Electron Transfer Photochemistry of Sabinene—Nucleophilic Capture of a Stereorigid Vinylcyclopropane Radical Cation

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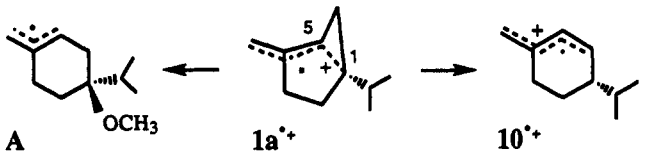
Received August 23, 1993. Revised Manuscript Received May 27, 1994®

Abstract: The electron transfer photoreaction of (1*R*,5*R*)-(+)-sabinene (**1**) with 1,4-dicyanobenzene and phenanthrene in acetonitrile/methanol gives rise to various optically active ring opened products. The stereochemical relationship between **1** and the products requires that the key intermediate retain the three-dimensional integrity of **1**. The results are rationalized via a radical cation, **1a**$^{\bullet+}$, in which a significant degree of bonding between C_1 and C_5 has been maintained; a ring-opened radical cation, in which C_1 would be planar, is clearly eliminated. **1a**$^{\bullet+}$ reacts primarily by nucleophilic capture of methanol at the quaternary carbon, generating radical **A** in regiospecific and stereoselective fashion. In addition, a hydride shift from C_6 to C_1 produces the β-phellandrene radical cation **10**$^{\bullet+}$, which is in turn captured by the nucleophile, also with a high degree of regioselectivity.

Introduction

The structures and reactions of organic radical cations have been the focus of much interest for the past decade.[1] In particular, the homoconjugative interactions of strained ring moieties with olefinic fragments have been probed to delineate changes in the molecular geometry upon oxidation and to assess the spin and charge density distributions in the resulting radical cations.[2] Among the reactions of these species, various rearrangements of the carbon skeleton have been reported, many of them resulting in the release of ring strain;[3] in some systems, ring opening is assisted by a nucleophile.[4] The simplest species containing both an olefinic moiety and a cyclopropane ring, the vinylcyclopropane radical cation, has not been characterized adequately, although several studies have been carried out. For example, a gas phase study of the reactivity of vinylcyclopropane molecular ion found characteristic changes in the mass spectrum of the product ion(s) as a function of the mode of ionization;[5] these were interpreted as evidence for a ring opening reaction, yielding the penta-1,3-diene radical cation. Of course, this type of chemistry is hardly expected in solution. In a theoretical approach, an STO-3G calculation of the vinylcyclopropane radical cation was carried out as a model for tricyclo[5.3.1.0^{1,7}]undeca-2,4,9-triene. In order to facilitate the calculations, a seriously restricted geometry was assumed, with the vinyl group and two cyclopropane carbons held coplanar.[6] Recently, the radical cations of bicyclo[3.1.0]-hex-3-ene and two bicyclo[4.1.0]hept-3-enes, containing *syn*-vinylcyclopropane systems, were characterized by CIDNP experiments.[7] Finally, several *p*-anisyl derivatives were found to undergo electron transfer induced vinylcyclopropane rearrangements.[3h,i] However, the corresponding radical cations probably are more appropriate models for divinyl- than for vinylcyclopropane radical cation.

In order to gain a more complete understanding of the radical cations derived from vinylcyclopropane systems, we have investigated the electron transfer induced photochemistry of a simple vinylcyclopropane system, in which the two functionalities are locked in the *anti* configuration, viz., 4-methylene-1-isopropylbicyclo[3.1.0]hexane (sabinene, **1**).



The product distribution and their stereochemistry elucidate various facets of the mechanism and reveal details of the reactivity and structure of the vinylcyclopropane radical cation, **1**$^{\bullet+}$. The results probe the significance of such factors as orbital overlap and charge stabilization factors in the radical cation,[4f] the regio- and stereochemistry of the nucleophilic attack on **1**$^{\bullet+}$, and the release of ring strain and the delocalization of spin density in the nucleophilic capture leading to **A**. The previously suggested greatly diminished steric hindrance in the transition state for a nucleophilic substitution on a cyclopropane radical cation[4e,g] is confirmed.

• Abstract published in *Advance ACS Abstracts*, July 1, 1994.

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Experimental Section

Materials and Solvents. (1*R*,5*R*)-(+)-Sabinene ($[\alpha]_D$ = +107°) (Fluka; puriss) was used as received. Phenanthrene (Aldrich; 98%) and 1,4-dicyanobenzene (Aldrich; 98%) were purified by recrystallization. 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.

Photosensitized Electron Transfer Reactions. Reaction mixtures, containing 0.1 M of sabinene, 0.1 M of 1,4-dicyanobenzene, and 0.02 M of phenanthrene in acetonitrile/methanol (3/1 by volume), were deoxygenated by purging with argon for 15 min and irradiated in a Rayonet RPR-100 photoreactor equipped with 16 RPR-3500 lamps. The progress of the reaction was monitored by gas chromatography on a GC/MS system (HP 5890 series II GC interfaced with an HP 5971 mass selective detector), using a 12 m × 0.2 mm × 0.33 μm HP-1 capillary column (cross-linked methyl silicone on fused silica). Analytical runs were carried out in 4-mm ID NMR tubes stoppered with latex stoppers, preparative runs in 30-mm ID tubes with central cooling fingers; the reaction mixtures were water-cooled.

Isolation of Products. Reaction products formed in yields > ~4% were isolated by a series of column chromatographic procedures, carried out using a set of 50-cm columns with IDs ranging from 1–5 cm, 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.

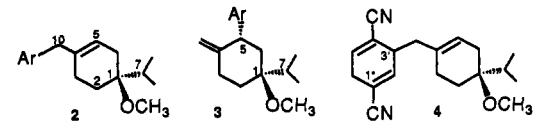
Characterization of Products. Structure assignments of isolated products are based on MS and NMR data. Proton NMR spectra were recorded on either a Varian XL-400 or a Varian VXR-200 spectrometer. ^{13}C and HETCOR spectra were recorded on a Varian VXR-200 spectrometer operating at 50.3 MHz. Optical rotations were measured on a Perkin-Elmer 141 polarimeter at room temperature. Typically, samples were measured at concentrations of 10–20 mg/mL in $CHCl_3$. Some samples were measured at lower concentrations in $CDCl_3$, prior to recording their NMR spectra.

Results

Irradiation of acetonitrile/methanol (3:1) solutions containing 0.1 M 1,4-dicyanobenzene (DCB), 20 mM phenanthrene (Ph), and 0.1 M of optically pure (1*R*,5*R*)-(+)-sabinene (**1**; $[\alpha]_D$ = +107°) gave rise to products of several different structure types. Five adducts each bear a methoxy and a cyanophenyl group: **2** (26%; $[\alpha]_D$ = +62°); **3** (9%; $[\alpha]_D$ = −25°); **5** ($[\alpha]_D$ = −86°); **6** ($[\alpha]_D$ = +30°); **5** + **6** (15%); and **7** (4%). One adduct, **4** ($[\alpha]_D$ = +45°), is substituted by a methoxy and a dicyanocyclohexadienyl group. Finally, a dimeric dimethoxy compound, **8** ($[\alpha]_D$ = +33°), is formed (the combined yields of products **4** + **8** is 7%) as well as a product, **9** (7%), consisting of two molecules of sabinene plus one molecule of methanol. Only combined yields were determined for products **4** + **8** and **5** + **6**. Products **7** and **9** were not isolated in sufficient quantities to measure their rotation.

The structural assignments rest on 1D ^1H, 2D COSY, and ^{13}C–^1H HETCOR, where appropriate. Extensive NOE difference spectra were taken to elucidate substituent stereochemistry and spatial relation between different groups and to confirm the structure. The spectral features allowing the assignment of the key products are briefly discussed below. In this description, products **2**–**7** are identified by their proper IUPAC names. However, for the reason of uniformity and for internal consistency all spectral data are labeled according to the terpene nomenclature convention for sabinene: the quaternary center is C_1, the external double bond occupies the 4-position, and the *exo*-methylene carbon is C_{10}.

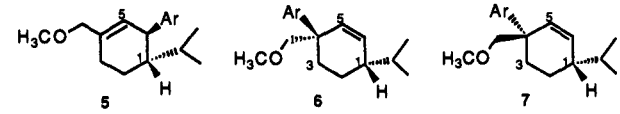
The major product, 1-(*p*-cyanobenzyl)-4-isopropyl-4-methoxycyclohexene (**2**), is characterized by a single olefinic resonance (H_5, 5.38 ppm) and the two allylic, benzylic signals (H_{10}, 3.32 and 3.35 ppm). Since H_7 appears as a pure septet, either the methoxy group or the aryl function must be attached to C_4. NOE experiments establish the proximity of the methoxy group to H_7 and H_{2eq} and of the aryl group to the allylic, benzylic signals (H_{10}).



The structure of *trans*-3-(*p*-cyanophenyl)-1-isopropyl-4-methylenecyclohexane (**3**) follows from two terminal olefinic protons (at 4.72 and 3.78 ppm, respectively). The unusual chemical shift of the latter is ascribed to pronounced shielding by the aryl group, establishing its presence near the *exo*-methylene function (at C_5). Since H_7 appears as a pure septet, the methoxy group must be attached to C_1. The steric relationship between the methoxy group and the aryl function follows from NOE experiments: the benzylic proton (H_{5ax}) interacts with the methoxy group, whereas the aryl function interacts with H_{6ax}.

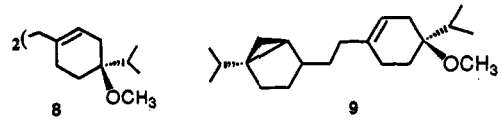
The spectrum of 1,4-dicyano-3-(4-isopropyl-4-methoxycyclohexenyl)methylcyclohexa-1,4-diene (**4**) is similar in the essential features to that of **2**, except that the aryl resonances of **2** (7.29 and 7.56 ppm, respectively) are replaced by two olefinic (6.56 and 6.61 ppm) and two doubly allylic resonances (3.2 ppm, 1H; 3.06 ppm, 2H). Essentially all resonances of the cyclohexadienyl function are doubled, suggesting that the isolated material apparently is a mixture of diastereomers, most likely differing in the configuration at $C_{3'}$.

trans-3-*p*-Cyanophenyl-4-isopropyl-1-methoxymethylcyclohexene (**5**) is characterized by a single olefinic resonance (H_5; 5.48 ppm) and its connectivity established through a 2D-COSY experiment. The position of the methoxy group on the side chain follows from an NOE experiment; similar experiments established a cis relationship between the aryl function and H_1.



cis- and *trans*-3-(*p*-Cyanophenyl)-6-isopropyl-3-methoxymethylcyclohexene (**6** and **7**, respectively) have two olefinic protons each and bear one allylic proton at C_1. The two isomers are differentiated by their NOE behavior; irradiating the aryl resonance of **6** causes a weak enhancement for H_{3ax}, whereas the identical treatment of **7** results in an enhancement of H_{3eq}.

Product **8** shows a weak molecular ion peak at *m/z* 334, corresponding to the composition of intermediate **A**, but to twice the molecular weight ($C_{22}H_{38}O_2$). The ^{13}C NMR spectrum shows only 11 signals, suggesting a symmetrical (dimeric) structure for the product. Characteristic peaks include two olefinic signals at 137.8 and 117.5 ppm as well as two alkoxy carbon signals at 76.5 (quaternary) and 48.1 ppm (methoxy), respectively. The ^1H NMR spectrum confirms the symmetrical nature of the product; it shows only one olefinic signal (2 H) at 5.3 ppm, one methoxy signal (6 H) at 3.2 ppm, and two doublets (6 H each), at 0.87 and 0.89 ppm, for the diastereotopic methyl groups of two equivalent isopropyl functions. The isopropyl methine resonance can be recognized at 1.98 ppm, overlapping with a group of unresolved allylic signals between 1.8 and 2.1 ppm (14 H).



Product **9** shows a molecular ion peak at *m/z* 304, $C_{21}H_{34}O$, corresponding to a monomethanol adduct of what is, formally, a sabinene dimer. The ^1H NMR spectrum shows one olefinic signal (5.4 ppm; 1 H), one methoxy signal (3.2 ppm; 3 H), and four doublets, representing two pairs of diastereotopic methyl groups (two nonequivalent isopropyl groups; 0.86, 0.87, 0.89,

and 0.96 ppm; 12 H). The 2D COSY spectrum shows strong crosspeaks between two doublets of doublets (0.15 and 0.38 ppm; 1 H each) and with a third resonance at 1.2 ppm. This combination is characteristic for a trisubstituted cyclopropane ring quite similar to that of the starting material, sabinene.

Discussion

Photoinduced Electron Transfer Reactions. When electron acceptors/sensitizer–cosensitizer systems (e.g., 1,4-dicyanobenzene–phenanthrene) are irradiated in the presence of suitable donors (D) and nucleophiles (CN^-, CH_3OH), electron transfer reactions may ensue, resulting either in simple addition products[8] or giving rise to more complex products. Under these general reaction conditions, a well established photochemical reaction sequence occurs,[4a–c,9] initiated by photoinduced generation of the radical cation ($D^{\bullet+}$) and the sensitizer radical anion ($DCB^{\bullet-}$; eq 1), followed by capture of $D^{\bullet+}$ by the nucleophile (eq 2). The resulting free radical(s) can add to the sensitizer or couple with the sensitizer radical anion (eq 3). For olefinic substrates, the reaction has been termed "photo-induced nucleophile-olefin-combination-aromatic-substitution (photo-NOCAS)".[9]

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

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

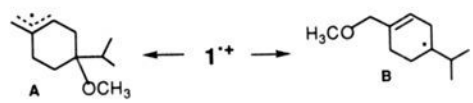
$$[\mathrm{D\text{-}OCH_3}]^{\bullet} + \mathrm{DCB}^{\bullet-} \rightarrow p\text{-}\mathrm{CN\text{-}C_6H_4\text{-}D\text{-}OCH_3} + \mathrm{CN}^- \quad (3)$$

This paper is concerned mainly with the relationship between the structures of sabinene, **1**, its radical cation, $\mathbf{1}^{\bullet+}$, and the free radicals generated by nucleophilic attack on $\mathbf{1}^{\bullet+}$. Accordingly, there appears to be no need to delineate the mechanism in any more detail. However, some facets particular to the electron transfer chemistry of **1** will emerge from the subsequent discussion.

The Electron Transfer Photochemistry of Sabinene. The various products resulting from the electron transfer photochemistry of sabinene provide mechanistic information on several levels: the nature of the products will identify the principal reaction types; the product distribution will establish the regiochemistry of the primary attack; finally, their stereochemistry will reveal stereochemical details of the initial attack.

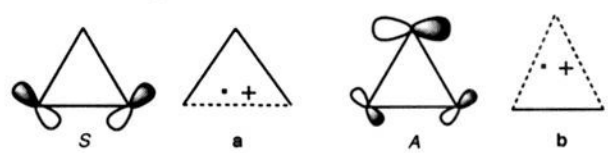
All reaction products resulting from the electron transfer photochemistry of sabinene have in common that they contain the methoxy group. Apparently, nucleophilic capture is the most significant reaction of the intermediate radical cation. The relative abundance of the products derived from attack at the competing sites reveal the regioselectivity of nucleophilic capture. The structures of the isolated reaction products, **2-9**, identify two principal sites of nucleophilic attack, the quaternary carbon (C_1) and the *exo*-methylene center. Any substitution at the tertiary and secondary cyclopropane carbons, C_5 and C_6, respectively, is limited to <5% of the overall reaction and, thus, is insignificant. The possibility of an attack at other centers was raised in connection with the electron transfer induced nucleophilic ring opening of several 1-phenyl- and 1,1-diphenyl-2-alkyl-substituted cyclopropanes.[4e–g] In these systems, nucleophilic attack occurred with a high degree of regioselectivity at C-2; no evidence for attack at C-3 (or C-1) was observed.

The main adduct, **2**, and four lesser products, **3**, **4**, **8**, and **9**, can be explained by nucleophilic attack at C_1, whereas the three adducts **5–7** are, at least formally, products of nucleophilic attack on the *exo*-methylene center in an apparent S_N2' reaction. Attack at the quaternary carbon would generate the free radical (**A**), whereas capture at the *exo*-methylene carbon is tentatively formulated as giving rise to **B**. The attack at C_1 accounts for ~50% of the products and, thus, predominates ~2.5:1 over attack at C_{10}, which accounts for ~20% of the products. These data suggest that nucleophilic attack on the sabinene radical cation occurs with a pronounced degree of regioselectivity.

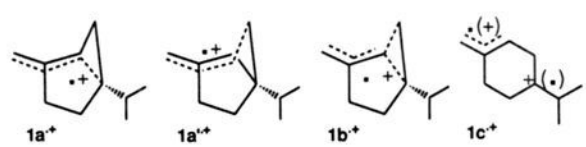


Potential Structures of Vinylcyclopropane Radical Cations. Having established the significance of nucleophilic capture and a degree of regioselectivity for this process, we consider the detailed stereochemistry of the products in an attempt to unravel the structural features of the sabinene radical cation as well as the stereochemical course of the primary attack. The key feature characterizing the structure of a cyclopropane radical cation in general, or of $\mathbf{1}^{\bullet+}$, in particular, lies in the distortion of the cyclopropane ring for optimal interaction with the substituents and in the distribution of spin and charge.

Two different structure types can be envisioned for the cyclopropane fragment of such a radical cation, either a "trimethylene" structure ($^2A_1$; **a**) derived from a symmetrical molecular orbital (as in *S*) or a "π-complex" ($^2B_2$; **b**) derived from an antisymmetrical molecular orbital (as in *A*).[1e,f,2a,b] The actual structure is determined by the substitution pattern; the (*exo*-methylene)bicyclo[3.1.0]hexane discussed here is a 1,1,2-trisubstituted cyclopropane; precedent[10,11] and ab initio molecular orbital calculations[12d] suggest that this substitution pattern may favor a "trimethylene" structure, $\mathbf{1a}^{\bullet+}$.



On the other hand, the radical cation of bicyclo[3.1.0]hex-3-ene favors a "trimethylene" structure with participation of the less highly substituted cyclopropane bond,[7] whereas benzobicyclo-[3.1.0]hexene was attacked at C_5 and C_6.[4f] Both results have been ascribed to better orbital overlap.[4f,7] If similar factors apply to **1**, one might expect structure $\mathbf{1a'}^{\bullet+}$ to be favored. Ring-opened trimethylene radical cations (e.g., $\mathbf{1c}^{\bullet+}$) have been discussed for some di-, tri-, and tetramethyl derivatives.[11c,d] However, this assignment has been challenged on the basis of ab initio calculations[12a–c] and other arguments.[12a] These structures would have the advantage of minimized strain, albeit at the expense of the delocalization of spin and charge.



Nucleophilic Attack at the Quaternary Carbon. The stereochemistry of products **2–4**, **8**, and **9** is incompatible with one of the radical cation structures. Nucleophilic attack at the quaternary carbon (C_1) of either $\mathbf{1a}^{\bullet+}$ or $\mathbf{1c}^{\bullet+}$ may generate the free radical, **A**, differing only in its optical activity. While attack on $\mathbf{1c}^{\bullet+}$ must be expected to generate a racemic mixture, the

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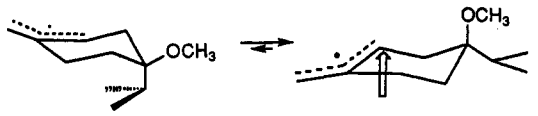
corresponding reaction of $1a^{\bullet+}$ may be envisaged as generating an enantiomerically enriched, or even pure, free radical, **A**. Since all products derived by attack at C_1 have retained significant optical activity (**2**, $[\alpha]_D = +62°$; **3**, $[\alpha]_D = -25°$; **4**, $[\alpha]_D = +45°$; **8**, $[\alpha]_D = +33°$; **9** was not isolated in sufficient quantity to measure its rotation), the radical cation must have retained the three-dimensional integrity of the substrate. These results suggest that the nucleophilic attack on C_1 is stereoselective and that the chiral species ($1a^{\bullet+}$) is a more prominent contributor to the radical cation structure than $1c^{\bullet+}$. Although the absolute stereochemistry of the major products has not been established, we assume that the reaction at C_1 occurs as a backside attack with inversion of configuration. The nucleophilic substitution of $1^{\bullet+}$ is analogous to the recent nucleophilic capture of a cyclopropane derivative, which was also explained via backside attack.[4g] We also note that the enantiomeric excess of products **2–4**, **8**, and **9** is not yet known; thus, the degree of stereoselectivity must await further studies.

All available evidence suggests that products **2–4**, **8**, and **9** are derived from free radical, **A**; the structures of these products also allow a more detailed description of the reaction pathway. Attack at the ipso carbon of the sensitizer (or its anion) with net loss of CN^- (e.g., eq 3) can form the NOCAS products **2** and **3**, containing one molecule each of the substrate, the nucleophile (methanol), and the electron acceptor (DCB) minus the elements of HCN. The failure to observe the diastereomer of **3** is interesting, since the allyl function of **A** appears to be essentially planar. We explain the selective formation of diastereomer **3** on the basis of conformational arguments. The two likely conformers of **A** should have an essentially planar allyl moiety, whereas the six-membered ring should exist in two quasi-chair conformers with either the isopropyl or the methoxy group in the quasi-axial position. The conformer with the (bulkier) isopropyl group in a quasi-equatorial position is clearly preferred. While access to the terminal allylic carbon (which leads to product **2**) appears to be unhindered, the quasi-axial substituent at the chiral carbon will interfere with the attack on the internal allylic center, thereby directing the attack to the face opposite to the quasi-axial methoxy function, generating **3**. These considerations account qualitatively for the 3:1 preference of **2** over **3** as well as for the suppression of the latter's diastereomer.



A related adduct, **4**, contains a (2,5-dicyanocyclohexa-2,5-dien-1-yl) function at C_{10} in addition to the methoxy function at C_1. This type of product has been reported less frequently than the NOCAS type; we have isolated only one related adduct in the electron transfer photoreaction of 7-methylenequadricyclane.[13] Product **4** can be explained via an attack of **A** at the ortho position of either the sensitizer or its radical anion. The approach of the free radical, **A**, to the ortho position should be subject to the same considerations as the attack on the ipso carbon of the sensitizer, namely, coupling at the *exo*-methylene carbon (C_{10}) and at C_3 should occur in a ratio similar to that established for products **2** and **3**. Therefore, we expect the cyclohexadienyl analog of **3** to be formed in $\sim 1/3$ the yield of **4**, i.e., in <2% yield. On the other hand, the lower symmetry of the cyclohexadienyl function compared to the *p*-cyanophenyl group leads us to expect the formation of diastereomers, having the same absolute configuration at C_1 but differing in their configuration at $C_{3'}$. The existence of diastereomers is indeed suggested by the NMR data.

The free radical dimer (**8**) and the radical addition product (**9**) also can be rationalized by reaction of **A** at the more easily accessible centers. The formation of these products shows that the aromatic substitution and addition reactions of **A** cannot be highly efficient. Analogs of **8** and **9** due to coupling at the more crowded site (C_5) are expected in lower yields, as discussed above for **4** and its analog.

Nucleophilic Attack on the *exo*-Methylene Function. In the preceding sections, we have discussed three aspects of our results: the products support nucleophilic capture as the most significant reaction of the electron transfer photochemistry of **1**; the product distribution identifies the primary attack as regioselective; and the optical activity of products **2–4**, **8**, and **9** documents stereoselective attack at the asymmetric carbon, C_1. The tentatively assigned degree of regioselectivity was based on the assumption that products **5–7** were due to nucleophilic capture at C_{10} via an S_N2' mechanism. A more detailed examination of products **5–7**, however, reveals two facts that are incompatible with this assumption and, specifically, with the involvement of **B**. First, products **5–7** show a significant degree of optical activity, whereas nucleophilic attack at C_{10} would generate racemic products. Second, the aryl substituents are attached in positions that do not bear spin density in either **B** or its cyclopropylcarbinyl isomer (**C**).

Free radical reactions of **B** should occur at C_1, whereas **C** should react at C_1 or C_4. In fact, however, the aryl groups are found at C_4 and C_6, suggesting an allylic free radical (**E**) as the most likely intermediate. Since this species is formed with significant retention of optical activity, it must be formed by a stereoselective cyclopropane to propene rearrangement of either $1^{\bullet+}$ or **C**.

The detailed discussion of this interesting conversion goes beyond the scope of the present paper; it will be presented elsewhere. We note, however, that (+)-**1** is converted to (+)-β-phellandrene (**10**) in the absence of methanol; furthermore, the electron transfer photochemistry of (+)-**10** gives rise to products **5–7** in the same ratio as formed from **1**.[14] These findings suggest that $1^{\bullet+}$ suffers ring opening with a hydride shift, generating $10^{\bullet+}$ which, in turn, reacts by nucleophilic capture, producing **E**. Accordingly, radical cation $1^{\bullet+}$ undergoes two reactions, bimolecular nucleophilic capture, giving rise to free radical **A**, in competition with the unimolecular hydride shift, generating radical cation $10^{\bullet+}$. In the light of this competition the modest regioselectivity derived from the product ratio (**2** + **3** + **4** + **8** + **9**)/(**5** + **6** + **7**) has to be revised: the nucleophilic capture of $1^{\bullet+}$ occurs exclusively at the quaternary center (C_1), i.e., it is regiospecific. Significantly, the nucleophilic capture of $10^{\bullet+}$ also is regiospecific; it occurs exclusively at the terminal olefinic position.

Factors Determining Radical Cation Reactivity. The previous sections have given a detailed description of the products derived

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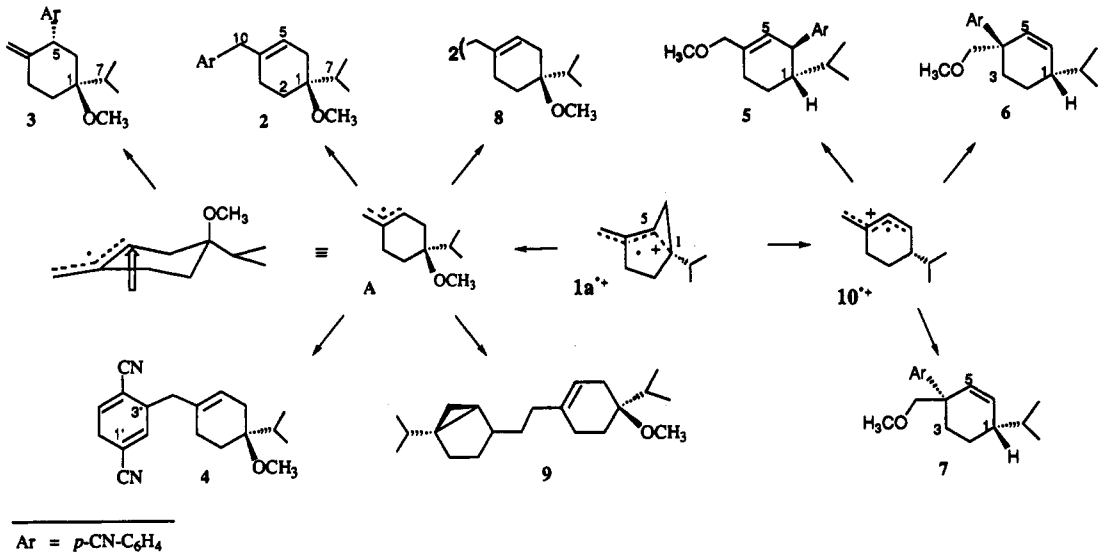
(12) (a) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1983**, *61*, 2310–2315. (b) Wayner, D. D. M.; Boyd, R. J.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 3283–3289. (c) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 3405–3412. (d) Krogh-Jespersen, K.; Roth, H. D. *J. Am. Chem. Soc.* **1992**, *114*, 8388–8394.

(13) Weng, H.; Du, X.-M.; Roth, H. D. *J. Am. Chem. Soc.*, submitted for publication.

(14) Weng, H.; Roth, H. D. *J. Am. Chem. Soc.*, submitted for publication.

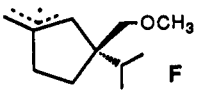
Scheme 1



from $1^{\bullet+}$. Can these results provide the basis for deriving some general principles of radical cation reactivity? It has long been recognized that the course of any reaction is dictated by the most favorable transition state (TS). Hammond recognized, in addition, that the structure of a TS may lie closer to the educt (early TS) or to the product (late TS).[15] Accordingly, factors that stabilize either educt or product may contribute to the stability of the TS. In the special case of radical cations, it has been shown that the reaction barriers may be significantly reduced.[3i,16] We suggest that the TSs of these reactions may reflect favorable (stabilizing) aspects of both educts and products.

The reactions discussed so far allow us to evaluate three factors affecting radical cation reactivity: (1) release of ring strain, (2) conjugation and optimal delocalization of spin and charge, and (3) steric factors. Both the nucleophilic capture (→ **A**) and the hydride shift (→ $\mathbf{10}^{\bullet+}$) fully release the ring strain present in $\mathbf{1}^{\bullet+}$ and lead to delocalized conjugated systems. On the other hand, $\mathbf{1}^{\bullet+}$ is attacked in the most hindered position, whereas $\mathbf{10}^{\bullet+}$ is attacked in the most easily accessible position. Obviously, in the formation of **A**, the relief of ring strain is more important than the steric hindrance in the TS.

However, the three factors delineated above fail to account for one significant detail: the complete absence of products due to nucleophilic capture of $\mathbf{1}^{\bullet+}$ at the secondary cyclopropane position, C_6. The generation of free radical **F** by this attack appears exceptionally favorable, as it would occur with release of ring strain, with formation of a conjugated π system, and with minimal steric hindrance. In order to explain the absence of any product derived via **F**, an additional enabling principle is required. The only element that may be missing from the TS for the formation of **F** is the presence of spin and charge in the C–C bond to be replaced. The significance of charge stabilization factors as well as orbital overlap have been discussed previously, specifically to explain nucleophilic attack at C_5 as well as C_6 of the radical cation of benzobicyclo[3.1.0]hex-2-ene[4f] and, more recently, to explain the structure assigned to the radical cation of bicyclo-[3.1.0]hex-2-ene.[7] Accordingly, we add the distribution of spin and charge in the radical cation as a fourth significant factor determining the reactivity of radical cations.



If the distribution of spin and charge is, indeed, essential for the nucleophilic attack, then the absence of products derived from **F** must indicate that its precursor, $\mathbf{1}^{\bullet+}$, does not have spin or charge on C_6. In the light of these considerations, we propose a more complete description of the sabinene radical cation. Earlier, we had eliminated structure $\mathbf{1c}^{\bullet+}$, because the products derived from **A** are optically active. We now eliminate both $\mathbf{1a}'^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$, because the observed reactivity does not support charge density at C_6, leaving structure $\mathbf{1a}^{\bullet+}$ as the most appropriate depiction of the sabinene radical cation. This assignment follows from the regiospecificity and stereoselectivity of the nucleophilic capture which, in turn, is based on the structure and stereochemistry of the products.

Conclusion

A detailed analysis of the products formed in the electron transfer photochemistry of sabinene has led to the assignment that nucleophilic capture of $\mathbf{1a}^{\bullet+}$ is regiospecific and stereoselective. Four factors have been identified as significant contributors in shaping radical cation reactivity: release of ring strain, optimal delocalization, steric factors, and the distribution of spin and charge in the intermediate. Work is in progress to further delineate these principles. We are also seeking to confirm the structure assignment to $\mathbf{1}^{\bullet+}$ by CIDNP experiments and ab initio calculations.

Acknowledgment. Support of this work by the National Science Foundation through Grant NSF CHE-9110487 and an equipment Grant NSF CHE-9107839 is gratefully acknowledged. The work of VS was supported by an NSF undergraduate equipment grant, NSF USE-9250530, for the purchase of a 200 MHz FT NMR spectrometer.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectral assignments, including 1D NOE and 2D COSY data for products **2–9** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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