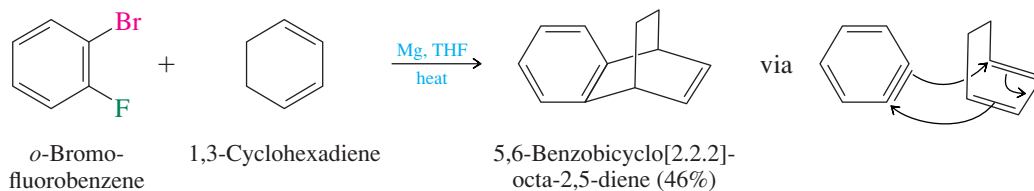


Its strained triple bond makes benzyne a relatively good dienophile, and when benzyne is generated in the presence of a conjugated diene, Diels–Alder cycloaddition occurs.

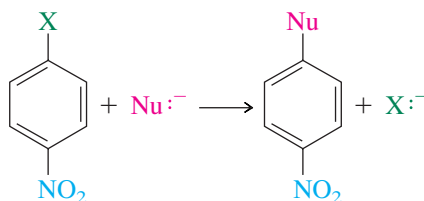


PROBLEM 23.9 Give the structure of the cycloaddition product formed when benzyne is generated in the presence of furan. (See Section 11.22, if necessary, to remind yourself of the structure of furan.)

Benzyne may also be generated by treating *o*-bromofluorobenzene with lithium. In this case, *o*-fluorophenyllithium is formed, which then loses lithium fluoride to form benzyne.

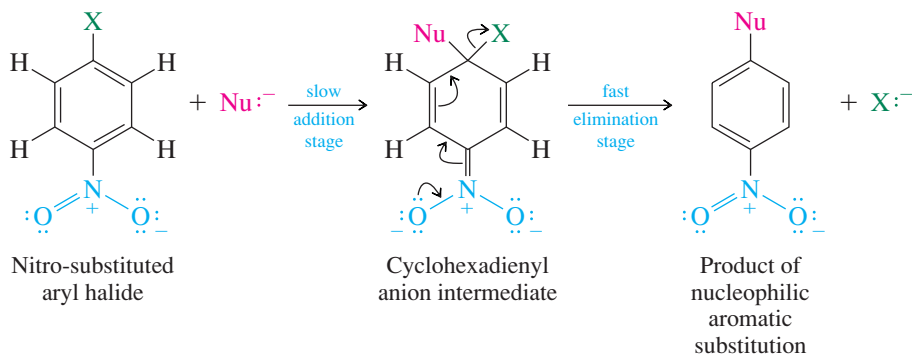
23.10 SUMMARY

- Section 23.1 Aryl halides are compounds of the type Ar—X where X = F, Cl, Br, or I. The carbon–halogen bond is stronger in ArX than in an alkyl halide (RX).
- Section 23.2 Some aryl halides occur naturally, but most are the products of organic synthesis. The methods by which aryl halides are prepared were recalled in Table 23.2
- Section 23.3 Aryl halides are less polar than alkyl halides.
- Section 23.4 Aryl halides are less reactive than alkyl halides in reactions in which C—X bond breaking is rate-determining, especially in nucleophilic substitution reactions.
- Section 23.5 Nucleophilic substitution in ArX is facilitated by the presence of a strong electron-withdrawing group, such as NO₂, ortho or para to the halogen.



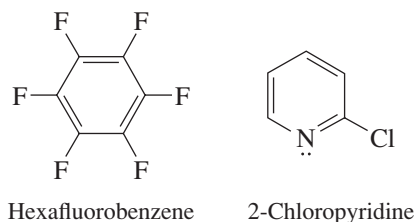
In reactions of this type, fluoride is the best leaving group of the halogens and iodide the poorest.

Section 23.6 Nucleophilic aromatic substitutions of the type just shown follow an **addition–elimination mechanism**.

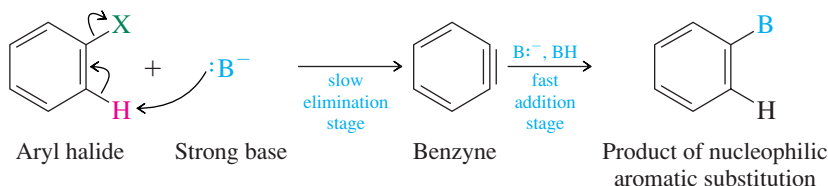


The rate-determining intermediate is a cyclohexadienyl anion and is stabilized by electron-withdrawing substituents.

Section 23.7 Other aryl halides that give stabilized anions can undergo nucleophilic aromatic substitution by the addition–elimination mechanism. Two examples are hexafluorobenzene and 2-chloropyridine.



Section 23.8 Nucleophilic aromatic substitution can also occur by an **elimination–addition mechanism**. This pathway is followed when the nucleophile is an exceptionally strong base such as amide ion in the form of sodium amide (NaNH_2) or potassium amide (KNH_2). **Benzynes** and related **arynes** are intermediates in nucleophilic aromatic substitutions that proceed by the elimination–addition mechanism.



Nucleophilic aromatic substitution by the elimination–addition mechanism can lead to substitution on the same carbon that bore the leaving group or on an adjacent carbon.

Section 23.9 Benzynes are reactive dienophiles and give Diels–Alder products when generated in the presence of dienes. In these cases it is convenient to form benzyne by dissociation of the Grignard reagent of *o*-bromofluorobenzene.