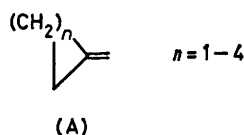


## Conformation of $\alpha$ -Substituted Cycloalkyl Radicals

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Radicals obtained by addition of  $\text{Et}_3\text{Si}^\cdot$  to the double bond of methylenecycloalkanes have been detected by e.s.r. at low temperature. The three-, four-, five-, and six-membered rings have been investigated. In the last case different splitting constants were detected for axial and equatorial hydrogens at low temperatures whereas a single average value is observed at higher temperatures. In the intermediate range line broadening effects allowed  $\Delta G^\ddagger$  5.2 kcal mol<sup>-1</sup> for the ring reversal process to be developed. In the case of the five-membered ring experimental evidence for a non-planar conformation has been also obtained. On the other hand the four-membered ring seems to be planar, at least within the approximation involved in these determinations.

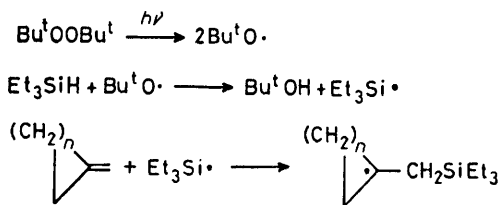
It has been shown recently that methylenecycloalkanes of general formula (A) undergo hydrogen abstraction by *t*-butoxyl radicals to give allylic radicals.<sup>1</sup> Interpretation of their e.s.r. spectra gave information upon the conformational arrangements of the cyclic moiety.



Krusic and Kochi showed that it is also possible to detect e.s.r. spectra of radicals generated by addition to double bonds.<sup>2-4</sup> We thus added the  $\text{Et}_3\text{Si}^\cdot$  radical to the aforementioned methylenecycloalkanes, and investigated the conformational behaviour of the resulting radicals.

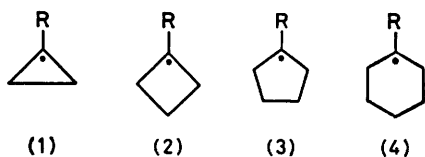
### RESULTS AND DISCUSSION

The addition of triethylsilyl radical to double bonds was accomplished by the reaction sequence in the Scheme.



SCHEME

The e.s.r. spectra of radicals (1)–(4) ( $\text{R} = \text{CH}_2\text{-SiEt}_3$ ) were observed at temperatures between  $-100^\circ$  and  $-130^\circ$ . In the case of methylenecyclopropane, in



addition to radical (1), a second radical was also observed in comparable amount. Its spectrum consists of a quartet ( $a_{\text{Me}}$  25.0 G) and large ( $a_{\text{H}}$  20.2<sub>5</sub> G) and small

doublets ( $a_{\text{H}}$  0.9<sub>5</sub> G). The latter value is strongly temperature dependent. This additional radical is not observed when  $\text{Me}_3\text{Si}^\cdot$  instead of  $\text{Et}_3\text{Si}^\cdot$  is added to the double bond. We suggest for this second radical a structure of the type  $\text{Et}_2\text{Si}(\text{CHR}_2)\text{-}\dot{\text{C}}\text{H-CH}_3$ , since the large splittings are equal to those reported<sup>5</sup> for  $\text{Et}_2\text{-SiH-CH-CH}_3$ , whereas the SiH splitting of the latter radical was not observed in our case.

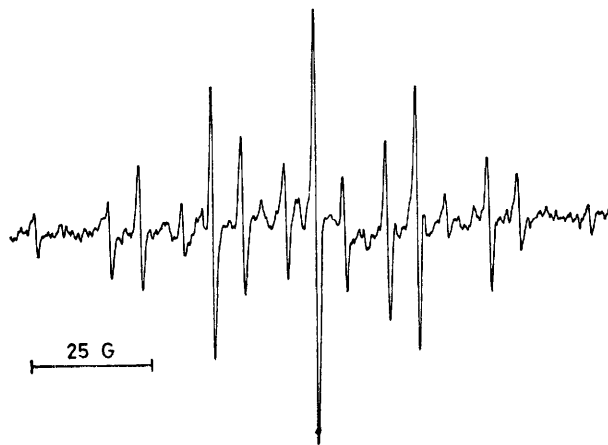


FIGURE 1 E.s.r. spectrum of (1;  $\text{R} = \text{Me}_3\text{SiCH}_2$ ) obtained from addition of trimethylsilyl radical to methylenecyclopropane at  $-120^\circ\text{C}$

The hyperfine splitting constants of radicals (1)–(4) are given in the Table; the assignments were made by analogy with the values of unsubstituted cycloalkyl radicals.<sup>6,7</sup>

In the case of the six-membered radical (4), two  $a_{\text{H}}$  values for the  $\beta$ -protons (axial and equatorial) were detected at  $-100^\circ$ . On raising the temperature, line broadening occurs and, at  $+120^\circ$ , a unique  $a_{\text{H}}$  value corresponding to four equivalent  $\beta$ -protons is observed. Similar behaviour was reported for the cyclohexyl radical in the solid state<sup>7</sup> and for other substituted cyclohexyl radicals.<sup>8-10</sup> Computer simulation (Figure 2) of the line shape affords the kinetic constants for the ring reversal process. The free energy of activation ( $\Delta G^\ddagger$ ) is independent of temperature within our experimental accuracy: an average value of  $5.2 \pm 0.3$  kcal

mol<sup>-1</sup> was determined, in agreement with the results in ref. 7.

In order to gain information on the conformational arrangement the well known relationship  $a_{H\beta} = A + B\cos^2\theta$  can be employed. Since we know the values

Proton splittings of radicals (1)–(4) at temperatures between  $-100$  and  $-130^\circ$

$(CH_2)_n$ $\beta$	Hyperfine splitting (G)			
	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$a_{\beta'}(H)$	16.00 (2 H)	17.00 (2 H)	15.50 (2 H)	15.38 (2 H) 6.25 (2 H)*
$a_{\beta}(H)$	21.60 (4 H)	34.00 (4 H)	32.10 (4 H)	38.50 (2 H)*
$a_{\gamma}(H)$	—	1.00 (2 H)	—	—

\* Average at  $+120^\circ C = 21.90$  G.

for axial and equatorial splitting in radical (4) the values of  $A$ ,  $B$ , and  $\theta$  can be derived if we also assume free rotation in the model radical  $Me_2\dot{C}CH_2SiEt_3$  (i.e.  $a = 22.25$  G =  $A + B/2$ ). The results obtained in this way ( $A$  3.8,  $B$  37.2,  $\theta -15^\circ$ ) show that  $\theta$  is midway between

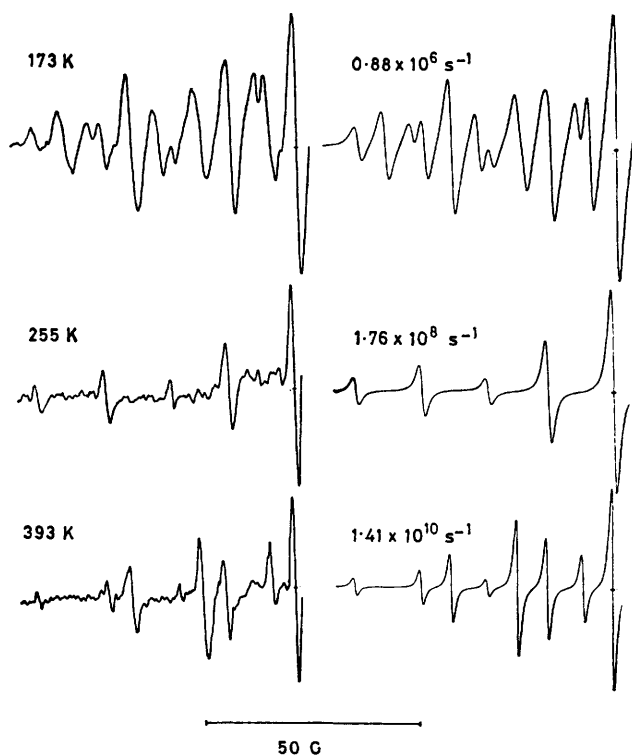


FIGURE 2 E.S.R. patterns (only half spectrum is reported) of radical (4) in cyclopropane at selected temperatures (left) with the corresponding computer simulation (right)

the angle expected for the chair and that for the half-chair: this result parallels that reported<sup>10</sup> for other cyclohexyl radicals. It seems therefore that these radicals have conformations corresponding to distorted chairs.

The information derived from the cyclohexyl radical

can be also used to assess the conformation of the other species if the same  $A$  and  $B$  values, as seems reasonable, are employed.

However, since in the other radicals the four  $\beta$ -hydrogens are equivalent, the average between the two equivalent situations has to be considered.\*

The result of the conformational analysis for the cyclopentyl radical (3) yields  $\theta$   $17.5^\circ$ , to be compared with  $-10^\circ$  for the envelope,  $+10^\circ$  for the half-chair, and  $+28^\circ$  for the planar conformation: clearly only the envelope can be safely dismissed. The  $a_H$  splittings calculated with this angle are 32.8 G for the planar and 30.8 G for the half-chair: both are too close to the experimental value (32.1) for an unambiguous determination. This same uncertainty has been already pointed out in the case of the analogous five-membered radicals.<sup>9,10</sup>

Gilbert and his co-workers solved this uncertainty<sup>10,11</sup> by studying monosubstituted five-membered radicals: the finding that two  $\beta$ -hydrogens have different splittings is in agreement only with a bent conformation. The conclusion that cyclopentyl radicals are not planar<sup>10</sup> was further confirmed by the report of different  $\beta$ -splittings in the radical obtained<sup>12</sup> by addition of methylthiyl (MeS $\cdot$ ) to cyclopentene. The deviation of  $\theta$  from the angle expected for a perfect half-chair probably indicates that also this structure is flattened.

If we try to employ the  $A$  and  $B$  values for checking the planarity of the cyclopropyl radical (1) an unacceptable value for  $\theta$  is obtained ( $\theta$  is expected to be  $18^\circ$  for the planar cyclopropyl).

Since the empirical values of  $A$  and  $B$  depend on the spin density, and therefore on the type of orbital bearing the unpaired electron, the anomalous finding indicates that different  $A$  and  $B$  values should be used for (1). This means that the orbitals of the trigonal carbon in the cyclopropyl radical are different with respect to those of the other cycloalkyl radicals.

This fact had been already pointed out<sup>13</sup> since the splittings of unsubstituted cyclopropyl do not follow the trend of the other cycloalkyl radicals. Rather than planar, the trigonal carbon of cyclopropyl is thought<sup>13</sup> to be bent by  $30$ – $35^\circ$ . On the other hand if the cyclobutyl radical (2) is planar at the radical centre the calculated value of  $\theta$   $18^\circ$  is quite close to that expected for a planar ring ( $\theta$   $25^\circ$ ). Conversely, using an angle of  $25^\circ$ , a value of 34.3 G is computed for a planar cyclobutyl ring, to be compared with an experimental splitting of 34.0 G. This correspondence encourages us to believe that the cyclobutyl radical is essentially planar and that the assumptions made in this work are reasonable.

#### EXPERIMENTAL

**Materials.**—All the compounds employed in this study were reagent grade commercial samples which were used

\* Note that  $\theta + \theta' = 60^\circ$  is true only for a six-membered ring but is  $56^\circ$  for a five-,  $50^\circ$  for a four-, and  $36^\circ$  for a three-membered ring.<sup>1</sup>

without further purification. Only methylenecyclohexane was distilled prior to use.

*E.s.r. Measurements.*—The e.s.r. spectrometer and the photolysis equipment were previously described.<sup>1</sup> The e.s.r. samples containing di-*t*-butyl peroxide, triethylsilane, and methylenecycloalkane were diluted *in vacuo* with sufficient cyclopropane to give a final ratio of *ca.* 1 : 2 : 2 : 4 (v/v). The sample containing methylenecyclohexane was saturated with nitrogen to avoid bubbling at the high temperatures. The temperature was measured by a copper-constantan thermocouple placed just below the sensitive part of the cavity in a sample tube containing Bu<sup>t</sup>OObu<sup>t</sup>, Et<sub>3</sub>SiH, and the substrate; we believe that the maximum error in the determination of the temperature of the sample is  $\pm 5$  °C.

Coupling constants were verified by computer simulation using a program in which a Lorentzian line shape was assumed. For radical (4) the experimental spectra were simulated with a computer program in which line broadening effect due to exchange is taken in account. Simulations were performed in the range where the chair-to-chair interconversion gives the maximum broadening effect. Five temperatures between  $-65$  and  $-18^\circ$  were used to obtain the rate constants, and the corresponding  $\Delta G^\ddagger$  values were averaged in that no appreciable differences were observed.

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