

Chapter 9. Benzene and Derivatives

Learning objectives:

1. Name benzene derivatives.
2. Recognize aromatic compounds using Huckel's criteria.
3. Explain the trend for the acidity of substituted phenol using the concept of electron-donating and electron-withdrawing groups, and inductive and resonance effects..
4. Write the oxidation of the benzylic groups with C-H bond(s) to benzoic acid.
5. Write the electron-pushing (arrow-pushing) mechanisms for the electrophilic aromatic substitution of benzene including halogenation, nitration, sulfonation, Friedel-Crafts alkylation, and Friedel-Crafts acylation.
6. Explain the trend for the reactivity of benzene toward electrophilic aromatic substitution using the concept of electron-donating and electron-withdrawing groups.
7. Recognize the reagents for reduction of nitro group to amino group.
8. Using the concept of electron-donating and electron-withdrawing groups, explain the regioselectivity (ortho/para versus meta) for the formation of di-substituted benzene derivatives.

Sections to be covered (in the order of delivery):

- 9.1 Introduction[#]
- 9.2 The Structure of Benzene
- 9.3 The Concept of Aromaticity^{*}
- 9.4 Nomenclature
- 9.5 Reactions of Benzene: Oxidation at Benzylic Position
- 9.6 Reactions of Benzene: Electrophilic Aromatic Substitution^{*}
- 9.7 Mechanism of Electrophilic Aromatic Substitution^{*}
- 9.8 Disubstitution and Polysubstitution^{*}
- 9.9 Phenols

* Sections that will be focused

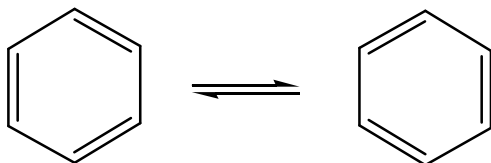
[#] Sections that will be skipped

Recommended additional problems

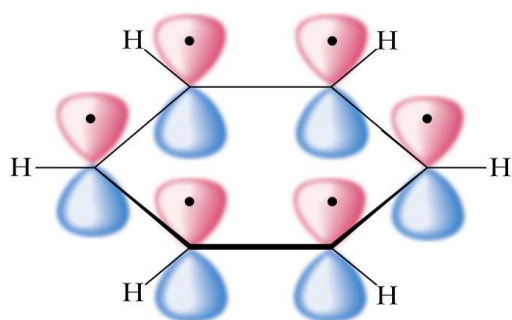
9.10 – 9.42

9.2 The Structure of Benzene

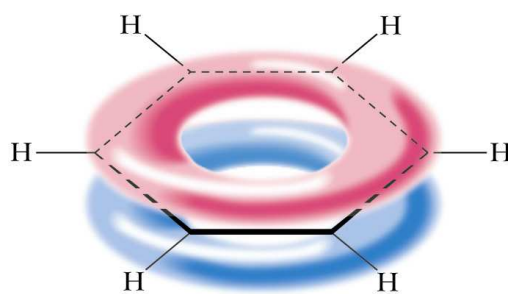
A. The Kekulé's Model of Benzene



B. The Orbital Model of Benzene

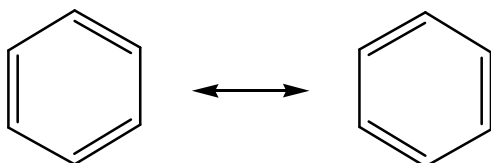


(a)

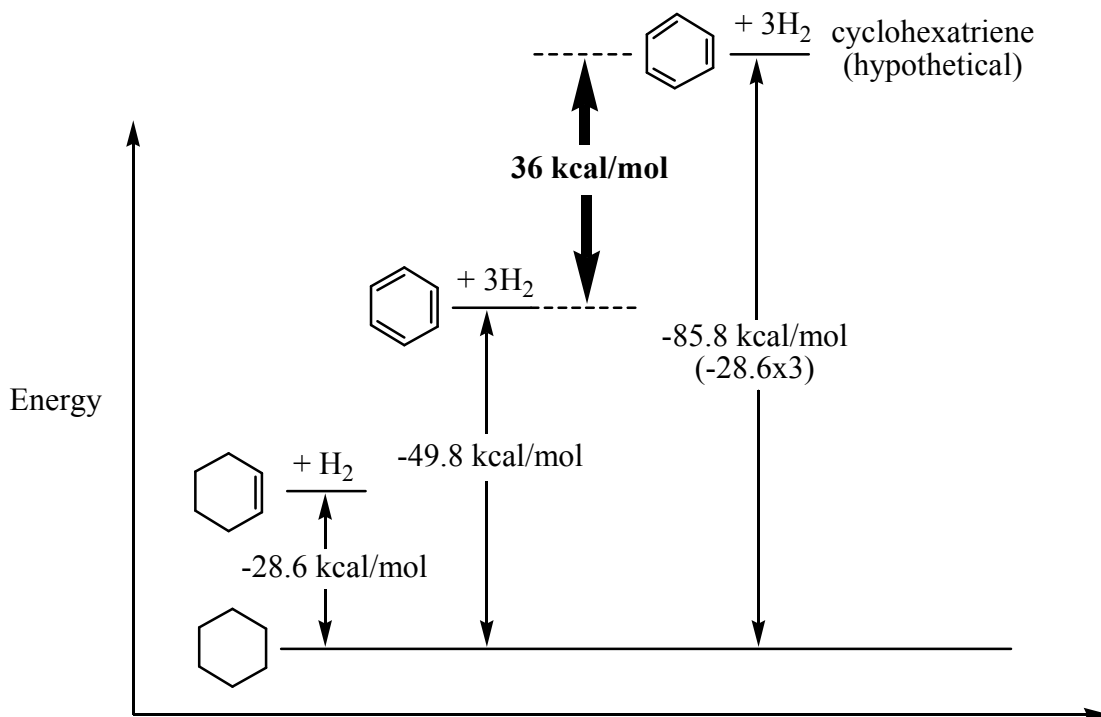
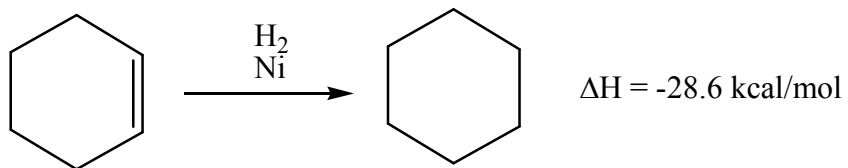


(b)

C. The Resonance Model of benzene



D. The Resonance Energy of Benzene

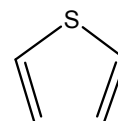
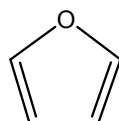
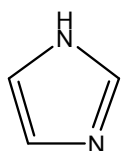
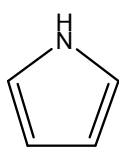
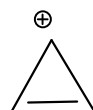
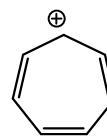
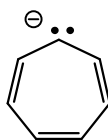
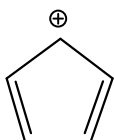
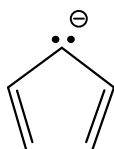
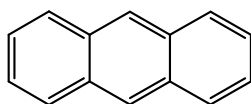
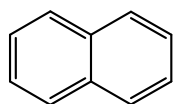
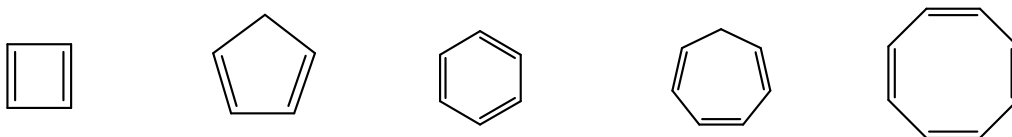


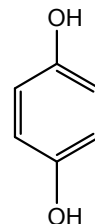
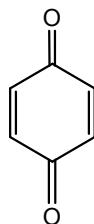
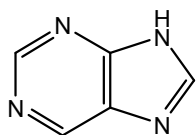
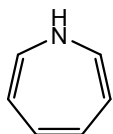
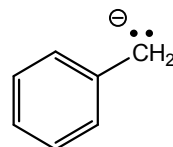
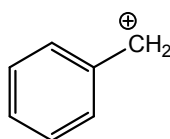
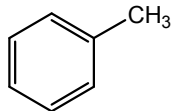
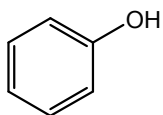
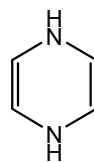
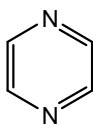
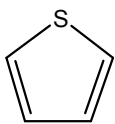
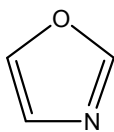
9.3 The Concept of Aromaticity

A. The Criteria of Being Aromatic

- (i) Cyclic molecule
- (ii) Every atom has p orbital
- (iii) Planar molecule
- (iv) Comply with $4n+2$ rule (as compared with $4n$ rule)

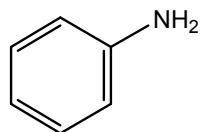
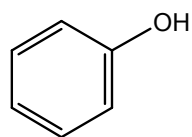
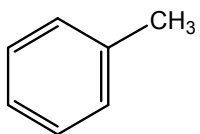
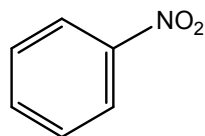
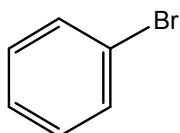
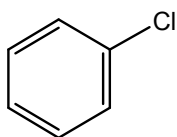
B. Examples

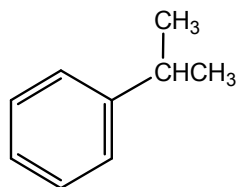
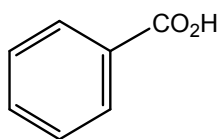
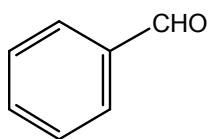
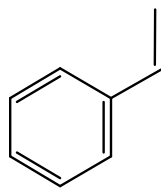
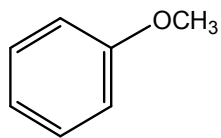
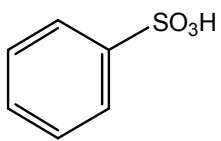




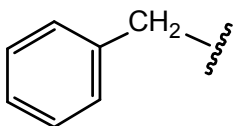
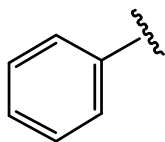
9.4 Nomenclature

A. Monosubstituted Benzenes

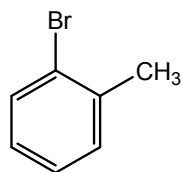
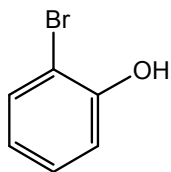
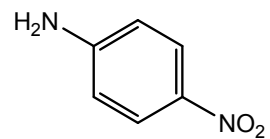
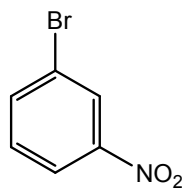
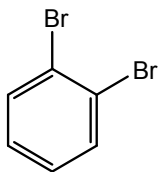




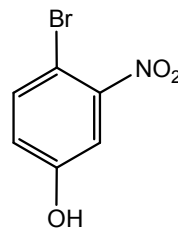
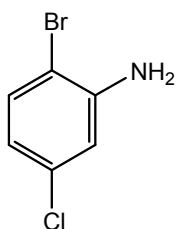
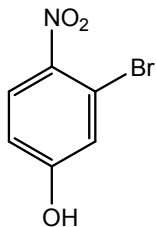
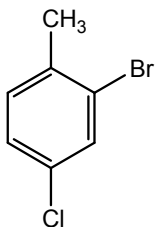
As substituent:



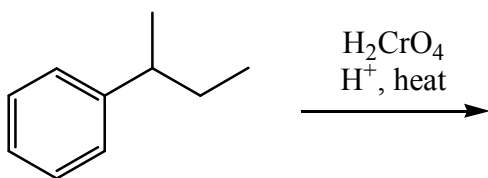
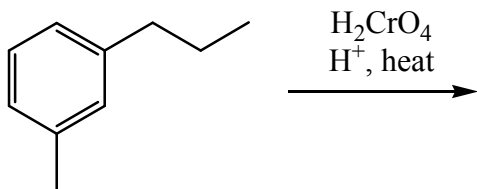
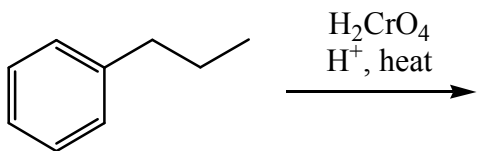
B. Disubstituted Benzenes

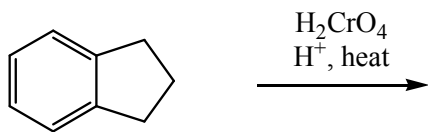
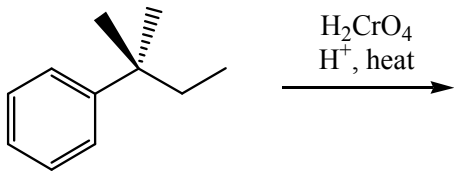


C. Polysubstituted Benzenes

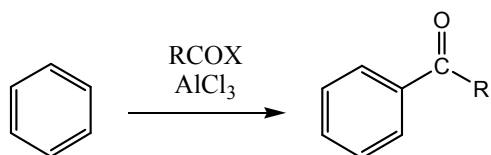
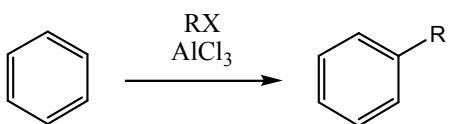
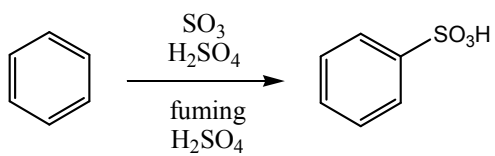
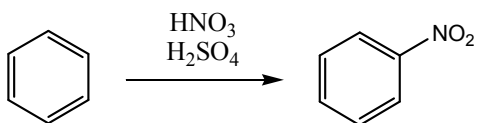
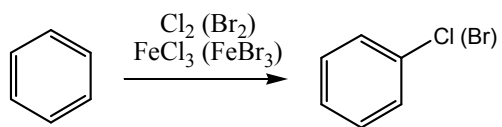
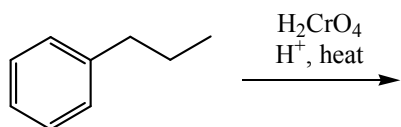


9.5 Reactions of Benzene: Oxidation at Benzylic Position





9.6 Reactions of Benzene: Electrophilic Aromatic Substitution



9.7 Mechanism of Electrophilic Aromatic Substitution

A. Chlorination and Bromination

B. Nitration and Sulfonation

C. Friedel-Craft Alkylation

D. Friedel-Craft Acylation

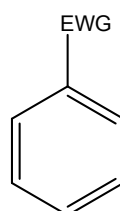
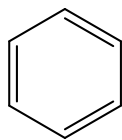
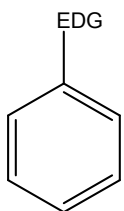
E. Other Electrophilic Aromatic Substitutions

9.8 Disubstitution and Polysubstitution

(i) Overview of Effect of Substituents on Benzene

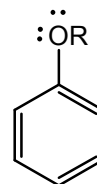
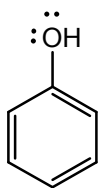
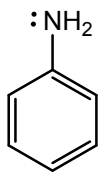
electron donation group (EDG)

electron withdrawing group (EWG)

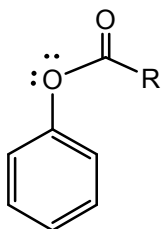
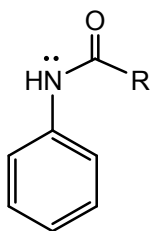


(ii) Analysis of Regioselectivity

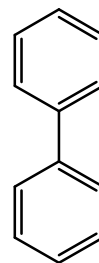
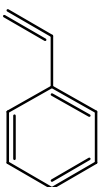
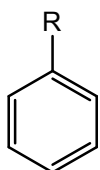
Strong activating groups (substituents)



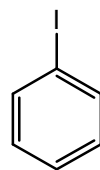
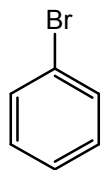
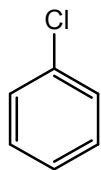
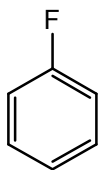
Moderate activating groups (substituents)



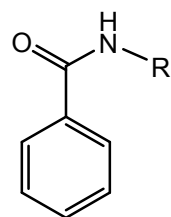
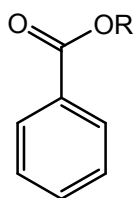
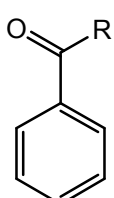
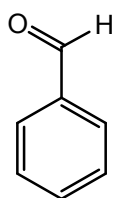
Weak activating groups (substituents)



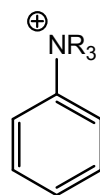
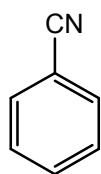
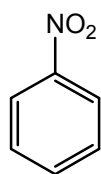
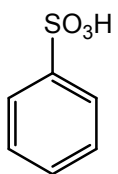
Weak deactivating groups (substituents)



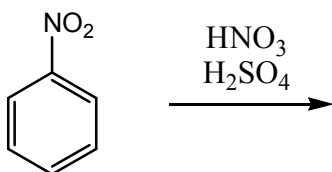
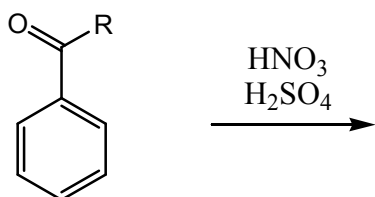
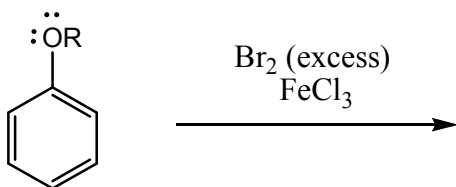
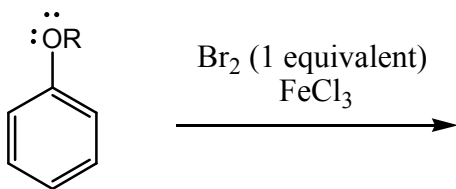
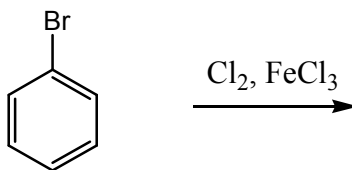
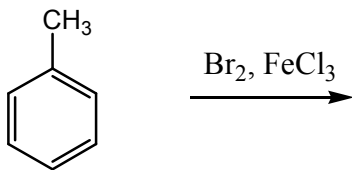
Moderate deactivating groups (substituents)



Strong deactivating groups (substituents)

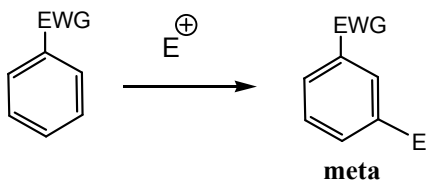
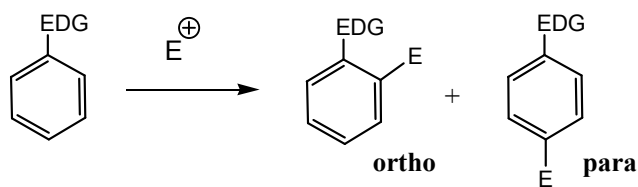
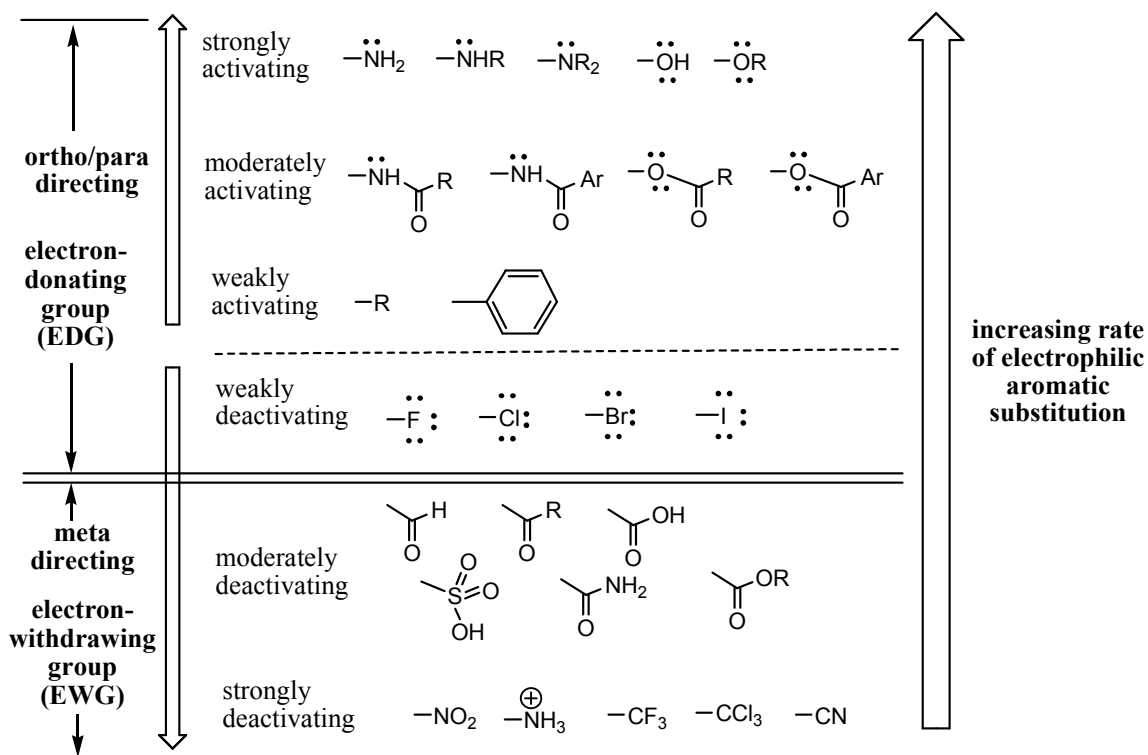


(iii) Examples



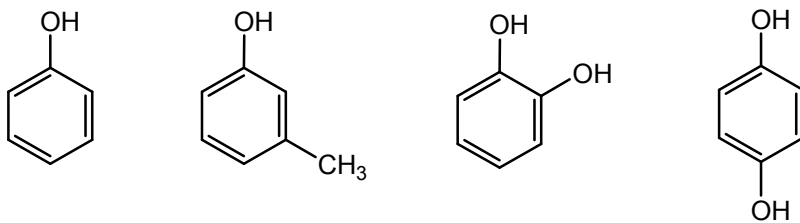
(iv) Summary

Effect of Substituents on Electrophilic Aromatic Substitution

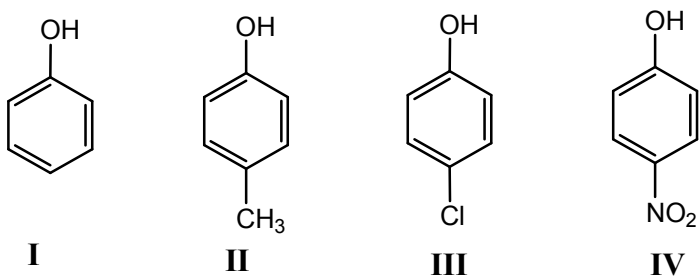


9.9 Phenols

A. Structure and Nomenclature



B. Acidity of Phenols



C. Acid-Base Reactions of Phenols

D. Phenols as Antioxidants

