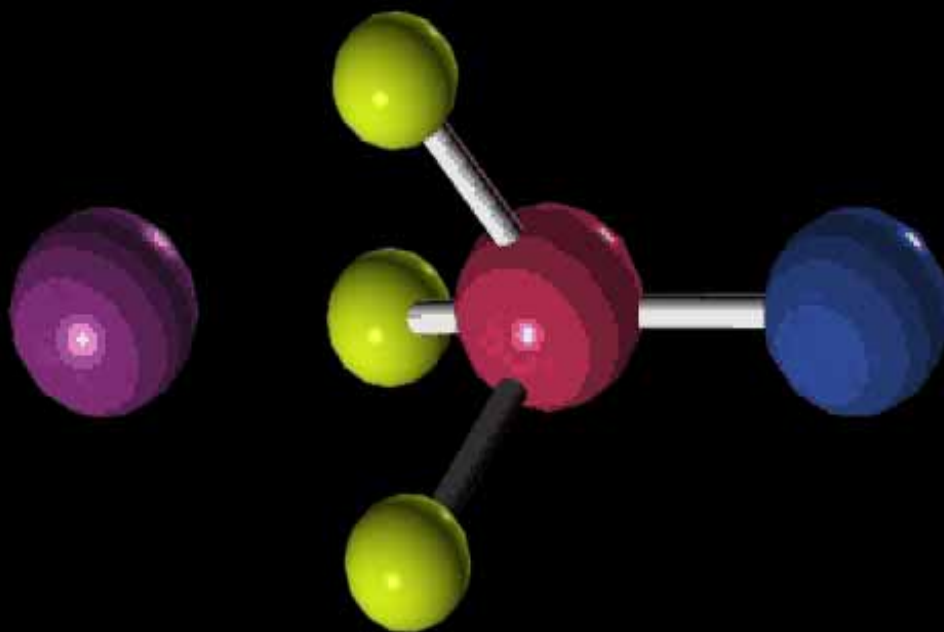
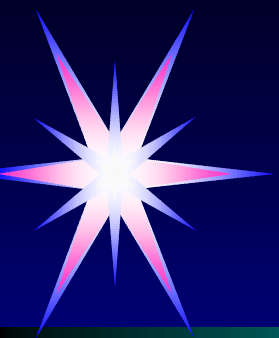


有机化学

(Organic Chemistry)

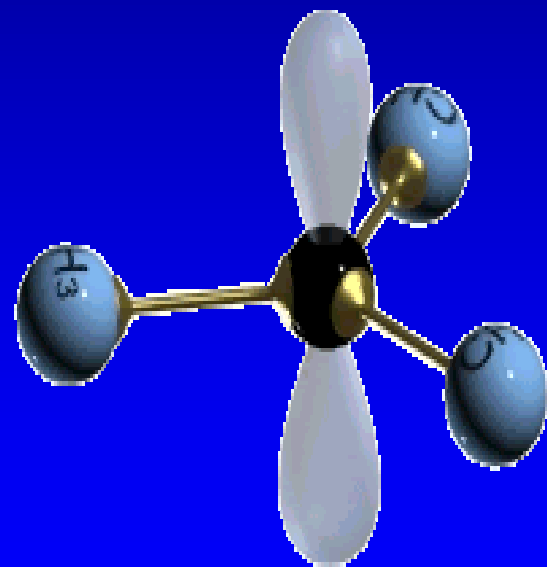


制作：付蕾 朱凤岗

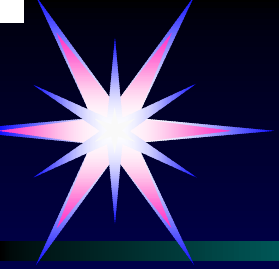


有机化学

(Organic Chemistry)



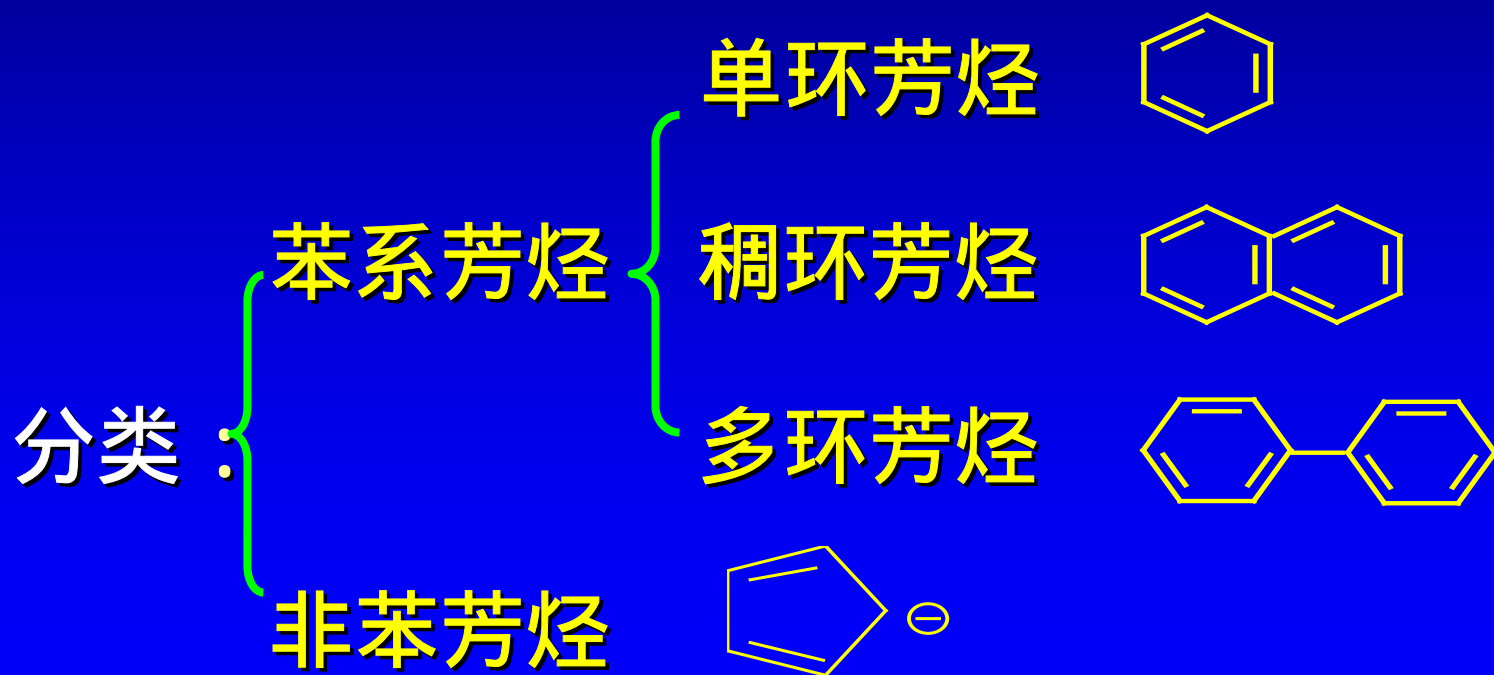
制作：付蕾 朱凤岗

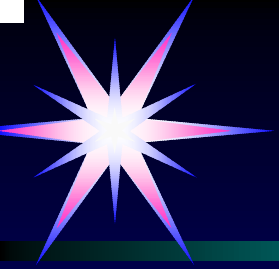


第四章

芳香烃 (Aromatic Hydrocarbons)

定义：苯及其化学性质类似于苯的化合物





芳香烃

(Aromatic Hydrocarbons)

第一节 单环芳烃

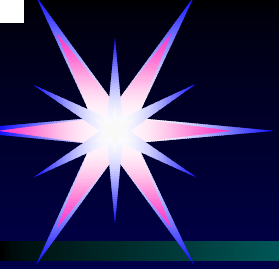
(Simple aromatic hydrocarbons)

第二节 稠环芳烃

(Fused polycyclic aromatic hydrocarbons)

第三节 非苯芳烃

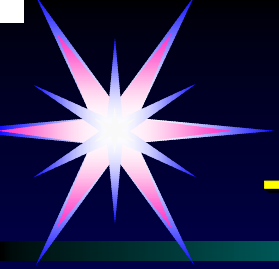
(Non-benzenoid aromatic hydrocarbons)



第一节 单环芳烃

(Simple aromatic hydrocarbons)

- 一、苯的分子结构
- 二、单环芳烃的同分异构和命名
- 三、单环芳香烃的性质
- 四、苯环上亲电取代的定位效应
及理论解释



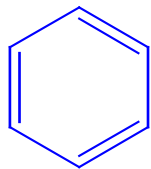
一、苯 的分子结构

(Structure of benzene)

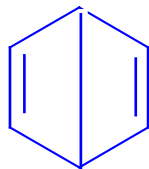
1 . Kekule结构式

1825 年

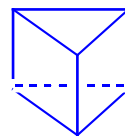
C_6H_6



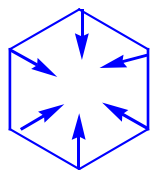
Kekul'e式



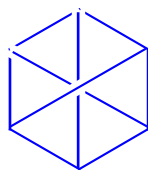
杜瓦苯



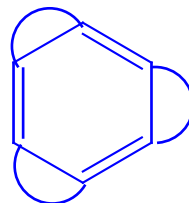
棱晶烷



向心结构式



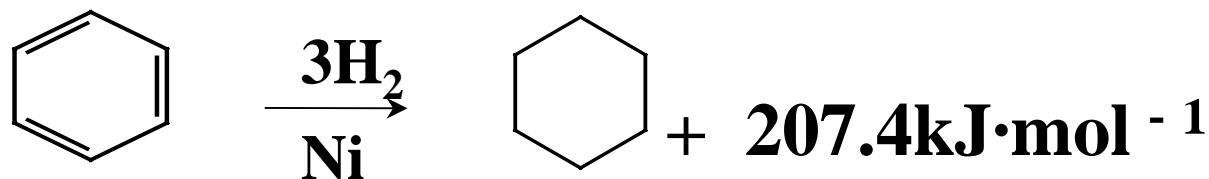
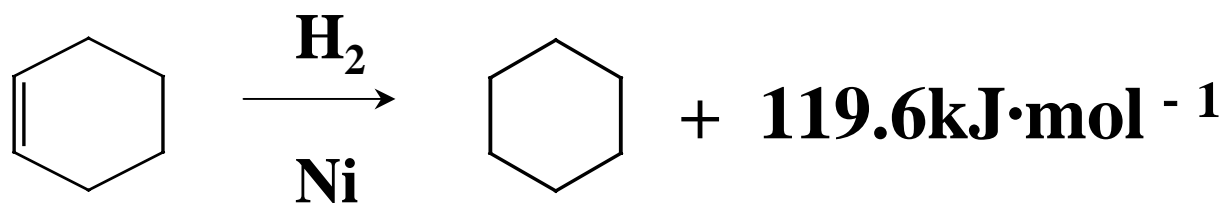
对位键



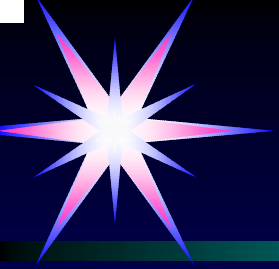
余价

未解决的问题

(1) 苯环有3个C=C，但不易加成，
环异常稳定

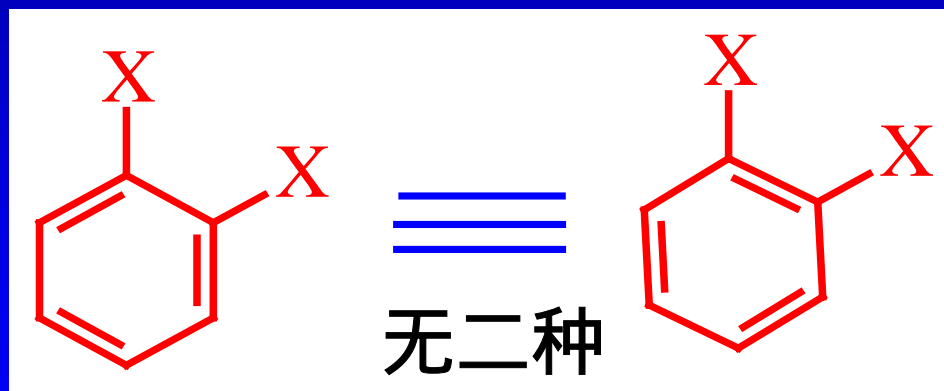


$$\text{差值 } 119.6 \times 3 - 207.4 = 151.4 \text{ kJ}\cdot\text{mol}^{-1}$$

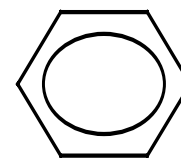
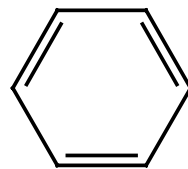
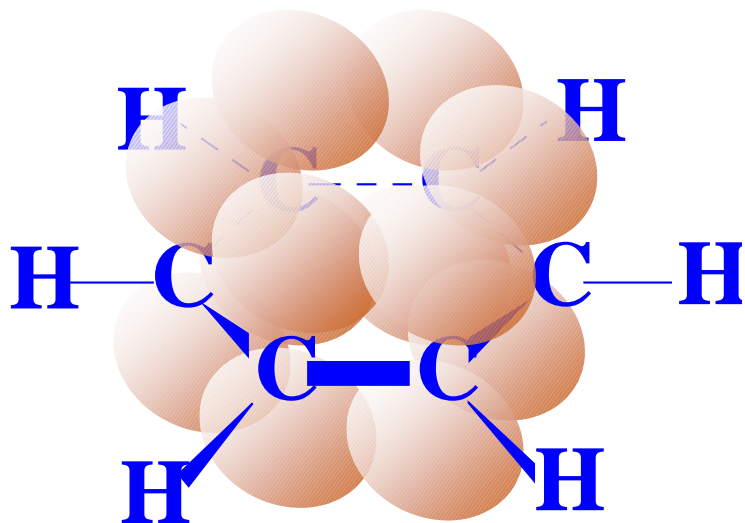
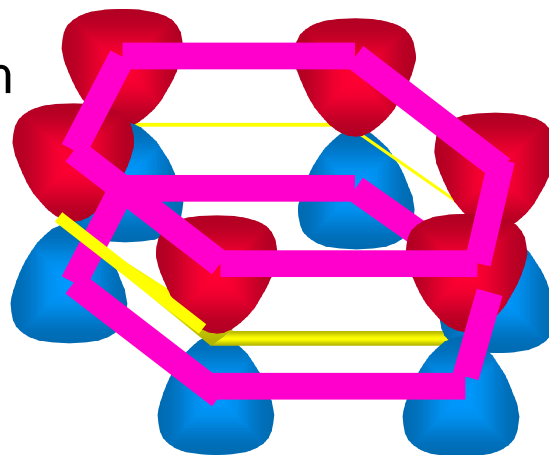
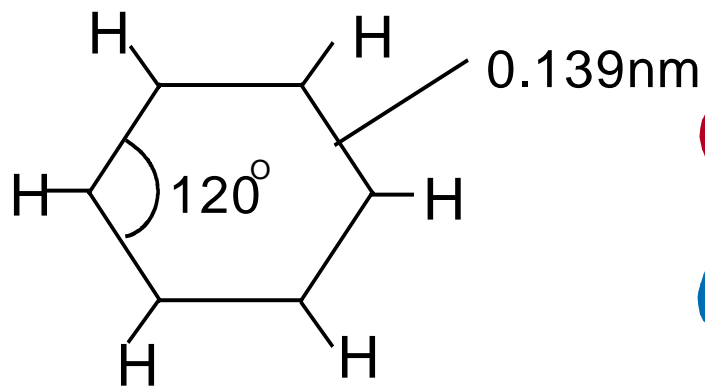


未解决的问题

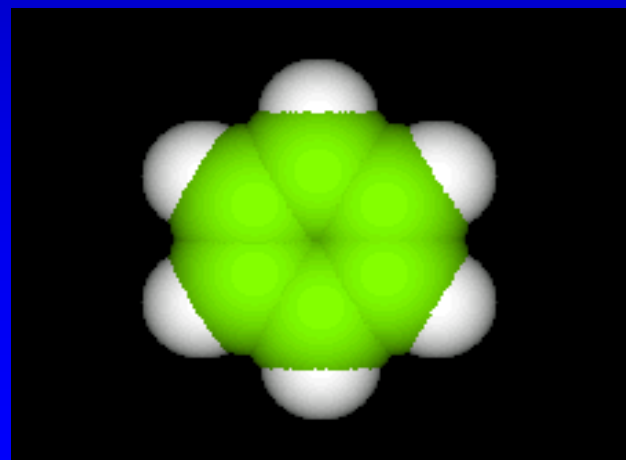
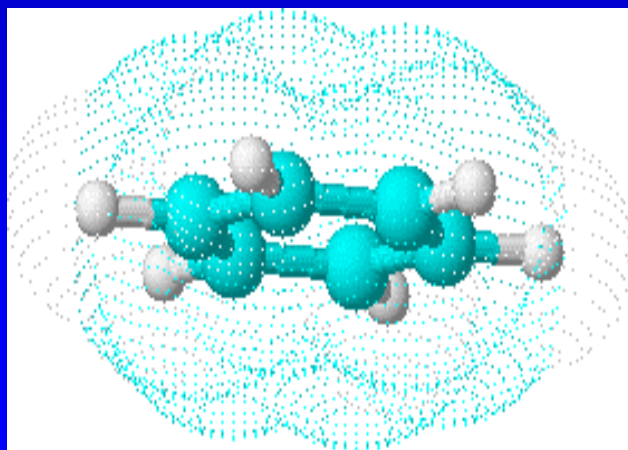
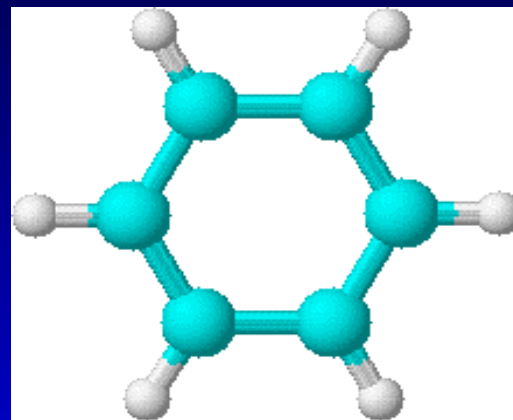
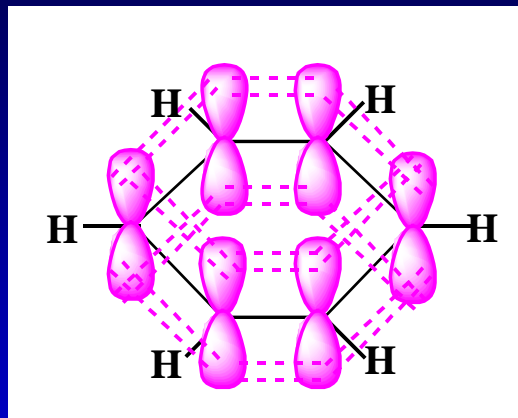
(2) 如果为单双键交替时，苯环为不等六边形，实验证明，6个C，6个H，6个边相同。



2. 苯分子结构的近代观点：



苯分子结构的近代观点



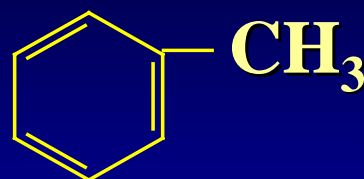
制作：付蕾 朱凤岗

二. 单环芳烃的同分异构和命名

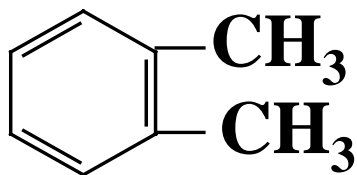
1. 同分异构现象

一元取代物：

二元取代物：

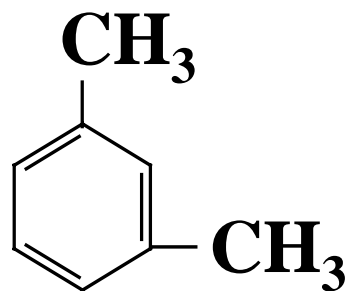


methylbenzene



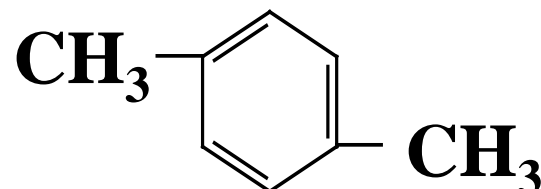
1, 2—二甲苯
邻二甲苯

o-dimethylbenzene



1, 3—二甲苯
间二甲苯

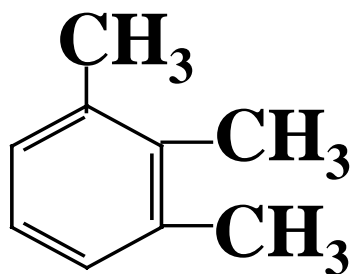
m-dimethylbenzene



1, 4—二甲苯
对二甲苯

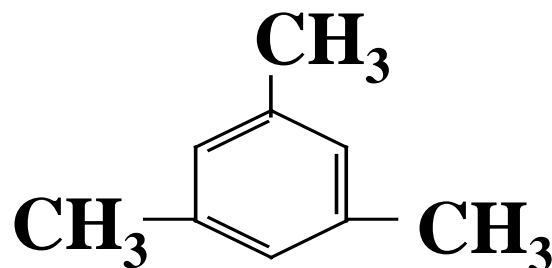
p-dimethylbenzene

三元取代物：



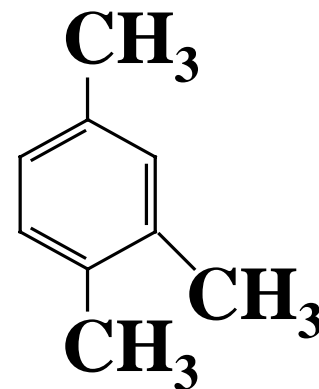
1, 2, 3—三甲苯
连三甲苯

vic-
trimethylbenzene



1, 3, 5—三甲苯
均三甲苯

sym-
trimethylbenzene



1, 2, 4—三甲苯
偏三甲苯

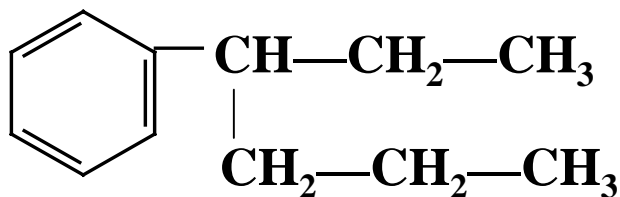
unsym-
trimethylbenzene

2. 命名 (nomenclature)

(1) 定母体

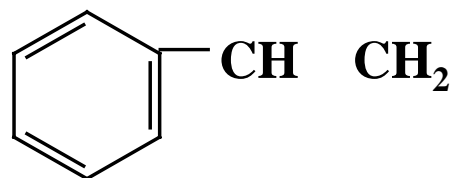
简单的取代基：环为母体

复杂的取代基：环为取代基



3 - 苯基己烷

3 - phenylhexane



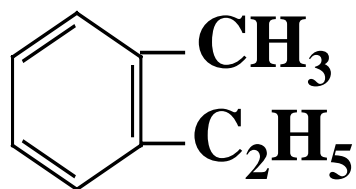
苯乙烯

phenyl ethylene

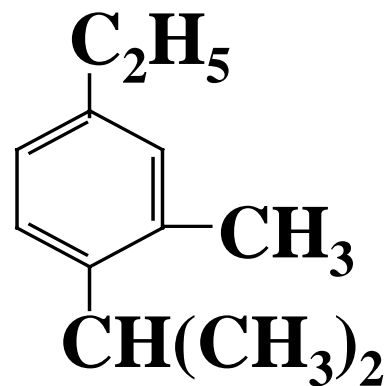
(2) 编号：

以小数字标小基团，和最小

可用：邻、间、对，连、均、偏
可用：阿拉伯数字



2 - 乙基甲苯

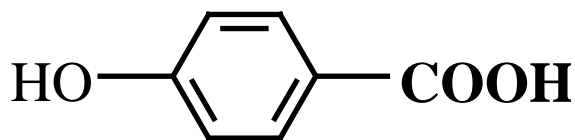


5 - 乙基 - 2 - 异丙基甲苯

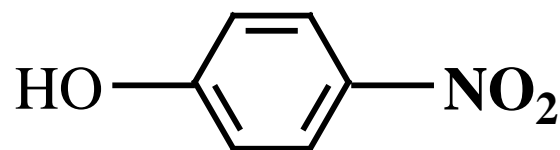
官能团优先次序

(Priority order of functional group)

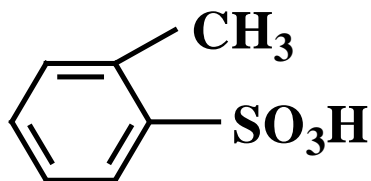
$-\text{COOH} > -\text{SO}_3\text{H} > -\text{COOR} >$
 $-\text{COX} > -\text{CONH}_2 > -\text{CHO} > -\text{CN} >$
 $-\text{OH} > -\text{NH}_2 > -\text{R} > -\text{NO}_2 > -\text{X}。$



4-羟基苯甲酸



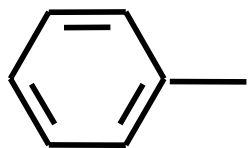
4-硝基苯酚



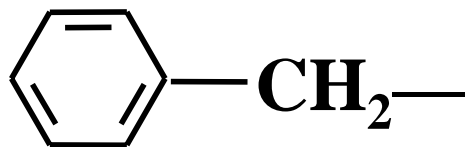
2-甲基苯磺酸

3. 芳基：

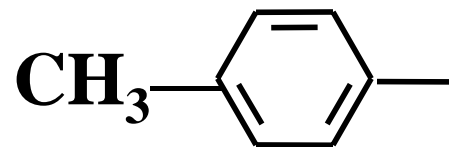
芳烃分子去掉一个或几个H 原子后剩余的基团，Ar -。



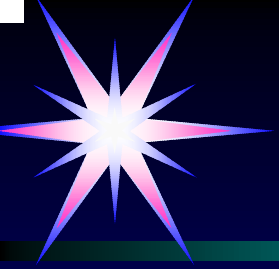
苯基 (Ph)



苯甲基 (苄基)



4—甲基苯基



三、单环芳香烃的性质（化性）

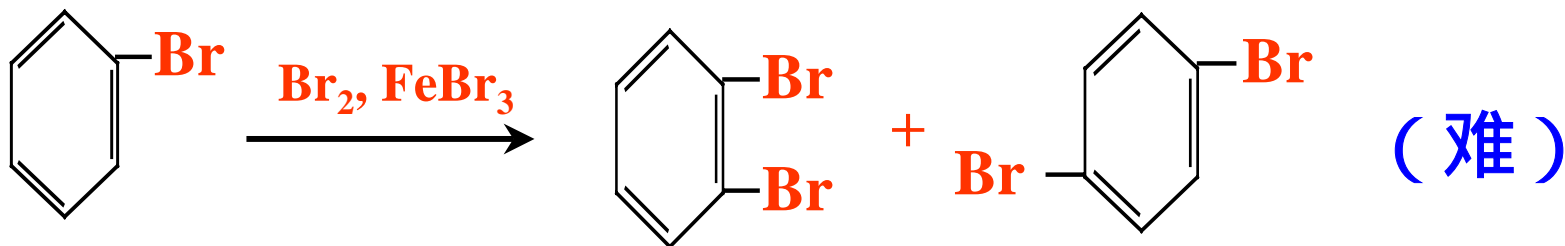
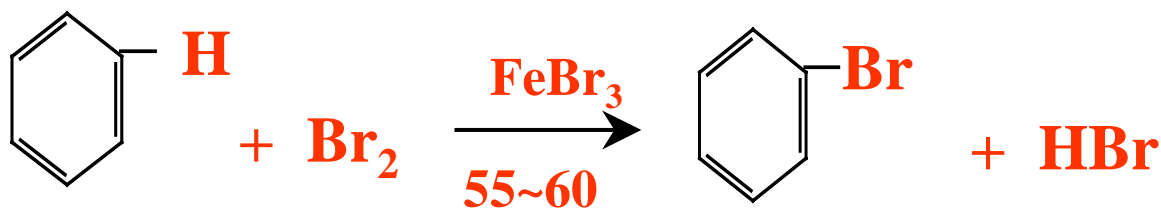
结构分析：



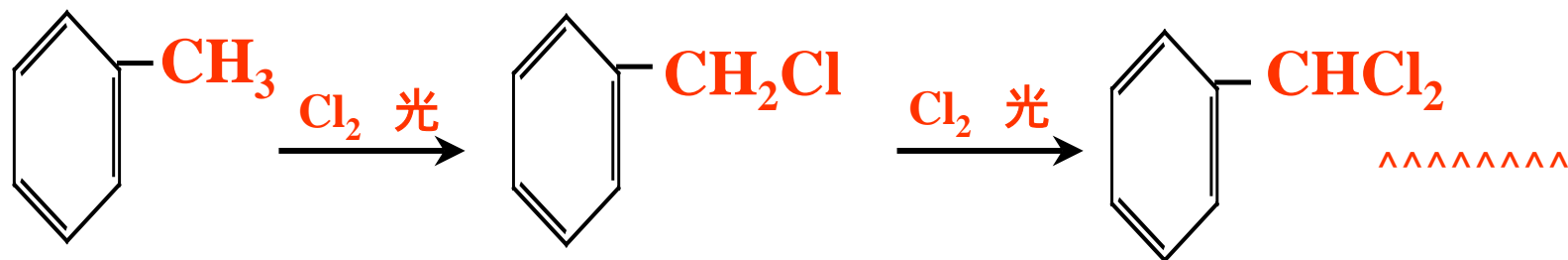
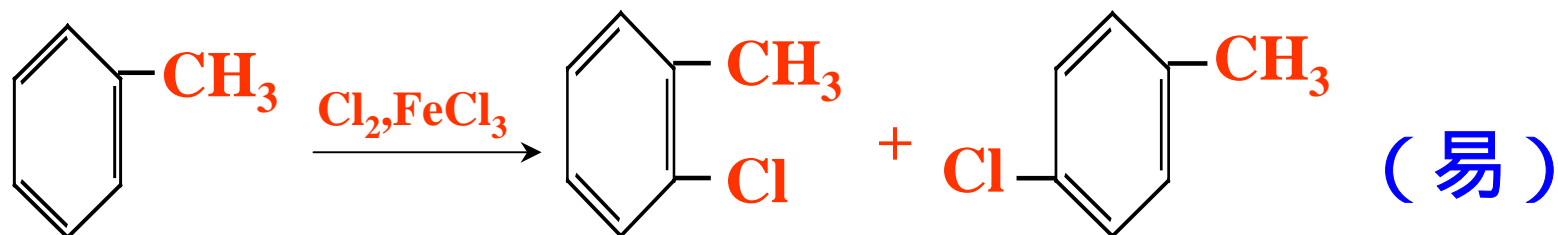
具芳香性：芳烃不易氧化，加成，
较易取代的性质。

1.取代反应 (Substitution reaction)

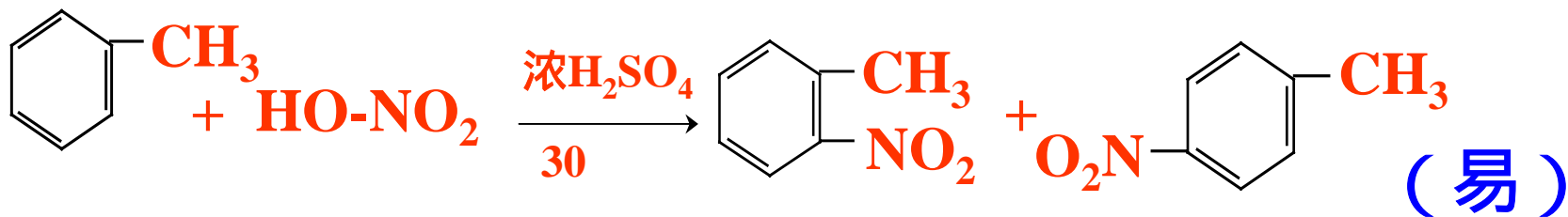
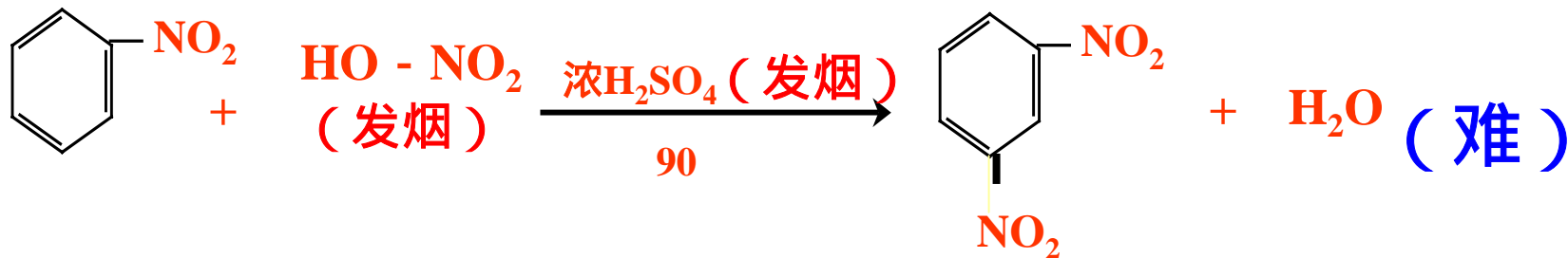
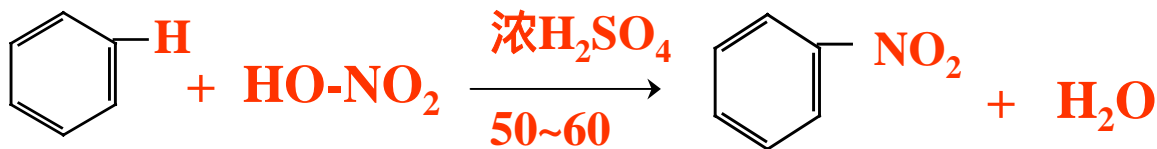
(1)卤代反应 (Hologenation)



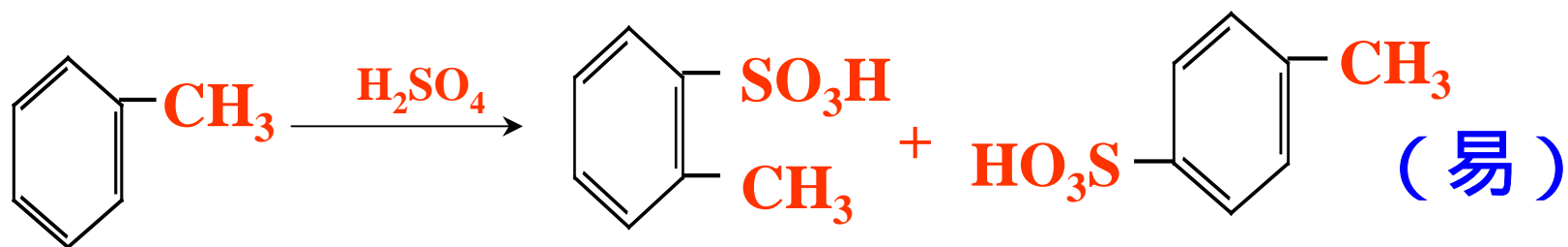
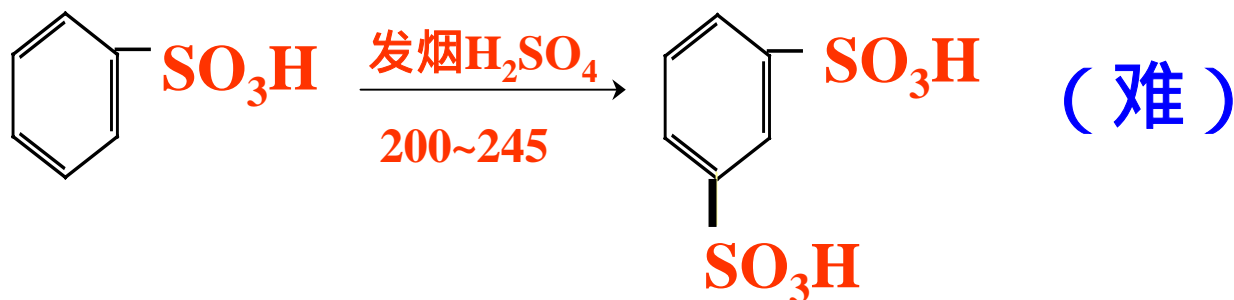
卤代反应 (Hologeneration)



(2) 硝化反应 (Nitration)

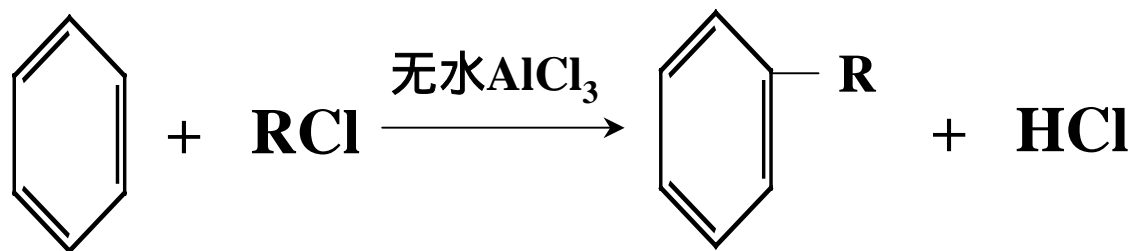


(3)磺化反应 (Sulfonation)



(4) 烷基化反应 (Alkylation)

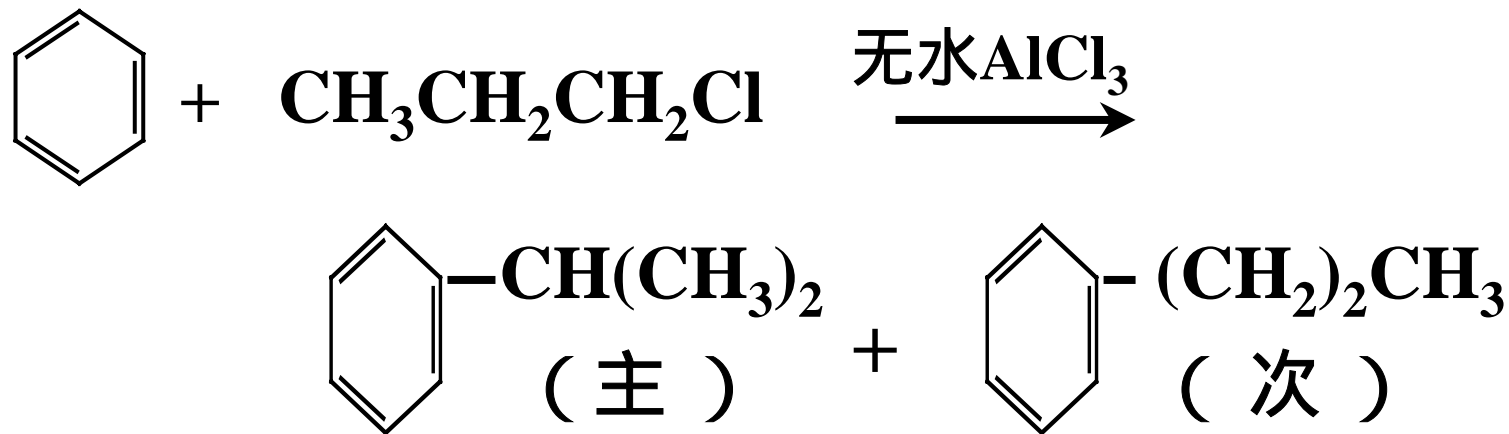
在无水 AlCl_3 的作用下，芳香烃与卤代烷生成烷基苯的反应





说明：

(1) C₃以上直链烷基异构化。



(2) 催化剂：FeCl₃, SnCl₄, HF, H₂SO₄.....

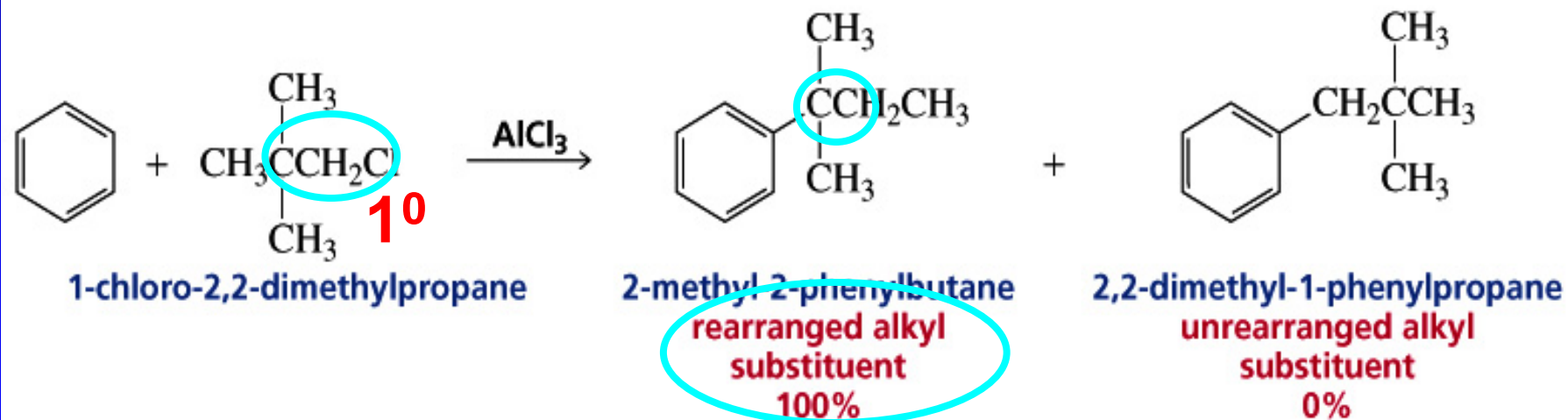
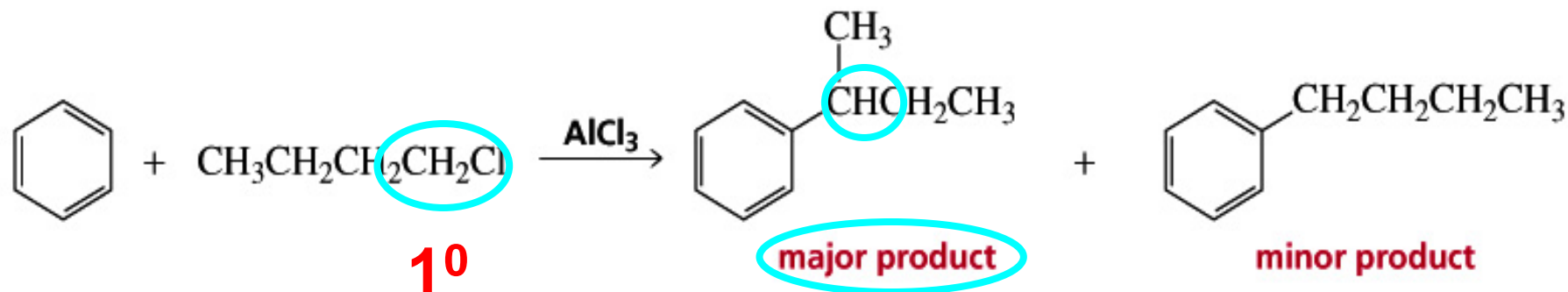
说明：

(3) 烷基化剂：烯烃，醇，卤代烷



(4) 当苯环上连有强吸电子基（ $-\text{NO}_2$ ， $-\text{CN}$ ， $-\text{SO}_3\text{H}$ ， $-\text{CO}-$ 等）时，不发生烷基化反应。

烷基化异构化

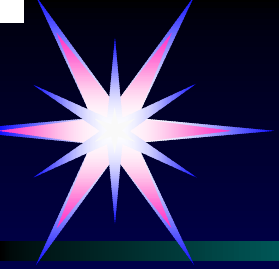




(5) 酰基化反应 (Acylation)

在无水 AlCl_3 的作用下，芳香烃与酰卤、酸酐生成芳香酮的反应



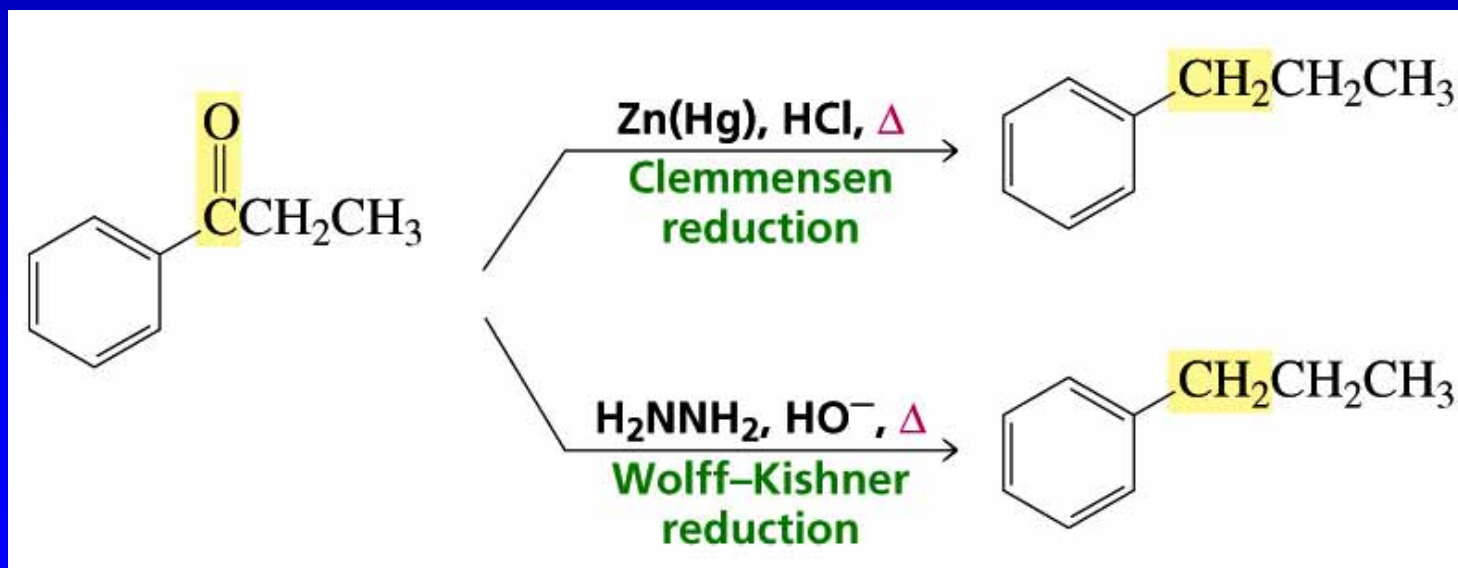
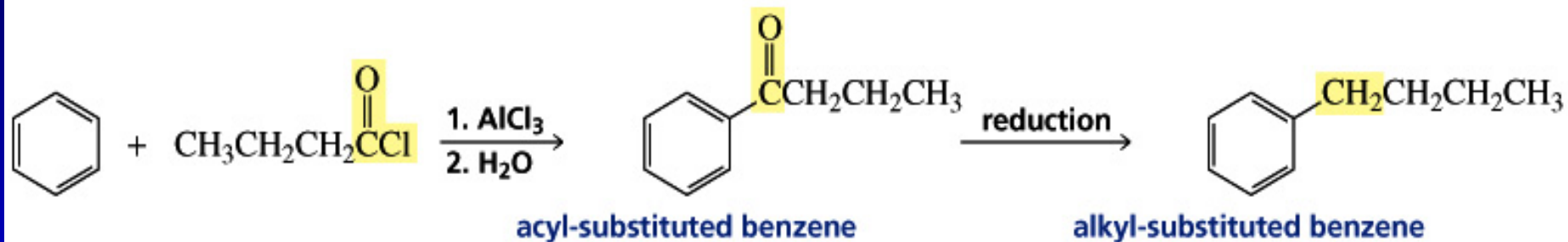


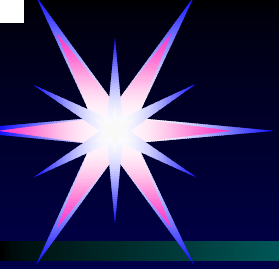
说明：

- (1) 当苯环上连有强吸电子基 ($-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{CO}-$ 等) 时 , 不发生酰基化反应
- (2) 酰基化不异构化
- (3) 酰基化试剂：酰卤、酸酐
- (4) 不生成多元取代产物

思考题：

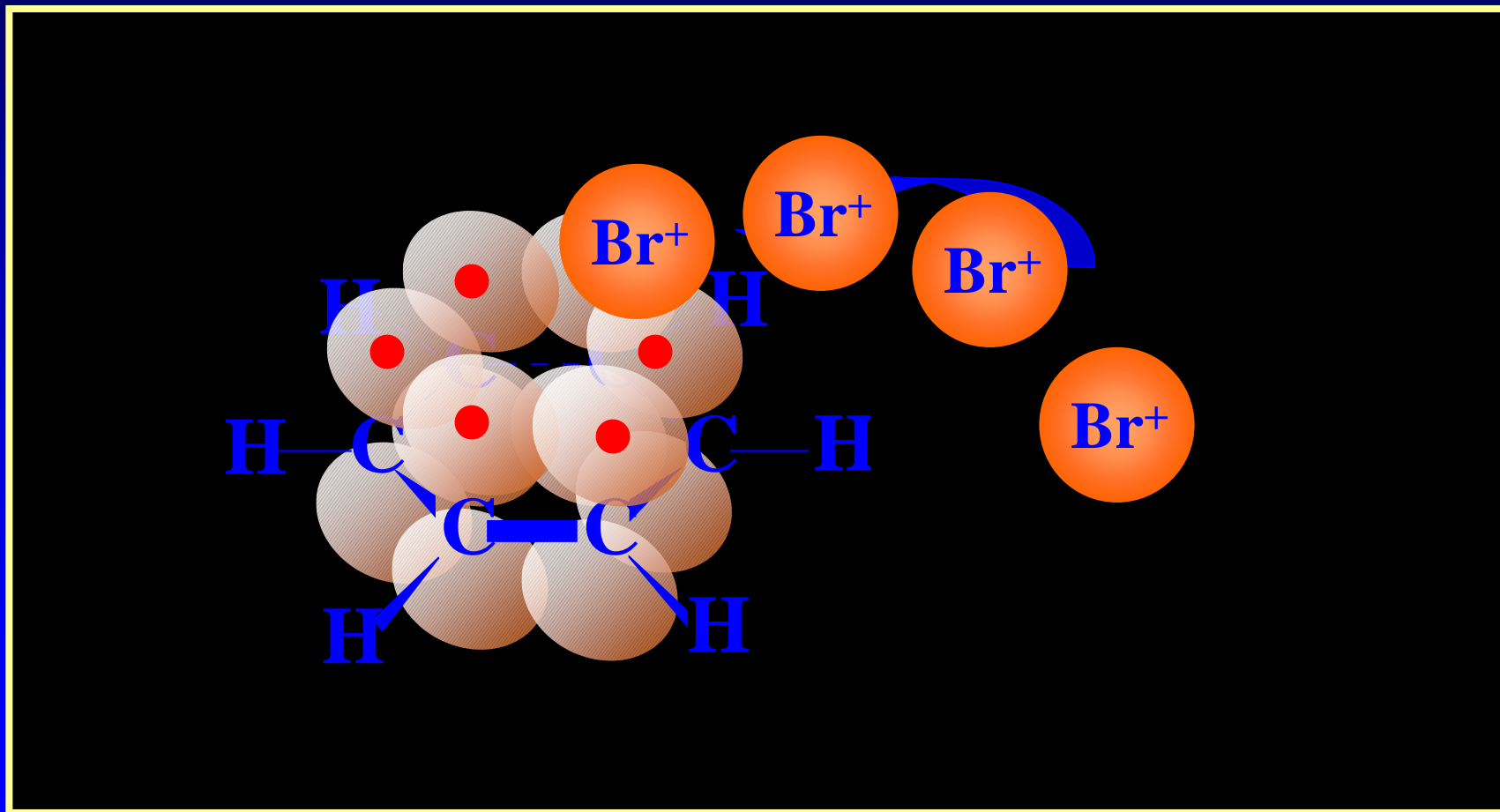
如何从苯合成正丁基苯？





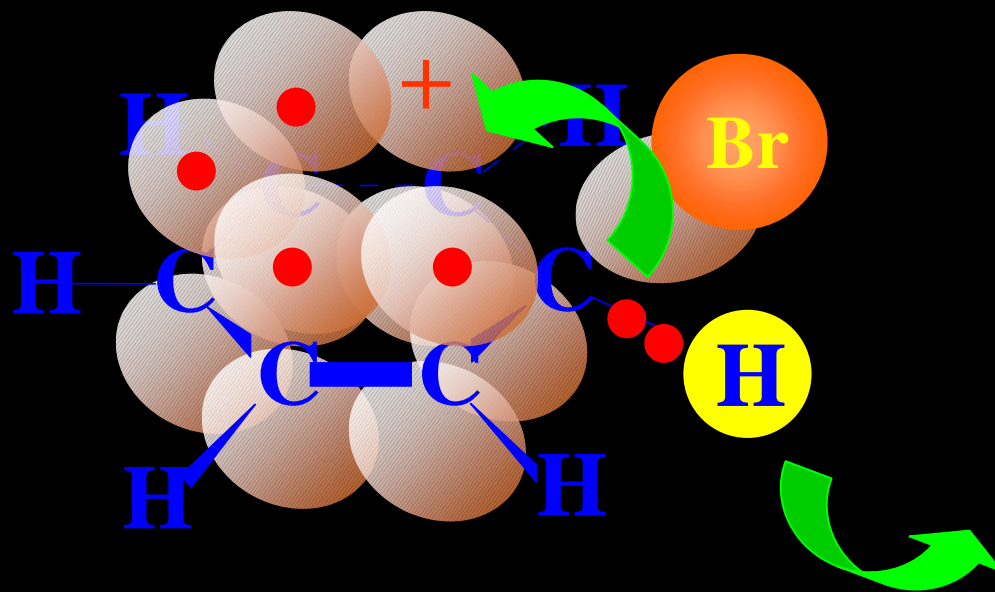
离子型亲电取代

Electrophilic substitution reaction



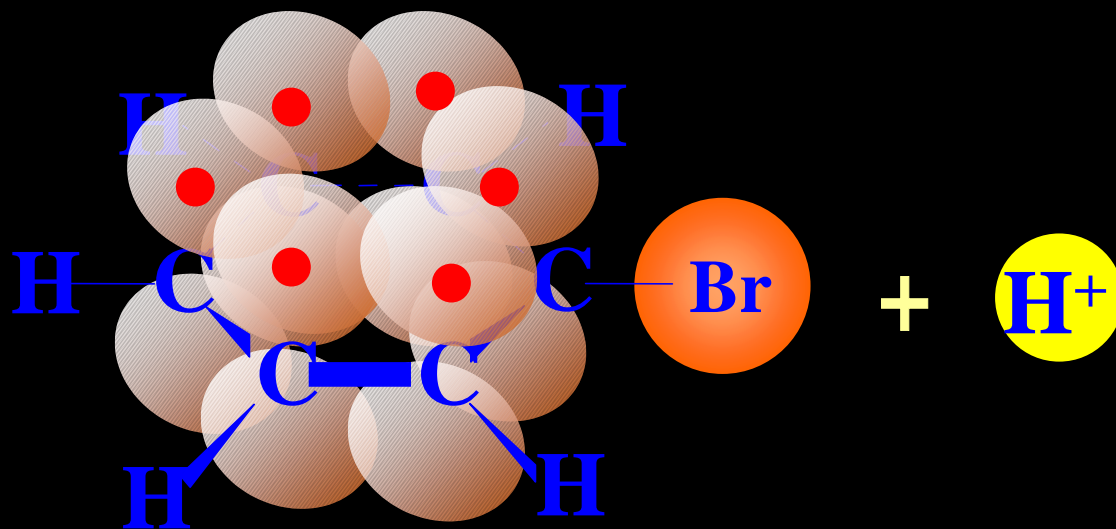
离子型亲电取代

Electrophilic substitution reaction



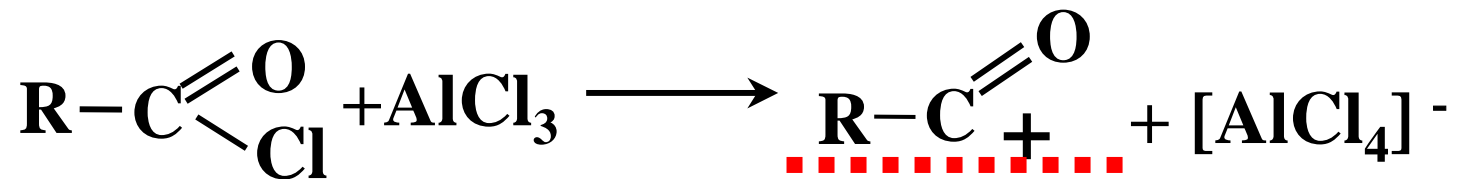
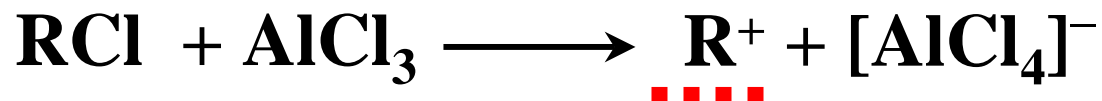
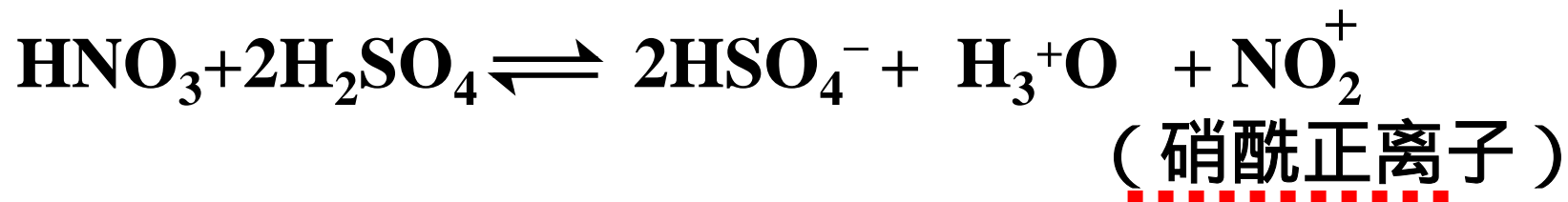
离子型亲电取代

Electrophilic substitution reaction

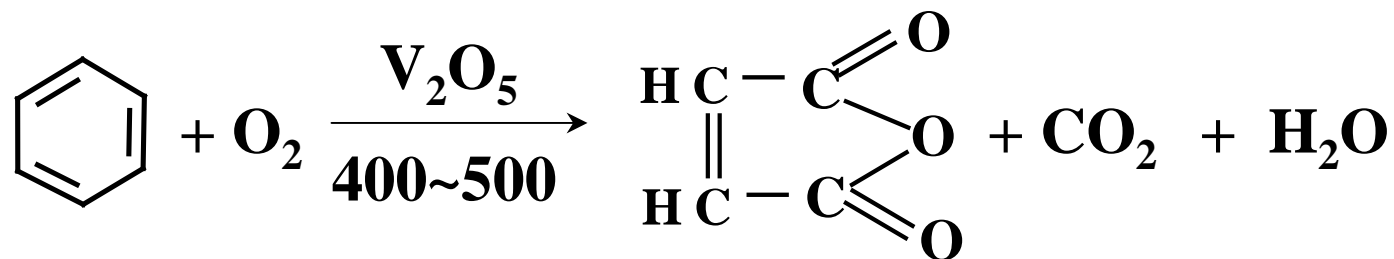
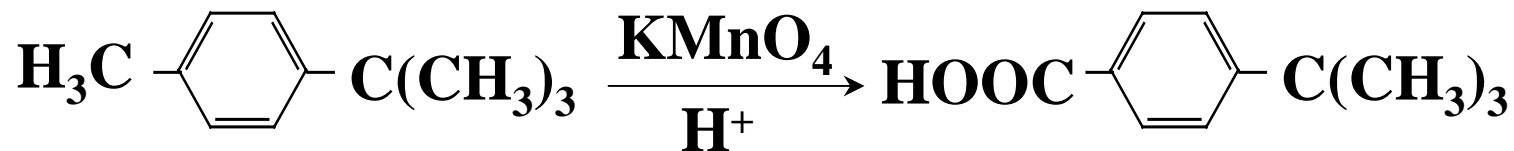


离子型亲电取代

Electrophilic substitution reaction



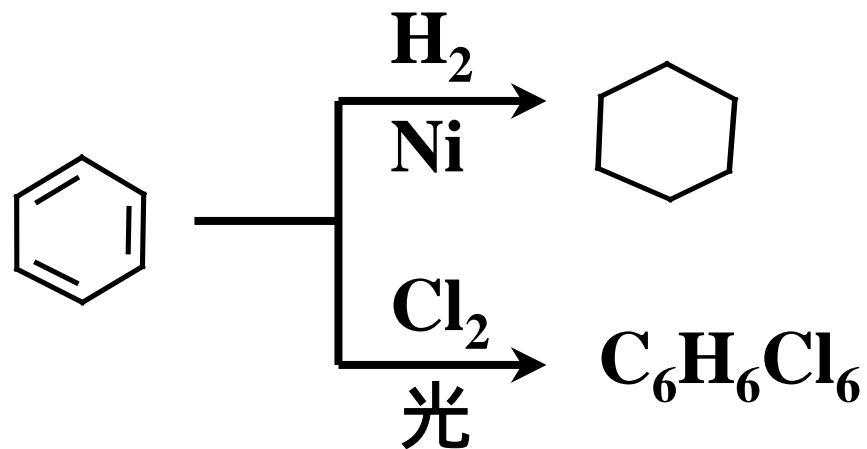
2. 氧化反应 (Oxidation)

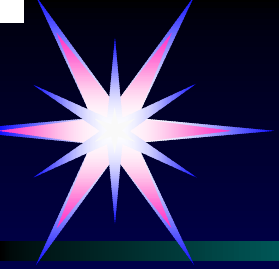


说明 (1) 含 -H

(2) 一律成 -COOH

3. 加成反应 (Addition)



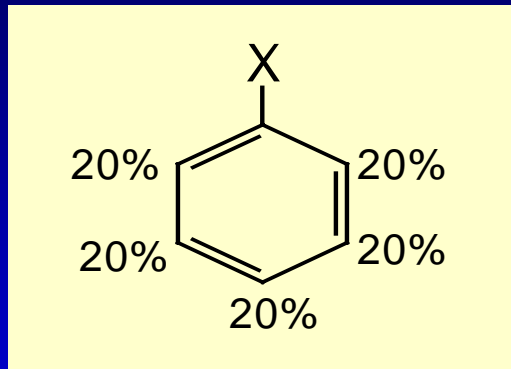


四、苯环上亲电取代的

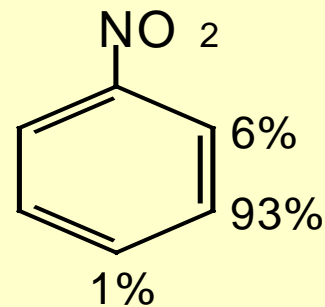
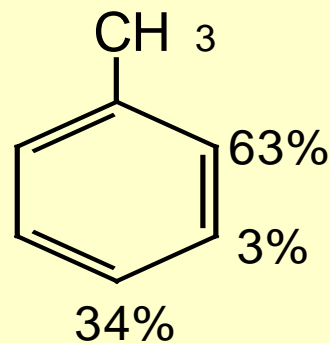
定位效应及理论解释

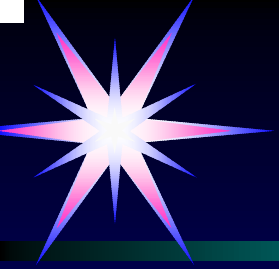
1、定位效应

从表面上看



事实上：



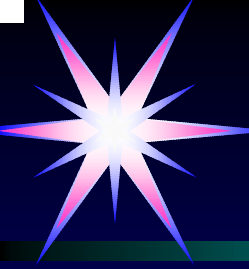


定位效应

定位基：苯环上原有的取代基。

定位效应：定位基对苯环上取代位置的影响（作用）。

{ 邻、对位定位基 (ortho/para directors)
 间位定位基 (meta directors)

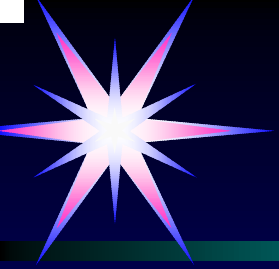


(1) 邻、对位定位基

作用： 使苯环活化，使苯环电子密度增加，亲电取代比苯易（卤素除外）
使第二个取代基主要进入原取代基的邻、对位。

基团： - NR₂ , - NH₂ , - OH , - OCH₃ ,
- NHCOCH₃ , - R , - X 等

特点： 与苯环直接相连的原子一般具有未成键的孤电子对



(2) 间位定位基

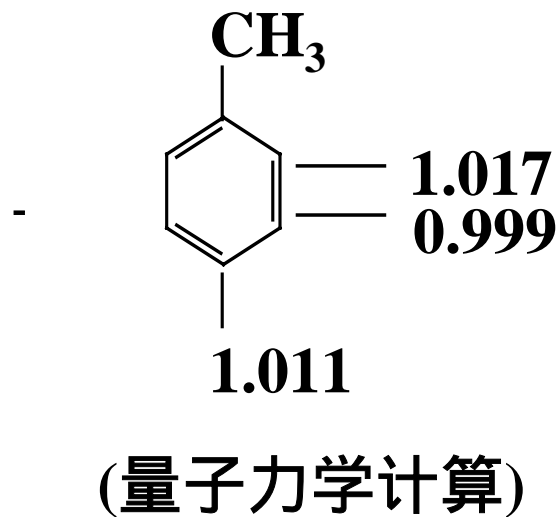
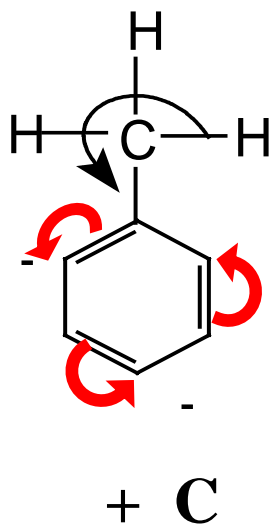
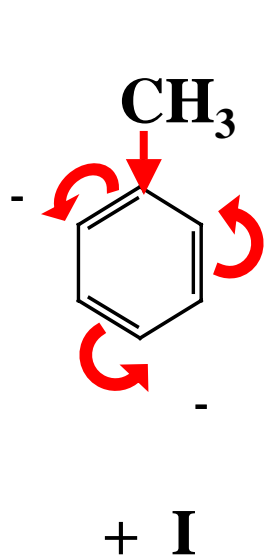
作用： 使苯环钝化，使苯环电子密度下降，亲电取代比苯难。
使第二个取代基主要进入原取代基的间位。

基团： $-\overset{+}{\text{N}}(\text{CH}_3)_3$, $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$, $-\text{CHO}$,
 $-\text{COOH}$, $-\text{COOR}$, $-\text{CONH}_2$

特点： 与苯环直接相连的原子一般具有双、叁键或带正电荷。

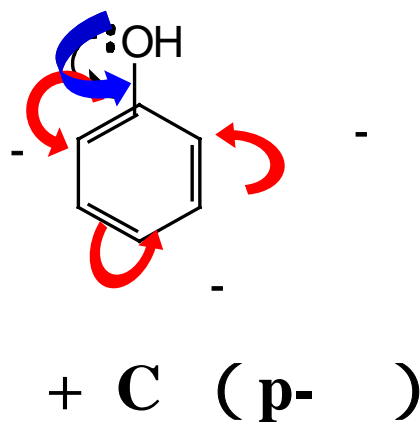
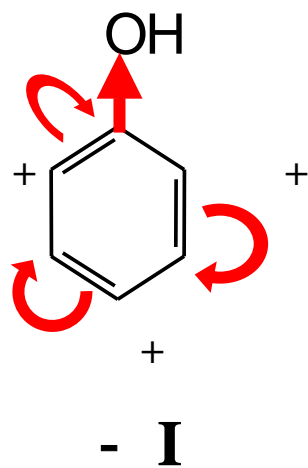
2. 定位规律的解释

解释基团：(1) 甲基



定位规律的解释

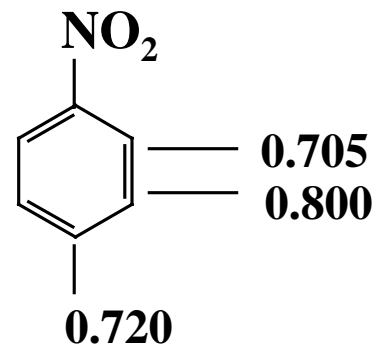
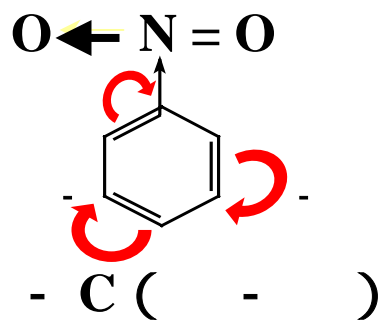
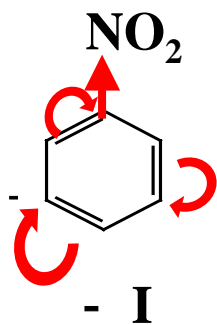
(2) 酚羟基



方向相反：
共轭 > 诱导

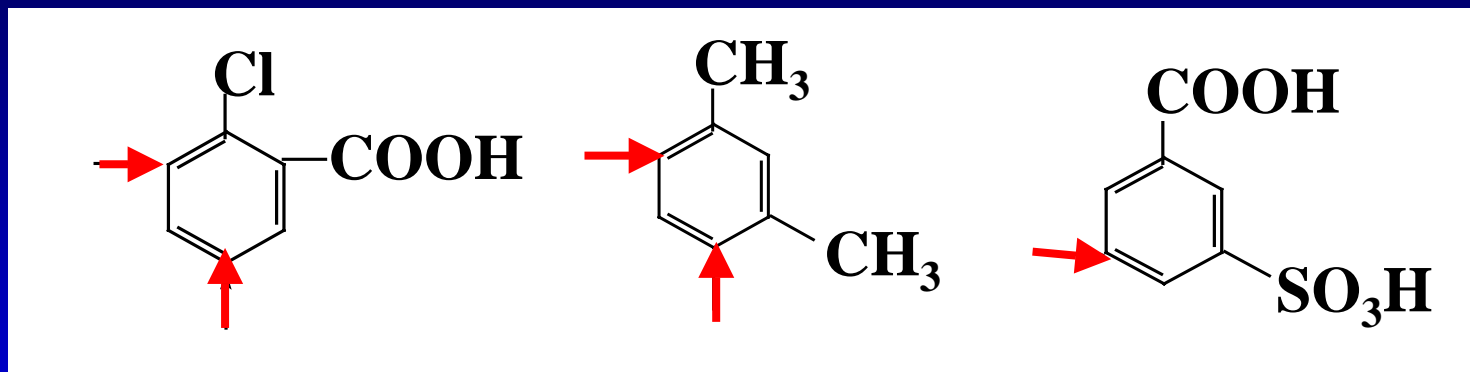
定位规律的解释

(3) 硝基



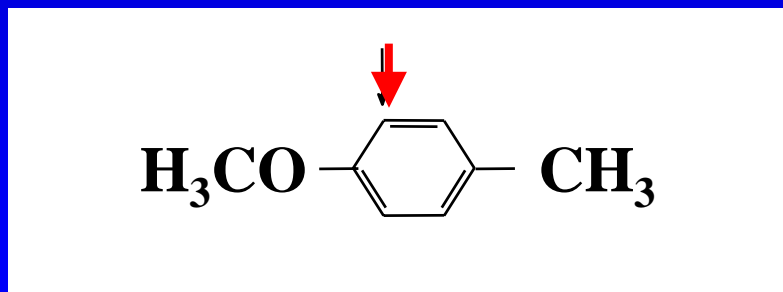
3. 二元取代物的定位规律

(1) 两个定位基定位一致服从共同确定的位置



(2) 作用矛盾

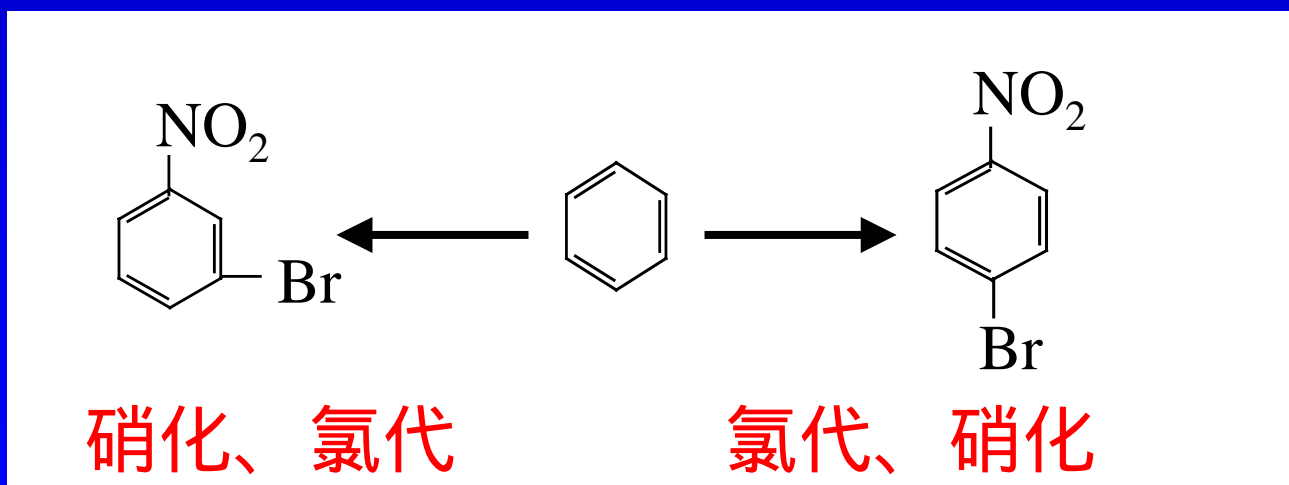
同类：服从强的



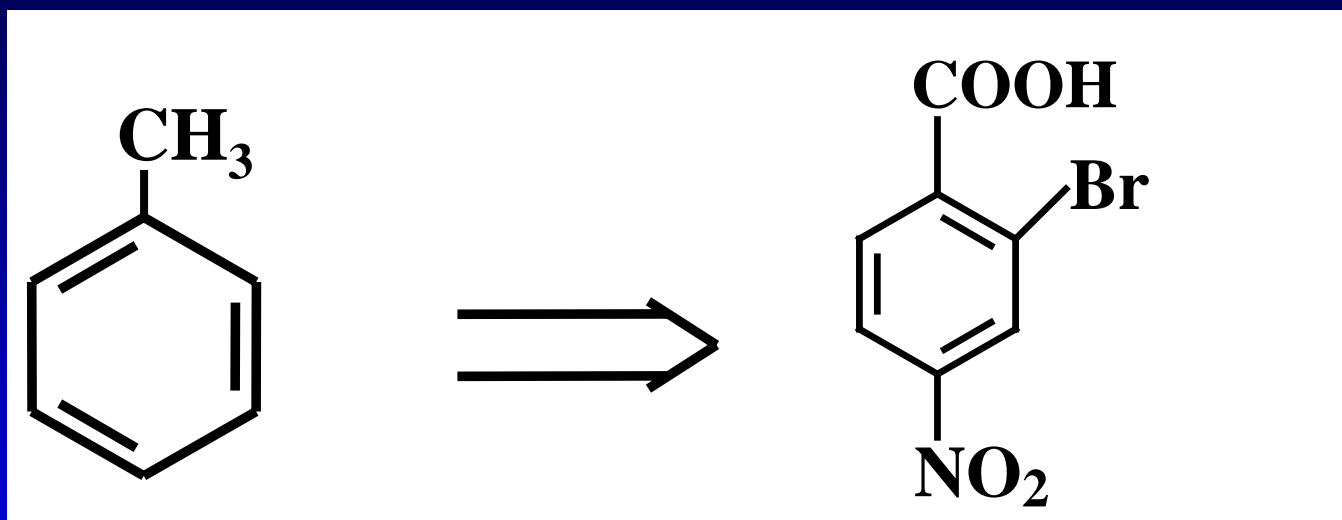
异类：服从第一类



- 用途** (1) 预测反应的主产物
(2) 选择正确的合成路线

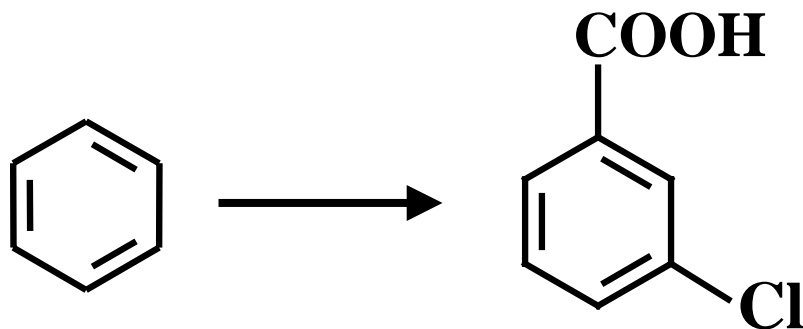


例1.



- A) 硝化、溴代、氧化 ●✓
- B) 溴代、硝化、氧化
- C) 氧化、硝化、溴代

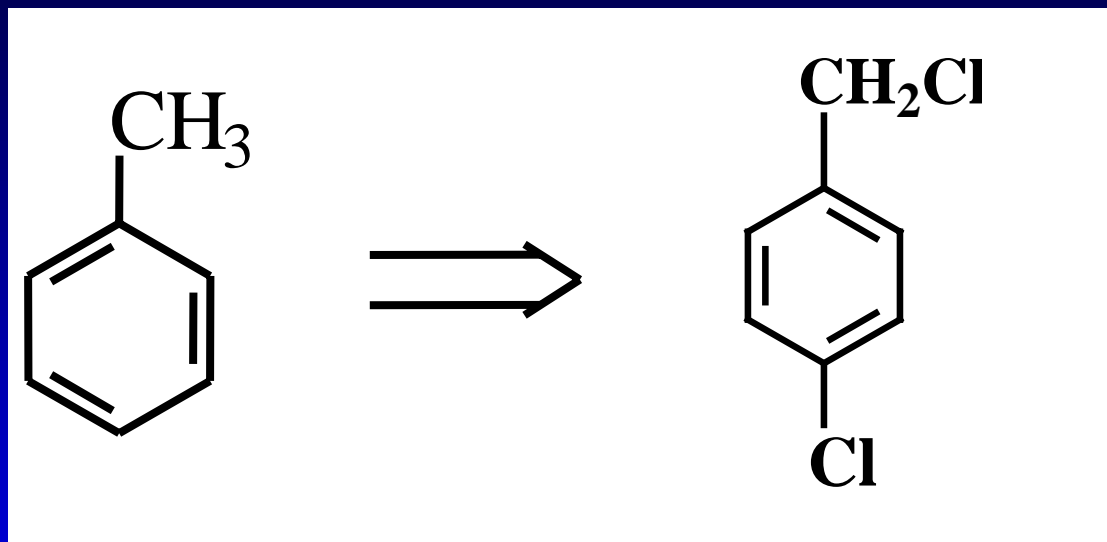
例2



A) 氯代、烷基化、氧化

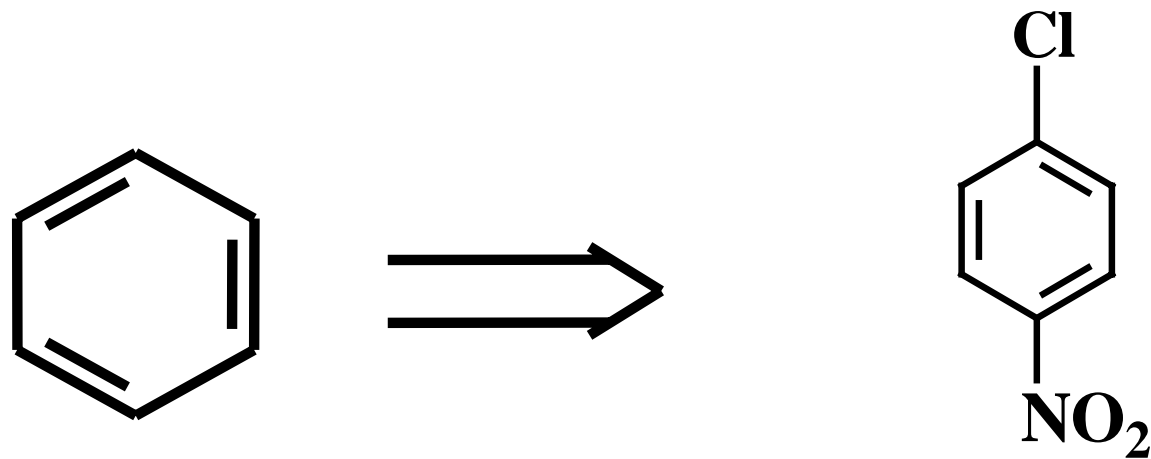
B) 烷基化、氧化、氯代 •✓

例3



- A) 氯代、光卤代 ●✓
B) 光卤代、氯代

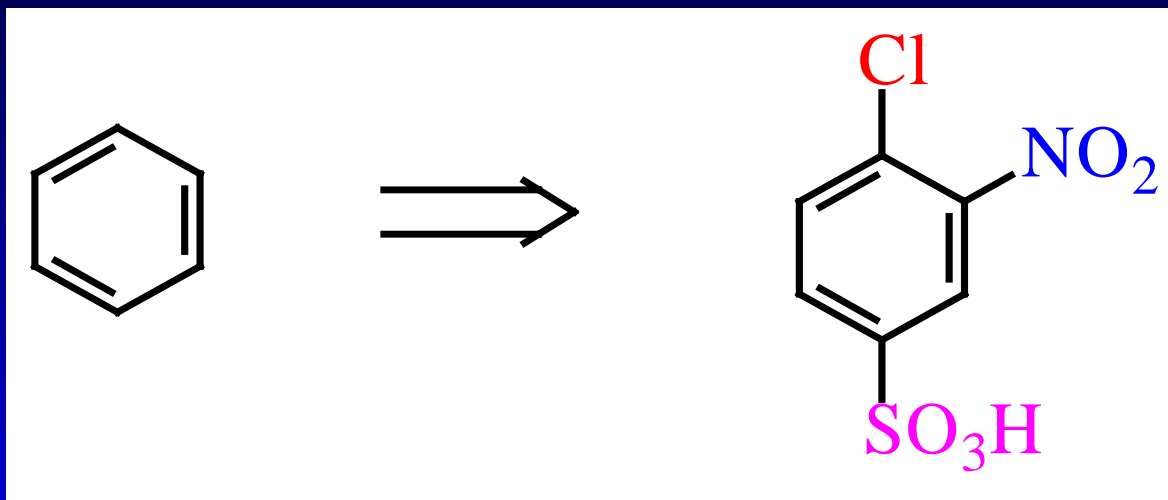
例4



A) 硝化、卤代

B) 卤代、硝化 ✓

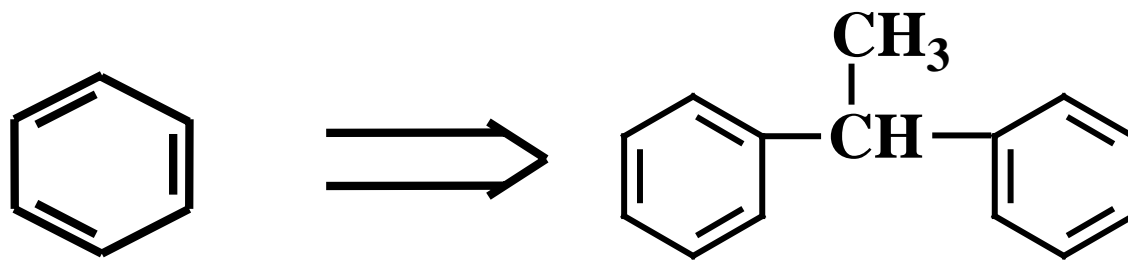
例5



- A) 硝化、氯代、磺化
- B) 硝化、磺化、氯代
- C) 氯代、硝化、磺化
- D) 氯代、磺化、硝化

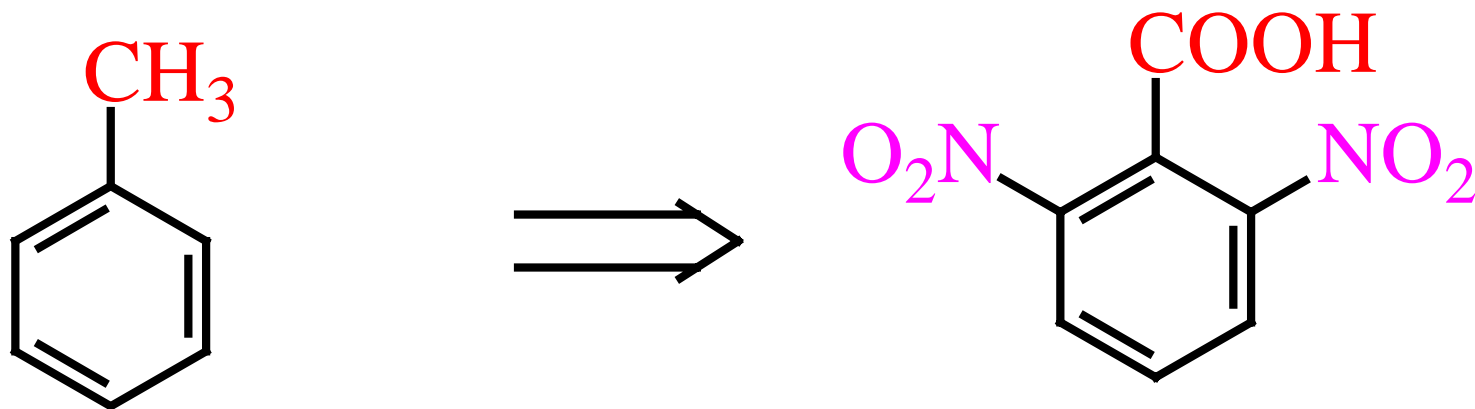


例6



烷基化、光卤代、烷基化

例7

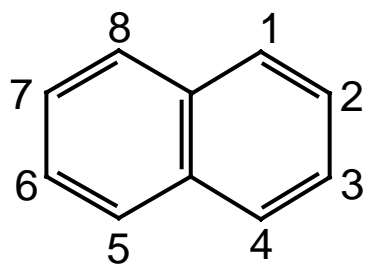


磺化、硝化、脱磺酸基、氧化

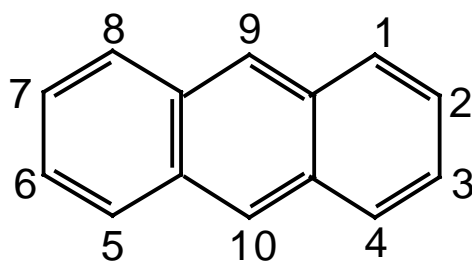
第二节

稠环芳香烃

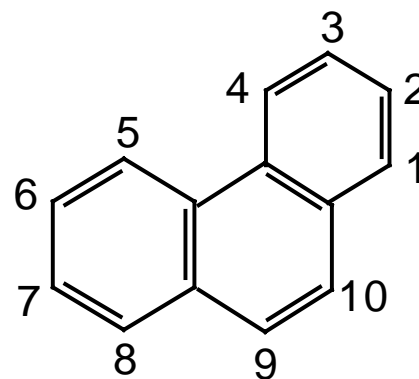
一、结构



萘



蒽



菲

二、异构

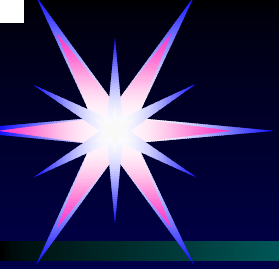
	萘	蒽	菲
一元	- , -	- , , -	5种
二元	相同10种 , 不同14种		

三、萘的化性

1、取代

2、氧化

3、加成



第三节 非苯芳烃

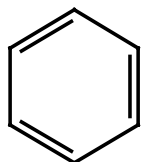
一、休克尔规则 (Hückel rule):

一个单环化合物只要它具有平面的闭合共轭体系，而且它的电子数目为 $4n+2$ ($n = 0, 1, 2, 3, \dots$) 就具有芳香性。

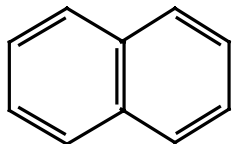
要点(Key notes) :

1. 单环
2. C sp^2
3. 电子 = $4n+2$

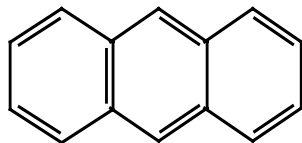
二、举例



$$4 \times 1 + 2 = 6$$

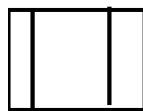


$$4 \times 2 + 2 = 10$$

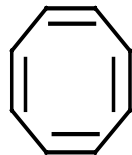


$$4 \times 3 + 2 = 14$$

已知有芳香性的苯系芳烃



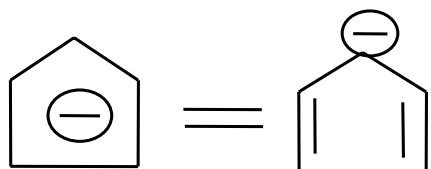
$$\text{电子} = 4$$



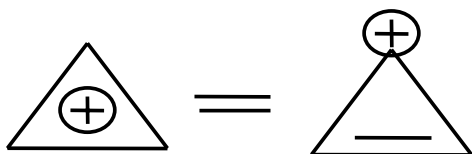
$$\text{电子} = 8$$

无芳香性

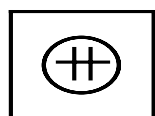
举例



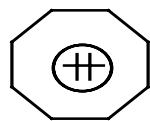
电子= 6



电子= 2

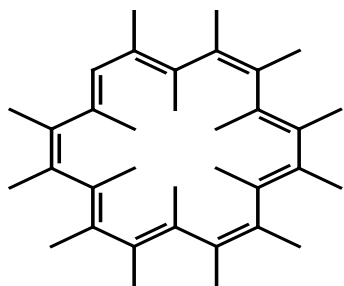


电子= 2



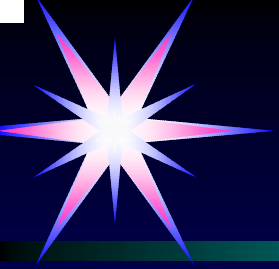
电子= 6

[18]-轮烯



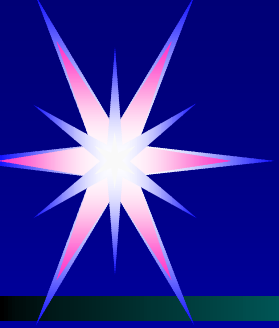
电子= 18

有芳香性



第四章重点讲解问题

1. 单环芳烃的命名和异构现象
2. 单环芳香烃的化学性质
3. 苯环的定位效应及理论解释
4. 稠环芳香烃和非苯芳烃



再见
Good-bye

