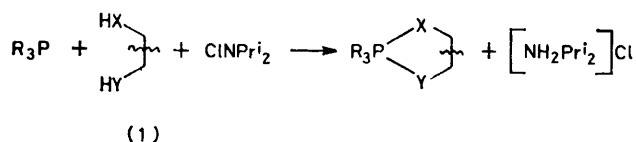


Further Syntheses of Quinquevalent Spirophosphoranes by using *N*-Chlorodi-isopropylamine

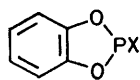
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Spirophosphoranes have been obtained from cyclic tervalent phosphorus compounds and 1,2-difunctional compounds $\text{HX}(\text{C})_2\text{YH}$ ($\text{X}, \text{Y} = \text{O}, \text{NR}, \text{or S}$), benzohydroxamic acid, benzohydrazide, or benzamidoxime in the presence of *N*-chlorodi-isopropylamine.

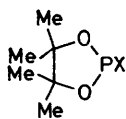
We previously showed¹ that quinquevalent phosphoranes are obtained in good yield from a wide range of tervalent phosphorus compounds and 1,2-diols or 1,2-dihydroxybenzenes (**1**; $\text{X}, \text{Y} = \text{O}$) in the presence of *N*-chlorodi-isopropylamine.



By using prolonged reaction times we have now extended the synthesis to include the thiols and amines (**1**; $\text{X}, \text{Y} = \text{O}, \text{NR}, \text{or S}$) listed in the Table, benzamidoxime, and, in their enol forms, benzohydroxamic acid, and benzohydrazide. The syntheses are exemplified using the tervalent species (**2**; $\text{X} = \text{OPh}$ or NMe_2) or (**3**; $\text{X} = \text{OMe}, \text{OPh}, \text{Ph}, \text{or NMe}_2$).



(2)



(3)

Most of the resulting phosphoranes would, in principle, be accessible by incorporating the sulphur and/or nitrogen(s) initially in a ring containing tervalent phosphorus and then adding a second ring using *N*-chlorodi-isopropylamine, or *via* for example exchange reactions.² However the method reported here is, in general, the

most convenient. The spirophosphoranes derived from *o*-aminophenol showed no evidence of the presence of the isomeric iminophosphoranes,³ presumably because of the relief of ring-strain in the five-co-ordinate form. Spirophosphoranes could not be isolated from reactions using *o*-phenylenediamine or 2-hydroxyethanethiol although there was ³¹P n.m.r. evidence for their formation.

Phosphoranes containing 3,1,2-thiazaphospholidine rings have previously been obtained by the deoxygenation with cyclic phosphites of aryl 2-nitrophenyl sulphides.⁴ *P*-H spirophosphoranes derived from benzamidoximes,⁵ benzohydroxamic acid,⁶ and benzohydrazide⁷ are well known, and spirophosphoranes containing two 1,3,4,2-oxadiazaphospholidine rings have recently been obtained from acyl hydrazides and phosphonic dichlorides.⁸

EXPERIMENTAL

General Procedure.—*N*-Chlorodi-isopropylamine (5 mmol) in ether (20 ml) was slowly added to a stirred solution of the tervalent phosphorus compound (5 mmol) and the 1,2-difunctional species (5 mmol) in ether (20 ml) at -40°C and the mixture set aside at room temperature until ³¹P n.m.r. spectra showed the reaction to be complete (1–24 days). The resulting suspension was filtered and the filtrate evaporated to dryness. The phosphoranes were then crystallised from ethyl acetate or dichloromethane by the addition of light petroleum although in some cases rapid chromatography on a short column of alumina was necessary in order to remove coloured impurities.

We thank the S.R.C. for support.

[7/2210 Received, 2nd December, 1977]

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² e.g. D. Bernard and R. Burgada, *Phosphorus*, 1975, 5, 285.

³ H. B. Stegmann, G. Bauer, E. Breitmaier, E. Herrmann, and K. Scheffler, *Phosphorus*, 1975, 5, 207.

⁴ J. I. G. Cadogan, R. O. Gould, and N. J. Tweddle, *J.C.S. Chem. Comm.*, 1975, 773.

⁵ L. Lopez and J. Barrans, *Compt. rend.*, 1971, 273C, 1540.

⁶ A. Munoz, M. Koenig, R. Wolf, and F. Mathis, *Compt. rend.*, 1973, 277C, 121.

⁷ A. Schmidpeter and J. Lubner, *Angew. Chem. Internat. Edn.*, 1972, 11, 306.

⁸ A. Schmidpeter and J. Lubner, *Chem. Ber.*, 1977, 110, 1124.

Spirophosphoranes prepared by using *N*-chlorodi-isopropylamine

(1)	Phosphorus compound	Phosphorane ^a	δ (³¹ P) ^b	Yield (%)	m.p. (°)	Analysis ^c			
						C	H	N	P
<i>o</i> -HOC ₆ H ₄ SH	(3; X = OPh)		14.5	89	91—92	58.8 (59.3)	6.0 (5.8)		8.35 (8.5)
	(2; X = OPh)		4.2	87	80—82	60.6 (60.7)	4.1 (3.7)		8.3 (8.7)
	(2; X = NMe ₂)		4.7 ^d	98	119—120	54.4 (54.7)	4.6 (4.6)	4.6 (4.6)	10.2 (10.1)
<i>o</i> -HSC ₆ H ₄ NHMe	(2; X = OPh)		4.4 ^e	79	82—83	61.8 (61.8)	4.4 (4.4)	3.7 (3.8)	8.4 (8.4)
	(3; X = OPh)		<i>e</i>	93	104—105	59.4 (60.4)	6.3 (6.4)	3.6 (3.7)	8.4 (8.2)
	(2; X = NMe ₂)		1.4 ^f	94	78—79	55.9 (56.2)	5.5 (5.3)	8.7 (8.7)	
	(3; X = NMe ₂)		17.1 ^g	94	136—137	55.1 (54.9)	7.6 (7.7)	8.4 (8.5)	
HOC ₂ H ₄ NHMe	(2; X = OPh)		40.9 ^h	70	116—117	58.95 (59.0)	5.35 (5.3)	4.6 (4.6)	
	(3; X = OPh)		48.1 ^h	79	89—90	57.5 (57.5)	8.2 (7.7)	4.3 (4.5)	
<i>o</i> -HOC ₆ H ₄ NH ₂	(2; X = NMe ₂)		31.6 ^j	93	103—104	57.4 (57.9)	5.3 (5.2)	9.7 (9.65)	
	(3; X = NMe ₂)		39.8 ^k	93	144—145	56.7 (56.4)	7.75 (7.8)	9.6 (9.4)	10.2 (10.4)
	(3; X = OMe)		38.0 ^l	80	123—124	54.7 (54.7)	6.8 (7.1)	4.7 (4.9)	
	(3; X OPh)		44.0 ^m	92	164—165	62.05 (62.25)	6.45 (6.4)	3.95 (4.0)	
			34.0 ⁿ	65	123—124.5	53.4 (53.4)	7.3 (7.1)	10.3 (10.4)	
PhC(=NOH)NH ₂	(3; X = Ph)		27.2 ^o	87	208—209	63.45 (63.7)	6.6 (6.4)	7.8 (7.8)	
PhCONHNH ₂	(3; X = Ph)		35.5 ^p	81	212—213	62.7 (63.6)	6.5 (6.5)	7.4 (7.8)	
PhCONHOH	(3; X = Ph)		17.1	86	124—125	63.1 (63.5)	4.0 (4.0)	6.15 (6.15)	

^a All phosphoranes showed the molecular ion and the expected fragmentation pattern in their mass spectra. ^b In CDCl₃. Positive values are to high field of external 85% H₃PO₄. ^c Found (required). ^d ³J_{PH} 12 Hz. ^e ³J_{PH} 14 Hz. ^f ³J_{PH} (NMe) 7 and (NMe₂) 13 Hz. ^g ³J_{PH} (NMe) 6 and (NMe₂) 13 Hz. ^h ³J_{PH} (NMe) 9 Hz. ⁱ ²J_{PH} 20, ³J_{PH} 12 Hz. ^k ²J_{PH} 19, ³J_{PH} 11 Hz. ^l ²J_{PH} 20, ³J_{PH} 16 Hz. ^m ²J_{PH} 19.5 Hz. ⁿ ²J_{PH} 18, ³J_{PH} (NMe₂) 11 Hz. ^o ²J_{PH} 18 Hz. ^p ²J_{PH} 38 Hz.