

§ 6. 脂环烃



§ 6.1 脂环烃的分类及命名

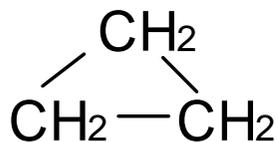
- 分类：

- 单环烃

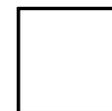
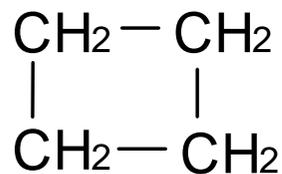
多环烃

{	桥环烃	公用两个以上碳原子
	螺环烃	公用一个碳原子(季碳)

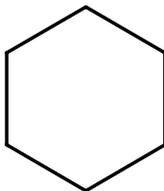
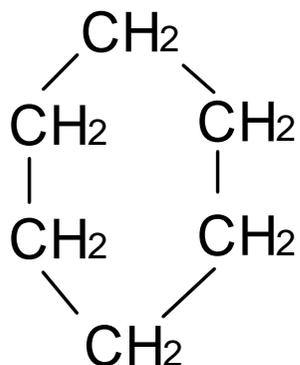
1. 单环烃



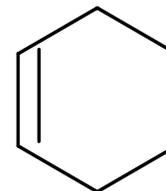
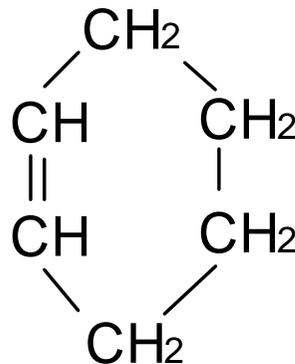
环丙烷



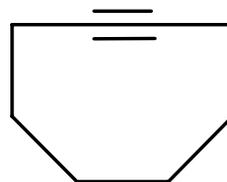
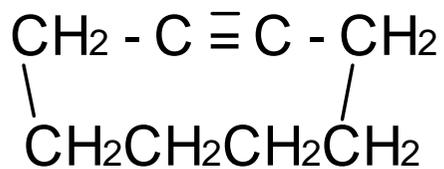
环丁烷



环己烷



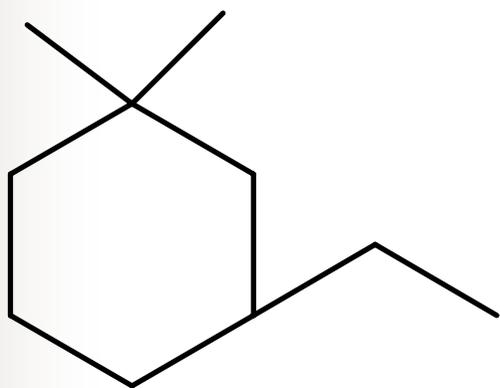
环己烯



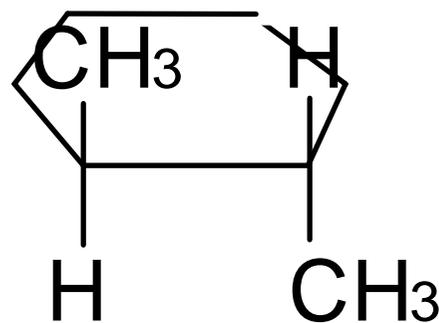
环己炔

A. 命名——单脂环烷烃

- a. 单脂环烃的命名与开链烷烃相同，名称前加“环”字；
- b. 有取代基时编号使取代基最小；



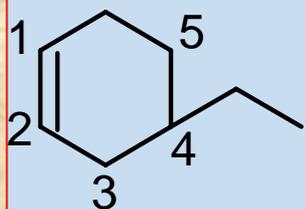
1,1-二甲基-3-乙基环己烷



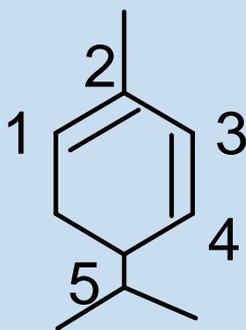
反-1,2-二甲基环己烷

8、命名——单脂环烯烃

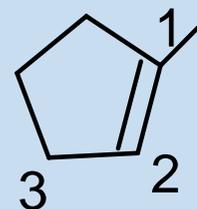
- a. 与开链烯烃相同，名称前加“环”字；
- b. 有取代基时，从双键处开始编号并使取代基位号最小。



4-乙基环己烯



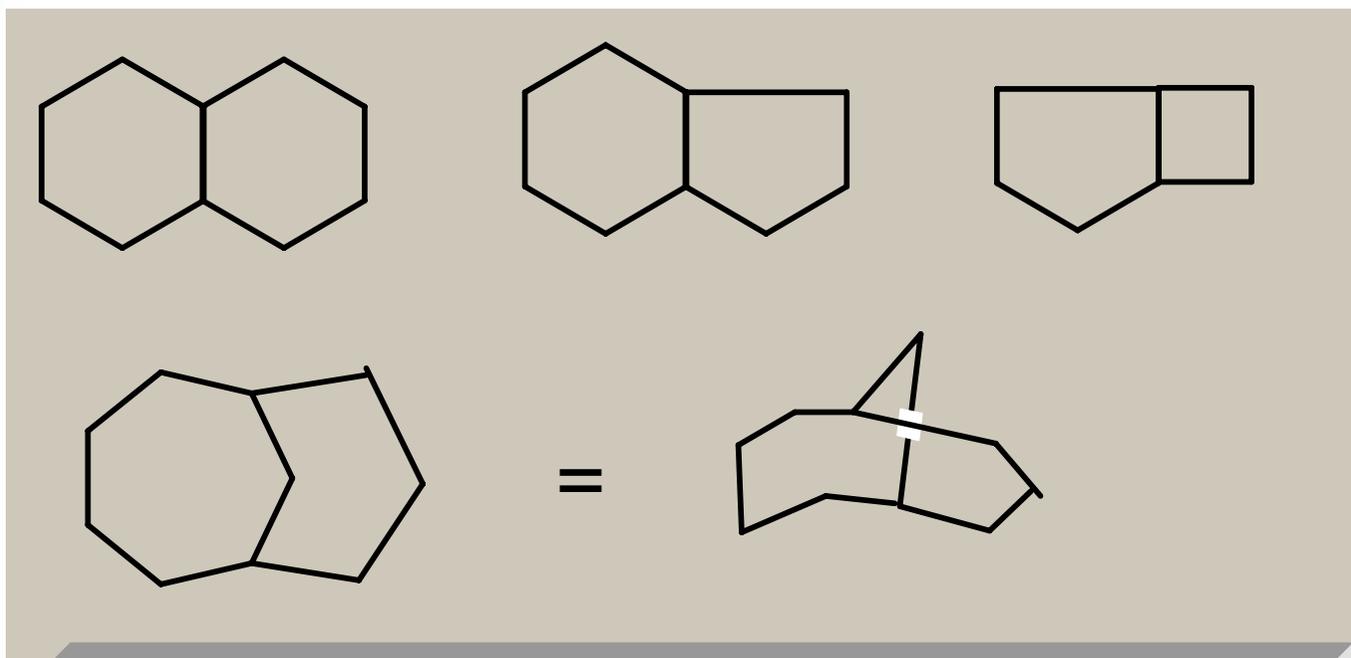
2-甲基-5-异丙基-1,3-环己二烯



1-甲基环戊烯

2. 多环烃

■ A. 桥环烃



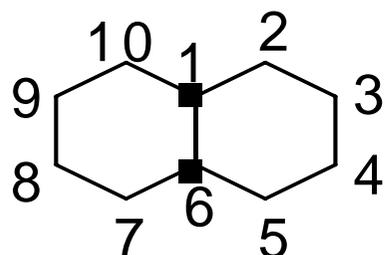
公用两个以上碳原子的环状烃
称为**桥环烃**
公用的碳原子称为**桥头碳**

■ 命名:

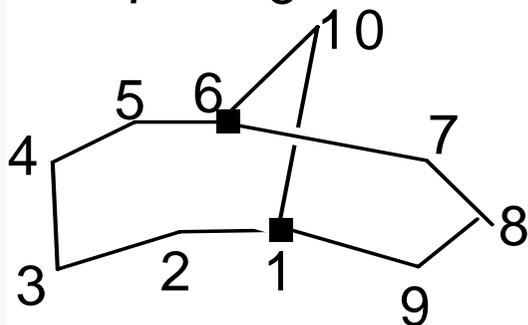
■ a. 确定环数: 如断开两个键就成链状烃的为双环

■ b. 从桥头碳原子开始编号, 从大环到中环再到小环并保证取代基位号最小

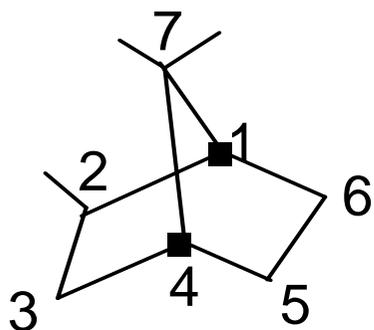
■ c. 书写顺序, 最后为母体名称, 前为[], []内为各环碳数从大到小, 再前为取代基。



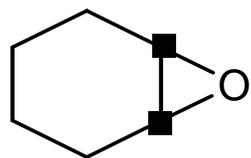
二环[4.4.0]癸烷



二环[4.3.1]癸烷

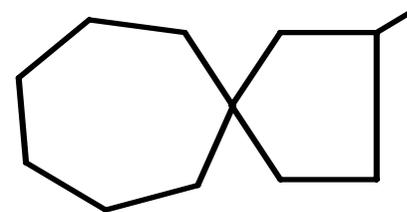
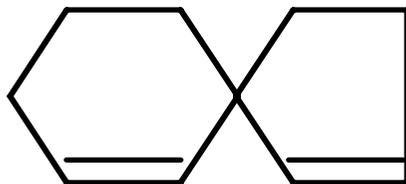
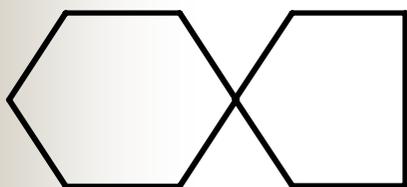


2,7,7-三甲基-二环[2.2.1]庚烷



7-氧代-二环[4.1.0]庚烷

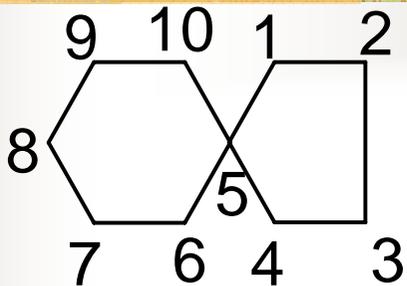
8、螺环烃



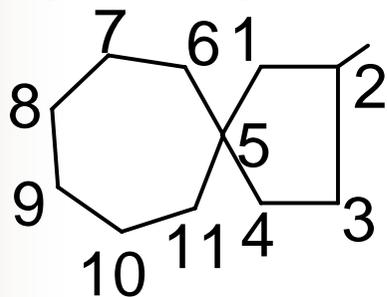
公用一个碳原子的环状烃称为**螺环烃**

命名：

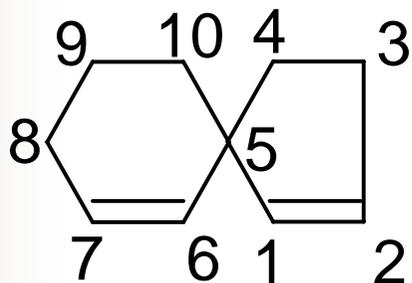
- 从螺碳原子旁边的碳原子开始编号；
- 从小到大环，并使双键及取代基位号最小；
- 书写顺序，最后为母体，前[]，[]内从小到大为环上碳数；前为“螺”字；最前为取代基。



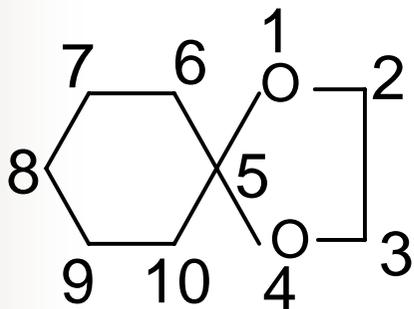
螺环[4.5]癸烷



2-甲基螺环[4.6]十一烷

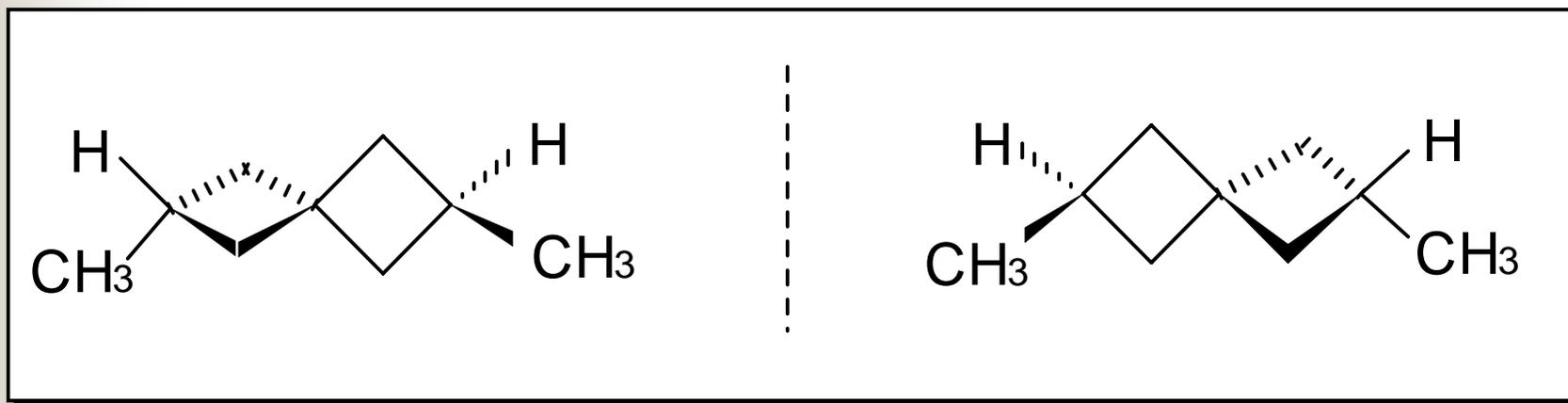


螺环[4.5]-1,6-癸二烯

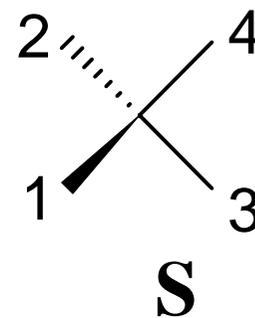
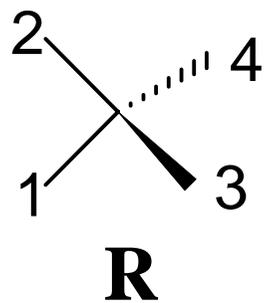


1,4-二氧代螺环[4.5]癸烷

c. 螺环化合物的手性



观察方向



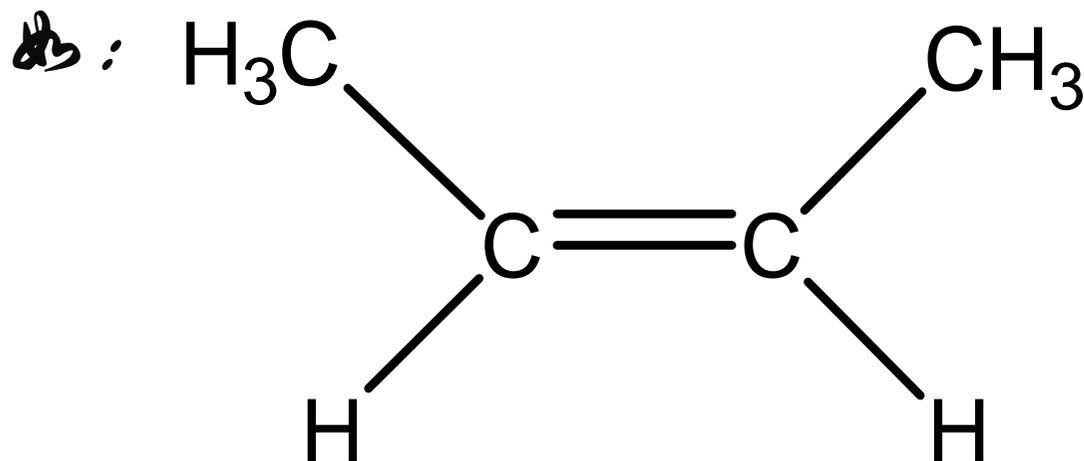
§ 6.2 脂环烃的立体异构

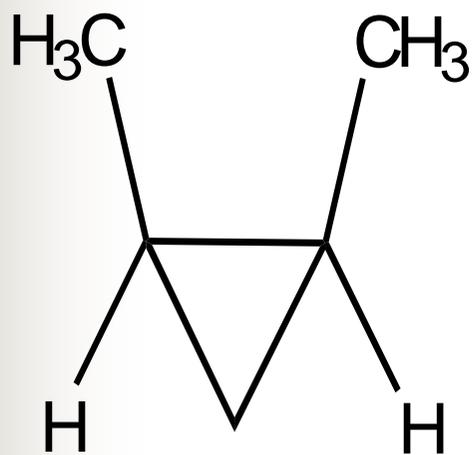
1、cis-/trans- 异构：

虽然 σ 键可任意旋转，但由于形成环后阻碍了其旋转，于是，类似于烯烃一样，就可产生顺/反异构，在脂环烃中我们称之为 cis-/trans- 异构。

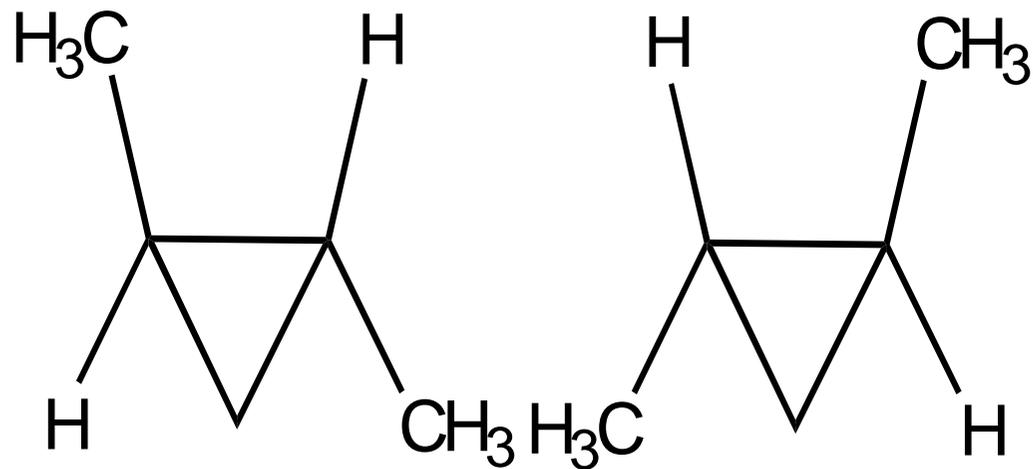
产生cis-/trans- (或顺/反) 异构的条件

- A. 分子中有阻碍旋转的因素。
- B. 在被阻碍旋转的碳原子上连有不同的原子或基团。

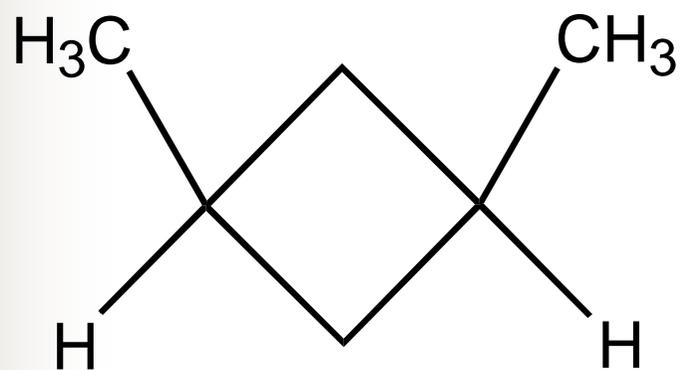




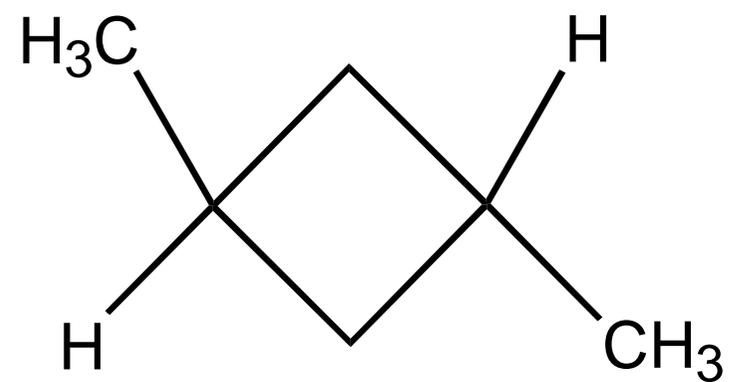
cis-1, 2-二甲基环丙烷



trans-1, 2-二甲基环丙烷

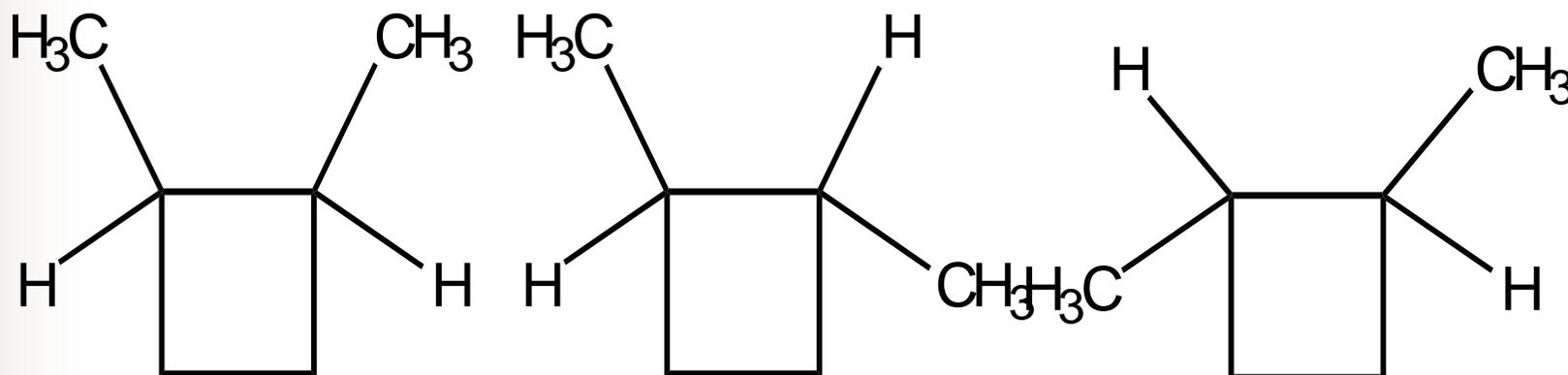


cis-1,3-二甲基环丁烷



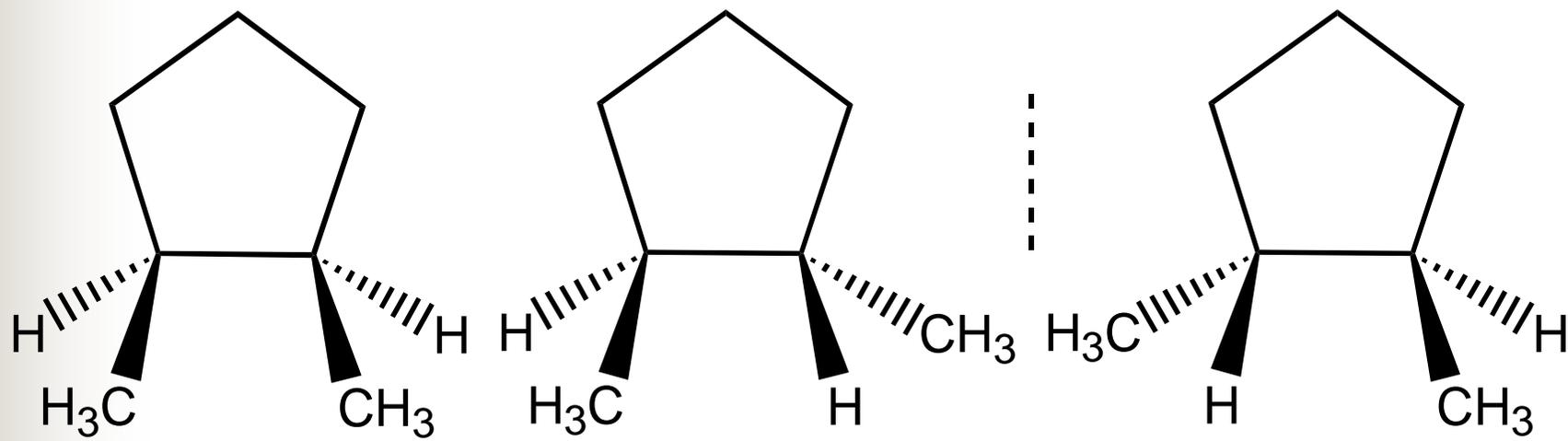
trans-1,3-二甲基环丁烷

2. 对映异构及非对映异构



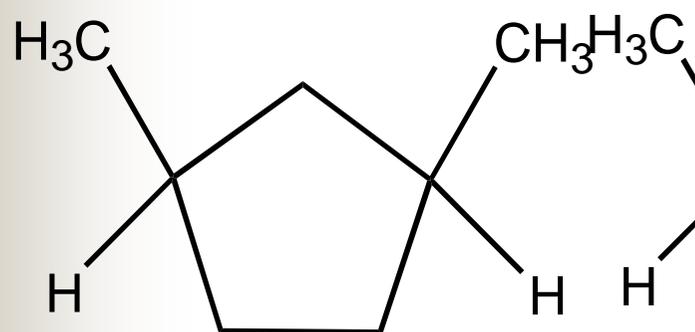
cis-1,2-二甲基环丁烷

trans-1,2-二甲基环丁烷

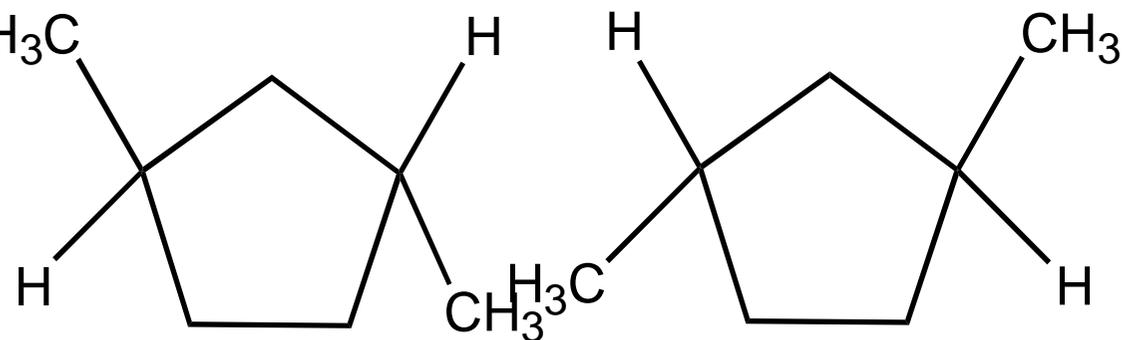


cis-1,2-二甲基环戊烷

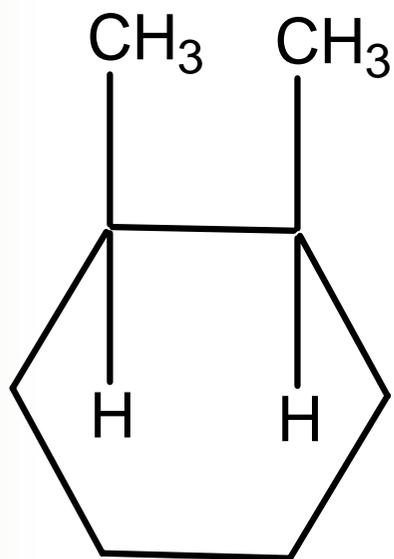
trans-1,2-二甲基环戊烷



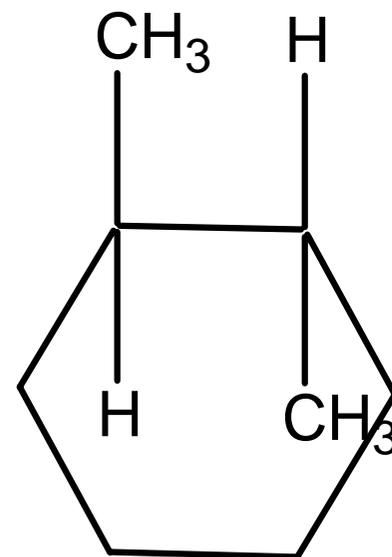
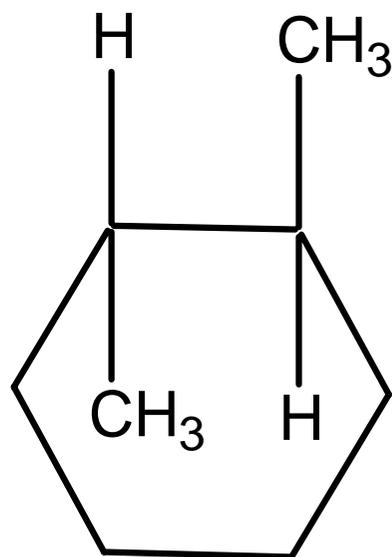
cis-1,3-二甲基环戊烷



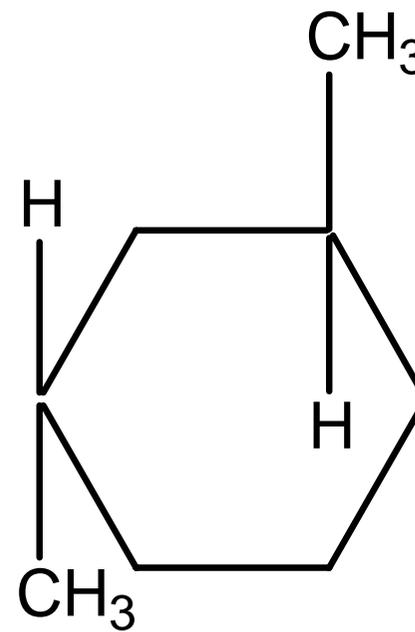
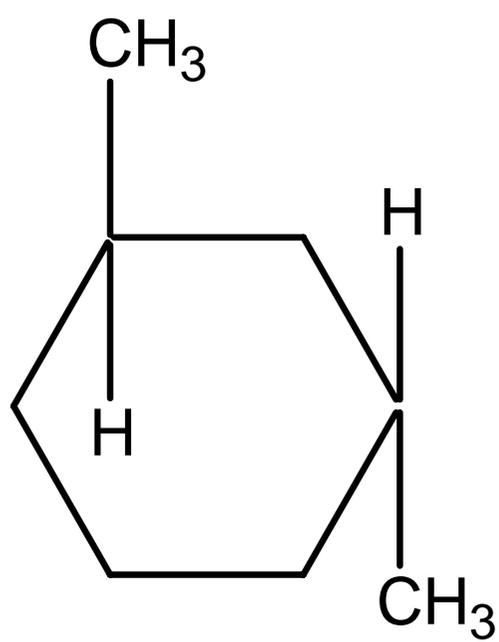
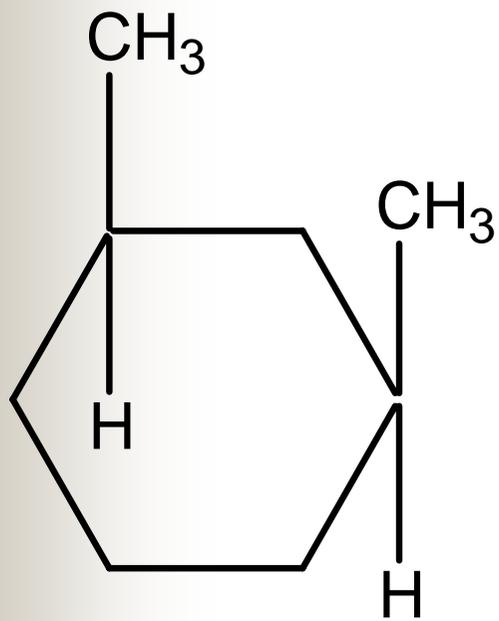
trans-1,3-二甲基环戊烷

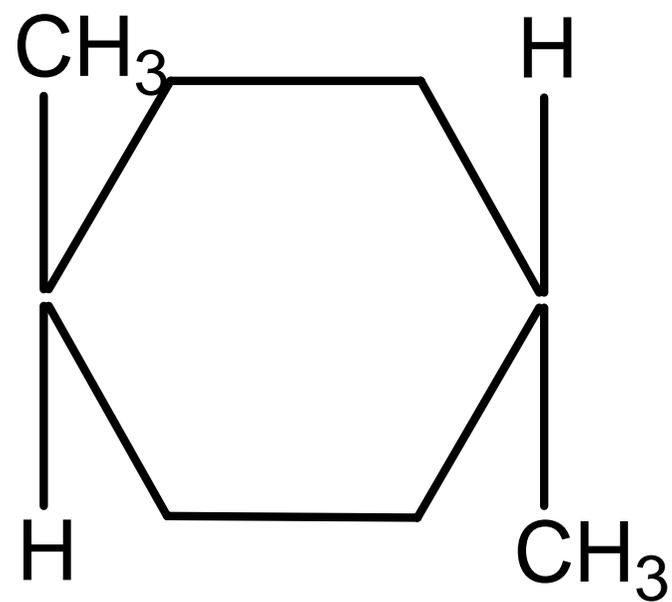
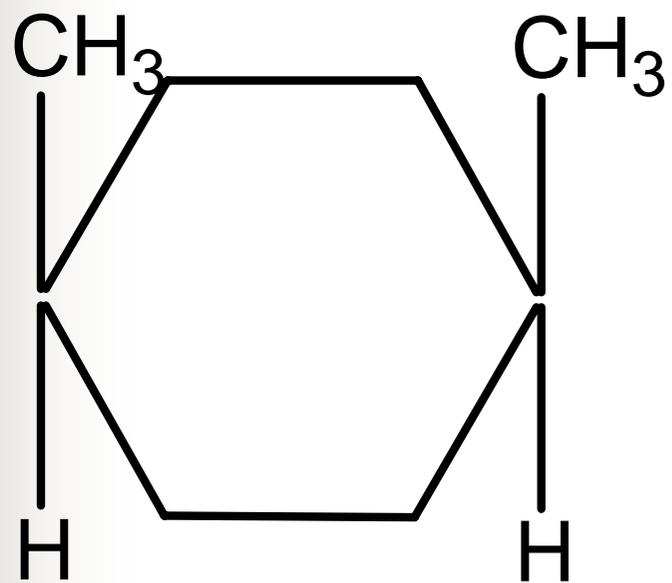


cis-1、2-二甲基环己烷

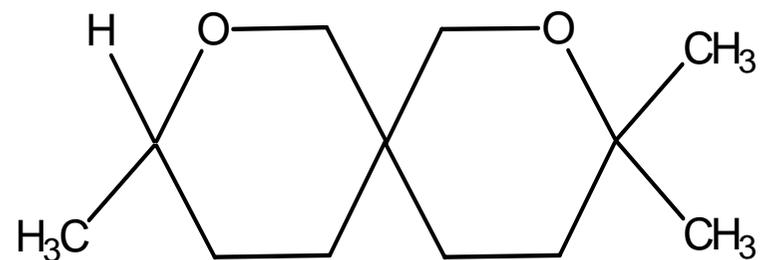
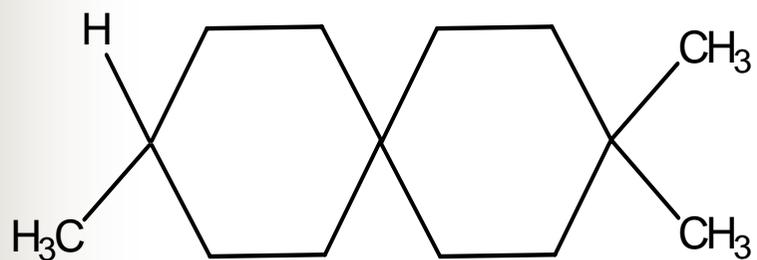
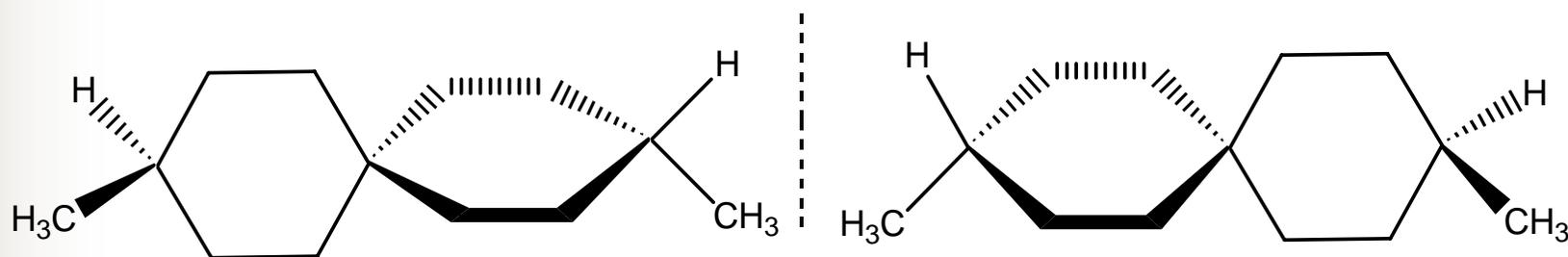


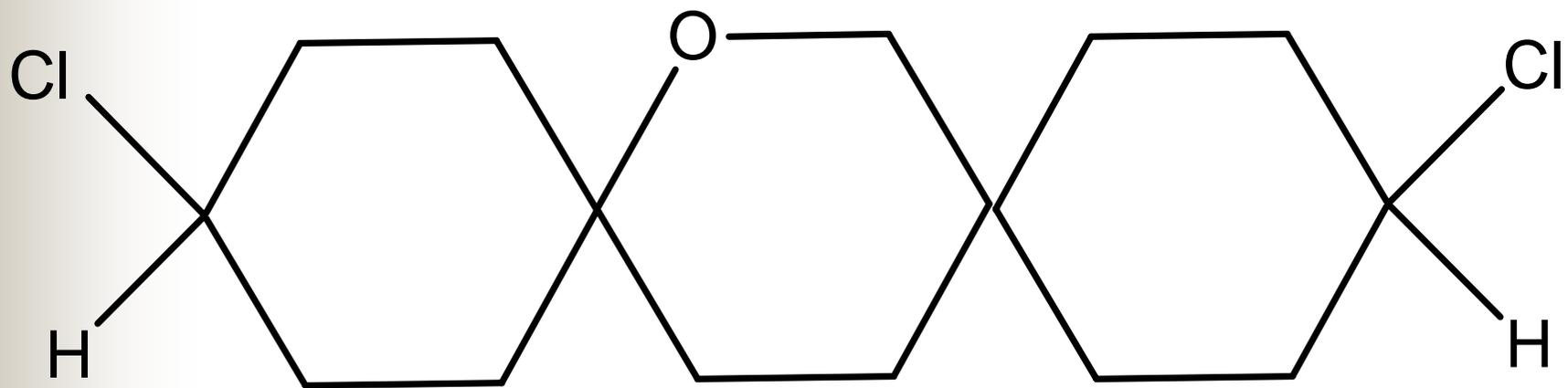
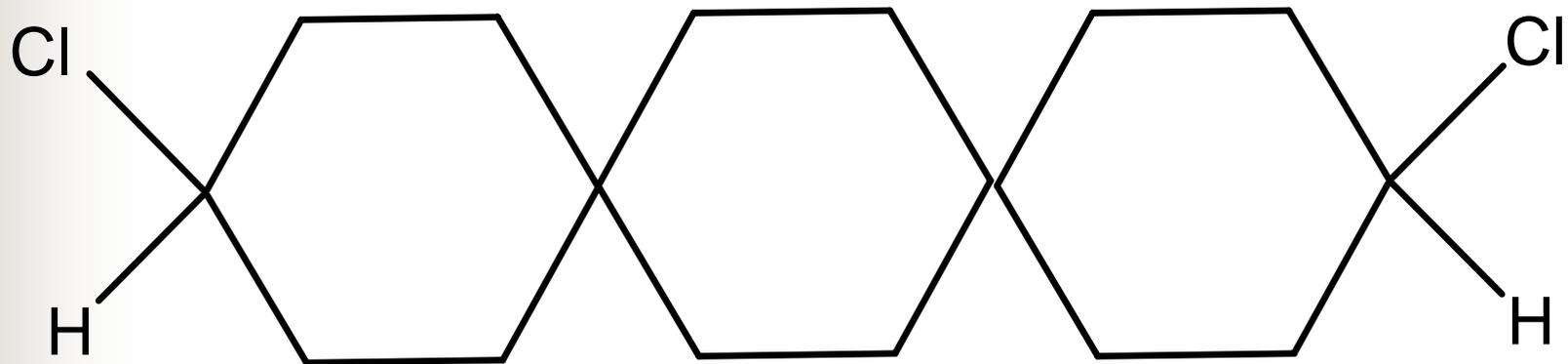
trans-1、2-二甲基环己烷

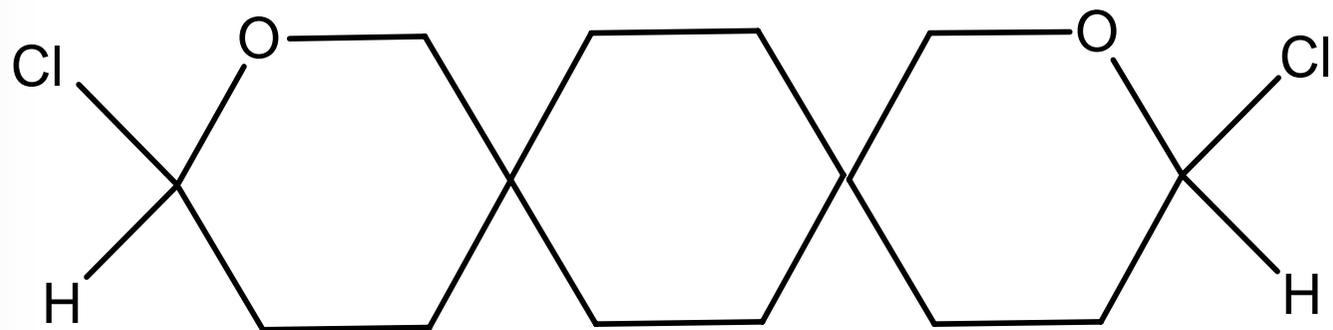
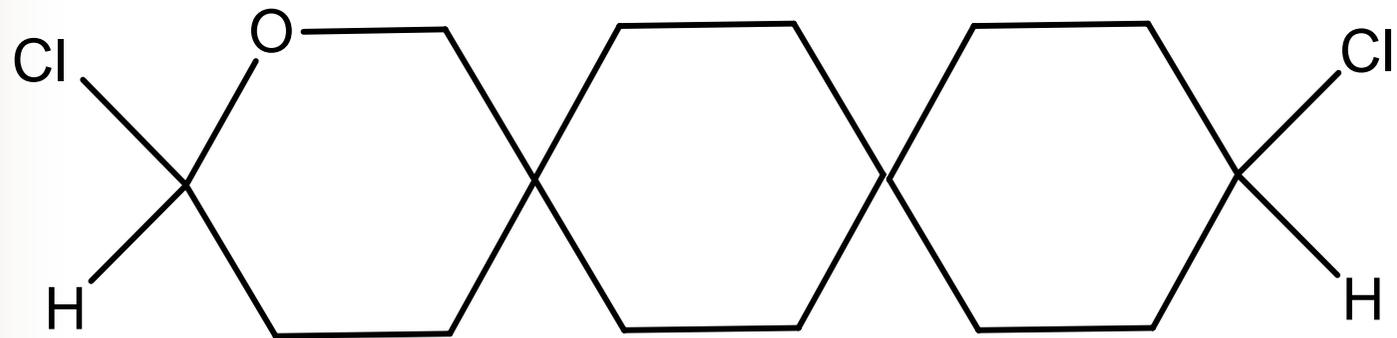




3. 螺环化合物的对映异构





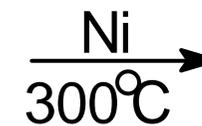
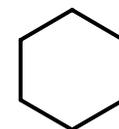
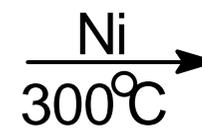
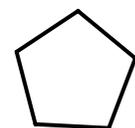
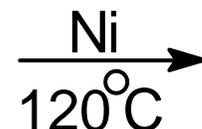
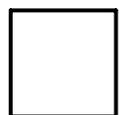
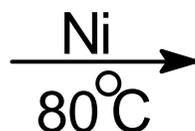


§ 6.3 化学性质

- 单环的分类:

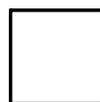
- 含 3~4 C 小环 性质类似于烯烃
 - 5~6 C 正常环
 - 7~11 C 中环
 - 12 C 以上 大环
- } 性质类似于烷烃

1. 开环反应——催化氢化



催化氢化开环反应的难度
随着环元数的增加而变难

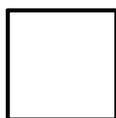
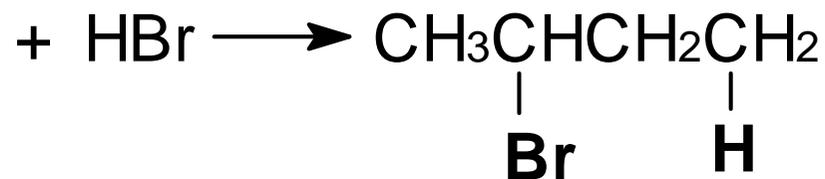
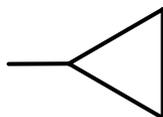
2. 小环烷烃的性质

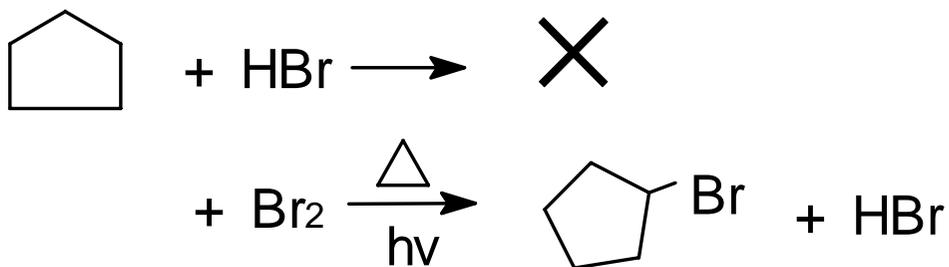


如同链状烷烃, 环烷烃不与 KMnO_4 反应



烯烃性质





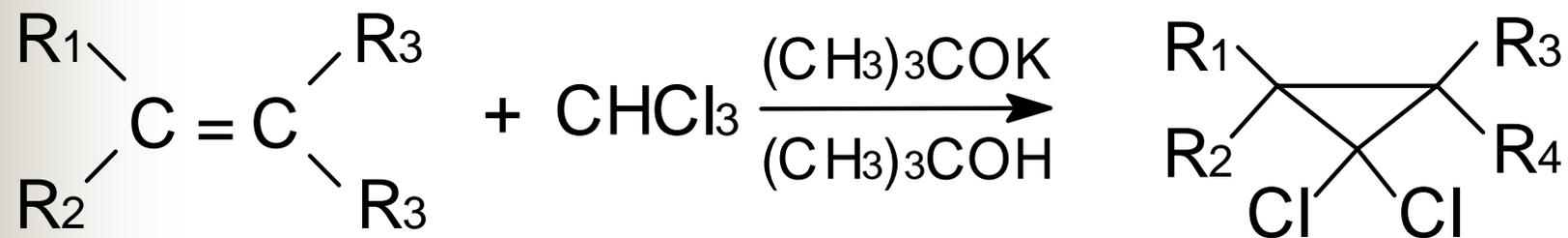
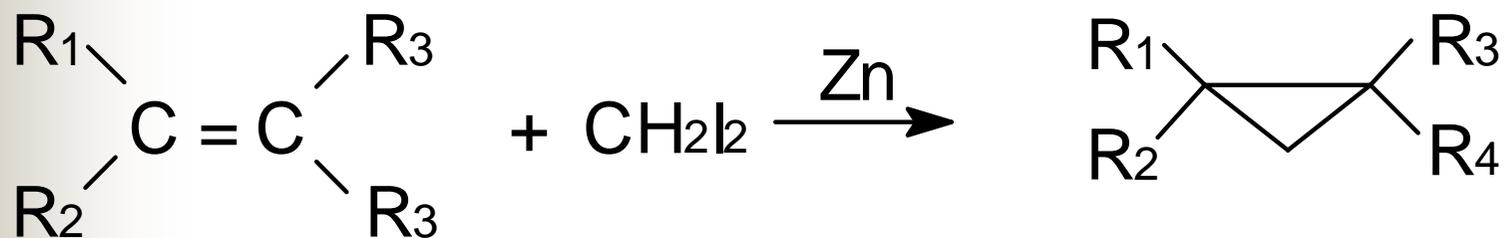
五元以上的脂环烃
具有烷烃的性质，
易发生取代反应

总结：

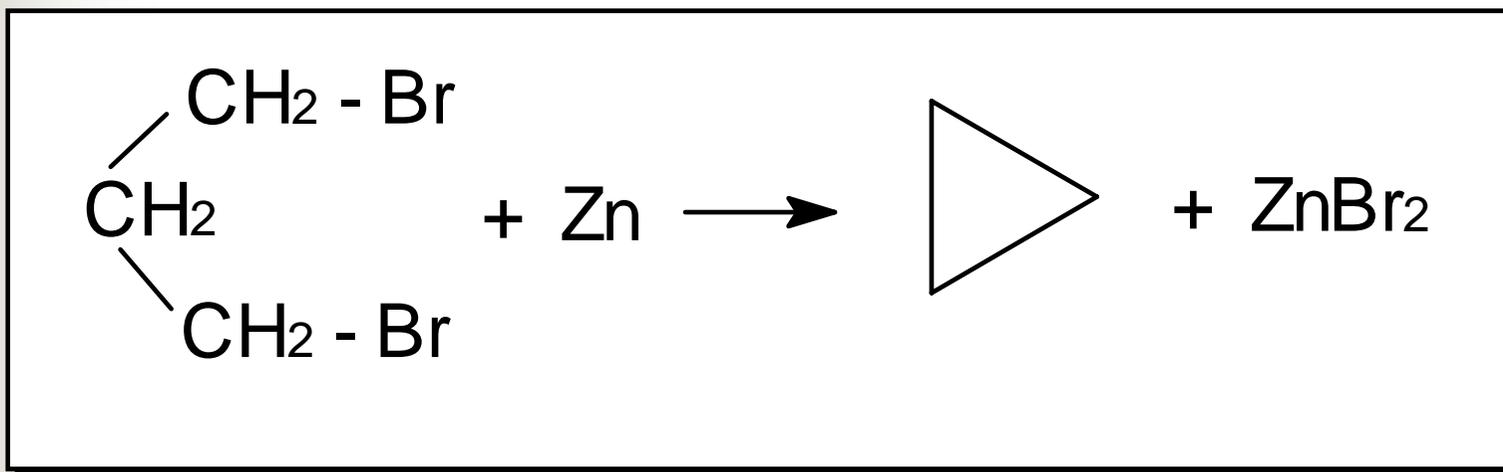
- 三元环具有烯烃的性质
- 四元环稍具烯烃的性质
- 五元以上不具烯烃的性质
- 脂环烃具有烷烃性质

3. 小环的制备方法:

■ A. 烯烃与卡宾反应



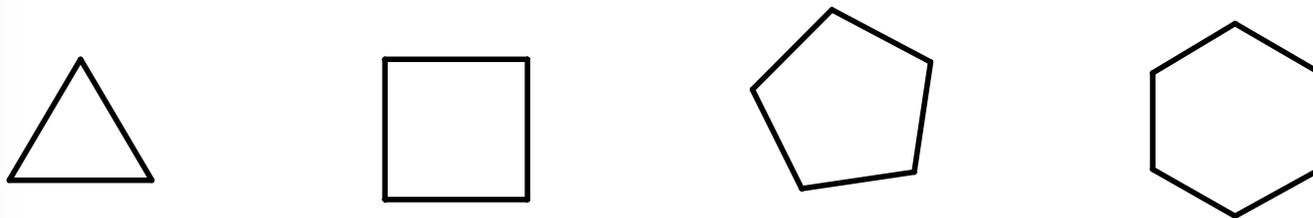
3、 α, ω -二卤代物与Zn反应



碳链长于6之后易发生分子间反应

§ 6.4 环的稳定性——Baeyer张力说

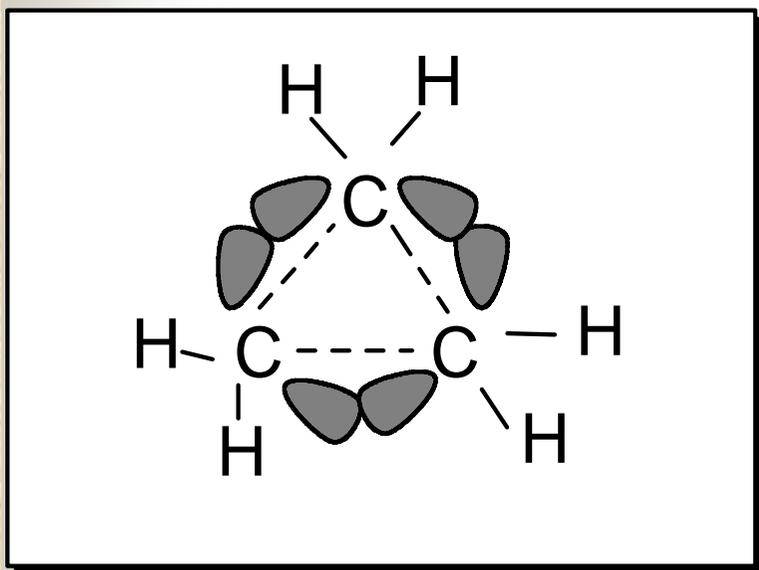
- 1. 假定:
- A. C为 sp^3 杂化
- B. 所有碳原子共平面



c. 与正常键角差值越大，环越不稳定；回复正常键角的力为角张力，得出五元环比六元环稳定的结论，但事实上六元环比五元环稳定，原因是没有考虑构象。

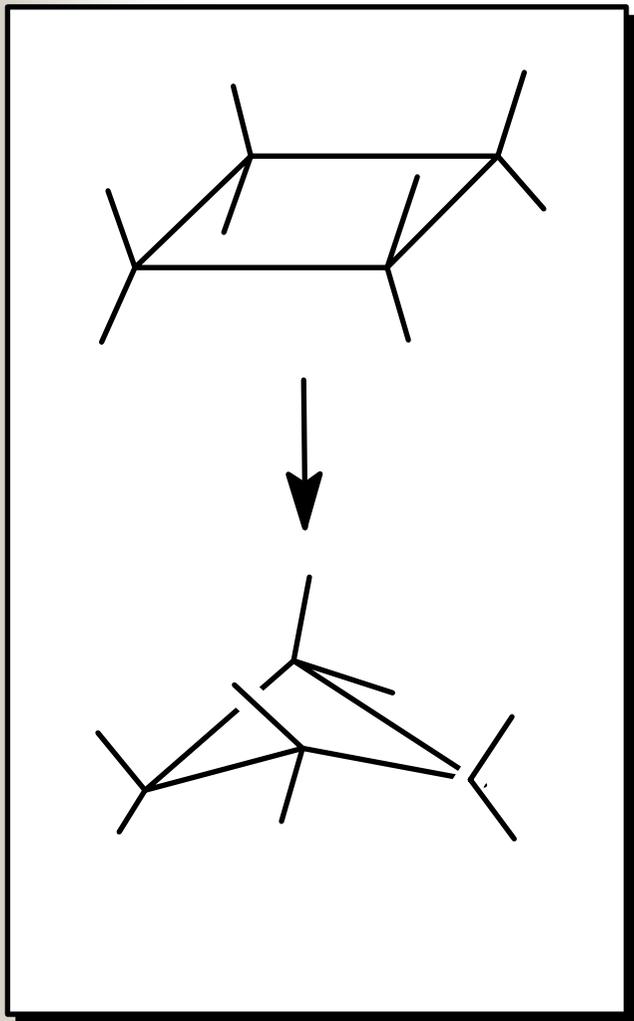
2. 环构象

A. 三元环



共平面夹角60 形成弯键
燃烧热为 697.1KJ/mol
开链烷烃 658.6KJ/mol
1mol物质完全燃烧生成
CO₂和H₂O所放出热量
燃烧热越小，则越稳定

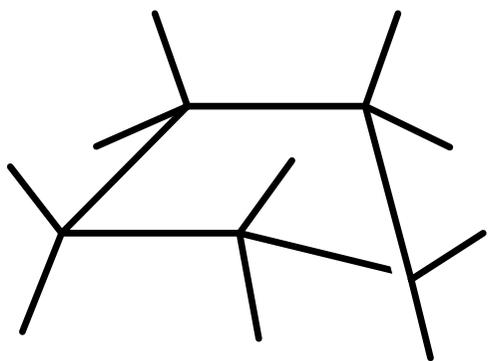
8. 四员环



如果共平面，夹角90 存在角张力。C-H之间彼此重叠排斥，有扭转趋势，存在扭张力

蝶式，夹角88 角张力升高，但C-H之间不重叠，扭张力下降，燃烧热为：
686.2KJ/mol - CH₂ -

c. 五员环

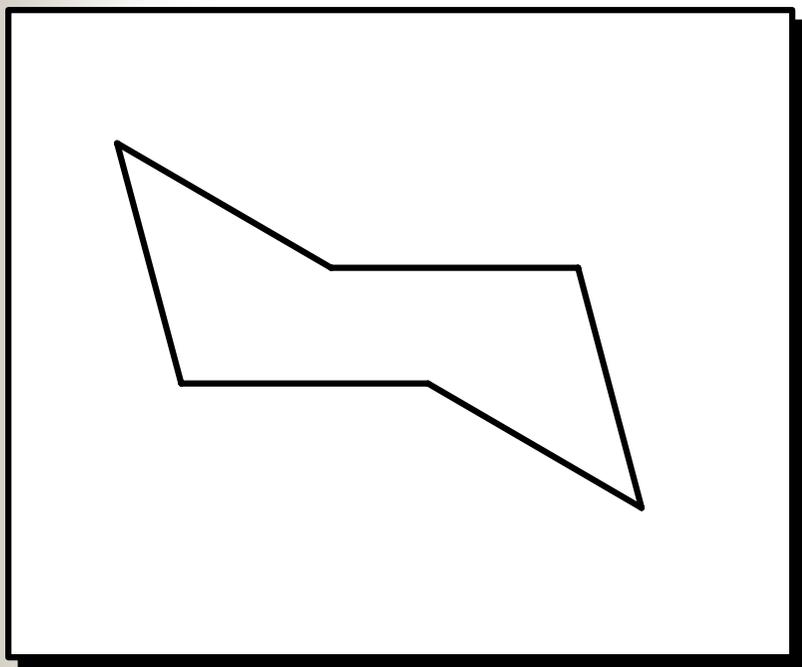


信封式，键角接近正常
值，无角张力

C-H成交叉式，无扭
张力燃烧热为：

664.4KJ/mol - CH₂ -

D、六员环

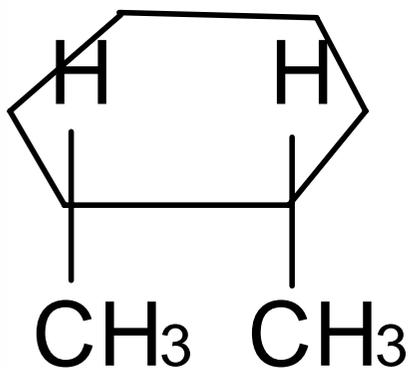


椅式键角 109.5° 无角张力, C-H交叉式, 无扭转张力, 燃烧热为 658.6 kJ/mol - CH_2 -

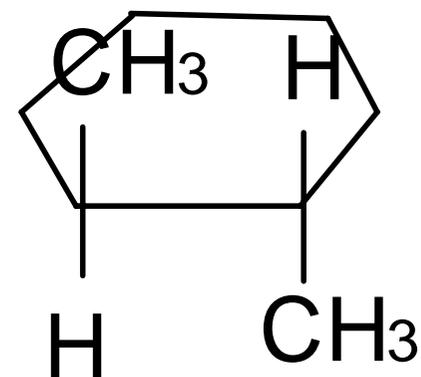
影响环稳定性因素: 角张力、扭转力

§ 6.5 环己烷的立体化学

■ 构型异构



顺-1,2-二甲基环己烷

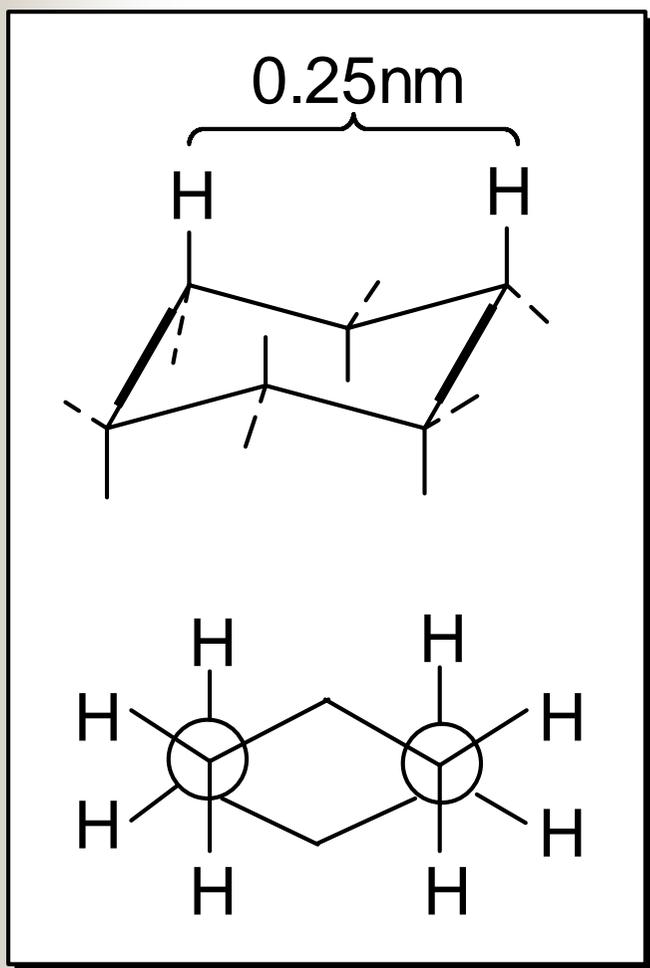


反-1,2-二甲基环己烷

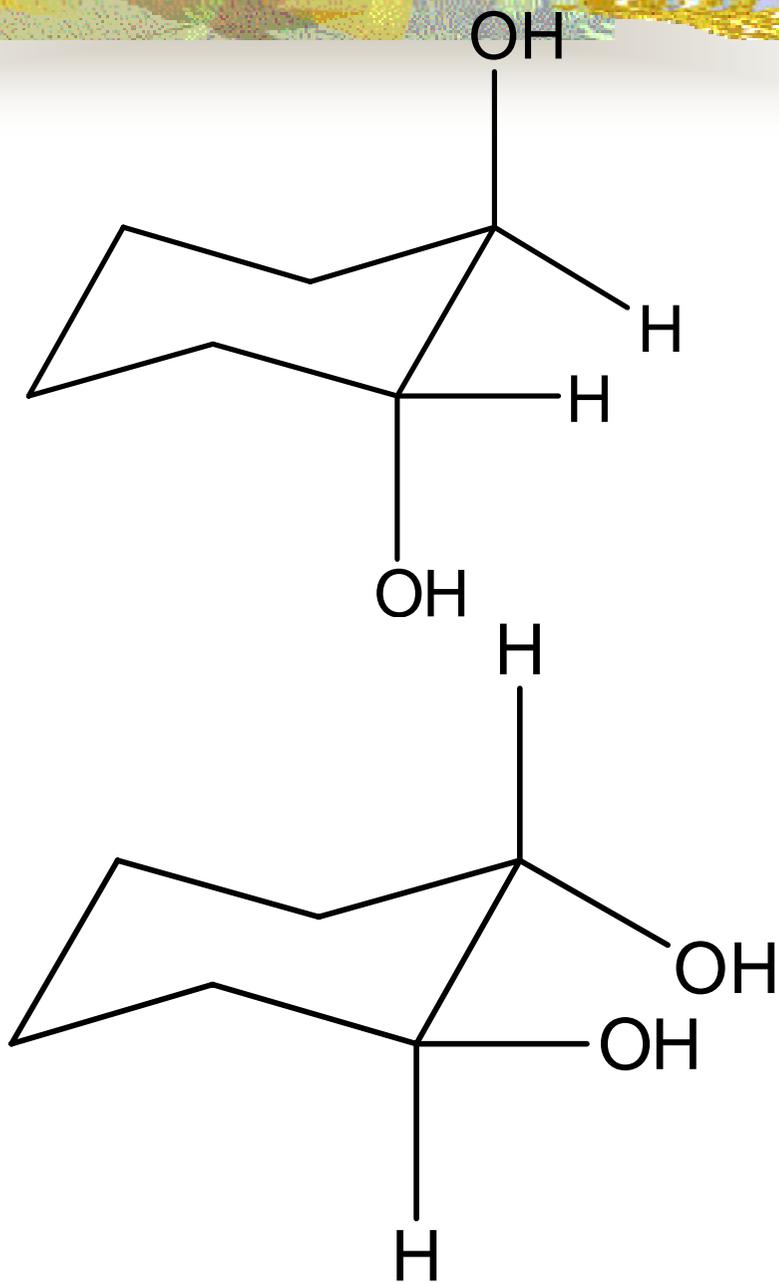
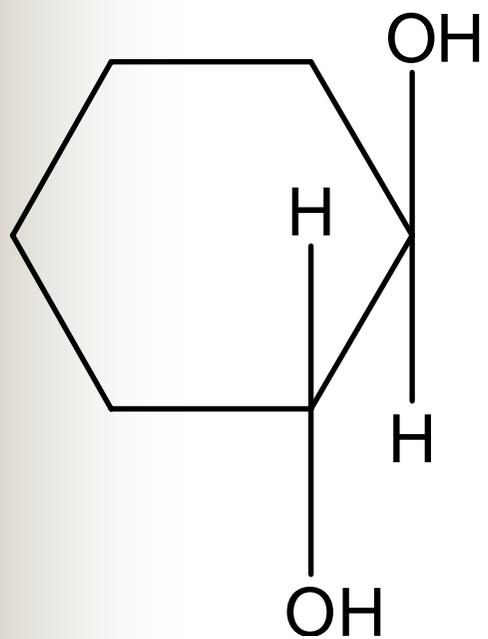
在每种构型异构下讨论构象问题

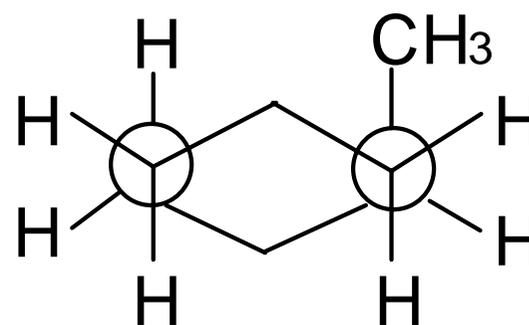
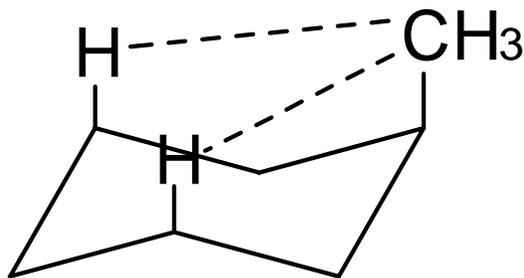
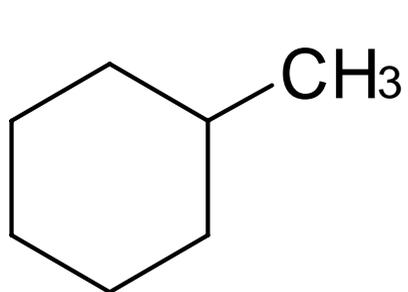
1. 环己烷构象

■ A. 椅式

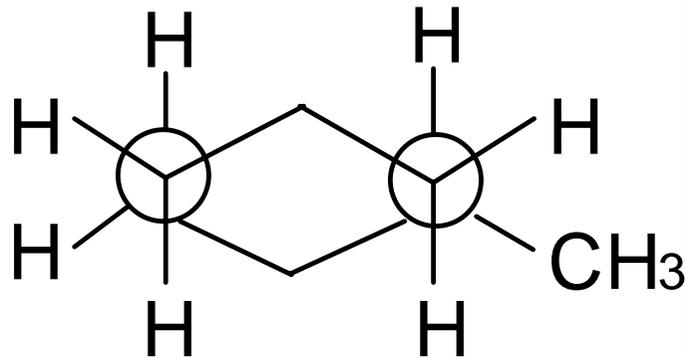
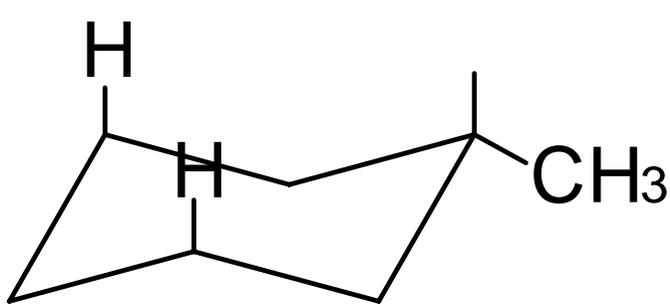


- a. 六个碳原子分属两个平面
面间距0.5nm
- b. 每个键角为109.5。
- c. 竖直键，**a**键；彼此平行平
伏键，**e**键；
- d. 各键彼此对位交叉
- e. 大取代基优先处于**e**键；
- f. 如能形成分子内氢键，则优
先形成氢键；



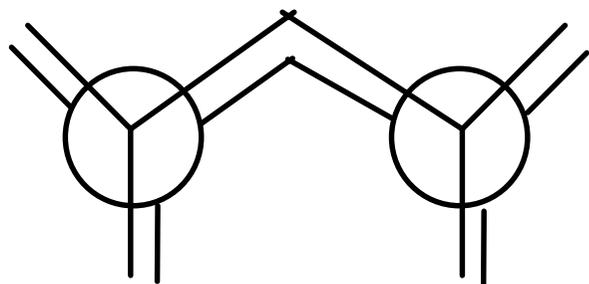
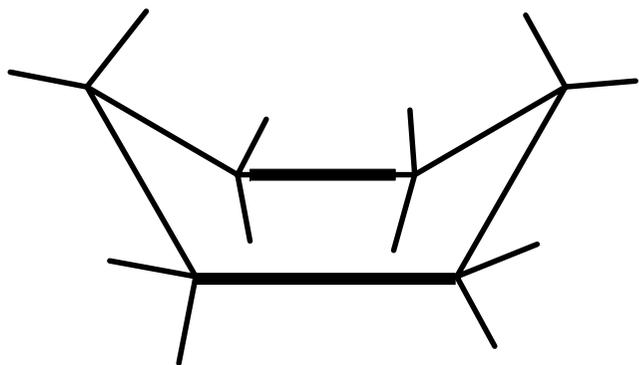


甲基处于a键上与H原子半径和大于0.25nm, 邻位交叉式内能为3.8kJ/mol, 不够稳定.

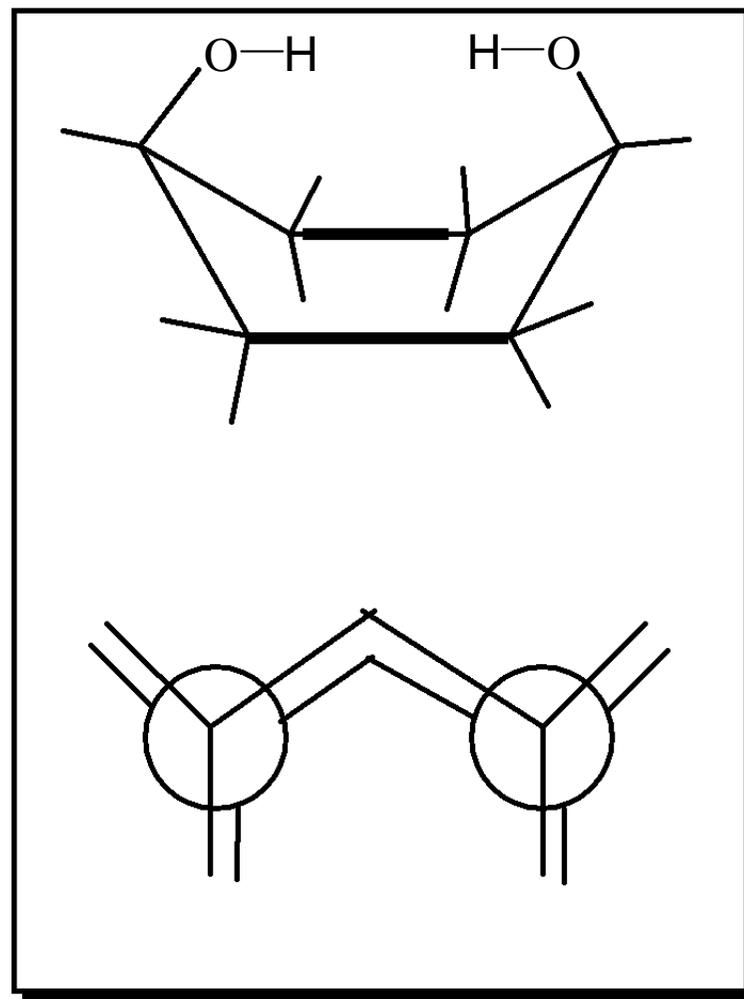
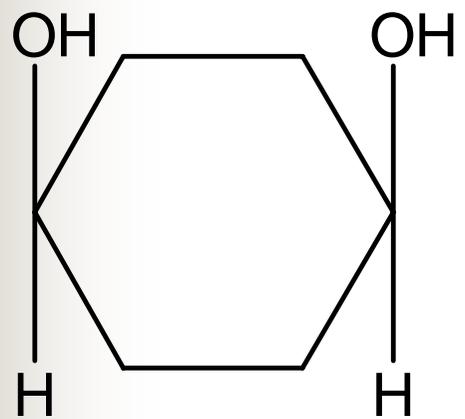


甲基处于e键上, 即在对位交叉式位, 稳定, 内能为 0 kJ/mol

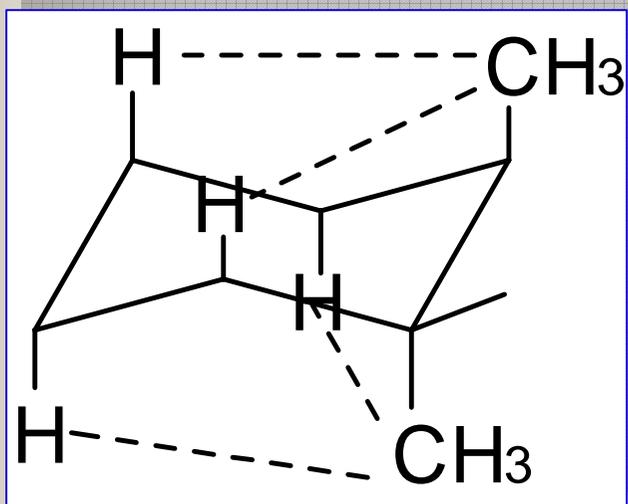
8. 船式



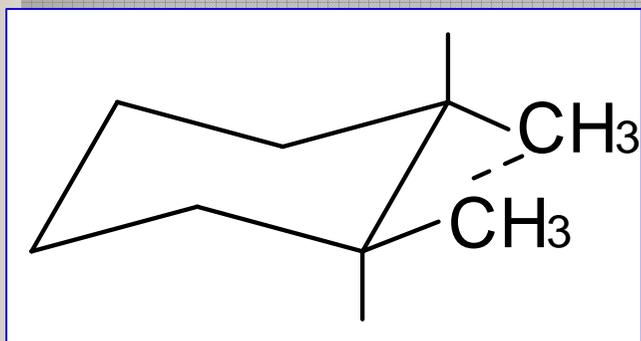
全重叠式，扭张力 > 0
内能比椅式高 28.9KJ/mol
如能形成氢键，则采用此
构象



6. 反-1,2-二甲基环己烷

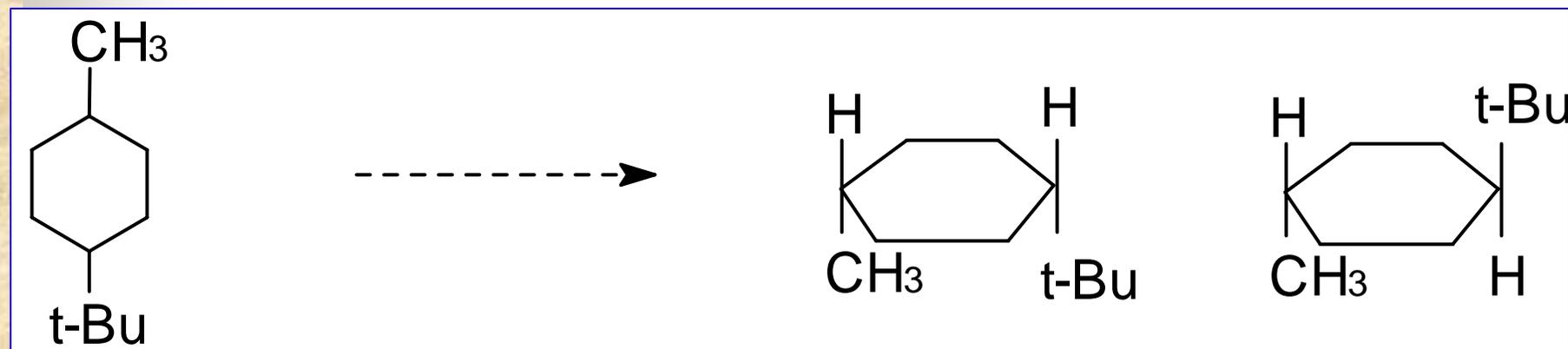


$$\begin{aligned} E_a &= 3.8 \times 2 + 3.8 \times 2 \\ &= 15.2 \text{ kJ/mol} \end{aligned}$$

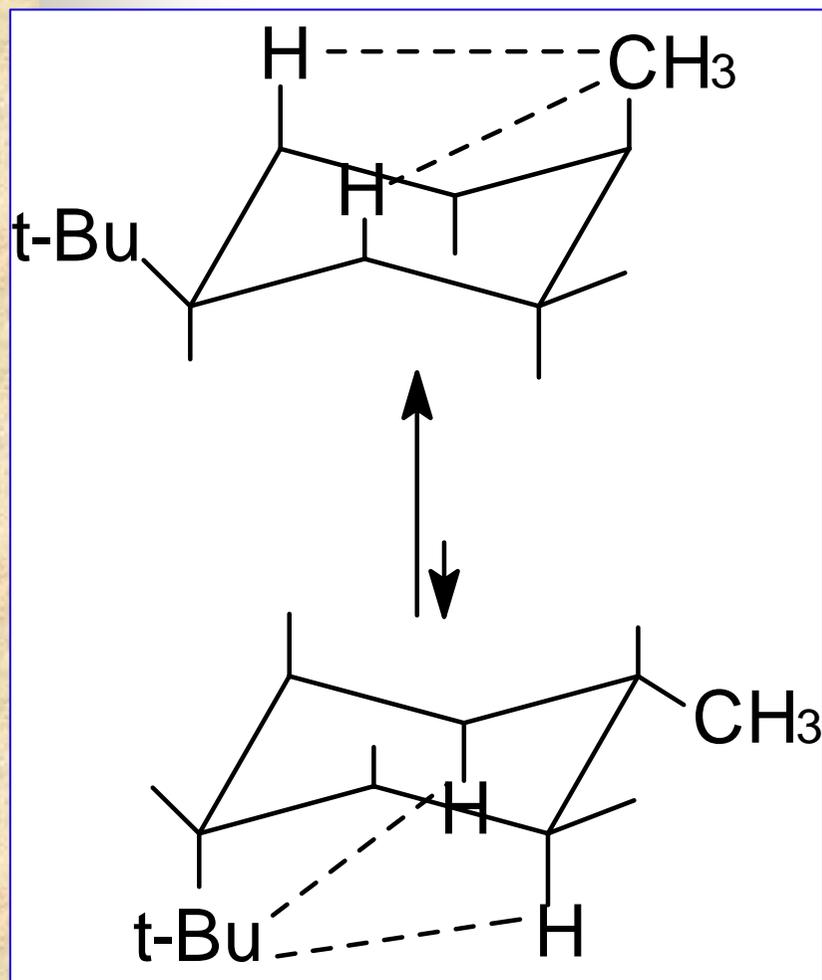


$$E_b = 3.8 \text{ kJ/mol}$$

8. 1-甲基-4-叔丁基环己烷



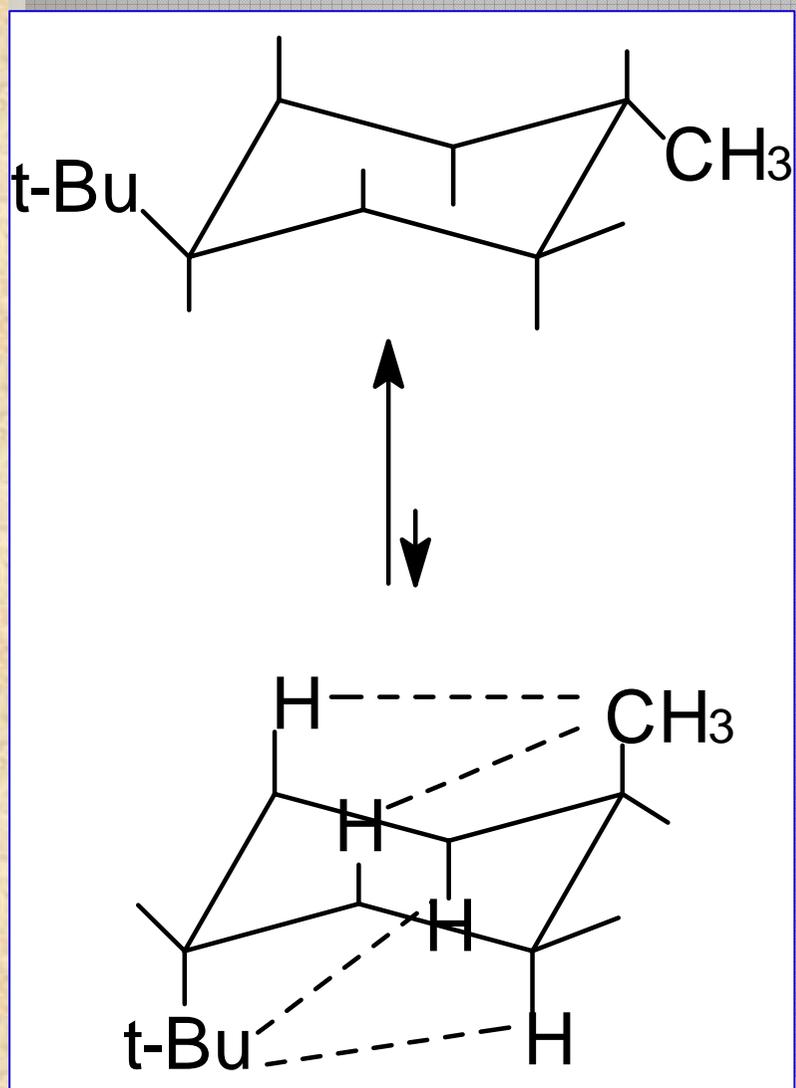
a、顺-1-甲基-4-叔丁基环己烷



$$E_a = 3.8 \times 2 = 7.6 \text{ kJ/mol}$$

$$E_b = 10.45 \times 2 = 20.9 \text{ kJ/mol}$$

6. 反-1-甲基-4-叔丁基环己烷



$$E_a = 0 \text{ kJ/mol}$$

$$\begin{aligned} E_b &= 10.45 \times 2 + 3.8 \times 2 \\ &= 28.5 \text{ kJ/mol} \end{aligned}$$



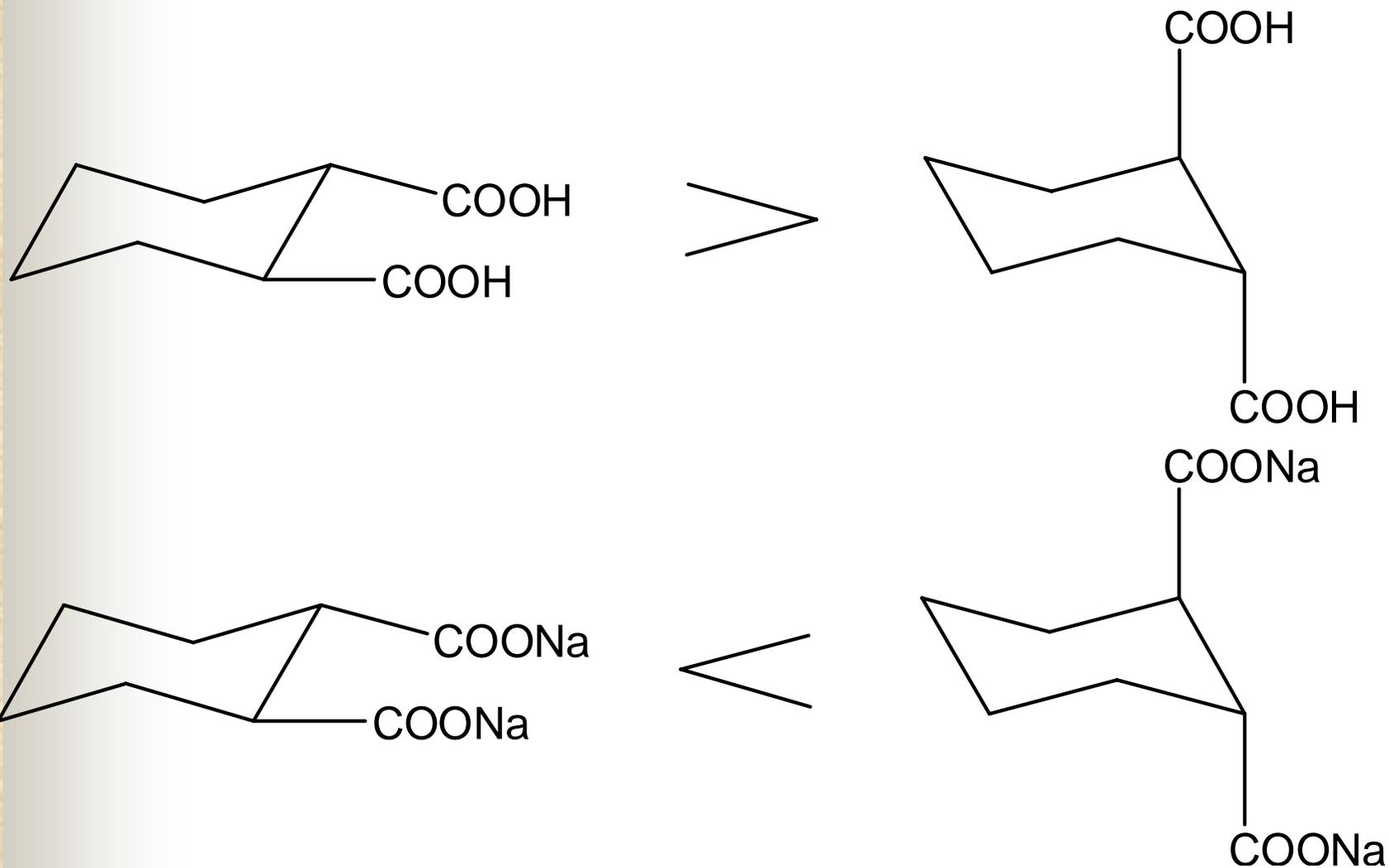
■ c. 计算:

■ a. 顺, 反-1,3-二甲基环己烷:

■ b. 顺, 反-1,4-二甲基环己烷

■ 已知: $-\text{CH}_3$ 之间1,3相互作用 15.04kJ/mol

3. 氢键及偶极-偶极相互作用



本章重点

- 1、脂环化化合物的立体异构
- 2、小环化合物的开环反应
- 3、环己烷的构象分析