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Photochemistry of Bichromophoric Molecules. Photochemistry and Photophysics of 2-Methylenebenznorbornene and Related Nonconjugated Aryl Olefins in Nonprotic Media[1]

Frank Scully, Tom Nylund, Fred Palensky, and Harry Morrison*

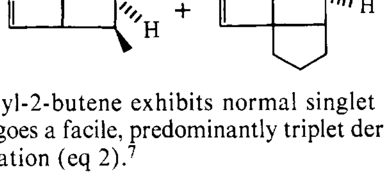
Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received April 25, 1978*

Abstract: Three nonconjugated aryl olefins, having well-defined but varied interorbital angles between the chromophores, have been studied: 2-methylenebenznorbornene (MBN), 2-ethylidene-1-methylindan (EMI), and 1-ethylidene-8,9-benzospiro[3.5]-nonane (ESO). The latter two are new compounds and their syntheses are detailed. In all cases, photoelectron, ultraviolet absorption, and fluorescence emission spectra have been measured. The solution-phase photochemistry of these molecules, using 254-nm irradiation, has been elaborated; MBN reacts primarily via a "diverted di-π-methane" reaction while EMI, ESO, and 2-isobutylidenebenznorbornene (IBN) undergo a facile olefin *E/Z* photoisomerization. Xenon perturbation methods have been used to gain insight into the relative involvement of singlet and triplet states in these reactions, and it appears that both states participate. Singlet interaction between the chromophores is a function of their geometry, being greatest in MBN (where appreciable charge transfer occurs in polar media), reduced in EMI, and minimal in ESO. Interaction at the triplet level is complete in all cases, there being no aryl phosphorescence observed for any of the substrates. An important feature of both MBN and EMI is extensive nonradiative decay from the singlet and triplet states; this decay is caused by the presence of the olefin moieties, does not involve olefin isomerization, and may well be general for nonconjugated aryl olefins.

The systematic study of bi- and polychromophoric molecules has generated considerable interest,[2,3] representing as it does the logical extension of the intensive surveys of monofunctional compounds which dominated photochemistry until recent years. Our own efforts in this area have proceeded at two levels: (a) we have been examining ground- and excited-state interactions between functionalities in conformationally mobile, acyclic systems[2] and (b) we have been studying these interactions in relatively rigid carbon frameworks. Each of the above has advantages with regard to obtainable information. Flexible systems provide a time-dependent spectrum of interchromophoric relationships which give rise to "preexcitation" and "postexcitation" interactions, and in fact may be used to obtain rate constants for bond rotations in chains.[4] By contrast, rigid molecules permit one to study interactions as a function of well-defined interchromophoric distances and angular relationships.[5]

Among the functional group pairs examined in these laboratories, the aryl olefins have proven particularly fruitful, giving rise in acyclic arrays to both triplet and singlet interactions upon excitation of the benzene ring. Thus 6-phenyl-2-hexene provided the first suggestion of, and evidence for, aryl olefin singlet exciplexes as precursors to cycloadducts.[6] Following excitation, the two functionalities achieve a collinear arrangement (allowed for by the trimethylene "bridge"), which permits rapid ($4 \times 10^8\ s^{-1}$) complexation, almost complete fluorescence quenching, and eventual photochemistry (eq 1).

$$\underset{(Z)}{Ph(CH_2)_3CH{=}CHCH_3} \xrightarrow[254\ nm]{h\nu}$$



(1)

By contrast 1-phenyl-2-butene exhibits normal singlet photophysics but undergoes a facile, predominantly triplet derived, *E/Z* photoisomerization (eq 2).[7]

$$\underset{(Z)}{PhCH_2CH{=}CHCH_3} \underset{254\ nm}{\overset{h\nu}{\rightleftarrows}} \underset{(E)}{PhCH_2CH{=}CHCH_3} \qquad (2)$$

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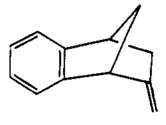
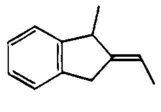
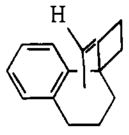
To further define the stereoelectronic requirements for aryl olefin excited- and ground-state interactions, we have synthesized a series of polycyclic molecules having different functional group orientations. These include 2-methylenebenznorbornene (MBN), 2-ethylidene-1-methylindan (EMI),


MBN


EMI

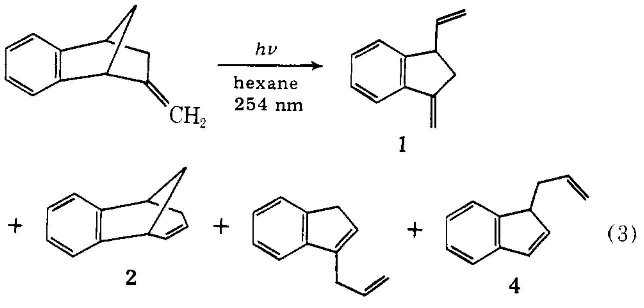


ESO

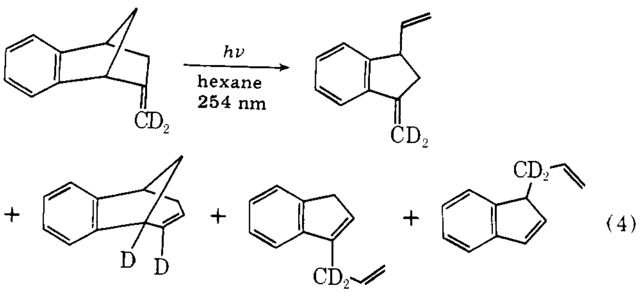
and 1-ethylidene-8,9-benzospiro[3.5]nonane (ESO). Our discussions will be restricted to the photochemistry and photophysics of these compounds in nonprotic media;[8] an elaboration of our observations in protic media[9] is presented in the accompanying paper.[10]

Results

Photochemistry of 2-Methylenebenznorbornene (MBN). Irradiation of a 0.01 M solution of MBN in *n*-hexane with a low-pressure mercury lamp results in the formation of four primary photoproducts (**1–4**) isomeric with the starting material.[11] The major product, **1**, is a new compound and has been identified as 1-methylene-3-vinylindan by spectroscopic analysis (cf. Experimental Section). Compound **2** (benzo[6.7]bicyclo[3.2.1]octa-2,6-diene), **3** (3-allyl-1*H*-indene), and **4** (1-allyl-1*H*-indene) have been previously characterized and were identified by comparison of spectra with authentic, independently synthesized samples. The reaction is summarized in eq 3.



Photochemistry of 2-Methylene-*d*-benznorbornene. MBN, deuterated in the methylene position, was readily prepared using triphenylmethyl-d_3-phosphonium bromide and benznorbornen-2-one. Photolysis was conducted under conditions identical with undeuterated material, products were isolated by VPC, and the location of the deuterium atoms was ascertained by NMR (see Experimental Section). The reaction is depicted in eq 4.



Quantum Efficiencies of Formation of Photoproduct[13] and Disappearance of MBN. Quantum efficiencies were determined in low-conversion runs and are as follows: **1**, 6.3×10^{-3}; **2**, 1.5×10^{-3}; **3**, 1.3×10^{-3}; **4**, 0.8×10^{-3}. The separately determined quantum efficiency for disappearance of MBN is 13×10^{-3}.

Effect of *trans*-2-Heptene on the Photochemistry of MBN. To confirm that the photochemistry caused by direct irradiation does not involve *inter*molecular aryl–olefin interactions, MBN was irradiated in the presence of an external olefin, *trans*-2-heptene. The use of molar quantities of the olefin 12–59-fold greater than MBN led to no observable quenching of the formation of **1**. In a separate experiment, the solutions were analyzed for formation of *cis*-2-heptene. Using 5.4×10^{-3} M MBN and olefin concentrations from 6.8×10^{-3} to 19×10^{-3} M, prolonged irradiation times were required before measurable amounts of cis isomer could be detected (i.e., under comparable photolysis conditions, of the order of 7% conversions to **1** could be achieved in ~6 h, whereas the 6.8 mM heptene tube required ~30 h for ~9% conversions to *cis*-2-heptene). Since secondary photoproduct formation would be significant with such long reaction times,[11] we interpret these results merely as confirmation of the short-lived, noninterceptable nature of the MBN triplet. These observations are substantiated by the lack of MBN phosphorescence (see below).

Photosensitized Rearrangement of MBN. We have demonstrated that the anti-Markownikoff addition of acetic acid to MBN proceeds from the excited singlet state.[9,10] This reaction can then serve as a probe for singlet energy transfer from a prospective triplet sensitizer. Thus, hexane solutions of toluene and MBN, in which toluene absorbed essentially all 254-nm incident radiation, gave rise to MBN rearrangement, but control studies indicated that acetic acid addition to MBN occurred as well. By contrast, *p*-xylene *did not* sensitize addition of acetic acid but *did* effectively cause MBN rearrangement. The product ratio, for 70% loss of MBN, is **1**, 90%; **2**, 5%; **3**, 4%; and **4**, 0%. These numbers may be compared with the ratio from low-conversion, direct irradiation quantum efficiency data: **1**, 62%; **2**, 19%; **3**, 13%; **4**, 5%. A quantitative comparison of these data is beclouded by the ambiguities of photosensitized secondary reactions (for example, there is a 9% formation of the di-π-methane photoproduct of **2**,[11] which explains the diminished presence of **2** in the sensitized run). However, the MBN triplet is clearly capable of giving rise to **1**, **2**, and **3**, and the absence of **4** and the increased proportion of **1** seem statistically significant.

Xenon Perturbation Studies on MBN. Varying amounts of xenon were added to degassed hexane solutions of MBN, and the yields of photoproducts compared with those obtained in the absence of xenon. The formation of all four photoproducts (**1–4**) was enhanced by xenon, the increases ranging from 50% (**1**) to over 100% (**4**). The degree of fluorescence quenching was measured simultaneously and plotted by the method of Fleming, Quina, and Hammond,[14] i.e., $[(F_0/F) - 1]$ vs. $[(F_0/F)(P/P_0) - 1]$. In these expressions, F_0 = fluorescence without xenon, F = fluorescence with varying xenon concentrations, P_0 = product formation without xenon, and P = product formation with varying xenon concentrations. Least-squares plots of the data of each of the products are shown in Figure 1; the slopes (which equal ϕ_{isc} when the product probe is 100% triplet derived; cf. the Discussion section) are **1**, 0.52 ± 04; **2**, 0.44 ± 0.06; **3**, 0.41 ± 0.04; and **4**, 0.32 ± 0.03.

Photochemistry of 2-Isobutylidenebenznorbornene (IBN). IBN was prepared by the Wittig olefination of benznorbornen-2-one, there being formed a 90:10 mixture of *Z* and *E* olefins. Larger quantities of the *E* isomer were prepared by 254-nm irradiation of the synthetic mixture. The *Z* and *E* isomers were separated by preparative VPC and characterized by ^{13}C NMR (cf. Experimental Section).

Irradiation of either isomer in hexane solutions using 254-nm light rapidly led to geometrical isomerization[15] (eq 5). Quantum efficiencies for these reactions are $\phi_{Z \to E} = 0.10$ and $\phi_{E \to Z} = 0 .08$ (under the conditions of these measure-

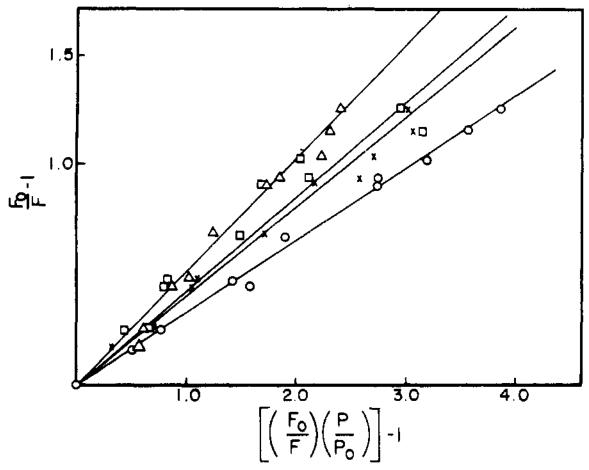


Figure 1. MBN xenon perturbation plots: **1** (△), **2** (□), **3** (×), **4** (○).

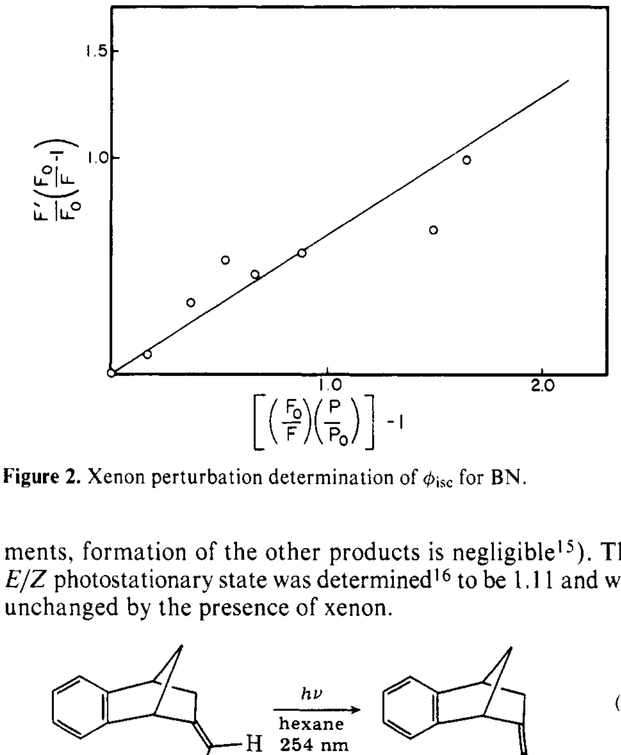
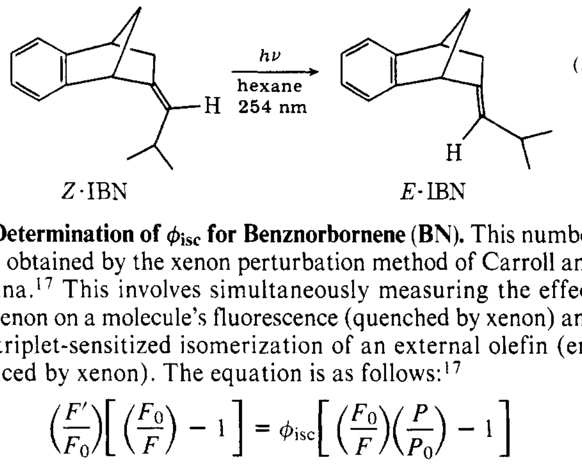


Figure 2. Xenon perturbation determination of ϕ_{isc} for BN.

ments, formation of the other products is negligible[15]). The E/Z photostationary state was determined[16] to be 1.11 and was unchanged by the presence of xenon.



(5)

Z-IBN E-IBN

Determination of ϕ_{isc} for Benznorbornene (BN). This number was obtained by the xenon perturbation method of Carroll and Quina.[17] This involves simultaneously measuring the effect of xenon on a molecule's fluorescence (quenched by xenon) and its triplet-sensitized isomerization of an external olefin (enhanced by xenon). The equation is as follows:[17]

$$\left(\frac{F'}{F_0}\right)\left[\left(\frac{F_0}{F}\right)-1\right] = \phi_{isc}\left[\left(\frac{F_0}{F}\right)\left(\frac{P}{P_0}\right)-1\right]$$

F' = fluorescence without olefin or xenon, F_0 = fluorescence without xenon, F = fluorescence with olefin and varying xenon concentrations, P_0 = olefin isomerization (*cis*-2-heptene) without xenon, and P = olefin isomerization with varying xenon concentrations. The data are plotted in Figure 2, with the least-squares-derived slope (ϕ_{isc}) equal to 0.59.

We had earlier done a more routine ϕ_{isc} determination on 2-methylbenznorbornene (MeBN), using *trans*-2-heptene as a triplet counter. Using a decay ratio equal to that for the toluene-sensitized isomerization of heptene, we obtained a ϕ_{isc} of 0.62 ± 0.04, in reasonable agreement with the benznorbornene value.

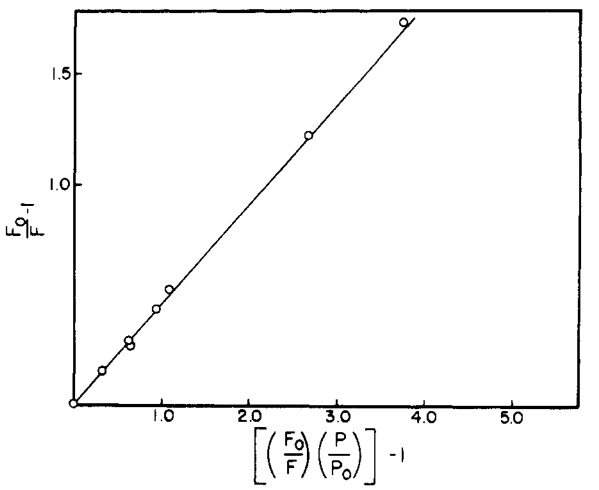


Figure 3. IBN xenon perturbation plot.

Xenon Perturbation Studies on IBN. Using a procedure identical with that discussed for MBN (cf. Figure 1), but employing Z to E photoisomerization of IBN as the product probe, gave the data plotted in Figure 3. The slope is 0.46.

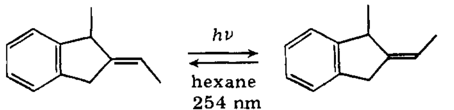
Spectroscopy of MBN. A. Absorption and Fluorescence. These spectra, taken in hexane at room temperature, are presented in Figure 4, with data for MeBN by way of comparison. ϕ_f values for these and related compounds are given in Table I together with singlet lifetimes. The reductions in ϕ_f for the unsaturated bicyclics at room temperature are observed as well as 77 K, i.e., the ϕ_f ratio for MBN:MeBN = 0.38 and **2**:**6** = 0.50, at 77 K.

B. Phosphorescence. None of the aryl olefins showed phosphorescence in an isopentane glass at 77 K. Both MeBN and **6** phosphoresce, with efficiencies of 1.70 and 0.71 relative to toluene.

C. Photoelectron Spectroscopy. Vertical ionization energies for MBN[19] and related molecules are presented in Table II.

Preparation of 2-Ethylidene-1-methylindan (EMI). EMI was prepared by the sequence outlined in Scheme I. This route provides a mixture of the isomers, with >98% E. Enrichment of the Z isomer was accomplished by irradiating the synthetic mixture. The isomers were separated by preparative VPC and structures assigned using ^{13}C NMR spectroscopy (cf. Experimental Section).

Photoisomerization of EMI. Irradiation of either EMI isomer led to rapid E/Z interconversion[22] (eq 6). The quantum



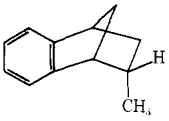
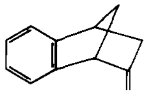
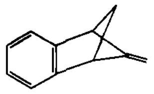
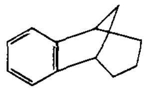
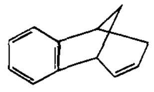
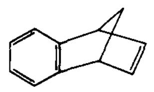
(6)

E Z

efficiency for $E \rightarrow Z$ is $\phi_{E\rightarrow Z} = 0.14_6 \pm 0.01_2$ and the photostationary state, $(E/Z)_{pss} = 0.88 \pm 0.02$. A combination of these data and the extinction coefficients at 254 nm (E, 401 M^{-1} cm^{-1}; Z, 409 M^{-1} cm^{-1}) gives $\phi_{Z\rightarrow E} = 0.13$. The photostationary state changes under the influence of xenon, to become $(E/Z)_{pss} = 0.99 \pm 0.02$. With p-xylene sensitization, $(E/Z)_{pss} = 1.10 \pm 0.01$. Photolysis of E-EMI in the presence of an equimolar concentration of *cis*-2-heptene gave 4% conversion to Z-EMI without any detectable formation of *trans*-2-heptene. The quantum efficiency for disappearance[22] of EMI = 0.01.

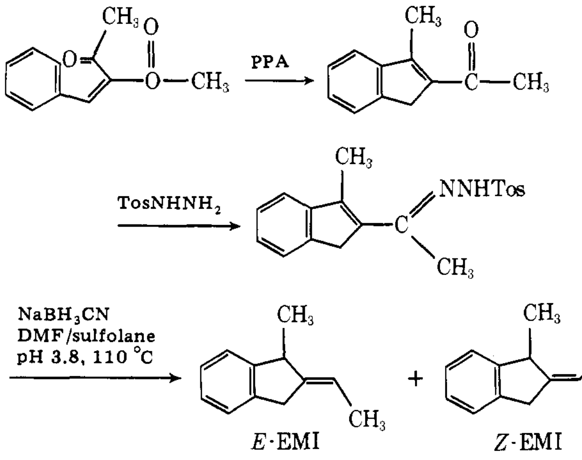
Xenon Perturbation Studies on EMI. Use of the procedure outlined earlier for MBN and IBN, in this case monitoring $E \rightarrow Z$ photoisomerization as a function of xenon concentration,

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

compd	ϕ_f[a]	$^1\tau$, ns[b]
	0.24	13.5
	0.08	4.5
 5		11.0
 6	0.25	14.0
 2	0.15	8.5
	<10^{-3}	

[a] All ϕ_f values were determined relative to toluene (ϕ_f = 0.14).[18]
[b] These values are considered accurate to ±1 ns.

Scheme I



gave the data plotted in Figure 5. The least-squares-derived slope is 0.61 ± 0.01.

Determination of ϕ_{isc} for 1-Methylindan. This measurement was done by the xenon perturbation method,[17] using *cis*-2-heptene as described above for benznorbornene. The data are plotted in Figure 6, with the least-squares-derived slope, $\phi_{isc} = 0.59 \pm 0.00_2$.

Spectroscopy of EMI. A. Absorption and Fluorescence. These spectra, taken in hexane at room temperature, are presented in Figure 7 together with data for 2-ethyl-1-methylindan (EMIH) as a model monochromophoric system. The ϕ_f's for *E*- and *Z*-EMI are both 0.22, whereas EMIH has ϕ_f = 0.34. The $^1\tau$'s reflect this difference, being 24 ns for EMIH and 18 ns each for the EMI isomers.

B. Phosphorescence. Neither of the EMI isomers shows phosphorescence in an ethanol glass at 77 K, whereas EMIH phosphoresces with an efficiency 0.77 that of toluene.

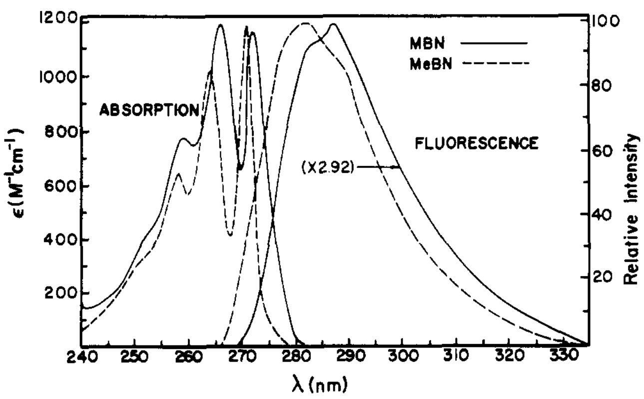


Figure 4. Absorption and fluorescence spectra for MBN and MeBN, in hexane at room temperature. (Note that the MBN fluorescence is scaled up by a factor of 2.92).

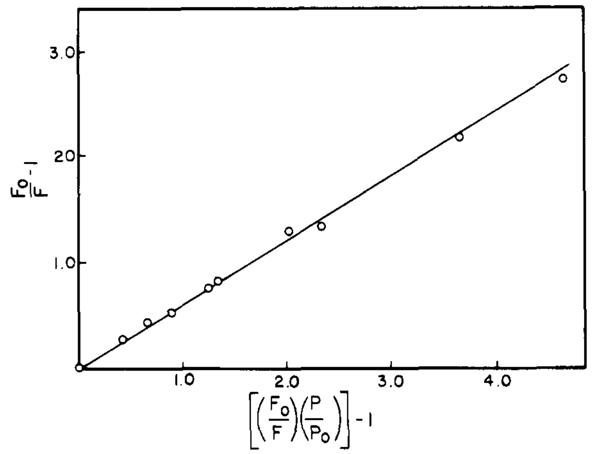
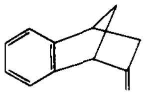
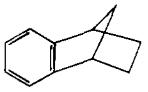
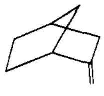
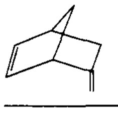


Figure 5. *E*-EMI xenon perturbation plot.

Table II. PES Values for MBN and Related Molecules

compd	vertical ionization potential, eV	assignment
	8.40 8.90 9.23	benzene S benzene A olefin
 BN	8.42^{20} 8.93	benzene S benzene A
	9.04^{21}	olefin
	9.01^{21} 9.38	olefin olefin

C. Photoelectron Spectroscopy. Vertical ionization energies[23] of the structurally simpler EMI analogue 2-methyleneindan,[24] and related molecules are presented in Table III.

Preparation of 1-Ethylidene-8,9-benzospiro[3.5]nonane (ESO). ESO was prepared by the sequence outlined in Scheme II. This route provided a mixture of isomers, with a *Z*:*E* ratio of 95:5. The isomers were separated by preparative VPC and assigned structures using ^{1}H NMR (cf. Experimental Section). Larger quantities of the *E* isomer could be prepared by irradiation of the synthetic mixture.

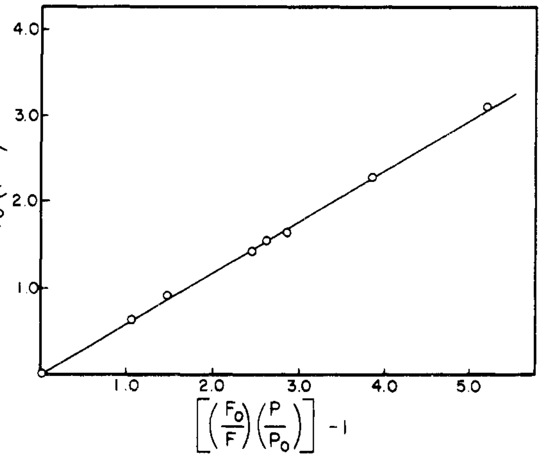
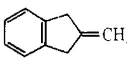
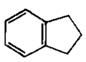
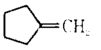


Figure 6. Xenon perturbation determination of ϕ_{isc} for 1-methylindan.

Table III. PES Values for 2-Methyleneindan and Related Molecules

compd	vertical ionization potential, eV	assignment
	8.61	benzene S
	9.14	benzene A
	9.45	olefin
	8.46[20]	benzene S
	9.04	benzene A
	9.15[21]	olefin

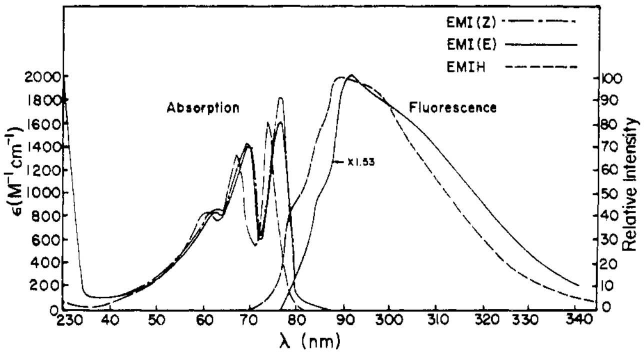
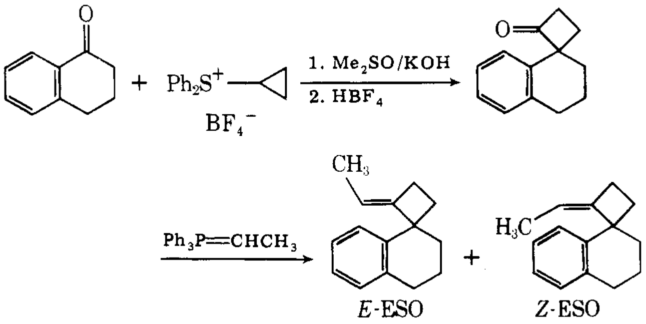
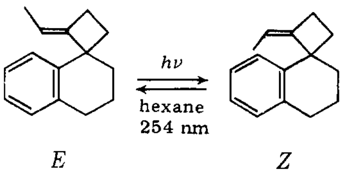


Figure 7. Absorption and fluorescence spectra for EMI and EMIH, in hexane at room temperature. (Note that the *E*-EMI fluorescence is scaled up by a factor of 1.53).

Scheme II



Photoisomerization of ESO. Irradiation of either ESO isomer led to rapid *E*/*Z* interconversion (eq 7). Quantum efficiencies are $\phi_{E\rightarrow Z} = 0.20_0 \pm 0.00_4$ and $\phi_{Z\rightarrow E} = 0.20_4 \pm 0.00_6$. The photostationary state, $(E/Z)_{pss} = 1.00 \pm 0.01$. Extended irradiations of equimolar concentrations of 1-methylene-8,9-benzospiro[3.5]nonane (MSO) and *cis*-2-heptene showed no measurable heptene isomerization.



(7)

Xenon Perturbation Studies on ESO. Xenon had essentially no effect on either ESO $Z \rightarrow E$ or $E \rightarrow Z$ isomerization, although xenon did quench ESO fluorescence. The model monochromophoric compound, 5,6-benzospiro[3.5]nonane, was prepared by the catecholborane reduction and decomposition of the tosylhydrazone of 8,9-benzospiro[3.5]nonan-1-one. Attempts to measure ϕ_{isc} for this compound by xenon-enhanced sensitization of a 2-heptene isomerization (as described above) were unsuccessful; again fluorescence quenching by xenon was observed, but no effect on 2-heptene isomerization was noted.

Spectroscopy of ESO. A. Absorption and Fluorescence. The absorption (>220 nm) and fluorescence spectra of *E*- and *Z*-ESO are essentially identical in band shape and intensity; they are also virtually superimposable on those of a monochromophoric model, 1-methyl-8,9-benzospiro[3.5]nonane (MSOH). The ϕ_f for the methylene analogue, MSO, was measured using toluene as a standard and found to be 0.18. The singlet lifetimes of ESO, MSO, and the related monochromophoric models are all 30.5 ns.

B. Phosphorescence. As with the other aryl olefins discussed above, ESO shows no phosphorescence at 77 K in an ethanol glass. Rather surprisingly, the monochromophoric analogue, MSOH, also shows no phosphorescence.

C. Photoelectron Spectroscopy. Vertical ionization energies[23] of MSO, MSOH, and related molecules are presented in Table IV.

Discussion

A. Photochemistry of MBN. 1. Products and Mechanism. The photochemical rearrangements of MBN (eq 3) are the most deep-seated of the transformations detailed in the Results section; photolysis of EMI and ESO leads primarily[21] to $E \rightleftarrows Z$ interconversion (eq 6 and 7). The experiment with deuterium-labeled MBN (eq 4) allows for a rationalization of the photolysis in terms of a "diverted di-π-methane" reaction[8a] (Scheme III). Excitation is followed by the usual[25] di-π-methane bond-making and bond-breaking steps to give the 1,3-diradical **8**. The ultimate formation of **2**, **3**, and **4** requires that the "normal", but highly strained, di-π-methane product **9** is formed as a transient.[26] However, the major pathway is fragmentation of **8** to the carbene **10**, which rearranges to **1**. Similar diversions from di-π-methane cyclization have been observed for dibenznorbornadienes[27] and triptycenes.[28]

When an appropriate label is present, such as the isopropyl group in IBN, geometrical isomerism of the olefin becomes evident (eq 5). Isomerization is far more efficient than rearrangement, for ϕ_{dis} of MBN is 0.013 where $\phi_{E\rightarrow Z} + \phi_{Z\rightarrow E}$ of IBN totals 0.18.

2. Excited State Multiplicity. In principle, both rearrangement and olefin isomerization could arise from singlet and/or triplet precursors. Formation of **1–4** primarily from the singlet is to be expected, since this is observed for di-π-methane rearrangements involving an isomerizable olefin.[25] Conversely, olefin isomerization is not normally competitive with singlet di-π-methane chemistry,[25,29] and one would therefore anticipate that the IBN isomerization is primarily due to a triplet, either via reversibility in the bridging step (**7**)[25] or through decay to a triplet localized at the double bond (intramolecular

Scheme III

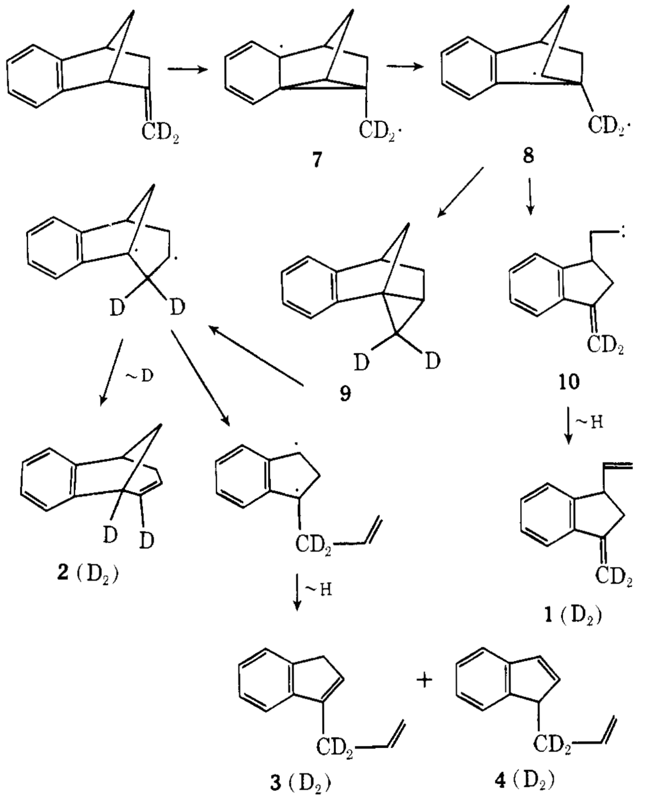
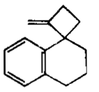
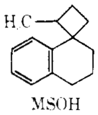
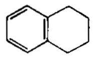
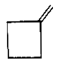


Table IV. PES Values for MSO and Related Molecules

compd	vertical ionization potential, eV	assignment
 MSO	8.40 8.65 9.10	benzene S benzene A olefin
 MSOH	8.35 8.72	benzene S benzene A
	8.44[20] 8.96	benzene S benzene A
	9.19[21]	olefin

triplet energy transfer).[7] The assignment of multiplicity to excited state precursors in bichromophoric aryl olefins is complicated by the very short triplet lifetimes (none of the unsaturated molecules under discussion phosphoresces). The lack of observable quenching by the usual triplet quenchers is therefore inconclusive. We have turned to xenon perturbation and photosensitization experiments for an insight into this problem.

As regards sensitization, *p*-xylene has been used successfully to selectively create the MBN triplet state.[30] The lack of singlet energy transfer is demonstrated by xylene's inability to induce a known MBN singlet reaction (anti-Markownikoff addition of acetic acid to the double bond).[8c,9,10,31] That xylene sensitization does yield **1**, **2**, and **3** therefore assures that an MBN triplet is at least capable of leading to these products.[32]

However, one must ultimately depend on perturbation experiments for information concerning the direct photolysis.[33] Such experiments are not without potential ambiguity, for when *both* singlet and triplet intermediates participate in a reaction, whether there is heavy-atom quenching or enhancement depends on the relative quantum efficiencies of singlet reactivity (ϕ_{RS}), intersystem crossing (ϕ_{isc}), and intrinsic triplet reactivity (ϕ_{RT}).[34] A kinetic analysis[34] indicates that (1) when $\phi_{isc} \geq 0.05$, enhancement of product formation (by, for example, xenon) is unambiguous and requires that the product be predominantly triplet derived (i.e., $\phi_{isc}\phi_{RT} > \phi_{RS}$); (2) when $\phi_{isc} \leq 0.05$, quenching unambiguously confirms a predominantly singlet derived product ($\phi_{RS} > \phi_{isc}\phi_{RT}$). Other combinations of ϕ_{isc} and enhancement or quenching are inconclusive in the absence of ϕ_{RS} and ϕ_{RT} data.[35] The ϕ_{isc} value for MBN is obviously critical, but because of the very short triplet lifetime, must be obtained indirectly. We have found ϕ_{isc} for a monochromophoric analogue, benznorbornene (BN), to be 0.59. If one assumes that the k_{isc} of BN is unchanged upon introduction of the double bond,[36] ϕ_{isc} can be calculated by

$$\phi^{BN}{}_{isc} = k^{BN}{}_{isc}{}^{1}\tau^{BN} \tag{8}$$

$$\phi^{MBN}{}_{isc} = k^{MBN}{}_{isc}{}^{1}\tau^{MBN} \tag{9}$$

assuming $k^{BN}{}_{isc} = k^{MBN}{}_{isc}$,

$$\phi^{MBN}{}_{isc} = \frac{\phi^{BN}{}_{isc}{}^{1}\tau^{MBN}}{{}^{1}\tau^{BN}} = 0.20 \tag{10}$$

The value so determined[38] is $\phi_{isc} = 0.20$; since xenon enhances the MBN rearrangement, the data fall in the inconclusive category.[35]

An alternative approach is to quantitate the xenon enchancement of product formation and the xenon quenching of fluorescence as a function of relative xenon concentration. This method has been successfully employed by Hammond and co-workers[14] using bromocyclopropane as the perturbing agent. When the probe product is 100% triplet derived, the equation

$$[(F_0/F) - 1] = \phi_{isc}[(F_0/F)(P/P_0) - 1] \tag{11}$$

applies (and may in fact be used to obtain ϕ_{isc}).[39] However, it is easily demonstrated[1b] that when the probe product is only partially triplet derived, a modified equation is applicable:

$$[(F_0/F) - 1] = \phi_{isc}\frac{\phi_p}{{}^{3}\phi_p}[(F_0/F)(P/P_0) - 1] \tag{12}$$

where ϕ_p is the total quantum efficiency of probe product formation and ${}^{3}\phi_p$ is the efficiency via the triplet manifold (i.e., $\phi_{isc}\phi_{RT}$). Thus the slopes of such plots, for a multiple product reaction, must increase as the singlet component increases; in no case can the slope be less than ϕ_{isc}. Plots for MBN are given in Figure 1 (Results section) with the slopes ranging from 0.32 to 0.52. If one again assumes $\phi_{isc} = 0.20$, all products are partially singlet derived (cf. Table V). *The same conclusion is required for IBN geometrical isomerization.*[40,41] The last observation is particularly noteworthy, and could be explained by invoking reversibility in a singlet-derived bridging step (**7** in Scheme III).[40b]

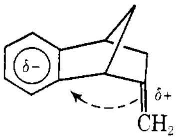
3. Nonradiative Decay of the MBN Excited States. It is instructive to calculate the total quantum efficiency for MBN product formation *out of the singlet manifold,* using the percentages given in Table V and including olefin isomerization as indicated by the IBN data. To the sum (0.10) may be added ϕ_f (0.08) and the assumed ϕ_{isc} (0.20). Clearly only a small portion (38%) of MBN singlets is accounted for, the nonradiative decay via internal conversion being ${}^{1}\phi_d = 0.62$. By contrast, ${}^{1}\phi_d$ for dihydro models equal ca. 0.17 ($1 - (\phi_f + \phi_{isc})$). In terms of rate constants, ${}^{1}k_d$ for MBN must be 1.4×10^8 s^{-1}, some tenfold greater than ${}^{1}k_d$ (1.3×10^7 s^{-1}) for MeBN.[42] *Introduction of a double bond at the 2 position has brought about a new singlet decay mode* which (a) presumably involves benzo-vinyl interaction; (b) does *not* involve rotation

Table V. Singlet Contribution to MBN Rearrangement and IBN Isomerization from Xenon Perturbation Studies

photoproduct	slope	% singlet[a]
1	0.52	62
2	0.44	55
3	0.41	51
4	0.32	38
IBN $Z \rightarrow E$	0.46	57

[a] Assuming $\phi_{\text{isc}} = 0.20$.

about the double bond; (c) undoubtedly involves significant charge transfer;[8b,c,9,10] (d) does not involve the formation of a full bond between the 2 and 6 carbons.[10] We would represent the form of this interaction in structural terms as **11.** Obviously, at some stage full 2,6 bonding does develop and brings about single-derived olefin isomerization and di-π-methane chemistry. Interception of an aryl excited singlet state by a nearby olefin, resulting in nonradiative decay without appreciable olefin isomerization, is well precedented.[6,7,43] *Perhaps more striking then is the evidence for a similar situation at the triplet level.* The modified form of the xenon perturbation equation (eq 12) can be used to provide ϕ_{RT}, the intrinsic triplet reactivity:



11

$$\text{slope} = \phi_{\text{isc}}(\phi_{\text{p}}/{}^3\phi_{\text{p}}) \tag{13}$$

$${}^3\phi_{\text{p}} = \phi_{\text{isc}}\phi_{\text{RT}} \tag{14}$$

$$\phi_{\text{RT}} = \phi_{\text{p}}/\text{slope} \tag{15}$$

Using the ϕ_{p} data for products **1-4** + $\phi_{E \rightleftarrows Z}$, and the slopes in Table V, one calculates a total ϕ_{RT} of 0.41; i.e., *despite the total absence of phosphorescence, only 41% of the MBN triplets are accounted for.*[44] Since nucleophilic addition to MBN is confined to the singlet state,[8b,c,9,10] the most economical rationale is to invoke a triplet equivalent to structure **11** which has a negligible charge-transfer component. *It must be emphasized that this interaction is competitive with localization of triplet energy at the double bond*[45] (with the latter viewed either as "triplet energy transfer" or $T_2 \rightarrow T_1$ decay), since localized (acyclic) olefinic triplets decay entirely by rotation. We are forced to similar conclusions for the indan, EMI.

A summary of MBN photochemistry and photophysics is given in Scheme IV.

4. Interaction between the Chromophores. To what extent is there interaction between the olefin and aromatic moieties in the ground state? What is the effect of the double bond on the $S_0 \rightarrow S_1$, transition and on S_1 itself? Despite the extensive research on bichromophores, these questions remain difficult to answer. We have utilized photoelectron, ultraviolet absorption, fluorescence, and phosphorescence spectroscopy to address these problems.

Scheme IV

$$\begin{tikzcd}
\text{MBN} \arrow[rr, "h\nu"] & & {}^1(\text{MBN})^* \arrow[dl, "8\%"'] \arrow[d, "62\%"] \arrow[dr, "10\%"] \arrow[rr, "20\%"] & & {}^3(\text{MBN})^* \arrow[d, "59\%"'] \arrow[dr, "41\%"] & \\
& \text{MBN} + h\nu & \text{MBN} & 1, 2, 3, 4, E \rightleftarrows Z & \text{MBN} & 1, 2, 3, 4\ E \rightleftarrows Z
\end{tikzcd}$$

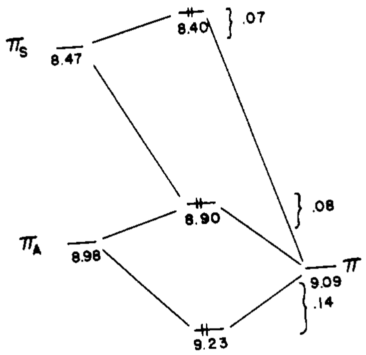
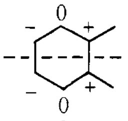
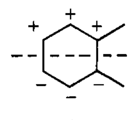


Figure 8. Orbital splitting diagram for MBN using corrected basis levels (see text).

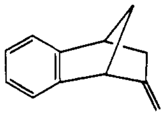
With regards to the MBN ground state, the PES data have been presented in Table II (Results), with the S and A assignments referring to a symmetry plane bisecting the benznorbornenyl ring system. Our treatment follows that of Heilbronner,[46] in which the basis energies are values from appropriate models, modified to reflect the inductive (through-bond) effect of the functional groups on one another. The inductive correction for the MBN models is the difference between the average of the energies of BN + **12** and the average of the energies of MBN:



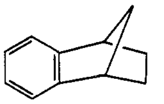
S



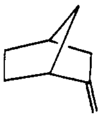
A



MBN



BN

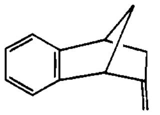
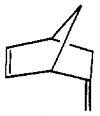
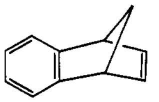
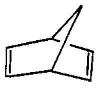


12

	MBN	BN	12
eV	8.40 S	8.42 S	
	8.90 A	8.93 A	
	9.23 π		9.04 π

$$\left(\frac{8.42 + 8.93 + 9.04}{3}\right) - \left(\frac{8.40 + 8.90 + 9.23}{3}\right) = -0.05\ \text{eV}$$

The correction (−0.05 eV), applied to BN and **12,** yields basis energies of 8.47 (S), 8.98 (A), and 9.09 (π) eV. Comparison of these data with those of MBN shows that the π level has been split by 0.14 eV, in good agreement with the sum of the benzene S and A splittings of 0.15 eV. An orbital interaction of 0.29 eV is not inconsequential, and approximates that calculated in like fashion for **13.**[21] The interaction energies for the endocyclic analogues **14**[47] and **15**[48] are expectedly higher, but it is somewhat surprising that the decrease from **15** to **14** is not reproduced in the exocyclic series. Despite the calculated interaction energy, the HOMOs of MBN and BN have almost identical energies, with the major perturbation occurring at the MBN olefin MO.

	MBN	13	14	15
orbital splitting, eV	0.29	0.30	0.46	0.86

The UV absorption spectra of MBN and MeBN are presented in Figure 4 (Results). There is a small (~2 nm) bathochromic shift of the B_{2u} band and some diminution of intensity upon introduction of the double bond. The spectrum of MBN has been discussed in detail,[49] with the conclusion that major perturbations are restricted to the E_{1ua} and B_{1u} transitions.[50] Similar conclusions have been reached using CD and ORD methods.[53] Nevertheless, there is general agreement[49,53] that the B_{2u} transition (which is responsible for the photochemistry under discussion) is slightly perturbed.

The fluorescence spectrum (Figure 4) of MBN is much more dramatically altered. Both ϕ_f and $^1\tau$ are reduced by 66% relative to MeBN (Table I); since $\phi_f = k_f{}^1\tau$, k_f is essentially unchanged (as one would anticipate from the absorption data). For reasons outlined above, the diminution in ϕ_f and $^1\tau$ can be ascribed to a much increased nonradiative decay mode which does not involve olefin rotation. It is clear from Figure 4 that the fluorescence of MBN is, like its absorption spectrum, slightly red shifted from that of MeBN.

In sum (1) *the HOMO and LUMO energies of MBN approximate those of model systems;* (2) *the* $S_0 \rightleftarrows S_1$ *transitions show a small but finite coupling of the chromophores;* (3) *the* S_1 *state is characterized by a markedly increased rate of nonradiative decay.* The ultimate question is whether **11** represents S_1, or is itself derived from a more "benzene-like" initially formed singlet state. We believe that latter possibility to be realistic, even with the relatively fixed nuclei of a bicyclic system; a more complete discussion may be found in the accompanying paper.[10,54] Its properties place MBN somewhere between 6-phenyl-2-hexene (where there is exclusively a post-excitation interaction[6]) and alkyl phenylacetates (where there is gross spectral distortion and the possibility of delocalized excitation into a "superchromophore"[55]).

B. Photochemistry and Photophysics of EMI. A primary objective of this study was to examine the photochemistry and photophysics of aryl olefin bichromophores as a function of geometry. The "interorbital angle" (i.e., the angle between the nodal planes of the two π systems, at a conformation intermediate between the conformational minima) and the "interorbital distance" (i.e., the closest distance between a carbon atom of the olefin, and an aryl carbon or aryl C–C bond, again in an intermediate conformation) are given in Table VI for several olefins of interest. As one would expect, photophysical properties (exemplified by $^1\tau$ in Table VI) vary appreciably; a discussion of the photochemistry of EMI and MSO follows (see Results for the synthesis of these compounds).

By contrast with MBN, photoisomerization is the primary[22] photoreaction of EMI (eq 6). The quantum efficiencies ($\phi_{E\rightarrow Z} = 0.15$, $\phi_{Z\rightarrow E} = 0.13$) are comparable to those observed for IBN and the parent acyclic molecule, 1-phenyl-2-butene. As with MBN, there is evidence for singlet involvement in the isomerization. For example, the photostationary state ($E/Z = 0.88$) is changed by xenon ($E/Z = 0.99$) in the direction of that observed for xylene triplet sensitization ($E/Z = 1.10$).[56,60] The extent of singlet participation can again be estimated from xenon perturbation studies, using the slopes of Figures 5 (0.61) and 6 (0.59), and the ϕ_{isc} (0.44) derived from $^1\tau$'s for EMI (18 ns) and 1-methylindan (1-MI) 24 ns, from EMIH). See eq 16–18.[61]

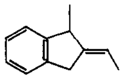
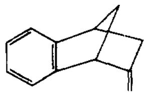
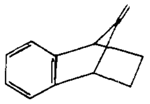
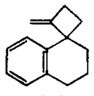
$$\phi^{\mathrm{EMI}}{}_{\mathrm{isc}} = \frac{\phi_{\mathrm{isc}}{}^{\mathrm{1\text{-}MI}}{}_{\mathrm{isc}}{}^{1}\tau^{\mathrm{EMI}}}{^{1}\tau^{\mathrm{1\text{-}MI}}} = 0.44 \qquad (16)$$

$$(\phi_p/{}^3\phi_p) = 0.61/0.44 = 1.39 \qquad (17)$$

$$\%\ \text{singlet} = 1 - ({}^3\phi_p/\phi_p) = 28\% \qquad (18)$$

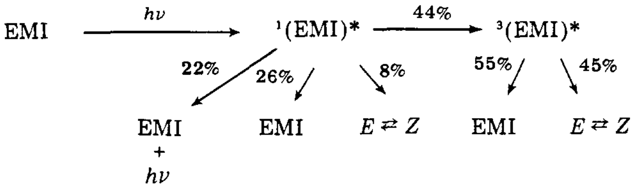
The 28% so calculated may be compared to the 57% calculated for IBN, the reduced singlet participation for EMI quite possibly reflecting the higher relative $^1\tau$ of this molecule (Table VI). As regards the singlet state, using 0.34 and 0.59 for ϕ_f and ϕ_{isc} yields a $^1\phi_d$ for EMIH of 0.07. For EMI, ϕ_f (0.22), ϕ_{isc} (0.44), and $^1\phi_{E\rightleftarrows Z}$ (0.08) leave a $^1\phi_d$ of 0.26. Introduction of the double bond leads to an additional 19% nonradiative decay, or in terms of ^1k_d, 1.4×10^7 s^{-1} (EMI) vs. 2.9×10^6 s^{-1} (EMIH). The fivefold increase in ^1k_d may be compared with the tenfold increment for MBN. Though EMI's geometry is clearly not as well suited for the partial bonding depicted in **11** (above), there is evidence for bond formation across the five-membered ring from the photoinduced skeletal rearrangement of indenes.[62,63] Once more, the triplet mimics the singlet; there is no phosphorescence and $^3\phi_{E\rightleftarrows Z} = 0.20$. Thus 55% of the EMI triplets are unaccounted for and decay is competitive with triplet localization at the double bond. Our observations are summarized in Scheme V.

Table VI. Aryl Olefin Interorbital Angles and Distances and Singlet Lifetimes

compd	angle, deg[a]	distance, Å[a]	$^1\tau$, ns	% $^1\tau$ of satd model
 EMI	180	2.2	18.0	75
	112	2.3	4.5	33
	125	2.0	11.0	75
 (MSO)	90	3.0	30.0	100

[a] Defined in the text.

Scheme V



Treatment of the PES data (Table III) as for MBN yields a −0.23 eV through-bond inductive effect, which applied to the model systems gives basis energies of 8.69 (S), 9.27 (A), and 9.38 (π) eV. For 2-methyleneindan, the corresponding values are 8.61, 9.14, and 9.45 eV, respectively; symmetry permits only a benzene (s)–π interaction which totals 0.15 eV. Though this number is relatively small, the HOMO of the aryl olefin is stabilized by 0.15 eV by comparison with indan; MBN has a greater calculated orbital interaction but virtually unchanged HOMO.

As with MBN, there is a small (ca. 2 nm) red shift in the UV absorption spectrum of EMI (Figure 7). Though the fluorescence intensity change is less marked (EMI/EMIH = 0.64; MBN/MeBN = 0.33), the band shape is more distorted and red shifted. The decrease in ϕ_f is attributable to ^1k_d, k_f being virtually unchanged. As noted above, EMI gives no detectable phosphorescence.

In sum, much of what has been observed for the photoisomerization and photophysics of MBN is reproduced with EMI. The degree of interaction between the chromophores has, however, been reduced by the collinear (EMI), as opposed to angular (MBN), relationship in the two molecules.

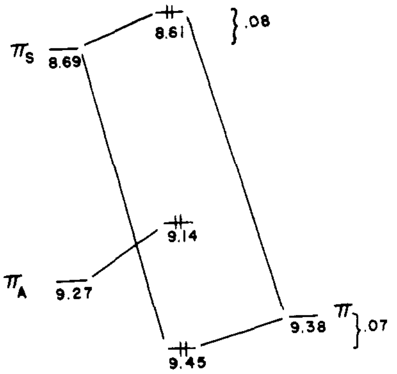


Figure 9. Orbital splitting diagram for 2-methyleneindan using corrected basis levels (see text).

C. Photochemistry and Photophysics of ESO. Of the cyclic substrates discussed herein, the spiro-fused ESO molecule is unique in that its $^1\tau$ is identical with that of the model system (Table VI). Nevertheless, ESO does undergo facile geometrical photoisomerization (eq 7); in fact, the quantum efficiencies ($\phi_{E\rightarrow Z} = \phi_{Z\rightarrow E} = 0.20$)[64] are the highest observed in this series. Evidence concerning reaction multiplicity is sparce. Though xenon quenches the fluorescence of both ESO and monochromophoric models, there is inexplicably no observable change in efficiency of internal or external probe isomerization. One can say that the $^1\tau$ data, which imply minimal singlet interaction, are supported by the absorption and fluorescence spectra which are identical in every way with those of model compounds. The PES data, corrected in the usual way for inductive effects (+0.03 eV), confirm the absence of ground-state interaction as well. One is tempted, on this basis, to characterize ESO as a molecule in which photoisomerization is exclusively the consequence of triplet localization at the double bond,[65] and the 90° relationship in this molecule to be one which virtually eliminates ground and singlet state interactions.

Conclusions

The photochemistry of these cyclic nonconjugated aryl olefins varies from the complex ("diverted di-π-methane") rearrangement of MBN to the simple $E \rightleftarrows Z$ isomerizations of IBN, EMI, and ESO. The relative participation of singlet and triplet states in the photochemistry has been deduced from xenon perturbation data, and compared with the degree of orbital interactions deduced from photoelectron, absorption, and emission spectroscopy. The singlet interactions strongly depend on geometry, with MBN and its angular atomic orbital relationship producing extensive interplay (cf. **11**) while ESO and its orthogonal arrangement yield minimal spectral distortion. The triplets are less sensitive to geometry, there being no phosphorescence and significant triplet derived olefin isomerization in all cases. *An important feature of both MBN and EMI is the extensive nonradiative decay from singlet as well as triplet states*; this decay is obviously caused by the double bond but is not due to its role as a "free rotor". This observation may well prove to be general for nonconjugated π systems (including di-π-methane molecules) and, in fact, *radiationless decay is fast becoming one of the most striking consequences of intramolecular bichromophoric interactions*.[2,3a,g,6,45a]

Experimental Section[1b]

Chemicals. Spectral quality solvents were used in all photochemical experiments. *n*-Pentane, cyclopentane, cyclohexane, and *n*-hexane were Burdick and Jackson "Distilled in Glass" and used as received. Spectroquality ethanol was prepared by distilling Commercial Solvents Gold Label ethanol from magnesium ethoxide under a nitrogen atmosphere, with the middle cut retained. Diethyl ether and tetrahydrofuran (THF) (MCB analytical reagent grade) were distilled under nitrogen from sodium benzophenone ketyl; benzene, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO) (MCB analytical reagent grade) were distilled from calcium hydride prior to use. *trans*-1-Phenyl-2-butene (ca. 97% trans, Aldrich) was purified by column chromatography on silver nitrate impregnated silica gel using hexane as eluent or by preparative VPC on column L at 105 °C (60 mL He/min). *cis*-2-Heptene (K and K; 95.5% cis, 4.0% trans, 0.5% unknown) was purified by VPC on column J at 50 °C (150 mL He/min) followed by column K at 45 °C (100 mL He/min); this procedure provides olefin which is at least 99.9% *cis*-2-heptene (column I).

Instrumentation. Infrared spectra were taken on a Perkin-Elmer 137 or 221 spectrophotometer; ultraviolet spectra were obtained on a Cary 15 or Beckman DUR with Gilford 222-A photometer; NMR spectra were taken on a Varian A-60A, Varian XL-100, or Perkin-Elmer R-32 spectrometer with Me_4Si as a reference (proton) or on a Varian CFT-20 spectrometer (carbon). Mass spectra were recorded by the Purdue Chemistry Department Mass Spectroscopy Center on a Hitachi RMU-6A or CE-110 spectrometer. Emission spectra were recorded on a custom-made right-angle spectrofluorimeter[66] using a low-pressure mercury lamp filtered by a 2537-Å interference filter. All spectra are fully corrected. Singlet lifetime measurements were made on a modified TRW nanosecond fluorimeter (Model 31A)[67] using a deuterium source and an RCA 1P28 photomultiplier. Preparative VPC was done on Varian Models A-90-P, A-700, or 90-P chromatographs, analytical work was on Varian 1200 or 1400 units using a Hewlett-Packard Model 3380-A digital recording integrator. Columns were as follows: A, stainless steel (ss) 5 ft × 0.125 in. 10% SE-30; B, ss 150 ft × 0.010 in. Golay column with UCON LB-550X; C, aluminum (Al) 5 ft × 0.25 in. 10% Carbowax 20M; D, Al 10 ft × 0.375 in. 30% Carbowax 20M; E, Al 7 ft × 0.375 in. 20% Carbowax 20M; F, ss 5 ft × 0.125 in. 10% Carbowax 20M; G, Al 10 ft × 0.25 in. 10% Carbowax 20M; H, Al 10 ft × 0.25 in. 10% SE-30. I, ss 20 ft × 0.125 in. 4% $AgBF_4$–10% UCON 2000 in series with a ss 20 ft × 0.125 in. 20% β,β'-oxydiproprionitrile; J, Al 15 ft × 0.375 in. 20% Carbowax 20M; K, ss 12 ft × 0.125 in. 10% $AgBF_4$–20% Carbowax 20M; L, Al 10 ft × 0.25 in. 10% $AgBF_4$–20% Carbowax 20M; M, copper 20 ft × 0.25 in. 30% SF-96. Column supports were A, 100/120 AW-DMCS Chromosorb W; C, G, H, J, 40/60 AW-DMCS Gas Pack W; D, K, L, M, 60/80 AW-DMCS Chromosorb W; E and back half of I, 60/80 AW Chromosorb P; F, 100/120 AW-DMCS Chromosorb W; front half of I, 100/120 AW-DMCS Gas Pack W.

Analyses. Quantum efficiencies were by uranyl oxalate actinometry or by reference to the *E* to *Z* isomerization of 1-phenyl-2-butene[7] using column K at 105 °C (25 mL N_2/min); all data were corrected for back reaction.[68] The equation used for this correction must be modified when photoproduct isomer is present prior to photolysis; the modified form[69] is

$$\beta' = \alpha - \beta_0 \ln \left(\frac{\alpha - \beta_0}{\alpha - \beta}\right)$$

where β' is the "true" isomerization or conversion of the compound, β_0 is the fraction of isomer before photolysis, and α is the fraction of isomer under observation, at the photostationary state. Analyses of *cis*- and *trans*-2-heptene were made on column I at ambient temperature (25 mL N_2/min).

Photochemical Apparatus. Most preparative and quantum yield work employed a Hanovia low-pressure mercury resonance lamp (Model 688A-45) made of Vycor and emitting principally 2537-Å light. Quantitative data were obtained using a rotating turntable with quartz tubes fitted with graded seals. Deoxygenation was via multiple freeze-pump-thaw cycles at less than 5×10^{-4} mm. Some early work employed Vycor tubes with argon degassing.

2-Methylenebenznorbornene (MBN). MBN was synthesized by the Wittig reaction on benznorbornen-2-one. It was isolated in 72% yield, bp 92–93 °C (4.5 mm), and had spectral properties identical with those of a known sample.[70]

2-Methylene-d_2-benznorbornene. The same procedure was used as for MBN except that methyl-d_3-triphenylphosphonium bromide (Aldrich) was employed. The dideuterio-MBN was isolated in 65% yield (bp 92–93 °C (4.5 mm)): NMR ($CDCl_3$) δ 7.09 (symmetrical m, 4 H), 3.66 (m, 1 H), 3.38 (m, 1 H), 2.50 (doublet of doublets, 1 H), 2.07–1.58 (m, 3 H) (plus residual signals at 5.08 and 4.68 δ integrating to 0.09 H); IR (neat) 6.13 μ; mass spectrum (70 eV) *m/e* 158 (M^+).

(*E*)- and (*Z*)-Isobutylidenebenznorbornene (IBN). A mixture of benznorbornen-2-one (3.0 g, 19.0 mmol), triphenylisobutylphosphonium bromide (10.0 g, 25.0 mmol), and potassium *tert*-butoxide (2.8 g, 25.0 mmol) in 20 mL of dry tetrahydrofuran was refluxed for 36 h under nitrogen. The mixture was cooled to room temperature, poured into 100 mL of water, and hexane extracted (2 × 50 mL). The extracts were water washed, dried over magnesium sulfate, and concentrated in vacuo. The resultant mixture of triphenylphosphine oxide and hydrocarbon product was placed on a 3.0 × 10 cm column packed with aluminum oxide and eluted with hexane. Removal of the hexane in vacuo gave 3.3 g (86.5%) of a colorless liquid. This material consisted of a mixture of ca. 90% (*Z*)- and 10% (*E*)-2-isobutylidenebenznorbornene. The isomers were separated at 180 °C on VPC column D (60 mL He/min). The *E* isomer eluted first with essentially base line separation between the isomers. Both isomers were prepared in greater than 99.5% isomeric purity as observed on analytical column B at 145 °C.

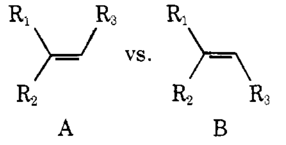
***Z*-IBN:** IR (neat) 3.32, 3.43, 5.92, 6.85 μ; NMR ($CDCl_3$) δ 7.10 (m, 4 H, aromatic), 4.90 (bd, 1 H, $J = 9.2$ Hz, vinyl), 3.92 (bs, 1 H, bridgehead), 3.35 (bs, 1 H, bridgehead), 2.90–2.30 (m, 2 H, 3 exo and methine), 1.95–1.60 (m, 3 H, 3 endo and bridge), 0.95 (d, 3 H, J = 7.0 Hz, CH_3), 0.87 (d, 3 H, J = 7.0 Hz, CH_3); high-resolution mass spectrum *m/e* 198.140 (calcd for $C_{15}H_{18}$, *m/e* 198.1408).

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

***E*-IBN:** IR (neat) 3.32, 3.43, 5.92, 6.85 μ; NMR ($CDCl_3$) δ 7.09 (m, 4 H, aromatic), 5.29 (bd, 1 H, $J = 9.2$ Hz, vinyl), 3.55 (bs, 1 H, bridgehead), 3.41 (bs, 1 H, bridgehead), 2.58–2.05 (m, 2 H, 3 exo and methine), 2.00–1.64 (m, 3 H, bridge and 3 endo), 0.93 (d, 3 H, J = 7.0 Hz, CH_3), 0.77 (d, 3 H, J = 7.0 Hz, CH_3); high-resolution mass spectrum *m/e* 198.141 (calcd for $C_{15}H_{18}$, *m/e* 198.1408).

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

Assignment of Configuration to IBN. The *Z* and *E* assignments rest on the ^1H and ^{13}C NMR chemical shifts. (1) An examination of molecular models indicates that the methyl groups for the *E* isomer should be more shielded by the aromatic ring than should those of the *Z* compound. The two methyl doublets are centered at δ 0.91 and 0.85 for the *Z* and *E* assignments as made above. (2) The configuration about a trisubstituted olefin can be assigned by use of the γ compression phenomenon, whereby a carbon resonance is shifted upfield when compressed by a γ carbon substituent, relative to the isomer without this compression[71,72] (i.e., R_1 will be upfield in A relative to its position in B). The C_1 resonance for *Z*-IBN comes at δ 47.5 whereas this carbon resonates at δ 52.8 in the *E* isomer (by comparison, the second bridgehead signal is almost invariant: δ 43.2 and 43.6 for *Z* and *E*, respectively). The complete ^{13}C NMR spectrum may be found in the thesis of Fred Palensky.

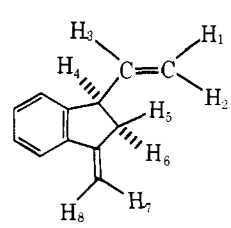


***endo*-2-Methylbenznorbornene (MeBN).** MBN was hydrogenated using a palladium on calcium carbonate catalyst, methanol/acetic acid (2:1) as solvent, and a Brown[2] hydrogenator. Preparative VPC on column M provided a pure sample: NMR ($CDCl_3$) δ 7.35–7.0 (m, 4 H, aromatic), 3.30 (m, 1 H, bridgehead), 3.15 (m, 1 H, bridgehead), 2.37 (m, 1 H, exo methine), 2.08 (broad doublet of doublets, 1 H, exo methylene H), 1.86 (doublet of quartets, 1 H, endo bridge H), 1.68 (doublet of triplets, 1 H, exo bridge H), 0.54 (d, 3 H, endo methyl), ~0.54 (m, 1 H, remaining endo methylene H).

Anal. ($C_{12}H_{14}$) C, H.

Photolysis of MBN. MBN (312 mg, 2 mmol) was dissolved in 200 mL of hexane, saturated for 1 h with argon, and irradiated with the low-pressure mercury lamp for 2 h, during which time about 20% of the starting material was consumed. The solvent was removed on a rotary evaporator and the oily residue molecularly distilled (60–110 °C (1.5 mm)). Preparative VPC on column M provided pure samples of **1**, **2**, and **3**. (Prolonged irradiations also produce the di-π-methane product of **2**, benzo[3.4]tricyclo[3.2.1.0^{2,7}]octene.)[73]

1-Methylene-3-vinylindan (1). IR (neat): 6.12 (olefin stretch), 10.10 + 10.93 (monosubstituted olefin), 11.45 μ (terminal methylene). The structural assignment follows from the NMR, which shows a four-proton multiplet at δ 7.65–7.05 (aromatic hydrogens); a typical monosubstituted olefin absorption with three eight-line patterns, δ_1 5.06 (J_{12} = 2.0, J_{13} = 9.8, J_{14} = 0.6 Hz), δ_2 5.14 (J_{23} = 17.1, J_{24} = 0.9 Hz), and δ_3 5.90 (J_{34} = 8.2 Hz); δ_4 3.82 (overlapping doublet of triplets broadened by long-range coupling to H_1 and H_2, J_{45} = 8.2, J_{46} = 6.0 Hz); a characteristic geminal group with two quartets of triplets, δ_5 3.06 (J_{56} = 16.5, J_{57} = J_{58} = 2.05 Hz) and δ_6 2.59 (J_{67} = J_{68} = 2.50 Hz); the exocyclic methylene hydrogens as two triplets, broadened due to long-range coupling, δ_7 5.05, δ_8 5.45 (J_{78} = 0.3 Hz). Mass spectrum (70 eV): *m/e* 156 (M^+).



Anal. ($C_{12}H_{12}$) C, H.

Benzo[6.7]bicyclo[3.2.1]octa-2,6-diene (2). This compound was identified by comparison of its spectra with those in the literature[74] and those obtained from an authentic sample.[75]

3-Allyl-1*H*-indene (3). This compound was identified by comparison of its spectra to those of a sample synthesized by published procedures.[76]

1-Allyl-1*H*-indene (4). This compound could not be isolated in pure form and was barely resolved on column B at 105 °C. It was formed most efficiently by photolysis of MBN (200 mg) in 25 mL of hexane saturated with xenon (~80 mL), in a Vycor tube irradiated for 4 h in the Rayonet reactor with the 254-nm lamps. Preparative VPC on column E at 159 °C (100 mL He/min) provided **4** as a 5% mixture in **1**. Nevertheless, a portion of the allylic methylene and the indene vinylic and benzylic protons of **4** are clearly visible in the 100-MHz spectrum and could be compared to the NMR of an authentic sample,[77] and to data in the literature.[76] Coinjection of the authentic sample and the **4**/**1** mixture on column B verified the assignment.

Photolysis of Dideuterio-MBN. Using identical procedures with those described above, the labeled MBN provided samples of the labeled **1**, **2**, **3**, and **4** (recovered starting material showed no evidence of scrambling). Assignments of the deuterium were as follows: **1**, the triplets due to H_7 (δ 5.04) and H_8 (δ 5.45) are absent; **2**, the multiplet due to H_2 (δ 6.15) and H_1 (δ 3.27) is absent;[78] **3**, the four-proton multiplet at δ 3.38 (benzylic and allyl methylenes) diminishes to a two-proton singlet lacking the 6-Hz allyl H–vinyl H coupling; **4**, the visible allylic methylene hydrogen (δ 2.28), which is normally a five-line multiplet which includes a 14-Hz coupling to its geminal partner, has been reduced to 0.22 H (0.15 H is predicted for the 85% deuterated MBN used in this experiment) and is a 7-Hz triplet (i.e., the 14-Hz geminal coupling has been removed by the presence of a geminal deuterium). The benzylic hydrogen at δ 3.52, normally split by the methylene into a 7-Hz triplet, is collapsed to a broad singlet.

3-Benzyl-2,4-pentanedione. This compound was prepared by addition of benzyl chloride to sodium acetylacetone in dimethyl sulfoxide.[79] The product was isolated in 40% yield, bp 106–108.5 °C (0.5 mm), and had an NMR spectrum identical with that reported.[80]

2-Acetyl-3-methylindene. A solution of 15.0 g (0.079 mol) of 3-benzyl-2,4-pentanedione in 150 g of polyphosphoric acid was warmed to 65 °C in a 300-mL three-neck flask equipped with an overhead stirrer and calcium chloride drying tube for 12 h. Upon cooling to room temperature the viscous, reddish-black solution was diluted with 300 mL of distilled water, extracted with ether (3 × 200 mL), washed with 5% sodium bicarbonate (2 × 200 mL), dried (anhydrous $MgSO_4$), concentrated in vacuo, and chromatographed on a 3.3 × 30 cm silica gel column, slurry packed in hexane. The column was eluted with 5% ether-pentane with 100-mL fractions taken. The desired product was obtained from the 8th through 13th fractions with the starting material concentrated in the 4th through 6th fractions. Concentration in vacuo of the product-containing fractions gave 6.45 g (47.5%) of a light yellow oil. VPC analysis on column A (150 °C, 30 mL N_2/min) showed the product to be approximately 99.8% pure: IR (neat) 3.25, 3.40, 6.00, 6.25, 6.35, 6.85 μ; NMR ($CDCl_3$) δ 7.60–7.20 (m, 4 H, aromatic), 3.65 (q, 2 H, J = 2.1 Hz, -CH_2), 2.50 (t, 3 H, J = 2.1 Hz, vinyl CH_3), 2.40 (s, 3 H, CH_3); mass spectrum (70 eV) *m/e* 172 (M^+).

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

(*E*)-2-Ethylidene-3-methylindan (*E*-EMI). This material was prepared by the general procedure of Hutchins.[81] To a solution of 2-

acetyl-3-methylindene (7.5 g, 43.6 mmol) and *p*-toluenesulfonylhydrazine (12.0 g, 64.0 mmol) in 120 mL of a 1:1 mixture of DMF–sulfolane containing 300 mg of *p*-toluenesulfonic acid at 100 °C was added sodium cyanoborohydride (7.6 g, 120.0 mmol). The solution was heated with stirring at 100–105 °C for 4 h under nitrogen. Upon cooling, the reaction mixture was poured into 150 mL of water, ether extracted (2 × 100 mL), washed with water (2 × 50 mL), dried (anhydrous $MgSO_4$), and concentrated in vacuo. The crude product was then passed through a 2.5 × 10 cm aluminum oxide (neutral) plug, eluting with hexane to remove residual sulfolane, concentrated in vacuo, and molecularly distilled to give 5.2 g (75.5%) of a colorless liquid. Analysis by VPC (column B, 140 °C) showed this material to be a mixture of *E*-EMI (90.0%), *Z*-EMI (1.4%), and internal olefin (8.6%). Preparative VPC on column C (140 °C, 100 mL He/min) provided pure *E*-EMI: IR (neat) 3.25, 3.35, 3.40, 6.30, 6.80, 6.90 μ; NMR ($CDCl_3$) δ 7.15 (m, 4 H, aromatic), 5.45 (m, 1 H, vinyl), 3.70–3.50 (m, 3 H, benzylic), 1.65 (ddm, 3 H, $J = 7.5, 2.0$ Hz, vinyl CH_3), 1.32 (d, 3 H, $J = 8.0$ Hz, benzylic CH_3); mass spectrum (70 eV) *m/e* 158 (M^+). Anal. ($C_{12}H_{14}$) C, H.

(*Z*)-2-Ethylidene-3-methylindan (*Z*-EMI). This isomer was prepared by photolyzing 480 mg of *E*-EMI (96% *E*) in 75 mL of degassed *n*-pentane for 2 h using the low-pressure mercury lamp. Removal of solvent and filtration through neutral aluminum oxide (pentane) gave 390 mg of a light yellow liquid consisting of a 41:59 ratio of *Z* and *E* isomers. Preparative VPC on column D at 155 °C gave >98.5% *Z*: IR (neat) 3.25, 3.35, 3.40, 3.45, 6.30, 6.80, 6.90 μ; NMR ($CDCl_3$) δ 7.18 (s, 4 H, aromatic), 5.47 (m, 1 H, vinyl), 4.10–3.35 (m, 3 H, benzylic), 1.69 (bd, 3 H, $J = 7.8$ Hz, vinyl CH_3), 1.30 (d, 3 H, $J = 7.8$ Hz, benzylic CH_3); mass spectrum (70 eV) *m/e* 158 (M^+).

Anal. ($C_{12}H_{14}$) C, H.

Assignment of Configuration to EMI. The *E* and *Z* assignment was made on the basis of ^{13}C NMR data, using the γ compression phenomenon,[71,72] as outlined above for IBN. The atoms of interest are C-1 and C-3; the *E* isomer should have C-1 shifted upfield while the *Z* isomer should have C-3 shifted upfield. In fact C-1 comes at δ 33.1 for *E* and δ 35.9 for *Z*; C-3 comes at δ 41.7 for *E* and δ 39.2 for *Z*. (The complete ^{13}C NMR spectrum may be found in the thesis of Fred Palensky.)

2-Methyleneindan (MI). To a mixture of methyltriphenylphosphonium iodide (10.0 g, 24.7 mmol) and potassium *tert*-butoxide (2.8 g, 24.7 mmol) in 100 mL of dry benzene (distilled from CaH_2), 2-indanone (3.2 g, 24.7 mmol) in 40 mL of dry benzene was added dropwise over 1.0 h at 25 °C. The resulting mixture was stirred at 25 °C for 25 h under nitrogen and poured into 200 mL of water. The benzene layer was separated and rotary evaporated, and the residue passed through an 8.0 × 15.0 cm aluminum oxide plug with hexane. Removal of solvent in vacuo gave 420 mg (13.4%) of a colorless liquid which was purified by preparative VPC at 145 °C on column E (400 mL He/min): IR (neat) 3.25, 3.47, 3.52, 6.02, 6.80, 6.90 μ; NMR ($CDCl_3$) δ 7.20 (s, 4 H, aromatic), 5.10 (p, 2 H, $J = 2.3$ Hz, vinyl), 3.70 (t, 4 H, $J = 2.3$ Hz, benzylic CH_2).

Anal. ($C_{10}H_{10}$) C, H.

1-Methylindan. This was prepared by hydrogenation of 3-methylindene using 10% Pd/C with ethyl acetate as solvent. VPC analysis (column E, 159 °C, 100 mL He/min) indicated a quantitative conversion, and preparative VPC (column E) provided pure material which had IR and NMR spectra identical with those reported.[82]

2-Ethyl-1-methylindan (EMIH). Identical material was made by reduction of EMI or by reduction of 2-ethyl-1-methylindene, in both cases using 10% Pd/C and dry tetrahydrofuran. Preparative VPC on column G provided EMIH, presumably the cis isomer: IR (neat) 3.35, 6.20, 6.28, 6.78, 6.86 μ; NMR ($CDCl_3$) δ 7.12 (s, 4 H, aromatic), 3.25–2.60 (m, 3 H, benzylic CH and CH_2), 2.30 (m, 1 H, $C(H)CH_2$), 1.42 (m, 2 H, $C(H_2)CH_3$), 1.04 (d, 3 H, $J = 7.5$ Hz, benzylic CH_3), 0.95 (t, 3 H, $J = 8.0$ Hz, $CH_2C(H_3)$).

Calcd for $C_{12}H_{16}$: *m/e* 160.125. Found: *m/e* 160.125.

1-Methylene-8,9-benzospiro[3.5]nonane (MSO). A mixture of 8,9-benzospiro[3.5]nonan-1-one[83] (0.50 g, 2.7 mmol), triphenylmethylphosphonium iodide (1.62 g, 4.1 mmol), and potassium *tert*-butoxide (0.37 g, 3.2 mmol) in 15 mL of dry tetrahydrofuran was refluxed for 18 h under nitrogen. Upon cooling, the reaction mixture was poured into 50 mL of water and extracted with 3 × 50 mL of hexane. The hexane extracts were passed through a 8.0 × 15.0 cm alumina plug followed by an additional 50 mL of hexane, combined, and concentrated in vacuo to give 0.40 g (80.4%) of MSO. The material was purified by preparative VP C on column H at 200 °C (60 mL He/min): IR (neat) 3.25, 3.40, 3.50, 6.00, 6.20, 6.35, 6.75, 6.92 μ; NMR (CCl_4) δ 7.30 (m, 1 H, aromatic), 6.95 (m, 3 H, aromatic), 4.78 (t, 1 H, $J = 2.0$ Hz, vinyl), 4.62 (t, 1 H, $J = 3.0$ Hz, vinyl), 2.72 (bt, 4 H, $J = 8.0$ Hz, benzylic CH_2 and allylic CH_2), 2.40–1.60 (m, 6 H, aliphatic CH_2); mass spectrum (70 eV) *m/e* 184 (M^+).

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

(*Z*)-1-Ethylidene-8,9-benzospiro[3.5]nonane (*Z*-ESO). A mixture of 8,9-benzospiro[3.5]nonan-1-one (1.0 g, 5.4 mmol), triphenylethylphosphonium iodide (8.4 g, 20.0 mmol), and potassium *tert*-butoxide (2.3 g, 20.5 mmol) in 25 mL of dry tetrahydrofuran was refluxed for 10 h under nitrogen. Workup as for MSO provided 1.0 g (94%) of ESO consisting of 95% *Z* isomer (as determined by VPC on column E, 100 mL He/min). The isomers were separated by preparative VPC on column E (170 °C) to provide pure *Z*-ESO: IR (neat) 3.40, 6.25, 6.78, 6.95 μ; NMR (CCl_4) δ 7.35 (m, 1 H, aromatic), 6.95 (m, 3 H, aromatic), 5.18 (m, 1 H, vinyl), 2.75 (m, 4 H, allylic CH_2 and benzylic CH_2), 1.95 (m, 6 H, ring CH_2), 1.20 (dt, 3 H, $J = 7.0, 2.4$ Hz, CH_3); mass spectrum (70 eV) *m/e* 198 (M^+).

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

(*E*)-1-Ethylidene-8,9-benzospiro[3.5]nonane (*E*-ESO). Portions (20 mL) of a solution of 500 mg of ESO (95% *Z*) in 100 mL of hexane were irradiated in 19-mm i.d. Vycor rubes which had been freeze–pump–thaw degassed and flame sealed. The source was a Rayonet reactor with 254-nm lamps. After 19 h, the solvent was concentrated in vacuo and the residue passed through a 2.5 × 8.0 cm alumina plug to give 485 mg of a 55:45 *Z*/*E* ratio of isomers. Preparative VPC on column E (170 °C, 100 mL He/min) provided pure *E*-ESO: IR (neat) 3.40, 6.25, 6.78, 6.95 μ; NMR (CCl_4) δ 7.25 (m, 1 H, aromatic), 6.95 (m, 3 H, aromatic), 5.00 (m, 1 H, vinyl), 2.70 (m, 4 H, allylic CH_2 and benzylic CH_2), 2.5–1.7 (m, 6 H, 4 and 6 ring CH_2), 1.55 (bd, 3 H $J = 7.0$ Hz, CH_3); mass spectrum (70 eV) *m/e* 198 (M^+).

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

Assignment of Configuration to ESO. The major synthetic isomer was assigned as *Z* on the basis of the chemical shift and coupling constants observed for the vinyl methyl signal. In this isomer, the methyl doublet is centered at δ 1.20 with 2.4-Hz triplet fine splitting; the *E* isomer is centered at δ 1.55 with no triplet fine splitting. The upfield signal in the *Z* isomer is consistent with the methyl's position relative to the benzene ring, whereby appreciable shielding would be anticipated. Likewise, the *Z* isomer has the methyl and allylic methylene groups in a transoidal relationship, for which a greater long-range coupling would be expected[84] than for the cisoid arrangement of the *E* isomer.

6-Methyl-8,9-benzospiran[3.5]nonane (MSOH). A solution of 96 mg of MSO in 20 mL of dry tetrahydrofuran was hydrogenated over 50 mg of 10% palladium on carbon catalyst for 20 h to afford a 95% conversion to MSOH, as analyzed at 130 °C on column F. The product was purified by preparative VPC at 150 °C on column G (60 mL He/min): IR (neat) 3.38, 6.24, 6.70, 6.90 μ; NMR ($CDCl_3$) δ 7.40 (m, 1 H, aromatic), 7.00 (m, 3 H, aromatic), 2.70 (m, 2 H, benzylic), 2.30 (m, 3 H, aliphatic), 1.75 (m, 6 H, aliphatic), 0.60 (d, 3 H, $J = 8.5$ Hz, CH_3).

Calcd for $C_{14}H_{18}$: *m/e* 186.141. Found: 186.141.

Xenon Perturbation Studies. The procedures are basically those of Carroll and Quina.[17] For ϕ_{isc} determinations using 2-heptene, stock solutions of the alkylaromatic were prepared in cyclopentane, to give an absorbance at 254 nm of 2.1–2.8. This solution (50 mL) was transferred to a volumetric flask and *cis*-2-heptene was added to make a 40–60 mM solution of olefin. Aliquots (4 or 5 mL) were pipetted into quartz photolysis tubes which had previously been matched to ±2.0% (using 1-phenyl-2-butene photoisomerization). Nevertheless, the tubes were matched for each individual study by finding the orientation of each tube in the cell holder, which gave maximum fluorescence emission (relative to that tube whose emission was strongest). After freeze–pump–thaw degassing (1) F'/F_0 was determined for pairs of tubes with and without heptene; (2) increments of xenon were added to a separate set of tubes, and (a) F was determined by rotating each tube to its maximum emission, (b) P/P_0 was determined by irradiation of the set followed by *trans*-2-heptene analysis by VPC (see analyses above). The procedure for bichromophoric molecules containing internal "product probes" was essentially identical with that described above, but without the need for added heptene and thus without an F'/F_0 determination.

A more detailed description of the experiment as well as a complete listing of the data for each compound may be found in the thesis of Fred Palensky.[85]

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References and Notes

(1) (a) Organic Photochemistry. 40. Part 39: M. Pallmer and H. Morrison, *J. Chem. Soc., Chem. Commun.*, 558 (1978). (b) Abstracted from the Doctoral Dissertations of Frank Scully (1973), Fred Palensky (1977), and Tom Nylund (1978), Purdue University.

(2) Leading references may be found in H. Morrison, V. Tisdale, P. J. Wagner, and K-C Liu, *J. Am. Chem. Soc.*, **97**, 7189 (1975).

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(4) T. J. Chuang, R. J. Cox, and K. B. Eisenthal, *J. Am. Chem. Soc.*, **96**, 6828 (1974).

(5) See ref 3b for a recent illustrative study.

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(7) H. Morrison, J. Pajak, and R. Peiffer, *J. Am. Chem. Soc.*, **93**, 3978 (1971); H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968).

(8) Portions of this research have been reported in preliminary form; cf. (a) F. Scully, J. Grutzner, and H. Morrison, *J. Am. Chem. Soc.*, **95**, 5100 (1973); (b) H. Morrison, T. Nylund, and F. Palensky, *J. Chem. Soc., Chem. Commun.*, 4 (1976); (c) H. Morrison and T. Nylund, *ibid.*, 104 (1977).

(9) H. Morrison and T. Nylund, *J. Chem. Soc., Chem. Commun.*, 785 (1976).

(10) T. Nylund and H. Morrison, *J. Am. Chem. Soc.*, following paper in this issue.

(11) A fifth product is benzo[3.4]tricyclo[3.2.1.$0^{2,7}$]octene; it is a secondary photoproduct not observed at low conversions, which is efficiently formed from **2** by a di-π-methane rearrangement.[12]

(12) R. C. Hahn and L. J. Rothman, *J. Am. Chem. Soc.*, **91**, 2409 (1969). We are grateful to Professor Hahn for spectra of this compound.

(13) These values differ slightly from those previously reported;[8a] they were obtained by a modification of the earlier analytical procedure and are considered to be more accurate.

(14) R. H. Fleming, F. H. Quina, and G. S. Hammond, *J. Am. Chem. Soc.*, **96**, 7738 (1974).

(15) Extended irradiation leads to other products which have not been further investigated. We suspect them to be homologues of the MBN products.

(16) Despite the good precision and reproductibility of the quantum efficiency and photostationary state data, the latter value is a little lower than would be predicted by the quantum efficiencies.

$$(E/Z)_{\mathrm{pss}} = \frac{\epsilon_Z\, \phi_{Z\rightarrow E}}{\epsilon_E\, \phi_{E\rightarrow Z}} = \frac{(422)(0.10)}{(412)(0.08)} \approx 1.28$$

(17) F. A. Carroll and F. H. Quina, *J. Am. Chem. Soc.*, **98**, 1 (1976).

(18) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, N.Y., 1970, p 122.

(19) We are grateful to Professor E. Heilbronner for the MBN data.

(20) F. Brogli, E. Giovanni, E. Heilbronner, and R. Schuster, *Chem. Ber.*, **106**, 961 (1973).

(21) P. Asmus and M. Klessinger, *Tetrahedron*, **30**, 2477 (1974).

(22) Prolonged irradiations give 2-ethyl-3-methylindene, an apparent product of a 1,3 hydrogen shift.

(23) We are grateful to Professor T. Fehlner for the 2-methyleneindan, MSO, and MSOH data.

(24) Surprisingly, we have found very little in the way of information on this aryl olefin in the literature. Its synthesis proved quite troublesome; see Experimental Section for details.

(25) For a review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(26) Further evidence for the intermediacy of **9** derives from products isolated in methanol, which result from 1,3 addition to the cyclopropane ring.[9,10] A product analogous to **9** has been isolated from the photolysis of 7-methylenedibenzobicyclo[2.2.2]octadiene; cf. S. J. Cristol and G. O. Mayo, *J. Org. Chem.*, **34**, 2363 (1969).

(27) J. Ipaktschi, *Chem. Ber.*, **105**, 1989 (1972).

(28) H. Iwamura and H. Tukada, *Chem. Lett.*, 1045 (1976), and references cited therein. See however, R. O. Day, V. W. Day, S. J. Fuerniss, J. R. Hohman, and D. M. S. Wheeler, *J. Chem. Soc., Chem. Commun.*, 853 (1976), for further discussions of the triptycene problem.

(29) For one possible exception, see S. S. Hixson and J. C. Tausta, *Tetrahedron Lett.*, 2007 (1974). A recent relevant discussion may be found in P. S. Mariano, D. G. Watson, and E. Bay, *Tetrahedron*, **33**, 11 (1977).

(30) Acetone is ineffective and reacts with the MBN.

(31) The successful choice of a sensitizer involves very subtle differences in energy levels. Toluene induces both singlet and triplet MBN photochemistry.

(32) The lack of **4** in the sensitized photoproduct mixture is anomalous; since its formation is enhanced by xenon (see below) we are exploring the possible involvement of an upper (T_2) triplet state.

(33) Reference 8b and references cited therein. See also G. Fischer and E. Fischer, *Mol. Photochem.*, **6**, 463 (1974); R. Korenstein, K. A. Muszkat, and E. Fischer, *J. Photochem.*, **5**, 345 (1976).

(34) J. B. Birks, *Photochem. Photobiol.*, **24**, 287 (1976); F. A. Carroll, *Mol. Photochem.*, **8**, 113 (1977).

(35) For example, xenon enhancement may be due (1) to a prediminantly triplet reaction which is increased by xenon induced intersystem crossing or (2) a predominantly singlet reaction for which ϕ_{RT} is high but ϕ_{isc} is low.

(36) We know of no conclusive evidence on this point for bichromophores. There is a claim (J. Tournon and M. A. El-Bayoumi, *J. Chem. Phys.*, **56**, 5128 (1972)) that benzyl derivatives exhibit a charge transfer induced increase in k_{isc}, but the basis for the claim is the false assumption of negligible internal conversion. In fact, k_{ic} is significant (34%) for toluene and it is it which increases upon benzylic substitution, an observation which may be related to the effects on k_{ic} which we are reporting. (Cf. V. M. Berenfeld and V. A. Krongauz, *Izv. Akad. Nauk SSR, Ser. Fiz.*, **32**, 1575 (1968).) The singlet state energies of BN and MBN are comparable (see below) and if this is so for the aryl triplet states as well, the known dependence of k_{isc} on the S–T energy gap (among other factors, of course)[37] implies a common k_{isc}. We do know that the k_f's for MBN and its dihydro analogue, MeBN, are identical (see below). The *inter*molecular interaction of olefins with aryl excited singlet states increases k_{ic} but does not appear to affect k_{isc} (L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969)).

(37) For example, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 296.

(38) Using $\phi_{isc}{}^{BN} = 0.59$, ${}^1\tau^{BN} = {}^1\tau^{MeBN} = 13.5$ ns.

(39) The terms in eq 11 have been defined in the Results section.

(40) (a) Note that the deviations in these slopes (cf. Results) make it quite possible that **1, 2, 3,** and the IBN $E \rightarrow Z$ reaction share a common slope (0.46) and singlet component (56%). (b) Subsequent to the completion of these studies Hammond and Weiss[3g] have reported that 5-*ethylidene*[2.2.1]*hept-2-ene also undergoes E/Z* isomerization out of the singlet state and in competition with a di-π-methane rearrangement.

(41) We recognize that were ϕ_{isc} assumed to be equal to the common value[40] of 0.46, four of the five products would be 100% triplet derived. The obvious problem of such an assumption is the low slope for **4** (a slope less than ϕ_{isc} is kinetically impossible). A value of $\phi_{isc} = 0.46$ requires a k_{isc} of 1.0×10^8 s^{-1}; the value for the monochromophoric models such as benznorbornane is ca. 4.3×10^7 s^{-1}.

(42) (a) Even were $\phi_{isc} = 0.46$[41], ϕ_d and ^1k_d for MBN would still be high (0.46 and 1.0×10^8 s^{-1}, respectively). (b) Hammond and Weiss[3g] suspected that such is the case for 5-ethylidene[2.2.1]hept-2-ene but had insufficient data to confirm their intuition. (c) We assume no appreciable difference in the photophysical properties of IPN and MBN. This assumption is substantiated by the identical ϕ_i values for MBN and 2-isopropylidenebenznorbornene.[10]

(43) A brief review may be found in the excellent chapter by R. S. Davidson in "Molecular Association", Vol. 1, R. Foster, Ed., Academic Press, New York, N.Y., 1975, p 302.

(44) Note the absence of ϕ_{isc} from eq 15 and this conclusion.

(45) (a) We have recently obtained xenon perturbation data for 1-phenyl-2-butene isomerization[7] which indicate that there is appreciable triplet decay without olefin isomerization (D. Giacherio, unpublished results). By contrast with MBN, there is no evidence for olefin-induced singlet decay. (b) Ketone triplets do form exciplexes with olefins, competitively with energy transfer: J. A. Gupta and G. S. Hammond, *J. Am. Chem. Soc.*, **98**, 1218 (1976), and references cited therein. We are not aware of similar observations for aryl triplets.

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(50) Of the three benzene transitions, typically the E_{1ua} (185–195 nm, ϵ ~50 000) and B_{1u} (200–210 nm, ϵ ~7000) are the most intense (B_{2u}, 260–270 nm, ϵ ~400). The N–V_1 band of 2-methylenenorbornane comes at 195 nm.[51] Since coupling of two transitions increases as (1) their transition moments increase and (2) their energy difference decreases,[49,52] one expects the primary aryl olefin coupling to occur within the two higher energy aryl transitions.

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(61) A constant k_{isc} is again being assumed.[36]

(62) F. Palensky and H. Morrison, *J. Am. Chem. Soc.*, **99**, 3507 (1977).

(63) We do not, however, see evidence for the charge transfer which characterized MBN (cf. **11**).

(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.
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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*

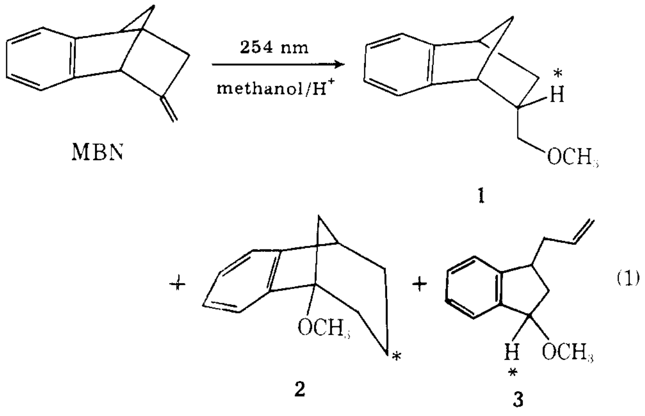
Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received April 25, 1978*

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_3MBN), 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_2SO_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_2SO_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-

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