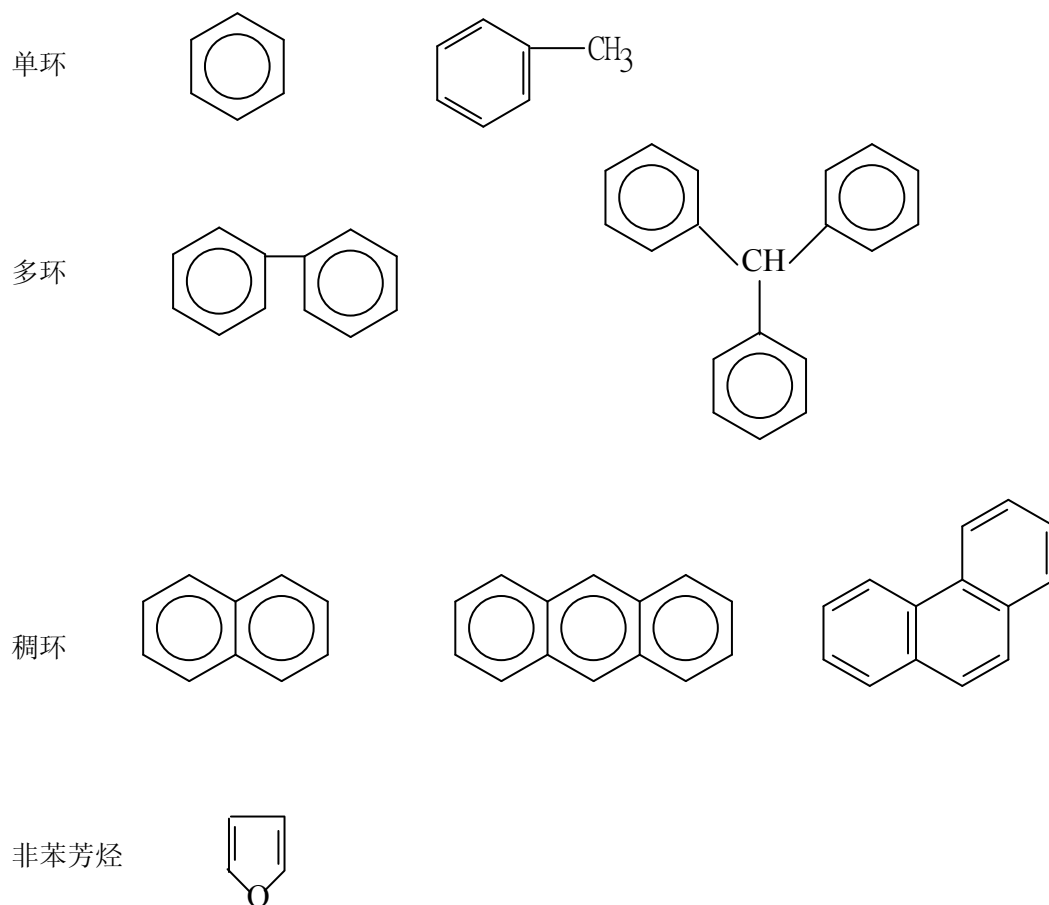


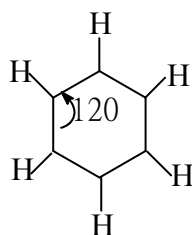
## 第六章 芳烃 芳香性



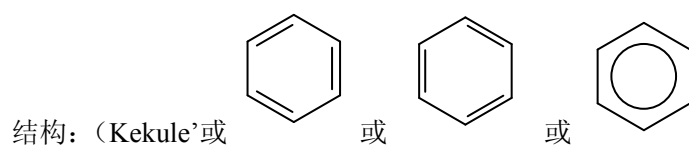
### (一) 苯的结构

#### 1. 价键理论

6 个 C, 6 个 H 在同一平面上

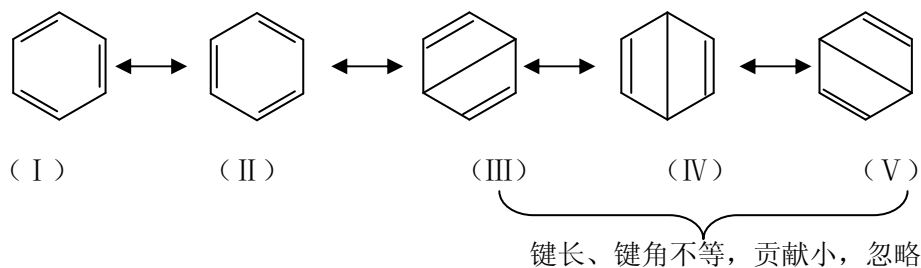


C 采用  $sp^2$  杂化 (2 个 C-C, 一个 C-H), 键长平均化 0.140nm  
 P 轨道侧面重叠— $\pi$  键



2. 分子轨道理论 P121

3. 共振论：苯的结构的表示方法



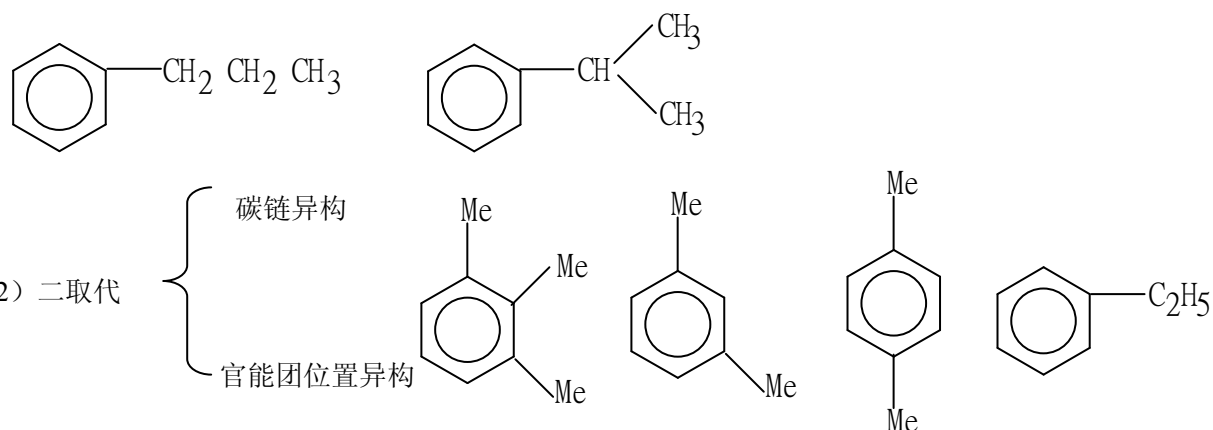
苯的结构介于 (I) 和 (II) 之间

4. 苯环的稳定性：(氢化热) P88-89

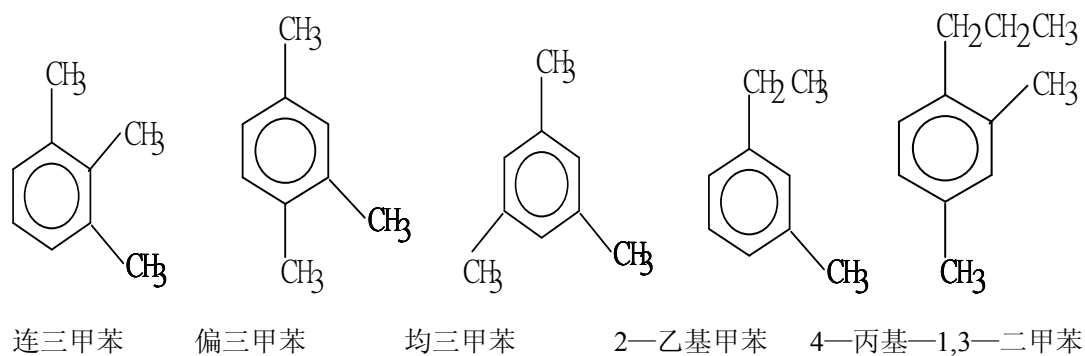
## (二) 单环芳烃的同分异构和命名

1. 同分异构

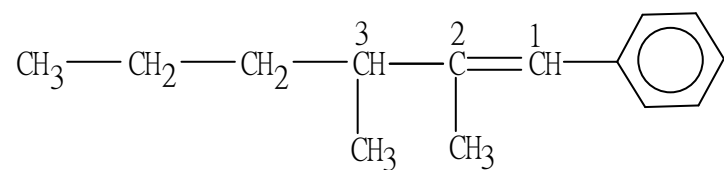
1) 一取代：(碳链异构)



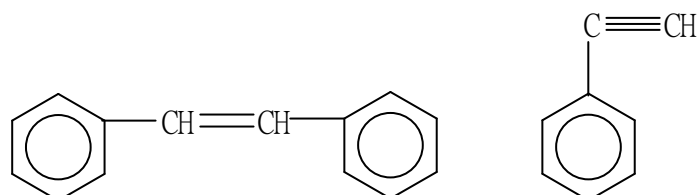
2. 命名：



当烃基结构复杂时，可以苯基为取代基，烃基为母体



2, 3-二甲基-1-苯基-1-己烯



二苯乙烯

苯乙炔

苄基:  $\text{C}_6\text{H}_5\text{CH}_2-$

芳基:  $\text{Ar}-$

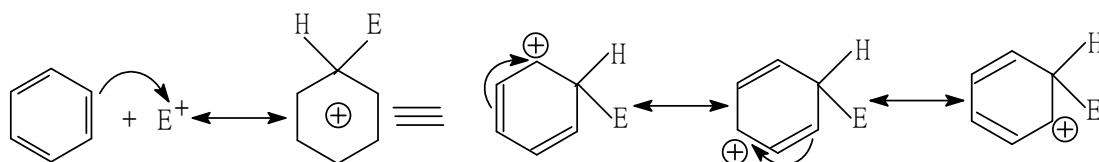
略(三) 单环芳烃的来源(自学) P155-156

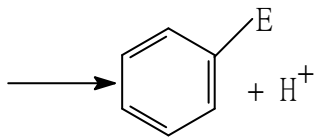
(三)、(四) 物性

1.  $d < 1$ , 溶于有机溶剂
2. 对位异构体的 mp 较高
3. 取代基增多, 稳定性增大
4. NMR、IR  $3030\text{cm}^{-1}$  伸缩 1625-1575 场面 1525-1475 (S) 两个峰, 指纹区: 环上邻接 C-H 的特征:

## 四 化性

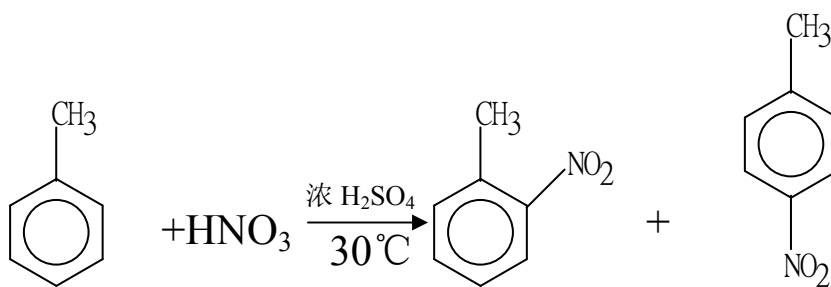
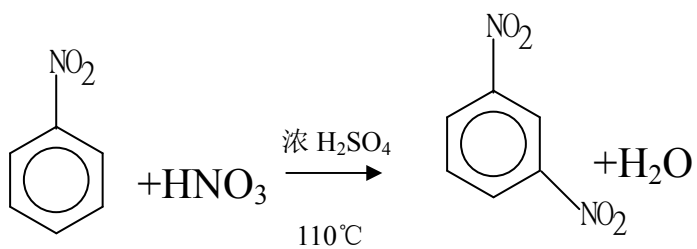
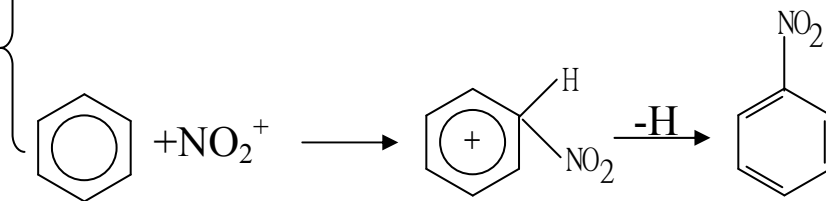
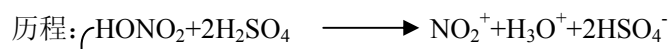
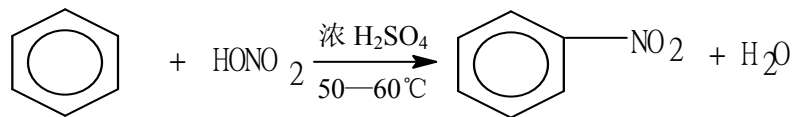
一、亲电取代反应 (electrophilic substitution)



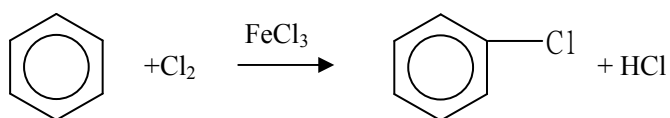


能量曲线图: P126 (照书讲)

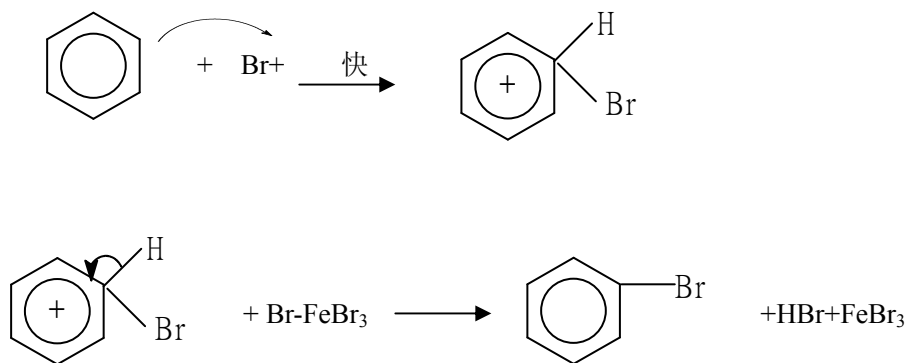
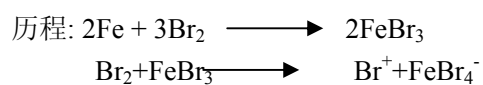
### 1. 硝化反应



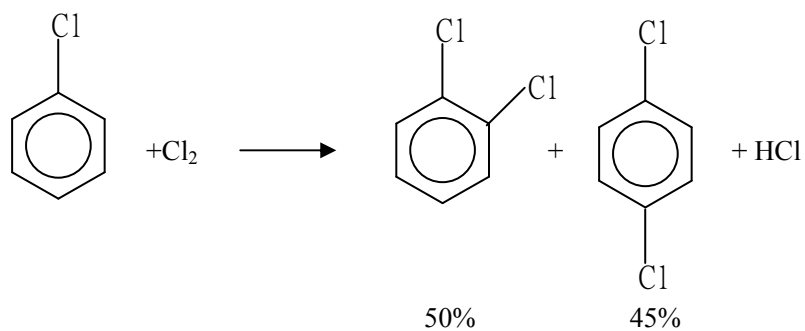
### 1. 卤化反应



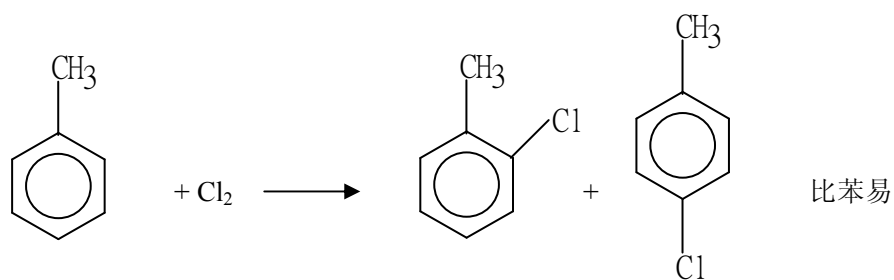
活性  $F_2 > Cl_2 > Br_2 > I_2$   
 常用



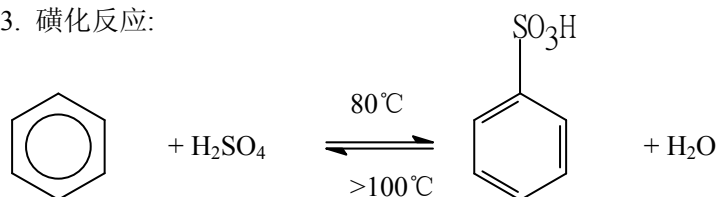
副反应



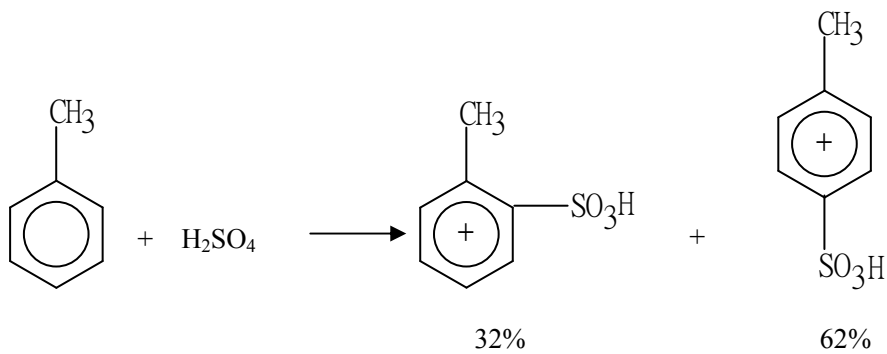
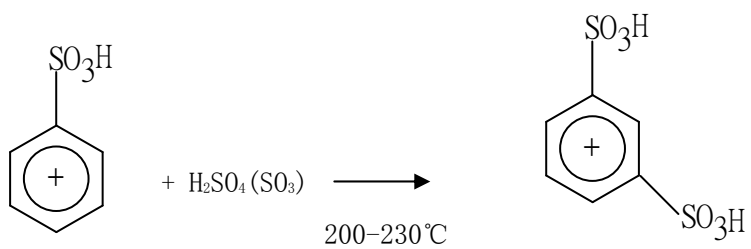
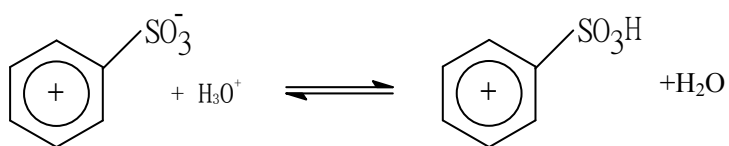
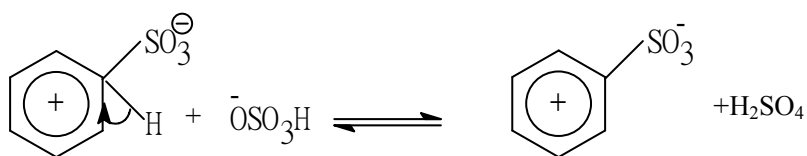
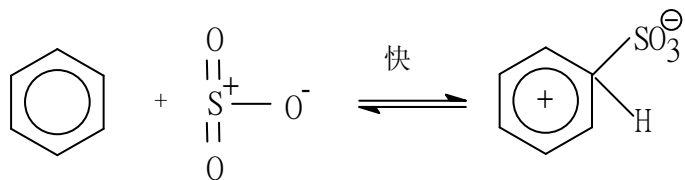
或甲苯



3. 磺化反应:



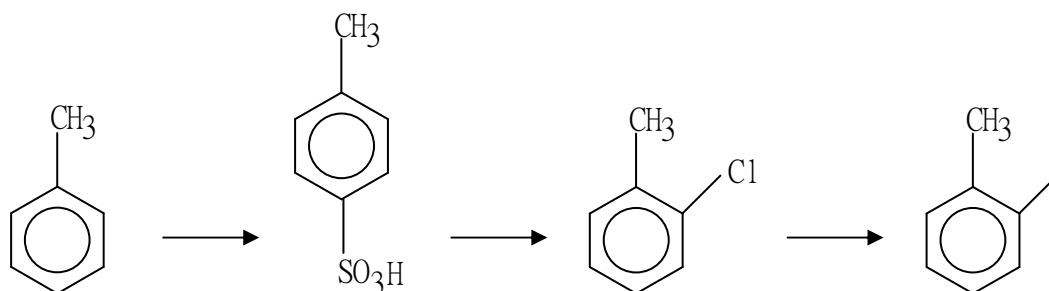
历程:



应用: 1. 引入  $\text{SO}_3\text{H}$ , 增加化合物的酸性和水溶性

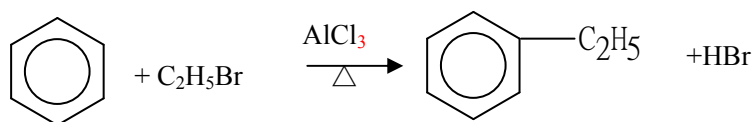
2. 保护基, 定位基

eg



#### 4. Friedel-Crafts 反应

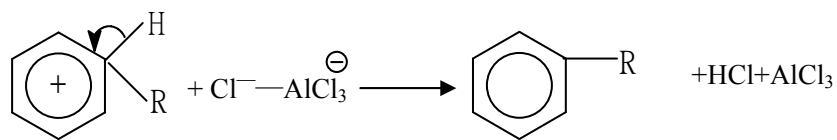
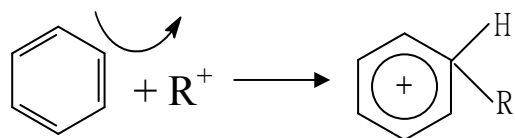
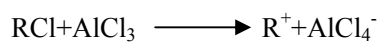
(1) 烷基化:



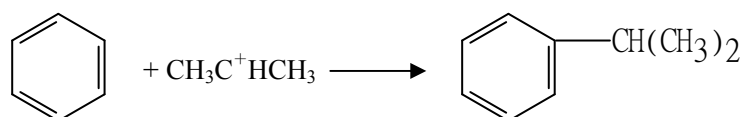
(卤代烃, 烯烃, 醇)

常用催化剂:  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{BF}_3$ ,  $\text{H}_2\text{SO}_4$  等

历程:

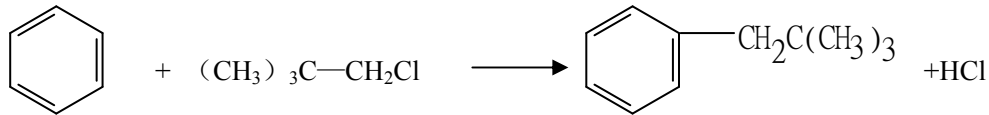


有重排:



70%

但若用  $\text{FeCl}_3$ , 则几乎无重排产物

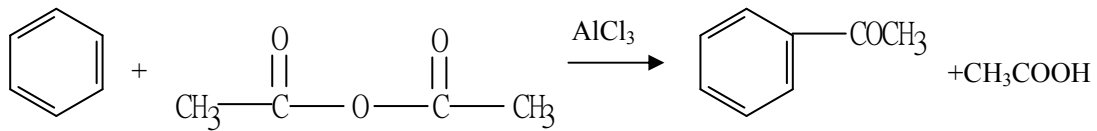
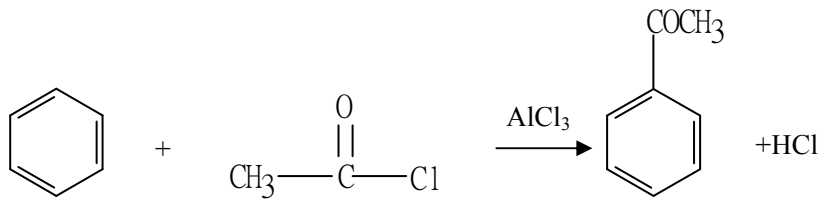


\*温度越低，重排产物越少

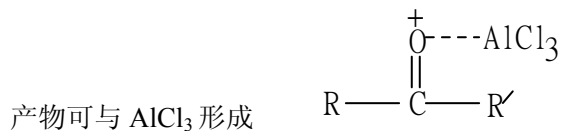
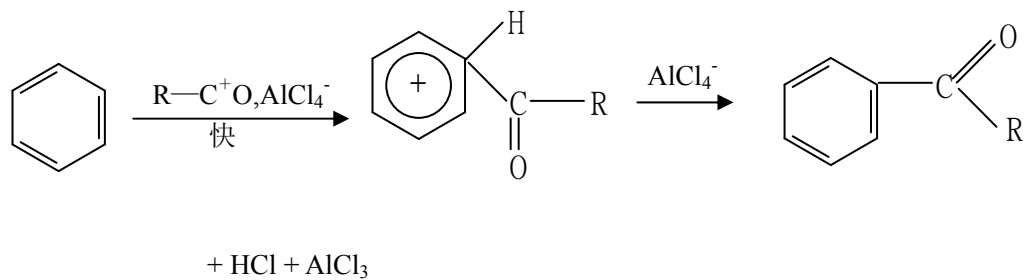
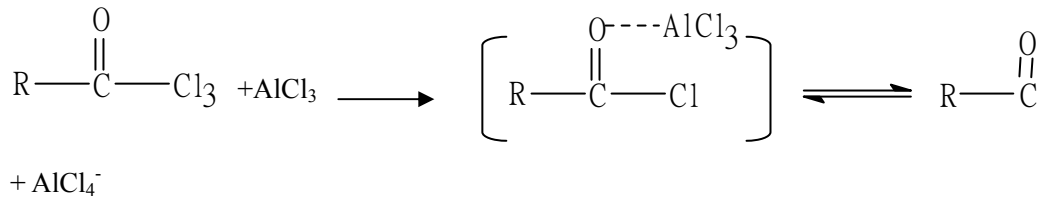
\*烷基苯比苯更容易反应，因而反应中带有多个烷基苯生成

\*芳烃 +  $\text{CHCl}_3 \xrightarrow{\text{AlCl}_3}$  深色（用于检验芳烃） P96

(2) 酰基化: (acylation)



历程:

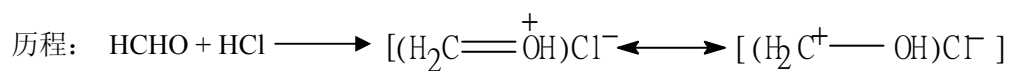
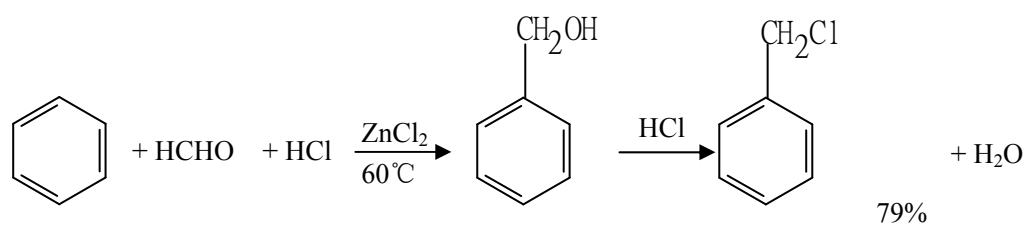


所以  $\text{AlCl}_3$  用量比烷基多 1mol

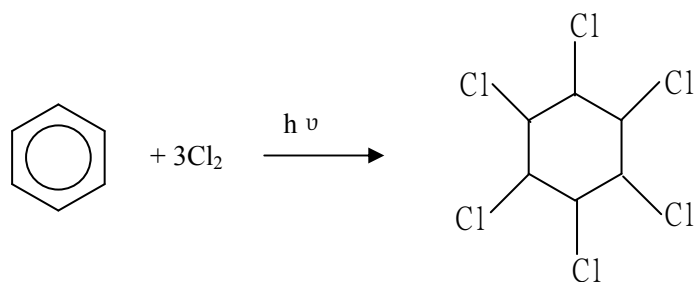
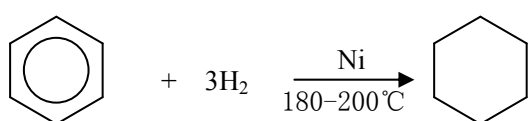
- 苯环上有强吸电子基时，不起付克反应
- 所以硝基苯可用作付克反应的溶剂



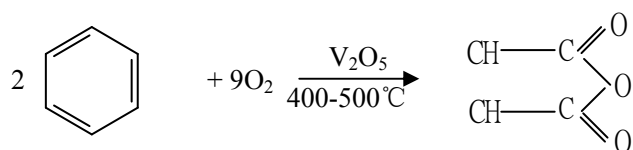
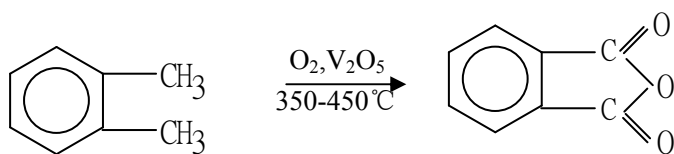
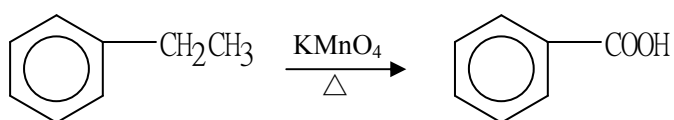
(3) 氯甲基化反应 (chloromethylation)



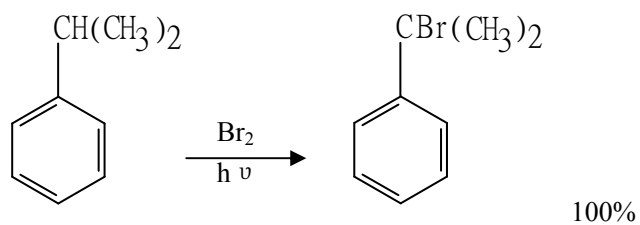
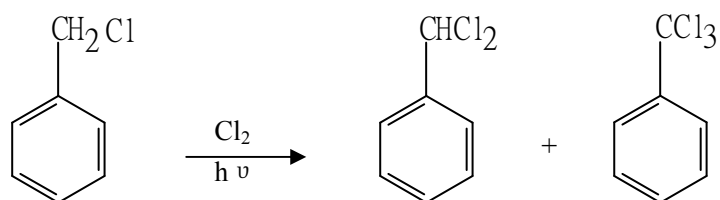
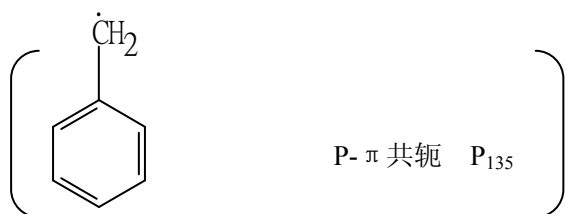
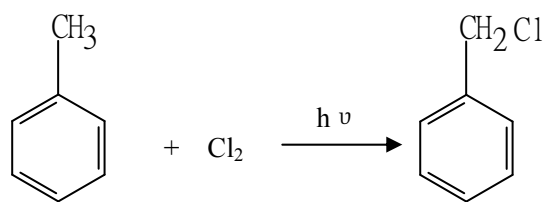
二、加成反应



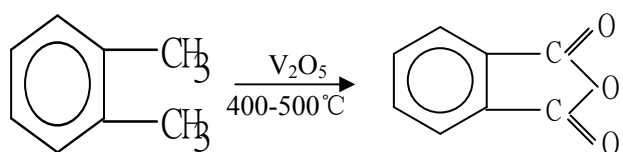
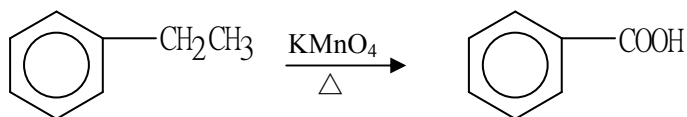
三. 氧化



四. 侧链  $\alpha$ -卤化反应:



烷基苯氧化—苯甲酸



(六) 取代定位规则

1. 两类定位基

(1) 第一类定位基 —邻对位定位基: (除卤素外, 活化苯环) **P136**

—O、—NR<sub>2</sub>、—NHR、NH<sub>2</sub>、—OH、—NHCOR、—OCOCH<sub>3</sub>、—CH<sub>3</sub> (—R)、—Cl、—Br、—I、—C<sub>6</sub>H<sub>5</sub> 等

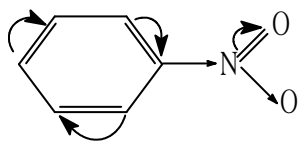
(2) 第二类定位基 —间位定位基: (吸电子基, 钝化苯环)

—NR<sub>3</sub>、—NO<sub>2</sub>、—CF<sub>3</sub>、—CCl<sub>3</sub>、—CN、—SO<sub>3</sub>H、—CHO、—COR、—COOH、—COOR、—CONH<sub>2</sub> 等

2. 定位规则的理论解释 (+I, +C, 活化苯环, —I, —C, 钝化苯环)

(1) 间位定位基对苯环的影响

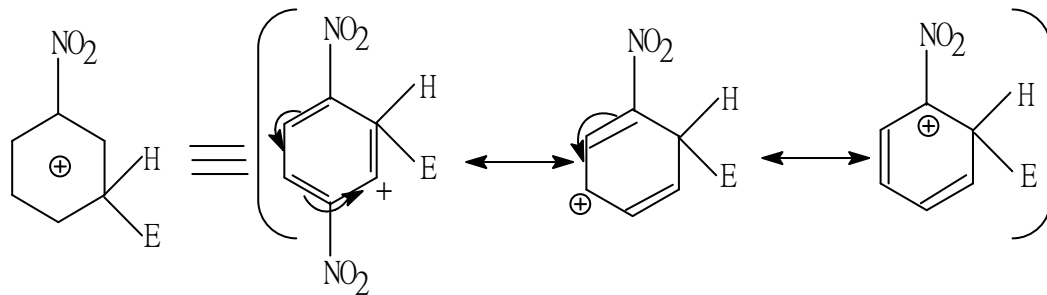
eg



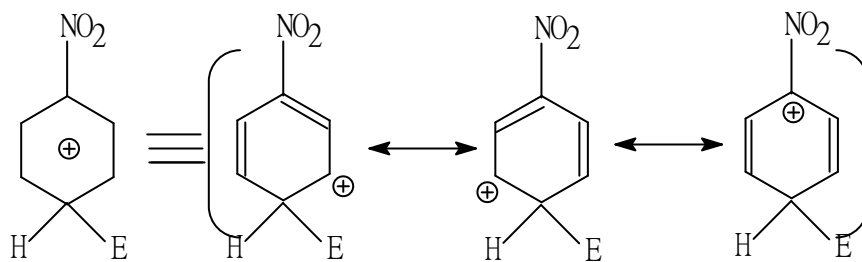
—I —C 硝基苯比苯活性小

共振论:

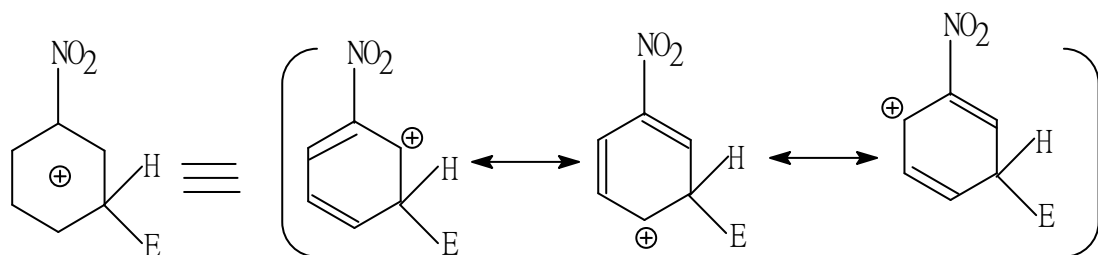
**P122** 邻



对

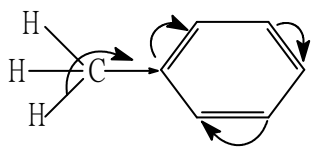


间



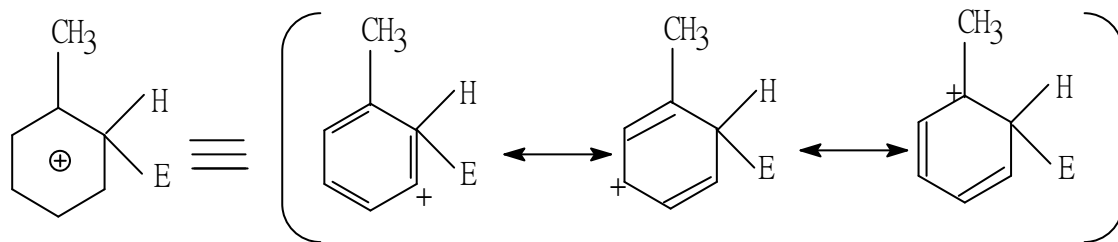
(2) 邻对位定位基对苯环的影响

(1) 甲基和烷基

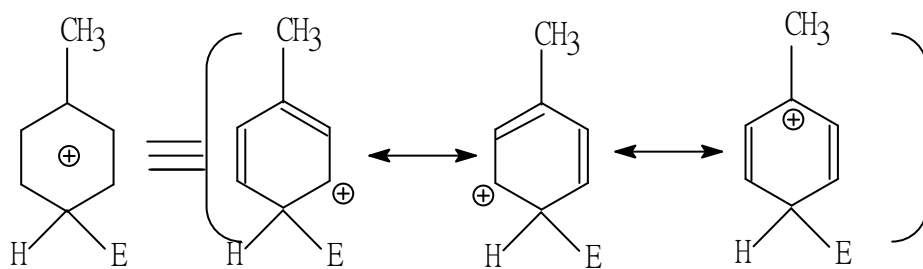


+H +C 甲苯比苯活性大

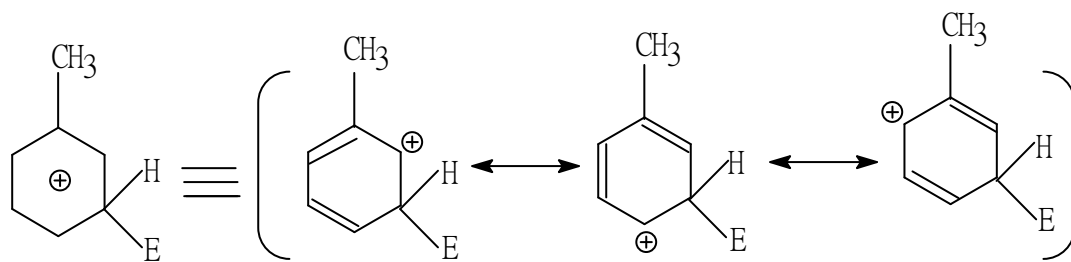
邻



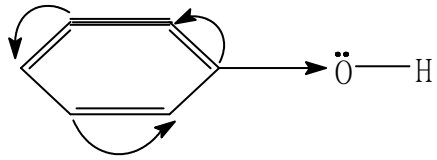
对



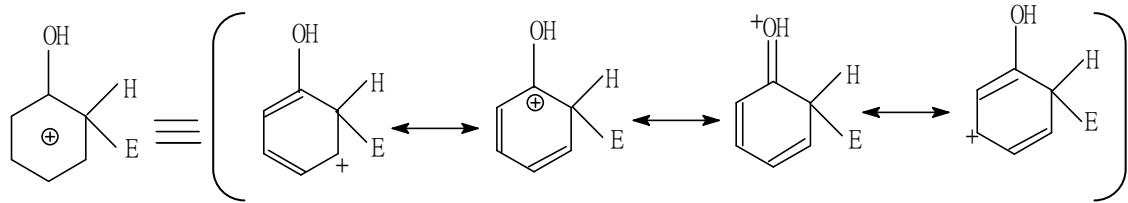
间



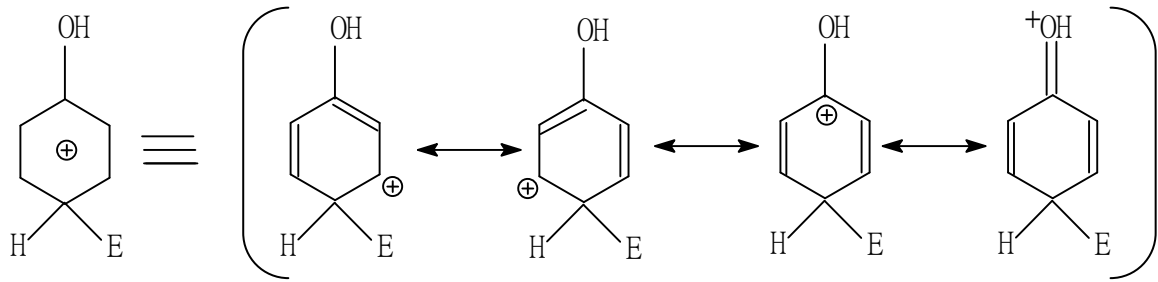
b) 羟基、氨基等 +C>—I 活化苯环 P141 照书讲



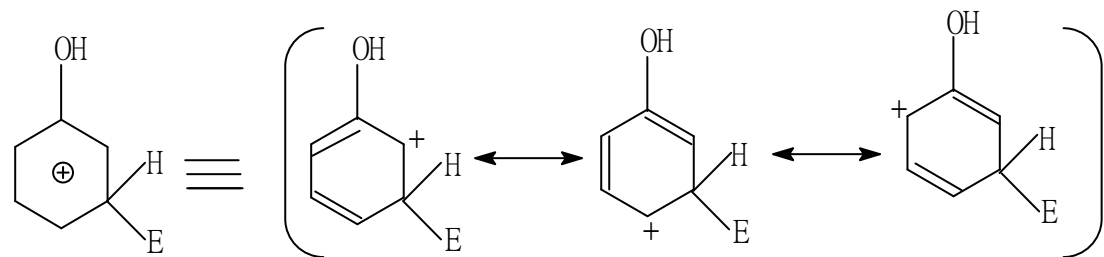
邻



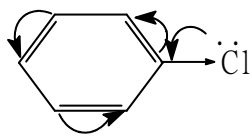
对



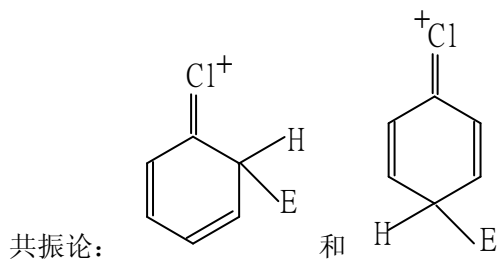
间



卤素：钝化苯环



—I>+C (邻对位电子云密度大于间位)



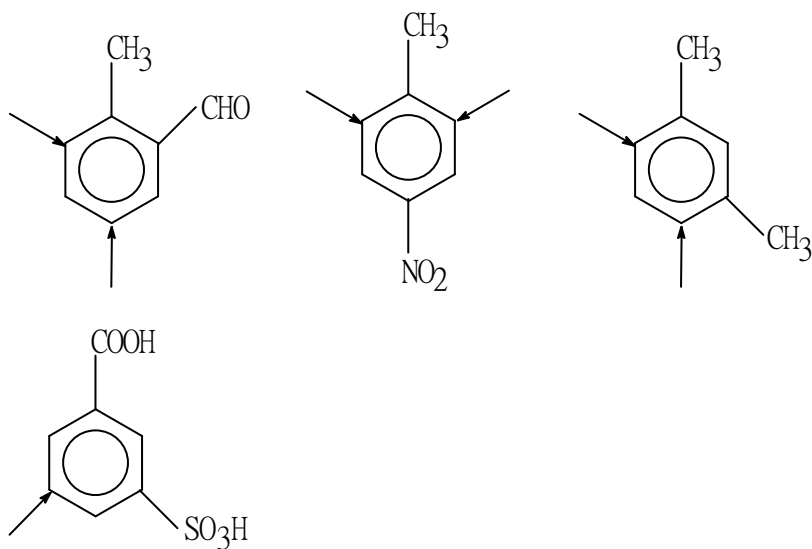
(3) 空间效应

a) 对第一类定位基而言: 取代基越大, 对位产物越多; 进攻基团越大, 对位产物越多 P143, 表 6-4, 6-5

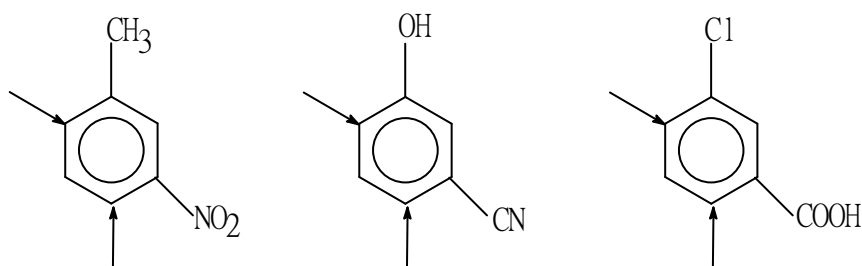
b) 两取代基互为间位时, 第三个取代基进入两取代基之间较少

(4) 两取代基的定位规律

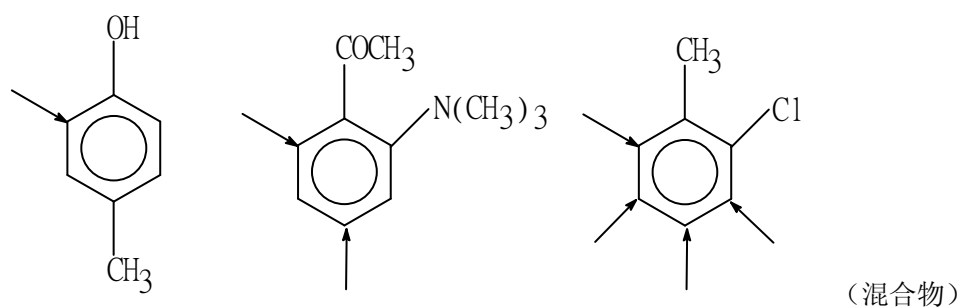
a) 两取代基定位效应一致



b) 两取代基定位效应不一致, 以第一类定位基为主

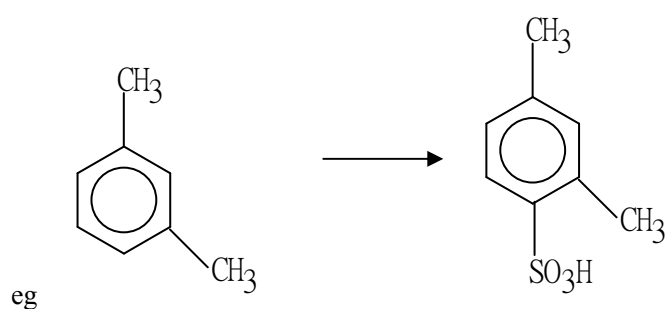


c) 两取代基为同一类，但定位效应不一致，由定位效应强的决定



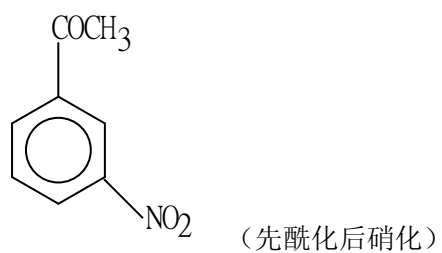
(5) 取代定位规律的应用

a) 预测反应产物

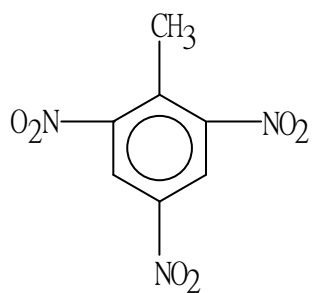


(且易于邻对二甲苯，工业用于分离纯化)

b) 设计合成路线



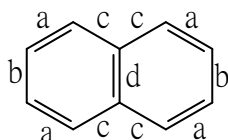
## (八) 重要的芳烃



(TNT) trinitrotoluene

## (九) 稠环芳烃

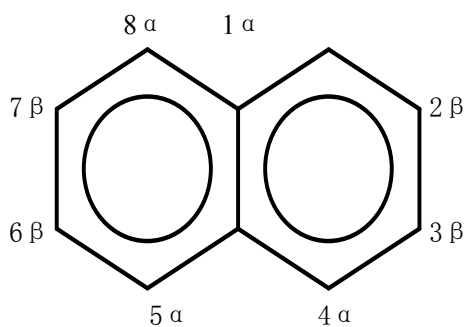
### 1. 萘 C<sub>10</sub>H<sub>8</sub>



#### 1) 结构 P147

a=0.136nm b=0.140nm c=0.142nm d=0.139nm

共平面



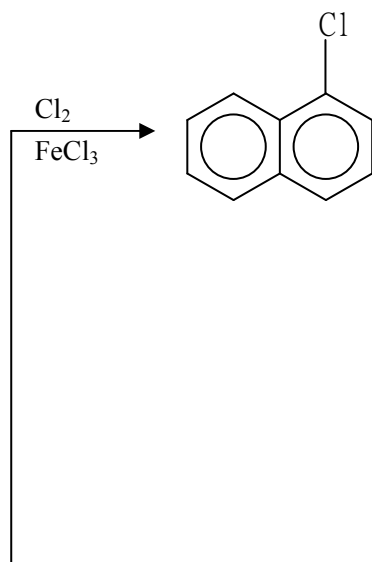
α—取代 (α 位电子云密度较高)

β—取代 (β 位电子云密度较低)

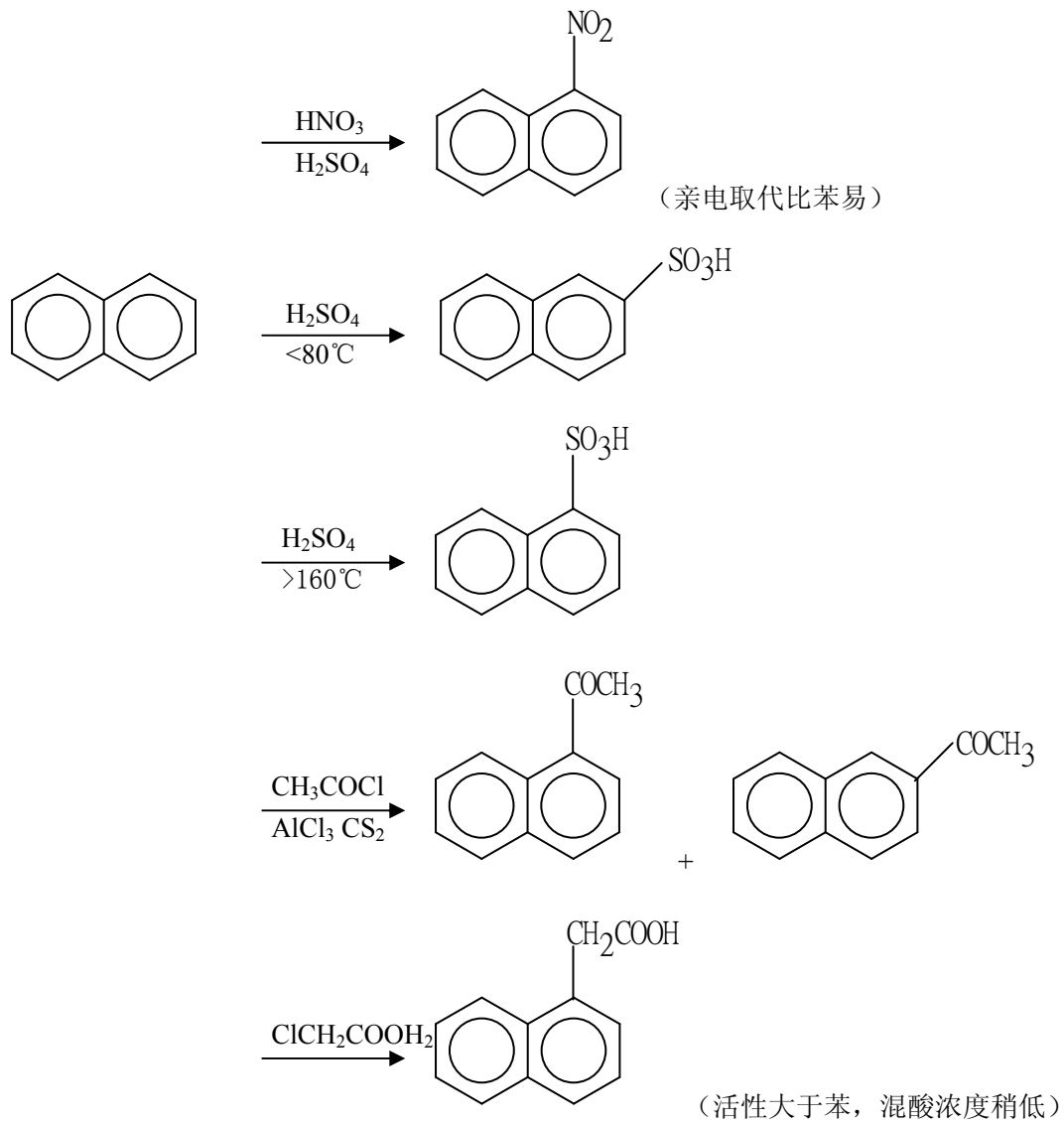
二取代的取代基相同时有 10 种, 不同时 14 种

2) 性质: mp 80.2°C, bp 218°C, 易升华

a) 取代反应:





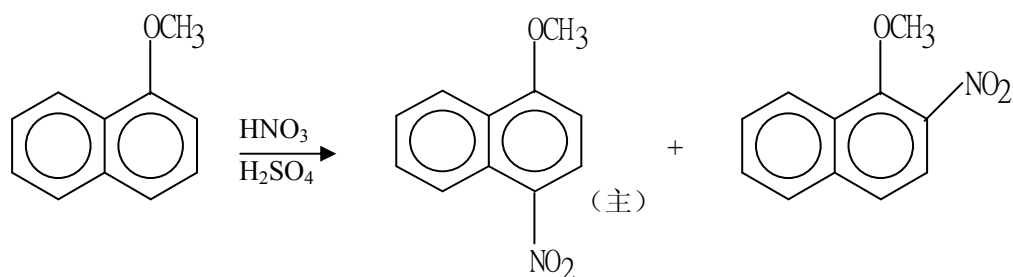


( $\alpha$ -萘乙酸), 植物生长调节剂, HAA, 对人蓄无害。

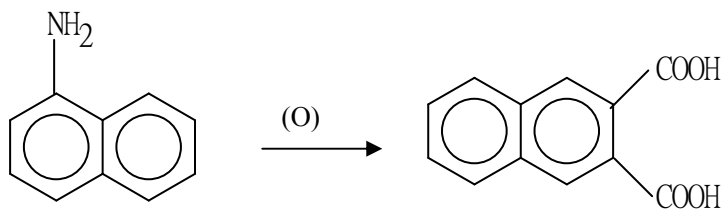
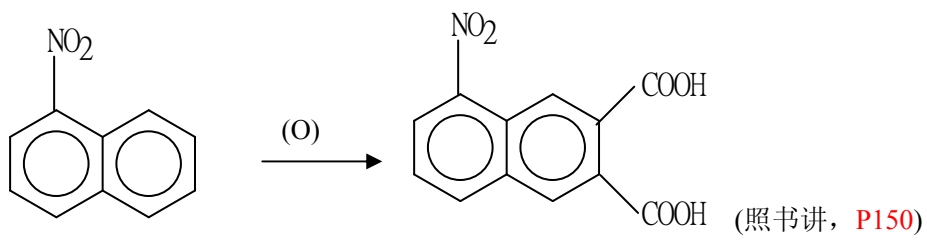
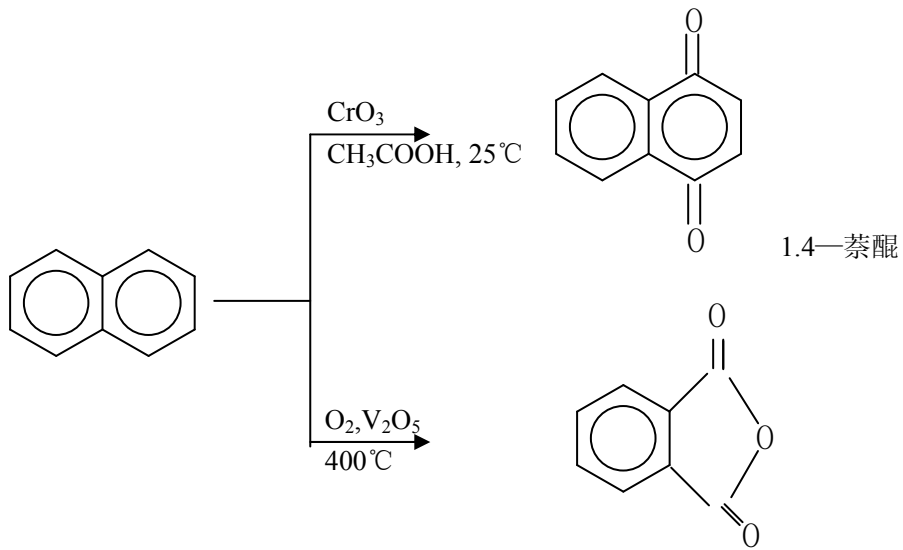
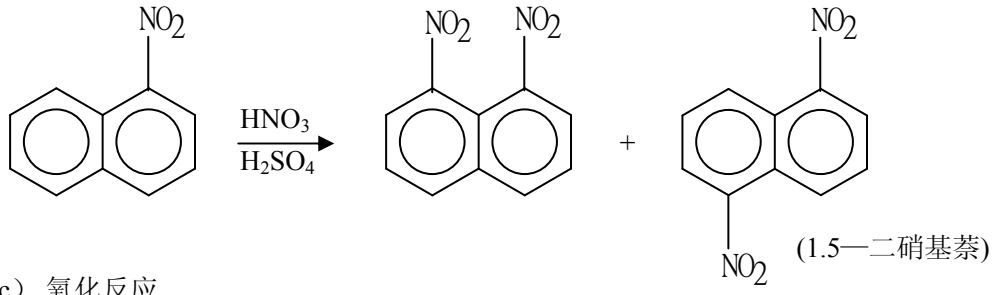
烷基化易生成多烷基萘，且萘环易破裂——无意义。

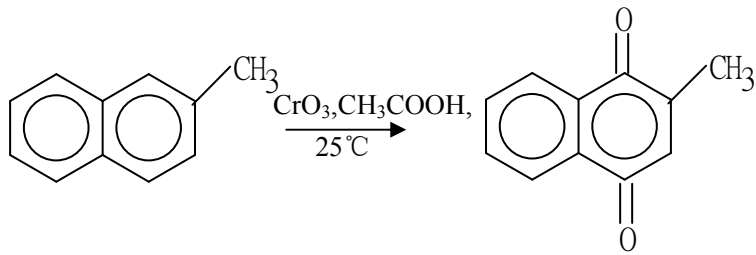
b) 定位规则

(1) 第一类定位基时——同环取代 ( $\alpha$  位为主)

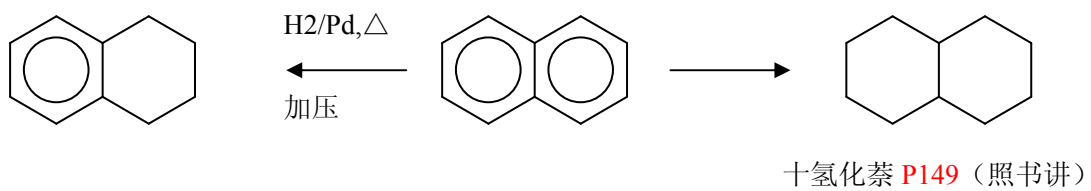
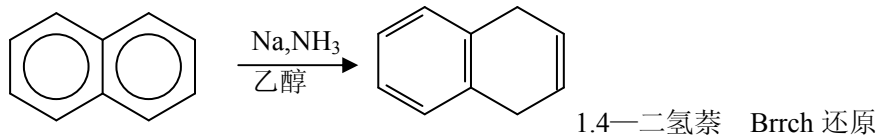


(2) 第二类定位基——异环取代 (一般  $\alpha$  位)

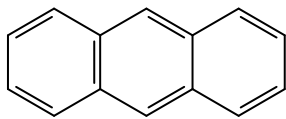




c) 还原

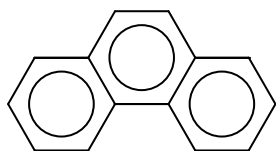


2. 蒽



取代、氧化、双烯合成

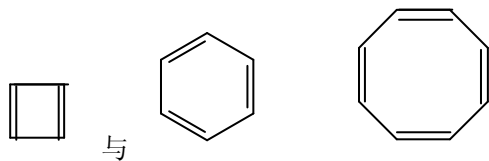
2. 菲



3. 其他: P150-151 照书讲

(十) 芳香烃 (aromaticity)

芳香烃的状态: 能量低, 稳定, 易取代, 难加成: 键长平均化 C/H 比例高  
人们发现:



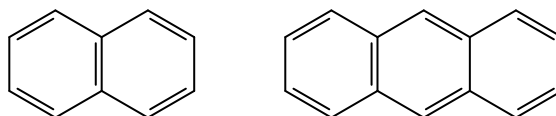
具有烯烃的性质

1. 芳香性和 Huckel 规则

单环共轭多烯分子与成环原子都处于同一平面，且离域的  $\pi$  电子数是  $4n+2$  时，该化合物具有芳香性——也称  $4n+2$  规则 ( $n=0, 1, 2, \dots$ )，具有  $4n$   $\pi$  电子的单环化合物不稳定，具有反芳香性。

(1) 苯 萘和蒽

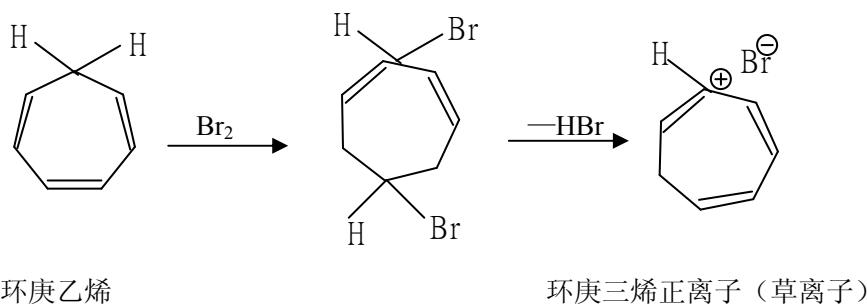
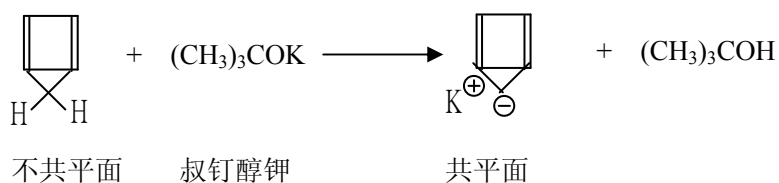
$C_6H_6$   $C_{10}H_8$   $C_{14}H_{10}$



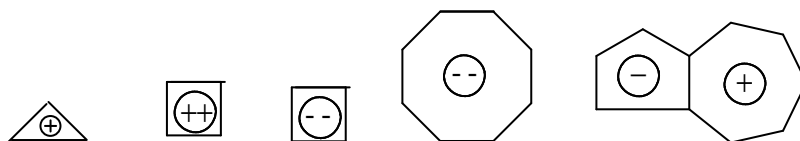
(2) 轮烯

P413 P114 特殊 [10] 轮烯不共平面，无芳香性

(3) 芳香离子



此外:

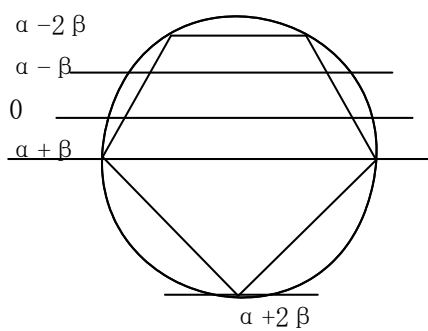


(天蓝色固体) mp:  $90^\circ C$

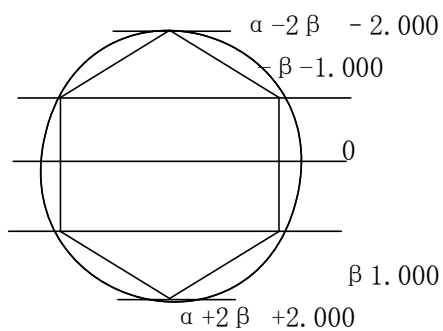
2. 芳香性和分子轨道理论: P153 照书讲

DRE(共轭能) $=E_\pi - E_{\text{定域}}$  Dewar 称之为共轭能

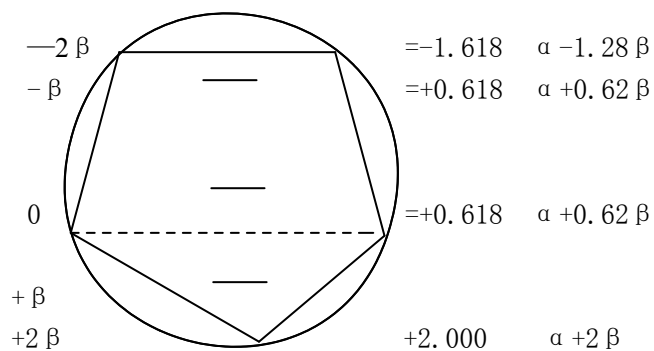
为了求得具有  $K$  个原子的环体系的分子轨道能级，Frost 和 Muoulin 作图法表示 Huckel 方程 ( $\beta$  为负值)



K=5



K=6



1. 下列反应有无错误？若有，请予以改正

