**Nucleophilic Aromatic Substitution — Aryl Halides**

\[
\text{Ar-X} + :\text{Nu} \rightarrow \text{Ar-Nu} + :\text{X}
\]

**Electron withdrawing** groups *ortho* or *para* to the site of attack **activate** the aryl halide toward **nucleophilic** substitution —

<table>
<thead>
<tr>
<th>Ar-X</th>
<th>Reaction Conditions</th>
<th>Ar-Nu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>aq. NaOH 350°C</td>
<td>Cl-</td>
</tr>
<tr>
<td>Cl-NO₂</td>
<td>aq. NaOH 160°C</td>
<td>Cl-NO₂</td>
</tr>
<tr>
<td>Cl-NO₂-NO₂</td>
<td>aq. Na₂CO₃ 130°C</td>
<td>Cl-NO₂-NO₂</td>
</tr>
<tr>
<td>Cl-NO₂-NO₂-NO₂</td>
<td>H₂O warm</td>
<td>Cl-NO₂-NO₂-NO₂</td>
</tr>
</tbody>
</table>

These nucleophilic substitutions do not take place by \( \text{S}_\text{N}1 \) or \( \text{S}_\text{N}2 \) mechanisms ---

\( \text{S}_\text{N}1 \) leads to unstable phenyl carbocation.

\( \text{S}_\text{N}2 \) requires backside attack: bad geometry!
A more feasible mechanism – addition-elimination also known as S_N Ar —

It turns out that this mechanism does NOT operate in the absence of powerful electron withdrawing groups ortho and/or para to the site of nucleophilic attack. Electron withdrawing groups stabilize the carbanion intermediate and the transition state leading to it; when they are not present the Meisenheimer carbanion does not form.
In the absence of electron withdrawing groups o/p to the site of nucleophilic attack reaction takes place by an elimination/addition sequence; this only happens with strong bases or vigorous conditions —

Benzyne is a reactive, unstable intermediate. The 6 aromatic π electrons have been shown as a circle here to emphasize that the new π bond is not part of the aromatic system, but is at right angles to it and lies in the plane of the carbon atoms. This π bond is highly reactive, having been formed from the not-so-parallel joining of two sp² (not p) orbitals.

Benzyne may form in a two-step process, as shown above, or the hydrogen and halogen may depart simultaneously, as in an E2 elimination.
Experimental evidence for elimination/addition in the absence of electron withdrawing groups o/p to nucleophilic attack —

\[
\begin{align*}
\text{Br} & \quad \text{NaNH}_2 \\
& \quad \text{NH}_3 \\
\Rightarrow & \quad \text{NH}_2
\end{align*}
\]

Elimination/addition leads to the 50:50 mixture as shown below; the carbanion mechanism would lead only to the first product.