O-(Diphenylphosphinyl)hydroxylamine

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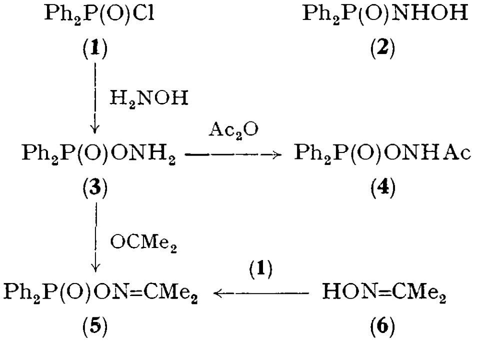
Summary The product from the reaction of hydroxylamine with diphenylphosphinic chloride (**1**) in benzene is *O*-(diphenylphosphinyl)hydroxylamine (**3**) rather than *N*-(diphenylphosphinyl)hydroxylamine (**2**); it forms an *N*-acetyl derivative (**4**) with acetic anhydride and condenses with acetone to give *O*-(diphenylphosphinyl)acetoxime (**5**).

KINETIC studies have shown that phosphorylating agents suffer initial attack by the hydroxy group of hydroxylamine,[1] but there are apparently no reports of the *O*-phosphorylhydroxylamines being isolated. Using diphenylphosphinic chloride (**1**) in benzene, Kreutzkamp and Schindler[2] obtained a derivative of hydroxylamine having m.p. 131 °C (decomp.) and analysing for $C_{12}H_{12}NO_2P$; this was designated *N*-(diphenylphosphinyl)hydroxylamine (**2**) although no chemical or spectroscopic evidence of structure was presented.

Following the reported procedure[2] we treated hydroxylamine (2·2 equiv.) with diphenylphosphinic chloride (**1**) in benzene (0·35 h at *ca.* 5 °C then 0·5 h at 5—15 °C) and collected the precipitate which was washed with iced water and crystallised from methanol (brief heating); it decomposed above 130 °C, had m/e 233 (M^+) and ν_{max} (Nujol) 3280, 3270, and 3180 cm^{-1}, and analysed for $C_{12}H_{12}NO_2P$ (92% yield before crystallisation). Although presumably the same as the product isolated by Kreutzkamp and Schindler, the properties of this compound suggest that it is in fact *O*-(diphenylphosphinyl)hydroxylamine (**3**).

Like *O*-acylhydroxylamines[3] it acts as an oxidising agent, liberating iodine from potassium iodide in acetic acid. It reacts readily with acetic anhydride in dichloromethane at room temperature to give a monoacetyl derivative (64%), m.p. 131—133 °C (from dichloromethane–ether), δ ($CDCl_3$) 11·8 br (1H, s), 8·1—7·2 (10H, m), and 1·90 (3H, s), ν_{max} ($CHCl_3$) 3120 and 1705 cm^{-1}.† The position of the i.r. carbonyl absorption supports the *N*-acetyl structure (**4**); in particular, a substantially higher frequency would be expected for the *O*-acetyl derivative of *N*-(diphenylphosphinyl)hydroxylamine (**2**).[4]

Especially convincing evidence for the structure (**3**) comes from the condensation of the phosphinylhydroxylamine with acetone (2 h at room temperature). The product (65%), m.p. 116—117·5 °C (from dichloromethane–ether), δ($CDCl_3$) 8·0—7·25 (10H, m), 2·06 (3H, s), and 1·91 (3H, s) is the phosphinyloxime (**5**), which is also formed by the reaction of acetoxime (**6**) with diphenylphosphinic chloride (Scheme).



SCHEME

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† All new compounds gave satisfactory elemental analyses.

O-(Di-*p*-tolylphosphinyl)hydroxylamine (73%), m.p. 112 °C (decomp.) (from dichloromethane–ether), and *O*-(di-*p*-anisylphosphinyl)hydroxylamine (89%), m.p. 92·5—93·5 °C (decomp.) (from methanol–ether), have been similarly prepared and characterised. It thus seems likely that *O*-phosphinylhydroxylamines will be generally accessible directly from hydroxylamine whereas *O*-acyl- and *O*-sulphonyl-hydroxylamines must usually be prepared by indirect methods.[5]

(*Received*, **14*th May*** 1979; ***Com.*** **514.**)

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[1] B. J. Jandorf, *J. Amer. Chem. Soc.*, 1956, **78**, 3686.

[2] N. Kreutzkamp and H. Schindler, *Arch. Pharm.*, 1960, **293**, 296; *Chem. Abs.*, 1964, **60**, 4179.

[3] P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, *J. Amer. Chem. Soc.*, 1964, **86**, 1139 and references therein.

[4] For example, W. P. Jencks, *J. Amer. Chem. Soc.*, 1958, **80**, 4581 reports ν_{max} ($CHCl_3$) 1710 and 1765 cm^{-1} for the *N*-acyl and *O*-acyl groups respectively in PhCONHOAc and O. Exner and M. Horák, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2992 (*Chem. Abs.*, 1960, **54**, 4370e) report ν_{max} (dioxan) 1725 and 1795 cm^{-1} for the corresponding groups in MeCONHOAc. See also O. Exner, *Dansk Tidsskr. Farm.*, 1968, **42**, 145.

[5] Y. Tamura, J. Minamikawa, and M. Ikeda, *Synthesis*, 1977, 1 and references therein.