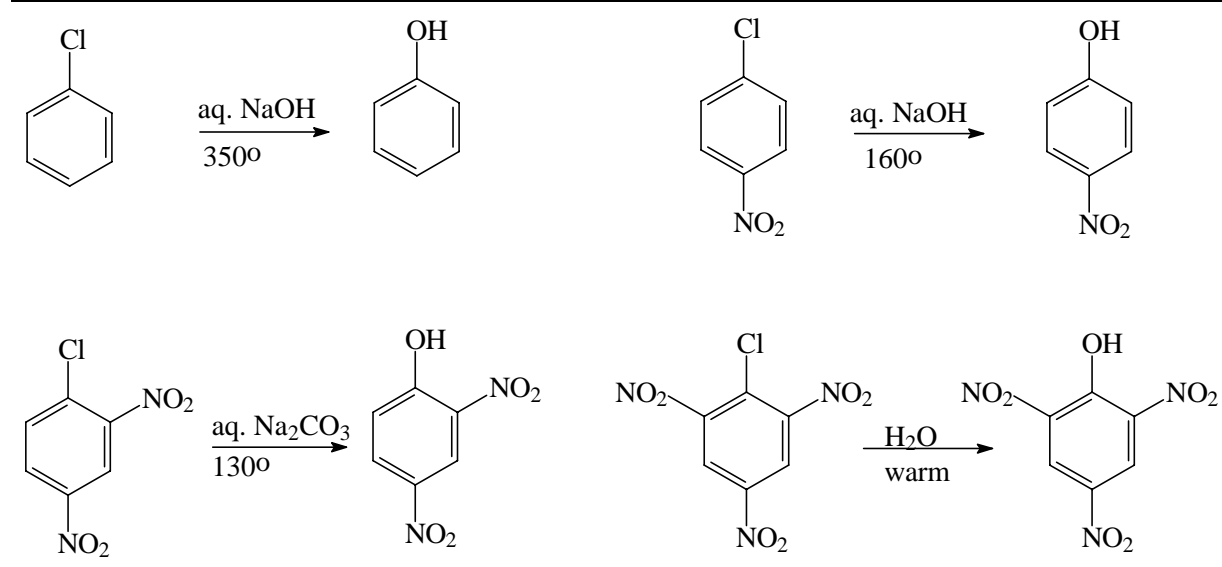


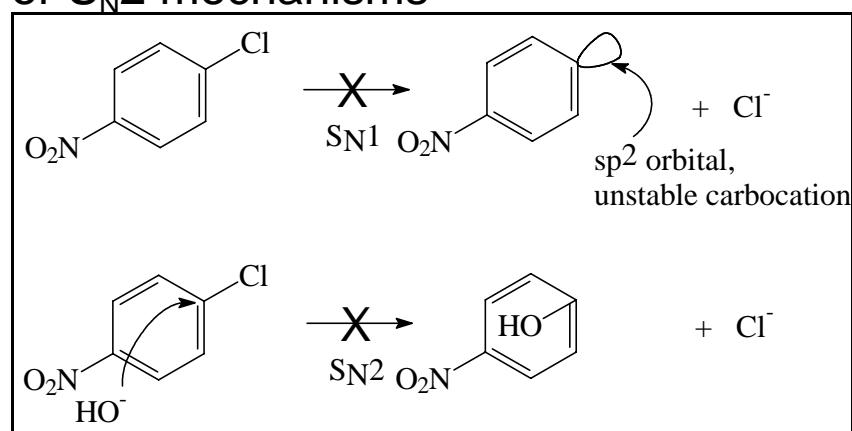
## Nucleophilic Aromatic Substitution — Aryl Halides



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



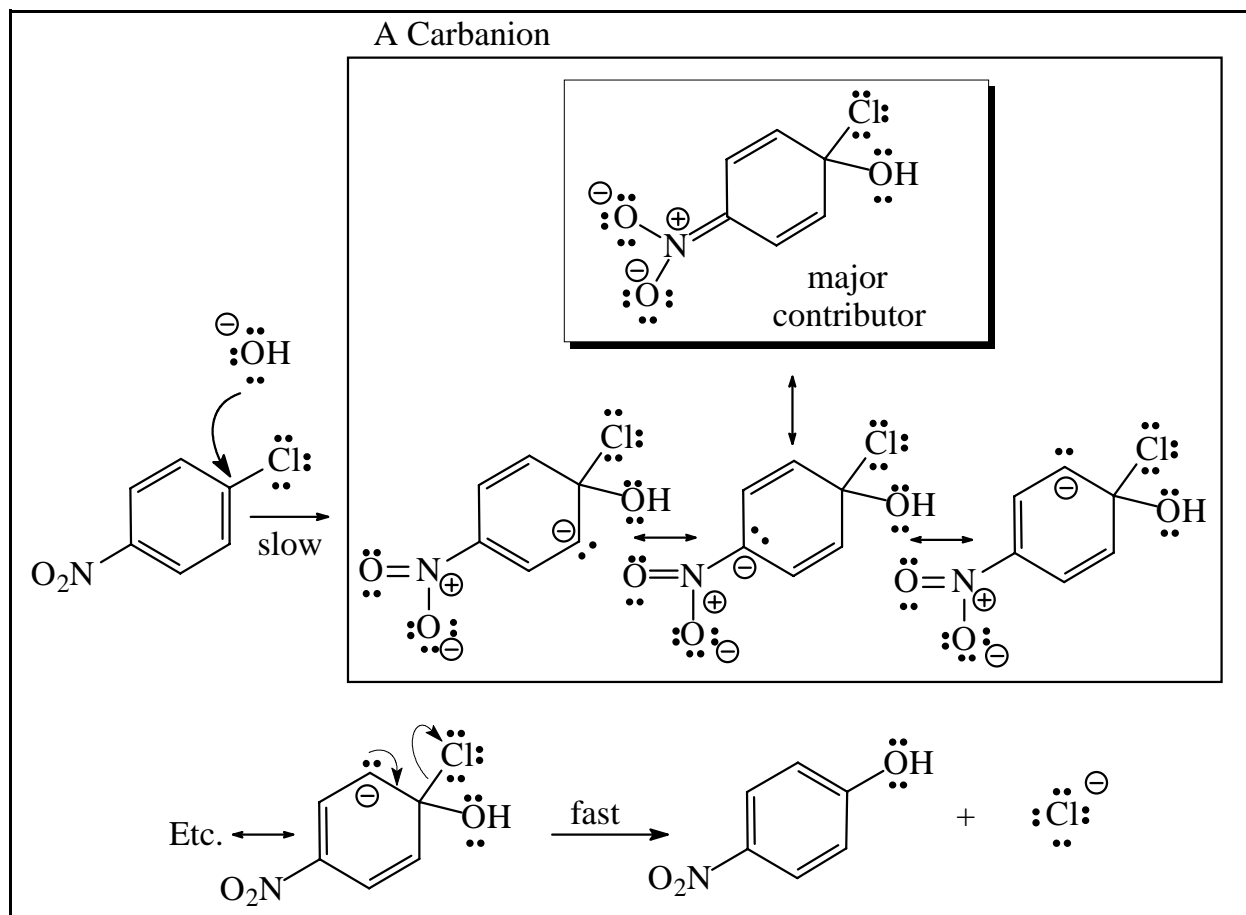
These nucleophilic substitutions do not take place by S<sub>N</sub>1 or S<sub>N</sub>2 mechanisms ---



S<sub>N</sub>1 leads to unstable phenyl carbocation.

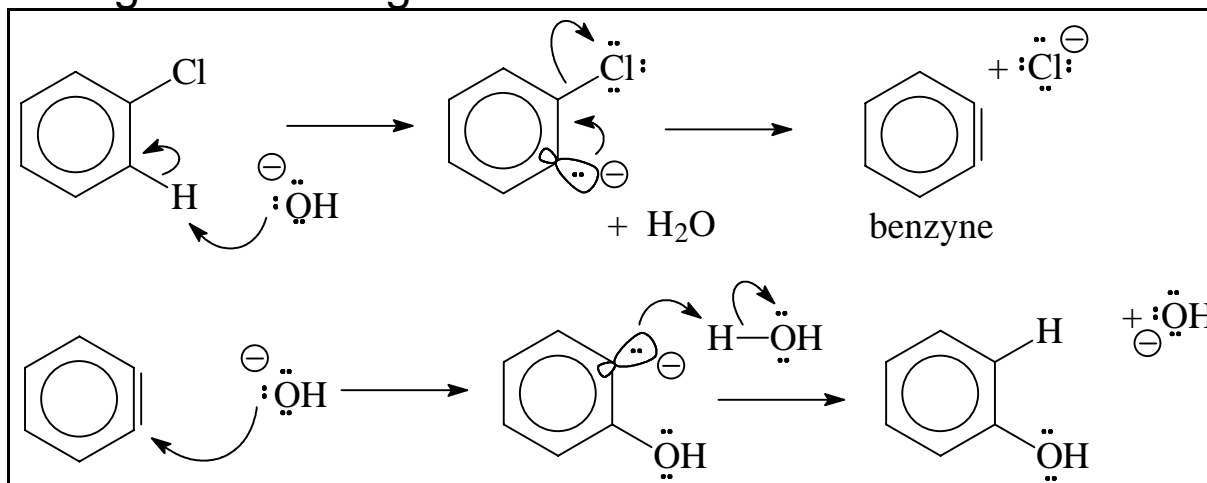
S<sub>N</sub>2 requires backside attack: bad geometry!

A more feasible mechanism –  
addition-elimination also known as  $S_NAr$  —

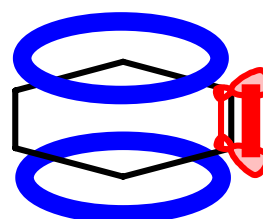


It turns out that this mechanism does *NOT* operate in the absence of powerful electron withdrawing groups *ortho* and/or *para* to the site of nucleophilic attack. Electron withdrawing groups stabilize the carbanion intermediate and the transition state leading to it; when they are not present the *Meisenheimer* 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  $\pi$  electrons have been shown as a circle here to emphasize that the new  $\pi$  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  $\pi$  bond is highly reactive, having been formed from the not-so-parallel joining of two  $\text{sp}^2$  (not  $p$ ) orbitals.

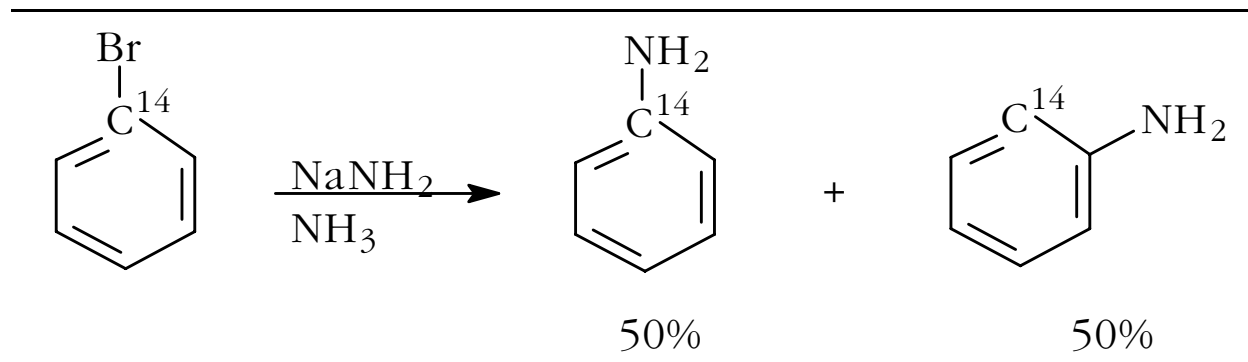


The six aromatic  $\pi$  electrons are shown in blue.

The additional  $\pi$  bond in benzyne, shown in red is in the plane of the carbons.

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 —



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

