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Alane – A Novel Way to Reduce Phosphine Oxides

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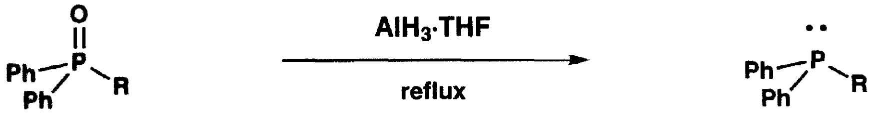
Abstract: Phosphine oxides may be reduced to phosphines in excellent yield using alane — AlH_3. An aqueous workup is not required.

The reduction of phosphine oxides to phosphines is an important reaction in organic chemistry and there are several methods available. Many of these methods have drawbacks of one kind or another. Any research worker who has reduced a phosphine oxide to a phosphine will be familiar with the small amount of reoxidation that always seems to accompany an aqueous workup.[1] However, an aqueous workup is essential in the case of reductions with $HSiCl_3$ or Si_2Cl_6[2, 3] and is also necessary when $LiAlH_4$, or one of its variants,[4] is used as the reducing agent. We have previously found the methodology developed by Lawrence *et al.*[1] to be excellent when a derivative phosphonium salt is made from the phosphine *in situ* but otherwise have had problems extracting some of our phosphines from the reaction mixture.[5]

We report here a method to reduce phosphine oxides to phosphines which is easy to perform, is very high yielding and does *not* require an aqueous work-up. A solution of alane in THF is prepared by the method of Brown and Yoon[6] by adding **concentrated** H_2SO_4 to a solution of $LiAlH_4$ in THF (CAUTION – addition of dilute H_2SO_4 will lead to an explosion). We have found that the resulting alane·THF solution may be conveniently titrated with the aid of a gas burette. Thus we measured the hydrogen evolved when 1 ml of the alane solution was syringed into a flask containing dry methanol.



A range of alkyldiphenylphosphine oxides were prepared by standard methods[7] and then reduced using between one and two equivalents of alane. The reactions were followed by TLC and were usually complete within 30 minutes.[8] There was no need for an aqueous workup — the reactions were quenched using anhydrous methanol and the reaction mixture filtered through celite. The yield was excellent in all the cases we examined.

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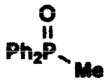
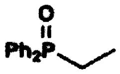
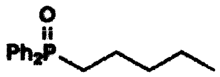
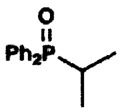
Table 1: Yields of Phosphines from Phosphine Oxides

Phosphine Oxide	Equivalents of $AlH_3{\cdot}THF$	Yield (%)
 $Ph_2P(O)Me$	1.1	96
	1.1	95
	1.1	97
	1.2	98
	1.1	98
Ph_3PO	1.0	97

Alane is known to have reactivity characteristics which differ from those of $LiAlH_4$ and is often more chemoselective.[6, 9] We expect this method to be useful to organic chemists where chemoselectivity is an issue. Investigations into chemoselectivity and into the stereoselectivity of reductions of phosphine oxides with a stereogenic phosphorus atom are in progress in our laboratories.

Typical procedure

iso-Propyldiphenylphosphine.— *iso*-Propyldiphenylphosphine oxide (109 mg, 0.455 mmol) was dissolved in dry THF (5.0 ml) and $AlH_3{\cdot}THF$ (490 µl of an 0.99 M solution in THF, 0.485 mmol) was added dropwise. The mixture was refluxed for 30 minutes, cooled and dry methanol (60 µl, 1.48 mmol) was added. The mixture was filtered through celite which was washed with hot THF (3 × 5 ml). The organic extract was evaporated under reduced pressure and purified by flash chromatography eluting with 9:1 40/60 pet. ether-EtOAc to yield the phosphine (102 mg, 98%).

Acknowledgements This work was inspired by an unpublished[10] observation made by Susan Armstrong.

References and Notes

1. Coumbe, T.; Lawrence, N. J.; Muhammad, F., *Tetrahedron Lett.*, **1994**, *35*, 625-628.
2. Naumann, K.; Zon, G.; Mislow, K., *J. Am. Chem. Soc.*, **1969**, *91*, 7012-7023.
3. Alkaline hydrolysis of the reaction mixture is necessary to liberate the phosphine.
4. Imamoto, T.; Takeyama, T.; Kusumoto, T., *Chem. Lett.*, **1985**, 1491-1492.
5. Warren, S.; Wyatt, P., *J. Chem. Soc., Perkin Trans. 1*, **1998**, 249-255.
6. Brown, H. C.; Yoon, N. M., *J. Am. Chem. Soc.*, **1966**, *88*, 1464-1472.
7. Buss, A. D.; Warren, S., *J. Chem. Soc., Perkin Trans. 1*, **1985**, 2307-2325.
8. Although all the reactions were completed under reflux, TLC often indicated a significant degree of reduction at room temperature.
9. Galatsis, P. in *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1995; vol. 1, pp. 161-164.
10. The related paper is – Armstrong, S. K.; Collington, E. W.; Knight, J. G.; Naylor, A.; Warren, S., *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1433-1447.