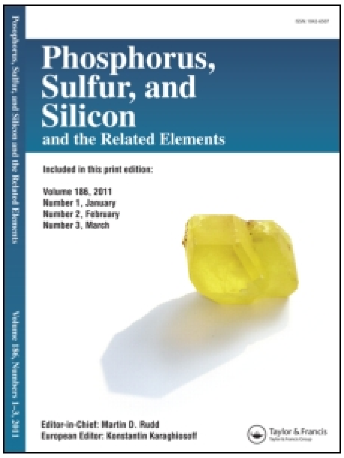

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOSPHORUS-NITROGEN COMPOUNDS. PART 70.[1] AMINOLYSIS OF *P*-TRICHLORO-*N*-DICHLOROPHOSPHORYLMONOPHOSPHAZENE, $C1_3P=N-P(O)Cl_2$

Adem Kilic[ab]; Zeynel Kilic[ac]; Robert A. Shaw[a]
[a] Department of Chemistry, Birkbeck College (University of London), London, UK. [b] Department of Chemistry, Science and Arts Faculty, Inönü University, Malatya, Turkey [c] Department of chemistry, Science Faculty, University of Ankara, Ankara, Turkey

To cite this Article Kilic, Adem , Kilic, Zeynel and Shaw, Robert A.(1991) 'PHOSPHORUS-NITROGEN COMPOUNDS. PART 70.[1] AMINOLYSIS OF *P*-TRICHLORO-*N*-DICHLOROPHOSPHORYLMONOPHOSPHAZENE, $C1_3P=N-P(O)Cl_2$', Phosphorus, Sulfur, and Silicon and the Related Elements, 56: 1, 157 — 164

To link to this Article: DOI: 10.1080/10426509108038078

URL: http://dx.doi.org/10.1080/10426509108038078

Phosphorus, Sulfur, and Silicon, 1991, Vol. 56, pp. 157-164
Reprints available directly from the publisher
Photocopying permitted by license only

PHOSPHORUS-NITROGEN COMPOUNDS. PART 70.[1] AMINOLYSIS OF *P*-TRICHLORO-*N*-DICHLOROPHOSPHORYLMONOPHOSPHAZENE, $Cl_3P{=}N{-}P(O)Cl_2$

ADEM KILIC,† ZEYNEL KILIC‡ and ROBERT A. SHAW*

Department of Chemistry, Birkbeck College (University of London), Gordon House, 29, Gordon Square, London WC1H OPP, UK.

(Received June 10, 1990; in final form July 10, 1990)

The reactions of $Cl_3P{=}N{-}P(O)Cl_2$ with primary and secondary amines have been studied. The following penta-amides $(R'RN)_3P{=}N{-}P(O)(NRR')_2$ were isolated: NRR' = NHE^{t}, NHPr^{i}, NHBu^{t}, NHPh, pyrrolidino, piperidino and morpholino. Symmetric hydrolysis products $(RR'N)_2P(O){-}NH{-}P(O)(NRR')_2$ were also obtained in lesser yields: NRR' = NHE^{t} NHPr^{i}, NHBu^{t}, pyrrolidino, piperidino and morpholino, A higher molecular weight tetranuclear phosphorus species was also tentatively characterised. ^{31}P, ^{1}H and ^{13}C n.m.r. spectra are reported.

Key words: *P*-Trichloro-*N*-dichlorophosphorylmonophosphazene, aminolysis, hydrolysis products, n.m.r. studies.

INTRODUCTION

P-Trichloro-*N*-dichlorophosphorylmonophosphazene, $Cl_3P{=}N{-}P(O)Cl_2$, (**1**), and its derivatives have aroused interest for a number of reasons:

(i) Thermolysis of compound (**1**) leads with elimination of phosphorus oxychloride, $P(O)Cl_3$, (**2**), to a polymeric chlorosphosphazene, $(NPCl_2)_n$.[2]

$$Cl_3P{=}N{-}P(O)Cl_2 \xrightarrow{\Delta} (NPCl_2)_n + P(O)Cl_3$$

(ii) The reversible silyl group migration ($O \rightleftharpoons O$)[3,4]

$$R_2(Me_3SiO)P{=}N{-}P(O)R_2 \rightleftharpoons R_2P(O){-}N{=}P(OSiMe_3)R_2$$

(iii) The irreversible ($O \rightarrow O$ and $O \rightarrow N$) migration of alkyl groups.[5,6]

$$(MeO)_3P{=}N{-}P(O)Et_2 \xrightarrow{\Delta} (MeO)_2P(O){-}NMe{-}P(O)Et_2 + (MeO)_2P(O){-}N{=}P(OMe)Et_2$$

(iv) The general preparative chemistry of a structurally relative simple dinuclear phosphorus compound with the nuclei in different chemical environments and which is fairly readily accessible.

Aspects of the above have been referred to in some general review articles.[7,8]

---

*Author to whom correspondence should be addressed.

†Present Address: Department of Chemistry, Science and Arts Faculty, Inönü University, Malatya, Turkey.

‡Present Address: Department of Chemistry, Science Faculty, University of Ankara, Ankara, Turkey.

A number of studies devoted to the complete alcoholyses of compound (**1**) have been reported.[9–11] Recently the replacement of one chlorine atom by the allyloxy group has been described.[12] One elegant study by Bulloch and Keat[13] was devoted to a partial aminolysis of the pentachloride (**1**); methylamine and *t*-butylamine were found to follow a different disubstitution pattern.

RESULTS AND DISCUSSION

We here report our findings, when compound (**1**) is subjected to reaction in acetonitrile with an excess of primary or secondary amines. The reaction products are surprisingly complex. No reaction system so far studied gave us fewer than two derivatives, some as many as six. We did obtain the expected penta-amides, $(RR'N)_3P{=}N{-}P(O)(NRR')_2$, (**3**), [NRR' = NHEt (**a**), NHPr^i (**b**), NHBu^t (**c**), NHPh (**d**), pyrrolidinio (**e**), piperidino (**f**) and morpholino (**g**)] as the major products.

Our choice of representative amines were based on the following; (i) Effect of primary versus secondary amines and mechanistic consequences. Secondary amines must act at phosphorus; primary amines have the choice of a similar reaction path or could react after the first replacement step by a proton abstraction—chloride elimination mechanism. With hexachlorocyclotriphosphazatriene ethylamine follows the former on disubstitution, whilst *t*-butylamine follows the latter. Experimentally we observed similar product patterns for both classes (primary and secondary) of amines. (ii) Effect of weak versus strong nucleophilicity (aniline versus *t*-butylamine, morpholine versus pyrrolidine). Again both extremes gave closely similar results. (iii) Steric effects: ethylamine, isopropylamine, *t*-butylamine. In contrast to the hexachlorocyclotriphosphazatriene system, where steric effects hindered complete substitution by *t*-butylamine, in the present study all amines allowed replacement of all chlorine atoms. Bulky steric effects increased the stability of the products, those based on ethylamine were found to be the least stable.

We had noticed in ^{31}P n.m.r. studies (see below) that in addition to the four line AX spectrum of the pentachloride (**1**), a singlet to low field was observed (~1 p.p.m.), which increased slowly on standing. It was proven not to be phosphorus oxychloride (**2**). We deduced it to be a hydrolysis product of the pentachloride (**1**), viz. a symmetrical dinuclear derivative, $Cl_2P(O){-}NH{-}P(O)Cl_2$, (**4**), whose presence in compound (**1**) was demonstrated by mass spectrometry. We duly isolated a number of tetra-amides $(RR'N)_2P(O){-}NH{-}P(O)(NRR')_2$, (**5**) [NRR' = NHEt (**a**), NHPr^i (**b**), NHBu^t (**c**), NHPh (**d**), pyrrolidino (**e**), piperidino (**f**) and morpholino (**g**)] based on the precursor chloride, (**4**). These tetra-amides (**5**) were always present in lower yields than the penta-amides (**3**).

Many of the compounds isolated showed ions in their mass spectra in excess of the molecular weights of the penta-amides (**3**) and tetra-amides (**5**) for the respective amines (see ^{31}P section).

^{31}P N.m.r. Studies

Comparison of the chemical shifts of the penta-amides (**3**) with those of the precursor chloride (**1**) shows in some cases a relationship. The low-field and high-field

signals of compound (**1**) have been assigned respectively to the $Cl_3P{=}N$— and to the —$P(O)Cl_2$ moieties.[13,14] If we assume approximate additivity of substituent effects for the amino groups (NRR′) we note that the shifts of the low-field and high-field signals move to lower field (except **3d**) and in a number of cases these are in the ratio of 3:2. This would confirm the earlier assignment.
The data are collected in Table I.

We report here on one higher molecular weight product, (**6**), derived from the reaction of the pentachloride (**1**) with *t*-butylamine. Its ^{31}P n.m.r. spectrum is complex and shows evidence of four different environments (**A**, **B**, **C**, and **D**). The chemical shifts of (**A**) and (**C**) (δ 4.77 p.p.m.) are superimposed, but these nuclei are not coupled to each other. Nucleus (**A**) couples weakly to (**B**) (~3 Hz). This is usually indicative of P—NH—P or P—NR—P, rather than of P=N—P coupling.[15,16] Nucleus (**B**) (δ 10.71 p.p.m.) couples moderately strongly to (**C**) (22.1 Hz). The latter also shows the strongest coupling in this system (33.4 Hz) to nucleus (**D**) (δ 1.22 p.p.m.). We ascribe to this compound a chain structure (**6**).

$$(Bu^tNH)_2\overset{(\mathbf{A})}{P}(O)\text{—}NH\text{—}\overset{(\mathbf{B})}{P}(NHBu^t)_2{=}N\text{—}\overset{(\mathbf{C})}{P}(NHBu^t)_2{=}N\text{—}\overset{(\mathbf{D})}{P}(O)(NHBu^t)_2 \quad (\mathbf{6})$$

^1H *n.m.r. Studies*

The data are presented in Table II. In the penta-amides (**3**) the $P(O)(NRR')_2$ and $P(NRR')_3$ environments can be distinguished in some cases, the latter being more deshielded than the former. The P(O)N*H* and N=PN*H* environments can also be distinguished in some cases.

TABLE I

^{31}P n.m.r. Data of Derivatives

Compound	$\delta P(O)(NRR')_2$[b]	$\delta P(NRR')_3$[b]	$2J(PP)$[c]
(**1**)	−2.7	−10.7	21.3
(**3a**)	11.6	14.4	35.1
(**3b**)	8.7	9.1	36.6
(**3c**)	4.4	−0.3	32.6
(**3d**)	−7.1[d]	−1.05[d]	46.5
(**3e**)	7.5	3.3	45.8
(**3f**)	8.7[d]	16.3[d]	51.3
(**3g**)	7.6[d]	15.9[d]	43.3
(**4**)	~1		
(**5a**)[e]	13.9		
(**5b**)	7.0		
(**5c**)	5.0		
(**5e**)	8.9		
(**5f**)	13.7		
(**5g**)	6.0		

[a] In $CDCl_3$ at room temperature at 24.15 and 161.903 MHz.
[b] In p.p.m.
[c] In Hz.
[d] Assignment uncertain.
[e] Not isolated, but detected by ^{31}P n.m.r. spectroscopy in reaction mixture.

TABLE II

^{1}H n.m.r. Data of Derivatives[a]

Compound	δα—C*H*[b]	δβ—C*H*[b]	δP(O)N*H*[b]	δN=PN*H*[b]
(3a) P(NRR')$_3$	2.84	1.02		3.52
P(O)(NRR')$_2$	2.80	0.99	2.00	
(3b) P(NRR')$_3$	3.34	1.10		2.78
P(O)(NRR')$_2$	3.28	1.07	1.87	
(3c) P(NRR')$_3$		1.32		3.09
P(O)(NRR')$_2$			1.30	2.09
(3e)[c] P(NRR')$_3$	3.18	1.81		
P(O)(NRR')$_2$	3.08	1.75		
(3f)[d] P(NRR')$_3$	3.06	1.50		
P(O)(NRR')$_2$				
(3g) P(NRR')$_3$	3.80	4.31	2.25	
P(O)(NRR')$_2$				
(5b)	3.44	1.19	4.67	2.87
(5c)		1.32	4.48	3.13
(5e)[e]	3.23	1.78		
(5f)[d]	3.12	1.54	2.25	
(5g)	3.11	3.63		

[a] In $CDCl_3$ (room temperature) at 199.5 and 399.95 MHz

[b] In p.p.m.

[c] $^3J(PNCH_2)$ 14.8 Hz, $^3J[P(O)NCH_2]$ 14.1 Hz.

[d] β—C*H* and γ—C*H*.

[e] $J[P(O)CH_2]$ 14.1 Hz.

^{13}C n.m.r. Studies

The data are presented in Table III. In the penta-amides (**3**), the two environments can be distinguished in all cases.

SUMMARY

In the reactions of the pentachloride, (**1**), with primary and secondary amines, the corresponding penta-amides, (**3**), were the major products in all cases. Lesser yields of a partial hydrolysis product, (**4**), leading to symmetrical tetra-amides, (**5**), were also obtained.

EXPERIMENTAL

Chemicals were obtained as follows: benzene, light petroleum (b.p. 40–60°C), anhydrous diethyl ether (May and Baker Ltd.), tetrahydrofuran (Fluka-Garantie 99.5%), deuteriated solvents n.m.r. spectroscopy, amines (Aldrich Chem. Co. Ltd.), phosphorus pentachloride, dichloromethane, 1,1,2,2-tetrachloroethane, (B.D.H. Chemical Co. Ltd.), and ammonium sulphate (Hopkins and Williams). Solvents were dried by conventional methods.

All reactions were monitored by using Kieselgel 60F 524 (Silica gel) precoated t.l.c. plates and sprayed with Ninhydrin (0.5 w/v%) in butanol solution, and developed at approximately 130°C. Separation of products were carried out by flash column chromatography[17] using Kieselgel 60. Melting points were determined on a Reichert-Kofler microheating stage and a Mettler FB 82 hot stage connected to a FP 800 Central Processor both fitted with a polarising microscope. ^{1}H n.m.r. spectra were recorded using a JEOL FX 200 spectrometer (operating at 199.5 MHz) and a Varian XL 400 spectrometer (operating at 399.95 MHz—University College, London). Samples were dissolved in $CDCl_3$, CD_2Cl_2 and $(CD_3)_2SO$ and placed in 5 mm n.m.r. tubes. Measurements were carried out using a $CDCl_3$ lock, TMS as internal reference and sample concentrations of 15–20 mg/cm^3.

TABLE III

^{13}C n.m.r. data of derivatives[a]

Compound	δα—C[b]	δβ—C[b]	δγ—C[b]	δδ—C[b]	$^2J(PC)$[c]	$^3J(PC)$	$^4J(PC)$[c]
(3a) $P(NRR')_3$	35.79	17.25				10.60	
$P(O)(NRR')_2$	35.27	17.17				7.80	
(3b) $P(NRR')_3$	43.06	26.03				6.23	
$P(O)(NRR')_2$	43.03	25.94				5.31	
	43.02	25.79				4.73	
(3c) $P(NRR')_3$	50.80	31.86			2.76	4.56	
$P(O)(NRR')_2$	49.98	31.93			1.10	4.57	
(3d) $P(NNR')_3$	142.99	116.76	128.08	118.40		7.32	
$P(O)(NRR')_2$	140.42	117.96	128.66	120.69		7.33	
(3e)[c] $P(NRR')_3$	46.98	26.52			4.30	7.20	
$P(O)(NRR')_2$	46.65	26.44			4.50	7.30	
(3f)[d] $P(NRR')_3$	46.13	26.84	25.32		1.07	6.99	1.07
$P(O)(NRR')_2$	45.97	26.40	24.84		2.68	6.45	1.08
(3g) $P(NRR')_3$	45.46	67.49			0.37	7.56	
$P(O)(NRR')_2$	45.39	66.89			0.73	6.47	
(5b)	43.32	25.71				5.18	
		25.63				6.30	
(5c)	51.06	31.62				5.01	
(5e)	46.26	26.58				8.30	
(5f)	45.73	26.19	24.72		1.47	5.87	
(5g)	45.39	67.47				7.40	

[a] In $CDCl_3$ (Room Temperature) at 50.10 and 100.577 MHz.

[b] In p.p.m.

[c] In Hz.

^{31}P N.m.r. spectra were recorded using a JOEL JNM FX-60 spectrometer (operating at 24.15 MHz), a Varian XL-200 spectrometer (operating at 80.98 MHz—University College, London), a Bruker WH 400 spectrometer (operating at 162.0 MHz—Queen Mary College), and a Varian VXR 400 spectrometer (operating at 162.0 MHz—University College, London), 85% H_3PO_4 was used as an external reference.

The mass spectra were recorded using a VG 7070 H Mass Spectrometer with Finnigan INCOS Data System at University College, London and a VG ZAB IF mass spectrometer at the School of Pharmacy.

Microanalyses were carried out by University College, London microanalytic service.

The starting material, *P*-trichloro-*N*-dichlorophosphorylmonophosphazene, $Cl_2P(O){\cdot}N{=}PCl_3$ (**1**), was prepared by the method of Emsley, Moore and Udy[18] and purified by vacuum distillation. The amino derivatives of (**1**) were synthesized from the reaction of (**1**) and primary and secondary amines. Two experiments are described below; the remainder were carried out in a similar manner. Experimental details are given in Table IV and the analytical data in Table V.

(**a**) *Reaction of* (**1**) *with an excess of isopropylamine in acetonitrile.* Isopropylamine (11.82 g, 220 mmol) in acetonitrile (40 cm^3) was cooled to 0°C and added dropwise to a stirred solution of compound (**1**) (5.4 g, 20 mmol) in acetonitrile (60 cm^3) cooled to ca. −78°C with solid CO_2. The reaction mixture was stirred (2 h) and then boiled under reflux (2.5 h) using a condenser fitted with a $CaCl_2$ drying tube. After the mixture was allowed to come to room temperature, the precipitated isopropylamine hydrochloride was filtered off and the solvent removed under vacuum. The oily residue was examined by t.l.c. using tetrahydrofuran-ethanol (5:1), and four components were detected. Using column chromatography (column length 65 cm, diameter 4 cm, 100 g silica gel for a 3 g mixture), they were separated. The structures of two compounds only (**3b** and **5b**) were deduced by analytical and spectroscopic methods. Both compounds, 1-(di-isopropylaminophosphinyl)-2,2,2-tri-isopropylaminophosphazene (**3b**) (2.3 g) 42.6%, m.p. 134°C and bis(di-isopropylaminophosphinoyl)amine (**5b**) (0.74 g, 13.7%, m.p. 175°C), were crystallised from dichloromethane-benzene (1:1) (see Table IV).

(**b**) *Reaction of* (**1**) *with an excess of t-butylamine in acetonitrile.* Conditions as for (**a**) using 6.67 g (25 mmol) of (**1**) in acetonitrile (65 cm^3) and *t*-butylamine (25 g, 342 mmol), eluent THF/dichlosomethane (3:2). The compounds were eluted in the following order and recrystallised as follows: (**6**), m.p. 172°C (PhH), (3^e, $NRR'{=}NHBu^t$), m.p. 120°C (light petroleum) and (5^e, $NNR'{-}NHBu^t$), m.p. 180°C [CH_2Cl_2/PhH] (1:1)

TABLE IV

Experimental details[a]

Starting Materials						
$Cl_2P(O)—N—PCl_3$(**1**)		Amine		Chromatographic eluent ratios (:)	Product	Yield g (%)
g (mmol)	in MeCN cm^3	g (mmol)	in MeCN (cm^3)			
		Ethylamine				
4.67 (17.5)	70	13.41 (297)	50	Benzene/EtOH (10:3)	(**3a**)	3.14 (58)
					(**5a**)[b]	
		Isopropylamine				
5.40 (20)	60	11.82 (200)	40	THF/EtOH (5:1)	(**3b**)	2.30 (42.6)
					(**5b**)	0.74 (13.7)
		t-butylamine				
6.67 (25)	65	25.00 (342)	45	THF/CH_2Cl_2 (3:2)	(**3c**)	3.50 (52.5)
					(**5c**)	1.90 (25.5)
					(**6**)	1.20 (18.0)
		Aniline				
5.21 (19.5)	65	27.25 (290)	40	THF/CH_2Cl_2 (3:2)	(**3d**)	3.41 (65.5)
		Pyrrolidine				
3.26 (12.2)	60	8.68 (122)	40	THF/CH_2Cl_2 (3:2)	(**3e**)	2.44 (74.8)
					(**5e**)	0.60 (18.4)
		Piperidine				
4.10 (15.4)	70	19.5 (230)	50	Benzene/EtOH (10:3)	(**3f**)	2.00 (48.9)
					(**5f**)	0.70 (17.1)
		Morpholine				
5.25 (19.7)	60	17.16 (197)	40	THF/EtOH (5:1)	(**3g**)	2.24 (42.7)
					(**5g**)	0.85 (16.19)

[a] All reactions were refluxed for 2.5 h in acetonitrile containing an excess of the amine. All products were recrystallised from a mixture of dichloromethane-benzene (1:1).

[b] Not isolated, but detected by ^{31}P n.m.r. spectroscopy in the reaction mixture.

TABLE V

Analytical data

		Found Required			Found (%)				Required (%)			
Compound	Formula	M.p. (°C)	*M*⁺	*M*	C	H	N	P	C	H	N	P
(3a)	$C_{10}H_{30}N_6P_2O$	57	312	312	37.91	9.42	26.21	19.70	38.46	9.68	26.91	19.83
(5a)	$C_8H_{25}N_5P_2O_2$[b]	—	—	—	—	—	—	—	—	—	—	—
(3b)	$C_{15}H_{40}N_6P_2O$	134	382	382	47.16	10.57	22.29	16.34	47.11	10.54	21.97	16.20
(5b)	$C_{12}H_{33}N_5P_2O_2$	175	341	341	42.24	9.51	20.69	18.14	42.22	9.74	20.52	18.15
(3c)	$C_{20}H_{50}N_6P_2O$	120	452	452	53.31	10.63	18.79	13.87	53.07	11.14	18.27	13.69
(5c)	$C_{16}H_{41}N_5P_2O_2$	180	397	397	48.66	10.21	17.94	15.68	48.35	10.40	17.62	15.58
(6)	$C_{32}H_{81}N_{11}P_4O_2$	172	761[c]	775	49.25	9.49	17.62	15.51	49.53	10.52	19.86	15.97
(3d)	$C_{30}H_{30}N_6P_2O$	234	552	552	64.75	5.39	14.29	10.68	65.21	5.47	15.21	11.21
(3e)	$C_{20}H_{40}N_6P_2O$	oil	442	442	53.73	9.02	18.68	13.65	54.28	9.11	18.99	14.00
(5e)	$C_{16}H_{33}N_5P_2O_2$	213	389	389	49.22	8.57	17.84	16.32	49.35	8.54	17.98	15.91
(3f)	$C_{25}H_{50}N_6P_2O$	60	512	512	57.95	9.61	16.06	11.89	58.57	9.83	16.39	12.08
(5f)	$C_{20}H_{40}N_6P_2O_2$	146	445	445	53.87	9.13	15.14	13.18	53.92	9.28	15.72	13.90
(3g)	$C_{20}H_{40}N_6P_2O$	169	522	522	45.41	7.70	15.68	11.80	45.97	7.71	16.08	11.86
(5g)	$C_{16}H_{33}N_5P_2O_6$	189	[d]	453	42.18	7.76	15.40	13.42	42.38	7.34	15.45	13.66

[a] Based on the mass of the most abundant isotope.

[b] Detected by ^{31}P n.m.r. spectroscopy in the reaction mixture.

[c] $(M—CH_3 + H)^+$.

[d] M^+ peak was not observed.

ACKNOWLEDGEMENTS

(A.K.) and (Z.K.) thank the Science Faculties of Inonu University and Ankara University, respectively for study leave. We are indebted to Queen Mary College and Kings College for n.m.r. measurements, and the School of Pharmacy for mass spectrometric data, all these being carried out under the auspices of the University of London Intercollegiate Research Services. We are grateful to Dr. H. G. Parkes and Mr. D. Shipp for n.m.r. measurements.

REFERENCES

1. Part 69. Alkubaisi, Contractor, Parkes, Shaw and Shaw, *Phosphorus, Sulfur, and Silicon*, **56,** 143 (1991).
2. M. Helioui, R. de Jaeger, E. Puskaric and J. Huebel, *Makromol. Chem.*, **183,** 1137 (1982).
3. M. I. Kabatschnik, N. N. Zaslavskaja, V. A. Giljarov, P. V. Petrovskij and V. A. Svoren, *Dokl. Akad. Nauk. S.S.S.R.*, **228,** 849 (1976).
4. L. Riesel, A. Claussnitzer and C. Ruby, *Z. Anorg. Allg. Chem.*, **433,** 200 (1977).
5. I. M. Filatova, E. L. Saizeva, A. P. Simonov and A. J. Jakubovitsch, *Zh. Obshch.*
6. M. I. Kabatschnik, V. A. Giljarov and Chang Cheng-De, *Ixzest. Akad. Nauk S.S.S.R. Ser. Khim.*, 665 (1965).
7. R. A. Shaw, *Pure and Appl. Chem.*, **52,** 1063 (1980).
8. R. A. Shaw, *J. Organomet. Chem.*, **341,** 357 (1988).
9. V. V. Kireev, G. S. Kolesnikov and S. S. Titov, *Zhur. Obshch. Khim.*, **40,** 2015 (1970).
10. A. A. Volodin, S. N. Zelenetskii, V. V. Kireev and V.V. Korshak, *Dokl. Akad. Nauk S.S.S.R. Ser. Khim.*, 1884 (1979).
11. A. A. Khodak, V. A. Gilyarov, I. I. Shcerbina and M. I. Kabachnik, *Izvest. Akad. Nauk S.S.S.R. Ser. Kim.*, 1884 (1979).
12. J. Heubel, A. Mazzah and R. de Jaeger, *Phosphorus Sulfur*, **40,** 53 (1989).
13. G. Bulloch and R. Keat, *Inorg. Chim. Acta*, **33,** 245 (1979).
14. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, *Topics in Phosphorus Chem.*, **5,** 346 (1967).
15. K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, T. S. Cameron, C. Chan, R. A. Shaw and M. Woods, *J. Chem. Soc., Chem. Commun.*, 231 (1980); K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *J. Chem. Soc., Dalton Trans.*, 1549 (1982).
16. K. S. Dathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *Inorg. Nucl. Chem. Lett.*, **15,** 109 (1979); K. S. Dhathathreyan, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *J. Chem. Soc. Dalton Trans.*, 1928 (1981).
17. W. C. Still, M. Kahn and A. Milton, *J. Org. Chem.*, **43,** 2923 (1978).
18. J. Emsley, J. Moore and P. B. Udy, *J. Chem. Soc. A.*, **2863,** (1971).