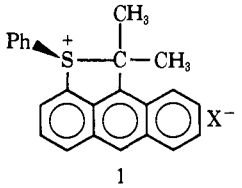
Syntheses of Sulfonium Ions Capable of Undergoing Degenerate Rearrangements. Derivatives of 1,8-Di(phenylthio)anthracene-9-carbinyl Cation

Robert J. Basalay[1] and J. C. Martin*

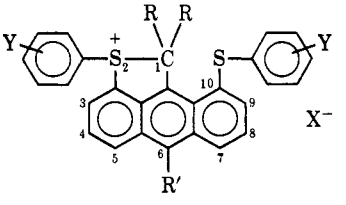
Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received August 4, 1972*

Abstract: Syntheses are described for a number of 9-substituted anthracenes bearing arylthio substituents at the 1 and 8 positions. Protonation of a 9-isopropenyl substituent in such a molecule can be carried out under a variety of conditions with simultaneous ring closure to form a cyclic sulfonium ion, a substituted 2-thioniaaceanthrene cation **1**, **2**, **3**, or **4**. Evidence is presented that this protonation is, in fact, anchimerically accelerated by neighboring sulfur participation. Analogous sulfonium ions (2-thioniaaceanthrene cations) in which the nonaromatic sulfonium bridging substituent is a methylene group rather than an isopropylidene group are also described.

The past few years have seen a number of investigations of systems in which geometric restraints provide a favorable environment for the stabilization of an electron-deficient center, such as a carbonium ion, by simultaneous bonding to two suitable neighboring nucleophilic groups.[2] The geometry of the 1,8,9-trisubstituted anthracene nucleus would seem, by virtue of the rigidity of the aromatic nucleus and the favorable geometric relationship between substituents, to provide a likely system for the study of pentacoordinate carbon intermediates in the SN2 reaction, if such are to be found. From the available choices of neighboring nucleophile, a variety of considerations led us to favor sulfide sulfur atoms in 1,8-di(arylthio)anthracene-9-carbinyl cations. This paper describes the synthesis and some of the reactions of ions **1**, **2**, **3**, and **4**. An accompanying paper[3] describes studies relevant to the question of the intermediacy of pentacoordinate carbon species in reactions of **2**, **3**, and **4**.



1



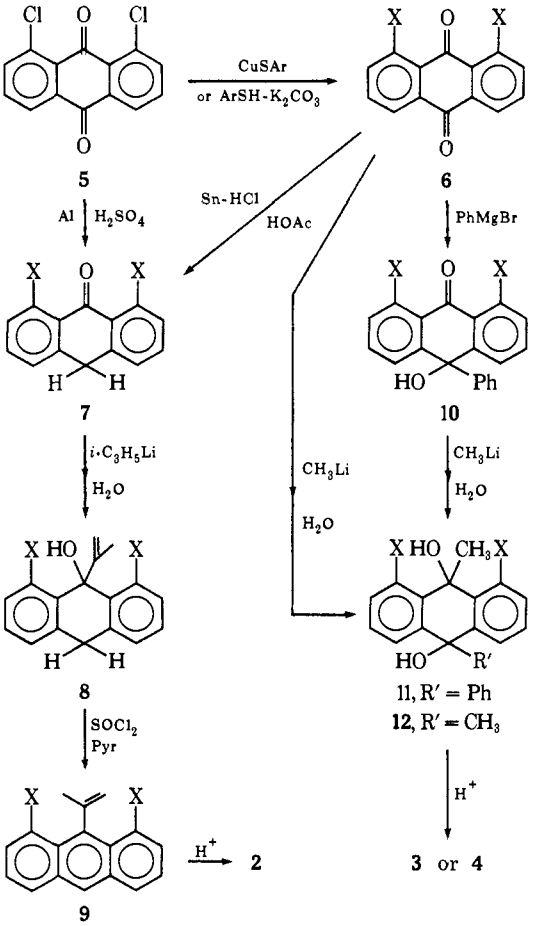
2, R = CH_3; R′ = H
3, R = H; R′ = CH_3
4, R = H; R′ = Ph

a, Y = H
b, Y = 4-CH_3
c, Y = 3-CH_3
d, Y = 4-$C(CH_3)_3$
e, Y = 4-OCH_3

Results and Discussion

Sulfonium ions **2**, **3**, and **4** were synthesized by the routes shown in Scheme I. Sulfonium ion **1** was prepared by a route, similar to that used for **2**, starting from 1-chloroanthraquinone (**13**). In the synthesis of **1** (Scheme II) the thionyl chloride dehydration was omitted since it was found that the direct base-catalyzed dehydration leading to **16**, using an excess of isopro-

Scheme I



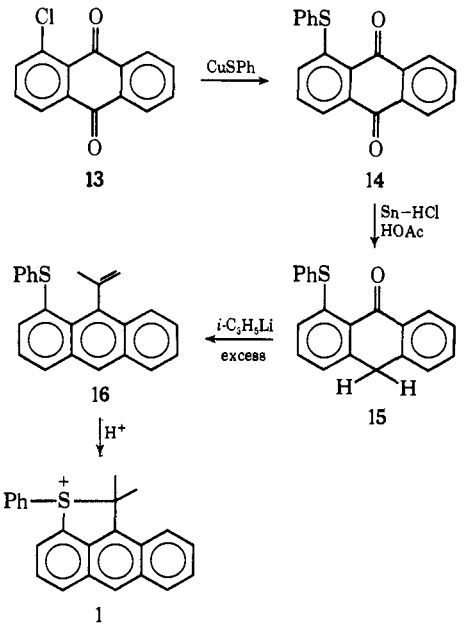
a, X = SC_6H_5
b, X = SC_6H_4Y; Y = 4-CH_3
c, X = SC_6H_4Y; Y = 3-CH_3
d, X = SC_6H_4Y; Y = 4-$C(CH_3)_3$
e, X = SC_6H_4Y; Y = 4-OCH_3
f, X = Cl

(1) Fellowships for R. J. B. were provided by the University of Illinois, the Proctor and Gamble Co., the National Science Foundation, and the National Institutes of Health.

(2) (a) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968); (b) R. Breslow, L. Kaplan, S. Garatt, and D. LaFollette, *J. Amer. Chem. Soc.*, **90**, 4051 (1968); R. Breslow, L. Kaplan, and D. LaFollette, *ibid.*, **90**, 4056 (1968); (c) R. Lustgarten, M. Brookhart, and S. Winstein, *Tetrahedron Lett.*, 141 (1971); (d) see, however, R. Firestone, *J. Org. Chem.*, **36**, 702 (1971).

(3) J. C. Martin and R. J. Basalay, *J. Amer. Chem. Soc.*, **95**, 2572 (1973).

Scheme II



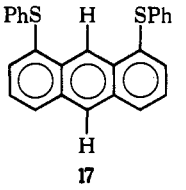
penyllithium, gave a good yield of **16**. Such a procedure was not effective for the conversion of **7** to **9**.

The preparation of diaryl sulfides by nucleophilic aromatic substitution of aromatic halides by the method of Adams[4] uses cuprous thiophenolates in quinoline at 200°, but the more reactive haloanthraquinones react under milder conditions with potassium carbonate and thiophenols in boiling *n*-amyl alcohol, to give thioaryl substituted anthraquinones. The method of Adams and Ferretti[4] was unsuccessful in converting 1,8-dichloroanthrone (**7f**) or 1,8-dichloro-9-isopropenylanthracene (**9f**) to the corresponding thioethers, **7a** and **9a**.

Anthrones and anthracenes might be expected, from a consideration of electronic effects, to be less reactive toward nucleophiles than are anthraquinones. In addition, the anthrones may react with a basic nucleophile to give the unreactive anthranolate anion, thus preventing the nucleophilic displacement from occurring. Another factor which may contribute to the greater reactivity of anthraquinone **5** is the relief of steric interactions between chlorine and carbonyl oxygen in the transition state for attack of nucleophile at positions 1 or 8.

A dramatic substituent effect is observed for the reduction of anthraquinones to anthrones. The reduction of 1,8-dichloroanthraquinone (**5**) with aluminum powder in sulfuric acid gives 1,8-dichloro-9-anthrone as the major product while tin and hydrochloric acid in acetic acid gives mainly 4,5-dichloro-9-anthrone.[5] Reduction of 1,8-diarylthioanthraquinone (**6**) with tin and hydrochloric acid in acetic acid gives the 1,8-di(arylthio)-9-anthrones (**7**). The favored site of reduction of anthraquinones changes from the 9 position to the 10 position on changing the 1,8-substituents from chloro to arylthio.

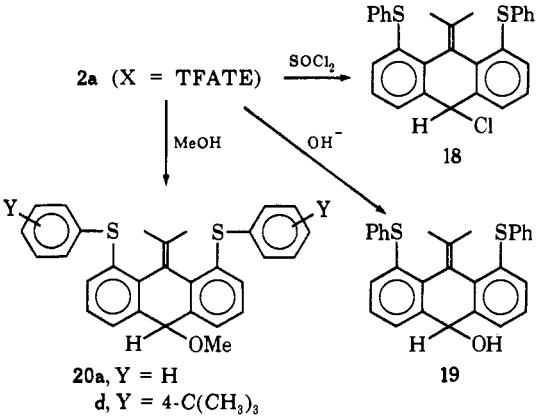
Anthracene **17** from the reduction of **6a** with zinc in aqueous ammonia has a characteristic nmr spectrum with the peak due to the 9 proton (between



17

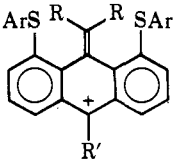
the two sulfur atoms) at δ 9.58 and the 10 proton at δ 8.37. The assignments of the anthracene ring protons given in the Experimental Section were made on the basis of analogy to the completely assigned 9-isopropenylanthracene (**9**) nmr spectra.

Protonations of **16** or **9** with trifluoroacetic acid (TFA) or anhydrous fluoroboric acid in TFA give **1** or **2**, but with hydrogen chloride or aqueous fluoroboric acid they give other products. Failure of the latter routes is perhaps explained by the observation that **2a** (X = trifluoroacetate, TFATE) is converted by the chloride ion in thionyl chloride to **18** and by sodium

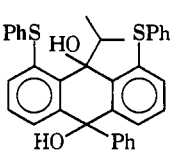


hydroxide to **19**, reactions involving attack by nucleophiles at the 10 position of the anthracene ring. Methanolysis of **2a** or **2d** leads to methyl ethers **20a** and **20d**. The chloride (**18**), when treated with BCl_3 or BF_3 in liquid SO_2, gave intractable tars containing none of sulfonium ion **2a**. It is suspected that our failure to find conditions for the purification of **2** by recrystallization is explicable in terms of the ease with which nucleophilic attack occurs on the anthracene ring.

Sulfonium ions **3** and **4** were prepared by routes taking advantage of the greater reactivity of the less hindered 10 carbonyl of **6**. The selectivity shown in the reaction by phenylmagnesium bromide was much greater than that seen for less bulky, more reactive methyllithium. The diols (**11** or **12**) obtained by this route undergo an acid dehydration to form sulfonium ion **3** or **4**, presumably *via* a cationic intermediate, or transition state, such as **21** (R = H).



21



22

Treatment of **22** with acid gave mixtures of products whose nmr spectra lacked methyl peaks. This failure to form sulfonium ion *via* **21** (R = CH_3), when contrasted with the high yield of the ring closure to give sulfonium ion when R = H, could reflect a steric

(4) (a) R. Adams and A. Ferretti, *J. Amer. Chem. Soc.*, **81**, 4927 (1959); (b) R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, **29**, 277 (1957).

(5) E. de B. Barnett, N. F. Goodway, and J. L. Wiltshire, *Chem. Ber.*, **63**, 472 (1930).

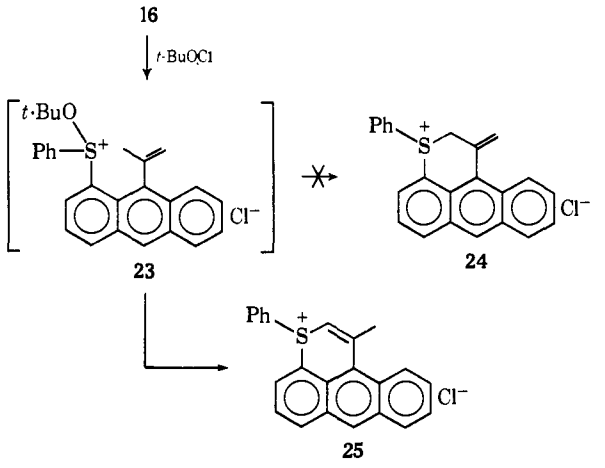
Table I. Nuclear Magnetic Resonance Parameters[a]

Compd	δ (2-H)	δ (3-H)	δ (4-H)	J_{23}	J_{34}	J_{24}	δ (Y)	Y =	δ (10-H)	δ (CH_3)	δ(C= CH)	δ(C= CH)	δ(9-CH_3)	δ(10-CH_3)
6a	7.07		8.00	7.0	7.5	1.5	7.3	H						
b	7.19	7.48	8.07	7.3	8.5	1.4	2.51	4-CH_3						
c	7.19		8.06	7.2	8.5	1.4	2.46	3-CH_3						
d	7.21	7.45	8.05	7.2	8.2	1.3	1.43	4-$C(CH_3)_3$						
e	7.12	7.33	8.02	7.7	8.2	1.4	3.96	4-OCH_3						
14	7.05		8.01		7.5	1.3								
7a			6.67		6.7	2.6	7.3	H	4.38					
b			6.78		7.8	1.8	2.45	4-CH_3	4.42					
d			6.75		6.8	2.4	1.38	4-$C(CH_3)_3$	4.34					
15	8.34[b]		6.20[c]	7.5[d]					4.38					
8a							7.35	H	4.21	1.53	5.71	5.23		
b							2.33	4-CH_3	4.15	1.52	5.70	5.25		
d							1.30	4-$C(CH_3)_3$	4.10	1.52	5.65	5.16		
f									4.12	1.27	5.58	5.25		
9a							7.4	H	8.50	2.88	5.72	5.45		
b			7.85		7.0	2.0	2.32	4-CH_3	8.33	2.82	5.66	5.45		
d	7.44		7.89[e]	7.2	7.8	1.6	1.32	4-$C(CH_3)_3$	8.36[e]	2.86	5.69	5.46		
f	7.95	7.55	8.13[e]	7.5	8.5	1.7			8.66[e]	2.70	5.85	5.33		
16							7.3	H	8.43	2.55	5.57	5.05		
10a	6.67			7.7		2.0								
b	6.75			8.0		2.0	2.44	4-CH_3						
11a							7.4	H					2.48	
b							2.35	4-CH_3					2.48	
12a[f]	6.90	7.14	7.67	6.5	7.5	1.5	7.4	H					2.28	1.45
b							2.35	4-CH_3					2.15	1.58
c							2.24	3-CH_3					2.11	1.55
d							1.25	4-$(C(CH_3)_3$					2.22	1.50
e							3.80	4-OCH_3					2.17	1.52

[a] Integrals of assigned peaks correspond within ±10%; in $CDCl_3$. [b] δ(8-H). [c] δ(5-H). [d] $J_{5,8}$. [e] $J_{4,10} = J_{5,10} = 0.5$ Hz. [f] In DMSO-d_6.

requirement for the process twisting the double bond of **21** by 90° to the geometry appropriate for the sulfonium ion.

Treatment of **16** with *tert*-butyl hypochlorite, in a



process presumed to involve the intramolecular oxidation of the isopropenyl group of **23** by the *tert*-butoxysulfonium chloride functional group,[6] did not give the expected allylic sulfonium ion **24**, but gave the same vinyl sulfonium cation (**25**) as did treatment of **16** with sulfuryl chloride. The nmr spectra of the products contain dissimilar aromatic peaks, but all have a one-proton quartet near δ 6.7 coupled (J = 1.3 Hz) with a three-proton doublet near δ 3.0. These peaks are assigned to the vinyl proton and methyl group of **25**. The elemental analysis of **25** from treatment of **16** with sulfuryl chloride was correct for the elemental composition of **25** plus a strongly coordinated molecule of hydrogen chloride.

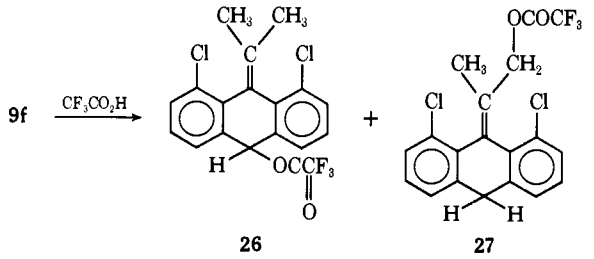
Structure assignments for the intermediates of importance in this synthesis study depend heavily upon nmr spectroscopy. Table I lists typical spectroscopic features for which assignments were made. Unassigned peaks are listed for individual compounds in the Experimental Section. Ring-current effects deshielding substituents at C_{10}, and to a lesser degree at C_4 and C_5, were important in providing a basis for making nmr assignments.[7] Long-range (4-bond) coupling of *ca.* 0.5 Hz could be resolved in some spectra (**9d** and **9f**) in peaks assigned to protons at C_4 and C_{10}. Spectroscopic parameters for the 2-thioniaaceanthrene cations (**1**, **2**, **3**, and **4**) are described in an accompanying paper which details the interpretation of temperature-dependent spectra of these species.

Anchimerically Accelerated Olefin Protonation. Isopropenylanthracenes **16** and **19a–e**, having neighboring arylthio substituents, are easily protonated at the isopropenylmethylene to give cyclic sulfonium ions **1** and **2**. Evidence that these protonation reactions are anchimerically accelerated by S–C bond formation simultaneous with C–H bond formation is seen in several observations. (a) The protonation of the isopropenylanthracene, **9f**, having poorly nucleophilic chloro substituents at positions 1 and 8, with trifluoroacetic acid in chloroform, is slow enough to be followed by nmr. Under identical conditions, protonations of isopropenylanthracenes **16**, **9a**, **9b**, and **9e**, all of which have neighboring arylthio substituents, are complete before a spectrum can be obtained. (b) The products seen in the nmr of the protonation reaction mixture involve protonation not only

(6) C. R. Johnson and J. J. Rigau, *J. Amer. Chem. Soc.*, **91**, 5398 (1969).

(7) See R. B. Mallion, *J. Chem. Soc. B*, 681 (1971), for a recent discussion of this point.

at the isopropenylmethylene to form **26** but also at



26 **27**

the anthracene 10 position to form **27**. The possible intermediacy of chloronium ions in the process leading to **26** and **27** cannot be ruled out. It is clear, however, that the protonation at the methylene is slow enough to allow protonation at the 10 position to compete. (c) Protonation of **16** with CF_3CO_2D is shown to be irreversible by the demonstration that only one deuterium atom is incorporated per molecule of **1** formed. (d) The incorporated deuterium is not equally distributed between cis and trans methyl groups of **1**. The cis/trans ratios were sometimes larger and sometimes smaller than unity, by factors as large as 2, depending on the solvent and conditions used for the protonation. The reasons for this variation are not understood.

This last observation tells us that the S–C bond formation must either be concerted with C–H bond formation or follow it within a period of time short relative to that required for conformational equilibration by rotation about an S–C bond. The earlier mentioned observations of more rapid protonation of the olefins with suitable neighboring sulfur substituents strongly suggest that the former is the case and that the reactions are anchimerically accelerated.

Experimental Section

Melting points are corrected. Infrared spectra were obtained with a Perkin-Elmer Model 137 Infracord and Model 237B spectrophotometer. Ultraviolet and visible spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer. The nmr spectra were obtained by Mr. R. Thrift and his associates. Microanalyses were carried out by Mr. J. Nemeth and his associates. Mass spectra were run on an Atlas CH4 mass spectrometer by Mr. J. Wrona. The listings of nmr peaks in the following sections omit data included in Table I.

General Method A for Preparation of Arylthio-Substituted Anthraquinones 6 and 14. To 500 ml of pyridine, 0.5 equiv of chloroanthraquinone and 0.55 mol of a cuprous thiophenolate[8] were added and heated to reflux with stirring under nitrogen. After 4 hr the resulting solution was poured onto a mixture of 500 ml of hydrochloric acid (concentrated) and *ca.* 1 kg of crushed ice. The precipitate was collected, dried *in vacuo*, and dissolved in chloroform, and this solution was dried with magnesium sulfate, filtered, and evaporated to give the crude product.

General Method B for Preparation of Arylthio-Substituted Anthraquinones (6). To 150 ml of *n*-amyl alcohol, 0.05 mol of 1,8-dichloroanthraquinone (**13b**), 0.105 mol of a thiophenol, and 0.125 mol of potassium carbonate were added, and the mixture was heated to boiling for 12 hr under nitrogen. The mixture was filtered on cooling, and the solids were washed thoroughly with ether. The organic product was extracted from the inorganic solids and evaporation of the resulting chloroform solution gave the crude product.

1-Phenylthioanthraquinone (14). On treatment with cuprous thiophenolate by method A, 1-chloroanthraquinone (**13**) gave two crops of yellow powder from benzene: mp 189–190° and mp 187–189° (total yield, 52%) (lit.[9] mp 185°); nmr ($CDCl_3$) δ 8.36–8.17 (m, 2.0, 5- and 8-H) and 7.81–7.27 (m, 8.1, phenyl protons and 3-, 6-, and 7-H); ir ($CHCl_3$) 1672 cm^{-1} (C=O).

1,8-Di(phenylthio)anthraquinone (6a). On treatment with cuprous thiophenolate by method A, 1,8-dichloroanthraquinone (**5**) gave an 80% yield of red-orange crystals from benzene: mp 187–188°; nmr ($CDCl_3$) δ 7.76–7.73 (m, 12.7, phenyl protons and 3- and 6-H); ir ($CHCl_3$) 1670 and 1640 cm^{-1} (C=O); uv (cyclohexane) 238 nm (ε 35,000), 266 (12,000), and 300 (8300). *Anal.* Calcd for $C_{26}H_{16}O_2S_2$: C, 73.55; H, 3.77; S, 15.11. Found: C, 73.42; H, 3.76; S, 15.14.

1,8-Di(4-tolylthio)anthraquinone (6b). On treatment with cuprous 4-thiocresolate[8] by method A, **5** gave a 31% yield of red-orange needles from chloroform, mp 256–257°, and on treatment with 4-thiocresol by method B, a yield of 32% was obtained: mp 254–256°; nmr ($CDCl_3$) δ 7.59 (d, 4.2, J = 7.7 Hz, phenyl protons) and 7.35 (d, 5.1, J = 7.6 Hz, phenyl protons and $CHCl_3$ imp); ir ($CHCl_3$) 1670 and 1640 cm^{-1} (C=O); uv (cyclohexane) 238 nm (ε 55,000), 268 (25,000), and 303 (13,000).

1,8-Di(3-tolylthio)anthraquinone (6c). On treatment with 3-thiocresol by method B, **5** gave a 54% yield of red-orange crystals from benzene: mp 176–179°; nmr ($CDCl_3$) δ 7.52–7.36 (m, 10.2, phenyl protons and 3- and 6-H); ir ($CHCl_3$) 1670 and 1640 cm^{-1} (C=O). *Anal.* Calcd for $C_{28}H_{20}O_2S_2$: C, 74.30; H, 4.45; S, 14.17. Found: C, 74.18; H, 4.71; S, 13.80.

1,8-Di(4-*tert*-butylphenylthio)anthraquinone (6d). On treatment with 4-*tert*-butylbenzenethiol by method B, **5** gave a 40% yield of red-orange cyrstals from benzene: mp 249–252°; nmr ($CDCl_3$) δ 7.58 (d, 8.1, J = 2.0 Hz, phenyl protons); ir ($CHCl_3$) 1670 and 1640 cm^{-1} (C=O). *Anal.* Calcd for $C_{34}H_{34}O_2S_2$: C, 75.80; H, 6.36; S, 11.90. Found: C, 75.98; H, 6.07; S, 11.94.

1,8-Di(4-anisylthio)anthraquinone (6e). On treatment with 4-methoxybenzenethiol by method B, **5** gave a 48% yield of red-orange crystals from chloroform: mp 264–268°; nmr ($CDCl_3$) δ 7.55 (d, 4.3, J = 8.8 Hz, phenyl protons) and 7.01 (d, 4.0, J = 8.8 Hz, phenyl protons); ir ($CHCl_3$) 1670 and 1640 cm^{-1} (C=O). *Anal.* Calcd for $C_{28}H_{20}O_4S_2$: C, 69.40; H, 4.16; S, 13.23. Found: C, 68.85; H, 4.35; S, 12.96.

General Method for Reducing Arylthioanthraquinones (6 and 14) to 9-Anthrones (7 and 15). To a mixture of 0.05 mol of anthraquinone and 10 g (0.085 g-atom) of granulated tin in 400 ml of boiling acetic acid, 24 ml (0.1 mol) of hydrochloric acid was added over 1 hr. After boiling for 2 hr, the precipitate that formed was collected, washed with ether, and dissolved in chloroform. The chloroform solution was washed with 5% sodium bicarbonate solution and water, dried ($MgSO_4$), and evaporated to give the crude product.

1-Phenylthio-9-anthrone (15). Recrystallization of the crude product from the reduction of **14** with chloroform gave two crops of yellow crystals: mp 159–160° and mp 155–157° (total yield, 80%); nmr ($CDCl_3$) δ 8.34 (d of multiplets, 1.0, J = 7.5 Hz, 8-H), 7.68–7.05 (m, 10.2, phenyl protons and 2-, 3-, 4-, 6-, and 7-H); ir ($CHCl_3$) 1650 cm^{-1} (C=O). *Anal.* Calcd for $C_{20}H_{14}OS$: C, 79.44; H, 4.67; S, 10.60. Found: C, 79.15; H, 4.70; S, 10.11.

1,8-Di(phenylthio)-9-anthrone (7a). The reduction of **6a** gave orange crystals which were recrystallized from benzene to give a 55% yield of product: mp 238–240°; nmr ($CDCl_3$) δ 7.32 (m, 10.9, C_6H_5S-) and 7.14–7.02 (m, 3.9); ir ($CHCl_3$) 1640 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 410 (100), 333 (32), 77 (9). *Anal.* Calcd for $C_{26}H_{18}OS_2$: C, 76.06; H, 4.42. Found: C, 76.35; H, 4.35.

1,8-Di(4-tolylthio)-9-anthrone (7b). Reduction of **6b** in 50% acetic acid–dioxane gave a 47% yield of **7b** on recrystallization from chloroform, mp 290–295°, nmr ($CDCl_3$) δ 7.57–7.05 (m, 13.0), ir ($CHCl_3$) 1640 cm^{-1} (C=O).

1,8-Di(4-*tert*-butylphenylthio)-9-anthrone (7d). Reduction of **6d** gave a 47% yield of yellow crystals, mp 227–230°, on recrystallization of the crude product from benzene, nmr ($CDCl_3$) δ 7.50–7.08 (m, 12.2), ir ($CHCl_3$) 1640 cm^{-1} (C=O).

1,8-Di(phenylthio)anthracene (17). A suspension of 10 g (23 mmol) of **6a** in 130 ml of 20% ammonia was heated on the steam bath and 33 g (0.5 g-atom) of zinc dust was added in 1.0-g portions over 1 hr. The mixture was then heated for 10 hr and filtered. The filtrate was extracted with acetone in a Soxhlet extractor, the acetone evaporated, and the residue dissolved in isopropyl alcohol. This alcohol solution was treated with a few drops of concentrated hydrochloric acid and the crystals which separated were collected and chromatographed with silica gel and benzene giving 1.54 g (17%) of a yellow solid, mp 144–150°. Recrystallization from benzene gave 0.9 g (12%); mp 148–149°; nmr ($CDCl_3$) δ 9.58 (s, 0.9, 9-H), 8.37 (s, 0.9, 10-H), 7.90 (d, 1.9, J = 7.5 Hz, 4- and 5-H), 7.62 (d, 2.0, J = 6.5 Hz, 2- and 7-H), and 7.43–7.03 (m, 12.5, phenyl

(8) Prepared by the method of ref 4.

(9) H. Decker and A. Wursch, *Justus Liebigs Ann. Chem.*, **348**, 238 (1906).

protons and 3- and 6-H). *Anal.* Calcd for $C_{26}H_{18}S_2$: C, 79.15; H, 4.60. Found: C, 79.11; H, 4.64.

Isopropenyllithium. To a stirred suspension of 1.4 g (0.2 g-atom) of freshly cut lithium wire in 100 ml of ether, 12.3 g (0.1 mol) of isopropenyl bromide (Aldrich, purissimus) was added, dropwise, at a rate sufficient to maintain reflux. After 1 hr, the concentration of lithium reagent was 0.6–0.7 *M* (60–70%) as determined by titration.[10]

1-Phenylthio-9-isopropenylanthracene (16). To 50 ml of 0.6 *M* isopropenyllithium in ether, 3.0 g (10.0 mmol) of **15** dissolved in 100 ml of benzene was added rapidly at room temperature, and after 10 min, the reaction mixture was poured onto crushed ice. The benzene–ether layer was separated, washed (H_2O), dried (Na_2SO_4), and evaporated and the residue recrystallized from benzene to give 1.65 g (51%) of yellow crystals: mp 114–115°; nmr ($CDCl_3$) 8.00 (m, 2.6), 7.49 (m, 4.44), and 7.27 (m, 5.8, C_6H_5S–). *Anal.* Calcd for $C_{23}H_{18}S$: C, 84.62; H, 5.56. Found: C, 84.46; H, 5.47.

General Method for Preparation of 9-Hydroxy-9-isopropenyl-9,10-dihydroanthracenes (8). A solution of 0.01 mol of an anthrone (7) in 500 ml of dry benzene or tetrahydrofuran (THF) was cooled to 0–5°. The solution was stirred under N_2 as isopropenyllithium (1.1 equiv in ether) was added. Immediately after the orange solution turned yellow, the reaction was quenched by adding 10 ml of 50% water–methanol solution. The solution was dried (Na_2SO_4) and evaporated, and the crude product was dissolved in chloroform for recrystallization.

1,8-Di(phenylthio)-9-isopropenyl-9-hydroxy-9,10-dihydroanthracene (8a). Treatment of 7a with isopropenyllithium in benzene gave a 70% yield of white powder: mp 208–209°; nmr ($CDCl_3$) δ 7.36 (m, 10.2, phenyl protons), 7.14 (m, 6.0), and 6.54 (s, 0.9, OH); mass spectrum (70 eV) *m/e* (rel intensity) 426 (11), 408 (94), 331 (34), 221 (100), 77 (15). *Anal.* Calcd for $C_{23}H_{24}OS_2$: C, 76.95; H, 5.34. Found: C, 76,28; H, 5.47.

1,8-Di(4-tolylthio)-9-isopropenyl-9-hydroxy-9,10-dihydroanthracene (8b). Treatment of a suspension of **7b** in THF with isopropenyllithium gave a poor yield (16%) of product (white powder, mp 254–259°) since the undissolved anthrone did not react; nmr ($CDCl_3$) δ 7.42–7.05 (m, 14.3, aromatic protons) and 6.55 (s, 1.1, –OH).

1,8-Di(4-*tert*-butylphenylthio)-9-isopropenyl-9-hydroxy-9,10-dihydroanthracene (8d). An 80% conversion of **7d** to product, as indicated by nmr spectroscopy, was obtained on treatment of its benzene solution with isopropenyllithium. The product was not purified further, and its nmr spectrum was determined by subtracting the peaks of the starting material from the spectrum of the crude product; nmr ($CDCl_3$) δ 7.30–7.05 (m, 16.3, aromatic protons) and 6.53 (s, 0.9, –OH).

1,8-Dichloro-9-isopropenyl-9-hydroxy-9,10-dihydroanthracene (8f). The crude product obtained on treatment of **7f** in benzene with isopropenyllithium was a mixture of starting material and **8f** (88%) as indicated by nmr spectroscopy. The carbinol **8f** was not isolated, and its nmr spectrum was obtained by subtracting the peaks due to starting material from the nmr spectrum of the mixture; nmr ($CDCl_3$) δ 7.38–7.06 (m, 6.3, aromatic protons) and 4.55 (s, 1.0, –OH).

General Method for Dehydration of 9-Hydroxy-9-isopropenyl-9,10-dihydroanthracenes (8) to 9-Isopropenylanthracenes (9). To an ice-cold solution of 10 mmol of the carbinol in 100 ml of ether and 3.5 ml (45 mmol) of pyridine, 1.0 ml (14 mmol) of thionyl chloride was added, and after standing at room temperature for 3 hr, the solution was poured onto *ca.* 50 g of crushed ice, and the precipitate was extracted with benzene. The benzene solution was washed with water and 2% HCl solution, dried ($MgSO_4$), and evaporated to give the crude product.

1,8-Di(phenylthio)-9-isopropenylanthracene (9a). Dehydration of **8a** gave an 81% yield of white crystals: mp 143–144°, on recrystallization of the crude product from ether; nmr ($CDCl_3$) δ 8.00–7.30 (m, 6.2) and 7.38 (m, 10.5, C_6H_5S–). *Anal.* Calcd for $C_{29}H_{22}S_2$: C, 80.15; H, 5.10; S, 14.75. Found: C, 79.84; H, 5.03; S, 14.51.

1,8-Di(4-tolylthio)-9-isopropenylanthracene (9b). Dehydration of **8b** gave a 75% yield of pale yellow crystals from 95% ethanol: mp 191–192°; nmr ($CDCl_3$) δ 7.42–7.00 (m, 13.2, aromatic protons). *Anal.* Calcd for $C_{31}H_{26}S_2$: C, 80.47; H, 5.66; S, 13.86. Found: C, 80.17; H, 5.62; S, 14.51.

1,8-Di(4-*tert*-butylphenylthio)-9-isopropenylanthracene (9d). Dehydration of crude **8d** (80% pure) gave an 17% overall yield of yellow crystals from benzene: mp 191–194°; nmr ($CDCl_3$) δ 7.31–7.14 (m, 11.0, phenyl protons and 3- and 6-H). *Anal.* Calcd for $C_{37}H_{38}S_2$: C, 81.42; H, 6.83; S, 11.75. Found: C, 81.08; H, 7.07; S, 11.88.

1,8-Dichloro-9-isopropenylanthracene (9f). Dehydration of crude **8f** (88% pure) gave a 25% yield overall, after chromatography of the crude product on Activity I Woelm alumina with benzene, of yellow platelets, mp 145–148°. *Anal.* Calcd for $C_{17}H_{12}Cl_2$: C, 71.09; H, 4.22; Cl, 24.69. Found: C, 70.73; H, 4.26; Cl, 25.22.

1,8-Di(phenylthio)-10-phenyl-10-hydroxy-9-anthrone (10a). To a solution of 2.2 g (5 mmol) of **6a** in dry THF at 0°, 5.0 ml (5 mmol) of 1.0 *M* phenylmagnesium bromide was added and the reaction quenched by adding 6 ml of a saturated ammonium chloride solution. The THF solution was decanted from the inorganic solids and evaporated to an oil which crystallized from ether giving 1.5 g (60%) of pale orange crystals; mp 240–244°; nmr ($CDCl_3$) δ 7.65–6.94 (m, 21.6, aromatic protons) and 3.02 (broad s, 0.9, OH); ir ($CHCl_3$) 3500 cm^{-1} (OH) and 1640 cm^{-1} (C=O).

1,8-Di(4-tolylthio)-10-hydroxy-9-anthrone (10b). To a suspension of 10 g (22 mmol) of **6b** in 250 ml of dry THF, 11 ml (22 mmol) of 2.0 *M* phenylmagnesium bromide was added and the mixture stirred for 1.0 hr while warming to room temperature before quenching the reaction with 25 ml of a saturated ammonium chloride solution. The solution was decanted and the inorganic "sludge" washed with more THF. After several recrystallizations of the crude product, from evaporation of the combined THF solutions, 3.0 g (25%) of bright yellow crystals were obtained: mp 268–270°; nmr ($CDCl_3$) δ 7.59–6.85 (m, 19.0, aromatic protons) and 2.98 (s, 1.0, OH): *Anal.* Calcd for $C_{34}H_{26}O_2S_2$: C, 76.95; H, 5.31; S, 12.08. Found: C, 77.08; H, 5.01; S, 12.28.

1,8-Di(phenylthio)-9-methyl-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (11a). To a solution of 1.5 g (3 mmol) of **10a** in 20 ml of ether, 40 ml (12 mmol) of 0.3 *M* methyllithium in ether was added and the reaction quenched with water. The ether extract was dried ($MgSO_4$), concentrated to 50 ml, and gave on standing 0.34 g (22%) of white solid: mp 210–220°; nmr ($CDCl_3$) δ 7.55–6.75 (m, 22.6, aromatic protons), 5.22 (s, 0.9, OH), and 2.38 (s, 0.6, OH).

1,8-Di(4-tolylthio)-9-methyl-10-phenyl-9,10-dihydroxy-9,10-dihydroanthracene (11b). To a solution of 2.65 g (5 mmol) of **10b** in 150 ml of dry THF at −78°, 5.9 ml (10 mmol) of 1.7 *M* methyllithium in ether was added and the reaction quenched by adding 10 ml of 50% methanol–water. The solution was evaporated and the residue extracted with methylene chloride, which gave 1.6 g (59%) of pale yellow crystals, mp 253–256°, after concentration to 20 ml and dilution with 20 ml of ether: nmr ($CDCl_3$) δ 7.44–6.74 (m, 20.3, aromatic protons), 5.20 (s, 1.0, OH), 2.48 (s, 2.7, 9-CH_3), and 2.35 (s, 6.7, $C_6H_3CH_3$ and OH).

1,8-Di(phenylthio)-9,10-dimethyl-9,10-dihydroxy-9,10-dihydroanthracene (12a). To a solution of 4.3 g (10 mmol) of **6a** in 100 ml of dry THF at −78°, 30 ml (21 mmol) of 0.7 *M* methyllithium in ether was added. The THF solution was poured into water (~500 ml) and the benzene extract of this mixture was washed with water, dried ($MgSO_4$), and evaporated to a reddish residue giving 3.4 g (74%) of white solid, mp 234–238°, on recrystallization with chloroform.

1,8-Di(4-tolylthio)-9,10-dimethyl-9,10-dihydroxy-9,10-dihydroanthracene (12b). To a solution of 10 g (22.2 mmol) of **6b** in 400 ml of dry THF at −78°, 27 ml (44.4 mmol) of 1.63 *M* methyllithium in ether was added and 10 ml of 50% CH_3OH–H_2O was added to quench the reaction. This solution was evaporated and the residue extracted with chloroform. The solution was concentrated to 50 ml and 3.6 g (34%) of white crystals formed: mp 234–236°; nmr ($CDCl_3$) δ 7.44–7.02 (m, 15.7, aromatic protons), 5.58 (s, 0.9, OH), and 5.24 (s, 1.0, OH).

1,8-Di(3-tolylthio)-9,10-dimethyl-9,10-dihydroxy-9,10-dihydroanthracene (12c). To a solution of 5 g (11 mmol) of **6c** in 100 ml of dry THF at −78°, 15 ml (22.5 mmol) of 1.4 *M* methyllithium in ether was added and the reaction quenched with 5 ml of water. The excess water was removed ($MgSO_4$) and the filtrate evaporated to a yellow residue which gave 0.9 g (17%) of crystals, mp 168–171°, after several recrystallizations from chloroform and benzene; nmr ($CDCl_3$) δ 7.42–7.01 (m, 15.1, aromatic protons) and 5.39 (s, 1.7, OH). *Anal.* Calcd for $C_{30}H_{28}O_2S_2$: C, 74.34; H, 5.82; S, 13.23. Found: C, 74.28; H, 5.92; S, 12.99.

1,8-Di(4-*tert*-butylphenylthio)-9,10-dimethyl-9,10-dihydroxy-9,10-dihydroanthracene (12d). To a solution of 5.3 g (10 mmol) of **6d** in 200 ml of dry THF at −78°, 12.4 ml (20 mmol) of 1.62 *M* methyllithium in ether was added and the reaction quenched with 50% methanol–water (10 ml). The solution was evaporated and the residue extracted with methylene chloride giving 0.9 g of yellow

(10) D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, 85, 743 (1963).

powder on dilution with methanol and cooling: nmr ($CDCl_3$) δ 7.2–6.7 (m, 14.8, aromatic protons), 5.33 (singlet, 1.3, OH), and 2.07 (s, 1.4, OH). Recrystallization from benzene gave 0.65 g of white solid, mp 143–144°. *Anal.* Calcd for $C_{36}H_{40}O_2S_2$: C, 76.01; H, 7.09. Found: C, 75.69; H, 7.01.

1,8-Di(4-methoxyphenylthio)-9,10-dimethyl-9,10-hydroxy-9,10-dihydroanthracene (20f). To a solution of 4.5 g (9.7 mmol) of **14f** in 400 ml of dry THF at −78°, 12 ml (19.5 mmol) of 1.62 *M* MeLi–ether was added and the reaction quenched with 50% methanol–water (10 ml). The solution was evaporated and extracted with methylene chloride, which gave 1.2 g of pale yellow crystals, mp 202–205°, on concentrating to 50 ml: nmr ($CDCl_3$) δ 7.45–6.87 (m, 14.0, aromatic protons) and 5.64 (s, 1.5, OH). *Anal.* Calcd for $C_{30}H_{28}O_4S_2$: C, 69.74; H, 5.46; S, 12.41. Found: C, 69.49; H, 5.39; S, 12.26.

1,8-Di(phenylthio)-9-isopropyl-10-phenyl-9,10-dihydroanthracene (22). To a solution of 1.0 g (2.0 mmol) of **10a** in 200 ml of benzene, 20 ml (6.0 mmol) of 0.3 *M* isopropyllithium[11] was added. After refluxing for 5 min, the reaction mixture was quenched with water, dried ($MgSO_4$), and reduced in volume to 25 ml. The crude product obtained on cooling was recrystallized (benzene) to give 230 mg of yellow needles: mp 226–228°; nmr ($CDCl_3$) δ 8.00 (d of d, 1.8, J = 3.0 and 6.0 Hz, 4- and 5-H), 7.60–7.00 (m, 21.2, aromatic protons), 5.10 (s, 1.2, OH), 2.43 (br s, 0.9, OH), 1.5 (m, 1.2, $CH(CH_3)_2$, and 0.88 (d, 5.9, J = 6.0 Hz, $CH(CH_3)_2$).

1,1-Dimethyl-2-phenyl-2-thioniaaceanthrene Tetrafluoroborate (1, X = BF_4). Anhydrous HCl gas was passed through a solution of 1.77 g (5.4 mmol) of **16** in 50 ml of ether for several hours. The solvent was replaced by methanol and 1.2 g (6.2 mmol) of $AgBF_4$ in methanol added. The product was precipitated by adding the methanol solution to ether giving 1.3 g (58%): mp 195–197°; nmr (ethylene carbonate) δ 8.89 (s, 1.0, 6-H), 8.65–7.45 (m, 13.2), 2.52 (s, 3.1, CH_3), and 2.08 (s, 2.9, CH_3). *Anal.* Calcd for $C_{23}H_{19}BF_4S$: C, 66.62; H, 4.49. Found: C, 66.45; H, 4.73.

Deuteration of 16. To a 200-mg sample of **16** in 0.4 ml of $CDCl_3$ was added 3 equiv (0.15 ml) of CF_3CO_2D. After 24 hr, the nmr spectrum indicated 98% conversion to sulfonium ion **1**. Integrals of the methyl region showed the δ 2.52 peak (tentatively assigned to the trans methyl) to be 15% larger than the δ 2.08 peak assigned to the cis methyl). This corresponds to a 60:40 preference for the protonation pathway leading to deuteration of the higher field methyl. A parallel experiment in which olefin **16** was suspended in solvent CF_3CO_2D gave clean incorporation of one deuteron per molecule (by comparison of aromatic and methyl peak integrals). The two methyl peaks were equal in area showing a lack of specificity under these conditions. In a third experiment, excess dry DCl in ether was added to an ether solution of **16**. The precipitate of sulfonium chloride **1**, which was formed over several hours, was dissolved in $CDCl_3$ for nmr examination. A 2:1 preference for deuteration of the *lower* field methyl was seen in this case.

1,1-Dimethyl-2-phenyl-10-phenylthio-2-thioniaaceanthrene Trifluoroacetate (2a, X = TEATE). Evaporation *in vacuo* of a methylene chloride solution of **9a** diluted with TFA gave an amorphous, dark residue: nmr at 0° (TFA) δ 9.03 (s, 0.9, 6-H), 8.62 (d, 0.8, J = 8 Hz, 5-H), 8.43 (d, 1.0, J = 8 Hz, 7-H), 8.21 (d, 1.8, J = 7 Hz, 3- and 9-H), 7.98 (m, 1.1, 4-H), 7.80 (m, 1.1, 8-H), 7.62 (m, 3.0, phenyl protons), 7.18 (m, 4.7, phenyl protons), 6.90 (m, 2.6, phenyl protons), 2.99 (s, 3.0, CH_3), and 2.50 (s, 3.0, CH_3).

1,1-Dimethyl-2-(4-tolyl)-10-(4-tolylthio)-2-thioniaaceanthrene Trifluoroacetate (2b, X = TFATE). Evaporation *in vacuo* of a methylene chloride solution of **9b** diluted with TFA gave an amorphous, dark residue: nmr at 0° (TFA) δ 8.95 (s, 0.9, 6-H), 8.58 (d, 1.0, J = 7.5 Hz, 5-H), 8.33 (d, 1.1, J = 7 Hz, 7-H), 8.12 (m, 1.9, 3- and 9-H), 7.94 (t, 1.0, J = 7.5 Hz, 4-H), 7.60 (t, 1.0, J = 6.5 Hz, 1.0, 8-H), 7.38 (m, 3.8, $^+SC_6H_4CH_3$), 7.05 (d, 2.0, J = 7 Hz, $SC_6H_4CH_3$), 6.87 (d, 2.0, J = 7 Hz, $SC_6H_4CH_3$), 2.94 (s, 3.0, CCH_3), 2.48 (s, 6.0, CCH_3 and $^+SC_6H_5CH_3$), and 2.29 (s, 3.1, $SC_6H_4CH_3$).

1,1-Dimethyl-2-(*tert*-butylphenyl)-10-(*tert*-butylphenylthio)-2-thioniaaceanthrene Fluoroborate (2d, X = BF_4). To a solution of 250 mg (0.45 mmol) of **9d** in 5 ml of methylene chloride, 0.65 ml (0.45 mmol) of 0.7 *M* fluoroboric acid in TFA–TFAA was added and the solution evaporated *in vacuo* to give an amorphous, dark residue: nmr at 0° (TFA) δ 9.00 (s, 0.9, 6-H), 8.61 (d, 0.9, J = 8 Hz, 5-H), 8.36 (d, 1.0, J = 8 Hz, 7-H), 8.23 (d, 0.9, J = 6 Hz, 3-H), 8.1–7.9 (m, 2.8, 9-H and $^+SC_6H_4$–), 7.60 (m, 2.0, $^+SC_6H_4$–), 7.47 (t, 1.0, J = 7 Hz, 4-H), 7.15 (d, 2.0, J = 7.5 Hz, SC_6H_4–), 7.05 (broad s, 1.2, 8-H), 6.8 1(d, 1.9, J = 7.5 Hz, SC_6H_4–), 2.95 (s, 2.8, CH_3), 2.48 (s, 2.8, CH_3), 1.34 (s, 9.1, $^+SC_6H_4C(CH_3)_3$), and 1.21 (s, 9.1, SC_6H_5-$C(CH_3)_3$).

General Method for Preparation of Sulfonium Ions (3 and 4) from Acidic Dehydration of 9,10-Dihydroxy-9,10-dihydroanthracenes. A suspension of 2.0 mmol of diol (**11** and **12**) in 50 ml of methanol was saturated with anhydrous HCl, and the residue, from evaporation of the resulting solution, dried *in vacuo* over KOH to give crude product.

2-Phenyl-6-methyl-10-phenylthio-2-thioniaaceanthrene Chloride (3a, X = Cl). Acidic dehydration of **12a** gave a 55% yield of yellow crystals from methanol: mp 194–197° dec; nmr (SO_2 at 50°) δ 3.27 (s, 3.0, 6-CH_3), 6.49 (d, 1.1, J = 17.5 Hz, $^+SCH_2$), 6.11 (d, 1.1, J = 17.5 Hz, $^+SCH_2$), 6.90–7.60 (complex m, 10.3, aromatic protons), 7.70–8.10 (quintet, 2.3, J = 8 Hz, 4- and 8-H), 8.31 (t, possibly overlapping doublets, 1.8, J = 7.0 Hz, and 3- and 9-H), and 8.85 (d, 1.8, J = 8.0 Hz, 5- and 7-H); nmr (SO_2 at 50°) δ 3.27 (s, 3.0, CH_3), 6.40 (s, 2.1, CH_2), 7.18 (s, 10.2, C_6H_5), 7.83 (t, 2.0, J = 7.0 Hz, 4- and 8-H), 8.14 (d, 1.9, J = 6.0 Hz, 3- and 9-H), and 8.67 (d, 1.9, J = 8.0 Hz, 5- and 7-H). *Anal.* Calcd for $C_{28}H_{21}S_2Cl$: C, 73.58; H, 4.63; S, 14.03. Found: C, 73.61; H, 4.88; S, 13.94.

2-Phenyl-6-methyl-10-phenylthio-2-thioniaaceanthrene Fluoroborate (3a, X = BF_4). To a solution of 1.0 g (2.2 mmol) of **3a** (X = Cl) in 50 ml of methanol, 0.5 g (2.5 mmol) of silver fluoroborate in 8 ml of methanol was added, and the yellow precipitate that formed was washed with methanol until white. The methanol washings were boiled down to 50 ml and 0.28 g (26%) of yellow crystals formed: mp 239–258° dec; nmr at 30° (TFA) δ 8.71 (d, 1.8, J = 9.0 Hz, 5- and 7-H), 8.14 (d, 1.9, J = 6.5 Hz, 3- and 9-H), 7.85 (t, 2.1, $J \simeq$ 8.0 Hz, 4- and 8-H), 7.06 (m, 9.8, C_6H_5), 6.47 (d, 1.1, J = 18 Hz, 1-H), 6.10 (d, 1.1, J = 18 Hz, 1-H), and 3.31 (s, 2.9, CH_3); nmr at −20° ($SOCl_2$) δ 8.62 (t, 1.8, J = 9 Hz, 5- and 7-H), 8.07 (t, 1.9, J = 7 Hz, 3- and 9-H), 7.84 (quartet, 2.1, J = 8 Hz, 4- and 8-H), 7.60–6.84 (m, 9.8, $^+SC_6H_5$ and SC_6H_5), 6.43 (d, 1.1, J = 18 Hz, 1-H), 6.10 (d, 1.1, J = 18 Hz, 1-H), and 3.26 (s, 2.9, CH_3). *Anal.* Calcd for $C_{28}H_{21}BF_4S_2$: C, 66.15; H, 4.16. Found: C, 66.08; H, 4.09.

2-(4-Tolyl)-6-methyl-10-(4-tolylthio)-2-thioniaaceanthrene Chloride (3b, X = Cl). Acidic dehydration of **12b** gave an 83% yield of yellow crystals from methanol: mp 196–199° dec; nmr at −10° (TFA) δ 8.70 (d, 1.0, J = 8.0 Hz, 5-H), 8.66 (d, 1.0, J = 8.0 Hz, 7-H), 8.11 (d, 1.0, J = 7.0 Hz, 3-H), 8.06 (d, 1.0, J = 7.0 Hz, 9-H), 7.86 (t, 1.0, J = 8.0 Hz, 4-H), 7.75 (t, 1.1, J = 8.0 Hz, 8-H), 7.19 (d, 2.0, J = 8.0 Hz, $^+SC_6H_4$), 7.03 (d, 1.9, J = 8.0 Hz, $^+SC_6H_4$), 6.81 (d, 1.9, J = 7.5 Hz, SC_6H_4), 6.61 (d, 1.9, J = 7.5 Hz, SC_6H_4–), 6.42 (d, 0.9, J = 17 Hz, CH_2), 6.05 (d, 1.0, J = 17 Hz, CH_2), 3.27 (s, 3.1, 10-CH_3), 2.45 (s, 3.0, $^+SC_6H_5CH_3$) and 2.16 (s, 3.0, SC_6H_4-CH_3); nmr at −15° (methanol-d_4) δ 8.56 (d, J = 8.0 Hz, 5-H), 8.52 (d, J = 8.0, 7-H), 8.19 (d, J = 7.0 Hz, 3-H), 7.95 (d, J = 7.0 Hz, 9-H), 7.70 (complex multiplet, 4- and 8-H), 7.08 (d, J = 8.0 Hz, $^+SC_6H_4$–), 6.99 (d, J = 8.0 Hz, $^+SC_6H_4$–), 6.76 (d, J = 9.0 Hz, SC_6H_4–), 6.59 (d, J = 9.0 Hz, SC_6H_4), 6.30 (d, J = 17 Hz, CH_2), 5.76 (d, J = 17 Hz, CH_2), 3.05 (s, 10-CH_3), 2.28 (s, $^+SC_6H_4CH_3$), and 2.05 (s, $SC_6H_5CH_3$); nmr at 90° (MeOH-d_4) δ 8.57 (d, J = 8.0 Hz, 5- and 7-H), 8.06 (d, J = 7.0 Hz, 3- and 9-H), 7.70 (d of d, J = 7.0 Hz and J = 8.0 Hz, 4- and 8-H), 6.97 (s, SC_6H_4–), 6.30 (s, CH_2), 3.14 (s, 10-CH_3), and 2.19 (s, $SC_6H_4CH_3$); nmr at −20° ($SOCl_2$) δ 8.63 (d, 2.0, J = 9 Hz, 5- and 7-H), 8.07 (overlapping, 2.0, 3- and 9-H), 7.76 (quintet, 2.1, J = 8 Hz, 4- and 8-H), 7.22 (d, 1.9, J = 9 Hz, $^+SC_6H_4$–), 7.12 (d, 2.0, J = 9 Hz, $^+SC_6H_4$–), 6.93 (d, 2.0, J = 8 Hz, SC_6H_4–), 6.77 (d, 2.0, J = 8 Hz, SC_6H_4–), 6.57 (d, 1.1, J = 17 Hz, 1-H), 6.39 (d, 1.0, J = 17 Hz, 1-H), 3.25 (s, 3.0, 6-CH_3), 2.36 (s, 3.0, $SC_6H_4CH_3$), and 2.20 (s, 2.9, $SC_6H_4CH_3$). *Anal.* Calcd for $C_{30}H_{25}ClS_2$: C, 74.27; H, 5.19. Found: C, 74.39; H, 5.04.

2-(3-Tolyl)-6-methyl-10-(3-tolylthio)-2-thioniaaceanthrene Chloride (3c, X = Cl). Acidic dehydration of **12c** gave a 75% yield of yellow crystals from methanol: mp 190–195° dec; nmr at −10° (TFA) δ 8.72 (t, 1.9, J = 7.5 Hz, 5- and 7-H), 8.17 (d, 2.0, J = 6.5 Hz, 3- and 9-H), 7.91 (t, 1.0, J = 1.5 Hz, 4-H), 7.78 (t, 0.9, J = 7.5 Hz, 8-H), 7.52 (d, 1.0, J = 8.0 Hz, aromatic proton), 7.30 (t, 1.1, J = 8.0 Hz, aromatic proton), 7.02–6.69 (m, 4.9, aromatic protons), 6.55–6.40 (m, 2.0, aromatic proton and a 1-H), 6.04 (d, 1.0, J = 16.0 Hz, 1-H), 3.31 (s, 3.0, 6-CH_3), 2.32 (s, 3.0, $^+SC_6H_4CH_3$), and 2.05 (s, 3.0, $SC_6H_4CH_3$); nmr at −20° ($SOCl_2$) δ 8.63 (overlapping doublets, 1.9, 5- and 7-H), 8.07 (t, 2.0, J = 9 Hz, 3- and 9-H), 7.76 (quintet, 2.0, J = 9 Hz, 4- and 8-H), 7.34–6.48 (complex m, 9.5, aromatic protons and a 1-H), 6.07 (d, 1.1, J = 16 Hz, 1-H), 3.25 (s, 2.9, 6-CH_3), 2.26 (s, 3.0, $^+SC_6H_4CH_3$), and 2.09 (s, 3.0, $SC_6H_4CH_3$).

(11) J. A. Landgrebe and J. D. Shoemaker, *J. Amer. Chem. Soc.*, 89, 4465 (1967).

2-(4-*tert*-Butylphenyl)-6-methyl-10-(4-*tert*-butylphenylthio)-2-thioniaaceanthrene Chloride (3d, X = Cl). Acidic dehydration of **12d** gave a 31% yield of yellow crystals from methanol: mp 190° dec; nmr at −20° ($SOCl_2$) δ 8.56 (d, 1.6, *J* = 8 Hz, 5- and 7-H), 8.05 (overlapping doublets, 2.1, 3- and 9-H), 7.85 (quintet, 2.2, *J* = 8 Hz, 4- and 8-H), 7.45 (d, 4.0, *J* = 8 Hz, $^+SC_6H_4$), 7.33 (d, 4.1, *J* = 8 Hz, $^+SC_6H_4$), 7.21 (d, 4.1, *J* = 8 Hz, SC_6H_4), 6.95 (d, 4.0, *J* = 8 Hz, SC_6H_4), 6.51 (d, 1.0, *J* = 16.5 Hz, 1-H), 6.25 (d, 1.0, *J* = 16.5 Hz, 1-H), 3.24 (s, 2.7, 6-CH_3), 1.26 (s, 8.9, $-C(CH_3)_3$), and 1.17 (s, 8.9, $-C(CH_3)_3$); nmr at −10° (TFA) δ 8.72 (d, 1.7, *J* = 9 Hz, 5- and 7-H), 8.02 (t, 2.0, *J* = 7 Hz, 3- and 9-H), 7.84 (t, 1.0, *J* = 7 Hz, 4-H), 7.70 (t, 1.0, *J* = 8 Hz, 8-H), 7.57 (d, 2.0, *J* = 8 Hz, $^+SC_6H_4-$), 7.26 (overlapping doublets, 3.8, $^+SC_6H_4-$ and SC_6H_4-), 6.84 (d, 1.9, *J* = 8 Hz, SC_6H_4-), 6.58 (d, 1.1, *J* = 16 Hz, 1-H), 6.27 (d, 0.9, *J* = 16 Hz, 1-H), 3.30 (s, 2.9, 6-CH_3), 1.35 (s, 9.1, $^+SC_6H_4C(CH_3)_3$), and 1.23 (s, 8.9, $SC_6H_4C(CH_3)_3$).

2-(4-Methoxyphenyl)-6-methyl-10-(4-methoxyphenylthio)-2-thioniaaceanthrene Chloride (3e, X = Cl). Acidic dehydration of **12e** gave a 26% yield of yellow crystals from methanol: mp 190° dec; nmr at −20° ($SOCl_2$) δ 8.85 (t, 2.0, *J* = 9 Hz, 5- and 7-H), 8.02 (d, 1.0, *J* = 8 Hz, 3-H), 7.89 (d, 1.0, *J* = 6 Hz, 9-H), 7.78 (t, 1.0, *J* = 6 Hz, 4-H), 7.65 (t, 1.0, *J* = 6 Hz, 8-H), 7.13 (d, 2.1, *J* = 8 Hz, aromatic protons), 6.86 (overlapping doublets, 4.2, aromatic protons), 6.66 (d, 1.8, *J* = 10 Hz, aromatic protons), 6.48 (d, 1.1, *J* = 16 Hz, 1-H), 6.07 (d, 1.0, *J* = 16 Hz, 1-H), 3.82 (s, 3.0, $^+SC_6H_4OCH_3$), 3.66 (s, 2.9, $SC_6H_4OCH_3$), and 3.19 (s, 2.7, 6-CH_3); nmr at −10° (TFA) δ 8.70 (d, 1.0, *J* = 9 Hz, 5-H), 8.56 (d, 1.0, *J* = 9 Hz, 7-H), 8.15 (d, 1.0, *J* = 6 Hz, 3-H), 8.03 (d, 1.0, *J* = 6 Hz, 9-H), 7.94 (t, 1.0, *J* = 9 Hz, 4-H), 7.70 (t, 1.0, *J* = 6 Hz, 8-H), 7.14 (d, 2.1, *J* = 8 Hz, $^+SC_6H_4OCH_3$), 6.93 (d, 2.1, *J* = 8 Hz, $^+SC_6H_4OCH_3$), 6.76 (d, 2.1, *J* = 7 Hz, $SC_6H_4OCH_3$), 6.65 (d, 2.1, *J* = 7 Hz, $SC_6H_4OCH_3$), 6.34 (d, 0.9, *J* = 17 Hz, 1-H), 5.98 (d, 0.9, *J* = 17 Hz, 1-H), 3.96 (s, 3.0, $^+SC_6H_4OCH_3$), 3.84 (s, 3.0, $SC_6H_4OCH_3$), and 3.23 (s, 2.9, 6-CH_3). *Anal.* Calcd for $C_{30}H_{25}O_2ClS_2$: C, 69.68; H, 4.87. Found: C, 69.68; H, 4.63.

10-(4-Tolyl)-6-phenyl-2-(4-tolylthio)-2-thioniaaceanthrene Chloride (4b, X = Cl). Acidic dehydration of **11b** gave a 71% yield of yellow crystals from methanol: mp 190° dec; nmr at −10° (TFA) δ 8.20–7.97 (m, 3.9, 3-, 5-, 7-, and 9-H), 7.70–7.11 (m, 10.8, 6-C_6H_5, 4-H, 8-H, and $^+SC_6H_4CH_3$), 6.88–6.62 (m, 5.2, $SC_6H_4CH_3$ and a 1-H), 6.24 (d, 1.1, *J* = 16 Hz, 1-H), 2.51 (s, 3.0, $^+SC_6H_4CH_3$), and 2.20 (s, 3.0, $SC_6H_4CH_3$). *Anal.* Calcd for $C_{35}H_{27}ClS_2$: C, 77.32; H, 4.87. Found: C, 77.56; H, 5.04.

10-(4-Tolyl)-6-phenyl-2-(4-tolylthio)-2-thioniaaceanthrene Fluoroborate (4b, X = BF_4). To a solution of 0.5 g (0.9 mmol) of **4b** (X = Cl) in 100 ml of methanol, 0.18 g (0.9 mmol) of silver fluoroborate in 7.6 ml of methanol was added and the precipitate filtered. The volume of the solution was reduced to 30 ml giving 0.22 g (24%) of yellow crystals: mp 190° dec; nmr at −10° (TFA) δ 8.18–7.93 (m, 4.1, 3-, 5-, 7-, and 9-H), 7.71–7.14 (m, 11.1, $^+SC_6H_4CH_3$, 6-C_6H_5, 4- and 8-H), 6.85–6.55 (m, 4.9, $SC_6H_4CH_3$ and a 1-H), 6.21 (d, 0.9, *J* = 17 Hz, 1-H), 2.49 (s, 3.0, $^+SC_6H_4CH_3$), and 2.19 (s, 3.0, $SC_6H_4CH_3$). *Anal.* Calcd for $C_{35}H_{27}BF_4S_2$: C, 70.23; H, 4.55. Found: C, 70.39; H, 4.42.

Protonation of 9f. A $CDCl_3$ solution of **9f** was treated with an approximately twofold excess of TFA, and the progress of the protonation reaction was followed by nmr. Starting material was still present after several minutes. Complete reaction (after 12 hr) gave a mixture of products with a nmr spectrum compatible with the postulated mixture of **26** and **27** (*ca.* 2:1): 100-MHz nmr ($CDCl_3$) δ 2.17 and 2.22 (unresolved singlets, 5.0, CH_3 of **26** and **27**), 4.06 and 4.12 (AB doublets, 0.8, $ArCH_2Ar$ of **27**, J_{AB} = 12 Hz), 5.26 and 5.52 (AB doublets, 0.7, $=CCH_2OCOCF_3$ of **27**, J_{AB} = 13), 6.3–6.5 (m, 2.0, from CH of **26** and **27**), 6.8–7.1 (m, 2.0, aromatic CH of **26** and **27**), 7.2–7.4 (m, 3.2, aromatic CH of **26** and **27**, $CHCl_3$, and $CHOCOCF_3$ of **26**).

1,8-Di(phenylthio)-9-dimethylmethylene-10-chloro-9,10-dihydroanthracene (18). A sample of **2a** (X = TFATE), prepared from 100 mg (0.23 mmol) of **9a** on treatment with TFA in methylene chloride, was dissolved in thionyl chloride, and on evaporation a yellow solid was obtained and recrystallized from benzene: mp 187–190°; nmr ($CDCl_3$) δ 7.37–6.92 (m, 16.2, aromatic protons), 5.80 (s, 0.9, 10-H), and 2.00 (s, 5.9, $=C(CH_3)_2$). *Anal.* Calcd for $C_{29}H_{23}ClS_2$: C, 73.94; H, 4.92. Found: C, 74.20; H, 4.93.

1,8-Di(phenylthio)-9-dimethylmethylene-10-hydroxy-9,10-dihydroanthracene (19). On treatment with TFA, 500 mg (1.1 mmol) of **9a** was converted to **2a** (X = TFATE), which was dissolved in 25 ml of dioxane with 0.3 g of sodium hydroxide, heated for 1 hr on a steam bath, diluted with water, and extracted with ether. The ether extract was washed (5% HCl and H_2O), dried ($MgSO_4$), and evaporated to a white powder, 320 mg (62%); nmr ($CDCl_3$) δ 7.36–6.95 (m, 17.1, aromatic protons), 5.40 (broad s, 0.9, OH, exchanges D_2O), 5.20 (s, 1.0, 10-H), and 2.01 (s, 5.8, $=C(CH_3)_2$).

Without further purification, the product was dissolved in thionyl chloride and heated on a steam bath for 1 hr. Evaporation of the solution gave a yellow solid, **18**: nmr ($CDCl_3$) δ 7.36–6.88 (m, 18.7, aromatic protons), 5.78 (s, 0.9, 10-H), and 1.94 (s, 6.0, $=C(CH_3)_2$).

1,8-Di(phenylthio)-9-dimethylmethylene-10-methoxy-9,10-dihydroanthracene (20). On treatment with TFA, 100 mg (0.23 mmol) of **9a** was converted to **2a** (X = TFATE), which was dissolved in chloroform and added to methanol. The resulting precipitate was collected, dried, and dissolved in chloroform-*d*: nmr ($CDCl_3$) δ 7.35–6.97 (m, 21.0, aromatic protons), 4.99 (s, 0.9, 10-H), 3.25 (s, 2.7, $-OCH_3$), and 2.00 (s, 6.0, $=C(CH_3)_2$).

1,8-Di(4-*tert*-butylphenylthio)-9-dimethylmethylene-10-methoxy-9,10-dihydroanthracene (28). On treatment with TFA, 100 mg (0.18 mmol) of **9d** was converted to **2d** (X = TFATE), which was dissolved in chloroform and added to methanol. The resulting precipitate was collected, dried, and dissolved in chloroform-*d*: nmr ($CDCl_3$) δ 7.28–6.92 (m, 13.9, aromatic protons), 4.96 (s, 0.9 10-H), 3.25 (s, 2.9, $-OCH_3$), 1.99 (s, 5.9, $=C(CH_3)_2$), and 1.30 (s, 18.3, $-C(CH_3)_3$).

1-Methyl-3-phenyl-3-thionia-3*H*-benzo[*m*,*n*]anthracene (25). To a solution of 1.0 g (3.0 mmol) of **16** in 50 ml of methylene chloride cooled in an ice bath, 0.25 ml (3.1 mmol) of sulfuryl chloride was added. On standing overnight at room temperature, red crystals formed, 0.68 g (60%); mp 212° dec; nmr (SO_2) δ 8.70 (s, 0.9, 7-H), 8.60–8.32 (m, 3.0), 8.15–7.65 (m, 6.3), 7.37–7.24 (m, 2.9), 6.83 (q, 1.1, *J* = 1.3 Hz, =CH), and 2.97 (d, 3.1, *J* = 1.3 Hz, $-CH_3$, double irradiation of this peak collapses the quartet at δ 6.83); nmr (TFA) δ 8.72 (s, 1.0, 7-H), 8.42 (s, 1.3), 8.38 (s, 1.7), 8.15–7.40 (m, 6.1), 7.33 (d, 2.9, *J* ≃ 2.0 Hz), 6.65 (q, 0.9, *J* = 1.3 Hz, =CH), and 3.02 (d, 2.9, *J* = 1.3 Hz, CH_3). *Anal.* Calcd for $C_{23}H_{18}SCl_2$: C, 69.52; H, 4.56; Cl, 17.85. Calcd for $C_{23}H_{17}SCl$: C, 76.54; H, 4.75; Cl, 9.82. Found: C, 69.83; H, 4.46; Cl, 19.72.

Treatment of 0.65 g (2.0 mmol) of **16** in 10 ml of methylene chloride with 0.25 ml (2.05 mmol) of *tert*-butyl hypochlorite at −70° in the dark gave, after standing at room temperature for 5 days, 0.33 g (45%) of red crystals: nmr (TFA) δ 8.88 (s, 1.0, 7-H), 8.68–8.47 (m, 3.0), 8.28–7.29 (m, 9.5), 6.85 (q, 1.0, *J* = 1.3 Hz, =CH), and 3.09 (d, 3.0, *J* = 1.3 Hz, $=CCH_3$).

Acknowledgment. Partial support for this research was provided by National Science Foundation Grant No. GP-13331, and through a Departmental grant from the National Science Foundation which provided partial funding for a 220-MHz nmr spectrometer.