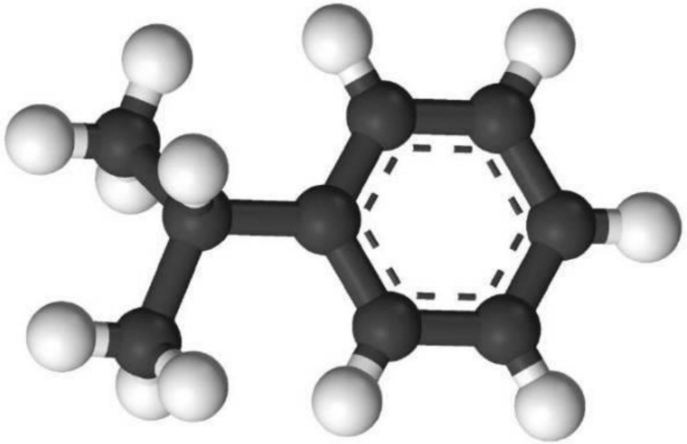
西安交通大學化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Organic Chemistry

西安交通大學化学学院
XI'AN JIAOTONG UNIVERSITY SCHOOL OF CHEMISTRY

Chapter 9

Benzene and Its Derivatives



9.1 What Is the Structure of Benzene?

9.2 What Is Aromaticity?

9.3 How Are Benzene Compounds Named, and What Are Their Physical Properties?

9.4 What Is the Benzylic Position, and How Does It Contribute to Benzene Reactivity?

9.5 What Is Electrophilic Aromatic Substitution?

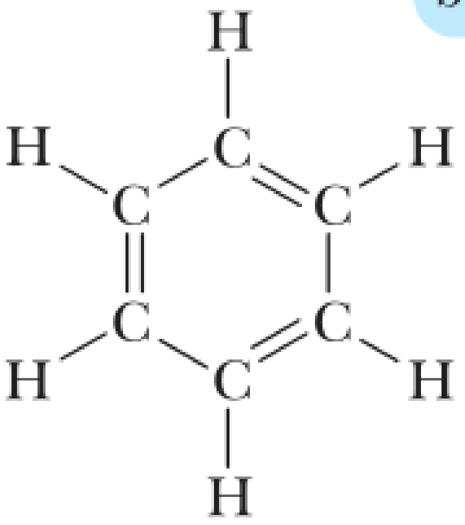
9.6 What Is the Mechanism of Electrophilic Aromatic Substitution?

9.7 How Do Existing Substituents on Benzene Affect Electrophilic Aromatic Substitution?

9.8 What Are Phenols?

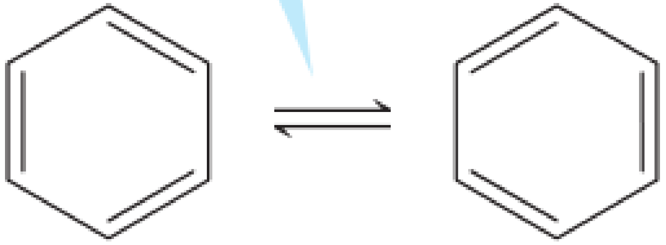
9.1 What Is the Structure of Benzene?

A. Kekulé's Model of Benzene



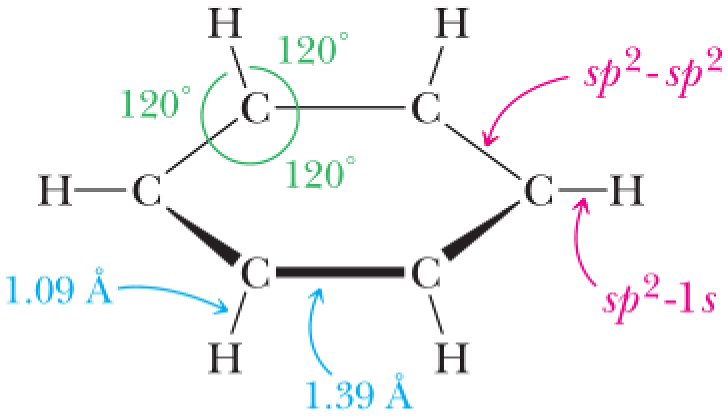
A Kekulé structure,
showing all atoms

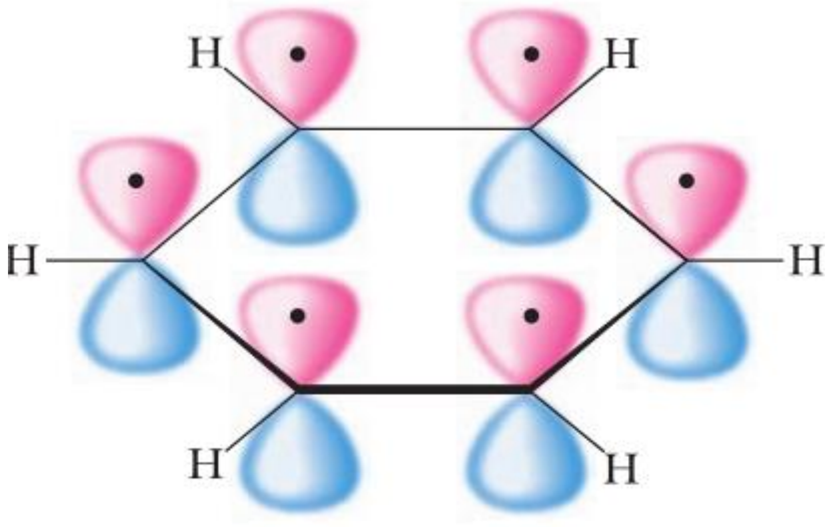
Kekulé incorrectly believed that the double bonds of benzene rapidly shift back and forth



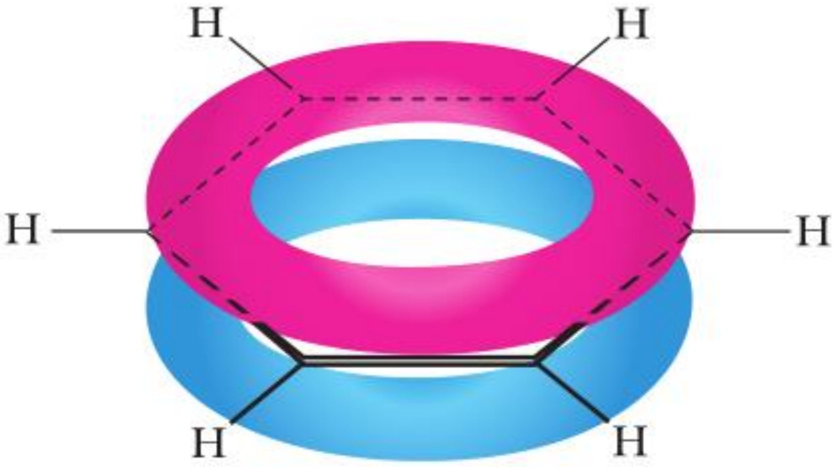
Kekulé structures
as line-angle formulas

B. The orbital overlap Model of Benzene



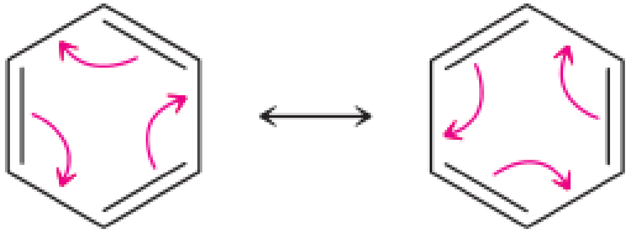


(a)



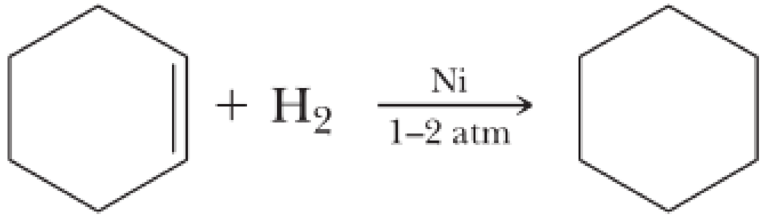
(b)

C. The Resonance Model of Benzene

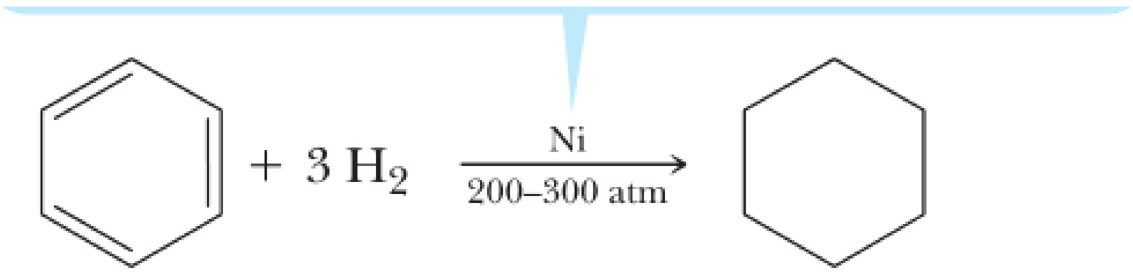


Benzene as a hybrid of two equivalent contributing structures

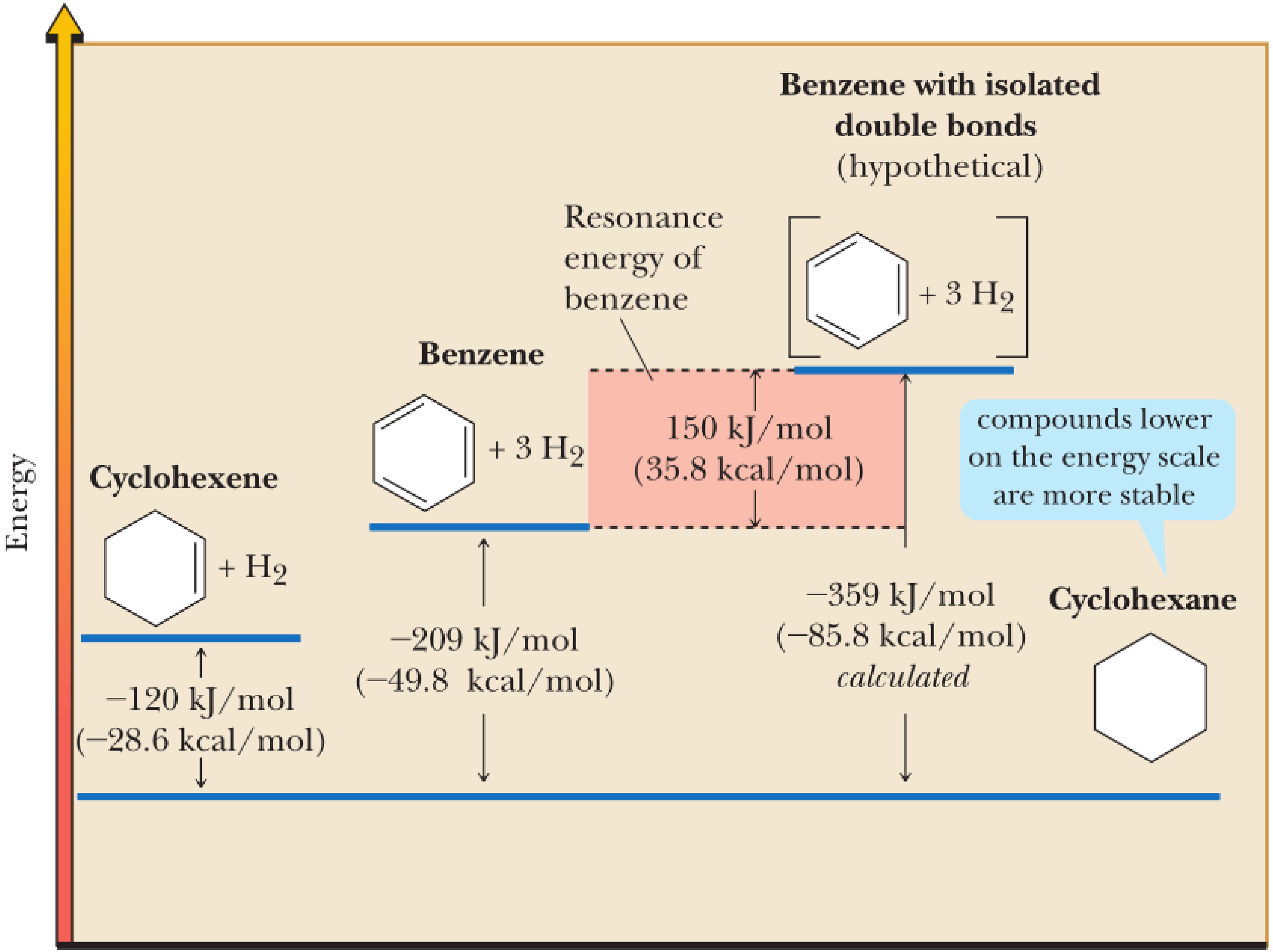
D. The Resonance Energy of Benzene

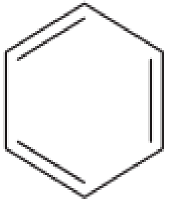


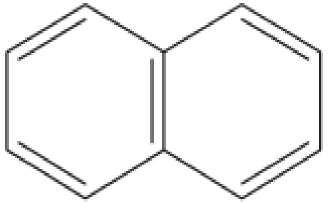
$\Delta H^0 = -120$ kJ/mol
(−28.6 kcal/mol)

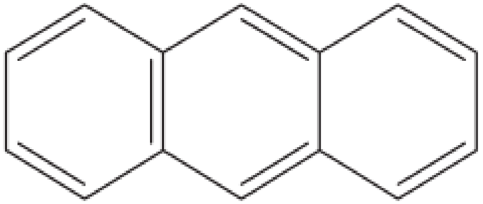


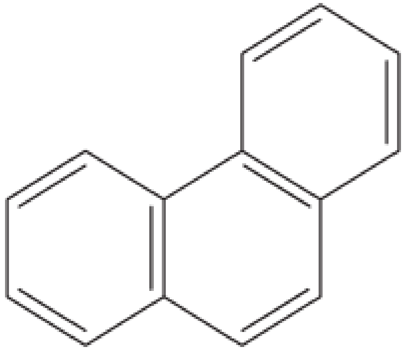
$\Delta H^0 = -209$ kJ/mol
(−49.8 kcal/mol)


Energy
Benzene with isolated double bonds (hypothetical)
+ 3 H_2
Resonance energy of benzene
Benzene
+ 3 H_2
150 kJ/mol
(35.8 kcal/mol)
compounds lower on the energy scale are more stable
Cyclohexene
+ H_2
−120 kJ/mol
(−28.6 kcal/mol)
−209 kJ/mol
(−49.8 kcal/mol)
−359 kJ/mol
(−85.8 kcal/mol)
calculated
Cyclohexane







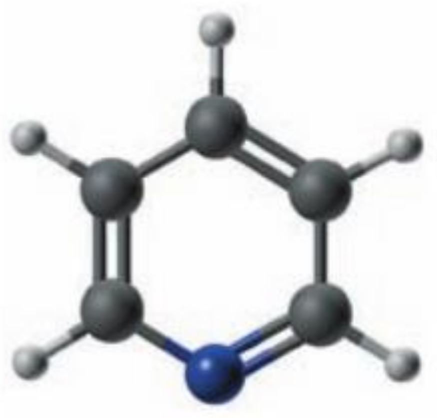


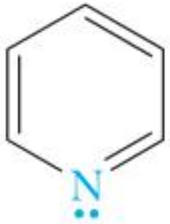
	Benzene	Naphthalene	Anthracene	Phenanthrene
Resonance energy [kJ/mol (kcal/mol)]	150 (35.8)	255 (60.9)	347 (82.9)	381 (91.0)

9.2 What Is Aromaticity?

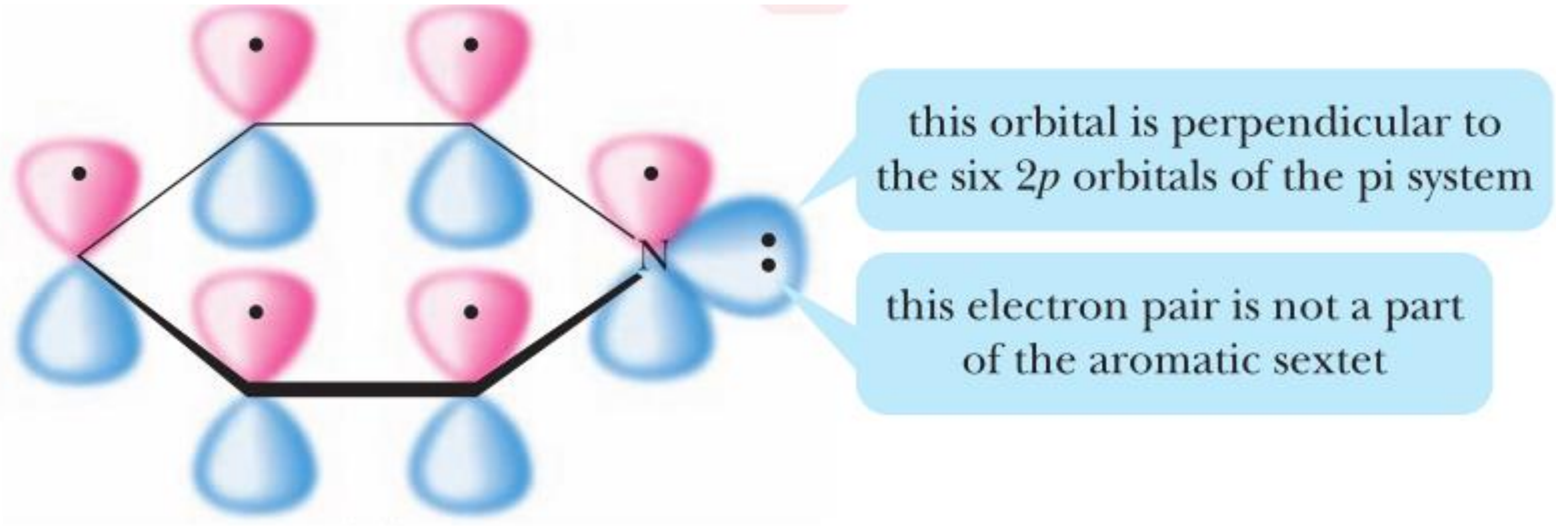
Hückel's criteria are summarized as follows. To be aromatic, a ring must

1. Have one 2*p* orbital on each of its atoms.
2. Be planar or nearly planar, so that there is continuous overlap or nearly continuous overlap of all 2*p* orbitals of the ring.
3. Have 2, 6, 10, 14, 18, and so forth pi electrons in the cyclic arrangement of 2p orbitals. (4*n*+2)





Pyridine

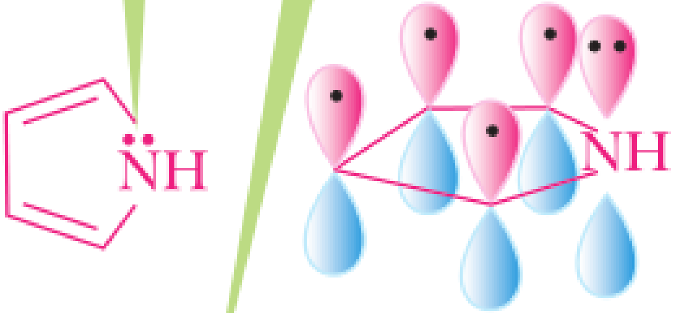


this orbital is perpendicular to the six 2*p* orbitals of the pi system

this electron pair is not a part of the aromatic sextet

Pyridine

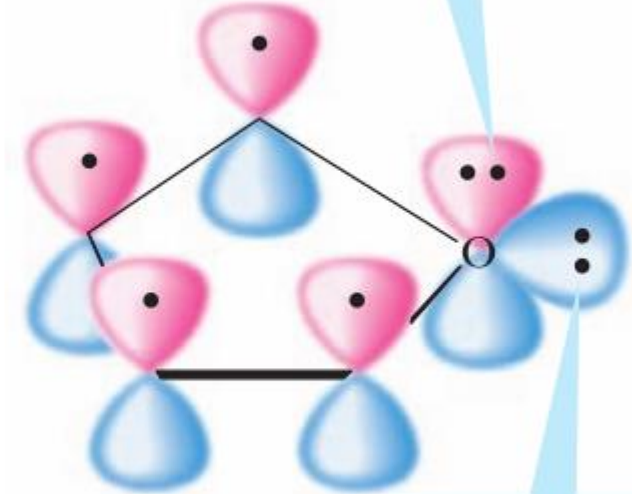
a nitrogen atom with three single bonds is normally *sp*^{3} hybridized. However, to determine if the lone pair of electrons belongs in the pi system, we must change the hybridization of nitrogen to *sp*^{2} so that the electrons can reside in a *p* orbital



The lone pair on nitrogen gives the pi system six electrons. Therefore, the nitrogen should be *sp*^{2} hybridized.

The lone pair gives the pi system eight electrons. Therefore, the nitrogen should not be *sp*^{2} hybridized.

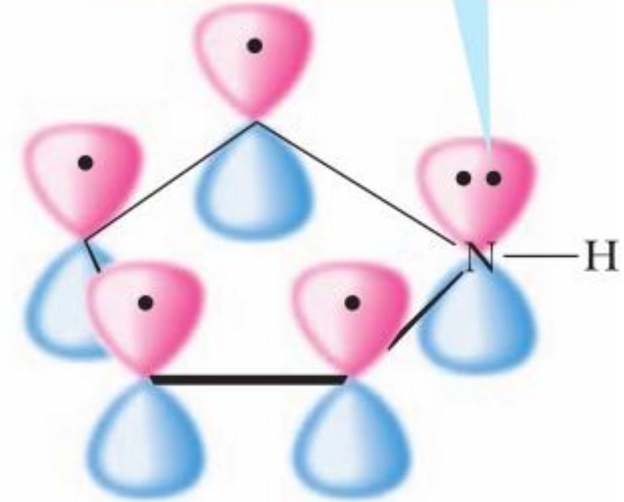
this electron pair is in a *p* orbital and is a part of the aromatic sextet



Furan

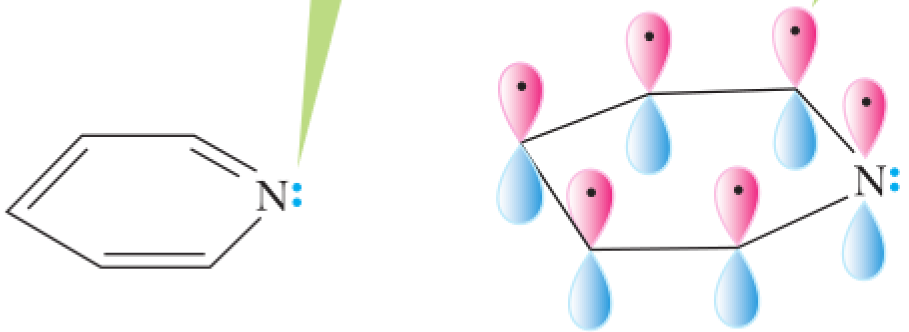
this electron pair is in an *sp*² orbital and is not a part of the aromatic sextet

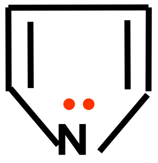
this electron pair is in a *p* orbital and is a part of the aromatic sextet



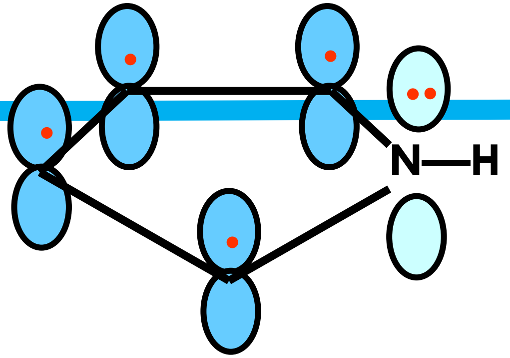
Pyrrole

this lone pair of electrons cannot be part of the aromatic pi system because the nitrogen is already sharing two electrons through the pi bond with carbon

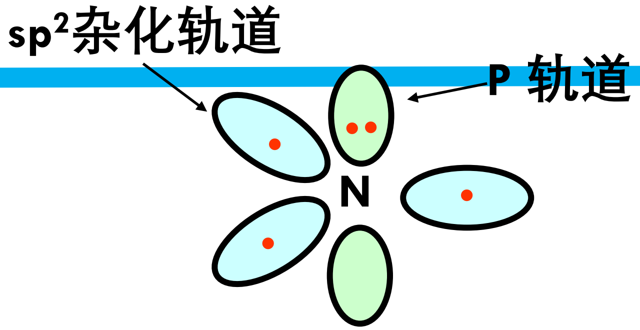




吡咯



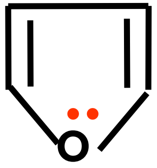
吡咯的分子结构



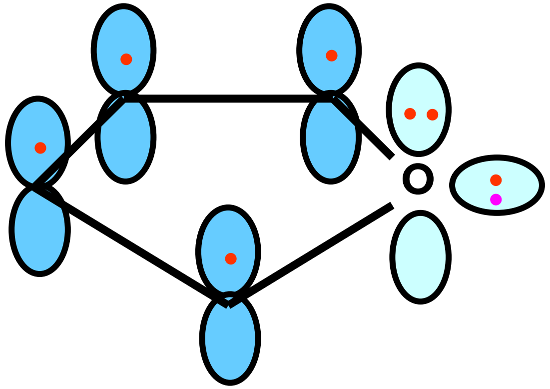
N原子杂化轨道

体系中π
电子数：
4 + 2 = 6

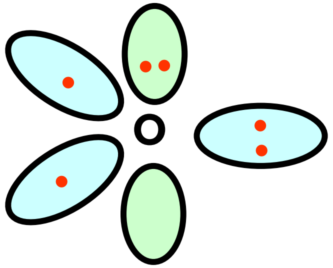
五中心六电子（富电子环）



呋喃

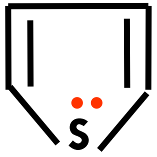


呋喃的分子结构

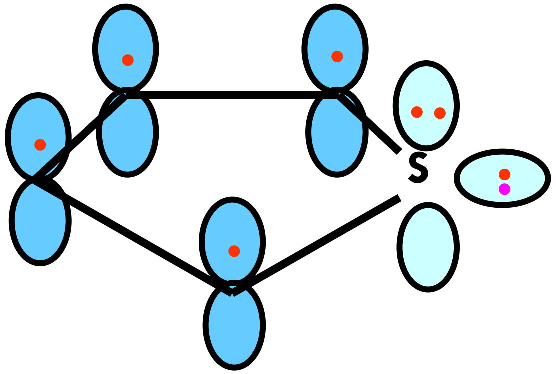


O原子杂化轨道

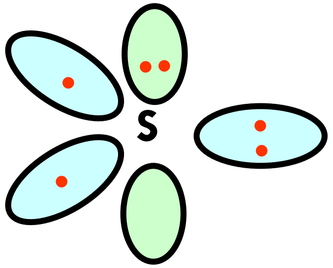
符合休克尔 4n + 2 规则，故三个杂环均具有芳香性



噻吩



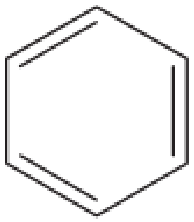
噻吩的分子结构

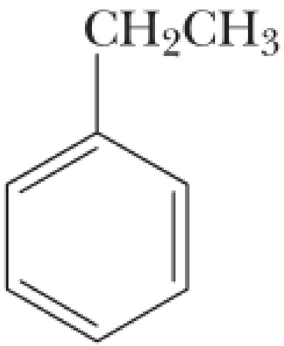


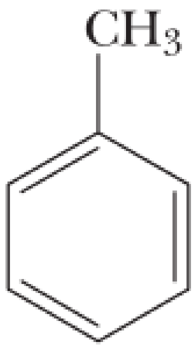
S原子杂化轨道

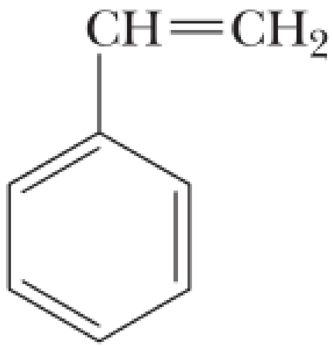
9.3 How Are Benzene Compounds Named, and What Are Their Physical Properties?

A. Monosubstituted Benzenes（一取代苯）



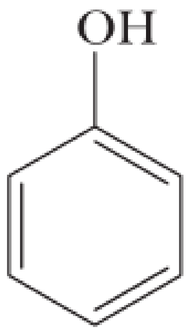






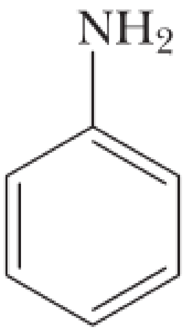
	Benzene	Ethylbenzene	Toluene	Styrene
mp (°C)	5.5	−95	−93	−31
bp (°C)	80	136	110	145

苯酚



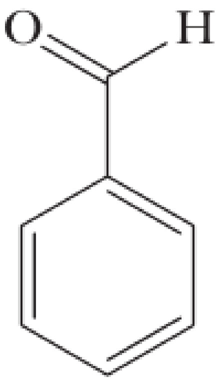
Phenol

苯胺



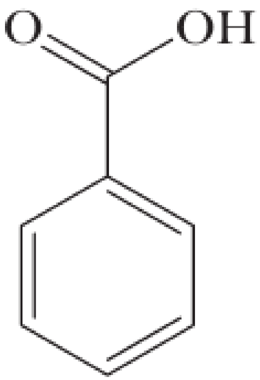
Aniline

苯甲醛



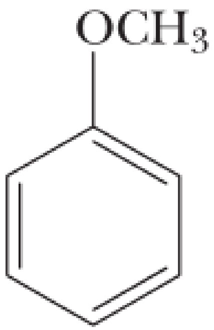
Benzaldehyde

苯甲酸



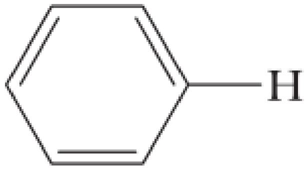
Benzoic acid

苯甲醚

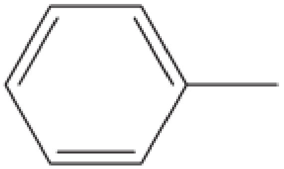


Anisole

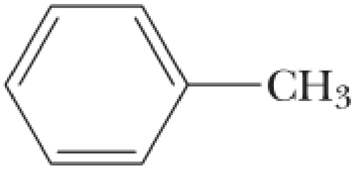
mp (°C)	41	−6	−26	123	−37
bp (°C)	182	184	178	249	154



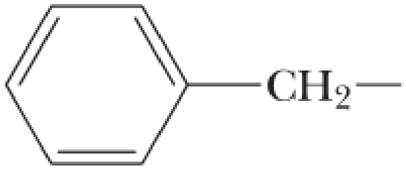
Benzene



Phenyl group (Ph)

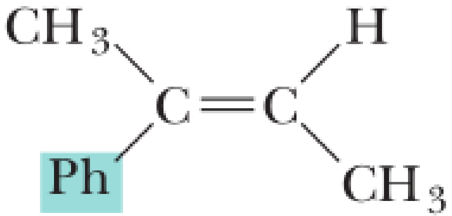


Toluene



Benzyl group (Bn)

苯甲基/卞基



(Z)-2-Phenyl-2-butene

$PhCH_2CH_2OH$

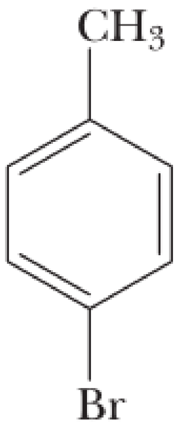
2-Phenylethanol

$PhCH_2Cl$

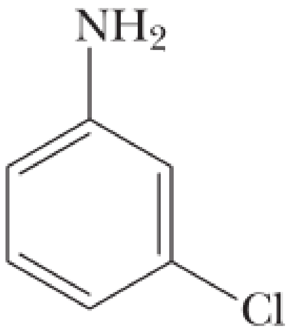
Benzyl chloride

苄基氯/苯甲烷

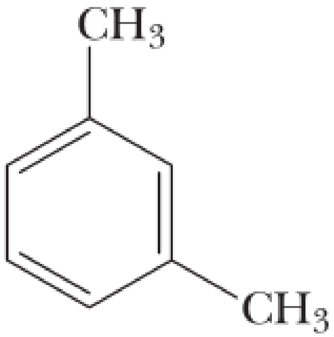
B. Disubstituted Benzenes



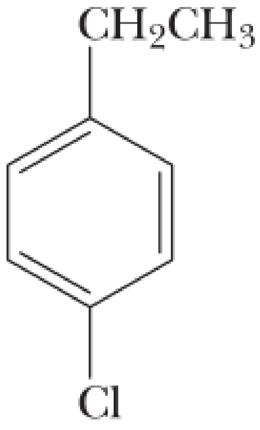
4-Bromotoluene
(*p*-Bromotoluene)



3-Chloroaniline
(*m*-Chloroaniline)



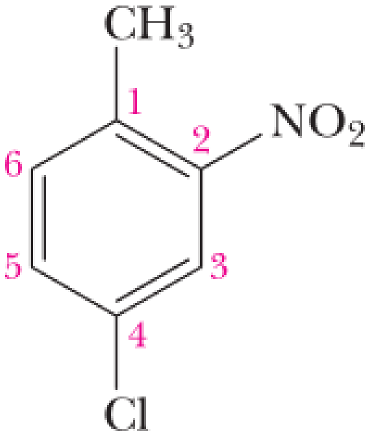
1,3-Dimethylbenzene
(*m*-Xylene)



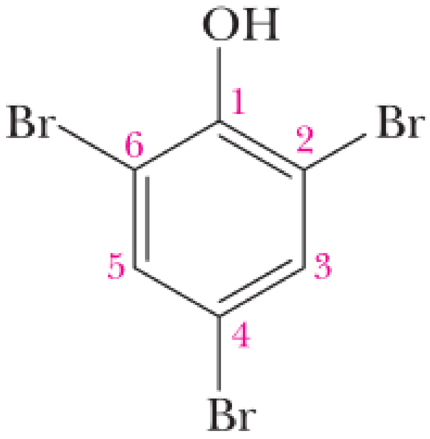
1-Chloro-4-ethylbenzene
(*p*-Chloroethylbenzene)

ortho (o): Refers to groups occupying positions 1 and 2 on a benzene ring.
Meta (m): Refers to groups occupying positions 1 and 3 on a benzene ring.
Para (p): Refers to groups occupying positions 1 and 4 on a benzene ring.

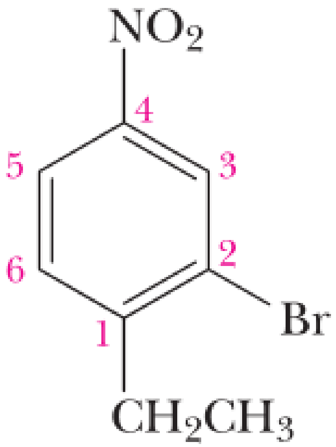
C. Polysubstituted Benzenes



4-Chloro-2-nitrotoluene



2,4,6-Tribromophenol



2-Bromo-1-ethyl-4-nitrobenzene

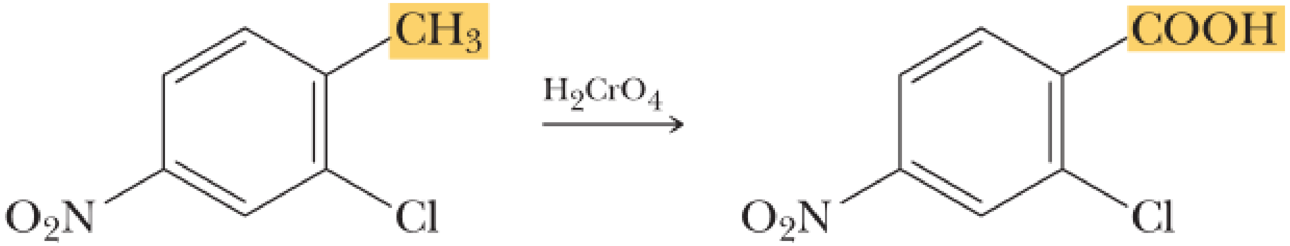
4-氯-2-硝基甲苯

2,4,6-三溴苯酚

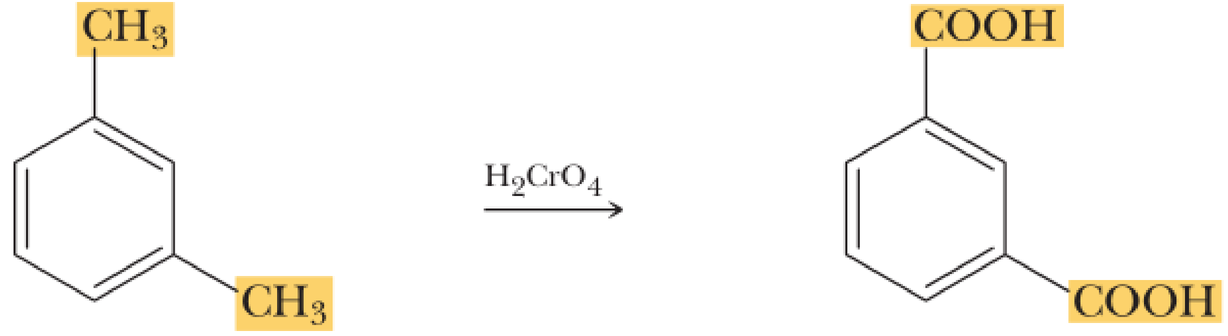
2-溴-1-乙基-4-硝基苯

9.4 What Is the Benzylic Position, and How Does It Contribute to Benzene Reactivity?

苯环侧链的氧化

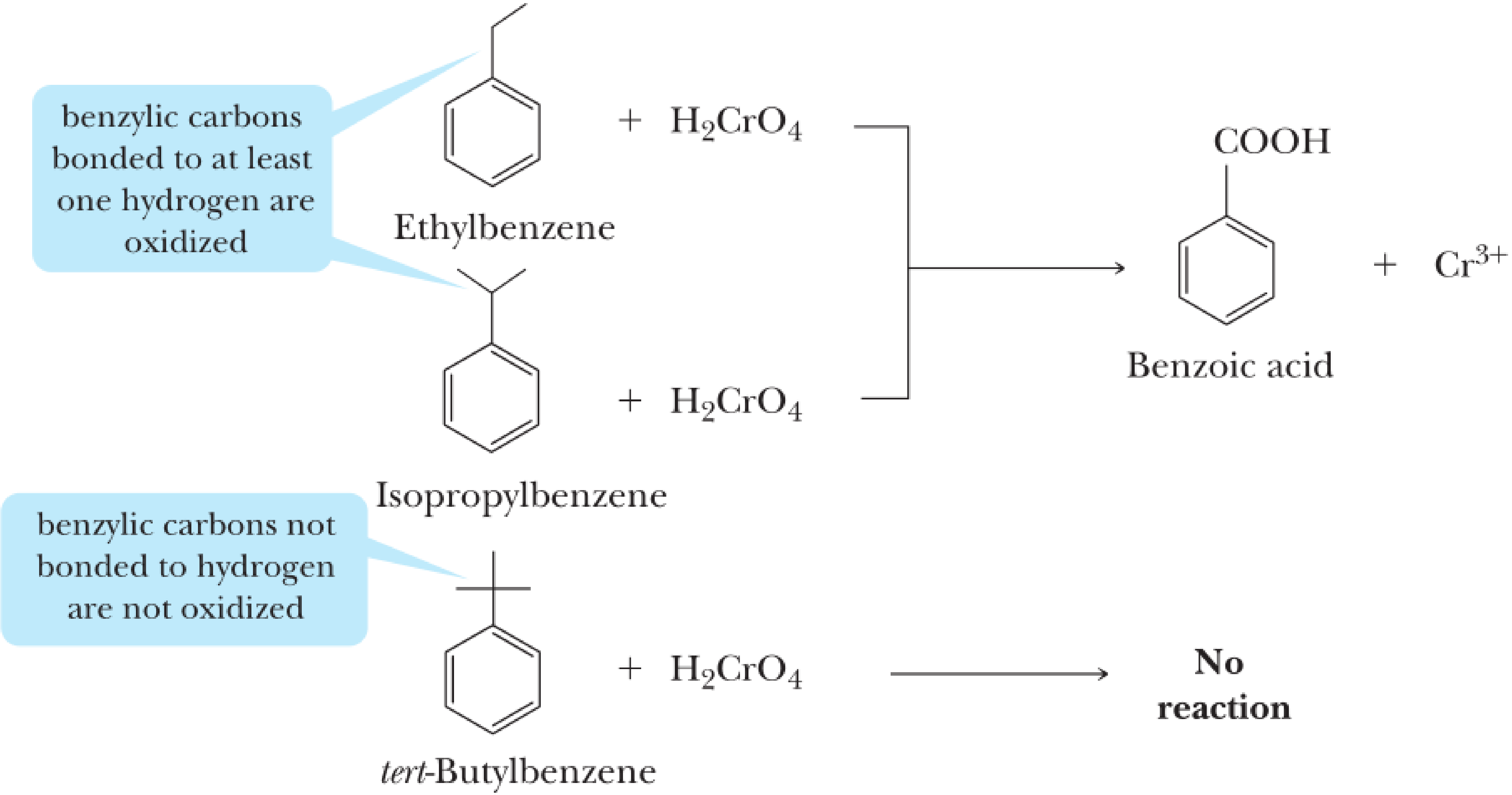


2-Chloro-4-nitrotoluene → 2-Chloro-4-nitrobenzoic acid



m-Xylene → 1,3-Benzenedicarboxylic acid
(Isophthalic acid)

苯环侧链的氧化： 有α-H的烷基苯



benzylic carbons bonded to at least one hydrogen are oxidized

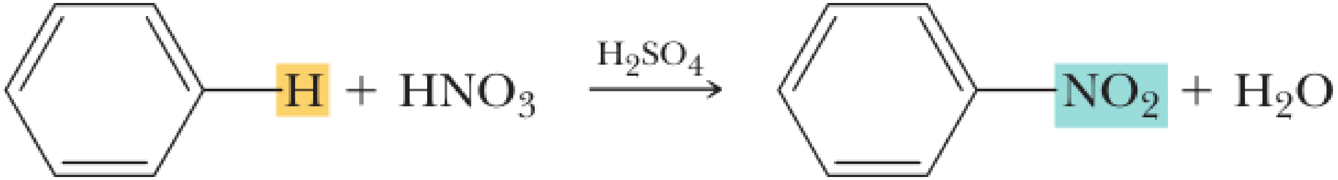
benzylic carbons not bonded to hydrogen are not oxidized

9.5 What Is Electrophilic Aromatic Substitution?（苯的亲电取代）

Halogenation:

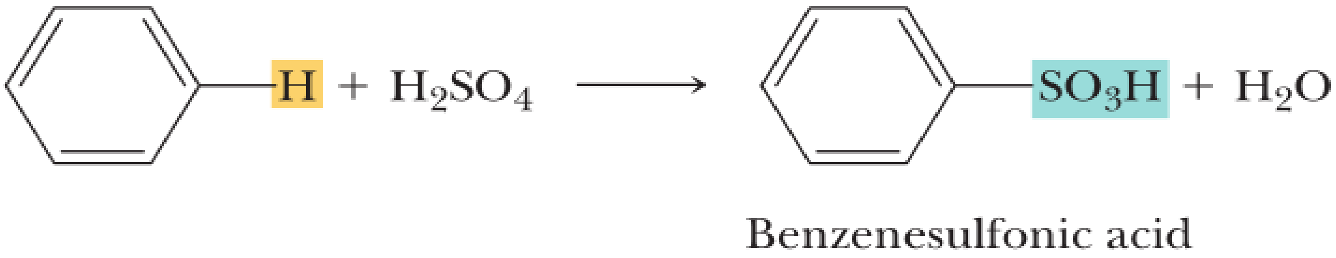
Chlorobenzene

Nitration:

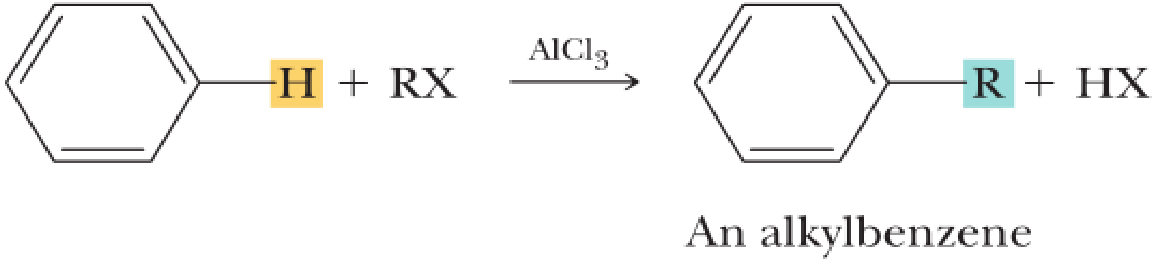


Nitrobenzene

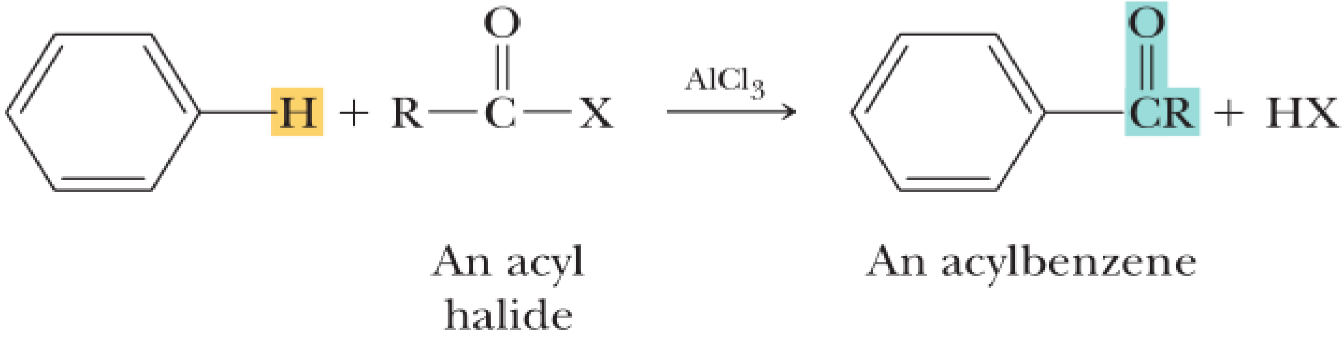
Sulfonation:



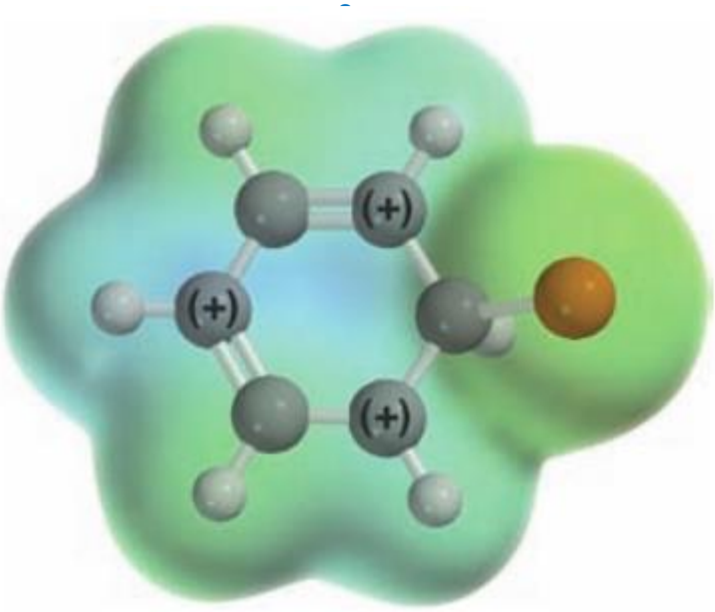
Alkylation:



Acylation:



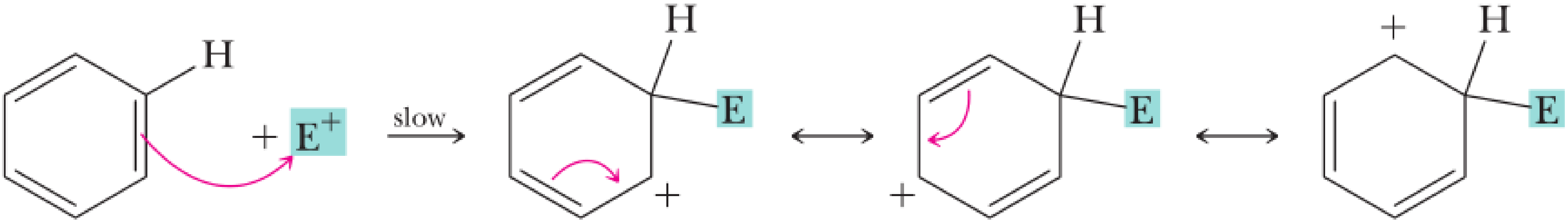
9.6 What Is the Mechanism of Electrophili Substitution?



Step 1: Generation of the electrophile.

$$\text{Reagent(s)} \longrightarrow E^+$$

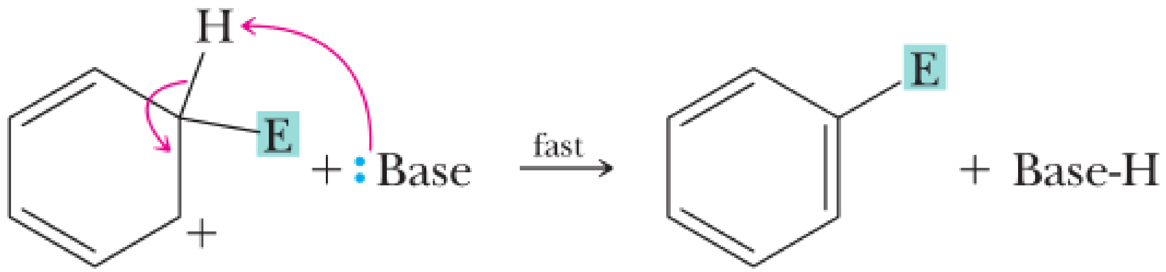
Step 2: Reaction of a nucleophile and an electrophile to form a new covalent bond.



(the nucleophile)

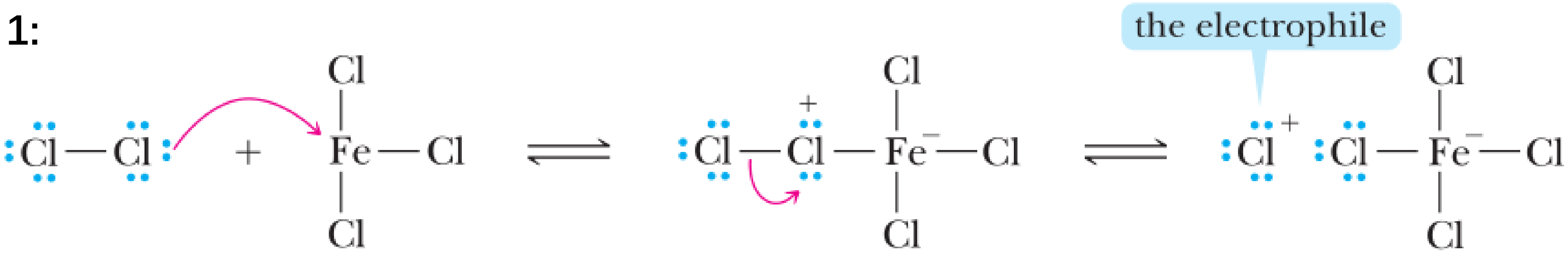
Resonance-stabilized cation intermediate

Step 3: Take a proton away. Proton transfer to a base to regenerate the aromatic ring:



A. Chlorination and Bromination

Step 1:



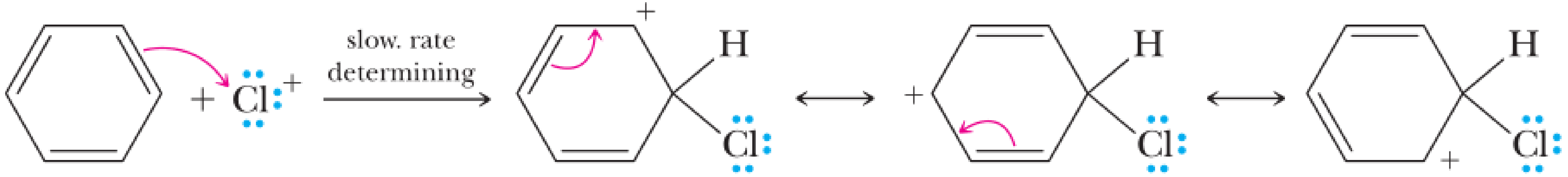
Chlorine
(a Lewis base)

Ferric chloride
(a Lewis acid)

A molecular complex with
a positive charge on chlorine
and a negative charge on iron

An ion pair containing
a chloronium ion

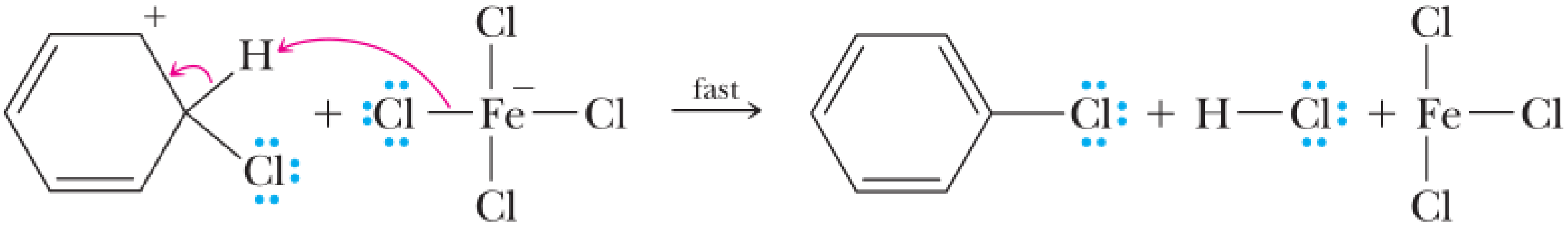
Step 2:



(the nucleophile)

Resonance-stabilized cation intermediate

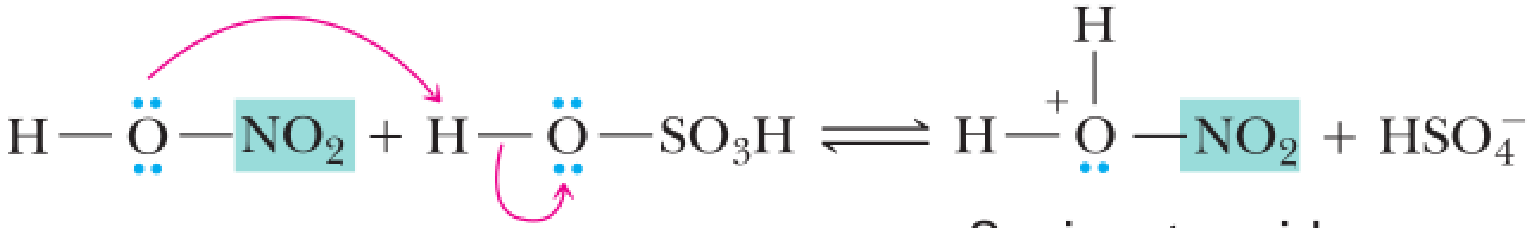
Step 3:



Cation intermediate

Chlorobenzene

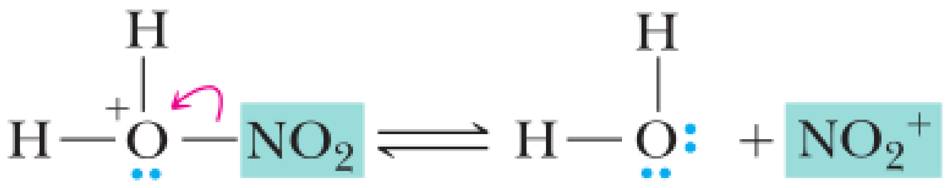
B. Nitration and Sulfonation



$$H-\ddot{O}-NO_2 + H-\ddot{O}-SO_3H \rightleftharpoons H-\overset{H}{\overset{|}{\overset{+}{O}}}-NO_2 + HSO_4^-$$

Nitric acid

Conjugate acid of nitric acid

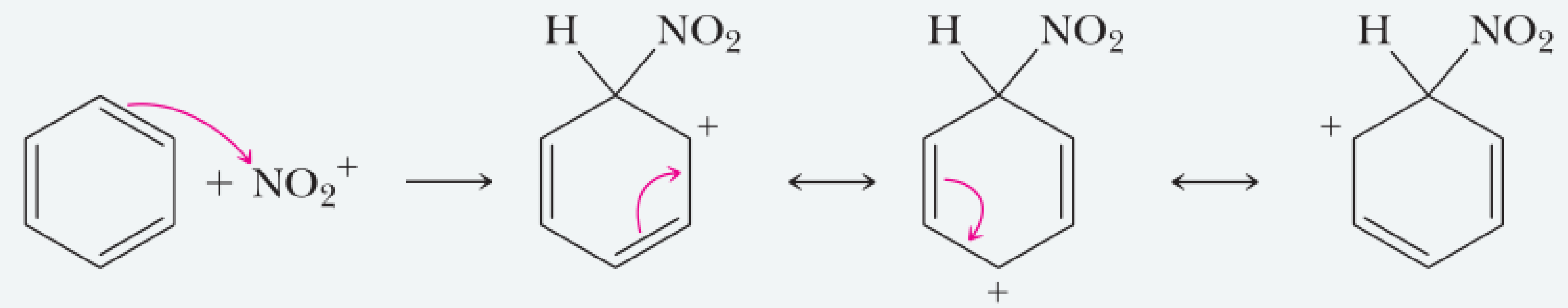


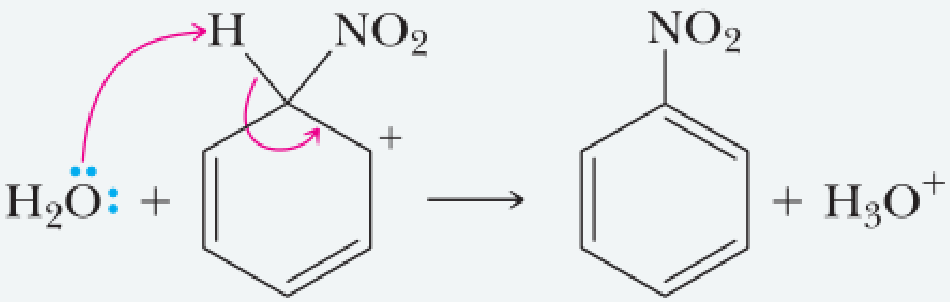
$$H-\overset{H}{\overset{|}{\overset{+}{O}}}-NO_2 \rightleftharpoons H-\overset{H}{\overset{|}{O}}: + NO_2^+$$

the electrophile

硝酰正离子

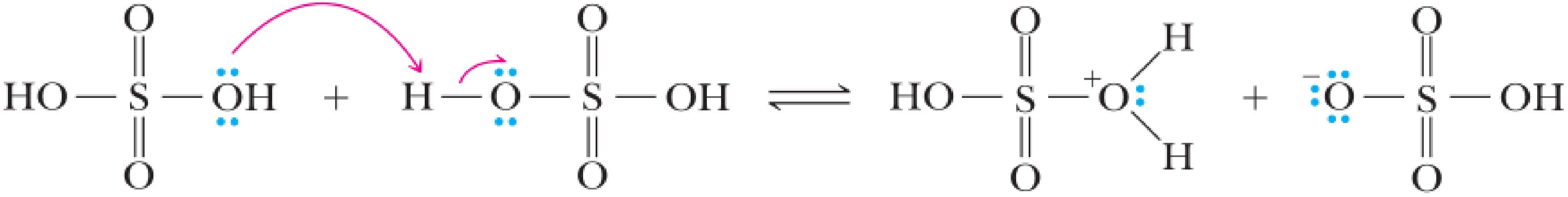
The nitronium ion



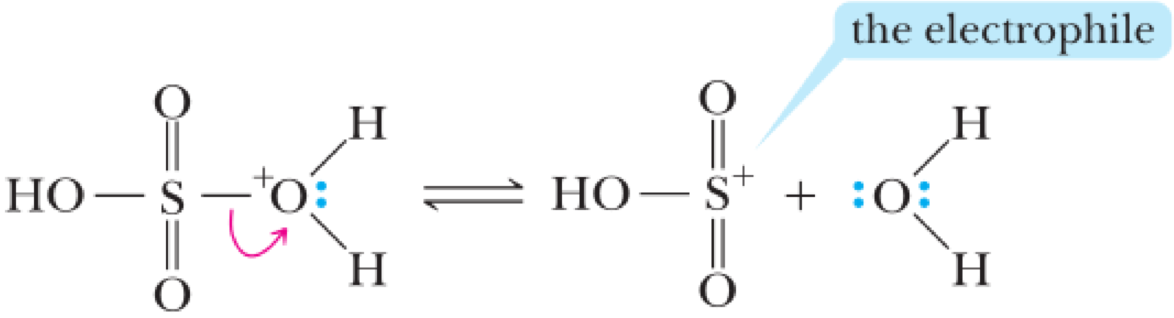


Nitrobenzene

磺化反应



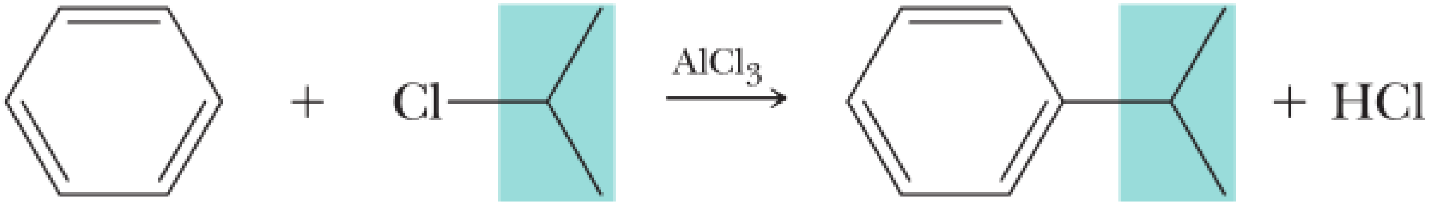
Sulfuric acid Sulfuric acid



the electrophile

The sulfonium ion

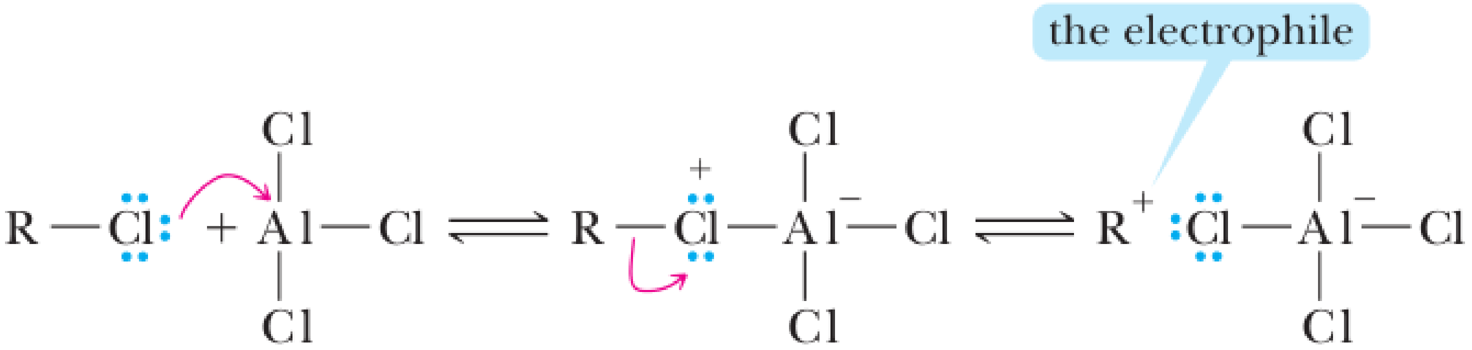
C. Friedel–Crafts Alkylation



Benzene

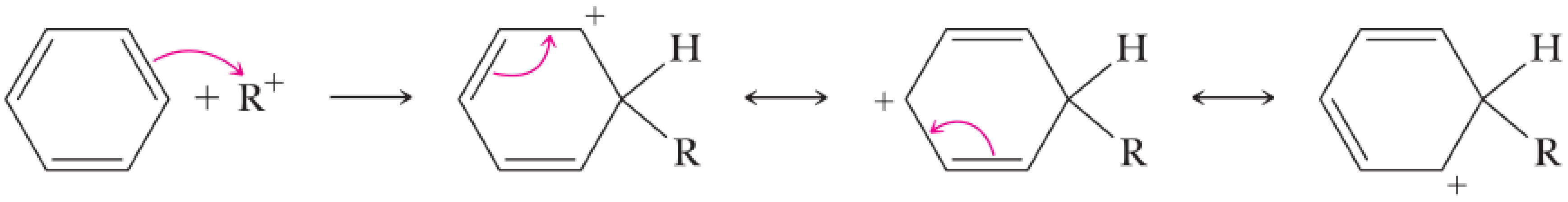
2-Chloropropane
(Isopropyl chloride)

Isopropylbenzene
(Cumene)

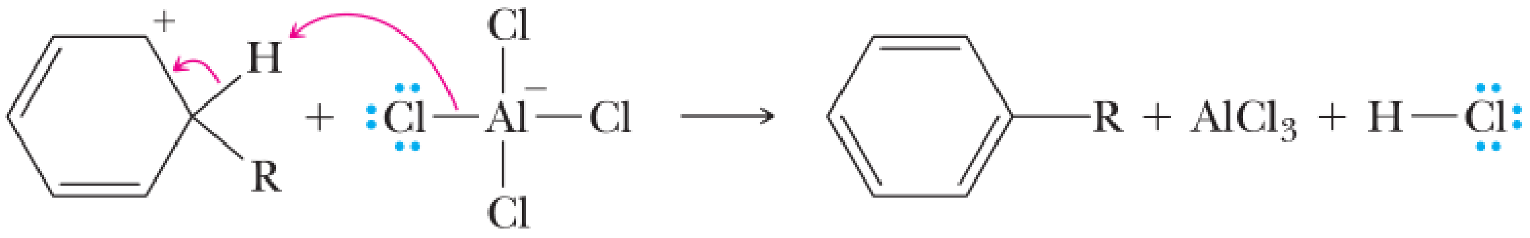


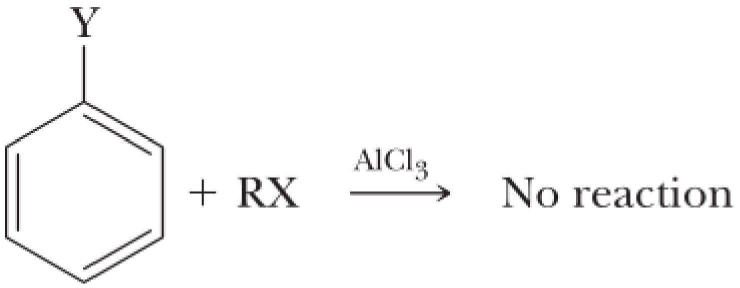
A molecular complex
with a positive charge on
chlorine and a negative
charge on aluminum

An ion pair
containing
a carbocation



The positive charge is delocalized onto
three atoms of the ring

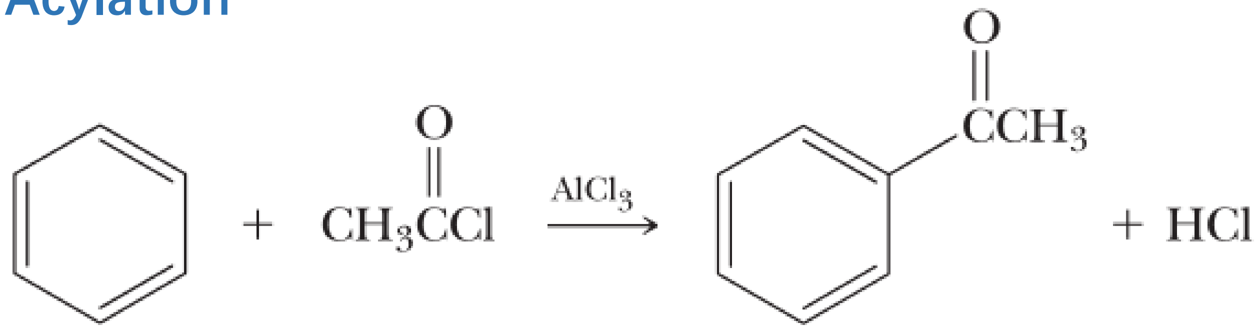




When Y Equals Any of These Groups, the Benzene Ring Does Not Undergo Friedel–Crafts Alkylation

$-\overset{O}{\overset{\|}{C}}H$	$-\overset{O}{\overset{\|}{C}}R$	$-\overset{O}{\overset{\|}{C}}OH$	$-\overset{O}{\overset{\|}{C}}OR$	$-\overset{O}{\overset{\|}{C}}NH_2$
$-SO_3H$	$-C\equiv N$	$-NO_2$	$-NR_3^{\,+}$	
$-CF_3$	$-CCl_3$			

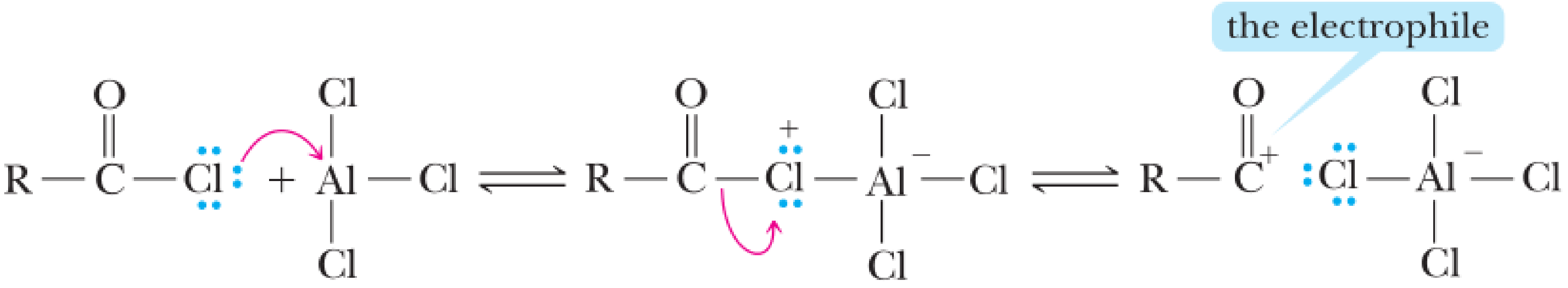
D. Friedel–Crafts Acylation



Benzene

Acetyl chloride
(an acyl halide)

Acetophenone
(a ketone)



the electrophile

An acyl
chloride
(a Lewis acid)

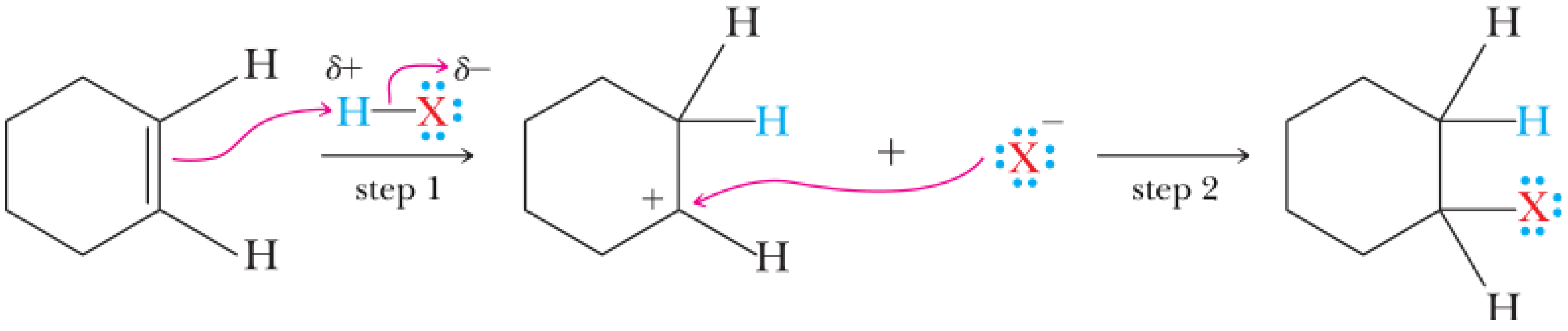
Aluminum
chloride
(a Lewis acid)

A molecular complex
with a positive charge on
chlorine and a negative
charge on aluminum

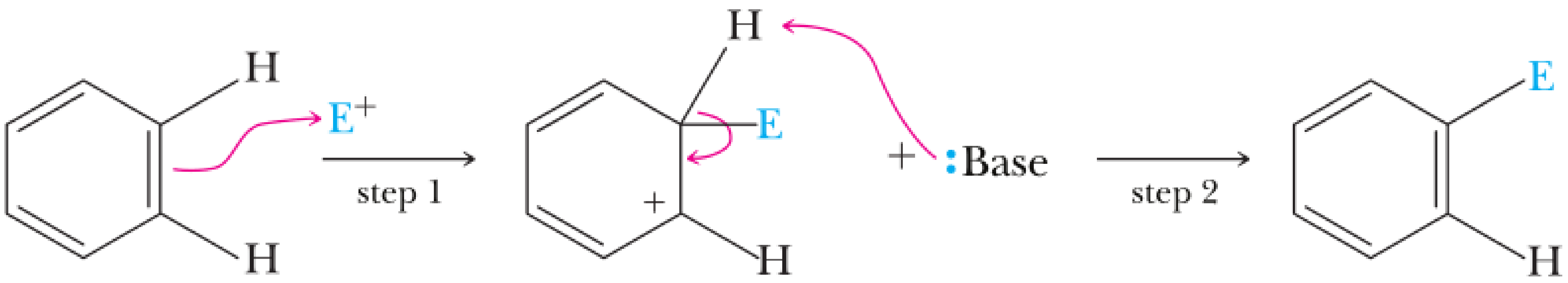
An ion pair
containing
an acylium ion

F. Comparison of Alkene Addition and Electrophilic Aromatic Substitution (EAS)（烯烃亲电加成与苯亲电取代的比较）

Addition to an Alkene



Electrophilic Aromatic Substitution

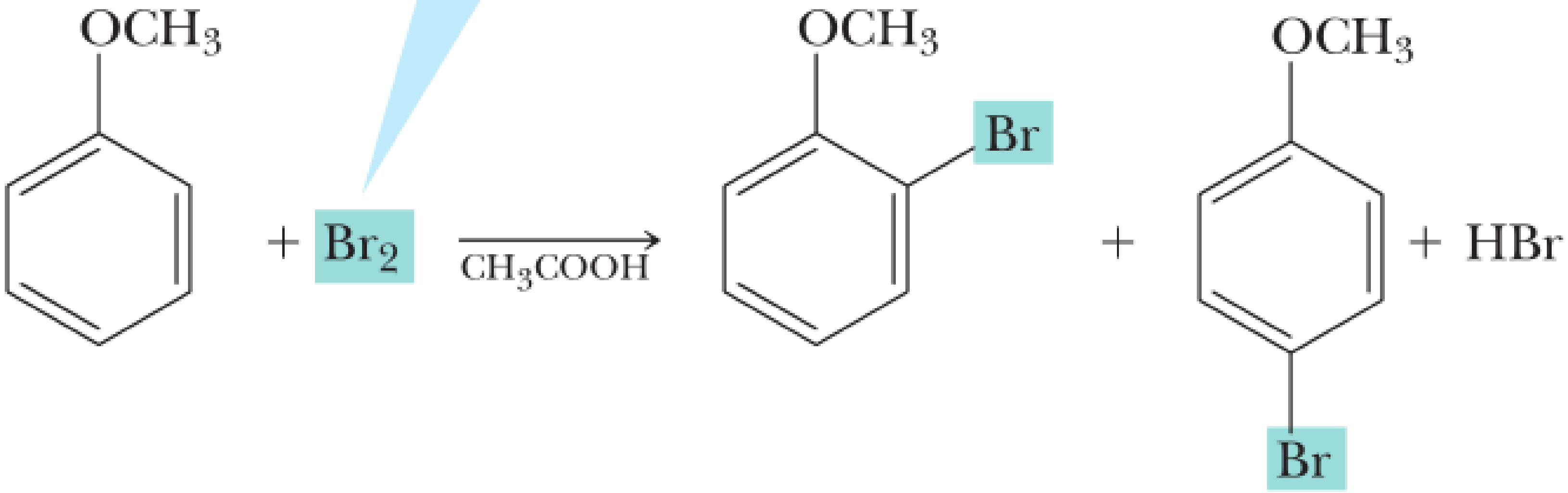


9.7 How Do Existing Substituents on Benzene Affect Electrophilic Aromatic Substitution?

1. Substituents affect the orientation of new groups. Certain substituents direct a second substituent preferentially to the ortho and para positions; other substituents direct it preferentially to a meta position. In other words, we can classify substituents on a benzene ring as ortho–para directing or meta directing.

2. Substituents affect the rate of further substitution. Certain substituents cause the rate of a second substitution to be greater than that of benzene itself, whereas other substituents cause the rate of a second substitution to be lower than that of benzene. In other words,we can classify groups on a benzene ring as activating or deactivating toward further substitution.

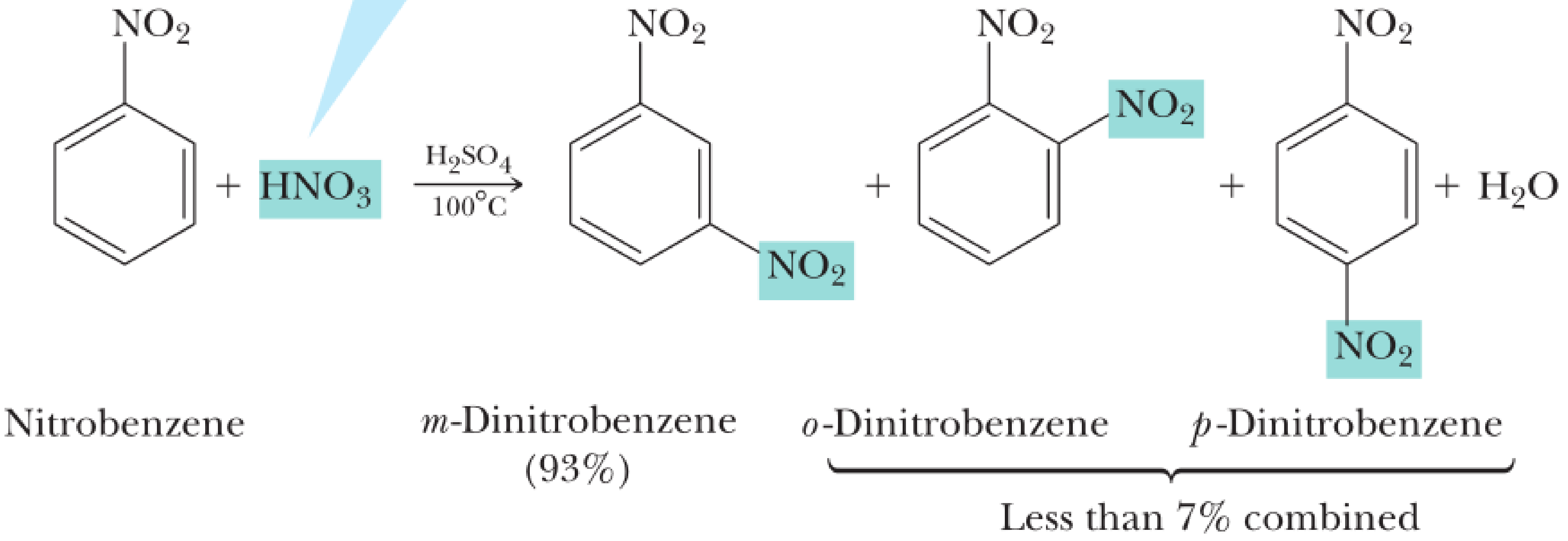
the bromination of anisole proceeds many times faster than the bromination of benzene. In fact, $-OCH_3$ is so activating that no catalyst is necessary in this reaction



Anisole

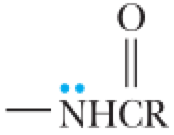
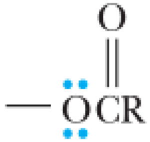
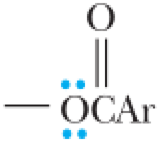
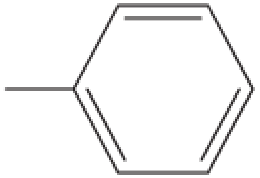
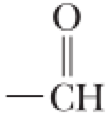
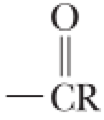
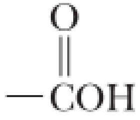
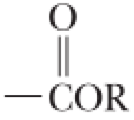
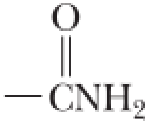
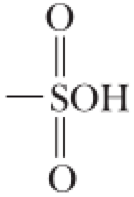
o-Bromoanisole (4%)

p-Bromoanisole (96%)



the nitration of nitrobenzene proceeds many times slower than the nitration of benzene

TABLE 9.1 Effects of Substituents on Further Electrophilic Aromatic Substitution

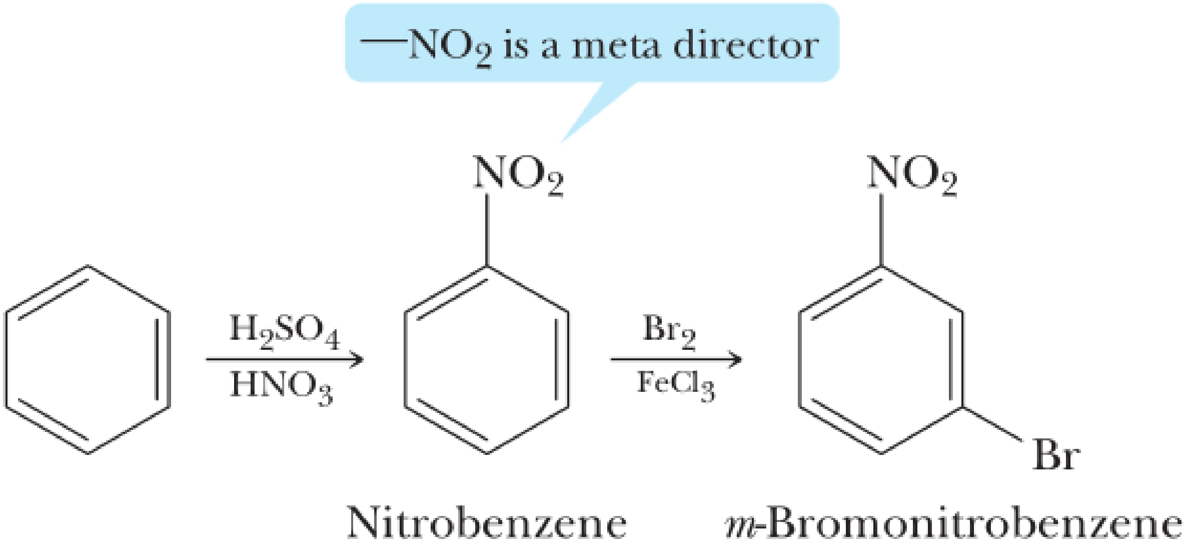
Ortho–Para Directing	strongly activating	$-\ddot{N}H_2$	$-\ddot{N}HR$	$-\ddot{N}R_2$	$-\ddot{\underset{\cdot\cdot}{O}}H$	$-\ddot{\underset{\cdot\cdot}{O}}R$	
	moderately activating	 $-\ddot{N}H\overset{\overset{O}{\|}}{C}R$	 $-\ddot{N}H\overset{\overset{O}{\|}}{C}Ar$	 $-\ddot{\underset{\cdot\cdot}{O}}\overset{\overset{O}{\|}}{C}R$	 $-\ddot{\underset{\cdot\cdot}{O}}\overset{\overset{O}{\|}}{C}Ar$		
	weakly activating	$-R$					
	weakly deactivating	$-\ddot{\underset{\cdot\cdot}{F}}:$	$-\ddot{\underset{\cdot\cdot}{Cl}}:$	$-\ddot{\underset{\cdot\cdot}{Br}}:$	$-\ddot{\underset{\cdot\cdot}{I}}:$		
Meta Directing	moderately deactivating	 $-\overset{\overset{O}{\|}}{C}H$	 $-\overset{\overset{O}{\|}}{C}R$	 $-\overset{\overset{O}{\|}}{C}OH$	 $-\overset{\overset{O}{\|}}{C}OR$	 $-\overset{\overset{O}{\|}}{C}NH_2$	 $-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}OH$
	strongly deactivating	$-NO_2$	$-NH_3{}^+$	$-CF_3$	$-CCl_3$		

Relative importance in directing further substitution

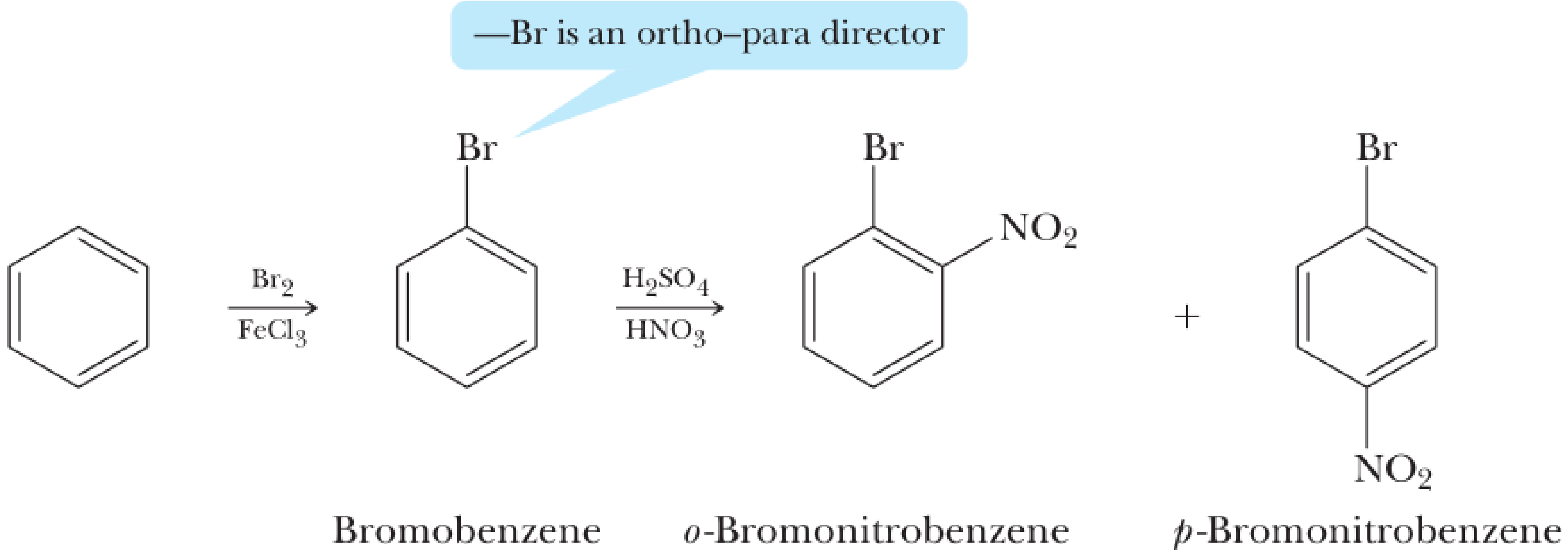
increasing reactivity relative to benzene

decreasing reactivity relative to benzene

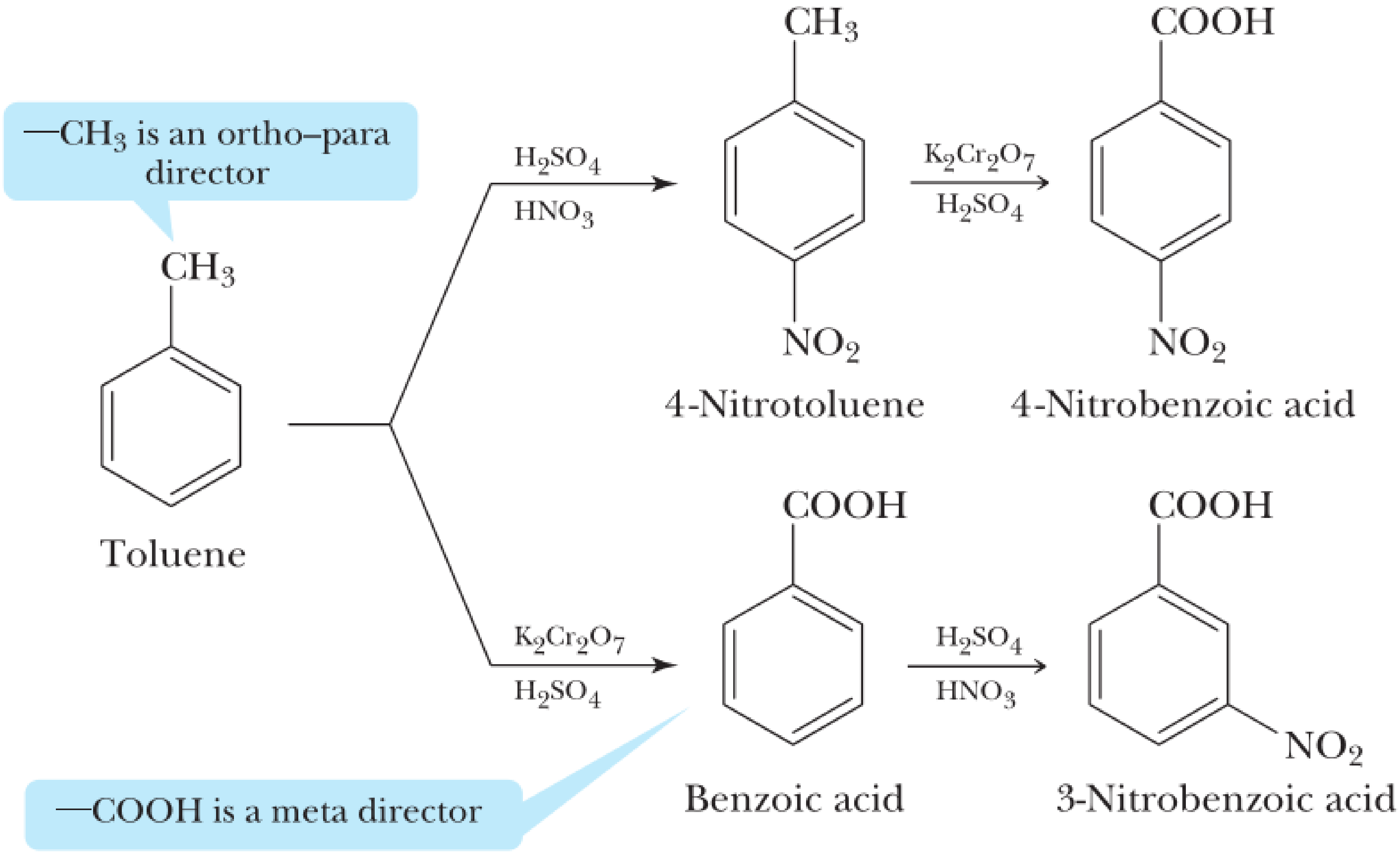
定位效应应用：指导合成



—NO_2 is a meta director



—Br is an ortho–para director



—CH_3 is an ortho–para director

—COOH is a meta director

Toluene

4-Nitrotoluene

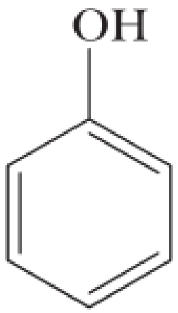
4-Nitrobenzoic acid

Benzoic acid

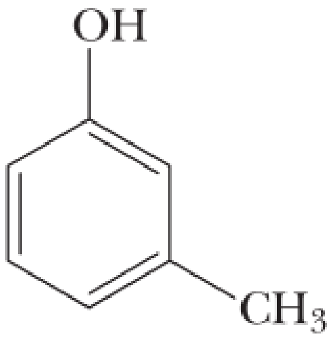
3-Nitrobenzoic acid

9.8 What Are Phenols?

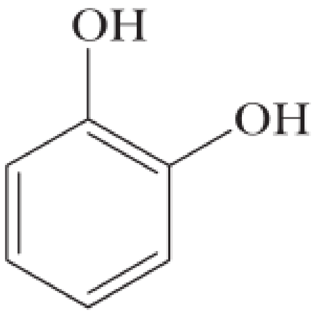
A. Structure and Nomenclature



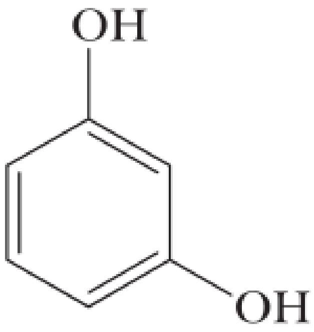
Phenol



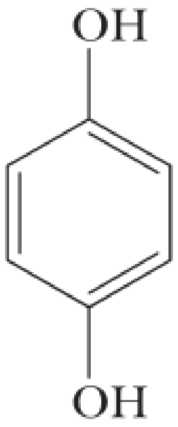
3-Methylphenol
(*m*-Cresol)



1,2-Benzenediol
(Catechol)

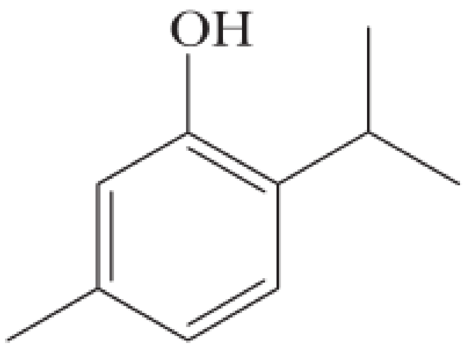


1,3-Benzenediol
(Resorcinol)



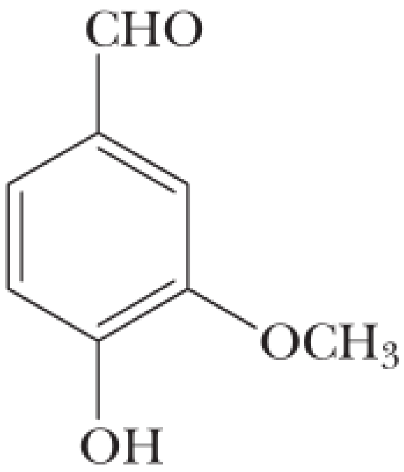
1,4-Benzenediol
(Hydroquinone)

百里香



2-Isopropyl-5-methylphenol
(Thymol)

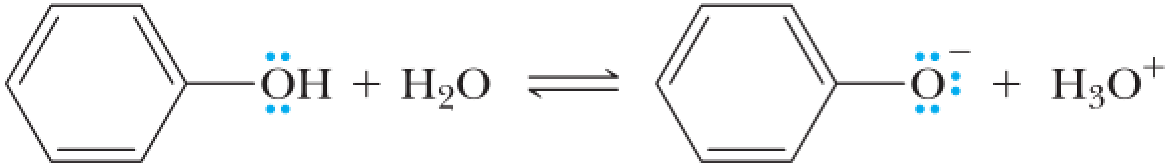
百里香酚



4-Hydroxy-3-methoxy-benzaldehyde
(Vanillin)

香草醛

B. Acidity of Phenols



Phenol Phenoxide ion

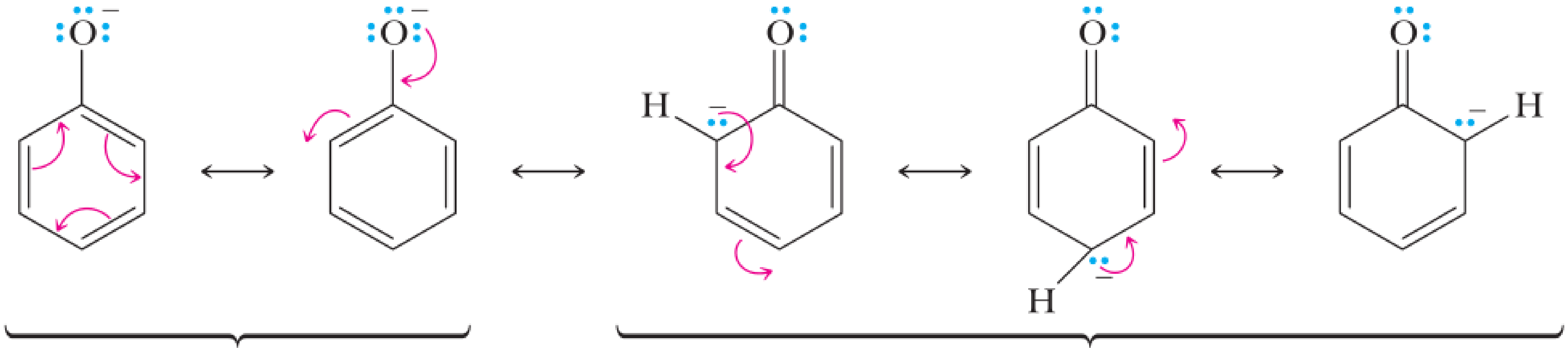
$K_a = 1.1 \times 10^{-10}$ $pK_a = 9.95$

$$CH_3CH_2\ddot{O}H + H_2 \rightleftharpoons CH_3CH_2\ddot{O}:^- + H_3O^+ \qquad K_a = 1.3 \times 10^{-16} \quad pK_a = 15.9$$

Ethanol Ethoxide ion

TABLE 9.2 Relative Acidities of 0.1-M Solutions of Ethanol, Phenol, and HCl

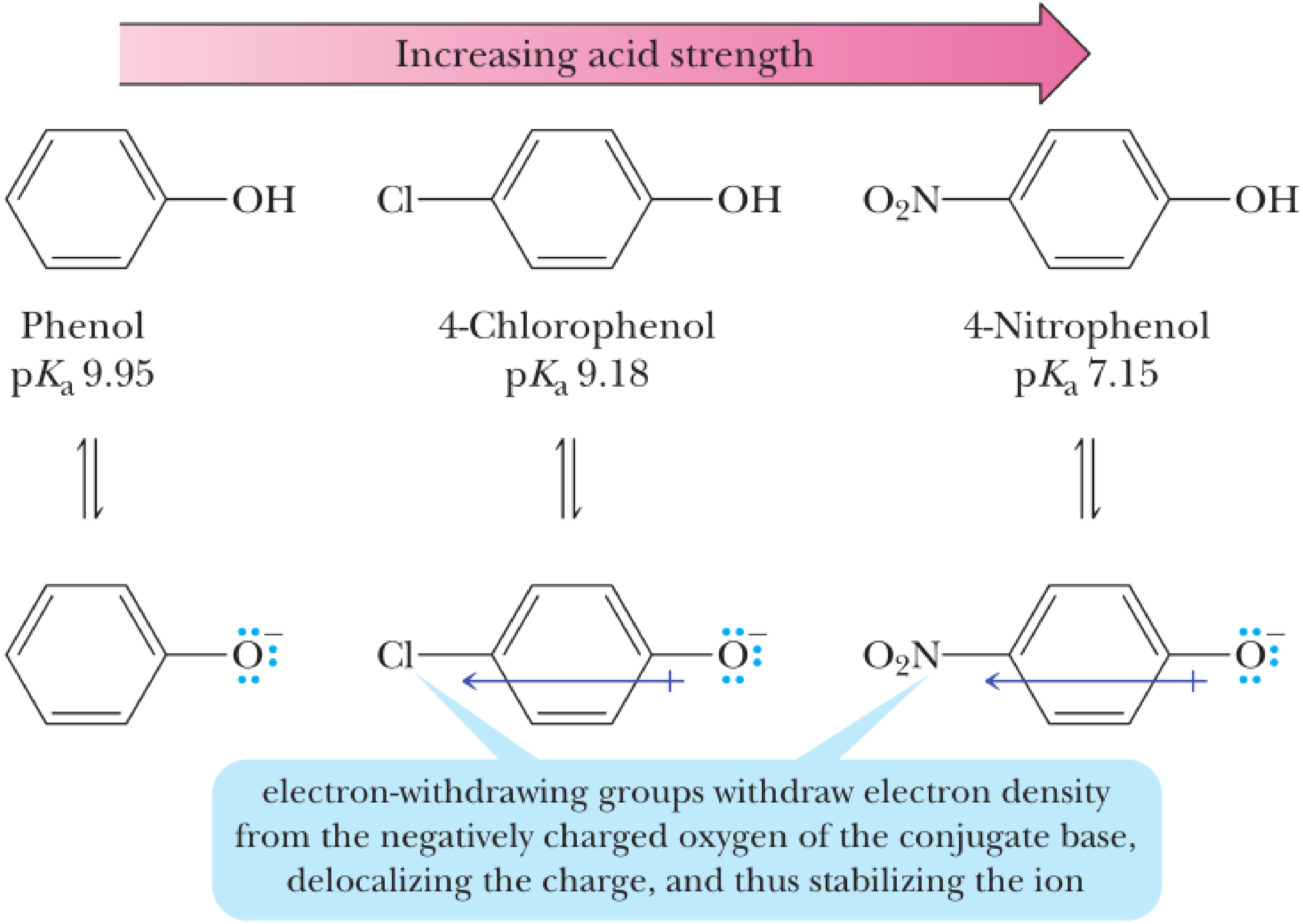
Acid Ionization Equation	$[H^+]$	pH
$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$	1×10^{-7}	7.0
$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3O^+$	3.3×10^{-6}	5.4
$HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$	0.1	1.0



These two Kekulé structures are equivalent

These three contributing structures delocalize the negative charge onto carbon atoms of the ring

试比较乙醇与苯酚的酸性并解释



Increasing acid strength

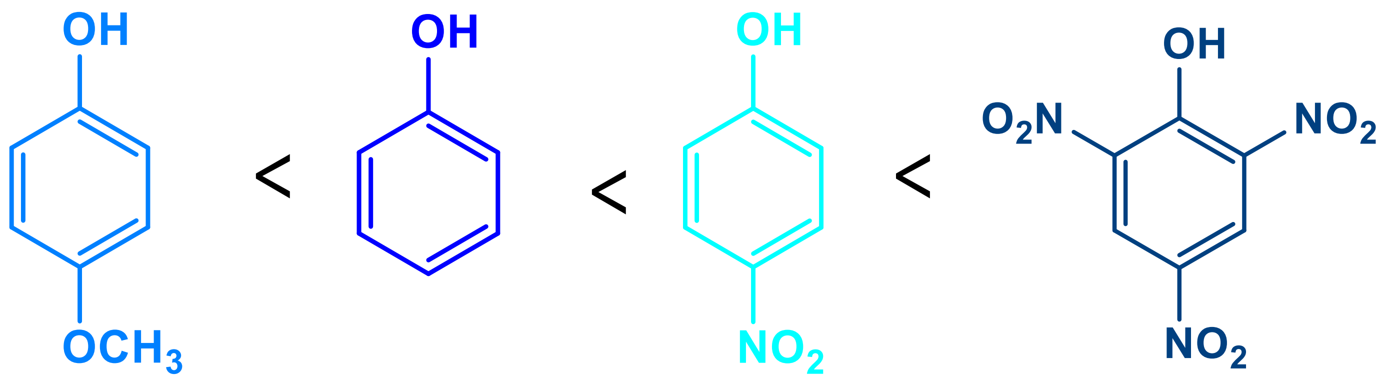
Phenol
pK_a 9.95

4-Chlorophenol
pK_a 9.18

4-Nitrophenol
pK_a 7.15

electron-withdrawing groups withdraw electron density from the negatively charged oxygen of the conjugate base, delocalizing the charge, and thus stabilizing the ion

取代苯酚的酸性强弱：



pKa 10.21 9.84 7.15 0.25

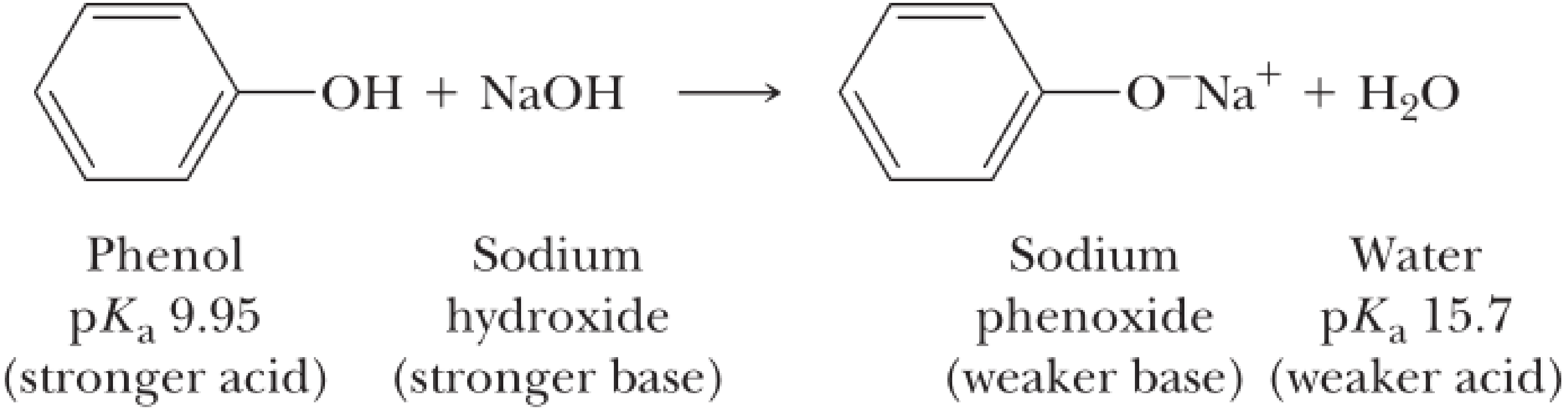
苯环上的取代基对酚酸性强弱的影响

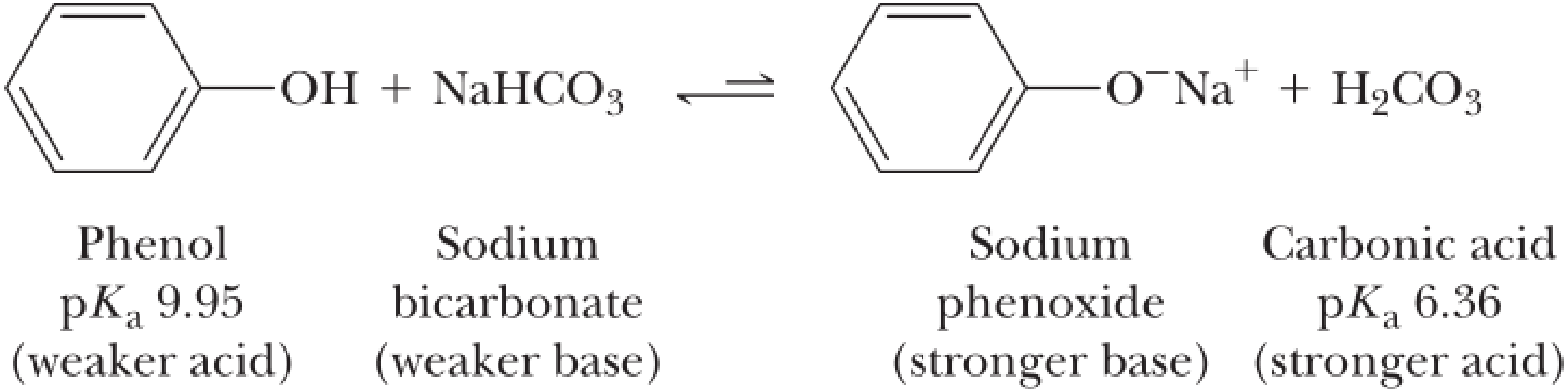
电子效应的影响：吸电子基团使酸性增强，给电子基团使酸性减弱(邻对位基团的影响大于间位)。

电荷分散, 负离子稳定化

电荷集中, 负离子去稳定化

C. Acid–Base Reactions of Phenols





作 业

9.11 、9.13（a、b、c、e、h）、9.18、
9.26（a、b、c、d）、9.31（a、c）、
9.37、、9.42（a、d、e、g）、
9.48（b、e、f、k）