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Photochemical Transformations. 44. Ground-State and Excited-State Reactions of Benzotricyclo[3.2.1.$0^{2,7}$]octenes[1]

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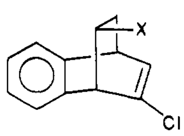
Irradiation of *anti*-6-X-7-chloro-3,4-benzotricyclo[3.2.1.$0^{2,7}$]oct-3-enes, **5**-X (X = Cl, OMs), at 254 nm in acetonitrile or acetic acid gives ionic (solvolysis and rearrangement) products, while similar irradiation of the syn epimers, **6**-X, gives only extremely slow decomposition to uncharacterizable products. **5**-OAc is inert in acetonitrile but is photoactive in acetic acid. The photoproducts are apparently derived from a short-lived singlet state. No products are observed in acetone-sensitized irradiations. The reactivity difference between **5** and **6** epimers is attributed, as in other previously studied homobenzyl systems, to the greater facility for excited electron transfer from the π^* orbital of the benzo group to the σ^* orbital of a carbon–nucleofuge bond when the nucleofuge is anti to the aromatic ring. It does not reflect comparable differences in ground-state reactivity in solvolysis. Unlike other systems (which give predominantly syn photo-Wagner–Meerwein rearrangements and rearrangement solvolyses), **5**-X species undergo cyclopropylcarbinyl-to-homoallyl rearrangement by migration of an anti bond to give *exo*-4-X-6-chloro-2,3-benzobicyclo[3.2.1]octa-2,6-dienes (exo-**4**-X), paralleling the ground-state carbocation rearrangement. The cyclopropyl chlorine at C-7 of the **5** and **6** compounds, which is also homobenzylic, is not photolabile.

The photoreactions of molecules containing aromatic chromophores and homobenzylic nucleofugal groups (β to the chromophores) have been of interest to our research group for some time.[2]

We became interested in the mode of excitation transfer from chromophore to reaction site and, as these reactions often involve rearrangements, in the stereochemistries of such rearrangements. In the course of these studies, the benzochlorobicyclo[2.2.2]octadienyl systems (**1**-Cl and **2**-Cl) and [3.2.1]octadienyl systems (*exo*- and *endo*-**3**-Cl and **3**-OMs) were investigated.[3,4] In addition, the benzylic isomers (**4**-Cl) have been studied.[1] We wish now to report results on the tricyclic species **5** and **6**, which are the cyclopropylcarbinyl isomers of the homoallylic isomers **1**, **2**, and **4**. These compounds are also homobenzylic and might therefore be expected[5] to react via $\pi^* \rightarrow \sigma^*$ electron transfer and perhaps to show stereochemical reactivity preferences[5-8] in their photosolvolysis and photorearrangement reactions.



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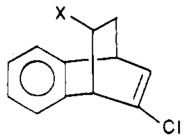

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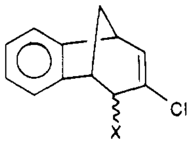

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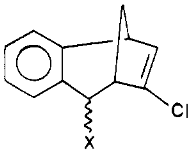

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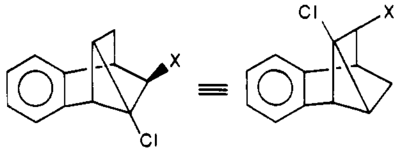

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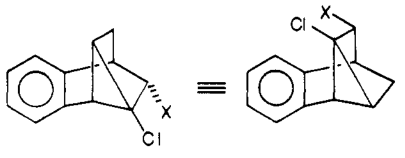

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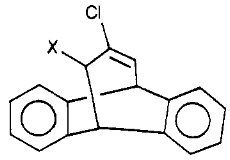
Systems **5** and **6** are useful substrates for stereochemical study as **5** has the nucleofugal group anti to the chromophoric benzene ring, while in **6** species the X group and the chromophore have a syn relationship.

An interesting feature of the photoreactions of *exo*- and *endo*-**3**-OMs[3] as well[9] as of the analogous dibenzobicyclononatriene **7**-OMs is the fact that irradiation leads to loss of methanesulfonate ion, rather than carbon–chlorine bond lysis. This is in sharp contrast to results with compounds such as **8**, where[10] irradiation leads cleanly to cleavage to chloride ion rather than to methanesulfonate ion. The greater reactivity of the carbon–chlorine bond over that of the carbon–oxygen bond in **8** species was ascribed to the lower cost of reduction in the electron transfer from the π^* orbital of the aromatic ring to the carbon–chlorine σ^* orbital over that to the carbon–oxygen σ^* orbital in elec-



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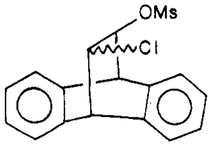

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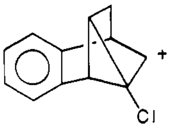

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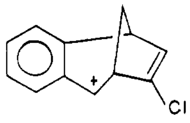

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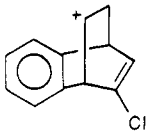

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tronically excited **8**. In **3**-OMs and in **7**-OMs, in contrast with **8**-OMs, the chlorine is γ to the chromophore[11] rather than β and is ethylenic as well,[12] while the methanesulfonate group is allylic.

5-OMs and **6**-OMs are similar to **8** in that both the chlorine and methanesulfonate groups are homobenzylic and thus the carbon–chlorine bond might be more likely to react, although (see below) the geometric attitudes of the aromatic ring and the carbon–chlorine bond are quite different in **5** (or **6**) and in **8** and, in addition, cyclopropyl halides are more difficult to reduce than are aliphatic halides.[14]

Results

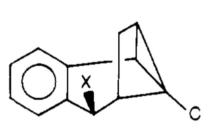
Ground State. The ground-state acetolysis of either **5**-OMs or **6**-OMs leads to a mixture of *exo*- and *endo*-**4**-OAc in a ratio[1,15] of about 3 to 1. That both epimers give identical product mixtures, without **3**-OAc being formed, suggests that ionization proceeds, before capture, either via **9**, or, without intervention of **9**, to its homoallylic and benzylic isomer **10** and that **11** is not involved either in rearrangement from **9** or in direct formation via anti bond participation from **6**. These conclusions are based upon the fact[3] that **1**-OMs is significantly more reactive in acetolysis (to give **3**-OAc) than is **2**-OMs (to give **5**-OAc and **6**-OAc). These observations suggest that migration of the benzo ring in **11** should be greatly favored over that of the chloroethenyl group and that **3**-OAc should thus result.

We decided to measure the rates of acetolysis of **5**-OMs and **6**-OMs. At 82 °C, with 1.0 M sodium acetate in acetic acid, **5**-OMs gave only **4**-OAc and no **5**- or **6**-OAc, On the other hand, **6**-OMs gave a trace of **5**-OAc (solvent or acetate participation), but the product mixture was almost entirely the **4**-OAc epimers. The rate constants were as follows: for **5**-OMs, $1.6 \times 10^{-4}\ \mathrm{s}^{-1}$, and for **6**-OMs, $2.4 \times 10^{-5}\ \mathrm{s}^{-1}$.

Irradiations. Irradiations of the anti epimeric chloride **5**-Cl[4] at 254 nm in acetonitrile-d_3 containing 2% D_2O gave an efficient photoreaction leading to 18% of *exo*-**4**-Cl, 9% of *endo*-**4**-Cl, 32% of *exo*-**4**-OH, 30% of **12**-OH, the di-π-methane product from **4**-OH, and 12% of *exo*-**4**-$NDCOCD_3$. The ratio of alcohol to amide products is very similar to that found when *exo*-**4**-Cl is photosolvolyzed under identical conditions,[1] and the ratio of exo-**4**-OH to **12**-OH varied with the extent of irradiation. The results are thus consistent with the intervention of **10** as the cationic species captured by the various nucleophiles.

When the irradiation was conducted in "dry" acetonitrile (trace of water present), the formation of the alcohol was reduced, the amount of chloride was increased somewhat, and the principal product (>50%) was the exo amide. A small amount of endo amide was also formed. The increase in **4**-Cl is likely due to the decreased solvent polarity,[16] giving more ion pair return; the increase in amide is to be expected.

When the syn chloride **6**-Cl was irradiated in "wet" acetonitrile, its photoactivity was much lower than that of its anti epimer. Thus, while about 60% of **5**-Cl reacted in 3 h, only 30% of **6**-Cl reacted in 85 h under similar conditions. The latter reaction gave no recognizable products, although trace amounts of **4** or **12** species would have been noted.



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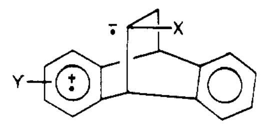

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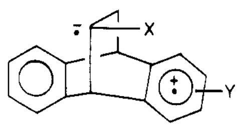

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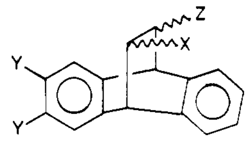

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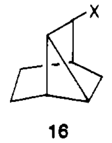

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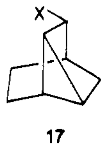

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The methanesulfonates showed photoactivities similar to the chlorides. In "wet" acetonitrile, the anti epimer **5**-OMs reacted rapidly (>80% in 3.5 h), while the syn epimer did not (~25% in 162 h under similar conditions). **5**-OMs gave largely *exo*-**4**-OH and its di-π-methane product, with some amide and some ion pair return product. As the latter is benzylic, it was rapidly lost by ground-state reaction and was seen in only one short-time irradiation. The syn epimer **6**-OMs gave no identifiable products.

While both **5**-OAc and **6**-OAc were only slowly decomposed by irradiation in "wet" acetonitrile, without formation of identifiable products, the anti epimer gave *exo*-**4**-OAc upon irradiation in acetic acid, although somewhat less efficiently than **5**-Cl or **5**-OMs. No such reaction was observed with the syn acetate. The requirement for acid catalysis in photosolvolysis of acetates has been reported earlier with **7**-OAc.[17]

The multiplicities of these photoreactions were briefly explored. The reactions would appear to involve short-lived singlet states. Irradiation of **5**-Cl or **5**-OMs in acetone with 300-nm light gave substantially no photoreaction and no **4** products. These results suggest that **5** triplets are unreactive but also permit the unlikely explanation that energy transfer from triplet acetone to **5** does not occur. In order to test this, we made use of the observation by Fischer and his co-workers[18] who noted that the reaction of the $n\pi^*$ triplet of acetone-d_6 with isopropyl alcohol results in the loss of isopropyl alcohol and the formation of acetone-d_0. Thus these phenomena are indicative of triplet acetone. When **5**-Cl was added to a solution of acetone-d_6 and isopropyl alcohol in acetonitrile-d_3, the formation of acetone-d_0 was quenched. This indicates that triplet transfer does occur to **5**-Cl, but that the triplet is unreactive.

It has previously been noted[19] that triplets in diarobicyclo[2.2.2]octadiene systems are generally unreactive toward photosolvolysis, as it is perceived that the energy of the triplet is insufficient to allow electron transfer to occur. The results with **5**-Cl and **5**-OMs are consistent with this view.

In confirmation of the result that the triplet of **5**-OMs was unreactive, we showed that the singlet reaction of **5**-OMs in acetonitrile-d_3 could be quenched with ace-

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[11] Unpublished experiments in our laboratory have shown that substituents γ to aromatic rings are less reactive than those β.

[12] Ethylenic halides are more difficultly reducible than corresponding saturated halides.[13]

[13] Miller, L. L.; Riekena, A. *J. Org. Chem.* **1969**, *34*, 3359.

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[17] Cristol, S. J.; Daussin, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2866.

[18] Blank, B.; Henne, A.; Laroff, G. P.; Fischer, H. *Pure Appl. Chem.* **1975**, *41*, 475.

[19] Cristol, S. J.; Bindel, T. H.; Hoffmann, D.; Aeling, E. O. *J. Org. Chem.* **1984**, *49*, 2368.

tone-d_6.[20] A Stern–Volmer plot of the quenching data gave values of $k_q\tau$ of 5 ± 2 L mol^{-1}. If one assumes a quenching rate constant of 2×10^{10} L mol^{-1} s^{-1},[22] the lifetime of the excited singlet of **5**-OMs may be computed to be approximately 0.2 ns.

Discussion of Results

This section is divided into three areas. The first of these is related to the stereochemistry of the excitation transfer process, the second to the question of regiochemistry of excitation transfer, and the third to the rearrangement stereochemistry.

The photoactivity of the anti epimers **5** upon irradiation, with substantial formation of **4** species (ionic products) in a few hours, is to be contrasted with the inertness of the syn epimers **6** (slow decomposition, without formation of **4** species, in periods greater than 100 h). It has been previously proposed[5] that this preference[6] for anti excitation transfer is a result of the lower free energy of transfer of the π^* electron of the π,π^* excited state to the σ^* orbital of an anti C–X bond (that is, to give a zwitterionic biradical, for example **13**) compared with that of a syn C–X bond, e.g., to give **14**. This is due to the fact that the σ^* orbital of the anti bond has its major lobe close to the π orbital of the aromatic ring while the syn bond orbital does not. A similar rationalization seems reasonable for **5** and **6** epimers. Thus the zwitterionic biradical resulting from **5** would have significantly greater coulombic stabilization than the analogous one from **6**.

An alternative explanation, that may be discarded, is that **5** and **6** species differ enough in energy that this could account for the photoreactivity difference. In fact, however, **5** species are somewhat more stable thermodynamically[4,23] than **6** species (of the order of magnitude of perhaps 1.0 kcal/mol).

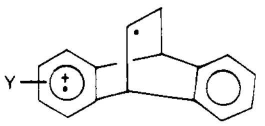
The energy difference between the ground-state solvolysis transition states, about 2 kcal/mol (derived by summing the stability and reactivity differences between **5** and **6**), is remarkably similar to that observed by LeBel[24] on the epimers **16** and **17**, analogous to **5** and **6**, but without the benzo rings on the tricyclic systems. In the LeBel system, however, the principal product of acetolysis (**16**-OAc) has the tricyclic system remaining, although small amounts of epimer **17**-OAc and homoallyl products were formed. The energy similarities suggest that the paths of solvolysis in our system and in LeBel's involve first the formation of the cyclopropylcarbinyl cation (in our case, **9**) followed by, in our case, rearrangement to **10**, rather than any rearrangement concerted with loss of nucleofuge.

While **5**-Cl and **5**-OMs lead to photosolvolysis, with loss of chloride ion and methanesulfonate ion, respectively, in acetonitrile, **5**-OAc is photoinert in this solvent. These results are analogous to those[17] in the **7** system, where **7**-Cl and **7**-OMs lead to ionic products in acetonitrile, while the acetate does not. Like **7**-OAc, **5**-OAc is photoactive in the ionic sense in acetic acid. The demonstration of acid catalysis in the **5** system confirms the idea[17] that these photoreactions do not involve cleavage into two radicals, followed by electron transfer, but that rather the nucleofuge separates with an electron pair in the initial cleavage reaction.

The lack of efficient photoactivity in all of the syn compounds deserves some comment. As mentioned above, the **6** (as well as **5**) compounds all have a β chlorine atom, which therefore might have reacted in the "ionic" sense. Even though it is not clear what products might have been anticipated from such a reaction, what is clear is that **6** species are relatively inert, surviving more than 100 h of irradiation. One may therefore conclude that electron transfer does not occur with any efficiency from the π^* orbital of **6** (or **5**) to the cyclopropyl chloride system. Two factors (both adverse) affect this possible transfer. The reduction potential[14] of cyclopropyl chlorides and the angle which the σ^* orbital of the carbon–chlorine bond makes with the ring are both unfavorable. Whether the latter contributes solely as a thermodynamic problem[25] or whether, in addition, there is a need for appropriate overlap geometry for efficient electron transfer remains to be learned.

The thermodynamics of the electron transfer[25] depend as well on the energy of the π,π^* state. As the energy of benzenoid triplets is well below that of singlets,[26] the photoinertness of the triplets of **5** and **6** is easily rationalized.[19]

Studies[6,10,19,27] on a variety of dibenzobicyclo[2.2.2]octadiene (**15**) systems have shown that, in sharp contrast to ground-state reactions, where clean anti migration is seen, there is a preponderance of syn (suprafacial) migration in the photo-Wagner–Meerwin rearrangements and in the rearrangements accompanying photosolvolysis. This is true whether or not the chromophoric ring is syn or anti to the nucleofuge and is seen as well in the **1** and **2** systems.[4,28] The results, and the failure to see clean stereospecificity, have been rationalized on the basis that two reaction channels may be utilized starting from the zwitterionic biradical. For example, starting with **13**, one may assume fragmentation at the radical anion site to give the biradical cation **18**. This species may subsequently suffer migration of either ring to give ultimately a mixture of benzylic cations, **19** and **20**, leading to product mixtures. An alternative fate proposed for **13** (or **14**) is migration of the ring syn to X, leading to **19** from **13** and **20** from **14**, *concerted* with the loss of X$^-$.



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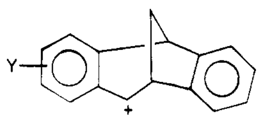

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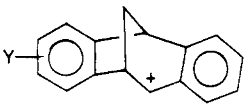

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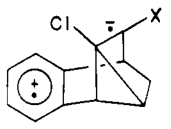

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Unlike these cases, the photoreactions of **5** species all are cleanly anti stereospecific. The two alternatives for syn migration from the zwitterionic biradical **21** would lead in one case to a severely strained ring system[1] or to a relatively unstable cation. Thus one may assume that fragmentation without migratory participation, followed by electron demotion, occurs, yielding the ion **9**, which, as

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[20] Acetone is known[21,22] to quench excited singlets of benzene and compounds containing benzene rings.

[21] Augustiniak, W. A.; Wiechowicz, E.; Wojtczak, J. *J. Photochem.* **1976/1977**, *6*, 229.

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[26] Murov, S. L. *Handbook of Photochemistry*; Marcel Decker: New York, 1973; Section I.

[27] Cristol, S. J.; Opitz, R. J. *J. Org. Chem.* **1985**, *50*, 4558.

[28] Cristol, S. J.; Fleming, M. S., unpublished work.

described above, rearranges to the benzylic ion **10** and to benzylic products.

Experimental Section

General Methods. ^1H NMR spectra were recorded on a Varian Associates EM-390 spectrometer in $CDCl_3$ solvent (with 1–5% Me_4Si) unless otherwise noted. Mass spectra were obtained on a Varian MAT CH-5 or CH-7 spectrometer. Melting points were determined with a Thomas-Hoover Unimelt apparatus and were corrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Certain oils described were difficult to purify and difficult to keep in pure form, so that elemental analyses were not attempted. Mass spectral data for these compounds are presented.

All irradiations were performed in a Rayonet Srinivasan-Griffin Photochemical Reactor (the Southern New England Ultraviolet Company) (referred to herein as the "Rayonet") with either RPR-2537Å (254 nm) or RPR-3000Å (300 nm) lamps. All irradiation samples were sealed with rubber septa and deoxygenated by bubbling N_2 through the solutions (10 min for NMR-tube irradiations, 30 min for larger samples) before irradiation. All NMR-tube irradiations were performed on a merry-go-round apparatus, Model MGR-100 (the Southern New England Ultraviolet Company). All quantitative values for destruction of starting material and formation of various products in NMR-tube irradiations were determined by integration of the signal in the ^1H NMR spectrum for the proton geminal to an electronegative functional group (H-6 for the **5** and **6** compounds, H-4 for **4**-Cl, and H-2 for the other compounds) with the total integration of the spectrum for δ 0–9 ppm (excluding residual protons on solvent) being used as an internal standard.

Direct Irradiation of *anti*-6,7-Dichloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (5-Cl) in Acetonitrile-d_3 Containing 2% D_2O. A solution of 35 mg (0.16 mmol) of **5**-Cl in 0.5 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was irradiated with 12 254-nm lamps in the Rayonet and monitored periodically by ^1H NMR. After 3.0-h irradiation, 55–60% of the starting material had reacted. Five products were observed. Together they accounted for 75–80% of the lost starting material. These products[1] were the exo- and endo-benzylic chlorides, *exo*- and *endo*-**4**-Cl, the exo-benzylic amide, *exo*-**4**-$NDCOCD_3$, the exo-benzylic alcohol, *exo*-**4**-OD, and the exo-[4.1.1.0^{5,7}] alcohol, **12**-OD. These products constituted approximately the following percentages of the total observed product: 18, 9, 11, 32, 30. After 10.0 h of irradiation, 85% of starting material had been lost. The ratio of products was similar to what was observed at 3.0 h (except that the proportion of **12** had increased, consistent with the idea that it was derived by a di-π-methane rearrangement from *exo*-**4**-OD[1]).

Large-Scale Direct Irradiation of 5-Cl in Acetonitrile. A solution of 324 mg (1.44 mmol) of **5**-Cl in 350 mL of "dry" CH_3CN in a large quartz tube was irradiated for 0.5 h with 16 254-nm lamps in the Rayonet. The solvent was removed. This gave 374 mg of light brown oil. The oil was packed onto silica gel and eluted with ether containing 25% hexanes on a dry column of silica gel treated with a fluorescence indicator. The following products were isolated and identified by ^1H NMR: band 2 (R_f 0.16) contained 78 mg of *exo*-**4**-NHAc; band 3 (R_f 0.34) contained 13 mg of material which was 60% *endo*-**4**-NHAc and 40% uncharacterizable material; band 5 (R_f 0.71) contained 16 mg of material which was 85% *exo*-**4**-OH and 15% uncharacterizable material. In addition, band 8 (R_f 0.95) contained 226 mg of material which was found to contain 80% starting material and 20% of *exo*- and *endo*-**4**-Cl, which were present in a 4:3 exo/endo ratio. (The other bands contained only very small amounts of material and had NMR spectra not consistent with those of known materials.)

Preparation of *syn*-6,7-Dichloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (6-Cl). A solution of 1.47 g (5.2 mmol) of **5**-OMs[29] and 7.56 g of LiCl in 50 mL of dimethylformamide was heated at 90 °C for 48 h. After the solution had cooled, 150 mL of water was added, followed by extraction with 100 mL of a 1:1 mixture of ether and hexanes. The organic phase was washed with saturated aqueous $NaHCO_3$, water, aqueous $Cu(NO_3)_2$ (twice), and water (twice) and dried ($MgSO_4$). Filtration and evaporation of solvent gave a quantitative yield of a yellow oil which was shown by ^1H NMR analysis to be a 4:3:3 mixture of *exo*- and *endo*-**4**-Cl and **6**-Cl. Small amounts of the formates *exo*- and *endo*-**4**-OCHO were also observed. A solution of this mixture in 160 mL of 35% acetone in water was heated at reflux for 12 h. The solution was allowed to cool. An additional 50 mL of water was added to the solution which was then extracted with two 100-mL portions of ether. The combined organic layers were washed with water and dried ($MgSO_4$). Filtration followed by removal of the solvent gave a yellow oil. ^1H NMR analysis showed that the benzylic chlorides had been converted to alcohols (**4**-OH) (exo:endo = 5:1) while the syn-tricyclic chloride had not reacted. Separation of 250 mg of **6**-Cl from the alcohols was achieved by elution of the mixture on a silica gel column. After recrystallization from hexanes: mp 86–88 °C; ^1H NMR δ 7.3 (m, 4 H, Ar H), 4.6 (d, 1 H, H-6, $J_{6,5} = 5$ Hz), 3.4 (t, 1 H, H-5, $J_{5,6} = 5$ Hz, $J_{5,8\mathrm{anti}} = 5$ Hz), 2.8 (d, 1 H, H-2, $J_{2,1} = 8$ Hz), 2.3 (m, 2 H, H-1 and H-8$_{\mathrm{anti}}$), 1.2 (d, H-8$_{\mathrm{syn}}$, $J_{8\mathrm{syn},8\mathrm{anti}} = 12$ Hz). Anal. Calcd for $C_{12}H_{10}Cl_2$: C, 64.03; H, 4.48. Found: C, 64.08; H, 4.53.

Direct Irradiation of *syn*-6,7-Dichloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-ene (6-Cl) in Acetonitrile-d_3 Containing 2% D_2O. A solution of 31 mg (0.14 mmol) of **6**-Cl in 0.4 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was irradiated with 13 254-nm lamps in the Rayonet. The solution was monitored both before and periodically during irradiation by ^1H NMR spectroscopy. Disappearance of some starting material was seen (30% after 85 h), but even after 152 h of irradiation, no characterizable products (and, in particular, no products in the benzylic (**4**) series of compounds) could be detected.

Direct Irradiation of 7-Chloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-en-*anti*-6-ol Methanesulfonate (5-OMs). A solution of 31 mg (0.11 mmol) of **5**-OMs in 0.5 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was irradiated with 13 254-nm lamps in the Rayonet. The experiment was monitored both before and periodically during irradiation by ^1H NMR spectroscopy. After 3.6 h, 80–85% of starting material had reacted. Five products were observed, which together accounted for 60% of the lost starting material. These products (and the proportion of the identified product which they represented) were *exo*-**4**-OD (24%); **12**-OD (30%); *exo*-**4**-$NDCOCD_3$ (16%); *endo*-**4**-$NDCOCD_3$ (19%) (this product was not observed at very short irradiation times and was presumably formed from the exo epimer); and a compound which was believed to be *exo*-**4**-OMs (11%). More of this last product was observed earlier in the experiment; however, it would not be expected to be very stable because of ground-state solvolysis. Both the H-2 and H-6 resonances of this compound were observed, with multiplicities and chemical shift values consistent with those expected for *exo*-**4**-OMs. While the product ratios changed considerably over the course of the experiment, it seemed clear that, even at very short irradiation times, solvolysis had predominated over rearrangement.

Direct Irradiation of 7-Chloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-en-*syn*-6-ol Methanesulfonate (6-OMs). A solution of 36 mg (0.13 mmol) of **6**-OMs[3a] in 0.5 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was irradiated in the Rayonet with 13 254-nm lamps and monitored periodically by ^1H NMR spectroscopy. After 162 h of irradiation, approximately 75% of the starting material remained. No products could be characterized, and, specifically, no products in the **4** system could be detected.

Direct Irradiation of 7-Chloro-3,4-benzotricyclo[3.2.1.0^{2,7}]oct-3-en-*anti*-6-ol Acetate in Wet Acetonitrile (5-OAc). A solution of 48 mg (0.19 mmol) of **5**-OAc in 0.5 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was irradiated with 14 254-nm lamps in the Rayonet and monitored as above. Significant destruction of starting material was observed (40–45% after 39 h of irradiation) but no characterizable products were observed. A significant amount of baseline elevation was observed in the δ 0.5–3.0 region of the ^1H NMR spectrum. At longer times, production of **5**-OH was observed. The speculation that this was an acid-catalyzed ground-state reaction product is supported by the fact that this reaction proceeded further during a period in which the sample tube was kept in the dark. No **4** compounds

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[29] **5**-OMs, which had previously[3a] been reported as an oil, was crystallized; mp 81–82 °C. Anal. Calcd for $C_{13}H_{13}O_3ClS$: C, 54.83; H, 4.60. Found: C, 54.95; H, 4.81.

were seen in 150 h of irradiation.

Preparation of 7-Chloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-en-*syn*-6-ol Acetate (6-OAc). To a solution of 1.08 g (5.2 mmol) of **6**-OH[3a] and 6 mL of pyridine in 24 mL of benzene was added 3 mL of acetic anhydride. After 56 h, the solution was diluted to 130 mL with water and extracted with two portions of ethyl ether. The combined ether layers were washed with 10% HCl and water (three times) and dried ($MgSO_4$). Filtration and evaporation of solvent gave 1.18 g (91%) of a light yellow oil which ^1H NMR analysis showed contained 10% of **6**-OH and 90% of **6**-OAc. Separation of the acetate from the alcohol was achieved by elution on a silica gel column: ^1H NMR δ 7.2 (m, 4 H, Ar H), 5.2 (d, 1 H, H-6, $J_{6,5}$ = 5 Hz), 3.5 (t, 1 H, H-5, $J_{5,6}$ = 5 Hz, $J_{5,8\text{anti}}$ = 5 Hz), 2.8 (d, 1 H, H-2, $J_{2,1}$ = 8 Hz), 2.4 (ddd, 1 H, H-8_{anti}, $J_{8\text{anti},1}$ = 3 Hz, $J_{8\text{anti},5}$ = 5 Hz, $J_{8\text{anti},8\text{syn}}$ = 11 Hz), 2.1 (dm, 1 H, H-1, $J_{1,2}$ = 8 Hz), 1.8 (s, 3 H, CH_3), 1.1 (d, 1 H, H-8_{syn}, $J_{8\text{syn},8\text{anti}}$ = 11 Hz); mass spectrum, **m/e** (rel intensity) M^+, 248 (60) $M^+ + 2$, 250 (20), $M^+ - 42$, 206 (100), $M^+ - 60$, 188 (33); $M^+ - 77$, 171 (41); $M^+ - 95$, 153 (49).

Direct Irradiation of 7-Chloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-en-*syn*-6-ol Acetate (6-OAc) in Wet Acetonitrile-*d*$_3$. Thirty-five milligrams (0.14 mmol) of **6**-OAc in 0.5 mL of CD_3CN containing 2% D_2O in a quartz NMR tube was irradiated with 14 254-nm lamps in the Rayonet and monitored periodically by ^1H NMR spectroscopy. After 28 h, loss of 35% of the starting material had occurred. A considerable amount of baseline elevation in the δ 0.8–3.0 region of the ^1H NMR spectrum was observed. The only identifiable product was **6**-OH. This alcohol accounted for only 20% of the loss of starting material. It was believed that this alcohol was the product of ground-state hydrolysis. This was supported by the observation that conversion of the starting material to this product continued when the sample tube was kept in the dark. Irradiation of the sample for up to 187 h still produced no compounds of the **4** series nor any other photochemical product which could be characterized.

Direct Irradiation of 7-Chloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-en-*anti*-6-ol Acetate (5-OAc) in Acetic Acid-*d*$_4$. A solution of 38 mg (0.15 mmol) of **5**-OAc in 0.5 mL of acetic acid-d_4 in a quartz NMR tube was irradiated at 254 nm in the small Rayonet with 13 lamps. After 4.1 h of irradiation, about 10% of the sample had been converted to *exo*-**4**-$OCOCD_3$. This product accounted for most of the loss of starting material.

Direct Irradiation of 7-Chloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-en-*syn*-6-ol Acetate (6-OAc) in Acetic Acid-*d*$_4$. An experiment, similar to that described for the anti isomer, was conducted with 42 mg (0.17 mmol) of **6**-OAc. After 100 h of irradiation, 70–75% of the starting material remained and, in particular, no products could be identified. No products of the **4** series of compounds could be detected.

Sensitized Irradiation of *anti*-6,7-Dichloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-ene (5-Cl). A solution of 24 mg of **5**-Cl in 0.5 mL of acetone-d_6 containing 3% D_2O in a Pyrex NMR tube was irradiated with five 300-nm lamps in the Rayonet. After 250 h of irradiation over 90% of the starting material remained. No products were observed.

Sensitized Irradiation of 7-Chloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-en-*anti*-6-ol Methanesulfonate (5-OMs). A solution of 41 mg of **5**-OMs in 0.5 mL of acetone-d_6 containing 3% D_2O was irradiated as above with 12 300-nm lamps. After 113 h of irradiation at least 95% of the starting material remained. No products were observed.

Triplet Quenching of Acetone-*d*$_6$ by *anti*-6,7-Dichloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-ene (5-Cl). Two 0.5-mL solutions of CD_3CN containing 2% D_2O and 1.0 M acetone-d_6 were prepared. Four microliters of isopropyl alcohol was added to each solution to make the solutions 0.1 M in isopropyl alcohol. In addition, 43 mg (0.19 mmol) of **5**-Cl was added to one solution. Each solution was filtered into a Pyrex NMR tube, and each was monitored periodically by ^1H NMR spectroscopy during irradiation. The solutions were irradiated with six 300-nm lamps in the Rayonet. After 22.8 h of irradiation, 70% of the isopropyl alcohol in the sample with no **5**-Cl had reacted. The major product in this experiment was acetone-d_0, as has been reported in a similar experiment.[18] At this time, however, little or no isopropyl alcohol had been lost in the tube containing **5**-Cl. In the sample which contained the chloride, approximately 80% of the isopropyl alcohol remained after 200 h of irradiation.

Singlet Quenching of 7-Chloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-en-*anti*-6-ol Methanesulfonate (5-OMs) by Acetone-*d*$_6$. Four solutions of 0.5 mL of CD_3CN containing 2% D_2O and varying amounts of acetone-d_6 were prepared. The acetone concentrations were 0.00 M (0%), 0.68 M (5%), 1.36 M (10%), and 2.65 M (19%). A sample of **5**-OMs (43 mg in each solution except 44 mg in the 2.65 M acetone-d_6 solution) (0.15 mmol) was added. Each solution was filtered into a quartz NMR tube. Each was then irradiated with 12 254-nm lamps in the Rayonet. The observed products were *exo*-**4**-OD, *exo*-**4**-$NDCOCD_3$, and **12**-OD. Analysis of the relative quantum yields of the various samples was made, based on observations at monitoring periods in which approximately comparable amounts of reaction had occurred. These times of irradiation and the percentages of conversion measured are as follows: 0.0 M acetone-d_6 sample, 0.2 h (12.7%); 0.68 M acetone-d_6 sample, 1.5 h (17.4%); 1.36 M acetone-d_6 sample, 1.5 h (11.0%); 2.65 M acetone-d_6 sample, 1.5 h (6.7%). The amount of light absorbed in each sample was assumed to be proportional to the time of irradiation (with correction being made for the light absorbed by acetone: 0, 4.5, 9, and 16% of the light for the respective samples, in order of increasing acetone-d_6 concentration). A small correction was made in the value for the 2.65 M acetone-d_6 sample to account for the fact that slightly more of the **5**-OMs was present in this tube. The relative quantum yields calculated are 1.0, 0.19, 0.13, and 0.086, in order of increasing acetone concentration.

Using the data for the two lower acetone concentrations, we computed a value of 5 ± 2 L mol^{-1} for the Stern–Volmer[30] constant, $k_q\tau$.

Determination of the Rate Constants for Acetolysis of the Anti and Syn Epimers of 7-Chloro-3,4-benzotricyclo$[3.2.1.0^{2,7}]$oct-3-en-2-ol Methanesulfonate (5-OMs and 6-OMs). Three samples, each containing 43 mg (0.15 mmol) of **5**-OMs or **6**-OMs, in 0.5 mL of acetic acid-d_4 containing 1.0 M NaOAc were placed in a constant temperature bath at 82.4 °C and monitored both before and periodically during solvolysis by ^1H NMR spectroscopy. Three products were observed from **5**-OMs, *exo*- and *endo*-**4**-OAc, and *exo*-**4**-OH. The proportion of each of the four compounds present in the samples (three products and starting material) was determined by repeated integration of resonances for these compounds in the ^1H NMR spectrum (H-6 for the tricyclic compound, H-2 for the others). The first-order rate constants for each sample were determined from these data. Least-squares lines were fitted to the data for each individual sample. The rate constants for **5**-OMs were 1.58, 1.55, and 1.52 $\times 10^{-4}\ s^{-1}$.

In the case of **6**-OMs, about 5% of **5**-OAc was observed as a product, in addition to those products obtained from **5**-OMs. It was not treated as a unimolecular product. (The resonance for H-6 of **5**-OAc was measured in the analysis.) Except for this, the analysis of the experiment was performed in the same way as that described for the determination of the rate constant for solvolysis of **5**-OMs. The rate constants for solvolysis of the syn-tricyclic methanesulfonate were 2.48, 2.29, and 2.47 $\times 10^{-5}\ s^{-1}$.

Ultraviolet spectra were taken in dry (distilled from CaH_2) acetonitrile on a Cary 17 or 219 spectrometer (λ_{max}, nm, (ϵ_{max})). **5**-Cl: 275 (250), 267 (310), 261 (200), 254 (not a maximum, 200); **6**-Cl: 273 (220), 265 (270), 263 (270), 258 (230), 254 (not a maximum, 180); **5**-OMs: 274 (430); 265 (500), 259 (420), 254 not a maximum, 320). There was no significant absorption by these compounds above 285–290 nm.

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Registry No. **5**-Cl, 75920-62-6; *exo*-**4**-Cl, 102306-41-2; *endo*-**4**-Cl, 102418-47-3; *exo*-**4**-$NDCOCD_3$, 102306-46-7; *exo*-**4**-OD, 103620-65-1; **12**-OD, 103620-66-2; **5**-OMs, 72204-36-5; **6**-Cl, 75947-49-8; *endo*-**4**-NHAc, 102418-48-4; *exo*-**4**-OMs, 103620-67-3; **6**-OMs, 72182-86-6; **5**-OAc, 72182-87-7; **6**-OAc, 103667-15-8; **6**-OH, 72182-84-4; *exo*-**4**-$OCOCD_3$, 103620-68-4.

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(30) Stern, O. v.; Volmer, M. *Physik. Z.* **1919**, *20*, 183.