

The Behaviour of *N*-*t*-Butyl-2,2'-iminodiethanol Towards some Trivalent Phosphorus Compounds

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Phosphorus trichloride and hexamethylphosphorus triamide react with *N*-*t*-butyl-2,2'-iminodiethanol (4) forming the 2:3 adduct *N,N*-bis[2-(6-*t*-butyl-1,3,6,2-dioxazaphosphoran-2-yloxy)ethyl-*t*-butylamine (5) which, on treatment with water (2 mol equiv.) is hydrolysed to give 6-*t*-butyl-1,3,6,2-dioxazaphosphocane 2-oxide (8) and *N*-*t*-butyl-2,2'-iminodiethanol (4). Compound (8) reacts with *o*-chloranil to produce a crystalline product which in solution gives an equilibrium mixture of six-coordinated phosphorus with a P-OH bond (9) and the phosphate ester (10). Phenylphosphonous dichloride and *N,N,N',N'*-tetramethyl-*P*-phenylphosphonous diamide react with (4) to give 2-phenyl-6-*t*-butyl-1,3,6,2-dioxazaphosphocane (11) which adds to *o*-chloranil to form a tautomeric equilibrium mixture of the four-co-ordinate and six-co-ordinate phosphorus compounds (13) \rightleftharpoons (14). Phenyl azide reacts with (11) to give 2-phenyl-2-phenylimino-6-*t*-butyl-1,3,6,2-dioxazaphosphocane (15). The structural assignments are based on analytical, chemical, and spectroscopic results.

It has been reported that the simplest diol, ethylene glycol, reacts with phosphorus trichloride, hexamethylphosphorus triamide, phenylphosphonous dichloride, and *N,N,N',N'*-tetramethyl-*P*-phenylphosphonous diamide to form 1:1 adducts, the 1,3,2-dioxaphospholanes (1).¹⁻⁶ Reaction of the 1,3,2-dioxaphospholanes (1a) and (1b) with another molecule of ethylene glycol led to the formation of either the trivalent phosphorus or the pentavalent phosphorus tautomer (2) or (3).^{7,8}

We report here the behaviour of *N*-*t*-butyl-2,2'-iminodiethanol (4) towards some trivalent phosphorus reagents, namely, phosphorus trichloride, hexamethylphosphorus triamide, phenylphosphonous dichloride, and *N,N,N',N'*-tetramethyl-*P*-phenylphosphonous diamide.

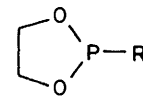
Results and Discussion

We have found that phosphorus trichloride reacts with *N*-*t*-butyl-2,2'-iminodiethanol (4), in benzene at 0°C, using triethylamine as a base, to give *N,N*-bis[2-(6-*t*-butyl-1,3,6,2-dioxazaphosphocan-2-yloxy)ethyl]-*t*-butylamine (5) in 85% yield. The other product (15%) could not be isolated. The ³¹P n.m.r. spectrum of the crude reaction mixture shows signals at δ 130.6 p.p.m., which corresponds to compound (5), and δ 137.7 p.p.m., presumably due to the unisolated product.

Similar results were obtained from the alcoholysis of hexamethylphosphorus triamide (2 mol equiv.) with *N*-*t*-butyl-2,2'-iminodiethanol (4) (3 mol equiv.), in boiling benzene. When equimolar amounts of the starting materials were used in benzene solution at room temperature the reaction was slow and all of (4) had reacted with about 65% of the hexamethylphosphorus triamide after about 21 days. The ³¹P n.m.r. spectrum of the crude reaction mixture showed the formation of compound (5) in quantitative yield (δ 130.6 p.p.m.).

From the above results, we conclude that *N*-*t*-butyl-2,2'-iminodiethanol (4) has a tendency to cyclise on reaction with either phosphorus trichloride in presence of triethylamine or hexamethylphosphorus triamide to form the transient intermediate eight-membered heterocyclic ring compound (6) which immediately reacts with (4) in the ratio 2:1 forming the main product (5) in quantitative yield. No spirophosphorane containing a P-H bond with a structure like (7) was formed.

Compound (5) was isolated as a stable crystalline product.

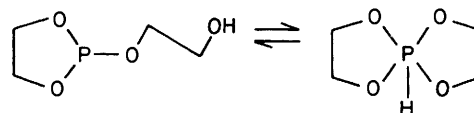


(1)

a; R = Cl

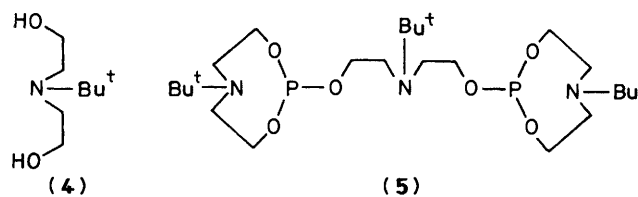
b; R = NMe₂

c; R = Ph



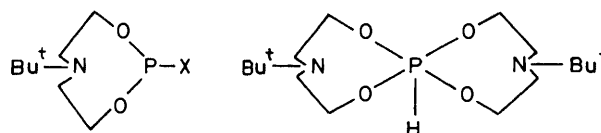
(2)

(3)



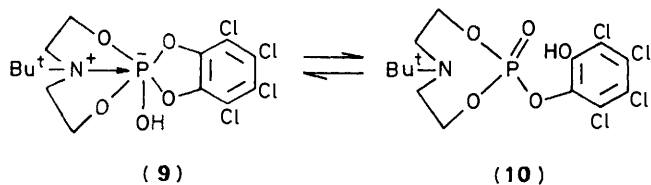
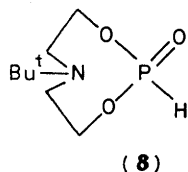
(4)

(5)

(6) X = Cl or NMe₂

(7)

The elemental analysis and the mass spectral data agree with the formula C₂₄H₅₁N₃O₆P₂. Its structure and configuration was established by ¹H and ³¹P n.m.r. spectroscopy. The ¹H n.m.r. spectrum in C₆D₆ shows two singlets at δ 0.90, 1.00 (27 H, *N*-*t*-butyl), and multiplets at δ 1.57–3.13 (12 H, NCH₂) and 3.60—



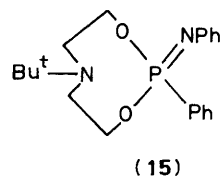
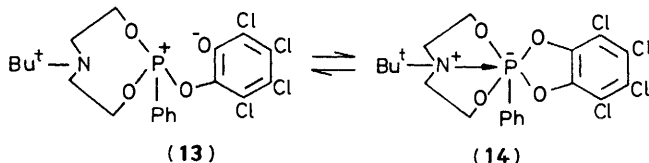
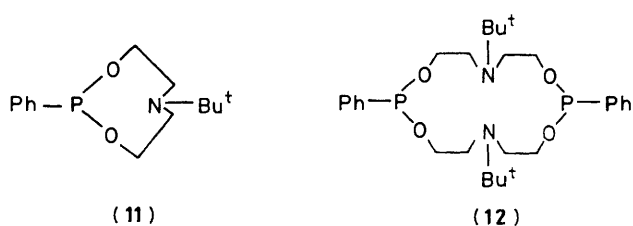
4.43 (12 H, OCH₂). Hydrolysis of compound (5) gave a mixture of the dioxazaphosphocane 2-oxide (8) and *N*-*t*-butyl-2,2'-iminodiethanol (4).

Compound (8) shows a strong P–H band⁹ near 2440 cm⁻¹ in its i.r. spectrum. The ³¹P n.m.r. spectrum, in benzene, exhibits a doublet with J_{P-H} 712 Hz at δ 4.6 p.p.m., while the ¹H n.m.r. spectrum, in C₆D₆, shows a singlet at δ 0.92 (9 H, *N*-*t*-butyl) and two multiplets at δ 1.73–2.80 (4 H, NCH₂) and 3.13–4.33 (4 H, OCH₂).

Compound (8) reacts with *o*-choranil, in benzene at 20 °C, to give a crystalline product which in solution gives an equilibrium mixture of a six-co-ordinated phosphorus compound with a P–OH bond (9) and the phosphate ester (10) in the ratio 2:3. Evidence for these came from the ³¹P n.m.r. spectrum in Me₂SO, which showed two signals at δ -95.91 and -2.34 p.p.m. corresponding to (9) and (10), respectively. A transannular phosphorus–nitrogen interaction is assumed to occur in structure (9) as observed in other eight-membered heterocyclic rings.^{10–25} To our knowledge, the observation of a six-co-ordinated phosphorus with a P–OH bond has not been reported.

The reaction of *N,N,N',N'*-tetramethyl-*P*-phenylphosphonous diamide with *N*-*t*-butyl-2,2'-iminodiethanol (4), in boiling xylene, gave 2-phenyl-6-*t*-butyl-1,3,6,2-dioxazaphosphocane (11) and another product believed to have structure (12), in the ratio 3:1. The product ratio was based on the ³¹P n.m.r. spectrum which shows two signals at δ 161.93 and 155.26 p.p.m. corresponding to (11) and (12), respectively. Using phenylphosphonous dichloride in the presence of triethylamine as base, the reaction gave a mixture of (11) and (12) in the ratio 1:2. The only product that could be isolated in quantitative yield, as colourless crystals, was (11), by distillation of the crude reaction mixture under reduced pressure; thus, the sixteen-membered ring dimer (12) had been converted into the parent eight-membered ring molecule (11). The structure of (11) was established from its elemental analysis and ¹H n.m.r., ³¹P n.m.r., and mass spectra. The ¹H n.m.r. spectrum, in C₆D₆, exhibits a singlet at δ 0.90 (9 H, *N*-*t*-butyl), and multiplets at 2.03–3.03 (4 H, NCH₂), 3.70–4.17 (4 H, OCH₂), and 7.00–8.00 (5 H, phenyl H).

The reaction of compound (11) with *o*-chloranil in benzene solution at room temperature gave a mixture of (13) and (14) in the ratio 3:2. The equilibrium between the four-co-ordinate and six-co-ordinate phosphorus compounds (13) \rightleftharpoons (14) was detected by ³¹P n.m.r. spectroscopy; the ³¹P n.m.r. spectrum of the reaction mixture, in benzene solution, shows two signals at δ 14.54 and -96.25 p.p.m., assigned to the four-co-ordinate phosphorus species (13) and the six-co-ordinate phosphorus compound (14) respectively. The transannular P←N bond is assumed to be present in (14) as in other heterocyclic eight-membered rings.^{10–25}



The behaviour of compound (11) towards phenyl azide was consistent with the Staudinger reaction of trivalent organophosphorus reagents with organic azides to give the corresponding imines;^{26–30} it reacts very rapidly and exothermically with phenyl azide (1 mol equiv.) to give colourless crystals of 2-phenyl-2-phenylimino-6-*t*-butyl-1,3,6,2-dioxazaphosphocane (15). The structure of compound (15) was elucidated on the basis of its elemental analysis, mass spectra, and n.m.r. spectra which were as expected. The ³¹P n.m.r. spectrum in benzene shows only one peak, at δ 4.25 p.p.m., and its ¹H n.m.r. spectrum, in C₆D₆, exhibits a singlet at δ 0.83 (9 H, *N*-*t*-butyl), and multiplets at 1.90–2.95 (4 H, NCH₂), 3.32–4.55 (4 H, OCH₂), and 6.75–8.18 (10 H, phenyl H).

Experimental

All reactions were carried out under nitrogen. The solvents were purified by standard methods. ³¹P N.m.r. spectra were recorded on a Perkin-Elmer R32 instrument, against an 85% H₃PO₄ solution as an external standard. Chemical shifts are positive to low field. The ¹H n.m.r. spectra were recorded, on a Varian T-60 spectrometer, using Me₄Si as internal standard. The i.r. spectra were obtained on Beckman spectrophotometer model 4220. The molecular weights were measured at 70 eV with a Varian MAT 112 mass spectrometer. Light petroleum refers to the fraction with b.p. 40–60 °C.

Reaction of N-t-Butyl-2,2'-iminodiethanol (4) (3 mol) with Phosphorus Trichloride (2 mol).—A solution of phosphorus trichloride (3.43 g, 0.025 mol) in dry benzene (20 ml) was added dropwise to a cooled solution of *N*-*t*-butyl-2,2'-iminodiethanol (4)³¹ (6.0 g, 0.037 mol) and freshly distilled triethylamine (10.5 ml, 0.075 mol) in dry benzene (50 ml). The mixture was then stirred overnight at room temperature. Triethylamine hydrochloride, thus obtained, was removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The resulting solid material (80%) was crystallized from benzene–light petroleum to give *N,N*-bis[2-(6-*t*-butyl-1,3,6,2-dioxazaphosphocane-2-yloxy)ethyl]-*t*-butylamine (5) as colourless crystals, m.p. 134–136 °C (Found: C, 53.2; H, 9.3; N, 7.6; P,

11.6%; M^+ , 539. Calc. for $C_{24}H_{51}N_3O_6P_2$: C, 53.41; H, 9.52; N, 7.78; P, 11.47%; M^+ , 539; ^{31}P n.m.r. (C_6H_6) δ 130.6 p.p.m. 1H n.m.r. (C_6D_6) δ 0.90, 1.00 (27 H, 2 s, *N*-*t*-butyl), 1.57—3.13 (12 H, m, NCH_2), and 3.60—4.43 (12 H, m, OCH_2).

Reaction of N-t-Butyl-2,2'-iminodiethanol (4) (1 mol) with Hexamethylphosphorus Triamide (1 mol).—A mixture of compound (4) (4.0 g, 0.025 mol) and hexamethylphosphorus triamide³² (4.1 g, 0.025 mol) in dry benzene (25 ml) was stirred at room temperature for about 21 days. Dimethylamine was evolved and the solid product, thus formed, was crystallized from benzene–light petroleum to give colourless crystals, identified as the tertiary amine (5) by m.p. and mixed m.p., comparative ^{31}P n.m.r., 1H n.m.r., and mass spectra with the authentic sample obtained from the reaction of phosphorus trichloride with (4). Changing the concentration of the benzene solution gave different quantities of (5) and unchanged hexamethylphosphorus triamide.

Reaction of N-t-Butyl-2,2'-iminodiethanol (4) (3 mol) with Hexamethylphosphorus Triamide (2 mol).—A solution of hexamethylphosphorus triamide (4.1 g, 0.025 mol) in benzene (10 ml) was added dropwise to a stirred solution of *N*-*t*-butyl-2,2'-iminodiethanol (4) (6.0 g, 0.037 mol) in benzene (25 ml). The mixture was heated under reflux for about 3 h. The dimethylamine evolved, titrated by sulphuric acid solution, represented 95% of the expected amount. After removal of the volatile materials under reduced pressure, the residue was triturated with light petroleum. The solid product was crystallized from benzene–light petroleum to give compound (5) as colourless crystals, m.p. 134—136 °C (90%).

*Hydrolysis of N,N-Bis[2-(6-*t*-butyl-1,3,6,2-dioxazaphosphocane-2-yloxy)ethyl]-*t*-butylamine (5).*—To a stirred solution of compound (5) (0.54 g, 0.001 mol) in benzene (10 ml), water (0.036 ml) was added. The mixture was heated under reflux for 2 h. Upon concentration of the benzene solution, the solid product, thus formed, was collected (0.37 g, 90%) and crystallized from benzene to give colourless crystals of 6-*t*-butyl-1,3,6,2-dioxazaphosphocane 2-oxide (8), m.p. 60—62 °C (Found: C, 46.4; H, 8.7; N, 6.7; P, 15.1%; M^+ , 207. Calc. for $C_8H_{18}NO_3P$: C, 46.37; H, 8.76; N, 6.76; P, 14.95%; M , 207; γ_{max} (KBr) 2 440 (P–H stretch),⁹ 1 245 (P=O), and 1 090 cm^{-1} (P–O–CH₂);⁹ ^{31}P n.m.r. (C_6H_6) δ 4.6 p.p.m. (d, J_{P-H} 712 Hz); 1H n.m.r. (C_6D_6) δ 0.92 (9 H, s, *N*-*t*-butyl), 1.73—2.80 (4 H, m, NCH_2), and 3.13—4.33 (4 H, m, OCH_2). The filtrate was evaporated to dryness and the residual substance was twice crystallized from benzene–light petroleum to give colourless crystals, shown to be *N*-*t*-butyl-2,2'-iminodiethanol (4) (m.p., mixed m.p., and comparative 1H n.m.r. spectra).

*Reaction of 6-*t*-Butyl-1,3,6,2-dioxazaphosphocane 2-Oxide (8) with *o*-Chloranil.*—The cyclic phosphonate (8) (0.20 g, 0.001 mol) in dry benzene (5 ml) was added to a suspension of *o*-chloranil (0.24 g, 0.001 mol) in dry benzene (10 ml) at 20 °C under nitrogen, and the red solution went colourless. After the benzene solution had been concentrated under reduced pressure and left in the refrigerator overnight, a colourless crystalline product was obtained. It was identified as a mixture of 4,5,6,7-tetrachloro-2'-hydroxy-6'-*t*-butylspiro[1,3,2-benzodioxaphosphole-2,2'-[1,3,6,2]dioxazaphosphocane] (N→P) (9) and 6-*t*-butyl-2-(3,4,5,6-tetrachloro-2-hydroxyphenoxy)-1,3,6,2-dioxazaphosphocane 2-oxide (10) {Found [mixture of (9) and (10)]: C, 36.9; H, 3.9; Cl, 31.2; N, 3.1; P, 7.0. Calc. for $C_{14}H_{18}Cl_4NO_5P$: C, 37.11; H, 4.00; Cl, 31.30; N, 3.09; P, 6.84%}; ^{31}P n.m.r. (Me_2SO) δ –95.91 [for (9)] and –2.34 p.p.m. [for (10)].

Reaction of N-t-Butyl-2,2'-iminodiethanol (4) with Phenylphosphonous Dichloride.—A solution of phenylphosphonous dichloride (6.7 g, 0.037 mol) in dry benzene (50 ml) was added dropwise during 1 h, into a solution of *N*-*t*-butyl-2,2'-iminodiethanol (4) (6.0 g, 0.037 mol) and triethylamine (10.5 ml, 0.075 mol) in dry benzene (150 ml) which had been cooled in an ice–water bath. The mixture was then stirred for another 6 h and triethylamine hydrochloride removed by filtration. After the solvent had been removed from the filtrate under reduced pressure, the residue was distilled under reduced pressure to give 2-phenyl-6-*t*-butyl-1,3,6,2-dioxazaphosphocane (11) (70%) as a colourless liquid, b.p. 110—112 °C (10^{-3} mmHg), which was solidified on cooling, m.p. 66—68 °C (Found: C, 62.7; H, 8.15; N, 5.2; P, 11.7%; M , 267. Calc. for $C_{14}H_{22}NO_2P$: C, 62.91; H, 8.29; N, 5.24; P, 11.59%; M , 267; ^{31}P n.m.r. (C_6H_6) δ 161.93 p.p.m.; 1H n.m.r. (C_6D_6) δ 0.90 (9 H, s, *N*-*t*-butyl), 2.03—3.03 (4 H, m, NCH_2), 3.70—4.17 (4 H, m, OCH_2), and 7.00—8.00 (5 H, m, phenyl H).

Reaction of N-t-Butyl-2,2'-iminodiethanol (4) with N,N,N',N'-Tetramethyl-P-phenylphosphonous Diamide.—A solution of *N,N,N',N'*-tetramethyl-*P*-phenylphosphonous diamide³³ (4.9 g, 0.025 mol) in dry xylene (10 ml) was added dropwise to a solution of (4) (4.0 g, 0.025 mol) in dry xylene (25 ml) which was heated under reflux at 140 °C (oil bath temperature). After about 4 h, 96% of the expected amount of dimethylamine evolved. The solvent and volatile materials were removed under reduced pressure and the oily residue was distilled under reduced pressure to give a colourless liquid, b.p. 110—112 °C (10^{-3} mmHg), which solidified on cooling; it was shown to be identical with (11) by m.p. and mixed m.p., comparative ^{31}P n.m.r., 1H n.m.r., and mass spectra with an authentic sample previously obtained from the reaction of (4) with phenylphosphonous dichloride.

*Reaction of 2-Phenyl-6-*t*-butyl-1,3,6,2-dioxazaphosphocane (11) with *o*-Chloranil.*—A solution of *o*-chloranil (0.49 g, 0.002 mol) in dry benzene (10 ml) was added dropwise to a cooled solution of the phosphocane (11) (0.53 g, 0.002 mol) in dry benzene (20 ml). The resulting yellow solution afforded, upon evaporation and addition of light petroleum, a yellow solid product containing a mixture of 3,4,5,6-tetrachloro-2-(2-phenyl-6-*t*-butyl-1,3,6,2-dioxazaphosphocane-2-*io*-oxy)phenolate (13) and 4,5,6,7-tetrachloro-2'-phenyl-6'-*t*-butylspiro[1,3,2-benzodioxaphosphole-2,2'-[1,3,6,2]dioxazaphosphocane](N→P)(14) {Found [mixture of (13) and (14)]: C, 46.6; H, 4.2; Cl, 27.5; N, 2.7; P, 6.12. Calc. for $C_{20}H_{22}Cl_4NO_4P$: C, 46.81; H, 4.32; Cl, 27.64; N, 2.73; P, 6.03%}; ^{31}P n.m.r. (C_6H_6) δ 14.54 [for (13)] and –96.25 p.p.m. [for (14)].

Reaction of Compound (11) with Phenyl Azide.—A solution of phenyl azide³⁴ (0.60 g, 0.005 mol) in dry benzene (10 ml) was added dropwise during 30 min to a stirred solution of the cyclic compound (11) (1.33 g, 0.005 mol) in dry benzene (20 ml) maintained at 0 °C. The reaction was rapid, and the evolution of nitrogen ceased after 1 h. The benzene solution was then concentrated and light petroleum added to give a solid product which was filtered off, and crystallized from benzene–light petroleum to give colourless crystals of 2-phenyl-2-phenylimino-6-*t*-butyl-1,3,6,2-dioxazaphosphocane (15) (90%), m.p. 75—76 °C (Found: C, 66.9; H, 7.4; N, 7.7; P, 8.8%; M^+ , 358. Calc. for $C_{20}H_{27}N_2O_2P$: C, 67.02; H, 7.59; N, 7.82; P, 8.64%; M , 358); ^{31}P n.m.r. (C_6H_6) δ 4.25 p.p.m.; 1H n.m.r. (C_6D_6) δ 0.83 (9 H, s, *N*-*t*-butyl), 1.90—2.95 (4 H, m, NCH_2), 3.32—4.55 (4 H, m, OCH_2), and 6.75—8.18 (10 H, m, phenyl H).

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