Photolytic Cleavage of Remote Functional Groups in Polyfunctional Molecules. Photolysis of *exo*- and *endo*-Benzobicyclo[2.2.2]octen-2-yl Chloride[1a]

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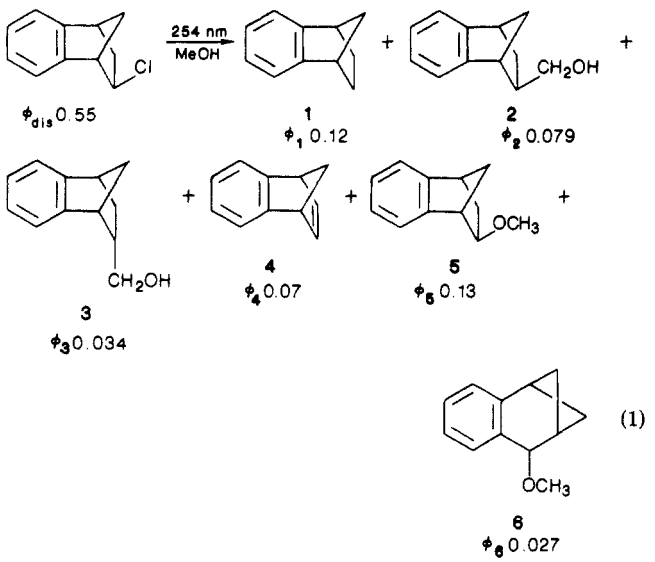
The aryl-induced photolytic cleavage of a remote C–Cl bond, earlier reported for the 2-position in the benzonorbornenyl series, is extended to the 2-position of the title compounds (*exo*-BBCl and *endo*-BBCl). Cleavage with 254-nm excitation is an efficient reaction (ϕ_{dis} = 0.45 and 0.005, exo and endo, respectively), involving the aryl singlet excited state. Radical and carbocation derived products are observed (eq 3), with the latter including an olefin (**8**), a cyclopropane (**9**), and rearranged ethers (**10** and **13**) attributed to "hot" cation intermediates. The rate constants for C–Cl cleavage are as follows: exo [2.2.1] 1.1×10^9 s^{-1}; exo [2.2.2], 3.8×10^8 s^{-1}; endo [2.2.1], 1.7×10^6 s^{-1}; endo [2.2.2], 2.7×10^5 s^{-1}. These rates are discussed within the context of previously proposed mechanisms.

As part of a broad program concerned with the photochemical and photophysical consequences of intramolecular interactions between nonconjugated functionalities, we have been studying the stereoelectronically controlled activation of C–Cl cleavage in benzobicyclic substrates.[2-4] An example is given in eq 1 where excitation of the aryl chromophore effects cleavage of the homobenzylic substituent. Both radical and carbocation derived products



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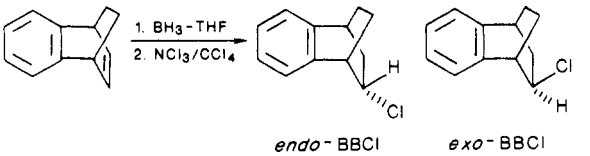
are formed, with the latter including a rearrangement product (**6**) not observed in ground-state solvolyses and to which we have attributed a "hot" carbocation precursor.[2b,c] This reaction has been shown to derive from the aryl excited singlet state, and the photoreactivity of the exo isomer is evident in a very large reduction of both ϕ_f and $^1\tau$ relative to benzonorbornene. By contrast, the endo isomer is considerably less reactive, with the k_r for C–Cl cleavage (1.7×10^6 s^{-1}) more than 600-fold smaller than that (1.1×10^9 s^{-1}) for the exo isomer.

We were led to extend these observations to the benzo[2.2.2] series for two reasons: (1) Though there are several examples of aryl photoactivated C–Cl cleavage in related [2.2.2] bicyclic hydrocarbons,[4] the substrates have been more complex (for example, dibenzo, benzo/vinyl, etc.), and a study of the basic ring system, comparable to our analysis in the [2.2.1] series, has not yet been done; (2) we have previously observed[5] a dramatic reduction in one of the several interactions available to an aryl excited singlet state with an olefin moiety, due to the change in interplanar angle which accompanies the expansion of a [2.2.1] to a [2.2.2] framework (see below), and we speculated that a substantial change in the exo/endo rate ratio might likewise be observed for C–Cl cleavage.

Results

A. Photochemistry of *exo*-Benzobicyclo[2.2.2]octen-2-yl Chloride (*exo*-BBCl). Synthesis. The title compound was prepared by the reaction sequence given in eq 2.[6] The exo and endo isomers are formed in a 55:45 ratio and were separated by preparative GLC. The ^{1}H NMR spectra of *exo*-BBCl has been reported.[7]



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The corresponding exo and endo alcohols were prepared in a 70:30 ratio by oxidation of the organoborane mixture. The ^{1}H NMR spectra were identical with those reported[7] and include a 0.1 upfield shift for the endo-2 proton in the exo alcohol and a distinct (ddd) splitting pattern for the

(1) (a) Organic Photochemistry. 63. Part 62: Morrison, H. *Photodermatology* **1985**, *2*, 158. Part 61: Morrison, H.; Mauclair, B.; Deibel, R. M.; Pandey, G.; Baird, W. M. *Photochem. Photobiol.* **1985**, *41*, 251. (b) Purdue University. (c) Ecole Normale Superieure de Saint Cloud.

(2) (a) Morrison, H.; Miller, A. *J. Am. Chem. Soc.* **1980**, *102*, 372. (b) Morrison, H.; Miller, A.; Pandey, B.; Pandey, G.; Severance, D.; Strommen, R.; Bigot, B. *Pure Appl. Chem.* **1982**, *54*, 1723. (c) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.* **1983**, *105*, 2398. (d) Morrison, H.; De Cardenas, L. M. *Tetrahedron Lett.* **1984**, *25*, 2527.

(3) For related studies, see: Cristol, S. J.; Bindel, T. H.; Hoffmann, D.; Aeling, E. O. *J. Org. Chem.* **1984**, *49*, 2368 and previous papers in the series. See also: Jaeger, D. A.; Bernhardt, E. A. *Tetrahedron Lett.* **1983**, 4521.

(4) For a review, see: Cristol, S. J.; Bindel, T. H. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker; New York, 1983; Vol. 6, pp 327-415.

(5) Neidigk, D.; Morrison, H. *J. Chem. Soc., Chem. Commun.* **1978**, 600.

(6) For the use of NCl_3/CCl_4 as a method of introducing chlorine through a free radical pathway, see: Brown, H. C.; DeLue, N. R. *J. Organomet. Chem.* **1977**, *135*, C57. DeLue, N. R., Ph.D. Thesis, Purdue University, 1977.

(7) Tanida, H.; Miyazaki, S. *J. Org. Chem.* **1971**, *36*, 425.

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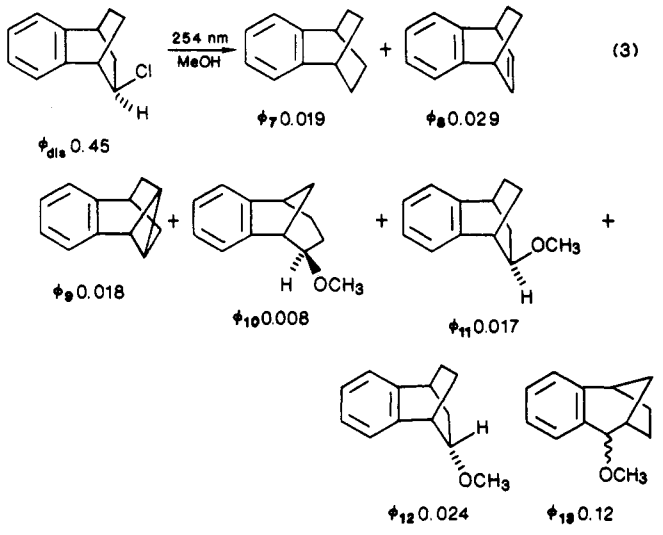
exo-3 proton in the endo alcohol. These characteristics are accentuated in the respective chlorides.[8] Further support for the assignments of configuration derived from solvolyses of 0.03 M solutions of the chlorides in methanol/water (9:1) mixtures containing 0.029 M silver nitrate for 15 h at room temperature.[9] The relative rate ratio for loss of the two isomers was exo/endo = 2.2 (the reported[7] rate ratio for solvolysis of the exo and endo brosylates is 2.9).

Attempts to synthesize these chlorides by HCl addition (SO_2(l)) or by substitutive chlorination of the alcohols (Ph_3P/CCl_4 or $SOCl_2$) gave mixtures containing appreciable amounts of rearranged product (*exo*-benzobicyclo[3.2.1]octen-2-yl chloride and *exo*- + *endo*-3,4-benzobicyclo[3,2,1]octen-2-yl chloride) with little or no *endo*-BBCl.[10]

Photolysis of *exo*-BBCl in Methanol. Irradiation of a 0.01 M solutioin in methanol with 254-nm light results in seven identifiable photoproducts (plus HCl and ethylene glycol). The reaction, with quantum efficiencies, is given in eq 3.[11] All products were identified by mass spectral and VPC comparison with independently synthesized samples (cf. Experimental Section).



Attempted Triplet Photosensitization of *exo*-BBCl in Methanol. *exo*-Benzobicyclo[2.2.1]hepten-2-yl chloride has been shown[2c] to be susceptible to triplet sensitization, albeit rather inefficiently. Photolysis of 0.01 M solutions of *exo*-BBCl (and *endo*-BBCl) and the *exo*-benzonorbornenyl chloride in methanol were conducted with 300-nm light and 10% (by volume) of acetone as the photosensitizer. Analyses showed the [2.2.2] substrates to be unaffected while the [2.2.1] homologue showed a 19% loss of starting material.

Table I. Emission Data for *exo*- and *endo*-BBCl

compd	solvent	ϕ_f	$^1\tau$, ns	$10^{-6}k_f$, s
exo-BBCl	cyclohexane	0.09_5	13.0	7.3
	methanol	0.01_5	1.2 ± 0.5	12.5
endo-BBCl	cyclohexane	0.12	21.7	5.5
	methanol	0.11	18.3	6.0
7	cyclohexane	0.20	25.0	8.0

Effect of (*E*)-2-Heptene on *exo*-BBCl Photochemistry in Methanol. Aliquots (4 mL) of a solution of *exo*-BBCl in methanol (9×10^{-3} M) were placed in four matched quartz tubes and degassed for 25 min with argon. (*E*)-2-Heptene (50 μL, 0.09 M) was added to two of the tubes, and all four were irradiated for 20 min with the low-pressure mercury lamp. GLC analysis indicated minimal quenching of starting material disappearance in the tubes containing heptene, and the product "fingerprint" was identical in the two sets of tubes. That the *exo*-BBCl triplet is completely quenched under these conditions is evidenced by the suppression of the *exo*-BBCl triplet-sensitized di-π-methane rearrangement of 8, normally observed as a secondary photoproduct.[12]

Photolysis of *exo*-BBCl in Cyclohexane. *exo*-Benzobicyclo[2.2.1]hepten-2-yl chloride exhibits C–Cl cleavage in cyclohexane, with ϕ_{dis} ca. 2-fold less than in methanol.[2c] However, under conditions where there was a 27% loss of 0.01 M *exo*-BBCl in methanol (254-nm excitation, low-pressure mercury lamps, 9 min), a similar irradiation of a 0.01 M cyclohexane solution of *exo*-BBCl gave no evidence of reaction. Prolonged irradiation (254 nm using a Rayonet reactor) gave benzobicyclo[2.2.2]-octene in 60% yield as the only detectable product.

B. Photochemistry of *endo*-Benzobicyclo[2.2.2.]-octen-2-yl Chloride (*endo*-BBCl). Synthesis. The title compound was prepared as indicated above in eq 2.

Photochemistry of *endo*-BBCl in Methanol. Irradiation of a 0.01 M solution in methanol with 254-nm light resulted in the formation of the same products isolated from the *exo*-BBCl reaction (cf. eq 3). The relative amounts of these products were **7** (10%), **8** (11%), **9** (2%), **10** (21%), **11** (42%), **12** (trace), and **13** (14%). By way of comparison, the exo isomer gave **7** (8%), **8** (12%), **9** (8%), **10** (4%), **11** (7%), **12** (10%), and **13** (51%) (see eq 3). The ϕ_{dis} for *endo*-BBCl was found to be 0.005.[13]

C. Spectroscopy. The absorption spectra of *exo*- and *endo*-BBCl are unexceptional, with ϵ_{254} 510 and 381 M^{-1} cm^{-1}, respectively. The fluorescence quantum efficiencies (ϕ_f), singlet lifetimes ($^1\tau$), and rate constants for fluorescence ($k_f = \phi_f/{}^1\tau$) are gathered in Table I. Data are presented for both cyclohexane and methanol solutions, with data for benzobicyclo[2.2.2]octene (**7**) included for purposes of comparison.

Discussion

Viewed in the light of our previous report on the *exo*- and *endo*-2-benzonorbornenyl chlorides,[2] we note that the major features of the [2.2.1] series are reproduced in the current study. Thus, the reaction shown in eq 3 for *exo*-BBCl confirms that the aryl-sensitized photolytic cleavage of the remote (i.e., β) C–Cl bond carries over into the basic [2.2.2] series.[3] As was noted with the benzonorbornenes, both free radical and carbocation derived products are observed, but two observations suggest that the tendency

(8) For the ^{1}H NMR spectral data of related *exo*- and *endo*-tetrafluorobenzobicyclo[2.2.2]octen-2-yl derivatives, see: (a) Slyn'ko, N. M.; Derendyaev, B. G.; Kollegova, M. I.; Barkhash, V. A. *Zh. Org. Khim.* **1973**, *9*, 2266. (b) Spivak, A. Y.; Chertok, V. S.; Derendyaev, B. G.; Barkhash, V. A. *Zh. Org. Khim.* **1973**, *9*, 2288. (c) Spivak, A. Y., Lobanova, T. P.; Chertok, V. S.; Podgornaya, M. I.; Barkhash, V. A. *Zh. Org. Khim.* **1976**, *12*, 1210.

(9) There is essentially no loss of the chlorides over this time period in the absence of the silver salt.

(10) For leading references on rearrangements from the [2.2.2] to the [3.2.1] bicyclic ring system, see: Monti, S. A.; Chen, S. C.; Yang, Y. L.; Yuan, S. S.; Bourgeois, O, P. *J. Org. Chem.* **1978**, *43*, 4062. See also ref 7.

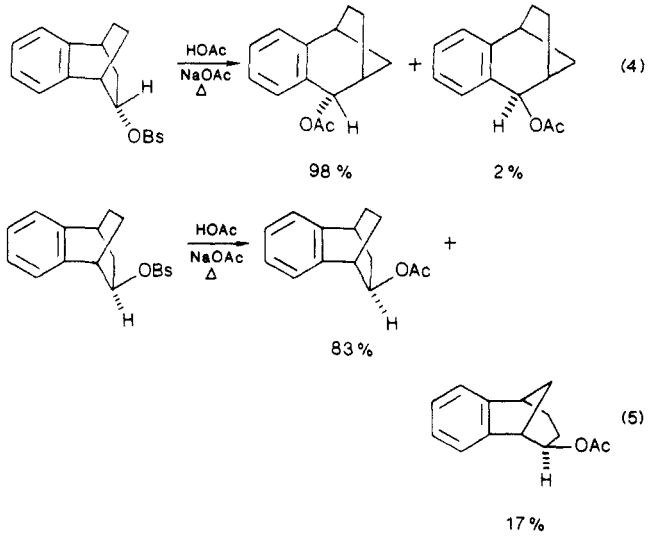
(11) The sum of the ϕ's for product formation represents 52% of ϕ_{dis}, by comparison with 84% obtained for *exo*-benzobicyclo[2.2.1]hepten-2-yl chloride. We observe, but have not identified, high-boiling products which may include hydroxymethyl compounds akin to **2** and **3** in eq 1. However, we estimate these longer retention time peaks only account for ca. 15% of the ϕ_{dis}.

(12) For the di-π-methane chemistry of analogues of **8**, see: Eckhard, I. F.; Heaney, H.; Marples, B. A. *Tetrahedron Lett.* **1969**, 3273. Hart, H.; Love, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4592. Triplet sensitization of **8** with acetophenone also leads to this product.

(13) The sum of the ϕ's for product formation equals 2×10^{-3}, i.e., 40% of ϕ_{dis} (cf. footnote 11).

to generate radical products has become significantly more disfavored, i.e., the reduction of *exo*-BBCl to the hydrocarbon 7 represents only 4% of ϕ_{dis} by contrast with the 22% observed for *exo*-2-benzonorbornenyl chloride, and the photoreactivity of *exo*-BBCl in cyclohexane (where only free radical products would be expected) is much more greatly reduced relative to reactivity in methanol than the factor of 2 observed for the exo [2.2.1] analogue. Cristol has reported[14,15] the complete absence of radical products in the photolysis of several related [2.2.2] and [3.2.1] systems, and it thus appears that the extensive formation of such products is characteristic of the benzonorbornenyl chloride.[16]

As was observed with the [2.2.1] substrates, extensive rearrangement accompanies these aryl-activated photosolvolyses. The migration of carbon–carbon bonds both syn and anti to the nucleofuge is evident, with the syn mode (51% for *exo*-BBCl to **13**; 21% for *endo*-BBCl to **10**) predominating over the anti mode (4% for *exo*-BBCl to **10**; 14% for *endo*-BBCl to **13**). This predominance of syn migration in the photolytic rearrangement contrasts with the totally anti rearrangement observed in the ground-state solvolyses of analogous derivatives (for example, eq 4 and 5).[7] Syn migration is also evident in the photolysis of



benzonorbornenyl chloride (cf. **6** in eq 1) though here anti migration still dominates.[2d] The preponderance of syn migration in [2.2.2] substrates has been noted for other analogues[15] and would appear to be general to this framework.

Cristol has proposed[7] that the principal origin of syn migration is via rearrangement proceeding in concert with loss of chloride ion. We have suggested[2c] that these syn rearrangements may result from the formation of a hot carbocation (i.e., unsolvated and possibly partially pyramidal) akin to that observed in the direct photolyses of alkyl halides.[17] Such hot ions characteristically deprotonate to olefins,[17] and olefin formation accompanies

(14) Cristol, S. J.; Klein, M. W.; Hendewerk, M. H.; Daussin, R. D. *J. Org. Chem.* **1981**, *46*, 4992.
(15) Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *J. Am. Chem. Soc.* **1983**, *105*, 7337.
(16) It is not obvious why this should be so, and a satisfactory explanation must await as yet unavailable data on the relative ease of formation of radicals at the 2-position in these systems.
(17) (a) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135. Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131. (b) It has been noted that carbene formation can make a minor contributioin to the formation of elimination products, cf.: Kropp, P. J.; Sawyer, J. A.; Snyder, J. J. *J. Org. Chem.* **1984**, *49*, 1583. We cannot rule out some involvement of carbene in the present study, though there was no evidence of such in the [2.2.1] photolysis.[2c]

Table II. Rate Constants for Photolytic Cleavage of the Benzobicyclo-2-yl Chlorides

chloride	k_r, s^{-1} [a]	chloride	k_r, s^{-1} [a]
exo [2.2.1]	1.1×10^9	endo [2.2.1]	1.7×10^6
exo [2.2.2]	3.8×10^8	endo [2.2.2]	2.7×10^5

[a] From $k_r = \phi_r/{}^1\tau$.

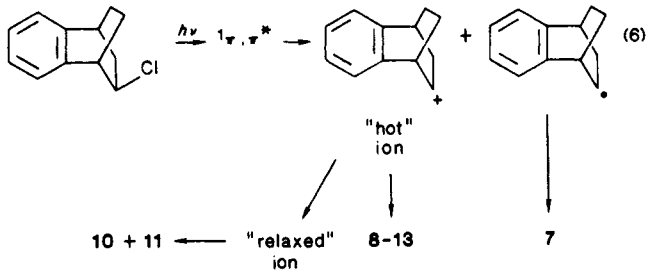
the photosolvolysis of both the [2.2.1] (eq 1) and [2.2.2] (eq 3) substrates. Furthermore, both *exo*- and *endo*-BBCl produce the cyclopropane **9**, and the formation of cyclopropanes from hot carbocations has been well documented.[17a,19] The cyclopropane is noticeably absent from the reported ground-state solvolyses (eq 4 and 5).[18] It is also interesting to note that the unrearranged acetate from solvolysis of the exo brosylate is entirely exo (eq 5), as expected from an extensively aryl stabilized carbocation, whereas the endo ether (**12** in eq 3) is actually favored in the photosolvolysis of *exo*-BBCl.[20,21] We therefore believe these new data lend further support to our proposal[2c] that a hot carbocation is formed in these photosolvolyses, the rearrangement and capture of which competes with decay to a relaxed, solvated cation.[22]

As previously observed in the benzonorbornenyl series,[2] the photochemical and photophysical evidence indicates that C–Cl cleavage derives from an excited singlet state. The reaction of *exo*-BBCl can neither be quenched nor sensitized,[23] and this substrate has an appreciably reduced ϕ_f and ${}^1\tau$ by comparison with the alkane **7** and the less reactive endo isomer (cf. Table I). Using $k_r = \phi_r/{}^1\tau$, where k_r is the rate constant for cleavage and $\phi_r = \phi_{dis}$,[24] the rate constants for cleavage are gathered in Table II.[25] These rate constants indicate (1) the [2.2.2] substrates are a factor of three or more less reactive than their [2.2.1] analogues, presumably a consequence of the increase in the interplanar angle in the larger bicyclic (for example, 110.8° in bicyclo[2.2.1]heptene[26] to 121.2° in bicyclo[2.2.2]octene[27])[28] and (2) the large exo/endo rate ratio (647) characteristic of the photosolvolysis of the [2.2.1] substrates is magnified (to 1400) in the [2.2.2] series (i.e., the endo [2.2.2] rate has dropped to a greater extent relative to its [2.2.1] homologue than has the exo isomer).[29] The latter observation is in

(18) It has been suggested that elimination (and also presumably cyclopropane formation) may be a consequence of the change in nucleofuge and reaction medium rather than the formation of a hot ion, cf.; Cristol, S. J.; Ali, M. Z. *Tetrahedron Lett.* **1983**, *24*, 5839.
(19) Keating, J. T.; Skell, P. S. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds., Interscience: New York, Vol. II, pp 573–654, 1976. See also Friedman, L., in the reference, pp 655–714.
(20) Note that by contrast with norbornenes, endo access is much more favorable in the [2.2.2] series, cf. eq 2.
(21) It is striking that the ground-state solvolysis of the exo brosylate occurs with minimal rearrangement, while rearrangement products constitute 55% of the products isolated from the photosolvolysis.
(22) Cristol[3,4] has proposed that biradical–cations precede the formation of the "relaxed" carbocations in these reactions; see further discussion below.
(23) If one assumes the [2.2.1] and [2.2.2] benzobicyclo chlorides to have comparable triplet energies, the acetone sensitization experiments indicate the [2.2.2] triplets to be appreciably less reactive than the [2.2.1] triplets.
(24) A reasonable assumption since only traces of *endo*-BBCl are occasionally observed from *exo*-BBCl so that internal return would appear to be minimal.
(25) The value of k_r for the endo [2.2.1] isomer is slightly higher than the 1.5×10^6 s^{-1} miscomputed in ref 2c.
(26) Chiang, J. F.; Chiang, R.; Lu, K. C.; Sung, E.-M.; Harmony, M. D. *J. Mol. Struct.* **1977**, *41*, 67.
(27) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1783.
(28) This increase in the interplanar angle and consequent reduction in available aryl participation during the departure of the exo nucleofuge is presumably the source of the very small exo/endo rate ratio for ground-state solvolysis of benzo[2.2.2] derivatives via à vis benzo[2.2.1] (i.e., 2.8 vs. 15 000).[7] Our MM2 derived interplanar angles were 112.8° and 120.2°.

marked contrast with the ground-state solvolytic exo/endo rate ratios.[27]

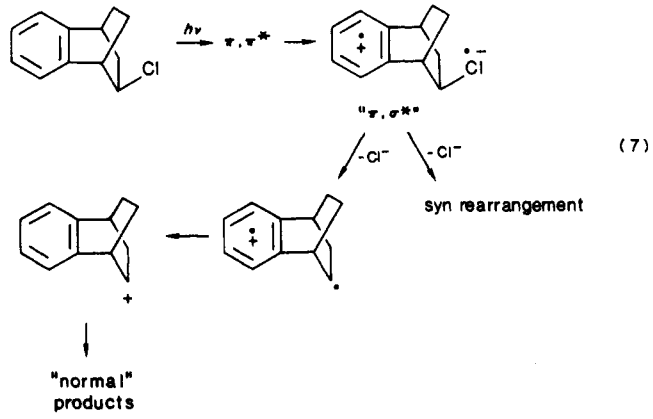
Exactly how the C–Cl bond becomes activated by 254-nm excitation remains unclear. We have proposed[2c] the use of the "natural correlation concept"[30] which views cleavage as resulting from the *continuous transformation* of the excited species from an initial π,π^* state into a dissociative, primarily σ,σ^* configuration as the carbon–nucleofuge bond weakens. This proposal and our earlier discussion lead to the mechanism outlined in eq 6.[31] The



(6)

key to relative reactivity is the interaction term $\langle\pi,\pi^*|\sigma,\sigma^*\rangle = H_{AB}$, which determines the degree of mixing at the transition state and therefore the extent of avoided crossing.[2c] Such terms are not readily calculated rigorously; approximations derived as in our earlier paper[2c] qualitatively predict a reduced rate for exo [2.2.2] vs. exo [2.2.1] but do *not* explain the very low rate for endo [2.2.2] (and thus the high exo/endo rate ratio).[32]

An alternative proposal is that suggested by Cristol and co-workers[3,4,15] and invokes activation via a *stepwise* electron transfer from the aryl π^* MO to the C–X σ^* MO (i.e., formation of a "π^*,σ^* zwitterionic biradical"). This species is then proposed to either undergo concerted (primarily syn) rearrangement or cleavage to a biradical cation. The latter species is then proposed to undergo intramolecular electron transfer to form a relaxed carbocation (cf. eq 7). Note that the hot cation intermediate



(7)

we discussed above is *not* included in Cristol's proposal though it could presumably be generated from the zwitterionic biracical.[33,35]

Studies designed to further probe the mechanistic details and stereoelectronic constraints of these photosolvolyses are in progres.

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained using a Perkin-Elmer R-32 (90 MHz), a Varian XL-200 (220 MHz), or a Nicolet NT-470 (470 MHz) spectrometer. ^{13}C NMR spectra were recorded on the XL-200 at 50 MHz with carbon assignments assisted by the APT ("attached proton test").[36] Chemical shifts are reported in ppm relative to Me_4Si with atom numbering as shown for compound **9**. Mass spectra were obtained with a Finnigan automated gas chromatograph EI/CI mass spectrometer. Ultraviolet spectra were recorded with a Cary Model 17D spectrometer. Vapor-phase chromatography utilized Varian Models 90-P, A-90-P, and A-700 for qualitative or preparative work and Models 1200 or 1400 FID chromatographs with a Hewlett-Packard 3380 or 3380-A digital integrator for quantitative studies. Flow rates were 60 and 30 mL/min, respectively, unless otherwise specified. Columns were as follows: (A) 15 ft × 0.125 in. 10% XF-1150 on 80/100 AW/DMCS Chromosorb W; (B) 10 ft × 0.125 in. 10% Carbowax 20 M on 80/100 AW/DMCS Chromosorb W; (C) 30 m × 0.25 mm Altech Superox capillary column, flow rate 1 mL/min; (D) 10 ft × 0.25 in. 20% XF-1150 on 40/60 AW/DMCS Chromosorb W; (E) 20 ft × 0.25 in. 20% XF-1150 on 40/60 AW/DMCS Chromosorb W; (F) 15 ft × 0.25 in. 20% Carbowax 20 M on 80/100 AW Chromosorb W. Internal standards used for quantitative work were as follows: bibenzyl to monitor the disappearance of *exo*-benzobicyclo[2.2.1]hepten-2-yl chloride on column B at 140 °C (response factor (RF) = weight(x)/weight(s) × area(s)/area(x) = 0.879), 2-bromonaphthalene to monitor the disappearance of both *exo*-BBCl and *endo*-BBCl on column A at 160 °C (*exo*-BBCl RF = 1.23, *endo*-BBCl assumed equal to *exo*-BBCl), and 2-bromonaphthalene to monitor the formation of *endo*-benzobicyclo[2.2.2]octen-2-yl methyl ether (**12**) on column C at 180 °C (RF = 1.54). The other photolysis products were assumed to have the same RF as **12**.

Photochemical studies mainly employed rotating turntables, quartz or Pyrex tubes, and a Hanovia Model 68814-45 low-pressure mercury arc lamp or a Rayonet photochemical reactor (New England Ultraviolet Corporation). Deoxygenation was performed by bubbling argon through the solution for at least 20 min. Actinometry was done with *exo*-benzobicyclo[2.2.1]hepten-2-yl chloride[2c] and with matched tubes.

Fluorescence quantum efficiencies were measured at room temperature by reference to toluene and are corrected for substrate absorbance. The ϕ_f for toluene in cyclohexane was taken to be 0.14.[37] Singlet lifetime measurements were done at room temperature with an Optitron Model-NF-100 nanosecond decay time fluorimeter, with interference filters at the excitation (254 nm) and emission (280 nm) windows. The details of the procedure have been previously described.[38]

***exo*- and *endo*-Benzobicyclo[2.2.2]octen-2-yl Chlorides (*exo*-BBCl and *endo*-BBCl).** Into a 50-mL three-necked round-bottomed flask, equipped with magnetic stirring bar and nitrogen inlet, was placed 8 mL (8 mmol) of 1 M BH_3–THF complex in THF. This was cooled to 0 °C, and about 2 g (12.8

(29) A preliminary report[2b] that *endo*-BBCl reacts more rapidly than *exo*-BBCl was in error. Early samples of the endo isomer were contaminated with undetected, highly photoactive, 3,4-benzobicyclo[3.2.1]octen-2-yl chloride.[10]

(30) Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009. Bigot, B.; Devaquet, A.; Turro, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 6.

(31) We are assuming the relaxed ion will exhibit chemistry analogous to that observed in the solvolysis of the brosylate, cf. eq 5.

(32) It has been suggested[3] that the correlation analysis should lead to a simple (but unobserved) correlation of relative reaction efficiency and the E_{0-0} of an aryl chromophore (if the nucleofuge is held constant). We believe any attempt to correlate photochemical reaction efficiencies rather than rate constants has obvious dangers. Furthermore, the proposal neglects the dependence of H_{AB} on the symmetry of the π,π^* state and especially the MO coefficients in the spatial region of maximum interaction.

(33) The key to activation within this proposal is the electron-transfer step. A detailed discussion of the energetics is presented in ref 15. We believe it worth noting that electron transmission spectral data place the σ^* MO of chloronorbornane (2.23 eV) considerably above the lowest π^* MO of aromatics such as *m*-xylene (1.12 eV).[34]

(34) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295. Jordan, K. D., private communication.

(35) One could well imagine the Cristol proposal becoming operative with a sufficiently electron affinic nucelofuge. This may be the case for a carbon–mercury bond in the dibenzo[2.2.2] series, where in fact the cation formed has no memory of the initial exo or endo stereochemistry.[18]

(36) LeCocq, C.; Lallemand, J. Y. *J. Chem. Soc., Chem. Commun.* **1981**, 150.

(37) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 5.

(38) Morrison, H.; Pandey, G. *Chem. Phys. Lett.* **1983**, *96*, 126.

mmol) of olefin 8 in 3 mL of dry THF was transferred into the reaction flask under a positive pressure of nitrogen. After the reaction mixture was stirred at room temperature for 12 h, THF was slowly evaporated under vacuo and replaced with 5 mL of CCl_4. To this was added about 25 mL (16.2 mmol) of 0.648 M NCl_3[39] in CCl_4 solution and the stirring continued for another 48 h in the presence of room light. The yellow color of NCl_3 slowly faded and a white precipitate formed. The reaction mixture was extracted with saturated sodium thiosulfate solution, the CCl_4 layer was filtered, and the solvent was evaporated to give an oil. Addition of hexane to the oil resulted in further precipitation of a solid, which was filtered to give about 1.7 g of crude product (6.9%). This was further purified by passing through 5 g of silica gel. The ^1H NMR spectrum of the crude product showed the absence of 3,4-benzobicyclo[3.2.1]octen-2-yl chloride and *exo*-benzobicyclo[3.2.1]octen-2-yl chloride and indicated the *exo*-BBCl and *endo*-BBCl to be in approximately an 11:9 ratio. VPC analysis showed the presence of some high retention time products which could not be removed by either molecular distillation or column chromatography with alumina or silica gel. *exo*-BBCl and *endo*-BBCl were successfully separated by using preparative VPC on column D at 150 °C. The *endo*-BBCl so obtained was always accompanied by 5–10% of *exo*- and *endo*-3,4-benzobicyclo-[3.2.1]octen-2-yl chloride formed in the gas chromatograph. This was converted to the ether mixture **13** before photolysis. Similarly, the *exo*-BBCl was contaminated with 5–10% of *exo*-benzobicyclo[3.2.1]octen-2-yl chloride.[40] Both samples also contained 1–2% of the cyclopropane **9**.

***exo*-BBCl**: ^1H NMR ($CDCl_3$, 90 MHz) δ 7.17 (m, 4 H, Ar), 4.00 (m, endo H_2), 3.15 (q, H_1), 2.98 (quintet, H_4) 1.20–2.60 (m, 6 H, exo H_3, endo H_3, and bridge methylene hydrogens), [reported[7]] 4.00 (m, endo H_2), 3.18 (q, H_1), 3.00 (quintet, H_4); GC–EIMS (70 eV), *m/e* 192 ($M^{\bullet+}$), 129 (base peak) [other major peaks are *m/e* 157 and 115].

***endo*-BBCl**: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.22 (m, 4 H, Ar), 4.38 (td, 1 H, exo H_2), 3.22 (q, H_1), 3.04 (quintet, H_4) 2.46 (ddd, exo H_3), 1.32–1.84 (m, 5 H, *endo* H_3 and bridge methylene hydrogens); GC–EIMS (70 eV), *m/e* 192 ($M^{\bullet+}$), 129 (base peak) [other major peaks are *m/e* 157 and 115].

***exo*- and *endo*-Benzobicyclo[2.2.2]octen-2-ol.** Into a 100-mL round-bottomed flask having a side arm and equipped with a nitrogen inlet and rubber septum was introduced 5 mL (5 mmol) of 1 M BH_3–THF complex in THF under nitrogen atmosphere with the flask cooled to 0 °C. Benzobicyclo[2.2.2]octa-2,5-diene (8)[41] (0.97 g, 6.2 mmol) dissolved in 3 mL of dry THF was syringed into the flask under a positive pressure of nitrogen with constant stirring. The mixture was stirred at 0–5 °C for 3 h and then at room temperature for 20 h. The reaction mixture was oxidized by adding 2 mL of 0.3 M NaOH followed by 4 mL of 30% H_2O_2. The solution was extracted with ether, washed with water and dried over anhydrous $MgSO_4$. Evaporation of the ether gave 1.05 g (97%) of a crude mixture of the alcohols in a ratio of endo/exo = 7:3 (as determined by VPC using column A at 180 °C). The pure alcohols were isolated by column (1 in. × 18 in.) chromatography over neutral alumina using hexane–benzene–methylene chloride mixtures as eluent. The exo alcohol was collected with 600 mL of a 1:1 hexane–benzene mixture and 800 mL of benzene and was rechromatographed to obtain pure samples. Recrystallization once from hexane gave mp 100–102.5 °C (lit.[42] mp 99.5–101.5 °C). Further elution with benzene and methylene chloride gave endo alcohol (recrystallized once from hexane, mp 104–106 °C (lit.[42] mp 103.5–104.5 °C).

Exo alcohol: ^1H NMR ($CDCl_3$, 90 MHz) δ 7.20 (m, 4 H, aryl), 3.93 (m, endo H_2), 3.00 (m, H_1 and H_4), 2.13–2.45 (m, exo H_3), 1.20–2.10 (m, 7 H, endo H_3, exo 2-OH, and bridge methylene hydrogens), [reported[7]] 3.90 (m, endo H_2) 3.00 (m, H_1 and H_4).

Endo alcohol: ^1H NMR ($CDCl_3$, 90 MHz) δ 7.20 (m, 4 H, aryl), 4.10 (dt, exo H_2), 3.06 (m, H_1 and H_4), 2.25 (ddd, exo H_3), 0.95–1.80 (m, 7 H, endo H_3, endo 2-OH, and bridge methylene hydrogens) [reported[7]] 4.00 (m, exo H_2), 3.00 (m, H_1 and H_4).

***exo*-Benzobicyclo[2.2.2]octen-2-yl Methyl Ether (11).** Into a 25-mL round-bottomed flask equipped with rubber stopper and nitrogen inlet was placed 25 mg of NaH (1 mmol). To this was added about 79 mg (0.45 mmol) of pure exo alcohol dissolved in 5 mL of dry ether, and the mixture was stirred under nitrogen atmosphere for 2 h. Then 0.2 mL (3.5 mmol) of methyl iodide was injected into the flask and the stirring continued overnight. Excess NaH was destroyed by adding 1 mL of methanol. The reaction mixture was diluted with 100 mL of ether, washed thoroughly with cold water, and dried over anhydrous $MgSO_4$. Evaporation of the ether gave 51 mg (60%) of 11. A pure sample of 11 was obtained by preparative VPC using column D at 150 °C: ^1H NMR ($CDCl_3$, 90 MHz) δ 7.18 (m, 4 H, aryl), 3.35 (m + s, 4 H, endo H_2 + CH_3O), 3.24 (m, H_1), 2.95 (m, H_4), 1.20–1.90 (m, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) 137.78 (C_6), 126.89 (C_5), 126.43, 125.94, 124.,5, 123.87 (C_9, C_{10}, C_{11}, and C_{12}), 78.56 (C_2), 56.67 (CH_3O), 37.86 (C_1), 36.66 (C_4), 34.76 (C_3), 26.27 (C_8), 18.38 (C_7) ppm; EIMS (70 eV), *m/e* 188 ($M^{\bullet+}$, 130 (base peak)) [other major peaks are *m/e* 156 and 115]. With CI, the M + 1 peak was located at *m/e* 189 and the base peak at *m/e* 157. Anal. ($C_{13}H_{16}O$) C, H.

***endo*-Benzobicyclo[2.2.2]octen-2-yl Methyl Ether (12).** The same procedure described for 11 was used. About 81 mg (0.47 mmol) of alcohol (endo/exo = 87.13), 30 mg (1.2 mmol) of NaH, and 0.2 mL (o.5 mmol) methyl iodide gave a mixture of 11 and 12. The pure endo isomer was isolated by preparative VPC using column D at 150 °C: ^1H NMR ($CDCl_3$, 90 MHz) δ 7.16 (m, 4 H, aryl), 3.68 (dt, exo H_2), 3.24 (m + s, 4 H, CH_3O + H_1), 3.02 (m, H_4), 2.12 (ddd, exo H_3), 1.10–1.70 (m, 5 H, endo H_3 and bridge methylene hydrogens); ^{13}C NMR ($CDCl_3$, 50 MHz) 143.44 (C_6), 139.68 (C_5), 126.35, 126.13, 125.59, 123.29 (C_9, C_{10}, C_{11} and C_{12}), 79.66 (C_2), 56.63 (CH_3O), 37.71 (C_1), 36.06 (C_3), 34.10 (C_4), 25.12, 22.71 (C_7 and C_8) ppm; EIMS (70 eV), *m/e* 188 ($M^{\bullet+}$), 130 (base peak) [other major peaks are *m/e* 156 and 115]. With CI, the M + 1 ion was found at *m/e* 189 and the base peak at *m/e* 157. Anal. ($C_{13}H_{16}O$) C, H.

3,4-Benzobicyclo[3.2.1]octen-2-yl Methyl Ether (13). Into a 25-mL round-bottoned flask was charged 0.19 g (1.1 mmol) of *endo*-benzobicyclo[2.2.2]octen-2-ol dissolved in 5 mL of benzene and 0.5 mL of freshly distilled thionyl chloride. The solution was stirred at room temperature for 12 h. The solvent was removed carefully under vacuo, and the residue was filtered through 2 g of silica gel using hexane. Evaporation of the hexane gave 0.17 g (77%) of a mixture of the benzylic chlorides (exo/endo = 5:1): ^1H NMR[43] ($CDCl_3$, 90 MHz) δ 6.90–7.40 (m, 4 H, Ar), 5.55 (d, 0.17 H, exo H_2), 4.97 (d, 0.83 H, *endo* H_2), 3.12 (m, H_1), 2.80 (m, H_5), 1.20–2.36 (m, 6 H, methylene hydrogens).

This mixture was dissolved in 5 mL of methanol and refluxed for 4 h. The solvent was removed under vacuo and the residue, upon VPC purification using column D at 150 °C, gave the mixture of isomers **13** (exo/endo = 86:14): ^1H NMR[43] ($CDCl_3$, 90 MHz) δ 6.90–7.40 (m, 4 H, Ar), 4.55 (d, 0.14 H, exo H_2), 3.89 (d, 0.86 H, endo H_2), 3.52 (s) + 3.49 (s) (3 H, OCH_3), 3.10 (m, H_1), 2.78 (m, H_5), 1.10–2.20 (m, 6 H, methylene hydrogens); EIMS (70 eV), *m/e* 188 ($M^{\bullet+}$), 129 (base peak) [other major peaks are *m/e* 157 and 115]; calcd for $C_{13}H_{16}O$ *m/e* 188.120, found *m/e* 188.116.

3,4-Benzobicyclo[3.2.1.$0^{2,7}$]octene (9).[44] Approximately 500 mg of a mixture of *exo*-BBCl (19%), *exo*-benzobicyclo[3.2.1]octen-2-yl chloride (2%), and *exo*- + *endo*-3,4-benzobicyclo-[3.2.1]octen-2-yl chlorides (79%) was prepared by addition of HCl (in SO_2 at −60 °C) to the olefin 8. The mixture was pyrolyzed at 180 °C by injection onto column D. The pyrolysate was collected and purified by reinjection onto column D at 150 °C. Compound **9** was obtained in ca. 20–25% yield. In an alternate preparation, a 5-mL solution of benzobicyclo[2.2.2]octen-2-one *p*-toluenesulfonylhydrazone (see below) (2.94 × 10^3 M) in ace-

(39) This reagent was prepared by a reported procedure. Kovacic, P.; Chaudhary, S. S. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 35.

(40) The ground-state rearrangements of *exo*- and *endo*-benzobicyclo[2.2.2]octen-2-yl derivatives occur with migration of the vicinal anti bond, see ref 7 and also: Barkhash, V. A. *Top. Curr. Chem.* **1984**, 116/117, 139.

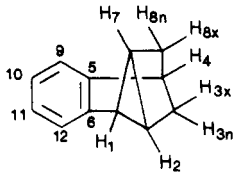
(41) Prepared from cyclohexadiene dimer by using DDQ and benzene by the procedure of: Kitahonoki, K.; Takano, Y. *Tetrahedron* **1969**, *25*, 2417. For a superb method of cyclohexadiene dimerization, see: Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.

(42) Kitahonoki, K.; Takano, Y. *Tetrahedron Lett.* **1963**, 1597.

(43) For the ^1H NMR spectral data of analogous derivatives, see: Tanida, H.; Miyargaki, S. *J. Org. Chem.* **1971**, *36*, 425.

(44) Hahn, R. C.; Rothman, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 2409.

tonitrile was irradiated with a medium-pressure mercury lamp through a Corex filter.[45] This yields a 1:1 mixture of **8** and **9**:



9

^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.13 (m, 4 H, Ar), 3.03 (t, $J_{4,3x} = J_{4,8x} = 4.9$ Hz, H_4), 2.13 (t, $J_{1,7} = J_{1,2} = 7$ Hz, H_1), 1.81 (m, $J =$ 4.9 and 11.6 Hz, H_{8x} and H_{3x}), 1.65 (d, $J_{1,7} = J_{1,2} = 7$ Hz, H_7 and H_2), 0.98 (d, $J_{3n,3x} = J_{8n,8x} = 11.6$ Hz, H_{8n} and H_{3n}); ^{13}C NMR ($CDCl_3$, 50 MHz) 140.86, 134.79 (C_5 and C_6), 126.12, 125.77, 124.08, 122.98 (C_9, C_{10}, C_{11}, and C_{12}), 36.33 (C_4), 28.64 ($C_3 = C_8$), 18.66 (C_1), 15.87 ($C_2 = C_7$); EIMS (70 eV), m/e 156 ($M^{\bullet+}$), 128 (base peak) [other major peaks are m/e 141, 115, 102, 89, 77]; CI showed the M + 1 peak at m/e 157. The ^{1}H NMR spectrum is in good agreement with that reported by Hahn.[44]

***exo*-Benzo[6,7]bicyclo[3.2.1]octen-2-yl Methyl Ether (10).** This compound was synthesized from the known[46] alcohol by using NaH and methyl iodide as described for **11**. The only chemical shifts reported for the alcohol are δ 3.87 for H_2 and δ 3.1 for H_1 and H_5. Our synthetic sample of the alcohol showed the following: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.28 (m, 4 H, Ar), 3.98 (m, H_2), 3.13 (m, H_1 and H_5), 1.20–2.39 (m, 7 H). The ether had the following spectral data: ^{1}H NMR ($CDCl_3$, 470 MHz) δ 7.20 (m, 4 H, Ar), 3.44 (s, 4 H, $OCH_3 + H_2$), 3.33 (m, 1 H, H_1), 3.18 (m, 1 H, H_5), 1.26–2.25 (m, 6 H, methylene hydrogens); EIMS (70 eV), m/e 188 ($M^{\bullet+}$), 130 (base peak); calcd for $C_{13}H_{16}O$ m/e 188.11979, found m/e 188.11978.

Benzobicyclo[2.2.2]octen-2-one. Into a 25-mL three-necked round-bottomed flask was placed 1 mL of 2 M BH_3/DMS solution (2 mmol). The system was flushed with nitrogen and under a positive pressure of nitrogen, and 0.5 g (3.2 mmol) of benzobicyclo[2.2.2]octadiene in 3 mL of dichloromethane (dried over P_2O_5) was added slowly by hypodermic syringe with magnetic stirring throughout. The solution was stirred for 10 h at room temperature. The solvent was removed by a stream of nitrogen leaving a colorless liquid, which was then added slowly to a flask (equipped with condenser and side arm) containing 3 g (14 mmol) of pyridinium chlorochromate in 10 mL of dichloromethane. The solution was refluxed for 4 h. After cooling to room temperature, the reaction mixture was diluted with 150 mL of diethyl ether and passed through a sintered-glass funnel packed with 20 g of Florisil. Evaporation of the ether gave 0.39 g (71%) of a colorless liquid, which was distilled at 98–103 °C (0.1 mm); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.2 (m, 4 H), 3.58 (m, 1 H), 3.40 (m, 1 H), 1.30–2.30 (m, 6 H).

A methanol (10 mL) solution of the ketone (10.3 g, 1.7 mmol) and (*p*-tolylsulfonyl)hydrazine (0.35 g, 1.8 mmol) was refluxed for 2 h. The solution was filtered while hot and then allowed to cool in a refrigerator. White needles were collected by filtration (0.37 g, mp 228–230 °C). Anal. ($C_{19}H_{20}N_2O_2S$) C, H, N, S.

Silver Ion Assisted Solvolysis of *endo*-BBCl and *exo*-BBCl. A 2-mL mixture of *endo*-BBCl (2.7×10^{-2} M) and *exo*-BBCl (3.3×10^{-2} M) and 10 mg of silver nitrate in a 9:1 methanol/water solution was stirred in the dark for 15 h at room temperature. The solution was treated with 10 mg of NaCl, and the precipitated silver chloride was filtered out. The filtrate was analyzed on column C at 180 °C. The losses observed were 10% and 22% for the endo and exo chlorides, respectively.

Photolysis of *exo*-BBCl in Methanol. Typically, a solution (5 mL) of *exo*-BBCl (0.01 M) in methanol was degassed with argon for 25 min and irradiated in a quartz tube with the low-pressure mercury arc for 30 min. Analysis of the reaction mixture on column C (180 °C) showed the presence of seven primary photoproducts at 3.4 (**7**),[41] 3.7 (**8**),[42] 4.3 (**9**),[44] 4.6 (**10**), 5.0 (**11**), 6.0 (**12**), and 6.2 (**13**) min. (Under these conditions *exo*-BBCl, *endo*-BBCl, and the internal standard elute at 6.3, 7.7, and 8.8 min, respectively).[47] The products were identified by GC–MS analysis and by coinjection with independently synthesized samples on columns C (180 °C), B (140 °C), and A (160 °C).

Photolysis of *endo*-BBCl in Methanol. Typically, a solution (5 mL) of *endo*-BBCl (0.01 M) in methanol was allowed to stand in the dark for 1 h to convert any contaminating 3,4-benzobicyclo[3.2.1]octen-2-yl chloride to the corresponding ether. (The amount of ether present was measured and subtracted from the product analysis after photolysis). The solution was then degassed and irradiated in a quartz tube with the low-pressure mercury arc for 20 h. Analysis of the reaction mixture on column C (180 °C) showed the presence of six of the previously observed *exo*-BBCl photolysis products (ether **12** was not formed in detectable amounts).

Photolysis of *exo*-BBCl in Methanol with (*E*)-2-Heptene. Aliquots (4 mL) of a 9×10^{-3} M solution of *exo*-BBCl in methanol were transferred into four matched quartz tubes and degassed for 25 min with argon. Into tubes 3 and 4 was syringed 50 μL (*E*)-2-heptene (0.09 M). All tubes were irradiated for 20 min with the low-pressure Hg lamp. Into each tube was added 1 mL of an internal standard solution containing 64 mg of 2-bromonaphthalene dissolved in 10 mL of methanol. Analysis was conducted on column A at 160 °C. The disappearances were (1) 32.5%, (2) 35.5%, (3) 25.7%, and (4) 36.3%, respectively.

Quantum Efficiency Determinations. The lamp was warmed up for 30 min prior to the experiment. The actinometer for these experiments was *exo*-benzobicyclo[2.2.1]hepten-2-yl chloride for which the quantum efficiency of disappearance in methanol is 0.55.[2c] Irradiation of quartz tubes containing 5-mL solutions, argon degassed and 1.08×10^{-2} M in substrate, with the low-pressure lamp for 5 min, gave 15% disappearance of the actinometer (with bibenzyl as internal standard on column B at 120 °C). This corresponds to 3.05×10^{16} photons/s. Simultaneously, a 9.58×10^{-3} M solution of *exo*-BBCl was photolyzed for 9 min. With 2-bromonaphthalene as internal standard, the sample was analyzed for both product formation (column C at 180 °C) and disappearance (column A at 160 °C). A 25.3% loss of *exo*-BBCl indicates $\phi_{dis} = 0.45$. The product formation percentages were 1.0_5, 1.6, 1.0, 0.46, 0.94, 1.3, and 6.8 for compounds **7–13**, respectively.

For ϕ_{dis} of *endo*-BBCl, 5-mL methanolic solutions of *endo*-BBCl (9.7×10^{-3} M) were irradiated for 984 min. The light intensity was also calculated toward the end of the photolysis by using an actinometer solution, and an average of 3.38×10^{16} photons/s was used in the ϕ calculations. Analysis by column B (at 140 °C) and column C (at 180 °C) showed 37% disappearance of *endo*-BBCl leading to $\phi_{dis} = 5 \times 10^{-3}$. The product formation percentages were 1.5%, 1.7%, 0.3%, 3.1%, 6.4%, and 2.0% for compounds **7–11** and **13**, respectively (after correction for **13** present at the outset).

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(45) Dauben, W. G.; Willey, F. G. *J. Am. Chem. Soc.* **1962**, *84*, 1497.

(46) Reduction of 2,3-benzobicyclo[2.2.2]octadiene-5-one with LAH has been shown to give a mixture of isomeric alcohols with a preponderance of the endo isomer (7:3), see: Tanida, H.; Tori, K.; Kitahonoki, K. *J. Am. Chem. Soc.* **1967**, *89*, 3212. We found it necessary to add sodium carbonate to the calcium carbonate used by Tanida to hydrolyze the allylic chloride to the allylic alcohol prior to reduction.

(47) At high conversions, a di-π-methane product of **8** is observed at a retention time of 4.0 min (cf. ref 12).