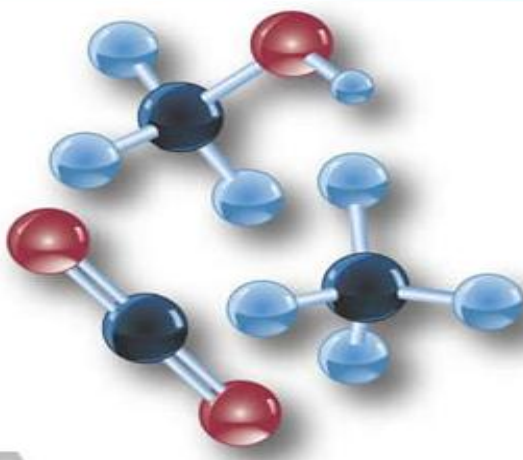


Organic Chemistry





胺的碱性

比较下列胺类化合物的碱性

	NH_3	MeNH_2	Me_2NH	Me_3N	PhNH_2
					
共轭酸	NH_4^+	MeNH_3^+	Me_2NH_2^+	Me_3NH^+	PhNH_3^+
pKa	9.26	10.64	10.72	9.74	4.6

共轭酸的酸性越强(或越稳定), 其对应的共轭碱的碱性越弱

水溶液中, 胺的碱性强弱次序为: 脂肪胺 ($2^\circ > 1^\circ > 3^\circ$) > 氨 > 芳香胺



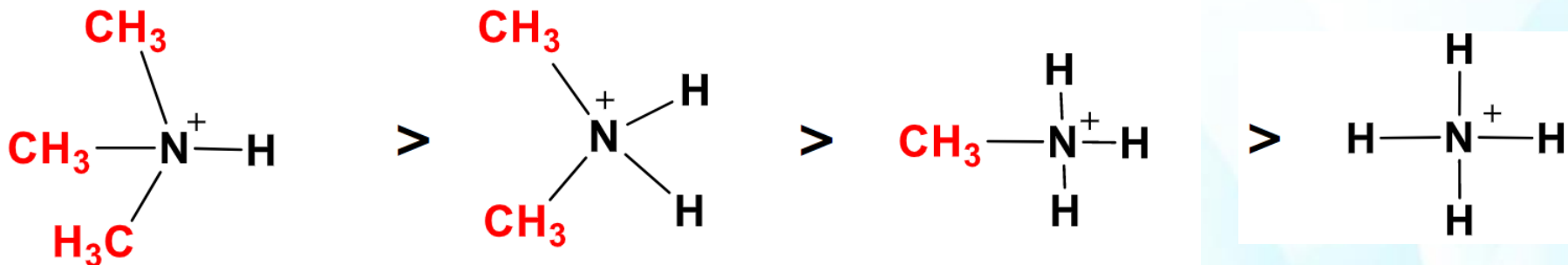


胺的碱性

脂肪胺碱性顺序: $2^\circ > 1^\circ > 3^\circ$

1) 电性效应

稳定性



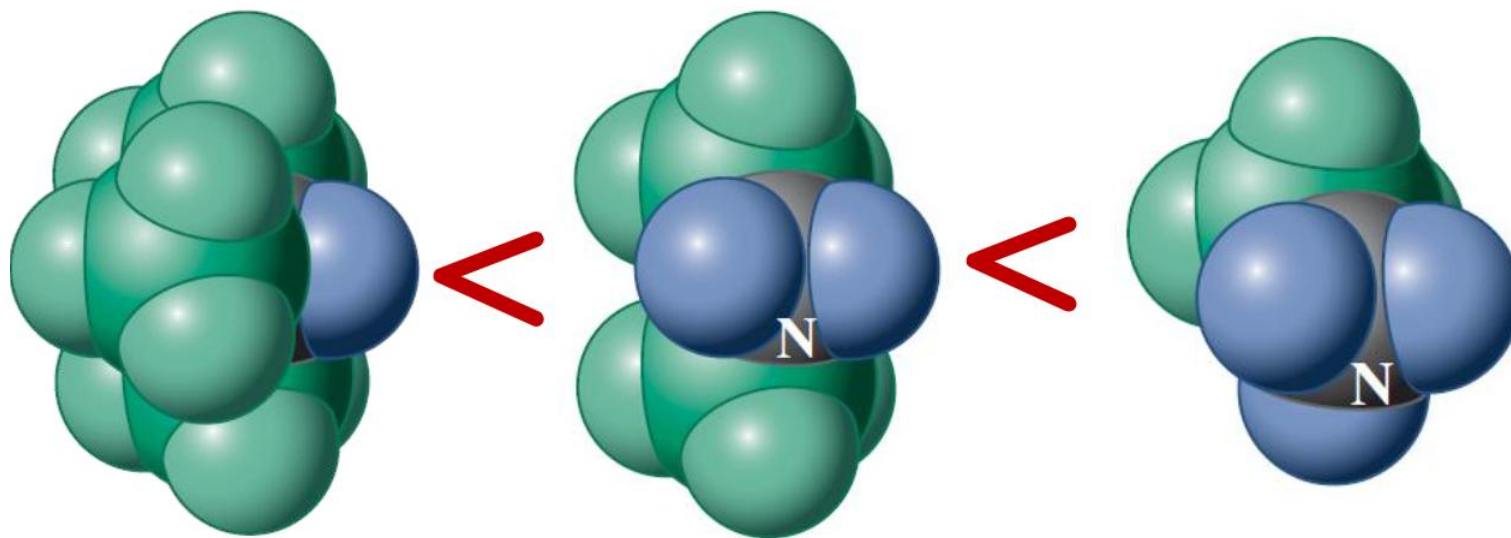
烷基超共轭效应稳定氮正离子，取代基越多共轭酸越稳定，则共轭酸酸性越弱，胺的碱性越强





胺的碱性

2) 空间位阻效应



3°

2°

1°

N原子上连接的基团越多越大，对N上孤对电子的屏蔽作用越大，N上孤对电子与 H^+ 结合就越难，碱性就越弱。

$$3^\circ < 2^\circ < 1^\circ$$

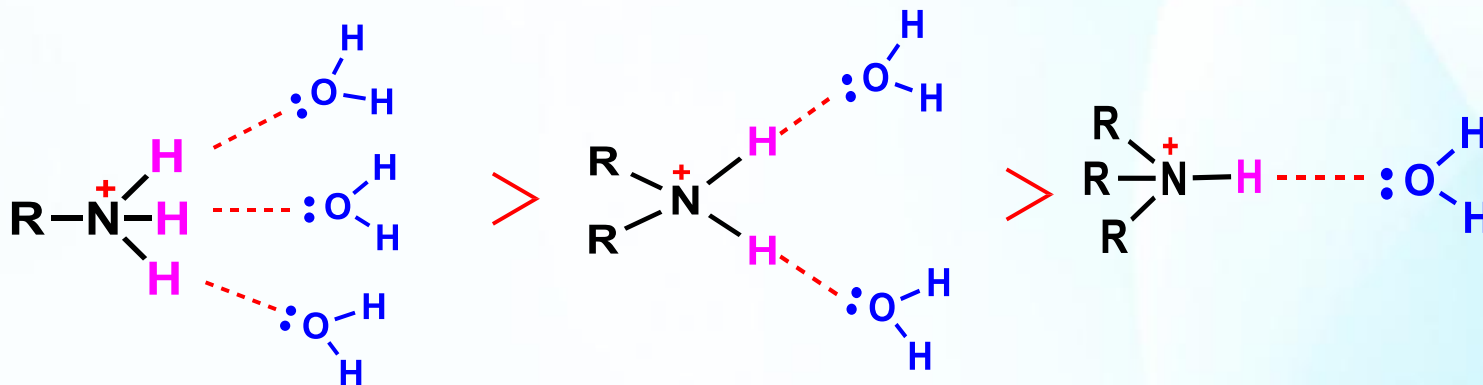


胺的碱性

3) 溶剂化效应



溶剂化程度越大，**铵正离子越稳定**，共轭酸酸性越弱，其**碱性越强**。



溶剂化效应导致脂肪胺类化合物的碱性由强到弱为： $3^\circ < 2^\circ < 1^\circ$



胺的碱性



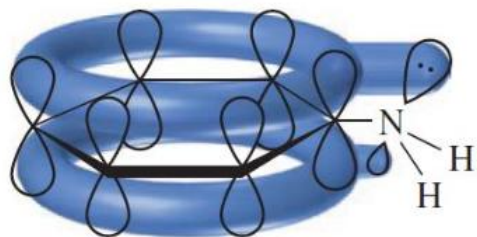
- ◆ 烷基超共轭效应: $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$
- ◆ 空间位阻效应: $3^\circ < 2^\circ < 1^\circ < \text{NH}_3$
- ◆ 溶剂化效应: $3^\circ < 2^\circ < 1^\circ < \text{NH}_3$

脂肪胺碱性顺序: $2^\circ > 1^\circ > 3^\circ$

多角度看问题的科学方法

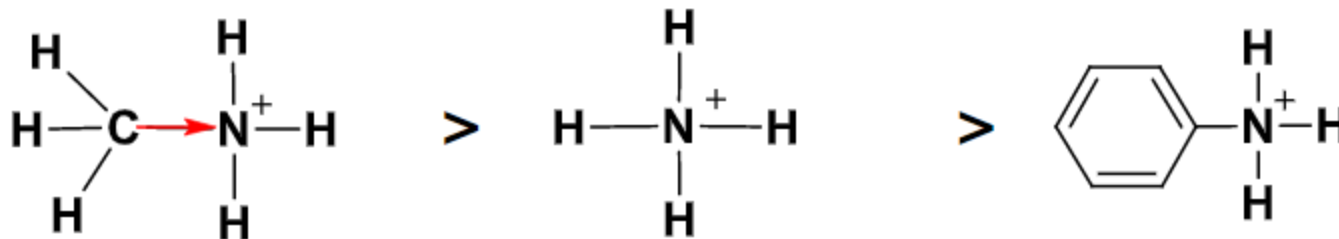
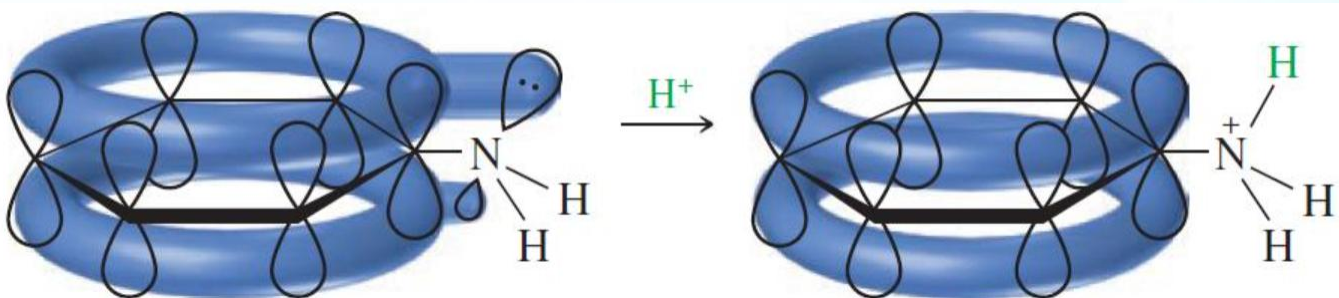


芳香胺的碱性



共轭作用

稳定性



◆ 苯胺正离子共轭作用消失

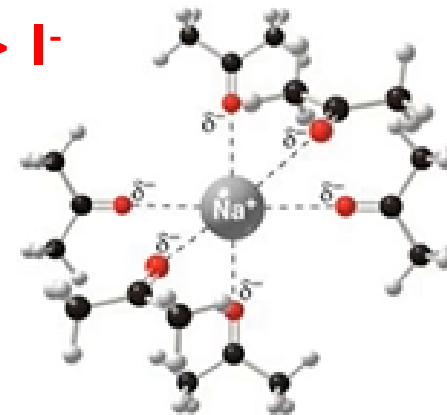
水溶液中，胺的碱性强弱次序为：脂肪胺 ($2^\circ > 1^\circ > 3^\circ$) > 氨 > 芳香胺

➤ 极性质子性溶剂中，亲核试剂发生溶剂化，溶剂化效应顺序： $F^- > Cl^- > Br^- > I^-$

溶剂化导致电荷分散，亲核活性降低，亲核活性顺序： $I^- > Br^- > Cl^- > F^-$

➤ 极性非质子性溶剂，抗衡阳离子被溶剂化，负离子本征活性

亲核活性与碱性一致： $F^- > Cl^- > Br^- > I^-$



Comparison of the Basicity of RO^- and RS^- and Their Nucleophilic Reactivity in Protic Solvents

Basicity $\text{RO}^- > \text{RS}^-$

Nucleophilicity $\text{RS}^- > \text{RO}^-$

可极化性：硫原子比氧原子体积大，电子云更松散，可极化性更强。可极化性强的亲核试剂更容易在进攻时发生电子云的形变，从而更容易与底物形成新的化学键（尤其是在 $\text{S}_{\text{N}}2$ 反应中）。

溶剂化效应：在质子性溶剂（如水、醇）中， RO^- 由于负电荷集中在体积小、电负性强的氧原子上，会与溶剂形成非常强的氢键，被紧密包裹，能量显著降低，导致其“有效亲核性”大打折扣。而 RS^- 负电荷较分散，与质子溶剂的氢键作用弱，溶剂化程度低，因此更“裸露”，反应活性更高。

在非质子极性溶剂中：溶剂化效应减弱。此时 RO^- 的碱性虽强，但亲核性仍受可极化性影响。在非质子溶剂中， RO^- 的亲核性会显著增强，甚至在某些情况下可与 RS^- 竞争，但 RS^- 由于可极化性优势，通常依然是更强的亲核试剂。



Chapter 15

Organic Compounds

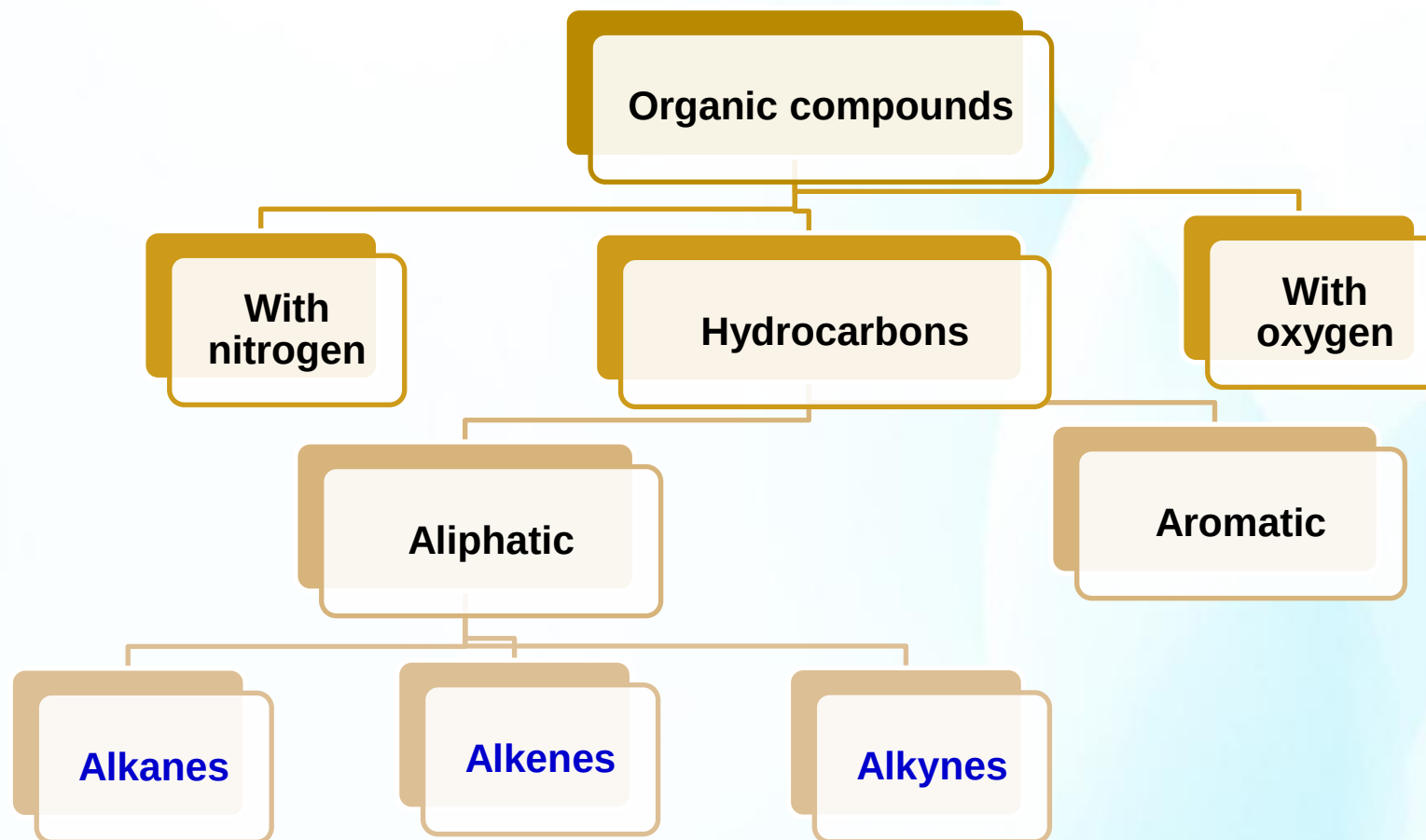
—— Hydrocarbon



- 1. What are Alkanes?**
- 2. What is constitutional isomerism in Alkanes?**
- 3. How do we name Alkanes?**
- 4. What is the IUPAC system of nomenclature?**
- 5. What are the conformations of alkanes ?**
- 6. What are the physical properties of Alkanes ?**
- 7. What are the characteristic reactions of Alkanes?**
- 8. What are the sources of Alkanes?**



Those that **have only carbons and hydrogens** and no other elements are called **hydrocarbons**.



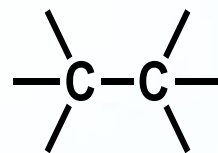


Hydrocarbons

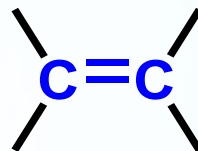
Family	General formula	Functional group	Specific example	
			Formula	IUPAC name
Alkane	RH	C – H and C – C bonds	CH ₃ CH ₃	Ethane
Alkene	RCH = CH ₂ RCH = CHR R ₂ C = CHR R ₂ C = CR ₂		CH ₂ = CH ₂	Ethene
Alkyne	RC ≡ CH RC ≡ CR	– C ≡ C –	HC ≡ CH	Ethyne
Aromatic hydrocarbon	ArH	Aromatic ring		Benzene
Haloalkane	RX		CH ₃ Cl	Chloromethane



Aliphatic hydrocarbons that have nothing but **single bonds** between carbons are called **alkanes**. They are also called saturated aliphatic hydrocarbons since they contain as many hydrogens as they can have.



Aliphatic hydrocarbons that have at least one **double bond** between carbons are called **alkenes**, the carbon-carbon double bonds being the functional group.



Aliphatic hydrocarbons that have at least one **triple bond** between carbons are called **alkynes**, the carbon-carbon triple bond being the functional group.



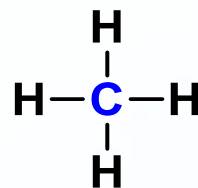


All open-chain alkanes fit the **general formula** C_nH_{2n+2} , where n is the number of carbon atoms in the molecule.

Methane

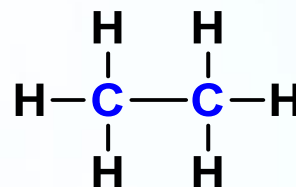
CH_4

Natural gas



Ethane

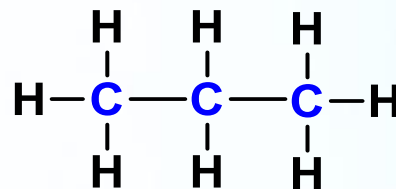
C_2H_6



Propane

C_3H_8

Barbeque grill fuel



• 烷烃的通式: C_nH_{2n+2}

(例: CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} ,)

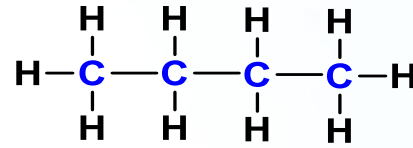
同系列

(同系物, Homologs)

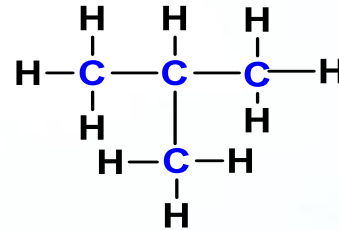
同系列: 有相同通式、结构上相差一定的“原子团”的一系列化合物。

同系物: 同系列中的化合物为同系物。

Butane



n-Butane



Iso-Butane

Isomers are compounds which have **the same molecular formula**, but **differ in** the way the atoms are **arranged**.

There are **three types** of isomers— constitutional, configurational, and conformational.

构造
构象

构造

构型

Constitutional isomers are compounds which have the same molecular formula but have the atoms **joined together in a different way**.

1.1.1 烷烃的同分异构

同分异构：分子式相同，结构不同。是不同的化合物。

构造异构：分子式相同，分子内原子间相互连接的顺序不同，即分子的构造不同。

碳架异构：分子式相同，碳的骨架不同。

C4 以上烷烃出现同分异构现象

同分异构体数

C_4H_{10}



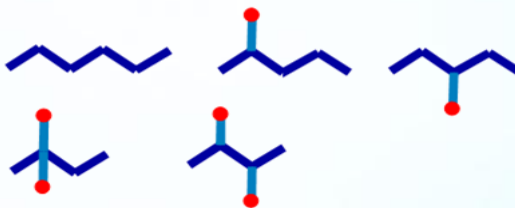
2

C_5H_{12}



3

C_6H_{14}



5

$C_{20}H_{42}$

366,319

Constitutional isomers have different physical and chemical properties.



Isomers abound in organic chemistry, and as the **number of carbons increases**, the **number of possible isomers increases** as well.

Carbon Atoms		Constitutional Isomers
5	C_5H_{12}	3
10	$\text{C}_{10}\text{H}_{22}$	75
15	$\text{C}_{15}\text{H}_{32}$	4,347
25	$\text{C}_{25}\text{H}_{52}$	36,797,588



- 普通命名法

用于简单化合物的命名

- IUPAC命名法（系统命名法）

（**IUPAC**: 国际纯粹与应用化学联合会，

International **U**nion of **P**ure and **A**ppplied **C**hemistry）

基础：普通命名法



1.2.2 普通命名法

		中文名	英文名
C1	CH ₄	甲烷	methane
C2	CH ₃ CH ₃	乙烷	ethane
C3	CH ₃ CH ₂ CH ₃	丙烷	propane

- 碳原子数目 + 烷
- 英文命名用词尾-ane表示烷烃

- 碳原子数为1~10用天干（甲、乙、丙、.....壬、癸）表示



Naming Alkanes

IUPAC Names for Alkanes and Alkyl Groups of Various Chain Lengths(International Union of Pure and Applied Chemistry, IUPAC)

Number of C Atoms	Name of Alkyl Group	Roots	Name of Alkane
1	Methyl	Meth-	Meth ane
2	Ethyl	Eth-	Eth ane
3	Propyl	Prop-	Prop ane
4	Butyl	But-	But ane
5	Pentyl	Pent-	Pent ane
6	Hexyl	Hex-	Hex ane
7	Heptyl	Hept-	Hept ane
8	Octyl	Oct-	Oct ane
9	Nonyl	Non-	Non ane
10	Decyl	Dec-	Dec ane



Naming Alkanes

$\text{CH}_3\text{—}$	methyl	甲基
	(Me)	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$	n-propyl	(正)丙基
	(n-pr)	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$	n-butyl	(正)丁基
	(n-Bu)	
$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH—} \\ \\ \text{CH}_3 \end{array}$	sec-butyl	仲丁基
	(s-Bu)	
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$	iso-butyl	异丁基
	(i-Bu)	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C—} \\ \\ \text{CH}_3 \end{array}$	tert-butyl	叔丁基
	(t-Bu)	
$\text{CH}_3\text{CH}_2\text{—}$	ethyl	乙基
	(Et)	
$\begin{array}{c} \text{CH}_3\text{CH—} \\ \\ \text{CH}_3 \end{array}$	iso-propyl	异丙基
	(i-pr)	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$	n-pentyl	(正)戊基
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$	iso-pentyl	异戊基
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{C—} \\ \\ \text{CH}_3 \end{array}$	tert-pentyl	叔戊基
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CCH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$	neo-pentyl	新戊基



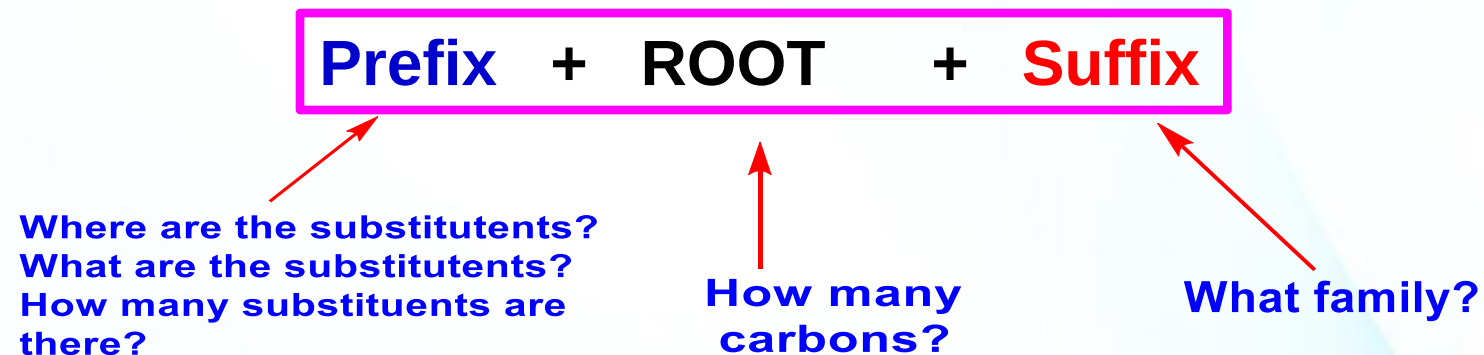
Naming Alkanes

	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	正丁烷	n-butane
C4	$\begin{array}{c}\text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_3\end{array}$	异丁烷	isobutane
<hr/>			
	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	正戊烷	n-pentane
C5	$\begin{array}{c}\text{CH}_3 \\ \\ \text{CH}_3\text{CHCH}_2\text{CH}_3\end{array}$	异戊烷	isopentane
	$\begin{array}{c}\text{CH}_3 \\ \\ \text{CH}_3\text{CCH}_3 \\ \\ \text{CH}_3\end{array}$	新戊烷	neopentane

- 异构词头用词头“正”、“异”和“新”等区分
- 相应的英文词头为 **n-** (normal)、**iso**和**neo** (注意不加“-”)



Rules for Naming an Organic Compound



1. Naming the longest chain (root)

- (a) Find the longest continuous chain of C atoms.
- (b) Select the root that corresponds to the number of C atoms in this chain.

2. Naming the compound type (suffix)

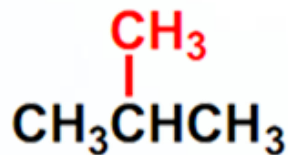
- (a) For alkanes, add the suffix **-ane** to the chain root.
- (b) If the chain forms a ring, the name is preceded by **cyclo-**.

3. Naming the branches (prefixes)

- (a) Each branch name consists of a root and the ending **-yl** to signify that it is **not part** of the main chain.
- (b) Branch names **precede** the chain name. When **two or more** branches are present, their names appear **in alphabetical order**.
- (c) To specify where the branch occurs along the chain, **number** the main-chain C atoms **consecutively**, starting **at the end closer** to a branch, to achieve the **lowest numbers** **连续地** for the branches. **Precede** each branch name **with the number** of the main-chain C to which that branch is **attached**.



IUPAC命名法, International Union of Pure and Applied Chemistry



普通命名法: 异丁烷

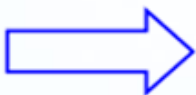
IUPAC命名法: 2-甲基丙烷

基本方法:

- 选定一条最长链作为主链 (以普通命名法命名)
- 其它支链作为主链上的取代基。

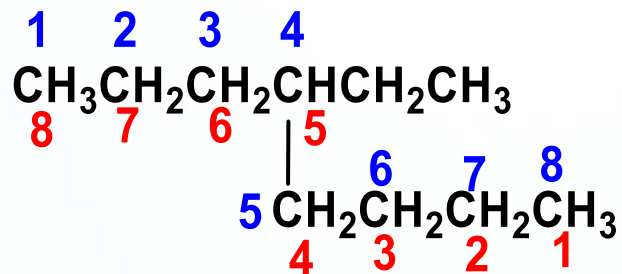
- 取代基 (烷基): 烷烃去掉一个氢原子后留下的原子团

烷烃



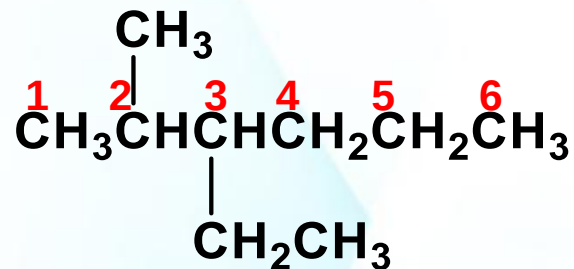
烷基





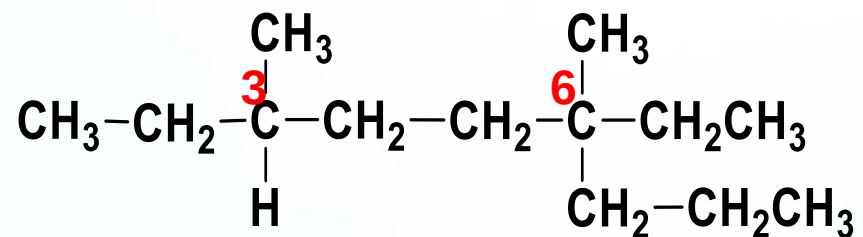
4-ethyloctane

- 最长链为主链
- 取代基编号数最小



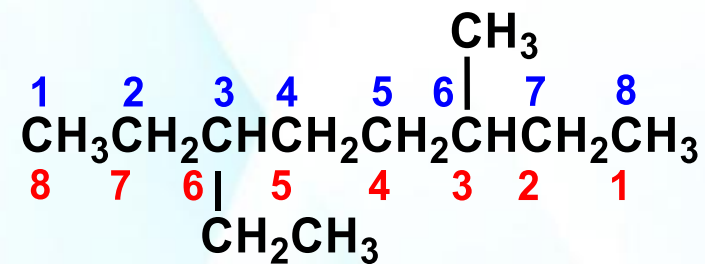
3-ethyl-2-methylhexane

- 取代基最多的链为主链
- 小基团排在前面（英文以字母顺序排列）



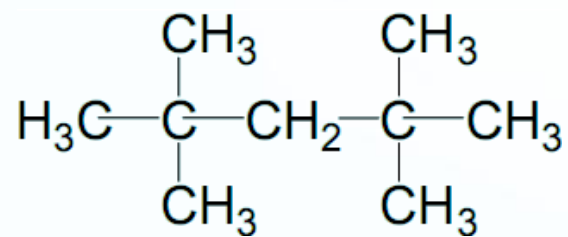
6-ethyl-3,6-dimethylnonane

➤ 不同基团编号相同时，使小取代基编号最小

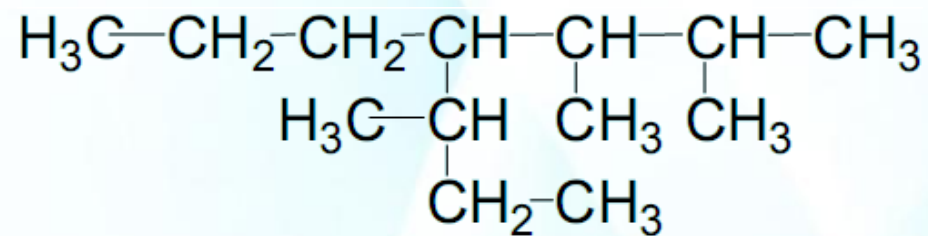


3-ethyl-6-methyloctane

相同取代基合并用大写数字表示（英文表示基团数目用词头 **di, tri, tetra, penta, hexa** 表示）



2,2,4,4-**tetra**methylpentane



2,3,5-**tri**methyl-4-n-propylheptane



Summary

Names all share a **common suffix**, i.e '....**ane**'

The suffix '...**ane**' indicates that the compound is an **alkane**

The **prefix** indicates **the number of carbons in the compound**

Substituents named in **alphabetical** order

Identical substituents grouped together with a **prefix**

- '**di**...' for **two** identical
- '**tri**...' for **three**
- '**tetra**...' for **four**

Di-, **tri-**, **tetra-**, **sec-**, **tert-** **ignored** when alphabetizing
iso, **neo** are **included** when alphabetizing.



一、不参与排序的前缀 (Di-, tri-, tetra-, sec-, tert-)

1. 数量前缀 (Di-, tri-, tetra-)

1. 这些前缀仅表示取代基的数量 (如 dimethyl 表示两个甲基) , 不影响取代基名称的主体部分。
2. **排序逻辑**: 取代基名称的主体 (如 methyl) 按字母顺序排列, 数量前缀被忽略。
 1. 例: 比较 dimethyl (视为 "methyl") 和 ethyl ("ethyl") 时, ethyl 优先 (e 在 m 前) 。

2. 结构前缀 (sec-, tert-)

1. 这些前缀描述取代基的连接方式 (如 sec - 表示仲, tert - 表示叔) , 属于取代基名称的修饰词。
2. **排序逻辑**: sec - 和 tert - 不被视为独立的首字母, 而是与主体名称合并排序。
 1. 例: sec-butyl (视为 "butyl") 和 ethyl ("ethyl") 比较时, ethyl 优先。

二、参与排序的前缀 (iso, neo)

1. iso 和 neo

1. 这些前缀被视为取代基名称的固定组成部分, 直接影响字母顺序。
2. **排序逻辑**: iso 和 neo 作为独立的首字母参与排序。
 1. 例: isopropyl ("i") 在 methyl ("m") 之前; neohexyl ("n") 在 ethyl ("e") 之后。

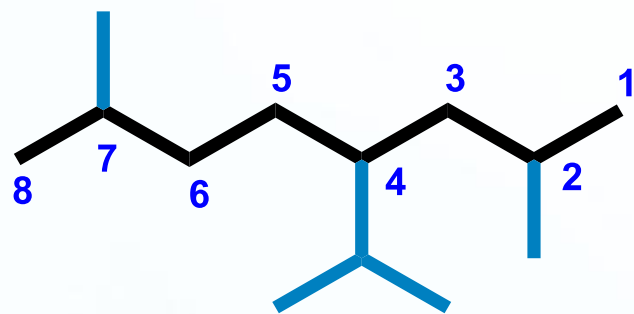
总结

-

不参与排序的前缀：Di-, tri-, tetra-, sec-, tert-（数量或结构修饰词，不影响主体名称）。

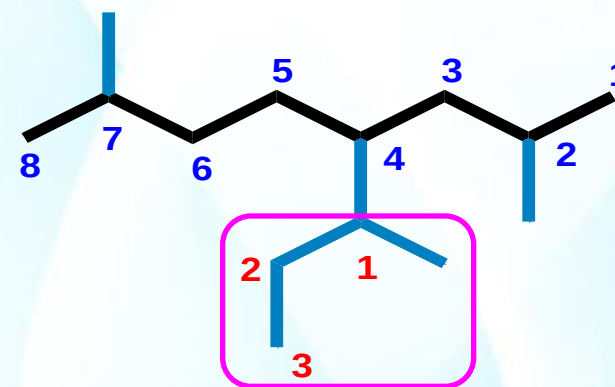
•**参与排序的前缀：**iso, neo（取代基名称的核心部分，直接影响字母顺序）。

•**核心原则：**以取代基名称的主体部分（如 methyl、ethyl）为基准，按字母顺序排列，忽略数量和非核心结构修饰词。



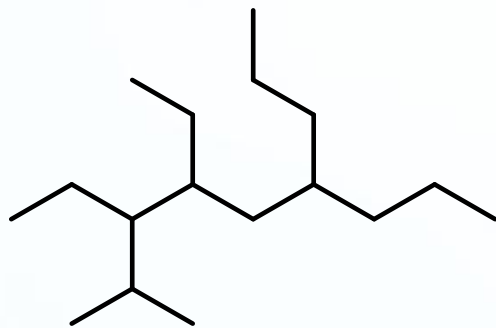
(1)

(1) 4-**i**sopropyl-2,7-di**m**ethyloctane

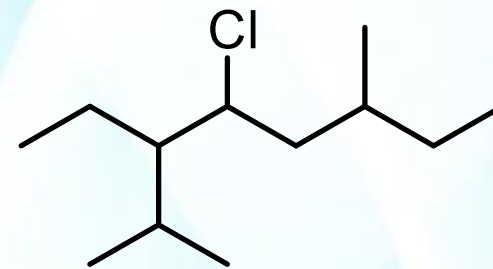


(2)

(2) 4-(sec-**b**utyl)-2,7-di**m**ethyloctane



3,4-diethyl-2-methyl-6-propylnonane

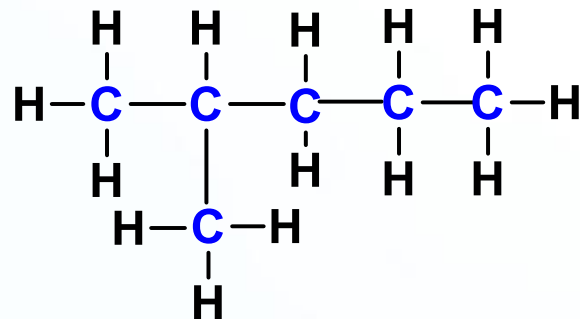


4-chloro-3-ethyl-2,6-dimethyloctane

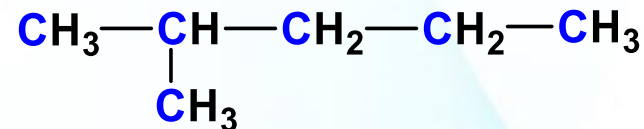


Depicting Alkanes with Formulas and Models

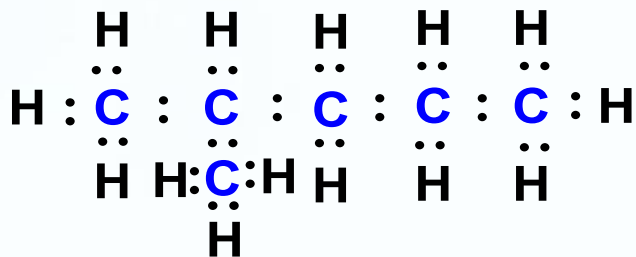
Several ways to depict organic compounds:



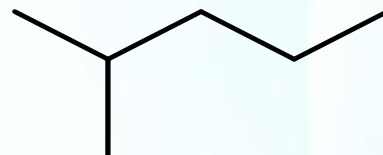
Expanded formula



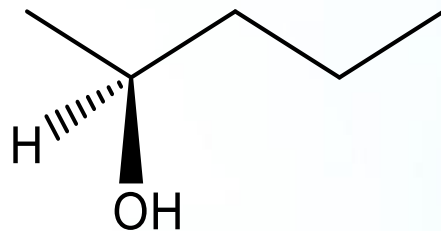
Condensed formula



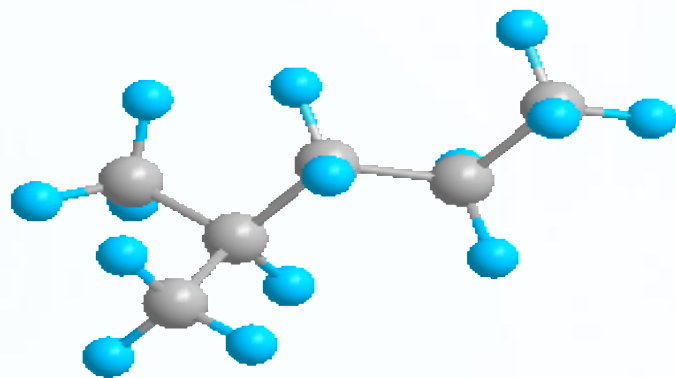
Electron formula



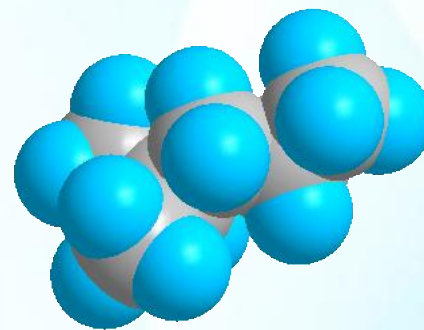
carbon-skeleton formula



Dashed-Wedged Line Notation



ball-and-stick model

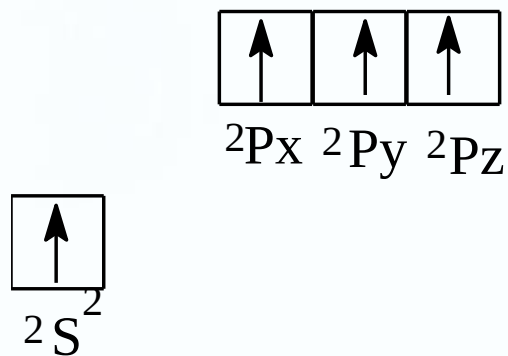
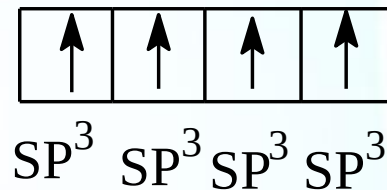
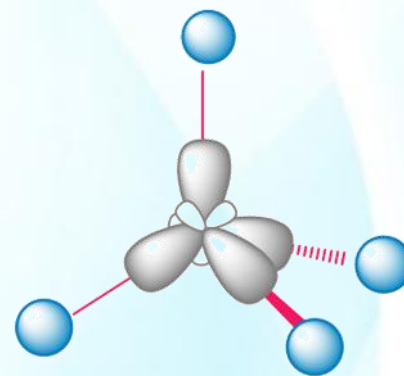
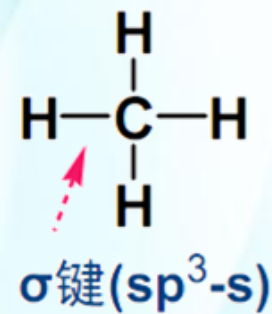


space-filling model



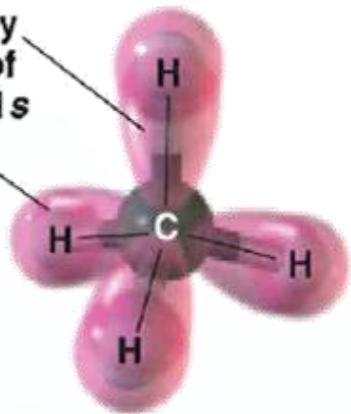
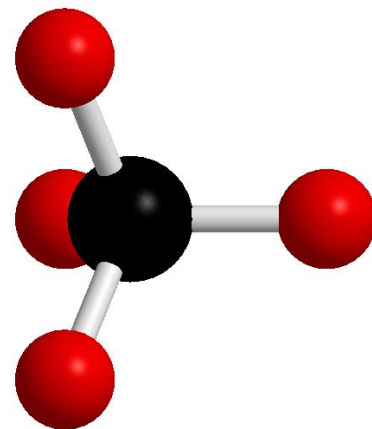
一个s轨道和三个p轨道杂化后，形成四个完全相等的杂化轨道，这种轨道称为 sp^3 杂化轨道

- 杂化轨道有更强的方向性；
- 四个 SP^3 杂化轨道完全等值；
- 四个键尽可能远离；
- 每两个杂化轨道之间的夹角都是 $109^\circ 28'$

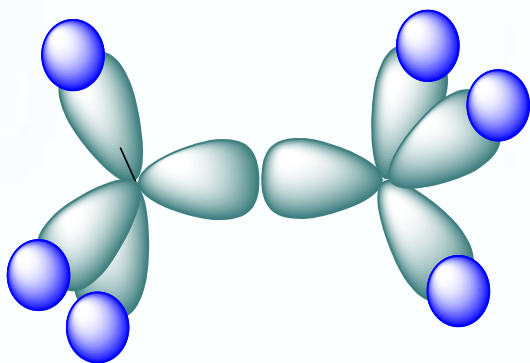
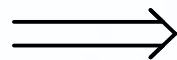
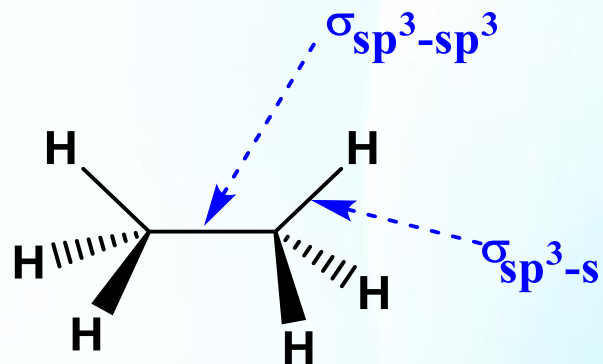


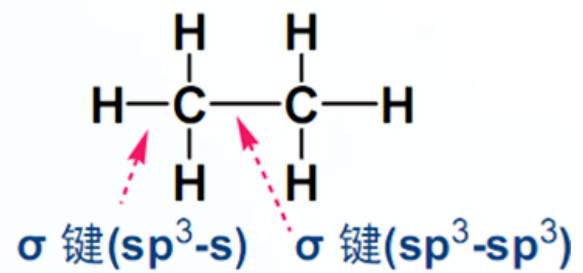


Sigma bonds
formed by
overlap of
 sp^3 and $1s$
orbitals

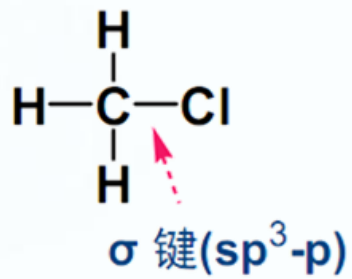


四面体构型





$sp^3-sp^3 \sigma$ 键

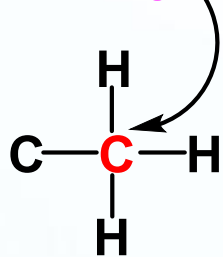


$sp^3-p \sigma$ 键

(1) Characteristics: C atom takes an **sp³** hybridization.

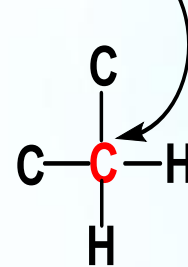
(2) Carbon atoms are classified into **four types** according to their degree of substitution by other carbons.

Primary carbon



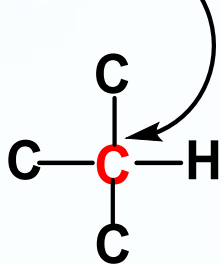
1°C

Secondary carbon



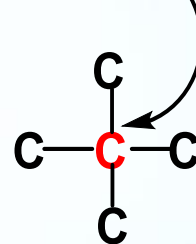
2°C

Tertiary carbon

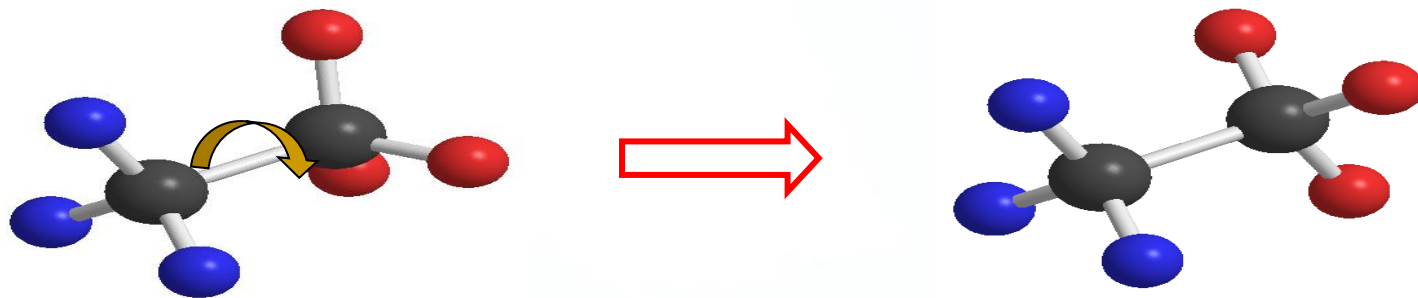


3°C

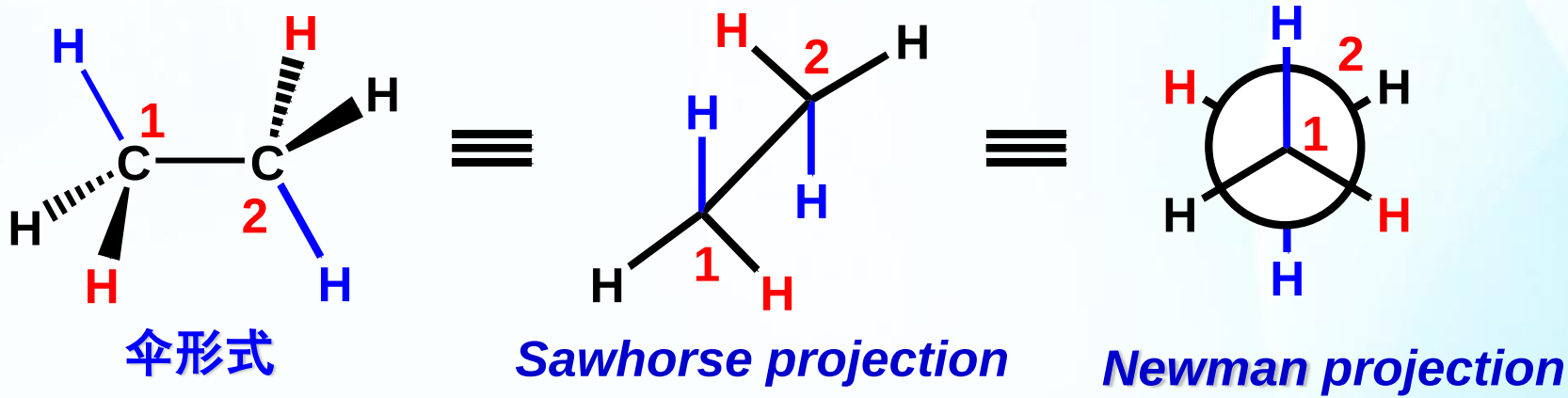
Quarternary carbon

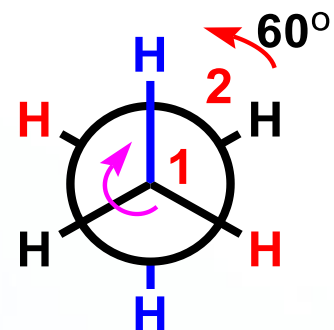


4°C



Conformational isomers are different shapes of the same molecule resulting from rotation round C-C single bonds.

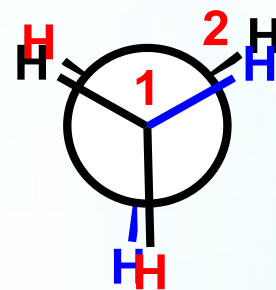




Energy Minimum

交叉式构象 最稳定

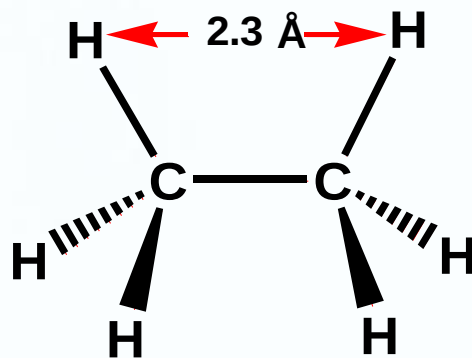
Staggered conformation



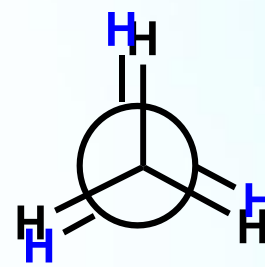
Energy Maximum

重叠式构象 最不稳定

Eclipsed conformation



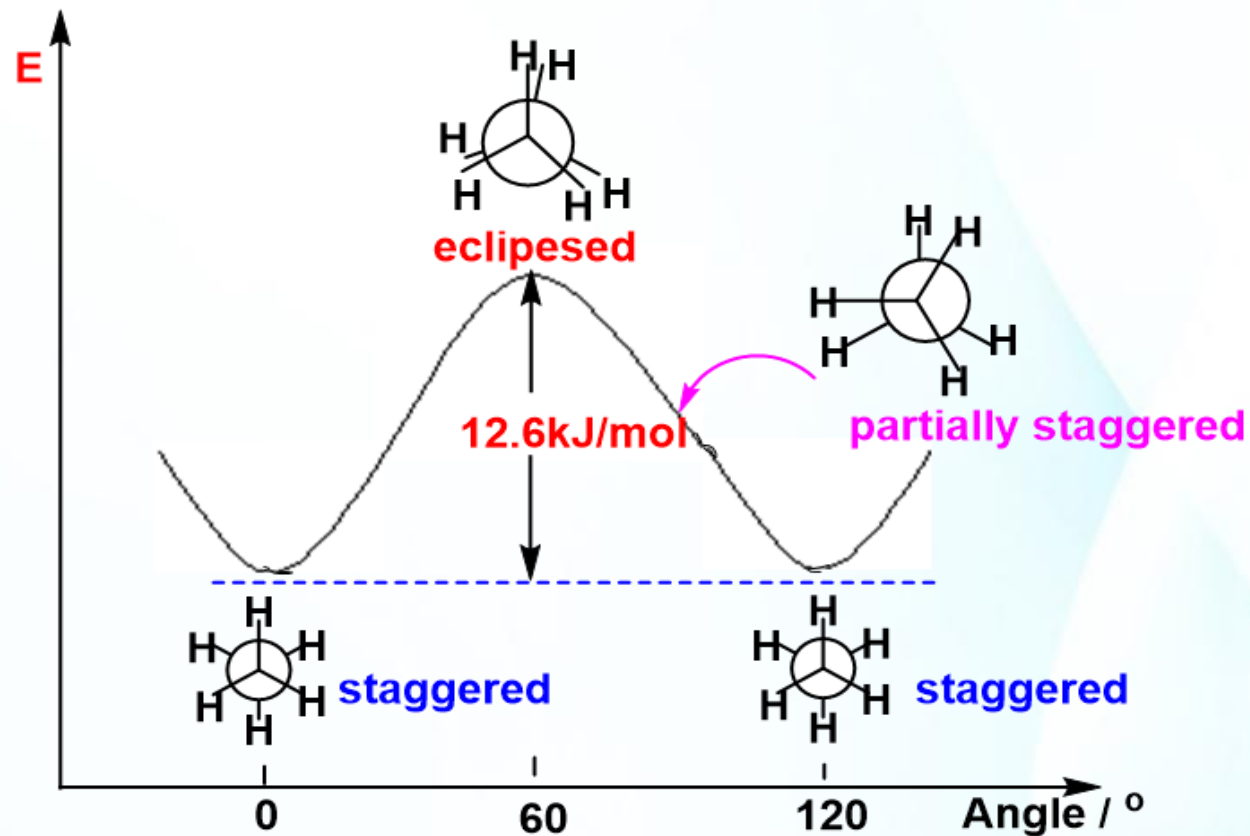
4 kJ mol⁻¹



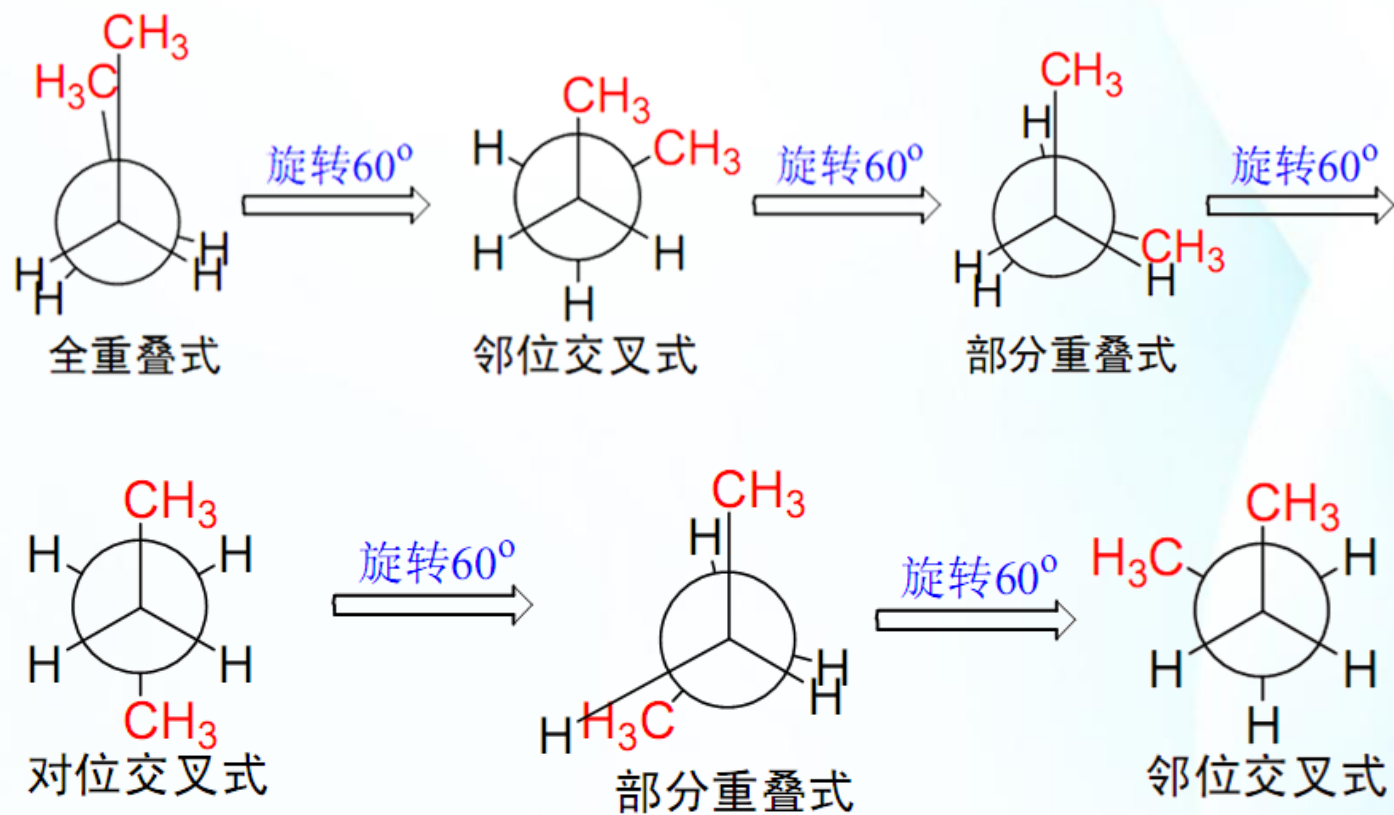
Total: 12 kJ mol⁻¹
torsional strain

4 kJ mol⁻¹

4 kJ mol⁻¹



Since rotation round a single bond normally occurs easily **at room temperature**, **conformational isomers** are **freely interconvertible**.

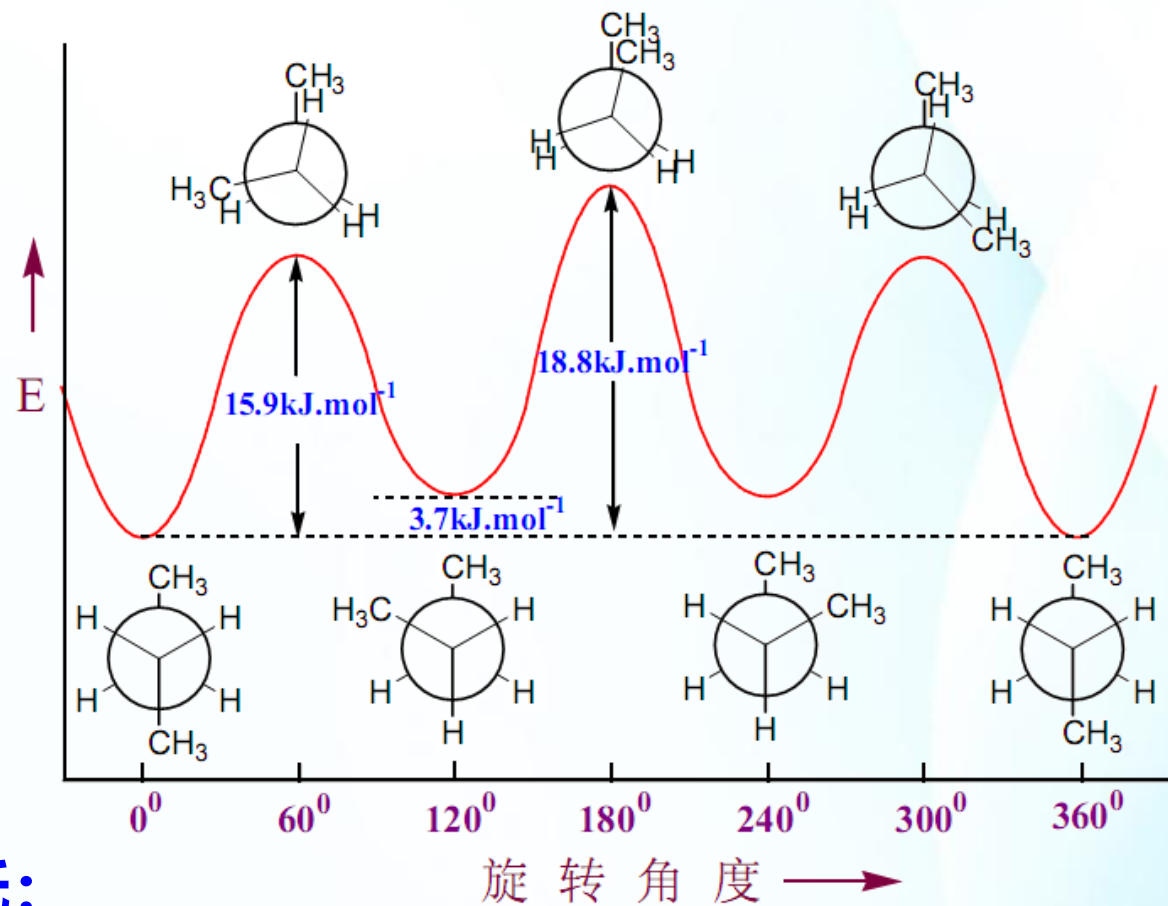


能量高低：

全重叠式 > 部分重叠式 > 邻位交叉式 > 对位交叉式

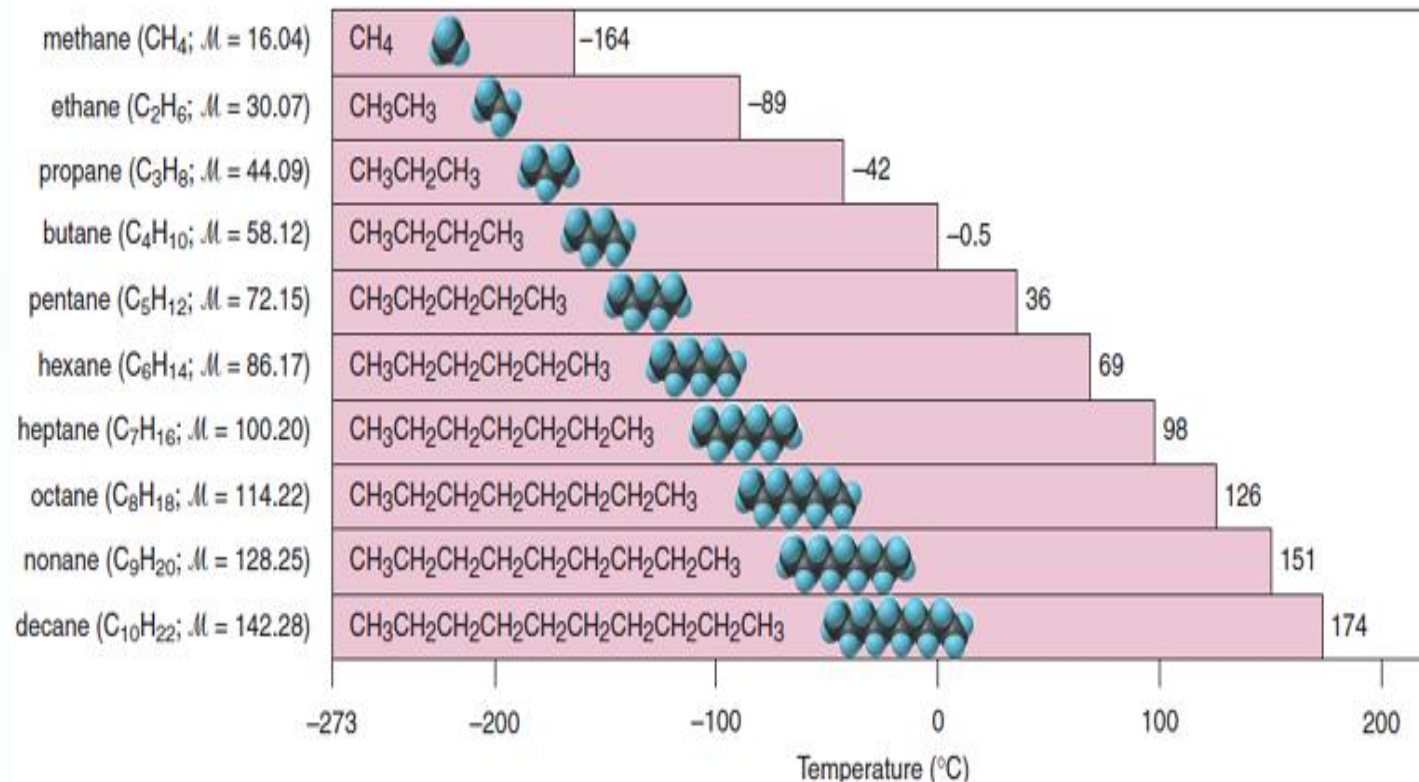


丁烷的各构象的能量变化



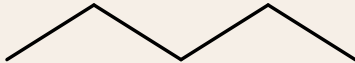
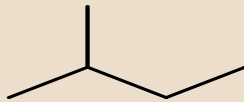
Boiling point

To the unbranched alkanes, the **longer** the chain, the greater the intermolecular contact, the stronger the dispersion forces (色散力), and the **higher** the **boiling point**.



沸点：主要看色散力、接触面积

To the branched alkanes, the **more spherical** member (*iso-* or *neo-*) boils **lower** than the more elongated one (*n-*).

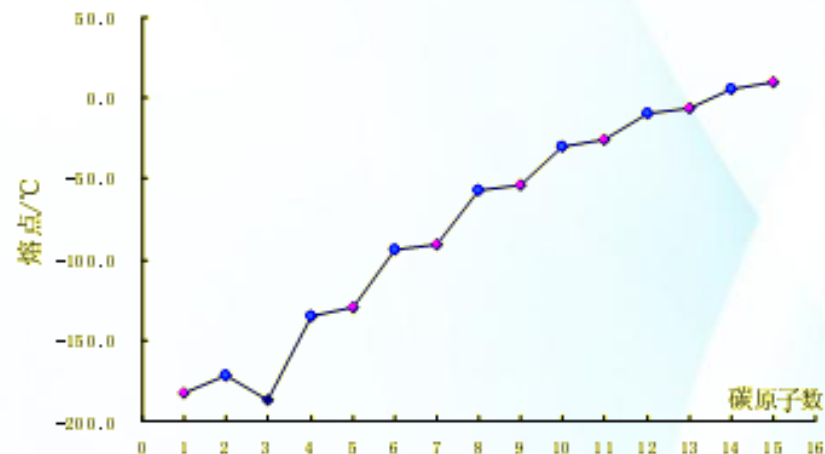
The Constitutional Isomers of C ₄ H ₁₀ and C ₅ H ₁₂			
Common Name	Skeleton Formulas	Density (g/mL)	Boiling Point (°C)
n-butane		0.579	-0.5
isobutane		0.549	-11.6
n-pentane		0.626	36.1
isopentane		0.620	27.8
neopentane		0.614	9.5

逐渐减少
↓

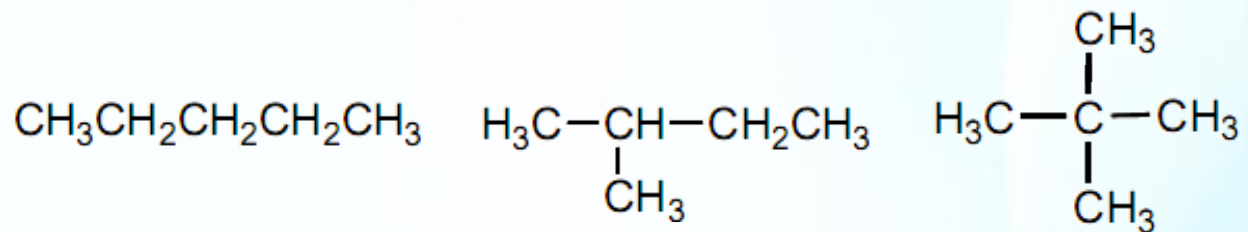


熔点：主要看分子对称性 + 晶格堆积紧密程度

➤ 分子量越大，熔点越高



➤ 对称性越好，熔点越高



正戊烷 (-129.7°C) 异戊烷 (-160°C) 新戊烷 (-17°C)

- 分子间引力决定: 随碳原子数增加而增大, 接近0.78
- 密度小于水

溶解性规律

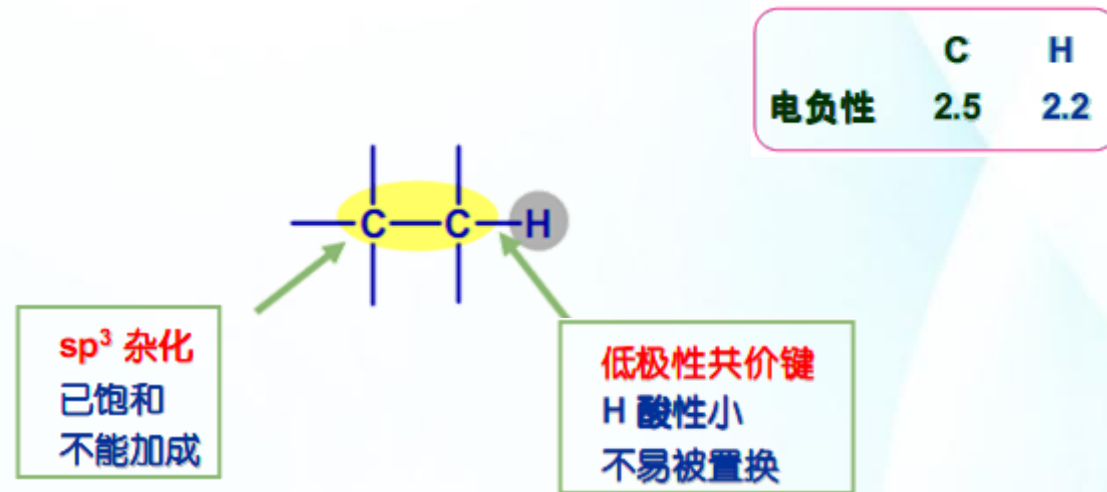
- 不溶于水, 易溶于有机溶剂, 尤其是烃类中, 相似相溶的规律
- 烷烃为非极性分子, 溶于极性小的有机溶剂, 不溶于极性溶剂

2.4.5 同分异构体的物理性质规律

- 沸点: 支链越多, 色散力越小, 沸点越低
- 熔点: 对称性越高, 熔点越高



烷烃的结构



- 一般情况下烷烃的化学性质不活泼、耐酸碱（常用作低极性的溶剂，如正己烷、石油醚）
- 烷烃可以与卤素发生自由基取代反应（烷烃的重要反应）

1. Combustion of Alkanes



2. Radical Substitution Reaction

➤ General reaction:

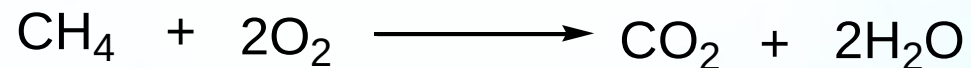
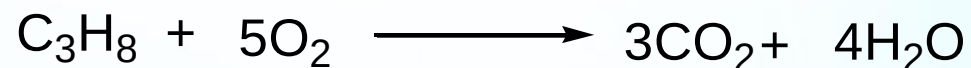
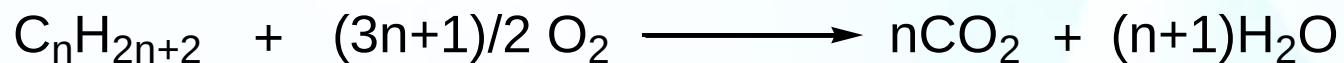


Reactivity activity of Halogen: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$





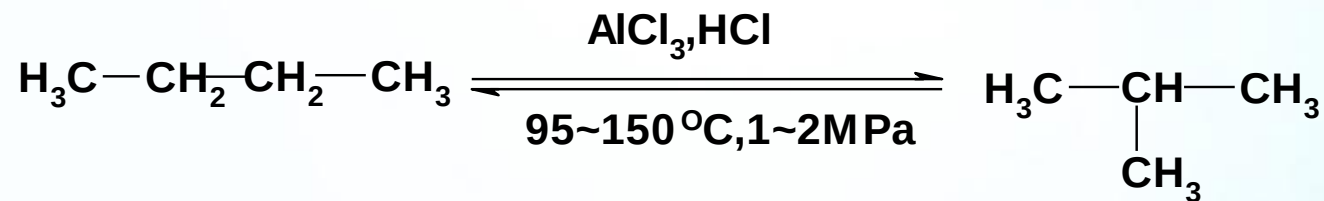
- 燃烧生成CO₂和水：高温和足够的空气中燃烧，完全氧化，生成CO₂和 水，大量放热



- 低级烷烃的蒸气和空气混合至一定比例，遇火爆炸，如煤矿中瓦斯爆炸。甲烷的爆炸极限是5.53%—14%；在这比例外，只燃烧不爆炸



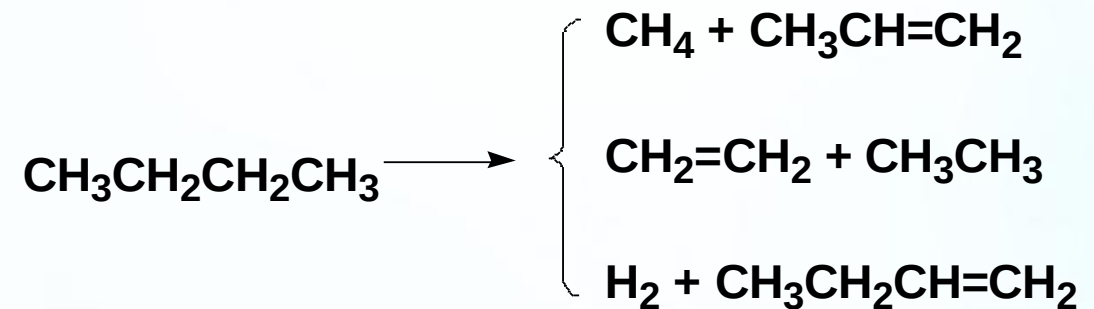
从化合物的一种异构体转变成另一种异构体的反应。



- 直链烷烃异构体为带支链的烷烃可以提高汽油的辛烷值，同时，因异构化产生叔碳原子而增加了化学反应的活性。

石油化工：汽油，辛烷值，
异辛烷值为100，正庚烷为0

裂化反应: 隔绝氧气,高温下,化合物发生键断裂的反应。一般生成分子量更小的烷, 烯和氢气。催化裂化, 又叫催化重整。



- **高温裂化, 又叫高温裂解, 一般高于750 °C裂化反应可以提高汽油的产量和质量**
- **催化裂化, 在催化剂的存在下的裂化, 长远的催化剂是硅酸铝**



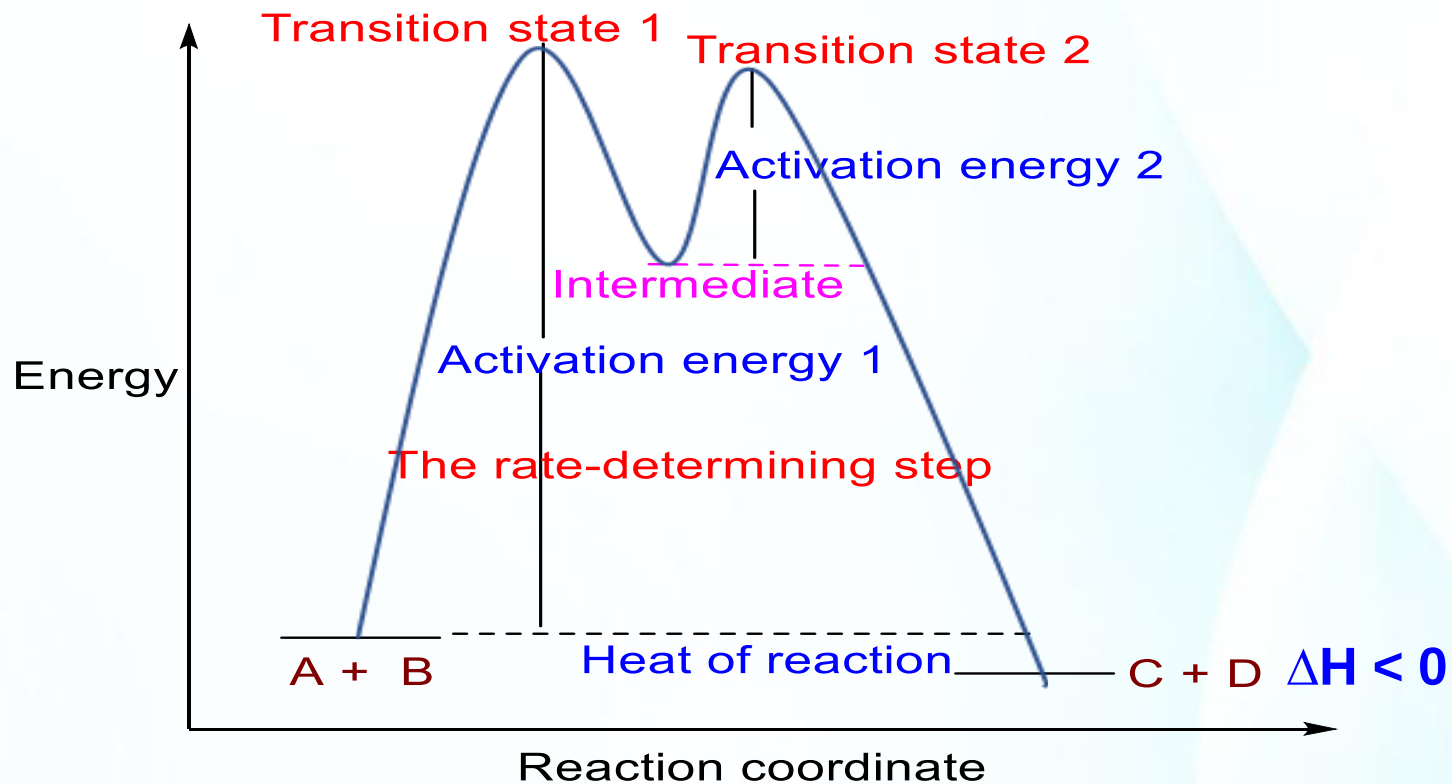
什么是反应机理：

反应机理是根据反应事实，对反应过程的详细描述和理论解释，应解释以下问题：

- 反应是如何开始的？
- 反应条件起什么作用？
- 产物生成的合理途径？
- 决速步骤是哪一步？
- 经过了什么中间体？
- 副产物是如何生成的？

研究反应机理的意义：

- 了解影响反应的各种因素，最大限度地提高反应的产率。
- 发现反应的一些规律，指导更深入的研究。

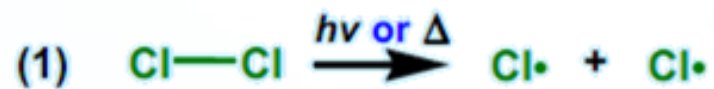


活化能：发生反应所需要的最低能量（反应物能量与过渡态能量之差）。

过渡态：由反应物到产物之间的新键未完全形成，旧键未完全断裂的能量最高的中间状态。



➤ Reaction mechanism:

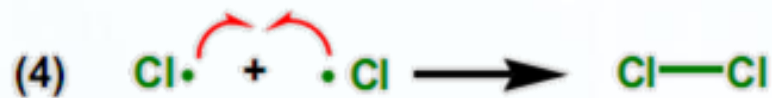
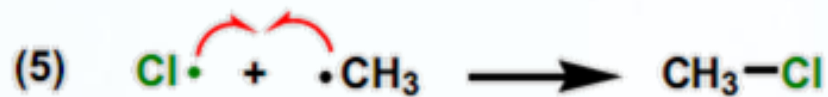
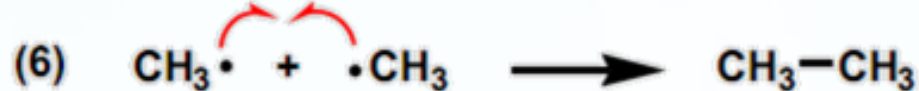


链引发
chain initiation



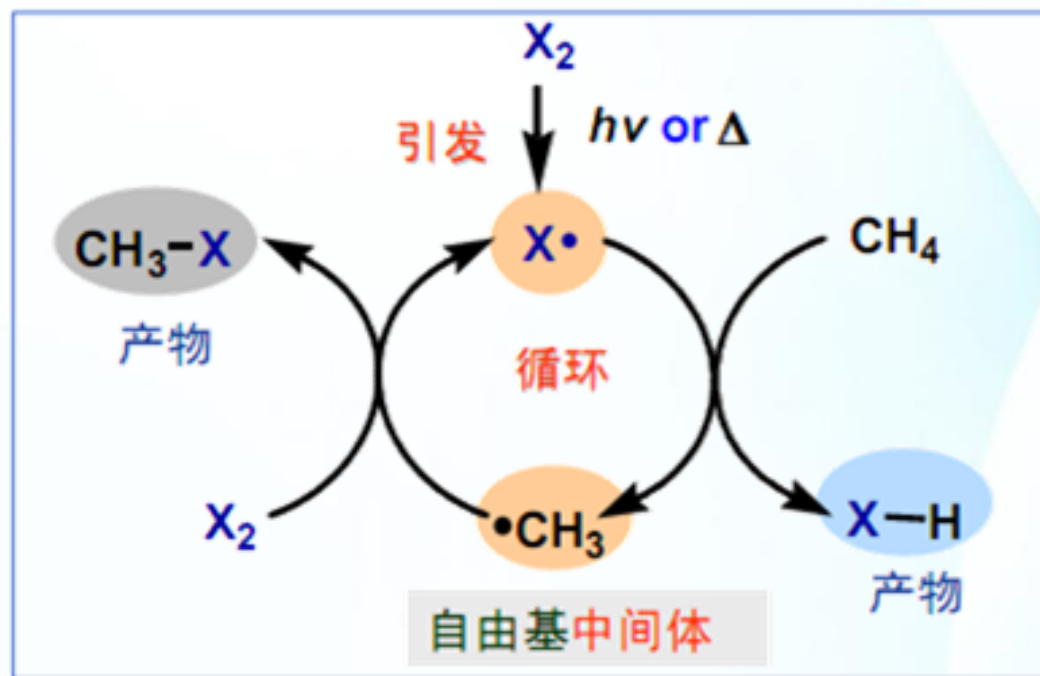
链转移
(链传递, 链增长)
chain
propagation

第(2), (3)步反应重复进行



链终止
chain termination

自由基型链反应 (chain reaction)



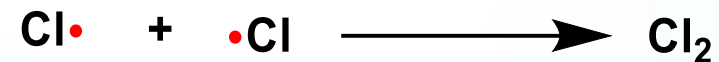
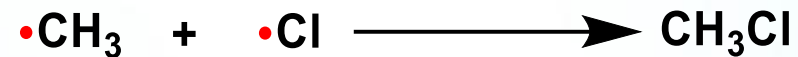
机理应解释
的实验现象

- ✓ 产物的生成
- ✓ 光或加热的作用
- ✓ 链现象

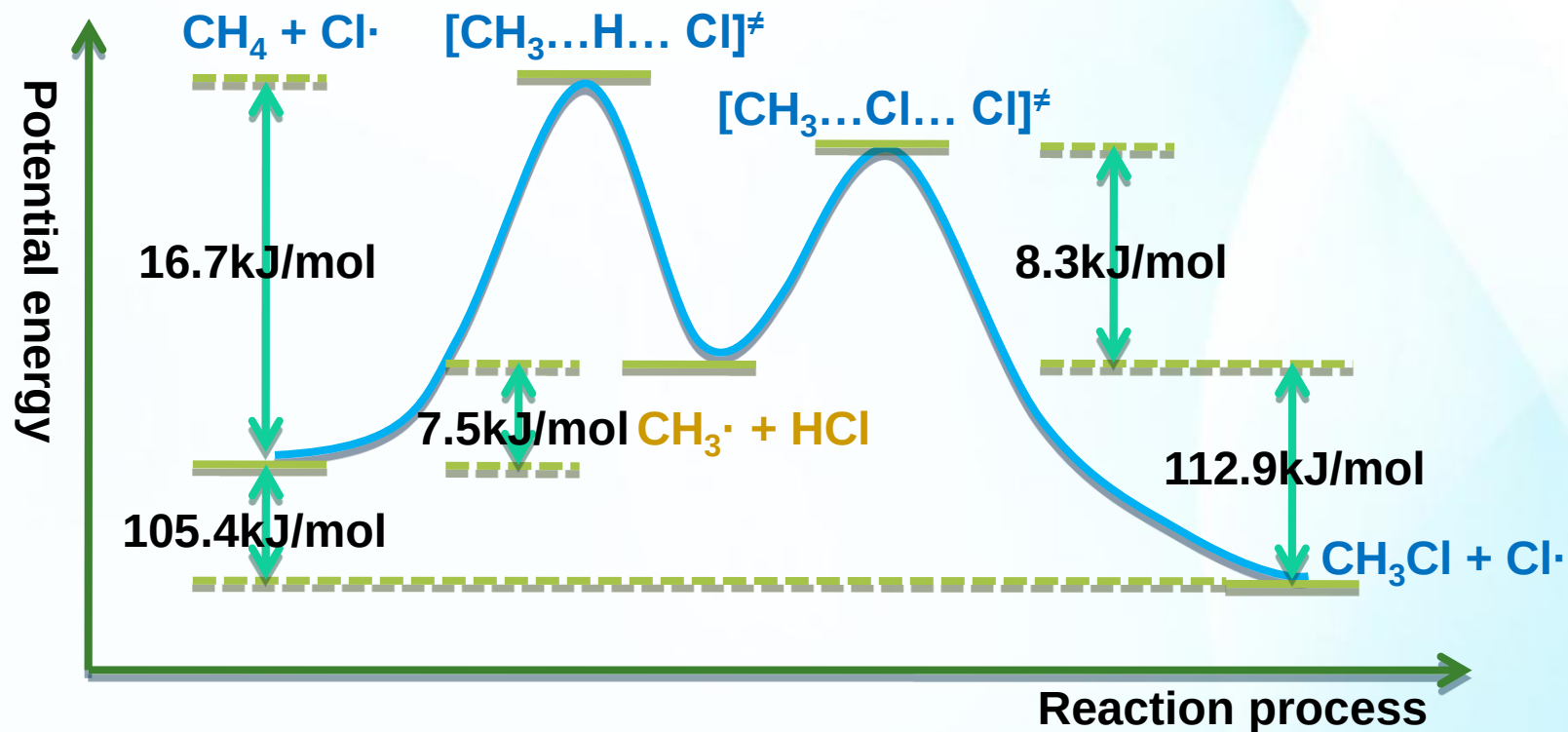
- ? O_2 存在时有延迟现象
- ? 反应速率: 氯代 > 溴代

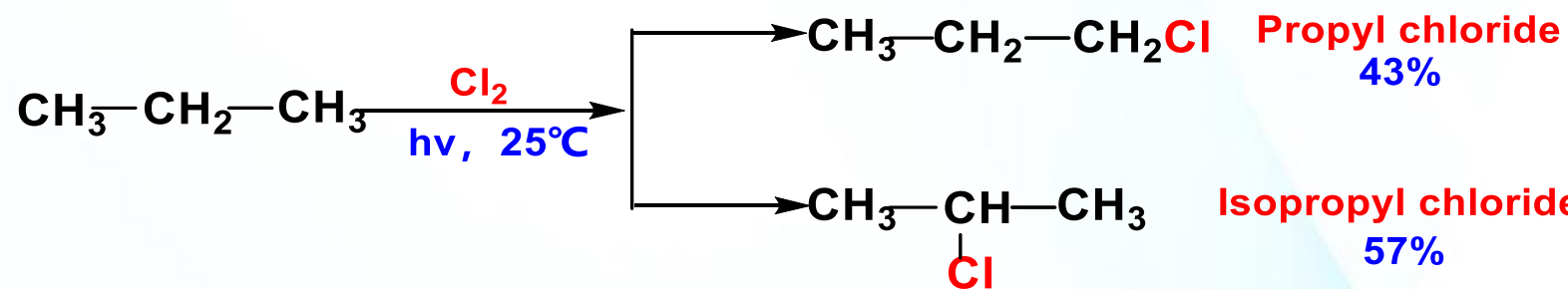
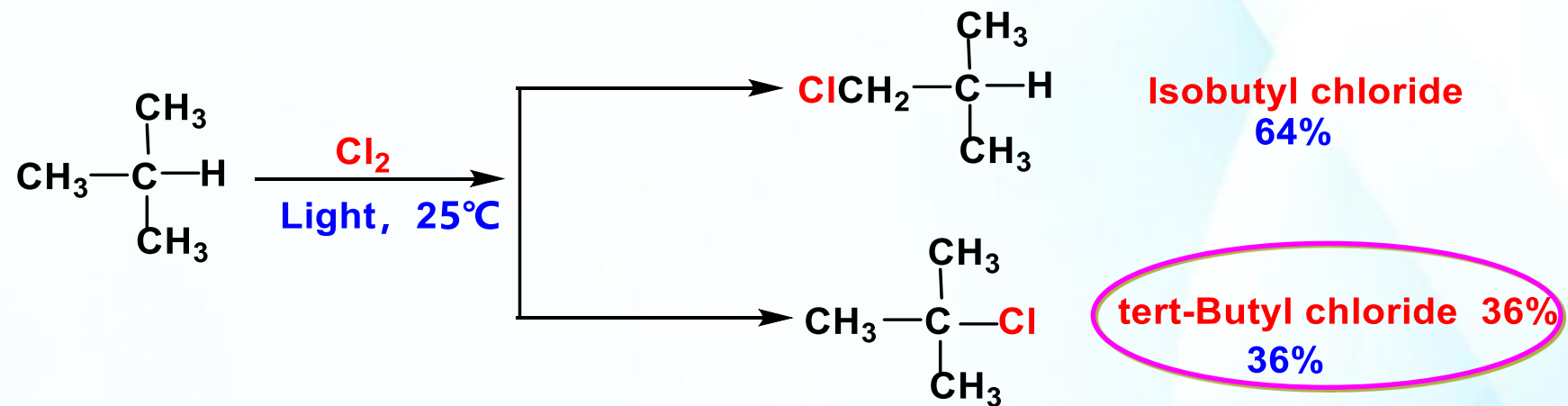
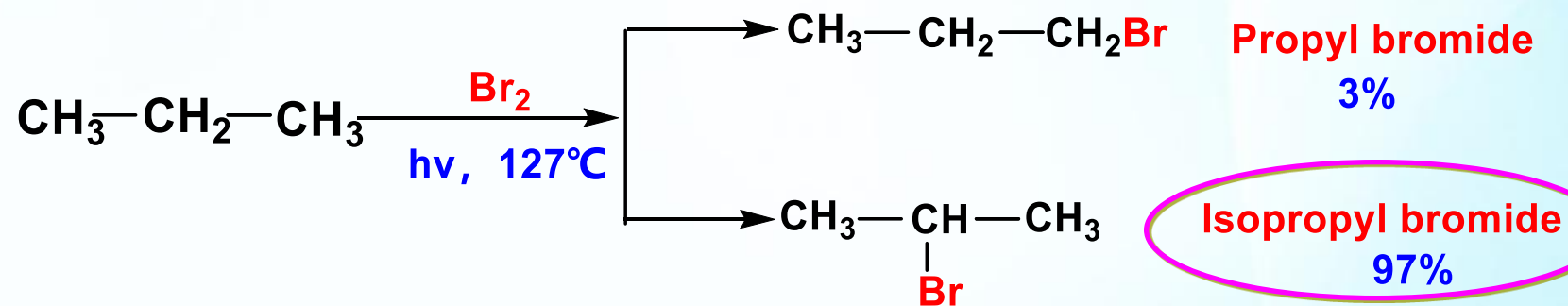


(c) Chain-terminating



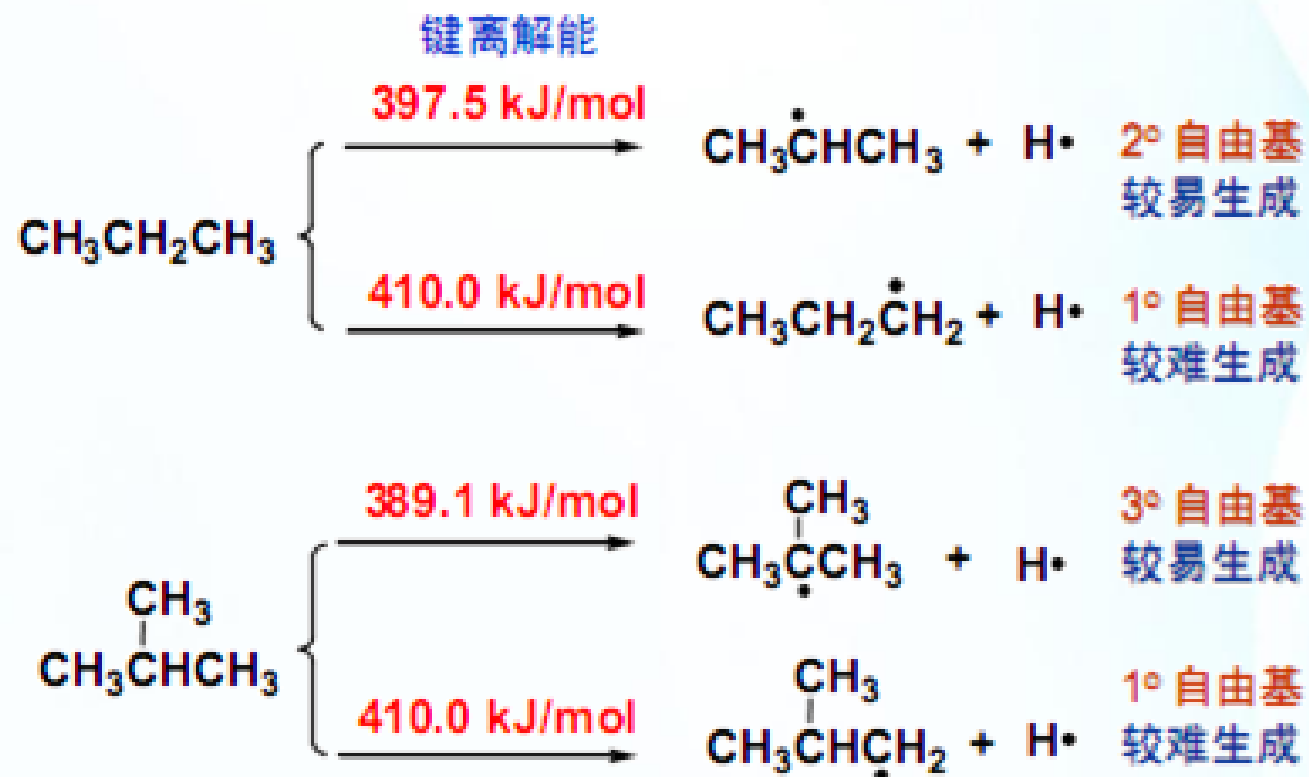
只消耗自由基而
不再产生自由基。







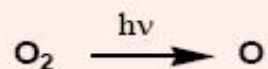
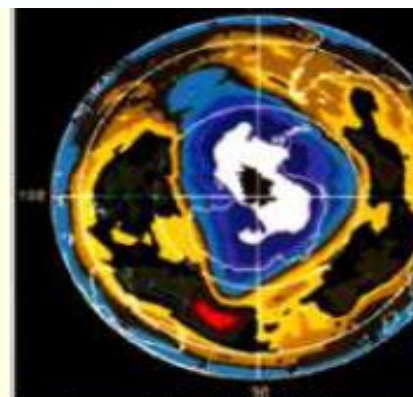
自由基的稳定性



自由基的相对稳定性: $3^\circ > 2^\circ > 1^\circ$



小常识：氟利昂 (氟氯烃)与臭氧层的破坏



气象卫星拍摄的南
臭氧层空洞照片



The Nobel Prize in Chemistry 1995

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"



Paul J. Crutzen



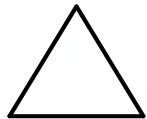
Mario J. Molina



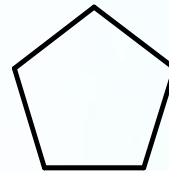
F. Sherwood Rowland



1. What are cycloalkanes?
2. What are the conformation of cycloalkanes?
3. What is *cis-trans* isomerism in cycloalkanes?
4. What are the characteristic reactions of cycloalkanes?



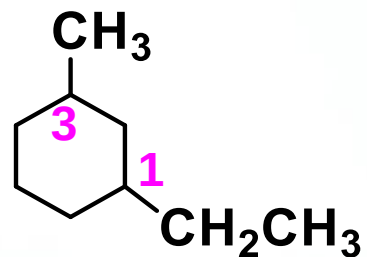
Cyclopropane



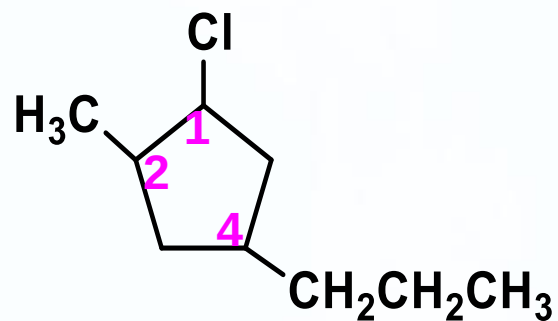
Cyclopentane

Cycloalkanes are named, under the IUPAC system, by adding the **prefix *cyclo-*** to the name of unbranch-ed alkane with the same number of carbons as the ring.

Cycloalkanes having several substituents are numbered such that the **substituent with alphabetical priority** is at position 1. Numbering is then carried out such that the **total obtained** from the substituent positions is a **minimum**.



1-Ethyl-3-methylcyclohexane



1-Chloro-2-methyl-4-propylcyclopentane

Ring Strain and the Structure of Cycloalkanes

Ring Strain in Cyclopropane



$$\Delta H_{\text{comb}}^{\circ}(\text{CH}_2) = 157.4 \text{ kcal}\cdot\text{mol}^{-1}$$

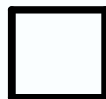
$$\Delta H_{\text{comb}}^{\circ}(\text{CH}_2) = -(3 \times 157.4) = -472.2 \text{ kcal}\cdot\text{mol}^{-1}$$

$$\text{Measured: } \Delta H_{\text{comb}}^{\circ} = -(3 \times 157.4) = -499.8 \text{ kcal}\cdot\text{mol}^{-1}$$

$$\text{Strain: } 499.8 - 472.2 = 27.6 \text{ kcal}\cdot\text{mol}^{-1}$$

The strain per CH_2 group is 9.2 kcal·mol⁻¹ .

Ring Strain in Cyclobutane



$$\text{Strain: } 26.3 \text{ kcal}\cdot\text{mol}^{-1}$$

The strain per CH_2 group is 6.6 kcal·mol⁻¹ .

Ring Strain in Cyclopentane

Strain: 6.5 kcal·mol⁻¹

Cyclohexane is virtually strain free.

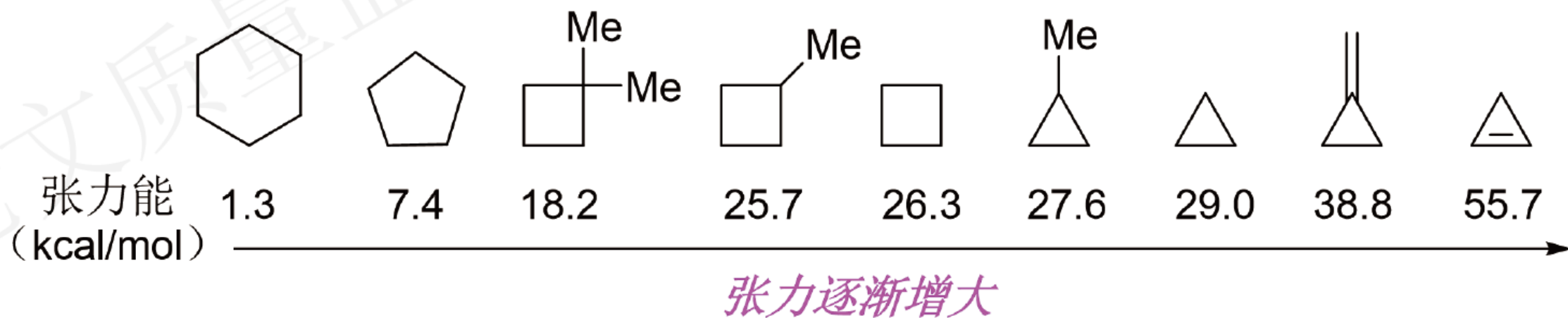
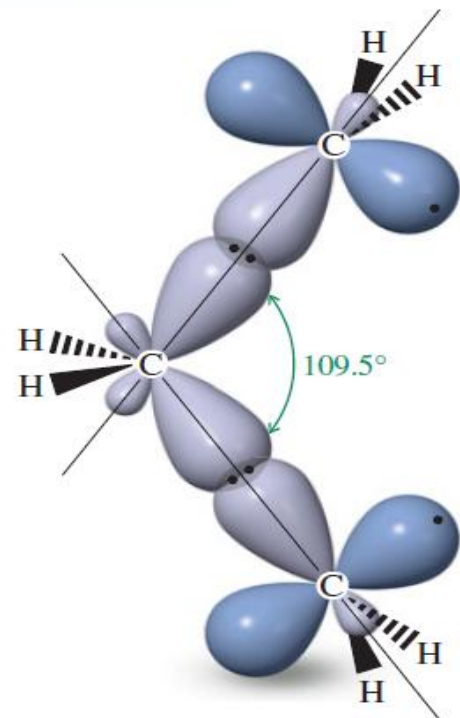


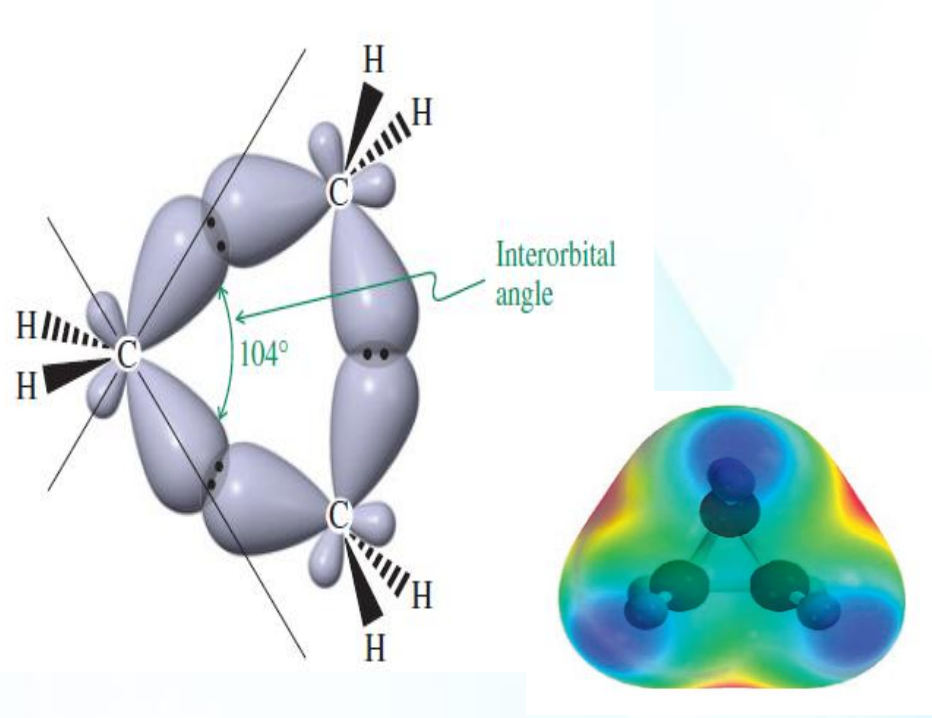
图 1.2 常见的环张力能数据



Cyclopropane



A normal C-C bond
in propane



A bent C-C bond
in cyclopropane



What kinds of effects contribute to the ring strain in cycloalkanes?

The reason is twofold: torsional strain (扭转张力) and bond-angle strain (键角张力)

To the structure of the cyclopropane molecule, **all methylene hydrogens are eclipsed**. (所有亚甲基氢都处于重叠式构象)

The energy of the eclipsed form is higher than that of the more stable staggered conformation because of eclipsing (torsional) strain.

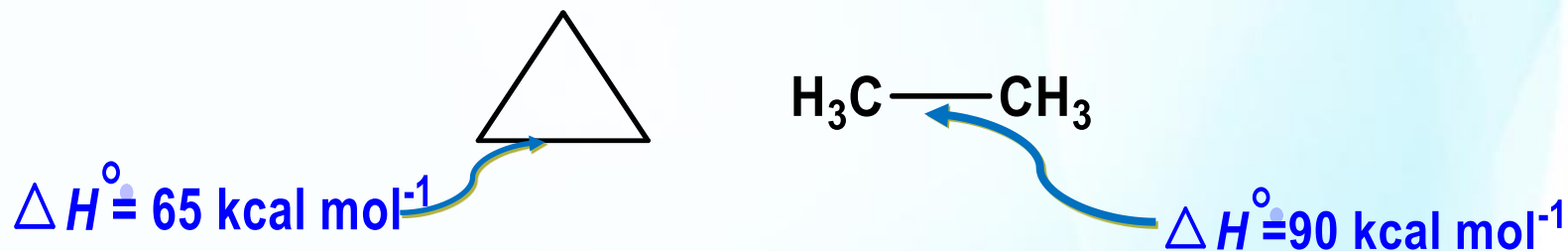
Moreover, the carbon skeleton in cyclopropane is by necessity **flat and quite rigid**, and **bond rotation** that might relieve eclipsing strain **is very difficult**.

Cyclopropane has C-C-C bond angles of 60° , a significant deviation from the “neutral” tetrahedral bond angle of 109.5° .

All three C-C bonds in cyclopropane **adopt a bent configuration** (interorbital angle 104°) **overlap** is sufficient for **bond formation**.

The energy needed to distort the tetrahedral carbons enough to close the ring is called **bond-angle strain**.

The ring strain in cyclopropane is derived from a **combination of eclipsing** and **bond-angle contributions**.

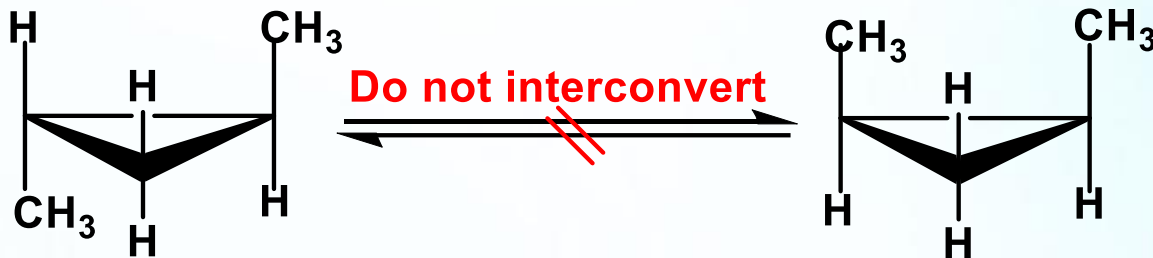




Isomers

Configurational isomers have the same molecular formula and the same bonds.

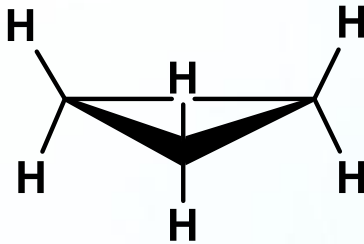
However, some of the atoms are arranged differently in space with respect to each other, and the isomers cannot be interconverted without breaking a covalent bond.



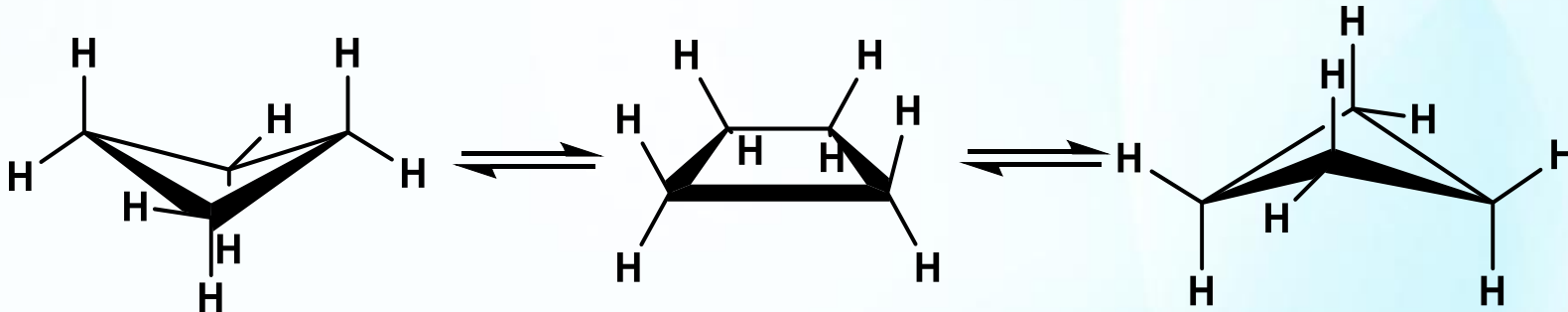
Substituted alkenes and cycloalkanes can exist as configurational isomers.

Conformational isomers are different shapes of the same molecule resulting from rotation round C-C single bonds.

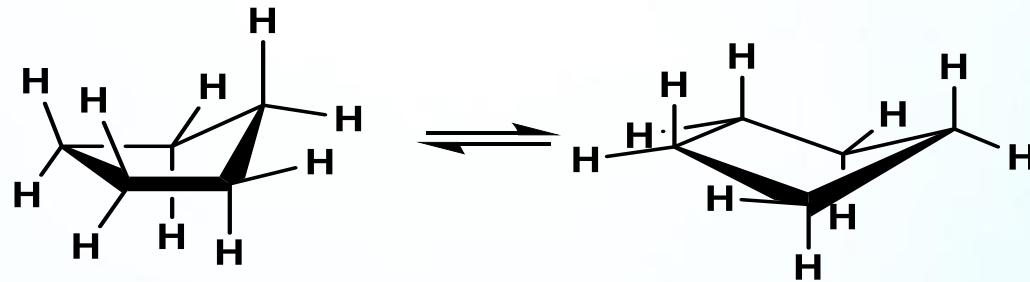
Cyclopropane is a flat molecule as far as the carbon atoms are concerned, with the hydrogen atoms situated above and below the plane of the ring. There are **no conformational isomers**.



Cyclobutane can form three distinct shapes- a planar shape and two 'butterfly' shapes.



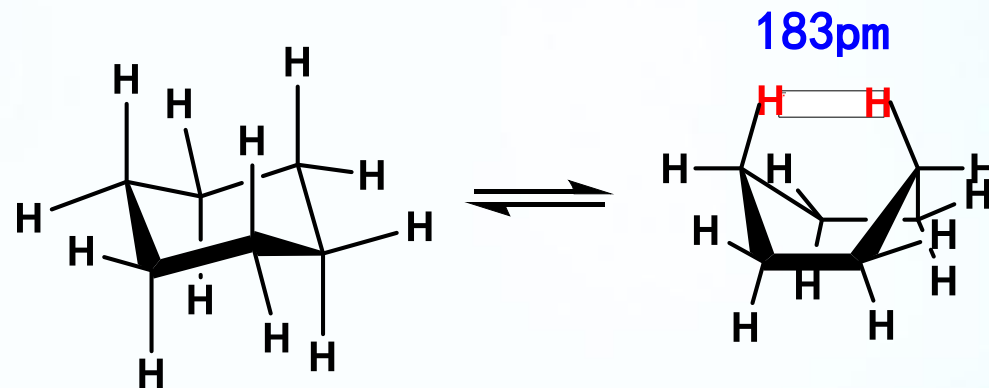
Cyclopentane can also form a variety of shapes or conformations.



Envelope

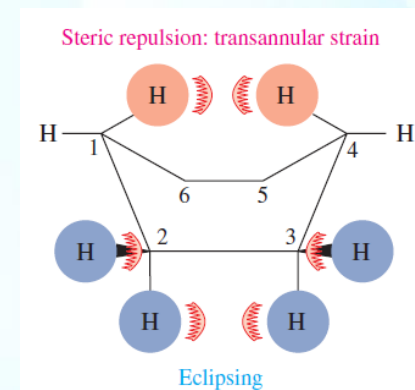
Half-chair

Cyclohexane can form two main conformational shapes- the chair and the boat.



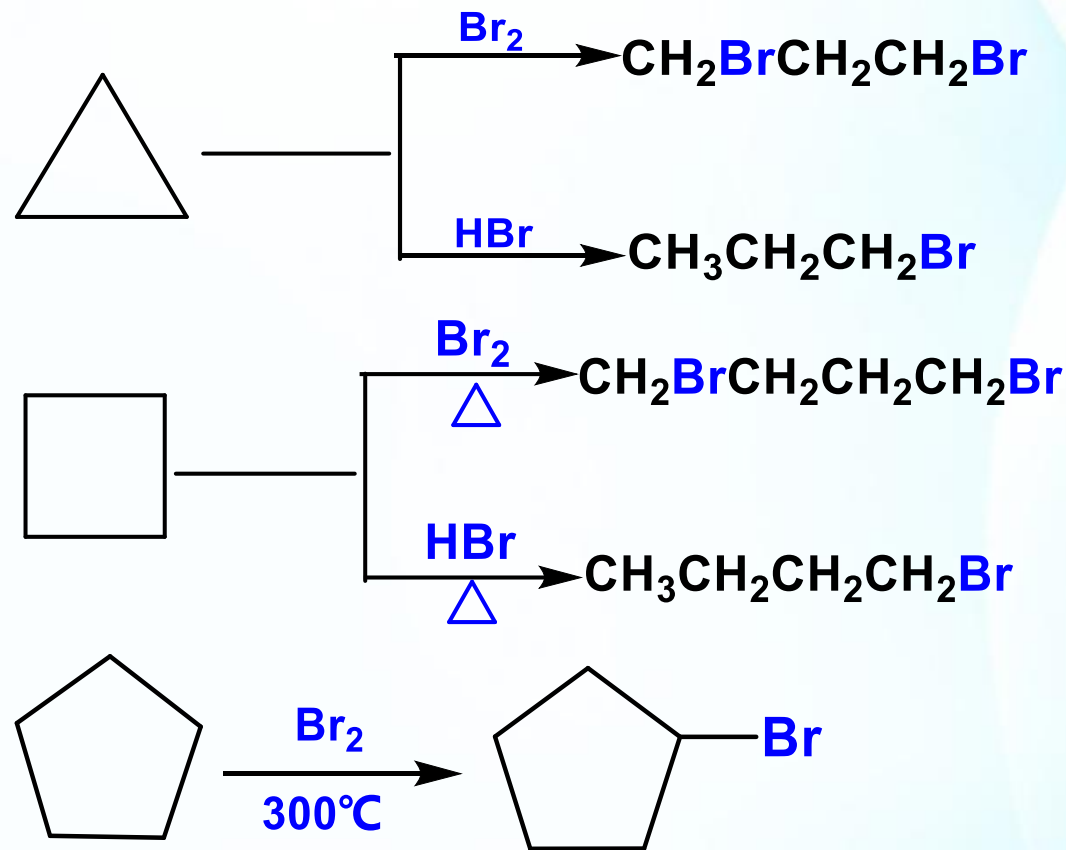
Chair (more stable)

Boat





Most cycloalkane are unreactive to chemical reagents. However, small three- and four-membered rings are reactive and behave like alkenes.



Summary

1. **烷烃**的定义、结构；
2. **烷烃**的命名；
3. **烷烃**的构象；
4. **烷烃**的化学反应；
5. **环烷烃**的分类与命名；
6. **环烷烃**的结构与张力；
7. **环烷烃**的构象(**环己烷**)；
8. **环烷烃**的化学反应。



本章作业:

P99: 3.24

P100: 3.35 3.36

P104: 2、 4、 5

P105: 6



也许有一天, 不知不觉, 你将渐渐活出写满答案的人生!