

Chem. 118B Workshop/Doug Kent/LSC: Electrophilic Aromatic Substitution Reactions Of Benzene From Chapter 15, Vollhardt & Schore, 4th Edition (Benzene = C₆H₅-H)

Reaction	Reagents/Catalysts	Electrophile	Product	Comments
Halogenation	X ₂ /MX ₃ [X = Cl or Br; M = Al or Fe (III)]	$\overset{+}{\text{X}} = \overset{-}{\text{X}} - \text{MX}_3$	C ₆ H ₅ -X (Chlorobenzene, Bromobenzene)	
Nitration	HNO ₃ /H ₂ SO ₄	$\overset{+}{\text{NO}_2}$	C ₆ H ₅ -NO ₂ (Nitrobenzene)	May be reduced to aniline (C ₆ H ₅ -NH ₂) by H ₂ /Ni, or Fe/HCl, etc. (Ch. 16)
Sulfonation	SO ₃ /H ₂ SO ₄	SO ₃	C ₆ H ₅ -SO ₃ H (Benzenesulfonic Acid)	Reversible (desulfonation) by hydrolysis using H ₂ O/Δ/H ₂ SO ₄ (catalyst)
Friedel-Crafts Alkylation	RCH ₂ X/MX ₃	$\overset{+}{\text{RCH}_2} - \overset{-}{\text{X}} - \text{MX}_3$	C ₆ H ₅ -CH ₂ R (Alkylbenzene)	Not generally useful due to possibility of rearrangements, polyalkylation, etc.
Friedel-Crafts Acylation	1) RCOCl/AlCl ₃ or RCO ₂ COR/AlCl ₃ 2) H ⁺ /H ₂ O or H ₂ O	$\overset{+}{\text{R}} - \overset{-}{\text{C}} = \text{O}$	C ₆ H ₅ -COR (acylbenzene = phenyl ketone)	need at least 1 equivalent amount of AlCl ₃ ; Product may be reduced to alkylbenzene (Ch.16)