Reaction of *N*-Methylphosphazenium Halides with Bases: a Phosphazene–Phosphorin Rearrangement

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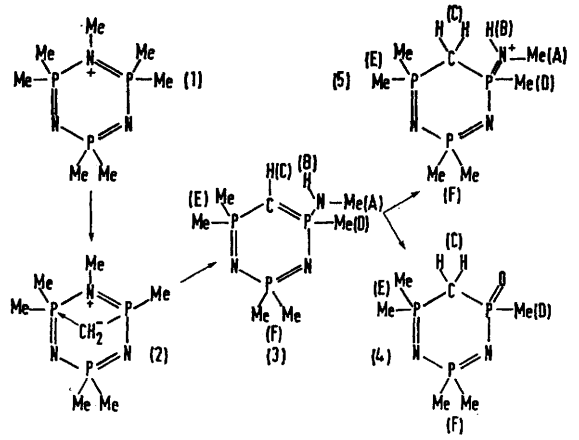
Summary On deprotonation by a sufficiently strong base, *N*-methylphosphazenium iodides $N_nP_nMe_{2n+1}I$ ($n = 3,4$) rearrange to phosphorins with exocyclic methylamino-groups.

QUATERNARY *N*-methylphosphazenium iodides $N_nP_nMe_{2n+1}I$ ($n = 3,4$) react with bases in at least two ways. The trimeric compound (**1**) reacts with sodium bis(trimethylsilyl)amide in octane, deprotonation occurring (as in the neutral methylphosphazenes $N_nP_nMe_{2n}$ [1]) at a PMe group (**2**), rather than at the NMe group, where much of the charge is localised.[2] The diazaphosphorin (**3**) is then formed in a carbanionic rearrangement similar to that which occurs with some silicon–phosphorus compounds,[3] but which is new to phosphazene chemistry.

Although the mobility of protons (B) and (C) in (**3**) prevents their detection by n.m.r. spectroscopy, the exocyclic position of the MeNH group, suggested by its n.m.r. parameters, is confirmed by hydrolysis of (**3**) to the phosphine oxide (**4**). The coupling of the (inequivalent) protons of the methylene group in (**4**) to two phosphorus atoms shows that the ring structure is maintained, and the formation of a C-hydriodide of (**3**) [cation (**5**)] without breaking the exocyclic P–N bond demonstrates the ylidic character of the P–C bonds; the hexaphenyl analogue of (**3**), prepared differently, is also protonated on carbon.[4] Nonamethylcyclotetraphosphazenium iodide $N_4P_4Me_9I$ undergoes analogous reactions, to give a triazatetraphosphorin (**6**), a phosphine oxide (**7**) and a cation (**8**), with n.m.r. parameters generally similar to those of (**3**)—(**5**). Introduction of carbon into both the 6- and 8-membered rings evidently decreases their flexibility, as (in contrast to the parent methiodides[2]) some geminal methyl groups are magnetically inequivalent.



If $N_4P_4Me_9I$ is deprotonated by potassium t-butoxide, the principal product (**6**) is accompanied by another compound, formulated as the linear phosphine oxide $MeNH(PMe_2N)_3PMe_2O$. The analogous compound $MeNH(PMe_2N)_2PMe_2O$

TABLE. N.m.r. parameters of diazatriphosphorin and triazatetraphosphorin derivatives[a]

Proton group	(3)[b]	(4)[c]	(5)[d]	(6)[b]	(7)[c]	(8)[d]
(A)	2·47(14·0)[e]	—	2·54(14·0)[f]	2·46(13·0)[e]	—	2·57(13·5)[g]
(B)	h,i	—	*ca.* 4·2	h,i	—	*ca.*3·9
(C)	h	1·95, 2·11(13·5)[j,k]	2·72, 2·86(13·5)[j,l]	h	2·31(12·5)	2·92, 3·10(13·5)[j,m]
(D)	1·45(14·0)	1·96(13·5)	1·81(14·0)	n	1·94(13·0)	1·81(13·5)
(E)	1·32(12·5)	1·61(14·0)	1·74(14·0)	n	1·56, 1·63(14·0)[o]	1·71(13·5)
(F)	1·39(13·5)	1·48, 1·53(15·0)[o,p]	1·53(14·5)	n	1·47, 1·54(13·0)[o,q]	1·47(14·0)[r]

[a] Analyses correct for all compounds. δ_H p.p.m. rel. to int. Me_4Si. J_{HP} (parentheses) in Hz. [b] In C_6D_6. [c] In $CDCl_3$. [d] In CD_3CN. [e] 2·57(12·8) in $N_3P_3(NHMe)_6$ (C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1965, **4**, 890). [f] $J_{H(A)H(B)}$ 13·5 Hz. [g] $J_{H(A)H(B)}$ 14·0 Hz. [h] Not observed. [i] ν(NH) 3180 cm^{-1}. [j] AB pattern. [k] J_{HH} 13·5 Hz. [l] J_{HH} *ca.* 16·0 Hz. [m] J_{HH} 14·0 Hz. [n] Unresolvable group of doublets at δ *ca.* 1·42. [o] Inequivalent geminal methyl groups. [p] Long range J_{HP} *ca.* 2 Hz. [q] F′ 1·44(14·0). [r] F′ 1·47(14·0); the fourth set of methyl groups (F′) lies between the E and F methyl groups.

is the only product in the reaction with $N_3P_3Me_7I$. These linear phosphine oxides are probably formed in a second type of reaction, the competitive nucleophilic attack of the t-butoxide ion on phosphorus, followed by elimination of isobutene (as in the reaction of chlorophosphazenes with sodium t-butoxide[5]) and ring cleavage.

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