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Reaction of 2-acetyl-5-methyl-2*H*-1,2,3-diazaphosphole with butane-2,3-diol

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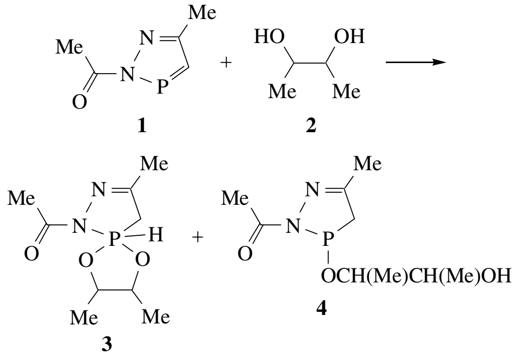
The reaction of 2-acetyl-5-methyl-2*H*-1,2,3-diazaphosphole with (*rac*)-butane-2,3-diol at temperatures below 0 °C leads to the formation of a hydrospirophosphorane containing both a diazaphospholene and a dioxaphospholane ring system and a β-hydroxy-alkoxy-1,2,3-diazaphospholene. On heating, these products form a hydrospirotetraoxaphosphorane, its tautomeric monocyclic β-hydroxyalkylphosphite and *N*-acetyl-*N′*-isopropylidene-hydrazine.

The interactions of heterocyclic two-coordinated phosphorus derivatives containing $\lambda^3\sigma^2$ P=C bonds with bifunctional nucleophilic reagents are poorly known. Here, we report on the interaction of 2-acetyl-5-methyl-2*H*-1,2,3-diazaphosphole **1** with (*rac*)-butane-2,3-diol **2**. Monitoring the reaction of a mixture of **1** and **2** in CH_2Cl_2 by ^{31}P NMR spectroscopy at –50 °C showed the appearance of signals at –33.3 ppm ($^1J_{PH}$ 807.9 Hz) and –40.2 ppm ($^1J_{PH}$ 731 Hz), which indicated the formation of hydrospirophosphoranes,[1] and signals at 109–114 ppm from the three-coordinated phosphorus atom in a 1,2,3-diazaphospholene ring with a P-OR substituent,[2] a signal at 236 ppm for diazaphosphole **1** was also present (Scheme 1). The simultaneous presence of 5-hydro-1-acetyl-3,7,8-trimethyl-1,2,5-diazaphospha-6,9-dioxaspiro[4.4]nonan-2-ene **3** and 3-(1′-methyl-2′-hydroxypropoxy)-2-acetyl-5-methyl-1,2,3-diazaphospholene **4** confirms the presence of the tautomeric equilibrium $P^{V} \rightleftharpoons P^{III}$ while the ratio of the tautomers [60:40] in the ^{31}P NMR spectrum shows this to be shifted towards the phosphorane. The examples of tautomeric equilibria between hydrospirophosphoranes and their β-hydroxyalkyl(aryl)phosphites or β-aminoalkyl(aryl)-phosphites have been described earlier.[3–7] The presence of two P^{V} signals in the ^{31}P NMR spectrum points to the chirality of PH spirophosphorane **3** and to the possibility of geometrical isomerism because the substituents can be in either *cis*- or *trans*-positions with respect to the hydrogen atom of the PH bond.[6,8,9] The presence of several ^{31}P NMR signals for the trivalent form of tautomers **4** is probably due to the presence of geometrical isomers: the OR substituent with its methyl groups can be *syn* or *anti* to the lone pair on the phosphorus.

Allowing the temperature of the reaction mixture to rise first to –30 °C and then to 0 °C leads to a gradual decrease in the intensity of the ^{31}P NMR signal at 236 ppm and to an increase in the resonances for compounds **3** and **4**. In comparison, the ^{31}P NMR spectrum of the reaction mixture at 30 °C shows the complete disappearance of signals at 236, –33.3 and –40.2 ppm and the appearance of new intense signals in the range from –31.5 to –32 ppm ($^1J_{PH}$ 791 and 825 Hz), typical of penta-coordinated phosphorus compounds, and at 136–137, 140–142, and 147 ppm, typical of tri-coordinated phosphorus derivatives.[6] A similar product mixture was observed in the ^{31}P NMR spectrum (CH_2Cl_2) of the product formed by stirring a mixture of compounds **1** and **2** at 5–10 °C. Keeping this reaction mixture in CH_2Cl_2 at 5–7 °C for several hours led to the formation of a suspension of small white crystals, which were difficult



Scheme 1

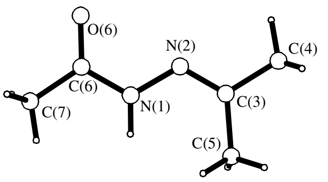
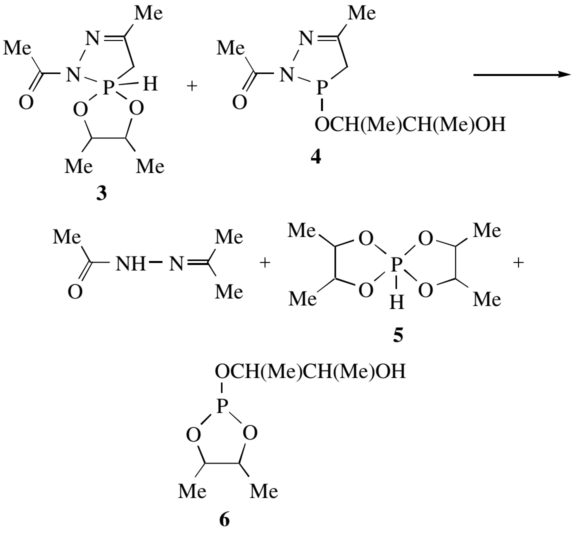


Figure 1 Molecular structure of *N*-acetyl-*N*′-isopropylidene-hydrazine. Selected bond lengths (Å): N(1)–N(2) 1.364(3), N(1)–C(6) 1.352(3), N(2)–C(3) 1.277(3), C(6)–C(7) 1.475(4), C(6)–O(6) 1.235(3).

to separate from solution.[†] Using benzene as a solvent for the reaction of diazaphosphole **1** with diol **2**, initially at 0–5 °C and then at 5–7 °C allowed us to isolate a crystalline compound,[‡] which gave a single-crystal X-ray diffraction[§] consistent with that of *N*-acetyl-*N*′-isopropylidene-hydrazine (Figures 1 and 2). It is well known that the reactions of 2*H*-1,2,3-diazaphospholes with excess alcohols result in diazaphospholene ring opening and formation of the corresponding hydrazones and phosphites.[10]

The mass-spectrometric analysis of the crystalline residue obtained after removing CH_2Cl_2 from the reaction mixture provided evidence for the ring-opening of diazaphospholene rings in **3** and **4** under the action of the diol (excess alcohol). The main quasimolecular ion $[MH]^+$ peaks in the mass spectra (chemical ionization) were at *m*/*z* 115, 209 and 251. Consequently, the masses of molecular ions of the compounds present in the reaction mixture were 114 (*N*-acetyl-*N*′-isopropylidene-hydrazine), 208 and 250. Based on a consideration of the fragment patterns for these ions, it follows that the molecular ion peak at *m*/*z* 208 corresponds to 5-hydro-2,3,7,8-tetramethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane **5** (δ_P –31 to –32 ppm) and its tautomeric form, phosphite 2-(1′-methyl-2′-hydroxypropoxy)-4,5-dimethyl-1,3,2-dioxaphospholane **6** (δ_P 136 to 137 ppm). The molecule with *m*/*z* 250 probably arises from the addition of water to compound **3**, which has a mass of 232. The formation and identification (by NMR spectroscopy, mass spectrometry and X-ray crystallography) of the reaction products allowed us to propose the following reaction scheme:



Scheme 2

Thus, the reaction of equimolar quantities of diazaphosphole **1** and butanediol **2** at temperatures below 0 °C proceeds with the formation of a mixture of hydrospirophosphorane **3** and diazaphospholene **4** in a tautomeric equilibrium. An increase in the temperature results in the fragmentation of the diazaphospholene ring in compounds **3** and **4** with the formation of

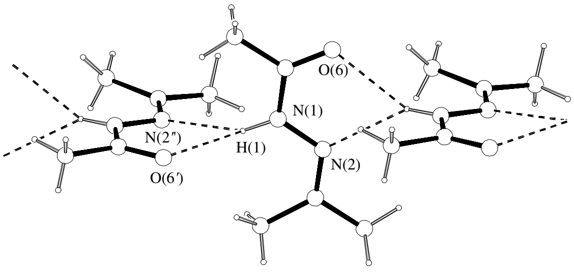


Figure 2 Hydrogen bonding in a crystal of *N*-acetyl-*N*′-isopropylidene-hydrazine. Parameters for intermolecular H-bonds: N(1)–H(1)···O(6′) (*x*, 1/2 – *y*, –1/2 + *z*), *d*[N(1)–H(1)] 0.91(2) Å, *d*[H(1)···O(6′)] 2.33(2) Å, *d*[N(1)···O(6′)] 3.088(2) Å, ∠N(1)H(1)O(6′) 140(2)°; N(1)–H(1)···N(2″) (1 – *x*, 1/2 + *y*, 1/2 - *z*), *d*[H(1)···N(2″)] 2.41(2) Å, *d*[N(1)···N(2″)] 3.204(2) Å, ∠N(1)H(1)N(2″) 148(2)°.

[†] The ^{1}H (300 MHz) and ^{31}P (122.4 MHz, 85% phosphoric acid) NMR spectra were obtained using a Varian Unity-300 NMR spectrometer.

Mass spectra were measured on a MAT-212 spectrometer (EI, 60 eV; emission, 0.1 mA), *m*/*z* (%). All reactions were carried out in an atmosphere of dry argon using dry solvents.

The interaction of diazaphosphole **1** *with butane-2,3-diol* **2**.

(*a*) A solution of 0.92 g (1.0 mmol) of butane-2,3-diol **2** in 5 ml of CH_2Cl_2 was added dropwise to a solution of 1.42 g (1.0 mmol) of diazaphosphole **1** at –30 °C. The ^{31}P NMR spectra of the reaction mixture gave δ: –40.2 ($^1J_{PH}$ 731 Hz), –33.3 ($^1J_{PH}$ 807.9 Hz), 109, 112.9, 114, 236. The mixture was stirred for 15 min to form a fine white suspension, which was difficult to separate from the liquid. The mixture was kept at 5–7 °C for 7–10 days, and the crystals of *N*-acetyl-*N*′-isopropylidene-hydrazine were removed and washed with CH_2Cl_2. ^{1}H NMR ($CDCl_3$) δ: 1.83 (s, 3H, *Me*C=), 1.98 (s, 3H, *Me*C=), 2.23 [s, 3H, *Me*C(O)], 8.67 (s, NH). ^{31}P NMR spectra of a liquid part of the reaction mixture, δ: –31.5 ($^1J_{PH}$ 791 Hz), –32 ($^1J_{PH}$ 825 Hz), 109.2, 113.3, 114.5, 135.5, 136, 137, 140.2, 141, 142, 147.

[‡] (*b*) Mixing a solution of 0.99 g (0.7 mmol) of diazaphosphole **1** in 5 ml of C_6H_6 with 0.63 g (0.7 mmol) of diol **2** at 0–5 °C and keeping the resulting reaction mixture at 5–7 °C for 2–3 days resulted in the formation of crystals of *N*-acetyl-*N*′-isopropylidene-hydrazine, mp 134 °C. Phosphorane **5** (mp 66–69 °C) was obtained after the evaporation of C_6H_6 from the liquid part of the reaction mixture.

[§] *X-ray crystallography of* N*-acetyl-*N′*-isopropylidene-hydrazine*. $C_5H_{10}N_2O$, *M* = 114.15, monoclinic, space group $P2_1/c$, a = 6.659(6), b = 13.236(6), c = 8.055(4) Å, β = 103.61(6)°, V = 689.9(8) Å^3, Z = 4, d_{calc} = 1.1 g cm^{-3}. Cell parameters and intensities of 720 independent reflections were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$-scan mode, $\theta \leq 24.62°$, using MoKα radiation with a graphite monochromator. Absorption correction was not applied. The structure was solved by a direct method using the SIR program[11] and refined by the full matrix least-squares using the MolEN program package.[12] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were solved from difference Fourier maps and refined isotropically in the last cycles. The final agreement factors are R_1 = 0.043 and wR_2 = 0.053 on 640 independent reflections with $F^2 \geq 3\sigma$. All calculations were performed on an Alpha Station 200 computer. The molecular structures were drawn with the PLATON program.[13]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 234488. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2004.

symmetrical hydrospirotetraoxaphosphorane **5**, hydroxyphosphite **6** and *N*-acetyl-*N*′-isopropylidene-hydrazine as the main products.

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