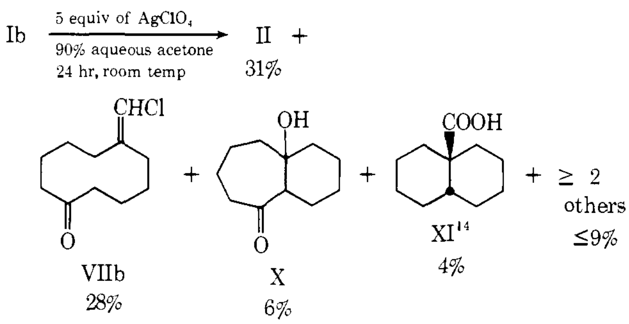
Table I. FT NMR Data for Enone II

Compound	Relative area: Carbonyl C	Relative area: C_α	Relative area: C_β	No. of pulses (20-sec intervals)
Unenriched II	1.02	0.62	(1.00)	2000
^{13}C enriched II	0.84	5.06	(1.00)	1710

Table II. Product Ratios For Various Aqueous Acetone Mixtures.

% H_2O (by volume)	(II + X)/ VIIa	% H_2O (by volume)	(II + X)/ VIIa
10	≥160	2	34
5	43	1	19

shown. While the major product was still enone II, the monocyclic ketone product, VIIb, clearly derived from bridgehead olefin IXb, was also formed in considerable quantity.[16] The presence of X[17] (later identified as a product from



Ia, too) proved to be a key finding; X is presumably cis-fused, although we have not shown that. Brief treatment of X with concentrated HCl (room temperature) gave II, as did exposure of X to the acidic solvolysis conditions.[12]

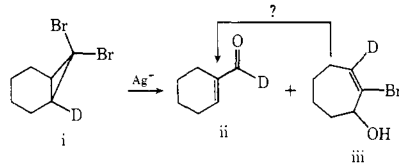
When Ib, enriched at C_{11} such that C_{11} contained 5.8% ^{13}C (high resolution mass spectrometry, hereafter, hrms), was treated with $AgClO_4$ as above, the enone II contained one carbon with 5.3% ^{13}C (hrms).[18] Unfortunately, the fragmentation of II did not separate the carbonyl carbon from C_α, and thus allowed no mechanistic conclusions. However, the application of ^{13}C NMR proved fruitful. The carbonyl, α, and β carbons of II resonate at 205, 135, and 153 ppm, respectively. Table I shows the integrated intensity of these three peaks after data collection at 20-sec pulse intervals. If C_β is taken as a standard (neither mechanism would place the label there), then it is seen that, within experimental error, *all of the label winds up at C_α* (which would contain 5.6% ^{13}C, in good agreement with the hrms results, especially considering the vagaries of integrating FT NMR spectra). This requires that II may be formed via the mechanism shown in Scheme II, i.e., *via protonation of the bridgehead double bond intermediate, IX.*

Since the mechanism given in Scheme II requires that the ratio of (II + X) to VII varies with the [H_2O] in the solvolytic medium, and since we have been unable to isolate XII,[12] we undertook a study of the aforementioned ratio, beginning with Ia. The results (GLC analysis), summarized in Table II, support Scheme II.

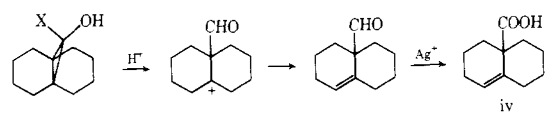
In conclusion, there yet appears to be no case in which an intramolecular shift process competes with ring opening of a "cyclopropyl cation".[19]

References and Notes

(1) For the previous paper in this series, see P. Warner, R. LaRose, and T. Schleis, *Tetrahedron Lett.*, 1409 (1974).
(2) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.
(3) D. B. Ledlie, *J. Org. Chem.*, **37**, 1439 (1972).
(4) C. B. Reese and M. R. D. Stebles, *Tetrahedron Lett.*, 4427 (1972).
(5) An analogous deuteride shift mechanism was postulated for the solvolysis of i.[4] This mechanism now appears incorrect (see text); we are further investigating this case and suspect ii arises from the predominant product, iii.



(6) C. B. Reese and M. R. D. Stebles, *J. Chem. Soc., Chem. Commun.*, 1231 (1972).
(7) P. Warner, J. Fayos, and J. Clardy, *Tetrahedron Lett.*, 4473 (1973).
(8) For rate comparisons in the presence of silver ion, see (a) D. B. Ledlie, J. Knetzer, and A. Gitterman, *J. Org. Chem.*, **39**, 708 (1974); (b) D. B. Ledlie and J. Knetzer, *Tetrahedron Lett.*, 5021 (1973).
(9) P. Warner and S. Lu, to be submitted for publication.
(10) VIII is formed via an addition–solvolysis mechanism and is almost the sole product when the acetic acid is unbuffered; VIII was identified by spectral comparison (NMR, uv) with the published data [S. Kabuss, H. Friebolin, and H. Schmid, *Tetrahedron Lett.*, 469 (1965); W. R. Moore, E. Marcus, S. E. Fenton, and R. T. Arnold, *Tetrahedron*, **5**, 179 (1959), respectively].
(11) We used a Perkin-Elmer 270 GLC-mass spectrometer fitted with a 10 ft × ⅛ in. 3% DEGS on Chromosorb P column; the temperature was programmed (50–180°). Analysis calculated for VIIa ($C_{11}H_{17}BrO$): *m/e* 244.0463; found, *m/e* 244.0473.
(12) All three mechanisms will be discussed in our full paper. Also, other work, based on the [4.3.1]- and [3.3.1]dibromopropellane series (P. Warner and S. Lu, to be submitted for publication), serves to establish the mechanism shown in Scheme II.
(13) E. Vogel, W. Wiedemann, H. Roth, J. Eimer, and H. Günther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972).
(14) Acid XI is formed from collapse of the initial ion with retention of the cyclopropane ring, followed by acid-catalyzed ring opening, and is precedented by the work of Groves.[15] Actually, XI appears to be a mixture (ca. 3:1) of XI and iv; iv may be formed via the same acid-catalyzed ring opening which leads to XI but with the proton going to C_{11} to give an aldehyde, which is subsequently oxidized by Ag^+



Both XI and iv are formed from Ia and Ib but in slightly different yields.
(15) (a) J. T. Groves and K. W. Ma, *Tetrahedron Lett.*, 909 (1974). (b) We thank Professor Groves (see ref 14 of ref 15a) for the ir spectra of XI and its trans isomer, which we utilized to identify XI.
(16) VIIb: calcd for $C_{11}H_{17}OCl$, 200.0968; found, 200.0975.
(17) The spectroscopic identification of X included the following highlights: MS parent ion at *m/e* 182 (rel intes = 10), (P − 18) at *m/e* 164 (rel intes = 100) at 70 eV; ir ν_{OH} 3450 (br), $\nu_{C=O}$ 1705 (s) cm^{-1}; ^{13}C NMR, the ^{13}C enriched sample of X, which gave enriched II as described, showed (relative to TMS) δ 215 (carbonyl carbon), 62 (tertiary carbon α to carbonyl-enriched), 73 ppm (carbon bearing OH).
(18) This figure was arrived at by assuming that only one carbon position in II was enriched. The natural abundance of ^{13}C for the other carbons was subtracted from the total ^{13}C content of II, and the remainder was the 5.3% indicated. *This includes the natural abundance of the enriched carbon.*
(19) Ledlie[8a] has overinterpreted our thermodynamic discussion for ring opening of cyclopropyl halides;[20] our remarks pertain to *uncatalyzed processes only.* However, once a "cyclopropyl cation" is formed, ring opening becomes a more facile process.
(20) P. Warner, R. LaRose, C. Lee, and J. Clardy, *J. Am. Chem. Soc.*, **94**, 7607 (1972).

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Δm = 3 Electron Spin Resonance in a Quartet Molecule

Sir:

In order to confirm the identification of a recently prepared series of organic molecules as electronic quartets,[1-5] we have sought for and observed the $\Delta m = 3$ transition in the electron spin resonance of one of them. The designation

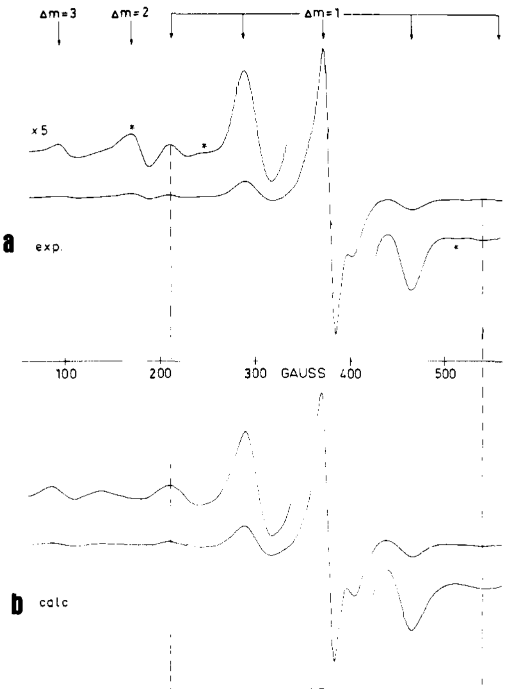


Figure 1. L Band ESR spectra of **1:** (a) experimental in a solid solution of polystyrene–2% divinylbenzene copolymer beads at 298°K; (b) computed for an ensemble of randomly oriented radicals on the basis of a second-order perturbation treatment, $D = 82$ G.

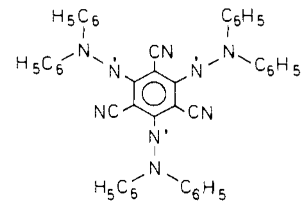
$\Delta m = 3$ refers to the transition between the levels identified by the approximate quantum numbers $m = -3/2$ and $m = +3/2$. The transition is observed because the magnetic dipolar interaction admixes, at most orientations of the molecule relative to the external field, components with $m = \pm 1/2$ into each of the levels $m = -3/2$ and $m = 3/2$. The amplitudes of the admixtures are of order D/H, D being the dipole–dipole coupling parameter and H the external field. Owing to the shifts in energy produced by the dipolar interaction and to the aforementioned admixtures, the spectrum at each orientation of the quartet molecule consists of three lines near $H = \omega/\gamma$ ($\Delta m = 1$), a pair of lines near $H = \omega/2\gamma$ ($\Delta m = 2$), and a single line at $H = \omega/3\gamma$ ($\Delta m = 3$). ω is the angular frequency of the radiation, H the field, and γ the magnetogyric ratio of the electron. Nonrotating randomly oriented molecules yield spectra with characteristic shapes in each of the three regions,[6] the $\Delta m = 3$ transition being a single fairly sharp line, just as is the $\Delta m = 2$ transition in a triplet molecule. Appearance of the sharp $\Delta m = 3$ transition requires that three electron spins be coupled to each other.

The intensities of the three transitions $\Delta m = 1$, 2, and 3 are in the approximate ratio $1:(D/H)^2:(D/H)^4$.[7]

The **1**,[8] whose spectrum we report here, has $D \sim 80$ G. At the commonly used X band frequency the intensity of the $\Delta m = 3$ transition would be only 3×10^{-5} relative to $\Delta m = 1$. It has, obviously, not been observed at X band despite careful search for it. We, therefore, turned to lower frequency, L band, with frequency 1×10^9 Hz. The L band spectrometer is less sensitive by a factor of about 100 in the minimum number of spins which it is capable of detecting than the X band one, but owing to the large volume of material which it accomodates, its concentration sensitivity appears to be superior.

The **1**, synthesized at the University of Freiburg,[5] was dissolved in a toluene solution of polystyrene–2% divinylbenzene copolymer beads. A uniformly colored solid remained after evaporation of the toluene. Its spectrum is characteristic of a randomly oriented solid solution. No signs of the spectrum of microcrystals of the radical are observed.

The L band spectrum at room temperature is shown in Figure 1a. A computed spectrum is shown in Figure 1b. The agreement is good except for the positions marked by asterisks. The extra feature at the latter positions arise from a contamination of bishydrazyl. The $\Delta m = 3$ resonance, which can arise only from molecules with three spins, stands out clearly.



Acknowledgments. The spectrometer has evolved over many years. It was perfected under a grant from the Hartford Foundation to Professor Barry Commoner. We are grateful to Professor Commoner for his generous permission to use the instrument. Its development was carried out by J. Townsend, S. Fuller, A. Lindauer, and R. Brennan. The compound was prepared by Dr. F. Rieser. Dr. E. Ohmes assisted in computation of the spectrum.

The work has been supported by the National Science Foundation, Deutsche Forschungsgemeinschaft, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) G. Kothe, J. Brickmann, and H. Zimmermann, *Adv. Mol. Relaxation Processes*, **5**, 277 (1973).
(2) G. Kothe and H. Zimmermann, *Tetrahedron*, **29**, 2305 (1973).
(3) C. Nowak, G. Kothe, and H. Zimmermann, *Ber. Bunsenges. Phys. Chem.*, **78**, 265 (1974).
(4) G. Kothe, and E. Ohmes, *Ber. Bunsenges. Phys. Chem.*, **78**, 924 (1974).
(5) J. Rieser, G. Kothe, and K. Wallenfels, *Justus Liebigs Ann. Chem.*, in press.
(6) G. Kothe and J. Brickmann, *J. Chem. Phys.*, **59**, 2807 (1973).
(7) One of us, S.I.W., was seduced into the present experiment by the erroneous belief that $\Delta m = 3$ would have intensity $(D/H)^2$ relative to $\Delta m = 1$. The phases of the admixture are such that cancellation of the components of order D/H in the transition moment occurs, leaving only a moment of order $(D/H)^2$ and intensity $(D/H)^4$. The transition is excited by the component of oscillating field rotating in the opposite sense to the normal one.
(8) 1,3,5-(2,4,6-Tricyanobenzenetriyl)tris(N^1,N^1-diphenylhydrazyl), 1

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Generation, Nuclear Magnetic Resonance Spectra, and Structure of 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl Cations

Sir:

The hydrolysis of 9-pentacyclo[4.3.0^{2,4}.0^{3,8}.0^{5,7}]nonyl *p*-nitrobenzoate (**1-OPNB**) proceeds with a very large rate enhancement (10^{10}–10^{12}) and leads to a statistical, but stereospecific, rearrangement which regenerates the parent pentacyclic alcohol (**1-OH**) with positions 6, 7, and 9 and positions 1, 5, and 8 each having been completely exchanged.[1] These observations were explained by ionization