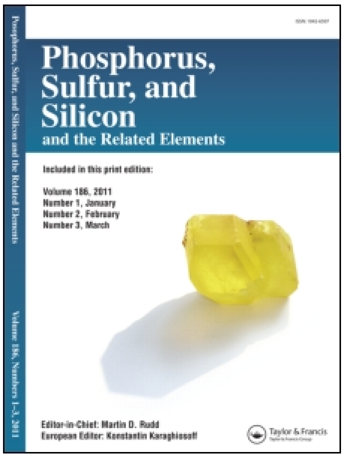


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Reaction of $N_4P_4Cl_8$ with Dibenzylamine: Formation of an Unusual Bicyclic Phosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$, by Dealkylation

P. M. Sundaram[a]; S. S. Krishnamurthy[a]; A. R. Vasudeva Murthy[a]; Robert A. Shaw[b]; Michael Woods[b]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India [b] Department of Chemistry, Birkbeck College (University of London), London, U.K.

To cite this Article Sundaram, P. M. , Krishnamurthy, S. S. , Murthy, A. R. Vasudeva , Shaw, Robert A. and Woods, Michael(1980) 'The Reaction of $N_4P_4Cl_8$ with Dibenzylamine: Formation of an Unusual Bicyclic Phosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$, by Dealkylation', Phosphorus, Sulfur, and Silicon and the Related Elements, 8: 3, 373 — 374
To link to this Article: DOI: 10.1080/03086648008078218
URL: http://dx.doi.org/10.1080/03086648008078218

Phosphorus and Sulfur, 1980, Vol. 8, pp. 373–374
0308-664X/80/0803–0373$04.50/0

SHORT COMMUNICATION

The Reaction of $N_4P_4Cl_8$ with Dibenzylamine: Formation of an Unusual Bicyclic Phosphazene, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$, by Dealkylation

P. M. SUNDARAM, S. S. KRISHNAMURTHY, and A. R. VASUDEVA MURTHY

*Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560012, India.*

and

ROBERT A. SHAW and MICHAEL WOODS

Department of Chemistry, Birkbeck College (University of London), London, WC1E 7HX, U.K.

(*Received November 24, 1979*)

The reactions of halogenocyclotetraphosphazatetraenes $N_4P_4X_8$, with nucleophiles have received little attention and only the reactions of the octachloride, $N_4P_4Cl_8$, with amines have been investigated in any detail.[1] Millington and Sowerby[2] studied the reaction of $N_4P_4Cl_8$ with dimethylamine and isolated the derivatives, $N_4P_4Cl_{8-n}(NMe_2)_n$, $n = 2, 3, 4, 5, 6, 8$; several *N*-methylanilino derivatives,

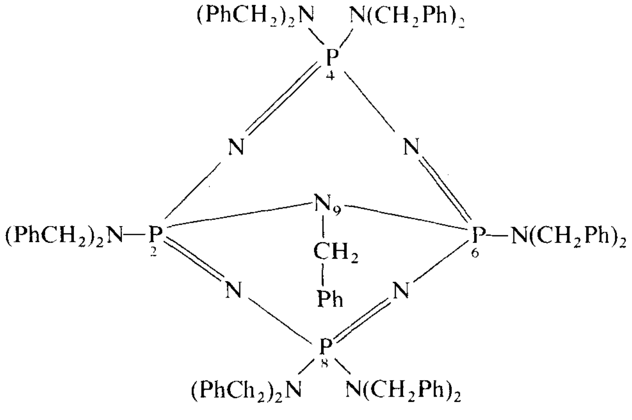
$N_4P_4Cl_{8-n}(NMePh)_n$,

$n = 1, 2, 3, 4, 6$, have been reported recently.[3] Numerous isomeric products were obtained in these reactions involving secondary amines; the replacement pattern is predominantly non-geminal in both cases.[2,3] We now report our preliminary findings on a reaction of $N_4P_4Cl_8$ with a secondary amine that gives rise to a bicyclic phosphazene.

The octachloride, $N_4P_4Cl_8$, reacts with dibenzylamine in boiling methyl cyanide to give a mixture of chloro(dibenzylamino) derivatives, $N_4P_4Cl_{8-n}[N(CH_2Ph)_2]_n$, $n = 1$–4 (yields 5–40% after column chromatography), and a small quantity of the compound,

$N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$

(**1**), mp 254°C (yield 3.5%) [m/e$^+$(obs) = 1460.635; $C_{91}H_{90}N_{11}P_4$ requires m/e$^+$ = 1460.633]. The 270 MHz ^{1}H nmr spectrum of compound (**1**) suggests that it has a bicyclic structure: a triplet (δ 4.57: N(9)C*H*$_2$) and three doublets (δ 4.38, 3.97, 3.92; intensity ratio 1 : 1 : 1) are observed (solvent: $CDCl_3$). Its $^{31}P\{^1H\}$ nmr spectrum is an A_2B_2 type with signals in the region of *ca.* 20 δ. The region of the spectrum is well separated from that associated with fully aminolysed cyclotetraphosphazatetraenes (*ca.* 4–10 δ)[1] and is characteristic of bicyclic phosphazenes.[4] The infrared spectrum of compound (**1**) has a strong band at 1200 cm^{-1} (ν P=N); the band at 792 cm^{-1} arises from the P(2)–N(9)–P(6) bridge—the phosphaz*ane* part of the bicyclic skeleton.[5] These distinctive features are also prominent in the infrared spectra of other bicyclic phosphazenes[4]



(**1**)

but are absent in the spectra of analogous monocyclic phosphazatetraenes [e.g., $N_4P_4(NRR')_8$, ν(P=N) is *ca.* 1250–1270 cm^{-1}].[1]

In our earlier studies, we observed that bicyclic phosphazenes were obtained only when the cyclotetraphosphazene possessed at least two primary amino substituents.[4] It seemed probable that a proton abstraction step followed by an intramolecular, *trans*-annular nucleophilic substitution was involved in the formation of this new type of phosphazene. In the present work, the formation of the bicyclic phosphazene (**1**) must involve a dealkylation step. Although dealkylation of secondary amines in the presence of chlorocyclophosphazenes and other phosphorus (V) chlorides has been noted previously,[6] this report is the first example of dealkylation accompanied by an intramolecular nucleophilic attack to give a bicyclic phosphazene. Also, the maximum number of chlorine atoms replaced by dibenzylamino groups for the *monocyclic* chlorophosphazenes, $N_3P_3Cl_6$ and $N_4P_4Cl_8$ is two[1] and four respectively. Hence, the large number of dibenzylamino substituents that can be accommodated by this bicyclic skeleton is somewhat unexpected.

We are indebted to the Overseas Development Administration, U.K. and the University Grants Commission, New Delhi, for support.

REFERENCES AND NOTES

1. S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Advances in Inorganic Chemistry and Radiochemistry*, H. J. Emeléus & A. G. Sharpe (Eds.), Academic Press Inc., New York, **21**, 41 (1978).
2. D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 2035 (1972).
3. S. S. Krishnamurthy, M. N. Sudheendra Rao, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods, *Inorg. Chem.*, **17**, 1527 (1978).
4. S. S. Krishnamurthy, K. Ramachandran, A. C. Sau, R. A. Shaw, A. R. Vasudeva Murthy, and M. Woods, *Inorg. Chem.*, **18**, 2010 (1979); S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *J. Ind. Inst. Sci.*, **61B**, 57 (1979).
5. T. S. Cameron and Kh. Mannan, *Acta Cryst.*, **B33**, 443 (1977); T. S. Cameron, R. E. Cordes and F. A. Jackman, *Acta Cryst.*, **B35**, 980 (1979).
6. S. S. Krishnamurthy, M. N. Sudheendra Rao, A. R. Vasudeva Murthy, R. A. Shaw, and M. Woods, *Ind. J. Chem.*, **14A**, 823 (1976); C. Y. Cheng and R. A. Shaw, *J.C.S. Perkin I*, 1739 (1976).