

The Reaction of *N*-Dichlorophosphoryl-*P*-trichlorophosphazene with Alkyl Grignard Reagents

F. Aslan,¹ A. I. Ozturk,¹ and M. Arslan²

¹Chemistry Department, Harran University, TR-63100 Sanliurfa, Turkey

²Chemistry Department, Firat University, TR-23169 Elazig, Turkey

Received 31 October 2002; revised 16 December 2002

ABSTRACT: The reactions of *N*-dichlorophosphoryl-*P*-trichlorophosphazene $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ (**1**) with benzylmagnesium bromide, 2-phenylethylmagnesium bromide, trimethylsilylmethylmagnesium chloride, *n*-butylmagnesium bromide, cyclohexylmagnesium bromide, cyclopentylmagnesium bromide, *tert*-butylmagnesium bromide, *iso*-propylmagnesium bromide, and ethylmagnesium bromide were studied. Tri- and pentaalkyl phosphazenes were obtained in very poor yield from trimethylsilylmethylmagnesium chloride and cyclohexylmagnesium bromide, respectively. Tri-alkylphosphoryl compounds formed from benzyl-, 2-phenylethyl-, and *n*-butylmagnesium bromide. No phosphorus compound could be isolated from the reaction of **1** with *t*-butyl-, cyclopentyl-, *iso*-propyl-, and ethylmagnesium bromide. © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:413–416, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10153

INTRODUCTION

Since short open-chain phosphazenes are sensitive to air and moisture, only a few of them have been characterized in detail [1–5]. The reactions of $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ (**1**) with amines and alcohols have

been reviewed [6,7]. The structures of **1** [8] and of pentaamino [9,10] and pentaalkoxy derivatives [11–15] have been obtained. The partial aminolysis and alcoholysis of **1** with methylamine and *tert*-butylamine [16], diisopropylamine [17], *o*-dichloro and *o*-dimethylphenol [18], 2,4,6-*tert*-butylphenol and 2,6-di-*tert*-butyl-4-methylphenol [19], and allyl alcohol [20] have been reported. These molecules can be used as structural models for phosphazene polymers with a large range of properties [2,21] and applications [22–29].

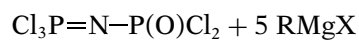
The reactions between halogenophosphazenes and main-group organometallic reagents can be complex [2,30,31]. Several transition-metal-containing cyclic phosphazenes have been synthesized [32]. In the synthesis of alkyl- and aryl-substituted phosphazenes, halophosphazenes are reacted with organolithium or Grignard reagents [33–39]. Although there are many publications about cyclic or polymeric alkyl- or arylphosphazenes [39–46], the synthesis of alkyl-substituted phosphazenes has been performed with only limited success [47–49]. Here we report the reactions of **1** with alkyl Grignard reagents.

RESULTS AND DISCUSSIONS

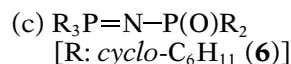
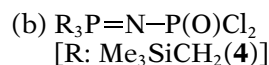
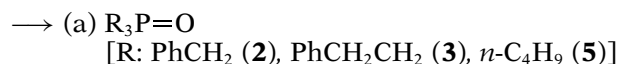
Tri- and pentasubstituted monophosphazenes **4** and **6** were obtained in 4 and 1% yield from the reaction of **1** with trimethylsilylmethylmagnesium chloride (b), and cyclohexylmagnesium bromide (c), respectively. Phosphoryl compounds **2**, **3**, and **5** were

Correspondence to: M. Arslan; e-mail: marslan07@yahoo.com.
Contract grant sponsor: Firat University Research Fund.
Contract grant number: FÜNAF-350.
© 2003 Wiley Periodicals, Inc.

detected from the reaction of **1** with benzyl-, 2-phenyl-ethyl-, and *n*-butylmagnesium bromide (a), respectively.



1



The products were isolated from the reaction mixture by column chromatography. All these compounds have been characterized by elemental analysis (Table 1), ^1H , ^{13}C , ^{31}P NMR, FT-IR, and mass spectrometry. From the analogous reaction of **1** with *tert*-butyl, cyclopentyl, *iso*-propyl, and ethylmagnesium bromide, no phosphorus compound could be isolated.

In the reactions of halophosphazene with organolithium or Grignard reagents, P–N bond cleavage can compete with halogen replacement [50]. The phosphoryl compounds **2**, **3**, and **5** also result only from a P–N bond cleavage.

The P=N and P=O stretching vibrations, 1220–1338 cm^{-1} and 1153–1263 cm^{-1} respectively (Table 2), are characteristic of phosphazenes. In the order of **1**, **4**, **6**, they are shifted to longer wavelengths.

The NMR data are presented in Tables 3–5. While both phosphorus signals for **1** are observed at high field, they move to lower field on alkyl substitution in **4** and **6** (Table 3). The ^{13}C NMR signals of the carbon atoms attached directly to phosphorus atoms

TABLE 1 MS and Analytical Data of 2–6

	Mol. Weight ^a			%	
	Calcd	Found		Calcd	Found
2	320	320	C	76.76	76.0
		91 (C_7H_7^+)	H	6.44	6.08
			N	—	—
3	362	No M^+	C	79.55	78.51
		91 (C_7H_7^+),	H	7.46	7.39
		105 (C_8H_9^+)	N	—	—
4	423	423	C	33.37	33.56
		73 (SiC_3H_9^+)	H	7.84	7.54
			N	3.30	3.18
5	218	218			
6	507	—			

^aMolecular ion and only the first one or two peaks of MS in the relative abundance order are shown.

TABLE 2 Characteristic IR Vibrations of 1–6 (cm^{-1})

	$\nu_{\text{C-H ar.}}$	$\nu_{\text{C-H al.}}$	$\nu_{\text{P=N}}$	$\nu_{\text{P=O}}$	$\nu_{\text{P-N}}$	$\nu_{\text{P-Cl}}$
1	—	—	1338	1263	770	650
2	3050	2900	—	1187	—	—
3	3050	2900	—	1153	—	—
4	—	2900–2800	1319	1251	761	536
5	—	2950–2850	—	1160	—	—
6	—	2930–2852	1220	1170	750	—

are generally observed at the lowest field and they show the largest J_{PC} values. In compound **6**, the POR_2 and PNR_3 environments can be distinguished, especially, C_i in PNR_3 are shielded more than in POR_2 (Table 5).

The electron impact MS spectra of **2** showed the well-defined molecular ion at m/z 320 (25%). The molecular ion peak of **3** was not observed, but the peaks at m/z values of 91 and 105 correspond to the loss of C_7H_7 and C_8H_9 groups. The peak at m/z 423 (10%) with the expected isotope pattern shows the molecular ion for **4**.

EXPERIMENTAL

General Remarks

Solvents were dried by conventional methods. All reactions were monitored by using Kieselgel 60 F254 (silica gel) precoated TLC plates and the separating conditions were determined. The separation of products was carried out by flash column chromatography using Kieselgel 60 (60–230 mesh).

IR spectra were recorded with an ATI Unicam Mattson 1000 FTIR spectrophotometer. ^1H , ^{13}C , and ^{31}P NMR spectra were recorded using a Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, 100.63, and 161.98 MHz, respectively. All data were recorded for solutions in CDCl_3 . The ^1H and ^{13}C chemical shifts were measured using SiMe_4 as an internal standard, and the ^{31}P chemical shifts were measured using 85% H_3PO_4

TABLE 3 ^{31}P NMR Data of 1–6

	δ_{PN}	δ_{PO}	J_{PNP}
1	–2.6	–10.6	21.3
2	—	41.8	—
3	—	47.2	—
4	33.5	–6.3	3.4
5	—	50.3	—
6	59.9	52.3	^a

^aNot determined.

TABLE 4 ^1H NMR Data of 2–6 (Coupling Constants J in Hz)

2	3.1 (CH_2 , $^2J_{\text{PH}}$: 13.8, 2H), 7.3–7.4 (5H)
3	2.1 (2-H, 2H), 2.9 (1-H, 2H), 7.2–7.3 (5H)
4	0.3 (CH_3 , 9H), 1.4 (CH_2 , $^2J_{\text{PH}}$: 16.2, 2H)
5	0.6 (4-H, 3H), 1.1 (3-H, 2H), 1.2 (2-H, 2H), 1.4 (1-H, 2H)
6	1.0–2.0 (20H), 3.9 (OPCH, 1H), 4.1 (NPCH, 1H)

as an external standard. Chemical shifts downfield from the standard are assigned positive δ values. Electron impact mass spectra were obtained by Micromass UK Platform-II spectrometer. Microanalysis was carried out by LECO 932 CHNS-O apparatus. The starting material **1** was prepared by the method of Emsley, Moore, and Udy and purified by vacuum distillation [51].

Reaction between **1** and Benzylmagnesium Bromide

Benzylmagnesium bromide (17 ml, 2 M in THF) was added dropwise to **1** (1.80 g, 7 mmol) in 150 ml of toluene by stirring for 0.5 h at ambient temperature. The mixture was then refluxed for 48 h. After the reaction was complete, the precipitated salt (MgBr_2) was filtered off and the solvent was removed under vacuum. The residue was examined by TLC using chloroform/acetone (3:1), $R_f = 0.66$, and separated by column chromatography. After the solvent was removed, a white solid (compound **2**) was obtained in 7% yield, m.p. 208°C.

Reaction between **1** and 2-Phenylethylmagnesium Bromide

2-Phenylethylmagnesium bromide (40 ml, 1 M in THF) and **1** (2.15 g, 8 mmol, in 150 ml of toluene) were used for the reaction as for **2**. The

TABLE 5 ^{13}C NMR Data of 2–6 (Coupling Constants J in Hz)

2	35.9 (CH_2 , $^1J_{\text{PC}} = 61.4$), 127.4 (C_p , $^5J_{\text{PC}} = 2.5$), 129.2 (C_m , $^4J_{\text{PC}} = 1.9$), 130.3 (C_o , $^3J_{\text{PC}} = 5.0$), 132.2 (C_i , $^2J_{\text{PC}} = 6.7$)
3	28.2 (2- CH_2 , $^2J_{\text{PC}} = 3.0$), 30.6 (1- CH_2 , $^1J_{\text{PC}} = 62.5$), 126.9 (C_p), 128.5 (C_m), 129.2 (C_o), 141.3 (C_i)
4	0.9 (CH_3 , $^3J_{\text{PC}} = 3.1$), 21.7 (CH_2 , $^1J_{\text{PC}} = 56.9$)
5	13.9 (CH_3), 24.0 (3- CH_2 , $^3J_{\text{PC}} = 3.8$), 24.5 (2- CH_2 , $^2J_{\text{PC}} = 14.4$), 28.0 (1- CH_2 , $^1J_{\text{PC}} = 65.1$)
6	Phosphinyl part: 25.2 (C_m , $^3J_{\text{PC}} = 2.7$), 26.3 (C_p), 26.6 (C_o), 36.0 (C_i , $^1J_{\text{PC}} = 7.4$) Phosphazene part: 26.4 (C_p), 26.6 (C_m , $^3J_{\text{PC}} = 2.6$), 27.2 (C_o , $^2J_{\text{PC}} = 11.6$), 35.2 (C_i , $^1J_{\text{PC}} = 22.8$)

residue was chromatographed ($R_f = 0.52$, chloroform/acetone 1:1). The white solid (compound **3**) was obtained in 7% yield, m.p. 154°C.

Reaction between **1** and Trimethylsilylmethylmagnesium Chloride

Trimethylsilylmethylmagnesium chloride (34 ml, 1 M in ether) and **1** (1.80 g, 7 mmol, in 150 ml of toluene) were used for the reaction as for **2**. The mixture was refluxed for 24 h, however. The residue was chromatographed ($R_f = 0.39$, chloroform). The white solid (compound **4**) was obtained in 4% yield, m.p. 109°C.

Reaction between **1** and *n*-Butylmagnesium Bromide

n-Butylmagnesium bromide (24 ml, 2 M in ether) and **1** (2.50 g, 9 mmol, in 150 ml of toluene) were used for the reaction as for **2**. The residue was chromatographed ($R_f = 0.39$, chloroform). The viscous compound (**5**) was obtained in 1% yield.

Reaction between **1** and Cyclohexylmagnesium Bromide

Cyclohexylmagnesium bromide (48 ml, 1 M in ether) and **1** (2.50 g, 9 mmol, in 150 ml of toluene) were used for the reaction as for **2**. The residue was chromatographed ($R_f = 0.53$, chloroform/acetone 1:1). The viscous compound (**6**) was obtained in 1% yield.

CONCLUSION

Tri- and pentasubstituted monophosphazenes were isolated from the reaction between *N*-dichlorophosphoryl-*P*-trichloromonophosphazene and trimethylsilylmethylmagnesium chloride, and cyclohexylmagnesium bromide, respectively. Phosphoryl compounds formed due to a P–N bond cleavage with benzyl-, 2-phenylethyl-, and *n*-butylmagnesium bromide. No phosphorus compound could be isolated with *tert*-butyl-, cyclopentyl-, *iso*-propyl- and ethylmagnesium bromide.

REFERENCES

- [1] Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972.
- [2] Evans, T. L.; Allcock, H. R. *J Macromol Sci Chem A* 1981, 16, 409.
- [3] Maracek, A. *Collect Czech Chem Commun* 1990, 55, 2453.
- [4] Kireev, V. V.; Kolesnikov, G. S.; Titov, S. S. *Zh Obshch Khim* 1970, 40, 2015.

- [5] Xu, K.; Angell, C. A. *Inorg Chim Acta* 2000, 298, 16.
- [6] Shaw, R. A. *Pure Appl Chem* 1980, 52, 1063.
- [7] Shaw, R. A. *J Organomet Chem* 1988, 341, 357.
- [8] Belaj, F. *Acta Crystallogr B* 1993, 49, 254.
- [9] Allcock, H. R.; Tollefson, N. M.; Arcus, R. A.; Whittle, R. R. *J Am Chem Soc* 1985, 107, 5166.
- [10] Kılıç, A.; Kılıç, Z.; Shaw, R. A. *Phosphorus, Sulfur and Silicon* 1991, 56, 157.
- [11] Khodak, A. A.; Gilyarov, V. A.; Shcherbina, T. M.; Kabachnik, M. I. *Izv Akad Nauk SSSR Ser Khim* 1979, 1884.
- [12] Allcock, H. R.; Ngo, D. C.; Parvez, M.; Whittle, R. R.; Birdsall, W. J. *J Am Chem Soc* 1991, 113, 2628.
- [13] Hökelek, T.; Akduran, N.; Begeç, S.; Kılıç, A.; Kılıç, Z. *Acta Crystallogr C* 2000, 56, 1404.
- [14] Öztürk, A. I. Master's thesis, Firat University, Elazığ, Turkey, 1995.
- [15] Çil, E.; Arslan, M.; Aslan, F.; Öztürk, A. I. *Phosphorus Sulfur Silicon* 2003, 178, 1–10 (in press).
- [16] Bullock, C.; Keat, R. *Inorg Chim Acta* 1979, 33, 245.
- [17] Kılıç, Z.; Gündüz, N.; Yıldız, M.; Kılıç, A.; Mor, S.; Ercan, F.; Hökelek, T.; Ülkü, D. *Heteroat Chem* 1994, 5, 349.
- [18] Allcock, H. R.; Ngo, D. C.; Parvez, M.; Visscher, K. J. *Chem Soc, Dalton Trans* 1992, 1687.
- [19] Kılıç, A.; Begeç, S.; Kılıç, Z.; Hökelek, T. *J Mol Struct* 2000, 516, 255.
- [20] Heubel, J.; Mazzah, A.; de Jaeger, R. *Phosphorus Sulfur Silicon* 1989, 40, 53.
- [21] Kartikeyan, S.; Neilson, R. H. *Inorg Chem* 1999, 38, 2079.
- [22] Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Olshavsky, M. A. *Inorg Chem* 1999, 38, 280.
- [23] Reed, C. S.; Taylor, J. P.; Guigley, U. S.; Coleman, M. M.; Allcock, H. R. *Polym Eng Sci* 2000, 40(2), 465.
- [24] Prange, R.; Allcock, H. R. *Macromolecules* 1999, 32, 6390.
- [25] Allcock, H. R.; Ravikiran, R.; O'Connor, S. J. M. *Macromolecules* 1997, 30, 3184.
- [26] Allcock, H. R.; Prange, R. *Macromolecules* 2001, 34, 6858.
- [27] Allcock, H. R.; Prange, R.; Hartle, T. J. *Macromolecules* 2001, 34, 5463.
- [28] Allcock, H. R.; Laredo, W. R.; de Denu, C. R.; Taylor, J. P. *Macromolecules* 1999, 32, 7719.
- [29] Förster, S.; Kramer, E. *Macromolecules* 1999, 32, 2783.
- [30] Harris, P. J.; Desorcie, J. L.; Allcock, H. R. *J Chem Soc, Chem Commun* 1981, 852.
- [31] Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* 1987, 6(2), 119.
- [32] Allcock, H. R.; Desorcie, J. L.; Wagner, L. J. *Inorg Chem* 1985, 24, 333.
- [33] Shaw, R. A.; Fitzsimmons, B. W.; Smith, B. C. *Chem Rev* 1962, 62, 207.
- [34] Allcock, H. R.; Patterson, D. B.; Evans, T. L. *J Am Chem Soc* 1977, 99, 6095.
- [35] Allcock, H. R.; Chu, C. T.-W. *Macromolecules* 1979, 12, 551.
- [36] Paddock, N. L.; Ranganathan, T. N.; Todd, S. M. *Can J Chem* 1971, 49, 164.
- [37] Biddlestone, M.; Shaw, R. A. *Phosphorus Relat Group V Elem* 1973, 3, 95.
- [38] Allen, C. W. *J Chem Soc, Chem Commun* 1970, 152.
- [39] Harris, P. J.; Williams, K. B.; Fisher, B. L. *J Org Chem* 1984, 49, 406.
- [40] Evans, T. L.; Allcock, H. R. *J Macromol Sci Chem A* 1981, 6, 409.
- [41] Harris, P. J.; Schwalke, M. A.; Liu, V.; Fisher, B. L. *Inorg Chem* 1983, 22, 1812.
- [42] Allcock, H. R.; Coggio, W. D. *Macromolecules* 1993, 26, 764.
- [43] Allen, C. W.; Moeller, T. *Inorg Chem* 1968, 7(11), 2177.
- [44] Harris, P. J.; Fadeley, C. L. *Inorg Chem* 1982, 22(3), 561.
- [45] Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J Am Chem Soc* 1981, 103(9), 2256.
- [46] Allcock, H. R.; Harris, P. J. *J Am Chem Soc* 1979, 101(21), 6221.
- [47] Vand, A. F.; Moeller, T. *Chem Ind* 1962, 221.
- [48] Moeller, T.; Vand, A. *J Am Chem Soc* 1962, 3511.
- [49] Arslan, M.; Aslan, F.; Ozturk, A. I. *Heteroat Chem* 2003, 14(2), 138.
- [50] Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg Chem* 1981, 20, 11.
- [51] Emsley, J.; Moore, J.; Udy, P. B. *J Chem Soc A* 1971, 2863.