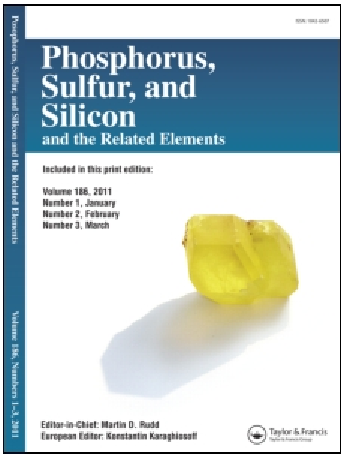
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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 60.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE AND OCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH GLYCEROL

Homaid A. Al-madfa[a]; Robert A. Shaw[a]
[a] Department of Chemistry, Birkbeck College (University of London), London, U.K.

To cite this Article Al-madfa, Homaid A. and Shaw, Robert A.(1989) 'PHOSPHORUS-NITROGEN COMPOUNDS. PART 60.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE AND OCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH GLYCEROL', Phosphorus, Sulfur, and Silicon and the Related Elements, 45: 1, 1 — 6

To link to this Article: DOI: 10.1080/10426508908046069

URL: http://dx.doi.org/10.1080/10426508908046069

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1989, Vol. 45, pp. 1–6
Reprints available directly from the publisher
Photocopying permitted by license only

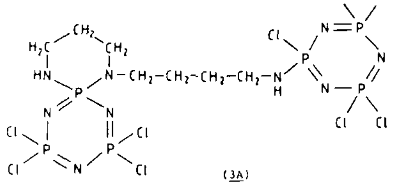
PHOSPHORUS-NITROGEN COMPOUNDS. PART 60.[1] THE REACTIONS OF HEXACHLOROCYCLOTRIPHOSPHAZATRIENE AND OCTACHLOROCYCLOTETRAPHOSPHAZATETRAENE WITH GLYCEROL.†

HOMAID A. AL-MADFA and ROBERT A. SHAW*
Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX, U.K.

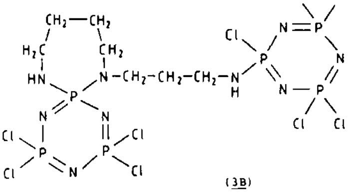
(Received October 17, 1988; in final form November 28, 1988)

The reactions of hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazatetraene with glycerol give rise to spiro-bridged derivatives, $N_3P_3Cl_4[OCH_2CHO(CH_2O)]N_3P_3Cl_5$ and $N_4P_4Cl_6[OCH_2CHO(CH_2O)]N_4P_4Cl_7$, as well as a spiro-monodentate derivative, $N_3P_3Cl_4$-$[OCH_2CHO(CH_2OH)]$. N.m.r. investigations of these products are reported.

The reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, (**1**), with monofunctional reagents, have received a great deal of attention.[2] Those of octachlorocyclotetraphosphazatetraene, $N_4P_4Cl_8$, (**2**), have also attracted interest.[3] The reactions of difunctional reagents, mainly with compound (**1**) or its derivatives, have recently come to the fore.[4–6] Only one study, that by Labarre's group in Toulouse, has been devoted to a trifunctional reagent. This is the reaction of compound (**1**) with a triamine, spermidine, $H_2N(CH_2)_3$-$NH(CH_2)_4NH_2$.[7,8] Only one product (**3**), was reported from this reaction[7] and this was shown by X-ray crystallography to have a six-membered spiro ring (**3A**), involving one N_3P_3 moiety and a bridge to a second such unit.[8] No evidence was found for the isomeric product (**3B**) containing a seven-membered spiro ring, or for monodentates based on (**3A**) or (**3B**). Both, six-membered and seven-membered spiro rings, are well documented in phosphazene chemistry.[9–11]



(3A)



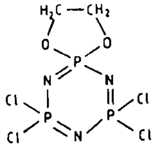
(3B)

---

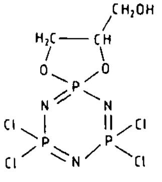
† Presented in part at the 4th International Symposium on Inorganic Ring Systems, Université Paris-Sud, France, September 1985.

RESULTS AND DISCUSSION

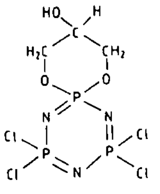
From the reaction of the hexachloride (**1**) with glycerol we isolated an oily and a crystalline product. The former was shown, by HPLC, to contain small amounts of the known five-membered spiro derivative, based on ethylene glycol, $N_3P_3[O(CH_2)_2O]Cl_4$, (**4**).[6,11] Analytical data of the major product from the oily fraction indicated a composition corresponding to $N_3P_3Cl_4(O_2C_3H_6)$. The mass spectrum showed a parent ion peak at 348. It had an isotope pattern characteristic of four chlorine atoms. Hydroxy compounds are known to lose water (−18) and to pick up a proton (+1) under mass spectrometric conditions.[12,13] Adding 17 to 348 gives 365, which corresponds to $N_3P_3^{35}Cl_4(O_2C_3H_6)$. Two isomeric structures (**5A** and **B**) would be in keeping with this.



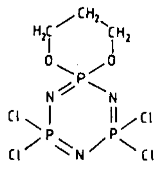
(4)



(5A)



(5B)



(6)

The ^{31}P n.m.r. spectrum of compound (**5**) [δ Pspiro 24.7, δ PCl_2 26.2 p.p.m., $^{2}J(\underline{PP})$ 64.7 Hz) (Figure 1) was closely similar to that of the five-membered spiro derivative (**4**)[6] [δ Pspiro 24.4, δ PCl_2 26.15 p.p.m., $^{2}J(\underline{PP})$ 67.4 Hz] and very different from that of its six-membered analogue (**6**).[6] Clearly, by analogy the oily derivative must be assigned the five-membered spiro structure (**5A**). The chemical shift values of the Pspiro and PCl_2 nuclei and the proximity of their

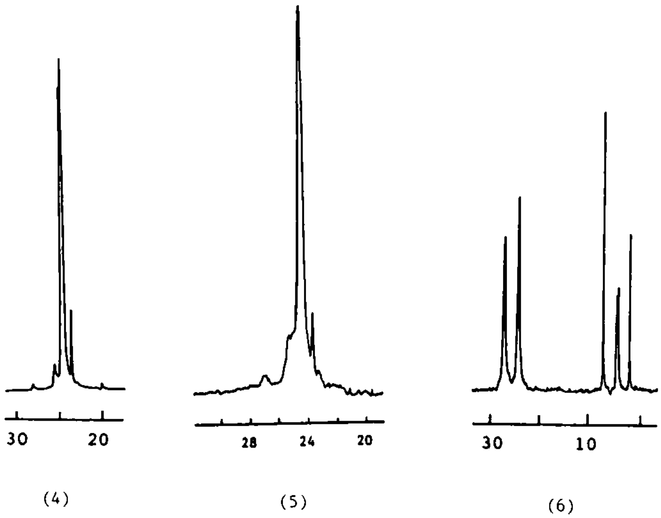
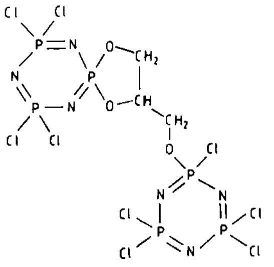
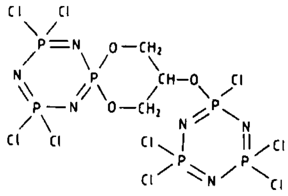


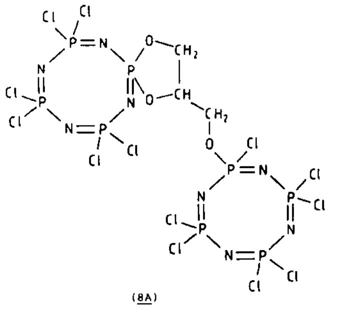
FIGURE 1 $^{31}P\{^{1}H\}$ n.m.r. spectra of compounds (**4**), (**5**), and (**6**) ($CDCl_3$ solution, room temperature at 24.15 MHz).

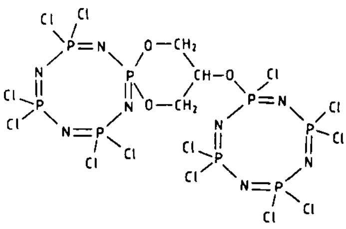
chemical shifts point decisively to a five-membered spiro moiety.[6] A relationship between ^{31}P chemical shift and OPO bond angles (and hence ring size) in PN_2O_2 tetrahedra has been demonstrated.[11] In studies of the reaction between benzaldehyde and glycerol the product based on a five-membered ring (oily) predominated over that with a six-membered ring (crystalline).[14]

The crystalline product (**7**) had a composition corresponding to $N_6P_6(O_2C_3H_5)Cl_9$ and its mass spectrum confirmed this (parent ion at 674). Two isomeric structures (**7A** and **7B**) would fit the above. The ^{31}P n.m.r. spectrum of compound (**7**) [δ Pspiro 24.2, δ PCl_2 26.25 p.p.m., $^2J(PP)$ 66.1 Hz (spiro moiety), δ PCl(OR) 16.8, δ PCl_2 23.5 p.p.m., $^2J(PP)$ 65.2 Hz (bridged moiety)] resembles closely the superposition of that of the oily product (**5A**) (and also of that of compound **4**) and that of the monoethoxy derivative, $N_3P_3Cl_5(OEt)$.[15] This strongly suggests that this derivative too is based on a five-membered spiro ring and this was confirmed by X-ray crystallography.[16] Thus the crystalline compound has the structure (**7A**) and like the oily derivative is based on a five-membered spiro ring. From the reaction of the octachloride, (**2**) with glycerol we isolated only one compound, a crystalline one (**8**). Its elemental analysis corresponded to $N_8P_8Cl_{13}O_2C_3H_5$ and its mass spectrum (which showed the presence of 13 chlorine atoms) confirmed this. Again we must consider for this spiro-bridged derivative two isomeric structures (**8A** and **8B**).


(7A)

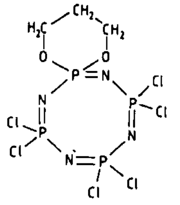

(7B)


(8A)


(8B)

The ^{31}P spectrum is complex [δ Pspiro, 7.8, δ $PCl_2(2)$ −2.8, δ $PCl_2(1)$ −4.7 p.p.m., $^2J(Pspiro\text{-}PCl_2)$ 58.7, $^2J(PCl_2-PCl_2)$ 28.2 Hz (spiro moiety), δ PCl(OR) −6.4, δ $PCl_2(2)$ −3.9, δ $PCl_2(1)$ −5.9 p.p.m., $^2J[PCl(OR)-PCl_2]$ 31.2, $^2J(PCl_2-PCl_2)$ 52.1 Hz (bridged moiety)], but indicates six groups of absorption signals. One would expect two independent patterns of the AB_2C or

AB_2X type. The proton coupled spectrum reveals an additional quarted fine structure at δ 7.8 and an additional triplet fine structure at δ −6.4. Thus the former can be assigned to the Pspiro group, the latter to the P(OR)Cl moiety. There appears to be no data available on five-membered spiro derivatives of compound (**2**) e.g. $N_4P_4Cl_6(O(CH_2)_2O]$. However, the six-membered analogue, $N_4P_4Cl_6[O(CH_2)_3O]$, (**9**) has its Pspiro absorption at δ −10.5.[17] In the cyclotriphosphazatriene series the Pspiro absorption for the five- and six-membered groupings occur at δ 24.5 and 3.4 respectively. The former thus absorbs 21.1 p.p.m. downfield from the latter. In the cyclotetraphosphazatetraene group, compound (**8**) has its Pspiro absorption 18.3 p.p.m. downfield from compound (**9**). Clearly the former has the structure (**8A**). The absence of a monodentate derivative, under our experimental conditions, is presumably related to the greater reactivity of the tetramer towards nucleophilic attack compared to that of the trimer.



(9)

Comparing the reactions of our tri-ol, glycerol, with that of the tri-amine, spermidine, we make the following observations. (i) In reactions with the hexachloride (**1**), we were able to observe and isolate a monodentate derivative (**5A**) with the tri-ol, none was reported for the triamine, presumably due to the greater reactivity of the latter. (ii) Having the choice between a five- and a six-membered spiro ring, the tri-ol prefers the former. By contrast, the triamine favours the six- over the seven-membered spiro moiety. Monodentate derivatives of bifunctional reagents have been previously reported.[18,19]

EXPERIMENTAL

The starting materials (**1**) and (**2**) were obtained as gifts from Shin Nisso Kako Co Ltd. All solvents used throughout this work were obtained from May and Baker Ltd. Glycerol and deuteriated solvent ($CDCl_3$) used for n.m.r. spectroscopy were obtained from Aldrich Chem. Co. Ltd. Pyridine, silica gel 60 for column chromatography and silica gel 60 254 tlc plates, with layer thickness of 0.25 mm, were obtained from BDH Chem. Co. Ltd. All reactions were monitored by using silica gel 60 precoated tlc plates and developed with ninhydrin (0.5% w/v) in butanol solution. To separate the products column chromatography was used (packed with silica gel mixed with a suitable solvent). The amount of silica gel used depended on the particular separation being carried out. However, 50 g of silica gel were normally used for each gram of the mixture to be separated. Melting points were measured on a Reichert–Kofler micro heating stage fitted with a polarising microscope.

Mass spectra (electron impact) were recorded on a VG 7070H mass spectrometer with Finnigan INCOS data system (University College, London) and VM 7070 and VG ZAB 1 F double focussing mass spectrometer with UV chart recorder system (The School of Pharmacy, London). ^1H n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 199.5 MHz), a Bruker

WH 250 spectrometer (operating at 250.48 MHz, Kings College, London) and a Varian XL 400 spectrometer (operating at 399.95 MHz, University College, London). Samples were dissolved in $CDCl_3$ 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. ^{31}P n.m.r. spectra were recorded using a JEOL JNM FX-60 spectrometer (operating at 24.15 MHz), Varian XL-200 spectrometer (operating at 80.98 MHz, University College, London) and a Varian XL 400 spectrometer (operating at 162.0 MHz, University College, London) with 85% H_3PO_4 used as external reference. Carbon-13 n.m.r. spectra were recorded using a JEOL FX-200 spectrometer (operating at 50.10 MHz), and a Bruker WH 400 spectrometer (operating at 100.62 MHz, Queen Mary College, London) and a Varian VXR 400 spectrometer (operating at 100.577 MHz, University College, London), TMS was used as an internal reference.

The reaction of (**1**) *with glycerol.* Pyridine (4.1 g, 51.90 mmol) was added dropwise to (**1**) (9 g, 25.86 mmol) in dichloromethane (200 cm^3). To this solution glycerol (2.4 g, 26.09 mmol) was added dropwise. The mixture was left to stir approx. 24 h at room temperature. It was then examined by tlc; three components were observed. The solvent was removed *in vacuo*. The residue was then applied to a chromatographic column.

The column was first eluted with a mixture of CH_2Cl_2/n-hexane (7:3), which eluted first, starting material, (**1**), (30%). Following this, an oily fraction was obtained, which was characterised by mass spectrometry and n.m.r. spectroscopy as the monodentate derivative (**5A**), yield 0.36 g (4%). The eluent was then changed to diethyl ether and this eluted the third component. This was recrystallised from benzene to give (**7A**), m.p. 96°C, yield 0.8 g (9%). [Found: C, 5.3; H, 0.8; N, 12.4%; $\underline{M}^+$ 674. $C_3H_5O_3N_6P_6Cl_9$ requires C, 5.3; H, 0.7; N, 12.4%; $\underline{M}$ (for $C_3H_5O_3N_6P_6{}^{35}Cl_9$) 674]. By using hplc (25 cm × 11 mm ID column system using S-20 m silica gel, 25% ethyl acetate in petroleum spirit as the mobile phase and a flow rate of 5.0 cm^3/min) compound (**4**). [Found: C, 7.1; H, 1.2; N, 12.5%; $\underline{M}^+$ 335. Calc. for $C_2H_4O_2N_3P_3Cl_4$ C, 7.1; H, 1.2; N, 12.5%, $\underline{M}$ (for $C_2H_4O_2N_3P_3{}^{35}Cl_4$) 335] was isolated in small yield from the oily fraction, which contained mainly the monodentate (**5A**). Ethylene glycol could not be detected in the original glycerol by mass spectrometry.

The reaction of (**2**) *with glycerol.* Compound (**2**) (5 g, 10.78 mmol) was dissolved in dioxane (200 cm^3). Pyridine (6.95 g, 87.97 mmol) was added dropwise. Then glycerol (8.1 g, 88.04 mmol) was added dropwise. The mixture was allowed to stir at room temperature for 24 h. Some insoluble residue resulted. The solution was filtered and the solvent removed on a rotary evaporator. Tlc of the residue showed the presence of starting material, (**2**), and one other compound. The residue was dissolved in dichloromethane and placed on a chromatographic column. Elution with dichloromethane/n-hexane (7:3) gave first starting material, (**2**), 40%, followed by the tetramer bridge compound (**8A**), recrystallised from benzene, m.p. 195°C, yield 0.75 g (15%). [Found: C, 3.9; H, 0.6; N, 12.5%; $\underline{M}^+$ 903.4339. $C_3H_5O_3N_8P_8Cl_{13}$ requires C, 4.0; H, 0.6; N, 12.4%; $\underline{M}$ (for $C_3H_5O_3N_8P_8{}^{35}Cl_{13}$) 903.4337].

ACKNOWLEDGEMENTS

One of us (H.A A.-M.) is indebted to the University of Qatar for a post-graduate studentship. We thank the Shin Nasso Kako Co Ltd for gifts of $N_3P_3Cl_6$ and $N_4P_4Cl_8$. 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 Mr H. G. Parkes and Mr D. Shipp for obtaining the n.m.r. data.

REFERENCES

1. Part 59. W. F. Deutsch, H. G. Parkes, and R. A. Shaw, *Magn. Reson. Chem.*, 1989, in the press.
2. For summaries see R. A. Shaw, *Z. Naturforsch.*, 1976, **31b**, 641; H. R. Allcock, Phosphorus-Nitrogen Compounds, Academic Press, New York, 1972; S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 41.
3. K. C. Kumara Swamy, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods. *Ind. J. Chem.* (*A*), 1986, **25**, 1004 and references therein.
4. A. H. Alkubaisi, W. F. Deutsch, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen), and R. A. Shaw, *Phosphorus Sulfur*, 1986, **28**, 229.

5. W. F. Deutsch and R. A. Shaw, *J. Chem. Soc., Dalton Trans.*, 1988, 1757.
6. A. H. Alkubaisi, H. G. Parkes, and R. A. Shaw, *Heterocycles*, 1989, in the press.
7. J.-F. Labarre, G. Guerch, F. Sournies, R. Lahana, R. Enjalbert and J. Galy, *J. Mol. Struct.*, 1984, **116,** 75.
8. G. Guerch, J.-F. Labarre, R. Lahana, F. Sournies, R. Enjalbert, J. Galy, and J. P. Declercq, *Inorg. Chim. Acta*, 1984, **83,** L33.
9. G. Guerch, M. Graffeuil, J.-F. Labarre, R. Enjalbert, R. Lahana, and F. Sournies, *J. Mol. Struct.*, 1982, **95,** 237.
10. G. Guerch, J.-F. Labarre, R. Rocques, and F. Sournies, *J. Mol. Struct.*, 1983, **96,** 113.
11. S. R. Contractor, M. B. Hursthouse, L. S. Shaw (née Gözen), R. A. Shaw, and H. Yilmaz, *Acta Crystallogr.*, Section B, 1985, **41,** 122.
12. D. H. Williams and I. Howe, Principles of Organic Mass Spectrometry, McGraw-Hill, London, 1972, p. 116.
13. F. W. McLafferty, Interpretation of Mass Spectra, 3rd Edn., University Science Books, Mill Valley, California, 1980, p. 166.
14. H. S. Hill, M. S. Whelen, and H. Hibbert, *J. Amer. Chem. Soc.*, 1928, **50,** 2235.
15. F. Heatley and S. M. Todd, *J. Chem. Soc.* (*A*), 1966, 1152.
16. H. A. Al-Madfa, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen), and R. A. Shaw, *Phosphorus Sulfur*, 1986, **28,** 203.
17. A. H. Alkubaisi, personal communication.
18. V. Chandrasekhar, S. S. Krishnamurthy, R. A. Shaw, A. R. Vasudeva Murthy and M. Woods, *Inorg. Nucl. Chem. Letters*, 1981, **17,** 181.
19. P. J. Harris and K. B. Williams, *Inorg. Chem.*, 1984, **23,** 1496.