

Preliminary communication

PERSISTENT TRIARYLGERMYL RADICALS $\dot{\text{G}}\text{eAr}_3$ (Ar = 2,6-Me₂C₆H₃ OR 2,4,6-Me₃C₆H₂): SYNTHESIS, ESR STUDIES, AND COMPARISONS WITH Si AND Sn ANALOGUES*

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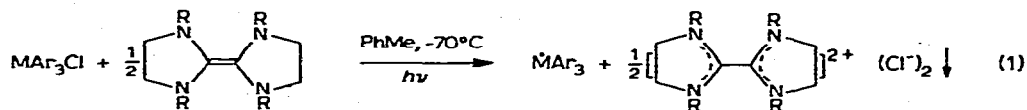
Summary

Persistent ($t_{1/2} > 24$ h in PhMe at 20°C) triarylgermyl radicals $\dot{\text{G}}\text{eAr}_3$ (Ar = 2,6-Me₂C₆H₃ or 2,4,6-Me₃C₆H₂) have been obtained from GeAr₃Cl and an electron-rich olefin [RNCH₂CH₂N(R)C=] (R = Me or Et) under UV irradiation in toluene at -70°C; the ESR spectra show coincidental equivalence of all proton couplings due to twisting of the aromatic rings into a propeller arrangement about the germanium; other syntheses are described, corresponding silicon and tin systems compared, and data provided on new compounds MAr₃X (M = Si, Ge, or Sn; X = H or Cl).

Recently there has been some interest in persistent metal-centred radicals $\dot{\text{M}}\text{X}_3$ of the Main Group IV elements Si, Ge, and Sn [1]. Species with half-lives > ca. 3 months in hydrocarbon solvents have been obtained ($\dot{\text{M}}\text{X}_3$ (M = Ge or Sn): X = CH(SiMe₃)₂ [2], N(SiMe₃)₂ or N(CMe₃)(SiMe₃) [2]; M(NR₂)₃ (R = GeMe₃ and M = Ge or Sn, or R = GeEt₃ and M = Sn) [3]), whereas others although still "persistent" are significantly shorter-lived (Si[CH(SiMe₃)₂]₃ [2] and $\dot{\text{S}}\text{n}(\text{CH}_2\text{-CMe}_2\text{Ph})_3$ [4]). We now report preliminary findings on the triarylgermyl radicals; while this work was being prepared for publication the radical $\dot{\text{G}}\text{e}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_3$ was obtained by a different procedure [5], but we observed superior resolution of its ESR spectrum, including ⁷³Ge satellites.

The principal method used for generating the metal-centred radical was that of eq. 1 (R = Me or Et) (cf. ref. 6). The following systems were examined: Ar = 2,4,6-Me₃C₆H₂ with M = Si, Ge, or Sn; and for M = Ge, Ar = 3,4-Me₂C₆H₃ or

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2,6-Me₂C₆H₃. Only the mesityl- or 2,6-xylyl-germanium radicals $\dot{\text{M}}\text{X}_3$ were detected by ESR spectroscopy (Table 1), although in every case except with Si(C₆H₂Me₃-2,4,6)₃Cl a reaction was observed. Thus during photolysis (250 W medium pressure Hg lamp) in the cavity of an ESR spectrometer, each solution remained colourless and (except for SiAr₃Cl) a white solid (probably the salt of eq. 1) was precipitated.

TABLE 1
ESR PARAMETERS AND HALF-LIVES OF PERSISTENT TRIARYLGERMYL RADICALS^a

Ar in $\dot{\text{G}}\text{eAr}_3$	g	$a(^1\text{H})$ (mT)	$a(^{73}\text{Ge})$ (mT)	$t_{1/2}$ (h)
2,4,6-Me ₃ C ₆ H ₂	2.0084	0.069	6.84	> 24
2,6-Me ₂ C ₆ H ₄	2.0080	0.065	6.69	> 24

^a Data are quoted for solutions in PhMe at 20°C, generated according to eq. 1.

The mesityl- and 2,6-xylyl-germyl radicals have long half-lives under ambient conditions (Table 1), but not comparable to $\dot{\text{G}}\text{e}[\text{CH}(\text{SiMe}_3)_2]_3$; the corresponding triaryltin radicals are expected to be less persistent as the larger tin atom can tolerate bulkier substituents and formation of the diamagnetic dimers Sn₂Ar₆ may have occurred.

The ESR spectrum of $\dot{\text{G}}\text{e}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_3$ shows a central eighteen line signal due to ¹H coupling, $a(\text{H})$, with satellites due to coupling with ⁷³Ge ($I = 9/2$, 7.6% abundance). The experimental spectrum is identical with a simulated one assuming that $a(\text{H})$ for *meta*-H and the 2-, 4-, or 6-Me groups are equivalent (i.e., coupling with 33 protons); thus the eighteen lines correspond in relative intensity to the central eighteen lines of the binomial expansion of 34. Similarly, the eighteen line central signal of $\dot{\text{G}}\text{e}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})_3$ (Fig. 1) has relative intensities corresponding to the central eighteen of the binomial expansion of 28, i.e., all H's have identical coupling constants. The coincidence of CH_3 and aromatic CH proton couplings contrasts with the situation in $\dot{\text{G}}\text{ePh}_3$ (where *o*-, *m*-, and *p*- $a(\text{H})$'s are 0.093, 0.046, and 0.093 mT, respectively [7]), but may be explained by the twisting of the aromatic rings for steric reasons; it has been shown [8] that such twisting causes $a(m\text{-H})$ to rise and $a(o\text{-H})$ and $a(p\text{-H})$ to fall.

Other methods which were used for the generation of $\dot{\text{G}}\text{e}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_3$ were by UV irradiation of (i) $\text{GeAr}_3\text{H}/\frac{1}{2}t\text{-Bu}_2\text{O}_2$ in *n*-C₆H₁₄ at 0°C [5] (this gave a much weaker signal); and (ii) $\text{GeAr}_3\text{H}/(\text{CH}_2)_5\text{C}=\text{O}$ in toluene at 0°C (quite a good spectrum). Similar irradiation of GeAr_3H with the nitron $\text{PhCH}=\text{N}(\text{t-Bu})\text{O}$ in PhMe at 20°C gave the nitroxide $\text{GeAr}_3\text{CH}(\text{Ph})\dot{\text{N}}(\text{t-Bu})\text{O}$ presumably via $\dot{\text{G}}\text{eAr}_3$ and its spin-trapping by the nitron [9]. However, the germylene $(\text{GeAr}_2)_n$ [10] in toluene did not ($h\nu$) give $\dot{\text{G}}\text{eAr}_3$, in contrast to $\text{Ge}[\text{CH}(\text{SiMe}_3)_2]_2$ [2] or $(\text{GePhCl})_n$ [9] which gave $\dot{\text{G}}\text{eR}_3$ ($\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$) or $\dot{\text{G}}\text{ePhCl}_2$ (identified by spin-trapping).

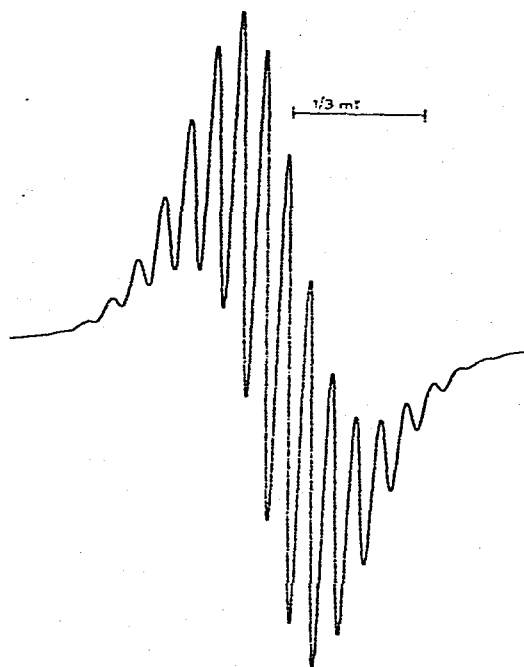


Fig. 1. The ESR spectrum of GeAr_3 (Ar = 2,6-Me₂C₆H₃) in toluene at 20°C. ⁷³Ge satellites not shown.

The tetravalent Group IV metal precursors for these experiments were prepared as follows: (a) SiAr_3H from SiCl_3H and LiAr ; (b) SiAr_3Cl from SiAr_3H and *N*-chlorosuccinimide in THF; (c) GeAr_3H from GeAr_3Cl and LiAlH_4 ; (d) GeAr_3Cl from GeCl_4 and ArMgBr , or GeAr_3H with CCl_4 or *N*-chlorosuccinimide; and (e) SnAr_3Cl from SnCl_4 and successively an excess of ArMgBr (to yield SnAr_4) and SnCl_4 . The new compounds include $\text{M}(\text{C}_6\text{H}_3\text{Me}_2\text{-2,6})_3\text{Cl}$ (M = Ge, m.p. 143°C; M = Sn, m.p. 165°C) and $\text{Si}(\text{C}_6\text{H}_2\text{-2,4,6})_3\text{Cl}$, b.p. 190–195°C/10⁻² mmHg.

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