Triplet Photoisomerization of 1-Substituted 6-Methoxybenzonorbornadienes. Excited-State Competition between Bridgehead and *m*-Methoxy Groups for Intramolecular Control of the Dual Channel Di-π-methane Pathway. The Vinyl Deuterium Isotope Effect

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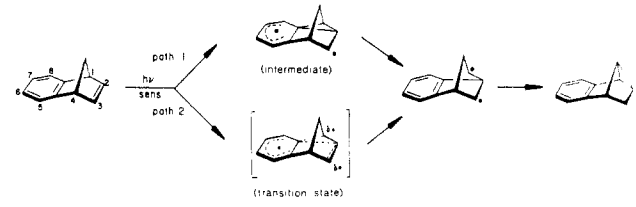
Abstract: Seven 1-substituted 6-methoxybenzonorbornadienes were prepared and subjected to acetophenone-sensitized photoisomerization. In the $-COOCH_3$, $-CONH_2$, $-COCH_3$, and $-CN$ examples, the excited-state 1,2-aryl shift was overwhelmingly controlled by the bridgehead substituent. As the electron-withdrawing character of this group is reduced as in $-C(CH_3)_2OH$, $-NHCOCH_3$, and $-CH_3$, the extent of proximal di-π-methane rearrangement falls off to a level as low as 55%. Notably, the otherwise well-established preference of *m*-methoxy to engage that aryl carbon positioned meta to it never dominates in this series. Quantum yield measurements have also been performed on 17 benzonorbornadienes. The results reveal particularly efficient processes at one end of the spectrum to 0% reaction in the 2-bromo example. The full range of the data provides an important glimpse into how triplet deactivation can be realized in rigid bichromophoric systems possessing well-defined geometry. Finally, the secondary deuterium isotope effect associated with triplet state di-π-methane rearrangement of benzonorbornadiene-d_2 has been determined to be greater than unity and quite large ($k_H/k_D = 1.34$). This partitioning, together with the global quantum efficiency and regioselectivity patterns, is discussed in mechanistic terms.

Recent elucidation of the appreciable regioselectivities which operate during triplet-sensitized di-π-methane photorearrangement of benzonorbornadienes is playing an important role in our development of a deeper understanding of mechanism and excited-state substituent effects. Benzonorbornadienes hold the distinction of being dual-channel di-π-methane substrates since aryl migration can occur to either vinyl carbon. As a result of the C_s symmetry of the parent hydrocarbon, its two possible isomerization pathways are enantiomerically related and consequently isoenergetic. Aryl, vinyl, or bridgehead substitution reduces this group symmetry, and the two possible rearrangement schemes consequently become intramolecularly competitive. The course of events followed by any given substrate is easily diagnosed by proper quantitative ^1H NMR analysis of the photoproduct(s).

Unambiguous demonstration of the following pronounced substituent effects has already been made as follows: (a) aryl substitution at C-6 by electron-acceptor groups results in overwhelming involvement of the para carbon atom; donor groups at the same site favor rebonding via the meta position.[2,3] (b) the same striking crossover is not seen upon substitution at C-5; in this instance, the ortho carbon atom is utilized irrespective of the nature of R.[4] (c) attachment of a substituent at bridgehead site C-1 promotes highly regioselective or fully regiospecific migration of the proximal aryl site; the only two known exceptions are Br (heavy atom effect) and D (isotopic control).[5] (d) in the case of 1-methoxy-4-substituted benzonorbornadienes, a single reaction channel again involving the aryl carbon proximal to R is favored; only when R is $NHCOCH_3$ or CH_3 is leveling encountered.[6] (e) a 2-cyano group strongly induces migration of the aryl site most remote from it;[7] the vinyl methyl effect is less pronounced.[8]

These findings, when combined with observations made in other laboratories,[9] have brought into question the exclusive operability of the aryl–vinyl bridging scheme (path 1) originally set forth by



Zimmerman.[10] The consequences of bridgehead substitution in particular suggest that the reaction mode involving "direct" 1,2-aryl migration may actually be preferred under certain circumstances. The possible intervention of cyclopropyldicarbinyl diradicals along these triplet di-π-methane rearrangement manifolds is compatible with molecular orbital calculations.[11] On this basis, path 2 is equally feasible and offers the advantage of minimizing the temporary disruption of benzenoid aromaticity. In actuality, it is entirely possible that there exists a gradient of mechanism between these two extremes similar to that detailed by Gajewski and Conrad for the Cope and Claisen rearrangements.[12]

It is necessary to recognize that explicit distinction between paths 1 and 2 is subtle because the "direct" 1,2-shift must also proceed geometrically via a bridged biradicaloid transition state. That pπ orbital involvement is necessary for rearrangement is reflected in the ease with which phenyl and vinyl migrate but allyl does not. The commonly accepted Zimmerman mechanism (path

(1) National Institutes of Health Postdoctoral Fellow, 1985-1986.
(2) (a) Paquette, L. A.; Cottrell, D. M.; Snow, R. A.; Gifkins, K. B.; Clardy, J. *J. Am. Chem. Soc.* **1975**, *97*, 3275. (b) Paquette, L. A.; Cottrell, D. M.; Snow, R. A. *Ibid.* **1977**, *99*, 3723.
(3) (a) Edman, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 3454; **1969**, *91*, 7103. (b) Liu, R. S. H.; Edman, J. R. *Ibid.* **1968**, *90*, 215; **1969**, *91*, 1492. (c) Hahn, R. C.; Johnson, R. P. *Ibid.* **1977**, *99*, 1508.
(4) (a) Santiago, C.; Houk, K. N.; Snow, R. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 7443. (b) Snow, R. A.; Cottrell, D. M.; Paquette, L. A. *Ibid.* **1977**, *99*, 3734.
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(7) (a) Paquette, L. A.; Ku, A. Y.; Santiago, C.; Rozeboom, M. D.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 5972. (b) Ku, A. Y.; Paquette, L. A.; Rozeboom, M. D.; Houk, K. N. *Ibid.* **1979**, *101*, 5981. (c) See, also: Bender, C. O.; O'Shea, S. F. *Can. J. Chem.* **1979**, *57*, 2804. (d) Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2883.
(8) Paquette, L. A.; Bay, E.; Ku, A. Y.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1982**, *47*, 422.
(9) For an overview, consult ref 5.
(10) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932. (b) Zimmerman, H. E.; Mariano, P. S. *Ibid.* **1969**, *91*, 1718. (c) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (d) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 16, pp 131-164.
(11) Quenemoen, K.; Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1985**, *107*, 5054 and relevant references cited therein.
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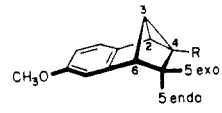
Table I. Chemical Shifts of the Aliphatic Protons in the 4-Substituted-9-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes[d]



R	H_2[c]	H_3[c]	H_{5exo}[c]	H_{5endo}[c]	H_6[c]	other
$COOCH_3$	3.27 (d, J = 5.6)	3.79 (m)[a]	3.00 (dd, J = 9.1, 8.9)	1.03 (dd, J = 9.0, 2.0)	3.29 (dd, J = 8.6, 2.9)	$COOCH_3$ (3.77, s)
$CONH_2$	3.26 (d, J = 5.3)	3.78 (m)[b]	2.90 (dd, J = 8.1, 8.0)	1.08 (dd, J = 8.2, 1.8)	3.34 (dd, J = 7.6, 2.1)	$CONH_2$ (5.57, br)
$COCH_3$	3.29 (d, J = 4.8)	3.85 (ddd, J = 5.0, 3.1, 2.2)	2.99 (dd, J = 9.0, 8.0)	1.08 (dd, J = 9.0, 2.0)	3.30 (dd, J = 7.4, 3.0)	$COCH_3$ (2.11, s)
CN	3.13 (d, J = 5.4)	3.31 (ddd, J = 5.2, 2.8, 2.6)	3.05 (dd, J = 8.4, 8.3)	1.07 (dd, J = 8.8 1.8)	3.39 (dd, J = 7.8, 3.0)	
$C(CH_3)_2OH$	2.63 (d, J = 5.4)	3.31 (ddd, J = 5.4, 2.7, 2.4)	2.78 (dd, J = 9.3, 8.2)	0.86 (dd, J = 8.6, 2.1)	3.21 (dd, J = 7.7, 2.8)	$C(CH_3)_2OH$ (1.68 br, O*H*, 1.41, s, 1.39, s)
$NHCOCH_3$	2.52 (d, J = 5.6)	3.80 (m)[b]	3.17 (dd, J = 8.2, 8.1)	1.16 (dd, J = 8.3, 2.5)	3.31 (dd, J = 7.8, 3.0)	$NHCOCH_3$ (6.47, br, N*H*, 1.95, s)
CH_3	2.22 (d, J = 5.2)	3.14 (ddd, J = 5.2, 2.8, 2.6)	2.56 (dd, J = 8.3, 8.0)	0.96 (dd, J = 8.8, 2.8)	3.27 (dd, J = 7.6, 2.9)	CH_3 (1.41, s)

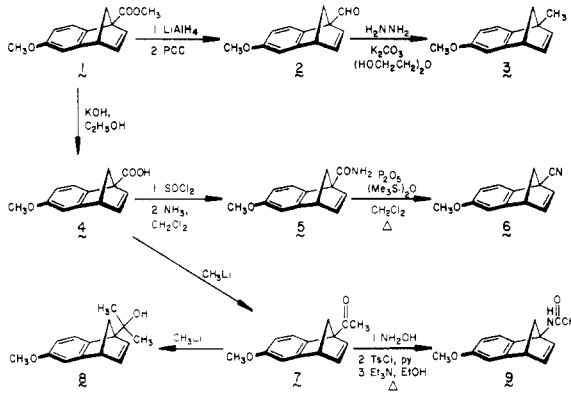
[a] Masked by carbomethoxy signal. [b] Masked by aryl methoxy signal. [c] J is measured in hertz. [d] 300 MHz, $CDCl_3$ solution, δ.

1) involves an actual, fully bonded, energy minimum cyclopropyl intermediate. A good deal of data uncovered in (a)–(e) suggests that the cyclopropyl species may often be only a partially bonded transition state, with the nonbridged 1,3-biradical serving as the true intermediate.

In an effort to gain additional clarification of these issues, we were led to investigate the fate of 1-substituted 6-methoxybenzonorbornadienes when subjected to triplet excitation. This class of molecules was selected in order to assess the results of intramolecular competition between the 6-OCH_3 group (known to favor meta-aryl migration) and various R groups at C-1 (known to direct shifting of the proximal aryl carbon that herein is para to methoxyl). In addition, quantum yield studies for a relatively large number of mono- and disubstituted benzonorbornadienes have been undertaken so as to set the overall mechanistic picture in a more quantitative setting.

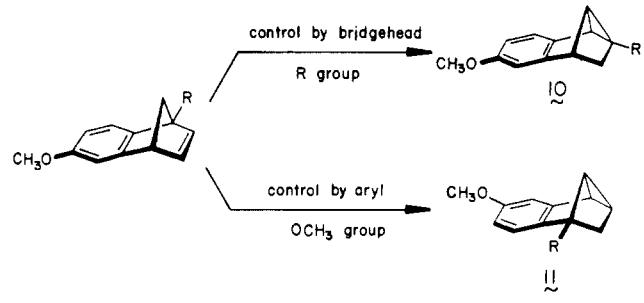
Results

Synthetic Considerations. No additional comment need be made about the preparation of the required ester **1** originally described several years ago by Wiesner and his co-workers.[13] The 11-step sequence starting with *p*-anisaldehyde was executed satisfactorily with only minor changes in detail. The conversion of **1** to the



bridgehead methyl derivative **3** was most effectively accomplished by Wolff–Kishner reduction of aldehyde **2**. Efficient arrival at the carboxamide **5** required that the acid chloride be condensed with anhydrous liquid ammonia (diluted with dichloromethane) rather than ammonium hydroxide or ethanolic ammonia solutions. Initially, the dehydration of **5** to give nitrile **6** proved problematical, perhaps as the combined result of steric inaccessibility to the carbonyl group and susceptibility of the benzonorbornadiene framework to electrophile-induced rearrangement. Mindful of the success enjoyed by Yokoyama et al. in their efforts to realize a similar transformation,[14] we turned to the use of (trimethylsilyl)polyphosphate. When the reaction was conducted in refluxing dichloromethane for 6 h, a 91% yield of **6** was realized. Methyl ketone **7** served as a convenient precursor to both the tertiary carbinol **8** and acetamido derivative **9**.

Photorearrangements. Triplet-sensitized (acetophenone, E_T = 73.6 kcal/mol) photoisomerization of the seven disubstituted benzonorbornadienes was performed on dilute deoxygenated benzene solutions at room temperature with 350-nm light (Rayonet reactor). Progress of the reactions was monitored by thin-layer chromatography. Following consumption of starting material, the solvent was removed in vacuo, and product composition was immediately assessed by ^{1}H NMR spectroscopy. When pairs of products resulted, their spectra proved sufficiently distinctive (see Tables I and II) to permit quantitative integration. In most cases, the products could be obtained in an isomerically pure state following spinning plate chromatography to remove the sensitizer. Proper structural assignment to each of the tetracyclo[5.4.0.3^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes was made possible by the fact that all five of the aliphatic protons in **10** and **11** possess



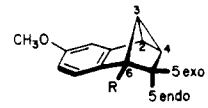
distinctively different chemical shifts. The distinction between the presence of R at C-4 (a cyclopropyl site) or C-6 (bridgehead position) is a particularly obvious one. The question of the position of the aryl methoxyl group is, of course, concomitantly resolved. Further substantiation of the structural relationships common to **10** and **11** was derived from their ^{13}C NMR spectra.

As can be seen from Table III, the excited-state rebonding preference adopted by **1**, **5**, **6**, and **7** is that which is overwhelmingly controlled by the bridgehead substituent. Thus, when R is electron-withdrawing, its ability to direct aryl migration overrides completely that otherwise dictated by *m*-OCH_3. As the scope of bridgehead substitution is expanded to include dimethylcarbinol **8**, acetamide **9**, and methyl derivative **3**, the extent of proximate

(13) Wiesner, K.; Ho, P.-T.; Jain, R. C.; Lee, S. F.; Oida, S.; Philipp, A. *Can. J. Chem.* **1973**, *51*, 1448.

(14) Yokoyama, M.; Yoshida, S.; Imamoto, T. *Synthesis* **1982**, 591.

Table II. Chemical Shifts of the Aliphatic Protons in the 6-Substituted-9-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]-undeca-1(7),8,10-trienes



R	H_2[c]	H_3[c]	H_4[c]	H_{5exo}[c]	H_{5endo}[c]	other
$C(CH_3)_2OH$	2.51 (dd, J = 5.2, 5.2)	3.16 (ddd, J = 5.1, 4.8, 2.2)	1.96 (ddd, J = 5.0, 4.7, 3.6)	2.84 (dd, J = 8.9, 3.5)	0.81 (dd, J = 8.8, 2.5)	$C(CH_3)_2OH$ (1.63, br, O*H*, 1.42, s, 1.40, s)
$NHCOCH_3$	2.57 (dd, J = 5.7, ×)[a]	3.86 (m)[b]	2.96 (ddd, J = 5.28 4.6, 3.4)	2.75 (dd, J = 8.2, 3.4)	1.33 (dd, J = 8.8, 2.4)	$NHCOCH_3$ (6.58, br, N*H*, 2.10 s, s)
CH_3	2.48 (dd, J = 5.2, 5.2)	3.07 (ddd, J = 5.2, 4.7, 2.7)	1.96 (ddd, J = 5.4, 4.3, 3.4)	2.41 (dd, J = 8.7, 3.3)	0.95 (dd, J = 8.8, 2.6)	CH_3 (1.50, s)

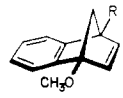
[a] Partially obscured by absorption from major peak (see text). [b] Masked by aryl methoxyl signal. [c] J is measured in hertz. [d] 300 MHz, $CDCl_3$ solution, δ.

Table III. Product Distributions Realized from Triplet-State Photoisomerization of **1–9**[a]

compd	R	bridgehead control **10**, %	aryl control **11**, %
1	$COOCH_3$	100	0
5	$CONH_2$	100	0
7	$COCH_3$	100	0
6	CN	100	0
8	$C(CH_3)_2OH$	77	23
9	$NHCOCH_3$	72.5 (±5)[b]	27.5 (±5)[b]
3	CH_3	55	45

[a] The limits of detection are considered to be ±3% except in the case of **9**. [b] The greater margin of error in this example arises because of the sensitivity of **10**-$NHCOCH_3$ to both $CDCl_3$ and the chromatographic conditions applied to product purification.

Table IV. Extent of Bridgehead Control as a Function of Additional Benzonorbornadiene Substitution (%)

R			
$COOCH_3$	100	100	100
$COCH_3$		100	100
$CONH_2$		100	100
CN	100	100	100
$NHCOCH_3$	100	62	72
CH_3	90	44	55

aryl carbon shift falls off to a level as low as 55%. Relevantly, the well-established preference of *m*-OCH_3 to engage that aryl carbon positioned meta to it never dominates in this series. Thus, the level of bridgehead control is striking.

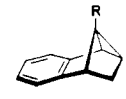
We now call attention to Table IV where the regioselectivity responses of three groups of benzonorbornadienes have been compiled. These data reveal that substitution at C-1 by $COOCH_3$, $COCH_3$, $CONH_2$, and CN results in total bridgehead domination, notwithstanding the *apparent* insulation of these groups from the obviously interactive aryl and vinyl moieties.

Bridgehead substitution by $NHCOCH_3$ continues to channel di-π-methane rearrangement into that sector of the benzonorbornadiene that is proximal, although it is only slightly more effective at doing so relative to a methoxyl group at C-4 or C-6. When a C-1 methyl group is present, its level of control is somewhat more efficacious than *m*-OCH_3 but less significant when pitted against a bridgehead methoxyl. The extent of domination by the latter two substituents can be more informatively indexed by comparison with the ratios of regioisomers formed following photoactivation of the relevant *mono*substituted compounds. On the premise that perfect additivity operates within **3**,[15,16] the predicted ratio for bridgehead/aryl control would be (3/97) × (90/10) = 22:78. The experimentally determined 55:45 composition indicates that C-1 methyl becomes a better controller of regioselectivity in **3** relative to when the aryl-OCH_3 is lacking. The same phenomenon arises in the acetamide series where perfect additivity would give a basal preference of 50:50. The actual value (72.5:27.5) again denotes improved directive capability.

Quantum Yield Measurements. Our past experience with variously substituted benzonorbornadienes has brought into focus a number of important mechanistic questions, more quantitative data about which could prove usefully informative. For example, if aryl–vinyl bridging according to path 1 did happen to be reversible under certain circumstances, the resulting energy dissipation would be revealed by a nonregular change in a relative rate profile. In the same vein, because substituents might exert long-range effects on nonradiative decay, quantum yields for the di-π-methane rearrangements become desirable reference points. Effects of this type, if operative, should be particularly noticeable when proceeding from non- to mono- to disubstituted reactants.

In an effort to gain information on these various issues, quantum efficiency determinations for a representative group of benzonorbornadienes under acetophenone-sensitized conditions were carried out and are collected in Table V. Although the overall quantum yield is the only kinetic parameter that can be measured directly for photochemical reactions performed under conditions of steady-state illumination,[17] the varied substitution plans examined herein provide a rare glimpse of how triplet deactivation can be realized in a rigid bichromophoric system possessing well-defined geometry.

Photoisomerization is seen to be particularly efficient in the parent hydrocarbon **12**[3b] and when the benzonorbornadiene frame carries a methyl or trimethylsilyl substituent at one of its bridgehead or vinyl sites as in **13–16** or a "meta"-methoxyl substituent as in **20**. To set matters in a more defined perspective, the regioselectivities observed for these substrates should be reviewed here. Whereas bridgehead trimethylsilyl causes all rebonding to occur proximal to it, a comparably positioned methyl group dictates that phenyl migrate in its immediate vicinity to the slightly reduced extent of 90%.[5] The vinyl methyl effect in **14** is such that **26a** and **27a** are produced in an 81:19 ratio.[8] For



26a, R = CH_3
b, R = $SiMe_3$

27a, R = CH_3
b, R = $SiMe_3$

trimethylsilyl analogue **16**, the distribution of **26b** and **27b** happens to be >99:1. Thus, the rather good capability of methyl to control di-π-methane regioselectivity is somewhat more enhanced in the case of Me_3Si.

(15) Examples of perfect additivity are known: ref 8 and Paquette, L. A.; Coghlan, M. J.; Cottrell, C. E.; Irie, T.; Tanida, H. *J. Org. Chem.*, in press.

(16) The ratios of 100:0 (only one regioisomer observed) are adjusted to ~97:3 to allow for possible detection limits.

(17) Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.

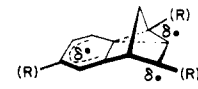
Table V. Quantum Yields

substrate	concentration, M	conversion, %	mass balance, %	Φ	Φ_{avg}
 **12**	0.0045	9.09	98.6	0.81	
 **13**	0.0043[a]	6.11–7.67	98.2–99.5	0.70	0.79
	0.0034	12.42	98.3	0.90	0.90
 **14**	0.0042	9.07	101.2	0.90	
	0.0045	9.03	100.0	0.84	0.82
 **15**	0.0042	8.96	96.5	0.80	
	0.0044	7.67	105.6	1.01	0.94
 **16**	0.0035	10.08	96.7	0.86	
	0.0041	10.02	99.1	0.85	0.83
 **17**	0.0036	8.21	99.6	0.81	
	0.0043	5.18		0.55	0.58
 **18**	0.0043	6.33	109	0.60	
	0.0042	5.44	97.4	0.50	0.50
 **19**	0.0042	6.52	92.8	0.49	
	0.0044	4.48	103.3	0.38	0.37
 **20**	0.0029	5.24	96.7	0.36	
	0.0041	9.89	102.8	0.80	0.77
 **21**	0.0041	6.88	96.5	0.74	
	0.0042	3.63	100.6	0.46	0.46
 **22**	0.0042	6.23	98.5	0.47	
	0.0042	3.75	104.0	0.28	0.28
 **23**	0.0042	4.70	110.0	0.29	
	0.0042	0	97.6	0.0	0.0
 **24**	0.0101	0	99.6	0.0	
	0.0042	8.44	94.4[b]	0.52	0.52
 **25**	0.0042	10.92	103.0	0.72	0.68
 **3**	0.0042	5.89	95.7	0.63	
	0.0042	7.99	108.2	0.75	0.67
 **1**	0.0042	6.73	92.0	0.63	
	0.0042	0.67	122.3	0.074	0.08
	0.0044	1.70	89.0	0.085	

[a] Average of four runs at this concentration. [b] Product decomposition occurs during the gas chromatographic analysis. The uncertainty in Φ is larger in this case.

When the lone substituent is 6-methoxyl, both possible rearrangement pathways again operate, with meta-aryl rebonding dominating over the para option to the extent of 78%.[2]

The combined data reveal that 1,2-aryl migration occurs very efficiently in these six compounds. Also clearly evident is the fact that there is a considerable buildup of odd-electron density at the substituted bridgehead and vinyl sites. The long-standing question now introduced is whether it is appropriate to view **28** or another of its weighted forms as a true intermediate on the energy surface. We will return to this specific mechanistic question in a later section with consideration of secondary deuterium isotope effects. Suffice it to say that earlier studies have shown that 1,3-biradical **29** does not return to the benzonorbornadiene,[18] and the high quantum yields suggest that triplet state **28** proceeds to product the majority of the time.



28

29

The exploration of substituent effects on Φ was continued with single electron-withdrawing groups typified by the vinyl and aryl cyano derivatives (**17** and **19**) as well as the bridgehead carbomethoxy and bromo compounds **18** and **21**. As Table V indicates, introduction of these particular groups somewhat reduces the photoisomerization efficiency, Φ dropping to levels 40–60% below those encountered above. Three causative factors could be at work.[19] One possibility is that the rates of energy transfer from acetophenone sensitizer to these particular benzonorbornadienes are significantly reduced. Although we did not directly measure the efficiency with which these compounds quench triplet acetophenone, precedence[19] suggests that there would be little difference in rate constants for energy transfer. Another probable cause would be an increase in k_d, the decay or intersystem crossing rate constant. This phenomenon is often difficult to distinguish from an overall reduction in the reaction rate, k_r, as defined below.

$$T_1 \xrightarrow{k_r} \text{product}$$

$$T_1 \xrightarrow{k_d} \text{starting material}$$

$$\phi r = \frac{k_r}{k_d + k_r}$$

During the course of these photorearrangements, the triplet state must revert to singlet in order to return to product. Any factor that selectively stabilizes the singlet is, of course, likely to facilitate the necessary intersystem crossing. In their detailed study of the photoactivation of chlorobenzobicyclo[2.2.2]octadienyl systems, Cristol, Dickenson, and Stanko noted that while the *anti*-7-chloro derivative is photoactive, giving rise to isomerized and solvolyzed products, the *syn*-8-chloride is inert.[20]

The photoreactivity of the first chloride was interpreted in terms of electron transfer from the benzene ring to the σ^* orbital of the carbon–chlorine bond, such that a zwitterionic biradical intervenes. Rapid decay of this species by loss of chloride ion is subsequently expected.[21,22]

In **17–19** and **21**, there exists no opportunity for photosolvolysis. However, these particular electron-withdrawing substituents may well introduce a competitive electron-transfer mode that enhances k_d and reduces overall efficiency. Stated differently, the lower quantum yields for these four systems are in evidence likely because of internal electron transfer, which allows the otherwise

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(19) Givens, R. S.; Chae, W. K.; Matuszewski, B. *J. Am. Chem. Soc.* **1982**, *104*, 2456.

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(21) (a) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707. (b) Critsol, S. J.; Strom, R. M. *Ibid.* **1980**, *102*, 5577. (c) Cristol, S. J.; Barbour, R. V. *Ibid.* **1968**, *90*, 2832.

(22) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734 and relevant references cited therein.

"forbidden" passage into the singlet manifold.

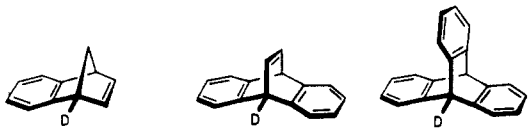
A comparison of the three isomeric bromides **21**, **22**, and **23** is particularly revealing. In the case of **22** where the bromine atom is present as an aryl substituent, a further attenuation of the quantum efficiency is seen. The effect appears too large to be attributed solely to inductive influences. Limited data exist on how the heavy-atom effect varies as a function of distance between the chromophore and the halogen.[23] Still controversial is the matter of whether a charge transfer[24] or electron exchange mechanism[24a,25] operates. The enhanced k_d in **22** may simply reflect the fact that its $T_1 \rightarrow S_0 + \Delta$ cascade may follow a different mechanism than that operative in **21**.

A most interesting example is vinyl bromide **23**, which exhibits no observable tendency to undergo excited-state di-π-methane rearrangement! This unique result can be understood in terms of **28**. As migration starts, spin density begins to build on the vinyl carbon that is substituted by bromine. As a consequence of the directly affixed heavy atom, the opportunity for spin-orbital coupling[24a,26] is maximized. The resultant molecular electronic state mixing evidently permits rapid return to the singlet ground state.

The disubstituted benzonorbornadienes **1**, **3**, **24**, and **25** constitute another intriguing subset of compounds. With the exception of **1**, the Φ values are quite similar (0.5–0.7). The relatively modest nature of these quantum efficiencies relative to those determined for **13**, **14**, and **20**, for example, may plausibly arise from charge-transfer interactions[27] operative in T_1. In this regard, the bridgehead methoxyl group in **24** is seen to add little to the quantum yield. Nor does $-OCH_3$ vie effectively against $-COOCH_3$ for control of regioselectivity in this derivative (Table IV). When the $-CH_3$ and $-OCH_3$ groups are positioned on the framework as in **3** and **25**, a true competition returns (Table IV). These influences are also reflected in lowered quantum yields. Suggested by this relationship is the possibility that the driving force for rearrangement can be undermined to some extent by the capacity of substituent groups to engage in intramolecular charge transfer.

This internal transmission of excitation energy between two pendant groups reaches a maximum in the case of **1** where Φ falls precipitously to 0.08. Since aryl migration in **1** is known to be entirely dominated by the bridgehead carbomethoxy group (Table IV), the bond between C1 and $C8_a$ is clearly weakened preferentially. The onset of this process presumably sets the stage for highly efficacious donor–acceptor interaction and triplet state deactivation.

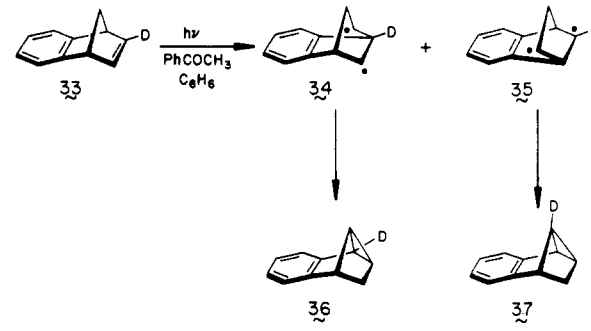
Secondary Deuterium Isotope Effect at the Vinyl Site. Paquette and Bay had previously subjected **30** and **31** to triplet-sensitized photoisomerization.[5] That direct control by bridgehead D on the course of the 1,2-aryl shift was significant was reflected in the fractionation factors which were greater than unity (k_H/k_D = 1.27 and 1.11, respectively). A study of the monodeuterated triptycene **32** by Hemetsberger and Neustern revealed a somewhat larger



30 31 32

isotope effect (2.2–2.4) in the same direction.[28] Consequently, the heavier bridgehead isotope prefers to avoid positioning itself at a fully bonded cyclopropyl (if pathway 1 is followed) or developing free-radical site (if the 1,2-aryl shift is "direct").

We have now made inquiry into the extent to which a vinyl deuterium atom as in **33** can exert control over electronic reorganization within the triplet state. In order to proceed to **37**,



33 34 35 36 37

the carbon bearing the deuterium must ultimately experience a change from initial alkene status to that of a secondary free radical site (see **35**). Little change in hybridization status can be anticipated to accompany this pathway. In direct contrast, progress along the reaction channel to **36** necessitates that the isotopically substituted site become tetrahedral in character (see **34**). Once **34** and **35** are reached, there is no reversal to **33**, and conversion to **36** and **37** follows mandatorily. In view of these substantive differences, an isotope effect differing from unity was anticipated.

To gain information on this question, benzene solutions of benzonorbornadiene-d_2 (**33**) containing acetophenone were sealed in individual NMR tubes and subjected to photoisomerization. The intact reaction mixtures were then analyzed by proton-decoupled ^2H NMR spectroscopy. Integration of the signal at 1.48 ppm due to **36** revealed its area to dominate over that due to **37** at 2.19 ppm by the ratio of 1.31–1.37 (±0.05).[29] The magnitude and direction of the rather high k_H/k_D value indicates that deuterium prefers to be positioned as in **34** and to a substantial degree.

The quantum yield for product formation in the case of **33** was determined to be 0.79. Consequently, the ratio of the quantum efficiencies $\Phi_{H,H}/\Phi_{H,D}$ is approximately unity. Observations have been made elsewhere[28,30] that an isotope effect on quantum yield is sometimes lower than the kinetic isotope effect.

Although the isotope effects are reasonable,[31] fundamental problems persist in their accurate interpretation. Thus, the quantum yield *may* be changing because of differences in radiationless decay along the reaction coordinate rather than because of differences in excited state rates. Deuterium is widely recognized to be capable of reducing rate constants for radiationless conversion to ground state.[31] Nonetheless, it remains difficult to *predict* with certainty the effect of D on competing *intramolecular* reaction rates or *differential* triplet decay.

If it is assumed that the observed k_H/k_D arises entirely from the different probabilities available to photoexcited **33** to pass from its triplet hypersurface to the hypersurfaces of one or the other intermediate biradical, then vibronic mixing of the triplet and intermediate hypersurfaces serves as the principal product-determining factor. The experimentally determined k_H/k_D value of 1.34 signifies that the probability of **33** leaving the triplet hypersurface via **34** is 1.34 times greater than that via **35**. Should the entire isotope effect stem from differences in reaction rates, the Franck–Condon requirements are that high-frequency vibrations be at play and that the electronic energy gap between triplet **33** and the primary photochemical intermediates be adequately large.[28,30] Both criteria are met in **12** and **33**.

Ancillary Mechanistic Considerations. The role of stabilizing substituents on the central carbon of nondual-channeled 1,4-dienes

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(29) The assignments were checked by recording the ^1H NMR spectrum of the **36**/**37** mixture in $CDCl_3$ solution. Upon dividing the area of the absorption centered at δ 3.26 (due to the bridgehead cyclopropyl proton) by that of the doublet positioned at δ 2.52 (site of the apical cyclopropyl proton signal), the isotope fractionation factor was determined to be 1.32.

(30) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 184, 189–190, 385.

(31) Swenton, J. S. In *Isotopes in Organic Chemistry, Volume 1*; Buncel, E., Lee, C. C.; Eds.; Elsevier: Amsterdam, 1975; Chapter 5.

in facilitating di-π-methane reactivity has been discussed in detail by Zimmerman.[32] In these papers, it is stated that selectivity may result from the second step of the di-π-methane mechanism and that substitution on the methano carbon accelerates the reaction by odd-electron stabilization of the ring opening process. Where benzonorbornadienes are concerned, the high quantum yield efficiencies observed in many cases suggest that the initial migration dictates regioselectivity and that energy-wasting return to starting material does not operate. Accordingly, it is possible that a different stage of the di-π-methane rearrangement is being probed in each case.

We find it imperative to note that Zimmerman recognized early that the various di-π-methane intermediate structures are "approximations of species along the reaction coordinate and are not necessarily intermediates (i.e., energy minima)."[10d] The popular view of the Zimmerman mechanism (path 1) oversimplifies and misconstrues this original statement. The full range of our studies in the benzonorbornadiene area reveals that a partially bridged *transition state* more satisfactorily accounts for the appreciable levels of regioselectivity. For this reason, path 2 must be accorded due consideration as an equally probable and perhaps more likely mechanistic rationalization in many di-π-methane processes.

Conclusion

In light of the above, it is clear that as aryl migration begins, the triplet benzonorbornadiene system does not require a covalently bridged intermediate as much as it demands completion of the 1,2-phenyl shift. Indeed, the key facet of regioselectivity control is heavily localized in the competitive formation of the two partially bonded intermediates and how effectively one or the other of their associated hypersurfaces can cut across those of the various geometric forms that eventually lead to product. This is not to say that fully bridged species are precluded as intermediates.[10,11] Rather, they are hardly mandatory resting points along the photoisomerization trajectory. A more detailed appreciation of the triplet potential surfaces of the various benzonorbornadienes would, of course, greatly facilitate our full understanding of these di-π-methane processes. In the interim, our earlier suggested methods for predicting rebonding preferences in these and related dual-channeled systems[4,5] are quite serviceable.

Experimental Section

6-Methoxybenzonorbornadiene-1-carboxaldehyde (2). A magnetically stirred slurry of lithium aluminum hydride (31.2 mg, 0.832 mmol) in anhydrous ether (5 mL) was added dropwise to a solution of ester **1** (191.3 mg, 0.832 mmol) in the same solvent (2 mL) at room temperature under argon. After 20 min, ethyl acetate (2 mL) was slowly introduced, followed by water (5 mL). The suspension was filtered through Celite, and the solids were extracted thoroughly with ether. The combined filtrates were washed with water, dried, and evaporated. The resulting colorless oil (158.3 mg, 94.2%) consisted of a mixture of the desired alcohol (75%) and its dihydro derivative (25%). The mixture was oxidized directly. A small sample of purified major product exhibited the following spectral properties: IR (film, cm^{-1}) 3600–3375, 2955, 2885; ^1H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, J = 7.9 Hz, 1 H), 6.87 (d, J = 2.2 Hz, 1 H), 6.80 (m, 1 H), 6.60 (dd, J = 5.3 Hz, 1 H), 6.43 (dd, J = 7.9, 2.2 Hz, 1 H), 4.31 (s, 2 H), 3.85 (br s, 1 H), 3.75 (s, 3 H), 2.33 (d, J = 6.8 Hz, 1 H), 2.18 (d, J = 6.8 Hz, 1 H), 1.9 (br, 1 H); MS, m/z calcd (M^+) 202.0993, obsd 202.1021.

A solution of the alcohol mixture (158.3 mg, 0.784 mmol) in dichloromethane (5 mL was treated with pyridinium chlorochromate (338 mg, 1.568 mmol), and the slurry was stirred at ambient temperature for 3 h under argon. Ether (100 mL) was introduced, and the supernatant solution was filtered through a pad of silica gel. Solvent evaporation afforded the mixture of aldehydes (138 mg, 88%) which proved prone to polymerization on standing at room temperature. Spinning plate chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) gave the purified 3:1 mixture of **2** and its dihydro derivative as a colorless oil (100 mg, 63.8%). For **2**: IR (film, cm^{-1}) 2980, 2870, 1720; ^1H NMR (300 MHz, $CDCl_3$) δ 10.26 (s, 1 H), 7.19 J = 7.9 Hz, 1 H), 6.88 (m, 3 H), 6.47 (dd, J = 7.9, 2.3 Hz, 1 H), 3.97 (br s, 1 H), 3.77 (s, 3 H), 2.55 (s, 2 H); MS, m/z calcd (M^+) 200.0837, obsd 200.0832.

6-Methoxy-1-methylbenzonorbornadiene (3). A mixture of aldehyde **2** (75% purity, 100 mg, 0.5 mmol), hydrazine hydrate (51.2 mg, 1.02 mmol), potassium carbonate (56.3 mg, 0.41 mmol), and diethylene glycol (51.2 mg, 0.48 mmol) was heated under reflux at 130 °C in an atmosphere of argon for 2 h. The reflux condenser was replaced with a short path distillation head, and the volatile liquids were allowed to distil during 1 h. After cooling, the glassware and residue were washed with a mixture of ether and water. The combined washings were placed in a separatory funnel and well shaken. The aqueous layer was removed, and the ethereal phase was washed with 10% hydrochloric acid and water, dried, and evaporated. The brown oil (83 mg) was initially purified by spinning plate chromatography on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 60 mg of a colorless oil consisting of **3** and its dihydro derivative in an approximate ratio of 2:1. Pure **3** was separated by preparative TLC on silica gel impregnated with 6% silver nitrate (same eluant as above). The desired hydrocarbon (25 mg, 27%) was obtained as a colorless oil: IR (film, cm^{-1}) 2990, 2960; ^1H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, J = 7.8 Hz, 1 H), 6.86 (d, J = 2.3 Hz, 1 H), 6.75 (m, 1 H), 6.49 (d, J = 5.5 Hz, 1 H), 6.46 (dd, J = 8.0, 2.5 Hz, 1 H), 3.78 (s, 4 H), 2.27 (dd, J = 6.9, 2.3 Hz, 1 H), 2.12 (d, J = 6.8 Hz, 1 H), 1.66 (s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 156.91, 154.88, 147.31, 145.97, 143.11, 119.43, 110.08, 107.02, 74.68, 55.46, 50.09, 29.64, 14.97; MS, m/z calcd (M^+) 186.1045, obsd 186.1063.

6-Methoxybenzonorbornadiene-1-carboxylic Acid (4). A solution of **1** (580 mg, 2.52 mmol) in ethanol (6 Ml) was treated with potassium hydroxide (750 mg, 13.4 mmol) and heated at the reflux temperature under argon for 8 h. The cooled reaction mixture was evaporated to leave a yellowish solid that was dissolved in water. Following extraction with ether (3×), the aqueous layer was acidified with concentrated hydrochloric acid, and the precipitated solid was taken up in ether. The combined organic phases were washed with water, dried, and evaporated to give 529 mg (97%) of **4** as a colorless solid, mp 141–142 °C (from ether): IR ($CHCl_3$, cm^{-1}) 1710; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 1 H), 6.90 (dd, J = 5.1, 2.3 Hz, 2 H), 6.83 (dd, J = 5.3, 3.1 Hz, 1 H), 6.49 (dd, J = 8.1, 2.4 Hz, 1 H), 3.94 (d, J = 1.7 Hz, 1 H), 3.78 (s, 3 H), 2.65 (dd, J = 7.1, 1.6 Hz, 1 H), 2.57 (d, J = 6.9 Hz, 1 H); MS, m/z calcd (M^+) 216.0787, obsd 216.0783.

6-Methoxybenzonorbornadiene-1-carboxamide (5). A solution of acid **4** (390 mg, 1.8 mmol) in dry dichloromethane (6 mL) was treated with thionyl chloride (0.5 mL, 6.95 mmol) and heated at reflux for 6 h. After cooling, the volatile components were removed in vacuo to leave the acid chloride as a yellow oil (418 mg, 99%). This material was dissolved in dry dichloromethane (15 mL) and slowly added under nitrogen to liquid ammonia (15 mL, distilled from sodium) at −78 °C during a period of 10 min. The solution was stirred at this temperature for 9 h and allowed to warm slowly to room temperature overnight as the excess ammonia evaporated. The reaction mixture was washed sequentially with water, 10% hydrochloric acid, saturated sodium bicarbonate solution, and finally water. Following drying and solvent evaporation, the residue was triturated with ether to give **5** as a colorless solid (375 mg, 98%), mp 128.5–130 °C (from ether): IR ($CHCl_3$, cm^{-1}) 3550, 3510, 3440, 3030, 1680, 1595; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.0 Hz, 1 H), 6.89 (dd, J = 4.9, 2.9 Hz, 2 H), 6.79 (dd, J = 3.1, 2.1 Hz, 1 H), 6.63 (br, 1 H), 6.45 (dd, J = 8.0, 2.4 Hz, 1 H), 5.91 (br, 1 H), 3.92 (br s, 1 H), 3.75 (s, 3 H), 2.55 (dd, J = 5.3, 1.3 Hz, 1 H), 2.45 (d, J = 6.6 Hz, 1 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 173.89, 157.60, 153.26, 142.16, 142.14, 141.43, 121.57, 110.58, 107.71, 72.13, 55.52, 50.41; MS, m/z calcd (M^+) 215.0947, obsd 215.0941. Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09. Found: C, 72.72; H, 6.11.

6-Methoxybenzonorbornadiene-1-carbonitrile (6). A solution of (trimethylsilyl)polyphosphate was prepared by refluxing 2 g of phosphorus pentoxide and 5 mL of hexamethyldisiloxane in dichloromethane (10 mL) for 1 h. The cooled solution was filtered to remove undissolved materials.

A mixture of amide **5** (134 mg, 0.332 mmol) and the (trimethylsilyl)polyphosphate solution prepared above (5.5 mL) in dichloromethane (2 mL) was heated at the reflux temperature for 6 h, cooled to room temperature, and diluted with dichloromethane and water. The organic phase was separated, and the aqueous layer was extracted with dichloromethane. The combined dichloromethane solutions were dried and concentrated to leave a colorless oil. Pure **6** was obtained by spinning plate chromatography on silica gel (elution with 2.5% ethyl acetate in petroleum ether), 112 mg (91%): IR (film, cm^{-1}) 2940, 2230; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 1 H), 6.88 (d, J = 2.3 Hz, 1 H), 6.84 (dd, J = 5.2, 3.3 Hz, 1 H), 6.74 (d, J = 2.3 Hz, 1 H), 6.51 (dd, J = 8.0, 2.4 Hz, 1 H), 3.92 (br d, J = 1.4 Hz, 1 H), 3.77 (s, 3 H), 2.72 (dd, J = 6.9, 1.6 Hz, 1 H), 2.58 (d, J = 6.7 Hz, 1 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 158.29, 150.31, 143.42, 141.00, 138.55, 121.06,

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119.57, 111.05, 108.10, 73.55, 55.62, 49.82, 48.89; MS, m/z calcd (M^+) 197.0840, obsd 197.0845.

1-Acetyl-6-methoxybenzonorbornadiene (7). A cold (0 °C), magnetically stirred solution of **4** (500 mg, 2.31 mmol) in dry ether (30 mL) was treated under nitrogen with methyllithium (4.0 mL of 1.6 M in ether, 6.4 mmol). The reaction mixture was stirred at 0 °C for 6 h, poured into ice water, and extracted with ether (3×). The combined organic layers were washed with water, dried, and evaporated. The residue was subjected to spinning plate chromatography on silica gel (elution with 2.5% ethyl acetate in petroleum ether). There was isolated 395 mg (80%) of ketone **7**, a colorless solid, mp 44–45 °C (from petroleum ether), and 32 mg (6%) of tertiary alcohol **8**.

For **7**: IR (film, cm^{-1}) 2940, 1705; ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 1 H), 6.91 (m, 2 H), 6.80 (dd, J = 5.2, 3.3 Hz, 1 H), 6.45 (dd, J = 8.0, 2.4 Hz, 1 H), 3.93 (br d, J = 1.4 Hz, 1 H), 3.76 (s, 3 H), 2.54 (d, J = 1.6 Hz, 2 H), 2.37 (s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 207.39, 157.47, 153.37, 143.20, 141.40, 121.44, 110.62, 107.55, 71.20, 55.45, 50.20, 28.22; MS, m/z calcd (M^+) 214.0994, obsd 214.0956. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.36; H, 6.66.

6-Methoxybenzonorbornadienyl-1-dimethylcarbinol (8). A solution of **7** (202 mg, 0.933 mmol) in ether (10 mL) cooled to −78 °C under nitrogen was treated with methyllithium (1.2 mL of 1.2 M in ether, 1.44 mmol). The reaction mixture was stirred at this temperature for 4 h, allowed to warm to 25 °C during 1 h, and quenched by the cautious addition of water (30 mL). The aqueous phase was extracted with ether (2 × 15 mL), and the combined organic layers were washed with water, dried, and concentrated. Purification was achieved by spinning plate chromatography on silica gel (elution with 15% ethyl acetate in petroleum ether) to give 174 mg (80%) of **8** as a colorless oil in addition to 31 mg of recovered starting material.

For **8**: IR (film, cm^{-1}) 3470, 2980, 2940; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 1 H), 6.86 (d, J = 2.4 Hz, 1 H), 6.81 (m, 2 H), 6.44 (dd, J = 8.0, 2.4 Hz, 1 H), 3.81 (d, J = 2.4 Hz, 1 H), 3.79 (s, 3 H), 2.29 (dd, J = 6.9, 1.6 Hz, 1 H), 2.22 (dd, J = 6.9, 1.0 Hz, 1 H), 1.76 nbr s, 1 H), 1.52 (s, 3 H), 1.49 (s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 156.70, 155.83, 144.00, 141.94, 123.03, 110.01, 107.60, 71.47, 69.89, 68.46, 55.40, 49.60, 28.22, 27.51; MS, m/z calcd (M^+) 230.1307, obsd 230.1309.

1-Acetamido-6-methoxybenzonorbornadiene (9). A mixture of ketone **7** (30 mg, 1.82 mmol), hydroxylamine hydrochloride (63 mg, 0.91 mmol), and anhydrous sodium acetate (149 mg, 1.82 mmol) in methanol (6 mL) was stirred under nitrogen at room temperature overnight. Water was added, the product was extracted into ether (2×), and the combined ether layers were washed with water, saturated sodium bicarbonate solution, and again with water. Drying and solvent evaporation left the oxime as a colorless solid (42 mg, 100%), mp 144–146 °C (from ether): IR ($CHCl_3$, cm^{-1}) 3300, 3010, 2940; MS, m/z calcd (M^+) 229.1103, obsd 229.1101.

A solution of the oxime (208 mg, 0.91 mmol) and p-toluenesulfonyl chloride (348 mg, 1.82 mmol) in dry pyridine (4 mL) was stirred under a nitrogen atmosphere for 4 days at room temperature. The reaction mixture was diluted with brine (50 mL) and extracted twice with ether. The combined ether phases were washed successively with water, 10% hydrochloric acid (2×), water, saturated sodium bicarbonate solution (2×), and water (2×). After drying and concentration, the oxime tosylate was obtained as a viscous yellow oil (312 mg, 89%): IR ($CHCl_3$, cm^{-1}) 3000, 2940, 1595, 1465, 1370; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 2 H), 7.33 (d, J = 8.0 Hz, 2 H), 6.84 (m, 4 H), 6.38 (dd, J = 8.0, 2.3 Hz, 1 H), 3.87 (d, J = 1.4 Hz, 1 H), 3.75 (s, 3 H), 2.45 (s, 3 H), 2.40 (s, 2 H), 2.15 (s, 3 H); MS, m/z calcd (M^+) 383.1191, obsd 383.1201.

A mixture of the oxime tosylate (401 mg, 1.05 mmol) and triethylamine (106 mg, 1.05 mmol) in 80% aqueous ethanol (20 mL) was heated at the reflux temperature for 24 h, diluted with brine (100 mL), and extracted with dichloromethane (5 × 20 mL). The combined organic layers were washed with water, dried, and concentrated to leave a residue that was purified by spinning plate chromatography (silica gel; elution with ether). There was isolated 182 mg (76%) of **9** as an off-white solid, mp 122–125 °C (from ether): IR ($CHCl_3$, cm^{-1}) 3440, 3000, 1675; ^1H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, J = 8.0 Hz, 1 H), 6.82 (dd, J = 7.0, 2.4 Hz, 2 H), 6.60 (dd, J = 5.3, 3.4 Hz, 1 H), 6.43 (dd, J = 8.0, 2.3 Hz, 1 H), 3.77 (br d, J = 1.7 Hz, 1 H), 3.74 (s, 3 H), 2.69 (dd, J = 6.4, 1.6 Hz, 1 H), 2.44 (d, J = 6.4 Hz, 1 H), 2.1 (s, 3 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 170.38, 157.47, 152.30, 143.67, 141.18, 119.66, 110.33, 107.58, 73.02, 71.55, 55.52, 47.92, 23.71; MS m/z calcd (M^+) 229.1103, obsd 229.1093.

Photoisomerization of 1. A solution of ester **1** (55 mg, 0.24 mmol) and acetophenone (ca. 0.05 mL) in benzene (50 mL) was deoxygenated with a gentle stream of nitrogen for 15 min. The mixture was irradiated at 350 nm in a Rayonet reactor for 1 h at ambient temperature under nitrogen. The solvent was removed in vacuo, and the product was purified by spinning plate chromatography on silica gel (elution with 5% ethyl acetate in petroleum ether). There was isolated 45 mg (82%) of **10**-$COOCH_3$: IR (film, cm^{-1}) 2950, 1720; ^1H NMR (see Table I); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 172.40, 158.56, 150.69, 132.54, 124.12, 110.56, 107.55, 55.51, 52.99, 51.62, 40.96, 37.79, 30.36, 28.94; MS, m/z calcd (M^+) 230.0943, obsd 230.0979.

Photoisomerization of 3. A solution of methyl derivative **3** (19.7 mg, 0.196 mmol) and acetophenone (2.6 mg) in benzene (16 mL) was irradiated as above for 65 min. The solvent was evaporated, and the product composition was assayed by ^1H NMR integration of the methyl signals at δ 1.50 and 1.41. Purification by spinning plate chromatography on silica gel did not result in their separation (7.5 mg, 38%). The spectral analyses were therefore carried out on the mixture. For **10**-CH_3: ^1H NMR (see Table I). For **11**-CH_3: ^1H NMR (see Table II); MS, m/z calcd (M^+) 186.1045, obsd 186.1053.

Photoisomerization of 5. A solution of amide **5** (40.3 mg) and acetophenone (ca. 0.05 mL) in benzene (35 mL) was irradiated in the predescribed manner for 75 min. The products from two identical runs were combined, leached with pentane, dissolved in dichloromethane, filtered, and concentrated. After being maintained in a high vacuum overnight, the sample was isolated as a colorless crystalline solid (80.7 mg, 100%) and identified as **10**-$CONH_2$, mp 201–203 °C dec (from ether): IR ($CHCl_3$ cm^{-1}) 3530, 3410, 3000, 1665, 1585; ^1H NMR (see Table I); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 169.54, 160.12, 152.45, 135.01, 124.55, 111.20, 103.13, 55.62, 51.98, 41.18, 37.03 (2 C's not observed); MS, m/z calcd (M^+) 215.0946, obsd 215.0953. Anal. Calcd for $C_{13}H_{14}NO_2$: C, 72.54; H, 6.09. Found: C, 72.65; H, 5.89.

Photoisomerization of 6. A solution of nitrile **6** (110 mg) and acetophenone (ca. 0.10 mL) in benzene (70 mL) was divided into 2 portions, and each was irradiated as outlined above for 80 min. Purification by spinning plate chromatography on silica gel (elution with 2.5% ethyl acetate in petroleum ether) afforded **10**-CN as a colorless solid (110 mg, 100%), mp 87–88 °C (from ether): IR ($CHCl_3$, cm^{-1}) 3020, 2940, 2220; ^1H NMR (see Table I); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 159.16, 149.27, 130.24, 124.72, 120.29, 111.27, 107.55, 55.45, 50.09, 41.67, 36.97, 31.55, 12.42; MS, m/z calcd (M^+) 197.0841, obsd 197.0847. Anal. Calcd for $C_{13}H_{11}NO$: C, 79.17; H, 5.62. Found: C, 79.23; H, 5.59.

Photoisomerization of 7. A solution of ketone **7** (47 mg) and acetophenone (ca. 0.05 mL) in benzene (40 mL) was irradiated as previously indicated for 60 min. The product, which was purified by spinning plate chromatography on silica gel (elution with 13% ethyl acetate in petroleum ether), exhibited a pronounced tendency for decomposition: IR (film, cm^{-1}) 2930, 1675; ^1H NMR (see Table I); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 206.09, 158.56, 151.02, 132.50, 124.06, 110.65, 107.58, 55.52, 54.88, 40.70, 39.93, 37.76, 30.86, 26.52; MS, m/z calcd (M^+) 214.0994, obsd 214.1000.

Photoisomerization of 8. A solution of alcohol **8** (174 mg) and acetophenone (ca. 0.10 mL) in benzene (70 mL) was divided into 2 equal portions, and each was irradiated as before for 75 min. After evaporation, the products were analyzed by ^1H NMR. The samples were combined and subjected to spinning plate chromatography on silica gel (elution with 15% ethyl acetate in petroleum ether). There was isolated 75 mg (43%) of **10**-$C(CH_3)_2OH$ and 30 mg (17%) of **11**-$C(CH_3)_2OH$, each as colorless viscous oils. Photoisomer **10**-$C(CH_3)_2OH$ was found to be unstable in $CDCl_3$ solution or on standing at room temperature.

For minor photoproduct **11**-$C(CH_3)_2OH$: IR (film, cm^{-1}) 3460, 2960, 2930; ^1H NMR (see Table II); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 158.45, 145.88, 139.92, 121.00, 110.07, 109.47, 71.58, 62.23, 55.45, 45.45, 30.03, 29.10, 26.91, 25.93, 17.45; MS m/z calcd (M^+) 230.1307, obsd 230.1307.

For major photoproduct **10**-$C(CH_3)_2OH$: IR (film, cm^{-1}) 3600–3200, 2900; ^1H NMR (see Table I); MS, m/z calcd (M^+) 230.1307, obsd 230.1299.

Photoisomerization of 9. A solution of acetamide **9** (182 mg) and acetophenone (ca. 0.10 mL) in benzene (70 mL) was divided into 2 equal portions, and each was irradiated as predescribed for 100 min. Following solvent removal, the samples were analyzed by ^1H NMR, then combined, and purified by spinning plate chromatography on silica gel (elution with 50% ethyl acetate in petroleum ether). Since the two photoisomers coeluted, characterization was performed on the mixture: IR ($CHCl_3$, cm^{-1}) 3440, 3400, 3300, 3000, 1675; ^1H NMR (see Tables I and II); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 171.14, 158.24, 151.35, 141.23, 134.07, 123.57, 118.16, 110.34, 110.23, 110.00, 108.10, 107.77, 55.56, 52.39, 52.17, 49.71, 40.31, 39.87, 38.67, 38.01, 36.31, 35.82, 35.39, 34.79, 28.83, 23.52, 21.34, 18.27; MS, m/z calcd (M^+) 215.0946, obsd 215.0953.

Photoisomerization of 16. 2-(Trimethylsilyl)benzonorbornadiene was prepared by the method of Ford[33] and separated from two concomitantly

formed positional isomers by chromatography on 2% silver nitrate impregnated silica gel. This purification afforded **16** in >98% purity. Material prepared in this fashion was employed for the quantum yield studies. Alternatively, **16** was prepared by adding a pentane solution of 2-bromobenzonorbornadiene[33] (0.50 g, 2.26 mmol) slowly to cold (−78 °C), magnetically stirred pentane solution (15 mL) of *tert*-butyllithium (3.0 mL, 4.75 mmol) under nitrogen. Anhydrous tetrahydrofuran (0.3 mL) was introduced, the reaction mixture was stirred at −78 °C for 15 min, and chlorotrimethylsilane (0.72 mL, 5.6 mmol) was added via syringe. The contents were alloed to warm slowly to room temperature, water was added, and the product was extracted into pentane. Purification by MPLC on silica gel (petroleum ether elution) afforded 470 mg (96%) of **16**; IR (neat, cm^{-1}) 3070, 3045, 2965, 1555, 1455, 1270, 1250, 1025, 920, 895, 865, 845, 750; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (m, 2 H), 6.99 (d, J = 2.9 Hz, 1 H), 6.90 (m, 2 H), 3.98 (s, 1 H), 3.92 (s, 1 H), 2.18 (t, J = 1.5 Hz, 2 H), 0.05 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 155.5, 152.2, 151.9, 151.2, 124.1, 123.9, 121.3, 69.4, 53.3, −1.9.

A benzene solution (2 mL) of **16** (190 mg) and acetophenone (50 μL) was transferred to an NMR tube, purged gently with nitrogen for 15 min, and photolyzed in a Rayonet reactor fitted with 3500-Å lamps. Monitoring of the progress of reaction by ^1H NMR showed **16** to be completely consumed after 8 h. Capillary VPC analysis showed only one product to be formed. Purification of this photoproduct by MPLC on silica gel gave 190 mg (100%) of **26b**: IR (neat, cm^{-1}) 3015, 2955, 2920, 2860, 1470, 1250, 1205, 1160, 1110, 1100, 1060, 985, 905, 895, 870, 845, 755, 680; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 7.2 Hz, 1 H), 7.12 (t, J = 7.2 Hz, 1 H), 7.00 (m, 2 H), 3.18 (dd, J = 2.1, 7.6 Hz, 1 H), 2.75 (td, J = 8.3, 3.3 Hz, 1 H), 2.47 (d, J = 5.0 Hz, 1 H), 1.92 (m, 1 H), 0.95 (d, J = 0.9 Hz, 1 H), 0.00 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 149.3, 142.5, 125.6, 124.6, 122.6, 119.8, 47.5, 44.2, 34.2, 29.2, 22.6, −2.6; MS, m/z calcd (M^+) 214.1178, obsd 214.1202.

Benzonorbornadiene-d_2 (33).[34] A 50-mL Schlenk flask containing a magnetic stirring bar was flame-dried in a stream of argon and charged with 884 mg (4 mmol) of 2-bromobenzonorbornadiene[35] and 10 mL of dry tetrahydrofuran after the flask had returned to room temperature. After being cooled to −78 °C, this solution was treated via syringe with 7 mL of *tert*-butyllithium in pentane (8 mmol). The reaction mixture was stirred for 15 min at this temperature and quenched by the addition of 2 mL of methanol-d_1. The cooling bath was removed, and following return to 20 °C the reaction mixture was diluted with water and extracted with pentane. The combined organic layers were dried and evaporated. The product was purified by preparative gas chromatography (15 ft × 0.25 in. 10% SE-30 on Chromosorb P, 200 °C) to give 463 mg (81%) of **33**. The level of deuterium incorporation was 94% (^1H NMR analysis).

Photoisomerization of 33. A 96-mg (0.67 mmol) sample of **33** in 300 μL of freshly distilled (from CaH_2) benzene was partitioned between two medium wall NMR tubes each containing 36 μL of acetophenone. Both solutions were degassed by 4 freeze–thaw cycles and irradiated in a Rayonet reactor equipped with a bank of 3500-Å lamps. The progress of the photoisomerization was monitored by ^1H NMR. After 3 h, the disappearance of the bridgehead protons in **33** at δ 3.3 was complete.

After recording of the ^2H NMR spectra,[36] the photoisomers were subjected to MPLC purification on silica gel to remove the acetophenone. There was isolated 96 mg of the **36**/**37** mixture.

Quantum Yield Studies. A. Materials. Commercial reagent grade benzene was washed with sulfuric acid, water, and sodium bicarbonate solution prior to fractional distillation from calcium hydride. Analytical reagent acetophenone (Mallinckrodt) and gold label decane (Aldrich) were redistilled at reduced pressure. The various benzonorbornadienes were prepared as previously described. Benzonorbornadiene was purified by spinning band distillation. The 6-cyano derivative was purified by chromatography and subsequent sublimation. The remaining substrates were subjected to preparative HPLC and finally distilled under reduced pressure in a Kugelrohr apparatus. Their purity in all cases was established by capillary GC analysis.

B. Preparation of Solutions. A stock sensitizer solution was prepared by dissolving 12.01 g of acetophenone in 1.00 L of benzene. Stock solutions of the benzonorbornadienes were prepared by transferring a known amount of each substrate and an appropriate amount of decane (internal standard) into a volumetric flask and diluting to the mark with the stock sensitizer solution. Appropriate concentrations could subsequently be arrived at by successive dilution as desired.

C. Actinometry. The photoreactor consisted of a 1000-W high-pressure mercury–xenon arc lamp. The light was passed through a 1.0 M aqueous cupric sulfate solution[37a] and subsequently through an Oriel 366-nm narrow band interference filter. The photolysis cell consisted of a dual-chambered cylindrical Pyrex vessel 10.0 cm in length and 1.5 cm in diameter. Both halves were equipped with short narrow necks at the top for the introduction of solutions. During use, the vessel was wrapped with black tape over all of its surface except, of course, for the ends through which the incident light was passed.

Lamp intensities were determined by ferric oxalate actinometry.[37b,c]

D. Photolysis Experiments. The actinometer solution (12.00 mL of known absorbance) was pipetted into the ear compartment of the cell, and 12.00 mL of the benzonorbornadiene/acetophenone/decane solution was transferred into the front compartment where it was capped with a rubber septum, purged with nitrogen for 15 min, analyzed by capillary gas chromatography, and immediately photolyzed for ca 1000 s while being thoroughly stirred with a miniature magnetic stirring bar. Subsequently, the front cell was analyzed by capillary GC to assess the percent photoisomerization, while an absorbance measurement was made of the actinometer solution in the rear cell. The front cell absorbed ca. 95% of the incident light.

E. Quantum Yield Calculations. The gas chromatographic analyses were performed on a Carlo Erba HRGC 4160 gas chromatograph fitted with FID detectors and J&W Durabond fused silica gel capillary column (30 m × 0.32 mm) and interfaced with a Hewlett-Packard 3392A recording integrator. The GC analyses assume that the benzonorbornadienes and their photoisomers have equal sensitivity to FID detection. However, a 100% mass balance was not assumed. Therefore, to determine the extent of product formation, the internal standard was utilized, and the response factor k was calculated from the proportionality relationships.

before photolysis

$$\frac{\text{area benzonorbornadiene}}{\text{area internal standard}} = k\frac{\text{mols benzonorbornadiene}}{\text{mols internal standard}}$$

after photolysis

$$\text{mols product} = \frac{1}{k} \times \frac{\text{area product}}{\text{area internal standard}} \times \text{mols internal standard}$$

The number of photons absorbed by the benzonorbornadiene/acetophenone/decane solution was ascertained by subtracting the number of photons entering the back cell from the total number of incident photons. Finally, the ratio of mmols of product formed to millieinsteins of light absorbed gives the quantum yield Φ.

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Registry No. 1, 42470-47-3; **1**-ol, 105040-08-2; **1**-ol (dihydro derivative), 105040-09-3; **2**, 105040-07-1; **2** (dihydro derivative), 105040-10-6; **3**, 105040-11-7; **3** (dihydro derivative), 105040-12-8; **4**, 105040-13-9; **4** (acid chloride), 105040-14-0; **5**, 105040-15-1; **6**, 105040-16-2; **7**, 105040-17-3; **7** (oxime), 105040-19-5; **7** (oxime tosylate), 105040-20-8; **8**, 105040-18-4; **9**, 105040-21-9; **10**-$COOCH_3$, 105040-22-0; **10**-CH_3, 105040-23-1; **10**-$CONH_2$, 105040-25-3; **10**-CN, 105040-26-4; **10**-$COCH_3$, 105040-27-5; **10**-$C(CH_3)_2OH$, 105040-28-6; **10**-$NHCOCH_3$, 105040-30-0; **11**-CH_3, 105040-24-2; **11**-$C(CH_3)_2OH$, 105040-29-7; **11**-$NHCOCH_3$, 105040-31-1; **12**, 4453-90-1; **13**, 31893-12-6; **14**, 31893-13-7; **15**, 31862-26-7; **16**, 31893-19-3; **17**, 71906-57-5; **18**, 5890-14-2; **19**, 16513-60-3; **20**, 4897-71-6; **21**, 23537-80-6; **22**, 4897-74-9; **23**, 23537-79-3; **24**, 91948-52-6; **25**, 91948-56-0; **26b**, 105040-32-2; **33**, 105040-33-3; **36**, 105040-34-4; **37**, 105040-35-5.

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