10 H); VPC mass spectrum (70 eV) m/e 214 ($M^{\cdot+}$), 157 (base peak).

7β-Hydroxy-13β-methyl-5,6,7,8,9,10,13β,14α-octahydrophenanthrene (1). Following further elution with 200 mL of the 90:10 mixture of benzene/diethyl ether (in which fraction eluted 57 mg of TAK), this compound (573 mg) was eluted with 600 mL of diethyl ether. This is a known compound[7,10] and was independently synthesized by $NaBH_4$ or $LiBH_4$ reduction of TAK: IR (neat) 3.00, 3.41, 6.75, 6.86, 6.95, 7.31, 7.52, 9.16, 9.47, 9.67, 13.20, 13.87 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.94–7.39 (m, aryl, 4 H), 3.65 (m, CHOH, 1 H), 2.81–3.05 (m, benzylic, 2 H), 1.45–2.40 (m, 10 H), 1.08 (s, CH_3, 3 H), 7α-hydroxy isomer has a characteristic CHOH signal at δ 4.1.

Photolysis of CAK in Methanol. Typically, a solution of 561 mg (2.62×10^{-2} M) of CAK in 100 mL of methyl alcohol containing ca. 1.0 g of $NaHCO_3$ was photolyzed with 254-nm light in an immersion well for 3 h with continuous argon degassing. The solvent was evaporated in vacuo at 40–50 °C and the residue chromatographed on 100 g of acid-washed alumina as described above for the TAK photolysis. Three major products were isolated:

Methyl 2-(1α-Ethyl-1β-methyl-1,2,3,4-tetrahydronaphthalen-2α-yl)ethanoate (8) and Methyl 3-(1β,2α-Dimethyl-1,2,3,4-tetrahydronaphthalen-1α-yl)propanoate (9). These esters could only be isolated as a mixture: 196 mg; IR (neat) 3.41, 5.76, 6.72, 6.95, 7.75, 7.97, 8.34, 8.65, 13.17, 13.69 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.90–7.40 (m, aryl, 4 H), 3.60 and 3.57 (both s, CH_3O, total of 3 H in a ratio of 2:1), 2.70–2.85 (m, benzylic, 2 H), 1.40–2.65 (m, 7 H), 1.15 (s, CH_3, 3 H), 0.90 (d), 0.70 (t) (total of 3 H in a ratio of 1:2). Anal. ($C_{16}H_{22}O_2$) C, H.

7α-Hydroxy-13β-methyl-5,6,7,8,9,10,13β,14β-octahydrophenanthrene (7). This compound[10] was isolated as 145 mg (26%) and proved to be identical with a sample independently synthesized by $NaBH_4$ reduction of CAK. It was readily purified by preparative VPC [column H at 180 °C, flow 60 mL/min, RT = 12 min]: IR (neat) 2.90, 3.40, 6.71, 6.90, 7.30, 13.10 μm; ^1H NMR ($CDCl_3$, 90 MHz) δ 6.94–7.32 (m, aryl, 4 H), 3.45–4.00 (m, CHOH, 1 H), 2.65–2.95 (m, benzylic, 2 H), 0.70–2.50 (m, including CH_3 at 1.10, 13 H). Anal. ($C_{15}H_{20}O$) C, H.

Quantum Efficiency Determinations. The actinometer for these experiments was *trans*-1-phenyl-2-butene, for which the quantum efficiency of formation of the cis isomer in cyclohexane is 0.20 ± 0.01.[39] Quartz tubes containing 4 mL of argon-degassed actinometer solutions, 1.0×10^{-2} M in substrate, were irradiated with the low-pressure lamp for 10 min. This produced 7.16% of *cis*-1-phenyl-2-butene, corresponding to 1.44×10^{16} photons/s (analysis by column E at 110 °C). An analogous determination at the end of the photolysis gave a value of 1.62×10^{16} photons/s, which two measurements were averaged to 1.53×10^{16} photons/s. Simultaneous photolysis of 1.0×10^{-2} M TAK in methanol and 7.0×10^{-3} M CAK in methanol, for 20 min, gave 20.6 and 19.7% loss, respectively (column D at 220 °C), corresponding to ϕ_{dis} = 0.27 and 0.17.

A more extended irradiation (40 min) gave $\phi_1 = 0.11 \pm 0.02$, $\phi_{2,3,4,6} = 0.13 \pm 0.01$, $\phi_7 = 0.048 \pm 0.002$, and $\phi_{8+9} = 0.13 \pm 0.005$.

Experiments with Cyclohexanone. These were carried out in the turntable with Vycor tubes, argon-degassed isopropyl alcohol solutions, and the low-pressure lamp. TAK was monitored on column D at 220 °C while cyclohexanone and cyclohexanol were monitored on column F at 100 °C. With equimolar (1.0×10^{-2} M) concentrations of TAK, CAK, and cyclohexanone and a 2-h photolysis, the loss of TAK, with and without added ketone, was 71 and 76%, respectively. The corresponding loss of CAK was 23 and 24%. Also a 71% loss of cyclohexanone was observed in the TAK solution (cyclohexanol formation accounted for ca. 39% of this loss); no loss of cyclohexanone nor evidence of cyclohexanol was found in the CAK solution.

In a second series of experiments, the tubes contained 1.0×10^{-2} M TAK or CAK plus cyclohexanone at 1.0×10^{-1} M. The irradiation was conducted for 2 h with the 300-nm lamps in a Rayonet reactor. The losses of TAK and CAK were 14 and 8%, respectively, while cyclohexanone losses were 32% (no TAK or CAK), 9% (with TAK), and 7% (with CAK). When a TAK (1.0×10^{-2} M) solution without cyclohexanone was irradiated (300 nm, 3 h) together with one containing 1.0×10^{-1} M cyclohexanone, the losses of TAK were 51 and 56%, respectively (we estimate only 8% of the incident light as absorbed by TAK in the second solution).

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Registry No. 1, 70524-87-7; 2, 104946-72-7; 3, 104946-73-8; 4, 104946-74-9; 7, 70524-92-4; 8, 104946-75-0; 9, 104946-76-1; TAK, 1686-50-6; CAK, 70524-91-3.

Photolytic Cleavage of Remote Functional Groups in Polyfunctional Molecules. Activation of a γ C–Cl Bond in the *endo*- and *exo*-Benzobicyclo[3.2.1]octen-3-yl Chlorides[1]

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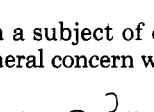
The aryl-induced photolytic cleavage of a distal C–Cl bond, earlier reported for a β-substituent in benzobicyclo[2.2.1] (eq 1) and -[2.2.2] (eq 2) substrates, has been extended to the γ position in the title compounds (*endo*-BBOC and *exo*-BBOC). Photolyses of these compounds in methanolic solution using 254-nm light primarily lead to products derived from carbocation intermediates (eq 4 and 5) with quantum efficiencies for loss of starting material $\phi_{dis} = 8.1 \times 10^{-2}$ and 7.6×10^{-3} (endo and exo, respectively). The greater reactivity of the endo isomer contrasts with that observed in the [2.2.1] and [2.2.2] series where large exo/endo rate ratios are the rule (Table III). This inverted reactivity pattern is attributed to the favorable aryl/chlorine relationship in the endo isomer (Figure 1), which compensates for the increased Ar–C_3 separation otherwise characteristic of these γ functionalities.

Introduction

The photolytic cleavage of a distal, relatively transparent nucleofuge upon excitation of a UV absorbing chromophore (cf. 1) has been a subject of continuing interest[2-5] as part of the more general concern with the photochemical



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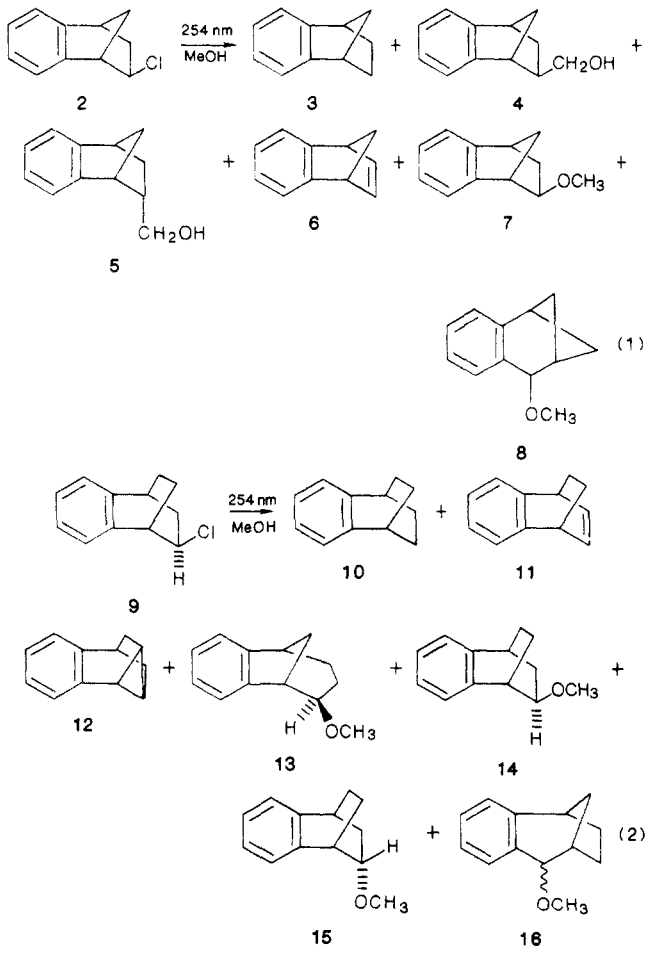
(1) Organic Photochemistry. 67. Part 66: Morrison, H.; Singh, T. V.; de Cardenas, L.; Severance, D.; Jordan, K.; Schaefer, W. *J. Am. Chem. Soc.* **1986**, *108*, 3862–3863.

0022-3263/86/1951-4681$01.50/0

and photophysical properties of polyfunctional molecules. One series of observations has centered on the aryl-initiated cleavage of a β C–X bond in both acyclic[3] and bicyclic[4,5] substrates. Examples of the latter are shown in eq 1[4c] and 2.[4f] Quantum efficiencies for C–Cl cleavage in

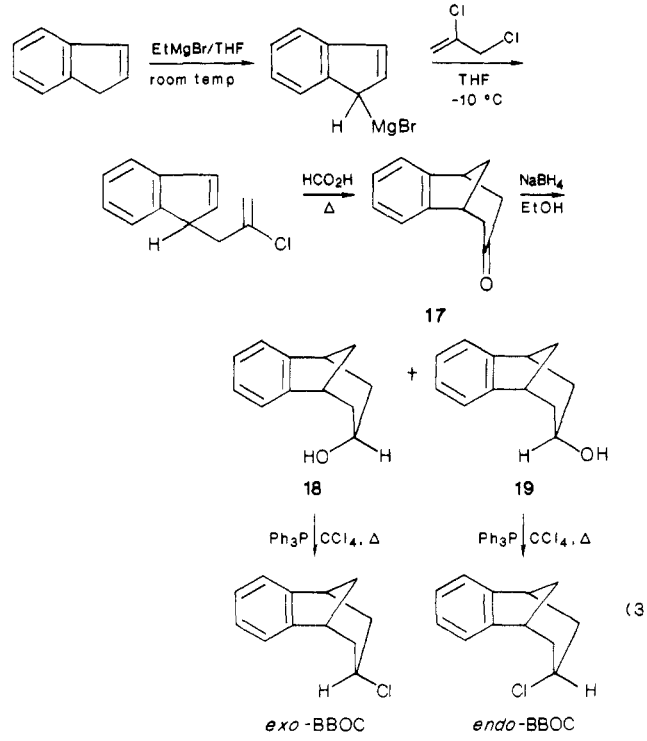


these benzobicyclics vary from 0.55 (exo [2.2.1]) to 0.005 (endo [2.2.2]) with characteristically large quantum efficiency and rate ratios for exo vs. endo cleavage (for example, the rate ratios for the [2.2.1] and [2.2.2] series are (k_{exo}/k_{endo}) = 647 and 1400, respectively). These singlet-state derived reactions are also characterized by extensive syn migration (for example, **2** → **8** (eq 1); **9** → **16** (eq 2)) and the formation of alkenes (**6**, **11**) and insertion products (**12**), all of which have been attributed to the formation of a hot carbocation intermediate.[4]

The observations described above[3-5] have been confined to the activation of a nucleofuge β to the aryl chromophore. We now report the first observation of aryl-initiated cleavage in a γ chloro substrate.

Results

A. Preparation of *endo*- and *exo*-Benzobicyclo[3.2.1]octen-3-yl Chlorides (*endo*-BBOC and *exo*-BBOC). The title compounds were prepared by the reaction sequence given in eq 3. This route gave the ketone (**17**)[6] in an overall yield of 22%. Reduction gave a 64%



18 and 36% **19** mixture of the two alcohols[7] which was separated by column chromatography. NMR analyses of **18** and **19** readily permitted their assignment. The general existence of members of the benzobicyclo[3.2.1]octenyl series as the chair conformers is well established,[8,9] as are the upfield shifts of endo groups at C-3, due to their location in the shielding region of the aromatic ring.[7,8,10] Thus, the 3-methine proton in the axial alcohol (**18**) appears at δ 3.88 (lit.[7] 3.70) while the corresponding hydrogen in the equatorial alcohol (**19**) appears at δ 3.03 (lit.[7] 2.90). This axial hydrogen also exhibits the expected, large axial–axial coupling constant (10.3 Hz). Substitution, with inversion, by triphenylphosphine in carbon tetrachloride[11] gave *exo*-BBOC from the endo alcohol and *endo*-BBOC from the exo alcohol (both in about 55% yield by GLC). The exo and endo chlorides are again readily distinguished by NMR spectroscopy, with *exo*-BBOC having its axial 3-methine proton upfield at δ 3.33 ($J_{H_{3ax}-H_{2ax}}$ = 10.8 Hz). The corresponding methine proton in *endo*-BBOC appears at δ 4.37.

Photolysis of *exo*-BBOC in Methanol. A 0.011 M solution (4 mL) of *exo*-BBOC in methanol was degassed

(2) Kuivila, H. G.; Maxfield, P. J.; Tsai, K.-H.; Dixon, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 104–109. Matuszewski, B. *Mol. Photochem.* **1977**, *8*, 89–120. Hamada, T.; Ohmori, M.; Yonemitsu, O. *Tetrahedron Lett.* **1977**, 1519–1522. Wagner, P. J.; Scheve, B. J. *J. Am. Chem. Soc.* **1979**, *101*, 378–383. Arad-Yellin, R.; Eaton, D. F. *Ibid* **1982**, *104*, 6147–6149.

(3) Jaeger, D. A.; Bernhardt, E. A. *Tetrahedron Lett.* **1983**, *4521*–4524. Jaeger, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6401–6402.

(4) (a) Morrison, H.; Miller, A. *J. Am. Chem. Soc.* **1980**, *102*, 372–373. (b) Morrison, H.; Miller, A.; Pandey, B.; Pandey, G.; Severance, D.; Stromen, R.; Bigot, B. *Pure Appl. Chem.* **1982**, *54*, 1723–1732. (c) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.* **1983**, *105*, 2398–2408. (d) Morrison, H.; DeCardenas, L. M. *Tetrahedron Lett.* **1984**, *25*, 2527–2530. (e) Morrison, H.; Singh, T. V.; Maxwell, B. *J. Org. Chem.* **1986**, *51*, 3707. (f) Morrison, H.; Muthuramu, K., Pandey, G., Severance, D., Bigot, B. *J. Org. Chem.* **1986**, *51*, 3358–3363.

(5) (a) Cristol, S. J., Bindel, T. H. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 327–415. (b) Cristol, S. J.; Bindel, T. H.; Hoffman, D.; Aeling, E. O. *J. Org. Chem.* **1984**, *49*, 2368–2375, and previous papers in this series.

(6) Lansbury, P. T.; Nienhouse, E. J.; Scharf, D. J.; Hilfiker, F. R. *J. Am. Chem. Soc.* **1970**, *92*, 5649–5657.

(7) Lansbury, P. T.; Boggs, N. T. *J. Chem. Soc., Chem. Comm.* **1967**, 1007–1008. These workers obtained a product mix of 85% 18, 15% 19; cf. Boggs, N. T. Ph.D. Thesis, State University of New York, Buffalo, NY, 1967. We are grateful to Prof. Lansbury for providing these data.

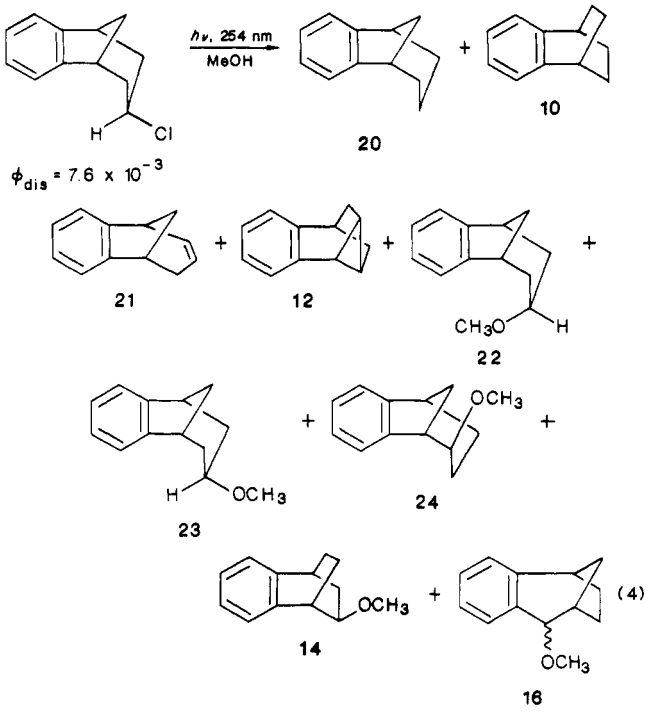
(8) Haslanger, M.; Zawacky, S.; Lawton, R. G. *J. Org. Chem.* **1976**, *41*, 1807–1810, and references therein.

(9) Fournier, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1973**, *1599*–1604.

(10) Stoll, A. P.; Loosli, H.-R.; Nicklaus, P.; Zardin-Tartaglia, T. *Helv. Chim. Acta* **1978**, *61*, 648–656.

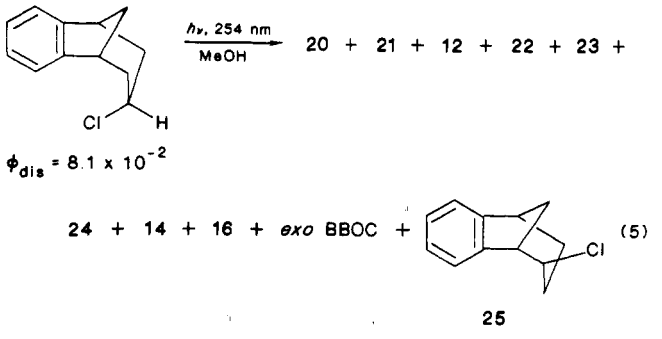
(11) Appel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 801–811.

for 25 min with argon and irradiated in a quartz tube for 2.5 h in a Rayonet reactor using five 254-nm lamps. A 15% loss of chloride occurred, with 11 primary photoproducts[12] observable by GLC. Nine of these (91 wt % of the total) could be identified by coinjection with authentic samples; these are shown in eq 4.



The relative mole percentages of the various products (as determined against an internal standard), are given in Table I. The quantum efficiency for loss of starting material was measured, using 1-phenyl-2-butene actinometry,[13] and gave a value of $\phi_{dis} = 7.6 \times 10^{-3}$.

Photolysis of *endo*-BBOC in Methanol. A 0.010 M solution (4 mL) of *endo*-BBOC in methanol was degassed for 25 min with argon and irradiated in a quartz tube for 15 min in a Rayonet reactor using five 254-nm lamps. A 22% loss of starting chloride occurred, with 16 primary photoproducts observable by GLC. Ten of these (71 wt % of the total) could be identified by coinjection with authentic samples and GC–mass spectrometry; these are shown in eq 5. The relative amounts of the various



products are given in Table I. The quantum efficiency for loss of starting material was measured with 1-phenyl-2-butene actinometry[13] and gave a value of $\phi_{dis} = 8.1 \times 10^{-2}$.

Photolysis of *exo*- and *endo*-BBOC in Cyclohexane. The quantum efficiencies for loss of the two chlorides were measured in identical fashion with that described above for the methanol solutions. *exo*-BBOC (4 mL, 0.013 M) and *endo*-BBOC (4 mL, 0.012 M) in cyclohexane were placed in quartz tubes, degassed for 25 min, and irradiated for 2.5 h and 15 min, respectively. Losses of starting material were 5.4 and 11.3%, yielding $\phi_{dis}^{exo} = 3.4 \times 10^{-3}$ and $\phi_{dis}^{endo} = 6.5 \times 10^{-2}$.

Triplet Sensitization of *endo*-BBOC in Methanol. A solution of *endo*-BBOC (0.013 M) and acetone (1.6 M) in methanol (3.6 mL) was irradiated for 25 h using the Rayonet reactor and 300-nm lamps. Glc analysis showed a 40% loss of starting material and the formation of three short retention-time products, one of which could be identified as the hydrocarbon, **20**. There was no evidence for the formation of **21** and **12** or any of the ethers (**14**, **16**, **22**–**24**).

Photolysis of *endo*-BBOC in Methanol with 2-Heptene. Solutions of *endo*-BBOC (0.018 M) in methanol (3.6 mL) were degassed for 20 min with argon in quartz tubes. (*E*)-2-Heptene (0.11 and 0.12 M) was added to two of the tubes with two others retained as controls. The four tubes were photolyzed for 35 min in a turntable using a Rayonet reactor and the 2537-Å lamps. GLC analysis showed identical loss (61%) of starting material in all four tubes; i.e., no quenching was observed. The product fingerprint remained the same, with and without olefin, except that the ratio of **21**:**12** was 0.30 without quencher and 1.3 with quencher. Formation of the cyclopropane, **12**, in the tubes with heptene occurred to the extent of 53% that of the tubes without heptene.

Ground-State Solvolyses of *exo*-BBOC and *endo*-BBOC. A mixture of *endo*-BBOC (0.021 M) and *exo*-BBOC (0.020 M) in 10:1 methanol/water (5.0 mL) containing silver nitrate (0.021 M) was stirred at 27 °C for 1.5 h. GLC analysis showed 47% and 3.7% loss of the endo and exo isomers respectively (rate ratio ca. 13:1). Product analysis in separate experiments indicated *exo*-BBOC solvolyzes to **21** (18%), the endo ether, **22** (45%), and the endo alcohol, **18** (37%). *endo*-BBOC gave **21** (56%) and the exo ether, **23** (56%), with just a trace of exo alcohol, **19**.

Spectroscopy of *exo*-BBOC and *endo*-BBOC. The absorption spectra of both isomers show fine structure centered at λ_{max} 268 nm (ϵ 568) and λ_{max} 270 nm (ϵ 744) in methanol. Other components of this band occur at 263 and 274 nm (exo) and 264 and 276 nm (endo). The spectrum of the endo isomer is virtually unchanged in cyclohexane while the exo isomer exhibits a 6-nm blue shift in this solvent. The parent hydrocarbon (**20**) shows broad, featureless absorption in both solvents, with λ_{max} 262 nm (ϵ 353) in methanol and λ_{max} 260 nm (ϵ 336) in cyclohexane.

Fluorescence spectra were obtained relative to a toluene standard in cyclohexane (ϕ_f 0.14)[14] and are presented in Table II. Singlet lifetimes are also included in this table.

Discussion

It is evident from eq 4 and 5 that (1) an aryl chromophore can initiate the photocleavage of a γ nucleofuge[15] and (2) the consistently high exo/endo quantum efficiency ratio characteristic of the [2.2.1] and [2.2.2] substrates is inverted in the BBOC series. Examining eq 4 and 5 and Table I in more detail, we note that several of the basic features of the earlier (β nucleofuge) studies are reproduced in these photolyses, but not without significant modifica-

(12) Several long retention-time peaks are noted at higher conversions and appear to be secondary photoproducts.

(13) Morrison, H.; Giacherio, D.; Palensky, F. *J. Org. Chem.* **1982**, *47*, 1050–1057. Scully, F.; Nylund, T.; Palensky, F.; Morrison, H. *J. Am. Chem. Soc.* **1978**, *100*, 7352–7364.

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

(15) Earlier studies[4c] have shown that, for example, *exo*-2-chloronorbornane, is not susceptible to *inter*molecular aryl sensitization.

Table I. Product Distribution upon Photolysis of *exo*- and *endo*-BBOC in Methanol[a,b]

	20	10	21	12	22	23	24	14	16	25	*exo*-BBOC
exo-BBOC	10	2	2	40	3	3	9	18	13	–	–
endo-BBOC	1	–	17	34	1	5	6	10	13	4	9

[a] Values are mole percentages of the total identifiable material observed by GLC. [b] 9% by weight of *exo*-BBOC and 29% by weight of *endo*-BBOC GLC-detectable material was unidentified.

Table II. Fluorescence Quantum Efficiencies and Singlet Lifetimes

compd	solvent	ϕ_f	$^1\tau$, ns
20	cyclohexane	0.32	21
exo-BBOC	cyclohexane	0.22	
	methanol	0.19	17
endo-BBOC	cyclohexane	0.054	
	methanol	0.046	11

Table III. Quantum Efficiencies and Rate Constants for Benzobicyclo Chloride Photolytic Cleavage

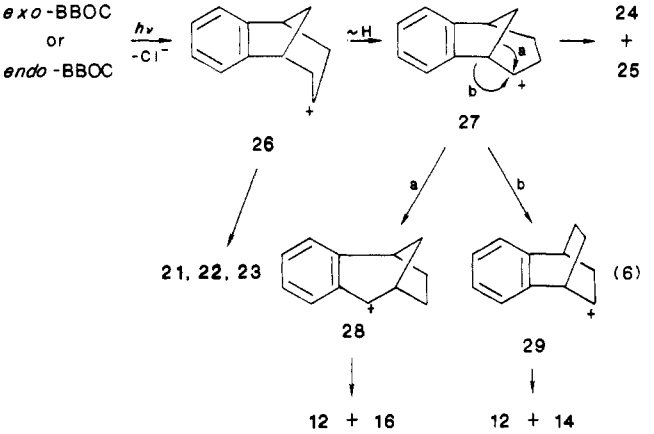
chloride[a]	ϕ_{dis}[b]	k_r, s^{-1} [c]
exo [2.2.1]	0.55	1.1×10^9
endo [2.2.1]	0.019	1.7×10^6
exo [2.2.2]	0.45	3.8×10^8
endo [2.2.2]	0.0050	2.7×10^5
exo-BBOC	0.0076	4.3×10^5
endo-BBOC	0.081	7.2×10^6

[a] Data for the [2.2.1] and [2.2.2] series from ref 4c and 4f, respectively. [b] In methanol. [c] From $\phi_{dis} = k_r{}^1\tau$.

tion. Thus, there is evidence for both free-radical and carbocation derived products, but the contribution of the former (i.e., **10** + **20**) is relatively minor (1%, *endo*-BBOC; 10% *exo*-BBOC) by comparison with 22% noted for *exo*-2-benzonorbornenyl chloride.[4c] A similar reduction in radical-derived products has been noted in the benzo[2.2.2] series,[4f,5] and *the dominance of carbocation chemistry in these photosolvolyses seems general.*[16]

Despite the small amount of reduction product, the overall amount of hydrocarbons formed from both *exo*- and *endo*-BBOC is ca. 50%, a much higher proportion than is seen in the [2.2.2] series (ca. 25%)[4f] and comparable to the 41% observed for the exo [2.2.1] chloride.[4c] The formation of the alkene, **21**, is unexceptional in these photosolvolyses, as is the benzo[2,3]tricyclo[3.2.1.$0^{4,6}$]octene (**12**), for **12** is the di-π-methane product expected from the triplet of this alkene.[17] Such (aryl chloride) triplet sensitized di-π-methane secondary photochemistry has been noted for the [2.2.1] and [2.2.2] substrates, but the 34–40% of **12** seen here is unusually high. Furthermore, the addition of ca. 0.1 M 2-heptene has generally been sufficient to quench all such secondary photoreactions in these systems,[4c,4f] but over 50% of the **12** formed from *endo*-BBOC proves to be *un*quenchable. Since **12** is also formed in modest amounts (2–8%) upon photolysis of the endo and exo [2.2.2] substrates (cf. eq 2), presumably by insertion of the initially generated cation, it seems reasonable that the same cation (**29**) is forming in the photolysis of BBOC and is a second source of **12** (as might be the ion **28**; see below).[18]

In fact, the product distributions in eq 4 and 5 indicate that a number of cations are sequentially formed in these photolyses (cf. **26**–**29** in eq 6). Several of these may well



be in equilibrium with one another since the photolytic generation of **29** from the [2.2.2] chlorides produces **16** (by **29** → **28**) and **24** (by **29** → **27**).[4f,19] Overall, rearrangements account for 82% and 76% of the identifiable exo and endo products, respectively. The extensive rearrangements caused by photolysis is in marked contrast to the ground-state, silver-assisted solvolyses where only alkene and *inverted*, *unrearranged* ethers (and alcohol) are formed.[20] The more extensive rearrangement and insertion chemistry seen in these BBOC photolyses, by comparison with the ground-state solvolyses, mirrors observations previously made in the benzo[2.2.1] and benzo[2.2.2] systems.[4,5]

The sensitization, quenching, and fluorescence studies are consistent with BBOC photochemistry that is aryl-excited singlet-state derived, as has been the case with previous homologues.[4] Quantum efficiencies and rate constants (using $\phi_{dis} = k_r{}^1\tau$)[21] are gathered in Table III. Moving the nucleofuge to a γ carbon has markedly reduced k_r for *exo*-BBOC relative to its [2.2.2] and [2.2.1] homologues, but surprisingly *endo*-BBOC is more reactive than the other endo isomers. *The net effect is an inversion of the high exo/endo rate ratio which until now has characterized these photolyses.*[4,5,22] It is interesting that, in the previously studied systems, the photolytically more reactive isomer has also been the more reactive isomer in ground-state solvolyses,[23] and our Ag(I) studies in meth-

(16) The origin of these photolytically generated carbocations has been discussed in detail in ref 4c. In summary, both heterolysis as well as homolysis followed by rapid electron transfer (cf.: Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* **1976**, *98*, 8135–8144) are viable possibilities.

(17) Hahn, R. C., Rothman, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 2409–2410.

(18) The alkene, **21**, also forms the di-π-methane product, **12**, via direct photolysis[17] so that some contribution towards the formation of **12** by secondary photolysis of the alkene may also be occurring. Note, however, the large amount of **12** formed from *endo*-BBOC at only 22% loss of starting material (Table I).

(19) Deprotonation of **26** to the alkene (**21**) followed by reprotonation may make a minor contribution to the formation of **27** (cf. reference 7). It is noteworthy that **27** is not formed with silver nitrate in the dark however. Protonation of **12** likewise provides an alternative route to **28**.

(20) Similar results are obtained in the buffered acetolysis of the exo tosylate; unbuffered acetolysis gives Wagner–Meerwein rearrangements leading primarily to the acetates of *exo*- and *endo*-benzobicyclo[2.2.2]-octen-2-ol.[7]

(21) These rate constants assume no internal return and are thus minimum values. The appearance of *exo*-BBOC in the *endo*-BBOC photolysis clearly suggests some internal return may be occurring.

(22) A preliminary report[4b] that such an inversion occurs in the [2.2.2] series was in error and has been corrected[4f] (as presented in Table II).

(23) Though the photolytic exo/endo rate ratio for the benzo[2.2.2]-chlorides (cf. Table II) is considerably larger than the ground-state solvolysis ratio of 2–3.

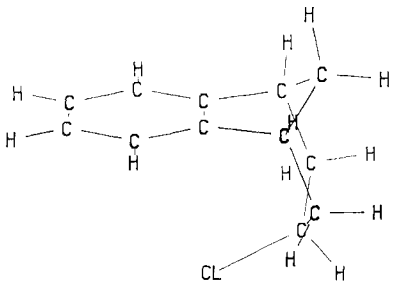
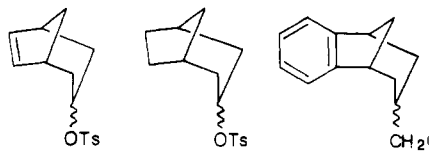


Figure 1. MM2 derived geometry for *endo*-BBOC.

anol give evidence that such is still the case. Though there are no comparable studies of exo/endo ground-state solvolytic reactivity in the benzobicyclo[3.2.1]octen-3-yl series, the analogous endo > exo reactivity pattern has been observed for the alkenes (**30**),[24] the alkanes (**31**),[25] and the



30 31 32

homologous pair of tosylates, **32**.[8] No anchimeric assistance by the double bound is observed for either isomer of **30**[24] and, since there is good spectral evidence that all of these structures exist in the rigid chair conformations shown,[8,9,24,26] one can attribute the greater ground-state reactivity of the endo isomers to the axial orientation of the nucleofuge.[24]

As to the *photolytic* reactivity of the BBOC isomers, we have proposed[4] that the C–Cl activation and stereoelectronic control observed in these photolytic solvolyses derive from a continuous transformation of the initially generated π,π^* state into a dissociative, primarily σ,σ^*, configuration, as a result of the avoided crossing of these states. The requisite mixing of the π,π^* and σ,σ^* states is overlap dependent and, in both the [2.2.1] and [2.2.2] series, is most favorable for the exo isomer where a "w-plan"-like relationship of the π and σ_{C-X} systems facilitates aryl interaction with the rear of the carbon side of the C–X bond. A molecular mechanics[27] analysis of the BBOC isomers indicates that C_3 is more distant from the aromatic ring in this series than is C_2 in the [2.2.1] and [2.2.2] substrates (2.8–2.9 Å vs. 2.4–2.5 Å), thus causing the drop in exo reactivity (cf. Table III). However, the chlorine atom in *endo*-BBOC is 3.08 Å from the aromatic ring, actually slightly *closer* than in the endo [2.2.2] (3.21 Å) and [2.2.1] (3.12 Å) substrates. More significant, we believe, is the propitious location of the chlorine atom virtually perpendicular to the π plane and just below the C_6–C_7 bond (cf. Figure 1). This position would be expected to diminish the negative interaction term which previous calculations indicated caused a reduction in the requisite mixing of the π,π^* and σ,σ^* states and rendered endo substrates relatively unreactive.[4c,28] Thus, *endo*-BBOC actually has the largest k_r of the endo series (cf. Table III) despite the gamma relationship of the nucleofuge. Furthermore, a vertical line dropped from the center of the C_6–C_7 aryl bond falls just to the *rear* of the chlorine atom; i.e., we believe *endo*-BBOC represents the first example in these studies where activation is occurring via a $\pi,\pi^*|\sigma,\sigma^*$ interaction primarily involving the backside of the nucleofuge.

Studies designed to further probe the limits of these aryl initiated photocleavage reactions are in progress.

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained using a Perkin-Elmer R-32 (90 MHz), a Varian XL-200 (200 MHz), or a Nicolet NT-470 (470 MHz) spectrometer. Chemical shifts are reported in ppm relative to Me_4Si. Mass spectra were obtained using a Finnigan automated gas chromatograph EI/CI mass spectrometer. Ultraviolet spectra were recorded using a Hewlett-Packard 8451A diode array spectrometer. Vapor-phase chromatography utilized a Varian Model 90-P for qualitative or preparative work, and Varian Models 1200 and 1400 or Hewlett-Packard Model 5710 A FID gas 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 20M on 80/100 AW/DMCS Chromosorb W; C, 30 meter × 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. Internal standards used for quantitative work were: hexadecane to monitor the disappearance of the *exo*- and *endo*-BBOC (response factor (RF) = weight(x)/weight(s) × area(s)/area(x) = 0.704) and to determine the weight percentages of the products (RF = 0.870 for hydrocarbon products, 0.720 for ether products, and 0.704 for the chlorides); 2-bromonaphthalene for ϕ_{14} (all ethers are assumed to have the same response factor as that of **23**, for which an RF of 1.092 was determined).

Photochemical studies mainly employed rotating turntables, quartz tubes, and a Hanovia model 68814-45 low-pressure mercury arc lamp or a Rayonet photochemical reactor (New England Ultraviolet Corp.). Deoxygenation was performed by bubbling argon through the solution for at least 20 min. Actinometry was done with 1-phenyl-2-butene by using matched quartz tubes.[13] Room-temperature fluorescence quantum efficiencies were measured by reference to toluene and are corrected for substrate absorbance. The ϕ_f for toluene in cyclohexane was taken to be 0.14.[29] Singlet lifetime measurements were done at room temperature using 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.[30]

Melting points were obtained on a Fisher-Johns melting point block and are uncorrected.

Chemicals. The following chemicals were used as received. Aldrich, 2,3-dichloro-1-propene, 2 M ethylmagnesium bromide in THF, 1 M BH_3–THF complex, 95–97% formic acid, Ph_3P; Mallinckrodt, silver nitrate, chromium trioxide, 30% H_2O_2, CCl_4; EM Science, iodomethane; J. T. Baker Chemical Co., sodium borohydride; Eastman Organic Chemicals, 2-bromonaphthalene. The following chemicals were modified or purified before use: sodium hydride (Metal Hydride Inc., dispersion in mineral oil) was washed with pentane, dried and kept under nitrogen atmosphere; indene (Aldrich), $SOCl_2$ (Mallinckrodt), (*E*)-2-heptene (Chemical Samples), and hexadecane (Columbia) were molecular distilled; Raney nickel catalyst (Aldrich) was washed with ethanol. Ether and THF (Mallinckrodt) were distilled under N_2 from sodium–benzophenone ketyl in a recycling still; methanol (Fisher Spectroscopic Grade), cyclohexane (Burdick and Jackson, distilled in glass), ethanol (U.S. Industrial Chemical Co.), and acetone and *tert*-butyl alcohol (Fisher Reagent Grade) were used as received.

(24) LeBel, N. A.; Maxwell, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 2307–2315.
(25) Banks, R. M.; Maskill, H. *J. Chem. Soc. Perkin Trans. 2* **1977**, 1991–1998, and references therein.
(26) Crist, B. V.; Rodgers, S. L.; Lightner, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 6040–6045.
(27) Allinger, N. L.; Yuh, Y. H. MM2, QCPE 395, 1980; Indiana University, Bloomington, IN.
(28) Cristol and co-workers[5] have suggested an electron-transfer mechanism for aryl activation of the C–Cl bond, which rationale would likewise predict greater reactivity for the more proximate endo isomer.
(29) Murov, S. L. *Handbook of Photochemistry* Marcel Dekker: New York, 1973, p 5.
(30) Morrison, H.; Pandey, G. *Chem. Phys. Lett.* **1983**, *96*, 126–128.

Alumina was Fisher, neutral, 80–200 mesh; silica was Davidson Grade 62, 60–200 mesh. Hexane and methylene chloride used for chromatography were bulk grade, distilled before use.

Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (17). This ketone was obtained by the method of Lansbury et al.,[6] mp 65–66 °C (lit.[6] 64–66), and its ^{1}H NMR spectral data were in agreement with the reported spectrum.[10] Mass spectrum, EI (70 eV): *m/e* (172 $M^{\bullet+}$), 130 (base peak); other major peaks are 129 and 115.

3-Chlorobenzo[6,7]bicyclo[3.2.1]octa-2,6-diene. This compound was isolated as a minor (9%) product in the preparation of 17.[6] ^{1}H NMR ($CDCl_3$, 90 MHz): 7.35 (m, 4 H, aromatic), 6.34 (d, 1 H, J = 9 Hz, vinyl), 3.30–3.55 (m, 2 H, bridgehead), 2.89 (m, 1 H, syn H_8), 2.12–2.43 (m, 2 H, H_2), and 2.01 (d, 1 H, anti H_8). Mass spectrum, EI (70 eV) *m/e* 190 ($M^{\bullet+}$), 192, 155 (base peak); other major peaks are 129 and 115.

Benzo[6,7]bicyclo[3.2.1]octa-2,6-diene (21). Into a 100-mL three-necked round-bottom flask equipped with a reflux condenser, a nitrogen inlet, and an addition flask was placed about 2.5 g of chopped sodium metal, 7 mL of *tert*-butyl alcohol, and 40 mL of THF, and the mixture was refluxed under a N_2 atmosphere. About 4.1 g (0.022 mol) of the chloroolefin in 10 mL of THF was added slowly from the addition flask and the refluxing continued for 36 h. The unreacted sodium metal was carefully removed by decanting and 20 mL of methanol was cautiously added to destroy residual sodium. Water (200 mL) was added and the organic layer extracted with ether. The ether was dried over anhydrous $MgSO_4$ and evaporated to give 2.98 g (88%) of an oily liquid. Mass spectrum, EI (70 eV): *m/e* 156 ($M^{\bullet+}$, base peak); other major peaks at 141, 128, and 115. The proton NMR spectrum was consistent with this known[31] compound.

Benzo[6,7]bicyclo[3.2.1]oct-6-ene (20).[32] About 0.59 g (3.1 mmol) of the chloro olefin was dissolved in 25 mL of ethanol and 0.5 g of Raney nickel catalyst was added. The reaction mixture was stirred overnight using a Brown-Squared hydrogenation apparatus. The ethanol solution was filtered through a sintered funnel to remove the catalyst and evaporated to give an oily liquid. The liquid was passed through 15 g of silica gel and eluted with hexane to obtain 0.29 g (59%) of **20**. A pure sample for spectroscopic study was obtained by molecular distillation at 105–110 °C/28 mm. ^{1}H NMR ($CDCl_3$, 470 MHz): δ 7.14 (s, 4 H, aromatic), 3.09 (m, 2 H, H_1 and H_5 (bridgeheads)) 2.22–2.26 (m, 1 H, syn H_8, $J_{syn\ 8\text{-}1}$ = 4.2 Hz, $J_{syn\ 8\text{-}eq\ 2}$ = 2.8 Hz, $J_{syn\ 8\text{-}anti\ 8}$ = 9.9 Hz), 1.63–1.70 (m, 3 H, anti H_8, eq H_2, eq H_4, $J_{eq\ 2\text{-}ax\ 3}$ = 6.1 Hz), 1.50–1.54 (m, 2 H, ax H_2, ax H_4, $J_{ax\ 2\text{-}ax\ 3}$ = 12.7 Hz, $J_{ax\ 2\text{-}eq\ 3}$ = 5.4 Hz), 1.36 (td, 1 H, eq H_3, $J_{eq\ 3\text{-}ax\ 3}$ = 14.1 Hz), 0.90 (ttd, 1 H, ax H_3, $J_{ax\ 3\text{-}eq\ 3}$ = 14.1 Hz). Mass spectrum EI (70 eV): *m/e* 158 ($M^{\bullet+}$), 129 (base peak), 115.

Benzo[2,3]tricyclo[3.2.1.0^{4,6}]oct-2-ene (12).[17] This compound was prepared by pyrolysis of a mixture of *exo*- and *endo*-benzo-[3,4]bicyclo[3.2.1]octen-2-yl chlorides. The details have been described elsewhere.[4f]

***exo*- and *endo*-Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-ol (19 and 18).**[7] To 1.0 g (5.8 mmol) of the ketone **17** dissolved in ethanol (10 mL) was added 0.28 g (7.4 mmol) of sodium borohydride. The reaction was stirred for 20 h at room temperature, poured into water, and extracted with ether. After drying over $MgSO_4$, the ether was evaporated to give an oily mixture consisting of **18**:**19** in a ratio of 1.8:1 (by VPC on column B at 160 °C). The alcohols were separated by chromatography on 100 g of alumina using hexane–dichloromethane mixtures as eluents. Elution with 90% hexane gave **18** as a viscous oil which solidified upon cooling (mp 31–32 °C). Elution with 50% hexane gave **19**, which was purified by treatment with activated charcoal and recrystallization from hexane (mp 76–77 °C). GC–mass spectrometry analysis of both **18** and **19**: EI (70 eV) *m/e* 174 ($M^{\bullet+}$), 115 (base peak); other major peaks at 156, 141, and 129.

Endo alcohol (18): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.13–7.32 (m, 4 H, aromatic), 3.88 (bs, 1 H, exo H_3, $J_{exo\ 3\text{-}eq\ 2}$ = 5.4 Hz), 3.16 (mm, 2 H, bridgeheads, $J_{1\text{-}syn\ 8}$ = 5.2 Hz), 2.39 (m, 1 H, syn H_8, $J_{syn\ 8\text{-}eq\ 2}$ = 2.6 Hz, $J_{syn\ 8\text{-}anti\ 8}$ = 10.4 Hz), 2.13 (ddd, 2 H, eq H_2, $J_{eq\ 2\text{-}ax\ 2}$ = 14.4 Hz), 1.94 (ddd, 2 H, ax H_2), 1.76 (d, 1 H, anti H_8), 0.40 (bs, 1 H, OH).

Exo alcohol (19): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.12 (s, 4 H, aromatic), 3.18 (m, 2 H, bridgeheads), 3.03 (tt, 1 H, endo H_3, $J_{endo\ 3\text{-}ax2}$ = 10.3 Hz, $J_{endo\ 3\text{-}eq\ 2}$ = 6.1 Hz), 2.13 (m, 1 H, syn H_8, $J_{syn\ 8\text{-}anti\ 8}$ = 10.2 Hz), 1.95–2.03 (m, 3 H, eq H_2 + OH, $J_{eq\ 2\text{-}ax\ 2}$ = 12.5 Hz), 1.64 (d, 1 H, anti H_8), 1.48 (t, 2 H, ax H_2).

***exo*-Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-yl Chloride (*exo*-BBOC).** To 0.66 g (3.8 mmol) of **18** in CCl_4 (15 mL) was added 1.04 g (3.96 mmol) of triphenylphosphine. The reaction mixture was refluxed with stirring for 16 h, cooled, and evaporated on a rotary evaporator. The residue was taken up in hexane (10 mL), filtered, and passed through silica (2–3 g). Evaporation gave 0.64 g of which analysis by VPC on columns A (160 °C) and B (140 °C) indicated the presence of alkene (**21**) (17%), **18** (16%) and *exo*-BBOC (67%). Preparative VPC on column D at 165–170° (retention time, 18 min) gave the product as a white solid (mp 51–52 °C).

^{1}H NMR ($CDCl_3$, 470 MHz): δ 7.16 (s, 4 H, aromatic), 3.33 (tt, 1 H, endo H_3, $J_{endo\ 3\text{-}ax\ 2}$ = 10.8 Hz, $J_{endo\ 3\text{-}eq\ 2}$ = 5.6 Hz), 3.23 (m, 2 H, bridgeheads), 2.21 (m, 3 H, syn H_8, eq H_2, $J_{syn\ 8\text{-}anti\ 8}$ = 10.8 Hz, $J_{eq\ 2\text{-}ax\ 2}$ = 12.7 Hz), 1.93 (t, 2 H, ax H_2), 1.77 (d, 1 H, anti H_8). Mass spectrum, EI (70 eV): *m/e* 194, 192 ($M^{\bullet+}$), 116 (base peak), 129; *m/e* 192.068 (calcd for $C_{12}H_{13}Cl$, *m/e* 192.071).

***endo*-Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-yl Chloride (*endo*-BBOC).** The exo alcohol (**19**, 0.28 g, 1.6 mmol) and triphenylphosphine (0.43 g, 1.65 mmol) were dissolved in CCl_4 (10 mL) in a 25-mL round-bottom flask and refluxed for 19 h. The reaction mixture was worked-up as described for *exo*-BBOC to give 0.23 g which VPC analysis on column A (160 °C) indicated was the desired product plus the alkene (**21**) (18%). Analytically pure samples were obtained by two recrystallizations from hexane (mp 85–86 °C).

^{1}H NMR ($CDCl_3$, 470 MHz): δ 7.16–7.23 (m, 4 H aromatic), 4.37 (t, 1 H, exo H_3, $J_{exo\ 3\text{-}eq\ 2}$ = 6.1 Hz), 3.19 (m, 2 H, bridgeheads, $J_{1\text{-}syn\ 8}$ = 5.2 Hz), 2.41 (m, 1 H, syn H_8, $J_{syn\ 8\text{-}eq\ 2}$ = 2.0 Hz, $J_{syn\ 8\text{-}anti\ 8}$ = 10.8 Hz), 2.32 (ddd, 2 H, eq H_2, $J_{eq\ 2\text{-}ax\ 2}$ = 15.5 Hz), 2.15 (d, 2 H, ax H_2), 1.72 (d, 1 H, anti H_8). Mass spectrum EI (70 eV): *m/e* 194, 192 ($M^{\bullet+}$), 116 (base peak), 129; *m/e* 192.068 (calcd for $C_{12}H_{13}Cl$, *m/e* 192.071).

***exo*-Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-yl Methyl Ether (23).** To 0.105 g (0.603 mmol) of **19** in dry THF (5 mL) was added NaH (25 mg, 1 mmol) and the mixture stirred at room temperature for 2 h under nitrogen. Methyl iodide (0.25 mL) was added and the reaction mixture further stirred overnight. Methanol (1 mL) was added, the reaction mixture was diluted with ether, and the organics washed with water. After drying over $MgSO_4$, the ether was evaporated to give 70 mg (62%) of product which was purified by VPC on column D (160 °C, retention time 12 min).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.14 (s, 4 H, aromatic), 3.23 (m, 2 H, bridgeheads, $J_{1\text{-}ax\ 2}$ = 2.2 Hz), 3.14 (s, 3 H, OCH_3), 2.66 (tt, 1 H, endo H_3, $J_{endo\ 3\text{-}ax\ 2}$ = 10.2 Hz, $J_{endo\ 3\text{-}eq\ 2}$ = 6.1 Hz), 2.08–2.23 (m, 3 H, syn H_8, eq H_2, $J_{syn\ 8\text{-}anti\ 8}$ = 10.6 Hz, $J_{eq\ 2\text{-}ax\ 2}$ = 12 Hz), 1.70 (d, 1 H, anti H_8), 1.51 (dt, 2 H, ax H_2). Mass spectrum, EI (70 eV): *m/e* 188 ($M^{\bullet+}$, base peak); other major peaks at 156, 129, 115; *m/e* 188.118 (calcd for $C_{13}H_{16}O$, *m/e* 188.120).

***endo*-Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-yl Methyl Ether (22).** This ether was prepared as described above for **23**. The endo alcohol (**18**, 0.135 g) provided a crude product (0.125 g, 86%) which was purified by VPC on column D (160 °C, retention time 10.5 min).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.04–7.16 (m, 4 H, aromatic), 3.44 (t, 1 H, exo H_3, $J_{exo\ 3\text{-}eq\ 2}$ = 4.8 Hz), 3.06 (q, 2 H, bridgeheads, $J_{1\text{-}syn\ 8} \approx$ 4.5 Hz), 2.81 (s, 3 H, OCH_3), 2.34 (m, 1 H, syn H_8, $J_{syn\ 8\text{-}anti\ 8}$ = 10.4 Hz, $J_{syn\ 8\text{-}eq\ 2} \approx$ 2.5 Hz), 1.85–2.06 (m, 4 H, ax and eq H_2), 1.75 (d, 1 H, anti H_8); Mass spectrum, EI (70 eV): *m/e* 188 ($M^{\bullet+}$, base peak); other major peaks at 156, 129, 115; *m/e* 188.118 (calcd for $C_{13}H_{16}O$, *m/e* 188.120).

***exo*-Benzo[6,7]bicyclo[3.2.1]oct-6-en-2-yl Methyl Ether (24).** This ether has been prepared and reported in previous studies.[4f]

***exo*-Benzobicyclo[2.2.2]octen-2-yl Methyl Ether (14).** This ether has been prepared and reported in previous studies.[4f]

Benzo[3,4]bicyclo[3.2.1]oct-3-en-2-yl Methyl Ether (16). This ether has been prepared and reported in previous studies.[4f] It is isolated as a mixture of exo and endo isomers which have proven to be unresolvable by VPC.

(31) Rosenthal, J. W.; Winstein, S. *Tetrahedron Lett.* **1970**, 2683–2686.
(32) Wilt, J. W.; Dabek, H. F.; Berliner, J. P.; Schneider, C. A. *J. Org. Chem.* **1970**, *35*, 2402–2410.

***exo*-Benzo[6,7]bicyclo[3.2.1]oct-6-en-2-yl Chloride (25).** This chloride has been previously reported[33] (though not characterized) and is obtained admixed (1:1) with *exo*-benzobicyclo[2.2.2]oct-5-en-2-yl chloride by treatment of *exo*-benzobicyclo[2.2.2]oct-5-en-2-ol with thionyl chloride in dry ether at room temperature. The chlorides are resolved analytically by VPC on column C at 150 °C (17.4 and 19.2 min for **25** and its isomer, respectively) but cannot be resolved by preparative VPC.

Photolyses of *exo*-BBOC and *endo*-BBOC in Methanol. Typically, 4 mL of the chloride (0.01 M) was degassed with argon for 20 min and irradiated in a quartz tube in the Rayonet reactor with the 254-nm lamps. Photolysis times were of the order of 2.5 h for exo and 15 min for endo chloride. Analysis by column C (150 °C) gave the products as: **20** (6.53 min), **10** (7.30 min), **21** (8.45 min), **12** (10.96 min), **22** (12.16 min), **23** (13.65 min), **24** (12.34 min), **14** (14.03 min), **25** (17.38 min) and **16** (19.28 min), with *exo*- and *endo*-BBOC at 18.10 and 27.91 min respectively. *exo*-BBOC gave unidentified[34] peaks at 5.40 and 24.38 min while *endo*-BBOC gave additional peaks at 5.16, 5.40, 6.16, 7.19, 14.17, and 14.38 min.

For the (*E*)-2-heptene quenching studies, a stock solution of *endo*-BBOC (1.18×10^{-2} M) and hexadecane (1.77 mg/mL) in methanol was prepared and 3.6 mL was transferred to each of four quartz tubes. The four solutions were degassed simultaneously with argon for 20 min, and two tubes were sealed. To the other two tubes was added 29.8 mg (0.11 M) and 41.8 mg (0.12 M) (*E*)-2-heptene, and all four tubes were then photolyzed for 35 min in a turntable using the Rayonet reactor and the 254-nm lamps. The four solutions as well as an unphotolyzed solution were analyzed on column C at 150 °C. An average of 31.3% loss of starting material was found in the control tubes and 31.2% found in the tubes containing quencher. There was only one observable difference in the product fingerprint between the two sets of tubes; i.e., the ratio of alkene (**21**) to di-π-methane product (**12**) was greatly increased in the tubes containing the triplet quencher. Quantitatively, the amount of **12** found in the tubes with heptene was 53% that formed in the controls.

The acetone sensitization experiment was done by using 0.013 M *endo*-BBOC plus 1.6 M acetone in methanol (the solution was degassed with argon prior to addition of the acetone). Photolysis was carried to 40% loss of starting material using the Rayonet reactor and 300-nm lamps. Analysis was on column C at 150 °C.

For the determination of ϕ_{dis}, the Rayonet reactor was equipped with five 254-nm lamps and a turntable. A solution of 1-phenyl-2-butene (1.72×10^{-2} M) in hexane was used for actinometry[13] and duplicate tubes, photolyzed for 15 min, provided a light intensity measurement of $(5.53 \pm .02) \times 10^{16}$ photons/s into the 4-mL solutions. Simultaneously, solutions of *endo*-BBOC in cyclohexane (1.19×10^{-2} M) and in methanol (1.04×10^{-2} M), and *exo*-BBOC in cyclohexane (1.30×10^{-2} M) and methanol (1.10×10^{-2} M), were charged with hexedecane, degassed, and irradiated in duplicate for 15 and 150 min, respectively. All analyses were by column C at 150 °C. Losses of starting material ranged from 5.4 to 22%, and ϕ_{dis} values were 0.081 (*endo*-BBOC/MeOH), 0.065 (endo-BBOC/cyclohexane), 0.0076 (*exo*-BBOC/MeOH), and 0.0034 (*exo*-BBOC/cyclohexane).

Ground-State Solvolyses. A 0.028 M solution of *endo*-BBOC in 10:1 methanol–water containing 0.027 M silver nitrate was stirred at room temperature for 2 h. After addition of several mg of NaCl, the solution was filtered and analyzed on column C at 150 °C. The products were **21** and **23** in a ratio of 56:44. In a comparable experiment with *exo*-BBOC, but for 48 h, **21** and **22** were observed, along with alcohol (**18**). Relative amounts were 18%:45%:37%, respectively. The rate study employed 22 mg of *endo*-BBOC (0.021 M) and 19 mg of *exo*-BBOC (0.020 M) in 5.5 mL of 10:1 methanol–water. An aliquot (0.5 mL) was removed for analysis, 8 mg of silver nitrate (0.021 M) was added, and the solution was stirred at 27 °C for 1.5 h. Several mg of NaCl was added, the solution filtered, and the filtrate analyzed on column C at 150 °C. Losses observed were 47.4% for *endo*-BBOC and 3.7% for *exo*-BBOC.

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Registry No. **12**, 24309-44-2; **14**, 84799-79-1; **16**, 105087-92-1; **17**, 13351-26-3; **18**, 105087-88-5; **19**, 105087-89-6; **20**, 15391-62-5; **21**, 24309-43-1; **22**, 105087-91-0; **23**, 105018-91-5; **24**, 84758-42-9; *exo*-BBOC, 105018-90-4; *endo*-BBOC, 105087-90-9; 3-chlorobenzo[6,7]bicyclo[3.2.1]octa-2,6-diene, 13351-27-4.

(33) Tanida, H.; Miyazaki, S. *J. Org. Chem.* **1971**, *36*, 425–435.

(34) These peaks did not match those for *endo*-benzobicyclo[2.2.2]-oct-5-en-2-yl methyl ether (retention time 18.7 min) or *endo*-benzo-[6,7]bicyclo[3.2.1]oct-6-en-2-yl methyl ether (retention time 15.8 min).

A Stereoselective Synthesis of α,β-Unsaturated Ketones Involving the Reactions of Organocuprates with β-Alkylthio α,β-Enones

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The substitution reactions of *E* and *Z* vinylogous thiol esters with organocuprates has been examined as a potential stereoselective synthetic route to α,β-enones. The stereoselectivities of the reactions were dependent upon substrate structure, cuprate reagent, cuprate transferable ligand, solvent, and temperature. The *E* vinylogous thiol esters all underwent reaction in THF with net retention of configuration except **26** which afforded net inversion with Me_2CuLi. In diethyl ether, the *E* vinylogous thiol esters generally afforded net inversion of configuration and only gave retention for enone **9** and for sterically hindered enone/cuprate pairs. The *Z* vinylogous thiol esters uniformly afforded reaction with net retention in either THF or diethyl ether with the exception of enone **34** which gave inversion with [*sec*-$Bu_2CuSCN]Li_2$. These results can be explained in terms of an addition–elimination pathway and several possible mechanisms are discussed.

We have, over the past few years, been exploring the chemistry of α-oxo ketene dithioacetals for use in the regio-, chemo-, and stereoselective construction of carbon–carbon bonds.[1] A full account of the chemo- and

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