Oxidation of Phenols to *ortho*-Quinones using Diphenylseleninic Anhydride

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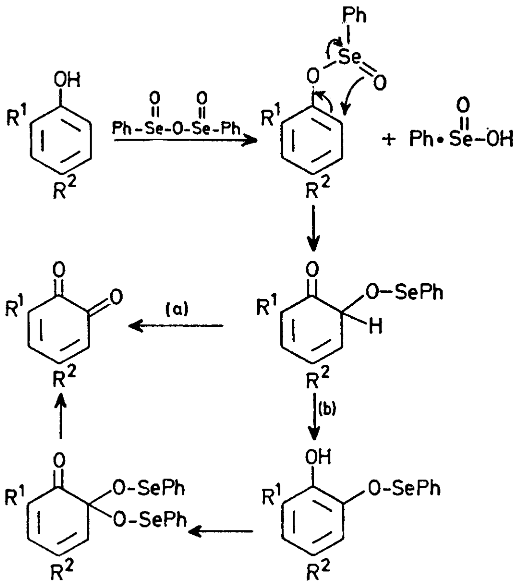
Summary Phenols, including examples with an unblocked *para*-position, are oxidised to the corresponding *ortho*-quinones using diphenylseleninic anhydride.

Although there are many methods[1] by which 1,2-dihydroxybenzenes (catechols) can be converted into *ortho*-quinones there are virtually no procedures which will directly convert phenols, particularly when the *para*-position is unblocked, into *o*-quinones. In view of the high *ortho*-selectivity of phenolate anion hydroxylation by diphenylseleninic anhydride[2] we were prompted, on mechanistic considerations, to investigate the possibility of using this reagent for *ortho*-quinone formation.

Typically, solutions of phenols in tetrahydrofuran were added to a stirred suspension of diphenylseleninic anhydride in tetrahydrofuran at 50 °C over 15 min. The reaction mixtures were worked up by washing with dilute $NaHCO_3$ solution (to remove phenylseleninic acid) followed by short column chromatography on silica gel to furnish the *ortho*-

quinones free from the by-product diphenyldiselenide (Table).



Scheme

In the case of α-naphthol oxidation a quantity of the *para*-quinone (10%) was also isolated. However in the remaining examples no *para*-oxidation was detected. Thus both thymol and carvacrol gave the *ortho*-quinone in good yield free from any *para*-isomer. Under less vigorous conditions β-naphthol gave a small amount of the α-phenylselenated naphthol which in a separate experiment could be oxidised by diphenylseleninic anhydride to the *ortho*-quinone (85%). Oxidation after prior conversion of the α- and β-naphthols into their corresponding anions using sodium hydride gave comparable yields of *ortho*-quinone.

Table. Oxidation of phenols with diphenylseleninic anhydride, $[PhSe(:O)]_2O$

Phenol	Product	Yield, % (recrystallized)
α-Naphthol	*o*-Naphthoquinone	62
β-Naphthol	,,	63
Carvacrol	3-Methyl-6-t-butyl-	60
Thymol	*o*-benzoquinone	59
2,4-Di-t-butylphenol	3,5-di-t-butyl- *o*-benzoquinone	68

In view of the high *ortho*-selectivity of the reaction we propose a mechanism as outlined in the Scheme. As yet we cannot distinguish between paths (a) and (b).

We have already shown[2] that hydroquinones afford *para*-quinones in high yield on oxidation with diphenylseleninic anhydride. Preliminary experiments show that catechols are similarly oxidised to *ortho*-quinones.

Clearly diphenylseleninic anhydride is a mild and selective oxidant of considerable application in organic synthesis.[3] All new compounds gave satisfactory analytical data.

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[1] S. Patai, 'The Chemistry of the Quinonoid Compounds,' Part 1, Wiley, New York.

[2] D. H. R. Barton, P. D. Magnus, and M. N. Rosenfeld, *J.C.S. Chem. Comm.*, 1975, 301. D. H. R. Barton, S. V. Ley, P. D. Magnus, and M. N. Rosenfeld, *J.C.S. Perkin I*, submitted for publication.

[3] *Cf.* M. R. Czarny, *J.C.S. Chem. Comm.*, 1976, 81.