Photochemical Transformations. 35. Stereochemistry of Electron Transfer from Photoexcited Aromatic Rings to Carbon–Chlorine Bonds. Syn Stereochemistry of Migration in Photo-Wagner–Meerwein Rearrangements[1]

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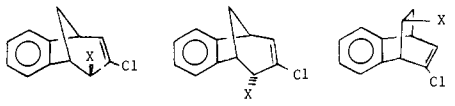
Abstract: Studies have been conducted on the ground-state and excited-state solvolyses of the isomeric 7,8-dichloro derivatives of benzonaphthobicyclo[2.2.2]octadiene and benzoveratrobicyclo[2.2.2]octadiene. The silver ion assisted ground-state reactions proceed, as anticipated, with clean anti stereochemistry (inversion at the migration terminus) reflected in the Wagner–Meerwein rearranged solvolysis products. Unlike the previously reported observations that excitation transfer from a photoexcited benzene ring to a β-carbon–chlorine bond requires anti stereochemistry, electron transfer from excited naphthalene or veratrole rings occurs to both syn and anti carbon–chlorine bonds, although that to the latter is preferred. The results are consistent with an electron-transfer process to give a zwitterionic biradical and are rationalized by the Weller equation. Separation of chloride ion from the presumed zwitterionic biradical is accompanied by "Wagner–Meerwein" rearrangement but is predominately *syn*, rather than *anti* as in the ground state. The rearrangement stereochemistry is consistent with the idea that, in the principal photochemical process, migration with retention of configuration is concerted with the loss of chloride ion.

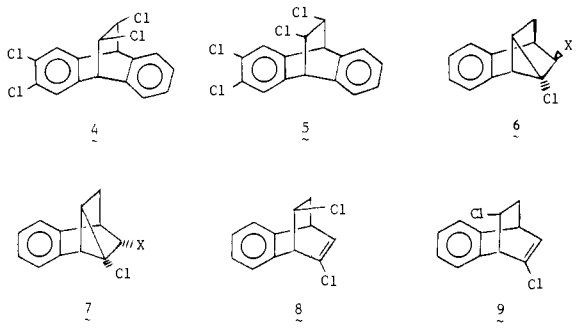
The study of photosolvolyses and photochemical Wagner–Meerwein rearrangements in certain bridged-ring systems containing aromatic chromophores and good nucleofugal groups has been of considerable interest in this laboratory.[2-5] These compounds are of interest because they act as probes into the as yet not fully understood photochemical mechanisms of intramolecular excitation transfer from a light-absorbing chromophore to a carbon–nucleofuge bond which is separated from the chromophore and of the resulting photoreactivity of that carbon–nucleofuge bond. The compounds are designed such that the aromatic chromophore and carbon–nucleofuge reactive center are separated by a rigid bridged-ring system and such that the aromatic chromophore or substituted aromatic chromophore absorbs substantially all of the light.

Study of these compounds has shown that there are stereo- and regiochemical requirements for both the excitation transfer and the subsequent rearrangements and solvolyses. What is known is that the homobenzyl allylic epimers **1** and **2** showed little



1 **2** **3**

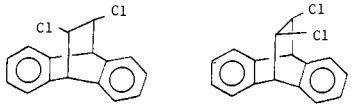
stereochemical requirement for photoreactivity, in that both epimers **1** and **2** (X = Cl or OMs) undergo photoreactions with 254-nm light in acetonitrile or acetic acid to give solvolysis products **1** or photo-Wagner–Meerwein rearrangement products **3** (X = Cl or OMs).[2,3] Unlike the homobenzyl allylic epimers **1** and **2**, the homobenzyl nonallylic systems, **4**, **5**, **6**, **7**, **8**, and **9** had the stereochemical requirement that the excitation transfer from the benzene or dichlorobenzene chromophore to the β-carbon–chlorine bond was anti-stereospecific; that is, when they were irradiated with 254- or 300-nm light in acetonitrile or in acetic acid, only



4 **5** **6**

7 **8** **9**

anti compounds **4**, **6**, and **8** underwent solvolyses and photo-Wagner–Meerwein rearrangements, whereas the syn compounds **5**, **7**, and **9** gave no such reactions.[4,5,7] The question of which ring migrated in the photo-Wagner–Meerwein rearrangement was also studied with **4**, **8**, **10**, and **11** (as well as others). In all cases,



10 **11**

the migrations were syn stereoselective, although they were by no means stereospecific.[4,5] These photochemical reactions have been shown not to be radical reactions,[8] and it was suggested[2-6] that the key to these reactions was an electron transfer from a π* orbital of the excited chromophore to the σ* orbital of the carbon–nucleofuge bond. This process seemed clearly to be favored by the proximity to the aromatic chromophore of the lobe of the σ* orbital anterior to the carbon atom of the carbon–nucleofuge bond.

In order to continue our studies, in our attempts to understand the driving forces for the presumed electron transfer and for the competitive syn vs. anti bond migrations, we synthesized the trans (**12** and **15**), anti-cis (**13** and **16**), and syn-cis (**14** and **17**) isomers of 7,8-dichloro-2,3-(2′,3′-naphtho)-5,6-benzobicyclo[2.2.2]octa-

(1) Paper 34. Cristol, S. J.; Hager, J. W. *J. Org. Chem.* **1983**, *48*, 2005. (Portions of this work were reported at the Sixth DOE Solar Photochemistry Research Conference in Boulder, Colorado, June 8, 1982 and at the Ninth IUPAC Symposium on Photochemistry in Pau, France, July 29, 1982).
(2) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 5577.
(3) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707.
(4) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977.
(5) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *J. Am. Chem. Soc.* **1983**, *105*, 1218.
(6) Cristol, S. J.; Graf, G. A. *J. Org. Chem.* **1982**, *47*, 5186.
(7) Compare: (a) Morrison, H.; Miller, A. *J. Am. Chem. Soc.* **1980**, *102*, 372. (b) Morrison, H.; Miller, A.; Pandey, B.; Pandey, G.; Severance, D.; Strommer, R.; Bigot, R. *Pure Appl. Chem.* **1982**, *54*, 1723. (c) Morrison, H.; Miller, A.; Bigot, B. *J. Am. Chem. Soc.* **1983**, *105*, 2398.
(8) Cristol, S. J.; Klein, M. W.; Hendewerk, M. H.; Daussin, R. D. *J. Org. Chem.* **1981**, *46*, 4992.

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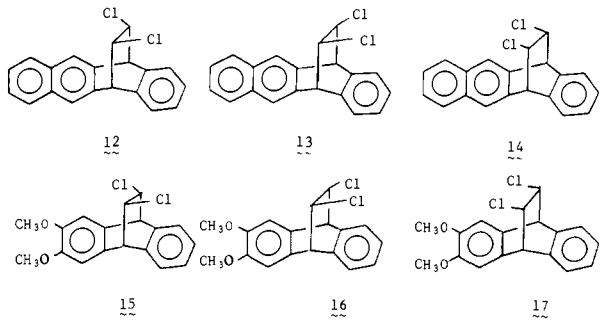


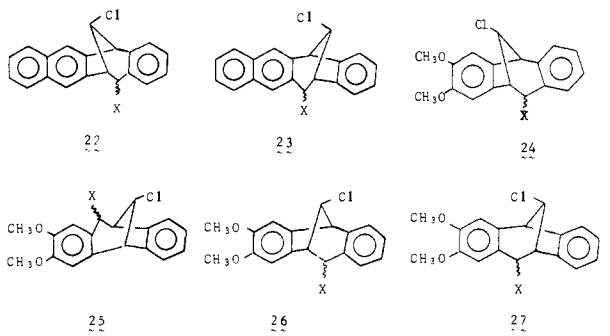
12 13 14

15 16 17

2,5-diene and 7,8-dichloro-10,11-dimethoxy-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-diene and studied their ground- and excited-state chemistries in acetic acid (or acetic acid and acetonitrile).

Results and Discussion

Compounds **12–14** were synthesized by reducing the commercially available naphthacenequinone to naphthacene by the Meerwein–Pondorff–Verley reduction according to the procedure of Kapovits and Tomasz,[9] followed by Diels–Alder reactions of the naphthacene with either *trans*- or *cis*-1,2-dichloroethene The *anti-cis*-**13** and *syn-cis*-**14** isomers were separated by fractional crystallization. The structures of the separated isomers were determined (Scheme I) by converting the isomers to their [3.2.1] monoacetates via silver ion assisted solvolysis with silver acetate in acetic acid.[10] This conversion involves a Wagner–Meerwein rearrangement which is known to proceed via anti participation and migration,[10] so that identification of the [3.2.1] acetates reveals the isomeric structure of the parent [2.2.2] compounds.[11] This was accomplished by converting the acetates to the ketones, for example, **20** or **21** [via methanolysis followed by chromium(VI) oxidation (Scheme I)]. The ketones were then easily distinguishable in their ^{1}H NMR spectra, by using data for both chemical shifts and multiplicities of the absorption of the aromatic protons ortho to the carbonyl group. As anticipated, silver ion assisted solvolysis of each cis isomer gave clean stereospecific participation and migration. Thus the anti-cis dichloride **13** gave the syn-8-chloro 4-acetates *exo*- and *endo*-**22**, and the syn-cis dichloride **14** gave the anti-8-chloro 4-acetates *exo*- and *endo*-**23**,

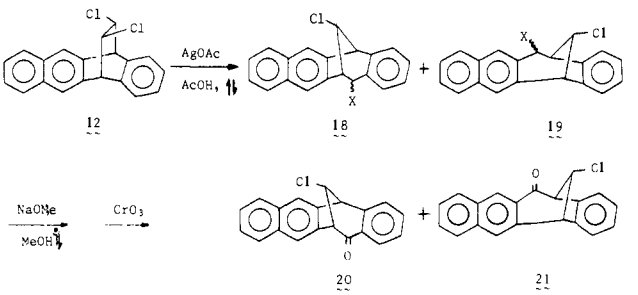


22 23 24

25 26 27

each without observable contamination with **18** or **19**. The trans dichloride gave two isomers in a ratio of 3:2. The major isomer was **18**, the result of anti migration of the naphtho ring, and the minor one **19**, that of anti migration of the benzo ring. It is of interest that the two rings are so similar in "migratory aptitude."[12]

Scheme I



12 18 19

20 21

Table I. Acetate Products from 300-nm Irradiations of the Dichlorides of the Naphthobenzo Systems 12–14

	composition of product mixture, %			
compd irradiated	18	19	22	23
trans-12	33	6	9	51
anti-cis-13	0	80	20	0
syn-cis-14	100	0	0	0

Table II. Products from 300-nm Irradiation of the Dichlorides of the Veratrobenzo Systems 15–17

	composition of product mixture, %			
compd irradiated	24	25	26	27
trans-15	6	0	26	66
anti-cis-16[17]	0	76	24	0
syn-cis-17	100	0	0	0

Excitation of the naphtho ring of the trans isomer **12** with 300-nm light in acetic acid gave four [3.2.1] acetates,[14] which were identified as **18**, **19**, **22** and **23** (Table I) by their ^{1}H NMR spectra. When anti-cis **13** was irradiated with 300-nm light in acetic acid, [3.2.1] acetates **19** and **22** were produced, whereas irradiation of syn-cis **14** with 300-nm light in acetic acid–acetonitrile (7:3) gave only [3.2.1] acetate **18**. The compositions of the product mixtures are given in Table I.

Compounds **15–17** were synthesized by the Diels–Alder reaction between 2,3-dimethoxyanthracene and either *trans*- or *cis*-1,2-dichloroethene. The 2,3-dimethoxyanthracene was synthesized by the general method[15a] of Iwata and Emoto for the synthesis of 2,3-dimethoxy-9-anthrone and the reduction of anthrones to anthracenes by the method of Criswell and Klanderman.[15b] The trans isomer **15** was known.[16] The *anti-cis*-**16** and *syn-cis*-**17** isomers were separated by fractional crystallization and their structures identified by conversion to the [3.2.1] ketones via the [3.2.1] acetates as described above for the naphthobenzo compounds.

The ground-state silver ion assisted solvolysis of the anti-cis dichloride **16** gave the [3.2.1] acetate **26**-OAc quite rapidly, while the syn-cis dichloride **17** was considerably less reactive, but proceeded cleanly to **27**-OAc. Both reactions thus proceeded with anti participation and migration, as anticipated,[10c] and the enhanced driving force due to the participation of the veratro ring over that of the benzo ring was also anticipated.[10c] The trans isomer similarly displayed the enhanced participation of the veratro ring with **24**-OAc as the sole isolated acetate.

Excitation with 300-nm light of the veratro ring of the trans isomer **15** in acetic acid gave [3.2.1] acetates and [3.2.1] dichlorides, which included **27** (X = Cl and OAc), as major product, with lesser amounts of **26** (X = Cl and OAc) and a small amount of **24**-OAc.[17] The [3.2.1] acetates were identified by comparison

(9) Kapovits, I.; Tomasz, J. *Ann. Univ. Sci. Budap. Rolando Eotvos Nominatae, Sect. Chim.* **1964**, *6*, 159; *Chem. Abstr.* **1964**, *62*, 13104*f*.

(10) (a) Cristol, S. J.; Parungo, F. P.; Plorde, D. E. *J. Am. Chem. Soc.* **1965**, *87*, 2870. (b) Cristol, S. J.; Bopp, R. J.; Johnson, A. E. *J. Org. Chem.* **1969**, *34*, 3574. (c) Cristol, S. J.; Kochansky, M. C. *Ibid.* **1975**, *40*, 2171.

(11) Also, [3.2.1] syn-8-chloro compounds (syn refers to the chlorine atom being on the same side of the bridge as the larger ring) are easily distinguishable from anti-8-chloro epimers as the H-8 absorption in the ^{1}H NMR spectrum of the syn-chloro compound is a triplet, whereas H-8 of the anti-chloro compound gives a singlet.

(12) It has been noted[10c] that the Brown–Okamoto[13] ρ^+ value for this reaction is −1.8. Using this value, we compute a σ^+ value of −0.10 for a meta, para benzo ring substituent.

(13) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

(14) The [3.2.1] dichlorides are also formed, but they photosolvolyze without rearrangement to give the [3.2.1] acetates.

(15) (a) Iwata, M.; Emoto, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1687. (b) Criswell, T. R.; Klanderman, B. H. *J. Org. Chem.* **1974**, *39*, 770.

(16) Bindel, T. H. Ph.D. Thesis, University of Colorado, Boulder, CO, 1980.

of their ^{1}H NMR spectra with the ^{1}H NMR spectra of those produced in the ground-state solvolyses of **15–17**. The [3.2.1] dichloro products were identified by hydrolyzing the benzylic chloride to the alcohols, oxidizing the resulting alcohols to the ketones, and interpreting the characteristic ^{1}H NMR spectra of the [3.2.1] ketones. In like manner, irradiation of the anti-cis isomer **16** was shown to give [3.2.1] acetates and [3.2.1] dichlorides **25** as major products, with a lesser amount of **26** (X = Cl). Irradiation of the syn-cis isomer **17** gave a mixture of [3.2.1] dichloride **24**-Cl and acetate **24**-OAc. The results are summarized in Table II.

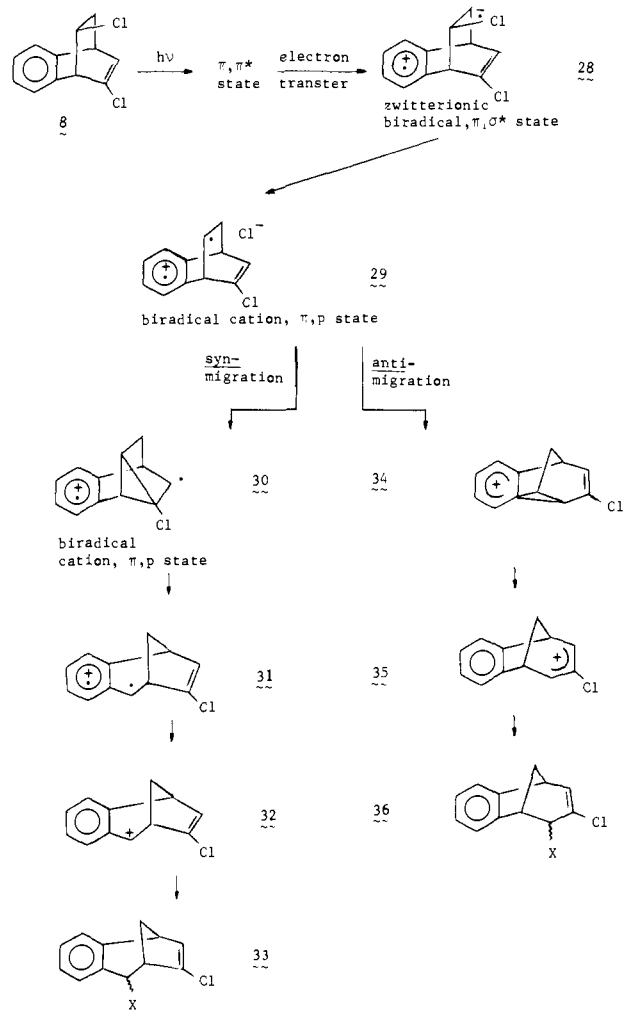
Our results clearly show that the photo-Wagner–Meerwein rearrangements go, as expected from the previous work, with migration of the aromatic ring syn to the chlorine nucleofuge predominating (syn stereoselectivity of the migration = 60–100%). On the other hand, excitation transfer from the naphtho or veratro ring to the β-carbon–chlorine bond is only anti-stereoselective (72–84% anti activation products), rather than stereospecific as it was in systems with benzene or dichlorobenzene rings as chromophores (**4–9**), or rather than with only slight stereoselectivity, as in the homobenzylic allylic epimers **1** and **2**.

Two interesting aspects of these reactions demand consideration in attempting to understand these photoreactions. These include the syn stereoselectivity in the ring migration, independent of whether the "chromophoric" ring is syn or anti and the question of syn vs. anti excitation transfer. Let us consider the latter question first. As noted above, earlier work[4,5] had shown that excitation transfer from benzo or dichlorobenzo rings to carbon–nucleofuge bonds seemed to have a requirement for anti geometry in [2.2.2] homobenzylic systems and a 20:1 advantage in quantum yield and a 700:1 advantage in rate over syn geometry in a [2.2.1] system.[7] Rationalization[4-6] of these results was based upon the assumption that the reactions involved photoexcitation to a π,π^* state followed by intramolecular transfer of the photoexcited electron into the σ^* orbital of the carbon–nucleofuge bond to give a π,σ^* zwitterionic biradical. It seems clear that such a process (or one analogous to it) is reasonable and required in order to allow for the loss of a chloride ion (or other anion) and the ultimate formation of a carbocationic species. An example[5] of this is given in Scheme II for the photoactive compound **8** in which the formation of **28** was assumed (the postulated decay process from **28** will be discussed below).

It was assumed[4,5] that the apparent requirement for the anti disposition of the donor and acceptor "chromophores" was a result of the greater overlap of the π^* orbital of the donor component and the lobe of the σ^* orbital of the acceptor bond anterior to the carbon atom in compounds with anti dispositions, compared with that to the opposite lobe of the σ^* orbital in compounds with syn dispositions. If this is reflected in extra work[18] (or extra activation energy) required in the electron transfer for syn groups over anti groups, the anti requirement (or preference) could be understood.

If one assumes that there is an energy barrier for the electron transfer from the π^* orbital to the σ^* orbital (or to a combination $\pi^*\sigma^*$ orbital) and that the barrier is greater in the syn than in the anti case, one might anticipate that the difference in barrier heights might decrease or become less significant as the electron transfers become more exergonic (or less endergonic). Weller and his co-workers[20] have developed a method for the computation of the free-energy change associated with the formation of radical cation–radical anion pairs by electron transfer to or from excited-state species and from or to ground-state species. The appropriate formulation for the process in which the excited-state species is the electron donor is given in eq 1, in which ΔG is the

Scheme II



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

free-energy change associated with the electron-transfer process, $E_{ox}(D/D^+)$ is the oxidation potential of the unexcited donor, $E_{red}(A/A^-)$ is the reduction potential of the acceptor, $^1E_{0\text{-}0}$ is the singlet excitation energy of the donor, N is Avogadro's number, e the charge on the electron, ϵ the effective dielectric constant of the medium separating the ions, and r is the distance between the ions. Two difficulties arise in the utilization of such an equation in our system. The first of these resides in the fact that thermodynamic reduction potentials for alkyl chlorides are, in principle, unknown, as electron transfer to an alkyl chloride is substantially irreversible—the resulting radical anions decompose "instantaneously" on the polarographic time scale. The half-wave reduction potential for a variety of secondary alkyl chlorides in dimethylformamide is reported[21] to be −2.65 V (vs. SCE), and we have used this value in our computations, even though $E_{1/2}$ is not E_0 and even though the solvent is not acetonitrile, which is the solvent for the reported oxidation potentials. Although it would be most useful, for the purposes of this discussion, to have absolute values of ΔG, use of an arbitrary value for the reduction potential will give relative values for various compounds that are discussable.

The second difficulty is in the Coulombic energy term, $E_c = -Ne^2/(\epsilon r)$, which reflects the stabilization gained by bringing two opposed single charges from infinity to separation distance r. As

(17) Some [3.2.1] dichlorides photosolvolze under these conditions to give primarily the unrearranged [3.2.1] acetates and some (1–2%) rearranged products.

(18) Calculations[19] show that the lobe of an occupied σ^* orbital in a carbon–halogen bond anterior to the carbon atom contains more electron density than does that exterior to the halogen atom.

(19) Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973; p 104. Jorgenson, W. L. *J. Am. Chem. Soc.* **1978**, *100*, 1049.

(20) Weller, A. In "Nobel Symposium 5th, Fast Reactions and Primary Processes in Chemical Kinetics"; Claesson, S., Ed.; Interscience: New York, 1967; pp 413–428.

(21) Lambert, F. L.; Ingall, G. B. *Tetrahedron Lett.* **1974**, 3231.

Table III. Computation of Free-Energy Differences Attributable to Electron Transfer between Aromatic Rings and Carbon–Chlorine Bonds, Neglecting Coulombic Interactions

compd	chromophore	$E(D/D^+)$ V[a]	$E(D/D^+)$ kcal/mol	$^1E_{o-o}$ nm[e]	$^1E_{o-o}$ kcal/mol	$\Delta G + Ne^2/(\epsilon r)$,[g] kcal/mol	syn-activation products
15	veratro	1.45[b]	33.4	315	90.8	+3.7	26%
12	naphtho	1.54[c]	35.5	330	86.7	+9.9	15%
10	benzo	2.30[d]	53.0	285	100.3	+13.8	*h*
4, 5	dichlorobenzo	>2.40[d]	>55.3	>305	<93.8	>+22.6	0

[a] Vs. SCE in acetonitrile. [b] Reference 24. [c] Reference 25. [d] Reference 26. [e] End absorbance of appropriately substituted dichlorodibenzobicyclo[2.2.2]octadiene.[f] [f] Reference 27. [g] Assumes $E(A/A^-)$ for all carbon–chlorine bonds is −2.65 V (61.1 kcal/mol). [h] Perceived to be small.[4,5,7]

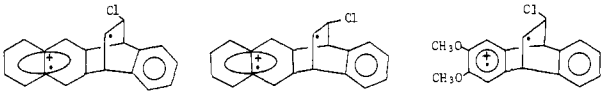
the value of Ne^2 is 330 kcal Å/mol, this makes an important contribution to the free energy of electron transfer. When solvent-separated ion pairs are involved, the effective dielectric constant is assumed[20] to be that of the medium. On the other hand, it is not so straightforward to set values for zwitterions,[22] either for the dielectric constant, where values lying between that of an aliphatic hydrocarbon (ca. 2) and that of the pure solvent may be considered, or for the distance between charges, particularly when such readily deformable orbitals as π and σ^* are involved. For this reason, we have chosen not to compute values of Coulombic energy, but rather to compute $\Delta G - E_c$ and to note that it is quite reasonable to assume that stabilization will certainly be greater for the anti case (where the anterior lobe of the σ^* orbital is close to the donor ring) than for the syn case (where the anterior lobe is more remote).

Computations of $\Delta G - E_c$ are listed in Table III. For this purpose, we have used data on oxidation potentials from the literature for benzene, naphthalene, and veratrole and have estimated a minimum value for dichlorobenzene as models for our compounds; we have used the ultraviolet absorption cutoff points ($\epsilon \sim 1$–10) of our compounds for singlet-energy values. It is interesting to note that the values of $\Delta G - E_c$ are substantially less endergonic (3.9 kcal/mol) for the naphtho system than for the benzo system, that the difference (10.1 kcal/mol) is greater for the veratro system, and that the dichlorobenzo ring suffers electron transfer 8.8 kcal/mol less readily than the benzo ring. It may not be coincidental, and we suggest by the arguments given above that the relationship is reasonable, that these values bear considerable relationship to the ability of the rings to suffer electron transfer to syn chlorine atoms, also summarized in Table III. Certain predictions are obvious from this idea, and we are in the process of testing them.

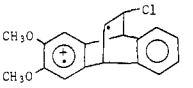
Morrison and his co-workers[7c] have discussed the preference for anti activation in their benzonorbornenyl system in terms of the "natural correlation" concept, that is, a quantum mechanical interpretation, as well as an energetic one such as we have suggested. In this treatment, the extent of orbital interaction in the transition states for bond cleavage is crucial for favored reaction. It is difficult to choose among these rationalizations at this stage of our knowledge, although more extended studies by workers in our laboratory are all consistent with the electron-transfer correlation. Complicating this problem is the report[7b] that the preferred stereochemistry for chloromonobenzobicyclo[2.2.2]-octenes is reversed from those systems we are reporting here or have reported earlier.[4,5] As experimental data are not available for these results, we prefer to defer comment on them.

Let us now turn to a discussion of the regioselectivity in the migration process. As noted above and in Scheme II, it has been suggested previously that the zwitterionic biradical produced by electron-transfer decays by loss of chloride ion (or other nucleofuge) to give a biradical cation (shown in the example in Scheme II as **29**), which then suffers rearrangement by migration of either the electron-deficient ring (the initial chromophore) to give a bridged ion, such as **34**, or of the non-electron-deficient moiety to give another (still excited) biradical cation, which ultimately decays to an ion isomeric with that of the alternative migration mode. This order of events in the decay mode, in which return to the ground-state surface is delayed, was suggested[4,5,27] in order to account for the fact that the distribution of products was not consistent with that anticipated from a ground-state cation.

The previous work in these systems, however, was lacking in an important regard, in that electron transfer always was anti, so that consideration of migration independent of electron-transfer stereochemistry was impossible. Put another way, there was only one way to prepare a presumed biradical cation intermediate, and therefore no way to get two independent confirmations of its fate. With the naphthobenzo and the veratrobenzo cases, where both syn and anti electron transfer are involved, tests of the validity of mechanisms analogous to that in Scheme II may be made. Thus, in the naphthobenzo system, anti electron transfer from the π,π^* state of the trans isomer **12** and syn transfer in the syn-cis isomer **14** should lead, after chloride ion loss, to the same biradical cation **37**. In like fashion, syn electron transfer for **12** and anti



37 38 39



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electron transfer from the anti-cis isomer **13**, should lead to the biradical cation **38**. Unless the chloride counterion has an unanticipated major effect in the rearrangements that follow, product mixtures should be identical from the two intermediates, **37** to give **18** and **23** and **38** to give **19** and **22**. In fact, the experimental results are quite inconsistent with this hypothesis (see Tables I and II). Thus **12** gives **18** and **23** in a ratio of 3:5, while **14** gives only **18**, results not at all predicted from a single intermediate **37**. A similar discrepancy is observed with the presumed intermediate **38**, where **12** gives a mixture of **19** and **22** in a ratio of 2:3, while **13** gives the same compounds but in an opposite ratio of 4:1. It should be noted that these represent a preponderance of syn migration over anti, independent of whether the syn ring is the benzo group or the naphtho group.

Analogously, in the veratrobenzo system, anti electron transfer from the π,π^* state of the trans isomer **15** and syn electron transfer in the syn-cis isomer **17** should lead, after chloride ion loss, to the biradical cation **39**, while **15** (syn transfer) and anti-cis-**16** should give **40**. **39** should lead to **24** and **27**, while **40** should give **25** and **26**. Again the experimental data do not fit the assumptions, **15** giving **24** and **27** in a ratio of 1:8, while only **24** was produced

(22) For a discussion of the computation of Coulombic energies of intramolecular charge interactions, see ref 23 and references therein.
(23) Cristol, S. J.; Hause, N. L.; Meek, J. S. *J. Am. Chem. Soc.* **1951**, *73*, 674.
(24) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124.
(25) Pysh, E. S.; Yang, N.-C. *J. Am. Chem. Soc.* **1963**, *85*, 2124.
(26) Estimate from data collected in: Mann, C. K.; Barnett, K. K. "Electrochemical Reactions in Non-Aqueous Systems"; Marcel Dekker: New York, 1970; p 225.
(27) Opitz, R. J. Ph.D. Thesis, University of Colorado, Boulder, CO, 1980.

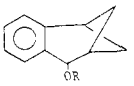
in measureable amounts from **17**. In the other set, **15** gave only **26**, while **16** gave **25** and **26** in a ratio of 3:1. Again, *syn* migration was predominant, independent of whether the migrating ring was benzo or veratro.

It seems clear from these results that the proposed biradical cation intermediates cannot represent the sole mechanism used in these photoreactions. As most of the reactions are not regiospecific, it is necessary to assume that (at least) two processes are generally involved. We see no reason to abandon the biradical cation as the intermediate responsible for the partial mixing of products, and we tentatively propose that a front-side (syn) rearrangement occurs concerted with loss of chloride ion, thus bypassing the biradical cation on the way to rearranged cation, for what appears to be the major mode of reaction, at least in this system.

Ground-state 1,2-sigmatropic rearrangements, whether of alkyl groups (σ participation), unsaturated groups (π participation), or groups donating n electrons, are well-known to proceed with inversion at the migration terminus, that is, in an anti fashion, as long as migration occurs in concert with loss of nucleofuge.[28] As the stereochemical consequences of orbital symmetry requirements are generally reversed in excited-state reactions, compared with analogous ground-state reactions,[29] it is reasonable to tie together concertedness and migration with retention in these excited-state rearrangements.

To the best of our knowledge, the question of stereochemistry in such excited-state rearrangements has not been addressed heretofore. There is, however a case in the literature that seems consistent with our results. As mentioned above, Morrison and Miller[7] have studied the photosolvolyses in methanol and in *tert*-butyl alcohol of the epimers of benzonorbornenyl chloride and methanesulfonate and have observed that the exo compounds (**41**) are substantially more photoactive than their endo isomers.

41



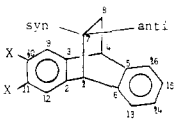
42

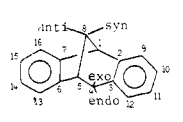
More to the point, however, is the observation that photosolvolyses of exo **41** result in substantial amounts of the [3.1.1] products **42**, which are not formed in ground-state solvolyses of **41**, but which are formed from the (endo) diazonium ion.[7c] These workers[7c] proposed that the ion leading to **42** is a "hot" (solvent-unencumbered) carbonium ion, as has been suggested for those produced by loss of nitrogen from diazonium ions[30] and those produced by direct irradiation of alkyl iodides.[31] We note, however, that **42** results from a suprafacial (syn) migration and suggest instead the same explanation for their results as given above for ours.

It may not be incorrect to assume that this type of rearrangement, with retention at the migration terminus, may be a model for S_N2-like displacements in such excited-state systems, that is, in systems involving five rather than four electrons, and may, therefore, give experimental insight into the general stereochemistry involved in such concerted displacements. It is our hope to explore this and other possible displacements further.

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):





All melting points were determined with a Thomas-Hoover or a Mel-Temp apparatus and were corrected. ^{1}H NMR spectra were obtained with the use of a Varian Associates EM-390 or a Bruker WM-250 instrument. Chemical shifts are reported in parts per million relative to tetramethylsilane. Mass spectra were obtained with the use of a Varian MAT CH-5 spectrometer. Ultraviolet spectra were obtained with a Cary 219 or Cary 17 spectrophotometer. Absorptions are reported in nanometers and extinction coefficients in liter mole^{-1} centimeter^{-1}. Elemental analyses were performed by Galbraith Laboratories, Inc. Irradiations with 254- and 300-nm light were carried out in a Srinivasen-Griffen photochemical reactor, hereafter referred to as a "Rayonet." All solvents and reagents were commercially available, reagent grade, and used without further purification unless otherwise stated.

Preparation of *trans*-7,8-Dichloro-2,3-(2′,3′-naphtho)-5,6-benzobicyclo[2.2.2]octa-2,5-diene (12). Naphthacene[9] (1.50 g, 6.6 mmol) and *trans*-1,2-dichloroethene (103 mL) were sealed in a large thick-walled glass combustion tube and heated at 153 ± 2 °C for 40 h. The tube was opened and the *trans*-1,2-dichlorethene was removed by reduced-pressure distillation. The residue was chromatographed on a 60–200 mesh silica gel column with hexanes/methylene chloride (2:1) as the eluent. The product fractions were combined and recrystallized from hexanes and/or toluene/ethyl acetate (80:20) to give 1.68 g (79%) of **12**, which upon further recrystallization had the following properties: mp 191.0–191.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.70 and 7.63 (two s, 4 H, H-1′, H-4′, H-5′, H-8′), 7.43–7.06 (m, 6 H, Ar H), 4.30 (br s, 2 H, H-7, H-8), 4.06 (d, 2 H, $J_{1,7} = J_{4,8} = 1.5$ Hz, H-1, H-4); mass spectrum, *m/e* (relative intensity) 328 (<1, M + 4), 326 (9, M + 2), 324 (14, M$^+$), 254 (6), 253 (12), 252 (12), 229 (23), 228 (100), 226 (12), 114 (9); ultraviolet spectrum (acetonitrile) λ_{max} (log ϵ) 320 (2.38), 316 (2.26), 307 (2.58), 300 (2.60, not a maximum), 288 (3.61), 277 (3.86), 271 (3.86), 266 (3.92, shoulder), 257 (3.81, shoulder), 233 (4.86), 215 (4.66). Anal. Calcd for $C_{20}H_{14}Cl_2$: C, 73.86; H, 4.34. Found: C, 73.61; H, 4.39.

Preparation of *anti*- and *syn-cis*-7,8-Dichloro-2,3-(2′,3′-naphtho)-5,6-benzobicyclo[2.2.2]octa-2,5-diene (13 and 14). Naphthacene (3.00 g, 13.2 mmol) and *cis*-1,2-dichloroethene (100 mL) were sealed in a thick-walled combustion tube and heated at 148 ± 2 °C for 72 h. The tube was opened, and the *cis*-1,2-dichloroethene was removed by reduced-pressure distillation. The brown residue (5.89 g) was decolorized with charcoal in toluene/ethyl acetate (4:1) and crystallized from toluene/ethyl acetate. The syn-cis isomer (**14**) predominated in the early crops and the anti-cis isomer (**13**) predominated in the later crops.

The syn-cis isomer (**14**) was recrystallized from hexanes, from toluene/ethyl acetate, and then from toluene/ethyl acetate/hexane to give small clear crystals: mp 264.0–264.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.90–7.70 (m, 2 H, H-5′, H-8′), 7.75 (s, 2 H, H-1′, H-4′), 7.53–7.10 (m, 6 H, Ar H), 4.53 (s, 2 H, H-1 and H-2 or H-7 and H-8), 4.51 (s, 2 H, H-7 and H-8 or H-1 and H-2); mass spectrum, *m/e* (relative intensity) 328 (<1, M + 4), 326 (10, M + 2), 324 (14, M$^+$), 254 (9), 253 (17), 252 (17), 250 (5), 229 (30), 228 (100), 227 (6), 226 (15), 114 (20); ultraviolet spectrum (acetonitrile) λ_{max} (log ϵ) 319 (2.40), 315 (2.30), 306 (2.59), 300 (2.45, not a maximum), 287 (3.62), 275 (3.88), 2.73 (3.89), 266 (3.94, shoulder), 257 (3.83, shoulder), 232 (4.86), 214 (4.68), 197 (4.69). Anal. Calcd for $C_{20}H_{14}Cl_2$: C, 73.86; H, 4.34. Found: C, 73.71; H, 4.41.

The anti-cis isomer (**13**) was recrystallized from hexanes then from toluene/ethyl acetate to give long colorless plates: mp 220.5–221.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.90–7.76 (m, 2 H, H-5′, H-8′), 7.78 (s, 2 H, H-1′, H-4′), 7.66–7.26 (m, 6 H, Ar H), 4.60 (s, 2 H, H-1 and H-4 or H-7 and H-8), 4.53 (br s, 2 H, H-7 and H-8 or H-1 and H-4); mass spectrum, *m/e* (relative intensity) 328 (<1, M + 4), 326 (13, M + 2), 324 (19, M$^+$), 254 (17), 253 (19), 252 (32), 229 (59), 228 (100), 227 (12), 226 (34), 114 (40); ultraviolet spectrum (acetonitrile) λ_{max} (log ϵ) 321 (2.64), 317 (2.34), 307 (2.72), 300 (2.59, not a maximum), 290 (3.60), 278 (3.81), 270 (3.88), 262 (3.79, shoulder), 232 (4.88), 213 (4.53). Anal. Calcd for $C_{20}H_{14}Cl_2$: C, 73.86; H, 4.34. Found: C, 73.77; H, 4.46.

Silver Ion Assisted Solvolysis of *trans*-7,8-Dichloro-2,3-(2′,3′-naphtho)-5,6-benzobicyclo[2.2.2]octa-2,5-diene (12). Compound **12** (122 mg, 0.38 mmol), silver acetate (63 mg, 0.38 mmol), and glacial acetic acid (50 mL) were heated at reflux with stirring until the reaction was complete (9.0 days) (additional silver acetate was added periodically). The yellow heterogeneous mixture was cooled and filtered. The acetic acid was evaporated in vacuo to give a yellow solid, which was dissolved in methylene chloride. The organic solution was washed with saturated sodium bicarbonate, dried ($MgSO_4$), filtered, and evaporated in vacuo to give an orange paste (191 mg), which was composed of a 3:2 mixture of [3.2.1] acetate **18**-OAc [^{1}H NMR ($CDCl_3$) δ 8.0–7.1 (m, 10 H, Ar

(28) de Mayo, P. "Molecular Rearrangements"; Interscience: New York, 1963.
(29) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; *Verlag Chemie*: Weinheim, 1970; Chapter 7.
(30) Keating, J. T; Skell, P. S. *Carbonium Ions* **1970**, *2*, 573.
(31) (a) Kropp, P. J.; Jones, T. H.; Poindexter, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 5420. (b) Poindexter, G. S.; Kropp, P. J. *Ibid.* **1974**, *96*, 7142. (c) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *Ibid.* **1976**, *98*, 8135.

H), 6.13 (d, 1 H, $J_{4,5}$ = 3 Hz, H-4), 5.06 (s, 1 H, H-8),[11] 4.36 (s, 1 H, H-1), 3.83 (br s, 1 H, H-5), 2.15 (s, 3 H, CH_3)] and [3.2.1] acetate **19**-OAc [^{1}H NMR ($CDCl_3$) δ 8.0–7.1 (m, 10 H, Ar H), 6.27 (d, 1 H, $J_{4,5}$ = 3 Hz, H-4), 5.10 (s, 1 H, H-8),[11] 4.41 (s, 1 H, H-1), 3.92 (br s, 1 H, H-5), 2.15 (s, 3 H, CH_3)].

Methanolysis of *anti*-8-Chloro-2,3-benzo-6,7-(2′,3′-naphtho)bicyclo-[3.2.1]octa-2,6-diene-*exo*-4-ol Acetate (*exo*-18-OAc) and *anti*-8-Chloro-2,3-(2′,3′-naphtho)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol Acetate (*exo*-19-OAc). The mixture of *exo*-**18**-OAc and *exo*-**19**-OAc (191 mg) produced as described in the preceding paragraph was heated at reflux for 10 min with saturated sodium methoxide in methanol. The methanol was evaporated in vacuo. The residue was diluted with ethyl ether and the ethereal solution was washed with 1 M HCl and water, dried ($MgSO_4$), filtered, and evaporated in vacuo to give 180 mg of a brown paste, which was composed of a 3:2 mixture of two [3.2.1] alcohols *exo*-**18**-OH and *exo*-**19**-OH. The crude product mixture was chromatographed on two 20 cm × 20 cm × 1 mm silica gel thin-layer chromatography (TLC) plates with hexanes/ethyl acetate (7:5) as the eluent to give the separated alcohols *exo*-18-OH [^{1}H NMR ($CDCl_3$) δ 7.85–7.20 (m, 10 H, Ar H), 5.05 (s, 1 H, H-8),[11] 4.92 (d, 1 H, $J_{4,5}$ = 3 Hz, H-4), 4.28 (s, 1 H, H-1), 3.86 (br s, 1 H, H-5), 2.2 (br s, 1 H, OH)] and *exo*-**19**-OH [^{1}H NMR ($CDCl_3$) δ 7.90–7.15 (m, 10 H, Ar H), 5.10 (m, 2 H, H-4, H-8),[11] 4.35 (s, 1 H, H-1), 3.86 (br s, 1 H, H-5), 2.0 (br s, 1 H, OH)].

Chromium(VI) Oxidation of *anti*-8-Chloro-2,3-benzo-6,7-(2′,3′-naphtho)bicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol (*exo*-18-OH). Compound *exo*-**18**-OH (45.3 mg, 0.18 mmol) was dissolved in acetone (5 mL). A slight excess of Jones' reagent[32] was added dropwise at room temperature. After 30 min, isopropyl alcohol (0.5 mL) was added. The mixture was diluted with water and washed 3 times with ethyl ether. The ethereal solution was washed with saturated sodium bicarbonate and water, dried ($MgSO_4$), filtered, and evaporated in vacuo to give 45.5 mg of an off-white solid (recrystallization from ethanol): mp 192–193 °C; ^{1}H NMR ($CDCl_3$) δ 8.01 (s, 1 H, benzo H ortho to keto), 7.97–7.75 (m, 3 H, Ar H), 7.67–7.30 (m, 5 H, Ar H), 5.02 (s, 1 H, H-8),[11] 4.59 (s, 1 H, H-1), 4.45 (s, 1 H, H-5). Anal. Calcd $C_{20}H_{13}ClO$: C, 78.82; H, 4.30. Found: C, 78.61; H, 4.59. On the basis of the ^{1}H NMR data, the product must be *anti*-8-chloro-2,3-benzo-6,7-(2′,3′-naphtho)bicyclo[3.2.1]octa-2,6-dien-4-one (**20** ketone).

Chromium(VI) Oxidation of *anti*-8-Chloro-2,3-(2′,3′-naphtho)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol (*exo*-19-OH). Compound *exo*-**19**-OH (47.5 mg, 0.15 mmol) was treated as above to give 58.8 mg of an off-white solid (recrystallization from ethanol): mp 235–236 °C; ^{1}H NMR ($CDCl_3$) δ 8.52 (s, 1 H, H-1′), 8.00–7.18 (m, 9 H, Ar H), 5.02 (s, 1H, H-8),[11] 4.57 (s, 1 H, H-1), 4.30 (s, 1 H, H-5); MS, *m/e* (relative intensity) 306 (14, M + 2), 305 (9, M + 1), 304 (40, M^+), 270 (22), 269 (100), 268 (27), 241 (17), 240 (16), 239 (50). On the basis of the ^{1}H NMR data, the product must be *anti*-8-chloro-2,3-(2′,3′-naphtho)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**21** ketone).

Silver Ion Assisted Solvolysis of *anti-cis*-7,8-Dichloro-2,3-(2′,3′-naphtho)-5,6-benzobicyclo[2.2.2]octa-2,5-diene (13). Compound **13** (49.2 mg, 0.15 mmol), silver acetate (95.1 mg, 0.57 mmol), and glacial acetic acid (50 mL) were heated at reflux with stirring for 18.5 days (additional silver acetate was added periodically). The reaction was worked up by following the procedure described above to give 117.5 mg of an orange paste. Chromatography of this material on a 20 cm × 20 cm × 1 mm silica gel TLC plate with methylene chloride/hexanes (5.7:1) as eluent gave a mixture of both epimers of [3.2.1] acetate **22**-OAc: 45.5 mg (87%); ^{1}H NMR of *exo*-**22**-OAc ($CDCl_3$) δ 8.00–7.25 (m, 10 H, Ar H), 5.93 (d, 1 H, $J_{4,5}$ = 1.5 Hz, H-4), 4.90 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 5 Hz, H-8),[11] 4.33 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1), 3.96 (dd, 1 H, $J_{5,8}$ = 5, $J_{5,4}$ = 1.5 Hz, H-5), 2.22 (s, 3 H, CH_3); ^{1}H NMR of *endo*-**22**-OAc ($CDCl_3$) δ 8.00–7.25 (m, 10 H, Ar H), 6.57 (d, 1 H, $J_{4,5}$ = 6 Hz, H-4), 4.90 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 5 Hz, H-8),[11] 4.28 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1), 4.12 (br t, 1 H, $J_{5,8}$ = 5, $J_{5,4}$ = 6 Hz, H-5), 2.17 (s, 3 H, CH_3).

Methanolysis of the *syn*-8-Chloro-2,3-benzo-6,7-(2′,3′-naphtho)bicyclo[3.2.1]octa-2,6-dien-4-ol Acetates (22-OAc). The epimeric mixture of **22**-OAc (33 mg, 0.09 mmol) was submitted to the same methanolysis and workup procedure as **18**-OAc and **19**-OAc to give 28 mg of an epimeric mixture of [3.2.1] alcohols **22**-OH: ^{1}H NMR ($CDCl_3$) δ 7.86–7.17 (m, 10 H, Ar H), 5.26 (d, $J_{4,5}$ = 6 Hz, H-4, endo isomer), 4.90 (m, 1 H, H-8, endo and exo isomers),[11] 4.62 (br s, H-4, exo isomer), 4.21 (d, $J_{1,8}$ = 5 Hz, H-1, exo isomer), 4.15 (d, $J_{1,8}$ = 5 Hz, H-1, endo isomer), 3.83 (m, 1 H, H-5, endo and exo isomers), 2.86 (br, 1 H, OH).

Chromium(VI) Oxidation of the *syn*-8-Chloro-2,3-benzo-6,7-(2′,3′-naphtho)bicyclo[3.2.1]octa-2,6-dien-4-ols (22-OH). The epimeric mixture (~28 mg, ~0.09 mmol) was oxidized as described above for **19**-OH to give a single ketone as an orange solid (20 mg) (recrystallization from ethanol): mp 150.0–150.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.93–7.20 (m, 10 H, Ar H), 5.06 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 3 Hz, H-8),[11] 4.41 (d, 1 H, $J_{5,8}$ = 3 Hz, H-5), 4.26 (d, 1 H, $J_{1,8}$ = 3 Hz, H-1). Anal. Calcd for $C_{20}H_{13}ClO$: C, 78.82; H, 4.30. Found: C, 78.64; H, 4.48. On the basis of the ^{1}H NMR data, the product must be *syn*-8-chloro-2,3-benzo-6,7-(2′,3′-naphtho)bicyclo[3.2.1]octa-2,6-dien-4-one (**22** ketone).

Silver Ion Assisted Solvolysis of *syn-cis*-7,8-Dichloro-2,3-(2′,3′-naphtho)-5,6-benzobicyclo[2.2.2]octa-2,5-diene (14). Compound **14** (42.7 mg, 0.13 mmol), silver acetate (large excess), and glacial acetic acid (20 mL) were heated at reflux with stirring for 18 days. The reaction was worked up as already described to give 234 mg of a brown solid which was chromatographed on a 20 cm × 20 cm × 2 mm silica gel TLC plate with methylene chloride/hexanes (2:1) as the eluent. This gave an epimeric mixture (endo/exo = 7:5) of [3.2.1] acetates **23**-OAc (47.2 mg): ^{1}H NMR of *endo*-**23**-OAc ($CDCl_3$) δ 7.97–7.17 (m, 10 H, Ar H), 6.63 (d, 1 H, $J_{4,5}$ = 6 Hz, H-4), 4.95 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 5 Hz, H-8),[11] 4.32 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1), 3.98 (br t, 1 H, $J_{5,4}$ = 6 Hz, $J_{5,8}$ = 5 Hz, H-5), 2.18 (s, 3 H, CH_3); ^{1}H NMR of exo-**23**-OAc ($CDCl_3$) δ 7.97–7.17 (m, 10 H, Ar H), 6.07 (br s, 1 H, H-4), 4.92 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 5 Hz, H-8),[11] 4.27 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1), 3.82 (dd, 1 H, $J_{5,4}$ = 1.5 Hz, $J_{5,8}$ = 5 Hz, H-5), 2.22 (s, 3 H, CH_3). The structure of **23**-OAc was verified as described below.

Irradiation of the Trans Isomer 12 with 300-nm Light. Compound **12** (175.2 mg, 0.54 mmol) was dissolved in glacial acetic acid (350 mL) in a thick-walled (3.5 mm) Pyrex tube. (Irradiation through 1-mm Pyrex gave essentially the same product mixture.) The sample was capped and deoxygenated by bubbling nitrogen gas through the solution for 15 min. The void space was wrapped with aluminum foil. The sample was irradiated with 300-nm light in a Rayonet for 88 h. The acetic acid was evaporated in vacuo at ≤40 °C. ^{1}H NMR spectroscopy revealed that trans isomer **12** had been ≥95% converted to the following five [3.2.1] acetates in the proportion indicated: *exo*-**18**-OAc (33%), *exo*-**19**-OAc (6%), *exo*-**22**-OAc (9%), and the two epimers of **23**-OAc (51%). Compounds *exo*-**18**-OAc, *exo*-**19**-OAc, and *exo*-**22**-OAc were identified by comparison of their ^{1}H NMR proton absorptions with the ^{1}H NMR spectra of the known compounds obtained from the ground-state solvolysis work. Compounds **23**-OAc were identified by conversion to the corresponding ketone, as described below.

A "dark reaction" was performed by wrapping a tube containing **12** in glacial acetic acid wth aluminum foil, irradiating it with 300-nm light for the same length of time as the irradiation of **12**, and working it up by the same method used for **12** except with excessive heating (80–100 °C) during solvent removal. The ^{1}H NMR spectrum of the final material showed only starting material (**12**); therefore, no ground-state solvolysis takes place under these conditions.

Methanolysis of *exo*- and *endo*-*syn*-8-Chloro-2,3-(2′,3′-naphtho)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-ol Acetates (23-OAc). A mixture of the epimers of **23**-OAc was obtained by silica gel TLC (eluent: hexanes/methylene chloride, 1:1) of the product mixture that resulted from 300-nm irradiation of **12** in glacial acetic acid. This mixture (225 mg, 0.64 mmol) was submitted to the same methanolysis and workup procedure previously described for *exo*-**18**-OAc and *exo*-**19**-OAc. This gave a mixture of the [3.2.1] alcohols **23**-OH (183.3 mg): ^{1}H NMR ($CDCl_3$) δ 8.00–7.10 (m, 10 H, Ar H), 4.95 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 5 Hz, H-8),[11] 4.80 (br s, 1 H, H-4), 4.23 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1), 3.77 (d, 1 H, $J_{5,8}$ = 5 Hz, H-5), 2.87 (br s, 1 H, OH).

Chromium(VI) Oxidation of *syn*-8-Chloro-2,3-(2′,3′-naphtho)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-ols (23-OH). The mixture of **23**-OH epimers described in the previous paragraph (184 mg, 0.60 mmol) was oxidized and worked up by the method described above to give a single ketone (198.4 mg) (recrystallization from hexanes): mp 178.0–178.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.60 (s, 1 H, H-1′) 8.00–7.17 (m, 9 H, Ar H), 5.20 (t, 1 H, $J_{8,5}$ = $J_{8,1}$ = 5 Hz, H-8),[11] 4.50 (d, 1 H, $J_{5,8}$ = 5 Hz, H-5), 4.25 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1). Anal. Calcd for $C_{20}H_{13}ClO$: C, 78.82; H, 4.30. Found: C, 78.80; H, 4.49. On the basis of the ^{1}H NMR data, the compound must be *syn*-8-chloro-2,3-(2′,3′-naphtho)-6,7-benzobicyclo-[3.2.1]octa-2,6-dien-4-one (**23** ketone).

Irradiation of *anti-cis*-13 with 300-nm Light. **13** (137 mg, 0.42 mmol) was dissolved in glacial acetic acid (350 mL) and irradiated with 300-nm light through 3.5-mm Pyrex for 102 h (irradiation through 1-mm Pyrex gave the same products). The method of sample preparation, irradiation, and workup was the same as already described for the irradiation of **12**. ^{1}H NMR spectroscopy revealed that *anti-cis*-**13** had been 88% converted to two [3.2.1] acetates in the proportions indicated: *exo*-**19**-OAc (80%) and *exo*-**22**-OAc (20%). Identification of the products was made by comparison of their ^{1}H NMR spectra with the ^{1}H NMR spectra of the known components.

Irradiation of *syn-cis*-14 with 300-nm Light. **14** (54.8 mg, 0.17 mmol) was dissolved in glacial acetic acid/acetonitrile (7:3, 300 mL) and irra-

(32) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 142.

diated with 300-nm light through 3.5-mm Pyrex for 17 days (irradiation through 1-mm Pyrex gave the same product). The method of sample preparation, irradiation, and workup was the same as already described for the irradiation of **12**. ^{1}H NMR spectroscopy revealed that 66% of **14** had reacted and that only *exo*-**18**-OAc had been formed. The product was identified by comparison of its ^{1}H NMR spectrum with the ^{1}H NMR spectrum of the known compound.

Preparation of 2,3-Dimethoxyanthracene. 2,3-Dimethoxyanthracene was made following the general procedure of Iwata and Emoto.[15a] In our hands, this procedure gave better results than that of Lagodzinski.[33] Phthalic anhydride (60 g, 0.40 mol) and aluminum chloride (100 g, 0.75 mol) were added to methylene chloride (1 L) at 0 °C. Veratrole (63 mL, 0.49 mol) was added dropwise (4–6 h) to this rapidly stirred mixture at 0 °C. The reaction was allowed to warm to room temperature and was stirred at room temperature overnight. Additional aluminum chloride (50 g, 0.38 mol) was added to the reaction at 0 °C, and the reaction was heated at reflux until no HCl gas evolved (24–48 h). The reaction was quenched by cooling it to 0 °C, dropwise addition (2 h) of ice water (100 mL), and the addition of concentrated HCl (20 mL). The precipitate was filtered, washed with 5% HCl, and then dissolved in 10% NaOH. The basic solution was washed with methylene chloride, acidified, cooled, filtered, and dried ($MgSO_4$) to yield 2-(2′,3′-dimethoxybenzoyl)benzoic acid: (60–90% yield); ^{1}H NMR (Me_2SO-d_6) δ 7.97 (dd, 1 H, $J_{6,5}$ = 6, $J_{6,4}$ = 3 Hz, H-6), 7.67 (d, 1 H, J = 4.5 Hz), 7.62 (d, 1 H, J = 4.5 Hz), 7.37 (br s, 1 H), 7.35 (dd, J = 6, J = 3 Hz), 6.93 (s, 2 H), 3.70 and 3.69 (two s, 6 H, OCH_3). The acid can be recrystallized from acetic acid but it was generally used without recrystallization.

2-(2′,3′-Dimethoxybenzyl)benzoic acid was made following the general procedure of Iwata and Emoto.[15a] 2-(2′,3′-Dimethoxybenzoyl)benzoic acid (89.2 g, 0.31 mol) was dissolved in 800 mL of 10% NH_4OH (in H_2O). $CuSO_4 \cdot 5H_2O$ (7.70 g, 0.03 mol) was added with vigorous stirring, followed by zinc dust (216 g, 3.3 mol). The reaction mixture was heated at reflux for 24 h and filtered hot; then the filtrate was cooled to 0 °C. HCl was added until no more acid precipitated. The mixture was cooled and filtered. The filter cake was dried to give 2-(2′,3′-dimethoxybenzyl)benzoic acid: 80–95% yield; ^{1}H NMR ($CDCl_3$) δ 8.20 (dd, 1 H, J = 7.5, 2 Hz), 7.66–7.25 (m, 3 H), 6.97–6.68 (m, 3 H), 4.39 (s, 2 H, CH_2), 3.83 and 3.81 (two s, 6 H, OCH_3). The acid can be recrystallized from acetic acid but it was generally used without recrystallization.

2,3-Dimethoxy-9-anthrone was synthesized by the procedure of Iwata and Emoto.[15a] 2-(2′,3′-Dimethoxybenzyl)benzoic acid (70 g, 0.26 mol) was added to concentrated H_2SO_4 (400 mL). The mixture was heated to a gentle boil for 20 min and then cooled. The solution was poured over ice to give a yellow-green solid, the anthrone, which was filtered and washed with base. The anthrone is air sensitive and was immediately reduced to the dimethoxyanthracene by the procedure of Criswell and Klanderman.[15b] The 2,3-dimethoxyanthracene was purified on an alumina column with dichloromethane as the eluent. 2,3-Dimethoxyanthracene was isolated in 50–70% yields. 2,3-Dimethoxyanthracene was recrystallized from ethanol: mp 200–202 °C (lit.[33] mp 204 °C); ^{1}H NMR ($CDCl_3$) δ 8.28 (s, 2 H, H-9 and H-10), 8.10–7.96 (dd, 2 H, J_{meta} = 3, J_{ortho} = 8 Hz, H-5 and H-8), 7.56–7.43 (dd, 2 H, J_{ortho} = 8, J_{meta} = 3 Hz, H-6 and H-7), 7.25 (s, 2 H, H-1 and H-4), 4.06 (s, 6 H, 2-OCH_3).

Synthesis of *anti-cis*-7,8-Dichloro-5,6-(10,11-dimethoxybenzo)-2,3-benzobicyclo[2.2.2]octa-2,5-diene (16) and *syn-cis*-7,8-Dichloro-5,6-(10,11-dimethoxybenzo)-2,3-benzobicyclo[2.2.2]octa-2,5-diene (17). 2,3-Dimethoxyanthracene (10 g, 30 mmol) was placed in a combustion tube along with 50 mL of *cis*-dichloroethylene and 80 mL of xylene. The tube was sealed and heated at 180–185 °C for 7–8 days. The *cis*-dichloroethylene was removed by simple distillation and the xylene by steam distillation. The residue was extracted with dichloromethane, and the solution was dried ($MgSO_4$). Removal of the solvent by distillation in vacuo left a residue which was purified by column chromatography. The top four-fifths of the column was silica gel (60–200 mesh), which had been activated by heating to 150–160 °C for 4–6 h and then stored at 100 °C until used. The bottom one-fifth was packed with alumina. Elution with dichloromethane gave 40–60% of **16** and **17** in the ratio of 1:15. The two isomers were separated by repeated crystallization in 95% ethanol. The major isomer **17**: mp 238.5–239.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.47–7.15 (m, 4 H, Ar H), 7.03 (s, 2 H, H-9 and H-12), 4.45 (br s, 4 H, H-2, H-1, H-7, and H-8), 3.88 (s, 6 H, 2 OCH_3); mass spectrum, *m/e* (relative intensity) 336 (13, M + 2), 334 (19, M^+), 264 (6), 239 (17), 238 (100), 195 (9), 165 (7), 151 (9), 119 (6); ultraviolet spectrum (acetonitrile), λ_{max} (log ϵ) 300 (2.95, not a maximum), 286.5 (3.72), 260 (3.32, shoulder). Anal. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.49; H, 4.81. Found: C, 64.55; H, 4.90. The minor isomer **16**: mp 206–207 °C; ^{1}H NMR ($CDCl_3$) δ 7.50–7.27 (m, 4 H, Ar H), 6.94 (s, 2 H, H-9 and H-12), 4.46 and 4.44 (two s, 2 H, H-8, H-7, H-1, and H-4), 3.86 (s, 6 H, 2 OCH_3); ultraviolet spectrum (acetonitrile) λ_{max} (log ϵ) 300 (3.37, not a maximum), 290 (3.71), 247 (3.16); mass spectrum, *m/e* (relative intensity) 336 (10, M + 2), 334 (15, M^+), 239 (18), 238 (100), 195 (11), 164 (6), 152 (6), 119 (7). Anal. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.49; H, 4.81. Found: C, 64.38; H, 5.02.

Synthesis of *trans*-7,8-Dichloro-5,6-(10,11-dimethoxybenzo)-2,3-benzobicyclo[2.2.2]octa-2,5-diene (15). The synthesis of **15** was similar to **16** and **17** except *trans*-dichloroethylene was used and no xylene was used. The reaction was worked up similarly. Compound **15** was recrystallized from 95% ethanol: mp 170.0–170.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.54–7.21 (m, 4 H, Ar H), 7.00 (s, 1 H, H-12), 6.92 (s, 1 H, H-9), 4.33 (d, 2 H, $J_{8,1}$ = $J_{7,4}$ = 1.5 Hz, H-7 and H-8), 4.17 (d, 2 H, $J_{1,8}$ = $J_{4,7}$ = 1.5 Hz, H-1 and H-4), 3.89 (s, 6 H, 2 OCH_3); ultraviolet spectrum (acetonitrile) λ_{max} (log ϵ), 300 (3.19, not a maximum), 287 (3.77), 250 (3.34, shoulder); mass spectrum, *m/e* (relative intensity) 336 (12, M + 2), 334 (19, M^+), 239 (14), 238 (100), 195 (10), 165 (6), 152 (8), 119 (8). Anal. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.49; H, 4.81. Found: C, 64.55; H, 4.90.

Silver Ion Assisted Solvolysis of *syn-cis*-7,8-Dichloro-5,6-(10,11-dimethoxybenzo)-2,3-benzobicyclo[2.2.2]octa-2,5-diene (17). Compound **17** (150 mg, 0.45 mmol), 20 mL of glacial acetic acid, and silver acetate (100 mg, 0.59 mmol) were heated at reflux for 6 days. After filtration and dilution with water, the reaction mixture was extracted with dichloromethane. The combined dichloromethane washings were washed with water and saturated sodium bicarbonate solution and dried ($MgSO_4$). The solvent was removed by distillation in vacuo. A light yellow oil was obtained (150 mg, 0.42 mmol, 93%) and identified as *syn*-8-chloro-2,3-(10,11-dimethoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*endo*-4-ol acetate (**27**-OAc): ^{1}H NMR ($CDCl_3$) δ 7.27–7.13 (m, 4 H, Ar H), 6.72 (s, 1 H, H-12), 6.70 (s, 1 H, H-9), 6.30 (d, 1 H, $J_{4,5}$ = 6 Hz, H-4, endo acetate), 4.84 (t, 1 H, $J_{8,5}$ = 4.5, $J_{8,1}$ = 4.5 Hz, H-8), 3.94–3.70 (m, 8 H, 2 OCH_3, H-1 and H-5), 2.13 (s, 3 H, $COCH_3$).

Methanolysis of 27-OAc to 27-OH. A solution of 150 mg (0.43 mmol) of **27-OAc**, 150 mg (3.1 mmol) of NaOH, and 10 mL MeOH was heated at reflux for 15 min. Water was added and the aqueous solution extracted with dichloromethane. The combined dichloromethane fractions were washed with water and dried ($MgSO_4$). The solvent was removed by distillation in vacuo. A light yellow oil (126 mg, 95%) was isolated and identified as *syn*-8-chloro-2,3-(10,11-dimethoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*endo*-4-ol (**27**-OH): ^{1}H NMR ($CDCl_3$) δ 7.48–7.15 (m, 4 H, Ar H), 7.00 (s, 1 H, H-12), 6.69 (s, 1 H, H-9), 5.13 (m, 1 H, H-4, upon addition of D_2O it simplified to a doublet, $J_{4,5}$ = 5.8 Hz), 4.86 (t, 1 H, $J_{8,5}$ = 4, $J_{8,1}$ = 4 Hz, H-8), 3.86 and 3.78 (two s, 6 H, OCH_3), 3.86–3.76 (m, 2 H, H-1 and H-5), 1.74 (br s, 1 H, OH, disappeared upon addition of D_2O).

Oxidation of 27-OH to 27 Ketone. The alcohol **27**-OH (126.4 mg, 0.40 mmol) was converted to *syn*-8-chloro-2,3-(10,11-dimethoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**27** ketone) according to the procedure of Ratcliffe and Rodehorst.[34] Ketone **27** was obtained as a white solid (107 mg, 85%) and was recrystallized from hexanes/ethanol: mp 144.0–144.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.45–7.11 (m, 4 H, Ar H), 7.43 (s, 1 H, H-12), 6.80 (s, 1 H, H-9), 5.11 (t, 1 H, $J_{8,5}$ = 4.5, $J_{8,1}$ = 4.5 Hz, H-8), 4.21 (d, 1 H, $J_{1,8}$ = 4.5 Hz, H-1), 4.10 (d, 1 H, $J_{5,8}$ = 4.5 Hz, H-5), 3.96 and 3.82 (two s, 6 H, OCH_3). Anal. Calcd for $C_{18}H_{15}O_3Cl$: C, 68.68; H, 4.80. Found C, 68.88; H, 4.90.

Silver Ion Assisted Solvolysis of *anti-cis*-7,8-Dichloro-5,6-(10,11-dimethoxybenzo)-2,3-benzobicyclo[2.2.2]octa-2,5-diene (16). A mixture of **16** and **17** (462.2 mg, 1.39 mmol; approximately 29% **16** and 71% **17**), 80 mL of glacial acetic acid, and silver acetate (62.5 mg, 0.37 mmol) was heated at reflux for 3 h. It was known that **15** (see Experimental Section) is converted to **26**-OAc in 3 h, due to assistance of the *p*-methoxy in the silver ion assisted solvolysis, whereas **17** requires 6 days to complete the same process, because no *p*-methoxy assistance is available. It was reasoned that if a mixture of **16** and **17** were subjected to silver ion assisted solvolysis, **16** would react quickly, on the order of 2–3 h, and **17** would react much more slowly (6 days). After the mixture of **16** and **17** was heated at reflux for 3 h, the reaction was worked up as usual, and the crude product mixture was chromatographed on 20 cm × 20 cm × 2 mm silica gel plates with 1% ether in dichloromethane as the eluent. Two bands were obtained (R_f 0.54 and 0.28). Band 2 (R_f 0.58, 331 mg, 72%) was identified by ^{1}H NMR as mostly **17** with a small amount, 2–4%, of **16**. Band 1 (R_f = 0.28, 120 mg, 34 mmol, 24%) was *syn*-8-chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**26**-OAc): ^{1}H NMR ($CDCl_3$) δ 7.43–7.17 (m, 3 H, Ar H), 7.01 (s, 1 H, H-13), 6.78 (s, 1 H, H-16), 5.82 (d, 1 H, $J_{4,5}$ = 1.5 Hz, H-4,

(33) Lagodzinski, K. *Justus Liebigs Ann. Chem.* **1905**, *342*, 90.

(34) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.

exo acetate), 4.83 (t, 1 H, $J_{8,5}$ = 4.5, $J_{8,1}$ = 4.5 Hz, H-8), 4.03 (d, 1 H, $J_{1,8}$ = 4.5 Hz, H-1), 3.85 and 3.80 (two s, 6 H, OCH_3), 3.69 (d, 1 H, $J_{5,8}$ = 4.5 Hz, H-5), 2.20 (s, 3 H, $COCH_3$).

Methanolysis of *syn*-8-Chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-ol Acetate (26-OAc). A solution of 120 mg (0.34 mmol) of **26**-OAc and 100 mg (2.5 mmol) of sodium hydroxide in 10 mL of methanol was heated at reflux for 15 min and worked up as described above for **27**-OH. *syn*-8-Chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-*exo*-ol (**26**-OH) was obtained as a yellow oil (100 mg, 93%): ^1H NMR ($CDCl_3$) δ 7.44–7.15 (m, 4 H, Ar H), 6.90 (s, 1 H, H-13), 6.74 (s, 1 H, H-16), 4.66 (m, 1 H, H-4, upon addition of D_2O it simplified to a doublet $J_{4,5}$ = 1 Hz, exo alcohol), 4.93 (t, 1 H, $J_{8,1}$ = 4.5, $J_{8,5}$ = 4.5 Hz, H-8), 4.00 (d, 1 H, $J_{1,8}$ = 4.5 Hz, H-1), 3.80 and 3.78 (two s, 6 H, OCH_3), 3.66 (br d, 1 H, $J_{5,8}$ = 4.5, $J_{5,4}$ = 2.0 Hz, H-5), 3.00 (br s, 1 H, OH, disappears upon addition of D_2O).

Chromium(VI) Oxidation of *syn*-8-chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-*exo*-ol (26-OH). Compound **26**-OH (100 mg, 0.32 mmol) was oxidized to the ketone according to the procedure of Ratcliffe and Rodehorst.[34] An oil (85 mg, 0.27 mmol, 79% yield) was obtained and identified by ^1H NMR as **26** ketone, *syn*-8-chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-one: mp, after recrystallization from 95% ethanol, 180.0–180.2 °C; ^1H NMR ($CDCl_3$) δ 8.00 (dd, 1 H, J_{ortho} = 7.5, J_{meta} = 3 Hz, H-12), 7.50–7.1 (m, 3 H, Ar H), 6.79 (s, 1 H, H-16), 6.90 (s, 1 H, H-13), 5.18 (t, 1 H, $J_{8,5}$ = 4.5, $J_{8,1}$ = 4.5 Hz, H-8), 4.26 (d, 1 H, $J_{1,8}$ = 4.5 Hz, H-1), 4.08 (d, 1 H, $J_{5,8}$ = 4.5 Hz, H-5), 3.80 (s, 6 H, 2 OCH_3). Anal. Calcd for $C_{18}H_{15}O_3Cl$: C, 68.68; H, 4.80. Found: C, 68.62; H, 4.88.

Conversion of 26-OH to 26-Cl. Compound **26**-OH (100 mg, 0.32 mmol) was dissolved in 5 mL of chloroform and cooled to 0 °C. Thionyl chloride (150 mg, 1.24 mmol) in 2 mL of chloroform was added dropwise with stirring. The reaction was stirred for 24 h at room temperature and then quenched with saturated sodium bicarbonate solution. Dichloromethane (10 mL) was added. The organic layer was washed with saturated sodium bicarbonate solution and dried ($MgSO_4$). The solvent was removed by distillation in vacuo. The residual oil (120 mg) was purified on a 20 cm × 20 cm × 1 mm silica gel TLC plate with 2.0% ethyl ether in dichloromethane as the eluent. Two bands were found after development (R_f 0.70, R_f 0.20). Band 1 (R_f 0.2, 20 mg, 20%) was the starting alcohol. Band 2 (R_f 0.70, 80 mg, 75% yield) was a mixture of the *endo*- and *exo*-**26**-Cl, *endo*- and *exo*-4-chloro-*syn*-8-chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-diene: ^1H NMR of *endo*-**26**-Cl ($CDCl_3$) δ 7.60–7.44 (m, 1 H, H-12), 7.42–7.16 (m, 3 H, Ar H), 7.06 (s, 1 H, H-13), 6.80 (s, 1 H, H-16), 5.74 (d, 1 H, $J_{4,5}$ = 5.5 Hz, H-4), 4.86 (t, 1 H, $J_{8,5}$ = 4.5, $J_{8,1}$ = 4.5 Hz, H-8), 3.78 and 3.82 (two s, 6 H, OCH_3), 3.70 (dd, 1 H, $J_{5,4}$ = 5.5, $J_{5,8}$ = 4.5 Hz, H-5); ^1H NMR of *exo*-**26**-Cl ($CDCl_3$) δ 6.92 (s, 1 H, H-13), 6.78 (s, 1 H, H-16), 5.12 (d, 1 H, $J_{4,5}$ = 2 Hz, H-4), 4.92 (t, 1 H, $J_{8,5}$ = 4.5, $J_{8,1}$ = 4.5 Hz, H-8), 4.02 (d, 1 H, $J_{1,8}$ = 4.5 Hz, H-1), 3.80 and 3.83 (two s, 6 H, OCH_3); ^1H NMR of *endo*-**26**-Cl (acetic acid-d_4) δ 7.56–7.35 (m, 1 H, H-12), 7.35–7.10 (m, 3 H, Ar H), 7.03 (s, 1 H, H-13), 6.85 (s, 1 H, H-16), 4.90 (d, 1 H, $J_{4,5}$ = 5 Hz, H-4), 4.35 (t, 1 H, $J_{8,1}$ = 5, $J_{8,5}$ = 5 Hz, H-8), 4.06 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1), 3.76 and 3.74 (two s, 6 H, OCH_3), 3.65 (t, 1 H, $J_{5,8}$ = 5, $J_{5,4}$ = 5 Hz, H-5); ^1H NMR of *exo*-**26**-Cl (acetic acid-d_4) δ 6.99 (s, 1 H, H-13), 6.79 (s, 1 H, H-6), 5.09 (br s, 1 H, $J_{4,5}$ = 1 Hz, H-4), 4.86 (t, 1 H, $J_{8,5}$ = 5, $J_{8,1}$ = 5 Hz, H-8), 4.00 (d, 1 H, $J_{1,8}$ = 5 Hz, H-1), 3.79 and 3.76 (two s, 6 H, OCH_3).

Silver Ion Assisted Solvolysis of trans-7,8-Dichloro-5,6-(10,11-dimethoxybenzo)-2,3-benzobicyclo[2.2.2]octa-2,5-diene (15). Compound **15** (463 mg, 1.35 mmol), glacial acetic acid (100 mL), and silver acetate (300 mg, 1.8 mmol) were heated at reflux for 3 h. The reaction was worked up as described above to give 470 mg (95%) of crude **24**-OAc, which crystallized from 95% ethanol as needles: mp 181.5–182.5 °C; ^1H NMR ($CDCl_3$) δ 7.38–7.24 (m, 4 H, Ar H), 7.03 (s, 1 H, H-13), 6.82 (s, 1 H, H-16), 5.99 (d, 1 H, $J_{4,5}$ = 2 Hz, H-4), 4.98 (s, 1 H, H-8), 4.06 (s, 1 H, H-1), 3.83 and 3.79 (two s, 6 H, OCH_3), 3.63 (d, 1 H, $J_{5,4}$ = 2 Hz, H-5), 2.17 (s, 3 H, $COCH_3$); ^1H NMR (acetic acid-d_4) δ 7.35–7.23 (m, 4 H, Ar H), 7.07 (s, 1 H, H-13), 6.88 (s, 1 H, H-16), 5.96 (d, 1 H, $J_{4,5}$ = 2.6 Hz, H-4), 4.95 (s, 1 H, H-8), 3.97 (s, 1 H, H-1), 3.79 and 3.74 (two s, 6 H, OCH_3), 3.61 (d, 1 H, $J_{5,4}$ = 2.6 Hz, H-5), 2.16 (s, 3 H, CH_3); mass spectrum, *m/e* (relative intensity) 360 (14, M + 2), 359 (10), M + 1), 358 (40, M^+), 302 (5), 300 (15), 279 (10), 265 (26), 264 (100), 263 (28), 250 (7), 249 (24), 238 (18), 234 (12), 233 (33), 221 (11), 206 (9), 202 (8), 189 (13), 179 (20), 165 (10), 152 (13). Anal. Calcd for $C_{20}H_{18}O_4Cl$: C, 66.94; H, 5.35. Found: C, 66.79; H, 5.54.

Methanolysis of *syn*-8-Chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-ol Acetate (24-OAc). Compound **24**-OAc (350 mg, 0.98 mmol), 10 mL of methanol, and sodium hydroxide (350 mg, 8.75 mmol) were heated at reflux for 15 min and worked up as described above. The [3.2.1] alcohol **24**-OH (289 mg, 93%) was obtained: ^1H NMR ($CDCl_3$) δ 7.23–7.00 (m, 4 H), 6.92 (s, 1 H, H-13), 6.78 (s, 1 H, H-16), 4.96 (s, 1 H, H-8), 4.80 (d, 1 H, $J_{4,5}$ = 2.5 Hz, H-4), 3.98 (s, 1 H, H-1), 3.78 and 3.76 (two s, 6 H, OCH_3), 3.60 (d, 1 H, $J_{5,4}$ = 2.5 Hz, H-5), 2.43 (br s, 1 H, OH, disappears upon addition of D_2O).

Conversion of *syn*-8-Chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-ol (24-OH) to 24-Cl. Alcohol **24**-OH (289 mg, 0.89 mmol) was dissolved in 10 mL of chloroform and cooled to 0 °C. Thionyl chloride (250 mg, 1.28 mmol) in 2 mL of chloroform was added with stirring. The reaction was warmed to room temperature and was allowed to react for another 2 h. It was then quenched with saturated sodium bicarbonate solution and worked up as described previously to give a light yellow oil (289 mg). It was purified on a 20 cm × 20 cm × 2 mm silica gel TLC plate with 2% ethyl ether in dichloromethane as the eluent. After development, two bands were present with R_f at 0.69 and 0.20. Band 1 (R_f 0.20, 80 mg) was the starting alcohol. Band 2 (R_f 0.69, 200 mg) was 4-chloro-*syn*-8-chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-diene (**24**-Cl): mp (after recrystallization from dichloromethane/hexane) 186–187 °C; ^1H NMR ($CDCl_3$) δ 7.43–7.15 (m, 4 H, Ar H), 7.02 (s, 1 H, H-13), 6.84 (s, 1 H, H-16), 5.28 (d, 1 H, $J_{4,5}$ = 2.5 Hz, H-4), 5.08 (s, 1 H, H-8), 4.06 (s, 1 H, H-1), 3.70 (s, 7 H, 2 OCH_3 and H-5); mass spectrum, *m/e* (relative intensity), 338 (12, M + 4), 337 (12, M + 3), 336 (13, M + 2), 334 (20, M^+), 333 (100, M − 1), 301 (8), 300 (8), 299 (27), 268 (6), 264 (14), 263 (17), 249 (8), 238 (16), 233 (13), 232 (7), 219 (7), 205 (7), 203 (7), 202 (7), 189 (8), 179 (12). Anal. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.49; H, 4.81. Found: C, 64.41; H, 4.89.

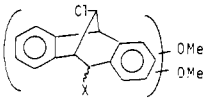
Chromium(VI) Oxidation of *syn*-8-Chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-ol (24-OH). The alcohol **24**-OH (163 mg, 0.51 mmol) was oxidized to *syn*-8-chloro-6,7-(14,15-dimethoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**24** ketone) according to the procedure of Ratcliffe and Rodehorst,[34] giving 130 mg of an oil: mp 201–202 °C (after recrystallization from 95% ethanol); ^1H NMR ($CDCl_3$) δ 8.10–7.90 (m, 1 H, H-12), 7.56–7.20 (m, 3 H), 7.03 (s, 1 H, H-13), 6.93 (s, 1 H, H-16), 5.00 (s, 1 H, H-8), 4.33 (s, 1 H, H-1), 4.13 (s, 1 H, H-5), 3.81 (two s, 6 H, 2 OCH_3). Anal. Calcd for $C_{18}H_{15}O_3Cl$: C, 68.68; H, 4.80. Found: C, 68.49; H, 5.08.

Irradiation of Trans Isomer 15 with 300-nm Light. A solution of **15** (275 mg, 0.82 mmol) in 275 mL of glacial acetic acid was placed in a thick-walled (3.5 mm) Pyrex tube. The tube was sealed with a rubber septum and parafilm The solution was deoxygenated by bubbling nitrogen gas through it. The void space was wrapped with aluminum foil. The tube was placed in a Rayonet and irradiated at 300 nm for 9 days. The solvent was removed by distillation in vacuo. The brown oil was chromatographed on a 20 cm × 20 cm × 2 mm silica gel TLC plate with 5% hexane in dichloromethane as the eluent. The plate was eluted twice. Three bands were observed after development with R_f's of 0.18, 0.46, and 0.66. Band 1 (R_f 0.18, 15 mg) was identified as a mixture of two [3.2.1] alcohols (**27**-OH and **26**-OH, from hydrolysis of the corresponding chlorides on the TLC plate, in a ratio of 1.8 to 1) by comparison of their proton absorptions in the ^1H NMR spectrum of the mixture with ^1H NMR spectra of authentic samples of **27**-OH and **26**-OH. The band with R_f of 0.46 (149.9 mg) was identified by ^1H NMR spectroscopy as being composed of [3.2.1] acetates and a small amount of alcohol. These compounds were further separated on a 20 cm × 20 cm × 2 mm silica gel TLC plate with 2% ethyl ether in dichloromethane as the eluent. After development, 3 bands were observed with R_f's of 0.25, 0.55, and 0.65. The band with R_f of 0.25 (10 mg) was [3.2.1] alcohol **26**-OH. The band with R_f 0.55 (26.5 mg) was [3.2.1] acetate which was identified as **26**-OAc by comparison of its ^1H NMR spectrum with that of an authentic sample. The ^1H NMR spectrum of the band with R_f 0.65 (116 mg) showed that two [3.2.1] acetates were present in a ratio of 11:1. These were identified by ^1H NMR spectroscopy as **27**-OAc and **24**-OAc, respectively. Last, the band from the original TLC plate with R_f 0.66 (80.3 mg) was identified by ^1H NMR spectroscopy to be starting material, [3.2.1] dichloride, and cis-dichloro isomer **16** or **17** in the ratio of 22:1.7:1. The cis dichloride is a secondary product and was only partially identified as either **16** or **17**. Identification of the [3.2.1] dichloride was achieved by conversion to the ketone. The mixture (80.3 mg) was dissolved in 50:50 acetone/water and heated at reflux for 7 days. The aqueous solution was extracted with dichloromethane. The organic solvent was dried ($MgSO_4$) and removed by distillation in vacuo. A yellow oil was obtained. The [3.2.1] dichloride had been converted to a [3.2.1] alcohol which was oxidized to a ketone by the procedure described earlier. A light yellow oil was obtained (68 mg), which was identified by ^1H NMR spectroscopy as **26** ketone.

Irradiation of the Cis-Syn Isomer 17 with 300-nm Light. A solution of cis-syn **17** (3.1 mg, 0.009 mmol) in 1.5 mL of acetic acid-d_4 was placed in a Pyrex NMR tube, deoxygenated as above, and sealed. The sample was irradiated for 1 h (30% conversion). The two photoproducts were identified as **24**-Cl and **24**-OAc (4.7:1) by comparison of the ^1H NMR

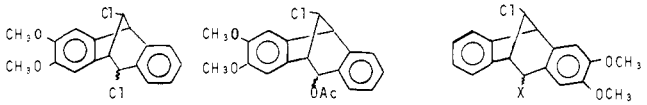
spectrum of the mixture with the ^1H NMR spectra of the authentic samples.

Irradiation of the Cis-Anti Isomer 16 at 300 nm. A solution of 2.9 mg of **16** (0.009 mmol) was dissolved in 1.0 mL of acetic acid-d_4 and placed in a Pyrex NMR tube. The solution was deoxygenated as described previously and sealed. The tube was irradiated at 300 nm for 1 h. Analysis of the ^1H NMR spectrum showed 70% conversion of starting material to products. The minor products (24%) were identified as **26**-Cl (endo:exo = 1:1) by comparison of the ^1H NMR spectrum to the ^1H NMR spectrum of an authentic sample of an epimeric mixture of **26**-Cl. The major products had the following type of [3.2.1] structure: **24**-Cl



X = Cl, OAc

and **24-OAc** are known compounds. The products were not **24** and,



therefore, must be **25** (of which 51% was **25**-Cl, endo:exo = 1.8, and 25% was **25**-OAc, endo:exo = 1:2.5).

"Dark Reactions" of 15, 16, and 17. "Dark reactions" were performed simultaneously with all three irradiations. Solutions were made up with similar concentrations, placed in similar tubes, wrapped in foil, and placed in the Rayonet beside the "light reactions". The "dark reactions" remained in the Rayonet for as long as the "light reactions". All "dark reactions" were worked up (if a workup was involved) in the same way as the "light reactions." For all three compounds, **15**, **16**, and **17**, no reaction was observed in the dark.

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Registry No. 12, 87567-71-3; **13**, 87637-73-8; **14**, 87637-74-9; **15**, 75920-61-5; **16**, 87637-75-0; **17**, 87637-76-1; *exo*-**18** (X = OH), 87567-74-6; *exo*-**18** (X = OAc), 87567-72-4; *exo*-**19** (X = OH), 87567-75-7; *exo*-**19** (X = OAc), 87567-73-5; **20**, 87567-76-8; **21**, 87567-77-9; **22** (X = O), 87637-60-3; *endo*-**22** (X = OH), 87637-58-9; *endo*-**22** (X = OAc), 87637-57-8; *exo*-**22** (X = OAc), 87637-56-7; *exo*-**22** (X = OH), 87637-59-0; **2** (X = O), 87637-65-8; *endo*-**23** (X = OH), 87637-63-6; *endo*-23 (X = OAc), 87637-61-4; *exo*-**23** (X = OH), 87637-64-7; *exo*-**23** (X = OAc), 87637-62-5; **24** (X = OAc), 87637-67-0; **24** (X = OH), 87637-68-1; **24** (X = Cl), 87637-69-2; **24** (X = O), 87637-70-5; *endo*-**25** (X = Cl), 87567-87-1; *endo*-**25** (X = OAc), 87637-71-6; *exo*-**25** (X = OAc), 87637-72-7; *exo*-**25** (X = Cl), 87637-77-2; **26** (X = 0), 87567-85-9; *endo*-**26** (X = Cl), 87567-86-0; *endo*-**26** (X = OAc), 87567-83-7; *exo*-**26** (X = OH), 87567-84-8; *exo*-**26** (X = Cl), 87637-66-9; **27** (X = O), 87567-82-6; *endo*-**27** (X = OAc), 87567-80-4; *endo*-27 (X = OH), 87567-81-5; 2-(2,3-dimethoxybenzoyl)benzoic acid, 76250-92-5; 2-(2,3-dimethoxybenzyl)benzoic acid, 87567-78-0; 2,3-dimethoxy-9-anthrone, 87567-79-1; naphthacene, 92-24-0; *trans*-1,2-dichloroethene, 156-60-5; *cis*-1,2-dichloroethene, 156-59-2; silver acetate, 563-63-3; 2,3-dimethoxyanthracene, 51790-19-3; phthalic anhydride, 85-44-9; veratrole, 91-16-7.

Synthesis of β-Lactam Antibiotics by the Sulfeno-Cycloamination

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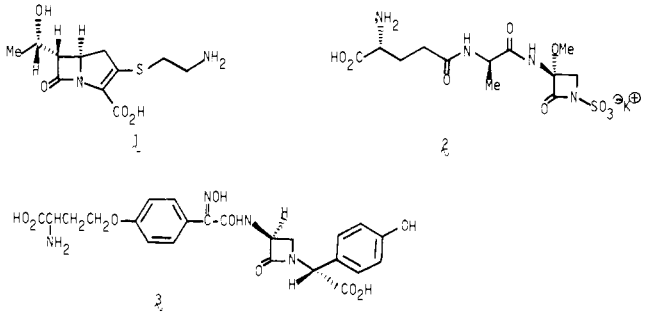
Abstract: A novel efficient β-lactam synthesis was achieved by two successive processes (sulfeno-cycloamination), addition of phenylsulfenyl chloride to α,β-unsaturated amides followed by base treatment. Key synthetic intermediates of monobactams and nocardicin derivatives were obtained via this method. Construction of the 1-carbapenam ring system by the sulfeno-cycloamination is also described.

The discovery of thienamycin (**1**), an unusually potent carbapenem antibiotic,[1,2] and the monobactams such as sulfazecin (**2**),[3,4] a family of monocyclic 2-oxoazetidine-*N*-sulfonic acids produced in bacteria, has led to intense activity in the synthesis of β-lactam antibiotics. These substances possess reactive β-lactam linkages, which show high antibacterial potency and a wide antibacterial spectrum. Among a variety of methods for the construction of the β-lactam ring,[5] the formation of the N–C_4 bond is known as a biomimetic process. Kishi first demonstrated this type of β-lactam formation by ring closure of β-halo amides,[6] and similar approaches were successfully extended by other workers.[7-13] Furthermore, β-hydroxy secondary amides were cyclized to β-lactams under the Mitsunobu reaction conditions.[14-17] We envisaged that a neighboring group effect would enhance β-lactam formation through addition of sulfenyl halides to α,β-unsaturated

Chart I



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