

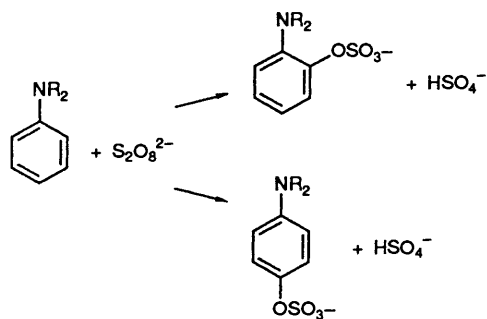
## An Arylhydroxylamine *O*-Sulfonate is the Probable Intermediate in the Peroxydisulfate Oxidation of Aromatic Amines

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*N,N*-Dimethylaniline *N*-oxide reacts with the sulfur trioxide–pyridine complex to give a product which upon treatment with water affords *o*-(dimethylamino)phenyl hydrogen sulfate in good yield.

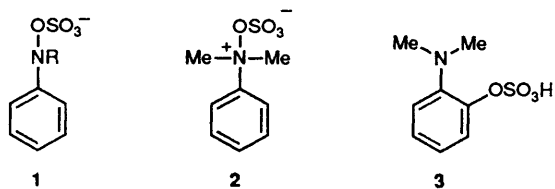
Aromatic amines react with peroxydisulfate ions to form, predominantly, the *o*-aminoaryl sulfate,<sup>1</sup> together with significant quantities of the *para*-sulfate<sup>2</sup> (Scheme 1). This reaction,



Scheme 1

known as the Boyland–Sims oxidation, contrasts with the reaction of phenols under the same conditions (the Elbs oxidation<sup>1</sup>) in which the *para*-sulfate is the major product.

The arylhydroxylamine *O*-sulfonate **1** has been postulated as a reasonable intermediate in the Boyland–Sims oxidation to account for the predominance of the *ortho*-product.<sup>3</sup> However, Edward and Whiting reported that (*N,N*-dimethylanilino)sulfate **2**, prepared by reaction of *N,N*-dimethylaniline *N*-oxide and sulfur trioxide, did not rearrange to the *ortho*-sulfate in water but rather underwent hydrolysis to the *N*-oxide and



sulfate ions.<sup>4</sup> Because of this report, other hypotheses were put forward including an *ipso* intermediate and a caged radical structure.<sup>5,6</sup>

A repeat of Edward and Whiting's work shows that their findings are incorrect. Reaction of *N,N*-dimethylaniline *N*-oxide with an equimolar amount of the sulfur trioxide–pyridine complex in dry pyridine produces material which, when treated with water, gives a 50% isolated yield of *o*-(dimethylamino)phenyl hydrogen sulfate **3** identified as authentic material<sup>7</sup> by its m.p., and its IR, UV and NMR spectra.

An *o/p* ratio of ca. 8:1 for the sulfate esters, determined from <sup>1</sup>H NMR spectra of crude reaction mixtures, was the same as that observed in the products of the peroxydisulfate oxidation of *N,N*-dimethylaniline.<sup>8</sup> This provides strong evidence that molecules of type **1** are intermediates in the Boyland–Sims oxidation.

**Typical Experimental Procedure.**—*N,N*-Dimethylaniline *N*-oxide (1.2 g, 10 mmol) was dissolved in dry pyridine (3 Å sieves) (25 cm<sup>3</sup>) and a slight excess of the sulfur trioxide–pyridine complex (Aldrich; 1.8 g, 13 mmol) was added to it all at once. The solution turned brown and warmed slightly. Since not all of the sulfur trioxide complex dissolved, additional *N*-oxide (0.6 g) was added to give an homogeneous solution; no gum, formed, however, as described by Edward and Whiting.<sup>4</sup> After ca. 2 h at room temperature, the mixture was diluted with hexane to precipitate the products and to extract the pyridine. The hexane-soluble fraction was decanted and the residue washed with five additional portions of hexane. The residue was then dried overnight *in vacuo* over P<sub>2</sub>O<sub>5</sub>–KOH to yield a brown hygroscopic solid. Water (25 cm<sup>3</sup>) was added to this dried material which, at first, failed to dissolve completely, but did so when heated in a boiling water-bath for 10 min. Upon cooling, a heavy precipitate formed which was filtered off and dried to give *o*-(dimethylamino)phenyl hydrogen sulfate (1.1 g, 45%), m.p. 215–218 °C (lit.,<sup>7</sup> 217–219 °C).

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