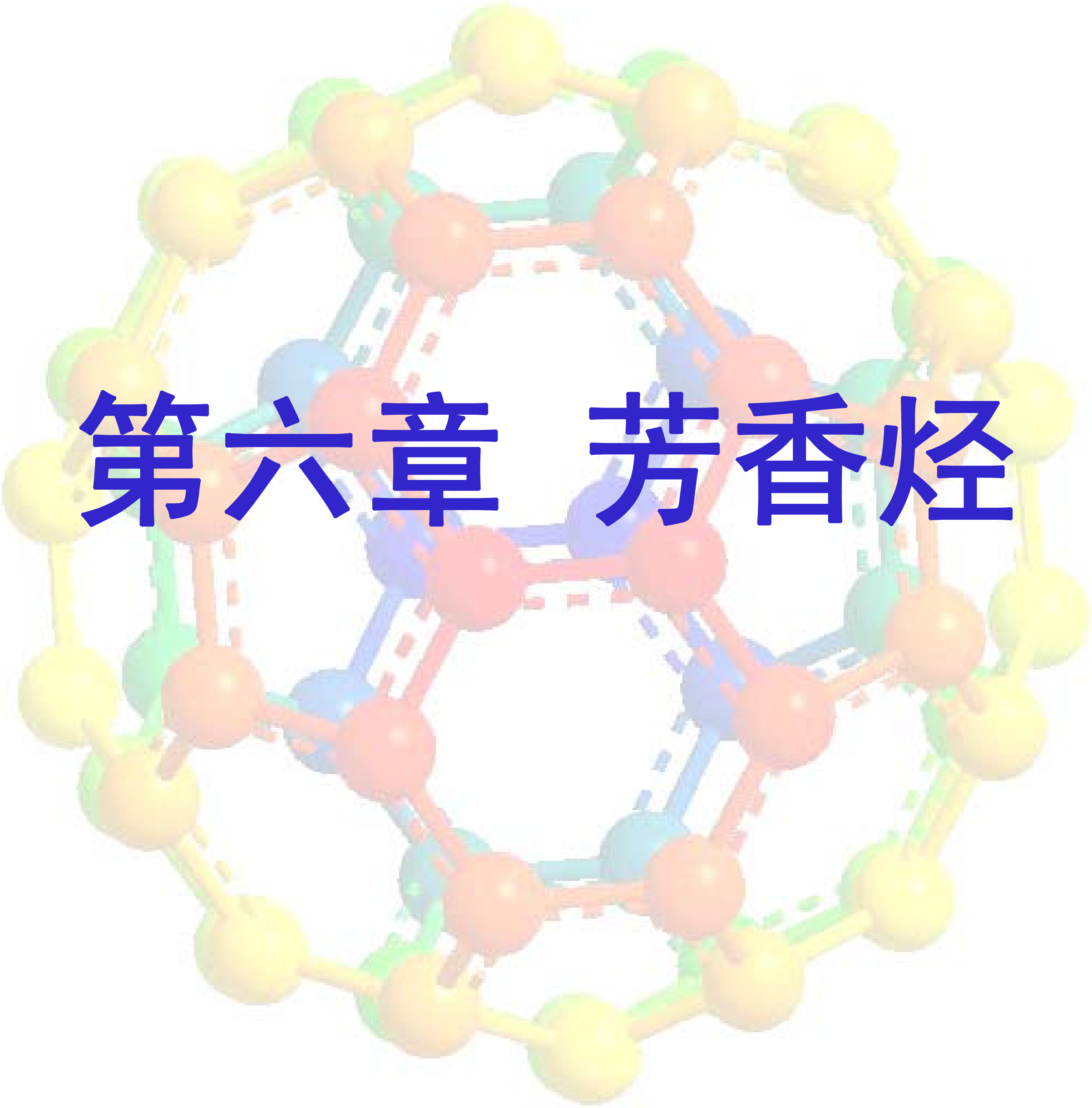
第六章 芳香烃

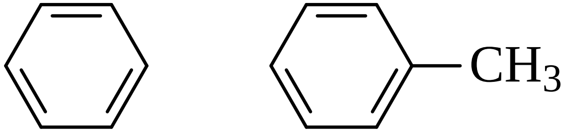


6.1 芳香烃的分类、结构及命名

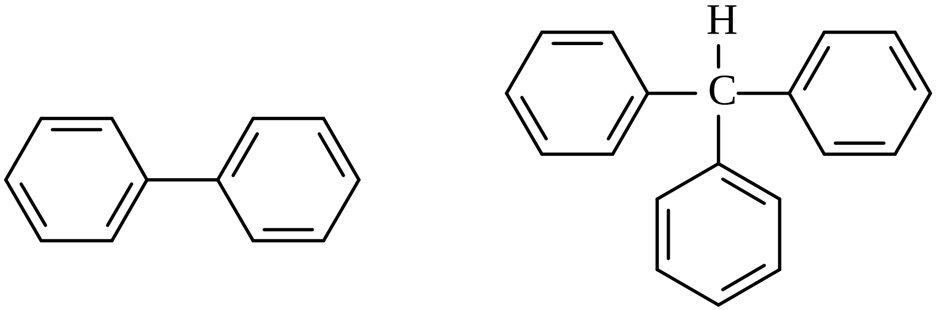
6.1.1 芳香烃的分类

芳香烃

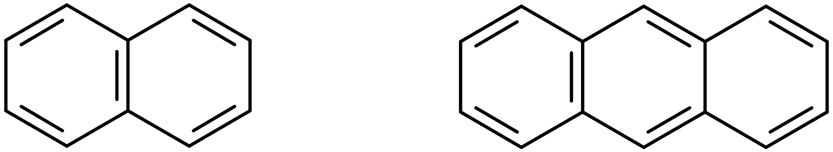
单环芳烃



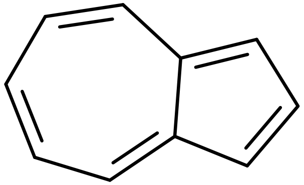
多环芳烃



稠环芳烃



非苯芳烃



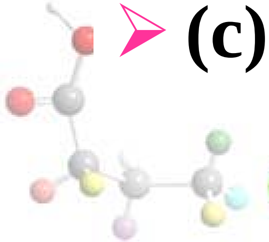
6.1.2 苯的结构

苯的特征:

- **(a) 分子式C_6H_6，C:H=1:1 , 不饱和程度高**
- **(b) 稳定性好—— 可由煤在1000°C制取；不被$KMnO_4$氧化，不易发生加成反应。**

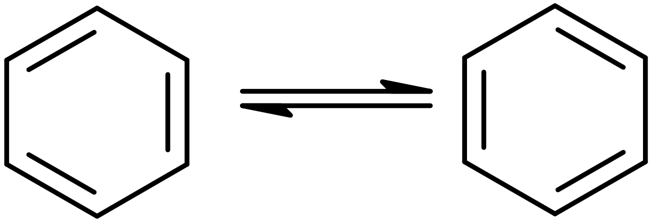
芳香族化合物的特性 —— 芳香性

- **(a) 苯环易发生取代，难发生加成反应**
- **(b) 不易氧化**
- **(c) 苯环具有特殊稳定性**



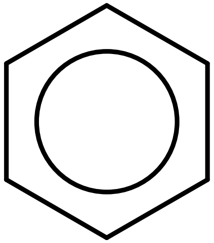
苯的结构表达式

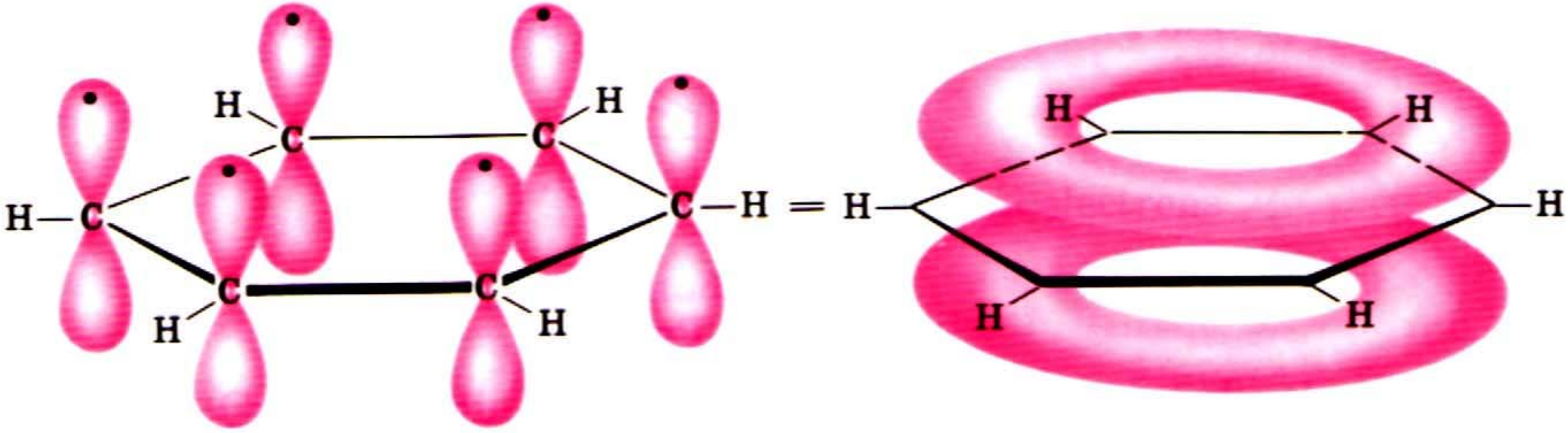
最为人们所普遍接受的是共轭环己三烯苯——Kekulé 苯



Kekulé 苯

Robinson 1925年建议用如下表达式



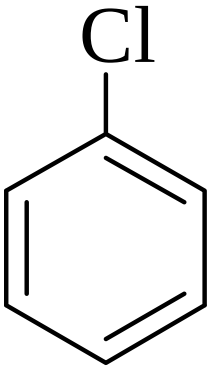


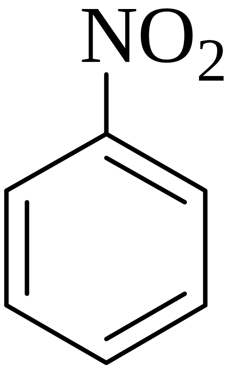
- 6个碳原子都是*sp*^{2}杂化
- 未参与杂化的*p* 轨道带着一个电子垂直于环平面，形成一个闭合环状的大 π键
- 苯的6个碳原子形成平面正六边形
- 碳-碳键长均等，为 140 pm
- 所有键角均为120°

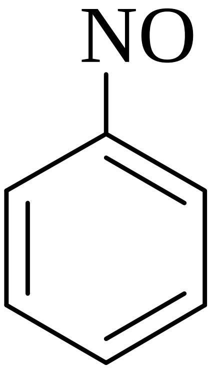
6.1.3 苯及其衍生物的命名和异构

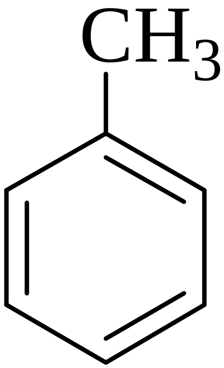
1. 一取代苯的命名

(1) 苯环作为母体：环上取代基为－X，－NO_2，－NO，简单烷基等基团


氯苯

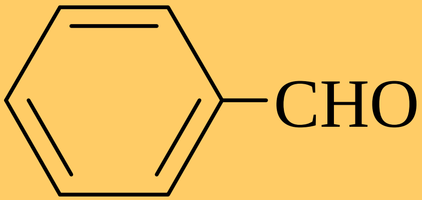

硝基苯


亚硝基苯

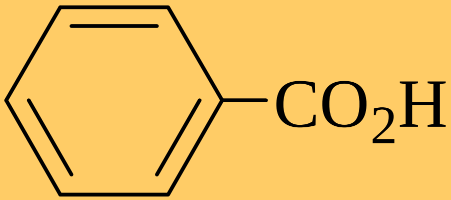

甲苯

(2) 苯环作为取代基

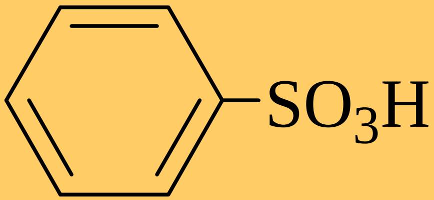
- 苯环连有母体官能团；
- 带较长烷基(>C_6)或取代基较复杂时；
- 分子中有多个苯环，以任一苯环为母体命名都有困难时；
- 取代基上带官能团时。



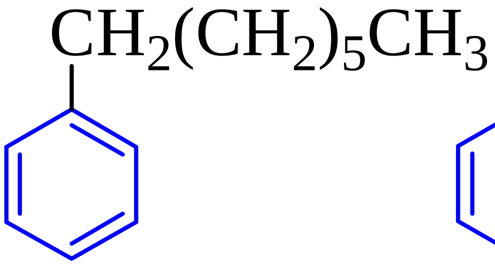
苯甲醛



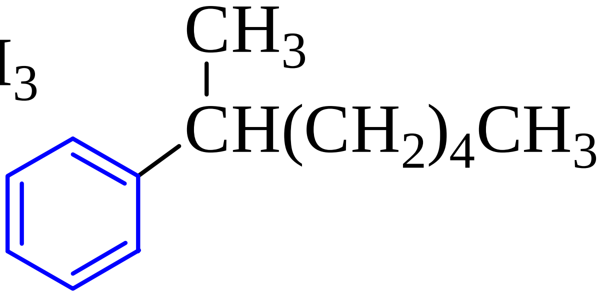
苯甲酸



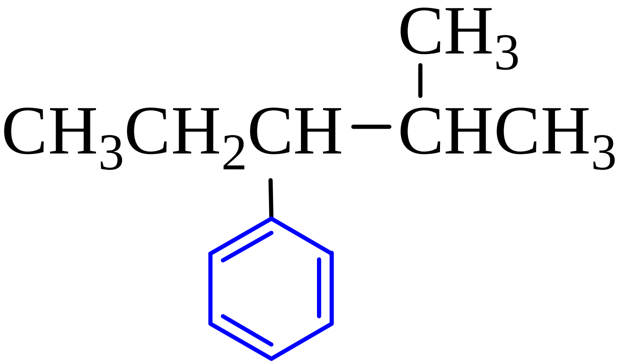
苯磺酸



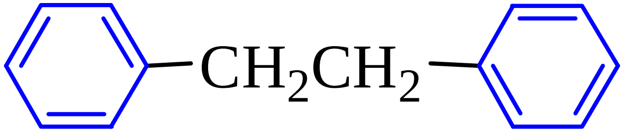
1-苯基庚烷



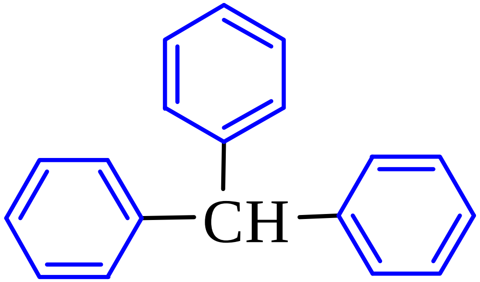
2-苯基庚烷



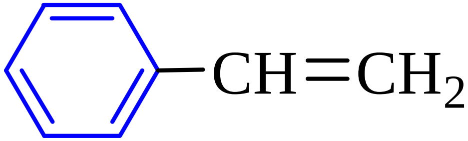
2-甲基-3-苯基戊烷



1,2-二苯基乙烷



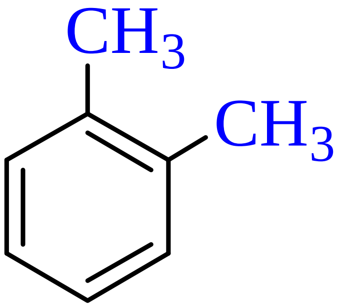
三苯基甲烷



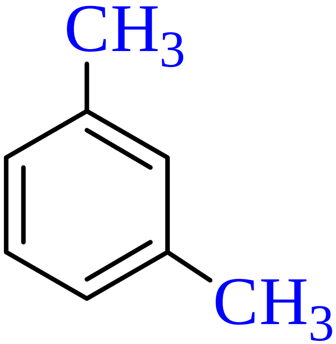
苯乙烯

2. 二取代苯的命名

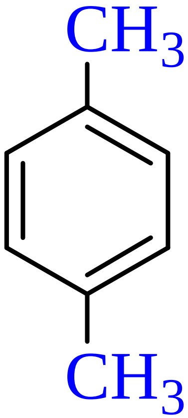
- 2个取代基非母体官能团(1,2– 邻–；1,3– 间–；1,4– 对–)
- 2个取代基中有母体官能团(确定主官能团，给最小位号)
- 多取代苯(确定主官能团，按最低系列原则编号)



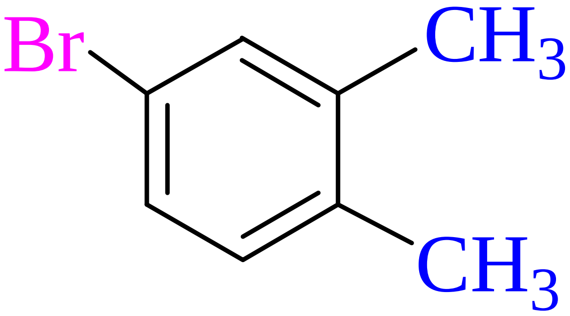
1,2–二甲苯
邻–二甲苯



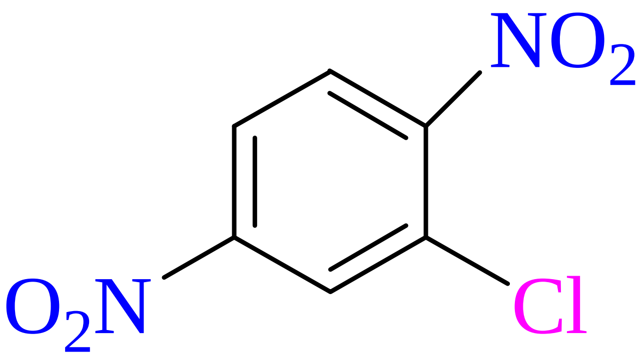
1,3–二甲苯
间–二甲苯



1,4–二甲苯
对–二甲苯



1,2–二甲基–4–溴苯



1,4–二硝基–2–氯苯

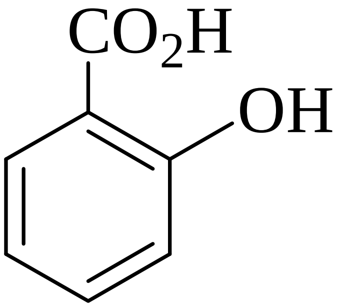
主官能团的确定

当化合物分子中含有2个以上官能团和取代基时，按下列顺序确定主官能团：

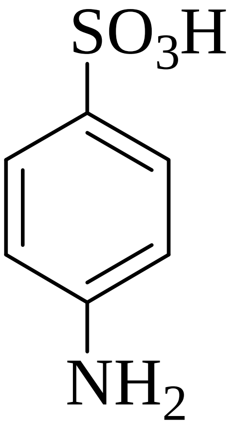
$-COOH$ $-SO_3H$ $-COOR$ $-COX$ $-CONH_2$

$-CN$ $-CHO$ $C=O$ **$-OH$** $-NH_2$ $-OR$ **$-R$**

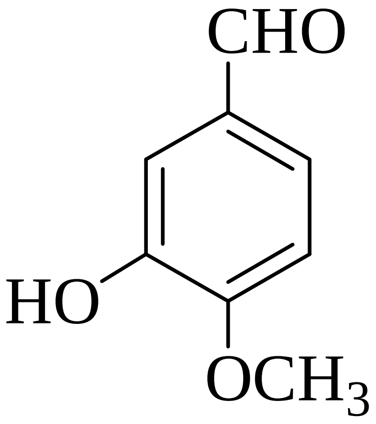
$-OH$, $-NH_2$与苯环一起构成母体"苯酚"、"苯胺"；**$-OH$**以前的基团与苯环相连时，苯环作为取代基命名。



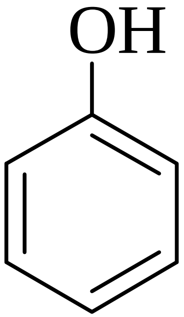
2–羟基苯甲酸



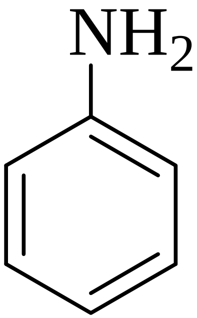
4–氨基苯磺酸



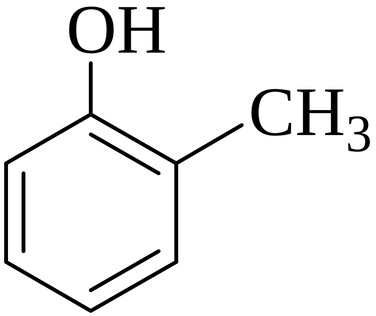
3–羟基–4–甲氧基苯甲醛



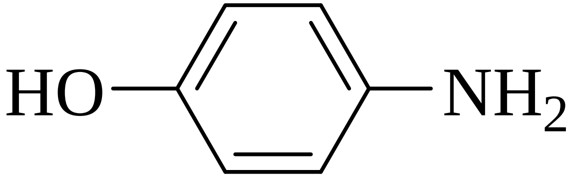
苯酚



苯胺



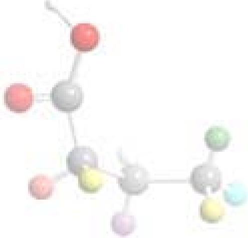
2–甲基苯酚



4–氨基苯酚

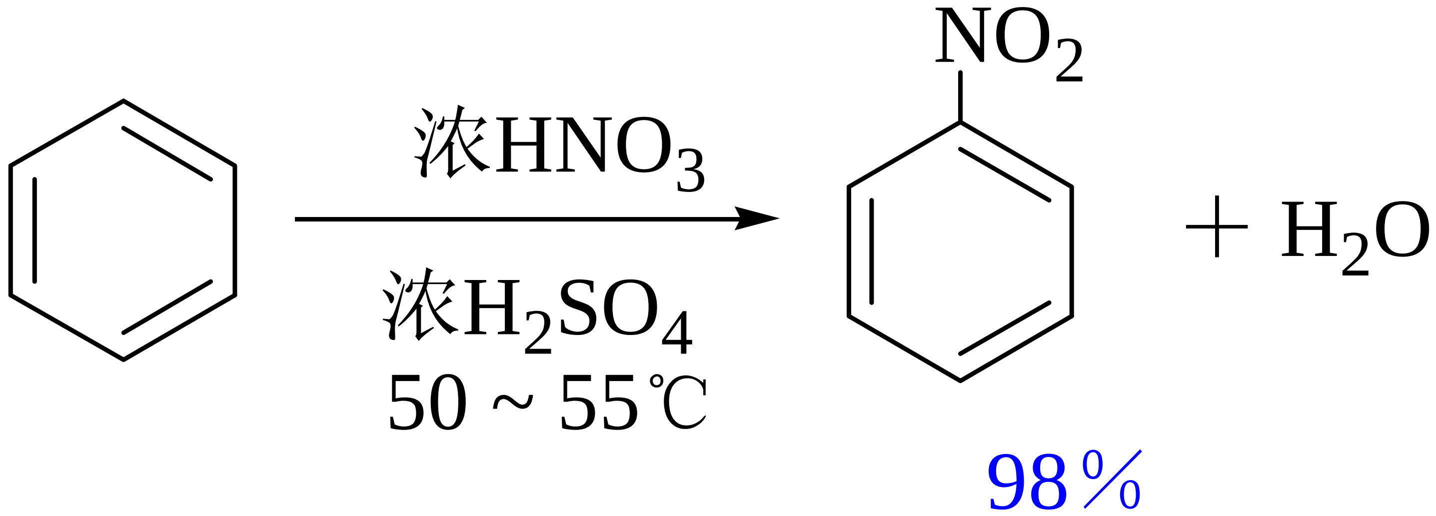
6.2 芳香烃的物理性质(自学)

6.3 芳香烃的化学性质



6.3.1 苯环上的亲电取代反应

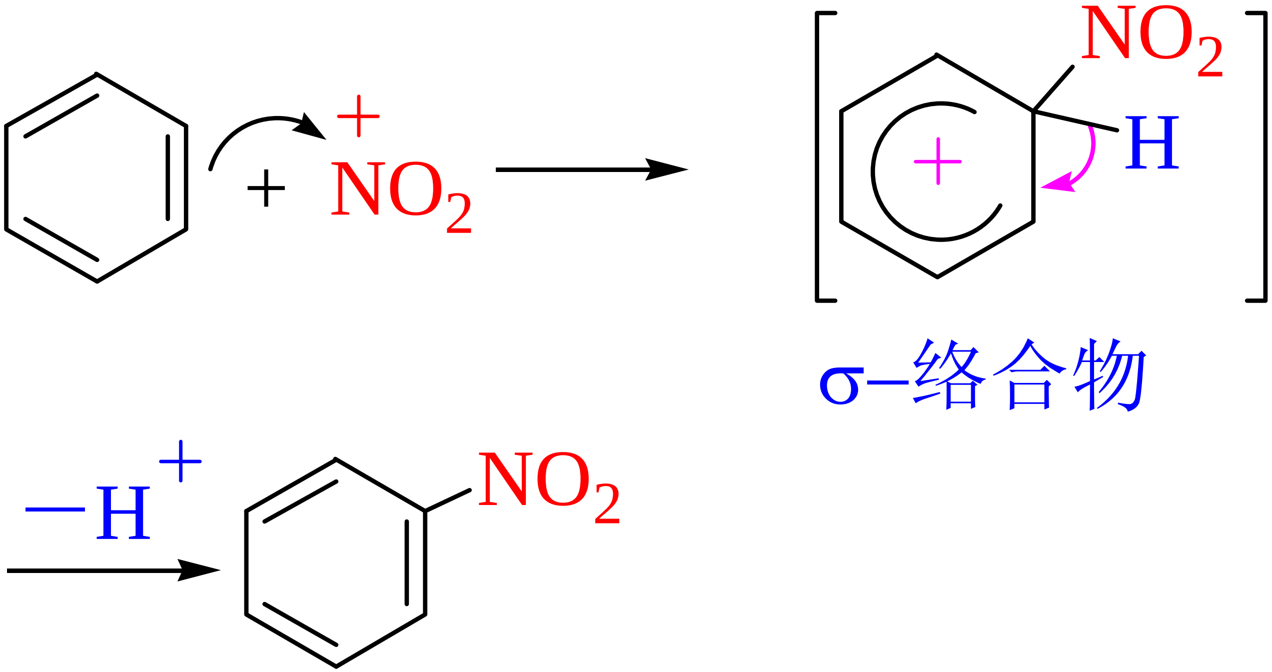
1. 硝化反应



反应机理

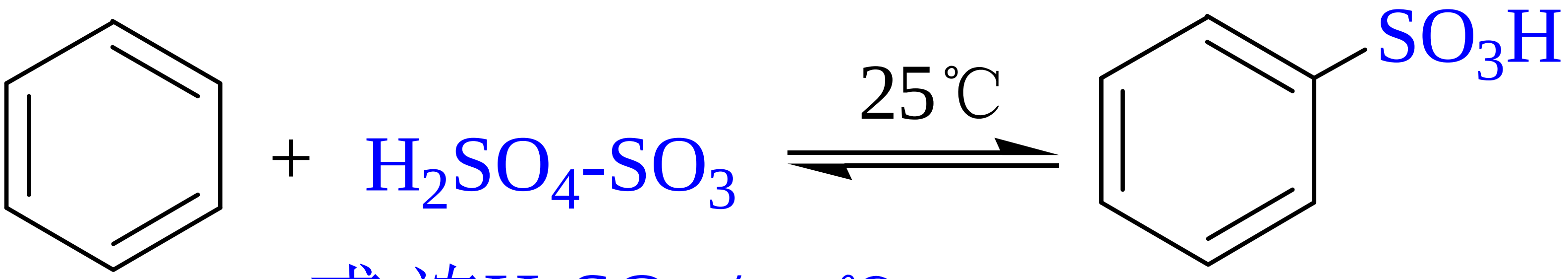
$$HONO_2 + H_2SO_4 \longrightarrow H_2\overset{+}{O}-NO_2 + HSO_4^-$$

$$H_2\overset{+}{O}-NO_2 + H_2SO_4 \longrightarrow H_3O^+ + \overset{+}{NO_2} + HSO_4^-$$



6.3.1 苯环上的亲电取代反应

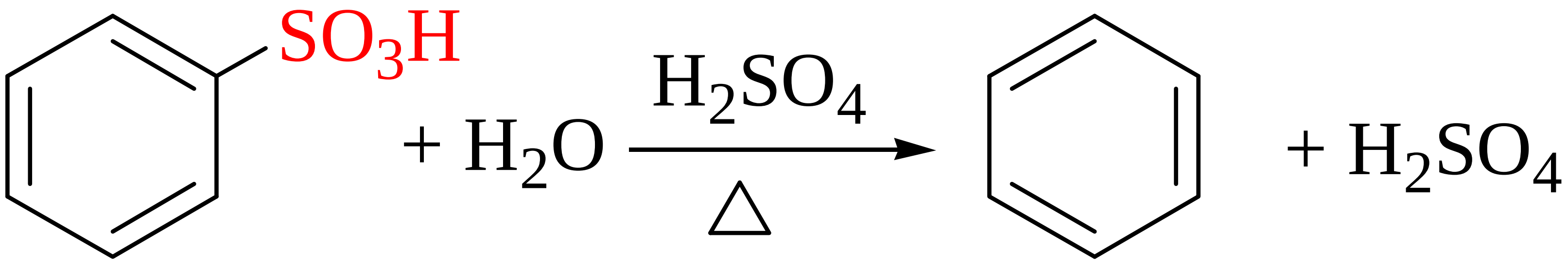
2. 磺化反应



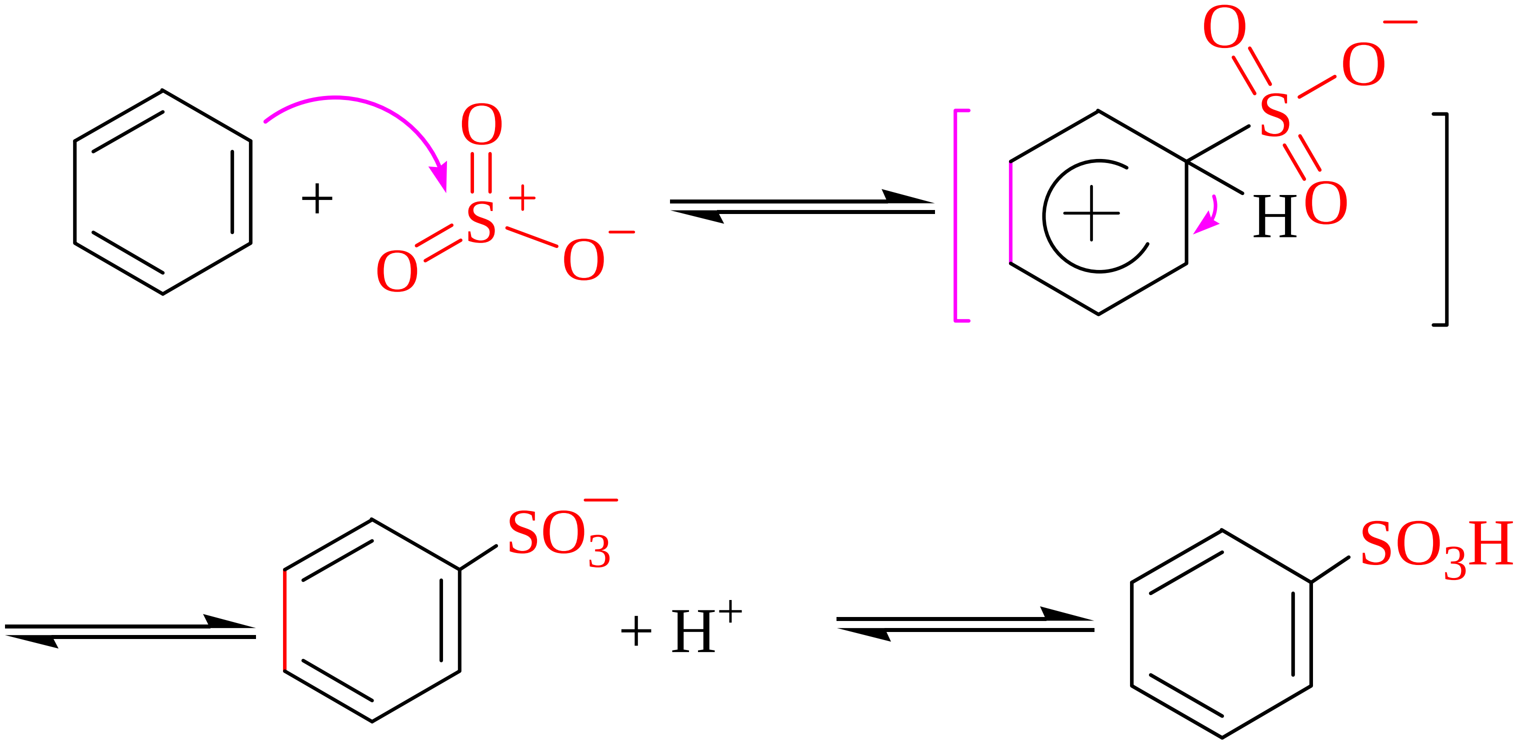
或 浓H_2SO_4 / 75℃

苯磺酸

苯磺酸在稀酸溶液中加热，磺酸基水解脱落

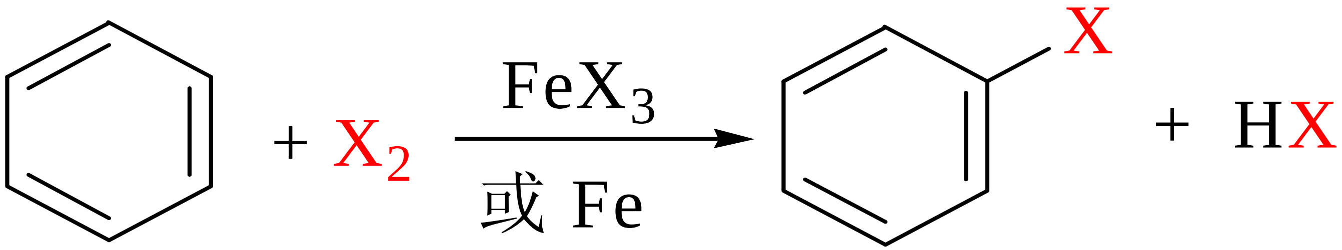


反应机理

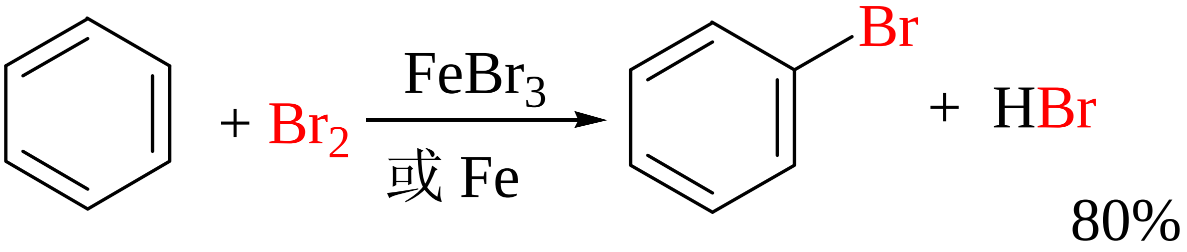


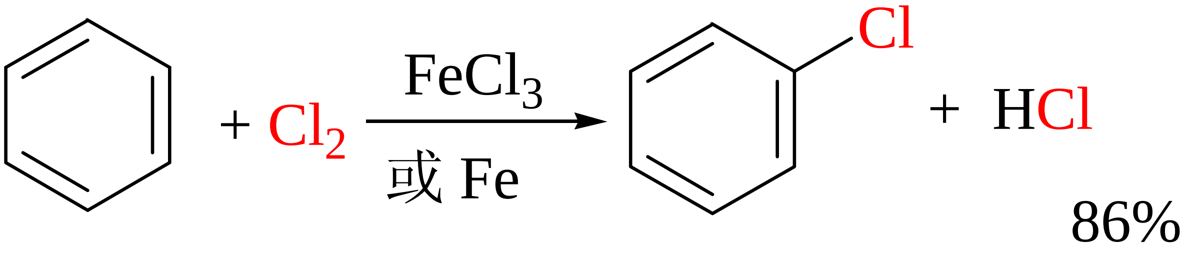
6.3.1 苯环上的亲电取代反应

3. 卤化反应



$X = Cl_2 , Br_2$

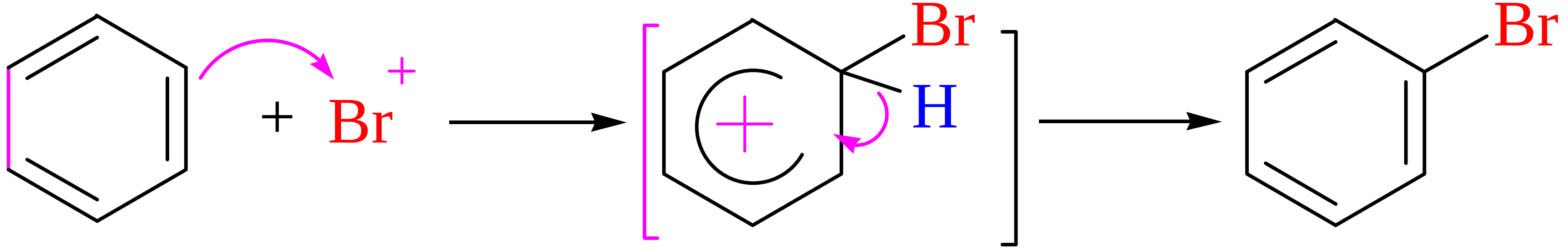




反应机理

$$Br_2 + Fe \longrightarrow FeBr_3$$

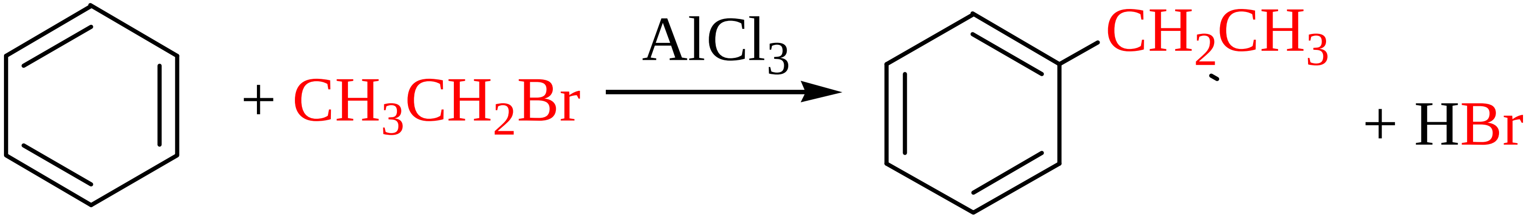
$$Br_2 + FeBr_3 \longrightarrow FeBr_4^- + Br^+$$

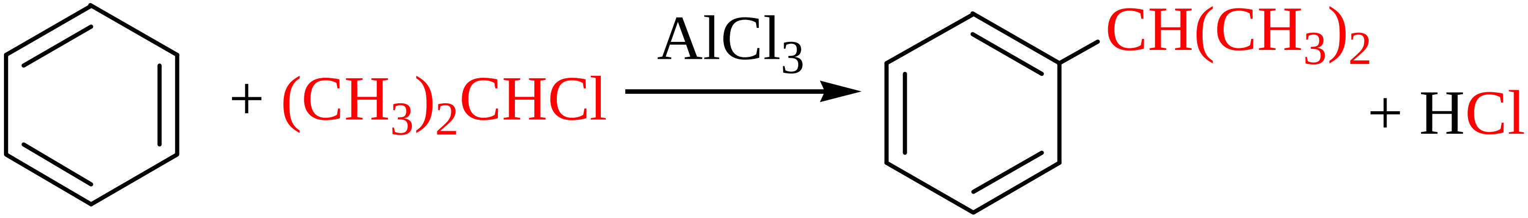


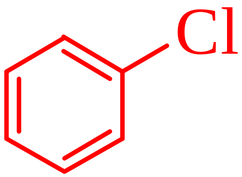
6.3.1 苯环上的亲电取代反应

4. Friedel—Crafts反应（傅－克反应）

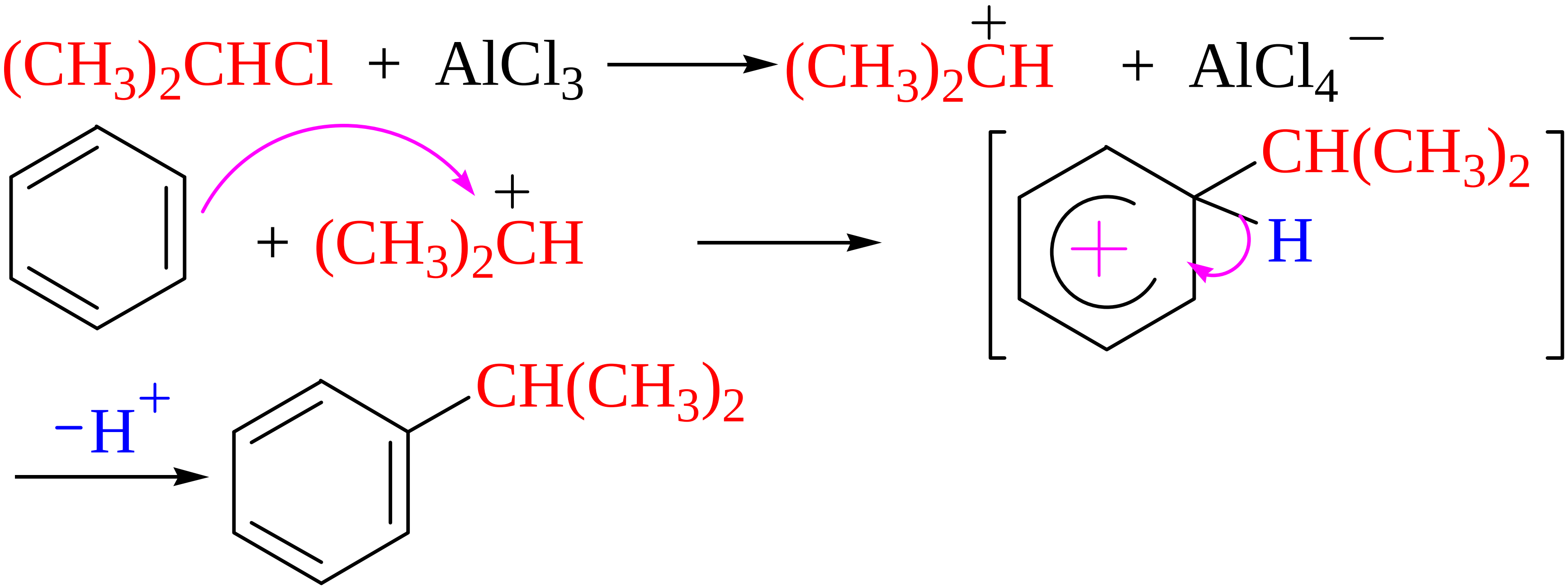
(A) 烷基化





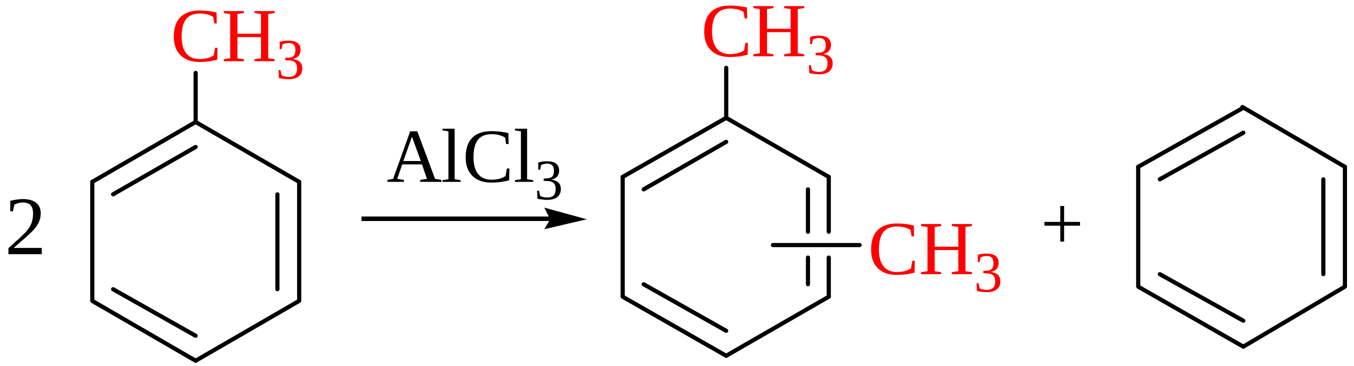
卤代烃用  $CH_2{=}CHCl$ 不能发生反应

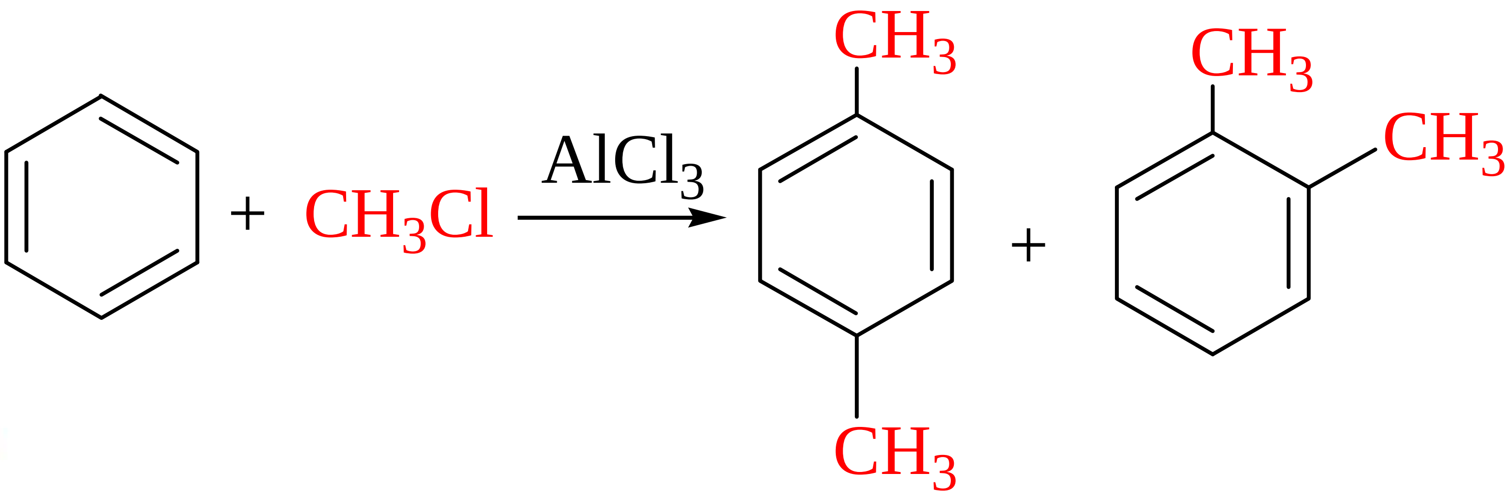
反应机理



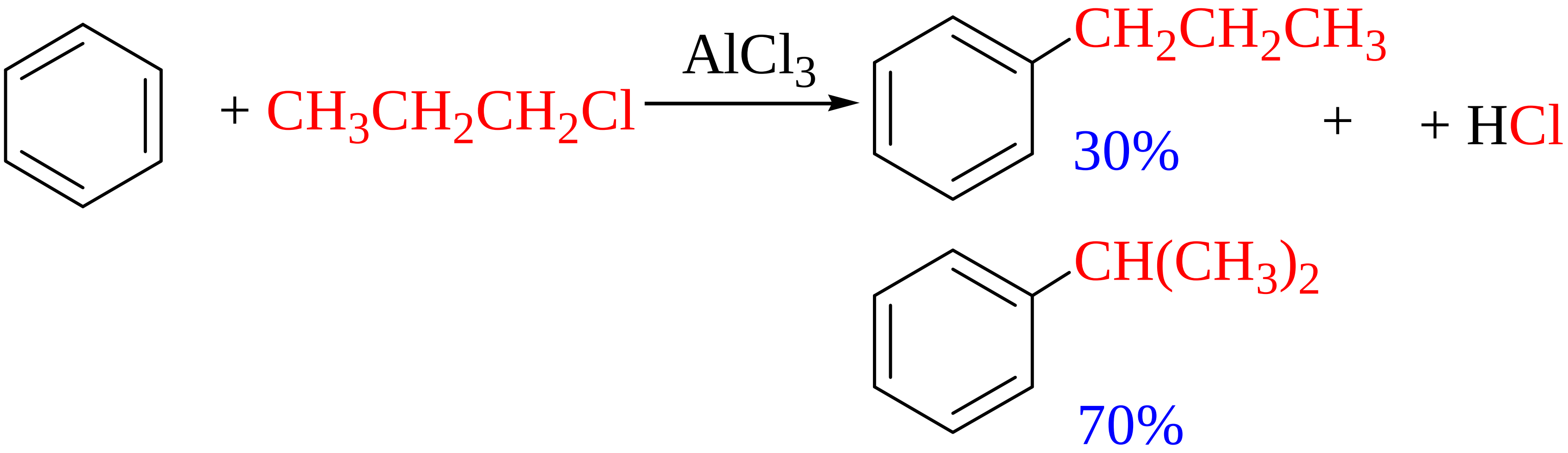
$$(CH_3)_2CHCl + AlCl_3 \longrightarrow (CH_3)_2\overset{+}{C}H + AlCl_4^{-}$$

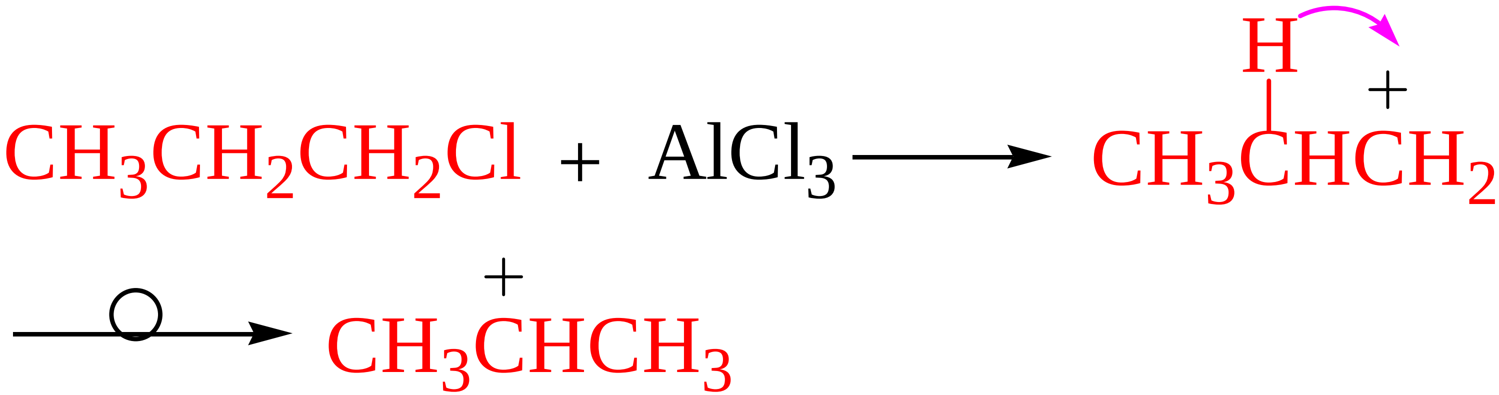
烷基化是可逆反应；易发生多取代现象





当RX超过3个碳原子时，可能发生重排反应





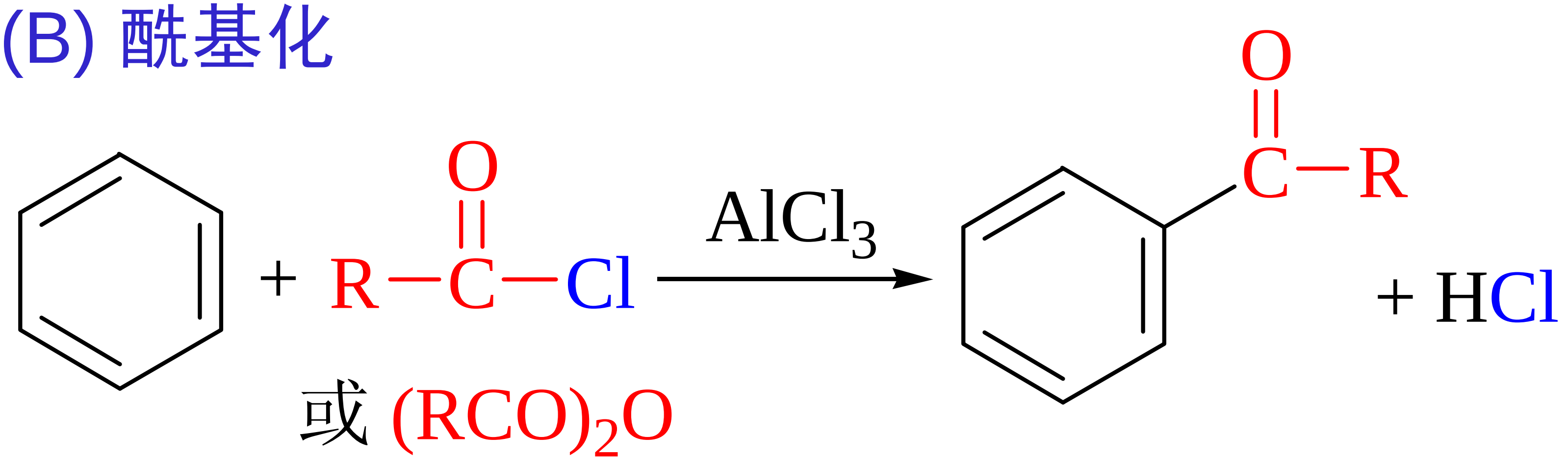
$$CH_3CH_2CH_2Cl + AlCl_3 \longrightarrow CH_3\overset{H}{C}H\overset{+}{C}H_2$$

$$\xrightarrow{\bigcirc} CH_3\overset{+}{C}HCH_3$$

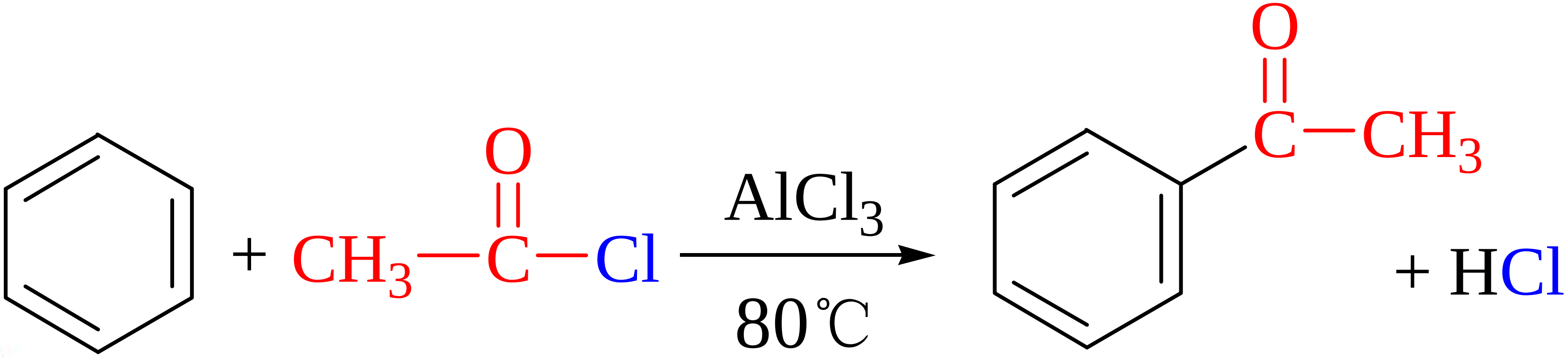
6.3.1 苯环上的亲电取代反应

4. Friedel—Crafts反应（傅－克反应）

(B) 酰基化

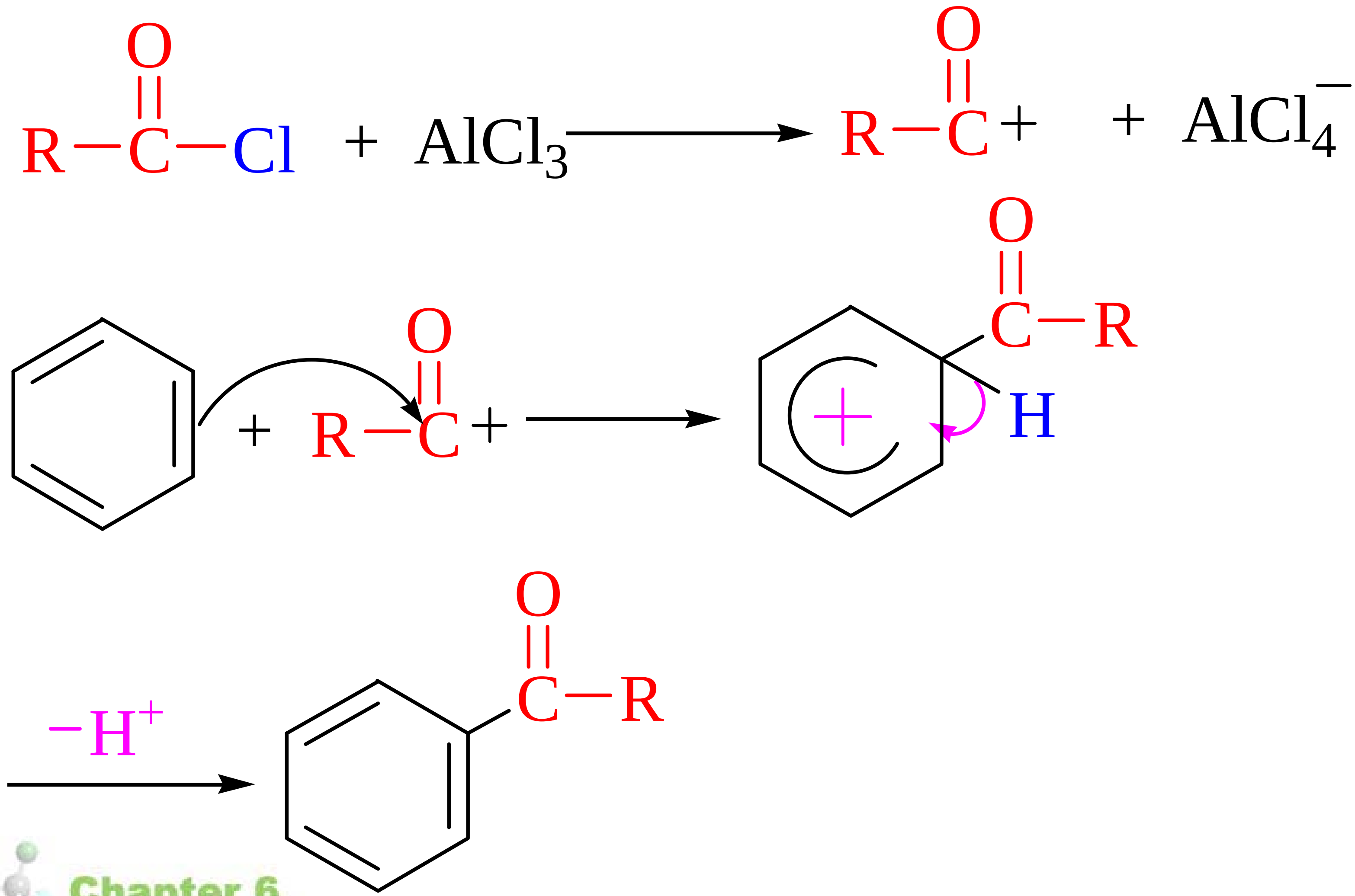


或 $(RCO)_2O$

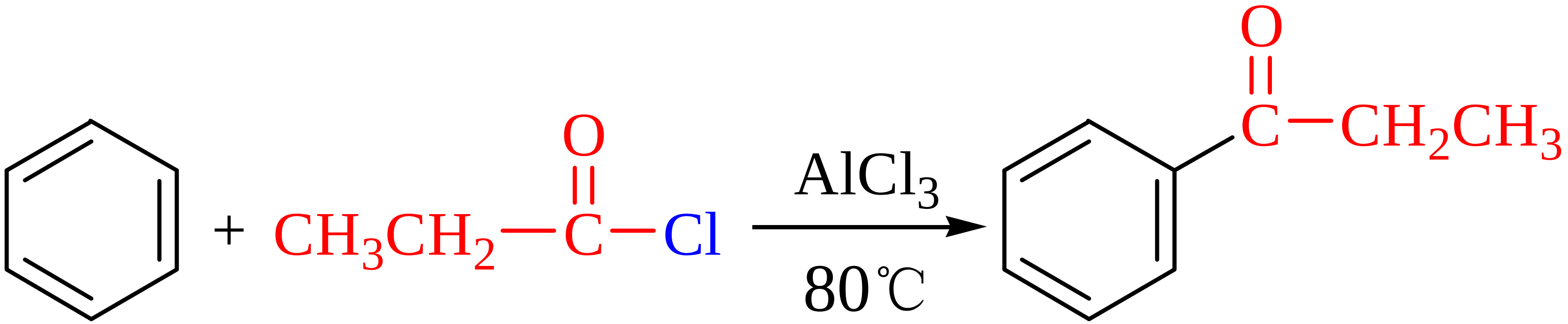


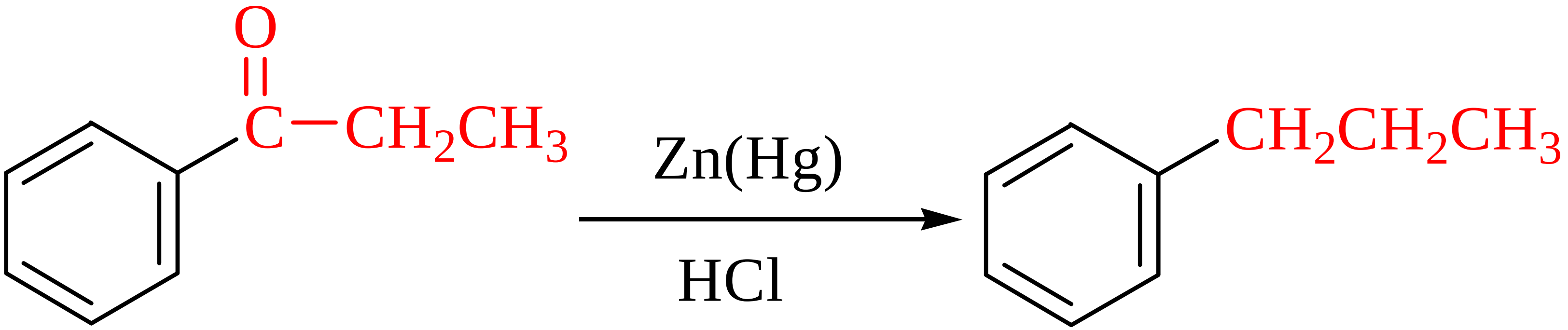
乙酰氯　　　　苯乙酮

反应机理



$$R-\overset{\overset{O}{\|}}{C}-Cl + AlCl_3 \longrightarrow R-\overset{\overset{O}{\|}}{C}{}^{+} + AlCl_4^-$$

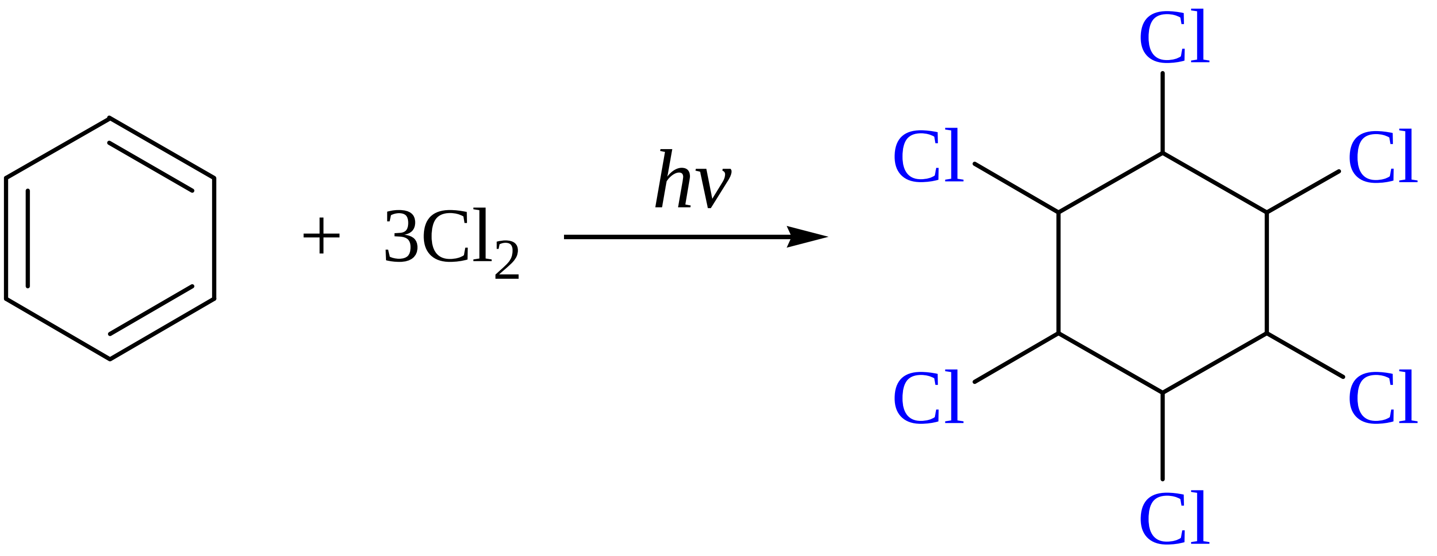




Clemmenson （克莱门森）还原

6.3.2 加成与还原反应

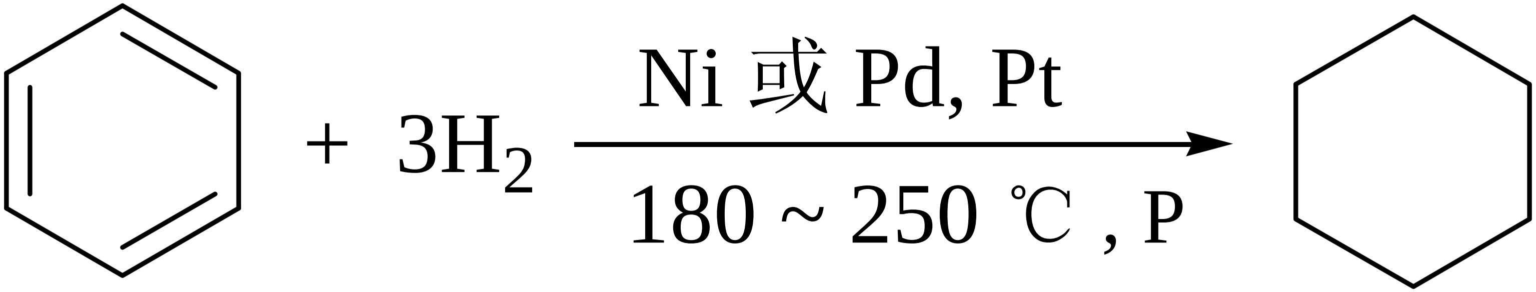
1. 与氯气加成



六氯化苯 “六六六”

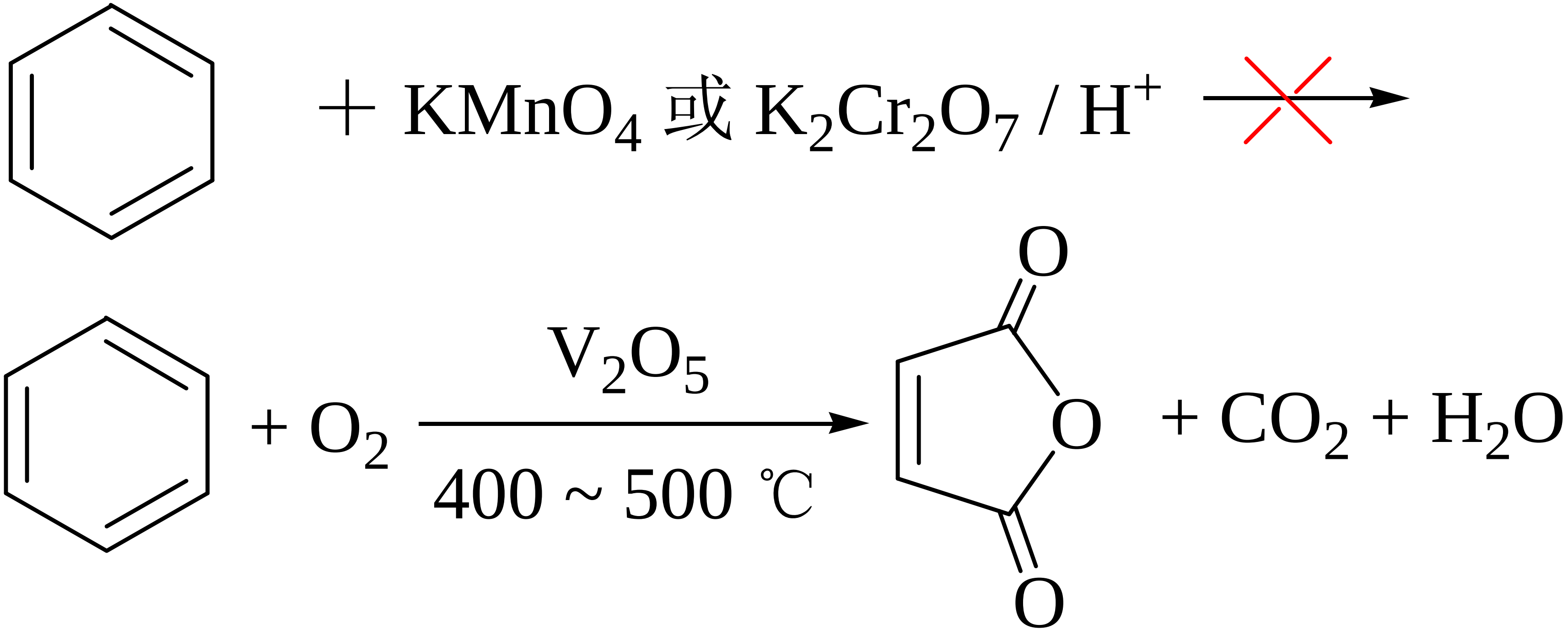
6.3.2 加成与还原反应

2. 加氢



6.3.3 氧化反应

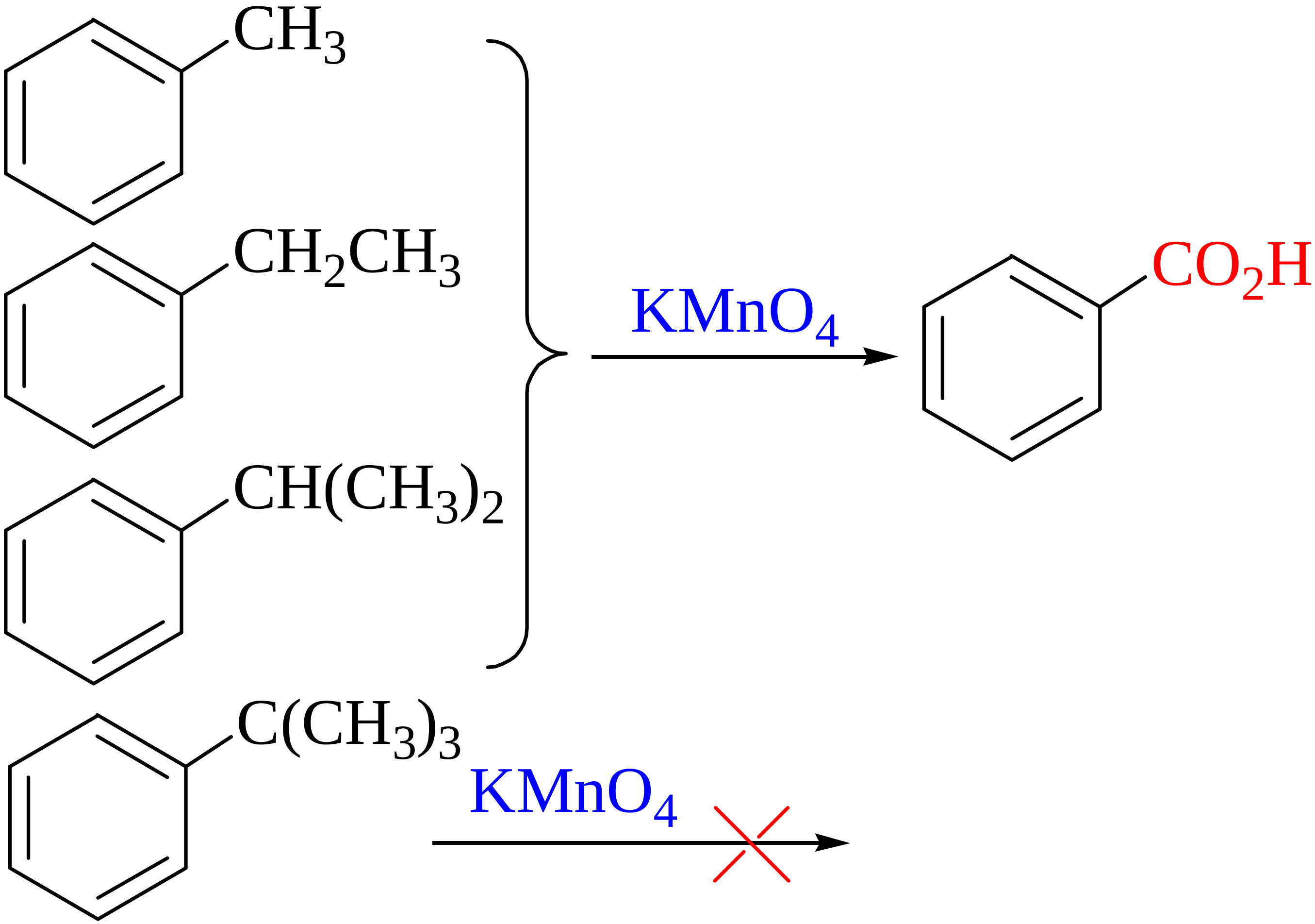
1. 苯环的氧化



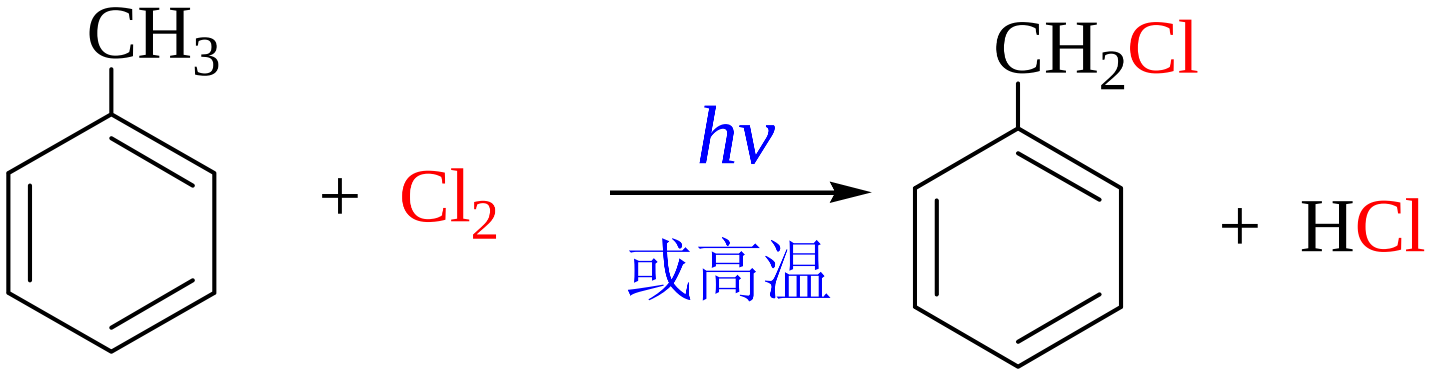
顺丁烯二酸酐

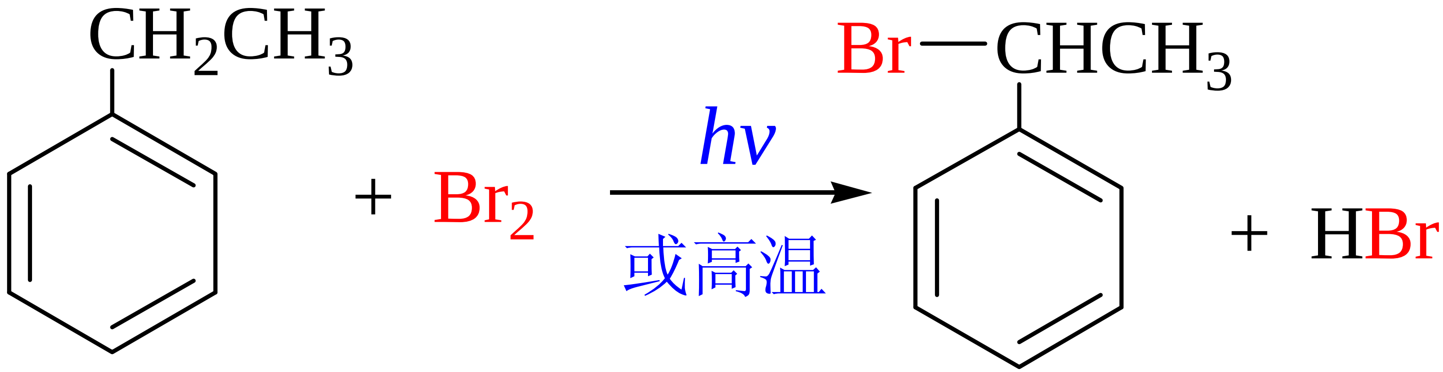
6.3.3 氧化反应

2. 侧链氧化

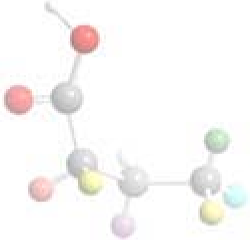


6.3.4 α−卤代反应

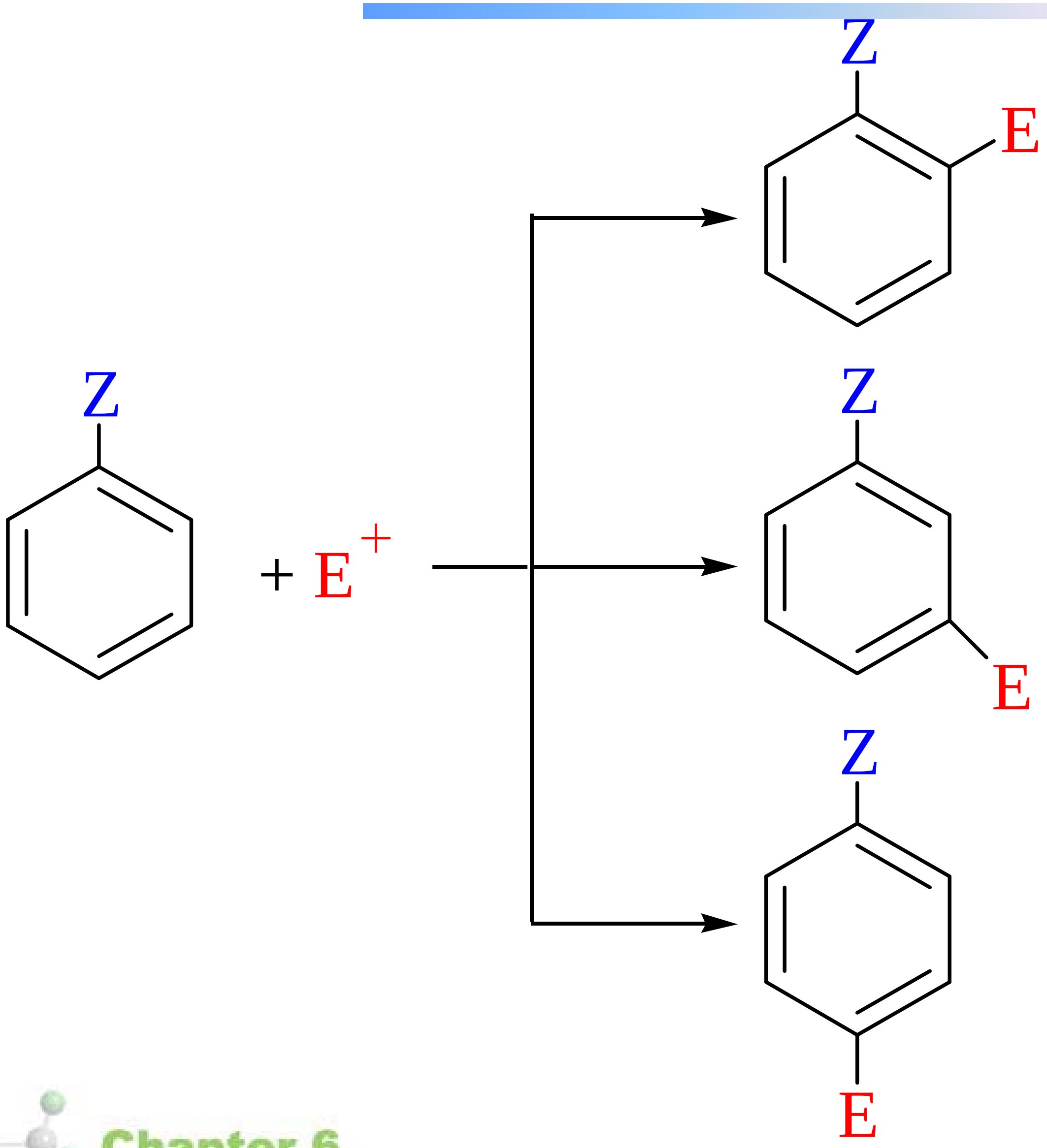




6.4 苯环上亲电取代的定位规律



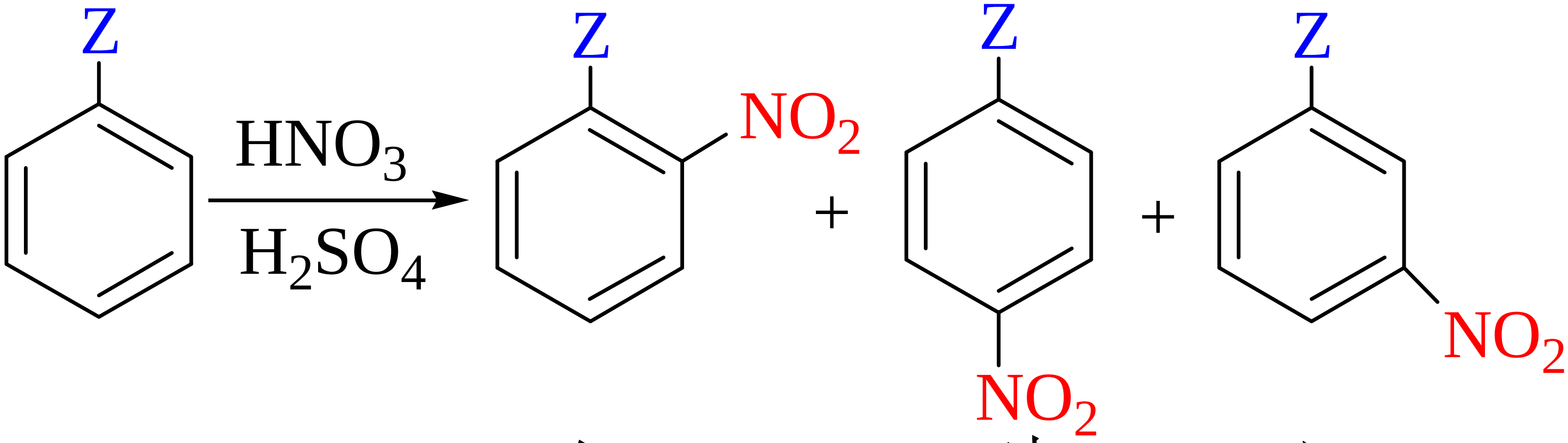
6.4.1 定位效应



邻位取代

间位取代

对位取代



邻 对 间

Z＝	OH	Me	Cl	NO_2	CN
邻(%)	40	58	30	6	17
对(%)	60	38	69	<1	2
间(%)	<1	4	1	93	81

取代基进入的位置受原有取代基的影响——定位效应

6.4.2 两类定位基团

1. 第一类定位基(邻对位定位基)

$-NR_2$ $-NHR$ $-NH_2$ $-OH$

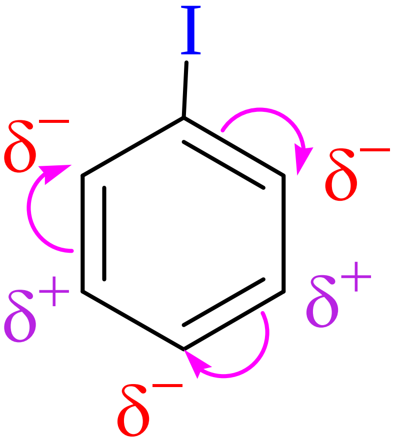
$-OR$ $-NHCOR$ $-OCOR$

$-R$ $-C_6H_5$ $-X$

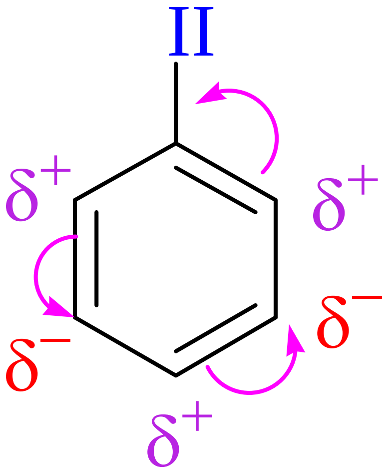
2. 第二类定位基(间位定位基)

$-\overset{+}{N}R_3$ $-NO_2$ $-CCl_3$ $-CN$ $-SO_3H$

$-CHO$ $-COR$ $-CO_2R$ $-CONH_2$



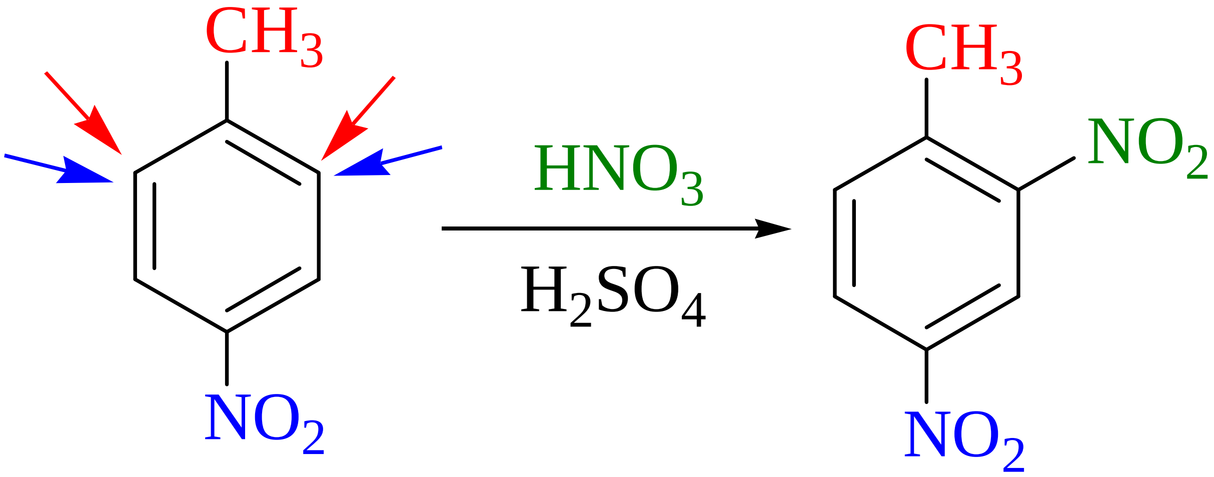
I 类定位基

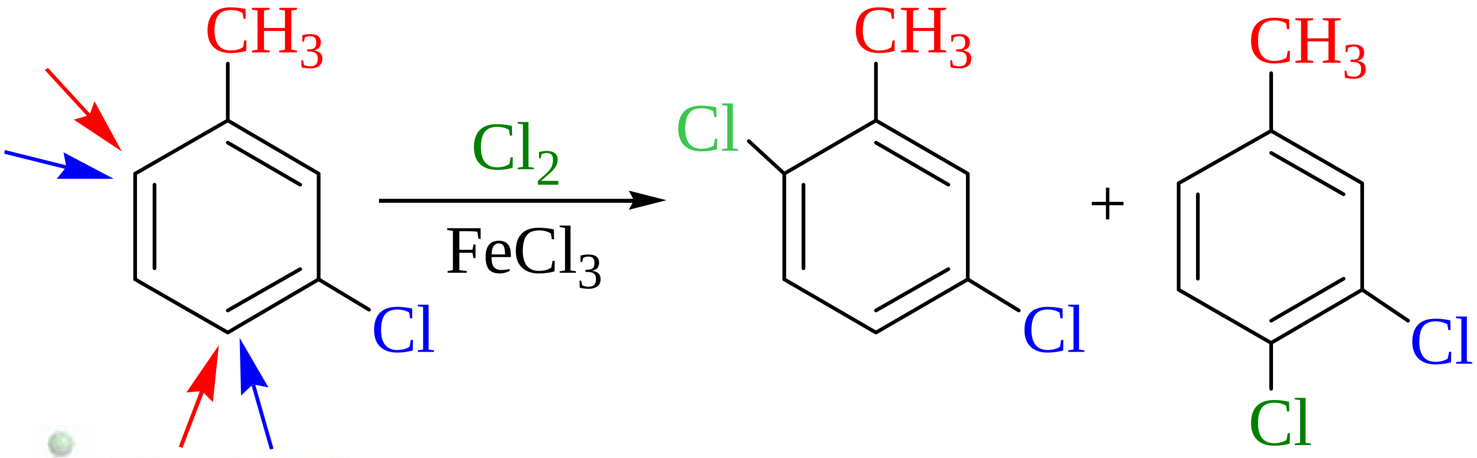


II 类定位基

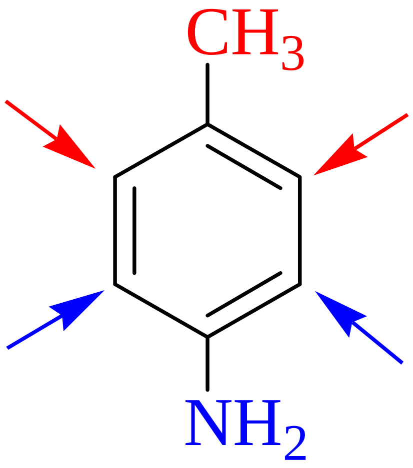
6.4.3 二元取代苯的定位

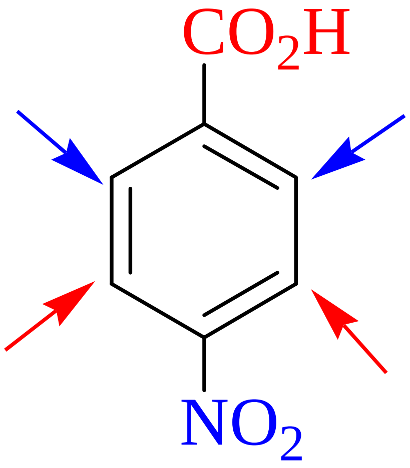
1. 两个取代基定位效应一致

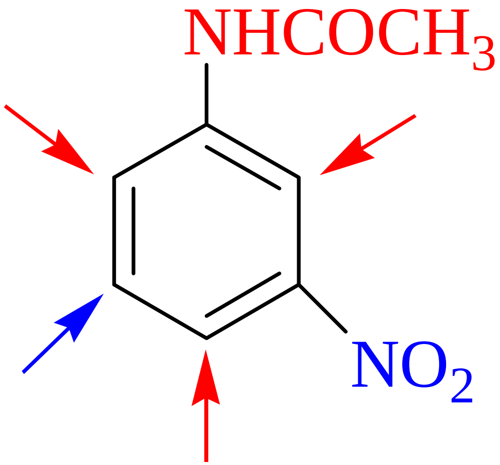


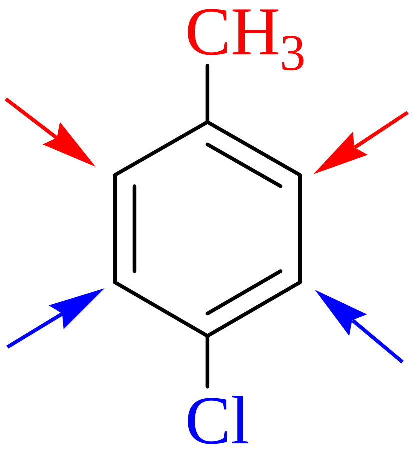


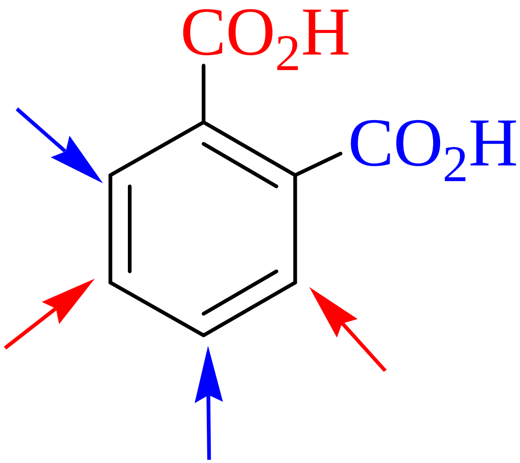
2. 两个取代基定位效应不一致



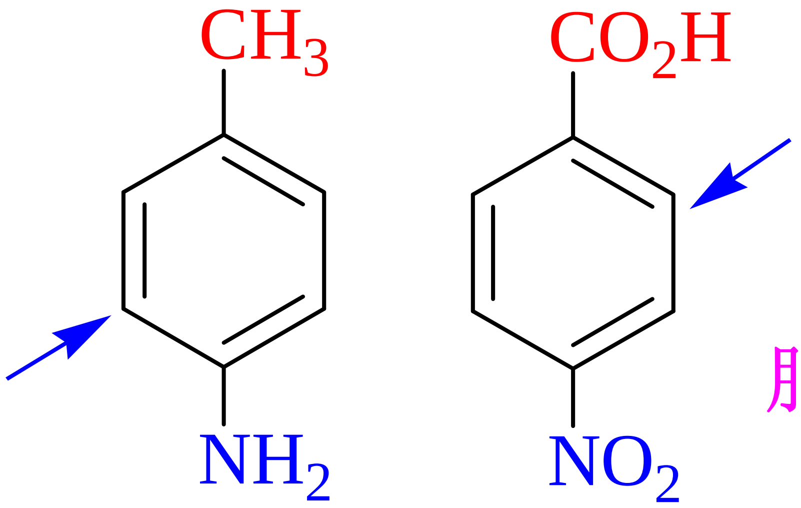




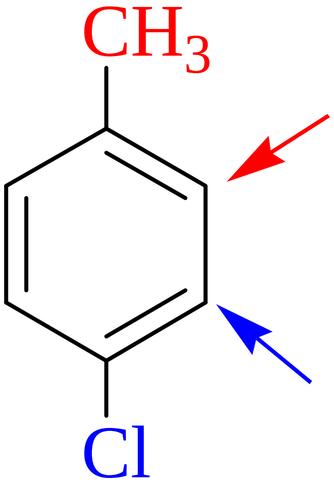




两个取代基同类

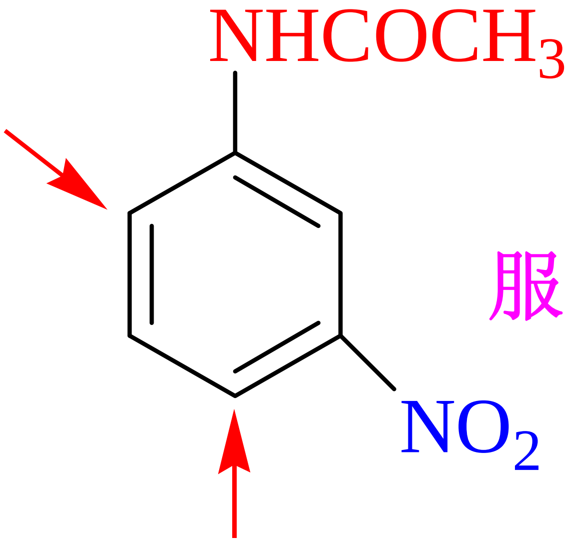


服从较强取代基的定位



定位能力差不多时
两者都有

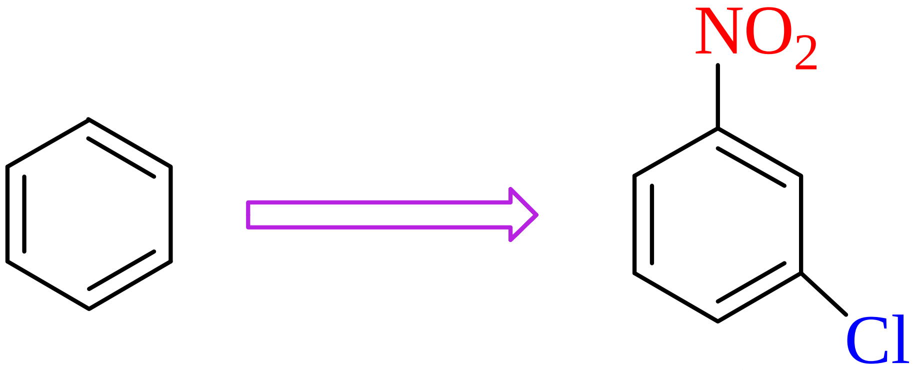
两个取代基不同类



服从一类定位基的定位

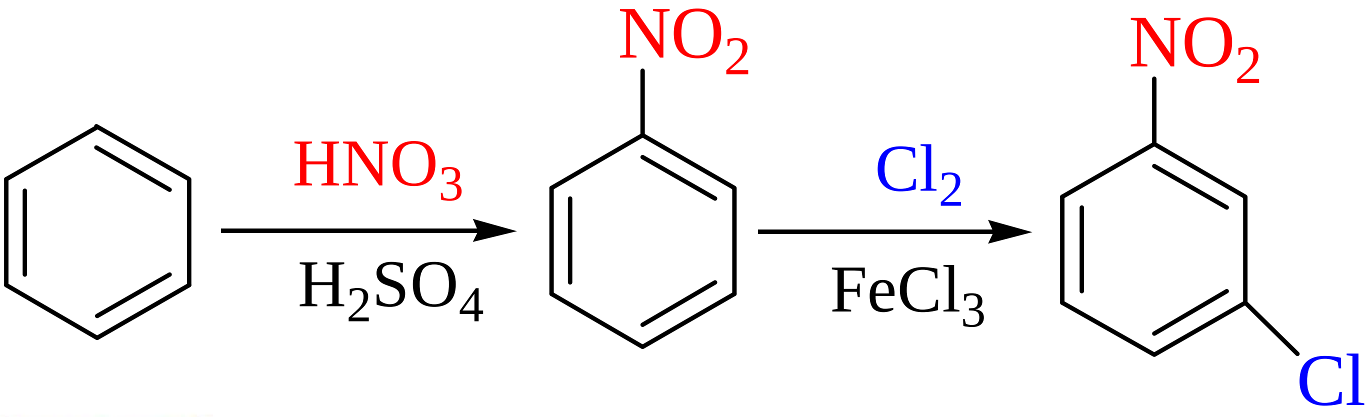
6.4.4 定位规律的应用

(1)

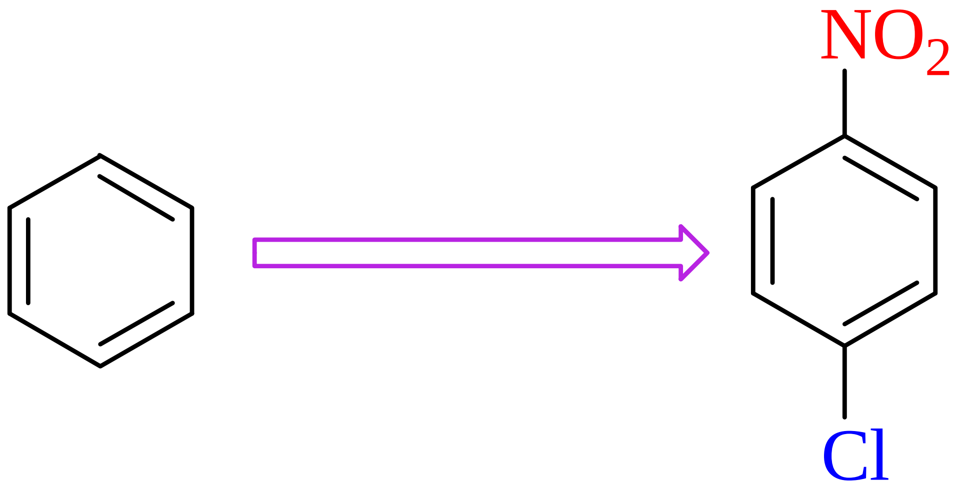


方法A： (1) 硝化 (2) 氯代

方法B： (1) 氯代 (2) 硝化

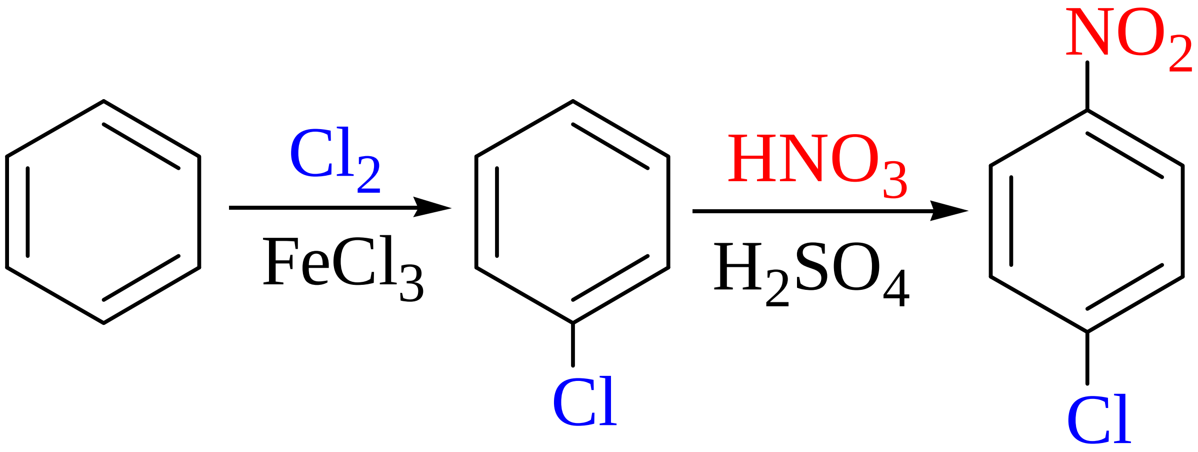


(2)

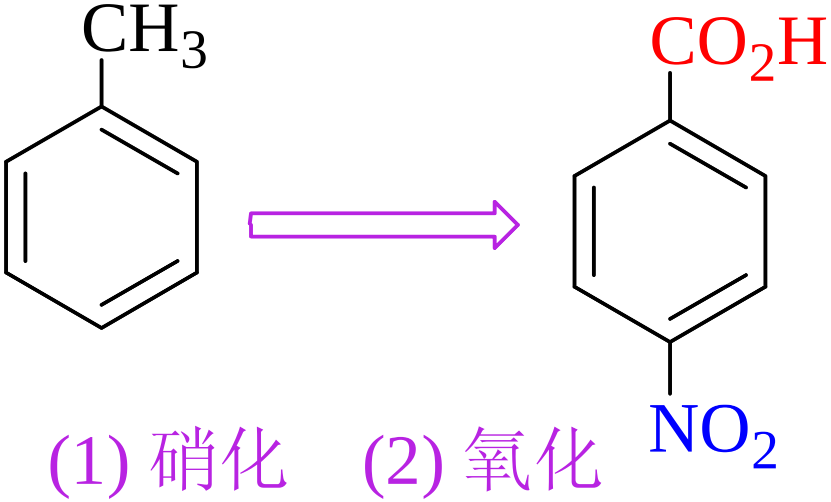


方法A： (1) 硝化 (2) 氯代

方法B： (1) 氯代 (2) 硝化

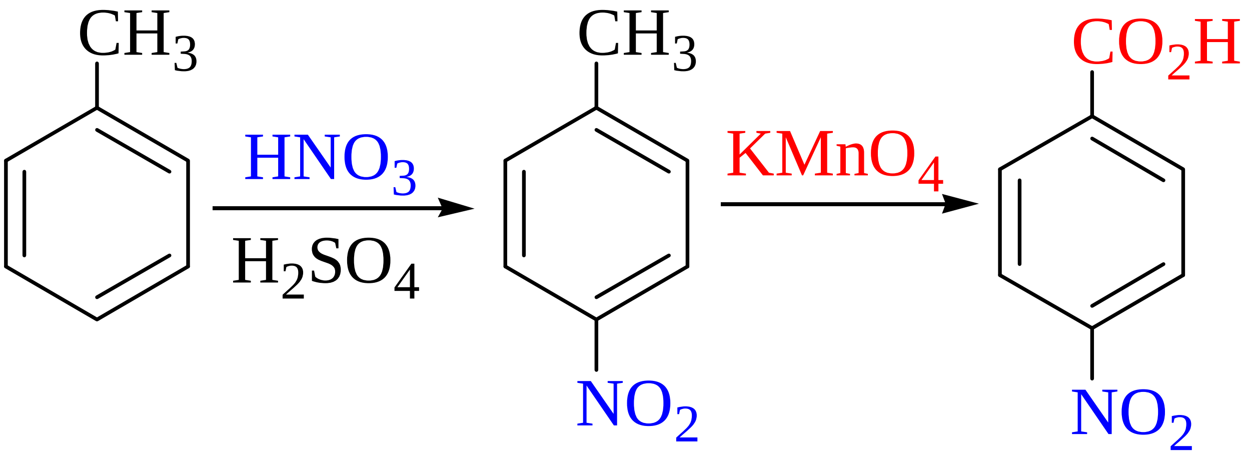


(3)



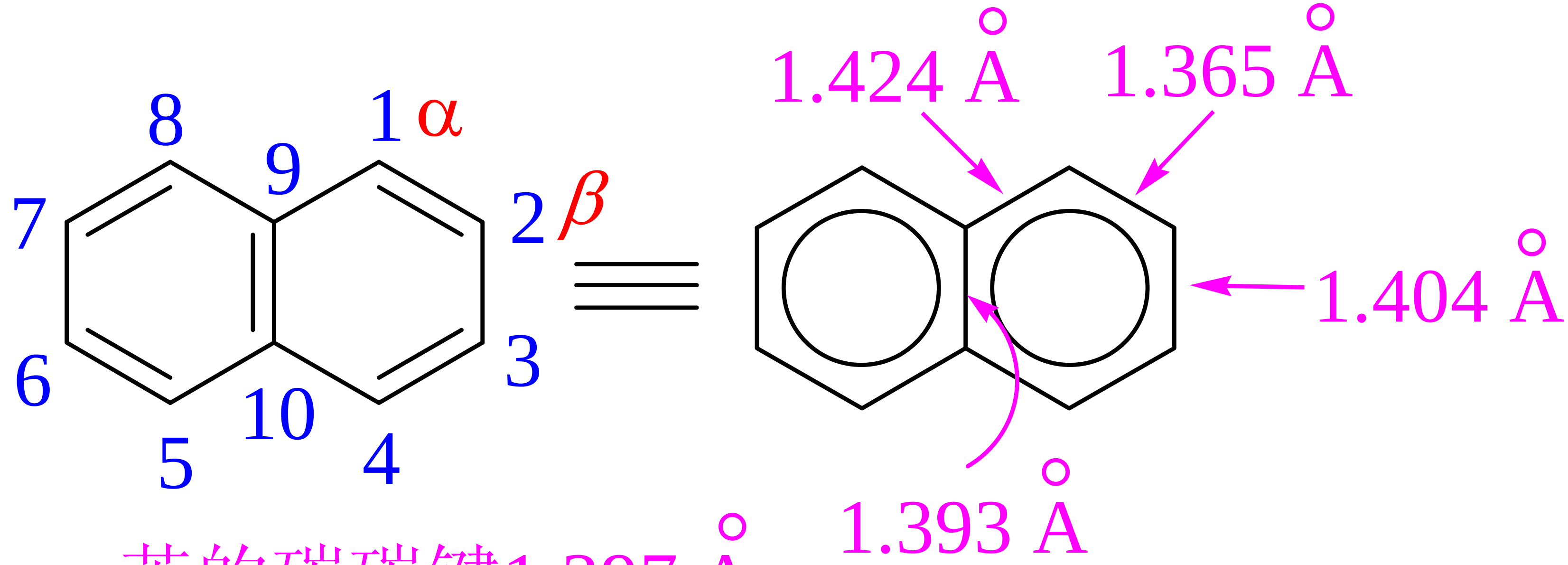
A： (1) 硝化 (2) 氧化

B： (1) 氧化 (2) 硝化



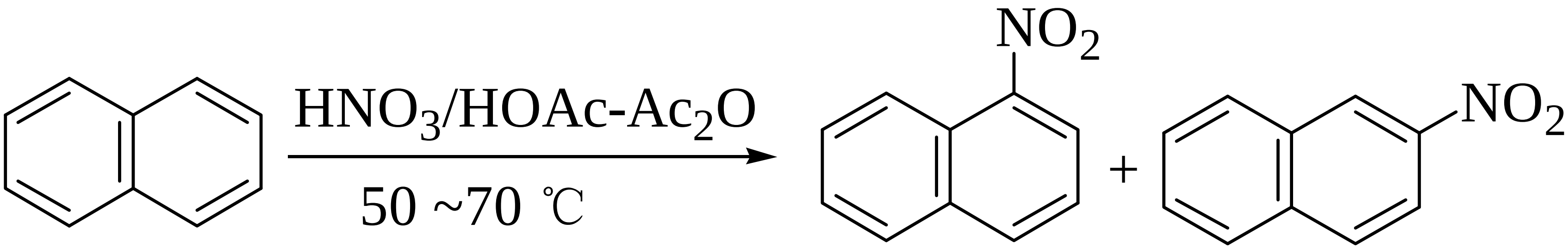
6.5 稠环芳烃

6.5.1 萘

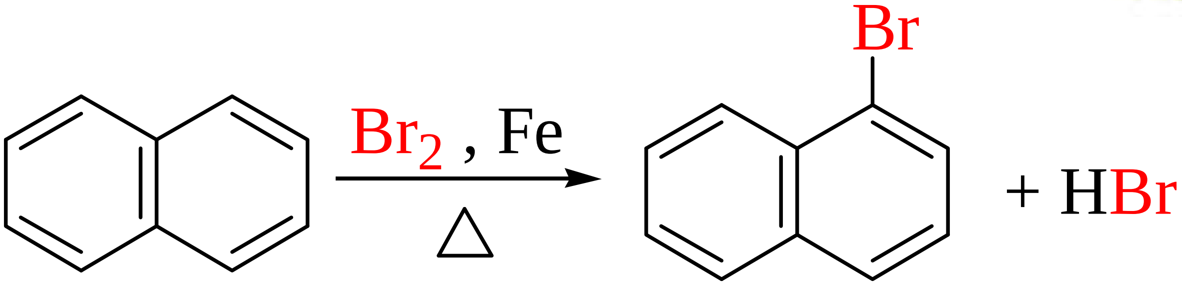


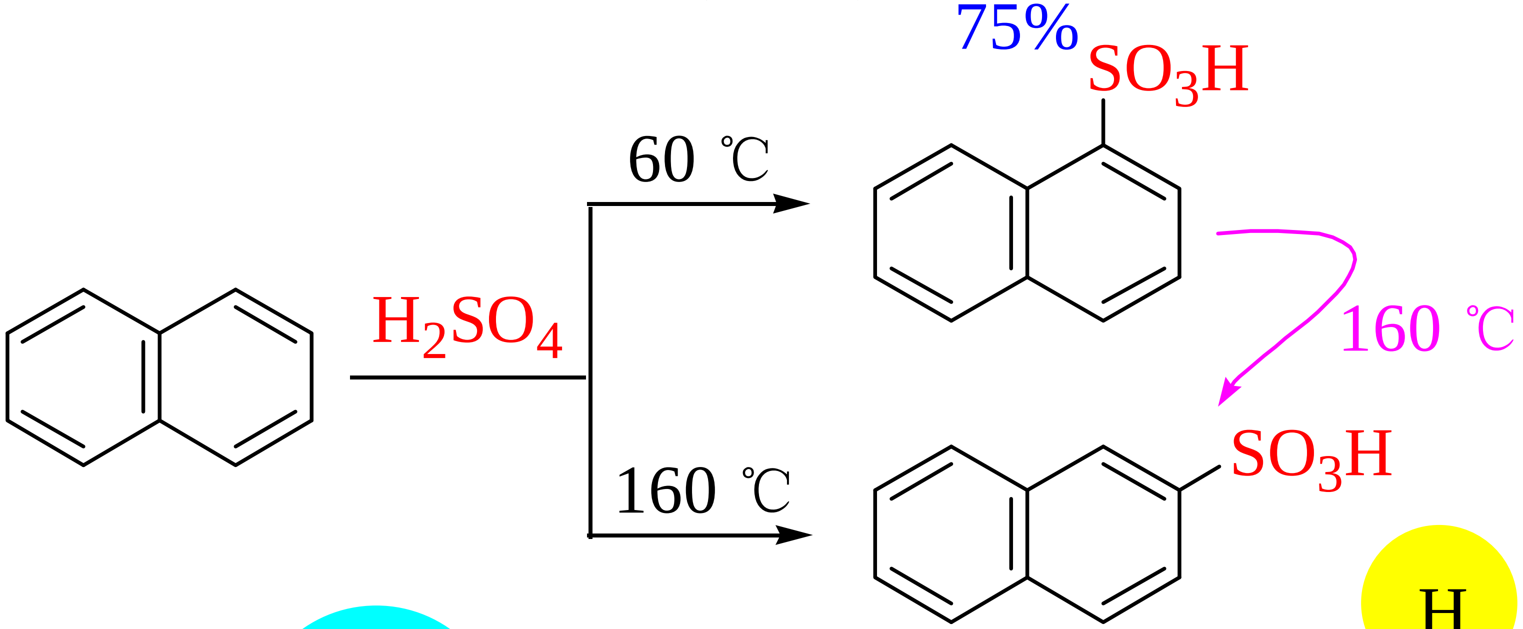
苯的碳碳键1.397 Å

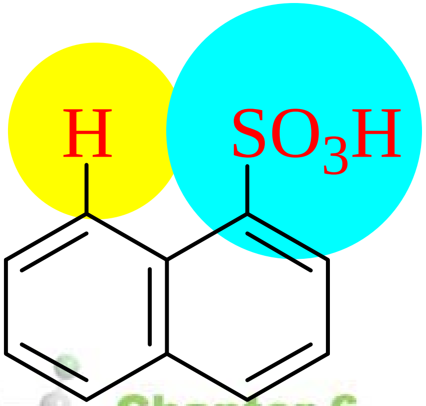
萘的亲电取代反应

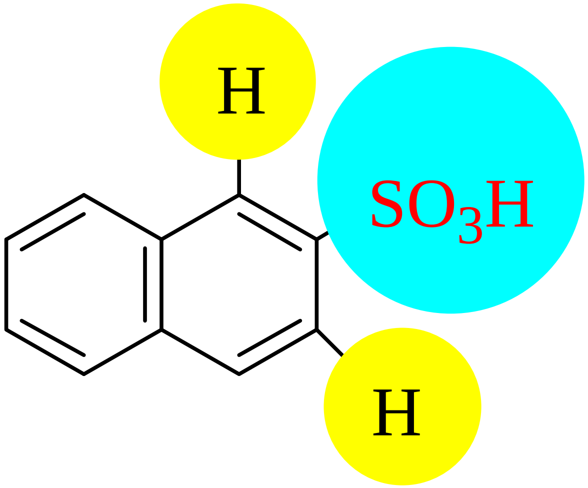


10 ： 1

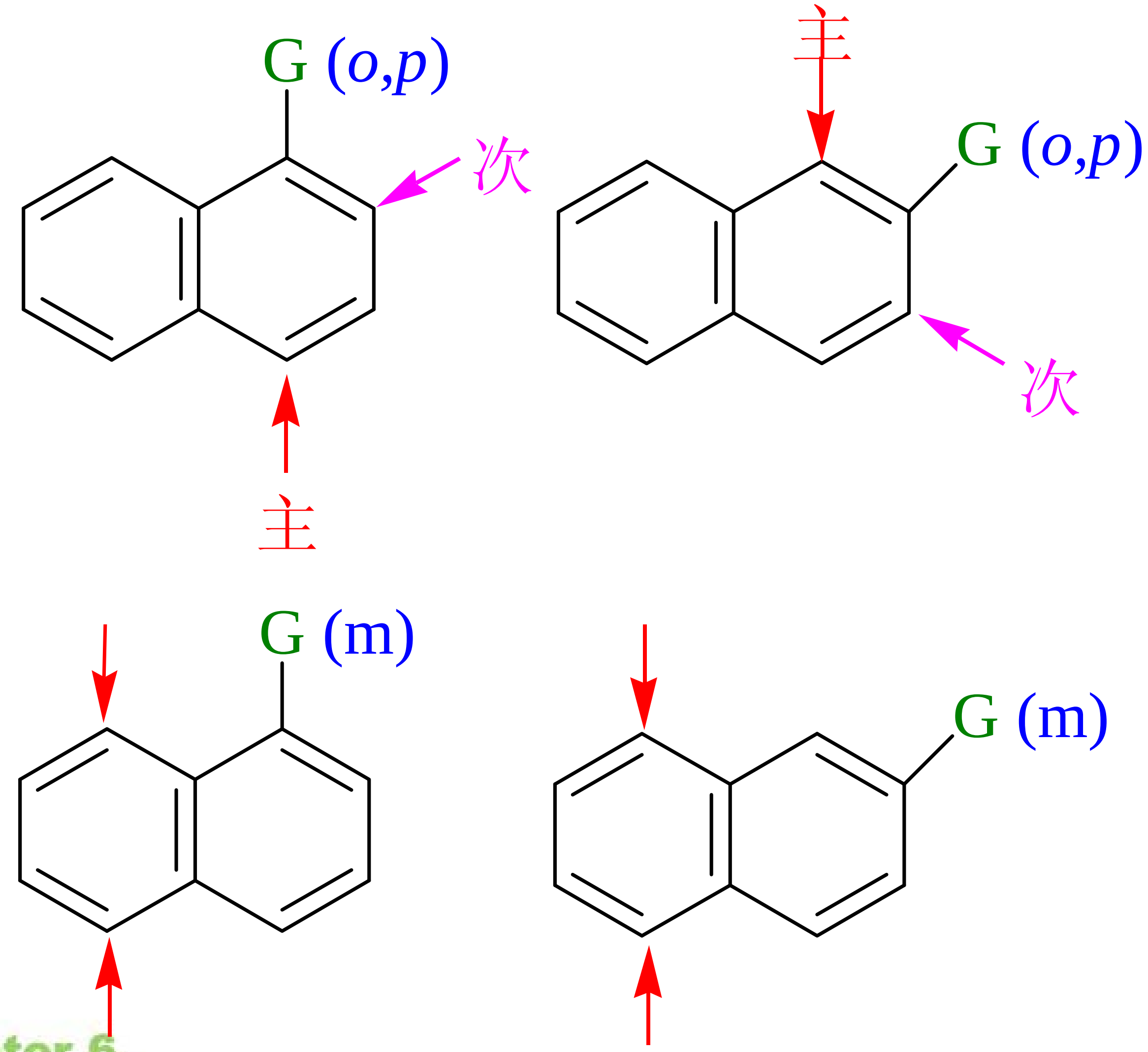

Br
Br_2 , Fe
△
+ HBr


75%
SO_3H
60 ℃
H_2SO_4
160 ℃
160 ℃
SO_3H

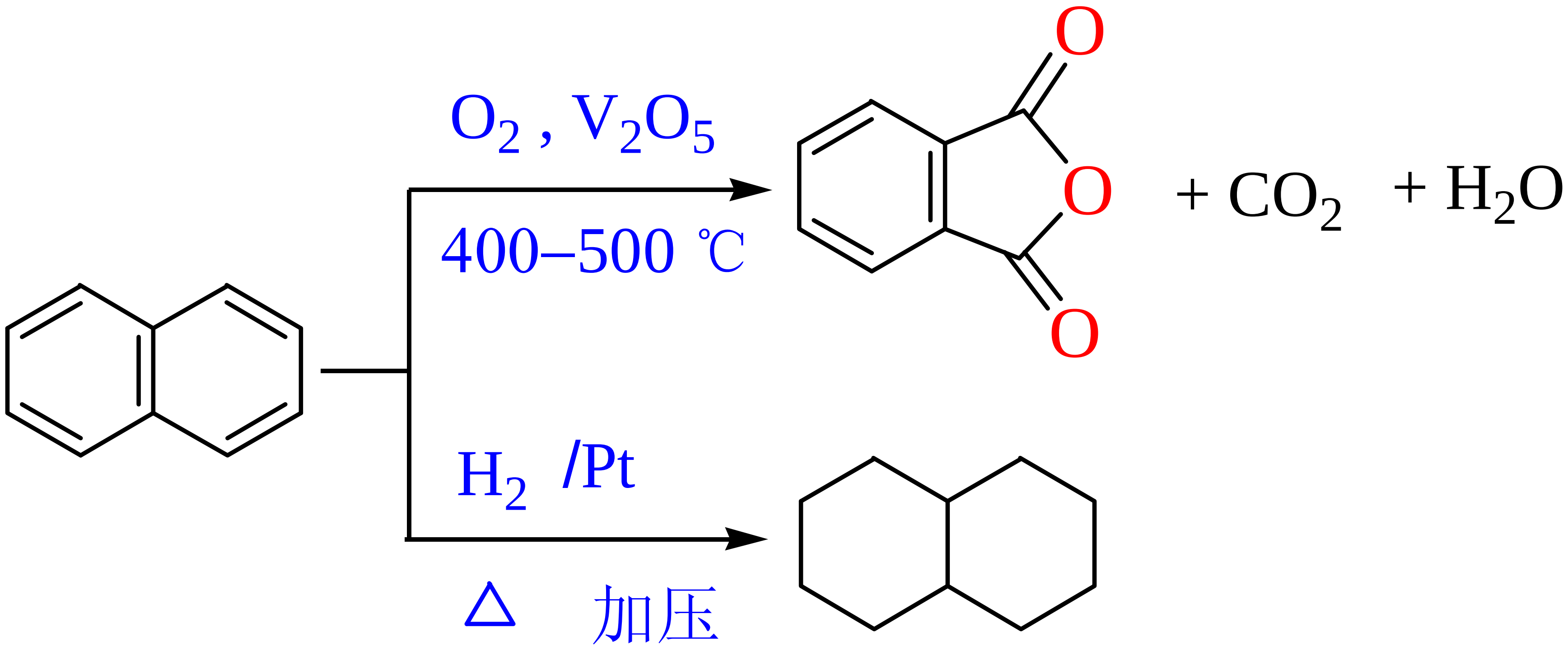

H
SO_3H


H
SO_3H
H

亲电取代反应的定位



萘的氧化还原反应

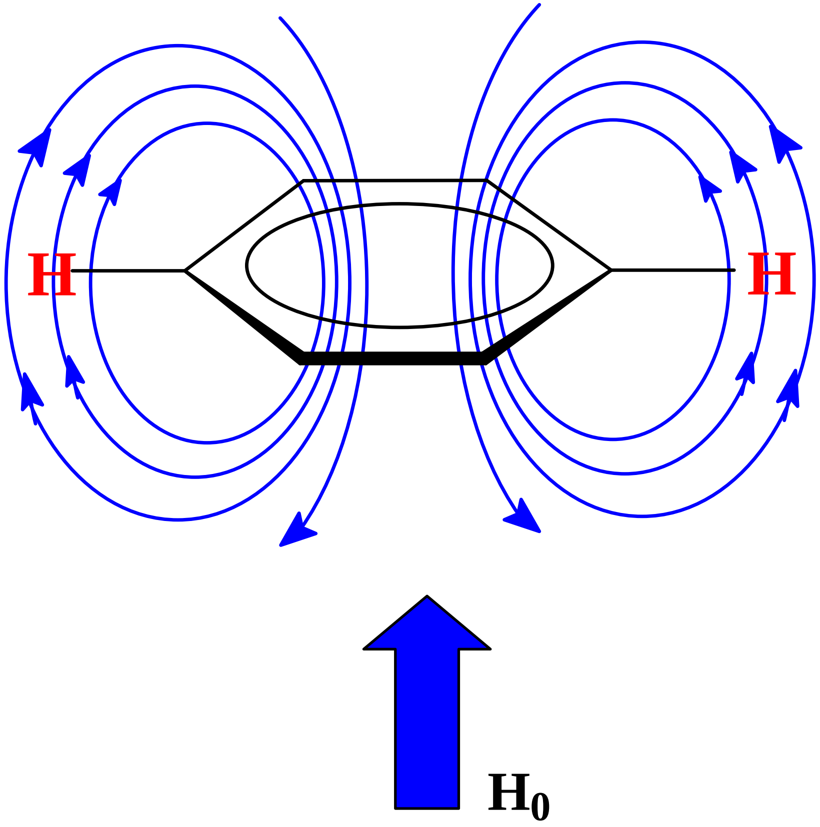


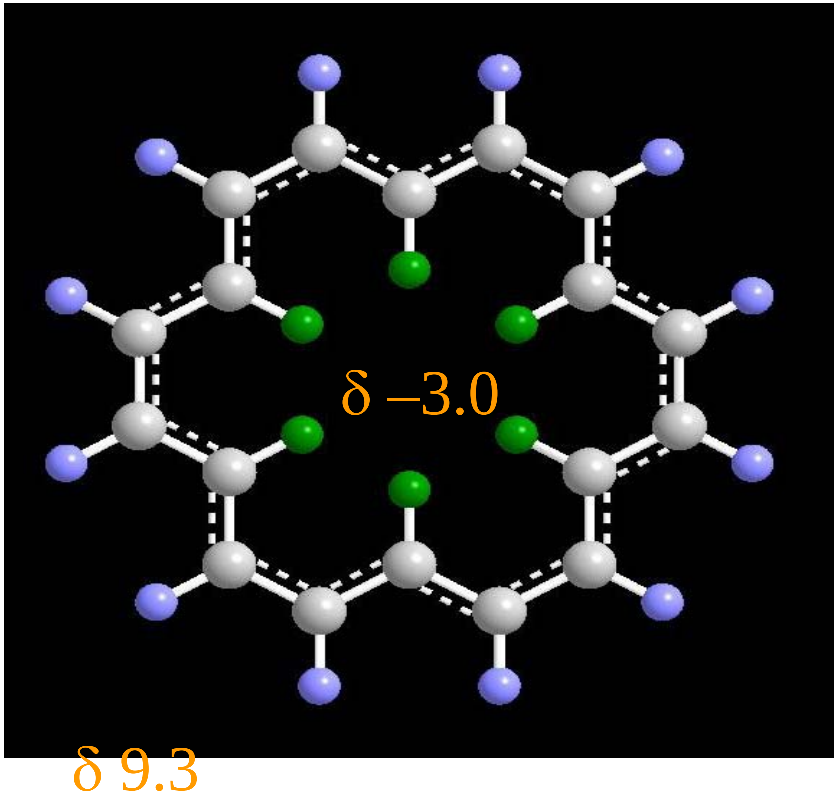
十氢萘

6.6 Hückel规则与芳香性

6.6.1 芳香性的特征

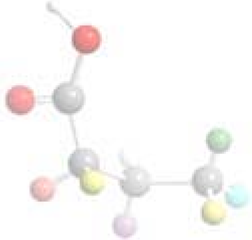
- C/H 比值大
- 具有特殊稳定性
- 易发生电取代反应，不易发生加成反应
- 核磁共振氢谱中环内外H化学位移差别大

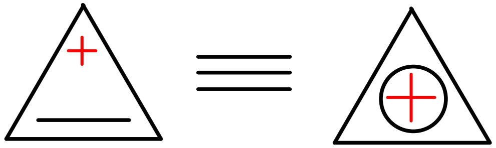

H
H
H_0

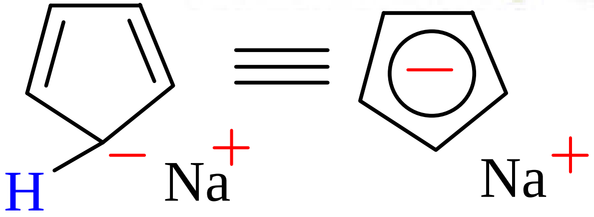

δ –3.0
δ 9.3

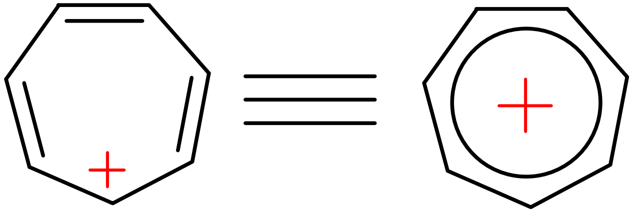
6.6.2 芳香性的判别

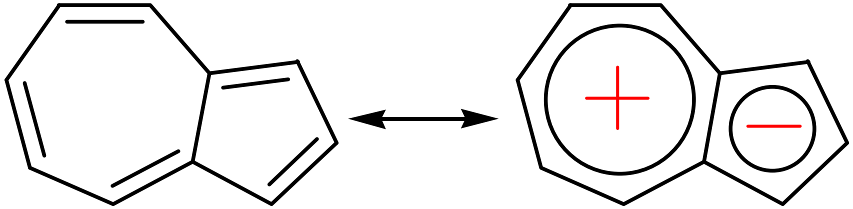
- 成环原子共处或者接近一个平面
- π键形成闭合环状共轭体系
- 闭合环状共轭体系 的π电子数符合**$(4n + 2)$**











薁