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ELECTRON TRANSFER PHOTOCHEMISTRY OF 7-(SPIROCYCLOPROPANE)QUADRICYCLANE: CAPTURE OF A RADICAL CATION AND SEQUENTIAL CYCLOPROPYLCARBINYL REARRANGEMENTS

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The electron transfer photo-sensitized reaction of 7-(spirocyclopropane)quadricyclane (1) with methanol produces two rearranged mono-methanol adducts, 2 and 3, and a bis-methanol adduct, 4. The products reveal that $1^{\bullet+}$ reacts by stereo- and regiospecific attack of methanol on one trisubstituted cyclopropane ring. The resulting free radical rapidly undergoes one or two (consecutive) cyclopropylcarbinyl to butenyl rearrangements. The mono-adducts are formed by net hydrogen abstraction, the di-adduct via a (secondary) electron transfer reaction of 3. © 1997 John Wiley & Sons, Ltd.

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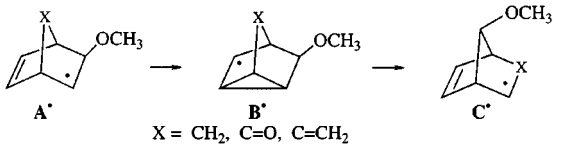
INTRODUCTION

Photo-induced electron transfer from norbornadiene (**N**) or quadricyclane (**Q**), or their 7-methylene- and 7-spirocyclopropane derivatives, to appropriate acceptor/sensitizers generates the respective radical cations, $\mathbf{N}^{\bullet+}$, $\mathbf{Q}^{\bullet+}$ or their derivatives.[1,2] Methanol attacks several of these species in stereospecific fashion from the *exo* face;[3–6] at 5 M methanol, nucleophilic capture is considerably faster than the valence isomerization of $\mathbf{Q}^{\bullet+}$ into $\mathbf{N}^{\bullet+}$.[1,7] The primary free radicals formed by nucleophilic capture undergo rapid molecular rearrangements; for example, *exo*-3-methoxybicyclo[2.2.1]hept-5-en-2-yl (**A**$^{\bullet}$, X = CH_2) rearranges to *anti*-5-methoxytricyclo[2.2.1.$0^{2,6}$]heptan-3-yl (**B**$^{\bullet}$, X = CH_2) which, in turn, rearranges to *syn*-7-methoxybicyclo-[2.2.1]hept-5-en-2-yl, (**C**$^{\bullet}$, X = CH_2). Free radicals **B**$^{\bullet}$ and **C**$^{\bullet}$ acquire a hydrogen atom (by reduction–protonation or hydrogen abstraction) or react with the sensitizer radical anion by aromatic substitution, generating a wide range of products.[3–6] Radical cations of 7-substituted derivatives undergo related reactions; thus, the electron transfer photoreaction of quadricyclanone in acetonitrile–methanol generates 7-*syn*-methoxybicyclo[2.2.1]hept-5-en-2-one via **B**$^{\bullet}$ (X = C═O) and **C**$^{\bullet}$ (X = C═O).[6]



The quadricyclane system (**1**) bearing a 7-spirocyclopropane group is a particularly attractive substrate because the strained ring in the 7-position might permit two consecutive cyclopropylcarbinyl-to-allylcarbinyl rearrangements. We therefore studied the electron transfer photochemistry of **1**. The structure of the corresponding radical cation has been established by CIDNP;[2] the spin density of $\mathbf{1}^{\bullet+}$ is essentially located on the pair of trisubstituted cyclopropane rings. This result was expected, because the frontier molecular orbitals of the quadricyclane and the spirocyclopropane fragments have incompatible symmetry, as the cyclopropane orbital lies in the nodal plane of the quadricyclane fragment.

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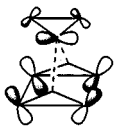
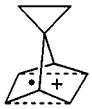




$1^{\bullet+}$

EXPERIMENTAL

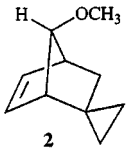
Materials and solvents. 7-(Spirocyclopropane)quadricyclane was prepared by reductive desulfonylation[8] of the Diels–Alder adduct between spiro[2,4]-hepta-4,6-diene[9] and *cis*-1,2-bis(phenylsulphonyl)ethylene. 7-Spirocyclopropanequadricyclane was prepared by benzoquinone photosensitized cyclization of 7-spirocyclopropanenorbornadiene.[10] 1-Cyanonaphthalene (Aldrich; 98%) was purified by recrystallization. Acetonitrile (Fischer) was distilled from calcium hydride. Methanol (Fischer, Spectranalyzed) was refluxed over *ca*2 g l^{-1} of sodium (freshly washed with methanol) and distilled. The solvents so dried were stored over 4A molecular sieve in brown bottles under an argon atmosphere.

Photo-reactions. Solutions containing appropriate concentrations of donor and acceptor were degassed by purging with argon for 15 min before irradiation. All irradiations were carried out in a Rayonet RPR-100 photoreactor equipped with 16 RPR-3500 lamps. The progress of the reactions was monitored by gas chromatography on a GC–MS system (HP 5890 Series II gas chromatograph interfaced with a HP 5971 mass-selective detector), using a 12 m × 0·20 mm i.d. 0·33 μm HP-1 capillary column (cross-linked methylsilicone on fused silica). Analytical runs were carried out in 5 mm NMR tubes and preparative runs in a 30 mm i.d. tube, water-cooled with a central cooling finger.

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

RESULTS

Irradiation of 1-cyanonaphthalene (CNN) as acceptor/sensitizer in the presence of 7-spirocyclopropanequadricyclane (**1**) in acetonitrile–methanol (3:1) generated two methanol adducts, 7-methoxy-5-spirocyclopropanebicylo[2.2.1]hept-2-ene (**2**, 30%) and 2-ethyl-7-methoxybicylo[2.2.1]hepta-2,5-diene (**3**, 15%), in addition to a bis-methanol adduct, 3,7-dimethoxy-6-ethylbicyclo[2.2.1]heptane (**4**, 25%). Irradiation of CNN as acceptor/sensitizer in the presence of **3** in acetonitrile–methanol (3:1) resulted in smooth conversion to the bis-methanol adduct,, **4**.



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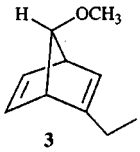

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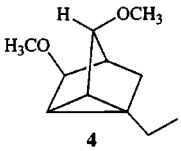

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Characterization of products

Structure assignments of the photoproducts are based on MS and NMR data. Proton NMR spectra were recorded on either a Varian XL-400 or a Varian VXR-200 spectrometer. The two mono-adducts, **2** and **3**, could be separated only with significant difficulties; they were characterized as a 2:1 mixture; there is no overlap between the signals of **2** and **3**. ^{13}C and HETCOR spectra were recorded on a Varian VXR-200 spectrometer operating at 50·3 MHz. The structural assignments are based on 1D ^{1}H, 2D COSY and ^{13}C–^{1}H HETCOR, where appropriate.

*7-Methoxy-5-spirocyclopropanebicylo[2.2.1]hept-2-ene (***2**)

^{1}H NMR: H-2, H-3, δ 6·13 ppm, d, 6·11 ppm, d (J = 2·2 Hz, H-1, H-4); H-7, δ 3·34 ppm, COSY cross peaks, H-1, H-4; CH_3O, δ 3·32 ppm, s; H-1, δ 2·74 ppm, m, including J = 3·7 Hz (H-6_{endo}), J = 2·2 Hz (H-2), J ≈ 2 Hz (H-7); H-4, δ 1.99 ppm, m, including J = 2·2 Hz (H-3), J ≈ 2 Hz (H-7); H-6_{exo}, δ 1·91 ppm, dd (^{2}J = 11 Hz, H-6_{endo}, ^{3}J = 3·7 Hz, H-1); H-6_{endo}, δ 1·15 ppm, d (^{2}J = 11 Hz, H-6_{exo}; ^{4}J ≈ 0·8 Hz, H-7); secondary cyclopropane resonances: δ 0·62 ppm, m, 2H; δ 0·36 ppm, m, 1H; δ 0·25 ppm, m, 1H. ^{13}C NMR: δ 88·5 ppm, tertiary alkoxy, C-7; δ 58·3 ppm, OCH_3.

*2-Ethyl-7-methoxybicylo[2.2.1]hepta-2,5-diene (***3**)

^{1}H NMR: H-5, H-6, δ 6·65, 6·66 ppm, d (J = 2·2 Hz, H-4, H-1); H-3, δ 5·96 ppm, bm; H-7, δ 3·54 ppm, m, including J ≈ 2 Hz (H-1, H-4); H-4, δ 3·45 ppm, m, including J = 2·2 Hz (H-5), J ≈ 2 Hz (H-3), J ≈ 2 Hz (H-7); H-1, δ 3·27 ppm, m, including J = 2·2 Hz (H-6), J ≈ 2 Hz (H-7); OCH_3, δ 3·23 ppm, s; allylic CH_2: δ 2·25 ppm, 2H, diastereotopic; δ 1·05 ppm, 3H, t (J = 7·4 Hz). ^{13}C NMR: δ 88·7 ppm, tertiary alkoxy, C-7; δ 58·2 ppm, OCH_3. MS [*m/z* (%, fragment or fragment lost)]: 150 (1, $M^{\bullet+}$), 149 (7, −H), 122 (34, $-C_2H_4$), 121 (100, $-C_2H_5$), 119 (24, $-CH_3O$), 118 (55, $-CH_3OH$), 117 (76, 149, $-CH_3OH$), 91 (74), 79 (27), 78 (12), 77 (36, C_6H_5), 65 (12), 45 (23), 39 (11).

3,5-Dimethoxy-1-ethyltricylo[2.2.1.$0^{1,6}$*]heptane (***4**)

^{1}H NMR: H-3, H-5, δ 3·59, 3·45 ppm, tertiary alkoxy ^{1}H; δ 3·36, 3·37 ppm, 2× OCH_3; H-4, δ 2·25 ppm, m, bridgehead ^{1}H between OCH_3 groups; H-7, δ 1·97 ppm, m, δ 1·38 ppm, m, geminal ^{1}H; δ 1·08 ppm, tertiary cyclopropane, H-2 or H-6; δ 1·34 ppm, 2H, 1 (J = 7·4 Hz); δ 0·9 ppm, 3H, t (J = 7·4

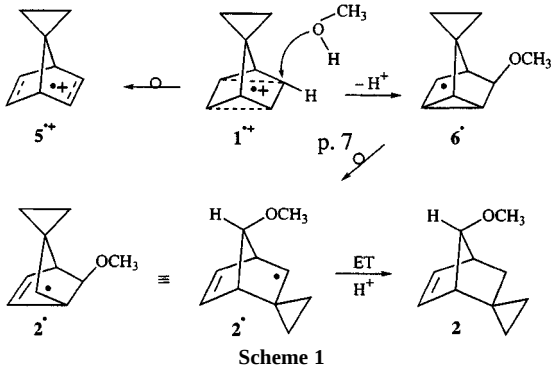
Hz), ethyl; the region 1·2–1·45 ppm shows overlapping signals due to one tertiary cyclopropane ^{1}H (H-6 or H-2), the CH_2 of the ethyl group and one of the geminal H-7. ^{13}C NMR: δ 88·9, 88[,]2 ppm, tertiary alkoxy, C-3, C-5; δ 58·2, 58·1 ppm OCH_3; δ 34·7 ppm, CH (C-4); δ 28·5 ppm, quarternary C-1; δ 27·9 ppm, CH_2; δ 20·5 ppm, CH; δ 19·4 ppm, CH_2; δ 17·4 ppm, CH; δ 17·4 ppm, CH; δ 12·1 ppm, CH_3. MS [*m/z* (%, fragment or fragment lost)]: 182 (1, $M^{\bullet+}$), 121 (11, $-OCH_3$, $-CH_2{=}O$), 109 (8), 103 (11), 91 (12), 75 (100, C_6H_3), 45 (14).

DISCUSSION

The electron transfer photo-reaction of CNN as acceptor/sensitizer with **1** generated not only the unexceptional methanol adduct, 7-methoxy-5-(spirocyclopropane)bicylo-[2.2.1]hept-2-ene (**2**) but also, in addition, the unprecedented mono-methanol adduct, 2-ethyl-7-methoxy-bicylo[2.2.1]hepta-2,5-diene (**3**), in addition to a related bis-methanol adduct, 3,7-dimethoxy-6-ethyl-bicylo[2.2.1]-heptane (**4**).

The norbornene skeleton of **2**, particularly the position of the methoxy group, is clearly supported by the ^{1}H and ^{13}C NMR spectra. The ^{1}H spectrum shows two olefinic resonances (δ 6·12 ppm; 't', J=2·2 Hz), each coupled with one bridgehead proton, H-1 and H-4, respectively. The position of the methoxy group at C-7 follows from the deshielded resonance of H-7 (δ 3·34 ppm), which is coupled to both bridgehead protons. The *syn* orientation of the methoxy group relative to the cyclopropane ring is borne out by a long-range ('W') coupling (^4J=1·8 Hz) between H-7 and the more shielded (*endo*-) proton at C-3.[11] The presence of two secondary cyclopropane carbons is indicated by the shielded resonances (δ 0·2–0·7 ppm; 4H). Product **3** lacks the secondary cyclopropane resonance; it shows, instead, an allylic ethyl function (δ 2·25 ppm, 2H; δ 1·05 ppm, 3H, t, J=7·4 Hz). Product **3** also shows three olefinic protons (δ 5·96 ppm, 1H; δ 6·65 ppm, 2H, J=2·2 Hz), a methoxy (δ 3·23 ppm) and a tertiary alkoxy resonance (δ 3·54 ppm), coupled to both bridgehead carbons. Finally, di-adduct **4** lacks olefinic resonances, but shows two tertiary cyclopropane protons (δ 1·08, 2·25 ppm), two methoxy (δ 3·36, 3·37 ppm) and two tertiary alkoxy resonances (δ 3·45, 3·6 ppm), as well as an ethyl group (δ 1·34 ppm, 2H; δ 0·9 ppm, 3H, t, J=7·4Hz).

The products reveal an interesting reaction sequence and identify the nature of the key intermediates. The reaction is initiated by electron transfer from **1** to the excited singlet state of **CNN**, generating the corresponding radical ion pair. In analogy to the parent radical cation, $\mathbf{Q}^{\bullet+}$,[5] and its 7-methylene and 7-keto derivatives,[4,6] the key radical cation, $\mathbf{1}^{\bullet+}$, may undergo three reactions: back electron transfer, (unimolecular) valence isomerization to the corresponding norbornadiene radical cation, $\mathbf{5}^{\bullet+}$, or (bimolecular) nucleophilic capture by methanol (Scheme 1). Back electron transfer lowers the efficiency of the overall reaction but does not affect the product distribution.

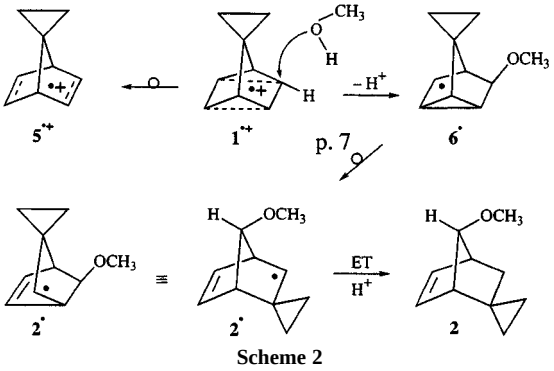


Scheme 1

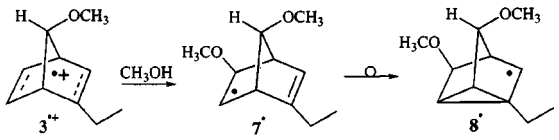
The valence isomerization of $\mathbf{1}^{\bullet+}$ to the spiro-norbornadiene radical cation, $\mathbf{5}^{\bullet+}$, has been documented;[2] its rate is slower than that of CIDNP induction ($ca 10^{-9}$ s^{-1}) and close to that of nuclear spin–lattice relaxation of free radicals (ca^{-6} s^{-+}).[12] Accordingly, the balance between valence isomerization and nucleophilic capture can be diverted by the concentration of methanol. For example, the rate constant for the addition of *tert*-butanol to quadricyclane radical cation is $k \approx 2 \times 10^6$ M^{-1} s^{-1}.[7] If the capture of $\mathbf{1}^{\bullet+}$ by methanol is similarly (or slightly more) efficient, the isomerization of $\mathbf{1}^{\bullet+}$ should be largely suppressed in the presence of 6 M methanol. Thus, $\mathbf{1}^{\bullet+}$ reacts preferentially or exclusively via nucleophilic capture, generating the methoxy-substituted free radical, 5-methoxy-7-(spirocyclopropane)-2-tricyclyl, $\mathbf{6}^{\bullet}$.

The strained free radical $\mathbf{6}^{\bullet}$ must have a very limited lifetime, since only rearranged adducts are formed. This requires that the cyclopropylcarbinyl-to-allylcarbinyl rearrangement generating $\mathbf{2}^{\bullet}$ is faster than any competing reaction that would preserve the connectivity of **1**, viz. hydrogen abstraction or electron transfer. The second rearrangement ($\mathbf{2}^{\bullet}$ to $\mathbf{3}^{\bullet}$), on the other hand, must be noticeably slower, since $\mathbf{2}^{\bullet}$ is intercepted. The conversion to the mono-adduct, **2**, could occur directly by hydrogen abstraction or by a two-step pathway, electron transfer from the sensitizer radical anion ($CNN^{\bullet}-$) to $\mathbf{2}^{\bullet}$, followed by protonation of the resulting anion, $\mathbf{2}^{-}$. Both processes are well documented[3–5] and, occasionally, compete with each other.[5] The noticeable rate difference between the rearrangement of $\mathbf{6}^{\bullet}$ to $\mathbf{2}^{\bullet}$ and that of $\mathbf{2}^{\bullet}$ to $\mathbf{3}^{\bullet}$ (or between the conversion of $\mathbf{6}^{-}$ to $\mathbf{2}^{-}$ and that of $\mathbf{2}^{-}$ to $\mathbf{3}^{-}$) is ascribed to the more limited stabilization of intermediates bearing spin or charge on a primary carbon.

The orientation of the methoxy groups in adduct **2** establishes the course of nucleophilic attack on the key intermediate, $\mathbf{1}^{\bullet+}$. The NMR data show clearly that the



Scheme 2



methoxy group of **2** is attached syn to the cyclopropane group. This stereochemistry requires stereospecific attack from the *exo* face, an approach that has been observed also in related 'substitution' reactions of cyclopropane,[13] bicyclobutane,[14] or vinylcyclopropane radical cations.[15] In each case, the alcohol attacks a one-electron bond from the backside, replacing a carbon-centered free radical as an 'intramolecular leaving group'. The radical cations have a strained-ring bond in common, containing a lengthened, formally one-electron bond, which maintains a sufficient degree of bonding to retain the stereochemical integrity of the strained ring.[16] These systems have in common that the nucleophilic substitution with replacement of carbon is favored by the release of ring strain.

The formation of **3** most likely involves an extension of the above mechanism. Since the methoxy group of **3** is attached syn to the ethyl group, in the orientation analogous to **2**, it is reasonable to conclude that **3** is formed via either **2**• or the respective anion, $\mathbf{2}^-$, and their conversion to **3**• or $\mathbf{3}^-$ by cyclopropylcarbinyl-to-butenyl rearrangement. Either rearrangement has precedent. Again, **3**• would be converted to the mono-adduct by either hydrogen abstraction or electron transfer/protonation; $\mathbf{3}^-$ simply requires protonation.

The bis(methanol)adduct, **4**, requires two separate oxidations, each followed by methanol capture with deprotonation. The fact that **4** has the ethyl group in common with **3** suggests that **4** may be derived from **3** reentering the reaction cycle. As an alkyl-substituted norbornadiene, **3** is a better electron donor than **2**, and should be preferentially oxidized. This possibility is supported by two lines of evidence: prolonged irradiation depletes **3** in favor of **4**; more directly, the electron transfer photoreaction of **3** produces **4** in excellent yield. Both experiments confirm **4** as a secondary product. The likely sequence of formation involves nucleophilic attack on the more accessible *exo* face of $\mathbf{3}^{\bullet+}$; the resulting free radical, **7**•, undergoes an allylcarbinyl-to-cyclopropylcarbinyl rearrangement, and the secondary free radical, **8**•, is converted to the bis-methanol adduct, **4**, by hydrogen abstraction or reduction/protonation[3–5] as discussed above.

In summary, the electron transfer photochemistry of 7-(spirocyclopropane)quadricyclane (**1**) in the presence of methanol proceeds via stereospecific nucleophilic capture (*exo* attack) of $\mathbf{1}^{\bullet+}$, and either one or two consecutive cyclopropylcarbinyl-to-butenyl rearrangements of the resulting free radical, **6**•. The free radicals, **2**• and **3**•, generate the products by hydrogen abstraction from the solvent or by a two-step pathway, involving electron transfer and protonation of the resulting anions, $\mathbf{2}^-$ and $\mathbf{3}^-$. Finally, the diene, **3**, reenters the reaction cycle, resulting in the formation of the diadduct, **4**. It is interesting that the rearrangments of **6**• and **2**• proceed with opening of the strained ring (type **B2•→C•**) whereas the butenyl-to-cyclopropylcarbinyl rearrangement of **7**• proceeds with formation of a cyclopropane ring (type **A•→B•**). Both modes of reaction have precedent in several free radicals formed by nucleophilic capture of norbornadiene or quadricyclane radical cations.[4–6]

ACKNOWLEDGMENTS

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