Tris(trimethylsilyl)methyl—a Relatively Stable Saturated Organic Radical

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Summary Tris(trimethylsilyl)methyl (II), prepared from the corresponding bromide or mercurial, is a relatively long-lived free radical: photolysis of the mercurial (V) to give (II) is believed to provide the first example of an e.s.r. spectrum of a radical produced directly by photolysis of an organomercurial.

WE have previously observed that many organic free radicals may be generated within the cavity of an e.s.r. spectrometer by photolysis of a mixture of the corresponding organic bromide with t-butyl peroxide and triethylsilane.[1] We have now found that tris(trimethylsilyl)methyl bromide[2] (I) gives rise to a particularly intense (*ca.* 1000 times that of typical organic radicals) e.s.r. spectrum (Figure), attributed to the tris(trimethylsilyl)methyl radical (II). The *g*-factor is 2·0027, and a computer simulation of the spectrum gives $a(\mathrm{H}) = 0{\cdot}375$, $a(^{13}\mathrm{C}_\gamma) = 5{\cdot}2$, and $a(^{29}\mathrm{Si}) = 13{\cdot}5\,\mathrm{G}$. The magnitudes of $a(\mathrm{H})$ and $a(^{29}\mathrm{Si})$ accord with those obtained for the radicals $\mathrm{Me_3SiCH_2}\cdot$[3] and $\mathrm{Et_3Si\dot{C}HCH_3}$.[4] We tentatively assign $a(^{13}\mathrm{C}_\alpha) = 26 \pm 3\,\mathrm{G}$: on account of the high local spin density on the $^{13}\mathrm{C}$ atom, lines due to $\mathrm{(Me_3Si)_3{}^{13}C}\cdot$ should be broader and of lower amplitude than other lines, particularly at low temperatures,[5,6] and are hence more difficult to locate. The low $^{13}\mathrm{C}_\alpha$-splitting indicates that the radical is planar, and that there is significant delocalization of the unpaired electron [$\mathrm{CH_3}\cdot$ has $a(^{13}\mathrm{C}) = 38\,\mathrm{G}$,[7] whereas $\mathrm{Ph_3C}\cdot$ has $a(^{13}\mathrm{C}_\alpha) = 26 \pm 3\,\mathrm{G}$ [6,8]].

$$\mathrm{(Bu^tO)_2} \xrightarrow{h\nu} \mathrm{2Bu^tO}\cdot \qquad (1)$$

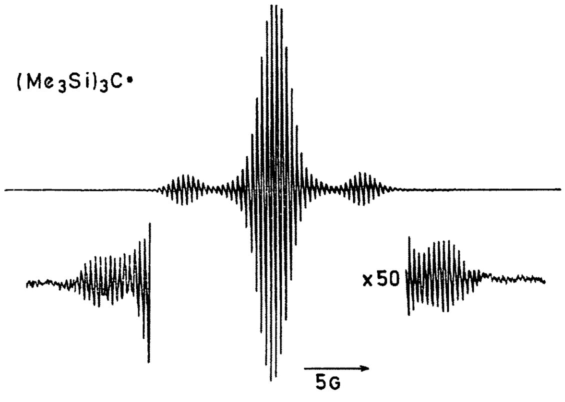
$$\mathrm{Bu^tO}\cdot + \mathrm{Et_3SiH} \rightarrow \mathrm{Bu^tOH} + \mathrm{Et_3Si}\cdot \qquad (2)$$

$$\mathrm{Et_3Si}\cdot + \underset{\text{(I)}}{\mathrm{(Me_3Si)_3CBr}} \rightarrow \mathrm{Et_3SiBr} + \underset{\text{(II)}}{\mathrm{(Me_3Si)_3C}\cdot} \qquad (3)$$

$$\mathrm{(Me_3Si)_3C}\cdot + \mathrm{Et_3SiH} \xrightarrow{\text{slow}} \underset{\text{(III)}}{\mathrm{(Me_3Si)_3CH}} + \mathrm{Et_3Si}\cdot \qquad (4)$$

$$\mathrm{2(Me_3Si)_3C}\cdot \not\rightleftharpoons \underset{\text{(IV)}}{\mathrm{(Me_3Si)_3C{-}C(SiMe_3)_3}} \qquad (5)$$

We suggest the reaction scheme (1—5). The only detected product derived from (II) is tris(trimethylsilyl)-methane (III); the absence of the dimer (IV) indicates that combination (reaction 5) is a very slow process. When the light is interrupted, the concentration of the radical (II) falls by a first order process with a half-life of about 5 sec. at −40°. We attribute this first-order decay to abstraction reactions of (II) yielding radicals which are rapidly lost by combination and disproportionation. The non-occurrence of reaction (5) is probably due to steric hindrance to combination: space-filling models indicate that, whilst there is little steric hindrance in the radical (II), there would be considerable hindrance in the dimer (IV). The relatively long life of the radical (II) may thus be ascribed to steric hindrance to combination (reaction 5), the non-availability of disproportionation reactions, and delocalization of the unpaired electron into the 3*d* orbitals of the three silicon atoms. Similar considerations apply to triphenylmethyl, though the relative importance of the factors may be different. We have been unable to add radical (II) to oct-1-ene: stabilization of the radical and steric hindrance may be responsible.



FIGURE

Finally, we have observed the e.s.r. spectrum of (II) on photolysis of bis[tris(trimethylsilyl)methyl]mercury (V).[9] We believe that this is the first example of an e.s.r. spectrum of a radical produced directly by photolysis of an organomercurial (although e.s.r. spectra of nitroxides, produced by addition of nitrones to the postulated organic radicals, have been observed.[10])

$$\underset{\text{(V)}}{\mathrm{[(Me_3Si)_3C]_2Hg}} \xrightarrow{h\nu} \mathrm{2(Me_3Si)_3C}\cdot + \mathrm{Hg} \qquad (6)$$

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