Chapter 23
Aryl Halides
23.1
Bonding in Aryl Halides
Aryl Halides

Aryl halides are halides in which the halogen is attached directly to an aromatic ring. Carbon-halogen bonds in aryl halides are shorter and stronger than carbon-halogen bonds in alkyl halides.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Type</th>
<th>Bond Energy: kJ/mol (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$X</td>
<td>$sp^3$</td>
<td>X = H: 410 (98)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>X = Cl: 339 (81)</td>
</tr>
<tr>
<td>H$_2$C$\equiv$CHX</td>
<td>$sp^2$</td>
<td>X = H: 452 (108)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>X = Cl: 368 (88)</td>
</tr>
<tr>
<td>X</td>
<td>$sp^2$</td>
<td>X = H: 469 (112)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>X = Cl: 406 (97)</td>
</tr>
</tbody>
</table>
Aryl halides are halides in which the halogen is attached directly to an aromatic ring. Carbon-halogen bonds in aryl halides are shorter and stronger than carbon-halogen bonds in alkyl halides. Because the carbon-halogen bond is stronger, aryl halides react more slowly than alkyl halides when carbon-halogen bond breaking is rate determining.
23.2
Sources of Aryl Halides
Preparation of Aryl Halides

Halogenation of arenes (Section 12.5)
The Sandmeyer reaction (Section 22.18)
The Schiemann reaction (Section 22.18)
Reaction of aryl diazonium salts with iodide ion (Section 22.18)
23.3

Physical Properties of Aryl Halides
Physical Properties of Aryl Halides

resemble alkyl halides
all are essentially insoluble in water
less polar than alkyl halides

\[ \mu \text{ 2.2 D} \]

\[ \mu \text{ 1.7 D} \]
23.4
Reactions of Aryl Halides:
A Review and a Preview
We have not yet seen any nucleophilic substitution reactions of aryl halides. Nucleophilic substitution on chlorobenzene occurs so slowly that forcing conditions are required.
Example

1. NaOH, H₂O
   
   370°C

2. H⁺

(97%)
Reasons for Low Reactivity

$S_N1$ not reasonable because:

1) C—Cl bond is strong; therefore, ionization to a carbocation is a high-energy process

2) aryl cations are less stable than alkyl cations
Reasons for Low Reactivity

$S_N2$ not reasonable because ring blocks attack of nucleophile from side opposite bond to leaving group.
23.5
Nucleophilic Substitution in Nitro-Substituted Aryl Halides
But... nitro-substituted aryl halides do undergo nucleophilic aromatic substitution readily.

\[
\begin{align*}
\text{Cl} & \quad \text{NO}_2 \\
+ & \quad \text{NaOCH}_3 \\
\xrightarrow{\text{CH}_3\text{OH}} & \quad 85^\circ\text{C} \\
\text{OCH}_3 & \quad \text{NO}_2 \\
\quad & \quad \text{NaCl} \\
\text{yield: } 92\% & \quad \text{(92%)}
\end{align*}
\]
Effect of nitro group is cumulative

especially when nitro group is ortho and/or para to leaving group

\[
\begin{align*}
&\text{Cl} & &\text{Cl} & &\text{Cl} & &\text{Cl} \\
&\text{NO}_2 & &\text{NO}_2 & &\text{NO}_2 & &\text{NO}_2 \\
&1.0 & &7 \times 10^{10} & &2.4 \times 10^{15} & &\text{too fast to measure}
\end{align*}
\]
follows second-order rate law:
rate = \( k[\text{aryl halide}][\text{nucleophile}] \)

inference:
both the aryl halide and the nucleophile are involved in rate-determining step
Effect of leaving group

unusual order: F > Cl > Br > I

\[
\begin{array}{c|c|c}
X & \text{Relative Rate}^* \\
\hline
\text{F} & 312 \\
\text{Cl} & 1.0 \\
\text{Br} & 0.8 \\
\text{I} & 0.4 \\
\end{array}
\]

*NaOCH\textsubscript{3}, CH\textsubscript{3}OH, 50°C
General Conclusions About Mechanism

bimolecular rate-determining step in which nucleophile attacks aryl halide
rate-determining step precedes carbon-halogen bond cleavage
rate-determining transition state is stabilized by electron-withdrawing groups (such as NO$_2$)
23.6
The Addition-Elimination Mechanism of Nucleophilic Aromatic Substitution
Two step mechanism:

Step 1) nucleophile attacks aryl halide and bonds to the carbon that bears the halogen
(slow: aromaticity of ring lost in this step)

Step 2) intermediate formed in first step loses halide
(fast: aromaticity of ring restored in this step)
Reaction

\[
\text{F} \begin{array}{c}
\text{NO}_2 \\
\end{array} + \text{NaOCH}_3 \xrightleftharpoons{\text{CH}_3\text{OH}}^{85^\circ\text{C}} \text{OCH}_3 \begin{array}{c}
\text{NO}_2 \\
(93\%) \\
\end{array} + \text{NaF}
\]
Mechanism

Step 1

bimolecular
consistent with second-order kinetics; first order in aryl halide, first order in nucleophile
Mechanism

Step 1

$\text{NO}_2$ $\text{NO}_2$ $\text{OCH}_3$ $\text{OCH}_3$ $\text{F}$ $\text{F}$

slow
intermediate is negatively charged formed faster when ring bears electron-withdrawing groups such as NO₂
Stabilization of Rate-Determining Intermediate by Nitro Group
Stabilization of Rate-Determining Intermediate by Nitro Group
Mechanism

Step 2

\[
\begin{align*}
&F \\
&\text{OCH}_3 \\
&\text{NO}_2
\end{align*}
\]
Mechanism

Step 2
Leaving Group Effects

F > Cl > Br > I is unusual, but consistent with mechanism

carbon-halogen bond breaking does not occur until after the rate-determining step

electronegative F stabilizes negatively charged intermediate
23.7
Related Nucleophilic Aromatic Substitution Reactions
Six fluorine substituents stabilize negatively charged intermediate formed in rate-determining step and increase rate of nucleophilic aromatic substitution.
2-Chloropyridine reacts 230,000,000 times faster than chlorobenzene under these conditions.
Example: 2-Chloropyridine

Nitrogen is more electronegative than carbon, stabilizes the anionic intermediate, and increases the rate at which it is formed.
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