CHAPTER OVERVIEW

3: CHEMISTRY OF BENZENE - ELECTROPHILIC AROMATIC SUBSTITUTION

LEARNING OBJECTIVES

When you have completed Chapter 16, you should be able to

1. fulfill all of the detailed objectives listed under each individual section.
2. solve road-map problems that require an understanding of the chemistry discussed in this chapter and those that preceded it.
3. design multistep syntheses using the reactions discussed in this and the preceding chapters. In particular you should be prepared to show how an aromatic compound containing two or more substituents could be synthesized, taking care to introduce the substituents into the ring in the correct order.
4. define, and use in context, the key terms introduced.

In the preceding chapter, you studied the concept of aromaticity and spent considerable time on the theoretical aspects of the chemistry of aromatic compounds. In this chapter, you will begin to study the chemical reactions of aromatic compounds, focusing in particular on electrophilic aromatic substitution, and to a lesser extent on nucleophilic aromatic substitution. We will discuss, in detail, the mechanism of electrophilic substitution, paying particular attention to the factors that determine both the rate and position of substitution in those aromatic compounds which already have one or more substituents present in the aromatic ring. When we discuss nucleophilic aromatic substitution, you will see that it can be achieved by two different mechanisms, one of which involves the formation of an unusual looking intermediate, benzyne.

You will also see how alkyl and acyl groups can be introduced on to an aromatic ring; how, once introduced, alkyl groups can be converted to carboxyl groups; and how bromine can be introduced to the alkyl side chain of alkylbenzene. The latter reaction is particularly useful because the benzylic bromide so produced undergoes the reactions of a typical alkyl bromide, thus providing us with a synthetic route to a large variety of compounds.

3.1: Introduction
3.2: Electrophilic Aromatic Substitution Reactions - Bromination
3.3: Other Aromatic Substitutions
3.4: Alkylation and Acylation of Aromatic Rings - The Friedel-Crafts Reaction
3.5: Substituent Effects in Substituted Aromatic Rings
3.6: An Explanation of Substituent Effects
3.7: Trisubstituted Benzenes - Additivity of Effects
3.8: Nucleophilic Aromatic Substitution
3.9: Benzyne
3.10: Oxidation of Aromatic Compounds
3.11: Reduction of Aromatic Compounds
3.12: Synthesis of Polysubstituted Benzenes
3.13: Additional Problems
3.S: Chemistry of Benzene - Electrophilic Aromatic Substitution (Summary)