is a reactive transient intermediate qualitatively comparable to species such as allyl or methyl with respect to dimerization or reaction with radicals, but which nevertheless has considerable stability compared to two acetylene molecules.[21] Its ionization potential is no higher than 8.6 eV and our best current value is 8.2 eV.

Acknowledgment. We acknowledge helpful discussions with F. P. Lossing concerning interpretation of the mass spectral data and Badische Anilin und Soda Fabrik for their generous gift of cyclooctatetraene.

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[21] Empirically, molecules having bonds with dissociation energies of about 20 kcal or less will not survive our conditions at pyrolysis temperatures of about 800°. Also, most of the observed acetylene can be accounted for by a process other than $C_4H_4 \rightarrow 2C_2H_2$.

[22] Union Carbide Corporation Postdoctoral Fellow, 1967–1968.

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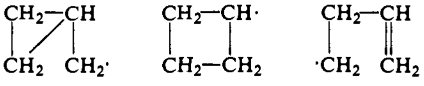
Received December 12, 1968

Homoallylic Rearrangement and Electron Spin Resonance of Cyclopropylcarbinyl Radicals

Sir:

Homoallylic rearrangements among cyclopropylcarbinyl (I), cyclobutyl (II), and allylcarbinyl (III) radicals and related systems have been extensively examined.[1] The problem is especially pertinent in view of the extremely facile rearrangement observed with the corresponding carbonium ions. In the latter case, the role of *nonclassical* carbonium ions has been the subject of considerable controversy.[2] The possibility of nonclassical free radicals in related systems has been considered,[3] and recently the 7-norbornenyl species has been presented as a nonclassical radical.[4]



I II III

Heretofore all discussions relating to the structure of these radicals have been based on inference from chemical studies. Direct observation of the electron spin resonance (esr) spectrum of these species would provide unequivocal evidence of their structure.

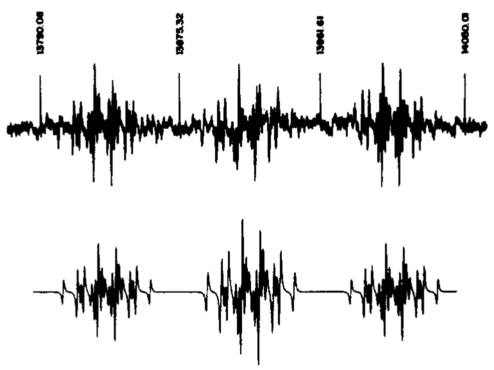


Figure 1. Esr spectrum of cyclopropylcarbinyl radical (−150°). The calculated spectrum includes second-order effects. The proton nmr frequency markers are in kilocycles per second.

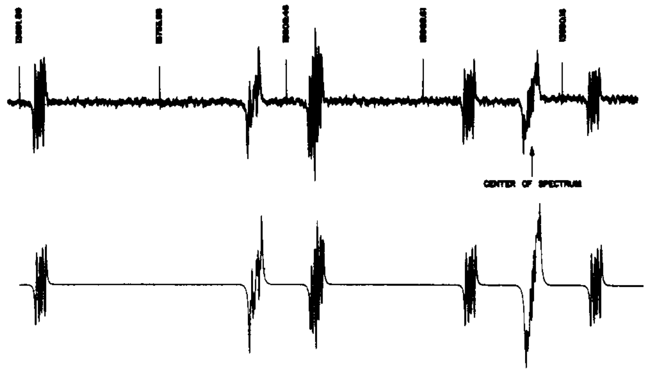
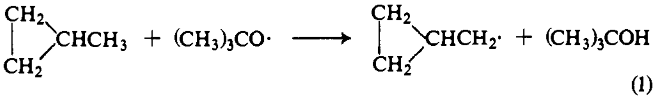


Figure 2. Experimental and calculated low-field halves of the esr spectrum of the allylcarbinyl radical showing second-order effects (−90°).

In this report we wish to present the esr spectrum of cyclopropylcarbinyl radicals in solution. A general method for the production of alkyl radicals from alkanes for esr studies, by the use of photochemically generated *t*-butoxy radicals from di-*t*-butyl peroxide, has been described previously.[5] *t*-Butoxy radicals react with methylcyclopropane by selective removal of one of the methyl hydrogens (eq 1).[6] The observed esr spectrum of the


(1)

resulting radical is highly dependent on the temperature. At temperatures less than −140°, the esr spectrum reproduced in Figure 1 was obtained. Between 0 and −100° the spectrum presented in Figure 2 was observed. At intermediate temperatures the esr spectrum consisted of a superposition of these two individual spectra. No exceptional line broadening was observed in these spectra to indicate the existence of any time-averaging phenomena.[7]

The esr spectrum presented in Figure 1 is clearly

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[1] (a) C. Walling, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 440 ff; (b) D. I. Davies and S. Cristol, *Advan. Free Radical Chem.*, **1**, 155 (1965); (c) J. C. Martin, J. E. Schultz, and J. W. Timberlake, *Tetrahedron Letters*, 4629 (1967); (d) M. Hanack and H. J. Schneider, *Forschr. Chem. Forsch.*, **8**, 554 (1967); (e) J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, **90**, 295 (1968).

[2] (a) P. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) M. Hanack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967); (c) D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (d) P. von R. Schleyer and G. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966); (e) R. Moss and F. Shulman, *ibid.*, **90**, 2731 (1968); *Tetrahedron*, **24**, 2881 (1968); (f) K. B. Wiberg and G. Szelmies, *J. Am. Chem. Soc.*, **90**, 4195 (1968).

[3] (a) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 3051 (1967); **89**, 923, 934 (1967); (b) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, **89**, 3051 (1967).

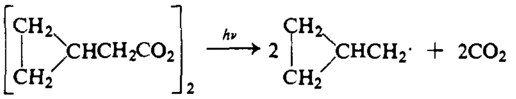
[4] J. Warkentin and E. Sanford, *ibid.*, **90**, 1668 (1968).

[5] P. J. Krusic and J. K. Kochi, *ibid.*, **90**, 7155 (1968).

[6] Similarly, product studies of the free-radical chain chlorination of methylcyclopropane by *t*-butyl hypochlorite require that the methyl hydrogens be abstracted by *t*-butoxy radical [C. Walling and J. Fredericks, *ibid.*, **84**, 3327 (1962)].

[7] This does not include broadening due to restricted rotation.

associated with the cyclopropylcarbinyl radical (I) and that presented in Figure 2[8] represents the allylcarbinyl radical (III).[9] The same spectra were obtained from the photolyses of cyclopropylacetyl peroxide (Figure 1, at temperatures less than −140°)[11] and allylacetyl peroxide (Figure 2),[11a] respectively.

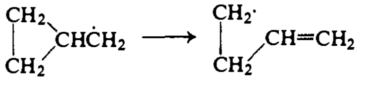


$$\left[\begin{array}{l}CH_2\\ |\;\;\rangle CHCH_2CO_2\\ CH_2\end{array}\right]_2 \xrightarrow{h\nu} 2\begin{array}{l}CH_2\\ |\;\;\rangle CHCH_2\cdot\\ CH_2\end{array} + 2CO_2 \qquad (2)$$

(2)

I

These results show that cyclopropylcarbinyl (I) and allylcarbinyl (III) are *discrete free radicals*, but that the cyclopropylcarbinyl radical rearranges rapidly to allylcarbinyl radical (eq 3) at temperatures higher than −120°.

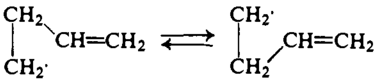


$$\begin{array}{l}CH_2\\ |\;\;\rangle \dot{C}HCH_2\\ CH_2\end{array} \longrightarrow \begin{array}{l}CH_2\cdot\\ |\;\;\rangle CH{=}CH_2\\ CH_2\end{array} \qquad (3)$$

(3)

I III

We could find no evidence for the presence of cyclopropylcarbinyl radical from the photolysis of allylacetyl peroxide even at temperatures less than −140°. Allylcarbinyl radical is the only species observed, and there is no evidence of reversibility in eq 3.[12] The spectra also indicate that the interconversion of allylcarbinyl radicals (eq 4) observed at higher temperatures[3a] is slow on the esr time scale at temperatures less than 0°.



$$\begin{array}{l}CH_2\\ |\;\;\backslash CH{=}CH_2\\ CH_2\cdot\end{array} \rightleftarrows \begin{array}{l}CH_2\cdot\\ |\;\;/ CH{=}CH_2\\ CH_2\end{array} \qquad (4)$$

(4)

The isotropic hyperfine coupling constants for I and III are presented in Table I. The electron spin resonance spectrum of the cyclobutyl radical obtained from cyclobutane by electron radiolysis[10] or by reaction with *t*-butoxy radical[5] has been recorded. The spectrum obtained from the photolysis of cyclobutanecarbonyl peroxide is reproduced in Figure 3, and the pertinent coupling constants are included in Table I for comparison.

The esr spectrum of cyclopropylcarbinyl radical shows a number of interesting features. The coupling constant of the single tertiary hydrogen is much smaller than is usual for a β hydrogen. It is deduced from this that the plane of the CH_2 group bisects the cyclopropane ring since this configuration places the single hydrogen in the node of the p orbital containing the spin, as shown in structure A.[13-16] The coupling constant for the α

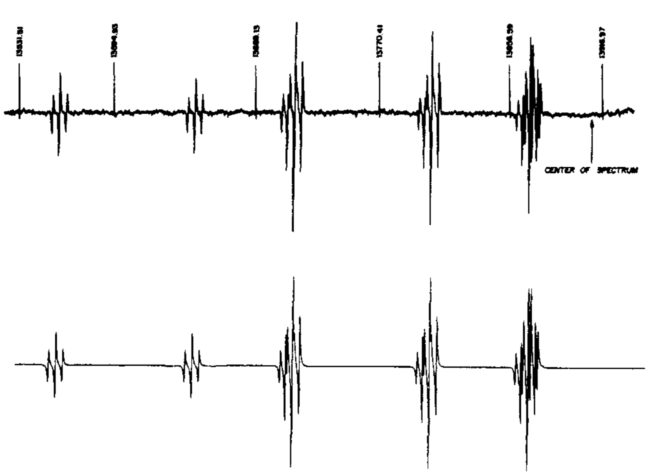
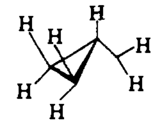


Figure 3. Experimental and calculated low-field halves of the esr spectrum of the cyclobutyl radical with resolved second-order splittings (−90°).

Table I. Hyperfine Coupling Constants for the Cyclopropylcarbinyl, Cyclobutyl, and Allylcarbinyl Radicals

Radical	Hyperfine coupling constants, Gauss			
	$a_{\alpha-H}$	$a_{\beta-H}$	$a_{\gamma-H}$	$a_{\delta-H}$
I	20.74	2.55	2.98 (*anti*)[a] 2.01 (*syn*)	
III[b]	22.17 (22.23)	28.53 (29.7)	0.61 (0.63)	0.35[c] (0.35)[c]
II[b]	21.30 (21.20)	36.77 (36.66)	1.09 (1.12)	

[a] These assignments are arbitrary and based on the applicability of Russell's studies on long-range hfs. (G. A. Russell, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, p 87 ff; these assignments of the hfs constants are also consistent with the odd-electron distribution [γ-H (*syn*) = 0.0006 and γ-H (*anti*) = 0.0041] calculated by the extended Hückel treatment for the bisected form of cyclopropylcarbinyl radical (private communication, Dr. Roald Hoffmann).) Further stereochemical studies are in progress. [b] Values in parentheses are from ref 10. [c] Due to only one δ hydrogen.



A

bisected conformer of the cyclopropylcarbinyl radical

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[8] A slightly larger line width for the lines corresponding to M = 0 for the α protons was used in the computer simulation to achieve agreement with the experimental spectrum. The broadening of these lines indicates a hindered rotation about the C_α–C_β bond. Furthermore, a small coupling constant of only one δ hydrogen suggests a favorable orientation of a single δ hydrogen relative to the α carbon. These features support the idea of a small resonance contribution from a three- or four-membered ring structure.

[9] The esr spectrum of the allylcarbinyl radical has also been observed during electron radiolysis of ethylene.[10]

[10] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[11] (a) J. K. Kochi and P. J. Krusic, to be published. (b) Only the spectrum of allylcarbinyl radical was observed during photolysis of cyclopropylacetyl peroxide at temperatures higher than −100°.

[12] If the exchange of the α and β carbons of the allylcarbinyl radical occurs *via* a cyclopropylmethyl radical,[3a] the concentration of this intermediate must be too low to observe under our conditions.

[13] See Table I, footnote *a*.

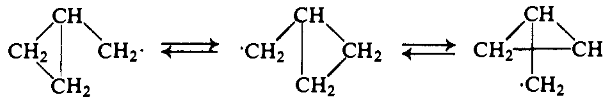
[14] A similar conclusion regarding geometry was drawn by Russell in a study of cyclopropyl semidione radical ions.[13]

[15] Interestingly, the preferred conformation of the cyclopropylcarbinyl radical proposed here is the same as that for analogous *cations* (C. U. Pittman and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5123 (1965); *cf.* also J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4311 (1968), for references to theoretical studies).

[16] The two α protons in the configuration A should be inequivalent. Our results show that their coupling constants are nearly if not completely equal.

hydrogens is a little smaller than expected. The CH_2 ring hydrogens also have significantly larger coupling constants (1–2 G) than expected even for favorably oriented γ hydrogens. Partial donation of the spin (about 5–10%) into an antibonding ring orbital which is antisymmetric with respect to the plane of symmetry of the molecule is indicated.

It should be noted that the three methylene groups in the cyclopropylmethyl radical are not equivalent. There may still be a rate process which exchanges these non-equivalent methylene groups. If there is, it is slow on the esr time scale, *i.e.*, the lifetime of a given structure in a process such as



is greater than ~10^{-7} sec.[17]

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(17) Deuterium labeling studies are in progress.

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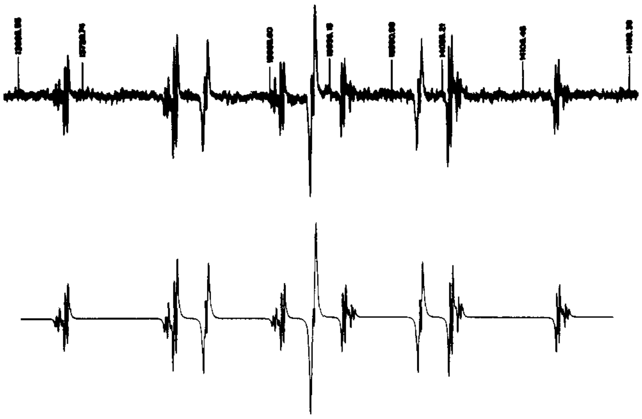


Figure 1. Esr spectrum of the substituted allylcarbinyl radical $\cdot CH_2CH_2CH{=}CHCH_3$ resulting by hydrogen atom abstraction from ethylcyclopropane at −80°. The spectrum is a superposition of spectra belonging to *cis* and *trans* isomers about the double bond. The less abundant isomer shows weak interactions with a γ and a δ proton of nearly equal magnitudes (small triplet splitting). The simulated spectrum implies equal *g* values and a ratio of concentrations of 1:2.4.

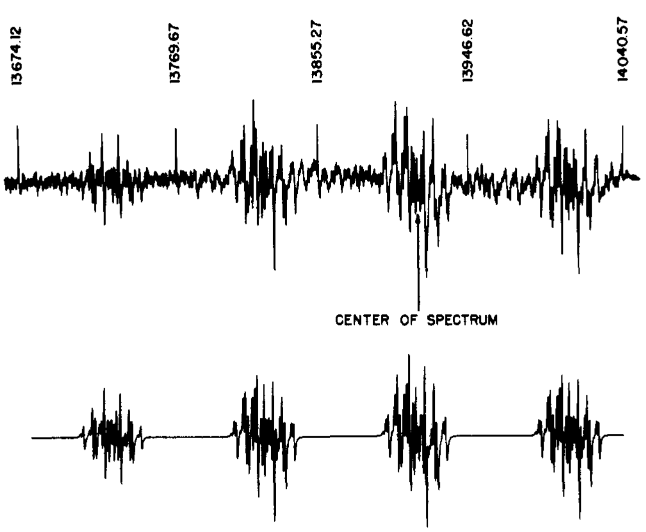
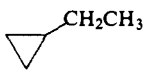


Figure 2. Esr spectrum of the substituted cyclopropylcarbinyl radical $C_3H_5\dot{C}(CH_3)_2$ at −150°. Four of the seven multiplets are shown. The calculated spectrum includes second-order effects.

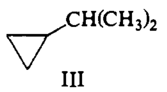
Electron Spin Resonance of Free Radicals from Alkylcyclopropanes

Sir:

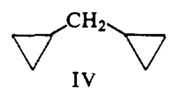
We wish to elaborate on the structures of cyclopropylcarbinyl radicals (I) and analogous radicals derived from alkylcyclopropanes II–VII and to relate their spontaneous homoallylic rearrangement with the earlier study.[1] The electron spin resonance study of cyclopropylcarbinyl radical (I) derived from methylcyclopropane by hydrogen abstraction with *t*-butoxy radical from the photolysis of di-*t*-butyl peroxide has been described.[1] Cyclopropane itself produces no esr signal under the conditions of these experiments and can be conveniently used as a solvent or diluent. For compounds II–V and VII hydrogen abstraction from the α position in the side chain is exclusively observed. The process of abstracting a secondary or tertiary hydrogen which occurs in compounds II, III, IV, and VII is analogous to reactions previously demonstrated in aliphatic hydrocarbons.[2] A primary hydrogen is abstracted from compounds V and VI as it is in the parent methylcyclopropane.[1]



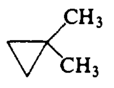
II



III



IV



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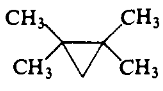
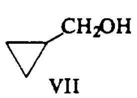


VI



VII

Each of these hydrocarbons yields two isomeric radicals, one of which is predominant at relatively high temperatures (> −100°). The other radical accounts for the spectrum obtained at low temperatures (< −140°). The rate of isomerization is slow on the esr time scale. Spectra illustrative of the high- and low-temperature radicals are shown in Figures 1 and 2, respectively. Analyses of the esr spectra indicate that the radicals have structures VIII (high temperature) and IX (low temperature) which are completely analogous to the allylcarbinyl

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(1) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, **91**, 1877 (1969).

(2) P. J. Krusic and J. K. Kochi, *ibid.*, **90**, 7155 (1968).