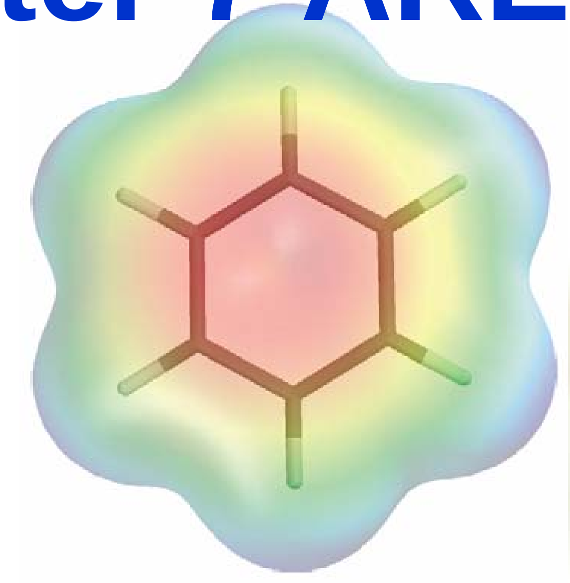
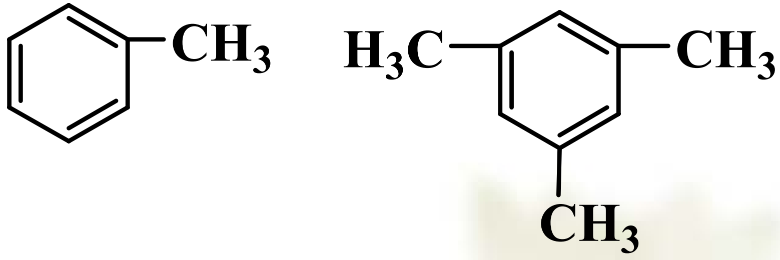
# Chapter 7 ARENES



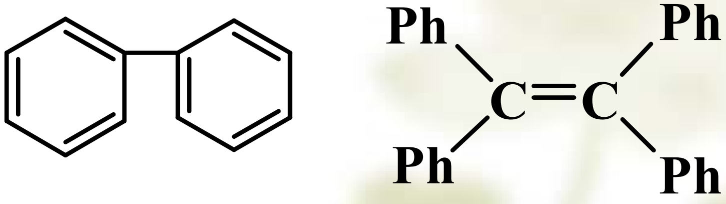
## Definition:

*Arenes* are hydrocarbons based on the benzene ring as a structural unit.

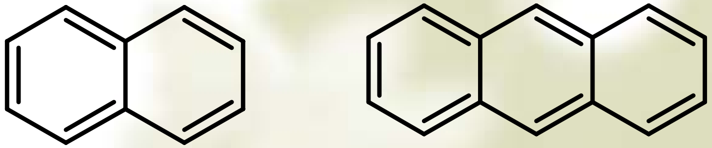
Arenes
- Monocyclic aromatics



- Polycyclic aromatics



- Condensed aromatics

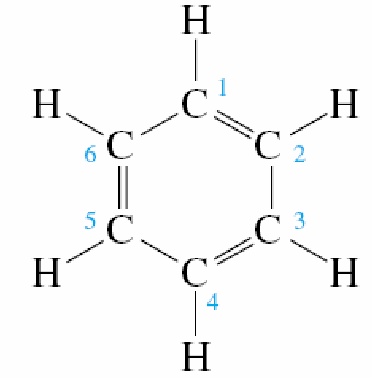


# 7.1 KEKULÉ AND THE STRUCTURE OF BENZENE

In 1825, Michael Faraday isolated a new hydrocarbon from illuminating gas, which he called “bicarburet of hydrogen.” Nine years later Eilhardt Mitscherlich of the University of Berlin prepared the same substance by heating benzoic acid with lime and found it to be a hydrocarbon having the empirical formula C*n*H*n*.

$$\underset{\text{Benzoic acid}}{C_6H_5CO_2H} + \underset{\text{Calcium oxide}}{CaO} \xrightarrow{\text{heat}} \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Calcium carbonate}}{CaCO_3}$$

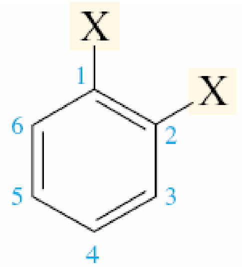
In 1866, only a few years after publishing his ideas concerning what we now recognize as the structural theory of organic chemistry, August Kekulé applied it to the structure of benzene.



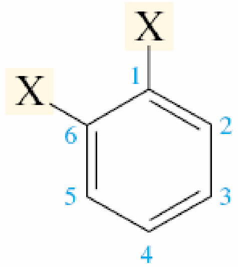
He based his reasoning on three premises:

- Benzene is $C_6H_6$.
- All the hydrogens of benzene are equivalent.
- The structural theory requires that there be four bonds to each carbon.

A flaw in Kekulé’s structure for benzene was soon discovered. Kekulé’s structure requires that 1,2- and 1,6-disubstitution patterns create different compounds (isomers).



1,2-Disubstituted derivative of benzene



1,6-Disubstituted derivative of benzene

Kekulé’s ideas about the structure of benzene left an important question unanswered. What is it about benzene that makes it behave so much differently from other unsaturated compounds?

**Benzene is *planar* and its carbon skeleton has the shape of a regular hexagon. There is no evidence that it has alternating single and double bonds. As shown in Figure 7.1, all the carbon–carbon bonds are the same length (140 pm) and the 120° bond angles correspond to perfect *sp*$^2$ hybridization. Interestingly, the 140-pm bond distances in benzene are exactly midway between the typical *sp*$^2$–*sp*$^2$ single-bond distance of 146 pm and the *sp*$^2$–*sp*$^2$ double-bond distance of 134 pm.**

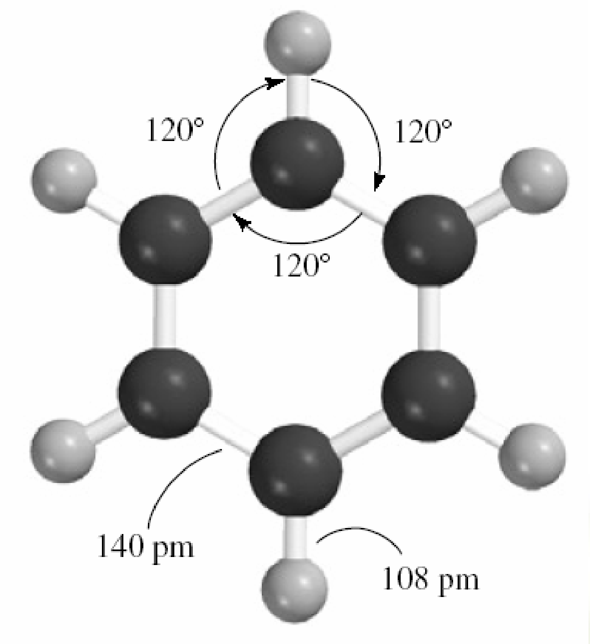


**FIGURE 7.1 Bond distances and bond angles of benzene.**

In addition to its three *sp*$^2$ hybrid orbitals, each carbon has a half-filled 2*p* orbital that can participate in  bonding.

Figure 7.2b shows the continuous system that encompasses all of the carbons that result from overlap of these 2*p* orbitals. The six electrons of benzene are delocalized over all six carbons.

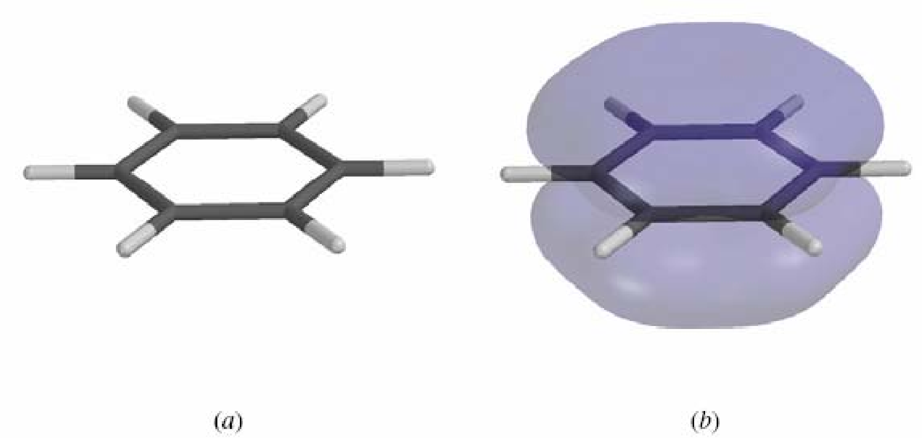
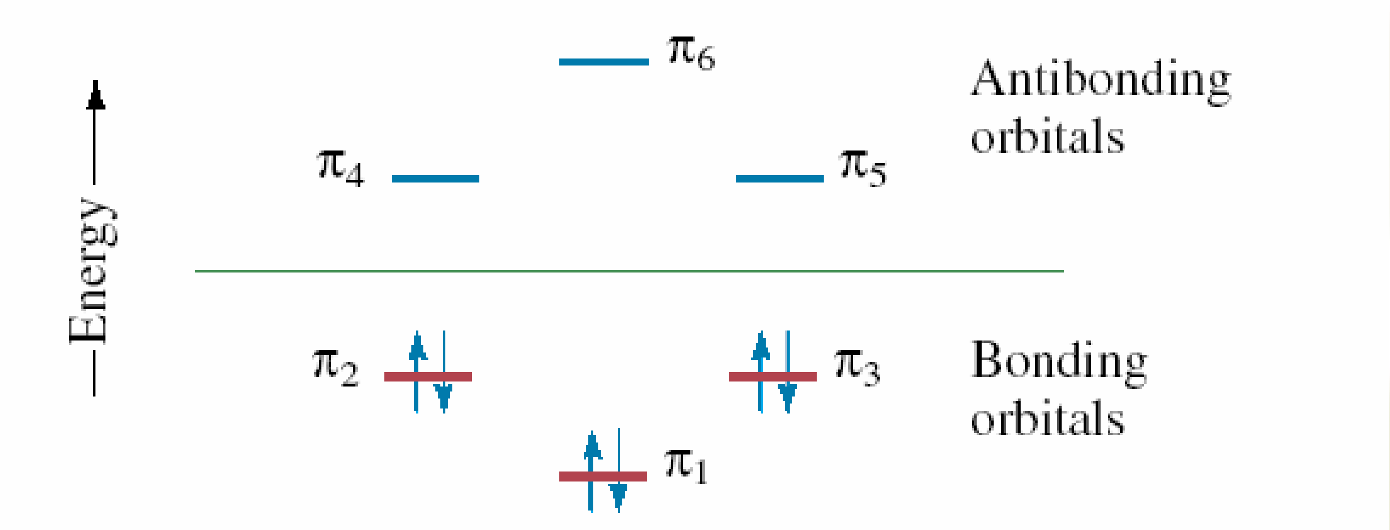
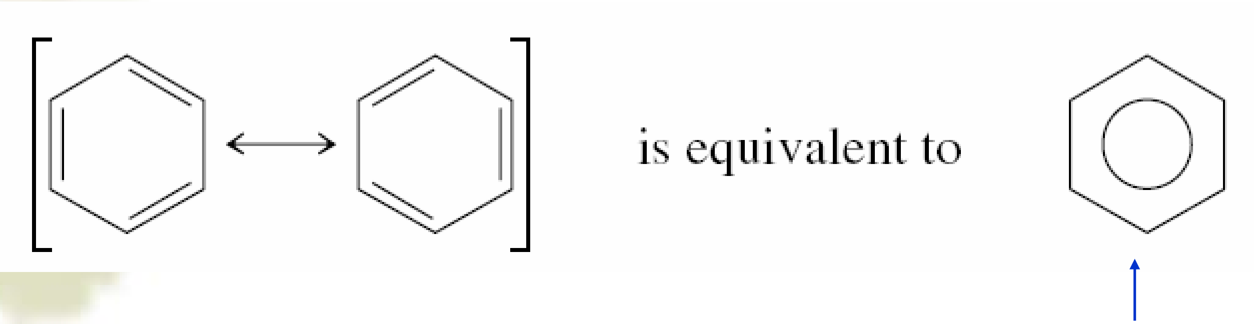


**Figure 7.2**

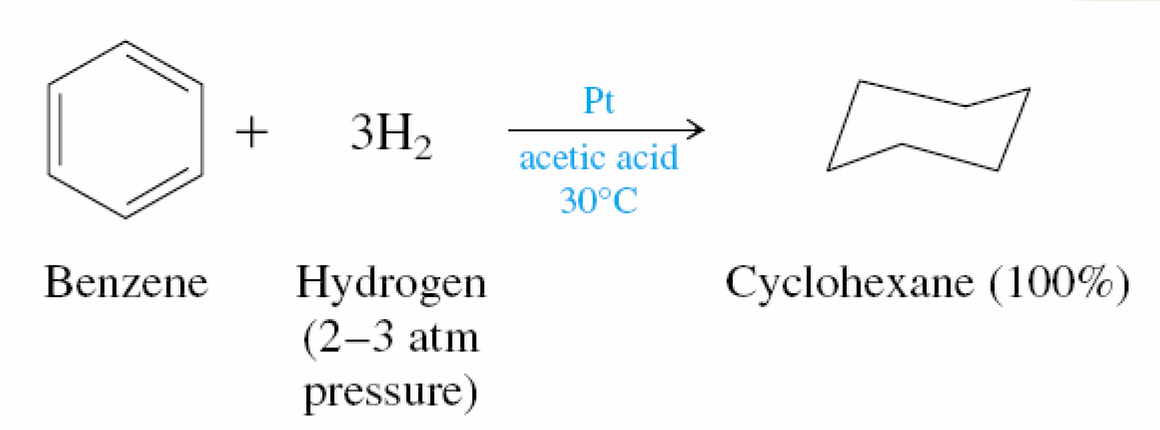
**A more rigorous molecular orbital analysis recognizes that overlap of the six 2*p* atomic orbitals of the ring carbons generates six molecular orbitals. These six molecular orbitals include three which are bonding and three which are antibonding.**





the circle-in-a-hexagon symbol

## THE STABILITY OF BENZENE



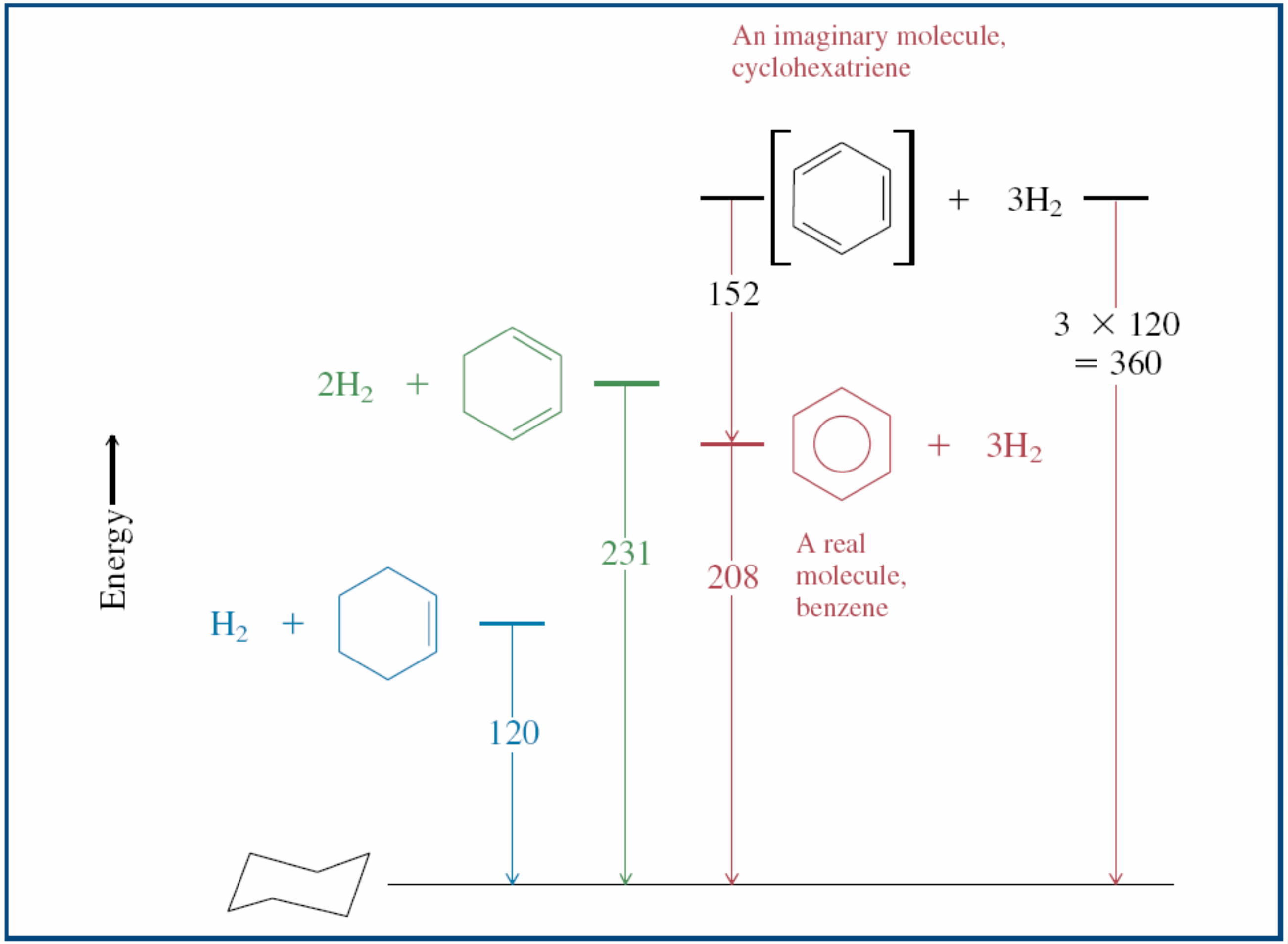


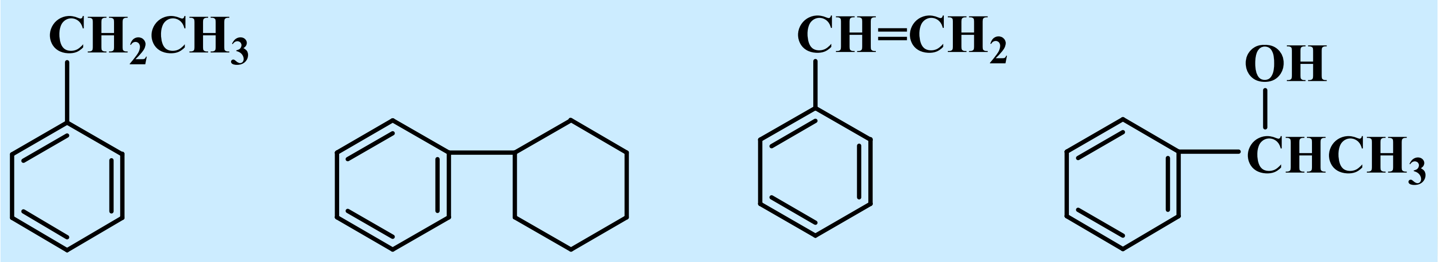
**FIGURE 7.3** **Heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, a hypothetical 1,3,5-cyclohexatriene, and benzene. All heats of hydrogenation are in kilojoules per mole.**

氢化热越小，体系内能越低，分子越稳定。

**150kJ/mol**的能量差正是由于苯环中存在共轭体系，π电子高度离域而造成苯特别稳定的结果。这叫共轭能或离域能。

# 7.2 SUBSTITUTED DERIVATIONS OF BENZENE AND THEIR NOMENCLATURE

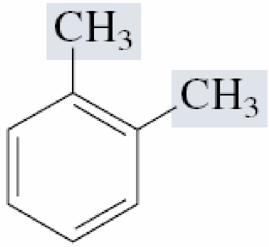
- 一取代芳烃没有异构体。

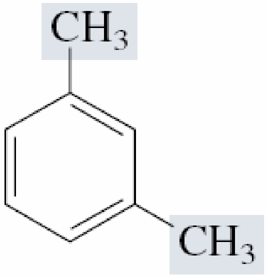


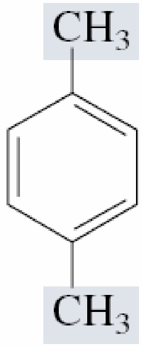
1-Ethylbenzene 1-Cyclohexylbenzene Styrene 1-Phenylethanol

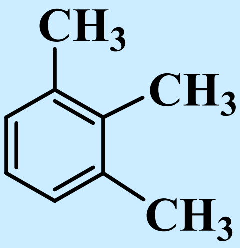
一般苯环作母体，取代基复杂或有不饱和键时，苯作取代基。

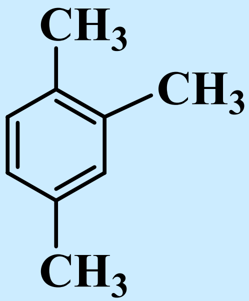
- 二、三...多取代芳烃才有异构化现象。

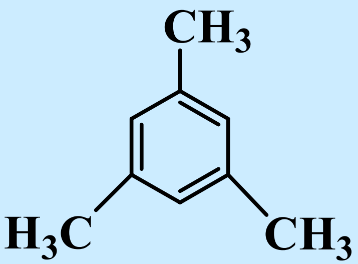

*o*-Xylene
(1,2-dimethylbenzene)


*m*-Xylene
(1,3-dimethylbenzene)


*p*-Xylene
(1,4-dimethylbenzene)

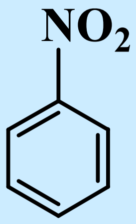

**1,2,3-Trimethylbenzene**


**1,2,4-Trimethylbenzene**

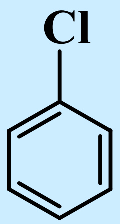

**1,3,5-Trimethylbenzene**

- 多元取代基的芳烃衍生物

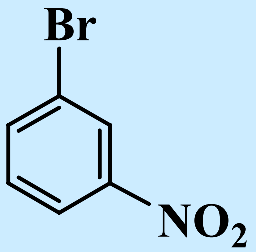
某些取代基如－$NO_2$，－NO，－X等通常只作取代基而不作母体。



1-Nitrobenzene

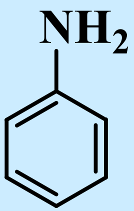


1-Chlorobenzene

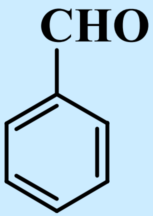


1-Bromo-3-nitrobenzene

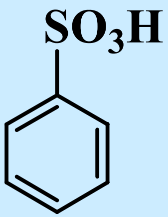
当取代基为－$NH_2$，－OH，－CHO，－COOH，－$SO_3H$等时，则把它们各看作一类化合物。



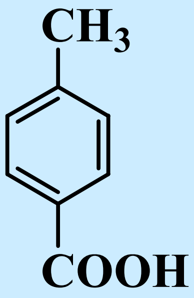
Aniline



Benzaldehyde

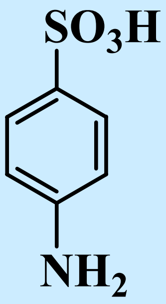


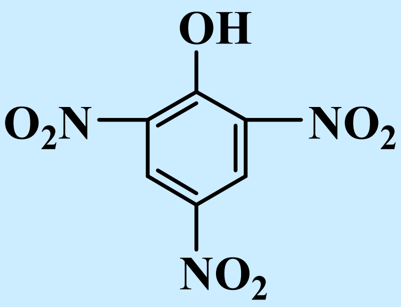
Benzenesulfonic acid

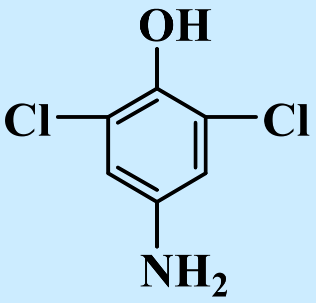


4-Methylbenzoic acid

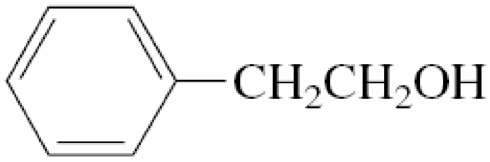
当环上有多种取代基时，选择母体的顺序见书P.152，排在后面的为母体。

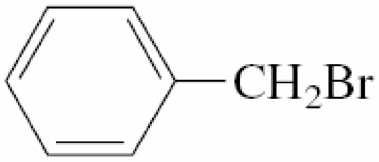

4-Aminobenzenesulfonic acid


Picric acid


4-Amino-2,6-dichlorophenol

**When the benzene ring is named as a substituent, the word "*phenyl*" stands for $C_6H_5-$. Similarly, an arene named as a substituent is called an *aryl* group. A *benzyl* group is $C_6H_5CH_2-$.**


2-Phenylethanol


Benzyl bromide

# 7.3 THE PROPERTIES OF MONOCYCLIC AROMATIC HYDROCARBONS

## 7.3.1 Physical Properties of Arenes

**In general, arenes resemble other hydrocarbons in their physical properties.**

***Nonpolar;***

***Insoluble in water;***

***Less dense than water.***

**Toluene has replaced benzene as an inexpensive *organic solvent*, which has not been determined to be carcinogenic in the cell systems at the dose levels that benzene is.**

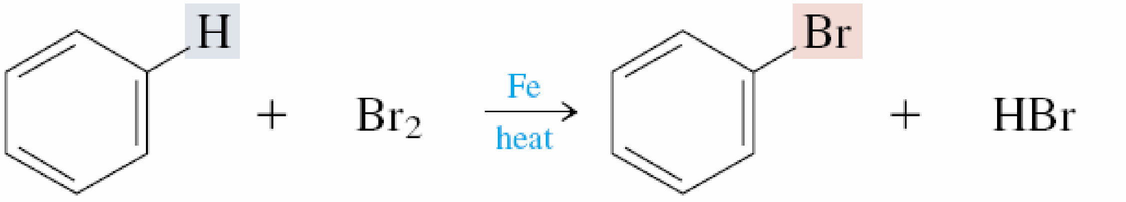
## 7.3.2 Chemical Properties of Arenes

**The classification of hydrocarbons as aliphatic or aromatic took place in the 1860s when it was already apparent that there was something special about benzene, toluene, and their derivatives. Their molecular formulas (benzene is $C_6H_6$, toluene is $C_7H_8$) indicate that, like alkenes and alkynes, they are unsaturated and should undergo addition reactions.**

**Under conditions in which bromine, for example, reacts rapidly with alkenes and alkynes, however, benzene proved to be inert. Benzene does react with $Br_2$ in the presence of iron(III) bromide as a catalyst, but even then addition isn't observed.** Substitution occurs instead!

## 7.3.2.1 Halogenation of Benzene

**According to the usual procedure for preparing bromobenzene, bromine is added to benzene in the presence of metallic iron (customarily a few carpet tacks) and the reaction mixture is heated.**



Bromine, although it adds rapidly to alkenes, is too weak an electrophile to react at an appreciable rate with benzene. A catalyst that increases the electrophilic properties of bromine must be present. Somehow carpet tacks can do this.

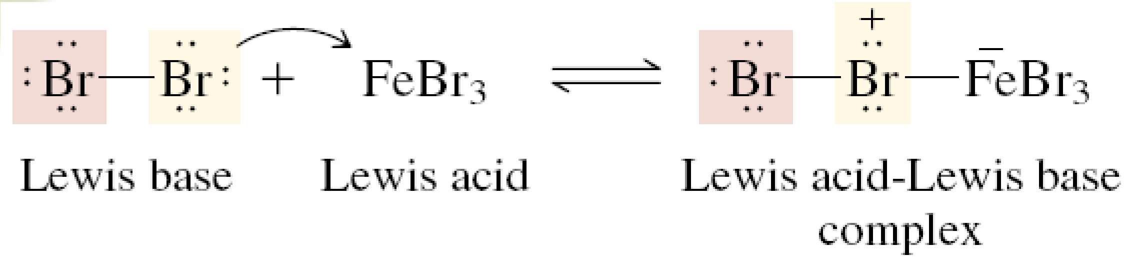
How?

**Mechanism:**

The active catalyst is not iron itself but iron(III) bromide, formed by reaction of iron and bromine.

$$\underset{\text{Iron}}{2\mathrm{Fe}} + \underset{\text{Bromine}}{3\mathrm{Br}_2} \longrightarrow \underset{\text{Iron(III) bromide}}{2\mathrm{FeBr}_3}$$

**Iron(III) bromide is a weak Lewis acid. It combines with bromine to form a Lewis acid-Lewis base complex.**



**Complexation of bromine with iron(III) bromide makes bromine *more electrophilic*.**

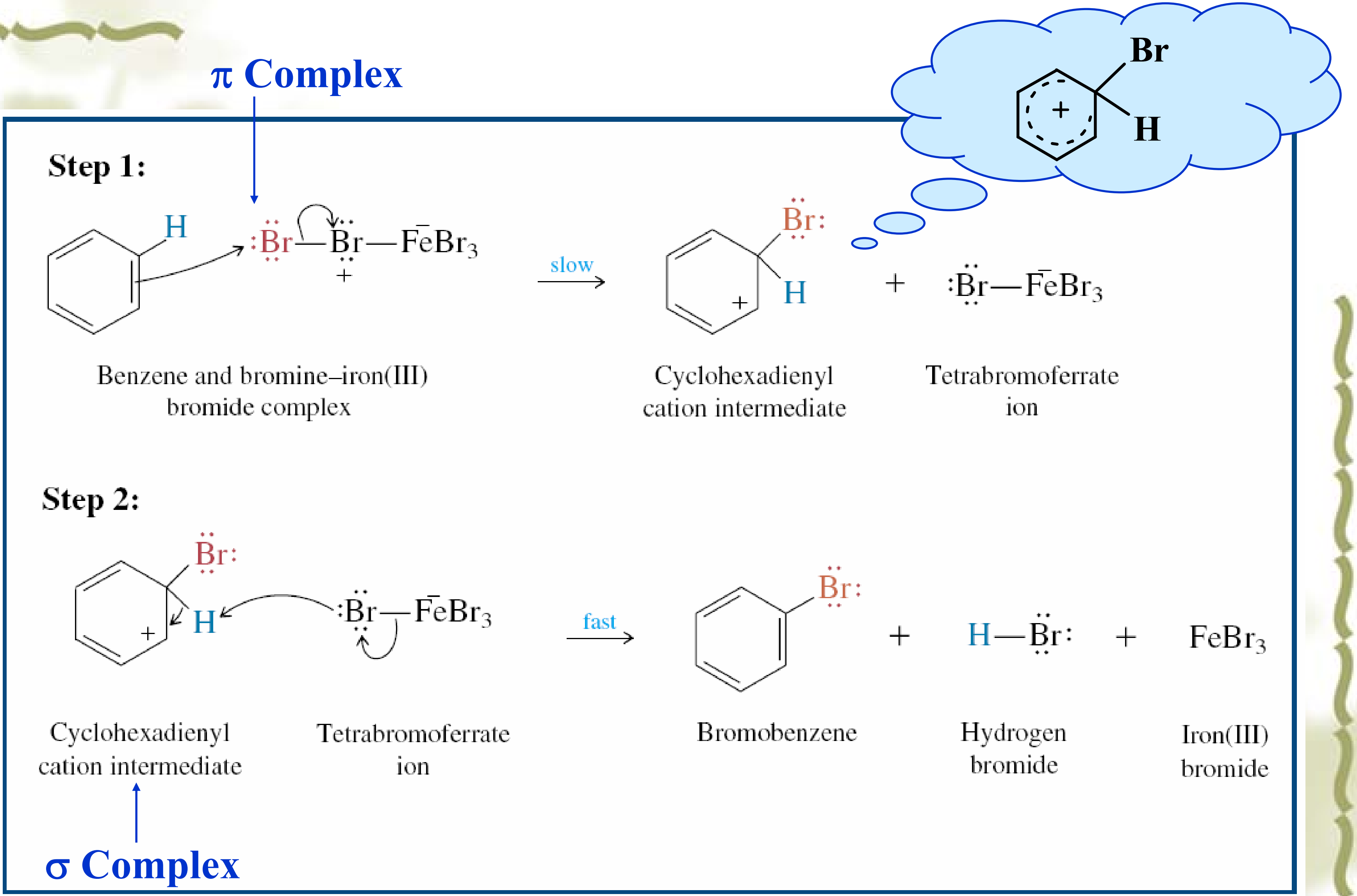
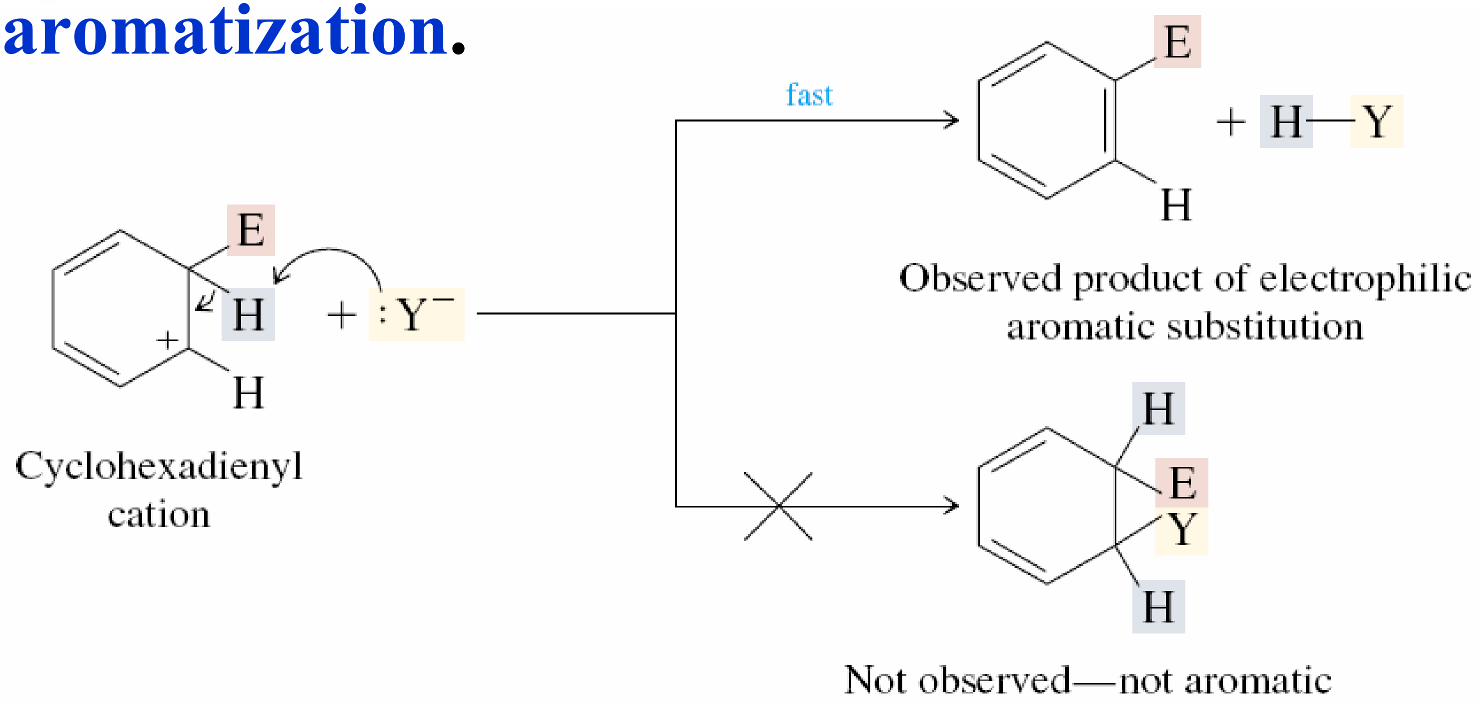


**FIGURE 7.4** **The mechanism of bromination of benzene.**

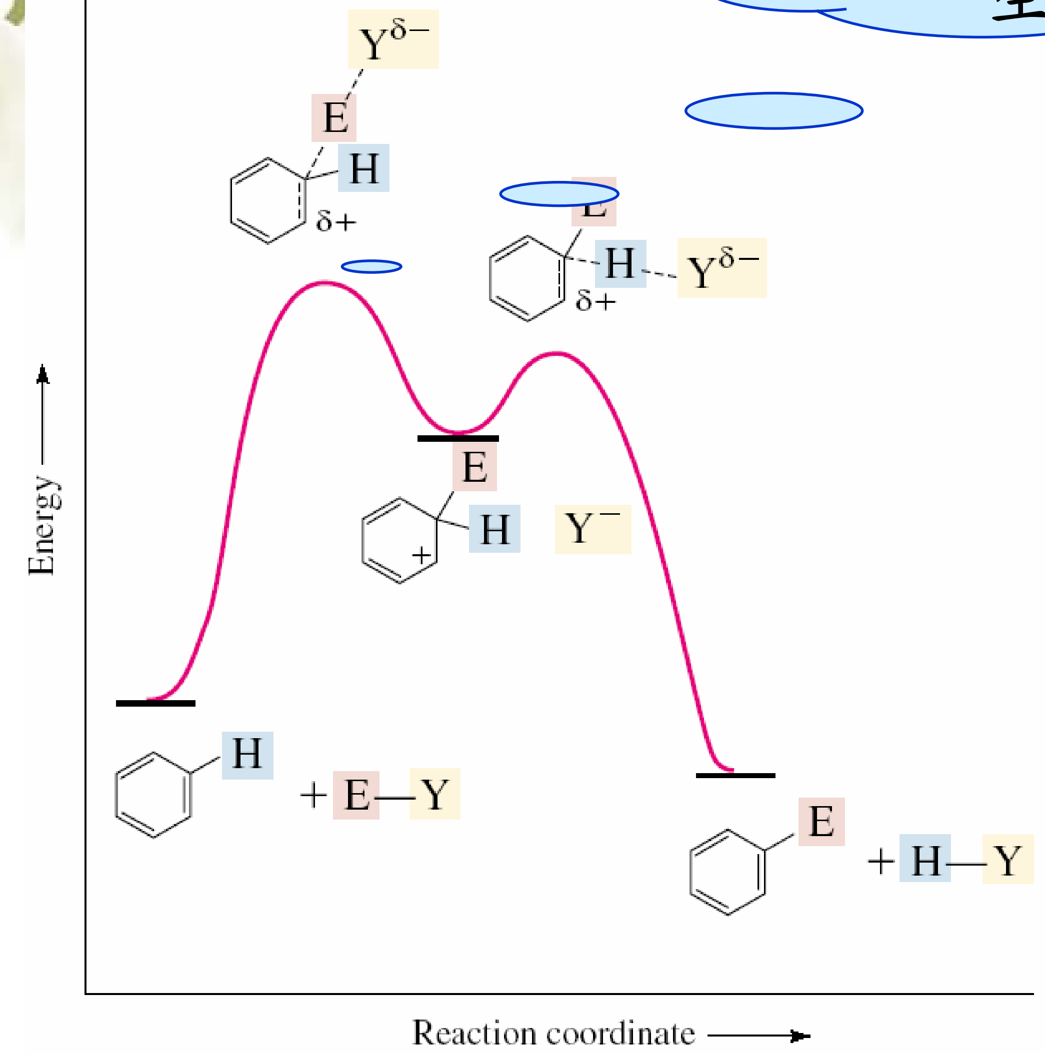
Addition and substitution products arise by alternative reaction paths of a cyclohexadienyl cation. Substitution occurs preferentially because there is a substantial driving force favoring rearomatization.



Cyclohexadienyl cation

Observed product of electrophilic aromatic substitution

Not observed—not aromatic



决速步骤：由π络合物
生成σ络合物

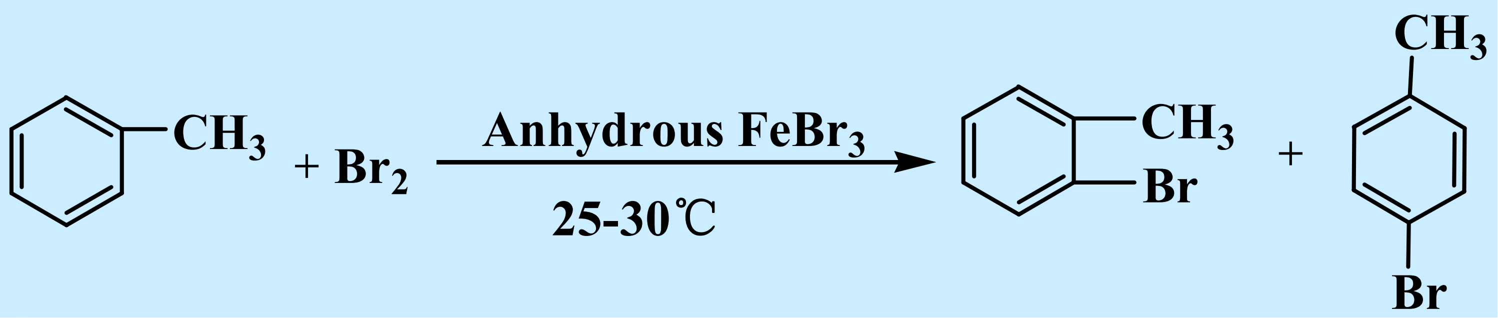
In order for electrophilic aromatic substitution reactions to overcome the high activation energy that characterizes the first step, the electrophile must be ***a fairly reactive one***. Many electrophilic reagents that react rapidly with alkenes do not react at all with benzene.

***Chlorination*** **is carried out in a manner similar to bromination and provides a ready route to chlorobenzene and related aryl chlorides.**

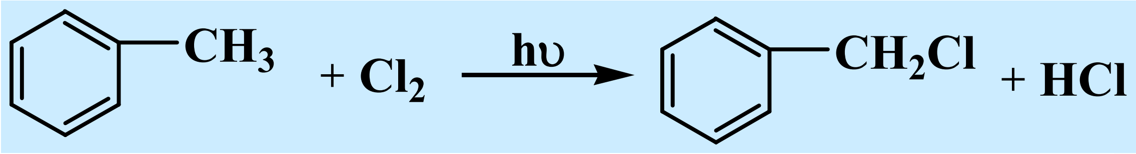
***Fluorination and iodination*** **of benzene and other arenes are rarely performed. Fluorine is so reactive that its reaction with benzene is difficult to control. Iodination is very slow and has an unfavorable equilibrium constant.**

**Syntheses of aryl fluorides and aryl iodides are normally carried out by way of functional group transformations of arylamines.**

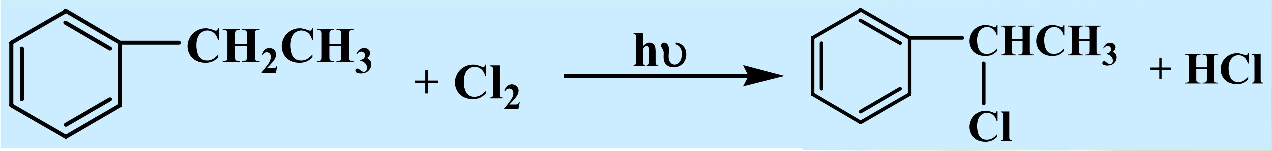
# Halogenation of Alkyl benzenes:



**Conclusion 1:** 烷基苯比苯容易发生亲电取代。



**Problem:**



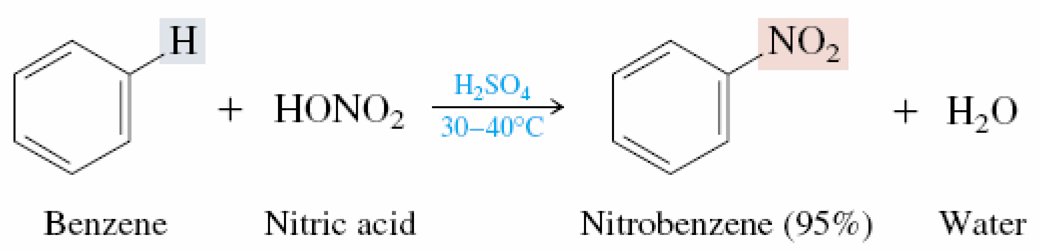
## Conclusion 2:

离子型取代历程

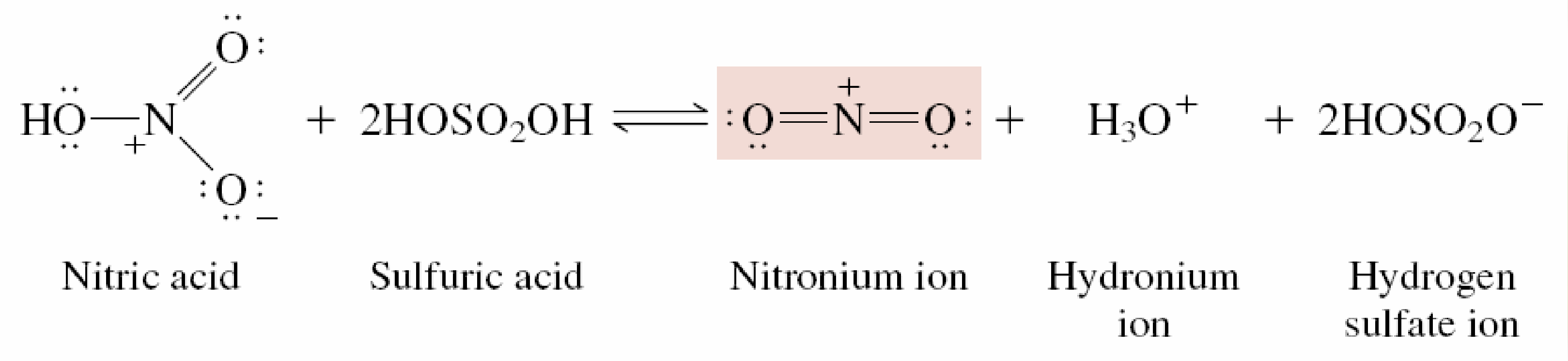
$$\text{烷基苯} + Cl_2 \begin{cases} \xrightarrow{\text{Fe}} \text{苯环取代产物} \\ \xrightarrow{\text{光照}} \text{侧链取代产物} \end{cases}$$

游离基取代历程

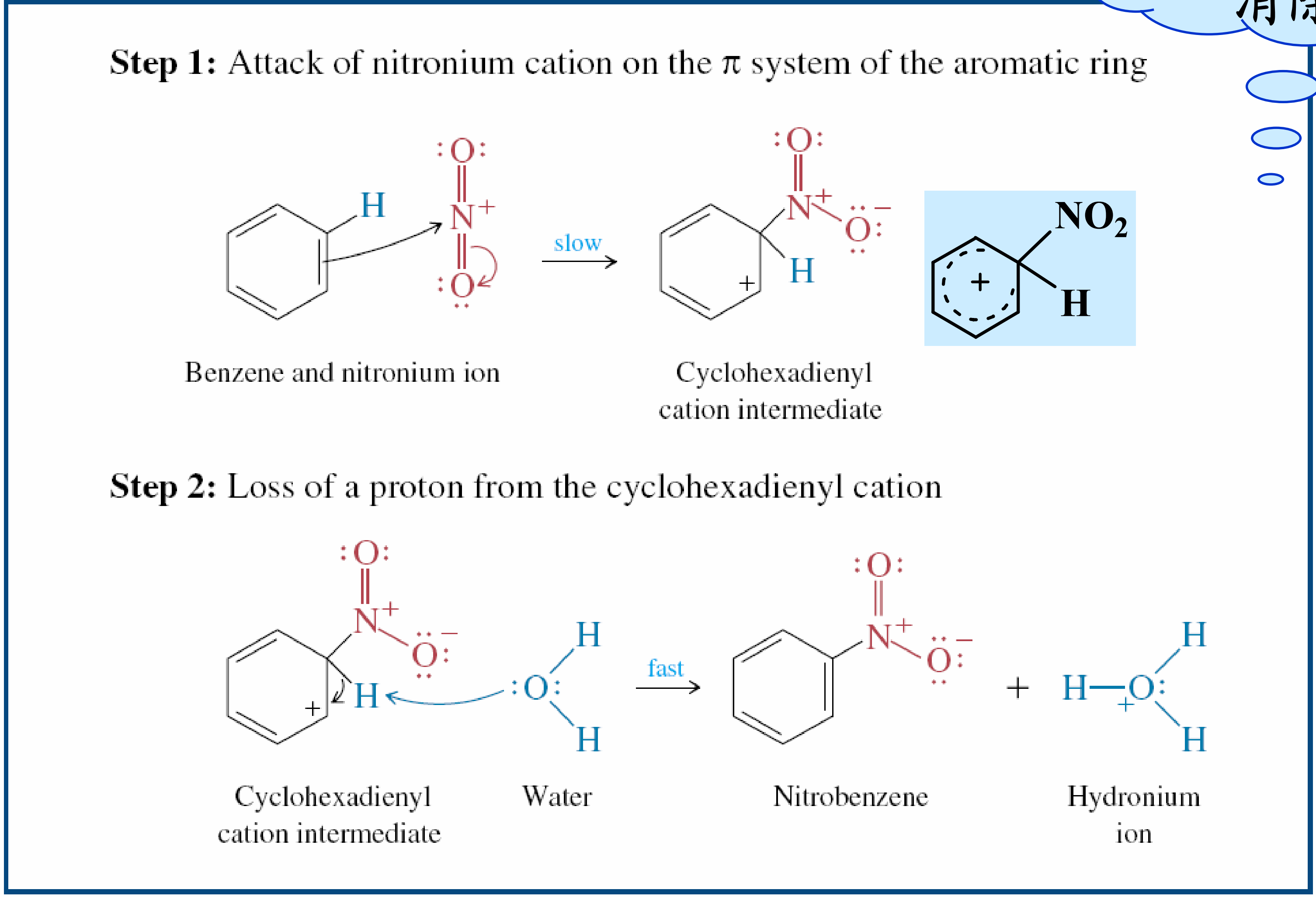
# 7.3.2.2 Nitration of Benzene



**The electrophile ($E^+$) that reacts with benzene is *nitronium ion* ($^+NO_2$).**



亲电加成-消除

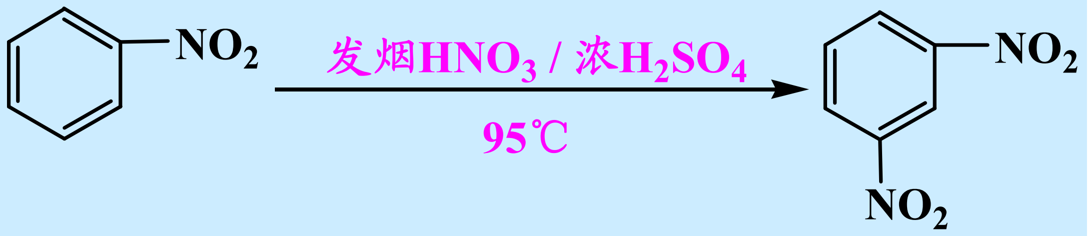


**Step 1:** Attack of nitronium cation on the π system of the aromatic ring

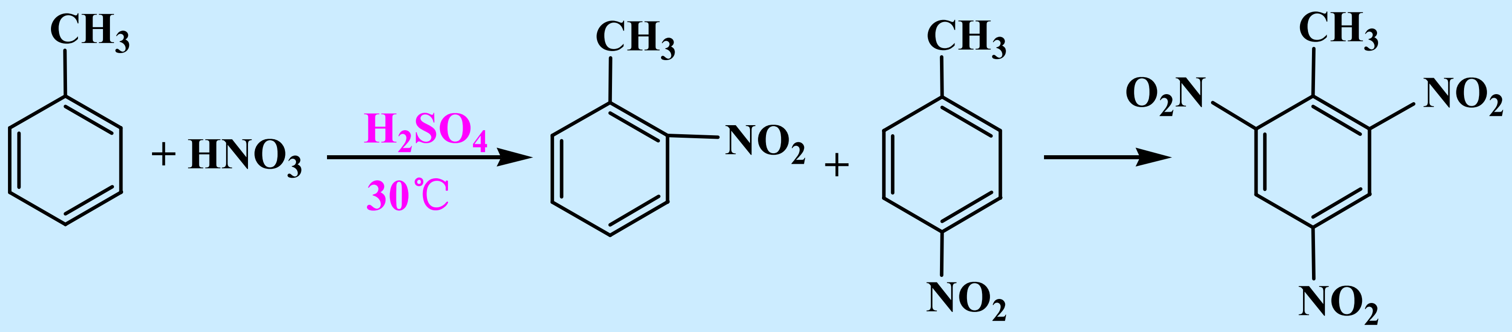
**Step 2:** Loss of a proton from the cyclohexadienyl cation

**FIGURE 7.5** **The mechanism of nitration of benzene.**

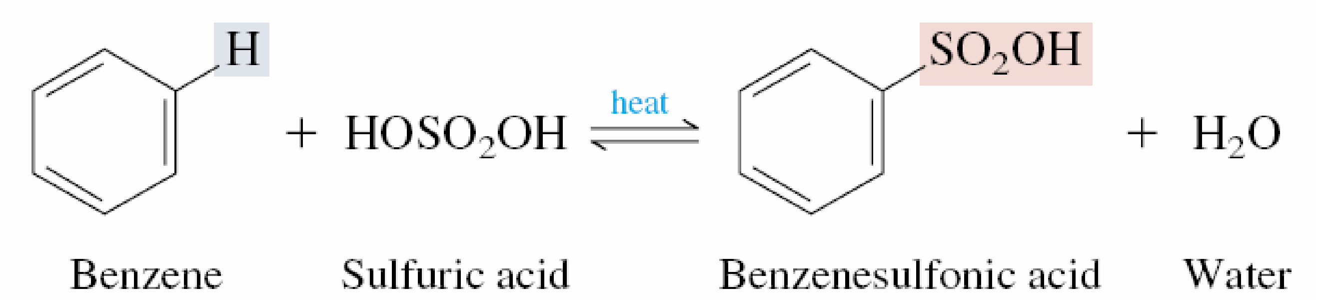
反应温度和酸的用量对硝化程度的影响很大。在过量混酸的存在下，苯可以硝化生成间二硝基苯。



硝基苯的硝化比苯困难，酸的浓度大，反应温度高，反应速度也慢得多。但如果是烷基苯，则硝化速度比苯快，甚至可以三硝化。

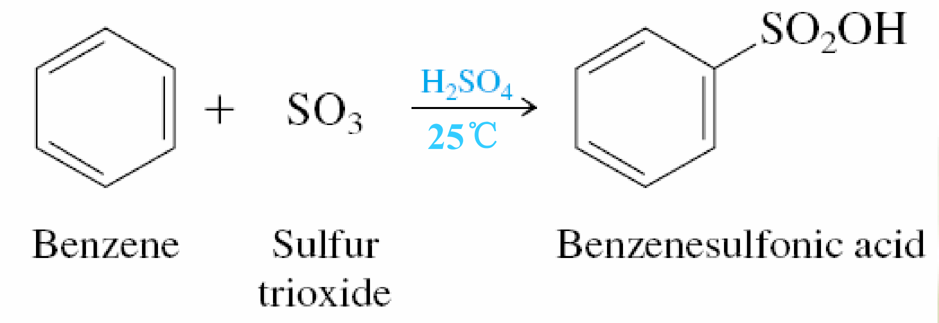


# 7.3.2.3 Sulfonation of Benzene



**The reaction of benzene with sulfuric acid to produce benzenesulfonic acid, is *reversible* but can be driven to completion by several techniques.**

When a solution of sulfur trioxide in sulfuric acid is used as the sulfonating agent, the rate of sulfonation is much faster and the equilibrium is displaced entirely to the side of products, according to the equation as follows.

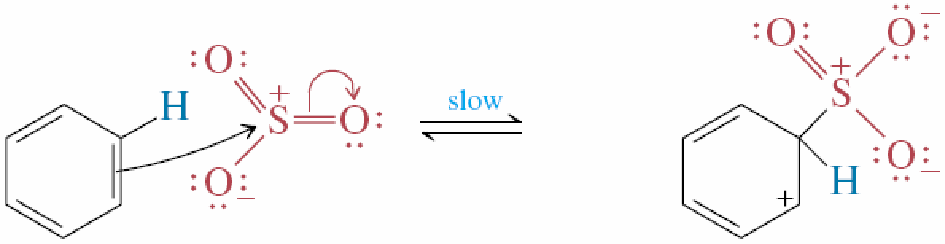


工业上常用的104.5% 的发烟硫酸(fuming sulfuric acid)中$SO_3$的含量是20 %。

**Among the variety of electrophilic species present in concentrated sulfuric acid, sulfur trioxide is probably the actual electrophile in aromatic sulfonation.**

## Mechanism:

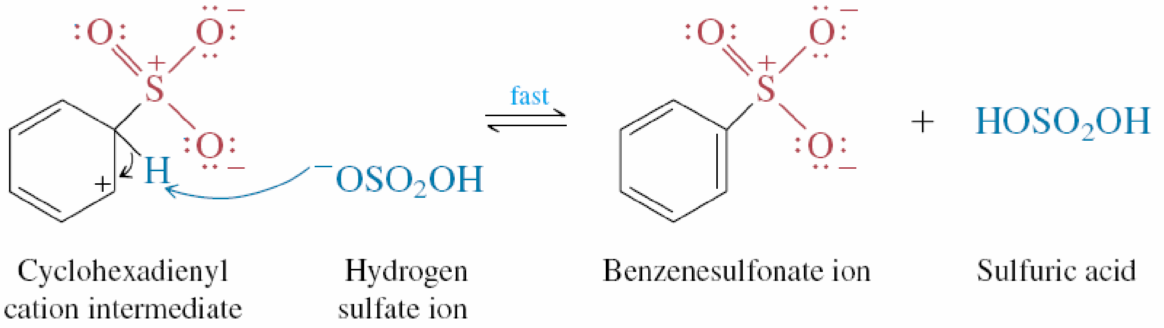
**Step 1:** Sulfur trioxide attacks benzene in the rate-determining step



Benzene and sulfur trioxide

Cyclohexadienyl cation intermediate

**Step 2:** A proton is lost from the $sp^3$ hybridized carbon of the intermediate to restore the aromaticity of the ring. The species shown that abstracts the proton is a hydrogen sulfate ion formed by ionization of sulfuric acid.



**Step 3:** A rapid proton transfer from the oxygen of sulfuric acid to the oxygen of benzenesulfonate completes the process.

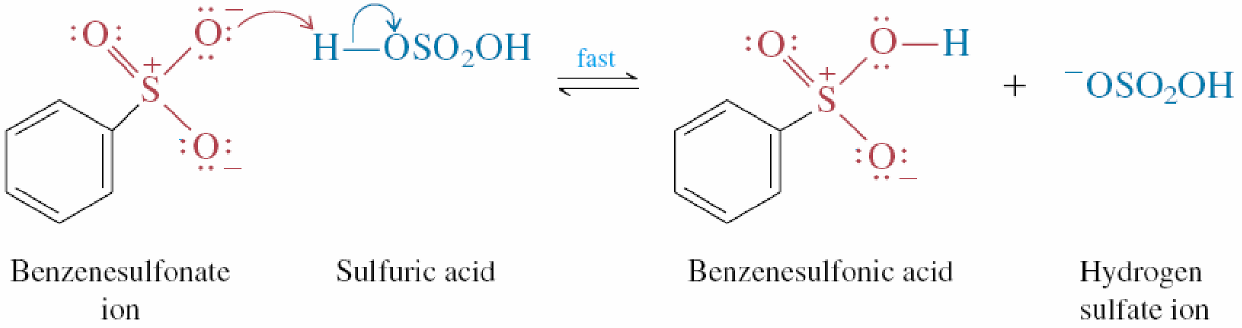
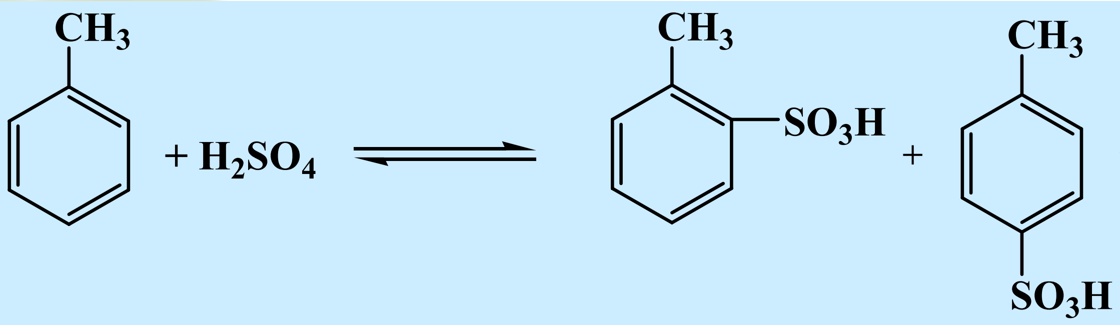


**FIGURE 7.5** **The mechanism of sulfonation of benzene.**

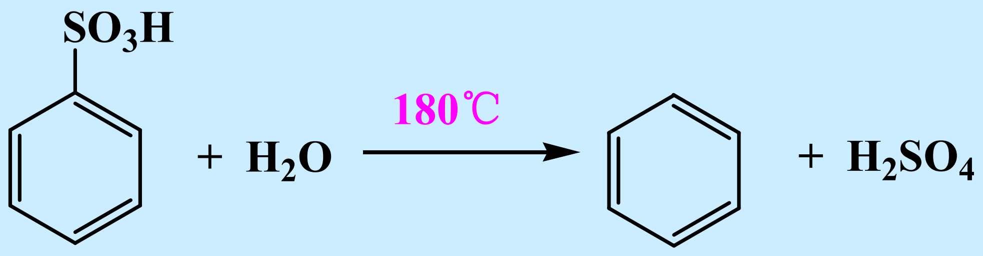
烷基苯的磺化比苯容易进行，用浓硫酸在常温下即可完成甲苯磺化。



高温时的主产物

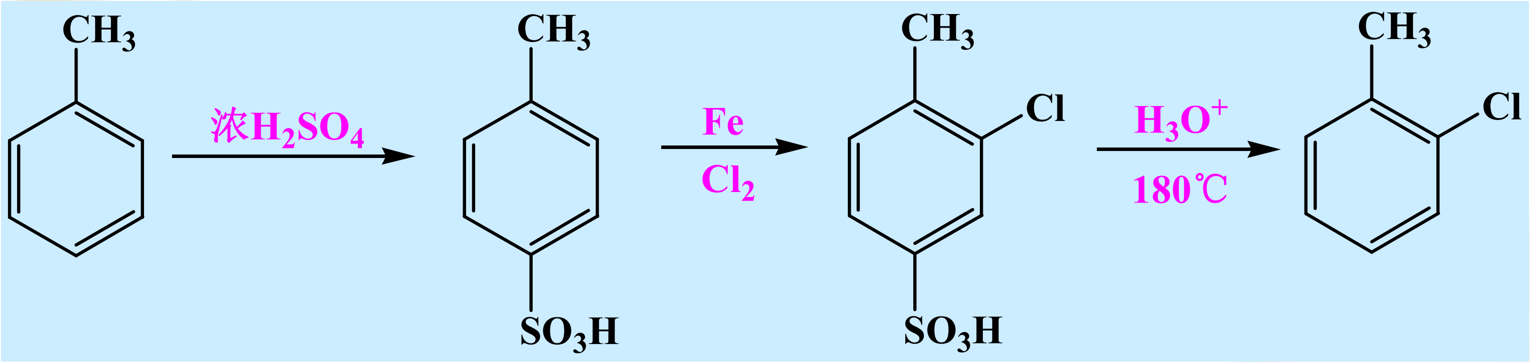
苯磺酸是有机强酸，在180 °C 的水蒸汽作用下可水解脱下磺酸基(desulfonation)。

加压得到



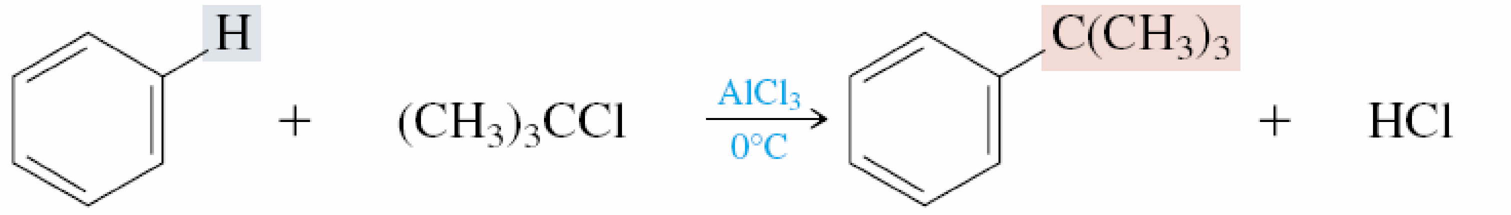
**Ex:** **Show how you might synthesize *o*-chlorotoluene starting with toluene.**

## Sample Solution:



***Tip: We may introduce a sulfonic acid group into a benzene ring to influence the course of some further reaction. Later, we may remove the sulfonic acid group by desulfonation.***

# 7.3.2.4 Friedel-Crafts Alkylation of Benzene



Benzene

*tert*-Butyl chloride

*tert*-Butylbenzene (60%)

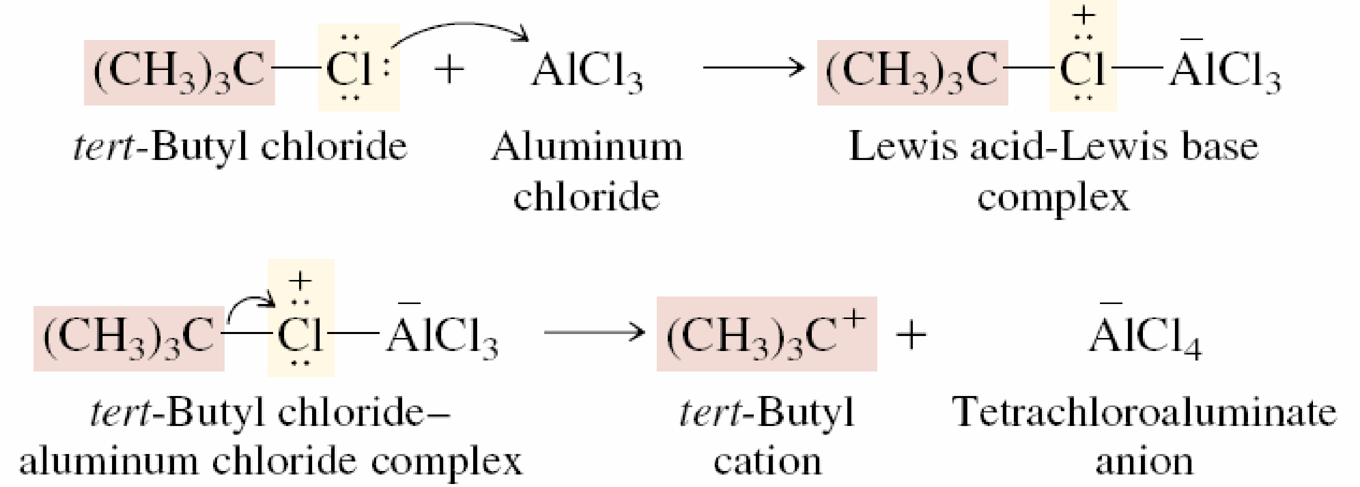
Hydrogen chloride

Alkyl halides by themselves are insufficiently electrophilic to react with benzene. Aluminum chloride serves as a **Lewis acid catalyst** to enhance the electrophilicity of the alkylating agent.

The commonly used Lewis acid catalysts:

$AlCl_3$、$ZnCl_2$、$FeCl_3$、$BF_3$…

With tertiary and secondary alkyl halides, the addition of aluminum chloride leads to the formation of carbocations, which then attack the aromatic ring.



$$(CH_3)_3C-\ddot{\underset{\cdot\cdot}{Cl}}: + AlCl_3 \longrightarrow (CH_3)_3C-\overset{+}{\underset{\cdot\cdot}{\ddot{Cl}}}-\overset{-}{Al}Cl_3$$

*tert*-Butyl chloride

Aluminum chloride

Lewis acid-Lewis base complex

$$(CH_3)_3C-\overset{+}{\underset{\cdot\cdot}{\ddot{Cl}}}-\overset{-}{Al}Cl_3 \longrightarrow (CH_3)_3C^+ + \overset{-}{Al}Cl_4$$

*tert*-Butyl chloride–aluminum chloride complex

*tert*-Butyl cation

Tetrachloroaluminate anion

Methyl and ethyl halides do not form carbocations when treated with aluminum chloride, but do alkylate benzene under Friedel–Crafts conditions.

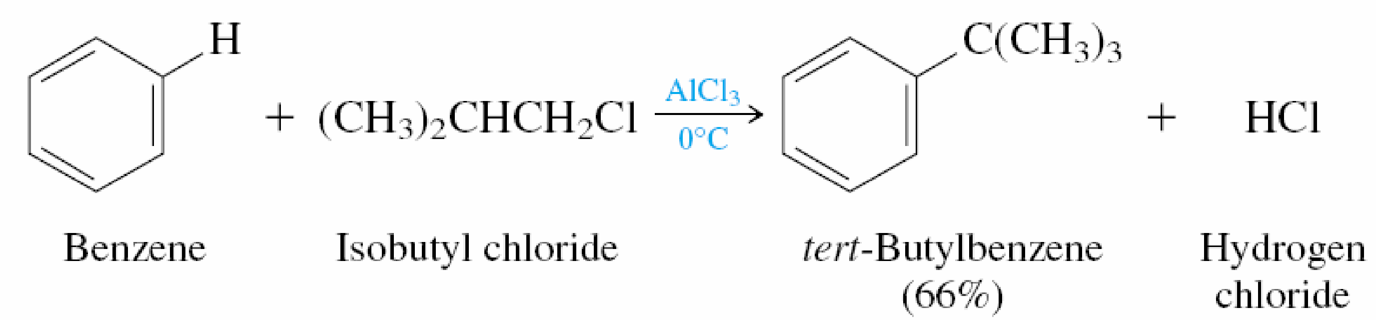
烷基化反应有三个主要特点:

a. 烷基化反应很难停留在一元取代阶段，通常生成多烷基产物。

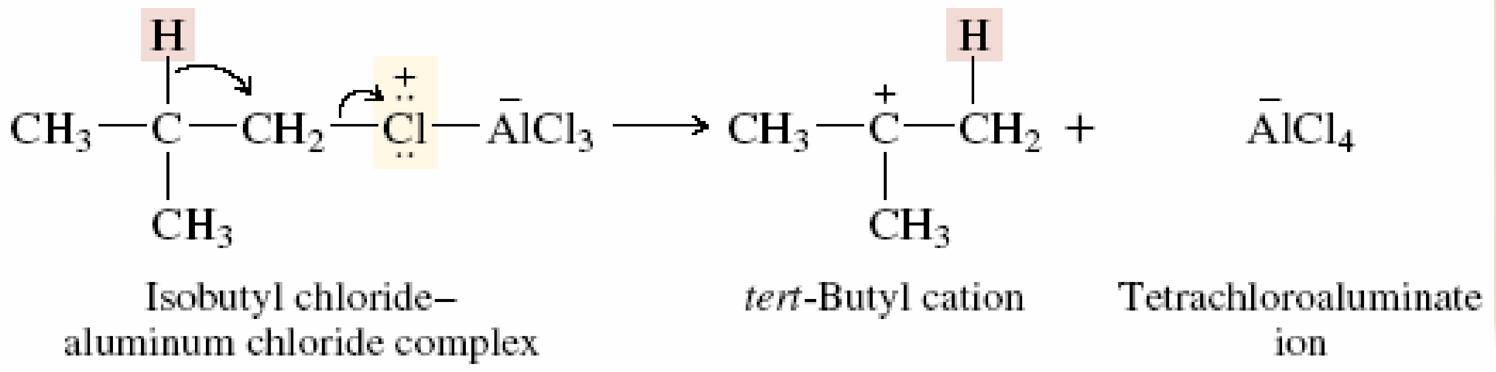
b. 烷基化反应可逆。

c. 当使用三个或以上碳原子的直链卤代烷作烷基化试剂时，会发生碳链异构化现象。

**One drawback to Friedel–Crafts alkylation is that rearrangements can occur, especially when primary alkyl halides are used.**

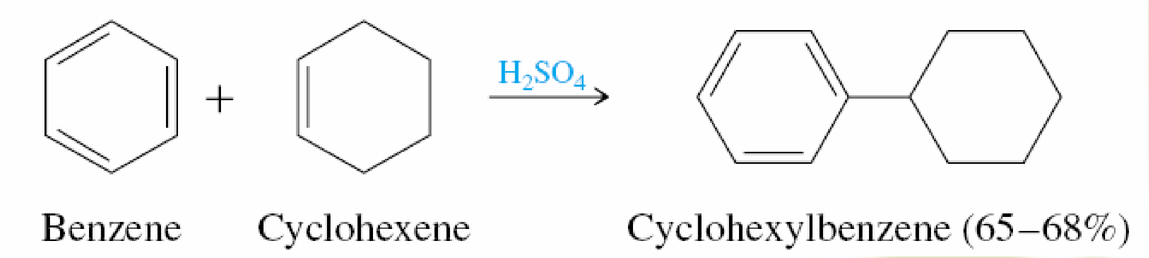


**Here, the electrophile is *tert*-butyl cation formed by a hydride migration that accompanies ionization of the carbon–chlorine bond.**

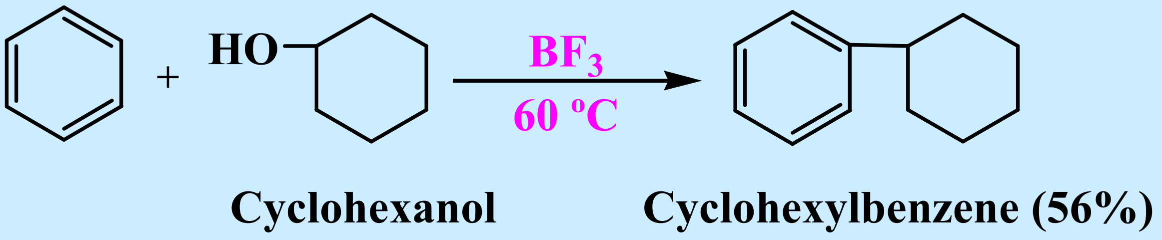


**Since electrophilic attack on benzene is simply another reaction available to a carbocation, other carbocation precursors can be used in place of alkyl halides.**

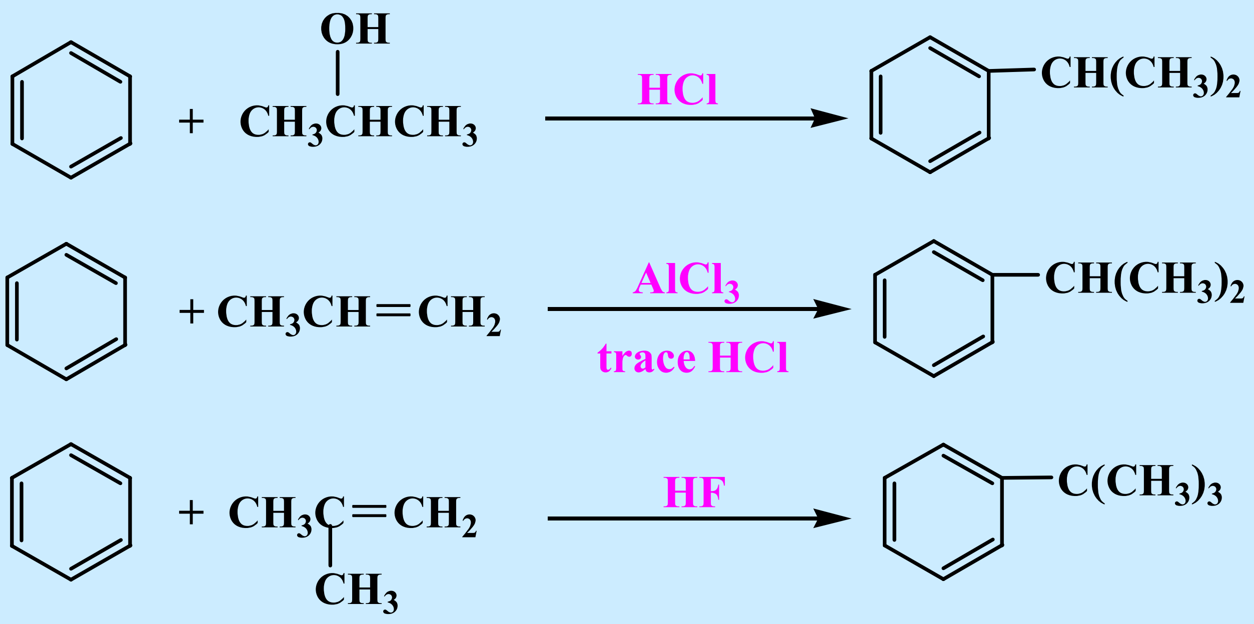
**For example, alkenes, which are converted to carbocations by protonation, can be used to alkylate benzene.**



**A mixture of an alcohol and an acid may also be used.**



**Ex:**



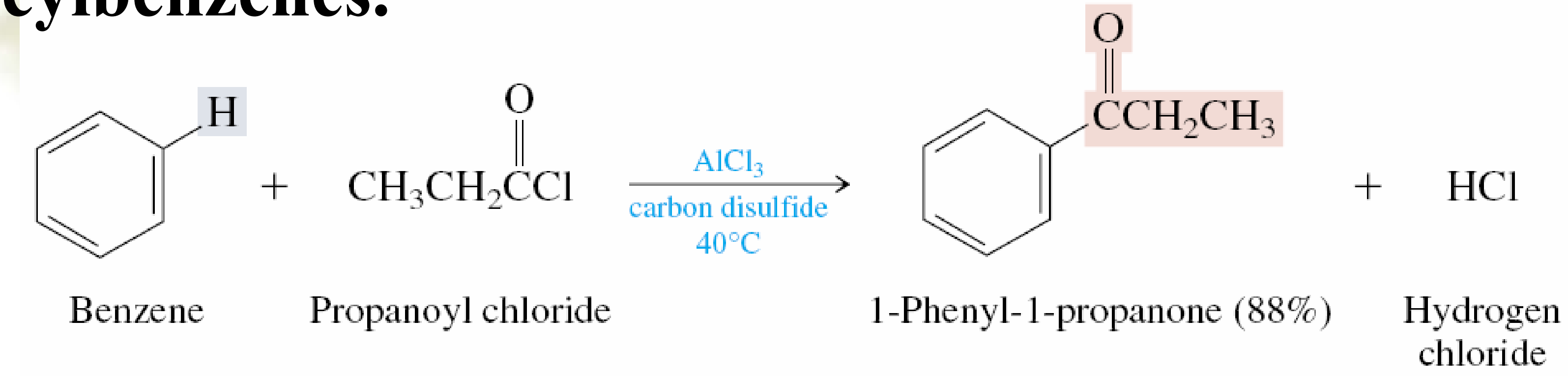
## Notice:

◆ 苯环上已有硝基等吸电子取代基时烷基化不能发生。

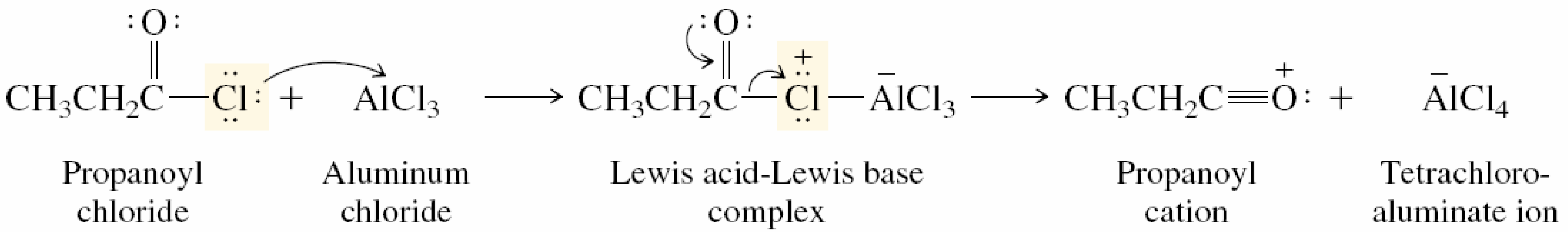
◆ **Alkenyl halides such as vinyl chloride ($CH_2$=CHCl) do *not* form carbocations on treatment with $AlCl_3$ and so cannot be used in Friedel-Crafts reactions.**

## 7.3.2.4 Friedel-Crafts Acylation of Benzene

**Another version of the Friedel–Crafts reaction uses acyl halides instead of alkyl halides and yields acylbenzenes.**



**The electrophile in a Friedel-Crafts acylation reaction is an acyl cation.**



The electrophilic site of an acyl cation is its **acyl carbon**. An electrostatic potential map of the acyl cation from propanoyl chloride illustrates nicely the concentration of positive charge at the acyl carbon.

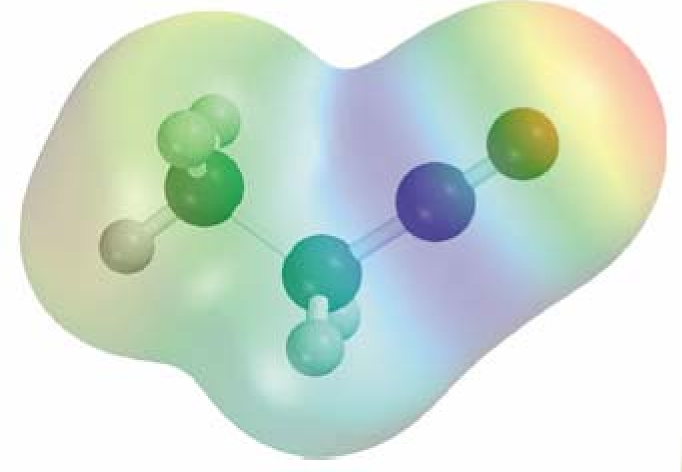
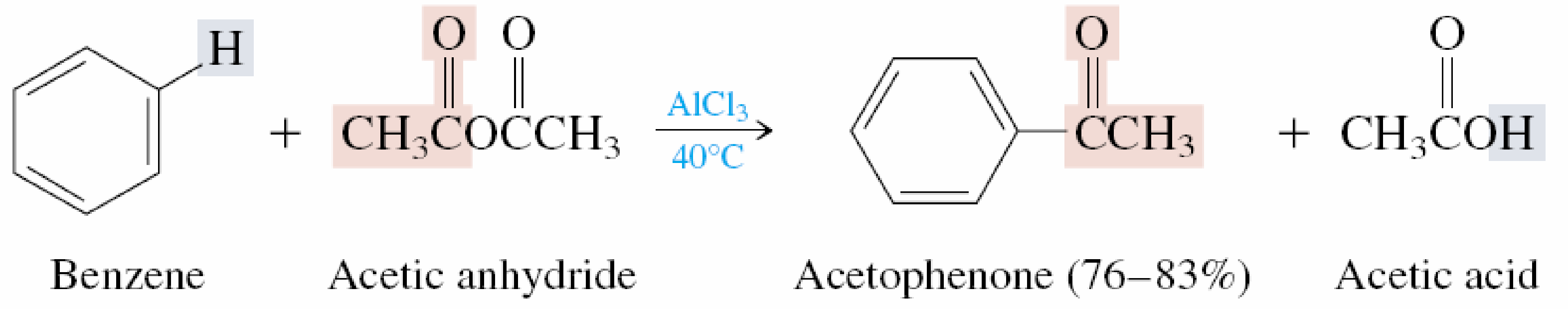


**FIGURE 7.6** Electrostatic potential map of propanoyl cation [$(CH_3CH_2C\equiv O)$]. The region of greatest positive charge (blue) is associated with the carbon of the C=O group.

**Carboxylic acid anhydrides can also serve as sources of acyl cations and, in the presence of aluminum chloride, acylate benzene.**

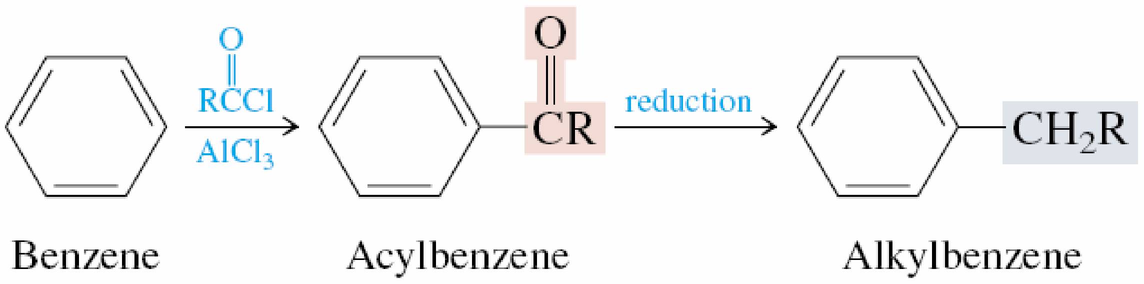
**One acyl unit of an acid anhydride becomes attached to the benzene ring, while the other becomes part of a carboxylic acid.**



*An important difference between Friedel-Crafts alkylations and acylations is that acyl cations do not rearrange.*

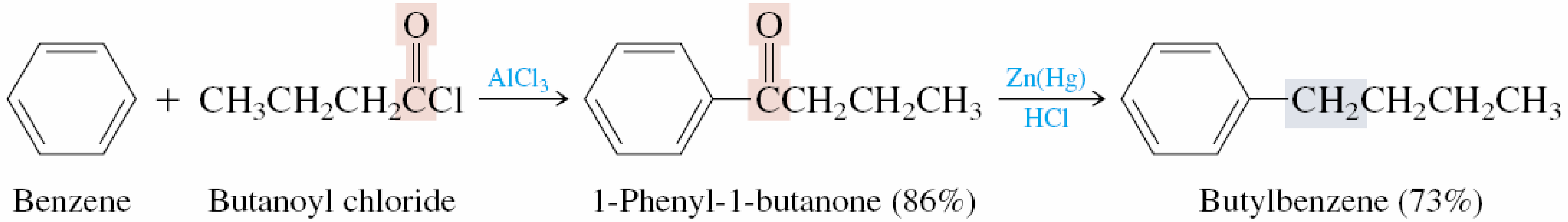
# 7.3.2.5 Synthesis of Alkylbenzene by Acylation-Reduction

**Because acylation of an aromatic ring can be accomplished without rearrangement, it is frequently used as the first step in a procedure for the *alkylation* of aromatic compounds by *acylation-reduction.***



**The most commonly used method for reducing an acylbenzene to an alkylbenzene employs a zinc–mercury amalgam in concentrated hydrochloric acid and is called the *Clemmensen reduction*.**

**Ex:** **Starting with benzene, outline a synthesis of *n*-butylbenzene.**

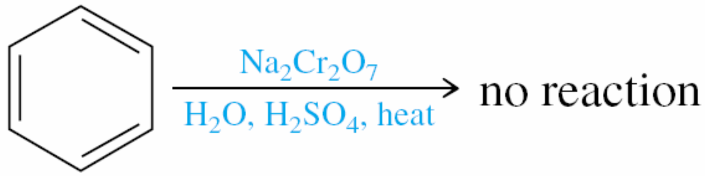


**Notice:** 跟烷基化相似，苯环上有硝基时，不能酰化。所以，硝基苯可以作为付-克反应的溶剂。

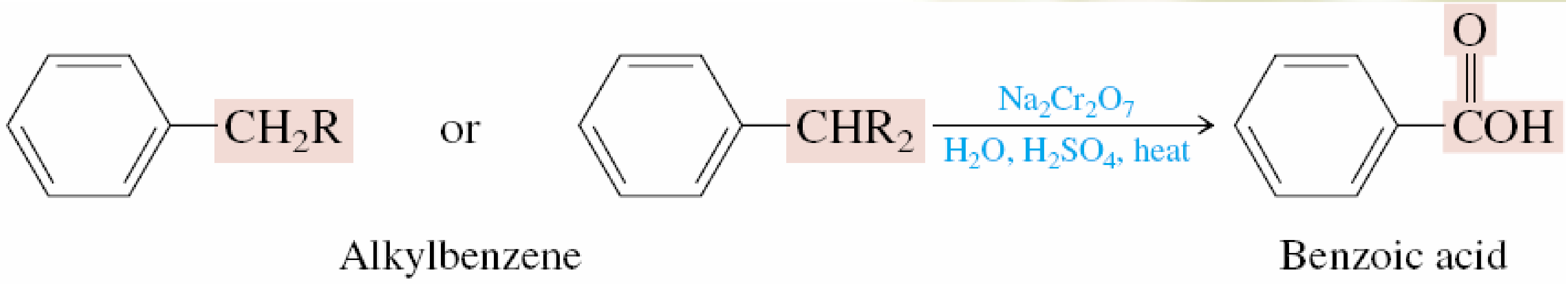
## 7.3.2.6 Oxidation of Alkylbenzenes

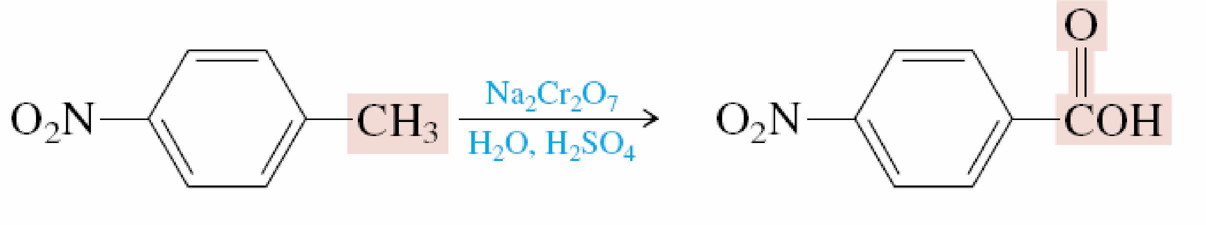
**Chromic acid is a strong oxidizing agent but does not react either with benzene or with alkanes.**

$$RCH_2CH_2R' \xrightarrow[H_2O,\ H_2SO_4,\ heat]{Na_2Cr_2O_7} \text{no reaction}$$



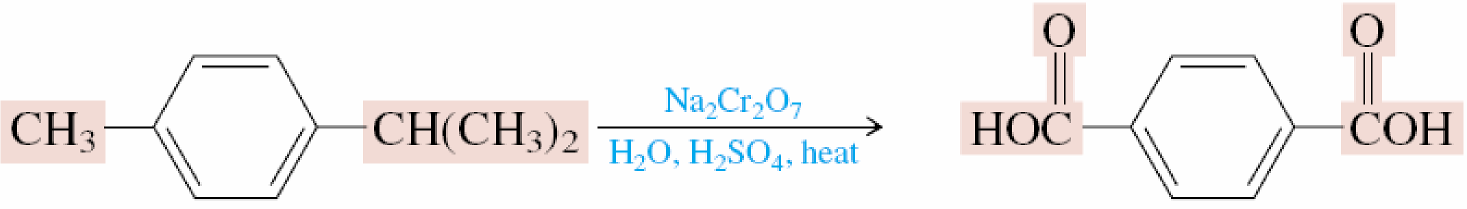
**However, an alkyl side chain on a benzene ring is oxidized on being heated with chromic acid. The product is benzoic acid or a substituted derivative of benzoic acid.**





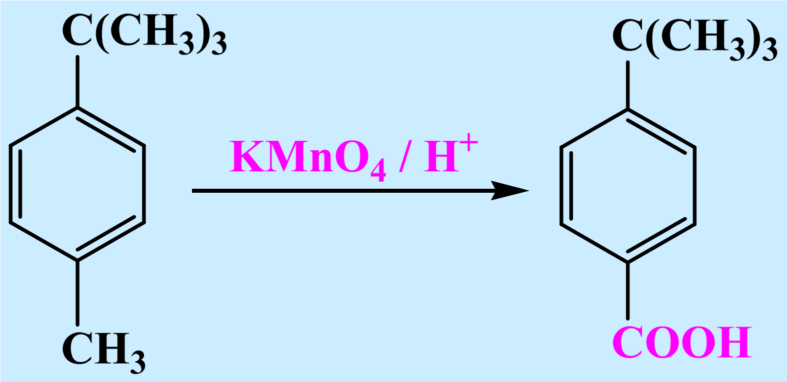
*p*-Nitrotoluene *p*-Nitrobenzoic acid (82–86%)

When two alkyl groups are present on the ring, both are oxidized. Note that alkyl groups, **regardless of their chain length**, are converted to carboxyl groups ( − $CO_2H$) attached directly to the ring.



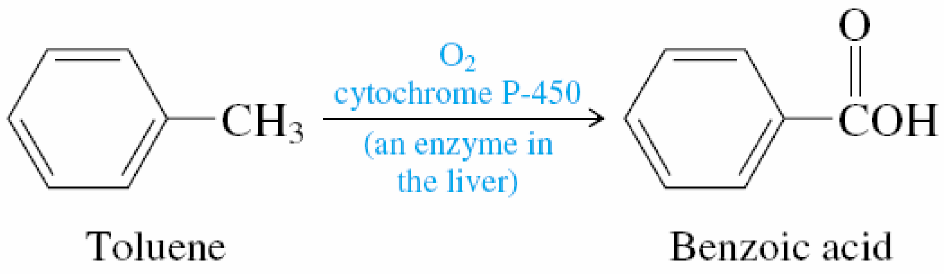
*p*-Isopropyltoluene *p*-Benzenedicarboxylic acid (45%)

An exception is a *tert*-alkyl substituent. Because it lacks benzylic hydrogens, a *tert*-alkyl group is not susceptible to oxidation under these conditions.



Side-chain oxidation of alkylbenzenes is important in certain metabolic processes. One way in which the body rids itself of foreign substances is by oxidation in the liver to compounds more easily excreted in the urine.

***Toluene*, for example, is oxidized to benzoic acid by this process and is eliminated rather readily.**

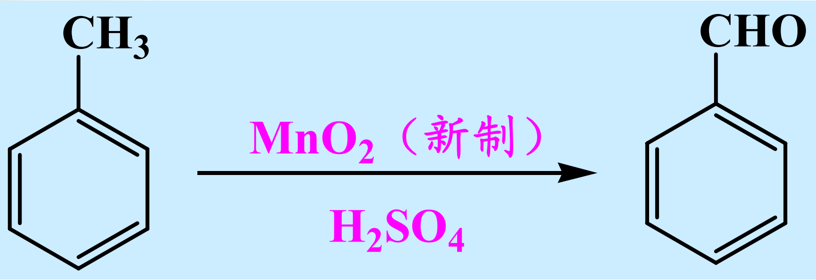


***Benzene*, with no alkyl side chain, undergoes a different reaction in the presence of these enzymes, which convert it to a substance capable of inducing mutations (突变) in DNA.**

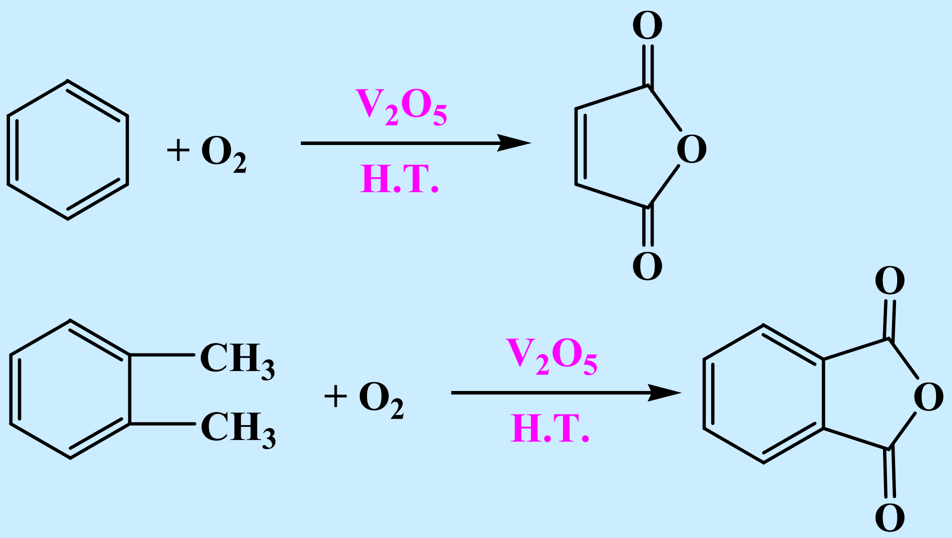
**This difference in chemical behavior seems to be responsible for the fact that benzene is carcinogenic (致癌的) but toluene is not.**

**Jones试剂**

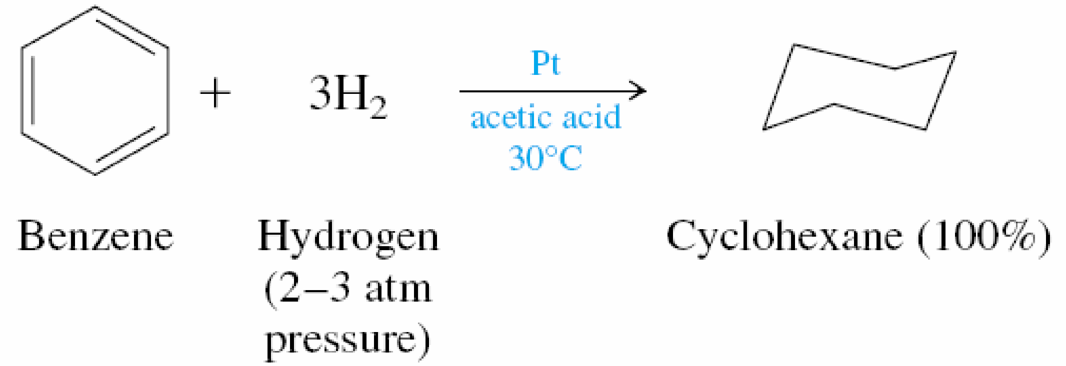
氧化剂若选择$MnO_2$(新制)$+H_2SO_4$，则:



氧化条件若激烈，则苯环断裂:



# 7.3.2.7 Reduction of Benzene

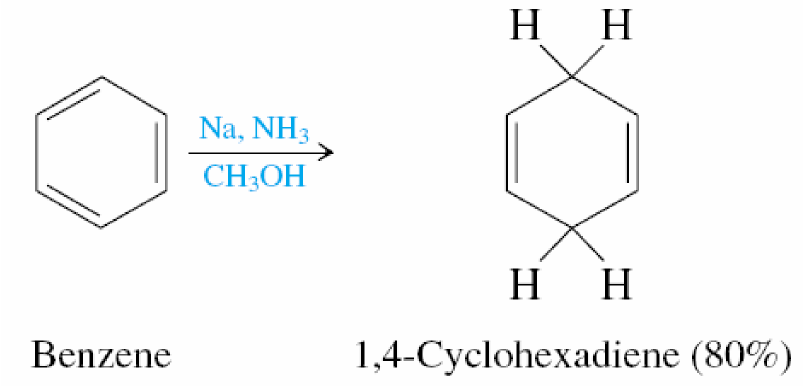


**Homogeneous catalyst: $(Ph_3P)_3RhCl$**

**(Willkinson catalyst)**

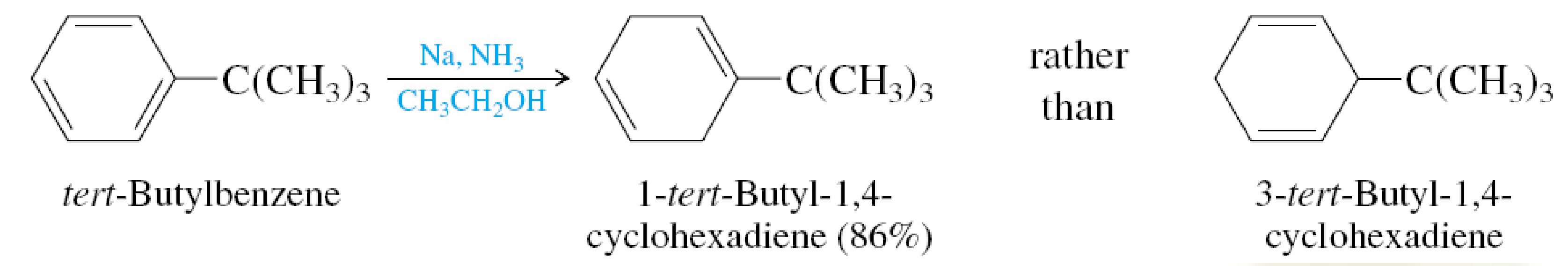
We saw that the combination of a Group I metal and liquid ammonia is a powerful reducing system capable of reducing alkynes to *trans* alkenes.

In the presence of an alcohol, this same combination *reduces arenes to nonconjugated dienes*.



Metal-ammonia-alcohol reductions of aromatic rings are known as Birch reductions.

**Alkyl-substituted arenes give 1,4-cyclohexadienes in which the alkyl group is a substituent on the double bond.**



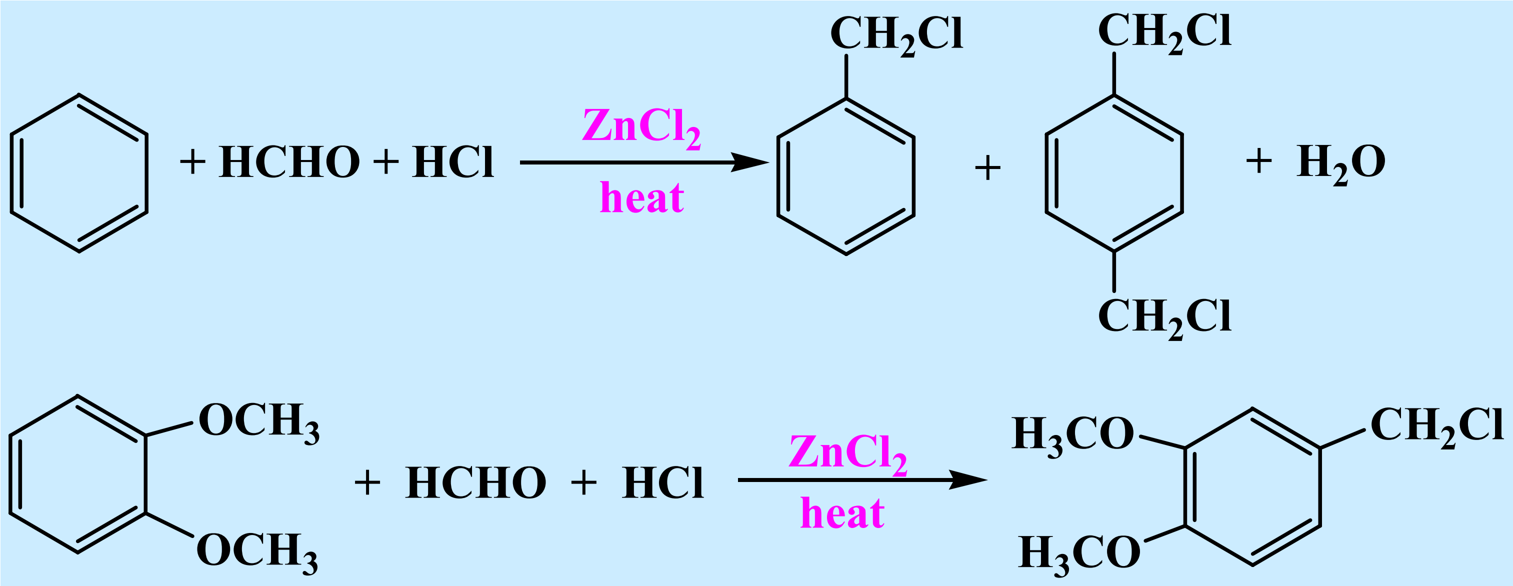
*tert*-Butylbenzene

1-*tert*-Butyl-1,4-cyclohexadiene (86%)

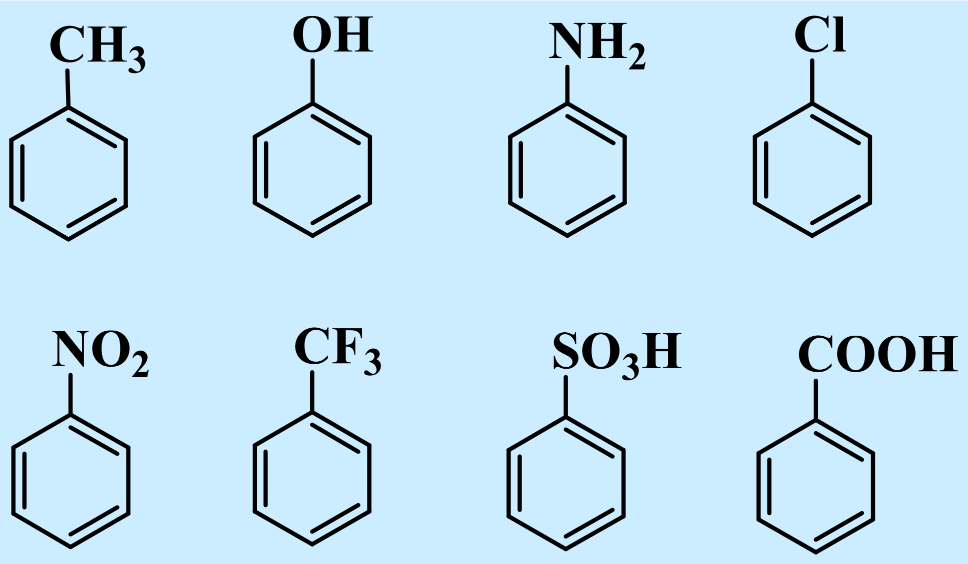
3-*tert*-Butyl-1,4-cyclohexadiene

## 7.3.2.8 Chloromethylation Reaction

芳烃、甲醛和氯化氢在无水$ZnCl_2$或$AlCl_3$等存在下进行反应，可以直接在芳环上引入氯甲基，这个反应叫做氯甲基化反应。



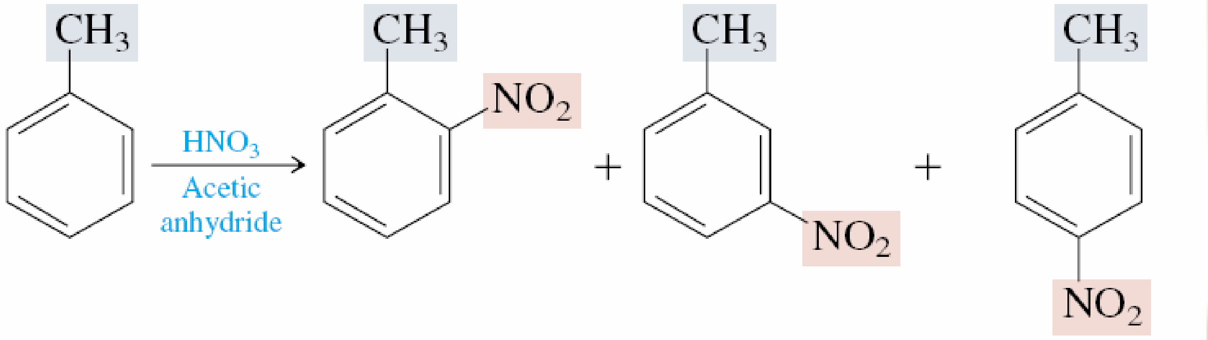
# 7.4 REGIOSELECTIVITY IN ELECTROPHILIC AROMATIC SUBSTITUTION (ORIENTATION EFFECT)



理论上：*o*- 40%; *m*- 40%; *p*- 20%

Three products are possible from nitration of toluene: *o*-nitrotoluene, *m*-nitrotoluene, and *p*-nitrotoluene. All are formed, but not in equal amounts.

Together, the ortho and para-substituted isomers make up 97% of the product mixture; the meta only 3%.



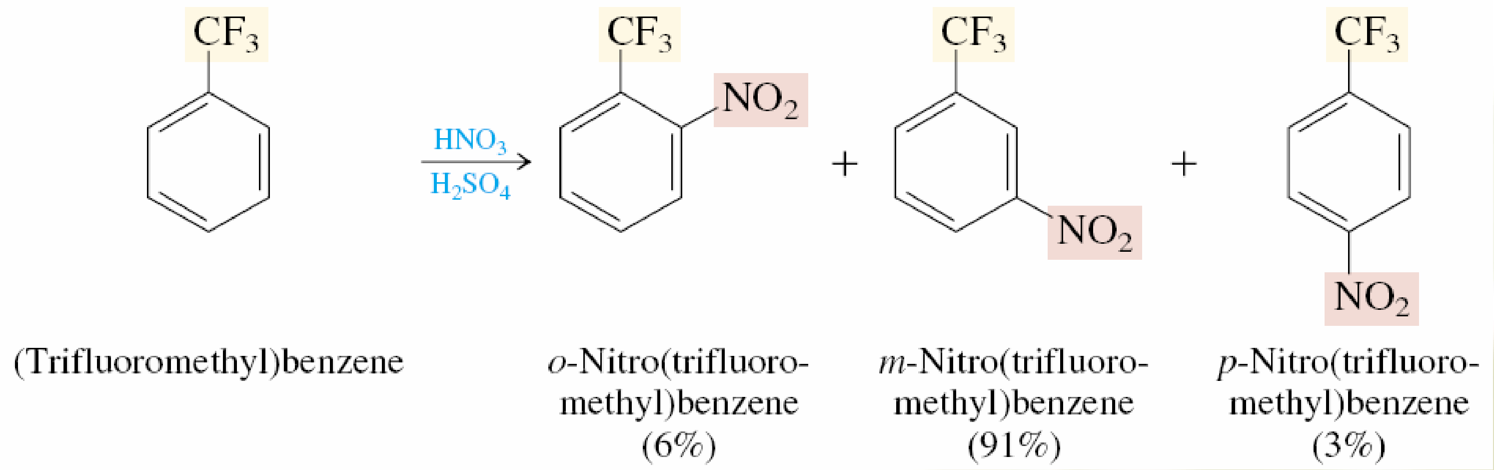
Toluene

*o*-Nitrotoluene (63%)

*m*-Nitrotoluene (3%)

*p*-Nitrotoluene (34%)

**Nitration of (trifluoromethyl)benzene, on the other hand, yields almost exclusively *m*-nitro-(trifluoromethyl)benzene (91%). The ortho- and para-substituted isomers are minor components of the reaction mixture.**



**What** is the effect of a substituent on the *regioselectivity* of electrophilic aromatic substitution?

**Why** substitution in toluene occurs primarily at positions ortho and para to methyl, however, substitution in (trifluoromethyl)-benzene occurs primarily at positions meta to the substituent?

## 7.4.1 Classification of Substituents in Electrophilic Aromatic Substitution Reactions

1. 苯环上新导入的取代基的位置主要与原有取代基的性质有关。原有的取代基称为定位基。

2. 根据定位基对苯环亲电取代反应的影响， 即新基导入的位置和反应的难易分成三类定位基。

# 第一类定位基：主要使反应易于进行，新基导入邻、对位。

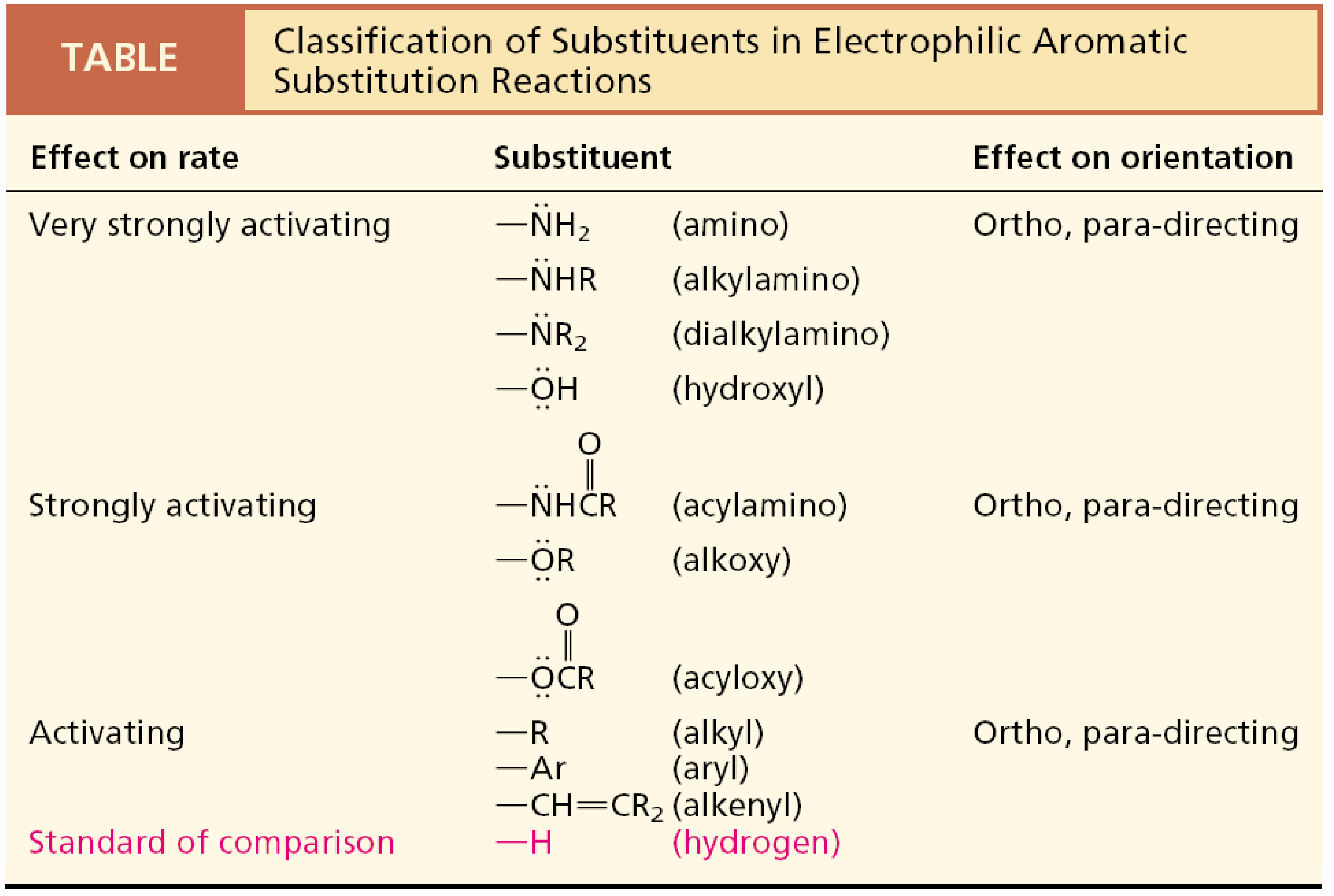


**TABLE** Classification of Substituents in Electrophilic Aromatic Substitution Reactions

| Effect on rate | Substituent | | Effect on orientation |
|---|---|---|---|
| Very strongly activating | $-\ddot{N}H_2$ | (amino) | Ortho, para-directing |
| | $-\ddot{N}HR$ | (alkylamino) | |
| | $-\ddot{N}R_2$ | (dialkylamino) | |
| | $-\underset{..}{\ddot{O}}H$ | (hydroxyl) | |
| Strongly activating | $-\ddot{N}H\overset{\overset{O}{\|}}{C}R$ | (acylamino) | Ortho, para-directing |
| | $-\underset{..}{\ddot{O}}R$ | (alkoxy) | |
| | $-\underset{..}{\ddot{O}}\overset{\overset{O}{\|}}{C}R$ | (acyloxy) | |
| Activating | $-R$ | (alkyl) | Ortho, para-directing |
| | $-Ar$ | (aryl) | |
| | $-CH{=}CR_2$ | (alkenyl) | |
| Standard of comparison | $-H$ | (hydrogen) | |

# 第二类定位基：主要使反应难于进行，新基导入邻、对位。

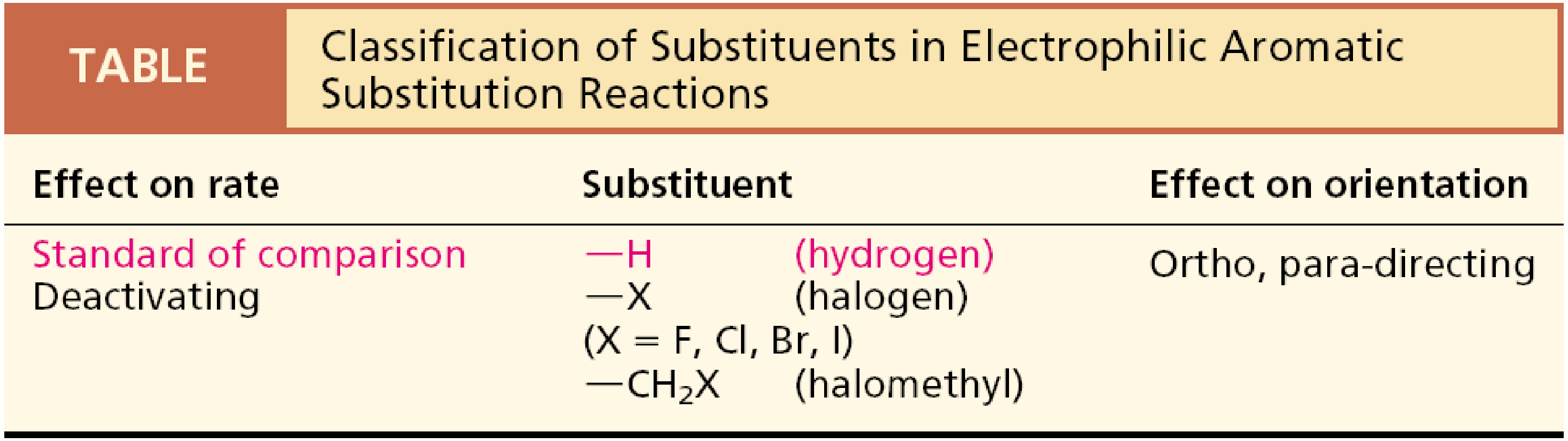


**TABLE** Classification of Substituents in Electrophilic Aromatic Substitution Reactions

| Effect on rate | Substituent | Effect on orientation |
|---|---|---|
| Standard of comparison | —H (hydrogen) | Ortho, para-directing |
| Deactivating | —X (halogen)<br>(X = F, Cl, Br, I)<br>—CH$_2$X (halomethyl) | |

# 第三类定位基：主要使反应难于进行，新基导入间位。

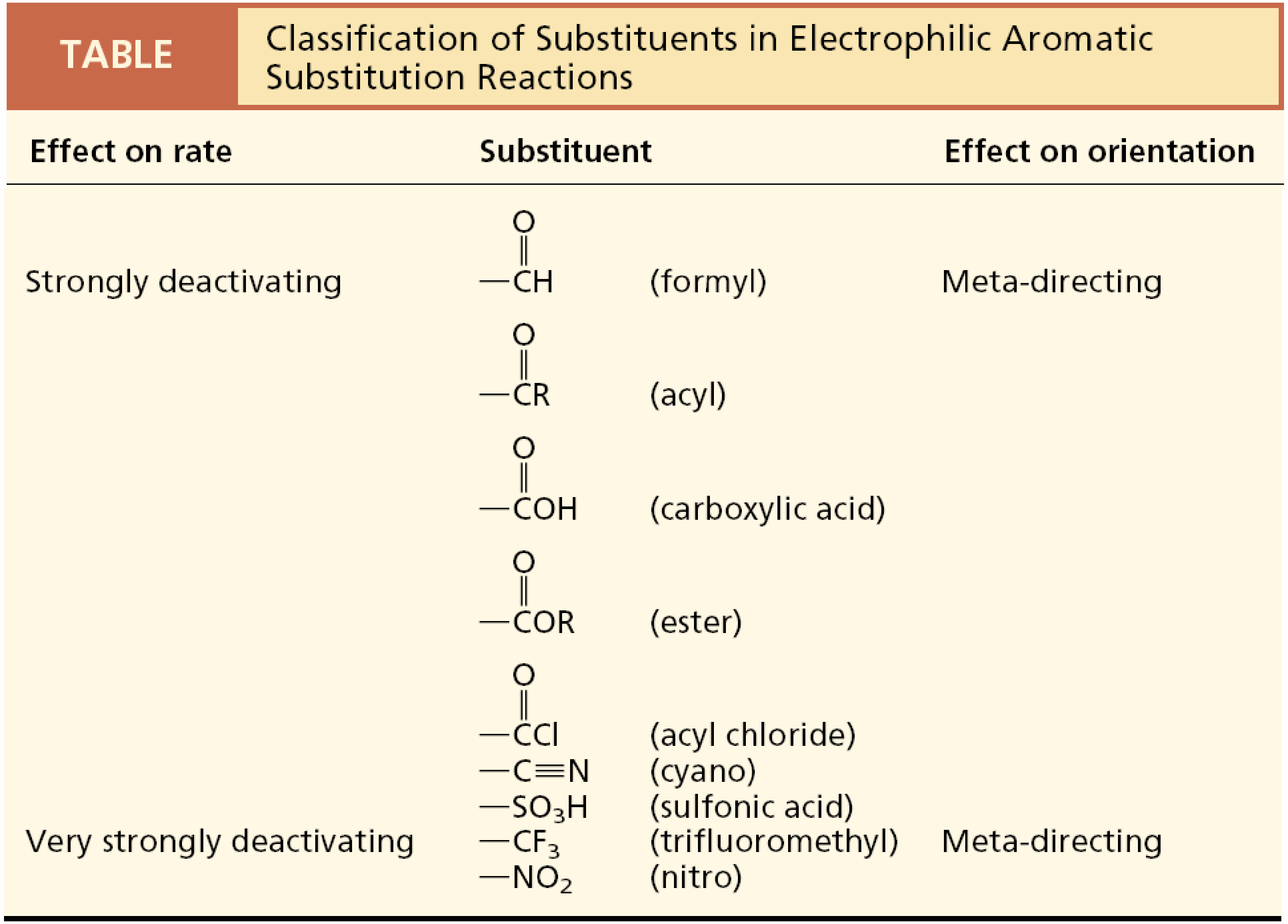


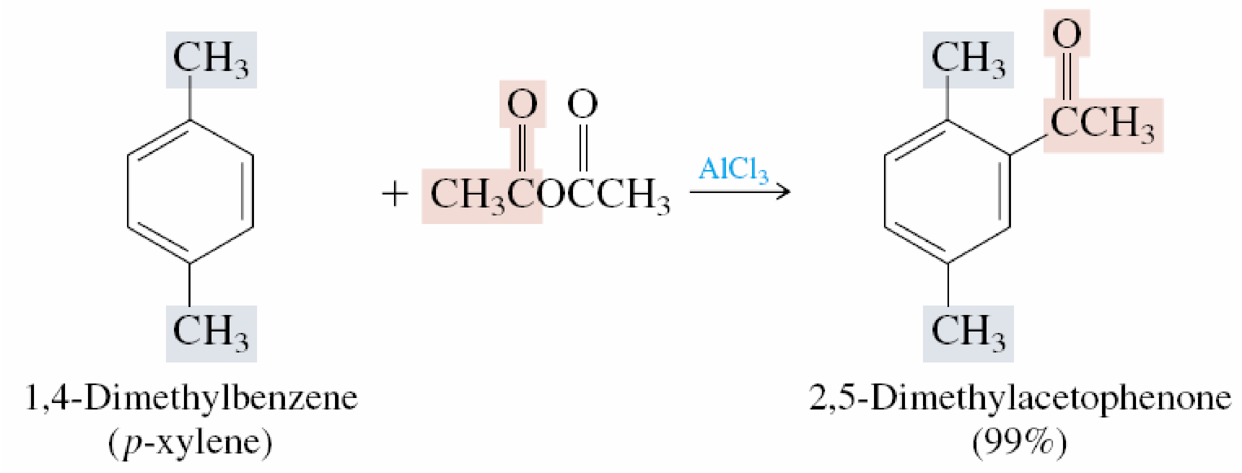
TABLE Classification of Substituents in Electrophilic Aromatic Substitution Reactions

| Effect on rate | Substituent | | Effect on orientation |
|---|---|---|---|
| Strongly deactivating | $-\overset{O}{\overset{\|}{C}}H$ | (formyl) | Meta-directing |
| | $-\overset{O}{\overset{\|}{C}}R$ | (acyl) | |
| | $-\overset{O}{\overset{\|}{C}}OH$ | (carboxylic acid) | |
| | $-\overset{O}{\overset{\|}{C}}OR$ | (ester) | |
| | $-\overset{O}{\overset{\|}{C}}Cl$ | (acyl chloride) | |
| | $-C\equiv N$ | (cyano) | |
| | $-SO_3H$ | (sulfonic acid) | |
| Very strongly deactivating | $-CF_3$ | (trifluoromethyl) | Meta-directing |
| | $-NO_2$ | (nitro) | |

## 7.4.2 Multiple Substituent Effects

**When a benzene ring bears two or more substituents, both its reactivity and the site of further substitution can usually be predicted from the cumulative effects of its substituents.**

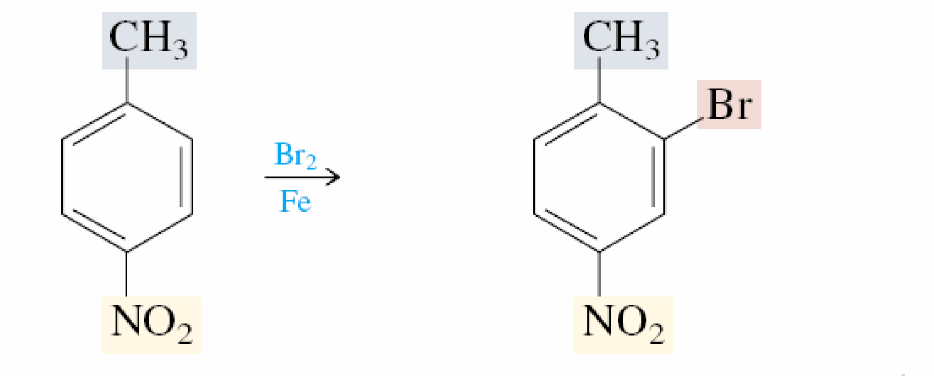
- **In the simplest cases all the available sites are equivalent, and substitution at any one of them gives the same product.**



1,4-Dimethylbenzene (*p*-xylene)

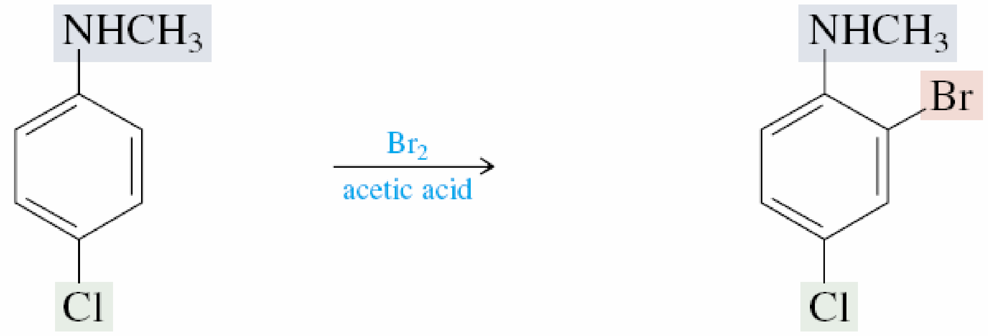
2,5-Dimethylacetophenone (99%)

◆ **Often the directing effects of substituents reinforce each other.**



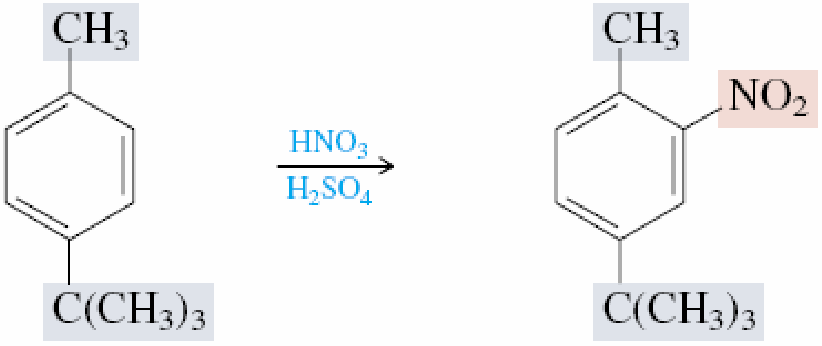
*p*-Nitrotoluene 2-Bromo-4-nitrotoluene (86–90%)

◆ **In almost all cases, including most of those in which the directing effects of individual substituents oppose each other,** ***it is the more activating substituent that controls the regioselectivity of electrophilic aromatic substitution.***

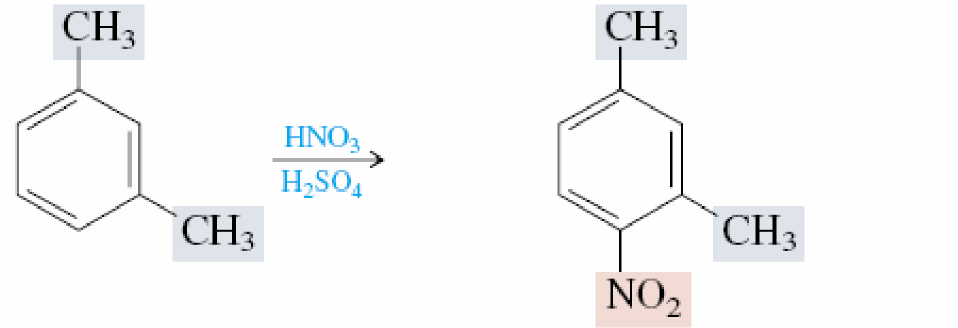


4-Chloro-*N*-methylaniline → 2-Bromo-4-chloro-*N*-methylaniline (87%)

◆ **When two positions are comparably activated by alkyl groups, substitution usually occurs at the *less hindered* site. Here is an example of a *steric effect*.**



*p*-*tert*-Butyltoluene → 4-*tert*-Butyl-2-nitrotoluene (88%)



*m*-Xylene 2,4-Dimethyl-1-nitrobenzene (98%)

**The ortho position between the two methyl groups is less reactive because it is *more sterically hindered*.**

**Conclusion:** 当苯环上有多个取代基时，确定新基导入位置的规则是：邻、对位定位基的定位能力大于间位定位基；有同一类定位基时要看相对强度；定位能力相当时再考虑立体位阻。

**Problem:** **Ex. 10 on page 186 in textbook**

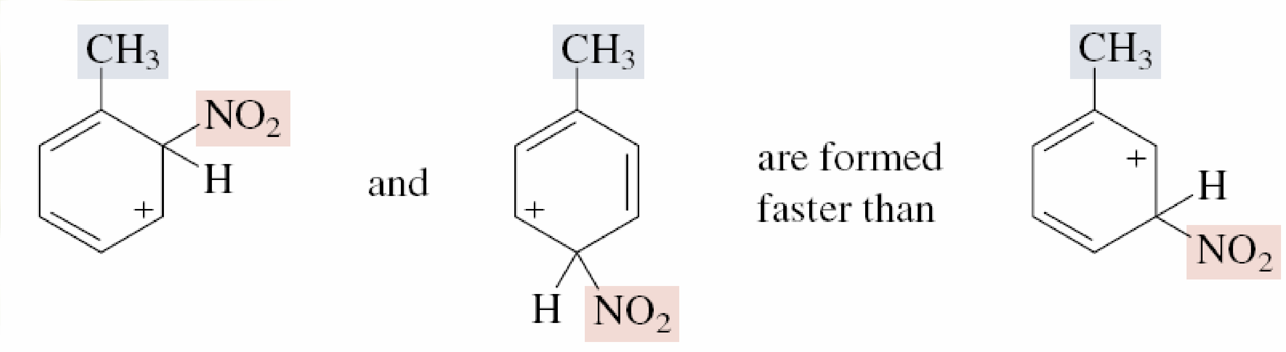
## 7.4.3 Explanation of Orientation Effect

**Why is there such a marked difference between methyl and trifluoromethyl substituents in their influence on electrophilic aromatic substitution?**

- 由中间体稳定性解释

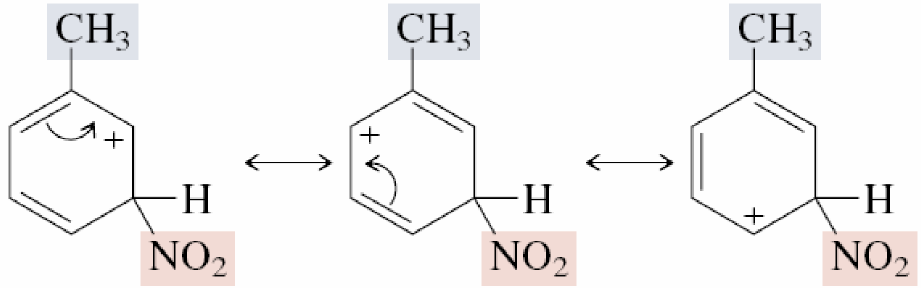
A more stable carbocation is formed faster than a less stable one.

## 7.4.3.1 Explanation for Nitration of Toluene



One way to assess the relative stabilities of these various intermediates is to examine electron delocalization in them using a resonance description.

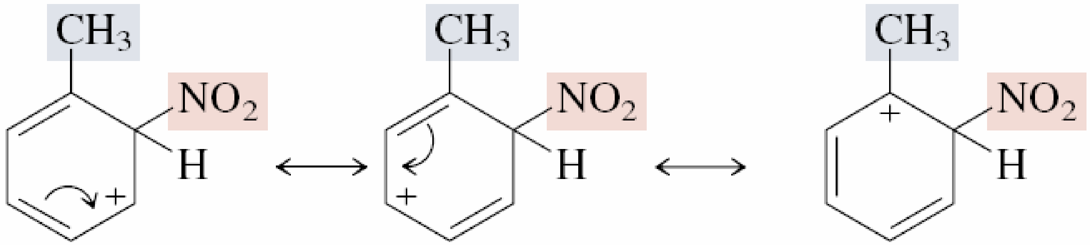
*Meta attack*



极限式

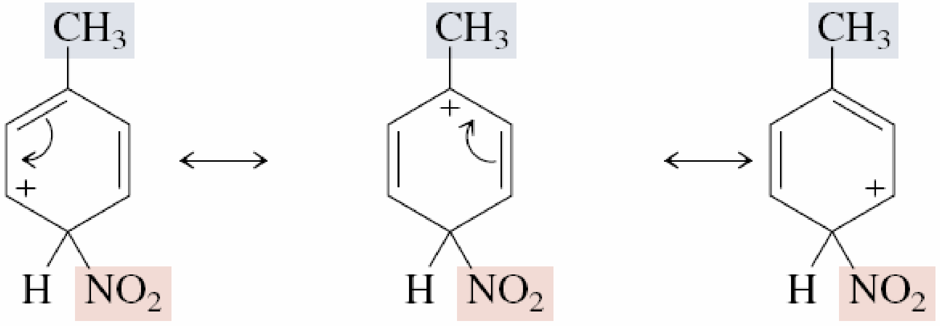
# The cyclohexadienyl cations leading to *o*- and *p*-nitrotoluene have tertiary carbocation character.

*Ortho attack*



This resonance form
is a tertiary carbocation

*Para attack*



This resonance form
is a tertiary carbocation

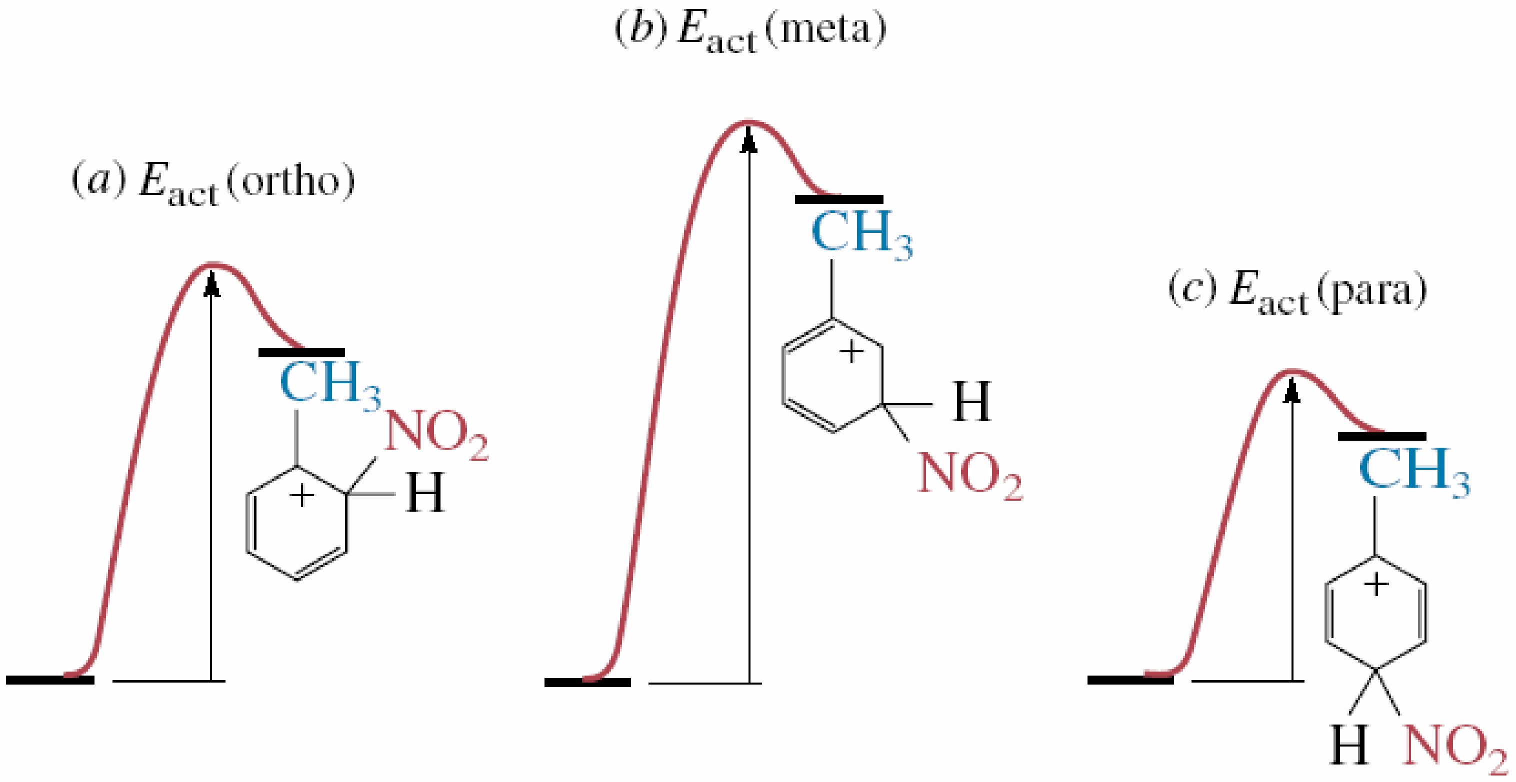
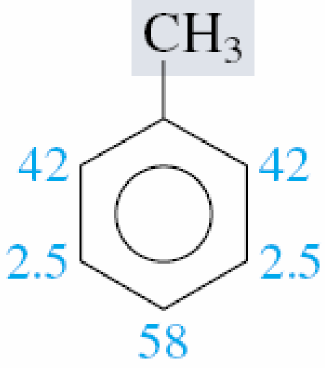


**Figure 7.9** **Comparative energy diagrams for nitronium ion attack at the (*a*) ortho, (*b*) meta, and (*c*) para positions of toluene.**

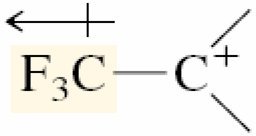
A methyl group is an *electron-releasing* substituent and activates *all* of the ring carbons of toluene toward electrophilic attack. The ortho and para positions are activated more than the meta positions.



The major influence of the methyl group is *electronic*. The most important factor is relative carbocation stability. To a small extent, the methyl group sterically hinders the ortho positions, making attack slightly more likely at the para carbon than at a single ortho carbon.

# 7.4.3.2 Explanation for Nitration of Trifluromethylbenzene

Because of their high electronegativity the three fluorine atoms polarize the electron distribution in their σ bonds to carbon, so that carbon bears a partial positive charge.

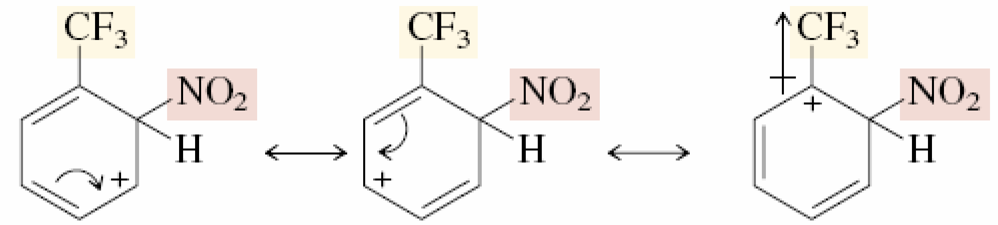


Trifluoromethyl group withdraws electrons, destabilizes carbocation

A trifluoromethyl group is a powerful *electron-withdrawing* substituent. Consequently, a $CF_3$ group *destabilizes* a carbocation site to which it is attached.

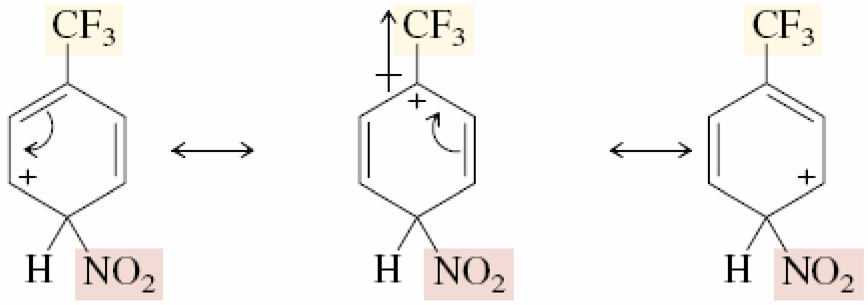
The cyclohexadienyl cation intermediates leading to *ortho and para* substitution are strongly destabilized.

*Ortho attack*



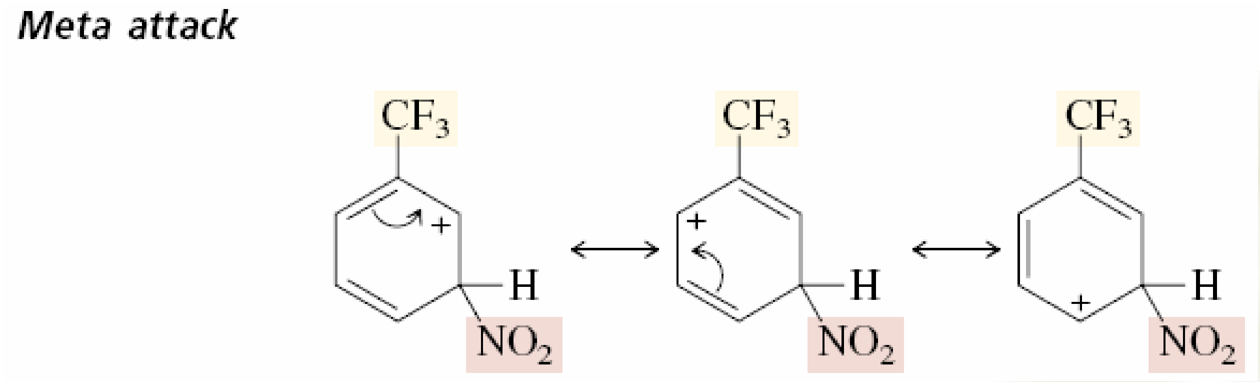
Positive charge on carbon bearing trifluoromethyl group; very unstable

*Para attack*



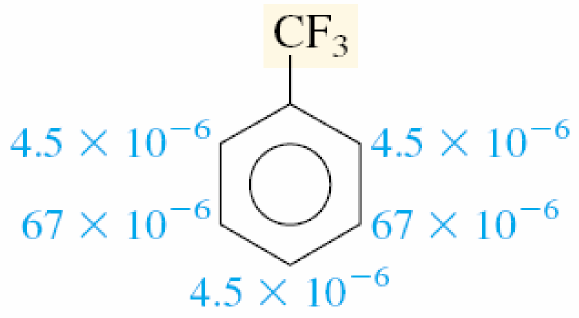
Positive charge on carbon bearing trifluoromethyl group; very unstable

**None of the three major resonance forms of the intermediate formed by attack at the meta position has a positive charge on the carbon bearing the trifluoromethyl substituent.**



Attack at the meta position leads to a more stable intermediate than attack at either the ortho or the para position, and so meta substitution predominates.

Even the intermediate corresponding to meta attack, however, is very unstable and is formed with difficulty.



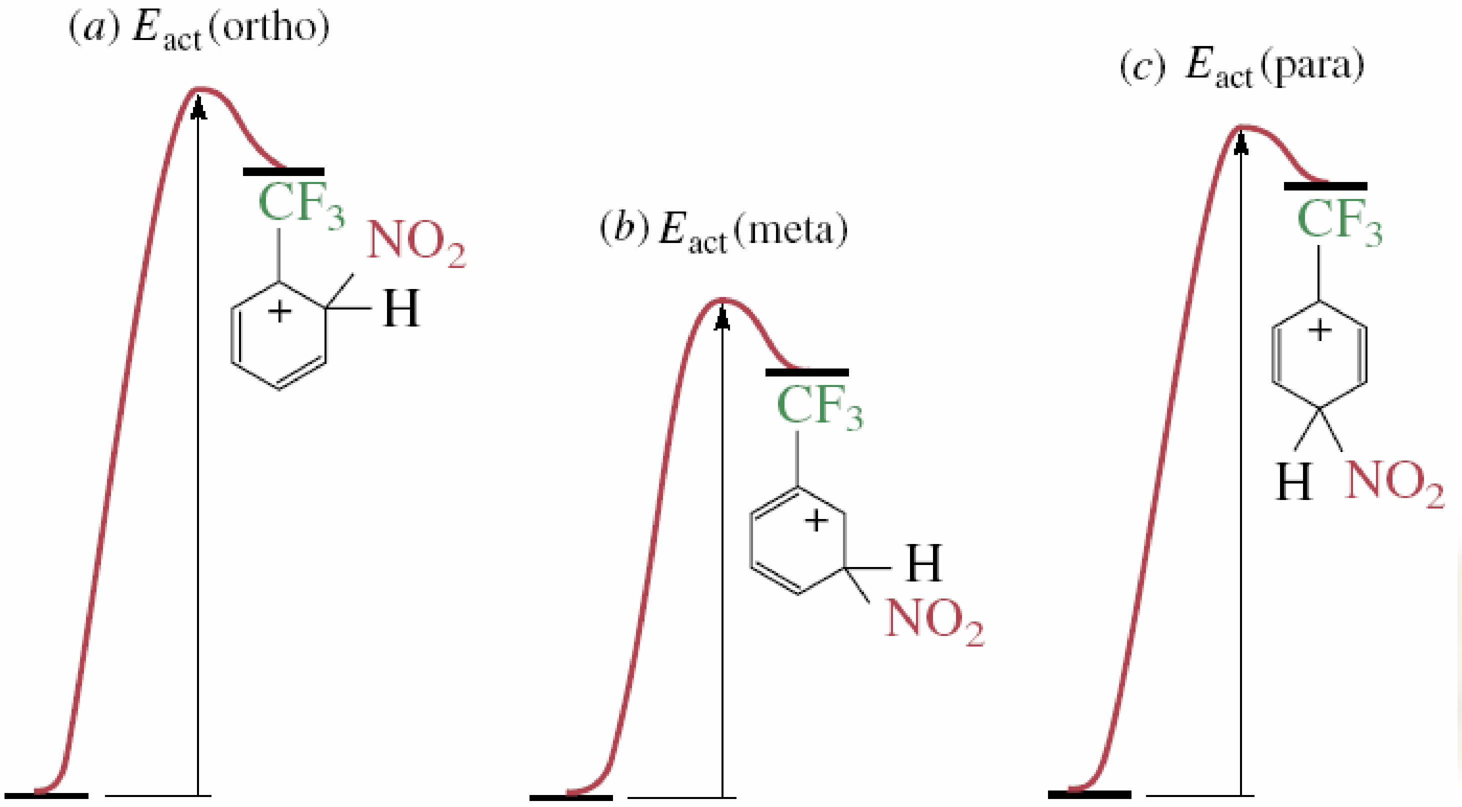
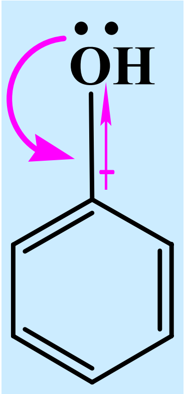


**FIGURE 7.10** Comparative energy diagrams for nitronium ion attack at the (*a*) ortho, (*b*) meta, and (*c*) para positions of (trifluoromethyl)-benzene.

# 7.4.3.3 Explanation for Hydroxyl and Alkoxy Group



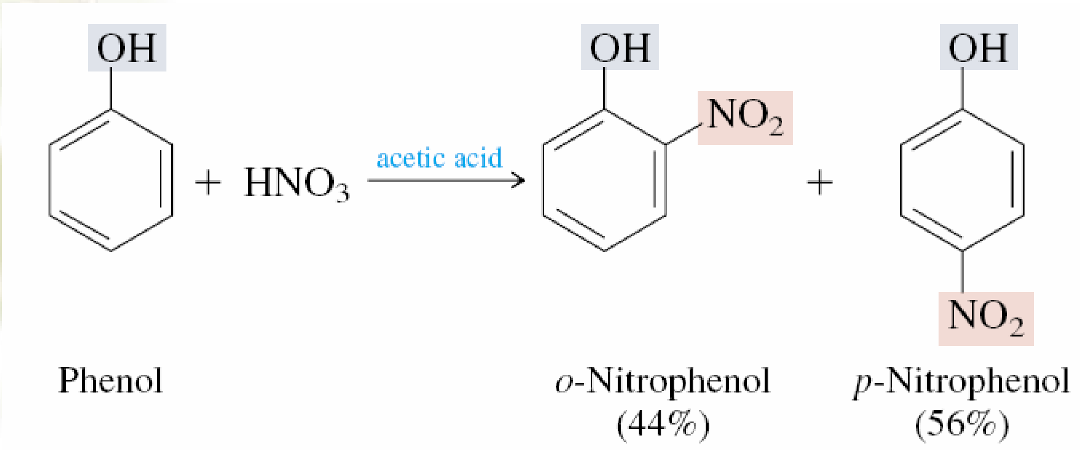
*p*- π conjugation effect

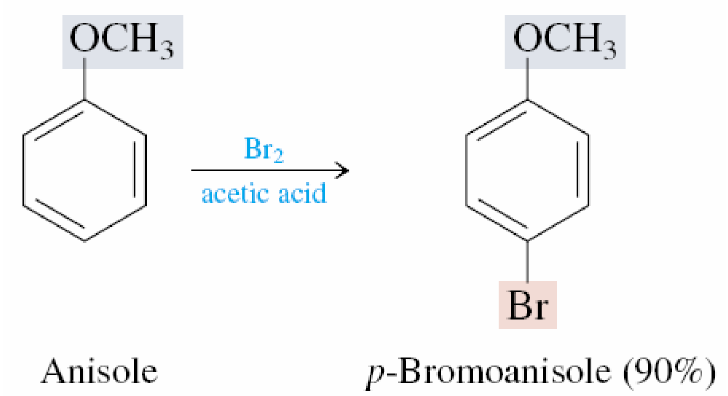
Strong

Inductive effect

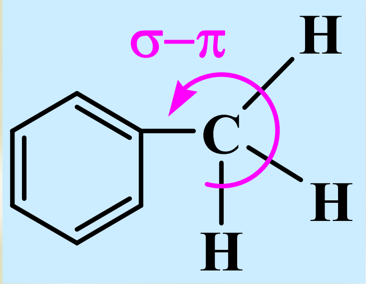
The inductive effect of hydroxyl and alkoxy groups is to withdraw electrons and would seem to require that such substituents be deactivating.

The electron-withdrawing inductive effect, however, is overcomed by a much larger electron-releasing effect involving the unshared electron pairs of oxygen.



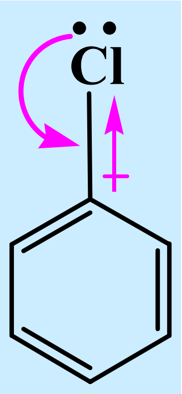


**Q:** 为什么羟基的定位能力大于甲基?



## 7.4.3.4 Explanation for Halogens

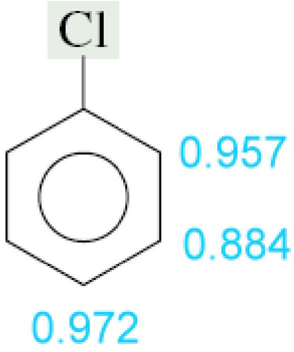
**Halogen substituents direct an incoming electrophile to the ortho and para positions but deactivate the ring toward substitution.**



***p*- π conjugation effect**

**Inductive effect**

**Strong**



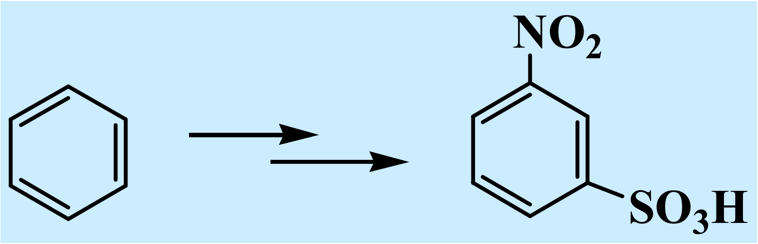
亲电取代反应活性比苯小33倍

## 7.4.4 Application of the Orientation Effect

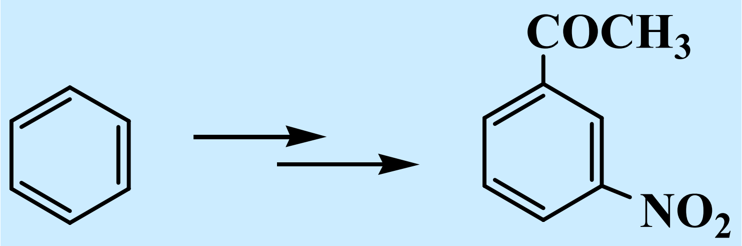
1. 预测主产物（major product)

2. 选择合成路线

**Ex 1:**

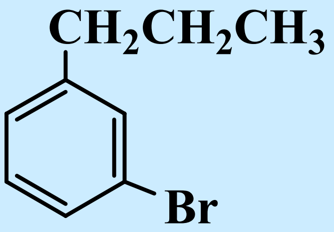


**Ex 2:**

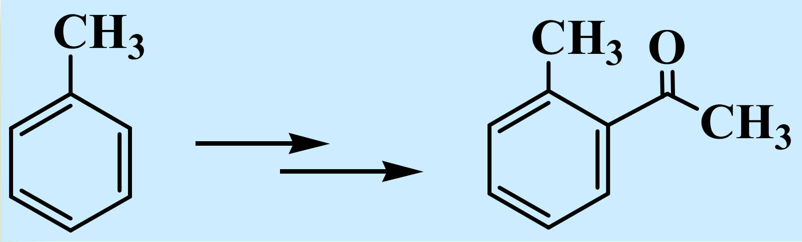


**Ex 3:**

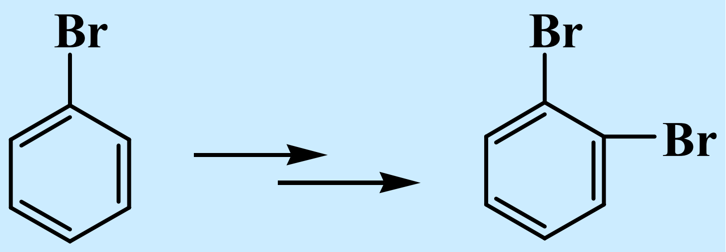
合成



**Ex 4:**



**Ex 5:**



# 7.5 SOME IMPORTANT MONOCYCLIC AROMATIC HYDROCARBONS

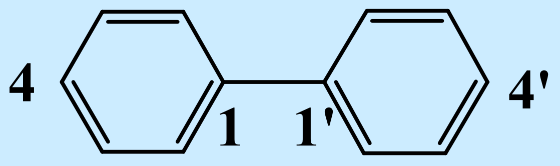
苯及其同系物都具有特殊（芳香）的气味，易燃，易溶于有机溶剂，本身也是良好的溶剂。有毒。

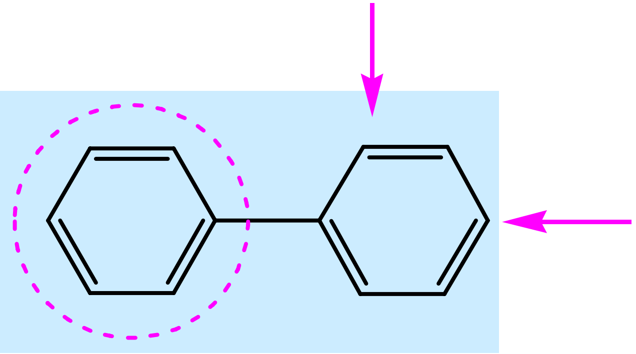
苯、甲苯、二甲苯目前都是重要的石油化工原料，用途广泛。由苯起始，可以合成橡胶、树脂、农药、合成燃料等；甲苯用来制造硝基甲苯、TNT、苯甲醛和苯甲酸等；二甲苯、乙烯苯是生产聚合物—涤纶和聚乙烯苯的重要单体。

烯烃比苯易加成，易还原

# 7.6 POLYCYCLIC AROMATICS

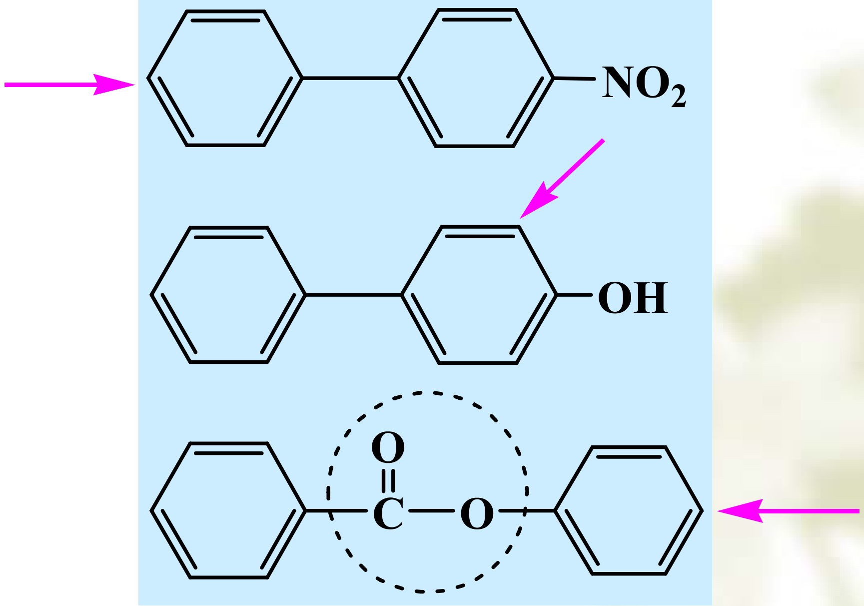
## 7.6.1 Biphenyl



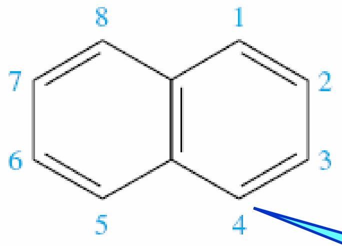


联苯比苯更容易发生亲电取代反应。

**Problem:**



# 7.6.2 Condensed Aromatics



Naphthalene

Most stable resonance form. Both rings correspond to Kekulé benzene.

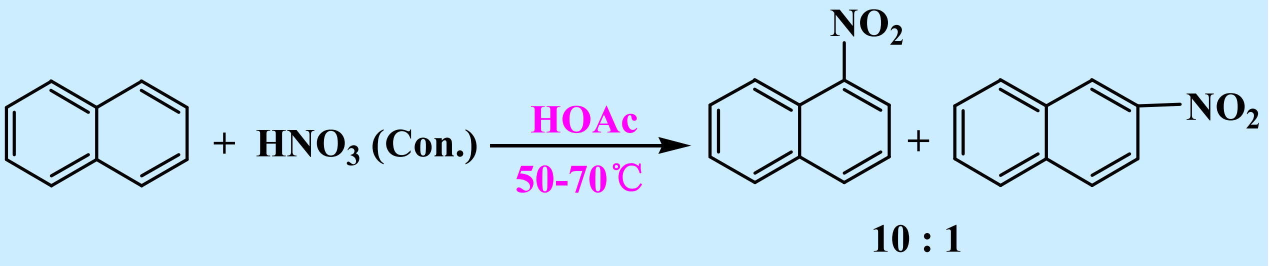
α position

Naphthalene is the most component in coal tar.

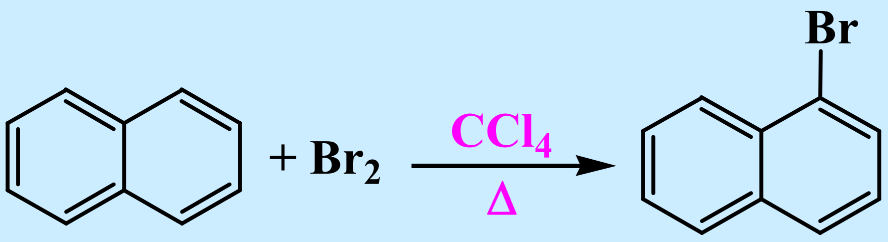
- White crystal
- Volatility

萘（$C_{10}H_8$），两个环共处于一个平面，大π体系，无定域的单、双键。相对来说，α位的电子云密度略高于β位，α位易发生亲电取代反应。

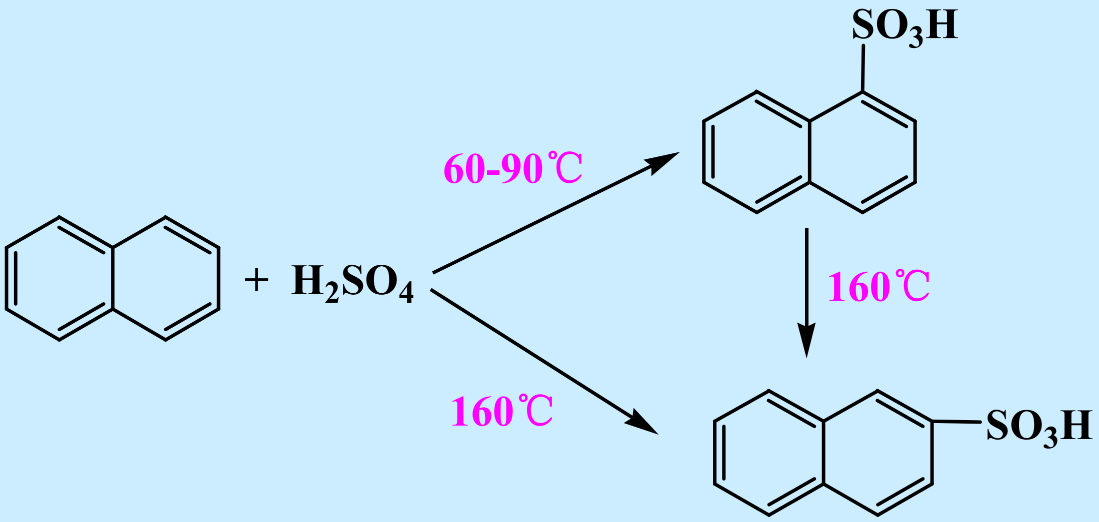
## ◆ Nitration



## ◆ Bromination



## ◆ Sulfonation



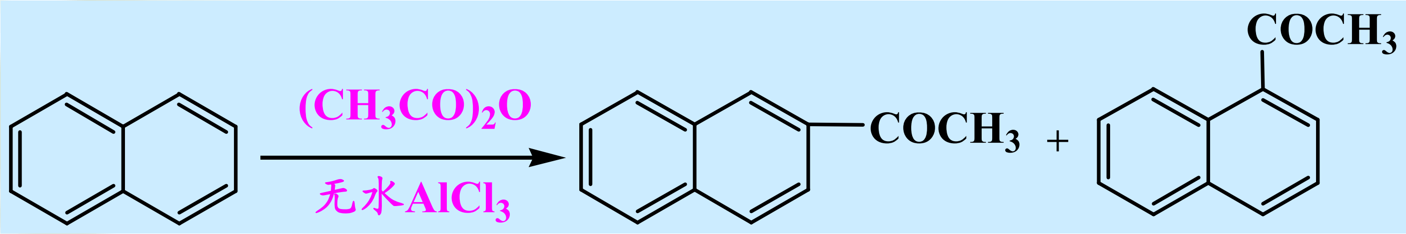
为什么磺化反应在低温时多为α位产物，高温时转化为β位产物?

首先，磺化反应是亲电取代反应，容易发生在电子云密度较高的位置。所以，反应一开始（小于60℃），就容易在电子云密度较高的α位发生，主要生成α位异构体。这时，β位磺化较困难。说明萘在α位磺化所需活化能比β位低。α位磺化速度快。此为速度控制。

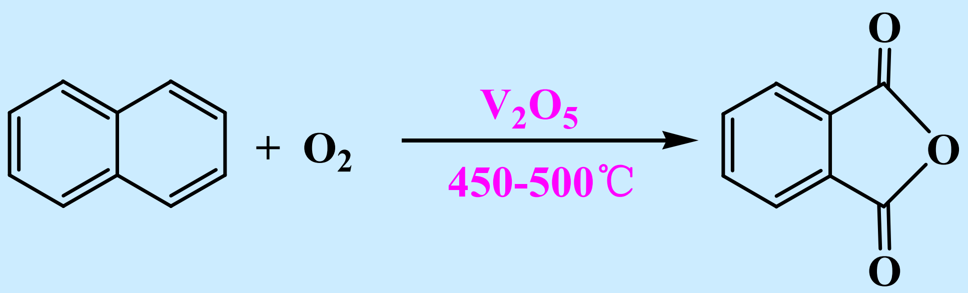
当反应温度大于160 ℃时， α位和β位磺化的速率都加快。但是对活化能较高的、生成β位异构体的反应速率的影响较大，因此又加速了β位异构体的生成。

磺化反应是可逆反应。低温时正反应速度慢，逆反应（即脱磺酸基）速度也慢。平衡尚未建立，所以低温以α位异构体为主。在高温时，正、逆反应速度都加快，由于α位异构体的分子内能高，所以逆反应速度加快， α位异构体转化了。而β位异构体的分子内能低（无位阻），脱磺酸基较难，所以生成β位异构体的反应成为主反应。此为平衡控制。

## ◆ Friedel-Crafts Reaction



## ◆ Oxidation Reaction

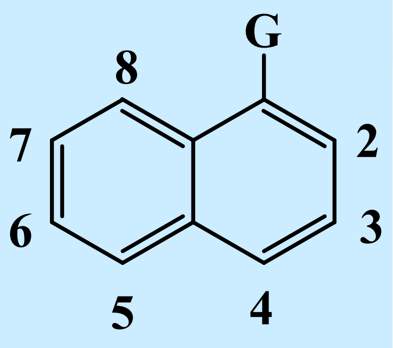


## ◆ Reduction Reaction

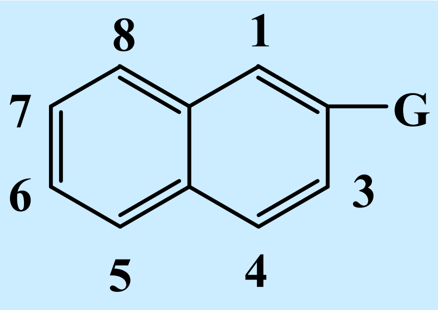
$Ni\ /H_2 \longrightarrow$ 四氢萘

$Pd-C\ /H_2 \longrightarrow$ 十氢萘

## ◆ 一取代萘的取代反应

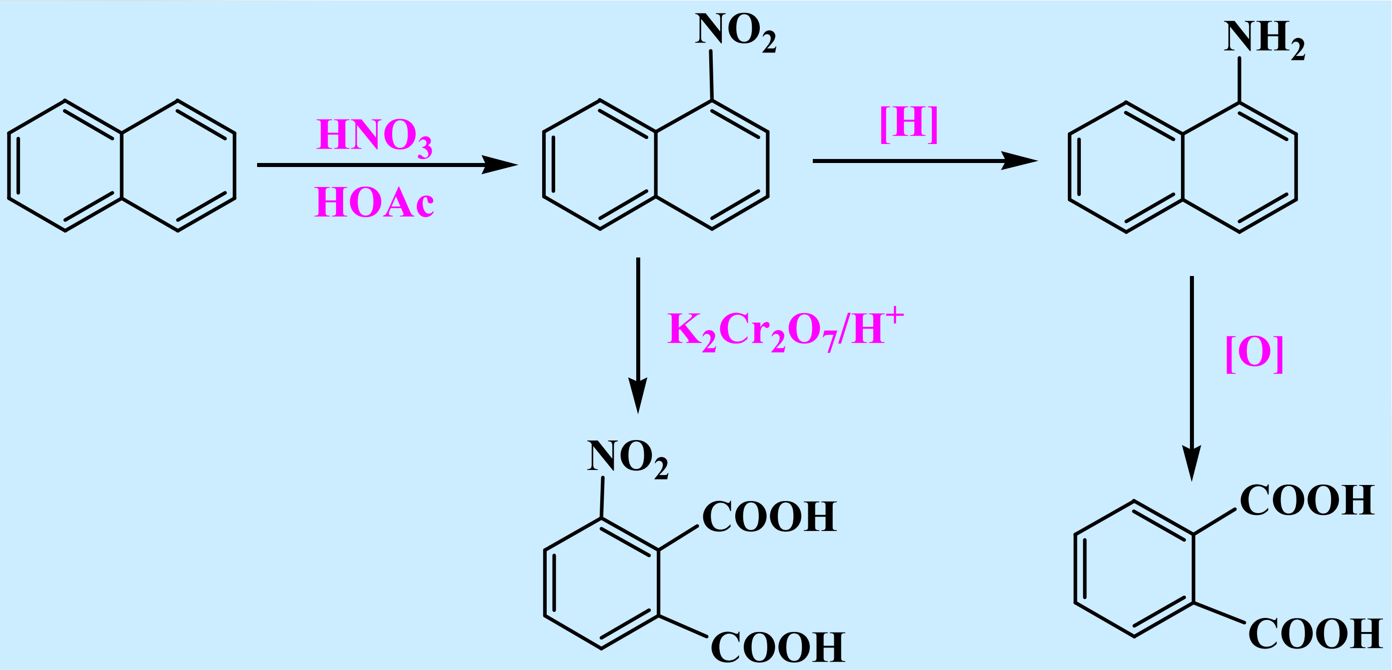


| 定位基类别 | 亲电取代的位置 |
|---|---|
| 邻、对位定位基 | 2，4位 |
| 间位定位基 | 5，8位 |



| 定位基类别 | 亲电取代的位置 |
|---|---|
| 邻、对位定位基 | 1，3位 |
| 间位定位基 | 5，6，8位 |

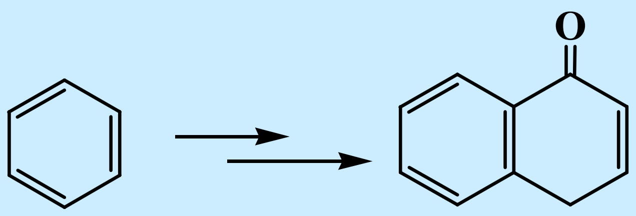
## ◆ 一取代萘的氧化反应



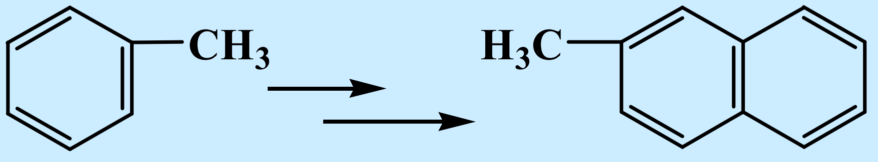
**Tip: 电子云密度较高的体系更容易发生氧化反应。**

## 7.6.3 Synthesis of Condensed Aromatics

**Ex 1.**



**Ex 2.**



**Ex 3.** 蒽的合成

# 7.7 NON-BENZENOID AROMATICS

## 7.7.1 Hückel’s Rule

**One of the early successes of molecular orbital theory occurred in 1931 when Erich Hückel discovered an interesting pattern in the π orbital energy levels of benzene, cyclobutadiene, and cyclooctatetraene. By limiting his analysis to monocyclic conjugated polyenes and restricting the structures to planar geometries, Hückel found that whether a hydrocarbon of this type was aromatic depended on its number of π electrons. He set forth what we now call *Hückel’s rule*.**

## Hückel's rule:

***Among planar, monocyclic, fully conjugated polyenes, only those possessing (4n+2) π electrons, where n is a whole number, will have special stability; that is, be aromatic.***

**Thus for this group of hydrocarbons, those with (4n+2) = 6, 10, 14, … π electrons will be aromatic. These values correspond to (4n+2) when n = 1, 2, 3, …**

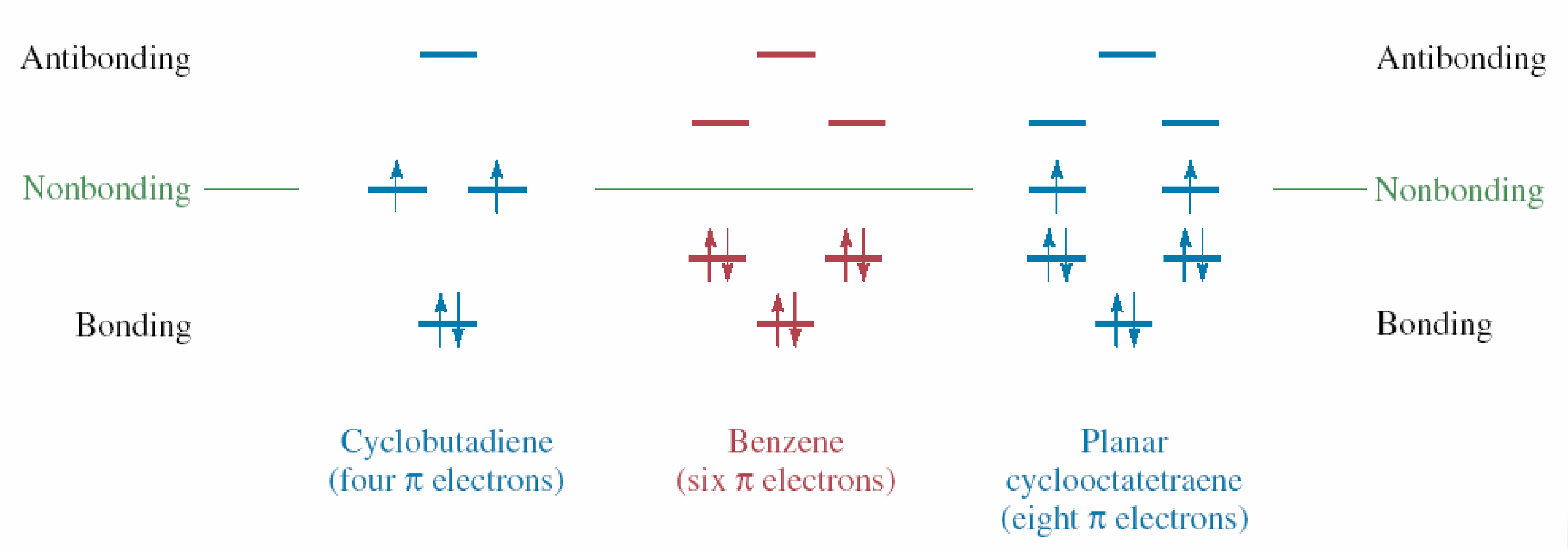
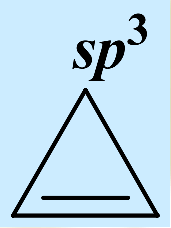
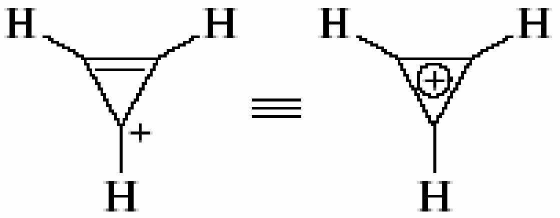


**FIGURE 7.11** **Distribution of molecular orbitals and electrons in cyclobutadiene, benzene, and planar cyclooctatetraene.**

## Cyclopropenyl cation

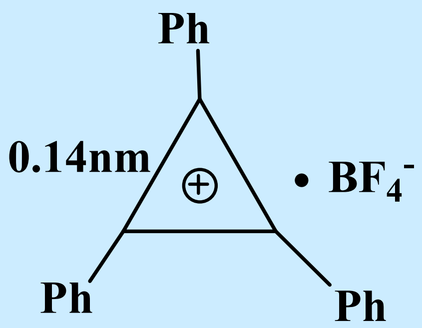


环丙烯3位碳上没有$p$轨道，分子中的2个π电子是定域的，所以整个分子不是一个共轭体系。

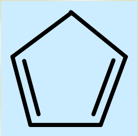


Cyclopropenyl cation

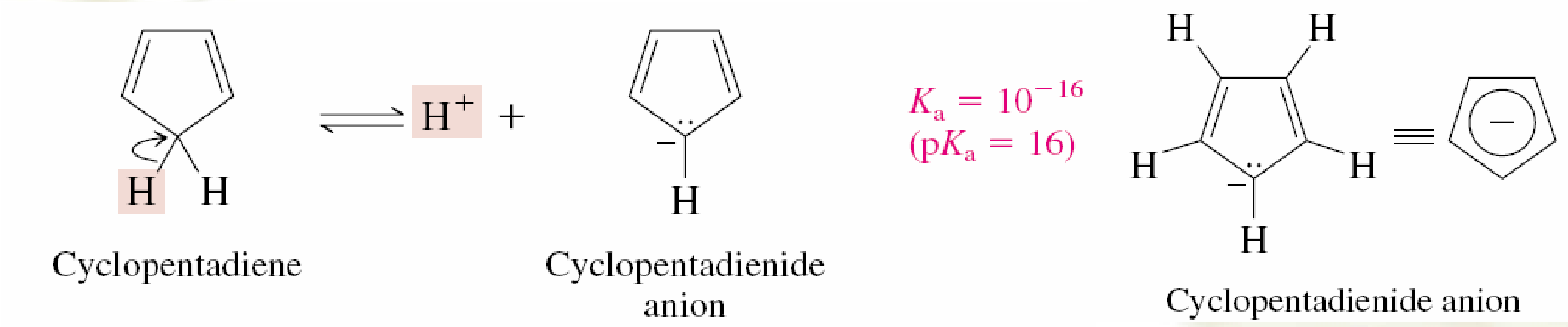
当环丙烯异裂为环丙烯正离子后，3位碳产生了一个空$p$轨道，这时分子中的π电子就可以离域，为3个碳原子的$p$轨道所共有，即3中心2电子体系。这样一个共轭体系就相当稳定，参与共轭的π电子数符合Hückel规则，是芳香性的。



## Cyclopentadienide anion

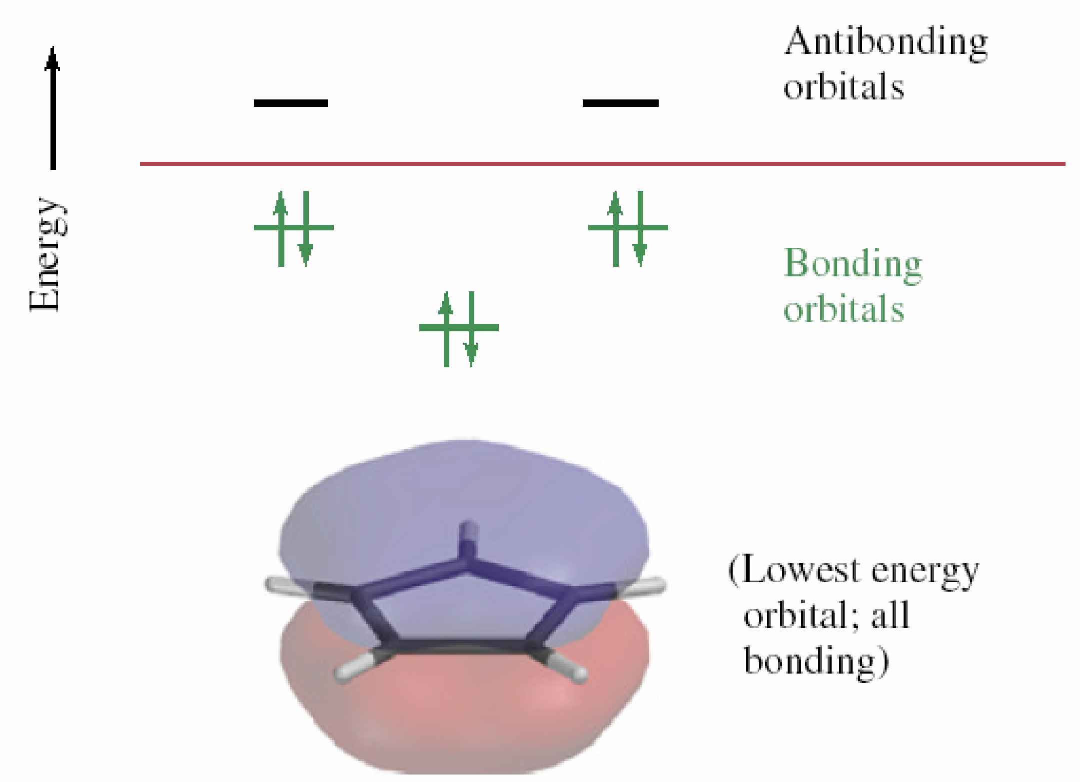


环戊二烯是4π电子体系，室温下自身D-A反应成二聚体。



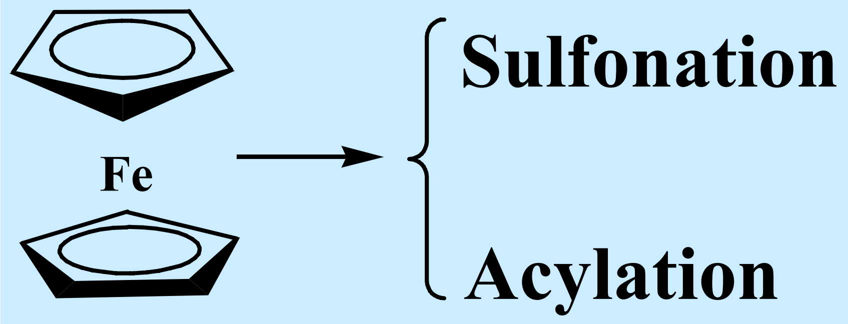
当生成环戊二烯负离子以后，碳碳键键长都为0.14nm，已没有单、双键之分，5个氢完全一样。

因为环戊二烯负离子中，参与共轭的π电子数为6个，5位碳上有充满的*p*轨道，它与另外4个碳上的*p*轨道侧面重叠，互相交盖，形成5中心6电子的芳香体系，所以特别稳定，键长平均化。



Cyclopentadiene is only a slightly weaker acid than water. The equilibrium for its deprotonation is more favorable than for other hydrocarbons because cyclopentadienide anion is aromatic.

1954年，合成了二茂铁（ferrocene）。



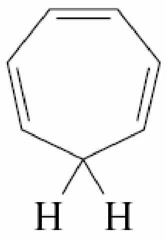
Sulfonation

Acylation

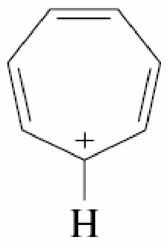
## Cycloheptatrienyl cation

Cycloheptatrienyl cation has a set of seven π molecular orbitals. Three of these are bonding and contain the six π electrons of the cation.

These six π electrons are delocalized over seven carbon atoms, each of which contributes one 2*p* orbital to a planar, monocyclic, completely conjugated system.

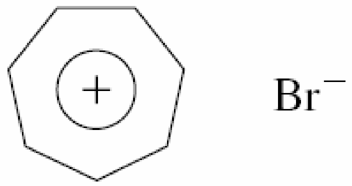


Cycloheptatriene



Cycloheptatrienyl cation (commonly referred to as *tropylium* cation)

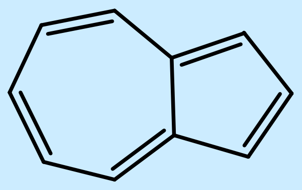
Cycloheptatriene has six  electrons in a conjugated system, but its  system does not close upon itself.



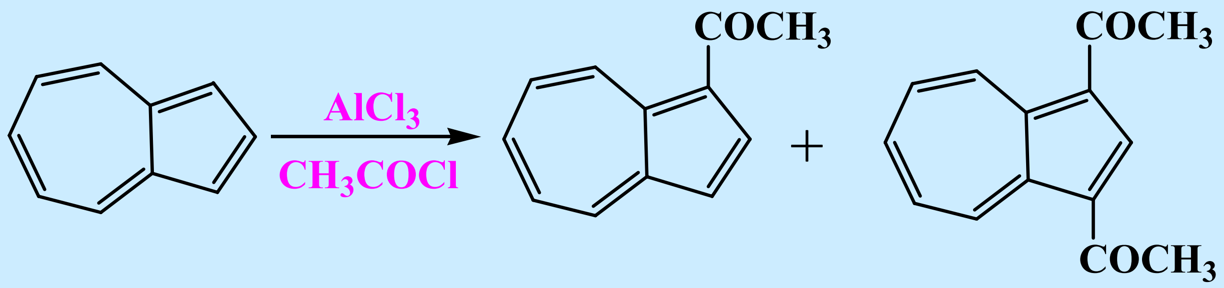
Tropylium bromide

Tropylium bromide was first prepared, but not recognized as such, in 1891. The work was repeated in 1954, and the ionic properties of tropylium bromide were demonstrated. The ionic properties of tropylium bromide are apparent in its unusually high melting point (203°C), its solubility in water, and its complete lack of solubility in diethyl ether.

- **Azulene**

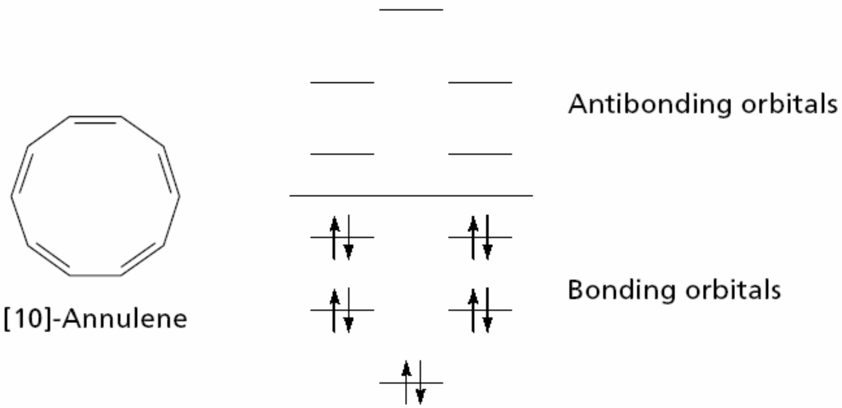


天蓝色片状固体，熔点90°C。含10个π电子，有芳香性，有明显的极性。



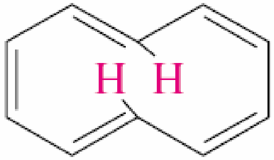
# ◆ Annulenes

## (1) [10]/[14] Annulenes



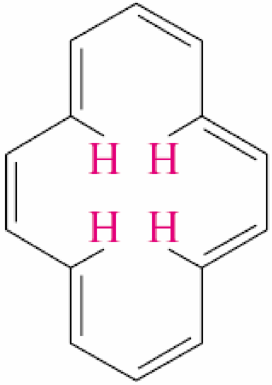
[10]-Annulene

π电子数虽然为10和14，但无芳香性



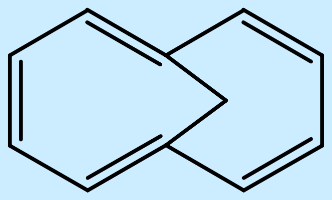
*cis,trans,cis,cis,trans*-
[10]-Annulene

Planar geometry required for aromaticity destabilized by van der Waals repulsions between indicated hydrogens



[14]-Annulene

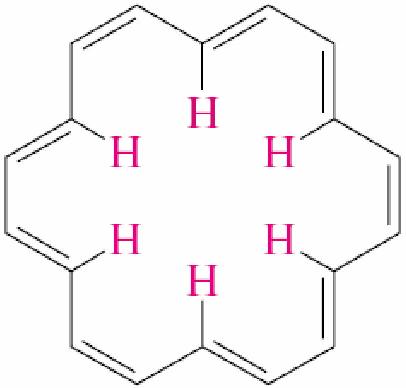
特别设计:



参与共轭的π电子数为10个，轮内两个氢原子为一个环外亚甲基所替代，环共平面，所以该分子有芳香性。

**(2) [18]Annulene**

**When the ring contains 18 carbon atoms, it is large enough to be planar while still allowing its interior hydrogens to be far enough apart that they do not interfere with one another. The [18]-annulene shown is planar or nearly so and has all its carbon–carbon bond distances in the range 137-143 pm—very much like those of benzene.**

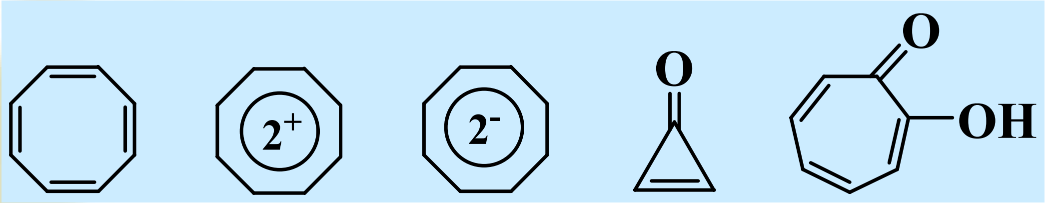


[18]-Annulene

No serious repulsions among six interior hydrogens; molecule is planar and aromatic.

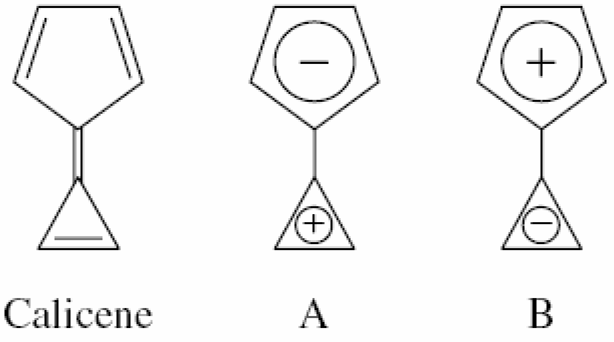
非苯芳烃的定义：没有苯环结构，但是π电子数符合4n+2规则，分子共平面，不易加成，易取代的烃。

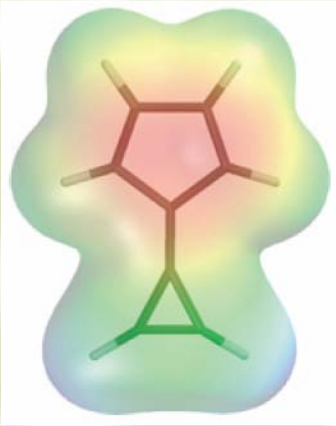
**Problem 1:** 判断下列结构是否具有芳香性。



无　有　有　有　有

**Problem 2:** Calicene is an unusually polar hydrocarbon. Which of the dipolar resonance forms, A or B, better corresponds to the electron distribution in the molecule? Why is this resonance form more important than the other?





# 7.8 CARBON CLUSTERS, FULLERENES, AND NANOTUBES

**The 1996 Nobel Prize in chemistry was awarded to Professors Harold W. Kroto (University of Sussex), Robert F. Curl, and Richard E. Smalley (both of Rice University) for groundbreaking work involving elemental carbon that opened up a whole new area of chemistry.**

**The work began when Kroto wondered whether polyacetylenes of the type $HC\equiv C\text{-}(C\equiv C)_n\text{-}C\equiv CH$ might be present in interstellar space（星际空间）and discussed experiments to test this idea while visiting Curl and Smalley at Rice in the spring of 1984.**

**When the experiment was carried out in the fall of 1985, Kroto, Curl, and Smalley found that under certain conditions a species with a molecular formula of $C_{60}$ was present in amounts much greater than any other.**

**On speculating about what $C_{60}$ might be, they concluded that its most likely structure is the *spherical cluster of carbon atoms* shown in Figure 7.8 and suggested it be called *buckminsterfullerene* because of its similarity to the geodesic domes popularized by the American architect and inventor R. Buckminster Fuller.**

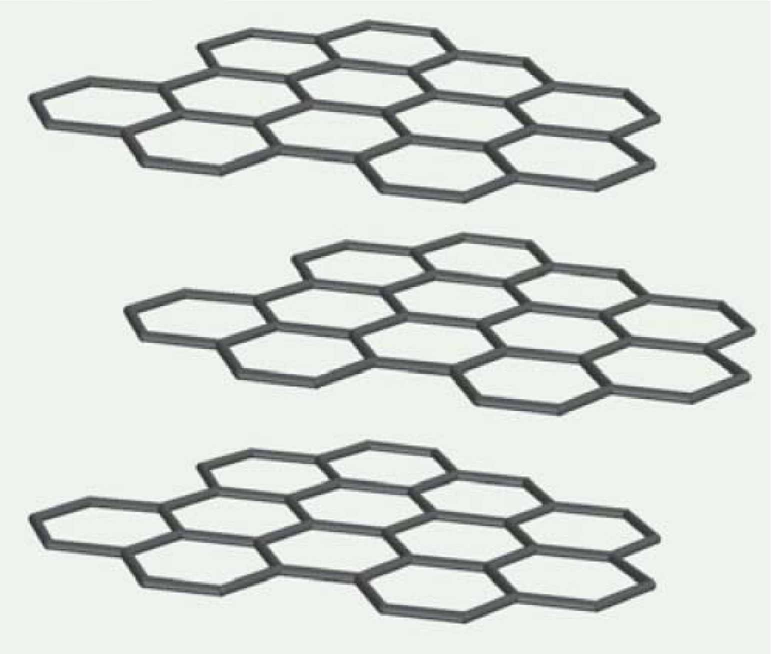


**FIGURE 7.7** Graphite is a form of elemental carbon composed of parallel sheets of fused benzene-like rings.

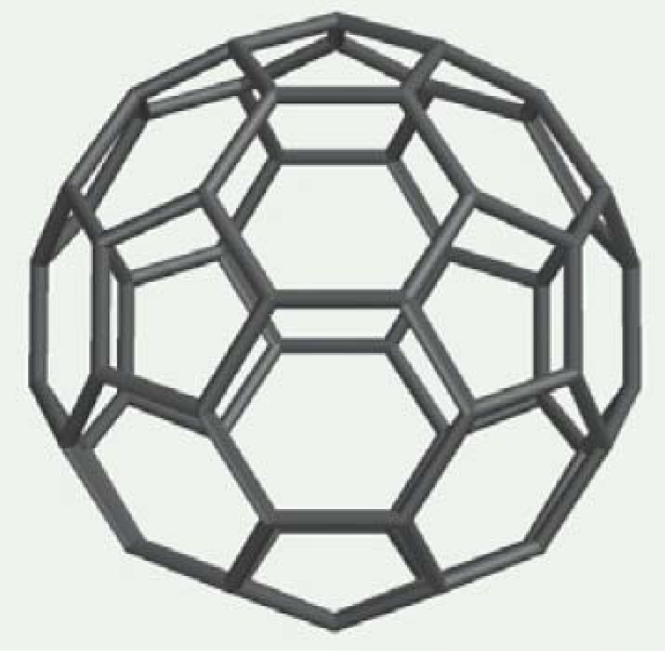


**FIGURE 7.8** Buckminsterfullerene ($C_{60}$). Note that all carbons are equivalent and that no five-membered rings are adjacent to one another.

**All of the carbon atoms in buckminsterfullerene are equivalent and are $sp^2$-hybridized; each one simultaneously belongs to one five-membered ring and two benzene-like six-membered rings. The strain caused by distortion of the rings from coplanarity is equally distributed among all of the carbons.**

**A quantum leap in fullerene research came in 1990 when a team led by Wolfgang Krätschmer of the Max Planck Institute for Nuclear Physics in Heidelberg and Donald Huffman of the University of Arizona successfully prepared buckminsterfullerene in amounts sufficient for its isolation, purification and detailed study.**

**It is now clear that $C_{60}$ is a relatively reactive substance, reacting with many substances toward which benzene itself is inert. Many of these reactions are characterized by the addition of nucleophilic substances to buckminsterfullerene, converting *sp*$^2$-hybridized carbons to *sp*$^3$-hybridized ones and reducing the overall strain.**

The field of fullerene chemistry expanded in an unexpected direction in 1991 when **Sumio Iijima** of the NEC Fundamental Research Laboratories in Japan discovered fibrous carbon clusters in one of his fullerene preparations. This led, within a short time, to substances of the type portrayed in Figure 7.9 called ***single-walled nanotubes***.

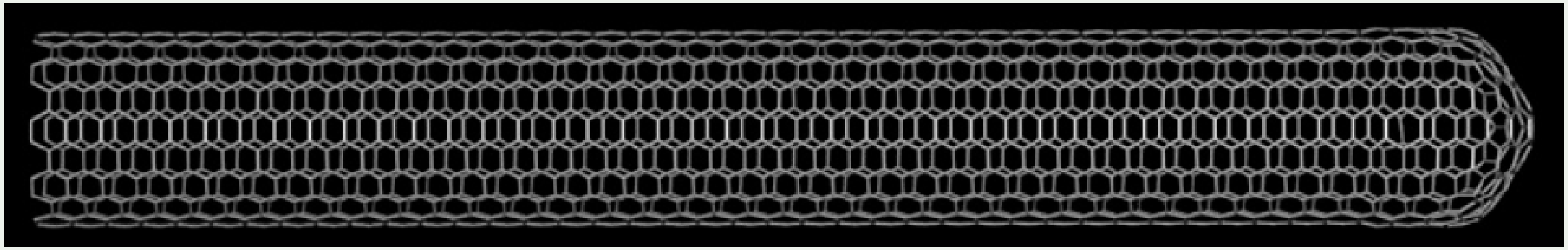


**FIGURE 7.9** A portion of a nanotube. The closed end is approximately one half of a buckyball. The main length cannot close as long as all of the rings are hexagons.

**Thus far, the importance of carbon cluster chemistry has been in the discovery of new knowledge. Many scientists feel that the earliest industrial applications of the fullerenes will be based on their novel electrical properties. Buckminster-fullerene is an insulator（绝缘体）, but has a high electron affinity（电子亲合性） and is a *superconductor* in its reduced form.**

**Nanotubes have aroused a great deal of interest for their electrical properties and as potential sources of carbon fibers of great strength.**