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Electron transfer photochemistry of bridged allylcyclopropane systems: novel substitution products via deprotonation

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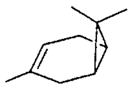
ABSTRACT: The electron transfer photochemistry of three rigid, bridged allylcyclopropane systems, 3-carene (**1**), tricyclo[4.3.1.$0^{1,6}$]dec-3-ene (**2**) and tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (**3**), is shown to take an unprecedented course: the major products are novel 'substitution' products, in which a hydrogen at an allylic carbon (C_2) of the substrate has been replaced by the *p*-cyanophenyl group. Copyright © 1999 John Wiley & Sons, Ltd.

INTRODUCTION

The structures and reactions of organic radical cations have attracted much attention during the past two decades.[1–13] Because of their dual nature, containing an unpaired spin as well as a positive charge, radical cations have an exceptional range of diverse reaction pathways available, such as rearrangements,[3–6] including sigmatropic shifts,[7] nucleophilic capture,[8,9] cycloadditions,[2d,10] as well as fragmentations[11] and cycloreversions.[12] Compared with the analogous reactions of the parent molecules, many radical cation reactions show a dramatic decrease in activation barriers,[11,13] one of the most striking aspects of radical cation chemistry.[3]

We are interested in conjugative and homoconjugative interactions in substrates containing olefinic moieties and cyclopropane rings.[2e,14–16] These interactions govern the structural changes that molecules undergo upon ionization, determine the distribution of spin and charge in the resulting radical cations, and govern the reactivity pattern of these species. Having studied the effects of conjugation on several vinylcyclopropane derivatives, we targeted homoconjugative interactions in substrates containing a cyclopropane ring and an alkene moiety linked symmetrically and held rigidly by two CH_2 groups. We selected three substrates of this structure type, viz. 3-carene (**1**), tricyclo[4.3.1.$0^{1,6}$]dec-3-ene (**2**) and tricyclo[4.4.1.$0^{1,6}$]undeca-3,8-diene (**3**), and studied their electron transfer photochemistry.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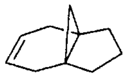
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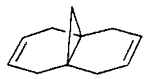
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When photo-induced electron transfer reactions are carried out in polar solvents containing a nucleophile (methanol), the radical cation may be captured in a nucleophilic fashion; the position of the alkoxy function in the products will reveal the site of nucleophilic attack. Substrates **2** and **3** contain a tetra-substituted cyclopropane bond and a di-substituted double bond; in this case the cyclopropane function should be the primary electron donating site and the nucleophile should attack a quaternary cyclopropane carbon.[7,8c,d,9b] On the other hand, the reactivity of **1** may be more complex. Because **1** has tri-substituted cyclopropane bonds and an alkene function, these moieties may compete as the primary electron donor function. Therefore, both functions are potential targets of nucleophilic attack; radical cation, $\mathbf{1}^{\cdot+}$, is more likely to have either a delocalized structure or several structures of comparable energies.

However, the electron transfer photochemistry of **1**–**3** took an unprecedented course. Although nucleophilic capture is not completely suppressed, the major products formed from **1**–**3** are novel 'substitution' products, in which an allylic hydrogen of the substrate has been replaced by the *p*-cyanophenyl group. The formation of these products reveals an interesting novel facet of radical cation chemistry.

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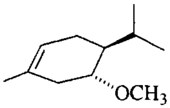
RESULTS

Electron transfer photochemistry of (+)-3-carene [1, (1S,6S)-3,7,7-trimethyl-bicyclo[4.1.0]hept-3-ene]

Irradiation of 1,4-dicyanobenzene (DCB), phenanthrene (Phen), and (1S,6S)-3-carene ($[\alpha]_{589} = 18.1°$), **1**, in acetonitrile–methanol gave rise to four products, all formed with significant retention of optical activity. A methanol adduct, **4**, resulting from anti-Markovnikov addition to the C_1–C_7-cyclopropane bond (6%, $[\alpha]_{589} = -25°$) and two ‘NOCAS’ products (**5**—17%, $[\alpha]_{546} = -13.0°$; and **6**—7%, $[\alpha]_{589} = 10.2°$), resulting from anti-Markovnikov attack on the cyclopropane function and the olefinic bond, respectively, are unexceptional products, apparently initiated by nucleophilic capture.



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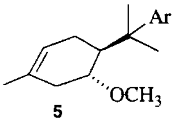

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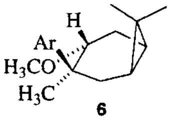

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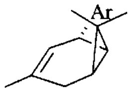
The major product, 2-*endo*-(*p*-cyanophenyl)-4,7,7-trimethylbicyclo[4.1.0]hept-3-ene (**7**—$[\alpha]_{546} = 143°$, ~50% yield) is formally a ‘substitution’ product, in which a hydrogen at an allylic carbon (C_2) of the substrate has been replaced by the *p*-cyanophenyl group.



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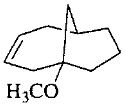
Electron transfer photochemistry of tricyclo-[4.3.1.0^{1,6}]dec-3-ene (2)

Irradiation of DCB, Phen and **2** gave rise to six different structure types. A methanol adduct (**8**) resulting from addition to the 4°–4°-cyclopropane bond and the corresponding aromatic substitution product (**9**) were isolated in yields of ~ 30% and ~ 5%, respectively. Both products were expected on the basis of the general spin density distribution established by CIDNP results for several analogs of **2**.[17]



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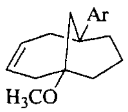

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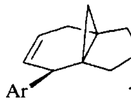
Products **10** and **11** (~25 and ~15% yield, respectively) arise formally by replacement of a hydrogen atom by the cyanophenyl group. They are accompanied by two additional products (**12, 13;** 15% combined yield), of the same composition as NOCAS products; however, the aryl group is attached in a position without spin or charge in **1**$^{\cdot+}$. Although these products could be rationalized via capture of the radical cation by methanol, and hydrogen migration before the ‘aromatic substitution’, this mechanism fails to account for the incorporation of deuterium into adducts **12** and **13**, when the reaction is carried out in CH_3–OD (see above).



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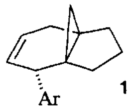

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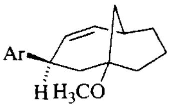

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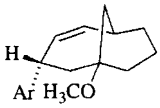

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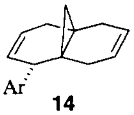
Electron transfer photochemistry of tricyclo-[4.4.1.0^{1,6}]undeca-3,8-diene (3)

Irradiation of DCB, Phen and **3** gave rise to products of at least four different structure types. The major product, **14** (12% yield), and several isomers of the same composition, including **15**, formally arise by replacement of an allylic hydrogen by the cyanophenyl group.



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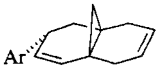

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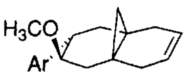
Several products are formed by incorporating a methoxy as well as a *p*-cyanophenyl group; among these, **16** may be a NOCAS product, or a methanol adduct formed by attack on the vinyl carbon of **15**. Adduct **17** is probably a secondary product, formed by addition of methanol to **15**.



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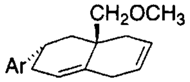

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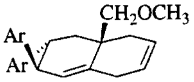
Two products, **18** and **19** (20 and 25% yield, respectively), contain two aryl functions and one methoxy group ($M^+ = 380$). They can be explained as NOCAS derivatives of primary arylation products, such as **15** or its syn-isomer.



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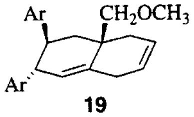

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DISCUSSION

The photo-induced reactions of the three substrates to be discussed here probably proceed via electron transfer from the substrates to a photo-excited acceptor. Irradiation of a sensitizer–co-sensitizer pair (such as 1,4-dicyanobenzene/phenanthrene, DCB, Phen) in the presence of suitable donors (D, viz. **1–3**) and nucleophiles (5 M CH_3OH) initiates a well-established photochemical reaction sequence with radical ion pairs ($D^{\cdot+}$, $DCB^{\cdot-}$) as key intermediates [Eqn. (1)]. Energetic considerations suggest that the electron transfer reactions generating the radical ion pairs are exothermic for all three substrates.* One typical reaction of the radical cations so generated is nucleophilic capture [Eqn. (2a)]; the resulting methoxy substituted free radicals either form simple methanol adducts [Eqn. (3)][8a,b] or generate more complex products by aromatic substitution at the ipso-carbon of the sensitizer radical anion [Eqn. (4a)].[8c,d,,9b]

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

$$\mathrm{D}^{\cdot+} + \mathrm{CH_3O\ H} \longrightarrow [\mathrm{D{-}OCH_3}]^{\cdot} + \mathrm{H}^+ \quad (2a)$$

$$\mathrm{D}^{\cdot+} + \mathrm{B}^- \longrightarrow \mathrm{D{-}({-}H)}^{\cdot} + \mathrm{B{-}H} \quad (2b)$$

$$[\mathrm{D{-}OCH_3}]^{\cdot} \longrightarrow \mathrm{H{-}D{-}OCH_3} \quad (3)$$

$$[\mathrm{D{-}OCH_3}]^{\cdot} + \mathrm{DCB}^{\cdot-} \longrightarrow p\text{-}\mathrm{CN\text{-}C_6H_4{-}D{-}OCH_3} + \mathrm{CN}^- \quad (4a)$$

$$\mathrm{D{-}({-}H)}^{\cdot} + \mathrm{DCB}^{\cdot-} \longrightarrow p\text{-}\mathrm{CN\text{-}C_6H_4{-}D{-}({-}H)} + \mathrm{CN}^- \quad (4b)$$

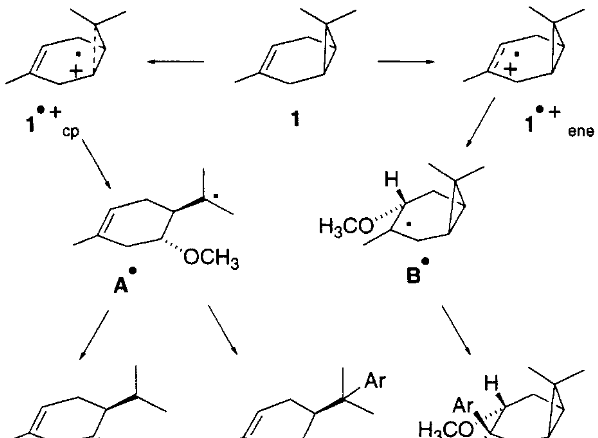
The detailed reaction sequence leading to the three-component products is particularly well-established for olefins; this variant is known as the photo-NOCAS reaction (for photo-induced nucleophile-olefin-combination-aromatic-substitution).[9b,c]

Nucleophilic capture

In the case of the bridged allylcylopropane systems, **1–3**, the nucleophile may attack either the cyclopropane function or an olefinic group. Our results provide evidence for both types of attack. For example, methanol adduct, **4**, and NOCAS product, **5**, are formed by attack on the cyclopropane function of $\mathbf{1}^{\cdot+}$. On the other hand, NOCAS product, **6**, requires attack on the alkene moiey; the attack at the strained ring is favored by 2.5:1. This competition is compatible with the presence of two separate localized radical cations of similar energy or with a delocalized radical cation, $\mathbf{1}^{\cdot+}$.

Nucleophilic capture of the radical cation(s), $\mathbf{1}^{\cdot+}$, leads to two free radicals, $A^{\cdot}$ and $B^{\cdot}$, both formed by anti-Markovnikov attack. The NOCAS products are readily explained by aromatic substitution of the free radicals on the sensitizer radical anion, $DCB^{\cdot-}$ [cf. Eqn. (4a)]. The final step in the formation of the methanol adduct, **4** [cf. Eqn. (3)], may involve one of two mechanistic variants, proceeding either via hydrogen abstraction or via reduction by the sensitizer radical anion followed by protonation; both reactions have precedent.[21]

The mechanisms can be differentiated by the use of methanol-OD as nucleophile. Under these conditions, a methoxy group is introduced in the primary reaction step. Subsequently, acetonitrile serves as the source for H atom abstraction, whereas methanol-OD serves to transfer D^+ to carbanion intermediates.[21] Consequently, the hydrogen abstraction mechanism leads to perprotio methanol adducts, whereas the reduction–'protonation' pathway generates methanol adducts containing one D. The electron transfer photochemistry of **1** using DCB-Phen in acetonitrile–methanol–OD produced 1:1 ratios of **4**-d_0 and **4**-d_1, and of **5**-d_0 and **5**-d_1, suggesting a competition between hydrogen abstraction and reduction mechanisms.



The other substrates discussed here have a tetrasubstituted cyclopropane ring and one (**2**) or two disubstituted alkene functions (**3**.) The spin density distribution of several compounds of this general structure type was probed by CIDNP studies,[17] which identified the most highly substituted (4°–4°) cyclopropane bond (e.g. of **3**) as the seat of spin and charge; little or no spin density was documented for the olefinic moieties. Accordingly, we expected nucleophilic capture mainly at the cyclopropane ring. Indeed, methanol adduct, **8**, and NOCAS product, **9**, are readily explained by attack on the cyclopropane function of $\mathbf{2}^{\cdot+}$, giving rise to radical $\mathbf{C}^{\cdot}$; no product

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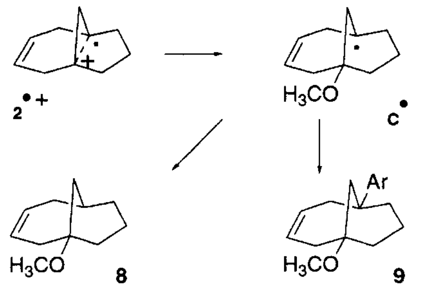
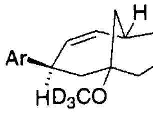
*The free energies of radical ion pair formation were calculated according to the Rehm–Weller equation, $-\Delta G^o = E_{(0,0)} - E^0_{D^{\cdot+}/D} + E^0_{A/A^{\cdot-}} - e^2/\varepsilon a$, where $E_{(0,0)}$ is the excitation energy, $E^o{}_{D^{\cdot+}}/D$, and $E^o{}_{A/A^{\cdot-}}$ are the redox potentials of donor and acceptor, respectively, and $e^2/\epsilon\, a$ is a Coulomb term accounting for ion pairing.[18] The oxidation potentials of **1–3** are estimated as ~2.0 V in analogy to limonene, ~2.1 V,[19] and methylcyclohexene, ~1.93 V.[20] Given the excitation energy [$E_{(0,0)} = 4.3$ eV] and reduction potential of DCB [$E_{(A^-/A)} = -1.60$ V],10a the oxidation of **1–3** by ^{1}DCB* [Eqn. (1)] is exergonic, $-\Delta G_{ET} = \sim 0.5$ eV.

suggests nucleophilic attack on the alkene moieties.



Reactions competing with nucleophilic capture

In contrast to the methanol adducts and NOCAS products, the remaining products require mechanisms not involving nucleophilic capture. This applies not only to products **7, 10** and **11**, or **14** and **15**, which lack the alkoxy substituent altogether, but also to products **12** and **13**, or **17–19**. This is shown quite clearly for the isomeric products **12** and **13** derived from **2**. Although they have the identical composition as NOCAS product **9**, the photoreaction with methanol–OD as nucleophile resulted in a 3:2 ratio of d_0:d_1-containing product; pure d_0 isotopomer is expected for a NOCAS product as is, indeed, observed for **9**. Clearly, a different radical cation mechanism must be responsible for these products.



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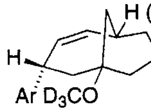

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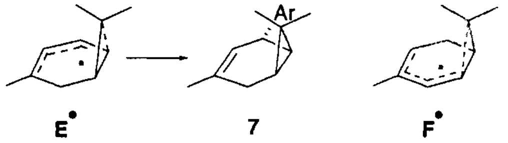
Among the potential reaction types open to radical cations, we consider hydrogen migration (sigmatropic shifts) and deprotonation. Several examples of [1,3] sigmatropic shifts have been documented for cyclopropane radical cations, leading to the isomeric propene radical cation; for example, sabinene radical cation is converted to β-phellandrene radical cation.[7] However, this reaction type cannot explain the formation of the major products, viz. **7** and **10**, which are formed with conservation of the three-membered ring and, in the case of **7**, with conservation of optical activity. The second reaction considered here, deprotonation, appears to be a more likely alternative.

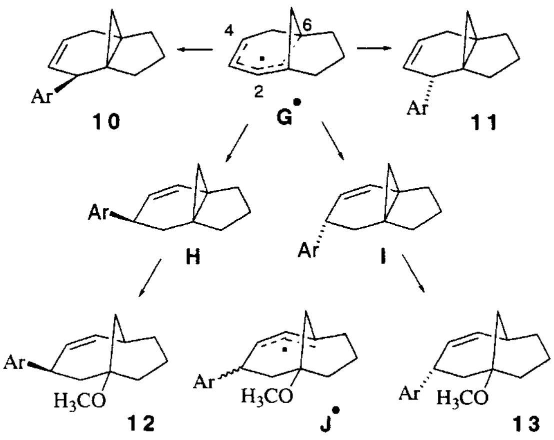
Deprotonations are characteristic reactions of some radical cations, converting them to neutral radicals. These conversions are particularly likely in the presence of relatively strong bases, such as semiquinone radical anions. For example, we found recently, that chloranil semiquinone deprotonates the α- and β-pinene radical cations; the products derived from the resulting neutral radicals demonstrated the existence of ring-closed vinylcyclobutane radical cations.[22] The radical cations discussed here, $\mathbf{1}^{\cdot+}$–$\mathbf{3}^{\cdot+}$, are deprotonated at a methylene group linking the cyclopropane and alkene moieties. Apparently, deprotonation is favored by the two adjacent functions, which allow the generation of resonance stabilized free radicals. Subsequent aromatic substitution of the free radicals on the sensitizer radical anion, $\mathbf{DCB}^{\cdot-}$, accounts for the formation of **7, 10** and **11**.



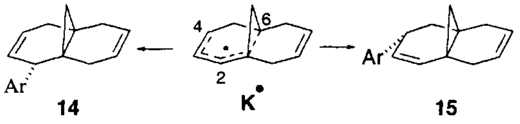
The formation of **7** from **1** shows significant regio- and stereospecificity. In principle, the deprotonation of $\mathbf{1}^{\cdot+}$ may give rise to two different neutral radicals, E$^{\cdot}$ and F$^{\cdot}$. Species E$^{\cdot}$ is stabilized by hyperconjugation between the methyl group and the allyl function; a similar stabilization is absent in F$^{\cdot}$ because the methyl group is attached at the node of the allyl function. The substantial yield of **7** and the absence of more than traces of the isomeric product show that free radical E$^{\cdot}$ is clearly favored, establishing the regiospecificity of deprotonation.

The stereo- as well as regiospecificity of the aromatic substitution step is also an interesting facet of this reaction; the sensitizer anion appears to approach exclusively from the surface opposite the cyclopropane ring; this can be explained by the significant steric hindrance due to the geminal dimethyl substitution. The significant preference for the substitution restoring an allylcyclopropane system is less readily explained.

Because of the symmetry inherent in $\mathbf{2}^{\cdot+}$ its deprotonation yields only one 'product', allyl radical, G$^{\cdot}$. This intermediate may undergo aromatic substitution at C_2, C_4, C_6 from the face of the CH_2 bridge (exo-) or from the opposite (endo-) face. The relative yields of **10** and **11** show moderate stereoselectivity, less pronounced than that of $\mathbf{1}^{\cdot+}$ because the steric bulk of the bridge (CH_2 for $\mathbf{2}^{\cdot+}$) is diminished relative to that of $\mathbf{1}^{\cdot+}$ [$C(CH_3)_2$]. The key to the regioselectivity of aromatic substitution lies in products **12** and **13;** although they have the composition of NOCAS products, they are probably formed via H and I. As vinylcyclopropane systems, these should undergo electron transfer more readily than **2**.



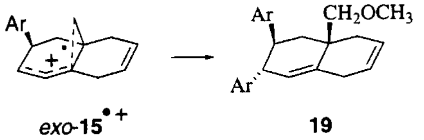
The degree of deuterium incorporation into **12** and **13** is rationalized via an allyl radical, endo- or exo-J$^{\cdot}$, generated from vinylcyclopropane radical cations, H$^{\cdot +}$ or I$^{\cdot +}$. The allylic radical should be more readily reduced than A$^{\cdot}$ or C$^{\cdot}$. If **12** and **13** are formed via this route, the regioselectivity of aromatic substitution is approximately 2:1 given by the relative yields of [**10** + **11**] vs [**12** + **13**].



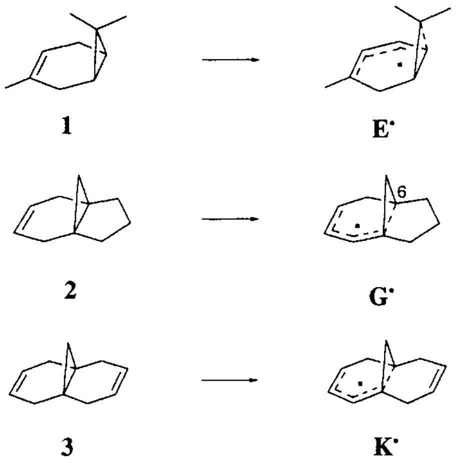
The reactions of the third substrate follow similar principles, yet offer additional interesting features. The key reaction appears to be deprotonation of **3**$^{\cdot +}$ to yield K$^{\cdot}$. This allylic radical can react with the sensitizer radical anion via endo-coupling, giving rise to allylcyclopropane **14** and vinylcyclopropane **15**.

Although both of these have been isolated, product **15**, as a vinylcyclopropane system, is oxidized more readily than both **3** and **14**. It is considered the key to three of the methoxy-substituted products, **17** and **18** are readily explained as methanol adduct and NOCAS product, respectively. In contrast to the formation of **12** and **13** from H and I, products **17** and **18** are formed by attack of methanol on the 2° and not the 4° cyclopropane carbon. Accordingly, the lateral bond of **15**$^{\cdot +}$ must be involved in delocalizing spin and charge whereas for H$^{\cdot +}$ and I$^{\cdot +}$ the internal (4°–4°) bond serves this function.

Product **16** could be formed by addition of methanol onto the vinyl carbon of **15**$^{\cdot +}$. This type of addition has precedent in the electron transfer photochemistry of vinylcyclopropane,[16b] although the conservation of the strained ring is unusual. Finally, product **19** is rationalized as a NOCAS product of the syn-isomer of **15**. Although syn-**15** is not isolated, it is most likely formed in low yield and should be quite readily oxidized.



The noteworthy result emerging from the electron transfer photochemistry of the (bridged) allylcyclopropane compounds, **1**–**3**, is the significant yield of products compatible with deprotonation of the corresponding radical cations. The deprotonation of **1**$^{\cdot +}$–**3**$^{\cdot +}$, even in the absence of strong bases, goes well beyond the degree previously observed for other structure types.[7,23] What causes this change in reactivity?



Deprotonation of allylcyclopropane radical cations involves doubly activated ^{1}H nuclei and gives rise to free radicals with extended conjugated π-systems E$^{\cdot}$, G$^{\cdot}$, and K$^{\cdot}$). This suggests that thermodynamic factors play a significant role in determining the reactivity of these radical cations. Thermodynamic ‘control’ was noted previously in the nucleophilic capture of various vinyl- or arylcyclopropane radical cations. For example, the radical cations of sabinene, thujene or 2-carene, as well as others, capture nucleophiles in such a fashion that allylic or benzylic radicals are formed. The results reported here identify another radical cation reaction type for which thermodynamic factors appear to play a major role.

CONCLUSION

The electron transfer photochemistry of three bridged allylcyclopropane systems, **1** –**3**, gives rise to a series of products compatible with deprotonation of the corresponding radical cations, **1**$^{\cdot +}$–**3**$^{\cdot +}$. The extent of deprotonation, even in the absence of strong base, goes well beyond the degree previously observed for other structure types.[7,23a] The deprotonations of **1**$^{\cdot +}$–**3**$^{\cdot +}$ have little or no synthetic utility, because of competing as well as secondary reactions. However, the results suggest that appropriate structure types can be designed whose deprotonation will lead to significant and useful reactions. We are currently evaluating the electron transfer induced deprotonation of several such structure types.

STRUCTURE ASSIGNMENTS

Because of the importance of the correct structure assignments for the mechanistic conclusions, the spectral features revealing key features of the products are briefly discussed below. In addition to ^{1}H and ^{13}C spectra, extensive NOE difference spectra elucidated substituent stereochemistry.

General features

All products containing the methoxy function show characteristic singlets (3.0–3.4 ppm) and multiplets for the tertiary alkoxy α-proton (3.0–3.8 ppm). The diastereotopic methoxymethylene protons of products **17**–**19** show pairs of doublets. All aryl substituted products show aromatic signals for the *p*-cyanophenyl group (7.10–7.70 ppm).

Products obtained from Δ^3-carene. Products **4** and **5** have similar NMR spectra except for the tertiary isopropyl multiplet of **4** (2.10 ppm), which is replaced by aryl resonances for **5**. The stereochemistry of these products rests on NOE experiments. Irradiation of the geminal methyl resonances (0.90 and 0.85 ppm) caused strong NOE enhancement of the single alkoxy resonances (3.31 ppm). Therefore, the isopropyl and methoxy groups of both compounds must be *trans* to each other.

For NOCAS product **6**, two cyclopropane resonances (0.92 and 0.72 ppm) and the absence of olefinic signals identify the double bond of **1** as the target of the nucleophile; the lack of a benzylic resonance indicates that the aryl substituent is attached to a quaternary carbon. The stereochemistry of **6** was deduced by an NOE experiment: pre-irradiation of the tertiary alkoxy resonance (3.25 ppm) caused enhancement of the syn-7-methyl group (1.04 ppm) and the aromatic ortho signals (7.49 ppm). Thus, the aryl group must be *trans* to the methoxy group and *cis* to the cyclopropane ring.

The spectrum of **7** has one olefinic and two cyclopropane protons (0.60 ppm, and ~0.9 ppm, overlapping one CH_3 resonance). The regiochemistry of the aryl group rests on the strong interaction between a benzylic allylic (3.33 ppm) and one olefinic proton (5.20 ppm; 2D-COSY). The stereochemistry of this group was probed by NOE: pre-irradiation of the allylic benzylic frequency (3.33 ppm) caused strong enhancement of the syn-7-methyl and the aromatic ortho frequencies (7.34 ppm); thus, the aryl group must occupy a position *trans* to the cyclopropane ring.

Products derived from tricyclo[4.3.1.0^{1,6}]dec-3-ene (2). The spectra of **8** and **9** are similar, except for the tertiary bridgehead resonance of **8**, which is replaced by cyanophenyl resonances in the spectrum of **9**. Both products lack tertiary alkoxy signals (DEPT), identifying a quaternary cyclopropane carbon as the point of attack by the methoxy group.

The structure of isomers **10** and **11** is indicated by the presence of two cyclopropane, two olefinic, one benzylic allylic, and two allylic resonances; the stereochemistry rests on NOE evidence. Pre-irradiation of the syn-cyclopropane resonance of **10** (0.49 ppm) caused NOE enhancement of the ortho aryl resonance (7.29 ppm) and one allylic signal (2.55 ppm); thus, the aryl group of **10** is attached *cis* to the cyclopropane ring. For **11**, pre-irradiation of the benzylic allylic resonance (3.80 ppm) caused NOE enhancement of one (syn-) cyclopropane signal (0.68 ppm), the ortho aryl resonance (7.19 ppm), and one olefinic signal (5.68 ppm); thus, the aryl group is *trans* to the cyclopropane ring.

The spectra of **12** and **13** feature two olefinic resonances as well as one allylic benzylic (**12**, 3.77 ppm; **13**, 3.95 ppm) and one allylic bridgehead signal (~2.75 ppm), each coupled to one olefinic proton. The position of the methoxy group is indicated by a quarternary (alkoxy) carbon resonance (~76.0 ppm). The stereochemistry of the aryl groups rests on NOE evidence. For **12**, pre-irradiation of one (syn-) bridge proton frequency (1.78 ppm) caused NOE effects for the ortho aryl, the geminal bridge proton (1.99 ppm), and the bridgehead signals; thus, the aryl group of **12** must occupy the position syn to the methylene bridge. For product **13**, irradiating a frequency where a bridge and the bridgehead proton overlap (~2.7 ppm) caused strong enhancement for the allylic benzylic, the other bridge proton (1.48 ppm) and one olefinic resonance (5.3 ppm). Thus, the aryl group must occupy the anti position. The NOE effect of the olefinic signal confirms the proposed regiochemistry.

Products derived from tricyclo[4.4.1.0^{1,6}]undeca-3-8-diene. The isomers **14** and **15** have several features in common, including two cyclopropane, one benzylic allylic, and four olefinic resonances. Because **14** has six allylic protons, the olefinic and cyclopropane functions must be isolated; since **15** has only four allylic protons, two of its functional groups must be conjugated. One olefinic signal (5.39 ppm) is not coupled to an allylic resonance; this double bond must be conjugated with the cyclopropane group. The aryl groups of both isomers are *trans* to the cyclopropane ring. For **14**, pre-irradiation of the allylic benzylic signal (3.59 ppm) caused NOE effects for the syn-cyclopropane signal (0.88 ppm). For **15**, pre-irradiating the cyclopropane resonances (0.90 and 0.95 ppm) caused enhancement of the allylic benzylic signal.

The general structure type of product **16** follows from the presence of two cyclopropane (0.46 and 0.80 ppm), four allylic (~2.6 ppm), and two olefinic protons (5.5 ppm). The stereochemistry of aryl and methoxy groups rests on NOE evidence. Pre-irradiation of the ortho aryl frequency (7.31 ppm) caused NOE effects for the 3° alkoxy and benzylic resonances (3.44 and 2.6 ppm, respectively). Also, pre-irradiation of the benzylic resonance caused enhancement of one cyclopropane resonance (0.46 ppm) and the ortho aryl signals, placing the methoxy group *trans* to the aryl group and *cis* to the cyclopropane ring.

Products **18** and **19** have similar spectra; pairs of strongly deshielded doublets (**18**, 3.21 and 3.65 ppm; **19**, 3.38 and 3.56 ppm) indicate that the three-membered ring of **3** has been opened by attack of methanol on the 2° carbon. The position of the double bonds follows from the presence of three olefinic protons (**18**, 5.56 ppm, s; 5.66 and 5.73 ppm, dm, $J = 12$ Hz; **19**, 5.54 ppm, s; 5.61 and 5.69 ppm, dm, $J = 12$ Hz), suggesting one bridgehead double bond; one pair of doubly allylic protons (**18**, 2.67 and 2.97 ppm, d, $J = 18.8$ Hz; **19**, 2.74 and 3.0 ppm, d, $J = 20.9$ Hz) confirms this assignment. The position of one aryl group is indicated by one allylic benzylic resonance each (**18**, 3.56 ppm; and **19**, 3.48 ppm).

The orientation of the aryl groups relative to each other and to the the methoxymethyl function is based on NOE evidence. For both products, pre-irradiation of a benzylic signal caused enhancement for both sets of aryl ortho resonances; therefore, the two aryl groups of either compound must be *trans* to each other. For **18**, irradiation of the (unusually deshielded) benzylic multiplet (3.56 ppm) caused enhancement of one methoxymethyl doublet and the resonance at 2.15 ppm. Therefore, the aryl function at C_3 is *cis* to the -CH_2OCH_3 group. For **19**, irradiating the benzylic resonance (3.14 ppm; H_4) caused enhancement for one set of ortho aryl signals, one methoxymethyl doublet (3.65 ppm), and weak effects for the allylic benzylic signal (3.56 ppm); thus the aryl group at C_4 must be *cis* to the -CH_2OCH_3 group.

EXPERIMENTAL SECTION

Materials and solvents

3-Carene (**1**, Aldrich; 95%; $[\alpha]_{589} = 18.1°$)[24] was used without further purification. Tricyclo[4.3.1.0^{1,6}]dec-3-ene (**2**)[25] and tricyclo[4.4.1.0^{1,6}]-undeca-3,8-diene (**3**),[26] were prepared according to literature procedures. 1,4-Dicyanobenzene (Aldrich; 98%) and phenanthrene (Aldrich; 98%) were purified by recrystallization. Acetonitrile (Fischer) and methanol (Fischer) were distilled from calcium hydride and stored over 4 Å molecular sieves.

Photosensitized electron transfer reactions

The reaction solutions contained 0.1 M of the donors and 0.05 M of 1,4-dicyanobenzene with 0.02 M of phenanthrene as co-sensitizer in acetonitrile/methanol (3:1). They 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 (crosslinked methyl silicone on fused silica). Analytical runs were carried out in 4 mm i.d. NMR tubes stoppered with latex stoppers, and preparative runs in 30 mm i.d. tubes with central cooling fingers (water-cooling).

Isolation of products

Reaction products formed in yields >5% were isolated by a series of column chromatographic procedures. Columns of 2.5 or 1.2 cm i.d., packed with ~10–15 cm of silica gel (VWR Scientific, 230–400 mesh), were eluted with solvent gradients, usually from light petroleum ether (b.p. <65 °C) to mixtures with ethyl acetate. Typically, several passes were required to isolate the products.

Characterization of products

Structure assignments of isolated products rest on MS and NMR data, including DEPT and 2D COSY experiments, and extensive NOE difference spectra, to confirm the proposed structures. Proton NMR spectra were recorded on either a Varian XL-400 or a Varian Gemini-200 spectrometer. ^{13}C spectra were recorded on the Gemini spectrometer, operating at 50.3 MHz.

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