Optically Active Phosphine Sulphides from Phosphine Oxides and Boron Trisulphide

By Bruce E. Maryanoff, Reginald Tang, and Kurt Mislow*
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08540)

Summary Boron trisulphide transforms tertiary phosphine oxides into the corresponding phosphine sulphides with high stereospecificity and net retention of configuration at phosphorus.

Recently, it was reported that phosphorus pentasulphide effects the conversion of the phosphoryl group into the thiophosphoryl group in a secondary phosphinate[1] and some phosphonothioates[2] with predominant retention of configuration at phosphorus. However, for optically active methylphenyl-n-propylphosphine oxide, this reaction afforded the racemic phosphine sulphide.[2b]

We now report a highly stereospecific, single-step transformation of tertiary phosphine oxides into phosphine sulphides, with boron trisulphide.[3] Previously, this conversion would have required stereospecific reduction of the phosphine oxide,[4] followed by treatment of the phosphine with sulphur[5] or other sulphurising agents.[5b]

Table

No.		Phosphine oxide, **a**[a] Optical purity (%) Starting	Recovered	Phosphine sulphide, **b** Conversion (%)	Yield[b] (%)	Optical purity[c] (%)
(**1**)	(+)-(*R*)-MePhPr^{n}PO	94	80	43	81	74
		94	88	59[d]	83[d]	68[d]
(**2**)	(+)-(*R*)-CyclohexylMePhPO ..	100	100	31	76	95
(**3**)	(+)-(*R*)-EtMePhPO	84	—	60[d]	—	69[d]
(**4**)[e]	2,2,3,4,4-Pentamethyl-1-phenyl-phosphetan oxide					
	trans	[97]	[97]	70	82	[97]
	cis	[100]	[100]	71	98	[100]

[a] Compounds (**1a**)—(**3a**) were prepared by the Grignard synthesis; values for optical purity are based on the highest reported rotation (O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4842). [b] Mol of (**b**) isolated/mol of (**a**) reacted. [c] See text. [d] 1 Mol. equiv. (relative to phosphine oxide) of triethylamine was present in the reaction mixture. [e] The starting phosphetan oxides were obtained according to a reported procedure (S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066); values in brackets denote diastereomeric purity (%).

Our results for a group of representative phosphine oxides are presented in the Table.† As can be seen, the stereospecificity‡ is dependably greater than *ca.* 65%, with predominant retention of configuration. The configurational correlations and the optical purities for the conversions are based on the following. Optically pure (+)-(*R*)-(**2a**) was converted[6] into (+)-(*R*)-(**2b**), $[\alpha]_D$ +25·4° (MeOH), by phenylsilane reduction and sulphurisation. Treatment of (+)-(*R*)-(**3b**), $[\alpha]_D$ +24·4° (MeOH), with $Me_3O^+SbCl_6^-$ followed by alkaline hydrolysis afforded (−)-(*S*)-(**3a**), $[\alpha]_D$ −14·6° (MeOH). Since the reaction sequence involving (**2**) occurs with net retention of configuration[4b] and the one involving (**3**) with net inversion,[7] the stereochemistry for these sulphides is thus as designated. The properties of (−)-(*S*)-(**1b**) have been reported.[7] Compounds (**1b**)—(**3b**) obtained in the boron trisulphide reaction were dextrorotatory at the D-line; therefore they are predominantly of the *R*-configuration. The properties of the phosphetan sulphides (**4b**) have been recently reported.[8]

The reaction is simple to perform and the products and unchanged starting materials can be readily separated, furnishing excellent material balances with high yields of the product. The recovered phosphine oxides, depending on the individual compound, may suffer a slight reduction in optical purity. A control experiment in which optically active sulphide (**1b**) was subjected to boron trisulphide under the conditions of the reaction revealed no measurable loss of optical purity for the recovered sulphide.

A typical experimental procedure for the sulphurisation is as follows. The phosphine oxide (0·4 mmol) and boron trisulphide (1·2 mmol) are stirred in dry benzene (3 ml) under nitrogen. The mixture, after 20—30 h of heating under reflux, is allowed to cool and subsequently hydrolysed with 15% HCl solution. It is then neutralised with $NaHCO_3$ and extracted with $CHCl_3$. The $CHCl_3$ solution

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† All new compounds gave satisfactory elemental analyses and ^1H n.m.r. spectra consistent with the assigned structures.

‡ As measured by percentage retention of enantiomeric or diastereomeric purity.

is dried and concentrated, and the residue is chromatographed on silica gel, with hexane as eluant to remove traces of sulphur, $CHCl_3$–hexane for the phosphine sulphide, and $CHCl_3$–EtOH for the unchanged phosphine oxide.

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[1] L. J. Szafraniec, L. P. Reiff, and H. S. Aaron, *J. Amer. Chem. Soc.*, 1970, **92**, 6391.

[2] (a) L. P. Reiff, L. J. Szafraniec, and H. S. Aaron, *Chem. Comm.*, 1971, 366; (b) J. Omelańczuk and M. Mikolajczyk, *Tetrahedron*, 1971, **27**, 5587.

[3] In similar experiments with silicon disulphide, the starting phosphine oxide was recovered and no phosphine sulphide was detected. The use of these two reagents was inspired by the work on thiones by F. M. Dean, J. Goodchild, and A. W. Hill, *J. Chem. Soc.* (*C*), 1969, 2192.

[4] See, *e.g.*, (a) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 7012; (b) K. L. Marsi, *ibid.*, 1971, **93**, 6341.

[5] (a) L. Horner and H. Winkler, *Tetrahedron Letters*, 1964, 175; (b) D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johnson, and C. A. VanderWerf, *ibid.*, p. 359.

[6] W. B. Farnham, unpublished results.

[7] G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 7023.

[8] G. A. Gray and S. E. Cremer, *J. Org. Chem.*, 1972, **37**, 3458.