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CONFIGURATIONAL CHARACTERIZATION OF THE 1-(TRIMETHYLSILYL)CYCLOPROPYL RADICAL

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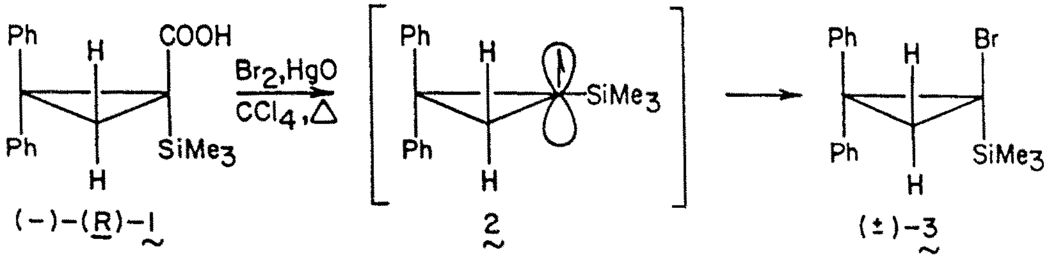
Summary: Reductive debromination of 1-bromo-1-(trimethylsilyl)cyclopropane-1-^{13}C produced the labeled radical, the EPR spectrum of which showed $a^{^{13}C\alpha}$ = 40.9 G, a^{H_β}(4H) = 27.0 G, and g = 2.00228, thereby confirming it to be planar, or nearly so.

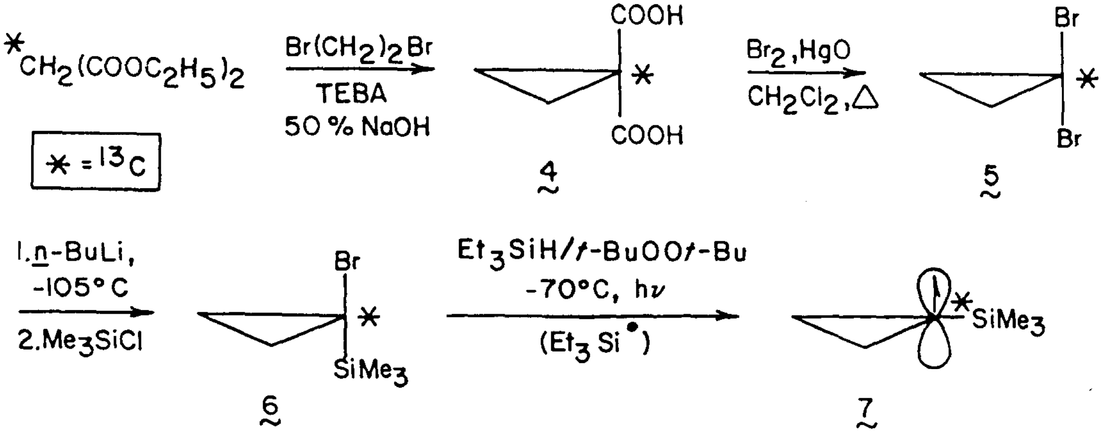
Although a great deal of interest surrounds the stereochemistry and reactivity of cyclopropyl radicals,[2] preparation of the first α-silyl derivative was reported only recently.[3] In this study, application of the Hunsdiecker reaction to optically pure (-)-(*R*)-1 yielded the racemic bromide 3. Failure of the intervening radical to maintain configuration contrasts with the nonracemizability of its carbanion analogue, reactions of which proceeded with complete retention of stereochemistry.[3] At least under these circumstances, therefore, the α-Me_3Si substituent is clearly unable to stabilize pyramidal character and the intermediate is most reasonably described as having effectively planar geometry (*viz.*, 2).



However, large groups positioned at C-2 (and C-3) are recognized to be capable of inducing the "flattening" of radical centers contained in three-membered rings. For example, whereas the 2,2-dimethylcyclopropyl radical is non-planar at C-1,[4] 2,2-di-*tert*-butyl-3,3-difluorocyclopropyl is planar.[5] Even relatively small 2-substituents may well exert steric influences adequate to reduce the inversion barrier relative to that for the parent radical.[6] The phenomenon is also seen with vinyl radicals, $(Me_3Si)_2C{=}\dot{C}SiMe_3$ being uniquely linear because of steric influences.[7]

Consequently, a reliable analysis of the α-$SiMe_3$ effect demands that the otherwise unsubstituted α-(trimethylsilyl)cyclopropyl radical be examined to determine if it is planar or not. The best technique for elucidating this point is measurement of the α-^{13}C hfs by EPR spectroscopy. Since it was considered unlikely that this parameter could be identified in natural abundance, a suitable isotopically labeled substrate was prepared.

Spiroalkylation of ^{13}C-malonic ester (99.5% isotopic purity) with 1,2-dibromoethane under phase transfer conditions[8] provided diacid **4**. Double Hunsdiecker degradation of **4** conveniently furnished dibromide **5**.[9] Sequential metalation-silylation leading to **6** was achieved with *n*-butyllithium and chlorotrimethylsilane in anhydrous ether at -105°C.[10] Compound **6** was dissolved in a 1:1 mixture of triethylsilane and di-*tert*-butyl peroxide and photolyzed directly in the cavity of a Varian E-104 EPR spectrometer at -70°C. The solvent mixture provided triethylsilyl radicals which abstracted bromine from **6** to yield the radical **7** : $a^{^{13}C_\alpha}$ = 40.9 G, a^{H_β}(4H) = 27.0 G, and g = 2.00228.



There can be no doubt that 7 is much more nearly planar than cyclopropyl and 1-methylcyclopropyl radicals for which we have found[11] $a^{^{13}C_\alpha} \approx 96$ and 98 G, respectively.[12] It is also probably more planar than the 2,2-di-*tert*-butyl-1,3,3-trifluorocyclopropyl radical for which $a^{^{13}C_\alpha} = 51.5$ G.[5] However, we believe that 7 may not be precisely planar, i.e., out-of-plane motion of the Me_3Si group is more probably governed by a double rather than by a single potential energy minimum function. We come to this conclusion because the Me_3Si group in a truly planar 7 would be expected to reduce $a^{^{13}C_\alpha}$ to a value even lower than the 38 G found for the planar methyl radical. For example, the $a^{^{13}C_\alpha}$ values for "planar" $(Me_3Si)_3C^\bullet$ and $(Me_3Si)_2CH\dot{C}(SiMe_3)_2$ are ~ 26 G[13] and 26.4 G,[14] respectively. Similarly, the "linear" $(Me_3Si)_2C{=}\dot{C}SiMe_3$ radical has $a^{^{13}C_\alpha} = 28.1$ G,[7] whereas the "bent" $Me_3Si(CF_3)C{=}\dot{C}SiMe_3$ and $Me_3Si(CCl_3)C{=}\dot{C}SiMe_3$ radicals have $a^{^{13}C_\alpha} = 47.7$ and 69.2 G, respectively.[7] We presume that the near planarity of 1-trimethylsilylcyclopropyl is a consequence of $d_\pi - p_\pi$ overlap or its equivalent.[15,16] Contributions of this type would have the net effect of favoring π radical status[2] and facilitating loss of configuration. They should also impart to 7 a certain kinetic stability relative to the cyclopropyl radical. Such would appear to be the case. Thus, the rate constant for H-atom abstraction by 7 from 1,4-cyclohexadiene at room temperature, *viz.* 1.2×10^6 M^{-1} s^{-1}, is appreciably smaller than the value previously reported for the cyclopropyl radical, *viz.*[17] 7.9×10^6 M^{-1} s^{-1}. Of course, some of this rate difference may be due to steric rather than to electronic factors.

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(12) At 27.0 G the a^{H_β}(4H) for 7 is appreciably larger than the values of 23.5 G and 19.5 G found for cyclopropyl and 1-methylcyclopropyl radicals,[11] which also argues strongly in favor of 7 being more planar than the other two radicals.

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