The Boyland-Sims Oxidation reaction uses an alkaline solution of peroxydisulfate salt to convert arylamines to o-aminophenols. The long-standing mechanism involves a nucleophilic attack by the amine leading to the formation of an arylhydroxylamine-O-sulfonate intermediate, which then rearranges to the arylamine o-sulfate. The long-standing mechanism of a nucleophilic attack by the amine on peroxide oxygen has been questioned by Marjanović et al. who have proposed a nitrenium ion intermediate as the reactive species rather than the uncharged amine. It has been challenged by a variety of experimental observations. We present here new computations at a high-level of density functional theory (B3LYP/6-311++G**) to model both arylhydroxylamine-O-sulfonate and nitrenium ion pathways in a series of aromatic amines. In this study, the energetics of reaction intermediates in both mechanisms are computed for aniline, 2,4-dinitroaniline, and N,N-dimethylaniline. To further support the pathways of the reaction, the calculations were performed to find the transition states involved in both mechanisms. The transition state calculations revealed two possible energetically feasible pathways for the rearrangement of arylhydroxylamine-O-sulfonate to arylamine o-sulfate. Our results indicate that the Boyland-Sims oxidation reactions proceed via arylhydroxylamine-O-sulfonate intermediate as predicted earlier.