Chapter 4: Aromatic Compounds





Bitter almonds are the source of the aromatic compound benzaldehyde

Sources of Benzene



Benzene, C₆H₆, is the parent hydrocarbon of the especially stable compounds known as **aromatic compounds**.

4.1 Some Facts About Benzene

-The carbon-to-hydrogen ratio in benzene, C₆H₆, suggests a highly unsaturated structure.

-Despite its molecular formula, benzene for the most part does not behave as if it were unsaturated.

- it does not decolorize bromine solutions .
- -it not easily oxidized by potassium permanganate.

Reacts mainly by substitution

$$C_{6}H_{6} + Br_{2} \xrightarrow{FeBr_{3}} C_{6}H_{5}Br + HBr$$

benzene bromobenzene
$$C_{6}H_{6} + Cl_{2} \xrightarrow{FeCl_{3}} C_{6}H_{5}Cl + HCl$$

benzene chlorobenzene

4.2 The Kekulé Structure for Benzene

In 1865, Kekulé proposed a reasonable structure for benzene



Kekulé's two structures for benzene *differ only* in the arrangement of the electrons; all of the atoms occupy the same positions in both structures.

4.3 The Resonance Structure of Benzene





Modern physical measurements support this model for the benzene structure:

- Benzene is planar.
- Each carbon atom is at the corner of a regular hexagon.

- All of the carbon-carbon bond lengths are identical: 1.39 Å, intermediate between typical single (1.54 Å) and double (1.34 Å) carbon-carbon bond lengths.

4.4 The Orbital Model for Benzene



The *p* orbitals on all six carbon atoms can overlap laterally to form pi orbitals that create a ring or cloud of electrons above and below the plane of the ring.

4.5 Symbols for Benzene



4.6 Nomenclature of Aromatic Compounds

Common names have acquired historic respectability and are accepted by IUPAC.

Monosubstituted benzenes with common names



Monosubstituted benzenes that do not have common names



When two substituents are present, we use prefixes *ortho-, meta-,* and *para-,* usually abbreviated as o-, m-, and p-, respectively.







(note alphabetical order)

For more than two substituents, their positions are designated by numbering the ring.





 $\begin{array}{c} CH_{3} \\ NO_{2} & 1 \\ 5 \\ & 1 \\ & 1 \\ & 1 \\ & 1 \\ & 1 \\ & 1 \\ & 2 \\ & 3 \\ & 4 \\ & NO_{2} \\ & 2,4,6-trinitrotoluene \\ & (TNT) \end{array}$

3,5-dichlorotoluene

Aromatic hydrocarbons, as a class called Arenes (Ar) the aryl groups are therefore aromatic substituents.







m-nitrobenzyl alcohol

PROBLEM 4.9 Draw the structure of

- a. dibenzyl
- b. cyclobutylbenzene c. benzyl iodide d. *p*-phenylstyrene





PROBLEM 4.10 Name the following structures:



- a. phenylcyclohexane or cyclohexylbenzene
- b. o-benzylphenol

4.7 The Resonance Energy of Benzene

- Hydrogenation of a carbon–carbon double bond is an exothermic reaction. The amount of energy (heat) released is about 26 to 30 kcal/mol. for each double bond.
- Hydrogenation of cyclohexene releases 28.6 kcal/mol.

$$C = C + H - H \longrightarrow -C - C - C + heat (26-30 \text{ kcal/mol})$$

• The complete hydrogenation of 1,3-cyclohexadiene should release twice that amount of heat, or 2 X 28.6 = 57.2 kcal/mol.

 The hypothetical *triene* 1,3,5-cyclohexatriene should correspond to that for three double bonds, or about 84 to 86 kcal/mol.

 That benzene is more difficult to hydrogenate than simple alkenes, and the heat evolved when benzene is hydrogenated to cyclohexane is much lower than expected: only 49.8 kcal/mol.

- We conclude that real benzene molecules are more stable than the contributing resonance structures (the hypothetical molecule 1,3,5- cyclohexatriene) by about 36 kcal/mol (86 - 50 = 36).
- The stabilization energy, or resonance energy, of a substance is the difference between the energy of the real molecule and the calculated energy of the most stable contributing structure.
- Benzene and other aromatic compounds usually react in such a way as to preserve their aromatic structure and therefore retain their resonance energy.



4.8 Electrophilic Aromatic Substitution

The most common reactions of aromatic compounds involve substitution of other atoms or groups for a ring hydrogen on the aromatic unit.





4.9 The Mechanisms of Electrophilic Substitutions

For Example, Chlorination of Benzene

Ferric chloride acts as a Lewis acid and converts chlorine to a strong electrophile by forming a complex and polarizing the Cl-Cl bond.





resonance forms of a benzenonium ion



composite representation of the benzenonium ion resonance hybrid







Reaction coordinate

Energy

b. Nitration





acid

d. Alkylation and Acylation (Friedel-Crafts reaction)



$\begin{array}{c} O \\ \parallel \\ CH_3CCl + AlCl_3 \rightleftharpoons CH_3\overset{+}{C} = O + AlCl_4^{-} \\ acetyl choride & acetyl cation \end{array}$



4.10 Ring-Activating and ring-Deactivating Substituents

Consider the relative nitration rates of the following compounds, all under the same reaction conditions:





In the electrophilic mechanism for substitution:

Substituents that donate electrons to the ring will increase its electron density and, hence, speed up the reaction.

Substituents that withdraw electrons from the ring will decrease electron density in the ring and therefore slow down the reaction.

4.11 Ortho, Para-Directing and Meta-Directing Groups

Substituents already present on an aromatic ring determine the position taken by a new substituent.



Groups (Groups are Listed in Decreasing Order of Activation)			
Ĺ	Substituent group	Name of group	
ecting	$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$	amino	
	-ён, -ёсн ₃ , -ёк	hydroxy, alkoxy	Acti
ho,Para-Di	0 ∥ −NHC—R	acylamino	vating
Ort	-CH ₃ , -CH ₂ CH ₃ , -R	alkyl	
	$-\ddot{\mathbf{F}}$:, $-\ddot{\mathbf{Cl}}$:, $-\ddot{\mathbf{Br}}$:, $-\ddot{\mathbf{I}}$:	halo	
	:o: :o: Ш —с—R —с—он	acyl, carboxy	
Meta-Directing	:0: :0: 	carboxamido, carboalkoxy	
	: о: ——s—он —— : : о:	sulfonic acid	eactivating
	- C≡=N:	cyano	
	-N Ö.	nitro	

Table 4.1 — Directing and Activating Effects of Common Functional Groups (Groups are Listed in Decreasing Order of Activation)

a. Ortho, Para-Directing Groups



Meta attack



Consider now the other *ortho,para*-directing groups. In each of them, the atom attached to the aromatic ring has an unshared electron pair.

$$-F: -OH -NH_2$$

This unshared electron pair can stabilize an adjacent positive charge.

Let us consider, as an example, the bromination of phenol.





In the case of *o*- or *p*- attack, one of the contributors to the intermediate benzenonium ion places the positive charge on the hydroxyl-bearing carbon.

Shift of an unshared electron pair from the oxygen to the positive carbon allows the positive charge to be delocalized even further, onto the oxygen.

b. meta-Directing Groups



Meta attack



One of the contributors to the resonance hybrid intermediate for *ortho* or *para* substitution (shown in the blue dashed boxes) has two adjacent positive charges, a highly undesirable arrangement, because like charges repel each other.

No such intermediate is present for *meta* substitution. For this reason, meta substitution is preferred.

All groups in which the atom directly attached to the aromatic ring is positively charged or is part of a multiple bond to a more electronegative element will be *meta* directing.



Y is an electron-withdrawing atom such as oxygen or nitrogen; atom X carries a positive charge in one of the resonance contributors.

c. Substituent Effect on Reactivity

In <u>all meta-directing groups</u>, the atom connected to the ring carries a full or partial positive charge and will therefore withdraw electrons from the ring.

All meta-directing groups are therefore ringdeactivating groups.

On the other hand, *ortho*, *para*-directing groups in general supply electrons to the ring and are therefore ring activating.

With the halogens (F, CI, Br, and I), two opposing effects bring about the only important exception to these rules. Because they are strongly electron withdrawing, the halogens are ring deactivating; but because they have unshared electron pairs, they are ortho, para-directing.

4.12 Importance of Directing Effects in Synthesis





meta

PROBLEM 4.16

Devise a synthesis for each of the following, starting with benzene:

- a. *m*-bromobenzenesulfonic acid
- b. *p*-nitrotoluene



• Homework

• 20 22 24 30 37 38 40 43 44