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Electron Spin Resonance Evidence for the Ring-Closed and Ring-Opened Forms of a Substituted Cyclopropane Radical Cation

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Gas-phase experiments[1,2] and solid-state ESR studies[3] have provided evidence that the radical cation derived from ethylene oxide (oxirane) is the ring-opened isomer $CH_2OCH_2^{+\cdot}$, a conclusion further supported by high-level ab initio calculations[4-6] and by measurements on the electronic absorption spectra of substituted oxirane cations.[7] In contrast, we find that the 1,1,2,2-tetramethylcyclopropane (TMCP) radical cation is stable in the ring-closed form at 77 K but rearranges to the ring-opened form above 110 K in the $CF_2ClCFCl_2$ matrix. As far as we are aware, this is the first study in which both the ring-closed and the ring-opened forms of a radical cation have been characterized by ESR spectroscopy.

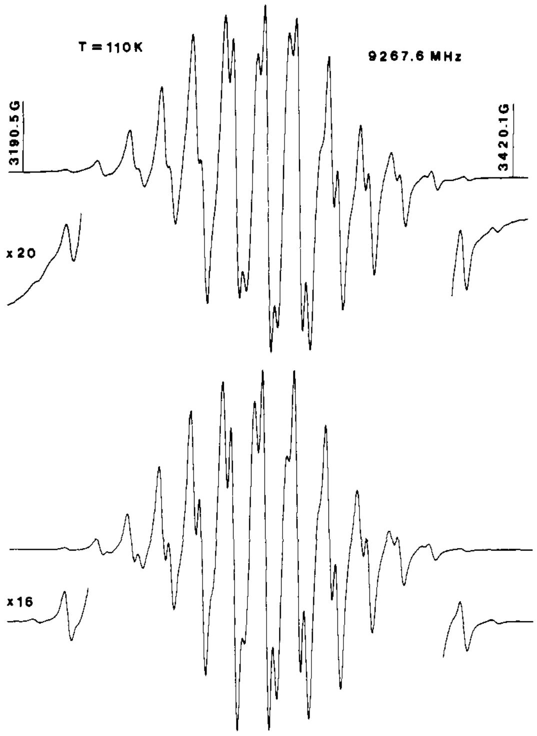


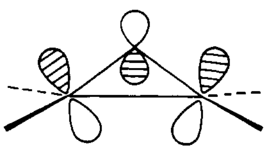
Figure 1. Observed (upper spectrum) and computer-simulated (lower spectrum) first-derivative ESR spectra of the ring-closed form of the radical cation of 1,1,2,2-tetramethylcyclopropane in $CF_2ClCFCl_2$. The upper spectrum was recorded at 109 K after γ-irradiation of a 0.8 mol % solution of the parent compound in this matrix at 77 K for a dose of 0.4 Mrad. The lower spectrum was simulated by using the ESR parameters in Table I and a Lorentzian line width of 2.5 G.

As shown in the upper half of Figure 1, the low-temperature ESR spectrum of the TMCP cation generated by radiolysis in the $CF_2ClCFCl_2$ matrix[8] consists of 15 almost evenly spaced components with a superimposed fine structure on at least 11 of these lines. It is noticeable, however, that this fine structure, which appears as a symmetric triplet on the center line, becomes increasingly distorted in the progression out toward the wings of the spectrum, the outside line in each of these distorted (and therefore apparent) triplets always gaining strength relative to the center component while the inside line loses strength correspondingly. Just such a pattern would be expected for a 13-line binomial set of lines further split into 1:2:1 triplets when the triplet splitting slightly exceeds that of the multiplet. The analysis is confirmed (Figure 1) by the excellent fit of the experimental spectrum to the spectrum simulated with the parameters $a(2\ H) = 18.7$ G and $a(12\ H) = 14.9$ G.

Table I. ESR Parameters for the Ring-Closed (**2**) and Ring-Opened (**3**) Forms of the 1,1,2,2-Tetramethylcyclopropane Radical Cation

radical cation	matrix	T/K	hyperfine couplings/G	g
	$CFCl_3$	145	18.7 (2 H), 15.0 (12 H)	2.0033
2	CF_3CCl_3[a]	145	18.1 (2 H), 14.7 (12 H)	2.0034
	$CF_2ClCFCl_2$	109	18.7 (2 H), 14.9 (12 H)	2.0032
3	$CF_2ClCFCl_2$	117	23.3 (6 H), 11.7 (2 H)	2.0029

[a] The spectrum of **2** was not as well resolved in CF_3CCl_3 as in the other two matrices.



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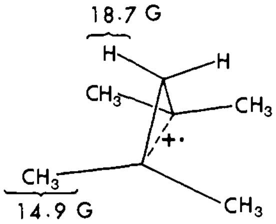

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These hyperfine interactions and coupling constants can be confidently assigned to the $^2A_1$ state of the ring-closed (C_{2v}) TMCP radical cation, the character of the SOMO being shown in **1**. This a_1 orbital is bonding between the two *gem*-dimethyl substituted carbon atoms, and so the C(1)–C(2) bond between these two atoms is expected to weaken and elongate in the radical cation,[9] as depicted in **2**. As in the case of the parent cyclopropane radical cation, which undergoes a Jahn–Teller distortion to the same C_{2v} symmetry,[10] INDO calculations predict that most of the spin density lies in the in-plane p orbitals of these two equivalent ring carbons. The coupling to the 12 equivalent methyl protons can therefore be considered as a β-proton hyperfine interaction originating from a carbon spin density of ca. 0.5, and its magnitude (14.9 G) is consistent with the results for simple alkyl radicals.[11] Also, the coupling of 18.7 G to the two equivalent methylene protons is in reasonable agreement with the value of 21 G reported for the corresponding protons in the C_{2v}-distorted cyclopropane cation.[10] Experiments in two other Freon matrices ($CFCl_3$ and CF_3CCl_3) gave similar ESR spectra and parameters for **2** (Table I).

The ring-closed cation (**2**) is unstable above about 110 K in the $CF_2ClCFCl_2$ matrix,[12] and Figure 2 shows the ESR spectrum which grows in irreversibly within 2 min at 120 K. This spectrum

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(1) Corderman, R. R.; Le Breton, P. R.; Buttrill, S. E.; Williamson, A. D.; Beauchamp, J. L. *J. Chem. Phys.* **1976**, *65*, 4929.

(2) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724; *J. Am. Chem. Soc.* **1979**, *101*, 540; *Adv. Mass Spectrom.* **1980**, *8B*, 178.

(3) Snow, L. D.; Wang, J. T.; Williams, F. *Chem. Phys. Lett.* **1983**, *100*, 193.

(4) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 3347; **1984**, *106*, 2513.

(5) Bouma, W. J.; Poppinger, D.; Saebo, S.; MacLeod, J. K.; Radom, L. *Chem. Phys. Lett.* **1984**, *104*, 198.

(6) Clark, T. *J. Chem. Soc., Chem. Commun.* **1984**, 666.

(7) Bally, T.; Nitsche, S.; Haselbach, E. *Helv. Chim. Acta* **1984**, *67*, 86.

(8) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180.

(9) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6805.

(10) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202.

(11) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(12) The lability of radical cations in this particular matrix has been observed for other species, the thermal dissociation of $t\text{-}BuSnMe_3^{+\cdot}$ to the *tert*-butyl radical also occurring at 110–120 K in the $CF_2ClCFCl_2$ matrix but not in the CF_3CCl_3 and $CFCl_3$ matrices, even at higher temperatures: Walther, B. W., Ph.D. Thesis, University of Tennessee, Knoxville, 1984.

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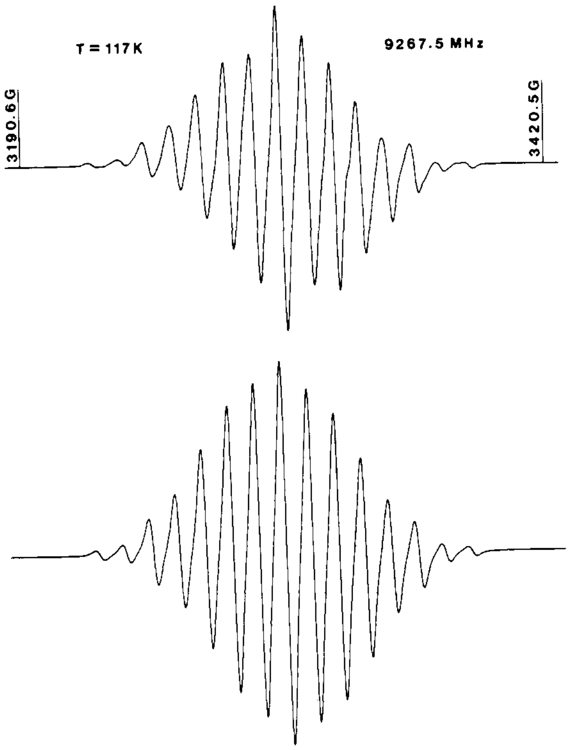
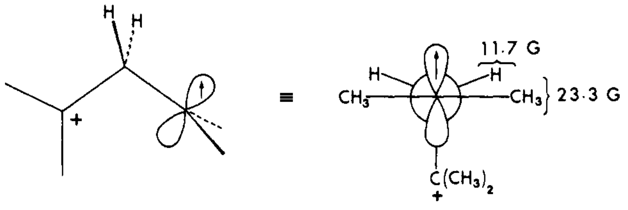


Figure 2. Observed (upper spectrum) and computer-simulated (lower spectrum) first-derivative ESR spectra of the ring opened form of the radical cation of 1,1,2,2-tetramethylcylopropane in $CF_2ClCFCl_2$. The upper spectrum was recorded at 117 K after a γ-irradiated 0.8 mol % solution of the parent compound in this matrix was thermally annealed above 110 K. Irradiation was carried out at 77 K for a dose of 0.4 Mrad. The lower spectrum was simulated by using the ESR parameters in Table I and a Lorentzian line width of 2.5 G.

consists of 15 evenly spaced lines with an apparent splitting of 11.7 G but the intensity ratios do not correspond to a binomial distribution. A clue to the analysis is provided by the relative intensity of the two outermost components in each wing, and the spectrum is satisfactorily simulated by the hyperfine parameters $a(6\ H) = 23.3$ G and $a(2\ H) = 11.7$ G, as shown in the lower half of Figure 2. The 23.3-G coupling to six equivalent hydrogens is characteristic of a simple α,α-dimethyl-substituted alkyl radical, and we assign the ESR parameters to structure 3. All the



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interacting protons are in β positions and both sets of couplings are in exact agreement with the $\cos^2\theta$ angular dependence.[13] Moreover, since the positively charged Me_2C^+ group should be similar in many respects to the electron-withdrawing CCl_3 group, the assignment is strongly supported by the fact that the hyperfine parameters are virtually identical with those of the $CCl_3CH_2CMe_2\cdot$ radical ($a(6\ H) = 23.52$ G and $a(2\ H) = 11.61$ G), which also possesses an eclipsed conformation at the radical center.[14] Evidently the thermal reacton described here is a simple isomerization,[15,16] a monorotatory ring opening at the weakened C(1)–C(2) bond of **2** giving rise to the orthogonal structure **3**.[17]

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Registry No. **1**, 56324-44-8; **3**, 93000-46-5.

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[13] Heller, C.; McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535.

[14] Chen, K. S.; Tang, D. Y. H.; Montgomery, L. K.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 2201.

[15] (a) The only other reasonable candidate for the radical product of the thermal reaction would seem to be the (1,1,3-trimethylallyl)carbinyl species $CH_2{=}C(Me)CH_2CMe_2\cdot$, which could be formed via ring opening followed by proton loss from the carbonium ion center in **3**. However, the methylene β-hydrogens in this radical are inequivalent below 170 K and give a triplet splitting of 17.5 G in the fast-exchange limit: Chen, K. S.; Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7036. (b) The ESR parameters for the secondary radical also appear to exclude the 2,4-dimethyl-2-pentene radical cation, $i\text{-PrCH}{=}CMe_2^{+\cdot}$, which could arise from **3** by a 1,2-hydride shift. Thus, the values of $a(6\ H)$ from the CMe_2 group in the radical cations of isobutene, trimethylethylene, and tetramethylethylene are all lower than 23 G and lie in a narrow range between 16.5 and 17.2 G; Toriyama, K.; Nunome, K.; Iwasaki, M. *Chem. Phys. Lett.* **1984**, *107*, 86 and references therein.

[16] The ring opening of **2** has also been proposed to explain the formation of products upon electrochemical oxidation: Shono, T.; Matsumura, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2861.

[17] **Note Added in Proof:** Recent work[18] has shown that the parent cyclopropane radical cation also isomerizes in the $CF_2ClCFCl_2$ matrix to a ring-opened orthogonal structure. However, the derived trimethylene radical cation adopts a bisected conformation at the radical center.

[18] Qin, X.-Z.; Williams, F. *Chem. Phys. Lett.*, in press.

Tandem Alkylation–Cycloadditions. Control by Transition-Metal Templates

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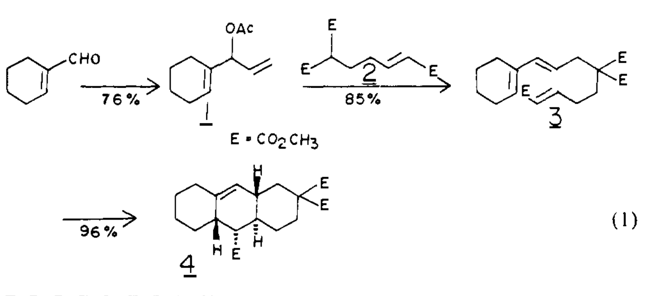
The intramolecular Diels–Alder reaction has become an exceedingly powerful tool in the total synthesis of natural products.[1] Limited methods exist for the synthesis of the requisite substrate; olefination reactions constitute the most important. Recent developments in controlling regioselectivity in allylic alkylations by variation of the metal templates[2-4] offer a versatile strategy to conjugated polyenes and consequently substrates for intramolecular Diels–Alder reactions, We wish to report a convergent approach in which the dienophile and diene fragments are joined using alkylations mediated by transition metals and the flexibility offered by the ability to manipulate the regioselectivity of alkylation.

The simplicity of this approach derives, in part, from the ready availability of the allylic carboxylates. For example, addition of vinylmagnesium bromide to an α,β-unsaturated aldehyde such



(1)

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[1] For recent review, see: Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. Taber, D. F. "Intramolecular Diels-Alder and Alder Ene Reaction"; Spring-Verlag: Berlin, 1984.

[2] Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 630. Akermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679. Keinan, E.; Sahai, M. *J. Chem. Soc., Chem. Commun.* **1984**, 648. Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

[3] Trost, B. M.; Lautens, M. *Organometallics* **1983**, *2*, 1687; *J. Am. Chem. Soc.* **1983**, *105*, 3343; **1982**, *104*, 5543.

[4] Trost, B. M.; Hung, M.-H. *J. Am. Chem. Soc.* **1983**, *105*, 7757.