

3.1: INTRODUCTION

OBJECTIVE

After completing this section, you should be able to identify electrophilic substitution as the single most important reaction of aromatic compounds.

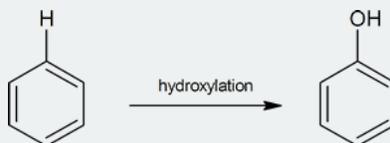
KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- acylation
- alkylation
- electrophilic substitution
- halogenation
- hydroxylation
- nitration
- sulfonation

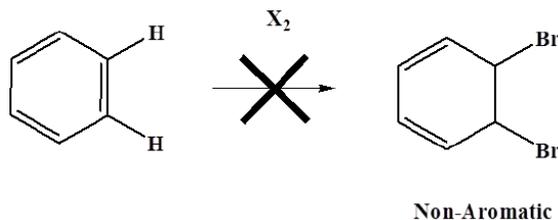
STUDY NOTES

In this chapter, you will study all of the reactions shown in the Reaction Type table. In addition to these five reaction types, we also add a sixth common electrophilic substitution known as hydroxylation.

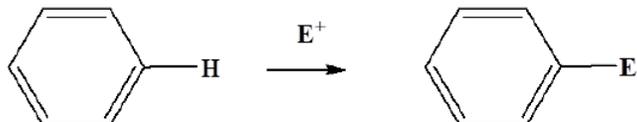


It is important that you recognize the similarities between these reactions to minimize the amount you must memorize.

The six pi electrons obey Huckel's rule so benzene is especially stable. This means that the aromatic ring wants to be retained during reactions. Because of this benzene does not undergo addition like other unsaturated hydrocarbons.



Benzene can undergo electrophilic aromatic substitution because aromaticity is maintained.



Product is Aromatic

OTHER EXAMPLES OF ELECTROPHILIC AROMATIC SUBSTITUTION

Many other substitution reactions of benzene have been observed, the five most useful are listed below (chlorination and bromination are the most common halogenation reactions). Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as **Electrophilic Aromatic Substitution**. The catalysts and co-reagents serve to generate the strong electrophilic species needed to effect the initial step of the substitution. The specific electrophile believed to function in each type of reaction is listed in the right hand column.

Reaction Type	Typical Equation			Electrophile E ⁽⁺⁾	
Halogenation:	C ₆ H ₆	+ Cl ₂ & heat FeCl ₃ catalyst	—————>	C ₆ H ₅ Cl + HCl Chlorobenzene	Cl ⁽⁺⁾ or Br ⁽⁺⁾
Nitration:	C ₆ H ₆	+ HNO ₃ & heat H ₂ SO ₄ catalyst	—————>	C ₆ H ₅ NO ₂ + H ₂ O Nitrobenzene	NO ₂ ⁽⁺⁾
Sulfonation:	C ₆ H ₆	+ H ₂ SO ₄ + SO ₃ & heat	—————>	C ₆ H ₅ SO ₃ H + H ₂ O Benzenesulfonic acid	SO ₃ H ⁽⁺⁾
Alkylation: Friedel-Crafts	C ₆ H ₆	+ R-Cl & heat AlCl ₃ catalyst	—————>	C ₆ H ₅ -R + HCl An Arene	R ⁽⁺⁾
Acylation: Friedel-Crafts	C ₆ H ₆	+ RCOCl & heat AlCl ₃ catalyst	—————>	C ₆ H ₅ COR + HCl An Aryl Ketone	RCO ⁽⁺⁾

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