10954 *J. Am. Chem. Soc.* **1996,** *118,* 10954−10962

Electron Transfer Photochemistry of Chrysanthemol: An Intramolecular S_N2' Reaction of a Vinylcyclopropane Radical Cation

Torsten Herbertz and Heinz D. Roth*

Contribution from the Department of Chemistry, Rutgers University, Wright-Rieman Laboratories, New Brunswick, New Jersey 08855-0939

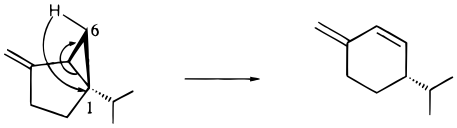
Received October 26, 1995[⊗]

Abstract: The electron transfer photochemistry of optically pure (1*R*,3*S*)-(+)-*cis*-chrysanthemol (*cis*-**2**) results in the formation of (*R*)-5-(1-(*p*-cyanophenyl)-1-methylethyl)-2,2-dimethyl oxacyclohex-3-ene (**4**) with significant retention of optical activity. The product is rationalized via nucleophilic attack of the alcoholic function of the radical cation on the terminal carbon of the vinyl group with simultaneous replacement of an isopropyl radical as an intramolecular leaving group in an apparent S_N2' reaction. This mode of attack is unprecedented in vinylcyclopropane radical cations and is interpreted as evidence for the significant role that relief of ring strain and its avoidance play in determining the course of nucleophilic capture in radical cationic systems.

Introduction

Radical cations of molecules containing strained ring moieties as well as olefinic fragments have been the focus of much interest in recent years;[1] the conjugative and homoconjugative interactions between the two types of functions have been of particular interest. Various substrates have been probed to delineate changes in the molecular geometry upon one-electron oxidation and to assess the spin and charge density distributions in the resulting radical cations.[2] Typically, the reactions of these species proceed with release of ring strain;[3−6] in some systems, ring opening is assisted by a nucleophile.[7−10]

Vinylcyclopropane radical cation, **1**$^{\bullet+}$, the simplest species containing an olefinic moiety and a cyclopropane ring, has not yet been characterized adequately, although several studies have been carried out recently.[10−14] Thus, the molecular ion of vinylcyclopropane undergoes rearrangement to penta-1,3-diene radical cation in the gas phase.[11] Related results of two rigidly linked vinylcyclopropane systems have been observed in solution; the electron transfer induced rearrangements of sabinene to *β*-phellandrene (shown below), and of α-thujene to α-phellandrene, were interpreted as novel examples of a sigmatropic shift.[12]



The spin density distributions of three radical cations containing *syn*-vinylcyclopropane systems, *viz.*, bicyclo[3.1.0]hex-2-ene, bicyclo[4.1.0]hept-2-ene, and its 3,7,7-trimethyl-derivative (2-carene) were characterized by CIDNP studies.[14] Theoretical calculations of the unsubstituted radical cation, **1**$^{\bullet+}$, so far have been limited to the STO-3G level of theory and a seriously

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

(1) (a) Forrester, R. A.; Ishizu, K.; Kothe, G.; Nelsen, S. F.; Ohya-Nishiguchi, H.; Watanabe, K.; Wilker, W. Organic Cation Radicals and Polyradicals. In *Landolt Börnstein, Numerical Data and Functional Relationships in Science and Technology*; Springer Verlag: Heidelberg, 1980; Vol. IX, Part d2. (b) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988. (c) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180. (d) Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269. (e) Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 133−245.

(2) (a) Haddon, R. C.; Roth, H. D. *Croat. Chem. Acta* **1984**, *57*, 1165. (b) Roth, H. D.; Schilling, M. L. M. *Can. J. Chem.* **1983**, 61, 1027. (c) Roth, H. D.; Schilling, M. L. M.; Schilling, F. C. *J. Am. Chem. Soc.* **1985**, *107*, 4152. (d) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *Tetrahedron* **1986**, *42*, 6157. (e) Roth, H. D.; Schilling, M. L. M.; Abelt, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 6098. (f) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343−350. (g) Roth, H. D.; Du, X-M.; Weng, H.; Lakkaraju, P. S.; Abelt, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 7744−7752. (h) Weng, H.; Du, X.-M.; Roth, H. D. *J. Am. Chem. Soc.* **1995**, *117*, 135−140.

(3) Quadricyclane to norbornadiene radical cation: (a) Roth, H. D.; Schilling, M. L. M.; Jones, G., II *J. Am. Chem. Soc.* **1981**, *103*, 1246−1248. (b) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1981**, *103*, 7210−7217.

(4) Methylenecyclopropane rearrangement: (a) Takahashi, Y.; Mukai, T.; Miyashi T. *J. Am. Chem. Soc.* **1983**, *105*, 6511−6513. (b) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079−1080.

(5) Bicyclobutane to cyclobutene rearrangement: (a) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1985**, *107*, 4075. (b) Gassman, P. G.; Hay, B. A. *J. Am. Chem. Soc.* **1986**, *108*, 4227. (c) Arnold, A.; Burger, U.; Gerson, F.; Kloster-Jensen, E.; Schmidlin, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 4271−4281.

(6) Vinylcyclopropane rearrangement: (a) Dinnocenzo, J. P.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561−1562. (b) Dinnocenzo, J. P.; Conlon, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 2324−2326.

(7) Cyclopropane systems: (a) Rao, V. R.; Hixson, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 6458−6459. (b) Mizuno, K.; Ogawa, J.; Kagano, H.; Otsuji, Y. *Chem. Lett.* **1981**, 437−438. (c) Mizuno, K.; Ogawa, J.; Otsuji, Y. *Chem. Lett.* **1981**, 741−744. (d) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6828. (e) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462−2464. (f) Hixson, S. S.; Xing, Y. *Tetrahedron Lett.* **1991**, *32*, 173−174. (g) Dinnocenzo, J. P.; Lieberman, D. R.; Simpson, T. R. *J. Am. Chem. Soc.* **1993**, *115*, 366−367.

(8) Bicyclobutane systems: (a) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. (b) Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740.

(9) Vinylcyclobutane systems: (a) Arnold, D. R.; Du, X. J. *J. Am. Chem. Soc.* **1989**, *111*, 7666−7667. (b) Arnold, D. R.; Du, X. *Can. J. Chem.* **1994**, *72*, 403−414. (c) Zhou, D.; Skeik, M.; Roth, H. D. *Tetrahedron Lett.* **1996**, *37*, 2385−2388.

(10) Vinylcyclopropane systems: (a) Weng, H.; Sethuraman, V.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 7021−7025. (b) Arnold, D. R.; Du, X.; de Lijser, H. J. P. *Can. J. Chem.* **1995**, *73*, 522−530.

(11) Dass, C.; Peake, D. A.; Gross, M. L. *Org. Mass. Spectrom.* **1986**, *21*, 741−746.

(12) Weng, H.; Sheik, Q.; Roth, H. D. *J. Am. Chem. Soc.* **1995**, *117*, 10655−10661.

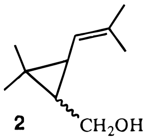
(13) Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1982**, *104*, 3659−3664.

(14) Roth, H. D.; Herbertz, T. *J. Am. Chem. Soc.* **1993**, *115*, 9804−9805.

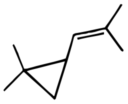
S0002-7863(95)03596-7 CCC: $12.00

restricted geometry.[13] In addition, two conformers of 2-carene radical cation were calculated recently, also at the STO-3G level.[10b]

In this publication we describe further attempts to illuminate the interactions between the olefinic and cyclopropane moieties of vinylcyclopropane radical cations. We selected three simple systems, in which the rotation of the vinyl group is, at least formally, unrestricted, a pair of geometric isomers, *cis*- and *trans*-chrysanthemol, **2**, and the bis-dimethyl-substituted derivative, **3**. We have approached the structure of the corresponding radical cations and their reactivity by two complementary methods: we probed the electron spin density distribution of the radical cations by chemically induced dynamic nuclear polarization (CIDNP); and we studied their electron transfer photochemistry with 1,4-dicyanobenzene and tetrachloro-*p*-benzoquinone (chloranil) as acceptor/sensitizer.



2



3

Irradiation of an electron acceptor sensitizer−co-sensitizer pair (DCB−Phen) in the presence of donors such as **2** or **3** (**D**) leads to the generation of the radical cation ($\mathbf{D}^{\bullet+}$) and the sensitizer radical anion ($\mathrm{DCB}^{\bullet-}$; eq 1); $\mathbf{D}^{\bullet+}$ is captured by a nucleophile (CH_3OH; eq 2) and the resulting free radical reacts with the radical anion by aromatic substitution (eq 3).[7a−c,9] For olefinic substrates, this reaction sequence has been termed a "photoinduced nucleophile-olefin-combination-aromatic-substitution" (photo-NOCAS).[9]

$$\mathrm{DCB{-}Phen} + \mathbf{D} \xrightarrow{h\nu} \mathrm{DCB}^{\bullet-} + \mathbf{D}^{\bullet+} + \mathrm{Phen} \qquad (1)$$

$$\mathbf{D}^{\bullet+} + \mathrm{CH_3OH} \rightarrow {}^{\bullet}[\mathbf{D}{-}\mathrm{OCH_3}] + \mathrm{H}^+ \qquad (2)$$

$${}^{\bullet}[\mathbf{D}{-}\mathrm{OCH_3}] + \mathrm{DCB}^{\bullet-} \rightarrow p\text{-}\mathrm{CN}\text{-}\mathrm{C_6H_4}{-}\mathbf{D}{-}\mathrm{OCH_3} + \mathrm{CN}^- \qquad (3)$$

The chrysanthemol isomers are of particular interest because their alcohol function may serve as an intramolecular nucleophile, intercepting the positive charge density on either the strained ring or the C═C double bond. The two chiral carbons of *cis*- and *trans*-**2** appear to be uniquely suited to elucidate the interactions between the three functional groups in any reaction initiated by electron transfer to a photo-excited sensitizer. To provide the proper perspective for the results obtained for **2**, we also discuss the electron transfer induced photoreactions of substrate **3** in the presence of an external nucleophile.

Experimental Section

The sensitizers and solvents used in this study are commercially available and were purified as described earlier.[10a] Similarly, the photoreactions were performed and the products were isolated and characterized according to previously described procedures.[10a]

Chrysanthemol. A mixture of *cis*- and *trans*-chrysanthemum monocarboxylic acid ethyl ester (Sigma, 95%) was hydrolyzed with aqueous KOH. Repeated fractional crystallization of the crude mixture of acids from ethyl acetate yields pure *cis*-chrysanthemic acid (mp 112−114 °C; lit.[15] mp 113−116 °C). In contrast, *trans*-chrysanthemic acid[16] was not obtained by crystallization; instead, it was prepared by epimerization of the mixed ethyl esters with potassium *tert*-amylate in benzene and subsequent alkaline hydrolysis. Enantiomerically enriched samples of (+)-*cis*- and (−)-*trans*-chrysanthemic acid were obtained by multiple fractional crystallization of the diastereomeric salts prepared from the acids and quinine (Janssen Chimica, 99%) from absolute ethanol and, subsequently, ethanol−water {(+)-*cis*-chrysanthemic acid quinine salt, mp 138−140 °C, $[\alpha]_D^{25}$ −102.4 ± 5°; *c* 1.29 in EtOH; lit. mp 127−135 °C, $[\alpha]_D^{25}$ −103.5°; (−)-*trans*-chrysanthemic acid quinine salt, mp 162 °C, $[\alpha]_D^{25}$ −112.5 ± 5.5°; *c* 1.08 in EtOH; lit. mp 159.5−161 °C, $[\alpha]_D^{25}$ −115.4°; *c* 1.018 in EtOH}.[17] The enantiomerically enriched acids were obtained by decomposing the purified salts with 2 M HCl and extracting with ether. In this fashion, optically pure (+)-*cis*-chrysanthemic acid ($[\alpha]_D^{25}$ +44.1 ± 2°; *c* 1.02 in EtOH; 100% ee; lit. $[\alpha]_D^{25}$ +40.8°; *c* 1.775 in EtOH) and enantiomerically enriched (−)-*trans*-chrysanthemic acid ($[\alpha]_D^{25}$ −10.5 ± 0.5°, 72 ± 3.5% ee, *c* 1.435 in EtOH; lit. $[\alpha]_D^{25}$ −14.45°; *c* 1.211 in EtOH) were obtained.

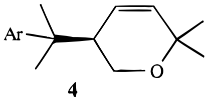
The pure cis and trans acids were reduced with $LiAlH_4$ in ether, yielding (+)-*cis*-chrysanthemol ($[\alpha]_D^{25}$ +26.0 ± 1°, *c* 1.56 in EtOH) and (−)-*trans*-chrysanthemol ($[\alpha]_D^{25}$ −39.1 ± 2°, *c* 1.15 in EtOH). For natural (+)-*trans*-chrysanthemol a rotation, $[\alpha]_D^{25}$ +49.7° (*c* 1.7 in methylcyclohexane), was measured.[18]

2,2-Dimethyl-1-(2-methyl-1-propenyl)cyclopropane. The crude pyrazoline resulting from conjugate addition of hydrazine hydrate to 2,6-dimethylhepta-2,5-dien-4-one (phorone; Aldrich, 97%) was pyrolyzed over KOH/Pt black at 150 °C, giving rise to 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane (bp 131 °C; ∼60% yield).[19]

CIDNP Experiments. Acetone-d_6 solutions containing 0.02 M donor and 0.01 M acceptor were irradiated in the probe of a Bruker 80-MHz NMR spectrometer. The collimated beam of a Hanovia 1000-W high-pressure Hg−Xe lamp was directed onto a fused silica light pipe in the NMR tube. This setup limits the useful concentration range of the light-absorbing sensitizer, as care has to be taken to ensure essentially uniform absorption throughout the volume in the receiver coil. Accordingly, the optical density of the sensitizer has to be kept low, OD ≤ 1.0. A total of 8 FIDs were collected before and during irradiation. Because of the relatively low sensitizer concentration and the relatively short irradiation time, there appeared to be no need to pass the light beam through a water or other filter solution. A pulse angle of 90° was used for all experiments.

Results

Photoreaction of (1*R*,3*S*)-(+)-*cis*-Chrysanthemol (*cis*-2). Irradiation of acetonitrile solutions containing 0.2 M 1,4-dicyanobenzene (DCB), 0.04 M phenanthrene (Ph), and 0.2 M of optically pure (1*R*,3*S*)-(+)-*cis*-chrysanthemol ($[\alpha]_D$ +26.0 ± 1°, *c* 1.56 in EtOH) leads to the formation of one major adduct, 5-(1-(*p*-cyanophenyl)-1-methylethyl)-2,2-dimethyloxacyclohex-3-ene, **4**, presumably the (R)-enantiomer, with significant retention of optical activity ($[\alpha]_D$ +26.3 ± 1°, *c* 1.255 in EtOH; 84% conversion after 7.5 h; 82% yield). Recovered starting material, (1*R*,3*S*)-(+)-*cis*-**2**, has retained its optical purity ($[\alpha]_D$ +26.4 ± 1°, *c* 0.74 in EtOH); no *trans*-chrysanthemol was detected by ^{1}H NMR.



4

The assignment of the oxacyclohexene structure to **4** is supported by the presence of 2 olefinic protons, H-3 (δ 5.35 ppm; J = 15.4 Hz) and H-4 (δ 5.70 ppm; J = 15.4, 9.4 Hz), one allylic proton (δ 2.45 ppm; ddd, J = 9.4, 9.4, 4.1 Hz, "t"d) coupled to H-4, H-6, and H-6′, and two alkoxy protons, H-6 (δ 3.4 ppm; dd, J = 9.4, 9.4 Hz, "t") and H-6′ (δ 3.5 ppm; dd, J = 9.4, 4.1 Hz). The presence of the 1-(*p*-cyanophenyl)-1-

---

[15] Campbell, I. G. M.; Harper, S. H. *J. Chem Soc.* **1945**, 283−286.

[16] Julia, S.; Julia, M.; Linstrumelle, G. *Bull. Soc. Chim. Fr.* **1966,** *11*, 3499−3507.

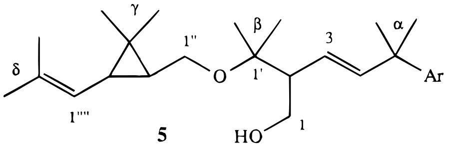
[17] Campbell, I. G. M.; Harper, S. H. *J. Sci. Food. Agric.* **1952,** *3*, 189−192.

[18] Epstein, W. W.; Alexander, K. *J. Org. Chem.* **1975**, *40*, 2576.

[19] Nelson, E. R.; Maienthal, M.; Lane, L. A.; Benderly, A. A. *J. Am. Chem. Soc.* **1957**, *79*, 3467−3469.

methylethyl function is documented by the dominant base peak of *m/z* 144 ($C_6H_4CNC_3H_6$).

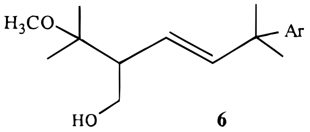
The DCB sensitized reaction also produced a photolabile adduct, **5** (∼15% yield at 84% conversion), with significantly higher GC retention time than **4**. The adduct apparently is formed by intermolecular capture of $\mathbf{2}^{\bullet+}$ at the quaternary cyclopropyl carbon by another molecule of chrysanthemol.



5

The structure of **5** is supported by the presence of 3 olefinic protons, H-3 (δ 5.42 ppm; J = 15.8, 9.5 Hz), H-4 (δ 5.71 ppm; J = 15.8 Hz), and H-1′′′′ (δ 4.88 ppm; broad multiplet), a tertiary allylic resonance, H-2 (δ 2.35 ppm; broad multiplet), an allylic cyclopropyl resonance, H-3′′′ (δ 1.36 ppm; broad multiplet), and four pairs of non-equivalent methyl resonances. The two allylic methyl groups (δ) are most deshielded (∼1.70 ppm), followed by the two methyl groups attached to the allylic-benzylic carbon, C-5 (α; ∼1.40 ppm). The pairs of methyl groups attached to the alkoxy-substituted carbon, C-1′ (β; 1.20 1.16 ppm), and the cyclopropane ring (γ; 1.11, 1.02 ppm). In essence, the spectrum of (*E*)-5-(*p*-cyanophenyl)-2-(1-(2,2-dimethyl-3-(2-methyl-1-propenyl))cyclopropylmethoxy-1-methylethyl)-5-methylhex-3-enol, **5**, is a superposition of the spectra of **2** and **6** (vide infra).

Photoreaction of (±)-*cis*-Chrysanthemol (*cis*-2) in the Presence of Methanol. Irradiation of acetonitrile/methanol (3/1 by volume) solutions containing 0.167 M DCB, 0.033 M Ph, and 0.167 M (±)-*cis*-chrysanthemol (4 h, 50% conversion) leads to the formation of a single NOCAS-adduct, (*E*)-5-(*p*-cyanophenyl)-2-(1-methoxy-1-methylethyl)-5-methylhex-3-enol (**6**).



6

The structure of **6** is supported by the presence of 2 olefinic protons, H-4 (δ 5.73 ppm; J = 15.7 Hz) and H-3 (δ 5.38 ppm; J = 15.7, 9.5 Hz), one allylic proton, (δ 2.39 ppm; ddd, J = 9.5, 6.7, 5.1 Hz), and two diastereotopic alkoxy protons (δ 3.64 ppm; ddd, J = 11.2, 5.6, 5.1 Hz; and δ 3.80 ppm; ddd, 11.2, 6.7, 5.6 Hz).

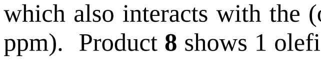
At lower methanol concentrations products **4** and **6** are formed competitively. CH_3CN solutions of 0.1 M DCB, 0.1 M *cis*-**2**, 0.02 M Ph, and varying concentrations of methanol (0.001, 0.01, 0.033, and 0.1 M) were irradiated simultaneously for 2 h. At 0.001 and 0.01 M methanol the relative yield of **4** is 5.5 and 0.75 times that of **6**, respectively.

Photoreaction of (1*S*,3*S*)-(−)-*trans*-Chrysanthemol (*trans*-2). Irradiation of acetonitrile solutions containing 0.175 M DCB, 0.035 M Ph, and 0.175 M (1*S*,3*S*)-(−)-*trans*-**2** ($[\alpha]_D$ −39.1 ± 2°, *c* 1.15 in EtOH, ∼72 ± 3.5% ee) generates the enantiomeric adduct (**4**; $[\alpha]_D$ −12.4 ± 0.5°, *c* 1.125 in EtOH, 90% yield; 100% conversion after 6 h). A photolabile adduct, analogous to **5**, was formed and identified by its mass spectrum. Starting material, (1*S*,3*S*)-(−)-*trans*-**2**, recovered after 77% conversion, showed reduced optical activity ($[\alpha]_D$ −16.8 ± 1°, *c* 0.715 in EtOH). However, *cis*-chrysanthemol is not detected by ^{1}H NMR.

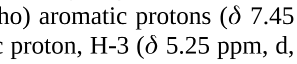
Comparative Irradiation of *cis*- and *trans*-2 under Identical Conditions. Simultaneous irradiation of acetonitrile solutions containing 0.2 M 1,4-dicyanobenzene (DCB), 0.04 M phenanthrene (Ph), and 0.2 M *cis*- or *trans*-**2**, respectively, in two NMR tubes did not indicate an appreciable difference in the rate of consumption of starting material by GC/MS monitoring.

Preparative Photoreaction of *cis*-2 with DCB−Phen in CH_3CN. A sample containing 3.08 g of *cis*-**2** (0.4 M), 2.56 g of DCB (0.4 M), and 0.72 g of Phen (0.08 M) in 50 mL of CH_3CN was irradiated in a 30-mm i.d. Pyrex tube for 41 h to ∼23% conversion of *cis*-**2**. The reaction mixture was concentrated to a volume of 5 mL, and the residue was loaded onto a silica gel column and eluted with methylene chloride containing ethyl acetate, gradually increasing from 0 to 20% v/v. The components of the reaction mixture are eluted in the following order: Phen, DCB, *cis*-**2**, and **4**. The fractions containing compound **4** were combined and concentrated; **4** was obtained as a 0.74-g sample of ∼90% purity (55% yield).

Photoreaction of 2,2-Dimethyl-1-(2-methyl-1-propenyl)-cyclopropane (3). Irradiation of acetonitrile/methanol (3/1 by volume) solutions containing 0.333 M DCB, 0.083 M Ph, and 0.333 M 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane leads to the formation of two NOCAS adducts, (*E*)-2-(*p*-cyanophenyl)-2,6-dimethyl-6-methoxy-3-heptene, **7**, and 4-(*p*-cyanophenyl)-2,6-dimethyl-6-methoxy-2-heptene, **8**, in yields of 63 and 37%, respectively (7.5 h; 81% conversion). No rearrangement of the vinylcyclopropane donor was observed. Product **7** is stable under the irradiation conditions (0.25 M DCB, 0.05M Ph, and 0.25 M **7**, in 2 mL of acetonitrile/methanol, 3/1 by volume, 2 h); in particular, it does not undergo a sigmatropic shift to **8**.



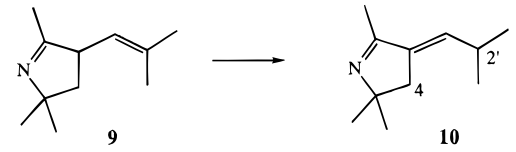
7



8

The structure of **7** rests on the presence of 2 olefinic protons, H-3 (δ 5.62 ppm, d, J = 15.6 Hz) and H-4 (δ 5.52 ppm, dt, 15.6, 6.0 Hz), and 2 allylic protons, H-5 (δ 2.24 ppm, d, J = 6.0 Hz). The 2D-COSY spectrum shows cross peaks between one olefinic (δ 5.52 ppm) and one methyl signal (δ 1.4 ppm), which also interacts with the (ortho) aromatic protons (δ 7.45 ppm). Product **8** shows 1 olefinic proton, H-3 (δ 5.25 ppm, d, J = 9.5 Hz), 1 allylic-benzylic proton, H-4 (δ 3.76 ppm, dt, J = 9.5, 6.6 Hz), and 2 allylic methyl groups (δ 1.66, 1.67 ppm).

Photoreaction of 3 in the Absence of Methanol. Irradiation of **3** (0.333 M) with DCB (0.333 M) and Ph (0.083 M) in acetonitrile solutions not containing methanol failed to show any rearrangement of the vinylcyclopropane donor; instead, an acetonitrile adduct, presumably 3-(2-methyl-1-propenyl)-2,5,5-trimethyl-1-pyrroline, **9**, is formed slowly (66% yield; 120 h; 35% conversion). The acetonitrile adduct has a very weak molecular ion peak (*m/z* 165; $C_9H_{16} + CH_3CN$); the base peak (*m/z* 109; C_8H_{13}; $C_{11}H_{19}N - CH_3CN - CH_3$) and a second strong peak (*m/z* 124; C_9H_{16}, $M^{+\bullet} - CH_3N$) document the incorporation of a labile acetonitrile function.



9 **10**

Upon chromatography on silica gel, the primary adduct rearranges to 2,5,5-trimethyl-3-(2-methylpropenylidene)-1-pyrroline, **10**. The stable molecular ion of **10** (*m/z* 165; C_9H_{16} +

Table 1. Summary of Electron Transfer Reactions

donor ($[\alpha]_D$)	solvent	time, conversion	products (yield; $[\alpha]_D$)
(+)-*cis*-**2** (+26.0°)	CH_3CN	7.5 h, 82%	**4** (82%; +26.3°) **5** (15%) *cis*-**2** (+26.4°)
(±)-*cis*-**2**	CH_3CN:CH_3OH, 3:1 v/v	4.0 h, 50%	**6** (100%)
(±)-*cis*-**2**	CH_3CN; 0.001 M CH_3OH	2.0 h	**4** (85%) **6** (15%)
(±)-*cis*-**2**	CH_3CN; 0.01 M CH_3OH	2.0 h	**4** (43%) **6** (57%)
(−)-*trans*-**2** (−39.1°)	CH_3CN	6.0 h, 100%	**4** (90%; −12.4°) **5** (10%) *trans*-**2** (−16.8°)
3	CH_3CN:CH_3OH, 3:1 v/v	7.5 h, 81%	**7** (63%) **8** (37%)
3	CH_3CN	120 h, 35%	**10** (66%)
3	CH_3NO_2	120 h, 0%	

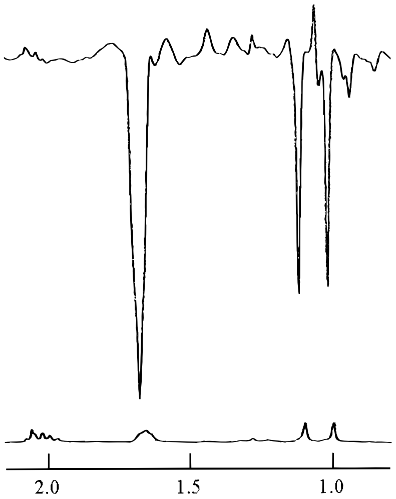


Figure 1. ^1H NMR spectra (80 MHz) of acetone-d_6 solutions containing 30 mM *cis*-chrysanthemol (*cis*-**2**) and 5 mM chloranil in the dark (bottom) and during UV irradiation (top). Only the resonances of the non-equivalent pairs of methyl groups (allylic, ~1.6 ppm; cyclopropane, ~1.1, 1.0 ppm) show significant polarization.

CH_3CN) and its base peak (m/z 150; $C_{10}H_{16}N$) document facile loss of CH_3 and insignificant loss of CH_3CN. The structure of **10** rests on the presence of 1 olefinic proton (δ 5.56 ppm, dt, $J = 9.15, 2.5$ Hz; H-1′) which is coupled to three allylic protons (δ 2.34 ppm, d, $J = 2.5$ Hz, H-4, 2H; and δ 2.37 ppm, dsep, $J = 9.15, 6.77$ Hz; H-2′, 1H) and on the fact that one allylic proton (H-2′) is coupled to two equivalent methyl groups (δ 1.02 ppm, d, $J = 6.77$ Hz).

The results are summarized in Table 1.

CIDNP Results. Irradiation of chloranil in the presence of *cis*- and *trans*-**2** as well as **3** resulted in strong CIDNP effects for the respective donor molecules. The CIDNP spectra of *cis*-**2** (Figure 1) and *trans*-**2** support radical cations of very similar spin density distributions. The two pairs of non-equivalent methyl groups at 1.6 and 1.1 and 1.0 ppm, respectively, of **2** show strong emission; the single olefinic resonance appears in weak emission (not shown). Similarly, the two pairs of non-equivalent methyl groups of **3** (Figure 2) show strong emission, as does the doublet of doublets of H-3_{trans} (0.65 ppm) and, to a lesser extent, the doublet of doublets of H-3_{cis} (0.18 ppm). The allylic cyclopropane proton (1.25 ppm) and the single olefinic proton show negligible polarization.

Discussion

The results discussed in this paper elucidate several diverse aspects, including the structure of the vinylcyclopropane radical cationic systems, $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, and the stereochemical details of their nucleophilic capture, which occurs in intramolecular or intermolecular fashion, respectively. The structural aspects are based on the CIDNP results.

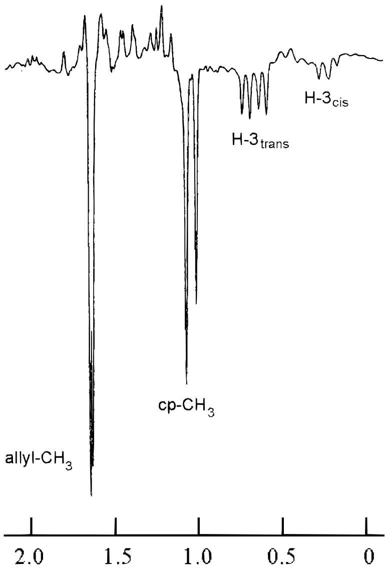


Figure 2. ^1H NMR spectra (80 MHz) of an acetone-d_6 solution containing 30 mM 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane (**3**) and 5 mM chloranil during UV irradiation. The non-equivalent pairs of methyl groups (allylic, ~1.65 ppm; cyclopropane, ~1.05, 1.0 ppm) show strong emission; in addition, the geminal protons, H-3_{trans} and H-3_{cis}, trans and cis to the isobutenyl group, show strong and moderate emission, respectively. The identity of the CIDNP signals is assigned in the figure.

Nuclear Spin Polarization: Structure of Vinylcyclopropane Radical Cations. In order to assign the structures of vinylcyclopropane radical cationic systems, we consider the frontier molecular orbital (FMO) of the cyclopropane unit and consequences for the interaction between the two moieties. MO calculations suggest that the vertical ionization of cyclopropane occurs from a degenerate pair of in-plane e′ orbitals (**s**, **a**) resulting in a doubly degenerate $^2\mathbf{E}'$ state;[20] first-order Jahn−Teller distortion leads to two non-degenerate electronic states, $^2\mathbf{A_1}$ and $^2\mathbf{B_2}$ (C_{2v} symmetry).[20] The $^2\mathbf{A_1}$ component (orbital **s** singly occupied) relaxes to a "one-electron-bonded trimethylene"

---

(20) (a) Haselbach, E. *Chem. Phys. Lett.* **1970**, *7*, 428. (b) Rowland, C. G. *Chem. Phys. Lett.* **1971**, *9*, 169. (c) Collins, J. R.; Gallup, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1530. (d) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21. (e) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283; *Can. J. Chem.* **1983**, *61*, 2310. (f) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405. (g) Krogh-Jespersen, K.; Roth, H. D. *J. Am. Chem. Soc.* **1992**, *114*, 8388−8394.

Scheme 1

$$\mathrm{A} \longrightarrow {}^{1}\mathrm{A}^{*} \longrightarrow {}^{3}\mathrm{A}^{*} \tag{4}$$

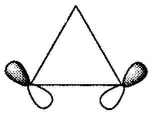
$${}^{3}\mathrm{A}^{*} + \mathrm{D} \longrightarrow {}^{3}\overline{\mathrm{A}^{\bullet -}\ \mathrm{D}^{\bullet +}} \tag{5}$$

$${}^{3}\overline{\mathrm{A}^{\bullet -}\ \mathrm{D}^{\bullet +}} \longrightarrow {}^{1}\overline{\mathrm{A}^{\bullet -}\ \mathrm{D}^{\bullet +}} \tag{6}$$

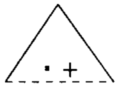
$${}^{1}\overline{\mathrm{A}^{\bullet -}\ \mathrm{D}^{\bullet +}} \longrightarrow \mathrm{A} + \mathrm{D} \tag{7}$$

$${}^{3}\overline{\mathrm{A}^{\bullet -}\ \mathrm{D}^{\bullet +}} \longrightarrow {}^{2}\mathrm{A}^{\bullet -} + {}^{2}\mathrm{D}^{\bullet +} \tag{8}$$

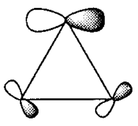
structure (type **A**) with one lengthened (but not broken) C−C bond. This structure type has been assigned to many cyclopropane radical cations, based on either CIDNP[2a,b,21] or low-temperature ESR spectra,[22] and they are consistent with various electron transfer induced ring opening reactions.[7]



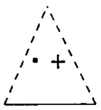
s



A



a



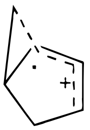
B

In the alternative $^{2}\mathbf{B}_{2}$ component the antisymmetrical molecular orbital **a** is singly occupied. The resulting structure has two lengthened C−C bonds; its cyclopropane fragment resembles a "π-complex" (type **B**).[1e,2a,b,f] This structure type may be stabilized by substitution at a single carbon as in the parent vinylcyclopropane radical cation.[23] The substrates discussed here are 1,1,2-trisubstituted cyclopropanes; precedent[2a,b] and ab initio MO calculations[20g] suggest that this substitution pattern favors a structure of the "one-electron-bonded trimethylene" type (**A**).

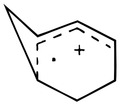
The structures of three vinylcyclopropane radical cations have been assigned previously based on (chemically induced) nuclear spin polarization (CIDNP) effects.[14] These effects may be induced, when photoinduced electron transfer reactions (eq 5) are carried out in the probe of an NMR spectrometer. The competing processes (eq 6−8), delineated in Scheme 1, give rise to a pattern of enhanced absorption or emission lines in the resulting NMR spectrum.

The polarization patterns observed for the reaction products are determined by four parameters, including the sign and magnitude of the hyperfine coupling constants (A) of the nuclei in the paramagnetic intermediate, the relative magnitude of the g-factor of the intermediate (Δg), the initial spin multiplicity of the radical ion pair (which is dictated by the precursor spin multiplicity; μ), and the mode of product formation (ϵ).[24−27]

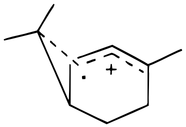
For three radical cations, $\mathbf{11}^{\bullet+}$−$\mathbf{13}^{\bullet+}$, in which the two functionalities are held rigidly in a syn orientation, three of the polarization-determining parameters are known with certainty (μ, $\epsilon > 0$; $\Delta g < 0$), the hyperfine coupling pattern can be derived from the observed polarization pattern, revealing the spin density distribution and, hence, the structure of the radical cationic intermediate.[2f] The three radical cations have in common that spin and charge are significantly delocalized between the strained ring and the vinyl group. They are formally related to structure type **A**, i.e., one cyclopropane bond participates in delocalizing spin and charge; the steric integrity of the three-membered ring is conserved in the radical cations. The participating bond is determined by stereoelectronic effects and the degree of substitution at the two allylic cyclopropane bonds. Thus, in the case of $\mathbf{12}^{\bullet+}$, the internal cyclopropane bond is involved, whereas for $\mathbf{11}^{\bullet+}$ and $\mathbf{13}^{\bullet+}$, the lateral allylic bond is weakened.



$\mathbf{11}^{\bullet+}$

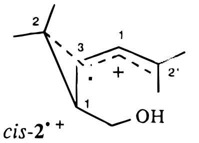


$\mathbf{12}^{\bullet+}$

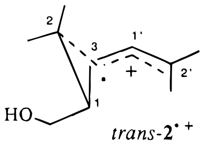


$\mathbf{13}^{\bullet+}$

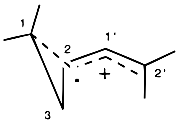
The CIDNP effects observed upon irradiation of chloranil (CA) in the presence of **2** and **3**, respectively, allow the unambiguous assignment of the respective radical cation structures. Photoinduced electron transfer from *cis*- and *trans*-**2** or **3** to ^{3}CA* generates radical ion pairs (eq 5); hyperfine-induced intersystem crossing (eq 6) forms singlet pairs which recombine regenerating the reactants (eq 7). Essentially identical polarization patterns are observed for *cis*- and *trans*-**2**; strong emission of the four methyl groups supports positive spin density for the cylopropane and olefinic carbons, C-2 and C-2′, respectively; weakly enhanced absorption for the olefinic proton (H-1′) indicates weak positive spin density at the adjacent carbon (C-1′). These results suggest radical cations, *cis*- and *trans*-$\mathbf{2}^{\bullet+}$, in which spin and charge are delocalized between the olefinic p-orbital and the Walsh orbital of the tri-substituted cyclopropane bond, with significant spin density at C-2 and C-2′ and very weak spin density at C-1′. The suggested structures are analogous to that of $\mathbf{13}^{\bullet+}$.



cis-$\mathbf{2}^{\bullet+}$



trans-$\mathbf{2}^{\bullet+}$



$\mathbf{3}^{\bullet+}$

The structure of radical cation, $\mathbf{3}^{\bullet+}$, is also quite similar. Strong emission of all methyl signals supports major spin density on C-2′ and C-1; spin and charge must be delocalized between the olefinic and the trisubstituted cyclopropane bond. The polarization of the geminal protons, H-3$_{\mathrm{syn,anti}}$, supports spin density on an adjacent carbon, C-1. The weak emission of H-2 rules out significant spin density at the allylic cyclopropane carbon, C-2.

Intramolecular Nucleophilic Capture. The intramolecular reactivity of *cis*- and *trans*-$\mathbf{2}^{\bullet+}$, particularly its regiochemistry, are of significant interest. The reactions of several radical cations of terpenoid vinylcyclopropane systems with (external) nucleophiles[10a,12] reveal three factors that may influence the regiochemistry of capture: (1) the attack occurs at a carbon bearing spin and charge density; (2) the attack occurs with relief of ring strain; and (3) the attack generates a delocalized (allylic) free radical. This precedent and the fact that the spin density distribution of *cis*-$\mathbf{2}^{\bullet+}$ is similar to that of other vinylcyclopropane radical cations may lead to the conclusion that the hydroxymethyl moiety attacks the quaternary carbon of the three-membered ring, forming the oxetane system, $\mathbf{14}^{\bullet}$. This reaction is an intramolecular S$_{\mathrm{N}}$2 process with an allyl radical as a leaving group, tethered to the newly formed ring.

---

(21) (a) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1980**, *102*, 7956−7958. (b) Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6805.

(22) (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202. (b) Qin, X. Z.; Snow, L. D.; Williams, F. *J. Am. Chem. Soc.* **1984**, *106*, 7640−7641. (c) Qin, X. Z.; Williams, F. *Tetrahedron* **1986**, *42*, 6301−6313.

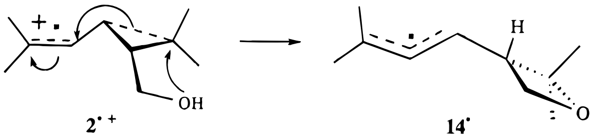
(23) Herbertz, T.; Roth, H. D. Unpublished results.

(24) Closs, G. L. *Adv. Magn. Reson.* **1974**, *7*, 157−229.

(25) Kaptein, R. *Adv. Free Radical Chem.* **1975**, *5*, 319−480.

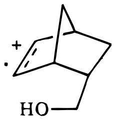
(26) Adrian, F. J. *Rev. Chem. Intermed.* **1979**, *3*, 3−43.

(27) Freed, J. H.; Pederson, J. B. *Adv. Magn. Reson.* **1976**, *8*, 2−84.

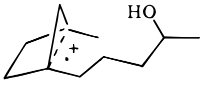


$2^{\bullet +}$ $14^{\bullet}$

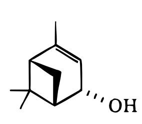
Intramolecular nucleophilic capture has precedent in the trapping of acyclic,[28,29] monocyclic,[30] or bicyclic[31,32] radical cations by carboxylic acid[28] or alcohol functions.[29−32] For example, the radical cationic site of $\mathbf{15}^{\bullet +}$ or $\mathbf{16}^{\bullet +}$ is captured by an alcohol function tethered to the system.[31,32] However, there is no precedent for nucleophilic capture via a four-membered transition state; thus, *cis*-verbenol, **17**, failed to undergo intramolecular capture upon electron transfer.[33] Given the strain inherent in the potential trapping product $\mathbf{14}^{\bullet}$ and that a four-membered transition state is required for its formation, we consider attack of the internal nucleophile at the terminal olefinic carbon, C-2′.



$15^{\bullet +}$

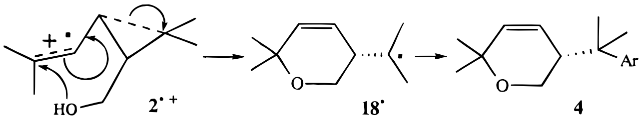


$16^{\bullet +}$



17

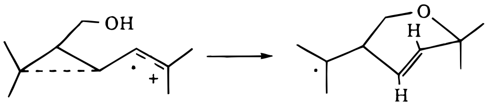
The reaction of *cis*-**2** with 1,4-dicyanobenzene and phenanthrene in acetonitrile generates a 1-(*p*-cyanophenyl)-1-methylethyl-substituted dihydro-2*H*-pyran (**4**) as the major product. No evidence for oxetane (**14**-C_6H_4-*p*-CN) formation was observed. Apparently, nucleophilic attack via a four-membered transition state is significantly disfavored relative to a six-membered transition state. The final step in this reaction, an aromatic substitution of free radical $\mathbf{18}^{\bullet}$ on the sensitizer radical anion, is unexceptional.[7a−c,9,34] The significant finding concerns the structure of the oxygen heterocycle formed in the preceding step. To our knowledge, the intramolecular capture of $\mathbf{2}^{\bullet +}$ is the only example in which a nucleophile attacks a vinylcyclopropane[10] (or vinylcyclobutane)[9] system at the terminal olefinic carbon. The unprecedented course of this reaction demonstrates that the reaction favors release of ring strain and avoids introducing additional strain. This reaction is an intramolecular S_N2' process with a tertiary carbon radical as a leaving group tethered to the newly formed ring.



$2^{\bullet +}$ $18^{\bullet}$ 4

The diamagnetic prototype of the S_N2' reaction has been documented most elegantly by the stereochemical consequences in isotopically labeled or chiral substrates.[35] The intramolecular nucleophilic capture discussed here is the first S_N2' reaction of a radical cation. The oxacyclohex-3-ene (dihydro-2*H*-pyran) structure clearly establishes the S_N2' reaction as a viable mechanism in radical cation chemistry. The electropositive nature of the vinylcyclopropane radical cation allows the substitution to proceed even with a weak nucleophile such as methanol. The stereochemical and chiral features of our substrate clearly document the stereochemical course of the reaction. Since the key chiral carbon atom (C-1) acts as a pivot in the conversion of **2** to **4**, the observed significant optical rotation of the S_N2' product is expected.

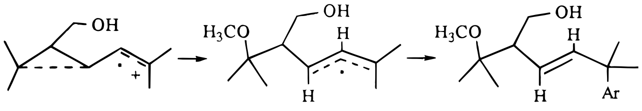
The geometry of the newly formed double bond of free radical, $\mathbf{18}^{\bullet}$ (and product **4**), is of interest because it is expected to reflect the conformation of the vinyl group relative to the cyclopropane moiety in $\mathbf{2}^{\bullet +}$. Since the terminal olefinic carbon and the cyclopropane ring are sterically congested (the syn conformer lies ~80 kJ mol^{-1} higher than the anti conformer; MM3), **2** should exist predominantly as the anti conformer. This may lead to the expectation that $\mathbf{2}^{\bullet +}$ should form a free radical with a *trans* double bond.



cis,anti-$2^{\bullet +}$ *trans*-$18^{\bullet}$

The olefinic coupling constant of **4** ($J = {\sim}15.4$ Hz) lies near the upper limit of the range (5 Hz $< J_{\text{cis}} <$ 14 Hz) typical for *cis* olefins,[36] and no unusual coupling constants have been reported for known derivatives of 5,6-dihydro-2*H*-pyran, including the 2,2-dimethyl derivative.[37] On the other hand, *trans*-cyclohexene systems assigned on the basis of emission spectra[38] or invoked as intermediates[39] have low barriers to cis−trans isomerization (~30 kJ mol^{-1}) and very short lifetimes (~10 μs).[38] Thus, it is unlikely that the *trans* olefin can be isolated at room temperature, even if it is formed initially.

Since the preferred conformer of *cis*-**2** is not accessible via intramolecular trapping, we investigated the electron transfer photochemistry of *cis*-**2** in the presence of methanol as an external nucleophile. Only one new product, **6**, is formed in this reaction; its formation can be explained via the acyclic allyl radical ($\mathbf{19}^{\bullet}$) and exclusive coupling of the sensitizer radical anion at the tertiary allyl terminus. Apparently, the $-CH_2OH$ and 2-methoxypropyl moieties of $\mathbf{19}^{\bullet}$ impede access to the monosubstituted allyl terminus at C3. The (trans) geometry of product **6** reflects the anti species as the preferred conformer of *cis*-$\mathbf{2}^{\bullet +}$, because the allyl radical ($\mathbf{19}^{\bullet}$) should be configurationally stable for its limited lifetime.[40]



cis,anti-$2^{\bullet +}$ $19^{\bullet}$ 6

The competitive formation of products **4** and **6** at low methanol concentrations makes it possible to estimate a rate

---

(28) (a) Gassman, P. G.; Bottorff, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 7547−7548. (b) Gassman, P. G.; De Silva, S. A. *J. Am. Chem. Soc.* **1991**, *113*, 9870−9872.

(29) (a) Jiang, Z. Q.; Foote, C. S. *Tetrahedron Lett.* **1983**, 24, 461−464. (b) Dai, S.; Wang, J. T.; Williams, F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1063−1064.

(30) (a) Du, X.; Arnold, D. R. Unpublished results, quoted in ref 9b. (b) Arnold, D. R.; McManus, K. A.; Coskun, D. Private communication.

(31) Weng, H.; Roth, H. D. Unpublished results.

(32) Adam, W.; Sendelbach, J. *J. Org. Chem.* **1993**, *58*, 5316−5322.

(33) Zhou, D.; Roth, H. D. Unpublished results.

(34) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012−3026.

(35) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901−1930.

(36) (a) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH Weinheim, 1993. (b) Günther, H. *NMR-Spectroscopy*; Wiley & Sons: New York, 1980.

(37) (a) Olsson, L.-I.; Claesson, A. *Synthesis* **1979**, 743−745. (b) Delaunay, J.; Lebouc, A.; Riobe, O. *Bull. Soc. Chim. Fr. Pt. 2* **1979**, 547−551.

(38) (a) Bonneau, R.; Joussot-Dubien, J.; Salem, L.; Yarwood, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 4329−4330. (b) Bonneau, R.; Joussot-Dubien, J.; Yarwood, A. J.; Pereyre, J. *Tetrahedron Lett.* **1977**, 235−238.

(39) (a) Kropp, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 4091−4092. (b) Kropp, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 1126−1134. (c) Kropp, P. J.; Krauss, H. J. *J. Am. Chem. Soc.* **1967**, *89*, 5199−5208. (d) Kropp, P. J. *Organic Chemistry*, Pawda, A., Ed., Marcel Dekker, New York, 1979; Vol. 4, p 1.

(40) Korth, H.-G.; Trill, H.; Sustmann, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 4483.

constant for intramolecular capture from the respective yields, φ_4 and φ_6, viz.,

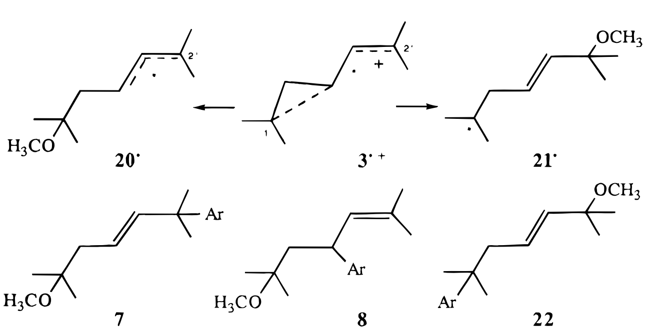
$$k_{\text{intra}} = k_{\text{inter}}[\text{MeOH}](\varphi_4/\varphi_6) \qquad (9)$$

A rate constant, $k = 3.2 \times 10^8$ M^{-1} s^{-1}, has been measured for the intermolecular capture of 1,1-diphenyl-2,2-dimethylcyclopropane radical cation by methanol.[7g] Assuming a similar rate constant for the intermolecular capture of *cis*-$\mathbf{2}^{\bullet+}$, the intramolecular capture should occur with an estimated rate constant of $k_{\text{intra}} \approx 2 \times 10^6$ s^{-1}; apparently, intramolecular capture is not very favorable, most likely because of steric factors.

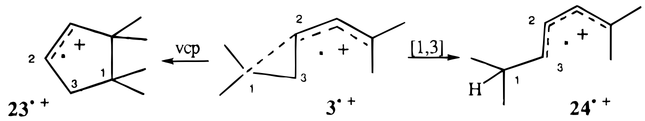
Electron Transfer Photochemistry of 2,2-Dimethyl-1-(2-methyl-1-propenyl)cyclopropane. We extended our studies to the electron transfer photochemistry of 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane, **3**. The nucleophilic capture of $\mathbf{3}^{\bullet+}$ should occur at a carbon bearing spin and charge density, i.e., at C-1 or C-2′. Attack at either carbon would break the cyclopropane ring, generating either an allylic free radical ($\mathbf{20}^{\bullet}$, attack at C-1) or a tertiary one ($\mathbf{21}^{\bullet}$, attack at C-2′). The intramolecular capture of *cis*-$\mathbf{2}^{\bullet+}$ suggests that reaction at C-2′ may be competitive; the precedence of several bicyclic vinylcyclopropane systems[10,12] and the intermolecular capture of *cis*-$\mathbf{2}^{\bullet+}$ lead us to expect attack at C-1.

The NOCAS products, **7** and **8**, resulting from the reaction of **3** show that the radical cation, $\mathbf{3}^{\bullet+}$, captures methanol exclusively at C-1, generating $\mathbf{20}^{\bullet}$; this result provides yet another example of a highly regiospecific nucleophilic capture. The subsequent aromatic substitution with DCB$^{\bullet-}$ occurs preferentially at the tertiary terminus of $\mathbf{20}^{\bullet}$, generating **7**. The fact that **8** is formed as a minor product shows that the reaction of $\mathbf{20}^{\bullet}$ is less regiospecific than that of $\mathbf{19}^{\bullet}$. Apparently, the 1-methoxy-1-methylethyl substituent shields the secondary terminus of $\mathbf{20}^{\bullet}$ less effectively than the pair of substituents shields that of $\mathbf{19}^{\bullet}$.

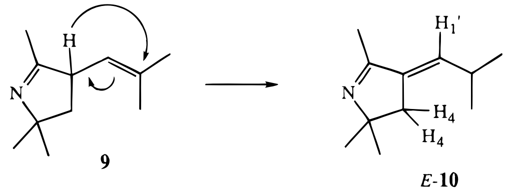
The structure of **7** rests on the 2D-COSY spectrum; cross peaks between one olefinic signal (δ 5.52 ppm) and the methyl resonance (δ 1.4 ppm) which also interacts with the *o*-aryl protons (δ 7.45 ppm) clearly establish the connectivity of these nuclei. The COSY spectrum is incompatible with structure **22** and, thus, rules out the alternative intermediate, $\mathbf{21}^{\bullet}$. The olefinic coupling constant ($J = 15.6$ Hz) identifies **7** as a *trans* alkene, suggesting that $\mathbf{3}^{\bullet+}$ exists predominantly as the *anti* conformer.



We also probed the potential involvement of intramolecular reactions, such as a vinylcyclopropane rearrangement,[6] or a [1,3] sigmatropic shift.[10a,12] A vinylcyclopropane rearrangement of **3** is expected to produce 3,3,4,4-tetramethylcyclopentene (**23**) whereas a [1,3] sigmatropic shift would generate 2,6-dimethylhepta-2,4-diene (**24**). The involvement of these reactions was probed by carrying out the photoreaction between DCB and **3** in the absence of an alcoholic nucleophile, i.e., in pure acetonitrile or nitromethane. The irradiation in nitromethane failed to show any reaction, whereas in acetonitrile the radical cation, $\mathbf{3}^{\bullet+}$, forms an adduct with the solvent.



The capture of radical cations by weak nucleophiles, such as acetonitrile, has been documented previously for vinylcyclopropane[12] and vinylcyclobutane[9] systems. The available precedent leads one to expect an adduct of structure **9**. However, the NMR data of the product suggest a different structure, 2,5,5-trimethyl-3-(2-methylpropenylidene)-1-pyrroline, **10**. The formation of this product is readily rationalized by a prototropic shift that moves the isobutenyl double bond into conjugation with the imine function during chromatography on silica gel.



The rearranged acetonitrile adduct, **10**, is tentatively identified as the *E* isomer because of the relatively large coupling constant between H$_4$ and H$_{1'}$ ($^4J_{4,1'} = 2.5$ Hz); this value lies near the upper limit for allylic coupling constants. Given that the protons H-4 have torsional/dihedral angles near ±30° relative to the olefinic p-orbitals, their coupling lies closer to the values expected for a transoid ($^4J \sim 2.5-3.0$ Hz) than a cisoid geometry ($^4J \sim 1.5-2$ Hz).[41] Molecular mechanics (MM3) calculations indicate that the energy of the *E* isomer lies ~2 kcal/mol below that of the *Z* isomer. Nevertheless, the assignment remains tentative, because ^4J couplings offer less insight into the stereochemistry of double bonds than ^3J coupling constants.

In summary, the vinylcyclopropane radical cation $\mathbf{3}^{\bullet+}$ reacts with nucleophiles, even as weak as acetonitrile, by nucleophilic capture at the quaternary cyclopropane carbon. Neither a vinylcyclopropane rearrangement nor a sigmatropic shift are competitive. The absence of the valence isomerization is readily explained by the preferred transoid geometry of the radical cation and by the apparently significant steric hindrance barring the approach of the dimethyl substituted vinyl group toward the cyclopropane ring.

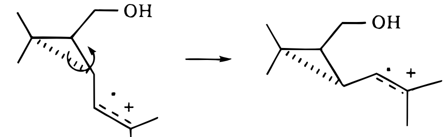
Electron Transfer Photochemistry of *trans*-Chrysanthemol. Interestingly, the dicyanobenzene-sensitized photoreaction of *trans*-chrysanthemol gives rise to the same product formed from the *cis* isomer. The apparent parallel reactivity of the geometric isomers is interesting; however, optically active samples show important differences. The electron transfer reaction of (1*R*,3*S*)-(+)-*cis*-**2** produces **4** with substantial optical rotation and the recovered starting material has fully retained its optical purity; the steric integrity of the three-membered ring of *cis*-**2** is conserved in its radical cation. In contrast, the reaction of (1*S*,3*S*)-(−)-*trans*-**2** produces **4** of lower optical purity; also, recovered starting material has suffered ~30% racemization (77% conversion); both results offer significant insight.

The conversion of *trans*-**2** to **4** requires rotation around one C−C bond, before capture by the internal nucleophile ($-$CH$_2-$OH). This reaction can be accommodated in a radical cation

---

(41) Sternhell, S. *Q. Rev.* **1969**, *23*, 236−270.

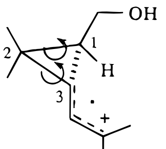
with one weakened bond (*trans*-$\mathbf{2}^{\bullet+}_{(\mathrm{C2}\cdots\mathrm{C3})}$), whose structure is supported by our CIDNP results. The isomerization of *trans*-$\mathbf{2}^{\bullet+}$ may proceed also by a two-bond rotation, around C1−C3 and C1−C2, as established for 1-phenyl-2-vinylcyclopropane radical cation.[6a] In the case of *trans*-$\mathbf{2}^{\bullet+}$, we cannot distinguish one-bond from two-bond rotation since the rotation around C1−C2 interchanges two identical groups.



trans-$\mathbf{2}^{\bullet+}_{(\mathrm{C2}\cdots\cdots\mathrm{C3})}$ *cis*-$\mathbf{2}^{\bullet+}$

Therefore, either a single rotation around C1−C3 or a two-bond rotation around C1−C3 and C1−C2 is expected to produce optically pure **4** because in either case the stereochemical integrity of C1 is conserved. The reduced optical purity of product **4** and the partial racemization of *trans*-**2** require at least one competing pathway.

The partial racemization of the starting material requires two rotations; it can be explained, for example, by concurrent (two-bond) rotation around C1−C2 and C2−C3 in a bifunctional radical cation, in which the C1−C3 bond is broken or weakened ($\mathbf{2}^{\bullet+}_{(\mathrm{C1}\cdots\mathrm{C3})}$). On the other hand, two consecutive single-bond rotations can be eliminated. One-bond rotation around C1−C2 or C2−C3, respectively, would convert *trans*-**2** to *cis*-**2** with either inversion or retention at C1. If one of these reactions were prominent, the reverse reaction, forming *trans*-**2**, should be faster because the heat of formation calculated for *cis*-$\mathbf{2}^{\bullet+}$ (HF/6−31G*) is 1.9 kcal mol^{-1} less negative than that of *trans*-$\mathbf{2}^{\bullet+}$. Yet, neither conversion of *cis*-**2** to *trans*-**2** nor racemization of recovered *cis*-**2** is observed. Clearly, the most likely pathway for the partial racemization involves concurrent rotations around the C1−C2 and C2−C3 bonds.



trans-$\mathbf{2}^{\bullet+}_{(\mathrm{C1}\cdots\mathrm{C3})}$

In summary, three different experimental results observed for *trans*-$\mathbf{2}^{\bullet+}$ require the existence of two different weakened cyclopropane bonds. The partial racemization of *trans*-**2** is readily accommodated by a lengthened C1---C3 bond, whereas the reduced optical purity of **4** as well as the CIDNP results suggest that the C2---C3 bond is weakened. Combined, these conclusions suggest that *trans*-$\mathbf{2}^{\bullet+}$ has an unsymmetrical (scalene) triangular structure.[20g] This possibility was probed by ab initio calculations[42] using an extended basis set, including p-type polarization functions on C (6−31G*), and appropriate levels of electron correlation (MP2). In order to limit the significant computing resources required for calculations at this level, we chose a slightly simpler model, in which the two methyl groups at the vinyl terminus are omitted, i.e., we optimized the structure of *trans*-3-ethenyl-1-(hydroxymethyl)-2,2-dimethylcyclopropane radical cation ($\mathbf{25}^{\bullet+}$). This change is expected to alter the FMO energy of the vinyl fragment and, thus, affect the extent of interaction with the cyclopropane function. However, the relative contribution of the C1---C3 and C2---C3 bonds to delocalizing spin and charge in $\mathbf{25}^{\bullet+}$ vs *trans*-$\mathbf{2}^{\bullet+}$ should be less significantly affected.

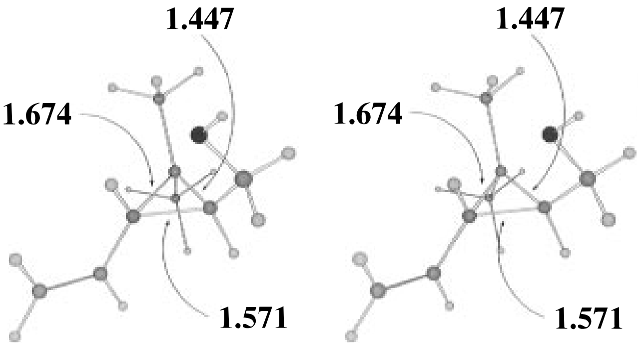
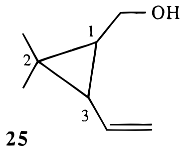
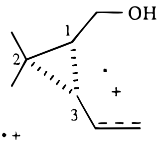


Figure 3. Stereoview of *trans*-3-ethenyl-1-hydroxymethyl-2,2-dimethylcyclopropane radical cation ($\mathbf{25}^{\bullet+}$) calculated at the MP2/6−31G* level of theory. The intermediate has cyclopropane bonds of three distinctly different bond lengths (Å).

Geometry optimization of $\mathbf{25}^{\bullet+}$ at the MP2/6−31G* level of theory supports an unsymmetrical (scalene) triangular structure (Figure 3) with two lengthened (and weakened) bonds, C2−C3 (1.674 Å) and C1−C3 (1.571 Å). Inasmuch as the calculated structure can be extrapolated to *trans*-$\mathbf{2}^{\bullet+}$, it is compatible with all experimental results in the electron transfer photochemistry of *trans*-**2** and reconciles any potential discrepancies. The longest (weakest) bond (C2−C3) determines the major electron spin density distribution; accordingly, it is reflected in the CIDNP results (Figure 2). This bond also allows concurrent rotations about C1−C2 and C1−C3, converting *trans*-$\mathbf{2}^{\bullet+}$ to *cis*-$\mathbf{2}^{\bullet+}$. The second weakened cyclopropane bond facilitates concurrent rotations about C1−C2 and C2−C3, explaining the observed racemization of *trans*-$\mathbf{2}^{\bullet+}$.



25



$\mathbf{25}^{\bullet+}$

Finally, in the light of the results observed for *trans*-$\mathbf{2}^{\bullet+}$ and the calculations for $\mathbf{25}^{\bullet+}$ and in the interest of "mechanistic unity", we note that *cis*-$\mathbf{2}^{\bullet+}$ may very well also have a second lengthened bond. However, we emphasize that the experimental results neither support nor eliminate this assignment. The CIDNP data (Figure 1) support a structure with electron spin density primarily at the two dimethyl-substituted carbons and a weakened bond between the allylic and the quaternary carbon (*cis*-$\mathbf{2}^{\bullet+}_{(\mathrm{C2}\cdots\mathrm{C3})}$). The high retention of optical activity in **4** requires that intramolecular nucleophilic capture is faster than any rearrangement of the radical cation. The bond rotation observed for *trans*-$\mathbf{2}^{\bullet+}$ becomes competitive only because the option of intramolecular nucleophilic capture has been removed. In this sense, the loss of optical purity of *trans*-**2** and **4** has provided significant insight.

Conclusion

The electron transfer photochemistry of three vinylcyclopropane systems illustrates the reactivity and structure of the respective radical cations and reveals the stereochemistry of their reactions. The radical cation of 2,2-dimethyl-1-(2-methyl-1-propenyl)cyclopropane, **3**, is captured by methanol at the quaternary cyclopropane carbon, a result anticipated from

---

[42] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J. P.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*; Gaussian, Inc., Pittsburgh, PA.

available precedent. This reaction is favored by release of ring strain and by the formation of a delocalized (allylic) free radical.

Optically pure (1*R*,3*S*)-(+)-*cis*-chrysanthemol (*cis*-**2**) forms an oxacyclohexene, **4**, with high optical purity. The alcohol function of *cis*-$\mathbf{2}^{\bullet+}$ reacts by nucleophilic attack on the terminal vinyl carbon, presumably because the alternative intramolecular attack on the quaternary cyclopropane carbon has an unfavorable (four-center) transition state. The conversion of *cis*-$\mathbf{2}^{\bullet+}$ to $\mathbf{4}^{\bullet}$ amounts to an S_N2' process, unprecedented in all of radical cation chemistry. The intermolecular capture of *cis*-$\mathbf{2}^{\bullet+}$ by methanol competes with the intramolecular capture, yielding an estimated rate constant for this process.

The electron transfer photochemistry of (1*S*,3*S*)-(−)-*trans*-**2**) generates **4**, apparently via *cis*-$\mathbf{2}^{\bullet+}$; both **4** and recovered *trans*-**2** are partially racemized. The results are rationalized by an unsymmetrical (scalene) triangular structure, allowing concurrent rotations around two different pairs of cyclopropane bonds of *trans*-$\mathbf{2}^{\bullet+}$. The assignments are supported by ab initio MO calculations (MP2/6−31G*) on a somewhat simplified model compound, *trans*-3-ethenyl-1-(hydroxymethyl)-2,2-dimethylcyclopropane radical cation ($\mathbf{25}^{\bullet+}$).

Acknowledgment. Financial support of this work by the National Science Foundation through grant NSF CHE-9414271 and equipment grants NSF CHE-9107839 and CHE-9520633 is gratefully acknowledged; the authors are indebted to Dr. G. Sluggett for technical assistance with the CIDNP spectra.

Supporting Information Available: NMR spectral assignments and MS data for products **4**−**8** and **10**; procedures for purification of solvents, photoreactions, isolation, and characterization of products (9 pages). See any current masthead page for ordering and Internet access instructions.

JA953596C