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# ELECTRON SPIN RESONANCE STUDY OF NEW N-ALKOXYPHOSPHORAMIDYL AND N-ALKYLPHOSPHORAMIDYL RADICALS

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Summary : The title radicals have been generated and studied by esr spectroscopy. The N-alkoxyphosphoramidyl radicals are formed by hydrogen abstraction from the corresponding protic parent compounds while the N-alkylphosphoramidyls can be generated by photolysis of cyclopropane solution of the corresponding N-bromo derivatives. Both types of radical exhibit esr data characteristic of a π electronic configuration.

The electronic structure of amidyl radicals $X\dot{N}R$ (X = RCO, $RSO_2$) and the corresponding N-alkoxyamidyls $X\dot{N}OR$ are of considerable interest and these radicals have been studied recently by both spectroscopic[2] (ESR) and chemical[3] techniques.

Esr evidence strongly favours a π ground electronic configuration for these radicals, however, the trends in isotropic nitrogen hyperfine splitting constants (hfscs) and g values exhibit some apparent anomalies which are not yet well-understood.

In this communication we report the first esr study of a series of simple N-alkoxyphosphoramidyl and their corresponding nitroxides as well as the esr data for the N-t-butyl phosphoramidyl radical $t\text{-Bu}\dot{N}P(O)(OEt)_2$.

N-alkoxyphosphoramidyls : the title radicals the spectral parameters of which are listed in Table I were generated by hydrogen abstraction from the protic parent compound using t-butoxyl radicals produced (a) by thermolysis at *ca* 30°C of di-t-butyl peroxyoxalate (DBPO) in benzene or (b) by u.v. photolysis of di-t-butyl peroxide in cyclopropane.

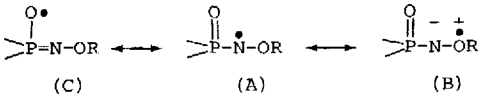
These radicals are quite long-lived and thus easily detected (in cyclopropane at 0°C radical **1f** decays by a first order process with a half-life of 2.7 s). The spectroscopic parameters are as expected if the unpaired electron occupies a π type orbital.

Table I : Hyperfine Splitting Constants (Gauss) and g values of N-alkoxyphosphoramidyls $RO\dot{N}P(O)L_2$ [(a)]

| R | L | $A_N$ | $A_P$ | $A_{H(R)}$ | g | |
|---|---|---|---|---|---|---|
| Me | EtO | 11.2 | 27.0 | 4.5(3H) | 2.0055 | **1a** |
| n-Hept | EtO | 10.7 | 25.0 | 3.7(2H) | 2.0055 | **1b** |
| Ø$CH_2$ | EtO | 11.5 | 26.5 | 3.7(2H) | 2.0054 | **1c** |
| iPr | EtO | 11.0 | 24.8 | 3.2(1H) | 2.0055 | **1d** |
| t-Bu | EtO | 11.5 | 26.0 | | 2.0055 | **1e** |
| t-Bu | Et | 11.7 | 23.4 | | 2.0055 | **1f** |
| t-Bu | ØO | 11.0 | 27.0 | | 2.0057 | **1g** |
| t-Bu | ØO | 11.2 | 21.5 | | 2.0057 | **1h** |
| $CH_3ONCH_3$[4] | | 14.3 | | 2.62($CH_3O$) | 2.0048 | |

(a) Generated in benzene (30°C) by hydrogen abstraction from the parent N-alkoxyphosphoramide using t-butoxyl radicals obtained by thermolysis of DBPO.

From table I it can be seen that the nitrogen and the hydrogen (from the N-alkoxy group) hfscs of the N-alkoxyphosphoramidyls are respectively ca 3G smaller and 1.5 to 2.0 G larger than those observed for alkoxyaminyls. These differences are probably due mainly to the strong electron withdrawing effect of the phosphonyl group which increases the weight of the canonical structure (B) relative to that of (A).



although a small contribution from the structure (C) cannot be excluded at present.
The related phosphonyloxyaminyl radicals can be generated by hydrogen abstaction from the parent O-phosphonyl hydroxylamines. Thus thermolysis of DBPO in the presence of O-diethoxyphosphonyl N-t-butyl hydroxylamine in benzene at 25 to 30°C leads to the observation of the corresponding phosphonyloxyaminyl :

$t\text{-}Bu\dot{N}OP(O)(OEt)_2$

$a_N14 = 15.0$ G, $a_N15 = 21.0$ G

$a_{C_\alpha}13 = 10.0$ G, $a_{C_\beta}13 = 8.0$ G

$a_P \simeq 0$ G , $g = 2.0047$

The esr spectral data may be compared with those of acyloxyaminyls[5] or alkylsufoxyloxyaminyls[2e] and are very similar. Delocalization of the unpaired electron onto oxygen represented by a contribution from structure (D) $(tBu\bar{N}-\overset{+}{\dot{O}}P(O)(OEt)_2)$ is now negligible because of the powerful electron withdrawing effect of the phosphonyl group and the nitrogen splitting closely resembles that for dialkylaminyl radicals. Furthermore, the lack of phosphorus coupling suggests a coplanar arrangement of the N-O-P fragment.

Phosphonyl alkoxy nitroxides - When the N-alkoxyphosphoramidyl radicals were generated in solvents which had been incompletely degassed another signal was detected initially and this second spectrum decayed as that of the phosphoramidyl radical increased in intensity with time. The initial spectrum was not detected when the solution was completely oxygen free and hence we attribute this signal to the phosphonyl alkoxynitroxide, formed by reaction of N-alkoxy-phosphoramidyl with small amounts of adventitious oxygen. The spectral parameters of this class of radical hitherto unreported, are listed in Table II.

Table II - Hyperfine Splitting Constants (Gauss) and g values of N-alkoxy phosphonylnitroxides $RON(\dot{O})P(O)L_2$

| R | L | $A_N$ | $A_P$ | | g | |
|---|---|---|---|---|---|---|
| Me | EtO | 17.0 | 12.5 | 1.0(3H) | 2.0055 | **1'a** |
| n-Hept | EtO | 16.5 | 9.7 | 0.7(2H) | 2.0055 | **1'b** |
| Ø$CH_2$ | EtO | 16.7 | 10.0 | 0.2(2H) | 2.0054 | **1'c** |
| iPr | EtO | 16.0 | 7.0 | | 2.0055 | **1'd** |
| t-Bu | EtO | 15.2 | 6.2 | | 2.0055 | **1'e** |
| t-Bu | Et$^{(i)}$ | 17.6 | 5.5 | | 2.0056 | **1'f** |
| t-Bu | ØO | 14.3 | 6.5 | | 2.0058 | **1'g** |
| t-Bu | Ø | 16.4 | 7.7 | | 2.0057 | **1'h** |

(i) generated in benzene from the corresponding phosphoramidyl by addition of t-butyl hydroperoxide.

Comparison of the $A_N$ values given in Table II with those of simple alkyl alkoxy nitroxides ($A_N \simeq$ 27-30 G) shows that the nitrogen hfscs are markedly larger for the latter. However for simple alkyl phosphonyl nitroxides $RN(\dot{O})P(O)L_2$ the $A_N$ values are about ca 5G smaller[6] than those observed for simple dialkyl nitroxides and thus the $A_N$ values for the N-alkoxy phosphonyl nitroxides might be expected to lie in the range 22 to 25 G. A relatively complex interplay of steric and electronic effects may be invoked to explain the observed discrepancy but we feel that detailed speculation is unjustified at this time.

Finally, we very recently found that simple phosphoramidyl radicals $RNP(O)L_2$ can be generated by photolysis of cyclopropane solution of the corresponding N-bromo derivative directly in the esr cavity at -100°C. The esr parameters[7] ($t\text{-}Bu\dot{N}P(O)(OEt)_2$ $a_N$= 13.0 G, $a_P$ = 35.0 G, $a_H$(tBu) = 0.67 G (from computer simulation)), g = 2.0052) are very similar with those of sulfonamidyl radicals.

Work is in progress to further elucidate the structure of the complete series (Table III) of phosphonyl aminyl radicals now observed in our laboratory.

Table III

| Radical | $a_N$ | $a_P$ | g |
|---|---|---|---|
| $t\text{-}Bu\dot{N}P(O)(OEt)_2$. | 13.0 | 35.0 | 2.0052 |
| $t\text{-}BuO\dot{N}P(O)(OEt)_2$ | 11.5 | 26.0 | 2.0055 |
| $t\text{-}Bu\dot{N}OP(O)(OEt)_2$ | 15.0 | $\simeq$ 0 | 2.0047 |
| $t\text{-}BuN(\dot{O})P(O)(OEt)_2$ | 10.0 | 12.2 | 2.0065 |
| $t\text{-}BuON(\dot{O})P(O)(OEt)_2$ | 15.2 | 6.2 | 2.0055 |
| $t\text{-}BuN(\dot{O})OP(O)(OEt)_2$ | 27.1 | $\simeq$ 0 | 2.0055 |

## References and notes

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7 - These e.s.r. data are in agreement with a π structure defined as one in which the unpaired electron resides in an $N_{2p}$ orbital perpendicular to the CNP plane. While it seems reasonable to expect amidyls to be "twisted" about the C(O)-N bond[2c] in order to reconcile the π structure and the favourable nitrogen lone-pair conjugation, conformation about the P(O)-N bond in phosphoramidyls appears more difficult to determine owing to the variou possibilities of $p_\pi$-$d_\pi$ interactions involving both the nitrogen lone pair and the semi occupied orbital.

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