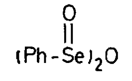
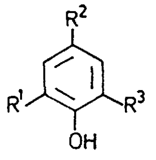
Oxidation of Phenols to Hydroxycyclohexadienones using Diphenylseleninic Anhydride

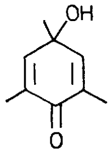
By Derek H. R. Barton,* Philip D. Magnus, and Moshe N. Rosenfeld
(Chemistry Department, Imperial College, South Kensington, London SW7 2AY)

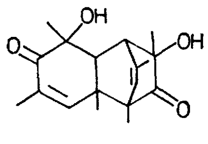
Summary Diphenylseleninic anhydride (**1**) reacts with phenols under neutral conditions to give *o*- and *p*-hydroxylation, whereas with phenolate anions only *o*-hydroxylation is observed.

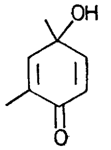
The conversion of a phenol into an *ortho*-hydroxycyclohexa-2,4-dienone has been carried out by us using a variety of oxidation systems.[1] Current interest in organoselenium chemistry[2] prompted us to examine the oxidising properties of an unexploited reagent, diphenylseleninic anhydride† (**1**).[3] Ozonolysis of diphenyldiselenide provides a convenient method of preparing crystalline diphenylseleninic anhydride (**1**).[3] Treatment of 2,4,6-trimethylphenol (**2**; $R^1 = R^2 = R^3 =$ Me) with diphenylseleninic anhydride (**1**) in dichloromethane at room temperature gave a rapid reaction yielding the *p*-hydroxycyclohexadienone (**3**) (30%) and the dimer of the *o*-hydroxycyclohexadienone (**4**)[4] (48%). Similarly, 2,4-dimethylphenol (**2**; $R^1 = R^2 =$ Me, $R^3 =$ H) and 2,6-dimethylphenol (**2**; $R^1 = R^3 =$ Me, $R^2 =$ H) were oxidised with diphenylseleninic anhydride in dichloromethane to give the *p*-hydroxycyclohexadienone (**5**) (18%) and 2,6-dimethylbenzoquinone (25%) or 2,2′,6,6′-tetramethyldiphenoquinone (40%) respectively. No *o*-hydroxylation was detected. The orcinol derivatives (**6**; R = OMe) and (**6**; R = NH_2) were treated with diphenylseleninic anhydride in dichloromethane to give the *ortho*-hydroxydienone (**7**; R = OMe) (35%) and (**8**; R = OMe) (55%), and (**7**; R = NH_2) (25%), the quinone (**9**) (20%) and (**8**; R = NH_2) (45%) respectively. Evidently, from these results, there is no selective *o*-attack by the electrophilic reagent. To produce selective *o*-hydroxylation, according to the Scheme,[1] the above phenols, in glyme were treated with sodium hydride (1 equiv.) and diphenylseleninic anhydride. The results are given in the Table. Using this procedure *p*-hydroxylation is entirely suppressed; the only by-products were selenated phenols.

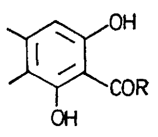

(1)

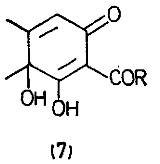

(2)

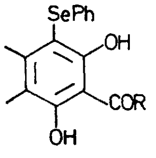

(3)

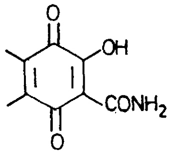

(4)


(5)


(6)

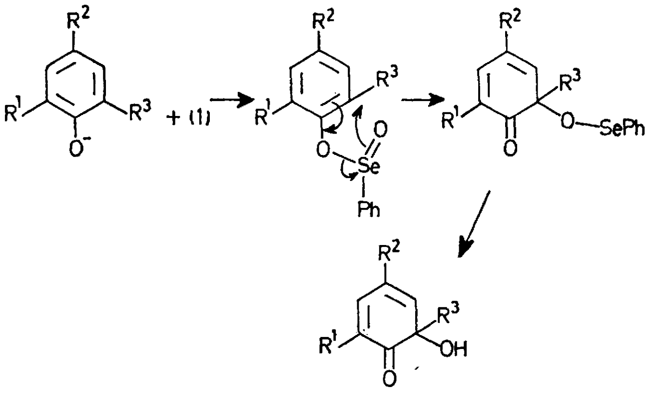

(7)


(8)


(9)

Table

Substrate	Product (% yield isolated pure)
(**2**; $R^1=R^2=$Me, $R^3=$H)	Dimer of *o*-hydroxydienone (37); no trace of (**5**) was present
(**2**; $R^1=R^3=$Me, $R^2=$H)	Dimer of *o*-hydroxydienone (44); no quinones were present
(**2**; $R^1=R^2=R^3=$Me)	*o*-Hydroxydienone dimer (**4**) (55); no trace of (**3**) was present
(**6**; R=OMe)	(**7**; R=OMe) (75) (**8**; R=OMe) (17)
(**6**; R=NH_2)	(**7**; R=NH_2) (68) (**8**; R=NH_2) (trace)


Scheme

All new compounds gave satisfactory spectral and microanalytical data.

(*Received, 12th February* 1975; *Com.* 176.)

---

† We have observed that diphenylseleninic anhydride reacts with the α-lithiosalt of esters ($LiNPr_2$ + ester) to give α,β-unsaturated esters without the need for *in situ* oxidation as used by other workers.[2]

[1] D. H. R. Barton, P. D. Magnus, and M. J. Pearson, *J. Chem. Soc.*, 1971, 2231; D. H. R. Barton, P. D. Magnus, and J. C. Quinney, *J.C.S. Perkin I*, in the press.

[2] K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Amer. Chem. Soc.*, 1973, **95**, 6137; H. J. Reich, I. L. Reich, and J. M. Renga, *ibid.*, 1973, **95**, 5813; D. L. J. Clive, *J.C.S. Chem. Comm.*, 1973, 695; K. B. Sharpless, M. Young, and R. F. Lauer, *Tetrahedron Letters*, 1973, 1979.

[3] G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 1962, 2089.

[4] E. Adler, J. Dahlen, and G. Westrin, *Acta. Chem. Scand.*, 1960, **14**, 1580.