The Putative Role of Homoconjugation in Radical Cations: Electron Transfer Photochemistry of 7-Methylenenorbornadiene and 7-Methylenequadricyclane

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Received September 15, 1994[⊗]

Abstract: Photoinduced electron transfer from 7-methylenenorbornadiene, **MN**, and 7-methylenequadricyclane, **MQ**, to an excited sensitizer/acceptor in the presence of methanol generates products of several structure types. All products require nucleophilic capture of the radical cations, $\mathbf{MN}^{\bullet+}$ and $\mathbf{MQ}^{\bullet+}$, by methanol, followed by rapid rearrangements of the resulting free radicals to $\mathbf{C}^{\bullet}$ as the key intermediate. The short lifetime of the primary products of capture is ascribed to the allylic nature of their C_4-C_5 bonds. The stereochemistry of the methoxy groups in the products indicates that the nucleophile attacks $\mathbf{MQ}^{\bullet+}$ exclusively from the "exo" face ("backside" attack), whereas $\mathbf{MN}^{\bullet+}$ shows, in addition, a limited degree of attack from the "endo" face.

Introduction

The structures and reactions of organic radical cations have been the focus of much interest for over a decade.[1] Particularly the interaction between nonconjugated olefinic functions or of strained ring moieties with olefinic fragments in organic radical cations has attracted considerable interest.[2-8] A rich variety of substrates have been investigated by an array of physical and chemical techniques for the purpose of delineating changes in molecular geometry upon one-electron oxidation, assessing the spin density distribution in the resulting radical cations, and elucidating the parameters affecting the structures and reactivities of these intermediates.[2-8] Radical cations derived from substrates containing strained rings as well as olefinic moieties in suitable orientations may be stabilized by cyclic homoconjugation.

We have a long standing interest in the radical cations ($\mathbf{N}^{\bullet+}$) of norbornadiene and ($\mathbf{Q}^{\bullet+}$) of quadricyclane and have probed their structures by CIDNP studies, time-resolved ESR spectroscopy, and ab initio calculations.[9] Furthermore, to study their reactivity, we have investigated the electron transfer photochemistry of **N** and **Q**.[10] We have also investigated the role of homoconjugation in the radical cations formed from **N** and **Q** systems bearing appropriate substituents in the 7-position.[11] For the radical cation of 7-methylenenorbornadiene ($\mathbf{MN}^{\bullet+}$), CIDNP results and ab initio calculations support the importance of homoconjugation; the results indicate significant spin density on the *exo*-methylene carbon (C_8) and noticeable negative hyperfine coupling constants (hfc) for the ^1H nuclei in this position. In contrast, strong positive hfcs are suggested for the *exo*-methylene protons of $\mathbf{MQ}^{\bullet+}$ along with substantial spin density on the bridge carbon (C_7) of this radical cation. One tentative explanation for these results is an exchange interaction between the $\mathbf{Q}^{\bullet+}$ fragment and the *exo*-methylene function, although this interaction is not prominently documented as a mechanism for hyperfine coupling.[11] In this paper, we report the results of an investigation into the electron transfer induced photochemistry of 7-methylenenorbornadiene (7-**MN**) and 7-methylenequadricyclane (7-**MQ**). The products resulting from this interaction further elucidate the role of homoconjugation in the resulting radical cations, $\mathbf{MN}^{\bullet+}$ and $\mathbf{MQ}^{\bullet+}$, and provide insight into the regio- and stereochemistry of nucleophilic capture by these intermediates.

Photoinduced Electron Transfer Reactions. When electron acceptors, such as 1,4-dicyanobenzene, are irradiated in the presence of suitable donors as well as of nucleophiles, the ensuing electron transfer reactions may lead either to simple addition products[12] or to more complex products involving nucleophilic capture of the radical cation followed by aromatic substitution by the adduct radical on the sensitizer-acceptor.[13,14] These reactions are carried out by irradiating either the sensitizer-acceptor or a co-sensitizer in polar solvents in the

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1994.

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0002-7863/95/1517-0135$09.00/0

Scheme 1

EXCITATION

$$A \longrightarrow {}^1A^* \quad (1)$$

$$co\text{-}S \longrightarrow {}^1co\text{-}S^* \quad (1a)$$

ELECTRON TRANSFER

$${}^1A^* + D \longrightarrow A^{\bullet-} + D^{\bullet+} \quad (2)$$

$${}^1co\text{-}S^* + A \longrightarrow co\text{-}S^{\bullet+} + A^{\bullet-} \quad (2a)$$

$$co\text{-}S^{\bullet+} + D \longrightarrow co\text{-}S + D^{\bullet+} \quad (2b)$$

NUCLEOPHILIC CAPTURE

$$D^{\bullet+} + CH_3OH \longrightarrow (D\text{—}OCH_3)^{\bullet} + H^+ \quad (3)$$

REARRANGEMENT OF ADDUCT RADICAL

$$(D\text{—}OCH_3)^{\bullet} \longrightarrow (D_{(r)}\text{—}OCH_3)^{\bullet} \quad (4)$$

REDUCTION

$$(D_{(r)}\text{—}OCH_3)^{\bullet} + A^{\bullet-} \longrightarrow (D_{(r)}\text{—}OCH_3)^{-} + A \quad (5)$$

PROTONATION

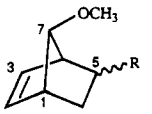
$$(D_{(r)}\text{—}OCH_3)^{-} + H^+ \longrightarrow H\text{—}D_{(r)}\text{—}OCH_3 \quad (6)$$

SUBSTITUTION

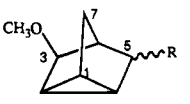
$$(D_{(r)}\text{—}OCH_3)^{\bullet} + A^{\bullet-} \longrightarrow A(\text{-}CN^-)\text{—}D_{(r)}\text{—}OCH_3 \quad (7)$$

presence of the substrate; the resulting reaction sequence appears well-established (Scheme 1).[12-14] Individual steps include photoexcitation of the acceptor (eq 1), generation of substrate radical cation by electron transfer from donor to electron acceptor (eq 2); capture of the radical cation by the nucleophile (eq 3), and reaction of the resulting free radical with the sensitizer radical anion by substitution at the ipso-carbon (eq 7). Possible reaction products include those derived simply by addition of methanol (eqs 3–6) as well as those involving further reaction with the sensitizer. The reaction sequence involving nucleophilic capture as well as coupling with the sensitizer has been denoted as photoinduced nucleophile–olefin combination aromatic substitution (photo-NOCAS).[14]

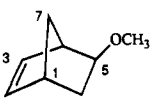
Electron transfer reactions of **N** and **Q** with 1-cyanonaphthalene (**CNN**)[15] and 1,4-dicyanobenzene (**DCB**)[10] as acceptor/sensitizer in either methanol or acetonitrile/methanol have been studied previously. With **DCB** as electron acceptor in acetonitrile/methanol, both **N** and **Q** led to the formation of methanol adducts (**1a, 2a**) and NOCAS products (**1b, 2b**). They are rationalized via the radical cations, $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$, stereospecific nucleophilic attack by methanol from the exo side, and either hydrogen abstraction from acetonitrile (→**1a,2a**) or coupling with $\mathbf{DCB}^{\bullet-}$ (→**1b,2b**) by the resulting methoxylated free radicals. The hydrogen abstraction is ascribed to the insufficient reducing ability of $\mathbf{DCB}^{\bullet-}$ and is supported by additional free-radical products and by isotopic labeling studies. With **CNN** as electron acceptor, a methanol adduct, **3a**, with unchanged carbon skeleton, was formed in addition to **1a** and **2a**; also, several cycloaddition products as well as 1:1:1 adducts containing **CNN**, **N**, and methanol were ascribed to exciplex intermediates.[10]



1 (a) R = H (b) R = *p*-C_6H_4CN



2 (a) R = H (b) R = *p*-C_6H_4CN



3

In order to evaluate the extent of homoconjugative interaction in the radical cations, $\mathbf{MN}^{\bullet+}$ and $\mathbf{MQ}^{\bullet+}$, we have investigated the electron transfer photochemistry of **MN** and **MQ** with 1,4-dicyanobenzene/phenanthrene as sensitizer and co-sensitizer, respectively. The structure and stereochemistry of the products formed from these substrates elucidate the significance of the homoconjugative interaction between the different functionalities in the corresponding radical cations and provide insight into the stereochemistry of nucleophilic capture by these intermediates. The presence of the *exo*-methylene function may change the resulting chemistry in several respects. Most importantly, the spin density in the *exo*-methylene function may result in the attack of the nucleophile at C_7 or C_8. Further, the free-radical rearrangements may be significantly affected by the potential conjugation with the olefin function. Finally, the rearranged free radicals derived from **MN** and **MQ** may be more readily reduced than their unsubstituted analogs, because they are delocalized.

Experimental Section

Materials and Solvents. Methylenequadricyclane was synthesized from 7-quadricyclanone[16,17] by Wittig reaction according to literature procedures[18] with minor modifications. Methylenenorbornadiene was prepared by valence isomerization of methylenequadricyclane catalyzed by bis(norbornadiene)palladium(II) chloride in refluxing toluene.[18] 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.

Photoreactions. Typical reaction mixtures, containing 0.1 M of the donor, 0.1 M of 1,4-dicyanobenzene, and 0.02 M of phenanthrene in acetonitrile/methanol (3/1 by volume), 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 GC interfaced with a 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 and preparative runs in 30-mm ID tubes with central cooling fingers; the reaction mixtures were water cooled.

Isolation of Products. Reaction products were isolated by both preparative GLC and liquid column chromatography. Preparative GLC was carried out on a 6-ft column packed with 10% CP-5 on a Chromosorb WHP support. Liquid chromatography was carried out using a set of 50-cm columns with IDs ranging from 1 to 5 cm. The columns were 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.

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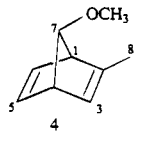
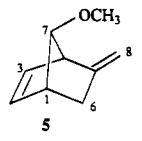
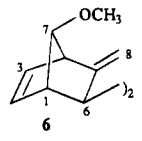
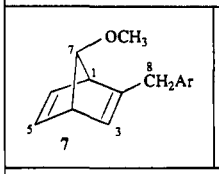
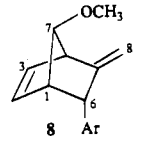
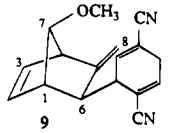
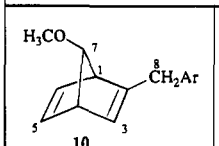
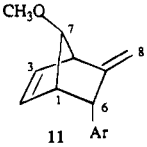
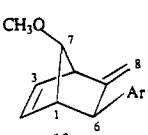
Table 1. Products of the Electron Transfer Photochemistry of 7-Methylenenorbornadiene and 7-Methylenequadricyclane

Methanol Adducts		Free Radical Dimers
 **4**	 **5**	 **6**
NOCAS – exo addition of Nucleophile		Aromatic Addition
 **7**	 **8** Ar	 **9**
NOCAS – endo Addition of Nucleophile		
 **10**	 **11** Ar	 **12**

^{13}C spectra were recorded on a Varian VXR-200 spectrometer operating at 50.3 MHz. The structural assignments are based on 1D ^1H and 2D COSY, where appropriate. Extensive NOE difference spectra were recorded to elucidate the structure and to probe substituent stereochemistry and the spatial relationship between the different functional groups. The spectral features allowing the assignment of the key products are briefly discussed below. A detailed compilation of spectral data is available as supplemental material.

Results

The electron transfer photochemistry of **MN** or **MQ** with 1,4-dicyanobenzene/phenanthrene in acetonitrile/methanol gives rise to four product types (Table 1), including (a) adducts of a net composition corresponding to addition of methanol to the substrate, (b) "dimeric" products containing two substrate molecules plus two methoxy groups, (c) adducts consisting of one molecule each of the substrate, the nucleophile (methanol), and the electron acceptor/sensitizer (DCB) without loss of HCN, and (d) adducts consisting of one molecule each of the substrate, the nucleophile (methanol), and the electron acceptor/sensitizer (DCB) with net loss of HCN (NOCAS products). **MN** and **MQ** give rise to similar reaction mixtures with small, yet significant differences as noted.

Two NOCAS products, **7** and **8**, are the most prominent products by far; they are formed in approximately 70% yield from both **MN** and **MQ**, however, in a slightly differing distribution (Table 2). A related adduct, containing a 7-methoxy function and a 6-(2,5-dicyanocyclohexa-2,5-dien-1-yl) substitutent (**9**), also is formed from both reagents. The lesser products include two simple methanol adducts, **4** and **5**; they are generated in comparable yields (3 vs 4%) from **MQ**, whereas **4** falls off significantly (<1 vs 5% for **5**) in the reaction of **MN**. In addition, a total of five "dimeric" methanol adducts are formed; these contain two substrate molecules plus two methoxy groups. They are formed in a total yield of 10% from **MQ**, but in considerably lower yield (2%) from **MN**. One of these "free radical dimers" was isolated and its structure assigned (**6**). Finally, the photoreaction of **MN** also gives rise to three additional NOCAS products, **10**–**12**, in a total yield of 7%. No such products are observed in the reaction of **MQ**.

Table 2. Product Yield (%) of the Electron Transfer Induced Photoreactions of 7-Methylenenorbornadiene and 7-Methylenequadricyclane[a]

product	4	5	6[b]	7	8	9	10	11	12
MN[c]	1	4	2	30	41	8	2	1	4
MQ[d]	3	4	10	36	33	10	0	0	0

[a] Based on GC/MS peak area percentage; reaction mixtures were irradiated with the 350 nm light of a Rayonet reactor. Reagent concentrations: [MN or MQ] = 0.1 mol/L, [DCB] = 0.1 mol/L, [Ph] = 0.02 mol/L in CH_3CN/CH_3OH (3:1 v/v). [b] There are at least five isomers of composition $C_{11}H_{22}O_2$ with essentially identical MS fragmentation patterns; isomer **6** could be isolated and was characterized. [c] At 30% conversion of MN. [d] At 20% conversion of MQ.

NMR Characterization. All products formed in the photoreactions of **MN** and **MQ** have in common a characteristic methoxy singlet (δ 3.0–3.4 ppm) and a singlet for the tertiary alkoxy α-proton at δ 3.0–3.8 ppm. In addition, the NOCAS products, **7**, **8**, and **10**–**12** show aromatic signals resembling two pairs of doublets (two protons each, $J \approx 8.2 - 8.4$ Hz) for the *p*-cyanophenyl group.

Products **4** and **7** are characterized by three endocyclic olefinic signals typical for a 2-alkylnorbornadiene,[19] i.e., a broad signal (δ ~6.0 ppm) and two mutually coupled signals at lower field (δ 6.5–6.7 ppm). Products **5**, **6**, **8**, and **9** have four olefinic signals typical for a 5-methylenenorbornene,[20] i.e., the two exocyclic protons resonate between δ 4.7–5.1 ppm, whereas the endocyclic protons show two mutually coupled resonances in the range δ 5.7–6.3 ppm. The presence of two double bonds in products **4**–**9** causes the resonances of the (doubly allylic) bridgehead protons to be significantly deshielded, close to the signal of the tertiary alkoxy proton. The detailed assignment rests on 2D COSY and NOE difference spectra.

The spectrum of the dimeric product **6** is similar to that of product **5** except that the signals of the geminal pair of protons at C_6 (H_{6x}, H_{6n}) are replaced by a single resonance (δ 2.42 ppm). The fact that this signal fails to show noticeable coupling with the bridgehead proton (H_1) identifies H_6 as occupying an *endo* position. Finally, product **9** (molecular ion *m/e* 264) shows two additional downfield olefinic resonances (δ 6.68 and 6.91 ppm) and two additionally doubly allylic resonances [δ 3.06 (1H), 3.66 (2H)], as expected for the 2,4-dicyanocyclohexa-2,4-dienyl group.

The spatial orientation of methoxy at C_7 is a key probe for the preferred direction of attack by methanol on the intermediate radical cation. The orientation of the methoxy group was deduced mainly from NOE experiments. For product **5**, the resonances of H_7 and H_{6n} show a weak cross peak in the 2D COSY spectrum, apparently due to "W-shape" long-range (^4J) coupling.[21] This orientation is possible only with the methoxy group positioned *anti* to the endocyclic double bond. For product **6**, only the *syn* relationship of methoxy and C_6 can account for the observed weak NOE enhancement of the methoxy signal upon irradiation of the H_6 resonance. For product **7**, the NOE enhancement observed for H_5 and H_6 upon preirradiation of H_7 indicates the spatial proximity of these nuclei and establishes the *syn* relationship between the methoxy and *p*-cyanobenzyl groups. The orientation of the methoxy functions in products **8** and **9** was established based on the NOE enhancement of the H_2 and H_3 signals upon pre-irradiation of the respective H_7 resonances. Similarly, the *endo* position of the aryl group of product **8** was established according to the

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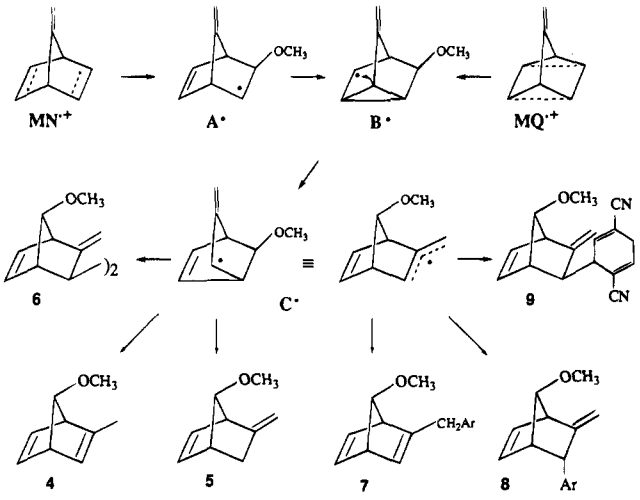
Scheme 2



noticeable NOE enhancement of methoxy signal upon irradiation of the (*exo*)-H_6 resonance. For product **9**, the presence of dicyanocyclohexadienyl group in the *exo* position was established by the NOE enhancement of an endocyclic olefinic proton [6.14 ppm (H_2)] upon pre-irradiation of H_6. Accordingly, H_6 must occupy the *endo* position.

Concerning the three NOCAS products formed only from MN, the ^{1}H NMR spectrum of **10** shows essentially the same features as that of its stereoisomer **7**. Its identification is tentative, since it was not isolated in sufficient quantity to allow thorough characterization. Products **11** and **12** differ from their stereoisomer **8** by the stereochemistry at C_7 (**11**) and C_6 and C_7 (**12**), respectively. The ^{1}H NMR spectroscopic features of all three compounds are very similar. NOE experiments were instrumental, once again, in delineating the key stereochemical differences. For product **11**, the strong NOE interactions between H_6 and H_7 revealed their proximity, which is possible only when the methoxy group is *syn* to the endocyclic double bond and the aryl group is in the *endo* position. For product **12**, preirradiation of H_7 resulted in strong NOE enhancements of the methoxy group and the *o*-aryl resonance at 7.47 ppm, establishing that the aryl group occupies the *exo* position and that the methoxy group is *syn* to the endocyclic double bond. The orientation of the aryl group was further confirmed by the strong NOE enhancement of the endocyclic olefinic proton H_2 upon irradiation of H_6, which, therefore, must be attached on the *endo* face.

Discussion

The structure and stereochemistry of the products formed from **MN** and **MQ** elucidate the significance of the homoconjugative interaction between the different functionalities in the corresponding radical cations and provide insight into the stereochemistry of nucleophilic capture by these intermediates. The methanol adducts and NOCAS products derived from **N** and **Q** provide the background for these assignments and serve as an interesting comparison.

The reaction products isolated from the electron transfer induced photoreactions of **MN** and **MQ** belong to four different structure types, including the following: two methanol adducts **4** and **5**; the bis-methoxy substituted "dimer", **6** (and its isomers), apparently formed via free-radical dimerization; two NOCAS products, **7** and **8**; and the unusual aromatic addition product **9** (Scheme 2). Altogether, products, **4**–**9** amount to 85% of the overall yield with **MN**, and to >95% with **MQ** as starting material. When **MN** serves as starting material, three additional NOCAS products, **10**–**12**, are obtained in low yields (~7% combined). These adducts differ from the major NOCAS products by the stereochemistry of the methoxy substituent. A plausible reaction mechanism for the sensitized electron transfer photochemistry of **MN** and **MQ** must account for the structure and stereochemistry of all products, and for any differences to the results observed for **N** and **Q**. All individual steps must be energetically feasible.

We will discuss the observed products in terms of a mechanism involving the following steps: (a) generation of the radical cations, **MN**$^{\bullet+}$ and **M**$^{\bullet+}$; (b) nucleophilic capture of the radical cations by methanol (Scheme 1, eq 3); (c) rearrangements and competing reactions of the primary free radicals (eqs 4–7); and (d) the formation of the various products.

Generation of Radical Cations. The free energy of formation of radical ion pairs by electron transfer from a donor to an acceptor excited state is dictated by the excited state energy, $E_{(0,0)}$, the reduction potential of the acceptor, $E_{(A^{\bullet-}/A)}$, and the oxidation potential of the donor, $E_{(D/D^{\bullet+})}$, as given by the Rehm-Weller equation:[22]

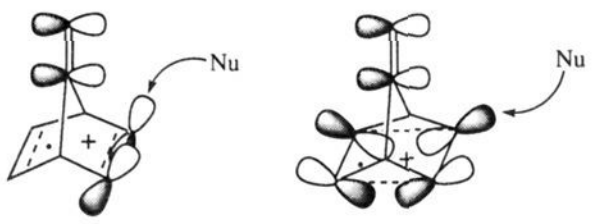
$$-\Delta G = E_{(0,0)} - E_{(D/D^{\bullet+})} + E_{(A^{\bullet-}/A)} + e^2/\epsilon a \qquad (1)$$

where the $e^2/\epsilon a$ term accounts for ion pairing. The sensitizer employed in the current study, **DCB**, has an excitation energy, $E_{(0,0)} = 4.29$ eV,[23] and a reduction potential, $E_{A^{\bullet-}/A} = -1.6$ V.[24] The oxidation potentials of the two substrates are not known but can be approximated by the oxidation potentials of **N** and **Q**. The Stern–Volmer constants of the four quenchers clearly show that the presence of the 7-methylene group in **MN** or **MQ** does not significantly alter their quenching abilities relative to those of **N** and **Q**.[11] Given the oxidation potential of **N** ($E_{D/D^+} = 1.5$ V)[25] and **Q** ($E_{D/D^+} = 0.9$ V),[25] the electron transfer from either substrate to ^{1}**DCB*** is strongly exergonic ($\Delta G = -1.2$ and -1.8 eV, respectively).

Although these considerations suggest that electron transfer from **MN** and **MQ** to ^{1}**DCB*** is viable, we did not approach the radical ions this way for the following reasons. First, the irradiation of **DCB** requires light of $\lambda \leq 300$ nm; these conditions cause **MN** to undergo side reactions in methanol solution even in the absence of DCB. Second, use of **DCB** as sensitizer causes a slow conversion of **MQ**. Third, light of $\lambda \leq 300$ nm will be absorbed by any products derived from DCB, particularly by any of the NOCAS products; this may cause secondary photoreactions. In order to avoid these potential complications, we elected an alternative approach to **MN**$^{\bullet+}$ and **MQ**$^{\bullet+}$ with phenanthrene (**Phen**) as a co-sensitizer in conjunction with DCB as electron acceptor. With light of $\lambda \geq 350$ nm, **Phen** serves as the only light-absorbing substance (Scheme 1; eq 1a). The excitation energy of **Phen**, $E_{(0,0)} = 3.58$ eV,[24] and its oxidation potential, $E_{D/D^{\bullet+}} = 1.58$ V,[24] renders the electron transfer from ^{1}**Phen*** to **DCB** exergonic by ~0.4 eV; this process should be efficient (Scheme 1; eq 2a). Once **Phen**$^{\bullet+}$ is formed, the generation of **MN**$^{\bullet+}$ and **MQ**$^{\bullet+}$ requires a secondary electron transfer from **MN** or **MQ** to **Phen**$^{\bullet+}$ (Scheme 1; eq 2b). Judged by the oxidation potential of **Phen** compared to those of **MN** or **MQ**, the electron transfer from **MQ** to **Phen**$^{\bullet+}$ is exergonic by ~0.7 eV and, thus, should be efficent.

(22) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 257.
(23) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931.
(24) Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233.
(25) Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

Scheme 3



On the other hand, the electron transfer from **MN** to **Phen**$^{\bullet+}$ is essentially thermoneutral; its completion may be aided by a fast nucleophilic attack on **MN**$^{\bullet+}$.

Nucleophilic Capture of Radical Cations by Methanol. All products isolated from the electron transfer induced photoreactions of **MN** and **MQ** contain the methoxy group, documenting the importance of nucleophilic capture as a primary radical cation reaction. The stereochemistry of the methoxy group in the products is of the utmost significance as it delineates the approach of the nucleophile to the radical cations. For the majority of products (**4**−**9**, ~85% yield from **MN**, >95% from **MQ**) the methoxy group occupies the position anti to the endocyclic double bond. This finding indicates that the attack of the nucleophile occurs from the exo face. Thus, the primary attack on **MN**$^{\bullet+}$ and **MQ**$^{\bullet+}$ is analogous to that established for **N**$^{\bullet+}$ and **Q**$^{\bullet+}$. It is noteworthy that no products were isolated that would identify the *exo*-methylene function as a target of nucleophilic capture. Although both CIDNP studies and ab initio calculations had indicated that the *exo*-methylene function participates in delocalizing spin (and charge) of at least one of the radical cations (**MN**$^{\bullet+}$),[11] this apparently does not manifest itself in the observed reactivity.

One of the most significant features of the photoreaction of **MN** is the formation of the three minor NOCAS adducts, **10**, **11**, and **12**, which are observed from **MN** only. These products differ from the major NOCAS adducts, **7** and **8**, by an inverted stereochemistry of the methoxy groups, syn to the endocyclic double bond. This stereochemistry requires attack of the nucleophile from the opposite, endo face of **MN**$^{\bullet+}$, in contrast to the exo approach leading to **4**−**9** (Scheme 3). The fact that products **10**−**12** are formed from **MN**, though in low yields, but not from **MQ**, leads to the conclusion that the nucleophile can attack **MQ**$^{\bullet+}$ only from the exo face. Apparently, the nucleophilic ring opening of the cyclopropane function of **MQ**$^{\bullet+}$ occurs exclusively by back-side attack with inversion of configuration (Scheme 3). This conclusion is fully compatible with several analogous nucleophilic capture (substitution) reactions of radical cations. For example, nucleophilic attack on 1-aryl-2-alkylcyclopropane radical cations,[26,27] capture of sabinene radical cation (a vinylcyclopropane derivative),[28] and attack on two isomeric tricyclane radical cations[29,30] all show this stereochemistry.

Rearrangements and Competing Reactions of the Primary Free Radicals. Another significant feature of the photoreactions of **MN** and **MQ** lies in the fact that all products derived from either **MN** or **MQ** have a rearranged carbon skeleton; the major products (**4**−**9**) are derived from the rearranged, allylic free radical **C**$^{\bullet}$, whereas the lesser products (**10**−**12**) are derived from the rearranged, allylic free radical **G**$^{\bullet}$. Apparently, the primary adducts, **A**$^{\bullet}$ (and **E**$^{\bullet}$) derived from **MN**$^{\bullet+}$ and **B**$^{\bullet}$ derived from **MQ**$^{\bullet+}$, rearrange efficiently to **C**$^{\bullet}$ (and **G**$^{\bullet}$), certainly faster than either the reduction (Scheme 1; eq 5) or the substitution (Scheme 1; eq 7).

The conversion of the primary free radicals to **C**$^{\bullet}$ and **G**$^{\bullet}$ is, of course, favored by their allylic stabilization, one of the manifestations of the *exo*-methylene function. Although this group has only a marginal effect on the oxidation potentials of **MN** or **MQ** (vide supra), it dramatically changes the relative stability of the methoxy-substituted radicals, **A**$^{\bullet}$ − **C**$^{\bullet}$ and **E**$^{\bullet}$ − **G**$^{\bullet}$ and also affects the redox properties of these species. The allylic radical is more stable than a nonallylic secondary alkyl radical by ≥10 kcal/mol.[31] The allylic stabilization causes **C**$^{\bullet}$ (and **G**$^{\bullet}$) to become the preferred intermediates and eliminates essentially all products derived from **A**$^{\bullet}$ and **B**$^{\bullet}$ as well as **E**$^{\bullet}$ and **F**$^{\bullet}$ (Schemes 2 and 4).

The increased stability of **C**$^{\bullet}$ (and **G**$^{\bullet}$) and the changed energetics of its reactions affect the subsequent reactions in several ways. In particular, the mechanism leading to the methanol adducts (**4** and **5**) is altered relative to the analogous reactions of the parent compound. In the photoreaction of **N** and **Q** the free radical intermediates complete the adduct formation by hydrogen abstraction from acetonitrile, as demonstrated by isotopic labeling experiments and by the identification of products clearly derived from cyanomethyl radicals. Because the allylic C−H bond (of **C**$^{\bullet}$) is considerably weaker than the C−H bond of acetonitrile,[32] the hydrogen abstraction is rendered unfavorable. On the other hand, the reduction potentials of allyl radicals are slightly more positive than those of secondary or tertiary radicals,[33] causing the electron transfer from **DCB**$^{\bullet-}$ to the allyl radical to be more favorable. In addition, the internal reorganization energy of the allyl radical to the corresponding anion is considerably smaller than that of converting a secondary or tertiary alkyl radical to an alkyl anion.[33,34] Combined, these factors favor the reduction of allyl radicals, **C**$^{\bullet}$ and **G**$^{\bullet}$, to the corresponding anions, **C**$^{-}$ and **G**$^{-}$. This conclusion is born out by experiments using methanol-*O-d* as nucleophile, which resulted in the complete incorporation of deuterium into the methanol adducts.

Products **4** and **5** can be ascribed to protonation at the internal and terminal carbons, respectively, of the anion **C**$^{-}$. The significantly lower yield of product **4** in the reaction of **MN** compared to that of **MQ** (Table 2) is ascribed to its depletion due to quenching; **4** should be a slightly better electron donor and, thus, a better quencher than **N**; therefore, it may be oxidized in competition with **MN**. Compared with **MQ**, on the other hand, **4** should be a less efficient quencher/electron donor, hence its accumulation in the reaction of **MQ**.

Although these results indicate that the reduction of **C**$^{\bullet}$ by **DCB**$^{\bullet-}$ has become viable, this reaction does not compete effectively with the formation of NOCAS products via aromatic substitution on DCB$^{\bullet-}$, which accounts for the major fraction of the products. Products **7** and **8** are formed by attack of the internal and terminal center of **C**$^{\bullet}$, respectively, on the radical anion, **DCB**$^{\bullet-}$. The attack of the internal carbon occurs from the endo face exclusively; apparently, the exo face is blocked by the 7-methoxy function (Scheme 5). As was the case for product **4**, the yield of product **7** is lower in the reaction of **MN** (Table 2). For the reasons discussed above for **4**, **7** may

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(28) Weng, H.; Sethuraman, V.; Roth, H. D. *J. Am. Chem. Soc.* **1994**, *116*, 7021.
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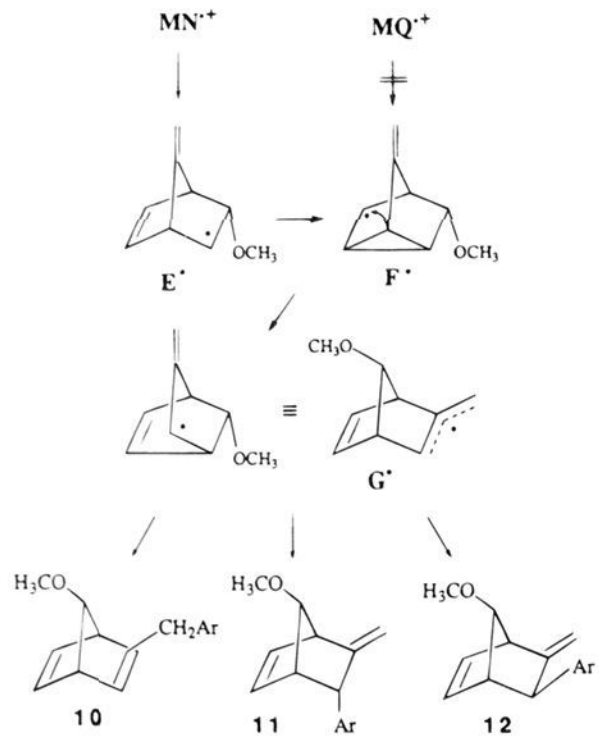
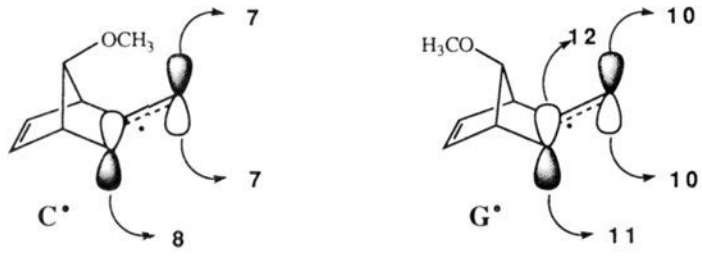
(33) (a) Occhialini, D.; Kristensen, J. S.; Daasbjerg, K.; Lund, H. *Acta Chem. Scand.* **1992**, *46*, 474. (b) Occhialini, D.; Pedersen, S. U.; Lund, H. *Acta Chem. Scand.* **1990**, *44*, 715.
(34) Mikkelsen, K. V.; Pederson, S. U.; Swanstron, P.; Lund, H. *J. Phys. Chem.* **1991**, *95*, 8892.

Scheme 4



Scheme 5



also compete with the reactions of **MN**, although the *p*-cyanophenyl moiety may retard its depletion somewhat. The depletion of products **4** and **7** is further supported by the appearance of trace products with molecular ion peaks of *m/z* 269, corresponding to NOCAS products of **4** or methanol adducts in **7** in the later stages of the **MN** reaction.

The stereochemistry of the three minor NOCAS products, **10**−**12**, indicates attack of the nucleophile from the endo side of the substrate, generating **E**•, which rearranges rapidly to **G**• (Scheme 4). Attack of the internal and terminal centers of **G**•, respectively, on **DCB**•⁻ leads to three NOCAS products. Two of the resulting products, **10** and **11**, are analogous to **7** and **8** with changed stereochemistry at the carbon bearing the methoxy group. The third product, **12**, corresponds to **8** with a change in two stereocenters, bearing the methoxy and *p*-cyanophenyl groups. Apparently, the internal carbon of the allyl function in **G**• can couple on the endo (→ **11**) or exo face, as the potential interference by the 7-methoxy group has been removed (Scheme 4). In fact, the exo attack generating **12** is now preferred. The failure to observe any methanol adduct resulting from endo attack is in line with the low yield of these adducts following exo attack. Given a similar ratio of reduction/protonation **(4, 5)** to substitution **(7, 8)** as documented for exo attack, the yield of methanol adducts from endo attack is expected to be negligible (<1%).

Two further reactions of the allylic free radical **C**• remain to be discussed, the apparent free radical dimerization, generating **6**, and the addition to the sensitizer, giving rise to **9**. The dimerization reaction indicates that the more familiar reactions of the allylic free radical, **C**•, aromatic substitution and reduction/protonation, are slow. Interestingly, **6** is yet another product, which is obtained in significantly higher yields with **MQ** than with **MN** as substrate. As discussed before, the quenching ability of some reaction products, including the dimers, may be comparable to **MN**, causing them to be depleted in the reaction of **MN**. On the other hand, their quenching abilities are inferior to that of **MQ**, allowing them to accumulate with **MQ** as starting material.

Finally, the aromatic addition product, **9**, containing the 2,5-dicyanocyclohexa-2,5-dien-1-yl function at C_6, belongs to a structure type which has been observed (or reported) less frequently than the NOCAS type. We have isolated only one related adduct in the electron transfer photoreaction of sabinene.[28] The aromatic addition product, **9**, can be explained via an attack of **C**• at the ortho position of either the sensitizer or its radical anion.

Conclusion

A detailed analysis of the products formed in the electron transfer photochemistry of 7-methylenenorbornadiene **(MN)** and 7-methylenequadricyclane **(MQ)** identifies nucleophilic capture as a significant reaction of the corresponding radical cations but fails to provide any indication that the *exo*-methylene function can be a target for this reaction. Only the olefinic carbons of **MN**•⁺ and the corresponding cyclopropane carbons of **MN**•⁺ are attacked. However, the 7-substituent significantly influences the reactivity of the resulting free radicals. Because of the allylic nature of the rearranged free radicals, **C**• and **G**•, they are favored relative to their isomers, both **A**•, **B**• and **E**•, **F**•, so that all products are derived from these two species. In addition, the more positive reduction potential of **C**• alters the pathway by which the methanol adducts, **4** and **5**, are formed.

Acknowledgment. Generous support of this work by the National Science Foundation through grants NSF CHE-9110487 and -9414271 and an equipment grant NSF CHE-9107839 is gratefully acknowledged.

Supplementary Material Available: Tables of ^{1}H and ^{13}C NMR spectral assignments, including 1D NOE and 2D COSY data for products **4**−**12** (9 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.

JA943048J