isolated from *Streptomyces spectabilis.*[3] Cbz-L-Thr-NMe-L-Trp-OMe (**10**) was converted to c(NMe-L-Trp-Dhb) (**11**) by tosylation and action of $Et_2NH$, mp 122-124 °C dec, mass spectrum $M^+$ 283, UV max (95% EtOH) 219 nm ($\epsilon$ 36 200) (lit.[3] mp 121-123 °C, UV max 220 nm ($\epsilon$ 34 900)).[17]

## References and Notes

(1) T. Ueno, T. Nakashima, Y. Hayashi, and H. Fukami, *Agric. Biol. Chem.*, **39,** 1115 (1975).

(2) S. Lee, H. Aoyagi, Y. Shimohigashi, N. Izumiya, T. Ueno, and H. Fukami, *Tetrahedron Lett.*, 843 (1976).

(3) K. Kakinuma and K. L. Rinehart, Jr., *J. Antibiot.*, **28,** 733 (1974).

(4) H. Poisel and U. Schmidt, *Chem. Ber.*, **106,** 3408 (1973).

(5) S. Akabori, T. Ikenaka, and K. Matsumoto, *Nippon Kagaku Zasshi*, **73,** 112 (1952).

(6) B. W. Bycroft and G. R. Lee, *J. Chem. Soc., Chem. Commun.*, 988 (1975).

(7) Abbreviations according to IUPAC-IUB commission, *Biochemistry*, **11,** 1726 (1972), are used throughout. Satisfactory elemental analyses and chromatographic data were obtained for the most crystalline compounds.

(8) D. E. Nitecki, B. Halpern, and J. W. Westley, *J. Org. Chem.*, **33,** 864 (1968).

(9) In determination of $[\alpha]_D$, 1% of a solution was used.

(10) I. Photaki, *J. Am. Chem. Soc.*, **85,** 1123 (1963).

(11) Y. Shimohigashi, S. Lee, and N. Izumiya, *Bull Chem. Soc. Jpn.*, **49,** 3280 (1976).

(12) We synthesized authentic c(L-Leu-L-Ala) and c(L-Leu-D-Ala) by Fischer's method, $R_f$ 0.46 and 0.54 (with 5:1 $CHCl_3$–MeOH), mp 240–242 °C and 244–246 °C (both dec), $[\alpha]^{20}{}_D$ −49.2 and +12.3° (DMF), respectively.

(13) E. Fischer, *Chem. Ber.*, **39,** 2893 (1906)

(14) Y. Shimohigashi, S. Lee, T. Kato, N. Izumiya, T. Ueno, and H. Fukami, *Agric. Biol. Chem.*, **41,** 1533 (1977).

(15) Meyer et al., *Biochem. Biophys. Res. Commun.*, **56,** 234 (1974), hydrogenated tentoxin, c(NMe-L-Ala$^1$-L-Leu$^2$-NMe-dehydroPhe$^3$-Gly$^4$) and isolated [NMe-D-Phe$^3$]-tentoxin as the sole product. Thus, it should be possible that dehydroamino acid residue in a certain peptide other than a type of dehydrodiketopiperazine is asymmetrically hydrogenated.

(16) E. J. Corey, H. S. Sachdev, J. Z. Gougoutas, and W. Saenger, *J. Am. Chem. Soc.*, **92,** 2488 (1970).

(17) Kakinuma and Rinehart[3] did not report whether Dhb was *E* or *Z* form. We assume that Dhb in synthetic c(NMe-L-Trp-Dhb) (**11**) from **10** will be *Z*, and are attempting to compare natural c(NMe-L-Trp-Dhb) with **11** and other synthetic c(NMe-L-Trp-*E*-Dhb) which is under synthesis from c(NMe-L-Trp-L-*allo*-Thr).

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## Structure of the *tert*-Butyl Radical

*Sir:*

The structure of the *tert*-butyl radical is still a controversial topic. One of us[1] has suggested that the equilibrium conformation of this radical is planar and that deviations from planarity in a solid matrix might arise from steric hindrance. A stable pyramidal structure was inferred by Wood et al.[2] from the negative temperature dependence of the $^{13}C$ coupling of the radical trapped in an adamantane matrix. Symons[3] gave another interpretation of our spectra and claimed to have given evidence for planarity of the *tert*-butyl radical. The problem is again discussed in two recent papers [4,5] in which the authors support the view of nonplanarity of the radical on the basis of a temperature dependence calculation of $^{13}C$ and H couplings. Since, as has already been suggested by Symons,[6] the negative temperature coefficient of H coupling may be caused by a medium effect, we have investigated the H coupling variation as a function of temperature in four different trapping matrices. We have irradiated at 77 K polycrystalline matrices of *tert*-butyl chloride, neopentane, and isobutane coming from quick freezing of the corresponding liquids, and neopentane in a xenon matrix containing 2% neopentane. Figure 1 shows that the variations of the H coupling $a^H$ as a function of temperature are different in the four matrices. Neither the slopes of the curves nor the position of the plateaus are the same. Our numerical results agree quite well with the values published by Fessenden et al.[7] for liquid neopentane (22.72 G at 260 K), solid neopentane (22.62 G at 213 K), and liquid isobutane (22.7 G at 128 K).

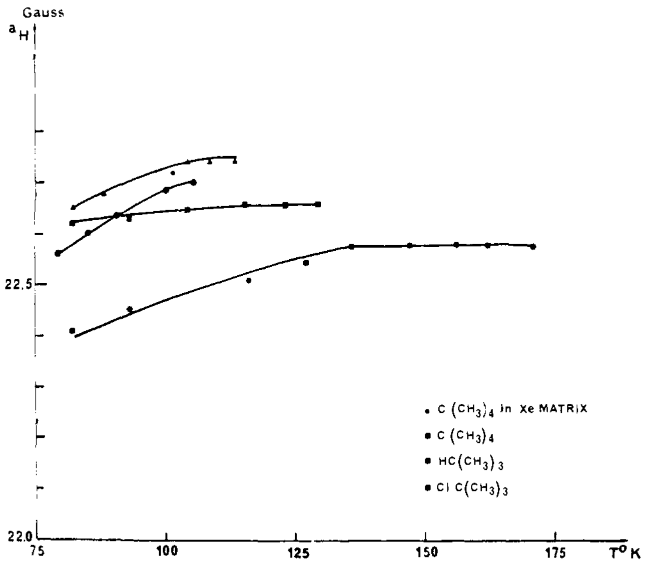

**Figure 1.** $a_{CH_3}{}^H$ coupling of $\dot{C}(CH_3)_3$ radicals as a function of temperature in four different trapping matrices: $ClC(CH_3)_3$, $C(CH_3)_4$, $HC(CH_3)_3$, $C(CH_3)_4$ in xenon.

These results show the influence of the matrix on the structure of the *tert*-butyl radical. This effect is not surprising since the deformation energy of the radical seems to be low.[2] Then, the temperature dependence of $^{13}C$ and H couplings observed by Wood et al. can adequately be interpreted in terms of the influence of the matrix: the radical, the equilibrium geometry of which would be planar, is distorted by the matrix; when the temperature is raised, it reverts toward its equilibrium structure because of the thermal expansion of the matrix. Thus, the $^{13}C$ coupling decreases and the H coupling increases as a function of temperature. Another factor[8] may also contribute to the observed temperature dependence of H couplings: electronic interactions of the unpaired electron with the matrix which slightly alter the observed splittings by perturbing the spin distribution in the radical and are temperature dependent owing to the thermal expansion of the matrix. The contribution of out-of-plane vibrations to the central carbon atom coupling, which certainly exists, is probably low compared to the effect of the matrix. These matrix effects vary with the matrix itself, and Figure 1 reflects the way in which equilibrium is achieved in each case. The present interpretation of the signs of the temperature coefficients of H and $^{13}C$ couplings does not imply a numerical value of the parameter $A_c$ (relating $^{13}C$ couplings to the 2s spin density), which would be in disagreement, as in ref 4 and 5 (407.3 G,[4] 435 G[5]) with the values calculated by different methods (1130 G,[9] 1191 G[10]).

Finally, we would like to point out that a negative temperature coefficient of $^{13}C$ coupling $a_{^{13}C}$ (or a positive temperature coefficient of H coupling $a_H$) is not an automatic consequence of a double minimum potential,[5] but depends on the shape of this potential. The sign of the temperature coefficient of $\langle Q^2\rangle$ (proportional to the coupling), as calculated from the expression

$$\langle Q^2\rangle = \frac{\sum_i \langle Q^2\rangle_i \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)}$$

where $E_i$ is the vibrational energy of the state *i*, *Q* the displacement coordinate, and *k* the Boltzmann constant, depends

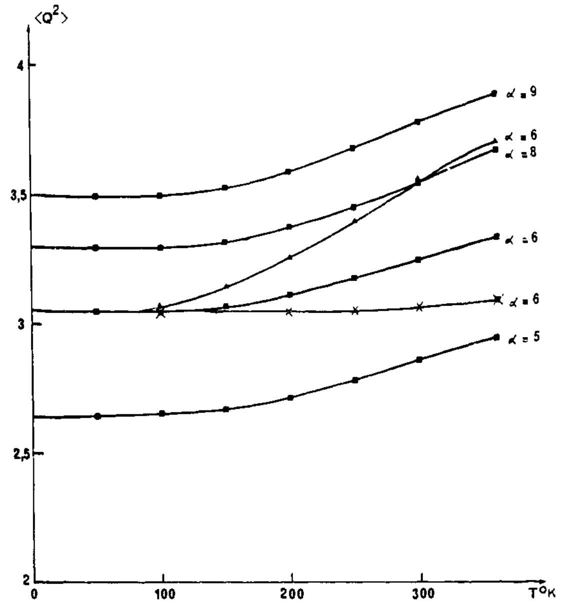

**Figure 2.** Calculated temperature dependence of $\langle Q^2 \rangle$ in the case of a Gaussian-barrier perturbed harmonic oscillator potential function: $\alpha h\nu_0$ represents the barrier height; ■, $h\nu_0 = 200\ \text{cm}^{-1}$; ×, $h\nu_0 = 400\ \text{cm}^{-1}$; ▲, $h\nu_0 = 130\ \text{cm}^{-1}$.

on the potential function chosen. As shown by Krusic et al.[5] the temperature dependence of $a_{^{13}\text{C}}$ is negative provided that the barrier is high enough for a potential $V(Q) = -AQ^2 + bQ^4$ ($a > 0$; $b > 0$); on the contrary, the temperature dependence of $a_{^{13}\text{C}}$ is positive if the chosen potential is[11]

$$V = h\nu_0[(Q^2/2) + \alpha \exp(-Q^2)]$$

as can be shown by using $\langle Q^2 \rangle_i$ calculated by Chan et al.[11] (see Figure 2).

## References and Notes

(1) C. Hesse and J. Roncin, *Mol. Phys.*, **19**, 803 (1970).
(2) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Am. Chem. Soc.*, **94**, 6241 (1972); D. E. Wood and R. F. Sprecher, *Mol. Phys.*, **26**, 1311 (1973).
(3) M. C. R. Symons, *Mol. Phys.*, **24**, 461 (1972).
(4) J. B. Lisle, L. F. Williams, and D. E. Wood, *J. Am. Chem. Soc.*, **98**, 227 (1976).
(5) P. J. Krusic and P. Meakin, *J. Am. Chem. Soc.*, **98**, 228 (1976).
(6) M. C. R. Symons, *Tetrahedron Lett.*, **3**, 207 (1973).
(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
(8) This interpretation of the experimental data has been suggested by one of the referees.
(9) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals", Elsevier, Amsterdam, 1967, p 21.
(10) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961).
(11) S. I. Chan and D. Steiman, *J. Chem. Phys.*, **39**, 545 (1963).

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## Reaction of Tri-*n*-butylstannyl with Oxygen. Electron Paramagnetic Resonance Evidence for a Pentacoordinate Stannylperoxy Radical[1,2]

*Sir:*

It has been well established[3,4] that trialkyl group 4b radicals, $R_3M$, where R is, for example, $CH_3$ and $C_6H_5$ and M is C, Si, Ge, Sn, and Pb, react rapidly with molecular oxygen to give the corresponding peroxy radicals $R_3MOO\cdot$. These radicals are characterized by high isotropic *g* factors, which in general increase down the series C < Si ~ Ge < Sn < Pb, and exhibit no detectable central atom hyperfine splitting.

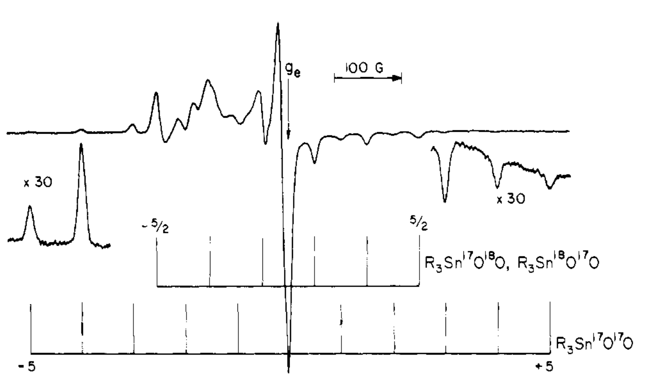


**Figure 1.** Anisotropic spectrum of $(n\text{-Bu})_3SnOO\cdot$ in cyclopropane at 93 K.

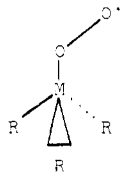
Alkylperoxy radicals enriched with oxygen-17 have an isotropic O hfsc of ~23 G from the terminal oxygen and an O hfsc of ~18 G from the penultimate oxygen.[5,6] The ratio of spin densities on the two oxygens is approximately 2:1, in favor of the terminal oxygen.[5] Trialkylsilylperoxy and trialkylgermylperoxy radicals also contain two inequivalent oxygen atoms with $a_O' \sim 25$ G and $a_O'' \sim 15$ G.[7]

The tri-*n*-butylstannyl radical, prepared by photolysis of a cyclopropane solution of di-*tert*-butyl peroxide and tri-*n*-butyltin hydride, reacted with oxygen enriched to 60% in oxygen −17 to give, at 213 K, an isotropic EPR spectrum consisting of an intense singlet ($g = 2.0265$) from a species with zero spin and *one* broad sextet, $a_O = 25$ G, with an identical *g* factor from a species with one oxygen nucleus ($I = 5/2$) or from a species with two *equivalent* oxygen nuclei, e.g., $R_3Sn^{17}OO\cdot$ and $R_3SnO^{17}O\cdot$. Transitions from a doubly substituted species ($R_3Sn^{17}O^{17}O\cdot$) were not detected.

When a solution containing the radical was rapidly cooled to 93 K, an anisotropic spectrum was observed with $g_x = 2.0019$, $g_y = 2.0084$, $g_z = 2.0661$, in which a set of six equally spaced lines centered about $g_x$ was resolved arising from the singly labeled species with $A_x(^{17}O) = 76.6$ G (Figure 1). In addition, 11 equally spaced sattelites were observed from the species where both oxygen nuclei were labeled. No oxygen-17 hyperfine interaction could be observed about $g_y$ or $g_z$ but, by analogy with the alkylperoxy radicals, it would be expected to be ~10 G.[8] No further changes occurred in the spectrum on cooling to 4.2 K.

It is clear from the powder spectrum that the reaction of $(n\text{-Bu})_3Sn\cdot$ with $O_2$ gives an oxy radical with two magnetically equivalent oxygen atoms. The failure to observe the isotropic spectrum from $(n\text{-Bu})_3Sn^{17}O^{17}O$ must be associated with the inherently broad line widths of this species, since, in the alkylperoxy radicals, the line widths of the doubly labeled species are two–four times greater than the singly labeled species.

We can, therefore, conclude from the results of this work that group 4b peroxy radicals down to germanium have the



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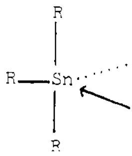

II

usual peroxy radical structure I while the tri-*n*-butylstannylperoxy radical prefers a structure in which both oxygens are equivalently bound to the tin nucleus. A possible structure for the radical, consistent with these observations, is the pentacoordinate, trigonal bipyramidal structure II in which the vacant Sn 5d orbitals are used to form a dative bond with the