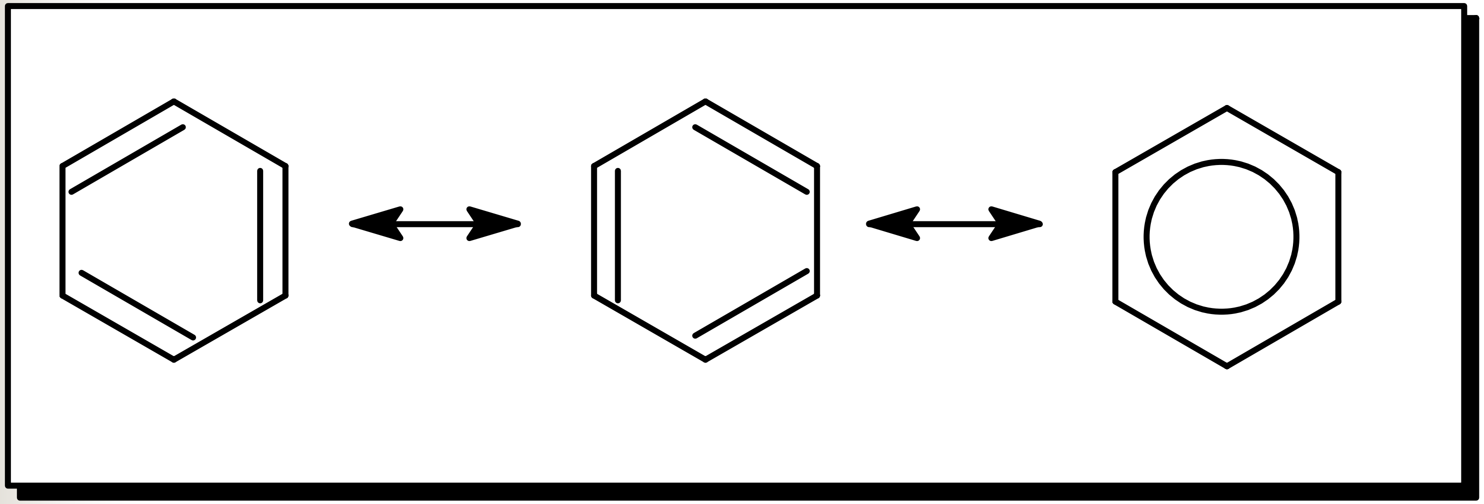
§7. 芳香烃

§7.1 芳香烃的结构及芳香性

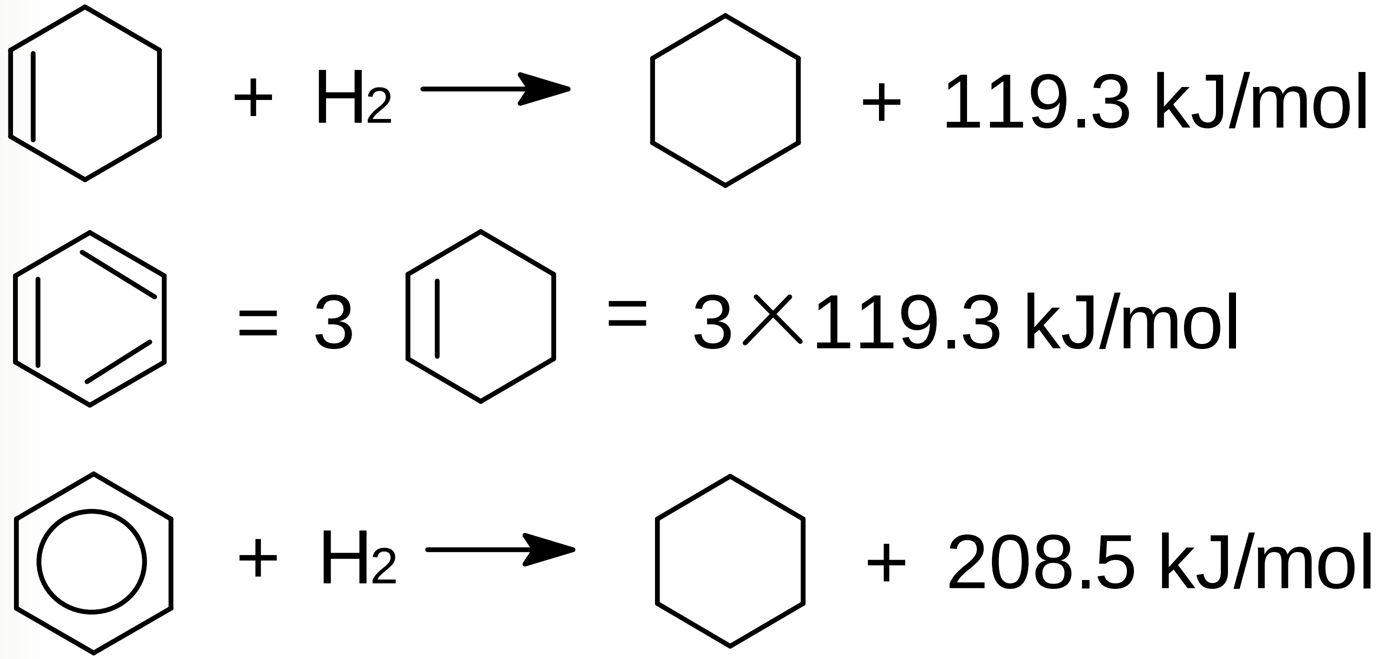
1, 苯的结构

A. 共振论

a. 苯有多个共振结构式



b.共振能=稳定结构式的能量 －杂化体的能量



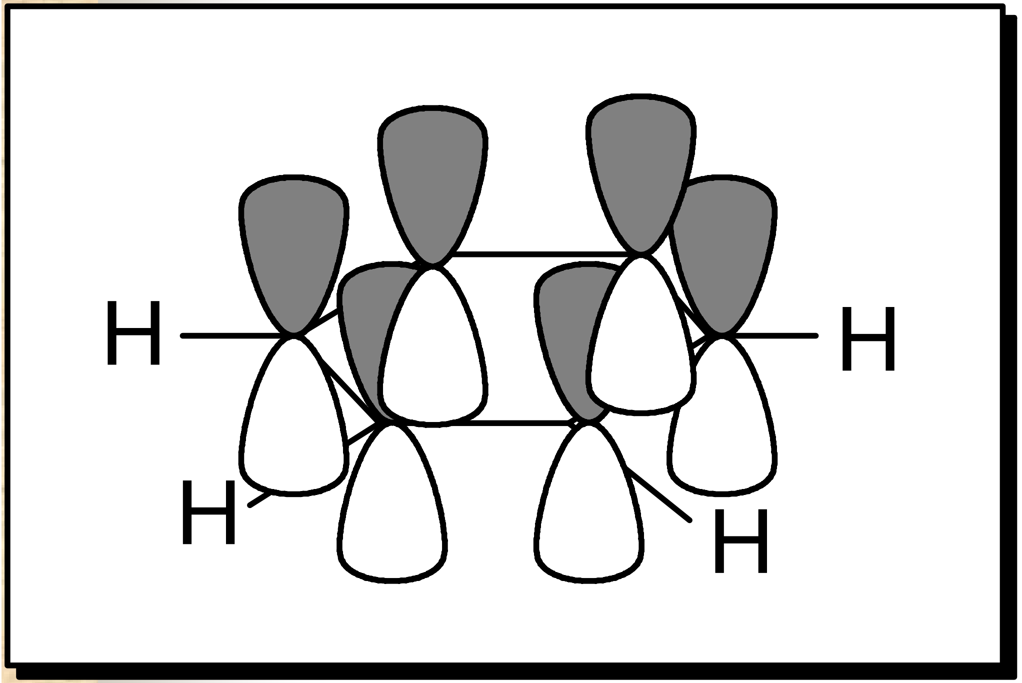
+ H_2 → + 119.3 kJ/mol

= 3 = 3×119.3 kJ/mol

+ H_2 → + 208.5 kJ/mol

共振能 ＝149.3 kJ/mol

B,分子轨道理论



a. 碳原子sp^2杂化,
形成C-C 0.139nm

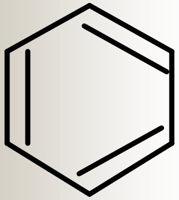
b. 平面型分子, 6个
p轨道肩并肩重
叠形成大π键;

c. 电子离域,为整个
分子所共有.

2. 芳香性

A.芳香性的定义

高度不饱和化合物难以氧化及加成，却易发生亲电取代反应的性质称为芳香性



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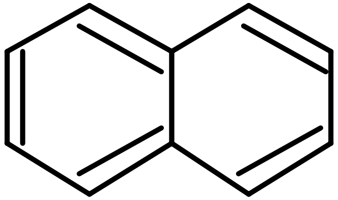

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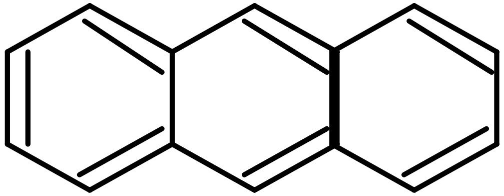

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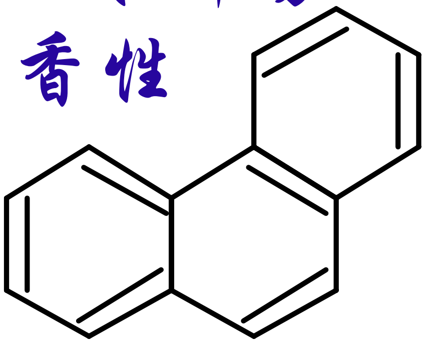


14e

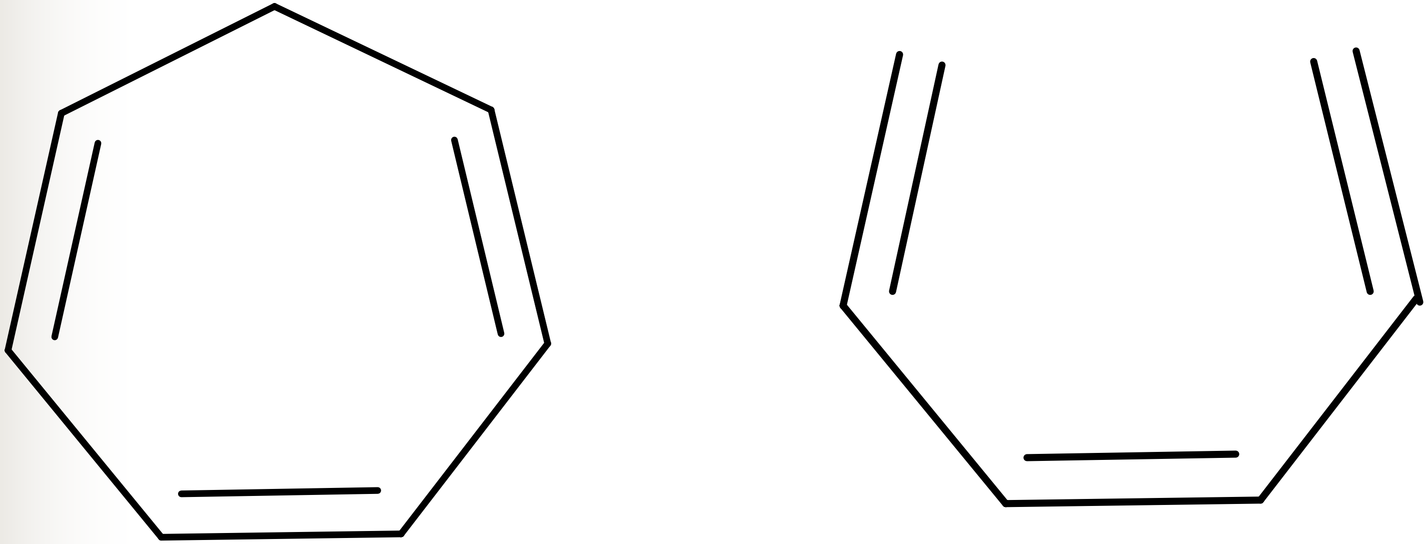
B.判断芳香性的原则－休克尔规则

a. 环状共轭闭合体系(全共轭)

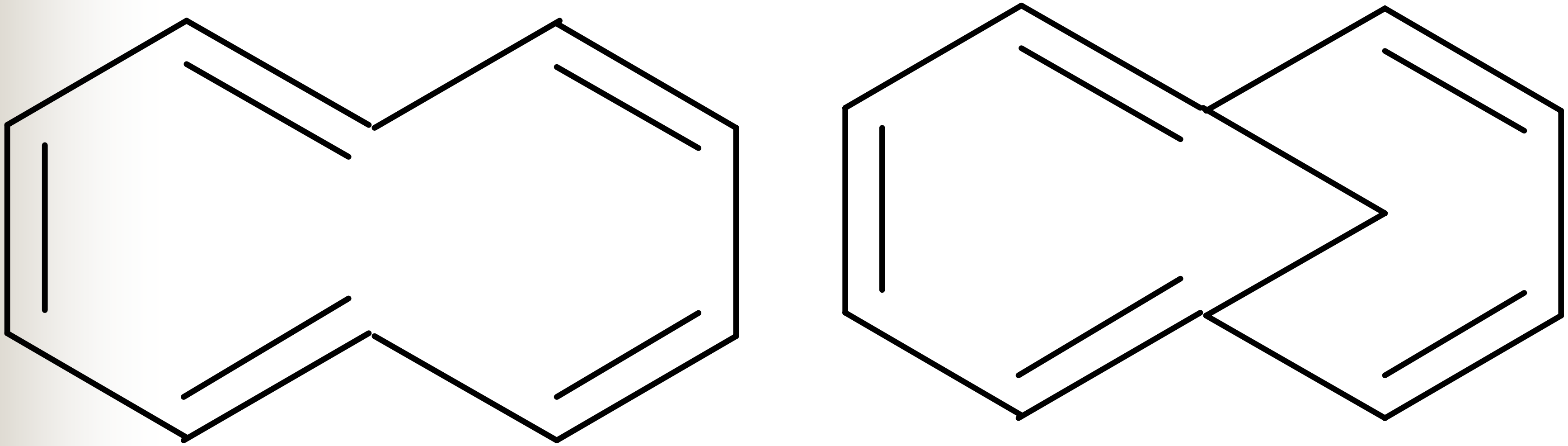
b. 共轭体系共平面(共平面)

c. 共轭体系p电子数为（4n+2）

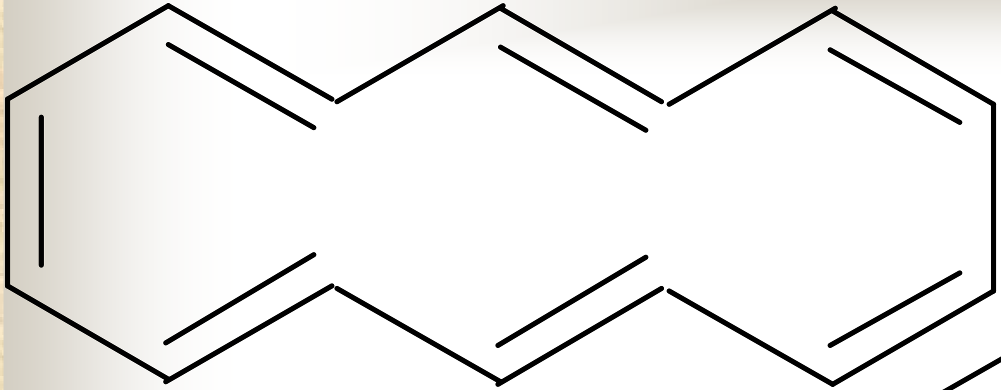
a.环状共轭闭合体系(-全共轭)



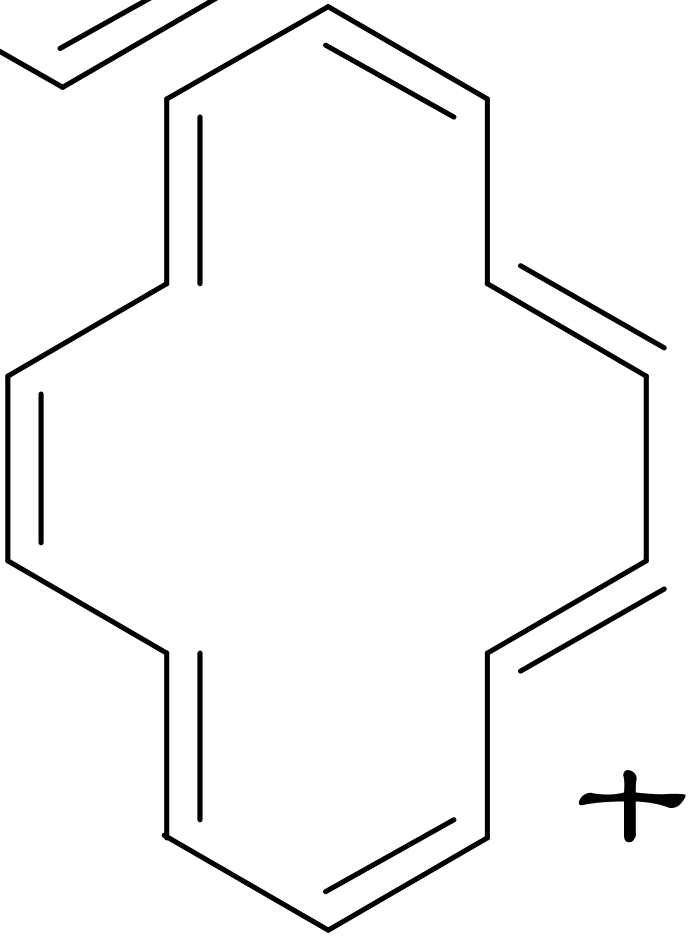
b.共轭体系共平面(-共平面)



十轮烯

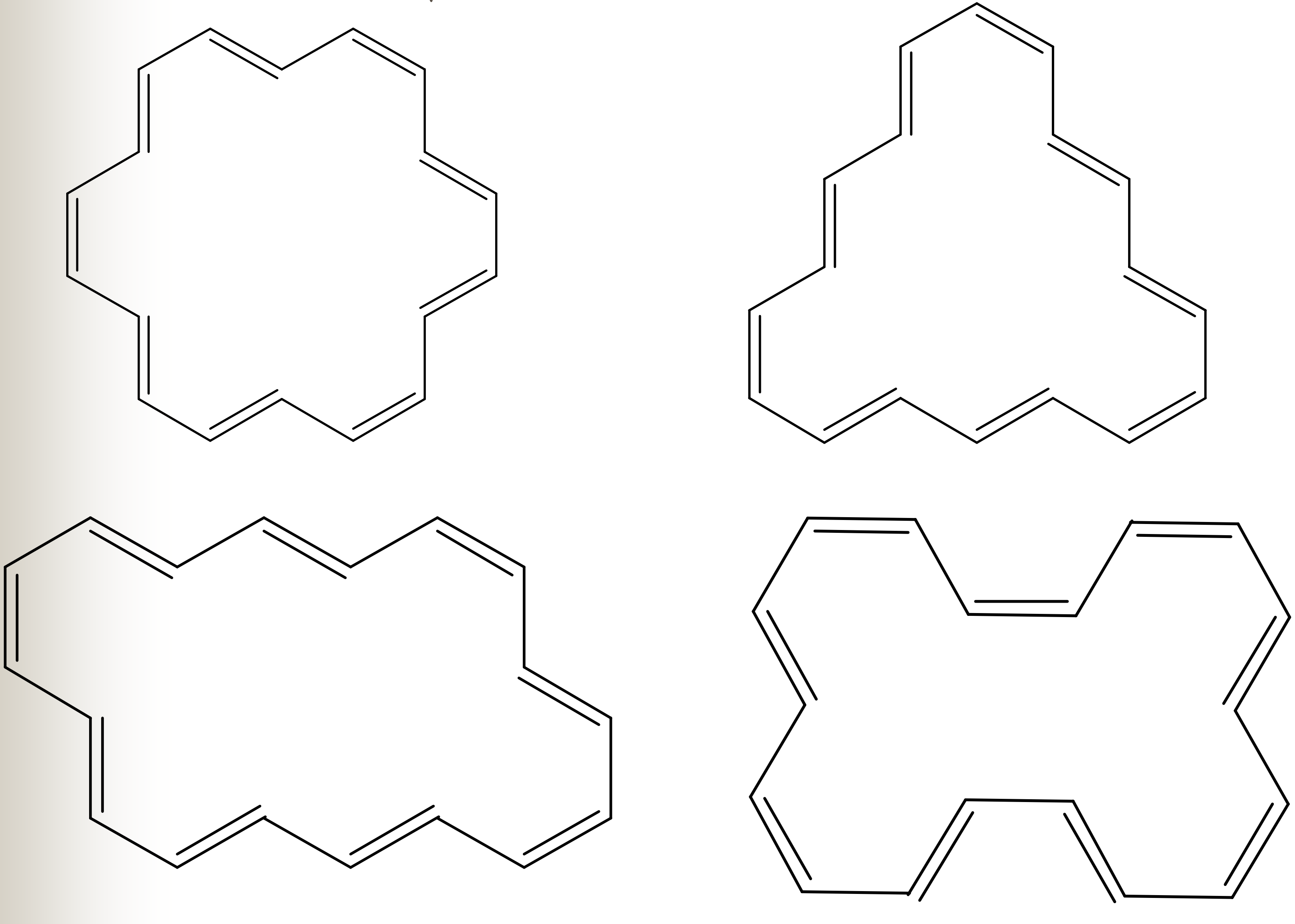


十四轮烯

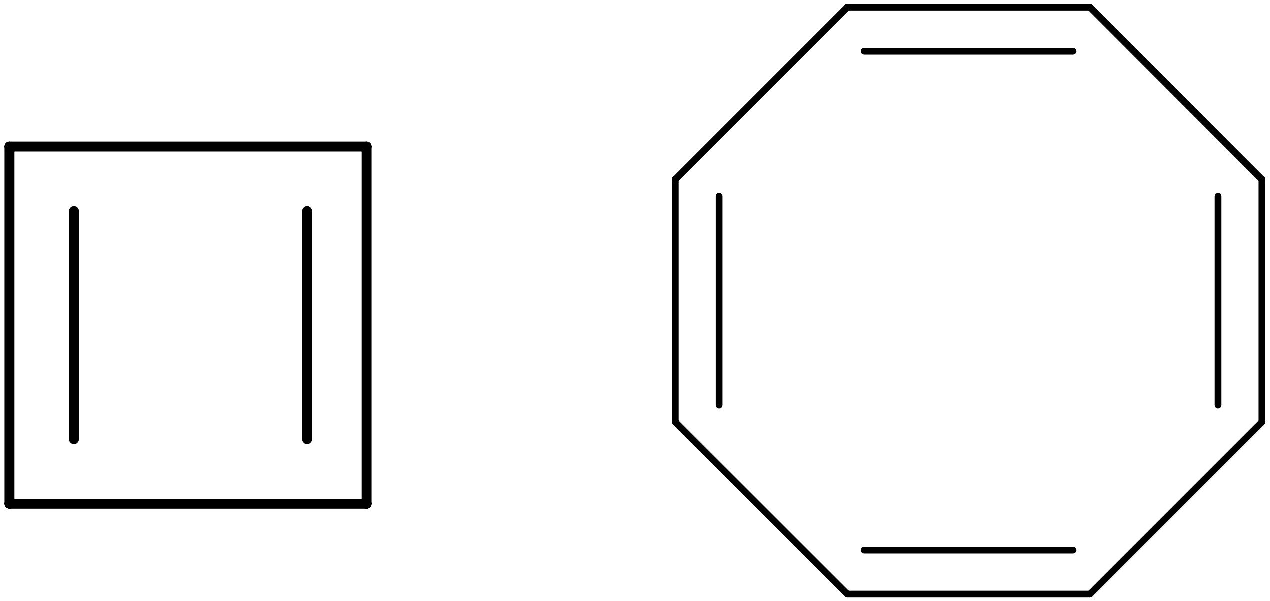


十四轮烯

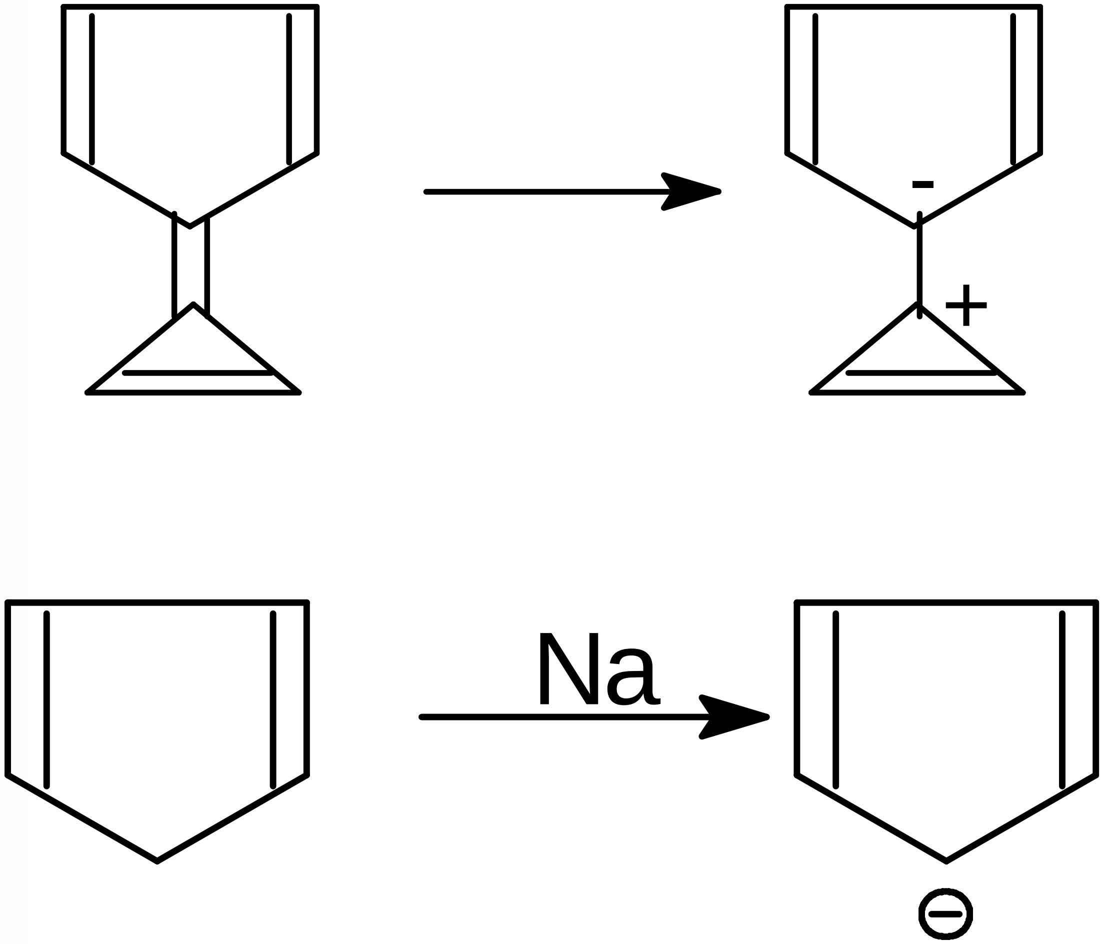
十八轮烯

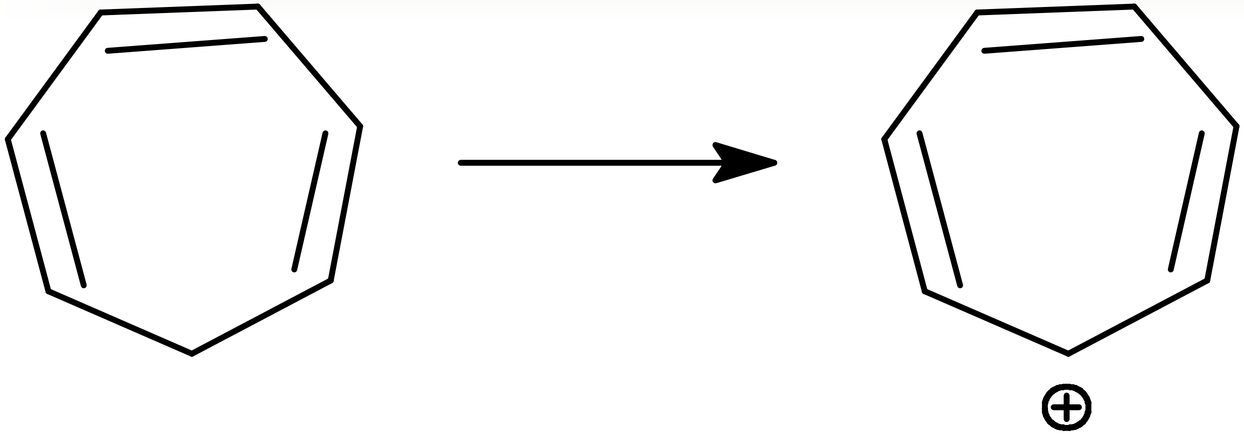


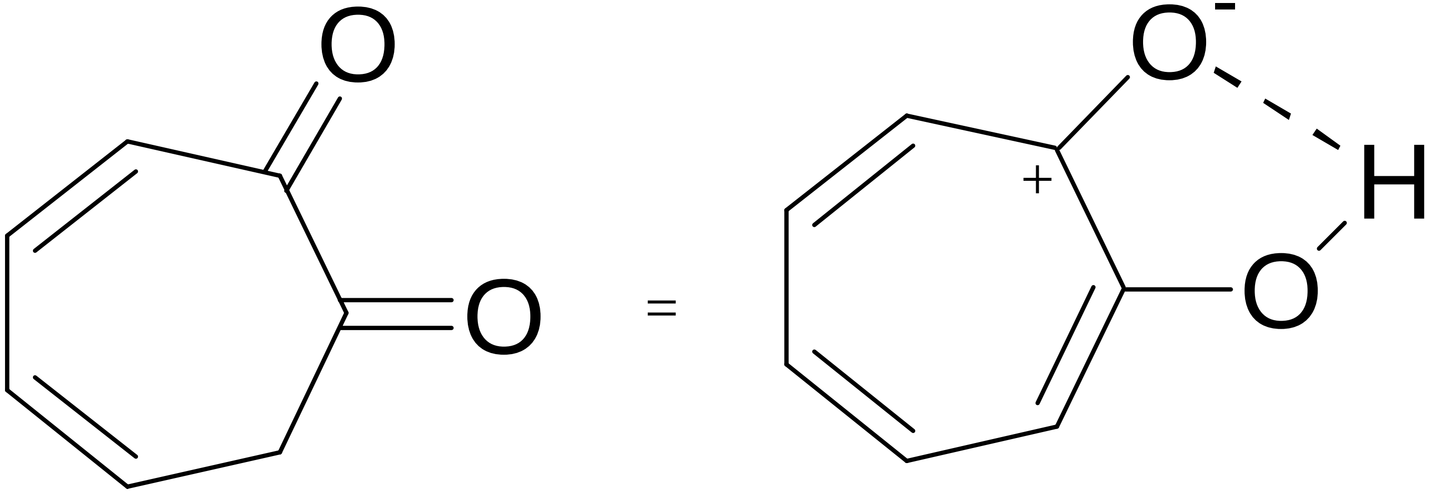
c. 共轭体系p电子数为4n+2



C. 非苯芳烃





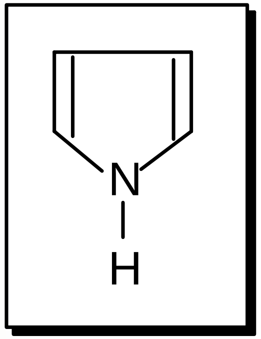


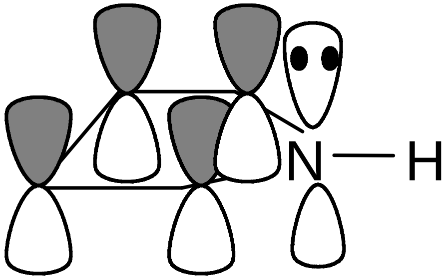
卓酚酮

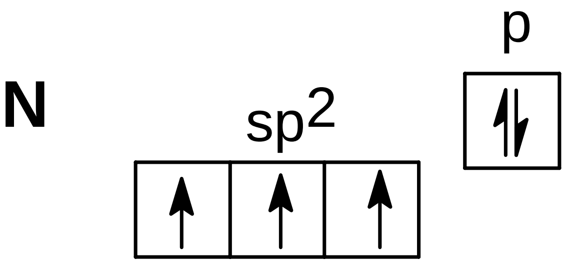
卓酚酮

D.芳香杂环

吡咯







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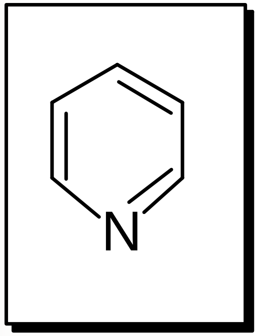

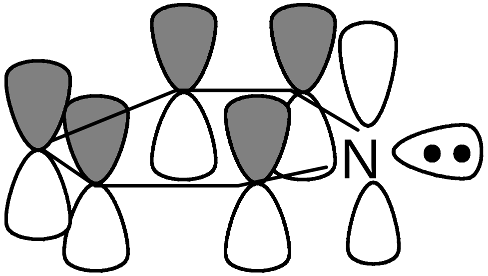

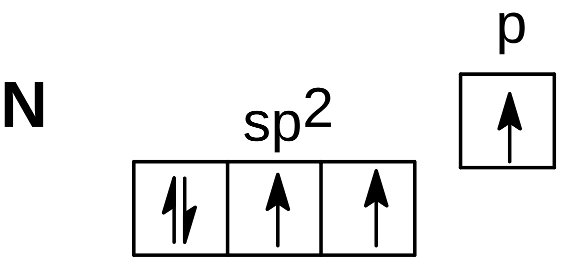

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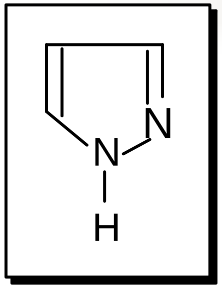

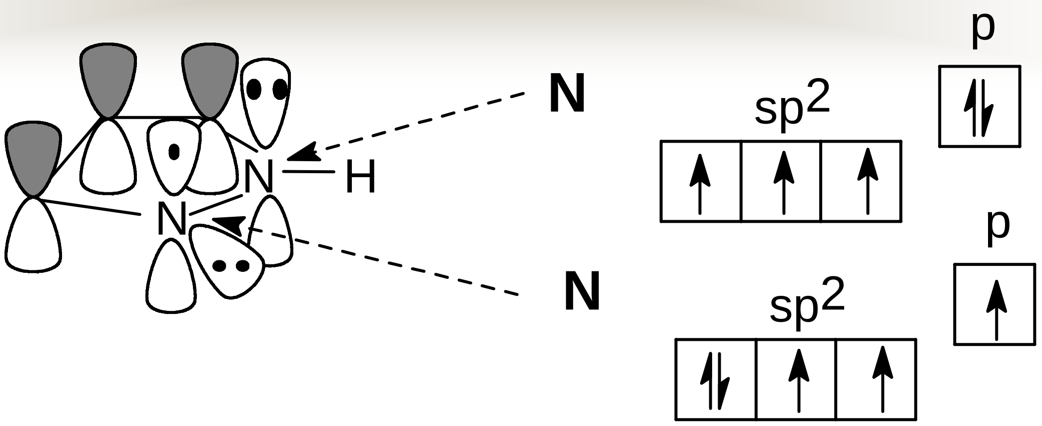

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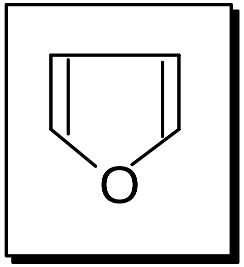

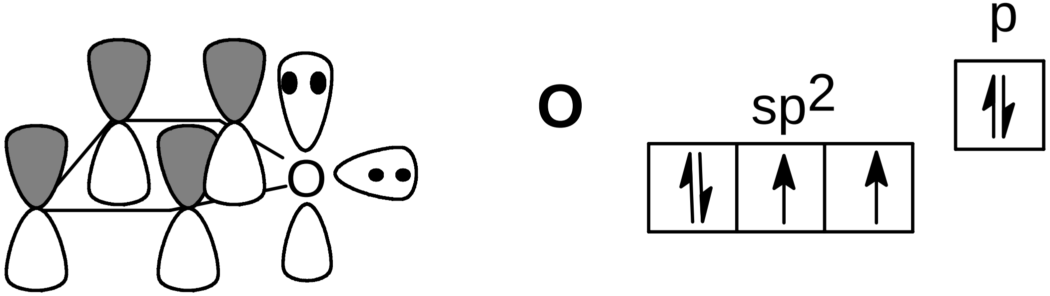

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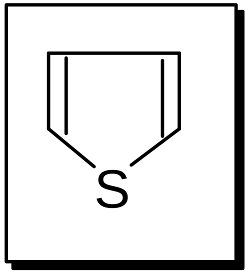

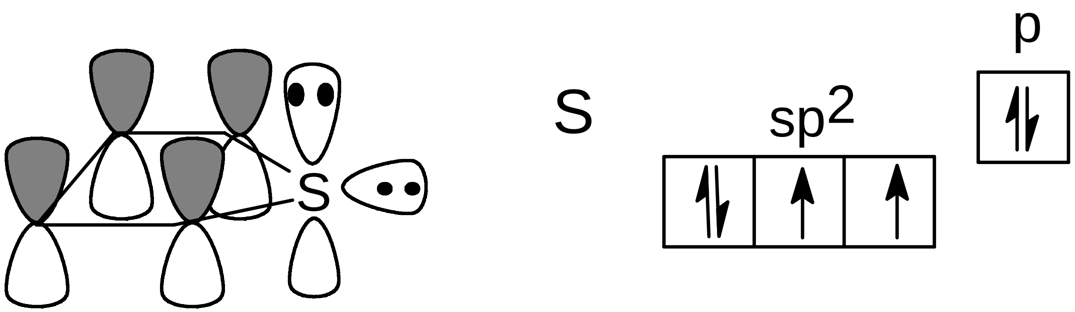

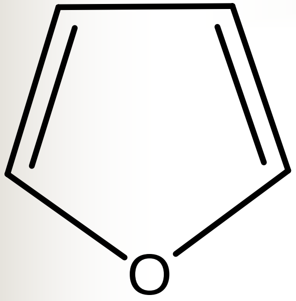

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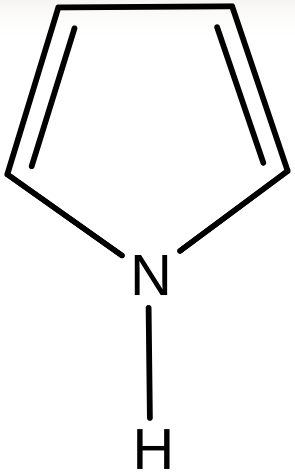

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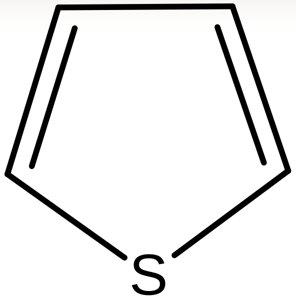

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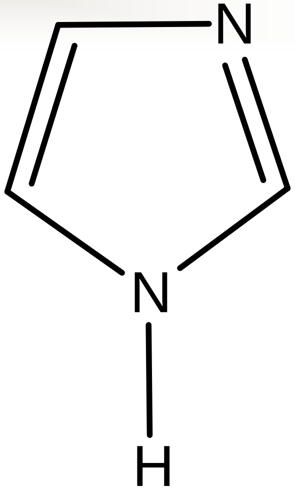

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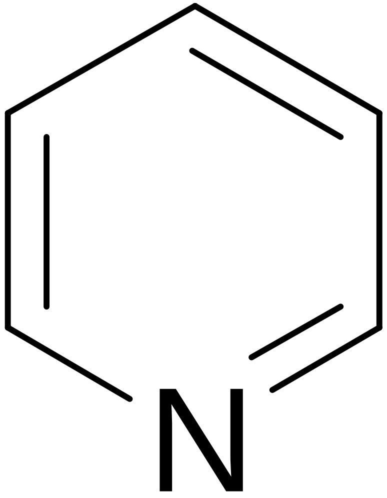
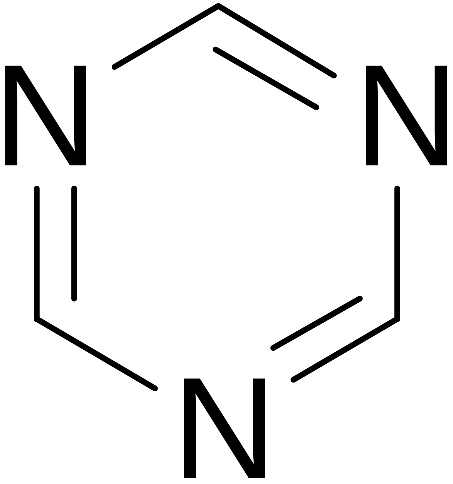
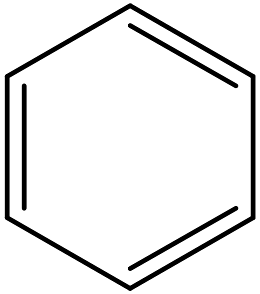


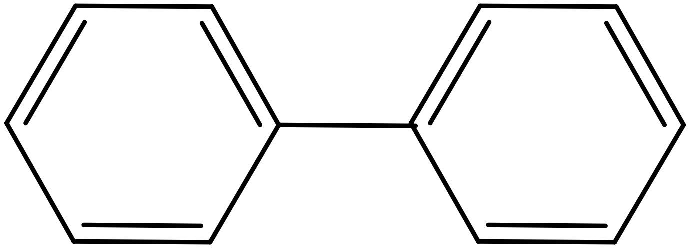


§ 7.2 芳香烃的分类及命名

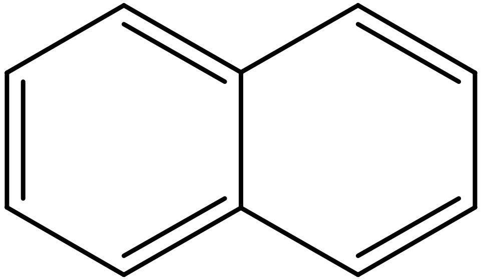
- 1，芳香烃的分类
- A.单环芳烃



- B.多环芳烃
- a.简单多环



- b.稠合多环

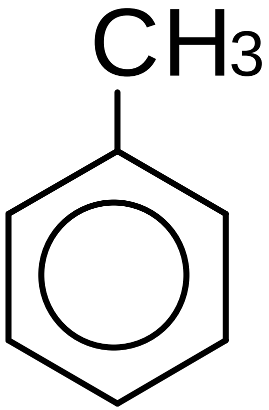


2，芳香烃的命名

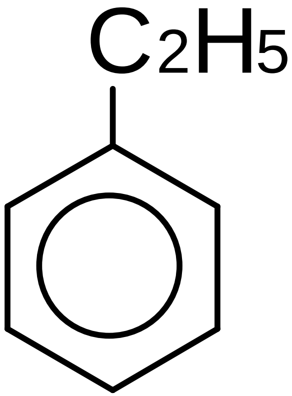
A.苯类芳香烃

a. 烃基取代

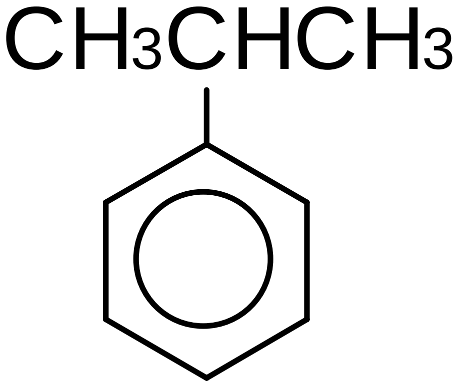
(1)以苯为母体，R为取代基



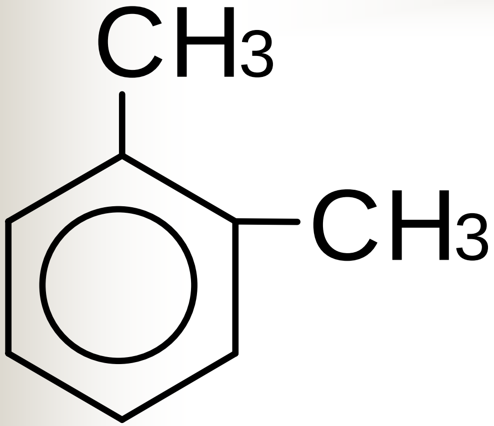
甲苯



乙苯



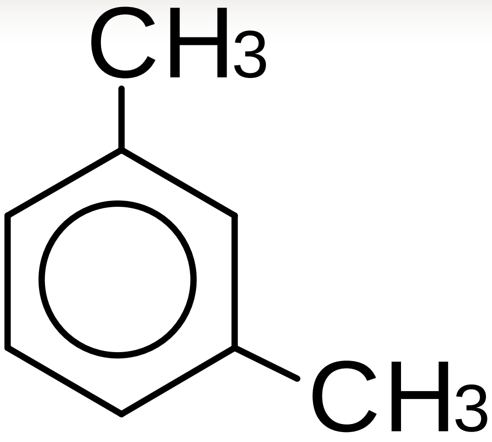
异丙苯



1,2-二甲苯

邻-二甲苯

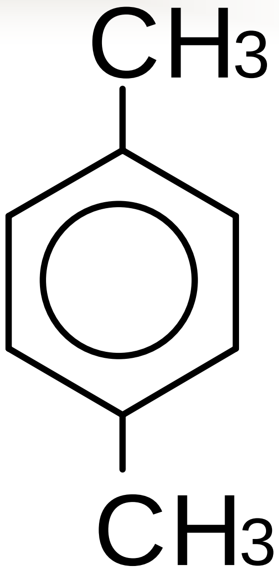
o-二甲苯



1,3-二甲苯

间-二甲苯

m-二甲苯

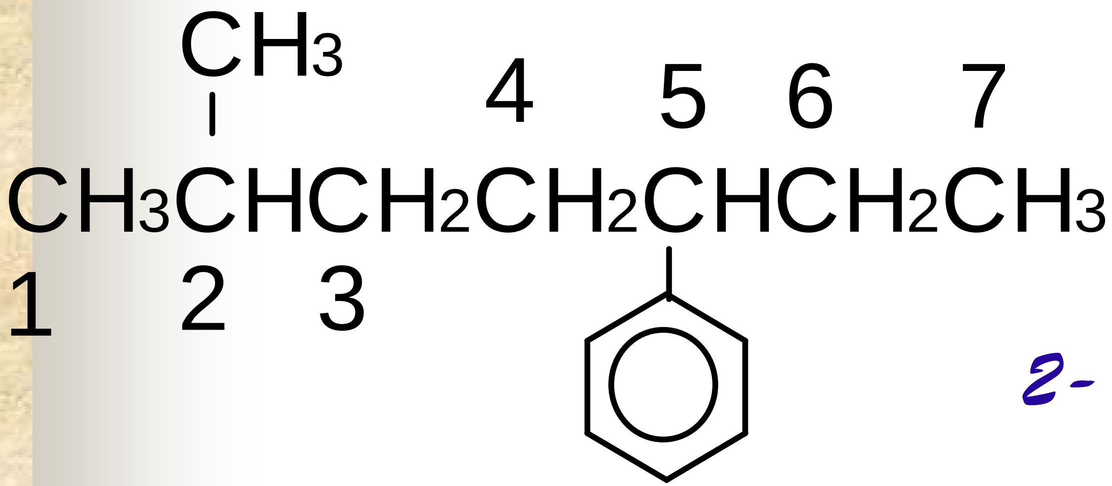


1,4-二甲苯

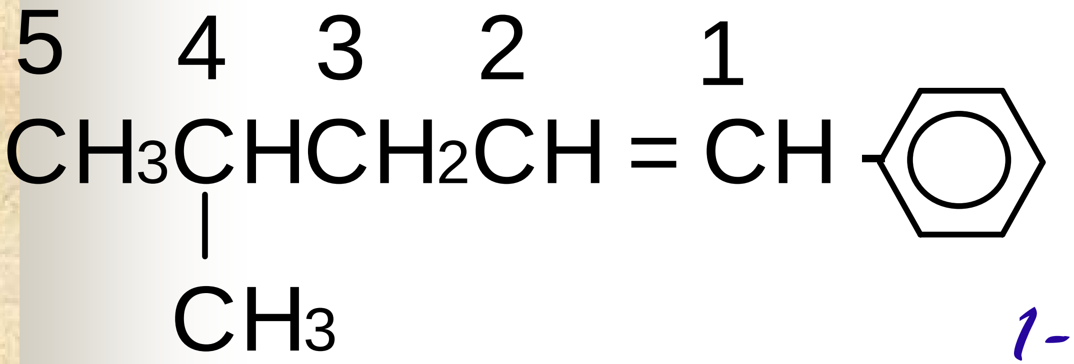
对-二甲苯

p-二甲苯

(2) 复杂烃基，以苯为取代基



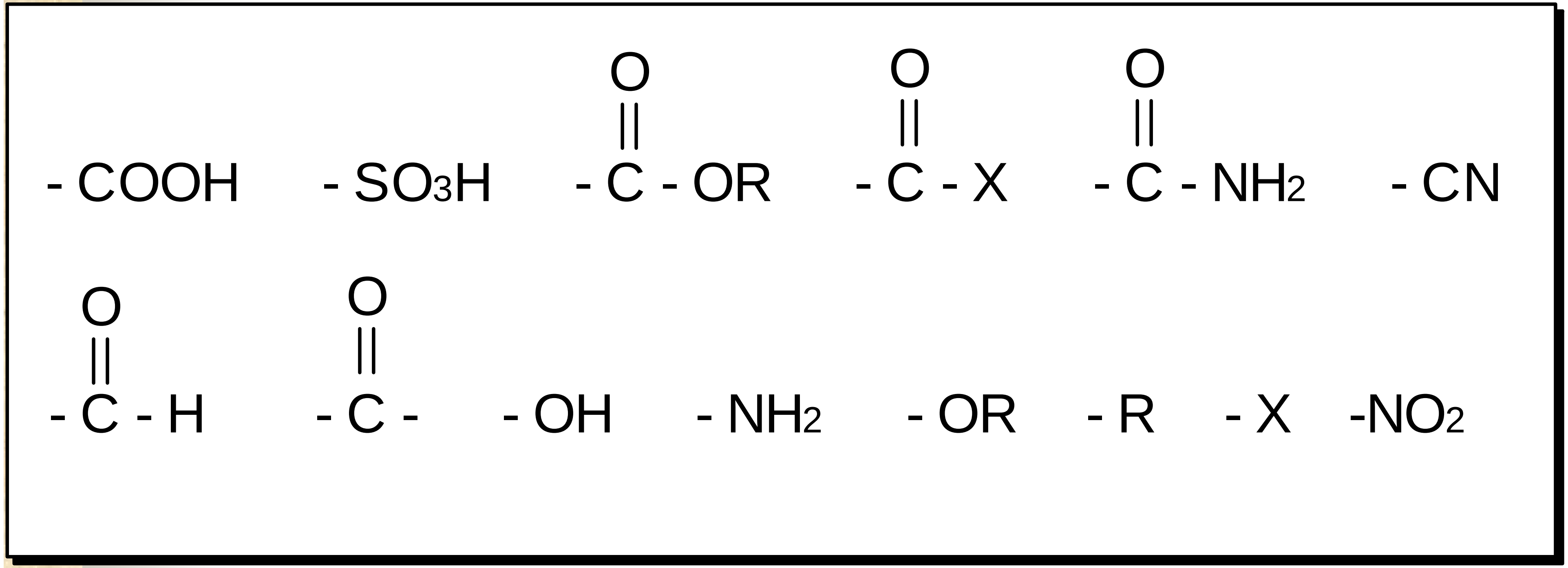
2-甲基-5-苯基庚烷



1-苯基-4-甲基-1-戊烯

b. 非烃基取代——取代基优先顺序

（仅用 于取代苯的命名）

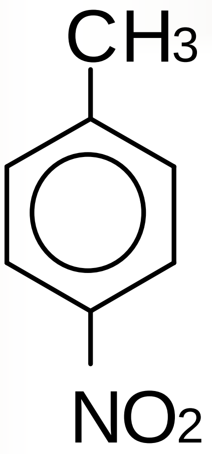


$-COOH$　$-SO_3H$　$-\overset{\overset{O}{\|}}{C}-OR$　$-\overset{\overset{O}{\|}}{C}-X$　$-\overset{\overset{O}{\|}}{C}-NH_2$　$-CN$

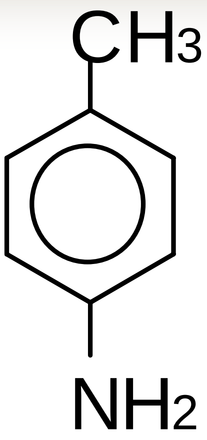
$-\overset{\overset{O}{\|}}{C}-H$　$-\overset{\overset{O}{\|}}{C}-$　$-OH$　$-NH_2$　$-OR$　$-R$　$-X$　$-NO_2$

优先基团作为母体

例：



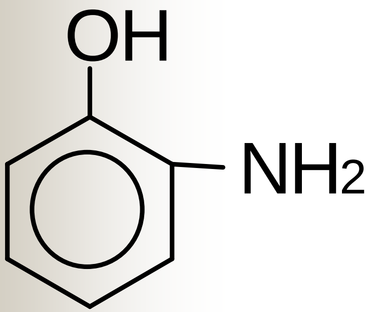
$-CH_3 > -NO_2$



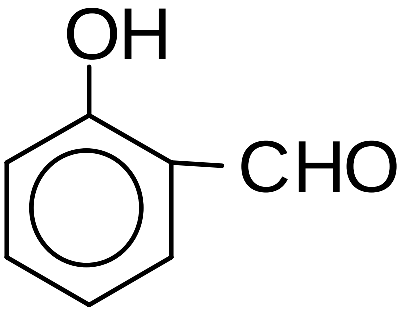
$-CH_3 < -NH_2$

对-硝基甲苯

对-甲基苯胺



$-OH > -NH_2$

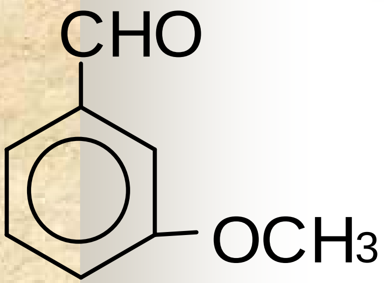


$-OH < -CHO$

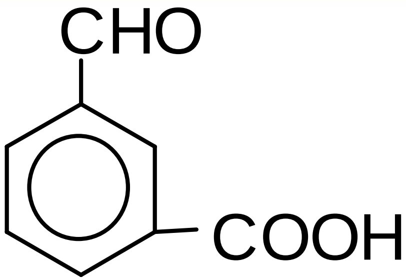
邻-氨基苯酚

邻-羟基苯甲醛

(-OH作为母体称为酚)(-OH作为取代基称为醛)



-CHO > -OCH$_3$

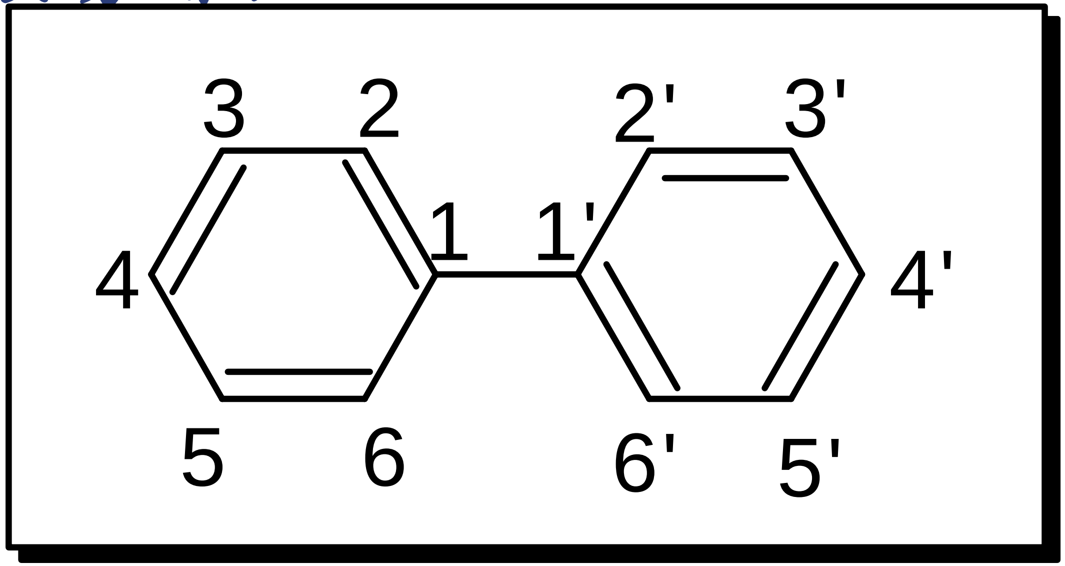


-CHO < -COOH

间-甲氧基苯甲醛　　间-甲酰基苯甲酸

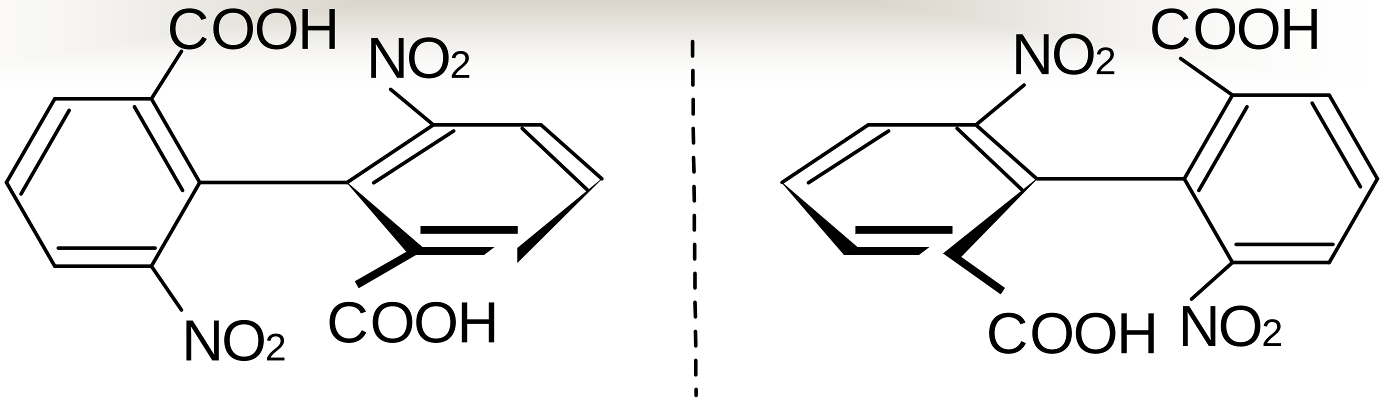
(-OCH3作为母体称为苯甲醚)(-CHO作为取代基称为甲酰基)

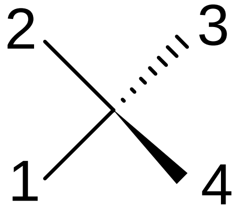
B. 联苯类芳香烃



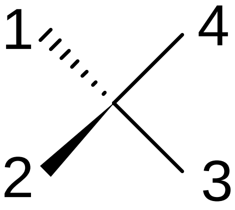
如果在2，2’和6，6’连有取代基，
而且取代基半径之和大于0.29nm，
使两个苯环旋转受阻，则可以产生手性

观察方向 →





S



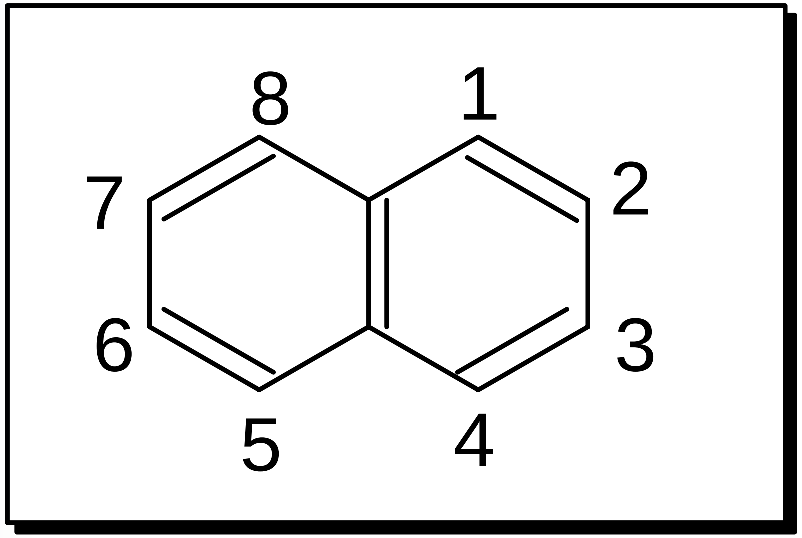
R

手性轴
- 聚集双键
- 螺环
- 联苯

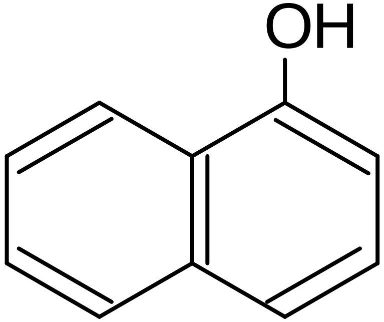
判断手性轴
- ①确定观察方向
- ②先看到的基团先比大小
  后看到的基团紧随其后
- ③应用R/S判断法

c.稠环芳烃——共用两个或两个以上碳原子的多环芳香烃

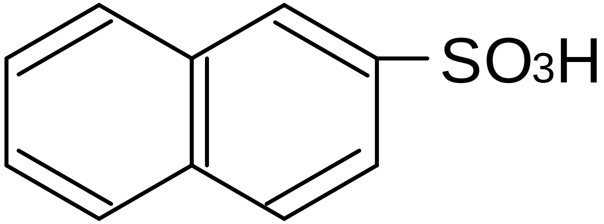
a. 萘



1,4,5,8位称为α位；
2,3,6,7位称为β位.

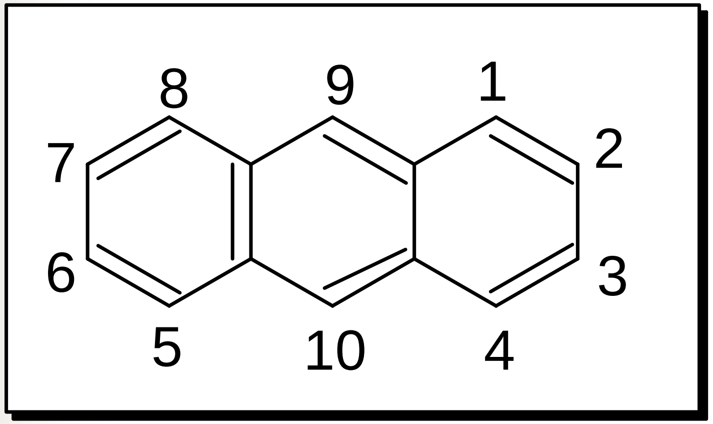


α-萘酚

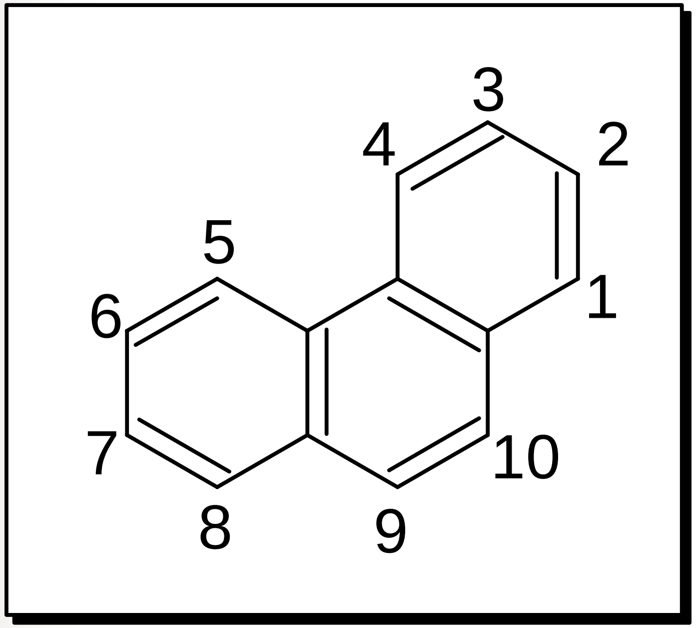


β-萘磺酸

6. 蒽，菲



1,4,5,8 位称为α位
2,3,6,7位称为β位
9,10 位称为γ位

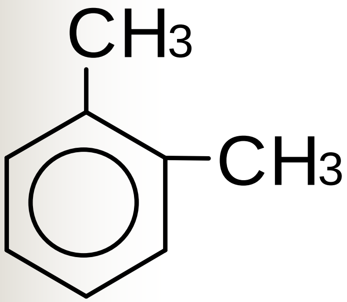


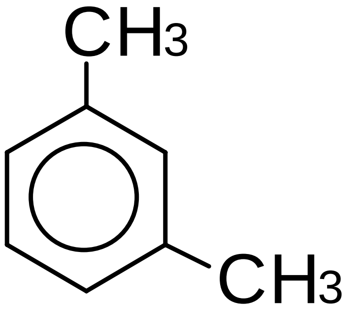
1,8 位称为α位
2,7 位称为β 位
9,10位称为γ 位

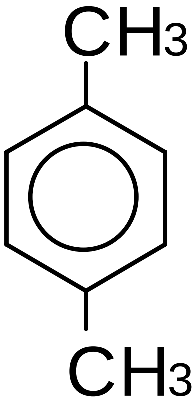
§ 7.3 芳烃的物理性质

1，苯和简单取代苯

苯—液体，有毒，不溶于水，$d<1$，可以与水共沸







b.p.	144°C	139°C	138°C
m.p.	-25°C	-48°C	13°C

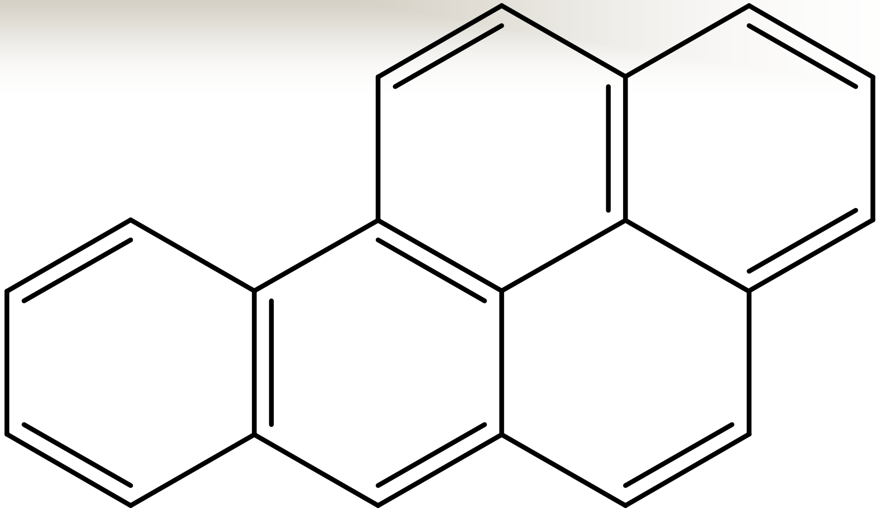
偶极矩 $\mu_o > \mu_m > \mu_p$

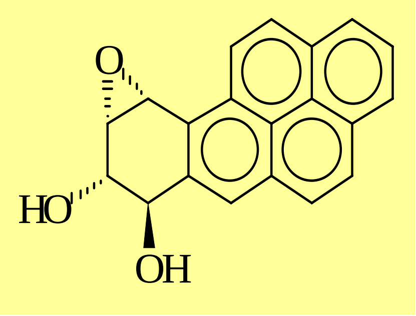
分子的对称性

2，稠环芳烃

有毒，致癌，固体

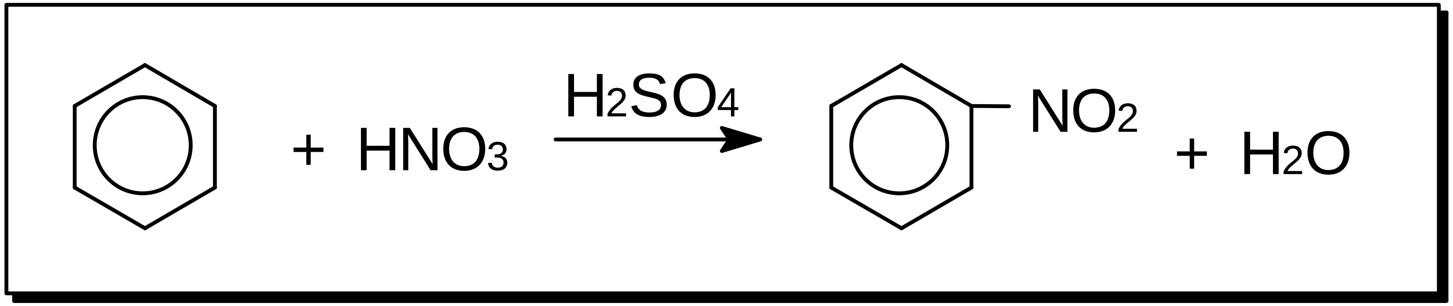
如：3,4-苯并芘(pì)

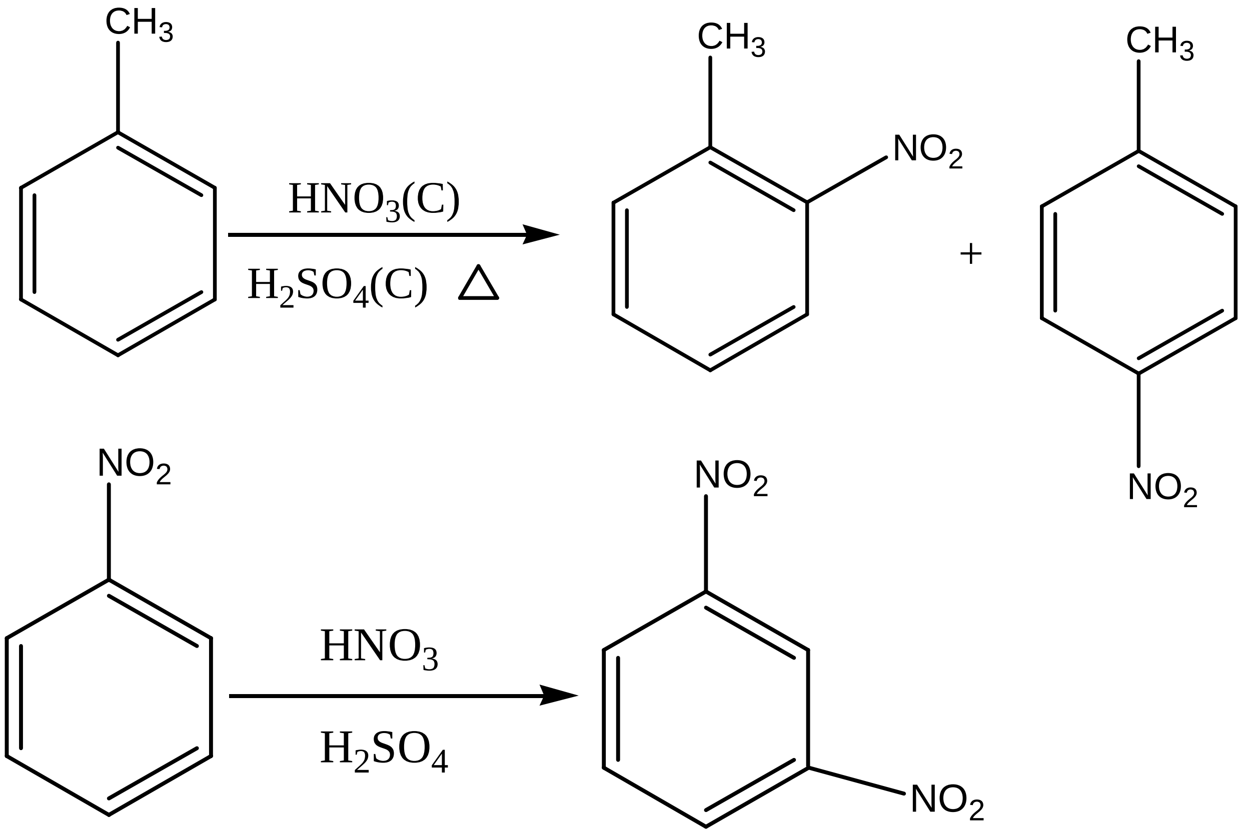


 苯并芘衍生物	（＋）强致癌物 （－）非致癌物

§ 7.4 苯的化学性质 I——亲电取代

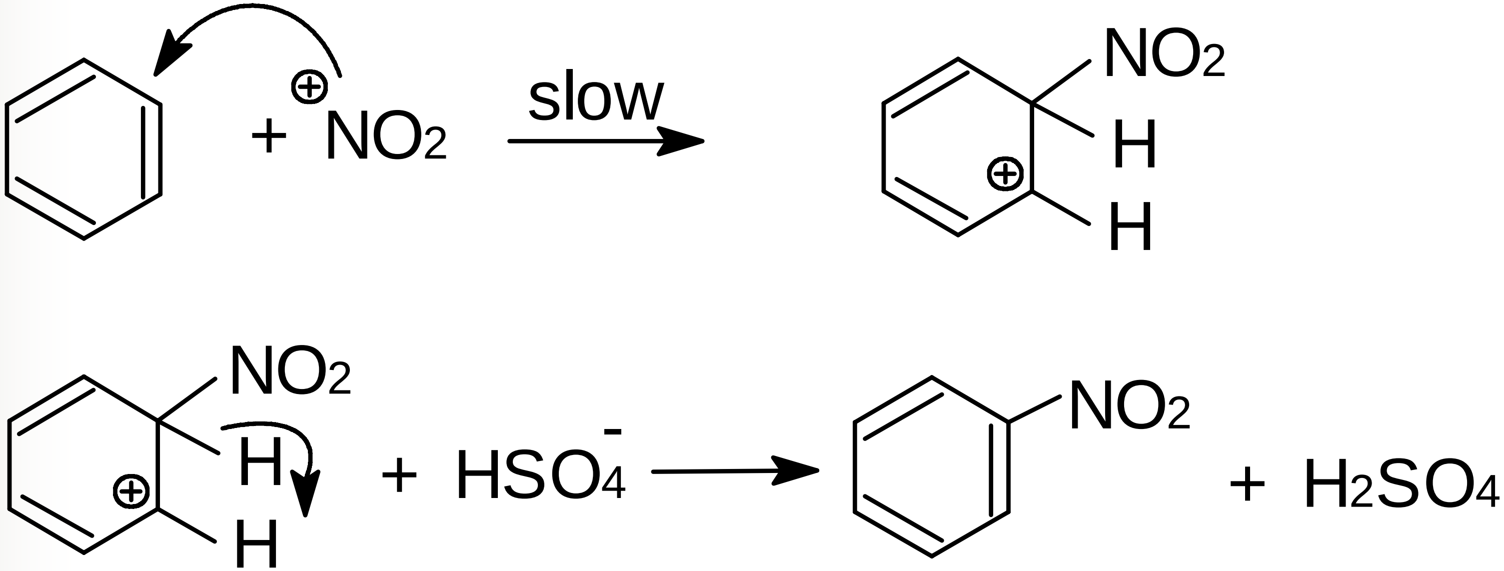
1，硝化：





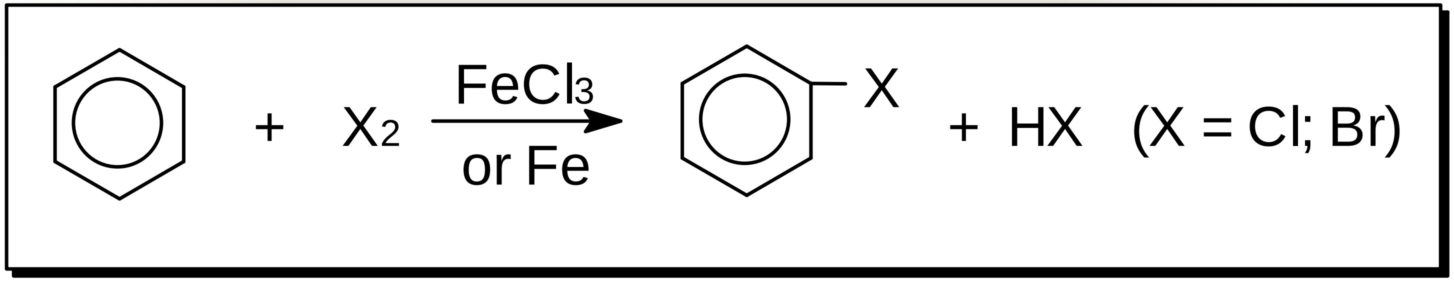
反应机理

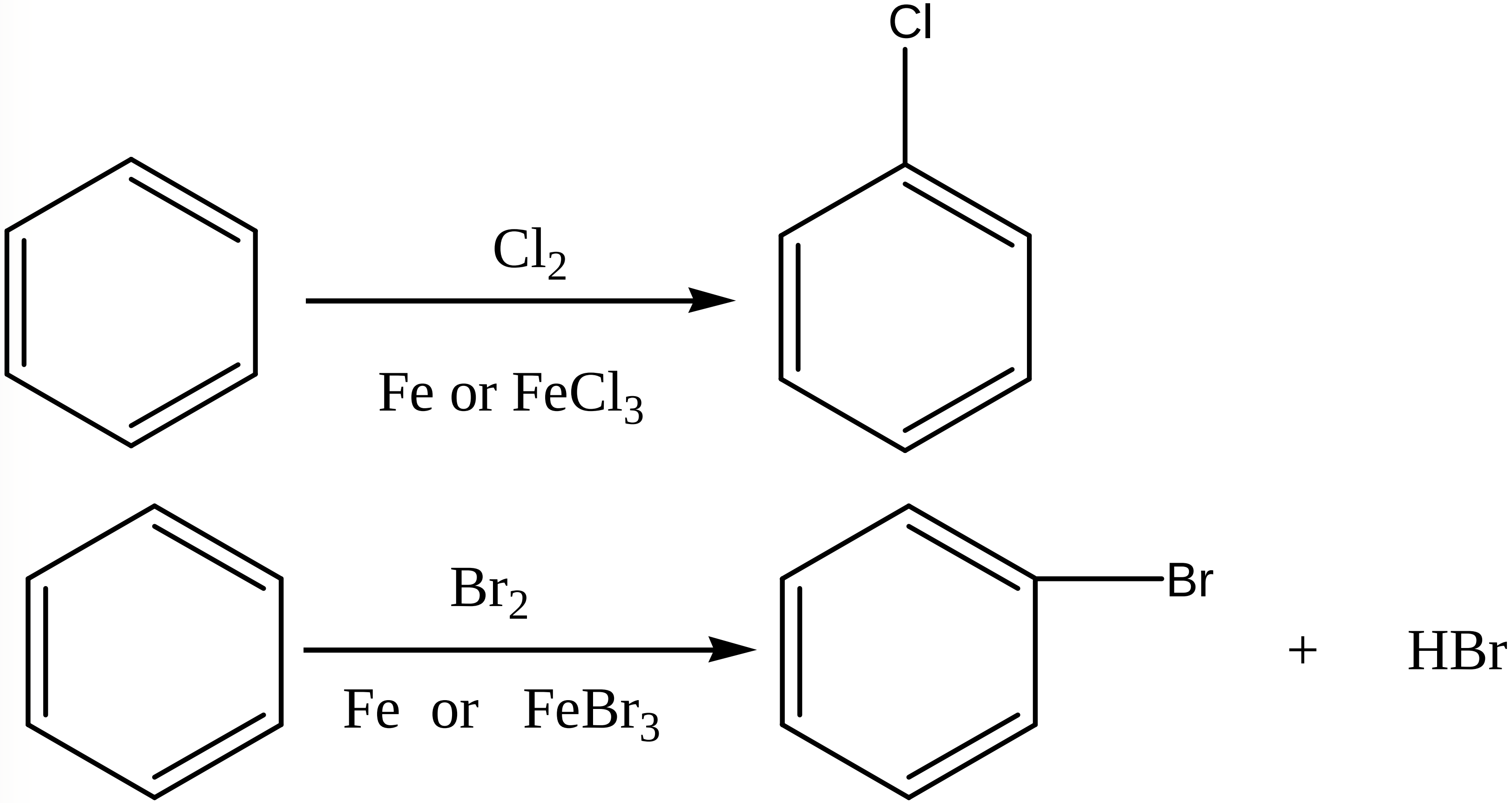
$$HO-NO_2 + 2\,H_2SO_4 \longrightarrow \overset{\oplus}{N}O_2 + H_3\overset{+}{O} + HSO_4^-$$



按价键理论理解，亲电试剂先对双键进行加成，形成一个正碳离子，然后进行消除，恢复共轭体系。

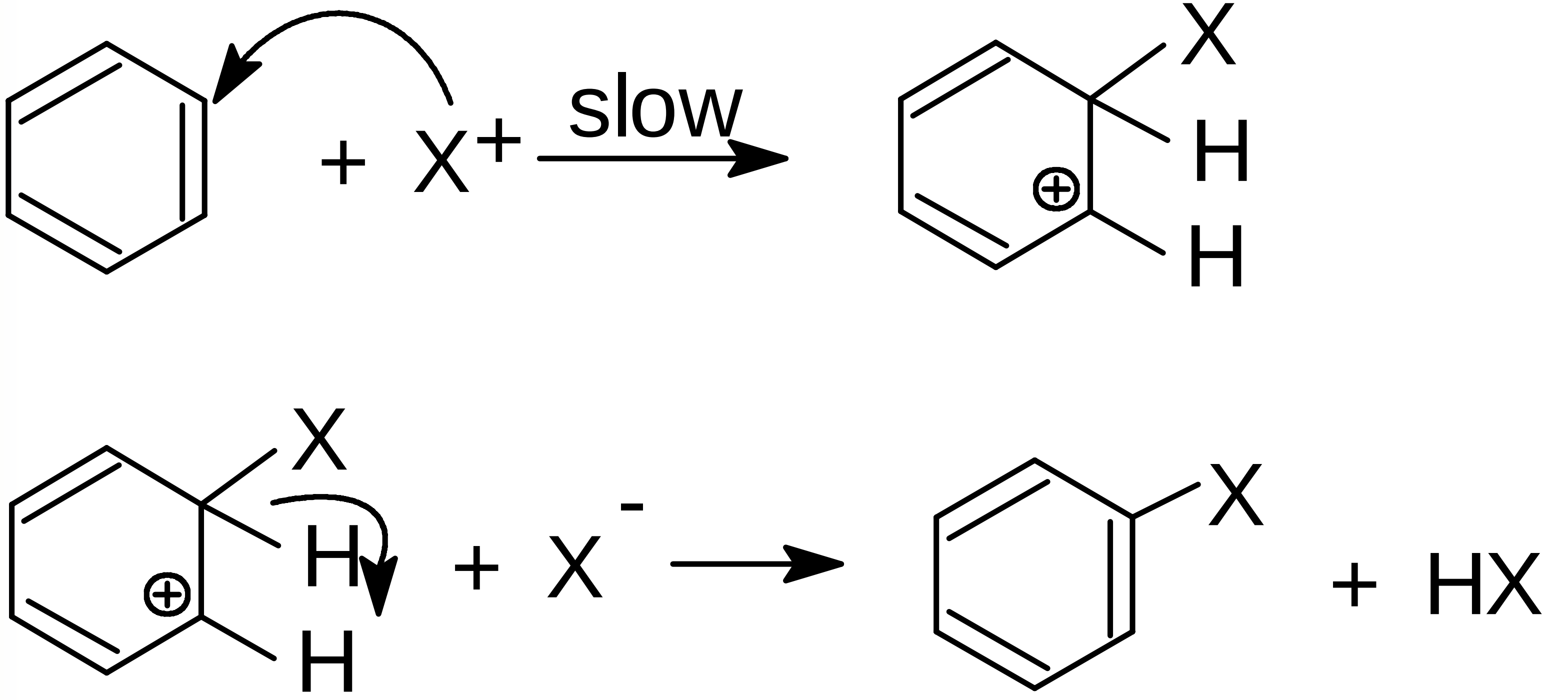
2，卤代：

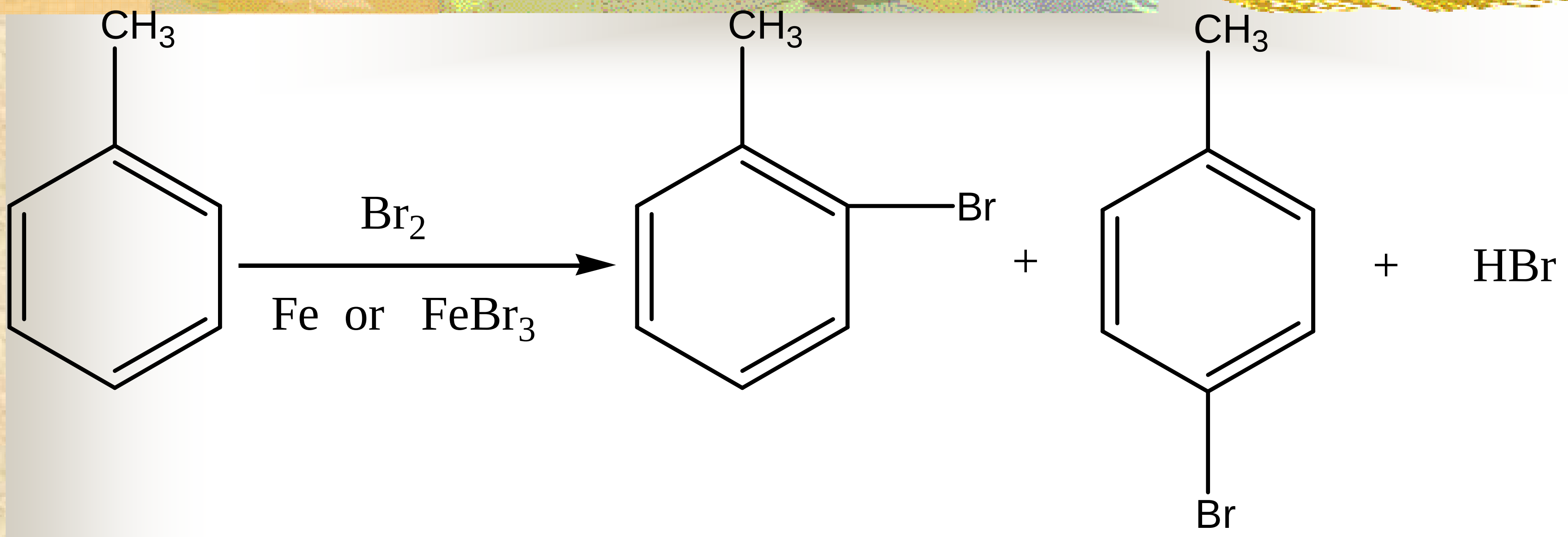

+
X_2
$FeCl_3$
or Fe
X
+ HX
(X = Cl; Br)

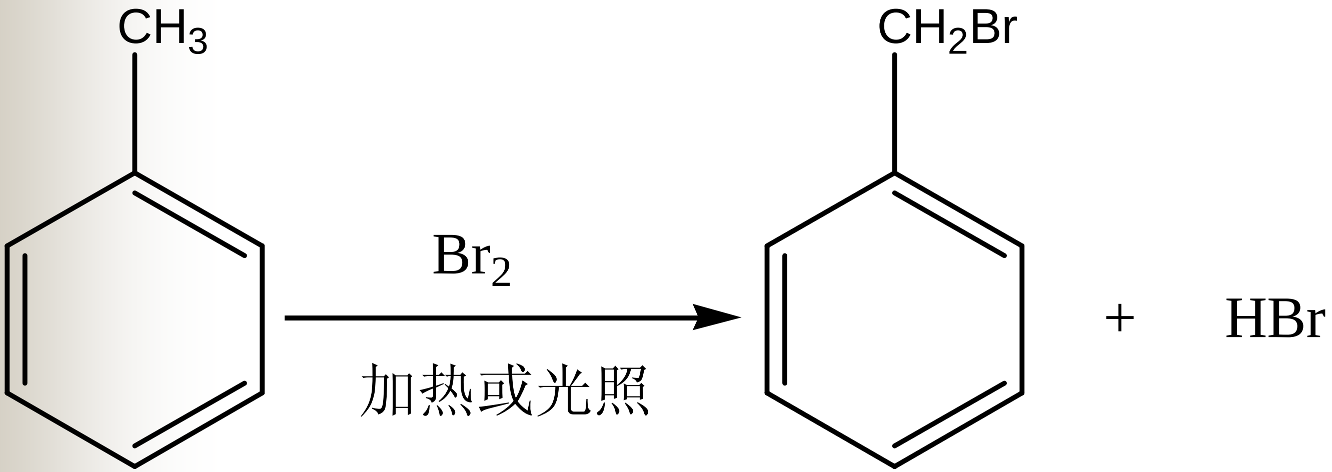

Cl
Cl_2
Fe or $FeCl_3$
Br_2
Fe or $FeBr_3$
Br
+
HBr

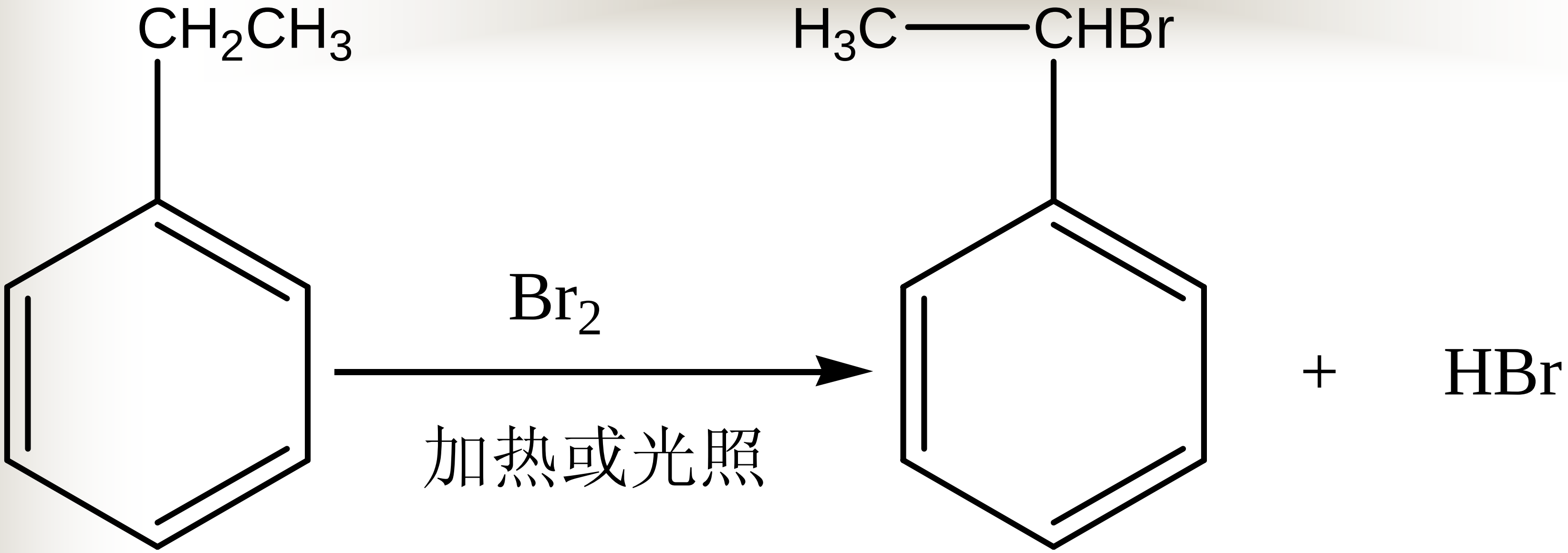
反应机理：

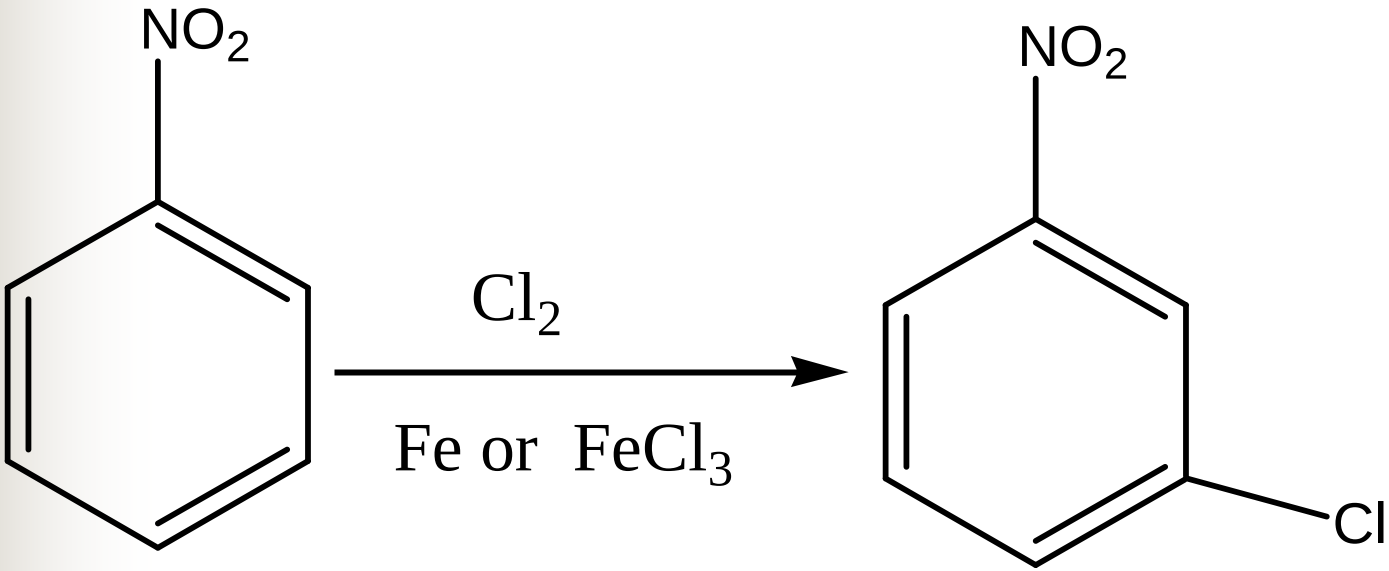
$$X - X + FeX_3 \longrightarrow X^+ + FeX_4$$



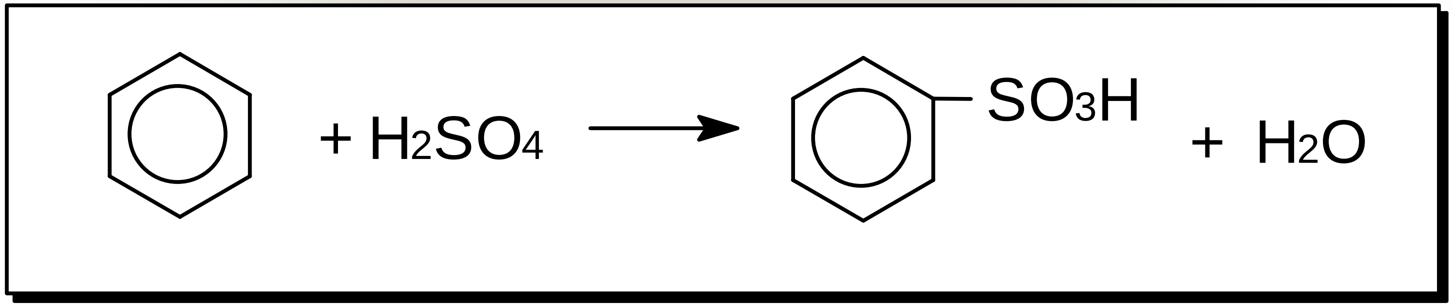

CH3
Br2
Fe or FeBr3
CH3
Br
+
CH3
Br
+
HBr

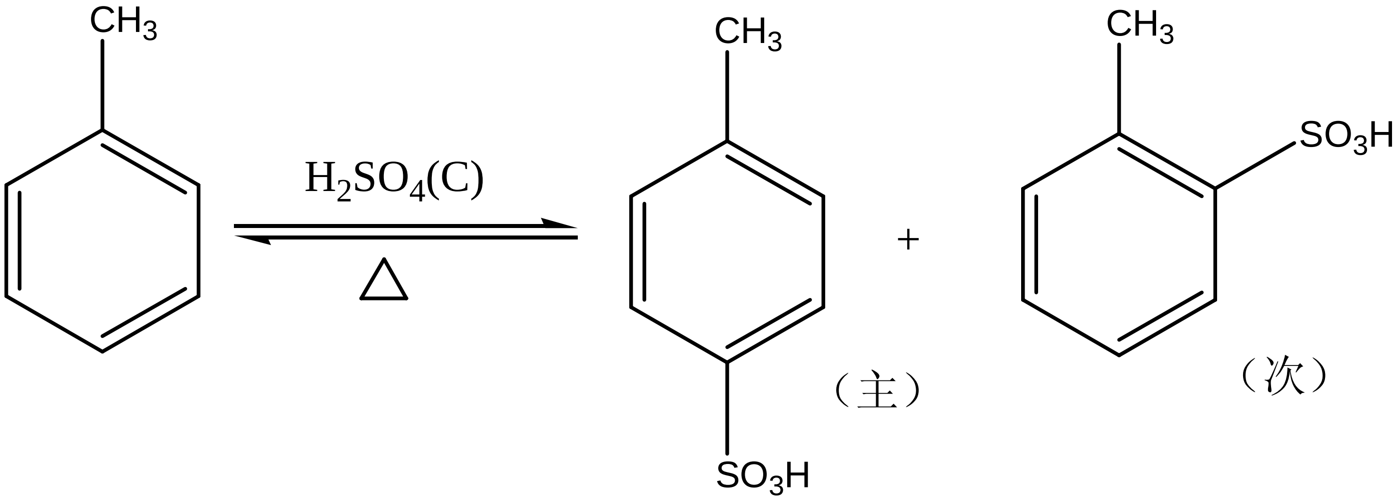

CH3
Br2
加热或光照
CH2Br
+
HBr

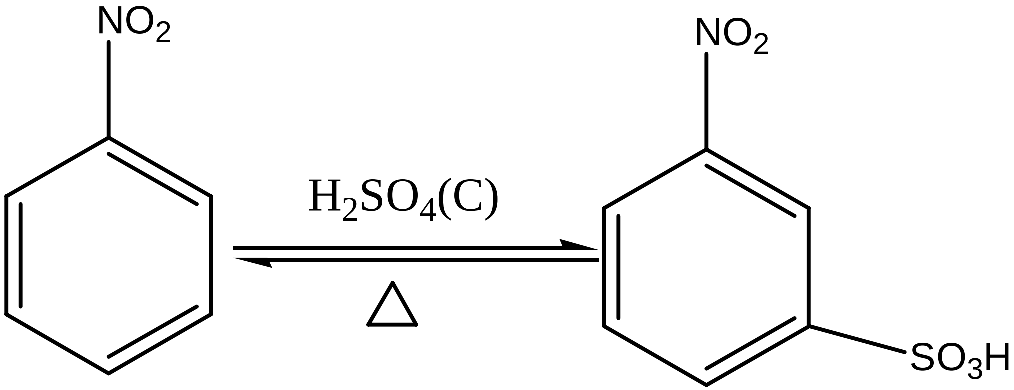

CH2CH3
Br2
加热或光照
H3C—CHBr
+ HBr


NO2
Cl2
Fe or FeCl3
NO2
Cl

3. 磺化：


+ H2SO4
SO3H
+ H2O


CH3
H2SO4(C)
△
CH3
SO3H
（主）
+
CH3
SO3H
（次）

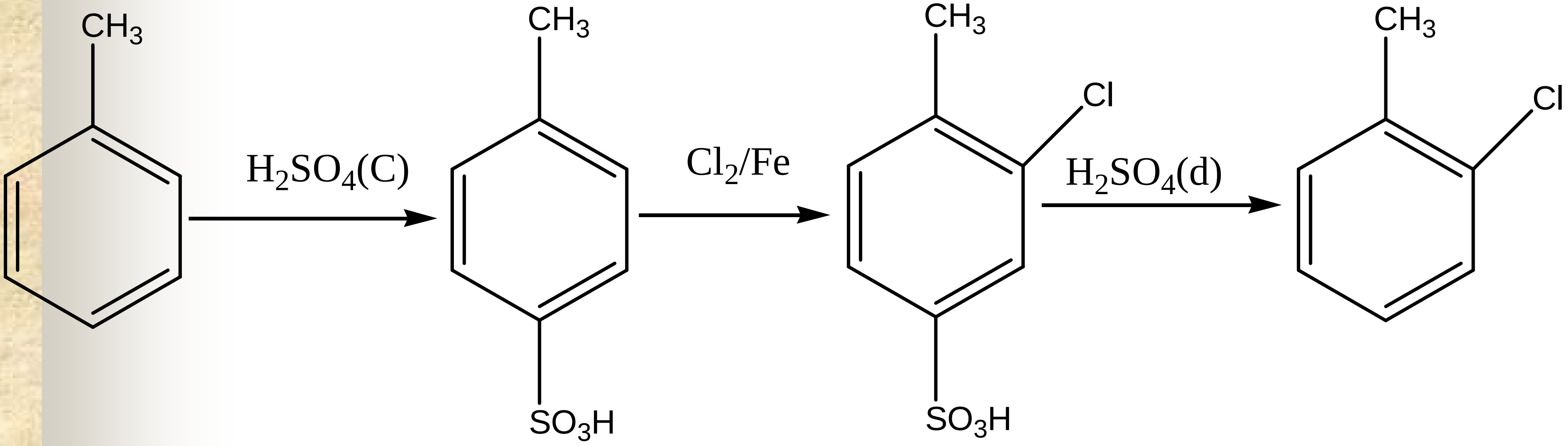

NO2
H2SO4(C)
△
NO2
SO3H

磺化反应的特点及应用：

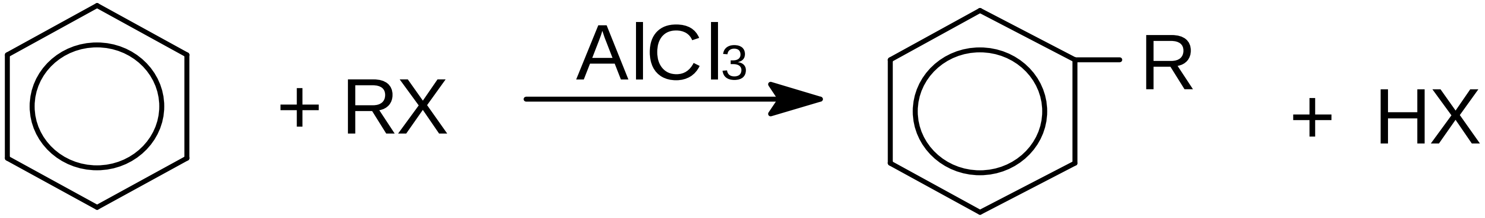
特点： a.可逆反应，除水利于向正向进行

b.水解可以除去$-SO_3H$

应用： 合成中阻位



4. Friedel-Crafts 烷基化反应



RX = 卤代烃

醇

烯

Cat. = AlCl3

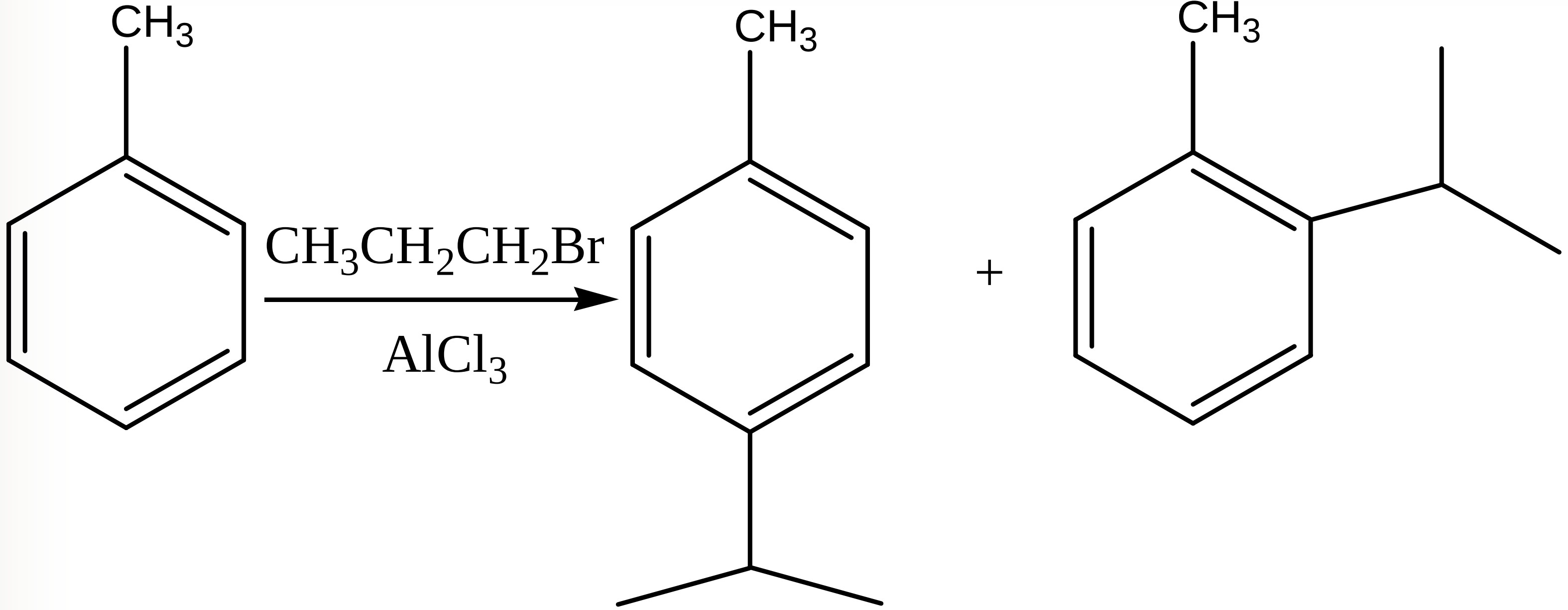
FeCl3

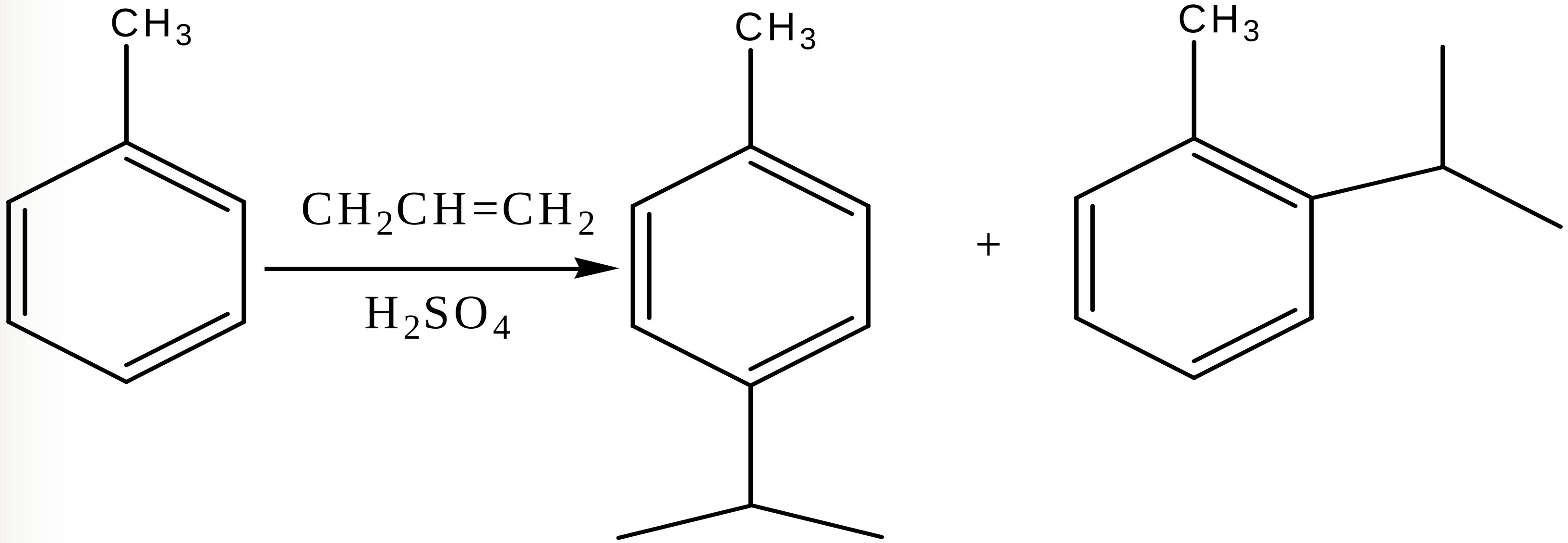
BF3

H2SO4

H3PO4

付氏烷基化反应实例：





反应机理

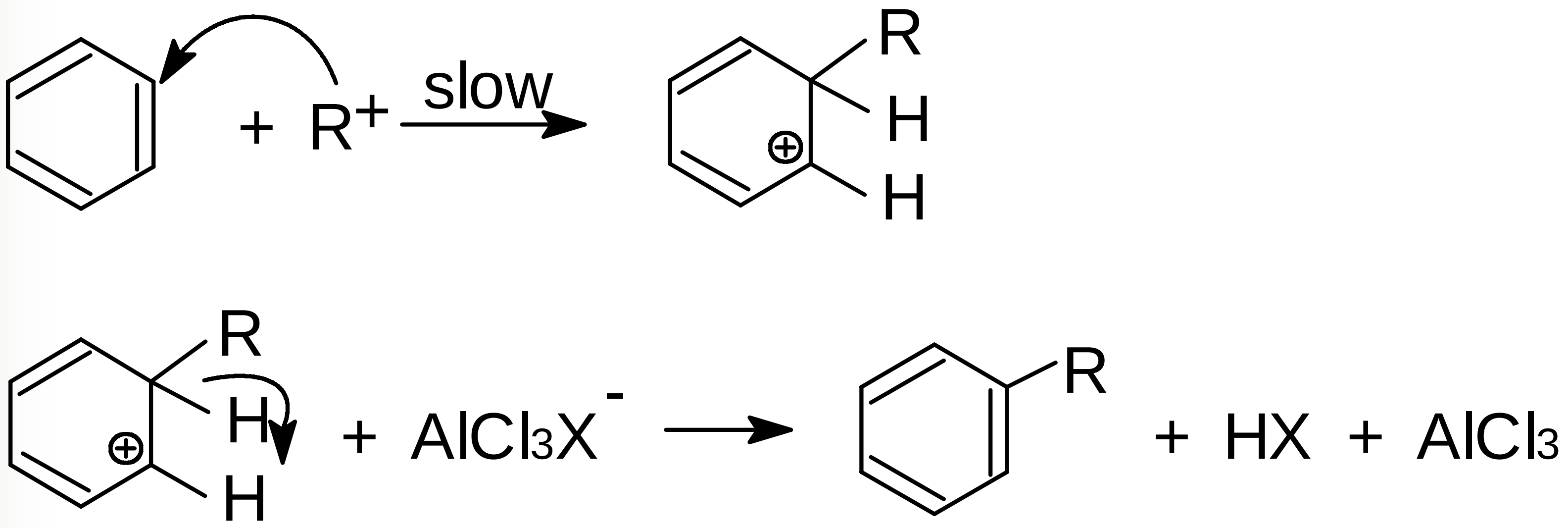
$R\text{-}X + AlCl_3 \longrightarrow R^+ + AlCl_3X^-$

$FeCl_3$

BF_3

H_2SO_4

H_3PO_4

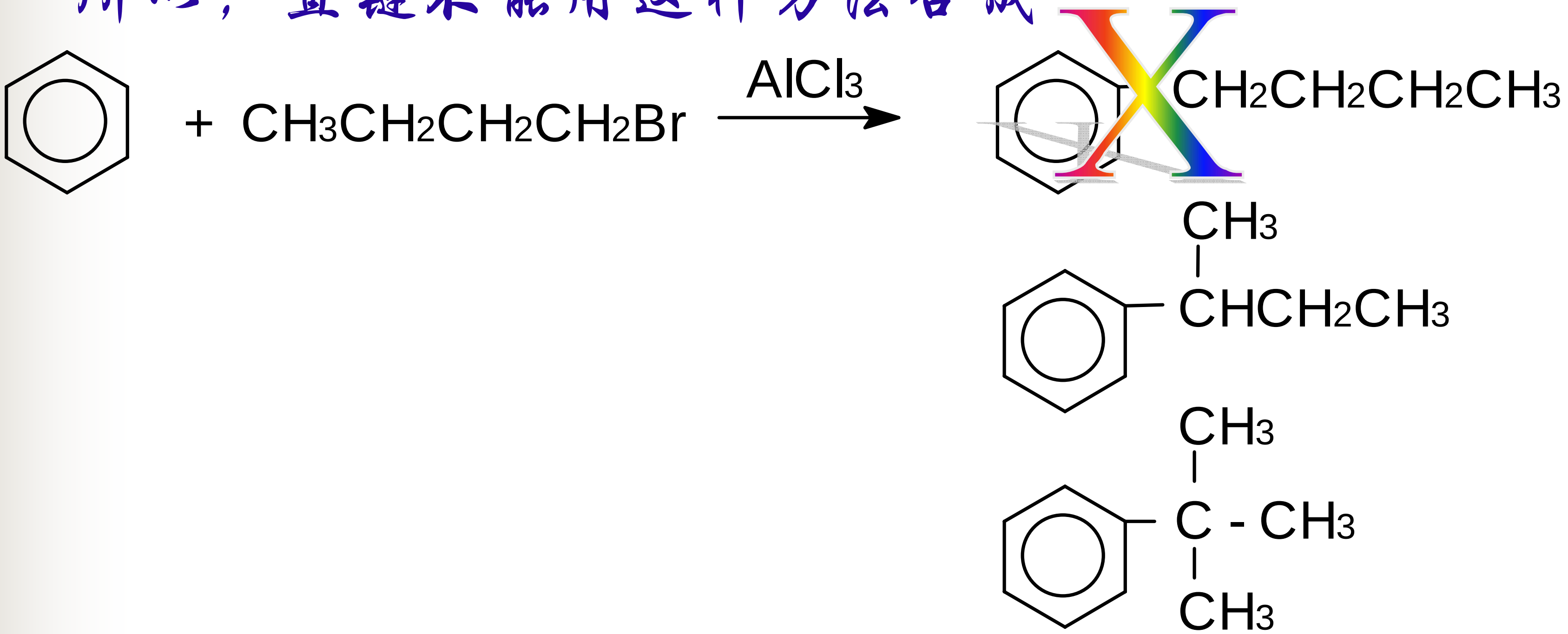


- 特点及应用：

a.可逆反应，苯需过量，$AlCl_3$需过量；

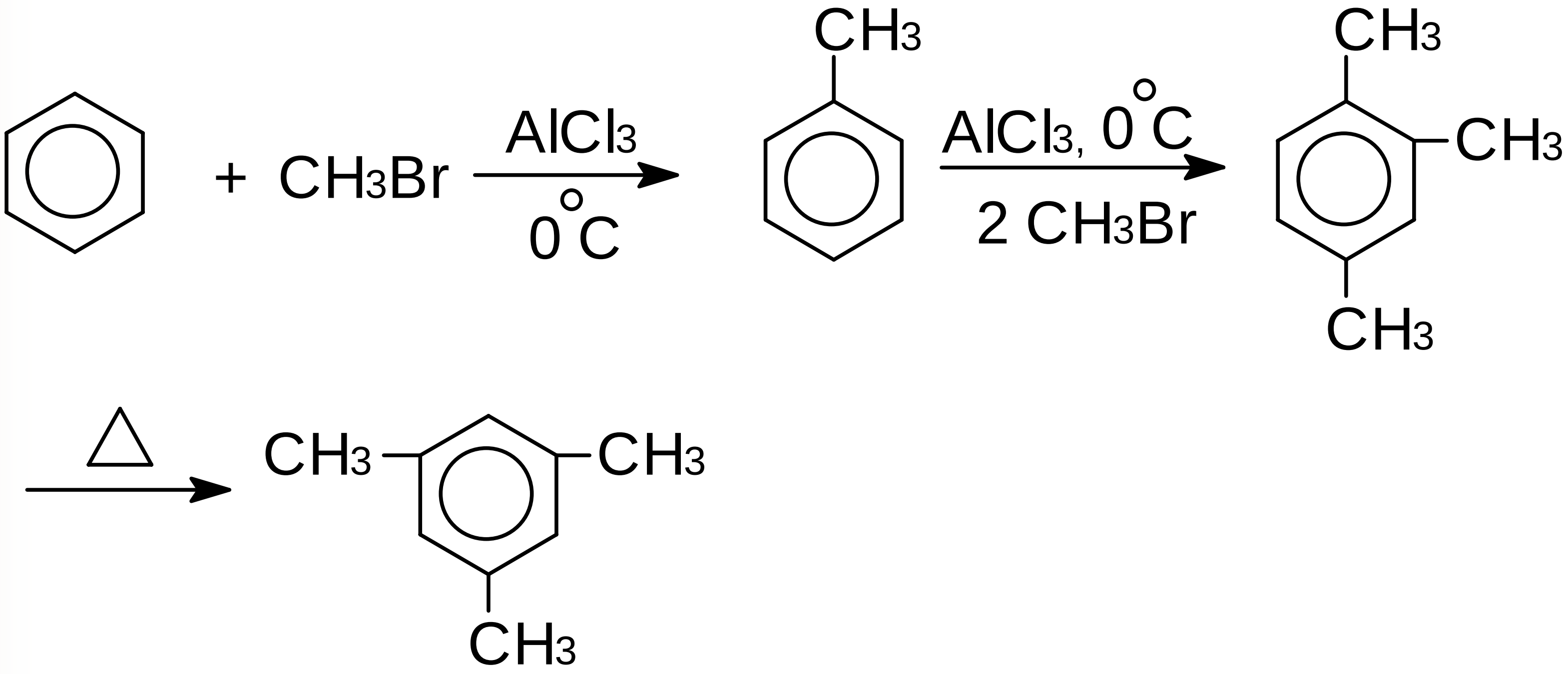
b.烷基正碳离子可以重排；

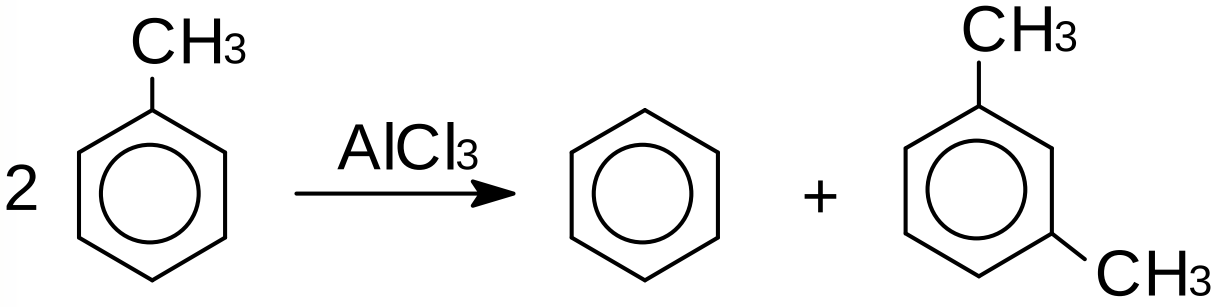
所以，直链不能用这种方法合成



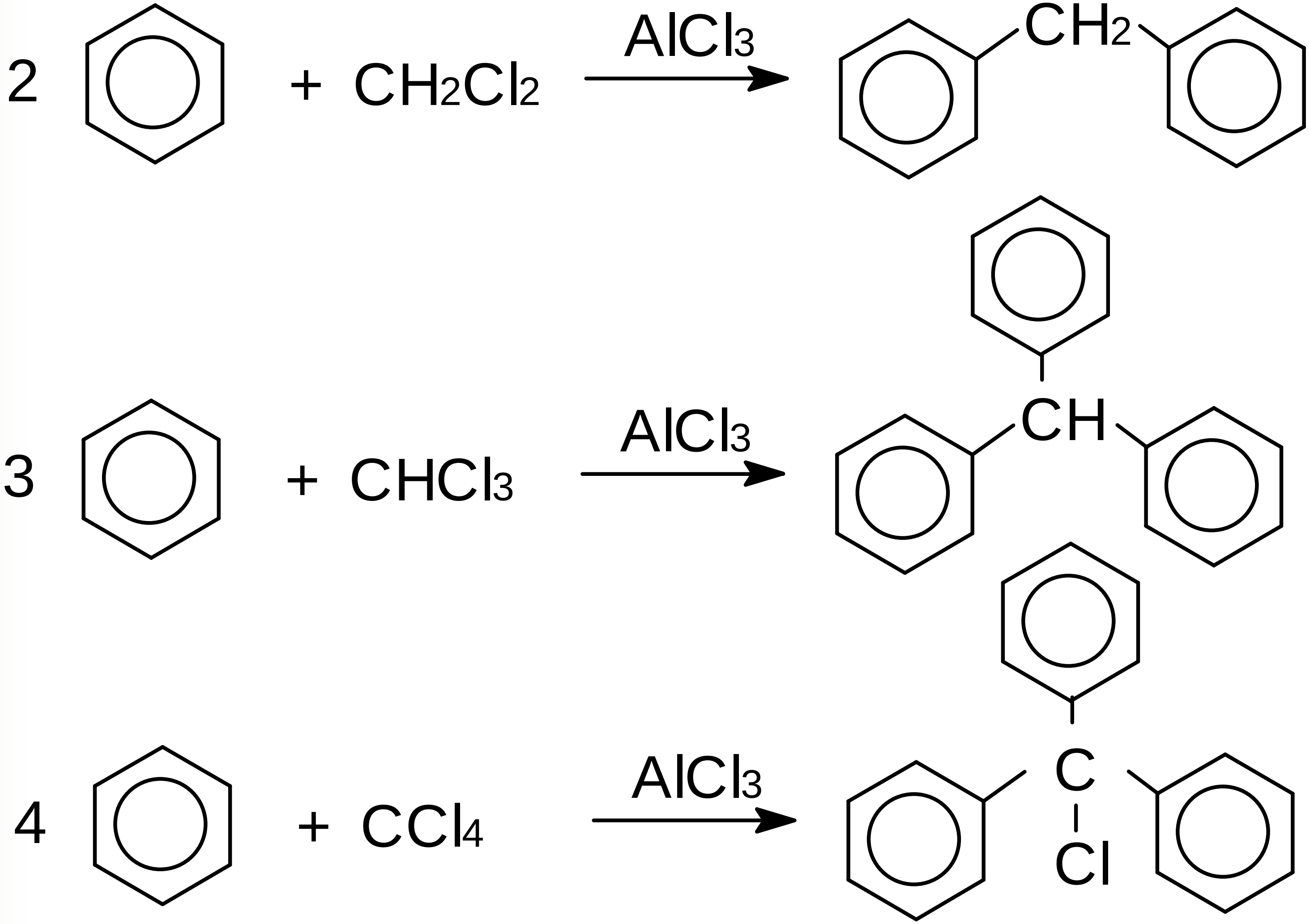
c. 易发生多烷基化，反应不易停留在一取代

在强催化剂条件下可以发生歧化反应：

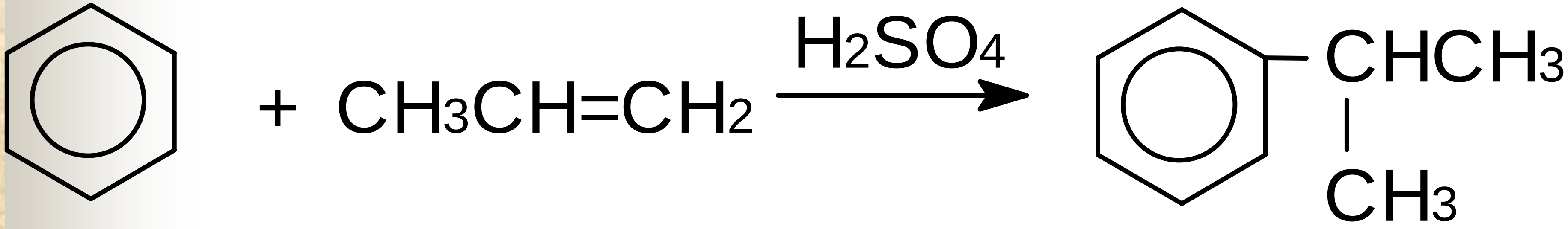


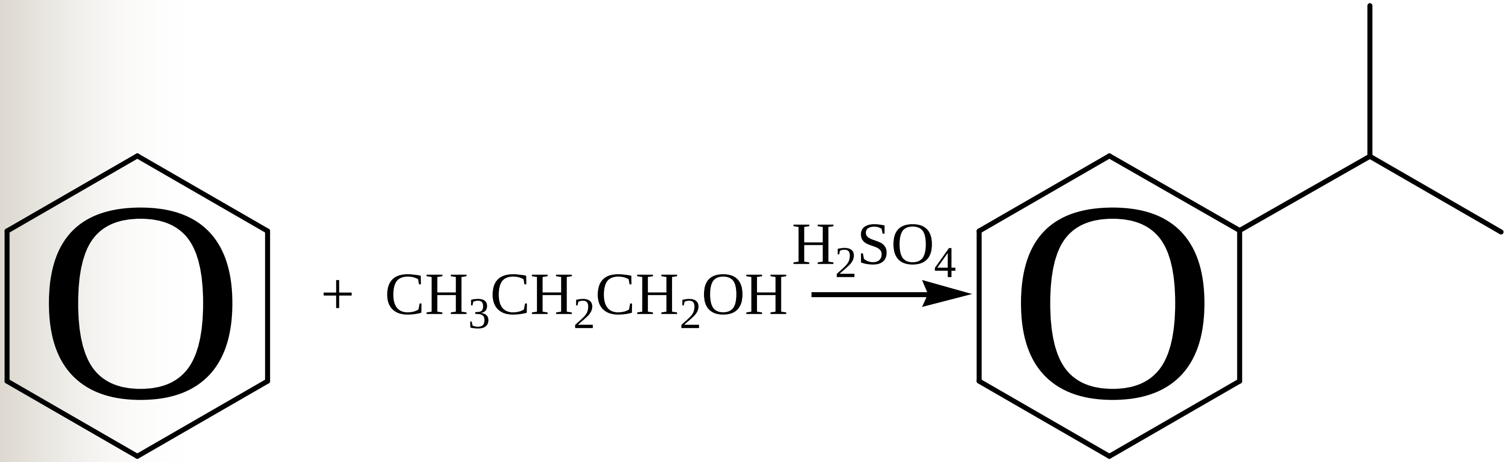


d. 多芳基化：—与多卤代烷的反应：

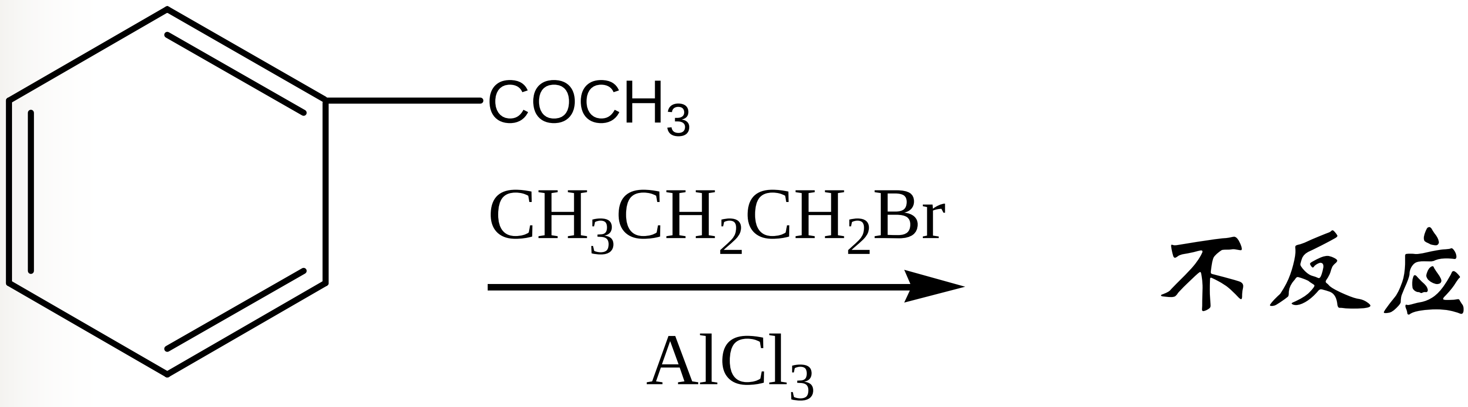


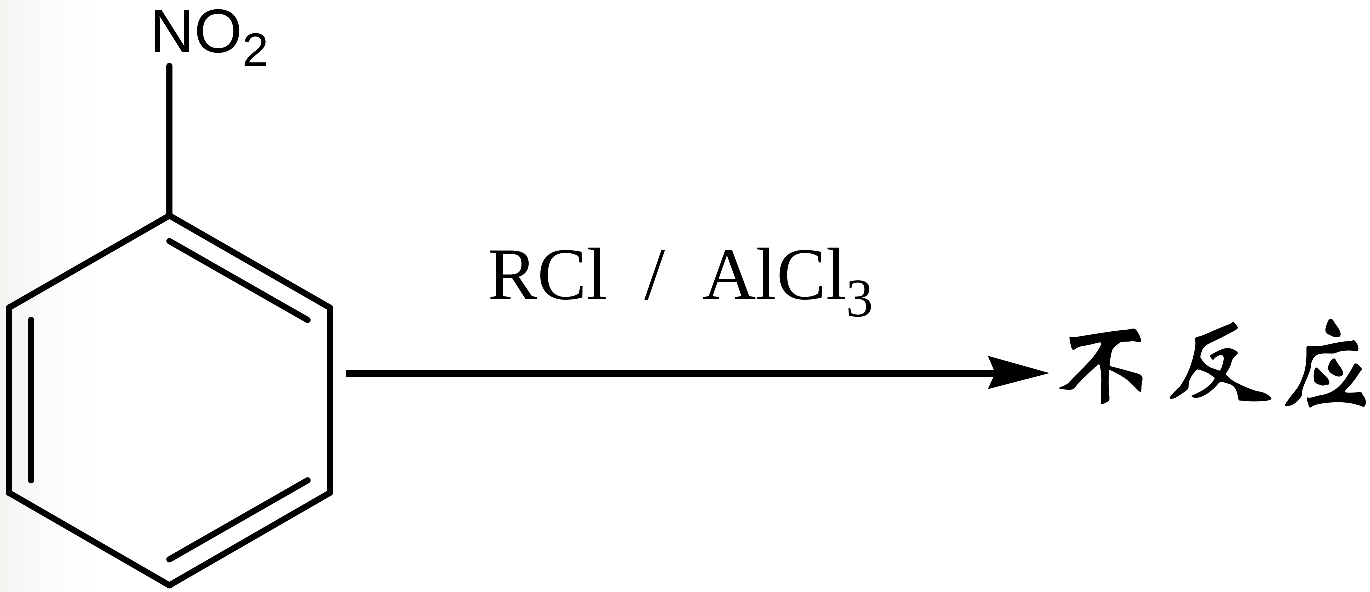
e. 质子酸可以催化烯烃或醇进行付氏烷基化反应



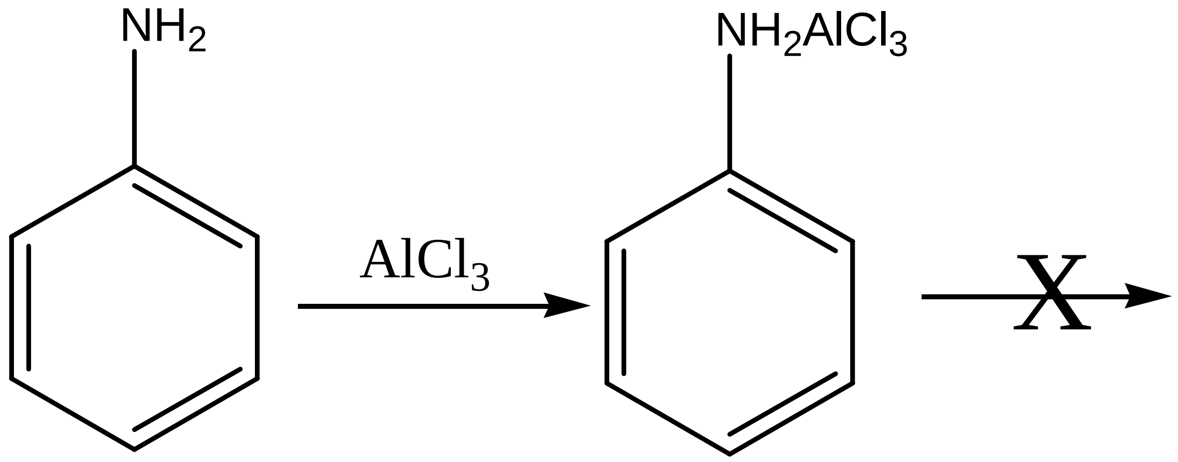


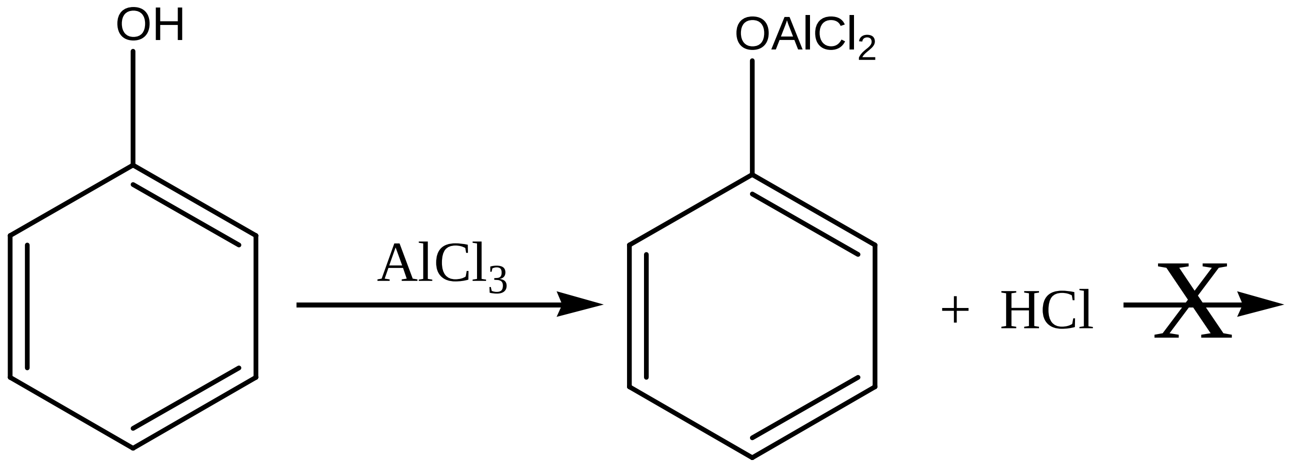
f. 如果苯环上有比卤素更强的吸电子基团，不反应



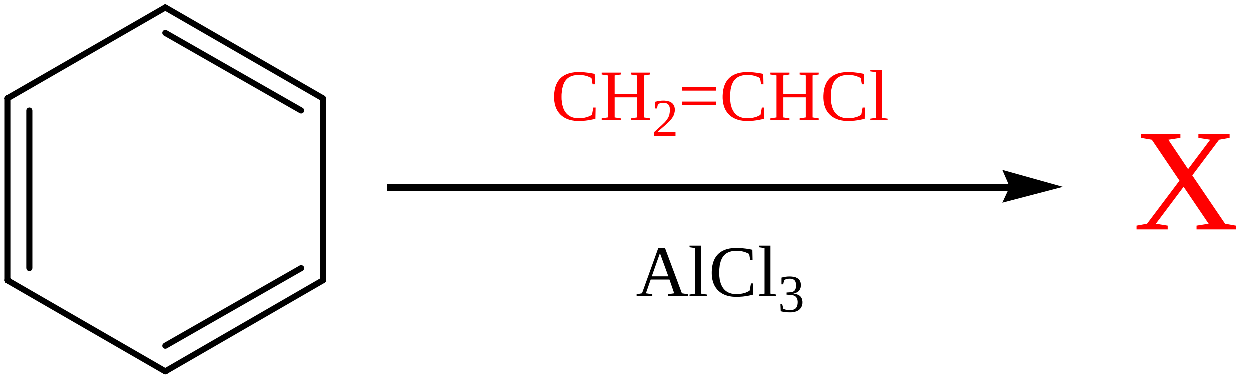


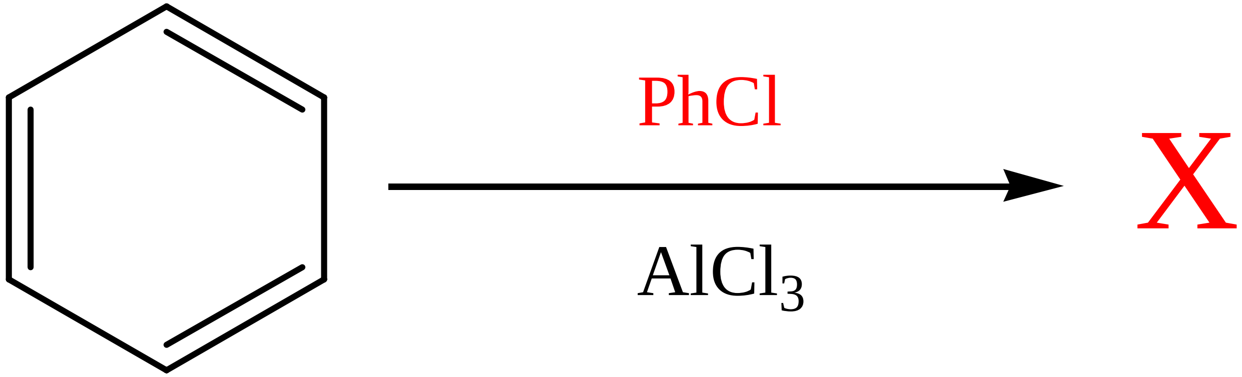
g. 如果含-NH2, -OH, -COOH等基团,会与AlCl3络合,催化剂失效,使反应不能进行



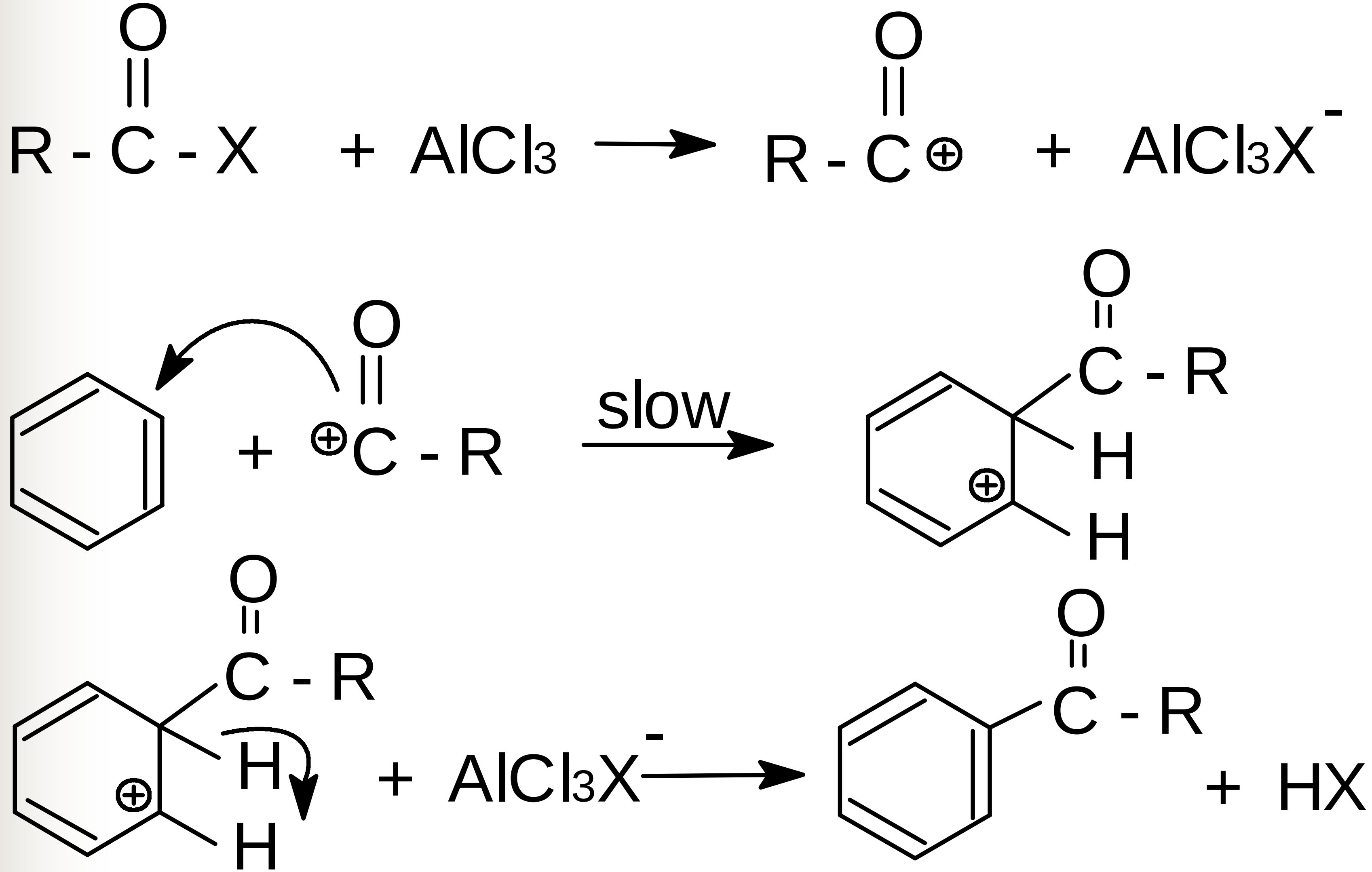


6. 氯乙烯、氯苯等惰性卤代烃不能用做付氏烷基化试剂。



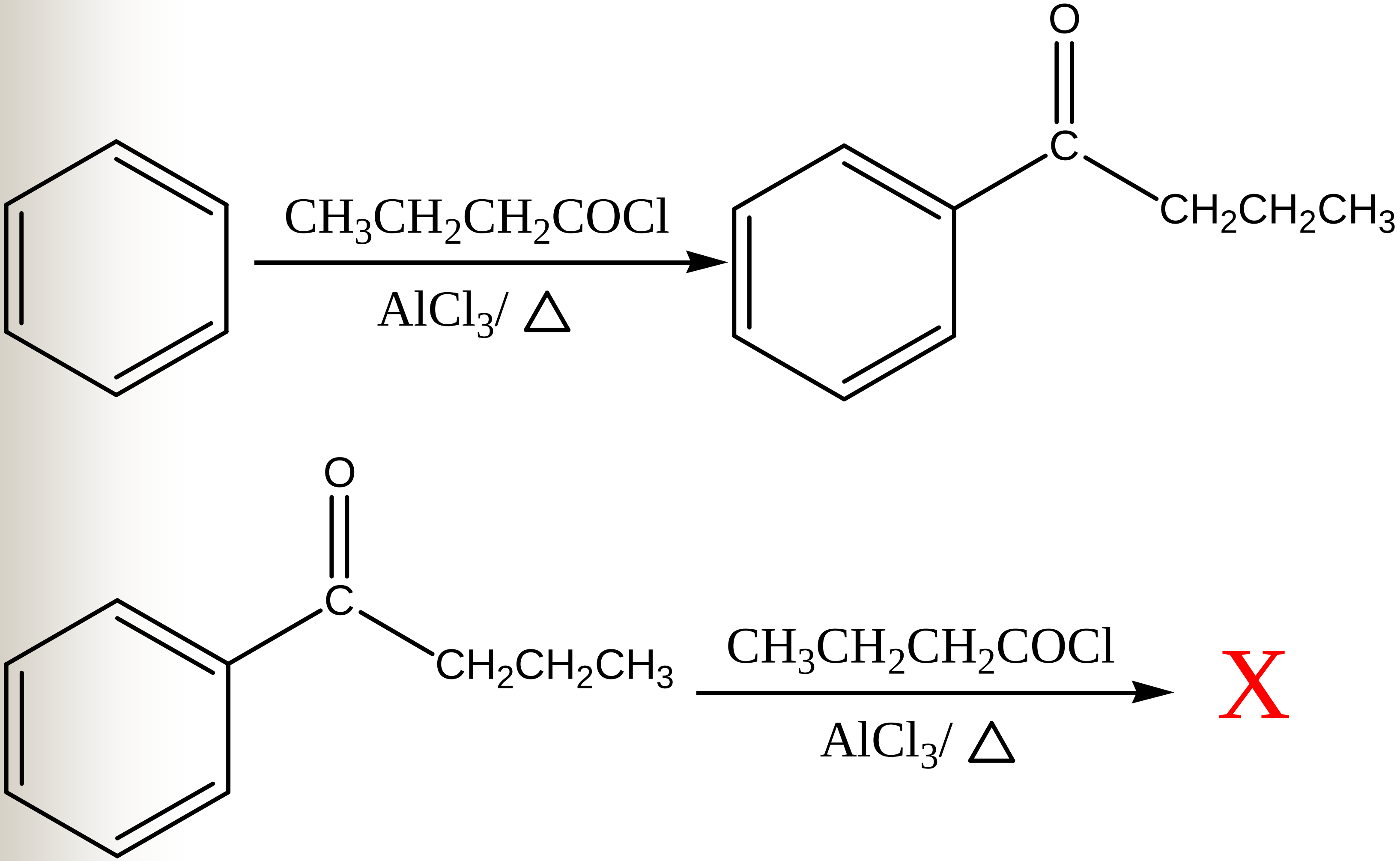


反应机理：

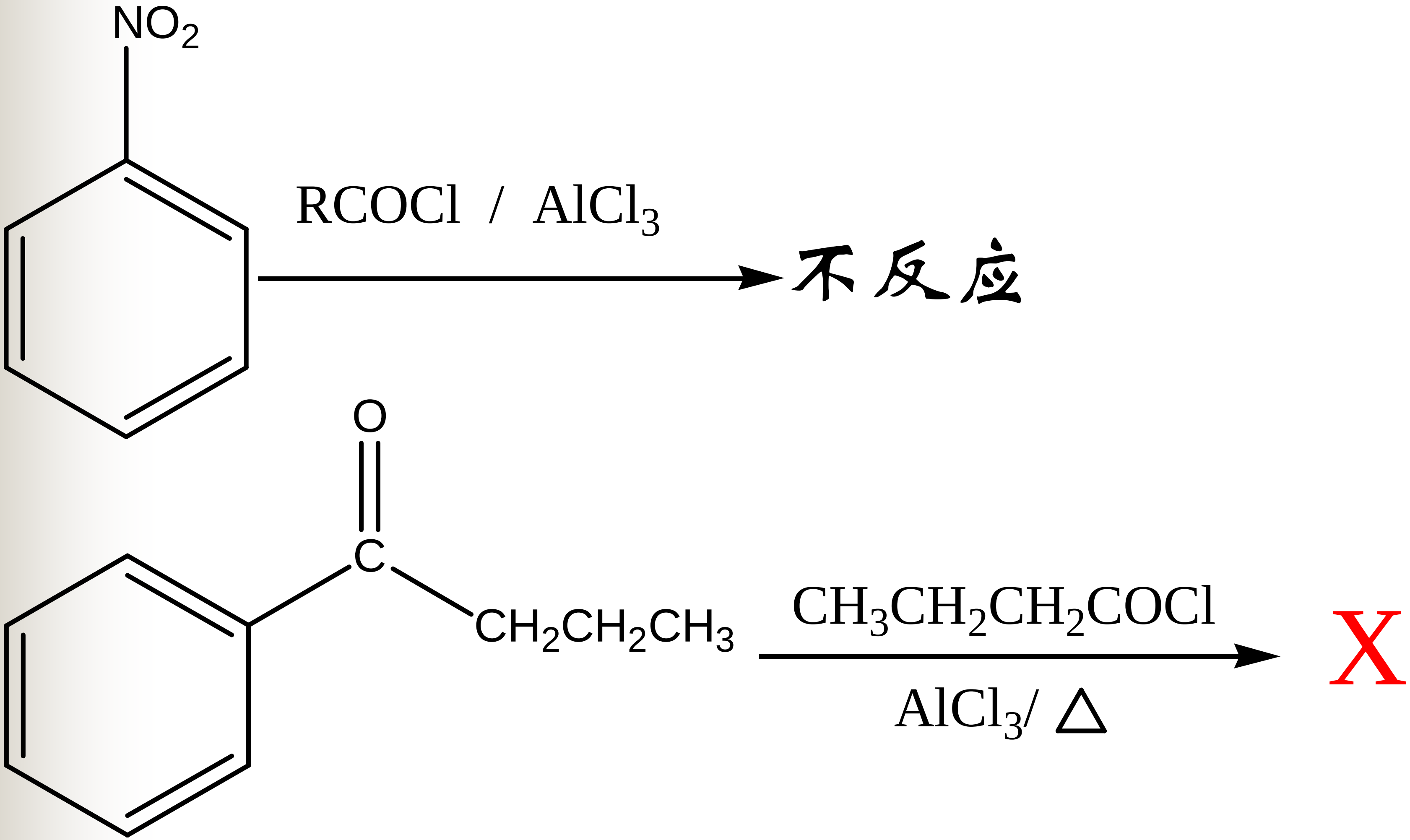


付氏酰基化反应的特点及应用：

a. 可用于合成芳酮；且无多取代问题；

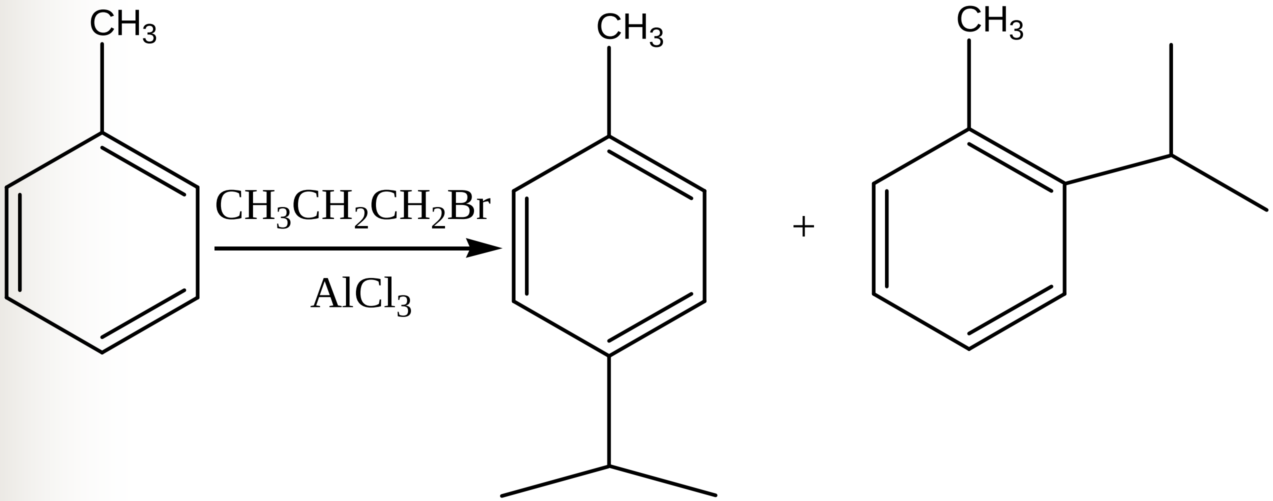


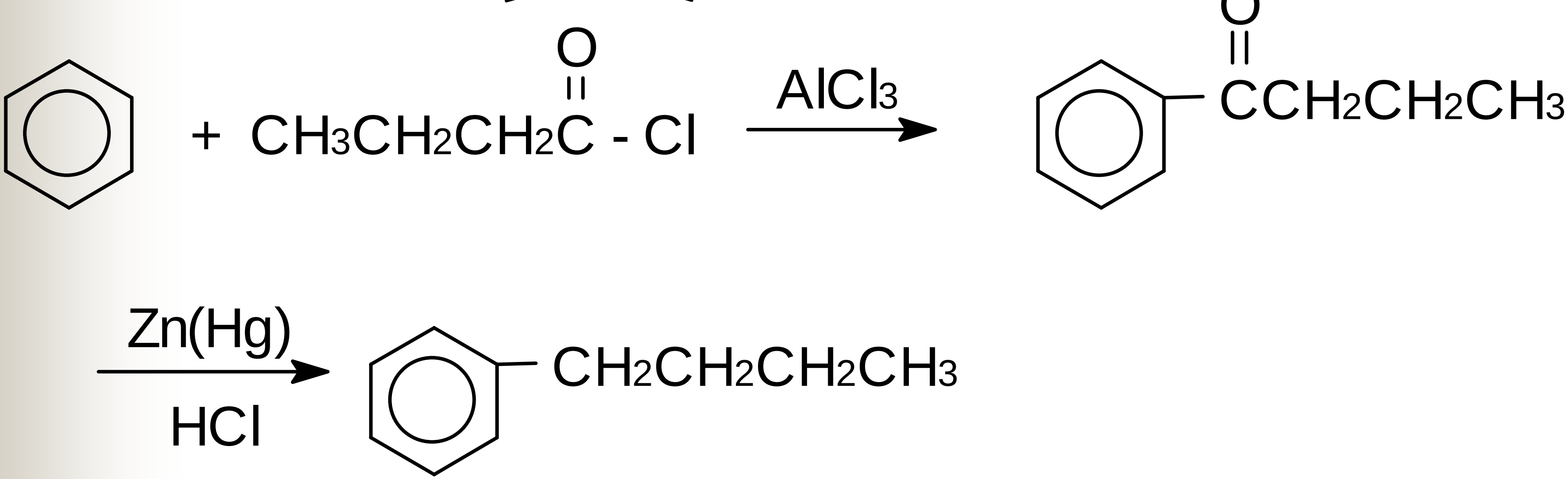
b. 如果苯环上含有比X更强的吸电子基团，则反应不进行；



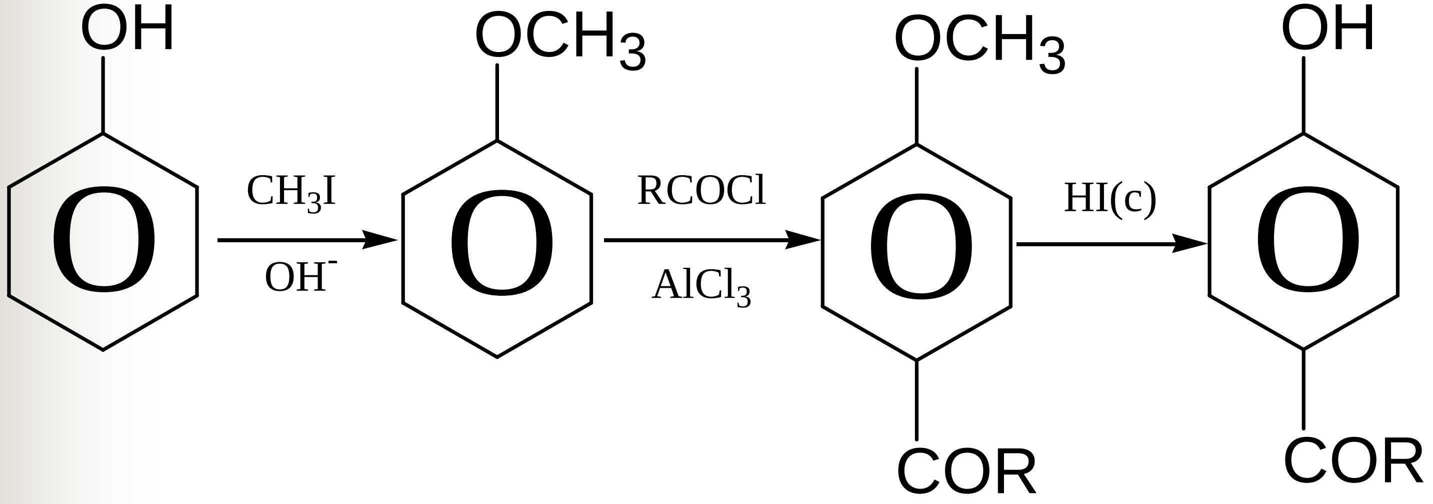
c.芳酮经还原可成烷基；无异构化问题；

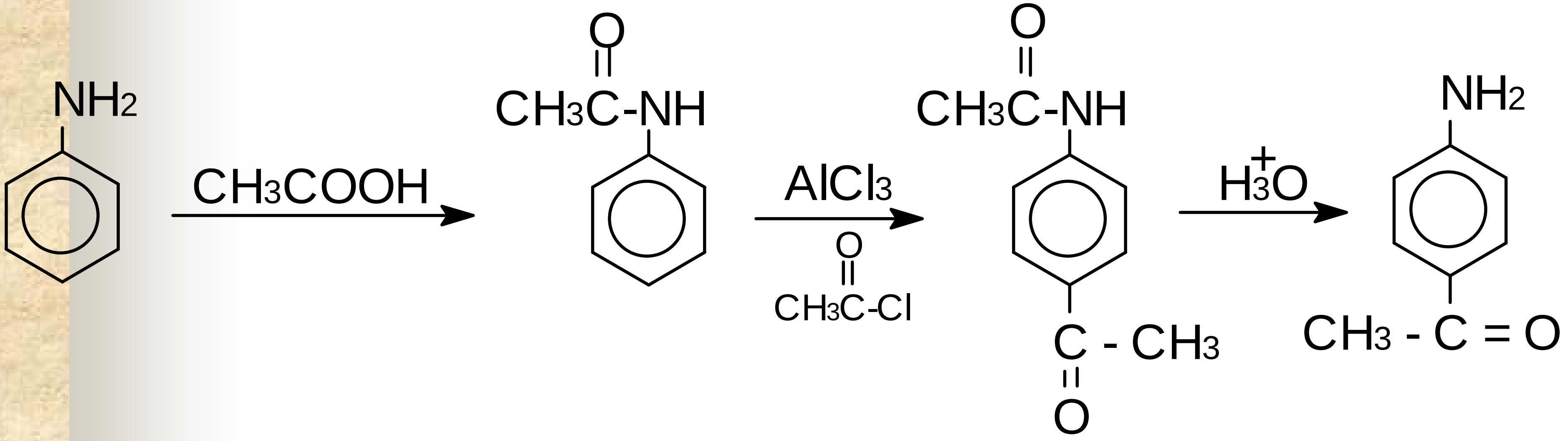
(还原条件：Zn(Hg)/HCl)



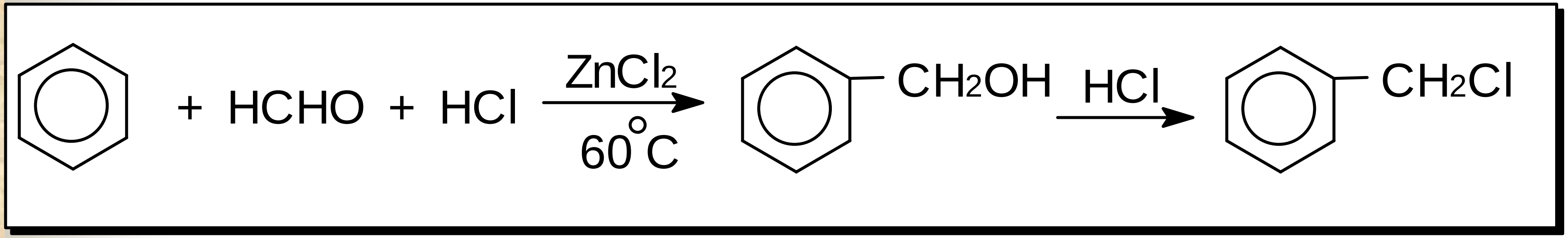


d. 如果苯环上含有-OH，-NH2等基团，可与催化剂络合，不反应，需先采用基团保护；

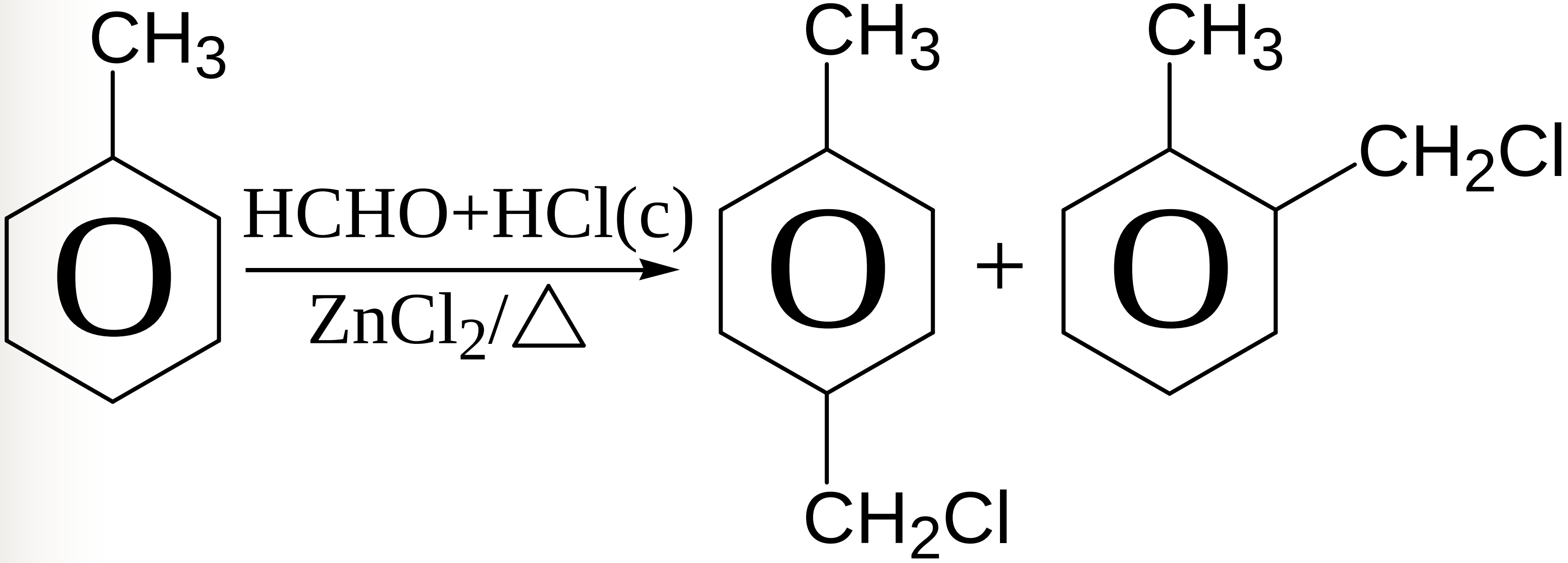




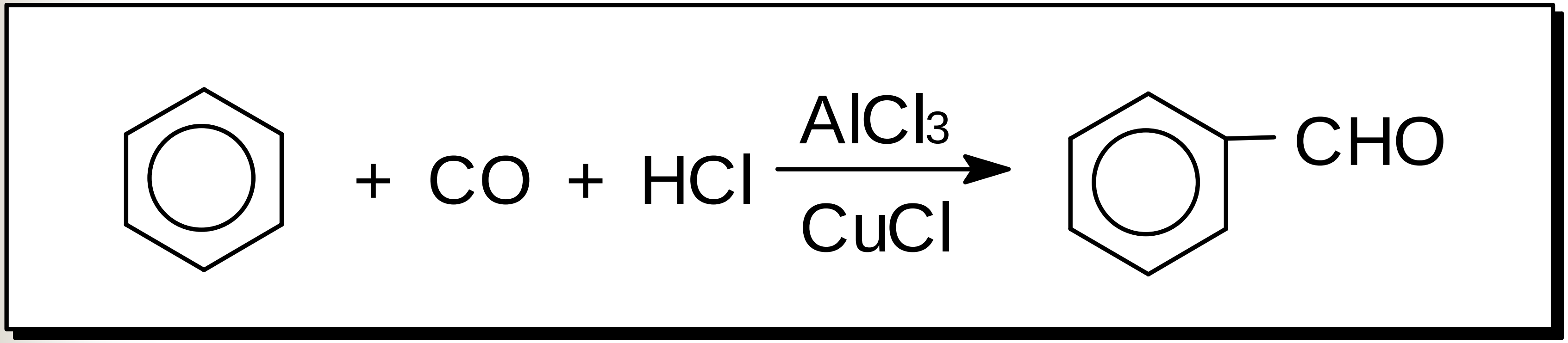
6. 氯甲基化反应


+ HCHO + HCl
$ZnCl_2$
60°C
CH_2OH
HCl
CH_2Cl

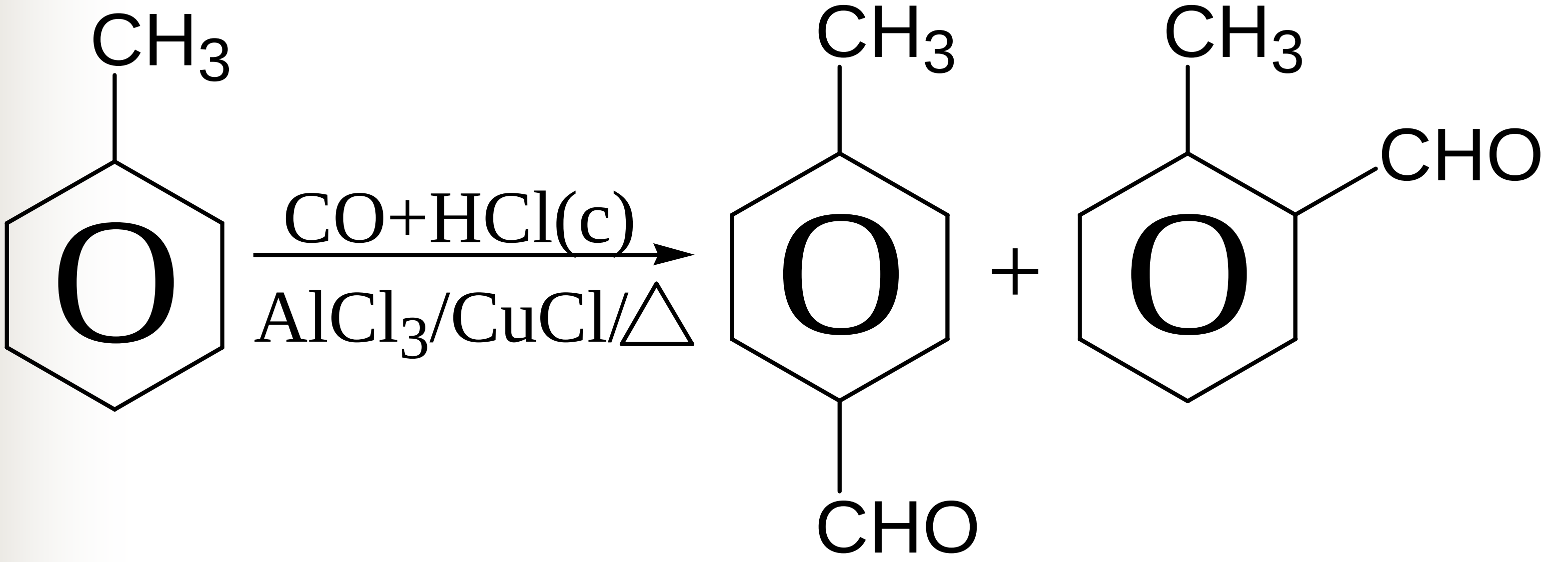
实例：


CH_3
HCHO+HCl(c)
$ZnCl_2$/△
CH_3
CH_2Cl
+
CH_3
CH_2Cl

7.Gattermann-Koch反应



实例：



亲电取代反应——总　结

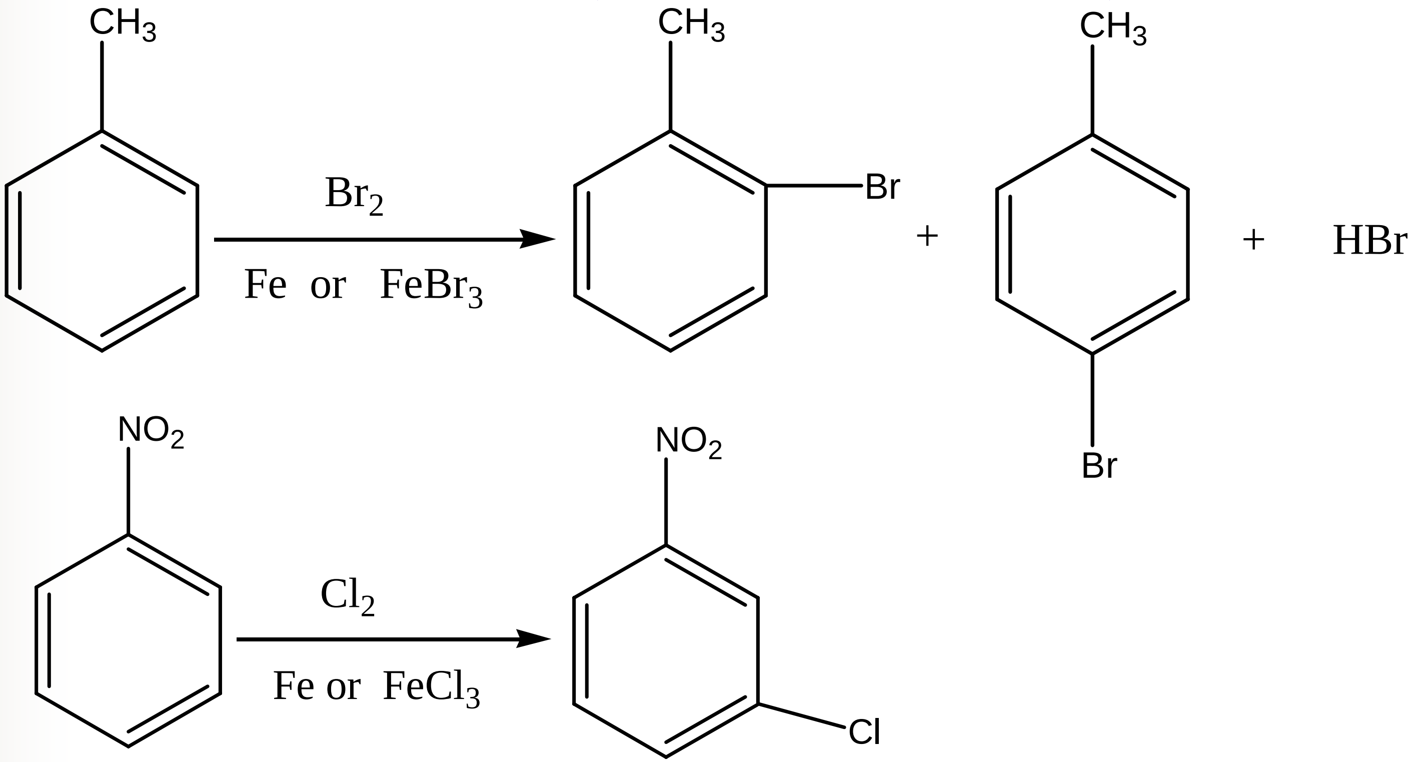
1.硝化、卤化、磺化、付氏烷（酰）基化

2.亲电取代机理-先加成后消除(Ad-E机理)

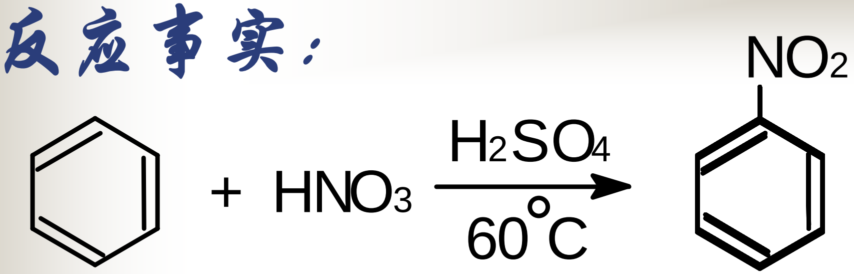
3.环上已有基团对欲上基团的取代难易程度和位置有一定的影响——定位效应。

§ 7.5 取代基的定位效应－定位律

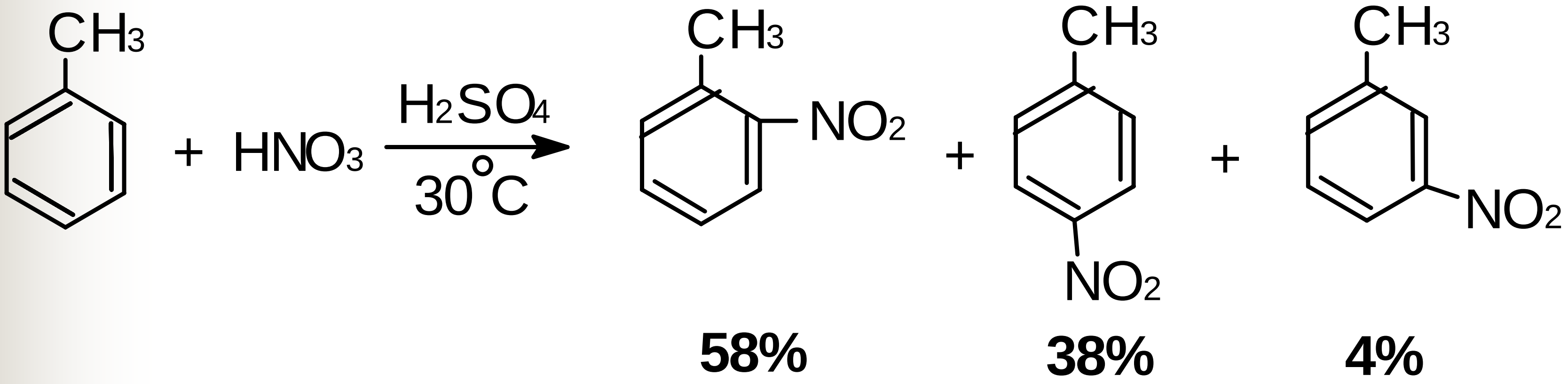
定位律：在芳烃发生亲电取代反应时，芳环上已有的取代基对取代位置的影响有一定的规律，这种定位的规律称之为定位律。



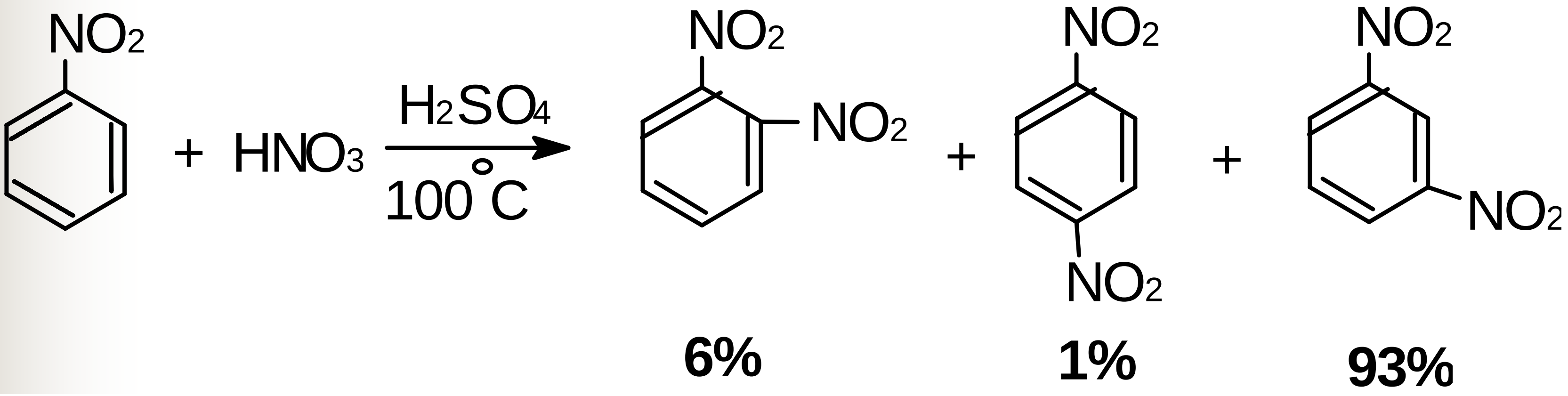
反应事实：



+ HNO_3
H_2SO_4
60°C
NO_2



CH_3
+ HNO_3
H_2SO_4
30°C
CH_3
NO_2
+
CH_3
NO_2
+
CH_3
NO_2
58%
38%
4%

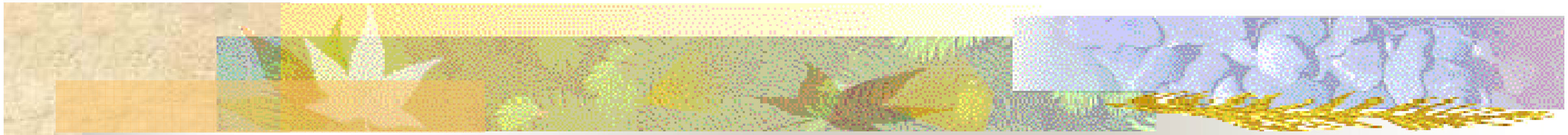


NO_2
+ HNO_3
H_2SO_4
100°C
NO_2
NO_2
+
NO_2
NO_2
+
NO_2
NO_2
6%
1%
93%

甲苯的硝化反应速度远远地高于硝基苯的硝化反应速度

说明：a. –CH_3活化苯环，且引导下一个基团进入邻位和对位；

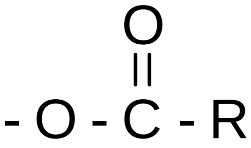
b. –NO_2钝化苯环，且引导下一个基团进入间位。



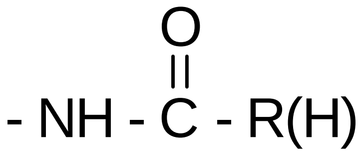
1.取代基的分类：

A. 第 I 类定位基（邻对位定位基）

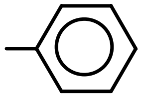
$-O^-$ $-NR_2$ $-NHR$ $-NH_2$ $-OH$ $-OR$



$-O-\overset{\overset{O}{\|}}{C}-R$



$-NH-\overset{\overset{O}{\|}}{C}-R(H)$



$-CH_3$ $-CR_3$

邻对位致

活定位基

$-X$ $-CH_2X$ $-CH=CHCOOH$ $-CH=CHNO_2$

邻对位致

钝定位基

特点：

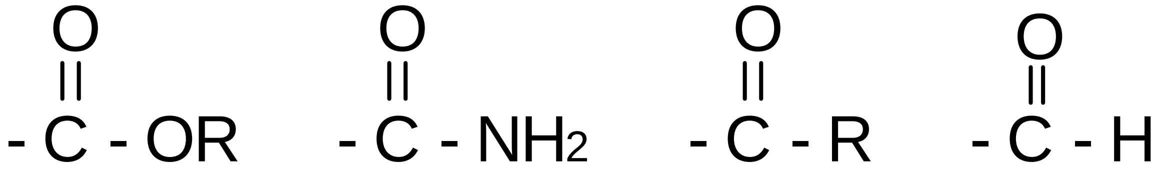
a. 都是邻对位定位基；

b. 含有氧、氮原子，虽然电负性较大，产生吸电子的诱导效应，但是孤对电子可以通过共轭效应共轭到环上，环上电子云密度加大，亲电反应活性提高；

c. 卤素等电负性太大，使环上电子云密度下降，亲电反应活性下降，但在反应过程中可以通过共轭效应将孤对电子共轭到环上而稳定中间体，仍是邻对位定位基

B. 第Ⅱ类定位基（间位定位基，致钝定位基）

$-\overset{+}{N}R_3$　$-CF_3$　$-CCl_3$　$-NO_2$　$-CN$　$-COOH$　$-SO_3H$



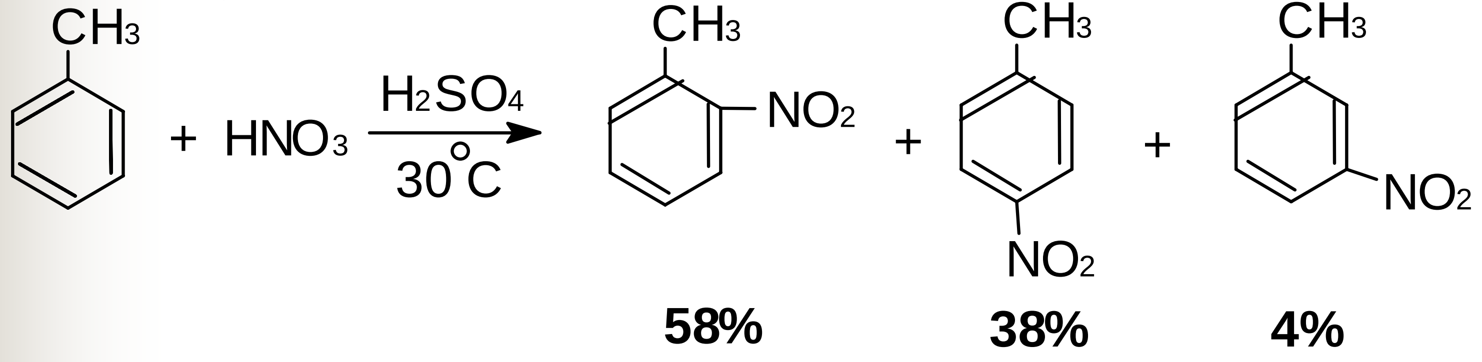
$-\overset{\overset{O}{\parallel}}{C}-OR$　$-\overset{\overset{O}{\parallel}}{C}-NH_2$　$-\overset{\overset{O}{\parallel}}{C}-R$　$-\overset{\overset{O}{\parallel}}{C}-H$

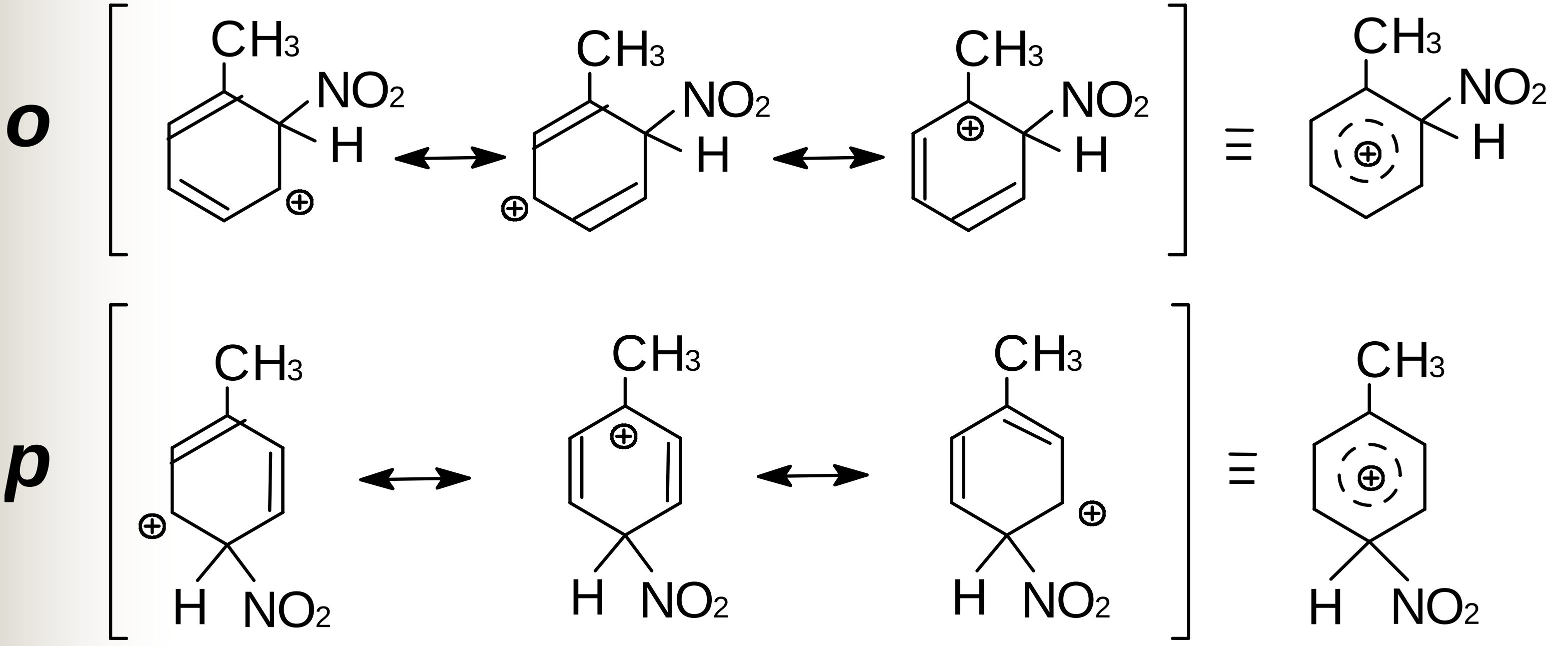
特点：a. 都是间位定位基；

b. 吸电子基团，使苯环电子云密度下降，亲电反应活性降低。

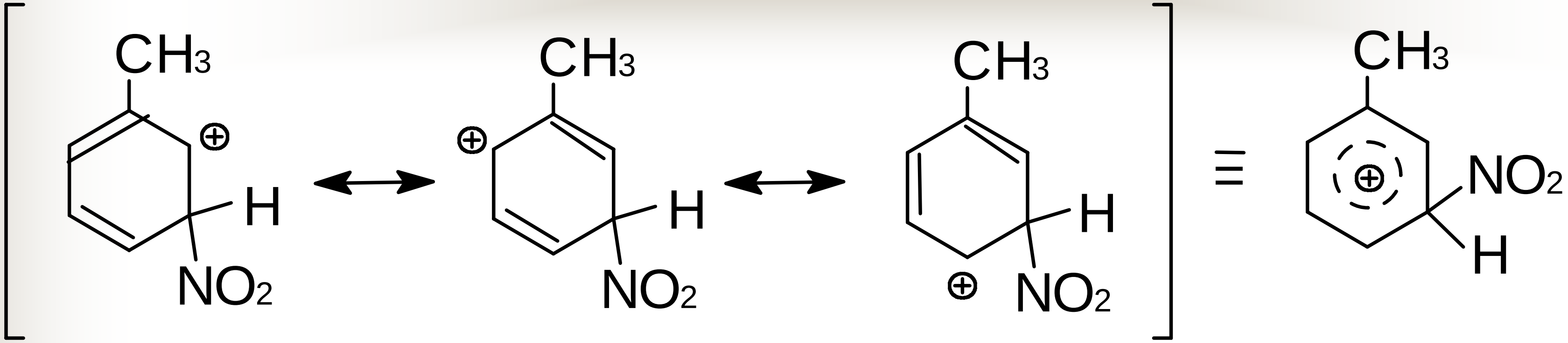
2. 定位效应 — 一取代芳烃的定位律

- A. 邻对位定位基



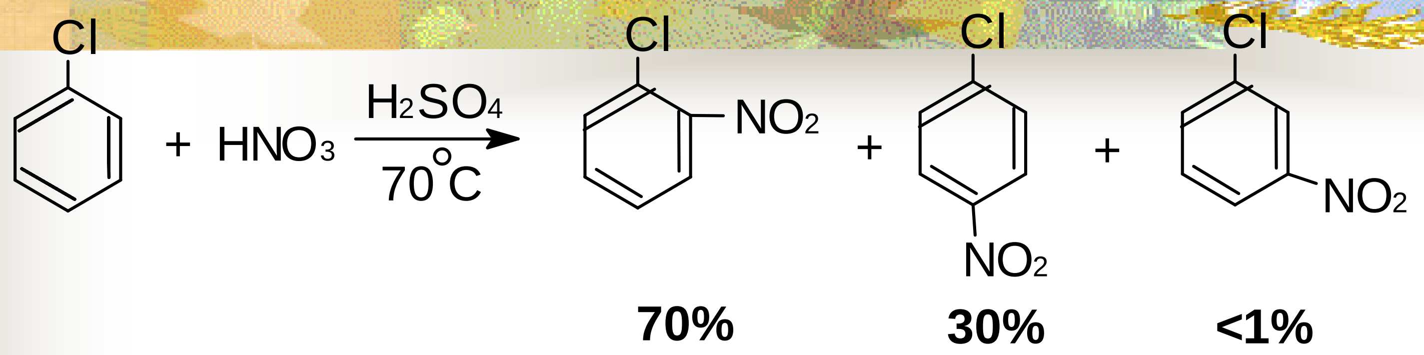


m

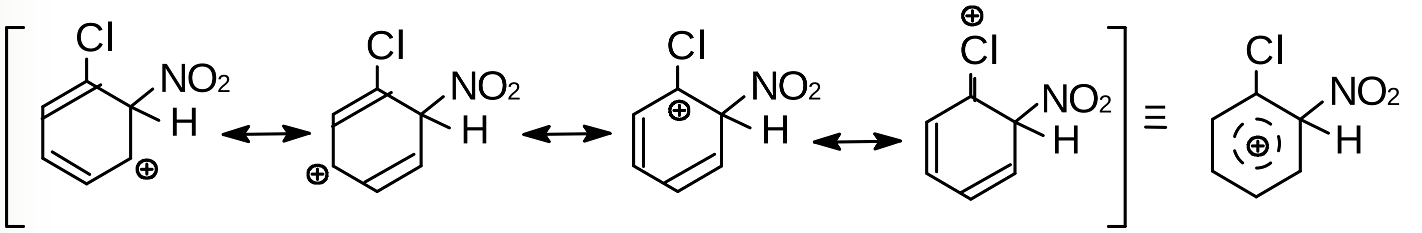


-CH_3是推电子基团，当亲电试剂加成到邻对位时，刚好能够形成正碳离子与-CH_3直接相邻的较稳定的共振式，而亲电试剂加成到间位时，不能够形成正碳离子与-CH_3直接相邻的较稳定的共振式，因此-CH_3为邻对位定位基。

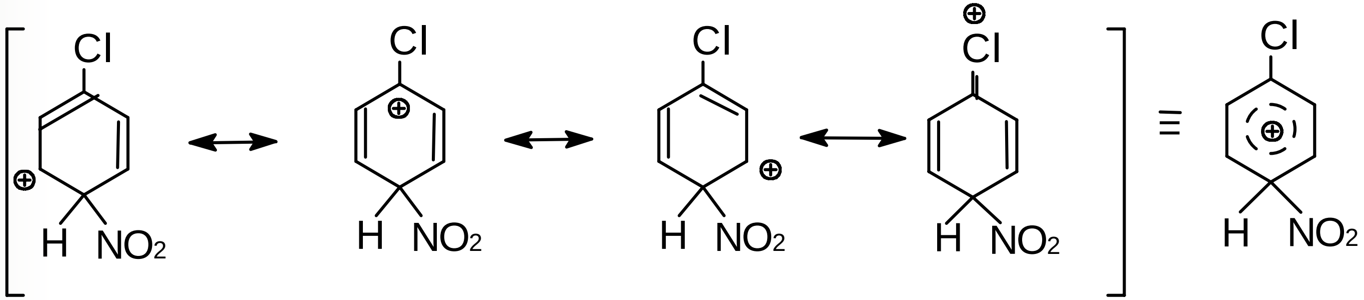
总结：正碳离子在苯环上共振，当连有第Ⅰ类定位基时，邻对位取代中间体可以被给电子基团稳定。


Cl
+ HNO3
H2SO4
70°C
Cl
NO2
+
Cl
NO2
+
Cl
NO2
70%
30%
<1%

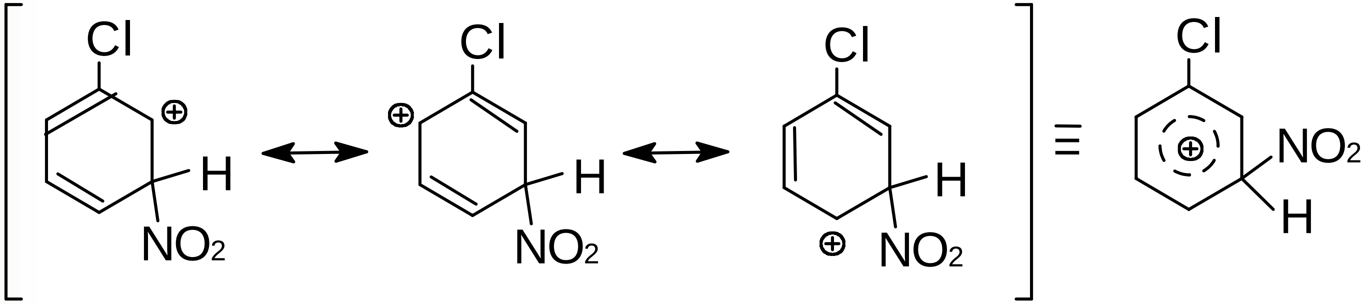
o

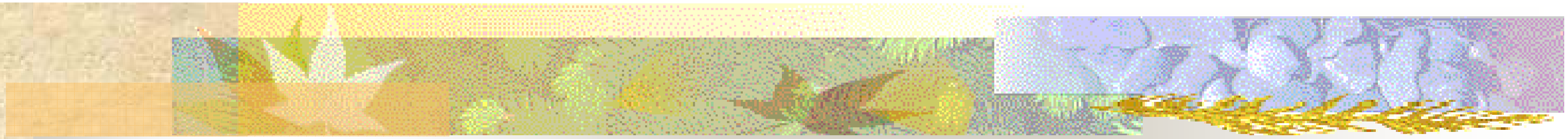

Cl
NO2
H
⊕
≡

p


Cl
H
NO2
⊕
≡

m

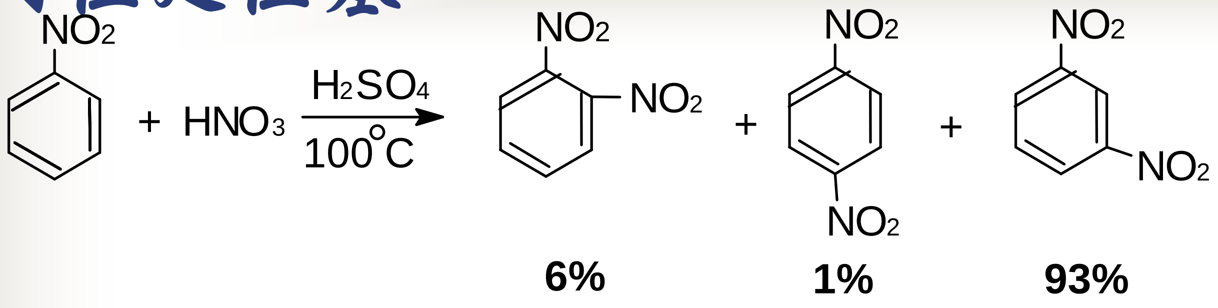

Cl
H
NO2
⊕
≡

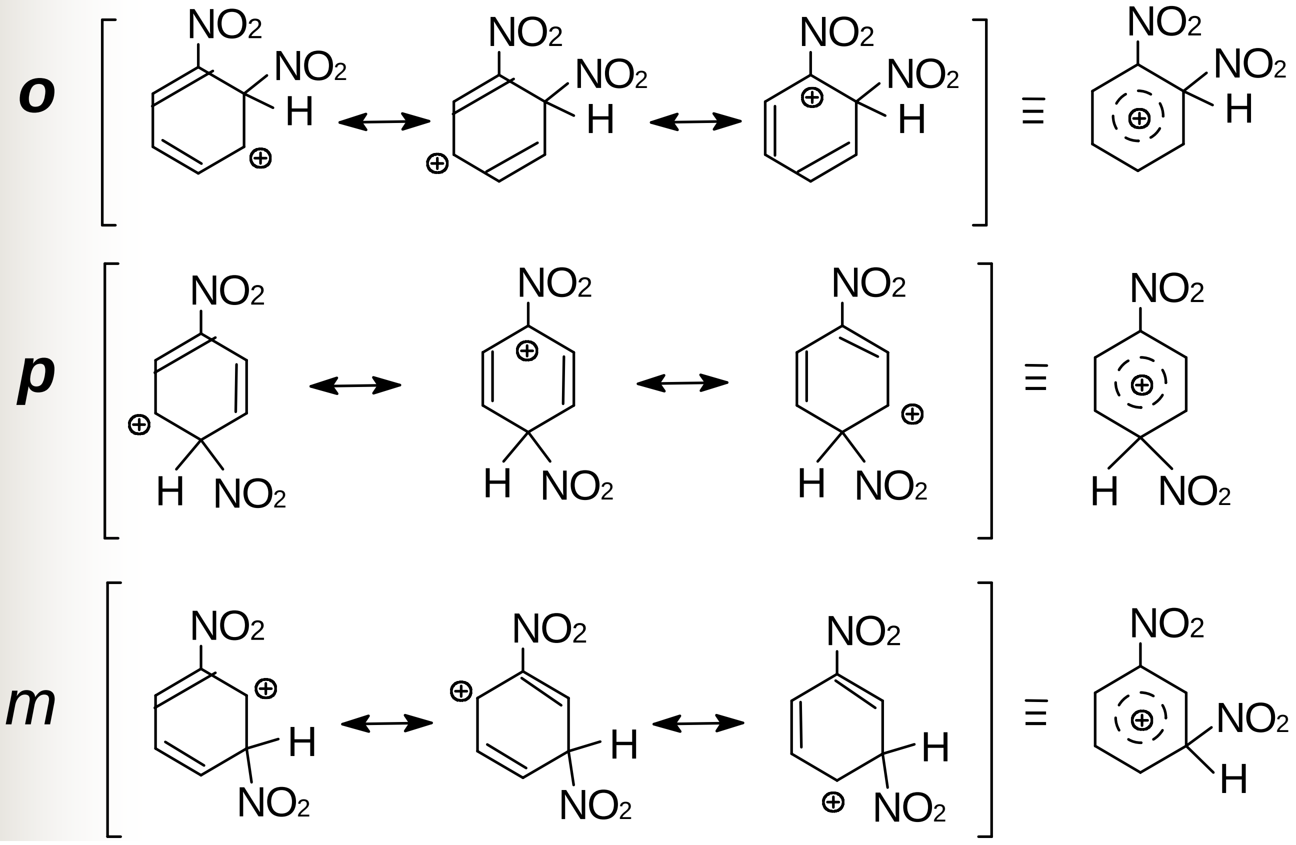


总结：

- a. 卤素吸电子诱导效应使苯环电子云密度下降，不利于反应；
- b. 卤素原子给电子共轭效应稳定邻对位取代时的正碳离子；
- c. 故卤素原子是致钝的邻对位定位基
- d. 诱导效应决定反应活性低；共轭效应决定反应取向为邻对位。

B. 间位定位基


NO2
+ HNO3
H2SO4
100°C
NO2
NO2
+
NO2
NO2
+
NO2
NO2
6%
1%
93%


o
NO2
NO2
H
⊕
≡
p
H
NO2
m

总结：

- a. 吸电子基团使苯环电子密度下降，不利于亲电反应；
- b. 正碳离子在苯环上共振，间位取代刚好能避开吸电子基团；
- c. 吸电子基团是间位定位基。

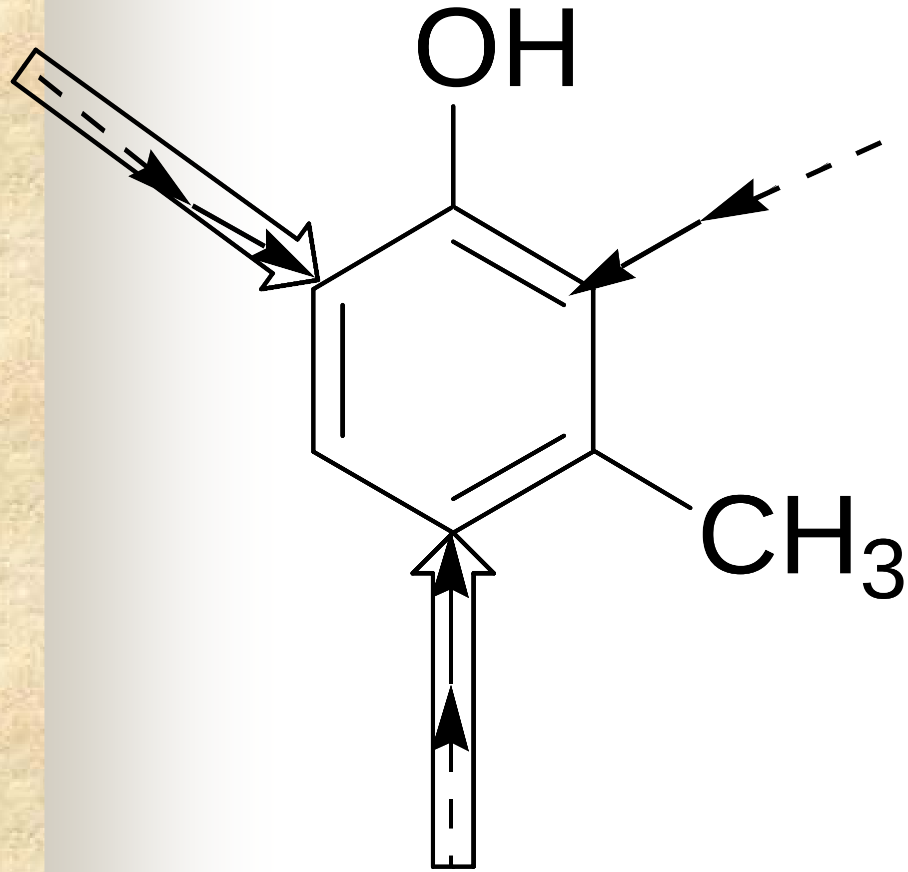
单取代芳烃的定位律总结：

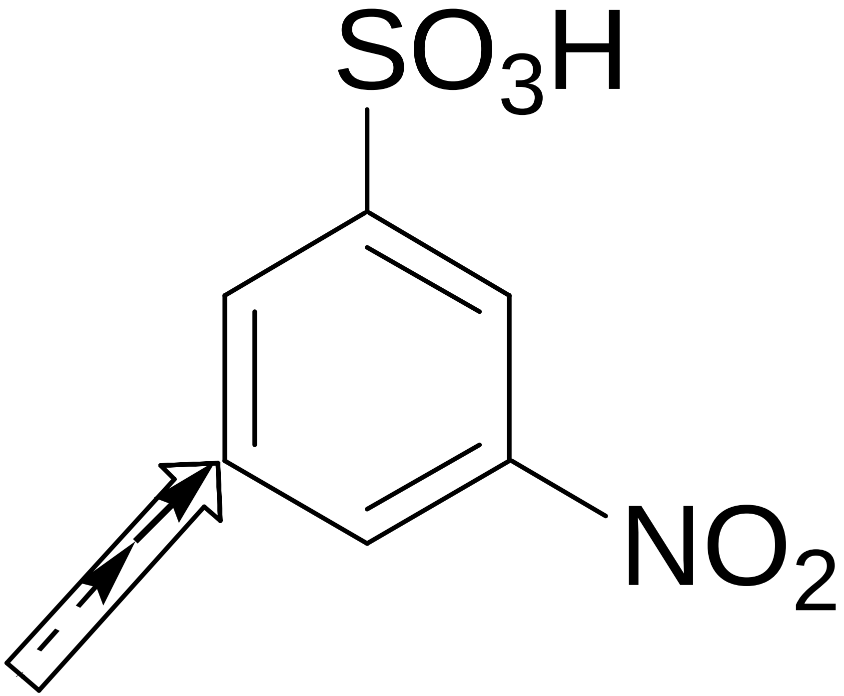
a.当连有**第Ⅰ类定位基**时，亲电取代主要反应发生在**邻、对位**。

b.当连有**第Ⅱ类定位基**时，亲电取代主要反应发生在**间位**。

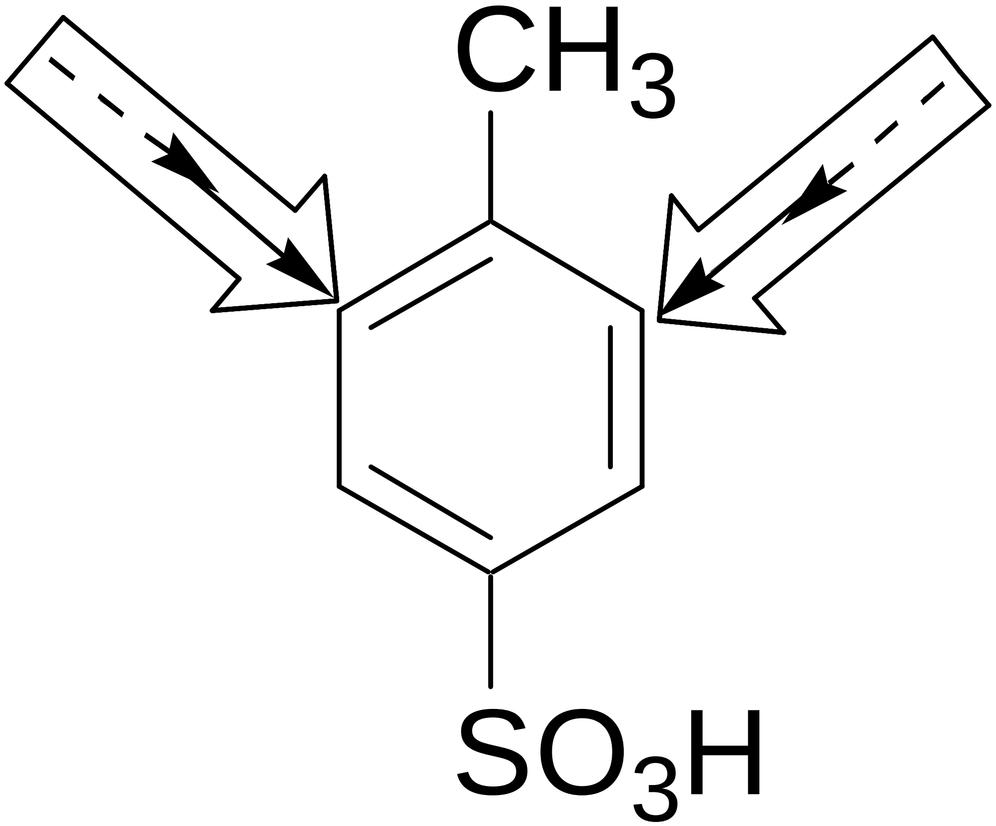
3.定位效应——双取代芳烃的定位律:

A.连有两个相同类型的定位基，且定位指向一致

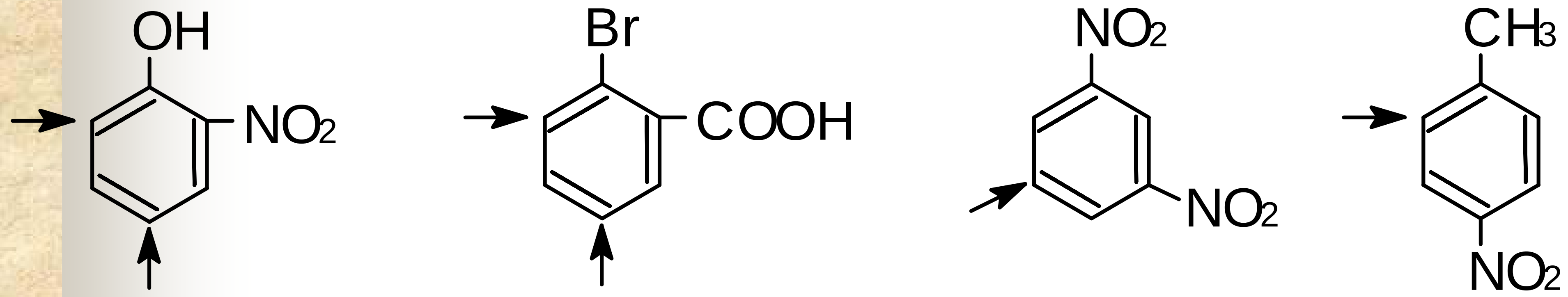




b. 连有两个不同类型的定位基，但定位指向一致



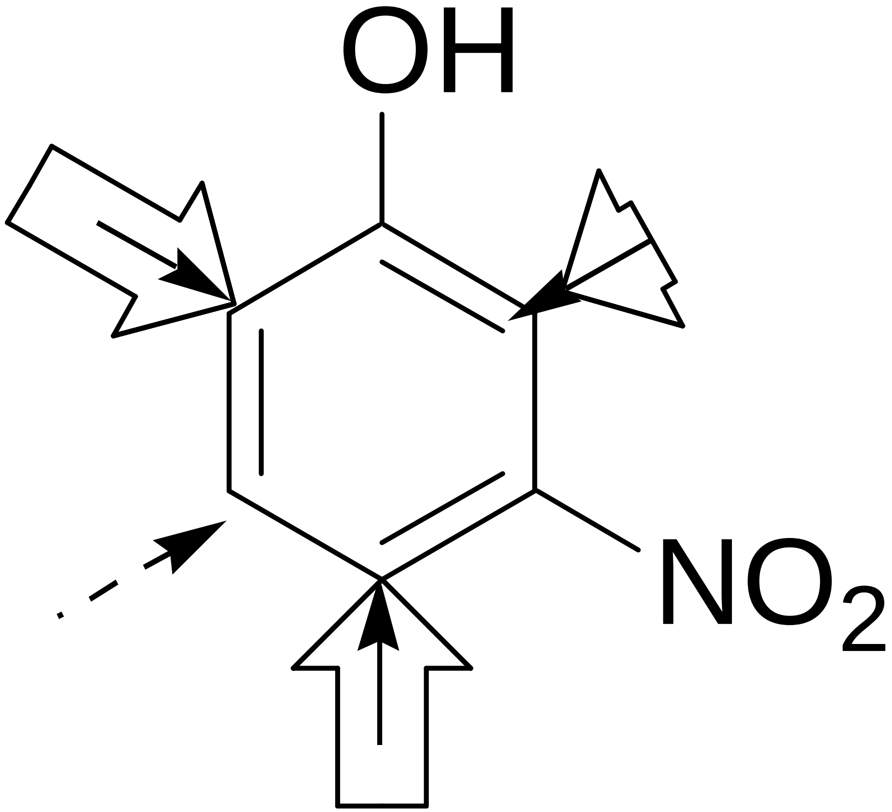
即：两取代基指向相同，第三个取代基进入指向的位置；

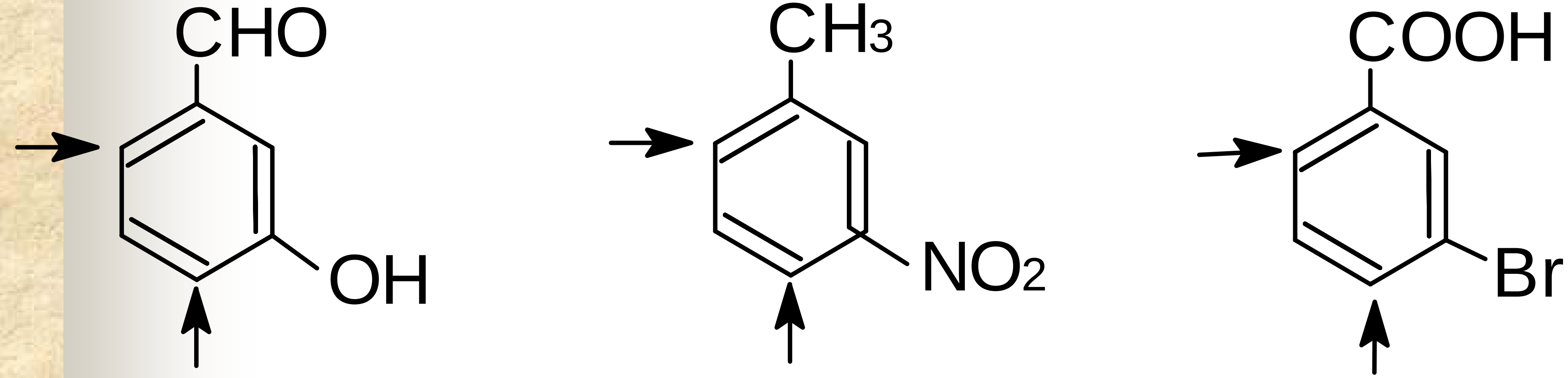


c. 连有两个不同类型的定位基，

且定位指向不一致

以第 I 类定位基定位为主

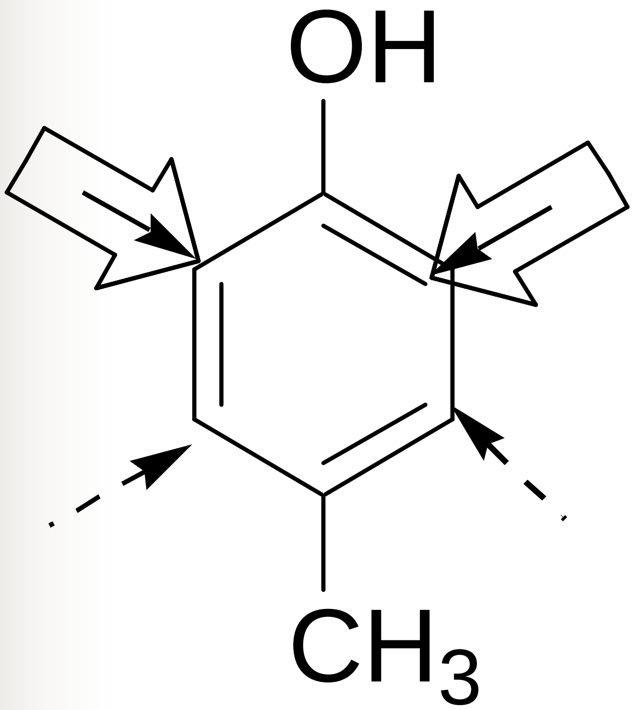


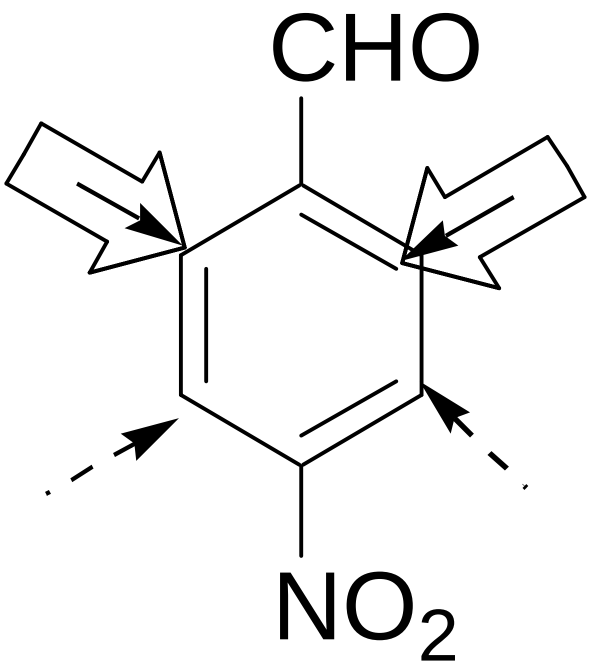

CHO
OH
CH3
NO2
COOH
Br

d. 连有两个相同类型的定位基，

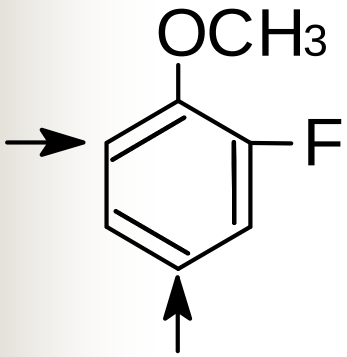
但定位指向不一致

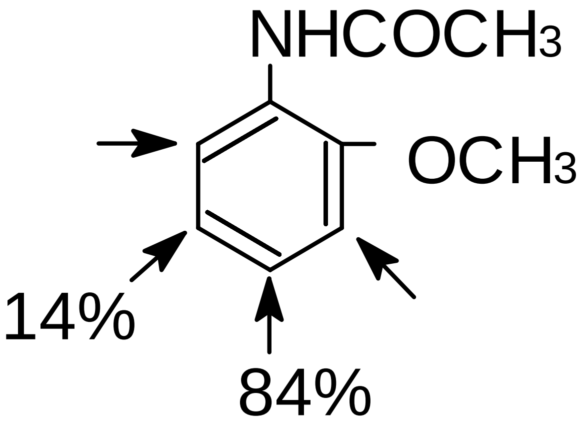
以相对定位能力强的定位基定位为主

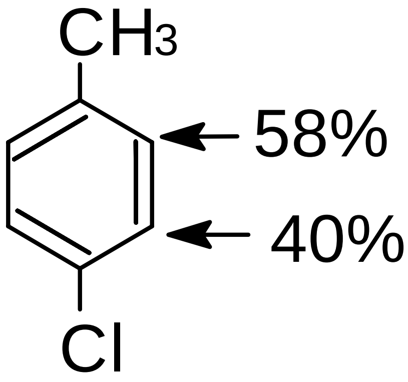


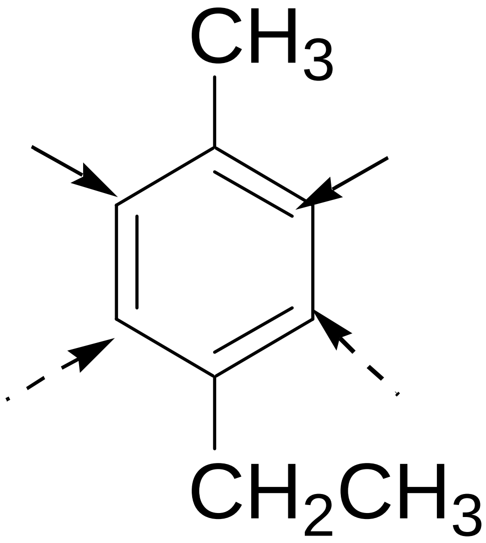


即：两个同种类型的取代基指向不同时，按定位能力强的指向；定位能力相似，则产物复杂；



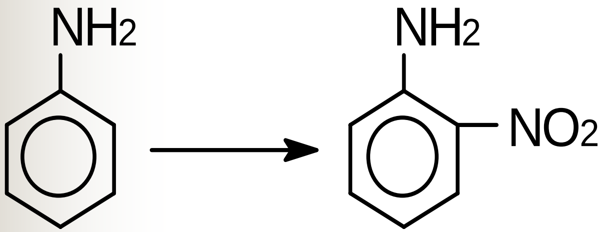


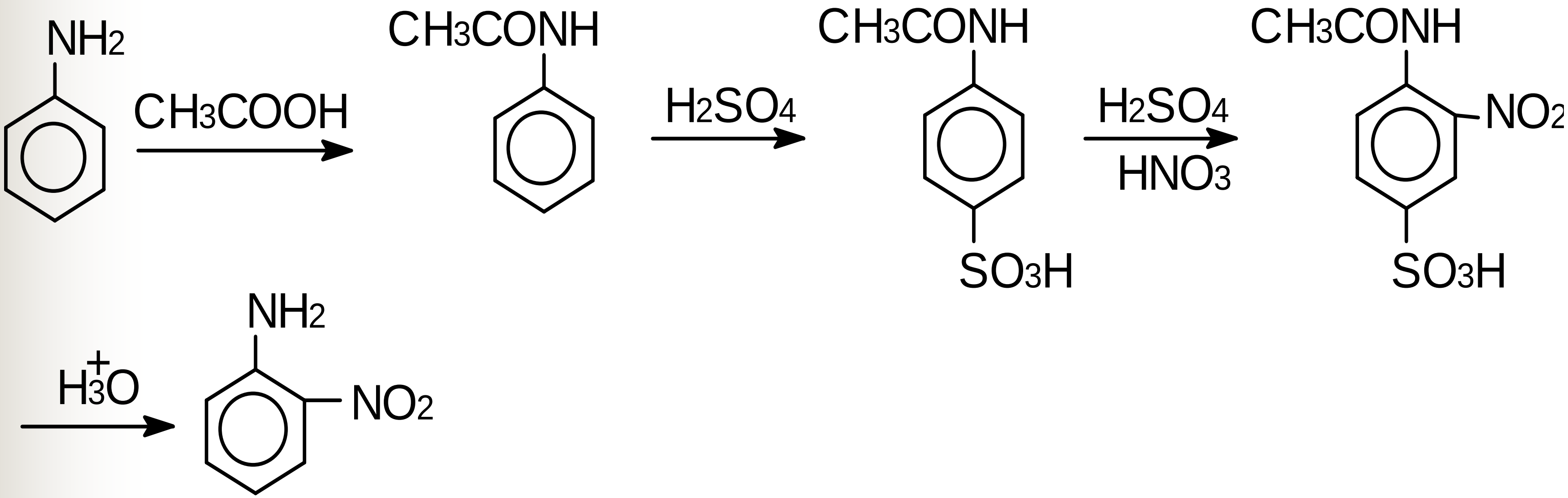




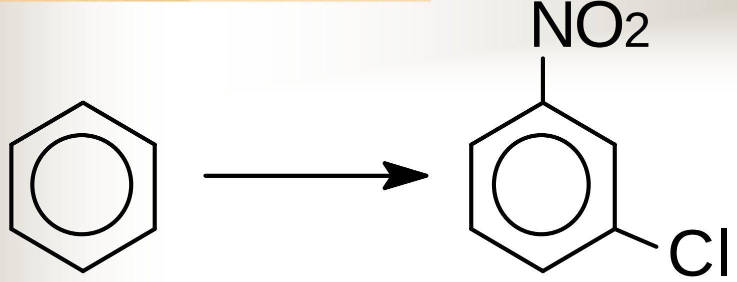
4、定位律在合成中的应用：

A.

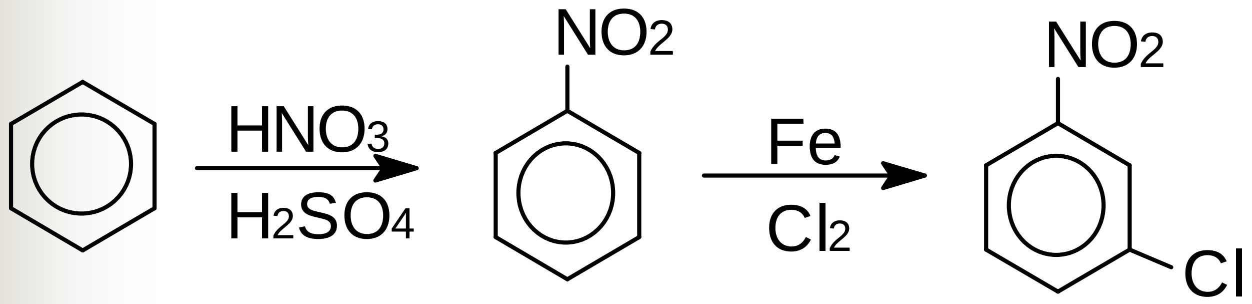




B.

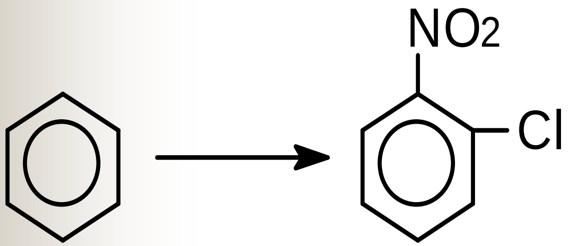


NO_2
Cl

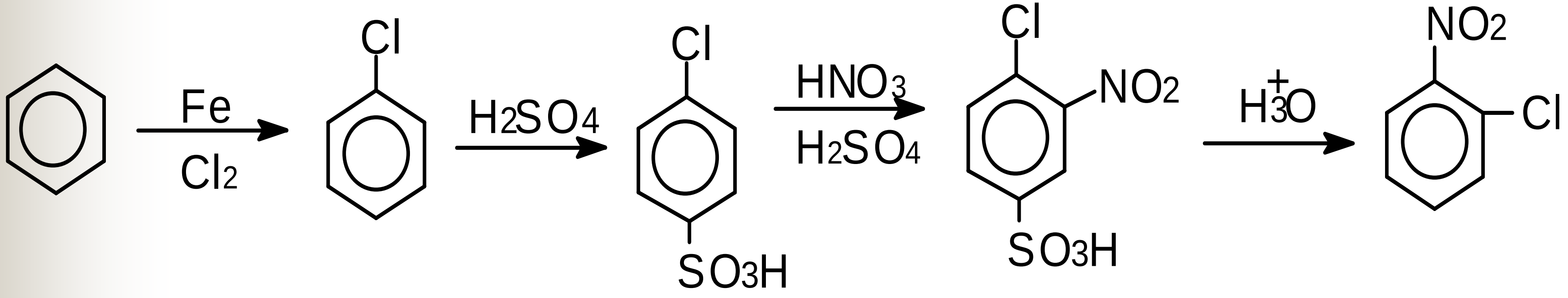


HNO_3
H_2SO_4
NO_2
Fe
Cl_2
NO_2
Cl

C.

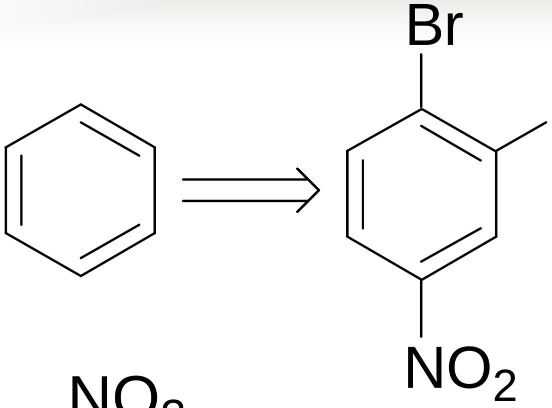


NO_2
Cl

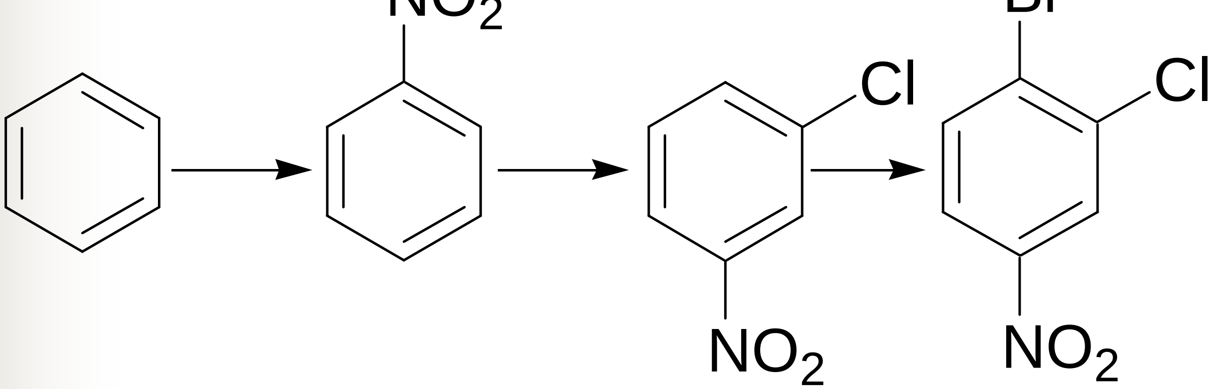


Fe
Cl_2
Cl
H_2SO_4
Cl
SO_3H
HNO_3
H_2SO_4
Cl
NO_2
SO_3H
$H_3\overset{+}{O}$
NO_2
Cl

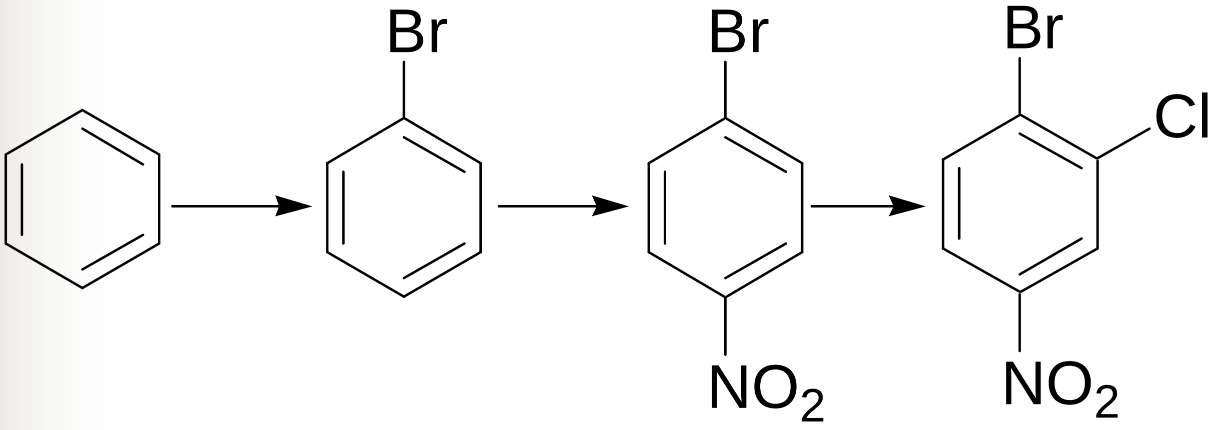
D.



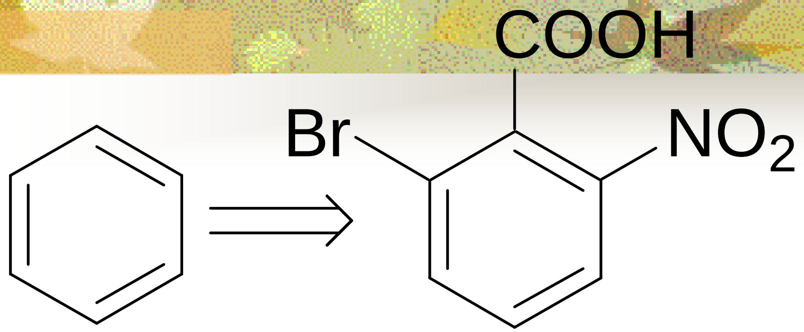
a.



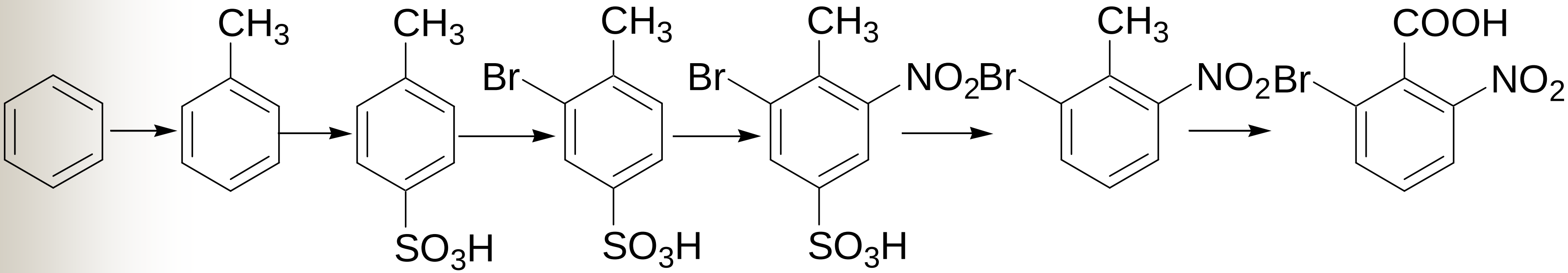
b.



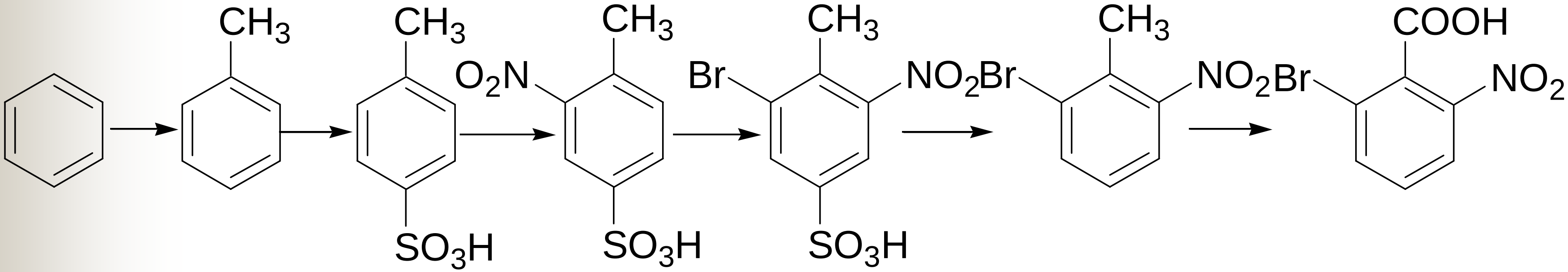
E.


COOH
Br
NO2

a.


CH3
CH3
SO3H
Br
CH3
SO3H
Br
CH3
NO2
SO3H
Br
CH3
NO2
Br
COOH
NO2

b.


CH3
CH3
SO3H
O2N
CH3
SO3H
Br
CH3
NO2
SO3H
Br
CH3
NO2
Br
COOH
NO2

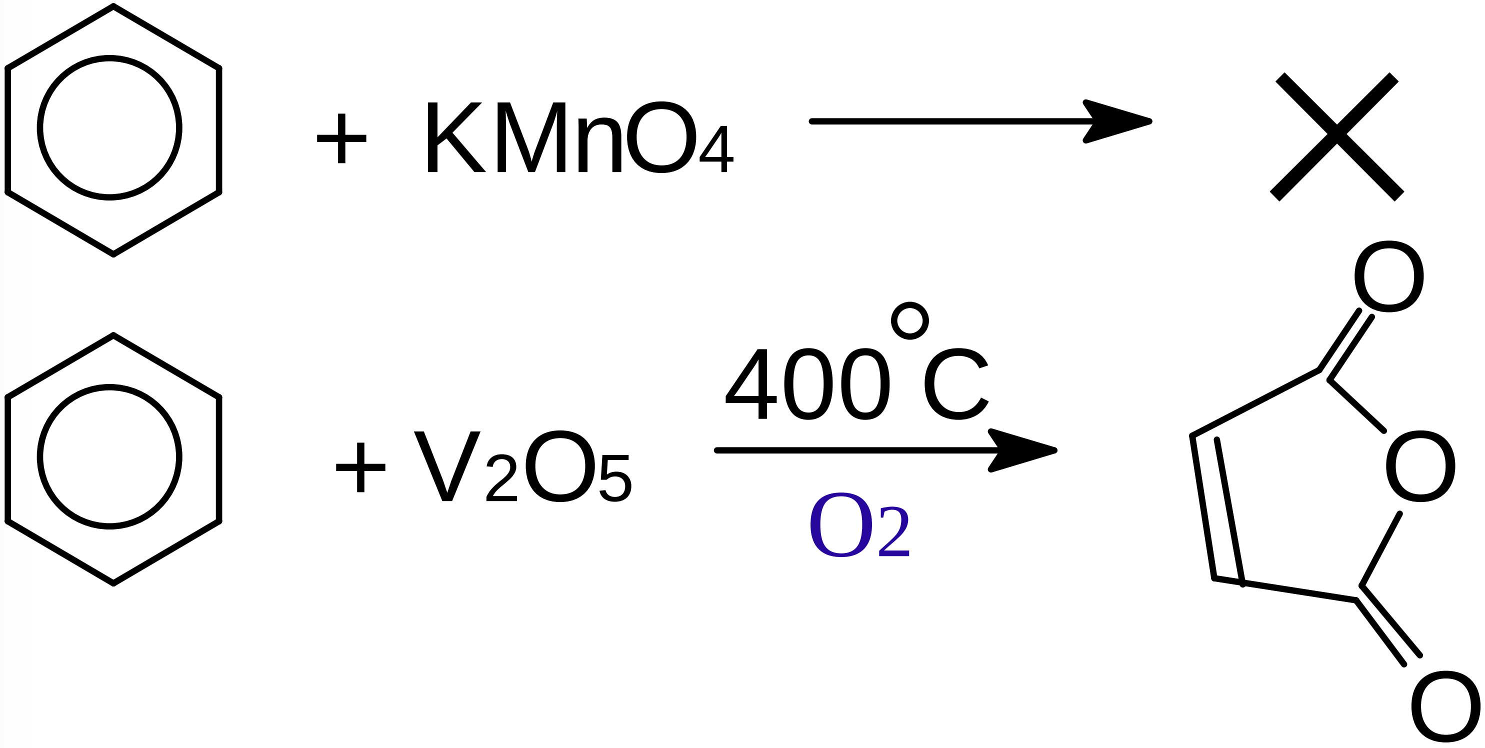
注意：

- a. 遇到-NH2，要先乙酰化保护；
- b. 欲生成邻位产物，要先磺化保护对位；
- c. 灵活运用各个基团的定位效应。

§ 7.6 苯的化学性质 Ⅱ

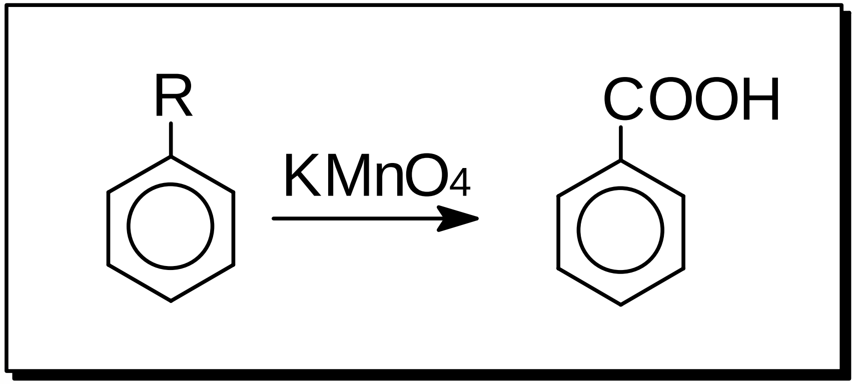
——氧化还原及侧链反应

1.苯环氧化反应:

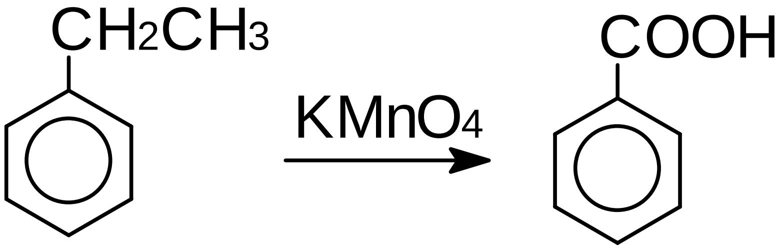


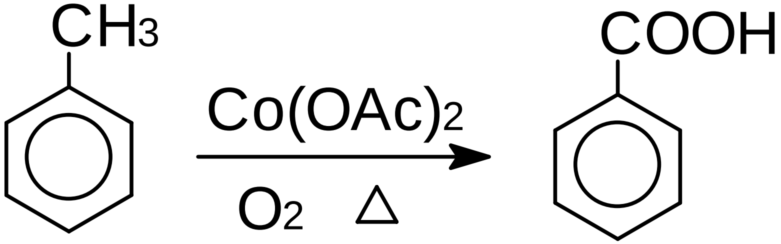
顺丁烯二酸酐

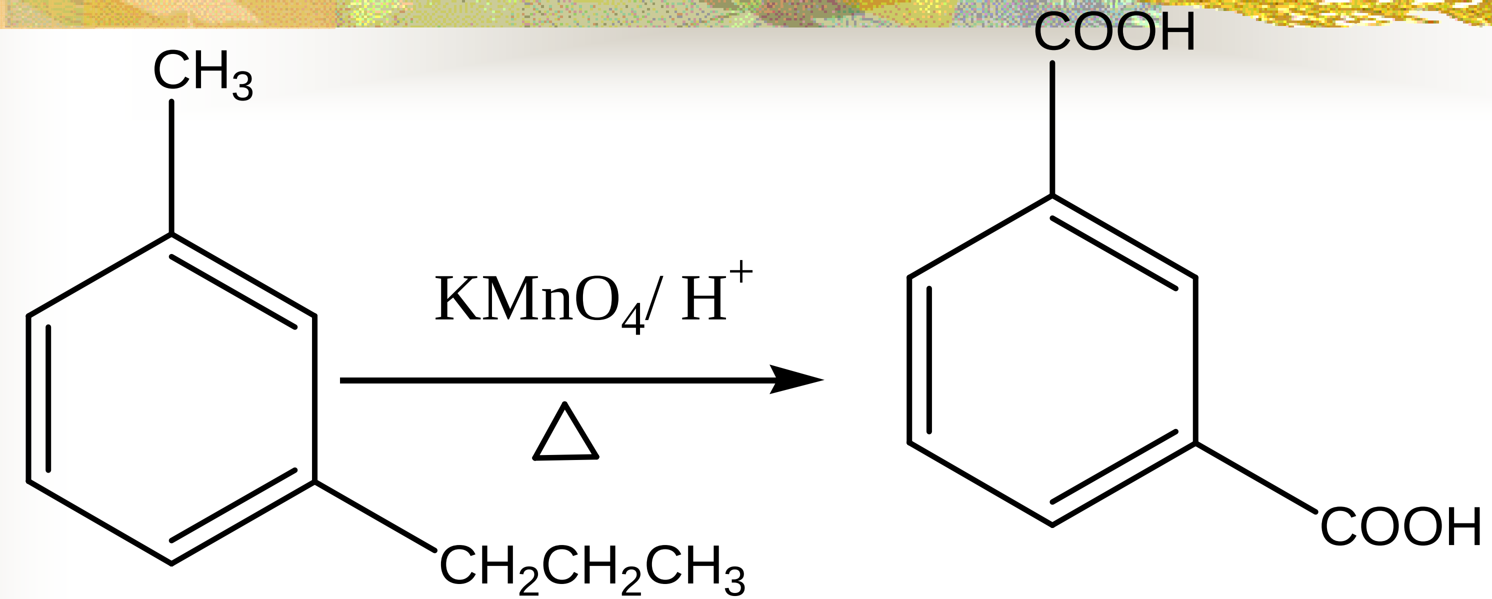
2. 苯环侧链反应——烷基苯的氧化反应

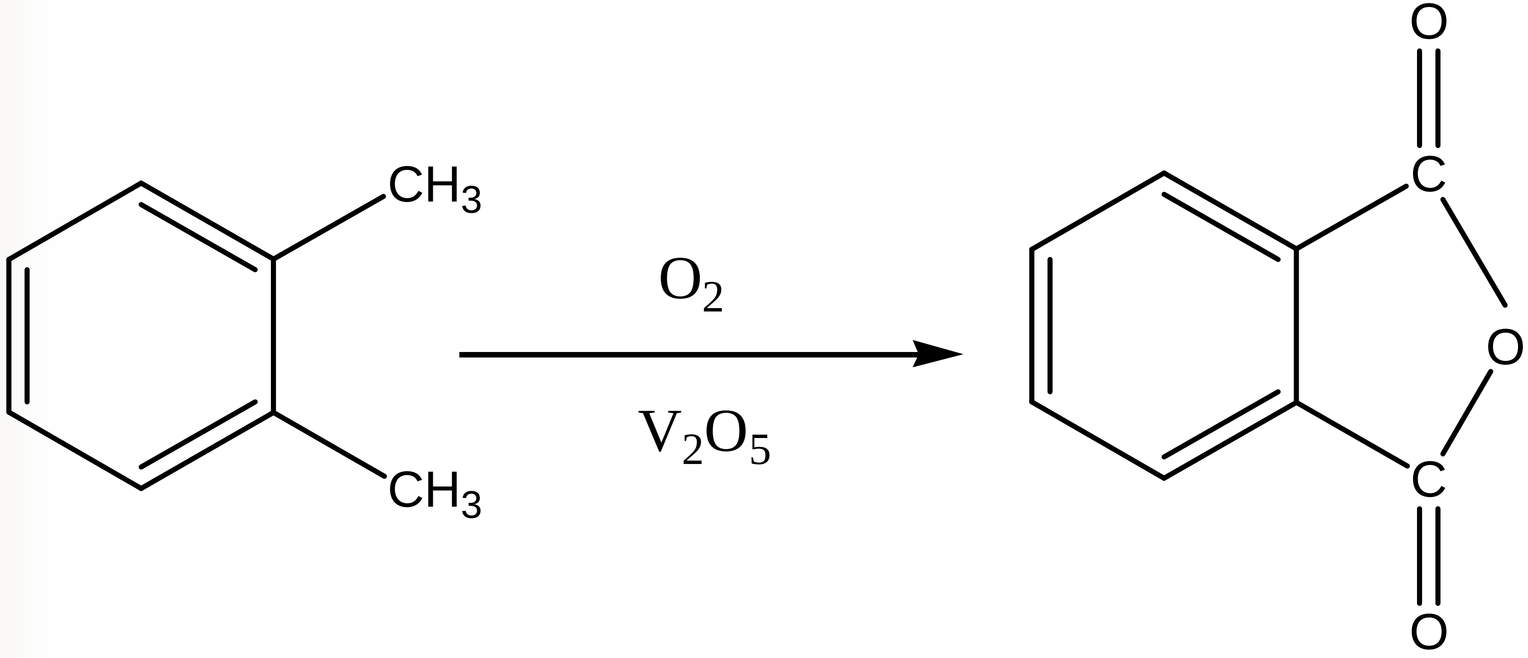


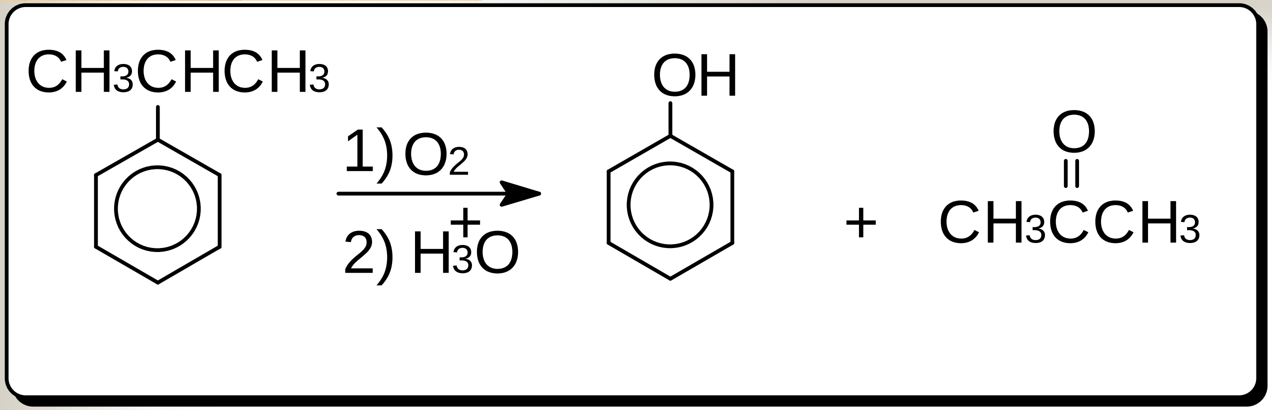
该反应要求苯环的α位上必须有H





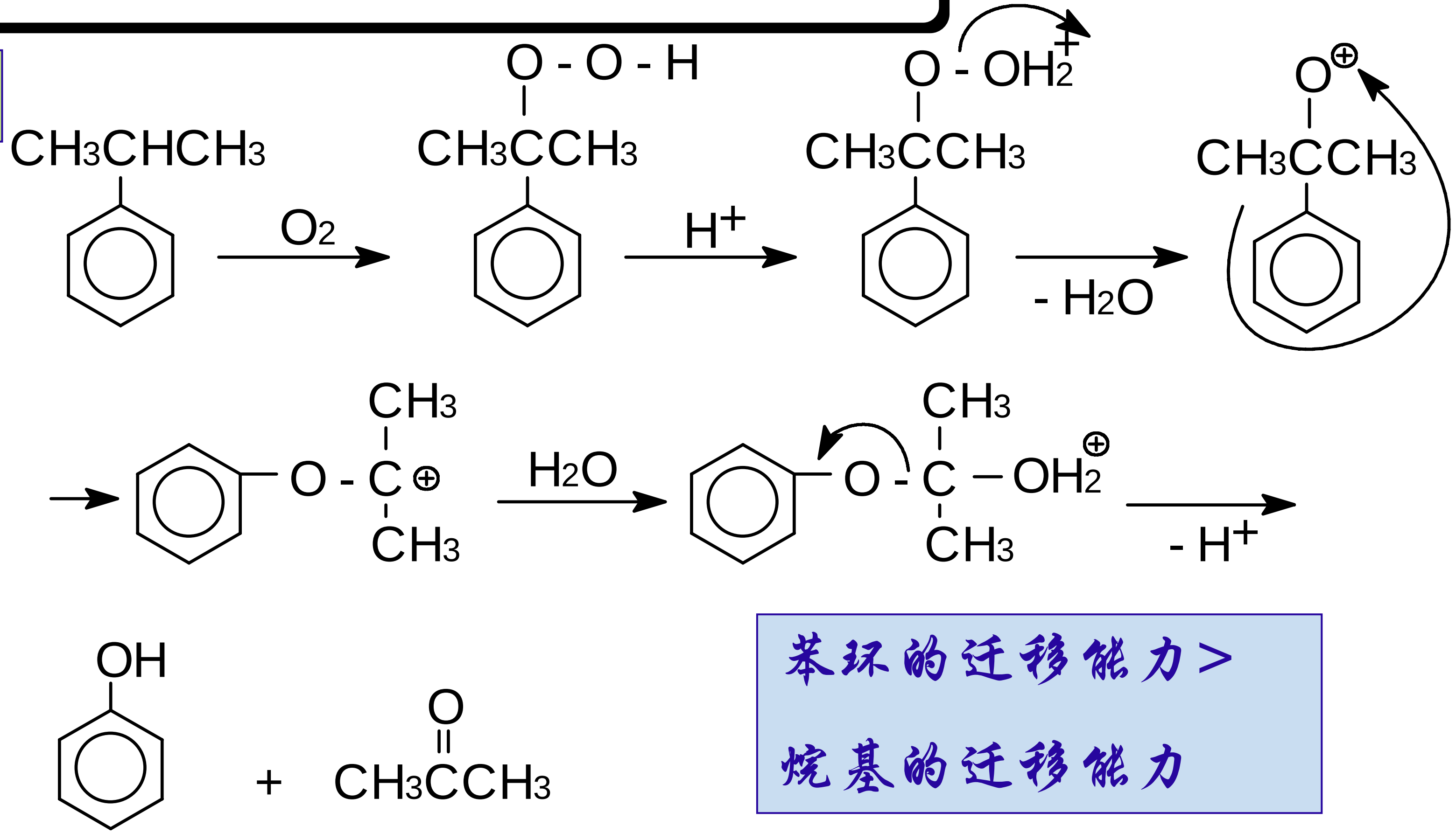

CH3
KMnO4/ H+
Δ
COOH
CH2CH2CH3
COOH


CH3
CH3
O2
V2O5
O
C
O
C
O



工业合成苯酚和丙酮的方法

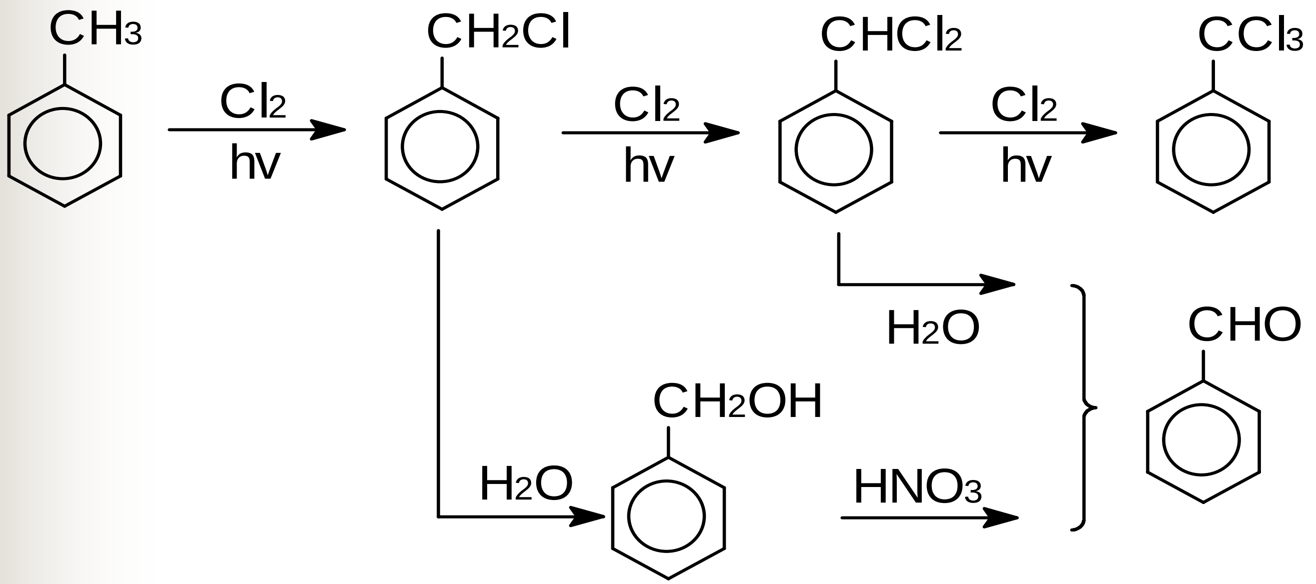
反应机理

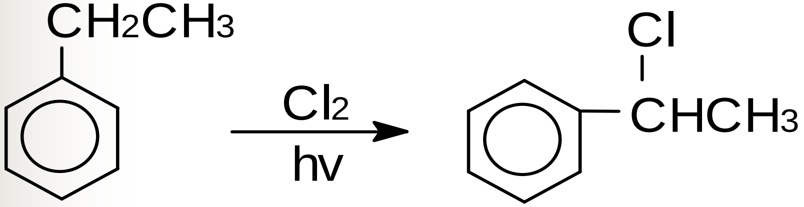


苯环的迁移能力>

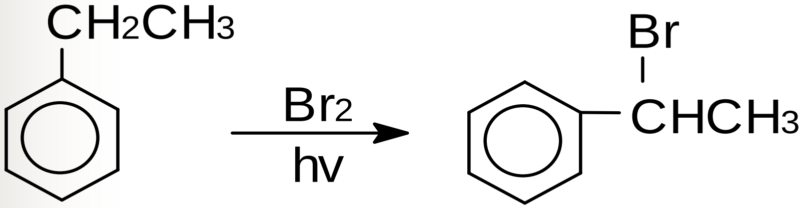
烷基的迁移能力

2. 苯环侧链反应——卤代反应





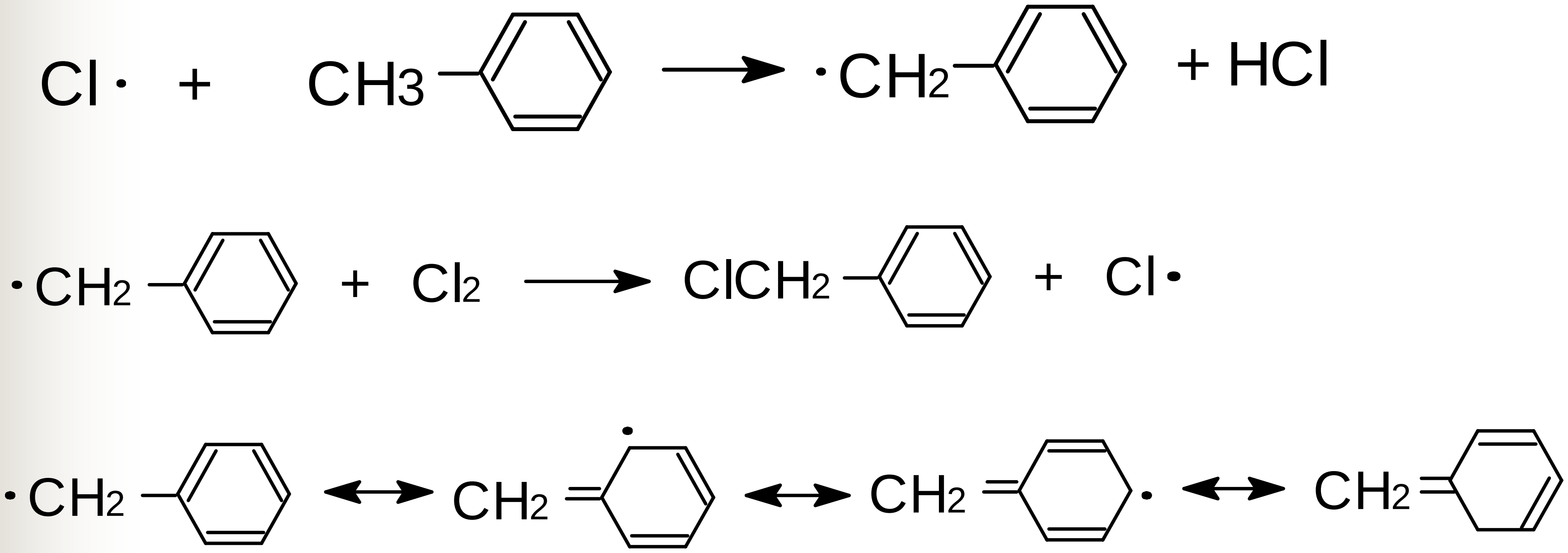
91%



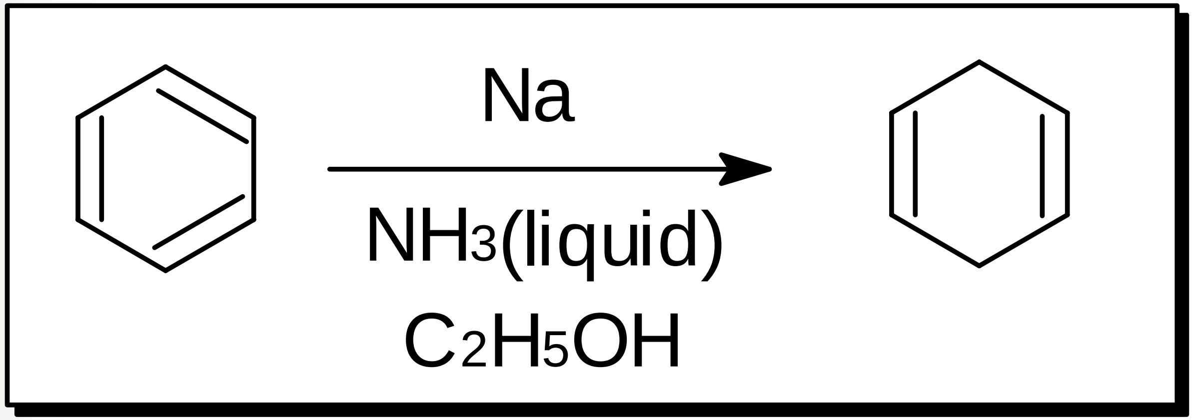
100%

反应机理：

$$Cl_2 \xrightarrow{hv} 2\ Cl\cdot$$

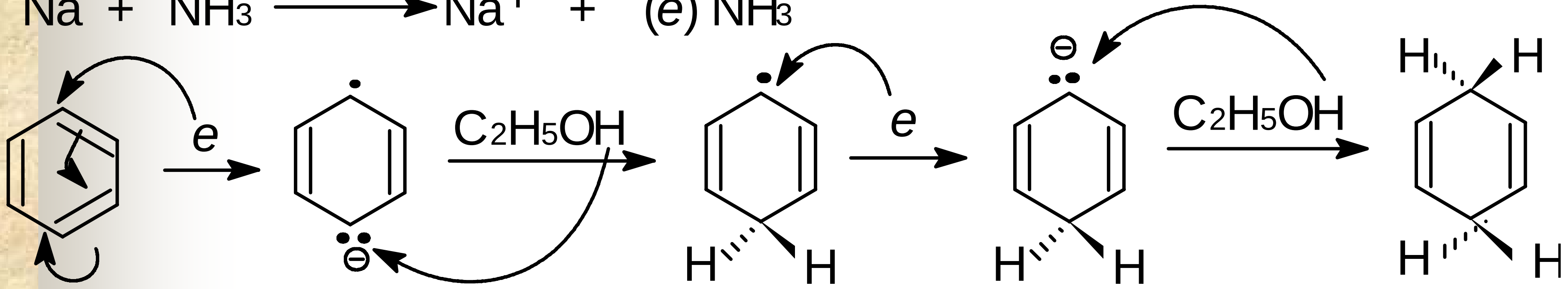


4. 苯环的还原反应——伯奇反应

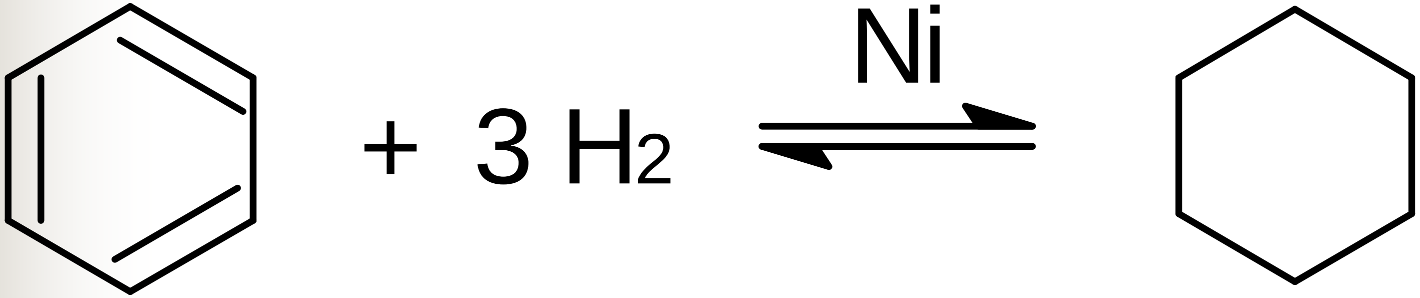


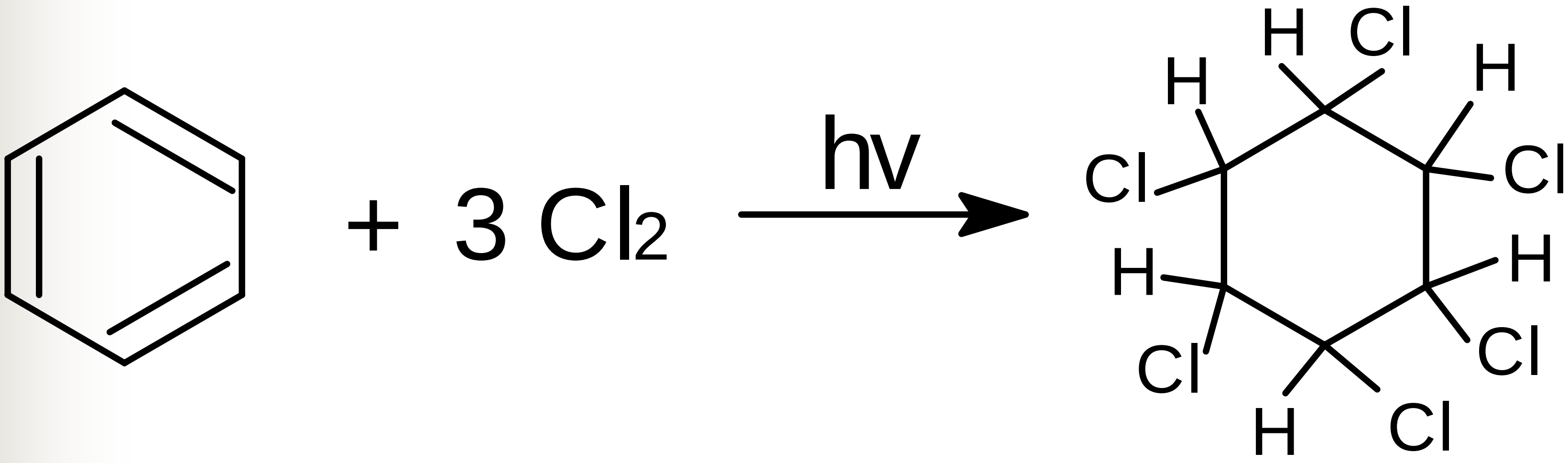
反应机理：

$$Na + NH_3 \longrightarrow Na^+ + (e)\,NH_3$$



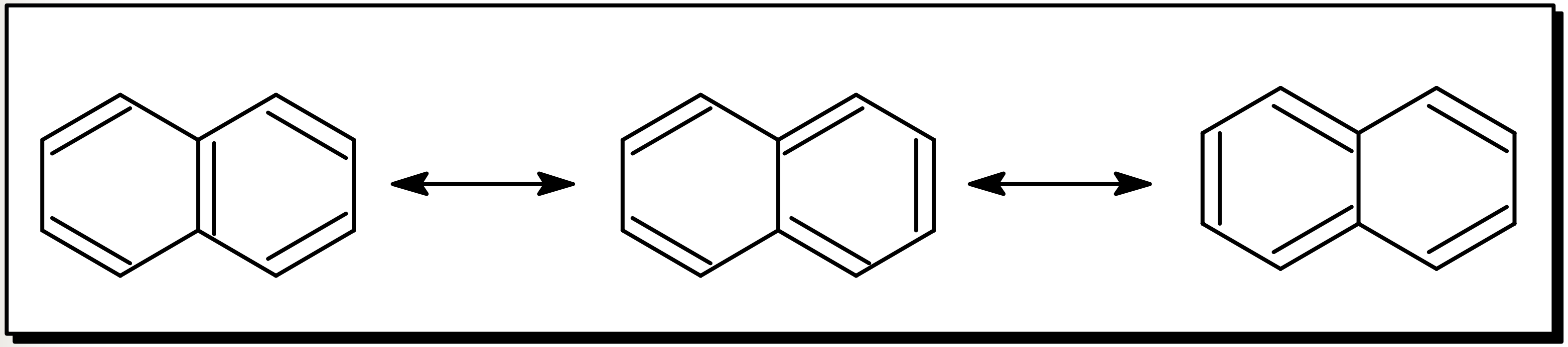
5. 苯环的加成反应





§7.7　萘的化学性质Ⅰ
——亲电取代

1.萘的结构



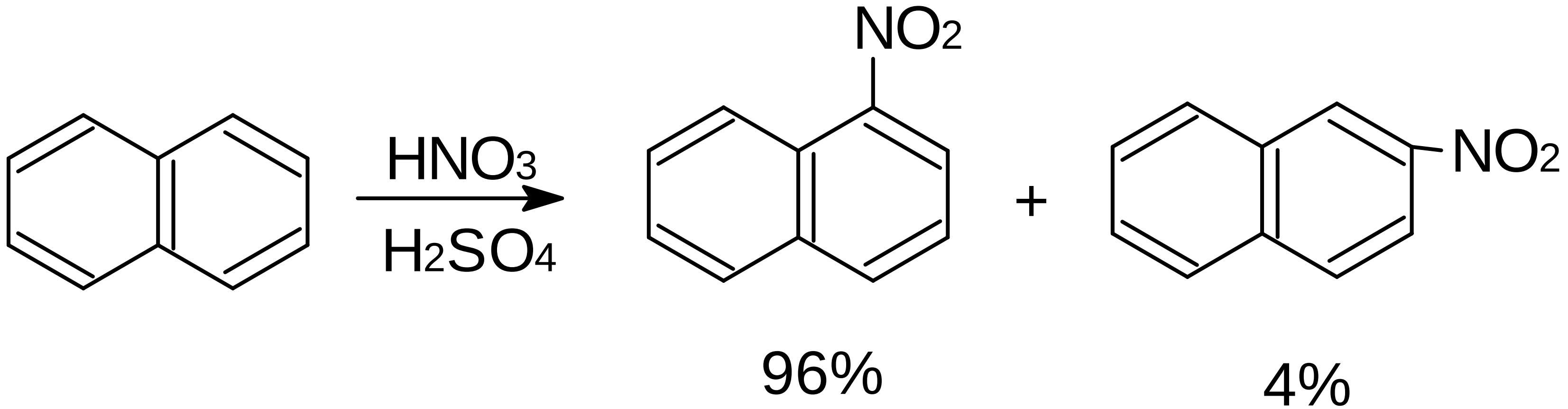
特点：a. 平面分子

b. 键长不平均化

Cα-Cβ两次双键,键长为0.136nm;

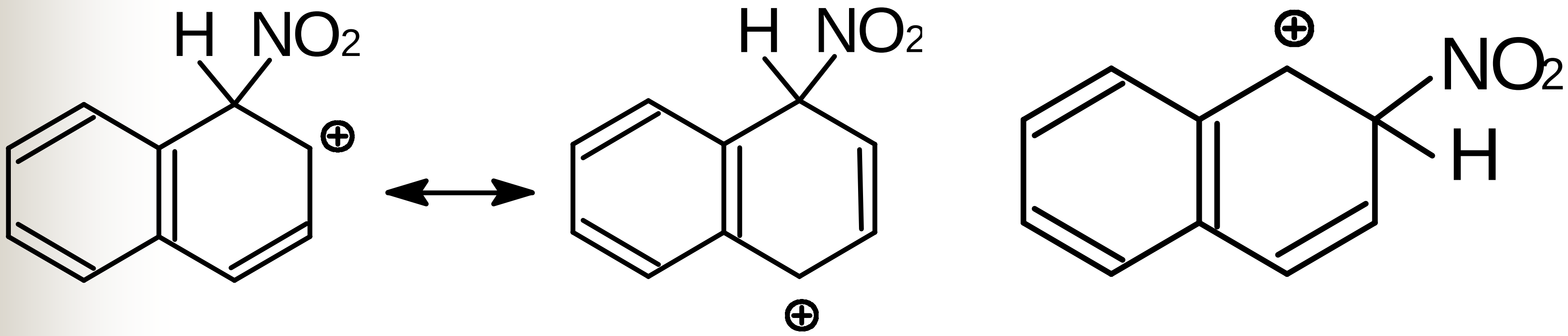
Cβ-Cβ一次双键,键长为0.140nm

2.硝化反应



反应机理：

亲电取代，取代α位和β位的中间体共振式不同

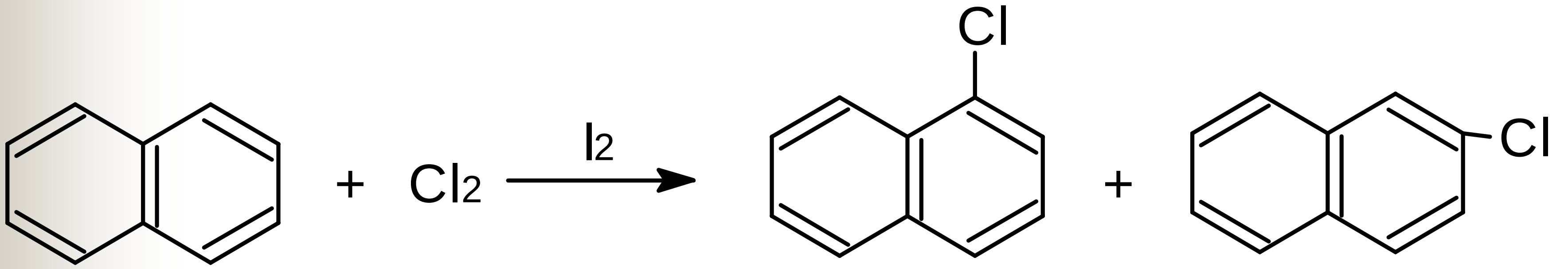


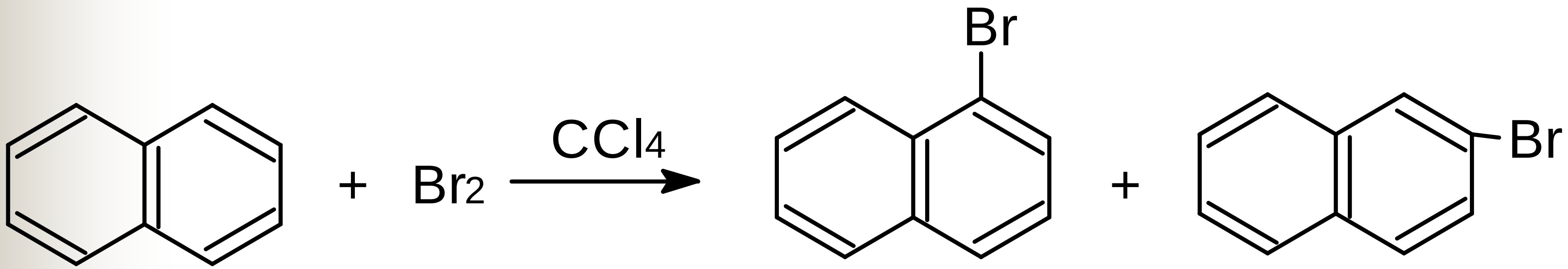
取代α位可以两次保持另一苯环不被破坏

取代β位只有一次保持另一苯环不被破坏

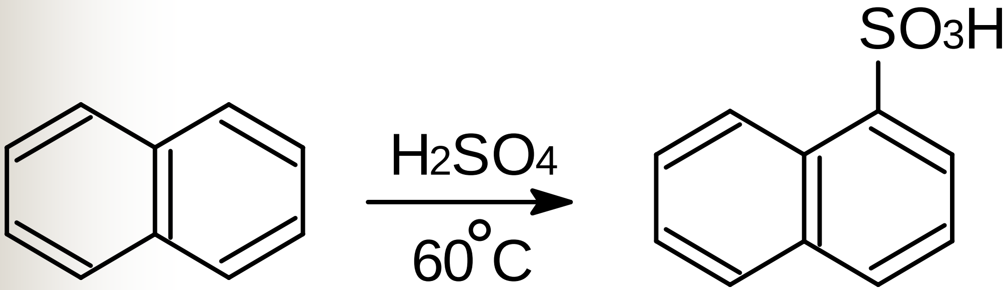
总结：进入α位更为有利。

3. 氯代反应

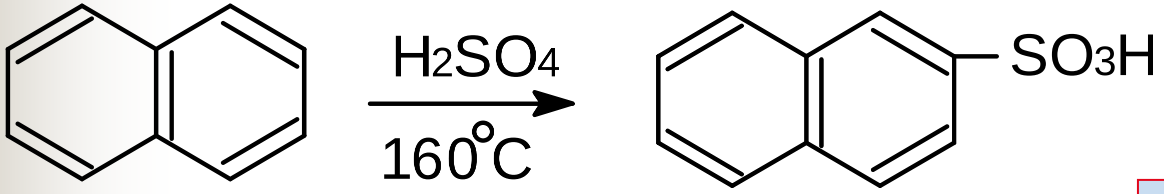




4.磺化反应

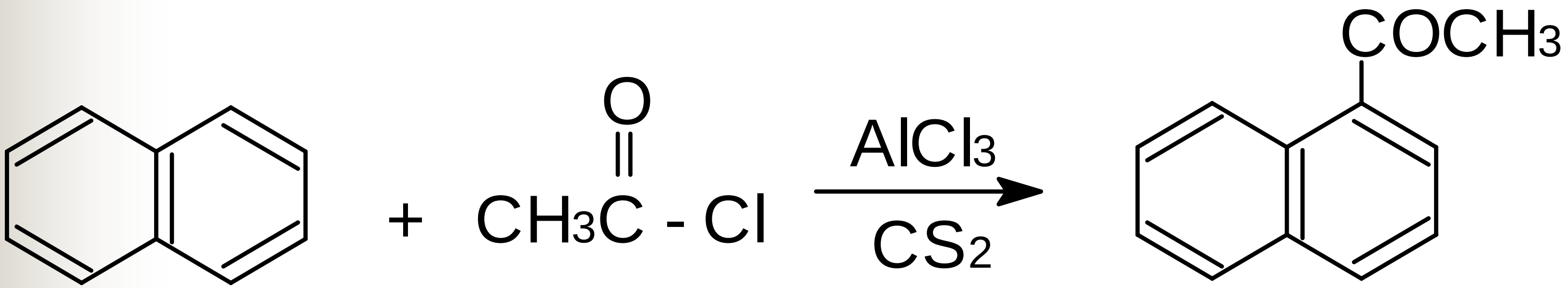


动力学控制

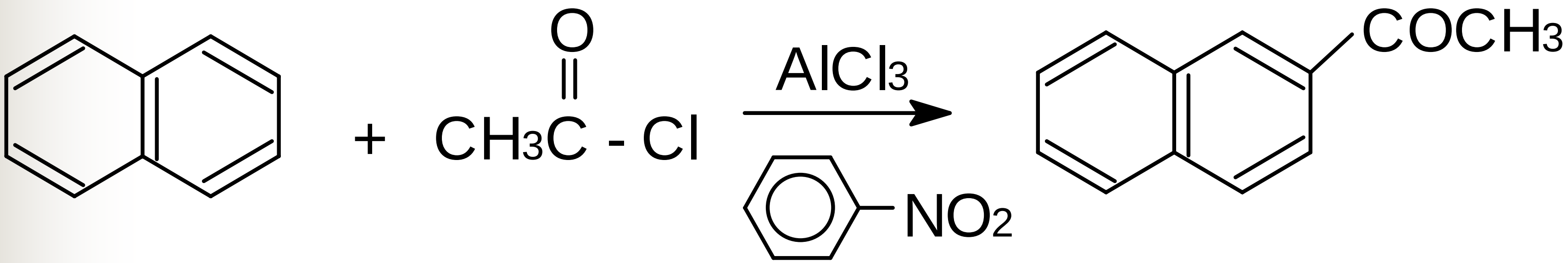


热力学控制

5.酰化反应

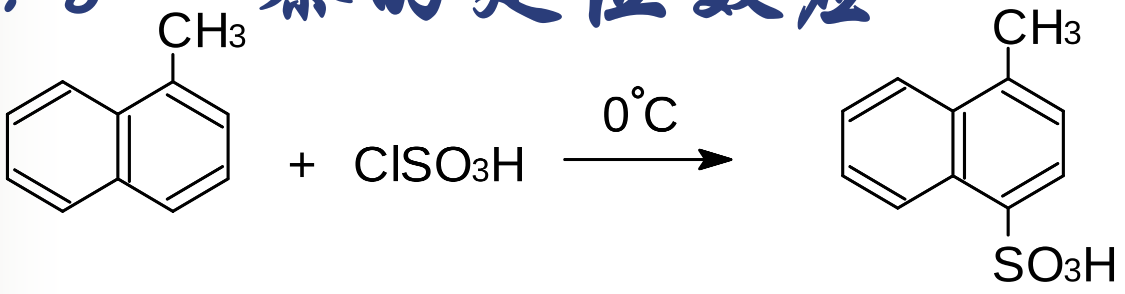


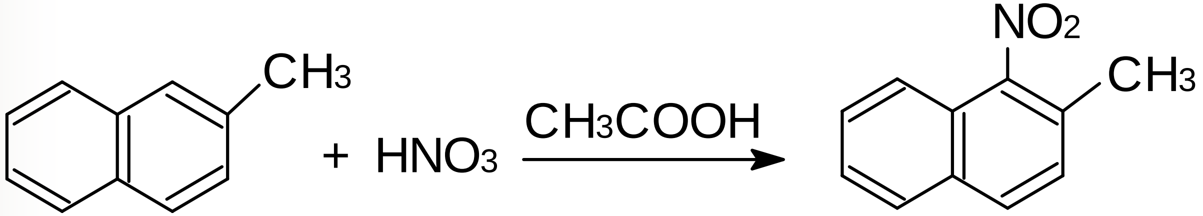
低沸点溶剂，动力学控制，进入α位

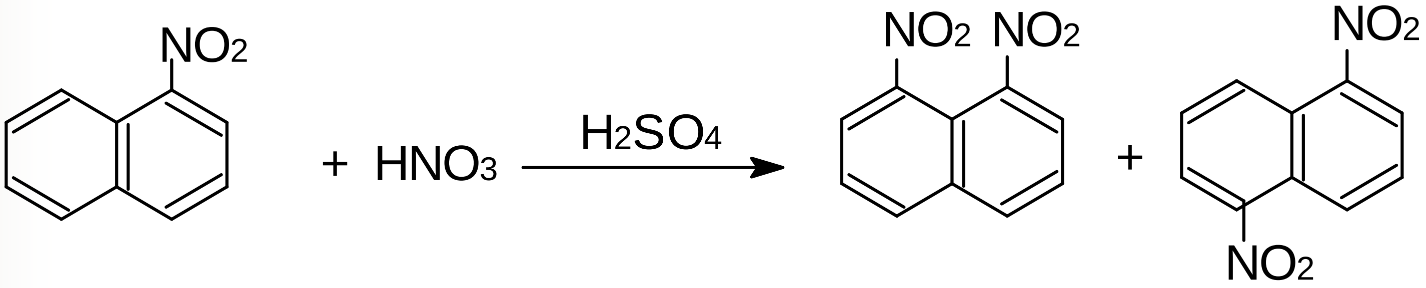


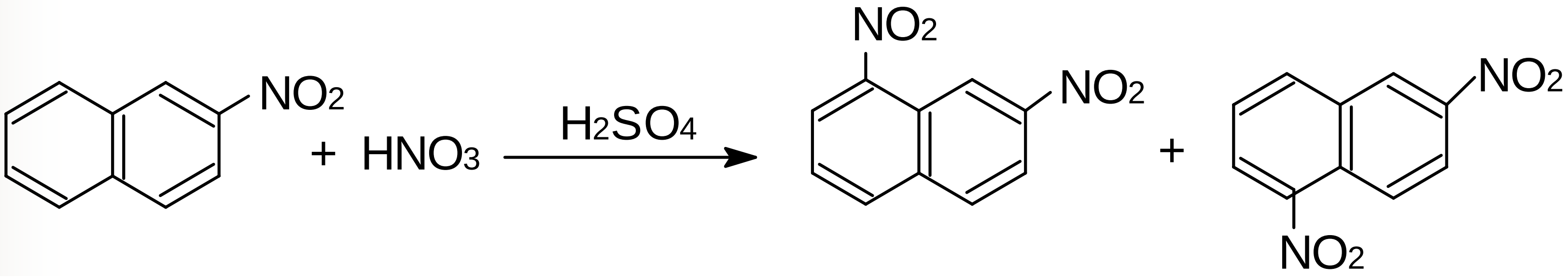
高沸点溶剂，热力学控制，进入β位

§ 7.8　萘的定位效应


CH3
+ ClSO3H
0°C
CH3
SO3H


CH3
+ HNO3
CH3COOH
NO2
CH3


NO2
+ HNO3
H2SO4
NO2 NO2
+
NO2
NO2


NO2
+ HNO3
H2SO4
NO2
NO2
+
NO2
NO2

总结：

- 第一类定位基引导下一个基团进入同环的α位

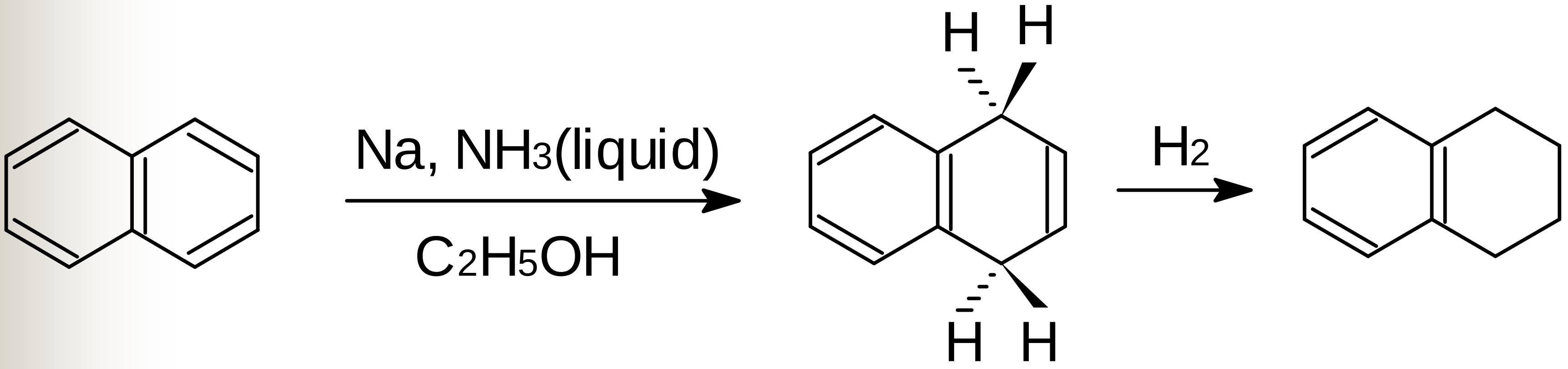
- 第二类定位基引导下一个基团进入异环的α位

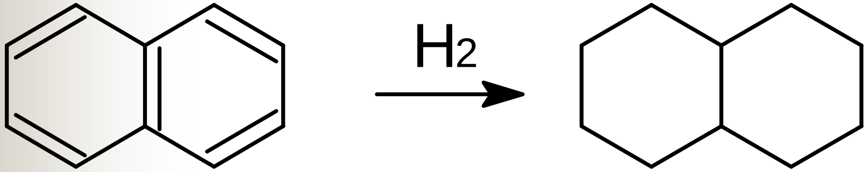
§7.9　萘的化学性质Ⅱ

——还原、氧化及加成

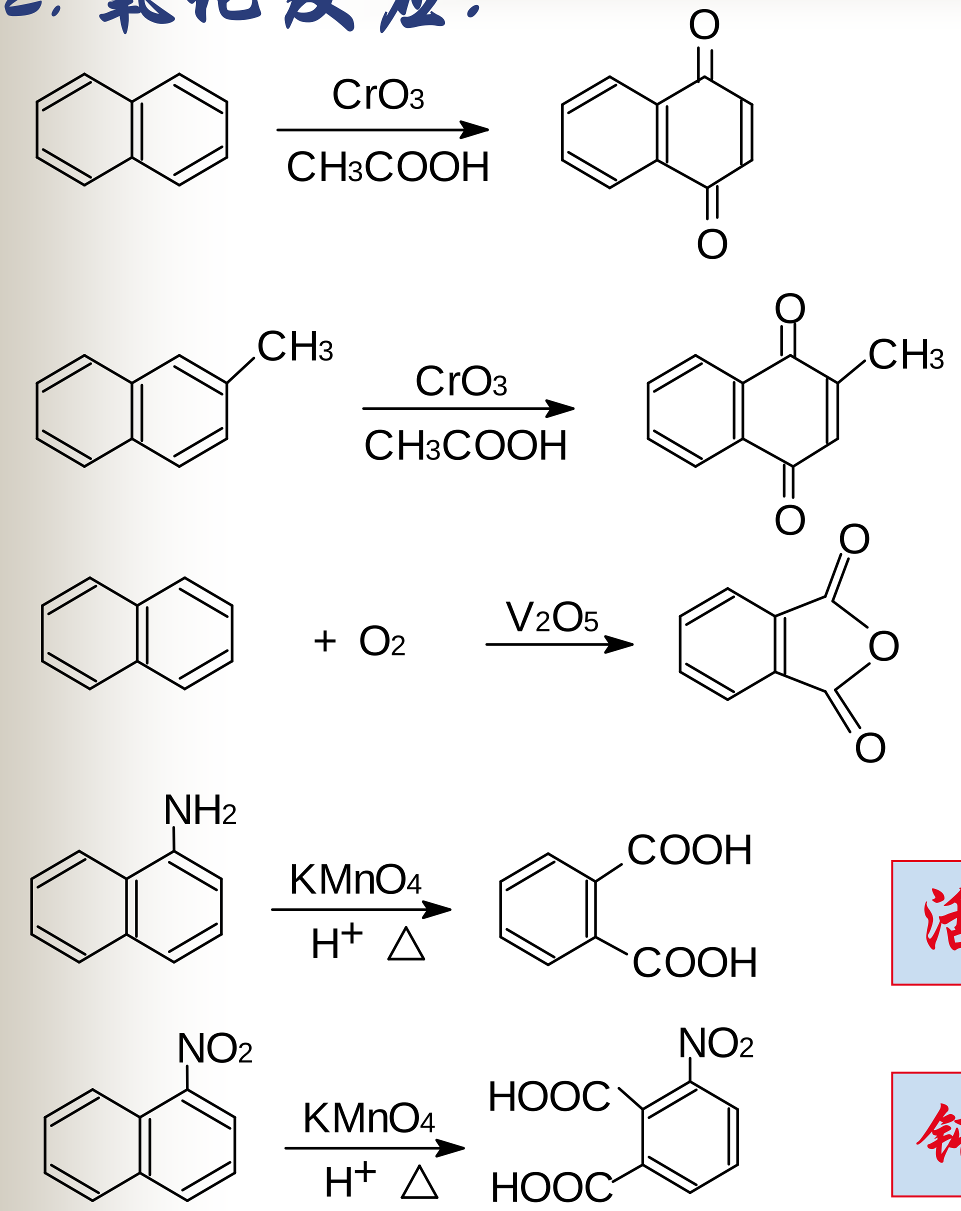
- 所有反应均比苯容易进行

1.还原反应





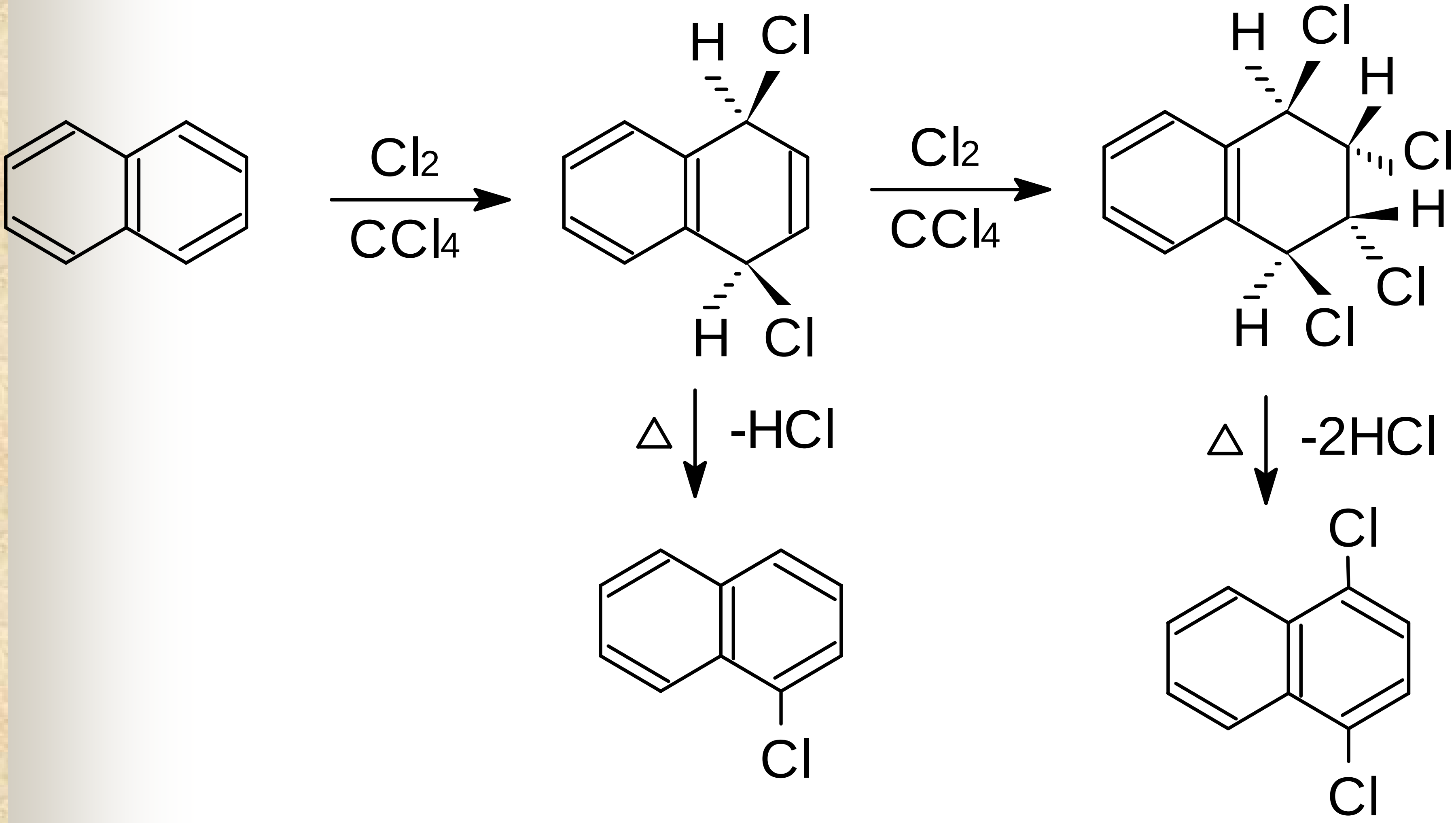
2. 氧化反应：



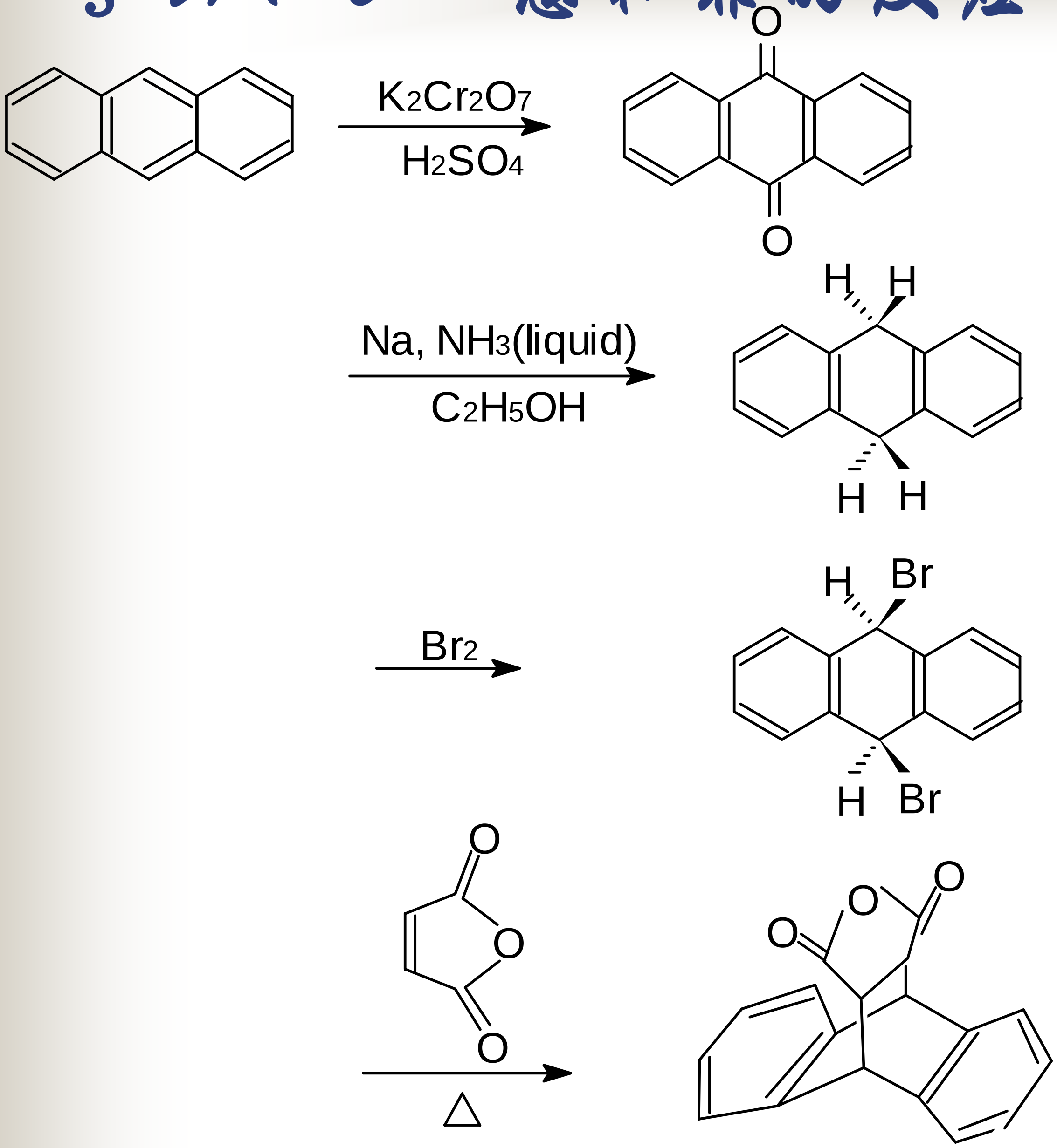
活化基团氧化同环

钝化基团氧化异环

3.加成反应



§7.10　蒽和菲的反应



总结：9，10位活泼，具有类似双键的性质。