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Synthesis and EPR Characterization of “Phosphaverdazyl” Radicals

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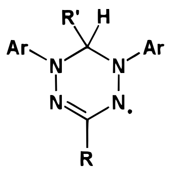
Two tetraazaphosphorines, 1,4,5,6-tetrahydro-1,5-dimethyl-3,6-diphenyl-1,2,4,5,6-tetrazaphosphorine 6-oxide (**4**) and 1,4,5,6-tetrahydro-1,5-dimethyl-3,3-diphenyl-1,2,4,5,3-tetrazaphosphorine 6-oxide (**6**), have been prepared and oxidized to form the corresponding stable “phosphaverdazyl” free radicals **5** and **7**, respectively. Solution EPR spectra of both radicals were obtained, from which phosphorus hyperfine coupling values of 5.2 G for **5** and ca. 0.2 G for **7** were determined by spectral simulation. The very small value of the latter *a*(P) was rationalized on the basis of orbital symmetry arguments and infers a planar geometry of the heterocycle. In contrast, the larger *a*(P) for **5** is indicative of a nonplanar geometry at the phosphorus atom, consistent with structures of related verdazyl radicals. These results represent the first systematic foray into so-called “heteroveradazyl” radicals and demonstrate the utility of incorporating phosphorus as an additional probe for EPR studies.

Although most free radicals are transient, highly reactive species, several families of stable free radicals are known.[1] Many of these examples have their unpaired electron delocalized over two or more nitrogen and/or oxygen atoms, such as the nitroxides, nitronyl nitroxides, and hydrazyl radicals.[2] Verdazyl radicals (**1**, **2**) are another such example.[3] Over the past three decades, synthetic routes to verdazyl radicals with a range of substituents on the nitrogen and carbon ring atoms have been established. The effects of substituents on the basic electronic structure and reactivity of the verdazyl ring are known to be minor. However, virtually nothing is known of the consequences of more drastic structural perturbations, i.e., alteration of the ring constituents.[4,5] Given the myriad uses of stable radicals, e.g., as spin probes,[6] as additives for “living” free radical based polymerizations,[7] and as components of solid state materials with conducting[8] or magnetic[9−13] properties, the synthesis and properties of new stable radicals comprise a research area of considerable interest. In this context we are embarking on a program of study aimed at preparing so-called “heteroverdazyls” (**3**) in which the basic verdazyl structure is maintained while the atoms in the 6 and 3 positions of the ring (X and Y, respectively) are altered. In this paper we report on our initial studies concerning the synthesis and EPR characterization of two “phosphaverdazyl” radicals in which a single phosphorus atom is incorporated into the heterocyclic system.



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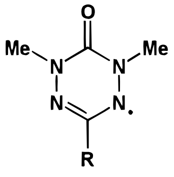

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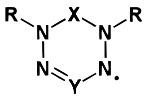

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The two phosphaverdazyl radicals were prepared as shown in eqs 1 and 2. The 1,2,4,5,6-tetrazaphosphorine **4** was prepared using a modified form of a procedure reported by Markovskii et al.[14] Thus, the bis(1-methyl hydrazide) of phenylphosphonic acid[15] was reacted with trimethyl orthobenzoate to give the 1,2,4,5-tetraza-6-phosphorine **4** in 50% yield (Equation 1). Using a similar methodology, the reaction of the bis(1-methylhydrazide) of carbonic acid[16] with trichlorodiphenylphosphorane in the presence of triethylamine produced the 1,2,4,5-tetraza-3-phosphorine **6** in 42% yield (Equation 2). Compounds **4** and **6** correspond to the reduced forms of the radicals **5** and **7** respectively (vide infra). The analogues of **4** and **6** (i.e. reduced forms) of parent verdazyls **1** and **2** are generally easily oxidized in air to the corresponding radicals. In contrast, **4** and **6** appear to be completely stable in solution and the solid state to air oxidation, thereby indicating that skeletal substitution of carbon by phosphorus has a significant effect on reactivity.

A variety of oxidants were used in attempts to prepare the phosphaverdazyl radicals. Literature methods for the synthesis of verdazyls of general structure **1** or **2** include ferricyanide, lead oxide, and substituted hydrazines.[2−4] In our hands, however,

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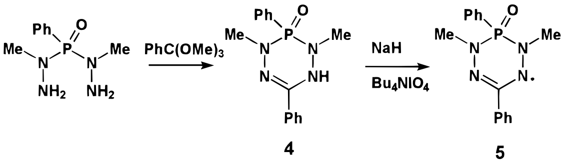
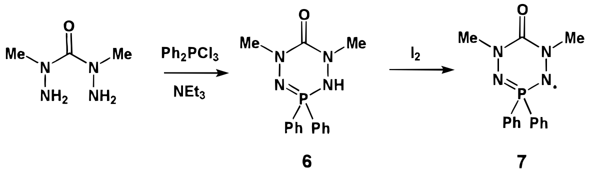


(1)



(2)

these reagents either did not react at all with **4** or **6** or produced EPR-active solutions which decayed within minutes. We therefore investigated other methods for the synthesis of radicals **5** and **7**. The 6-phosphorine **4** could be quantitatively deprotonated (NaH, THF) to generate oxygen-sensitive solutions of the corresponding anion and then oxidized with tetrabutylammonium periodate to produce red ($\lambda_{\max}$ 585 nm) solutions of 6-phosphaverdazyl **5**. The 3-phosphaverdazyl radical was most efficiently prepared by treating **6** with iodine in benzene to generate red/orange ($\lambda_{\max}$ 525 nm) solutions of radical **7**. The radicals could be isolated by evaporating the solvent, dissolving the residue in a solvent in which the salt byproducts are insoluble (typically benzene), and evaporating the filtrate to dryness. In the solid state both radicals are red-brown semisolids, and they appear to be indefinitely stable when stored as solids at −30 °C. At room temperature or in solution, however, **5** and **7** decompose over a period of 1−2 weeks, primarily back to **4** and **6**, respectively, with substantial amounts of (unidentified) byproducts also generated in the decomposition of **7**. Treatment of freshly prepared solutions of the radicals with ascorbic acid quantitatively regenerates the corresponding leuco compounds, thereby providing evidence that the observed EPR signals are in fact due to structures **5** and **7**.

The EPR spectra of **5** and **7** are shown in Figure 1. Spectral simulations afforded the hyperfine coupling constants given in Table 1; also listed are the hyperfine data for the 1,5-dimethyl-3-phenyl-6-oxoverdazyl radical (**2**, R = Ph),[17] an appropriate “reference” for both phosphorus-containing radicals. Comparison of the EPR parameters of the three species reveals some interesting trends. The hyperfine parameters of **7** and **2** are nearly identical; more striking is the negligible (within the resolution limits provided by the spectrum; estimated to be ca. 0.2 G) hyperfine coupling to the phosphorus atom in **7**, particularly compared to the larger a(P) value observed in **5**. At first glance this result seems somewhat counterintuitive, given that in both **5** and **7** the phosphorus atoms are adjacent to nitrogen centers bearing substantial spin density.

Verdazyl derivatives of type **2** (i.e., bearing a carbonyl group at C6) are known to have essentially planar structures. Extended Hückel calculations on **2** (R = H) using structural parameters taken from crystallographically characterized derivatives of **2**[18,19] indicate that the unpaired electron resides in a delocalized π-molecular orbital (Figure 2a). One of the two nodal planes in this orbital intersects C3 and C6, thereby precluding direct coupling to these atoms at the HMO level. By analogy, the very small a(P) value in **7** is strongly suggestive of a planar structure, at least at the NPN moiety (vide infra). The inferred geometry at phosphorus is in fact reminiscent of the structures observed in some cyclotriphosphazenes.

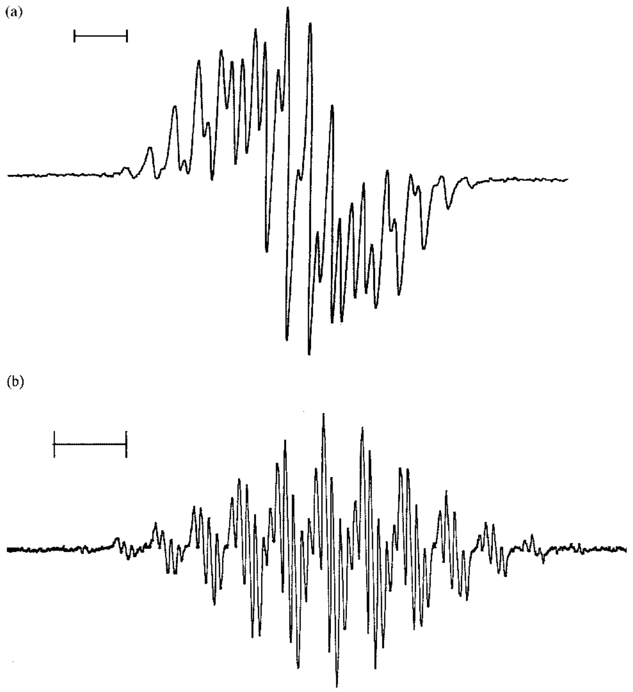


Figure 1. Solution EPR spectra of (a) **5** and (b) **7**. Both spectra were obtained in benzene solution at ambient temperature. The horizontal lines represent a 10 G scale.

Table 1. EPR Parameters for Selected Verdazyl Radicals[a]

	5	**7**	**2** (R = Ph)[b]
g value	2.0038	2.0038	2.0037
$a(N_{1,5})$	4.4	5.3	5.3
$a(N_{2,4})$	6.4	6.4	6.5
$a(CH_3)$	4.6	5.4	5.3
a(P)	5.2	0.2	

[a] Hyperfine coupling constants are given in gauss. $N_{1,5}$ are the three-coordinate nitrogen atoms and $N_{2,4}$ are the two-coordinate nitrogen atoms. [b] Reference 17.

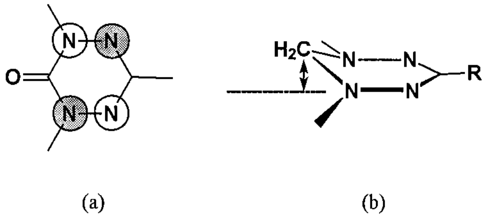


Figure 2. (a) Singly occupied molecular orbital of **2**. (b) Schematic geometry of **1** (R = Ar = Ph, R′ = H) indicating the nonplanar geometry of the methylene carbon.

Why, then, is a(P) larger in **5**, particularly given the fact that it is formally not part of the conjugated π system? The planarity in **2** (and, as described above, presumably **7**) arises from interaction of the heterocyclic π system with the C=O π* orbital (i.e., amide-type resonance of N1 and N5 with the carbonyl group). In contrast, verdazyl radicals lacking the carbonyl group at C6 (i.e., **1**) have no such orbitals with which to stabilize the planar geometry; thus, in 1,3,5-triphenylverdazyl (**1**; R = Ar = Ph, R′ = H) the methylene carbon is 0.62 Å above the plane of the rest of the verdazyl ring (Figure 2b).[20] Similarly, in **5** there are no exocyclic orbitals of suitable symmetry to strongly overlap with the verdazyl π framework. The resulting nonplanar

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geometry permits mixing of the σ and π systems, thereby leading to spin leakage onto the phosphorus atom. It is worth noting that the magnitude of observed coupling to phosphorus is relatively small; coupling constants of several hundred gauss have been observed in phosphoranyl radicals with spin density directly on the phosphorus.[21,22] The present systems, particularly with respect to the magnitude of a(P) in **5**, more closely resemble other related phosphorus−sulfur−nitrogen based heterocyclic radicals.[23−25]

In summary, we have prepared two phosphorus-containing verdazyl derivatives, including the heretofore unknown 3-phosphaverdazyl **7**, and characterized each by EPR spectroscopy. The introduction of another spin-active nucleus (^{31}P) into the odd-electron framework has provided additional means of probing general structural features of these novel systems. It is interesting to speculate on the possible substituent effects at the phosphorus atom on ring structure, as such behavior has been noted.[26] Unfortunately, our efforts to obtain crystals of **5** and **7** suitable for crystallographic studies have been thwarted. We are currently pursuing other derivatives of these systems; by altering the ring substituents it is hoped that structural data will become possible. Further studies on the present species, including variable temperature EPR and electrochemical measurements of redox potentials, are underway and will reported in a future publication.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. Solvents were dried and distilled under argon prior to use (CH_2Cl_2, CaH_2; benzene, toluene, and THF, Na/benzophenone). All reagents were purchased from Aldrich and used as received. Phenylphosphonic acid bis(1-methylhdriazide)[15] and carbonic acid bis(1-methylhydrazide)[16] were prepared according to literature methods. NMR spectra were recorded on a Bruker AMX360 spectrometer. EPR spectra were recorded on a Varian E6S instrument, and the spectra so obtained were simulated using the SIMFONIA program contained in the WINEPR suite of programs provided by Bruker. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, BC, Canada. Extended Hückel MO calculations were carried out using the HyperChem suite of programs.

Synthesis and Characterization of 1,2,5,6-Tetrahydro-1,5-dimethyl-3,6-diphenyl-1,2,4,5,6-tetrazaphosphorine 6-Oxide (4). A solution of phenylphosphonic acid bis(1-methylhydrazide) (1.70 g, 7.95 mmol), trimethyl orthobenzoate (1.36 mL, 7.95 mmol), and $BF_3{\cdot}Et_2O$ (5 drops) was stirred for 16 h in 50 mL of CH_2Cl_2. The solvent was then removed and the residue chromatographed (SiO_2, 1:1 CH_2Cl_2:CH_3CN) to give **4**, yield 1.20 g (50%). ^{1}H NMR ($CDCl_3$): δ 7.3−7.7 (m, 10H), 6.3 (d, 1H, J = 8.7 Hz), 3.23 (d, 3H, J = 6.0 Hz), 2.87 ppm (d, 3H, J = 10.3 Hz). ^{13}C NMR ($CDCl_3$): δ 140.1 (d, J = 9.3 Hz), 132.3 (d, J = 3 Hz), 132.0, 131.2 (d, J = 10 Hz), 130.0, 128.5, 128.3, 126.3, 37.2 (d, 4.5 Hz), 37.0 ppm (d, 4 Hz). ^{31}P NMR ($CDCl_3$): δ 12.8 ppm. Anal. Calcd for $C_{15}H_{17}N_4OP$: C, 60.00; H, 5.71; N, 18.66. Found: C, 59.85; H, 5.65; N, 18.40.

Synthesis and Characterization of 1,2,5,6-Tetrahydro-1,5-dimethyl-3,3-diphenyl-1,2,4,5,3-tetrazaphosphorine 6-Oxide (6). A solution of Ph_2PCl_3 (prepared from Ph_2PCl and SO_2Cl_2 in hexanes) (1.90 g, 6.52 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of carbonic acid bis(1-methylhydrazide) (0.81 g, 6.85 mmol) and excess triethylamine (3.0 mL) in 25 mL of CH_2Cl_2. After the reaction mixture was stirred for 2 h, the light brown solution was extracted with aqueous sodium carbonate, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography (SiO_2, CH_3CN) to give **5** as a very hygroscopic solid, yield 820 mg (42%). The solid was dried by being stored over P_2O_5 under vacuum. ^{1}H NMR ($CDCl_3$): δ 7.9−7.4 (m, 10H), 6.0 (d, 1H, J = 19 Hz), 3.0 (s, 3H), 2.8 ppm (s, 2H). ^{13}C NMR ($CDCl_3$) δ 165.4 (d, J = 2 Hz), 132.1 (d, J = 10 Hz), 132.0, 130.5 (d, J = 128 Hz), 128.2 (d, J = 11 Hz), 44.3 (d, J = 2 Hz), 40.7 ppm. ^{31}P NMR ($CDCl_3$): δ 24.1 ppm. Anal. Calcd for $C_{15}H_{17}N_4OP$: C, 60.00; H, 5.71; N, 18.66. Found: C, 59.71; H, 6.03; N, 18.52.

Oxidation of 4 to "6-Phosphaverdazyl" 5. A solution of phosphorine **4** (330 mg, 1.10 mol) in THF (25 mL) was added via dropping funnel to a slurry of NaH (30 mg, 1.25 mmol) in 20 mL of THF. The solution immediately turned bright yellow/orange, and the color change was accompanied by hydrogen evolution. After 15 min of stirring at room temperature, a solution of $Bu_4N^+IO_4^-$ (480 mg, 1.11 mmol) in 30 mL of THF was added, causing the solution to immediately turn deep magenta/red. The reaction mixture was stirred for 1 h and then evaporated to near dryness. Benzene was added, and the insoluble byproducts were filtered off, giving a clear deep red filtrate of **5**, which was evaporated to give a red-brown solid.

Oxidation of 6 to "3-Phosphaverdazyl" 7. A solution of iodine (97 mg) in 10 mL of benzene was added to a solution of phosphorine **6** (220 mg, 0,73 mmol) and NEt_3 (0.1 mL) in 50 mL of benzene. The dark red/purple solution was stirred for 2 h. The off-white filtrate so obtained was filtered off under argon, and the filtrate was evaporated and pumped overnight to remove residual iodine, giving a dark red/brown solid sample of **7**.

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