and to T. W. Stevens for recording the mass spectra.

Registry No. **1a**, 32040-07-6; **1a** (X = H), 25912-16-7; **1b**, 32040-06-5; **1b** (X = H), 27292-50-8; **1c**, 32040-09-8; **1c** (X = H), 27292-49-5; **2a**, 96648-99-6; **2b**, 96649-01-3; **2c**, 96649-02-4; **3a**, 96649-00-2; **4a**, 96649-03-5; **4b**, 96649-04-6; **4c**, 96649-06-8; **5a**, 96649-07-9; **5b**, 96649-09-1; **5c**, 96649-11-5; **6a**, 96649-08-0; **6b**, 96649-10-4; **6c**, 96649-12-6; **7a**, 96649-13-7; **7a** (X = H), 82961-68-0; **8a**, 96649-14-8; **9a**, 96649-15-9; **9a** (6-lithio deriv), 96665-97-3; **9b**, 96649-16-0; **9d**, 63907-38-0; **9d** (6-lithio deriv), 96665-98-4; **10a**, 96649-17-1; **10a** (6-lithio deriv), 96688-67-4; **10d**, 96649-18-2; **10d** (6-lithio deriv), 96688-68-5; **11a**, 96649-19-3; **11b**, 96649-20-6; **11d**, 96649-22-8; **12a**, 74427-40-0; **12b**, 96649-21-7; **12d**, 41602-56-6; **13a**, 96649-23-9; **13d**, 96649-24-0; **14a**, 96649-25-1; **14d**, 96649-26-2; **15a**, 96649-27-3; 3-$CH_3OC_6H_4NH_2$, 536-90-3; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $(Br(CH_2)_2)_2O$, 5414-19-7; 3-$HOC_6H_4NH_2$, 591-27-5; $ClCH_2OCH_3$, 107-30-2; 3-$CH_3OCH_2OC_6H_4NH_2$, 96649-05-7; $ClCONEt_2$, 88-10-8; Me_3SiCl, 75-77-4.

Photochemical Transformations. 39. Effects of Ring Substituents and Leaving Groups on Photo-Wagner-Meerwein Rearrangements and Their Ground-State Analogues

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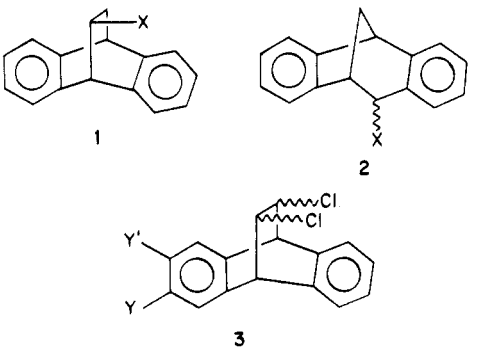
Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Received December 12, 1984

A variety of diarobicyclo[2.2.2]octa-2,5-dienes, substituted on the saturated bridge at C-7 or disubstituted at C-7 and C-8, have been subjected to direct irradiation in acetic acid, as well as to ground-state solvolysis. The ground-state reactions proceed as anticipated, occurring with preferred loss of the nucleofuge anti to the better participating ring, or with loss of the better nucleofuge, and with clean anti Wagner–Meerwein rearrangement to the diarobicyclo[3.2.1]octadienyl system, with one exception. The photoreactions proceed with reaction at the more readily reduced carbon–nucleofuge bond (chloride loss rather than methanesulfonate) with the dibenzo system. The (methylsulfonyl)oxy group is photoinert with both benzo rings unsubstituted but is photoactive with the better electron-donating veratrolo ring. The photo-Wagner–Meerwein rearrangements and photosolvolyses all proceed with preponderant or stereospecific syn migration, in contrast to the ground-state reactions. The photoreactivities are consistent with the requirement that electron transfer of an excited π^* electron to the σ^* orbital of the carbon–nucleofuge bond must occur faster than electron-demotion processes occur. The stereochemical results are accommodated by the assumption that the resulting zwitterionic biradical has two possible competing fates leading to products. One involves loss of nucleofuge concerted with a syn 1,2-migration, and the other is a nonconcerted process in which loss of nucleofuge results in formation of a biradical cation, which is nonstereospecific in its ultimate rearrangement.

The photoreactions of benzo- and diarobicyclo[2.2.2]-octadienes containing an aromatic light-absorbing ring and a remote reactive center have been studied extensively in this laboratory.[1-7] Irradiation excites the aromatic chromophore, which then, under favorable conditions, transfers excitation to the reactive center (generally a β-carbon–nucleofuge bond).

This results ultimately in a photo-Wagner–Meerwein rearrangement and/or a rearrangement with solvolysis; e.g., 1-Cl gives 2-Cl and 2-OAc (in acetic acid).[8] Results on isomeric dichlorides 3 with different Y and Y′ substituents[5,7] were consistent with the idea that the excitation transfer leading to fragmentation to chloride ion and an excited carbocation is an electron transfer from the π^* orbital of the photoexcited ring to the σ^* orbital of the carbon–chlorine bond. In particular, comparison of calculations from the Weller equation[9] (eq 1) (where ΔG is



$$\Delta G = E_{oxid}(D/D^+) - E_{red}(A/A^-) - E_{0-0}(D) - Ne^2/\epsilon r \quad (1)$$

the energy of electron transfer of the π^* electron to the carbon–nucleofuge bond, $E_{oxid}(D/D^+)$ is the oxidation potential of the aromatic ring, $E_{red}(A/A^-)$ is the reduction potential of the carbon–nucleofuge bond, E_{0-0} (D) is the excitation energy (0–0 band) of the aromatic ring, N is Avogadro's number, e is the charge on the electron, ϵ is the dielectric constant, and r is the charge separation) with

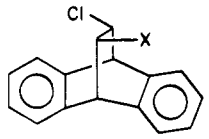
(1) Previous paper in series: Cristol, S. J.; Ali, M. Z. *J. Org. Chem.*, in press. A portion of this work was presented at the Xth IUPAC Symposium on Photochemistry in Interlaken, Switzerland, in July, 1984.
(2) (a) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707. (b) *Ibid.* **1980**, *102*, 5577.
(3) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977.
(4) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 1218.
(5) Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *J. Am. Chem. Soc.* **1983**, *105*, 7337.
(6) Cristol, S. J.; Ali, M. Z. *Tetrahedron Lett.* **1983**, *24*, 5839.
(7) Cristol, S. J.; Bindel, T. H.; Hoffmann, D.; Aeling, E. O. *J. Org. Chem.* **1984**, *49*, 2368.
(8) Opitz, R. J. Ph.D. Dissertation, University of Colorado—Boulder, 1980.
(9) Weller, A. In "5th Nobel Symposium, Fast Reactions and Primary Processes in Chemical Kinetics"; Claesson, S., Ed.; Interscience: New York, 1967; pp 413-428.

0022-3263/85/1950-2698$01.50/0

experimental results showed that highly unfavorable values of $\Delta G - E_c$ ($E_c = -Ne^2/\epsilon r$) led to no photoreaction (where Y = NO_2, $COCH_3$, CN; Y′ = H), intermediate values led only to loss of the anti chlorine (Y = Y′ = Cl, Y = Y′ = H), and relatively favorable values led to loss of both syn and anti chlorine atoms (Y, Y′ = benzo; Y = Y′ = OCH_3).

In all of these cases, changes in the ring substituents affected the first and third terms of eq 1, while the second term was kept constant. The purpose of this paper is to report our initial results on changes in nucleofugal group on these photochemical reactions, that is, changes the affect the second term of the Weller equation, to see how reduction potential values affect photoreactivity.

To this end we scrutinized the ground-state and excited-state chemistry of compounds of systems **1**, **4**, **5**, **6**, and **7**, with the differing candidate nucleofugal groups X = chlorine, (methyl)sulfonoxy, and acetoxy.



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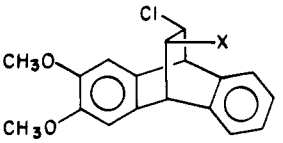

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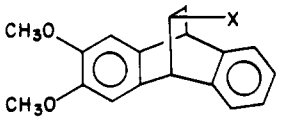

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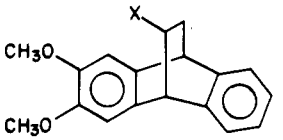

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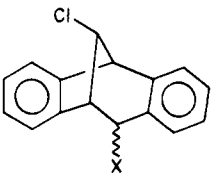
The ground-state chemistry of **1**-OTs has already been reported,[10] as has that of a variety of similar compounds. Solvolysis in acetic acid proceeds with Wagner–Meerwein rearrangement to give the [3.2.1] acetates **2**-OAc. A similar result was obtained with **1**-OMs. While **1**-Cl is photoactive[8] upon irradiation with 254-nm light, in acetic acid giving **2**-OAc and in wet acetonitrile giving **2**-$NHCOCH_3$, the corresponding methanesulfonate was found to be photoinert in either solvent. This results was surprising, when it was first noted some time ago, as methanesulfonates in other systems had been noted to be photoactive by members of our research group[2,3] and earlier by others[11,12] as well. At the time of that observation, we still had been perceiving the fragmentation as one into an almost "normal" cation and an anion formed as the result of an energy transfer rather than that of an electron transfer. Thus, it was not then clear to us why the better ground-state leaving group would not also be the better one in the photoreaction.

With knowledge of the photoinertness of **1**-OMs at hand and with the idea developing at the time[3] that electron transfer of the π^* electron to the σ^* orbital required an anti geometry (it is *now* clear, as stated above, that syn activation is also seen with **5**-Cl), a study of **4**-OMs and **5**-OMs seemed appropriate. As anticipated, ground-state acetolysis of **4**-OMs led cleanly to **8**-OAc, the result of the greater nucleofugacity of the (methylsulfonyl)oxy group and the anti migration reported earlier in such reactions.[13] The photochemical results were quite different. No products from loss of methanesulfonate were observed; instead, the product mixture from irradiation in aceto-



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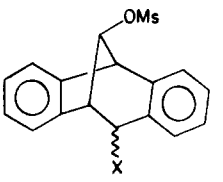

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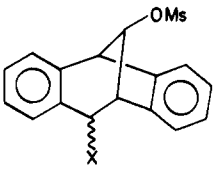

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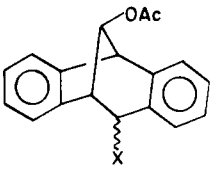

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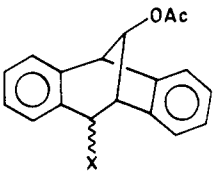

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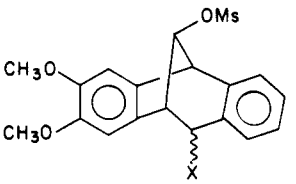
nitrile containing 5% water with 254-nm light comprised 75% of **9**-$NHCOCH_3$, **9**-Cl, and **9**-OH and 25% of **10**-$NHCOCH_3$, **10**-Cl, and **10**-OH. The former set of products comes from loss of chloride and migration of the ring syn to the nucleofuge and the latter from loss of chloride and anti migration. Loss of chloride rather than of methanesulfonate is consistent with the photoactivity of **1**-Cl and inertness of **1**-OMs, and the predominance of syn migration is consistent with earlier work.[3,5,7] The acetoxy chloride **4**-OAc was similarly photoactive. Irradiation in either acetic acid or acetonitrile gave about 80% of syn migration products **11** and 20% of anti migration products **12**. No product deriving from loss of acetate was observed.

The results with **5**-OMs are of particular interest. Irradiation with 300-nm light should produce an excited state in which the excitation is largely localized in the veratrole ring.[5] At the time this experiment was begun, we believed (erroneously, of course) that electron transfer occurred only with anti nucleofuges, and we thus expected that methanesulfonate loss would be seen, rather than chloride loss. In fact, however, the products (solvent 2:1 acetonitrile–acetic acid) were entirely those of chloride ion loss. Thus a 9:2 mixture of **13**-X (X = Cl, OAc, $NHCOCH_3$) (syn migration) and **14**-X (anti migration) was produced. Clearly the syn carbon–chlorine bond was a better electron acceptor than an anti carbon–methanesulfonate bond. The ground-state solvolysis, as anticipated,[10,13] gave only the expected **15** acetate from loss of methanesulfonate.



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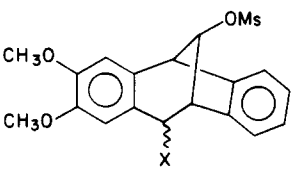

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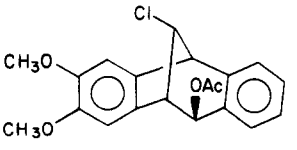
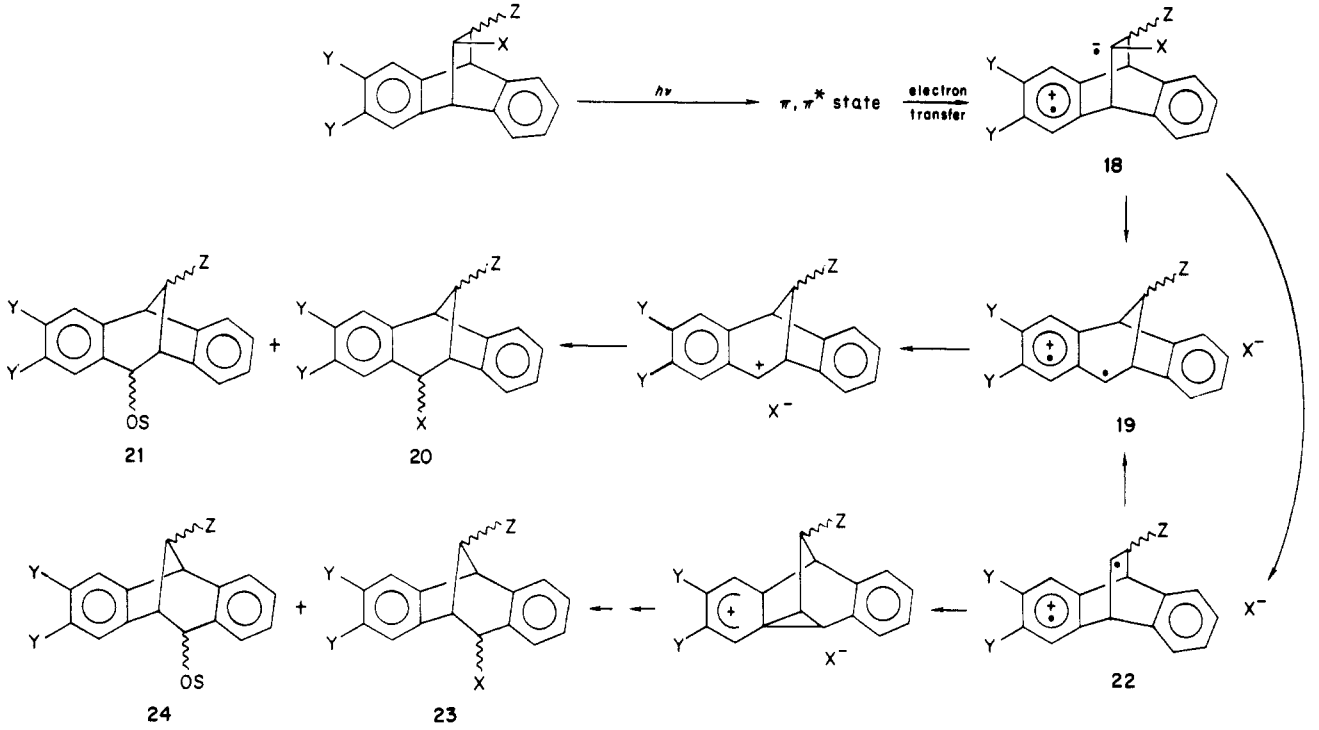


15

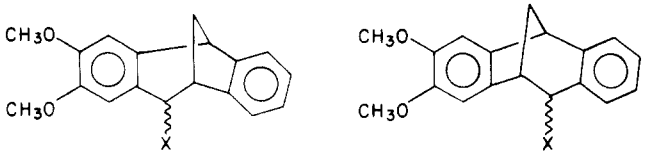
We then decided to study the anti and syn derivatives of the veratrolo–benzo systems **6** and **7**, respectively, with

(10) Cristol, S. J.; Mohrig, J. R.; Tiedeman, G. T. *J. Org. Chem.* **1972**, *37*, 3239.
(11) Cristol, S. J.; Bindel, T. H. *Org. Photochem.* **1983**, *6*, 327–415.
(12) Jaeger, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6401.
(13) (a) Cristol, S. J.; Parungo, F. P.; Plorde, D. E. *J. Am. Chem. Soc.* **1965**, *87*, 2870. (b) Cristol, S. J.; Kochansky, M. C. *J. Org. Chem.* **1975**, *40*, 2171.

Scheme I



the idea that, in the absence of a competing carbon–chlorine bond, electron transfer to a carbon–oxygen bond from the excited veratrolo ring might occur. First the chlorides were studied. Both epimers were photoactive: *anti*-6-Cl gave the product of syn (benzo) migration, 16-Cl,



16 17

when irradiated at 300 nm in 2:1 acetic acid–acetonitrile (acetonitrile was added to inhibit ground-state solvolysis); 16-Cl was converted to 16-OAc and 16-$NHCOCH_3$ with continued irradiation. Under similar conditions, irradiation of the syn epimer 7-Cl gave its syn (veratrolo) migration product 17-Cl as the initial product, with a quantum yield approximately half that of 6-Cl. Continued irradiation of 17-Cl led, interestingly enough, to 16 solvolysis products.

The acetates 6-OAc and 7-OAc and the alcohols 6-OH and 7-OH were photoinert. On the other hand, both methanesulfonates react upon irradiation at 300 nm in acetonitrile–acetic acid. 6-OMs gave largely the syn migration product 16-OAc; some amide was also produced. Analogously, 7-OMs gave the syn migration product 17-OAc. (Like the chloride, 17-OAc was converted photochemically to 16-OAc). Thus, the combination of the veratrolo ring with the (methylsulfonyl)oxy group leads to compounds that are photoactive.

Discussion of Photochemical Reactivities. Correspondence with Electron-Transfer Hypothesis. Several points are clear from the results described above. Unlike the ground-state reactions, where methanesulfonate is a significantly better nucleofuge than is chloride, the reverse is true for photofugacity, even when the (methylsulfonyl)oxy group has the preferred anti disposition with respect to a veratrolochromophoric ring. When the photoexcited aromatic ring is a relatively poor[3,5] electron donor, that is, in the 1 series, with only hydrogens in the ring, loss of methanesulfonate does not occur while loss of chloride does occur.[14] When the excited ring is a better[3] electron donor, that is, in the veratrole systems 6 and 7, loss of methanesulfonate does occur, although loss of acetate is not observed.

These results thus are in accord with the ideas developed in the early section of this paper regarding variation in the carbon–nucleofuge bond. Clearly, rather than correlating with nucleophilicity, photoreactivity is correlated with reduction potential, or more precisely with a combination of oxidation potential of the excited donor [$E_{oxid}(D/D^+) - E_{0\text{-}0}(D)$] and the difficulty of reduction of the C–X bond [$E_{red}(A/A^-)$]. Put another way, the thermodynamics of electron transfer play a crucial role in determining whether these reactions proceed.[14]

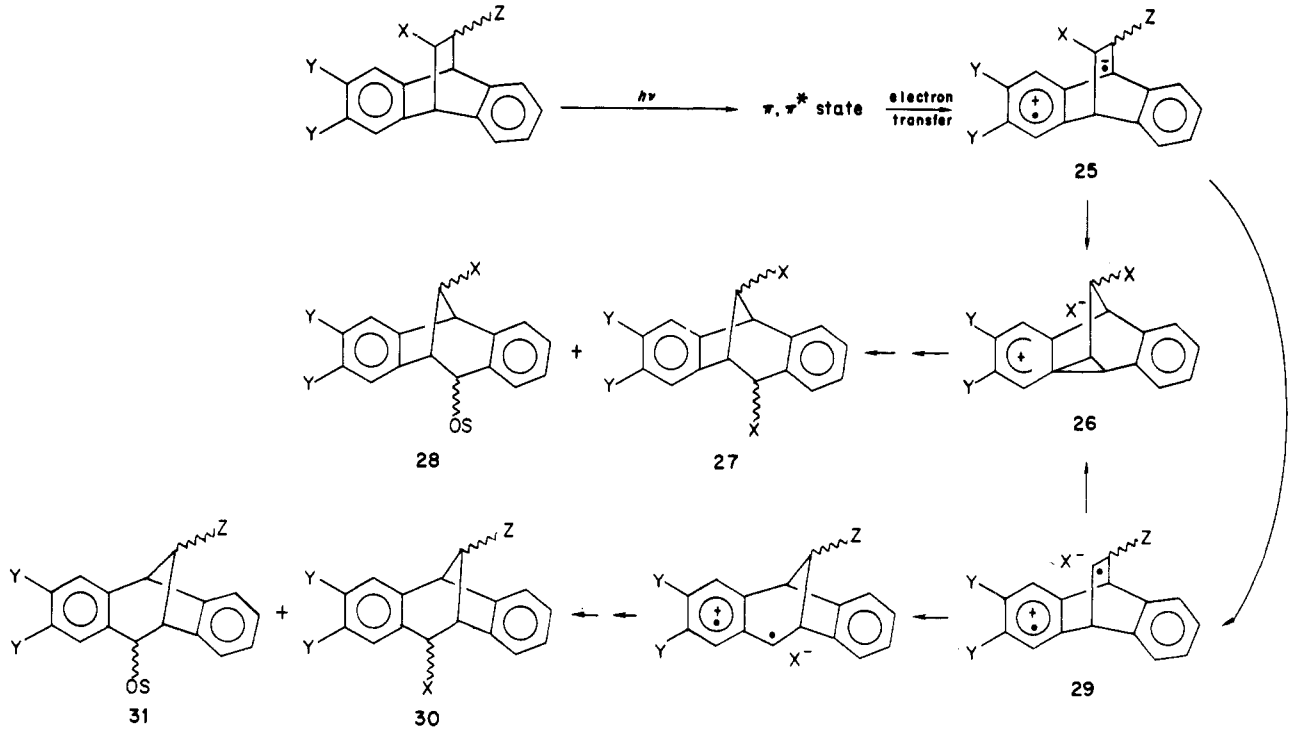
Discussion of Photochemical Reactions. Stereochemistry of Photo-Wagner–Meerwein Rearrangements. It has been proposed[3,5] that the paths for the photochemical reactions of the anti isomers are those shown in Scheme I, where, as described above, the key to reactivity is the formation of the zwitterionic biradical 18 by electron transfer from the π,π^* state. We have also proposed[5,7] that there is usually a branching at the next stage, where, in one fate, loss of X^- is accompanied by syn migration of, in this case, the nonactivated π-electron-complete ring to give the rearranged species 19, which ultimately decays to syn migration products 20 and/or 21. An alternative fate proposed for 18 was loss of X^- to give the [2.2.2] unrearranged biradical cation 22, which may suffer migration of either the initial syn or anti ring.[16] Scheme II gives the similar proposed paths for those

(14) The half-wave reduction potentials of a variety of acetates, methanesulfonates, and chlorides (and the quenching of 1,4-dimethoxybenzene fluorescence with which they correlate)[15] give quantitative validity to these arguments.

(15) Carroll, F. A.; McCall, M. Y.; Hammond, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 315.

(16) An alternative explanation[8] for the anti migration generally observed to be a minor path may be internal conversion of the π,π^* state to a vibrationally excited ground state, which may then undergo normal anti migration in the formation of the ion pair.

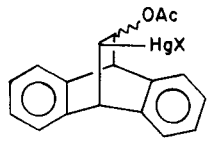
Scheme II



compounds with a syn disposition of the chromophore and the leaving group X. Here the presumably concerted syn migration involves the activated π-electron-deficient ring.

We have noted earlier[3,5,7] that, with chloride as nucleofuge, migration of the syn aromatic ring is preferred over that of the ring anti to the leaving group, *independent* of whether or not the syn ring is the electron donor. We have ascribed[5] the observed syn stereochemistry to a migration *concerted* with loss of nucleofuge and have suggested that this stereochemistry may be general when such displacements occur at C–X bonds whose σ* orbitals are already (partially) occupied. The present results are consistent with these ideas—that is, that a concerted displacement goes with retention of configuration and that loss of nucleofuge prior to rearrangements leads to loss of stereospecificity in such rearrangements.

It had also been proposed[6] that the competition between loss of nucleofuge preceding migration vs. that accompanied by migration is strongly affected by the excess energy involved in the electron transfer. Thus, when the electron transfer is highly exothermic, as for example when transfer occurs to a readily reducible carbon–mercury bond, as in the isomeric **32** species, the migration was observed to be



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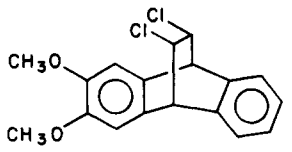

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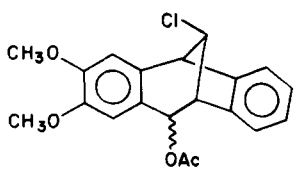


34

stereoconvergent,[6] both cis and trans isomers giving a mixture of 60% of **12** and 40% of **11**. These results were ascribed to complete utilization of the path via the biradical cation. The presently reported results offer support to this idea.

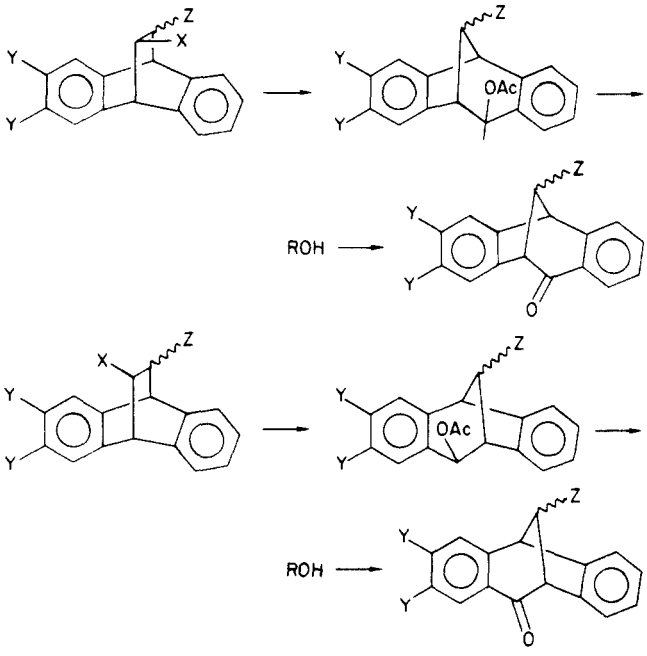
In work described earlier[3-8] and in work described above, almost all of the compounds containing electron-attracting substituents on both C-7 and C-8 (the bridge carbon atoms) give mixtures resulting from both syn and anti migration.[17] We now observe that when there is no substituent at C-8, that is with **6**-Cl, **6**-OMs, **7**-Cl, and **7**-OMs, the migrations are stereospecifically syn (independent of whether or not the light-absorbing ring is syn or anti). We suggest that the fact that vicinal dihalides may be presumed[18] to be more readily reduced than monochlorides may not be coincidental, that is, that electron transfer to monochlorides or methanesulfonates give zwitterionic biradicals that are not energetic enough to lose nucleofuge without the anchimeric assistance of the syn migrating group. Put another way, our results can be rationalized on the assumption that the concerted reaction has an additional driving force above that of the fragmentation without migration.

The results given above, regarding the exclusive syn migration seen in the reactions of **7**-Cl, **7**-OMs, and **33**, are those of short irradiation periods. Thus **7**-Cl gave largely **17**-Cl, with some **17**-OAc, **7**-OMs gave **17**-OAc, and **33** gave **15**. While analogues of these products are generally photostable, except for photosolvolysis and/or epimerization at C-4, this was not true for **17** and **15** species. These were transformed fairly rapidly into their C-8 bridge migration products; that is, **17** gave **16** and **15** gave **34**. This behavior was limited to the veratrolo compounds and was seen in ground-state reactions as well. A number of possible paths for such reactions may be conceived,[19] but, in the absence

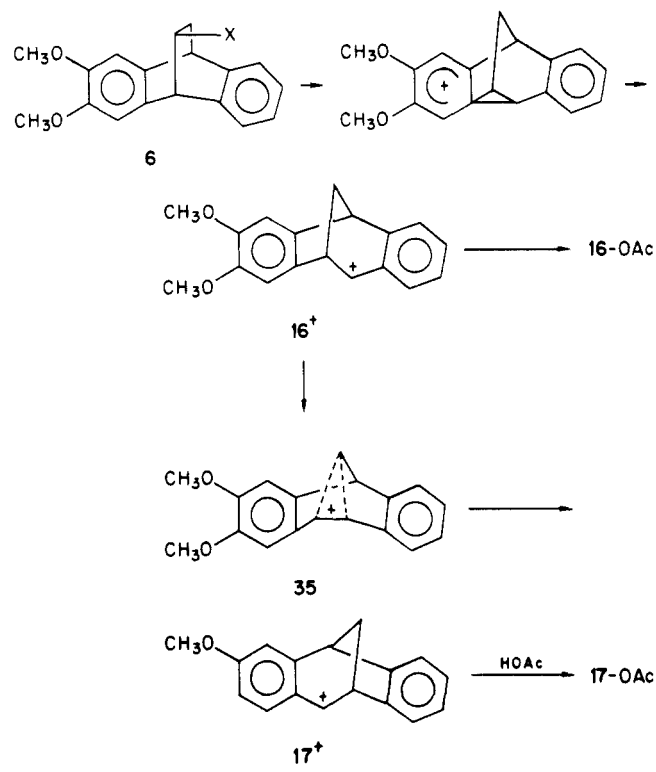
(17) The cis dichlorides, syn to naphtho or veratrolo rings, e.g., **33**, are unusual in that they give *only syn* migration.[5]

(18) (a) Reported $E_{1/2}$'s for vicinal dihalides are for two-electron processes.[18b,c] However, electron-attracting groups are reported to lower $E_{1/2}$ values for alkyl halides.[18d,e] (b) Bard, A. J., Lund, H. Eds. "Encyclopedia of Electrochemistry of the Elements", 2nd ed.; Marcel Dekker: New York, 1973; Vol. 14 pp 36–48, 161. (c) O'Connell, K. M.; Evans, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 1473. (d) Reference 18b, Chapter 14. (e) Sease, J. W.; Burton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968**, *90*, 2595.

Scheme III



Scheme IV



of labeling experiments, nothing definite may be said. A reasonable path involves the direct migration of C-8 from C-5 to C-4, which would transform a benzylic cation to a more stable veratrylic one.

Discussion of Photochemical Reactions. Solvolysis vs. Ion-Pair Return. When chloride was the leaving group, the initial benzylic (or veratrylic) products were the [3.2.1] chlorides, produced, one assumes, by ion-pair return. These were more or less slowly solvolyzed[20] into the corresponding acetates or, when acetonitrile was present, in part to amides. With methanesulfonates, the first products seen were the solvolysis products. As benzylic (or veratrylic) methanesulfonates are very reactive and would give the same products, we are unable to judge whether or not ion-pair return is important in these systems.[21]

Synthesis and Proofs of Structure of Products. All of the diarobicyclo[2.2.2]octadienes were prepared by Diels–Alder reactions between the appropriately substituted anthracenes and the appropriate olefins. Structures of the new [2.2.2] compounds were determined by ground-state solvolysis to [3.2.1] acetates, hydrolysis to the corresponding alcohols, and oxidation to ketones (Scheme III). Combination of consideration of the spectra of the [2.2.2] and [3.2.1] compounds and the assumption[13] of anti migration in the Wagner–Meerwein transformations accompanying solvolysis led, without difficulty, to structural assignments, as, with one exception, the migrations were clean.

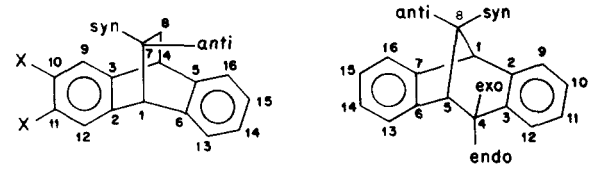
The exception, and the only one we have observed in our numerous studies in these systems, occurred with the *anti*-7-chloro dimethoxy system **6**-Cl and the analogous methanesulfonate **6**-OMs. For example, treatment of the chloride with silver acetate in acetic acid (heating to reflux) gave a mixture of acetates containing 75% of **16**-OAc (that expected by anti migration) and 25% of **17**-OAc (the unexpected one). This composition did not change upon continued heating in acetic acid (AgOAc present) for an additional 3 h, so we presume that these were kinetically controlled products. Such rearrangements have been considered to be involved in [3.2.1] ⇌ [2.2.2] systems lacking ring methoxy substituents but only in situations where the conditions are extremely severe, that is, when the carbocation manifold is entered repeatedly[19] or when there is neighboring group participation,[22] while they have been observed in analogous [3.2.2] systems[23] to occur quite regularly.

In similar fashion, **6**-OMs, upon heating in acetic acid containing sodium acetate, gave a mixture of 88% of **16** and 12% of **17**. We assume that ion pairing in the methanesulfonate experiment leads to a product mixture different from that of the chloride.

The reaction path in Scheme IV accommodates the observations, but no experiments have been done as yet to test this. We presume the ready formation of the bridged ion **35** (possibly a transition state), as opposed to the similar ion lacking the methoxy groups, is undoubtedly due to the veratrylic stabilization.

Experimental Section

The locant systems used in this paper for indicating the structures and names of compounds are as follows (in order to avoid confusion, the locants are based on the hydrocarbon numbering system).



Melting points were determined with a Thomas-Hoover apparatus and are corrected. ^{1}H NMR spectra were obtained with a Varian Associates EM-390 or a Bruker WM-250 instrument. Chemical shifts are reported in ppm relative to tetramethylsilane.

(19) Cristol, S. J.; Bopp, R. J. *J. Org. Chem.* **1974**, *39*, 1336.
(20) The photoreactions of these [3.2.1] compounds will be described later.
(21) Ion-pair return in photoreactions of other systems involving methanesulfonates has been observed previously.[2]
(22) (a) Cristol, S. J.; Parungo, F. P.; Plorde, D. E.; Schwarzenbach, K. *J. Am. Chem. Soc.* **1965**, *87*, 2879. (b) Cristol, S. J.; Caple, R.; Sequeira, R. M.; Smith, L. O., Jr. *Ibid.* **1965**, *87*, 5679.
(23) Cristol, S. J.; Noreen, A. L. *J. Org. Chem.* **1976**, *41*, 4016.

Mass spectra were obtained with a Varian MAT CH-5 spectrometer. Ultraviolet spectra were obtained with a Cary 219 spectrophotometer; absorptions are reported in nanometers and extinction coefficients in L mol^{-1} cm^{-1}. Elemental analyses were performed by Galbraith Laboratories.

General Photochemical. Irradiations with 254- and 300-nm light were carried out either in a Srinivasan–Griffin (Rayonet) photochemical reactor or in an R.S. photochemical reactor. Irradiations at 300 nm were run in Pyrex vessels while those at 254 nm were run in quartz vessels. The compound to be irradiated was placed in a tube, and the appropriate solvent was added to dissolve the compound. The tube was sealed with a septum and Parafilm. If methanesulfonate was to be irradiated, a 10–20% molar excess of anhydrous sodium acetate was added to the tube to neutralize the methanesulfonic acid produced. The solution was deoxygenated by nitrogen bubbling. The void space was then wrapped with foil, to avoid any possible irradiation of solid compounds on the walls of the tube. "Dark" reactions were prepared similarly and treated identically with the sample to be irradiated but were wrapped completely in foil and placed alongside the "light" reaction in the Rayonet.

Ground-State Solvolyses. The ground-state solvolyses of [2.2.2] chlorides were carried out according to the procedure of Cristol, Parungo, and Plorde.[13a] The methanesulfonates were dissolved in glacial acetic acid or glacial acetic acid–acetonitrile, and an excess of anhydrous sodium acetate was added. The reaction mixture was heated to the desired temperature. When the reaction was complete, the solution was cooled and water added. The mixture was extracted with dichloromethane. The combined dichloromethane layers were washed with water and with sodium bicarbonate solution and then dried ($MgSO_4$). Following filtration, the solvent was removed by distillation in vacuo. Purification followed, when appropriate.

Conversion of Acetates to Alcohols. The acetate was dissolved in methanol, and an excess of sodium hydroxide was added. The basic solution was heated at reflux for 5–10 min and then cooled. Water was added, and the mixture was extracted with dichloromethane; the combined dichloromethane layers were washed with water, dried ($MgSO_4$), and filtered, and the solvent was removed by distillation in vacuo. The resulting oil was usually purified by chromatography followed by recrystallization.

Oxidation of alcohols to ketones was conducted according to the procedure of Ratcliffe and Rodehorst.[24]

Conversion of alcohols to methanesulfonates was conducted according to the procedure of Crossland and Servis.[25]

Conversion of alcohols to chlorides was carried out according to the procedure of Kirner and Windus.[26]

Direct Irradiation of *trans*-8-Chloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-dien-7-ol Acetate (4-OAc). A solution of 61 mg (0.20 mmol) of 4-OAc[13a,22] in 0.6 mL of CD_3CN and 0.05 mL of H_2O was irradiated for 16 days. The major product had a triplet ^1H NMR pattern centered at 5.50 ppm (relative to internal Me_4Si), consistent with a [3.2.1] product with a syn C-8 acetoxy group,[27] and the minor product had a singlet centered at 5.45 ppm, consistent with a [3.2.1] product with an acetoxy anti on the bridge.[27] The syn product and the anti acetoxy products were present in a ratio of 4:1. No absorptions were observed in the ^1H NMR spectrum at 4.95–5.1 ppm which were attributable[27] to compounds that contained a chlorine on the C-8 bridge, that is, to 8 or its C-8 epimer.

Direct Irradiation of 4-OAc in Acetic Acid. A solution of 236 mg (0.79 mmol) of 4-OAc in 5 mL of glacial acetic acid was irradiated at 254 nm for 90 h. The solvent was removed by distillation in vacuo, and a brown oil (248 mg) was isolated. The ^1H NMR spectrum showed the oil to be 75% product and 25% starting material. The oil was separated by silica gel TLC. The plate was developed with 5% ethyl acetate in dichloromethane. After development, the plate showed two bands with R_f's of 0.7 and 0.2. The band with R_f 0.7 was a broad band that was divided in half and removed as two separate bands. The less polar section of the broad band (77.1 mg) contained starting material and a [3.2.1] acetoxy chloride. The ^1H NMR spectrum showed the acetoxy chloride to contain a singlet at 5.55 ppm due to H-8, a singlet at 5.18 ppm attributable to the proton geminal to an exo chloride at C-4, and a doublet at 5.60 ppm due to the proton geminal to the C-4 endo chloride. Broad peaks were also seen at 3.73 and 3.96 ppm, corresponding to H-5 and H-1 and an acetate methyl peak at 2.01 ppm. These ^1H NMR data are consistent with those for *endo*- and *exo*-4-chloro-2,3:6,7-dibenzobicyclo-[3.2.1]octa-2,6-dien-*anti*-8-ol acetates (**12**-Cl). Starting material and **12**-Cl were present in a ratio of 3.2:1. The more polar portion of the broad band (71 mg) contained a trace of starting material and a [3.2.1] acetoxy chloride. The ^1H NMR showed the [3.2.1] acetoxy chloride had the following absorptions: δ 5.58 (d, exo H-4), 5.30 (t, H-8), 4.80 (d, endo H-4), 3.95 (d, H-5), 3.85 (d, H-1), and 2.01 (OAc). These ^1H NMR data are consistent with the compounds *endo*- and *exo*-4-chloro-2,3:6,7-dibenzobicyclo[3.2.1]-octa-2,6-dien-*syn*-8-ol acetate (**11**-Cl). The most polar band (67.6 mg) contained a mixture of **11**-OAc and **12**-OAc in a ratio of 3:1. These diacetates were identified by comparison of their ^1H NMR spectra with those of authentic samples.[27]

Synthesis of *trans*-8-Chloro-2,3:5,6-dibenzobicyclo-[2.2.2]octa-2,5-dien-7-ol Methanesulfonate (4-OMs). 4-OMs was prepared from the chloro alcohol 4-OH:[13a] mp 154–156 °C (after recrystallization from ether–hexanes); ^1H NMR ($CDCl_3$) δ 7.19–7.55 (m, 8 H, Ar H), 4.94 (t, 1 H, H-8, $J_{8,4}$ = 3 Hz, $J_{8,7}$ = 3 Hz), 4.60 (d, 1 H, H-4, $J_{4,8}$ = 3 Hz), 4.42 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.06 (t, 1 H, H-7, $J_{7,8}$ = 3 Hz, $J_{7,1}$ = 3 Hz), 3.02 (s, 3 H, methanesulfonate); UV spectrum (CH_3CN) λ_{max} (log ϵ) 271 (2.96), 264 (2.90), 258 (2.79, shoulder), 251 (2.69, shoulder). Anal. Calcd for $C_{17}H_{15}O_2ClS$: C, 60.99; H, 4.51. Found: C, 61.16; H, 4.60.

Ground-State Acetolysis of 4-OMs. A solution of 4-OMs (347 mg, 0.97 mmol) and 83 mg of anhydrous sodium acetate in 5 mL of acetic acid was heated at 70 °C for 2 h and then worked up, giving 250 mg of a pale yellow oil. The ^1H NMR spectrum was identical with that[27] of *anti*-8-chloro-*exo*-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-4-ol acetate (8-OAc). No loss of the chloride was observed, even when the reaction was repeated with 1.1 molar equiv of silver acetate.

Irradiation of 4-OMs in Acetonitrile. A solution of 212 mg (0.59 mmol) of 4-OMs and 55 mg of anhydrous sodium acetate in 5 mL of spectrograde acetonitrile and 0.1 mL of water was irradiated at 254 nm for 54 h. A dark reaction of similar concentration was run beside the light reaction. In each reaction, the solvent was removed by distillation in vacuo. No product formation was observed in the dark reaction. In the light reaction, a brown oil (245.6 mg) was left. The ^1H NMR spectra showed little or no starting material. The oil was separated by silica gel TLC. Four bands containing products were obtained: R_f 0.5 (14.0 mg), R_f 0.2 (100.5 mg), R_f 0.1, and R_f 0.05 (combined 119.4 mg). ^1H NMR spectra were taken of each band in Me_2SO-d_6. That of the least polar band showed a triplet at 5.57 ppm and a singlet at 5.47 ppm, consistent with those of (methylsulfonyl)oxy groups on the bridge, doublets at 4.10 and 3.73 ppm, and peaks at about 3.10 ppm (CH_3SO_2). The product in this band was **9**-Cl, *endo*- and *exo*-4-chloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*syn*-8-ol methanesulfonate, with a trace of **10**-Cl, *endo*- and *exo*-4-chloro-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*anti*-8-ol methanesulfonate. The next band, 100.5 mg, contained mostly [3.2.1] methanesulfonate alcohols. The ^1H NMR spectrum showed a singlet at 5.70 ppm, a singlet at 4.45 ppm, a singlet at 3.77 ppm, and a singlet at 3.20 ppm (methanesulfonate), consistent with that anticipated for *exo*-4-hydroxy-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*anti*-8-ol methanesulfonate **10**-OH. However, the larger absorptions in the ^1H NMR spectra were one at 5.54 ppm (t, J = 3 Hz), a doublet at 4.51 ppm (d, J = 3 Hz), doublets at 4.26 and 3.73 ppm (J = 3 Hz), and a singlet at 3.2 ppm (CH_3SO_2). These NMR data are consistent with those anticipated for *exo*-4-hydroxy-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*syn*-8-ol methanesulfonate (**9**-OH). The two isomeric alcohols **9**-OH and **10**-OH were present in a ratio of 6.8:1.0. The two most polar bands, R_f 0.1 and 0.05, contained amides. The minor amide had the following ^1H NMR (Me_2SO-d_6) spectrum: δ 8.86 (d, J = 8 Hz, 6.96–7.44 (m), 5.59 (s), 5.01 (d, J = 8 Hz), 4.35 (s), 3.48 (s),

(24) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.
(25) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.
(26) Kirner, W. R.; Windus, W. "Organic Syntheses"; Wiley, New York, 1943; Collect. Vol. 2, p 136.
(27) (a) Cristol, S. J.; Mohrig, J. R.; Plorde, D. E. *J. Org. Chem.* **1965**, *30*, 1956. (b) Cristol, S. J.; Russell, T. W.; Mohrig, J. R.; Plorde, D. E. *Ibid.* **1966**, *31*, 581.

3.22 (s), 1.95 (s). These data are consistent with the structure *exo*-4-acetamido-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*anti*-8-ol methanesulfonate (**10**-NHCOCH$_3$). The major amide product had the following ^{1}H NMR (Me_2SO-d_6) spectrum: δ 8.01 (d, J = 8 Hz), 7.45–6.97 (m), 5.45 (d, J = 3 Hz), 4.85 (d, J = 8 Hz), 4.26 (d, J = 3 Hz), 3.62 (d, J = 3 Hz), 3.25 (s), 2.10 (t). These data *exo*-4-acetoamido-2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*syn*-8-ol *exo*-4-acetoamido-2,6:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-*syn*-8-ol methanesulfonate (**9**-NHCOCH$_3$). The ratio of **9**-amide to **10**-amide was 6.0:2.4. No product was observed that contained a proton resonance appropriate for a compound with a chlorine on the bridge.

Synthesis of *syn*-8-Chloro-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-*anti*-7-ol Acetate (5-OAc). A solution of 2.2 g (6.1 mmol) of **15**-OAc,[5] 1.75 mL of perchloric acid, and 4.0 mL of acetic anhydride in 75 mL of acetic acid was heated at 70 °C until rearrangement to **5**-OAc was complete (monitored by ^{1}H NMR spectroscopy). The reaction mixture was poured onto ice and then extracted 3 times with dichloromethane. The combined organic layers were washed twice with water, twice with saturated sodium bicarbonate, and twice with brine. The organic layer was dried ($MgSO_4$) and filtered. The solvent was removed by distillation in vacuo, and 2.1 g (96%) of crude **5**-OAc was obtained. This was dissolved in hot ethanol, decolorized, and allowed to crystallize. The first crop (1.69 g, 77%) had mp 163.0–164.0 °C: ^{1}H NMR ($CDCl_3$) δ 7.52–7.27 (m, 4 H, Ar H), 7.03 (s, 2 H, H-9, H-12), 5.10 (t, 1 H, H-7, $J_{7,8}$ = 3 Hz, $J_{7,1}$ = 3 Hz), 4.43 (d, 1 H, $J_{1,7}$ = 3 Hz, H-5), 4.35 (d, 1 H, H-4, $J_{4,8}$ = 3 Hz), 3.98 (t, 1 H, H-8, $J_{8,4}$ = 3 Hz, $J_{8,7}$ = 3 Hz), 3.89 (s, 6 H, 2 OCH$_3$), 1.98 (s, 3 H, C(O)CH$_3$); mass spectrum, m/e (relative intensity) 361 (9, M + 3), 360 (28.4, M + 2), 359 (21.3, M + 1), 358 (41.3, M$^+$), 263 (12), 251 (29.7), 240 (15.6), 239 (51.3), 238 (100), 224 (32.4), 222 (15.2), 196 (16.9), 195 (40.8), 194 (15.1), 178 (21.5), 177 (24.0), 164 (38.9), 151 (38.3), 45 (22.8), 43 (38.5), 31 (33.6), 28 (30.5); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (3.05, not a maximum), 287 (3.73), 255 (3.38, shoulder). Anal. Calcd for $C_{20}H_{19}O_4Cl$: C, 66.94; H, 5.35. Found: C, 67.08; H, 5.43.

***syn*-8-Chloro-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-*anti*-7-ol (5-OH)** was prepared by methanolysis from 1.54 g of **5**-OAc. After recrystallization from ethanol, 1.38 g (93%) was obtained, mp 212–213 °C: ^{1}H NMR ($CDCl_3$) δ 7.54–7.20 (m, 4 H, Ar H), 6.99, 6.91 (s, s, 2 H, H-12 and H-9), 4.31 (d, 1 H, H-4), 4.20–4.08 (m, 2 H, H-7 and H-8), 3.86 (s, 6 H, OCH$_3$), 3.79 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (2.93, not a maximum), 286.5 (3.72), 259 (3.16). Anal. Calcd for $C_{18}H_{17}O_3Cl$: C, 68.25; H, 5.41. Found: C, 68.17; H, 5.38.

Synthesis of *syn*-8-Chloro-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-*anti*-7-ol Methanesulfonate (5-OMs). Compounds **5**-OH (1.0 g, 3.1 mmol) was converted to the methanesulfonate **5**-OMs in 100% crude yield (1.23 g). The methanesulfonate is not particularly stable and attempts at recrystallization from hot solution caused decomposition. Recrystallization could be accomplished by dissolving in dichloromethane–hexane at room temperature and cooling in an acetone–dry ice bath. The compound, if stored at room temperature, turned brown: mp 201 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 7.68–7.05 (m, 6 H, Ar H, H-12, and H-9), 4.85 (t, 1 H, H-7, $J_{7,8}$ = $J_{7,1}$ = 3 Hz), 4.65 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.54 (d, 1 H, H-4, $J_{4,8}$ = 3 Hz), 4.25 (t, 1 H, H-8, $J_{8,7}$ = $J_{8,4}$ = 3 Hz), 3.76 (s, 6 H, 2 OCH$_3$), 3.26 (s, 3 H, methanesulfonate); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (3.02, not a maximum), 286.5 (3.79), 254 (3.46, shoulder); mass spectrum, m/e (relative intensity) 397 (11.0, M + 3), 396 (38.2, M + 2), 395 (27.4, M + 1), 394 (41.4, M$^+$), 359 (10.5), 301 (14.1), 299 (34.9), 264 (27.6), 263 (22.8), 252 (38.9), 240 (17.7), 239 (48.5), 238 (100.0), 222 (16.4), 207 (24.0), 194 (15.0), 178 (30.6), 177 (29.2), 176 (15.1), 164 (37.5), 151 (37.2), 95 (30.0), 85 (23.6), 83 (33.5), 78 (37.8), 52 (17.6), 49 (36.2), 28 (31.8).

Ground-State Solvolysis of 5-OMs. Compound **5**-OMs (101 mg, 0.26 mmol), dissolved in 10 mL of acetic acid containing 100 mg of anhydrous sodium acetate, was heated at 70 °C for 10 min. Workup gave a yellow oil; examination by ^{1}H NMR spectroscopy showed that the product was entirely **15**-OAc.[28]

Direct Irradiation of 5-OMs in Acetonitrile–Acetic Acid. Three solutions of **5**-OMs were prepared, each containing 100–102 mg of **5**-OMs, 32 mg of sodium acetate, and 100 mL of 3:1 v/v acetonitrile–acetic acid. Sample 1 was irradiated in a merry-go-round apparatus in a 300-nm Rayonet for 1 h and sample 2 for 4.25 h, and sample 3 (dark reaction) was wrapped in foil and placed on the merry-go-round for 4.25 h. After the appropriate time, the samples were removed, poured into 100 mL of water, and extracted 3 times with dichloromethane. The combined organic layers were washed with water, saturated sodium bicarbonate, and brine, dried ($MgSO_4$), and filtered, and the solvent was removed by distillation in vacuo. The residues were analyzed by ^{1}H NMR spectroscopy. The dark sample comprised about 6% of **15**-OAc and 94% of starting material; sample 1 had about one-third of starting material left, while none could be detected in sample 2.

Samples 1 and 2 were each separated on silica gel TLC 2.0-mm plates, by elution with 10% hexanes in dichloromethane. Sample 1, after development, showed four bands on the TLC plate. The least polar band (band 4) weighted 30.9 mg and contained some starting material but was mostly **15**-OH.[28] Since no **15**-OH appeared in the original NMR spectrum of the total irradiation mixture, it must have been due to solvolysis of **5**-OMs on the TLC plate. Band 3 (32.4 mg) contained some **15**-OH (20%) and **14**-OAc and **13**-OAc. Incomplete ^{1}H NMR spectral data, which could be sorted out, were as follows. **14**-OAc: δ 7.58–7.14 (m, 4 H, Ar H), 6.68, 6.63 (2 s, 2 H, H-9 and H-12), 5.98 (d, 1 H, J = 2.5 Hz, H-4), 5.65 (s, 1 H, H-8), 4.23 (s, 1 H, H-1), 3.86, 3.72 (2 s, 6 H, 2 OCH$_3$) (H-5 is probably under the many peaks in the methoxy region), 2.98 (s, 3 H, OMs), 2.17 (s, 3 H, OAc). **13**-OAc: δ 7.35–7.10 (m, 4 H, Ar H), 6.73 (2 s, 2 H, H-16, H-13), 5.85 (d, 1 H, $J_{4,5}$ = 2 Hz, H-4), 5.45 (t, 1 H, $J_{8,1}$ = $J_{8,5}$ = 4 Hz), 3.82, 3.78 (2 s, 6 H, 2 OCH$_3$) (H-1 and H-5 are probably under the many peaks in the methoxy region), 2.92 (s, 3 H, OMs), 2.17 (s, 3 H, OAc). The ratio of **14**-OAc to **13**-OAc was 1:1.3. This mixture was methanolized to give the alcohols, which were then oxidized to the ketones. The following data were isolated from the ^{1}H NMR spectrum: **13**-ketone, δ 7.93 (dd, 1 H, J_{ortho} = 8 Hz, J_{meta} = 2 Hz, H-12), 5.70 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 5 Hz, H-8), ~3.8 (s, 6 H, 2 OCH$_3$), 2.83 (s, 3 H, OMs) (the signals for H-1 and H-5 were obscured by the many signals in the 4.1–3.7-ppm region); **14**-ketone (no proton absorption for **14**-ketone down in the 8-ppm range was present; therefore, the keto group must be next to the substituted ring), δ 5.55 (s, 1 H, H-8), 4.14 (s, 1 H, H-1), ~3.8 (s, 6 H, 2 OCH$_3$), 2.90 (s, 3 H, OMs) (H-5 must be under the methoxy peaks). Bands 1 and 2 (39.7 mg) appeared to be only one product: *exo*-4-acetamido-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-*syn*-8-ol methanesulfonate (*exo*-**13**-NHCOCH$_3$). The ^{1}H NMR spectrum showed the following: δ 7.40–7.20 (m, 4 H), 7.0 (s, 1 H), 6.76 (s, 1 H), 5.50 (t, 1 H, J = 3.5 Hz), 5.26 (dd, 1 H, J = 9 Hz), 4.07 (d, 1 H, J = 3.5 Hz), 3.80, 3.76 (2 s, 6 H, 2 OCH$_3$), 2.97 (s, 3 H, OMs), 2.08 (s, 3 H, NCOCH$_3$). To confirm the structure of this amide, 33.2 mg of the amide was treated with thionyl chloride in chloroform for 24 h.[29] The reaction was worked up, and the products were separated on a silica gel TLC, eluting with 5% EtOAc–CH_2Cl_2. After development, two bands were present. The most polar band (14.6 mg) was the amide and the other (12.3 mg) an alcohol, resulting from hydrolysis of the chloride on the TLC plate. The alcohol was oxidized to the ketone by the standard procedure to give a ketone with a ^{1}H NMR spectrum identical with the proton spectrum of **13**-ketone.

Sample 2, which had been irradiated for 4.25 h, was also separated by silica gel TLC. After development with 3% ethyl acetate in dichloromethane, three bands were observed. The least polar band (20.4 mg) was a mixture of **13**- and **14**-OAc in a 1:4 ratio. The two most polar bands (67.9 mg) were **13**-amide. No starting material or **15**-OH was seen. All products were identified by comparison with the ^{1}H NMR spectrum of each band to those of the 1-h irradiation products.

Synthesis of 2,3:5,6-Dibenzobicyclo[2.2.2]octa-2,5-dien-7-ol Methanesulfonate (1-OMs). The alcohol 1-OH[13a] (700 mg, 3.15 mmol) was converted to **1**-OMs: mp 124 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.56–7.10 (m, 8 H, Ar H), 5.17 (dt, 1 H, H-7, $J_{7,8_{cis}}$ = 9 Hz, $J_{7,8_{trans}}$

(28) Bindel, T. H. Ph.D. Dissertation, University of Colorado–Boulder, 1980.

(29) Vaughan, W. R.; Carlson, R. D. *J. Am. Chem. Soc.* **1962**, *84*, 1976.

= 3 Hz, $J_{7,1}$ = 3 Hz), 4.75 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.31 (t, 1 H, H-4, $J_{4,8}$ = 3 Hz), 2.90 (s, 3 H, methanesulfonate), 2.48 (ddd, 1 H, H-8_{cis}, $J_{8_{gem}}$ = 14 Hz, $J_{8_{cis},7}$ = 9 Hz, $J_{8_{cis},4}$ = 3 Hz), 1.77 (dt, 1 H, H-8_{trans}, $J_{8_{gem}}$ = 14 Hz, $J_{8_{trans},7}$ = 3 Hz, $J_{8_{trans},4}$ = 3 Hz); mass spectrum, *m/e* (relative intensity) 302 (<1, M + 2), 301 (<1, M + 1), 300 (M, 2.1), 221 (2.9), 220 (1.3), 208 (1.4), 207 (2.1), 206 (17.5), 205 (39.8), 204 (37.0), 203 (39.1), 191 (19.2), 189 (15.7), 180 (11.5), 179 (79.6), 178 (100.0), 177 (28.8), 176 (36.5), 164 (13.8), 151 (23.7), 150 (17.1), 78 (12.8); UV spectrum (acetonitrile) λ_{max} (log ϵ) 271 (3.09), 264 (3.01), 257 (2.85, shoulder), 250 (2.72, shoulder). Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.98; H, 5.37. Found: C, 67.73; H, 5.34.

Ground-State Solvolysis of 1-OMs. A solution of 52 mg (0.17 mmol) of 1-OMs and 15 mg of sodium acetate was dissolved in 10 mL of glacial acetic acid, heated to reflux, cooled, and worked up. A yellow oil (42.3 mg, 0.16 mmol, 94%) of 2,3:6,7-dibenzobicyclo[3.2.1]octa-2,6-dien-4-ol acetate (2-OAc) was obtained identified by ^{1}H NMR comparison with an authentic sample.[13a,27]

Irradiation of 1-OMs. A series of solutions containing 55–60 mg of 1-OMs and 15–20 mg of NaOAc in (a) CD_3CN, (b) 70% CD_3CN–30% CD_3CO_2D, or (c) 66% CH_3CN–*tert*-butyl alcohol were subjected to irradiation in a 254-nm Rayonet. In solvents a and b, similar small amounts of solvolysis were observed in both light and dark reactions. In solvent c no reaction occurred in 24 h in the dark. Some photoreaction occurred in the irradiation; the product mixtures had increased ratios of aromatic to aliphatic protons (NMR analysis). While the products were not characterized, it was clear that neither alcoholysis nor rearrangement to [3.2.1] products had occurred.

Synthesis of *syn*- and *anti*-2,3-(10,11-Dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol Acetate (6-OAc and 7-OAc). A mixture of 15 g (0.063 mol) of dimethoxyanthracene,[5] 50 mL of vinyl acetate, and 50 mL of xylene in a sealed heavy-walled combustion tube was heated at 185 ± 5 °C for 6 days. After workup, one isomer, *syn*-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol acetate (7-OAc), was crystallized from ethanol: mp 175.0–176.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.52–7.10 (m, 4 H, Ar H), 6.96, 6.93 (2 s, 2 H, H-9 and H-12), 5.09 (dt, 1 H, H-7, $J_{7,8_{trans}}$ = 9 Hz, $J_{7,1}$ = $J_{7,8_{cis}}$ = 3 Hz), 4.49 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.21 (t, 1 H, H-4, $J_{4,8_{cis}}$ = $J_{4,8_{trans}}$ = 2.5 Hz), 3.87 (s, 6 H, 2 OCH_3), 1.95 (s, 3 H, $COCH_3$), 2.32 (ddd, 1 H, H-8_{trans}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{trans},7}$ = 9 Hz, $J_{8_{trans},4}$ = 3 Hz), 1.49 (dt, 1 H, H-8_{cis}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{cis},7}$ = $J_{8_{cis},4}$ = 3 Hz); mass spectrum, *m/e* (relative intensity) 324 (41.1, M^+), 240 (21.2), 239 (51.7), 238 (100.0), 222 (15.7), 196 (24.3), 195 (46.7), 194 (22.6), 186 (16.9), 178 (29.4), 177 (32.6), 166 (19.6), 165 (21.5), 164 (39.3), 152 (15.4), 151 (40.9), 43 (37); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (2.94, not a maximum), 286 (3.76). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.26. Found: C, 74.05; H, 6.36.

The second isomer, *anti*-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol acetate (6-OAc), was also crystallized from ethanol: mp 150.0–151.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.52–7.10 (m, 4 H, Ar H), 7.00, 6.90 (2 s, 2 H, H-9 and H-12), 5.13 (dt, 1 H, H-7, $J_{7,8_{trans}}$ = 9 Hz, $J_{7,1}$ = $J_{7,8_{cis}}$ = 3 Hz), 4.50 (d, 1 H, H-1, $J_{1,8}$ = 3 Hz), 4.24 (t, 1 H, H-4, $J_{4,8_{cis}}$ = $J_{4,8_{trans}}$ = 2.5 Hz), 3.85 (s, 6 H, 2 OCH_3), 1.90 (s, 3 H, $COCH_3$), 2.37 (ddd, 1 H, H-8_{trans}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{trans},7}$ = 9 Hz, $J_{8_{trans},4}$ = 3 Hz), 1.51 (dt, 1 H, H-8_{cis}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{cis},7}$ = $J_{8_{cis},4}$ = 3 Hz); mass spectrum, *m/e* (relative intensity) 325 (12.8, M + 1), 324 (52.8, M^+), 281 (4.9), 265 (7.1), 240 (12.1), 239 (58.1), 238 (100.0), 222 (9.6), 196 (10.8), 195 (53.1), 178 (11.4), 177 (12.9), 164 (31.3), 151 (34.0), 43 (14.9), 28 (16.7); UV spectrum (acetonitrile) λ_{max} (log ϵ), 300 (2.97, not a maximum), 285 (3.80). Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.26. Found: C, 73.92; H, 6.32.

Methanolysis of 7-OAc gave *syn*-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol, 7-OH, which, after recrystallization from ethanol, had the following: mp 190.0–190.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.49–7.12 (m, 4 H, Ar H), 7.03, 6.97 (2 s, 2 H, H-9 and H-12), 4.41–4.16 (m, 3 H, H-7, H-4, and H-1), 3.86 (s, 6 H, 2 OCH_3), 2.32 (ddd, 1 H, H-8_{trans}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{trans},7}$ = 9 Hz, $J_{8_{trans},4}$ = 3 Hz), 1.40 (dt, 1 H, H-8_{cis}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{cis},7}$ = $J_{8_{cis},4}$ = 3 Hz); mass spectrum, *m/e* (relative intensity) 282 (5.3, M^+), 266 (5.4), 239 (20.9), 238 (100.0), 195 (16.8), 164 (10.6), 151 (14.9), 32 (31.8), 28 (99.8); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (3.01, not a maximum), 286.5 (3.76). Anal. Calcd for $C_{18}H_{18}O_3$: C, 75.57; H, 6.43. Found: C, 75.64; H, 6.68.

The alcohol 7-OH was converted to ***syn*-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol methanesulfonate** (7-OMs), which was crystallized by dissolving in a minimum amount of hexane–dichloromethane at room temperature and cooling to −73 °C: mp 150 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.49–7.12 (m,4 H, Ar H), 7.02, 6.92 (2 s, 2 H, H-9 and H-12), 5.13 (dt, 1 H, H-7, $J_{7,8_{trans}}$ = 8.5 Hz, $J_{7,8_{cis}}$ = $J_{7,1}$ = 3.5 Hz), 4.77 (d, 1 H, H-1, $J_{1,7}$ = 3.5 Hz), 4.25 (t, 1 H, H-4, $J_{4,8_{cis}}$ = $J_{4,8_{trans}}$ = 3 Hz), 3.87, 3.84 (2 s, 6 H, 2 OCH_3), 2.93 (s, 3 H, OMs), 2.45 (ddd, 1 H, H-8_{trans}, $J_{8_{gem}}$ = 13.5 Hz, $J_{8_{trans},7}$ = 8.5 Hz, $J_{8_{trans},4}$ = 3 Hz), 1.73 (dt, 1 H, H-7_{cis}, $J_{8_{gem}}$ = 13.5 Hz, $J_{8_{cis},7}$ = $J_{8_{cis},4}$ = 3 Hz); mass spectrum, *m/e* (relative intensity) 361 (5.4, M + 1), 360 (20.3, M^+), 281 (7.9), 280 (30.0), 266 (29.2), 265 (10.5), 249 (10.6), 239 (21.9), 238 (100.0), 195 (14.3), 178 (8.5), 164 (18.2), 151 (10.6), 28 (9.9); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (2.70, not a maximum), 286 (3.58). No elemental analysis was obtained, as the compound was unstable.

Ground-State Solvolysis of 7-OMs in Acetic Acid. A solution of 150 mg (0.42 mmol) of 7-OMs and 50 mg of NaOAc in 10 mL of glacial acetic acid was heated to reflux, cooled, and worked up as usual. The product (122.2 mg, 0.377 mmol), *exo*-2,3-(10,11-dimethoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-ol acetate (16-OAc), was obtained as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.55–7.10 (m, 4 H, Ar H), 6.71 (br s, 2 H, H-9 and H-12), 5.81 (d, 1 H, H-4, $J_{4,5}$ = 2 Hz), 3.94–3.74 (m, 8 H, 2 OCH_3, H-5, and H-1), 2.50 (m, 2 H, H-8_{anti} and H-8_{syn}), 2.12 (s, 3 H, $OCOCH_3$).

Methanolysis of 122 mg (0.38 mmol) of 16-OAc gave 101 mg (95%) of **2,3-(10,11-dimethoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-ol (16-OH)**: ^{1}H NMR ($CDCl_3$) δ 7.52–7.09 (m, 4 H, Ar H), 6.99, 6.67 (2 s, 2 H, H-9 and H-12), 5.01 (d, 1 H, H-4, $J_{4,5}$ = 4 Hz), 3.92–3.60 (m, 8 H, 2 OCH_3, H-5, and H-1), 2.70–2.50 (m, 2 H, H-8_{syn} and H-8_{anti}). 16-OH was not purified but was oxidized to **2,3-(10,11-dimethoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (16-ketone)**, which was purified on silica gel TLC (eluting solvent was 100% dichloromethane). The ketone could not be induced to crystallize: ^{1}H NMR ($CDCl_3$) δ 7.57–7.30 and 7.25–7.06 (2 m, 4 H, Ar H), 7.46 (s, 1 H, H-12), 6.87 (s, 1 H, H-9), 4.12 (t, 1 H, H-5, $J_{5,8_{syn}}$ = $J_{5,8_{anti}}$ = 3 Hz), 4.00 (t, 1 H, H-1, $J_{1,8_{syn}}$ = $J_{1,8_{anti}}$ = 3 Hz), 3.98, 3.86 (2 s, 6 H, 2 OCH_3), 2.85 (m, 2 H, H-8_{anti} and H-8_{syn}); mass spectrum, *m/e* (relative intensity) 281 (19.9, M + 1), 280 (100.0, M^+), 279 (12.6), 249 (26.5), 221 (10.0), 164 (19.5).

Methanolysis of 6-OAc gave ***anti*-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol (6-OH).** The crude material was crystallized from dichloromethane–hexane: mp 192–193 °C; ^{1}H NMR ($CDCl_3$) δ 7.45–7.12 (m, 4 H, Ar H), 6.94, 6.87 (2 s, 2 H, H-9 and H-12), 4.35–4.07 (m, 3 H, H-1, H-4, and H-7), 3.83 (s, 6 H, 2 OCH_3), 2.31 (ddd, 1 H, H-8_{trans}, $J_{8_{trans},8_{cis}}$ = 13 Hz, $J_{8_{trans},7}$ = 9 Hz, $J_{8_{trans},4}$ = 3 Hz), 1.32 (dt, 1 H, H-8_{trans}, $J_{8_{cis},8_{trans}}$ = 13 Hz, $J_{8_{cis},7}$ = $J_{8_{cis},4}$ = 3 Hz; mass spectrum, *m/e* (relative intensity) 282 (10.5, M^+) 240 (3.3), 239 (33.8), 238 (100.0), 195 (31.3), 177 (6.8), 164 (15.7), 151 (18.0), 119 (6.8), 43 (3.7). Anal. Calcd for $C_{18}H_{18}O_3$: C, 75.57; H, 6.43. Found: C, 75.41; H, 6.56.

Alcohol 6-OH was converted to ***anti*-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol methanesulfonate (6-OMs)**, but, upon normal workup, only [3.2.1] alcohols were recovered, due to the high lability of the methanesulfonate in contact with water. The reaction was repeated with exactly 1 equiv of methanesulfonyl chloride and a small excess (3–4%) of triethylamine. The usual workup was not employed: rather, after a suitable reaction time had elapsed, the solvent and the excess amine were removed by distillation in vacuo. the residue was examined by ^{1}H NMR spectroscopy and showed 6-OMs and triethylamine hydrochloride. removal of this salt proved impossible, although some was removed by washing the product with dichloromethane; the methanesulfonate was more soluble in dichloromethane than the salt. thus, every reaction with 6-OMs is contaminated with the amine salt: ^{1}H NMR ($CDCl_3$) δ 7.52–7.11 (m, 4 H, Ar H), 7.00, 6.91 (2 s, 2 H, H-9 and H-12), 5.11 (dt, 1 H, H-7, $J_{7,8_{trans}}$ = 9 Hz, $J_{7,8_{cis}}$ = $J_{7,1}$ = 3 Hz), 4.65 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.26 (t, 1 H, H-4, $J_{4,8_{cis}}$ = $J_{4,8_{trans}}$ = 3 Hz), 3.81 (s, 6 H, 2 OCH_3), 2.95 (s, 3 H, OMs) (H-8_{cis} and H-8_{trans} were quite difficult to see because of the amine salt impurity but did appear to be at approximately 2.4 and 1.7 ppm); mass spectrum, *m/e* (relative intensity), 360 (2.2, M^+), 302 (12.4), 300 (27.8), 283 (16.8), 282 (60.1), 276 (12.1), 265 (12.3), 264 (20.9), 251

(22.0), 249 (22.8), 239 (40.6), 238 (100.0), 233 (28.0), 195 (41.3), 178 (24.5), 164 (27.1), 151 (32.8), 84 (39.8).

Ground-State Acetolysis of 6-OMs in Acetic Acid. Compound 6-OMs (150 mg, contaminated with the trimethylamine hydrochloride) was added along with 50 mg of NaOAc to 10 mL of acetic acid and warmed to reflux. The solution was cooled and worked up as usual. The residue (105 mg) appeared to be a mixture of an alcohol and an acetate. The acetate, the major product, was 6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo-[2.2.2]octa-2,6-dien-*exo*-4-ol acetate (17-OAc): ^{1}H NMR ($CDCl_3$) δ 7.51–7.13 (m, 4 H, Ar H), 6.97–6.87 (2 s, 2 H, H-16 and H-13), 5.84 (d, 1 H, H-4, J = 2 Hz), 3.78 (m, 8 H, 2 OCH_3, H-1 and H-5), 2.11 (s, 3 H, $COCH_3$). The minor product was 16-OH. Compounds 17-OAc and 16-OH were present in a ratio of 7:1.

This mixture was treated with methanol and base to give a mixture of 17-OH and 16-OH. The ^{1}H NMR spectrum of 17-OH could be resolved from that of the mixture: ^{1}H NMR ($CDCl_3$) δ 7.45–7.10 (m, 4 H, Ar H), 6.94, 6.77 (2 s, 2 H, H-13 and H-16), 4.30 (t, 1 H, H-1, $J_{1,8_{anti}} = J_{1,8_{cis}} = 3$ Hz), 3.81–3.76 (2 s, 8 H, 2 OCH_3, H-5 and H-4), 2.44 (m, 2 H, H-8_{anti} and H-8_{syn}).

Oxidation of the mixture of alcohols gave a ketone mixture, which was separated into two bands on a silica gel TLC plate by development with dichloromethane. Band 1 was 16-ketone (~12%) (^{1}H NMR spectrum); the major band was 17-ketone (88%): ^{1}H NMR ($CDCl_3$) δ 7.98 (dd, 1 H, H-12, $J_{12,11}$ = 9 Hz, $J_{12,10}$ = 2 Hz), 7.52–7.17 (m, 3 H, Ar H), 7.02, 6.89 (2 s, 2 H, H-13 and H-16), 4.11 (br s, 1 H, H-1), 3.96 (d, 1 H, $J_{5,8_{syn}}$ = 3.5 Hz), 3.82 (s, 6 H, 2 OCH_3), 2.86 (m, 2 H, H-8_{anti} and H-8_{syn}); mass spectrum, m/e (relative intensity), 281 (40.3, M + 1), 280 (100, M^+), 265 (20.5), 250 (26.3), 249 (83.0), 237 (42.6), 221 (77.7), 209 (21.2), 178 (33.0), 165 (22.7), 164 (60.7).

Preparation of *anti*-7-Chloro-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-diene (6-Cl). Treatment of 1.00 g (3.6 mmol) of 6-OH with thionyl chloride by the standard procedure gave 17-Cl. Once the reaction was complete (monitored by TLC), the solvent and excess $SOCl_2$ were removed by distillation in vacuo. The [3.2.1] chloride was dissolved in 50 mL of carbon tetrachloride, and 50 mg of ferric chloride was added to catalyze the [3.2.1]-to-[2.2.2] rearrangement. The mixture was heated at reflux for 6 h. After being cooled, the solution was filtered, washed with saturated sodium bicarbonate and with water, dried ($MgSO_4$), and filtered. The solvent was removed by distillation in vacuo. The resulting black oil was purified by (activated silica gel, 60–200 mesh) chromatography. The column separated 17-OH (presumably from solvolysis of unrearranged 17-Cl on the column) from 6-Cl (0.92 g, 86% yield). 6-Cl was recrystallized from ethanol: mp 135.5–136.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.54–7.12 (m, 4 H, Ar H), 6.88, 6.85 (2 s, 2 H, H-9 and H-12), 4.48–4.09 (m, 3 H, H-1, H-5, and H-7), 3.75 (s, 6 H, 2 OCH_3), 2.42 (ddd, 1 H, H-8_{trans}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{trans},7}$ = 9 Hz, $J_{8_{trans},1}$ = 3 Hz), 1.75 (dt, 1 H, H-8_{cis}, $J_{8_{gem}}$ = 13 Hz, $J_{8_{cis},7} = J_{8_{cis},1}$ = 3 Hz); mass spectrum, m/e (relative intensity) 302 (37.5, M + 2), 301, 21.8 M + 1), 300 (49.1, M^+), 266 (8.31), 265 (13.5), 264 (10.9), 240 (12.5), 239 (48.9), 238 (100), 196 (11.1), 195 (47.6), 178 (22.9), 177 (22.4), 176 (13.2), 164 (44.7), 151 (47.6), 150 (13.9), 119 (43.4), 28 (19.5); UV spectrum λ_{max} (log ϵ) 300 (3.18, not a maximum), 287 (3.74). Anal. Calcd for $C_{18}H_{17}O_2Cl$: C, 71.88; H, 5.70. Found: C, 71.68; H, 5.84.

***syn*-7-Chloro-2,3-(10,11-dimethoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-diene (7-Cl).** We were unable to prepare 7-Cl from 7-OH via the method described for 6-Cl, as the attempt at rearrangement from 16-Cl was accompanied by significant decomposition. It was prepared from the syn dichloride[5] by treatment with tri-*n*-butyltin hydride and butanethiol in benzene.[30] After recrystallization from ethanol the following data were obtained: mp 173.5–175.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.45–7.12 (m, 4 H, Ar H), 7.01, 6.94 (2 s, 2 H, 286.5 and H-12), 4.50–4.20 (m, 3 H, H-1, H-4, and H-7), 3.87 (s, 6 H, 2 OCH_3), 2.51 (ddd, 1 H, H-8_{trans}, $J_{8_{gem}}$ = 14 Hz, $J_{8_{trans},7}$ = 9 Hz, $J_{8_{trans},1}$ = 3 Hz), 1.85 (dt, 1 H, H-8_{cis}, $J_{8_{gem}}$ = 14 Hz, $J_{8_{cis},7} = J_{8_{cis},1}$ = 3 Hz); mass spectrum, m/e (relative intensity) 302 (11.4, M + 2), 301 (8.1, M + 1), 300 (35.1, M^+), 266 (4.8), 240 (5.5), 239 (40.4), 238 (100.0), 196 (5.1), 195 (31.4), 178 (7.6), 177 (8.9), 164 (17.3), 151 (23.9), 119 (12.3); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (2.98, not a maximum), 286.5 (3.76). Anal. Calcd for $C_{18}H_{17}O_2Cl$: C, 71.88; H, 5.70. Found: C, 72.08; H, 5.83.

Silver-Ion-Assisted Solvolysis of 6-Cl. A solution of 18.3 mg (0.061 mmol) of 6-Cl and 13.0 mg of silver acetate in 5 mL of glacial acetic acid was heated to reflux. After workup, the products were analyzed by ^{1}H NMR spectroscopy. A 3:1 mixture of acetates 17-OAc and 16-OAc was observed. No starting material remained. This mixture of acetates was redissolved in 5 mL of acetic acid, 9.0 mg of silver acetate was added, and the reaction was heated at reflux for 3 h. The reaction was then worked up and the product analyzed by ^{1}H NMR spectroscopy. No change in product composition was observed.

Silver-Ion-Assisted Solvolysis of 7-Cl. A solution of 60 mg (0.20 mmol) of 7-Cl and 10 mg of silver acetate in 10 mL of acetic acid was heated to reflux, and a small portion was removed, worked up, and then analyzed by ^{1}H NMR spectroscopy. About 75% of the 7-Cl remained; the sole product was 16-OAc. The remaining acetic acid solution was heated at reflux and monitored by TLC. After about 30 min, the reaction appeared complete and was worked up and analyzed by ^{1}H NMR. No starting material remained; the sole product was 16-OAc.

Direct irradiations of 6-OH, 7-OH, 6-OAc, and 7-OAc were carried out in approximately 0.2 M solutions in acetic acid at 300 nm for 8 days. No apparent reaction occurred in any of these solutions.

Direct Irradiations of 6-OMs and 7-OMs. Solutions containing 40 mg of 7-OMs and 12–15 mg of sodium acetate in 1.00 mL of 2:1 CD_3CN–CD_3CO_2D were prepared, as were solutions of 36 mg of 6-OMs and 10–13 mg of sodium acetate in 9:1 CD_3CN–CD_3CO_2D. The acetonitrile was added to minimize, as much as possible, competing ground-state acetolyses. Irradiation was carried out in the 300-nm Rayonet, with dark samples alongside. The reactions were monitored by ^{1}H NMR spectroscopy. 7-OMs showed slow ground-state solvolysis to 16-OAc. The irradiated sample gave largely 17-OAc and some 16-OAc. But 16-OAc is either a secondary product or a ground-state product, as it was not observed initially, but only after about 15% conversion. 6-OMs unfortunately underwent a facile ground-state reaction to give 17-OAc. The irradiated sample gave a 2:1 mixture of 17-OAc and 16-OAc; our estimate is that most, if not all, of the 17-OAc was due to the ground-state reaction. Upon longer irradiation times, the product acetates underwent solvolysis to give amides. The structure of these amides was not investigated.

Irradiation of 6-Cl and 7-Cl. Solutions containing 20 mg of either 6-Cl or 7-Cl in 0.5 mL of 2:1 CD_3CN–CD_3CO_2D were irradiated in the 300-nm Rayonet. The irradiations were monitored by ^{1}H NMR spectroscopy. Compound 6-Cl underwent rearrangement about twice as fast as 7-Cl. At low (10–15%) conversions, each gave only one chloride product; 6-Cl gave 16-Cl and 7-Cl gave 17-Cl. In addition, very small amounts of corresponding acetates were formed. As the chlorides are extremely labile in the presence of water, each product was treated at room temperature with silver perchlorate in acetone–water. The product from irradiation of 6-Cl was 16-OH, identified by comparison of the ^{1}H NMR of the irradiation product with that of an authentic sample.[7] Similarly, the product from 7-Cl was 17-OH, identified by ^{1}H NMR spectral comparison with that of an authentic sample.[7] When the irradiations were continued past 20% conversion, secondary photoproducts were seen in both irradiation samples. The photoproduct of 6-Cl, that is, 16-Cl, underwent solvolysis to give amide and acetate products. The structure of the amide was not investigated. The acetate was 16-OAc. The photoproduct of 7-Cl (17-Cl) was also photochemically reactive, giving 16-Cl and 16-OAc (^{1}H NMR analysis).

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Registry No. 1-OH, 1521-59-1; 1-OMs, 96690-20-9; 2-OAc, 6682-28-6; 4-OAc, 2732-77-6; 4-OH, 2734-16-9; 4-OMs, 96690-08-3; 5-OAc, 96690-12-9; 5-OH, 96690-13-0; 5-OMs, 96690-14-1; 6-OAc, 96745-34-5; 6-OH, 96745-35-6; 6-OMs, 96745-36-7; 6-Cl, 96690-30-1;

(30) We are indebted to Dr. M. Z. Ali for this preparation.

7-OAc, 96690-21-0; 7-OH, 96690-22-1; 7-OMs, 96690-23-2; 7-Cl, 96745-37-8; 8-OAc, 3123-86-2; *endo*-9-Cl, 96690-09-4; *exo*-9-Cl, 96745-27-6; 9-OH, 96745-30-1; 9-NHAc, 96745-31-2; *endo*-10-Cl, 96745-28-7; *exo*-10-Cl, 96745-29-8; 10-OH, 96690-10-7; 10-NHAc, 96690-11-8; *endo*-11-Cl, 96745-25-4; *exo*-11-Cl, 96745-26-5; *endo*-12-Cl, 96690-07-2; *exo*-12-Cl, 96745-24-3; 13-OAc, 96690-15-2; 13 (ketone), 96690-17-4; 13-NHAc, 96690-19-6; 14-OAc, 96690-16-3; 14 (ketone), 96690-18-5; 15-OAc, 96745-32-3; 15-OH, 96745-33-4; 16-OAc, 96690-24-3; 16-OH, 96690-25-4; 16 (ketone), 96690-26-5; 16-Cl, 96690-32-3; 17-OAc, 96690-27-6; 17-OH, 96690-28-7; 17 (ketone), 96690-29-8; 17-Cl, 96690-31-2; 33, 87637-76-1; 2,3-dimethoxyanthracene, 51790-19-3; vinyl acetate, 108-05-4.

Neighboring Group Participation by Oxygen in the Solvolysis of Acyclic γ-Alkoxy Substituted *p*-Toluenesulfonates

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Methanolysis of branched 3-(benzyloxy)propyl *p*-toluenesulfonates, $PhCH_2OCR^1R^2CR^3R^4CHR^5OTs$ (R^1 = Me, R^2–R^5 = H; R^1 = R^2 = Me, R^3–R^5 = H; R^1 = R^2 = R^5 = Me, R^3 = R^4 = H; R^1 = R^2 = R^4 = R^5 = H, R^3 = Me; R^1 = R^2 = R^5 = H, R^3 = R^4 = Me) proceeds with partial rearrangement, implying neighboring group participation, only when there are geminal methyl groups in the 2- or 3-position (R^3 = R^4 = Me or R^1 = R^2 = Me). Addition of lithium perchlorate enhances the extent of rearrangement. No or negligible anchimeric assistance is manifest either in the absence or in the presence of the salt. Participation thus seems to occur past the transition state. The primary 3-substituted alcohol precursors of the *p*-toluenesulfonates are synthesized by solvomercuration–borohydride reduction of α,β-unsaturated acids followed by reduction with lithium aluminum hydride or diborane; the corresponding secondary alcohol is similarly obtained from 4-methyl-3-penten-2-ol, $(CH_3)_2C{=}CHCHOHCH_3$, by solvomercuration–borohydride reduction.

In a previous paper[2] we presented evidence, from both product and kinetic studies, that whereas the methanolysis of $PhCH_2SCH_2CH_2CH_2OTs$ and $PhCH_2SCH_2CH_2CH$-MeOTs proceeds without neighboring group participation, both rearrangement and anchimeric assistance occur when the tosylate is substituted at the 2- or 3-position with one or more alkyl groups. Moreover, neighboring group participation with rearrangement is found even in the unbranched primary and secondary tosylates shown above when the solvolysis is carried out in 2,2,2-trifluoroethanol, CF_3CH_2OH.

The present study was designed to probe whether similar participation might occur in the corresponding oxygen analogues, $C_6H_5CH_2OC$–C–COTs. RO participation involving five- and six-membered rings has been demonstrated repeatedly in the literature[3] and RO-3 participation is also known,[4] though it occurs less readily than RS-3 participation and apparently only in relatively highly branched compounds. The requirement for branching suggests that a Thorpe–Ingold effect[5,6] is at work, as we had also postulated in RS-4 participation.[2] RO-4 participation, has, to the best of our knowledge, not been demonstrated in acyclic systems but does occur in some cyclic[7] and bicyclic[8] systems where the participating group is located close to the reaction center in space and entropic considerations are therefore favorable.

Table I. Percentage of Rearranged Product in Methanolysis of 3-(Benzyloxy)propyl *p*-Toluenesulfonates

entry	compound	% rearranged product	sulfur series[a]
1	$PhCH_2OCMe_2CH_2CHMeOTs$	45	100
2	$PhCH_2OCMe_2CH_2CH_2OTs$	3.5	100
3	$PhCH_2OCHMeCH_2CH_2OTs$	0	20
4	$PhCH_2OCH_2CMe_2CD_2OTs$	33[b]	50[c]
5	$PhCH_2OCH_2CHMeCHDOTs$	0	12[d]

[a] Corresponding results with S in place of O, from ref 2. [b] This corresponds to 66% cyclic intermediate. [c] This corresponds to 100% cyclic intermediate. [d] This corresponds to 24% cyclic intermediate.

Table II. Methanolysis Rates[a]

entry	compound	k^a	k_{rel}[b]	k_O/k_{model}[c]	k_S/k_{model}[d]
1	$XCHMeCH_2CH_2OTs$	4.71	1	0.67	3.6
2	$XCMe_2CH_2CH_2OTs$	1.91	0.41	0.79	90.7
3	$XCMe_2CH_2CHMeOTs$	39.1	8.3	0.63	8.0

[a] $\times 10^6$ s^{-1} at 60 °C; X = $PhCH_2O$. [b] Relative to $PhCH_2OCHMeCH_2CH_2OTs$. [c] Rates for X = $PhCH_2O$ relative to X = CH_3.[2] [d] Rates for X = $PhCH_2S$ relative to X = CH_3, from ref 2.

Results and Discussion

Product studies in the methanolysis of variously substituted 3-(benzyloxy)propyl *p*-toluenesulfonates are summarized in Table I. Corresponding percentages from the 3-benzylthio series (S in place of O) are given in the last column.

Not unexpectedly the extent of neighboring group participation, as indicated by the extent of rearrangement, is considerably less in the oxygen than in the sulfur series. In fact, the 3-(benzyloxy)propyl compounds rearrange only if there are geminal methyl substituents at the 2- or 3-

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