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# *N*-(Diphenylphosphinothioyl)hydroxylamine Transposition of O and S in its *O*-Benzoyl Derivative

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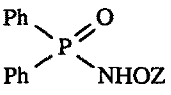
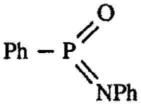
***Abstract***: *N*-(Diphenylphosphinothioyl)hydroxylamine has been prepared from $Ph_2P(S)Cl$ using $H_2NOSiMe_3$. The derivative $Ph_2P(S)NHOCOPh$ rearranges to $Ph_2P(O)NHSCOPh$ with base; this transposition of O and S seems to require a 3-membered ring comprising P, S and N atoms.

A group migrates from P to N when derivatives of *N*-phosphinoylhydroxylamines such as **1** (Z = H) rearrange with base, e.g. the sulphonyl derivative **1** ($Z = SO_2Me$) gives the phosphonamidate **3** with NaOMe in MeOH.[1] Formally these rearrangements proceed via 3-co-ordinate $P^V$ intermediates (e.g. **2**), analogous to the isocyanates formed in Lossen rearrangements. Such intermediates are also formed in other types of reaction, not involving rearrangement.[2,3] For these, replacing P = O by P = S has little effect on the rate in some cases,[2] but in others it makes the 3-co-ordinate $P^V$ species easier to form.[3] We therefore wanted to discover how changing P = O to P = S influences the reactivity of compounds such as **1** (Z = leaving group).



**1**



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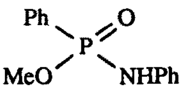
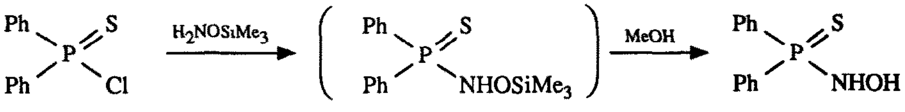


**3**

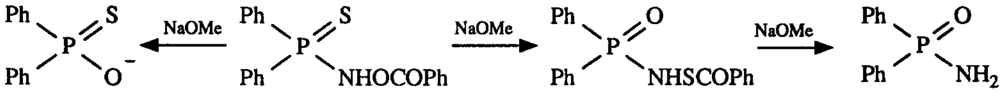
The phosphinothioic chloride **4** was allowed to react with $H_2NOSiMe_3$-$Et_3N$ in $CH_2Cl_2$ overnight. Removal of the TMS protecting group with MeOH gave the *N*-phosphinothioylhydroxylamine **5** as a stable crystalline solid (71 %), m.p. 120 - 121 °C. This is apparently the first thiophosphoryl hydoxylamine to be prepared,[4] but its structure seems secure: *m/z* 249 ($M^+$, 30%) and 217 ($M^+$ – NHOH, 100); $\nu_{max.}$(Nujol) 3305 and 3195 $cm^{-1}$; $\delta_P$ ($CH_2Cl_2$) 66.6; $\delta_H$ ($CD_3SOCD_3$) 8.36 (1 H, d, $J_{PH}$ 7.9), 8.14 (1 H, d, $J_{PH}$ 8.6) and 7.9 - 7.4 (10 H, m). Attempts to prepare sulphonyl derivatives were unsuccessful (they seem to be unstable), but with PhCOCl-$Et_3N$ the benzoate **7** was readily obtained: m.p. 95.5 - 97 °C; *m/z* 353 ($M^+$, 20 %) and 105 (100); $\nu_{max.}$ (Nujol) 3180 and 1730 $cm^{-1}$; $\delta_P$ ($CDCl_3$) 65.4; $\delta_H$ ($CDCl_3$) 8.38 (1 H, s, NH) and 8.15 - 7.2 (15 H, m).



**4** **5**

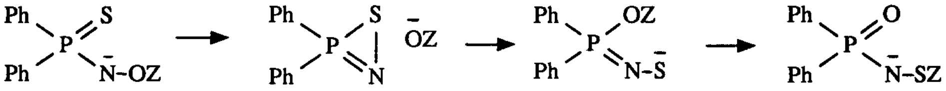
With MeOH-NaOMe (1.2 mol equiv.), the benzoate **7** dissolved and reacted over 15 min, but not by a

Lossen-like rearrangement. The dominant product ($\delta_P$ 25.6; 91 %) was the phosphinic amide **9**,[5] having both Ph groups still attached to P, but with O in place of S. The minor product was the phosphinothioate **6** ($\delta_P$ 56.3; 9 %), and methyl benzoate (~ 83 % by GLC) and sulfur were byproducts. Monitoring the reaction by $^{31}P$ NMR spectroscopy revealed that the phosphinic amide was not formed directly, but rather via a short-lived intermediate, $\delta_P$ 31.8. By using a lower temperature (*ca.* 5 °C) and vigorous shaking, and quenching the reaction ($CF_3CO_2H$) after 3 min, it was possible to isolate the intermediate in a sufficiently pure state for tentative identification as the rearrangement product **8**: *m/z* 353 ($M^+$, 25 %) and 105 (100); $\nu_{max}$ (Nujol) 3060, 2700, 1685 (C = O) and 1200 $cm^{-1}$ (P = O). In support of this, treatment of **1** (Z = $SO_2Me$) with NaSCOPh gave a product (m.p. 155 – 156 °C) having the same $R_f$ and $\delta_P$ values, and similar spectroscopic characteristics. This product, moreover, was converted quantitatively into the phosphinic amide **9** and methyl benzoate with MeOH-NaOMe. It therefore seems clear that the principal primary reaction of the benzoate **7** with base is indeed rearrangement to **8**, with transposition of S and O atoms. Remarkable though this is, there are some precedents for the interchange of S and O atoms in the chemistry of thiophosphoryl compounds.[6]



**6** **7** **8** **9**

As regards the mechanism of the rearrangement, the function of the base must surely be to generate the nitrogen anion **10** (Z = COPh); transposition of the S and O atoms might then proceed as shown, leading to the rearranged nitrogen anion **11**. Whatever the precise detail, the crucial point is surely that the S atom on phosphorus, rather than a Ph group, displaces the leaving group from nitrogen. Phenyl migration to the N atom is suppressed, and Lossen-like rearrangement does not occur.



**10** **11**

## REFERENCES AND NOTES

1. Harger, M. J. P.; Smith, A. *J. Chem. Soc., Perkin Trans. 1* 1985, 1787; 1987, 683.
2. Kawashima, T.; Miki, Y.; Tomita, T.; Inamoto, N. *Chem. Lett.* 1986, 501; Jankowski, S.; Quin, L. D. *J. Am. Chem. Soc.* 1991, **113**, 7011, and references cited in these.
3. Breslow, R.; Katz, I. *J Am. Chem. Soc.* 1968, **90**, 7376; Gerrard, A. F.; Hamer, N. K. *J. Chem. Soc. (B)* 1969, 369; Harger, M. J. P. *J. Chem. Soc., Perkin Trans. 2* 1991, 1057.
4. New compounds **5**, **7** and **8** were fully characterised by spectroscopy and elemental analysis.
5. Harger, M. J. P. *J. Chem. Soc., Perkin Trans* 2 1980, 154.
6. Creary, X.; Inocencio, P. A. *J. Am. Chem. Soc.* 1986, **108**, 5979; DeBruin, K. E.; Boros, E.E. *Phosphorus, Sulfur and Silicon* 1990, **49/50**, 139; *J. Org. Chem.* 1990, **55**, 6091.

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