Tetrahedron Vol. 42, No. 10, pp. 2703 to 2706, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00
Pergamon Journals Ltd.

OXIDATION OF AMINES WITH BIS-(DIPHENYLPHOSPHINYL)PEROXIDE TO GIVE O-PHOSPHINYLATED AMINATING REAGENTS

GERNOT BOCHE* and REINHARD H. SOMMERLADE

Fachbereich Chemie der Philipps-Universität Marburg,
Hans-Meerwein-Strasse, D-3550 Marburg, FRG

(*Received in Germany* 18 *February* 1986)

Abstract - Oxidation of primary and secondary amines with bis-(diphenylphosphinyl)peroxide 8 conveniently leads to the O-(diphenylphosphinyl)hydroxylamines 1a-n.

N,N-disubstituted O-(diphenylphosphinyl)hydroxylamines[1a-i] and O-(diphenylphosphinyl)hydroxylamine[1j,2] (1) are useful reagents in electrophilic amination reactions to yield the amines 2, as we[1a-j] and others[2b] have amply shown in recent years (equation (1)).

$$\underset{\mathbf{1}}{RR'N\text{-}O\overset{O}{\overset{\|}{P}}Ph_2} \xrightarrow{R_3C^-M^+} \underset{\mathbf{2}}{RR'N\text{-}CR_3} + Ph_2PO_2^-M^+; \quad R,R' = \text{alkyl or H} \qquad (1)$$

Both types of reagents 1 have been prepared so far from the corresponding hydroxylamines 3 and diphenylphosphinyl chloride (4) in the presence of a base (equation (2))[1,2].

$$\underset{\mathbf{3}}{RR'N\text{-}OH} + \underset{\mathbf{4}}{Cl\text{-}\overset{O}{\overset{\|}{P}}Ph_2} \xrightarrow{\text{base}} \mathbf{1}; \qquad R,R' = \text{alkyl or H} \qquad (2)$$

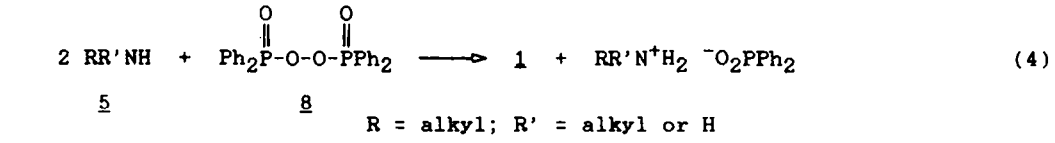
Although reaction (2) leads to 1 in good yields the preparation of the hydroxylamines 3 requested in this procedure is often tedious[3]. The one-step transformation of primary[4] and secondary[5,6] amines RR'NH 5 by means of dibenzoylperoxide (6) into the O-benzoylated hydroxylamines 7 (equation (3)),

$$2\ \underset{\mathbf{5}}{RR'NH} + \underset{\mathbf{6}}{(PhCO_2)_2} \longrightarrow \underset{\mathbf{7}}{RR'N\text{-}\overset{O}{\overset{\|}{C}}Ph} + RR'NH_2^+PhCO_2^- \qquad (3)$$

R = alkyl; R' = alkyl or H

and the related reaction of primary amines with bis-(arylsulfonyl)peroxides to give the corresponding N-alkyl-O-(arylsulfonyl)hydroxylamines[7] suggested a similar pathway for the preparation of the O-phosphinylated hydroxylamimes 1 by means of bis-(diphenylphosphinyl)peroxide 8[8].

We describe here the preparation of the N,N-disubstituted (1a-i) and the N-monosubstituted O-(diphenylphosphinyl)hydroxylamines 1j-n by means of 8 and secondary and primary amines 5, respectively, (equation (4))[9].



$$2\ \underset{5}{RR'NH} + \underset{8}{Ph_2P(O)\text{-}O\text{-}O\text{-}P(O)Ph_2} \longrightarrow 1 + RR'N^+H_2\ {}^-O_2PPh_2 \qquad (4)$$

R = alkyl; R' = alkyl or H

Table 1 summarizes the O-(diphenylphosphinyl)hydroxylamines 1a-n which have been prepared according to (4).

Table 1. O-(Diphenylphosphinyl)hydroxylamines 1a-n prepared via route (4).

1	R	R'	yield of 1(%)	1	R	R'	yield of 1(%)
a	CH_3	CH_3	98	h	n-C_4H_9	C_2H_5	93
b	C_2H_5	C_2H_5	92	i	-CH=CH-CH=CH-		73
c	i-C_3H_7	i-C_3H_7	70	j	i-C_3H_7	H	89
d	C_6H_{11}	i-C_3H_7	84	k	n-C_4H_9	H	90
e	C_6H_{11}	C_6H_{11}	60	l	$CH_2C_6H_5$	H	96
f	-$(CH_2)_4$-		63	m	$CH_2CH{=}CH_2$	H	82
g	-$(CH_2)_5$-		97	n	CH_3	H	60

Since the peroxide 8 is easily accessible from the diphenylphosphinyl chloride 4 and disodium peroxide[8] reaction (4) is the method of choice for the preparation of the N,N-disubstituted and N-monosubstituted O-(diphenylphosphinyl)hydroxylamines 1. The procedure simply requires the addition of two molar equivalents of the amines 5 to the cold (-60°C) solution of the peroxide 8 in methylene chloride, warming up of the solution over night, removal of the ammonium phosphinate with water, drying of the methylene chloride solution and evaporation of the solvent.

Acknowledgement: We are grateful to the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

Experimental part

General procedure for the preparation of 1a-n (1j): A solution of 0.53 g (8.96 mmol) isopropyl amine in 30 ml of dry CH_2Cl_2 was added under stirring over a period of 1 h to a solution of 2.00 g (4.60 mmol) 8 in 50 ml dry CH_2Cl_2 cooled to -60°C. The reaction mixture was allowed to warm to 0°C over night, washed four times with cold water and dried over $MgSO_4$. After removal of CH_2Cl_2 a residue resulted which was crystallized from dimethoxyethane/diethyl ether to yield 1.13 g (89%) of colorless needles; m.p. 125-126°C.

Characterization and properties of 1a-n:

1a: m.p. 134-135°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 2.75 (6H, s, N($\underline{CH_3}$)$_2$), 7.37-8.10 (10H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1})): 3060, 2975, 1590, 1235 (P=O), 890; MS (FD) m/z: 262 (MH^+, 100%)
$C_{14}H_{16}NO_2P$ (261.26) found C 64.60 H 6.09 N 5.29 calc. C 64.36 H 6.17 N 5.36

1b: m.p. 90-91°C (65-67°C)[9]; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 0.98 (6 H, t, -CH_2-$\underline{CH_3}$; J = 7.08 Hz), 3.00 (4 H, q, N-$\underline{CH_2}$-CH_3, J = 7.08 Hz), 7.38-7.96 (10 H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1})): 3070, 2990, 2960, 2890, 1600, 1450, 1240 (P=O), 910; MS (EI, 70 eV) m/z: 219 (($C_6H_5)_2P(OH)_2^+$, 100%)
$C_{16}H_{20}NO_2P$ (289.31) found C 66.06 H 6.88 N 4.65 calc. C 66.42 H 6.97 N 4.84

1c: m.p. 62-64°C (oil)[9]; ^{1}H-NMR ($CDCl_3$/TMS, δ (ppm)): 1.03 (12H, d, -CH($\underline{CH_3}$)$_2$, J = 6.59 Hz), 3.31 (2 H, sept., -$\underline{CH}$(CH_3)$_2$, J = 6.59 Hz), 7.31-7.94 (10 H, m, H_{arom}); IR (KBr disk (cm^{-1}): 3070, 2980, 2950, 2890, 1600, 1445, 1240 (P=O), 1135, 890; MS (FD) m/z: 318 (MH^+, 100%).
$C_{18}H_{24}NO_2P$ (317.37) found C 68.01 H 7.60 N 4.34 calc. C 68.12 H 7.62 N 4.41

1d: m.p. 109-111°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 1.00 (6 H, d, CH($\underline{CH_3}$)$_2$, J = 6.59 Hz, 0.86-1.73 (10 H, m, ($\underline{CH_2}$)$_5$), 2.90 (1 H, m, N-$\underline{CH}$(CH_2)$_5$), 3.30 (1 H, sept., N-$\underline{CH}$(CH_3)$_2$, J = 6.59 Hz), 7.26-7.93 (10 H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1})): 3090, 2990, 2950, 2880, 1600, 1450, 1235 (P=O), 1135, 890; MS (FD) m/z: 358 (MH^+, 100%)
$C_{21}H_{28}NO_2P$ (357.43) found C 70.76 H 7.98 N 3.96 calc. C 70.57 H 7.90 N 3.92

1e: m.p. 77-78°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 0.85-2.05 (20 H, m, -$(CH_2)_5$-), 2.90 (2 H, m, N-$\underline{CH}$(CH_2)$_5$), 7.06-7.95 (10 H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1}): 3090, 2990, 2880, 1600, 1450, 1235 (P=O), 1135, 890; MS (FD) m/z: 398 (MH^+, 100%)
$C_{24}H_{32}NO_2P$ (397.50) found C 72.19 H 8.06 N 3.45 calc. C 72.52 H 8.11 N 3.52

1f: m.p. 115-116°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 1.87 (4 H, m, N-CH_2-$\underline{CH_2}$-), 3.18 (4 H, m, N-$\underline{CH_2}$-CH_2), 7.20-8.10 (m, 10H, $H_{arom.}$); IR (KBr disk (cm^{-1})): 3070, 2995, 2960, 2940, 2880, 1600, 1450, 1230 (P=O), 1145, 1130, 910; MS (EI, 70 eV) m/z: 41 ($C_3H_5^+$, 100%), 219 (($C_6H_5)_2P(OH)_2^+$, 34%)
$C_{16}H_{18}NO_2P$ (287.30) found C 66.84 H 6.55 N 4.67 calc. C 66.89 H 6.31 N 4.87

1g: m.p. 124-125°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 1.15-1.70 (6 H, m, 3.4.5-$\underline{CH_2}$), 2.72-2.77 (2 H, m, N-$\underline{CH_2}$), 3.32-3.35 (2H, m, N-$\underline{CH_2}$-), 7.28-7.87 (10 H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1})): 3080, 3030, 2980, 2960, 2930, 2850, 1600, 1445, 1230 (P=O), 1135, 920, 885; MS (EI, 70 eV) m/z: 83 ($N(CH_2)_5^+$, 63%), 219 (($C_6H_5P(OH)_2^+$, 100%)
$C_{17}H_{20}NO_2P$ (301.32) found C 67.51 H 6.60 N 4.42 calc. C 67.76 H 6.69 N 4.65

1h: oil; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 0.79 (3 H, t, N-$(CH_2)_3$-$\underline{CH_3}$, J = 7.10 Hz), 0.99 (3 H, t, N-CH_2-$\underline{CH_3}$, J = 7.10 Hz), 1.07-1.45 (4 H, m, N-CH_2-$\underline{CH_2}$-$\underline{CH_2}$-CH_3), 2.92 (2 H, t, N-$\underline{CH_2}$-CH_2-, J = 7.10 Hz), 3.01 (2 H, t, N-$\underline{CH_2}$-CH_3, J = 7.10 Hz); IR (film on NaCl): 3070, 2985, 2960, 2890, 1600, 1455, 1240 (P=O), 910; MS (FD) m/z: 317 (M^+, 100%)
$C_{18}H_{24}NO_2P$ (317.37) found C 67.94 H 7.60 N 4.18 calc. C 68.12 H 7.62 N 4.41

1i: oil; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 6.22-6.4, 6.78-6.89 (2 H, m, N-CH=$\underline{CH}$-$\underline{CH}$=CH-), 7.27-7.85 (12 H, m, N-$\underline{CH}$=CH + $H_{arom.}$); MS (FD) m/z: 284 (MH^+, 100%)
$C_{16}H_{14}NO_2P$ (283.27)

1j: m.p. 125-126°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 1.10 (6 H,d, $CH(\underline{CH_3})_2$, J = 6.70 Hz), 3.38 (1 H, sept., $\underline{CH}(CH_3)_2$, J = 6.70 Hz), 5.32 (1 H, s, broad, D_2O exch., NH), 7.40-8.17 (10 H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1})): 3210 (NH), 3070, 2980, 2920, 2870, 1590, 1440, 1235 (P=O), 1210, 1130, 880; MS (FD) m/z: 275 (M^+, 100%)
$C_{15}H_{18}NO_2P$ (275.29) found C 65.53 H 5.57 N 5.11 calc. C 65.45 H 6.59 N 5.09

1k: m.p. 115-116°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm): 0.85 (3 H, t, $\underline{CH_3}$-CH_2, J = 6.35 Hz), 1.05-1.54 (4 H, m, CH_3-$\underline{CH_2}$-$\underline{CH_2}$-CH_2-N), 3.08 (2 H, t, N-$\underline{CH_2}$-CH_2, J = 6.35), 6.10 (1 H, s, broad, D_2O exch., NH), 7.35-7,97 (10 H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1}): 3230 (NH), 3080, 2960, 2990, 2880, 2840, 1600, 1455, 1230 (P=O), 1140, 890; MS (EI, 70 eV) m/z: 219 ($((C_6H_5)_2P(OH)_2^+$, 100%);
$C_{16}H_{20}NO_2P$ (289.31) found C 66.51 H 6.94 N 4.80 calc. C 66.42 H 6.97 N 4.84

1l: m.p. 118-119°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 4.17 (2 H, m, -$\underline{CH_2}$-C_6H_5), 6.30 (1 H, s, broad, D_2O exch., NH), 7.26 (5 H, s, CH_2-$\underline{C_6H_5}$), 7.28-7.90 (10 H, m $H_{arom.}$); IR (KBr disk, (cm^{-1})): 3210 (NH), 3070, 3040, 2970, 2940, 2900, 1600, 1440, 1225 (P=O), 1135, 855; MS (EI, 70eV), m/z: 217 ($((C_6H_5)_2PO^+$, 100%), 219 ($((C_6H_5)_2P(OH)_2^+$, 20%)
$C_{16}H_{20}NO_2P$ (289.31) found C 66.51 H 6.94 N 4.80 calc. C 66.42 H 6.97 N 4.84

1m: m.p. 98-100°C; ^{1}H-NMR ($CDCl_3$/TMS; δ (ppm)): 3.67 (2 H, d, N-$\underline{CH_2}$-CH=CH_2, J = 6.38 Hz), 5.19 (2 H, m, -CH=$\underline{CH_2}$), 5.26 (1 H, s, broad, D_2O exch., NH), 5.83 (1 H, m, -$\underline{CH}$=CH_2), 7.21-7.91 (10 H, m, $H_{arom.}$); IR (KBr disk, (cm^{-1})): 3220 (NH), 3090, 3020, 2960, 2920, 1600, 1455, 1230(P=O), 1140, 875; MS (FD) m/z: 273 (M^+, 100%), 274 (MH^+, 37%)
$C_{15}H_{16}NO_2P$ (273.27) found C 65.98 H 5.86 N 5.01 calc. C 65.93 H 5.90 N 5.13

1n: m.p. 106-107°C; ^{1}H-NMR ($CDCl_3$/TMS, δ (ppm)): 2.90 (3 H, s, N-$\underline{CH_3}$), 6.17 (1 H, s, broad, D_2O exch., NH), 7.41-7.91 (10 H, m, $H_{arom.}$); IR (KBr disk): 3220 (NH), 3080, 3020), 2980, 2950, 1590, 1440, 1215 (P=O), 1125, 865; MS (FD) m/z: 248 (MH^+, 100%)
$C_{13}H_{14}NO_2P$ (247.23) found C 63.28 H 5.71 N 5.30 calc. C 63.16 H 5.71 N 5.66

Literature and References

1. a. M. Bernheim, G. Boche, Angew. Chem. 92, 1043 (1980); Angew. Chem. Int. Ed. Engl. 19, 1010 (1980); b. M. Bernheim, Dissertation, Universität München 1981; c. G. Boche, F. Bosold, M. Nießner, Tetrahedron Lett. 1982, 3255; d. G. Boche, W. Schrott, Tetrahedron Lett. 23, 5403 (1982); e. G. Boche, M. Bernheim, M. Nießner, Angew. Chem. 95, 48 (1983); Angew. Chem. Int. Ed. Engl. 22, 53 (1983); Angew. Chem. Suppl. 1983, 34; f. M. Nießner, Dissertation, Universität Marburg 1984; g. W. Schrott, Dissertation, Universität Marburg 1984; h. K.-P. Stahl, G. Boche, W. Massa, J. Organomet. Chem. 227, 113 (1984); i. R.H. Sommerlade, Diplomarbeit, Universität Marburg 1983; j. G. Boche, M. Bernheim, W. Schrott, Tetrahedron Lett. 1982, 5399.
2. a. M.J.P. Harger, J. Chem. Soc. Chem. Commun. 1979, 768; b. W. Klötzer, H. Baldinger, E.M. Karpitschka, J. Knoflach, Synthesis 1982, 592.
3. For the preparation of hydroxylamines, see, e.g., B. Zeeh, H. Metzger in Houben-Weyl, Vol. X/1, Thieme Verlag, Stuttgart 1971, p. 1071.
4. a. G. Zinner, Arch. Pharm. (Weinheim) 296, 57 (1963); b. M. Psiorz, G. Zinner, Synthesis 1984, 217.
5. S. Gambarjan, Ber. Dtsch. Chem. Ges. 58, 1775 (1925).
6. A.J. Biloski, B. Ganem, Synthesis 1983, 537.
7. R.V. Hoffman, E. Belfoure, Synthesis 1983, 34.
8. For the preparation of 8 see R.L. Dannley, K.R. Kabre, J. Am. Chem. Soc. 87, 4805 (1965).
9. A recent publication on the nucleophilic oxidation of six secondary amines with 8 to give the corresponding N,N-dialkyl-O-(diphenylphosphinyl)hydroxylamines 1 (J.J. Yaouanc, G. Masse, G. Sturtz, Synthesis 1985, 807) prompts us to report our results[11,10].
10. R.H. Sommerlade, Dissertation in progress.