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Benzyne Mechanism

Halobenzenes with out electron-withdrawing substituents don't react with nucleophiles under most conditions. At high temperature and pressure, however, even chlorobenzene can be forced to react. Chemists at the Dow Chem ical Company discovered in 1928 that phenol could be prepared on a large industrial scale by treatment of chlorobenzene with dilute aqueous NaOH at 340 °C under 170 atm pressure

A similar substitution reaction occurs with other strong bases. Treatment of bromobenzene with potassium amide (KNH₂) in liquid NH₃ solvent, for instance, gives aniline. Curiously, though, when bromobenzene labeled with radioactive ¹⁴C at the C1 position is used, the substitution product has equal amounts of the label at both C1 and C2, implying the presence of a symmetrical reaction intermediate in which C1 and C2 are equivalent.