New Reagents for Deoxygenation of Sulphoxides: Use of Compounds with Selenium–Boron Bonds

By Derrick L. J. Clive* and Steven M. Menchen

(Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2)

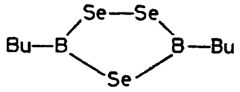
Summary Compounds (**1**), (**2**), and (**3**) are efficient reagents for deoxygenation of sulphoxides.

Although a number of organic compounds containing selenium–boron bonds have been known for some years[1] their potential as reagents for functional group interconversion has not been adequately recognised. Tris(phenylseleno)borane (**1**) is useful for converting ketones,[2] aldehydes,[2] and acetals,[3] into the synthetically important[4] selenoacetal compound class. We report that this reagent, as well as the related compounds (**2**)[5] and (**3**)[6] deoxygenate sulphoxides efficiently in a fairly rapid process that occurs at, or below, room temperature.[7]

$B(SeX)_3$

(**1**) X = Ph

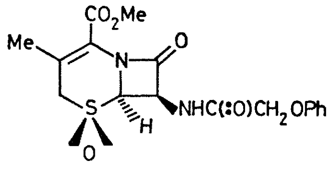
(**2**) X = Me



(**3**)

$(PhCH_2)_2S\approx Se$

(**4**)



(**5**)

Table[a]

Starting material	Reagent	Amount (equiv.)	Temp./°C; time	% Yield of sulphoxide reduction product
1: $(PhCH_2)SO$	(1)	1·17	−30; 1 h	91
2: "	(2)	1·15	0, 15 min; then room temp., ⩽2·5 h[b]	88
3: "	(3)	1·28[c]	−30, 1·5 h	74
4: $Bu^t{}_2SO$	(1)	1·12	0 to room temp.; 1 h[d]	(83·6)
5: Ph_2SO	(1)	1·11	0, 0·5 h; then room temp., 1 h[b]	(96·9)
6: $Me[CH_2]_{14}C(:O)CH_2S(:O)Me$[e] ..	(1)	1·09	0, 1 h; then room temp., 1 h[b]	90
7: $BuCH{=}CHS(:O)Me$[f]	(1)	1·15	0, 30 min	86[g]
8: 8-Methylquinoline *N*-oxide ..	(1)	1·30	−30, 50 min	84
9: (5)	(3)	3·89	$CHCl_3$ at reflux, 24 h	25

[a] All reactions were run in dry $CHCl_3$ using < 2·5 mmol of sulphoxide. Yields in parentheses were determined by v.p.c. using an internal standard and in these cases specimens of the products were isolated and identified by comparison with authentic samples; [b] Ice bath removed after specified period at 0 °C and mixture worked up after the further period indicated; [c] A 1 : 1 molar stoicheiometry was used; [d] Ice bath removed immediately after mixing the reagents; [e] M.p. 96—97·5 °C. Made by method of E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1345; [f] B.p. 120 °C (0·2 mmHg). *E*-Isomer as judged by n.m.r. spectroscopy. Made by method of B. M. Trost and A. J. Bridges, *J. Org. Chem.*, 1975, **40**, 2014; [g] Stereochemistry of vinyl sulphide not determined.

Our results are summarised in the Table.† Reductions were carried out in chloroform, the reagents (**2**) and (**3**) being added as neat liquids to a solution (*ca.* 0·2—0·4 M) of the sulphoxide. With the crystalline compound (**1**), a solution of the sulphoxide (*ca.* 0·6—2·3 M) was added to a solution (*ca.* 0·2—0·4 M) of the reagent.

In the experiment with compound (**3**) [see Table, entry 3] selenium is deposited at the end of the reaction but a selenosulphoxide (**4**)[8] does not appear to be involved (at least as a persistent intermediate) since an n.m.r. spectrum taken at −60 °C *before* the appearance of selenium showed that all the $(PhCH_2)_2S{=}O$ had been converted into the sulphide.

When using $B(SeMe)_3$ to make relatively non-volatile sulphides, the selenium-containing byproduct (MeSeSeMe) can be removed *in vacuo* rather than by chromatography. The reagents (**1**)—(**3**) do not deoxygenate triphenylphosphine oxide or di-n-butyl sulphone,[9] but 8-methylquinoline *N*-oxide, the only amine oxide tested, does react readily (see Table).

We observed that the selenium reagents reported here have very different behaviour from that of $Me_2AlSeMe$.[10] This compound partially deoxygenates esters[10] but it does not appear to reduce sulphoxides under our conditions, as judged by tests with $(PhCH_2)_2S{=}O$. Conversely, methyl palmitate is inert to $B(SePh)_3$ in chloroform solution, but the reaction mixture, after 12 h at room temperature, still retains the capacity to reduce $(PhCH_2)_2S{=}O$; the sulphide can be isolated in 84% yield and the ester recovered (78% recovery).

Entry 6 (see Table) shows that although $B(SePh)_3$ reacts with ketones,[2] highly selective deoxygenation of keto-sulphoxides[11] can be achieved. Finally, the deoxygenation of vinyl sulphoxides makes these compounds synthetically equivalent to acetylenes.[12]

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† Satisfactory (±0·3%) combustion analytical data were obtained for all new compounds.

[1] 'Gmelin Handbuch der Anorganischen Chemie,' **19**, Teil 3, Springer-Verlag, Heidelberg, 1975, 83.

[2] D. L. J. Clive and S. M. Menchen, *J.C.S. Chem. Comm.*, 1978, 356.

[3] D. L. J. Clive and S. M. Menchen, described in part at 12th Middle Atlantic Regional Meeting, Baltimore, April 5-7, 1978.

[4] For uses of selenoacetals see D. L. J. Clive, *Tetrahedron Report No.* 50, *Tetrahedron*, 1978, **34**, 1049; D. Labar, W. Dumont, L. Hevesi, and A. Krief, *Tetrahedron Letters*, 1978, 1145; D. Seebach and A. K. Beck, *Angew. Chem. Internat. Edn.*, 1974, **13**, 806; D. Clive, G. Chittattu, and C. K. Wong, *J.C.S. Chem. Comm.*, 1978, 41.

[5] W. Siebert, W. Ruf, and R. Full, *Z. Naturforsch.*, 1975, **30B**, 642.

[6] B. M. Mikhailov and T. A. Shchegoleva, *Bull. Acad. Sci., U.S.S.R.*, 1959, 331.

[7] For methods of sulphoxide reduction see: J. Drabowicz, T. Numata, and S. Oae, *Organic Preparations and Procedures International*, 1977, **9**, 63. For use of Me_3SiI, which is not applicable to dibenzyl sulphoxide, see G. A. Olah, B. G. B. Gupta, and S. C. Narung, *Synthesis*, 1977, 583. For other silicon-based reagents see H. S. D. Soysa and W. P. Weber, *Tetrahedron Letters*, 1978, 235.

[8] *Cf.* R. D. Baechler and S. K. Daley, *Tetrahedron Letters*, 1978, 101.

[9] *Cf.* J. N. Gardiner, S. Kaiser, A. Krubiner, and H. Lucas, *Canad. J. Chem.*, 1973, **51**, 1419.

[10] A. P. Kozikowski and A. Ames, *J. Org. Chem.*, 1978, **43**, 2735.

[11] *Cf.* H. D. Durst, J. W. Zubrick, and G. R. Kieczykowski, *Tetrahedron Letters*, 1974, 1777.

[12] C. A. Brown, *J. Org. Chem.*, 1978, **43**, 3083.