Synthesis of the First Examples of 1*H*- and 4*H*-1,2,4,3λ^3-Triazaphospholes *via* Unexpected Ring-contraction Reactions

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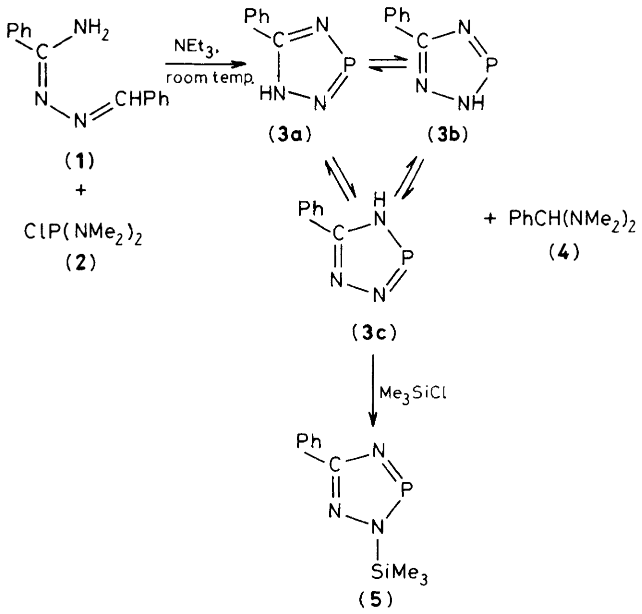
The reaction of the Schiff bases of benzamidrazone or diaminomaleonitrile with bis(dimethylamino)chlorophosphine or tris(dimethylamino)phosphine affords new 1*H*-, 2*H*-, or 4*H*-1,2,4,3λ^3-triazaphospholes or 1,3,2λ^3-diazaphospholes with the formation of triaza- or diaza-phosphorines as intermediates.

There has been increasing interest recently in the synthesis and reactivity of unusually hybridized phosphorus compounds.[1] Until now only a few examples of five-membered ring compounds containing two-co-ordinated phosphorus with an >N–P=N– skeleton have been described.[2,3] To the best of our knowledge analogous six-membered-ring compounds have not yet been reported. The reaction of a Schiff base (**1**) or (**11**) with a phosphorus derivative such as bis(dimethylamino)chlorophosphine (**2**) or tris(dimethylamino)phosphine (**6**) would be expected to give this type of compound.

However, unexpected ring-contraction reactions, which occurred surprisingly with phosphorus–carbon bond cleavage, were observed instead in these cases, leading to the first examples of 1*H*- and 4*H*-1,2,4,3λ^3-triazaphospholes or to 1,3,2λ^3-diazaphospholes. We also report here: (i) the synthesis of a new 2*H*-1,2,4,3λ^3-triazaphosphole,† and (ii) the full characterisation of a derivative of the previously unknown 3,4-dihydro-1,4,2λ^5-diazaphosphorine (**12**) as a stable intermediate.

Treatment of the chlorophosphine (**2**) with the Schiff base (**1**) in the presence of triethylamine in benzene at 0 °C gave (**4**)



Scheme 1

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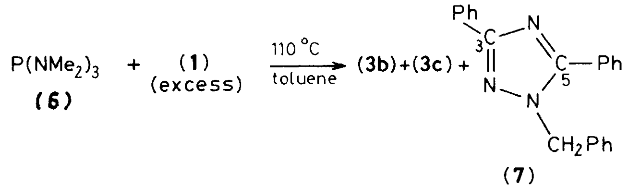
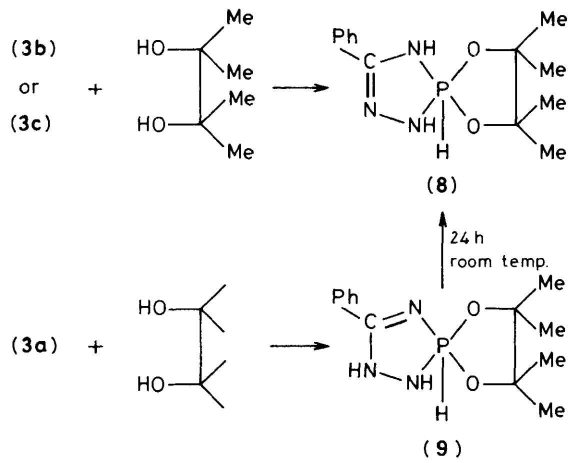
† The first example of 2*H*-1,2,4,3λ^3-triazaphosphole was described by Schmidpeter *et. al.*[3b]



Scheme 2



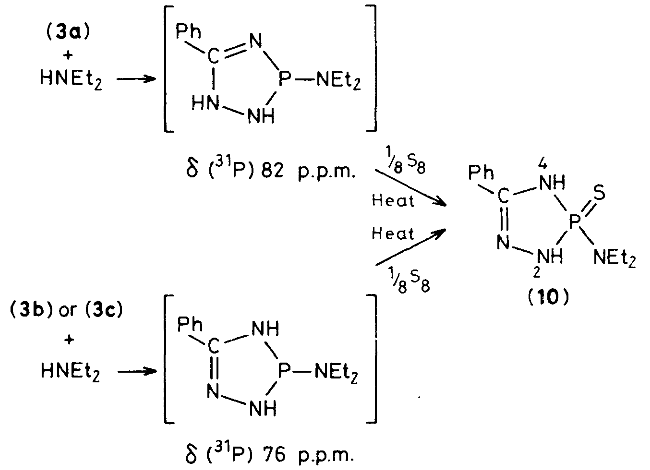
Scheme 3

(b.p. 30 °C at 0.1 mmHg)[4] and the new two-co-ordinate phosphorus compound (**3**) [^{31}P n.m.r. δ 254 p.p.m.; ^{1}H n.m.r. δ 7.15 (5H, one broad signal) and 2.2 (1H, no detectable J_{HNP}); major ions in mass spectrum (70 eV) at *m/z* 163, 146, 134, 119 and 104]. The ^{1}H n.m.r. data strongly support the structure (**3a**), the first example of a 1*H*-1,2,4,3λ^3-triazaphosphole, for (**3**).[5] In benzene solution (**3a**) was slowly converted into its isomer (**3b**).

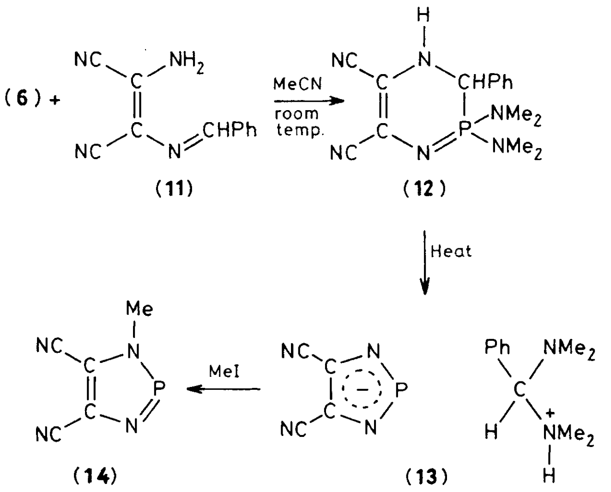
The reaction of (**3**) with trimethylchlorosilane resulted in the exclusive formation of (**5**), probably because of steric hindrance [(**5**),‡ b.p. 89 °C at 0.1 mmHg; ^{31}P n.m.r. δ 280 p.p.m.; ^{1}H n.m.r. δ 0.5 (9H, s). 7.2 (3H, m), and 8.3 (2H)].

The isomers (**3b**) and (**3c**), the latter being the first example of a 4*H*-1,2,4,3λ^3-triazaphosphole, can be prepared by addition of tris(dimethylamino)phosphine (**6**) to an excess of (**1**) in boiling toluene [(**3b**): ^{31}P n.m.r. δ 251.5 p.p.m., J_{PNH} 27.6 Hz); (**3c**) ^{31}P n.m.r. 249 p.p.m., J_{PNH} 24.9 Hz]. This reaction also provides a route to 1-benzyl-3,5-diphenyl-1,2,4-triazole (**7**)‡ [m.p. 104 °C; ^{1}H n.m.r. δ 5.34 (2H) and 7—8.2 (5H); ^{13}C n.m.r. δ 52.6 (CH_2), 126—136.5 (C_6H_5), and 155.9 and 161.7 p.p.m. (C-3 and C-5)]. The identity of the novel triazole (**7**) was confirmed by its independent synthesis by heating the Schiff base (**1**) with (**4**) in refluxing toluene (yield 90%). A similar trapping reaction of (**4**) must also occur in the reaction of (**1**) with (**6**) (Scheme 2).

Additional proof of the structure of compounds (**3a**—**c**) is provided by the following reactions. (i) Addition of pinacol to (**3b**) or (**3c**), a reaction which is characteristic of cyclic two-co-ordinated phosphorus compounds,[2,6] gave rise, as expected, to the formation of the spirophosphorane (**8**)[7] (m.p. 198 °C; ^{31}P n.m.r. δ −62 p.p.m. J_{PH} 766 Hz); the same reaction with the isomer (**3a**) afforded first another spirophosphorane (**9**) (^{31}P n.m.r. δ −55 p.p.m., J_{PH} 752 Hz) which was slowly converted into (**8**). (ii) Diethylamine reacts at the phosphorus–nitrogen double bond of (**3a**—**c**) giving unstable P^{III} derivatives which are transformed into the corresponding



Scheme 4



Scheme 5

P^{IV} product (**10**) on addition of sulphur in refluxing benzene [(**10**), m.p. 135 °C; ^{31}P n.m.r. δ 68 p.p.m., ^{1}H n.m.r. δ 9.45 (d, $^2J_{NHP}$ 33 Hz, N^2-H) and 8.8 (d, $^2J_{NHP}$ 24 Hz, N^4-H)].

^{13}C N.m.r. data for the species (**3**) are consistent with structures (**3a**—**c**) (a weak doublet at δ 166 p.p.m., $^2J_{CP}$ 14 Hz for the carbon atom of the triazaphosphole ring, analogous to the case of *N*-substituted triazaphospholes[8]).

It is of interest that a transient intermediate [δ (^{31}P) 27 p.p.m.] is formed during the reactions in Schemes 1 and 2. This species can be isolated when (**6**) is treated with the Schiff base (**11**) (Scheme 5). In a typical experiment the phosphine (**6**) (0.05 mol) in acetonitrile (20 ml) was slowly added, at room temperature, to (**11**) (0.05 mol) also in acetonitrile (20 ml). Removal of acetonitrile followed by extraction with chloroform and recrystallisation from hexane gave compound (**12**)‡ (50% yield), which is stable in the solid state [m.p. 136 °C (decomp.); ^{31}P n.m.r. δ 27 p.p.m.; ^{1}H n.m.r. δ 2.16 (3H, d, J_{PH} 10 Hz), 2.51 (3H, d, J_{PH} 10 Hz), 4.0 (1H), 4.4 (1H, d, J_{PH} 6 Hz), and 7.5 (5H, m); ^{13}C n.m.r. δ 122.6, 119.6 (sp^2); 116, 106 (CN); 50 (P–C, d, J_{PC} 90 Hz): 126—136 p.p.m. (C_6H_5); ν_{NH} 3200, $\nu_{P=N}$ 1275 cm^{-1}; major ions in mass spectrum (70 eV) at *m/z* 314, 312, and 196].

In acetonitrile solution (**12**) is slowly converted into (**13**) at room temperature (3 days) by an unexpected ring contraction reaction involving an unusual cyclic phosphorus–carbon bond cleavage under very mild conditions. In this reaction (**4**) is trapped in its protonated form, the counter-anion being the

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‡ Satisfactory elemental analyses were obtained.

cyclic phosphorus derivative. Addition of methyl iodide to (**13**) gives (**14**).[3c,6]

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References

1 See *e.g.* E. Fluck, *Top. Phosphorus Chem.*, 1980, **10**, 193: R. Appel, F. Knoll, and I. Ruppert, *Angew, Chem., Int. Ed. Engl.*, 1981, **20**, 731.

2 Y. Charbonnel and J. Barrans, *C.R. Acad. Sci., Ser. C*, 1974, **278**, 355; *Tetrahedron*, 1976, **32**, 2039; C. Malavaud, M. T. Boisdon, Y. Charbonnel, and J. Barrans, *Tetrahedron Lett.*, 1979, 447; C. Malavaud, T. N'Gando M'Pondo, L. Lopez, and J. Barrans, *Can. J. Chem.*, in the press.

3 (a) A. Schmidpeter, J. Luber, and H. Tautz, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 546; (b) A. Schmidpeter and H. Tautz, *Z. Naturforsch., Teil B*, 1980, **35**, 1222; (c) A. Schmidpeter and K. Karaghiosoff, *ibid.*, 1981, **36**, 1273.

4 S. V. Lieberman, *J. Am. Chem. Soc.*, 1955, **77**, 1114.

5 Y. Charbonnel, Thèse doctorat d'état, no. 656, University of Toulouse III, 1975.

6 K. Karaghiosoff, J. P. Majoral, A. Meriem, J. Navech, and A. Schmidpeter, *Tetrahedron Lett.*, 1983, 2137; A. Meriem, Thèse de 3ème cycle, University of Toulouse III, 1983.

7 Y. Charbonnel and J. Barrans, *C.R. Acad. Sci., Ser. C*, 1972, **274**, 2209.

8 J. Barrans, M. Th. Boisdon, and M. Haddad, unpublished work.