Bitter almonds are the source of the aromatic compound benzaldehyde.

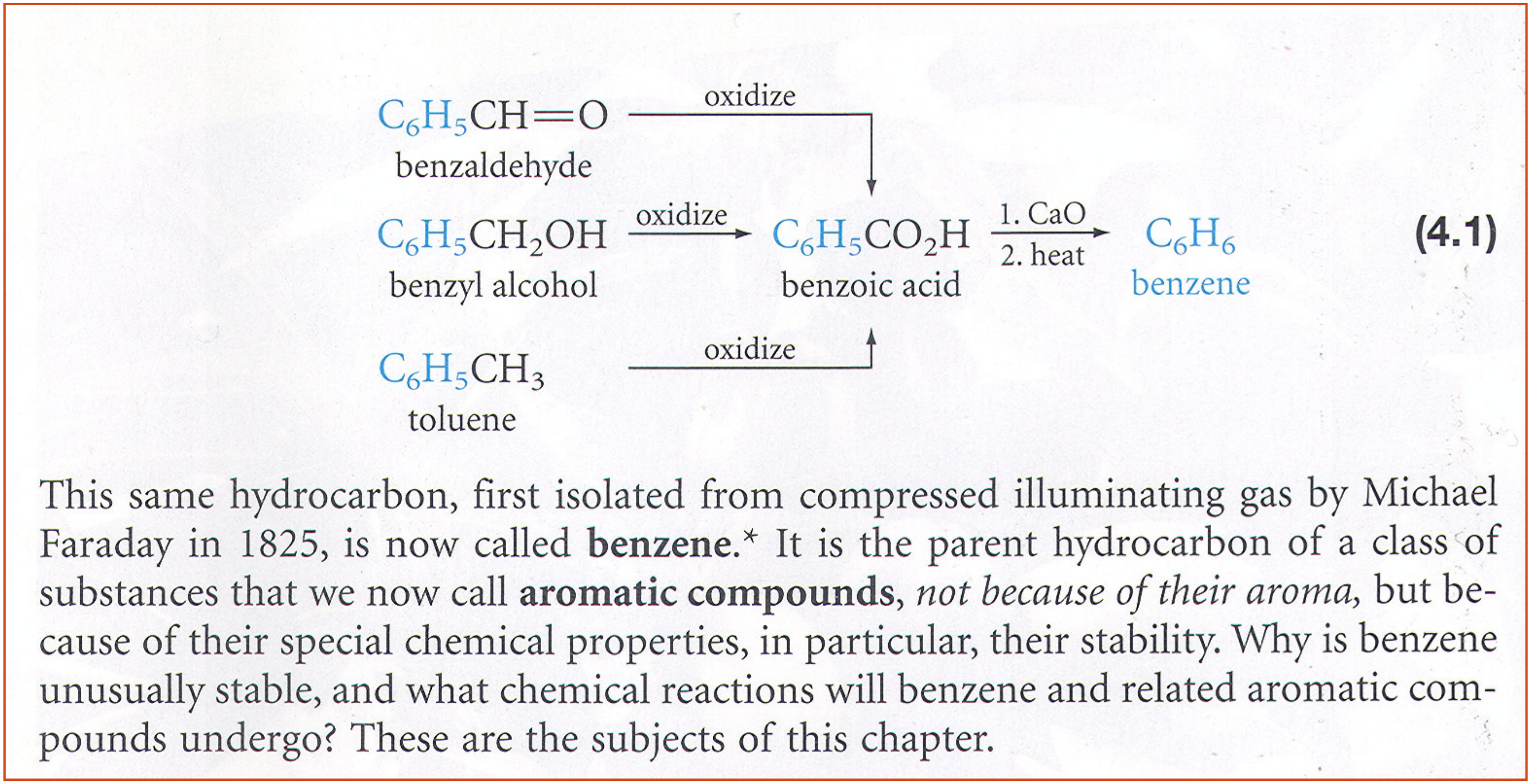
4

Aromatic Compounds

Introduction

- Aromatic compounds are common in spices and herbs.
- Spices and herbs were among the first natural products studied by organic chemists.
- It turned out that many of these aromatic substances have rather simple structures.
  - Many contain very stable 6-carbon unit, C_6H_5-.
  - For example: **benzaldehyde** (*isolated from bitter almond*), **benzyl alcohol** (*isolated from gum benzoin*), and **toluene** (*isolated from tolu balsam*)

Introduction



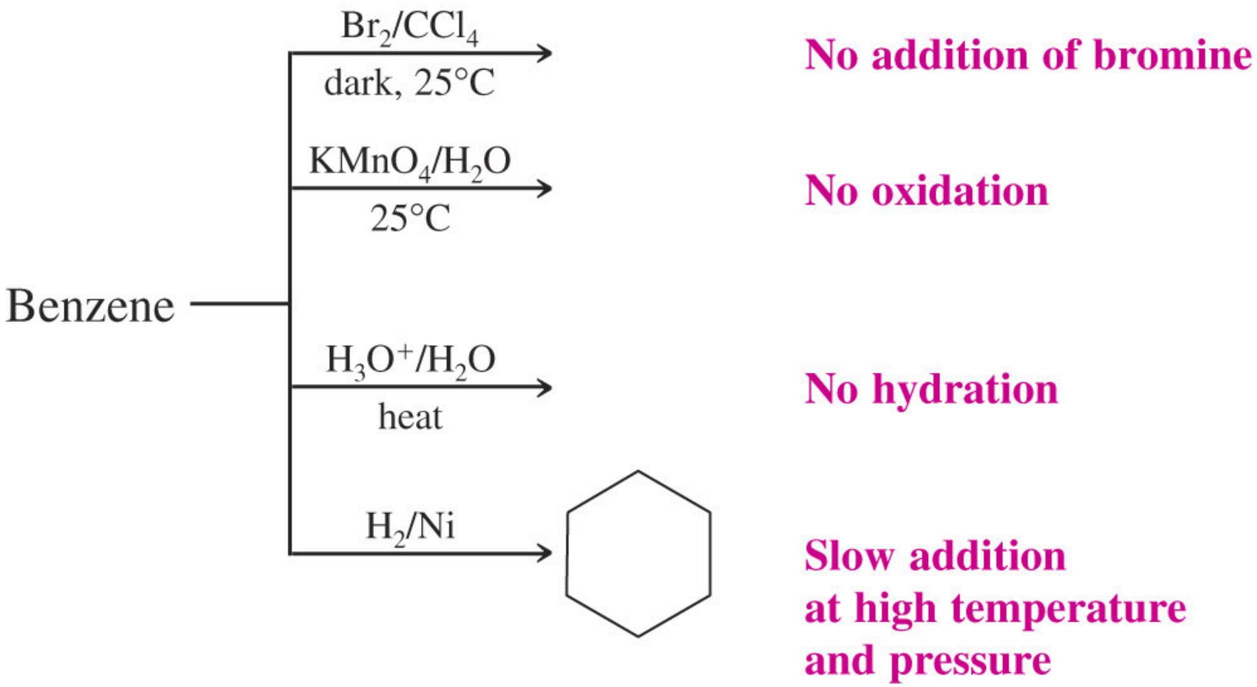
$$\begin{tikzcd}
\underset{\text{benzaldehyde}}{C_6H_5CH{=}O} \arrow[dr, "\text{oxidize}"] & & \\
\underset{\text{benzyl alcohol}}{C_6H_5CH_2OH} \arrow[r, "\text{oxidize}"] & \underset{\text{benzoic acid}}{C_6H_5CO_2H} \arrow[r, "\text{1. CaO}", "\text{2. heat}"'] & \underset{\text{benzene}}{C_6H_6} \\
\underset{\text{toluene}}{C_6H_5CH_3} \arrow[ur, "\text{oxidize}"'] & &
\end{tikzcd}$$

(4.1)

This same hydrocarbon, first isolated from compressed illuminating gas by Michael Faraday in 1825, is now called **benzene**.* It is the parent hydrocarbon of a class of substances that we now call **aromatic compounds**, *not because of their aroma*, but because of their special chemical properties, in particular, their stability. Why is benzene unusually stable, and what chemical reactions will benzene and related aromatic compounds undergo? These are the subjects of this chapter.

4.1 Some Facts About Benzene

- Reactions of Benzene
  - Even though benzene is highly unsaturated it does not undergo any of the regular reactions of alkenes such as addition or oxidation



Benzene

$\xrightarrow[\text{dark, 25°C}]{Br_2/CCl_4}$ **No addition of bromine**

$\xrightarrow[\text{25°C}]{KMnO_4/H_2O}$ **No oxidation**

$\xrightarrow[\text{heat}]{H_3O^+/H_2O}$ **No hydration**

$\xrightarrow{H_2/Ni}$ **Slow addition at high temperature and pressure**

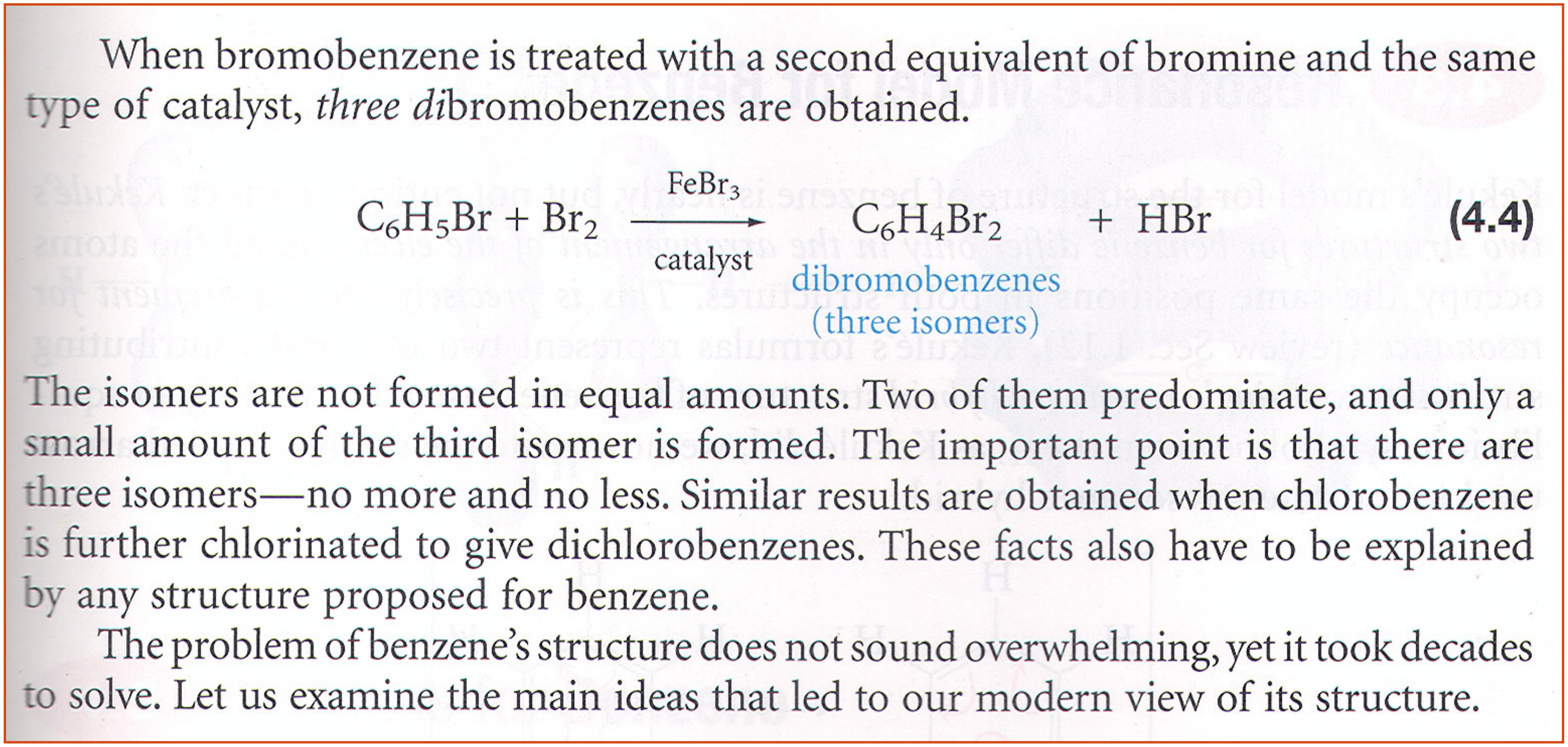
- Benzene can be induced to react with bromine if a Lewis acid catalyst is present however the reaction is a *substitution* and not an addition
  - Benzene produces only one monobrominated compound, which indicates that all 6 carbon-hydrogen bonds are equivalent in benzene

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$ **Observed**

$$C_6H_6 + Br_2 \not\longrightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6$$ **Not observed**

Chlorine, with a ferric chloride catalyst, reacts similarly.

$$\underset{\text{benzene}}{C_6H_6} + Cl_2 \xrightarrow[\text{catalyst}]{FeCl_3} \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl$$



When bromobenzene is treated with a second equivalent of bromine and the same type of catalyst, *three di*bromobenzenes are obtained.

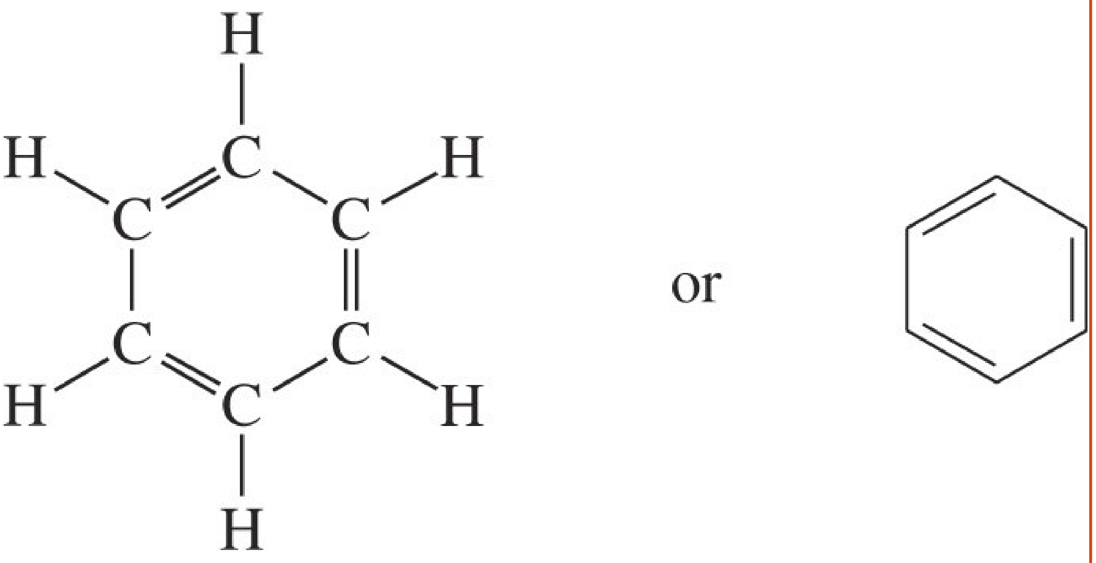
$$C_6H_5Br + Br_2 \xrightarrow[\text{catalyst}]{FeBr_3} \underset{\substack{\text{dibromobenzenes} \\ \text{(three isomers)}}}{C_6H_4Br_2} + HBr \qquad \textbf{(4.4)}$$

The isomers are not formed in equal amounts. Two of them predominate, and only a small amount of the third isomer is formed. The important point is that there are three isomers—no more and no less. Similar results are obtained when chlorobenzene is further chlorinated to give dichlorobenzenes. These facts also have to be explained by any structure proposed for benzene.

The problem of benzene's structure does not sound overwhelming, yet it took decades to solve. Let us examine the main ideas that led to our modern view of its structure.

4.2 The Kekule Structure for Benzene

- Kekule (1829-1896) was the first to formulate a reasonable representation of benzene (1865)

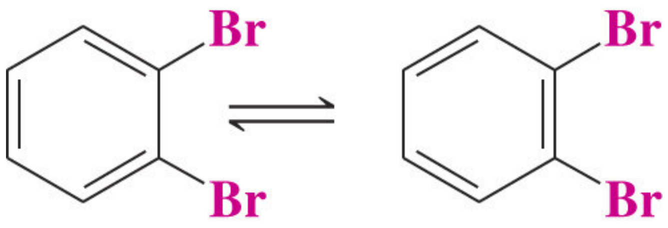


The Kekulé formula for benzene

Friedrich August Kekulé.

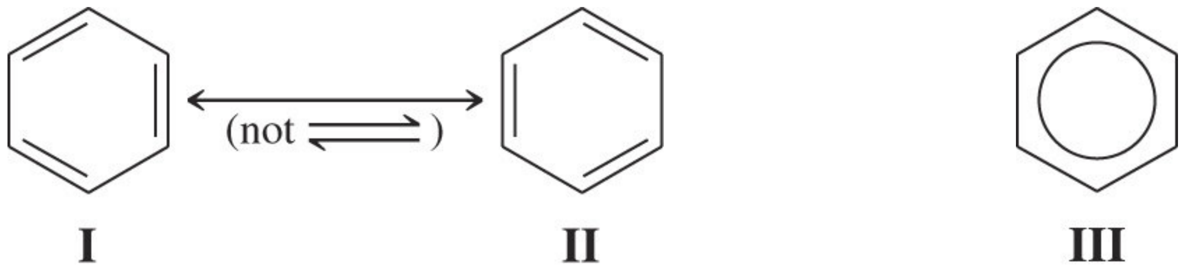
- The Kekule structure suggests alternating double and single carbon-carbon bonds
  - Based on the Kekule structure one would expect there to be two different 1,2-dibromobenzenes **but there is only one**

  - Kekule suggested an equilibrium between these compounds to explain this observation **but it is now known no such equilibrium exists**



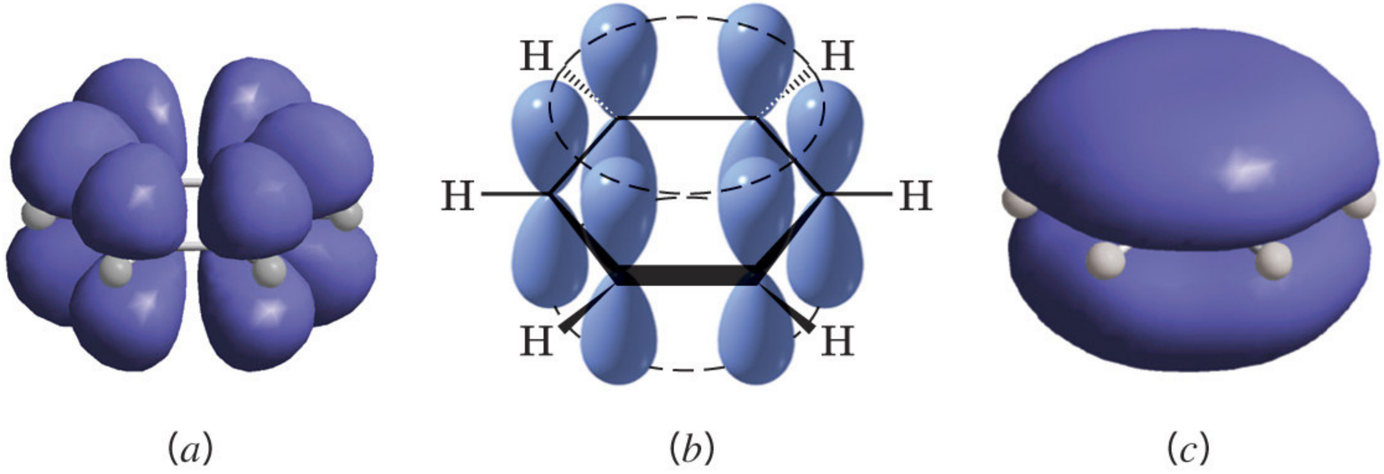
4.3 Resonance Model for Benzene

- Modern Theories of the Structure of Benzene
  - The Resonance Explanation of the Structure of Benzene
    - Structures I and II are equal resonance contributors to the real structure of benzene
      - Benzene is planar and particularly stable because it has two equivalent and important resonance structures
      - Each carbon-carbon bond is 1.39 Å, which is between the length of a carbon-carbon single bond between *sp*^{2} carbons (1.47Å) and a carbon-carbon double bond (1.33 Å)
      - Often the hybrid is represented by a circle in a hexagon (III)



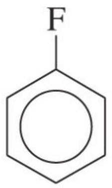
4.4 Orbital Model for Benzene

- The carbons in benzene are sp^2 hybridized with *p* orbitals on all 6 carbons (a)
  - The *p* orbitals overlap around the ring (b) to form a bonding molecular orbital with electron density above and below the plane of the ring (c)
  - This model explains nicely the planarity of benzene
  - It also explains its hexagonal shape, with H-C-C and C-C-C angles of 120°

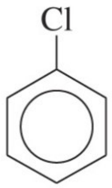


4.6 Nomenclature of Benzene Derivatives

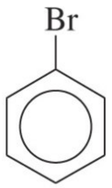
- Benzene is the parent name for some monosubstituted benzenes; the substituent name is added as a prefix



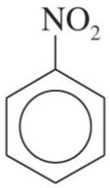
Fluorobenzene



Chlorobenzene

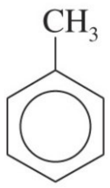


Bromobenzene

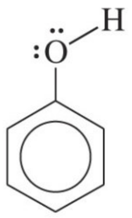


Nitrobenzene

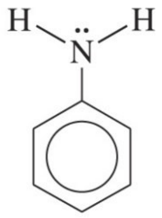
- For other monosubstituted benzenes, the presence of the substituent results in a new parent name



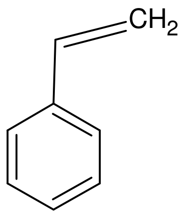
Toluene



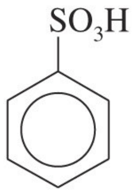
Phenol



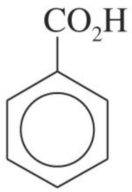
Aniline



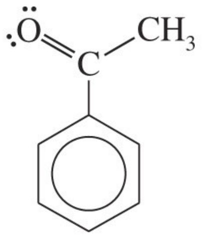
Styrene



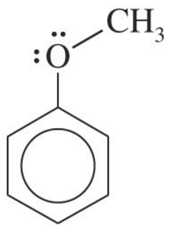
Benzenesulfonic acid



Benzoic acid

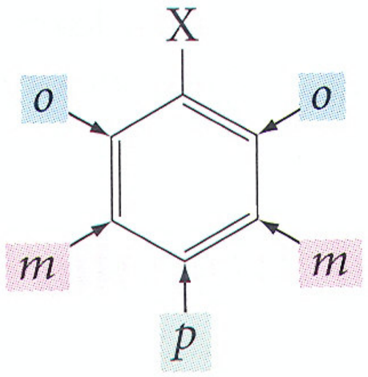


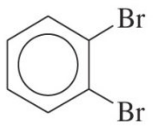
Acetophenone



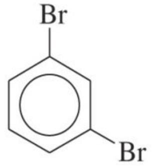
Anisole

When two substituents are present their position may be indicated by the prefixes *ortho*, *meta*, and *para* (*o*, *m* and *p*) or by the corresponding numerical positions

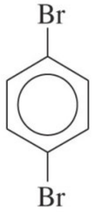




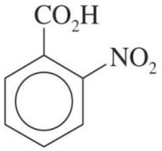
1,2-Dibromobenzene
(*o*-dibromobenzene)
ortho



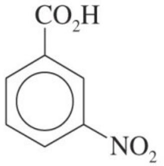
1,3-Dibromobenzene
(*m*-dibromobenzene)
meta



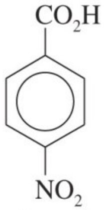
1,4-Dibromobenzene
(*p*-dibromobenzene)
para



2-Nitrobenzoic acid
(*o*-nitrobenzoic acid)



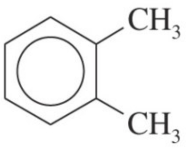
3-Nitrobenzoic acid
(*m*-nitrobenzoic acid)



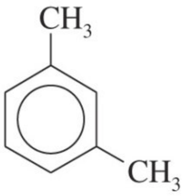
4-Nitrobenzoic acid
(*p*-nitrobenzoic acid)

CH_3 CH_3

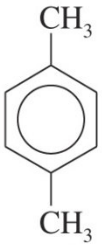
Dimethyl substituted benzenes are called xylenes



1,2-Dimethylbenzene
(*o*-xylene)

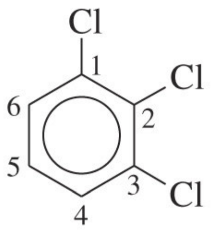


1,3-Dimethylbenzene
(*m*-xylene)

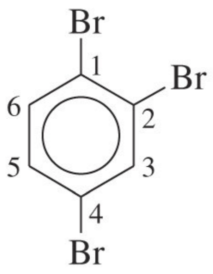


1,4-Dimethylbenzene
(*p*-xylene)

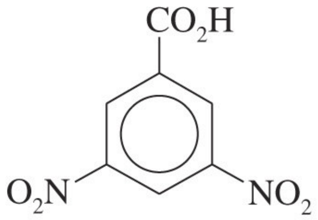
- Numbers must be used as locants when more than two substituents are present
  - The lowest possible set of numbers should be given to the substituents
  - The substituents should be listed in alphabetical order
  - If one of the substituents defines a parent other than benzene, this substituent defines the parent name and should be designated position 1



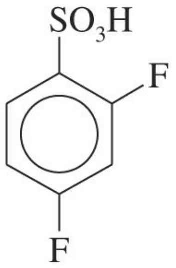
1,2,3-Trichlorobenzene



1,2,4-Tribromobenzene
(*not* 1,3,4-tribromobenzene)

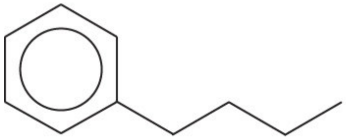


3,5-Dinitrobenzoic acid

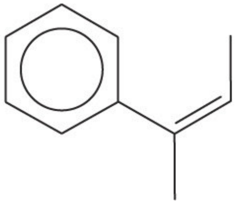


2,4-Difluorobenzenesulfonic acid

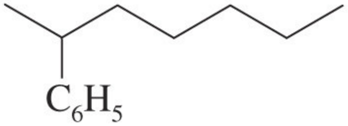
- The C_6H_5- group is called phenyl when it is a substituent
  - Phenyl is abbreviated Ph or Φ
  - A hydrocarbon with a saturated chain and a benzene ring is named by choosing the larger structural unit as the parent
  - If the chain is unsaturated then it must be the parent and the benzene is then a phenyl substituent



Butylbenzene

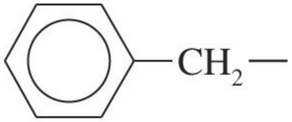


2-Phenyl-2-butene

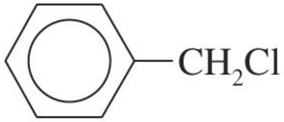


2-Phenylheptane

- The phenylmethyl group is called a benzyl (abbreviated Bz)

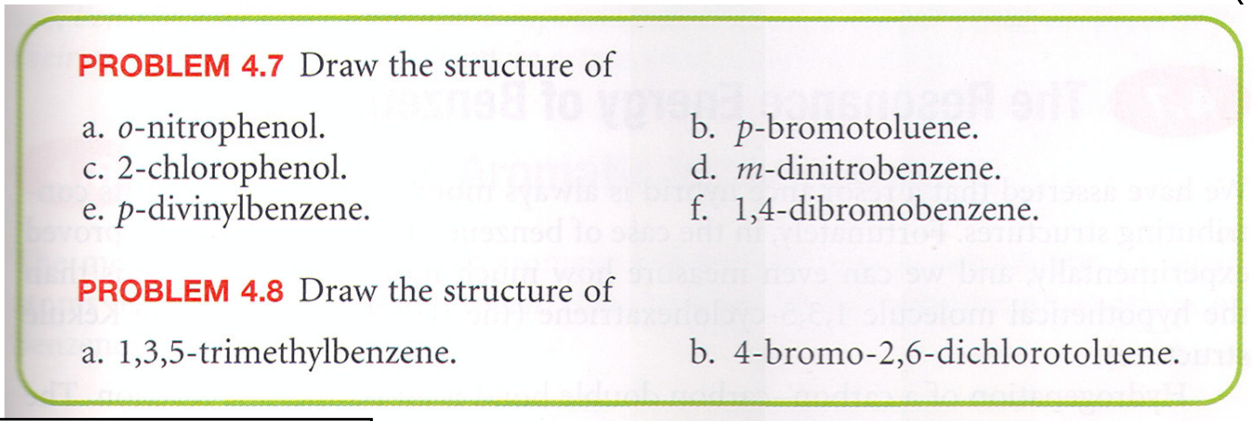


The benzyl group (the phenylmethyl group)



Benzyl chloride (phenylmethyl chloride or BzCl)

examples

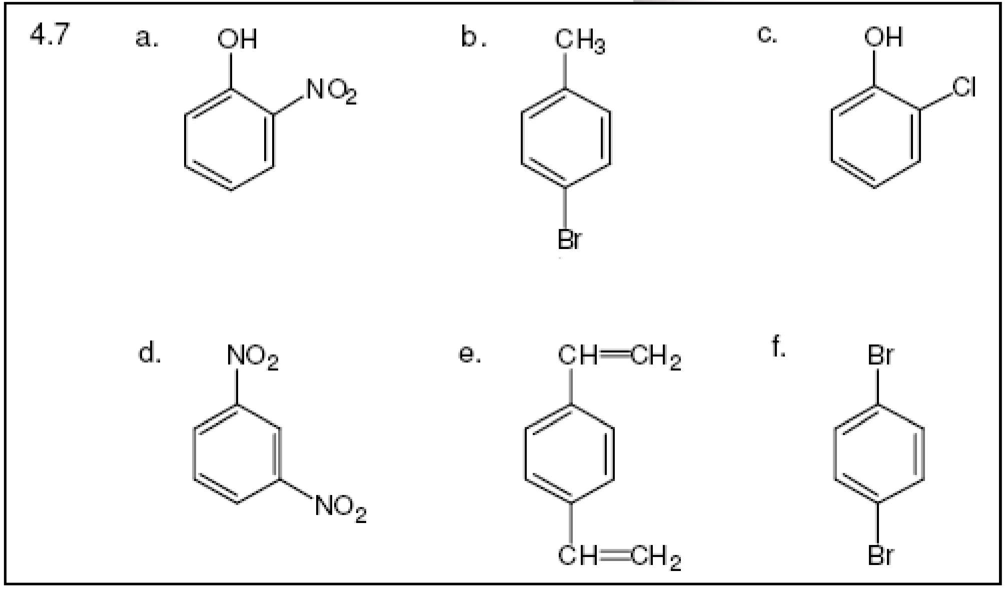


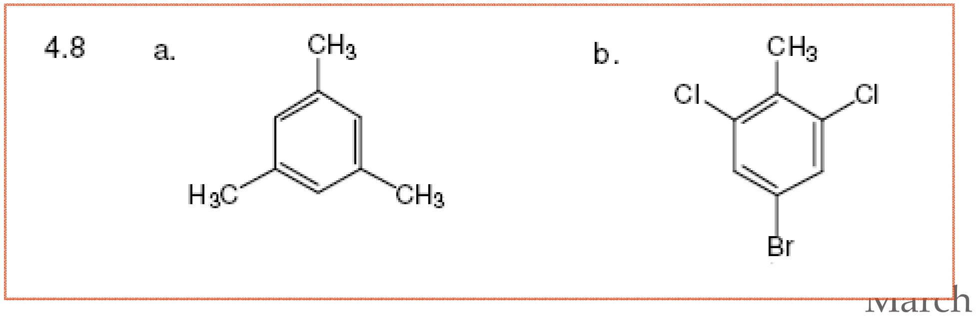
PROBLEM 4.7 Draw the structure of

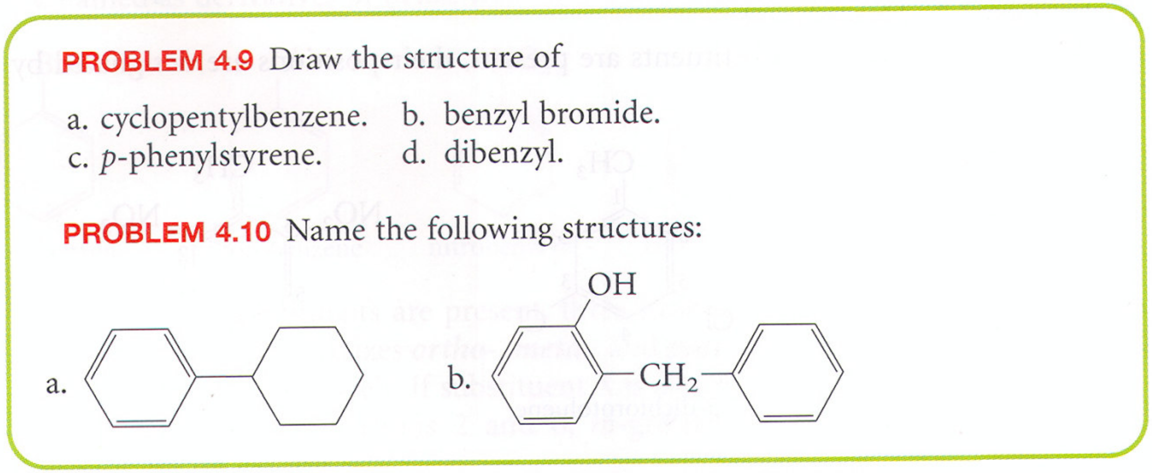
a. *o*-nitrophenol.
b. *p*-bromotoluene.
c. 2-chlorophenol.
d. *m*-dinitrobenzene.
e. *p*-divinylbenzene.
f. 1,4-dibromobenzene.

PROBLEM 4.8 Draw the structure of

a. 1,3,5-trimethylbenzene.
b. 4-bromo-2,6-dichlorotoluene.







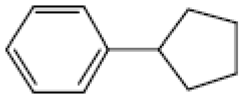
PROBLEM 4.9 Draw the structure of

a. cyclopentylbenzene.
b. benzyl bromide.
c. *p*-phenylstyrene.
d. dibenzyl.

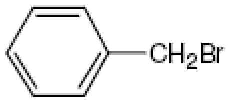
PROBLEM 4.10 Name the following structures:

4.9

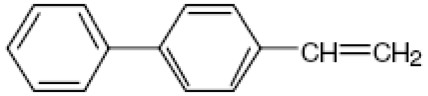
a.



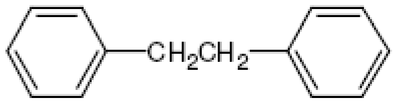
b.



c.



d.



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

4.7 the Resonance Energy of Benzene

The Stability of Benzene

Benzene is much more stable than would be expected

Based on calculations for "cyclohexatriene"

A reasonable prediction for the heat of hydrogenation of hypothetical cyclohexatriene is 86 kcal mol^{-1} (3 times that of cyclohexene, -28.6 kcal mol^{-1})

The experimentally determined heat of hydrogenation for benzene is 49.8 kcal mol^{-1} . 36 Kcal mol^{-1} more stable than hypothetical Cyclohexatriene This difference is called the **resonance Energy (or Stabilization Energy)**