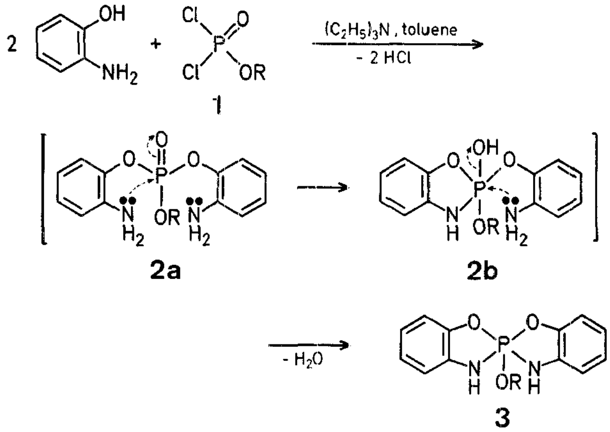
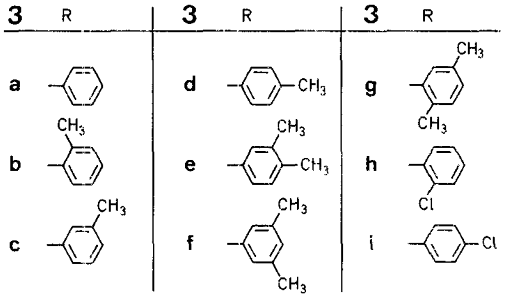




Synthesis of 2-Phenoxy-2,2′(3*H*,3′*H*)-spirobi[1,3,2-benzoxazaphosphole]

C. Devendranath Reddy*, S. Sreerami Reddy, M. S. R. Naidu

Department of Chemistry, Sri Venkateswara University, Tirupati 517502, India

The chemistry of cyclic phosphoranes is a rapidly growing field drawing much attention in recent times[1-5]. Only trace amounts of pentacoordinate phosphorus spiro compounds have been isolated by Koizumi et al.[6] while investigating the reaction between 2-aminophenol and phenyl phosphorodichloridate. During our studies on the synthesis of organophosphorus heterocyclic compounds, we found that 2-(substituted phenoxy)-2,3-dihydro-1*H*-1,3,2-benzodiazaphosphole 2-oxides were easily prepared by the condensation of *o*-phenylenediamine with substituted phenyl phosphorodichloridates[7,8]. In continuation of this study, we undertook the synthesis of 2-substituted phenoxy-2,3-dihydro-1,3,2-benzoxazaphosphole 2-oxides by the same procedure but obtained 2-phenoxy-2,2′(3*H*,3′*H*)-spirobi[1,3,2-benzoxazaphosphole] in good yields.

The mechanism of the formation of the bicyclic compounds **3** appears to be complex. However, we assume that the condensation of 2-aminophenol with the aryl phosphorodichloridate **1** proceeds via the phosphate intermediates **2a** and **2b**.

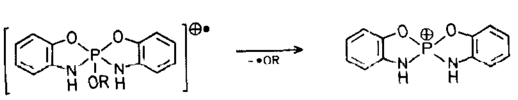
The I.R. spectra of products **3** show characteristic bands of P—NH[9], P—O—C_{arom}[10], and P—N—C_{arom}[11] stretching vibrations and are thus compatible with the structure **3**. In the ^{1}H-N.M.R. spectra, all compounds **3** show a doublet in the region $\delta = 8.55-8.70$ ppm with $J_{P-N-H} = 24$ Hz for the NH protons which are coupled to the P-atom[12]. Compounds **3a, b, c, d, i** show a down-field one-proton doublet with a coupling constant 7–9 Hz which could be assigned to one of the *o*-protons of the aryloxy group. The non-observance of similar down-field proton signals with compounds **3e, f, g** indicates the prevalance of *o*-aryl conformation different from that of the above compounds due to the presence of *ortho* and *meta* substituents. The chemical shifts of the two methyl groups of **3f** could not be differentiated; the 6.05 ppm signal of this compound could be assigned to the *O*-aryl *para* proton. The chemical ionization mass spectra of all compounds **3** show peaks corresponding to $(M+2)^+$, $(M+1)^+$, M^+, and $(M-OR)^+$, thus corroborating the assigned structures.

Table 1. 2-Phenoxy-2,2′(3*H*,3′*H*)-spirobi[1,3,2-benzoxaphospholes] (**3**)

3	Yield[a] [%]	m.p. [°C] (solvent)	Molecular formula[b]
a	56	209–211° (2-propanol)	$C_{18}H_{15}N_2O_3P$ (338.2)
b	59	231–232° (2-propanol)	$C_{19}H_{17}N_2O_3P \cdot \frac{1}{2}H_2O$ (361.2)
c	61	219–221° (2-propanol)	$C_{19}H_{17}N_2O_3P$ (352.2)
d	61	218–220° (2-propanol)	$C_{19}H_{17}N_2O_3P$ (352.2)
e	63	231–233° (2-propanol/DMF)	$C_{20}H_{19}N_2O_3P$ (366.3)
f	65	234–236° (2-propanol)	$C_{20}H_{19}N_2O_3P$ (366.3)
g	60	235.5–236.5° (2-propanol/DMF)	$C_{20}H_{19}N_2O_3P$ (366.3)
h	68	239–240° (2-propanol)	$C_{18}H_{14}ClN_2O_3P$ (372.65)
i	70	197–199° (2-propanol)	$C_{18}H_{14}ClN_2O_3P$ (372.65)

[a] Yield after one recrystallization.

[b] All products gave satisfactory microanalyses: C, ±0.43; H, ±0.20. The analyses were performed by Dr. R. D. MacDonald, Australian Microanalytical Service, CSIRO, University of Melbourne, Victoria, Australia, 3001 and at C.D.R.I., Lucknow, India.



3a *m/e* = 338 (M⁺) *m/e* = 245 (M−OR)⁺

0039-7881/80/1232-1004 $ 03.00

Table 2. Spectral Data of Compounds **3**

3	C.I. Mass Spectra[a] (m/e)				I.R. (Nujol)[b] ν [cm^{-1}]			^{1}H-N.M.R. (DMSO-d_6)[c] δ [ppm]
	$(M+2)^+$	$(M+1)^+$	M^+	$(M-OR)^+$	P—N—H	P—N—C_{arom}	P—O—C_{arom}	
a	340	339	338	245	3420	1320, 915	1235, 960	8.64 (d, 2H, NH, J=24 Hz); 7.23 (d, 1H, J=7 Hz); 6.62–6.87 (m, 12H)
b	354	353	352	245	3500	1330, 920	1240, 960	8.60 (d, 2H, NH, J=24 Hz); 7.01 (d, 1H, J=7 Hz); 6.56–6.93 (m, 11H); 2.00 (s, 3H)
c	354	353	352	245	3420	1320, 920	1238, 955	8.57 (d, 2H, NH, J=24 Hz); 7.04 (d, 1H, J=7 Hz); 6.53–6.93 (m, 11H); 2.10 (s, 3H)
d	354	353	352	245	3500	1330, 920	1242, 955	8.58 (d, 2H, NH, J=24 Hz); 7.08 (d, 1H, J=9 Hz); 6.58–6.88 (m, 11H), 2.22 (s, 3H)
e	368	367	366	245	3450	1328, 910	1240, 950	8.55 (d, 2H, NH, J=24 Hz); 6.40–7.00 (m, 11H); 2.10 (s, 3H); 2.03 (s, 3H)
f	—	367	366	245	3500	1330, 910	1245, 950	8.57 (d, 2H, NH, J=24 Hz); 6.05 (s, 1H); 6.60–6.87 (m, 11H); 2.10 (s, 6H)
g	368	367	—	245	3500	1325, 914	1240, 955	8.60 (d, 2H, NH, J=24 Hz); 6.47–7.10 (m, 11H); 1.95 (s, 3H); 2.07 (s, 3H)
h	373	372	371	245	3400	1320, 910	1220, 950	8.70 (d, 2H, NH, J=24 Hz); 7.57–7.53 (m, 12H)
i	373	372	371	245	3495	1325, 910	1230, 955	8.66 (d, 2H, NH, J=24 Hz); 7.32 (d, 1H, J=9 Hz); 6.63–6.97 (m, 11H)

[a] Recorded with a CEC (Dupont) 21-110B Mass spectrometer. Reactant gas: methane for **3a** and **3g** and isopentane for others.
[b] Measured on a Perkin-Elmer Model 137 infrared spectrometer.
[c] Recorded at 60 MHz on a Varian T 60 NMR spectrometer.

The phenyl phosphorodichloridates (**1**) are prepared by the procedure described in Ref.[7,8].

2-Phenoxy-2,2′(3*H*,3′*H*)-spirobi[1,3,2-benzoxazaphospholes] (3a); General Procedure:

A solution of the phenyl phosphorodichloridate (**1**; 0.025 mol) in dry toluene (20 ml) is added dropwise over a period of 20 min to a stirred and refluxing solution of 2-aminophenol (3.46 g, 0.05 mol) and triethylamine (5.06 g, 0.05 mol) in dry toluene (70 ml). Stirring and refluxing is continued for 4 h. Triethylamine hydrochloride is removed by filtration and the solvent is removed in a rotavapor. The residue is washed with water and recrystallized three times from isopropanol.

We are thankful to Dr. Kurt L. Loening, Nomenclature Director, Chemical Abstract Service, Columbus, Ohio-43210 for suggesting names to these compounds. The authors are also thankful to Dr. M. S. Raju of the Rockefeller University for the ^{1}H-N.M.R. spectra and to U. G. C., New Delhi for financial assistance.

Received: April 14, 1980

* Address for correspondence.
[1] F. H. Westheimer, *Acc. Chem. Res.* **1**, 70 (1968).
[2] F. Ramirez, *Acc. Chem. Res.* **1**, 168 (1968).
[3] S. Trippet, *Phosphorus and Sulphur* **1**, 89 (1976).
[4] F. Mathis, *Phosphorus and Sulphur* **1**, 109 (1976).
[5] M. A. Pudovik, S. A. Terenteva, N. P. Anoshina, A. N. Pudovik, *Zh. Obshch. Khim.* **47**, 1230 (1977); *J. Gen. Chem. USSR* **47**, 1133 (1977).
[6] T. Koizumi, Y. Watanabe, Y. Yoshida, E. Yoshii, *Tetrahedron Lett.* **1974**, 1075.
[7] M. S. R. Naidu, C. Devendranath Reddy, *Indian J. Chem.* **12**, 349 (1974).
[8] M. S. R. Naidu, C. Devendranath Reddy, *Indian J. Chem.* (in press).
[9] J. R. Pustinger, W. T. Cane, M. L. Neilson, *Spectrochem. Acta* **15**, 909 (1959).
[10] A. C. Chapman, R. Harper, *Chem. Ind. (London)* **1962**, 985.
[11] N. B. Colthup, L. H. Daly, S. E. Wilberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964, p. 305.
[12] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon Press, New York, 1959, p. 73.

0039-7881/80/1232–1005 $ 03.00