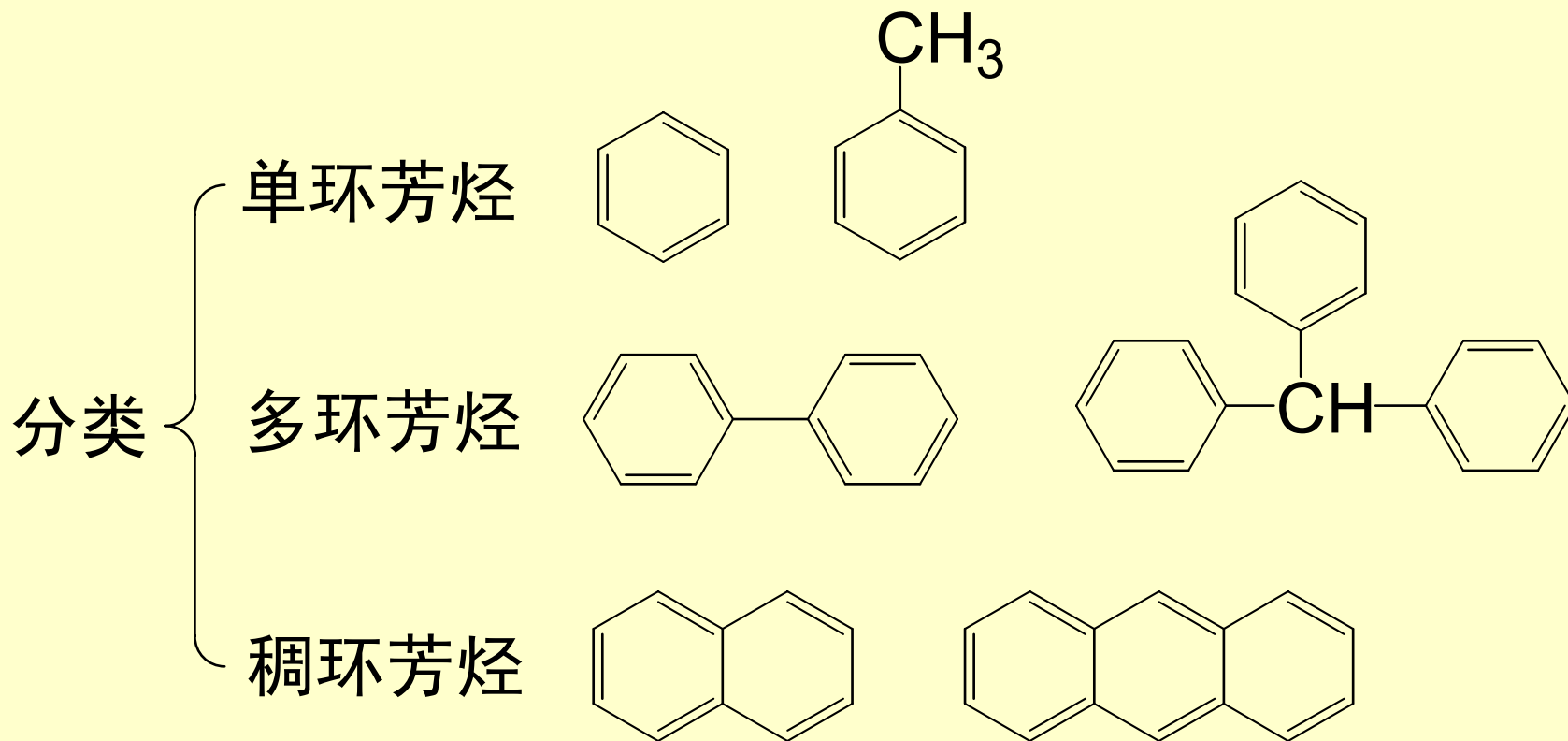


# 第七章

# 芳 烃

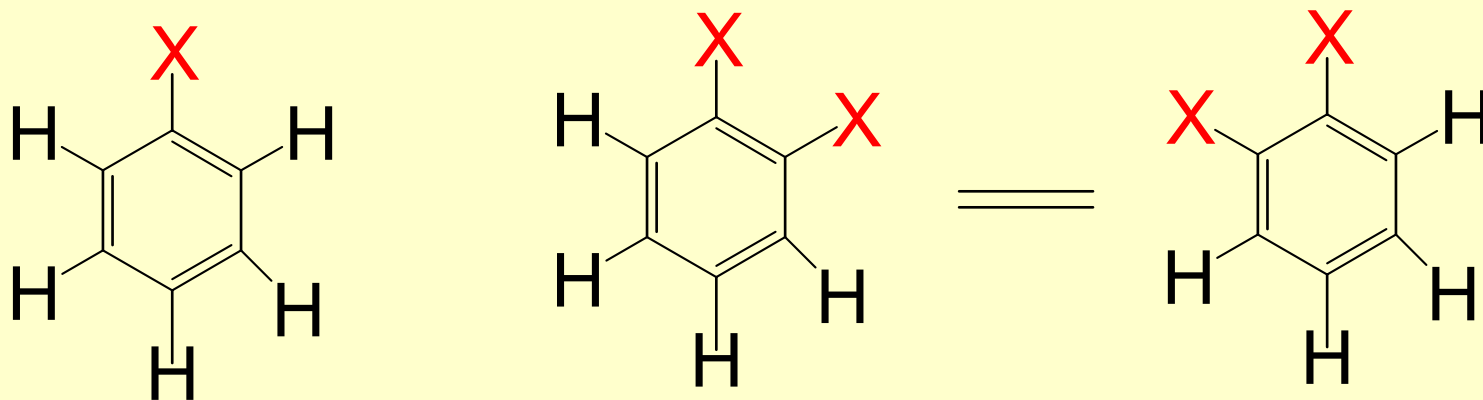
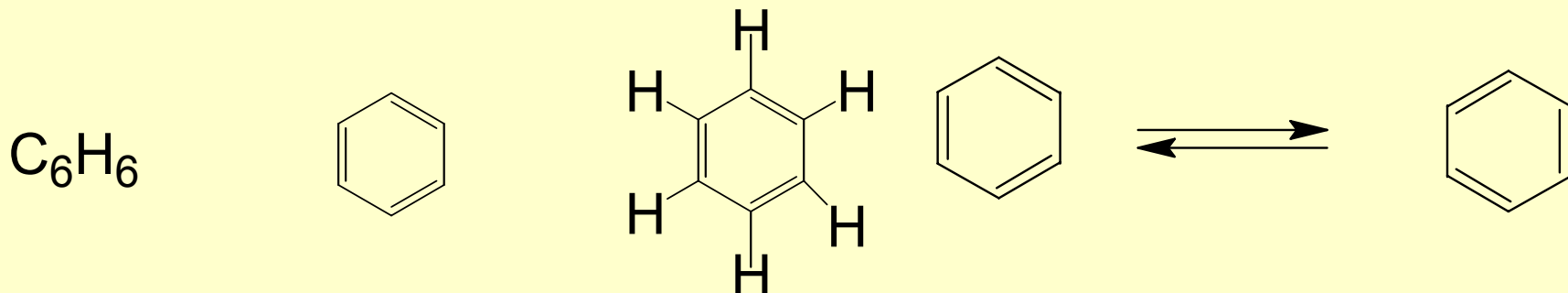
*Aromatic hydrocarbon*

# 苯型芳香烃的分类

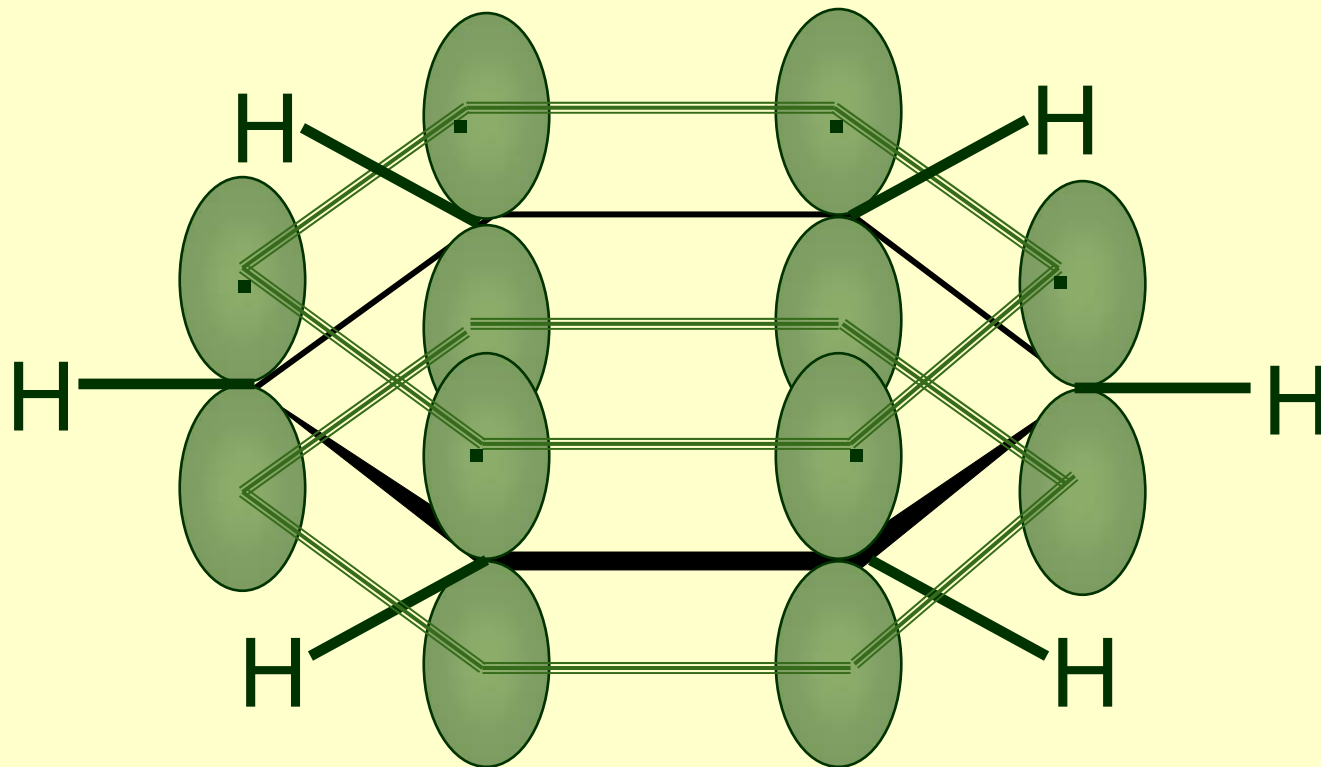


# 第一节 苯的结构

## 一、苯的Kekulé结构式



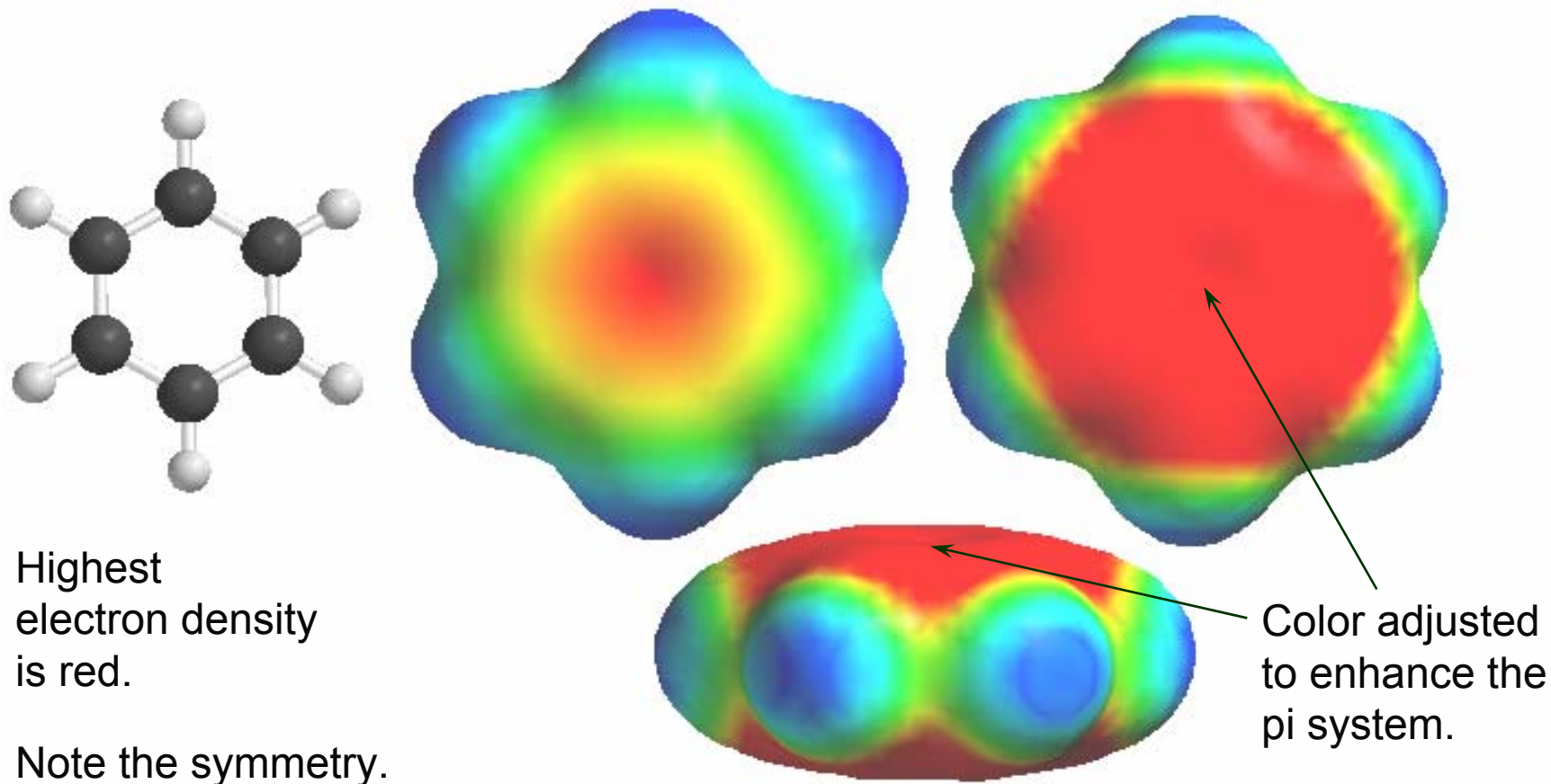
## 二、苯的分子结构



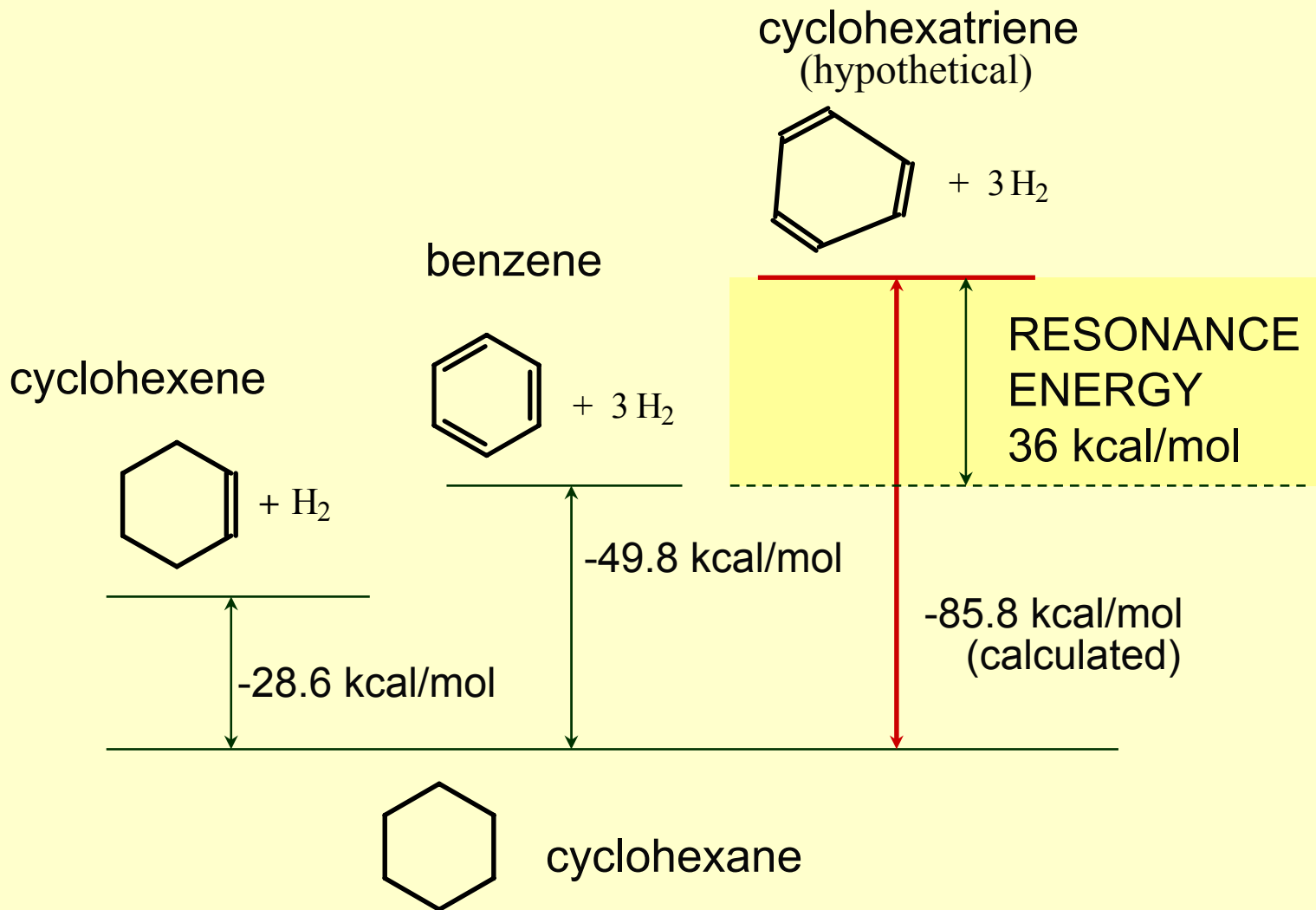
All 2p orbitals overlap equally.

## 二、苯的分子结构

Isodensity surfaces - electron potential mapped in color.  
(van der Waal's)

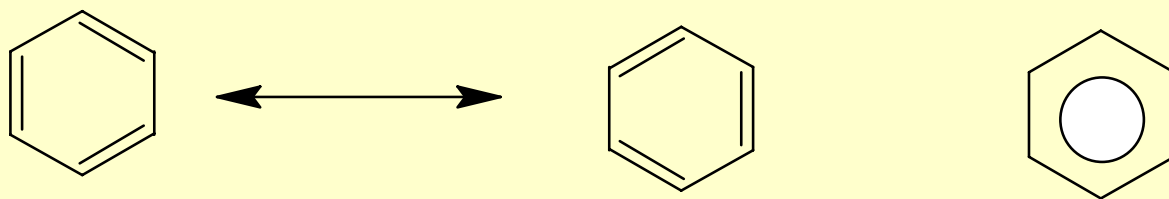


## 二、苯的分子结构



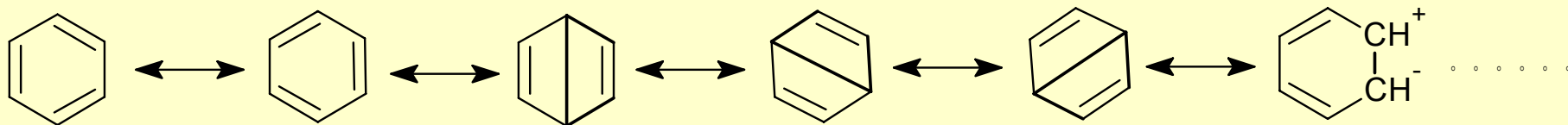
### 三、共振论简介

共振论认为苯的结构式主要由二个Kekule式的共振杂化体表示：



共振论是Pauling 在1930年提出，基本要点如下：

1. 当一个分子、离子、或自由基按照价键理论可写出二个以上的经典结构式时，这些结构式成为参加共振的一员，例苯：



### 三、共振论简介

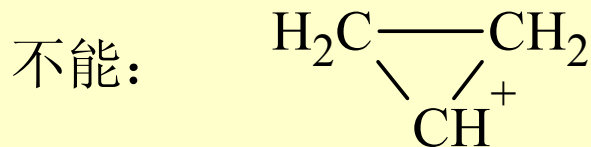
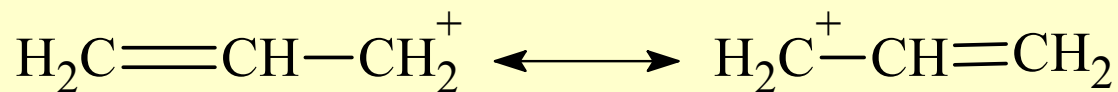
2. 分子的稳定程度可用共振能表示，共振结果使体系内能降低。对一个化合物的分子来说，每个极限式对共振杂化体的贡献不同，越稳定的极限式贡献越大（共价键较多的稳定，贡献大。电荷式不稳定，贡献小）。

3. 书写极限式必须遵守一定的规则：

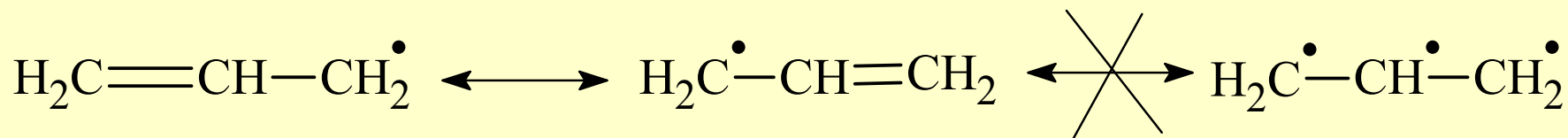


### 3. 书写极限式必须遵守一定的规则:

- (1) 遵守价键理论, 氢外层电子不能超2个, 碳不能超八个。
- (2) 原子核位置相对不变, 只允许电子排布有差别:



- (3) 在所有极限式中, 未共用电子数必需相等。



## 第二节 芳烃的异构和命名

### 一、异构

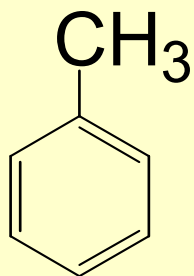
### 二、命名

1、当苯环上连的是简单的烷基（R-）， $-\text{NO}_2$ ， $-\text{X}$ 等基团时，则以苯环为母体，叫做某基苯。

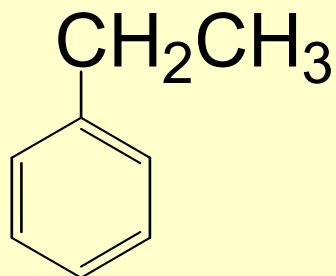
2、当苯环上连有 $-\text{COOH}$ ， $-\text{SO}_3\text{H}$ ， $-\text{NH}_2$ ， $-\text{OH}$ ， $-\text{CHO}$ ， $-\text{CH}=\text{CH}_2$ 或R较复杂时，则把苯环作为取代基。

**多个取代基时选择母体顺序：** $-\text{NO}_2$ 、 $-\text{X}$ 、 $-\text{OR}$ （烷氧基）、 $-\text{R}$ （烷基）、 $-\text{NH}_2$ 、 $-\text{OH}$ 、 $-\text{COR}$ 、 $-\text{CHO}$ 、 $-\text{CN}$ 、 $-\text{CONH}_2$ （酰胺）、 $-\text{COX}$ （酰卤）、 $-\text{COOR}$ （酯）、 $-\text{SO}_3\text{H}$ 、 $-\text{COOH}$ 、 $-\text{N}^+\text{R}_3$ 等

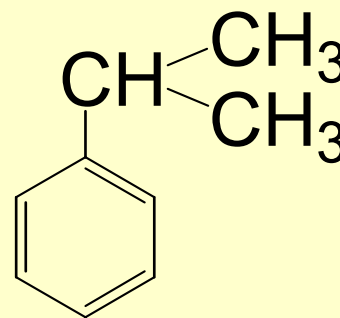
## 二、命名



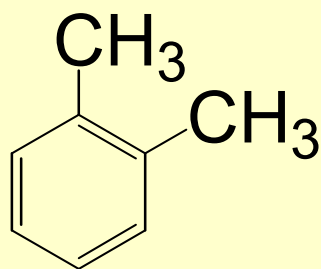
甲苯



乙苯 ethylbenzene

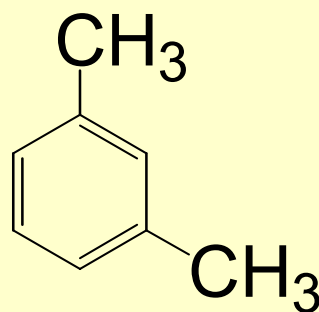


异丙苯



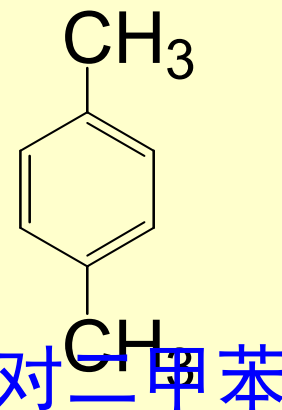
邻二甲苯

*o*-二甲苯



间二甲苯

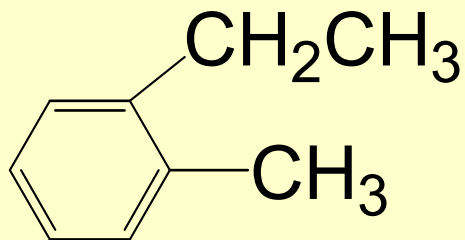
*m*-二甲苯



对二甲苯

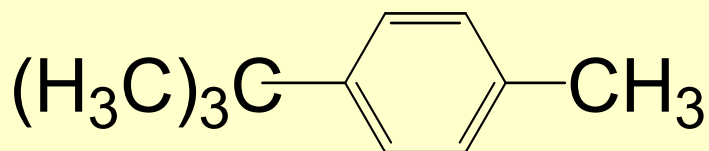
*p*-二甲苯

## 二、命名



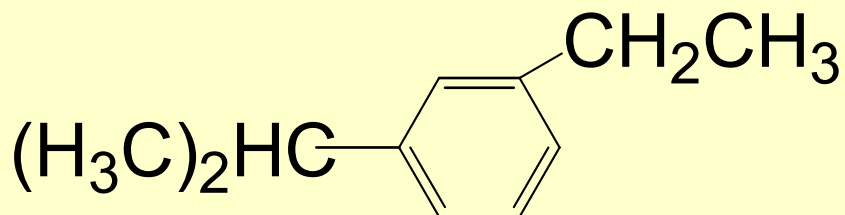
邻甲乙苯

1-甲基-2-乙苯



对甲叔丁苯

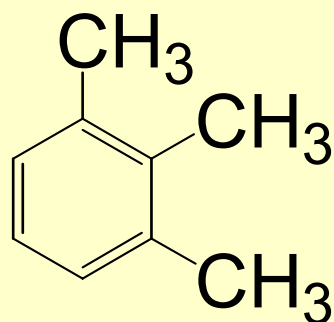
1-甲基-4-叔丁基苯



间乙异丙苯

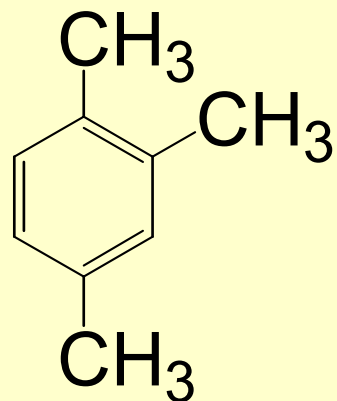
1-乙基-3-异丙苯

## 二、命名



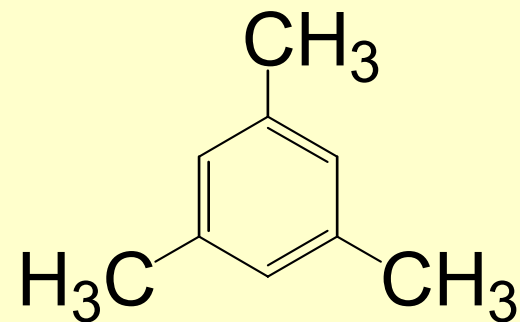
连三甲苯

1, 2, 3-三甲苯



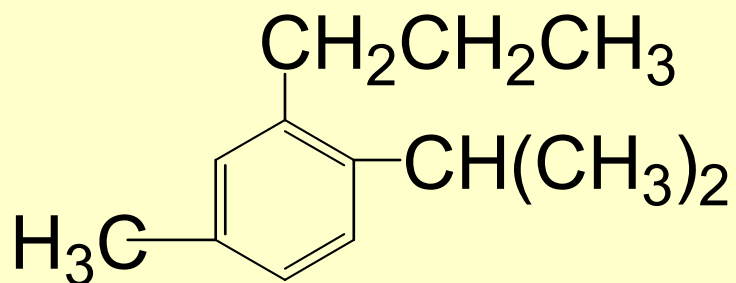
偏三甲苯

1, 2, 4-三甲苯



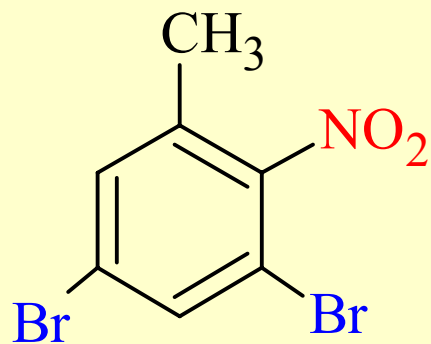
均三甲苯

1, 3, 5-三甲苯

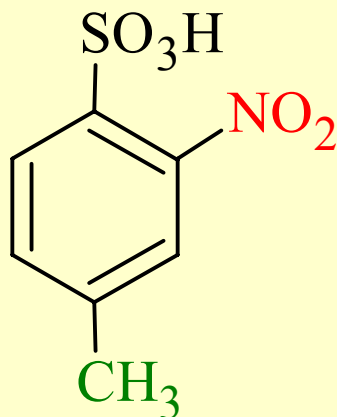


1-甲基-3-丙基-4-异丙苯

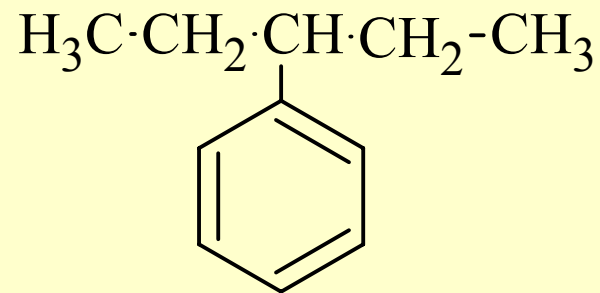
## 二、命名



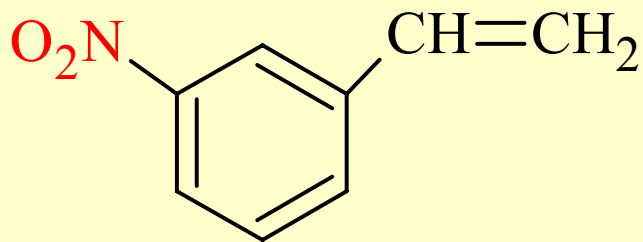
3, 5-二溴-2-硝基甲苯



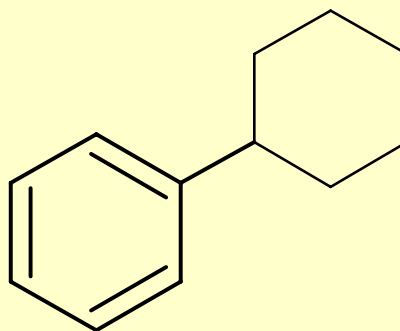
2-硝基对甲苯磺酸



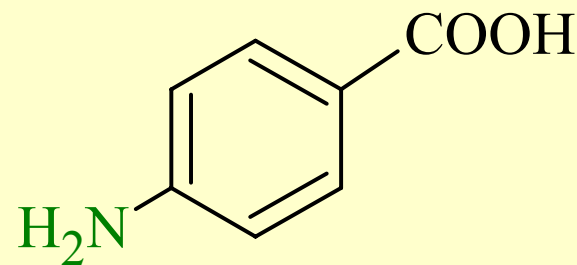
3-苯基戊烷



3-硝基苯乙烯

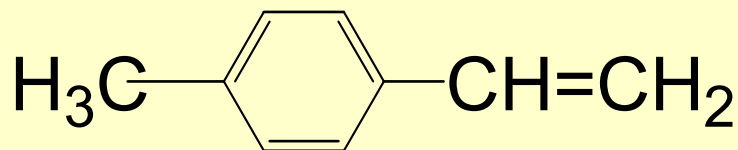


环己基苯

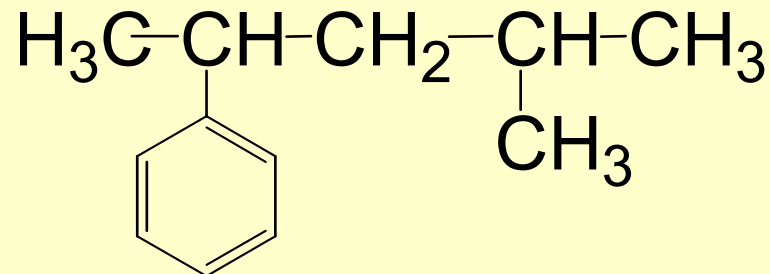


对氨基苯甲酸

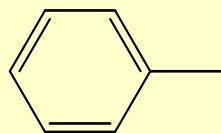
## 二、命名



对甲苯乙烯



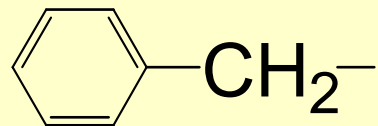
2-甲基-4-苯基-戊烷



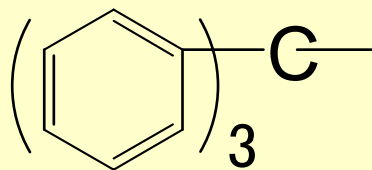
$\text{C}_6\text{H}_5-$

ph-

苯基



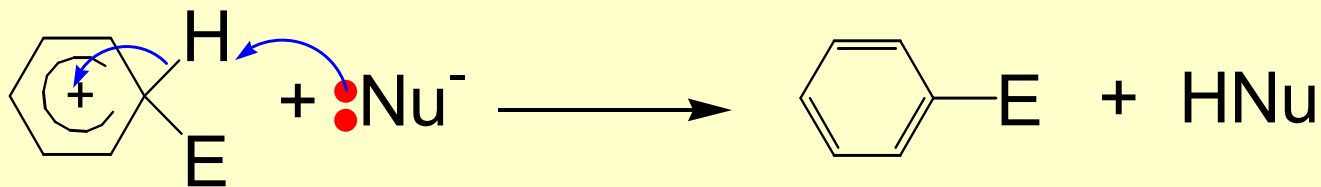
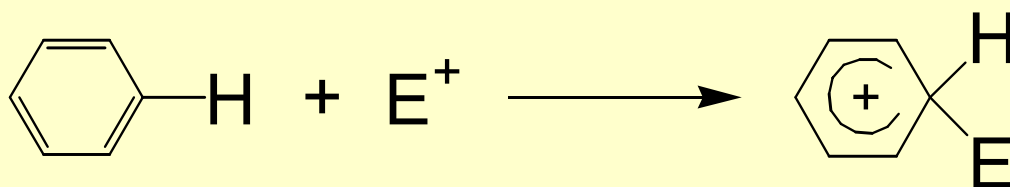
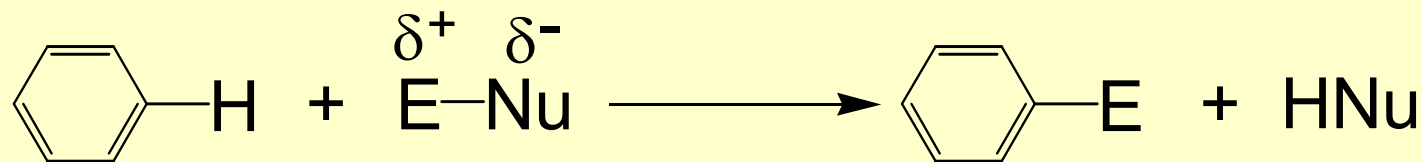
苯甲基 (或苄基)



三苯甲基

# 第三节 单环芳烃的性质

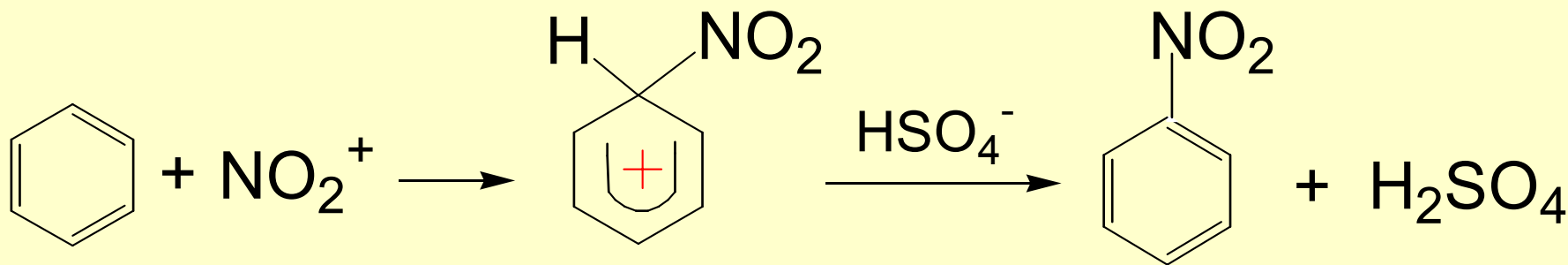
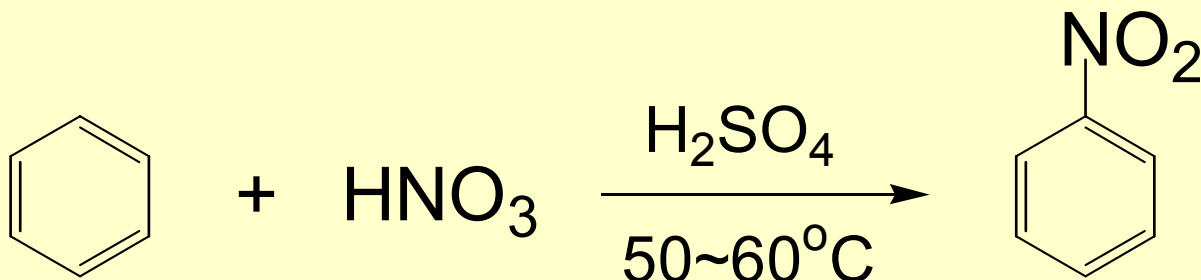
## 一、亲电取代反应



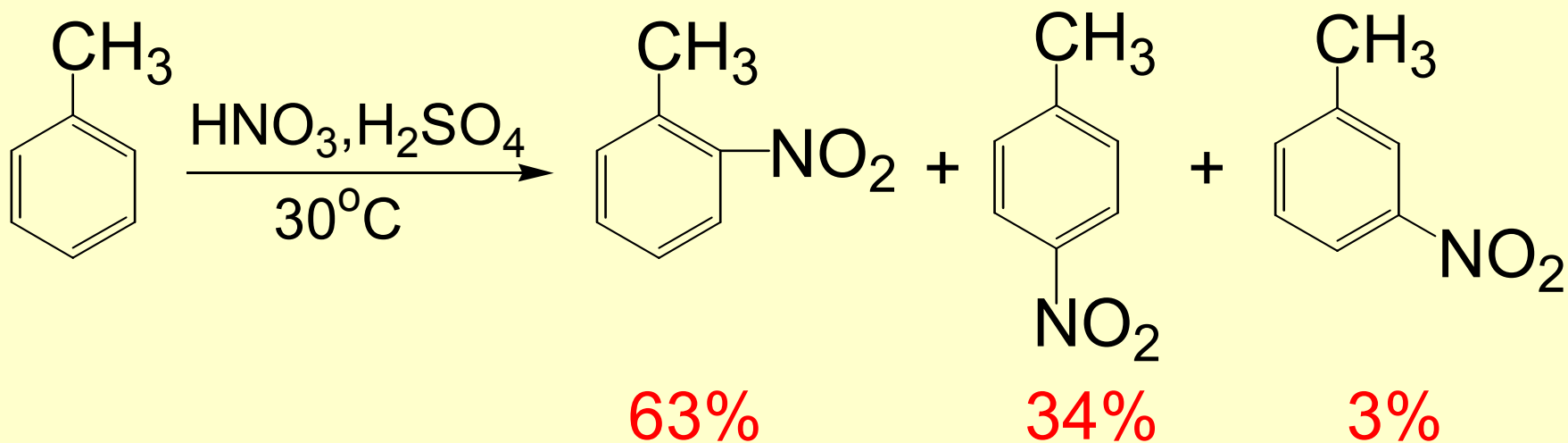
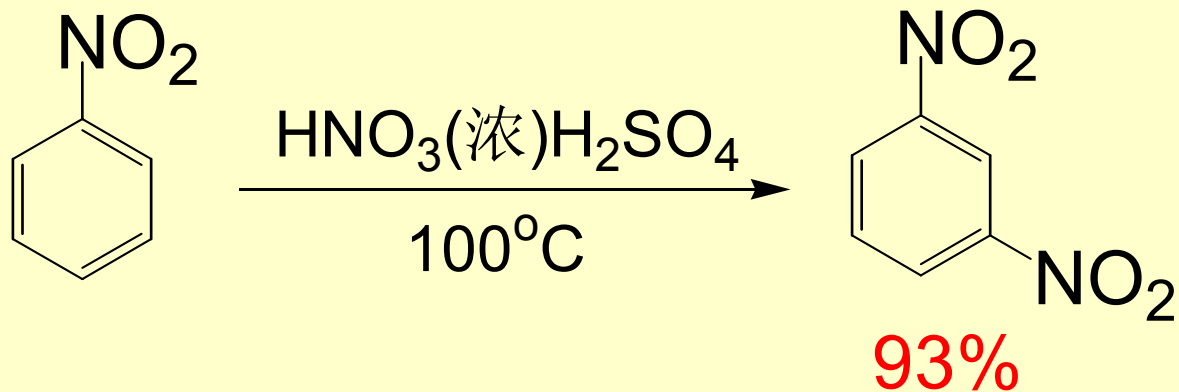


# 一、亲电取代反应

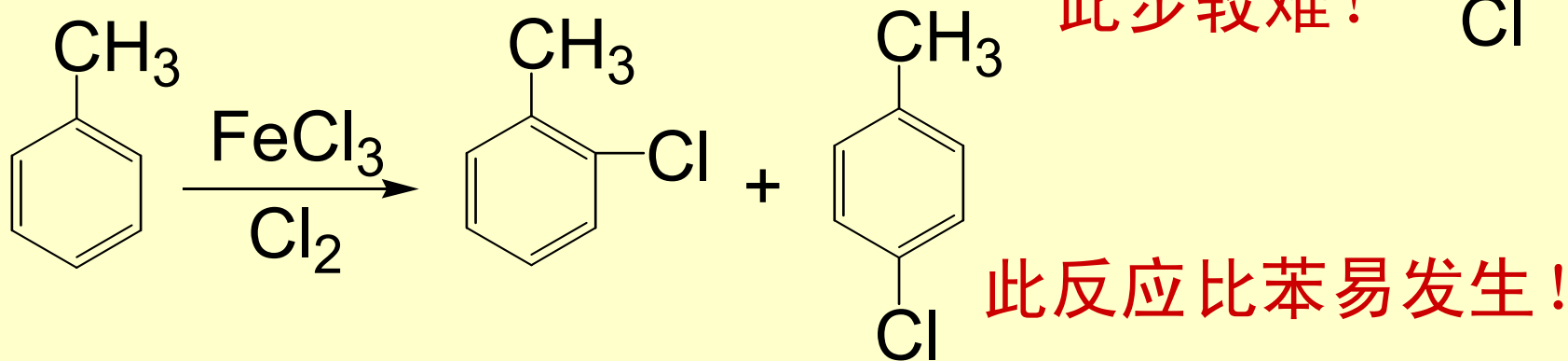
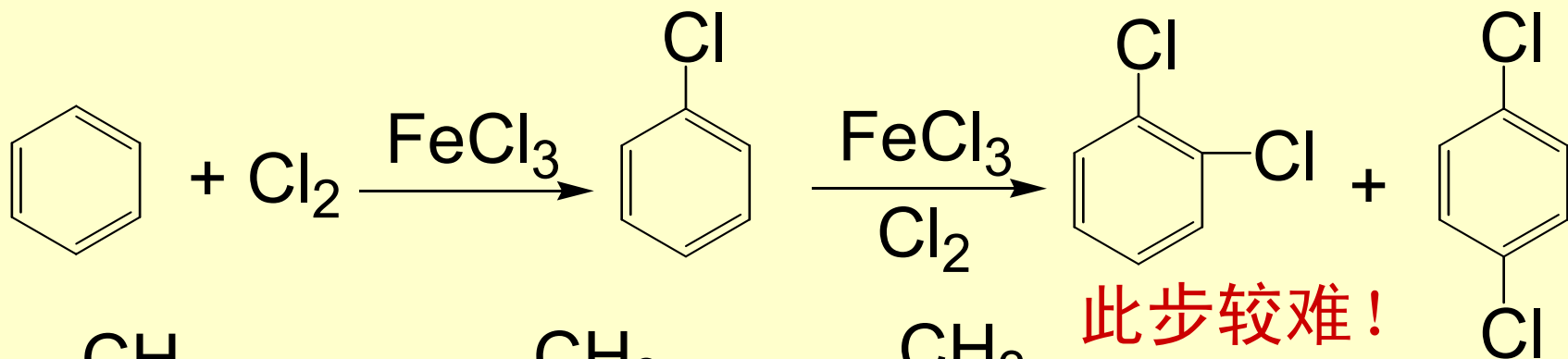
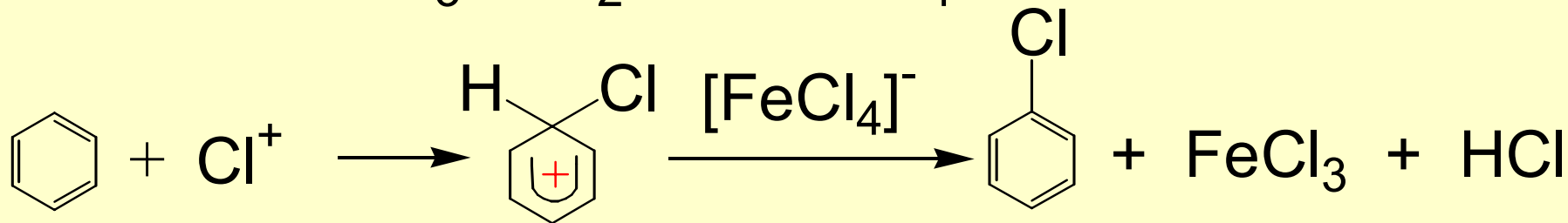
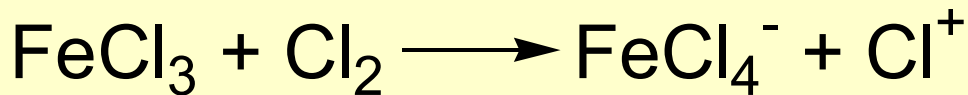
## 1、硝化反应



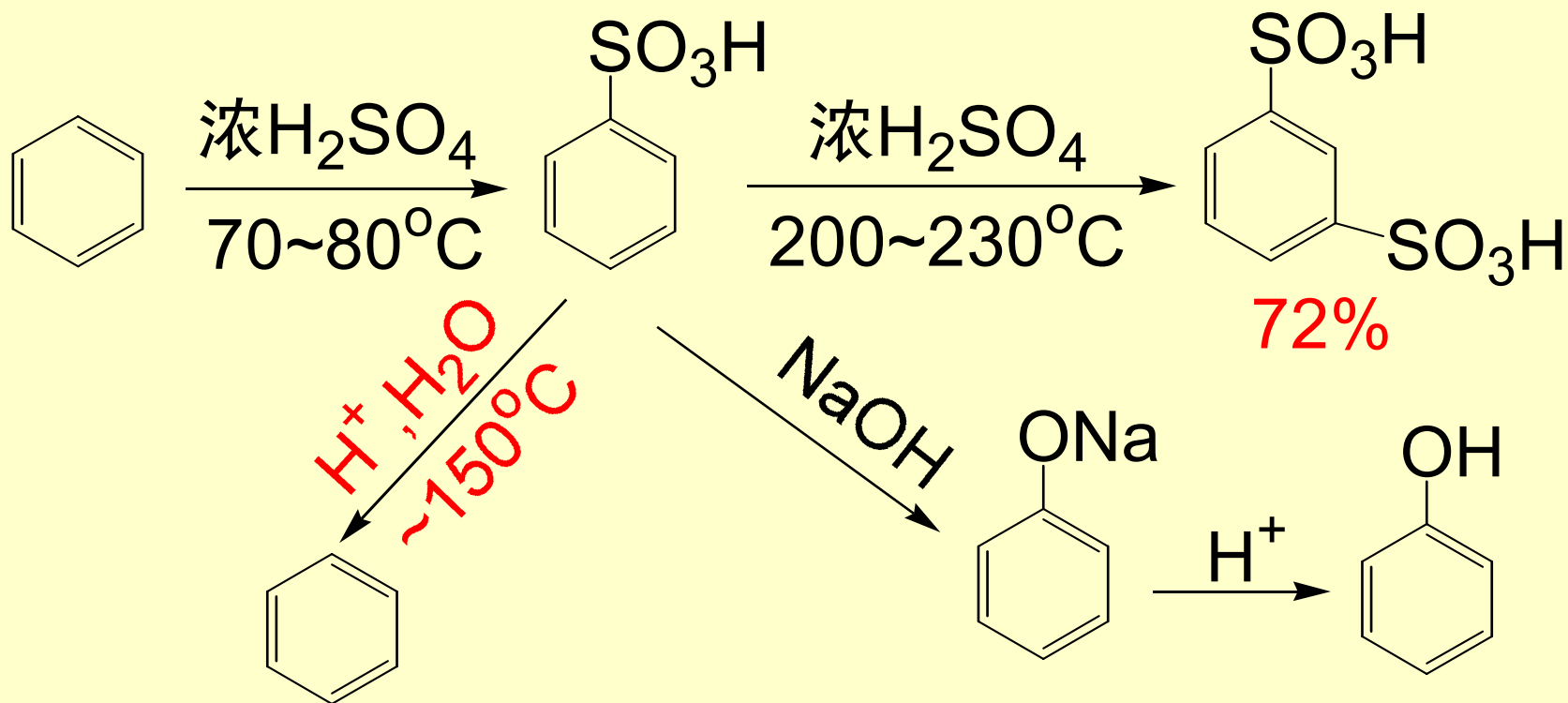
# 1、硝化反应



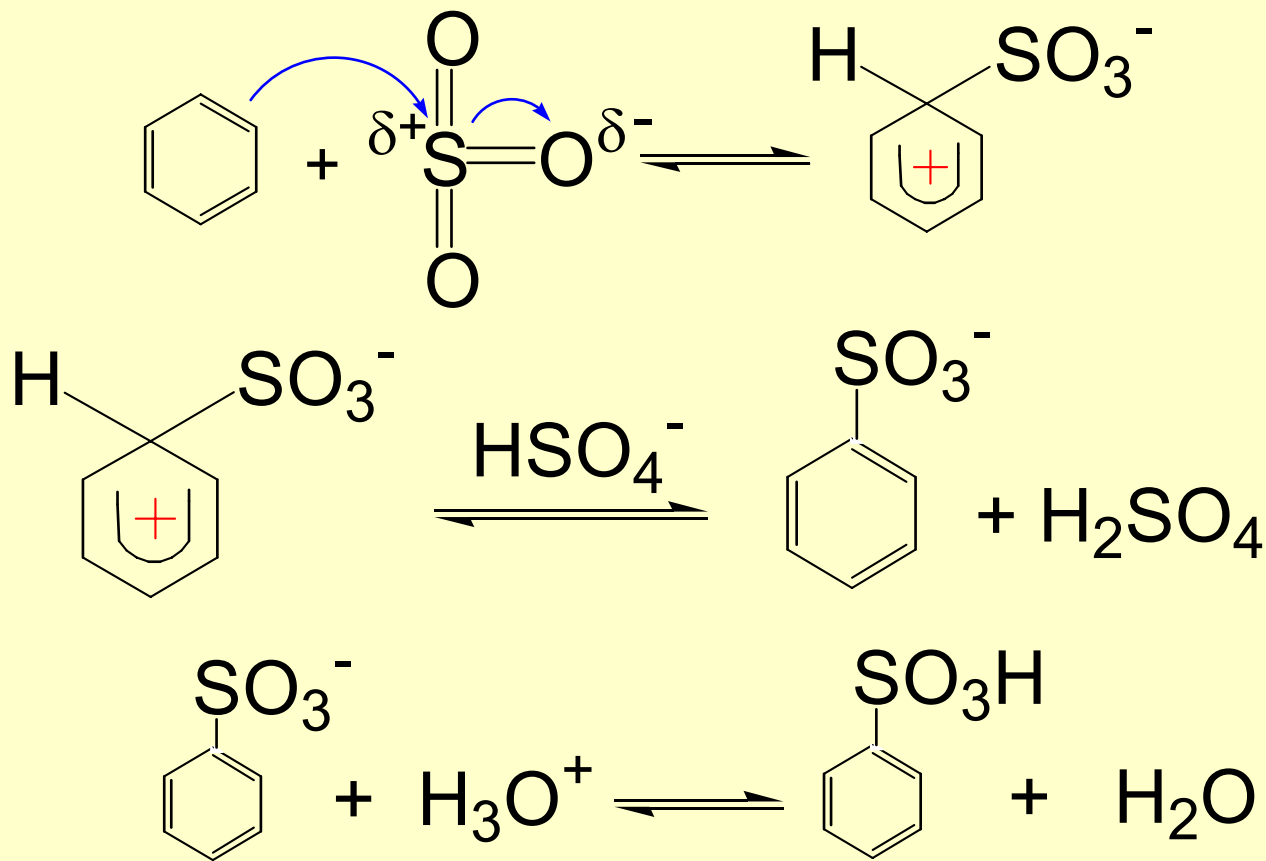
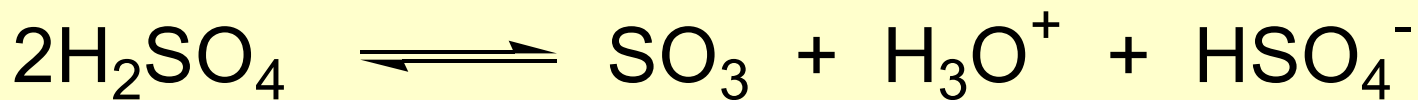
## 2、卤代反应



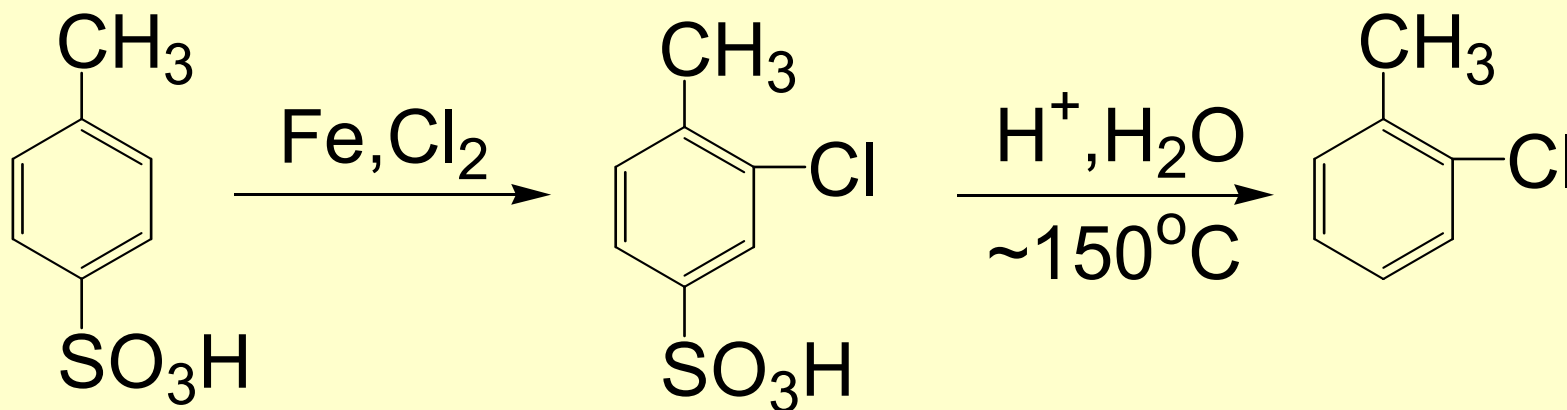
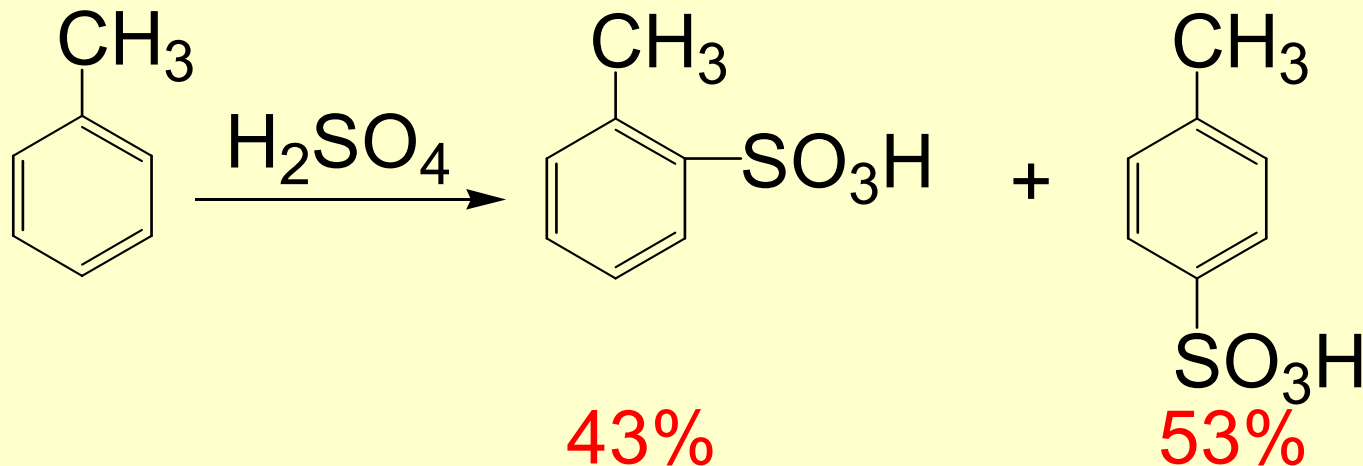
# 3、磺化反应



# 3、磺化反应

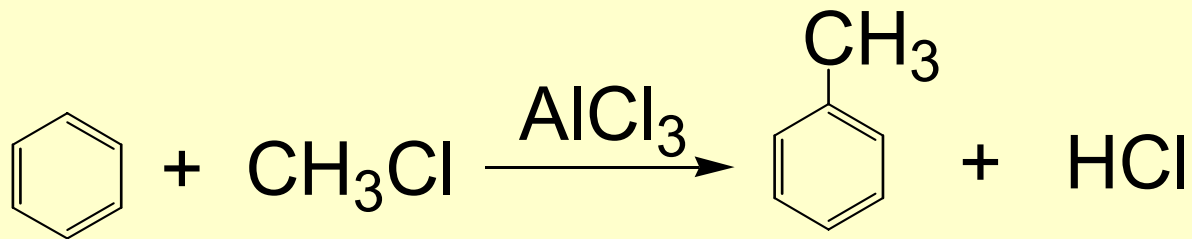


如何由甲苯制得邻氯甲苯而产品中不含有对氯甲苯？

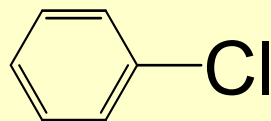
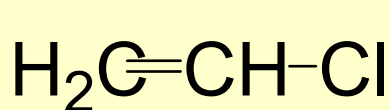
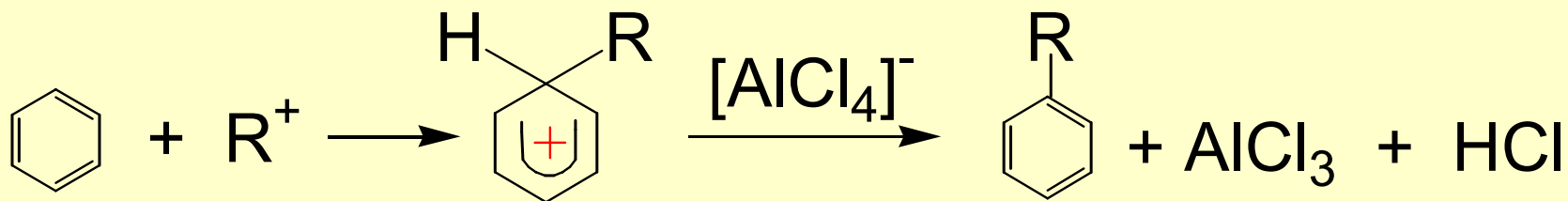
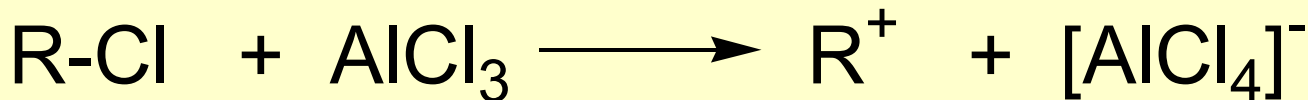


# 4、Fridel-Crafts反应

## (1) 傅-克烷基化

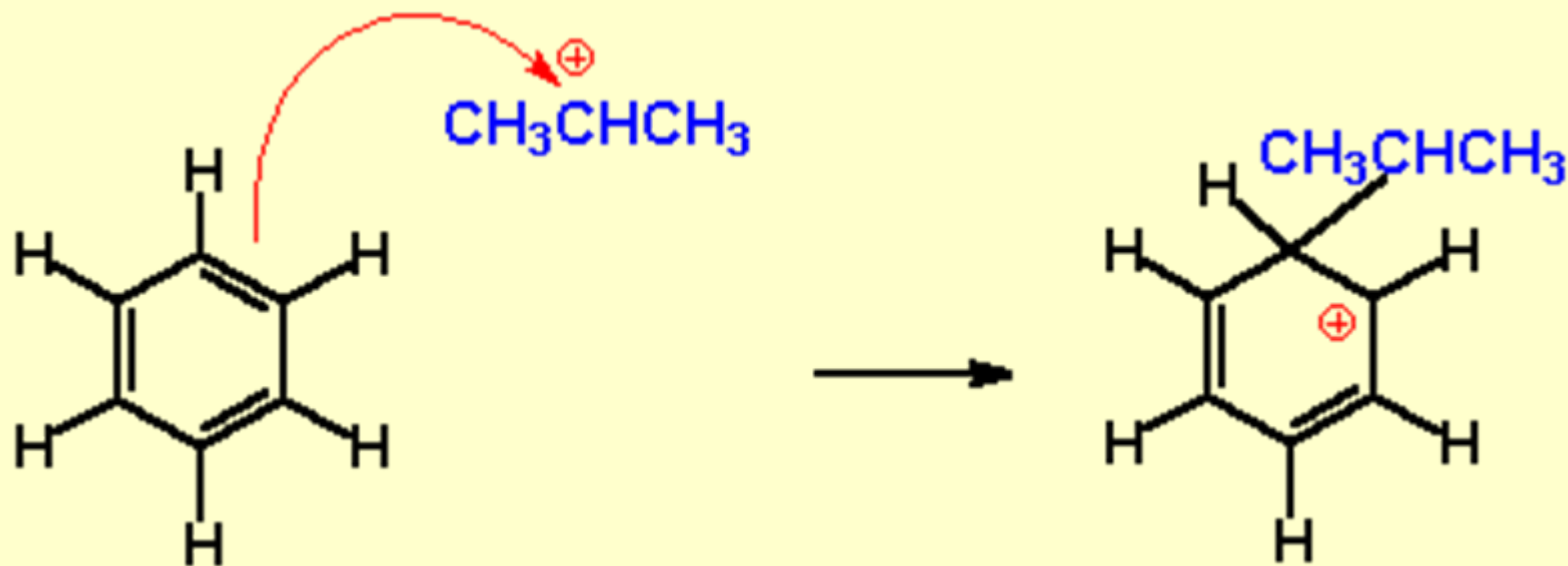


历程:



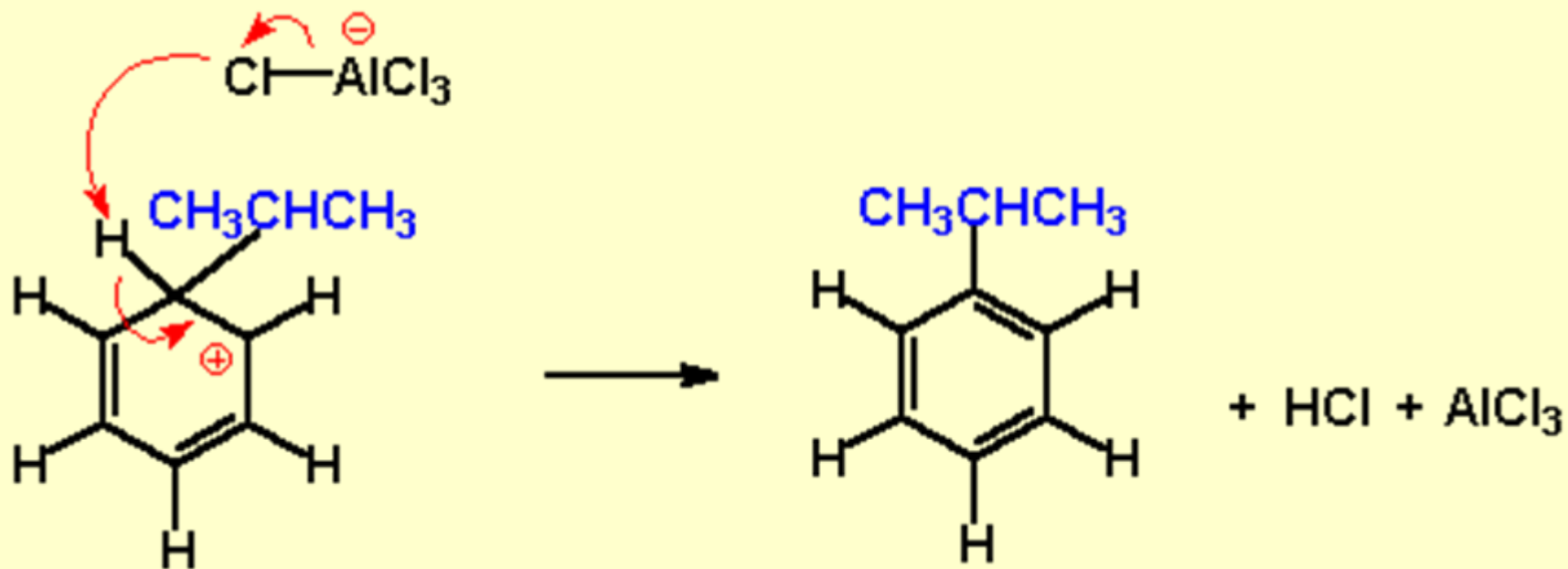
不发生此反应

# 历程:



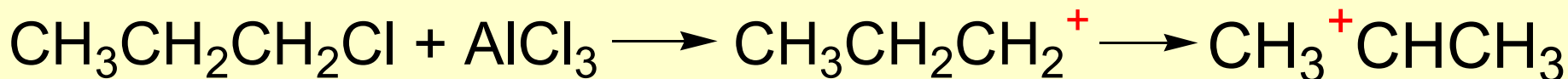
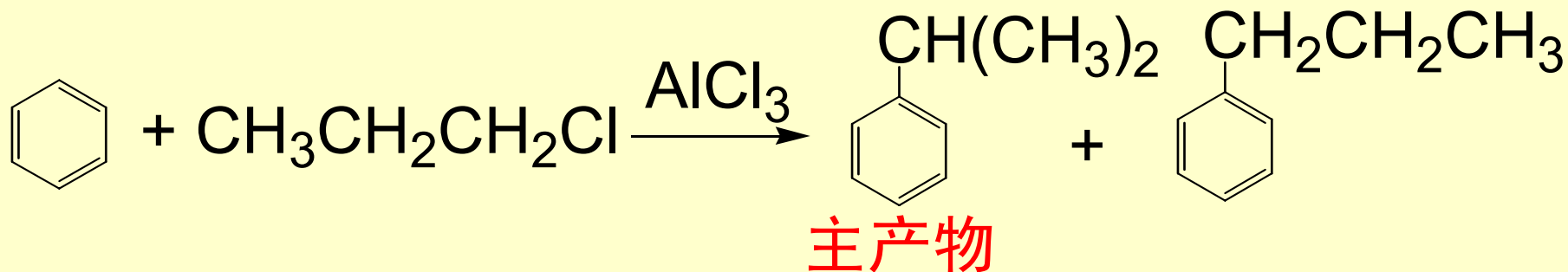
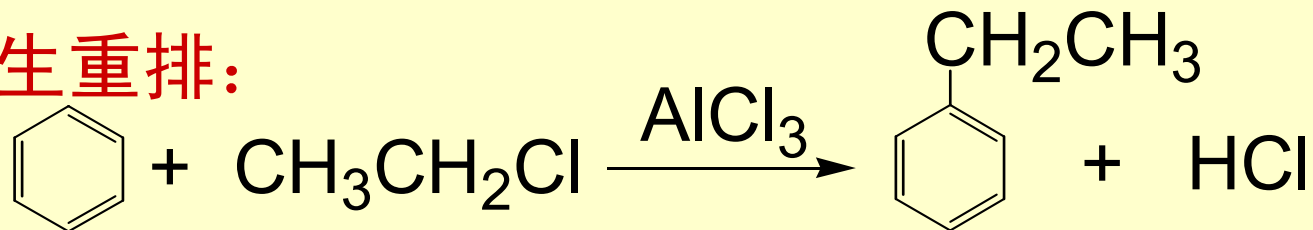


# 历程:

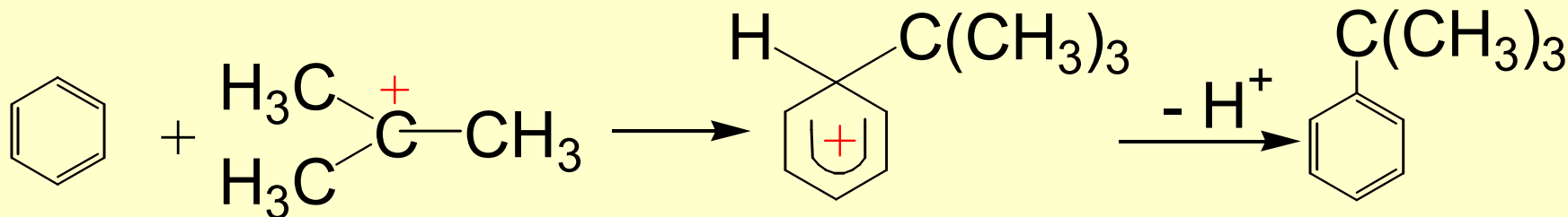
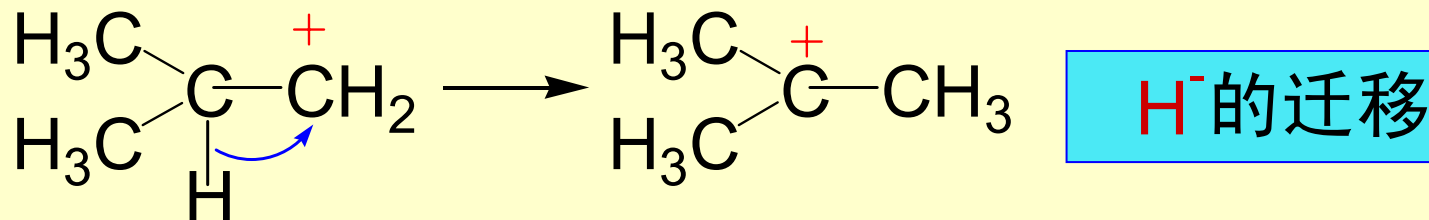
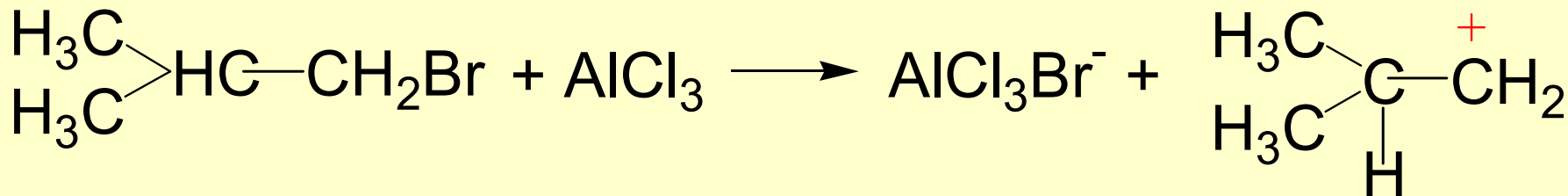
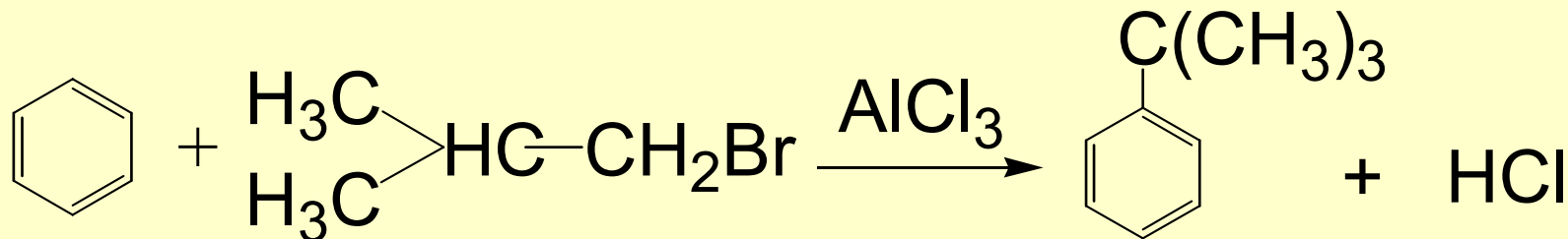


# (1) 傅-克烷基化

易发生重排:



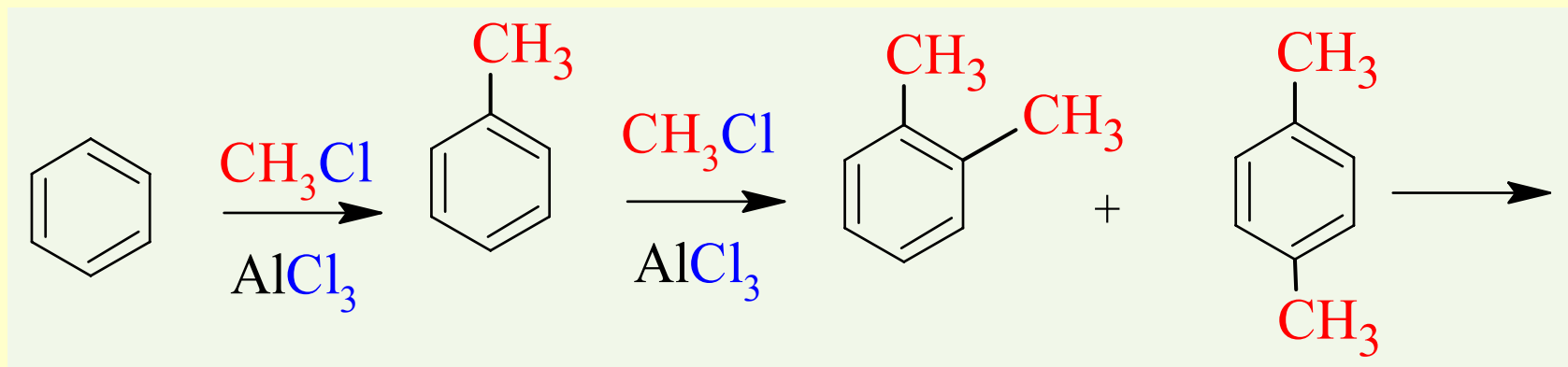
# (1) 傅-克烷基化



# (1) 傅-克烷基化

注意:

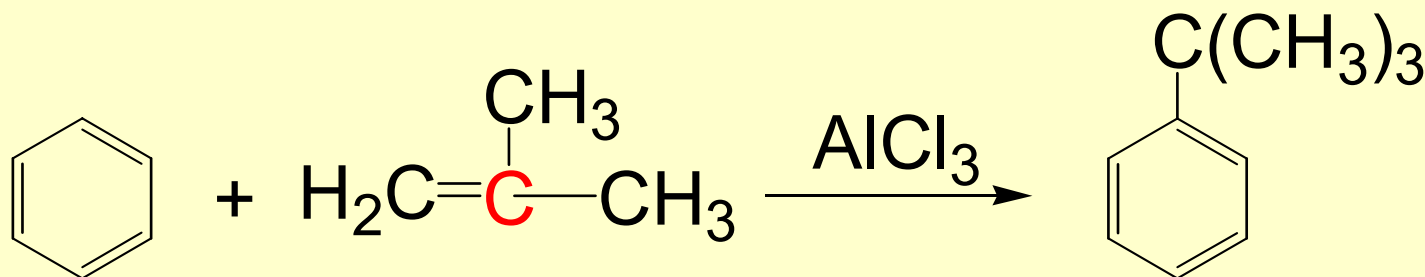
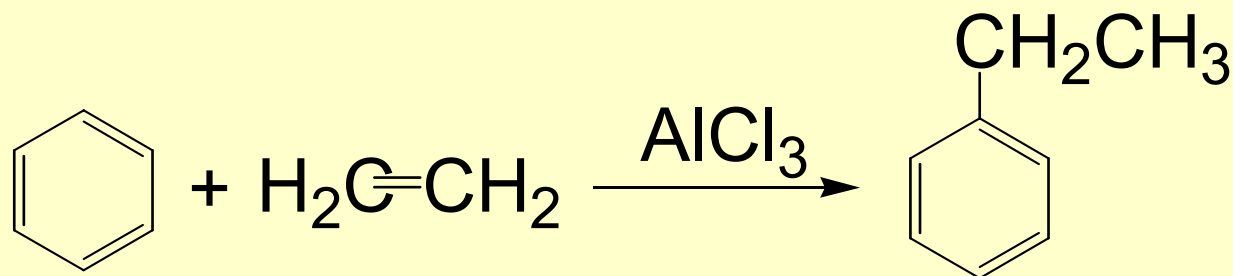
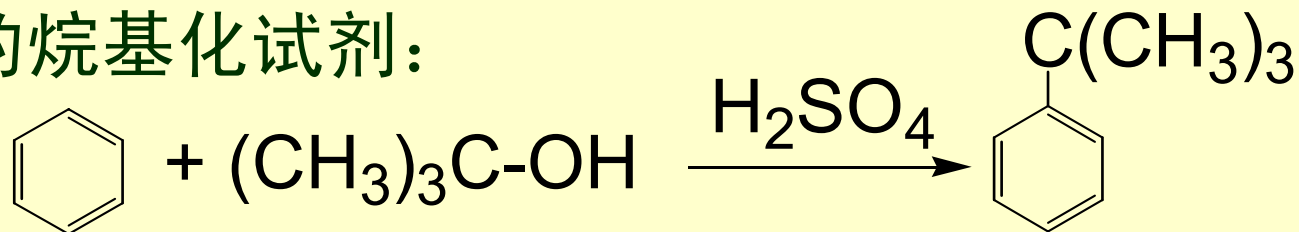
烷基化反应不易停留在一元取代阶段，可进一步生成多烷基苯：



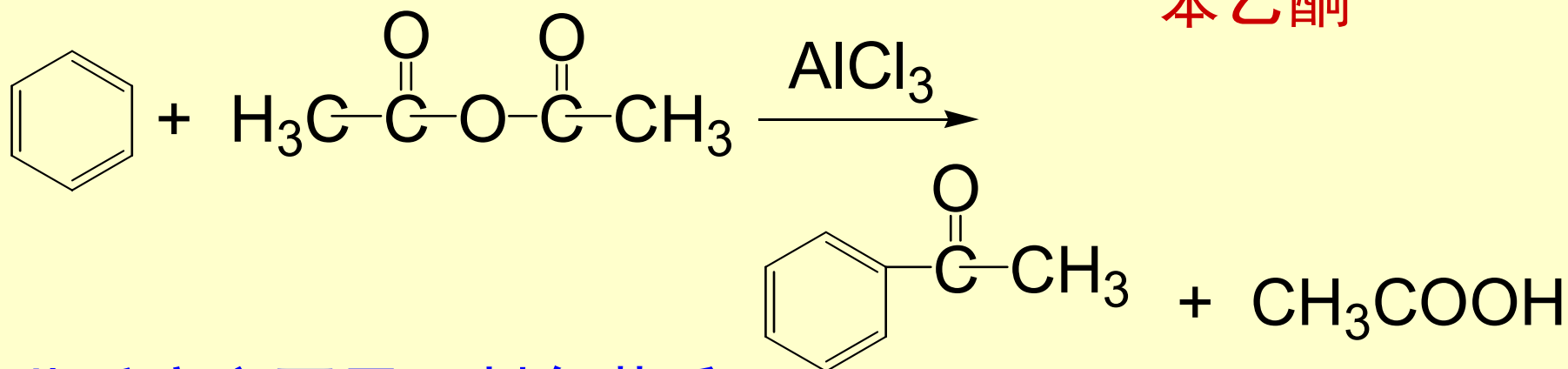
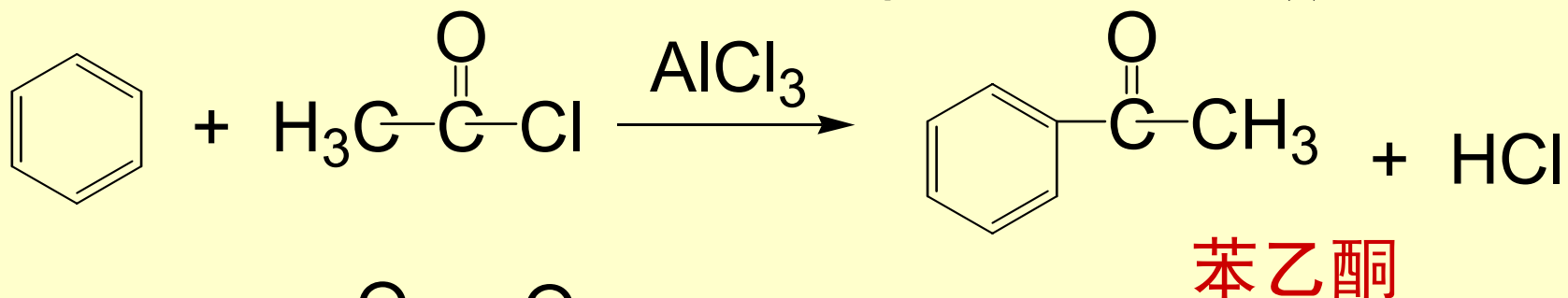
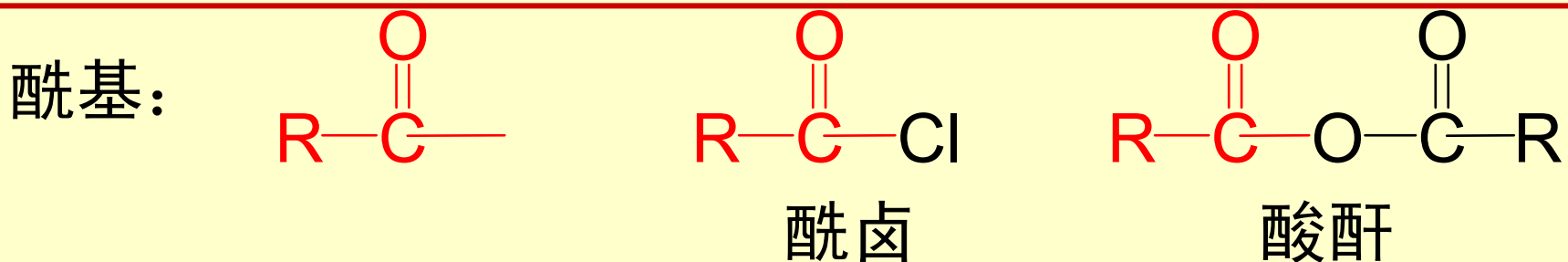
烯烃或醇也可作为烷基化试剂，但苯环上有了 $-\text{NO}_2$ 等吸电子取代基后，烷基化反应不能发生：

# (1) 傅-克烷基化

其它的烷基化试剂:

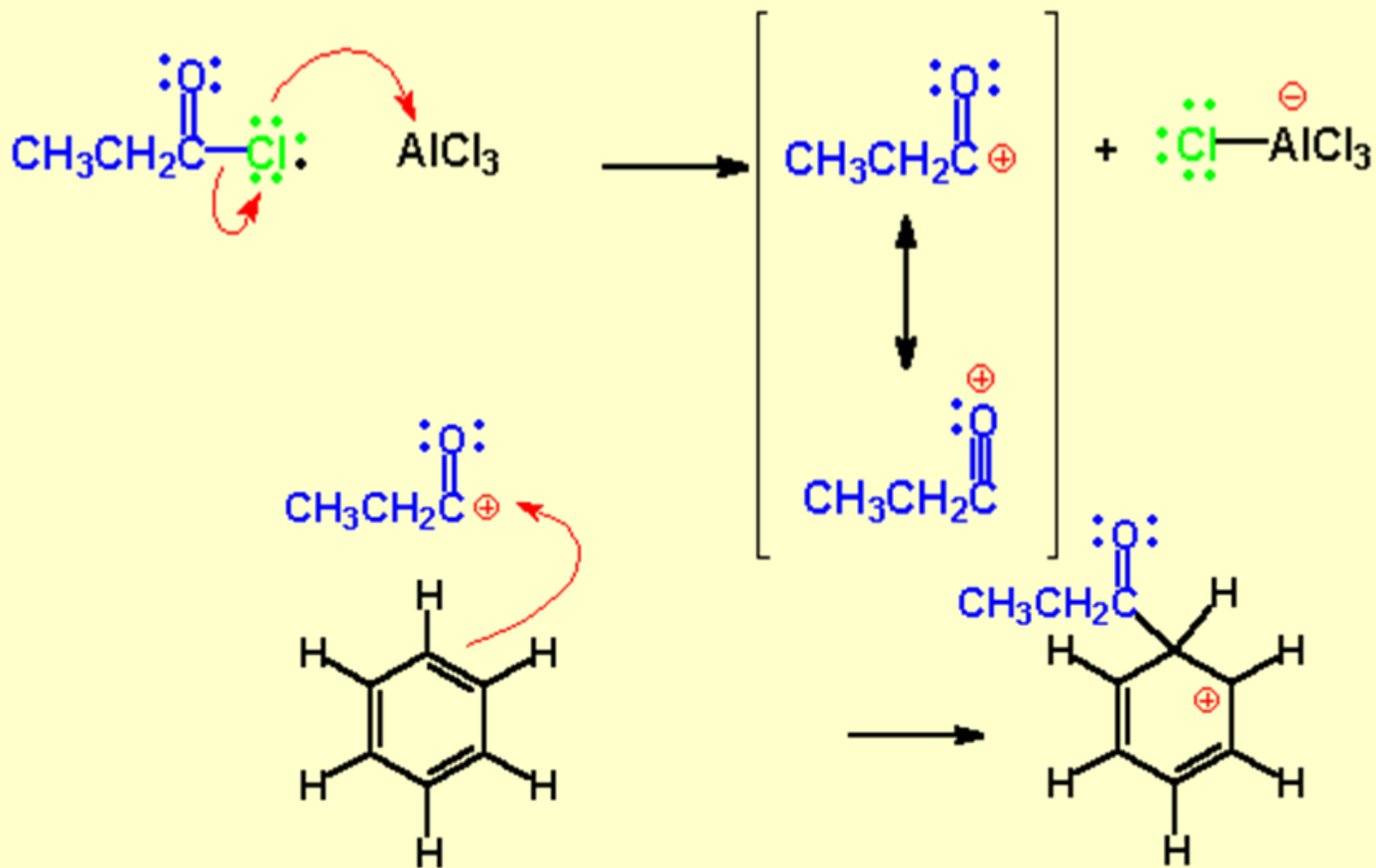


## (2) 傅-克酰基化

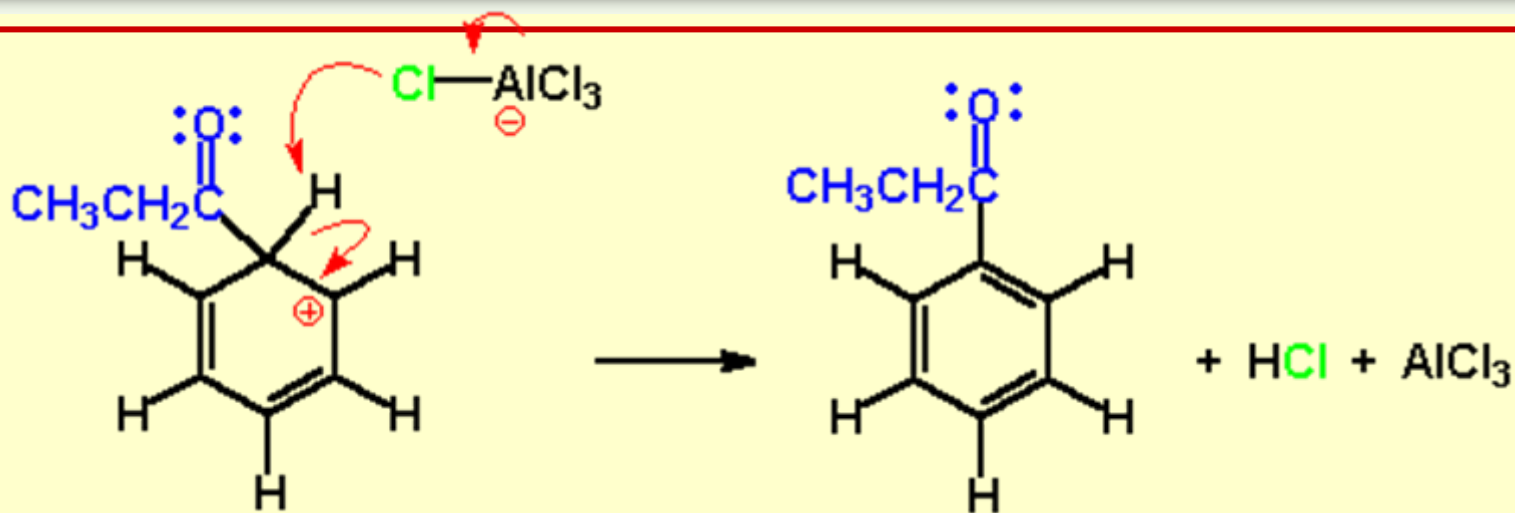


此反应主要用于制备芳香酮。

# 反应机理:



## (2) 傅-克酰基化

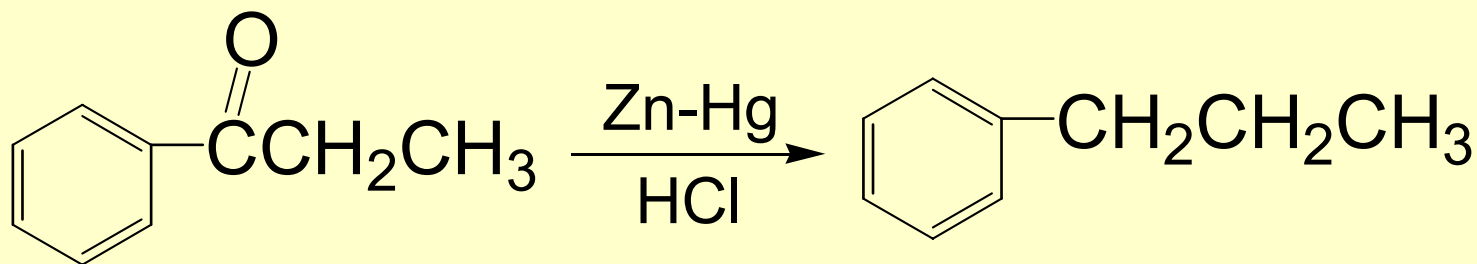
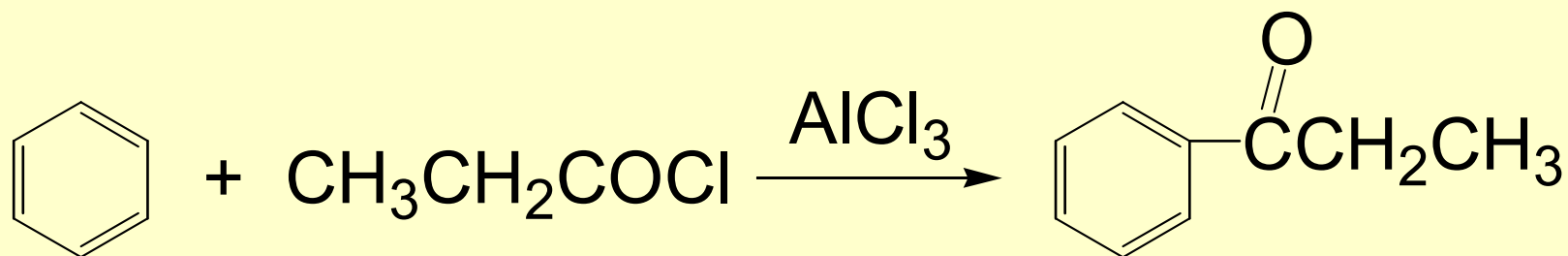
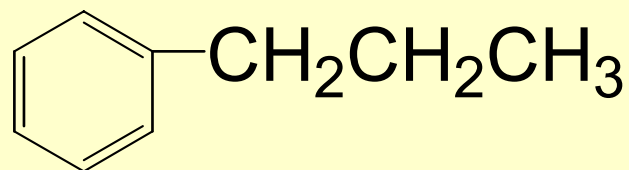


特点： 只发生一元取代，且不发生重排



## (2) 傅-克酰基化

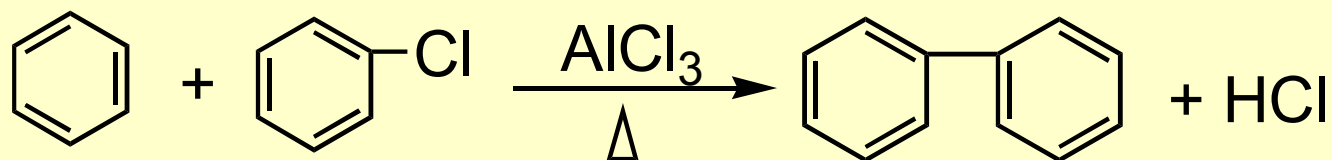
问：如何合成



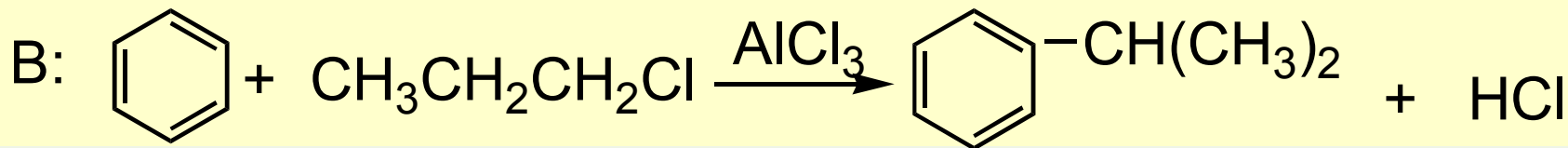
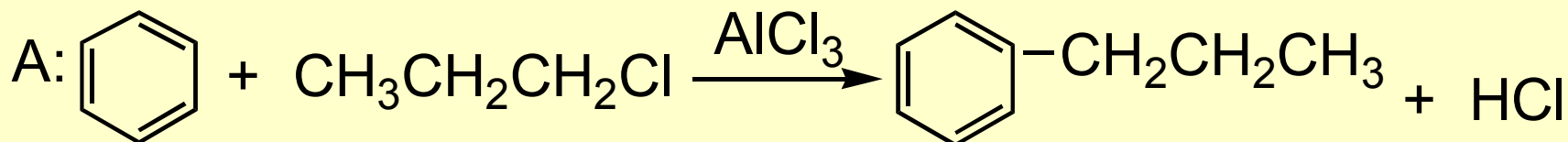
# 例题与讨论

解释下列有关Friedel-Crafts烷基化反应的事实：

(1) 苯用RX在AlCl<sub>3</sub>存在下进行烷基化时需要过量的苯。(2) 苯酚与苯氨的烷基化产率极差。(3) Ph-Ph不能用下面反应制得。



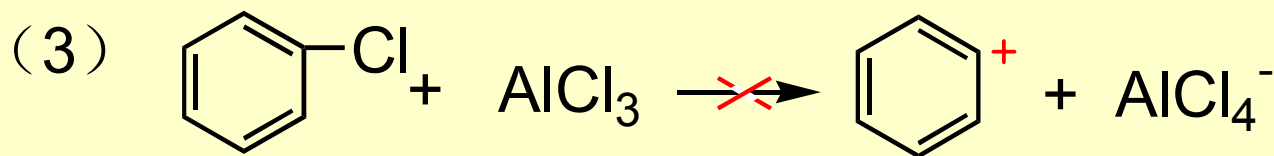
(4) 反应A产率极差，而反应B反应有很好的产率。

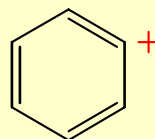


# 例题与讨论

解：（1）因为R-为致活基团，一烷基化产物 $C_6H_5R$ 比 $C_6H_6$ 本身更活泼，故 $C_6H_5R$ 将进一步反应生成 $C_6H_5R_2$ 和 $C_6H_5R_3$ 。为了避免多烷基化，使用过量的苯以增加 $R^+$ 和 $C_6H_6$ 之间的碰撞机会和减少 $R^+$ 和 $C_6H_5R$ 之间的碰撞机会。

（2）-OH和-NH<sub>2</sub>均能跟催化剂反应而使其失去活性。

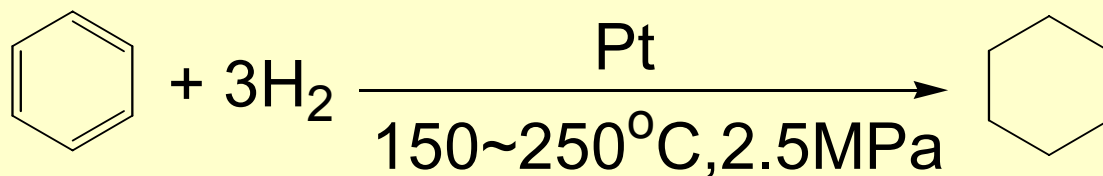


 的焓很高，不能形成。

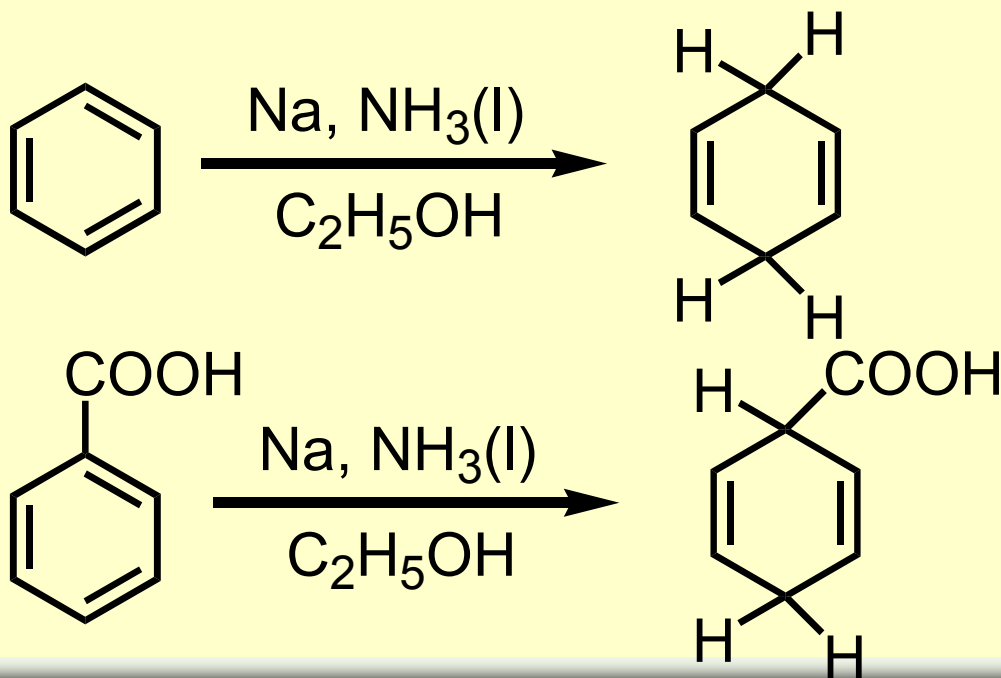
（4）中间体 $R^+$ ，特别是 $1^\circ RH_2C^+$ 能发生重排，重排反应如下：  
 $CH_3CH_2CH_2^+ \longrightarrow CH_3CH^+CH_3$  所以，B的反应产物高。

## 二、加成反应

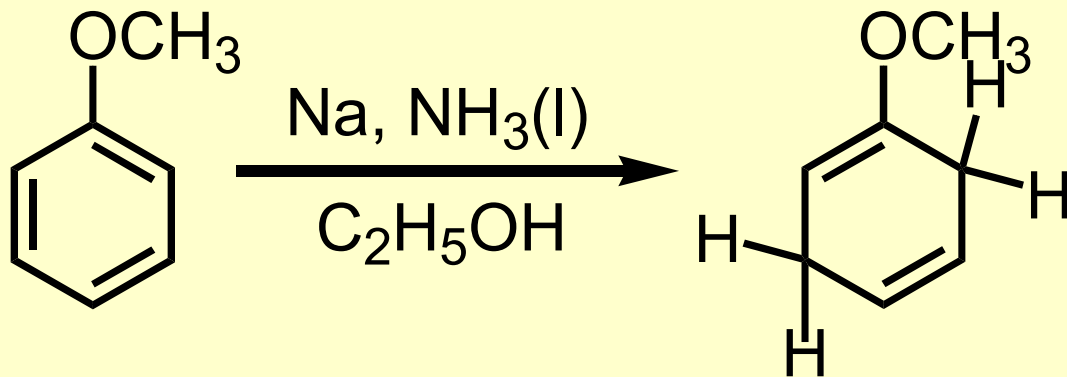
### 1、催化加氢



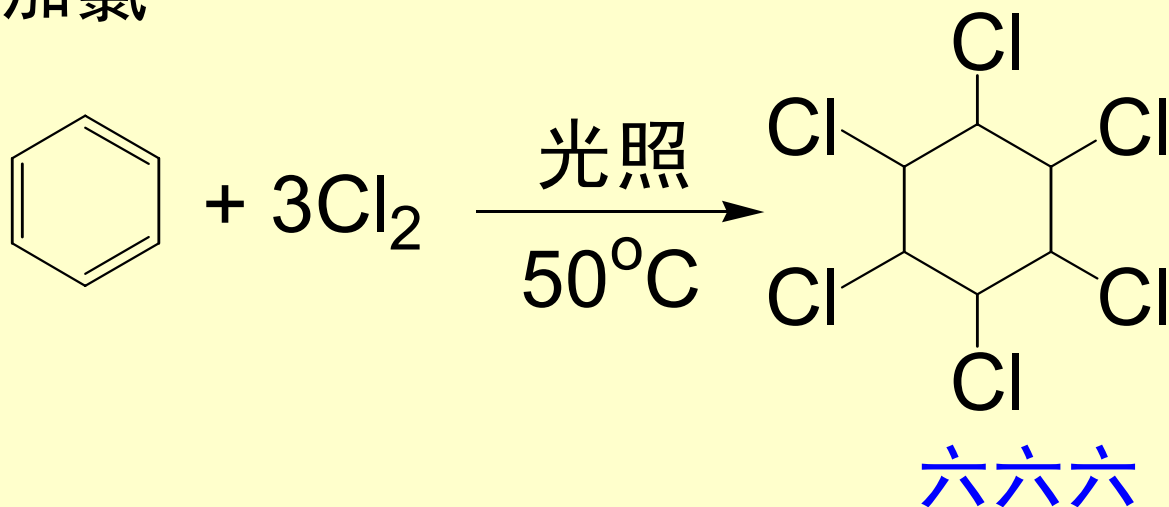
### 2、伯奇反应 (Birch)



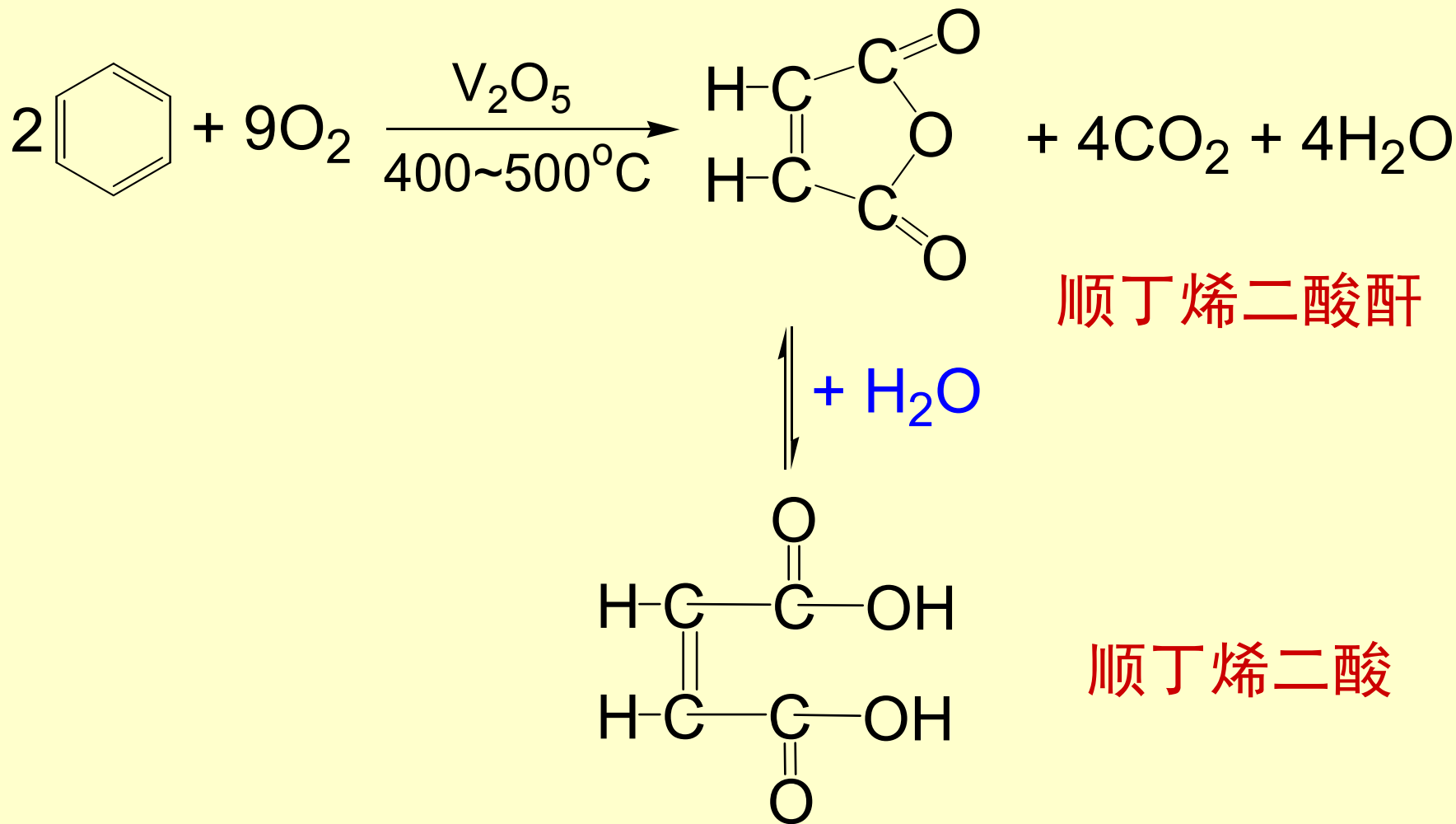
## 二、加成反应



### 3、加氯

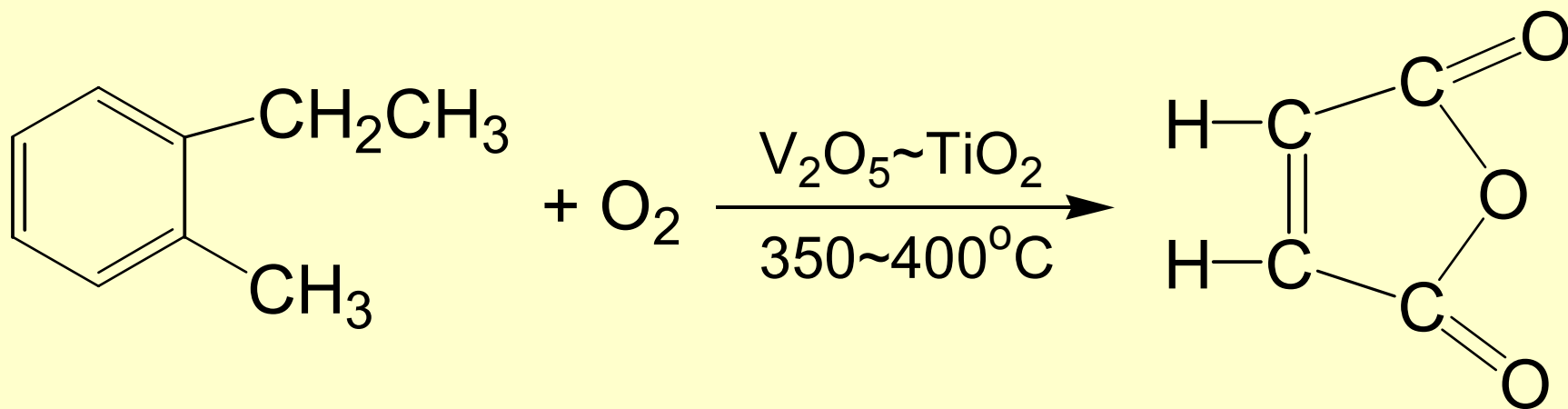
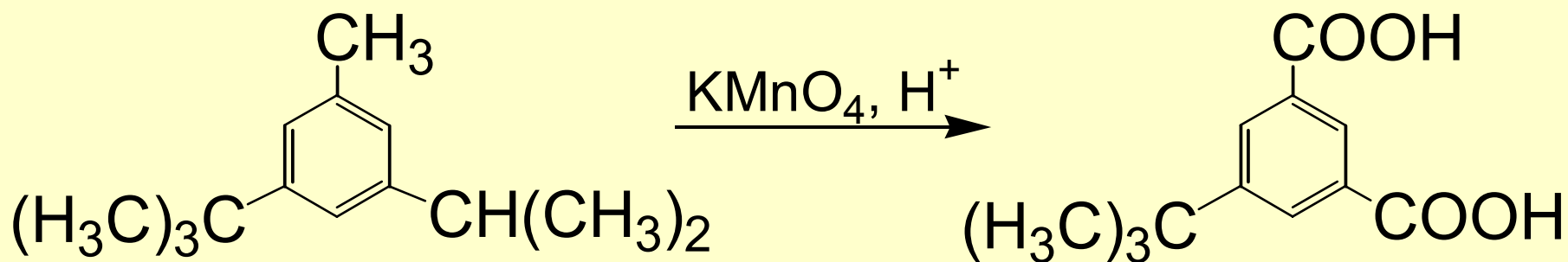


### 三、氧化反应

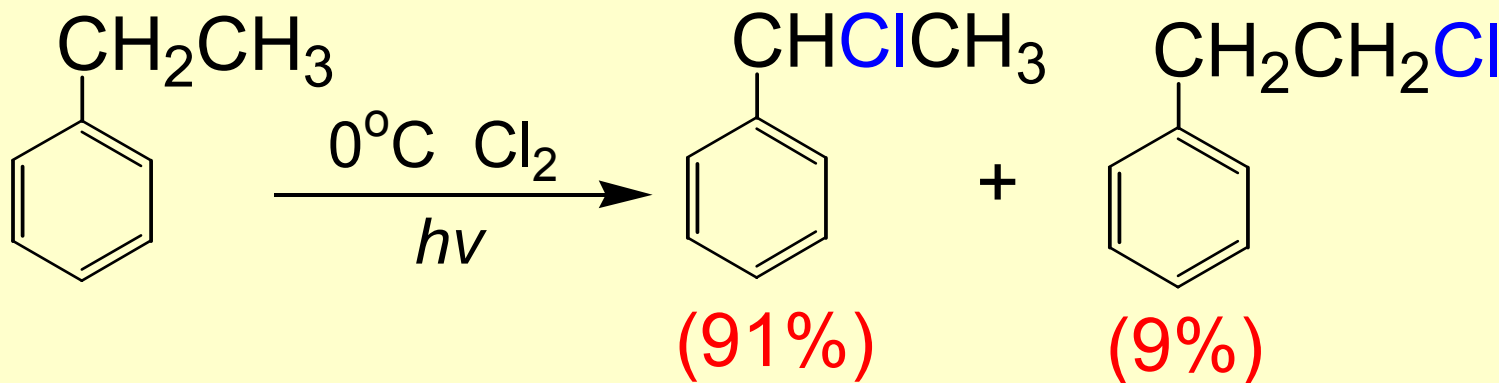
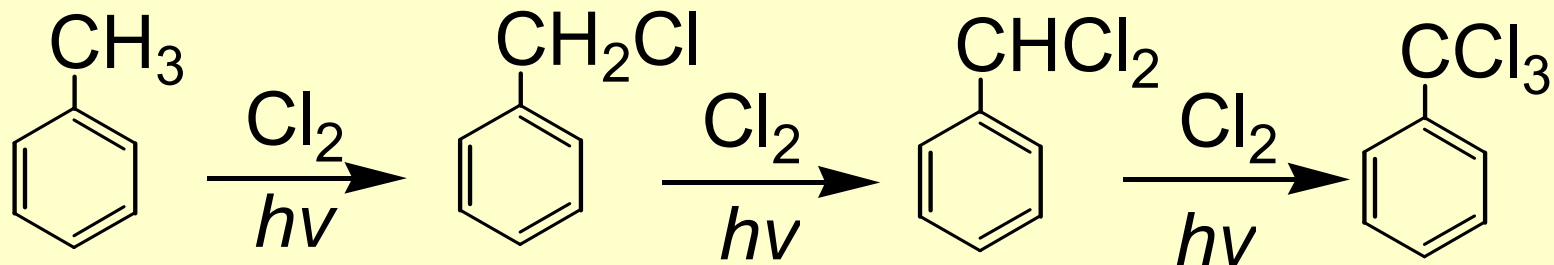


### 三、氧化反应

苯环侧链上有  $\alpha$ -H，则可被氧化为-COOH。

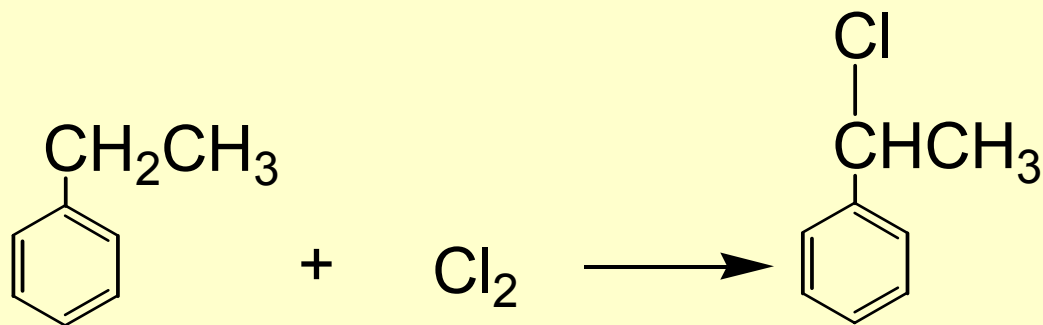
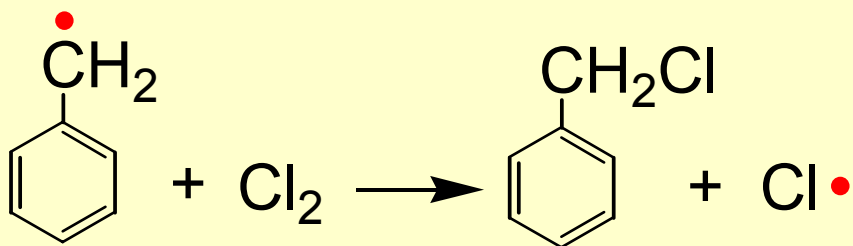
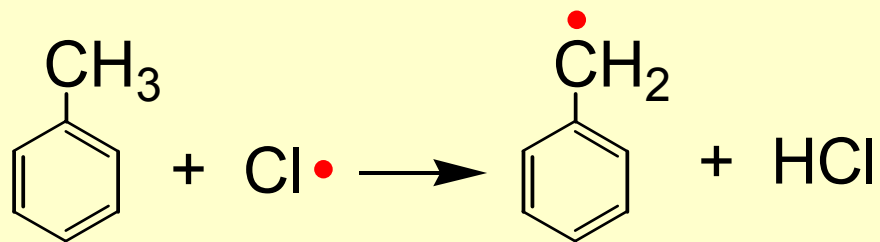
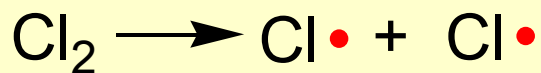


## 四、烷基苯侧链上的卤化反应

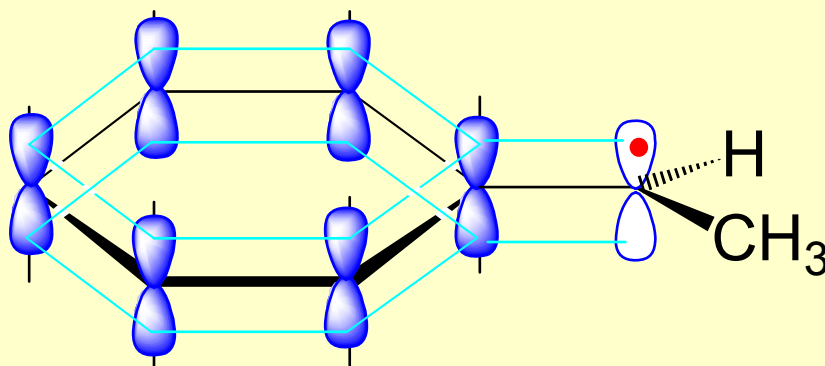
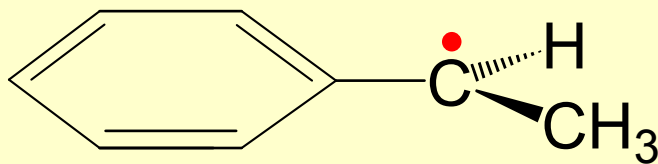




# 侧链卤代反应的历程

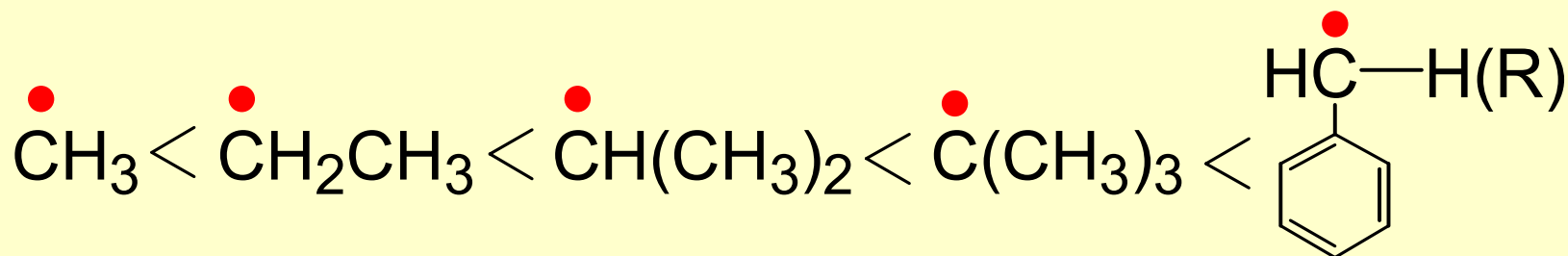


# 侧链卤代反应的历程

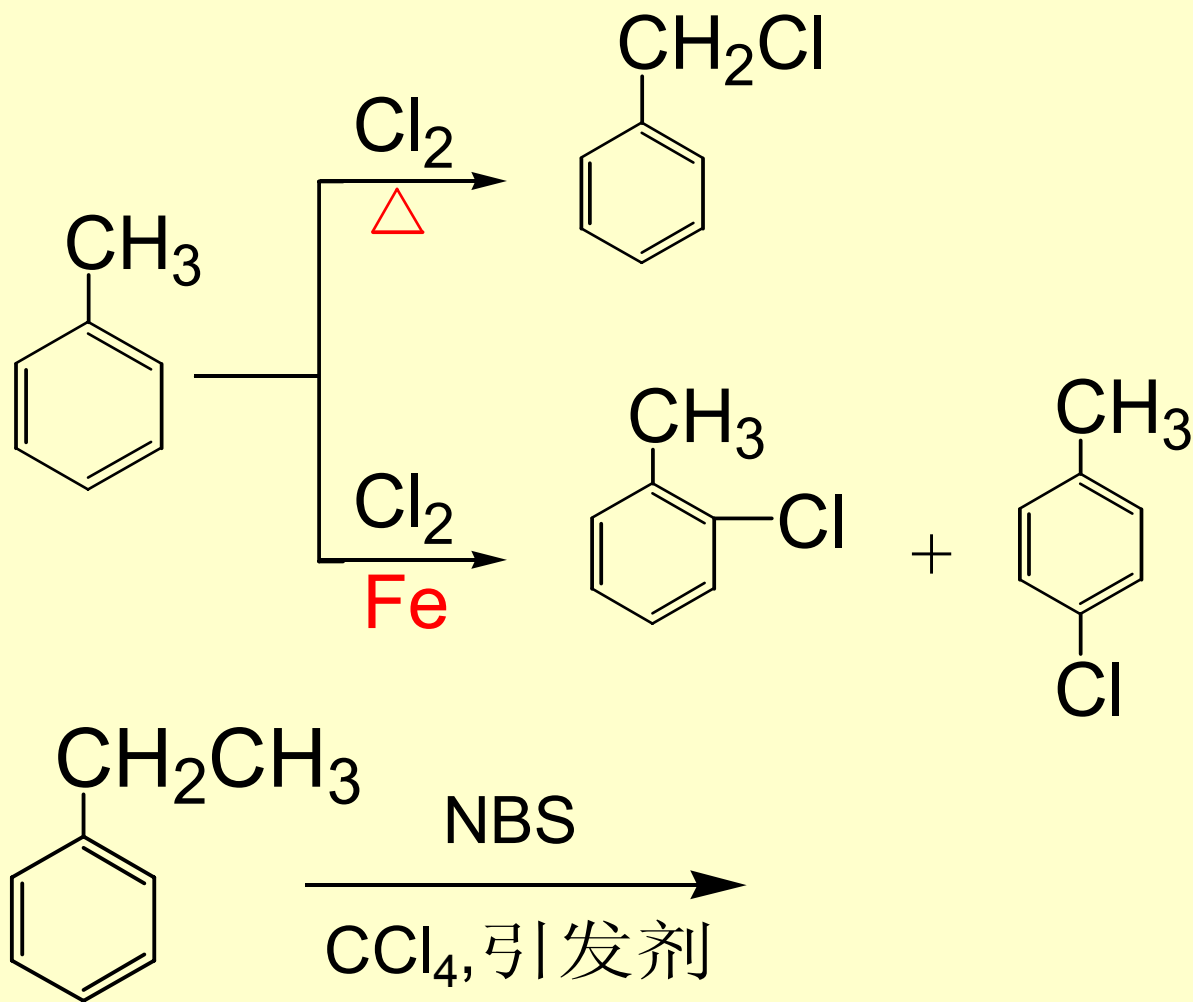


p-π共轭

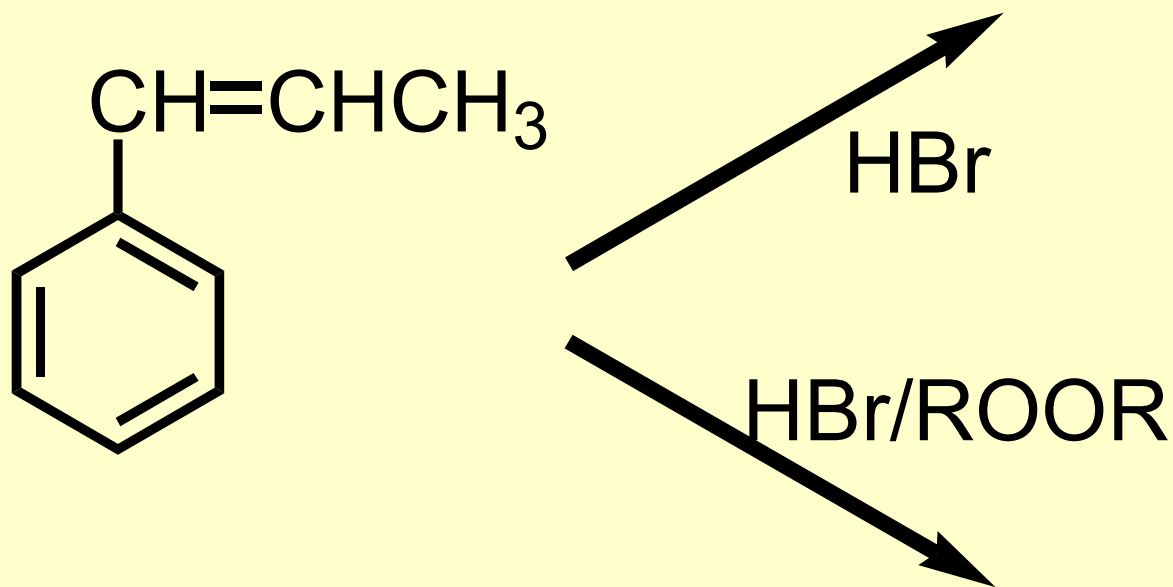
自由基的稳定顺序:



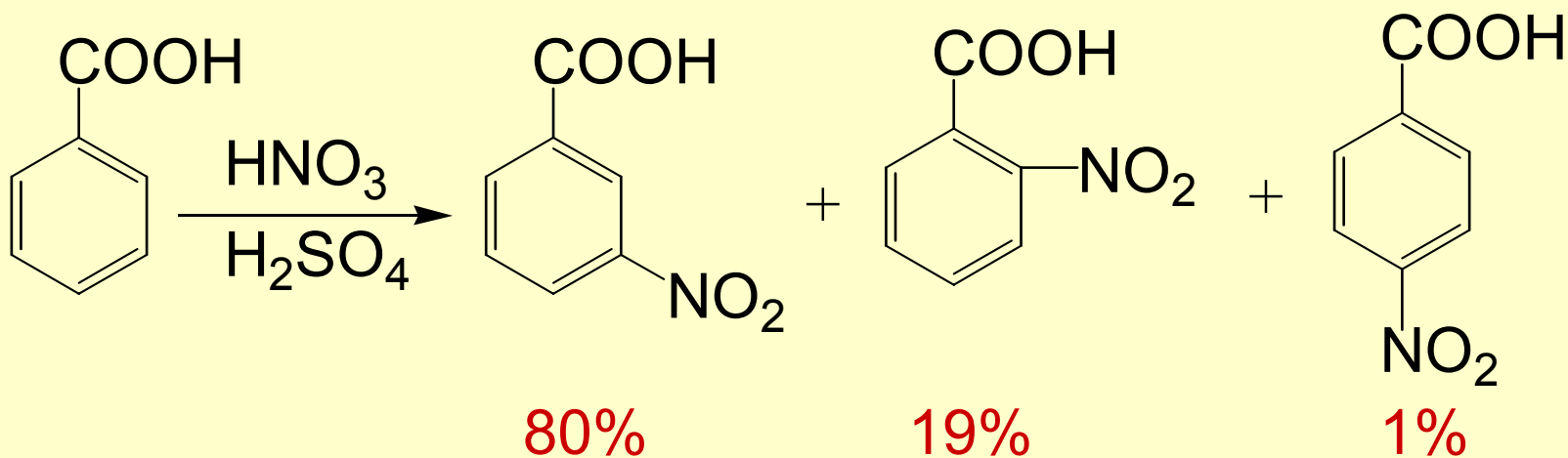
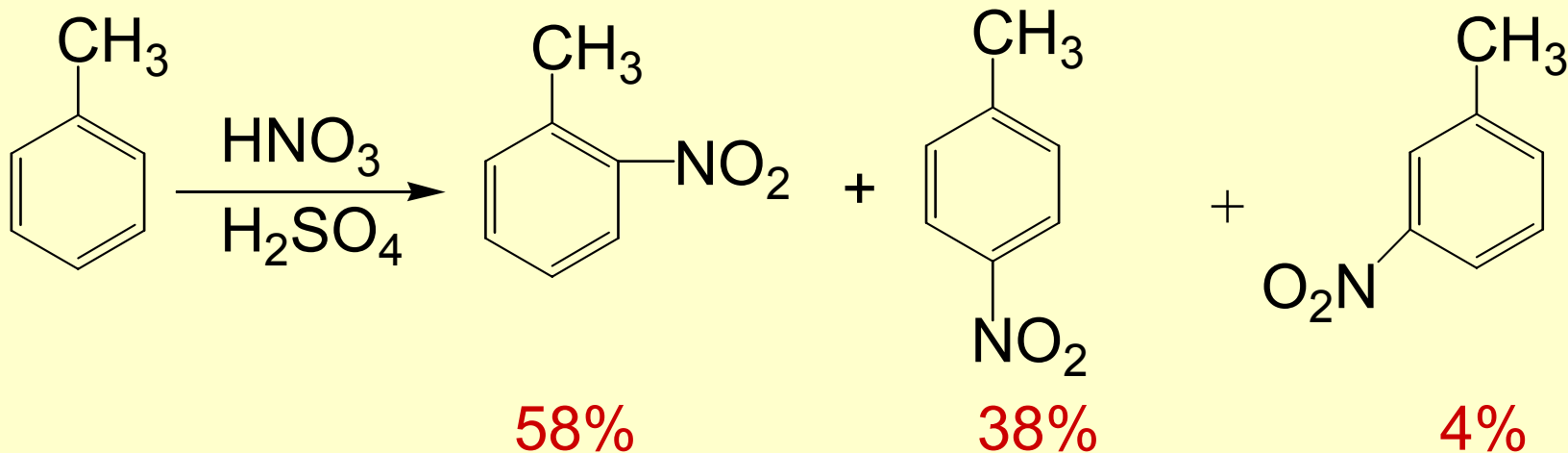
## 四、烷基苯侧链上的卤代反应



## 五、烯基苯的反应



# 第四节 苯环亲电取代的定位规律



## 第五节 苯环亲电取代的定位规律

**第一类定位基**——**邻对位定位基**：苯环上原有取代基指导新引入的取代基主要进入其邻位和对位(邻对位取代物之和  $> 60\%$ )，称为邻对位取代基。一般为活化基团。

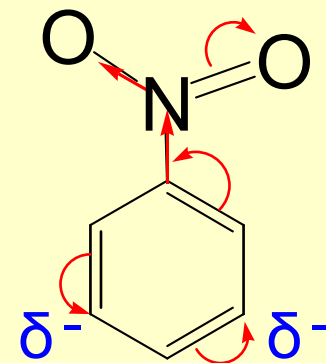
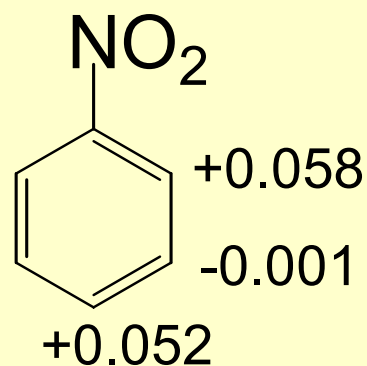
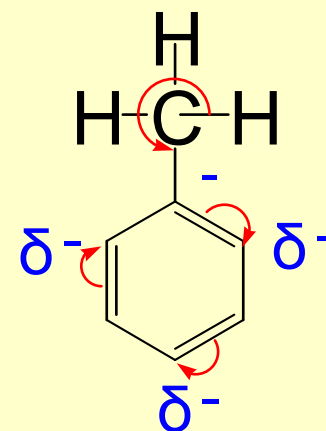
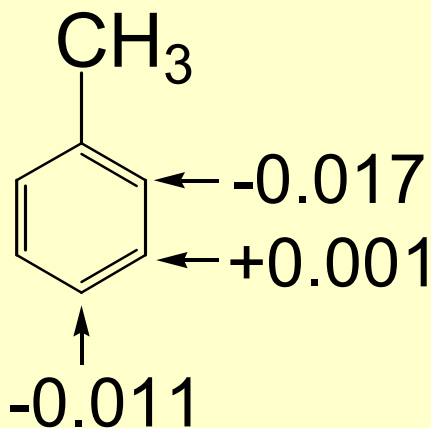
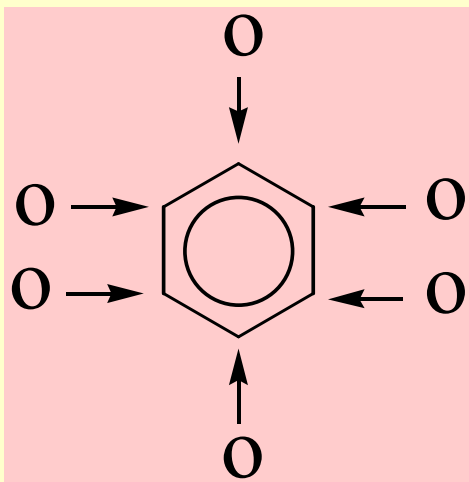
-R. -X. -OH. -OR. -NH<sub>2</sub>. -NHR. -OOCR

**第二类定位基**——**间位定位基**：苯环上原有取代基指导新引入的取代基主要进入其间位(邻对位取代物  $> 40\%$ )，称为间位取代基。一般为钝化基团。

-NO<sub>2</sub>. -CN. -SO<sub>3</sub>H. -CHO. -COOH

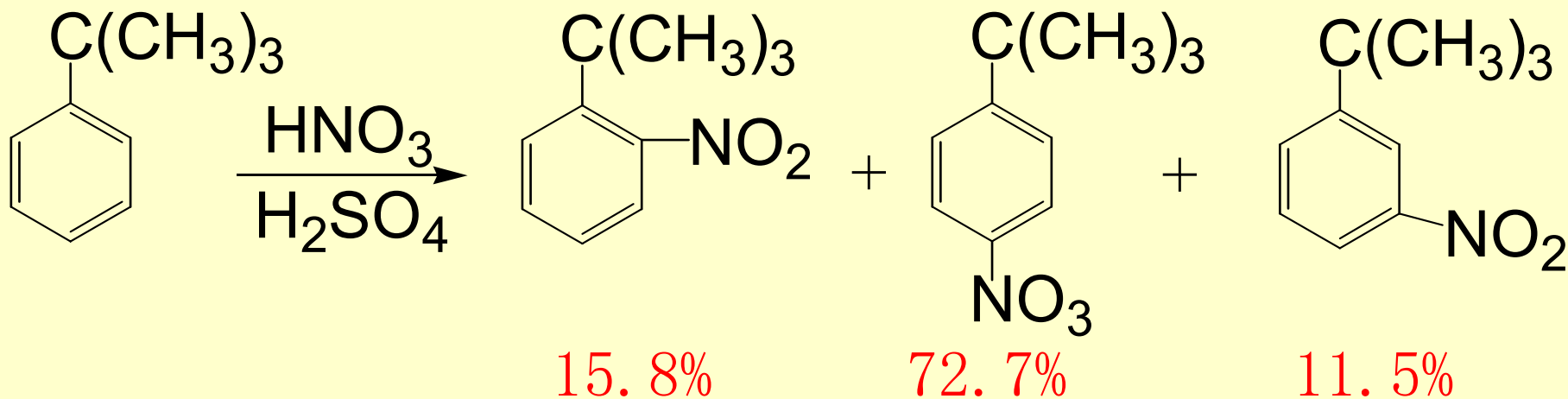
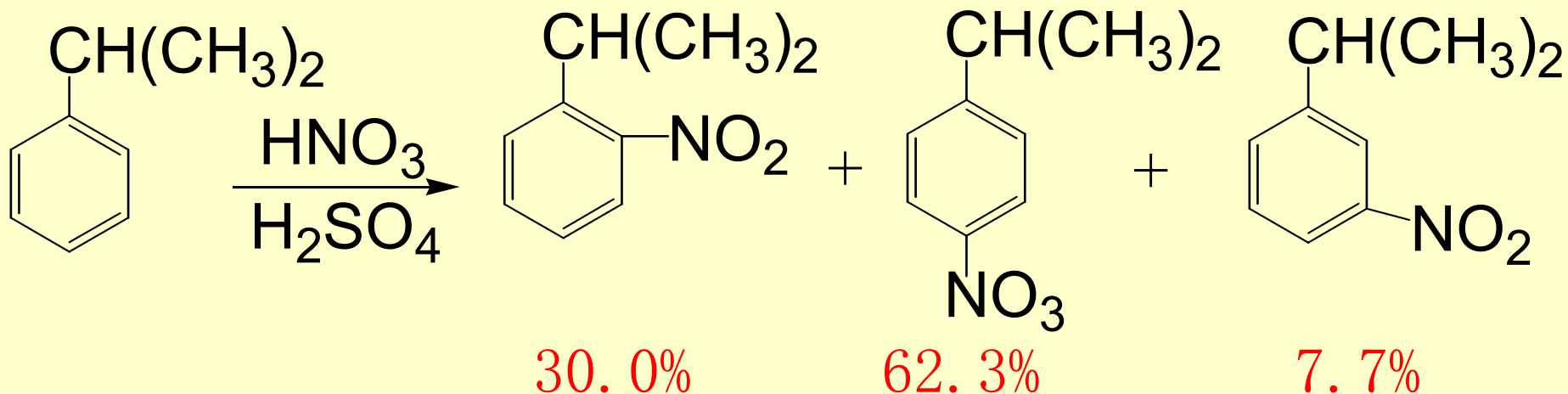
# 苯环取代的定位效应的解释

## 1、取代基的电子效应



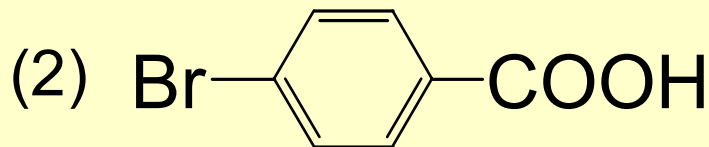
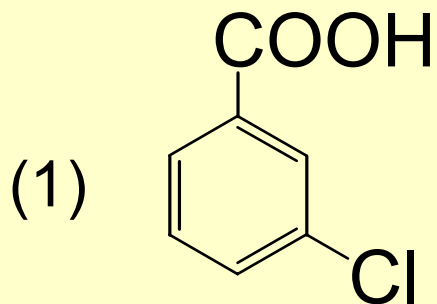
# 苯环取代的定位效应的解释

## 2、取代基的空间效应



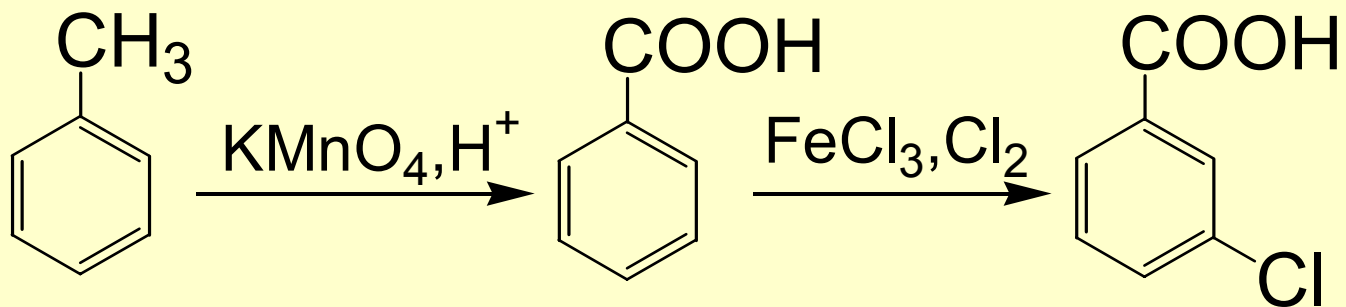


# 例题：用甲苯合成下列化合物

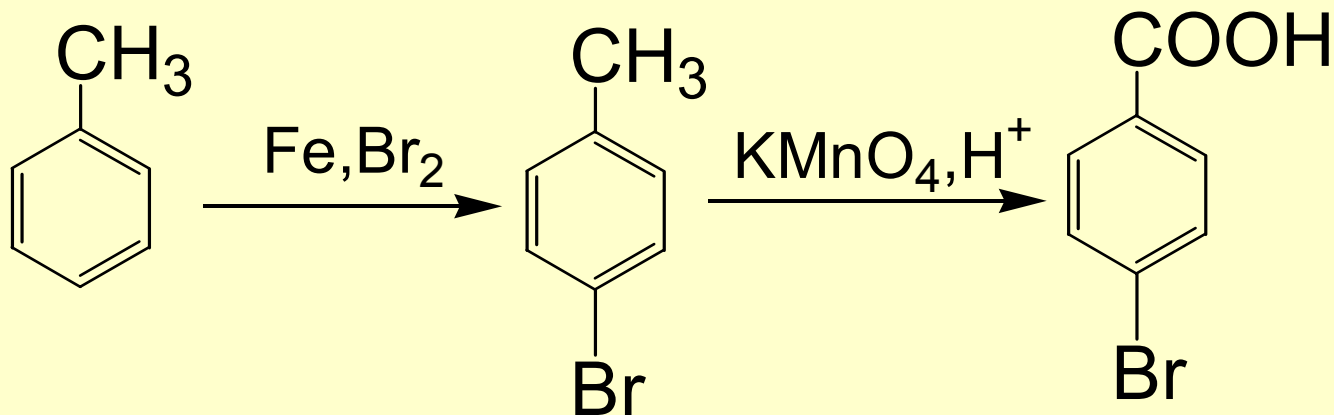


解：

(1)



(2)



# 例题与讨论

写出下列化合物的苯环硝化活性由强到弱顺序：

1、 苯、1,3,5-三甲基苯、甲苯、间二甲苯、对二甲苯

2、 苯、溴苯、硝基苯、甲苯

3、 2,4-二硝基氯苯、2,4-二硝基酚

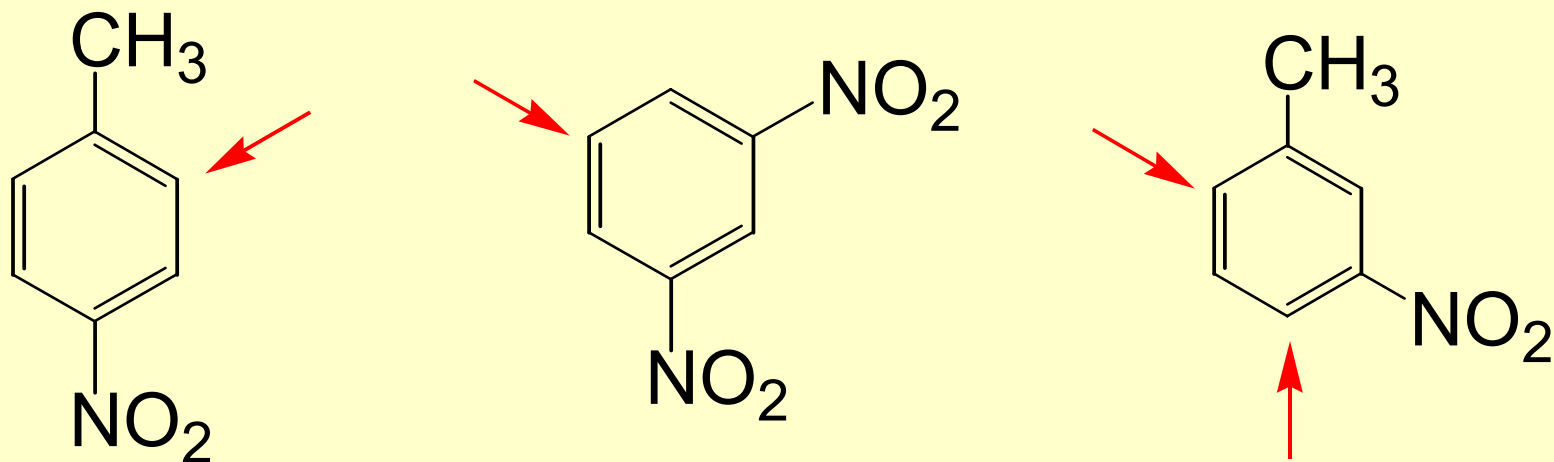
**解：**（a）1,3,5-三甲基苯、间二甲苯、对二甲苯、甲苯、苯

（b）甲苯、苯、溴苯、硝基苯

（c）2,4-二硝基酚、2,4-二硝基氯苯

# 二元取代苯的取代反应的定位规律

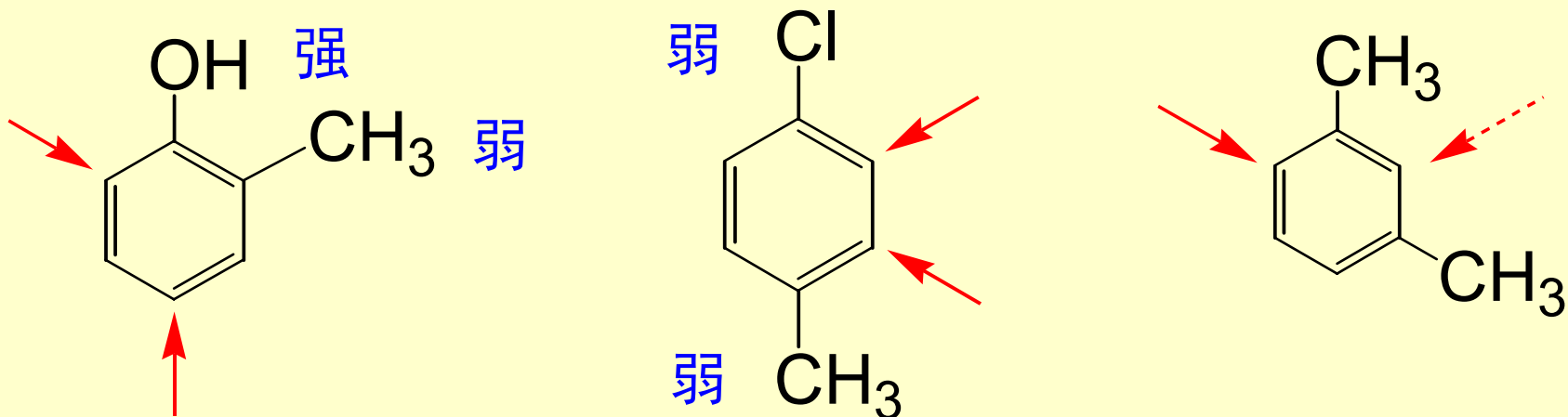
①若原有的两个取代基相互一致而增强，引入第三个取代基的定位不成问题。



②当一个为邻、对位定位基而另一个为间位基时，由邻、对位基控制定位。

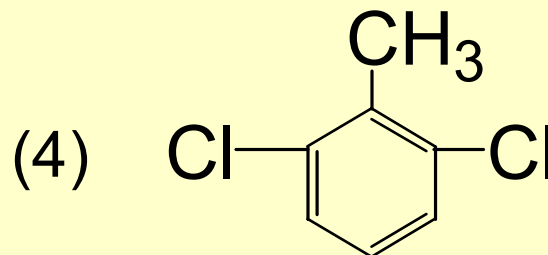
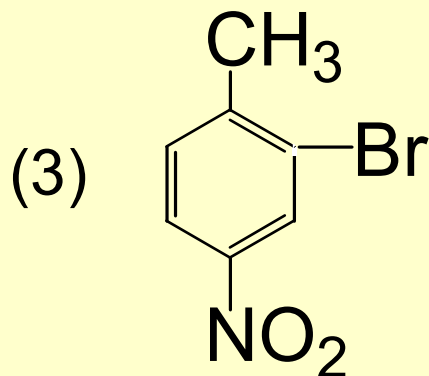
# 二元取代苯的取代反应的定位规律

③当较强的活化基团与较弱的活化基团竞争时，由较强的活化基团控制定位。强度相同，得到差不多相等数量的异构体。



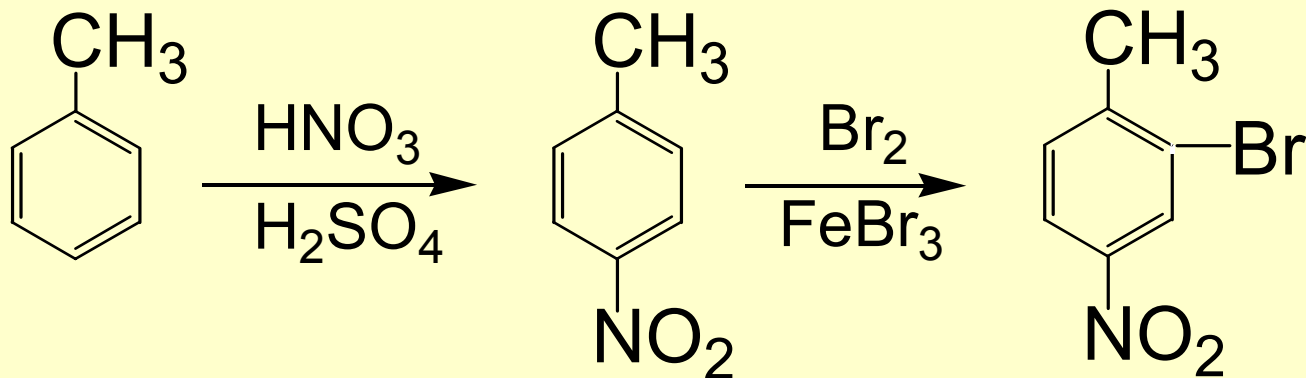
④在两个相互处于间位的取代基之间，由于空间阻碍，很少会发生亲电取代反应。

# 例题：用甲苯合成下列化合物



解：

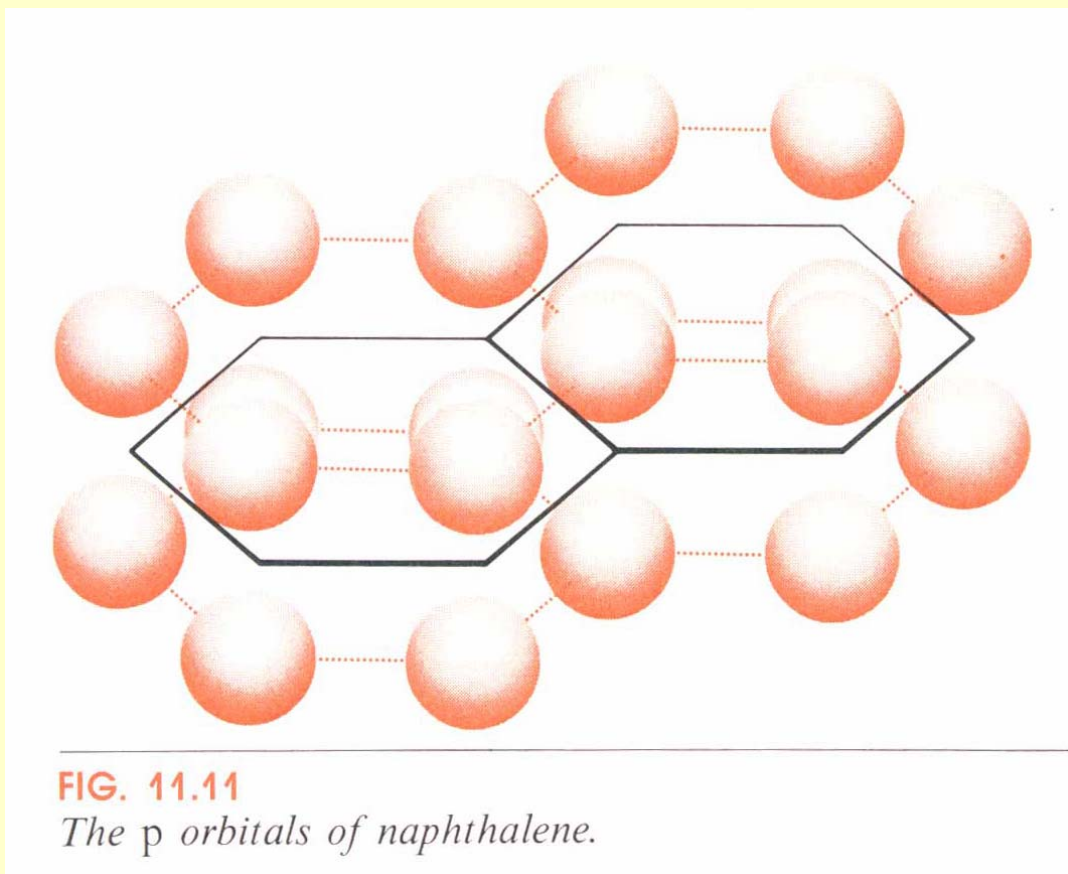
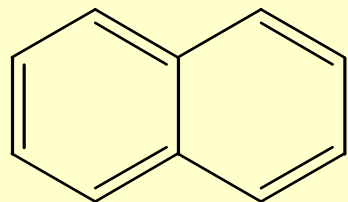
(3)



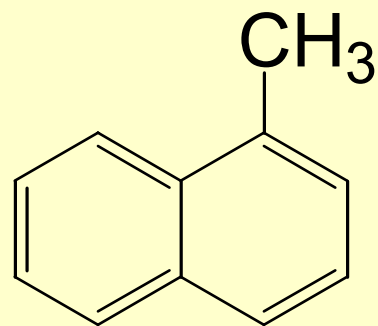
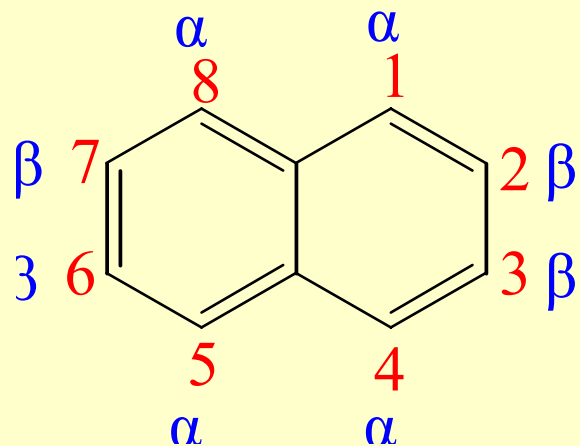
# 第六节 多环芳烃

## (一) 稠环芳烃

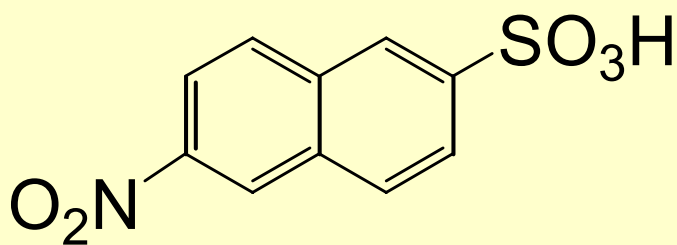
### 1、萘的结构



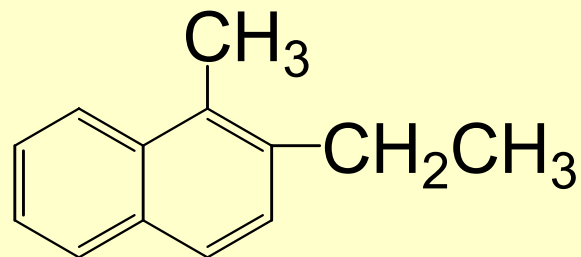
## 2、萘的命名



1-甲基萘 ( $\alpha$ -甲基萘)

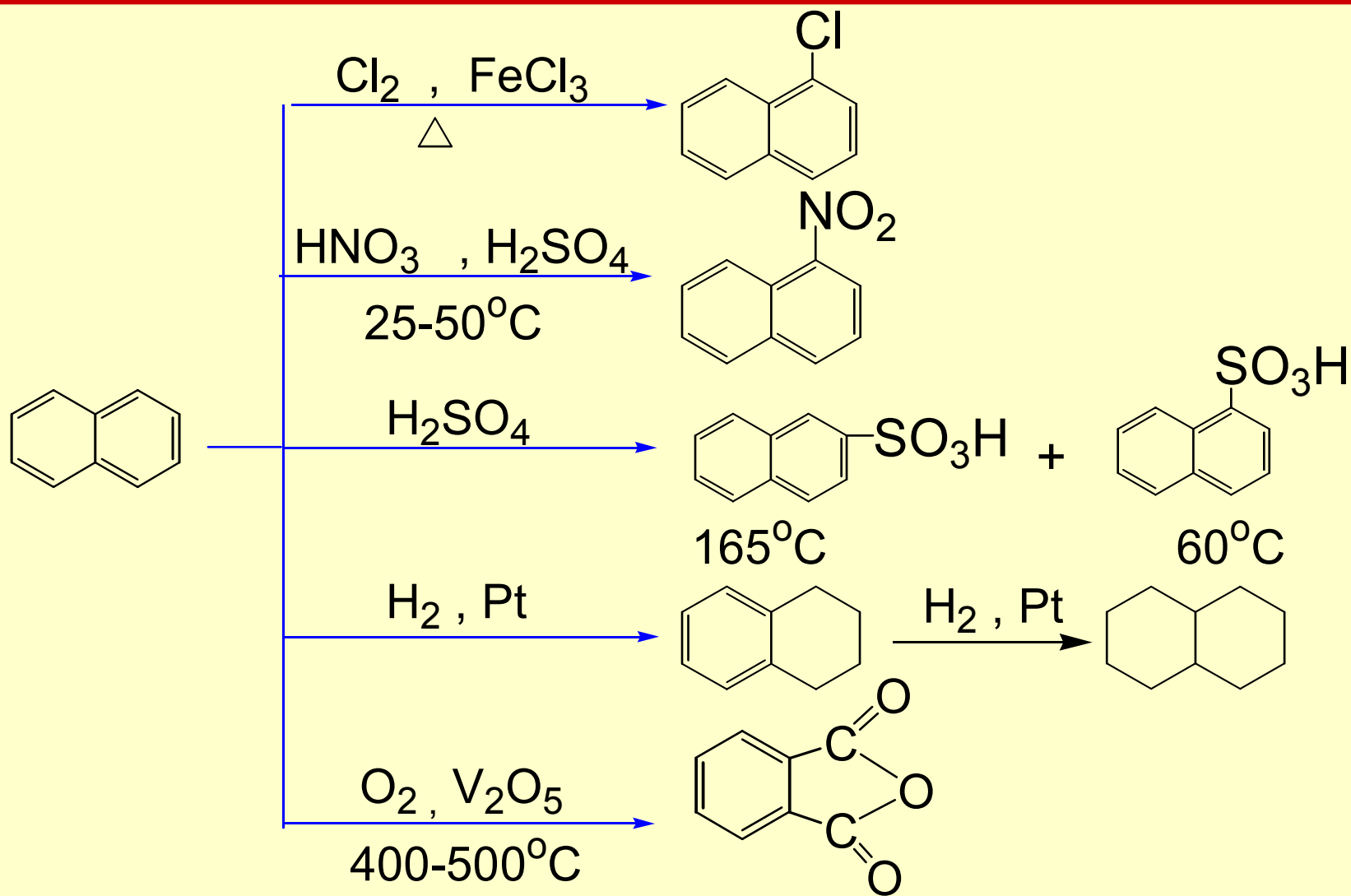


6-硝基-2-萘磺酸



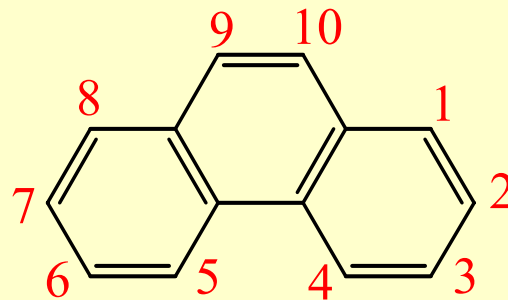
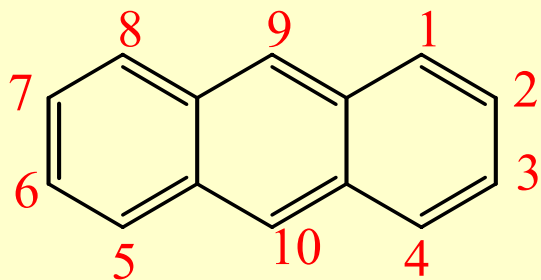
1-甲基-2-乙基萘

# 3、萘的化学性质

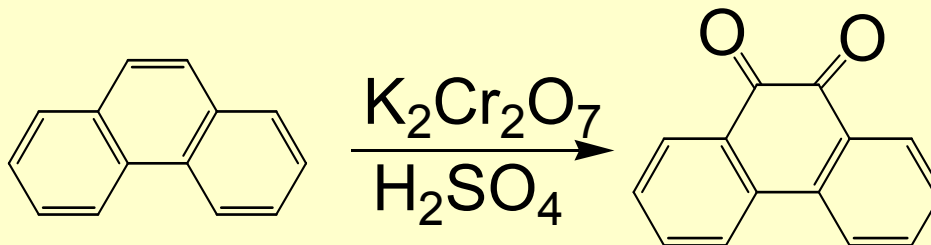
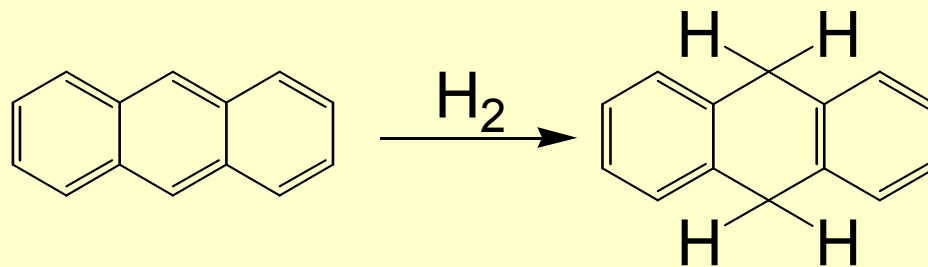




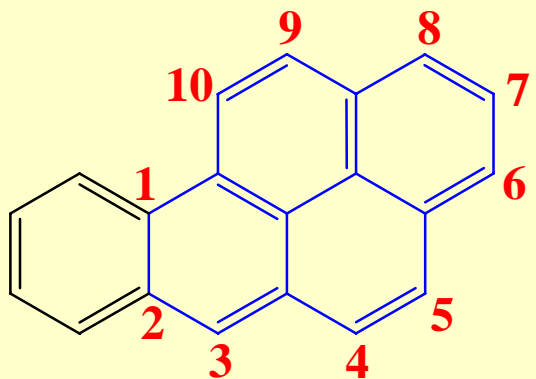
# 4、蒽和菲



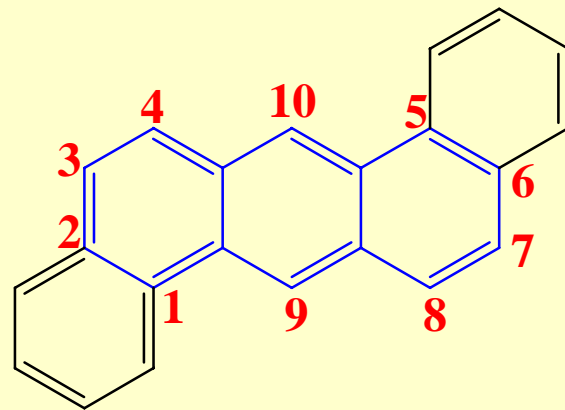
化学性质在9，10位较活泼



## 5、致癌芳香烃



1, 2-苯并芘



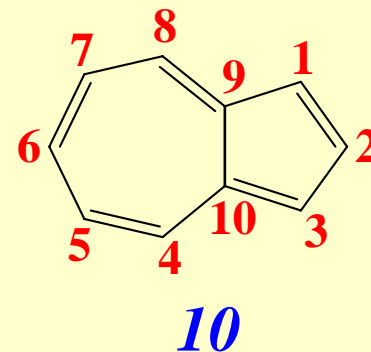
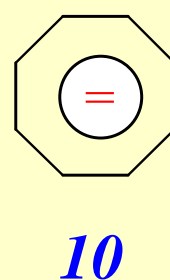
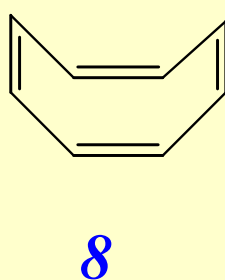
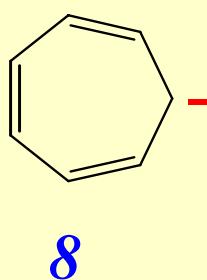
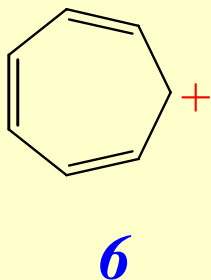
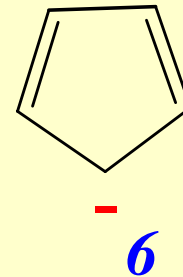
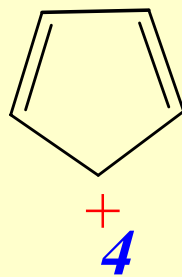
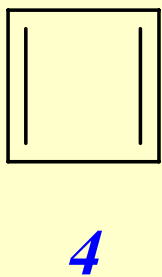
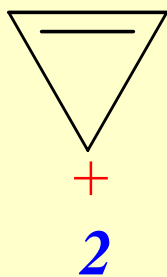
1, 2, 5, 6-二苯并蒽

苯并芘是煤焦油的主要成分，食物烟熏过程中会遭受污染。1kg烟熏羊肉中的苯并芘 $\approx$ 250支卷烟。

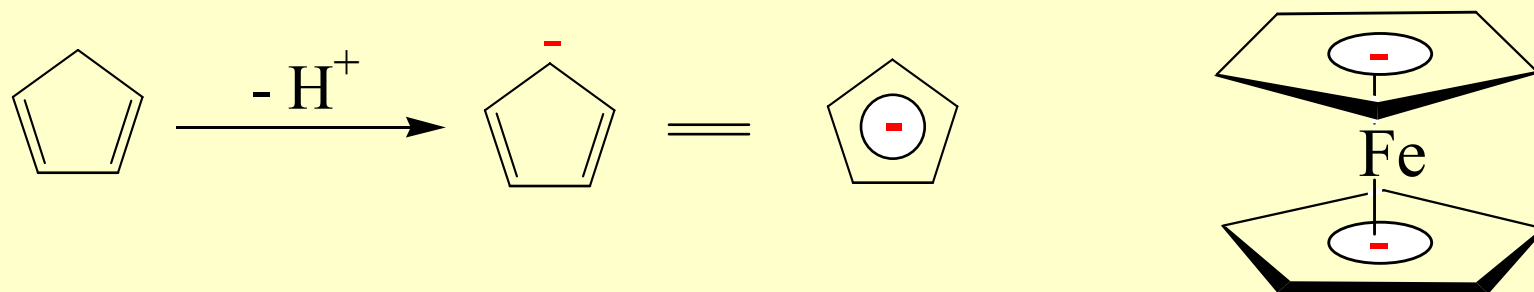
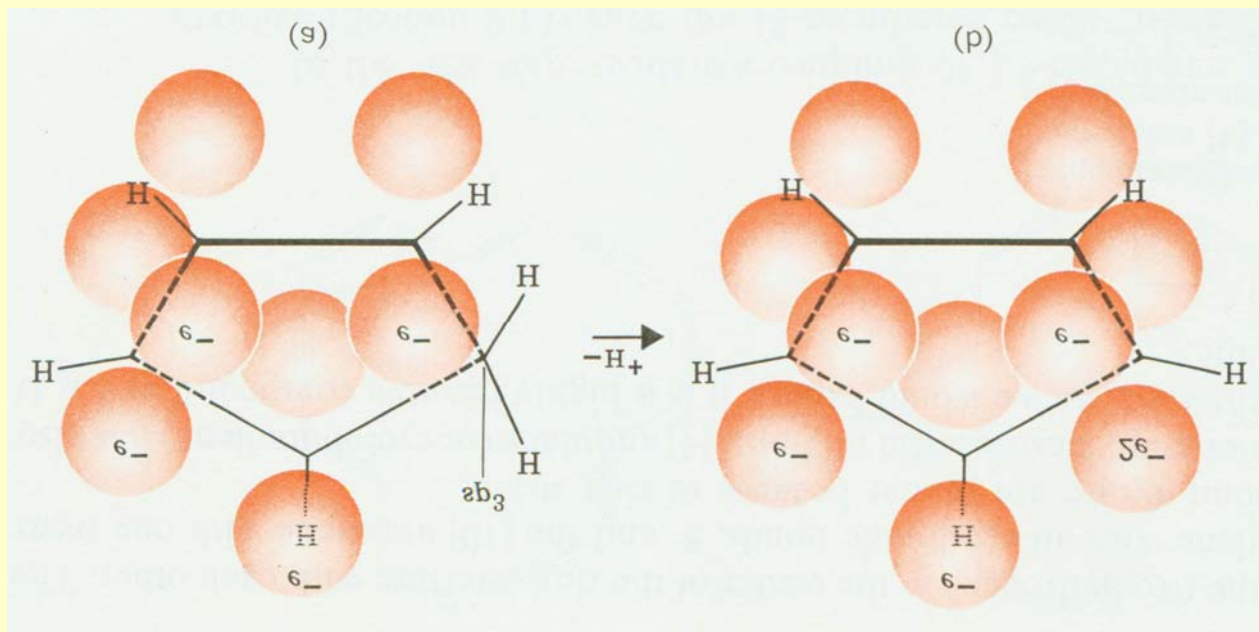
# 第七节 非苯系芳香烃

芳香性(aromaticity): 环稳定, 易取代, 难加成。

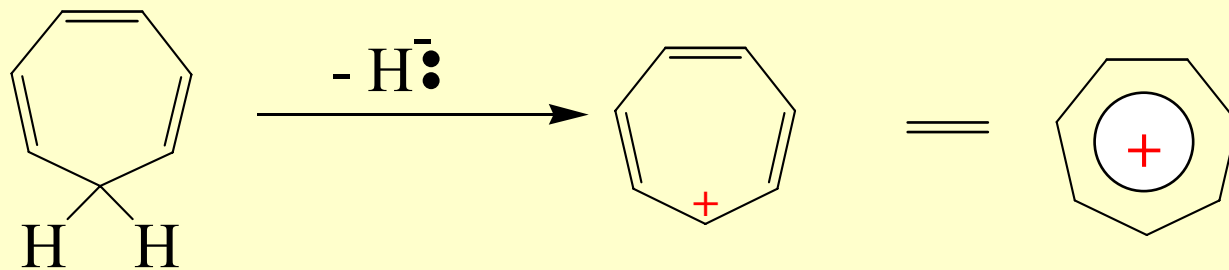
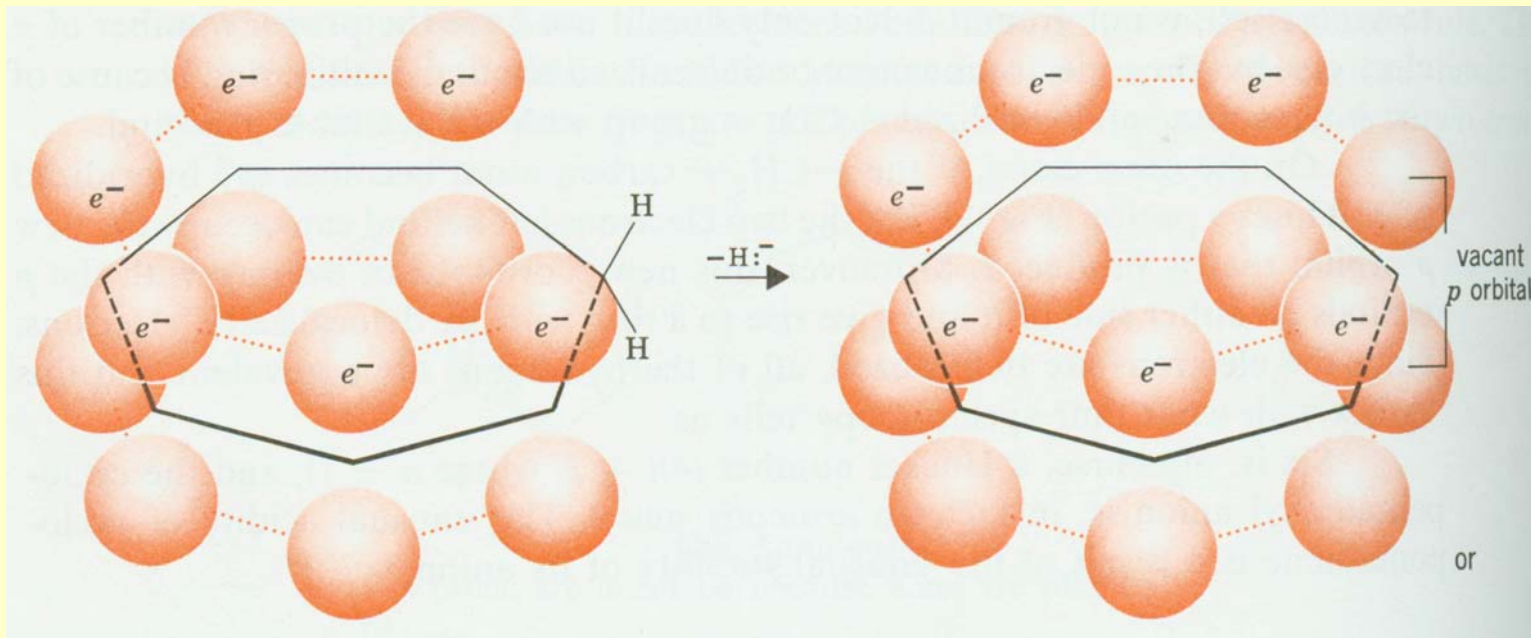
Hückel规则: 环多烯化合物中, 具有共平面的离域体系, 其  $\pi$  电子数等于  $4n+2$  ( $n=0, 1, 2, 3\dots$ ), 此化合物具有芳香性。



# 非苯型芳香烃



# 非苯型芳香烃



# 例题与讨论

用化学方法区别下列化合物：

(1) 苯与甲苯

(2) 环戊二烯和环戊二烯负离子

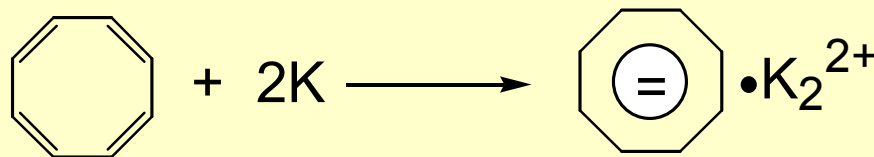
解：（1）分别取两物质于两个试管中，分别加入酸性高锰酸钾溶液，使高锰酸钾褪色的是甲苯，不褪色的是苯。

（2）分别取两物质于两个试管中，分别加入金属钠，有气体产生的是环戊二烯，无气体产生的是环戊二烯负离子。

# 例题与讨论

2mol K与1mol 1,3,5,7-环辛四烯反应(不放出H<sub>2</sub>)生成的一个稳定化合物，该化合物不溶于非极性溶剂，而易溶于极性溶剂，说明理由。

解：两个K原子提供两个电子给1,3,5,7-环辛四烯，生成1,3,5,7-环辛四烯二负离子的钾盐。因为是盐，所以，不溶于非极性溶剂，而易溶于极性溶剂。该反应方程式为：



1,3,5,7-环辛四烯二负离子是稳定的共轭体系，符合休克尔规则，具有芳香性，性质较稳定。