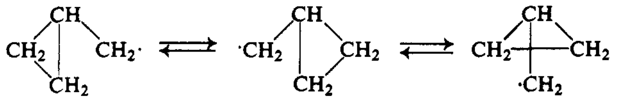
hydrogens is a little smaller than expected. The CH_2 ring hydrogens also have significantly larger coupling constants (1–2 G) than expected even for favorably oriented γ hydrogens. Partial donation of the spin (about 5–10%) into an antibonding ring orbital which is antisymmetric with respect to the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

[17] Deuterium labeling studies are in progress.

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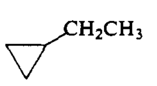
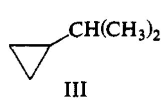
Electron Spin Resonance of Free Radicals from Alkylcyclopropanes

Sir:

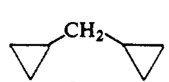
We wish to elaborate on the structures of cyclopropylcarbinyl radicals (I) and analogous radicals derived from alkylcyclopropanes II–VII and to relate their spontaneous homoallylic rearrangement with the earlier study.[1] The electron spin resonance study of cyclopropylcarbinyl radical (I) derived from 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



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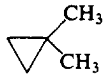

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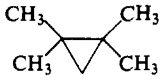
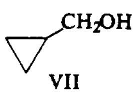


VI



VII

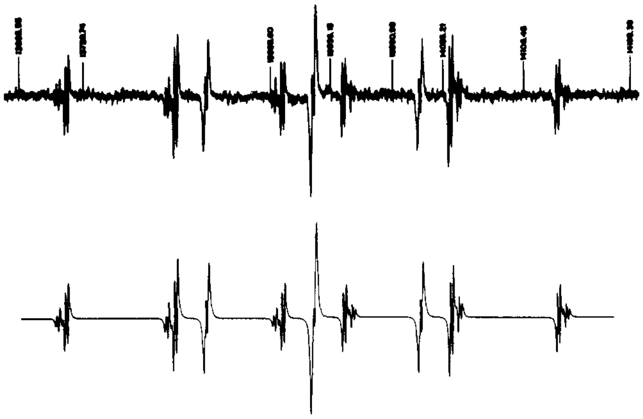


Figure 1. Esr spectrum of the substituted allylcarbinyl radical $\cdot CH_2CH_2CH{=}CHCH_3$ resulting by hydrogen atom abstraction from ethylcyclopropane at −80°. The spectrum is a superposition of spectra belonging to *cis* and *trans* isomers about the double bond. The less abundant isomer shows weak 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.

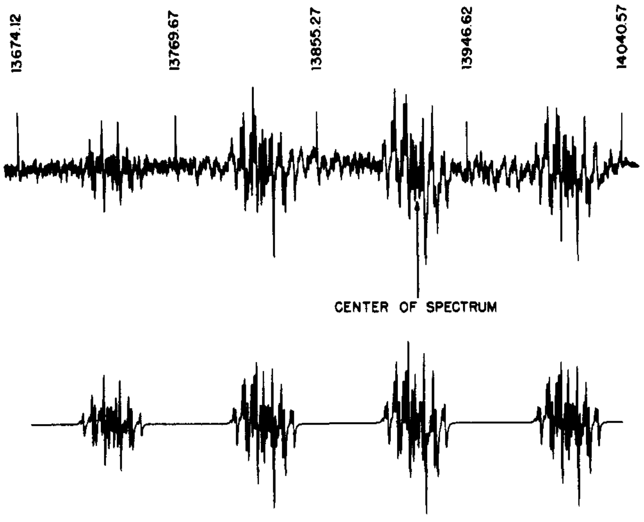


Figure 2. Esr spectrum of the substituted cyclopropylcarbinyl radical $C_3H_5\dot{C}(CH_3)_2$ at −150°. Four of the seven multiplets are shown. The calculated spectrum includes second-order effects.

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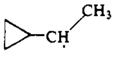
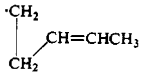
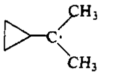
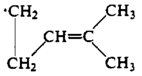
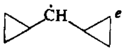
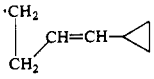
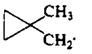
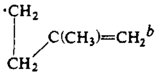
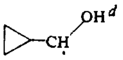
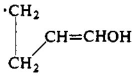
[1] J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, **91**, 1877 (1969).

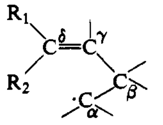
[2] P. J. Krusic and J. K. Kochi, *ibid.*, **90**, 7155 (1968).

Table I. Electron Spin Resonance Coupling Constants of Substituted Cyclopropylcarbinyl and Allylcarbinyl Radicals[a]

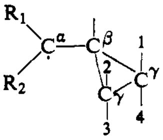
Alkylcyclopropane	Cyclopropylcarbinyl radical	Temp, °C	Coupling constants, G	Allylcarbinyl radical	Temp, °C	Coupling constants, G *trans*	*cis*
II		−153	$\mathrm{CH_3} = 22.3$ $\alpha\mathrm{H} = 22.3$ $\beta = 2.9$ $\gamma_1\gamma_2 = 1.9$ $\gamma_3\gamma_4 = 1.1$		−114	$\alpha = 22.3$ $\beta = 29.3$ $\gamma = 0.7$	$\alpha = 22.3$ $\beta = 30.9$ $\gamma = 0.7$ $\delta = 0.7$
III		−150	$\mathrm{CH_3} = 21.7_6$ $\beta = 2.2_7$ $\gamma_1\gamma_2 = 1.6_9$ $\gamma_3\gamma_4 = 1.2_7$		−73	$\alpha = 21.9_8$ $\beta = 30.0_5$ $\gamma = 0.6_7$	
IV	[e]	−153	$\alpha = 19.5_0$ $\beta = 4.0_4$ $\gamma_1\gamma_2 = 2.2_7$ $\gamma_3\gamma_4 = 1.7_5$		−78	$\alpha = 22.0_6$ $\beta = 28.3_7$ $\gamma = 0.6_3$	$\alpha = 22.0_6$ $\beta = 29.8_6$ $\gamma = 0.6_1$ $\delta = 0.6_1$
V		−131	$\alpha = 20.6_0$ $\mathrm{CH_3} = 0.7_8$ $\gamma_1\gamma_2 = 3.5_1$ $\gamma_3\gamma_4 = 1.9_5$	[b]	−70	$\alpha = 22.1_8$ $\beta = 26.8_6$	
VII[c]	[d]				−48	$\alpha = 21.9_6$ $\beta = 28.2_6$ $\gamma = 0.6_9$	$\alpha = 21.9_6$ $\beta = 29.6_4$ $\gamma = 0.6_1$ $\delta = 0.6_1$

[a] From photolysis of solutions of alkylcyclopropanes containing approximately 10% v/v di-*t*-butyl peroxide. [b] Slightly broader lines observed, probably due to unresolved δ hyperfine. [c] Diluted approximately 50% by volume with cyclopropane. [d] See text. [e] Splittings are: β, triplet; $\gamma_1\gamma_2$, quintet; $\gamma_3\gamma_4$, quintet.

and cyclopropylcarbinyl radicals, respectively, described earlier.[1]



VIII

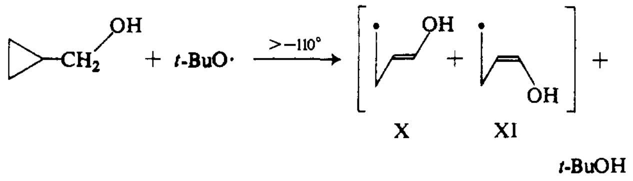


IX

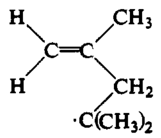
The coupling constants relevant to the substituted *cyclopropylcarbinyl* radicals (IX) are presented in Table I. The single β hydrogen in the ring of those radicals derived from hydrocarbons II–IV all exhibit small coupling constants, whereas the coupling constants of the two pairs of γ hydrogens are larger than usual. Thus, the substituted cyclopropylcarbinyl radicals are structurally analogous to the previously described cyclopropylcarbinyl radical I.[1]

The spectra of the substituted *allylcarbinyl* radicals (VIII) for which $R_1 \neq R_2$ (from compounds II, IV, and VII) show two sets of lines arising from a mixture of *cis* and *trans* isomers. Both sets of coupling constants are included in Table I.[3] The *cis* and *trans* isomers are not present in equal concentrations, and the isomer placing the bulkier groups *trans* predominates.

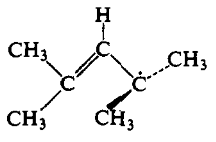
Cyclopropylcarbinol reacts with *t*-butoxy radicals in cyclopropane solutions to produce a mixture of *trans* and *cis* enol radicals X and XI at temperatures greater than −110°. In contrast to allylcarbinyl radicals derived from hydrocarbons II and IV, the *cis* isomer XI predominates over the *trans* by a factor of 4 at −48° and is virtually the only species observed at −110°. The same spectra were obtained from cyclopropylcarbinol-*d*. We were unable to examine the spectrum of the hydroxycyclopropylcarbinyl radical at lower temperatures because of difficulties with crystallization.



The spectra obtained from tetramethylcyclopropane VI are anomalous in several respects. Again both high-temperature and low-temperature spectra are observed, but the low-temperature form is maintained to a much higher temperature and is still significantly intense even at −50°. The high-temperature spectrum consists of nine symmetric lines consistent with the expected radical XII in which all the β couplings are equal. The lines are rather broad, probably due to unresolved smaller coupling from the γ $\mathrm{CH_3}$. (This is also observed in the analogous radical from V.) The low-temperature spec-



XII (temperature −54°; $a_\beta = 23.0_2$ G)



XIII (temperature −126°; $a_{\mathrm{CH_3}} = 23.1_0$ G, $a_\mathrm{H} = 34.9_4$ G)

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(3) Only one of these isomers, which we tentatively assume to be the *trans* species, shows hyperfine splitting by a single δ hydrogen. A similar situation prevails in the parent allylcarbinyl radical VIII ($R_1 = R_2 = \mathrm{H}$).[1] A more rigorous identification is in progress.

trum is comprised of two septets and is assigned to XIII.[4] This is not an allylic radical since models indicate that the four methyl groups will not allow coplanarity of the carbons.[5] The large CH coupling, indicating that the H is in the antinode of the p orbital, supports this conclusion. Since no rearrangement of the previously discussed radicals to allylic structures is observed even where there is the possibility of gaining resonance energy, it is inferred that abstraction from a ring CH_2 group has occurred.[6] Apparently four methyl groups activate the ring sufficiently to make this the preferred process, but abstraction from side chain CH_3 is becoming competitive at high temperatures.

It is not, of course, possible to make unambiguous mechanistic deductions from esr structural data, but there is a rather obvious rationalization of the relationship between radicals VIII and IX. IX is the initial product of hydrogen abstraction, and it requires some activation energy to get to VIII. If the rate of isomerization is less than the reciprocal of the lifetime of the radical (as it could be at low temperatures), VIII will not be observed. The activation process could be associated with rotation about the $R_2\dot{C}$–cyclopropyl bond since a $\pi/2$ rotation will leave the p orbital containing the odd electron in position to interact with the ring antibonding orbital symmetric with respect to the plane of symmetry of the molecule.[7] Strong interaction with this orbital is to be anticipated since it is antibonding between the ring carbon centers adjacent to the substituent, and rearrangement to VIII seems to be a natural consequence.

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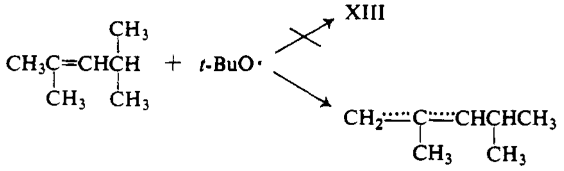
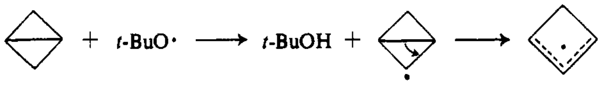
(4) Attempts to prepare XIII from 2,4-dimethyl-2-pentene and *t*-butoxy radical led only to the isomeric *cis*- and *trans*-2,4-dimethyl-1-penten-2-yl radicals. Hydrogen abstraction from the methyl groups is, thus, preferred to the isopropyl hydrogen in this alkene. The unreactivity of the tertiary isopropyl hydrogen in this alkene is consistent with the nonstabilization of XIII.



(5) A similar nonbonded interaction of methyl groups has recently been discussed relative to rotational barriers in methylated allylic cations [G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **90**, 6082 (1968)]. These increased steric effects can be reflected in decreased delocalization energy in the allylic radical as well as the cations [*cf.* P. Schleyer, *et al.*, *ibid.*, **88**, 2868 (1966)].

(6) Abstraction of a methylene hydrogen from a cyclopropane ring by *t*-butoxy radical has also been observed in bicyclobutane. The bicyclobutyl radical so formed undergoes spontaneous ring opening to cyclobutenyl radical. The latter process can be retarded only at very low temperatures (to be published).



(7) For discussions related to bonding in these compounds see J. P. Pete, *Bull. Soc. Chim. France*, 357 (1967); C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4311 (1968).

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Book Reviews

The Computer and Chemistry. An Introduction to Programming and Numerical Methods. By T. R. Dickson, Orange Coast College. W. H. Freeman and Co., 660 Market St., San Francisco, Calif. 1968. viii + 216 pp. 6 × 24 cm. $5.75.

Though timely in purpose, this book is somewhat less than successful in execution. The treatise promised by the author's ambitious title ("The Computer and Chemistry") is not to be found. Rather, the reader is offered a less than satisfying primer on the Fortran language and a glib discussion of fundamental numerical methods.

Study panels within both the National Academy of Sciences and the National Science Foundation recently recommended the teaching of numerical methods and computer programming during the early stages of undergraduate education. It is viewed that such early training will extend the range of problems with which a developing scientist can deal, will help to acquaint him with an evolving computer environment which is playing a more and more significant role in research, and should serve to encourage more imaginative utilization of computers later in the student's career. In coupling a discussion of the rules of Fortran programming with an introduction to numerical methods, Dickson's book is indeed timely. That it is incomplete may be more a reflection of publishing priorities than the author's judgment. Whatever the case, the book is not strongly recommended. It is intended primarily for second year undergraduate students, according to the author; and despite suggestions to the contrary, researchers are not likely to find the volume valuable for reference. The book relates to chemistry in the choice of problems and applications with which the subject is illustrated.

The book is divided into three sections. The first section is devoted to the Fortran languages (II and IV); the second part, roughly half the volume, treats numerical methods and computer applications; and the last section is composed of four appendices, only one of which is generally useful.

The aware reader may become disappointed early in the text as the author uses an introductory chapter to give the impression that the computer is little more than a replacement for the desk calculator. This is untrue, as many of us appreciate and perhaps more of us should. The computer is an immensely powerful tool with an unbounded range of application. The student should come to appreciate this and make use of it early in his career, for there is little doubt but that the computer is destined to have far-reaching effects upon our execution of science. Dickson offers no assistance toward this end; rather his text reflects a peculiarly narrow outlook.

Although the writing is generally lucid, all too often the author rejects explicit discussion and illustrations, choosing instead to demonstrate coding variations implicitly, by example. As this produces apparent contradictions, it results in a clumsy presentation