found in the corresponding competition experiment. These mixtures were dissolved in DMF (10% solutions), combined with equimolar amounts of triethylamine, and kept at -78 °C for 3 h. Each binary mixture of authentic peptides was then precipitated in 0.05 N HCl overnight and recovered by the chromatography extraction procedure used in the competition experiments. Determination of the composition of each recovered mixture from its rotatory magnitude established two points: First, it showed that neither the experimental conditions used in the competition reactions nor those of the isolation procedure caused a significant change in any of the binary peptide compositions, thus eliminating any isomerization effects. Second, the small difference between the initial composition and the chiroptically determined composition of each recovered authentic pair was used as the error of the corresponding competition experiment.

Photochemical Transformations. 45. Orbital Overlap Preferences in Excited-State Intramolecular Electron Transfers[1]

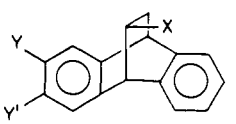
Stanley J. Cristol,* Ellen O. Aeling, and Richard Heng

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80309-0215. *Received July 9, 1986*

Abstract: Syntheses of a number of meta-methoxy-substituted 2,3;6,7-dibenzobicyclo[2.2.2]octadienes, substituted as well on the ethano bridge, have been carried out. These included the four acetates produced by Diels-Alder reactions between 2-methoxyanthracene and vinyl acetate. The acetates were converted to alcohols and to methanesulfonates. Ground-state acetolysis of each methanesulfonate led to a unique dibenzobicyclo[3.2.1]octadienol acetate (discounting exo-endo isomerism) via Wagner-Meerwein skeletal rearrangement, whose conversion to alcohol and oxidation to ketone showed clean anti aryl participation in the rearrangement. The isomer with the anti-homopara relationship between the methoxy group and the carbon bearing the methanesulfonate group was substantially more reactive than the other three isomers, which had approximately equivalent reactivities. Reaction of 2-methoxyanthracene with *cis*-1,2-dichloroethene gave a mixture of cis-anti and cis-syn 7,8-dichloro compounds, and the reaction with the *trans*-dichloroethene gave a mixture of the two trans dichlorides. In ground-state acetolyses promoted by silver acetate, those isomers with anti-homopara chlorine atoms reacted rapidly, while those without reacted more slowly. Conversion to 8-chlorodibenzobicyclo[3.2.1]octadien-4-ol acetates occurred, which in turn were converted to alcohols and ketones. ^{1}H NMR spectra were used to confirm structures of all compounds, and typical anti migrations were observed. Mixture compositions matched those anticipated from relative reactivities. Irradiations of the methanesulfonates were conducted in acetic acid-acetonitrile with 300-nm light. Of the four isomers, only the one with the anti-homometa relationship between the methanesulfonate group and the ring methoxy substituent was photoactive. The [3.2.1] product acetate resulted from syn (benzo) migration, rather than anti (anisolo) migration. All four isomeric dichlorides were photoactive (300-nm light in acetic acid), giving photo-Wagner-Meerwein rearranged [3.2.1] chlorides and acetates. The two isomers with anti-homometa chlorine atoms were considerably more photoactive than the other two. The syn-homometa and syn-homopara chlorines were less reactive than the anti-homometa chlorines, and the anti-homopara chlorines were almost photoinert. Differences between these results and those reported previously on analogous systems are noted. All products arose from Wagner-Meerwein skeletal rearrangements, with syn migration predominating over anti, regardless of whether the migration involved the benzo or anisolo ring.

Members of our research group have been interested for some time[2] in photoinduced solvolysis reactions and in the rearrangements which accompany them. As a result of these studies, it has been concluded that, for homobenzyl chlorides (or β-arylethyl compounds with other nucleofugal groups, such as bromides, methanesulfonates, or mercurials), the key requirement for reactivity, following excitation of the aromatic ring chromophore, is electron transfer of the π^* electron to the σ^* orbital of the carbon-nucleofuge bond.[3]

In the experiments reported earlier, electron transfer was observed to occur more readily (higher quantum yields) when the chromophoric ring had an anti disposition with respect to the carbon-nucleofuge bond, as, for example, in **1**, where Y and Y′ are auxochromic groups, rather than a syn disposition, as in **2**. A number of such examples were noted, and it was suggested that the favoring of electron transfer into anti C-X bonds could be



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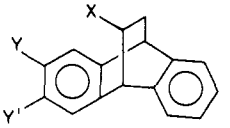

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rationalized by the coulombic advantage in the resulting zwitterionic biradical over that in the syn system. Occupied σ^* orbitals of carbon-halogen bonds have a large fraction of their electron density in a lobe anterior to the carbon atom,[4] and one may estimate,[5] from a study of models, that electron transfer may be about 10 kcal/mol more favorable in the anti case.

All of the reactive systems reported thus far have been disubstituted (or nonsubstituted) in the light-absorbing ring, and reactivity correlations were made on the basis of Weller[6] electron-transfer free-energy calculations. Put another way, it was assumed that the electron transferability, as measured by relative

(1) Paper 44. Cristol, S. J.; Dickenson, W. A. *J. Org. Chem.* **1986**, *51*, 3625.

(2) (a) Cristol, S. J.; Mayo, G. O.; Lee, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 914. (b) Cristol, S. J.; Schloemer, G. C. *Ibid.* **1972**, *94*, 5916.

(3) (a) Cristol, S. J.; Opitz, R. J.; Bindel, T. H.; Dickenson, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 7977. (b) Cristol, S. J.; Dickenson, W. A.; Stanko, M. K. *Ibid.* **1983**, *105*, 1218. (c) Cristol, S. J.; Seapy, D. G.; Aeling, E. O. *Ibid.* **1983**, *105*, 7337. (d) Cristol, S. J.; Ali, M. Z. *Tetrahedron Lett.* **1983**, *24*, 5839. (e) Cristol, S. J.; Bindel, T. H.; Hoffmann, D.; Aeling, E. O. *J. Org. Chem.* **1984**, *49*, 2368. (f) Cristol, S. J.; Aeling, E. O. *Ibid.* **1985**, *50*, 2698.

(4) (a) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; p 104. (b) Jorgensen, W. L. *J. Am. Chem. Soc.* **1978**, *100*, 1049. (c) Canadell, E.; Karafiloglou, P.; Salem, L. *Ibid.* **1980**, *102*, 855.

(5) Aeling, E. O. Ph.D. Dissertation, University of Colorado-Boulder, 1984.

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

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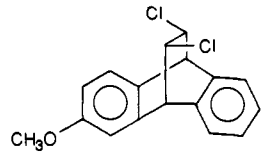
reactivity (quantum yield ratios), is related solely (or largely, at least) to the thermodynamics of the system and is path independent and does not depend upon orbital overlap. We decided to study a monosubstituted ring in order to test that assumption, which, as described below, turned out to be incorrect.

We chose to study the various isomers of 7,8-dichloro-10-methoxy-2,3;5,6-dibenzobicyclo[2.2.2]octa-2,5-diene (**3**–**6**), as our experience with the 9,10-dimethoxy (veratrolo) compounds[3c,f]



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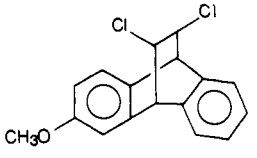

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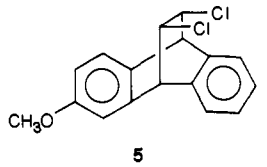

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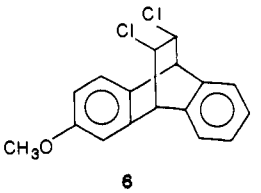

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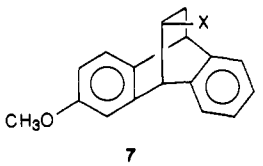

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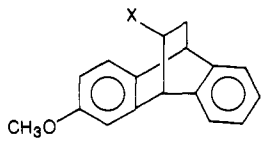
indicated that, of the auxochromic groups studied, the methoxy group was the most active in allowing electron transfer from a photoexcited ring to both syn and anti carbon–nucleofuge bonds. We also decided to study the methanesulfonates **7**–**10** to compare them with the corresponding pair of veratrolobenzo compounds **11** and **12**, whose ground-state chemistry and photochemistry have already been reported.[3f]



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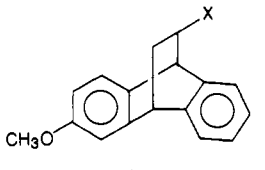

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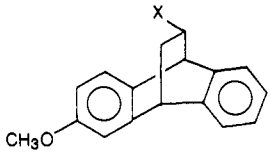

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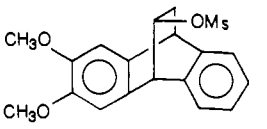

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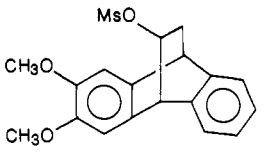

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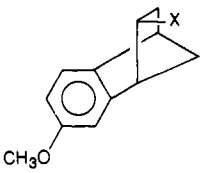
Preparation of Compounds, Ground-State Reactions, and Structure Proofs. All of the compounds were prepared by Diels–Alder reactions of 2-methoxyanthracene.[7] Addition of the anthracene to *trans*-1,2-dichloroethene gave a mixture of **3** and **4**; similar reaction with the cis isomer gave **5** and **6**; these results are from the known stereochemistry of the diene synthesis. (Each mixture was separated by fractional crystallization.)

The acetates **7**-OAc, **8**-OAc, **9**-OAc, and **10**-OAc were prepared by reaction with vinyl acetate and, as we were unable to separate this mixture, were methanolized to a mixture of the corresponding alcohols, whose separation by repeated column chromatography and repeated fractional crystallization was tedious but not impossible.

It had previously been shown[8] that solvolyses of compounds of this type proceed with Wagner–Meerwein rearrangement to [3.2.1] compounds and that the rearrangements involve π participation by the anti aromatic ring in the ionization step. Further it has been shown,[9–11] from studies in 6- and 7-methoxybenzonorbornyl systems (**13**–**16**), compared with the unsubstituted benzonorbornyl



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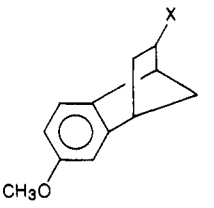

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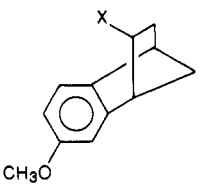

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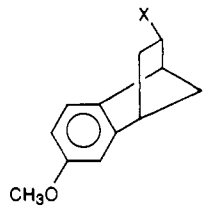

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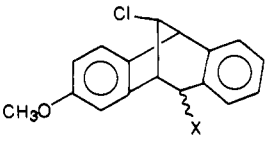
systems, that (a) an anti (exo)-homopara methoxy substituent, as in **14**, furnishes a large rate-enhancing effect (100–200 times) and (b) that only minor rate effects are caused by an anti (exo)-homometa methoxy substituent, as in **13**, or by syn (endo) substituents, as in **15** and **16**. Thus we are able to predict with confidence that the anti-homopara compound **9**-OMs will be substantially more reactive than its isomers **7**, **8**, and **10**-OMs.

Further we may predict that treatment of **3** with silver acetate will give a mixture containing substantial amounts of **17**-OAc and **18**-OAc; that is, the chlorines at both C-7 (anti to benzo ring)



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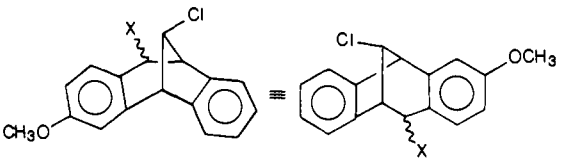

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and C-8 (anti-homometa methoxy) will have approximately equal reactivity. On the other hand, treatment of the other trans isomer, **4**, with silver acetate should lead to **19**-OAc (loss of the anti-homopara chlorine at C-7) in preference to **20**-OAc (loss of the chlorine at C-8 anti to benzo ring). With the anti–cis dichloride **5**, one would predict the formation of a mixture containing more of **21**-OAc (loss of anti-homopara chlorine) than of **22**-OAc (loss of anti-homometa chlorine), while **6** should give roughly equal amounts of **23**-OAc and **24**-OAc (loss of chlorines anti to benzo ring). While there are 16 different acetates (counting exo and endo epimers but not enantiomers) and corresponding alcohols, the problems of analysis are substantially reduced by conversion to ketones.

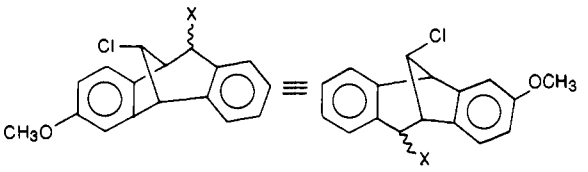
(7) Iwata, M.; Emoto, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1687.

(8) Cristol, S. J.; Kochansky, M. C. *J. Org. Chem.* **1975**, *40*, 2171.

(9) Braddon, D. V.; Wiley, G. A.; Dirlan, J.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 1901.

(10) Tanida, H.; Ishitobi, H.; Irie, T. *J. Am. Chem. Soc.* **1968**, *90*, 2688.

(11) Brown, H. C.; Tritle, G. L. *J. Am. Chem. Soc.* **1968**, *90*, 2689.



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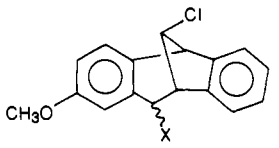

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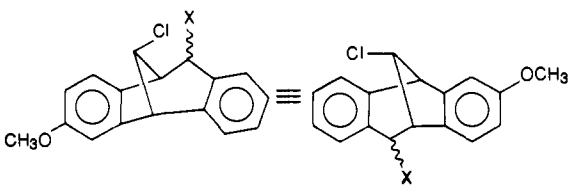

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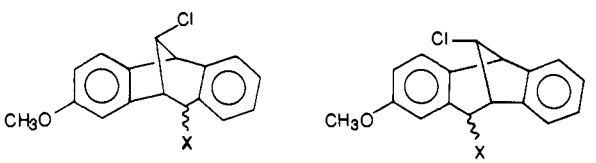

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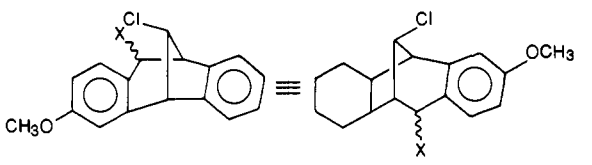

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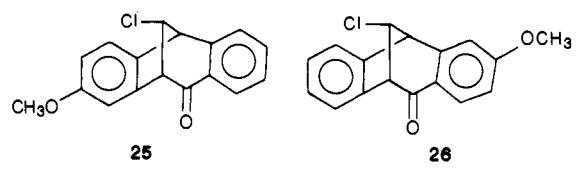
The ketones may be identified by a combination of knowledge of their sources and ^{1}H NMR spectra.[3c,8,12] In particular, the syn-8 protons in **25**, **26**, **27**, and **28** have small coupling constants (<1 Hz) with those at C-1 and C-5, while the anti-8 protons in **29**, **30**, **31**, and **32** have coupling constants about 4.5 Hz with the protons at C-1 and C-5. The protons ortho to the carbonyl group are shifted downfield significantly from the other aromatic protons,[8] have coupling constants of ca. 3 Hz (meta proton coupling) when the methoxy group is ortho to it (as in **28** and **31**), ca. 9 Hz (ortho coupling) when the methoxy group is meta to it (as in **26** and **32**), and give rise to a doublet of doublets (J ca. 3 and 9 Hz) when the ring is unsubstituted (as in **25**, **27**, **29**, and **30**). In the acetates and alcohols from which the ketones are derived, exo–endo assignments were made by the coupling between the protons at C-4 and C-5. Exo protons have coupling constants greater than 5 Hz and endo protons less than 3 Hz.[12]

Of the two trans isomers, the lower melting one required about 60–70 h of treatment with silver acetate in refluxing acetic acid for complete acetolysis, while the higher melting isomer reacted under similar conditions in 2–3 h. As **4** has an anti-homopara chlorine, the higher melting point compound could be assigned that structure, and the lower melting point compound was thus assigned structure **3**.

Acetolysis of compound **3** gave two exo acetates in a ratio of about 2:3, which were separated, with difficulty, by chromatography. The major isomer led to a ketone whose ^{1}H NMR spectrum was consistent with anticipation, showing a syn-8 proton ($J \sim 0$ Hz) and a proton ortho to a carbonyl and with a meta methoxy group ($J \sim 9$ Hz). The ketone, therefore, was the anti-8-chloro-10-methoxy-4-one **26** and the major acetate was thus



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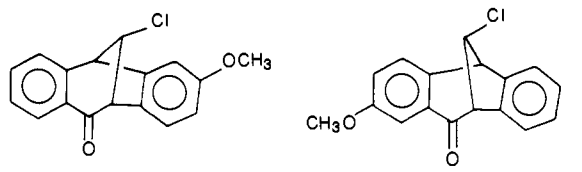

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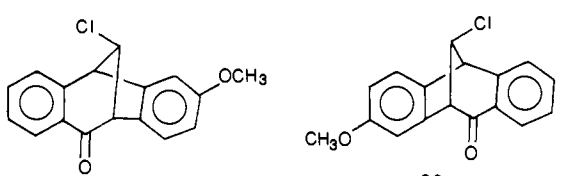

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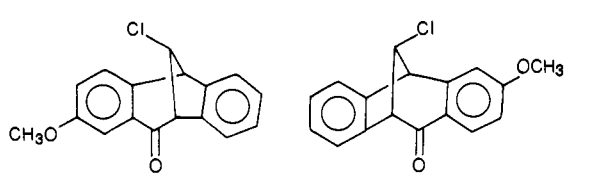


31 32

the anti-8-chloro-10-methoxy acetate *exo*-**18**-OAc. The minor acetate led to a ketone with a syn-8 proton ($J \sim 0$ Hz) and a proton ortho to the keto group which gave rise to a doublet of doublets (J = 3.5, 9 Hz). The ketone was thus the anti-8-chloro-14-methoxy-4-one **25** and its progenitor acetate was the anti-8-chloro-14-methoxy acetate *exo*-**17**-OAc. These assignments confirm structure **3** for the dichloride.

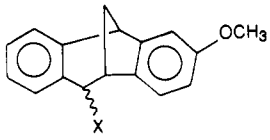
When **4** was acetolyzed, the exo acetate mixture comprised about 90% of one isomer and about 10% of the other. Structure *exo*-**19**-OAc (the anti-8-chloro-15-methoxy acetate) was tentatively assigned for the major product and *exo*-**20**-OAc (the anti-8-chloro-11-methoxy acetate) to the minor product. The acetates were not separated but were converted to the ketones, which were separable. The major isomer had a ^{1}H NMR spectrum anticipated for the anti-8-chloro-15-methoxy-4-one **27** (singlet for H-8; doublet of doublets for the ortho proton). The minor isomer had a spectrum anticipated for the anti-8-chloro-11-methoxy-4-one **28** (singlet for H-8; doublet, J = 2.5 Hz for the ortho proton). These data confirm the assignments for the acetates and those derived from the solvolysis rates and products for the dichlorides.

In similar fashion, the two cis dichlorides were identified. The diene synthesis gave two products. The major product (80%) had the higher melting point. The minor product reacted completely, when treated with silver acetate in refluxing acetic acid, in 3 h, while the major product required 60 h. Accordingly the anti–cis structure **5** was tentatively assigned to the minor product and the syn–cis structure **6** to the major product. Acetolysis of **5** led to the syn-8-chloro-15-methoxy acetate **21**-OAc. Measurable amounts of the syn-8-chloro-14-methoxy acetate **22**-OAc were not produced, demonstrating the greater reactivity of the anti-homopara chlorine. On the other hand, acetolysis of **6** gave two products in a ratio of 3:2. The major isomer was identified as the syn-8-chloro-10-methoxy acetate **24**-OAc and the minor as the syn-8-chloro-11-methoxy acetate **23**-OAc by conversion to the corresponding ketones. The solvolysis rate and product data and ^{1}H NMR spectra were all consistent with those anticipated for the assigned structures (see Experimental Section).

Of the four methanesulfonates, one was substantially (200–600 times more reactive to acetolysis than the other three or the unsubstituted compound **1** (Y = Y′ = H, X = OMs)). It was thus assigned structure **9** (anti-homopara). This structure was

(12) Cristol, S. J.; Mohrig, J. R.; Plorde, D. E. *J. Org. Chem.* **1965**, *30*, 1956. Note that our usual practice of using the hydrocarbon numbering is followed in the present paper.

confirmed by acetolysis to the 15-methoxy acetate **33**-OAc followed by oxidation to the 15-methoxy ketone **34**. Structures of



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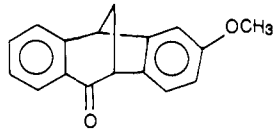

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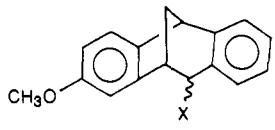
each of the other methanesulfonates were similarly assigned, based upon the assumption of anti Wagner–Meerwein migration and ^{1}H NMR spectra of the ketones produced. Thus the anti-homometa **7**-OMs gave the 14-methoxy acetate **35**-OAc and ketone **36**; the 11-methoxy acetate **8**-OMs gave the 11-methoxy acetate **37**-OAc, leading to 11-methoxy ketone **38**, and the syn-homopara **10**-OMs gave the 10-methoxy acetate **39**-OAc and ketone **40**. In each case, only one ketone was formed, demonstrating that the ground-state acetolyses were stereospecific, as anticipated.[8]



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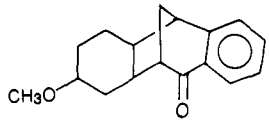

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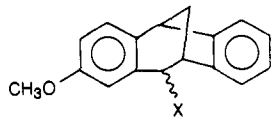

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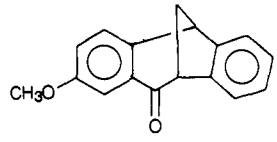

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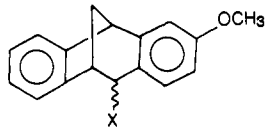

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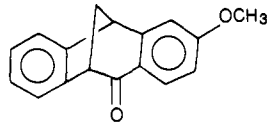

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Photochemical Results. With all of the compounds known (save for **22**-species and its ketone **30**), we were now in a position to answer our original question of whether or not there would be a directive kinetic effect on electron transfer superimposed upon the thermodynamic effects observed earlier. In Zimmerman's original work[13] on photosolvolysis, it was shown that meta methoxy groups were much more effective in promoting photosolvolysis in benzylic systems than were para groups. This effect was ascribed to the preponderance of electron density in anisole derivatives at the meta (and ortho) positions in the first excited state and its deficiency at the para position. Recently, this effect has been confirmed by Turro and Wan[14] on benzyl alcohols, who also noted significantly higher quantum yields for the acid-catalyzed "photosolvolysis" of meta methoxy over those for para methoxy compounds. It is not clear[15] that photosolvolysis of benzylic systems involves electron transfer preceding formation of ion pairs, as is the case in homobenzylic systems such as we are studying. Nonetheless, just as in the ground state, where para effects are reflected in homopara reactivities,[9-11] it might be anticipated that similarities would be observed in excited-state reactions.

We have previously[3f] shown that, in the veratrolobenzo system, both the syn **12** and anti **11** methanesulfonates are photoactive. As the Weller equation, as we used it, does not discriminate between homopara and homometa electron acceptors, it might have been anticipated that all of the anisolobenzomethanesulfonates **7–10** would be photoactive or all would be photoinert. In fact, however, only the anti-homometa isomer **7** was photoactive, when irradiated in acetonitrile–acetic acid at 300 nm. Like its veratrolobenzo analogues, **7**, upon loss of methanesulfonate ion, suffers clean syn migration, the sole product being **37**-OAc. We have previously noted[3f] that loss of methanesulfonate, a rather poor "nucleofuge" in these electron-transfer-mediated photoreactions, is one that favors migration concerted with loss from the biradical cation intermediate (see below).

On the basis of these results, one might predict those dichloride isomers with anti-homometa chlorine atoms, that is **3** and **5**, would have the greatest photoactivity. On the basis of previous results with the veratrolo compounds, one might also predict that anti-homopara loss as in **4** and **5** would compete better than syn-homopara loss. Finally, one might predict that, whatever the attitude of the photonucleofugal group, syn migration would be favored over anti migration. As we describe below, the results are not quite so simple.

When **3** was irradiated in acetic acid with either 300- or 254-nm light, products derived from both anti-homometa and syn-homopara activation were observed. Of the products, the former class (anti-homometa) included 50% of **23**-OAc and 19% of **23**-Cl, products of syn (benzo) migration, and 7% of **17**-OAc and 6% of **17**-Cl, products of anti (anisolo) migration. The latter class (syn-homopara activation) comprised 8% of **21**-OAc and 4% of **21**-Cl, products of syn (anisolo) migration, and 6% of **18**-OAc, product of anti (benzo) migration.

Similar irradiation of the other trans isomer **4** gave only a trace of **24**-Cl, the product of anti-homopara activation (syn migration), with substantially all of the products the result of syn-homometa activation. These included 57% of **22**-OAc and 30% of **22**-Cl, products of syn (anisolo) migration, and 5% of **20**-OAc and 8% of **20**-Cl, products of anti (benzo) migration.

The anti–cis isomer **5** gave, upon 300-nm irradiation, only homometa chloride loss with formation of 70% of **20**-OAc and 14% of **20**-Cl, products of syn (benzo) migration, and 8% each of **22**-OAc and **22**-Cl, products of anti (anisolo) migration. No product of loss of the anti-homopara chloride was seen.

When the syn–cis dichloride **6** was similarly irradiated, the product mixture comprised 58% of **17**-OAc and 21% of **17**-Cl, products of homometa reaction and syn (anisolo) migration, and 12% of **19**-OAc and 8% of **19**-Cl, products of homopara reaction and syn migration. In all of the irradiations of **6**, a small amount of **23**-X was found. In short irradiation times, about 2% of the product was **23**, and, in time, this increased to about 15%. Thus **23** was a secondary product.[16]

While quantum yield studies were not made, qualitative estimates of relative quantum yields were made by measuring the times required for partial reaction. Compounds **3** and **5**, which have chlorine atoms that are both homometa and anti were substantially (4–10 times) more reactive than **4** and **6** (where homometa chlorines are syn). These results are as predicted above.

Also as predicted, loss of anti-homometa chlorine atoms occurs more readily than that of other chlorine atoms. Thus, in the trans dichloride **3**, the anti-homometa chlorine was lost 4.6 times as readily as the syn-homopara chlorine. In the anti–cis dichloride **5**, all of the products seen were those of loss of the homometa chlorine. Surprisingly, the anti-homopara chlorine atom was inert. The inertness of the anti-homopara chlorine atom was also seen in the reactions of the trans dichloride **4**, where only a trace of product from its loss was seen, even though its competition was with a syn (but homometa) chlorine atom. Reactivity of the syn-homopara chlorine was noted in the reactions of the syn–cis dichloride **6** (as well as in **3**), where it was one-fourth as reactive as the syn-homometa chlorine atom.

The "meta effect" in photochemistry demonstrated two decades ago by Zimmerman and Sandel[13] thus has been extended to a homometa situation. This suggests that orbital overlap and thermodynamics are both important factors in assessing photoreactivity in these homobenzyl (β-arylethyl) electron-transfer reactions. The preference for anti-homometa geometry is seen in both the methanesulfonate and dichloride systems. Zimmerman and Sandel ascribe the "meta effect" and a corresponding an-

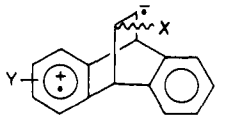
(13) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 913.
(14) Turro, N. J.; Wan, R. *J. Photochem.* **1985**, *28*, 93.
(15) Cristol, S. J.; Opitz, R. J.; Aeling, E. O. *J. Org. Chem.* **1985**, *50*, 4834.

(16) Compare the similar situation in the veratrolobenzo system.[3f]

ticipated "ortho effect" to excess electron densities at these positions in the first excited state of anisole. We see no reason to disagree with a similar rationalization for the ready electron transfer to the anti-homometa substituents. In previous work[3e] on the veratrolobenzo system we have noted that electron transfer from the excited ring to anti chlorines occurs about 3 times more readily than to syn chlorines. A similar effect is seen here in the homometa series.

What is still a problem to understand are the relative reactivities of the syn- and anti-homopara chlorine atoms. From previous work,[3a,e] we had anticipated that the anti chlorine would have been more reactive. In fact, the opposite was true, as the anti-homopara chlorine was inert in **5** and almost inert in **4**, while the syn-homopara chlorine is active in both **3** and **6**. A plausible rationalization of these results may lie in the fact that these chlorine atoms are vicinal to homometa chlorine atoms and that electron transfer may occur sequentially from excited aromatic ring to homometa chlorine and then perhaps to the homopara chlorine. A study of the monochloro derivatives **7**, **8**, **9**-, and **10**-Cl would certainly be of interest in this regard.

Like our previous work in the mono- and dibenzobicyclo[2.2.2]octadienyl systems, the stereochemistry of migration ranges from stereoselectively to stereospecifically syn, independent of whether the migrating group is the chromophoric ring or not. We have discussed this previously in terms of two fates of the zwitterionic biradical **41** resulting from electron transfer. One of these



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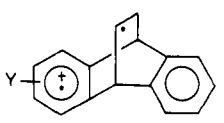

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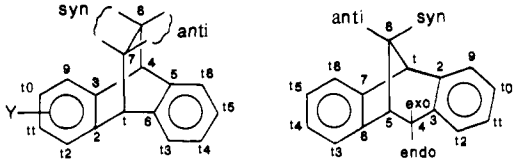
involves a suprafacial (syn) migration to a radical anion (5 electron) carbon-nucleofuge site concerted with loss of nucleofuge (to give the [3.2.1] system. The competitive mode of reaction involves fragmentation of the intermediate to nucleofugal anion and a biradical cation **42** preceding migration, which allows either syn or anti migration to the [3.2.1] system. The present results are consistent with these ideas.

Experimental Section

The locant systems used for the 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 apparatus and are corrected. ^{1}H NMR spectra were obtained with the use of a Varian Associates EM-390 (90-MHz) or a Bruker WM-250 (250-MHz) instrument. Chemical shifts are reported in ppm relative to Me_4Si. Mass spectra were obtained with the use of a Varian MAT CH-5 spectrometer. UV spectra were obtained with a Cary 219 spectrophotometer with 10^{-4}–10^{-5} M solutions in spectrograde solvents. 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 in either a Srinivasan–Griffin photochemical reactor or an R.S. Photochemical reactor, set up as described previously.[17] Irradiations at 300 nm were run in Pyrex vessels, including NMR scale irradiations (Wilmad no. 507-PP tubes). Irradiations at 254 nm were run in quartz vessels, including NMR scale irradiations (Wilmad no. 702-PQ tubes). Irradiations were set up in the following manner. The compound to be irradiated was placed in a tube. The appropriate solvent was added, the compound was dissolved, and the tube was sealed with a septum and para film. If a compound containing a methanesulfonate group was to be irradiated, a 10–20% molar excess of anhydrous sodium acetate was added to the tube to neutralize any methanesulfonic acid produced during the irradiation. After the tube was sealed, the solution was deoxygenated by bubbling a stream of nitrogen through it. The void space was then wrapped with foil, to avoid any possible irradiation of solid compound on the walls of the tube. "Dark" reactions were prepared similarly and treated identically to the sample to be irradiated but were wrapped completely in foil and placed alongside the "light" reaction in the Rayonet.

Methanolysis, Conversion of Acetates to Alcohols. The acetate to be converted to an alcohol 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 aqueous solution 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 Rodehurst.[18]

Synthesis of *syn*-7-*anti*-8-Dichloro-2,3-(10-methoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-diene, 3, and *anti*-7-*syn*-8-Dichloro-2,3-(10-methoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-diene, 4. Solutions of 10.0 g (0.048 mol) of 2-methoxyanthracene[7] and 0.5–1.0 g of pyrocatechol in 50 mL of *trans*-dichloroethylene and 50 mL of xylene were sealed in a combustion tube and heated at 185–195 °C for 3–5 days. The reactions were worked up as described previously for similar reactions.[3c] The two isomers were separated by repeated recrystallization from 95% ethanol. The first compound to crystallize was **3**: mp 131–132 °C (after recrystallization); ^{1}H NMR ($CDCl_3$) δ 7.60–7.20 (m, 5 H, Ar H and H-12), 6.97 (d, 1 H, H-9, $J_{9,11}$ = 2 Hz), 6.80 (dd, 1 H, H-11, $J_{11,12}$ = 9 Hz, $J_{11,9}$ = 3 Hz), 4.36 (d, 2 H, H-7 and H-8, $J_{7,1} = J_{8,4}$ = 1.5 Hz), 4.15 (d, 2 H, H-1 and H-4, $J_{1,7} = J_{8,4} \sim 2$ Hz), 3.75 (s, 3 H, OCH_3); MS, *m/e* (rel intensity) 306 (14, M + 2), 305 (6, M + 1), 304 (22, M$^+$), 269 (8), 234 (16), 233 (16), 209 (65), 208 (100), 189 (32), 165 (17), 164 (71), 104 (19); UV spectrum (acetonitrile) λ max (log ϵ) 300 (1.2, not a maximum), 284 (2.95), 278 (3.03), 268 (2.89 shoulder). Anal. Calcd for $C_{17}H_{14}OCl_2$: C, 66.90; H, 4.62. Found: C, 66.75; H, 4.84.

The second crop of crystals contained **4**: mp 139–140 °C after recrystallization; ^{1}H NMR ($CDCl_3$) δ 7.61–7.25 (m, 5 H, Ar H and H-12), 7.09 (d, 1 H, H-9, $J_{9,11}$ = 3 Hz), 6.84 (dd, 1 H, H-11, $J_{11,12}$ = 8.5 Hz, $J_{11,9}$ = 3 Hz), 4.40 (d, 2 H, H-7 and H-8, $J_{7,1} = J_{8,4}$ = 2 Hz), 4.20 (d, 2 H, H-1 and H-4, $J_{1,7} = J_{4,8}$ = 2 Hz), 3.81 (s, 3 H, OCH_3); MS, *m/e* (rel intensity) 306 (13, M + 2), 305 (4, M + 1), 304 (19, M$^+$), 269 (6), 234 (12), 233 (12), 209 (45), 208 (100), 189 (24), 165 (10), 164 (67), 104 (10); UV spectrum λ max (log ϵ) 300 (1.3, not a maximum), 284 (3.48), 278 (3.50), 268 (3.37, shoulder). Anal. Calcd for $C_{17}H_{14}OCl_2$: C, 66.90; H, 4.62. Found: C, 66.79; H, 4.70.

Synthesis of *anti-cis*-7,8-Dichloro-2,3-(10-methoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-diene, 5, and *syn-cis*-7,8-Dichloro-2,3-(10-methoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-diene, 6. The syntheses of **5** and **6**, the cis dichlorides, were similar to those of the trans isomers **3** and **4**, except that *cis*-dichloroethylene was used. Compound **6**, the cis–syn isomer, was the major isomer (80%), and **5** was the minor isomer (20%). These isomers were separated by repeated recrystallization. The major isomer **6** had mp 172.5–173.5 °C: ^{1}H NMR ($CDCl_3$) δ 7.48–7.16 (m, 5 H, Ar H and H-12), 7.02 (d, 1 H, H-9, $J_{9,11}$ = 3 Hz), 6.81 (dd, 1 H, H-11, $J_{11,12}$ = 8.5 Hz, $J_{11,9}$ = 3 Hz), 4.50 (br s, 4 H, H-1, H-4, H-8, and H-7), 3.83 (s, 3 H, OCH_3); MS, *m/e* (rel intensity) 306 (10, M + 2), 305 (3, M + 1), 304 (15, M$^+$), 269 (7), 234 (15), 233 (12), 209 (50), 208 (100), 189 (20), 164 (75), 104 (12); UV spectrum (acetonitrile) λ max (log ϵ) 300 ($\sim$1.0, not a maximum), 284 (3.32), 278 (3.35), 268 (3.22, shoulder). Anal. Calcd for $C_{17}H_{14}OCl_2$: C, 66.90; H, 4.62. Found: C, 66.90; H, 4.82.

The minor isomer **5** had mp 147–148 °C: ^{1}H NMR ($CDCl_3$) δ 7.60–7.20 (m, 5 H, Ar H and H-12), 6.96 (d, 1 H, H-9, $J_{9,11}$ = 3 Hz), 6.77 (dd, 1 H, H-11, $J_{11,12}$ = 8.5 Hz, $J_{11,9}$ = 3 Hz), 4.47 (s, 4 H, H-1, H-4, H-7, and H-8), 3.86 (s, 3 H, OCH_3); MS, *m/e* (rel intensity), 306 (9, M + 2), 305 (3, M + 1), 304 (14, M$^+$), 269 (10), 234 (13), 233 (13), 209 (48), 208 (100), 189 (19), 164 (70), 104 (14); UV spectrum (acetonitrile) λ max (log ϵ) 300 (1.2, not a maximum), 284 (3.51), 278 (3.49), 268 (3.39, shoulder). Anal. Calcd for $C_{17}H_{14}OCl_2$: C, 66.90; H, 4.62. Found: C, 66.58; H, 5.06.

Silver-Ion-Assisted Solvolysis of 4. The anti-7-syn-8 dichloride **4** (405 mg, 1.33 mmol) was treated with excess silver acetate in refluxing acetic acid as described earlier for similar reactions.[3c] The reaction was complete in 3 h. An oil (405 mg, 1.23 mmol) was isolated. Initially only one acetate product was apparent, *anti*-8-chloro-6,7-(15-methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate, **19**-OAc, but upon closer examination a small amount (10–12%) of a minor product, *anti*-

(17) Cristol, S. J.; Micheli, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 854.

(18) Ratcliffe, R.; Rodehurst, J. *J. Org. Chem.* **1970**, *35*, 4000.

8-chloro-2,3-(11-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate, **20**-OAc, was also observed. Compound **19**-OAc: ^{1}H NMR ($CDCl_3$) δ 7.45–7.09 (m, 5 H, Ar H and H-13), 6.83 (d, 1 H, H-16, $J_{16,14}$ = 3 Hz), 6.70 (dd, 1 H, H-14, $J_{14,13}$ = 8.5 Hz, $J_{14,16}$ = 3 Hz), 6.00 (d, 1 H, endo-H-4, $J_{4,5}$ = 3 Hz), 4.97 (s, 1 H, H-8), 4.10 (s, 1 H, H-1), 3.75 (d, 1 H, H-5, $J_{5,4}$ = 3 Hz), 3.70 (s, 3 H, OCH_3), 2.14 (s, 1 H, $OCOCH_3$). Compound **20**-OAc: ^{1}H NMR ($CDCl_3$) δ 6.95 (d, H-9, $J_{9,11}$ = 3 Hz), 6.76 (dd, 1 H, H-11, $J_{11,12}$ = 8.5 Hz, $J_{11,9}$ = 3 Hz), 3.65 (s, 3 H, OCH_3). No attempt was made to separate the two isomers.

Methanolysis of 19-OAc and 20-OAc. The mixture of **19**-OAc and **20**-OAc obtained in the above reaction was converted to the alcohols by methanolysis. A yellow solid (376 mg, 1.31 mmol) was isolated. By ^{1}H NMR, only **19**-OH was apparent. (After oxidation, the next experiment, some ketone **28**, was isolated from this sample. Thus **20**-OH must have a ^{1}H NMR spectrum similar to that of **19**-OH and was not obvious.) Compound **19**-OH: ^{1}H NMR ($CDCl_3$) δ 7.45–7.10 (m, 5 H, Ar H and H-13), 6.83 (d, 1 H, H-16, $J_{16,14}$ = 3 Hz), 6.67 (dd, 1 H, H-14, $J_{14,13}$ = 9 Hz, $J_{14,16}$ = 3 Hz), 4.98 (s, 1 H, H-8), 4.80 (br s, 1 H, *endo*-H-4), 4.07 (s, 1 H, H-1), 3.70 (s, 3 H, OCH_3), 3.64 (br s, 1 H, H-5), 2.25 (br s, 1 H, OH).

Oxidation of 19-OH and 20-OH to Their Respective Ketones. The mixture of alcohols (**19**-OH and **20**-OH, 376 mg) was oxidized to the ketones. The major isomer, *anti*-8-chloro-6,7-(15-methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**27**) was crystallized from the mixture from ethanol: mp 141–142 °C; ^{1}H NMR ($CDCl_3$) δ 7.95 (dd, 1 H, H-12, $J_{12,11}$ = 9 Hz, $J_{12,10}$ = 2.5 Hz), 7.63–7.20 (m, 4 H, H-11, H-10, H-9, and H-13), 6.92 (d, 1 H, H-16, $J_{16,14}$ = 3 Hz), 6.69 (dd, 1 H, H-14, $J_{14,13}$ = 9 Hz, $J_{14,16}$ = 3 Hz), 4.97 (s, 1 H, H-8), 4.30 (s, 1 H, H-1), 4.08 (s, 1 H, H-5), 3.75 (s, 3 H, OCH_3); MS, *m/e* (rel intensity) 286 (27, M + 2), 285 (13, M + 1), 284 (73, M^+), 250 (19), 249 (100), 248 (23), 221 (20), 219 (20), 218 (11), 217 (11), 189 (18), 178 (48), 177 (13), 176 (18). Anal. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60. Found: C, 71.66; H, 4.59.

After the major isomer was crystallized, the mother liquor was separated on a silica gel TLC plate. An impure sample of *anti*-8-chloro-2,3-(11-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**28**) was obtained: ^{1}H NMR ($CDCl_3$) δ 7.59 (d, 1 H, H-12, $J_{12,10}$ = 2.5 Hz), 7.55–7.10 (m, 5 H, Ar H and H-9), 6.89 (dd, 1 H, H-10, $J_{10,9}$ = 8 Hz, $J_{10,12}$ = 2.5 Hz), 4.99 (s, 1 H, H-8), 4.25 (s, 1 H, H-1), 4.12 (s, 1 H, H-5), 3.71 (s, 3 H, OCH_3).

Silver-Ion-Assisted Solvolysis of 3. Compound **3** (1.47 g, 4.82 mmol) was converted to the [3.2.1] acetates with silver acetate in acetic acid. The reaction was complete in 55 h. After workup, a yellow oil was obtained. This oil was separated on an activated silica gel (60–200 mesh) column, by using as eluent 2% ethyl acetate in dichloromethane. Partial separation of the two isomers, *anti*-8-chloro-6,7-(14-methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**17**-OAc) and *anti*-8-chloro-2,3-(10-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**18**-OAc), was achieved. Compound **17**-OAc (40% of mixture): ^{1}H NMR ($CDCl_3$) δ 7.40–7.16 (m, 5 H, Ar H and H-16), 7.13 (d, 1 H, H-13, $J_{13,15}$ = 3 Hz), 6.76 (dd, 1 H, H-15, $J_{15,16}$ = 8.5 Hz, $J_{15,13}$ = 3 Hz), 6.05 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 5.01 (s, 1 H, H-8), 4.14 (s, 1 H, H-1), 3.72 (s, 3 H, OCH_3), 3.69 (d, 1 H, H-5, $J_{5,4}$ = 2.5 Hz), 2.14 (s, 3 H, $OCOCH_3$). Compound **18**-OAc (60% of mixture); ^{1}H NMR ($CDCl_3$) δ 7.65–7.50 (m, 1 H, H-12), 7.35–7.10 (m, 4 H, Ar H), 6.75 (m, 2 H, H-9 and H-11), 6.09 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 5.00 (s, 1 H, H-8), 4.12 (s, 1 H, H-1), 3.79 (s, 3 H, OCH_3), 3.76 (d, 1 H, H-5, $J_{5,4}$ = 2.5 Hz), 2.15 (s, 3 H, $OCOCH_3$).

Conversion of 17-OAc to 17-OH. Compound **17**-OAc (163 mg, 0.496 mmol) was converted to **17**-OH by methanolysis, giving a yellow oil (137 mg, 0.478 mmol): ^{1}H NMR ($CDCl_3$) δ 7.53–7.14 (m, 5 H, Ar H and H-16), 7.03 (d, 1 H, H-13, $J_{13,15}$ = 3 Hz), 6.70 (dd, 1 H, H-15, $J_{15,16}$ = 8.5 Hz, $J_{15,13}$ = 3 Hz), 4.97 (s, 1 H, H-8), 4.84 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 4.08 (s, 1 H, H-1), 3.74 (s, 3 H, OCH_3), 3.66 (d, 1 H, H-5, $J_{5,4}$ = 2.5 Hz), 2.50 (br s, 1 H, OH).

Oxidation of 17-OH to 25. The alcohol **17**-OH (135 mg, 0.471 mmol) was oxidized to *anti*-8-chloro-6,7-(14-methoxybenzo)-2,3-benzobicyclo-[3.2.1]octa-2,6-dien-4-one (**25**) in 91% yield. It was crystallized from ethanol/hexane: mp 152–153 °C: ^{1}H NMR ($CDCl_3$) δ 7.98 (dd, 1 H, H-12, $J_{12,11}$ = 9 Hz, $J_{12,10}$ = 3.5 Hz), 7.65–7.25 (m, 4 H, H-9, H-10, H-11, and H-16), 7.11 (d, 1 H, H-13, $J_{13,15}$ = 2.5 Hz), 6.78 (dd, 1 H, H-15, $J_{15,16}$ = 8.5 Hz, $J_{15,13}$ = 2.5 Hz), 4.97 (s, 1 H, H-8), 4.31 (s, 1 H, H-1), 4.16 (s, 1 H, H-5), 3.73 (s, 3 H, OCH_3); MS, *m/e* (rel intensity), 286 (10, M + 2), 285 (5, M + 1), 284 (30, M^+), 250 (19), 249 (100). Anal. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60. Found: C, 71.60; H, 4.80.

Conversion of 18-OAc to 18-OH. Compound **18**-OAc (512 mg, 1.56 mmol) was converted to 409 mg (1.42 mmol) of *anti*-8-chloro-2,3-(10-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol, **18**-OH, by methanolysis: ^{1}H NMR ($CDCl_3$) δ 7.53–7.06 (m, 5 H, Ar-H and H-12), 6.77 (m, 2 H, H-9 and H-11), 4.92 (s, 1 H, H-8), 4.73 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 4.03 (s, 1 H, H-1), 3.74 (s, 3 H, OCH_3), 3.62 (d, 1 H, H-5, $J_{5,4}$ = 2.5 Hz), 4.55 (br s, 1 H, OH).

Oxidation of 18-OH. Compound **18**-OH (409 mg, 1.43 mmol) was oxidized to give 379 mg (1.33 mmol) of *anti*-8-chloro-2,3-(10-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**26**): mp 175.5–176.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 1 H, H-12, $J_{12,10}$ = 9 Hz), 7.50–7.15 (m, 4 H, Ar H), 6.85 (m, 2 H, H-9 and H-11), 4.96 (s, 1 H, H-8), 4.35 (s, 1 H, H-1), 4.20 (s, 1 H, H-5), 3.83 (s, 3 H, OCH_3); MS, *m/e* (rel intensity), 286 (30, M + 2), 285 (17, M + 1), 284 (79, M^+), 250 (49), 249 (100), 248 (30), 221 (28), 206 (22), 204 (20), 189 (22), 178 (56), 177 (22), 176 (23), 151 (17), 150 (13). Anal. Calcd for $C_{17}H_{13}ClO_2$: C, 71.71; H, 4.60. Found: C, 71.71; H, 4.59.

Silver-Ion-Assisted Solvolysis of 5. Dichloride **5** (115 mg, 0.337 mmol) was converted to the [3.2.1] acetate by treatment with silver acetate in acetic acid. After 3 h, no starting material remained. A yellow oil (120 mg, 0.365 mmol), *syn*-8-chloro-6,7-(15-methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-*exo*-4-ol acetate (**21**-OAc) was obtained: ^{1}H NMR ($CDCl_3$) δ 7.50–7.20 (m, 5 H, Ar H and H-13), 6.83 (m, 2 H, H-14 and H-16), 5.80 (br s, 1 H, H-4), 4.80 (t, 1 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3.5 Hz), 4.08 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 3.65 (s, 3 H, OCH_3), 3.60 (br d, 1 H, H-5, $J_{5,8}$ = 3.5 Hz), 2.15 (s, 3 H, $OCOCH_3$). By ^{1}H NMR, no **22**-OAc was apparent, and there was no reaction of the chlorine at C-8.

Conversion of 21-OAc to 21-OH. Conversion of 120 mg (0.365 mmol) of **21**-OAc gave 101 mg (0.352 mmol) of **21**-OH as an oil: ^{1}H NMR ($CDCl_3$) δ 7.50–7.10 (m, 5 H, Ar H and H-13), 6.65 (m, 2 H, H-14 and H-16), 4.90 (t, 1 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3.5 Hz), 4.55 (br s, 1 H, H-4), 4.00 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 3.70 (s, 3 H, OCH_3), (H-5 is under the methoxy peak at ca. 3.65 ppm).

Oxidation of 21-OH. Oxidation of 101 mg (0.36 mmol) of **21**-OH gave 94 mg (0.33 mmol) of *syn*-8-chloro-6,7-(15-methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**29**). The oil obtained was crystallized from ethanol: mp 141–142 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (dd, 1 H, H-12, $J_{12,11}$ = 8.5 Hz, $J_{12,10}$ = 2 Hz), 7.55–7.10 (m, 4 H, H-9, H-10, H-11, and H-13), 6.84 (d, 1 H, H-16, $J_{16,14}$ = 2.5 Hz), 6.63 (dd, 1 H, H-14, $J_{14,13}$ = 8.5 Hz, $J_{14,16}$ = 2.5 Hz), 5.03 (t, 1 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3 Hz), 4.16 (d, 1 H, H-5, $J_{5,8}$ = 3 Hz), 4.02 (d, 1 H, H-1, $J_{1,8}$ = 3 Hz), 3.32 (s, 3 H, OCH_3); MS, *m/e* (rel intensity), 286 (31, M + 2), 285 (18, M + 1), 284 (100, M^+), 250 (21), 249 (63), 248 (44), 219 (50), 218 (19), 205 (18), 202 (17), 189 (25), 178 (45). Anal. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60. Found: C, 71.55; H, 4.78.

Silver-Ion-Assisted Solvolysis of 6. The cis–syn dichloride **6** (1.432 g, 4.695 mmol) was converted to the [3.2.1] acetates **23**- and **24**-OAc by treatment with silver acetate in acetic acid.[3] The reaction was complete in 60–70 h. The resulting oil (1.50 g, 4.56 mmol) was a mixture of two acetates. The major acetate (60%) was *syn*-8-chloro-2,3-(10-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-*endo*-4-ol acetate, **24**-OAc, and the minor product (40%) was *syn*-8-chloro-2,3-(11-methoxybenzo)-6,7-benzobicyclo-[3.2.1]octa-2,6-dien-*exo*-4-ol acetate, **23**-OAc.

Compound ***endo*-24-OAc**: ^{1}H NMR ($CDCl_3$) δ 7.37–7.06 (m, 5 H, Ar H and H-12), 6.77 (m, 2 H, H-9 and H-11), 6.36 (d, 1 H, H-4, $J_{4,5}$ = 6 Hz), 4.91 (t, 1 H, H-8, $J_{8,1}$ = $J_{8,5}$ = 3.5 Hz), 4.00 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 3.86 (dd, 1 H, H-5, $J_{5,4}$ = 6 Hz, $J_{5,8}$ = 3.5 Hz), 3.71 (s, 3 H, OCH_3), 2.09 (s, 3 H, $OCOCH_3$).

Compound ***exo*-23-OAc**: ^{1}H NMR ($CDCl_3$) δ 7.58–7.40 (m, 1 H, H-9), 7.37–7.06 (m, 4 H, Ar H), 6.77 (m, 2 H, H-10 and H-12), 5.79 (s, 1 H, H-4), 4.87 (t, 1 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3.5 Hz), 4.06 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 3.67 (m, 4 H, H-5, OCH_3), 2.17 (s, 3 H, $OCOCH_3$). No attempt was made to separate **23**-OAc and **24**-OAc.

Conversion of 23-OAc and 24-OAc to 23-OH and 24-OH. Methanolysis of the mixture of acetates from the above reaction gave an oil (1.263 g, 4.40 mmol) from which these spectra could be deduced. Compound *endo*-**24**-OH: ^{1}H NMR ($CDCl_3$) δ 7.49–7.11 (m, 5 H, Ar H and H-12), 6.74 (m, 2 H, H-9 and H-11), 5.13 (d, 1 H, H-4, $J_{4,5}$ = 5.5 Hz), 4.86 (t, 1 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3.5 Hz), 3.94 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 3.72 (m, 4 H, H-5, OCH_3). Compound **23**-OH: ^{1}H NMR ($CDCl_3$) δ 7.49–7.11 (m, 5 H, Ar H and H-9), 7.05 (d, 1 H, H-12, $J_{12,10}$ = 2.5 Hz), 6.80 (dd, 1 H, H-10, $J_{10,9}$ = 8.5 Hz, $J_{10,12}$ = 2.5 Hz), 4.91 (t, 1 H, H-8, $J_{8,1}$ = $J_{8,5}$ = 3.5 Hz), 4.53 (br s, 1 H, H-4), 4.02 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 3.71 (m, 4 H, H-5, OCH_3).

Oxidation of 23-OH and 24-OH to 31 and 32. The mixture of alcohols from the above reaction was oxidized to the ketones *syn*-8-chloro-2,3-(10-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**32**) and *syn*-8-chloro-2,3-(11-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**31**). The mixture of ketones (1.19 g, 4.19 mmol) was separated by repeated recrystallization from ethanol and then ethanol/hexane. The major isomer, **32**, had mp 182–183 °C: ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 1 H, H-12, $J_{12,11}$ = 9 Hz), 7.61-7.22 (m, 4 H, Ar H), 6.90 (m, 2 H, H-9 and H-11), 5.17 (t, 1 H, H-8, $J_{8,1}$ = $J_{8,5}$ = 3.5 Hz), 4.32 (d,

1 H, H-1, $J_{1,8}$ = 3.5 Hz), 4.08 (d, 1 H, H-5, $J_{5,8}$ = 3.5 Hz), 3.89 (s, 3 H, OCH_3); MS, *m/e* (rel intensity), 286 (17, M + 2), 285 (10, M + 1), 284 (46, M^+), 250 (30), 249 (100), 248 (71), 206 (14), 205 (21), 189 (12), 178 (26). Anal. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60. Found: C, 71.61; H, 4.65.

The minor isomer, **31**, had mp 132–133 °C: ^1H NMR ($CDCl_3$) δ 7.52 (d, 1 H, H-12, $J_{12,10}$ = 3 Hz), 7.40–7.13 (m, 5 H, Ar H and H-9), 7.05 (dd, 1 H, H-10, $J_{10,9}$ = 8.5 Hz, $J_{10,12}$ = 3 Hz), 5.17 (t, 1 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3.5 Hz), 4.25 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 4.13 (d, 1 H, H-5, $J_{5,8}$ = 3.5 Hz), 3.70 (s, 3 H, OCH_3); MS, *m/e* (rel intensity), 286 (17, M + 2), 285 (10, M + 1), 284 (46, M^+), 250 (15), 249 (100), 248 (48), 221 (11), 206 (11), 205 (21), 189 (13), 178 (31). Anal. Calcd for $C_{17}H_{13}O_2Cl$: C, 71.71; H, 4.60. Found: C, 72.00; H, 4.87.

Synthesis of 7-, 8-, 9-, and 10-OH. A solution of 15.1 g (0.073 mol) of 2-methoxyanthracene, 37 mL of vinyl acetate, and 100 mL of xylene was heated in a heavy-walled combustion tube at 195 ± 5 °C for 6 days. It was then worked up as described earlier. The four isomers, *syn*-2,3-(11-methoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol acetate (**8**-OAc), *anti*-2,3-(11-methoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol acetate **7**-OAc), *syn*-2,3-(10-methoxybenzo)-5,6-benzobicyclo-[2.2.2]octa-2,5-dien-7-ol acetate (**10**-OAc), and *anti*-2,3-(10-methoxybenzo)-5,6-benzobicyclo[2.2.2]octa-2,5-dien-7-ol acetate (**9**-OAc), proved difficult to separate. The mixture of all four acetates was therefore converted to the alcohols, which were separated by repeated column chromatography to obtain samples significantly enriched in one isomer, followed by repeated recrystallizations. Eventually, all four isomers were separated.

Compound 8-OH: mp 137.5–138.5 °C: ^1H NMR ($CDCl_3$) δ 7.51–7.06 (m, 5 H, Ar H and H-9), 7.03 (d, 1 H, H-12, $J_{12,10}$ = 2.5 Hz), 6.78 (dd, 1 H, H-10, $J_{10,9}$ = 8 Hz, $J_{10,12}$ = 2.5 Hz), 4.15 (m, 3 H, H-1, H-4, and H-7), 3.75 (s, 3 H, OCH_3), 2.30 (ddd, 1 H, H-8_{anti}, J_{8gem} = 14 Hz, $J_{8anti,7}$ = 8 Hz, $J_{8anti,4}$ = 3 Hz), 1.38 (dt, 1 H, H-8_{syn}, J_{8gem} = 14 Hz, $J_{8syn,7}$ = $J_{8syn,4}$ = 3 Hz), 1.30 (br s, 1 H, OH); MS, *m/e* (rel intensity) 252 (5, M^+), 209 (27), 208 (100), 178 (6), 164 (63); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (~1.0 not a maximum), 284 (3.50), 278 (3.48), 267 (3.29 shoulder). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.51; H, 6.86.

Compound 7-OH: mp 115–117 °C; ^1H NMR ($CDCl_3$) δ 7.46–7.02 (m, 5 H, Ar H, and H-9), 6.90 (d, 1 H, H-12, $J_{12,10}$ = 2.5 Hz), 6.60 (dd, 1 H, H-10, $J_{10,9}$ = 7.5 Hz, $J_{10,12}$ = 2.5 Hz, 4.30–3.95 (m, 3 H, H-1, H-4, and H-7), 3.75 (s, 3 H, OCH_3), 2.22 (ddd, 1 H, H-8_{syn}, $J_{8syn,8anti}$ = 14 Hz, $J_{8syn,7}$ = 8 Hz, $J_{8syn,4}$ = 3 Hz), 1.70 (br s, 1 H, OH), 1.27 (dt, 1 H, H-8_{anti}, $J_{8anti,8syn}$ = 14 Hz, $J_{8anti,7}$ = $J_{8anti,4}$ = 3 Hz); MS, *m/e* (rel intensity) 253 (1, M + 1), 252 (6, M^+), 209 (32), 208 (100), 178 (7), 164 (74); UV spectrum (acetonitrile) λ_{max} (log ϵ) 300 (~1.3, not a maximum), 284 (3.36), 278 (3.42), 267 (3.32, shoulder). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.47; H, 6.89.

Compound 10-OH: mp 143–144 °C; ^1H NMR ($CDCl_3$) δ 7.46–7.02 (m, 5 H, Ar H and H-12), 6.95 (d, 1 H, H-9, $J_{9,11}$ = 2.5 Hz), 6.74 (dd, 1 H, H-11, $J_{11,12}$ = 7.5 Hz, $J_{11,9}$ = 2.5 Hz), 4.39–4.07 (m, 3 H, H-1, H-4, and H-7), 3.75 (s, 3 H, OCH_3), 2.28 (ddd, 1 H, H-8_{anti}, J_{8gem} = 14 Hz, $J_{8anti,7}$ = 7 Hz, $J_{8anti,4}$ = 3 Hz), 1.32 (dt, 1 H, H-8_{syn}, J_{8gem} = 14 Hz, $J_{8syn,7}$ = $J_{8syn,4}$ = 3 Hz), 1.28 (br s, 1 H, OH); MS, *m/e* (rel intensity) 253 (<1, M + 1), 252 (2, M^+), 234 (1), 221 (2), 210 (4), 209 (37), 208 (100), 178 (7), 165 (15), 164 (82); UV spectrum, λ_{max} (log ϵ) 300 (~1.0 not a maximum), 284 (3.52), 278 (3.56), 267 (3.34, shoulder). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.53; H, 6.83.

Compound 9-OH: mp 165–166 °C; ^1H NMR ($CDCl_3$) δ 7.54–7.13 (m, 5 H, Ar H and H-12), 6.87 (d, 1 H, H-9, $J_{9,11}$ = 3 Hz), 6.67 (dd, 1 H, H-11, $J_{11,12}$ = 8 Hz, $J_{11,9}$ = 3 Hz), 4.32–4.09 (m, 3 H, H-1, H-4, and H-7), 3.74 (s, 3 H, OCH_3), 2.30 (ddd, 1 H, H-8_{syn}, J_{8gem} = 13 Hz, $J_{8syn,7}$ = 8 Hz, $J_{8syn,4}$ = 3 Hz), 1.40 (dt, 1 H, H-8_{anti}, J_{8gem} = 13 Hz, $J_{8anti,7}$ = $J_{8anti,4}$ = 3 Hz), 1.26 (br s, 1 H, OH); MS, *m/e* (rel intensity) 253 (<1, M + 1), 252 (4, M^+), 222 (2), 209 (19), 208 (100), 164 (41); UV spectrum (acetonitrile) λ max (log ϵ) 300 (~1.2, not a maximum), 283 (3.41), 279 (3.45), 266 (3.18, shoulder). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.52; H, 6.81.

Conversion of 7-OH, 8-OH, and 10-OH to Methanesulfonates. Samples of each alcohol (~300 mg, 1.19 mmol) were converted to methanesulfonates according to the procedure of Crossland and Servis.[19] The crude products were dissolved at room temperature in a minimum amount of 1:1 dichloromethane:hexane. Cooling in dry ice–acetone gave off-white powders. As the esters were only modestly stable, they were kept in a refrigerator.

Compound 8-OMs: dec point 114 °C; ^1H NMR ($CDCl_3$) δ 7.50–7.11 (m, 5 H, Ar H and H-9), 7.02 (d, 1 H, H-12, $J_{12,10}$ = 3 Hz), 6.76 (dd, 1 H, H-10, $J_{10,9}$ = 8 Hz, $J_{10,12}$ = 3 Hz), 5.13 (dt, 1 H, H-7, $J_{7,8anti}$ = 9 Hz, $J_{7,8syn}$ = $J_{7,1}$ = 3 Hz), 4.67 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.25 (t, 1 H, H-4, $J_{4,8syn}$ = $J_{4,8anti}$ = 3 Hz), 3.76 (s, 3 H, OCH_3), 2.92 (s, 3 H, OMs), 2.44 (ddd, 1 H, H-8_{anti}, J_{8gem} = 14 Hz, $J_{8anti,7}$ = 10 Hz, $J_{8anti,4}$ = 3 Hz), 1.73 (dt, 1 H, H-8_{syn}, J_{8gem} = 14 Hz, $J_{8syn,7}$ = $J_{8syn,4}$ = 3 Hz); MS, *m/e* (rel intensity) 331 (8, M + 1), 330 (35, M^+), 236 (9), 235 (29), 234 (13), 209 (69), 208 (100), 164 (70).

Isomer 7-OMs: dec point 125 °C; ^1H NMR ($CDCl_3$) δ 7.53–7.10 (m, 5 H, Ar H and H-9), 7.00 (d, 1 H, H-12, $J_{12,10}$ = 2.5 Hz), 6.70 (dd, H-10, $J_{10,9}$ = 7 Hz, $J_{10,12}$ = 2.5 Hz), 5.13 (dt, 1 H, H-7, $J_{7,8syn}$ = 8 Hz, $J_{7,8anti}$ = $J_{7,1}$ = 3 Hz), 4.67 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.21 (t, 1 H, H-4, $J_{4,8syn}$ = $J_{4,8anti}$ = 3 Hz), 3.75 (s, 3 H, OCH_3), 2.90 (s, 3 H, OMs), 2.42 (ddd, 1 H, H-8_{syn}, J_{8gem} = 14 Hz, $J_{8syn,7}$ = 9 Hz, $J_{8syn,4}$ = 3 Hz), 1.72 (dt, H-8_{anti}, $J_{8anti,8syn}$ = 14 Hz, $J_{8anti,7}$ = $J_{8anti,4}$ = 3 Hz); MS, *m/e* (rel intensity), 331 (8, M + 1), 330 (31, M^+), 278 (26), 236 (20), 235 (39), 209 (68), 208 (100), 164 (69).

Isomer 10-OMs: dec point 95 °C; ^1H NMR ($CDCl_3$) δ 7.45–7.03 (m, 5 H, Ar H and H-12), 6.91 (d, 1 H, H-9, $J_{9,11}$ = 3 Hz), 6.70 (dd, 1 H, H-11, $J_{11,12}$ = 8 Hz, $J_{11,9}$ = 3 Hz), 5.07 (dt, 1 H, H-7, $J_{7,8anti}$ = 8 Hz, $J_{7,8syn}$ = $J_{7,1}$ = 3 Hz), 4.63 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.18 (t, 1 H, H-4, $J_{4,8anti}$ = $J_{4,8syn}$ = 3 Hz), 3.72 (s, 3 H, OCH_3), 2.87 (s, 3 H, OMs), 2.40 (ddd, 1 H, H-8_{anti}, J_{8gem} = 13 Hz, $J_{8,anti,7}$ = 8 Hz, $J_{8anti,4}$ = 3 Hz), 1.71 (dt, 1 H, H-8_{syn}, J_{8gem} = 13 Hz, $J_{8syn,7}$ = $J_{8syn,4}$ = 3 Hz); MS, *m/e* (rel intensity) 331 (2, M + 1), 330 (3, M^+), 250 (5), 236 (13), 235 (16), 209 (22), 208 (90), 164 (30), 95 (56), 78 (66).

Synthesis of 9-OMs. The [2.2.2] alcohol **9**-OH (520 mg, 2.06 mmol) was converted to the methanesulfonate[19] and worked up as above. ^1H NMR spectroscopy revealed the residue to be a 50:50 mixture of **9**-OMs and the rearranged [3.2.1] alcohol **33**-OH. The synthesis was repeated. Rather than an aqueous workup, the solvent was removed from the reaction by distillation in vacuo. The residue was then washed with dichloromethane. The product is soluble in dichloromethane, whereas the salt of the triethylamine was not. Thus, the contamination of the amine salt was reduced although not completely removed. The compound used was contaminatd with the amine salt. This isomer decomposed rapidly at room temperature, was stored, therefore, at 0 °C and used promptly: ^1H NMR ($CDCl_3$) δ 7.46–7.11 (m, 5 H, Ar H and H-12), 7.05 (d, 1 H, H-9, $J_{9,11}$ = 2.5 Hz), 6.99 (dd, 1 H, H-11, $J_{11,12}$ = 8 Hz, $J_{11,9}$ = 2.5 Hz), 5.15 (dt, 1 H, H-7, $J_{7,8syn}$ = 9 Hz, $J_{7,1}$ = $J_{7,8anti}$ = 3 Hz), 4.69 (d, 1 H, H-1, $J_{1,7}$ = 3 Hz), 4.20 (t, 1 H, H-4, $J_{4,8syn}$ = $J_{4,8anti}$ = 3 Hz), 3.75 (s, 3 H, OCH_3), 2.89 (s, 3 H, OMs), 2.43 (ddd, 1 H, H-8_{syn}, J_{8gem} = 14 Hz, $J_{8syn,7}$ = 9 Hz, $J_{8syn,4}$ = 3 Hz), 1.73 (dt, 1 H, H-8_{anti}, J_{8gem} = 14 Hz, $J_{8anti,7}$ = $J_{8anti,1}$ = 3 Hz); MS, *m/e* (rel intensity) 330 (<1, M^+), 294 (42), 272 (42), 270 (88), 236 (40), 234 (100), 220 (33), 219 (88), 209 (42), 208 (97), 204 (43), 203 (88), 191 (76), 189 (51), 164 (89), 78 (39), 43 (97).

Relative Rates of Acetolysis of Methanesulfonate Esters. Samples of 42–51 mg of each methanesulfonate were dissolved in 0.75 mL of 7:3 CD_3CN:CD_3CO_2D containing 15–25 mg of NaOAc. The reactions were run in the dark at 37 °C and analyzed periodically by ^1H NMR spectroscopy, by using the ratio of absorption intensities for H-7 of the [2.2.2] reactants and H-4 of the [3.2.1] products. Results are given in Table I.

Table I. Results for Methanesulfonate Solvolyses

time (h)	approximate % conversions for compd				
	9-OMs	**10**-OMs	**7**-OMs	**8**-OMs	**1**-OMs (Y = Y′ = H)
0	0	0	0	0	0
0.12	8	0	0	0	0
1.5	50	0	0	0	0
3	60	0	0	0	0
17	100	2	0	0	0
68		12	5	5	5
186		35		15	15

Ground-State Acetolyses of Methanesulfonates and Conversion to Alcohols and Ketones. The methanesulfonate (ca. 1.0 mmol) was dissolved in 10 mL of glacial acetic acid containing ca. 2.0 mmol of anhydrous sodium acetate. The reaction mixture was heated to reflux. After a few minutes, the solution was cooled, and water was added. The mixture was extracted with dichloromethane. The combined dichloromethane layers were washed with water and sodium bicarbonate solution and then dried over magnesium sulfate. The solution was filtered, and the solvent was removed by distillation in vacuo. The acetate could then be purified.

The acetates were methanolized to alcohols as described above, and the alcohols were oxidized to ketones.[18] All of the reactions were close to quantitative, and only one ketone was derived from each methanesulfonate. Properties of the products were as follows.

7-OMs Gave *exo*-6,7-(14-Methoxybenzo)-2,3-benzobicyclo[3.2.1]-octa-2,6-dien-4-ol Acetate (*exo*-35-OAc). ^1H NMR ($CDCl_3$) δ 7.35–7.05 (m, 5 H, Ar H and H-16), 6.79 (d, 1 H, H-13, $J_{13,15}$ = 3 Hz), 6.71 (dd,

(19) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.

1 H, H-15, $J_{15,16}$ = 8 Hz, $J_{15,13}$ = 3 Hz), 5.89 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 3.90 (br t, 1 H, H-1, $J_{1,8}$ = 3 Hz), 3.70 (s, 3 H, OCH_3), 3.53 (br t, 1 H, H-5, $J_{5,4}$ = 2.5 Hz, $J_{5,8}$ = 3 Hz), 2.48 (m, 2 H, H-8), 2.18 (s, 3 H, $OCOCH_3$).

***exo*-35-OH**: ^{1}H NMR ($CDCl_3$) δ 7.45–7.03 (m, 5 H, Ar H and H-16), 6.97 (d, 1 H, H-13, $J_{13,15}$ = 2.5 Hz), 6.60 (dd, 1 H, H-15, $J_{15,16}$ = 9 Hz, $J_{15,13}$ = 2.5 Hz), 4.65 (d, 1 H, H-4, $J_{4,5}$ = 3 Hz), 3.83 (br t, 1 H, H-1, $J_{1,8}$ = 3 Hz), 3.70 (s, 3 H, OCH_3), 3.46 (br t, 1 H, H-5, $J_{5,4}$ = $J_{5,8}$ = 3 Hz), 2.44 (m, 2 H, H-8).

6,7-(14-Methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-one (36): ^{1}H NMR ($CDCl_3$) δ 7.94 (dd, 1 H, H-12, $J_{12,11}$ = 8 Hz, $J_{12,10}$ = 2 Hz), 7.53–7.09 (m, 4 H, H-9, H-10, H-11, H-16), 7.01 (d, 1 H, H-13, $J_{13,15}$ = 2.5 Hz), 6.64 (dd, 1 H, H-15, $J_{15,16}$ = 9 Hz, $J_{15,13}$ = 2.5 Hz), 4.08 (d, 1 H, H-1, $J_{1,8}$ = 4 Hz), 3.92 (d, 1 H, H-5, $J_{5,8}$ = 4 Hz), 3.75 (s, 3 H, OCH_3), 2.81 (m, 2 H, H-8); MS, *m/e* (rel intensity) 251 (20, M + 1), 250 (100, M^+), 249 (9), 235 (6), 222 (11), 207 (20), 191 (11), 179 (16), 178 (30).

8-OMs Gave *exo*-2,3-(11-Methoxybenzo)-6,7-benzobicyclo[3.2.1]-octa-2,6-dien-4-ol Acetate (*exo*-37-OAc). ^{1}H NMR ($CDCl_3$) δ 7.44–7.03 (m, 5 H, Ar H and H-9), 6.83–6.60 (m, 2 H, H-10 and H-12), 5.82 (d, 1 H, H-4, $J_{4,5}$ = 2 Hz), 3.90 (t, 1 H, H-1, $J_{1,8}$ = 2.5 Hz), 3.70 (s, 3 H, OCH_3), 3.60 (br t, 1 H, H-5, $J_{5,8}$ = 2.5 Hz, $J_{5,4}$ = 2 Hz), 2.50 (m, 2 H, H-8), 2.20 (s, 3 H, $OCOCH_3$).

***exo*-37-OH**: ^{1}H NMR ($CDCl_3$) δ 7.50–7.01 (s, 5 H, Ar H and H-9), 6.89 (d, 1 H, H-12, $J_{12,10}$ = 3 Hz), 6.71 (dd, 1 H, H-10, $J_{10,9}$ = 8 Hz, $J_{10,12}$ = 3 Hz), 4.60 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 3.86 (br t, 1 H, H-1, $J_{1,8}$ = 2.5 Hz), 3.69 (s, 3 H, OCH_3), 3.48 (br t, 1 H, H-5, $J_{5,8}$ = $J_{5,4}$ = 2.5 Hz), 2.41 (m, 2 H, H-8).

2,3-(11-Methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (38): mp 130–131 °C; ^{1}H NMR ($CDCl_3$) δ 7.45 (d, 1 H, H-12, $J_{12,10}$ = 3 Hz), 7.36–6.98 (m, 5 H, Ar H and H-9), 6.88 (dd, 1 H, H-10, $J_{10,9}$ = 8 Hz, $J_{10,12}$ = 3 Hz), 4.30 (d, 1 H, H-1, $J_{1,8}$ = 4 Hz), 4.02 (d, 1 H, H-5, $J_{5,8}$ = 4 Hz), 3.71 (s, 3 H, OCH_3), 2.80 (br t, 2 H, H-8, $J_{8,1}$ = $J_{8,5}$ = 4 Hz); MS, *m/e* (rel intensity) 251 (38, M + 1), 250 (100, M^+), 249 (28), 235 (15), 222 (21), 221 (19), 207 (32), 179 (32), 178 (55).

9-OMs Gave *exo*-6,7-(15-Methoxybenzo)-2,3-benzobicyclo[3.2.1]-octa-2,6-dien-4-ol Acetate, *exo*-33-OAc: ^{1}H NMR ($CDCl_3$) δ 7.45–7.06 (m, 5 H, Ar H and H-13), 6.77 (d, 1 H, H-16, $J_{16,14}$ = 3 Hz), 6.53 (dd, 1 H, H-14, $J_{14,13}$ = 7 Hz, $J_{14,16}$ = 3 Hz), 5.83 (d, 1 H, H-4, $J_{4,5}$ = 2 Hz), 3.88 (br t, 1 H, H-1, $J_{1,8}$ = 2.5 Hz), 3.76 (s, 3 H, OCH_3), 3.49 (br t, 1 H, H-5, $J_{5,4}$ = $J_{5,8}$ = 2.5 Hz), 2.45 (m, 2 H, H-8), 2.10 (s, 3 H, $OCOCH_3$).

***exo*-33-OH**: ^{1}H NMR ($CDCl_3$) δ 7.44–7.06 (m, 5 H, Ar H, H-13), 6.75 (d, H-16, $J_{16,14}$ = 2 Hz), 6.58 (dd, 1 H, H-14, $J_{14,13}$ = 7 Hz, $J_{14,16}$ = 2 Hz), 4.55 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 3.80 (br t, 1 H, H-1, $J_{1,8}$ = 3 Hz), 3.62 (s, 3 H, OCH_3), 3.31 (br t, 1 H, H-5, $J_{5,4}$ = 2.5 Hz, $J_{5,8}$ = 3 Hz), 2.36 (m, 2 H, H-8).

6,7-(15-Methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-one (34): ^{1}H NMR ($CDCl_3$) δ 7.97 (dd, 1 H, H-12, $J_{12,11}$ = 9 Hz, $J_{12,10}$ = 3 Hz), 7.50–7.10 (m, 4 H, H-9, H-10, H-11, and H-13), 6.99 (d, 1 H, H-16, $J_{16,14}$ = 3 Hz), 6.61 (dd, 1 H, H-14, $J_{14,13}$ = 8 Hz, $J_{14,16}$ = 3 Hz), 4.06 (d, 1 H, H-1, $J_{1,8}$ = 4 Hz), 3.93 (d, 1 H, H-5, $J_{5,8}$ = 4 Hz), 3.66 (s, 3 H, OCH_3), 2.76 (t, 2 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 4 Hz); MS, *m/e* (rel intensity) 251 (18, M + 1), 250 (100, M^+), 249 (18), 222 (17), 221 (12), 219 (19), 208 (16), 207 (25), 179 (35), 178 (49).

10-OMs Gave a Mixture of endo and exo Isomers (Largely exo) of 2,3-(10-methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-ol Acetate, 39-OAc: ^{1}H NMR ($CDCl_3$) δ 7.40–6.96 (m, 5 H, Ar H and H-12), 6.70 (d, 1 H, H-9, $J_{9,11}$ = 2 Hz), 6.64 (dd, 1 H, H-11, $J_{11,12}$ = 8 Hz, $J_{11,9}$ = 2 Hz), 6.18 (d, *exo*-H-4, $J_{4,5}$ = 6 Hz), 5.80 (d, *endo*-H-4, $J_{4,5}$ = 2.5 Hz), 3.85 (br t, 1 H, H-1, $J_{1,8}$ = 3 Hz), 3.74 (s, 3 H, OCH_3), 3.51 (m, 1 H, H-5), 2.50 (br t, 2 H, H-8), 2.15 (s, 3 H, $OCOCH_3$).

***exo*-39-OH**: ^{1}H NMR ($CDCl_3$) δ 7.50–7.02 (m, 5 H, Ar H and H-12), 6.87–6.60 (m, 2 H, H-9 and H-11), 4.46 (d, 1 H, H-4, $J_{4,5}$ = 2.5 Hz), 3.81 (br t, 1 H, H-1, $J_{1,8}$ = 2.5 Hz), 3.71 (s, 3 H, OCH_3), 3.41 (br t, 1 H, H-5, $J_{5,4}$ = $J_{5,8}$ = 2.5 Hz), 2.40 (m, 2 H, H-8).

2,3-(10-Methoxybenzo)-6,7-benzobicyclo[3.2.1]octa-2,6-dien-4-one (40): mp 118–121 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 1 H, H-12, $J_{12,11}$ = 8 Hz), 7.53–7.24 (m, 4 H, Ar H), 6.78–6.64 (m, 2 H, H-9 and H-11), 4.08 (d, 1 H, H-1, $J_{1,8}$ = 3.5 Hz), 3.90 (d, 1 H, H-5, $J_{5,8}$ = 3.5 Hz), 3.70 (s, 3 H, OCH_3), 2.75 (t, 2 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3.5 Hz); MS, *m/e* (rel intensity) 252 (7, M + 2), 251 (67, M + 1), 250 (100, M^+), 249 (79), 235 (16), 233 (18), 222 (16), 221 (17), 219 (41), 207 (60), 191 (21), 189 (26), 179 (47), 177 (21), 176 (20).

Direct Irradiation of Methanesulfonates 7, 8, 9, and 10. Two solutions, each containing ca. 50 mg (0.15 mmol) of a methanesulfonate ester and ca. 20 mg (0.25 mmol) of NaOAc in 0.75 mL of 7:3 CD_3CN:CD_3CO_2D, were prepared and placed in Pyrex NMR tubes. After deoxygenation, one of each set was wrapped in foil (dark reaction), and all tubes were placed in the 300-nm Rayonet reactor and monitored by ^{1}H NMR spectroscopy. The dark reaction tubes containing **7**-OMs, **8**-OMs, and **10**-OMs showed no reaction in 3 h nor did the irradiated tubes containing **8**-OMs and **10**-OMs. The irradiated tube containing **7**-OMs underwent reaction, giving **37**-OAc as the sole product, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. Compound **9**-OMs underwent very rapid solvolysis in the dark as well as under irradiation to give **33**-OAc. In CD_3CN, **9**-OMs reacted much more slowly with no significant difference between the dark and irradiated samples.

Direct Irradiation of 3 in Glacial Acetic Acid at 300 nm. Compound **3** (770 mg, 2.52 mmol) dissolved in 60 mL of HOAc in a thin-walled Pyrex tube was irradiated for 8 days in a 300-nm Rayonet. The sample was poured into 100 mL of dichloromethane and extracted 3 times with water, twice with saturated $NaHCO_3$, and once with brine. The organic layer was dried ($MgSO_4$) and filtered, and the solvent was removed by distillation in vacuo. The brown oil was separated by silica gel TLC. Four bands were obtained: band 4 (least polar) 250 mg, starting material and [3.2.1] dichlorides in a ratio of 4.4:1; band 3, 85 mg [3.2.1] dichlorides; band 2, 312 mg [3.2.1] acetates; band 1, 39 mg [3.2.1] acetates. The bands containing [3.2.1] dichlorides (bands 4 and 3) were dissolved in acetone:water (75:25) and heated at reflux for 7 days, giving the [3.2.1] alcohols. The [3.2.1] alcohols were separated from the [2.2.2] dichlorides by silica gel TLC and were oxidized to the ketones. The ketones were analyzed by ^{1}H NMR spectroscopy and were found to be **31**, **25**, and **29** ketones in a ratio of 3.2:1.0:0.7, respectively.

The acetate bands (bands 2 and 1) were converted to the alcohols by methanolysis and oxidized to the ketones. The ketones were analyzed by ^{1}H NMR spectroscopy and were found to be **31**, **25**, **29**, and **26** ketones in a ratio of 8.6:1.2:1.3:1.0. This irradiation was repeated in a heavy-walled tube; much longer times (30–45 days) were necessary, but no significant changes in the product mixture were observed.

Irradiation of 3 in Acetic Acid at 254 nm. Compound **3** (454 mg, 1.49 mmol) in 20 mL of HOAc in a quartz tube was irradiated for 24 h in the 254-nm Rayonet. The sample was worked up and analyzed as in the 300-nm irradiation. There was significantly more [3.2.1] acetate product in the 254-nm irradiation, but, aside from this, no significant difference in product ratio was observed. Whether this greater amount of solvolysis product was due to secondary photoreaction of the [3.2.1] dichlorides was not ascertained.

Irradiation of 4 in Glacial Acetic Acid at 300 nm. Compound **4** (287 mg, 0.939 mmol) was irradiated as above in 45 mL of HOAc at 300 nm for 4.6 days. After workup, ^{1}H NMR analysis showed quite incomplete reaction. The sample was redissolved in 100 mL of acetic acid, deoxygenated, and irradiated for 10 more days. The residue was separated by silica gel TLC, giving two bands: the less polar band (138 mg) was [3.2.1] dichlorides and [2.2.2] starting material in a ratio of 2:1, and the more polar band (141 mg) was a mixture of [3.2.1] acetates. Workup and reaction of the dichlorides led to a ketone mixture. The major product had a ^{1}H NMR proton absorbance at 7.99 (dd, J = 8.5 Hz, J = 2 Hz) and a triplet at 5.15 (3 Hz coupling), consistent with structures **29** and **30**, that is, with the methoxy group at either C-14 or C-15. Compound **29** is described above, and its ^{1}H NMR spectrum was different from that for the new ketone; therefore, the product must be *syn*-8-chloro-6,7-(14-methoxybenzo)-2,3-benzobicyclo[3.2.1]octa-2,6-dien-4-one (**30**): ^{1}H NMR δ 7.99 (dd, 1 H, H-12, $J_{12,11}$ = 8.5 Hz, $J_{12,10}$ = 2 Hz), 7.7–7.1 (m, 4 H, H-9, H-10, H-11, H-16), 6.90 (d, 1 H, H-13, $J_{13,15}$ = 2 Hz), 6.72 (dd, 1 H, H-15, $J_{15,16}$ = 8 Hz, $J_{15,13}$ = 2 Hz), 5.15 (t, 1 H, H-8, $J_{8,5}$ = $J_{8,1}$ = 3 Hz), 4.25 (d, 1 H, H-5, $J_{5,8}$ = 3 Hz), 4.15 (d, 1 H, H-1, $J_{1,8}$ = 3 Hz), 3.76 (s, 3 H, OCH_3). (Note: **21**-X, the precursors to **29**, could not arise directly from the starting material **4** as the relative stereochemistry of the chlorine on the bridge and the methoxy on the ring in **4** and **21**-X are opposite.) The minor product was **28**, and a trace of **32** was also present. The ratio of **30**:**28** was 3.9:1.0.

The acetate band was also converted to the ketones. The ratio of **30**:**28** was 10.4:1.

Direct Irradiation of 5 in Glacial Acetic Acid at 300 nm. Compound **5** (111 mg, 0.36 mmol) was dissolved in 110 mL of HOAc and was irradiated at 300 nm for 24 h. After the solvent was removed by distillation in vacuo, the residue was examined by ^{1}H NMR spectroscopy. The residue, after workup, was about 85% products. Silica gel TLC gave two bands. The less polar band (39 mg) was starting material and [3.2.1] dichlorides in a ratio of 1:1.2. The more polar band (83 mg) was [3.2.1] acetates.

The dichloride band was heated with silver perchlorate in acetone–water at reflux for 2 min to give starting material and [3.2.1] alcohols. Workup and conversion as above gave a ketone mixture of **28** and **30** in a ratio of 1.8:1. The acetate band gave a ketone mixture comprised of **28** and **30** in a ratio of 9.0:1.

Irradiation of 6 in Glacial Acetic Acid at 300 nm. Dichloride **6** (511 mg, 1.68 mmol) was dissolved in 110 mL of HOAc. The sample was

irradiated for 10 days. Examination by ^{1}H NMR spectroscopy of the residue after workup showed 30% products. The residue was separated by silica gel TLC, giving two bands. The less polar band (392 mg) was starting material **6** and [3.2.1] dichlorides in a ratio of 3.9:1. The more polar band (188 mg) was [3.2.1] acetates.

The [3.2.1] dichloride band was heated at reflux with silver perchlorate in 50:50 acetone:water mixture for 2 min. The [3.2.1] alcohols were separated from the [2.2.2] dichlorides by silica gel TLC. After oxidation of the [3.2.1] alcohols (82 mg), the ketone products were **25** and **27** in a ratio of 2.6:1.

The [3.2.1] acetates were converted to a ketone mixture of **25** and **27** in a ratio of 4.7:1.0.

The irradiation of **6** at 300 nm was repeated in a heavy-walled Pyrex tube. The irradiated sample required 45 days to go to 40% conversion, and no significant difference in products was found.

In all the irradiations of **6** a small amount of **23**-X was observed, but the relative amount of **23** was time-dependent. Short irradiation samples showed 2-3%, whereas long irradiation samples showed 10-15%. This is indicative of **23** being a secondary product.

Irradiation of 6 in Glacial Acetic Acid at 254 nm. Compound **6** (439 mg, 1.44 mmol) was dissolved in 110 mL of HOAc and irradiated for 48 h in the 254-nm Rayonet. After workup, the residue showed no starting material, and only [3.2.1] acetate products were visible. The products were **17**-OAc, **19**-OAc, and **23**-OAc in a ratio of 5:1:1, as measured by ^{1}H NMR spectroscopy of the acetate mixture.

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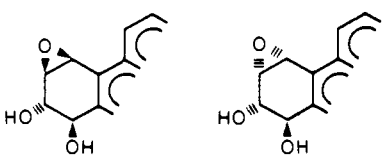
Effects of a 6-Fluoro Substituent on the Solvolytic Properties of the Diastereomeric 7,8-Diol 9,10-Epoxides of the Carcinogen Benzo[*a*]pyrene

H. Yagi,[†] J. M. Sayer,[†] D. R. Thakker,[†,‡] W. Levin,[§] and D. M. Jerina*[†]

Contribution from the Section on Oxidation Mechanisms, Laboratory of Bioorganic Chemistry, NIDDK, The National Institutes of Health, Bethesda, Maryland 20892, and the Laboratory of Experimental Carcinogenesis and Metabolism, Roche Institute of Molecular Biology, Nutley, New Jersey 07110. *Received July 21, 1986*

Abstract: 6-Fluorinated analogues of the mutagenic and carcinogenic benzo[*a*]pyrene 7,8-diol 9,10-epoxides have been synthesized by epoxidation of metabolically formed (−)-*trans*-(7*R*,8*R*)-7,8-dihydroxy-7,8-dihydro-6-fluorobenzo[*a*]pyrene to produce (7*R*,8*S*,9*R*,10*S*)-7,8-dihydroxy-9,10-epoxy-7,8,9,10-tetrahydro-6-fluorobenzo[*a*]pyrene (**1a**) and (7*R*,8*S*,9*S*,10*R*)-7,8-dihydroxy-9,10-epoxy-7,8,9,10-tetrahydro-6-fluorobenzo[*a*]pyrene (**2a**). NMR spectra indicate that the 7,8-diol group of **1a** is almost exclusively pseudoaxial whereas the diol group in **2a** prefers the pseudoaxial orientation to a lesser extent. In both cases the preference for the pseudoaxial conformation of the diol group is much stronger in the fluorinated diol epoxides than in the corresponding benzo[*a*]pyrene derivatives. Like the benzo[*a*]pyrene diol epoxides, **1a** and **2a** undergo hydrolysis and rearrangement in aqueous solutions to give tetraols and a 9-keto 7,8-diol, according to the rate law $k_{obsd} = k_H a_{H^+} + k_0$. Studies with 9,10-epoxy-7,8,9,10-tetrahydro-6-fluorobenzo[*a*]pyrene (**3a**) and its corresponding benzo[*a*]pyrene derivative **3b** indicated that the electronic effect of the 6-fluoro group decreases k_H by ~7-fold and k_0 by ~11-fold. Relative magnitudes of k_H for the fluorinated and unfluorinated diol epoxides can be accounted for solely by this electronic effect. On the other hand, k_0 for **1a** is much smaller and k_0 for **2a** is much larger than predicted when only the electronic substituent effect of fluorine is considered. The pH-independent rates for solvolysis of the fluorinated diol epoxides are thus markedly affected by their altered conformational equilibria due to the presence of fluorine. The observed differences in conformation of the fluorinated diol epoxides may account for the reduced mutagenicity of **1a** and **2a** as well as the lack of high tumorigenicity for **2a** relative to their benzo[*a*]pyrene counterparts, since bay-region diol epoxides in which the hydroxyl groups prefer the pseudoaxial conformation are known not to be highly carcinogenic.

Diol epoxides whose epoxide group forms part of a bay region are the only known metabolically formed ultimate carcinogens from the polycyclic aromatic hydrocarbons.[1] Since such diol epoxides are formed from *trans*-dihydrodiols, two diastereomers are possible, in which the benzylic hydroxyl group and the epoxide



diastereomer-1 diastereomer-2

oxygen are cis (diastereomer 1) or trans (diastereomer 2). In the absence of specific structural features, the benzo-ring *trans*-dihydrodiol precursors markedly prefer the conformation in which the hydroxyl groups are pseudoequatorial.[2] Although this conformational preference is maintained for the derived diol epoxide 2 diastereomers, the diol epoxide 1 diastereomers have a small preference for the conformation in which the hydroxyl groups are

[†] National Institutes of Health.
[§] Roche Institute of Molecular Biology.
[‡] Present address: Center for Drugs and Biologies, FDA.

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