Thiabenzenes. IV. Synthesis and Ylidic Properties of 1-Methyl-3,5-diphenylthiabenzene and 1-Aryl-2-methyl-2-thianaphthalenes[1a]

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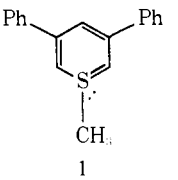
Abstract: The synthesis of 1-methyl-3,5-diphenylthiabenzene (**1**) and 1-aryl-2-methyl-2-thianaphthalenes (**16** and **17**) by proton abstraction from the corresponding thiinium (**9**) or thiochromenium (**15b, c**) salts is described. Nmr and uv spectral data and deuterium exchange studies are discussed in light of possible bonding descriptions for the tetravalent sulfur atom incorporated in the ring systems examined. An ylidic (as opposed to aromatic) bonding structure is proposed for the "thiaaromatics." The data presented in support of ylidic character in **1**, **16**, and **17** are consistent with those previously reported in support of ylidic character in thiabenzene 1-oxides (*e.g.*, **2**).

Continuing interest[2-6] in the study of $p\pi$–$d\pi$ type bonds resulting from overlap of d AO's of second-row elements with p AO's of carbon or other first-row elements has prompted our further consideration of the possibility of transmission of conjugative effects through a tetravalent sulfur center. The potential of either "ylidic" or "aromatic" character in a system possessing such a sulfur atom in a conjugated ring system having $4n + 2$ π electrons has led us to the study of *S*-methylthiabenzenes[7] and *S*-methylthianaphthalenes, both novel classes of compounds having unusual bonding requirements and characteristics.

Since the initial discovery that 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2**) could be readily prepared by the reaction of dimethyloxosulfonium methylide with 1,3-diphenylpropynone,[8a] and that this reaction had reasonably general applicability for the preparation of other 1-methyl-3,5-disubstituted-thiabenzene 1-oxides,[8b,9] we have concentrated our efforts on means of converting these thiabenzene 1-oxides, specifically **2**, to 1,3,5-trisubstituted thiabenzenes having tetravalent sulfur in a conjugated six π-electron system. Whereas the 1-oxides were required by the oxidation state of sulfur to invoke $2p\pi$–$3d\pi$ overlap at the C–S–C linkage, the thiabenzenes suffer no such restriction. In fact, Price and coworkers[10-12] during the last 13 years have set forth several bonding proposals for the related *S*-arylthiabenzenes and *S*-arylthianaphthalenes which they have prepared, some involving the use of sulfur d orbitals and others requiring only s and p orbitals for conjugative overlap at the C–S–C linkage. Other bonding schemes for related heterocyclic systems having second-row elements with available d orbitals have also been proposed.[2-4,13,14] These theoretical bonding descriptions have raised the question of whether or not *through* conjugation may occur at the heteroatom and have led us to undertake this study of the preparation of *S*-methylthiabenzenes and *S*-methylthianaphthalenes in hope of obtaining physical data which would provide a clearer picture of bonding in these unusual heterocycles.

1-Methyl-3,5-diphenylthiabenzene

Our interest in the reduction of thiabenzene 1-oxides[8b] has been focused mainly on the possibility of cleaving the sulfoxide S–O bond in **2** to give 1-methyl-3,5-diphenylthiabenzene (**1**) directly. Thiabenzene **1**



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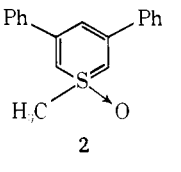


2

would be of particular interest because it would have different proton substitution on the S-ring than thiabenzene I and related S-aryl 2,4,6-trisubstituted thiabenzenes reported by Price, *et al.*[11,15] Hence it should be possible to observe by ^1H nmr the effective shielding of the protons at the 2, 4 and 6 positions of the S-ring of **1** and thereby determine whether ylene-like resonance

(1) (a) Abstracted in part from the Ph.D. Dissertations of Ronald Lee Harris, Washington University, 1970, and James Allen Miles, Washington University, 1973; (b) Alfred P. Sloan Foundation Fellow, 1973–1975; (c) National Science Foundation Trainee, 1968–1969; (d) NDEA Predoctoral Trainee, 1969–1970; National Institutes of Health Predoctoral Fellow, 1970–1972.

(2) (a) K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969), and references cited therein; (b) "Organic Compounds of Sulfur, Selenium and Tellurium," Vol. 2, D. H. Reid, Sr. Ed., The Chemical Society, London, 1973, pp 341–351.

(3) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, pp 158–176.

(4) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 430–436.

(5) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970); W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 6205 (1971); A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *ibid.*, **93**, 6507 (1971).

(6) K. Zahradnik, *Advan. Heterocycl. Chem.*, **5**, 1 (1965).

(7) A preliminary report describing the preparation and properties of 1-methyl-3,5-diphenylthiabenzene (1) has been published: A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

(8) (a) A. G. Hortmann, *J. Amer. Chem. Soc.*, **87**, 4972 (1965); (b) A. G. Hortmann and R. L. Harris, *ibid.*, **93**, 2471 (1971).

(9) Several recent reports which describe preparations of other novel thiabenzene 1-oxides include (a) T. R. Williams and D. J. Cram, *J. Org. Chem.*, **38**, 20 (1973); (b) A. C. Barnes, P. D. Kennewell, and J. B. Taylor, *J. Chem. Soc., Chem. Commun.*, 776 (1973); (c) E. Cohnen and J. Mahnke, *Chem. Ber.*, **106**, 3368 (1973); Y. Tamura, T. Miyamoto, H. Taniguichi, K. Sumoto, and M. Ikeda, *Tetrahedron Lett.*, 1729 (1973); C. M. Harris, J. J. Cleary, and T. M. Harris, *J. Org. Chem.*, **39**, 72 (1974). See also ref 18–22 cited in ref 8b.

(10) C. C. Price, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 6N.

(11) (a) C. C. Price and G. Suld, *J. Amer. Chem. Soc.*, **84**, 2090 (1962); (b) C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971); (c) C. C. Price and H. Pirelahi, *ibid.*, **37**, 1718 (1972).

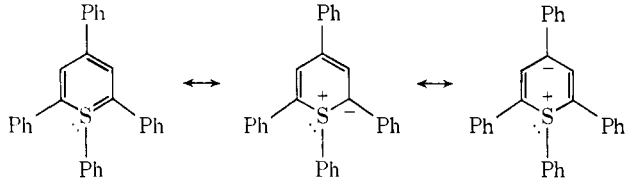
(12) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962.

(13) D. P. Craig, *Chem. Soc., Spec. Publ.*, No. 12, 343 (1958).

(14) M. J. S. Dewar, E. A. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

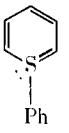
(15) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 1770 (1961).

forms or ylide-like resonance forms are more important contributors to the structure of monocyclic thiabenzenes.



I Ia IIb

Price, *et al.*, have suggested that the bonding about tetravalent sulfur in I and related compounds permits a ring current which causes the deshielding of the ring protons on the periphery of the S-ring.[11] They have used this theory to explain the low-field chemical shifts (7–8 ppm) observed for the S-ring protons at the 3 and 5 positions in I and related thiabenzenes[11] and similar shifts noted *for all of the protons* on the S-ring of II.[16]



II

On the other hand, the chemical and physical properties found to be characteristic of 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2**) are strongly suggestive of an ylide-like, rather than ylene-like or aromatic system.[8] If the bonding in **1** were similar to that in **2** (with an electron pair in **1** replacing the oxygen atom in **2**) it might be expected on the basis of generally observed trends among sulfur ylides that the sulfonium ylide **1** would be more ylide like (more basic) than the sulfoxonium ylide **2** and hence that **1** would display even more carbanionic character at C-2, C-4, and C-6 than that already established by several techniques (^{1}H nmr, ^{13}C nmr, deuterium exchange studies)[8b] for **2**. This prediction is obviously incompatible with the conclusions of Price, *et al.*, with regard to the aromatic character presumed to be displayed by I and especially II (nmr, uv, dpm data).[11,16] Therefore, it was felt that a comparison of the properties of **1**, especially with regard to uv spectra and to the chemical shifts of the S-ring protons with those of I and II, as well as with those of various other "thiaaromatics" described by Price, *et al.*,[11,17] would aid in the determination of the predominant bonding situation in these compounds.

Results

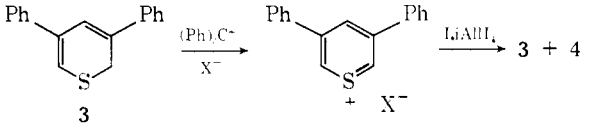
Attempts to Prepare 1-Methyl-3,5-diphenylthiabenzene *via* Direct Deoxygenation of the 1-Oxides. Several attempts to prepare **1** by direct deoxygenation of **2** have been previously described.[8b] An alternative approach to this reduction proved much more useful. Horner and Balzer[18] have reported that optically active phosphine oxides could be readily reduced to optically active phosphines by trichlorosilane. It, therefore, seemed logical to extend the scope of the trichlorosilane reduction to include sulfoxide bonds and, in particular, the sulfoxide bond of **2**. Treatment of **2** with 1 mol equiv of trichlorosilane in benzene at reflux temperature for 9–12 hours did not yield the desired 1-methyl-3,5-diphenylthiabenzene (**1**); instead, the crude product obtained was a mixture of 2*H*- and 4*H*-3,5-diphenylthiopyrans (**3** and **4**, respectively) along with small amounts

3 4

of a third unidentified material. The ratio of the 2*H* and 4*H* isomers varied from 2:1 to 5:4 as determined by nmr analysis of the crude products obtained from several reaction mixtures.[19] The purification of the 2*H* isomer could be effected by recrystallization of the isomer mixture; however, decomposition of the 4*H* isomer was observed to occur in the course of this procedure.

Since the 4*H* isomer decomposed in the purification procedure, efforts were directed to other means of separating and purifying both of the components of the reaction mixture. Chromatography on Florisil or alumina was unsuccessful. However, washing a petroleum ether solution of the crude trichlorosilane reduction product with saturated silver nitrate solution selectively extracted most of the 2*H* isomer into the aqueous layer. Mixtures of 2*H* and 4*H* isomers which were enriched in the 4*H*-thiopyran, **4**, could thus be obtained from the petroleum ether layer; the minor unidentified product mentioned above was also present in the solution enriched in the 4*H* isomer. In several attempts which were made to recrystallize the enriched samples of the 4*H*-thiopyran, **4**, from ethanol, it was noted that only small amounts of the 4*H* compound, but greater amounts of the 2*H* isomer than were originally present, were present in the mother liquors and the crops of crystals obtained. This observation indicated that isomerization of the 4*H*-thiopyran was occurring during recrystallization. Extensive efforts to pinpoint the exact conditions (*e.g.*, thermal, acid catalyzed, Ag^+ catalyzed, etc.) under which this isomerization was occurring using enriched samples of **4** came to naught.[19]

Treatment of a mixture of **3** and **4** (obtained by $HSiCl_3$ reduction of **2**) with trityl tetrafluoroborate[20–22] in methylene chloride yielded, upon addition of diethyl



3 5a, X = BF_4 5b, X = I

(16) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969).

(17) (a) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 2090 (1962); (b) *ibid.*, **84**, 2094 (1962); (c) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963); (d) C. C. Price and D. M. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).

(18) L. Horner and W. Balzer, *Tetrahedron Lett.*, 1157 (1965), and references therein.

(19) Compounds **3** and **4** were readily differentiated by comparison of resonances for the C-2, C-4, and C-6 protons of **3** at δ 3.60 (t, 2, $J \sim 0.7$ Hz), 6.40 (q, 1, $J \sim 0.6$ Hz), and 6.54 (q, 1, $J \sim 0.9$ Hz) with those of the S-ring protons of **4** at δ 3.50 (t, 2, $J = 1.0$ Hz) and 6.33 (t, 2, $J = 1.0$ Hz).

(20) T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, 32, 1558 (1967); 33, 1306 (1968).

(21) I. Degani, R. Fochi, and C. Vincenzi, *Gazz. Chim. Ital.*, **94**, 203 (1964).

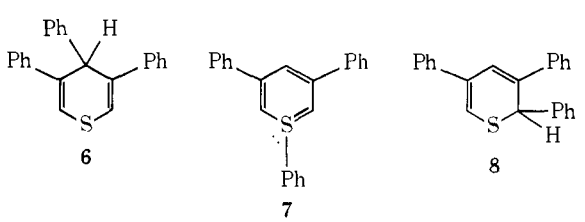
(22) H. Dauben, L. Honnen, and K. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

ether, the novelly substituted thiopyrylium tetrafluoroborate (**5a**) which was also converted to the corresponding iodide (**5b**) with sodium iodide *via* a simple metathesis reaction. Reduction of **5a** with lithium aluminum hydride gave a 1:1 mixture of **3** and **4** only.[23,24] The 4*H* isomer **4** was obtained in low yield and in *ca.* 90% purity after removal of the 2*H* isomer by repeated washings of the mixture of **3** and **4** in petroleum ether with silver nitrate solution.

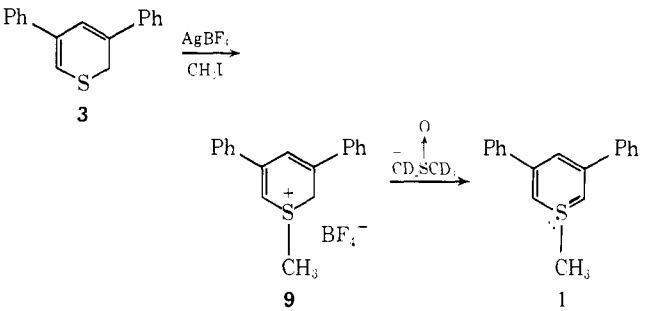
To the best of our knowledge, the procedures developed here represent at present the only published route to simple 3,5-disubstituted thiopyrans and thiopyrylium salts.

Generation and Properties of 1-Methyl-3,5-diphenylthiabenzene. Although the reduction of 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2**) did not yield **1** directly,[8b] the 2*H*- and 4*H*-3,5-diphenylthiopyrans (**3** and **4**) obtained *via* reduction of **2** with trichlorosilane were ideally suited to two potential routes to 1,3,5-trisubstituted thiabenzenes.

The first route explored for the purpose of preparing a 1-substituted 3,5-diphenylthiabenzene had some precedent in the literature and was explored briefly. Price and coworkers have reported on the synthesis of a series of thiabenzenes[11,15–17a,b] by a coupling reaction of aryllithium reagents with thiopyrylium salts. (Other aryl or alkyl metal reagents such as Grignard reagents apparently cannot be used; Degani,[24] Dimroth,[25] and Lüttringhaus[26] all have found that alkyl or aryl magnesium halides undergo reaction at the C-2 and C-4 positions of the S-ring rather than at the sulfonium center.) The goal, then, was to treat 3,5-diphenylthiopyrylium tetrafluoroborate (**5a**) with aryllithium reagents. When **5a** was treated with phenyllithium in diethyl ether at −10°, the crude product had an nmr spectrum which showed absorption peaks at δ 6.10 (d, 1, J = 2.4 Hz), 6.58 (dd, 1, J = 2.4, 0.8 Hz), 6.86 (d, 1, J = 0.8 Hz), and 7.0–7.6 (m, 15).[27a] A recrystallized sample exhibited the same spectrum. The presence of three nonequivalent protons ruled out a symmetrical thiopyran (**6**) and the thiabenzene (**7**) and left as a probable structure 2,3,5-triphenylthiopyran (**8**).[27b] The latter could have been formed by rearrangement of **7**,[11,17b] or it might have been formed by direct attack of phenyllithium at C-2 of **5a**.[24–26]



Another approach, which was investigated concurrently with the method just described was more fruitful and resulted in a two-step synthesis of 1-methyl-3,5-diphenylthiabenzene (**1**). 2*H*-3,5-Diphenylthiopyran (**3**) was first alkylated with excess methyl iodide in the presence of silver tetrafluoroborate to give 1-methyl-3,5-diphenyl-2*H*-thiinium tetrafluoroborate (**9**). (Silver tetrafluoroborate has been used previously to facilitate the alkylation of diphenyl sulfide[28] and 1,4-dithiins[29].) Compound **9** was characterized by microanalytical data and by its nmr spectrum which showed absorption at δ 2.97 (s, 3), 4.78 (d, 2, J ~ 1.0 Hz, H-2), 6.78 (d, 1, J ~ 0.7 Hz, H-6), 7.28 (q, 1, J ~ 0.9 Hz, H-4), and 7.37–7.93 (m, 10). Next, a relatively acidic proton at the methylene group of **9** was removed by base to yield **1** which was characterized by nmr and uv spectroscopy.[30]



A typical nmr experiment for the generation of **1** follows. A solution of **9** in DMSO-d_6 under nitrogen in an nmr tube was treated with 1 mol equiv of *tert*-butyllithium in pentane. An nmr spectrum obtained on the lower DMSO solution (yellow-pale orange) within minutes after generation of **1** remained unchanged during the following 0.5 hr at *ca.* 35°. Peaks at δ 0.85, 1.11, and 1.23 and an absorption envelope beneath these peaks were attributed to dissolved pentane and 2-methyl-2-propane-2-*d* and possibly *tert*-butyl compounds (other than *tert*-butyllithium) which were originally present in the *tert*-butyllithium solution before reaction.[31] A singlet which appeared at δ 1.73 (2.5 H)[32] was assigned to the protons of the *S*-methyl group of **1**. The missing 0.5 proton was found in the DMSO-d_x peak as a result of the occurrence of exchange of some of the *S*-methyl protons of the thiabenzene (**1**) with (presumably) local excesses of methylsulfinyl carbanion-d_5 before complete mixing of the reagents and hence complete generation of **1** had occurred. A doublet at δ 4.03 (2 H, J = 1.7 Hz) was assigned to the H-2 and H-6 protons and a triplet at δ 6.18 (1 H, J = 1.7 Hz) was assigned to H-4. Absorption in the phenyl region between δ 7.21 and 7.82 corresponded to ten protons. The DMSO-d_x peak in the spectrum of **1** had actually increased by ~1.7 protons (±~10%) since the dimethylsulfinyl carbanion-d_5, formed from the reaction of *tert*-butyllithium with DMSO-d_6, had abstracted one proton from C-2 of **9** in

(23) Degani and coworkers[24] had previously demonstrated that lithium aluminum hydride reduction of thiopyrylium iodide gave a mixture of 2*H*-thiopyran and 4*H*-thiopyran in a ratio of 1:9.

(24) I. Degani, R. Fochi, and C. Vincenzi, *Gazz. Chim. Ital.*, **97**, 397 (1967).

(25) K. Dimroth, *Justus Liebigs Ann. Chem.*, **678**, 183 (1964).

(26) A. Lüttringhaus, N. Englehard, and A. Kolb, *Justus Liebigs Ann. Chem.*, **654**, 189 (1962).

(27) (a) These were the only peaks in the spectrum of crude or recrystallized materials. (b) Lack of sufficient material prevented obtention of an analytical sample. The probability that the product was **8** (*cf.* ref 11) led us to abandon this reaction as a promising route to **1**.

(28) V. Franzen, J. F. Schmidt, and C. Mertz, *Chem. Ber.*, 94, 2942 (1961).

(29) T. E. Young and R. Lazarus, *J. Org. Chem.*, **33**, 3370 (1968).

(30) This method has also been applied to the synthesis of phosphabenzenes: G. Märkl, *Angew. Chem.*, **75**, 168, 669, 1121 (1963).

(31) A control sample of *tert*-butyllithium in pentane (1.24 *M*, 0.25 ml) added to 0.2 ml of dimethyl-d_6 sulfoxide showed similar absorption in this region.

(32) In other experiments, the area under the resonance peak for the *S*-methyl group varied over a range corresponding to 0–3 (±10%) protons depending upon the mode of mixing of the DMSO-d_6 and the *tert*-butyllithium solutions during addition of the latter in the generation of **1**.

the formation of **1** and an additional 0.5 proton of the *S*-methyl group of **1** (as mentioned above) before mixing was complete.

As further proof of the existence and structure of **1**, the solution of **1** in the nmr tube was acidified with 1 mol equiv of fluoroboric acid in water to regenerate the starting thiinium salt **9** which showed peaks at δ 2.97 (s), 6.70 (s), and 7.23 (s) corresponding to the peaks of the starting material.[33] (The peak at δ 4.8 present in the spectrum of the starting salt **9** was obscured by the absorption due to water in the solution of the regenerated salt.) The regenerated thiinium salt was recovered by dilution of the nmr sample with acetone, evaporation of the solvent, and addition of water and petroleum ether to the resulting oil; **9** slowly crystallized from the aqueous layer (46% recovery). The recovered material had an nmr spectrum (DMSO-d_6) which showed absorption peaks at δ 2.97 (2.5 H, the same value observed for the *S*-methyl protons in **1**),[32] 4.78 (2 H), 6.77 (1 H), 7.23 (1 H), and 7.40–7.97 ppm (10 H).

In another experiment, thiabenzene **1** was generated by adding *tert*-butyllithium to a solution of **9** in DMSO and then extracted (under nitrogen) into diethyl ether to yield a yellow solution which was evaporated under vacuum without exposing the thiabenzene to air. The resulting orange sticky material was dissolved in CCl_4 and found to contain 50 ± 5% of **1** by nmr analysis.[34] The nmr spectrum (CCl_4 solution) showed resonance peaks at δ 1.72 (s), 3.85 (d, J = 1.7 Hz), and 6.17 (t, J = 1.7 Hz) which were assigned to the S–CH_3, H-2, H-6, and H-4 protons, respectively. The thiabenzene, however, was not stable in CCl_4 and decomposed over the next 1.3 hr to the extent of about 80% as evidenced by nmr monitoring.

Thiabenzene **1** was also generated by reaction of a suspension of **9** in diethyl ether with *tert*-butyllithium under nitrogen at −10°; the resulting yellow solution was concentrated under vacuum giving a yellow gum which immediately turned purple when exposed to air. An nmr spectrum of the purple material in $CDCl_3$ revealed that *ca.* 37 ± 5% of the material was the thiabenzene **1**,[34] but it also decomposed appreciably during about 1 hr.

Further evidence confirming the existence of **1** was obtained in a uv experiment. The thiabenzene **1** was generated by addition of carbonate- and oxygen-free standard sodium hydroxide solution (0.5 ml of 0.101 *N* Fisher reagent) to 2.0 ml of a degassed ethanolic solution of **9** in a cuvette and under argon. The uv spectrum of the thiabenzene showed absorption peaks at 245 (ε 33,700), 275 (ε 14,300, shoulder), and 437 nm (ε 3200). Addition of an equivalent amount of fluoroboric acid solution to neutralize the base present in the cell regenerated the thiinium salt **9**. In a similar uv experiment it was observed that the thiabenzene **1** did not decompose to any significant extent over a period of 1 hr in the basic aqueous medium. It is notable that thiabenzene **1** is quite stable in the polar DMSO and EtOH–H_2O media in which it has been generated, but apparently undergoes rapid decomposition in nonpolar solvents (CCl_4, Et_2O) and in the presence of oxygen.

Deuterium Exchange Experiments with 1-Methyl-3,5-diphenylthiabenzene in Protic Media. Since it had been observed[8] that 1-methyl-3,5-diphenylthiabenzene 1-oxide (**2**) exchanged S-ring protons for deuterium rapidly when solutions of **2** in chloroform-*d* were treated with acetic-d_4 acid and slowly when a solution of **2** in DMSO-d_6 was treated with D_2O, similar experiments were performed with **1**. When a solution of **1** in DMSO-d_6 in an nmr tube (generated as previously described[35]) was treated with acetic-d_4 acid (14 mol equiv excess), an nmr spectrum[36] showed that **1** had rapidly undergone exchange of its S-ring protons for deuterium *and was further deuterated to yield* **9**-d_3 (in contrast to the behavior of **2** in $CDCl_3$[8b] or DMSO-d_6). The nmr spectrum of **9**-d_4 exhibited peaks at 3.00 (s, *2*,[35] S–$CH_{3-x}D_x$), 2.52 (m, DMSO-d_5), and 7.21–7.80 (m, 10) indicating that little, if any, exchange of S-methyl protons occurred. The rapid generation of the spectrum of **9**-d_4 implies that the thiabenzene **1** is a stronger base than acetate ion (in DMSO) and that the deuteron-mediated equilibration between **9**-d_{x+1} ⇌ **1**-d_x in the presence of excess acetic acid-d_1 continues to occur rapidly while the spectrum of **9**-d_1 is being observed but is relatively slow on the nmr time scale.

When a solution of **1** in DMSO-d_6[37] was treated with 10 μl of deuterium oxide, nmr analysis revealed that the S-ring protons exchanged slowly. Approximately 83% of H-2 and H-6 and *ca.* 12% of H-4 in **1** had exchanged in 19 min at *ca.* 35°. The exchange observed here was much faster than that of H-2, H-6 and H-4 of thiabenzene 1-oxide **2** in a similar experiment.[8b] As was observed for S–CH_3 in the latter experiment with **2**, the *S*-methyl protons of **1** also apparently do not undergo exchange under these conditions. Nmr spectra recorded 36 min after the addition of deuterium oxide to the sample of **1** showed no further exchange at H-2 and H-6, some slight additional exchange at H-4, and some decomposition of the thiabenzene **1** as indicated by the appearance of new resonance peaks (of undetermined origin) at 6.72 and 6.65 ppm.

The observation of exchange of the S-ring protons of **1** for deuterium indicates that equilibria may exist between **1**, **9**, and **9a** in the presence of H_2O in DMSO but that the equilibria lie strongly in favor of **1** in this medium. This conclusion suggested the experiment of treating a solution of **9** (25 mg in 0.20 ml of DMSO-d_6) with deuterium oxide (10 μl). Nmr analysis indicated partial exchange of protons on C-2 and C-4 of **9**;[38]

(33) Addition of fluoroboric acid solution to the thiabenzene solution generated some heat and may, as a result, have caused some decomposition of the thiabenzene. The height of the *S*-methyl peak in regenerated **9** was about one-half that in **1**. The heat generated and the consequent dilution of the DMSO-d_6 with water also resulted in loss of pentane from the DMSO-d_6 layer of the sample, as evidenced by changes in the nmr spectrum in the region of δ 0.6–1.4.

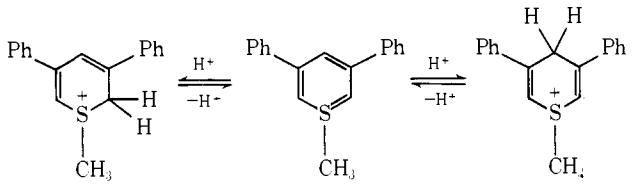
(34) Based on a comparison of the total area of peaks in the phenyl region of the spectrum with the area under peaks due to H-2 and H-6 of **1**.

(35) The spectrum of **1** in DMSO-d_6 used in this experiment exhibited resonance peaks at δ 1.78 (s, 2 [due to partial exchange at S–CH_3 of **1** during generation], S–$CH_{3-x}D_x$), 2.52 (m, DMSO-d_5), 4.08 (d, 2, J = 1.7 Hz, H-2, H-6), 6.19 (t, 1, J = 1.7 Hz, H-4), and 7.21–7.82 (m, 10, Ar–H) prior to treatment of the nmr solution with acetic acid-d_4.

(36) This spectrum was run immediately after mixing the solution of **1** and acetic acid-d_4; the deep orange-red color of the solution of **1** turned to light yellow upon mixing with acetic acid-d_4.

(37) The thiabenzene **1** was generated by treating a solution of **9** (35 mg, 0.1 mmol) in DMSO-d_6 (0.2 ml) in an nmr tube under N_2 at 15° with 0.08 ml (0.1 mmol) of 1.24 *M* *t*-BuLi in pentane.

(38) A known amount of *tert*-butylbenzene had been added as an internal integration standard; its presence obscured the resonance peak due to H-6. Only peaks due to **9** were observable; no peaks due to **9a** were detectable.



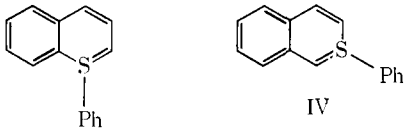
9 1 9a

little or no exchange of the protons of the *S*-methyl group had occurred. A 52% deuterium incorporation at C-2 and a 14% incorporation at C-4[38] was observed after 0.4 hr at *ca.* 35° (probe temperature) followed by 6.9 hr at room temperature; only very small increases (~10%) in the deuterium content at these positions occurred during the next 15.6 hr.[39]

In a similar experiment, the per cent deuterium present at C-2, C-4, and C-6 in the spectrum of **9** after an exchange time of 23 hr was 60, 40, and 15%, respectively.[40] The area under the *S*-methyl resonance peak (compared with that of the Ar–H resonance peak) 23 hr after addition of deuterium oxide was the same (within experimental error) as the area measured 20 min after the addition.

1-Aryl-2-methyl-2-thianaphthalenes

Due to the obvious utility of the method of proton abstraction from thiinium salt **9** in the generation of 1-methyl-3,5-diphenylthiabenzene (**1**), the possibility of extending this method to the generation of other tetravalent sulfur heterocycles, *e.g.*, *S*-alkylthianaphthalenes, seemed promising. Adding to our desire to extend these studies to the preparation of thianaphthalenes was the observation of such diverse chemical and spectral characteristics between 1-*methyl*thiabenzene, **1**, and 1-*phenyl*-thiabenzene (II),[16] in spite of their apparently similar structural characteristics,[41] and the fact that Price and coworkers[17c,d] have also reported on the preparation and properties of several presumably aromatic *S*-arylthianaphthalenes which include III and IV.[42] The need for comparison of the chemical and physical characteristics of III and IV with *S-methyl*thianaphthalenes, hopefully to be prepared by the procedure used for generation of **1**,[43] was thus clear.



III IV

(39) The data recorded after 7.3 hr indicate that there was no exchange (detectable by nmr) of the *S*-methyl protons. A small decrease (~9%) noted in the area under the *S*-methyl resonance after 22.9 hr was probably due to slow decomposition of **9**.

(40) Since the previous experiment indicated little, if any, exchange of the *S*-methyl protons, the area under the peak due to S–CH_3 was taken as an integration standard instead of the –$C(CH_3)_3$ peak of *tert*-butylbenzene.

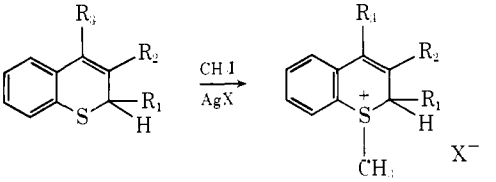
(41) The major difference between 1 and II lies in the marked upfield shifts noted for the S-ring protons of 1 in its nmr spectrum, when compared with the observation that all the protons in II are located in the aromatic region. Thiabenzene II was also noted to have a uv spectrum (max at 246 nm) similar to that of biphenyl, whereas the uv spectrum of 1 has absorption in the visible region (437 nm).

(42) All claimed to be delocalized, aromatic systems on the basis of nmr and dpm data.

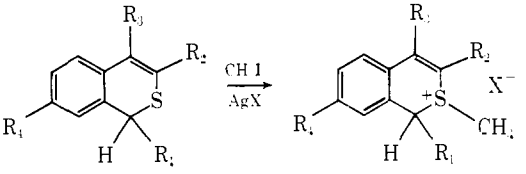
(43) In all cases,[17c,d] the *S*-arylthianaphthalenes were generated *via* coupling of an aryllithium or aryl Grignard reagent with the corresponding thianaphthalenium salt. In two cases,[17d] generation *via* proton abstraction from thiochromenium salts was also claimed.

Results

The presence in the literature of practical methods for the preparation of a variety of substituted and unsubstituted thiochromenes (**12a–e**, **14a–f**)[44–51] opened a



12a,[44–47] $R_1 = R_2 = R_3 = H$ — **13a**. X = BF_4
12b,[48] R_1 = Ph; $R_2 = R_3 = H$ — **13b**. X = ClO_4
12c,[49] R_1 = H; $R_2 = CH_3$; $R_3 = H$ — **13c**. X = BF_4
12d,[26] $R_1 = R_2$ = H; R_3 = Ph — **13d**. X = BF_4
12e,[50] R_1 = H; R_2 = Ph; $R_3 = H$ — **13e**. X = BF_4



14a,[46] $R_1 = R_2 = R_3 = R_4 = H$ — **15a**. X = BF_4
14b. R_1 = Ph; $R_2 = R_3 = R_4 = H$ — **15b**. X = BF_4
14c. R_1 = *p*-ClPh; $R_2 = R_3 = R_4 = H$ — **15c**. X = ClO_4
14d. $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$ — **15d**. X = BF_4
14e. $R_1 = R_2$ = Ph; R_3 = H; R_4 = OCH$_3$ — **15e**. X = BF_4
14f,[51] R_1 = H; R_2 = Ph; R_3 = H; R_4 = OCH$_3$ — **15f**. X = BF_4

ready route to a variety of sulfonium (thiochromenium) salts (**13a–e**, **15a–f**) analogous to the thiinium salt **9** and, therefore, a potentially general procedure[52] for preparation of *S*-methylthianaphthalenes whose chemical and spectral characteristics could be compared to those *S*-arylthianaphthalenes previously reported[17c,d] and claimed to be aromatic in character. This procedure for the generation of thianaphthalenes *via* proton removal from thiochromenium salts is in marked contrast to that used for the preparation of *S*-phenylthianaphthalenes by Price, *et al.*,[17c,d,46] which generally involved coupling of thianaphthalenium salts (V and VI) with phenyllithium.[43,53]

Unfortunately, the procedure used for generating **1** from **9** proved to be less than general for the generation of *S*-methylthianaphthalenes. Despite repeated attempts under a variety of conditions and with diverse solvent–base combinations, conclusive evidence for the

(44) T. L. Gresham, J. E. Jansen, F. W. Shaver, R. A. Bankert, W. L. Beears, and M. G. Prendergast, *J. Amer. Chem. Soc.*, 71, 661 (1949).

(45) F. Krollpfeifer and H. Schultze, *Chem. Ber.*, **56**, 1819 (1923).

(46) D. M. Follweiler, Ph.D. Thesis, University of Pennsylvania, 1968, pp 92–109.

(47) J. v. Braun and K. Weissbach, *Chem. Ber.*, **62**, 2416 (1929); W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961).

(48) F. Arndt, *Chem. Ber.*, **56**, 1269 (1923).

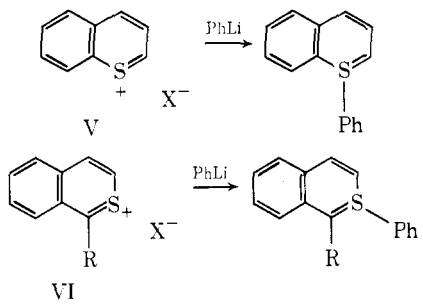
(49) B. D. Tilak, H. S. Desai, C. V. Deshpande, S. K. Jain, and V. M. Vaidya, *Tetrahedron*, **22**, 7 (1966).

(50) G. F. Katekar and R. M. Thomson, *Aust. J. Chem.*, **25**, 647 (1972).

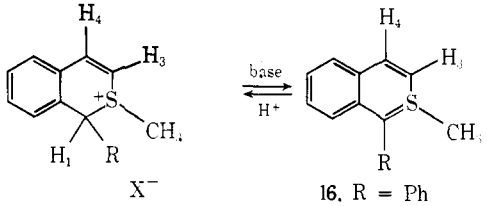
(51) In the preparation of **14f** a sample of 7-methoxy-3-phenyl-2-thio-4-chromanone (kindly provided by Dr. R. N. Crenshaw of Bristol Laboratories, Syracuse, N. Y.) was reduced with sodium borohydride in methanol and the resulting thiochromanol was dehydrated by heating in benzene containing phosphorus pentoxide.

(52) At least formally, any of the thiochromenium salts **13** and **15** could be treated with strong base in DMSO solution in a manner identical with that used for the generation of **1** to yield thianaphthalenes.

(53) It is noteworthy that Price and Follweiler[17d] also claim to have generated colored 1,2-diphenyl-2-thianaphthalene and 1-*tert*-butyl-2-phenyl-2-thianaphthalene by titration of the corresponding thiochromenium perchlorates with base. *However, it should be noted that the reversibility of these reactions was not definitely established.*



generation of 1-methyl-1-thianaphthalenes from the thiochromenium salts **13a–e** could not be obtained. Using the conditions for the generation of **1** as a model, only broad, poorly resolved resonance peaks, none of which were interpretable as *S*-methyl singlets, were generally observed in the nmr spectra of solutions of the supposed 1-methyl-1-thianaphthalenes; furthermore, it was not possible to regenerate the spectra of the starting thiochromenium salts upon addition of acid. In the attempts to generate 2-methyl-2-thianaphthalenes only **15b** and **15c** upon treatment with base gave species in



15b, R = Ph; X = BF_4
15c, R = *p*-ClPh; X = ClO_4

solution having nmr spectra consistent with the presence of the desired *S*-methylthianaphthalenes.[54]

Generation of 2-Methyl-1-phenyl-2-thianaphthalene and 2-Methyl-2-(*p*-chlorophenyl)-2-thianaphthalene. When a solution of **15b** or **15c** in DMSO-d_6 was treated under an inert atmosphere in an nmr tube with *tert*-butyllithium in pentane, or potassium *tert*-butoxide in DMSO-d_6,[55] a deep red solution free of any suspended particles was formed. An nmr spectrum recorded immediately after the addition of base showed that all of the starting salt **15b** or **15c** had been consumed and that the corresponding 1-aryl-2-methyl-2-thianaphthalenes **16** and **17** had been generated. In the case of **16**, the new spectrum showed a sharp singlet at δ 1.87 assigned to the *S*-methyl group, a pair of doublets centered at δ 5.64 and 7.75 (J = 8 Hz) assigned to H-3 and H-4, respectively, and a well-resolved multiplet at δ 6.8–7.7; the areas under the singlet and doublets integrated in a ratio of 3:1:1, while the area of the aromatic region integrated for approximately 15–18 H, nearly twice the expected amount. Upon acidification of the solution in the nmr tube with dilute fluoroboric acid, **15b** was regenerated as shown by reappearance of the resonance peaks due to **15b** at δ 3.01 and 6.5–6.7. Again, however, the integrated area of the aromatic region of the spectrum was approximately twice the calculated amount based on the *S*-methyl resonance of **15b** at 3.01 ppm. Isolation of the material in the nmr tube gave a 50% recovery of **15b**, mp 156–162° (pure **15b** melts at 167–169°).[56]

As expected, **15c** behaved in the same fashion as **15b** when treated with *tert*-butyllithium or potassium *tert*-butoxide with only slight changes in chemical shifts of the protons of the generated thianaphthalene **17**. The nmr spectrum of **17** exhibited a 3 H singlet at δ 1.85, 1 H doublets centered at δ 5.75 and 7.65 (J = 8 Hz), and a multiplet from δ 6.5 to 7.6 integrating for 12–16 protons. Based on integration of the area beneath the singlet at 1.85 ppm and comparison with the area of peaks in the phenyl region, a maximum of ~55% of **17** was present in several experiments. Acidification of the solution with dilute acid regenerated **15c** in approximately 50% yield.

The source of the 45–50% extra absorption in the phenyl region of **16** and **17** was of major concern. An attempt to find a valid explanation of this discrepancy was made by studying the spectrum, shortly after generation, of **17** kept in the nmr probe at ~40° for an extended period. It was noted that under these conditions the *S*-methyl singlet at δ 1.85 exhibited a somewhat broadened base, and scans taken within minutes of the first scan showed the emergence of a new singlet at δ 1.90. The increase in this new peak occurred at the expense of the singlet at δ 1.85 and the doublet at δ 5.75. That this occurrence was temperature dependent was confirmed by recording the spectrum at 20–22°. After 1.5 hr at this lower temperature, the spectrum of **17** showed no significant change; the new singlet at δ 1.90 did not appear. Although it was evident that a new product was forming from **17** after its generation at 40° these observations did not, however, afford a simple explanation for the generation of **17** in a maximum yield of only about 50% *at the time of introduction of base*.[57]

The identification of the new product observed to form from **17** at 40° in the nmr probe was accomplished by generating **17** from **15c** on a preparative scale in DMSO under an inert atmosphere with potassium *tert*-butoxide as the base. The deep red solution which was formed was stirred for 24 hr at 40° during which time the color of the solution had faded to a pale orange. Work-up[58] followed by chromatography on neutral alumina gave one pure product, shown by its nmr and mass spectral characteristics to be 1-methyl-1-*p*-chlorophenyl-2-thio-3-chromene (**18**). The methyl group of **18** appears as a singlet at 1.90 ppm, in exact agreement with the position of the new signal which appeared several minutes after the generation of **17** at 40° in the earlier experiment.

A second product, **14c**, was also found in small amounts in later chromatography fractions. Its pres-

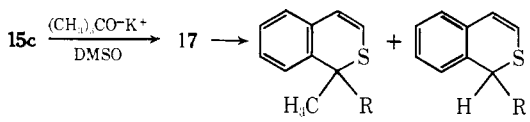
(54) In all other cases, no clearly discernible products were obtained nor could the thiochromenium salts be regenerated upon addition of acid.

(55) When potassium *tert*-butoxide was used inverse addition was necessary. A suspension of 1 mol equiv of dry potassium *tert*-butoxide in DMSO-d_6 in an nmr tube under nitrogen was treated (*via* syringe) with the salt **15b** or **15c** dissolved in DMSO-d_6.

(56) The material in the nmr tube was diluted with acetone which also aided in its removal from the nmr tube; volatile material was removed under high vacuum and the residue was crystallized from acetone and ether.

(57) Depending upon the particular experiment in which generation of **17** was studied, the singlet at δ 1.90 was either completely absent or could already be recognized when the initial nmr scan was recorded. Nevertheless, when no singlet at δ 1.90 was present in the first scan, the excess 45–50% absorption in the aromatic region was already present, indicating that the discrepancy in the initial integration was not associated with the new peak at δ 1.90.

(58) The orange solution was acidified with dilute fluoroboric acid and poured into ice water. Thorough extraction with ether was followed by the usual work-up to give the crude residue.



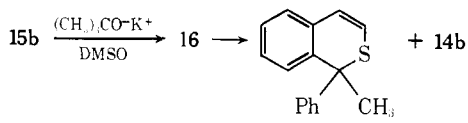
18 14c

R = *p*-ClPh

ence was established by a comparison of the nmr spectrum of the known thiochromene (prepared as an intermediate in the synthesis of **15c**) with the nmr spectrum of the chromatography fraction in which it was found. Compound **14c** presumably arises by displacement of the methyl group at sulfur in **15c** by the base, instead of proton abstraction by the base at C-1.

Only 85% of the calculated amount of organic material was recovered, of which about 40% was **18**, 10% was **14c**, and the remaining 50%, which presumably consisted of the unknown product formed *immediately* upon generation of **17**, was uncharacterizable.[59]

The same apparent rearrangement was observed for **16** formed by treatment of **15b** with potassium *tert*-butoxide. After a rapid nmr scan to confirm the presence of **16** (present in about 50% yield), the solution was acidified. After work-up, a 25% recovery of crude organic-soluble[58] material was obtained as a 12:1 mixture of **19** and **14b**. No effort was made to reisolate **15b** from the aqueous layer. Clearly, the pro-



19

tonated **16** (*i.e.*, **15b**) could represent, at best, only two-thirds of the 75% of material unaccounted for, material which was presumably lost in the water washes. Therefore, a definitive explanation of the excess area in the phenyl region of the nmr spectra of **16** and **17** immediately after generation was not forthcoming. These preparative scale studies did, however, serve as additional support for the presence of thianaphthalenes **16** and **17**, since both were shown to rearrange to thiochromenes **19** and **18**, respectively.

Deuterium Exchange Studies on 2-Methyl-2-thio-3-chromenium Salts. Deuterium exchange studies on thiabenzene 1-oxide (**2**) have been reported.[8] The present investigation has further shown that thiabenzene **1** exchanges its S-ring protons in a manner similar to **2**, and that thiabenzene **1** is in equilibrium with thiinium salt **9** in the presence of protic solvents. These data suggested ylidic character for both **1** and **2**. It was felt that an observation of comparable deuterium exchange in thiochromenium salts (**15a–e**) might give information as to the rate of deprotonation of these salts to give 2-methyl-2-thianaphthalenes in the process of exchange of their C-1 and C-3 protons (this assumes that exchange does, in fact, occur *via* an intermediate ylidic thianaphthalene). However, when **15a–c** and **15e** were treated with D_2O in DMSO-d_6, absolutely no exchange of either the *S*-methyl or S-ring protons was noted after as long as 3 weeks as determined by nmr monitoring. In contrast **15b**, **15c**, and **15e** gave nearly instantaneous exchange of their C-1 protons when a DMSO-d_6 solution of the salt was treated with 1 equiv of D_2O containing less than 0.01 equiv of KOD (prepared by dissolving known amounts of potassium *tert*-butoxide in D_2O); exchange of the C-3 protons or *S*-methyl protons was not observed. When **15a** was treated under the same conditions, clear evidence of simple exchange was not derivable from the nmr spectrum.[60]

(59) The 50% of recovered material which could not be characterized was found in the chromatography fractions containing **14c**. It exhibited multiple absorptions from δ 0.90 to 2.4, 5.6 to 6.6, and 6.7 to 7.8, even after repeated chromatography.

Characterization of Bonding in 1-Methyl-3,5-diphenylthiabenzene and 1-Aryl-2-methyl-2-thianaphthalenes

The preparation of, and evidence for, the existence of the novel heterocyclic compounds 1-methyl-3,5-diphenylthiabenzene (**1**) and 1-aryl-2-methyl-2-thianaphthalenes, **16** and **17**, has been presented in the preceding discussion. The method of proton abstraction used in their generation did not prove to be of general utility as first believed. However, in the case of formation of **1**, **16**, and **17** the procedure was successful, and the following discussion is directed toward those properties of **1**, **16**, and **17** which indicate that ylide-type bonding, as opposed to aromatic-type bonding, predominates in these cyclic, conjugated heterocycles.

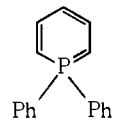
1-Methyl-3,5-diphenylthiabenzene. The presence of ylide-type bonding in **1** rather than aromatic character is evident from several pieces of data. First, the H-2 and H-6 protons of **1** are *upfield from the normal olefinic region* of the nmr spectrum and not in the aromatic region. This indicates that a ring current, the effects of which are usually invoked to explain the downfield nmr shift of peripheral ring protons in conjugated ring systems of $4n + 2$ π electrons and commonly used as a criterion for aromaticity, is not present in **1**. In fact, the chemical shift, 4.03 ppm, of the H-2 and H-6 protons of **1** indicates a high degree of electron density at C-2 and C-6 and is compatible with ylide-type bonding in this compound. The high-field chemical shift observed for these protons is in direct contrast to the shift one might expect if **1** were aromatic in character; for example, a chemical shift for H-2 and H-6 similar to that of the 2 and 5 protons of thiophene,[61] which exhibit a resonance peak at 7.30 ppm, might be expected.

Secondly, the presence of ylide-type bonding in **1** is strongly evidenced by the observations discussed above which show that **1** protonates readily in weakly acidic media (as opposed to any tendency of **9** to spontaneously lose a proton to form a resonance-stabilized species) and that the exchange of H for D occurs more rapidly at C-2 and C-6 than at C-4. The latter observation also indicates that there is probably a greater electron density at C-2 and C-6 than at C-4 in **1**, a supposition also supported by the fact that the resonance peak (4.03 ppm) of H-2 and H-6 is shifted quite far upfield from that of H-4 (6.19 ppm). It is also notable that the interconversion of the thiinium salt **9** and the thiabenzene **1** outlined here is similar to that noted for the analogous cyclic phosphonium ylides (VII, VIII) reported by Märkl.[30]

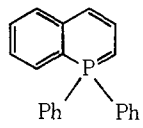
A comparison of the nmr data for the S-ring and *S*-

(60) The C-1 protons of **15a** apparently did not undergo exchange. Decomposition of **15a** appeared to take place instead. The nmr absorption of the C-1 protons did decrease relative to that of the *S*-methyl absorption; however, no concomitant increase in the intensity of the HOD absorption could be observed.

(61) N. S. Bhacca, L. F. Johnson, and J. N. Holland, "High Resolution Nmr Spectra Catalog," Varian Associates, 1962.



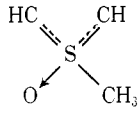
VII



VIII

methyl protons of **1** with those of the corresponding thiabenzene 1-oxide, **2**, is also very interesting. The chemical shifts of H-2 and H-6 and the *S*-methyl group of **2** are at much lower field (6.28 and 3.75 ppm, respectively in DMSO) than those of the corresponding protons in **1** (4.03 and 1.73 ppm, respectively). The greater deshielding observed for these protons of **2** might be partly attributed to more effective deshielding due to the presence of an additional sulfoxide oxygen in **2** and, in addition, to the possibility of more effective overlap of the d orbitals of sulfur with the termini of the cyclopentadienyl system in **2**. The net consequence of the latter effect should be a more stable $p\pi$–$d\pi$ bond (*i.e.*, more delocalization of electrons into the C–S–C region) and less carbanionic character at the C-2 and C-6 positions in **2** than in **1**. This supposition would appear to be borne out further by the observation that, whereas **1** is readily deuterated by acetic acid-d_4 in DMSO-d_6 to yield **9**-d_4 quantitatively, no such favoring of the corresponding thiinium 1-oxide occurs on treatment of **2** with acetic acid-d_4 in $CDCl_3$ or DMSO-d_6.

One additional comparison that can be made from the nmr data for **1** and **2** is that there is little difference in the chemical shift of H-4 in **1** and **2** (6.18 and 6.28 ppm, respectively); this suggests that the more highly positively charged sulfur of **2** (compared to that of **1**) exerts only a minor effect on the electron density at C-4 in comparison with the large effect observed at the C-2 and C-6 positions and the *S*-methyl group. This would seem to indicate that the electronic structures of **1** and **2** are probably similar except for the additional deshielding and $p\pi$–$d\pi$ bond-stabilizing effect of the S=O bond in the



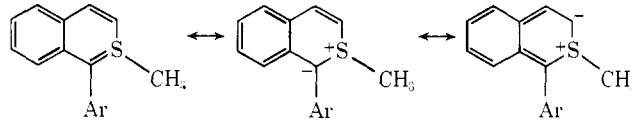
system of **2**.

A comparison of the ultraviolet spectra of **1** and the corresponding 1-oxide **2** is also interesting. The thiabenzene **1** has absorption maxima at 437, 275 (shoulder), and 240 nm; 1-oxide **2** has absorption peaks at 364 and 240 nm. The significant difference is the hypsochromic shift of the long wavelength band from 437 nm in **1** to 364 nm in **2**. It is likely that this shift is due to the extra stability of the $p\pi$–$d\pi$ interaction in the thiabenzene 1-oxide. It is important to note that it is these long wavelength absorptions which disappear when **1** (*vide supra*) and **2** (see ref 8) are exposed to acidic media and they may well involve excitation of electrons associated with the $p\pi$–$d\pi$ bond.

The long wavelength absorption of **1** is also interesting since other analogous compounds which can be viewed as having an ylidic $2p\pi$–$3d\pi$ bond incorporated into a cyclic system also exhibit high wavelength absorptions. For example, VII has a long wavelength absorption at 407 nm and VIII has absorption bands at 402 and 360 nm.

A comparison of the ultraviolet and nmr spectra of **1** with those of 1-phenylthiabenzene (II) is puzzling. The uv spectrum of **1** does not resemble those of analogous carbon aromatic systems. On the other hand, it is reported[16] that the uv spectrum of II resembles that of biphenyl and that II has *all* of its proton resonance peaks in the aromatic region of the nmr spectrum. The discrepancy between the ylidic and aromatic bonding claimed for **1** and II, respectively, remains unresolved at present.

1-Aryl-2-methyl-2-thianaphthalenes. The presence of ylidic bonding in 1-phenyl-2-methyl-2-thianaphthalene (**16**) and 1-*p*-chlorophenyl-2-methyl-2-thianaphthalene (**17**) also appears evident from several pieces of data. First, H-3 in **16** and **17** is found in the olefinic region of the nmr spectrum (approximately δ 5.70 in both cases). This parallels the behavior of the H-2 and H-6 protons of **1** and **2**. That the H-3 proton of **16** and **17** is not as highly shielded as the H-2 and H-6 protons in **1** can possibly be explained as follows. The C-1 position in **16** and **17** is doubly benzylic and can be expected to more effectively stabilize electron density at that position than at C-3. The C-3 position has only the flanking sulfonium center to aid in stabilizing electron density. The observed lower field shift of H-3 in **16** and **17** compared to H-2 and H-6 in **1** can also be rationalized in part by the fact that negative charge in a bicyclic system can be delocalized over more atoms thereby leaving less charge density at each carbon relative to the situation in a monocyclic system. Also, disruption of the benzenoid portion of a thianaphthalene is required in the resonance contributor which has a negative charge at C-3. This contrasts with resonance forms for **1** (and **2**)[8] in which important resonance contributors having a negative charge at C-2 and C-6 can be written without destroying the aromaticity of phenyl substituents. The importance of contributing structures showing negative charge at C-3 in **16** or **17** would, therefore,



16. Ar = Ph
17. Ar = *p*-ClPh

be less than those bearing charge at C-1. The net result is less shielding of H-3 in **16** and **17** than H-2 and H-6 in **1** and, consequently, a lower field chemical shift for H-3.

More evidence supporting ylidic character for thianaphthalenes **16** and **17** comes from a comparison of the *S*-methyl resonances of **16** and **17** with the methyl resonances of known "aromatic" compounds such as toluene. The methyl absorption in **16** and **17** occurs at approximately 1.85 ppm, nearly 0.6 ppm higher field than that of toluene whose methyl resonance is found at 2.4 ppm. The value of 1.85 ppm in **16** and **17** is also consistent with the chemical shift of the *S*-methyl resonance in **1**, which was found at 1.73 ppm. This abnormally high chemical shift suggests electronic shielding due to a high measure of charge density at the carbons adjacent to the positive sulfonium center, *i.e.*, an ylidic type of bonding representation.

A final criterion for ylidic bonding in **16** and **17**, or for that matter in **1**, comes from the fact that **16** and **17** can be readily protonated to regenerate the thiochro-

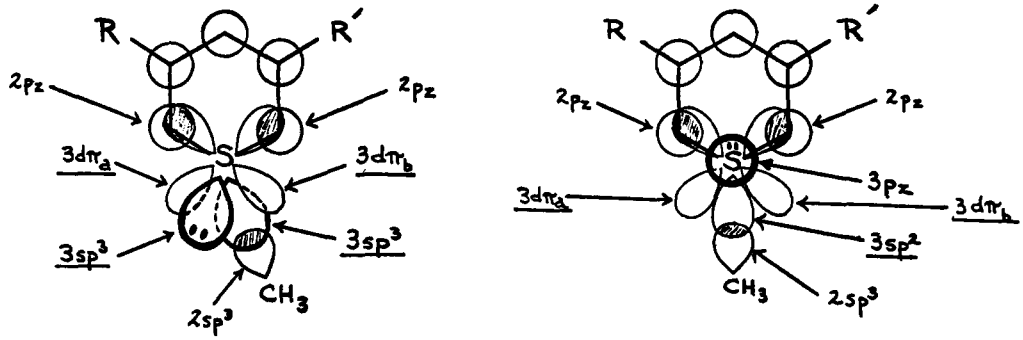
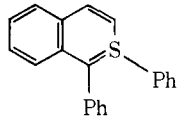


Figure 1. Possible bonding structures for ylidic thiabenzenes (inversion at sulfur possible for either form): A, left; B, right.

menium salts (**15b, c**) from which they were generated. This is also in accord with Märkl's observations[30] on phosphabenzenes for which an ylidic bonding scheme is proposed. In this respect there is also a marked similarity between *S*-methylthiabenzenes (and *S*-methylthianaphthalenes) and simple acyclic sulfonium ylides[62] which can also be reversibly generated. These observations differ from those made on *S*-arylthianaphthalenes by Price, *et al.*[17c,d] The latter compounds, with one possible exception, cannot be reversibly generated from the corresponding thiochromenium salts.[17d,53] (However, it should be noted that this behavior in *S*-arylthiaaromatics would seem to be in agreement with the claim of Price, *et al.*, for aromaticity in these compounds.) It is possible that *S*-alkyl and *S*-aryl thiaaromatics might differ widely in their bonding characteristics, although, *a priori*, it is difficult to envision such a large disparity. In this regard efforts have been under way in this laboratory to compare more closely and under similar conditions the physical characteristics of **16** and the analogous *S*-aryl compound IX recently described by Price and Follweiler.[17d]



IX

Bonding Model for 1-Methyl-3,5-diphenylthiabenzene and 1-Aryl-2-methyl-2-thianaphthalenes. A model for bonding in **1** which is consistent with its chemical and spectral properties would be the ylidic model set forth previously for thiabenzene 1-oxide **2**,[8b] *i.e.*, a delocalized pentadienyl anion (C-2–C-6) overlapping weakly at its termini with the positively charged sulfonium center. The model for **1** (and **2**[8b]) is based primarily on Dewar's arguments[14] and is one which has six π electrons distributed in seven π-atomic orbitals,[30] *i.e.*, five p orbitals on the carbon atoms of the pentadienyl unit of the S-ring and two orthogonal (and presumably noninteracting) hybrid d orbitals ("$d\pi_a$" and "$d\pi_b$")[14] on sulfur, each of which overlaps with one adjacent carbon $2p_z$ orbital (see Figure 1). A slightly modified model based on the resonance contributors shown above for **16** and **17** would also be in agreement with the ylidic properties of *S*-methylthianaphthalenes.

We further suggest, based on the similarities of the nmr data for **1** and **2** (after taking the deshielding effect of the sulfoxide bond of **2** into account), that the sulfur atom in both is tetrahedral, the oxygen in **2** replacing the electron pair in a $3sp^3$ orbital in **1**. In this model for **1** (Figure 1A, R = R′ = Ph) sulfur is $3sp^3$ hybridized. An alternative model for **1** (Figure 1B) has sulfur planar and $3sp^2$ hybridized with the unshared electron pair in a $3p_z$ orbital. (In both models, A and B, it is assumed that the unshared electron pair on sulfur is not interacting with the six π-electrons in the seven-πAO system.) A third possible model for ylidic thiabenzenes has A rapidly interconverting with its mirror image (R $\neq$ R′) *via* B as the transition state. Such inversion has already been demonstrated in phospholes, phosphindoles, and dibenzophospholes.[5] A distinction between these bonding models would seem a worthwhile subject for further study, as would the apparent disparity in the bonding properties of the *S*-methylthiabenzenes and thianaphthalenes described here *vs.* the *S*-aryl analogs[11,16,17] reported by Price, *et al.*[63]

Experimental Section[64]

Generation of 1-Methyl-3,5-diphenylthiabenzene (1). Nmr Experiments. A solution of *tert*-butyllithium in pentane (0.19 ml of

(62) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

(63) The observed alternation of negative charge densities in the carbanions studied by Bates, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), and Kloosterziel, *et al.*, *Recl. Trav. Chim. Pays-Bas*, **89**, 300, 368, 413 (1970), and the fact that protons on β-carbon atoms in vinyl sulfonium salts are strongly deshielded (M. C. Caserio, *et al.*, *J. Amer. Chem. Soc.*, **88**, 5747 (1966)) point out that ylidic character cannot necessarily be discounted for 1,2,4,6-tetraphenylthiabenzene (I)[11a] or the more recently reported 1-(*p*-dimethylaminophenyl) analog[11c] of I on the basis of the nmr data reported by Price, *et al.* Also, the low dipole moment (1.88 D) cited in support of aromatic character for I[17c] might be explained as the resultant arising from a higher localization of negative charge at C-2 and C-6 than at C-4 in the S-ring of (ylidic) I.

(64) Melting points were determined on a Thomas H. Hoover Co. Unimelt apparatus and are uncorrected unless specified otherwise; boiling points are uncorrected. Nmr spectra were obtained at 60 MHz using a Varian A-60A spectrometer with approximately 20% solutions unless specified otherwise. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) as an internal standard. In the generation of **1**, **16**, and **17**, chemical shifts are correlated with the quintet resulting from residual DMSO-d_5 centered at 2.52 ppm. Coupling constants (*J*) are given in hertz; s, d, t, and q refer to singlet, doublet, triplet, and quartet, respectively. Infrared spectra were obtained on a Perkin-Elmer Model 457 infrared spectrophotometer using approximately 10% solutions or Nujol mulls as specified. Ultraviolet spectra were obtained on a Cary Model 14 spectrometer. Mass spectra were obtained on a Varian Model M-66 spectrometer. Peak heights are based on the parent peak being of 100% intensity. Elemental analyses were performed by Mikroanalytisches Laboratorium, Institut für Physikalischem Chemie, Vienna, Austria, or Galbraith Laboratories, Knoxville, Tenn., or Atlantic Microlabs, Atlanta, Ga. The petroleum ether used had bp 63–69°.

a 1.24 *M* solution, 0.24 mmol) was added *via* syringe to a solution of **9** (85 mg, 0.24 mmol) in 0.30 ml of DMSO-d_6 in an nmr tube at room temperature and under N_2. The pentane and DMSO-d_6 solutions were mixed by slowly drawing the syringe needle through the solution during the addition and by slowly revolving the nmr tube after addition was complete. An nmr spectrum of the material in the DMSO-d_6 layer (orange solution) revealed that the only peaks present (excluding those of pentane and other compounds initially present in the *tert*-butyllithium solution) were at δ 1.73 (s, 2.5), 4.03 (d, 2, J = 1.7 Hz), 6.18 (t, 1, J = 1.7 Hz), and 7.21–7.82 (m, 10); there was an increase of 1.7 protons in the dimethyl-d_x sulfoxide peak (determined by comparison of one proton and two proton peaks in **9**, and in **1**, with the DMSO-d_x peak) indicating that the S–CH_3 protons of the initially formed thiabenzene **1** underwent partial exchange with the methylsulfinyl carbanion-d_5 formed from the reaction of *tert*-butyllithium with DMSO-d_6 before complete mixing had taken place. The sample was left in the nmr probe (*ca.* 35°); spectra recorded 0.5 and 0.7 hr later revealed that very little decomposition of **1** had occurred. After 1.1 hr, 0.24 mmol of HBF_4 (10% aqueous solution) was added to the nmr tube (which contained some solid at this point) giving a pale yellow solution containing some suspended solid. An nmr spectrum of the sample exhibited peaks due to **9** at δ 2.97 (s), 6.70 (s), 7.23 (br s), and 7.40–7.95 (m). The peak at δ 4.78 in the spectrum of **9** was under the peak due to H_2O introduced upon addition of the HBF_4 solution. The nmr sample was diluted with acetone, and the resulting solution was evaporated under vacuum leaving a yellow liquid which was treated with petroleum ether (6 ml) and H_2O (10 ml); the H_2O layer was separated, and the thiinium salt was allowed to slowly crystallize. Filtration, followed by drying of the thiinium salt at 0.05 mm for several hours, yielded 39 mg (46% recovery) of **9** as pale yellow needles, mp 142.6–143.9° dec (corr) (evacuated tube): nmr (DMSO-d_6) δ 2.97 (s, 2.5), 4.78 (s, 2), 6.77 (s, 1), 7.23 (s, 1), and 7.40–7.97 (m, 10). The petroleum ether layer was evaporated giving 16 mg of an orange oil that showed only a broad peak in the phenyl region in its nmr spectrum.

Attempts to generate **1** in a similar manner in Et_2O and under N_2 using a double Schlenk tube led to decomposition of the solid yellow product during recrystallization. Attempts were also made to generate **1** in Et_2O followed by removal of Et_2O and dissolution in CCl_4 or $CDCl_3$. Decomposition of **1** was found (by nmr) to be rapid at room temperature in nonpolar solvents.

Uv Experiments. A degassed standard solution of 1-methyl-3,5-diphenylthiinium tetrafluoroborate (**9**) (5.07×10^{-3} mg/ml) in absolute EtOH was prepared, and a uv spectrum of 2 ml of the standard EtOH solution and 1 ml of boiled and degassed deionized H_2O showed uv(max) at 244 (ϵ 32,300), 291 (ϵ 15,600), and 331 nm (ϵ 11,300). The thiabenzene **1** was generated by adding 0.5 ml of standard degassed NaOH solution (0.101 *N* Fisher reagent, carbonate free) to 2 ml of the standard EtOH solution. The two solutions were mixed by bubbling argon through the sample in the cuvette: a uv spectrum of the thiabenzene **1** showed uv(max) at 245 (ϵ 33,700), 275 (ϵ 14,300 shoulder), and 437 nm (ϵ 3200); the extinction coefficients were corrected for dilution changes in concentration and for a blank absorption of 0.5 ml of the standard aqueous NaOH solution in EtOH. Addition of a 0.0562 *M* HBF_4 solution (degassed) to the solution of thiabenzene **1** in the cuvette regenerated the thiinium tetrafluoroborate (**9**): absorption (max) at 242, 290, and 330 mμ.

In a similar experiment the thiabenzene **1** generated had uv(max) at 247 (OD 0.451), 275 (0.205), and 437 mμ (0.050): a spectrum of the same solution run 68 min later showed uv(max) at 247 (OD 0.439), 275 (0.205), and 437 mμ (0.048).

2*H*- and 4*H*-3,5-Diphenylthiopyrans (3 and 4). Method A. By Reduction of 1-Methyl-3,5-diphenylthiabenzene 1-Oxide (2) with Trichlorosilane. Trichlorosilane (2.71 g, 0.02 mol) was injected *via* syringe into a stirring solution of **2** (5.60 g, 0.02 mol) in benzene (40 ml). A fine, yellow precipitate formed after 1 min and disappeared as the mixture was brought to reflux. The mixture was refluxed for 9 hr, cooled, poured into $CHCl_3$ (50 ml), and washed with 10% NaOH solution (50 ml). The organic layer was washed with H_2O and brine and dried ($MgSO_4$). Evaporation of the solvent under vacuum left 5.07 g (100%) of yellow solid. The crude material was adsorbed on Florisil (100 g, 100–200 mesh) and rapidly eluted with 2.5 l. of petroleum ether (bp 33–37°). Evaporation of the solvent afforded 4.36 g (87%) of a mixture of 2*H*- and 4*H*-thiopyrans **3** and **4**, in a ratio of 3:2 (90% pure and 10% of a related impurity by nmr assay). Recrystallization led to apparent loss of the 4*H* isomer (**4**). In a similar experiment, 4.3 g (representing a 96% yield) of a mixture of **3** and **4** (2:1) obtained from a similar reduction (12 hr of reflux) was recrystallized twice from absolute EtOH to yield 1.96 g (44%) of the 2*H*-thiopyran, **3**, as yellow flakes, mp 97–102°. The mother liquors were chromatographed on Florisil (75 g, 100–200 mesh, packed wet in petroleum ether (bp 33–58°)). Elution with petroleum ether containing increasing amounts of benzene afforded (after recrystallization) a further 0.49 g (11%) of **3**, mp 100–103°. An analytical sample of **3** had mp 104.6–106.1° (corr): ir (CCl_4) 1599, 1494, 1446, and 648 cm^{-1}; uv(max) (EtOH) 364 (ϵ 4900) and 270 nm (ϵ 30,600); nmr (CCl_4) δ 3.60 (t, 2, $J \sim 0.6$–0.9 Hz), 6.40 (q, 1, $J \sim 0.6$ Hz), 6.54 (q, 1, $J \sim 0.9$ Hz), and 7.2–7.8 (m, 10). *Anal.* Calcd for $C_{17}H_{14}S$: C, 81.56; H, 5.64; S, 12.80. Found: C, 81.39; H, 5.51; S, 12.84.

Method B. By Reduction of 5a with $LiAlH_4$. Purified $LiAlH_4$ (11 mg, 0.3 mmol) was added to a cold solution (−10°) of **5a** (100 mg, 0.3 mmol) in anhydrous Et_2O under N_2. The mixture was stirred for 1 hr at −5 to −10° and then diluted with Et_2O and H_2O. The organic layer was washed with brine and dried (Na_2SO_4) at 0°. The solvent was removed under vacuum leaving 74 mg (99%) of **3** and **4** (solely) as yellow plates (~1:1 by nmr analysis). Mixtures enriched in the 4*H* isomer (**4**) could be obtained by extraction of the 2*H* isomer (**3**) into aqueous $AgNO_3$ solution. In a typical experiment, 350 mg of a mixture of **3** and **4** was dissolved in petroleum ether (110 ml). The filtered petroleum ether solution was washed twice with saturated $AgNO_3$ solution (100 ml, 20 ml) followed with H_2O and brine and dried ($MgSO_4$). The petroleum ether was removed under vacuum at 25° to afford 90 mg of yellow flakes consisting of **4** and **3** (90% pure) in a ratio of 7:2, respectively. (Other experiments gave **4** and **3** in ratios of 9:1, 6:1, and 9:2.) Recrystallization of the product (90 mg) from *cold* EtOH–Et_2O gave 40 mg of ~90% pure 4*H*-thiopyran **4**: nmr ($CDCl_3$) δ 3.62 (t, 2, J = 1.0 Hz), 6.47 (t, 2, J = 1.0 Hz), and 7.2–7.7 (m, 10); uv(max) (EtOH) 336 (ϵ 6400), 273 (ϵ 8600), and 237 nm (ϵ 14,800). The product contained ~10% of **3** (nmr analysis).

Dilution of the $AgNO_3$ extracts with H_2O and extraction with CH_2Cl_2 followed by a normal work-up procedure gave 170 mg of yellow gum which contained the 2*H* isomer (**3**) and considerable amounts of impurities (nmr analysis).

3,5-Diphenylthiopyrylium Tetrafluoroborate (5a). Trityl tetrafluoroborate (4.0 g, 0.012 mol) was added as a powder to a solution of **3** and **4** (3.0 g, 0.012 mol; prepared by method A) in CH_2Cl_2 (115 ml) under N_2. The mixture was stirred for 2.5 hr at room temperature. The solution was treated with 125 ml of anhydrous Et_2O yielding, after filtration, 3.6 g (95%) of **5a** as a powdery solid. Recrystallization from acetone afforded 2.2 g (58%) of **5a** as pale yellow needles: mp 154° (partial melting), 163–165° dec (evacuated tube); second crop, 0.7 g (16%), mp 154–162° dec (evacuated tube). Recrystallization from 10% fluoroboric acid afforded an analytical sample: mp 169.5–171.0° dec (corr); uv(max) (4:1 EtOH–H_2O containing 1% fluoroboric acid) 283 (ϵ 38,600) and 205 nm (ϵ 44,800); nmr (DMSO-d_6) δ 7.5–7.8 (m, 6), 7.8–8.2 (m, 4), 9.40 (t, 1, J = 1.4 Hz) and 10.47 (d, 2, J = 1.4 Hz). *Anal.* Calcd for $C_{17}H_{13}BF_4S$: C, 60.74; H, 3.90; F, 22.61; S, 9.54. Found: C, 60.89; H, 3.88; F, 22.39; S, 9.37.

3,5-Diphenylthiopyrylium Iodide (5b). NaI (1.9 g) was added to a solution of **5a** in acetone–H_2O. A rust-colored solid began to precipitate after 2 min. After 2.5 hr at room temperature the precipitate was filtered and recrystallized twice from acetic acid–H_2O (1:2) to yield **5b** as crimson needles: mp 161.5–163.3° (corr); ir (KBr) 2888, 1534, 1510, 1488, 1370, 1228, 758, 689, 592, and 468 cm^{-1}; nmr (DMSO-d_6) δ 7.6–7.9 (m, 6), 7.9–8.2 (m, 4), 9.45 (t, 1, J = 1.4 Hz), and 10.67 (d, 2, J = 1.4 Hz).

1-Methyl-3,5-diphenyl-2*H*-thiinium Tetrafluoroborate (9). $AgBF_4$ (2.1 g, 0.011 mol) was added at room temperature to a solution of **3** (2.5 g, 0.01 mol) in purified CH_3I (17 ml). After the pasty mixture was stirred at room temperature under N_2 for 2.5 hr, the solid material was collected by suction filtration. The filter cake was extracted with boiling acetone (60 ml) and then boiling CH_2Cl_2 (20 ml). The extracts were treated with charcoal, and the solvent was removed under vacuum at 40° leaving 3.2 g (90%) of a pale yellow solid, mp 143.9° dec (evacuated tube). The crude material was dissolved in acetone, and petroleum ether was added to the cloud point; the yield of **9** as slightly off-white needles was 2.5 g (71%): mp 144.4–145.9° dec (corr) (evacuated tube): ir (KBr) 3170, 1541, 1497, 1391, 1320, 1287, 1226, 1188, 1056 (broad), 870, 758, 696, 590, 578, and 497 cm^{-1}; uv(max) (EtOH–H_2O) [2:1]) 244 (ϵ 32,300), 291 (ϵ 15,600), and 331 nm (ϵ 11,300); nmr (DMSO-d_6) δ 2.97 (s, 3), 4.78 (d, 2, $J \sim 1.0$ Hz), 6.78 (d, 1, $J \sim 0.7$ Hz), 7.28 (q, 1, $J \sim 0.9$ Hz), and 7.37–7.97 (m, 10). *Anal.* Calcd for $C_{18}H_{15}BF_4S$: C, 61.39; H, 4.87; F, 21.57; S, 9.10. Found: C, 61.44; H, 4.91; F, 21.28; S, 9.25.

Methyl 2-Phenyl-3-mercaptophenylpropionate. Methyl atropate[65] (4.10 g, 0.025 mol) was combined with thiophenol (5.4 g, 0.05 mol) in 25 ml of CH_3OH. Sodium (0.04 g, 0.0017 mol) was added to the stirred solution at room temperature. After 18 hr, the solvent was removed *in vacuo*, and other readily volatile materials were removed by distillation at high vacuum. The undistilled pot residue (6.3 g) was crystallized from CH_3OH–H_2O to give methyl 2-phenyl-3-mercaptophenylpropionate as a pale yellow solid (6.0 g, 88%), mp 29–30°. Two additional recrystallizations gave an analytical sample as colorless plates: mp 33.7–34.5°; nmr ($CDCl_3$) δ 3.0–4.0 (m (with singlet at 3.55 ppm), 6) and 7.1–7.5 (s, 10); ir (CCl_4) 1745, 720, and 695 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 272 (M^+, 100), 273 ($M^+ + 1$, 17.9), 274 ($M^+ + 2$, 7.2), calcd for $C_{16}H_{16}O_2S$: ($M^+ + 1$, 18.6) and ($M^+ + 2$, 6.2). *Anal.* Calcd for $C_{16}H_{16}O_2S$: C, 70.70; H, 5.91; S, 11.75. Found: C, 71.23; H, 5.91; S, 11.76.

2-Phenyl-3-mercaptophenylpropionic Acid. A mixture of methyl 2-phenyl-3-mercaptophenylpropionate (4.0 g, 0.0147 mol), anhydrous lithium iodide[66,67] (11.7 g, 0.087 mol) and anhydrous pyridine (100 ml) was refluxed for 7 hr. The reaction mixture was diluted with 100 ml of ether and 50 ml of CCl_4 and washed with 6 *M* HCl. The acidic washings were back-extracted with ether, and the organic extracts were combined. Following drying over $MgSO_4$, the organic extracts were concentrated under reduced pressure to leave a brown oil which was dissolved in a minimum amount of ether. A brown tar which separated was discarded. Removal of the ether gave 2.5 g (65%) of 2-phenyl-3-mercaptophenylpropionic acid as a colorless oil.

An alternate procedure for preparation of the acid entailed refluxing the ester in a 1:1 mixture of 3 *M* HCl and acetone for 12 hr. The heterogeneous reaction mixture was extracted with ether. The ether extracts were washed with saturated $NaHCO_3$ solution, and the washings were carefully acidified with dilute HCl. Extraction of the acidified washings with ether followed by drying of the ether extracts with $MgSO_4$ gave, after removal of solvent, the same colorless 2-phenyl-3-mercaptophenylpropionic acid[50] which could not be crystallized: nmr (CCl_4) δ 2.9–3.8 (m, 3), 7.0–7.5 (m, 10), and 10.6 (s, 1).

Alternate Preparation of 2-Phenyl-3-mercaptophenylpropionic Acid. Sodium thiophenolate (9.7 g, 0.0756 mol) and sodium 3-bromo-2-phenylpropionate (prepared by dissolution of 3-bromo-2-phenylpropionic acid[68] in an equivalent amount of aqueous $NaHCO_3$) were dissolved in 150 ml of H_2O and stirred overnight at room temperature. The aqueous solution was washed once with ether and acidified with dilute HCl. The cloudy solution was extracted with ether, and extracts were washed with brine and dried ($MgSO_4$). Concentration of the extracts under reduced pressure gave the oily acid (13.0 g, 65%). Nmr analysis indicated that the product was identical with that obtained by treatment of methyl 2-phenyl-3-mercaptophenylpropionate with LiI–pyridine or HCl–acetone–H_2O.

3-Phenyl-1-thio-4-chromanone. Crude 2-phenyl-3-mercaptophenylpropionic acid (6.7 g, 0.026 mol) was dissolved in 75 ml of $POCl_3$ and refluxed for 30 min. The mixture was poured into ice water and worked up as usual to give 5.0 g of a brown oil. The oil was chromatographed on 100 g of silica gel. Elution with 600 ml of 15% ether in petroleum ether gave uncharacterized products. Further elution with 500 ml of 22% ether in petroleum ether gave 3.6 g (60%) of a colorless solid. Recrystallization of the latter from ether–petroleum ether gave the desired chromanone as fluffy white crystals (3.2 g, 53%), mp 61.3–62° (lit.[50] bp 171–176° (0.5 mm)); nmr (CCl_4) δ 2.8–4.1 (m, 3), 6.8–7.4 (m, 8), and 7.9–8.2 (m, 1); ir (CCl_4) 1690, 1605, 1450, 710, and 600 cm^{-1}. *Anal.* Calcd for $C_{15}H_{12}OS$: C, 75.00; H, 5.00; S, 13.34. Found: C, 75.22; H, 5.08; S, 13.34.

2-Phenyl-1-thio-4-chromanone. A solution of 3-phenyl-3-mercaptophenylpropionic acid (13.0 g, 0.051 mol)[48] in 60 ml of $POCl_3$ was refluxed for 35 min as described previously by Arndt.[48] The dark red solution was poured onto crushed ice in a larger beaker. The resulting aqueous mixture was extracted several times with methylene chloride, and the extracts were combined, worked up, and dried ($MgSO_4$) as usual. Removal of the solvent under reduced pressure gave 10 g of a black oil which was chromatographed on 200 g of neutral alumina (Woelm, activity grade 1). Elution with petroleum ether gave 1.9 g of crude 4-chloro-2-phenyl-1-thio-2-chromene or 4-chloro-2-phenyl-1-thio-3-chromene: bp 148–152° (0.05 mm); nmr (CCl_4) δ 4.75 (d, 1, J = 5 Hz), 6.15 (d, 1, J = 5 Hz), 6.7–7.4 (m, 8), and 7.5–7.8 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 258 (M^+, 100), 259 ($M^+ + 1$, 34), 260 ($M^+ + 2$, 40); also 257 ($M^+ - 1$, 40), 223 ($M^+ - 35$, 200), and 221 ($M^+ - 37$, 80). Further elution of the column with ethyl acetate gave 5.0 g of a yellow oil. Distillation afforded 4.0 g of a pale yellow oil, bp 190–195° (0.20 mm), which crystallized with much difficulty from petroleum ether–ether to give the desired 2-phenyl-1-thio-4-chromanone as colorless crystals: mp 51.5–52.2° (lit.[48] mp 55–56°); nmr ($CDCl_3$) δ 2.9–3.6 (m, 2), 4.5–4.8 (dd, 1, J = 9.5, 6.5 Hz), 6.9–7.7 (m, 8), and 8.0–8.3 (m, 1).

In the foregoing procedure for the preparation of 2-phenyl-1-thio-4-chromanone, the product ratio varied widely. In another preparation of the ketone, 20 g of the acid was refluxed in 100 ml of $POCl_3$ for 40 min. Following the work-up and isolation procedure described above, *no* 4-chloro-2-phenyl-1-thio-2-chromene was obtained. Instead, elution with petroleum ether gave 2-phenyl-1-thio-2-chromene (1.0 g, 5.8%) as pale yellow needles from CH_3OH: mp 60–61° (lit.[69] mp 60–61.5°); nmr (CCl_4) δ 3.45 (d, 2, J = 5 Hz), 6.10 (t, 1, J = 5 Hz), and 6.8–7.6 (m, 9).[70] The yield of the chromanone was 4.0 g (oil) in this preparation.

General Procedure for the Reduction of Thiochromanones to Thiochromanols. The thiochromanones were dissolved in anhydrous CH_3OH (1.0 g/25 ml) and cooled in an ice bath. While the solution was stirred vigorously, an equimolar amount of $NaBH_4$ was added in very small portions. After all the reducing agent had been added, the solution was refluxed for 1 hr. After cooling, the excess $NaBH_4$ was destroyed by addition of 10% H_2SO_4. The resulting mixture was poured into ice water, extracted with ether, and worked up as usual. Isolation afforded quantitative yields of oily alcohols which were used directly for dehydration.

General Procedure for Dehydration of Thiochromanols to Thiochromenes. With the exception of 1-thio-4-chromanol and 2-thio-4-chromanol, which were distilled directly from potassium pyrosulfate according to the literature procedures,[44–47] the following procedure was employed. The thiochromanol was refluxed for 1.5–3.0 hr with an equal weight of phosphorus pentoxide in benzene (1.0 g/50 ml). After reflux had begun, a gummy residue settled out of solution and stirring (magnetic stirrer) became difficult. After the allotted time, the reaction mixture was poured into ice water. Extraction with ether followed by a normal work-up afforded oils which were either distilled or chromatographed on neutral alumina. The oily thiochromenes were either stored at low temperature or, preferably, used as soon as possible due to their general instability in air at room temperature.

2-Phenyl-1-thio-3-chromene (12b). Essentially pure 2-phenyl-1-thio-4-chromanone (1.75 g, 0.0073 mol) was reduced with $NaBH_4$ in CH_3OH according to the general procedure. Work-up afforded the alcohol as a tan solid which was recrystallized from petroleum ether to give 1.62 g (93%) of 2-phenyl-1-thio-4-chromanol as a nearly colorless solid, mp 144–145° (lit.[26] mp 144–145°). The alcohol was refluxed in 125 ml of dry benzene containing 2.7 g of phosphorus pentoxide for 1.5 hr. After the usual work-up, a dark red oil (1.27 g) was isolated. Attempts to crystallize the oil from CH_3OH failed despite a literature report which describes a thiochromene obtained in the same manner as a solid.[26] Distillation afforded **12b** as a pale yellow oil (1.0 g, 67%), bp 135–140° (0.05 mm) (lit.[26] bp 138–145° (0.1 mm)). The distilled material also failed to crystallize: nmr (CCl_4) δ 4.77 (dd, 1, J = 5, 2 Hz), 5.82 (dd, 1, J = 10, 5 Hz), 6.50 (dd, 1, J = 10, 2 Hz), and 6.9–7.4 ppm (m, 9).

General Procedure for the Methylation of Thiochromenes and for the Preparation of the Corresponding *S*-Methylthiochromenium Salts. The thiochromene was dissolved in CH_3I (1.0 g in 20 ml) under an inert atmosphere and the solution was cooled in an ice bath. While the solution was stirred vigorously, a 5–10% molar excess of either $AgBF_4$ or $AgClO_4$ was added in portions. The solution was stirred for 1.5–3 hr at room temperature. The resulting slurry of AgI and product was filtered through a sintered glass filter and the filter cake was washed with anhydrous ether. The filtrates were discarded, and the filter cake was washed repeatedly

(65) Prepared by addition of α-styrylmagnesium bromide to Dry Ice followed by acidification to the free atropic acid and esterification with diazomethane. See H. Normant and P. Maitte, *Bull. Soc. Chim. Fr.*, 1439 (1956).

(66) F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 43, 113 (1960).

(67) W. L. Meyer and A. S. Levinson, *J. Org. Chem.*, **28**, 2184 (1963).

(68) F. Merling, *Justis Liebigs Ann. Chem.*, **209**, 1 (1881).

(69) W. D. Cottrell, *J. Chem. Soc., Perkin Trans. 1*, 817 (1972).

(70) The reasons for the marked variations observed in the yields of side products (previously unreported by Arndt[48]) were not determinable.

with hot CH_2Cl_2 and hot acetone. The washings were combined and concentrated *in vacuo* to leave colorless to brown residues. When the residue was an oil, it was dissolved in a minimum amount of acetone and ether was added to the cloud point. Cooling generally gave the thiochromenium salt as colorless to pale yellow crystals of high purity. Solids could be recrystallized by the same procedure with either acetone–ether or CH_2Cl_2–petroleum ether as a solvent pair.

1-Methyl-1-thio-3-chromenium Tetrafluoroborate (13a). Alkylation of 1-thio-3-chromene (**12a**)[44-47] with CH_3I and $AgBF_4$ by the general procedure gave **13a** as white crystals after recrystallization from CH_2Cl_2 and petroleum ether: mp 90.8–91.6° dec; yield 70–80% in several preparations; nmr (DMSO-d_6) δ 3.00 (s, 3), 4.0–4.9 (m, 2), 6.1–6.5 (m, 1), 7.13 (dd, 1, J = 2.5, 10.5 Hz), and 7.5–8.2 (m, 4); ir (Nujol) 1295, 1150, 960, 830, 770, and 710 cm^{-1}. *Anal.* Calcd for $C_{10}H_{11}BF_4S$: C, 48.03; H, 4.43; S, 12.82; F, 30.40. Found: C, 47.96; H, 4.44; S, 13.03; F, 30.58.

1-Methyl-2-phenyl-1-thio-3-chromenium Perchlorate (13b). Using the general procedure, 2-phenyl-1-thio-3-chromene (**12b**) (1.0 g, 0.00134 mol) was alkylated with both $AgBF_4$ and $AgClO_4$ in combination with CH_3I. Only the perchlorate salt would solidify, yielding **13b** as an amorphous yellow solid which remained amorphous during repeated attempts at recrystallization from a variety of polar solvents. Therefore, it was used as obtained (85–90% pure by nmr integration), and no analytical data were obtained: nmr (DMSO-d_6) δ 3.35 (s, 3), 6.12 (d, 1, J = 6.5 Hz), 6.58 (dd, 1, J = 10.5, 6.5 Hz), and 7.2–8.05 (m, 10).

1,3-Dimethyl-1-thio-3-chromenium Tetrafluoroborate (13c). A sample of 3-methyl-1-thio-4-chromanone[71] (7.0 g, 0.0395 mol) was reduced by the general procedure and dehydrated by distillation of of the crude alcohol directly from potassium pyrosulfate (8.2 g). Colorless 3-methyl-1-thio-3-chromene (**12c**) was obtained as an oil (4.2 g, 70%): bp 105–109° (18 mm) (lit.[49] 110–115° (5mm)); nmr (CCl_4) δ 1.9 (broad s, 3), 3.2 (broad s, 2), 6.18 (m, 1), and 6.8–7.2 (m, 4). The thiochromene (**12c**) darkened rapidly at room temperature. Consequently, it was either stored at −20° or, preferably, used immediately. Alkylation of 3-methyl-1-thio-3-chromene (**12c**) was effected by the general procedure using CH_3I and $AgBF_4$. Isolation gave **13c** as colorless crystals (75%): mp 124.8–125.7° (from acetone–ether); nmr (DMSO-d_6) δ 2.1 (s, 3), 2.95 (s, 3), 4.0 and 4.6 (pair of d, 2, J = 17.5 Hz, AB pattern with low-field doublet broadened considerably), 6.72 (s, 1), and 7.3–8.2 (m, 4). *Anal.* Calcd for $C_{11}H_{13}BF_4S$: C, 50.00; H, 4.94; S, 12.10. Found: C, 49.79; H, 4.90; S, 12.32.

1-Methyl-4-phenyl-1-thio-3-chromenium Tetrafluoroborate (13d). Alkylation of 4-phenyl-1-thio-3-chromene (**12d**)[26] with CH_3I and $AgBF_4$ according to the general procedure gave **13d** as colorless needles in 68% yield: mp 123.0–123.8°; nmr (DMSO-d_6) δ 3.15 (s, 3), 4.3–4.9 (m, 2), 6.15–6.4 (m, 1), 7.15–7.8 (m, 8) and 8.0–8.2 (m, 1); ir (Nujol) 1370, 1100, 1040, 820, 770, 735, 720 and 690 cm^{-1}. *Anal.* Calcd for $C_{16}H_{15}BF_4S$: C, 58.93; H, 4.65; S, 9.83. Found: C, 58.70; H, 4.92; S, 10.00.

1-Methyl-3-phenyl-1-thio-3-chromenium Tetrafluoroborate (13e). A sample of 3-phenyl-1-thio-4-chromanone[50] (3.0 g, 0.0125 mol) was reduced and dehydrated according to the general procedure to give 3-phenyl-1-thio-3-chromene (**12e**) as a yellow oil (2.3 g, 89% from the ketone) which was used as soon as possible and without further purification: nmr (CCl_4) δ 3.65 (d, 2, J = 1.4 Hz), 6.7 (s, 1), and 6.9–7.6 (m, 9). The alkylation of 3-phenyl-1-thio-3-chromene was effected according to the general procedure with CH_3I and $AgBF_4$ to give an essentially quantitative yield of solid product. Recrystallization from acetone–ether gave **13e** as colorless crystals (2.65 g, 75%): mp 186.2–188.0°; nmr (DMSO-d_6) δ 3.3 (s, 3), 5.0–5.3 (m, 2), and 7.3–8.2 (m, 10); ir (Nujol) 1410, 1250, 1000–1070, 990, 890, 760, 730, 710, and 690 cm^{-1}. *Anal.* Calcd for $C_{16}H_{13}BF_4S$: C, 58.93; H, 4.65; S, 9.83. Found: C, 59.11; H, 4.75; S, 9.73.

1-Phenyl-2-thio-3-chromene (14b). 1-Phenyl-2-thio-3-chromene was prepared by a modification of the procedure of Price and Follweiler.[17d,46] To a slurry of 2-thianaphthalenium perchlorate[72] (30 g, 0.122 mol) in 1000 ml of anhydrous ether was added, during 30 min, 100 ml of 2.72 M phenylmagnesium chloride (0.272 mol) in THF under N_2. After stirring rapidly overnight at room temperature, the flask was cooled in an ice bath and saturated NH_4Cl solution was added. The entire mixture was filtered, and the two layers of filtrate were separated. The ether layer was washed with brine and dried over $MgSO_4$. Volatile material was removed under reduced pressure to leave a dark purple oil (19.1 g) which smelled strongly of biphenyl. The oil was chromatographed on 200 g of neutral alumina (Woelm, activity grade 1). Elution with petroleum ether gave crystalline biphenyl (5.5 g) followed by 11.9 g of a pale yellow oil. Distillation of the oil gave pure **14b** (9.0 g, 32%): bp 124–126° (0.10 mm) (lit.[46] 131–132° (0.15 mm)); nmr (CCl_4) δ 5.07 (s, 1), 6.18 (dd, 1, J = 10, 1 Hz), 6.65 (d, 1, J = 10 Hz), and 6.7–7.3 (m, 9).

1-(*p*-Chlorophenyl)-2-thio-3-chromene (14c). A suspension of 2-thianaphthalenium perchlorate[72] (10.0 g, 0.041 mol) in 150 ml of anhydrous ether under N_2 was treated with 35 ml of 2 M *p*-chlorophenylmagnesium chloride (0.070 mol) in THF over 15 min. A deep purple color developed. Vigorous stirring was maintained overnight. The solution was quenched with saturated NH_4Cl solution at 0° and worked up in the same manner as used for the isolation and purification of 1-phenyl-2-thio-3-chromene (**14b**). Elution with petroleum ether gave 4,4′-dichlorobiphenyl in small amounts. Further elution with petroleum ether–benzene (3:2) gave 6.6 g of colorless solid. Recrystallization from petroleum ether afforded 6.0 g (60%) of **14c** as colorless crystals: mp 62.5–64°; nmr (CCl_4) δ 5.0 (s, 1), 6.2 (dd, 1, J = 10, 1 Hz), 6.7 (d, 1, J = 10 Hz), and 6.75–7.30; mass spectrum (70 eV) m/e (rel intensity) 258 (M^+, 100), 259 ($M^+ + 1$, 44), 260 ($M^+ + 2$, 37); also 257 ($M^+ - 1$, 78). *Anal.* Calcd for $C_{15}H_{11}ClS$: C, 69.75; H, 4.26; S, 12.40. Found: C, 69.50; H, 4.30; S, 12.37.

1-Methyl-2-thio-3-chromene (14d). In 25 ml of anhydrous ether under N_2 at 0° was suspended 2-thianaphthalenium perchlorate[72] (3.1 g, 0.0125 mol). While vigorous stirring was maintained, methylmagnesium bromide (0.018 mol, 6 ml of a 3 M solution in ether) was added *via* syringe. The solution gradually turned an amber color with disappearance of the dark perchlorate salt. After 30 min, the reaction mixture was quenched with cold saturated NH_4Cl solution at 0°. A solid residue was removed by filtration, and the ether layer was separated, dried over $MgSO_4$, and concentrated under reduced pressure to leave a wine-colored oil. Distillation afforded **14d** as a colorless oil (1.3 g, 65%), bp 62–65° (0.15 mm), which yellowed rapidly in air at room temperature: nmr (CCl_4) δ 1.4 (d, 3, J = 7 Hz), 3.75 (dq, 1, J = 7, 1.5 Hz), 6.15 (dd, 1, J = 9, 1.5 Hz), 6.55 (d, 1, J = 9 Hz), and 6.7–7.2 (m, 4). The oil was alkylated immediately without further purification.

1,3-Diphenyl-7-methoxy-2-thio-3-chromene (14e). In 25 ml o-anhydrous ether cooled to −70° was dissolved 7-methoxy-3-phenylf 2-thio-3-chromene (**14f**)[51] (2.5 g, 0.0098 mol). A solution of 3.0 ml of sulfuryl chloride in 20 ml of anhydrous ether was also cooled to −70° and added dropwise to the thiochromene solution in a procedure patterned after that of Lüttringhaus and Engelhard[72] for the preparation of 2-thianaphthalenium perchlorate. A brown solid which precipitated was filtered as quickly as possible through a precooled sintered glass filter and suspended in 50 ml of anhydrous ether at −70°. A syringe was used to add 15 ml of 70% perchloric acid (cooled to −30°) to the suspension. The mixture was allowed to warm slowly to room temperature over 15 min. A yellow-orange precipitate which formed was collected and recrystallized from glacial acetic acid to yield (presumably) 7-methoxy-3-phenyl-2-thianaphthalenium perchlorate as cinnamon-colored crystals (2.3 g, 66%). The product was not further characterized. Instead, a portion (1.0 g, 0.0023 mol) was suspended in 25 ml of anhydrous ether under N_2. The suspension was stirred vigorously as 4.0 ml of 2.72 M phenylmagnesium chloride (0.0109 mol) in THF was added over 5 min. After stirring for 20 min at room temperature, the deep red solution was quenched at 0° with saturated NH_4Cl solution. The entire mixture was poured into water and thoroughly extracted with ether. The combined ether extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give 0.90 g of an orange solid. The solid was washed thoroughly with petroleum ether to remove any biphenyl present. The pale yellow solid (0.60 g) which remained was recrystallized from hot acetone to give thiochromene **14e** as hard, colorless crystals (0.50 g, 15%): mp 157–158°; nmr (acetone-d_6) δ 3.90 (s, 3), 5.6 (s, 1), 6.8–7.2 (m, 3), and 7.2–7.9 (m, 11); mass spectrum (70 eV) m/e (rel intensity) 330 (M^+, 100), 331 ($M^+ + 1$, 26.5), 332 ($M^+ + 2$, 7.9), and 253 ($M^+ - 77$, 80). *Anal.* Calcd for $C_{22}H_{18}OS$: C, 80.00; H, 5.56; O, 4.87. Found: C, 79.77; H, 5.60; O, 5.29.

7-Methoxy-3-phenyl-2-thio-3-chromene (14f). The reduction and dehydration of 7-methoxy-3-phenyl-2-thio-4-chromanone,[51] carried out according to the general procedure, gave **14f**, mp 94–95°, as colorless flakes from either petroleum ether–ether or anhydrous CH_3OH in yields of 55–70% in several preparations: nmr ($CDCl_3$) δ 3.70 (s, 3), 3.85 (s, 2), and 6.68–7.85 (m, 9). *Anal.* Calcd for

(71) J. C. Petropoulous, M. A. McCall, and D. S. Tarbell, *J. Amer. Chem. Soc.*, **75**, 1130 (1953).

(72) A. Lüttringhaus and N. Engelhard, *Chem. Ber.*, **93**, 1525 (1960).

$C_{16}H_{14}OS$: C, 75.60; H, 5.51; S, 12.60. Found: C, 75.42; H, 5.63; S, 12.77.

2-Methyl-2-thio-3-chromenium Tetrafluoroborate (15a). Using the procedure of Price and Follweiler,[17d] 2-thio-3-chromene (**14a**) (bp 84–90° (0.20 mm)) was prepared in 63% yield by slowly heating 2-thio-4-chromanol with potassium pyrosulfate followed by distillation of the volatile material at high vacuum. The yield could be increased to nearly 85% (based on 2-thio-4-chromanone) if the crude oily alcohol was not crystallized and purified but instead used as obtained. Following the general procedure, 2-thio-3-chromene (**14a**) (0.70 g, 0.0047 mol) was alkylated with CH_3I and $AgBF_4$ to give **15a** as colorless plates (1.0 g, 67%) from acetone–ether: mp 92.4–93.2°; nmr (DMSO-d_6) δ 2.75 (s, 3), 4.5–5.1 (m, 2), 6.6 (d, 1, J = 10 Hz), 7.4–7.7 (broad s, 4), and 7.8 (d, 1, J = 10 Hz); uv(max) (H_2O) 242 (ϵ 12,250), 266 (ϵ 5750), and 295 nm (shoulder); ir (CH_2Cl_2) 3100–2950, 1600, 1510, 1480, 1200, 1100, and 840 cm^{-1}. *Anal.* Calcd for $C_{10}H_{11}BF_4S$: C, 48.03; H, 4.43; S, 12.82. Found: C, 48.10; H, 4.33; S, 13.09.

1-Phenyl-2-methyl-2-thio-3-chromenium Tetrafluoroborate (15b). Alkylation of 1-phenyl-2-thio-3-chromene (**14b**) with CH_3I and $AgBF_4$ by the general procedure gave 92–95% yields (in several preparations) of **15b** as a crude white solid. Recrystallization from methylene chloride and petroleum ether afforded **15b** as colorless crystals: mp 168–169°; nmr (DMSO-d_6) δ 3.01 (s, 3), 6.5–6.7 (broad singlet overlapping high field peak of a doublet with J = 9 Hz, 2), 7.2–7.8 (m, 9), and 8.0 (d, 1, J = 9 Hz); uv(max) (50% EtOH) 226 (ϵ 23,800) and 287 nm (ϵ 9150). *Anal.* Calcd for $C_{16}H_{15}BF_4S$: C, 58.93; H, 4.65; S, 9.83; B, 3.39. Found: C, 59.07; H, 4.65; S, 9.73; B, 3.31.

1-(*p*-Chlorophenyl)-2-methyl-2-thio-3-chromenium Perchlorate (15c). A sample of 1-(*p*-chlorophenyl)-2-thio-3-chromene (**14c**) (0.60 g, 0.0023 mol) was alkylated according to the general procedure with CH_3I and $AgClO_4$ to yield **15c** as a pale yellow powder (0.72 g, 84%). Recrystallization from acetone–petroleum ether gave **15c** as colorless crystals (0.55 g, 64%): mp 183–184°; nmr (DMSO-d_6) δ 3.01 (s, 3), 6.5–6.7 (broad singlet overlapping high-field portion of a doublet, 2, J = 9.5 Hz), 7.2–7.9 (m, 8), and 8.0 (d, 1, J = 9.5 Hz); uv(max) (EtOH) 227 (ϵ 25,200) and 289 nm (ϵ 7020). *Anal.* Calcd for $C_{16}H_{14}Cl_2O_4S$: C, 51.50; H, 3.76; S, 8.58; Cl, 19.00. Found: C, 51.59; H, 3.82; S, 8.36; Cl, 18.74.

1,2-Dimethyl-2-thio-3-chromenium Tetrafluoroborate (15d). Freshly prepared 1-methyl-2-thio-3-chromene (**14d**) (0.92 g, 0.0057 mol) was alkylated with CH_3I and $AgBF_4$ according to the general procedure to give a yellow solid (0.89 g, 60%). Recrystallization from acetone–ether gave **15d** as colorless crystals (0.73 g, 48%): mp 95.5–96°; nmr (DMSO-d_6) δ 1.6 (d, 3, J = 6.8 Hz), 2.77 (s, 3), 5.01 (dq, 1, J = 6.8, 1.7 Hz), 6.64 (dd, 1, J = 9.5, 1.7 Hz), 7.6 (s, 4), and 7.87 (d, 1, J = 9.5 Hz). *Anal.* Calcd for $C_{11}H_{13}BF_4S$: C, 49.92; H, 4.96; S, 12.14; B, 4.17. Found: C, 49.97; H, 4.90; S, 11.85; B, 4.02.

1,3-Diphenyl-7-methoxy-2-thio-3-chromenium Tetrafluoroborate (15e). The alkylation of 1,3-diphenyl-7-methoxy-2-thio-3-chromene (**14e**) (0.71 g, 0.002 mol) with CH_3I and $AgBF_4$ was carried out according to the general procedure except that the reaction was allowed to proceed for 4 hr. Isolation gave a yellow-brown solid (0.60 g, 64%) which was recrystallized from acetone–ether to yield 0.52 g (56%) of **15e** as pale yellow crystals: mp 165–166°; nmr (DMSO-d_6) δ 3.10 (s, 3), 3.90 (s, 3), 6.70 (s, 1), 7.2–7.8 (m, 12), 7.9 (d, 1, J = 10 Hz), and 8.33 (s, 1); uv(max) (50% EtOH) 354 (ϵ 16,800) and 255 nm (ϵ 16,800). *Anal.* Calcd for $C_{23}H_{21}BF_4OS$: C, 64.00; H, 4.87; S, 7.39. Found: C, 63.55; H, 5.05; S, 7.16.

7-Methoxy-2-methyl-3-phenyl-2-thio-3-chromenium Tetrafluoroborate (15f). The alkylation of 7-methoxy-3-phenyl-2-thio-3-chromene (**14f**) was carried out according to the general procedure with CH_3I and $AgBF_4$. A pale yellow solid (recrystallized from acetone–ether), mp 215–216°, was obtained in 80–90% yields in several preparations: nmr (DMSO-d_6) δ 2.70 (s, 3), 3.90 (s, 3), 4.90 and 5.25 (AB pattern, 2, J = 17 Hz), and 7.05–8.18 (m, 9). *Anal.* Calcd for $C_{17}H_{17}BF_4OS$: C, 56.91; H, 4.77; S, 9.01. Found: C, 57.14; H, 4.81; S, 9.19.

General Procedure for the Generation or Attempted Generation of Thianaphthalenes. Method A. A sample of thiochromenium salt (0.0001–0.0004 mol) was dissolved in 0.20–0.30 ml of DMSO-d_6 in an nmr tube. The tube was capped with a rubber serum cap and a long needle was passed through the serum cap into the solution. With a short needle also in the serum cap, the solution was degassed by passing either N_2 or argon through it for 15–20 min. An equivalent amount of *tert*-butyllithium (purchased from Foote or Alfa Chemical as a 1.2–1.35 *M* solution in pentane) was slowly released, *via* a syringe equipped with a long needle, into the solution of the salt in DMSO-d_6 as the tip of the needle was gradually withdrawn from the base of the nmr tube. The short pressure-release needle was removed when bubbling had stopped. To ensure complete mixing, the nmr tube was shaken once, taking care to see that the serum cap fit tightly. Some additional gas pressure occasionally had to be released with a syringe needle at this point. The solutions generated in this manner were normally transparent (and highly colored) with varying amounts of pentane layered on the surface of the DMSO-d_6. Small amounts of pentane dissolved in the DMSO-d_6 produced very large absorptions in the nmr spectrum from 0.85 to 1.25 ppm. The chemical shifts of protons were determined by using the DMSO-d_5 multiplet at 2.52 ppm as an internal standard. Resolution was a problem at times, presumably due to varying degrees of solution homogeneity and viscosity.

Method B. A slight variation of procedure A was used when the proton-abstracting base was potassium *tert*-butoxide. Potassium *tert*-butoxide (0.0001–0.0004 mol) was partially dissolved in 0.20 ml of DMSO-d_6 and the suspension was degassed with N_2 or argon by the method described in procedure A. An equivalent amount of of the thiochromenium salt in 0.10–0.20 ml of DMSO-d_6 was then injected slowly at the bottom of the potassium *tert*-butoxide–DMSO-d_6 suspension. The syringe needle was withdrawn, and the tube was shaken once. The reaction mixture was generally deep wine-red in color and transparent at this point. Nmr spectra were obtained as quickly as possible. Resolution was not a problem when procedure B was employed.

General Procedure for Protonation and Reisolation of Starting Thiochromenium Salt after Generation or Attempted Generation of the Corresponding Thianaphthalene. After the addition of *tert*-butyllithium or potassium *tert*-butoxide to the thiochromenium salt in DMSO-d_6 under argon in an nmr tube, a general reisolation procedure was followed, whether or not the thianaphthalene was observed or was suspected to be present based on the nmr spectrum. The solution (usually highly colored) was quenched in the nmr tube with a slight excess of 20–35% fluoroboric or perchloric acid (injected *via* microliter syringe). The color of the solution invariably vanished instantly when the acid was added and the tube shaken. Some solid material often precipitated. An nmr spectrum of the acidified solution (or suspension) was obtained directly when practical. If too much solid material was present in the nmr tube to obtain a meaningful spectrum, the following procedure was used. The content of the nmr tube was diluted with acetone, the suspension was filtered to remove insoluble material, and the filtrate was concentrated under high vacuum. The oily residue was either observed directly in the nmr in acetone-d_6 solution or attempts were made to crystallize the residue from a suitable solvent pair. When the acidified solution was suspected to contain organic-soluble material rather than the water-soluble tetrafluoroborate or perchlorate salt, the content of the nmr tube was poured into water and thoroughly extracted with ether. The ether extracts were dried ($MgSO_4$), and solvent was removed *in vacuo* to yield the organic-soluble material for nmr analysis.

Generation of 1-Phenyl-2-methyl-2-thianaphthalene (16). A solution of 1-phenyl-2-methyl-2-thio-3-chromenium tetrafluoroborate (**15b**) (0.086 g, 0.00026 mol) in 0.200 ml of DMSO-d_6 under N_2 in an nmr tube was treated, according to the general procedure, with *tert*-butyllithium (0.22 ml of a 1.24 *M* solution in pentane, 0.00026 mol). An immediate deep wine-red color was produced. An nmr spectrum recorded within 3–5 min of the addition of base gave evidence for the generation of **16**: nmr (DMSO-d_6) δ 1.87 (s, 3), 5.64 (d, 1, J = 8 Hz), 6.8–7.7 (m, 15–18), and 7.75 (d, 1, J = 8 Hz). The only other peaks in the spectrum were attributable to the hydrocarbon solvent of the *tert*-butyllithium solution and several small extraneous signals. After 10 min at a probe temperature of 40°, the spectrum was essentially unchanged except for the appearance of a small singlet at 1.90 ppm. A slight excess of dilute fluoroboric acid was added. The nmr spectrum of the starting salt (**15b**) was regenerated as evidenced by the reappearance of nmr signals at δ 3.01, 6.5–6.7, 7.2–7.8, and 8.0 ppm. The acidified material in the nmr tube was isolated according to the general procedure to give 0.043 g (50%) of **15b** as pale yellow crystals, mp 156–162° (pure **15b**, mp 168–169°).

Determination of the Decomposition Products of 1-Phenyl-2-methyl-2-thianaphthalene (16). A suspension of potassium *tert*-butoxide (0.034 g, 0.304 mol) in 0.20 ml of DMSO-d_6 under N_2 in an nmr tube was treated according to the general procedure with a solution of 1-phenyl-2-methyl-2-thio-3-chromenium tetrafluoroborate (**15b**) (0.099 g, 0.00029 mol) dissolved in 0.20 ml of DMSO-d_6. The deep red solution was scanned quickly by nmr to confirm the presence of **16** (present in 50% yield). The solution was acidi-

fied with dilute fluoroboric acid, diluted with acetone, poured into H_2O, and extracted thoroughly with ether. The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give an orange oil (0.022 g) whose nmr spectrum indicated the presence of 1-methyl-1-phenyl-2-thio-3-chromene (**19**) (~48%), 1-phenyl-2-thio-3-chromene (**14b**) (~7%), and unknown material (~45%). The products were not separated. No attempt was made to reisolate the **15b** regenerated upon acidification from the aqueous extracts.

The decomposition of 1-phenyl-2-methyl-2-thianaphthalene (**16**) was studied on a preparative scale. Into a solution of potassium *tert*-butoxide (0.216 g, 0.00193 mol) in 30 ml of DMSO under N_2 was injected 1-phenyl-2-methyl-2-thio-3-chromenium tetrafluoroborate (**15b**) (0.629 g, 0.00193 mol) dissolved in 10 ml of DMSO. The solution immediately turned deep red. The reaction mixture was stirred at 40° for 4 hr during which the color of the mixture had faded to a yellow-orange. It was poured into H_2O and extracted with ether, and the extracts were washed thoroughly with H_2O. The extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give 0.440 g of a brown oil. Chromatography on neutral alumina (Woelm, activity 1) (4:1 petroleum ether–benzene) gave 0.217 g of essentially pure 1-methyl-1-phenyl-2-thio-3-chromene (**19**): nmr (CCl_4) δ 1.90 (s, 3), 6.15 (d, 1, J = 10 Hz), 6.55 (d, 1, J = 10 Hz), and 6.7–7.7 (m, 9); mass spectrum (70 eV) *m/e* (rel intensity) 238 (M^+, 100), 239 ($M^+ + 1$, 18.8), 240 ($M^+ + 2$, 5.75), calcd for $C_{16}H_{14}S$ ($M^+ + 1$, 18.3) and ($M^+ + 2$, 5.8). Further elution with 50% benzene–ether gave 0.169 g of an orange oil showing absorption signals assignable to 1-phenyl-2-thio-3-chromene (**14b**) (25%) and multiple absorptions from 0.70 to 2.4 and 6.6 to 7.8 ppm (75%), the origin of which was indeterminate.

Generation of 1-(*p*-Chlorophenyl)-2-methyl-2-thianaphthalene (17). A solution of 1-(*p*-chlorophenyl)-2-methyl-2-thio-3-chromenium perchlorate (**15c**) (0.073 g, 0.000196 mol) was dissolved in 0.20 ml of DMSO-d_6 and injected into a suspension of potassium *tert*-butoxide (0.022 g, 0.000196 mol) in DMSO-d_6 under a N_2 atmosphere in an nmr tube according to the general procedure. A deep red solution was produced whose nmr spectrum (obtained within 3 min of generation) exhibited signals attributable to **17**: δ 1.85 (s, 3), 5.75 (d, 1, J = 8 Hz), 6.5–7.60 (m, 15), and 7.65 (d, 1, J = 8 Hz). Several experiments in which **17** was generated by the same general procedure gave **17** in amounts ranging from 50 to 54% based on comparison of the integration of the signals at 1.85, 5.75, and 6.5–7.60 ppm. Acidification of the solution in the nmr tube after 5 min in the nmr probe with dilute $HClO_4$ regenerated the spectrum of the starting salt, **15c**, in approximately 50% yield, although the material was not reisolated.

When **17** was generated at room temperature and maintained at 40° in the nmr probe, new peaks began to appear after a few minutes. The intensity of the doublet at 5.75 ppm began to decrease and the multiplet from 6.8 to 7.7 ppm began to show more peaks in the region 6.5–7.0 ppm. The general appearance of the phenyl region changed while a singlet began to appear at 1.90 ppm at the expense of the singlet at 1.85 ppm. After 15 min, 50% of **17** had been converted to another product, based on integration of the doublet at 5.75, the singlet at 1.87, and the emerging singlet at 1.90 ppm.

The generation and observation of **17** were also performed at a temperature of 20–22°. Thianaphthalene, **17**, was initially generated in the same 50–54% yields as outlined above. However, the lowered temperature prevented any noticeable decomposition from occurring for as long as 90 min.

Determination of the Decomposition Products of 1-(*p*-Chlorophenyl-2-methyl-2-thianaphthalene (17). Into a suspension of potassium *tert*-butoxide (0.061 g, 0.00055 mol) in 15 ml of DMSO (stirred under a nitrogen atmosphere) was injected 1-(*p*-chlorophenyl)-2-methyl-2-thio-3-chromenium perchlorate (**15c**) (0.200 g, 0.00054 mol) dissolved in 1.0 ml of DMSO. The solution turned cherry red and was maintained at 37–40° for 24 hr. After that time, the solution had faded to a yellow-orange. The reaction mixture was poured into H_2O and extracted thoroughly with ether, and the extracts were washed thoroughly with water. The extracts were dried over $MgSO_4$ and concentrated under reduced pressure to give an orange oil (0.142 g, 85%). Chromatography on neutral alumina (Woelm, activity grade 1), eluting first with petroleum ether mixtures containing up to 50% benzene, gave 0.058 g of a pale yellow oil, identified by its spectral characteristics as 1-(*p*-chlorophenyl)-1-methyl-2-thio-3-chromene (**18**): nmr (CCl_4) δ 1.90 (s, 3), 6.20 (d, 1, J = 10 Hz), 6.62 (d, 1, J = 10 Hz), and 6.9–7.4 (m, 8); mass spectrum (70 eV) *m/e* (rel intensity) 272 (M^+, 100), 273 ($M^+ + 1$, 19), and 274 ($M^+ + 2$, 39). Further elution with 50% benzene–ether gave 0.081 g of an orange oil whose nmr spectrum indicated that it was approximately 30% 1-(*p*-chlorophenyl)-2-thio-3-chromene (**14c**), identified by comparison of the nmr spectrum with that of authentic **14c**: nmr (CCl_4) δ 5.0 (s), 6.2 (d), and 6.7–7.6 (m), also 0.90–2.4 (m), 5.6–6.6 (m), and 6.7–7.8 (m).

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Structure of a Hydrazino-Bridged [12]Annulene. A 12π Monocyclic Antiaromatic Compound

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Abstract: The crystal structure of 8b,8c-diazacyclopent[*fg*]acenaphthylene has been determined from three-dimensional X-ray data measured by counter methods. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 7.643 (4), b = 4.138 (3), c = 13.452 (6) Å, β = 90.38 (5)°, and ρ_{calcd} = 1.41 g/cm^3 for Z = 2. Least-squares refinement gave a conventional R factor of 0.076 for 349 unique observed reflections. The molecular framework of this hydrazino-bridged [12]annulene is planar to within 0.02 Å. This fact, and the presence of a nitrogen–nitrogen single bond, establish its structure. The X-ray and pmr data establish that this compound is a planar 12-π-monocyclic antiaromatic compound.

An understanding of the net energy changes associated with π-electron delocalizations remains one of the basic questions in organic chemistry. Molecular orbital theory predicts[1] that π-electron delocalization may have one of three possible effects on the net energy of the system: it may increase, decrease, or have no effect on that energy. The $4n + 2$ monocyclic systems, aromatic compounds, represent an experimental verification of those instances where an energy decrease accompanies π-electron delocalizations. The

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