fore did not interfere with the analysis. A typical run consisted of eight to nine points plus an infinity sample.

Deuterium exchange reaction kinetics were run with 250–300 mL of substrate in 10 mL of alcoholic alkoxide solution. Aliquots (~ 1 cm^3) were syringed into a separatory funnel containing 50 mL of ca. 1 N aqueous HCl and 0.5 mL of CCl_4. The substrate was isolated from the CCl_4 by preparative gas chromatography and then submitted for mass spectral analysis. A typical run consisted of six to eight points plus an infinity sample.

Detritiation kinetics were run with 10–40 μL of substrate in 15 mL of alcoholic sodium alkoxide. Aliquots were taken by a 1-cm^3 glass Luer-lok syringe equipped with a 4.5-in. stainless steel needle. Nine points and an infinity sample was taken for each run. The same size sample (0.90–1.00 mL) was taken with a separate syringe for each point. The aliquot was syringed into a 125-mL separatory funnel (with a Teflon stopcock) that contained 50.0 mL of 0.2–0.3 N aqueous HCl and 15.0 mL of toluene. The funnel was shaken for a set time for each run (usually 30–60 s) and then allowed to sit for ca. 10 min prior to draining the lower water layer. The toluene layer was then poured into a 25-mL Erlenmeyer containing Drierite. After the solution dried, 10.0 mL of the toluene solution was added to a scintillation vial containing 10.0 mL of scintillation cocktail (4 g of PPO, 1 g of POPOP in 1.0 L of toluene). After dark adapting for 30–60 min, the samples were counted.

The results and calculated activation parameters are reported in Table I. The temperature range and number of total runs used for the calculations are also given. Normally we would measure rate constants at 10-deg intervals and a reported range of 50–80 °C with 4 runs would translate to single kinetic runs at 50, 60, 70, and 80 °C. Occasionally a kinetic run would be off the Arrhenius plot and was therefore not included in the calculations.

Acknowledgment. We are grateful to the donors of Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for a Cottrell College Science Grant for support of this research. We thank Jerry Kresge and William Tumas for helpful suggestions and discussions, and J. van Thuijl, W. C. M. M. Luyten, and J. J. van Houte for the mass spectral data used to calculate the hydrogen and deuterium exchange rates.

Registry No. D_2, 7782-39-0; H_2, 1333-74-0; T_2, 10028-17-8; EtOD, 925-93-9; MeOD, 1455-13-6; $C_6H_5CHClCF_3$, 384-65-6; $C_6H_5CH(CF)_2$, 3142-78-7.

Photolytic Cleavage of Remote Functional Groups in Polyfunctional Molecules. Photolysis of *exo*- and *endo*-2-Benzonorbornenyl Chlorides and Methanesulfonates[1a,b]

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Abstract: The photochemistry and photophysics of the title compounds are reported. The exo chloride exhibits a facile cleavage of the C–Cl bond upon excitation of the aryl chromophore (eq 1–3). The reaction has a rate >700-fold larger than that observed with the endo isomer, derives from the singlet excited state, and leads to the formation of "hot" carbocations as well as free radicals. The exo mesylate shows similar characteristics (eq 4). A mechanism (Scheme II) is suggested which incorporates both heterolytic fission as well as sequential homolytic fission (to a polarized radical pair), followed by electron transfer to form an ion pair. The stereoelectronically controlled activation of the C–Cl and C–OMs moieties is explained by a correlation diagram (Figure 5) which depicts the π,π^* state as correlating with the diradical product state through an avoided crossing with the C–X σ,σ^* state. Calculations indicate that this avoided crossing is considerably larger (and the barrier to reaction therefore considerably smaller) when the C–X unit in the 2-benzonorbornenyl series is exo.

Introduction

The photochemical and spectroscopic consequences of intramolecular interactions between nonconjugated functionalities remains a subject of considerable interest.[2] There is now ample evidence that only by a systematic investigation of model bifunctional substrates can the organic photochemist expect to understand and utilize the diverse chemistry to be found in complex multifunctional compounds. Toward these ends we have earlier presented a preliminary report[3] on an unusual, stereoelectronically controlled, photolytic cleavage of the chloro and methanesulfonyl (mesyl) groups in the benzonorbornenyl series. In this paper, we summarize our detailed studies on these interesting examples of the photoactivation of remote functional groups.

Results

A. Photochemistry and Spectroscopy of *exo*-2-Benzonorbornenyl Chloride (exoClBNB). Photochemistry of exoClBNB in Cyclohexane. The title compound was prepared by hydrochlorination of benzonorbornadiene.[4] Irradiation of a 0.02 M solution in cyclohexane at 254 nm produces HCl and two volatile photoproducts which have been identified as benzonorbornene (**1**) and bicyclohexyl (**2**) by comparison of spectra with authentic samples.[5] Quantum efficiencies were determined in low conversion runs and are given in eq 1.[6]

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[1] (a) Organic Photochemistry. 54. Part 53: Morrison, H.; Giacherio, D.; Pandey, G. *Tetrahedron Lett.* **1982**, 3437. Part 52: Morrison, H.; Miller, A.; Pandey, B.; Pandey, G.; Severance, D.; Strommen, R.; Bigot, B. *Pure Appl. Chem.* **1982**, *54*, 1723. Part 51: Morrison, H.; Giacherio, D. *J. Org. Chem.* **1982**, *47*, 1058. (b) Abstracted, in part, from the Doctoral Dissertation of A. M., Purdue University, 1980. (c) Purdue University. (d) Universitē Pierre et Marie Curie.

[2] (a) For a review and leading references, see: Morrision, H. *Acc. Chem. Res.* **1979**, *12*, 383. (b) Additional examples include Lin, C-I; Singh, P.; Maddox, M., Ullman, E. F. *J. Am. Chem. Soc.* **1980**, *102*, 3261. Studebaker, J.; Srinivasan, R.; Ors, J. A.; Baum, T. *Ibid.* **1980**, *102*, 6872. McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L., Faggiani, R. *Ibid.* **1980**, *102*, 7782. Manning. T. D. R.; Kropp, P. J. *Ibid.* **1981**, *103*, 889. Calcaterra, L. T.; Schuster, D. I. *Ibid.* **1981**, *103*, 2460. Castellan, A.; Desvergne, J.-P.; Bouas-Laurent, H. *Chem. Phys. Lett.* **1980**, *76*, 390. Cristol, S. J.; Opitz, R. J.; Bindel, T. H. Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977.

[3] Morrison, H.; Miller, A. *J. Am. Chem. Soc.* **1980**, *102*, 372.

[4] Wilt, J. W.; Gutman, G.; Ranus, W. J., Jr.; Zigman, A. R. *J. Org. Chem.* **1967**, *32*, 893.

[5] Several high molecular weight products are also detectable, the principal two being tentatively assigned as *exo*- and *endo*-2-cyclohexylbenzonorbornene on the basis of ^{1}H NMR and mass spectral data.

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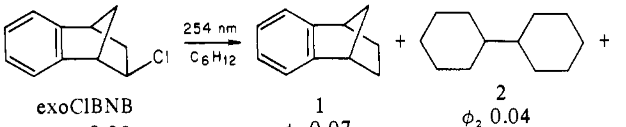


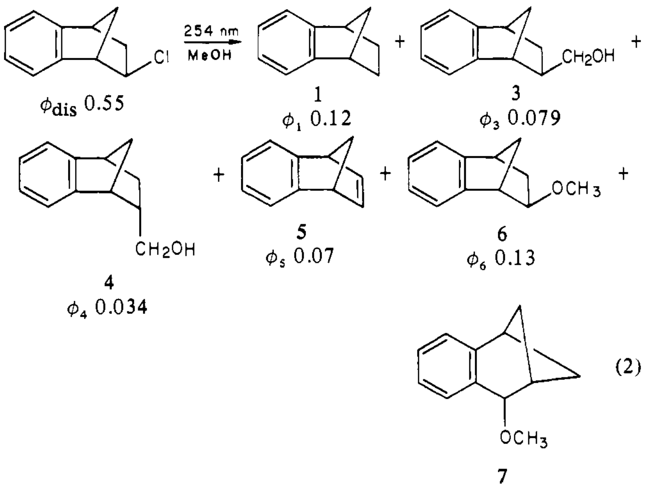
exoClBNB ϕ_{dis} 0.25 **1** ϕ_1 0.07 **2** ϕ_2 0.04 HCl (1)

ϕ_{HCl} 0.18

Photosensitization of exoClBNB in Cyclohexane. Photolysis of 0.015 M solutions of exoClBNB in cyclohexane with 3.3 M *p*-xylene at 254 nm results in only a trace of **2** and a 98% reduction in the formation of **1**. Since *p*-xylene[7] and exoClBNB[8] have triplet energies of about 80 kcal/mol, the efficiency of energy transfer in this experiment could be considered suspect; however, we have observed that triplet transfer from *p*-xylene to exoClBNB in methanol is relatively efficient (see below).

Xenon Perturbation Study of exoClBNB in Cyclohexane. The addition of xenon to freeze–pump–thaw degassed exoClBNB resulted in a 65% quenching of the formation of **1** and a 48% quenching of the formation of **2**.

Photochemistry of exoClBNB in Methanol. Irradiation of 0.02 M exoClBNB in methanol at 254 nm results in six primary photoproducts (in addition to HCl). The reaction and quantum efficiencies are given in eq 2.



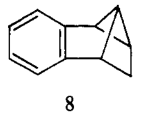
ϕ_{dis} 0.55 **1** ϕ_1 0.12 **3** ϕ_3 0.079

4 ϕ_4 0.034 **5** ϕ_5 0.07 **6** ϕ_6 0.13

(2)

7 ϕ_7 0.027

Products **4** (*endo*-benzonorbornen-2-ylmethanol) and **5** (benzonorbornadiene) are known compounds and were identified by spectal comparison with authentic samples. Product **3** (*exo*-benzonorbornen-2-ylmethanol) was identified by its spectral data (cf. Experimental Section) and by conversion into the known *exo*-benzonorbornen-2-ylcarboxylic acid.[9] The ethers **6** (*exo*-benzonorbornen-2-yl methyl ether) and **7** (1,3-methanonaphthalen-4-yl methyl ether) were identified by their spectral data (cf. Experimental Section). An additional photoproduct begins to appear at very low conversions (~4% disappearance of exoClBNB) and has been identified (VPC retention time vs. an independently synthesized sample) as **8** (tetracyclo-



8

$[5.4.0.0^{2,4}.0^{3,6}]$undeca-1(7),8,10-triene). This is the di-π-methane, triplet-sensitized, rearrangement product of **5** (known not to be formed by direct photolysis of **5**[10]). The ratio of **5** and **8** varies inversely with irradiation time and **8** is assigned as a secondary photoproduct.[11]

Table I. Effect of (*E*)-2-Heptene on the exoClBNB/MeOH Photoreaction[a]

	1	3	4	5	8	(5 + 8)	6	7
% change in ϕ	+21	−32	−32	+71	−63	0	−8	−7

[a] 0.1 *m* (*E*)-2-heptene.

Table II. Effect of PrSH on the exoClBNB/MeOH Photoreaction

[PrSH] (*m*)	% change in ϕ						
	1	3	4	5	8	6	7
0.04	+92	−86	−100	−100	−100	−23	−31
0.12	+75	−88	−100	−100	−100	−23	−38

Table III. Effect of Oxygen on the exoClBNB/MeOH Photoreaction

	1	3	4	5	8	(5 + 8)	6	7
% change in ϕ	−100	−86	−90	−33	−71	−49	−36	−33

Photolysis of ExoClBNB in the presence of *exo*-norborn-2-yl chloride at 254 nm in methanol, to 90% loss of the aryl chloride, gave no loss of the aliphatic substrate (nor, in fact, did the direct irradiation of a methanolic solution of norbornyl chloride with 254-nm light).

Photosensitization of exoClBNB in Methanol. A photolysis of 0.015 M exoClBNB in methanol with 3.3 M *p*-xylene (the latter absorbing all the incident light) was conducted simultaneously with a direct photolysis of the halide. Product formation was normalized to the formation of **1** by direct excitation; the data are presented as the ratios for direct vs. sensitized photolysis: **1**, 1.00:0.13; **3**, 0.55:trace; **4**, 0.26:trace; **5**, 0.38:trace; **6**, 2.01:1.16; **7**, 0.11:trace.

Photolysis of 0.02 M exoClBNB in 10% (by volume) of acetone in methanol with 300-nm light resulted in a 72% loss of the starting material and the following products: **1**, 1.9%; **3**, trace; **4**, trace; **5**, 12.6%; **6**, 57%; **7**, not detected.

It may be noted that neither aryl (i.e., toluene) nor acetone sensitization leads to fragmentation of *exo*-norborn-2-yl chloride.

Effect of (*E*)-2-Heptene on exoClBNB Photochemistry in Methanol. Irradiation of 0.018 M exoClBNB in methanol with 0.1 M (*E*)-2-heptene at 254 nm gave the results shown in Table I. The principal observations are the following. (1) There is an increase in **1** ($\Delta\phi$ = +0.025) which approximates the total diminution in **3** and **4** ($\Delta\phi$ = −0.036). We presume this is due to hydrogen abstraction from the heptene by the benzonorbornenyl radical before the latter can couple with hydroxymethylene radicals.[12] (2) The di-π-methane reaction (**5** → **8**) is quenched, but there is no change in the sum of **5** + **8**.[13] (3) Ether formation is not much affected by the heptene, and, in fact, there is little net quenching; i.e., the sum of **1**, **3**, and **4** decreases by 5% and that of the ethers by ~8%.

Effect of *n*-Propyl Mercaptan on exoClBNB Photochemistry in Methanol. Irradiation of 0.022 M exoClBNB in methanol at

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(6) The ϕ_{HCl} was determined in *n*-hexane. A previously reported[3] value for ϕ_1 represented an average of data obtained in cyclohexne and *n*-hexane.

(7) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(8) Estimated from the onset of the 0–0 band in the phosphorescence emission spectrum at 77 K (1:1 pentane/cyclopentane glass).

(9) We are grateful to Professor J. W. Wilt for a sample of this acid.

(10) Edman, J. R. *J. Am. Chem. Soc.* **1969**, *91*, 7103.

(11) The ϕ's given in eq 2 were measured at 9% loss of exoClBNB, whence over 50% of **5** has rearranged to **8**. Since an accurate ϕ_5 could not be determined at the conversions (≤4%) needed to prevent formation of **8**, and since **8** is the only sensitized photoproduct of **5**,[10] ϕ_5 was taken as the sum of **5** + **8**.

(12) *trans*-Piperylene (0.04 M) eliminates *all* the radical products but has no effect on **5**, **6**, or **7**; the other multiplicity data make it apparent that the diene is reacting chemically with the norbornyl radical.

(13) Since heptene (E_T ~ 75 kcal/mol)[14] quenching of **5** (E_T ~ 70 kcal/mol)[10] should be endothermic, and kinetically not competitive with the intramolecular di-π-methane reaction, we believe heptene is quenching the triplet which sensitizes **5** (i.e., exoClBNB).

(14) By comparison with similar olefins in ref 7.

Table IV. Effect of Water on the exoClBNB/MeOH Photoreaction

% H_2O	% change in ϕ							
	1	3	4	5	8	(5 + 8)	6	7
10	−27	−38	−44	−18	−34	−29	−4	+9
20	−52	−58	−59	−36	−52	−47	−1	+21
30	−64	−74	−76	−50	−70	−64	−5	+9
40	−74	−82	−85	−64	−82	−76	−5	+4

Table V. Product Ratios for Silver-Ion-Assisted Ground-State Solvolysis vs. Photolysis of exoClBNB in Methanol/Water Mixtures

% water	9/6	
	solvolysis	photolysis
10	0.50	0.18
20	0.76	0.40
30	1.36	0.75

Table VI. Photolysis of exoClBNB in MeOH, *i*-PrOH, and *t*-BuOH

solvent	ϕ_{dis}	quantum efficiencies[a]					
		1	"3"	"4"	(5 + 8)	"6"	"7"
MeOH	0.55	0.12	0.079	0.034	0.070	0.13	0.027
i-PrOH	0.48	0.29	0.027	0.010	0.084	0.037	0.002
t-BuOH	0.38	0.03	0.050	0.017	0.14	0.019	0.002

[a] Products "3", "4", "6" and "7" refer to the pairs of alcohols and ethers formed in each of the solvents; cf. eq 2 and 3.

Table VII. Fluorescence Quantum Efficiencies for exoClBNB in Various Solvents

solvent	ϕ_f	ϵ[a]
hexane	0.065	1.90
t-BuOH	0.010	12.50
i-PrOH	0.010	19.41
EtOH	0.007	24.33
MeOH[b]	0.007	32.62
CH_3CN/1% H_2O	0.004	36.02
EtOH/20% H_2O	0.002	~35.1

[a] Dielectric constants from reference 19; the values for the mixed media were approximated by assuming a linear relationship between solvent composition and dielectric constant. [b] The ϕ_f in MeOH was unchanged by the addition of 10^{-3} *n* HCl or $NaHCO_3$ (to saturation).

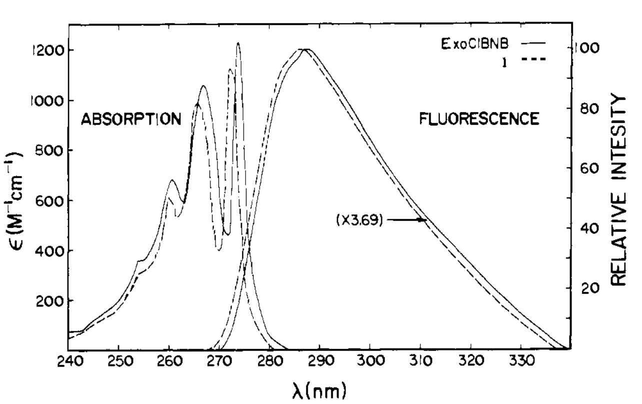


Figure 1. Absorption and fluorescence spectra of exoClBNB and benzonorbornene (1).

254 nm, with two concentrations of mercaptan, gave the results shown in Table II (data are corrected for partial light absorption by the mercaptan). ϕ_{dis} for the chloride is virtually unchanged by added mercaptan; i.e., ϕ_{dis} (0.04 M PrSH) = 0.53, ϕ_{dis} (0.12 M PrSH) = 0.55.

As observed with *trans*-2-heptene, $\Delta\phi_1$ (+0.09, 0.12 M PrSH) approximates $\Delta\phi_{3+4}$ (−0.10), though the mercaptan is even more efficient in trapping the norbornyl radical. By contrast with the heptene data, **5** + **8** are now eliminated, presumably because of reaction of PrSH with **5**. There is also a reduction in ether formation which may be attributed to some reaction of carbocation(s) with the mercaptan.[15]

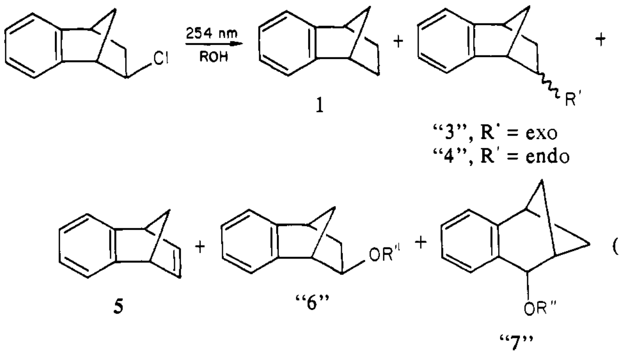
Effect of Oxygen on exoClBNB Photochemistry in Methanol. Irradiation of 0.018 M exoClBNB in oxygen-saturated methanol at 254 nm gave the results shown in Table III. The formation of *exo*-benzonorbornen-2-ol in the oxygenated solution is detectable by VPC. Note that there is virtually complete quenching of **1**, **3**, and **4**, an inhibition of the di-π-methane reaction (**5** → **8**), and partial quenching of (**5** + **8**), **6**, and **7**. We also observe that ϕ_{dis} for the chloride is 0.37 in the presence of oxygen (i.e., −33%), and fluorescence measurements, with and without oxygen, show that there is a reduction in ϕ_f in the presence of oxygen of −37%.

Effect of Water on exoClBNB Photochemistry in Methanol. Irradiation of 0.015 M exoClBNB in methanol/water mixtures at 254 nm gave the results shown in Table IV. In addition, the formation of *exo*-benzonorbornen-2-ol (**9**) was assayed, and the data for ϕ_9 are: 10% H_2O, ϕ_9 0.022; 20% H_2O, ϕ_9 0.052% 30% H_2O, ϕ_9 0.093; 40% H_2O, ϕ_9 0.15.[16] The ϕ_{dis} value for the chloride is virtually unchanged by the added water, i.e., 10% H_2O, ϕ_{dis} 0.57; 20% H_2O, ϕ_{dis} 0.55; 30% H_2O, ϕ_{dis} 0.53; 40% H_2O, ϕ_{dis} 0.50. Thus, there is extensive quenching of **1**, **3**, **4**, and (**5** + **8**), a minimal effect on **6** or **7**, and formation of **9** which is appreciable but does not seem to effect ϕ_{dis} and must therefore be coming at the expense of the quenched products.

In a separate experiment, photolyses in aqueous methanol were carried out with 0.06 M *n*-propyl mercaptan. The results were qualitatively similar to those given in Table II. i.e., enhancement of **1**, large diminution in **3**, **4**, **5**, and **8**, and small reductions in **6** and **7**. Alcohol **9** was virtually unaffected by added mercaptan.

Ground-State Solvolysis of exoClBNB in Methanol/Water Mixtures. Solvolyses of 0.015 M substrate were conducted in methanol/water mixtures containing 0.035 M silver nitrate for 20 h at 25 °C.[17] The formation of the alcohol **9** and ether **6**[18] was measured by VPC, and the ratios are presented in Table V, together with corresponding data from the photolyses. The selectivity of the carbocation precursor to **9** and **6** is clearly dependent on the method of generation. One can use the product yields and nucleophile concentrations to calculate k_{MeOH}/k_{H_2O} ("capture ratios"); for ground-state solvolyses the average ratio is 0.66 ± 0.10, while for the photolyses the value is 1.36 ± 0.06.

Photolysis of exoClBNB in Isopropyl Alcohol and *tert*-Butyl Alcohol. Irradiation of 0.02 M exoClBNB in these alcohols at 254 nm gives photoproducts analogous to those observed with methanol; cf. eq 3 (structure assignments are described in the



(3)

(a) R = *i*-Pr; R' = $-C(OH)(CH_3)_2$; R'' = −O-*i*-Pr
(b) R = *t*-Bu; R' = $-CH_2C(OH)(CH_3)_2$; R'' = −O-*t*-Bu

Experimental Section). Table VI presents the comparative quantum efficiencies for these products, as well as ϕ_{dis}, in the three alcoholic solvents. It may be noted that the $\sum\phi/\phi_{dis}$ for photolysis

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[15] No specific attempt was made to detect or assay thioether formation.

[16] No new product which could be attributed to rearranged alcohol was detected, but there are differences between the sum of the ϕ's for product formation vs. ϕ_{dis} which could reflect the presence of such a product.

[17] There is essentially no loss of the chloride over this time period in the absence of the silver salt.

[18] There is very little (<5%) formation of the olefin **5** in the ground-state reactions.

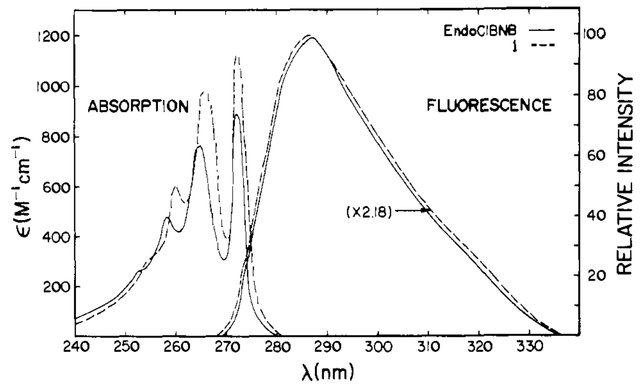

Figure 2. Absorption and fluorescence spectra of endoClBNB and benzonorbornene (1).

in MeOH, *i*-PrOH, and *t*-BuOH are 0.84, 0.94, and 0.68, respectively.

Spectroscopy of exoClBNB. The absorption and fluorescence spectra of ExoClBNB in hexane at room temperature are shown in Figure 1, together with the corresponding spectra for benzonorbornene (**1**). The ϕ_f values for the two substrates are 0.06_5 and 0.24, respectively, although the k_f values (from $\phi_f = k_f{}^1\tau$; see below) are comparable: 1.4×10^7 and 1.9×10^7 s^{-1}. There is a pronounced solvent effect on exoClBNB emission wherein ϕ_f decreases in more polar media, though ϕ_f is not affected by the pH of the medium (cf. Table VII). Neither **1** nor the endo chloride (see below) shows any such solvent sensitivity.

The singlet lifetime ($^1\tau$) for exoClBNB in hexane is 4.8 ns compared with 12.7 ns for **1**. The chloride lifetime diminishes markedly in methanol; by direct measurement we can say it is <1 ns, while by calculation of k_f from absorption data and the use of $\phi_f = k_f{}^1\tau$, we can estimate $^1\tau$ to be 0.5 ns.

The phosphorescence spectra for exoClBNB and **1** (in a 50:50 pentane/cyclopentane glass at 77 K) are qualitatively similar, but ϕ_p for the chloride is larger by a factor of 2.6. Vertical ionization energies were obtained from photoelectron spectra,[20] and the ionization potentials (in eV) for the two highest occupied molecular orbitals are: **1**, 8.45, 8.95; exoClBNB, 8.80, 9.24.

B. Photochemistry and Spectroscopy of *endo*-2-Benzonorbornenyl Chloride (endoClBNB). Photochemistry of endoClBNB in Cyclohexane and in Methanol. The title compound was prepared by a modification of the literature procedure[4] and irradiated as a 0.015 M solution in cyclohexane with 254-nm light. Both **1** and **2** were formed, but very inefficiently ($\phi_1 = 4.4 \times 10^{-4}$, $\phi_2 = 8.8 \times 10^{-4}$, $\phi_{dis} = 0.013$). Photolysis of a 0.02 M solution in methanol gave **1** ($\phi_1 = 1.1 \times 10^{-3}$) and **6** ($\phi_6 = 1.1 \times 10^{-2}$), but only trace quantities of **3**, **4**, **5**, and **7**. The quantum efficiency for disappearance is $\phi_{dis} = 0.019$.

When endoClBNB is irradiated in methanol with xenon, **1** is reduced to only trace quantities and the formation of **6** is quenched by 43%. Acetone sensitization of an equal mixture of the endo and exo chlorides gave a ratio of ϕ_{dis}^{sens}(endo/exo) = 0.13. Note that the comparable ratio for direct photolysis is ϕ_{dis}(endo/exo) = 0.019/0.55 = 0.034.

Spectroscopy of endoClBNB. The absorption and fluorescence spectra of endoClBNB in hexane at room temperature are shown in Figure 2, together with the corresponding spectra for **1**. The ϕ_f and $^1\tau$ values for the endo chloride are 0.11 and 12.6 ns, respectively, with $k_f = 8.7 \times 10^6$ s^{-1}. Though not reduced as much as with the exo chloride, the ϕ_f is low compared to that of **1** ($\phi_f = 0.24$), a consequence primarily of the reduced k_f (k_f for **1** = 19×10^6 s^{-1}). (The $^1\tau$'s for endoClBNB and **1** are identical within experimental error.) The reduction in the rate of the radiative transition for endoClBNB is evident from it absorption spectrum, integration of which provides $k_f = 7.6 \times 10^6$ s^{-1}. There is no significant change in either ϕ_f or $^1\tau$ for endoClBNB in methanol relative to hexane; values in methanol are 0.11 and 10.9 ns.

Table VIII. Perturbation of the exoMsBNB/*t*-BuOH Photoreaction

perturber	% change in ϕ				
	5	**8**	(**5** + **8**)	"**6**"	"**7**"
xenon	−46	−66	−61	−44	−79
oxygen	+111	−95	−31	−56	−31
(*E*)-2-heptene					
0.1 M	+217	−88	+38	−7	+85
0.2 M	+138	−94	0	−28	+54

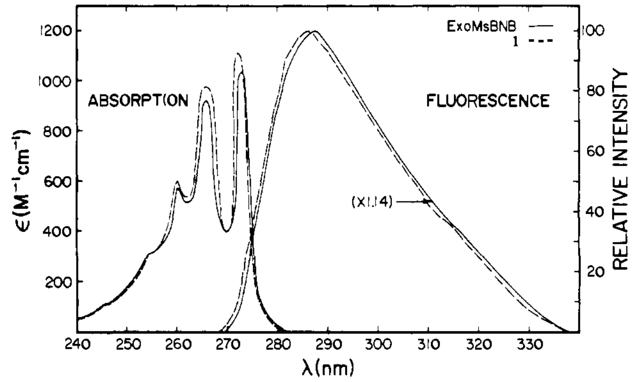

Figure 3. Absorption and fluorescence spectra of exoMsBNB and benzonorbornene (1).

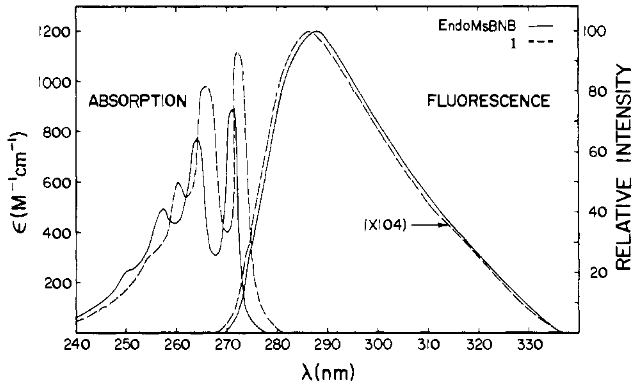

Figure 4. Absorption and fluorescence spectra of endoMsBNB and benzonorbornene (1).

The phosphorescence spectra for endoClBNB and **1** (in a 50:50 pentane/cyclopentane glass at 77 K) are qualitatively similar with ϕ_p for the chloride larger by a factor of 1.6 (but 62% that of ϕ_p for the exo chloride). Ionization poentials for the two highest occupied molecular orbitals are 8.66 and 9.12 eV.[20]

C. Photochemistry and Spectroscopy of *exo*- and *endo*-Benzonorbornen-2-yl Methanesulfonate (exoMsBNB and endoMsBNB). Photochemistry of exo- and endoMsBNB. These compounds were prepared from the corresponding alcohols using methanesulfonyl chloride in pyridine. endoMsBNB is photoinert at 254 nm in cyclohexane; in *tert*-butyl alcohol, $\phi_{dis} \leq 3 \times 10^{-3}$. exoMsBNB reacts inefficiently at 254 nm in cyclohexane to give trace amounts of **1**. Irradiation in *tert*-butyl alcohol produces **5** and the *tert*-butyl ethers corresponding to "**6**" and "**7**", but no **1** (even with 0.2 M *n*-propyl mercaptan), "**3**", or "**4**". The reaction is given in eq 4; quantum efficiencies have been corrected for ground-state solvolysis (ca. 4% of the loss of starting material and ~15% of **5** and "**6**" are due to a dark reaction).

Sensitization and Quenching of the Photoreaction. Photolysis of 0.017 M exoMsBNB in *tert*-butyl alcohol with 3.3 M *p*-xylene gave no "**7**", trace amounts of **5**, and a conversion to "**6**" only 2.9% of that obtained in a corresponding unsensitized photolysis. Acetone sensitization also gave a trace of **5** and some "**6**" but no "**7**". The effects of other perturbing agents are presented in Table

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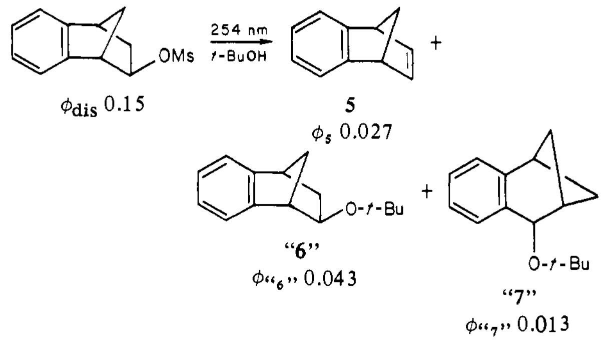
(19) Abraham, M. H. *Prog. Phys. Org. Chem.* **1974**, *11*, 1.

(20) We are grateful to Professor Kenneth Houk for these data. The spectra were run on a Perkin-Elmer Ps-18 operating at a resolution of approximately 20 MeV, with xenon and argon as internal claibrants. The maxima were taken as the vertical ionization potentials, and values are the average of five determinations. The positions are accurate within ±0.05 eV.



(4)

VIII. Oxygen was found to quench the fluorescence of exoMsBNB by 45%.

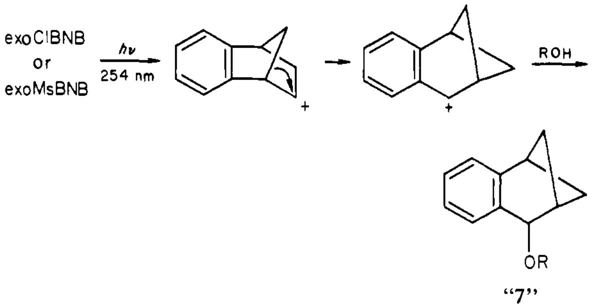
Spectroscopy of exo- and endoMsBNB. The absorption and fluorescence spectra of the two mesylates in hexane at room temperature are shown in Figures 3 and 4, together with the corresponding spectra for benzonorbornene (**1**). The exo isomer has ϕ_f and $^1\tau$ equal to 0.21 and 15.6 ns in hexane, with ϕ_f in *t*-BuOH reduced to 0.09$_5$. The endo isomer has corresponding values of 0.25 and 18.3 ns (hexane) and 0.20 (*t*-BuOH). Both the exo and endo isomers showed very little phosphorescence relative to **1** (3.3% in each case), with the emission anomalously shifted from (λ_{max}) 387 nm (**1**) to 460 nm (exo) and 470 nm (endo) and therefore suspect (data at 77 K in a 1:1 pentane/cyclopentane glass).

Discussion

A. A Summary of the Qualitative Features of Benzonorbornen-2-yl Chloride and Mesylate Photochemistry. Equations 1–4 in the Results section illustrate that the photolysis of exoClBNB and exoMsBNB with 254-nm light results in a facile cleavage of the 2-substituent. Quantum efficiencies range from 0.25 to 0.55 for disappearance of the chloride (depending on the solvent), and the mesylate disappears with $\phi = 0.15$ in *t*-BuOH. By way of comparison, benzyl chloride photosolvolyzes with ϕ's ranging from 0.26 (*t*-BuOH)[21] to 1.0 (CH_3OH)/H_2O),[22] while we find that *exo*-norborn-2-yl chloride is photoinert under our photolytic conditions. Two aspects of our observations are particularly striking: (1) *the reactions involve intramolecular activation of the remote functionality by the aryl chromophore* and (2) *the activation is strongly stereoelectronically controlled.* Thus we have noted above that *exo*-norborn-2-yl chloride is not cleaved by direct irradiation with 254-nm light, and it is also photoinert when admixed with exoClBNB. The stereoelectronic effect is evident from the reduced reactivity of endoClBNB. The ϕ_{dis} values in methanol for the exo and endo chlorides are 0.55 and 0.019, respectively; since the reactions are singlet derived (see below) one can estimate the k_r values for cleavage using $\phi = k_r{}^1\tau$ and the $^1\tau$ values of ~0.5 and 12.6 ns, respectively. *The rates so calculated are 1.1 × 10^9 s^{-1} and 1.5 × 10^6 s^{-1}, respectively, a relative rate factor of 733*! We likewise observe endoMsBNB to be virtually photoinert (as, incidentally, is 2-chloroethylbenzene).

The products of the exo chloride reaction include structures derived from free radical precursors (e.g., **1**, **3**, and **4**)[23] as well as those derived from carbocations (**6** and **7**).[25] Benzonorbornadiene (**5**) has several possible precursors; we favor a carbocation because **5** mimics the ethers in its response to the addition of perturbing agents to the reaction mixture, and there is ample evidence[24,27,28] that cations formed by the direct photolysis of alkyl halides readily deprotonate to olefins.[29] Compound **8** is the product of the triplet di-π-methane rearrangement of **5**,[10] and studies at low conversions confirm that it is indeed a secondary photoproduct. The addition of triplet quenchers (2-heptene, oxygen) reduces the formation of **8** and increases **5** (cf. Tables I, III, and VIII), and exoClBNB is the probable triplet sensitizing agent (we have shown that it can initiate the conversion of **5** to **8**).

The formation of the [3.1.1] bicyclic ether **7** and the olefin **5** in these photolyses is noteworthy. Rearrangement to the [3.1.1] series is not at all observed in ground-state solvolyses of benzonorbornenyl derivatives, and elimination to olefin is usually quite minor.[30] Our own "dark reaction" data with AgCl/MeOH/H_2O confirm those observations.[18] (Note that **5** accounts for 13 and 20% of the ϕ_{dis} for the chloride and mesylate, respectively; cf. eq 2 and 4.) We successfully generated **7**, which derives from a 1,2 migration of the C-9 bridge (eq 5), by photolyzing an alkaline methanolic solution of 2-benzonorbornenone tosylhydrazone[31] (conditions known to produce "hot" (i.e., "free") carbocations via decomposition of an intermediate diazonium ion).[32,33] As noted above, olefin formation is likewise a characteristic product of reactions involving "hot" carbocations. We conclude that, as in the direct photolysis of bromides and iodides,[24,27,28,34] *the photochemistry of exoClBNB and exoMsBNB involves the generation of a "hot" carbocation which is neither appreciably stabilized by the aryl group nor extensively solvated*, and *thus exhibits chemistry quite distinct from that created via ground-state solvolysis*.[35]



(5)

B. Multiplicity of the Excited-State Precursors to the Photoproducts. *There is considerable evidence that the primary pho-*

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[21] Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951.

[22] Ivanov, V. B.; Ivanov, V. L.; Kuz'min, M. G. *J. Org. Chem. USSR* (*Eng. Transl.*) **1973**, *9*, 345.

[23] There is precedent[24] for formation of **1** via a carbanion, but irradiation of exoClBNB in basic MeOD results in less than 2% deuterium incoporation in **1** (by ^{1}H NMR and mass spectrometry).

[24] Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135.

[25] There is evidence for carbene formation in the photolysis of alkyl iodides,[26] but irradiation of ExoClBNB in MeOD gave less than 2% isotope incorporation in **6** and **7**. Compound **7** could conceivably arise from ring opening of **8**, but this possibility can be ruled out since (1) **7** is formed at low (<1%) conversions when **8** is unobservable, (2) the formation of **7** is not enhanced by acid, (3) there is no incorporation of deuterium into **7** when MeOD is the solvent, (4) **7** is minimally quenched under conditions where **8** is virtually eliminated, and (5) we have found neitherr ground- nor excited-state conditions which convert **8** to **7**. See also: Kouwenhoven, A. P.; van Noort, P. C. M.; Cerfontain, H. *Tetrahedron Lett.* **1981**, 1745.

[26] Sawyer, J. A.; Kropp, P. J. Southeast/Southwest Regional Meeting of the American Chemical Society, New Orleans, LA Dec 10–13, 1980; Abstr. 365.

[27] Kropp, P. J., Jones, T. H.; Poindexter, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 5420.

[28] Kropp, P. J.; Gibson, J. R.; Snyder, J. J.; Poindexter, G. S. *Tetrahedron Lett.* **1978**, 207.

[29] We cannot rule out some contribution from a carbene intermediate,[25] and experiments with the appropriately 2-deuterio-substituted exo chloride are in progress.

[30] See, for example: Goering, H. L.; Chang, C.-S.; Masilamani, D. *J. Am. Chem. Soc.* **1978**, *100*, 2506, and references therein.

[31] Ethers **6** and **7** were formed in a 16:1 ratio; no olefin (**5**) was detectable by VPC.

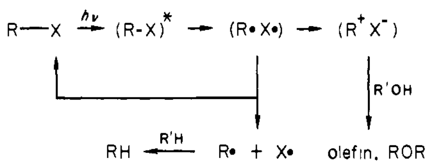
[32] Dauben, W. G.; Willey, F. G. *J. Am. Chem. Soc.* **1962**, *84*, 1497.

[33] An anlogous rearrangement has been observed upon photolysis of 5-norbornen-2-one tosylhydrazone in aqueous sodium hydroxide; cf. Kirmse, W.; Kroppfel, N.; Loosen, K.; Siegfried, R.; Wroblowsky, H.-J. *Chem. Ber.* **1981**, *114*, 1187. These workers also report the formation of the 3:2:1 product from nitrous acid deamination of *endo*-5-norbornen-2-amine, but observe no such rearrangement of the exo amine. They therefore propose that an endo diazonium ion is required for bridge migration; clearly our photochemically induced rearrangement has no such requirement.

[34] Takaishi, N.; Miyamoto, N.; Inamoto, Y. *Chem. Lett.* **1978**, 1251. Gokhale, P. D.; Josh, A. P.; Sahni, R.; Naik, V. G.; Damodara, N. P.; Nayak, U. R.; Dev, S. *Tetrahedron* **1976**, *32*, 1391.

[35] Cristol and co-workers[52] have proposed that syn migration, as in the formation of "7", is generally preferred over anti migration in analogous systems. Experiments with 2-deuterio exoClBNB are needed to establish the extent of anti migration for the exo halide and are currently in progress.

Scheme I



toproducts from exoClBNB and exoMsBNB are principally derived from the singlet excited state. To enumerate: (1) The addition of xenon to exoClBNB in cyclohexane led to a 65% quenching of **1**. We have shown elsewhere[36] that heavy-atom quenching in excess of 50% confirms a dominant singlet-state reaction (in fact, ≥67% of the reaction is singlet derived).[37]

(2) Irradiation of exoClBNB in methanol with 0.1 M *trans*-2-heptene results in 63% quenching of the triplet derived di-π-methane product (**8**) with only a minimal (5–8%) effect on the other products.

(3) Photolysis of exoClBNB in oxygen-saturated methanol leads to a quenching of product formation (34%) comparable to the observed decrease in substrate fluorescence (37%). Again, the di-π-methane reaction serves as an excellent probe of triplet quenching, and **8** is quenched by 71%.

(4) Though photosensitization of exoClBNB by *p*-xylene and acetone successfully generates the unrearranged ether (**6**), there is very little formation of **1**, **3**, **4**, **5**, or **7**.[38]

(5) There is a good correlation of substrate fluorescence and reactivity. Thus, ϕ_f(exoClBNB) < ϕ_f(endoClBNB), and both ϕ_f and $^1\tau$ for exoClBNB in methanol are less than the corresponding values in cyclohexane (while endoClBNB exhibits no such solvent effect). In each case, the reductions in ϕ_f are accompanied by an appreciable increase in ϕ_{dis}.

C. Relevant Literature. Before presenting a more detailed picture of the exoClBNB photolysis, we briefly summarize here prior studies which most directly relate to our observations, i.e., reports on the direct photolysis of alkyl halides, the photolysis of benzyl chloride, and the photochemistry of several other aryl chlorides where "remote activation" has also been observed.

Direct excitation of the n → σ^* transition of the C–Cl chromophore (for example, at 185 nm) results in efficient homolytic cleavage and free radical chemistry.[41] However, carbocation as well as free radical chemistry has been observed upon the photolysis of alkyl bromides and iodides, and relatively "hot" carbocations can be prepared in this way.[24] Thus, photolysis of 1-iodonorbornane in methanol results in a 76% yield of 1-methoxynorbornane (plus 8% norbornane), and the contrasting photochemistry and ground-state solvolysis of 1-iodooctane[24] are illustrated in eq 6 and 7. Alkyl bromides give a higher proportion of the radical-derived products; for 1-bromonorbornane, the yields

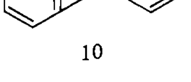
$$n\text{-}C_7H_{15}CH_2I \xrightarrow[MeOH]{h\nu} \underset{56\%}{n\text{-}C_6H_{13}CH{=}CH_2} + \underset{6\%}{n\text{-}C_4H_9CH\overset{\cdot\cdot}{=}CH\overset{\cdot\cdot}{=}CHCH_3} + \underset{38\%}{n\text{-}C_7H_{15}CH_3} \quad (6)$$

$$n\text{-}C_7H_{15}CH_2I \xrightarrow[\substack{MeOH\\ AgClO_4}]{\Delta} n\text{-}C_7H_{15}CH_2OCH_3 \quad (7)$$

of ether and hydrocarbon are 30 and 55%, and only *n*-octane is observed upon photolysis of 1-bromooctane.[24] Kropp has proposed[24] the mechanism in Scheme I to explain the bulk of these results.[23,25] Among the more significant experimental observations in support of this scheme are: (1) the ability of oxygen to quench the ethers as well as the hydrocarbons, presumably by intercepting the caged radical pair before recombination or electron transfer (because recombination is impeded, starting material disappearance is increased by oxygen); (2) the fact that a viscous medium, ethylene glycol, increases carbocation products, attributed to an increased lifetime of the caged radical pair and thus a greater opportunity for electron transfer.

It has been known for some time that benzyl derivatives ($C_6H_5CH_2Y$) are susceptible to cleavage of the C–Y bond by 254-nm light; examples include Y = OAc,[40] $^+N(CH_3)_3$,[42] I,[40,43] Br,[40] and Cl.[40,44] Products derived from radicals and carbocations have been observed, and the mechanism of the photosolvolysis of benzyl chloride has been the subject of considerable study. This latter system is characterized by the apparently anomalous observation that direct photolysis preferentially produces radical products while photosensitization primarily affords cation (i.e., benzyl ether) products.[21] The "capture ratios" for methanol vs. isopropyl alcohol are comparable for the sensitized photosolvolysis and silver-ion promoted ground-state solvolysis,[45] suggesting that the cation generated in the sensitization experiment is "cold". A similar result has been reported for methanol vs. water in the direct photolysis.[46] The detailed nature of the fragmentation step (homolytic, heterolytic, or some combinatioon of the two (see below)) is still in question.[21] Singlet and triplet states have been invoked for the direct photolysis,[40] and there is a recent proposal that the reactive triplet, under these conditions, is an upper (T_2) state.[44]

By contrast with the benzyl system, aralkyl chlorides having the halogen more remote from the aryl chromophore have not been extensively studied. As regards acyclic substrates, we see no evidence of reactivity upon photolysis of 1-chloro-2-phenylethane, though photosolvolysis of analogous mesylates having oxygen substituents on the aromatic ring has been reported,[47] as has the 254-nm-induced homolytic cleavage of the C–Br bond in 1-bromo-2-phenylpropane.[48] A more closely related series of studies is that of Cristol and co-workers. The bulk of this work has involved allylic chlorides and mesylates such as **10**[49] and **11**.[50]



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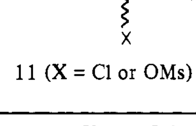

11 (X = Cl or OMs)

$R{\cdot}Cl{\cdot} \longleftrightarrow R^+Cl^-$

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(36) Morrison, H.; Miller, A. *Tetrahedron* **1981**, *37*, 3405.

(37) The number follows from an estimate of the maximum ϕ_{isc} as 0.93 (from the fluorescence data) and the equations[36] $\phi_s/\phi_T\phi_{isc} = [1/\phi_{isc}(1 - Q)] - 1 = 2.07$; $\phi_s + \phi_T\phi_{isc} = \phi_1 = 0.10$. ($\phi_S$ and ϕ_T are the singlet and triplet quantum efficiencies, and Q represents the fraction of quenching (i.e., 0.65).

(38) The sensitization studies indicate that the triplet state gives only a "cold" carbocation and is ineffective in producing free radicals. Both results are puzzling and we can only speculate on their origin. We note that heterolytic fission of the C–Cl bond from T_1 is spin forbidden. Since exoClBNB has a T_1 energy of ~82 kcal/mol (the 0,0 transition in the phosphorescence emission is at 350 nm) and the bond dissociation energy of a secondary C–Cl bond is ca. 81 kcal/mol,[39] homolytic fission will be only marginally exothermic and should yield a caged radical pair with very little excess kinetic or vibrational energy (and possibly a greater degree of aryl participation). The "colder" radicals may have a longer lifetime within the cage and thus undergo more complete electron transfer (no radical products) to form a correspondingly "colder" carbocation (no rearrangement). Benzyl chloride shows a similar preference for ionic and radical products upon sensitization and direct irradiation, respectively, and logic similar to the above could apply.[40] See also: Schaffner, K.; Jeger, O. *Tetrahedron* **1974**, *30*, 1891, for similar observations upon photolysis of α-mesyl ketones.

(39) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(40) For another view, see: Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 87, and references therein. Larson, J. R.; Epiotis, N. D.; McMurchie, L. E.; Shaik, S. S. *J. Org. Chem.* **1980**, *45*, 1388.

(41) Shold, D. M.; Ausloos, P. J. *J. Photochem.* **1979**, *10*, 237, and references therein.

(42) Lillis, V.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Williams, I. H. *J. Chem. Soc. Perkin Trans. 2* **1980**, 83, and references therein.

(43) See also: Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 4625.

(44) Cristol, S. J.; Bindel, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 7287, and references therein.

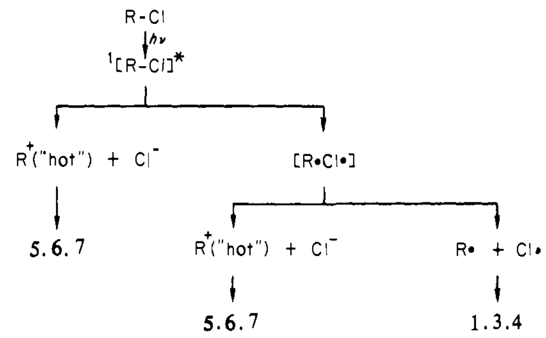
(45) Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105.

(46) Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Chem. Commun.* **1977**, 108.

(47) Jaeger, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6401. See also: Jaeger, D. A.; Angelos, G. H. *Tetraheron Lett.* **1981**, 803.

(48) Dannenberg, J. J.; Dill, K.; Waits, H. P. *J. Chem. Soc., Chem. Commun.* **1971**, 1348. Dannenberg, J. J.; Dill, K. *Tetrahedron Lett.* **1972**, 1571.

Scheme II

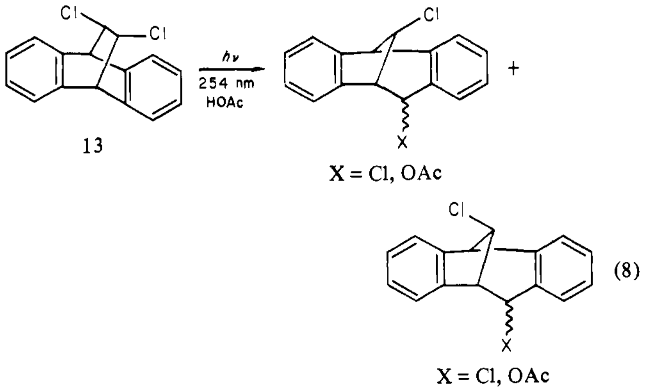


Photosolvolyses are observed, and the authors have proposed[49a] that the fragmentation proceeds via an "intimate ion-radical pair" (**12**) which may then dissociate to a pair of radicals or a pair of

$$R{\cdot}Cl{\cdot} \leftrightarrow R^+Cl^-$$

12

ions depending on the polarity of the medium. Activation of the C–Cl bond in these substrates is suggested to occur via an electron transfer from the aromatic ring π,π^* state to the C–Cl σ^* orbital.[50,51] A nonallylic substrate, more closely related to our benzo[2.2.1] series, is **13** which photosolvolyzes in acetic acid to give rearrangement products (eq 8),[52] Preferential fragmentation of a chlorine atom anti to an aromatic ring is proposed.[53]



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(8)

D. A General Mechanistic Scheme for exoClBNB Photolysis. With the above serving as a brief background, we suggest that the data in hand are best accomodated by the mechanism outlined in Scheme II (wherein exoClBNB is represented by R–Cl). Our logic and an analysis of our data in the light of this scheme follow.

There is ample evidence that the singlet excited state is the principal source of the direct excitation photochemistry (cf. section B above), and that C–Cl cleavage from S_1 is favored by more polar media. The benzonorbornenyl radical (R·) and cation (R^+) are being formed, with the cation reacting quite differently from that generated by ground-state solvolysis. We have characterized the photogenerated cation as being "free" or "hot" (cf. section A above), and, for example, it presumably derives little or no stabilization from the aromatic ring. This is not true of the triplet-derived cation which gives neither rearrangement nor olefin formation.[38]

Table IX. Radical vs. Carbocation Derived Products from exoClBNB Photolysis in Alcohols

solvent	$\Sigma\phi_{R\cdot}{}^a$	$\Sigma\phi_{R^+}{}^b$
MeOH	0.23	0.23
i-PrOH	0.33	0.12
t-BuOH	0.097	0.16

[a] $\phi_1 + \phi_{\text{“}3\text{”}} + \phi_{\text{“}4\text{”}}$. [b] $\phi_{5+8} + \phi_{\text{“}6\text{”}} + \phi_{\text{“}7\text{”}}$.

Though homolysis within the S_1 state is clearly required by the appearance of radical-derived products in both cyclohexane and methanol, the details of the sequence leading to the "hot" cation are less certain. The rates of C–Cl cleavage in cyclohexane and methanol may be estimated from the ϕ_{dis} and $^1\tau$ data as 5.2×10^7 and $\sim 110 \times 10^7$ s^{-1}, respectively. The greater than 20-fold increase in the more polar medium would certainly seem to argue for a heterolytic fragmentation. However, the fact that radical-derived products are formed as efficiently in methanol as in cyclohexane (cf. the quantum efficiencies in eq 1 and 2), despite the shortened $^1\tau$ in methanol, requires that homolysis is also favored by the more polar medium (one can calculate that the rate of homolytic cleavage in methanol must be more than twice that in cyclohexane even were one to assume that the ϕ for bond cleavage in the hydrocarbon solvent is 1.0). *Homolysis must therefore be proceeding via a polarized transition* state[54] ($R^{\delta+}{\cdots\cdots}{}^{\delta-}Cl$) as has been suggested for a related system by Cristol.[49a] The final proportion of solvent-separated radicals vis-ã-vis ions, as a function of solvent polarity, may either then be thought of in terms of the degree of charge separation in the ion-radical pair, or within the framework of the electron-transfer mechanism proposed by Kropp.[24] With this discussion in mind, we have, nevertheless, chosen to include heterolysis as a distinct step in the fragmentation because of (1) the very large dependence of the fragmentation rate on solvent polarity (see above) and (2) the difference between T_1 and S_1 generated cations (the former presumably being derived from initial homolysis).[40,55]

In fact, a number of experiments described in the Results section were designed to specifically test the proposition that a radical pair is a precursor to the carbocation. As mentioned above, Kropp succeeded in establishing such a sequence by showing that oxygen quenched cation as well as radical-derived products upon photolysis of alkyl iodides. When oxygen is incorporated into an ExoClBNB photolysis, we likewise observe the complete elimination of the normal free radical products and partial quenching of the ethers and olefin (cf. Table III). However, we note that the degree of quenching of the ethers is the same as the extent of the quenching of substrate fluorescence and thus *cannot* be ascribed to interception of the radical pair. In fact, though Kropp observed that oxygen *increases* alkyl halide disappearance (by preventing radical pair recombination), we see an oxygen-induced *decrease* in ϕ_{dis} which matches the decrease in ϕ_f. We conclude that, in our case, the lifetime of the radical pair is too short to permit interception by oxygen.

Because of the limitation on quencher concentration imposed by the use of oxygen, we turned to *n*-propyl mercaptan. With 0.12 M mercaptan as an additive in methanol, we again noted no increase in ϕ_{dis} though the increase in ϕ_1 and the large decrease in ϕ_3 and ϕ_4 attest to the effectiveness of this hydrogen atom donor (cf. Table II). We then considered that the most effective quencher of the solvent-caged radical pair should be the solvent molecules making up the cage, and examined the effect of changing from methanol to the better hydrogen atom donor,

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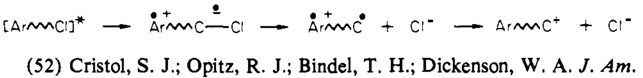
(49) (a) Cristol, S. J.; Stull, D. P.; Daussin, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 6674. (b) Cristol, S. J.; Daussin, R. D. *Ibid.* **1980**, *102*, 2866.

(50) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707; **1980**, *102*, 5577.

(51) This electron-transfer mechanism appears to be unable to rationalize the formation of radical-derived products or to give species such as **12**. Dissociation following electron transfer would be expected to lead to a carbocation intermediate, i.e.



(52) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7978.

(53) Though this report is consistent with our 2:2:1 studies, we have recently observed that in the simple benzo[2.2.2] series there is a small but significant preference for cleavage of the endo C–Cl bond: Morrison, H.; Pandey, G., to be submitted for publication, cf. ref 1, Part 52.

(54) Walling, C.; Waits, H. P.; Milovanovic, J.; Pappiaonnou, C. G. *J. Am. Chem. Soc.* **1970**, *92*, 4927.

(55) One might well expect Cristol's[50] π,π^* to C–Cl σ^* electron-transfer process to also be promoted by polar media, and the three-step sequence in footnote 51 may be taken as equivalent to a concerted heterolysis.

isopropyl alcohol. *tert*-Butyl alcohol was included in the study to test the effect of solvent polarity. The data, tabulated for the purpose of the present discussion, are presented in Table IX (from Table VI in the Results section); in Table IX, $\sum\phi_{R\cdot} = \phi_1 + \phi_{"3"} + \phi_{"4"}$ and $\sum\phi_{R+} = \phi_{5+8} + \phi_{"6"} + \phi_{"7"}$. One notes that upon changing from methanol to isopropyl alcohol, (1) the sum of the radical-derived products increases at the expense of the carbocation products, and (2) the effect is reversed in *tert*-butyl alcohol, where the $\sum\phi_{R^+}$ actually is greater than that for isopropyl alcohol. The second observation precludes the change in solvent dielectric as the source of the isopropyl alcohol/methanol perturbation. Rather, we believe that the reduction in the $\sum\phi_{R^+}$ in isopropyl alcohol is a consequence of our first successful interception of the caged radical pair and concomitant inhibition of the radical pair electron-transfer mechanism.[56] It is interesting to note that, even for isopropyl alcohol, ϕ_{dis} does not increase, and thus we have no evidence for cage recombination. A similar picture emerges from the aqueous methanol studies (Table IV) where, as one might expect, an increase in water content is accompanied by a decrease in $\sum\phi_{R\cdot}$, an increase in $\sum\phi_{R^+}$, and no change in ϕ_{dis}.

In sum, as regards the source of the singlet-derived "hot" carbocations, each of the potential pathways (heterolysis and radical pair electron transfer) can be supported, and there is no conclusive evidence to rule out either of them. In the absence of such, both pathways are included in Scheme II.[57]

E. Mechanism of exoMsBNB Photolysis. The mesylate analogue of exoClBNB is also photoreactive with 254-nm light. The ϕ_{dis} value in *tert*-butyl alcohol (0.15) is about a factor of 2 less than that (0.38) for the chloride. As in the halide series, the mesylates show a large exo/endo reactivity ratio and the ExoMsBNB generates a "hot" carbocation (cf. eq 4). Though triplet sensitization and xenon perturbation experiments indicate that the olefin and rearranged ether are primarily singlet derived, the unrearranged ether does not respond to triplet quenchers (heptene, oxygen) in the same fashion as the other two products.[58] We attribute this to a triplet component to the formation of the unrearranged ether (we can estimate that about 40% of this product is triplet derived). One significant feature of the exoMsBNB photolysis is the absence of free-radical-derived products, so that a single heterolytic fragmentation now suffices to explain all the data in hand.[59]

F. Theoretical Rationale for the Remote Activation and the Stereoelectronic (Exo/Endo) Effect. Two questions not yet addressed are how C–X cleavage is initiated by light primarily absorbed by the aryl chromophore, and why the photoactivation shows a large exo/endo effect. The first of these has been touched on by Cristol and co-workers, who have suggested[50] a reduction of the C–Cl unit in related molecules by electron transfer from the aryl π,π^* excited state (see section C above). We have employed the Weller equation[60] to estimate whether such a process would be favorable. Using the oxidation potential of *o*-xylene (+1.89 eV),[61] the reduction potential of methyl chloride (−2.23 eV),[61] a coulombic term of ca. 4.40 kcal/mol (estimated using ϵ(MeOH) = 36.7 and r = 7 Å), and $\Delta E_{0\text{-}0}$ of 103 kcal/mol, ΔG for electron transfer is predicted to be exergonic by 12 kcal/mol.

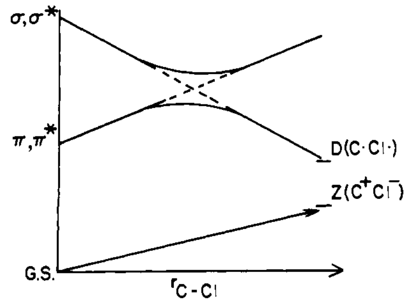


Figure 5. Correlation diagram for 254-nm-induced fragmentation in the benzonorbornenyl series.

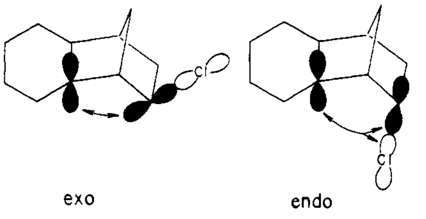


Figure 6. Pictorial representations of $\langle\pi\pi^*|\sigma\sigma^*\rangle$ for the *exo*- and *endo*-2-benzonorbornenyl chlorides.

However, the difficulty in explaining radical-derived products by such a sequence has already been touched upon,[51] and the source of the stereoelectronic preference for exo activation is not defined. It is clear, for example, that spatial separation is not a factor, for the distance between the aryl and Cl units is appreciably smaller in the endo isomer.

As an alternative approach we turned to the "natural correlation" concept.[62] The sequence of steps in this analysis are the following: (1) an MO natural correlation diagram is drawn for the reaction path while considering the conservation of the MO phase and location properties along the reaction coordinate; (2) a configuration correlation diagram is deduced based on the conservation of the electron occupancy of the natural correlation MO's; and (3) a final-state correlation diagram is determined by considering the various mixings of configurations as well as the avoided crossings which occur along the reaction paths between the different correlated configurations. The avoided crossings generate potential energy barriers, the magnitudes of which are inversely related to the interaction term, H_{AB} $(=\langle S_A|1/r_{AB}|S_B\rangle)$, between the states "A" and "B" involved in the crossing; i.e., the larger H_{AB}, the greater the mixing and the smaller the barrier (see Figure 5 below).

In the benzonorbornenyl system, it is clear from the spectral data that the initially created excited state is mainly localized on the aryl chromophore and is of the π,π^* type (one reaches the same conclusion from CNDO/S calculations). In the product which results from σ bond breaking, there will be a diradical-type electronic state with an electron located on each fragment of the broken bond (i.e., C·X·). (The corresponding ion-pair-type state (C$^+$X$^-$) may well be below the diradical state in solvents of high polarity.) From a natural correlation point of view, the diradical state correlates with the high-lying σ,σ^* excited state of the initial benzonorbornenyl molecule (σ and σ^* referring to the bonding and antibonding orbitals of the bond involved in the fragmentation), while the initial aryl π,π^* state correlates with a corresponding π,π^* plate of the product (cf. Figure 5). It is clear from the figure that there is an intended crossing of these correlation paths, but this crossing will be "avoided" to the extent dictated by $H_{AB} = \langle\pi\pi^*|\sigma\sigma^*\rangle$. If, to a first approximation, we consider the aryl and σ_{C-X} moieties to be independent, the slopes and positions of the various correlation lines in the benzonorbornenyl isomers will be the same no matter which of the C–X isomers is being calculated, and *the relative reactivity of the exo and endo*

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[56] The increase in $\sum\phi_{R^+}$, on going from *i*-PrOH to *t*-BuOH, may be due to a combination of *i*-PrOH interception of the radical pair (thus hindering electron transfer) and the increased viscosity of the *t*-BuOH cage (thus prolonging cage lifetime and promoting electron transfer). See ref 24 for such a viscosity effect using ethylene glycol.

[57] Scheme II does not include a "cold" carbocation in the singlet mechanism. Though we have no evidence on this point, it is certainly possible that the "hot" ion, in part, "relaxes" prior to the formation of 6.

[58] There is a curious enhancement observed for (5 + 8) and 7 when heptene is added; we have no explanation of this anomaly though enhancements by "quenchers" have been reported and attributed to exciplex formation. Cf. Saltiel, J.; Townsend, D. E.; Watson, B. D.; Shannon, P. *J. Am. Chem. Soc.* **1975**, *97*, 5688, and references therein.

[59] As, of course, could homolysis followed by 100% efficient electron transfer.

[60] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[61] "Techniques of Chemistry-Technique of Electroorganic Synthesis", Part 2; Weissberger, A., Weinberg, N. L., Eds.; Wiley: New York, 1975; Vol. 5, pp 667–1055.

[62] Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009. Bigot, B.; Devaquet, A.; Turron, N. J. *Ibid.* **1981**, *103*, 6.

isomers will be determined exclusively by the magnitude of H_{AB} at the transition states. Since the determination of the geometries of the transition states is not feasible (it would require a calculation of the complete energy profiles for the two reaction paths), we have assumed that the interaction term at the transition state is proportional to the value of H_{AB} in the reactant.

The H_{AB} terms were estimated by first using CNDO/S[63] calculations on the exo and endo benzonorbornenyl alcohols[64] to obtain sets of molecular orbitals. A localization procedure[65] was then used to get the σ orbitals relative to the substituted σ bonds. These localized orbitals were, in turn, used to compute[66] the H_{AB} terms. **To review, this analysis presumes that the larger the H_{AB}, the greater the degree of avoided crossing, the smaller the transition state barrier, and the greater the reactivity of that isomer.** Pictorial representations of the state/state interactions are given in Figure 6. The principal distinction between the exo and endo orientations is the partial cancellation of the $\pi\pi^*|\sigma\sigma^*$ interaction in the endo isomer due to the positive and negative overlap created in the latter. Computation gives $H_{AB}(\text{exo}) = 30.4$ kcal/mol and $H_{AB}(\text{endo}) = 18.4$ kcal/mol, in good qualitative agreement with the stereoelectronic features of the benzonorbornenyl photofragmentation.

Conclusion

This work extends our earlier studies on 2-methylenebenzonorbornene wherein several modes of aryl/olefin interaction in the excited state were identified.[67] We may now add photofragmentation of the remote 2-substituent to the list of known consequences of photoexcitation in these rigid bifunctional molecules. The large exo/endo reactivity ratio we have noted is particularly intriguing, and studies in related systems are being directed toward a further understanding of the stereoelectronic aspects of the remote activation phenomenon. These studies will also help test the correlation analysis theory we have put forward as a rationale for our observation.

Experimental Section

The experimental details for this work may be found in the Ph.D. thesis of A.M.[1b] The most cogent data are reproduced below.

Instrumentation. The basic analytical and photochemical techniques and instrumentation have been previously described.[68] ^{1}H NMR spectra were obtained on a Perkin-Elmer R-32 90-MHz spectrometer or on a Nicolet NT-360 MHz spectrometer. Vapor-phase chromatography utilized Varian Models 90-P, A-90-P, and A-700 for qualitative or preparative work and a Varian Model 1200 or 1400 FID chromatograph with a Hewlett-Packard 3380 or 3380-A digital integrator for quantitative studies (internal standards were used throughout). Flow rates were 60 mL of He/min. (0.25-in. columns) or 30 mL of N_2/min. (0.125-ins. columns) unless otherwise specified. Columns were as follows: (A) 20 ft × 0.25 in. 20% XF-1150 on 40/60 AW-DMCS Gas Pack W; (B) 10 ft × 0.25 in. 30% Apiezon L on 60/80 AW-DMCS Chromosorb W; (F) 10 ft × 0.125 in. 26% Apiezon L on 60/80 Chromosorb W; (H) 20 ft × 0.125 in. 10% XF-1150 on 60/80 AW-DMCS Chromosorb W; (I) 10 ft × 0.125 in. 5% SF-96 on 60/80 AW-DMCS Chromosorb W; (K) 5 ft × 0.125 in. 5% Carbowax 20 M on Gas Pack; (L) 10 ft × 0.25 in. 10% XE-60 on Gas Pack; (N) 4 ft × 0.25 in. 10% SF-96 on 60/80 AW-DMCS Chromosorb W; (O) 12 ft × 0.125 in. 10% $AgBF_4$ and 20% Carbowax 20 M on 100/120 AW-DMCS Chromosorb W; (P) 20 ft × 0.25 in. 20% DC-550 on 60/80 Chromosorb W.

All quantitative determinations for HCl were conducted by titrating the acidic solution with a standardized NaOH solution and measuring pH for each increment of NaOH added. The pH was measured using a calibrated Beckman Zeromatic pH meter equipped with a Sargent-Welsh combination microelectrode, and the equivalence point was taken as that where $\Delta\text{pH}/\Delta M(\text{NaOH})$ was maximum. This corresponds to the inflection point in this strong acid–strong base titration curve.

Photochemical studies typically employed rotating turntables, quartz, Vycor, or Pyrex tubes (matched within 3% by uranyl oxalate actinometry), and a Hanovia Model 68814-45 low-pressure mercury lamp or a Rayonet Photochemical Reactor (New England Ultraviolet Corp.). Deoxygenation was by bubbling a slow stream of argon through the solution for at least 10 min or by freeze–pump–thawing the tubes through at least four cycles below 10^{-4} mmHg. Actinometry was with 1-phenyl-2-butene[68] using matched tubes and solutions having $A_{254}^{1\text{cm}} \geq 4.0$ (noting that the equivalent path length of a cylindrical tube is $l \simeq \pi d/4$, where d = inner diameter of the tube and l = the equivalent path length for a rectangular cell.

Room-temperature fluorescence quantum efficiencies were obtained by comparing computer-corrected[69] fluorescence areas of a sample of known absorbance with that of a toluene sample of known absorbance and correcting for differing light absorbance. The ϕ_f for toluene in hexane was taken to be 0.12.[70] Lifetime measurements were done at room temperature using equipment and procedures previously described.[68] Phosphorescence spectra were recorded at 77 K in a 50:50 pentane/cyclopentane glass.

Chemicals. The following chemicals were used as received from the respective chemical companies: anthranilic acid, isoamyl nitrite, propylene oxide, iodobenzene, triethylamine, sodium azide, and bibenzyl (Matheson Coleman and Bell); mercuric acetate and silver nitrate (Mallinckrodt); 1 M BH_3–THF complex, 3-amino-2-naphthoic acid (technical grade, 80%), norbornylene, tosylhydrazine, hexachlorocyclopentadiene, pyridinium chlorochromate, *n*-heptadecane, and *trans*-stilbene (Aldrich); dicyclopentadiene and 10% Pd/C (Eastman); 5% Pd/$BaSO_4$ (Pfaltz and Bauer); 30% H_2O_2 and naphthalene (Baker); lithium aluminum hydride, sodium borohydride, aluminum *tert*-butoxide, and *n*-butyllithium (2.1 M in hexane) (Alfa-Ventron Inorganics); sodium methylate (Olin); 1-cyclohexylcyclohexene (Frinton Labs); potassium *tert*-butoxide (M.S.A. Research Corp.); methyl iodide (Columbia Organic Chemicals).

The following chemicals were modified or purified before they were used. Sodium hydride (Metal Hydrides Inc., dispersion in mineral oil) was washed with hexane, dried, and kept under a N_2 atmosphere. (*E*)-2-Heptene (Chemical Samples) was molecularly distilled before use. Undecane (Phillips) was stirred over concentrated H_2SO_4 overnight, washed with water, dried over $MgSO_4$, and distilled. Potassium hydrogen phthalate (Mallinckrodt, P.S.S.) was dried in a 120 °C oven overnight and kept in a vacuum dessicator. Propyl mercaptan (Aldrich) was distilled under nitrogen before use. Pure *trans*-1-phenyl-2-butene (Aldrich, 97% trans) was obtained by preparative VPC on column O. The following were also prepared by VPC before use: (3-chloropropyl)benzene (Chemical Samples) on column B, (2-chloroethyl)benzene (Aldrich) on column B, phenethyl alcohol (Aldrich) on column P, and 3-phenylpropanol (Aldrich) on column P. Acetophenone (Baker) was distilled before use.

With regards to reaction solvents, ether and tetrahydrofuran (Mallinckrodt) were distilled under nitrogen from sodium–benzophenone ketyl in a recycling still. Benzene and pyridine (Mallinckrodt, AR) were distilled from calcium hydride, toluene (Baker) was passed through alumina (neat) and molecularly distilled, and chloroform (Mallinckrodt, AR) was washed with water, dried over $MgSO_4$, and distilled from P_2O_5. All other solvents were bulk grade and were used after distillation. For photolyses, *n*-hexane, cyclohexane, and isopropyl alcohol were Burdick and Jackson "Distilled in Glass" spectroquality solvents and were used as received. *tert*-Butyl alcohol (Mallinckrodt) was dried over molecular sieve (Linde Type 4A, MCB) and distilled to give a sample with suitable UV transparency ($A_{254}^{1\text{cm}} = 0.004$), and no fluorescence emission between 250 and 500 nm when excited at 254 nm. Methanol (MCB or Fisher Spectroquality grades) showed suitable UV transmittance, but showed 254-nm stimulated emission from 287 to 500 nm at sensitive instrument settings. This emission could not be removed by passing the methanol through alumina, distillation, or distillation from $NaBH_4$. Burdick and Jackson methanol was superior in its emission characteristics, showing only traces of fluorescence emission between 287 and 350 nm. Acetone (Fisher spectroquality grade) was used as received. *p*-Xylene (MCB) was passed through a column of alumina (neat) and molecularly distilled.

***exo*-2-Benzonorbornenyl Chloride (exoClBNB).** Benzonorbornadiene (2 g, 0.014 mol) was stirred at room temperature in 10 mL of HCl (concn) for 14 h to give a black solution. This solution was diluted with 50 mL of H_2O and extracted four times with 30-mL portions of hexane. The hexane layers were combined, washed with 5% $NaHCO_3$ (2 × 100 mL) and H_2O (2 × 100 mL), and dried over $MgSO_4$. Removal of solvent

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(63) Del Bene, J. E.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807. Ellis, R. L.; Kuehnlenz, G.; Jaffé, H. H. *Theor. Chim. Acta* **1972**, *26*, 131.

(64) The hydroxy substituents were used in place of chlorine because of the lack of available parameters in the CNDO program.

(65) Del Re, G. *Theor. Chim. Acta* **1963**, *1*, 188.

(66) The bielectronic integrals were calculated with Gaussian 70: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. QCPE 238, Indiana University, Bloomington, In.

(67) Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383.

(68) Scully, F.; Nylund, T.; Palensky, F.; Morrison, H. *J. Am. Chem. Soc.* **1978**, *100*, 7352. Morrison, H.; Giacherio, D.; Palensky, F. *J. Org. Chem.* **1982**, *47*, 1051.

(69) Brainard, R. B. Ph.D. Thesis, Purdue University, 1970.

(70) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970; p 126.

left an oil which was dissolved in hexane and passed through a 10-g plug of alumina with hexane. Removal of solvent left 2.198 g (0.012 mol, 86%) of the desired product. The product had IR and ^{1}H NMR spectra identical with those reported.[71] This material was used in all preparative photoreactions without further purification; however, for all experiments in which quantitative data were obtained, the exoClBNB was purified by preparative VPC before use, using column A, 165 °C, retention time (t_R) 26 min. Neither VPC nor spectral data give any indication of contamination by endoClBNB.

***endo*-2-Benzonorbornenyl Chloride (endoClBNB).** 2-Chlorobenzonorbornadiene[71] (0.310 g, 1.76 mmol) was dissolved in 20 mL of absolute ethanol and stirred with 1.11 g of 5% Pd/BaSO$_4$ at room temperature using a "Brown^2" hydrogenator. After 3 h, VPC analysis on column H, 168 °C, showed benzonorbornene/2-chlorobenzonorbornadiene/endo-ClBNB = 16.0/5.83/5.0. The product was isolated by preparative VPC on column L, 145 °C, t_R 11.5 min, to give 173 mg (55.2%) of the chloride. The product shows ^{1}H NMR and IR spectra identical with those reported.[71] Neither VPC nor spectral data give any indication of contamination by exoClBNB.

***exo*-2-Benzonorbornenyl Mesylate (exoMsBNB).** Into a 15-mL, flame-dried, pear-shaped flask with side arm and septum was syringed 3 mL of dry pyridine followed by 65 μL (*d* 1.48, 0.827 mmol) of methanesulfonyl chloride. The solution was cooled in ice and into it was syringed 100 mg (0.625 mmol) of *exo*-benzonorbornen-2-ol[72] dissolved in 2 mL of dry THF. The solution was stirred overnight, after which the mixture was filtered and diluted with 50 mL of Et$_2$O. The ether layer was washed with saturated CuSO$_4$ solution (5 × 50 mL) and with H$_2$O (2 × 50 mL) and dried over MgSO$_4$. Removal of solvent left 107 mg (0.448 mmol, 72%) of the desired material as an oil, which solidified upon standing. The solid was recrystallized from hexane to give fine, white needles (mp 67–69 °C). Although this compound has been reported,[73] no spectral data were given. Therefore, the compound was identified by its following spectral data: IR (KBr pellet) 3.49, 7.58, 8.64, 9.97, 10.22, 10.62, 10.83, 11.12, 11.58, 12.05, 12.25, 13.18, 13.61 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.99–7.35 (m, aryl, 4 H), 4.65–4.82 (m, endo-2H, 1 H), 3.64 (m, bridgehead, 1 H), 3.41 (m, bridgehead, 1 H), 3.02 (s, methyl, 3 H), 1.85–2.15 (m, 4 H); *m/e* 238.064 (calcd for C$_{12}$H$_{14}$O$_3$S, *m/e* 238.066).

***endo*-2-Benzonorbornenyl Mesylate (endoMsBNB).** The procedure used was identical with that described for the exo isomer except that the mixture was stirred for 30 h. From 100 mg (0.625 mmol) of *endo*-benzonorbornen-2-ol[72,74] there was obtained 138.7 mg (5.81 mmol, 93%) of a pale yellow solid which upon five recrystallizations from Et$_2$O gave the desired product as white crystals (mp 85–85.5 °C). Although this compound has been reported,[73] no spectral data were given; therefore, it was identified by its following spectra data: IR (CH$_2$Cl$_2$) 3.35, 6.95, 7.05, 7.39, 7.49, 7.90, 8.49, 9.86, 10.35, 11.02, 11.45, 13.10, 13.9 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.00–7.45 (m, aryl, 4 H), 5.34–5.60 (m, exo-2H, 1 H), 3.60–3.80 (m, bridgehead, 1 H), 3.27–3.45 (m, bridgehead, 1 H), 2.85 (s, methyl, 3 H), 2.28–2.62 (m, exo-3H, 1 H), 1.80–2.06 (m, 1 H), 1.60–1.80 (m, 1 H), 1.10–1.40 (d of t, *J* = 13, 2 Hz, endo-3H); *m/e* 238.065 (calcd for C$_{12}$H$_{14}$O$_3$S, *m/e* 238.066).

***exo*-Benzonorbornen-2-yl Methyl Ether (6).** Into a 100-mL three-neck round-bottom flask equipped with a magnetic stir bar, rubber stopple, and N$_2$ inlet was added 110 mg (4.6 mmol) of NaH followed by 20 mL of dry THF and 325 mg (2.03 mmol) of *exo*-benzonorbornen-2-ol[70] dissolved in THF. This mixture was stirred for 2 h, after which 200 μL (3.2 mmol) of CH$_3$I was added and the solution was stirred overnight. Removal of solvent and excess CH$_3$I left a residue which was dissolved in 75 mL of ether; the ether layer was washed with water (2 × 50 mL) and dried over MgSO$_4$. Removal of solvent left 334 mg (1.92 mmol, 95%) of the desired product. An analytical sample was isolated from column A, 172 °C, t_R 16.5 min. Although this compound is formed in the ground-state methanolysis of exoClBNB, spectral data have not been reported. Therefore, it was identified by its following spectral data: IR (neat) 3.45, 6.89, 7.45, 7.85, 8.02, 8.19, 8.35, 9.05, 9.20, 9.89, 10.29, 10.47, 11.19, 13.40 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.00–7.45 (m, aryl, 4 H), 3.27–3.68 (m, bridgeheads, H 2-endo-H, 3 H), 3.42 (s, methyl, 3 H), 1.62–2.16 (m, 4 H); *m/e* 174.103 (calcd for C$_{12}$H$_{14}$O, *m/e* 174.104).

Preparative Photolysis of exoClBNB in Methanol. A solution (50 mL) of exoClBNB (2.8 × 10^{-2} M) in methanol was degassed for 20 min with argon and irradiated with 15 254-nm lamps in the Rayonet reactor for 150 min. The solution was neutralized with excess solid Na$_2$CO$_3$, the solvent was removed in vacuo, and the residue was taken up in hexane. The oil obtained from removal of the hexane was separated by VPC on column B, 180 °C, to give six products. Compound **1** (t_R 17.3 min) had spectral properties identical with those reported.[69] Compound **3** (t_R 79 min) had the following spectral data: IR (neat) 3.00, 3.40, 6.77, 9.11, 9.36, 9.68, 10.23, and 13.19 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.00–7.35 (m, aryl, 4 H), 3.58–3.88 (m, α to OH, 2 H), 3.20–3.41 (m, bridgeheads, 2 H), 1.22–1.96 (m, 6 H); *m/e* 174.101 (calcd for C$_{12}$H$_{14}$O, *m/e* 174.104). Oxidation with Jones reagent provided *exo*-benzonorbornenyl-2-carboxylic acid, identical with a known sample.[9] Compound **4** (t_R 64.5 min) was identical with an authentic sample prepared by hydroboration/oxidation of 2-methylenebenzornorbornene.[75] The synthetic sample had mp 96–98 °C with the following spectral data: IR (KBr pellet) 3.12, 3.40, 6.89, 7.58, 9.51, 9.86, 9.92, 10.45, 10.9, 13.3, and 14.05 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.0–7.3 (m, aryl, 4 H), 3.38 (m, bridgehead, 1 H), 3.28 (m, bridgehead, 1 H), 3.13 (dd, *J* = 10 and 6 Hz, endo methylene, 1 H), 2.78 (t, *J* = 10 Hz, endo methylene, 1 H), 2.3–2.8 (m, H$_{2ex}$), 2.07 (ddd, *J* = 11, 10, and 4 Hz, H$_{3ex}$), 1.87 (dq, *J* = 9 and 2 Hz, H$_{7en}$), 1.65 (dt, *J* = 9 and 1.5 Hz, H$_{7ex}$), 1.36 (s, hydroxy), 0.64 (ddd, *J* = 11, 4, and 2 Hz, H$_{3en}$). Anal. (C$_{12}$H$_{14}$O) C, H. Compound **5** is not detected under these conditions, but was seen at low conversions with a retention time of 15.8 min and was identified by comparison with an authentic sample. Compound **6** (t_R 31.6 min) has spectral data identical with those of an authentic sample (see above). Compound **7** (t_R 45.5 min) has the following spectral data: IR (neat) 3.41, 6.72, 7.35, 8.09, 8.37, 9.13, 10.22, 13.11 and 13.57 μm; ^{1}H NMR (CDCl$_3$, 360 MHz) δ 6.97–7.45 (m, aryl, 4 H), 4.60 (d, *J* = 2.16 Hz, H$_3$), 3.54 (s, methyl, 3 H), 3.07 and 3.01 (overlapping m, H$_1$ and H$_2$), 2.56 (m, 1 H), 2.31 (m,1 H), 1.72 (t, *J* = 8.65 Hz, 1 H), 1.57 (t, *J* = 8.64 Hz, 1 H); ^{1}H NMR (C$_6$D$_6$, 360 MHz) δ 4.39 (d, *J* = 2.16 Hz, 1 H), 3.28 (s, methyl, 3 H), 2.85 (q, *J* $\simeq$ 5.5 Hz, 1 H), 2.70 (m, 1 H), 2.25 (m, 1 H), 2.07 (m, 1 H) (the protons at δ 2.25 and 2.07 show *identical* coupling patterns), 1.85 (t, *J* = 8.65 Hz, 1 H), 1.41 (t, *J* = 8.65 Hz, 1 H); *m/e* 174.103 (calcd for C$_{12}$H$_{14}$O, *m/e* 174.104). The product was also prepared by photolysis of a basic methanol solution of benzonorbornen-2-one tosylhydrazone; comparison was made on column H, 168 °C (t_R 14.4 min) and column F, 172 °C, (t_R 23.1 min). The ^{1}H NMR spectrum is virtually identical with that of 1,3-methanonaphthalen-4-yl *tert*-butyl ether, prepared by photolysis of ExoMsBNB in *tert*-butyl alcohol (see detailed NMR assignments below). Compound **8** (t_R 23.7 min) had an identical retention time with an authentic sample on column B, column H (162 °C; t_R 8.3 min), and column I (120 °C; t_R 2.5 min).

Preparative Photolysis of exoClBNB in Isopropyl Alcohol. A 50-mL Vycor tube containing 45 mL of a 0.107 M exoClBNB solution in isopropyl alcohol and 300 mg of NaHCO$_3$ was degassed with argon for 30 min and irradiated with 15 254-nm lamps in a Rayonet for 5 h. Upon removing solvent, dissolving the residue in Et$_2$O, filtering, and removing solvent, there was left 660.58 mg of a clear, yellow-green oil. A 568.24-mg portion of the photoproduct mixture was eluted on a 15 × 2.5 cm column of silica gel (60–200 mesh), in the following manner (taking 20-mL fractions): 400 mL of hexane, 200 mL of 5% benzene in hexane, 200 mL of 5% benzene plus 5% methanol in hexane, and 300 mL of 5% benzene plut 10% methanol in hexane. There was obtained 266.9 mg of a clear, colorless oil in fractions 1–19, which showed three peaks isolable on column A, 170 °C, and shown to be **1**, **5**, and **8**. Fractions 38–55 (285.5 mg) gave a yellow oil which showed five peaks on VPC. Each was isolated by preparative VPC from column N, 155 °C.

***exo*-Benzonorbornen-2-yl Isopropyl ether ("6")** (t_R 15.5 min) had the following data: IR (neat) 3.41, 6.81, 7.28, 7.51, 8.68, 8.83, 9.21, 9.41, 9.98, 13.26 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.98–7.35 (m, aryl, 4 H), 3.68 (heptet, *J* $\simeq$ 7 Hz) overlapping 3.54–3.70 (m, endo-2-H) (2 H total), 3.31 (m, bridgeheads, 2 H), 1.37–2.20 (m, 4 H), 1.22 (d, *J* $\simeq$ 7 Hz) overlapping 1.18 (d, *J* $\simeq$ 7 Hz) (6 H total); *m/e* 202.133 (calcd for C$_{14}$H$_{18}$O, *m/e* 202.136). This product was independently synthesized by the Ag$^+$-assisted ground-state solvolysis of exoClBNB. **1,3-Methanonaphthalen-4-yl isopropyl ether ("7")** (t_R 20 min) could only be isolated in sufficient quantity for a high-field NMR spectrum (360 Mz, CDCl$_3$): δ 6.90–7.41 (m, aryl, 4 H), 4.75 (d, *J* = 3.28 Hz, 1 H), 3.91 (heptet, *J* = 6.10 Hz, 1 H), 3.07 (q, *J* = 5.46 Hz, 1 H), 2.86 (m, 1 H), 2.52 (1 H) and 2.30 (1 H) (identical multiplets), 1.75 (t, *J* = 8.46 Hz, 1 H), ~1.57 (multiplicity uncertain because of overlapping with H$_2$O peak), 1.41 (d, *J* = 6.10 Hz, CH$_3$), 1.29 (d, *J* = 6.10 Hz, CH$_3$). **2-(Benzonorbornen-*endo*-2-yl)-2-hydroxypropane ("4")** (t_R 23.0 min) had spectral data identical with those reported[73] and was identified by comparison with an independently synthesized sample[75] (see below). **2-(Benzonorbornen-*exo*-2-yl)-2-hydroxypropane ("3")** (t_R 29 min) had IR (neat) 2.98, 3.41,

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(74) Trittle, G. L. Ph.D. Thesis, Purdue University, 1966.

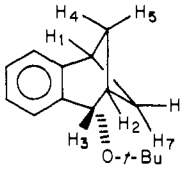
(75) Nylund, T. W. Ph.D. Thesis, Purdue University, 1978.

6.79, 7.28, 7.78, 8.58, 9.82, 10.60, 13.12, 13.55 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 7.00–7.32 (m, aryl, 4 H), 3.25–3.45 (m, bridgeheads, 2 H), 1.20–2.05 (m) overlapping 1.33 (s, methyl) overlapping 1.25 (s, methyl) (12 H total); *m/e* 202.137 (calcd for $C_{14}H_{18}O$, *m/e* 202.136). The compound was independently synthesized by Wittig olefination of 2-benzonorbornen-2-one with ethyltriphenylphosphonium iodide, hydroboration, Jones oxidation, and Grignard addition of methylmagnesium iodide (a mixture of "**3**" and "**4**" is obtained).[75]

Preparative Photolysis of exoClBNB in *tert*-Butyl Alcohol. Irradiation of an argon degassed, 0.075 M solution of exoClBNB (45 mL) in a Vycor photolysis tube for 5 h with 15 254-nm lamps in the Rayonet gave a solution which was neutralized with solid NaHCO$_3$ (300 mg), evaporated in vacuo, taken up in ether (100 mL), washed with water (1 × 60 mL), and dried over MgSO$_4$. Removal of solvent left 531 mg of a yellow oil. Five of the seven photoproducts detected in the photoproduct mixture had already been isolated by VPC and structurally characterized in detail: 1, **5**, and **8** from the photoreaction of exoClBNB in methanol, and *exo*-benzonorbornen-2-yl *tert*-butyl ether ("**6**") and 1,3-methanonaphthalen-4-yl *tert*-butyl ether ("**7**") from the photoreaction of exoMsBNB in *tert*-butyl alcohol (see below). The remaining two photoproducts were isolated from column N, 160 °C. 1-**(Benzonorbornen-*endo*-2-yl)-2-methyl-2-hydroxypropane** ("4") had IR (neat) 2.97, 3.40, 6.80, 7.25, 8.61, 8.88, 10.90, 13.24 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.90–7.26 (m, aryl, 4 H), 3.12–3.32 (m, bridgeheads, 2 H), 2.00–2.55 (m, exo-2-H and exo-3-H, 2 H), 1.00–1.90 (m) overlapping 1.12 (s, 12 H total); *m/e* 213.152 (calcd for $C_{15}H_{20}O$, *m/e* 213.151).

1-**Benzonorbornen-*exo*-2-yl)-2-methyl-2-hydroxypropane** ("**3**") had IR (CCl$_4$) 2.97, 3.41, 6.79, 7.29, 8.65, 8.88, 10.42, and 10.95 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.97–7.30 (m, aryl, 4 H), 3.29 (m, bridgehead 4H, 1 H), 3.08 (m, bridgehead 1H, 1 H), 1.41–1.87 (m, 7 H), 1.22 (s, methyls, 6 H); *m/e* 213.152 (calcd for $C_{15}H_{20}O$, *m/e* 216.151). This compound was independently synthesized by oxidation of *endo*-benzonorbornen-2-yl-methanol (4) with pyridinium chlorochromate, Wittig olefination with isopropyltriphenylphosphonium iodide, and oxymercuration–demercuration.

Preparative Photolysis of exoMsBNB in *tert*-butyl Alcohol. Irradiation of 150 mL of a 0.011 M exoMsBNB solution in *tert*-butyl alcohol, in two 50-mL and three 25-mL Vycor photolysis tubes (after degassing 15 min with argon), with 16 254-nm lamps in the Rayonet reactor for 8 h, gave a solution which was diluted with 200 mL of water and extracted with ether (4 × 100 mL). The ether layers were combined and washed with water (2 × 60 mL) and 5% NaHCO$_3$ (1 × 60 mL) and dried over MgSO$_4$. Removal of ether in vacuo left 432.2 mg of an orange-yellow oil which by VPC on column A (170 °C) showed four products, two of which had been characterized as **5** and **8** (t_R 13 and 18 min, respectively). The remaining two photoproducts were isolated from column A (170 °C). (No photoproducts derived from a free radical process could be detected on columns H or K.) ***exo*-Benzonorbornen-2-yl *tert*-butyl ether** ("**6**") (t_R 28 min): IR (neat) 3.36, 6.01, 7.22, 7.34, 8.36, 8.60, 9.28, 9.44, 9.75, 10.00, 10.22, 13.21, 13.34 μm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 6.90–7.25 (m, aryl, 4 H), 3.61 (m, endo-2-H, 1 H), 3.20 (m, bridgehead-4-H, 1 H), 3.08 (m, bridgehead-1-H, 1 H), 1.48–2.16 (m, 4 H), 1.19 (s, *t*-Bu, 9 H); *m/e* 216.150 (calcd for $C_{15}H_{20}O$, *m/e* 213.151). This compound was independently synthesized via ground-state solvolysis of ExoMsBNB. **1,3-Methanonaphthalen-4-yl *tert*-butyl ether** ("**7**"): IR (neat) 3.40, 6.70, 6.83, 7.30, 8.10, 8.34, 9.38, 9.74, 13.14, 13.56 μm; ^{1}H NMR (CDCl$_3$, 360 MHz) δ 6.75–7.35 (m, aryl, 4 H), δ_3 4.83 (d, $J_{32} = 3.2$ Hz), δ_1 3.00 (q, $J_{12} \simeq J_{15} = J_{16} \simeq 5.8$ Hz), δ_2 2.69 (m, $J_2 \simeq 5.8$, $J_{23} = 3.2$, $J_{25} = J_{26} \simeq 7.0$ Hz), δ_5 2.42 (m, $J_{51} \simeq 5.8$, $J_{52} \simeq 7.0$, $J_{54} \simeq 8.3$ Hz), δ_6 2.26 (m, $J_{61} \simeq 5.8$, $J_{62} \simeq 7.0$, $J_{67} \simeq 8.3$ Hz), δ_7 1.72 (t, $J_{74} = J_{76} \simeq 8.3$ Hz), δ_4 1.53 (t, $J_{45} = J_{47} \simeq 8.3$ Hz), δ 1.35 (s, *t*-Bu, 9 H), where the following numbering applies:



m/e 216.151 (calcd for $C_{15}H_{20}O$, *m/e* 216.151).

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Registry No. 1, 4486-29-7; **3**, 73176-49-5; "3" (R′ = Cl), 7605-04-1; "3" (R′ = CH$_3$SO$_2$O), 31351-14-1; "**3**" (R′ = OH), 13153-47-4; "**3**" (R′ = OPr), 84988-56-7; "**3**" (R′ = C(CH$_3$)$_2$OH), 85027-46-9; "**3**" (R′ = *t*-BuO), 73151-76-5; 4, 69103-46-4; "4" (R′ = Cl), 7605-05-2; "4" (R′ = CH$_3$SO$_2$O), 31351-15-2; "4" (R′ = OH), 13153-75-8; "4" (R′ = C(CH$_3$)$_2$OH), 84988-58-9; "4" (R′ = CH$_2$C(CH$_3$)$_2$OH), 84988-59-0; **5**, 4453-90-1; **6**, 73151-73-2; **7**, 73151-74-3; "**7**" (R″ = Pr), 84988-57-8; "**7**" (R″ = *t*-Bu), 73151-75-4; 2-chlorobenzonorbornadiene, 7605-08-5; benzonorbornen-2-one tosylhydrazone, 84988-55-6; benzonorbornen-2-one, 7374-90-5; 2-methylenebenzonorbornene, 7525-44-2; ethyltriphenylphosphonium iodide, 4736-60-1; (*E*)-2-heptene, 14686-13-6; oxygen, 7782-44-7; water, 7732-18-5; PrSH, 107-03-9; MeOH, 67-56-1; *i*-PrOH, 67-63-0; *t*-BuOH, 75-65-0.

Optical Rotatory Dispersion Studies. 135.[1] Synthesis and Chiroptical Properties of (*S*)- and (*R*)-(3-$^{2}H_{1}$)-2,2-Dimethylcyclobutanone. Evidence for Conformational Effects in Substituted Cyclobutanones

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Abstract: The synthesis, proof of absolute configuration, and other chiroptical properties of both (*S*)- and (*R*)-(3-$^{2}H_{1}$)-2,2-dimethylcyclobutanone (**5** and **6**) are reported. Both **5** and **6** exhibited temperature-dependent Cotton effects in their CD spectra characteristic of compounds having conformational mobility.

The use of circular dichroism (CD) as a tool for studying subtle conformational effects in cyclic ketones having isotopically engendered chirality is now well established.[2] However, of the examples reported so far, attention has focused mainly on the cyclohexanone and cyclopentanone systems with deuterium as the

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(1) For preceding paper, see ref 4b.

(2) For review, see: Barth, G.; Djerassi, C. *Tetrahedron* **1981**, *37*, 4123–4142.

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