

BOOKS

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry, Jonathan Clayden Nick Greeves Stuart Warren, 2th Edition
- 4) Organic Chemistry, John E. McMurry, 8th. Edition
- 5) Reaksiyon Mekanizmaları: Metin Balcı, 2. Baskı.

1. REACTIONS OF AROMATIC COMPOUNDS

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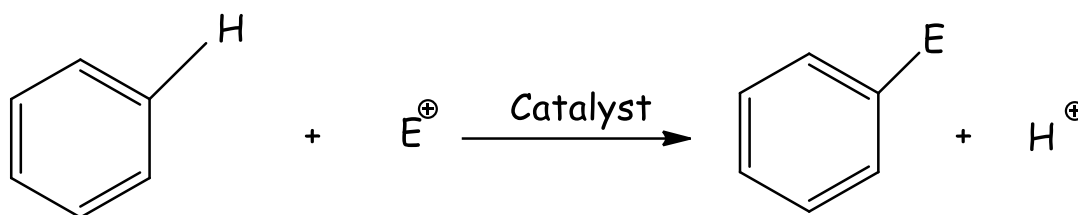
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1. Reactions of Benzene

1.1 Electrophilic Aromatic Substitution Reactions

Some of the most important reactions of aromatic compounds are those in which an electrophile replaces one of the hydrogen atoms of the ring.



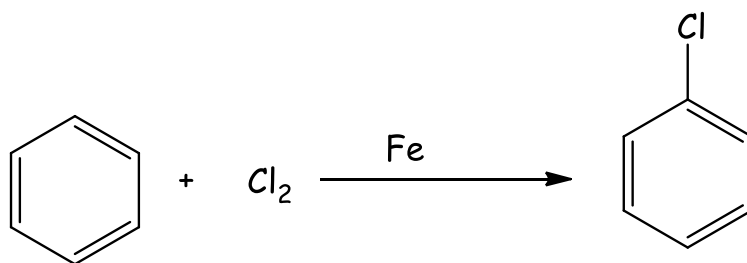
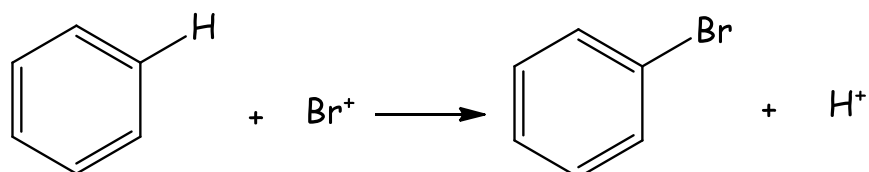
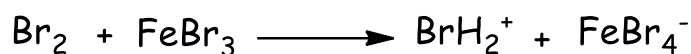
E^+ = Electrophile; Cl_2 , Br_2 , RX ($\text{X} = \text{Cl}, \text{Br}$), HNO_3 , H_2SO_4 etc.

These reactions, called **electrophilic aromatic substitutions (EAS)**, allow the direct introduction of groups onto aromatic rings such as benzene, and they provide synthetic routes to many important compounds.

1.1.1 Halogenation of Benzene

The Lewis acids typically used are aluminum chloride (AlCl_3) and iron chloride (FeCl_3) for chlorination, and iron bromide

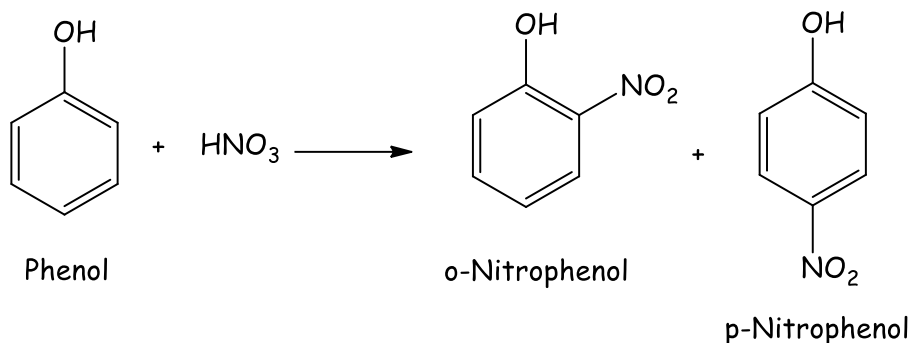
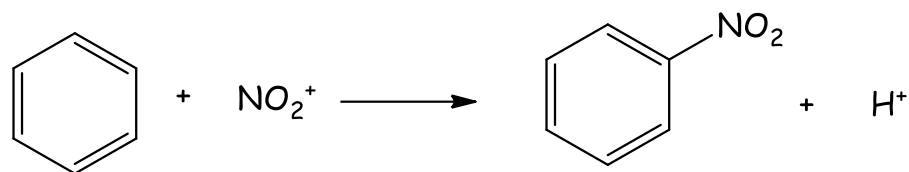
(FeBr₃) for bromination. The purpose of the Lewis acid is to make the halogen a stronger electrophile.



1.1.2 Nitration of Benzene

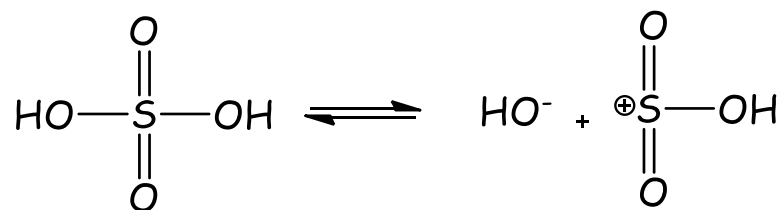
Benzene undergoes nitration on reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid. Concentrated sulfuric acid increases the rate of the reaction by increasing the concentration of the electrophile, the nitronium ion (NO₂⁺),

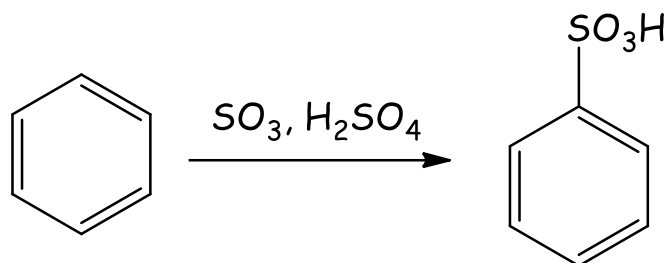
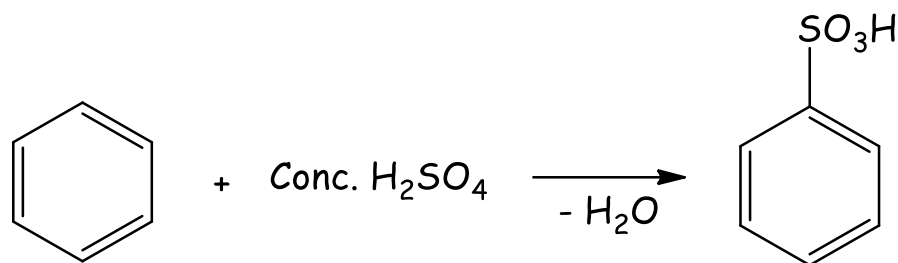




1.1.3 Sulfonation of Benzene

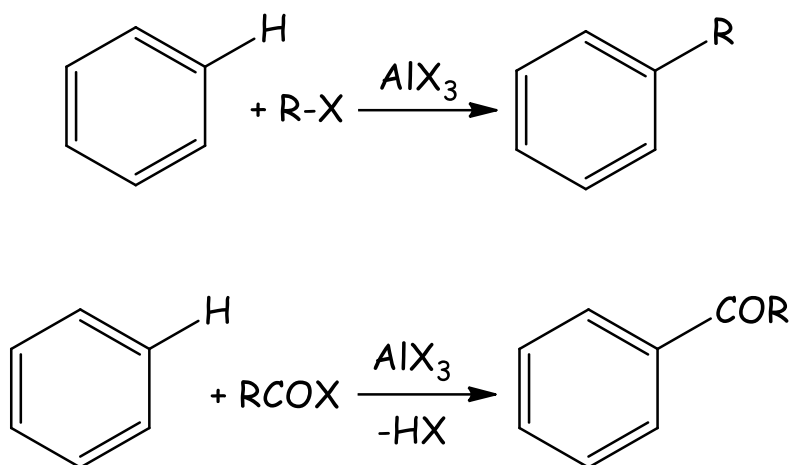
Benzene reacts with fuming sulfuric acid at room temperature to produce benzenesulfonic acid. Fuming sulfuric acid is sulfuric acid that contains added sulfur trioxide (SO_3). Sulfonation also takes place in concentrated sulfuric acid alone, but more slowly. Under either condition, the electrophile appears to be sulfur trioxide.





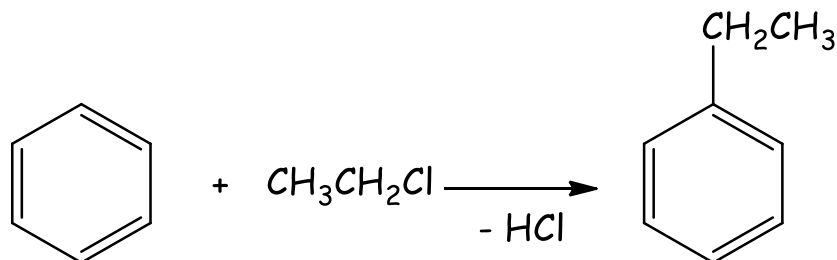
1.1.4 Friedel-Crafts Alkylation and Acylation

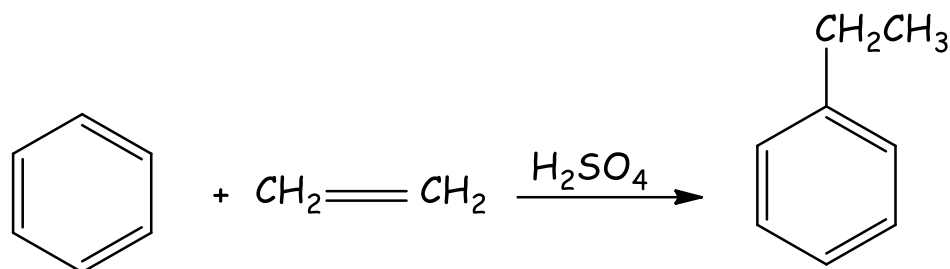
Charles Friedel, a French chemist, and his American collaborator, James M. Crafts, discovered new methods for the preparation of alkylbenzenes (ArR) and acylbenzenes (ArCOR) in 1877. These reactions are now called the Friedel-Crafts alkylation and acylation reactions. Friedel-Crafts alkylations are usually used to alkyl halides and aluminum chloride. Other pairs of reagents that form carbocations (or species like carbocations) may be used in Friedel-Crafts alkylations as well.



The Friedel-Crafts acylation reaction is often carried out by treating the aromatic compound with an acyl halide (often an acyl chloride). Unless the aromatic compound is one that is highly reactive, the reaction requires the addition of at least one equivalent of a Lewis acid (such as AlCl_3) as well. The product of the reaction is an aryl ketone.

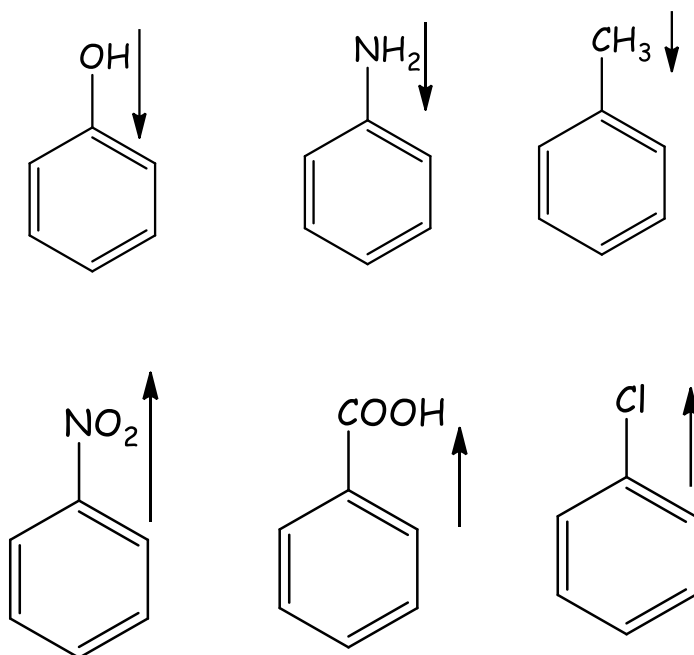
Examples;





1.2 Electron-Donating and Electron-Withdrawing Substituents

A substituent group already present on a benzene ring can affect both the reactivity of the ring toward electrophilic substitution and the orientation that the incoming group takes on the ring. A substituent can make the ring **more reactive** than benzene (i.e., it can make the compound react faster than benzene reacts). Such a group is called an **activating group**. A substituent can make the ring **less reactive** than benzene (i.e., it can make the compound react more slowly than benzene reacts). Such groups are called **deactivating groups**.



1.3 Groups: Ortho-Para-Meta Directors

A substituent on the ring can also affect the **orientation** that the incoming group takes when it replaces a hydrogen atom on the ring. Substituents fall into two general classes:

Ortho-para directors predominantly direct the incoming group to a position ortho or para to itself. All electron-donating groups are activating groups and all are ortho-para directors. Halogen substituents are weakly deactivating groups and are ortho-para directors.

Meta directors predominantly direct the incoming group to a position meta to itself. With the exception of halogen substituents, all electron-withdrawing groups are deactivating groups and all are meta directors.