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: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,

4) Organic Chemistry : A Brief Course, R. C. Atkins, F.A. Carey

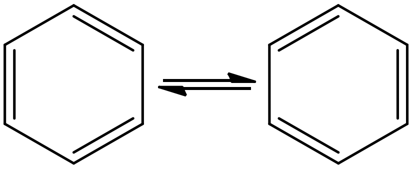
4. AROMATIC COMPOUNDS

4. AROMATIC COMPOUNDS

Benzene has only as many hydrogen atoms as it has carbon atoms. Benzene, having the formula of C_6H_6, should be a highly unsaturated compound because it has an index of hydrogen deficiency equal to 4. Eventually, chemists began to recognize that benzene was a member of a new class of organic compounds with unusual and interesting properties. Benzene does not show the behavior expected of a highly unsaturated compound.

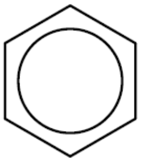
4.1 The Structure for Benzene

In 1865, August Kekulé, proposed the first definite structure for benzene, a structure that is still used today. Kekulé suggested that the carbon atoms of benzene are in a ring, that they are bonded to each other by alternating single and double bonds, and that one hydrogen atom is attached to each carbon atom. This structure satisfied the requirements of the structural theory that carbon atoms form four bonds and that all the hydrogen atoms of benzene are equivalent:



Experimental evidence bears this out. Spectroscopic measurements show that the molecule of benzene is planar and that all of its carbon–carbon bonds are of equal length. Moreover, the carbon–carbon bond lengths in benzene are 1.39 Å, a value in between that for a carbon–carbon single bond between sp^2-hybridized atoms (1.47 Å) and that for a carbon–carbon double bond (1.34 Å).

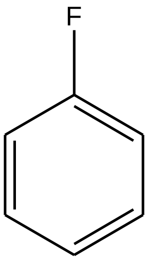
The hybrid structure of benzene is represented by inscribing a circle inside the hexagon as shown in formula below.



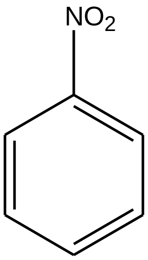
4.2 Nomenclature of Benzene Derivatives

Two systems are used in naming monosubstituted benzenes.

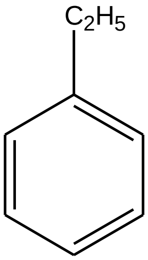
- In many simple compounds, benzene is the parent name and the substituent is simply indicated by a prefix.



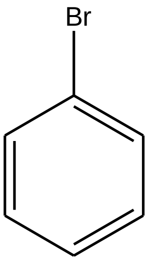
Fluorobenzene



Nitrobenzene

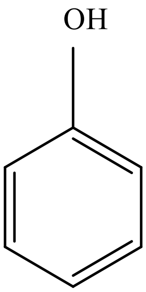


Ethylbenzene

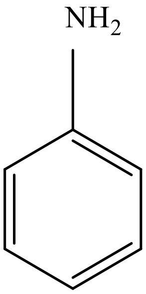


Bromobenzene

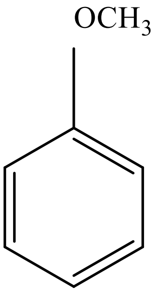
- For other simple and common compounds, the substituent and the benzene ring taken together may form a commonly accepted parent name.



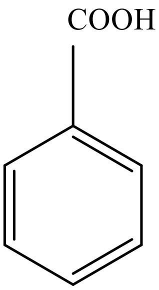
Hydroxybenzene
Phenol



Benzeneamine
Aniline

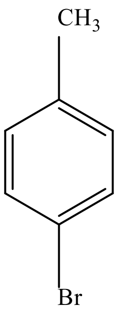


Methoxybenzene
Anisole

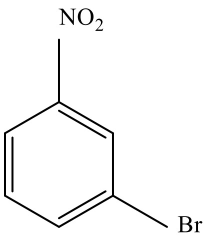


Benzenecarboxylic acid
Benzoic acid

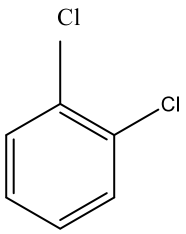
- When two substituents are present, their relative positions are indicated by the prefixes ortho-, meta-, and para- (abbreviated o-, m-, and p-) or by the use of numbers



1-Bromo-4-methylbenzene
p-Bromotoluene

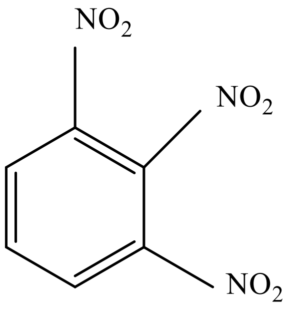


1-Bromo-3-nitrobenzene
m-Bromonitrobenzene

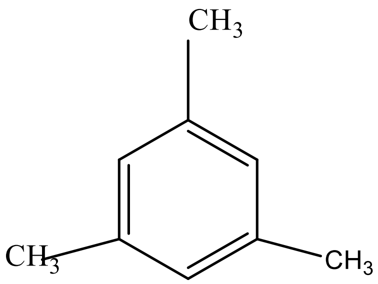


1,2-Dibromobenzene
o-dichlorobenzene

- If more than two groups are present on the benzene ring, their positions must be indicated by the use of *numbers*.



1,2,3-Trinitrobenzene
Mesitilene



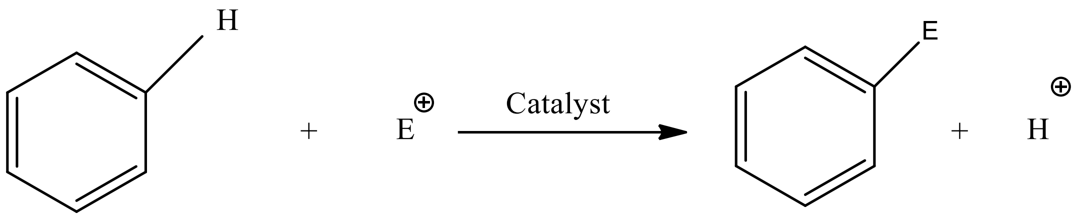
1,3,5-Trinitrobenzene

4.3 The Resonance Explanation of the Structure of Benzene

The difference in energy between hypothetical 1,3,5-cyclohexatriene (which if it existed would have higher energy) and benzene is called *resonance energy*, and it is an indication of the extra stability of benzene due to electron delocalization.

4.4 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.



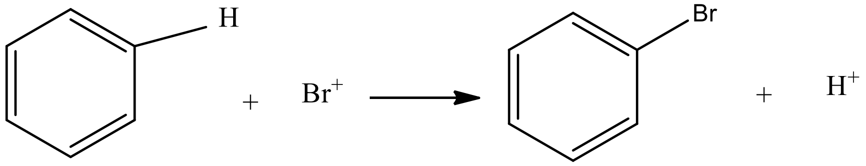
E^+ = Electophile; Cl_2, Br_2, RX (X= Cl, Br), HNO_3, H_2SO_4 etc.

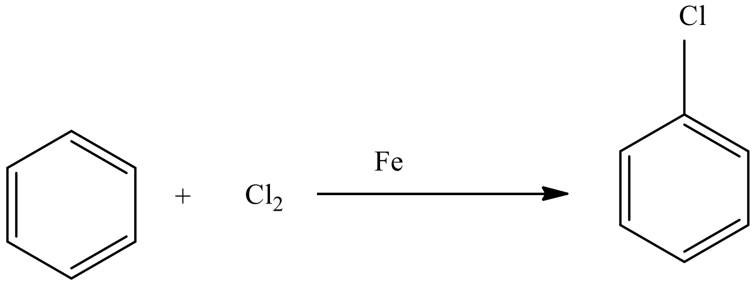
These reactions, called **electrophilic aromatic substitutions (EAS)**, allow the direct introduction of groups onto aromatic rings such as benzene, and they provide synthetic routes to many important compounds.

4.4.1 Halogenation of Benzene

The Lewis acids typically used are aluminum chloride ($AlCl_3$) and iron chloride ($FeCl_3$) for chlorination, and iron bromide ($FeBr_3$) for bromination. The purpose of the Lewis acid is to make the halogen a stronger electrophile.

$$Br_2 + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$$

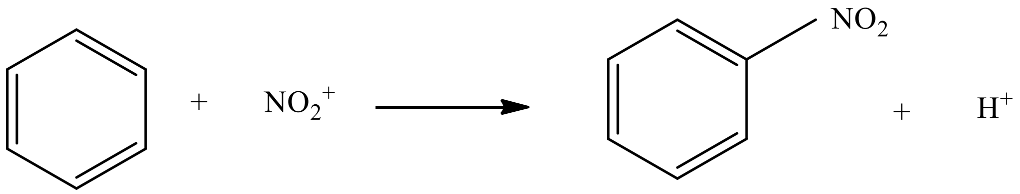


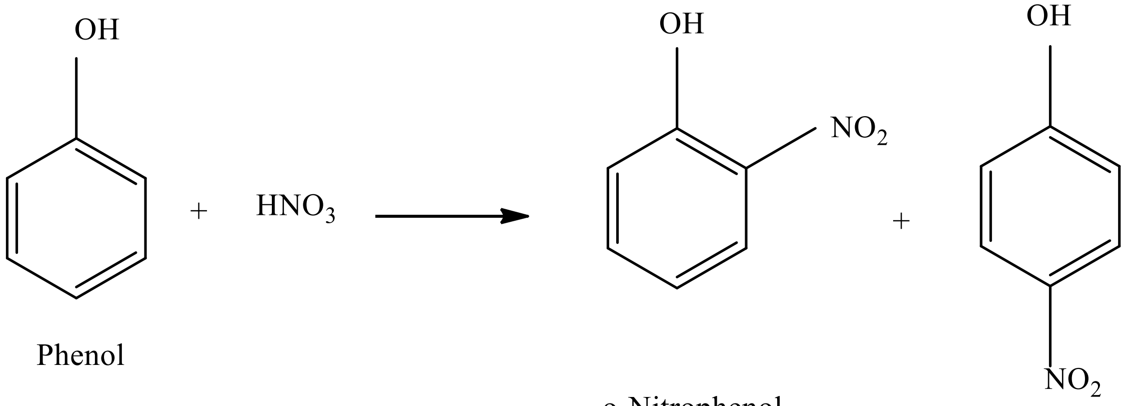


4.4.2 Nitration of Benzene

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 (NO_2^+),

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2O + NO_2^+ + HSO_4^-$$





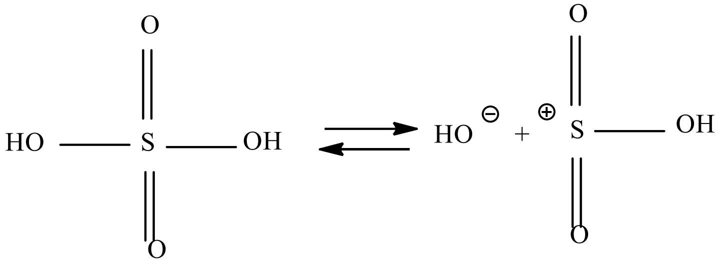
Phenol

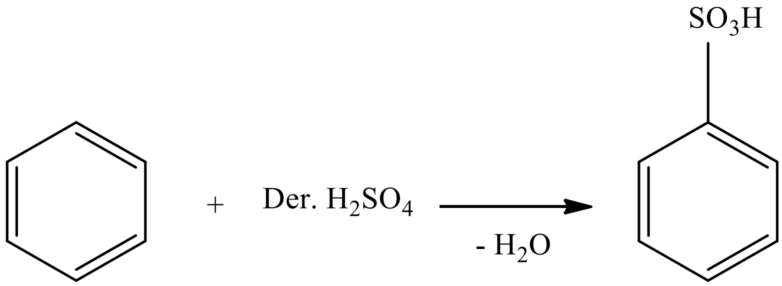
o-Nitrophenol

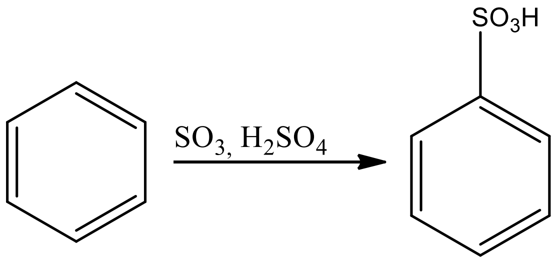
p-Nitrophenol

4.4.3 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.

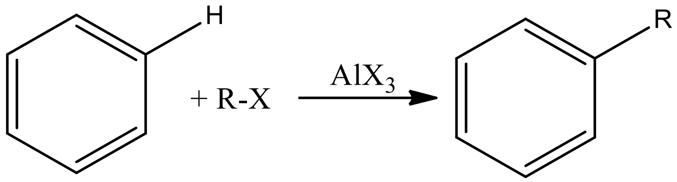


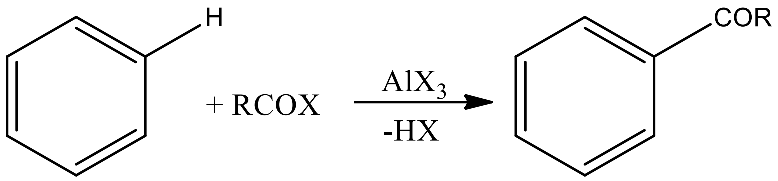




4.4.4 Friedel–Crafts Alkylation and Acylation

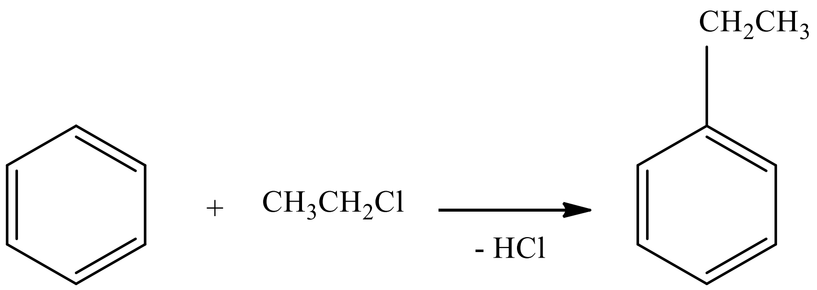
Charles Friedel, a French chemist, and his American collaborator, James M. Crafts, discovered new methods for the preparation of alkylbenzenes (ArR) and acylbenzenes (ArCOR) in 1877. These reactions are now called the Friedel–Crafts alkylation and acylation reactions. Friedel–Crafts alkylations are usually 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.

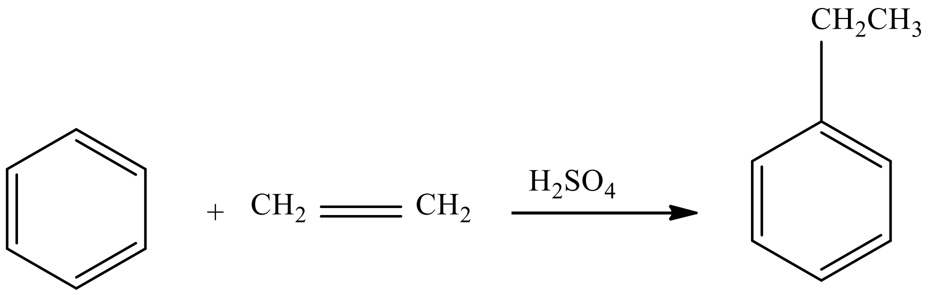




The Friedel–Crafts acylation reaction is often carried out by treating the aromatic compound with an acyl halide (often an acyl chloride). Unless the aromatic compound is one that is highly reactive, the reaction requires the addition of at least one equivalent of a Lewis acid (such as $AlCl_3$) as well.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

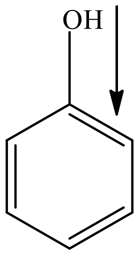
Examples;

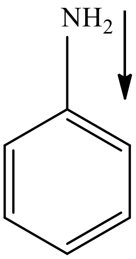


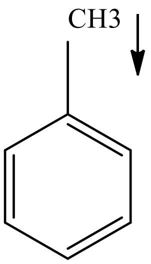


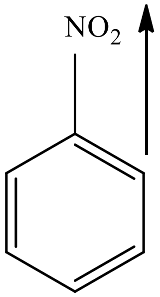
4.5 Electron-Donating and Electron-Withdrawing Substituents

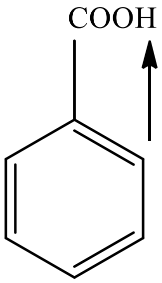
A substituent group already present on a benzene ring can affect both the reactivity of the ring toward electrophilic substitution and the orientation that the incoming group takes on the ring. A substituent can make the ring **more reactive** than benzene (i.e., it can make the compound react faster 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**.

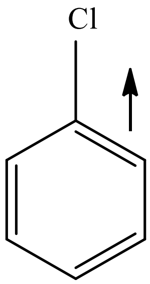












4.6 Groups: Ortho–Para-Meta Directors

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.

Ortho- , para- Activating Group

Strong	Middle	Weak
NR_2	OR	R
NH_2	NHCOR	Ar
OH		

Ortho- , para- Deactivating Group

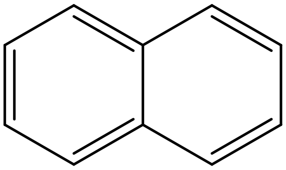
Weak
Halogens

Meta- Deactivating Group

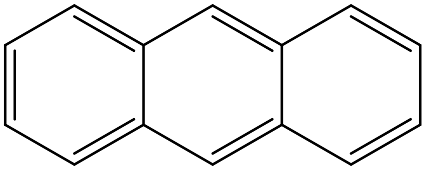
Strong	Middle
$-NR_3$	-COOH
$-NO_2$	-COOR
$-SO_3H$	$-CONH_2$
	-CHO
	-COR
	-CN

4.7 Benzenoid Aromatic Compounds

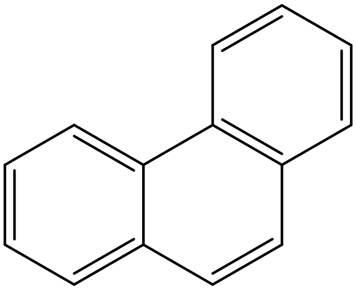
Representatives of one broad class of benzenoid aromatic compounds are called polycyclic aromatic hydrocarbons (PAH). Benzenoid polycyclic aromatic hydrocarbons consist of molecules having two or more benzene rings fused together.



Naphtalene



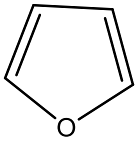
Antracene



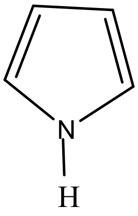
Phenantrene

4.8 Heterocyclic Aromatic Compounds

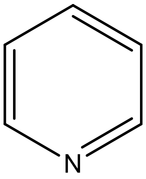
Cyclic compounds that include an element other than carbon are called heterocyclic compounds. Heterocyclic compounds containing nitrogen, oxygen, or sulfur are by far the most common.



Furane



Pyrole



Pyridine