Bimolecular Nucleophilic Substitution of an Anion by an Anion. A Theoretical Study of Phenylboronic Acids as a Source of Phenyl Anions.

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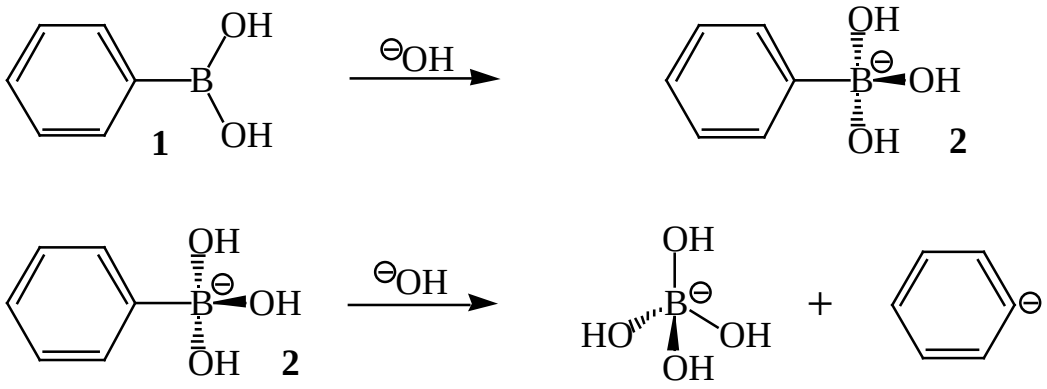
Phenylboronic acid, **1**, is a source of reactive phenyl anions and therefore of great interest in synthetic organic chemistry. It is thought that the treatment of phenylboronic acid with strong nucleophiles, such as hydroxide ion, leads to the formation of $B(OH)_4^-$ and phenyl anion in two steps as outlined in the Scheme.



The first step consists in the addition of hydroxide ion to phenylboronic acid to generate the anion **2**. The second step involves the nucleophilic substitution of a phenyl anion in **2** by a hydroxide nucleophile. Bimolecular nucleophilic substitutions of anions by anions have received relatively little attention and there is the question as to whether the reaction follows a typical SN2 mechanism or whether it is more like an elimination-addition process. In this presentation, we will discuss the reaction paths of the nucleophilic substitutions of the parent system, the automerization reaction of OH^- with $B(OH)_4^-$, and of **2** with OH^- to yield $B(OH)_4^-$ and phenyl anion.

The potential energy surfaces of orthoboric acid, $B(OH)_3$, and two hydroxide ions and of phenylboronic acid, $PhB(OH)_2$, and two hydroxide ions were explored at the theoretical levels RHF/6-31+G* and B3LYP/6-31+G*. Energies also were determined at B3LYP/6-311++G**// B3LYP/6-31+G*.

Results of population analyses will be presented to discuss the nature of the bonding in **2**. In particular, we will address the issue as to whether **2** may be considered the result of dative bonding between phenyl anion and orthoboric acid.