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Ring Opening of Vinylcyclopropane Radical Cations via Stereoselective Sigmatropic Shifts

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Abstract: The electron transfer photoreaction of (1*R*,5*R*)-(+)-sabinene (4-methylene-1-(1-methylethyl)bicyclo[3.1.0]-hexane; **1**) with 1,4-dicyanobenzene and phenanthrene gives rise to (*S*)-(+)-β-phellandrene (3-methylene-6-(1-methylethyl)cyclohexene; **3**), whereas (1*S*,5*S*)-(+)-α-thujene (2-methyl-5-(1-methylethyl)bicyclo[3.1.0]hex-2-ene; **2**) is converted to (*S*)-(+)-α-phellandrene (2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene; **7**). Both products can be rationalized via stereoselective sigmatropic shifts in the corresponding radical cations. For $\mathbf{1}^{\bullet+}$, a [1,3] sigmatropic shift transfers a hydrogen from C_6 to C_1 with inversion of stereochemistry at C_1. For $\mathbf{2}^{\bullet+}$, experiments with **2**-3-d_1 indicate that a [1,3] sigmatropic shift (from C_6 to C_1) competes with a homo-[1,5] sigmatropic shift (from C_2 to C_1); the latter migration is slightly favored. The stereochemical relationship between the chiral educts, **1** and **2**, and the ring-opened products, **3** and **7**, requires that the radical cations, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, retain the chirality of their precursors; they cannot be ring-opened. The rearrangement of $\mathbf{2}^{\bullet+}$ takes a significantly different course from the thermal isomerization of its parent, **2**, which proceeds via the vinylcyclopropane rearrangement. The stereochemical course established for the rearrangement of $\mathbf{2}^{\bullet+}$ is the first case of competing sigmatropic shifts in radical cations.

Introduction

The structures and reactions of organic radical cations have been the focus of much attention for more than two decades.[1,2] Particularly, organic radical cations containing strained ring moieties as well as olefinic fragments have attracted considerable interest.[1e,2c] These species may undergo a wide range of reactions. For example, various rearrangements of the carbon skeleton have been reported, many of them resulting in the release of ring strain.[3−6] In some instances, ring opening is assisted by a nucleophile.[7−9] The simplest species containing an olefinic moiety and a cyclopropane ring, the parent vinylcyclopropane radical cation, has been the target of some investigations,[10,11] as have several derivatives.[6,12,13] The reactivity of this species has been examined in the gas phase, where changes in the mass spectrum of the resulting ion(s) as a function of varying modes of ionization indicate ring opening to penta-1,3-diene radical cation.[10] An STO-3G calculation for the prototype radical cation was carried out with the vinyl group coplanar to two cyclopropane carbons.[11] Dinnocenzo and colleagues studied the electron transfer induced chemistry of various *p*-anisyl derivatives and observed rearrangements of the vinylcyclopropane type.[6] We have studied several aspects of this interesting system, including the electron transfer induced CIDNP effects of simple bicyclic derivatives, in which the two functionalities are locked in a syn configuration,[12] and the electron transfer photochemistry of sabinene, which contains the two functionalities in the anti configuration.[13] In spite of these studies, the structure of the vinylcyclopropane radical cation has not been adequately characterized by experiment or calculation.

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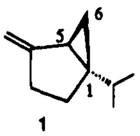
The vinylcyclopropane system can undergo two rearrangements that would relieve its ring strain, either a valence isomerization or a hydrogen shift. The vinylcyclopropane rearrangement would generate a cyclopentene system, whereas hydrogen (hydride) transfer would lead to pentadiene derivatives. In this publication, we report the electron transfer induced isomerization of two chiral vinylcyclopropane systems in which the two functionalities are locked in the anti (sabinene, **1**) or syn orientation (α-thujene, **2**). Both systems are converted to less strained, fully conjugated products.



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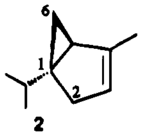

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Photoinduced Electron Transfer Reactions. Irradiation of an electron acceptor sensitizer—cosensitizer system (e.g., 1,4-dicyanobenzene—phenanthrene) in the presence of suitable donors (D, viz. **1** and **2**) and nucleophiles (CN^-, CH_3OH) initiates a well-established photochemical reaction sequence,[7a,9b] generating radical ion pairs ($D^{\bullet+}$, $DCB^{\bullet-}$; eq 1). The radical cation may rearrange (eq 2) or undergo nucleophilic capture (eq 3); rearranged radical cations ($D_r^{\bullet+}$) generate rearranged products by electron return from the sensitizer anion (eq 4). The free radical(s) formed by nucleophilic capture react with the sensitizer radical anion by aromatic substitution (eq 5). The reaction sequence leading to the three-component product was studied in detail for olefins; it has become known as the photo-NOCAS reaction (for "photoinduced nucleophile olefin combination aromatic substitution").[9b]

$$\mathrm{Ph + DCB + D \xrightarrow{h\nu} Ph + DCB^{\bullet-} + D^{\bullet+}} \tag{1}$$

$$\mathrm{D^{\bullet+} \rightarrow D_r^{\bullet+}} \tag{2}$$

$$\mathrm{D^{\bullet+} + CH_3OH \rightarrow [D{-}OCH_3]^{\bullet} + H^+} \tag{3}$$

$$\mathrm{D_r^{\bullet+} + DCB^{\bullet-} \rightarrow [D{-}OCH_3]^{\bullet} + H^+} \tag{4}$$

$$\mathrm{[D{-}OCH_3]^{\bullet} + DCB^{\bullet-} \rightarrow \mathit{p}\text{-}CNC_6H_4{-}D{-}OCH_3 + CN^-} \tag{5}$$

This paper is concerned mainly with the relationship between the structures of sabinene and α-thujene radical cations and those of their rearrangement products. Accordingly, there appears to be no need to delineate the mechanism in any more detail. However, some facets particular to individual reactions will emerge from the subsequent discussion.

Experimental Section

Materials. (1*R*,5*R*)-(+)-Sabinene (4-methylene-1-(1-methylethyl)-bicyclo[3.1.0]hexane; $[\alpha]_{546}$ = +125°, "puriss.") was obtained from Fluka; (1*S*,5*S*)-(+)-α-thujene (2-methyl-5-(1-methylethyl)bicyclo[3.1.0]-hex-2-ene; $[\alpha]_{546}$ = +33°, ~60% ee) was isolated by gas chromatography from a sample of (*R*)-(−)-α-phellandrene (2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene; Fluka, "techn., ~50%,"); (1*R*,5*R*)-(−)-α-thujene was synthesized by reaction of the toluene-*p*-sulphonylhydrazone of (1*R*,5*R*)-(−)-thujone (4-methyl-1-(1-methylethyl)bicyclo[3.1.0]hexan-3-one; Aldrich) with butyl lithium.[14] α-Thujene-3-d_1 was prepared from (−)-thujone and $LiAlD_4$ via pyrolysis of a xanthate intermediate according to a procedure of Doering and Lambert.[15] Simultaneously formed (1*R*,5*R*)-β-thujene (4-methyl-1-(1-methylethyl)bicyclo[3.1.0]hex-2-ene) was removed by GC separation. 1,4-Dicyanobenzene (Aldrich; 98%) and phenanthrene (Aldrich; 98%) were purified by recrystallization. (Throughout the remaining sections, the stereochemical indicators are denoted by the terpene nomenclature convention, in which, e.g., the quaternary center of sabinene is C_1.)

Solvents. Acetonitrile (Fischer) was distilled from calcium hydride. Methanol (Fischer, Spectranalyzed) was refluxed over ~2 g/L of sodium (freshly washed with methanol) and distilled. The solvents so dried were stored over 4A molecular sieve in brown bottles under argon atmosphere.

Photoreactions. Solutions containing appropriate concentrations of donor and acceptor were degassed by purging with argon for 15 min before irradiation. All irradiations were carried out in a Rayonet RPR-100 photoreactor equipped with 16 RPR-3500 lamps. The progress of the reactions was monitored by gas chromatography on a GC/MS system (HP 5890 series II GC interfaced with a HP 5971 mass selective detector), using a 12 m × 0.20 mm × 0.33 μm HP-1 capillary column (cross-linked methyl silicone on fused silica). Analytical runs were carried out in 5-mm NMR tubes stoppered with latex stoppers, preparative runs in 30-mm-i.d. tubes, water-cooled with central cooling fingers.

Isolation of Products. Reaction products were isolated by both preparative GLC and liquid column chromatography. Preparative GLC was carried out on a 6-ft column packed with 10% CP-5 on a Chromosorb WHP support. Liquid chromatography was carried out using a set of 50-cm columns with i.d.'s ranging from 1 to 5 cm. The columns were packed with ~15 cm of TLC standard grade silica gel (Aldrich; without binder) and eluted with solvent gradients, usually from light petroleum ether (bp < 65 °C) to mixtures with either methylene chloride or ethyl acetate. Typically, several passes were required to isolate the products.

Characterization of Products. Structure assignments of isolated products are based on MS and NMR data. Proton NMR spectra were recorded on either a Varian XL-400 or a Varian VXR-200 spectrometer. ^{13}C and HETCOR spectra were recorded on a Varian VXR-200 spectrometer operating at 50.3 MHz. The structural assignments are based on 1D ^1H, 2D COSY, and $^{13}C{-}^1H$ HETCOR, where appropriate. Extensive NOE difference spectra were recorded to elucidate the structure and to probe substituent stereochemistry and the spatial relationship between the different functional groups.

Results

Irradiation of (1*R*,5*R*)-(+)-Sabinene (1). Irradiation of acetonitrile solutions containing 0.1 M 1,4-dicyanobenzene (DCB), 0.02 M phenanthrene (Ph), and 0.05 M optically pure (1*R*,5*R*)-(+)-sabinene ($[\alpha]_D$ = +107°, $[\alpha]_{546}$ = +125°)[16] causes isomerization to (*S*)-(+)-β-phellandrene (**3**; $[\alpha]_{546}$ = +21°, ee < 30%; 25% yield at ~40% conversion)[17] and formation of two acetonitrile adducts, **4** (12%) and **5** (11%), as well as several dimeric hydrocarbons (M^+ = 272; ~50%); the dimers were not separated. Product **5** was characterized only by its MS pattern as it was hydrolyzed upon chromatography on silica gel, yielding the bicyclic ketone **6** ($[\alpha]_{546}$ = −188°). Recovered sabinene essentially retains its optical activity ($[\alpha]_{546}$ = +122°). Prolonged irradiation depletes product **3** and leads to a more complex dimer mixture.

Irradiation of (1*S*,5*S*)-(+)-α-Thujene (2). Irradiation of acetonitrile solutions containing 0.1 M DCB, 0.02 M Ph, and 0.05 M (1*S*,5*S*)-(+)-α-thujene ($[\alpha]_{546}$ = +33°, ee ~ 60%)[18]

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(14) Doering, W. von E.; Schmidt, E. K. G. *Tetrahedron* **1971**, *27*, 2005–2030.

(15) Doering, W. von E.; Lambert, J. B. *Tetrahedron* **1963**, *19*, 1989–1994.

(16) The highest recorded specific rotation for (+)-sabinene is $[\alpha]_D$ = +105°: Baganz, H.; Teichert, P. *Arch. Pharmacol.* **1959**, *292*, 442.

(17) The highest recorded specific rotation for (*R*)-β-phellandrene is $[\alpha]_D$ = −74.2°: Acheson, G. G.; West, T. F. *J. Chem. Soc.* **1949**, 812.

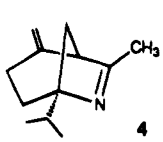
(18) The highest recorded specific rotation for (−)-α-thujene is $[\alpha]_D$ = −52.6°: Shabalina, V. I.; Dembutskii, A. D.; Goryaev, M. I. *Zh. Obshch. Khim.* **1964**, *34*, 3855.

gives rise to (*S*)-(+)-α-phellandrene (**7**; $[\alpha]_{546} = +19°$, ee < 7%;[19] 13% yield at ~30% conversion), 14% cymene (**8**), and an acetonitrile adduct ($M^+ = 177$; 10%) as well as several dimeric hydrocarbons ($M^+ = 272$; ~60%); the dimers were not separated. Recovered α-thujene essentially retains its optical activity ($[\alpha]_{546} = +32°$).

Irradiation of **2**-3-d_1 under the same conditions produced α-phellandrene-d_1; NMR analysis showed this product to be a mixture of **7**-1-d_1 and **7**-3-d_1 in the ratio of 45:55.

Irradiation of an acetonitrile/methanol (3:1) solution 0.1 M DCB, 0.02 M Ph, and 0.05 M (1*R*,5*R*)-(−)-**2** ($[\alpha]_D = -42°$; optically pure) gave rise to the dehydrogenation product, cymene (**8**, 4%), three products of the "NOCAS"-type,[9b,20] **9** (43%; $[\alpha]_D = +19°$), **10** (26%; $[\alpha]_D = 0°$), and **11** (14%; $[\alpha]_D = +29°$), and a novel ring-opened "substitution" product, **12** (5%), in which a hydrogen atom has been replaced by a cyanophenyl group.

NMR Characterization. Product **4** (M^+ 177, $C_{10}H_{16} + CH_3CN$) shows a pair of terminal olefinic protons (δ 4.68, 4.74 ppm) as well as a broad signal at δ 2.01 ppm (3H) for the methyl group attached to the imine carbon. A significantly deshielded signal (δ 3.16 ppm) supports the presence of a doubly allylic bridgehead proton; it appears as a doublet ($J = 5.8$ Hz), coupled to only one of the bridge protons, suggesting a twisted bicyclic structure. The isopropyl group is attached to a quaternary carbon since its methine proton is coupled only to the two methyl groups. The regiochemistry of the imine methyl group was established by NOE experiments; irradiation of the doubly allylic bridgehead proton caused (medium) enhancement of the imine methyl resonance.



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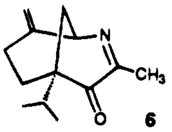
Product **5** (M^+ 204, $C_{10}H_{16} + CH_3CN + HCN$) was converted to product **6** (M^+ 205, $C_{10}H_{16} + C_3H_3NO$) upon chromatography on silica gel, apparently by replacement of an imine function by a carbonyl group. Product **6** shows proton resonances similar to those of product **4**, viz. signals characteristic for terminal olefinic (δ 4.77, 4.86 ppm), isopropyl, and imine methyl functions (δ 2.18 ppm). The ^{13}C spectrum shows 13 signals including carbonyl (δ 192 ppm) and imine (δ 164 ppm) as well as internal (δ 143 ppm) and terminal olefinic resonances (δ 111 ppm). The orientation of the imine function is deduced from the fact that the methyl group shows no NOE effects with any other proton.



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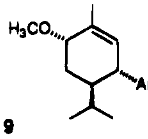
The three NOCAS-type products, **9**−**11** (M^+ 269, $C_{18}H_{23}NO$), have several features in common, including the methoxy singlets (δ 3.2−3.4 ppm) and the characteristic AA′BB′ resonances of the cyanophenyl group ($^3J \sim 8$ Hz). The following assignments are fully compatible with 2-D COSY spectra.

(*r*)-3-(*p*-Cyanophenyl)-*trans*-4-isopropyl-*cis*-6-methoxy-1-methylcyclohexene (**9**)[21] has resonances at δ 3.58 and 3.17 ppm, characteristic for an alkoxy and an allylic benzylic proton, respectively. Since the isopropyl methine signal appears as a doublet of septets, the isopropyl group must be attached to a tertiary carbon (C_4). Irradiation of the resonance at δ 1.71 ppm (H_4) causes medium NOE enhancement for two resonances representing (1) one of a pair of diastereotopic methylene protons (H_5) and (2) the ortho aryl protons. The latter fact requires that aryl and isopropyl groups are trans to each other. Irradiation of the alkoxy resonance (H_6, δ 3.59 ppm) causes NOE enhancement of the second resonance (δ 1.30 ppm) ascribed to H_5, establishing that the methoxy and isopropyl groups are trans to each other.



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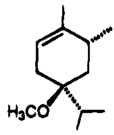
trans-6-(*p*-Cyanophenyl)-4-isopropyl-4-methoxy-1-methylcyclohexene (**10**) has a single olefinic resonance (H_2, 5.56 ppm). A multiplet at 3.43 ppm, assigned to the allylic, benzylic proton H_6, shows strong mutual NOE effect with the ortho aryl resonance. The isopropyl methine proton appears as a septet, establishing that the isopropyl and methoxy groups are attached to the same carbon (C_4). Irradiation of the benzylic resonance (H_6) causes medium NOE enhancement of the methoxy singlet, establishing a *cis*-1,3-diaxial relationship and suggesting that the methoxy group is axial.



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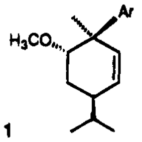
(*r*)-3-(*p*-Cyanophenyl)-*cis*-6-isopropyl-*trans*-4-methoxy-3-methylcyclohexene (**11**) has two internal olefinic resonances (δ 5.55, 5.93 ppm; $J = 10.2$ Hz). The isopropyl methine shows an eight-line pattern due to coupling with an allylic proton (δ 1.75 ppm) as well as two methyl protons. Irradiating the *ortho*-aryl resonance causes strong NOE enhancements of one olefinic (δ 5.55 ppm, H_2), the alkoxy (δ 3.46 ppm, H_4), and one methyl resonance (1.42 ppm). Apparently, the aryl function is attached to the methyl-bearing carbon (C_3) and trans to the methoxy group. Irradiation of the alkoxy resonance (H_4) caused noticeable NOE enhancement of the isopropyl methine proton, establishing the trans relationship between methoxy and isopropyl groups.



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Discussion

A vinylcyclopropane radical cation can, in principle, undergo two rearrangements that would relieve its ring strain: a

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[19] The highest recorded specific rotation for (*R*)-α-phellandrene is $[\alpha]_D = -217°$: *Dictionary of Organic Compounds*; 5th ed.; Chapman and Hall: New York, 1982; Vol. 3. (−)-α-Phellandrene (Fluka, puriss.) has a specific rotation of $[\alpha]_{546}$ value of −288°.

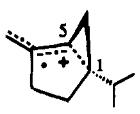
[20] Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012.

[21] In order to unambiguously designate the stereochemical relationship in monocyclic compounds with more than two chiral atoms, the configuration of each group is given with respect to a reference group (r) attached to the lowest-numbered ring member; see: March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; Wiley-Interscience: New York, 1992; Chapter 4.

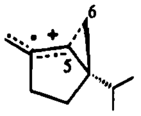
vinylcyclopropane-type rearrangement generating a cyclopentene system or a hydrogen (hydride) transfer forming pentadiene derivatives, containing either a conjugated (1,3-) or a nonconjugated (1,4-) diene system. Both types of reactions have been observed for a number of radical cations. For example, several *p*-anisyl derivatives were reported to undergo vinylcyclopropane rearrangements upon electron transfer to dioxygenyl cation.[6] Hydrogen migrations have been demonstrated or invoked in many radical cations; the involvement of hydride shifts is postulated on the basis of experimental data, such as EPR[22,23] or CIDNP spectra,[24,25] the structure of reaction products, or theoretical calculations.[26] Thus, the conversion of cyclohexane-1,4-diyl[22] radical cation to cyclohexene radical cation or of bicyclo[2.1.0]pentane radical cation[23] to cyclopentene radical cation rests on EPR evidence. CIDNP data support the involvement of radical cationic species in the conversion of benzonorcaradiene to 1- and 2-methylnaphthalene[24] and of tricyclo[4.1.0.0^{2,7}]heptane to bicyclo[4.1.0]hex-2-ene.[25] The conversion of cyclopropane to propene radical cation has been studied in considerable detail by ab-initio calculations.[26] Although the detailed course of these reactions has not been established, some migrations clearly involve a hydride shift to an adjacent carbon (formally 1,2-shift),[22,24] whereas others involve transfer across several C−C bonds.[25]

The two vinylcyclopropane systems that are the subject of this publication contain the two potentially interacting functionalities in rigid arrangements, locked in either the anti (sabinene, **1**) or the syn orientation (α-thujene, **2**). The anti stereochemistry of sabinene precludes the vinylcyclopropane rearrangement whereas the syn stereochemistry of α-thujene would, in principle, permit this reorganization. However, the structure of **2** causes this rearrangement to be degenerate; therefore, it can be evaluated only for isotopically labeled or chiral substrates. Upon photoinduced electron transfer, both systems undergo rearrangements to less strained, fully conjugated products: the reaction of (1*R*,5*R*)-(+)-**1** gives rise to (*S*)-(+)-β-phellandrene (**3**),[17] whereas (1*S*,5*S*)-(+)-**2** is converted to (*S*)-(+)-α-phellandrene (**7**).[18] The stereochemical relationship between the chiral vinylcyclopropane compounds and the ring-opened hydrocarbons, **3** and **7**, obtained from them illuminates the nature of the radical cations, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, and reveals mechanistic details of the pathway connecting them to $\mathbf{3}^{\bullet+}$ and $\mathbf{7}^{\bullet+}$. Both results are compatible with sigmatropic shifts between adjacent carbons, but the results observed for the two reactions show significant and interesting differences.

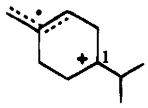
Rearrangement of Sabinene Radical Cation. We consider three structure types for the radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$: "trimethylene" structures with one lengthened (but not broken) cyclopropane bond, either the internal bond (C_1-C_5; structures $\mathbf{1-2a}^{\bullet+}$), or the lateral one (C_5-C_6; structures $\mathbf{1-2b}^{\bullet+}$), or ring-opened bifunctional structures ($\mathbf{1-2c}^{\bullet+}$), which have the advantage of minimized strain energies, albeit at the expense of diminished delocalization. Structures with one lengthened cyclopropane bond have been assigned to many cyclopropane radical cations, based on CIDNP[27] or low-temperature ESR spectra;[28] most recently, CIDNP results identified two structure types, in which an internal or a lateral cyclopropane bond are involved in delocalizing spin and charge.[12] Ring-opened structures formally related to type **c** have been invoked for 1-aryl-2-vinylcyclopropane radical cations.[6]



$\mathbf{1a}^{\bullet+}$



$\mathbf{1b}^{\bullet+}$



$\mathbf{1c}^{\bullet+}$

The electron transfer induced rearrangement of (1*R*,5*R*)-(+)-**1** to (*S*)-(+)-**3** occurs with significant, though not complete, retention of optical activity. The retention of optical activity by the rearranged hydrocarbons is most significant. For example, the enantiomeric excess (33% ee) in **3** precludes the significant involvement of a "ring-opened" radical cation, $\mathbf{1c}^{\bullet+}$, in which the quaternary carbon center, C_1, would be planar. The intermediate radical cation must retain the chirality of the parent; this species can only be described as a "closed-ring" intermediate, $\mathbf{1a}^{\bullet+}$, with substantial residual bonding between the quaternary and allylic cyclopropane carbons. The conservation of chiral integrity in $\mathbf{1a}^{\bullet+}$, is further supported by the high optical purity ($[\alpha]_{546} = +122°$) of recovered starting material.

The hydride shift converting $\mathbf{1a}^{\bullet+}$ to $\mathbf{3}^{\bullet+}$ occurs with a significant degree of stereoselectivity. The structural relationship between **1** and **3** indicates that the migration occurs from C_6 to C_1, and the known absolute configurations of educt and product[17] unambiguously define the hydrogen migration as occurring with inversion of stereochemistry at the receiving carbon, C_1. On the other hand, the results do not provide any direct information about the stereochemical origin of the migrating H. We favor involvement of the *syn*-6-H for several reasons. Because the steric integrity of the three-membered ring is maintained in the radical cation, a suprafacial shift of *syn*-6-H is attractive as it would utilize the back lobe of the p-orbital developing at C_1; this assignment is consistent with the stereochemistry of nucleophilic attack on radical cations of cyclopropane systems[7e,g,13] or quadricyclane and derivatives.[29] This conversion may be considered a [1,3] sigmatropic shift in an open-shell system.

The involvement of *syn*-6-H in the conversion is supported by the precedent of *anti*-5-methyl-bicyclo[2.1.0]pentane radical cation observed by Williams and co-workers; this radical cation (which contains a *syn*-5-H) rearranges to 1-methylcyclopentene radical cation, whereas the *syn*-5-methyl isomer (which contains an *anti*-5-H) fails to undergo the corresponding reorganization.[23] Combined, the results observed for the radical cation of **1** reported here and of the isomeric 5-methylbicyclo[2.1.0]pentane radical cations unambiguously delineate the stereochemical course of the sigmatropic shifts in these radical cations.

It is interesting to consider the failure of this rearrangement to fully transfer the optical purity of the educt **1** to the product **3**. This is especially noteworthy since there is neither any loss of optical purity in recovered starting material nor any evidence for a degenerate rearrangement of the product. Alternative sigmatropic shifts, either the suprafacial migration of the *anti*-

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[28] (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.

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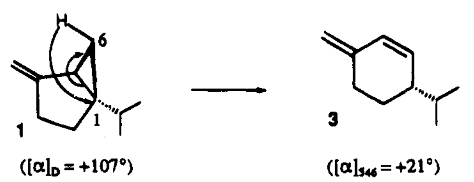
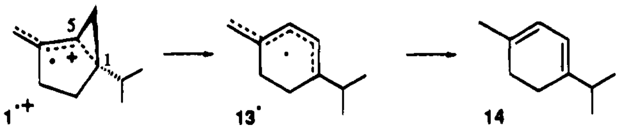


6-H or the antarafacial migration of the *syn*-6-H, appear unlikely in view of the precedent of the 5-methylbicyclo[2.1.0]pentane radical cations;[23] however, they cannot be eliminated with certainty. Because of the potential significance of these processes for the observed loss of optical activity, we are pursuing two stereospecifically monodeuterated analogs of **1** and their electron transfer photochemistry.

Another possible mechanism involves deprotonation of sabinene radical cation with ring opening followed by (random) reprotonation at the isopropyl-bearing carbon. Deprotonations of several bifunctional radical cations have, indeed, been observed;[30] in fact, several products obtained in the electron transfer photochemistry of α-thujene require deprotonation of its radical cation as a key step (vide infra). However, protonation of the free radical, $\mathbf{13}^{\bullet}$, at the exocyclic methylene group would produce the conjugated diene, α-terpinene, **14**, which is not observed. Also, we have no other evidence for deprotonation in the electron transfer photochemistry of **1**. In summary, it is not clear by which mechanism the optical purity of product **3** is reduced.

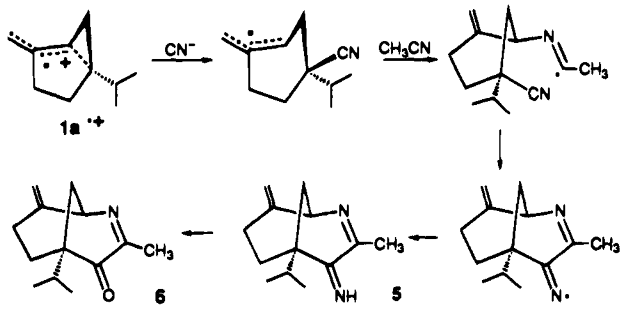


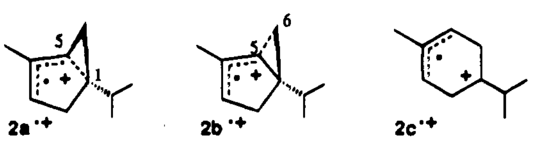
Two additional products observed during the reaction of **1** are formed by interaction with the solvent, acetonitrile. The bicyclic acetonitrile adduct **4** has precedent in the electron transfer photochemistry of α- and β-pinene.[9b] The formation of product **5** is an unprecedented extension, requiring that $\mathbf{1}^{\bullet+}$ react with cyanide anion as well as acetonitrile (Scheme 1).

Although acetonitrile is a poor nucleophile, it may react with the radical cation because of its high concentration, possibly via a ternary complex of the solvent with the ion pair. The association of polar solvent molecules with exciplexes or ion pairs has been demonstrated.[31] The attack of cyanide ion on $\mathbf{1}^{\bullet+}$ is interesting; DCB appears to be the only reasonable source for cyanide ion. The formation of products **4** and **5** define a scale of relative rates for the reactions of $\mathbf{1}^{\bullet+}$: the "bimolecular" reactions with the solvent and with cyanide ion compete efficiently with the sigmatropic shift leading to product **3**. The high retention of optical activity in ketone **6** ($[\alpha]_{546} = -188°$), formed by hydrolysis of the imine, **5**, once again supports the retention of optical purity of $\mathbf{1}^{\bullet+}$.

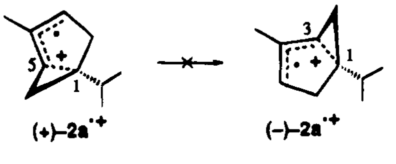
Rearrangement of α-Thujene Radical Cation. In view of the structure assigned to sabinene radical cation and considering the mechanism discussed for its rearrangement, we considered an analogous structure for the α-thujene radical cation, $\mathbf{2}^{\bullet+}$, and an analogous sigmatropic shift from the secondary to the quaternary cyclopropane carbon for its conversion to α-phellandrene (**7**). However, compared to the significant enantiomeric excess observed for **3**, the optical purity of **7** obtained from (1*S*,5*S*)-(+)-**2** is quite low (~9% ee) and the preferred enantiomer, (+)-**7**, is incompatible with a suprafacial shift from C_6 to C_1.

Scheme 1





The significant loss of optical purity could be explained either by a non-chiral radical cation intermediate, such as $\mathbf{2c}^{\bullet+}$, or by the (rapid) racemization of a chiral radical cation (+)-$\mathbf{2a}^{\bullet+}$ via the vinylcyclopropane rearrangement, followed by a (slower) sigmatropic shift from C_6 to C_1 analogous to that observed for $\mathbf{1a}^{\bullet+}$. However the experimental findings support neither possibility. The starting material recovered from this reaction ($[\alpha]_{546} = +32°$) shows essentially complete retention of chirality, eliminating both the nonchiral radical cation, $\mathbf{2c}^{\bullet+}$, and any significant involvement of the vinylcyclopropane rearrangement. The failure of $\mathbf{2}^{\bullet+}$ to undergo the valence isomerization may be related to the degenerate nature of the rearrangement and the absence of a significant driving force. Although it has long been recognized that many radical cation reactions have considerably lower barriers than do the corresponding reactions of their neutral diamagnetic precursors,[6,7e,32] it has also been noted that the potential energy surfaces of radical cationic systems may have significantly different topologies compared to those of their precursors. Accordingly, it is a distinct possibility that the vinylcyclopropane rearrangement of $\mathbf{2}^{\bullet+}$ is accelerated to a lesser extent than are several competing pathways.



Significantly, the residual optical activity of **7** is incompatible with a suprafacial hydride shift from C_6 to C_1, analogous to that established for $\mathbf{1a}^{\bullet+}$. The formation of (+)-**7** suggests retention at C_1, and not inversion, as observed in the rearrangement of **1** to **3**; this result would require an antarafacial shift to C_1, if the migrating hydrogen originated exclusively at C_6; this process does not appear very likely. An alternative mechanism compatible with the observed de facto racemization involves competing stereoselective processes in a chiral intermediate ($\mathbf{2a}^{\bullet+}$). Because C_2 is allylic, a homo-[1,5] sigmatropic shift

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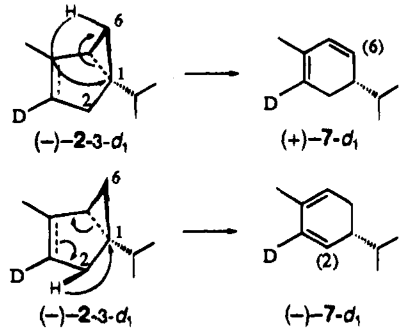
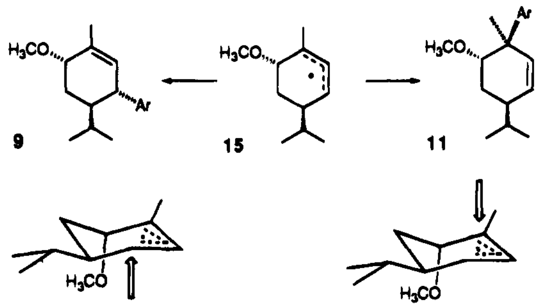
Scheme 2



Scheme 3

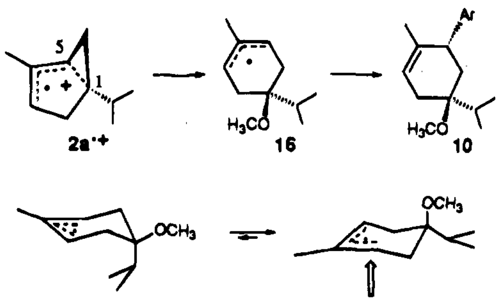


from C_2 to C_1 might compete with the migration from C_6 to C_1. We were able to demonstrate the feasibility of this process for an isotopically labeled derivative of **2**. A material labeled with D in the 3-position is readily available by $LiAlD_4$ reduction of (+)-thujone and dehydration of the resulting alcohol.[15] The electron transfer photochemistry of (−)-**2**-3-d_1 gave rise to (−)-**7**-d_1, with the label distributed between C_3 (5.46 ppm; 53%) and C_5 (5.78 ppm; 47%) in a ratio of 1.1:1. This finding is most readily explained by competing sigmatropic shifts: a [1,3] sigmatropic shift (from C_6 to C_1) gives rise to **7**-5-d_1, whereas a homo-[1,5] sigmatropic shift (from C_2 to C_1) generates **7**-3-d_1; the latter process is marginally favored. Since there is only a slight isotopic excess, the slight enantiomeric excess suggests a competition between two pathways, each of which might occur with a significant degree of stereoselectivity (Scheme 2).

The generation of the rearranged radical cation, $\mathbf{7}^{\bullet+}$, with some residual optical activity is also supported by two NOCAS products isolated from the reaction of **2** in the presence of methanol as a nucleophile. The adducts **9** and **11** can be rationalized by attack of methanol on $\mathbf{7}^{\bullet+}$ from the face opposite to the isopropyl group, generating an allylic free radical, **15**, with a slight enantiomeric excess. Both termini of the allylic moiety undergo aromatic substitution with the sensitizer derived radical anion. The substituents on the two faces of **15** direct the attack to the terminus farthest away from them; the methoxy group directs the attack to the less substituted terminus three bonds away (→ **9**), whereas the isopropyl moiety directs the attack to the more highly substituted terminus, also three bonds away (→ **11**; Scheme 3).

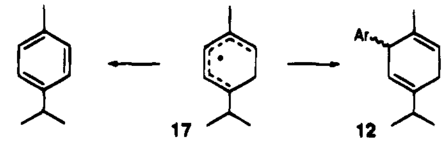
Competing Reactions of α-Thujene Radical Cation. The remaining products generated by the electron transfer reaction of **2** in the presence of methanol are of interest because they document two additional reactions competing with the sigmatropic shift, viz. nucleophilic capture and deprotonation of $\mathbf{2}^{\bullet+}$. Nucleophilic attack of methanol at C_1, generating the free radical **16**, is less prominent than in the case of $\mathbf{1a}^{\bullet+}$;[13] the subsequent aromatic substitution occurs in stereospecific fashion from the face bearing the isopropyl moiety. This observation can be explained based on considerations similar to those delineated for the analogous reaction of sabinene.[13] The free radical **16** is achiral and likely exists in two quasi-chair conformers with essentially planar allyl moieties and either the methoxy or the isopropyl group in a quasi-axial position. The conformer with the (bulkier) isopropyl group in a quasi-equatorial position is preferred; its quasi-axial methoxy group interferes with the approaching nucleophile, thus directing the attack to the opposite face (→ **10**; Scheme 4).

Scheme 4



Since the NOCAS products derived from the rearranged radical ion, $\mathbf{7}^{\bullet+}$, are formed in higher yields (57%) than the NOCAS product derived from $\mathbf{2}^{\bullet+}$ (26%), the sigmatropic shifts must compete more prominently with nucleophilic capture than in the case of $\mathbf{1a}^{\bullet+}$.[13]

The second reaction type competing with the intramolecular hydrogen shift is identified by products **8** and **12**. Deprotonation at either C_1 or C_6 would generate a delocalized free radical, **17**, which, in turn, may undergo aromatic substitution with the sensitizer derived radical anion (→ **12**) or lose a hydrogen atom with formation of an aromatic ring system (→ **8**). We have observed similar deprotonation reactions, once again followed by either aromatic substitution or aromatization in the electron transfer photochemistry of various bifunctional substrates. These reactions will be discussed in detail in a forthcoming publication.[30] Interestingly, product **12** is not observed when the photoreaction is carried out in pure acetonitrile. This finding suggests that methanol is involved in the deprotonation process, possibly as the base.



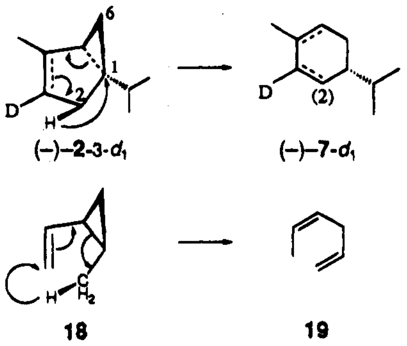
Conclusion

The electron transfer photochemistry of the vinylcyclopropane systems **1** and **2** proceeds via strain-releasing reactions of their radical cations. These rearrangements can be described as sigmatropic shifts with inversion of configuration at the carbon receiving the migrating H. For $\mathbf{1}^{\bullet+}$, the migrating H originates at the secondary cyclopropane carbon, C_6; in contrast, $\mathbf{2}^{\bullet+}$ undergoes competing H shifts from the allylic carbon, C_2, as well as from C_6. In competition with the sigmatropic reactions, the radical cation $\mathbf{2}^{\bullet+}$ is deprotonated, also with ring opening. Accordingly, the sigmatropic shifts are observed most readily with sensitizers whose radical anions are weak bases. In the presence of strongly basic radical anions the intramolecular H transfer would be defeated in favor of a "base"-induced deprotonation of the radical cation.

The sigmatropic reactions observed for the radical cations have no precedent in the thermal chemistry of the parent vinylcyclopropane systems. Although this finding may, at first glance, appear surprising, it does not come completely unexpected. It has long been recognized that many radical cation reactions have considerably lower barriers than do the corresponding reactions of their neutral diamagnetic precursors.[31] It has also been noted that the potential energy surfaces of radical cationic systems may have significantly different topologies compared to those of their precursors. For example, the free energy differences, ΔE, between corresponding pairs of minima may be substantially changed, even inverted.[33] Furthermore, the geometries of energy minima may be dramatically changed; in fact, several systems are known for which the radical cation potential surfaces have energy minima, whose geometries correspond to saddle points on the potential surfaces of the parent molecules.[34−37] In view of these observations, it was to be expected that the reactivity pattern of a radical cation may differ substantially from that of its diamagnetic precursor. The vinylcyclopropane derivatives discussed here appear to be excellent examples for systems in which the neutral diamagnetic precursors and the radical cations react by divergent pathways.

Thermal rearrangements of appropriate vinylcyclopropane derivatives include the valence isomerization to cyclopentene systems, including the degenerate rearrangement of **2**,[14,15] as well as homo-[1,5] sigmatropic shifts.[38] In contrast, the radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ fail to undergo the vinylcyclopropane rearrangement, even though $\mathbf{2}^{\bullet+}$ has the appropriate stereochemistry. Furthermore, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ utilize sigmatropic shifts without precedent in neutral diamagnetic parent systems. Although the rearrangement of (−)-**2**-3-d_1 to (−)-**7**-3-d_1 proceeds as a homo-[1,5] sigmatropic shift, as does the prototypical example, **18** → **19**, closer inspection (Scheme 5) reveals that the two systems utilize entirely different pathways. Also, no homo-[1,5] sigmatropic shift was found in the thermal reorganization of **2**, which has been studied in significant detail.[14,15]

Scheme 5



The recognition that radical cations and their neutral diamagnetic precursors may undergo significantly divergent reactions, even in their intramolecular rearrangements, is an interesting observation; we do not expect this to be limited to the species studied here. Additional substrates which may provide examples of sigmatropic shifts in radical cations are under investigation.

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Supporting Information Available: Tables of NMR spectral assignments and MS data for products **4**−**6** and **9**−**12** (7 pages). This material is available in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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