Preparation of *N*-(Diphenylphosphinyl)hydroxylamine and Lossen-like Rearrangement of its *O*-Methanesulphonate

By MARTIN J. P. HARGER
(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary *N*-(Diphenylphosphinyl)hydroxylamine (**4a**) can be prepared from diphenylphosphinic chloride using *O*-trimethylsilylhydroxylamine; it forms *O*-acetyl (**5a**) and *O*-methanesulphonyl (**6a**) derivatives, the latter undergoing Lossen-like rearrangement in t-butylamine.

HYDROXYLAMINE reacts with diphenylphosphinic chloride (**1a**) in benzene to give a monosubstituted derivative thought originally to be the *N*-phosphinyl-hydroxylamine (**4a**).[1] That being so, the behaviour of phosphinic chlorides towards hydroxylamine would resemble the usual behaviour of acylating[2,3] and sulphonylating[3] agents under preparative conditions. However, it now seems that the products formed by phosphinic chlorides (**1**) and hydroxylamine are in fact the *O*-phosphinyl derivatives (**2**),[4] and that a different method is required to obtain *N*-phosphinyl-hydroxylamines (**4**).

Diphenylphosphinic chloride (**1a**) reacts with *O*-trimethylsilylhydroxylamine[5] (1·3 equiv.) and triethylamine (1·2 equiv.) in dichloromethane at room temperature (1·5 h). If sufficient solvent is used (*ca.* 3·5 ml per mmol), Et_3NHCl does not precipitate out and a clear solution results. The product is presumably the silylated compound (**3a**) but this has not been isolated. Rather, the trimethylsilyl group is removed by addition of methanol (3–4 equiv.), together with triethylamine (0·5—1·0 equiv.) to minimise the risk of acid-catalysed methanolysis of the P–N bond. *N*-(Diphenylphosphinyl)hydroxylamine (**4a**) (75%), m.p. 145—146 °C (decomp.), *m/e* 233 (M^+, 19%), 217 (51), 216 (65), and 201 (100); ν_{max} (Nujol) 3250, 3180, and 1165 cm^{-1}; $\delta(CD_3SOCD_3)$ 8·4—8·2 (2H, m, simplified by decoupling of phosphorus, NHOH) and 8·0—7·35 (10H, m), crystallises out over 2—3 h.† The related compounds (**4b**) (64%), m.p. 143—144 °C (decomp.), and (**4c**) (79%),

† The new compounds (**4**)—(**7**) all gave satisfactory elemental analysis results. Some samples of (**4a**) melted with decomposition at temperatures differing somewhat (±5 °C) from that noted above.

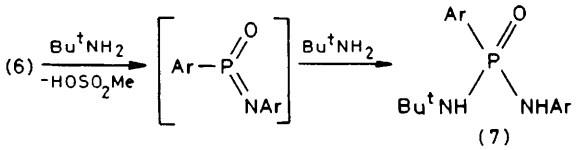
m.p. 139—140 °C (decomp.), can be prepared in similar ways from the phosphinic chlorides (**1b**) and (**1c**) respectively.‡

$Ar_2P(O)Cl$ (**1**)	$Ar_2P(O)ONH_2$ (**2**)	$Ar_2P(O)NHOSiMe_3$ (**3**)
$Ar_2P(O)NHOH$ (**4**)	$Ar_2P(O)NHOAc$ (**5**)	$Ar_2P(O)NHOSO_2Me$ (**6**)

a; Ar = Ph **b**; Ar = *p*-MeC_6H_4 **c**; Ar = *p*-$MeOC_6H_4$

The *N*-phosphinyl-hydroxylamines (**4**) are distinguished from the products (**2**) obtained using unprotected hydroxylamine[4] by their failure to liberate iodine immediately from potassium iodide in acetic acid, and also by their acetyl derivatives; for example (**4a**) reacts with acetic anhydride in dichloromethane containing triethylamine at room temperature to give a mono-acetate (83%), m.p. 164—165 °C; ν_{max} (Nujol) 3100 (NH) and 1785 cm^{-1} (C=O); ν_{max} (CH_2Cl_2) 1755 cm^{-1} (C=O); δ($CDCl_3$) 8·32 (1H, s, NH), 8·0—7·25 (10H, m), and 2·04 (3H, s, Me). These derivatives have i.r. carbonyl frequencies (1755—1760 cm^{-1} in CH_2Cl_2) that are in accord with the *O*-acetyl structures (**5**), being substantially higher than those (*ca.* 1705 cm^{-1} in $CHCl_3$) of the *N*-acetyl derivatives formed by the compounds (**2**).[4]

In the hope of observing a Lossen-like rearrangement[6] in phosphorus chemistry, the hydroxamic acid analogues (**4**) have been treated with methanesulphonyl chloride in pyridine (5—10 min at room temperature followed by



(7)

quenching with water) to give the crystalline methanesulphonates (**6**), *e.g.* (**6a**) (79%), m.p. 149 °C (decomp.), *m/e* 311 (M^+, 18%); ν_{max} (Nujol) 3140 cm^{-1}; δ(CD_3SOCD_3) 10·91 (1H, d, J_{PH} 11 Hz, NH), 8·0—7·3 (10H, m), and 3·26 (3H, s, Me). These methanesulphonates react exothermically with t-butylamine to give the products (**7**) of Lossen rearrangement in >90% yield. For example, (**6a**) gives (**7**, Ar = Ph), m.p. 176—178 °C, *m/e* 288 (M^+, 100%); ν_{max} (Nujol) 3380 and 3240br cm^{-1} (NH); δ($CDCl_3$) 8·0—7·3 (5H, m, PPh), 7·2—6·8 (5H, m, NPh), 5·24br (1H, d, J_{PH} 9 Hz, NH), 2·79br (1H, d, J_{PH} 11 Hz, NH), and 1·32 (9H, s, Bu^t), essentially identical with an authentic sample prepared by sequential reaction of $PhP(O)Cl_2$ with t-butylamine and aniline.

(*Received*, 16*th July* 1979; *Com.* 761.)

‡ With (**1b**) and (**1c**) the reaction time was increased to 16 h although this is probably not necessary. The stated yields of (**4b**) and (**4c**) include additional material (10 and 25% respectively) isolated by finally evaporating off the solvent, adding water to dissolve Et_3NHCl, and collecting the insoluble product.

[1] N. Kreutzkamp and H. Schindler, *Arch. Pharm.*, 1960, **293**, 296 (*Chem. Abs.*, 1964, **60**, 4179).
[2] H. L. Yale, *Chem. Rev.*, 1943, **33**, 209.
[3] Y. Tamura, J. Minamikawa, and M. Ikeda, *Synthesis*, 1977, 1.
[4] M. J. P. Harger, *J.C.S. Chem. Comm.*, 1979, 768.
[5] U. Wannagat and O. Smrekar, *Monatsh.*, 1969, **100**, 750.
[6] L. Bauer and O. Exner, *Angew. Chem. Internat. Edn.*, 1974, **13**, 376.