

## Oxidation of Catechols *via* Oxysulphonium Cations

By JOSEPH P. MARINO\* and ALAN SCHWARTZ

(Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104)

**Summary** A new and mild method for the oxidation of catechols and para-hydroquinones is described which uses the succinimidodimethylsulphonium cation (**1**).

IN 1965, two groups independently reported that the oxidation of phenols under Pfitzner–Moffatt conditions resulted in the formation of *o*-(methylthiomethylene)phenols.<sup>1</sup> This transformation has been interpreted as involving a ready sigmatropic rearrangement of the presumed aryloxysulphonium ylide of the type (**3a**) (path a).<sup>2</sup> Recently, similar results have been reported using the azasulphonium intermediate (**1**; X = Cl), which was generated *in situ* from

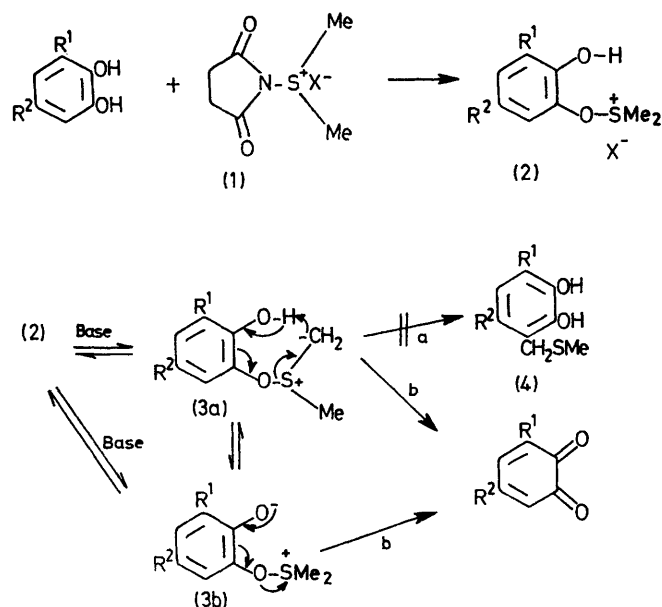
*N*-chlorosuccinimide (NCS) and Me<sub>2</sub>S.<sup>3</sup> We describe here the fate of an aryloxysulphonium cation (**2**) which is generated from a catechol or a hydroquinone. We find that the second *o*- or *p*-hydroxy-group directs the aryloxysulphonium ylide† (**3a**) or phenoxide (**3b**) to the oxidized *o*- or *p*-quinone (path b) instead of the *ortho*-rearranged product (**4**) (path a), thus constituting an extremely mild and easy method for the oxidation of dihydroxybenzene derivatives.

The oxidations can be carried out in CH<sub>2</sub>Cl<sub>2</sub> or MeCN at low temperatures (–20 to –50 °C) with 1 equiv. of the preformed succinimido-sulphonium fluoborate (**1**; X = BF<sub>4</sub><sup>–</sup>)‡ or the corresponding chloride (**1**; X = Cl) (generated

† The intervention of an aryloxysulphonium ylide (**3a**), while not a mechanistic necessity, would be possible under the reaction conditions, since such ylides are presumed to form even in the presence of proton donors (ref. 2).

‡ Succinimidodimethylsulphonium fluoborate, m.p. 167–169 °C, was prepared by treating a suspension in CH<sub>2</sub>Cl<sub>2</sub> of the corresponding chloride with a solution in MeCN of AgBF<sub>4</sub> at –20 °C.

*in situ* from NCS and Me<sub>2</sub>S). Oxidation of 4-*t*-butylcatechol (R<sup>1</sup> = H, R<sup>2</sup> = Bu<sup>t</sup>), 3,5-di-*t*-butylcatechol (R<sup>1</sup> = R<sup>2</sup> = Bu<sup>t</sup>), and *p*-hydroquinone produced the corresponding



quinones in quantitative yield only after addition of triethylamine (1 mol. equiv.). A control experiment with the fluoborate salt of (1) and 3,5-di-*t*-butylcatechol without base did not yield any *o*-quinone even in refluxing CH<sub>2</sub>Cl<sub>2</sub>. Similarly, a mixture of NCS and the catechol does not result in clean oxidation; instead, a complex mixture of *o*-quinone, ring chlorinated products, and catechol is obtained. The oxidations of electron-rich catechols proceed to completion in a matter of minutes after addition of the base.

Some of the merits of this method (see ref. 4 for other oxidation methods) for oxidizing catechols and hydroquinones include: (a) the availability of inexpensive reagents; (b) efficiency of 1:1 stoichiometry for large-scale oxidations; (c) low temperature reaction conditions which would extend the lifetime of sensitive *o*-quinones; and (d) the absence of deleterious by-products which could further react with the *o*-quinones. This last point is especially significant since over-oxidation and nucleophilic additions are precluded by the self-destruction of the aryl-oxysulphonium ylide (3a) or phenoxide (3b) to an unreactive sulphide.

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<sup>2</sup> J. P. Marino, K. E. Pfitzner, and R. A. Olofson, *Tetrahedron*, 1971, **27**, 4181.

<sup>3</sup> P. G. Gassmann and D. R. Amick, *Tetrahedron Letters*, 1974, 889.

<sup>4</sup> For a review of some other oxidizing methods see: (a) V. Balogh, M. Fetizon, and M. Golfier, *J. Org. Chem.*, 1971, **36**, 1339; M. F. Ansell, A. J. Bignold, A. F. Gosden, V. J. Leslie, and R. A. Murray, *J. Chem. Soc. (C)*, 1414; A. J. Fatiadi, *Synthesis*, 1974, (4), 229.