

## Tri-isopropylmethyl: an Aliphatic Hydrocarbon Radical of Remarkable Stability

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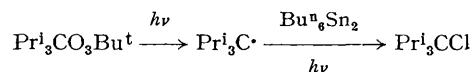
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*Summary* Tri-isopropylmethyl is one of the most stable aliphatic hydrocarbon radicals known, and displays an e.s.r. spectrum indicative of an  $sp^2$  hybridization with the three  $\beta$ -hydrogens symmetrically aligned in the plane orthogonal to the  $p$ -orbital containing the unpaired electron.

RECENTLY it has been discovered that hydrocarbon radicals substituted with two or more *t*-butyl groups are highly stabilized.<sup>1-3</sup> The *t*-butyl groups lack  $\beta$ -hydrogens, which are labile to disproportionation, and their bulk retards bimolecular dimerization and disproportionation of any  $\beta$ -hydrogens on the remaining substituent.

We have now prepared tri-isopropylmethyl from two different sources, and find that this radical, which possesses no *t*-butyl groups, is extremely stable.

Tri-isopropylmethyl was obtained by photolysis of *t*-butyl tri-isopropylperoxyacetate in cyclopropane, or by photolysis of tri-isopropylmethyl chloride (obtained from tri-isopropylmethanol and phosgene) and hexabutylditin in cyclopropane, and had a  $g$  value of 2.0023. After gener-



ation from the chloride the decay of the radical at 20 °C without irradiation could be monitored by e.s.r. spectroscopy and at an initial concentration of  $10^{-5}$  mol l<sup>-1</sup> followed second-order kinetics,  $2k_t = 8 \times 10^2$  l mol<sup>-1</sup> s<sup>-1</sup>. The peroxyester was not a suitable radical precursor for decay kinetics since it generated the radical thermally at an appreciable rate at 25°:  $k = 5.67 \times 10^{-6}$  s<sup>-1</sup>,  $\Delta H^\ddagger = 26.6$  kcal mol<sup>-1</sup>,  $\Delta S^\ddagger = 6.7$  cal K<sup>-1</sup> mol<sup>-1</sup>. The products of the bimolecular decay of the radical are under examination.

The e.s.r. spectrum from either source varied with temperature in the range -60 to +60 °C. The central lines covered a total range of ca. 14 G at all temperatures,

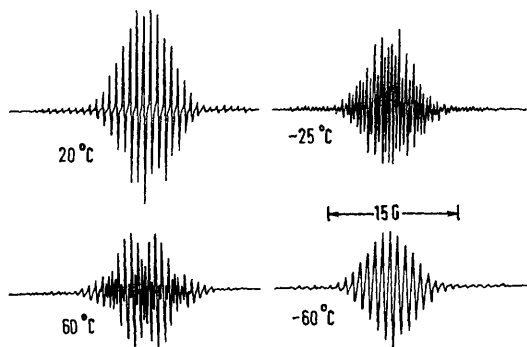


FIGURE 1. E.s.r. spectra of tri-isopropylmethyl.

but the number of lines visible in the central region of the spectrum varied from 16 or less at 20 °C and -60 °C to 24 or more at -25 °C and +60 °C. These changes were completely reversible, with or without continued irradiation (Figure 1).

The spectrum at -25 °C could be matched by a simulated spectrum with  $a^H(\beta)$  2.4 G, and  $a^H(\gamma)$  0.6 G. Such parameters are reasonable for a symmetrical conformation of tri-isopropylmethyl with all three  $\beta$ -hydrogens in the plane orthogonal to the central  $p$  orbital. A molecular

model suggests this conformation is highly favoured (Figure 2). Similar e.s.r. parameters have been reported for the isopropyl groups in isopropyl-di-*t*-butylmethyl<sup>2a</sup> and the radical anion of isopropyl *t*-butyl ketone.<sup>4</sup>

The temperature dependence of the spectrum is apparently due to small variations in the hyperfine couplings which cause some of the predicted 76 lines due to proton couplings to move in and out of coincidence.

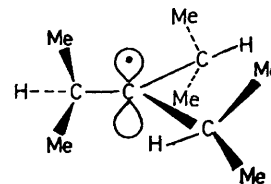


FIGURE 2. Tri-isopropylmethyl.

The high stability of tri-isopropylmethyl can be ascribed to the prohibitive strain that is obvious in a model of the dimer. Disproportionation is hindered by the location of the  $\beta$ -hydrogens in the central plane shielded by the methyl groups. Unimolecular decomposition is probably less likely than in di- and tri-*t*-butylmethyl,<sup>1a</sup> since tri-isopropylmethyl appears less strained than these species, and will have a smaller driving force for fragmentation or intramolecular hydrogen atom shift, the routes postulated for the former cases.<sup>1a</sup> Quantitative comparisons are difficult on the various stable radicals which have been reported,<sup>1-3</sup> but tri-isopropylmethyl is one of the longest lived aliphatic hydrocarbon radicals yet prepared.<sup>5</sup>

The structure of tri-isopropylmethyl is reminiscent of those of hexaisopropyl-<sup>6a</sup> and hexaisopropenyl-benzene,<sup>6b</sup> which also have the planes of the substituent groups parallel to the adjacent  $p$ -orbitals.

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