(64) Nicely confirmed by the $(E/Z)_{pss}$ value of 1.00. The extinction coefficients for Z and E are 176 and 178 cm^{-1} M^{-1}, respectively.
(65) ESO does not phosphoresce, but the significance of this observation is mitigated bt the lack of phosphorescence in the model spiro alkane.
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Photochemistry of Bichromophoric Molecules. Photochemistry and Photophysics of 2-Methylenebenznorbornene and Related Molecules in Protic Media[1]

Tom Nylund and Harry Morrison*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received April 25, 1978

Abstract: A novel, acid-catalyzed, photochemical anti-Markownikoff addition of methanol and other nucleophiles to 2-methylenebenznorbornene (MBN) is described. The effect of structure on this reaction has been studied using 2-isopropylidenebenznorbornene (IPBN), 6- and 7-methoxy-2-methylenebenznorbornene (MeOMBN), 6- and 7-trifluoromethyl-2-methylenebenznorbornene (CF$_3$MBN), and 1-methoxymethyl-2-methylene-d_2-benznorbornene (MMBN). The chemical and photophysical data suggest a mechanism involving three sequential intermediates: **27** (the fluorescent singlet state), **28** (a nonfluorescent, intramolecular charge-transfer state), and **29** (a protonated radical cation). Both **28** and **29** provide efficient radiationless decay paths which result in diminished fluorescent yields and lifetimes for the aryl olefins. The role of acid is especially noteworthy in that it allows for an otherwise endothermic electron transfer from the double bond to the aromatic ring; a similar role is likely in other acid-assisted photochemical reactions of aromatics.

The accompanying paper[1a] details the photochemistry and photophysics of the title compound (MBN) in hydrocarbon media. During the course of that study we observed that photolysis of MBN in methanol gives rise to a new reaction path, i.e., anti-Markownikoff addition of solvent to the double bond.[2] The fact that such addition was unprecedented for a nonconjugated olefin, and the potential relationship of this reaction to the greatly increased radiationless decay characteristic of MBN,[1a] led us to explore in detail the photochemistry and photophysics of MBN in protic media.

Results

Photochemistry of 2-Methylenebenznorbornene (MBN) in Methanol. Irradiation of a 0.02 M solution of MBN in methanol with 0.001 N H$_2$SO$_4$ at 254 nm with a low-pressure mercury lamp results in the formation of three photoproducts. All were independently synthesized and have been identified as **1** (*endo*-2-methoxymethylbenznorbornene), **2** (1-methoxybenzo[6.7]bicyclo[3.2.1]oct-6-ene), and **3** (*cis*- and *trans*-1-allyl-3-methoxyindan). Quantum efficiencies are $\phi_{dis} = 0.056 \pm 0.004$, $\phi_1 = 0.027 \pm 0.001$, $\phi_2 = 0.012 \pm 0.001$, $\phi_3 = 0.0038 \pm 0.0002$. The positions of deuterium incorporation when methanol-d was used as solvent were ascertained by ^{1}H NMR analysis and are designated by an asterisk in eq 1. There was no deuterium incorporation in the recovered MBN.

Photochemistry of 2-Methylene-d_2-benznorborene. This
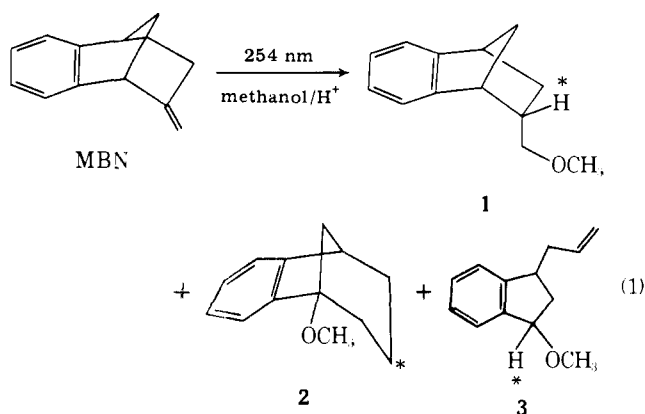
photolysis was conducted using conditions identical with those described above. The position of the deuterium atoms was determined by ^{1}H NMR; cf. eq 2.
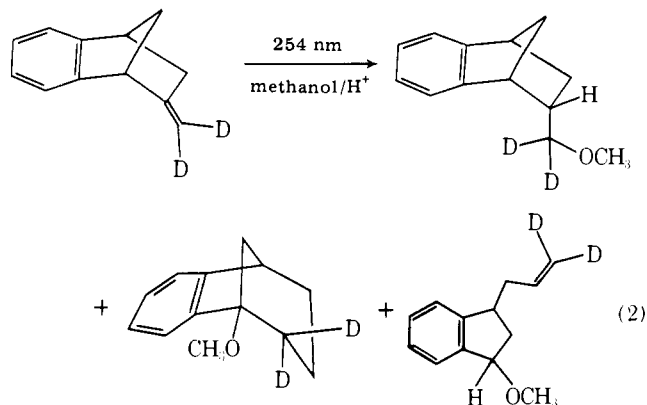
Photosensitized Reaction of MBN. Irradiation of a 0.01 M solution of MBN with 2 M p-xylene and 0.001 N H$_2$SO$_4$ to low conversion gave the following product ratio: **1**, 5%; **2**, 71%; **3**, 24%. These numbers may be compared with those obtained upon direct photolysis: **1**, 63%; **2**, 28%; **3**, 9%.

Xenon Perturbation Study of MBN. MBN was irradiated in methanol with xenon and compared to simultaneous pho-

Table I. Quantum Efficiencies of Fluorescence and Singlet Lifetimes of MBN and Related Molecules

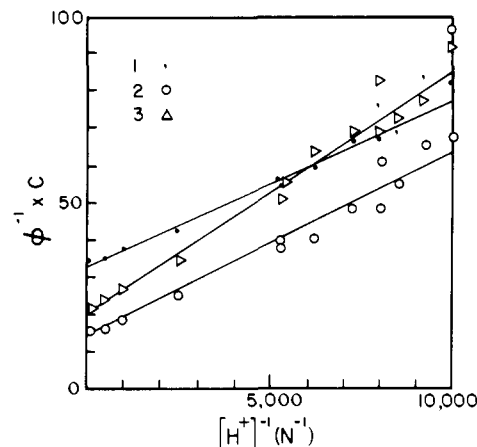| compd	solvent	$\Phi_f{}^a$	$^1\tau$, ns^b
endo-2-isobutylbenz-norbornene	hexane		14.7
	methanol + 0.001 N HCl		10.2
2-methylenebenznorbornene (MBN)	hexane	0.08	4.5
	methanol + 0.001 N HCl	0.033	2.3
	methanol + NaHCO₃	0.033	
2-isopropylidenebenz-norbornene (IPBN)	hexane	0.075	4.2
	methanol + 0.001 N HCl		3.8
	methanol + NaHCO₃		3.8
methoxy-*endo*-2-methyl-benznorbornene	hexane	0.25	5.4
methoxy-2-methylenebenz-norbornene (MeOMBN)	hexane	0.22	4.7
trifluoromethyl-*endo*-2-methylbenznorbornene	hexane	0.17	11.5
trifluoromethyl-2-methy-lenebenznorbornene (CF₃MBN)	hexane	0.046	4.2^c

^{a} All Φ_f values were determined relative to toluene ($\phi_f = 0.14$).[3] ^{b} These values are considered accurate to ±1 ns. ^{c} This value is anomalously high (36% of its saturated model) compared to its Φ_f value (27% of the model compound).

Figure 1. Plot of ϕ^{-1} vs. $[H^+]^{-1}$ for **1**, **2**, and **3**. $C = 1, 0.2$, and 0.1 for **1**, **2**, and **3**, respectively.

N HCl leads to the formation of **4** plus three other products, **5** (benznorbornen-*endo*-2-ylmethyl chloride), **6** (1-benznor-bornen-*endo*-2-ylmethoxy-2-(2-chloroethoxy)ethane), and **7** (1-(2-(2-chloroethoxy)ethoxy)benzo[6.7]bicyclo[3.2.1]-oct-6-ene). Compound **5** was identified by independent synthesis and **6** and **7** were characterized spectroscopically (Experimental Section). The reaction is depicted in eq 3. Quantum

tolyses without xenon. Product **1** was quenched 42% by xenon while **2** and **3** were both formed 2.12 times more efficiently with xenon.
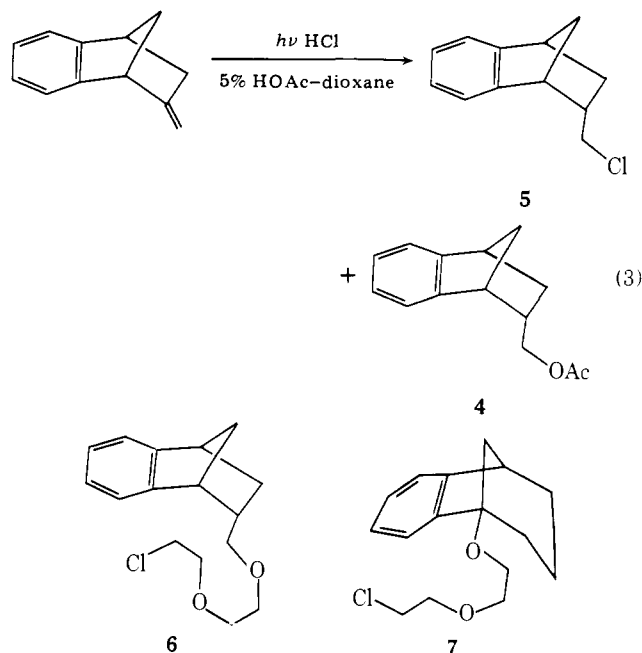
Effect of Acid on the Photochemistry of MBN. Compounds **1**, **2**, and **3** form 30–300-fold more slowly in basic methanol. In order to determine the role of acid in the catalysis, the quantum efficiencies of product formation were determined as a function of acid concentration. The responses of **2** and **3** to changes in acid concentration are identical, each forming 4.3 times more efficiently in 0.01 N than 0.0001 N H₂SO₄. The rate of formation of **1** is less sensitive, increasing only 2.5-fold over the same range of acid concentrations. The results are plotted as Φ^{-1} vs. $[H^+]^{-1}$ in Figure 1. In a second experiment, MBN was photolyzed using sensitization conditions previously described, but in methanol saturated with NaHCO₃. Neither **2** nor **3** was produced, *indicating sensitivity of even the triplet manifold to catalytic amounts of acid.*

Photochemistry of MBN in 5% Acetic Acid–Dioxane. Photolysis of a 0.02 M solution of MBN in 5% acetic acid–dioxane at 254 nm gives a 65% isolated yield of **4** (benznor-bornen-*endo*-2-ylmethyl acetate), identified by independent synthesis. Irradiation under the same conditions but with 0.025

efficiencies are ϕ_{dis} (0.001 N HCl) = 0.05 ± 0.02, ϕ_4 (no HCl) = 0.035 ± 0.002, ϕ_4 (0.024 N HCl) = 0.006, ϕ_5 (0.024 N HCl) = 0.025, ϕ_6 (0.024 N HCl) = 0.009, ϕ_7 (0.024 N HCl) = 0.019. When MBN was photolyzed with 2 M *p*-xylene in 5% acetic acid–dioxane + 0.025 N HCl, none of the photoproducts could be detected.

Spectroscopy of MBN. The absorption and fluorescence spectra of MBN in methanol are identical with those recorded in hexane,[1a] and are unaffected by 10^{-3} N HCl or NaHCO₃. The fluorescence quantum yields and singlet lifetimes for MBN and related molecules are given in Table I.

Photochemistry of 2-Isopropylidenebenznorbornene (IPBN). IPBN was prepared in two steps by reaction of isopropyllithium with benznorbornen-2-one, followed by dehydration of the resultant alcohol with POCl₃ in pyridine. Irradiation of a 0.01 M solution of IPBN in hexane with 10^{-3} N HCl at 254 nm results in the formation of three photoproducts. Compounds
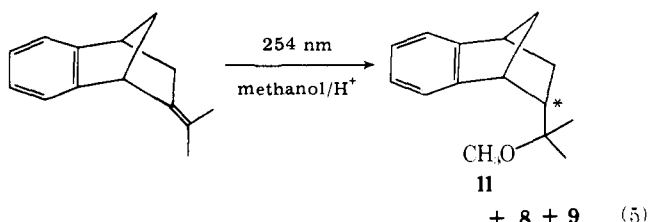
Table II. Photosensitized Reaction of IPBN

solvent		product ratios, %			
		8	9	10	11
hexane	direct	16	47	37	
	sensitized	79	15	6	
methanol	direct	3	13	<1	83
	sensitized	56	22	2	20

8 (1-isopropenylbenznorbornene) and **9** (*endo*-2-isopropenylbenznorbornene) were identified by independent synthesis, and **10** (1-isopropylidene-3-vinylindan) was characterized spectroscopically. Irradiation in hexane containing 0.001 N D₂SO₄ and saturated with methanol-*d* gave products containing deuterium in the positions denoted by asterisks in eq 4. Under these conditions, **10** could not be isolated in sufficient

(4)
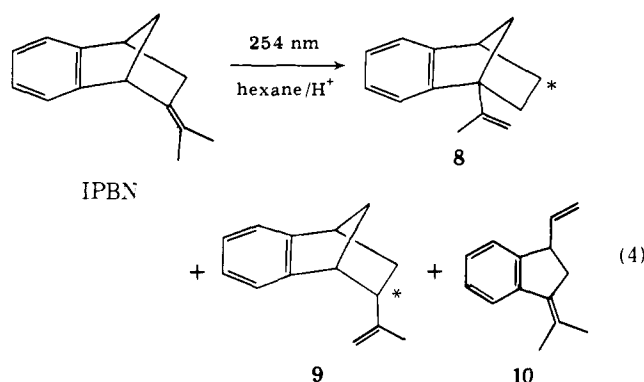
quantity for analysis; there was no deuterium incorporated in recovered IPBN.

Irradiation of a 0.01 M solution of IPBN in methanol with 0.001 N H₂SO₄ at 254 nm results in the formation of **8, 9,** and the major photoproduct, **11** (2-(benznorbornen-*endo*-2-yl)-2-methoxypropane). The position of deuterium incorporated in **11** when methanol-*d* was used as solvent was ascertained by ¹H NMR and is designated by an asterisk in eq 5. Quantum


efficiencies in methanol are $\phi_{dis} = 0.24 \pm 0.03$; **8,** 0.0053 ± 0.0005, **9,** 0.045 ± 0.004; **11,** 0.22 ± 0.02.

Photosensitized Reaction of IPBN. Irradiation of 0.013 M solutions of IPBN with 0.001 N H₂SO₄ and 4 M *p*-xylene in methanol or hexane gave the results shown in Table II. The values are compared to those obtained upon direct photolysis.

Xenon Perturbation Study of IPBN. IPBN was photolyzed to low conversion in methanol or hexane with xenon and compared to simultaneous photolyses without xenon. In hexane, xenon quenched (91%) the formation of **9,** had no effect on **8,** and enhanced (67%) **10.** In methanol, **11** was quenched (61%) by xenon.

Effect of Acid on the Photochemistry of IPBN. Product **11** forms ten times more efficiently in methanol with 0.001 N H₂SO₄ than in methanol saturated with NaHCO₃. In hexane under direct and sensitized conditions, respectively, **8** forms 32 and 1.1 times more efficiently with 0.001 N H₂SO₄, while **9** is produced 14 and 1.4 times more efficiently under identical conditions. The rate of formation of **10** is unaffected by acid.

Scheme I
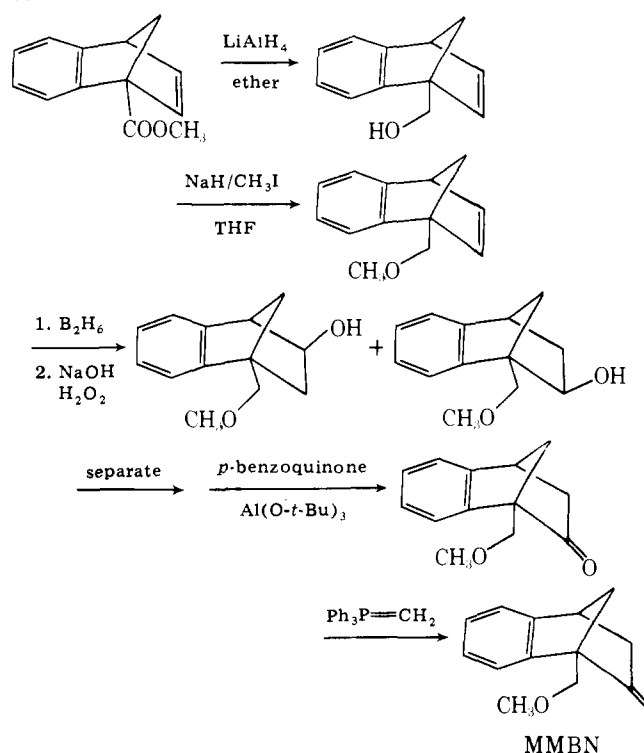
Spectroscopy of IPBN. The absorption and fluorescence spectra of IPBN taken in hexane at room temperature are presented in Figure 2 with data for MBN. The values of Φ_f and ¹τ are given in Table I. Although Φ_f of IPBN in methanol was not determined, the spectra recorded in methanol saturated with NaHCO₃ or with 0.001 N H₂SO₄ are identical.

Preparation of 1-Methoxymethyl-2-methylenebenznorbornene (MMBN). MMBN was prepared by the sequence outlined in Scheme I. The alcohols were separated by silica chromatography and were identified by europium shift ¹H NMR experiments.

Photochemistry of MMBN. Irradiation of a 0.0075 M solution of MMBN in methanol with 0.001 N H₂SO₄ at 254 nm results in the formation of three major products, **12** (*endo*-2,1-bis(methoxymethyl)benznorbornene), **13** (*exo*-3-methoxy-3-methoxymethylbenzo[6.7]bicyclo[3.2.1]oct-6-ene), and **14** (5-methoxy-5-methoxymethylbenzo[1.2]bicyclo[3.2.1]oct-1-ene). Each product was identified spectroscopically. MMBN was irradiated under identical conditions in methanol-*d*. The positions of deuterium incorporation were determined by ¹H NMR analysis and are designated with an asterisk in eq 6. Photolysis of 1-methoxymethyl-2-meth-
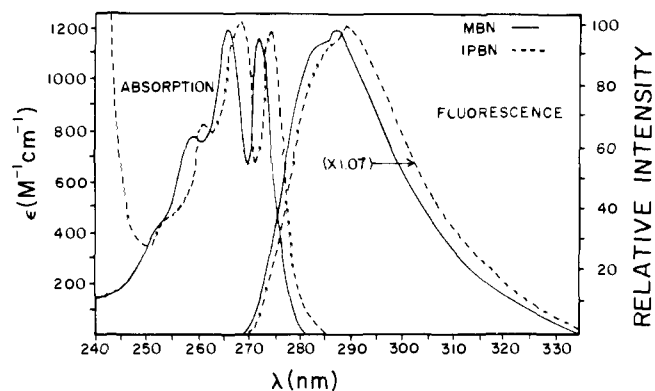

(6)
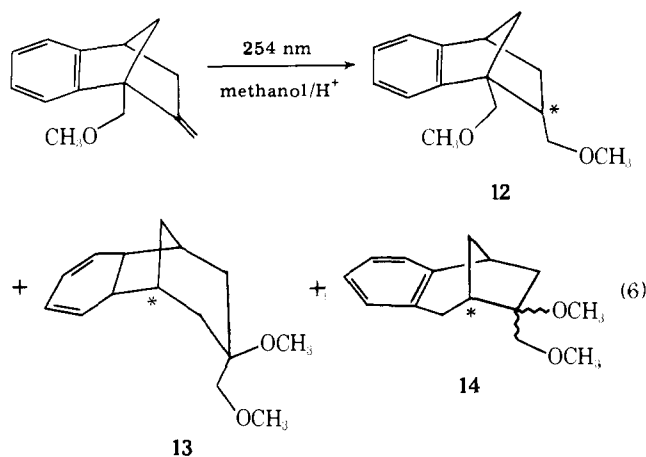
Figure 2. Absorption and fluorescence spectra of MBN and IPBN, in hexane at room temperature. (Note that the IPBN fluorescence is scaled up by a factor of 1.07.)
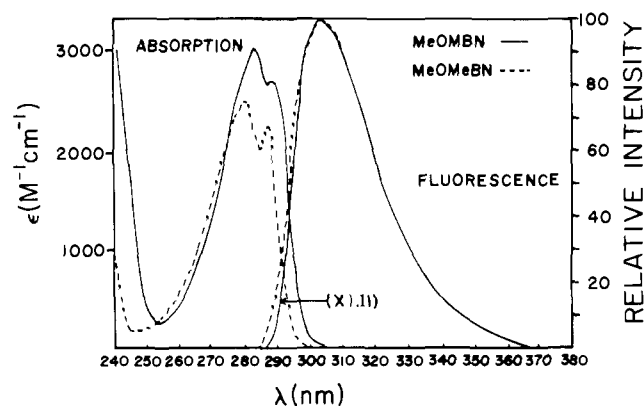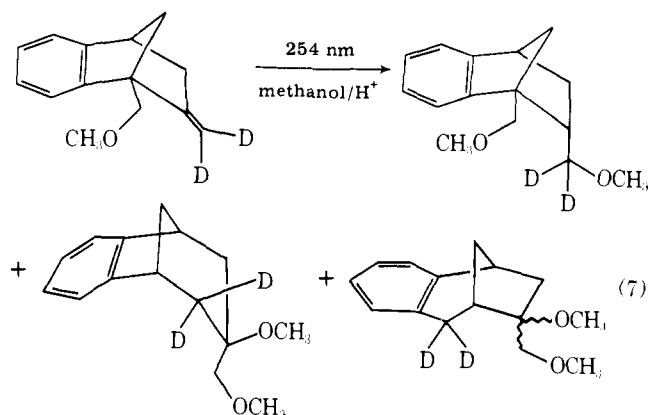

Figure 3. Absorption and fluorescence spectra of MeOMBN and MeO-MeBN, in hexane at room temperature. (Note that the MeOMBN fluorescence is scaled up by a factor of 1.11.)

ylene-d_2-benznorbornene under identical conditions gave the results shown in eq 7.

Quantum efficiencies for MMBN follow: **12**, 0.019 ± 0.001; **13**, 0.018 ± 0.001; **14**, 0.019 ± 0.001.

Effects of Sensitizer, Xenon, and Acid on MMBN. Photolysis of a 0.02 M solution of MMBN in methanol with 0.001 N H_2SO_4 and 1 M p-xylene gave the following ratio: **12**, 13%; **13**, 74%; **14**, 13%. The values obtained upon direct photolysis follow: **12**, 34%; **13**, 32%; **14**, 34%. When MMBN was irradiated in methanol with xenon, the rates of formation of **12** and **14** were diminished by 35% but product **13** was enhanced by 54%. Under direct and sensitized conditions, respectively, **13** forms 5.6 and 3.0 times more efficiently in methanol with 0.001 N H_2SO_4 than in methanol saturated with $NaHCO_3$. Compounds **12** and **14** do not form under either condition in basic methanol.

Photochemistry of 6- and 7-Methoxy-2-methylene-benznorbornene (MeOMBN). The 1:0.7 mixture of isomeric starting materials was synthesized from the corresponding ketones[4] by a standard Wittig reaction. Irradiation at 254 nm of a 0.008 M solution of MeOMBN in methanol results in the formation of **15**, identified spectroscopically as a mixture of 1,10- and 1,11-dimethoxybenzo[6.7]bicyclo[3.2.1]oct-6-ene, and **16**, a mixture of *cis*- and *trans*-5,3- and 6,3-dimethoxy-1-allylindan. The isomers of **15** could be separated by VPC and were found to form at identical rates (i.e., the ratio of isomers did not change from 10% to total conversion of starting material). The isomers of **16** could not be separated. The reaction is summarized in eq 8. The anti-Markownikoff adducts analogous to **1** were independently synthesized and shown by VPC to be absent from the reaction mixture. Quantum efficiencies follow: **15**, 0.012$_5$ ± 0.002; **16**, 0.002 ± 0.0004. Absorption and fluorescence spectra, taken in hexane, are presented in Figure 3 together with those of the reduced (i.e., *endo*-2-methyl)
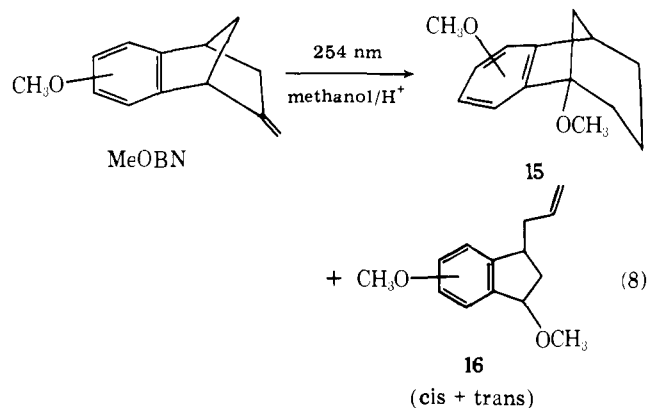
analogue for purposes of comparison. ϕ_f and $^1\tau$ data are in Table I.

Photochemistry of 6- and 7-Trifluoromethyl-2-methylenebenznorbornene (CF$_3$MBN). A 1:1 mixture of starting materials was prepared from the carbonyl precursors[4] by reaction with methylenetriphenylphosphorane. Photolysis of a 0.0013 M solution of CF$_3$MBN in methanol with 0.001 N H_2SO_4 at 254 nm gave **17**, a mixture of 6- and 7-trifluoromethyl-*endo*-2-methoxymethylbenznorbornene. Two minor products were observed but were not isolated. The isomers could be separated analytically by VPC and were found to form at identical rates. The reaction is depicted in eq 9. The quantum
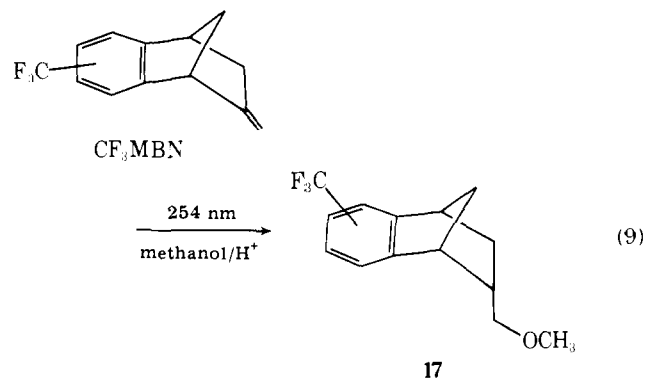
efficiency for **17** is 0.044$_5$ ± 0.001; it is not formed at all in methanol saturated with sodium bicarbonate. Absorption and fluorescence spectra, taken in hexane, are presented in Figure 4 with those of the reduced (i.e., *endo*-2-methyl) analogue for purposes of comparison. ϕ_f and $^1\tau$ data are in Table I.

Discussion

The photoproducts formed by irradiation of MBN and its analogue in protic media can be conveniently divided into two
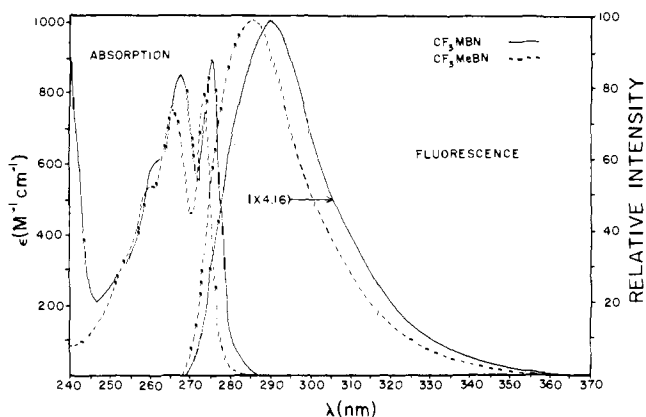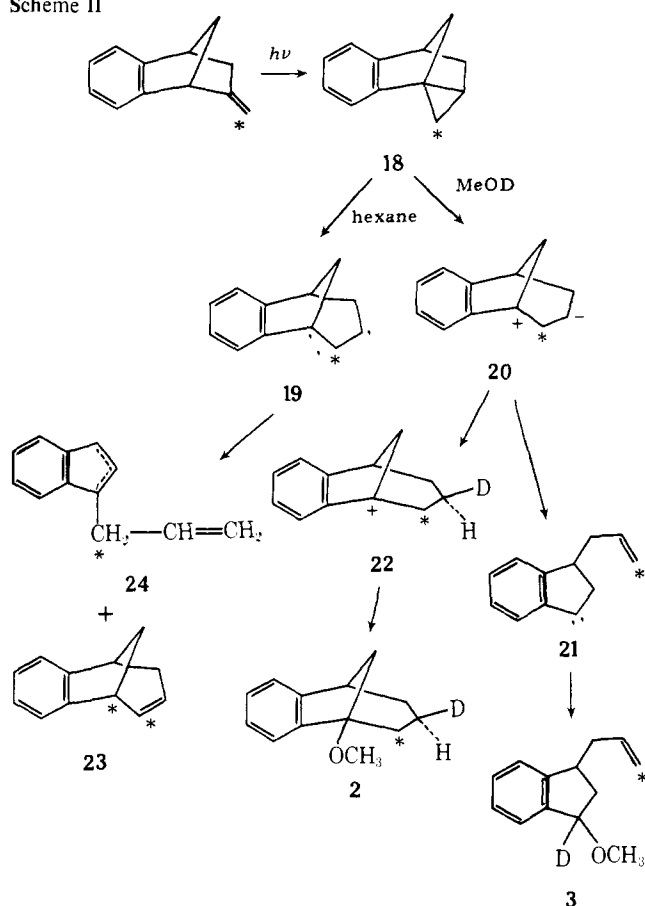
Figure 4. Absorption and fluorescence spectra of CF₃MBN and CF₃MeBN, in hexane at room temperature. (Note that the CF₃MBN fluorescence is scaled up by a factor of 4.16.)

Scheme II

groups: those which arise via di-π-methane bonding[1a] and those which form through polarization of the olefin. The former are of interest in that they represent additional support for the mechanism outlined in the preceding paper;[1a] they will be discussed briefly in this context. The bulk of our Discussion will then focus on the charge-transfer chemistry and its relationship to the facile radiationless decay which characterizes MBN and related bichromophores.

Di-π-methane Chemistry. Of the photoproducts of MBN in methanol, compounds **2** and **3** appear to derive from a di-π-methane rearrangement to **18** (Scheme II; the asterisks locate the site of deuterium labeling when MBN-*d*₂ is irradiated; the deuterium atoms explicitly shown are those which are incorporated by photolysis of MBN in a deuterated medium). Homolytic fission of the highly strained **18** has been previously
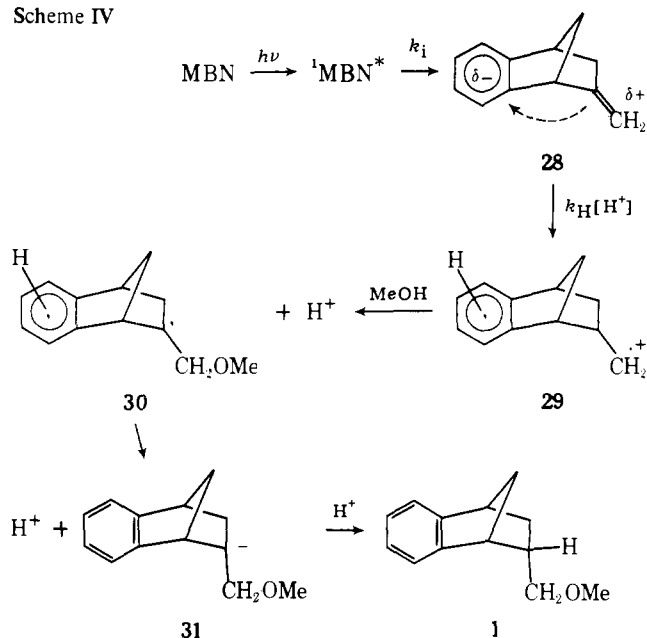
Scheme III
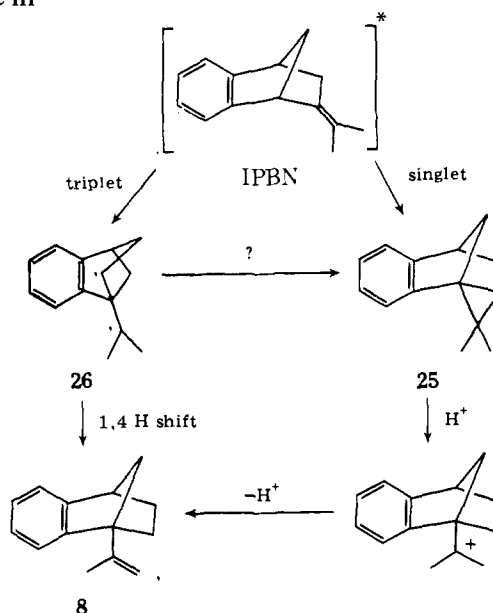
shown to accommodate the products (**23, 24**) formed in hexane.[1a] We suggest that in methanol, bond fission is heterolytic and provides the zwitterion **20**. Formation of **2** from **20** is straightforward[5] but cleavage of **20** to the carbene **21** is, to our knowledge, unprecedented.[6] The xenon data indicate that **2** and **3** are at least in part derived from an MBN triplet; the sum of ϕ_2 and ϕ_3 (16×10^{-3}) exceeds ϕ_{23} and ϕ_{24} (3.6×10^3), thus suggesting that the di-π-methane reaction has been enhanced in the more polar medium.[7]

Products related to **2**, and presumably formed by an analogous route, have been isolated from MBN in HOAc/HCl/dioxane (**7**) and MeOMBN in methanol (**15**). The methoxymethyl group of MMBN inverts the polarity of **20** so that protonation occurs at the bridgehead to give **13**. Of the 2-isopropylidenebenznorbornene (IPBN) photoproducts, **10** is a "diverted di-π-methane" product analogous to that isolated from MBN.[1a] Compound **8** appears to be formed by two different routes, since direct photolysis only gives this product when acid is present whereas sensitization (*p*-xylene) is efficient with or without acid. A rationale is presented in Scheme III. The singlet rearrangement to **25** either bypasses **26** (i.e., is concerted) or involves ring closure too rapid for the competitive 1,4 hydrogen shift (therefore requiring acid).

A final point worth noting is the lack of a positional substituent effect on the di-π-methane reaction of the 6- and 7-methoxy-MBN. The two isomers of **15** are found to form at identical rates, a fact which contrasts with the report[8] that meta bridging is preferred over para bridging in 6- and 7-methoxybenznorbornadiene. The simple molecular orbital rationale[9] (in which bridging is proposed to involve the aromatic ring carbon with the largest orbital coefficient in the LUMO), which accommodates Paquette's data, also predicts an unobserved preference for meta bridging in MeOMBN.

Polarization of the Double Bond. The most striking aspect of MBN photochemistry in methanol (eq 1) is the anti-Markownikoff addition of solvent to the double bond. Such addition to an unconjugated olefin is unprecedented, though there are several reports of sensitized anti-Markownikoff additions involving a styrene chromophore.[10] As regards MBN, the susceptibility to nucleophilic attack on the terminus of the double bond is general, with the chloride anion, acetic acid, and even dioxane[11] capable of intercepting the responsible intermediate (eq 3). The reaction efficiency is a function of acid concentration, aryl substitution, and olefin alkylation, with ϕ reaching 0.22 for methanol addition to IPBN at 10^{-3} N H₂SO₄ (eq 5).

Scheme IV

28

30   + H$^+$ $\xleftarrow{\text{MeOH}}$ **29**

31 $\xrightarrow{\text{H}^+}$ **1**

Scheme V

MMBN

32

"a" cleavage   "b" cleavage

(none observed)   (sole adduct)

The combination of xenon quenching[12] and lack of xylene sensitization confirm that the reaction derives from the excited singlet state.[13]

The mechanism we suggest for these reactions is patterned after Arnold's rationale of his electron-transfer, sensitized additions,[10c] and is outlined in Scheme IV. A justification of this mechanism, and specifically its invocation of several discrete intermediates, follows.

Several key observations relevant to Scheme IV come out of our associated photophysical studies (Table I). (a) The fluorescence and singlet lifetime of MBN in hexane are reduced by 67% relative to a dihydro model, indicating that interaction between the two chromophores has introduced a significant new radiationless decay path.[1a] (b) The phenomenon is accentuated by methanol with MBN's fluorescence diminished a further 40% in this solvent. This suggests that the new singlet decay involves some polarization of the molecule. Since CF$_3$MBN shows a 73% decrease in its ϕ_f relative to a dihydro model and IPBN a 71% reduction in its $^1\tau$, charge transfer is from the olefin to the aromatic ring (cf. k_i and **28**). The methoxy-substituted analogue (MeOMBN) would be expected to resist such a polarization and indeed does, with ϕ_f and $^1\tau$ only 11% less than the dihydro model. (c) Despite the requirement for acid catalysis in order to see significant amounts of photoaddition, *acid has no effect on the ϕ_f of MBN or the $^1\tau$ of IPBN.* This indicates that the emitting species (**27**) is not being protonated and is further evidence for a discrete species (**28**) between **27** and the protonated intermediate (**29**). (The nonlinearity of plots of ϕ vs. [H$^+$] and linearity of ϕ^{-1} vs. [H$^+$]$^{-1}$ (Figure 1) require that protonation occurs after, rather than before, excitation.)

The intermediate **29** is represented as an aryl-proton π complex[14] in which neither a full C–H nor a bridged C$_2$–C$_6$ bond is formed.[15] There are several facts which support this view. (1) The use of deuterated media leads to no observable deuteration of the aromatic ring, such as one would expect if reversible σ C–H (D) bonding were occurring. (2) The two CF$_3$MBN isomers add methanol to the double bond at identical rates, a fact inconsistent with the formation of a C$_2$–C$_6$ bridge and creation of negative charge specifically at the ortho and para positions. (3) Were such bridging occurring, deuterium-labeled MMBN would eventually give rise to an intermediate (**32**, Scheme V) having appreciable symmetry. Such symmetry would be expected to lead to comparable efficiencies
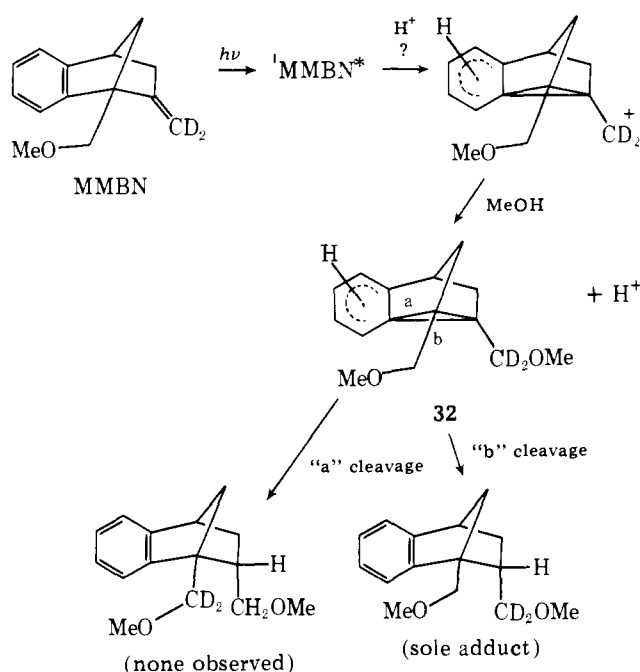
for cleavage of bonds "a" and "b"[17] with deuterium appearing at both the bridgehead and C$_2$ methoxymethylene groups. We take the fact that no such scrambling is observed as further evidence for a charge-transfer interaction which does not involve discrete bonding (**28** and **29**). Note that since di-π-methane chemistry is proceeding simultaneously with addition, we are suggesting that di-π-methane (C$_2$–C$_6$) bonding and charge-transfer polarization involve distinctly different interactions (and consequently have different stereoelectronic requirements; see below).

Returning again to Scheme IV, it should be noted that the full transfer of an electron to the aromatic ring is avoided until the proton is brought into play (**28** → **29**). The free-energy

28 $\xrightarrow{?}$

33
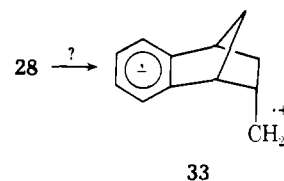
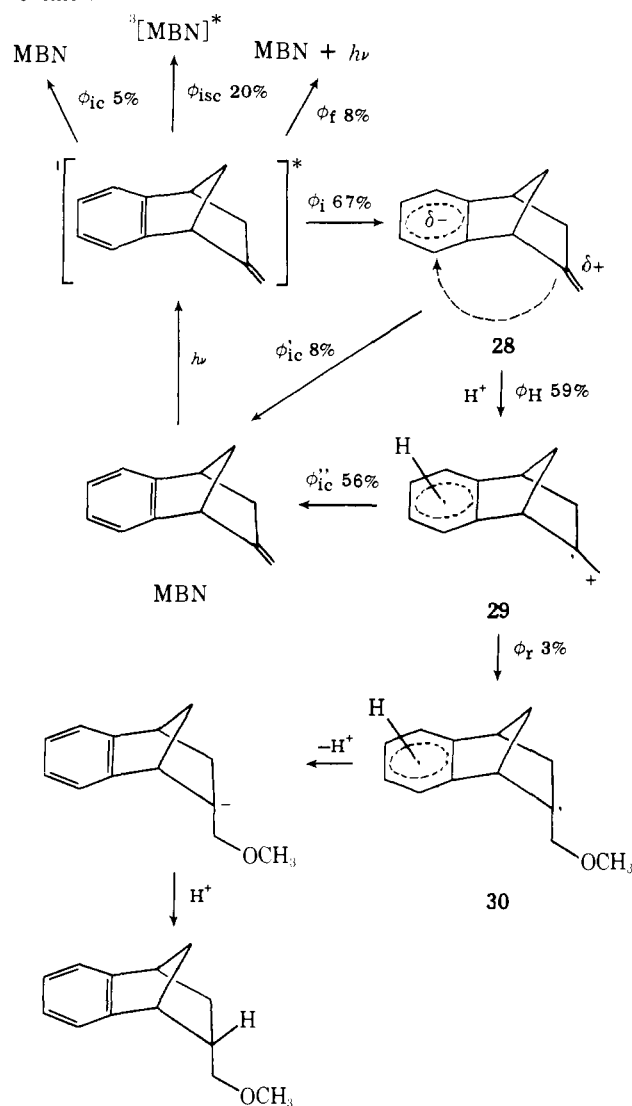change associated with an electron transfer without proton assistance (i.e., **28** → **33**) can be roughly estimated using the equation[18]

$$\Delta G \text{ (kcal/mol)} = 23.06[E(D/D^+)_V - E(A/A^-)_V]$$
$$- 1.29 \times 10^{40} \left(\frac{e_0^2}{\epsilon\alpha}\right) - \Delta E_{0\text{-}0} \quad (10)$$

In this equation $E(D/D^+)_V$ = oxidation potential of the donor (in volts), $E(A/A^-)_V$ = reduction potential of the acceptor (in volts), $\Delta E_{0\text{-}0}$ = singlet energy of the excited species (kcal/mol), and $1.29 \times 10^{40}(e_0^2/\epsilon\alpha)$ is the "Coulombic attraction term" (kcal/mol) with e_0 = electronic charge (1.6×10^{-19} C), ϵ = the dielectric constant, and α = the encounter distance of the ions (in Å).[19] The reduction potential for xylene is unknown but can be estimated as -3.25 V from a plot of $E(A/A^-)_V$ vs. orbital coefficients of the LUMO.[20] For the other values we have used the oxidation potential for 2-methyl-2-butene (2.3 V),[21] the singlet energy of MBN (102.6 kcal/mol) calculated from the intersection of the absorption and fluorescence spectra, and a Coulombic attraction term of 4.40 kcal/mol (using $\alpha = 2.3$ Å and $\epsilon_{\text{methanol}} = 32.6$). With these data, one
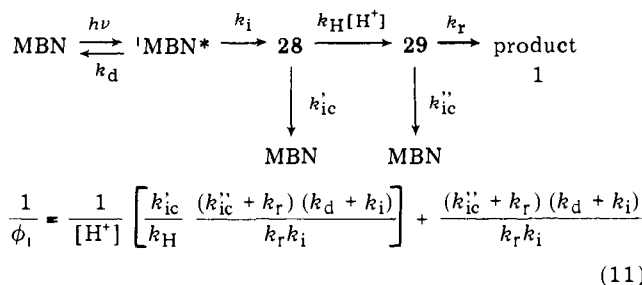
Scheme VI

$$\text{MBN} \quad \overset{3[\text{MBN}]^*}{\underset{}{\longrightarrow}} \quad \text{MBN} + h\nu$$

ϕ_{ic} 5% ϕ_{isc} 20% ϕ_f 8%

ϕ_i 67%

$h\nu$ ϕ_{ic}' 8%

28

H^+ ϕ_H 59%

ϕ_{ic}'' 56%

MBN

29

ϕ_r 3%

$-H^+$

OCH$_3$ OCH$_3$

30

H^+

OCH$_3$

calculates $\Delta G = +21$ kcal/mol for formation of **33**, with the free-energy change remaining positive (+5 kcal/mol) even for CF$_3$MBN. Though the absolute magnitudes of these values are certainly ill defined, it seems reasonable to conclude that a simple electron transfer would be endothermic, with proton assistance necessary for the formation of the radical cation. The acid thus allows for an electron transfer which others have observed only by using aromatics bearing electron-withdrawing groups (e.g., methyl *p*-cyanobenzoate).

As regards the disposition of the radical cation, **29**, reaction with nucleophiles occurs so as to produce the most stable, homoconjugated radical **30**.[10c] The intermediate **29** can also be invoked to rationalize formation of **9** from IPBN (via deprotonation of the isopropylidene methyl group) and formation of **14** from MMBN (via a 1,3 phenyl shift).

A composite picture of MBN's photochemistry and photophysics in methanol is presented in Scheme VI. All ϕ's in Scheme VI represent fractions of ^{1}MBN*. The ϕ_f is an experimental value, ϕ_{isc} (= $k_{isc}^1\tau$) and ϕ_{ic} (= $k_{ic}^1\tau$) are calculated from the observed $^1\tau$ and rate constants obtained from the dihydro model,[1a] and $\phi_i = 1 - (\phi_f + \phi_{isc} + \phi_{ic})$. A simplified version of Scheme VI is presented in Scheme VII, for which a kinetic analysis provides eq 11. The experimentally determined slope and intercept for formation of the anti-Markownikoff product (**1**) as a function of acid (Figure 1) are 4.28×10^{-3} and 33 respectively. Therefore $k_{ic}'/k_H = 1.30 \times 10^{-4}$ and when $[H^+] = 10^{-3}$ M, $k_{ic}'/k_H[H^+] = 0.130$. Thus,

Scheme VII

$$\text{MBN} \underset{k_d}{\overset{h\nu}{\rightleftharpoons}} \, ^1\text{MBN}^* \xrightarrow{k_i} 28 \xrightarrow{k_H[H^+]} 29 \xrightarrow{k_r} \text{product}$$
$$1$$

k_{ic}' k_{ic}''

MBN   MBN

$$\frac{1}{\phi_1} = \frac{1}{[H^+]} \left[\frac{k_{ic}'}{k_H} \frac{(k_{ic}'' + k_r)(k_d + k_i)}{k_r k_i} \right] + \frac{(k_{ic}'' + k_r)(k_d + k_i)}{k_r k_i} \tag{11}$$

at 10^{-3} N acid, 11.5% of **28** decays to MBN (ϕ_{ic} = 8%) and 88.5% of **28** is protonated (ϕ_H = 59%). Since ϕ_1 = 3%, if one assumes no diversion between **30** and product, an appreciable amount of decay to MBN is introduced at **29** (ϕ_{ic}^* = 56%).

There are several places in the overall mechanism where structural changes in the substrate could affect the anti-Markownikoff addition. For example, substituents on the benzene ring affect ϕ_i as follows: MBN (67%), CF$_3$MBN (73%), MeOMBN (11%). In rate terms, k_i's are (10^8 s^{-1}) MBN (1.5), CF$_3$MBN (2.4), MeOMBN (0.3).[22] The absence of anti-Markownikoff addition to MeOMBN undoubtedly reflects this inefficiency of initial charge transfer. It should be noted that a large, olefin-induced increase in aryl radiationless decay need *not* be associated with olefin polarization. For example, 6-phenyl-2-hexene is very short lived owing to the efficient formation of an intramolecular exciplex;[23] yet it fails to show the alcohol addition (attempts to "switch on" the acid-assisted polarization using appropriately substituted analogues are in progress). Likewise, the additional singlet decay intrinsic to 2-methyleneindan[1a] does not lead to alcohol addition. Perhaps most striking, 2-methylenebenzobicyclo[2.2.2]oct-5-ene also resists the reaction even though it structurally resembles the [2.2.1] system[24] and exhibits an additional decay component (58%) comparable to that of MBN.[25] In this case, it may be that ϕ_{ic}' now greatly exceeds ϕ_H. The competition between ϕ_{ic}^* and ϕ_r is most dramatically illustrated with IPBN. This molecule has a ϕ_i (67%) identical with that of MBN, can obviously do little to improve on the 88% of **28** which goes on to **29**, and yet forms the methanol adduct with a quantum efficiency tenfold greater than MBN (0.22 vs. 0.026). The primary effect of the olefin alkyl groups is therefore a very large change in the ratio of ϕ_{ic}^* to ϕ_r.

Conclusions

Whereas the photochemistry of MBN in hexane proceeds through initial "di-π-methane" bridging, photolysis in protic media gives rise to anti-Markownikoff adducts as the major products. These adducts are the end products of a sequence initiated by a singlet-state interaction involving charge transfer from the double bond to the aromatic ring (**28**) followed by a proton-assisted electron transfer forming the radical cation **29**. This radical cation can be intercepted by a variety of nucleophiles. In the absence of acid, or in the case of molecules for which proton-assisted electron transfer is not competitive, the initial charge-transfer process nevertheless provides a facile radiationless decay path which can appreciably shorten the singlet-state lifetime of nonconjugated aryl olefins.

Experimental Section

0.125 in. 3% SE-30; F, 10 ft. × 0.250 in. 10% SE-30; G, 20 ft × 0.25 in. 20% XF-1150; H, 4 ft × 0.25 in. 10% SE-30; I, 20 ft × 0.25 in. 25% SE-30. Column supports were B, 60/80 AW-DMCS Chromosorb W; D, 60/80 AW Chromosorb P; F, G, H, I, 40/60 AW-DMCS Gas Pack W; C, 100/120 AW-DMCS Chromosorb W.

exo-2-Isopropylbenznorbornen-endo-2-ol. Isopropyllithium (12.8 mL of 1.5 M in hexane-ether) was stirred at −78 °C under nitrogen. Benznorbornen-2-one (3.0 g, 19.2 mmol) in ether (30 mL) was added dropwise over a 1-h period. The mixture was quenched with water, washed with 10% sulfuric acid and water, dried over anhydrous magnesium sulfate, and evaporated under vacuum to give 3.7 g of an oil. The oil was found to be 75% pure by analytical VPC on column C but could not be purified by column chromatography because a large percentage of the material decomposed on the column. An analytical sample was purified by VPC on column F.

The spectral data follow: IR (neat) 2.85, 3.35, 6.84, 6.88, 7.39, 8.46, 9.91, and 13.25 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.0–7.3 (m, aryl, 4 H), 3.2–3.35 (m, bridgehead, 2 H), 1.75–2.2 (m, 4 H), 0.95–1.15 (t, $J = 6$ Hz, 7 H), and 0.61 (s, hydroxy); mass spectrum m/e 202 (molecular ion) and 116 (base ion).

Anal. (C$_{14}$H$_{18}$) C, H.

2-Isopropylidenebenznorbornene (IPBN). Phosphorus oxychloride (3.0 g, 0.02 mol) was added to the crude alcohol from the previous reaction (2.0 g) in pyridine (14 g, 0.18 mol). The mixture was refluxed for 2 h, taken up in ether, washed with 10% sulfuric acid and water, and reduced under vacuum to give an oil. The oil was passed through alumina with hexane and the hexane was reduced. The product (1.0 g, 46% yield from benznorbornen-2-one, based on pure product) was 90% pure by VPC on column C. The major impurity was exo-2-chlorobenznorbornene.

An analytically pure sample was prepared by preparative gas chromatography on column G and had the following spectral data: IR (neat) 3.40, 6.86, 7.35, 7.91, 8.92, 9.92, 10.1, 13.4, and 14.0 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.9–7.5 (m, aryl, 4 H), 3.88 (s, H$_1$), 3.32–3.45 (m, H$_4$), 2.25–2.55 (dm, $J = 14$ Hz, 1 H), 1.60–2.00 (m, 3 H), 1.74 (s, methyl, 3 H), and 1.47 (s, methyl, 3 H); mass spectrum m/e 184 (molecular ion) and 141 (base ion).

Anal. (C$_{14}$H$_{16}$) C, H.

Benznorborna-2,5-diene-1-carbinol. Lithium aluminum hydride (1 M) in ether (200 mL) was added dropwise to methyl benznorborna-2,5-diene-1-carboxylate (5.3 g, 26.5 mmol) in ether (150 mL) under nitrogen. The mixture was stirred overnight and ethyl acetate was added to destroy the excess reagent. Hydrochloric acid (50%) was added until a pH of 2 was obtained and the mixture was extracted with ether. The ether was washed with sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and evaporated in vacuo to give the desired alcohol[26] (4.61 g) containing a 3% impurity. An analytical sample was purified by gas chromatography on column F.

The spectral data follow: IR (neat) 2.95, 3.40, 6.93, 7.62, 9.50, 9.69, 9.98, 13.2, 13.4, 13.7, and 14.35 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.05–7.28 (m, aryl, 2 H), 6.75–7.0 (m, aryl and vinyl, 3 H), 6.57 (d, $J = 6$ Hz, vinyl, 1 H), 4.28 (s, methylene adjacent to the hydroxy, 2 H), 3.86 (bs, bridgehead, 1 H), 2.19–2.34 (AB pattern, H$_{7en}$ and H$_{7ex}$), and 1.87 (s, hydroxy); mass spectrum m/e 172 (molecular ion) and 141 (base ion).

Anal. (C$_{12}$H$_{12}$O) C, H.

1-Methoxymethylbenznorborna-2,5-diene. Benznorborna-2,5-diene-1-carbinol containing a 3% impurity (4.6 g, 26.8 mmol) and sodium hydride (0.96 g, 40 mmol) were placed in a round-bottom flask and the system was flushed with nitrogen. Tetrahydrofuran (70 mL) was added and the solution stirred for 30 min. Methyl iodide (15 mL) was then added and the solution stirred for an additional 36 h. The solvent and methyl iodide were evaporated, and the residual oil taken up in ether. The ethereal solution was washed with water, dried, and evaporated to give 5.13 g of the product. An analytical sample was prepared by gas chromatography on column H at 150 °C.

The spectral data follow: IR (neat) 3.45, 6.93, 7.65, 8.38, 8.57, 9.08, 9.97, 13.25, 13.4, 13.7, and 14.5 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.05–7.30 (m, aryl, 2 H), 6.75–7.05 (m, aryl and vinyl, 3 H) 6.56–6.73 (m, vinyl, 1 H), 4.10 (d, $J = 9$ Hz, methylene adjacent to ether, 1 H), 3.97 (d, $J = 9$ Hz, methylene adjacent to ether, 1 H), 3.85 (bs, bridgehead, 1 H), 3.48 (s, methyl, 3 H), and 2.19–2.37 (AB pattern, H$_{7en}$ and H$_{7ex}$); mass spectrum m/e 186 (molecular ion) and 45 (base ion).

Anal. (C$_{13}$H$_{14}$O) C, H.

1-Methoxymethylbenznorbornen-exo-2-ol. Crude 1-methoxybenznorborna-2,5-diene (5.13 g, 27.5 mmol) from the above reac-

tion, sodium borohydride (0.522 g, 13 mmol), and dry THF (50 mL) were stirred at 10 °C under nitrogen. Boron trifluoride etherate (2.81 g, 19.8 mmol) was added while maintaining the temperature between 10 and 20 °C. The mixture was stirred for an additional 1 h at ambient temperature and water (8 mL) then added cautiously. This was followed by 3 N sodium hydroxide (7.9 mL) and 30% hydrogen peroxide (7.9 mL), maintaining the temperature below 30 °C. The mixture was stirred for 1 h at room temperature, taken up in ether, and washed twice with water and twice with brine. The ether layer was dried over anhydrous magnesium sulfate and evaporated to give 5.54 g of an oil. Elution through alumina (750 g) with chloroform, or silica with chloroform/ether (4:1), gave the desired alcohol (0.96 g), the exo-3-ol (1.0 g), and an equal mixture of the two (1.75 g). The alcohols were identified by europium shift ^{1}H NMR experiments, i.e., in the 3-ol, the bridgehead proton shifted 3.4 times faster than the methoxymethylene CH$_2$ hydrogens, whereas in the 2-ol, the bridgehead proton shifted about 0.3 times that for the CH$_2$ group. Analytical samples of each isomer were prepared by preparative gas chromatography on column F.

The spectral data of the exo-2-alcohol follow: IR (neat) 2.90, 3.40, 6.85, 6.90, 8.90, 9.16, 9.43, 9.68, and 13.35 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.90–7.25 (m, aromatic, 4 H), δ_8 4.17 (d, $J_{89} = 10$ Hz), δ_9 3.94 (d, $J_{98} = 10$ Hz), δ_{2en} 3.76–4.05 (m), δ 3.41 (s, methoxy, 3 H), δ 3.00–3.30 (m, H$_4$ and hydroxy), δ_{7ex} 2.11 (bd, $J_{7ex7en} = 9$ Hz), δ 1.54–1.85 (m, H$_{3ex}$, H$_{3en}$, and H$_{7en}$); mass spectrum m/e 204 (weak, molecular ion) and 128 (base ion).

Anal. (C$_{13}$H$_{16}$O$_2$) C, H.

The spectral data for the exo-3-alcohol follow: IR (neat) 2.98, 3.40, 6.83, 6.90, 8.28, 8.41, 9.10, 9.45, 9.83, 10.45, and 13.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.92–7.25 (m, aromatic, 4 H), δ_{3en} 3.80–4.05 (m), δ 3.86 (s, H$_8$ and H$_9$), δ 3.41 (s, methoxy, 3 H), δ 3.14 (bs, hydroxy, 1 H), δ_4 3.03–3.20 (m), δ_{7ex} 2.12 (bd, $J_{7ex7en} = 9$ Hz), δ 1.45–1.90 (m, H$_{2ex}$, H$_{2en}$, and H$_{7en}$); mass spectrum m/e 204 (molecular ion) and 128 (base ion).

Anal. (C$_{13}$H$_{16}$O$_2$) C, H.

1-Methoxymethylbenznorbornen-2-one. 1-Methoxymethylbenznorbornen-exo-2-ol (0.90 g, 4.41 mmol), benzoquinone (1.0 g, 9.3 mmol), and aluminum tert-butoxide (3.83 g, 16.9 mmol) were refluxed in benzene (100 mL) for 48 h. Washing with 10% H$_2$SO$_4$ (2 × 50 mL) and 10% NaOH (5 × 50 mL), followed by evaporation of the solvent, gave 0.79 g (88%) of the ketone. An analytical sample was prepared by gas chromatography on column F at 190 °C.

The spectral data follow: IR (neat) 3.45, 5.75, 6.85, 8.36, 8.54, 9.08, 9.23, 10.35, and 13.25 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.05–7.35 (m, aryl, 4 H), 4.03 (AB pattern, $J = 10$ Hz, methylene adjacent to ether, 2 H), 3.60 (bs, bridgehead, 1 H), 3.42 (s, methoxy, 3 H), 2.17–2.52 (m, 3 H), and 2.01 (dd, $J = 17$ and 4 Hz, H$_{3en}$); mass spectrum m/e 202 (molecular and base ions).

Anal. (C$_{13}$H$_{14}$O$_2$) C, H.

1-Methoxymethyl-2-methylene-d_2-benznorbornene (MMBN-d_2). n-Butyllithium (4.25 mmol) was added to a slurry of methyl-d_3-triphenylphosphonium iodide (2.02 g, 4.95 mmol) in dry THF (15 mL) under nitrogen, and the mixture stirred for 1 h. 1-Methoxymethylbenznorbornen-2-one (500 mg, 2.47 mmol) was added and the mixture refluxed for 12 h. Evaporation of the solvent, trituration with hexane, washing of the hexane layer with water, drying over MgSO$_4$, and evaporation provided an oil which was filtered through alumina with hexane to give 400 mg (80%) of the >95% deuterated olefin. An analytically pure sample was prepared by gas chromatography on column F.

The spectral data follow: IR (neat) 3.40, 6.16, 6.84, 7.02, 7.23, 8.38, 8.45, 8.81, 9.00, 9.11, 10.3, 13.3, and 14.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.0–7.2 (m, aryl, 4 H), 4.02 (AB pattern, $J = 10$ Hz, methylene adjacent to methoxy, 2 H), 3.45 (s, methoxy, 3 H), 3.35 (bs, bridgehead, 1 H), 2.63 (dd, $J = 13$ and 4 Hz, H$_{3ex}$), and 1.65–2.15 (m, 3 H); mass spectrum m/e 202 (molecular ion) and 171 (base ion).

Anal. (C$_{14}$H$_{14}$D$_2$O) C, H, D.

1-Methoxymethyl-2-methylenebenznorbornene (MMBN). This preparation mirrored that of MMBN-d_2. The product was obtained in 72% yield and had a ^{1}H NMR spectrum identical with that of MMBN-d_2, except for two broad singlets integrating to one proton each, at δ 4.73 and 4.86.

Methoxy-2-methylenebenznorbornene (MeOMBN). A 1:0.7 mixture of 6- and 7-methoxybenznorbornen-2-one[4] (620 mg, 3.3 mmol), methyltriphenylphosphonium iodide (2.02 g, 5 mmol), and potassium tert-butoxide (0.560 g, 5 mmol) was refluxed in THF (20 mL) under

nitrogen for 18 h. The mixture was cooled, poured into water, and extracted with hexane. Workup as for MMBN-d_2 provided a 1:0.7 mixture of the 6- and 7-methoxy-substituted olefins (490 mg, 83%). The methoxy peaks of the two isomers were resolved by addition of europium shift reagent but the assignment of which isomer is in excess cannot be made.

The spectral data of the mixture follow: IR (neat) 3.37, 6.02, 6.22, 6.31, 6.80, 7.02, 7.77, 7.86, 8.02, 8.16, 8.93, 9.35, 9.75, and 11.4 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.03 (d, J = 8 Hz, aryl, 1 H), 6.77 (d, J = 3 Hz, aryl, 1 H), 6.54 (dd, J = 8 and 3 Hz, aryl, 1 H), 5.04 (bs, vinyl, 1 H), 4.67 (bs, vinyl, 1 H), 3.71 (s, methoxy, 3 H), 3.62 (bs, H$_1$), 3.22-3.42 (m, H$_4$), 2.50 (dm, J = 15 Hz, H$_{3ex}$), and 1.67-2.04 (m, 3 H); mass spectrum m/e 186 (molecular and base ions).

An analytically pure sample of the mixture of isomers was prepared by gas chromatography on column 1 at 230 °C.

Anal. (C$_{13}$H$_{14}$O) C, H.

Methoxy-*endo*-2-methylbenznorbornene. Methoxy-2-methylene-benznorbornene (30 mg) and 10% palladium on charcoal (10 mg) were reacted in ethyl acetate (2 mL) under hydrogen (3.6 atm) in a Parr hydrogenator. Filtration and evaporation of the solvent gave an oil (30 mg) with a 10% impurity. The product was purified by gas chromatography on column 1 at 230 °C and gave a mixture of the 6- and 7-methoxy derivatives.

The spectral data follow: IR (neat) 3.35, 6.23, 6.30, 6.78, 7.45, 7.86, 8.00, 8.89, 9.32, 9.68, 12.2, and 13.65 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.01 (d, J = 8 Hz, aryl, 1 H), 6.75 (d, J = 3 Hz, aryl, 1 H), 6.57 (dd, J = 8 and 3 Hz, aryl, 1 H), 3.73 (s, methoxy, 3 H), 3.15 (bs, bridge-head, 1 H), 3.00 (bs, bridgehead, 1 H), 2.15-2.45 (m, H$_{2ex}$), 2.08 (dt, J = 4 and 10 Hz, H$_{3ex}$) 1.53-1.87 (m, bridge methylene, 2 H), and 0.55 (d over m, J = 7 Hz, H$_{3en}$ and methyl); mass spectrum m/e 188 (molecular ion).

Calcd for C$_{13}$H$_{16}$O: m/e 188.120. Found: m/e 188.120.

Trifluoromethyl-2-methylenebenznorbornene (CF$_3$MBN). A mixture of 6- and 7-trifluoromethylbenznorbornen-2-one[4] (430 mg, 1.9 mmol), methyltriphenylphosphonium iodide (2.02 g, 5 mmol), and potassium *tert*-butoxide was refluxed in THF (20 mL) under nitrogen for 18 h. Workup as for MBN-d_2 gave a 1:1 mixture of the 6- and 7-trifluoromethyl-substituted olefins (200 mg, 46%). The isomer ratios were determined by ^{13}C NMR but the assignment of which isomer is in excess cannot be made. An anlytically pure sample of the mixture of isomers was prepared by VPC on column G.

The spectral data for the 1:1 mixture follow: IR (neat) 3.38, 6.01, 7.38, 7.52, 7.83, 8.85, 10.05, 11.45, and 12.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.18-7.50 (m, aryl, 3 H), 5.12 (bs, vinyl, 1 H), 4.70 (bs, vinyl, 1 H), 3.69 (bs, H$_1$), 3.36-3.48 (m, H$_4$), 2.53 (dm, J = 15 Hz, H$_{3ex}$), and 1.69-2.06 (m, 3 H); mass spectrum m/e 224 (molecular ion) and 209 (base ion).

Anal. (C$_{13}$H$_{11}$F$_3$) C, H, F.

Trifluoromethyl-*endo*-2-methylbenznorbornene. CF$_3$MBN (10 mg), 10% palladium on charcoal (5 mg), and ethyl acetate (2 mL) were placed in the reaction flask of a (Brown)[2] hydrogenator. The apparatus was flushed with nitrogen and 1 M sodium borohydride (30 mL) was injected into the acetic acid flask. After filtration of the catalyst, the solvent was filtered through alumina and evaporated to give 10 mg of an oil. Purification by gas chromatography on column 1 at 200 °C gave the mixture of isomers.

The spectral data follow: IR (neat) 3.35, 6.25, 6.30, 6.79, 7.45, 9.13, 10.85, and 12.2 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.16-7.48 (m, aryl, 3 H), 2.23-2.37 (bs, bridgehead, 1 H), 2.09-2.23 (m, bridgehead, 1 H), 2.03-2.56 (m, H$_{2ex}$), 2.19 (dt, J = 4 and 10 Hz, H$_{3ex}$), 1.63-1.94 (m, bridge methylene, 2 H), and 0.43-0.70 (d over m, J = 7 Hz, H$_{3en}$ and methyl).

Calcd for C$_{13}$H$_{13}$F$_3$: m/e 226.098. Found: m/e 226.099.

Photoreaction of MBN in Methanol. A solution of MBN (1.9 × 10^{-2} M) in methanol (100 mL) with 1 N H$_2$SO$_4$ (100 μL) was degassed for 30 min with argon and irradiated for 3 h at 254 nm in a photolysis well. The solution was neutralized with sodium bicarbonate and evaporated in vacuo. The resultant oil was taken up in chloroform and dried over anhydrous magnesium sulfate and the solvent was reduced under vacuum. Separation by gas chromatography on column B gave three photoproducts.

***endo*-2-Methoxymethylbenznorbornene (1).** The spectral data follow: IR (neat) 3.35, 3.45, 6.84, 6.91, 8.50, 8.76, 8.87, 9.10, 10.7, and 13.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.0-7.25 (m, aromatic, 4 H), δ 3.18 (s, methoxy, 3 H), δ 2.35-2.90 (m, H$_{2ex}$, H$_8$, and H$_9$), δ_4 3.20-3.32 (m), δ_1 3.30-3.43 (m), δ_{3ex} 2.05 (ddd, J_{3ex3en} = 12, J_{3ex2ex}

= 9, J_{3ex4} = 4.5 Hz), δ_{7en} 1.82 (dm, J_{7en7ex} = 9, J_{7en3en} = 2.5, J_{7en1} = J_{7en4} = 1.6 Hz), δ_{7ex} 1.62 (dt, J_{7ex7en} = 9, J_{7ex1} = J_{7ex4} = 1.6 Hz), δ_{3en} 0.59 (ddd, J_{3en3ex} = 12, J_{3en2ex} = 4, J_{3en7en} = 2.5 Hz); mass spectrum m/e 188 (molecular ion) and 116 (base ion).

Anal. (C$_{13}$H$_{16}$O) C, H.

This product was independently synthesized by hydroboration of MBN and methylation of the resultant alcohol. Photolysis of MBN-d_2 yields 1 lacking two protons from the three-proton multiplet at δ 2.58-2.75 (H$_{2ex}$, H$_8$, H$_9$). Since the couplings of 2-exo to 3-exo and 3-endo can still be seen, it is the methoxymethylene (H$_8$, H$_9$) group which is deuterated. Likewise, photolysis of MBN in CH$_3$OD yields 1 for which H$_{2ex}$ is now missing.

1-Methoxybenzo[6.7]bicyclo[3.2.1]oct-6-ene (2). The spectral data follow: IR (neat) 3.40, 6.80, 6.87, 7.56, 7.84, 8.18, 8.51, 8.79, 8.84, 9.22, 9.30, 9.76, 10.4, and 13.25 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.1-7.35 (m, aromatic, 4 H), δ 3.33 (s, methoxy, 3 H), δ_5 3.20-3.40 (m), δ_{8en} 2.48-2.70 (m), δ_{2ex} 1.90 (dt, J_{2ex2en} = J_{2ex3en} = 12, J_{2ex3ex} = 5.5 Hz), δ_{8ex} 1.57 (d, J_{8ex8en} = 10 Hz), δ 1.43-1.75 (m, 4 H), δ_{3en} 0.48-1.00 (m); mass spectrum m/e 188 (molecular ion), 159 (base ion).

Anal. (C$_{13}$H$_{16}$O) C, H.

This product was independently synthesized by methylation of benzo[6.7]bicyclo[3.2.1]oct-6-en-1-ol.[27] Photolysis of MBN-d_2 yields 2 in which the two-proton multiplet (H$_{2ex}$ and H$_{2en}$) at δ 1.68-2.03 is absent. Likewise, photolysis of MBN in CH$_3$OD yields 2 in which the four-proton multiplet (H$_{3ex}$, H$_{4en}$, H$_{4ex}$, and H$_{8ex}$) at δ 1.22-1.50 has been reduced to a three-proton multiplet and the doublet of triplets at δ_{2ex} 1.86 (J_{3ex2ex} = 5.5, J_{2ex2en} = J_{2ex3en} = 12 Hz) has become a triplet.

1-Allyl-3-methoxyindan (3). The spectral data of the trans isomer follow: IR (neat) 3.40, 6.11, 6.81, 6.90, 7.01, 7.46, 8.42, 9.06, 9.25, 10.15, 11.0 and 13.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.28-7.64 (m, aromatic, 4 H), δ_1 5.75-6.16 (m, J_{12} = 17.6, J_{13} = 9.9, J_{17} = 7.4, J_{16} = 6.5 Hz), δ_2 5.18 (dm, J_{21} = 17.6, J_{23} = 2.2, J_{26} = J_{27} ≈ 1.5 Hz), δ_3 5.15 (dm, J_{31} = 9.9, J_{32} = 2.2, J_{36} = J_{37} ≈ 1.5 Hz), δ_4 4.86 (dd, J_{49} = 6.2, J_{48} = 3.0 Hz), δ_5 ≈ 3.4 (obscured by methoxy), δ 3.42 (s, methoxy, 3 H), δ_6 (pm, J_{67} = 14.2, J_{61} = 6.5, J_{65} = 5.5, J_{63} = J_{62} ≈ 1.5 Hz), δ_7 2.22 (bm), δ_8 2.26 (ddd, J_{89} = 14, J_{85} = 7.5, J_{84} = 3.0 Hz), δ_9 2.00 (5-line pattern, J_{98} = 14, J_{95} = 7.0, J_{94} = 6.2 Hz); mass spectrum m/e 188 (molecular ion) and 115 (base ion).

Anal. (C$_{13}$H$_{16}$O) C, H.

This product was independently synthesized by alkylation of indenyllithium with allyl bromide, followed by acid-catalyzed addition of methanol. Photolysis of MBN-d_2 yields 3 in which the signals due to H$_2$ (5.18 δ) and H$_3$ (5.15 δ) are absent. Photolysis of MBN in CH$_3$OD yields 3 in which the doublet of doublets (δ_4 4.86) is absent.

Photoreaction of MBN in Acetic Acid–Dioxane. A solution of MBN (2 × 10^{-2} M) in 5% acetic acid-dioxane (100 mL) was degassed for 30 min with argon and irradiated for 2.5 h at 254 nm in a photolysis well. The solution was evaporated in vacuo to 5 mL, taken up in water (40 mL), and extracted with ether (2 × 30 mL). The extracts were washed with saturated sodium bicarbonate and brine, dried over anhydrous magnesium sulfate, and evaporated in vacuo to give an oil. Molecular distillation gave a 65% isolated yield of 4. When a solution of MBN (1.3 × 10^{-2} M) with hydrochloric acid (2.4 × 10^{-2} N) in 5% acetic acid-dioxane (100 mL) was irradiated (30-min degassing, 1.75-h photolysis), identical workup and separation on column B gave 4–7.

Benznorbornen-*endo*-2-ylmethyl Chloride (5). The spectral data follow: IR (neat) 3.37, 3.85, 3.90, 3.95, 7.69, 7.83, 8.04, 8.74, 8.84, 9.92, 13.3, 13.9, and 14.21 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.0-7.29 (m, aromatic, 4 H), δ_1 3.35-3.46 (m), δ_4 3.20-3.34 (m), δ 2.39-3.12 (m, H$_{2ex}$, H$_8$, and H$_9$), δ_{3ex} 2.10 (dd, J_{3ex3en} = 12, J_{3ex2ex} = 9.5, J_{3ex4} = 4.5 Hz), δ_{7en} 1.84 (dm, J_{7en7ex} = 9 Hz), δ_{7ex} 1.62 (dm, J_{7ex7en} = 9 Hz), δ_{3en} 0.60 (ddd, J_{3en3ex} = 12, J_{3en2ex} = 4, J_{3en7en} = 2.5 Hz); mass spectrum m/e 192 (molecular ion, M + 2 is one-third as intense) and 116 (base ion).

Anal. (C$_{12}$H$_{13}$Cl) C, H, Cl.

This product was independently synthesized by chlorination of *endo*-benznorbornen-2-ylmethanol with thionyl chloride.

Benznorbornen-*endo*-2-ylmethyl Acetate (4). The spectral data follow: IR (neat) 3.36, 5.77, 6.85, 6.90, 7.27, 7.40, 7.90, 8.15, 9.28 and 13.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.00-7.25 (m, aromatic, 4 H), δ_8 3.63 (dd, J_{89} = 11, J_{82ex} = 7 Hz), δ 3.23-3.39 (m, H$_1$ and H$_4$), δ_9 3.15 (dd, J_{98} = 11, J_{92ex} = 9 Hz), δ_{2ex} 2.40-2.77 (m), δ_{3ex} 2.09 (ddd,

$J_{3ex3en} = 12$, $J_{3ex2ex} = 9$, $J_{3ex4} = 4.5$ Hz), δ 2.01 (s, methyl, 3 H), δ_{7en} 1.85 (dm, $J_{7en7ex} = 9$ Hz), δ_{7ex} 1.63 (dm, $J_{7exen} = 9$ Hz), δ_{3en} 0.68 (ddd, $J_{3en3ex} = 12$, $J_{3en2ex} = 4$, $J_{3en7en} = 2.5$ Hz); mass spectrum m/e 216 (molecular ion) and 116 (base ion).

Anal. ($C_{14}H_{16}O_2$) C, H.

This product was independently synthesized by acetylation of *endo*-benznorbornen-2-ylmethanol with acetic acid and acetic anhydride.

1-(Benznorbornen-*endo*-2-ylmethoxy)-2-(2-chlorethoxy)ethane (6). The spectral data follow: IR (neat) 3.43, 6.84, 6.88, 7.44, 7.78, 9.0, and 13.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.05-7.26 (m, aromatic, 4 H), δ 3.55-3.85 (m, side-chain methylene, 8 H), δ_4 3.20-3.33 (m), δ_1 3.33-3.45 (m), δ 2.40-3.01 (m, H$_{2ex}$, H$_8$, and H$_9$), δ_{3ex} 2.04 (m, $J_{3ex2ex} = 9$ Hz, the other coupling constants are not discernible owing to poor signal to noise), δ_{7en} 1.83 (dm, $J_{7en7ex} = 9$ Hz), δ_{7ex} 1.63 (dm, $J_{7ex7en} = 9$ Hz), δ_{3en} 0.58 (dm, $J_{3en3ex} = 12$ Hz); mass spectrum m/e 280 (molecular ion, M + 2 is one-third as intense) and 84 (base ion).

Calcd for $C_{16}H_{21}ClO_2$: m/e 280.122. Found: m/e 280.122.

1-(2-(2-Chloroethoxy)ethoxy)benzo[6.7]bicyclo[3.2.1]oct-6-ene (7). The spectral data follow: IR (neat) 3.40, 6.81, 6.89, 7.58, 7.76, 7.85, 8.21, 8.95, 9.30, 9.90, and 13.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.05-7.35 (m, aromatic, 4 H), δ 3.52-3.93 (m, side-chain methylene, 8 H), δ_5 3.15-3.34 (m), δ_{8en} 2.41-2.65 (m), δ_{2ex} 1.87 (dt, $J_{2ex3ex} = 5.5$, $J_{2ex2en} = J_{2ex3en} = 12$ Hz), δ 1.35-1.78 (m, H$_{2en}$, H$_{4ex}$, and H$_{4en}$), δ_{8ex} 1.57 (d, $J_{8ex8en} = 10$ Hz), δ_{3en} 0.44-1.05 (m); mass spectrum m/e 280 (molecular ion, M + 2 is one-third as intense) and 84 (base ion).

Calcd for $C_{16}H_{21}ClO_2$: m/e 280.122. Found: m/e 280.121.

Photoreaction of IPBN in Hexane. A solution of IPBN (138 mg, 7.5×10^{-3} M) in hexane (100 mL) was degassed with argon and irradiated for 90 min at 254 nm in a photolysis well. Evaporation and gas chromatography on column G afforded **10.** When *exo*-2-chlorobenznorbornene (which photolyzes to give HCl) was present, **8** and **9** could also be isolated.

1-Isopropenylbenznorbornene (8). The spectral data follow: IR (neat) 3.40, 6.09, 6.80, 6.88, 7.31, 7.90, 8.88, 8.97, 9.91, 11.25, and 13.4 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.17-7.33 (m, aromatic, 4 H), δ 5.17 (bs, vinyl, 1 H), δ 5.06 (bs, vinyl, 1 H), δ_4 3.33-3.45 (m), δ 1.90 (s, methyl, 3 H), δ 1.85-2.10 (m, H$_{7en}$, H$_{2ex}$, and H$_{3ex}$), δ_{7ex} 1.49 (d, $J_{7ex7en} = 9$ Hz), and δ 1.23 (dm, $J = 9$ Hz, H$_{2en}$ and H$_{3en}$); mass spectrum m/e 184 (molecular ion) and 156 (base ion).

Anal. ($C_{14}H_{16}$) C, H.

This product was independently synthesized by hydrogenation of methyl benznorborna-2,5-diene-1-carboxylate, reaction with methylmagnesium iodide, and dehydration with phosphorus oxychloride in pyridine.

endo-2-Isopropenylbenznorbornene (9). The spectral data follow: IR (neat) 3.39, 6.09, 6.86, 6.90, 7.35, 7.88, 8.71, 8.86, 8.95, 9.91, 11.35, and 13.4 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.00-7.26 (m, aromatic, 4 H), δ 4.47 (bs, vinyl, 1 H), δ 4.02 (bs, vinyl, 1 H), δ 3.27-3.45 (m, H$_1$ and H$_4$), δ_{2ex} 2.77-3.06 (m), δ_{3ex} 2.08 (ddd, $J_{3ex3en} = 12$, $J_{3ex2ex} = 9$, $J_{3ex4} = 4.5$ Hz), δ_{7en} 1.87 (dm, $J_{7en7ex} = 9$ Hz), δ_{7ex} 1.68 (dm, half of doublet is obscured), δ 1.61 (s, methyl, 3 H), δ_{3en} 1.20 (ddd, $J_{3ex3en} = 12$, $J_{3en2ex} = 4.5$, $J_{3en7en} = 2$ Hz); mass spectrum m/e 184 (molecular ion) and 116 (base ion).

Calcd for $C_{14}H_{16}$: m/e 184.125. Found: m/e 184.125.

This product was independently synthesized by reaction of benznorbornen-2-one with ethylenetriphenylphosphorane followed by hydroboration, oxidation with chromium trioxide in water, and reaction with methylenetriphenylphosphorane.

1-Isopropylidene-3-vinylindan (10). The spectral data follow: IR (neat) 3.44, 6.10, 6.27, 6.85, 6.89, 7.36, 9.25, 10.15, 11.0, 13.25, and 13.65 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.52-7.68 (m, aromatic, 1 H), δ 7.12-7.36 (m, aromatic, 3 H), δ_3 5.90 (ddd, $J_{32} = 17$, $J_{31} = 10$, $J_{34} = 8$ Hz), δ_2 5.17 (dd, $J_{23} = 17$, $J_{21} = 2$ Hz), δ_1 5.08 (dd, $J_{12} = 2$, $J_{13} = 10$ Hz), δ_4 3.79 (dt, $J_{43} = J_{45} = 8$, $J_{46} = 6$ Hz), δ_5 3.06 (ddm, $J_{54} = 8$, $J_{56} = 16$ Hz), δ_6 2.52 (ddm, $J_{65} = 16$, $J_{64} = 6$ Hz), δ 2.09 (s, methyl, 3 H), δ 1.90 (s, methyl, 3 H); mass spectrum m/e 184 (molecular ion) and 43 (base ion).

Calcd for $C_{14}H_{16}$: m/e 184.125. Found: 184.123.

Photoreaction of IPBN in Methanol. A solution of IPBN (200 mg, 1.1×10^{-2} M) with sulfiric acid (5×10^{-4} N) in methanol (100 mL) was degassed with argon and irradiated for 45 min at 254 nm in a photolysis well. The reaction mixture was reduced in vacuo to 10 mL and washed with water. The organics were extracted with cyclohexane.

The solvent was evaporated under vacuum and the major photoproduct was purified on column G.

2-(Benznorbornen-*endo*-2-yl)-2-methoxypropane (11). The spectral data follow: IR (neat) 3.40, 6.84, 6.90, 7.29, 7.39, 7.86, 8.70, 8.89, 9.13, 9.31, 9.42, 9.53, 9.91, 13.3, 13.55, and 14.2 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.9-7.2 (m, aromatic, 4 H), δ 3.15-3.35 (m, H$_1$ and H$_4$), δ 2.96 (s, methyl, 3 H), δ_{2ex} 2.27-2.58 (m), δ_{3ex} 1.95 (ddd, $J_{3ex3en} = 12$, $J_{3ex2ex} = 10$, $J_{3ex4} = 4.5$ Hz), δ 1.52-1.8 (m, H$_{7ex}$ and H$_{7en}$), δ 0.78 (s, methyl, 3 H), δ 0.56 (s, methyl, 3 H), H$_{3en}$ is hidden under methyl group; mass spectrum m/e 216 (molecular ion) and 58 (base ion).

Anal. ($C_{15}H_{20}O$) C, H.

Photoreaction of 1-Methoxymethyl-2-methylenebenznorbornene (MMBN). A solution of MMBN (150 mg, 7.5×10^{-3} M) and sulfuric acid (10^{-3} N) in methanol was degassed with argon and irradiated for 1 h at 254 nm in a photolysis well. The acid was neutralized with solid sodium bicarbonate and the solvent was evaporated in vacuo. Separation on column G at 185 °C gave **12, 13,** and **14.**

endo-2,1-Bis(methyoxymethyl)benznorbornene (12). The spectral data follow: ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.98-7.15 (m, aromatic, 4 H), δ_{10} 4.05 (d, $J_{10,11} = 10$ Hz), δ_{11} 3.90 (d, $J_{11,10} = 10$ Hz), δ 3.41 (s, methoxy, 3 H), δ_4 3.22 (bs), δ 3.13 (s, methoxy, 3 H), δ 2.40-2.91 (m, H$_{2ex}$, H$_8$, and H$_9$), δ_{3ex} 2.22 (ddd, $J_{3ex3en} = 11$, $J_{3ex2ex} = 10$, $J_{3ex4} = 4$ Hz), δ 1.66-1.96 (m, H$_{7ex}$ and H$_{7en}$), δ_{3en} 0.74 (ddd, $J_{3en3ex} = 11$, $J_{3en2ex} = 4$, $J_{3en7en} = 2$ Hz); mass spectrum m/e 232 (molecular ion) and 160 (base ion).

Dideuterated **12,** formed upon photolysis of MMBN-d_2, was independently synthesized by hydroboration of MMBN-d_2 followed by methylation of the resultant alcohol.

Anal. ($C_{15}H_{18}D_2O_2$) C, H, D.

exo-3-Methoxy-*endo*-3-methoxymethylbenzo[6.7]bicyclo[3.2.1]-oct-6-ene (13). The spectral data follow: ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.1 (s, aromatic, 4 H), δ 3.12 (s, methoxy, 3 H), δ 2.88 (s, methoxy, 3 H), $\delta_{1,5}$ 3.10-3.25 (m, 2 H), δ_{8en} 2.1-2.45 (m), $\delta_{9,10}$ 1.98 (s, 2 H), δ_{8ex} 1.82 (d, $J_{8ex8en} = 10$ Hz), δ 1.74-2.0 (m, H$_{2ex}$, H$_{2en}$, H$_{4ex}$, and H$_{7en}$); mass spectrum m/e 232 (molecular ion) and 187 (base ion) (Calcd: m/e 232.146. Found: m/e 232.147); ^{13}C NMR (CDCl$_3$, 20 MHz) δ 36.5 (t), 40.4 (d), 45.9 (t), 48.6 (q), 58.6 (q), 75.3 (t), 76 (s), 122.7 (d), 126.9 (d), and 146.7 (s).

The ^{1}H NMR of **13**-d_2 shows two protons missing from the four-proton multiplet at δ 1.74-2.00. Two consecutive hydrogen shifts would be necessary to put one deuterium on C$_2$ and one on C$_4$. Since this is unlikely for a primary photoproduct, it is believed that both deuterium atoms reside on the same carbon.

5-Methoxy-5-methoxymethylbenzo[1.2]bicyclo[3.2.1]oct-1-ene (14). The spectral data follow: IR (melt) 3.42, 6.75, 6.90, 8.39, 9.03, 9.22, 9.50, 10.8, 11.9, 13.0, and 13.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.9-7.2 (m, aromatic, 4 H), δ_9 3.48 (d, $J_{9,10} = 11$ Hz), δ 3.32 (s, methoxy, 3 H), δ 3.23 (s, methoxy, 3 H), δ_{10} 3.13 (d, $J_{10,9} = 11$ Hz), δ 2.9-3.2 (m, H$_7$, H$_{3ex}$, and H$_{3en}$), δ_4 2.50 (m), δ_{8ex} 2.27 (ddd, $J_{8ex8en} = 11$, $J_{8ex4} = 5$, $J_{8ex7} = 4$ Hz), δ_{6ex} 2.10 (dd, $J_{6ex6en} = 14$, $J_{6ex7} = 7$ Hz), δ_{8en} 1.76 (bd, $J_{8en8ex} = 11$ Hz), δ_{6en} 1.51 (dd, $J_{6en6ex} = 14$, $J_{6en8en} = 2$ Hz); mass spectrum m/e 232 (weak molecular ion) and 185 (base ion); ^{13}C NMR (CDCl$_3$, 20 MHz) δ 33 (t), 34.5 (t), 41 (d), 42.5 (d), 45.5 (t), 50 (q), 59 (q), 73.5 (t), 87 (s), 125 (d), 126.5 (d), 126.7 (d), 129 (d), 134 (s), and 145.5 (s).

Anal. ($C_{15}H_{20}O_2$) C, H.

The ^{1}H NMR of **14**-d_2 shows that two protons are absent from the three-proton multiplet at δ 2.9-3.2. The signal for H$_7$ is present and $J_{6ex7} = 7$ Hz can be seen in the H$_{6ex}$ multiplet at δ 2.10.

Photoreaction of MeOMBN. A solution of a mixture of isomers (1:0.7) of MeOMBN (150 mg, 8×10^{-3} M) in methanol with sulfuric acid (10^{-3} N) was degassed with argon and irradiated for 55 min at 254 nm in a photolysis well. Solid sodium bicarbonate was added and the methanol was reduced in vacuo. The photoproducts were purified on column G at 175 °C to give the two isomers of **15** (ratio by VPC was 1:0.7) and **16.**

1,10- and 1,11-Dimethoxybenzo[6.7]bicyclo[3.2.1]oct-6-ene (15). The spectral data follow: IR (neat, major isomer) 3.42, 6.21, 6.30, 6.79, 7.58, 7.80, 7.90, 8.15, 8.26, 8.38, 8.53, 8.92, 9.4, 9.75, and 12.35 μ; IR (neat, minor isomer) 3.41, 6.23, 6.31, 6.79, 6.90, 7.60, 7.90, 8.01, 8.14, 8.55, 8.69, 8.98, 9.32, 9.80, 10.40, and 12.35 μ; the ^{1}H NMR spectra (CDCl$_3$, 90 MHz) are the same for each isomer (except for slight differences in the aromatic multiplet at δ 6.65-6.85) and show δ 7.04 (d, $J = 8.5$ Hz, aromatic, 1 H), δ 6.65-6.85 (m, aromatic, 2 H), δ 3.78 (s, methoxy, 3 H), δ 3.30 (s, methoxy, 3 H), δ_5 3.15-3.30 (m),

δ_{8en} 2.43–2.67 (m), δ_{2ex} 1.87 (dt, J_{2ex3ex} = 5.5, J_{2ex3en} = J_{2ex2en} = 12 Hz), δ_{3ex} 1.57 (d, J_{8ex8en} = 10 Hz), δ 1.40–1.75 (m, H_{2en}, H_{3ex}, H_{4en}, and H_{4ex}), δ_{3en} 0.65–1.0 (m); mass spectrum m/e 218 (molecular and base ions).

Major isomer. Anal. ($C_{14}H_{18}O_2$) C, H.

Minor isomer. Anal. ($C_{14}H_{18}O_2$) C, H.

cis- and *trans-***5,3-** and **-6,3-Dimethoxy-1-allylindan (16).** The spectral data follow: IR (neat) 3.41, 6.10, 6.22, 6.31, 6.74, 6.85, 7.00, 7.8, 8.0, 8.13, 8.45, 8.75, 8.92, 9.10, 9.3, 9.73, 10.1, 11.0, 11.85, and 12.3 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.7–7.3 (m, aromatic, 3 H), δ_1 5.6–6.1 (m), δ_2 5.08 (dm, J_{12} = 16 Hz), δ_3 5.05 (dm, J_{31} = 10 Hz), δ_4 5.77 (dd, J_{49} = 6, J_{48} = 3.5 Hz), δ 3.79 (s, methoxy, 3 H), δ 3.45 and 3.36 (singlets, methoxy peaks of cis and trans isomers (1:3.2), 3 H), δ 2.0–3.0 (m, 5 H) (the ^{1}H NMR is complicated by the presence of an impurity); mass spectrum m/e 218 (molecular and base ions). Anal. ($C_{14}H_{18}O_2$) C, H.

Photoreaction of CF$_3$MBN. A solution of CF$_3$MBN (22 mg, 1.3 $\times$ 10^{-3} N) and sulfuric acid (10^{-3} N) in methanol (75 mL) was degassed with argon and irradiated for 60 min at 254 nm in a photolysis well. Solid sodium bicarbonate was added and the solvent was evaporated in vacuo. The remaining oil was taken up in pentane, dried over anhydrous magnesium sulfate, concentrated, and purified on column G at 150 °C.

6- and 7-Trifluoromethyl-*endo*-2-methoxymethylbenznorbornene (17). The spectral data follow: IR (neat) 3.37, 3.46, 6.17, 6.85, 6.98, 7.39, 7.57, 7.75, 7.85, 8.6, 8.9, 9.24, 9.30, 9.48, 10.5, 11.2, and 11.95 μ; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.29–7.49 (m, aromatic, 3 H), δ 3.48 (bs, H$_1$ or H$_4$), δ 3.36 (bs, H$_1$ or H$_4$), δ 3.22 (s, methoxy, 3 H), δ 2.33–3.0 (m, H$_{2ex}$, H$_{10}$, and H$_{11}$), δ_{3ex} 2.13 (ddd, J_{3ex3en} = 12, J_{3ex2ex} = 9, J_{3ex4} = 4.5 Hz), δ_{9en} 1.78 (dm, J_{9en9ex} = 9 Hz), δ_{9ex} 1.67 (bd, J_{9ex9en} = 9 Hz), δ_{3en} 0.63 (dm, J_{3en3ex} = 12 Hz, width of multiplet is 7 Hz); mass spectrum m/e 256 (molecular ion) and 184 (base ion). Calcd for $C_{14}H_{15}F_3O$: m/e 256.107. Found: m/e 256.108.

References and Notes

(1) (a) Organic Photochemistry. 41. Part 40: F. Scully, T. Nylund, F. Palensky, and H. Morrison, *J. Am. Chem. Soc.*, preceding paper in this issue. (b) Abstracted from the Doctoral Dissertation of T.N., Purdue University, 1978.

(2) Portions of this research have been reported in preliminary form; cf. H. Morrison and T. Nylund, *J. Chem. Soc., Chem. Commun.*, 785 (1976); H. Morrison, T. Nylund, and F. Palensky, *ibid.*, 4 (1976); 4; H. Morrison and T. Nylund, *ibid.*, 104 (1977).

(3) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970.

(4) We are grateful to Professor H. C. Brown for providing the ketone precursors of MeOMBN and CF$_3$MBN.

(5) Acid-assisted opening of **18** to give **22** directly represents a reasonable

(6) The *photochemical* transformation of **18** to **21** is well precedented (R. G. Weiss and G. S. Hammond, *J. Am. Chem. Soc.*, **100**, 1172 (1978), and references cited therein) but there is no evidence that **3** is a secondary photoproduct.

(7) Methanol is reported to cause a "surprising" twofold increase in the di-π-methane rearrangement of 1-methylene-4,4-diphenyl-2-cyclohexene; cf. H. E. Zimmerman and G. E. Samuelson, *J. Am. Chem. Soc.*, **91**, 5307 (1969).

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(27) We are grateful to Professor J. Wilt for a sample of this alcohol.

alternate path to **2** but **20** (or some other intermediate) is necessary to rationalize **3**.[6]