cooled solution was added hydrocloric acid (35%, 10 mL), and subsequently the system was carefully treated with KOH (vigorous reaction) to give a liquid that after extraction with ether and elimination of the solvent yielded 3.8 g of 7: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.75–0.9 (6 H, m, 2 Me), 1.2 (1 H, m, HC*H*), 1.45 (1 H, m, *H*CH), 2.15 (6 H, s, Me_2N), 2.3 (1 H, m, CH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 11.0 (CH_3), 13.2 (CH_3), 26.1 (CH_2), 40.7 (NCH_3), 60.8 (NCH).

***N,N*-Dimethylisobutylamine**[33] **(8)** was obtained with the same procedure as 7. 8: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.87 (6 H, d, *Me*$_2$CH), 1.70 (1 H, m, CH), 1.97 (2 H, d, CH_2), 2.17 (6 H, s, Me_2N); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.4 (CH_3), 26.7 (CH), 46.5 (NCH_3), 69.2 (NCH_2).

NMR Spectra. The spectra were run on a Varian Gemini spectrometer operating at 200 MHz. The 300-MHz spectra of 7 were run on a Bruker CXP 300. The variable-temperature devices were calibrated with the standard methanol sample. For temperatures lower than the freezing point of methanol, a sample containing CH_3OH, CD_3OD, and CHF_2Cl was employed. The chemical shift differences between CH_3 and OH in this sample were measured, with the help of a thermistor, at 100 MHz down to −125 °C. The same sample was subsequently used in the 200- and 300-MHz spectrometers when required. The samples containing CHF_2Cl were prepared by sealing the NMR tubes connected to a vacuum line. The chemical shift differences of the diastereotopic NMe groups were found to depend upon the molar ratio of the Pirkle alcohol. As the chemical shift differences decrease on raising the temperature they were measured at various temperatures below the exchange region and the extrapolated values were employed for the line-shape simulation. The results turned out to be more reliable when relatively small $\Delta G^{\ddagger}$'s are involved: in fact in the case of 5, where the barrier is much larger, the shift difference becomes negligible before reaching the temperature where the exchange occurs. The advantage of using the highest available magnetic fields is clearly illustrated by the case of 6. At 200 MHz the chemical shift difference between the diastereotopic NMe groups was quite small (e.g. 7.5 Hz at −90 °C) so that the rate constant obtained by simulation at the coalescence (6 s^{-1} at −77 °C) was possibly affected by a large error. The value was indeed quite dependent upon the choice of the line width in absence of exchange (4.7 Hz at −77 °C). This parameter had been taken equal to that of the NCH_2 quartet[35] at the same temperature since they had been found to have equal values when the methyl signals did not undergo dynamic exchange (e.g., at −90 °C). The same sample examined at 300 MHz (Figure 1) yielded, at the coalescence, a larger rate constant (14 s^{-1} at −74 °C) that was therefore affected by a smaller uncertainity. It is gratifying however to realize that the $\Delta G^{\ddagger}$ values obtained at two different frequencies are essentially equal within the errors.

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Supplementary Material Available: Proton (200 MHz) and ^{13}C (50.3 MHz) NMR spectra in $CDCl_3$ for compounds 4, 5, 7, and 8 (8 pages). Ordering information is given on any current masthead page.

(35) In principle the geminal protons of the CH_2 group should display two different shifts owing to the presence of the chiral alcohol: the difference was probably too small in the examined sample to be detectable. The same happened for the CH_2 group in 8 where, on the contrary, the methyl groups of the diastereotopic isopropyl moiety display the expected chemical shift difference induced by the presence of the chiral alcohol.

Photochemistry of Stilbenes. 8. Eliminative Photocyclization of *o*-Methoxystilbenes[1]

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The synthetic value of the eliminative photocyclization of *o*-methoxystilbenes to give phenanthrenes with loss of the elements of methanol has been enhanced by the use of *tert*-butyl alcohol as the solvent and sulfuric acid as a catalyst. 2-Methoxy-5-X-stilbenes and 2-methoxy-3-X-stilbenes undergo this photoreaction to produce the corresponding 2-X-phenanthrenes and 4-X-phenanthrenes, respectively. This regioselective photochemical route to these particular types of substituted phenanthrenes represents an improvement synthetically over the well-known oxidative photocyclization method with meta-substituted stilbenes, from which approximately 1:1 mixtures of 2-substituted and 4-substituted phenanthrenes usually are obtained. An attempt to extend the scope of this eliminative photocyclization method to the synthesis of benz[*a*]anthracene by the ultraviolet irradiation of 3-methoxy-2-styrylnaphthalene was not successful, but this synthetic objective was achieved in an alternative way by the eliminative photocyclization of 5,6,7,8-tetrahydro-3-methoxy-2-styrylnaphthalene followed by oxidation of the resulting 8,9,10,11-tetrahydrobenz[*a*]anthracene with DDQ.

The photocyclization reaction exemplified by the conversion of *cis*-stilbene to phenanthrene through ultraviolet irradiation in solution in the presence of iodine and dissolved oxygen is a valuable synthetic method for the preparation of a wide variety of carbocyclic and heterocyclic systems.[2a] There is, however, an unfortunate limitation in the synthetic utility of this venerable photoreaction: simple meta-substituted stilbenes usually give approximately 1:1 mixtures of 2-substituted and 4-substituted phenanthrenes.[3] This presents practical difficulties for two reasons: not only is there an upper limit of about 50% on the yield of either phenanthrene isomer, but also the mixture of the two isomers often is very dif-

(1) (a) Part 7: Mallory, F. B.; Mallory, C. W.; Sen Loeb, S. E. *Tetrahedron Lett.* **1985**, *26*, 3773. (b) Taken from the Ph.D. Dissertation of M. J. Rudolph, Bryn Mawr College, 1988.

(2) (a) Mallory, F. B.; Mallory, C. W. *Org. React. N.Y.* **1984**, *30*, 1–456. (b) Reference 2a, page 34. (c) Reference 2a, page 48.

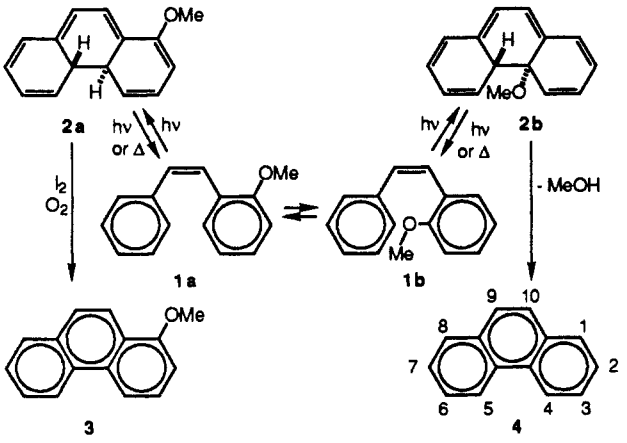
(3) Product ratios skewed in favor of the 2-substituted phenanthrene have been found, however, for stilbenes with certain strongly electron-withdrawing[4] or sterically demanding[5] meta substituents.

(4) (a) Gore, P. H.; Kamonah, F. S. *Synth. Commun.* **1979**, *9*, 377. (b) Kende, A. S.; Curran, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1857. (c) Joly, M.; Defay, N.; Martin, R. H.; Declerq, J. P.; Germain, G.; Soubrier-Payen, B.; Van Meerssche, M. *Helv. Chim. Acta* **1977**, *60*, 537.

(5) (a) Mallory, F. B.; Mallory, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6041. (b) Dickerman, S. C.; Zimmerman, I. *J. Org. Chem.* **1974**, *39*, 3429. (c) Mallory, F. B.; Mallory, C. W.; Cheng, L.-L.; Oh, S. M., unpublished results.

0022-3263/89/1954-4619$01.50/0

Scheme I

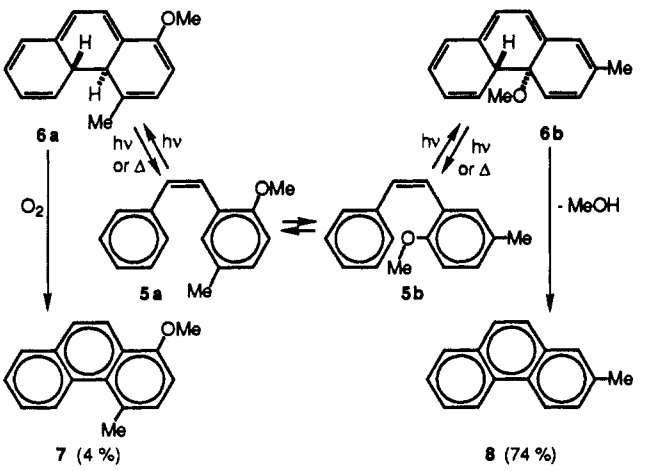


ficult to separate into its pure components. We set out to develop an experimental method to overcome this lack of regioselectivity, following the strategy proposed earlier[2b] involving the use of an *o*-methoxy substituent to direct the photocyclization in a controlled manner.

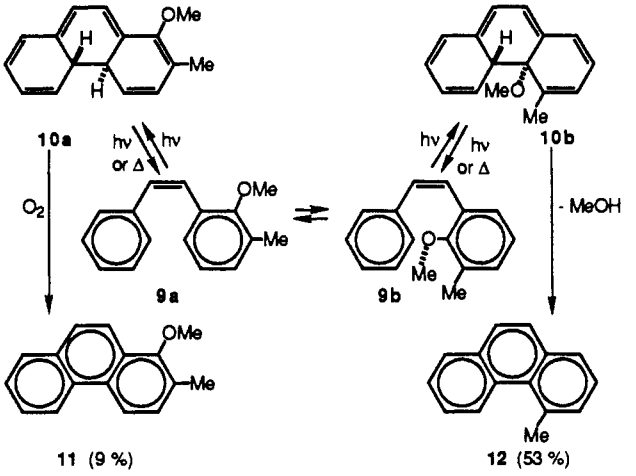
The eliminative photocyclization of *o*-methoxystilbenes was discovered inadvertently by our early observation[6] that the oxidative photocyclization of *cis*-*o*-methoxystilbene[7] (**1**) in cyclohexane solution in the presence of iodine and dissolved oxygen gave, in addition to 1-methoxyphenanthrene (**3**) as the main product, phenanthrene itself (**4**) as a minor side product.[8] As illustrated in Scheme I, this result can be viewed as the outcome of the competition between oxidative trapping of intermediate **2a** and eliminative trapping of intermediate **2b**. Other workers subsequently found[9] that the elimination pathway predominated (58% yield of **4**) when **1** was irradiated in cyclohexane solution under a nitrogen atmosphere in the absence of iodine, although the oxidative pathway remained operative to a troublesome extent (15% yield of **3**), presumably owing to the trapping of **2a** by residual dissolved oxygen. We reasoned that it might be possible to achieve a higher **4**/**3** product ratio, thereby enhancing the synthetic value of the eliminative photocyclization reaction, by increasing the rate of trapping of **2b** through the use of an acid catalyst and a solvent capable of facilitating proton transfers. We began our studies by evaluating the effectiveness of a number of such catalysts and solvents using the parent system **1** as a test case.

We found that the photocyclization of **1** in methanol as solvent led to the formation of small amounts of 9,10-dihydrophenanthrene in addition to **3** and **4**, presumably through a photoreduction process involving the CH bonds of the methanol. To avoid this complication, we settled on *tert*-butyl alcohol as our solvent of choice, either neat or as a 9:1 v/v mixture of the alcohol with benzene as a diluent to facilitate handling of the solvent by lowering its freezing point. We evaluated three candidates for the acid catalyst and found that sulfuric acid (1 drop per 300 mL of solvent) was more suitable than phosphoric acid or hydrochloric acid. Under our standard conditions, a solution of the stilbene in the acidified solvent was stirred magnetically and purged with nitrogen gas both prior to and during its irradiation with a 450-W Hanovia medium-pressure mercury lamp that was contained in a water-cooled Pyrex or quartz immersion well. Treatment of **1** in this way on a 0.6–1.9-g scale led to the formation of the elimination product **4** in 69% yield, accompanied by the unwanted oxidation product **3** in 4% yield.

Scheme II



Scheme III



We chose 2-methylphenanthrene (**8**) and 4-methylphenanthrene (**12**) as the target molecules to demonstrate that our improved eliminative photocyclization procedure could provide a viable solution for the general regiochemical problem mentioned above. Using the oxidative photocyclization method, as reported previously,[5a] these two phenanthrenes are available only as a very difficultly separated 51/49 mixture from the irradiation of *m*-methylstilbene in solution in the presence of iodine and oxygen.[5a] Using our eliminative photocyclization method, as shown in Scheme II, we obtained 2-methylphenanthrene (**8**) in 74% yield from the irradiation of *cis*-2-methoxy-5-methylstilbene[7] (**5**); the unwanted side product 1-methoxy-4-methylphenanthrene (**7**), presumably the result of oxidative trapping of intermediate **6a** by residual dissolved oxygen, was produced in only 4% yield. Similarly, we obtained 4-methylphenanthrene (**12**) in 53% yield, along with 9% of the unwanted oxidative trapping product **11**, from the eliminative photocyclization of *cis*-2-methoxy-

(6) Wood, C. S.; Mallory, F. B. *J. Org. Chem.* **1964**, *29*, 3373.

(7) For each photocyclization experiment explicitly discussed or depicted in this paper, the actual starting material was the trans isomer of the stilbene derivative, from which the cis isomer that is required mechanistically for the ring closure was generated in situ by trans-to-cis photoisomerization.

(8) Eliminative photocyclization with loss of methanol also has been found for the conversions of the stilbene-like *o*-methoxybenzanilides to the corresponding phenanthrene-like phenanthridones. Leading references: (a) Kanaoka, Y.; Itoh, K. *J. Chem. Soc., Chem. Commun.* **1973**, 647. (b) Lenz, G. R. *J. Org. Chem.* **1974**, *39*, 2839.

(9) (a) Cresp, T. M.; Giles, R. G. F.; Sargent, M. V.; Brown, C.; Smith, D. O'N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2435. (b) Giles, R. G. F.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2447. (c) Giles, R. G. F.; Mitchell, P. R. K.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2147.

3-methylstilbene[7] (9) as shown in Scheme III.

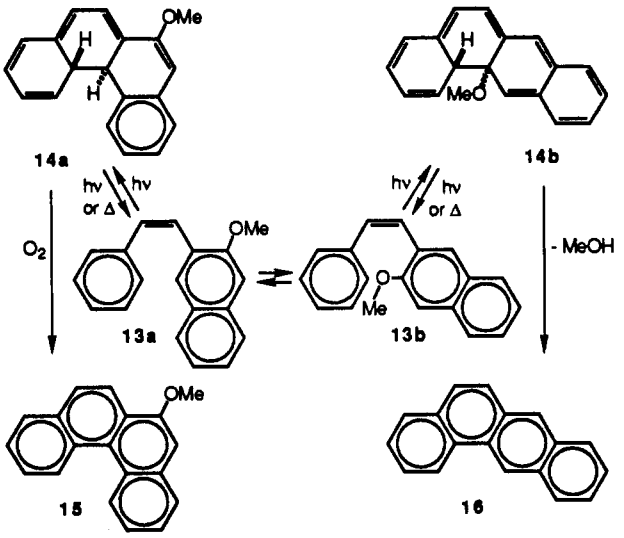
Based on the irradiation times required for product formation under the irradiation conditions we employed, eliminative photocyclizations appear to be less efficient than their oxidative photocyclization counterparts by factors of about 2–4. Thus we found that rather long irradiation times (about 30–175 h) were needed for the eliminative photocyclizations that we carried out on a 9-mmol scale.

Under our standard eliminative photocyclization conditions, the apparent quantum efficiency of product formation from stilbene 9 appears to be only about one-fourth that from stilbene 5. We speculate that this difference arises because the methoxy substituent in 9, being flanked by other substituents on both sides, is forced sterically to adopt a conformation in which its *O*-methyl group is turned out of the plane of the benzene ring to which the oxygen atom is attached, whereas the methoxy substituent in 5 is free to adopt a conformation in which the *O*-methyl group lies in the ring plane (pointing toward the sterically accommodating hydrogen substituent at the 3-position). Based on previous studies of the conformational dependence of the π-conjugation between the oxygen atom and the benzene ring in anisole derivatives,[10] we expect that the methoxy group in 9 would have a net *electron-withdrawing* effect on the ring (its inductive effect outweighing its small conjugative effect), whereas the methoxy group in 5 would have a net *electron-supplying* effect on the ring (its large conjugative effect outweighing its inductive effect).[11] One can then rationalize the observation that product formation is less efficient from 9 than from 5 by invoking the finding[12] from previous studies of related systems that electron-withdrawing substituents decrease the quantum yields for the photocyclization of stilbenes to the corresponding 4a,4b-dihydrophenanthrenes.

The fact that the chemical yield of 4-methylphenanthrene (12) from the eliminative photocyclization of stilbene 9 is significantly less than the chemical yield of 2-methylphenanthrene (8) from the eliminative photocyclization of stilbene 5 (53% compared to 74%) can be explained by noting that the prolonged irradiation period required for the former photoreaction allows more opportunity for competing photodegradation reactions to take place. We believe that this longer irradiation time also accounts for the fact that a larger amount of the unwanted oxidative trapping product is obtained from 9 than from 5 (9% compared to 4%).

As a further test of the viability of our method, the eliminative photocyclization of 2,5-dimethoxystilbene[7] was investigated.[13] The results were analogous to those illustrated in Scheme II for the methoxymethylstilbene 5: the desired elimination product 2-methoxyphenanthrene was produced in 54% yield, along with the unwanted oxidation product 1,4-dimethoxyphenanthrene in 3% yield.

Scheme IV



Additionally, as expected by analogy with Scheme III, the eliminative photocyclization[13] of 2,3-dimethoxystilbene[7] gave a mixture of 4-methoxyphenanthrene and 1,2-dimethoxyphenanthrene, but the isolated yield of 4-methoxyphenanthrene was so low (3%), owing to extensive photodecomposition under the irradiation conditions, that this particular transformation appears to have no synthetic value.

An analogous attempt to develop a regioselective photocyclization method to produce 2-substituted phenanthrenes has been reported[14] in which base-catalyzed eliminative photocyclizations[15] of 2-bromo-5-X-stilbenes in the presence of sodium methoxide in methanol were carried out under a nitrogen atmosphere to try to avoid the competing oxidative photocyclizations of these stilbenes to the corresponding 1-bromo-4-X-phenanthrenes. This approach to 2-substituted phenanthrenes was only modestly successful: in the six reported examples, the yields of the desired elimination products ranged from 20 to 60%, while the yields of the undesired products apparently arising from oxidative trapping ranged as high as 49%.[14] These same 2-bromo-5-X-stilbenes were found to be quite useful, however, in providing a practical synthetic method for the regioselective formation of 4-substituted phenanthrenes through a two-stage sequence involving oxidative photocyclization followed by debromination of the resulting 1-bromo-4-X-phenanthrenes.[14] For example, 4-methylphenanthrene was obtained in 65% yield overall by the action of lithium aluminum hydride on the crude product[16] derived from the oxidative photocyclization of 2-bromo-5-methylstilbene in cyclohexane containing iodine.[14]

Next we turned to the more challenging regiochemical problem associated with the photocyclizations of a special type of meta-substituted stilbenes, namely the 2-styrylnaphthalenes. For simple meta-substituted stilbenes like those discussed above, the intrinsic photoreactivities to-

(10) Baddeley, G.; Smith, N. H. P.; Vickars, M. A. *J. Chem. Soc.* **1956**, 2455.

(11) Consistent with this presumption that there is significant π-conjugation between the benzene ring and the singly flanked but not the doubly flanked methoxy substituents in our systems, the long-wavelength region of the ultraviolet absorption spectrum is quite different for the trans isomer of stilbene 9 (only one broad absorption band at 299 nm) than for the trans isomer of stilbene 5 (two broad absorption bands at 323 nm and 289 nm) or the trans isomer of stilbene 1 (two broad absorption bands at 316 nm and 287 nm).

(12) (a) Mallory, F. B.; Gordon, J. T.; Wood, C. S. *J. Am. Chem. Soc.* **1963**, *85*, 828. (b) Mallory, F. B.; Mallory, C. W.; Varimbi, S. P.; Yaffe, R. A.; Colman, T. E., unpublished results.

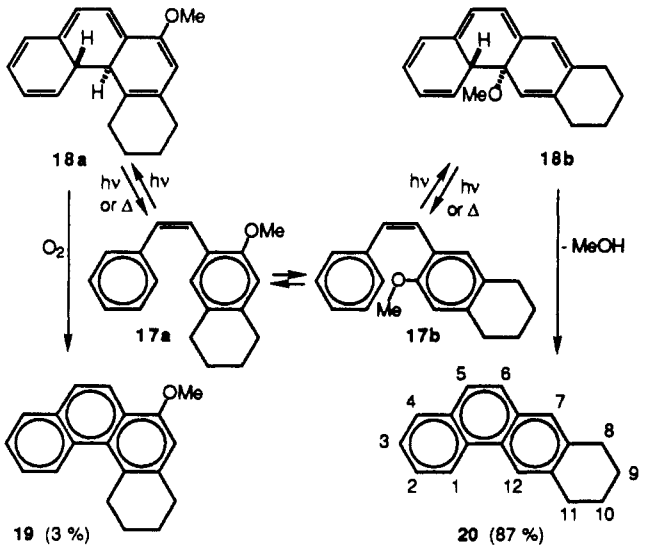
(13) S. M. Oh obtained better results in this dimethoxy system using potassium bisulfate as the acid in a 9:3:1 v/v/v mixture of *tert*-butyl alcohol, cyclohexene, and toluene as the solvent rather than using our standard conditions.

(14) Olsen, R. J.; Pruett, S. R. *J. Org. Chem.* **1985**, *50*, 5457.

(15) These eliminative photocyclizations are believed to involve trapping of the photochemically generated 4a-bromo-4a,4b-dihydrophenanthrene intermediates by an E2 elimination of the elements of HBr induced by the attack of methoxide ion at the 4b-hydrogen atom. (a) Cava, M. P.; Mitchell, M. J.; Havlicek, S. C.; Lindert, A.; Spangler, R. J. *J. Org. Chem.* **1970**, *35*, 175. (b) Cava, M. P.; Stern, P.; Wakisaka, K. *Tetrahedron* **1973**, *29*, 2245. (c) Cava, M. P.; Libsch, S. S. *J. Org. Chem.* **1974**, *39*, 577.

(16) This crude product already contained some 4-methylphenanthrene that had originated from the debromination of the main product, 1-bromo-4-methylphenanthrene, in a secondary photoreaction under the conditions employed for the oxidative photocyclization.

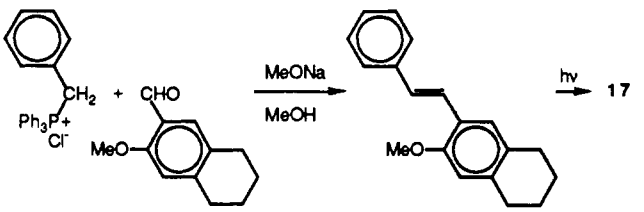
Scheme V



ward cyclization at the two different positions on the benzene ring ortho to the styryl group are essentially equal (as judged, for example, by the 51/49 product distribution in the oxidative photocyclization of *m*-methylstilbene). In contrast, for 2-styrylnaphthalenes the photocyclization is strongly biased toward the 1-position rather than the 3-position on the naphthalene ring (as judged, for example, by the fact that the parent 2-styrylnaphthalene undergoes oxidative photocyclization to give almost exclusively benzo[*c*]phenanthrene with only traces of benz[*a*]anthracene).[17] Thus oxidative photocyclization is an excellent synthetic method for benzo[*c*]phenanthrenes, but is of no practical value for the synthesis of benz[*a*]anthracenes. We hoped that this regiochemical bias might be reversed through an eliminative photocyclization approach of the type illustrated in Scheme IV, leading to a useful new synthetic method for the preparation of benz[*a*]anthracenes, a class of compounds of considerable chemical and biochemical interest.

Accordingly, we irradiated *cis*-3-methoxy-2-styrylnaphthalene[7] (**13**) under our standard conditions for eliminative photocyclization and also under many variations of those conditions. To our disappointment, all of these experiments led only[18] to the destruction of **13** without yielding any detectable amount of benz[*a*]anthracene (**16**). The results of control experiments permitted several conclusions: (a) the desired product **16** is stable under our irradiation conditions, and therefore apparently is not being formed; (b) at least conformer **13a** is capable of photocyclizing to intermediate **14a**, because 6-methoxybenzo[*c*]phenanthrene (**15**) is produced by irradiating **13** under the usual oxidative photocyclization conditions in the presence of iodine and oxygen; and (c) the starting material **13** is stable in the reaction mixture in the dark. One interpretation of these results would be that the photocyclization of **13b** to **14b** is so unfavorable[20] that it cannot compete effectively with some destructive photoreactions (perhaps involving intermediate **14a**) whose nature we are not yet able to specify on the basis of the available evidence. An alternative interpretation would be that the photocyclization of **13b** to **14b** does take place, but the very high-energy[20] intermediate **14b** is consumed rapidly in some unknown way under the reaction conditions. We decided not to pursue this matter further.

Scheme VI



Although our attempt to produce benz[*a*]anthracene (**16**) by the eliminative photocyclization of **13** was thwarted, we did accomplish this synthetic objective by the two-stage method outlined in Scheme V, starting from the tetrahydronaphthyl analogue[7] **17**. Thus eliminative photocyclization of **17** gave 8,9,10,11-tetrahydrobenz[*a*]anthracene (**20**) in 87% yield (accompanied by the side product from oxidative photocyclization in only 3% yield), and subsequent oxidation of hydrocarbon **20** by DDQ gave benz[*a*]anthracene (**16**) in 92% yield.

As shown in Scheme VI, we synthesized the trans isomer[7] of precursor **17** from the readily available 5,6,7,8-tetrahydro-3-methoxy-2-naphthaldehyde[22] by a Wittig reaction with the phosphonium salt prepared from triphenylphosphine and benzyl chloride. Although we have done no experiments to test explicitly the adaptability of our approach to the synthesis of substituted benz[*a*]anthracenes, we anticipate that by carrying out the Wittig reaction in Scheme VI starting with various ortho-substituted or para-substituted benzyl chlorides, subjecting these analogues of **17** to eliminative photocyclization under our standard irradiation conditions, and oxidizing the resulting photocyclization products with DDQ, one should be able to extend the scope of the synthetic method illustrated in Scheme V to include the preparation of the corresponding 4-substituted and 2-substituted benz[*a*]anthracenes, respectively.

Experimental Section

General. Melting points were determined with a Thomas-Hoover oil bath apparatus and are uncorrected. Elemental

(17) The amount of benz[*a*]anthracene obtained from this reaction ranges from 0% to 1%, depending on the concentration of the iodine used as the oxidative trapping agent (unpublished results of F. B. Mallory, C. W. Mallory, and E. J. Halpern).

(18) There is one exception to this statement: when we carried out the irradiation of **13** under a modified version of our standard conditions in which anthracene and Rose Bengal were included in the reaction mixture (for reasons that need not be considered here), we obtained benzo[*c*]phenanthrene in good yield.[19] Although we certainly do not have the experimental evidence that would be required for a secure mechanistic understanding of this rather obscure result, it can be rationalized by the following speculations: (1) the added anthracene and Rose Bengal may exert an inner filter effect that protects the putative intermediate **14a** from absorbing light and thereby suffering photodegradation; (2) this may give **14a** time to undergo isomerization by a series of proton transfers to and from the substrate to give 5,6-dihydro-6-methoxybenzo[*c*]phenanthrene, an intermediate that presumably would undergo acid-induced elimination of methanol to give benzo[*c*]phenanthrene.

(19) This product did not arise from 6-methoxybenzo[*c*]phenanthrene as a precursor, as shown by a control experiment with an authentic sample of this compound.

(20) In a 2-styrylnaphthalene system (e.g., **13**), the 4a,4b-dihydrophenanthrene intermediate (e.g., **14b**) that is produced by photocyclization at C-3 has lost all of the aromaticity of the starting material, whereas the isomeric intermediate that is produced by photocyclization at C-1 (e.g., **14a**) possesses the resonance stabilization of a benzene ring. It has been argued that this large difference in the energies of the two intermediates is related to the marked preference for cyclization at the 1-position rather than the 3-position.[2c] This regioselectivity also has been accounted for by the results of various molecular orbital calculations on 2-styrylnaphthalene in its excited singlet state.[21]

(21) (a) Laarhoven, W. H.; Cuppen, Th. J. H. M.; Nivard, R. J. F. *Tetrahedron* **1970**, *26*, 4865. (b) Tinnemans, A. H. A.; Laarhoven, W. H.; Sharafi-Ozeri, S.; Muszkat, K. A. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 239.

(22) Hunsberger, I. M.; Gutowsky, H. S.; Powell, W.; Morin, L.; Bandurco, V. *J. Am. Chem. Soc.* **1958**, *80*, 3294.

analyses were performed by M-H-W Laboratories, Phoenix, AZ. ^{1}H NMR spectra were obtained in $CDCl_3$ solution with Me_4Si as an internal standard either at 300 MHz with an IBM AF-NR/300 spectrometer, at 270 MHz with an IBM AF-270 spectrometer, or at 90 MHz with a Perkin-Elmer R-32 spectrometer. Spectral assignments for all previously unknown compounds were made with the help of COSY 2D NMR spectroscopy. Ultraviolet spectra were obtained with a Perkin-Elmer/Hitachi Model 200 spectrometer. Analyses by gas chromatography (GC) were accomplished with glass capillary columns and flame-ionization detection using either a Hewlett-Packard 5700A or a Hewlett-Packard 5890 gas chromatograph. Analyses by combined gas chromatography and mass spectrometry (GC/MS) were carried out using a Hewlett-Packard 5890 gas chromatograph interfaced with a Hewlett-Packard 5970 mass selective detector. High-resolution mass spectra were obtained at the University of Pennsylvania with a VG 70-70 Micromass double-focusing spectrometer. Column chromatography employed either Woelm neutral aluminum oxide, activity grade I, or EM Science Kieselgel 60 silicic acid (70–230 mesh). Sublimations were done at pressures less than 0.01 Torr using a previously described apparatus.[23]

Wittig reactions were carried out at room temperature under a nitrogen atmosphere by magnetically stirring a mixture of 1 equiv of the appropriate phosphonium salt and 1.6 equiv of solid sodium methoxide in dry methanol for 30 min to generate the ylid and then adding dropwise over 30 min a dry methanol solution of the appropriate aldehyde. After the resulting mixture had been stirred for several hours, enough water was added to bring the solvent composition to 60% methanol and 40% water, and the mixture was cooled in an ice bath. The crude product, consisting of a mixture of the cis and trans isomers of the styrylarene contaminated by a small amount of triphenylphosphine oxide was collected by suction filtration (or by using a separatory funnel if the crude product was an oil). The aqueous methanol filtrate (or layer) was extracted with hexane and the extract was combined with the solid (or the oil) obtained initially. The resulting hexane solution was subjected to column chromatography on either alumina or silicic acid, and a mixture of the two isomeric styrylarenes was obtained by rotary evaporation of the eluate. This isomer mixture was dissolved in toluene along with a small amount of iodine, and the solution was irradiated with a 100-W incandescent bulb for several hours until the isomerization to the trans isomer was judged by GC to be complete. The toluene was removed by rotary evaporation, the residue was dissolved in hexane, and the hexane solution was passed through a column of alumina or silicic acid. Rotary evaporation of the eluate gave the desired *trans*-stilbene analogue.

Unless otherwise noted, preparative-scale eliminative photocyclizations were carried out in an Ace Glass photoreactor using a 450-W Hanovia medium-pressure mercury arc lamp mounted in a water-cooled quartz or Pyrex immersion well to irradiate 300–900 mL of a magnetically stirred 10^{-2} M solution of the appropriate *trans*-stilbene analogue in a 9:1 (v/v) mixture of *tert*-butyl alcohol and benzene containing 1 drop of concentrated sulfuric acid per 300 mL of solvent; dry nitrogen gas was bubbled steadily through the reaction mixture, beginning at least 2 h before the lamp was started and continuing throughout the irradiation. When the reaction was judged by GC to be complete, the solvents were removed by rotary evaporation, and the residue was purified by chromatography with hexane as the eluent on a column of alumina or silicic acid topped with diatomaceous earth; the desired phenanthrene analogue resulting from eliminative photocyclization eluted first, followed by the side product resulting from oxidative photocyclization.

Preparative-scale oxidative photocyclizations were carried out in a fashion similar to the preparative-scale eliminative photocyclizations described above, except that the solvent was cyclohexane containing 10^{-3} M iodine, the reaction vessel was open to the air, and the crude product was isolated by passing the entire reaction mixture through a column of alumina, eluting with additional cyclohexane, and rotary evaporating the eluate.

***trans*-2-Methoxystilbene.** A sample originally prepared by C. S. Wood[6] was sublimed and recrystallized from methanol to give material with mp 59.4–60.0 °C (lit.[6] mp 58.6–59.5 °C): UV (methanol) λ_{max} nm (log ϵ) 325 (sh) (4.26), 316 (4.26), 299 (4.23), 287 (4.26), 229 (4.18).

Phenanthrene (4). Eliminative photocyclization of 1.90 g (9.0 mmol) of *trans*-2-methoxystilbene by 11 h of irradiation in 900 mL of acidified *tert*-butyl alcohol gave 1.48 g of material shown by GC/MS comparisons with authentic samples[6] to contain 1.11 g (69%) of phenanthrene (**4**) and 0.07 g (4%) of 1-methoxyphenanthrene (**3**). Recrystallization from methanol gave 0.87 g (54%) of **4** (99% pure by GC/MS). A further recrystallization from methanol gave 0.63 g (39%) of **4**, mp 98.8–99.8 °C (lit.[24] mp 99.15 °C).

***trans*-2-Methoxy-5-methylstilbene.** Treatment[25] of 235 g (1.92 mol) of *p*-methylanisole with $ZnCl_2$, 37% aqueous formaldehyde, and HCl gas gave 146 g (45%) of 2-(chloromethyl)-4-methylanisole as a clear liquid, bp 192 °C (26 Torr) (lit.[25] bp 124 °C (16 Torr)): ^{1}H NMR (90 MHz) δ 7.06 (br s, 1 H, H-3), 7.01 (br d, 1 H, H-5, J_{56} = 8.5 Hz), 6.67 (d, 1 H, H-6, J_{56} = 8.5 Hz), 4.56 (s, 2 H, benzylic), 3.72 (s, 3 H, methoxy), 2.22 (s, 3 H, methyl).

Treatment of 34 g (0.2 mol) of 2-(chloromethyl)-4-methylanisole with 52 g (0.2 mol) of triphenylphosphine in refluxing xylene gave 56.5 g (65%) of the corresponding phosphonium salt. A Wittig reaction of 13 g (30 mmol) of this salt and 3.1 mL (3.2 g, 30 mmol) of benzaldehyde produced 5.0 g (75%) of a yellow oil that gave, after molecular distillation, 4.0 g (59%) of *trans*-2-methoxy-5-methylstilbene, mp 34.2–38.5 °C: UV (methanol) λ_{max} nm (log ϵ) 329 (4.20), 323 (4.20), 289 (4.28), 224 (4.23); ^{1}H NMR (270 MHz) δ 7.53 (dd, 2 H, H-2′ and H-6′, $J_{2'3'} = J_{5'6'}$ = 8.6 Hz, $J_{2'4'} = J_{4'6'}$ = 1.4 Hz), 7.46 (d, 1 H, H-α, $J_{\alpha\alpha'}$ = 16.6 Hz), 7.41 (d, 1 H, H-6, J_{46} = 2.0 Hz), 7.37–7.20 (m, 3 H, H-3′, H-4′, and H-5′), 7.10 (d, 1 H, H-α′, $J_{\alpha\alpha'}$ = 16.5 Hz), 7.04 (dd, 1 H, H-4, J_{34} = 8.3 Hz, J_{46} = 2.0 Hz), 6.80 (d, 1 H, H-3, J_{34} = 8.3 Hz), 3.86 (s, 3 H, methoxy), 2.32 (s, 3 H, methyl); mass spectrum, *m/e* (relative intensity) 224 (M^+, 100). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.87; H, 6.93.

2-Methylphenanthrene (8). Eliminative photocyclization of 2.02 g (9.0 mmol) of *trans*-2-methoxy-5-methylstilbene by 40 h of irradiation in 900 mL of acidified *tert*-butyl alcohol/benzene (9:1, v/v) gave, after chromatography on silicic acid with pentane as eluent, an early fraction consisting of 1.28 g (74%) of 2-methylphenanthrene (**8**) (99.6% pure by GC/MS) and a later fraction consisting of 0.09 g of a mixture shown by GC/MS to contain about 0.07 g (4%) of 1-methoxy-4-methylphenanthrene (**7**) and about 0.02 g of recovered *trans*-2-methoxy-5-methylstilbene. The 1.28-g sample was recrystallized from methanol to give 0.88 g (51%) of **8**, mp 56.7–57.2 °C (lit.[26] mp 57–59 °C): ^{1}H NMR (270 MHz) δ 8.64 (br d, 1 H, H-5, J_{56} = 8.0 Hz), 8.56 (d, 1 H, H-4, J_{34} = 8.5 Hz), 7.86 (dd, 1 H, H-8, J_{78} = 7.8 Hz, J_{68} = 1.4 Hz), 7.70 and 7.66 (AB q, 2 H, H-9 and H-10, $J_{9,10}$ = 8.9 Hz), 7.66 (br s, 1 H, H-1), 7.66–7.52 (m, 2 H, H-6 and H-7), 7.47 (dd, 1 H, H-3, J_{34} = 8.5 Hz, J_{13} = 1.7 Hz), 2.55 (s, 3 H, methyl); mass spectrum *m/e* (relative intensity) 192 (M^+, 100).

1-Methoxy-4-methylphenanthrene (7). Oxidative photocyclization of 0.67 g (3.0 mmol) of *trans*-2-methoxy-5-methylstilbene by 7 h of irradiation in 300 mL of a 10^{-3} M solution of I_2 in cyclohexane gave 0.25 g of a clear oil shown by GC/MS to contain about 0.22 g (34%) of 1-methoxy-4-methylphenanthrene (**7**) and about 0.03 g (5%) of 2-methylphenanthrene (**8**). Chromatography of this oil on silicic acid with pentane as eluent gave **7**, mp 53.4–53.8 °C: ^{1}H NMR (270 MHz) δ 8.92 (X part of ABX, 1 H, H-5, $J_{56} + J_{57}$ = 9.4 Hz), 8.30 (d, 1 H, H-10, $J_{9,10}$ = 9.1 Hz), 7.90 (X part of ABX, 1 H, H-8, $J_{78} + J_{68}$ = 9.4 Hz), 7.72 (d, 1 H, H-9, $J_{9,10}$ = 9.1 Hz), 7.62–7.55 (m, 2 H, H-6 and H-7), 7.39 (d, 1 H, H-3, J_{23} = 8.1 Hz), 6.92 (d, 1 H, H-2, J_{23} = 8.1 Hz), 3.99 (s, 3 H, methoxy), 3.07 (s, 3 H, methyl); mass spectrum *m/e* (relative intensity) 222 (M^+, 100). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.26; H, 6.40.

***trans*-2-Methoxy-3-methylstilbene.** Benzylic bromination of 25 g (0.18 mol) of 2,6-dimethylanisole with 32 g (0.18 mol) of *N*-bromosuccinimide and a small amount of benzoyl peroxide in refluxing CCl_4 gave 21.8 g (56%) of 2-(bromomethyl)-6-methyl-

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anisole as a clear liquid (*CAUTION*, lachrymator), bp 131–140 °C (21 Torr): ^{1}H NMR (90 MHz) δ 7.20–6.80 (m, 3 H, H-3, H-4, and H-5), 4.50 (s, 2 H, benzylic), 3.79 (s, 3 H, methoxy), 2.25 (s, 3 H, methyl).

Treatment of 21.8 g (0.10 mol) of 2-(bromomethyl)-6-methylanisole with 26.2 g (0.10 mol) of triphenylphosphine in refluxing xylene gave 16.1 g (34%) of the corresponding phosphonium salt. A Wittig reaction starting with 9.6 g (20 mmol) of this phosphonium salt and 2 mL (2.1 g, 20 mmol) of benzaldehyde yielded 3.1 g (70%) of *trans*-2-methoxy-3-methylstilbene as a clear oil. Molecular distillation gave *trans*-2-methoxy-3-methylstilbene as a white solid, mp 19–21 °C (lit.[27] bp 130–140 °C (0.05 Torr)): UV (methanol) λ_{max} nm (log ε) 298 (4.41), 228 (4.20); ^{1}H NMR (270 MHz) δ 7.55 (br d, 2 H, H-2′ and H-6′, $J_{2'3'} = J_{5'6'} = 7.7$ Hz), 7.49 (dd, 1 H, H-6, $J_{56} = 7.5$ Hz, $J_{46} = 1.5$ Hz), 7.42 (d, 1 H, H-α, $J_{\alpha\alpha'} = 16.5$ Hz), 7.41–7.23 (m, 3 H, H-3′, H-4′, and H-5′), 7.12 (d, 1 H, H-α′, $J_{\alpha\alpha'} = 16.5$ Hz), 7.11 (dd, 1 H, H-4, $J_{45} = 7.5$ Hz, $J_{46} = 1.5$ Hz), 7.04 (t, 1 H, H-5, $J_{45} = J_{56} = 7.5$ Hz), 3.76 (s, 3 H, methoxy), 2.32 (s, 3 H, methyl); mass spectrum, *m/e* (relative intensity) 224 (M^+, 100). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.42; H, 7.03.

4-Methylphenanthrene (12). Eliminative photocyclization of 2.02 g (9.0 mmol) of *trans*-2-methoxy-3-methylstilbene by 175 h of irradiation[28] in 900 mL of acidified *tert*-butyl alcohol/benzene (9:1, v/v) gave, after two chromatographic separations on silicic acid, first with cyclohexane and then with pentane as eluent, an early fraction consisting of 0.91 g (53%) of 4-methylphenanthrene (**12**) (99.5% pure by GC) and a later fraction consisting of 0.18 g (9%) of 1-methoxy-2-methylphenanthrene (**11**) (100% pure by GC). The 0.91-g sample was recrystallized from methanol/water (1:1, v/v) to give 0.57 g (33%) of **12**, mp 52.0–52.3 °C (lit.[30] mp 52.0–52.5 °C): ^{1}H NMR (270 MHz) δ 8.91 (X part of ABX, 1 H, H-5, $J_{56} + J_{57} = 9.3$ Hz), 7.91 (X part of ABX, 1 H, H-8, $J_{78} + J_{68} = 9.4$ Hz), 7.77 (X part of ABX, 1 H, H-1, $J_{12} + J_{13} = 9.3$ Hz), 7.71 (s, 2 H, H-9 and H-10), 7.66–7.55 (m, 2 H, H-6 and H-7), 7.51–7.47 (m, 2 H, H-2 and H-3), 3.15 (s, 3 H, methyl); mass spectrum *m/e* (relative intensity) 192 (M^+, 100).

1-Methoxy-2-methylphenanthrene (11). The 0.18-g sample obtained as a side product from the eliminative photocyclization described in the preceding paragraph was recrystallized from methanol to give 1-methoxy-2-methylphenanthrene (**11**), mp 81.0–81.3 °C: ^{1}H NMR (270 MHz) δ 8.64 (br d, 1 H, H-5, $J_{56} = 8.0$ Hz), 8.38 (d, 1 H, H-4, $J_{34} = 8.5$ Hz), 8.07 (d, 1 H, H-10, $J_{9,10} = 9.1$ Hz), 7.89 (dd, 1 H, H-8, $J_{78} = 7.5$ Hz, $J_{68} = 1.6$ Hz), 7.76 (d, 1 H, H-9, $J_{9,10} = 9.1$ Hz), 7.66–7.54 (m, 2 H, H-6 and H-7), 7.48 (d, 1 H, H-3, $J_{34} = 8.5$ Hz), 3.94 (s, 3 H, methoxy), 2.51 (s, 3 H, methyl); mass spectrum, *m/e* (relative intensity) 222 (M^+, 100). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.42; H, 6.42.

***trans*-2,5-Dimethoxystilbene.** A Wittig reaction of 10.0 g (60 mmol) of 2,5-dimethoxybenzaldehyde with 23.4 g (60 mmol) of benzyltriphenylphosphonium chloride gave, after recrystallization of the crude product from hexane, 6.52 g (45%) of *trans*-2,5-dimethoxystilbene, mp 46.2–47.5 °C (lit.[31] mp 51 °C): ^{1}H NMR (300 MHz) δ 7.56–7.53 (m, 2 H, H-2′ and H-6′), 7.46 (d, 1 H, H-α, $J_{\alpha\alpha'} = 16.5$ Hz), 7.37–7.33 (m, 2 H, H-3′ and H-5′), 7.28–7.25 (m, 1 H, H-4′), 7.15 (d, 1 H, H-6, $J_{46} = 2.8$ Hz), 7.09 (d, 1 H, H-α′, $J_{\alpha\alpha'} = 16.5$ Hz), 6.80 (dd, 1 H, H-4, $J_{34} = 8.8$ Hz, $J_{46} = 2.8$ Hz), 6.65 (d, 1 H, H-3, $J_{34} = 8.8$ Hz), 3.85 (s, 3 H, methoxy), 3.83 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 240 (M^+, 100).

2-Methoxyphenanthrene. Eliminative photocyclization of 0.74 g (3.1 mmol) of *trans*-2,5-dimethoxystilbene by 43 h of irradiation in 270 mL of *tert*-butyl alcohol, 30 mL of toluene, and 100 mL of cyclohexene containing 3.5 g of potassium bisulfate gave a mixture of 2-methoxyphenanthrene and 1,4-dimethoxyphenanthrene in a 94/6 ratio. Chromatographic purification gave 0.34 g (54%) of 2-methoxyphenanthrene, mp 93.5–94.5 °C (lit.[32] mp 99 °C): ^{1}H NMR (300 MHz) δ 8.60 (br d, 2 H, H-4 and H-5, $J_{34} = J_{56} = 8.6$ Hz), 7.87 (dd, 1 H, H-8, $J_{78} = 7.9$ Hz, $J_{68} = 1.2$ Hz), 7.73 and 7.68 (AB q, 2 H, H-9 and H-10, $J_{9,10} = 8.8$ Hz), 7.66–7.51 (m, 2 H, H-6 and H-7), 7.31–7.26 (m, 2 H, H-3 and H-1), 3.98 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 208 (M^+, 100).

1,4-Dimethoxyphenanthrene. Oxidative photocyclization of 0.72 g (3.0 mmol) of *trans*-2,5-dimethoxystilbene by 10 h of irradiation in 300 mL of a 10^{-3} M solution of I_2 in cyclohexane gave, after purification of the crude product by column chromatography and recrystallization from methanol, 0.40 g (56%) of 1,4-dimethoxyphenanthrene, mp 115–118 °C (lit.[33] mp 123.5–124.5 °C): ^{1}H NMR (300 MHz) δ 9.70 (dd, 1 H, H-5, $J_{56} = 8.4$ Hz, $J_{57} = 1.4$ Hz), 8.25 and 7.77 (AB q, 2 H, H-9 and H-10, $J_{9,10} = 9.1$ Hz), 7.89 (dd, 1 H, H-8, $J_{78} = 7.3$ Hz, $J_{68} = 2.1$ Hz), 7.63–7.58 (m, 2 H, H-6 and H-7), 7.08 and 6.98 (AB q, 2 H, H-2 and H-3, $J_{23} = 8.7$ Hz), 4.08 (s, 3 H, methoxy), 4.01 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 238 (M^+, 79), 223 (100).

***trans*-2,3-Dimethoxystilbene.** A Wittig reaction of 5.0 g (30 mmol) of 2,3-dimethoxybenzaldehyde with 11.7 g (30 mmol) of benzyltriphenylphosphonium chloride gave, after recrystallization of the crude product from hexane, 6.0 g (83%) of *trans*-2,3-dimethoxystilbene, mp 38.2–39.2 °C: ^{1}H NMR (300 MHz) δ 7.55 (br d, 2 H, H-2′ and H-6′, $J_{2'3'} = J_{5'6'} = 7.4$ Hz), 7.46 and 7.13 (AB q, 2 H, H-α and H-α′, $J_{\alpha\alpha'} = 16.5$ Hz), 7.36 (br t, 2 H, H-3′ and H-5′, $J_{2'3'} = J_{3'4'} = J_{4'5'} = J_{5'6'} = 7.4$ Hz), 7.26 (br t, 1 H, H-4′, $J_{3'4'} = J_{4'5'} = 7.4$ Hz), 7.25 (dd, 1 H, H-6, $J_{56} = 8.1$ Hz, $J_{46} = 1.3$ Hz), 7.06 (t, 1 H, H-5, $J_{45} = J_{56} = 8.1$ Hz), 6.84 (dd, 1 H, H-4, $J_{45} = 8.1$ Hz, $J_{46} = 1.3$ Hz), 3.88 (s, 3 H, methoxy), 3.85 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 240 (M^+, 100). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.95; H, 6.72.

4-Methoxyphenanthrene. Eliminative photocyclization of 0.72 g (3.0 mmol) of *trans*-2,3-dimethoxystilbene by 60 h of irradiation in 270 mL of *tert*-butyl alcohol, 30 mL of toluene, and 100 mL of cyclohexene containing 2 g of $KHSO_4$ gave, after purification of the crude product by chromatography and recrystallization from hexane, only 0.02 g (3%) of 4-methoxyphenanthrene: ^{1}H NMR (300 MHz) δ 9.67 (br d, 1 H, H-5, $J_{56} = 8.3$ Hz), 7.88 (dd, 1 H, H-8, $J_{78} = 7.7$ Hz, $J_{68} = 1.6$ Hz), 7.74 and 7.71 (AB q, 2 H, H-9 and H-10, $J_{9,10} = 8.8$ Hz), 7.67–7.51 (m, 4 H, H-1, H-3, H-6, and H-7), 7.16 (X part of ABX, 1 H, H-3, $J_{34} + J_{13} = 9.2$ Hz), 4.14 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 208 (M^+, 100). A second product was identified as 1,2-dimethoxyphenanthrene by GC and MS comparisons with an authentic sample prepared as described below.

1,2-Dimethoxyphenanthrene. Oxidative photocyclization of 0.72 g (3.0 mmol) of *trans*-2,3-dimethoxystilbene by 15 h of irradiation in 300 mL of cyclohexane containing 25 mg (0.1 mmol) of I_2 gave, after purification of the crude product by chromatography and recrystallization from absolute ethanol, 0.45 g (63%) of 1,2-dimethoxyphenanthrene, mp 98–100 °C (lit.[34] mp 100–102 °C): ^{1}H NMR (300 MHz) δ 8.59 (br d, 1 H, H-5, $J_{56} = 8.1$ Hz), 8.43 (d, 1 H, H-4, $J_{34} = 9.2$ Hz), 8.09 (d, 1 H, H-10, $J_{9,10} = 9.2$ Hz), 7.86 (br d, 1 H, H-8, $J_{78} = 7.8$ Hz), 7.74 (d, 1 H, H-9, $J_{9,10} = 9.2$ Hz), 7.65–7.52 (m, 2 H, H-6 and H-7), 7.38 (d, 1 H, H-3, $J_{34} = 9.2$ Hz), 4.04 (s, 3 H, methoxy), 4.02 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 238 (M^+, 100).

***trans*-3-Methoxy-2-styrylnaphthalene.** A Friedel–Crafts reaction[35] of *o*-methylanisole with succinic anhydride and $AlCl_3$ gave 3-(4′-methoxy-3′-methylbenzoyl)propanoic acid, mp 146–147 °C (lit.[36] mp 152 °C). Recrystallization from a mixture of cyclohexane and isopropyl alcohol (3:1, v/v) gave a sample with mp 166.4–169.2 °C: ^{1}H NMR (270 MHz) δ 7.85 (dd, 1 H, H-6′, $J_{5'6'} = 8.5$ Hz, $J_{2'6'} = 2.2$ Hz), 7.80 (br s, 1 H, H-2′), 6.85 (d, 1 H, H-5′, $J_{5'6'} = 8.6$ Hz), 3.90 (s, 3 H, methoxy), 3.27 (t, 2 H, H-3, $J_{23} = 6.6$ Hz), 2.79 (t, 2 H, H-2, $J_{23} = 6.6$ Hz), 2.25 (s, 3 H, methyl); mass spectrum, *m/e* (relative intensity) 222 (M^+, 21), 149 (100).

Wolff–Kishner reduction[37] of the preceding keto acid with

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hydrazine hydrate and KOH gave, after recrystallization of the product from hexane, a sample of 4-(4′-methoxy-3′-methylphenyl)butanoic acid, mp 56.0–57.5 °C (lit.[38] mp 59.5–60.5 °C): ^{1}H NMR (270 MHz) δ 6.97–6.67 (m, 3 H, H-2′, H-5′, and H-6′), 3.80 (s, 3 H, methoxy), 2.58 (t, 2 H, H-4, J_{34} = 7.5 Hz), 2.36 (t, 2 H, H-2, J_{23} = 7.5 Hz), 2.20 (s, 3 H, methyl), 1.92 (pentet, 2 H, H-3, J_{23} = J_{34} = 7.5 Hz); mass spectrum, *m/e* (relative intensity) 208 (M^+, 27), 148 (31), 135 (100).

Treatment[39] of the preceding carboxylic acid with polyphosphoric acid gave, after purification of the product by distillation at reduced pressure and recrystallization from a mixture of methanol and water, a sample of 7-methoxy-6-methyl-1-tetralone, mp 45.6–46.1 °C (lit.[38] mp 44–45 °C): ^{1}H NMR (270 MHz) δ 7.45 (s, 1 H, H-8), 7.02 (s, 1 H, H-5), 3.86 (s, 3 H, methoxy), 2.86 (t, 2 H, H-4, J_{34} = 6.0 Hz), 2.62 (t, 2 H, H-2, J_{23} = 6.5 Hz), 2.25 (s, 3 H, methyl), 2.10 (pentet, 2 H, H-3, J_{23} = J_{34} = 6.3 Hz); mass spectrum, *m/e* (relative intensity) 190 (M^+, 100).

Reduction[40] of the preceding ketone with sodium borohydride gave, after recrystallization of the product from hexane, a sample of 7-methoxy-6-methyl-3,4-dihydro-2*H*-naphthalen-1-ol, mp 66.0–67.5 °C (lit.[41] mp 63 °C): ^{1}H NMR (270 MHz) δ 6.89 (s, 1 H, H-5 or H-8), 6.87 (s, 1 H, H-8 or H-5), 4.75–4.71 (m, 1 H, H-1), 3.82 (s, 3 H, methoxy), 2.77–2.55 (m, 2 H, H-4), 2.18 (s, 3 H, methyl), 2.04–1.68 (m, 4 H, H-2 and H-3); mass spectrum, *m/e* (relative intensity) 192 (M^+, 49), 174 (100).

Dehydration[42] of a sample of 43 g (0.25 mol) of the preceding alcohol with 0.2 g of *p*-toluenesulfonic acid in 1.1 L of benzene with azeotropic removal of water by means of a Dean–Stark trap gave, after workup, 37 g (86%) of an oil that solidified in a freezer. Purification by chromatography on silicic acid with pentane as the eluent followed by recrystallization from methanol gave 1,2-dihydro-6-methoxy-7-methylnaphthalene as colorless plates, mp 49.0–49.5 °C: ^{1}H NMR (270 MHz) δ 6.88 (br s, 1 H, H-5 or H-8), 6.53 (br s, 1 H, H-8 or H-5), 6.42 (br d, 1 H, H-4, J_{34} = 9.6 Hz), 5.98 (dt, 1 H, H-3, J_{34} = 9.6 Hz, J_{23} = 4.5 Hz), 3.81 (s, 3 H, methoxy), 2.69 (t, 2 H, H-1, J_{12} = 8.2 Hz), 2.32–2.24 (m, 2 H, H-2), 2.18 (s, 3 H, methyl); mass spectrum, *m/e* (relative intensity) 174 (M^+, 100). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.59; H, 8.05.

The preceding dihydronaphthalene (18.5 g, 0.11 mol) was oxidized by treatment[43] with 27 g (0.12 mol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 1.5 L of refluxing benzene for 4 h. Filtration of the cooled reaction mixture through alumina, rotary evaporation of the solvent, chromatography of the residue on silicic acid with cyclohexane as the eluent, and rotary evaporation of the eluate gave 15 g (80%) of 3-methoxy-2-methylnaphthalene, mp 73.2–74.1 °C (lit.[44] mp 75–76 °C): ^{1}H NMR (270 MHz) δ 7.72–7.68 (m, 2 H, H-5 and H-8), 7.57 (br s, 1 H, H-1), 7.41–7.26 (m, 2 H, H-6 and H-7), 7.07 (br s, 1 H, H-4), 3.94 (s, 3 H, methoxy), 2.37 (s, 3 H, methyl); mass spectrum, *m/e* (relative intensity) 172 (M^+, 100).

Benzylic bromination of 15.6 g (90 mmol) of 3-methoxy-2-methylnaphthalene with 16 g (90 mmol) of *N*-bromosuccinimide and a small amount of benzoyl peroxide in refluxing CCl_4 gave 21 g (93%) of 2-(bromomethyl)-3-methoxynaphthalene. Recrystallization from hexane gave yellow prisms, mp 149.5–150.0 °C: ^{1}H NMR (300 MHz) δ 7.81 (br s, 1 H, H-1), 7.75–7.71 (m, 2 H, H-5 and H-8), 7.44 (ddd, 1 H, H-6 or H-7, J_{56} or J_{78} = 8.1 Hz, J_{67} = 6.9 Hz, J_{68} or J_{57} = 1.3 Hz), 7.34 (ddd, 1 H, H-6 or H-7, J_{56} or J_{78} = 8.1 Hz, J_{67} = 7.0 Hz, J_{68} or J_{57} = 1.1 Hz), 7.13 (br s, 1 H, H-4), 4.71 (s, 2 H, CH_2Br), 4.00 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 252 (M^+, 28), 250 (M^+, 28), 171 (100); exact *m/e* calcd for $C_{12}H_{11}O^{81}Br$ 251.9973, obsd 251.9962; exact *m/e* calcd for $C_{12}H_{11}O^{79}Br$ 249.9993, obsd 249.9989.

Treatment of 21 g (83 mmol) of 2-(bromomethyl)-3-methoxynaphthalene with 22 g (83 mmol) of triphenylphosphine in refluxing xylene gave 36 g (84%) of the corresponding phosphonium salt. A Wittig reaction of this salt (36 g, 70 mmol) with 7.1 mL (7.4 g, 70 mmol) of benzaldehyde gave 8.3 g (46%) of *trans*-3-methoxy-2-styrylnaphthalene. Recrystallization from methanol gave material with mp 103.0–103.8 °C: UV (methanol) λ_{max} nm (log ε) 330 (4.41), 318 (4.45), 278 (4.48), 273 (4.48), 226 (4.56); ^{1}H NMR (300 MHz) δ 8.02 (br s, 1 H, H-1), 7.79 (br d, 1 H, H-8, J_{78} = 8.0 Hz), 7.71 (br d, 1 H, H-5, J_{56} = 8.6 Hz), 7.58 (d, 1 H, H-α, $J_{\alpha\alpha'}$ = 16.5 Hz), 7.44–7.24 (m, 7 H, H-6, H-7, and phenyl), 7.28 (d, 1 H, H-α′, $J_{\alpha\alpha'}$ = 16.5 Hz), 7.13 (br s, 1 H, H-4), 4.00 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 260 (M^+, 100). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.44; H, 6.41.

6-Methoxybenzo[*c*]phenanthrene (15). Oxidative photocyclization of 1.56 g (6 mmol) of *trans*-3-methoxy-2-styrylnaphthalene by 80 min of irradiation in 600 mL of a 10^{-3} M solution of iodine in cyclohexane gave, after chromatography on silicic acid with hexane as eluent followed by recrystallization from methanol, 0.46 g (30%) of 6-methoxybenzo[*c*]phenanthrene (**15**) as pale yellow prisms, mp 84.0–84.2 °C (lit.[45] oil): ^{1}H NMR (300 MHz) δ 9.10 (br d, 1 H, H-12, $J_{11,12}$ = 8.0 Hz), 9.00 (br d, 1 H, H-1, J_{12} = 8.2 Hz), 8.36 (d, 1 H, H-7, J_{78} = 8.8 Hz), 8.02 (dd, 1 H, H-4, J_{34} = 7.1 Hz, J_{24} = 2.2 Hz), 7.97 (d, 1 H, H-8, J_{78} = 8.7 Hz), 7.90 (d, 1 H, H-9, $J_{9,10}$ = 6.9 Hz), 7.69–7.49 (m, 4 H, H-2, H-3, H-10, and H-11), 7.17 (s, 1 H, H-5), 4.12 (s, 3 H, methoxy); mass spectrum, *m/e* (relative intensity) 158 (M^+, 100). Anal. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.45; H, 5.55.

***trans*-5,6,7,8-Tetrahydro-3-methoxy-2-styrylnaphthalene.** Treatment of 25 g (0.17 mol) of 5,6,7,8-tetrahydro-2-naphthol with 40 g (0.32 mol) of dimethyl sulfate and 10 g (0.25 mol) of sodium hydroxide in 500 mL of refluxing dry ethanol for 5 h gave, after workup, 26 g (94%) of 5,6,7,8-tetrahydro-2-methoxynaphthalene (99.4% pure by GC/MS) as an oil: ^{1}H NMR (300 MHz) δ 6.96 (d, 1 H, H-4, J_{34} = 8.3 Hz), 6.66 (dd, 1 H, H-3, J_{34} = 8.4 Hz, J_{13} = 2.6 Hz), 6.60 (d, 1 H, H-1, J_{13} = 2.6 Hz), 3.75 (s, 3 H, methoxy), 2.75–2.67 (m, 4 H, H-5 and H-8), 1.79–1.74 (m, 4 H, H-6 and H-7); mass spectrum, *m/e* (relative intensity) 176 (M^+, 100).

Treatment[22] of 25 g (0.15 mol) of the preceding oil with 38 mL (42 g, 0.31 mol) of *N*-methylformanilide and 33 mL (54 g, 0.35 mol) of phosphorus oxychloride gave 24 g (82%) of 5,6,7,8-tetrahydro-3-methoxy-2-naphthaldehyde. Chromatography on silicic acid with pentane as eluent gave 17.5 g (60%) of material with mp 51.6–52.2 °C (lit.[22] mp 51.6–52.0 °C): ^{1}H NMR (300 MHz) δ 10.38 (s, 1 H, formyl), 7.53 (s, 1 H, H-1), 6.66 (s, 1 H, H-4), 3.88 (s, 3 H, methoxy), 2.81–2.71 (m, 4 H, H-5 or H-8), 1.81–1.76 (m, 4 H, H-6 and H-7); mass spectrum, *m/e* (relative intensity) 190 (M^+, 100).

A Wittig reaction of 10 g (53 mmol) of the preceding aldehyde with 23 g (60 mmol) of benzyltriphenylphosphonium chloride gave 4 g (29%) of *trans*-5,6,7,8-tetrahydro-3-methoxy-2-styrylnaphthalene, mp 78.8–79.5 °C. Recrystallization from methanol gave material with mp 79.5–80.0 °C: UV (methanol) λ_{max} nm (log ε) 333 (4.28), 325 (4.28), 291 (4.30), 226 (4.34); ^{1}H NMR (300 MHz) δ 7.52 (br d, 2 H, H-2′ and H-6′), 7.43 (d, 1 H, H-α, $J_{\alpha\alpha'}$ = 16.5 Hz), 7.36–7.19 (m, 3 H, H-3′, H-4′, and H-5′), 7.33, (br s, 1 H, H-4), 7.06 (d, 1 H, H-α′, $J_{\alpha\alpha'}$ = 16.5 Hz), 6.59 (br s, 1 H, H-1), 3.84 (s, 3 H, methoxy), 2.78–2.72 (m, 4 H, H-5 and H-8), 1.82–1.78 (m, 4 H, H-6 and H-7); mass spectrum, *m/e* (relative intensity) 264 (M^+, 100). Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.46; H, 7.63.

8,9,10,11-Tetrahydrobenz[*a*]anthracene (20). Eliminative photocyclization of 2.0 g (7.6 mmol) of *trans*-5,6,7,8-tetrahydro-3-methoxy-2-styrylnaphthalene by 26 h of irradiation in 900 mL of acidified *tert*-butyl alcohol/benzene (9:1, v/v) gave, after chromatography on silicic acid with pentane as eluent, 1.53 g (87%) of 8,9,10,11-tetrahydrobenz[*a*]anthracene (**20**), mp 87–89 °C. Recrystallization from methanol gave **20** with mp 89.4–90.0 °C (lit.[46] mp 88.5–89.5 °C): ^{1}H NMR (300 MHz) δ 8.63 (br d, 1 H, H-1, J_{12} = 7.9 Hz), 8.37 (s, 1 H, H-12), 7.83 (dd, 1 H, H-4, J_{34} = 7.8 Hz, J_{24} = 1.2 Hz), 7.63–7.51 (m, 4 H, H-2, H-3, H-5, and

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H-6), 7.62 (s, 1 H, H-7), 3.08-2.98 (m, 4 H, H-8 and H-11), 1.93-1.88 (m, 4 H, H-9 and H-10); mass spectrum, *m/e* (relative intensity) 232 (M^+, 100).

1,2,3,4-Tetrahydro-6-methoxybenzo[*c*]phenanthrene. Further elution with pentane of the silicic acid column described in the preceding paragraph yielded 0.05 g (3%) of 1,2,3,4-tetrahydro-6-methoxybenzo[*c*]phenanthrene (**19**) (97% pure by GC/MS). Recrystallization from pentane gave 0.02 g of **19**, mp 96.2-96.5 °C: ^{1}H NMR (300 MHz) δ 8.79 (X part of ABX, 1 H, H-12, $J_{11,12} + J_{10,12} = 9.6$ Hz), 8.23 (d, 1 H, H-7, $J_{78} = 9.0$ Hz), 7.89 (X part of ABX, 1 H, H-9, $J_{9,10} + J_{9,11} = 9.5$ Hz), 7.67 (d, 1 H, H-8, $J_{78} = 9.0$ Hz), 7.58-7.50 (m, 2 H, H-10 and H-11), 6.77 (s, 1 H, H-5), 4.00 (s, 3 H, methoxy), 3.47 (t, 2 H, H-1, $J_{12} = 5.8$ Hz), 3.08 (t, 2 H, H-4, $J_{34} = 6.6$ Hz), 2.00-1.76 (m, 4 H, H-2 and H-3); mass spectrum, *m/e* (relative intensity) 262 (M^+, 100). Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.10; H, 6.98.

Benz[*a*]anthracene (16). Treatment of 100 mg (0.43 mmol) of 8,9,10,11-tetrahydrobenz[*a*]anthracene with 215 mg (0.95 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 10 mL of refluxing dry benzene for 20 min gave, after chromatography on alumina, 90 mg (92%) of benz[*a*]anthracene (**16**), mp 158-161 °C. Recrystallization from methanol gave **16** with mp 161.0-161.8 °C (lit.[47] mp 160.5-161.0 °C): mass spectrum, *m/e* (relative intensity) 228 (M^+, 100).

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Macrocycles Containing Tin. Preparation of Macrobicyclic Lewis Acidic Hosts Containing Two Tin Atoms and ^{119}Sn NMR Studies of Their Chloride and Bromide Binding Properties in Solution

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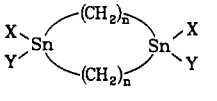
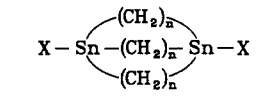
The preparation of eight symmetrical, macrobicyclic hosts containing two chloride- or bromide-substituted tin atoms at the bridgehead positions and linking chains of 6, 7, 8, 10, or 12 methylene groups are described. In solution, the smaller members exist as one isomer with the halogens outside of the cavity (out-out isomer), but the larger members exist as a mixture of the major out-out isomer and a minor in-out isomer that contains one halogen inside the cavity. Complexation of chloride anion by the five chloride-substituted hosts and of bromide anion by the three bromide-substituted hosts in halogenated solvents was studied by ^{119}Sn NMR spectroscopy. All of the bicyclic hosts that bind halide form complexes with 1:1 stoichiometry with a guest anion encrypted within the cavity of the host. Equilibrium constants for formation of the complexes were measured. Temperature-dependent dynamic NMR behavior was observed for four bicyclic hosts binding chloride and for one host binding bromide, and simulations of the spectra measured at various temperatures provided rate constants for binding guest anion within the cavity and for dissociation of the guest anion from the cavity. Arrhenius functions for these processes were calculated. Size-selective binding was observed in both chloride and bromide binding. For chloride complexation, the rate of formation of complexes at 20 °C increased monotonically as a function of the linking chain length, but the rate of dissociation did not.

The binding of anions and basic donors in organic media by multidentate Lewis acidic hosts is relatively unexplored.[1] Our group has studied the use of Lewis acidic tin atoms in macrocyclic[2] and macrobicyclic[3] compounds as hosts for anionic guests. Simple macrocycles containing two Lewis acidic sites (**1**) were found to bind chloride ion with little size selectivity,[2] but incorporation of a third linking chain between the acidic sites to give bicycles **2** provided hosts that bound chloride in a size-selective manner.[3a] This size-selective binding of chloride by hosts **2** and the anion-specific binding of fluoride ion by host **2a**[3b] suggested that bicyclic compounds included halide ions within their cavities, and this feature was confirmed in recent solid-state studies of a complex formed from host **2a** and tetrabutylammonium fluoride and a complex formed from host **2c** and benzyltriphenylphosphonium chloride.[4]



1: X=Y=Cl; n = 8, 10, 12
4: X=C_4H_9, Y=Cl, n=10



2: X=Cl 3: X=Br
a:n=6; b:n=7; c:n=8
d:n=10; e:n=12

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