Allylic Radicals from Methylenecycloalkanes

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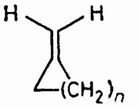
Abstraction of an allylic hydrogen in methylene cyclo-propane, -butane, -pentane, and -hexane affords the corresponding allylic radicals. Their e.s.r. spectra can be detected in appropriate conditions below −100 °C. In the case of the six-membered ring radical the two pseudoaxial and the two pseudoequatorial hydrogens are diastereotopic, thus indicating that, as expected, a half-chair conformation is adopted. On the other hand the five-membered ring radical prefers an envelope conformation, whereas the four-membered ring radical (and obviously the three-membered) are planar.

HYDROGEN abstraction from CH_3, CH_2, or CH α to a double bond yields allylic radicals that can be detected by e.s.r. spectroscopy.[1,2] Both the *cis*- and *trans*-alkyl substituted isomers of the open-chain allylic radicals have been obtained.[2] Recently an allylic-like radical, having three nitrogen instead of three carbon atoms, has also been reported.[3] Cyclic allylic radicals have been obtained only in the *cis*-configuration: [2,4,5] we report here the e.s.r. detection of cyclic allylic radicals with the ring substituent in a *trans*-configuration.

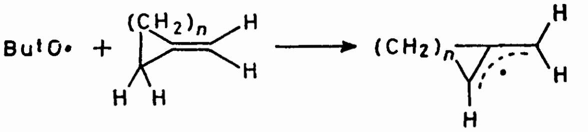
The radicals were obtained by photolysis of Bu^tOOBu^t in presence of the methylenecycloalkanes (1)—(4).

(1) $n = 1$
(2) $n = 2$
(3) $n = 3$
(4) $n = 4$



Reactions (1) and (2) occur.

$$\mathrm{Bu^tOOBu^t} \xrightarrow{h\nu} 2\mathrm{Bu^tO}\cdot \qquad (1)$$



(2)

(1) - (4)

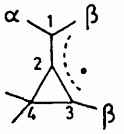
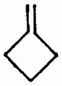
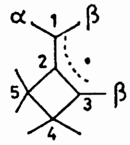
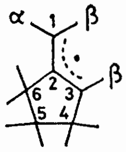
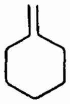
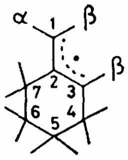
(5) - (8)

In the case of $n = 2$—4 only the corresponding allylic radicals (6)—(8) were observed, whereas in the case of $n = 1$ (methylenecyclopropane) a second radical, in addition to 2-methylenecyclopropyl (5), has been detected with similar intensity. Its e.s.r. spectrum consists of two triplets (a_H 26.8 and 21.8 G respectively), further split in two doublets (a_H 0.55 and 0.26 G). Most likely we have been observing the allylmethyl radical $\cdot CH_2$-CH_2-CH=CH_2, arising from ring opening, followed by rearrangement. The same radical has also been reported in the photolysis of methylcyclopropane.[2]

A sample spectrum of these allylic radicals is shown in Figure 1 [radical (6) from methylenecyclobutane]. In the Table the hyperfine splitting constants (a_H) of radicals (5)—(8) are reported.

The assignment of the a_H values has been performed by analogy with those of the corresponding open-chain *trans*-substituted allylic radicals.[2] In the three-membered radical (5) the β-hydrogens of the allylic moiety (1β- and 3β-H) (see Table for numbering) have quite different splittings, whereas these splittings become almost degenerate in radicals with larger rings [*i.e.* (6)—(8)]. It appears then that the strain of the three-membered ring affects the geometry of the allylic group, thus modifying the symmetric spin density distribution on the β-hydrogens in position 1 and 3. The equivalence of the cor-

Hyperfine coupling for the allyl radicals (5)—(8) constants

Substrate	Allyl radical	(a_H)	Coupling constants (G)
 (1)	 (5)	$a_{1\alpha}$ $a_{1\beta}$ $a_{3\beta}$ $a_{4,4}$	15.63 13.25 12.45 19.00
 (2)	 (6)	$a_{1\alpha}$ $a_{1\beta}$ $a_{3\beta}$ $a_{4\,4'}$ $a_{5,5'}$	14.10 13.50 13.90 24.25 4.10
 (3)	 (7)	$a_{1\alpha}$ $a_{1\beta,3\beta}$ $a_{4,4'}$ $a_{6,6'}$	14.38 13.50 22.75 3.63
 (4)	 (8)	$a_{1\alpha}$ $a_{1\beta,3\beta}$ $a_{4\,ax}$ $a_{4'\,eq}$ $a_{7,7'}$ $a_{7\,ax}$ $a_{7'\,eq}$	14.50 13.75 28.00 15.00 3.75 at −100 °C $\left.\begin{array}{l}4.75\\2.75\end{array}\right\}$ at −120 °C

responding a_H values, in fact, is observed not only in (6)—(8) but also in the open-chain *trans*-allylic radical (*trans*-but-2-enyl) [2] where there is no strain whatsoever.

The splittings of the hydrogen atoms of methylene group bonded to one of the terminal carbons (C-3) of the allylic moiety appear to be much larger than those of CH_2 bonded to the central allylic C-2. The spin density on C-1 and -3 is known to be larger than that on C-2. In connection with this fact it is interesting to observe that in (5) where C-4 is bonded to both C-2 and -3, the a_H splitting of 4-H is almost equal to the difference of those of 4- and 5-H of the four-membered radical (6), thus suggesting that the latter couplings have opposite sign.

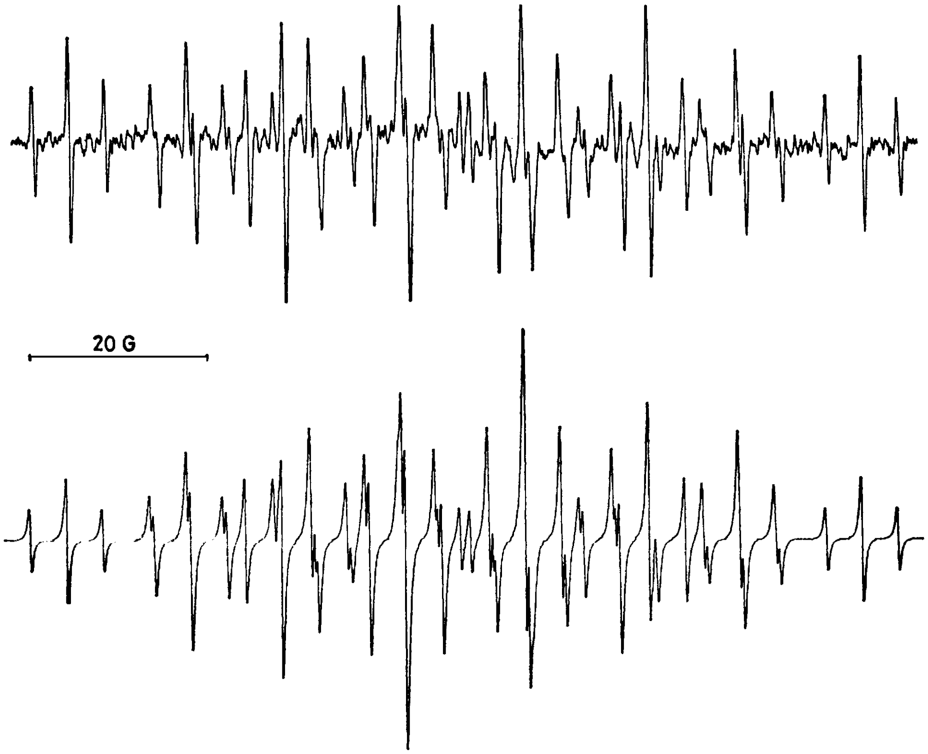


FIGURE 1 Experimental and computer simulated (line width 0.3 G) e.s.r. spectra of 2-methylenecyclobutyl radical (6) at −100 °C in cyclopropane

The hyperfine splitting constants of the pair of hydrogens in position 4 are equal in (5)—(7) and so are those of the hydrogens in positions 5 and 6 in (6) and (7). This means that either the conformation of these rings is planar or that the rings interconvert rapidly through a dynamic plane of symmetry. Planarity is compulsory for the three-membered ring [radical (5)] and very likely for the four-membered ring of (6) owing to the presence of a partial double-bond: for radical (7), on the contrary a non-planar conformation is possible. In the radical (8) the a_H values in position 4 are non-equivalent at −100° (see Table), whereas those in position 7 are equal ($a_{7',7\text{-H}}$ 3.7_5 G). However, some spectral lines are broader than others, thus indicating that a dynamic process (most likely interconversion between two equivalent conformations) occurs in a time scale comparable with the spin lifetime. This is confirmed by the fact that, at −120°, the 1 : 2 : 1 triplet due to the 7- and 7′-H pair becomes a pair of doublets, the average of the new splittings (2.7_5 and 4.7_5 G) being equal to that of the former triplet. Therefore at −100° the interconversion is slow enough as to show different splittings for those diastereotopic hydrogens (such as 4- and 4′-H) with large a_H differences whereas it is still too fast to distinguish between the diastereotopic 7- and 7′-H which have a much smaller Δa_H. Unfortunately the low signal-to-noise ratio and the complexity of the spectrum at −120° did not allow a reliable line-shape analysis for measuring the interconversion barrier. However, a knowledge of the two a_H values for the diastereotopic hydrogens can give information about the ring conformation of radical (8). In principle two conformations deserve consideration, the envelope [6] (sometime called ' sofa ') and the half-chair [6] (sometime referred to as twisted). Both conformations (Figure 2) can interconvert into an enantiomeric form *via* ring inversion, thus accounting for the observed line-shape effect. In the envelope form one of the two pairs of hydrogens has the dihedral angles θ (*i.e.* the angles between the CH bond and the π orbital bearing the unpaired electron) equal, respectively, to 0 and 60°; the other pair has two equivalent dihedral angles, each equal to 30°. The a_H values of the protons in position β to the unpaired electron are known [7] to depend on θ according to equation (3).

$$a_H = A + B\cos^2\theta \qquad (3)$$

As a consequence this envelope conformation cannot account for the four different a_H values experimentally observed, since two hydrogens, although diastereotopic, have equal θ, and thus should have almost equal splittings. On the other hand, the half-chair conformation has a pseudoaxial (θ 10°) and a pseudoequatorial (θ 50°) hydrogen on both C-4 and -7 (Figure 2) and therefore four different splittings can, in principle, be observed. To confirm the half-chair arrangement we must obtain $\theta \cong 10°$ using the experimental splittings to fit equation (3). It should be remembered that θ 50° for the pseudoequatorial hydrogens will then be a consequence of the relationship $\theta_{ax} + \theta_{eq} = 60°$, which holds for a six-membered ring. It is also worth mentioning that in smaller rings the sum of the angles θ is smaller: it is in fact *ca.* 56° in the five-, 50° in the four-, and 36° in the three-membered rings. In the case of radical (8) two independent equations (4) and (5) can be derived for the splittings of the two hydrogens in position 4.

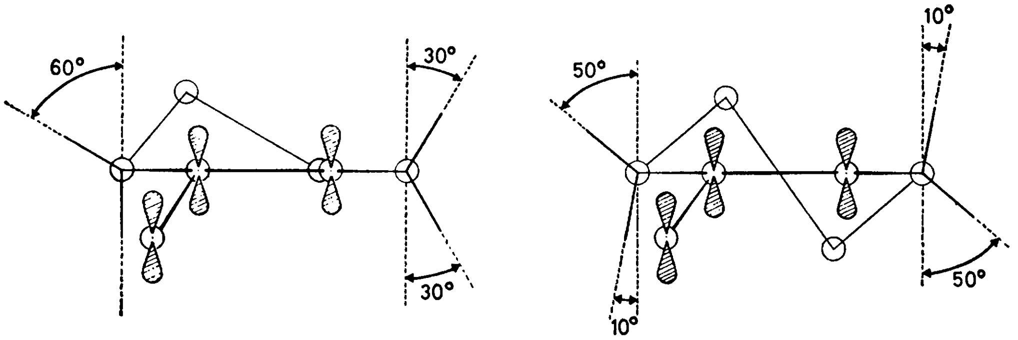


FIGURE 2 Schematic drawing of the envelope (left) and half-chair (right) conformation of 2-methylenecyclohexyl radical (8)

$$28\ \mathrm{G} = A + B\cos^2\theta \qquad (4)$$

$$15\ \mathrm{G} = A + B\cos^2(60 - \theta) \qquad (5)$$

Since, in addition to θ, A and B are also not known, a third independent equation is required. If a very similar radical (*trans*-but-2-enyl) is considered,[2] its a_{Me} splitting can be used to fit the free rotation equation (6).

$$a_{Me} = 16.4\ \mathrm{G} = A + \frac{B}{2\pi}\int_0^{2\pi}\cos^2\theta\, d\theta = A + B/2 \qquad (6)$$

The same approach can be repeated to generate a second set of three equations using the two $a_{7\text{-H}}$ splittings (see Table) and a_{Me} 3.2 G taken from the isobutenyl radical.[2] The results of both sets of equations are expected, in addition, to fulfil the following conditions: (i) the term A has to be small, *i.e.* lying within the theoretically expected zero and the largest values empirically observed (3—4 G);[8,9] (ii) within the experimental uncertainty the θ value calculated from one set of equations must be equal to that derived from the second set, since the half-chair conformation of (8) has a centre of symmetry with respect to the cyclic moiety.

The solution of the first set (values for 4- and 4'-H). yields A 3.6 G, B 25.5 G, and θ 12°; the solution of the second set (for 7- and 7'-H) gives A 1.5 G, B 3.3 G, and θ 8°. There is little doubt that the average value, θ 10 ± 2°, fits expectations for a half-chair conformation.

With the assumption that A and B maintain the same values it is possible to investigate the conformation of the five-membered ring radical (7). This assumption can be tested with the four-membered radical (6) which is expected to be planar; for the ring to assume a puckered conformation the allylic moiety of (6) should, in fact, lose its planarity. The experimental splittings of 1α-, 1β-, and 3β-H have values very close to those of all the other planar allylic radicals.[2] In a planar conformation the θ value of (6) is expected to be *ca.* 25°: the use of the relation (3), with the A and B values already determined, gives θ 25.7°. This confirms that the same values can be also used for assigning the conformation of (7).

The possible arrangements of (7) are the planar (two equal θ of 28°) and the envelope conformation (θ_1 15 and θ_2 56 − 15°). Since it was not possible to observe two different $a_{4\text{-H}}$ splittings, as in the case of (8), the average of the two possible values has to be considered. The equation thus becomes (7) where A and B have the

$$a_{4\text{-H}} = 22.7_5\ \mathrm{G} = A + B\,[\cos^2\theta + \cos^2(56° - \theta)]/2 \qquad (7)$$

same values as in (8) (3.6 and 25.5 G, respectively). The solution affords θ 16° which fits expectations for an envelope conformation. So far only half-chair conformations had been reported for five-membered radicals:[9,10] however no double bond, or partial double bond, was present in these examples. The strain due to the allylic bond in (7) is such as to modify the half-chair into an envelope.

EXPERIMENTAL

The e.s.r. spectra were recorded with a Varian E 104 spectrometer equipped with standard temperature devices. The light source was a high-pressure mercury 1 kW lamp; the optical system consisted of Suprasil quartz lenses. Coupling constants were verified by computer simulation using a program in which a Lorentian line-shape was assumed.

All materials employed in this study were reagent grade commercial samples, most of which were used without further purification.

A small amount of di-t-butyl peroxide was introduced in a Suprasil e.s.r. tube followed by the desired amount of hydrocarbon. The contents were thorougly degassed on a vacuum line by the freeze–thaw technique, after which the desired amount of solvent (cyclopropane) was introduced into the sample tube by bulb-to-bulb distillation: the tube was then sealed off in vacuum with a flame.

G. P. thanks the C.N.R., Ozzano E., for financial support.

[9/904 *Received, 12th June,* 1979]

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