Triphenylpyrylium Tetrafluoroborate-Sensitized Photochemistry of the Terpenes Sabinene, α-Phellandrene, and α- and γ-Terpinene

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The triphenypyrylium tetrafluoroborate (TPT)-sensitized reactions of several terpene donor molecules, including sabinene (**1**), α-phellandrene (**4**), α-terpinene (**5**) and γ-terpinene (**6**) give rise to significantly different products than reactions induced by other electron-transfer sensitizers, such as 1,4-dicyanobenzene (DCB). The divergent reactions require decidedly different key intermediates; the products obtained with TPT can be explained by dissociative recombination of the intermediate radical–radical cation pair in the triplet state, generating donor-derived biradicals.

Introduction

The structures and reactions of organic radical cations have attracted much interest for over two decades.[1–10] The structures of these species have been probed by physical and chemical techniques.[1–8] Their reactions have also attracted considerable attention.[9–15] As intermediates with both an unpaired spin and a positive charge, radical cations can undergo a variety of reactions characteristic of either free radicals or carbocations. Bimolecular reactions, such as additions to alkenes[12,13] and the nucleophilic capture by alcohols[14,15] lead to C–C and C–O bond formation, respectively. Among unimolecular reactions, geometric isomerizations[16,17] and several molecular rearrangements,[18–20] including sigmatropic shifts,[21,22] have been studied.

The electron transfer photoreactions of terpenes have provided interesting results. The radical cations of strained-ring terpenes were generated with 1,4-dicyanobenzene/phenanthrene as sensitizer/co-sensitizer in the presence of 5 M methanol as nucleophile. Under these conditions the radical cations are scavenged by methanol and the resulting methoxy-substituted free radicals form simple methanol adducts,[14,15] or more complex products by aromatic substitution at the *ipso*-carbon of the sensitizer radical anion.[23–25] Details of the reaction sequence leading to the three-component products are particularly well-established for olefins; this reaction is known as the photo-NOCAS reaction (for "photo-induced **n**ucleophile-**o**lefin-**c**ombination-**a**romatic-**s**ubstitution").[24,25] The terpenes studied under these conditions include cyclopropane derivatives (tricyclane),[26] vinylcyclopropane systems [sabinene (**1**),[27] α- (**2**) and β-thujene,[28] 2-carene],[29] and vinylcyclobutane species (α- and β-pinene).[25,26,30] In a few cases, the intramolecular capture of terpene radical cations by tethered nucleophiles (OH functions) was probed. For example, intramolecular capture was observed for the radical cations of chrysanthemol,[31] homo-chrysanthemol,[32] and geraniol (**8**).[33]

The reaction of terpene radical cations in the absence of nucleophiles has been studied to a lesser extent. Unimolecular reactions were observed for the radical cations of sabinene, $\mathbf{1}^{\bullet+}$, and α-thujene, $\mathbf{2}^{\bullet+}$, which undergo sigmatropic shifts to generate the radical cations of β- and α-phellandrene, **3** and **4**, respectively.[22] The radical cations of α- and β-pinene were deprotonated by the sensitizer radical anion (tetrachlorosemiquinone); β-pinene was converted into α-pinene, whereas α-pinene was dehydrogenated with formation of verbenene.[30]

We have carried out a detailed study of the electron-transfer photosensitized reactions of terpenes with triphenylpyrylium tetrafluoroborate (TPT) as sensitizer in dichloromethane. The use of this sensitizer has the advantage that the resulting donor-radical cation is paired with a neutral radical; the absence of Coulomb forces causes significantly increased radical cation yields.[34] In this paper we report results obtained in the TPT-sensitized photochemistry of sabinene (**1**), and of the products generated in this reaction, α-phellandrene (**4**) and α- (**5**) and γ-terpinene (**6**).

Results

Irradiation of triphenylpyrylium tetrafluoroborate (TPT) in the presence of sabinene (**1**), yielded 35% α-terpinene (**5**), 40% γ-terpinene (**6**), and 2% α-phellandrene (**4**), in addition to 20% *p*-cymene (**7**). Under similar conditions, the photoreaction with α-phellandrene gave rise to 40% α-terpinene and 30% *p*-cymene. Finally, the photo-sensitized reaction of α-terpinene or γ-terpinene yielded mostly *p*-cymene. These conversions are summarized in Scheme 1.

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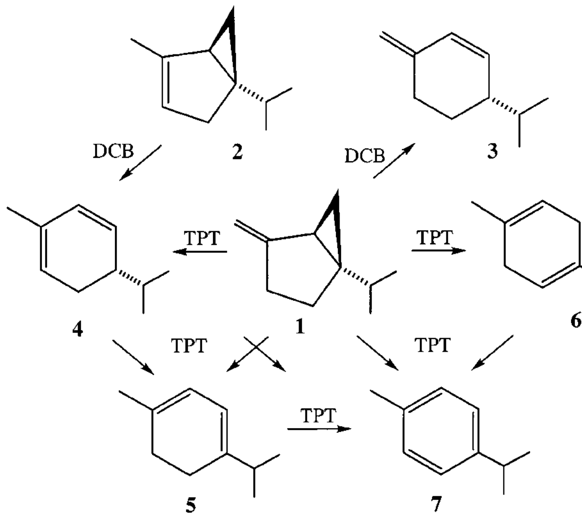


Scheme 1. Photochemical conversions of selected terpenes

Discussion

The course of the TPT-sensitized reaction of sabinene in dichloromethane is clearly different from that followed with 1,4-dicyanobenzene (DCB) in acetonitrile. This is shown most clearly by the fact that β-phellandrene (**3**), the main product formed with DCB as sensitizer,[27] is not observed at all in the TPT-sensitized reaction. The divergent course of the reactions induced by the two sensitizers can be explained only if they proceed via different key intermediates. The energetics of the electron-transfer reactions with the different sensitizers are possible factors determining the different outcome of the reactions.

The energetics of an electron transfer reaction provides a convenient measure for its feasibility. The free energies of radical ion pair generation were calculated according to a modified Weller Equation accounting for different solvent polarities,[35]

$$-\Delta G^0_{\text{gen}} = E_{(0,0)} - E^0_{(\text{D/D+})} + E^0_{(\text{A-/A})} - [2.6\ \text{eV}/\varepsilon - 0.13\ \text{eV}] \qquad (1)$$

where $E_{(0,0)}$ is the excitation energy of the photoexcited state initiating the electron transfer, $E^0_{(\text{D/D+})}$ and $E^0_{(\text{A-/A})}$ are the one-electron oxidation and reduction potentials of the donor and acceptor, respectively, measured in acetonitrile, and [2.6 eV/ε – 0.13 eV] is an empirical term correcting for changes in solvent polarity. According to this equation, the excitation energy of 1,4-dicyanobenzene (DCB) ($E_{0,0}$ = 4.3 eV)[36] and its reduction potential ($E^0_{(\text{A-/A})}$ = –1.60 V),[37] ensure efficient electron transfer from **1** to ^{1}DCB* in CH_3CN, ε = 37.5 (**1** is estimated to have an oxidation potential, 1.8 V > $E^0_{(\text{D/D+})}$ ≥ 1.4 V; the latter value is that of 2-carene).[29] A driving force, $-\Delta G_{\text{ET}} \geq 0.5$ eV, is typically sufficient to generate solvent separated radical ion pairs (SSRIP).

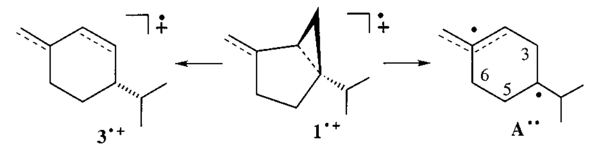
Concerning the TPT sensitized reactions in CH_2Cl_2 (ε = 9), the reduction potential ($E^0_{(\text{A-/A})}$ = –0.29 V vs SCE)[34] and excitation energy ($E_{0,0}$ = 2.8 eV)[34] of TPT indicate that the singlet state ($^*E^0_{(\text{A-/A})}$ = 2.5 V) should readily oxidize donors with oxidation potentials up to ≈ 2.3 V, sufficient for most unsaturated or strained-ring terpenes. On the other hand, the excited state reduction potential of the TPT triplet state (E_T = 2.2 eV; $^*E^0_{(\text{A-/A})}$ = 1.9 V)[34] may be too low for the oxidation of some terpenes. To preclude any potential problems, we chose donor concentrations to ensure essentially complete singlet quenching.

These considerations indicate that the radical cation $\mathbf{1}^{\bullet+}$ should be formed as the primary intermediate with DCB as well as TPT as sensitizer. Accordingly, the course of the reaction must diverge at a later stage. The conversion of radical cation $\mathbf{1}^{\bullet+}$ in acetonitrile was ascribed to a [1,3]-sigmatropic shift, generating β-phellandrene ($\mathbf{3}^{\bullet+}$); subsequent electron return from the sensitizer anion $\text{DCB}^{\bullet-}$ to the rearranged radical cation generates **3**. The nature of the reaction is firmly supported by the retention of absolute configuration at the center bearing the isopropyl group.

The sigmatropic shift can be essentially suppressed in the presence of 5 M methanol due to nucleophilic capture. In the TPT-sensitized reaction the sigmatropic shift must be suppressed by a different process not available to the radical pair, $\mathbf{1}^{\bullet+}$–$\text{DCB}^{\bullet-}$. We propose dissociative recombination of triplet radical ion pairs, $^3[\mathbf{1}^{\bullet+}\text{–TP}^{\bullet}]\cdot\text{T}^-$, yielding the allylic-tertiary biradical $\mathbf{A}^{\bullet\bullet}$, and ground-state TPT. Considering the free energies of the radical (ion) pairs formed from the two sensitizers,

$$-\Delta G^0_{\text{SSRP}} = -E^0_{(\text{D/D+})} + E^0_{(\text{A-/A})} - [2.6\ \text{eV}/\varepsilon - 0.13\ \text{eV}] \qquad (2)$$

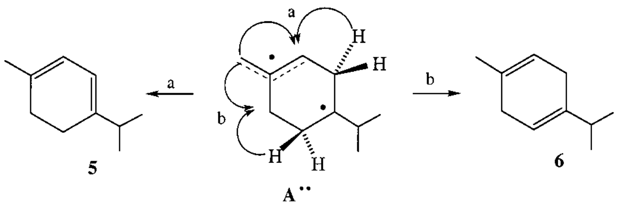
we note that the low reduction potential of TPT causes the corresponding pair to have a much lower free-energy (1.8 vs 3.1 eV). Accordingly, it may lie very close to the suggested biradical allowing for rapid recombination (Scheme 2).



Scheme 2. Divergent reactions of sabinene radical cation ($\mathbf{1}^{\bullet+}$) paired with either 1,4-$\text{DCB}^{\bullet-}$ or $\text{TPT}^{\bullet}$

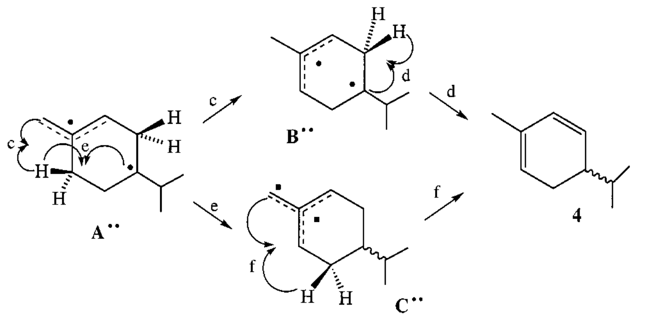
Triplet recombination of radical ion pairs has been invoked in several cases, based on optical[38–40] or CIDNP results.[41–44] The recombination of triplet pairs generates reagent triplet states or biradicals, which may initiate interesting reactions if their structures allow rearrangements. The aromatic donors and acceptors readily studied by flash spectroscopy[38–40] fail to rearrange. On the other hand, olefins[41] and strained ring systems[42–44] readily undergo rearrangements. Triplet ion pairs containing "vertical", "bifunctional", or "twisted" radical cations may generate biradicals, triplet states of changed geometry, or "perpendicular" triplet states. Compared to the geometry of the precursor, the biradical may contain a newly formed bond ("associative" return electron-transfer; e.g., formation of the "pre-quadricyclane" triplet state from the norbornadiene radical cation)[43] or a "broken" bond ("dissociative" return electron-transfer; i.e., formation of a "ring-opened" triplet state from the diphenylcyclopropane radical cation).[42,44,45] The formation of $\mathbf{A}^{\bullet\bullet}$ from $\mathbf{1}^{\bullet+}$ would be a "dissociative" return electron-transfer.

Given the formation of $\mathbf{A}^{\bullet\bullet}$, the terpinenes **5** and **6** are accessible by a single hydrogen shift, whereas the formation of **4** requires a more complex mechanism. The aromatic product, *p*-cymene (**7**), must be a secondary product as it requires loss of two hydrogen atoms in addition to the reorganization of the carbon framework. The proposed mechanism for the formation of products **4–6** is discussed in more detail below. The key intermediate, the biradical $\mathbf{A}^{\bullet\bullet}$, contains three pairs of activated hydrogens in the 3-, 5-, and 6-positions (in decreasing order of presumed migratory aptitude). A 1,4-hydrogen migration of one of the doubly activated hydrogens from C3 to C1′ (pathway a) would generate α-terpinene (**5**). Although **5** is readily formed in the electron transfer photochemistry of α-phellandrene (**4**), it is more likely formed directly from $\mathbf{A}^{\bullet\bullet}$ and not as a secondary product. The formation of γ-terpinene (**6**) can be explained similarly by a 1,4-hydrogen migration of a singly activated hydrogen from C5 to C1′ (pathway b, Scheme 3).



Scheme 3. Mechanistic formulation of sabinene photoproducts

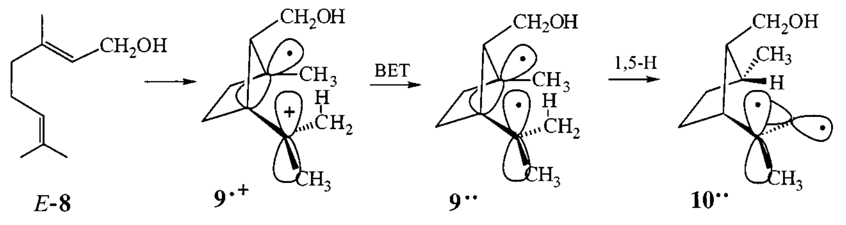
Intramolecular hydrogen migrations in biradicals have precedent; for example, the generation of *cis*-2-(2-propenyl)-*trans*-5-methylcyclopentanemethanol (**10**) from *E*-3,7-dimethylocta-2,6-dien-1-ol (geraniol; *E*-**8**) was rationalized by a 5-center C–C cyclization, generating $\mathbf{9}^{\bullet+}$, subsequent back-electron-transfer giving the di-tertiary, 2,α-bifunctional methylene-cyclopentyl biradical $\mathbf{9}^{\bullet\bullet}$, and a 1,5-H shift yielding $\mathbf{10}^{\bullet\bullet}$ (Scheme 4).[33] The formation of α-phellandrene is more complex; the net conversion of **1** (or $\mathbf{A}^{\bullet\bullet}$) to **4** requires two separate hydrogen migrations, from C6 to C1′, forming biradical $\mathbf{B}^{\bullet\bullet}$ (pathway c, Scheme 5) and, subsequently, from C3 or C5 to C4 (pathway d, Scheme 5), yielding the product. Alternatively, hydrogen migration from C6 to C4 would generate a trimethylenemethane biradical, $\mathbf{C}^{\bullet\bullet}$ (pathway e, Scheme 5), whose conversion into **4** requires, in addition, a hydrogen migration from C3 or C5 to C1′ (pathway f, Scheme 5). The complexity of this reaction sequence is in line with the low yield of **4**. In view of this complexity it is unlikely that **4** serves as an intermediate in the formation of terpinenes, **5** and **6** (vide supra).



Scheme 5. Mechanistic rationalization of the formation of α-phellandrene

The formation of *p*-cymene (**7**) is considered a secondary photoreaction of the terpinenes. This view is supported by the ready conversion of **5** and **6** to **7**. This reaction can be formulated via three key steps, beginning with generation of the respective radical cations, $\mathbf{5}^{\bullet+}$ and $\mathbf{6}^{\bullet+}$; it further requires deprotonation and loss of a hydrogen atom. The one-electron oxidation of **5** and **6** is entirely reasonable in view of the energetics delineated above. The second of the envisaged steps, deprotonation, is well established for many radical cations.[30,46–48] The proton-accepting base may be the counter-ion generated in the electron transfer reaction[30] or an adventitious reaction partner.[47] Deprotonation may become the major reaction for substrates with doubly activated ^{1}H nuclei, including doubly allylic ones and those between an unsaturated and a cyclopropane moiety.[49,50] Thus, the radical cations of α- and γ-terpinene should be readily deprotonated.

The fate of the resulting cyclohexadienyl free radical(s) will depend on the nature of the sensitizer-derived geminate intermediate. With DCB as sensitizer, the geminate radical anion is a poor base as well as a poor hydrogen-atom acceptor; however, it readily undergoes aromatic substitution with loss of cyanide ion.[23–27] As a result, appropriate donor molecules may undergo a net conversion amounting to "substitution" of an activated H atom by a *p*-cyanophenyl group. Several examples of such a three-step substitution have been documented.[49,50]



Scheme 4. 1,5-H shift in the biradical generated from the 1,5-cyclized geraniol radical cation

On the other hand, with triphenylpyrylium ion as sensitizer, the electron-transfer reaction generates the neutral radical, triphenylpyranyl, a considerably better hydrogen receptor, and is unlikely to undergo "substitution". Hence, it allows the smooth conversion of **5** and **6** to **7**.

Conclusion

The TPT-induced electron-transfer photochemistry of sabinene takes a decidedly different course from the reaction initiated by DCB. Although both reactions proceed via the radical cation $\mathbf{1}^{\bullet+}$, the nature of the geminate free-radical partner causes the reactions to diverge. The absence of a suitable nucleophile in the TPT reaction, the increased pair lifetime intrinsic to TPT sensitization, and the low pair-energy enables the pair $\mathbf{1}^{\bullet+}$–$(\mathbf{TP}^{\bullet}\mathbf{T})^{-}$, to undergo triplet recombination. This process forms biradical $\mathbf{A}^{\bullet\bullet}$, which is the key intermediate in the formation of the divergent products. Triplet recombination is not limited to the system TPT–sabinene. TPT-induced reactions of other terpenes may also involve this interesting key step and selected systems are currently under investigation.

Experimental Section

Materials: Sabinene, α-phellandrene, α- and ß-terpinene, *p*-cymene and TPT were purchased from Sigma–Aldrich and used without further purification.

Irradiation Procedure: Solutions of terpene (20 mg) and TPT (5 mg) in $CDCl_3$ (0.5 mL) were irradiated under argon with a 125 W medium-pressure mercury lamp in Pyrex tubes surrounding a centrally positioned quartz cooling jacket. A potassium chromate/sodium carbonate solution was employed as filter to prevent direct light absorption by the substrate. The progress of the reaction was monitored by a Hewlett–Packard 5988 A GC/MS with a mass selective detector.

Under these conditions, sabinene **(1)** yielded 35% α-terpinene **(5)**, 40% γ-terpinene **(6)**, and 2% α-phellandrene **(4)**, in addition to 20% *p*-cymene **(7)**; α-phellandrene gave rise to 40% α-terpinene and 30% *p*-cymene (90% conversion after 1.5 h); γ-terpinene yielded 40% *p*-cymene (40% conversion after 4.5 h); and α-terpinene yielded only *p*-cymene (100% conversion after 6.5 h). The conversion of α-terpinene to *p*-cymene occurred at a slower rate upon direct irradiation (≈20% conversion after 6.5 h) whereas direct irradiation of γ-terpinene yielded *p*-cymene at rates very similar to the TPT-sensitized conversion.

Product Identification: The reaction mixtures were analyzed by ^{1}H NMR spectroscopy (Varian VXR-400S, 400 MHz) and GC-MS (Hewlett–Packard, HP 5988 A, 70 eV, electron impact ionization) provided with a capillary column (SPB-5, 30m × 0.25 mm × 0.25 mm). The photoproducts were identified by comparison of their spectra with those of authentic samples.

Acknowledgments

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