Electron Transfer Photochemistry of Norbornadiene and Quadricyclane. Nucleophilic Capture of Radical Cations, Free-Radical Rearrangements, and Hydrogen Abstraction

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The photoinduced electron donor–acceptor reactions between norbornadiene (**N**) or quadricyclane (**Q**) and acceptor/sensitizers generate products of several structure types, depending on the nature of sensitizers and solvents. Irradiation of 1,4-dicyanobenzene (**DCB**) in acetonitrile/methanol leads to methanol adducts **2** and **3**, NOCAS products **4**–**7**, and two acetonitrile adducts **8** and **9**, which are formed only from **N**. The products are rationalized via stereospecific nucleophilic attack by methanol on the radical cations, $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$, from the exo-face. The resulting free radicals, *exo*-3-methoxybicyclo[2.2.1]hept-5-en-2-yl ($\mathbf{N}^{\bullet+} \rightarrow CH_3O\text{–}\mathbf{B}^{\bullet}$) and *anti*-5-methoxytricyclo[2.2.1.0^{2,6}]heptan-3-yl ($\mathbf{Q}^{\bullet+} \rightarrow CH_3O\text{–}\mathbf{C}^{\bullet}$) undergo rapid molecular rearrangements to $CH_3O\text{–}\mathbf{C}^{\bullet}$ and *syn*-7-methoxybicyclo[2.2.1]hept-5-en-2yl, ($CH_3O\text{–}\mathbf{E}^{\bullet}$), respectively, before forming products **2**–**7**. The methanol adducts **2** and **3** are ascribed to hydrogen abstraction by $CH_3O\text{–}\mathbf{C}^{\bullet}$ and $CH_3O\text{–}\mathbf{E}^{\bullet}$, most likely due to the insufficient reducing ability of $\mathbf{DCB}^{\bullet-}$. The abstraction reaction is supported by isotopic labeling studies and by acetonitrile adducts **8** and **9** formed by attack of $^{\bullet}CH_2CN$ on **N**. The reduced singlet energy of 1-cyanonaphthalene (**CNN**) causes the electron transfer from **N** to be less favorable, whereas the reducing ability of $\mathbf{CNN}^{\bullet-}$ is increased. The reaction leads to methanol adducts **1**–**3**, [2 + 2]-cycloadducts, and several 1:1:1 adducts of **CNN**, **N**, and methanol. The formation of methanol adducts is initiated by nucleophilic capture of the radical cations; isotopic labeling studies suggest a competition between hydrogen abstraction and reduction/protonation mechanisms.

Introduction

Structures and reactions of organic radical cations have been the focus of much interest for more than two decades.[1,2] Particularly the interaction between two or more adjacent moieties, either strained rings or olefinic fragments, in organic radical cations has been of much interest.[3–8] A wide range of substrates has been investigated by physical and chemical techniques to delineate 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.[3–8]

The valence isomers, norbornadiene (**N**) and quadricyclane (**Q**), have been the target of considerable attention for the past two decades. Both systems contain two identical groups, either ethene units or cyclopropane moieties, held rigidly in orientations allowing the study of through-space or through-bond interactions, respectively.[9] The valence isomers also have received attention because of their potential for the storage of solar energy[10] or as the basis of an optical memory system.[11] The corresponding radical cations, $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$, also have long been a target of interest.[12] In this paper, we report results of an investigation into the electron donor/acceptor photochemistry of **N** and **Q**. The products resulting from this interaction support the intermediacy of exciplexes as well as radical cations, elucidate the stereochemistry of nucleophilic capture by radical cations,

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Scheme 1

Excitation

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

Electron Transfer

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

Nucleophilic Capture

$$D^{\bullet+} + CH_3OH \longrightarrow CH_3O{-}D^{\bullet} + H^+ \quad (3)$$

Reduction

$$CH_3O{-}D^{\bullet} + A^{\bullet-} \longrightarrow CH_3O{-}D^- + A \quad (4)$$

Protonation

$$CH_3O{-}D^- + H^+ \longrightarrow CH_3O{-}D{-}H \quad (5)$$

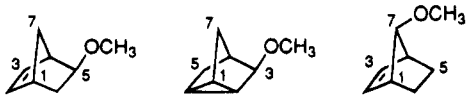
Coupling/Substitution

$$CH_3O{-}D^{\bullet} + A^{\bullet-} \longrightarrow CH_3O{-}D{-}A^- \quad (6)$$

give insight into free-radical rearrangements, and show that the solvent serves as a target for hydrogen abstraction.

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[13] or to more complex products involving nucleophilic capture of the radical cation followed by aromatic substitution by the adduct radical on the sensitizer–acceptor.[13e,14] These reactions are carried out by irradiating a sensitizer–acceptor in polar solvents in the presence of the substrate; the resulting reaction sequence appears well-established (Scheme 1).[13,14] Individual steps include the following: photoexcitation of the acceptor (eq 1); generation of the donor radical cation by electron transfer (eq 2); capture of the radical cation by the nucleophile (eq 3); and reduction of the resulting free radical by the sensitizer radical anion (eq 4) followed by protonation (eq 5). The reduction/protonation pathway is supported by quantitative deuterium incorporation into the methanol adducts in experiments employing CH_3OD as nucleophie.[13d,f] Alternatively, the free radical may react with the sensitizer radical anion by coupling at the ipso-carbon (eq 6) followed by loss of cyanide ion. The reaction sequence involving nucleophilic capture (eq 3) as well as coupling with the sensitizer (eq 6) has become known as photoinduced nucleophile-olefin-combination-aromatic-substitution (photo-NOCAS).[14]

The electron transfer reaction of **N** with 1-cyanonaphthalene (**CNN**) as acceptor in methanol has been studied previously; it led to net addition of methanol to the electron donor, with unchanged (**1**) or rearranged carbon skeleton (**2, 3**).[12e] Apparently, the rearrangement occurs after nucleophilic capture of the substrate-derived radical cation. For the reaction of **Q** under the same reaction conditions, rapid isomerization to **N** was reported,[12e] without nucleophilic capture of the well-established radical cation, $\mathbf{Q}^{\bullet+}$.[12b,c,15] These results seem to be at odds with recent findings which show clearly that capture of $\mathbf{Q}^{\bullet+}$ even by *tert*-butyl alcohol is competitive with isomerization to $\mathbf{N}^{\bullet+}$.[15] In order to resolve the apparent discrepancy, we have reinvestigated the 1-cyanonaphthalene-sensitized photochemistry of **N** and **Q**. We have also studied their reactions with 1,4-dicyanobenzene (**DCB**) as sensitizer in the presence of phenanthrene (**Ph**) as cosensitizer, which we found to be efficient in reactions with other donor systems, including several vinylcyclopropane derivatives.[16]



1 2 3

Experimental Section

Materials and Solvents. Norbornadiene (Aldrich; 99%) was purified by fractional distillation; quadricyclane (Aldrich; 99%) was used as received. Phenanthrene and 1,4-dicyanobenzene (both from 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 sieves in brown bottles under argon atmosphere. Methanol-d_1 (Aldrich, 99.5+ atom % D) was used as received; its purity was confirmed by NMR.

Photoreactions. Solutions containing appropriate concentrations of the donor, the sensitizer, and a cosensitizer were purged with argon for 15 min before irradiation. All irradiations were carried out in a Rayonet RPR-100 photoreactor equipped with 16 RPR-3500 or RPR-3000 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 × 0.2mm × 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 caps, preparative runs in 30-mm i.d. tubes with central (water) cooling fingers.

Three different combinations of sensitizers and solvents were employed. Reaction A was carried out with solutions containing 0.2 M donor, 0.1 M 1,4-dicyanobenzene, and 0.02 M phenanthrene in acetonitrile/methanol (3/1 by volume); reaction B was carried out under the conditions of Gassman and Olson,[12e] with 0.47 M donor and 0.22 M 1-cyanonaphthalene (**CNN**) in methanol; reaction C was run with 0.1 M donor and 0.1 M **CNN** in acetonitrile/methanol (3/1 by volume). The reaction mixtures of reaction type A were irradiated with 350 nm light; those of types B and C were performed with 300 nm light.

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Table 1. Product Yields of the Photosensitized Reactions of Norbornadiene and Quadricyclane

		product distribution (%)[a]											
		CH_3OH adducts			photo-NOCAS products				CH_3CN adducts		CNN	1:1:1	2:1
reagents	solvents	1	2	3	4	5	6	7	8	9	adducts[b]	adducts[c]	adducts[d]
N, DCB/Ph	CH_3CN/CH_3OH	<1	18	24	6	5	6	3	3	7			13
Q, DCB/Ph	CH_3CN/CH_3OH	<1	33	42	5	4	4	2	–	–			–
N, CNN	CH_3OH	4	3	3							~50	~35	
	CH_3CN/CH_3OH	5	13	14					<1	2	~40	~20	trace
N, CNN[e]	CH_3OH	10	33	33									

[a] Normalized product distribution according to GC peak area percentage. [b] Combined yield of [2 + 2] cycloadducts between **CNN** and **N**. [c] Combined yield of adducts containing **N**:**CNN**:CH_3OH in the ratio 1:1:1. [d] Combined yield of 2:1 adducts between **N** and CH_3OH. [e] Reference 12e.

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 i.d.'s ranging from 1 cm 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.

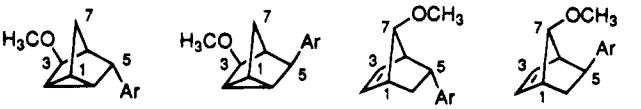
Deuterium Incorporation Experiments. In order to probe the final step in the formation of the methanol adducts (**1**–**3**), the photoreactions were carried out under the different experimental conditions, with CH_3OD as nucleophile. In the resulting reaction mixture, the ratio of ions $m/z = 125$ ($C_8H_{11}DO$) to $m/z = 124$ ($C_8H_{12}O$) observed for each adduct was corrected for contributions to the $m/z = 125$ peak due to $C_8H_{12}O$ containing ^{13}C at natural abundance and to the $m/z = 124$ peak due to M − 1 fragmentation (loss of ^1H) of $C_8H_{11}DO$. The correction for the presence of ^{13}C is the same for all adducts (for C_8, $8 \times 1.1/100 = 0.088$).[17] The extent of M − 1 fragmentation, on the other hand, differs significantly; adducts **1**, **2**, and **3** showed (M − 1)/M ratios of 0.085, 0.43, and 0.24, respectively. With these corrections, the ratio of D/H was calculated according to eq 7; the results are summarized in Table 2.

$$\frac{D}{H} = \frac{A_{125}/A_{124} - 0.088}{1 - (M-1)/M \times A_{125}/A_{124}} \qquad (7)$$

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. ^{13}C spectra were recorded on a Varian VXR-200 spectrometer operating at 50.3 MHz. The structural assignments are based on ^1H and ^{13}C spectra as well as 2D COSY, where appropriate. Extensive NOE difference spectra were recorded to elucidate structural details, particularly, 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.

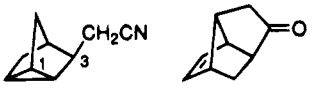
Results

Electron Transfer Photochemistry of Norbornadiene and Quadricyclane. Reaction A. The irradiation of 1,4-dicyanobenzene/phenanthrene (**DCB/Ph**) as sensitizer/cosensitizer with **N** and **Q**, respectively, in acetonitrile/methanol (3:1) as solvent/nucleophile system gave rise to two addition products **2** and **3** and to four NOCAS products **4**–**7** (Table 1). Two of the NOCAS products have bicyclo[2.2.1]hept-2-ene structures with a 7-methoxy substituent anti to the double bond and a 5-*p*-cyanophenyl group (Ar) in either endo- (**6**) or exo-orientation (**7**). The remaining NOCAS products have tricyclo[2.2.1.$0^{2,6}$]heptane structures with *exo*-7-methoxy groups and a 5-*p*-cyanophenyl group in either endo- (**4**) or exo-position (**5**).



4 **5** **6** **7**

In addition, the reaction of **N**, but not that of **Q**, also gave rise to a product, **8**, corresponding to the net addition of acetonitrile, H−CH_2CN, to a rearranged carbon skeleton, and a (tricyclic) imine, **9**, of the same composition ($C_9H_{11}N$; parent peak, m/e 133). Upon chromatography on silica gel this product is converted to the tricyclic ketone **10**. Products **8** and **9** were formed only in the presence of methanol.



8 **10**

The reaction of **N**, but not **Q**, also gave rise to a mixture of several products containing two C_7H_8 molecules plus one molecule of methanol. The individual components showed very similar chromatographic behavior; we did not succeed in the separation of the components.

Reaction B. Irradiation of 1-cyanonaphthalene (**CNN**) in the presence of **N** in methanol produced methanol adducts **1**, **2** and **3** in yields of 4, 3, and 3%, respectively, significantly lower than the reported values of 10, 33, and 33%.[12e] The sensitizer, **CNN**, was consumed in this reaction and two types of molecular adducts, containing either **N** and **CNN** in a ratio of 1:1 (M^+ m/z 245; in ~45% combined yield) or composed of **N**, **CNN**, and CH_3OH in a ratio of 1:1:1 (M^+ m/z 277; in ~35% yield), were formed as the major products. The structure and stereochemistry of the products containing **CNN** probe some interesting mechanistic aspects concerning the reactivities of exciplex intermediates.

Reaction C. The irradiation of 1-cyanonaphthalene in acetonitrile/methanol (3:1) containing 0.1 mol of **N** led to increased yields of methanol adducts (**1**, 5%; **2**, 14%; **3**, 13%). Again, the 1:1 (~35%) and 1:1:1 adducts (~25%) were formed in significant yields. In addition, minor amounts of the acetonitrile adducts **8** (2%) and **9** (<1%) and trace amounts of adducts containing **N** and CH_3OH in a ratio of 2:1 were observed.

Deuterium Incorporation Experiments. The different reaction conditions with CH_3OD as nucleophile

(17) McLafferty, F. W. *Interpretation of Mass Spectra*, 2nd ed.; University Science Books: Mill Valley, Califonia, 1980; Chapter 2.

Table 2. Deuterium Incorporation in Methanol Adducts

reagents	solvents	deuterium incorporation (%) 1	2	3
N, DCB/Ph	CH_3CN/CH_3OD		4 ± 2	4 ± 2
Q, DCB/Ph	CH_3CN/CH_3OD		4 ± 2	4 ± 2
N, DCB	CH_3CN/CH_3OD		4 ± 2	3 ± 2
N, CNN	CH_3OD	96 ± 5	47 ± 2	50 ± 2
	CH_3CN/CH_3OD	85 ± 5	32 ± 2	29 ± 2

resulted in different degrees of deuterium incorporation. With **DCB** as electron acceptor in CH_3CN/CH_3OD (reaction A), minimal deuterium incorporation was observed for adducts **2** and **3**; the yield of adduct **1** was too low to allow an accurate measure of deuterium incorporation. On the other hand, **CNN** sensitization (reactions B, C) resulted in significant deuterium incorporation for all methanol adducts; particularly adduct **1** showed essentially quantitative deuterium incorporation (Table 2).

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 ^1H and ^{13}C spectra, 2D COSY experiments provided significant structural details. Extensive NOE difference spectra were recorded to elucidate substituent stereochemistry and spatial relation between different groups.

General Features. With the exception of **8** and **10**, each of the products shows a characteristic methoxy singlet (δ 3.0–3.4 ppm) and a singlet resonance for the tertiary alkoxy α-proton (δ 3.0–3.8 ppm). In addition, the NOCAS products **4**–**7** show an aromatic AA'BB' system resembling two pairs of doublets (2 protons each, $J = 8.2$–8.4 Hz) for the *p*-cyanophenyl group. Products **2**, **4**, and **5** show no olefinic resonances; instead, they each feature three broad triplets (δ 1.1–1.6 ppm) for their three cyclopropane protons; the splitting ($J \sim 5.5$ Hz) is characteristic for the cis-coupling in cyclopropane systems. Each product further has a broad singlet at ~2.0 ppm, typical for the bridgehead proton H_4.

Methanol Adducts and NOCAS Products. Methanol adducts **1** and **2** show two pairs of geminal protons (at C_7 and C_6 or C_5), whereas the NOCAS products **4** and **5** have only one pair of geminal protons (at C_7) each. For compounds **4** and **5**, the stereochemistry at C_3 and C_5 was elucidated by NOE experiments. In case of **4**, preirradiation of the alkoxy (H_3) resonance causes strong NOE enhancement of the ortho aryl signal (7.41 ppm); thus, the methoxy (exo-) and the aryl group (endo-) are trans to each other. Similarly, the strong mutual NOE interactions between H_3 and H_5 of product **5** establish that these protons are on the endo-face and, correspondingly, the methoxy and the aryl group occupy exo-positions.

Products **1**, **3**, **6**, and **7** show typical norbornene features,[18] i.e., (a) two deshielded endocyclic olefinic signals (δ 5.7–6.3 ppm), (b) strongly shielded resonances for *endo*-H_5, H_6 (0.6–1 ppm upfield from the corresponding exo-protons), and (c) a typical set of coupling constants, $^2J_{H6x-6n} \approx 10$–12 Hz, $^3J_{H5x-6x}$ and $^3J_{H5n-6n} \approx 9$ Hz, $^3J_{H5x-6n}$ and $^3J_{H5n-6x} \approx 5$ Hz, $^3J_{H5x-4}$ and $^3J_{H6x-1} \approx 3$–4 Hz, $^3J_{H5n-4}$ and $^3J_{H6n-1} < 1$ Hz, $^3J_{H2-3} \approx 6$ Hz, $^3J_{H3-4}$ and $^3J_{H2-1} \approx 3$–4 Hz. Because of its symmetry, adduct **3** has a much simpler spectrum than its isomers. For products **1**, **3**, and **6**, the anti relationship between methoxy group and endocyclic double bond was deduced from the unusual upfield shift of the tertiary alkoxy resonance (H_{7s}, δ 3.37, 3.13, and 3.31 ppm, upfield of the corresponding methoxy signals, δ 3.34, 3.25, and 3.34, respectively), apparently due to their location in the shielding cone of the endocyclic double bond.[19] In contrast, the methoxy signal of compound **7** was shifted upfield (δ 2.98), indicating its position near the shielding region of the aryl group.

Acetonitrile Adducts. Concerning the acetonitrile adducts, product **8** has a characteristic parent ion (M^+ $m/z = 133$, $C_7H_8 + CH_3CN$). Its ^1H NMR spectrum is quite similar to that of product **2**, except that the two alkoxy singlets of **2** are replaced by a triplet (H_3; δ 1.89, $J \approx 8$ Hz) and two strongly coupled resonances, respectively, representing the diastereotopic protons of the cyanomethyl function (δ 2.14, d(d), $J = 17.0$, 8.1 Hz, and, δ 2.21, d(d), $J = 16.9$, 7.8 Hz). The ^{13}C NMR spectrum shows the cyano carbon at δ 119.4 and eight additional resonances at δ 10–42 ppm.

Product **9** is identified by its mass spectrum (M^+ $m/z = 133$, $C_7H_8 + CH_3CN$; base peak $m/z = 132$, M − 1). It is hydrolyzed to the corresponding ketone, **10**, during attempts to separate it chromatographically. Product **10** (M^+ $m/z = 134$) has spectral features similar to product **7**, except that the signals of the methoxy and aryl groups of **7** are replaced by two strongly coupled protons (δ 2.03, d(d), $J = 18.5$, 4.8 Hz, and δ 2.11, d(br), $J = 18.5$ Hz). The ^{13}C spectrum shows a carbonyl signal at δ 229, two olefinic signals at δ 130 and δ 141, and six other resonances at δ 29–55 ppm. The unusually large value of the geminal *J*-couplings between two pairs of protons for products **8** and **10** (vide supra) suggest that they are located in the vicinity of an electron-withdrawing group (viz., the CN or C=O function, respectively).[20]

Discussion

The products resulting from the donor–acceptor photochemistry of **N** and **Q** reveal interesting mechanistic facets: they elucidate the stereochemistry of nucleophilic capture by the corresponding radical cations, $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$; they document the rapid rearrangement of the resulting adduct radicals and demonstrate their involvement in various competing reactions. The methanol adducts and NOCAS products derived from **N** and **Q** show interesting differences compared to the analogous reactions of derivatives of **N** and **Q** bearing either a 7-*exo*-methylene[21a] or a 7-spirocyclopropane function.[21b]

The isolated products require at least two primary intermediates, each reacting by various competing pathways; the ultimate products are determined by factors such as solvent polarity, the nature of the electron acceptor, and the energetics of the competing reactions. We consider primary intermediates of two types, an excited-state complex (exciplex) between **CNN** and **N**, and the radical cations, $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$. Since nucleophilic capture by alcoholic solvents is one of the best-known

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Scheme 2

Excitation

$$\mathbf{Ph} \longrightarrow {}^1\mathbf{Ph}^* \quad (8)$$

Electron Transfer

$${}^1\mathbf{Ph}^* + \mathbf{DCB} \longrightarrow \mathbf{Ph}^{\bullet+} + \mathbf{DCB}^{\bullet-} \quad (9)$$

$$\mathbf{Ph}^{\bullet+} + \mathbf{D} \longrightarrow \mathbf{Ph} + \mathbf{D}^{\bullet+} \quad (10)$$

radical cation reactions, the methanol adducts **1**–**3**, and the NOCAS products, **4**–**7** will be ascribed to a radical cation mechanism. On the other hand, the cycloadducts between **CNN** and **N** are typical products of an exciplex; we also ascribe the 1:1:1 adducts between **CNN**, **N**, and methanol to an exciplex pathway. These adducts will be discussed in a separate publication. Finally, the formation of products **8** and **9** and the limited extent of deuterium incorporation into the methanol adducts **2** and **3** elucidate a new mechanism by which the adduct free radicals are converted to the methanol adducts.

Energetics of Electron Transfer. The free energy of formation of radical ion pairs generated by electron transfer between a donor and an acceptor (Scheme 1; eq 2) is determined by the excited state energy, $E_{0,0}$, the reduction potential of the acceptor, $E_{(A^-/A)}$, the oxidation potential of the donor, $E_{(D/D^+)}$, and a term accounting for ion pairing:[22]

$$-\Delta G = E_{(0,0)} - E_{(D/D^+)} + E_{(A^-/A)} - e^2/\epsilon a \quad (7)$$

This is known as the Rehm–Weller equation; in polar solvents, the $e^2/\epsilon a$ term has a value of ~0.06 eV.

The two sensitizer systems employed in the current study, **DCB/Ph** and **CNN**, differ in several respects. With the **DCB/Ph** sensitizer pair, light of wavelength 350 nm can be employed, and the radical cations are generated via an indirect pathway (Scheme 2). Following excitation of **Ph**, electron transfer occurs from ^{1}**Ph*** to **DCB**; this process is exergonic by 0.34 eV (**Ph**, $E_{(0,0)}$ = 3.58 eV;[23] E_{D/D^+} = 1.58 V;[23] **DCB**, $E_{A^-/A}$ = −1.60 V)[23] and, thus, should be very efficient. The second electron transfer is stongly exergonic for the reaction of **Q** ($E_{D/D^{\bullet+}}$ = 0.91 V;[24] ΔG = −0.67 eV), but essentially thermoneutral for **N** ($E_{D/D^{\bullet+}}$ = 1.54 V;[24] ΔG = −0.04 eV). Its completion may be aided by fast nucleophilic attack on $\mathbf{N}^{\bullet+}$.[25] One significant advantage of this method of radical cation formation lies in the fact that exciplex formation between **N** and **DCB** is unlikely under the conditions of indirect (two-step) oxidation. On the other hand, the reduction potential of **DCB** ($E_{A^-/A}$ = −1.6 V) is only marginal for the reduction of some free radicals generated by nucleophilic capture.

Given the excitation energy ($E_{(0,0)}$ = 3.75 eV)[23] and reduction potential ($E_{A^-/A}$ = −1.98 V)[26] of **CNN**, the electron transfer from **N** to ^{1}**CNN*** is only modestly exergonic (ΔG = −0.17 eV) and very likely inefficient; thus, exciplex formation should become competitive in the **CNN** sensitized photoreaction. On the other hand, $\mathbf{CNN}^{\bullet-}$ has greater reducing power than $\mathbf{DCB}^{\bullet-}$, sufficient to reduce the free radicals resulting from nucleophilic capture.

Structural Features of Radical Cations $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$. The radical cations $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$ have long been targets of interest, and their principal structural features are well established. The structure of $\mathbf{N}^{\bullet+}$ rests on the polarization pattern of the CIDNP spectrum,[12b,c] ab initio molecular orbital calculations,[12h] and the hyperfine coupling pattern from ESR and ENDOR data.[12f,27] All three methods agree that spin (and charge) is delocalized over the four equivalent olefinic carbons; these centers are the primary targets for nucleophilic capture.

Many attempts to observe $\mathbf{Q}^{\bullet+}$ directly have failed; in some cases rearranged radical cations have been observed.[12g,i,28] CIDNP results[12b,c] and ab initio molecular orbital calculations[12h] indicated that the spin (and charge) density of $\mathbf{Q}^{\bullet+}$ is delocalized over the four cyclopropane carbons corresponding to the olefinic carbons of $\mathbf{N}^{\bullet+}$. This assignment has been confirmed by a recent time-resolved (TR) ESR study, the first unambiguous direct observation of $\mathbf{Q}^{\bullet+}$.[15] The good agreement between the spin density distributions obtained by three different methods for $\mathbf{Q}^{\bullet+}$ (as well as $\mathbf{N}^{\bullet+}$) gives us confidence that the structures are described adequately. On the other hand, the hyperfine pattern of a difference spectrum recently ascribed to $\mathbf{Q}^{\bullet+}$[29] deviates substantially from the (TR) ESR results[15] and also appears incompatible with the CIDNP pattern[12b,c] and the ab initio results.[12h,29] Regardless of the actual values of the hfcs, nucleophilic capture clearly is expected at one of the four equivalent cyclopropane carbons. This expectation is born out by the observed methanol adducts and NOCAS products, which indicate that attack on $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$ occurs at the four olefinic or cyclopropane carbons, respectively.

Several interesting rearrangements have been reported following the one-electron oxidation of **N** or **Q** in cryogenic matrices.[12g,28a] For example, argon resonance photoionization of both **Q** and **N** led to the absorption spectra of cycloheptatriene and methylenecyclohexadiene radical cations.[12g] Radiolysis of **Q** in chlorofluorocarbon matrices produced the ESR spectrum of bicyclo[3.2.0]hepta-2,6-diene radical cation ($\mathbf{BH}^{\bullet+}$).[28a] We have carefully searched for any products that may reflect the intermediacy of these rearranged radical cations; however, the isolated products fail to support any of these rearrangements in solution. The divergent results found in the matrix and solution experiments may be due to one or more of a variety of reasons, including matrix effects, the significant temperature difference, the possibility of excited-state reactions of $\mathbf{Q}^{\bullet+}$ or $\mathbf{N}^{\bullet+}$ in the matrix, which is prevented in solution due to their rapid depletion by nucleophilic capture. Whatever the specific reasons, there can be no doubt that the conversion of $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$ to $\mathbf{BH}^{\bullet+}$ or other radical cations does not occur under the conditions of conventional photochemistry in solution.

DCB/Ph Sensitized Reactions. The **DCB/Ph** sensitized reactions of **N** and **Q** lead to a variety of products,

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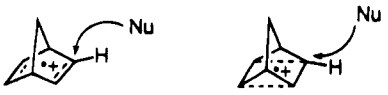
Scheme 3



including methanol adducts, NOCAS products, and two acetonitrile adducts **8** and **9**, which are formed only from **N**. The methanol adducts and NOCAS products belong to two different structure types; products **3**, **6**, and **7** have 7-substituted norbornene frames, whereas products **2**, **4**, and **5** have tricyclo[2.2.1.$0^{2,6}$]heptane (tricyclane) structures.

It is noteworthy, that the reactions of **N** and **Q** produce very similar ratios of norbornene to tricyclane structure types for both methanol adducts (**2**:**3**) and photo-NOCAS products, [(**4** + **5**) : (**6** + **7**)] (Table 1). It is tempting to interpret this finding as evidence that all reaction products are derived from a single radical cation $\mathbf{N}^{\bullet+}$, after conversion of **Q** to **N**; this possibility was considered by previous investigators.[12e] However, under the conditions employed in our experiments, this rearrangement can be eliminated unambiguously for several reasons. First, products **2** and **3** clearly begin to build up with the onset of irradiation, well before the putative rearrangement product **N** can compete as a quencher with **Q**. The involvement of **N** is unfavorable, because **Q** is four times more efficient a quencher than **N** ($K_{SV;Q} = 260$ vs $K_{SV;N} = 65$).[30] Second, several additional products are formed in the reaction of **N** exclusively, indicating the existence of pathways open only to the diolefinic, less strained substrate **N**. In view of these findings, the rearrangement of **Q** to **N** cannot account for the products derived from **Q** under the conditions of our experiments. Most significantly, it has been shown that the rearrangement from $\mathbf{Q}^{\bullet+}$ to $\mathbf{N}^{\bullet+}$ is slower than nucleophilic capture by *tert*-butyl alcohol[15] and, therefore, certainly slower than capture by methanol. Clearly, $\mathbf{Q}^{\bullet+}$ is captured directly by the nucleophile, generating an adduct radical.

Stereochemistry of Nucleophilic Capture. The stereochemistry of the methoxy groups in these structures is of particular interest, because their orientation identifies the preferred direction of nucleophilic attack upon the intermediate radical cations $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$. Although the resulting primary radicals undergo significant structural rearrangements (vide infra), the reaction products reveal the stereochemistry of nucleophilic capture (as well as the course of the rearrangement). According to detailed NOE experiments, the nortricyclane derivatives (**4**, **5**) contain a 3-*exo*-methoxy group; this stereochemistry is compatible with stereospecific nucleophilic attack exclusively from the exo position of $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$. The norbornene structures (**3**, **6**, **7**) each contain a 7-*anti*-methoxy group, which is also compatible with exo-attack. For the nucleophilic attack on the cyclopropane function of $\mathbf{Q}^{\bullet+}$ these results support a back-side attack with inversion of configuration (→ $CH_3O-\mathbf{C}^{\bullet}$), fully compatible with several analogous "substitutions" on cyclopropane radical cations,[16,31,32] including a vinylcyclopropane ring opening.[16] For the attack on $\mathbf{N}^{\bullet+}$, the stereochemistry (→ $CH_3O-\mathbf{B}^{\bullet}$) may be determined by steric factors.

Interconversion and Competing Reactions of Free Radicals $CH_3O-C_7H_8^{\bullet}$. Having eliminated the involvement of only one radical cation as key intermediate, we explain the similar product ratios obtained in the electron transfer photochemistry of **N** and **Q** by the involvement of several rapidly interconverting secondary intermediates. Based on precedent established for the *tert*-butoxy-substituted system,[33] we assume that the free radical $CH_3O-\mathbf{B}^{\bullet}$, formed by nucleophilic capture of $\mathbf{N}^{\bullet+}$, undergoes a rapid allylcarbinyl–to–cyclopropylcarbinyl rearrangement to $CH_3O-\mathbf{C}^{\bullet}$, the species generated by capture of $\mathbf{Q}^{\bullet+}$, and that the latter exists in a cyclopropylcarbinyl–allylcarbinyl equilibrium with $CH_3O-\mathbf{E}^{\bullet}$.

Following their intramolecular equilibration, the free radicals, $CH_3O-\mathbf{B}^{\bullet}$, $CH_3O-\mathbf{C}^{\bullet}$, and $CH_3O-\mathbf{E}^{\bullet}$, may undergo bimolecular reactions, leading to the various products. Typical processes to be considered under the reaction conditions include the following: reduction by the sensitizer radical anion (k_{red}); coupling with the sensitizer radical anion (k_c); addition to an olefinic reagent (**N**; k_{add}); and hydrogen abstraction from the solvent (k_h). All observed products can be traced back to competing reactions of $CH_3O-\mathbf{C}^{\bullet}$ and $CH_3O-\mathbf{E}^{\bullet}$ (Scheme 4).

The four NOCAS products (**4**–**7**) apparently are formed by *coupling* of the free radicals, $CH_3O-\mathbf{C}^{\bullet}$ and $CH_3O-\mathbf{E}^{\bullet}$, respectively, with $\mathbf{DCB}^{\bullet-}$, followed by loss of cyanide ion. In contrast to the nucleophilic attack on the radical cations $\mathbf{N}^{\bullet+}$ and $\mathbf{Q}^{\bullet+}$ (vide supra), the coupling reaction is essentially stereorandom. The steric relationship between the methoxy function and the unpaired spin causes some differences in the stereochemical behavior of $CH_3O-\mathbf{C}^{\bullet}$ and $CH_3O-\mathbf{E}^{\bullet}$, respectively. Attack on the two faces of $CH_3O-\mathbf{C}^{\bullet}$ generates products **4** and **5**, essentially indiscriminately. In contrast, the reaction of $CH_3O-\mathbf{E}^{\bullet}$, giving rise to product **6** by endo-attack and generating product **7** by exo-attack, shows an element of stereoselectivity (Table 1). The attack from the endo-side (→ **6**) is preferred, presumably because the 7-methoxy group interferes with the attack on the exo-face (→ **7**) (Scheme 5).

In analogy to ample precedent,[13] the formation of the methanol adducts **2** and **3** might be formulated via *reduction* of $CH_3O-\mathbf{C}^{\bullet}$ and $CH_3O-\mathbf{E}^{\bullet}$ by $\mathbf{DCB}^{\bullet-}$ and protonation of the resulting anions (*cf.*, Scheme 1, eqs 4, 5). However, the reduction of these secondary free radicals by $\mathbf{DCB}^{\bullet-}$ ($E_{(A^-/A)} = -1.6$ V) may be slightly endergonic ($\Delta G \sim 0$), if their reduction potential is similar to that of norbornyl-2-yl radical ($E_{(A^-/A)} = -1.67$ V vs SCE).[34] In fact, with CH_3CN/CH_3OD as solvent/nucleophile the adducts **2** and **3** showed only 4 ± 2% deuterium incorporation, far shy of the quantitative deuterium incorporation required by the reduction–protonation mechanism. Clearly, **2** and **3** must be formed by an alternative mechanism, most likely *hydrogen abstraction* from the solvent(s), CH_3CN or CH_3OD. This mechanism is supported by the formation of the acetonitrile adducts **8** and **9** (vide infra).

The formation of the 2:1 adducts of C_7H_8 and CH_3OH in the reaction of **N** but not **Q** indicate a third competing reaction of the methoxylated radicals, viz., *addition* to the olefinic π bond of **N**. This process would generate

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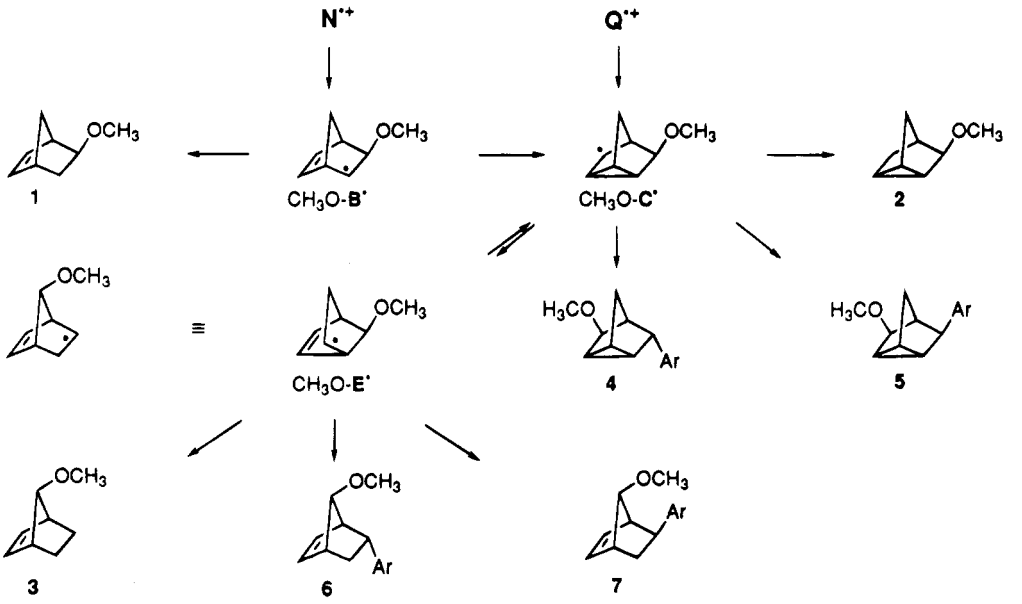
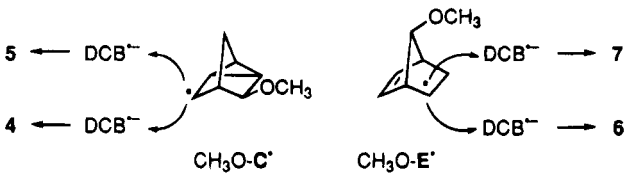
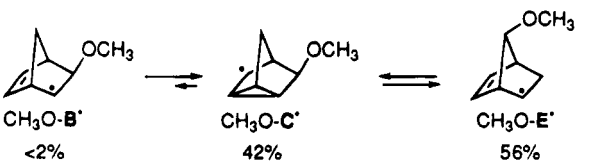
Scheme 4



Scheme 5



Scheme 6



adduct radicals (CH_3O–**C**–)–**B**• and (CH_3O–**E**–)–**B**•; rapid rearrangement to (CH_3O–**C**–)–**C**• and (CH_3O–**E**–)–**C**• is expected as is the further equilibration with (CH_3O–**C**–)–**E**• and (CH_3O–**E**–)–**E**•. The last four intermediates, finally, could form the 2:1 adducts by hydrogen abstraction. Free-radical additions to the π bonds of alkenes are firmly established as significant initiation and propagation steps of many free-radical chain reactions and have been studied in some detail.[35]

In contrast, cyclopropane derivatives undergo free-radical additions less readily, although the addition of chlorine atoms to cyclopropane systems has been observed in some cases, when tertiary or otherwise stabilized radicals are formed.[36,37] On the other hand, cyclopropyl radicals can be generated by hydrogen abstraction from cyclopropane systems.[38] In view of these considerations it is not surprising that the electron transfer reaction of **Q** does not lead to products originating from free radical additions.

Relative Reactivity of Free Radicals CH_3O–C_7H_8•. The products derived from the **DCB/Ph** sensitized reactions enable us to evaluate the various competing reactions available to the free radicals, CH_3O–**C**• and CH_3O–**E**•; i.e., rearrangement, hydrogen abstraction, reduction by **DCB**•⁻, coupling with **DCB**•⁻, and addition to olefinic π bonds. According to the relative yields of product obtained in the reaction of **N** (Table 1), and considering the results of the deuterium incorporation experiment, the reactivity of the methoxy-substituted free radicals is clearly differentiated, as shown below. Moreover, since the reactions of **N** and **Q** lead to methanol adducts and NOCAS products with similar ratios of norbornene to nortricyclane skeletons, the intramolecular rearrangements (k_{isom}) between CH_3O–**B**•, CH_3O–**C**•, and CH_3O–**E**• must be faster than any intermolecular reaction.

$$k_{isom} > \underset{(\sim 40\%)}{k_{abstr}[CH_3CN]} > \underset{(\sim 20\%)}{k_{coupl}[\mathbf{DCB}^{\bullet -}]} \geq \underset{(\sim 15\%)}{k_{olefin}[\mathbf{N}]} \gg \underset{(\sim 2\%)}{k_{et}[\mathbf{DCB}^{\bullet -}]}$$

Finally, since the intramolecular interconversions of the radical intermediates are faster than their bimolecular reactions, we use the ratio of norbornene to nortricyclane products to derive approximate equilibrium concentrations of the corresponding free radicals. Assuming that the hydrogen abstraction of the three secondary radicals CH_3O–**B**•, CH_3O–**C**•, and CH_3O–**E**• proceed at comparable rates, then the observed product ratios indicate approximate equilibrium concentrations of <2:42:56%, respectively (Scheme 6). These values are consistent with a qualitative result derived for the *tert*-butoxy substituted system (t-C_4H_9-O-C_7H_8).[33] An EPR study of the addition of t-butoxy radical to **N** provided evidence for the existence of both t-BuO–**C**• (at −130 °C) and t-BuO–**E**• (at −70 °C), but failed to reveal any evidence for t-BuO–**B**• at either temperature.[33]

Products Derived by Free Radical Addition of Cyanomethyl. A plausible mechanism for the formation of adducts **8** and **9** involves hydrogen abstraction from acetonitrile, addition of the resulting cyanomethyl radical to **N**, and a second hydrogen abstraction by the adduct radical $NCCH_2$–**B**•. This mechanism resembles a reaction sequence developed by Lewis and co-workers for the metal ion catalyzed addition of acetonitrile to nor-

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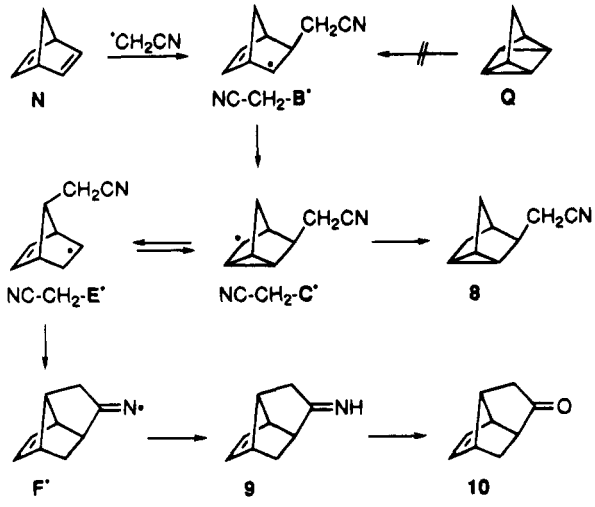
Scheme 7



bornene.[39] A related adduct formed in the electron transfer photochemistry of 5-benzylnorbornene[40] can be rationalized by an analogous mechanism.

Two types of species need to be considered for the initial hydrogen abstraction from the solvent, either the substrate radical cation $\mathbf{N}^{\bullet+}$ or the adduct radicals $CH_3O-\mathbf{C}^{\bullet}$ and $CH_3O-\mathbf{E}^{\bullet}$. Although norbornene radical cation reportedly abstracts hydrogen from CH_3CN,[39] the analogous reaction of $\mathbf{N}^{\bullet+}$ can be eliminated, because the acetonitrile adducts were suppressed in the absence of methanol. Apparently, the presence of the second double bond in our substrate (**N**) reduces the efficiency of hydrogen abstraction. On the other hand, hydrogen abstraction by $CH_3O-\mathbf{C}^{\bullet}$ or $CH_3O-\mathbf{E}^{\bullet}$ from acetonitrile is exergonic by ~4 kcal/mol, as estimated from the bond dissociation energies (BDE) of the secondary C–H bonds of **2** and **3** (secondary norbornenyl C–H, BDE 96.7 ± 1 kcal mol^{-1})[41] and the primary bond of acetonitrile (H–CH_2CN, BDE 93 ± 2.5 kcal mol^{-1}).[41] Hydrogen abstraction from methanol is marginally exergonic (~3 kcal mol^{-1}) for the methyl group (H–CH_2OH, BDE 94 ± 2 kcal mol^{-1}),[41] whereas the hydroxyl group is an unlikely target because of its high BDE (104 ± 1 kcal mol^{-1}).[41] Clearly, acetonitrile is the primary target for hydrogen abstraction.

Once the free radical addition product $NCCH_2-\mathbf{B}^{\bullet}$ is formed, the second double bond causes molecular rearrangements similar to those discussed for $CH_3O-\mathbf{B}^{\bullet}$ (Scheme 3). The structures of the isolated products **8** and **10** suggest that $NCCH_2-\mathbf{B}^{\bullet}$ rearranges to $NCCH_2-\mathbf{C}^{\bullet}$ and $NCCH_2-\mathbf{E}^{\bullet}$. One of these species, $NCCH_2-\mathbf{C}^{\bullet}$, generates **8** by hydrogen abstraction from the solvent. In keeping with the addition–abstraction sequence, adduct **8** is formed without incorporation of deuterium (Scheme 7). The isomeric intermediate $NCCH_2-\mathbf{E}^{\bullet}$ generates the iminyl radical $\mathbf{F}^{\bullet}$ by intramolecular free radical addition to the cyanoalkyl function. Subsequently, the imine **9** is formed via hydrogen abstraction or by reduction/protonation. This product showed significant D incorporation, supporting a major contribution due to reduction/protonation. The extent of D incorporation was not assessed quantitatively, because loss of the iminyl hydrogen (deuterium) is a prominent fragmentation process of the imine molecular ion; this process removes the distinction between **9**-H and **9**-D.

The intramolecular free-radical addition to a C≡N bond has precedent;[42] for example, 4-cyanobutyl radical undergoes fast 1,5-cyclization to an analogous iminyl radical.[42c] On the other hand, several disubstituted iminyl radicals undergo fragmentation to nitriles and alkyl radicals.[43] For example, benzylphenylchlorimine undergoes a thermally induced free-radical chain decomposition, yielding benzonitrile and benzyl chloride in high yields.[43] Analogous iminyl fragmentions have been documented in several steroid systems; in these cases, cleavage is favored by a β-hydroxy function and results in the formation of a γ-cyano ketone.[42a,b] In our system, the intramolecular addition is favored significantly over fragmentation, as indicated by the conversion of $\mathbf{F}^{\bullet}$ to **9** rather than hydrogen abstraction by $NCCH_2-\mathbf{E}^{\bullet}$.

In view of the earlier considerations concerning free radical addition to cyclopropane functions, it is not surprising that the electron transfer photochemistry of **Q** failed to show any evidence for products **8** or **9**. This finding raises the question of other pathways for the depletion of cyanomethyl radical, viz., dimerization or reduction. Since we could not find any evidence for the dimerization product, succinonitrile, the reduction of cyanomethyl radical by $\mathbf{DCB}^{\bullet-}$ must be an important termination pathway, particularly when **Q** serves as the substrate. Reduction of $^{\bullet}CH_2CN$ by $\mathbf{DCB}^{\bullet-}$ ($E_{(A^{\bullet}/A)}$ −1.6 V) appears energetically feasible, since an estimated reduction potential, $E_{(A^{\bullet}/A)} = -0.7$ V (vs SCE), can be derived from a thermochemical cycle[44] using the C–H BDE and the pK_a of acetonitrile (31.3 in DMSO).[45] Indirect support for the reduction of $^{\bullet}CH_2CN$ is provided by several experimental observations. For example, the ratio of NOCAS products to methanol adducts in the reaction of **Q** is smaller than that observed in the reaction of **N** (Table 1); this is consistent with a greater fraction of $\mathbf{DCB}^{\bullet-}$ being depleted by cyanomethyl radical, since the latter cannot add to **Q**. Also, in the reaction of **N**, the ratio of acetonitrile to methanol adducts is much smaller than unity. Apparently, a significant fraction of $^{\bullet}CH_2CN$ is depleted by a pathway other than free radical addition, even though there can be no doubt about the free radical addition to **N**. The reactions summarized in Scheme 7 amount to a free radical chain process, albeit with a limited chain length due to inefficient propagation steps. This process must be considered for the formation of methanol adducts, when the well established reduction/protonation sequence is energetically disfavored. The necessity to consider the hydrogen abstraction pathway may not be generally appreciated.

Acetonitrile may also participate in radical cation reactions via a different pathway, namely cycloaddition. Thus, the electron transfer photochemistry of phenylethyne leads to a cycloadduct containing two molecules of the donor plus acetonitrile.[46] Similarly, α- (**11**) and

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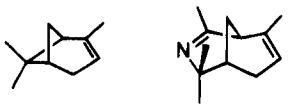
(46) Mattes, S.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1981**, 138.

β-pinene form cycloadducts (e.g., **12**) corresponding to the addition of acetonitrile to the four-membered ring or to a ring-opened bifunctional intermediate.[47] Finally, the **DCB** sensitized photochemistry of sabinene in acetonitrile in the absense of methanol leads to both cycloadduct and free-radical addition product.[48]



11 **12**

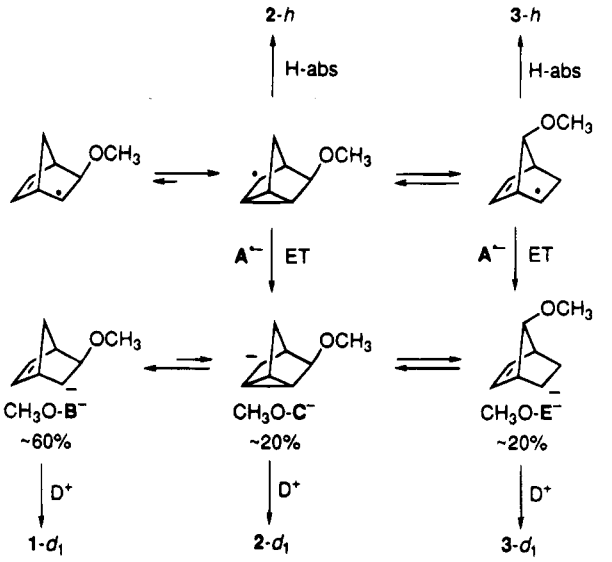
Reactions Sensitized by 1-Cyanonaphthalene. The results of the **DCB/Ph** sensitized reactions of **N** and **Q** presented in the previous section stand in interesting contrast to an earlier report concerning the **CNN** sensitized reaction of **N** in methanol.[12e] Only the methanol adducts, **1**, **2**, and **3**, were reported in yields of 10%, 33%, and 33%, respectively. The remarkable difference to the findings discussed above, particularly our failure to observe more than traces of methanol adduct **1**, caused us to carry out the reaction under the conditions employed by Gassman and Olson.[12e] Furthermore, to gain additional mechanistic insights, the reaction was carried out with methanol-OD. The results obtained under these conditions show striking differences, both compared to the **DCB/Ph** sensitized reaction and to the earlier litererature report.[12e]

We found the methanol adducts to be only minor products (~10%; Table 1); the majority of products are 1:1 adducts between **CNN** and **N** (45%) or 1:1:1 adducts between **CNN**, **N**, and methanol (~35%). Significantly, the methanol adducts showed increased degrees of deuterium incorporation, suggesting that reduction of the free radicals, CH_3O–**B**•, CH_3O–**C**•, and CH_3O–**E**•, is competitive with **CNN**•⁻ as reducing agent. Interestingly, adduct **1** was found to incorporate a substantially higher degree of deuterium (96% d) than adducts **2** (47% d) and **3** (50% d) (Table 2). These results suggest that adduct **1** is formed exclusively via the protonation of CH_3O–**B**⁻, whereas products **2** and **3** are formed in comparable quantities by hydrogen abstraction and by reduction/protonation, respectively.

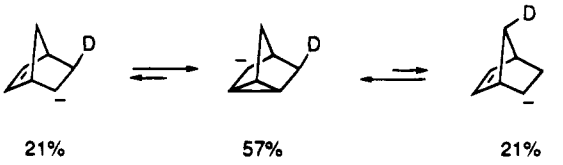
We rationalize the formation of methanol adducts with different degrees of deuterium incorporation by subtle changes in the balance between rearrangement, hydrogen abstraction, and reduction of the free radicals CH_3O–**B**•, CH_3O–**C**•, and CH_3O–**E**• (Scheme 8). When the reduction is inefficient, and hydrogen abstraction is slower than rearrangement, the observed methanol adducts reflect the equilibrium mixture of free radicals. These conditions prevail in the **DCB/Ph** sensitized reaction in CH_3CN/CH_3OH, giving rise to minimal yields of adduct **1**, comparable yields of adducts **2** and **3**, and essentially no deuterium incorporation.

In contrast, when the reduction is more efficient than hydrogen abstraction, the product ratio will be determined by the equilibrium between the anions, CH_3O–**B**⁻, CH_3O–**C**⁻, and CH_3O–**E**⁻. Products formed under these conditions are expected to show quantitative deuterium incorporation. The **CNN** sensitized reactions in methanol-OD or in acetonitrile/methanol fall short of this limit. In methanol-OD, reduction is slightly faster than hydrogen abstraction, yielding ~50% deuterium incorporation for adducts **2** and **3** and showing a slight preference for adduct **1**. In acetonitrile/methanol, hydrogen abstraction is marginally preferred, reflecting the slightly lower C–H bond dissociation energy of acetonitrile compared to that of methanol. Accordingly, deuterium incorporation in adducts **2** and **3** is limited (~30%), as is the relative yield of adduct **1**.

Scheme 8



Scheme 9



Based on the relative yields of the methanol adducts and on the extent of deuterium incorporation under different reaction conditions, the approximate equilibrium populations of the three anions, CH_3O–**B**⁻, CH_3O–**C**⁻, and CH_3O–**E**⁻ can be assigned. The results (Scheme 8) indicate that adduct **1** will be formed preferentially, when reduction is sufficiently fast to prevent hydrogen abstraction by the free radical intermediates. The postulated interconversion of the three anions has precedent in the interconversion of norbornenyl and nortricyclyl anions, a reaction which also equilibrates a deuterium label between the exo-5 and the anti-7 positions (at 60 °C; Scheme 9).[49] The different distribution of the three structures observed for the parent system can be ascribed to an effect of the methoxy group on the equilibrium populations.

The competition between hydrogen abstraction and reduction/protonation was further probed by studying the charge transfer photochemistry of **CNN** and **N** in *tert*-butyl alcohol. This change in solvent/nucleophile will affect the rates of several key processes; its overall effect on the mechanistic scheme is difficult to predict with certainty. For example, the reduced solvent polarity is expected to result in lower radical cation yields, and the decreased mobility of the alcohol may result in a reduced yield of nucleophilic capture. Concerning the ensuing free radical reactions, hydrogen abstraction should be significantly retarded because of the higher C–H bond

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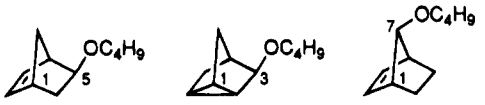
dissociation energy (~100 vs 94 kcal mol^{-1}), whereas the reduction step is more difficult to predict. In principle, the yield of **CNN**$^{\bullet-}$ (like the yield of **N**$^{\bullet+}$) is quite low; however, the reduction may occur in a geminate cage, since **CNN**$^{\bullet-}$ is generated as geminate counter ion of **N**$^{\bullet+}$; yet, any time elapsed before nucleophilic capture will diminish the probability of a reactive (re)-encounter; the reduction of the free radicals may also be affected because of the presence of the *tert*-butoxy group. Once the anions, t-C_4H_9O–**B**$^-$ etc., are formed, their protonation may be slowed because of the higher pK_a of *tert*-butyl alcohol. Finally, the presence of the *tert*-butoxy group may affect the free radical as well as the anion equilibria.

The significantly reduced yields of alcohol adducts (≤1%) observed in this reaction confirm substantially diminished radical cation formation. In addition, the 1:1:1 adducts are completely suppressed, whereas four [2 + 2]-cycloadducts are obtained as major products. Although formed in negligible yields, the ratio of the three *tert*-butyl alcohol adducts **13**–**15** (3:1:1) reflects the expected involvement of the seemingly unrearranged anion, t-C_4H_9O–**B**$^-$. This assignment is supported further by the fact that adduct **13** shows essentially quantitative deuterium incorporation with *tert*-butyl alcohol-OD as solvent/nucleophile. On the other hand, adducts **14** and **15** show only ~30% deuterium incorporation.



13 **14** **15**

While these results are consistent with the mechanistic scheme delineated above, only a minor fraction of the overall reaction in *tert*-butyl alcohol follows this pathway. The major portion of the charge transfer photochemistry of **CNN** with **N**, leading to [2 + 2]-cycloadducts in *tert*-butyl alcohol, and to [2 + 2]-cycloadducts and 1:1:1 adducts in methanol, proceeds via an entirely different mechanism. These products show various interesting features; for example, the [2 + 2]-cycloadducts are formed by approach of the sensitizer from the exo-face of **N**, whereas the 1:1:1 adducts contain the sensitizer on the endo- and the methoxy groups on the exo-face. Significantly, any rearrangement of the norbornyl system can be eliminated, since there is no evidence for either the tricyclyl or the 7-methoxynorbornyl structure. Apparently, the alcohol captures an aggregate of **CNN** and **N** in a manner similar to the attack on **N**$^{\bullet+}$ which forms CH_3O–**B**$^{\bullet}$ (vide supra). However, the mechanistic details of these products go beyond the radical cation chemistry, which is the principal topic of the paper presented here. The pathways leading to [2 + 2]-cycloadducts and 1:1:1 adducts will be communicated separately.

Conclusion

The alcohol adducts and NOCAS products formed in the electron transfer photochemistry of **N** and **Q** reveal details of the reaction mechanism. With **DCB** as sensitizer, radical cations, **N**$^{\bullet+}$ and **Q**$^{\bullet+}$, are key intermediates. Both species generate free radicals, CH_3O–**B**$^{\bullet}$ and CH_3O–**C**$^{\bullet}$, respectively, by stereospecific nucleophilic attack from the exo face. CH_3O–**B**$^{\bullet}$ rearranges rapidly to CH_3O–**C**$^{\bullet}$, which exists in equilibrium with CH_3O–**E**$^{\bullet}$. Methanol adducts **2** and **3** are formed by hydrogen abstraction; this mechanism is supported by the failure to incorporate deuterium and by the formation of acetonitrile adducts **8** and **9** generated by attack of $^{\bullet}CH_2CN$ on **N**. The reduction–protonation mechanism can be eliminated, because the reducing ability of **DCB**$^{\bullet-}$ is insufficient. The ratio of adducts **2** and **3** reflects the equilibrium concentrations of CH_3O–**C**$^{\bullet}$ and CH_3O–**E**$^{\bullet}$.

With 1-cyanonaphthalene as sensitizer, the electron transfer from **N** is less favorable, causing significantly reduced yields of **N**$^{\bullet+}$. On the other hand, the increased reducing ability of **CNN**$^{\bullet-}$ causes the reduction–protonation mechanism to compete. The reaction leads to methanol adducts **1**–**3**; the degree of deuterium incorporation reflects the participation of the anions, CH_3O–**B**$^-$, CH_3O–**C**$^-$, and CH_3O–**E**$^-$; the ratio of the adducts **1**–**3** is determined by the equilibrium concentrations of free radicals as well as anions.

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Supplementary Material Available: Detailed ^1H and ^{13}C NMR spectral assignments, including 1D NOE and 2D COSY data for products **1**–**8** and **10** and data used to calculate the reduction potential of $^{\bullet}CH_2CN$ (9 pages). This material is available in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see current masthead page for ordering information.

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