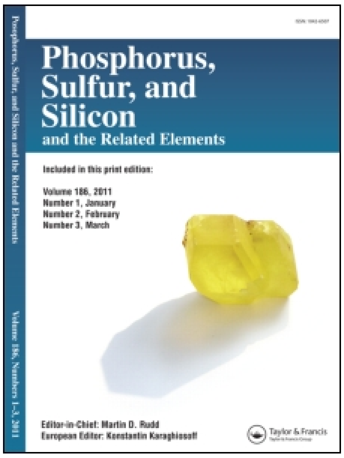

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THE BEHAVIOR OF 2,2'-(TERT-BUTYLIMINO) DIETHANOL TOWARDS FIVE-MEMBERED HETEROCYCLES CONTAINING PHOSPHORUS(III)

F. H. Osman[a]; W. S. El-hamouly[a]; M. M. Abdel-gawad[a]; M. M. Abbasi[b]
[a] National Research Center, Dokki, Cairo, Egypt [b] Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

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THE BEHAVIOR OF 2,2′-(TERT-BUTYLIMINO) DIETHANOL TOWARDS FIVE-MEMBERED HETEROCYCLES CONTAINING PHOSPHORUS(III)

F. H. OSMAN, W. S. EL-HAMOULY, M. M. ABDEL-GAWAD
National Research Center, Dokki, Cairo, Egypt
and
M. M. ABBASI
Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

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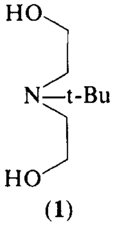
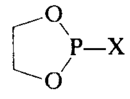
The reaction of 2,2′-(*tert*-butylimino)diethanol (**1**) with dioxaphospholanes (**2a**) and (**2b**) leads to the formation of (*tert*-butylimino)diethylene cyclic ethylene bisphosphite (**4**). Thermal reaction of the biphosphite (**4**) with (**1**) gives a complete rearrangement yielding a mixture of spirophosphorane (**7**), (*tert*-butylimino)diethylene cyclic bis[(*tert*-butylimino)diethylene] bis(phosphite) (**9**) and traces of another product. The biphosphite (**4**) reacts with phenyl azide to give a mixture of penta- and tetracoordinated phosphorus structures (**10**) and (**11**), respectively. Biacetyl condenses with (**4**) to give 2′,2″-bis[2,3-dimethyl-1,4,6,9-tetraoxa-5-phospha(5-P^V)spiro[4.4]non-2-en-5-yl)oxy]-1,1-dimethyltriethylamine (**12**). The reaction of dioxaphospholane (**3a**) with (**1**) yields a mixture of the biphosphite (**9**) and another product believed to be either triethylammonium tris(o-phenylenedioxy) phosphate (**15**) or spirobenzodioxaphospholane (**16**). On the other hand, dioxaphospholane (**3b**) reacts with (**1**) forming a mixture of 4-*tert*-butyl-1,1-dimethylpiperazinium tris[pyrocatecholato(2-)] phosphate(1-) (**17**) and cyclic (*tert*-butylimino)diethylene phosphonate (**18**). Structural assignments are based on chemical and spectroscopic evidence.

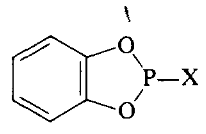
We have recently reported[1] our observations on the behavior of 2,2′-(tert-butylimino)diethanol (**1**) towards phosphorus trichloride, hexamethylphosphorus triamide, phenylphosphonous dichloride and *N,N,N′,N′*-tetramethyl-P-phenylphosphonous diamide. The present work describes the reaction of (**1**) with simple compounds of five-membered heterocycles containing tricoordinated phosphorus such as 1,3,2-dioxaphospholanes (**2**) and (**3**).



(1)



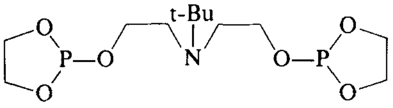
(2)



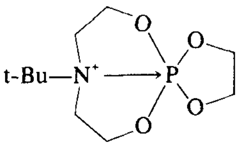
a, X = Cl
b, X = NMe₂

(3)

We found that when 2-chloro-4,5-dihydro-1,3,2-dioxaphospholane (**2a**) was allowed to react with (**1**) in benzene at 0° using triethylamine as catalyst, the colorless liquid (*tert*-butylimino)diethylene cyclic ethylene bis(phosphite) (**4**) is obtained. 2-Dimethylamino-4,5-dihydro-1,3,2-dioxaphospholane (**2b**) reacts similarly with (**1**) in boiling benzene to give compound (**4**) in quantitative yield. The expected hexacoordinated phosphorus compound (**5**) could not be obtained when (**1**) was treated with equimolar amounts of either (**2a**) or (**2b**). The structure of the biphosphite (**4**) was



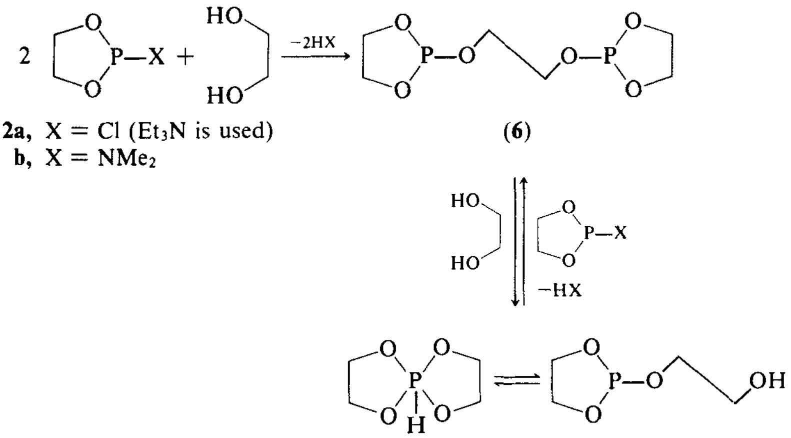
(4)



(5) not formed

established by its ^{31}P NMR spectra which gave only one peak at $\delta = 132.8$ ppm (in benzene) which corresponds to structure (**4**). Full elemental analysis as well as the mass spectrum agree with the formula $C_{12}H_{25}NO_6P_2$. In addition, its ^{1}H NMR spectrum in C_6D_6 exhibits a singlet at $\delta = 0.90$ ppm (due to protons in the *N*-*tert*-butyl, "9H") and the triplet centered at $\delta = 2.57$ ppm (for the *N*—CH_2 protons) and the multiplet falls in the region $\delta = 3.40$–4.10 ppm (due to O—CH_2protons, "12H").

Burgada and coworkers[2] reported the formation of biphosphite (**6**) from the reaction of (**2**) with ethylene glycol in the ratio 2 : 1 or by the reaction of spirophosphorane (**7**) in its tricoordinated tautomeric form (**8**) with an equimolar amount of (**2**). Also, they reported

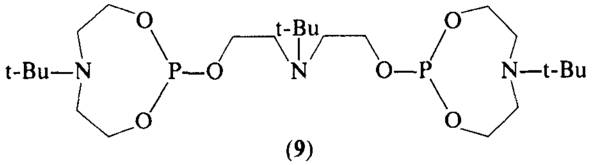


2a, X = Cl (Et_3N is used)
b, X = NMe_2

(**6**)

(**7**) (**8**)

that the biphosphite (**6**) was converted into spirophosphorane (**7**) upon heating with one mole of ethylene glycol at 150°C. The existence of a tautomeric equilibrium between pentacoordinated phosphorus (**7**) and its tricoordinated form (**8**) was first suggested by Burgada *et al.*[3,4] and was confirmed by infrared[5] and by ^{31}P NMR spectroscopy[2,6] at different temperatures. In our work, the thermal reaction of (**4**) with compound (**1**) in a 2 : 1 molar ratio caused a rearrangement giving rise to a mixture consisting mainly of compound (**7**), (*tert*-butylimino)diethylene cyclic bis(*tert*-butylimino)diethylene bis(phosphite) (**9**), together with a small amount of another product which could not be isolated. Examination

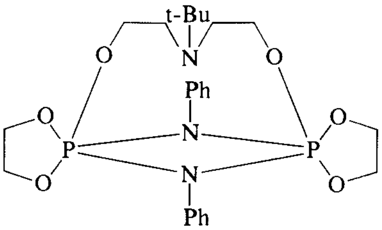


(**9**)

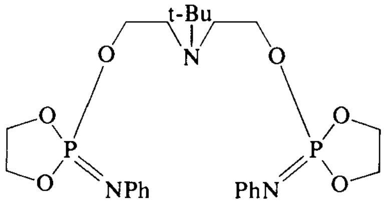
of the ^{31}P NMR spectrum of the reaction mixture showed the presence of signals at $\delta = 130$ ppm, which corresponds to the biphosphite (**9**),[1] and at $\delta = 137.8$ ppm presumably due to the unisolated product, and a doublet at $\delta = -25.2$ ppm with $J_{P\text{-}H} = 827$ Hz due to the spirophosphorane with P—H bond (**7**).[2]

The biphosphite compound (**9**) was isolated as a crystalline product and its identity was established by its m.p., mixed m.p. and comparative IR, NMR, and mass spectra with specimens[1] prepared from the reaction of (**1**) with either hexamethylphosphorus triamide or phosphorus trichloride in the presence of triethylamine as a base. Recently, the molecular structure of (**9**) has been determined by X-ray analysis.[7]

The biphosphite (**4**) reacts very rapidly and exothermically with two mol equivalents of phenyl azide in benzene to give a mixture consisting of compounds (**10**) and (**11**). The structures of



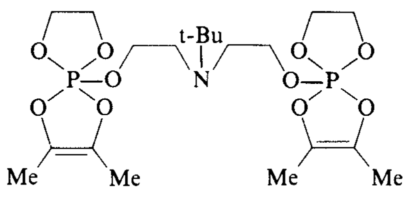
(**10**)



(**11**)

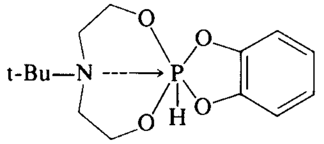
both compounds are supported by their ^{31}P NMR spectra which show two signals at $\delta = -58.5$ ppm and $\delta = 10.5$ ppm which correspond to (**10**) and (**11**), respectively. Compound (**10**) could be isolated in a crystalline form from the mixture and its structure was confirmed by elemental analysis and mass spectrometry.

Biacetyl, a reactive α-diketone, condenses very readily with (**4**) at room temperature to give a non-distillable product whose ^{31}P NMR chemical shift ($\delta = -28.5$ ppm) is consistent with other dispirophosphoranes[8] and has the structure (**12**)

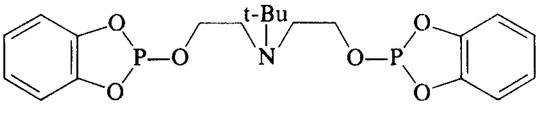


(**12**)

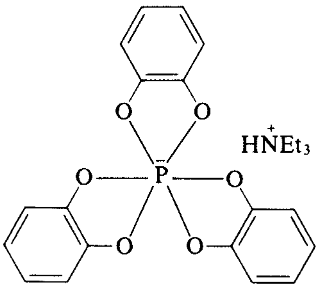
It was of interest to examine the reaction of both 2-chloro-4,5-benzo-1,3,2-dioxaphospholane (**3a**) and 2-dimethylamino-4,5-benzo-1;3;2-dioxaphospholane (**3b**) with compound (**1**). Thus, equimolar amounts of dioxaphospholane (**3a**) and (**1**) in benzene at 0° lead to the formation of a mixture composed of compound (**9**) (as indicated from its spectral data and by comparison with an authentic sample.[1]) and another product we believe to have either structure (**15**) or (**16**). The expected compounds (**13**) and (**14**) analogous to (**4**) formed by the reaction between (**1**) and (**2**) were not formed.



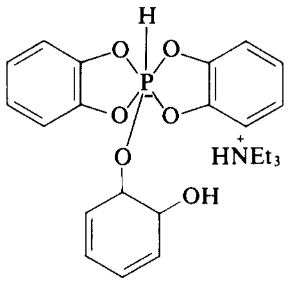
(13)



(14)

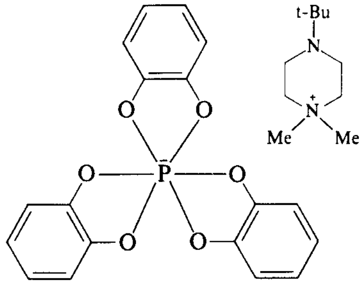


(15)

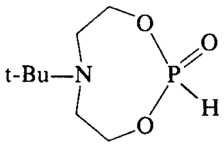


(16)

on the other hand, reaction of **(3b)** and **(1)** in boiling benzene leads to the formation of compounds assigned structures **(17)** and **(18)**, with the evolution of dimethylamine (70% of the expected amount).



(17)



(18)

The phosphonate compound **(18)** was found to be identical in physical and chemical properties with that obtained from the hydrolysis of the biphosphite **(9)** with two mole-equivalents of water.[1]

EXPERIMENTAL

All melting points are uncorrected. The reactions were carried out under nitrogen. The solvents were purified by standard methods. ^{31}P NMR spectra were recorded on a Perkin-Elmer R32 instrument, against an 85% H_3PO_4 solution as an external standard. Chemical shifts are positive to low field. The ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer using TMS as internal standard. The IR spectra were obtained on Beckman spectrophotometer Model 4220. The molecular weights were obtained at 70 eV with a Varian MAT 112 mass spectrometer.

*Reaction of 2,2′-(*tert*-butylimino)diethanol* (**1**) *(1 mol) with 2-chloro-4,5-dihydro-1,3,2-dioxaphospholane* (**2a**) *(2 mol)*

A solution of dioxaphospholane **2a**[9] (6.3 g, 0.05 mol) in 50 ml of dry benzene was added drop by drop over a period of 1 hr, into a solution of **1**[10] (4.0 g, 0.025 mol) and freshly distilled triethylamine (5.5 g, 0.05 mol) in 100 ml of dry benzene which had been cooled in an ice-water bath. The mixture was then stirred for another 10 hr at room temperature. Triethylamine hydrochloride (6.5 g) was removed by filtration. After the solvent had been removed under reduced pressure from the filtrate, the residue was distilled to give a colorless liquid, (*tert*-butylimino)diethylene cyclic ethylene bis(phosphite) (**4**) (yield 90%), b.p. 122–124° (10^{-3}mm Hg).

Anal. Calcd for $C_{12}H_{25}NO_6P_2$: C, 42.23; H, 7.38; N, 4.11; P, 18.15. Found: C, 42.06; H, 7.30; N, 4.00; P, 18.03. Mol. Wt.: Calcd 341. Found (MS) 341. ^{31}P NMR (C_6H_6): signal at $\delta = 132.8$ ppm. ^{1}H NMR (C_6D_6): signals at $\delta = 0.90$ (9H, singlet, *N-tert*-butyl), $\delta = 2.57$ (4H, triplet, *N*—CH_2) and $\delta = 3.40$–4.10 (12H, multiplet, OCH_2).

Reaction of 2,2'-(tert-*butylimino*)*diethanol* (**1**) (*1 mol*) *with 2-dimethylamino-4,5-dihydro-1,3,2-dioxaphospholane* (**2b**) (*2 mol*)

A solution of dioxaphospholane **2b**[11] (6.75 g, 0.05 mol) in 20 ml of dry benzene was added dropwise to a stirred solution of **1** (4 g, 0.025 mol) in 50 ml of dry benzene. The mixture was heated under reflux (bath temperature 90°) for about 6 hr. The dimethylamine evolved was titrated with sulfuric acid solution and represented 98% of the expected amount. After the solvent had been removed under reduced pressure, the residue was distilled under vacuum (10^{-3} mm) to give a colorless liquid proved to be identical with (*tert*-butylimino)diethylene cyclic diethylene bis(phosphite) (**4**) by comparison of ^{31}P NMR, ^{1}H NMR and mass spectra with an authentic sample previously obtained from the reaction of **1** with **2a**.

Thermal Reaction of (tert-*butylimino*)*diethylene cyclic diethylene bis*(*phosphite*) (**4**) *with 2,2'-*(tert-*butylimino*)*diethanol* (**1**)

A mixture of biphosphite (**4**) (6.8 g, 0.02 mol) and 2,2'-(*tert*-butylimino)diethanol (**1**) (1.6 g, 0.01 mol) was heated under vacuum in a sealed tube (bath temperature 150°) for 20 minutes. Distillation of the reaction mixture under reduced pressure gave a colorless liquid spirophosphorane with P—H bond (**7**), b.p. 98–100 (10^{-3} mm Hg) (comparative chemical shift and coupling constant $J_{P\text{-}H}$ in ^{31}P NMR spectra).[2] The non-distillable material was triturated with benzene-light petroleum to give mainly a solid product, which was crystallized from benzene-light petroleum. It was found to be identical with the biphosphite (**9**) (mp, mixed mp and comparative IR, NMR and mass spectra).[1]

Reaction of (tert-*butylimino*)*diethylene cyclic diethylene bis*(*phosphite*) (**4**) *with phenyl azide*

A solution of phenyl azide[12] (1.20 g, 0.01 mol) in 10 ml of dry benzene was added drop by drop to a stirred solution of the biphosphite (**4**) (1.70 g, 0.005 mol) in 20 ml of dry benzene. The mixture was heated gently (bath temperature 50°) for about 3 hr and left overnight at room temperature. Nitrogen was evolved and the solution was examined by ^{31}P NMR spectrum, and showed two signals at $\delta = -58.5$ ppm and $\delta = 10.5$ ppm corresponding to 5'-*tert*-butyl-10',11'-diphenyldispiro[1,3,2-dioxaphospholane-2,1'-[2,8]dioxa[5,10,11]triaza[1,9]diphosphabicyclo[7.1.1]undecane-9',2''-[1,3,2]dioxaphospholane] (**10**) and (*tert*-butylimino)diethylene cyclic diethylene bis(phenylphosphorimidate) (**11**), respectively. A few drops of light petroleum was added to the solution of the reaction mixture and left in the refrigerator for 5 days; the solid product thus formed was filtered and crystallized from benzene-light petroleum to give 10 as colorless crystals (yield 23%), mp 92–93°. Anal. Calcd for $C_{24}H_{35}N_3O_6P_2$: C, 55.05; H, 6.74; N, 8.03; P, 11.83. Found: C, 54.89; H, 6.62; N, 7.91; P, 11.59%. Mol. Wt.: Calcd 523. Found (MS) 523. The filtrate contains compound **11** which could not be isolated owing to the presence of a quantity of compound **10** in the solution.

Reaction of (tert-*butylimino*)*diethylene cyclic diethylene bis*(*phosphite*) (**4**) *with biacetyl*

To a solution of biacetyl (0.86 g, 0.01 mol) in 5 ml of dry benzene was added a solution of biphosphite (**4**) (1.7 g, 0.005 mol) in 10 ml of dry benzene. The mixture was heated under reflux (bath temperature 60°) for 6 hr. After removal of the volatile materials under reduced pressure, the nondistillable viscous liquid, 2',2''-bis[(2,3-dimethyl-1,4,6,9-tetraoxa-5-phospha(5-P^V)spiro[4.4]non-2-en-5-yl)oxy]-1,1-dimethyltriethylamine (12) was obtained and characterized by its chemical shift $\delta = -28.5$ ppm in ^{31}P NMR spectrum.

*Reaction of 2,2'-(*tert*-butylimino)diethanol* (**1**) *with 2-chloro-4,5-benzo-1,3,2-dioxaphospholane* (**3a**)

A solution of dioxaphospholane **3a**[13] (8.7 g, 0.05 mol) in 50 ml of dry benzene was added dropwise over a period of 1 hr into a stirred solution of **1** (8.0 g, 0.05 mol) and freshly distilled triethylamine (7 g, 0.07 mol) in 150 mol of dry benzene which had been cooled in an ice-water bath. The mixture was kept with continuous stirring for an additional 12 hr at room temperature. The precipitate (13.5 g) thus formed was filtered. It contained triethylamine hydrochloride with another product that could not be separated or examined by ^{31}P NMR spectra, and is believed to be triethylammonium tris(o-phenylenedioxy)phosphate (**15**) or spirobenzodioxaphospholane (**16**). The filtrate was evaporated under reduced pressure to remove the volatile materials. The residue was triturated with ether to give colorless crystals (6.4 g), proved to be identical with the biphosphite (**9**) by its mp and mixed mp, comparative IR, ^{31}P NMR, ^{1}H NMR and mass spectra with an authentic sample previously prepared.[1]

*Reaction of 2,2'-(*tert*-butylimino)diethanol* (**1**) *with 2-dimethylamino-4,5-benzo-1,3,2-dioxaphospholane* (**3b**)

A solution of dioxaphospholane **3b**[14] (4.6 g, 0.025 mol) in 10 ml of dry benzene was added dropwise to a stirred solution of **1** (4.0 g, 0.025 mol) in 15 ml of dry benzene which was heated under reflux for 3 hr. The dimethylamine evolved was titrated with sulfuric acid solution and represented 70% of the expected amount. The solid product (4.5 g), thus formed, was filtered and crystallized from acetonitrile to give colorless crystals of 4-*tert*-butyl-1,1-dimethylpiperazinium tris[pyrocatecholato(2-)]phosphate (1-) (**18**), mp 293–295°C. Anal. Calcd for $C_{28}H_{36}N_2O_6P$: C, 63.75; H, 6.88; *N*, 5.31; P, 5.87. Found: C, 63.45; H, 6.57; *N*, 5.30; P, 6.15%. ^{31}P NMR (DMF): signal at $\delta = -84.6$ ppm. ^{1}H NMR (DMSO-d_6): signals at $\delta = 1.00$ (9H, singlet, *N-tert*-butyl), $\delta = 2.60$–2.93 (4H, multiplet, N—CH$_2$), $\delta = 3.07$ (6H, singlet, $\overset{+}{N}Me_2$), $\delta = 3.23$–3.53 (4H, multiplet, N—CH$_2$) and $\delta = 6.61$ (12H, singlet, aromatic protons). The filtrate was evaporated under reduced pressure to remove the volatile materials. The residual substance was distilled under vacuum to give a colorless liquid, b.p. 85–87°(10^{-3} mm Hg) which solidified on cooling (2.6 g) and proved to be identical with cyclic (*tert*-butylimino)diethylene phosphonate (**18**) (mp and mixed mp, comparative IR, NMR and mass spectra).[1]

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