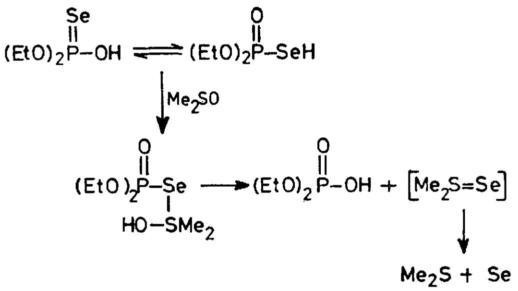
New Method for Deoxygenation of Sulphoxides: Use of *OO*-Diethyl Hydrogenphosphoroselenoate

By Derrick L. J. Clive,* William A. Kiel, Steven M. Menchen, and Chi Kwong Wong
(*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada* T6G 2G2)

Summary *OO*-Diethyl hydrogenphosphoroselenoate, readily available from its sodium salt, reduces sterically accessible sulphoxides in high yield.

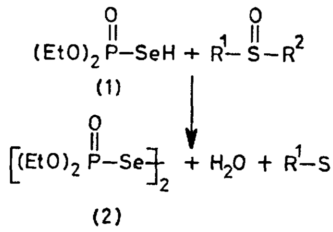
The use of selenium reagents to reduce oxygenated functions has been well developed only in the case of oxirans.[1] We now report that *OO*-diethyl hydrogenphosphoroselenoate (**1**) reduces sulphoxides efficiently to sulphides[2] (see Table).

When neat Me_2SO is added to the acid (**1**) a reaction occurs, which, on the basis of the data then available, was described previously[3] by Scheme 1. In general, compounds



Scheme 1.

possessing an SeH-group are oxidised to diselenides and, because of the unusual nature of Scheme 1, we have re-investigated the reaction. Our experiments confirm the production of Me_2S and also, under appropriate conditions, of metallic selenium, but we have found that there is another, faster, process occurring which constitutes a general method for reducing sulphoxides (Scheme 2).†



SCHEME 2.

TABLE

Sulphoxide (equiv. of reagent used)	Solvent	Temp.	Time/h	% Yield[a]
Me_2SO (1)	$CDCl_3$	41 °C	0·5	93[b]
			1·0	97[b]
$Bu^n{}_2SO$ (1·1)	CH_2Cl_2	Room temp.	1·5	92[c]
$(PhCH_2)_2SO$ (1·61[d])	CH_2Cl_2	Room temp.	3	92
Ph_2SO (2·17[e])	CH_2Cl_2	Reflux	28	94[c]
$MeSOC_6H_4Me$-*p* (1·3)	$CHCl_3$	Room temp.	1	78[c]
		then 35 °C	0·5	
$C_5H_{10}SO$[f] (1·62)	$CHCl_3$	Room temp.	2·25	74[g]
$MeSOBu^t$ (2·9[h])	CH_2Cl_2	Reflux	25	79[g]
$Bu^t{}_2SO$ (2·11)	$CHCl_3$	Reflux	14	14[g]

[a] Yields refer to pure, isolated materials unless indicated otherwise. [b] Yield determined by n.m.r. spectroscopy. [c] > 99% pure by g.l.c. [d] Reagent added in 2 portions during first 1 h. [e] Reagent added in 6 portions during first 21 h. [f] $C_5H_{10}SO$ = thiopyran *S*-oxide. Reagent added in 3 portions during 1·5 h. [g] Absolute yield determined by g.l.c. relative to an internal standard. [h] Reagent added in 3 portions during first 13 h.

Compound (**1**) is susceptible to aerial oxidation and must be used in an inert atmosphere. However, its crystalline sodium salt,[4] which can be made in 86% yield by dissolving Se shot in ethanolic sodium diethyl phosphite, can be stored for months. Acidification of an aqueous solution of the salt releases compound (**1**) [90—97% yield, $\delta(^{31}P)$ ($CDCl_3$) $-59·8$ p.p.m.]. A $CHCl_3$ or CH_2Cl_2 solution of (**1**) (1 equiv.) is added to a solution of the sulphoxide in the same solvent and, when the reduction is complete (see Table) the sulphide can be isolated‡ with the results shown. Yields are high but, evidently, the reagent is sensitive to steric factors and $Bu^t{}_2SO$ is not reduced in synthetically useful yields.

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, the National Research Council of Canada, and the University of Alberta.

(*Received*, 10*th June* 1977; *Com.* 570.)

---

† The diselenide (**2**) (ref. 4a) slowly reduces Me_2SO and selenium is deposited.

‡ In large-scale runs it is convenient to remove most of the selenium and phosphorus species by washing an ethereal solution of the total product with 0·2 M K_2CO_3 before chromatography.

[1] (a) D. L. J. Clive and C. V. Denyer, *J.C.S. Chem. Comm.*, 1973, 253; (b) F. Mathey and G. Muller, *Compt. rend.*, 1975, **281**, 881; V. Calò, L. Lopez, A. Mincuzzi, and G. Pesce, *Synthesis*, 1976, 200.

[2] For reduction of Me_2SO by 2-dimethylaminoethylselenol in hypophosphorus acid see W. H. H. Günther, *J. Org. Chem.*, 1966, **31**, 1202.

[3] M. Mikolajczyk, *Chem. and Ind.*, 1966, 2059.

[4] (a) O. Foss, *Acta Chem. Scand.*, 1947, **1**, 8; (b) P. Pistschimuka, *J. prakt. Chem.*, 1911, **84**, 746.

[5] For leading references to methods for deoxygenation of sulphoxides see: H. C. Brown and N. Ravindran, *Synthesis*, 1973, 42; R. G. Nuzzo, H. J. Simon, and J. San Filippo, Jr., *J. Org. Chem.*, 1977, **42**, 568.