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Strained-ring silicon-centred radicals: silacyclobut-1-yl and related radicals *

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Abstract

Silacyclobut-1-yl, 1-methylsilacyclobut-1-yl and 3-methylsilacyclobut-1-yl radicals have been prepared by γ-irradiation of the parent silane in adamantane matrices. Electron paramagnetic resonance studies show that the radicals have non-planar rings; the SOMO on silicon is pseudo-equatorial. There is a substantial long range coupling of 16.4 G to the pseudo-equatorial γ-proton in the silacyclobut-1-yl radical and a smaller δ-coupling is shown to the pseudo-equatorial methyl protons in the 3-methylsilacyclobut-1-yl radical. In fluid solution at −40 °C t-butoxy radicals react with silacyclobutane by an S_H2 reaction at silicon to give 4-t-butoxy-4-silabut-1-yl radicals, rather than by the expected hydrogen abstraction to give silacyclobut-1-yl radicals.

We and others have explored various aspects of the structure of silicon-centred free radicals [1,2]. Small ring compounds offer the interesting features of angle strain and relatively rigid geometries. We report here our results on silacyclobut-1-yl and related radicals.

Results and discussion

Silacyclobut-1-yl (I), 1-methylsilacyclobut-1-yl (II) and 3-methylsilacyclobut-1-yl (III) radicals were prepared by γ-irradiation of the corresponding silanes in adamantane or perdeuterioadamantane matrices at 77 K.

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* Dedicated to Professor Colin Eaborn on his 65th birthday in recognition of his important contributions to organometallic chemistry.

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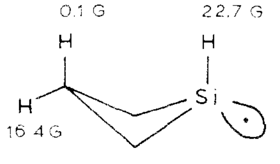
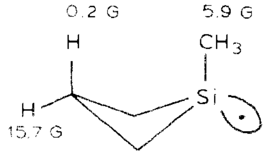


(I)



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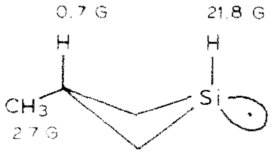


(III)

The EPR spectrum shown in Fig. 1a was obtained in adamantane at −45 °C, and is interpreted by correlation analysis (Fig. 1b) [3] in terms of two doublet splittings of 16.3 and 22.8 G and two triplet splittings of 2.6 and 2.1_5 G. Silicon-29 satellites were visible with the expected low intensity, giving $a(^{29}\mathrm{Si})$ 171.9 G at −53 °C. The corresponding spectrum obtained in adamantane-d_{16} at −58 °C shows sharper lines, but contains a central impurity signal. Coupling constants are 16.4 and 22.7 G (doublets) and 2.7 and 2.0 G (triplets). Both spectra have line-shapes consistent with the remaining proton having a coupling of approximately 0.1 G. We assign the larger doublet splitting as due to Si–H by analogy with the silacyclopent-1-yl (23.4 G) [4] and dimethylsilyl radicals (17.0, 17.3 G) [5], and by comparison of the spectrum with that of the 1-deuteriosilacyclobut-1-yl radical (Fig. 1c), which may be analysed better for replacement of the 22.7 G doublet by a 1/1/1 triplet with 1/6.514 coupling, than by similar replacement of the smaller doublet coupling. In matching the experimental spectrum (Fig. 1c) with a simulation, the central region where an impurity peak is present is ignored. The spectrum of the 1-methylsilacyclobut-1-yl radical (discussed below), in which a 5.9 G methyl quartet replaces the 22.7 G coupling, also supports this assignment.

The most surprising feature of the spectrum of the silacyclobut-1-yl radical is the doublet coupling of 16.4 G which we attribute to the pseudo-equatorial 3-proton. This assignment also involves a non-planar ring structure and a pseudo-equatorial

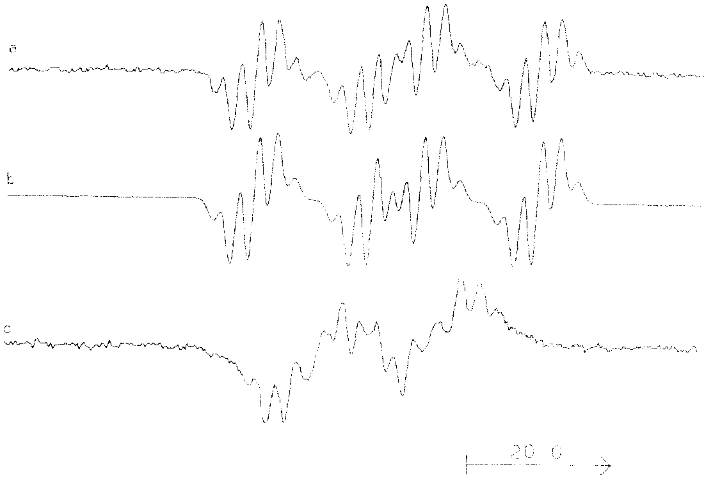
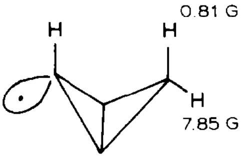


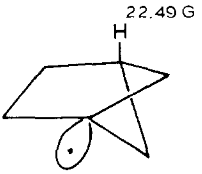
Fig. 1. (a) The EPR spectrum of the silacyclobut-1-yl radical in adamantane at −45 °C; (b) simulation of (a); (c) the EPR spectrum of the 1-deuteriosilacyclobut-1-yl radical in adamantane at −40 °C.

SOMO (singly occupied molecular orbital) on silicon. Silacyclobutane is non-planar [6,7], with a dihedral angle between the Si, C(2), C(4) and the C(2), C(3), C(4) planes of ca. 30°. A similar non-planar structure is to be expected for the radical, in which similar structural features (in particular, all but two of the potentially eclipsing H–C–C–H and H–C–Si–H interactions) are present. UMINDO [8] calculations tend to give cyclic structures that are more planar than those found experimentally: silacyclobutane is predicted to be planar, and the fully optimised silacyclobut-1-yl radical shows a Si, C(2), C(4)/C(2), C(3), C(4) dihedral angle of only about 11°, with the SOMO on silicon in the pseudo-equatorial position. By keeping the shape of the radical the same as that found experimentally for silacyclobutane [6], but allowing optimization of the Si–H bond length and C–Si–H angle, we obtain two conformations of the radical, of which the more stable by 18.5 kJ mol^{-1} is the radical with the pseudo-equatorial SOMO.

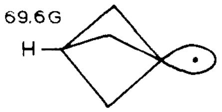
The pseudo-equatorial conformation is consistent with the large γ-proton coupling. With a non-planar radical centre and puckered ring, a "W"-conformation conducive to a substantial long-range coupling is produced. UMINDO annihilated *s* spin densities at the γ protons are calculated to be 0.0356 and 0.0026 for the pseudo-equatorial and pseudo-axial protons in the conformation of the radical with the pseudo-equatorial SOMO on silicon, but only 0.0002 and 0.0035 for the corresponding protons in the pseudo-axial radical. Cyclobutyl radicals, which are approximately planar at the radical centre, show γ-couplings of only 1.12 G [9]. The γ-couplings in the silacyclobut-1-yl radical are by far the largest γ-couplings so far observed for a silicon-centred radical. Values of 0.2–0.5 G are typical for non-cyclic systems [10], and in the cyclic 1-silacyclo[2.2.2]octyl radical [11], the low value of 0.37 G shown by the γ-positions reflects the "non-W" conformational relationship of the SOMO with the γ-C–H bonds. Larger values of γ-coupling constants have been observed in carbon-centred radicals, but only in strained fused ring systems such as IV, V and VI [12–15], where the strained ring system promotes non-planarity at the radical site as well as the favourable "W"-arrangement of the interacting orbitals. In the silacyclobut-1-yl radical, the silicon-centred radical is pyramidal even without a strained ring system, and in this cyclic system the through-space and through-bond effects should reinforce [14] to give a large coupling constant.



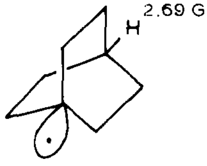
(IV) [13]



(V) [14]



(VI) [15]



(VII) [14]

The two β-proton triplet splittings of 2.7 and 2.0 G are more consistent with the 'electron diffraction' geometry than with the fully optimized UMINDO geometry, which predicts that one of the triplets should have nearly the same coupling constant as the "W"-conformation γ-proton, but the agreement is not very good.

There is a barrier to interconversion of the two equivalent forms of silacyclobutane of 5.3 kJ mol^{-1} [7]. In the radical, the pseudo-equatorial form is almost certainly the most stable conformation, but it is not certain whether the pseudo-axial conformation is a true minimum or not. UMINDO calculations based on fully optimized geometry, but allowing variation of the Si, C(2), C(4)/C(2), C(3), C(4) dihedral angle do not indicate the existence of a second (pseudo-axial) energy minimum, but these calculations, as mentioned earlier, overestimate the planarity of the molecule and may fail to locate a second minimum for the radical, if it exists.

At −133°C the silacyclobutyl radical spectrum collapses to a broad doublet of doublets (18.7 and 22.9 G) with $a(^{29}Si)$ 171.6 G. The α-H doublet value remains constant, the γ-H coupling is significantly increased, and the two β-proton triplets disappear. This temperature dependence could be due to changes in the inversion frequency of the ring with temperature, with accompanying effects on coupling constants, but is more likely due to a loss of rotational freedom at low temperatures [16] as the plastic phase of adamantane is replaced by a more ordered structure.

The ^{29}Si coupling constant at 171.9 G is slightly less than that found is non-cyclic analogues such as the dimethylsilyl radical [5]. However J(Si–H) in the parent silane is 197 Hz [17], consistent with larger than normal s-character in the extra-cyclic orbital. Application of the regression equation developed in reference [2] to link J(Si–H) for the silane with $a(^{29}Si)$ in the radical leads to a predicted value of 196.2 G for the ^{29}Si coupling constant. The fact that the observed value is about 24 G less than this suggests, that there is some unusual feature in the radical: the other radicals that we have studied which have $a(^{29}Si)$ significantly lower than predicted by the regression line have either chlorine or silicon substituents, which delocalize spin density in the radical. This suggests that delocalization is similarly responsible for stabilization of the pseudo-equatorial form of the silacyclobut-1-yl radical, with significant contributions to the SOMO from other orbitals in the ring system, with a concomitant reduction in spin density at the silicon atom. In qualitative accord with this, our UMINDO calculations show a lesser spin density at silicon (0.553) in *eq*-silacyclobut-1-yl than in the axial conformer (0.642), or in the silacyclopent-1-yl radical (0.679).

The EPR spectrum of the 1-methylsilacyclobut-1-yl radical (II) in perdeuterioadamantane at −85°C is shown in Fig. 2a. Analysis of this spectrum (Fig. 2b) gives a quartet (5.9 G), a doublet (15.7 G) and two triplets (ca. 1.3 and 1.0 G), with a further possible doublet of ca. 0.2 G buried in the line width. The quartet splitting has a value appropriate to a methyl group directly attached to a silicon centre and the doublet splitting is very similar to that attributed to the pseudo-equatorial proton in the unsubstituted radical. The two triplet splittings are similarly attributed to the β-protons. The spectrum is essentially invariant over the temperature range −119 to −65°, and no silicon satellites could be discovered. We conclude that this radical has the same pseudo-equatorial conformation as unsubstituted silacyclobut-1-yl.

The EPR spectrum of the 3-methylsilacyclobut-1-yl radical (III) in adamantane at −50°C is shown in Fig. 2c. Analysis of this spectrum (Fig. 2d) is in terms of an α-proton doublet of 21.8 G, a methyl quartet of 2.7 G and two β-proton triplets of 3.2 and 3.8 G, and a possible further buried doublet coupling of ca. 0.7 G. The α-proton doublet is normal, and the replacement of the large γ-H doublet by a smaller quartet is strong evidence that the methyl group is in the pseudo-equatorial position. UMINDO calculations with the ring carbons, silicon and β-protons fixed in the silacyclobutane positions [6], and the other parameters optimized, show that the conformation with the methyl group and the silicon SOMO both pseudo-equa-

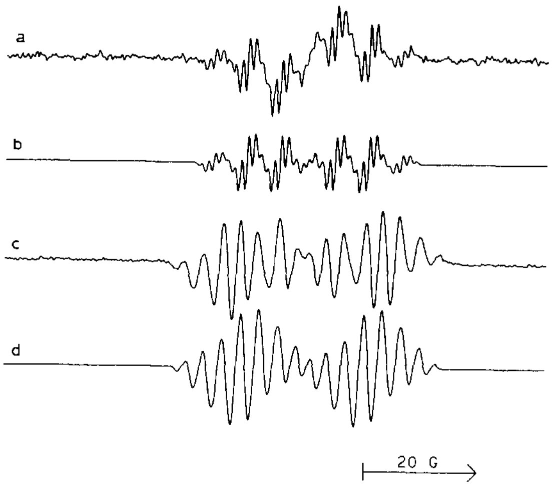
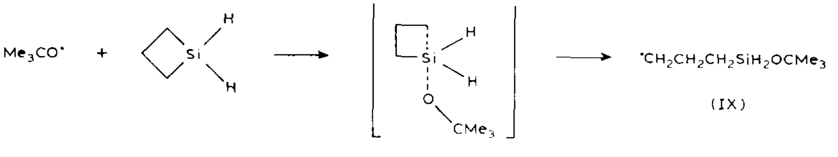


Fig. 2. (a) The EPR spectrum of the 1-methylsilacyclobut-1-yl radical in perdeuterioadamantane at −85 °C; (b) simulation of (a); (c) the EPR spectrum of 3-methylsilacyclobut-1-yl radical in adamantane at −50 °C; (d) simulation of (c).

torial is the most stable of the four permutations of pseudo-axial and pseudo-equatorial conformations, and that the spin density on the δ-protons of the methyl groups should be the greatest in this conformation. The δ proton couplings are similar in magnitude than those observed in the bicyclo[2.2.2]octyl radical (VII) [18]; it has been noted that for long range δ-couplings (in contrast to γ-couplings), the through-space and through-bond contributions to spin density at the remote position oppose rather than reinforce each other [14]. The UMINDO calculations referred to above also indicate that the radical centre has a greater pseudo-equatorial/pseudo-axial conformational preference (19 kJ mol^{-1}) than does the methyl group (6 kJ mol^{-1}).

The greater value of $a(^{29}\mathrm{Si})$ for the 3-methylsilacyclobut-1-yl radical (178.2 G) than that observed for the silacyclobut-1-yl radical itself accords with a reduced delocalization of the spin density from silicon in the substituted radical.

Reaction of the t-butoxy radical with silacyclobutane in solution. In structural studies of silicon-centred radicals, the method of choice for generating the radical is the reaction of photolytically produced t-butoxy radicals with the corresponding silane. Resolution of solution spectra is usually better than that obtained in an adamantane matrix. However, photolysis of a solution of silacyclobutane in $Me_3COOCMe_3$ at −40 °C gave a triplet of triplets (22.1 and 28.4 G), incompatible with any radical formed by α-, β- or γ-proton abstraction. This suggested that S_H2 attack has been taken place at silicon to give the 4-(t-butoxy)-4-silabutyl radical (IX) according to eq. 1. The triplet splittings agree well with those obtained for 1-octyl radicals at the same temperature (22.1 and 28.3 G) [19]. We believe



(VIII)

(IX)

(1)

that this S_H2 attack at a silicon-centre containing Si–H bonds is unprecedented, though S_H2 reactions at silicon have been postulated in other reactions, for example, the reaction of iodine with hexamethyldisilane, (eq. 2) [20].

$$\tfrac{1}{2}I_2 \rightleftharpoons I^{\cdot} \xrightarrow{Me_3SiSiMe_3} Me_3SiI + Me_3Si^{\cdot} \xrightarrow{I_2} Me_3SiI + I^{\cdot} \qquad (2)$$

The greater ease of S_H2 attack at silicon in silacyclobutane has an analogy in the greater ease of S_N2 reactions in such systems. One of the possible reasons for such behaviour [21] is that in the transition state, or intermediate VIII for an S_H2 reaction, the trigonal bipyramidal geometry offers relief of the steric strain inherent in the four-membered ring.

Experimental

Silacyclobutane (X) [22], 1-methylsilacyclobutane (XI) [23], silacyclobutane-1,1-d_2 (XII) [22], and 3-methylsilacyclobutane (XIII) [24] were prepared by literature procedures. All had purities > 99% by GLC.

Matrix samples of the above compounds were made in purified adamantane (Aldrich, puriss grade) or perdeuterioadamantane (97.7 atom % D, Merck, Sharp and Dohme of Canada, Ltd.) by the method of ref. 16. To avoid polymerization during the preparation of the matrix, compounds X and XII were heated only to 60–70 °C, whereas XI and XIII were heated to 100 °C. Pellets, made in an evacuated Beckman IR die, at 50 tons in^{-2} pressure, were cut up and introduced into quartz sample tubes. The tube was sealed off under vacuum and γ-irradiated on the ^{60}Co source (4 h, 0.6 krad min^{-1}) at 77 K by immersion in liquid nitrogen. After irradiation, the end of the tube with the sample was kept in liquid nitrogen, while the other end was warmed to red heat to remove impurity signals. The tube was then cooled and inverted so that the sample slipped to the signal-free end.

The EPR (Varian E104A EPR spectrometer connected to a Strumech SEED microcomputer) measurements and computations were carried out as described previously [2,25].

Acknowledgement

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