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N - tert - BUTYL - N - PHOSPHONYLOXYAMINYLS
A NEW CLASS OF PERSISTENT RADICALS

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SUMMARY : The title radicals have been generated by hydrogen abstraction from the corresponding hydroxylamines in benzene solution. In the absence of oxygen these radicals are extremely persistent and their esr data (a_N14, a_N15 and a_C13, determined without isotopic enrichment) are characteristic of a Π electronic configuration.

The number of reports on persistent organic-free radicals different from nitroxides or hydrazyls underwent explosive growth since Ingold clearly stated that the kinetic stability of a radical can be achieved by steric crowding of the radical center[2]. However while the list of persistent carbon-centered radicals is now rather long[2] only a few heteroatom-centered persistent radicals have been reported[3].

In this note we present esr data of a new class of persistent aminyl radicals bearing a phosphorus group : ${}^{t}Bu\text{-}\dot{N}\text{-}O\text{-}P(O)L_2$. Radicals 1., 2., 3. and 4. (Table I), were generated in benzene by hydrogen abstraction from the protic parent compounds (t-Bu N(H)OP(O)L_2) using t-butoxyl radicals produced (a) by thermolysis at ca 30°C of di-t-butyl peroxyoxalate (DPBO) or (b) by u.v. photolysis of di t-butyl peroxide.

If the foregoing procedures, were carried out under oxygen-free conditions, using thoroughly degassed benzene and reagents, high concentrations of N-tert-butyl-N-phosphonyloxyaminyl radicals could be generated. The radicals obtained in this way, were extremely persistent, showing no appreciable decay over many days at room temperature.

When t-butylbenzene solutions of radicals 1.-4. were cooled to -30°C, the esr signals rapidly faded and they reappeared on raising back to room temperature. This cycle was completely reversible and from this observation radicals 1.-4. were found to be in equilibrium with their corresponding dimers in solution. This finding is very interesting for the carbon analog[3b] 5. (Table I) shows no sign of dimerization to form a diamagnetic product at temperature down to -80°C.

When contacted with oxygen the radicals 1.-4. were definitely less persistent, especially when they were generated by photolysis. Moreover, during photolysis relatively intense spectra of ter-butoxy-tert-butyl nitroxide and di tert-butyl nitroxide could be observed.

The esr parameters for the four radicals studied in this work are listed in Table I.

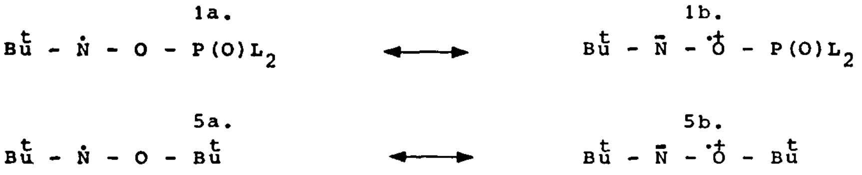
Table I. ESR Parameters for Me$_3$C$\dot{N}$OP(O)L$_2$ Radicals$^{(a)}$

Radical	L	a_N^{14}	$aC\alpha^{13}$	$aC\beta^{13}$	a^{other}	
1.	EtO	14.9	9.9	8.0	20.8(N^{15})	2.0047
2.	ϕO	15.0	9.5	8.2	-	2.0047
3.	Et	14.9	9.7	7.8	-	2.0047
4.	ϕ	15.0	10.0	8.0	1.0(P^{31}) 21.2(N^{15})	2.0047
$\overset{t}{Bu}\dot{N}O\overset{t}{Bu}$, 5.^{3b}		14.1	9.1	7.0	11.4(O^{17})	2.0049

(a) In benzene at 30°C. Hyperfine splittings (hfs) are given in gauss.

The spectra of all radicals were sufficiently intense for the C^{13} satellites to be observed and the C^{13} hfs to be determined as well as the N^{15} hfs for 1. and 4. .

Radical 4. was the only case leading to a small phosphorus hfs observation. Because of the electron- withdrawing effect of the phosphonyl group, the dipolar canonical structure 1b. will contribute less to the resonance hybrid of 1., than does the corresponding dipolar canonical structure 5b. to the hybrid of 5.



1a. 1b.

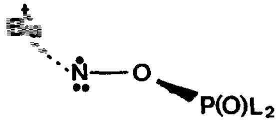
$$\overset{t}{\mathrm{Bu}} - \dot{\mathrm{N}} - \mathrm{O} - \mathrm{P(O)L_2} \longleftrightarrow \overset{t}{\mathrm{Bu}} - \overset{-}{\mathrm{N}} - \overset{\cdot +}{\mathrm{O}} - \mathrm{P(O)L_2}$$

5a. 5b.

$$\overset{t}{\mathrm{Bu}} - \dot{\mathrm{N}} - \mathrm{O} - \overset{t}{\mathrm{Bu}} \longleftrightarrow \overset{t}{\mathrm{Bu}} - \overset{-}{\mathrm{N}} - \overset{\cdot +}{\mathrm{O}} - \overset{t}{\mathrm{Bu}}$$

Conjugative electron delocalization, is therefore less important in 1. than 5., and the g values and nitrogen hfs for the four radicals (1. - 4.) are intermediate between those of di-alkylaminyls[4] and those of alkoxyalkylaminyls[5]. A high ρ_N value for radicals 1. - 4. is indicated by the magnitude of their N^{14} and N-ter-butyl C^{13} hfs (Table I) as well as by their behavior towards dimerization (ρ_N should be greater than 0.7 a value estimated from O^{17} in the case of 5.).

The lack of resolved phosphorus hfs for the radicals 1., 2., 3., and the small value observed for the radical 4., suggest that these radicals adopt the following staggered conformation A,



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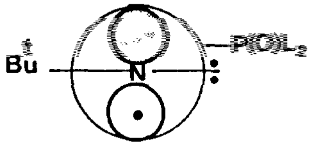
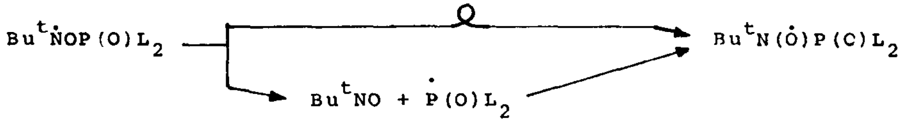


A

which has been previously proposed for the N-2,4,6 - tri - t - buty phenyl - O - phosphonyl aminyls[6].

Moreover, the staggered conformation (A) is consistent with the high persistence of the radicals 1.-4., since it is not consistent with a β scission which would require the overlap of the semioccupied orbital with the O-P(O)L$_2$ bond[9]



The great persistence of the N-tert-butyl-N-phosphonyloxyaminyls stands in contrast to the behavior of the trialkylsilytrialkylsilyloxyaminyls 6.which are unknown since they rearrange to the bis (trialkylsilylnitroxide) even at -80°C, presumably via an intramolecular 1,2 migration[10].

Since both silicon and phosphorus have low-lying vacant d orbitals which could accomodate the unpaired electron in the transition state of an intramolecular 1,2 migration it seems likely that the different persistence of radicals 1. - 4. and 6., is a consequence of different conformational preference. Like the analogs Bu^{t}ṄCH$_2$SiEt$_3$[11] and F$_2$ĊOSiEt$_3$[12] the transient radical 6. is believed to adopt an eclipsed conformation.

Chemical studies are in progress to isolate the dimers of radicals 1. to 4. and to investigate the thermodynamic parameters for the equilibria.

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