Diazadiphosphetidine Ring Systems

By R. JEFFERSON, J. F. NIXON,* and T. M. PAINTER

(*Chemical Laboratory, University of Sussex, Brighton, Sussex* BN1 9QJ)

DIAZADIPHOSPHETIDINE ring systems, $(RNPX)_2$ (I) (R = alkyl, aryl; X = chlorine), containing tervalent phosphorus, which are isomeric with phosphonitrilic compounds (II) $(RXP{=}N)_n$ are said to be formed[1,2] in reaction between:

(a) an amine hydrochloride and phosphorus trichloride[1] (R = Ph, X = Cl)

(*b*) a disilazane $(R_3Si)_2NR$ and phosphorus trichloride[2] (R = Me, X = Cl)

On the other hand there is a report that aniline hydrochloride and phosphorus trichloride afford only the *non-cyclic* product $RN(PCl_2)_2$ (III) (R = Ph, X = Cl), which on elimination of phosphorus trichloride gives $(Ph_3N_3P_2)_2$ rather than $(PhNPCl)_n$.[3]

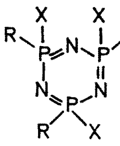
We showed previously[4] that alkylaminobisdichlorophosphines (III; R = Me, Et; X = Cl) could be synthesised by route (a) and more recently we have extended this method to the phenyl and *m*-chlorophenyl derivatives.[5]

We now report that route (b) above also provides a synthetic route to these non cyclic compounds (III; R = Me, X = Cl) when 1 : 1 molar ratios are used:

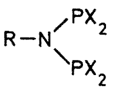
$$(Me_3Si)_2NMe + 2PCl_3 \rightarrow MeN(PCl_2)_2 + 2Me_3SiCl$$

the products being identical with those formed *via* route (a), subsequent fluorination affording *only* (III; R = Me, X = F) (62%), with no evidence for formation of a stable diazadiphosphetidine ring. The identity of the compounds was confirmed by elemental analyses and by the characteristic ^{19}F and ^{31}P n.m.r. spectra of the fluoro-derivative which is an example of the XX′AA′X″X‴ spin system (neglecting further interaction with the R-group).[6]

(I)



(II)



(III)

Similarly *no* evidence for ring formation was found in the following reactions:

(1) dehydrofluorination of methylaminodifluorophosphine, $MeNHPF_2$,[7] using tertiary base or caesium fluoride.

(2) formation of trimethyltin fluoride in the reaction between PF_3 or $MeN(PF_2)_2$ and heptamethyldistannazane $(Me_3Sn)_2NMe$.

(3) thermal elimination of phosphorus trichloride from $MeN(PCl_2)_2$.

(4) elimination of trimethylchlorosilane from $MeN(PCl_2)_2$ and $(R_3Si)_2NMe$ *i.e.*

$$MeN(PCl_2)_2 + (Me_3Si)_2NMe \not\longrightarrow (MeNPCl)_2 + 2Me_3SiCl.$$

Instead reaction (4) carried out with either a deficiency or an excess of (III) produced the known "cage" aminophosphine, tetraphosphorus hexamethylhexaimide, $P_4(NMe)_6$,[8]

$$2MeN(PCl_2)_2 + 4(Me_3Si)_2NMe \rightarrow P_4(NMe)_6 + 8Me_3SiCl$$

Exchange of groups on phosphorus leading to some $MeN(PCl_2)_2$ formation was also observed during ^1H n.m.r. studies of mixtures of PCl_3 and $P_4(NMe)_6$ at room temperature.

$$(MeN)_6P_4 + 8PCl_3 \rightleftharpoons 6MeN(PCl_2)_2$$

It is worth noting that although phosphorus pentafluoride and its derivatives, R_nPF_{5-n}, readily react with disilazanes to form the well established *cyclic* compounds, $(RNPF_2R)_2$,[9,10] containing quinquevalent phosphorus; there is no analogous reaction using trifluorophosphine.[9] Likewise deamination of di(alkylamino)phenyl phosphines, $[PhP(NHR)_2]$,[11] produced the cyclic polyphosphine, $(PhP)_4$, rather than the P–N ring compound, while several careful attempts to prepare the related trifluoromethyl-phosphorus derivatives[12] (I; R = Me, X = CF_3) were also unsuccessful.

It therefore appears that the existence of these interesting cyclic P^{III}–N compounds (I) is as yet not well established.

We thank Messrs. Albright and Wilson and the S.R.C. for financial support.

(*Received, February 21st, 1969; Com.* 246.)

---

[1] A. Michaelis and G. Schröeter, *Chem. Ber.*, 1894, **27**, 490.
[2] E. W. Abel and G. R. Willey, *Proc. Chem. Soc.*, 1962, 308; E. W. Abel, D. A. Armitage, and G. R. Willey, *J. Chem. Soc.*, 1965, 57.
[3] S. Goldschmidt and H. L. Krauss, *Annalen*, 1955, **595**, 193.
[4] J. F Nixon, *Chem. Comm.*, 1967, 669; *J. Chem. Soc.* (*A*), 1968, 2689.
[5] J. F Nixon and T. M. Painter, unpublished results.
[6] J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 1087.
[7] C. G. Barlow, R. Jefferson, and J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2692.
[8] R. R. Holmes and J. A. Forstner, *J. Amer. Chem. Soc.*, 1960, **82**, 5509; 1961, **83**, 1334.
[9] R. Schmutzler, *Chem. Comm.*, 1965, 19; *U.S.P.*, 3,287,406 (1966).
[10] G. C. Demitras, R. A. Kent, and A. G. MacDiarmid, *Chem. and Ind.*, 1964, 712; G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 1903.
[11] A. P. Lane and D. S. Payne, *Proc. Chem. Soc.*, 1964, 403; A. P. Lane, D. A. Morton-Blake, and D. S. Payne, *J. Chem. Soc.* (*A*), 1967, 1492.
[12] J. Heners and A. B. Burg, *J. Amer. Chem. Soc.*, 1966, **88**, 1677.