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Electron Transfer Induced Deprotonation of α- and β-Pinene: Evidence for Ring–Closed Vinylcyclobutane Radical Cations

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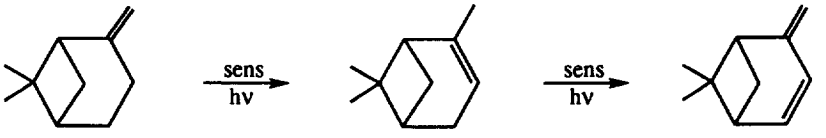
Abstract

Electron transfer from α- (**1**) or β-pinene (**2**), to 2,3,5,6-tetrachlorobenzoquinone generates radical cations, which are rapidly deprotonated by the semiquinone radical anion. (1S,5S)-**2** is converted to (1S,5S)-**1** and (1R,5R)-**1** yields a dehydrogenation product, verbenene, (1R,5R)-**9** with essentially quantitative retention of optical activity. The results support chiral, "ring-closed" radical cation structures in which the allylic–quaternary cyclobutane C–C bond retains a significant degree of bonding.

The structures and reactions of organic radical cations have been the focus of much interest for over two decades.[1,2] Particularly the interaction of strained ring moieties with olefinic fragments in organic radical cations[2] has attracted considerable interest.[2-4] A rich variety of substrates have been investigated by both physical and chemical techniques to probe the spin density distribution in the resulting radical cations and elucidate their structures and reactivities.[2-4] In this Letter we report results pertinent to the radical cations of two bridged vinylcyclobutane derivatives, α- (**1**) and β-pinene (**2**). Arnold and co-workers found that the electron transfer photochemistry of α-pinene with 1,4-dicyanobenzene in acetonitrile-methanol leads to racemic NOCAS products (**5**) and acetonitrile adducts; the analogous reaction of β-pinene generates the corresponding product types, which are, however, optically active.[3] These observations were interpreted as evidence for the capture of ring-opened radical cations, **1-o**$^{\bullet+}$ and **2-o**$^{\bullet+}$, by the solvent-nucleophile methanol.[3]

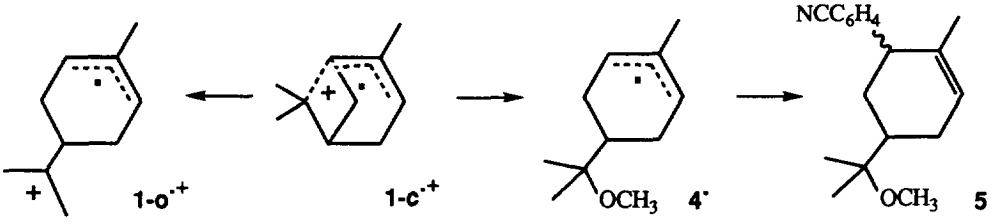


2 **1** **3**

It is interesting to compare the proposed intermediates with the structure types proposed for vinylcyclopropane radical cations.[4] Although ring-opened structures has been postulated for radical cations of vinylcyclopropane[4c,d] derivatives, most species clearly maintain a sufficient degree of bonding to conserve the stereochemical integrity of their precursors. For example, the electron transfer photo-chemistry of sabinene, a

bridged vinylcyclopropane derivative, generates optically active products, supporting a chiral "ring-closed" intermediate.[4a] Because of the potential relationship between vinylcyclopropane and vinylcyclobutane radical cation structures we are interested in the structures of **1**$^{\bullet+}$ and **2**$^{\bullet+}$.

We note that the major products derived from **1** or **2** do not strictly eliminate the ring-closed radical cations, **1-c**$^{\bullet+}$ and **2-c**$^{\bullet+}$. In fact, neither the optical purity of the NOCAS products nor that of the acetonitrile adducts have any bearing on the structure of the radical cations. The products derived from α-pinene would likely be racemic, regardless of whether the radical cation is **1-c**$^{\bullet+}$ or **1-o**$^{\bullet+}$. Conversely, the chirality of β-pinene would be conserved, regardless of whether the radical cation is **2-c**$^{\bullet+}$ or **2-o**$^{\bullet+}$.

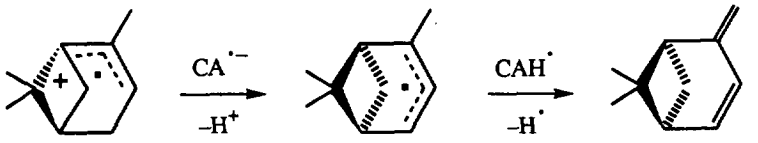


In the case of **1**, the racemic nature of the products (e.g., **5**) is sufficiently explained by the intermediacy of symmetrical, ring-opened free radicals (e.g., **4**•). These species could arise by nucleophilic attack at an achiral species, such as **1-o**$^{\bullet+}$, as suggested,[3] but equally well by nucleophilic "substitution" at a chiral radical cation, **1-c**$^{\bullet+}$, a process that has precedent in the reaction of sabinene,[4a] except for the loss of chirality, which is rooted in the symmetry of **4**•.

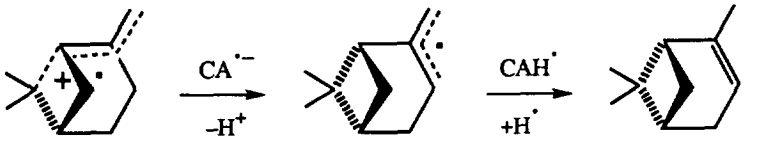
We have approached the radical cations of **1** and **2** by electron transfer to sensitizers, such as 1,4-benzoquinone and derivatives, whose radical anions are strong bases. Deprotonations are characteristic reactions of many radical cations, converting them to neutral radicals. Because proton transfer may be quite fast, the stereochemical integrity of a radical cation may be conserved, particularly in (hypothetical) cases where a short-lived ring-closed species, e.g. **1-c**$^{\bullet+}$, precedes a ring-opened radical cation, e.g. **1-o**$^{\bullet+}$. An appropriate subsequent reaction will then transfer the stereochemical features of the free radical to a diamagnetic product. Any degree of chirality found in the product will reflect the chirality of the radical cation and free radical precursors.

Irradiation of 2,3,5,6-tetrachlorobenzoquinone (chloranil, **CA**) in the presence of (1R,5R)-**1** ($[\alpha]_{589}$ = +48°; 92% e.e.)[5] produced the known acetonitrile adduct[3] in 35% yield; in addition, a dehydrogenation product, verbenene, (1R,5R)-**3** ($[\alpha]_{589}$ = –86°; 92% e.e.)[6] was formed in ~10% yield. The quantitative retention of optical activity in this product is incompatible with an achiral intermediate, particularly, **1-o**$^{\bullet+}$. The formation of **3** can be visualized via an allylic free radical, **6**•, which may be generated by either of two competing mechanisms, hydrogen abstraction by triplet **CA*** from **1** or deprotonation of **1-c**$^{\bullet+}$ by **CA**$^{\bullet-}$. Both pathways would be completed by hydrogen transfer from **6**• to the semiquinone radical, **CAH**•.

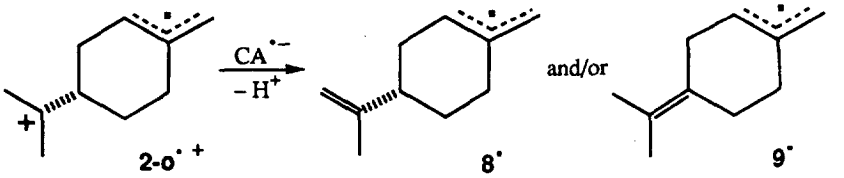
The pathway involving hydrogen abstraction by ^{3}**CA*** can be ruled out on the basis of the observed solvent dependence. The conversion of **1** to **3** proceeds smoothly in polar solvents, such as acetonitrile or acetone, but it is significantly suppressed in non-polar media, such as cyclohexane. These results strongly support the deprotonation mechanism with the ring-closed radical cation, **1-c**$^{\bullet+}$ as the key intermediate.



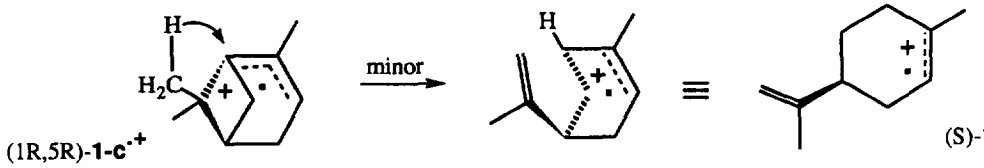
Similarly, irradiation of chloranil in the presence of (1S,5S)-**2** ($[\alpha]_{589}$ = –21°; 98% e.e.)[7] generated the isomer, (1S,5S)-**1** ($[\alpha]_{589}$ = –48.7°; 94% e.e.) in ~80% yield. This reaction once again is rationalized via a ring-closed allylic free radical, **7•**, formed by deprotonation, and hydrogen "return" to it. The high retention of optical activity in the product is incompatible with the involvement of a ring-opened intermediate, **2-o•+**.



Ring-opened species (**2-o•+**) would most likely be deprotonated in the side chain, yielding **8•** and/or **9•**. Analoga of such radical cations can be generated by photo-induced electron transfer from monocyclic terpenes containing an alkene function in a side chain. However, limonene, **10**, failed to form intramolecular cyclization products under these conditions; therefore, it appears unlikely that ring-opened species, **1-o•+** or **2-o•+**, would undergo re-cyclization. In the light of these considerations, the conversion of **2** to its endocyclic isomer, **1**, strongly supports the intermediacy of the ring-closed radical cation, **2-c•+**.



The experiments reported here clearly establish the existence of ring-closed radical cations, **1-c•+**, **2-c•+**, with lifetimes sufficiently long to allow deprotonation by **CA•−**. We emphasize that we cannot rule out the existence of ring-opened radical cations, **1-o•+**, **2-o•+**, under different conditions; the formation of **10** in the 1,4-dicyanobenzene/biphenyl sensitized reaction of **1**[3] argues strongly for **1-o•+**. We have probed the nature of the intermediate by isolating **10** [(1R,5R)-**1**; 92% e.e.; —> (S)-**10**; $[\alpha]_{546}$ = – 8.2°; 7% e.e.).[8] The high degree (>90%) of racemization suggests the achiral **1-o•+**; yet, the residual rotation (8% retention) of **10** requires limited participation of a chiral intermediate; the conversion is tentatively ascribed to a hydrogen shift in **1-c•+**. Theoretical calculations also support **1-c•+**, **2-c•+**[3] and other vinylcyclobutane radical cations.[9]



Hydrogen migrations have been demonstrated for several radical cations, based on EPR or CIDNP spectra,[10a-e] isotopic labeling studies,[10f] or theoretical calculations.[11] The conversion of cyclohexane-1,4-diyl to cyclohexene[10a,b] or cyclopentane-1,3-diyl to cyclopentene[10c] radical cations rests on EPR evidence; the conversion of benzonorcaradiene to 1- and 2-methylnaphthalene,[10d] and of tricyclo[4.1.0.$0^{2,7}$]heptane to bicyclo[4.1.0]hex-2-ene[10e] is based on CIDNP data; the hydrogen migration in sabinene radical cation rests on the chirality of the product, β-phellandrene;[10f]and the conversion of cyclopropane to propene radical cation has been investigated by ab-initio calculations.[11] The minor pathway tentatively proposed for the conversion of **1** to **10** would be a 1,3-hydrogen shift; this interesting reaction type is under active investigation.

Acknowledgement

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