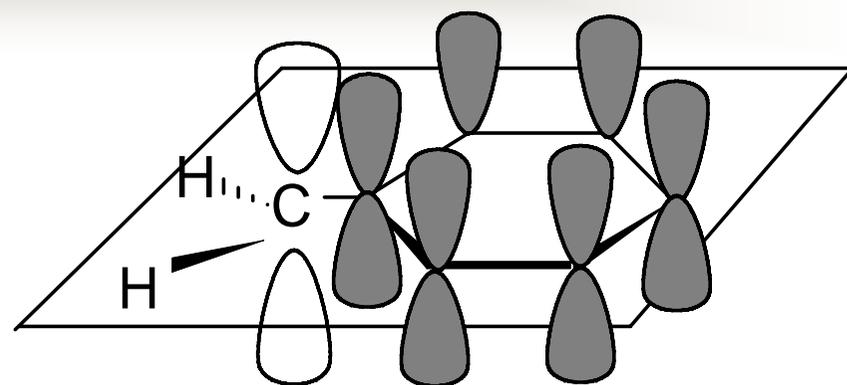


b. 反应机理——自由基机理





烯丙基自由基结构



苄基自由基结构

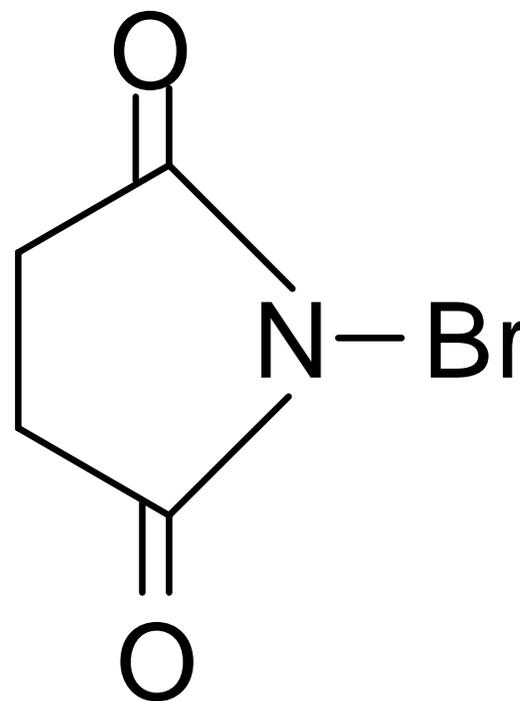
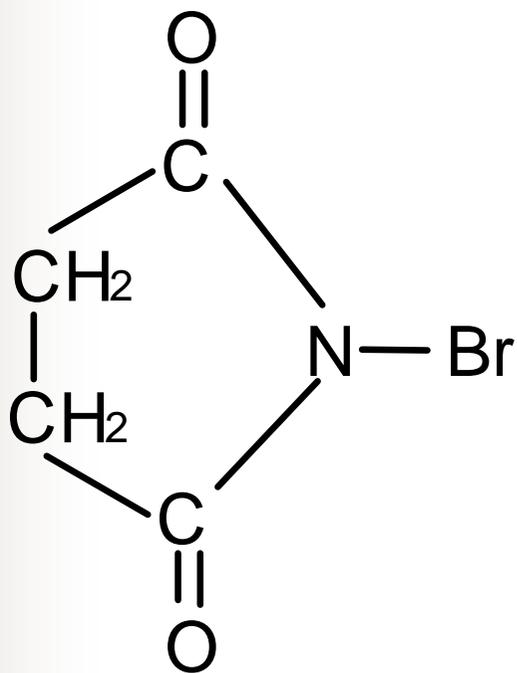
p - π 共轭

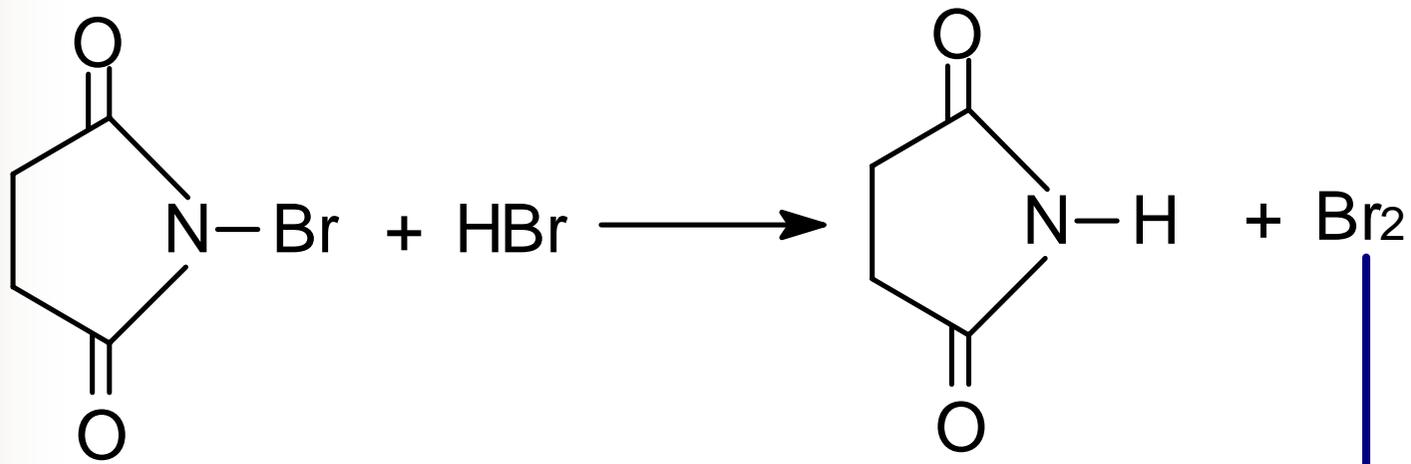
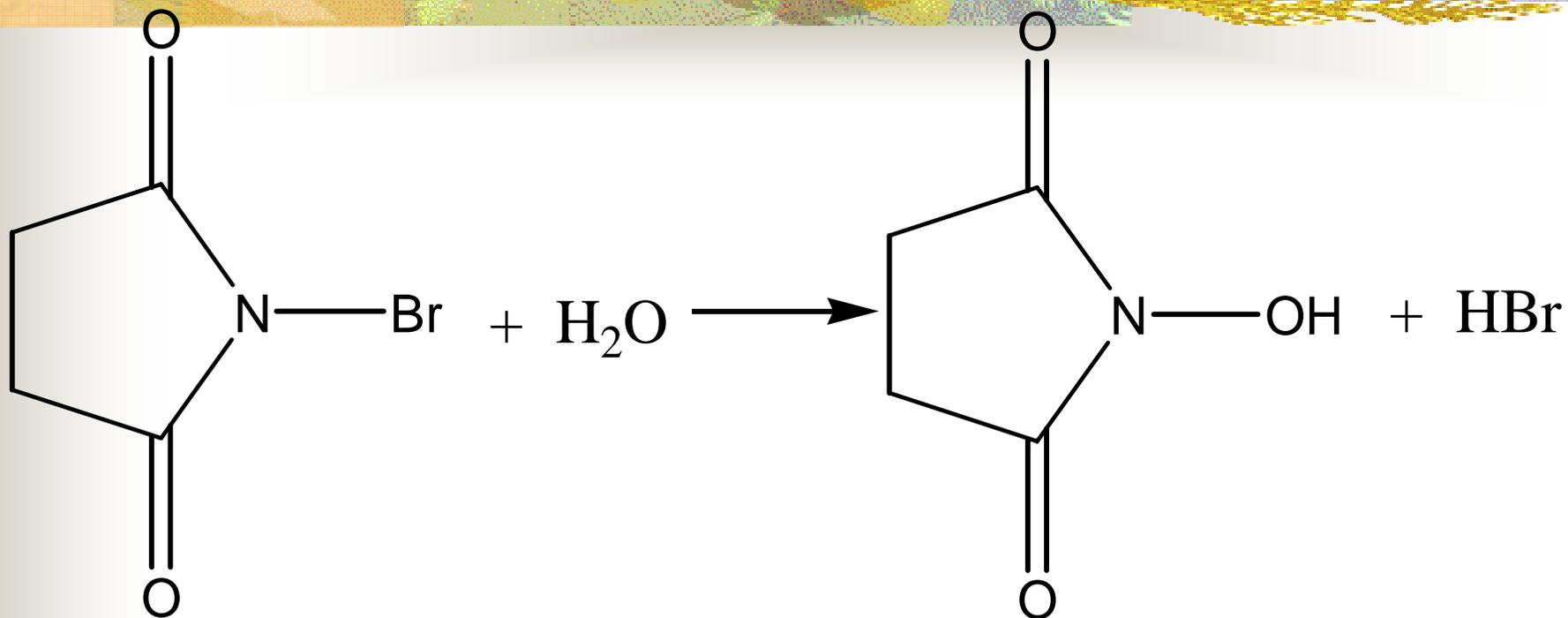
自由基稳定顺序:

苄基; 烯丙基 > 3° > 2° > 1° > CH₃·

6. 烯丙基位及苄基位专用溴代试剂——NBS

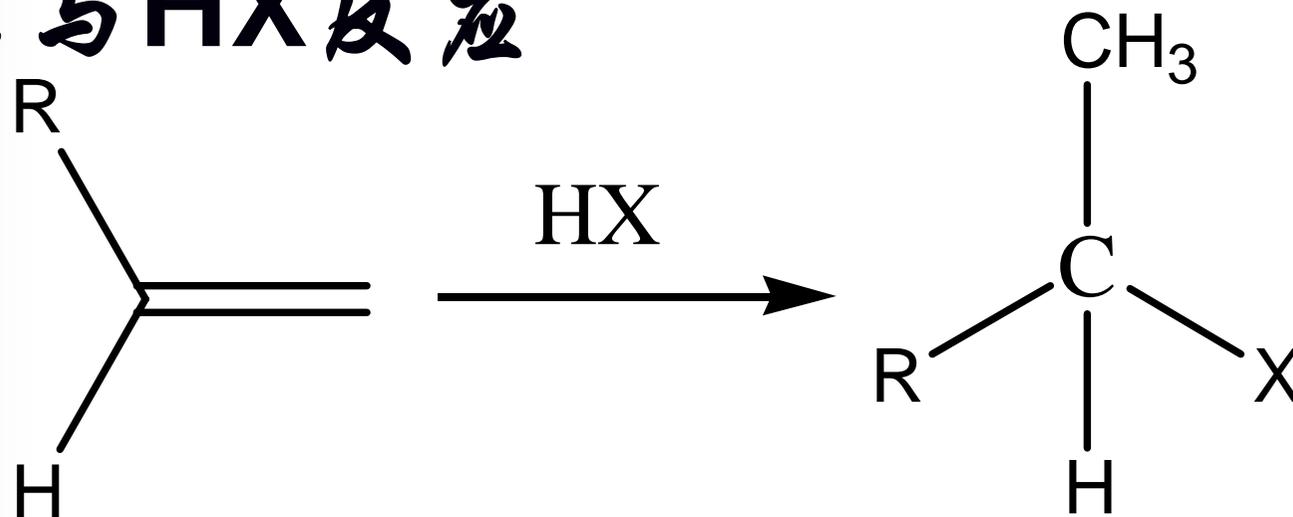
■ N-溴代丁二酰亚胺





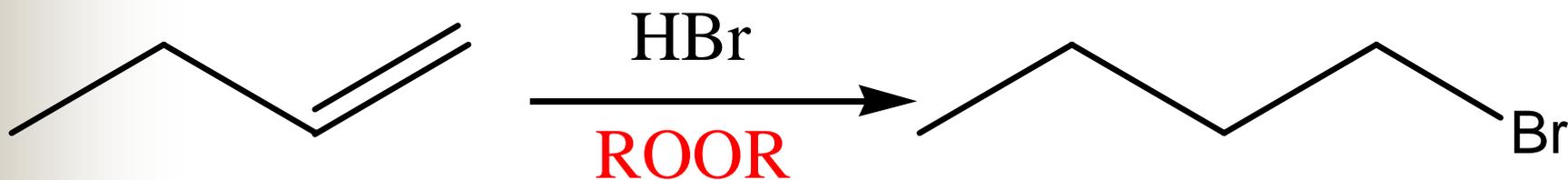
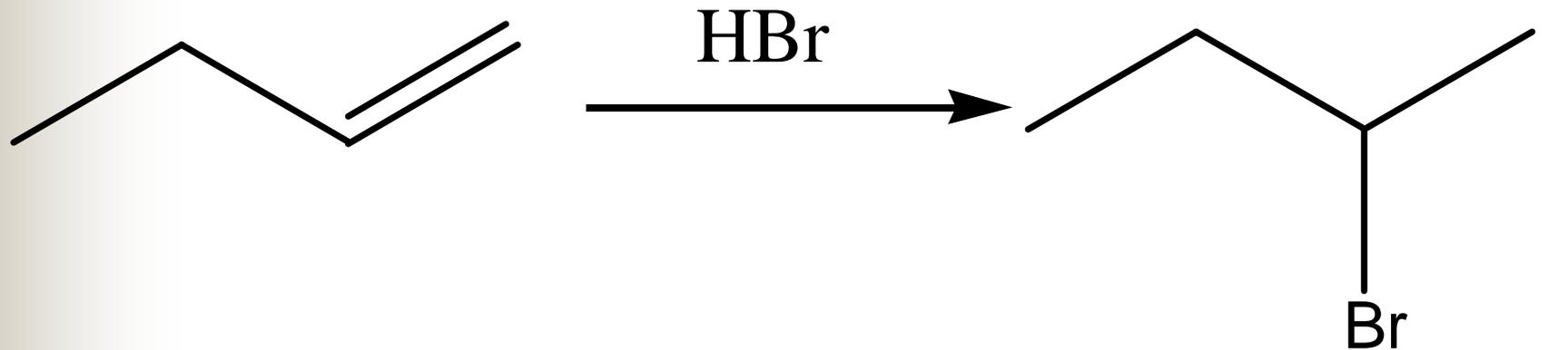
参与自由基反应

2. 与HX反应

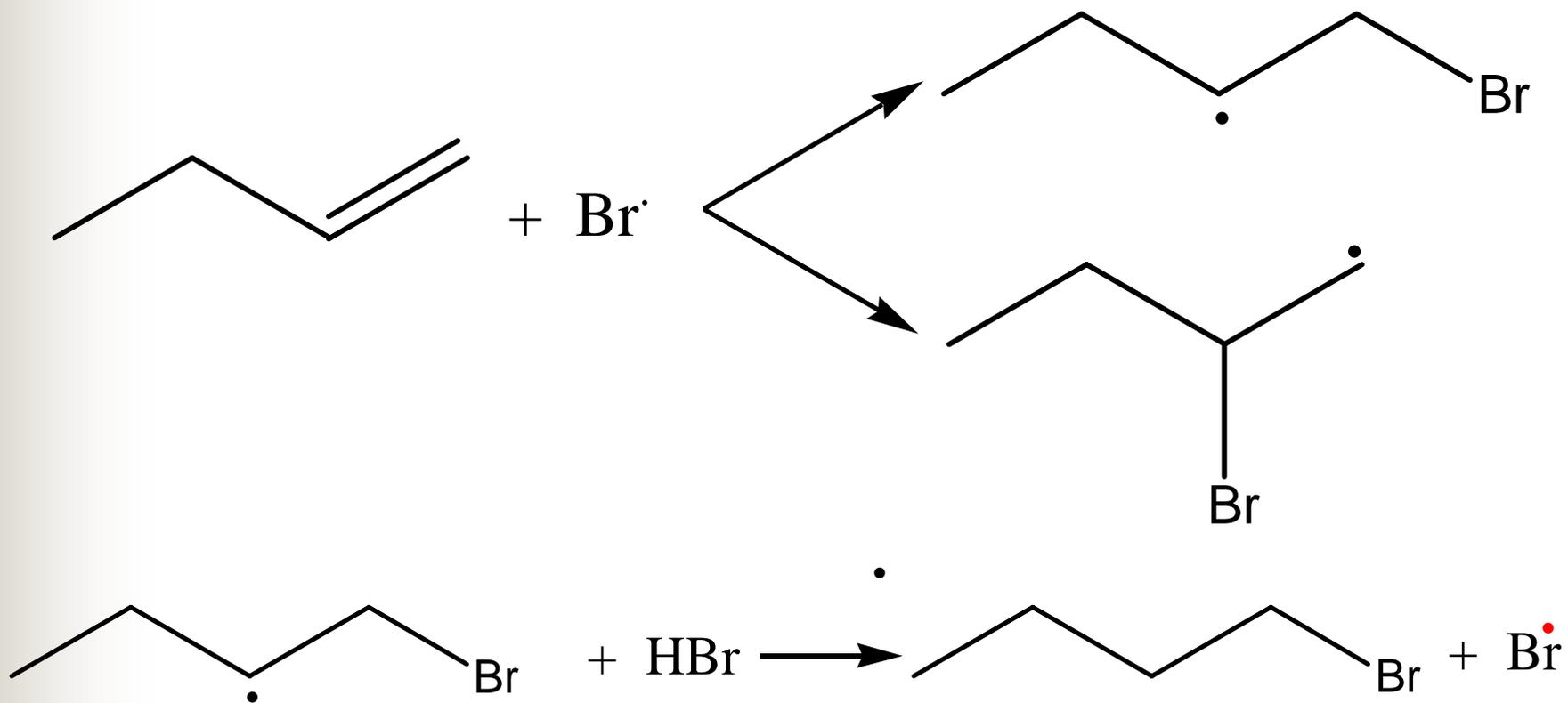


- 1、HX= HCl , HBr , HI
- 2、遵循马氏规则
- 3、用于制备卤代烃

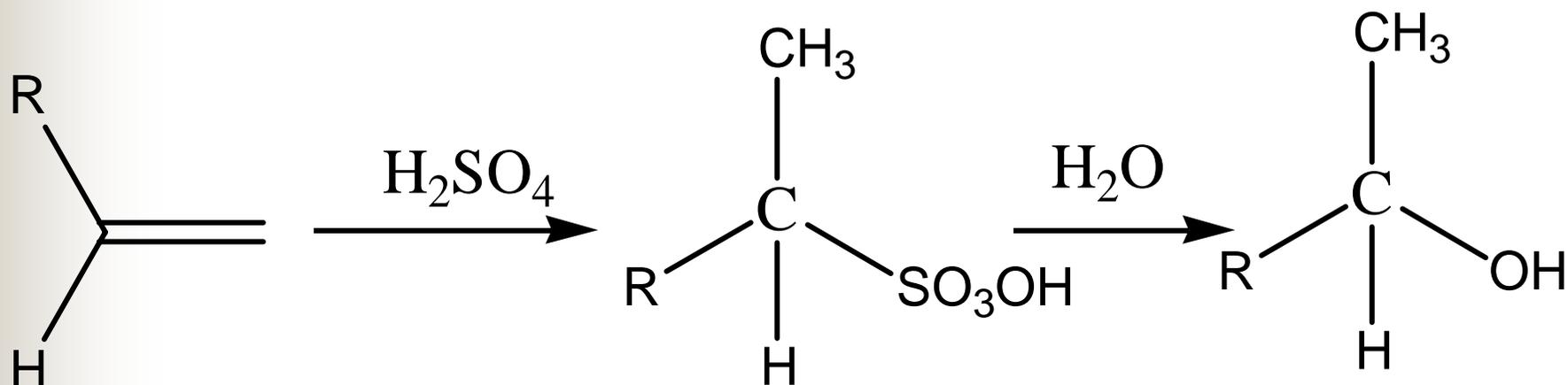
与HBr加成时的过氧化物效应 - 反马氏规则



原因:

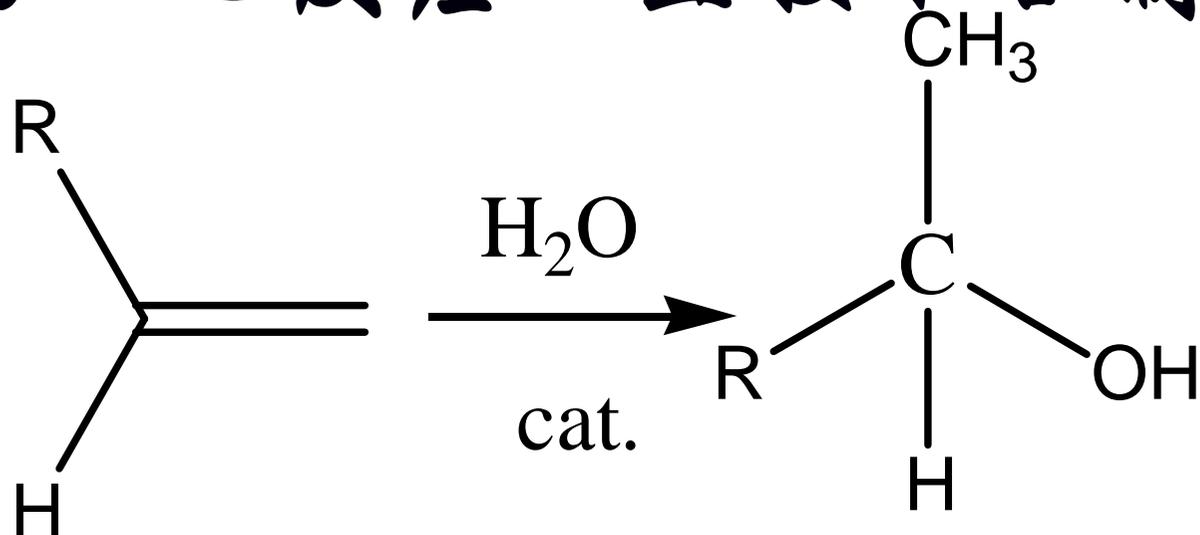


3. 与 H_2SO_4 反应 - 间接水合制醇



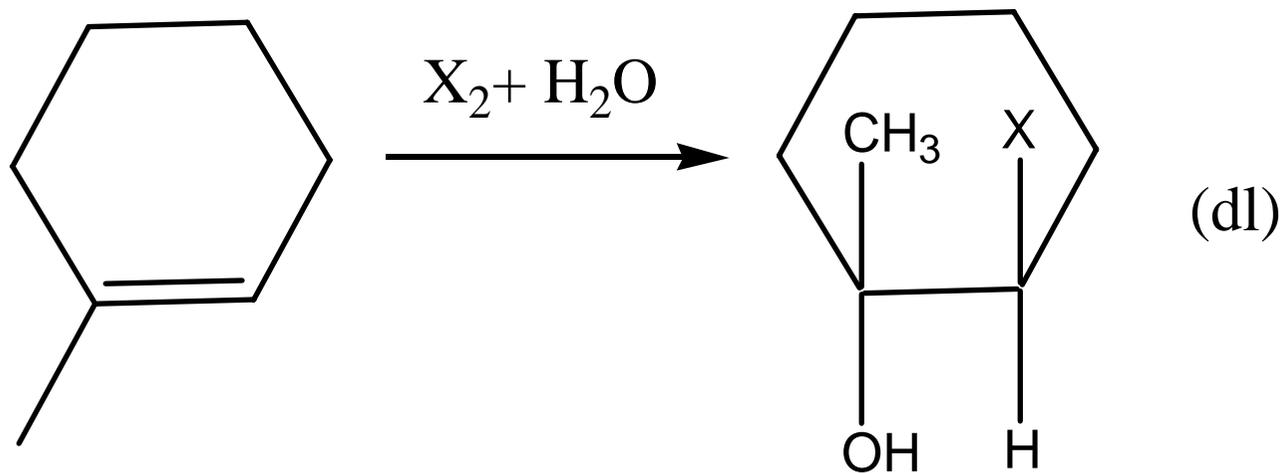
- 1、需用浓硫酸
- 2、遵循马氏规则
- 3、用于制备醇

4. 与H₂O反应 - 直接水合制醇



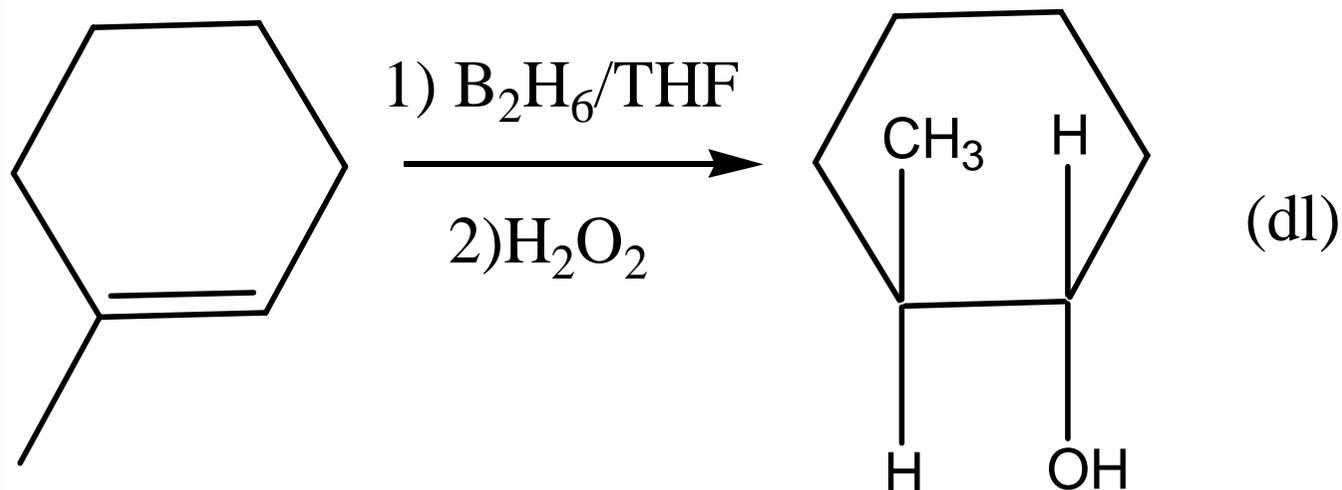
- 1、Cat.= H₃PO₄ , H₂SO₄ , 分子筛
- 2、遵循马氏规则
- 3、用于制备醇

5. 与卤素+H₂O反应



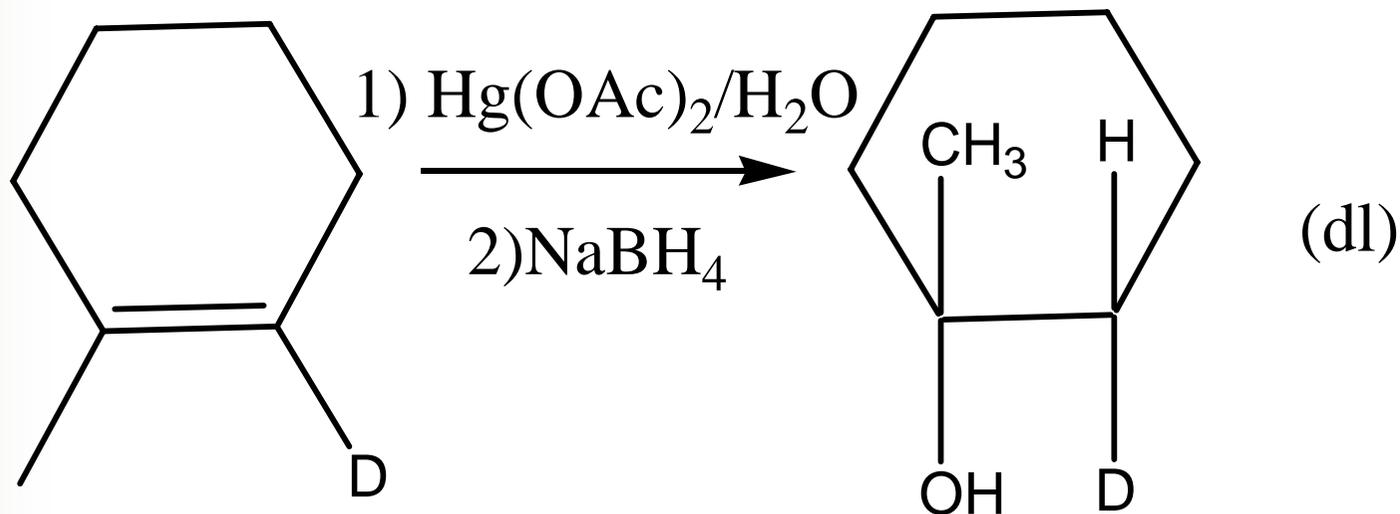
1. $X_2 = Cl_2, Br_2$
2. 遵循马氏规则
3. 用于制备卤代醇
4. 加成反应的立体化学为反式加成

6. 硼氢化 - 氧化反应



1. 遵循反马氏规则
2. 用于制备醇
3. 加成反应的立体化学为顺式加成

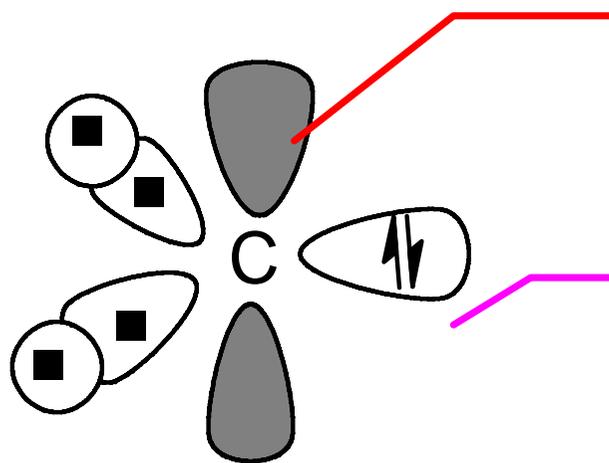
7. 羟汞化-脱汞反应



1. 遵循马氏规则
2. 用于制备醇
3. 加成反应的立体化学为反式加成

8. 与卡宾反应

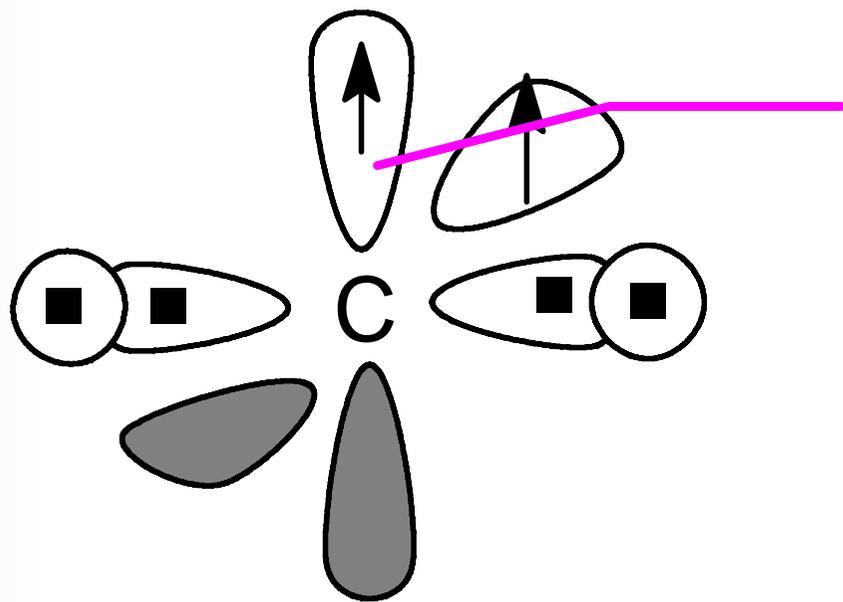
- A. 卡宾的结构
- a. 单线态卡宾
- $:\text{CH}_2$ C带有6个电子; C sp^2 杂化



空 p 轨道
缺电子

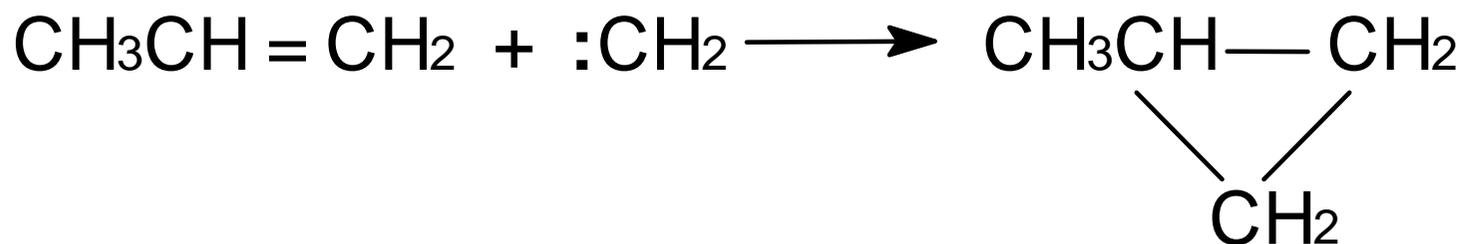
一对自旋相反
的电子添入一
个 sp^2 中
能量高

- *b.* 三线态卡宾
- $\cdot\text{CH}_2\cdot$ C带有6个电子; C sp杂化

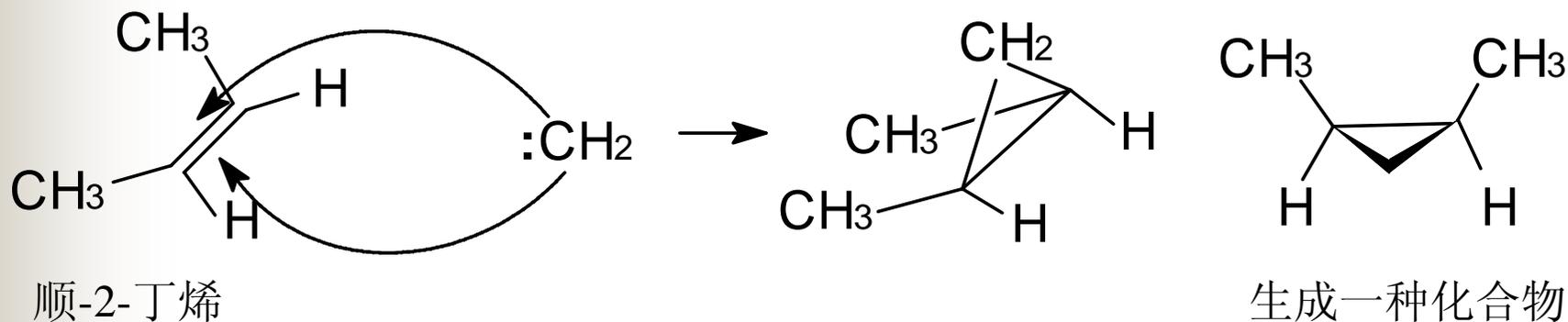


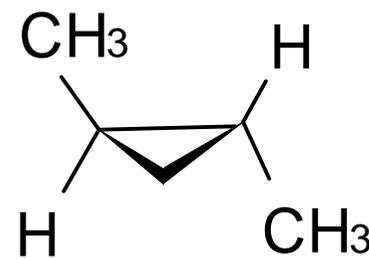
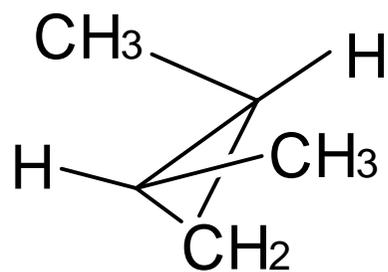
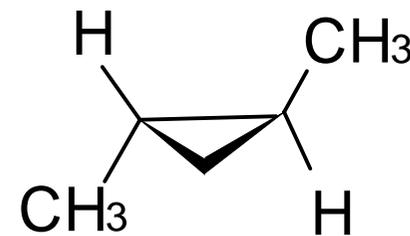
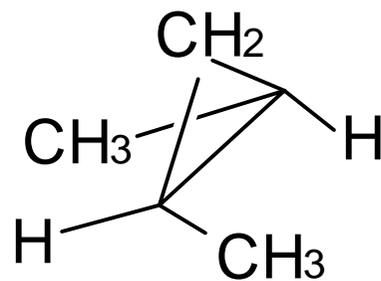
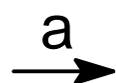
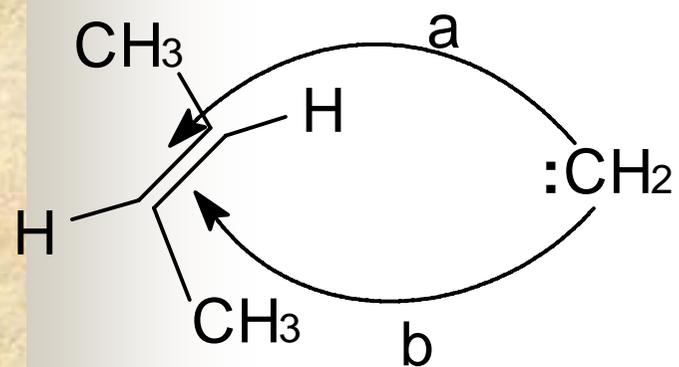
两个电子平行
自旋添入两个 p
轨道中
能量低

8. 单线态卡宾的加成——立体专一



反应机理：

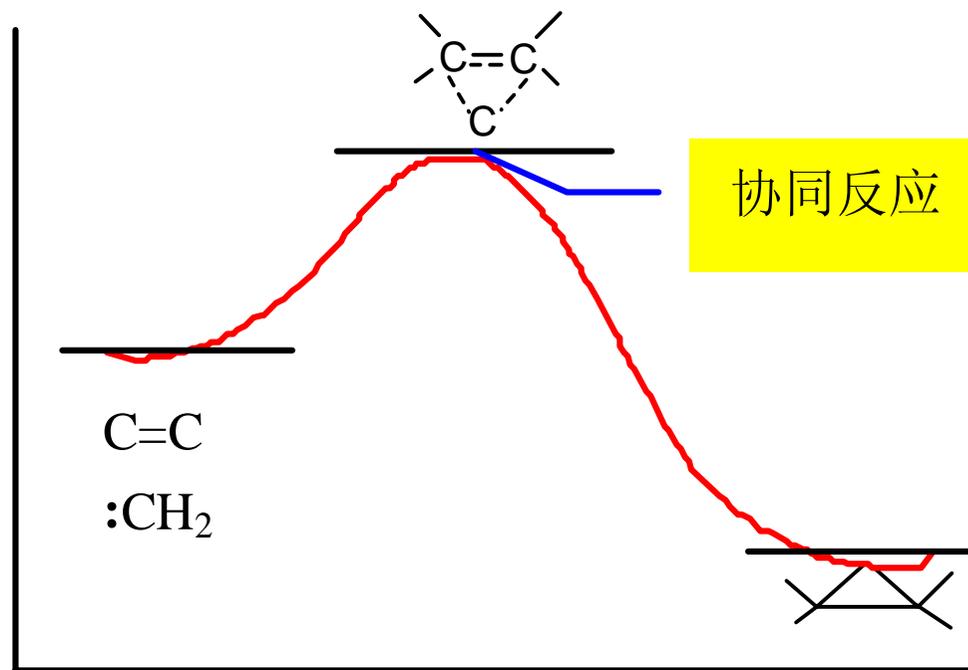




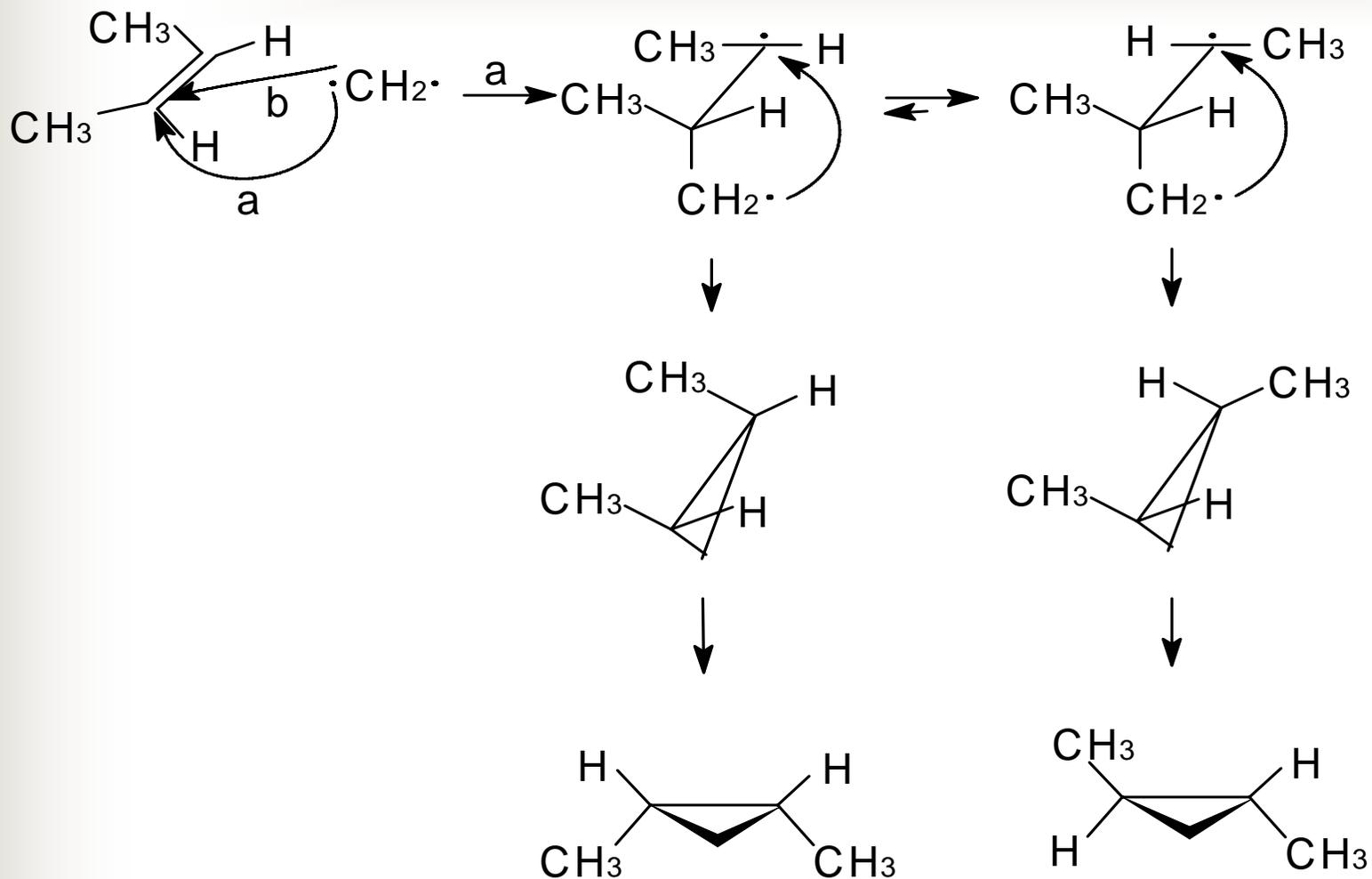
反-2-丁烯

生成一对对映体

- **立体专一反应**：从一种立体有別化合物出发得到另一种立体有別化合物(包括一对对映体), 称为立体专一反应。
- **协同反应**：不经任何中间体的反应称为协同反应。

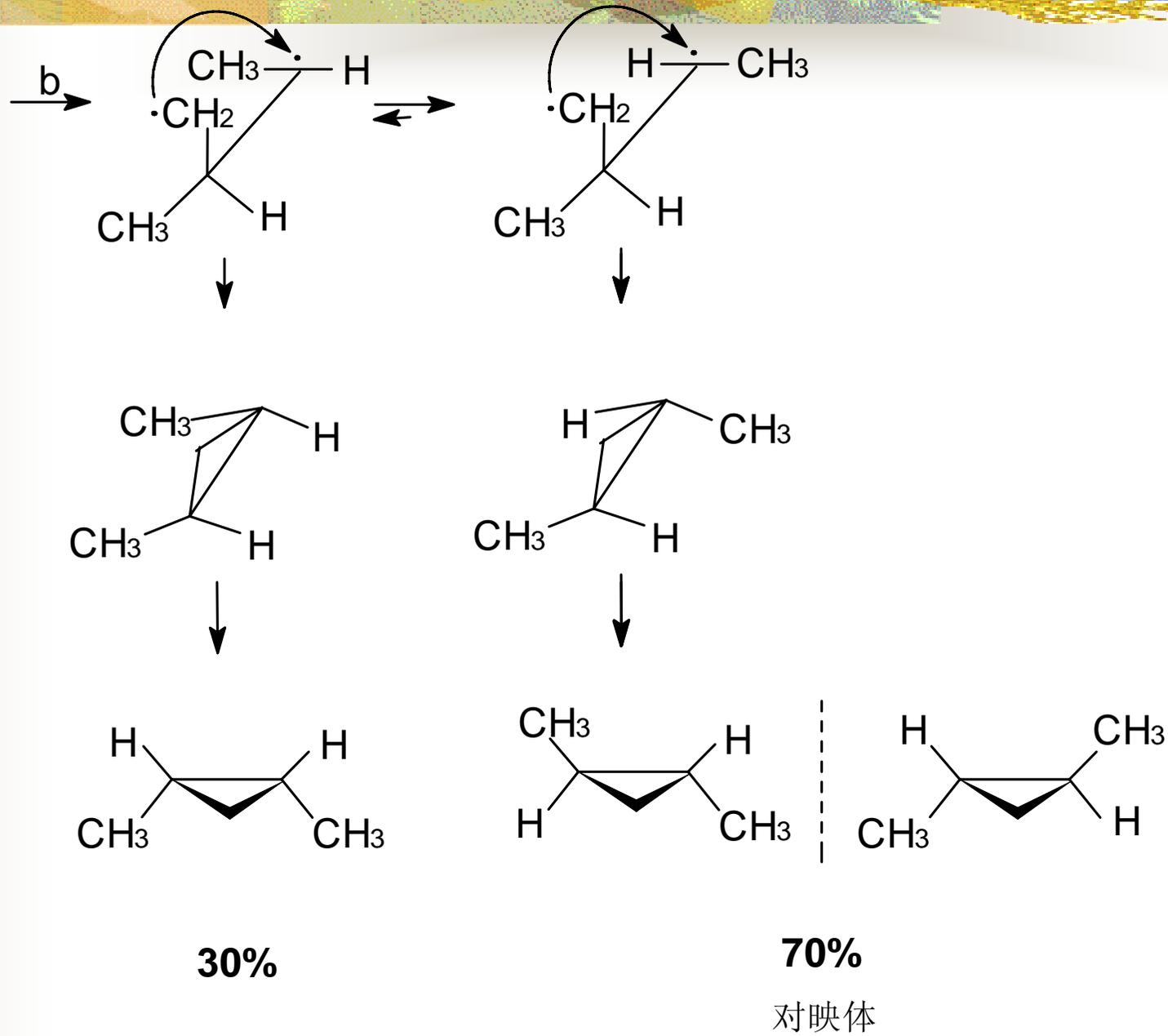


C. 三线态卡宾的加成



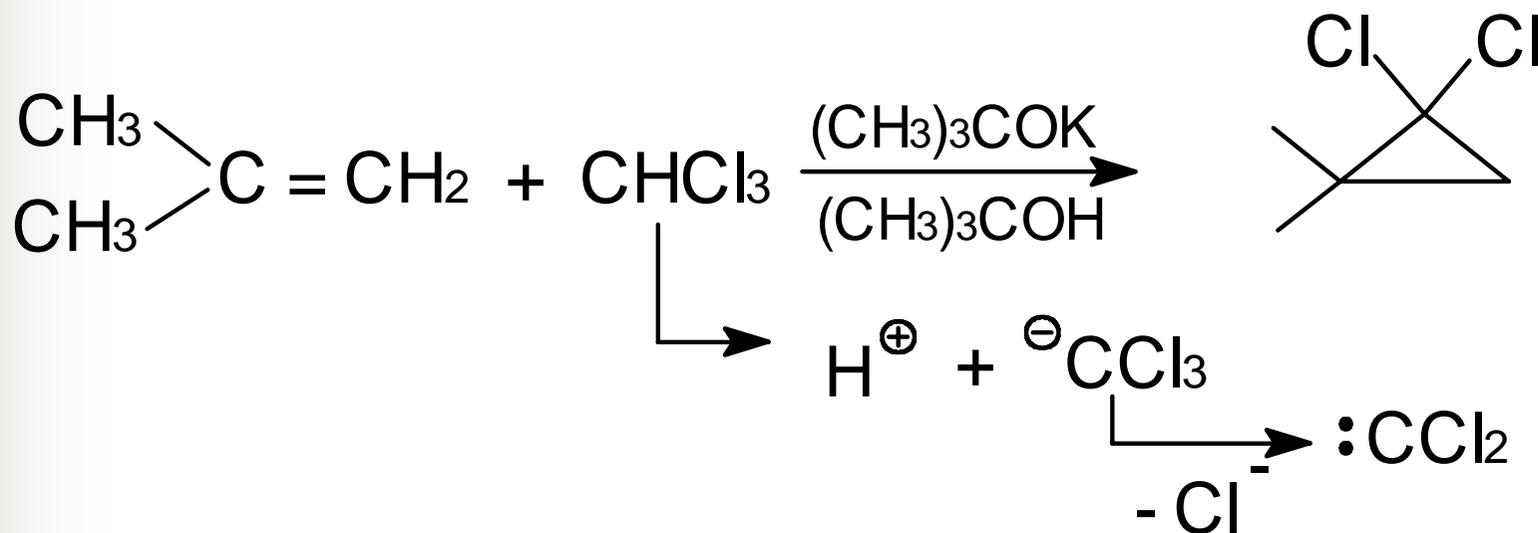
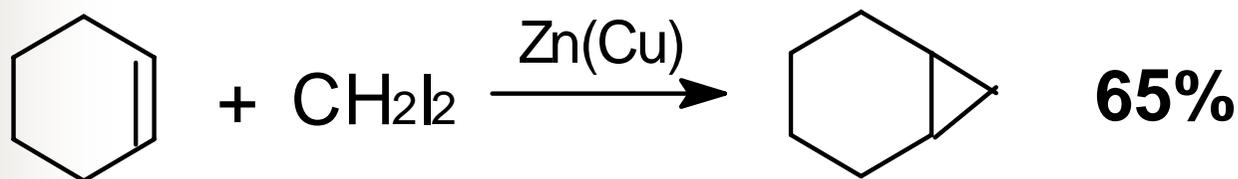
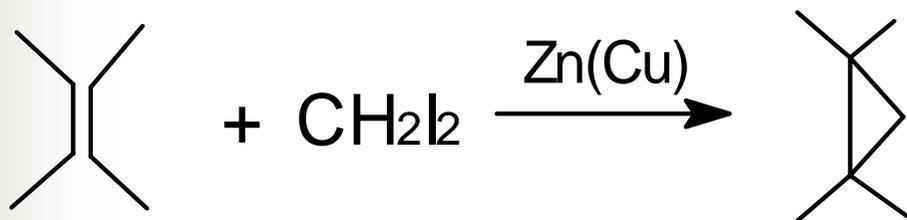
次产物

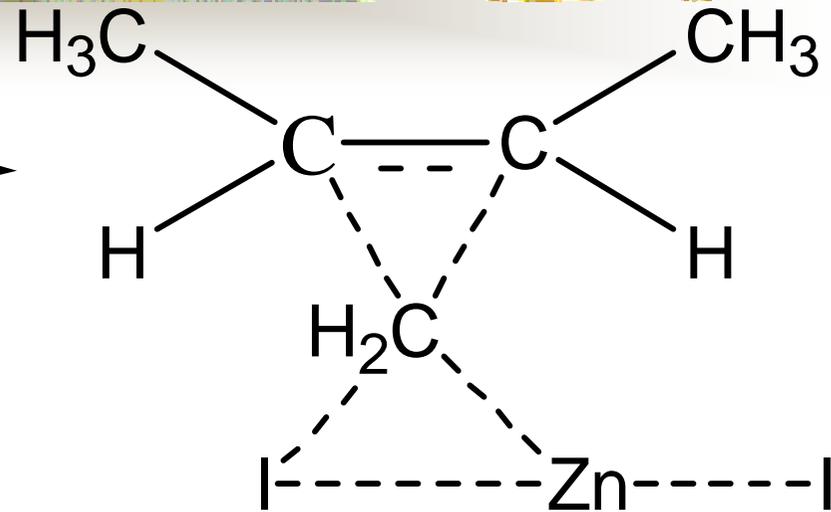
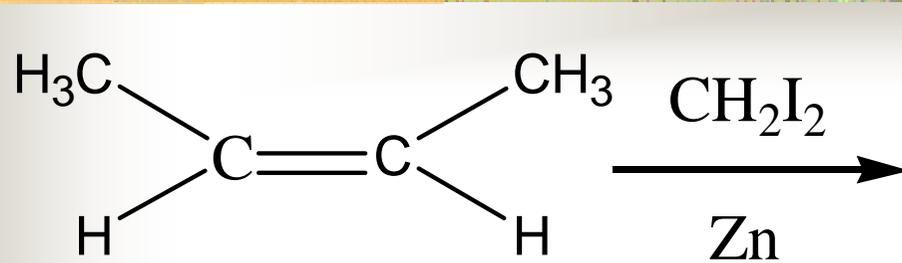
主产物
中间体构象稳定



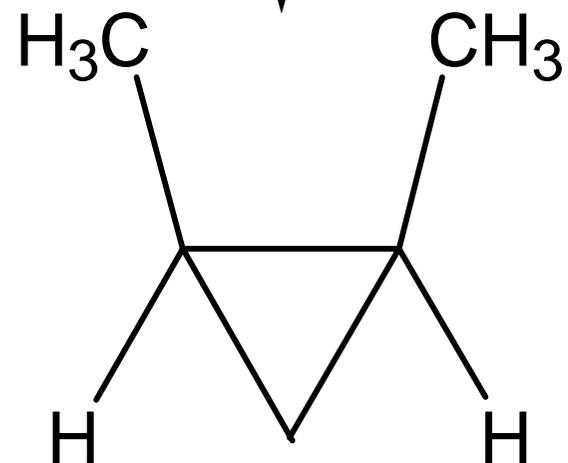
- 
- **立体选择性反应**：从立体有別化合物能够得到几种立体有別化合物时，有一种占优势则称该反应为立体选择性反应。

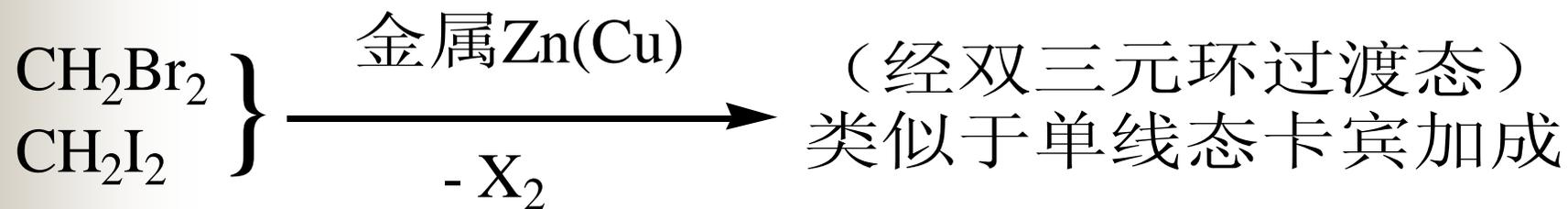
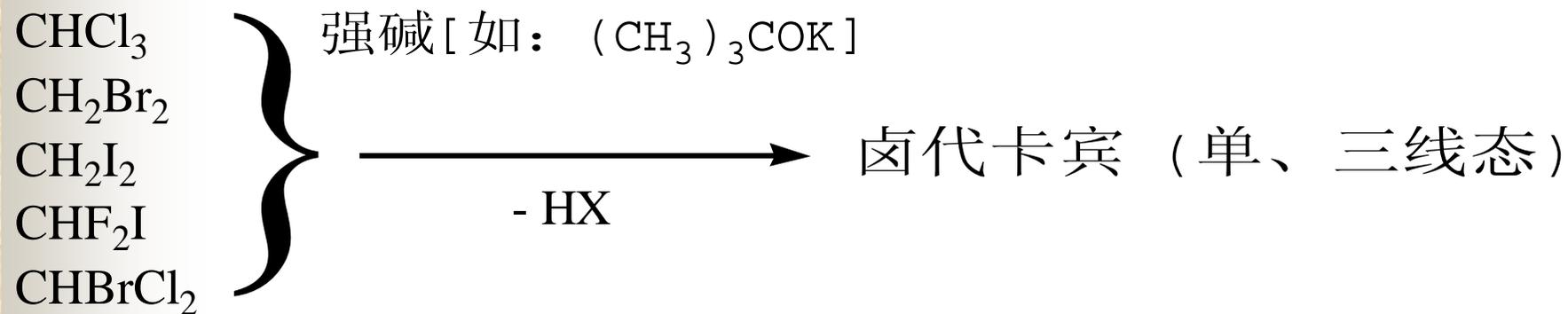
D. 产生卡宾的条件及卡宾衍生物





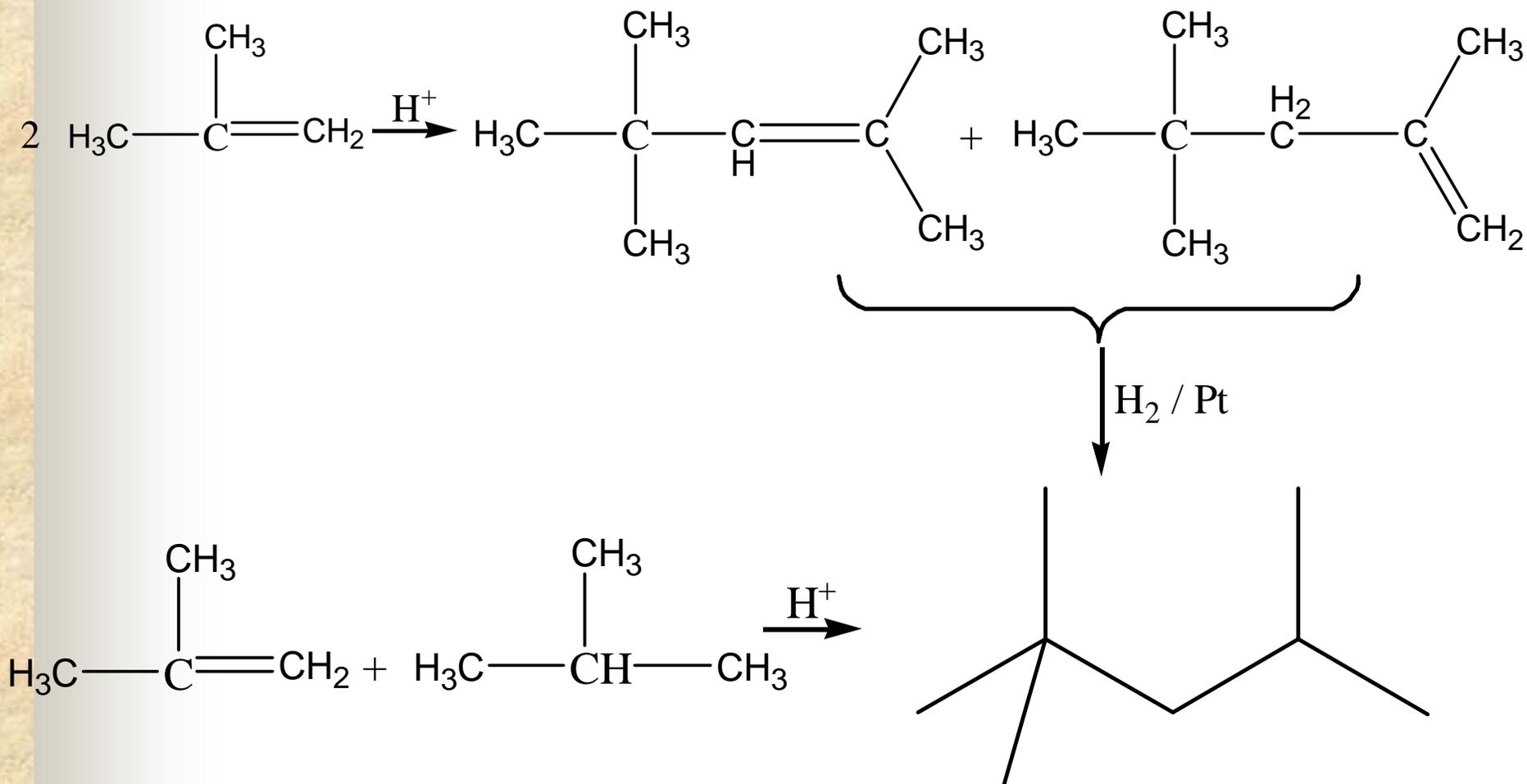
$$- \text{ZnI}_2$$





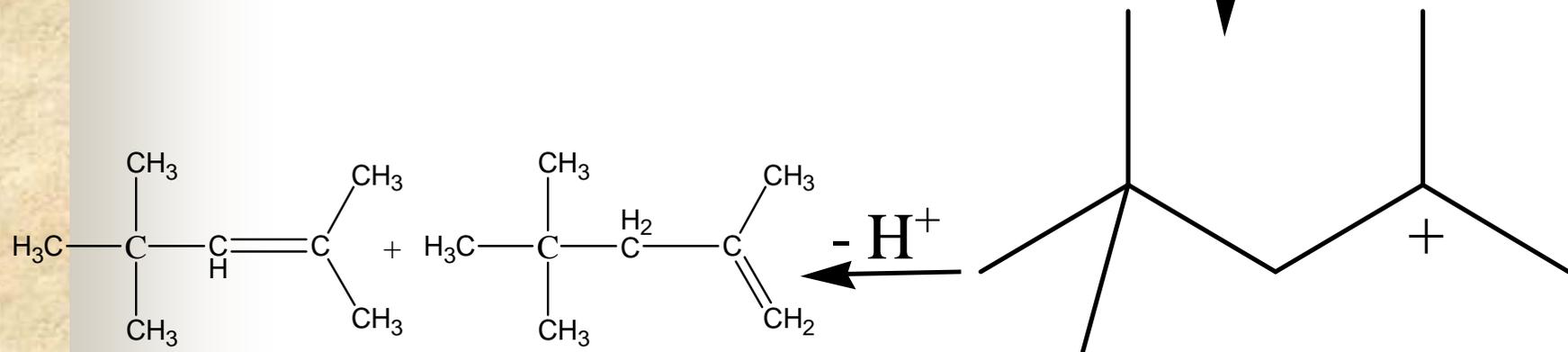
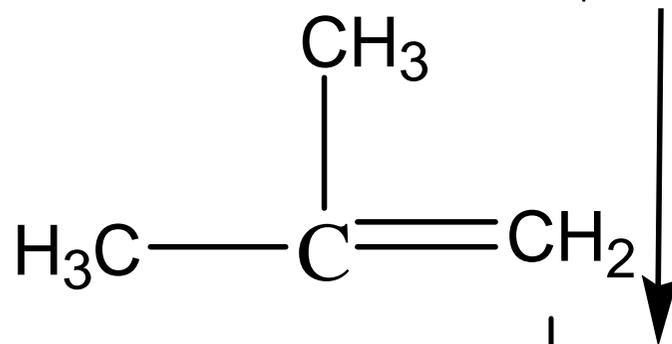
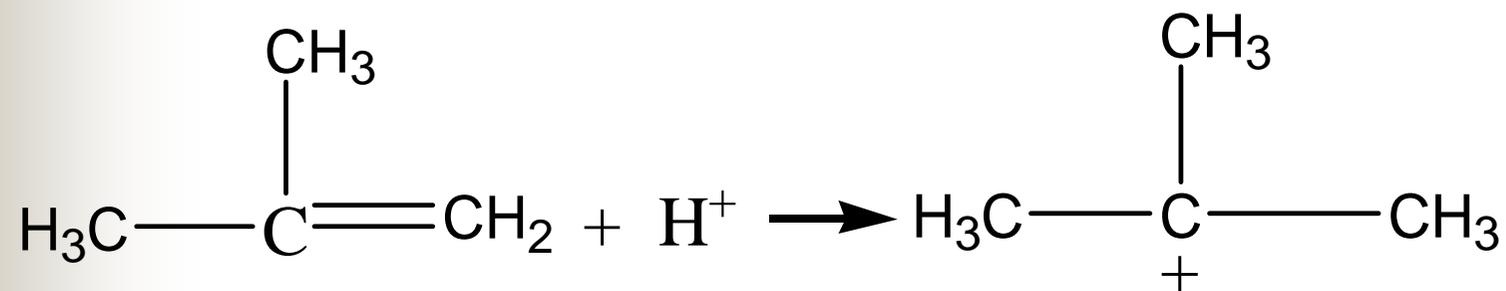
9. 烯烃二聚及烷基化反应

■ A. 反应实例:

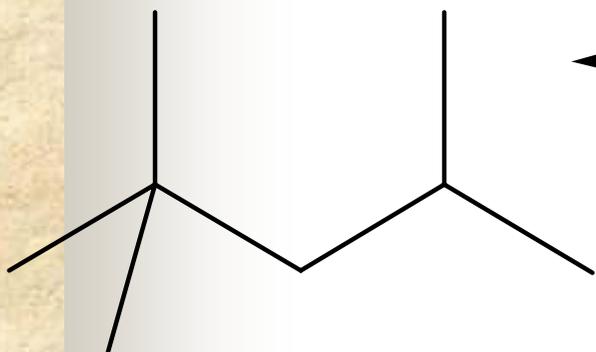
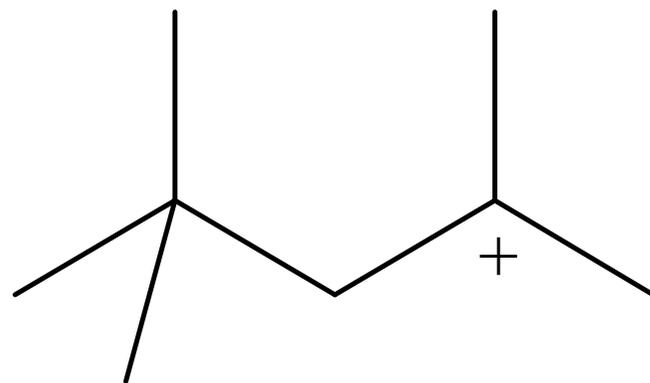
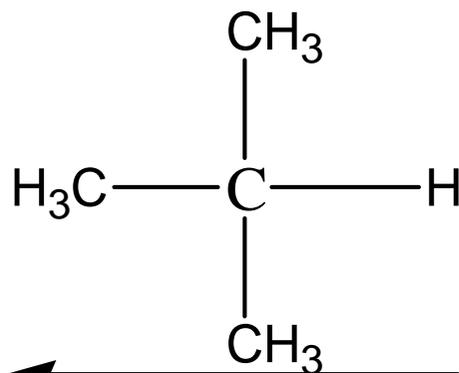
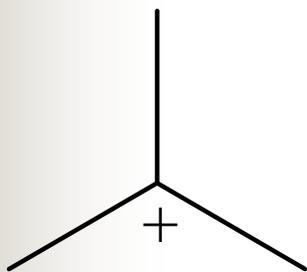
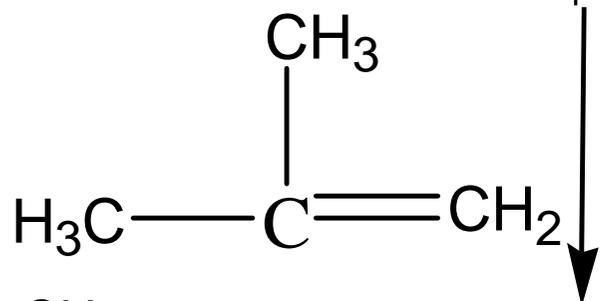
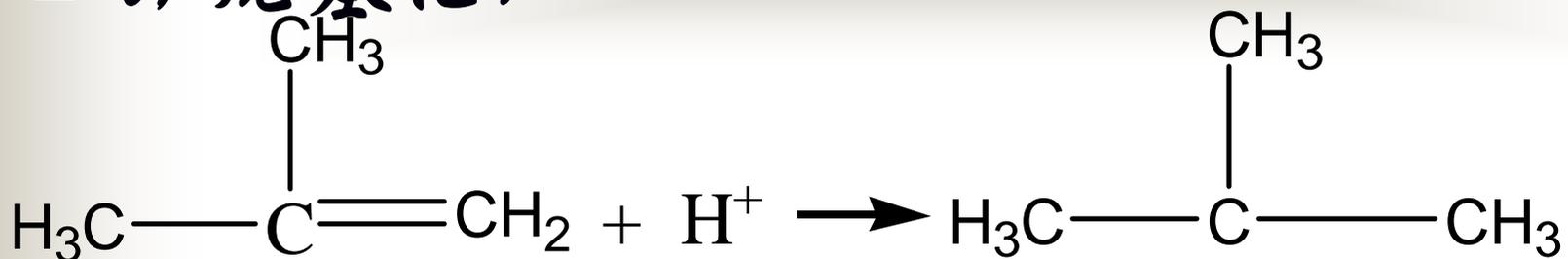


■ B. 反应机理:

■ a. 二聚:

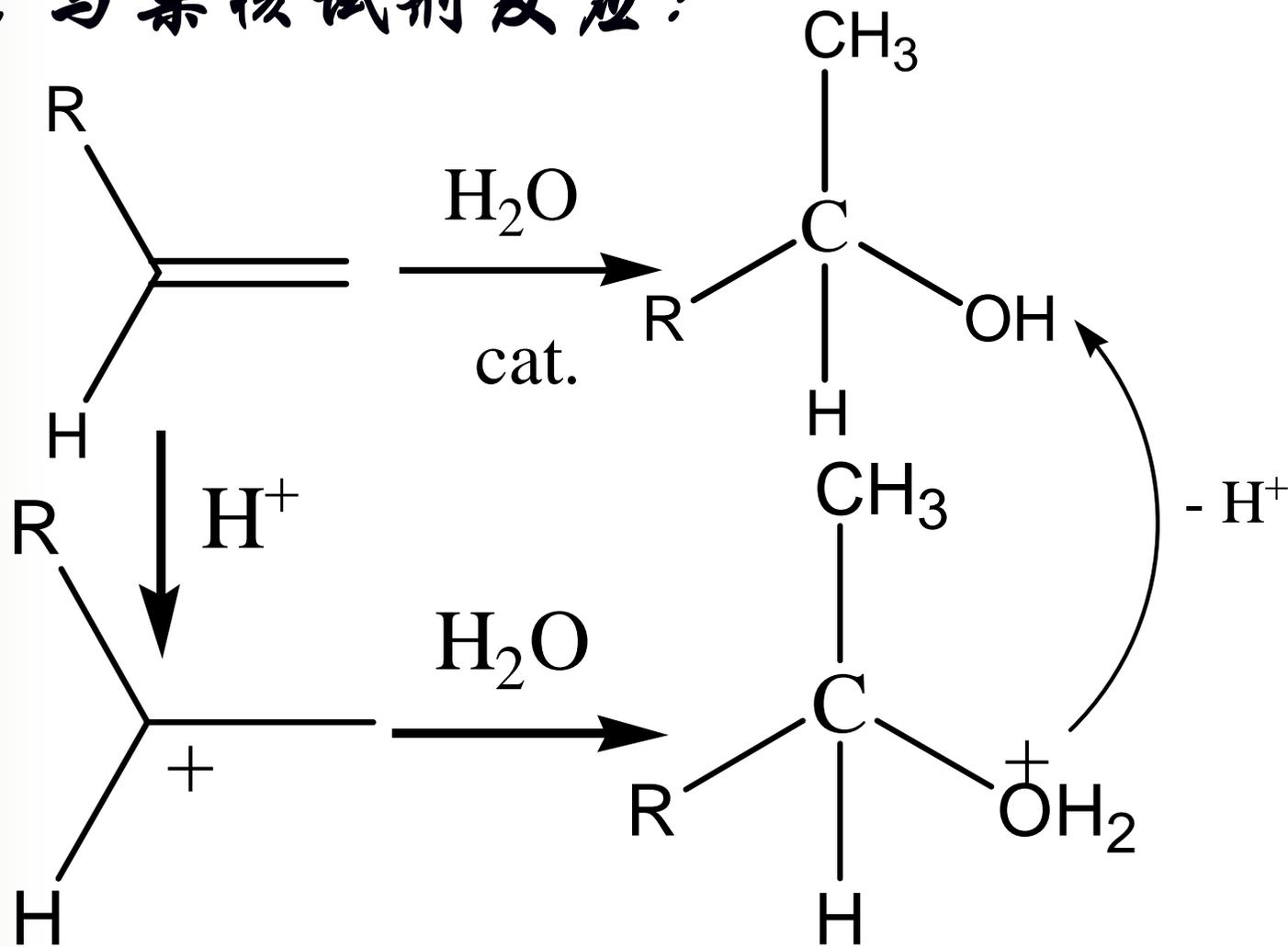


■ 6. 烷基化:

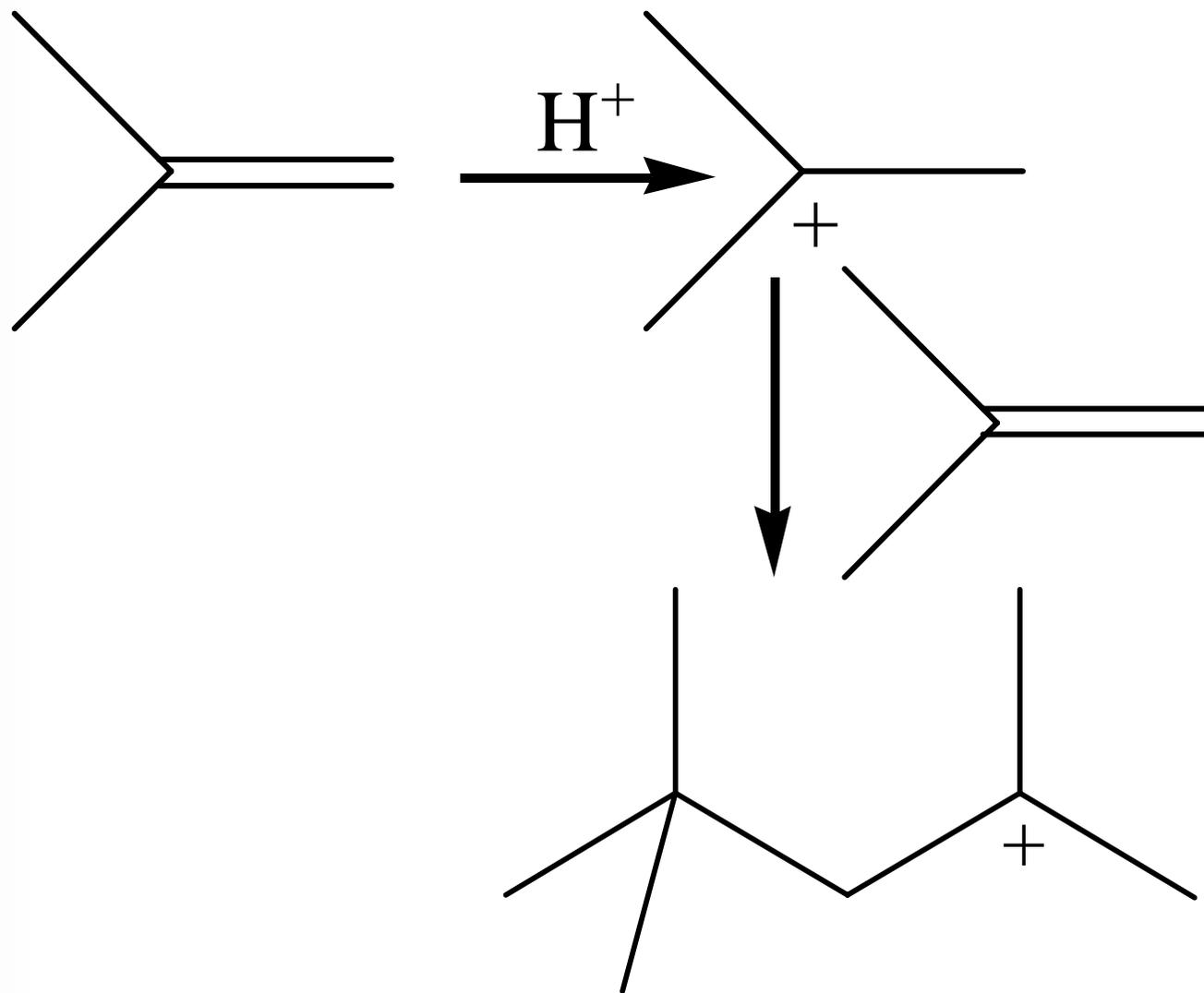


■ c. 碳正离子可进行的反应:

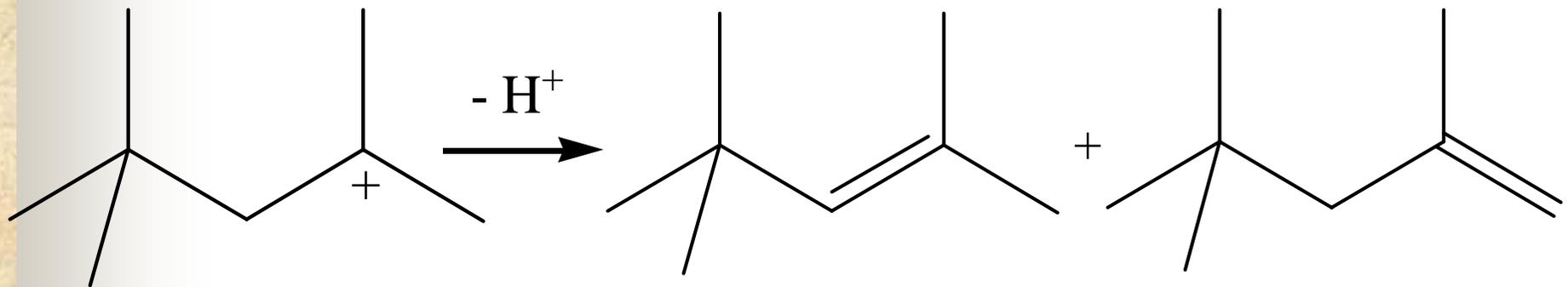
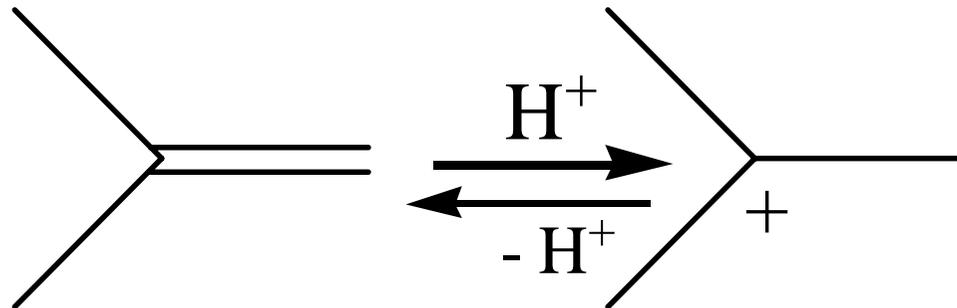
■ a. 与亲核试剂反应:



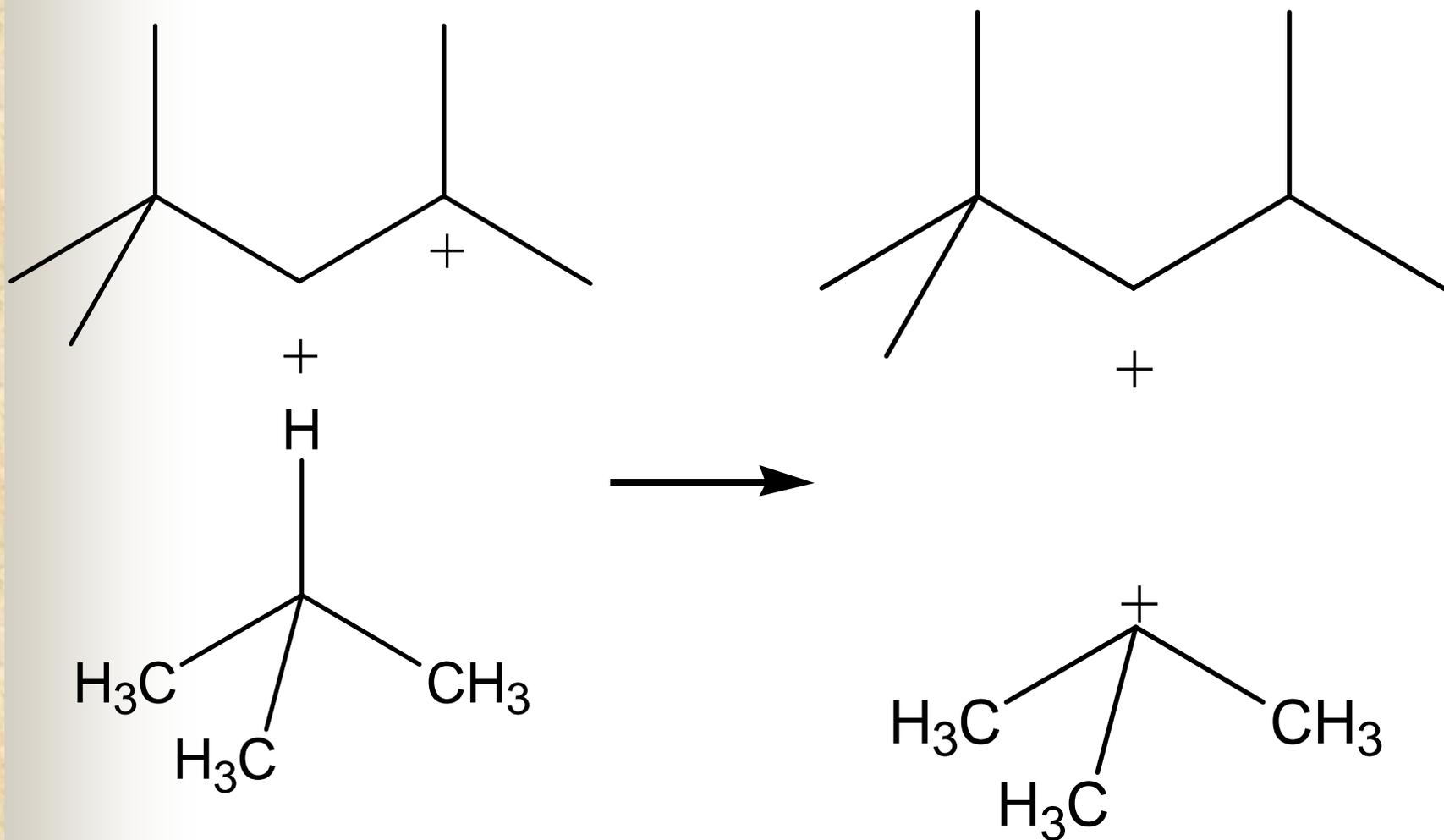
■ 6. 作为亲电试剂参与反应:



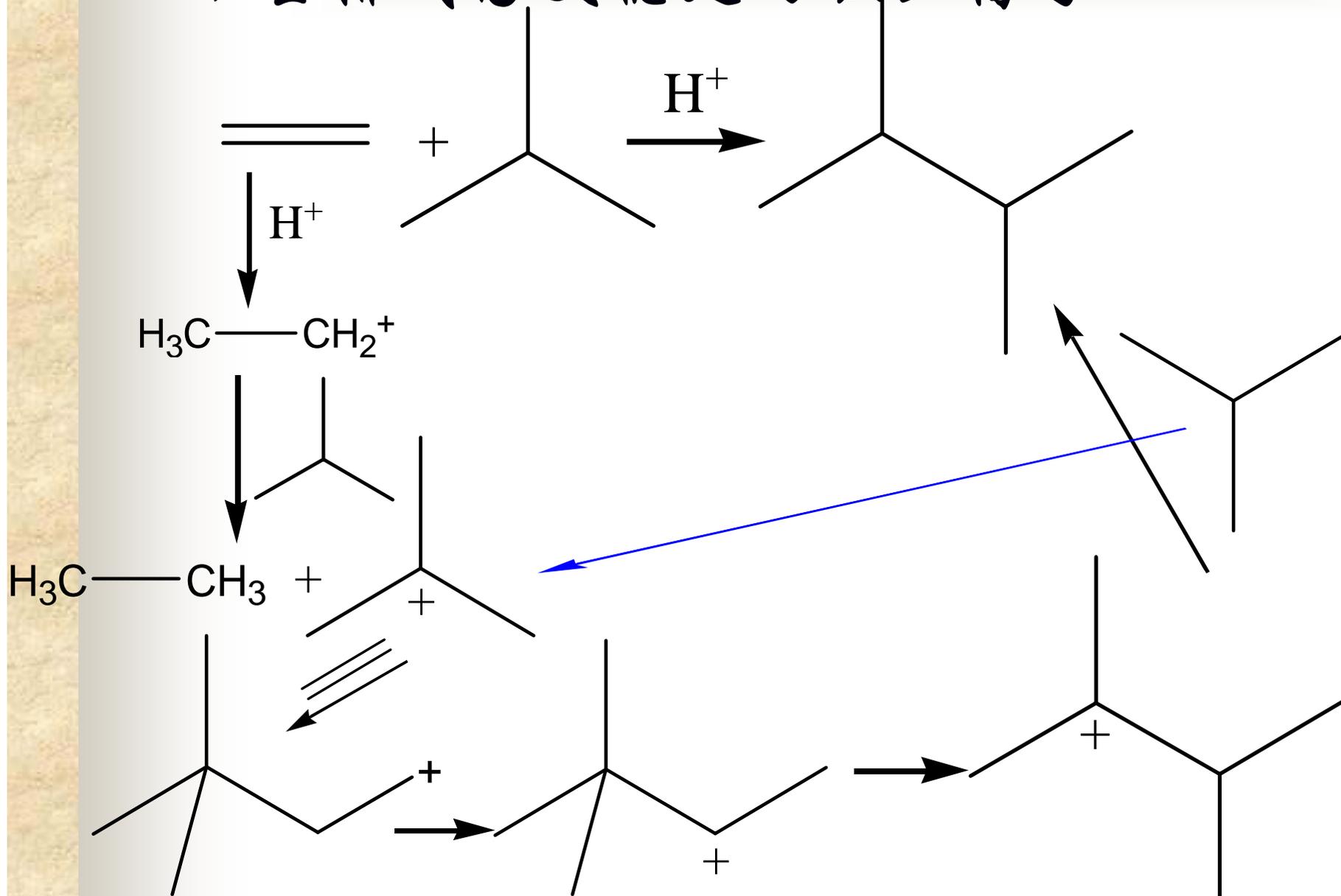
■ c, 脱去质子氢成为烯烃:



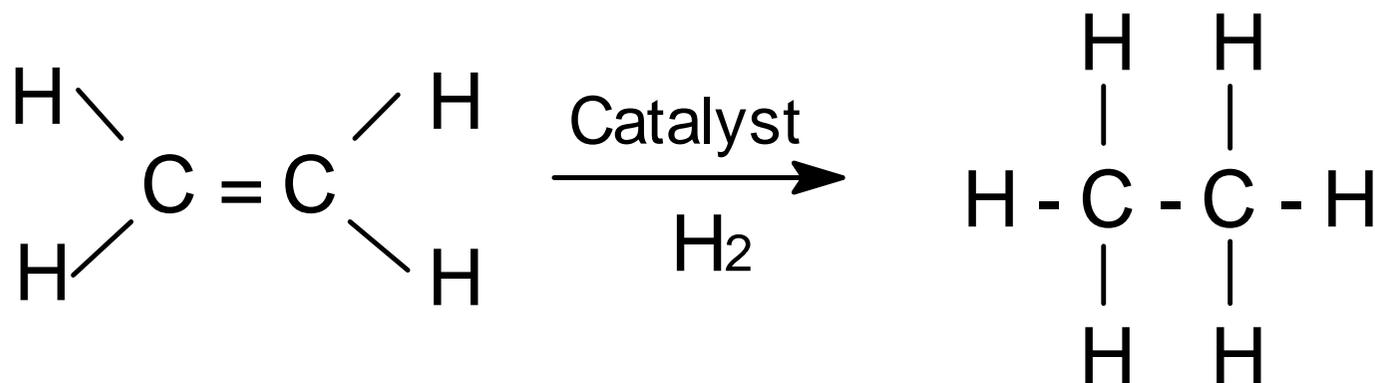
■ d. 拔取负氢成为烷烃——拔氢反应:



■ e, 重排成为更稳定的碳正离子:



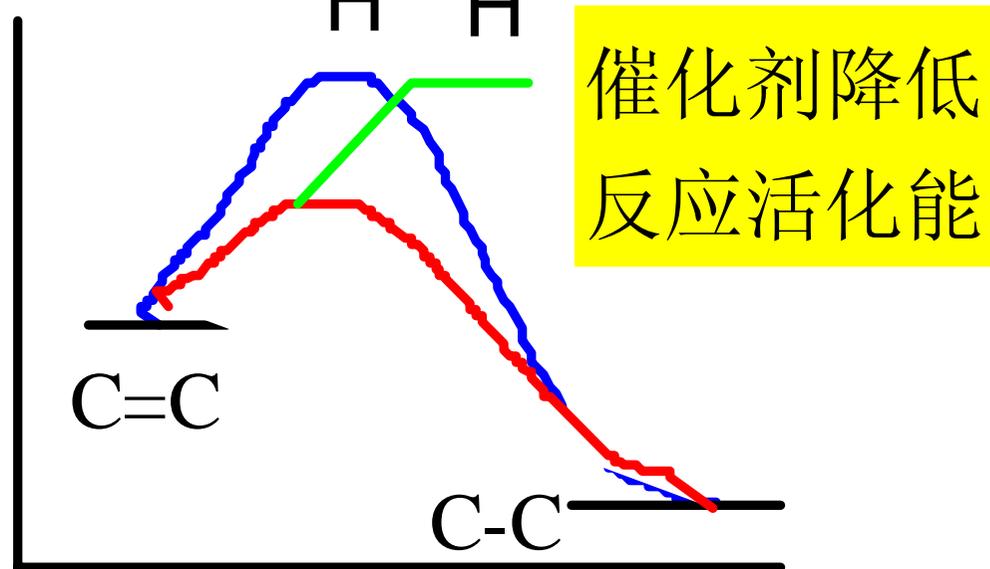
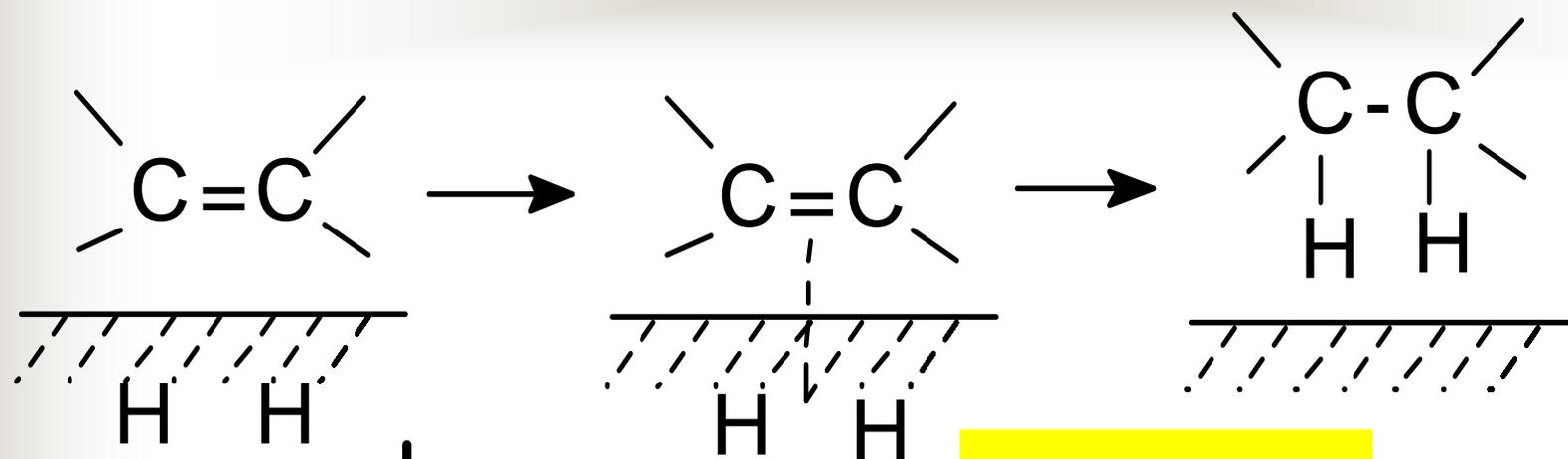
§ 4.5 化学性质 II —— 催化加氢



1. 催化剂

A. 异相催化剂

催化活性 $\text{Pt} > \text{Pd} > \text{Ni}$



Raney Ni: Ni Al合金 NaOH Ni (多孔超微粉)

■ B. 均相催化剂

$[(C_6H_5)_3P]RhCl$ 金属有机化合物

■ C. 反应特点

a. 顺式加成

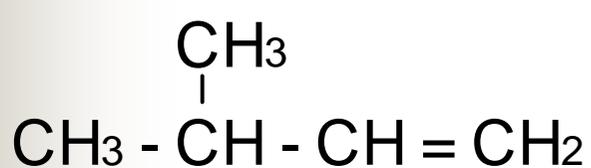
b. 取代基少 \Rightarrow 空间阻碍小 \Rightarrow 加氢速度快

2. 氢化热与烯烃稳定性

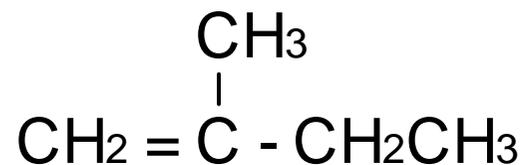
A. 氢化热

氢化热: 1 mol 不饱和化合物加氢生成饱和化合物所放出的热量为氢化热。

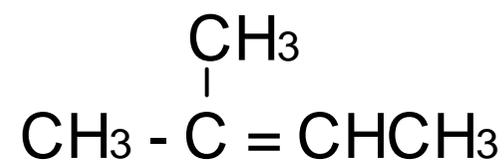
B. 烯烃稳定性



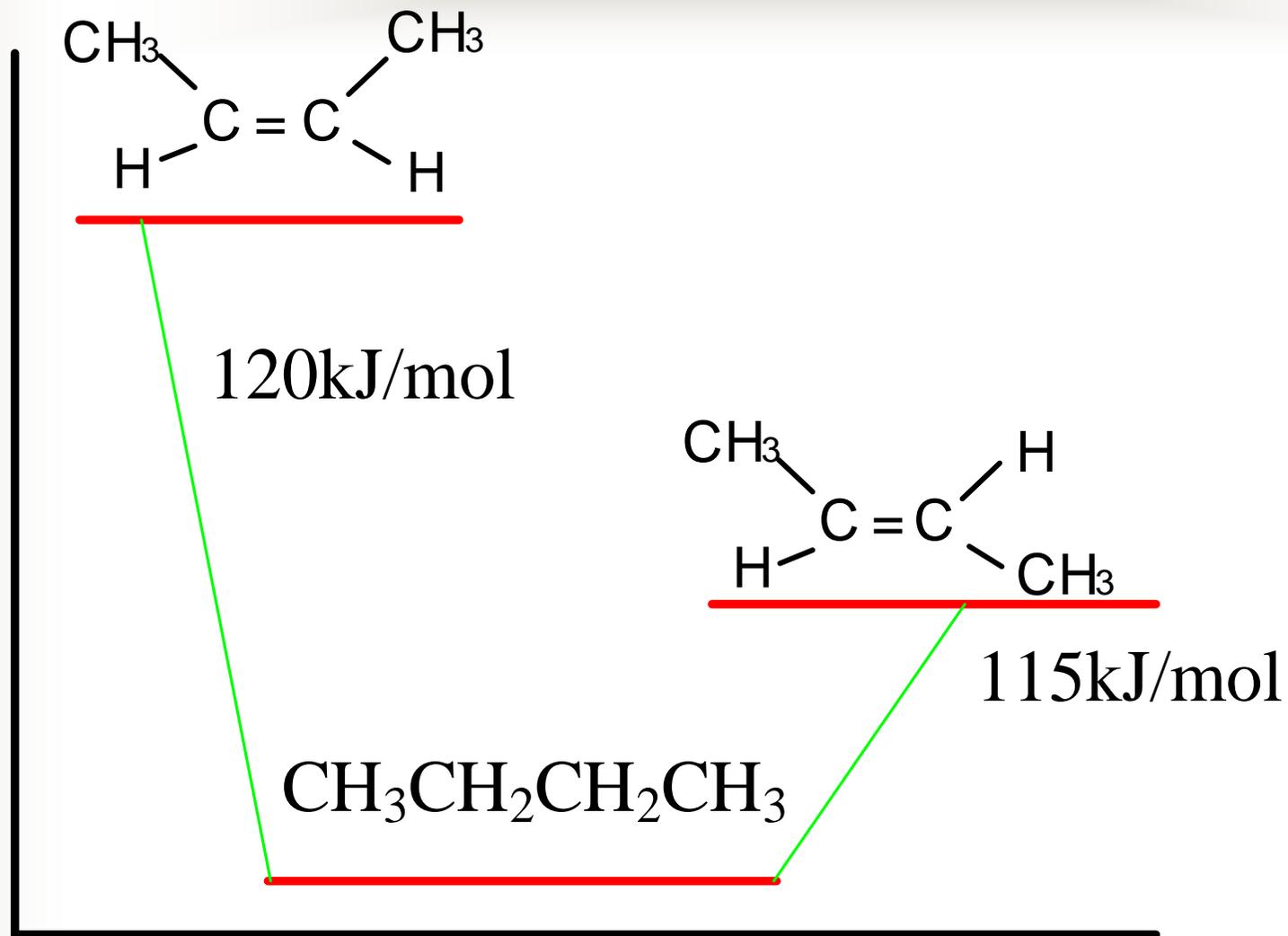
$$\Delta H = 127 \text{kJ/mol}$$



$$120 \text{kJ/mol}$$

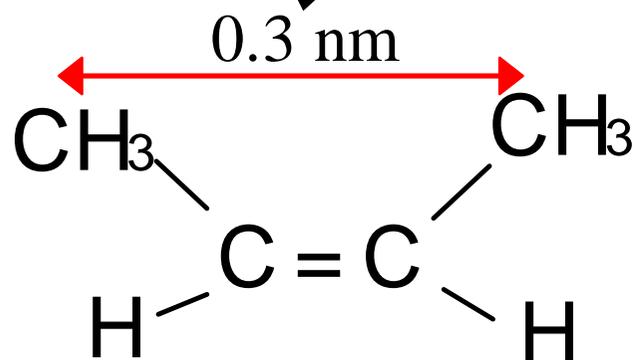


$$113 \text{kJ/mol}$$

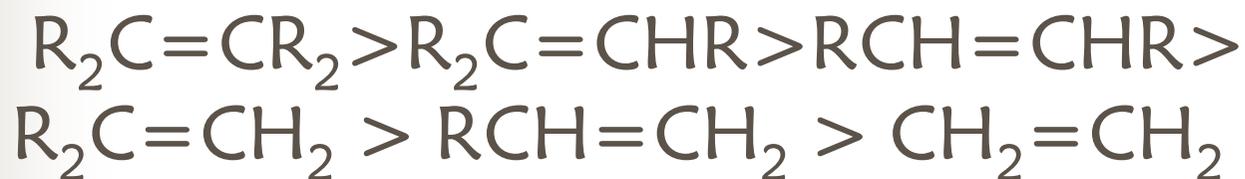


CH₃ 半径 0.2 nm

斥力较大



总结：烯烃稳定性

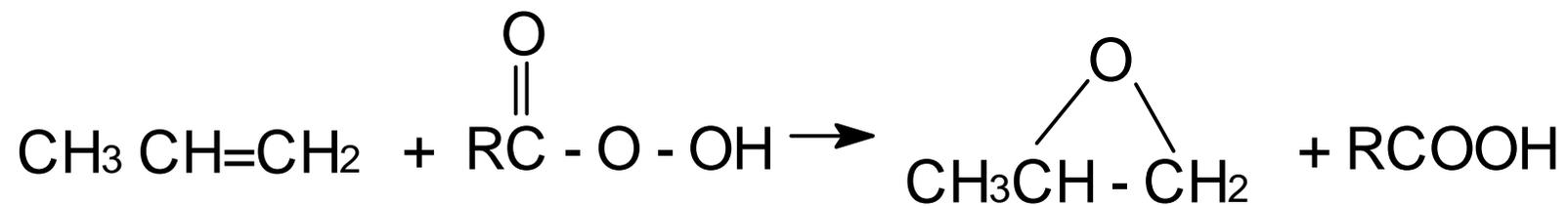


a. 取代基越多越稳定；

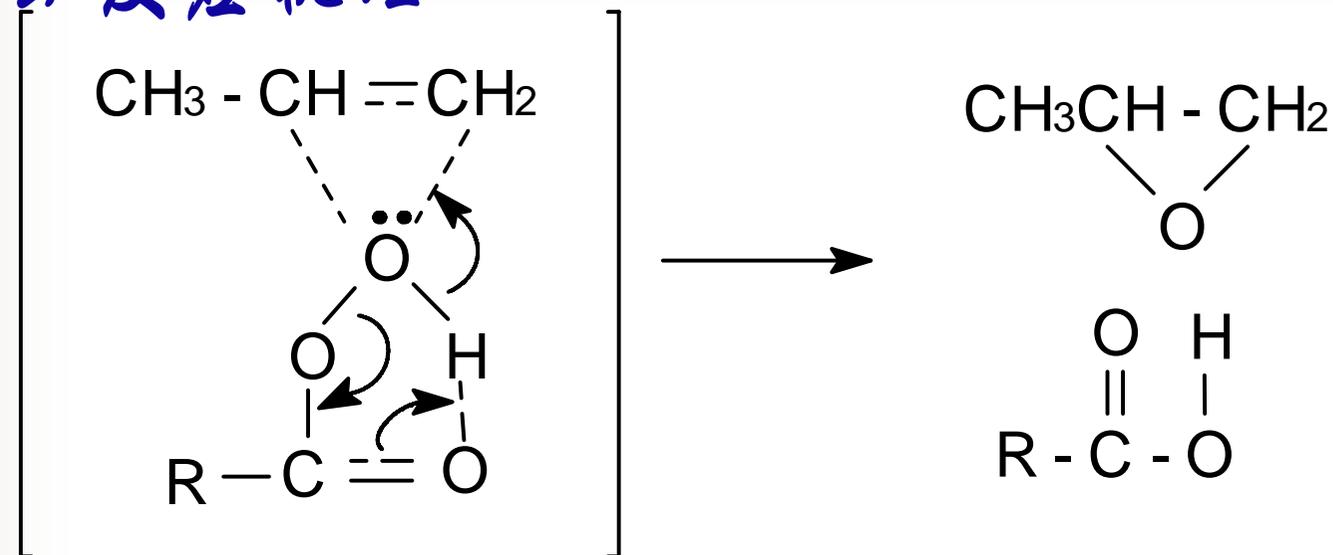
b. 反式比顺式稳定；

§ 4.6 化学性质 III —— 氧化反应

1. 过氧酸氧化



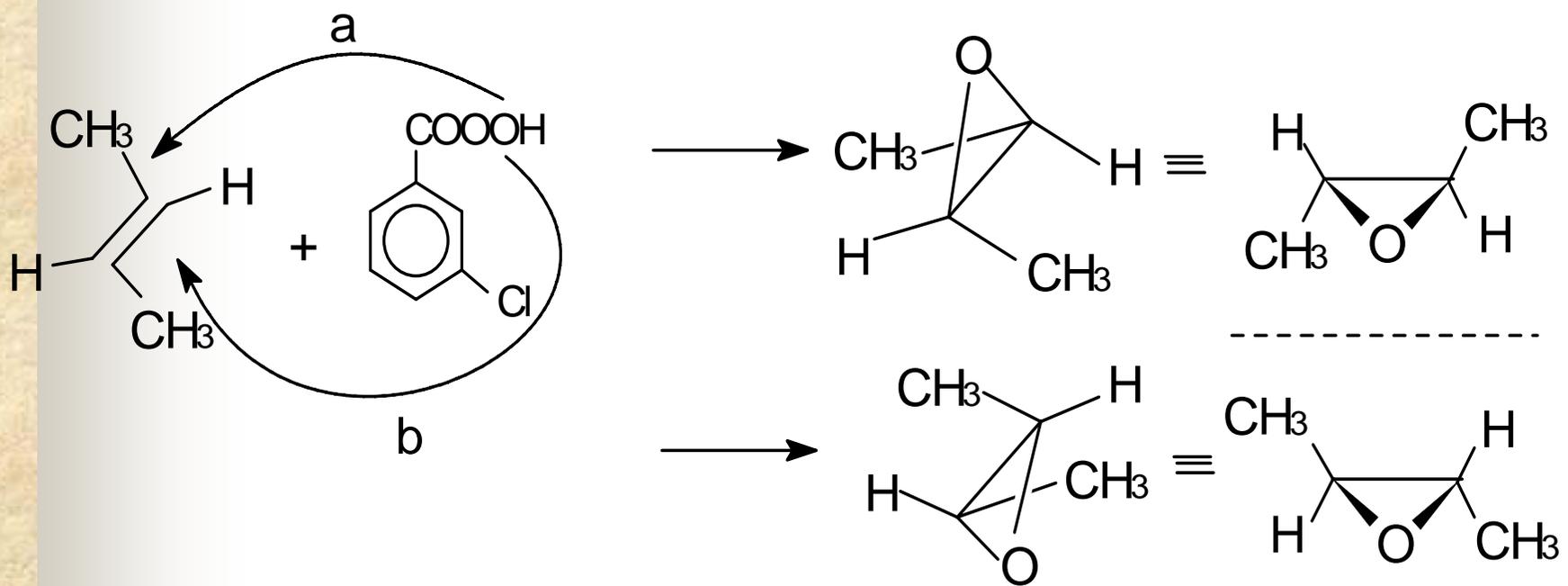
A. 反应机理



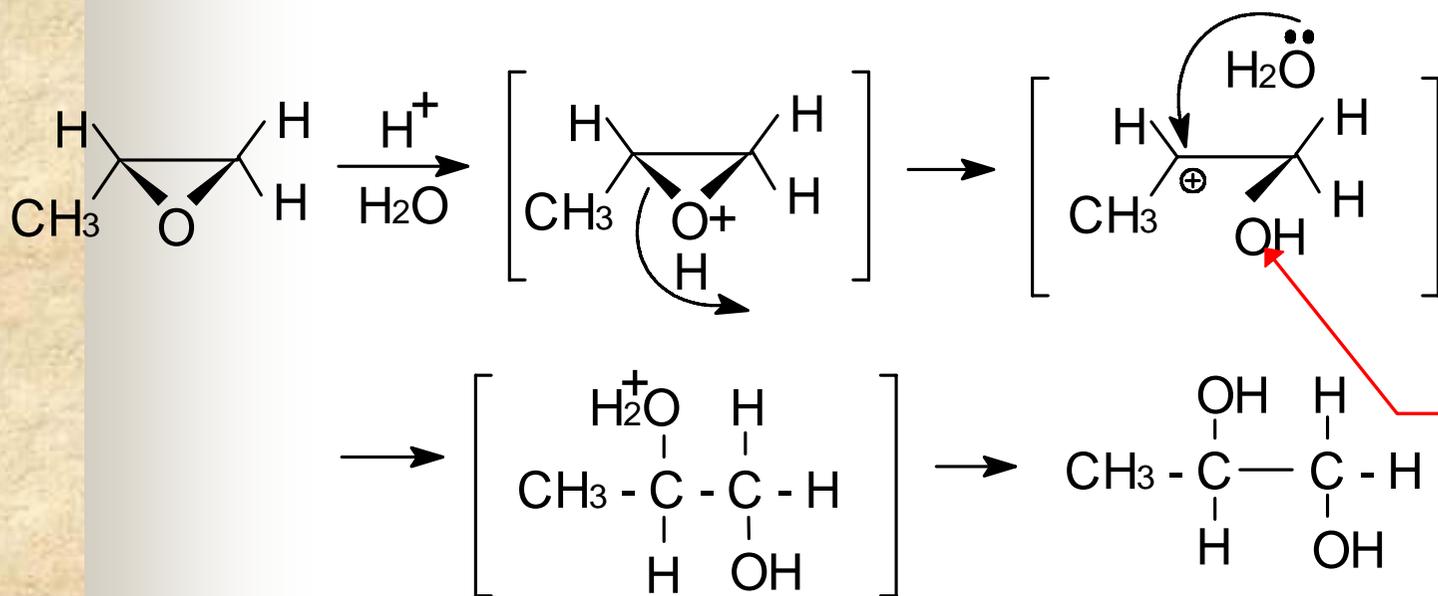
B. 特点

- 制备环氧化合物；
- 顺式加成，立体专一；
- 产物水解制备连二醇。

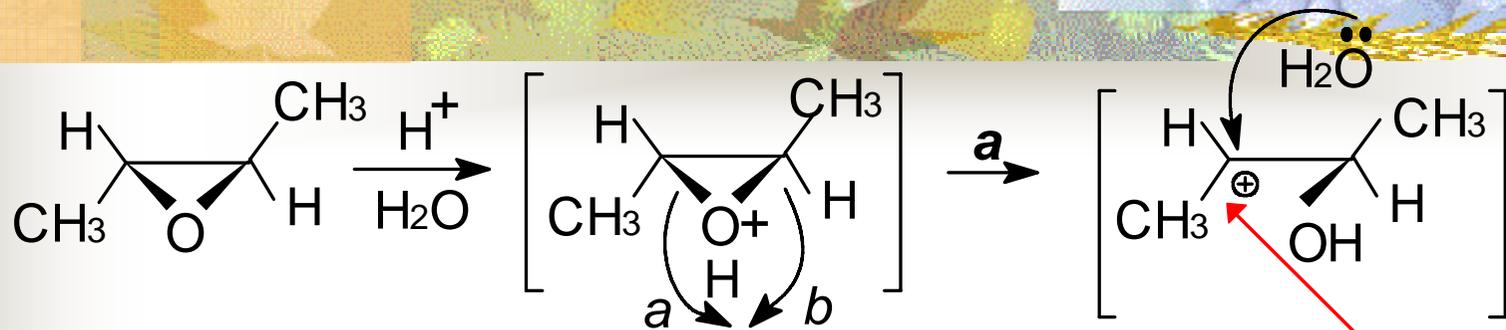
c. 环氧化合物水解反应



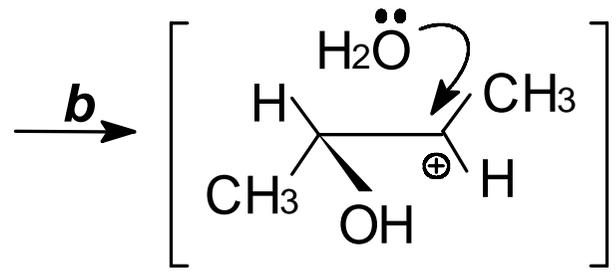
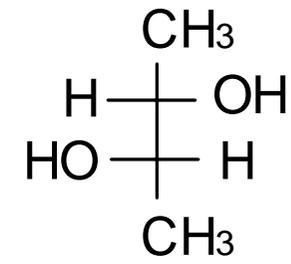
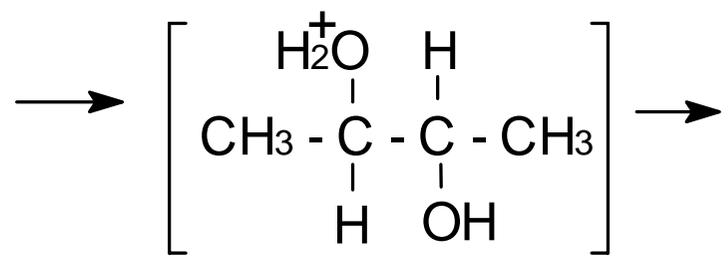
酸性介质水解



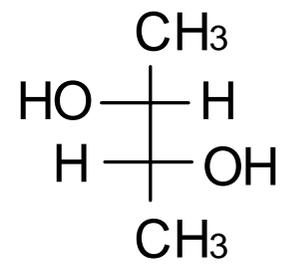
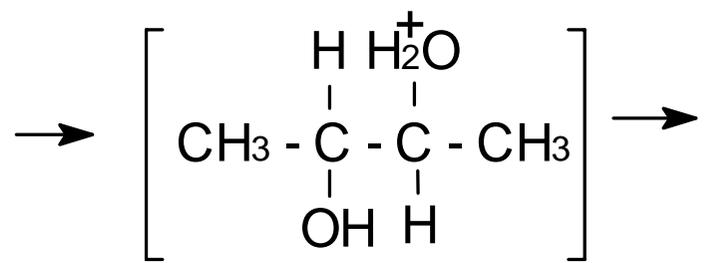
形成一个稳定的正碳离子中间体



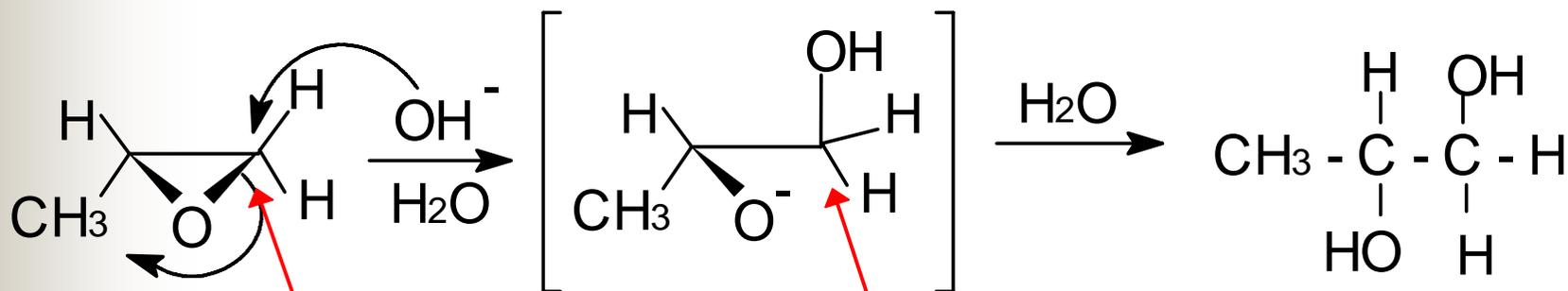
反式共平面进攻正碳离子



对映体



碱性介质水解



特点:

进攻空间阻碍
小的位置

反式共平面

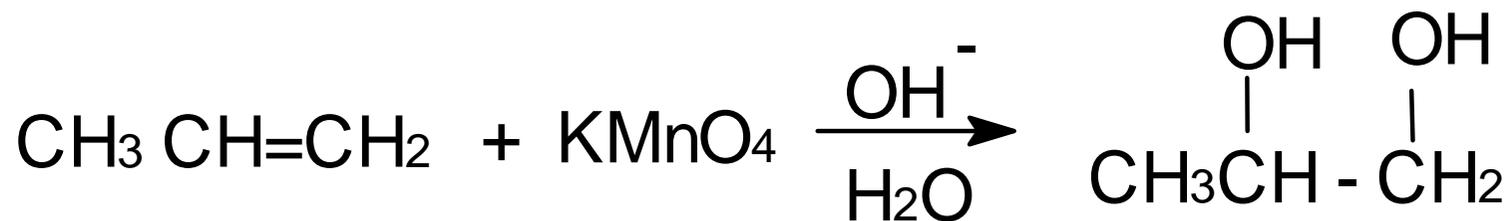
a. 制备连二醇:

b. 为反式加成产物:

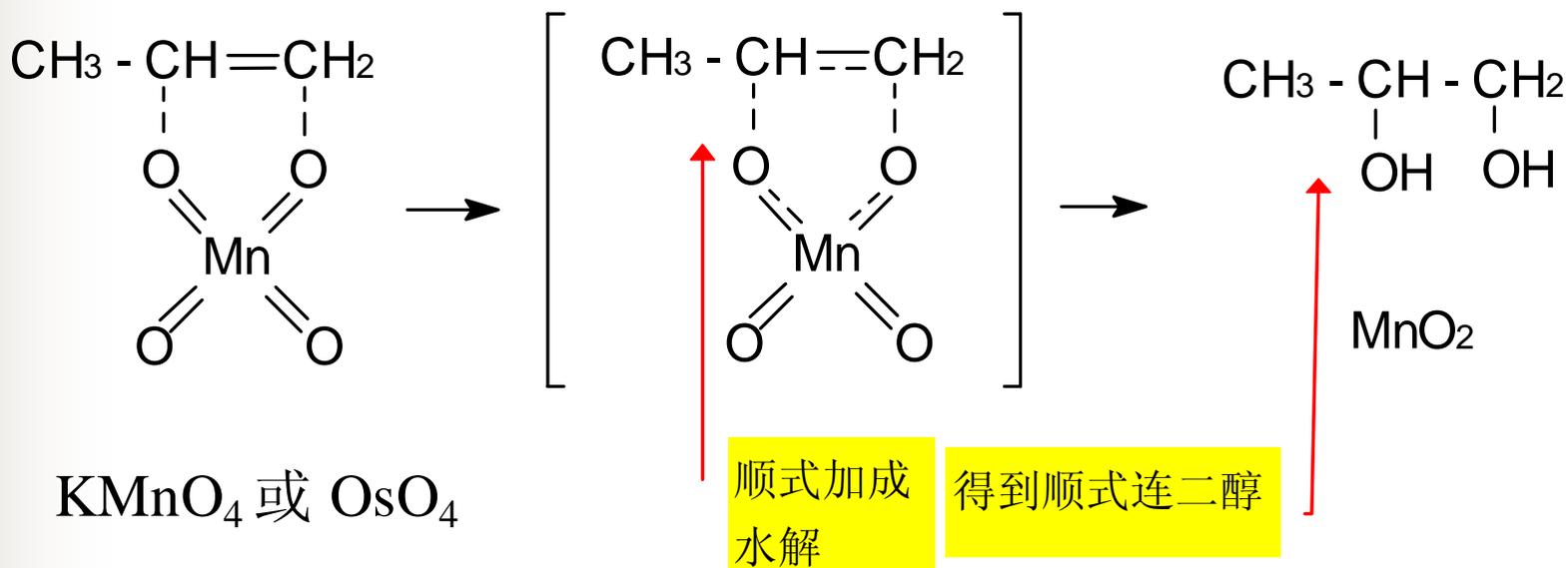
c. 酸性介质水解需经历稳定的正碳离子中间体:

碱性介质水解需进攻空阻碍小的位置。

2. 碱性KMnO₄ 氧化



A. 反应机理



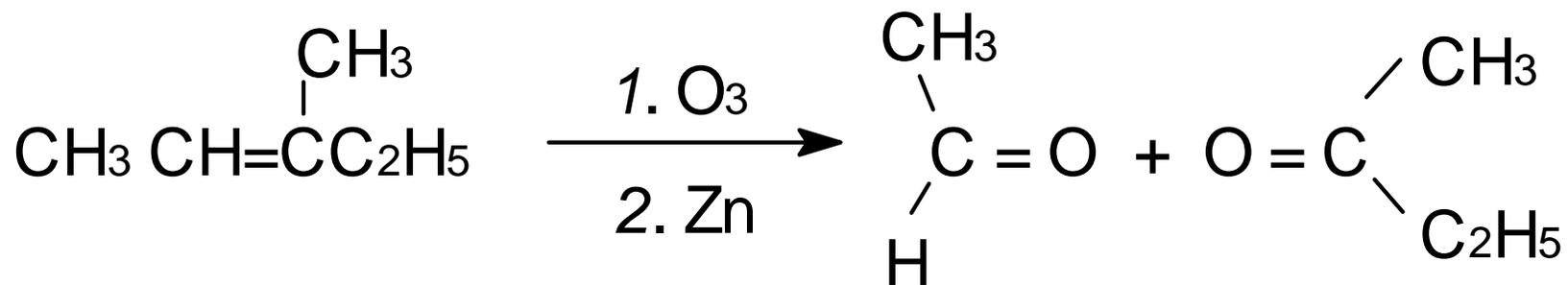
8. 特点

a. 制备连二醇; 顺式加成

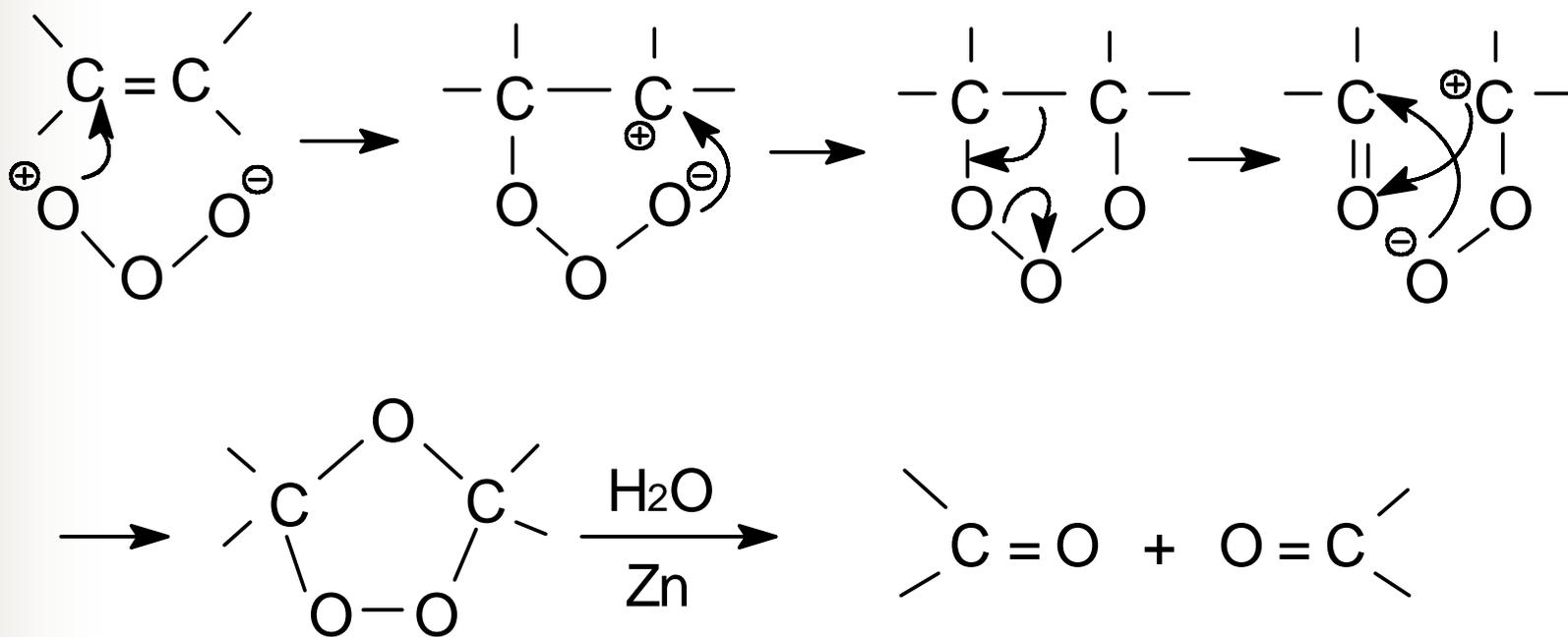
b. 低温下反应, 不易控制;

c. OsO_4 效果好, 但很昂贵。

3. 臭氧氧化



A. 反应机理:



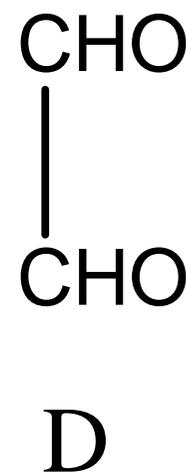
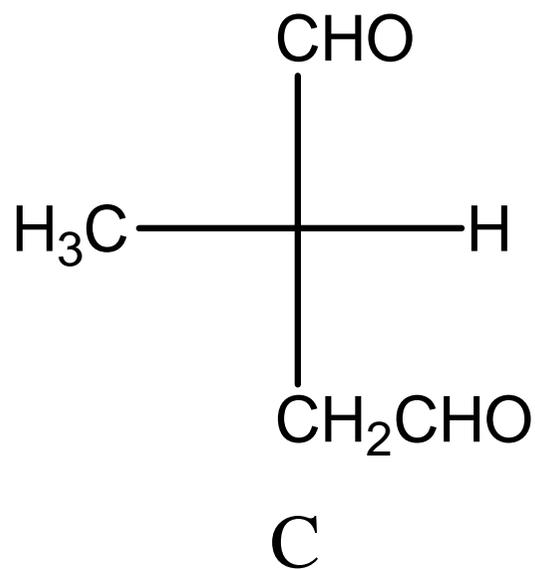
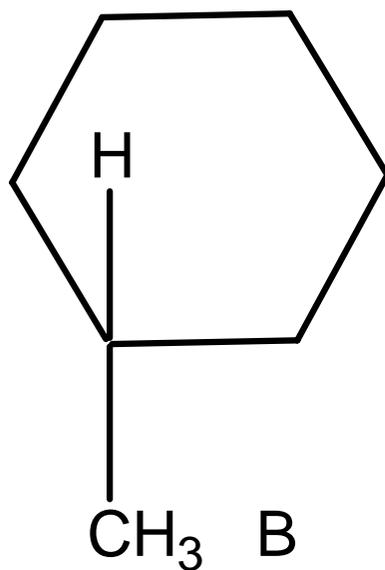
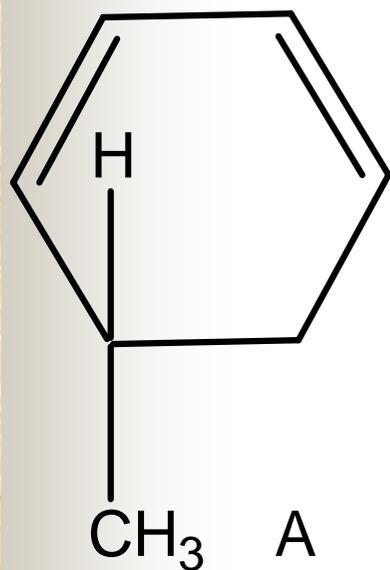
8. 特点

a. 产率高, 易操作;

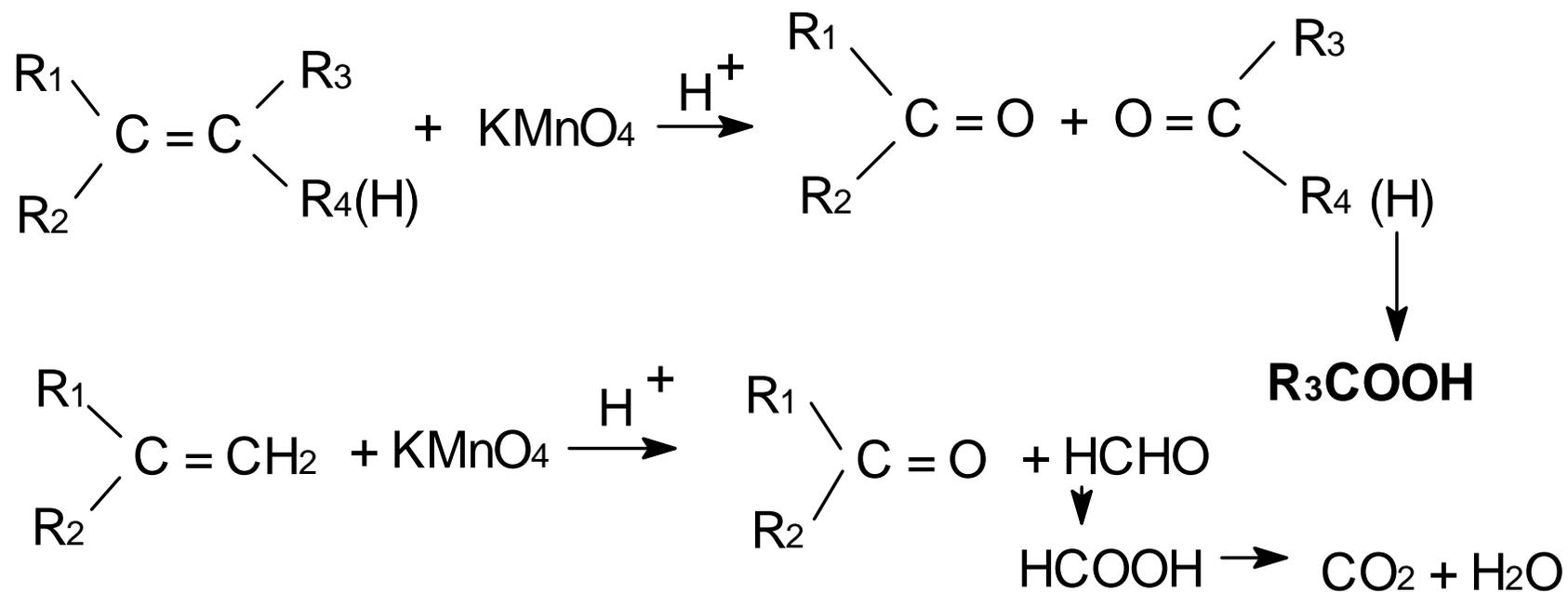
b. 测定双键位置;

c. 工业合成醛酮。

某一化合物A (C_7H_{10})，有旋光性，经催化加氢后得无旋光性的化合物B (C_7H_{14})；A用臭氧氧化后在Zn保护下水解可得一个有旋光性的二醛C ($C_5H_8O_2$) 和一个无旋光性的二醛D ($C_2H_2O_2$)，请写出A, B, C, D, 的可能结构(A, C需用立体结构表达)。



4. 酸性 KMnO_4 氧化



总结

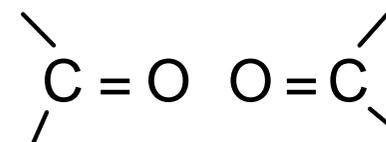
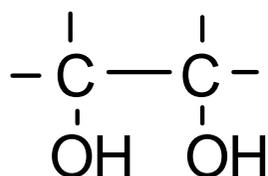
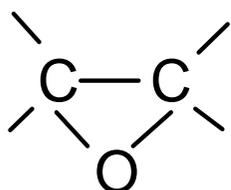
环氧化合物

顺式连二醇

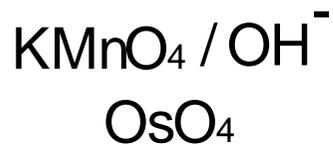
酮; 醛

酮; 酸

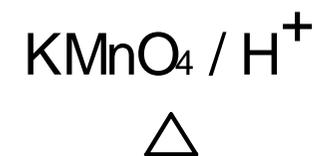
Products



Oxidants



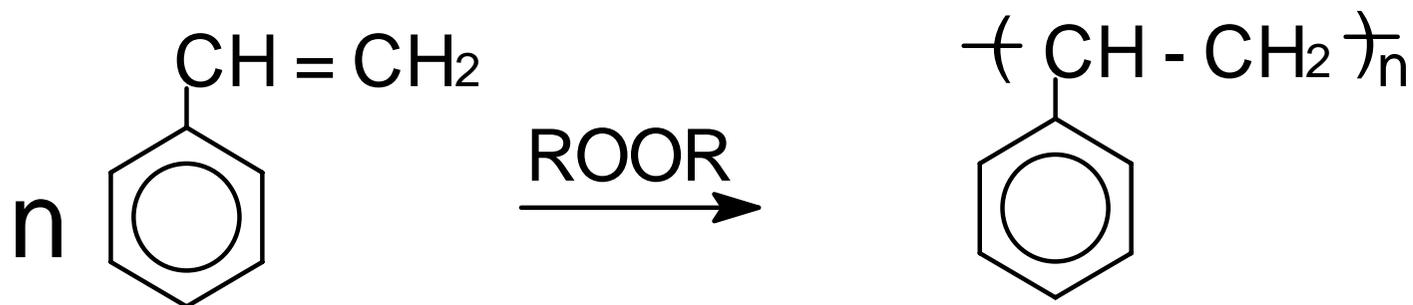
1. O₃
2. Zn



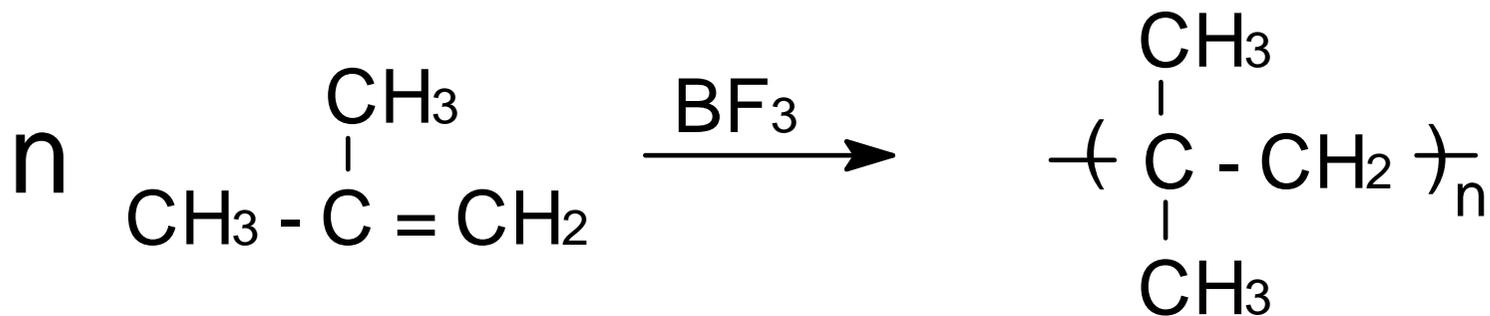
氧化性加强

§ 4.7 化学性质 IV——聚合反应

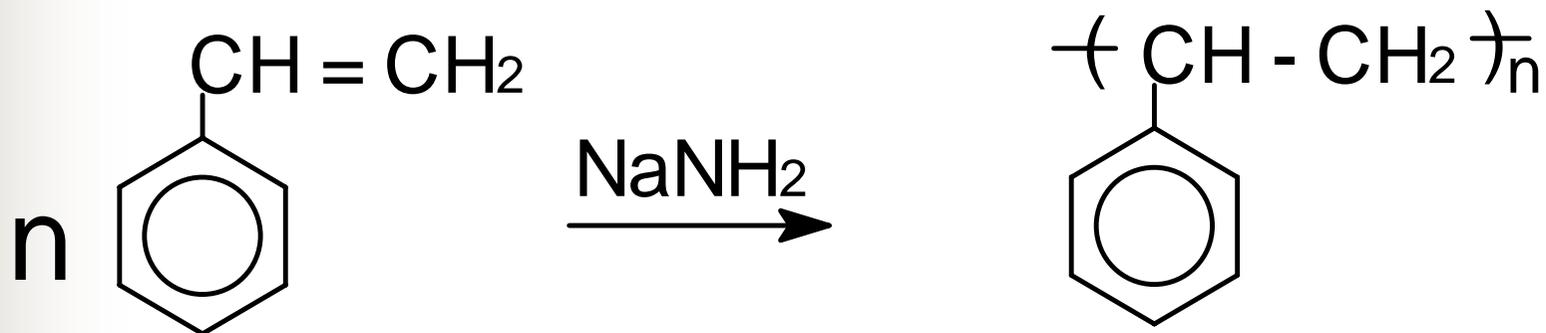
■ 1. 自由基聚合



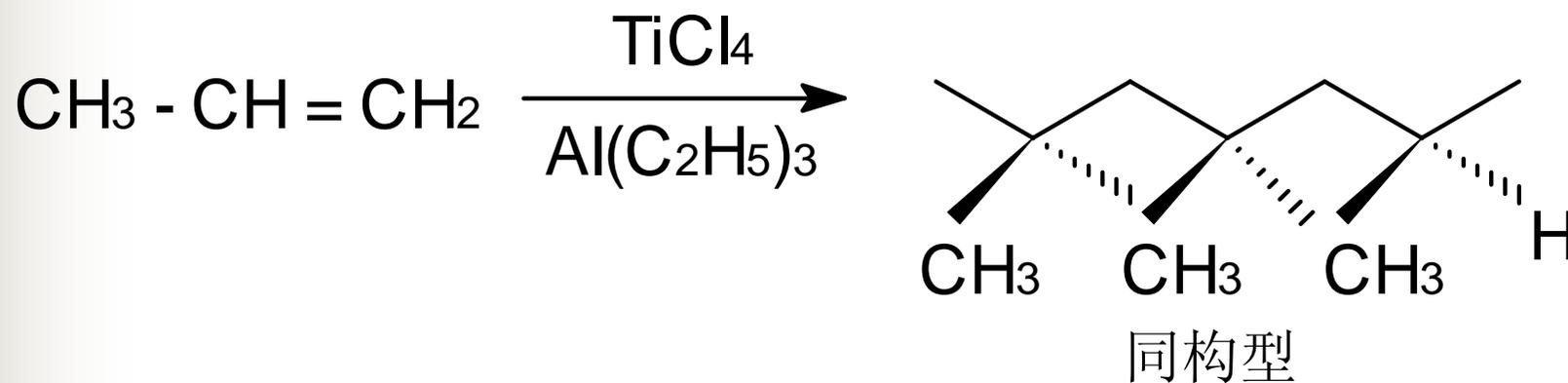
■ 2. 阳离子聚合



■ 3. 阴离子聚合



■ 4. 配位聚合



§ 4.8 烯烃的合成

- 醇脱水
- 脱卤素
- 脱卤化氢