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Preliminary communication

ORGANOSILYL SUBSTITUTED PHOSPHORANYL RADICALS

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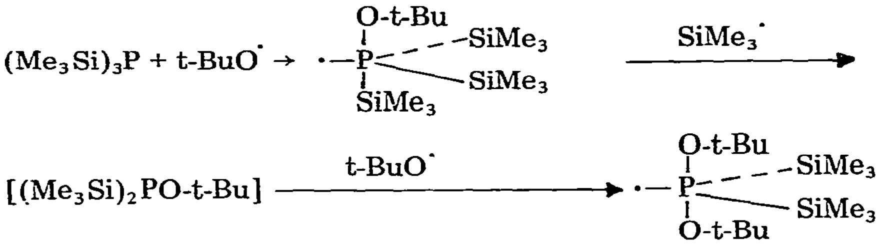
Summary

Organosilyl substituted phosphoranyl radicals were generated by the addition of t-butoxyl radical to $(Me_3Si)_3P$ and $MeP(SiMe_2)_n$ (n = 5,6) and studied by ESR spectroscopy. $(Me_3Si)_3\dot{P}O$-t-Bu, the initial phosphoranyl radical formed from $(Me_3Si)_3P$, undergoes α-cleavage and formation of a second radical species, $(Me_3Si)_2\dot{P}(O\text{-t-Bu})_2$. Kinetic measurements of the decay of these phosphoranyl radicals are reported.

Phosphoranyl radicals, $R_3\dot{P}O$-t-Bu, have previously been generated by the addition of t-butoxy radical to tricoordinate phosphines, and have been studied by electron spin resonance (ESR) spectroscopy [1—4]. They are known to have a trigonal bipyramidal structure with two axial and two equatorial ligands [5], and to undergo α- or β-cleavage involving loss of $R^\cdot$ or t-butyl radical, respectively. We report here the formation and ESR spectra of phosphoranyl radicals from three organosilylphosphines.

The compounds studied were tris(trimethylsilyl)phosphine (I) and the cyclic phosphasilanes, $MeP(SiMe_2)_n$ (n = 4, 5, 6) [6]. A solution of the phosphine, di-t-butyl peroxide and cyclopropane (1/1/5 v/v/v) at −100°C was irradiated with a super pressure Hg UV source while the solution was in the ESR cavity. With I, an ESR signal consisting of a doublet with a(P) 452 G is immediately observed. However, after several minutes of irradiation a second doublet with a(P) 574 G appears (Fig. 1). Silicon satellites (a(Si) 65.8 G) are observed about the doublet with 452 G splitting but not with the doublet of larger splitting constant (Fig. 2).

The initial doublet of 452 G is most likely due to the primary adduct, $(Me_3Si)_3\dot{P}O$-t-Bu (eq. 1). The observed silicon satellites of 65.8 G are probably due to the axial silicon, with the equatorial silicon atoms having a coupling less than the line width of approximately 8 G. By comparison, the t-butoxy radical adduct of phosphine, t-$BuO\dot{P}H_3$, exhibits an axial hydrogen coupling constant of 139.6 G while the equatorial hydrogens have a coupling constant of 10.8 G.



(1)

The secondary doublet of 574 G is probably due to the t-butoxy radical adduct of (Me$_3$Si)$_2$PO-t-Bu which arises from α-cleavage of the primary adduct. The trimethylsilyl radical was not observed under our reaction conditions. According to apicophilicity rules [7,8], the trigonal bipyramidal structure of (Me$_3$Si)$_2\dot{P}$(O-t-Bu)$_2$ should have axial t-butoxy groups and equatorial trimethylsilyl groups. This secondary phosphoranyl radical, (Me$_3$Si)$_2\dot{P}$(O-t-Bu)$_2$, would thus nicely account for the absence of silicon satellites about the doublet of 574 G.

Kinetic measurements of the decay of these phosphoranyl radicals have been obtained and are consistent with the above assignments. At −100°C (Me$_3$Si)$_3\dot{P}$O-t-Bu

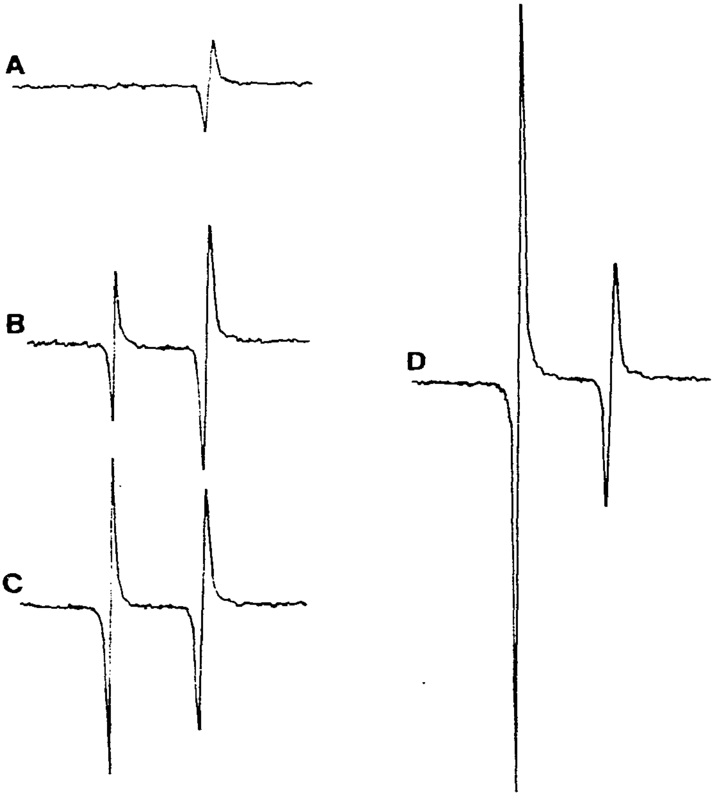


Fig. 1. Low-field half of the ESR spectrum obtained by photolysis of (Me$_3$Si)$_3$P and di-t-butyl peroxide at −100°C: A, immediately after the start of photolysis only the doublet a(P) 452 G is observed; B, 3 minutes after the start of photolysis the doublet a(P) 574 G is also observed; C, 5 minutes; D, 15 minutes.

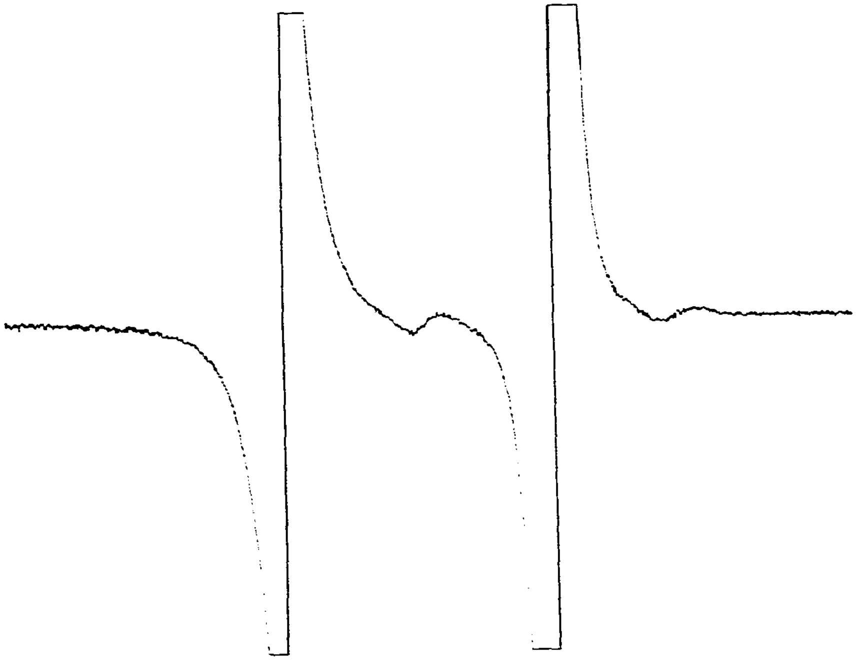


Fig. 2. Low-field half of the ESR spectrum obtained by photolysis of $(Me_3Si)_3P$ and di-t-butyl peroxide at −100°C showing the ^{29}Si satellites (a(Si) 65.8 G) about the doublet of 452 G.

disappeared instantaneously on shuttering the light while $(Me_3Si)_2\dot{P}(O\text{-t-Bu})_2$ decayed with first-order kinetics (Fig. 3). At −120°C both $(Me_3Si)_3\dot{P}O\text{-t-Bu}$ and $(Me_3Si)_2\dot{P}(O\text{-t-Bu})_2$ decayed with first-order kinetics when the light was shuttered. The decay rates and half-lives are summarized in Table 1. As expected [3,4] the phosphoranyl radical species with two t-butoxy substituents, $(Me_3Si)_2\dot{P}(O\text{-t-Bu})_2$, is much more stable than the initial t-butoxy adduct, $(Me_3Si)_3\dot{P}O\text{-t-Bu}$.

When a solution of $MeP(SiMe_2)_5$ was irradiated under the same conditions, a doublet (a(P) 407 G) was immediately observed. This signal grows in intensity somewhat with irradiation but no additional resonances are observed. Using analogous conditions the spectrum of $MeP(SiMe_2)_6$ also exhibits only one doublet (a(P) 403 G). However no radical species were detected for $MeP(SiMe_2)_4$ under similar conditions. Evidently the angle strain caused by an equatorial five-membered ring in the trigonal bipyramidal structure of $t\text{-BuO(Me)}\dot{P}(SiMe_2)_4$ results in its immediate decomposition. Pseudorotation which would relieve angle strain but result in a structure with an apical silicon atom is presumably disfavored.

The phosphorus coupling constants observed for the silicon-substituted phosphoranyl radicals described above are significantly less than those reported for typical phosphoranyl radicals previously observed (Table 2). The decrease in phosphorus splittings for the organosilicon-substituted radicals may result from decreased electronegativity of silicon compared to the other substituents which have been studied, leading to lower *s*-orbital contribution in the orbital containing the odd electron.

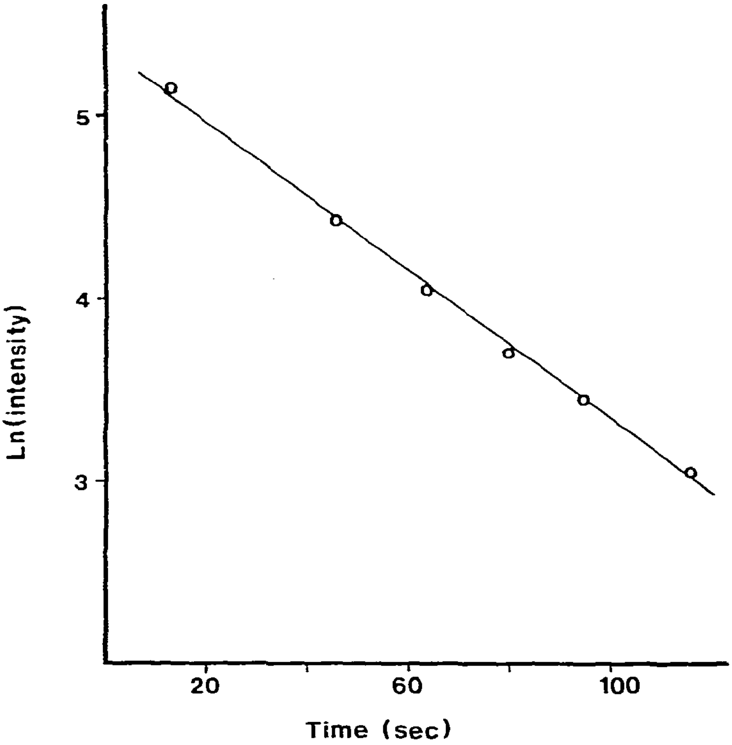


Fig. 3. Natural logarithm of the intensity of the ESR signal as a function of time for the decay of $(Me_3Si)_2\dot{P}(O\text{-}t\text{-}Bu)_2$ at −100°C.

TABLE 1

DECAY RATES AND HALF-LIVES OF THE ORGANOSILYL SUBSTITUTED PHOSPHORANYL RADICALS $(Me_3Si)_3PO\text{-}t\text{-}Bu$ AND $(Me_3Si)_2P(O\text{-}t\text{-}Bu)_2$

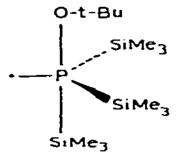
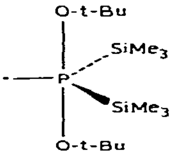
Compound	Temperature (°C)	K (sec^{-1})	$t_{1/2}$ (sec)
	−120	0.060	12
	−100	instantaneous decay	
	−120	1.4×10^{-4}	4900
	−100	0.020	35

TABLE 2

PHOSPHORUS COUPLING CONSTANTS OF PHOSPHORANYL RADICALS

Radical	a(P) (G)	Reference
PF_4	1330	9
PCl_4	1210	10
$(t\text{-}BuO)_4P$	918	2
$(t\text{-}BuO)_2PMe_2$	714	1
$t\text{-}BuOPMe_3$	619	1
$(t\text{-}BuO)_2P(SiMe_3)_2$	574	this work
$t\text{-}BuOP(SiMe_3)_3$	452	this work
$t\text{-}BuO(Me)P(SiMe_2)_5$	407	this work
$t\text{-}BuO(Me)P(SiMe_2)_6$	403	this work

The phosphorus coupling constants of the ring species, $t\text{-}BuO(Me)\dot{P}(SiMe_2)_n$ (n = 5,6), are smaller than the coupling observed for $t\text{-}BuO\dot{P}(SiMe_2)_3$. This difference may be due either to changes in the phosphorus bond angles, which will change the amount of *s* character of the orbital possessing the lone electron, or to removal of spin density from the phosphorus into the polysilane moiety. However ^{29}Si satellites are not observed for the phosphoranyl radicals of the ring compounds; therefore, a(Si) is less than the line width of 10 G. It is apparent that the odd electron in the heterocyclic compounds $Me(t\text{-}BuO)\dot{P}(SiMe_2)_n$ (n = 5,6) is primarily localized at the phosphorus, even though the odd electron is delocalized in the anion radicals of the cyclopolysilanes $(Me_2Si)_n$ (n = 5,6) [11].

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