Thiabenzenes. Reassessment of Their Chemical and Physical Properties[1,2]

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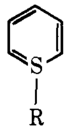
Abstract: The syntheses of divers thiabenzene systems are described, and several chemical and physical properties of this class of compounds are evaluated. Observations are recorded which point to the similarity between thiabenzenes and acyclic sulfonium ylides: both classes of compounds are stabilized toward thermal decomposition by substituents which delocalize or stabilize electronic charge, both classes undergo thermal Stevens rearrangements, and both classes are stably pyramidal at sulfur with a barrier to pyramidal inversion >20 kcal/mol. These observations, as well as the marked upfield chemical shifts noted for protons on carbons α to sulfur in thiabenzene systems, rule out an aromatic bonding description for thiabenzenes and can be reconciled only with the view of thiabenzenes as cyclic sulfonium ylides.

In the course of our studies on pyramidal inversion,[3] we had occasion to develop a specially parametrized CNDO/2 scheme[4] which proved useful in providing reliable quantitative estimates for barriers to pyramidal inversion in systems containing elements from the first and second row of the periodic table. These calculations also offered many predictions which, it was hoped, would stimulate and direct further experimentation.



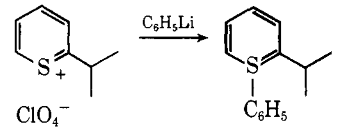
1, R = CH_3
2, R = C_6H_5

One such prediction was that 1-methylthiabenzene (**1**) should have a relatively high barrier to pyramidal inversion at sulfur (ca. 43 kcal/mol).[4] As was subsequently pointed out,[3] this high barrier contrasts sharply with a previously expressed opinion that 1-phenylthiabenzene (**2**), and other similar unhindered thiabenzenes, should be planar or have a very low bending barrier for the sulfur-phenyl bond.[5-8]

To resolve these conflicting views, we decided to resort to an experimental test. Nuclear magnetic resonance spectroscopy is a convenient technique for gaining insight into the question of pyramidality. By incorporation of groups containing enantiotopic nuclei, which become diastereotopic in the chiral molecular environment that would be associated with appropriately substituted pyramidal sulfur, one could probe the conformation of thiabenzenes.[9] If thiabenzenes proved to be nonplanar, on the time scale of the NMR observations, then dynamic nuclear magnetic resonance (DNMR) would provide a means of determining the inversion barrier so long as the activation energies were in the range of ca. 5-25 kcal/mol. Hence, the synthesis of an appropriately substituted thiabenzene was undertaken.

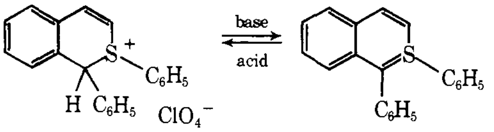
Since **2** was reported[5] to be quite stable, and since S-arylthiabenzenes might be expected[10] to be more stable than S-alkylthiabenzenes (and thus **2** more stable than **1**), we felt that a derivative of **2** would be ideally suited for a preliminary study along the lines described above. Accordingly, we attempted to synthesize 2-isopropyl-1-phenylthiabenzene (**3b**), in which the sulfur atom serves as a potential center of chirality, by the route that was employed for the preparation of **2** (eq 1).[5]

The reaction of **3a**[11] with phenyllithium was examined by NMR spectroscopy. In an NMR tube under a dry nitrogen atmosphere, **3a** (1.0 mol equiv) was combined with purified phenyllithium (1.0 mol equiv). Dry toluene-d_8 was then added to the tube cooled at −78°, immediately resulting in the formation of a dark-red color and precipitate. After centrifugation (−78°), the ^1H NMR spectrum of the clear supernate was recorded at −30°. Surprisingly, three broad, unresolved, envelope absorptions centered at δ 7.1 ($W_{1/2}$ = 0.3 ppm), 5.8 ($W_{1/2}$ = 0.4 ppm), and 1.1 ($W_{1/2}$ = 0.35 ppm) were observed; the broad, unresolved methyl region was especially puzzling. The unexpected failure of this reaction to form a clean product induced us to seek another synthetic route to **3b**.

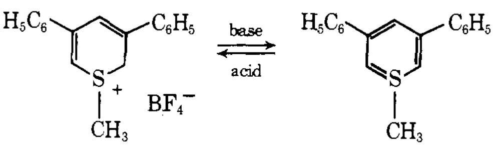


3a **3b** (1)

Deprotonation of 1,2-diphenyl-2-thiochromenium perchlorate (**4a**) with base had been reported by Price and Follweiler[7] to give 1,2-diphenyl-2-thianaphthalene (**4b**) (eq 2). Evidence for the formation of **4b** was derived from the intense purple color formed on deprotonation of **4a** and the observation that addition of acid (aqueous NH_4Cl) to the purple solution could regenerate **4a**.[7] Deprotonation was also used by Hortmann and Harris[12] to generate orange solutions of 1-methyl-3,5-diphenylthiabenzene (**5b**) (eq 3) which regenerated **5a** on acidification with 48% HBF_4. As noted by these workers, the ^1H NMR spectrum of **5b** featured a markedly upfield chemical shift for the 2,6 protons of the thiabenzene ring (δ 4.03, Me_2SO-d_6), which was taken to indicate an ylide-like structure for **5b**.[12] This spectrum was dramatically different from the one reported for **2** ("... a single absorption centered at τ 2.8."),[5] a discrepancy which prompted Hortmann and Harris[12] to question the claimed synthesis of **2**. However, the spectral differences were subsequently rationalized by Price et al.[8a] as arising



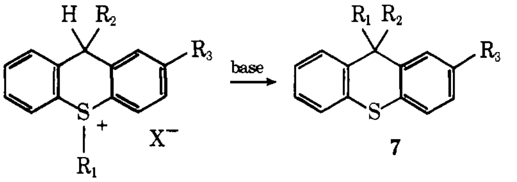
4a **4b** (2)



5a **5b** (3)

from a possible difference in the nature of *S*-alkylthiabenzenes as compared with *S*-arylthiabenzenes.

While the above deprotonation experiments[7,12] appeared to be successful in generating thiabenzenes, thus affording ample precedent for a possible synthesis of **3b**, we noted with concern a report[13] that the deprotonation of 10-alkyl- or 10-arylthioxanthenium salts (type **6**) did not yield 10-alkyl- or 10-aryl-10-thiaanthracenes but gave instead the corresponding 9-alkyl- or 9-arylthioxanthenes (type **7**). Since 10-aryl-10-thiaanthracenes had previously been claimed to be stable, isolable species,[6] an obvious inconsistency existed which we felt obliged to resolve before continuing the main thread of our investigation.



(4)

6 → **7**

6

a, R_1 = phenyl; R_2 = H; R_3 = H
b, R_1 = 2,5-xylyl; R_2 = H; R_3 = H
c, R_1 = 2,5-xylyl; R_2 = H; R_3 = Cl
d, R_1 = mesityl; R_2 = H; R_3 = H
e, R_1 = methyl; R_2 = H; R_3 = H
f, R_1 = methyl; R_2 = *p*-tolyl; R_3 = H
(**6a**–**6d**, X = ClO_4^-; **6e**, **6f**; X = BF_4^-)

Accordingly, thioxanthenium salts **6a**–**6f** were prepared,[14] and their deprotonation was studied using dimsyl anion.[15] Table I summarizes the results of these experiments. In every case, rearrangement products **7a**–**7f** were observed, in agreement with the observation of Hori et al.[13] In addition to these rearrangement products, escape products (see below) were also detected from the deprotonation of **6d**–**6f**. We shall return to a discussion of the mechanism of these rearrangements and a rationalization of the formation of the escape products in a subsequent section.

Although deprotonation of **6a** should give directly 10-phenyl-10-thiaanthracene (**8**), a purportedly stable species,[6] no such substance was isolated. However, we did note that all the reactions (eq 4) initially produced intense colors,[16] which could be maintained at low temperatures (<0°), and which were subsequently discharged on warming to ca. 25°. Indeed, the ^1H NMR spectrum at −45° of the orange reaction mixture obtained by the low-temperature deprotonation of **6e** with dimsyl-d_5-lithium in 80% toluene-d_8–20% dimethoxyethane exhibited not only the resonances attributable to the methyl group of **7e** [δ 1.27 (d, J = 7 Hz)] but also singlet resonances of another species at δ 6.01 and 1.05 (ratio 1:3). As the reaction mixture was allowed to warm to ca. 40°, the orange color was discharged, and the signals at δ 6.01 and 1.05 concurrently disappeared, leaving only rearrangement products. This spectral evidence strongly suggests that highly colored 10-thiaanthracenes are initially formed on deprotonation and subsequently undergo rapid rearrangement to the thioxanthenes shown in Table I.

By demonstrating that 10-thiaanthracenes are extremely unstable species,[17] these results necessarily contradicted the picture[6] of 10-thiaanthracenes as isolable red-brown amorphous solids that could be boiled in acetic acid without change, and that were very resistant to Raney nickel desulfurization. Hence, this outcome raised a serious question regarding the identity of the material characterized[6] as **8** and reinforced the doubts first expressed by Hortmann and Harris,[12] concerning the identity of the material previously characterized[5] as **2**. Since thiabenzenes have been widely accepted in the literature[18] as an interesting class of heteroaromatic species, we felt compelled to launch a broad inquiry into the chemistry of thiabenzenes in order to reconcile the mounting body of evidence that explicitly disputed previously reported[5,6] observations and interpretations.

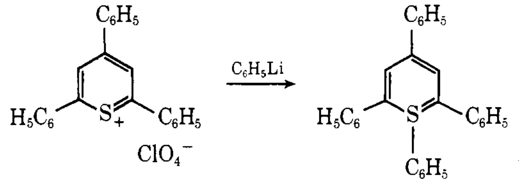
Table I. Deprotonation of 10-Substituted Thioxanthenium Salts

	Yield of rearrangement products (%)[a]	
Compd	9-Substituted thioxanthene (**7**)	Thioxanthene (**7**, $R_1 = R_2 = R_3$ = H)
6a	90	
6b	90	
6c	71[c]	
6d	36	5
6e	34	13
6f	50	26[b]

[a] Yields were determined (±3%) by GLC using 9-*p*-tolylthioxanthene or 9-phenylthioxanthene as an internal standard, unless otherwise indicated. Detector response factors were determined on authentic samples of the major observed rearrangement products. [b] This value represents the observed yield of 9-*p*-tolylthioxanthene. [c] This value is an isolated yield obtained by column chromatography of the reaction mixture.

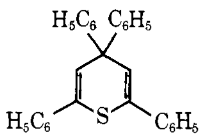
Results and Discussion

1,2,4,6-Tetrasubstituted Thiabenzenes. 1,2,4,6-Tetraphenylthiabenzene (**10**) was the first thiabenzene for which a synthesis was reported.[19] This compound was generated by treatment of 2,4,6-triphenylthiopyrylium perchlorate (**9**) with an excess of phenyllithium (eq 5). Suld and Price[19] initially obtained a violet resin which was converted to a finely divided, amorphous, violet solid by precipitation from ether. This solid was assigned structure **10** chiefly on the basis of its absorption in the visible region, molecular weight, elemental analysis,[20] and chemical reactivity. The chemical evidence for **10** consisted of the isolation of 2,4,4,6-tetraphenylthiopyran (**11**) (25% yield) from the thermal decomposition of the purple solid and the formation of betaine **12** (60% yield), in addition to the qualitative presence of thiophenol and phenyl disulfide, from treatment of the purple resin with oxygen followed by hydrogen chloride. This information implicates the formation of **10** but, while later work[8a,21] with similar systems lent additional support to structures of this type, we felt it worthwhile to reexamine the reaction of eq 5 in more detail in order to provide a foundation for further work.



(5)

9 → **10**



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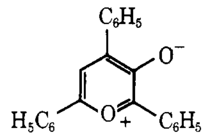
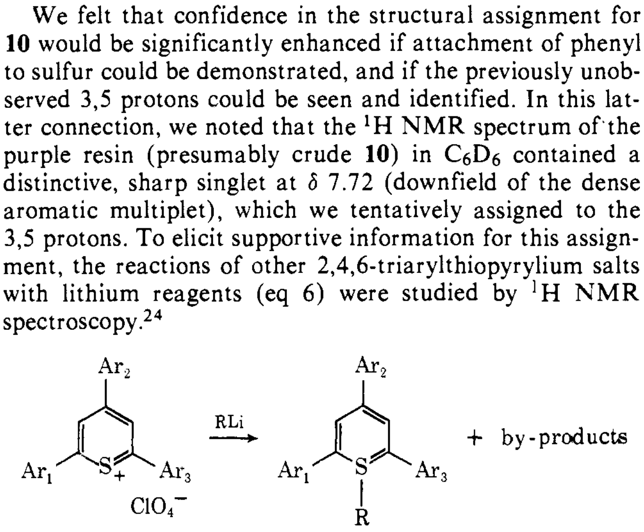


12

The purple substance from eq 5 was prepared exactly according to the published procedure.[19b] The resulting crude purple resin could be stored without apparent decomposition under an inert atmosphere, in the dark, and in the cold (below 0°). The ir spectrum (thin film) exhibited characteristic bands[19] at 1415 and 1250 cm^{-1}, the intensities of which diminished as the purple color was discharged. The electronic spectrum in the visible region showed an absorption maximum at 521 nm in isooctane (lit.[22] 524 nm). Mass spectra at 20 and 70 eV were qualitatively alike and featured an intense parent ion at 402 and the base peak at 325, with very minor peaks at *m/e* 448 and 496. No peaks were observed from *m/e* 500–1000. The ^1H NMR spectrum (CCl_4) was composed of a dense collection of peaks between δ 7.8 and 6.8, which exhibited resolved fine structure; there were no resonances attributable to complexed ethyl ether. The resin was purified by the published procedure[19b] to afford a deep violet, amorphous solid, mp 46–62° (lit.[6] 43–65°). The ir spectrum of the solid had less intense (relatively) 1415 and 1250 cm^{-1} peaks, and its ^1H NMR spectrum (CCl_4) showed a broad, poorly resolved signal between δ 7.8 and 6.8 (again, no ether resonances were observed).[23] Fresh solutions of the purple solid decolorized much more readily than those of the crude purple resin, even when sealed under vacuum.

We felt that confidence in the structural assignment for **10** would be significantly enhanced if attachment of phenyl to sulfur could be demonstrated, and if the previously unobserved 3,5 protons could be seen and identified. In this latter connection, we noted that the ^1H NMR spectrum of the purple resin (presumably crude **10**) in C_6D_6 contained a distinctive, sharp singlet at δ 7.72 (downfield of the dense aromatic multiplet), which we tentatively assigned to the 3,5 protons. To elicit supportive information for this assignment, the reactions of other 2,4,6-triarylthiopyrylium salts with lithium reagents (eq 6) were studied by ^1H NMR spectroscopy.[24]



13 **14** (6)

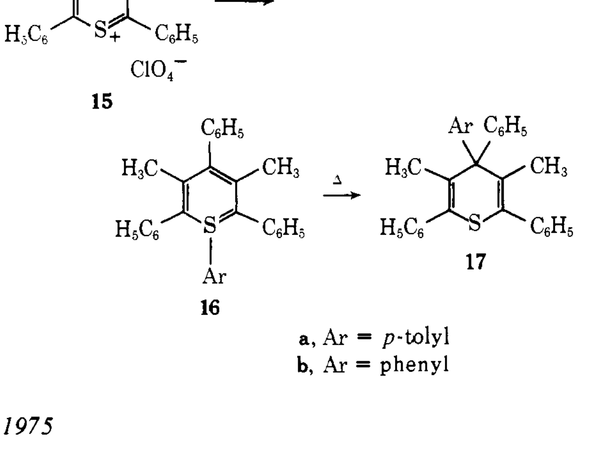
a, $Ar_1 = Ar_2 = Ar_3 = R =$ *p*-tolyl
b, $Ar_1 = Ar_2 = R =$ *p*-tolyl; $Ar_3 =$ *p*-anisyl
c, $Ar_1 = Ar_3 =$ *o*-isopropylphenyl; $Ar_2 = R =$ phenyl
d, $Ar_1 = Ar_2 = Ar_3 =$ phenyl; $R =$ *o*-tolyl
e, $Ar_1 = Ar_3 =$ phenyl; $Ar_2 = R =$ *o*-tolyl
f, $Ar_1 = Ar_2 = Ar_3 =$ phenyl; $R =$ methyl

To simplify the aromatic spectral region, and thus to simplify the analysis of the NMR spectrum, we undertook a study of 1,2,4,6-tetra-*p*-tolylthiabenzene (**14a**). The ^1H NMR spectrum of the deep purple C_6D_6 solution (produced directly in the NMR tube, under nitrogen, from a slight excess of **13a** and purified *p*-tolyllithium)[25] showed a set of discrete signals between δ 7.8 and 6.4 and another set between δ 2.2 and 1.8. In the aromatic region, there was a sharp singlet integrating for two protons at lowest field (δ 7.78), which was tentatively assigned to the 3,5 protons of **14a**. In the methyl region, an intense peak at δ 2.18 (12 H), a singlet at δ 1.82 (3 H), and less intense resonances at δ 2.13 (1.5 H) and 2.07 (1.5 H) were present. The unique *p*-tolyl methyl signal (δ 1.82) was assigned to the *p*-tolyl group attached to sulfur in **14a** for two reasons. First, the large upfield chemical shift of this resonance, compared with the other *p*-tolyl methyl signals, all of which are attributed to *p*-tolyl groups on carbon, sets it apart in a class of its own. Second, this signal disappears concurrently with decolorization of the sample, presumably because of a gross change in environment accompanying decomposition. The singlets at δ 2.13 and 2.07 are assigned to *p*-tolyl methyl groups of isomeric thiopyrans, and the peak at δ 2.18 is assigned to a combination of the 2,4,6-*p*-tolyl methyl groups of **14a** (9 H) and the *p*-tolyl methyl groups of isomeric thiopyrans (3 H). Hence, the ratio of **14a** to isomeric thiopyrans formed in the initial reaction mixture is ca. 2:1.

It remained further to ensure against any possible ambiguity in the assignment of the 3,5 protons. Accordingly, a small excess of **13b** was reacted with purified *p*-tolyllithium in an NMR tube. The ^1H NMR spectrum (C_6D_6) of the deep-magenta solution revealed single absorptions at δ 1.86 (3 H, S-$C_6H_4CH_3$ of **14b**), 2.11 and 2.17 (4 H), 2.23 (6 H, 2,4-*p*-$C_6H_4CH_3$ of **14b**), 3.32 (1 H, *p*-$C_6H_4OCH_3$ of thiopyrans), 3.42 (3 H, *p*-$C_6H_4OCH_3$ of **14b**) and a complex band of signals from δ 6.4 to 7.7, the low-field end of which displayed a pair of singlets at δ 7.80 and 7.87 (2 H, 3 and 5 protons of **14b**). Notably, desymmetrization (in this case, removal of the σ) of the thiabenzene ring resulted in two singlets (δ 7.80 and 7.87), with integrated intensities of 1:1, in the spectral region expected to contain the signals of the thiabenzene 3,5 protons. Again, a singular upfield *p*-tolyl methyl singlet was evident which disappeared on decolorization of the sample. As before, this signal is ascribable to the *S-p*-tolyl group of **14b**, and the integrated area of this peak was totally consistent with that of the 3 and 5 protons (i.e., 3:1:1). These data also show that initial reaction of the lithium reagent with **13b** yields an approximately 3:1 mixture of **14b** and isomeric thiopyrans.

Sharp downfield singlets, attributable to the 3,5 protons, were also present in the ^1H NMR spectra (C_6D_6) of other 1,2,4,6-tetrasubstituted thiabenzenes (**14**) that had a σ, i.e., in which $Ar_1 = Ar_3$: **14c** (δ 7.42), **14d** (δ 7.72), **14e** (δ 7.27), **14f** (δ 7.61).

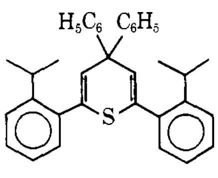
As previously mentioned, Suld and Price[19] had reported the rearrangement of **10** to an isomeric thiopyran. Evidence that this rearrangement is not restricted to compounds bearing only hydrogen atoms in the 3,5 positions was provided by the following experiment, which will be dealt with in more detail in the discussion on the thermal stability of thiabenzenes. Thiopyrylium salt **15** was combined with purified *p*-tolyllithium (eq 7) at −78° and allowed to warm to ca. 5° in C_6D_6. The deep red-orange solution thus obtained was monitored by ^1H NMR spectroscopy at ca. 5°. The spectrum featured absorptions at δ 7.6–6.6 (m, 19 H), 2.12 (s, 6 H), and 1.98 (s, 3 H), compatible with structure **16a**. When the solution was allowed to stand at room temperature (21°), in the dark, changes in the spectrum were observed. New peaks appeared at δ 1.53 (6 H, vinyl CH_3) and 2.18 (3 H, *p*-$C_6H_4CH_3$), while the signals at δ 1.98 and 2.12 disappeared (the color being discharged at the same time). This phenomenon is readily explicable by initial formation of **16a** with subsequent thermal rearrangement to an isomeric thiopyran, presumably **17a** (eq 7).



(7)

a, Ar = *p*-tolyl
b, Ar = phenyl

Treatment of **13c** with purified phenyllithium generated a magenta solution, the color of which did not persist long at room temperature. In fact, we were thwarted in our attempts to obtain a ^{1}H NMR spectrum of **14c** uncomplicated by large amounts of other substances (thiopyrans).[26] After combining the reactants at −78° and warming enough (ca. 0°) to effect the reaction with vigorous shaking, the solution was composed of 40% thiabenzene **14c** and 60% isomeric thiopyrans (based on the ^{1}H NMR intensities of the isopropyl resonances). The ^{1}H NMR spectrum of the mixture in toluene-d_8 featured absorptions at δ 1.14 [d, J = 7 Hz, CH(CH_3)$_2$ of isomeric thiopyrans], 1.26 [d, J = 7 Hz, CH(CH_3)$_2$ of **14c**], 3.62 [m, CH(CH$_3$)$_2$], 4.35 (s), 5.75 (s, vinylic protons of isomeric thiopyrans), 6.7–7.5 (m, aromatic H), 7.42 (s, 3,5 protons of **14c**). When the reaction was allowed to warm, the doublet centered at δ 1.14 and the singlet at δ 5.75 increased in intensity, while the doublet centered at δ 1.26 and the singlet at δ 7.42 decreased. Since we have established that a sharp, downfield singlet is a characteristic of 1,2,4,6-tetrasubstituted thiabenzenes, it is clear that **14c** is produced, in part, thereafter undergoing facile thermal rearrangement to thiopyrans. In this case, again, it seems that one thiopyran is principally formed, probably **18**.



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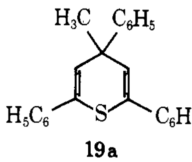
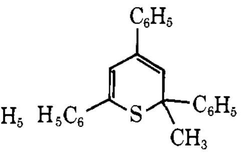


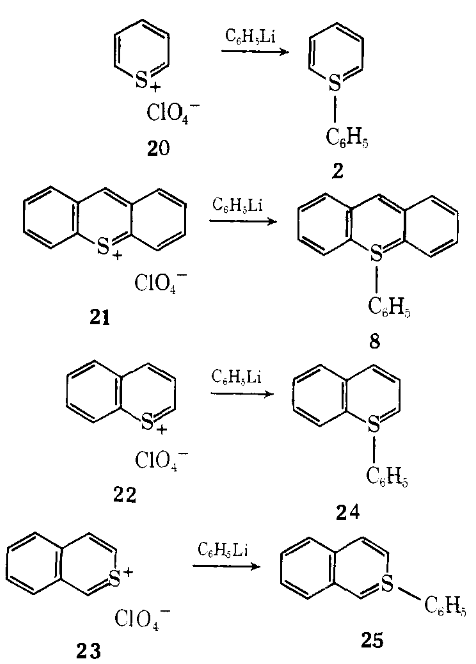
19a



19b

The slow thermal rearrangement of 1,2,4,6-tetraarylthiabenzenes to thiopyrans had been reported for a number of derivatives by Price and coworkers.[8a,19,21] On the other hand, Suld and Price[10] found that the rearrangement of 1-alkyl-2,4,6-triphenylthiabenzenes, presumed to be formed initially by the vivid, transient magenta color, take place much more readily. As a natural extension of our broad inquiry into thiabenzene chemistry, we reexamined the synthesis and facile rearrangement of **14f**, a representative 1-alkyl-2,4,6-triarylthiabenzene, by the NMR spectral method employed in the study of the tetraaryl systems. When **9** in C_6D_6 was treated with methyllithium in ethyl ether (0°), a deep-magenta solution was produced. The ^{1}H NMR spectrum (5°) revealed singlets at δ 1.32 (S-CH_3) and 7.61 (3,5 protons of **14f**), in addition to aromatic absorptions (δ 7.0–7.7). On warming the sample at 20°, the singlets at δ 1.32 and 7.61 gradually faded away and new peaks at δ 1.52, 1.68, 5.88, and 6.87 grew in.[27] These new signals are assigned to **19a** and **19b**, formed in approximately equimolar ratio. In a similar experiment using methylmagnesium iodide in 1,2-dimethoxyethane, the same results were recorded. It should be pointed out that for both reactions, the initial solutions of **14f** could be maintained without rearrangement for an extended period of time at low temperatures (e.g., 5°). Work-up of the methyllithium reaction mixture, after rearrangement, easily furnished crystalline **19a** [^{1}H NMR: δ_{CCl_4} (Me$_4$Si) 1.67 (s, 3 H), 5.86 (s, 2 H), 7.0–7.7 (m, 15 H)]; the residue was enriched in **19b** [the ^{1}H NMR spectrum featured additional singlets at δ 1.88 (3 H) and 6.80 (1 H)].[27]

Oligomeric Nature of "Stable Thiabenzenes".[28] In an extension of their earlier studies of thiabenzenes, Price and coworkers[5,6] examined the reaction of thiopyrylium salts **20–23** with phenyllithium (eq 8), by analogy with their syntheses of **10** and **14f**. Red-brown amorphous solids were isolated, which were characterized as the "stable thiabenzenes" **2, 8, 24,** and **25.**



(8)

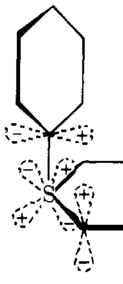
As the evidence discussed above (see introductory section) raised serious doubts concerning the identity of the materials characterized[5,6] as **2** and **8**, we repeated the reactions shown in eq 8. Reaction of **20–23** with phenyllithium under a dry nitrogen atmosphere employing the reported reaction conditions and described work-up[5,6] in each case gave red-brown amorphous solids, whose uv, ir, and ^{1}H NMR spectra were consistent with the reported spectral characteristics.[5,6,29] The elemental analyses of these solids proved to be erratic, although analyses in agreement with those reported[5,6,29] could be obtained for samples of material resulting from addition of phenyllithium to **21** and **23**.[25] All samples of material obtained from the reactions shown in eq 8, using the described reaction conditions and work-up,[5,6,29] were found to have molecular weights three to six times greater than expected for the monomeric species (osmometric determinations in benzene).[25] Thus the red-brown amorphous solids which were previously characterized as "stable thiabenzenes" **2, 8, 24,** and **25**[5,6] are in fact oligomeric[30] materials of undetermined structure and composition.

The oligomeric nature of these materials is entirely consistent with *all* of the observations reported on "stable thiabenzenes", with the singular exception of the previously reported[5,6,29a] molecular weight determinations.[31] The following examples may be cited: (a) the unresolved ^{1}H NMR[29] and ^{13}C NMR spectra, which featured only envelope absorptions; (b) the lack of distinct absorption maxima in the visible region (". . . the characteristic 'long tail' absorption out into the visible without a maximum . . ." [8a]);[33] (c) the low dipole moments;[5,6] (d) the behavior noted on heating, i.e., softening with no distinct melting point;[5,34] (e) the amorphous nature of these materials;[5,6] (f) the peaks in the mass spectra of "stable thiabenzenes" at m/e values substantially higher than expected for a monomer;[8a,35] and (g) the reported lack of chemical reactivity (i.e., resistance to oxidation, desulfurization, boiling in acetic acid, etc.).[5,6]

Subsequent work by Hori et al.[36] has provided other examples of the isolation of stable amorphous solids, generated by the addition of excess phenyllithium to diversely substituted thioxanthylium perchlorates, which have been characterized as stable 10-thiaanthracenes. The results presented in the present paper serve to nullify all of these claims. In fact, the stable brown powders alleged to be 10-thiaanthracenes[6,36] are, with no known exception, oligomeric materials of undetermined composition and structure. Indeed, it must be emphasized that *all presently known thiaanthracenes are notably unstable compounds which readily undergo rearrangement to thioxanthenes and which can only be observed as transient reaction intermediates.* Isolation of these elusive compounds thus remains a challenge for the future.[37]

Similarly, the claims by Hori et al.[13b,38a] to the synthesis of 10-selenaanthracenes, brown powders with properties remarkably similar to those reported for the "stable thiaanthracenes", have also been refuted.[38b] In point of fact, these products are not authentic selenaanthracenes but are oligomeric materials of undetermined structure and composition.

It is important to note that, as a result of the conviction that they were dealing with monomeric species, Price and coworkers were forced to postulate a number of ad hoc hypotheses in order to reconcile the experimental observations on "stable thiabenzenes" with their portrayal of them as authentic thiabenzenes. For example, the observation that "stable thiabenzenes" were much more stable than **10** was explained in terms of a scheme that postulates two conformers, each with "... a continuous π-molecular orbital, conjugating the aromatic rings through sulfur and permitting a cyclic aromatic ring current in the thiabenzene ring".[8a] In the first conformer, **26**, sulfur utilizes p^3 orbitals for σ bonding, with the lone pair remaining in an s orbital and with cyclic conjugation achieved through involvement of a single $3d_{xz}$ orbital on sulfur. In the second conformer, **27**, sulfur utilizes sp^2 orbitals for the σ bonds, and the nonbonded electron pair is promoted to a d orbital. The $3p_z$ orbital is used in constructing a continuous cyclic delocalized system. In **26**, sulfur is pyramidal, whereas in **27** it is planar. It was argued that the planar form (**27**) should be inherently more stable than the pyramidal form (**26**), and that unhindered thiabenzenes (having a very low "... barrier to bending at the S-phenyl bond, with virtually no barrier between conformers ..." [8a]) should therefore be much more stable than ortho-substituted thiabenzenes, in which the pyramidal conformer (**26**) would be favored on steric grounds.[5-8] Thus this steric argument was invoked to explain the observation that "stable thiabenzenes" resisted Raney nickel desulfurization under forcing conditions and could be boiled in acetic acid without change,[6] whereas **10** was unstable to heat, light, oxygen, and acid.



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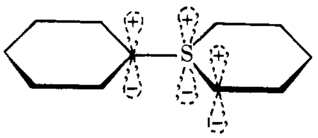


27

A similar explanation was used to account for the amorphous nature of these compounds, for it was reasoned[6] that rapid motion of the phenyl group on sulfur moving above and below the plane of the sulfur ring (i.e., rapid interconversion of conformers **26** and **27**) retarded crystallization. However, we note that there are numerous examples of crystalline compounds whose molecules have low barriers for pyramidal inversion, and we know of no precedent for the postulated effect on crystallinity.

The peaks in the mass spectra of several of the "stable thiabenzenes" at *m/e* values higher than those expected for the monomeric compound were explained as arising from ion-molecule reactions in the mass spectrometer.[8a] No precedents were given, nor do they exist to our knowledge for ion-molecule reactions between molecules and fragments of the molecular weights required to explain the reported observations under the normal operating pressures employed. No reference was made to the use of high-pressure mass spectrometry under which ion-molecule reactions are usually studied.[39]

Table II. Volatile Products formed in the Reaction of Thiopyrylium Salts with *p*-Tolyllithium

	Yields (%)[a,b]		
Compd	Toluene	*p*-Tolyl sulfide	*p*-Tolyl carbon adduct[c]
20[d]	32	27	<1
20[e]	40	17	<1
20[f]	36	28	<1
22[d]	36	1	9
22[e]	53	<1	3
22[f]	42	2	15
23[d]	33[g]	37	5
23[e]	55	24	2
23[f]	41	41	7
28[d]	31[h]	51	8
29[d]	34[i]	36	

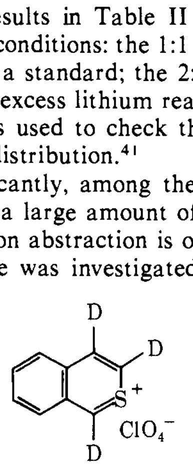
[a] Yields were determined (±3%) by GLC analysis and are based on *p*-tolylithium. [b] Traces of 4,4'-bitolyl (<3%) are present in all reaction mixtures. [c] Product yields refer to sulfides formed either by direct *p*-tolyllithium attack on carbon or rearrangement of a transient thiabenzene (see Scheme I, pathways b''' and c). For example, **23** yields 1-*p*-tolyl-2-thio-3-chromene. [d] $C_6D_6-Et_2O$, 5–30°, 1:1 ratio of salt to *p*-tolyllithium. Similar results were obtained using Et_2O at temperatures <0°. [e] $C_6D_6-Et_2O$, 5–30°, 1:1 ratio of salt to *p*-tolyllithium. [f] $C_6D_6-Et_2O$, 5–30°, 1:1 ratio of salt to *p*-tolyllithium, reaction quenched with H_2O. [g] No deuterium incorporation found in toluene. A similar result was obtained when the reaction was run in C_6D_6–THF-d_8. [h] Toluene-d_1 (80–83% D) formed in the reaction as determined by GLC–mass spectrometry. [i] Toluene-d_1 (8–10% D) formed in the reaction as determined by GLC–mass spectrometry.

As was noted before, the marked difference in properties reported by Hortmann and Harris[12] for **5b**, compared with the properties reported by Price and coworkers[5] for the material which they characterized as **2**, was rationalized as arising from a possible difference in the nature of *S*-alkyl- compared with *S*-arylthiabenzenes.[8a] Given the broad, unresolved ^1H NMR spectrum reported for the material characterized as **2**[29a,b] and the well-resolved spectrum that one obtains on deprotonation of **5a**,[12,25] this explanation is unconvincing.

In light of the conclusions with regard to the alleged syntheses of **2**, **8**, **24**, and **25**, one may wonder what is the actual course of events when aryllithium reagents react with thiopyrylium salts **20–23**. To gain insight into this question, and to develop at least the beginnings of an explanation for the formation of the red-brown oligomers, we examined the reactions of *p*-tolyllithium with **20**, **22**, and **23**. In each case, the reaction was carried out in an NMR tube, under nitrogen, by addition of purified *p*-tolyllithium to the thiopyrylium salt suspended in the indicated solvent (Table II).[25] ^1H NMR spectra were immediately recorded for each reaction mixture to obtain an assay for all the products. Thereafter, the volatile components of each mixture were identified by GLC–mass spectrometry and comparison with authentic samples (GLC, ^1H NMR). The mixtures were analyzed quantitatively by GLC (see data in Table II). Product mixtures representing the reaction of *p*-tolyllithium with **20**, **22**, and **23** were subjected to bulb-to-bulb distillation [80° (5 × 10^{-6} Torr)], the progress of which was monitored by ^1H NMR, to remove the volatile substances.[40] The ^1H NMR spectra of the red-brown, nonvolatile residues thus obtained appeared remarkably similar to those of the aforementioned red-brown oligomers.

The results in Table II are derived from three sets of reaction conditions: the 1:1 *p*-tolyllithium–salt ratio was selected as a standard; the 2:1 ratio was designed to test the effect of excess lithium reagent, and the quenching experiment was used to check the effect of added water on the product distribution.[41]

Significantly, among the variety of products from each reaction, a large amount of toluene was present indicating that proton abstraction is of major importance. Production of toluene was investigated further by the reaction of **28** (95% D) with *p*-tolyllithium. In addition to the products from the reaction of **23** (exclusive of deuterium substitution), a 31% yield of toluene-d_1 (80–83% D) was found; this result conclusively demonstrates that proton abstraction from the thiopyrylium salt or products derived therefrom is the predominant cause of the toluene formation.[42] Moreover, the reaction of **29** with *p*-tolyllithium illustrates that at least some abstraction occurs from the 1 position.[43a]



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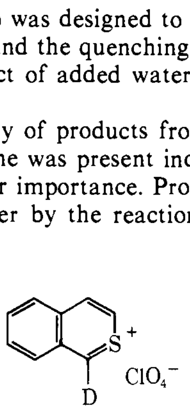

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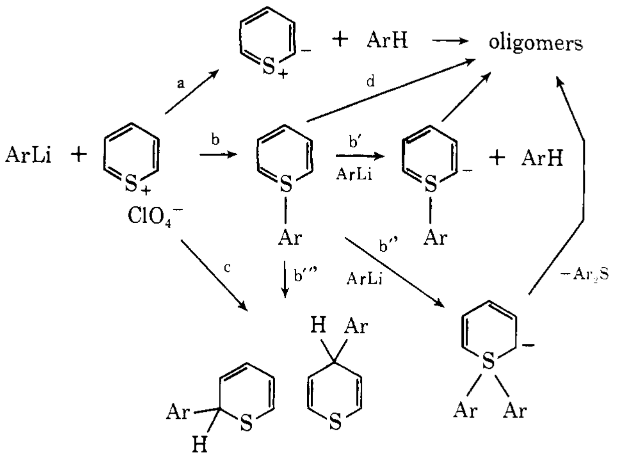
p-Tolyl sulfide was the other major product formed in these reactions, and a discussion of its possible origins follows.

Several mechanistic pathways (Scheme I)[43b] can be envisioned to account for the observed products (Table II).

Scheme I



Pathway a depicts direct proton abstraction from the thiopyrylium salt to generate a thiopyrylium ylide, a presumably reactive intermediate which may be a source of oligomeric material. This possibility derives support from the fact that isoelectronic N-substituted pyridinium salts readily exchange their 2,6 protons for deuterium merely by the action of aqueous base.[44] Facile deprotonation also occurs in thiazolium,[45a] benzthiazolium,[45b] and dithiolium[45c] salts, producing ylides (resonance-stabilized, nucleophilic carbenes).[46] In pathway b the thiopyrylium salt is first attacked at sulfur giving a thiabenzene. This central intermediate may suffer deprotonation (b′), forming a thiabenzene anion and then oligomers, or addition of another aryllithium (b″) to create a σ-sulfurane anion. Ejection of aryl sulfide from this latter species would disintegrate the original ring system, and the fragmentary by-products might constitute yet another source of oligomeric material.[47] The intermediate thiabenzene may also undergo rearrangement to thiopyrans (b‴), wherein the aryl group is transferred from sulfur to carbon (see discussion on thiabenzene rearrangements below). Pathway c involves direct attack on carbon by the aryllithium reagent, again leading to formation of thiopyrans. It is also evident from our studies on the thermal decomposition of thiabenzenes (see below) that thiabenzenes can decompose directly without rearrangement or attack by a lithium reagent (pathway d), and this may be yet another source of oligomeric material.

From the preceding data (see Table II), it is evident that a proton-abstraction step (pathways a, b–b′) is preeminent in the reactions of *p*-tolyllithium with **20, 22,** and **23,** the toluene originating only from this source. Unfortunately, the data do not permit determination of the relative importance of the two possible pathways. Secondly, the formation of large amounts of *p*-tolyl sulfide in the reactions of *p*-tolyllithium with **20** and **23** requires, at least in these cases, that pathway b–b″ be of considerable significance. The small yields of thiopyrans attest to the minor importance of pathways b‴ and c. In any event, it is clear that several pathways are accessible which could lead to the destruction of thiabenzenes initially formed in these reactions.

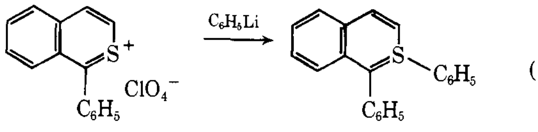
The formation of both toluene and *p*-tolyl sulfide clearly signifies that extensive destruction of the sulfur-ring system takes place in the reactions of **20, 22,** and **23** with *p*-tolyllithium under conditions even milder than those previously reported.[5,6,25] In retrospect, it is now apparent that the isolated oligomers are only the embryonic stages of a much more complex polymeric mixture as evinced by the fact that, in the addition of phenyllithium to **20–23,** evaporation of the organic layer after reaction work-up[5,6,25,29] initially leads to a dark brown to red-brown, highly viscous residue. It was refined portions of these tars that were isolated and characterized as **2, 8, 24,** and **25.**[5,6,29]

While the above discussion shows that thiabenzenes cannot be observed in the addition of phenyllithium to thiopyrylium salts **20–23,** *the addition of aryllithium reagents to certain more highly substituted thiopyrylium salts is a viable means of forming thiabenzenes.* For example, 1,2,4,6-tetraarylthiabenzenes (see preceding section) can be generated by the addition of aryllithium reagents to 2,4,6-triarylthiopyrylium salts, though the syntheses are not always free of side reactions arising from direct attack of the aryllithium reagent on carbon (pathway c). Furthermore, as will be discussed later, addition of aryllithium reagents to 1-substituted 2-thianaphthalenium perchlorate salts provides a route to the generation of 1,2-disubstituted 2-thianaphthalenes, though again these reactions are not entirely free of contaminants, possibly because of proton abstraction (pathways a and/or b′). That these synthetic routes lead to the desired product, in contrast to the reactions discussed above, is readily understandable in terms of the mechanistic pathways depicted in Scheme I. First, proton abstraction, whether by pathway a or b′, is much less likely in these more highly substituted systems than in thiopyrylium salts **20–23.** Second, a steric effect may operate in these more highly substituted thiopyrylium salts, in contrast to **20–23,** which impedes the second addition of aryllithium reagent to an initially formed thiabenzene, to give a σ-sulfurane anion (pathway b″). Hence, in our view, the accessibility of pathways leading to the destruction of any thiabenzene formed in the reaction of phenyllithium with thiopyrylium salts **20–23** precludes the observation of thiabenzenes **2, 8, 24,** and **25,** while, conversely, the inhibition of these pathways by the presence of suitable substituents permits the generation of thiabenzenes in these more highly substituted systems.

In the introductory section to this paper, we noted the apparently successful generation of thiabenzenes **4b**[7] and **5b**[12] by deprotonation of appropriately substituted sulfonium salts. In light of the many inconsistencies already recorded, we decided to reexamine this work as well.

Hortmann and Harris[12] produced an orange solution on deprotonation of **5a** (Me_2SO-d_6), whose ^1H NMR spectrum was taken as the main evidence for the synthesis of **5b**. In our hands, deprotonation of **5a** with dimsyl-d_5-lithium[25] in C_6D_6 also gave a bright-orange solution. The ^1H NMR spectrum of this solution showed absorptions at δ 1.28 (s, S-CH_3), 3.91 (d, 2,6 protons), 6.57 (t, 4 proton), and 7.18–7.88 (m, aromatic H), entirely consistent with the reported spectrum of **5b**.[12] Over a period of a few hours, we noted appreciable decomposition, but the composition of the resulting decomposition mixture was not explored. In short, our experience with **5b** was substantially in accord with that of Hortmann and Harris.[12]

In their work, Price and Follweiler[7] obtained a purple solution on deprotonation of **4a**, which faded with the passage of days. This was advanced as the primary evidence for **4b** but, in addition, they reported that **4b** could be prepared in solution by the reaction of **30** with excess phenyllithium (eq 9) and subsequently isolated as a purple, amorphous solid, softening at 60–100°. The ^1H NMR spectrum of this solid exhibited a broad, unresolved signal from δ 7.8 to 6.6,[7,48] in good agreement with the spectrum of the purple material retrieved from deprotonation of **4a**. Although this information was all too reminiscent of the previously discussed situation involving the oligomers, two observations nevertheless spoke for the generation of **4b** from **30** or **4a**: the intense purple color which faded on standing, and the regeneration of **4a** by treatment of a fresh purple solution with aqueous NH_4Cl.

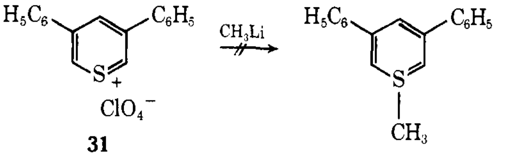


30 **4b** (9)

In our hands, deprotonation of **4a** was accomplished with dimsyl-d_5-lithium in C_6D_6, generating a deep-purple solution.[25] The ^1H NMR spectrum of the solution featured absorptions at δ 5.15 (d, 1 H, J = 8 Hz) and 6.6–8.2 (m, 15 H). The aromatic region was sharply defined, wholly unlike the reported spectrum of **4b**.[7,48] The marked upfield signal (δ 5.15), by analogy with the upfield 2,6 protons in **5b**, can be assigned to the 3 proton. The companion doublet for the 4 proton is presumably obscured by the aromatic proton signals.[49] On standing for ca. 24 hr at room temperature (ca. 22°), the purple color (λ_{max} 519 nm) of an isooctane solution of **4b** had vanished (protected from light and air).

Concerned by the disparity between the ^1H NMR spectra, we proceeded to study the reaction in eq 9 using the NMR technique. Addition of purified phenyllithium to **30** suspended in C_6D_6-Et_2O afforded a deep-purple solution that featured absorptions in its ^1H NMR spectrum at δ 5.26 (d, J = 8 Hz) and 6.6–8.2 (m, aromatic H + 4-proton). This spectrum obviously corresponded to the spectrum of **4b** obtained by deprotonation of **4a**, taking into account solvent effects on chemical shifts. Thus the difference between the published spectra of **4b**[7,48] (the isolated purple solid) and ours derives from the fact that the former were recorded on material which was largely decomposed. Indeed, when the purple solutions produced in our reexamination were permitted to decompose, their ^1H NMR spectra began to resemble, more and more, the ones reported by Price and Follweiler[7,48] (i.e., a broad unresolved envelope, δ 6.6–7.8). Eventually, a red-brown solution was obtained whose ^1H NMR spectrum exhibited only a broad hump (δ 6.6–7.8).

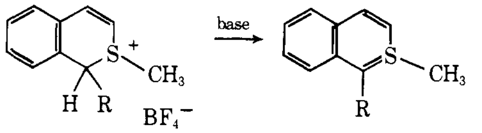
Using the route involving addition of a lithium reagent to a thiopyrylium salt, we tried unsuccessfully to synthesize **5b** (eq 10). This result is consistent with the negative report of Harris with respect to the reaction of **31** (BF_4^- salt) with phenyllithium,[50] and with the failure of **20** to form an observable thiabenzene.



31 **5b** (10)

Our reinvestigation affords the conclusion that, even though prior claims[5,6] for "stable thiabenzenes" are invalid, certain, more highly substituted thiabenzenes (e.g., **10, 4b, 5b**) can be, and have been,[7,8a,10,12,19,21] prepared. However, it is important to remark that, in some instances, the characterization of the generated thiabenzenes has been marred by the failure to appreciate more fully the significant instability of these compounds.[51] For example, in the course of the "purification" employed in the synthesis of **10**[19] and the isolation of **4b** as a purple solid,[7] severe decomposition of the thiabenzenes undoubtedly took place.[51a]

Thermal Stability of Thiabenzenes. As an integral part of our study of thiabenzene chemistry, we investigated the factors which influence thermal stability in these compounds. Toward this end, we examined a series of 1,2-disubstituted 2-thianaphthalenes (**33**), synthesized by deprotonation of appropriately substituted sulfonium salts (**32**) (eq 11), an extension of the synthesis of **4b** (eq 2).[7]



32 **33** (11)

a, R = phenyl
b, R = *o*-isopropylphenyl
c, R = pentafluorophenyl
d, R = H

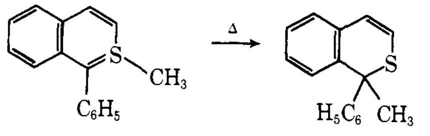
Sulfonium salts **32a–32d** were readily prepared by alkylation of the corresponding sulfides with CH_3I-$AgBF_4$.[52] Deprotonation of **32a–32c** with dimsyl-d_5-lithium produced intensely colored solutions whose ^1H NMR spectra are summarized in Table III. The spectra data are consistent with generation of **33a–33c**, and the 3 protons of these thiabenzenes exhibit the same marked upfield shift as was manifested by the 2,6 protons of **5b**.[12] *This feature seems to be a general characteristic for all ortho protons in thiabenzenes.*[52a] Addition of 48% fluoboric acid to solutions of **33a** and **33b** at ca. 10° regenerated the sulfonium salts **32a** and **32b**.[53]

Solutions of **33c** (red) could be warmed to ca. 40° with no apparent change in their color or NMR spectra. However, solutions of **33a** (purple), on warming to ca. 40°, changed color to pale red, and their new ^1H NMR spectra featured absorptions at δ 1.85 (s, 3 H, CH_3), 6.13 and 6.47 (AB q, 2 H, J = 9.5 Hz, olefinic H), 6.7–7.7 (m, 9 H, aromatic H), indicative of 1-methyl-1-phenyl-2-thio-3-chromene (**34**) (eq 12). This structural assignment was verified by an independent synthesis of **34** by the addition of methylmagnesium iodide to **30**.[25,54]

Table III. The 60-MHz ^{1}H NMR Spectral Data for Some 2-Thianaphthalenes

	Chemical shifts (δ)[a]			
Compd	Aromatic H	3-H ($^3J_{HH}$)[b]	4-H[c]	S–CH$_3$
33a[d]	8.2–6.8 (m)	4.47 (d, 8 Hz)	6.72 (d)	0.92 (s)
33b[e]	7.4–6.9 (m)	4.53 (d, 8 Hz)	6.92 (d)	1.04 (s)
33c[f]	7.3–6.7 (m)	4.76 (d, 8 Hz)	6.82 (d)	1.27 (s)

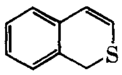
[a] The chemical shifts noted are strongly solvent dependent. For example, the spectrum of 33c in CDCl$_3$ featured absorptions at δ 7.4–6.7 (m, aromatic H and 4-H), 5.55 (d, J = 8 Hz, 3-H), 1.97 (s, S–CH$_3$). Aromatic solvent-induced shifts (ASIS) are well established and should be expected in systems which possess dipolar character such as sulfonium ylides [R. D. Bertrand, R. D. Compton, and J. G. Verkade, *J. Am. Chem. Soc.*, 92, 2702 (1970); J. Ronayne and D. H. Williams, *Annu. Rev. NMR Spectrosc.*, 2, 83 (1969)]. See also the excellent discussions of this effect by P. Laszio in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 3, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, New York, N.Y., 1967, pp 348–389, and by L. M. Jackman and S. Sternhell in "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, New York, N.Y., 1969, pp 104–113 and 246–248. [b] Assignment of the 3-H is based on the chemical shift observed for the 2,6 protons of 5b (δ, 4.03 Me$_2$SO-d_6,[12] 3.91 C$_6$D$_6$). [c] Assigned by strong irradiation (spin-decoupling) of the 3-H. [d] Spectrum recorded at −35° in toluene-d_8–C$_6$D$_6$ (2:1). [e] Spectrum recorded at 5° in toluene-d_8–C$_6$D$_6$ (2:1); isopropyl group: δ 1.09 (pr of d, J = 7 Hz, Δν = 4.4 Hz) and 3.25 (m). [f] Spectrum run at ambient probe temperature (ca. 38°) in C$_6$D$_6$.



33a **34** (12)

The deprotonation of **32d** differs from the others in that, even at −65°, it was not possible to prepare and observe **33d**. Analysis of the warmed reaction mixture (GLC–mass spectrometry) permitted identification of the principal volatile products as 1-methyl-2-thio-3-chromene (**35**), 10% yield, and 2-thio-3-chromene (**36**), 1% yield.[25,55] This observation is most reasonably attributed to the intermediate presence of **33d**, which rapidly rearranges to **35** (see discussion on thermal rearrangements below). Hence, it is evident that **33d** is significantly less stable than **33a–33c**.

35



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The qualitative ordering of stabilities for **33a–33d** (**33c** > **33a** > **33d**) suggested that delocalization of charge is important in determining the thermal stability of thiabenzenes. To gain further information on this topic, we monitored the characteristic visible absorption of a number of diversely structured thiabenzenes[56] as a function of time (Table IV). The relative thermal stabilities of the thiabenzenes are reflected in their first half-lives (i.e., the time for 50% decomposition).

Several trends are apparent from the data (Table IV): (1) *S*-phenyl substitution stabilizes thiabenzenes compared with *S*-methyl substitution (cf. **10** vs. **14f**; **4b** vs. **33a**);[57] (2) particular stability derives from substitution of a strongly electron-withdrawing group (e.g., pentafluorophenyl) on the thiabenzene α-carbon atom (cf. **33c** vs. **33a**); and (3) increasing stability seems to go hand in hand with increasing solvent polarity (cf. entries for **33a** and **33c**), an effect that had been noted previously by Hortmann and Harris in their consideration of the properties of **5b**.[12]

Table IV. Thermal Stability of Thiabenzenes

Compd (λ_{max}, nm)	Time, hr, for 50% decomposition[a] (°C, solvent)
10 (524)[b]	8.2 (22, benzene)
(521)[b]	3.5 (23, isooctane)
14c (495)[b]	5.0 (23, benzene)
14f (527)[c]	0.35 (21, benzene)
16b (490)[b]	1.5 (21, benzene)
5b (439)[d,e]	ca. 4 (22, benzene)
4b (518)[d]	3.9 (21, benzene)
(519)[d]	1.5 (23, isooctane)
33a (511)[d]	0.83 (27, dimethyl sulfoxide)
(519)[d]	0.39 (22, benzene)
d,f	<0.1 (25, isooctane)
33c (480)[d]	249 (23, dimethyl sulfoxide)
(485)[d]	65 (20, benzene)

[a] Decomposition rates were measured on solutions prepared under a dry nitrogen atmosphere in diffuse light with oxygen-free, dry solvents, and retained in a ground-glass stoppered cuvette. Since rates of decomposition are highly sensitive to oxygen, which cannot be totally excluded by this technique, the reported values are dependent on our choice of conditions and may not represent the thermal stability of thiabenzenes under other conditions. The values are the maximum observed first half-lives and, under consistent experimental conditions, accurately reflect *relative* thermal stability. [b] Generated by addition of phenyllithium to the appropriate thiopyrylium salt. [c] Generated by addition of CH$_3$MgI to 9. [d] Generated by deprotonation of the corresponding sulfonium salt with dimsyl anion. [e] Value is approximate because of spectral interference by decomposition products. [f] Decomposition was too fast to allow monitoring of the solution by this method.

The remarkable stability of **33c** has permitted isolation and rigorous characterization of this particular thiabenzene. Dilution of a methylene chloride solution of **33c** with hexane gave an orange-red crystalline solid (mp 107–108° dec), the identity of which was established as **33c** by several independent methods. The ^{1}H NMR spectrum of the crystalline material coincided with the one initially recorded on deprotonation of **32c**. Elemental analysis, exact mass (mass spectrometry), and solution molecular weight (osmometry in benzene) were consistent with the assigned structure.[25] The crystallinity of **33c** was confirmed by the X-ray powder pattern of the solid.[58]

The noise-decoupled ^{13}C NMR spectrum[59] of **33c** in CDCl$_3$ features absorptions at 137.1 (C-9); 135.6, 130.9, 129.7, 123.7 (C-5 to C-8); 123.2 (C-10); 117.7 (C-4); 92.5 (C-3); 31.9 (*S*-methyl); and 27.9 (C-1) ppm downfield from Me$_4$Si. The assignments for C-4 and C-3 were made by specific decoupling of the C-4 proton. The upfield shift noted for C-3 is indicative of increased electron density at this carbon, and it is consonant with the upfield shift of the 3 proton observed in the ^{1}H NMR spectrum of **33c**. The chemical shift noted for C-3 is also similar to chemical shifts observed in pentadienyl anion systems.[60] The assignment of the weak absorption at 27.9 ppm to C-1 is tentative and based largely on the observation of similar chemical shifts in stabilized phosphonium ylide systems.[61] A further complication is introduced by the observation that this signal collapses on off-resonance decoupling; however, the possibility of coupling to the fluorines of the pentafluorophenyl group leaves the low signal intensity and off-resonance decoupling result open to interpretation. Until more chemical-shift data are available on sulfonium ylide and thiabenzene systems, the assignment offered here for C-1 should be viewed with caution.

In addition to the electronic effects detailed above, there appears to be an effect stemming from steric interactions between substituents. Comparison (Table IV) of the relative thermal stabilities of **16b** and **10** reveals that the former is somewhat less stable. The relative destabilization of **16b** can be rationalized on the basis that nonbonded repulsion between the 3,5-methyl and 2,4,6-phenyl groups lessens the ability of the phenyl groups on the carbon framework of **16b** to delocalize charge. The slight reduction in the thermal stability of **14c** may be due to a similar steric effect. The large hypsochromic shifts (Table IV) of the absorption maxima for **16b** and **14c** (compared with **10**) are in accord with this interpretation.

From the accumulated experimental information bearing on the thermal stability of thiabenzenes, a general picture emerges that can be used as a guide for predicting the relative stabilities of these compounds. Notably, all of our experimental observations are satisfactorily accounted for if thiabenzenes are portrayed as sulfonium ylides; specifically, *structural elements that can delocalize or stabilize a positive charge on sulfur and/or a negative charge on the adjacent carbon* (*or one conjugated to it*) *will contribute to the stabilization of thiabenzenes.*

Thermal Rearrangements of Thiabenzenes. Many thiabenzenes undergo thermal rearrangements involving the transfer of an aryl or alkyl group from sulfur to carbon. These migrations appear to be a general chemical property of thiabenzenes and may be formally described as four-electron [1,2] and six-electron [1,4] sigmatropic shifts, processes that have been recognized in a variety of carbanionic species including acyclic sulfonium ylides (Stevens rearrangement).[62]

Migration of *S*-aryl substituents has been observed both in 1,2,4,6-tetraarylthiabenzene and in 10-aryl-10-thiaanthracene systems. We have previously mentioned that Price and coworkers reported the rearrangement of **10**,[19] and of related derivatives,[8a] to thiopyrans, with a large predominance of the 2,4,4,6-tetraaryl isomer (4 adduct).[63] In our studies on **16** and **14c**, we had an opportunity to monitor directly thermal aryl migration by ^{1}H NMR spectroscopy (see above). In each rearrangement, only one product was detected by ^{1}H NMR and thin-layer chromatography; each product was later isolated and characterized as a thiopyran (presumably the 4 adduct). Thus the aryl rearrangements, in these cases, are relatively clean.

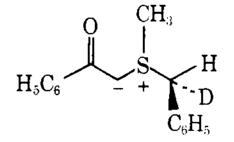
Hori et al. reported the isolation of rearrangement products from the deprotonation of 10-arylthioxanthenium salts.[13] Although they had failed to acknowledge the intermediacy of 10-thiaanthracenes in these reactions, we have presented evidence (see above) which attests to the existence of such thermally unstable species in these reactions. The results of our studies on the rearrangements of 10-aryl-10-thiaanthracenes (Table I) show that the 10-phenyl and 10-(2,5-xylyl) systems undergo relatively clean rearrangements, but that the 10-mesityl system suffers a marked decrease in the yield of rearrangement product (**7d**). This may indicate the operation of unfavorable steric interactions in the transition state that leads to rearranged product.

S-Alkyl rearrangements in thiabenzenes were first suggested by Suld and Price[10] to explain the fact that reactions of alkyl Grignard reagents with **9** produced a transient magenta color in the process of forming isomeric thiopyrans. Our aforementioned experiments involving the reaction of **9** with methyllithium and methylmagnesium iodide established the intermediacy of **14f** by monitoring the progress of this thermal rearrangement by ^{1}H NMR spectroscopy. It was found that signals ascribed to **14f** uniformly decayed as new absorptions assigned to **19a** and **19b** (ca. 1:1 ratio) developed. Since the reaction mixture was comprised of only the two thiopyrans, this methyl rearrangement was apparently clean. *S*-Methyl group migrations were also observed in thiaanthracene and thianaphthalene systems, the details of which have already been presented.

In many of the thermal rearrangements of thiabenzenes that we have described, products arising from loss of the migrating substituent (earlier referred to as escape products) were detected. The relevance of these products on the general mechanism of the rearrangements will be considered below.

In order to gain some insight into the mechanism, a crossover experiment was performed. Deprotonation of an intimate mixture of **6a** and **6c** led to a product mixture containing **7a** and **7c**, in which no **7b** could be detected. The failure to discover any crossover product **7b** indicates that the 10-aryl-10-thiaanthracene rearrangement is substantially intramolecular.[64,64a] In the following discussion, we shall presume predominant intramolecularity for other thiabenzene rearrangements as well.

It is tempting to consider the mechanistic possibilities which accommodate our experimental observations on these rearrangements.[65] However, differentiation between these possibilities would require knowledge of the stereochemical consequences of the rearrangement on the migrating substituent and would entail the use of quantitative CIDNP.[67]

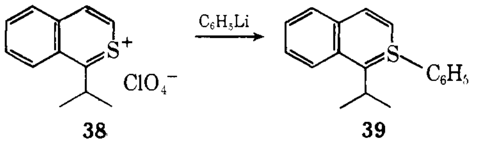


37

In an intramolecular [1,2] rearrangement of sulfonium ylide **37**, Baldwin et al.[69] observed simultaneous CIDNP and net retention (36%) of stereochemistry in the migrating group in accord with a radical-pair process. However, Ollis et al.[70] have recently suggested that, in a number of [1,2] anionic rearrangements, assignment of an exclusive radical-pair mechanism on the basis of the mere detection of CIDNP is unfounded and thus remains uncertain in the absence of more compelling evidence. Recent discussions concerning orbital symmetry-forbidden concerted reactions[71,72] are strikingly pertinent to the results and suggestions of Ollis et al.[70] (i.e., competition between concerted-forbidden and radical-pair mechanisms). Our observation of products arising from loss of the S substituent (i.e., thioxanthenes and thiochromenes) may be rationalized in terms of radicals escaping from an intimate radical pair; the radicals then proceed to abstract hydrogen atoms from the solvent.[73]

We feel that the straightforward analogy that can be drawn between the thermal rearrangements of thiabenzenes and the rearrangements of acyclic sulfonium ylides is not fortuitous but is an experimental expression of the inherent sulfonium ylide character of thiabenzenes.

Pyramidal Stability. With a much improved understanding of the physical and chemical properties of thiabenzenes, we were in a tenable position to return to our original objective—the determination of the barrier to pyramidal inversion in a member of this class of compounds. Our first attempt in this direction foundered on our inability to prepare reasonably pure samples (in solution) of **14c**.[26] In our second attempt, we proceeded to synthesize 1-isopropyl-2-phenyl-2-thianaphthalene (**39**) by way of 1-isopropyl-2-thianaphthalenium perchlorate (**38**), an approach which allowed a degree of flexibility. Treatment of **38** with purified phenyllithium in C_6D_6 afforded a purple solution (eq 13).



38 **39** (13)

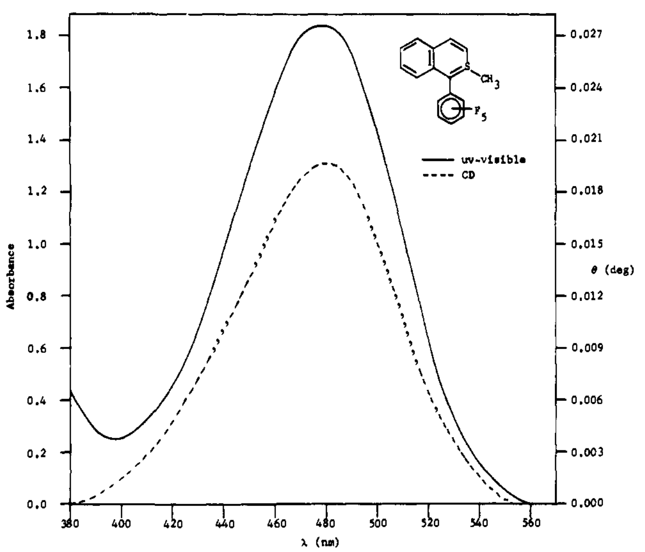


Figure 1. The electronic spectrum of optically active **33c** (generated by deprotonation of **32c** with brucine) in the region of the characteristic absorption band (solid line) and the observed circular dichroism in the same region (dashed line). Solvent is dimethyl sulfoxide.

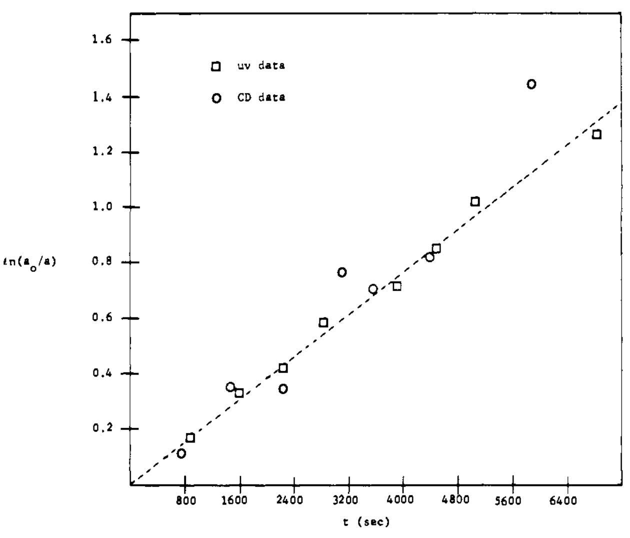


Figure 2. The decrease in the intensity of the uv absorption at 480 nm (squares) and the decrease in the CD band at 480 nm (circles) of optically active **33c** (generated by brucine deprotonation of **32c**) are plotted as first-order reactions. Solvent is dimethyl sulfoxide, 29°. The dashed line is obtained from a least-squares treatment of the uv data.

The ^1H NMR spectrum of this solution at 37° displayed a well-resolved pair of doublets for the isopropyl group (δ 1.35, 1.42; J = 6.5 Hz), as well as a doublet at δ 5.00 (J = 8 Hz), the characteristic 3-proton signal of the 2-thianaphthalene ring (see discussion on thermal stability above). The presence of a signal assignable to the 3 proton ensured that **39** was in fact being generated.[74] On standing at probe temperature, these absorptions disappeared, and the purple color changed to light brown. The decomposition mixture did not contain 1-phenyl-1-isopropyl-2-thio-3-chromene (**40**), which was prepared by an independent synthesis. Thus, like the decomposition of **4b** and unlike that of **33a,** the decomposition of **39** does not entail migration of the S substituent to the 1 position (i.e., a Stevens rearrangement).[63]

The presence of diastereotopic isopropyl methyl signals in **39** discloses that inversion at pyramidal sulfur is slow on the NMR time scale.[75] Heating of the sample above ambient probe temperature to ca. 60° resulted in rapid decomposition; thus the actual inversion barrier for **39** is inaccessible by this method, and we must content ourselves with reporting a *lower limit* of 16.8 kcal/mol.[76]

Since the calculated barrier to pyramidal inversion[4] for **1** exceeds the limits of DNMR, an alternative approach to the problem lay in the preparation of an optically active thiabenzene. Since **33c** possesses a markedly enhanced thermal stability resulting from incorporation of the strongly electron-withdrawing pentafluorophenyl group (see thermal stability section above), this compound was selected for our study. Optically active **33c** was prepared by deprotonation of **32c**[78] with brucine in anhydrous dimethyl sulfoxide under a dry nitrogen atmosphere.[25] The optical activity of the orange solution of **33c** thus generated was detected by circular dichroism (CD)[79] at the frequency of the characteristic thiabenzene absorption band in the visible region (Figure 1). This solution of optically active **33c** was much less stable than solutions of **33c** generated by deprotonation of **32c** with dimsyl anion; the time for 50% decomposition for solutions of **33c** generated by brucine deprotonation was 1.0 hr as compared with 249 hr for solutions generated by deprotonation with dimsyl anion. As the absorption in the visible region decreased, a parallel decrease in rotational strength (CD) was also observed (Figure 2), indicating that racemization proceeded *no faster* than decomposition. We determined that the unexpectedly rapid decomposition was caused by the presence of brucine hydrofluoroborate, generated on deprotonation of **32c**. This difficulty was overcome by treating the freshly prepared solution of optically active **33c** with anhydrous sodium methoxide, resulting in a solution of optically active **33c** which showed stability comparable to samples generated by deprotonation with dimsyl anion. It thus became possible to monitor the CD over an extended period of time.[80] The solution showed negligible diminution of optical activity (less than a 10% change as monitored by CD) and negligible thermal decomposition (less than a 2% change as monitored by uv) over a period of 200 min at 24 ± 1°. This observation assures that the barrier to pyramidal inversion in **33c** must be *at least* 23.7 kcal/mol.[81]

Prior studies have established a pyramidal structure for the sulfur center in acyclic sulfonium ylides.[82,83] The pyramidal inversion barrier for ethylmethylsulfonium phenacylide was determined to be 23.3 kcal/mol.[83] Our estimate of a *lower limit* for pyramidal inversion of 16.8 kcal/mol in **39** and of 23.7 kcal/mol in **33c** is therefore at least consistent with the view that thiabenzenes are ylide-like in character.

This description of thiabenzenes sharply contrasts with the model proposed by Price and coworkers[5-8] to rationalize their observations. As previously discussed in our consideration of "stable thiabenzenes", Price and coworkers proposed that thiabenzenes were most stable in a planar conformation (i.e., like **27**), and they declared that "The remarkable amorphous character and color of these compounds [i.e., the "stable thiabenzenes"] still seem best explained by an extremely low barrier to bending at the sulfur-phenyl bond." [5] This model was supported by related Hückel calculations on 2-phenyl-2-thianaphthalene which predicted a planar structure (like **27**), with a barrier to out-of-plane bending at the S-phenyl bond of less than 5.0 kcal/mol.[29c] In light of our experimental findings, it is apparent that these calculations led to the wrong conclusion, and that criteria such as "amorphous character" and "color" are not meaningful when considering pyramidality at sulfur.

The pyramidal inversion process constitutes a sensitive probe into the nature of bonding in certain cyclic, conjugated systems.[3,4,84] In the transition state for inversion, a p orbital on the inverting center, containing an electron pair, becomes parallel to an adjacent set of p orbitals, allowing strong interactions between the two electronic systems. Such conjugative interactions are somewhat diminished in the pyramidal configuration. The magnitude of the energy change, which results from the geometric change between the pyramidal ground state and the planar transition state, may be perceived as a measure of the strength of these conjugative interactions. It should be pointed out that, if conjugation plays an important role in the bonding of thiabenzenes, the pyramidal, six-electron ground state would be stabilized and the planar, antiaromatic, eight-electron transition state destabilized relative to an unconjugated structure (i.e., a model acyclic sulfonium ylide).[3]

Our findings cast little light on the importance of d-orbital participation in the bonding of thiabenzenes, other than to exclude a planar aromatic ring such as proposed by Price and coworkers (**27**).[8a] The bonding role of d orbitals in systems that contain second or higher row elements of the periodic table and their potential for interaction with a neighboring π system have been controversial topics,[85,86] centering mainly on phosphonitrilic halides, but also having been extended to thiabenzenes.[86b] All discussions thus far on this subject are of a qualitative character; the problem of the precise nature of bonding in such systems remains open but is under active investigation.[87]

Conclusions

In the present study, we have provided evidence on the basis of which a reasonable bonding model for thiabenzenes, consistent with experimental observation and with chemical intuition, can be formulated. Our studies of the factors which influence the thermal stability of thiabenzenes have pointed to a similarity between thiabenzenes and sulfonium ylides, both being stabilized by effects (ring substituents, solvent) which delocalize or stabilize electronic charge. The marked upfield shifts for α protons in **5b**[12] and 1,2-disubstituted thianaphthalene systems is nicely accommodated by this ylide model. The rearrangements that occur in a broad range of thiabenzenes indicate a close resemblance to the Stevens rearrangements, which are well established for sulfonium ylides. Finally, from our probe of pyramidality at sulfur in thiabenzenes, we have found that the sulfur center in these molecules, as in sulfonium ylides, is stably pyramidal, with a barrier to pyramidal inversion of at least 23 kcal/mol.

On the basis of the above experimental observations, we have been led to the ineluctable conclusion that thiabenzenes are best depicted as cyclic sulfonium ylides. This conclusion totally supports the one initially proposed in the pioneering work by Hortmann and Harris[12,90] on thiabenzenes and thiabenzene 1-oxides.[91]

The present study has also served to illuminate some of the physical and chemical properties which characterize thiabenzenes, such as the already referred to upfield shifts for α protons and the distinct absorption bands in the visible region of the electronic spectrum. Above all, thiabenzenes, without known exception, are inherently unstable compounds under ordinary conditions,[51] even though degrees of instability are discernible which are, as we have been able to show, related to the sulfonium ylide character of these molecules. Suitably substituted thiabenzenes, such as 1-pentafluorophenyl-2-methyl-2-thianaphthalene, are therefore capable of isolation.

Experimental Section[93]

General Procedure for the Preparation of Purified Lithium Reagents. Aryllithium Reagents. These were prepared by a modification of the method of Schlosser and Ladenberger,[94] by an exchange reaction between butyllithium and the appropriate aryl halide at low temperature in anhydrous ether under a dry nitrogen atmosphere. The solutions were allowed to warm, and the solvent was removed under reduced pressure. The white solids were warmed with hexane (dried over sodium) under a dry nitrogen atmosphere and allowed to settle, the hexane was removed by syringe, and the resulting solids were vacuum dried. The crude solids were dissolved in anhydrous ether under a dry nitrogen atmosphere, and the solutions were cooled to ca. −78°. White crystals formed in ca. 0.5 hr, and the supernatant liquids were removed by syringe. The process was repeated, and the resulting white crystals were vacuum dried for ca. 24 hr to give white powders. These were stored under a dry nitrogen atmosphere at ca. 5° and were pyrophoric in air.

Ethyllithium. Commercial ethyllithium in benzene was warmed to 60° and filtered through glass wool into a flask under a dry nitrogen atmosphere. The solvent was removed under reduced pressure, and the resulting brown solid was dissolved in hexane (dried over sodium). The solution was cooled to ca. −78°, and crystals formed. The supernate was removed by syringe, and the process was repeated. The resulting material was vacuum dried for ca. 12 hr to furnish a tan powder. The ^{1}H NMR spectrum of this solid was consistent with the assigned structure.

2-Isopropylthiopyrylium Perchlorate (3a). The method used for the synthesis of **3a** was a modification of the method used by Degani and Vincenzi[11] in the preparation of 2-methylthiopyrylium perchlorate. Sodium metal (30.0 g, 1.3 mol) was dissolved in methanol (550 ml) under a dry nitrogen atmosphere. The solution was cooled to ca. 0°, and methyl thioglycolate (142.0 g, 1.3 mol) was added rapidly with stirring. While the reaction mixture was maintained at ca. 0°, 3-chloro-4-methylpentan-2-one[95] (180.0 g, 1.3 mol) was added dropwise. After the addition was completed, the cooling bath was removed, and the reaction mixture was refluxed for 1 hr (NaCl precipitate was evident). The reaction mixture was suction filtered, and the filtrate was distilled under reduced pressure to remove most of the methanol. The resulting oil was diluted with water (500 ml), and this aqueous mixture was extracted with ether (3 × 250 ml). The combined ether extracts were then washed with dilute aqueous sodium bicarbonate and dried with anhydrous $MgSO_4$. The ether was removed under reduced pressure, and the resulting oil was fractionally distilled to give methyl (α-isopropylacetonyl)mercaptoacetate (178.0 g, 67%), bp 81–82° (0.2 mm). The ^{1}H NMR spectrum of this oil featured absorptions at δ 3.70 (s, 3 H, $O-CH_3$), 3.20 (s, 2 H, $S-CH_2$), 3.07 (d, 1 H, J = 9.5 Hz, S-CH), 2.27 (s, 3 H, $COCH_3$), 2.07 [m, 1 H, $CH(CH_3)_2$], 1.10 and 0.97 [pr of doublets, 6 H, J = 6.5 Hz, $CH(CH_3)_2$].

Cyclization to the desired diketone was accomplished by simultaneous addition of the mercaptoacetate (178.0 g, 0.87 mol) and commercial $NaOCH_3$ (100.0 g, 1.6 mol) to benzene (1000 ml) cooled to ca. 5° in an ice bath. The reaction mixture was mechanically stirred for ca. 1 hr with continued cooling, and the thick yellow mixture was then poured into an ice-cold solution of concentrated hydrochloric acid (200 ml) in water (1000 ml). After rapid agitation for 5 min, the benzene layer was separated, and the aqueous layer was extracted with chloroform (10 × 100 ml). The organic extracts were combined and dried with anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave a yellow solid which was washed with ether to give 2-isopropyltetrahydrothiopyran-3,5-dione (74.0 g, 50%) as a colorless crystalline solid, mp 69.5–70.5°. The ^{1}H NMR spectrum featured absorptions at δ 1.08 and 1.10 [pr of doublets, 6 H, J = 6.5 Hz, $CH(CH_3)_2$], 2.25 [m, 1 H, $CH(CH_3)_2$], 3.20 (d, 1 H, J = 8 Hz, S-CH), 3.38 (br s, 2 H, $S-CH_2$), 3.53 (br s, 2 H, CH_2); ir (KBr) 2950, 2920, 2900, 2860, 1745, 1715, 1480, 1410, 1370, 1345, 1290, 1245, 1190, and 1135 cm^{-1}.

Anal. Calcd for $C_8H_{12}O_2S$: C, 55.79; H, 7.02; S, 18.61. Found: C, 55.86; H, 7.10; S, 18.46.

Reduction was accomplished by adding a solution of the diketone (20.0 g, 0.12 mol) in anhydrous ether (100 ml) dropwise to a suspension of lithium aluminum hydride (20.0 g, 0.53 mol) in anhydrous ether (200 ml) under a dry nitrogen atmosphere. After the addition was completed, the reaction mixture was cooled in an ice bath and carefully treated in turn with water (20 ml), 15% NaOH (aqueous) (20 ml), and water (60 ml). This gave an easily filtered white solid which was washed with ether. The ether washings and filtrate were combined and dried with anhydrous $MgSO_4$. Removal of the ether under reduced pressure gave a pale-yellow oil which was used without further purification. The oil was dehydrated with potassium pyrosulfate (40 g, 0.19 mol) by heating the mixture to 130° (15 mm). Over a 2-hr period, a mixture of a low-boiling oil and water was collected in a receiver flask cooled in an ice bath. This oil was dissolved in ether and dried with anhydrous $MgSO_4$. Removal of the ether under reduced pressure gave a crude oil (1.1 g, mixture of dienes) which was dissolved in acetonitrile (30 ml) and treated with trityl perchlorate.[96] Addition of ether gave a white precipitate which was recrystallized from acetonitrile–ether to give **3a** (400 mg, 1.5% based on diketone),[97] mp 103–105°. The ^1H NMR spectrum of **3a** featured absorption at δ_{CD_3CN} (Me_4Si) 1.54 [d, 6 H, J = 6.5 Hz, $CH(CH_3)_2$], 3.82 [septet, 1 H, $CH(CH_3)_2$], 8.63–9.16 (m, 3 H, meta and para ring H), 10.01 (m, 1 H, ortho ring H).

Anal. Calcd for $C_8H_{11}O_4SCl$: C, 40.26; H, 4.65; S, 13.43; Cl, 14.85. Found: C, 40.05; H, 4.42; S, 13.14; Cl, 14.83.

Attempted Synthesis of 2-Isopropyl-1-phenylthiabenzene (3b). Purified phenyllithium (22 mg, 0.26 mmol) was combined with **3a** (62 mg, 0.26 mmol) in an NMR tube under a dry nitrogen atmosphere. The NMR tube was capped with a rubber septum and immersed in an acetone–Dry Ice bath (ca. −78°). Anhydrous toluene-d_8 (0.5 ml) was added to the mixture, and the tube was removed from the cooling bath and vigorously shaken producing an immediate red-brown color and dark precipitate. The tube was then replaced in the cooling bath and this mixing–cooling cycle was repeated several times. The NMR tube was then centrifuged (−78°) to give a clear red supernate. The ^1H NMR spectrum of this supernate at −30° featured three broad, unresolved, envelope absorptions at $\delta_{C_7D_8}$ (Me_4Si) 7.1 ($W_{1/2}$ = 0.3 ppm), 5.8 ($W_{1/2}$ = 0.4 ppm), and 1.1 ($W_{1/2}$ = 0.35 ppm). A sharp singlet at δ 7.2 suggested that some benzene had been formed, presumably from proton abstraction by phenyllithium. The broad signal in the methyl region, which did not change on warming the sample to ca. 40°, was not in accord with the doublet (rapid pyramidal inversion) or pair of doublets (slow pyramidal inversion on the nmr time scale) anticipated for **3b** and clearly signaled the failure of this route to yield the desired product.

1,2-Diphenyl-2-thiochromenium Perchlorate (4a). This salt was prepared by the method of Price and Follweiler.[7,48] Treatment of **30** (0.5 g, 1.55 mmol) in anhydrous ether with excess commercial phenylmagnesium chloride (8.0 mmol) under a dry nitrogen atmosphere at 0° gave an intensely purple reaction mixture. Quenching of this reaction mixture with ice-cold aqueous NH_4Cl precipitated an off-white solid which on recrystallization from acetonitrile–ether gave **4a** (310 mg, 50%), mp 168–168.5° dec (lit.[7] 160° dec). The ^1H NMR spectrum of this salt featured absorptions at $\delta_{C_3D_6O}$ (Me_4Si) 6.84 (s, 1 H, 1-H), 6.92 (br d, 1 H, J = 9 Hz, 3-H), 7.27–8.04 (m, 14 H, aromatic H), 8.44 (d, 1 H, J = 9 Hz, 4-H).

Anal. Calcd for $C_{21}H_{17}O_4SCl$: C, 62.92; H, 4.27; S, 8,00; Cl, 8.84. Found: C, 62.68; H, 4.27; S, 8.20; Cl, 8,55.

Generation of 1,2-Diphenyl-2-thianaphthalene (4b) by Deprotonation of 4a. Ethyllithium (94 μl. of a 1.6 M solution in benzene-d_6) was added to a solution of anhydrous dimethyl-d_6 sulfoxide (11 μl., 0.15 mmol) in benzene-d_6 (0.2 ml) under a dry nitrogen atmosphere in an NMR tube. The mixture was degassed with freeze–thaw cycles under vacuum to remove the ethane-d_1 formed on deprotonation, and the dimsyl-d_5-lithium–benzene-d_6 mixture was frozen. Under a dry nitrogen atmosphere, **4a** (60.1 mg, 0.15 mmol) was added to the NMR tube. After sealing the tube with a rubber septum cap, the reaction mixture was warmed to ca. 5°, and the reaction was allowed to proceed with mixing–cooling cycles to ensure that the temperature of the mixture remained below ca. 15°. Tetramethylsilane was added as an internal reference, and the purple reaction mixture in the NMR tube was centrifuged. The ^1H NMR spectrum of the clear, deeply purple supernate featured distinct absorptions at $\delta_{C_6D_6}$ (Me_4Si) 8.2–6.6 (m, 15 H, aromatic H + 4-H), 5.15 (d, 1 H, J = 8 Hz, 3-H).[93b] The spectrum showed signs of thermal decomposition with time; electronic integration revealed that the intensity of the 3-H doublet decreased relative to the aromatic region. On standing for ca. 24 hr at room temperature (ca. 22°), the intense purple color had faded to a red-brown color, and the ^1H NMR spectrum showed only a broad, unresolved absorption in the aromatic region.

The thermal decomposition of **4b** was also evident in the uv-visible spectrum (300–700 nm). A freshly prepared solution of **4b** in isooctane featured a distinct absorption in the visible region (λ_{max} 519 nm) in addition to two shoulder absorptions evident at 400 and 350 nm.[93b] On standing for ca. 24 hr at room temperature (ca. 22°), protected from light and air, the spectrum over the same region showed only a single smooth absorption extending into the visible region without a maximum (A = 2.0 at 300 nm, A = 0.0 at 490 nm).[93b]

The thermal decomposition product was isolated from a solution of **4b**, generated by deprotonation of **4a** (50 mg, 0.125 mmol) with dimsyllithium (0.15 mmol) in anhydrous benzene under a dry nitrogen atmosphere at ca. 5°, after allowing the solution to stand for 2 days at room temperature (protected from light). The mixture was washed with water, the organic layer was separated, and the solvent was removed under reduced pressure. The brown residue was dried in a vacuum desiccator to give a semisolid.

Anal. Calcd for $C_{21}H_{16}S$ (mol wt 300): C, 83.96; H, 5.37. Found [mol wt 438 (osmometry in benzene)]: C, 62.89; H, 5.68.

Generation of 4b by Addition of Phenyllithium to 30. In an NMR tube, **30** (50 mg, 0.155 mmol) was suspended in benzene-d_6 (0.5 ml) under a dry nitrogen atmosphere. The tube was placed in an ice bath, and purified phenyllithium (155 μl., 1 M in ether) was added slowly to give a deep-purple reaction mixture. Centrifugation gave a clear, intensely purple supernate that featured ^1H NMR absorptions at $\delta_{C_6D_6\text{-}Et_2O}$ (Me_4Si) 8.13–6.71 (m, aromatic H + 4-H), 5.23 (d, J = 8 Hz, 3-H) in addition to signals due to ether. The spectrum was in good agreement with that of **4b** obtained by deprotonation of **4a,** taking into account the changes in chemical shift caused by the change in solvent. A sharp singlet at δ 7.2 indicated that some proton abstraction by phenyllithium had occurred. Allowing the sample to stand at room temperature (ca. 22°) for ca. 24 hr resulted in the loss of the initially formed purple color. The ^1H NMR spectrum of this decomposition mixture featured only a broad, envelope absorption (δ 7.8–6.6) in addition to the benzene singlet (δ 7.2) and the ether signals. Both the decomposition product obtained from **4b** generated by deprotonation and the decomposition product obtained from **4b** by addition of phenyllithium to **30** exhibited spectral features that closely resembled those previously reported for **4b** itself.[7,48] It is thus apparent that the material formerly characterized as **4b** was largely decomposed material.

1-Methyl-3,5-diphenyl-2*H*-thiinium Tetrafluroborate (5a). This salt was synthesized by the method of Hortmann and Harris.[12] 1-Methyl-3,5-diphenylthiabenzene 1-oxide[90] (4.0 g, 0.014 mol) was dissolved in anhydrous benzene (50 ml) under a dry nitrogen atmosphere. Trichlorosilane (1.94 g, 0.014 mol) was added to this solution with stirring and the reaction mixture was refluxed for 9 hr. After cooling the reaction mixture in an ice bath, 20% aqueous KOH (5 ml) was added slowly, producing a white precipitate. Suction filtration furnished a clear yellow benzene solution which gave a red-brown solid residue on removal of the solvent under reduced pressure. This solid was chromatographed on Florisil (60–100 mesh) with petroleum ether (bp 60–70°) as eluent to give a yellow solid which on recrystallization from ethanol gave yellow platelets of 2*H*-3,5-diphenylthiopyran (1.24 g, 35%), mp 102–104° (lit.[12] mp 104.6–106.1°). The ^1H NMR spectrum of this solid featured absorptions at δ 7.58–7.22 (m, 10 H, aromatic H), 6.73 (m, 1 H, vinylic H), 6.62 (m, 1 H, vinylic H), and 3.73 (m, 2 H, S-CH_2), in good agreement with the spectral features previously reported.[12]

The thiopyran (1.0 g, 4.0 mmol) was alkylated using a modification of the method of Young and Lazarus[52] by dissolving it in a mixture of nitromethane (25 ml), dichloromethane (50 ml), and methyl iodide (5 ml). Silver tetrafluoroborate (1.3 g, 6.7 mmol) was dissolved in a minimum amount of acetonitrile (ca. 5 ml) and diluted with nitromethane (25 ml). This solution was then added to the thiopyran solution, and the reaction mixture was stirred for 24 hr while protected from light. Suction filtration (using Celite filter aid) gave a clear yellow filtrate which was boiled with activated charcoal to remove the color. The clear solution was evaporated under reduced pressure to give an off-white solid which on recrystallization from acetonitrile–ether gave **5a** (1.0 g, 71%), mp 144.5–145° dec (lit.[12] mp 144.4–145.8° dec). This salt gave a ^1H NMR spectrum that featured absorptions at δ_{CD_3CN} (Me_4Si) 7.88–7.47 (m, 10 H, aromatic H), 7.27 (m, 1 H, vinylic H), 6.55 (br s, 1 H, vinylic H), 4.52 (d, 2 H, J = ca. 1 Hz, S-CH_2), and 2.92 (s, 3 H, S-CH_3), in good agreement with the values previously reported.[12]

Generation of 1-Methyl-3,5-diphenylthiabenzene (5b) by Deprotonation of 5a. Treatment of **5a** (70 mg, 0.2 mmol) with dimsyl-d_5 lithium (0.2 mmol, generated from deprotonation of dimethyl-d_6 sulfoxide with ethyllithium) in benzene-d_6 gave a bright-orange reaction mixture. The ^{1}H NMR spectrum of the clear orange supernate obtained on centrifugation featured absorptions at $\delta_{C_6D_6}$ (Me_4Si) 7.88–7.18 (m, 10 H, aromatic H), 6.57 (t, 1 H, J = 1.6 Hz, 4-H), 3.91 (d, 1.6 H, J = 1.6 Hz, 2,6-H), and 1.28 (s, 2.5 H, S-CH_3) in agreement with the spectral features previously reported for **5b**[12] (small impurity absorptions were also noted at δ 1.60 and 0.82).[93b] On standing at room temperature under a dry nitrogen atmosphere and protected from light, **5b** underwent thermal decomposition.

10-Phenylthioxanthenium Perchlorate (6a). This salt was prepared by the general method of Andersen et al.[14] Thioxanthene 10-oxide[98] (1.0 g, 4.65 mmol) was dissolved in benzene (20 ml), and the solution was cooled to ca. 5° in an ice bath. Concentrated sulfuric acid (4 ml) was added dropwise with stirring to this cold solution, and the red reaction mixture was allowed to warm to room temperature and stirred for 48 hr. The reaction mixture was poured over ice, and the aqueous layer (some white precipitate present) was extracted with ether (3 × 100 ml). The aqueous layer was then cooled to 0°, and perchloric acid (5 ml, 70%) was added with stirring. After 1 hr at 0°, the mixture was filtered, washed with water and ether, and air dried. Recrystallization from acetone–ether gave **6a** (230 mg, 13%), mp 177–179°. The ^{1}H NMR spectrum of **6a** featured absorptions at $\delta_{C_3D_6O}$ (Me_4Si) 8.68–7.52 (m, 13 H, aromatic H), 4.63 and 4.30 (AB q, 2 H, J = 20 Hz, 9-H).

Anal. Calcd for $C_{19}H_{15}O_4SCl$: C, 60.88; H, 4.03; S, 8.56. Found: C, 60.24; H, 4.06; S, 8.94.

10-(2,5-Xylyl)thioxanthenium Perchlorate (6b). Using the procedure described for the preparation of **6a**,[14] thioxanthene 10-oxide[98] (1.0 g, 4.65 mmol) was treated with p-xylene and sulfuric acid followed by treatment with perchloric acid. Recrystallization of the crude salt from acetone–ether gave **6b** (430 mg, 23%), mp 157–158° (lit.[14] mp 158°). The ^{1}H NMR spectrum of **6b** featured absorptions at $\delta_{C_3D_6O}$ (Me_4Si) 8.32–7.50 (m, 10 H, aromatic H), 7.07 (br s, 1 H, aromatic H), 4.67 (br s, 2 H, 9-H), 2.79 (br s, 3 H, CH_3), 2.25 (br s, 3 H, CH_3), in agreement with the reported values.[14]

2-Chloro-10-(2,5-xylyl)thioxanthenium Perchlorate (6c). 2-Chlorothioxanthene (3.0 g, 13 mmol, material from Chem. Procurement Labs, recrystallized from 95% ethanol) was mixed with glacial acetic acid (20 ml), and H_2O_2 (5 ml, 30%) was added to the stirred mixture. After 6 hr, a slight cloudiness was evident and, on dilution with water (100 ml), an oil separated which solidified on stirring at 5° overnight. The liquid was decanted, the solid was dissolved in chloroform, and the organic solution was dried (K_2CO_3). The residue from evaporation of the solvent was dissolved in hot heptane with the aid of some chloroform, and the solution was seeded with a sample of solid retained from the prior crystallization. This furnished a tan solid (2.1 g, 65%) which contained ca. 4% of sulfone (by NMR) and no starting sulfide. The ^{1}H NMR spectrum of the sulfoxide featured absorptions at δ 3.72 and 4.08 (AB q, 2 H, J = 17 Hz, 9-H), 7.2–8.0 (m, 7 H, aromatic H). The sulfoxide (1.0 g, 4 mmol) was combined with p-xylene (20 ml) and sulfuric acid (4 ml), and the reaction mixture was stirred for 4 hr. Work-up as previously described gave a crude solid which on recrystallization from acetonitrile–ether gave **6c** (880 mg, 50%) as colorless prisms, mp 194–195.5°. The ^{1}H NMR spectrum of **6c** featured absorptions at δ_{CD_3CN} (Me_4Si) 2.24 (s, 3 H, m-CH_3), 2.72 (s, 3 H, o-CH_3), 4.47 (s, 2 H, 9-H), 6.86 (br s, 1 H, aromatic H), 7.37–7.97 (m, 9 H, aromatic H).

Anal. Calcd for $C_{21}H_{18}O_4SCl$: C, 57.67; H, 4.15; Cl, 16.21. Found: C, 58.01; H, 4.13; Cl, 16.97.

10-Mesitylthioxanthenium Perchlorate (6d). Using the previously described procedure,[14] **6d** was obtained by treatment of thioxanthene 10-oxide[98] (2.15 g, 10 mmol) with mesitylene (20 ml) and sulfuric acid (5 ml) followed by treatment with perchloric acid. The crude product was recrystallized from acetone–ether to give **6d** (1.85 g, 44%), mp 281–282° (lit.[14] >245°). The ^{1}H NMR spectrum of **6d** featured absorptions at $\delta_{CD_2Cl_2}$ (Me_4Si) 7.95–7.13 (m, 10 H, aromatic H), 4.62 and 4.38 (AB q, 2 H, J = 19 Hz, 9-H), 2.50 (s, 3 H, p-CH_3), 2.17 (s, 6 H, o-CH_3), in agreement with the values previously reported.[14]

10-Methylthioxanthenium Tetrafluoroborate (6e). This salt was prepared by alkylation of thioxanthene using a modification of the procedure of Young and Lazarus.[52] Thioxanthene (1.0 g, 5 mmol) was dissolved in a mixture of methylene chloride (25 ml), nitromethane (15 ml), and methyl iodide (10 ml). Silver tetrafluoroborate (1.0 g, 5 mmol) was dissolved in a minimum amount of acetonitrile (ca. 5 ml) and diluted with nitromethane (15 ml). This solution was added to the thioxanthene solution, and the reaction mixture was stirred for 24 hr (protected from light). The reaction mixture was suction filtered (Celite filter aid), and the clear filtrate was diluted with ether (500 ml). An off-white precipitate formed which on recrystallization from acetonitrile–ether gave **6e** (520 mg, 35%) as white needles, mp 192–194° dec. The ^{1}H NMR spectrum of **6e** featured absorptions at $\delta_{CDCl_3\text{-}CD_3CN(50:50)}$ (Me_4Si) 8.20–7.45 (m, 8 H, aromatic H), 4.55 (br s, 2 H, 9-H), 3.23 (s, 3 H, S-CH_3).

Anal. Calcd for $C_{14}H_{13}SF_4B$: C, 56.03; H, 4.37; S, 10.68. Found: C, 56.28; H, 4.71; S, 10.95.

9-*p*-Tolylthioxanthene. This thioxanthene derivative was prepared by modification of the method of Price et al.[6] Freshly prepared p-tolylmagnesium bromide (50 ml, 1.6 M solution in ether) was added to a suspension of **21** (7.7 g, 26 mmol) in anhydrous ether (100 ml) over a 10-min period under a dry nitrogen atmosphere. The reaction mixture was stirred for 0.5 hr and quenched with aqueous NH_4Cl. The reaction mixture was then extracted with ether (3 × 100 ml), and the ether extracts were washed with water and dried with anhydrous $MgSO_4$. Removal of the ether under reduced pressure gave a crude solid which was recrystallized from methanol to give 9-p-tolylthioxanthene (5.7 g, 76%), mp 148–150°. This sulfide featured absorptions in its ^{1}H NMR spectrum at $\delta_{C_6D_6}$ (Me_4Si) 7.48–6.73 (m, 12 H, aromatic H), 5.13 (br s, 1 H, 9-H), 2.03 (s, 3 H, CH_3).

Anal. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59; S, 11.12. Found: C, 83.06; H, 5.69; S, 11.21.

9-*p*-Tolyl-10-methylthioxanthenium Tetrafluoroborate (6f). 9-p-Tolylthioxanthene (2.0 g, 6.9 mmol) was methylated in a manner identical with that described for the preparation of **6e**.[52] Recrystallization of the crude solid from acetonitrile–ether gave **6f** (1.90 g, 73%), mp 212–214°. The ^{1}H NMR spectrum of the product featured absorptions at δ_{CD_3CN} (Me_4Si) 8.23–7.57 (m, 8 H, aromatic H), 7.01 (m, 4 H, p-tolyl aromatic H), 5.93 (br s, 1 H, 9-H), 2.80 (s, 3 H, S-CH_3), 2.27 (s, 3 H, CH_3).

Anal. Calcd for $C_{21}H_{19}SF_4B$: C, 64.63; H, 4.91; F, 19.47. Found: C, 64.94; H, 4.94; F, 19.61.

General Procedure for Deprotonation of 6a, 6b, 6d–6f. The thioxanthenium salt (ca. 0.1 mmol) and 9-p-tolylthioxanthene or **7a** (ca. 0.05 mmol, internal standard for the determination of yields) were placed in an NMR tube. Toluene (0.5 ml) was added, and the tube was degassed with freeze–thaw cycles under vacuum. The tube was then sealed with a rubber septum cap under a dry nitrogen atmosphere, and the mixture was cooled in an ice bath. Dimsyllithium (1.0 mol equiv, standard solution in dimethyl sulfoxide) was introduced with a microsyringe. Vigorous shaking produced an initial intense color which could be maintained for ca. 10 min at ca. 0°, but which was rapidly discharged (<3 min), as the solution was allowed to warm to room temperature (ca. 22°), to give a pale-yellow reaction mixture. The solution was analyzed by GLC (5 ft × 0.25 in. 10% OV-1 on Chromosorb W column), employing a thermal conductivity detector. Detector-response factors were determined on independently synthesized samples of the rearrangement products, and yields were determined (±3%) from peak areas. The data are presented in Table I.

Identification of the rearrangement products obtained on deprotonation of the thioxanthenium salts was made by GLC (coinjection with authentic compounds) and ^{1}H NMR spectral comparisons. Spectra were obtained on solutions from the deprotonation of these salts under conditions similar to those employed in the deprotonation of **4a**. The initially produced intense colors were allowed to fade, and the ^{1}H NMR spectra were recorded for the rearrangement mixtures. These spectra were then compared with those of authentic rearrangement products, i.e., **7a, 7b, 7d–7f.**

As a typical example, **6a** (38.0 mg, 0.101 mmol), with 9-p-tolylthioxanthene (32.5 mg, 0.113 mmol) as internal standard, was deprotonated with dimsyl anion (0.10 mmol). After ca. 5 min of shaking at ca. 22°, the initially formed intense purple color had faded to light yellow. Examination of this solution revealed that **7a**

(90 ± 3%) was formed as the exclusive volatile rearrangement product.

In the deprotonation of **6d**, product analysis revealed that **7d** (36 ± 3%) was formed as the major volatile rearrangement product, but that thioxanthene (ca. 5%) and at least three other minor volatile products were also formed during deprotonation and/or rearrangement. Similarly, in the deprotonation of **6e**, **7e** (34 ± 3%) and thioxanthene (13 ± 3%) were formed as the major reaction products. There were also at least three other minor volatile products formed in the reaction sequence. Finally, in the deprotonation of **6f**, analysis revealed that **7f** (50 ± 3%) and 9-*p*-tolylthioxanthene (26 ± 3%) were formed as the major volatile reaction products, and that at least one other minor volatile product was formed.

Deprotonation of 6c. Powdered **6c** (87 mg, 0.2 mmol) was suspended in anhydrous benzene in an NMR tube under a dry nitrogen atmosphere, the tube was sealed with a rubber septum cap, and the mixture was frozen in an acetone–Dry Ice bath. Dimsyllithium (0.20 mmol) was generated in the tube above the frozen mixture, as follows. Dimethyl sulfoxide (20 μl., 0.20 mmol) was first injected, followed by a solution of ethyllithium in benzene (133 μl., 1.5 *M*). Local heating (by hand) was used to melt the Me_2SO sufficiently to cause it to react with the ethyllithium. On warming with shaking (ca. 10°), an intense purple color was generated which faded at 25° to light red. Two drops of water and benzene (0.5 ml) were added, and the layers were separated. The residue from evaporation of the benzene solution was chromatographed on silica gel (hexane–chloroform eluent) giving a tan viscous oil (48 mg, 71%). Spectral data recorded on this material were consistent with **7c**. Its identity was further confirmed by comparison with an authentic sample.

Low-Temperature Deprotonation of 6e. Direct Observation of 10-Methyl-10-thiaanthracene. The products formed on deprotonation of **6e**, as well as the initially produced intense orange color, suggested the intermediacy of 10-methyl-10-thiaanthracene. A low-temperature deprotonation experiment was therefore carried out. Dimsyl-d_5-lithium (0.2 mmol) was prepared from dimethyl-d_6 sulfoxide in toluene-d_8 by addition of purified ethyllithium in a manner identical with that previously described for the deprotonation of **4a**. The dimsyl-d_5-lithium–toluene-d_8 mixture was frozen in liquid nitrogen, and **6e** (60.0 mg, 0.2 mmol) was added under a dry nitrogen atmosphere. The NMR tube was sealed with a rubber septum cap, and dry dimethoxyethane (0.1 ml) was added to increase the solubility of the reactants at low temperature. The contents of the NMR tube were then warmed to ca. −78° and, with rapid shaking–cooling cycles, the reaction was allowed to proceed while maintaining the mixture below ca. −40°. The bright-orange reaction mixture, which contained some precipitate, was then centrifuged in the NMR tube (−78°). The ^{1}H NMR spectrum of the clear orange supernate at −45° featured absorptions at δ 7.42–6.56 (m, aromatic H), 6.01 (s, 9-H of thiaanthracene), 1.27 (d, J = 7 Hz, CH_3 of **7e**), 1.05 (s, S–CH_3 of thiaanthracene) in addition to signals due to the solvent mixture.[93b] The ratio of peak areas for the singlets at δ 6.01 and 1.05 was 1:3. The orange reaction mixture was allowed to warm to ca. 40°, and the signals at δ 6.01 and 1.05 concurrently disappeared with a concomitant increase in the doublet at δ 1.27.[93b] On warming, the color of the reaction mixture changed from bright orange to pale yellow.

9-Phenylthioxanthene (7a). Using the procedure described for the synthesis of 9-*p*-tolylthioxanthene, **21** (2.0 g, 6.8 mmol) was allowed to react with phenylmagnesium chloride (15 ml, 2.72 *M* solution in tetrahydrofuran) in anhydrous ether. After reaction work-up as previously described, the crude solid obtained was recrystallized from methanol to give **7a** (1.42 g, 76%), mp 95.5–96° (lit.[6] mp 99°). The ^{1}H NMR spectrum of **7a** featured absorptions at $\delta_{C_6D_6}$ (Me_4Si) 7.47–6.72 (m, 13 H, aromatic H), 5.13 (s, 1 H, 9-H).

Anal. Calcd for $C_{19}H_{14}S$ (mol wt 274): C, 83.17; H, 5.14; S, 11.69. Found [mol wt 276 (osmometry in benzene)]: C, 83.26; H, 5.43; S, 11.41.

Raney nickel desulfurization of **7a** (200 mg, 0.73 mmol) in refluxing ethanol gave triphenylmethane (120 mg, 67%), mp 92.5–93.5°.

9-(2,5-Xylyl)thioxanthene (7b). Using the previously described method of synthesis, **21** (0.89 g, 3.0 mmol) was allowed to react with 2,5-xylylmagnesium bromide (8.0 mmol) in anhydrous ether. After work-up, the crude solid was recrystallized three times from ethanol to give **7b** (0.49 g, 54%), mp 125–126°. The ^{1}H NMR of **7b** featured absorptions at $\delta_{C_6D_6}$ (Me_4Si) 7.55–6.75 (m, 11 H, aromatic H), 5.13 (br s, 1 H, 9-H), 2.12 (s, 3 H, CH_3), and 2.01 (s, 3 H, CH_3).

Anal. Calcd for $C_{21}H_{18}S$: C, 82.71; H, 6.25. Found: C, 82.65; H, 5.94.

2-Chloro-9-(2,5-xylyl)thioxanthene (7c). 2-Chlorothioxanthen-9-one (3.1 g, 12.5 mmol) was allowed to react with 2,5-xylylmagnesium bromide (25 mmol) in anhydrous ether. After hydrolysis with saturated aqueous NH_4Cl, work-up in the usual manner gave the crude alcohol (oil) which was suspended in ether and cooled to −78°. Perchloric acid (7 ml) was mixed with glacial acetic acid (20 ml), and this mixture was added dropwise to the cooled suspension. The red reaction mixture, after warming to ca. −10°, was filtered to give an orange solid, which was washed with ether and dried to give crude 2-chloro-9-(2,5-xylyl)thioxanthylium perchlorate (2.51 g). Recrystallization of this salt (1.25 g) from acetonitrile–ether furnished an orange solid (630 mg): mp 264–265° dec; ^{1}H NMR: δ_{CD_3CN} (Me_4Si) 1.88 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 7.18 (s, 1 H, aromatic H), 7.56 (s, 2 H, aromatic H), 8.0–9.0 (m, 7 H, aromatic H). The purified salt was dissolved in ethanol (0.1 ml) and dichloromethane (0.5 ml), and $NaBH_4$ (ca. 20 mg) was added until the red color was discharged. Water (0.5 ml) was added to the reaction mixture, and the organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to give **7c** as a pale-yellow resin (100 mg) that would not crystallize (homogeneous by TLC): ^{1}H NMR $\delta_{C_6D_6}$ (Me_4Si) 1.93 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 4.99 (s, 1 H, 9-H), 6.8–7.8 (m, 10 H, aromatic H); mass spectrum *m/e* (rel intensity, %) 339 (3), 338 (13), 337 (11), 336 (30), 335 (11), 321 (6), 233 (26), 232 (17), 231 (100); exact mass (calcd for $C_{21}H_{17}ClS$, 336.0739) 336.0726. A sample which had been chromatographed on silica gel, then on alumina (neutral), eventually crystallized. Recrystallization from absolute ethanol furnished colorless prisms, mp 89.5–91°.

Anal. Calcd for $C_{21}H_{17}SCl$: C, 74.87; H, 5.09; S, 9.52. Found: C. 74.74; H, 5.19; S, 9.61.

9-Mesitylthioxanthene (7d). Using the synthetic route previously described, **21** (2.0 g, 6.8 mmol) was allowed to react with mesitylmagnesium bromide (20 mmol, 1 *M* solution in tetrahydrofuran) in anhydrous ether. After stirring for 2 hr, reaction work-up gave a crude solid which was recrystallized from methanol–chloroform to give **7d** (1.95 g, 91%), mp 155–157°. The ^{1}H NMR spectrum of **7d** featured absorptions at δ 7.53–6.68 (m, 10 H, aromatic H), 5.43 (br s, 1 H, 9-H), 2.37 (s, 3 H, *p*-CH_3), and 2.03 (s, 6 H, *o*-CH_3).

Anal. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37; S, 10.13. Found: C, 83.02; H, 6.46; S, 10.52.

The ^{1}H NMR spectrum of **7d** at −60° features three methyl resonances at δ 2.42, 2.35, and 1.76. As the temperature is raised, the methyl signals at δ 2.35 and 1.76 broaden, coalesce, and sharpen into a singlet at δ 2.03. The presence of three distinct methyl resonances at −60° clearly indicates restricted rotation about the mesityl–C_9 single bond. The Gutowsky–Holm approximation[77] yielded a rate constant for exchange of the magnetic environments of the *o*-methyl groups (k_c = 79.2 sec^{-1}) at the coalescence temperature (−14°). Substitution of these values into the Eyring equation, assuming a transmission coefficient of unity, gave $\Delta G^{\ddagger}_{-14}$ for the rotational process of 12.8 ± 0.3 kcal/mol. This compares with a value of $\Delta G^{\ddagger}_{25}$ of 17.6 ± 0.5 kcal/mol for 9-mesitylxanthene.[100]

9-Methylthioxanthene (7e). Using the synthetic method described above, **21** (2.0 g, 6.8 mmol) was allowed to react with excess methylmagnesium bromide (20 mmol, 2 *M* solution in tetrahydrofuran–benzene) in anhydrous ether. After stirring for 1 hr, reaction work-up gave a crude solid which was recrystallized from methanol to give **7e** (0.95 g, 66%), mp 82–84° (lit.[6] mp 84.5°). The ^{1}H NMR of **7e** featured absorptions at δ 7.53–6.97 (m, 8 H, aromatic H), 3.99 (q, 1 H, J = 7 Hz, 9-H), and 1.44 (d, 3 H, J = 7 Hz, CH_3), in agreement with the values previously reported.[101]

9-Methyl-9-*p*-tolylthioxanthene (7f). Thioxanthen-9-one (26.5 g, 0.125 mol) was dissolved in benzene and allowed to react with *p*-tolylmagnesium bromide (0.25 mol, solution in ether) under a dry nitrogen atmosphere. After the addition was complete, the reaction mixture was refluxed for 1 hr, cooled, and hydrolyzed with an aqueous saturated NH_4Cl solution. The organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. The solvent was then removed under reduced pressure to give a crude solid that was recrystallized from methanol to give 9-*p*-tolylthioxanthenol (25.1 g, 66%), mp 158–161°. This product was suspended in anhydrous ether (600 ml) and cooled to −78°. Perchloric acid (45 ml, 70%) was mixed with glacial acetic acid (150 ml), and this mixture was added to the cooled suspension over a period of 1 hr. The reaction mixture was warmed to room temperature, and the red precipitate was collected by suction filtration. Recrystallization from glacial acetic acid (1% perchloric acid) gave 9-*p*-tolylthioxanthylium perchlorate (23.5 g, 74%) as red platelets, mp 222–224°.

Anal. Calcd for $C_{20}H_{15}O_4SCl$: C, 62.10; H, 3.91; S, 8.29. Found: C, 62.48; H, 4.06; S, 8.44.

Reduction of this salt with lithium aluminum hydride gave 9-*p*-tolylthioxanthene, identical with that prepared by the addition of *p*-tolylmagnesium bromide to **21.**

The perchlorate salt (1.0 g, 2.6 mmol) was suspended in anhydrous ether (50 ml) under a dry nitrogen atmosphere, and methylmagnesium bromide (10 mmol, 2 *M* solution in tetrahydrofuran-benzene) was added with stirring. After ca. 30 min, a saturated aqueous NH_4Cl solution was added and the organic layer separated, washed with water (3 × 50 ml), and dried over anhydrous $MgSO_4$. Distillation of the solvent under reduced pressure gave a crude solid which on recrystallization from ethanol gave **7f** (650 mg, 82%), mp 153–154°. The ^1H NMR of **7f** featured absorptions at $\delta_{C_6D_6}$ (Me_4Si) 7.47–6.77 (m, 12 H, aromatic H), 2.07 (s, 3 H, CH_3), and 1.87 (s, 3 H, CH_3).

Anal. Calcd for $C_{21}H_{18}S$: C, 83.40; H, 6.00; S, 10.60. Found: C, 83.39; H, 6.23; S, 10.78.

2,4,6-Triphenylthiopyrylium Perchlorate (9).[102] A mixture of 2,4,6-triphenylpyrylium perchlorate[103] (8.2 g, 20 mmol) and acetone (400 ml) was warmed to ca. 40°, and a solution of sodium sulfide nonahydrate (10 g) in distilled water (100 ml) was added, producing a deep ruby-red color. After 30 min, perchloric acid (100 ml, 20%) was added, followed by distilled water (400 ml). The mixture was allowed to stand for 2 hr, then cooled to 5°, and the bright-yellow, fluffy needles which formed were collected. The solid was washed well with ethanol–acetone (19:1), affording 6.25 g of dried material, mp 210–212° (lit.[19,102] mp 211–212°, 210–211°). The ^1H NMR spectrum of this material indicated that starting material was present to the extent of ca. 5%.[104] Recrystallization from dichloromethane–pentane furnished **9** free from the contaminating pyrylium salt (as determined by ^1H NMR), mp 214–215°.

Reaction of 9 with Phenyllithium. Under a dry nitrogen atmosphere, **9** (2.5 g, 5.9 mmol) was suspended in anhydrous ether (70 ml), and commercial phenyllithium [21 mmol, 2.3 *M* solution in benzene–ether (70:30)] was slowly added with stirring. The mixture turned from red to deep purple, with all of the salt dissolving after 1 mol equiv of the lithium reagent had been added. The reaction was quenched after 5 min with degassed aqueous saturated NH_4Cl (15 ml), and the aqueous phase was removed with a syringe. The ether layer was washed with degassed water (15 ml), and the water washings were removed with a syringe. Anhydrous K_2CO_3 was added to the ether solution and, after 15 min, the mixture was filtered under a dry nitrogen atmosphere. The clear solution was cooled at −78° for 30 min and decanted from a colorless solid (acetone insoluble, water soluble). Pentane was then added to the ether solution and, on cooling to −78°, more solid was deposited (biphenyl). Rapid filtration and evaporation of the solvent at ca. 15° under reduced pressure gave a dark-purple resin. Residual solvent was removed under high vacuum. The resin was stored under a dry nitrogen atmosphere at 5° in the dark. The ir spectrum (thin film) of the neat resin featured bands at 3040, 3010, 1590, 1570, 1480, 1438, 1415, 1250, 1072, 1028, 812, 750, and 690 cm^{-1}. The mass spectrum (70 and 20 eV, 80° inlet) of the resin showed no mass peaks in the region of *m/e* 500–1000; minor peaks were present at *m/e* 448 and 496; the major peaks occurred at *m/e* 402, 326 (100%), 269, 220, 191, 154, 110, 105. The ^1H NMR spectrum (CCl_4) of the crude purple resin featured absorptions at δ 7.88–6.80 (m), in addition to a small, sharp absorption at δ 6.28, and the presence of signals due to hydrocarbons (from minor high-boiling impurities in the pentane). No signals due to ether were observed in the spectrum. Attempted chromatography (silica gel, alumina) under a dry nitrogen atmosphere of the resin resulted in instant decolorization. The color did persist for 1–2 min on acetyl cellulose.

The purple resin was immediately dissolved in anhydrous ether (20 ml), and pentane (175 ml) was added. The solution was cooled to −78° and filtered rapidly to give a red-violet solid, mp 44–60° (sealed), 46–62° (open) (lit.[6] shrinking at 43–45°, mp 65°). The ir spectrum of this red-violet solid showed that the characteristic bands at 1415 and 1250 cm^{-1} were decreased in intensity relative to the rest of the spectral absorptions; furthermore, these characteristic bands decreased in intensity as the color faded (CCl_4). The ^1H NMR spectrum of the red-violet solid in C_6D_6, CCl_4, and $CDCl_3$ was much broader and showed much less fine structure than the spectrum of the crude purple resin. Its chief feature was a broad envelope absorption centered at δ 7.2 ($W_{1/2}$ = 1 ppm). A small sharp peak was present at δ 7.50 (CCl_4) or at δ 7.70 (C_6D_6), which disappeared on decolorization. Attempted repurification of this sample resulted in complete loss of the purple color.

2,4,6-Tri-*p*-tolylthiopyrylium Perchlorate (13a). 2,4,6-Tri-*p*-tolylpyrylium perchlorate was prepared (32% yield) by a modification of the method of Wizinger et al.[103] The product had mp 317–318° dec. The ^1H NMR spectrum of this salt featured absorptions at $\delta_{CH_2Cl_2}$ (Me_4Si) 8.48 (s, 2 H, 3,5-H), 840–8.00 (m, 6 H, aromatic H), 7.70–7.30 (m, 6 H, aromatic H), 2.52 (s, 6 H, CH_3), 2.40 (s, 3 H, CH_3). This pyrylium salt was converted to **13a** by the method previously described for the preparation of **9.**[102] Recrystallization from dichloromethane–hexane[104] gave **13a** (40%), mp 273–274° dec. The ^1H NMR spectrum of **13a** featured absorptions at $\delta_{CH_2Cl_2}$ 8.66 (s, 2 H, 3,5-H), 8.25–7.70 (m, 6 H, aromatic H), 7.65–7.30 (m, 6 H, aromatic H), 2.42 (s, 9 H, CH_3), with chemical shifts referenced to the dichloromethane singlet at δ 5.28.

Anal. Calcd for $C_{26}H_{23}O_4SCl$: C, 66.87; H, 4.96; S, 6.87; Cl, 7.59. Found: C, 66.04; H, 5.01; S, 6.86; Cl, 7.67.

2,4-Di-*p*-tolyl-6-*p*-anisylthiopyrylium Perchlorate (13b). *p*-Methylacetophenone (13.62 g, 0.102 mol) was added to a solution of NaOH (5 g) in water (50 ml)–ethanol (30 ml). The mixture was chilled in ice to 20°, and *p*-tolualdehyde [14.2 g, 0.118 mol (97% assay)] was added with stirring, while the temperature was maintained between 20 and 30°. The reaction mixture was then stirred vigorously for 15 min and allowed to stand for 18 hr. A pale-yellow crystalline mass separated which was removed by filtration and washed with 60% ethanol (50 ml) followed by an abundance of ice-cold water. The crude 4,4′-dimethylchalcone (17.5 g, 79%) was dried under vacuum and used without further purification.

The chalcone (4.72 g, 20 mmol) was mixed with *p*-methoxyacetophenone (3.10 g, 21 mmol) and $POCl_3$ (7 ml).[103] The reaction mixture was heated on a steam bath with protection from moisture for 1.5 hr, and the remaining $POCl_3$ was removed by distillation under reduced pressure to give a dark residue. Careful dissolution (exothermic) of this residue in ethanol gave a solution which was treated with perchloric acid (2 ml, 70%), cooled, and filtered. The resulting solid was rinsed with ethanol and air dried to give crude 2,4-di-*p*-tolyl-6-*p*-anisylpyrylium perchlorate (4.75 g, 51%) as a rust-colored solid, mp 335–338° dec. The ^1H NMR spectrum of this product featured absorptions at δ_{CD_3CN} (Me_4Si) 2.50 (s, 6 H, CH_3), 3.97 (s, 3 H, O-CH_3), 7.2–7.65 (m, 6 H, aromatic H), 7.95–8.20 (m, 6 H, aromatic H), 8.83 (s, 2 H, 3,5-H).

The crude pyrylium salt (4.0 g, 8.55 mmol) was converted to **13b** by the method previously described for the preparation of **9.**[102] Fractional recrystallization from dichloromethane–pentane[104] of the crude red-orange solid eliminated contamination by the pyrylium salt and gave bright-orange **13b** (750 mg, 18%), mp 275–280° dec. The ^1H NMR spectrum of **13b** featured absorptions at δ_{CD_3CN} (Me_4Si) 2.43 (s, 6 H, CH_3), 3.88 (s, 3 H, O-CH_3), 7.0–7.5 (m, 6 H, aromatic H), 7.75–8.20 (m, 6 H, aromatic H), 8.60 (s, 2 H, 3,5-H).

Anal. Calcd for $C_{26}H_{23}O_5SCl$: C, 64.66; H, 4.80. Found: C, 64.42; H, 4.74.

2,6-(*o*-Isopropylphenyl)-4-phenylthiopyrylium Perchlorate (13c). Employing a modification of the procedure of Wizinger et at.,[103] *o*-isopropylphenyl methyl ketone[105] (10.3 g, 63.5 mmol), benzaldehyde (3.4 g, 32.1 mmol), and $POCl_3$ (14 ml) were heated to 65° for 3 hr with stirring. The resulting red reaction mixture was distilled under reduced pressure to remove the remaining $POCl_3$, giving a red-brown residue. This residue was dissolved in ethanol (100 ml) and treated with perchloric acid (4 ml, 70%). Hexane was added until two phases formed (ca. 100 ml), and the reaction mixture was poured into water, resulting in the separation of a red oil.

The mixture was stirred for 48 hr until the oil solidified. The solid was collected by suction filtration, dried, and recrystallized from dichloromethane–hexane at −78° to give 2,6-(*o*-isopropylphenyl)-4-phenylpyrylium perchlorate (2.05 g, 13%), mp 223.5–225.5° dec. The ^{1}H NMR spectrum of the yellow crystalline solid featured absorptions at δ 8.30 (s, 2 H, 3,5-H), 8.28–7.30 (m, 13 H, aromatic H), 3.26 [m, 2 H, $CH(CH_3)_2$], 1.30 [d, 12 H, J = 7 Hz, $CH(CH_3)_2$].

This pyrylium salt was converted to **13c** by the method previously described for the preparation of **9**.[102] Recrystallization from dichloromethane–hexane[104] of the crude product gave pure **13c** (85%), mp 277–279° dec. The ^{1}H NMR spectrum of **13c** featured absorptions at $\delta_{CH_2Cl_2}$ 8.70 (s, 2 H, 3,5-H), 8.10–7.30 (m, 13 H, aromatic H), 3.08 [m, 2 H, $CH(CH_3)_2$], 1.30 [d, 12 H, J = 7 Hz, $CH(CH_3)_2$], with chemical shifts referenced to the singlet of dichloromethane at δ 5.28.

Anal. Calcd for $C_{29}H_{29}O_4SCl$: C, 68.42; H, 5.74. Found: C, 68.29; H, 5.88.

2,6-Diphenyl-4-*o*-tolylthiopyrylium Perchlorate (13e). 2,6-Diphenyl-4-*o*-tolylpyrylium tetrachloroferrate was prepared by the method of Dilthey[106] as an orange-brown powder (30%), mp 205–207° dec. This pyrylium salt was converted to **13e** by a modification of the method of Wizinger and Ulrich.[102] An eightfold excess of $Na_2S \cdot 9H_2O$ was used, and the reaction mixture was filtered before addition of perchloric acid and water. The product was recrystallized once from glacial acetic acid to give crude **13e** (20%). This solid was recrystallized from dichloromethane–pentane to give orange crystals. The ^{1}H NMR spectrum of this product indicated that it was an approximately 60:40 mixture of **13e** and the pyrylium salt. The mother liquor from this recrystallization was treated with pentane yielding orange crystalline **13e** (200 mg, 1.5%), mp 197–198° dec (pure by ^{1}H NMR spectroscopy). The ^{1}H NMR spectrum of **13e** featured absorptions at δ_{CD_3CN} 8.80 (s, 2 H, 3,5-H), 8.20–7.40 (m, 14 H, aromatic H), 2.47 (s, 3 H, CH_3), with all signals referenced to the center of the CD_2HCN multiplet, δ 1.96.

Anal. Calcd for $C_{24}H_{19}O_4SCl$: C, 65.67; H, 4.36. Found: C, 65.52; H, 4.28.

General Procedure for Reaction of 13a–13e with Aryllithium. Generation of 14a–14e. The thiopyrylium salt (ca. 0.2 mmol) was placed in a 5-mm NMR tube under a dry nitrogen atmosphere, and benzene-d_6 (0.5 ml) was added. The purified dry aryllithium reagent (1.0 mol equiv) was then added under nitrogen to this frozen mixture, and the NMR tube was sealed with a rubber septum cap. Anhydrous ether (ca. 30 μl.) was added to the frozen mixture, and the reaction was initiated by warming the mixture to ca. 5°; the temperature was maintained below ca. 15° by cooling–mixing cycles. The intensely purple reaction mixture was then centrifuged in the NMR tube and the ^{1}H NMR spectrum of the clear supernate recorded. The ^{1}H NMR spectral features for **14a–14c** are reported in the text. The ^{1}H NMR spectrum of **14d** featured absorptions at $\delta_{C_6D_6\text{-}Et_2O}$ (Me_4Si) 7.72 (s, 2 H, 3,5-H), 7.6–6.6 (m, 19 H, aromatic H), 2.15 (s, 3 H, CH_3). The ^{1}H NMR spectrum of **14e** featured absorptions at $\delta_{C_6D_6\text{-}Et_2O}$ (Me_4Si) 7.27 (s, 2 H, 3,5-H), 7.7–6.6 (m, 18 H, aromatic H), 2.02 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3).

Reaction of 9 with Methyllithium. Generation of 14f. The thiopyrylium salt (85 mg, 0.2 mmol) was placed in an NMR tube, and benzene-d_6 (0.5 ml) was added. The tube was then flushed with dry nitrogen and sealed with a rubber septum cap. The mixture was cooled in an ice bath, and methyllithium (1.0 mol equiv) in ether was added to the tube. The reaction was allowed to proceed with mixing–cooling cycles while maintaining the temperature below ca. 10°. The deep-magenta reaction mixture was then centrifuged in the NMR tube. The ^{1}H NMR spectrum (5°) of the clear supernate featured absorptions at δ 1.32 (s, 3 H, CH_3), 7.61 (s, 2 H, 3,5-H), and 7.0–7.7 (m, 15 H, aromatic H). On warming, the singlets at δ 1.32 and 7.61 diminished as new singlets at δ 1.52, 1.68, 5.88, and 6.87 appeared. The reaction was carried out on a preparative scale by the reaction of **9** (425 mg, 1.0 mmol) with methyllithium (1.0 mol equiv) in anhydrous ether under a dry nitrogen atmosphere. The initially produced magenta color faded over the course of 1.5 hr, and dilute aqueous NH_4Cl solution was then added. The ether layer was separated, washed with water, dried with anhydrous K_2CO_3, and evaporated under reduced pressure to give a brown oil (320 mg). The oil was dissolved in acetone–methanol, and a tan solid was collected on cooling. Recrystallization from ethanol gave crystalline 2,4,6-triphenyl-4-methylthiopyran (**19a**), mp 96–98° (lit.[10] 97°). The ^{1}H NMR spectrum of **19a** featured absorptions at δ_{CCl_4} (Me_4Si) 1.67 (s, 3 H, CH_3), 5.86 (s, 2 H, 3,5-H), 7.0–7.7 (m, 15 H, aromatic H). The mother liquor from this recrystallization was enriched in 2,4,6-triphenyl-2-methylthiopyran (**19b**) which featured additional singlets at δ 1.88 (3 H, CH_3) and 6.80 (1 H, vinylic H).[27]

Similar results were obtained using methylmagnesium bromide in place of methyllithium.

The Reaction of 13c with Phenyllithium. Generation of 1,4-Diphenyl-2,6-(*o*-isopropylphenyl)thiabenzene (14c) and Thermal Rearrangement to 4,4-Diphenyl-2,6-(*o*-isopropylphenyl)thiopyran (18). Thiopyrylium salt **13c** (242 mg, 0.48 mmol) was suspended in anhydrous ether (20 ml) under a dry nitrogen atmosphere. Purified phenyllithium (48 mg, 0.58 mmol) was added to the suspension, and the reaction mixture turned deep purple. The reaction was stirred for 36 hr during which time the color faded to tan. The reaction mixture was chromatographed on silica gel (hexane eluent) to give a colorless oil which slowly crystallized to give **18** (170 mg, 74%), mp 98–102°. The ^{1}H NMR spectrum of **18** featured absorptions at $\delta_{C_6D_6}$ (Me_4Si) 7.70–6.85 (m, 18 H, aromatic H), 5.95 (s, 2 H, 3,5-H), 3.55 [m, 2 H, $CH(CH_3)_2$], 1.15 [d, 12 H, J = 7 Hz, $CH(CH_3)_2$]. Mass spectrum (120° inlet): *m/e* (rel intensity, %) 488 (15, P + 2), 487 (41, P + 1), 486 (98, P), 411 (12), 410 (39), 409 (100), 367 (46), 230 (12), 167 (16), 165 (13), 163 (11), 161 (12), 149 (10), 147 (10), 143 (16), 131 (14), 130 (10), 129 (41), 128 (15), 115 (16), 91 (32), and 57 (11). The identity of this compound as the 4 isomer (as opposed to the 2 isomer) is based chiefly on the observation of a sharp singlet for the 3,5 protons at δ 5.95.

2,4,6-Triphenyl-3,5-dimethylthiopyrylium Perchlorate (15). The pyrylium salt corresponding to **15** was prepared by the method of Wizinger et al.[103] by heating benzaldehyde (17.4 g, 0.16 mol) and phenyl ethyl ketone (46.6 g, 0.35 mol) with $POCl_3$ (56 ml). Work-up by the previously described method with ethanol and perchloric acid gave yellow needles of 2,4,6-triphenyl-3,5-dimethylpyrylium perchlorate (13.7 g, 19%), mp 298–299° dec. The ^{1}H NMR spectrum of the salt featured absorptions at δ_{CD_3CN} (Me_4Si) 8.1–7.3 (m, 15 H, aromatic H) and 2.26 (s, 6 H, CH_3).

Conversion of this pyrylium salt to **15** was accomplished by the procedure previously described for the preparation of **9**.[102] Recrystallization of the crude solid from acetonitrile–ethanol gave **15** (27%), mp 314–315° dec. The ^{1}H NMR spectrum of **15** featured absorptions at δ_{CD_3CN} (Me_4Si) 7.75–7.20 (m, 15 H, aromatic H) and 2.21 (s, 6 H, CH_3).

Anal. Calcd for $C_{25}H_{21}O_4SCl$: C, 66.29; H, 4.67. Found: C, 66.29; H, 4.86.

Reaction of 15 with Aryllithium Reagents. Generation of 1-*p*-Tolyl-2,4,6-triphenyl-3,5-dimethylthiabenzene (16a) and Its Thermal Rearrangement to 4-*p*-Tolyl-2,4,6-triphenyl-3,5-dimethylthiopyran (17a). A nitrogen-filled vessel was charged with **15** (136 mg, 0.3 mmol), benzene (4 ml), and anhydrous ether (50 μl.). The mixture was treated with purified *p*-tolyllithium (26 mg, 0.295 mmol) to give a red solution (see text). This solution was refluxed for 8 hr in the absence of light, producing a pale-yellow solution. Evaporation of the solvent under reduced pressure gave a residue that was chromatographed on silica gel. The first band [hexane–chloroform (2:1) eluent] furnished **17a** (81.5 mg, 62% based on *p*-tolyllithium), mp 161–164°. Ethyl acetate eluent gave a second band due to unreacted **15** (59.6 mg, 0.13 mmol). The yield of **17a** based on the amount of **15** converted was ca. 95%. The ^{1}H NMR spectrum of **17a** featured absorptions at δ 1.35 (s, 6 H, 3,5-CH_3), 2.37 (s, 3 H, CH_3), 7.0–7.7 (m, 19 H, aromatic H).

Thiopyrylium Perchlorate (20). This salt was prepared by the method of Degani et al.,[107] as modified by Strating et al.[108] Freshly distilled glutaraldehyde (23.3 g, 0.22 mol) was dissolved under a dry nitrogen atmosphere in degassed dichloromethane (500 ml) at −78° (Dry Ice–acetone bath). Hydrogen chloride and hydrogen sulfide were then bubbled through the solution in a ratio of ca. 2:1. The temperature was allowed to warm to ca. −30°, and the reaction mixture was maintained at this temperature for ca. 2 hr. The gas addition was then stopped, and the reaction was cooled to −78° without stirring. The ice crystals which formed were removed by rapid suction filtration, and the filtrate was dried with anhydrous magnesium sulfate, while the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure without heating to give a viscous oil which was carefully mixed with freshly distilled *N,N*-diethylaniline (200 ml) and then heated under a dry nitrogen atmosphere to 130° for ca. 45 min. The orange-red reaction mixture (some precipitate) was allowed to cool to room temperature and vacuum distilled with the receiver flask cooled to −78°. A fraction was collected at 30-60° (16 mm) which on redistillation gave γ-thiopyran (2.0 g, 9%), bp 40-43° (15 mm) [lit.[108] bp 30° (12 mm)]. This air-sensitive compound gave a ^{1}H NMR spectrum that featured absorptions at δ 6.26-5.21 (m, 4 H, vinylic H) and 2.99-2.74 (m, 2 H, CH_2), in agreement with the values previously reported.[29b]

The γ-thiopyran (2.0 g, 20.4 mmol) was dissolved in acetonitrile (50 ml) and cooled in an ice bath under a dry nitrogen atmosphere. Trityl perchlorate[96] (6.9 g, 20.2 mmol) was then added slowly with stirring (some white solid was evident after ca. half of the addition was completed). The mixture was diluted with anhydrous ether, and the resulting white solid was filtered and washed with anhydrous ether to give **20** (3.4 g, 85%), mp 336° (*explosion*) [lit.[29b] mp 336° (*explosion*)]. (*Warning:* this explosion is very violent, and only minute amounts of material should be used.) The uv spectrum [CH_3CN (1% perchloric acid)] featured absorptions at λ_{max} (log ϵ) 284 nm (3.59) and 245 (3.82) [lit.[107] 284 nm (3.54) and 245 (3.76)].

Thioxanthylium Perchlorate (21). This salt was prepared, by following exactly the procedure of Price et al.,[6] from thioxanthen-9-ol and perchloric acid. The crude salt was recrystallized from acetic acid (1% perchloric acid) to give **21**, mp 230-232° dec (lit.[6] mp 229° dec). The uv spectrum [acetic acid (1% perchloric acid)] displayed absorptions at λ_{max} (log ϵ) 280 nm (4.95), 380 (4.33), 484 (3.50), and 510 (3.40).[109]

1-Thianaphthalenium Perchlorate (22). This salt was prepared as previously described.[111] Recrystallization from glacial acetic acid (2% acetic anhydride) gave yellow-green needles of **22**, mp 219-220° dec (lit.[112] mp 219-220° dec). The uv spectrum of **22** [acetic acid (1% perchloric acid)] featured absorptions at λ_{max} (log ϵ): 258 nm (4.54), 335 (3.71), and 385 (3.56) [lit.[110] 258 nm (4.53), 335 (3.70), and 384 (3.50)].

2-Thianaphthalenium Perchlorate (23). This salt was prepared as previously described.[6] Recrystallization from glacial acetic acid (2% acetic anhydride) gave **23**, mp 190-191° (lit.[6] 189-190°). (*Warning:* While this perchlorate salt was handled over a period of several months without incident, one preparation, on attempted recrystallization from acetic acid, exploded violently while being heated to achieve dissolution. Although this explosion was presumably due to an impurity not present in the other preparations, it points up the fact that these materials are perchlorate salts, and every precaution should therefore be taken in their preparation and handling. We also note that **23** is sensitive to abrasion.) The uv spectrum [acetic acid (1% $HClO_4$)] of **23** featured absorptions at λ_{max} (log ϵ) 258 nm (4.65), 306 (3.71), 317 (3.69), and 384 (3.63) [lit.[112] 257 (4.61), 307 (3.66), 316 (3.64), and 384 (3.60)].

Reaction of 20 with Phenyllithium. Following exactly the procedure described by Price and coworkers,[5] **20** (1.20 g, 6.29 mmol) was suspended in anhydrous ether (100 ml) under a dry nitrogen atmosphere at −78°. Commercial phenyllithium (25 mmol, 2.3 *M* solution in benzene-ether) was then added dropwise with stirring to give a red reaction mixture. This mixture was then warmed to ca. 0° (the color turned green), and an ice-cold saturated aqueous NH_4Cl solution (40 ml) was added. This produced a deep red organic layer and an orange aqueous layer, in addition to an insoluble material. The reaction mixture was filtered, and the organic layer was separated, washed with water (10 × 100 ml), and evaporated under reduced pressure to give a dark (almost black) highly viscous oil, tarry in appearance. This tarry oil was extracted with benzene (100 ml), and the red solution was filtered to remove an insoluble residue. The clear solution was dried over anhydrous $MgSO_4$, filtered, and evaporated to give a dark viscous oil which was dried under vacuum. The tarry oil was extracted with anhydrous ether (20 ml), and the red solution was again filtered to remove the insoluble portion of the material. The solution was cooled to ca. 0° and then diluted with 30-60° petroleum ether (100 ml). This resulted in the formation of a flocculant precipitate which was collected by filtration, dissolved in a minimum amount of benzene and freeze-dried to give a red-brown electrostatic solid (89 mg).

Anal. Calcd for $C_{11}H_{10}S$ (mol wt 174): C, 75.82; H, 5.78; S, 18.40. Found [mol wt 968 (osmometry in benzene)]:[113] C, 68.11; H, 5.05; S, 16.94.

On heating this material, at 60°, the first signs of shrinking occurred, and the material increased in fluidity until no form was maintained at 120-125°. The ^{1}H nmr spectrum (CCl_4) of this material featured two broad envelope absorptions centered at δ 7.26 ($W_{1/2}$ = 0.25 ppm) and 6.17 ($W_{1/2}$ = 0.7 ppm) in addition to some minor absorptions in the aliphatic region which may be due to occluded solvent.[93b,114] The ir spectrum (KBr) of this solid had absorptions at 3040, 3005, 1650, 1600, 1475, 1435, 1020, 740, and 690 cm^{-1} in agreement with the reported[5] values. The uv spectrum (ethanol) of this material showed a λ_{max} (log ϵ) at 250 nm (3.66); the reported[5] maximum at 202 nm (ethanol) is due to the uv cutoff of the solvent. The mass spectrum (85° inlet) of this material featured peaks at *m/e* (rel abundance, %) 469 (10), 393 (10), 350 (10), 349 (15), 275 (12), 274 (39), 273 (78), 271 (15), 241 (12), 239 (15), 218 (16), 212 (16), 219 (31), 218 (78), 217 (100), 186 (16), 185 (13), 184 (14), 174 (2), 165 (60), 154 (26), 152 (28), 115 (20), 110 (60), 105 (35), 91 (35), 78 (35), and 77 (50) (only peaks of rel intensity ≥20% are given for *m/e* values below 174). The reported[5] mass spectrum of "**2**" showed that the major observed peaks were at *m/e* 186, 154, and 97. The peak at 186 was attributed[5] to an ion-molecule reaction producing phenyl sulfide. Based on our investigation of the processes that occur on addition of an aryllithium reagent to **20**, it is more reasonable to believe that the observed phenyl sulfide was formed in the course of the reaction and not in the mass spectrometer.

Reaction of 21 with Phenyllithium. Following exactly the procedure of Price et al.,[6] **21** (8.0 g, 26 mmol) was suspended in anhydrous ether (100 ml) under a dry nitrogen atmosphere. Commercial phenyllithium (57 mmol, 2.3 *M* solution in benzene-ether) was added, and the reaction mixture was shaken to achieve dissolution of **21**. A red-brown reaction mixture was produced, along with some precipitate. The reaction mixture was cooled in an ice bath, and an ice-cold saturated aqueous NH_4Cl solution (40 ml) was added with shaking. This produced a deep red organic layer with some more precipitate. The mixture was suction filtered and the solid retained. The clear organic layer was separated, washed with water (5 × 100 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give a dark, highly viscous, tarry-appearing oil. This tarry oil was extracted with 30-60° petroleum ether (3 × 20 ml) and the insoluble residue chromatographed on neutral alumina (ether eluent). The resulting oil was dissolved in a minimum amount of ether, and 30-60° petroleum ether was added to give a solid which was filtered and washed with cold 30-60° petroleum ether. After drying under vacuum, an electrostatic brown powder (480 mg) was obtained.

Anal. Calcd for $C_{19}H_{14}S$ (mol wt 274): C, 83.17; H, 5.14; S, 11.69. Found [mol wt 831 (osmometry in benzene)]:[113] C, 83.07; H, 5.08; S, 11.33.

Visual inspection of a sample of this material on heating showed that shrinking began to occur at ca. 110°, and that the fluidity of the material increased until all form was lost at 140-150°. Differential thermal analysis[93a] performed on this material revealed that no endothermic reaction occurred up to 200°, although a decomposition exotherm was noted in some runs at about 105°. The ^{1}H NMR spectrum (CCl_4) of this material featured a broad envelope absorption in the aromatic region centered at δ 7.12 ($W_{1/2}$ = 0.5 ppm) in addition to some minor signals in the aliphatic region that may be due to occluded solvent.[93b] The ^{13}C NMR spectrum ($CDCl_3$)[59] was wholly inconsistent with monomeric **8**. Instead of eight intense signals and three weak signals (quaternary carbons) that would be expected for the noise-decoupled spectrum of **8**, merely a broad envelope absorption was evident, centered at ca. 126 ppm downfield from Me_4Si.[93b] The ir spectrum (KBr) of this material had absorptions at 3055, 1580, 1460, 1430, 740, and 695 cm^{-1}. The uv spectrum (dioxane) featured absorptions at λ_{max} (log ϵ) 265 nm (3.80) and 420 (2.05). The mass spectrum (95° inlet) exhibited peaks at *m/e* (rel intensity, %) 349 (2), 348 (2), 347 (5), 288 (3), 287 (4), 286 (5), 274 (6), 213 (100), 197 (24), 184 (45), 97 (20), 95 (23), 94 (40), and 91 (20) (only peaks of rel intensity ≥20% are given for *m/e* values below 274). The previously reported[8a] mass spectrum of "10-phenyl-10-thiaanthracene" exhibited peaks at *m/e* values out to 546 amu. In retrospect, these peaks bespeak the oligomeric nature of this amorphous material.

Reaction of 22 with Phenyllithium. Following the procedure of Price et al.,[6] **22** (2.5 g, 10 mmol) was suspended in anhydrous ether (50 ml) under a dry nitrogen atmosphere. Over a 20-min period, commercial phenyllithium (46 mmol, 2.3 *M* solution in benzene–ether) was added with shaking to achieve dissolution of the thianaphthalenium salt and to produce a brown reaction mixture with some precipitate. After ca. 0.5 hr of stirring, the reaction mixture was cooled in an ice bath, and an ice-cold saturated aqueous NH_4Cl solution (40 ml) was added with shaking. The deep red organic layer was separated, washed with water (5 × 30 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give a red viscous oil. This was dissolved in ether and filtered (to remove some insoluble material), and the clear filtrate was diluted with 30-60° petroleum ether to give a yellow-orange precipitate. This solid was filtered, washed with 30-60° petroleum ether, and dried under vacuum to give a brown electrostatic powder (480 mg).

Anal. Calcd for $C_{15}H_{12}S$ (mol wt 224): C, 80.31; H, 5.39; S, 14.29. Found [mol wt 1380 (osmometry in benzene)]:[113] C, 77.29; H, 5.03; S, 18.00.

In a second run, the thianaphthalenium salt **22** (10 g, 41 mmol) was allowed to react with phenyllithium (81 mmol) in anhydrous ether (150 ml) under conditions identical with those described above. The initially produced viscous oil was chromatographed on neutral alumina (ether eluent) to give a brown powder (225 mg).

Anal. Calcd for $C_{15}H_{12}S$ (mol wt 224): C, 80.31; H, 5.39; S, 14.29. Found [mol wt 980 (osmometry in benzene)]:[113] C, 76.86; H, 5.03; S, 17.14.

This solid on heating began to soften at ca. 120° and continued to increase in fluidity until all form was lost between 135–145°. The ^1H NMR spectrum (CCl_4) of this material featured a broad envelope absorption centered at δ 7.14 ($W_{1/2}$ = 0.5 ppm), in addition to some weak absorptions in the aliphatic region which may be due to occluded solvent. The ir (KBr) featured absorptions at 3050, 3015, 2940, 1575, 1460, 1430, 1065, 1030, 730, and 690 cm^{-1}. The uv spectrum (cyclohexane) showed no distinct absorption band but did exhibit two shoulders at λ_{max} (log ϵ) 285 nm (3.68) and 245 (4.01). The mass spectrum (200° inlet) of this material had peaks at *m/e* (rel intensity, %) 594 (3), 592 (3), 516 (3), 514 (3), 446 (7), 444 (10), 367 (20), 293 (12), 279 (10), 253 (10), 236 (12), 234 (12), 224 (55), 223 (85), 210 (20), 147 (100), and 134 (29) (only peaks of rel intensity ≥20% are given for *m/e* values below 224). The reported mass spectrum[29b] of "1-phenyl-1-thianaphthalene" [*m/e* (rel intensity, %) 155 (15), 154 (100), 153 (33), 152 (22), 105 (12), 91 (16), 77 (26), 76 (29), 64 (12), 63 (11), 51 (19), 50 (11), 44 (58), and 43 (17) (only peaks of rel intensity ≥10% are given)] is remarkably similar to that reported[115] for biphenyl [*m/e* (rel intensity, %) 156 (7), 155 (13), 154 (100), 153 (26), 152 (21), 151 (7), 115 (5), 77 (10), 76 (17), 64 (7), 63 (7), 51 (10), and 50 (6)].

Reaction of 23 with Phenyllithium. Following the procedure described by Price et al.,[6] **23** (2.5 g, 10 mmol) was suspended in anhydrous ether (75 ml) under a dry nitrogen atmosphere. Commercial phenyllithium (35 mmol, 2.3 *M* solution in benzene–ether) was added with shaking to give a brown reaction mixture with some precipitate. After the addition was completed, the reaction mixture was cooled in an ice bath, and an ice-cold saturated aqueous NH_4Cl solution (20 ml) was added with shaking. The organic layer was separated, washed with water (2 × 50 ml), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give a dark, viscous, tarry oil. This tarry oil was extracted with 30-60° petroleum ether (5 × 20 ml), the residue was dissolved in a minimum amount of ether, and 30-60° petroleum ether was added to precipitate the solid material. This solid was filtered, washed with 30-60° petroleum ether, and dried under vacuum to give a brown electrostatic powder (260 mg).

Anal. Calcd for $C_{15}H_{12}S$ (mol wt 224): C, 80.31; H, 5.39; S, 14.29. Found [mol wt 1261 (osmometry in benzene)]: C, 81.27; H, 5.67; S, 13.43.

The reaction was repeated by the addition of phenyllithium (81 mmol) to **23** (6 g, 24 mmol), using the conditions described above. The crude oil initially obtained was chromatographed on neutral alumina (ether eluent). The collected ether eluate was reduced in volume to ca. 30 ml, and ice-cold 30-60° petroleum ether was added. This gave a yellow solid which was filtered, washed with 30-60° petroleum ether, and dried under vacuum to give a brown electrostatic powder (255 mg).

Anal. Calcd for $C_{15}H_{12}S$ (mol wt 224): C, 80.31; H, 5.39; S, 14.29. Found [mol wt 919 (osmometry in benzene)]:[113] C, 80.52; H, 5.36; S, 13.65.

Visual inspection on heating revealed that this material began to soften at ca. 105°, and that the fluidity increased until all form was lost at 120-130°. Differential thermal analysis[93a] on this material revealed a glass transition temperature at 81° but no true phase transition (melting point). The ^1H NMR spectrum (CCl_4) featured a broad envelope absorption centered at δ 7.15 ($W_{1/2}$ = 0.7 ppm). The ir (KBr) featured bands at 3040, 3010, 1580, 1465, 1430, 1100, 1080, 1020, 750, and 690 cm^{-1}. The uv spectrum (cyclohexane) did not show a distinct uv maximum but did feature a shoulder at λ_{max} (log ϵ) ca. 300 nm (3.90). The reported[6] uv maximum at 207 nm (ethanol) is actually the uv cutoff for the solvent. The mass spectrum (95° inlet) of this material exhibited peaks at *m/e* (rel intensity, %) 450 (1), 448 (1), 372 (1), 370 (1), 341 (2), 340 (5), 338 (4), 337 (4), 306 (6), 305 (7), 304 (5), 302 (6), 292 (11), 291 (6), 289 (5), 244 (5), 229 (12), 228 (11), 224 (27), 223 (20), 192 (27), 191 (22), 189 (76), 149 (20), 148 (65), 147 (100), 115 (25), 110 (100), 109 (38), 78 (20), 77 (41), and 66 (38) (only peaks of rel intensity ≥20% are given for *m/e* values below 224).

9-Phenylthioxanthylium Perchlorate. Thioxanthen-9-one (8.48 g, 40 mmol) was suspended in anhydrous ether (100 ml) under a dry nitrogen atmosphere, and commercial phenyllithium (80 mmol, 2.3 *M* solution in 70:30 benzene–ether) was added with stirring. After 8 hr, the reaction mixture was hydrolyzed with a saturated aqueous NH_4Cl solution. The organic layer was separated, washed with water (3 × 50 ml), dried over anhydrous $MgSO_4$, and evaporated to give an oil which on trituration with heptane gave a crude tan solid. Recrystallization from chloroform–heptane gave crude 9-phenylthioxanthen-9-ol (9.1 g) which was used without further purification.

The crude alcohol (8.0 g, 27.6 mmol) was converted to the corresponding perchlorate salt using the method described by Price et al.[6] Treatment of an ether solution of the alcohol with perchloric acid (11 ml, 70%) at low temperature, followed by recrystallization of the crude salt from glacial acetic acid gave 9-phenylthioxanthylium perchlorate (9.2 g, 90%), mp 238.5–239.5° dec (lit.[6] mp 239°).

Reaction of 9-Phenylthioxanthylium Perchlorate with Phenyllithium. Following the basic procedure of Price et al.,[6] 9-phenylthioxanthylium perchlorate (1.6 g, 4.8 mmol) was suspended in anhydrous ether (30 ml) under a dry nitrogen atmosphere, and phenyllithium (9.4 mmol, freshly prepared from *n*-butyllithium and bromobenzene in anhydrous ether) was added with stirring. After 2 hr, the red-brown reaction mixture was quenched with an ice-cold saturated aqueous NH_4Cl solution. The organic layer was separated, washed with water, dried over anhydrous Na_2CO_3, and evaporated under reduced pressure to give a dark oil. This oil was dissolved in ether and the solution diluted with hexane. Evaporation of this solution under reduced pressure to a small volume gave a red-brown precipitate. This solid was chromatographed on neutral alumina (ether eluent) to give a red-brown oil which was freeze-dried from benzene to give a red-brown solid (80 mg).

Anal. Calcd for $C_{25}H_{18}S$ (mol wt 350): C, 85.67; H, 5.18; S, 9.15. Found [mol wt 757 (osmometry in benzene)]:[113] C, 84.46; H, 5.91; S, 8.73.

The red-brown electrostatic solid on heating began to soften at 120° and increased in fluidity until all form was lost at 140-145°. The ^1H NMR spectrum (CCl_4) of this material featured a broad envelope absorption centered at δ 7.2 ($W_{1/2}$ = 0.5 ppm) in addition to several minor absorptions in the aliphatic region that may be due to occluded solvent. The ir spectrum (KBr) featured bands at 3055, 1580, 1450, 1430, 750, and 700 cm^{-1}. The uv spectrum (dioxane) featured an absorption at λ_{max} (log ϵ) 273 nm (4.00). The mass spectrum (100° inlet) featured peaks at *m/e* (rel intensity, %) 427 (6), 426 (12), 425 (5), 350 (21), 349 (47), 274 (42), 273 (79), 271 (21), 251 (16), 198 (10), 197 (65), 78 (100), and 77 (18) in addition to minor peaks over 500 (only peaks of rel intensity ≥10% are given for *m/e* values below 350). The reported[29b] mass spectrum of "9,10-diphenyl-10-thiaanthracene" exhibited peaks in excess of 900 amu. In retrospect, the presence of these high mass peaks provides further evidence for the oligomeric nature of the material previously claimed as a monomeric species.

General Procedure for the Addition of *p*-Tolyllithium to 20, 22, 23, 28, and 29. The thiopyrylium salt [ca. 0.2 mmol, dried for ca. 12 hr at 80–115° (0.05 mm)] was weighed into an NMR tube under a dry nitrogen atmosphere. Benzene-d_6 (0.6-0.9 ml, dried over sodium) was added to the tube, the tube was sealed with a rubber septum cap, and the suspension was then frozen in an acetone-Dry Ice bath. Purified *p*-tolyllithium (1.0 or 2.0 mol equiv) was added to the frozen suspension under a dry nitrogen atmosphere, and the NMR tube was resealed with a wired-on rubber septum cap. Ether (15-30 μl., dried over sodium) was then added to the mixture, and the reaction was initiated by allowing the tube to warm to ca. 5°. Mixing-cooling cycles assured that the temperature remained below ca. 30°. The NMR tube containing the reaction mixture was centrifuged to give a clear supernate and a small plug of salts; the ^{1}H NMR spectrum of this supernate was recorded as an assay of the products formed in the reaction.[116] A known amount of mesitylene (internal standard) (ca. 0.05 mmol, dried over sodium) was then added to the reaction mixture with mixing, and GLC analysis using either a 5 ft × 0.25 in. OV-1 column (10% on Chromosorb W) or a 6 ft × 0.25 in. XE-60 column (5% on Chromosorb W) was carried out. Product identification was accomplished by comparison of the ^{1}H NMR spectra of authentic compounds with the spectrum of the reaction mixture, by coinjection with authentic compounds, and by GLC-mass spectrometric analysis (10% OV-1 column). Quantitative yields were determined from peak areas after detector-response factors were established. The results of this study are collected in Table II.

In a negative control reaction, the same procedure described above was followed with the exception that no thiopyrylium salt was used. After the addition of mesitylene and before GLC analysis, the *p*-tolyllithium was quenched with chlorotrimethylsilane (distilled from quinoline). The amount of toluene formed was determined by GLC analysis. It was found to be typically 5% of that formed in the thiopyrylium salt reactions, and this was assumed to arise from handling errors with the lithium reagent. The values reported in Table II are corrected to account for this factor. The activity of the *p*-tolyllithium was determined by quenching with nitrogen-purged water followed by quantitative GLC analysis of the amount of toluene formed (mesitylene as internal standard). The activity was typically 95-100% of that expected on a weight basis.

The GLC-mass spectrometric analyses of these crude reaction mixtures typically showed the presence of β- and γ-thiopyran (for **20**), 1-thio-2- and 1-thio-3-chromene (for **22**), and 2-thio-3-chromene (for **23**), though the ^{1}H NMR spectra of the reaction mixtures themselves did not indicate the presence of these compounds. Thus, they may be attributable to pyrolysis during GLC analysis. These products occurred only when a salt to lithium reagent ratio of 1:1 was employed.

Bulb-to-bulb distillations were carried out on the crude reaction mixtures [80° (5 × 10^{-6} mm), 4-6 days], the progress of which was monitored by examination of the ^{1}H NMR spectra of the pot residues. The distillates contained the same materials previously indicated by GLC analysis, with the exception of the olefin products discussed above. The residues were orange-brown solids, whose ^{1}H NMR spectra were remarkably similar to those of the "stable thiabenzenes".[5,6,29] GLC analysis of these residues did show the presence of the olefin products discussed above. It is therefore likely that these products arise by pyrolysis of the nonvolatile materials.

1-*p*-Tolyl-2-thio-3-chromene. Thianaphthalenium salt **23** (4.0 g, 16 mmol) was added portionwise to an excess of *p*-tolylmagnesium bromide (freshly prepared in ether) under a dry nitrogen atmosphere with stirring. The reaction mixture was then refluxed for 0.5 hr, cooled, and quenched with an ice-cold saturated, aqueous NH_4Cl solution. The organic layer was separated, washed with water, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give a brown oil. Kugelrohr distillation [130-135° (0.05 mm)] gave a yellow oil which slowly crystallized to give a waxy solid, 1-*p*-tolyl-2-thio-3-chromene (2.8 g, 74%), mp 52-58°. The ^{1}H NMR spectrum of this sulfide featured absorptions at $\delta_{C_6D_6}$ 2.07 (s, 3 H, CH_3), 5.04 (br s, 1 H, CH), 6.11 and 6.54 (AB q, 2 H, *J* = 9 Hz, vinylic H), 6.7-7.3 (m, 4 H, aromatic H) (all signals are referenced to the center of the ethyl ether triplet δ 1.12). Mass spectrum (60° inlet): *m/e* (rel intensity, %) 240 (10, P + 2), 239 (27, P + 1), 238 (100, P), 237 (40), 233 (16), 221 (16), 205 (25), 149 (10), 148 (20), 147 (28), and 146 (10).

4-*p*-Tolyl-1-thio-2-chromene and 2-*p*-Tolyl-1-thio-3-chromene. Thianaphthalenium salt **22** (1.0 g, 4.1 mmol) was added to an excess of *p*-tolylmagnesium bromide in anhydrous ether under a dry nitrogen atmosphere. The reaction mixture was refluxed for 1 hr and quenched with an ice-cold aqueous NH_4Cl solution. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to give a brown oil. Kugelrohr distillation [130-135° (0.05 mm)] gave a tan oil (0.61 g). The ^{1}H NMR spectrum of this product was consistent with an approximately 1:1 mixture of the desired sulfides and featured absorptions at $\delta_{C_6D_6}$ 2.05 (s, 3 H, CH_3), 2.10 (s, 3 H, CH_3), 4.45 (d, 1 H, *J* = 5 Hz, CH), 4.69 (dd, 1 H, *J* = 5, *J* = 1 Hz, CH), 5.78 (dd, *J* = 10 Hz, *J* = 5 Hz, vinylic H),[117] 5.84 (dd, *J* = 10, *J* = 5 Hz, vinylic H),[117] 6.19 (d, 1 H, *J* = 10 Hz, vinylic H), 6.42 (dd, 1 H, *J* = 10, *J* = 1 Hz, vinylic H), 6.7-7.4 (m, 16 H, aromatic H) (all signals are referenced to the center of the ethyl ether triplet at δ 1.12). Mass spectrum (100° inlet): *m/e* (rel intensity, %) 240 (8, P + 2), 239 (22, P + 1), 238 (100, P), 237 (62), 223 (27), 221 (16), 148 (11), and 147 (83).

2-Thianaphthalenium-*1,3,4*-d_3 Perchlorate (28). Following the general method of Price et al.[6] for the synthesis of **23**, 2-thiochroman-4-one[6] (in benzene) was treated with NaOD-D_2O to furnish 2-thiochroman-4-one-*3,3*-d_2. The ketone (10.6 g, 64 mmol) was reduced with $LiAlD_4$ (2.7 g, 64 mmol) in anhydrous ether to give, after the usual reaction work-up, crude 2-thiochroman-4-ol-*3,3,4*-d_3. This alcohol was dehydrated with potassium pyrosulfate (10 g) to give the crude olefin, which on Kugelrohr distillation [65-75° (0.01 mm)] gave 2-thio-3-chromene-*3,4*-d_2 (6.4 g, 67%), mp 35-36°. The olefin was dissolved in acetonitrile and treated with trityl perchlorate[96] to give 2-thianaphthalenium-*3,4*-d_2 perchlorate (7.9 g, 72%), mp 189-191° dec. Reduction of this salt with $LiAlD_4$ followed by hydride abstraction with trityl perchlorate gave ca. 70% deuterium incorporation in the 1 position. This cycle was repeated three times to give **28** (2.9 g, 18% from the ketone), mp 188-190° dec. Reduction of a sample of **28** with $LiAlD_4$ gave 2-thio-3-chromene-*1,1,3,4*-d_4. The ^{1}H NMR spectrum of this sulfide assured that **28** had ca. 95% deuterium incorporation in the 1, 3, and 4 positions.

2-Thianaphthalenium-*1*-d_1 Perchlorate (29). This salt was prepared in a manner similar to that employed for the synthesis of **28** by reduction of **23** (3.4 g, 13 mmol) with $LiAlD_4$ (1.0 g, 24 mmol) followed by hydride abstraction with trityl perchlorate.[96] This cycle was repeated three times to give **29** (1.4 g, 43%), mp 189-190°. Reduction of a sample of **29** with $LiAlD_4$ gave 2-thio-3-chromene-*1,1*-d_2 which had ca. 95% deuterium incorporation at the 1 position as determined by ^{1}H NMR spectroscopy.

1-Phenyl-2-thio-3-chromene. This sulfide was prepared using the method of Price and Follweiler[7,48] by the addition of phenylmagnesium chloride to **23**. The crude product was Kugelrohr distilled to give an amber oil, bp 130-134° (0.13 mm) [lit.[7] bp 132-133° (0.15 mm)]. The ^{1}H NMR spectrum of this sulfide featured absorptions at δ 7.53-7.03 (m, 9 H, aromatic H), 6.78 and 6.36 (AB q, 2 H, *J* = 9 Hz, vinylic H), and 5.20 (br s, 1 H, 1-H).

1-Phenyl-2-thianaphthalenium Perchlorate (30). This salt was prepared as previously described[7,48] by the addition of sulfuryl chloride to 1-phenyl-2-thio-3-chromene (1.2 g, 5.4 mmol) at low temperature in ether. Treatment of the solid obtained in this reaction with 70% aqueous perchloric acid in ether gave the crude salt which was recrystallized from acetonitrile-ether to give **30** (1.2 g, 69%), mp 185-186° (lit.[7] mp 184-185°). The ^{1}H NMR spectrum of **30** featured absorptions at δ_{CH_3CN} (Me_4Si) 8.82 and 8.74 (AB q, 2 H, *J* = 9.5 Hz, 3,4-H), 8.22-7.57 (m, 4 H, aromatic H), 7.37 (m, 5 H, aromatic H).

3,5-Diphenylthiopyrylium Perchlorate (31). 2*H*-3,5-Diphenylthiopyran (1.0 g, 4.0 mmol) was dissolved in acetonitrile (50 ml), and trityl perchlorate[96] (1.35 g, 3.9 mmol) was added. The reaction mixture was warmed on a steam bath for 5 min and then cooled in an ice bath. Slow addition of ether (ca. 150 ml) precipitated a yellow crystalline solid which was filtered, washed with ether, and air dried to give **31** (1.09 g, 78%), mp 180-182°.

Attempted Generation of 5b from 31 and Methyllithium. A suspension of **31** (42 mg, 0.12 mmol) in anhydrous benzene-d_6 (0.3 ml), contained in an NMR tube under a dry nitrogen atmosphere, was treated with methyllithium (0.12 mmol, 2.2 *M* solution in ether) to give an orange mixture. The ^{1}H NMR spectrum (ca. 38°) of the clear orange supernate, obtained after centrifugation, did not feature any absorptions that could be assigned to **5b**; rather, the spectral features consisted of a broad, unresolved aromatic resonance (δ 6.6-7.8) in addition to signals due to ether. A similar result was obtained when phenyllithium was used.

1-Phenyl-2-methyl-2-thiochromenium Tetrafluoroborate (32a). Using the procedure of Young and Lazarus,[52] 1-phenyl-2-thio-3-chromene (1.0 g, 4.5 mmol) was dissolved in a mixture of dichloromethane (25 ml), nitromethane (10 ml), and methyl iodide (5 ml). Silver tetrafluoroborate (0.85 g, 4.3 mmol) was dissolved in a minimum amount of acetonitrile, and the solution was diluted with nitromethane (15 ml). The two solutions were combined and stirred for ca. 12 hr while protected from light. The mixture was filtered (Celite filter aid) to give a clear filtrate which was diluted with ether (600 ml) to precipitate a grey solid. This solid was dissolved in acetonitrile, and the solution was boiled with activated charcoal. Filtration gave a clear solution which on slow dilution with ether gave **32a** (1.0 g, 68%), mp 181–182° dec. The ^{1}H NMR spectrum of **32a** featured absorptions at $\delta_{\mathrm{Me_2SO}\text{-}d_6}$ (Me_4Si) 3.01 (s, 3 H, S–CH_3), 6.45 (s, 1 H, 1-H), 6.57 (d, 1 H, J = 9 Hz, 3-H), 7.05–7.95 (m, 9 H, aromatic H), 7.97 (d, 1 H, J = 9 Hz, 4-H).

Anal. Calcd for $C_{16}H_{15}SF_4B$: C, 58.92; H, 4.64; S, 9.83. Found: C, 58.77; H, 4.80; S, 10.05.

1-(*o*-Isopropylphenyl)-2-methyl-2-thiochromenium Tetrafluoroborate (32b). Powdered **23** (3.09 g, 12.5 mmol) was suspended in anhydrous ether (25 ml) under a dry nitrogen atmosphere, and freshly prepared *o*-isopropylphenylmagnesium bromide (25 mmol, ether) was added in small portions. After the addition was complete, the yellow reaction mixture was stirred for 1 hr and hydrolyzed with a saturated aqueous NH_4Cl solution. The organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give a tan solid. Two recrystallizations from heptane gave 1-(*o*-isopropylphenyl)-2-thio-3-chromene (1.72 g, 52%), mp 104–107°. The ^{1}H NMR spectrum of this sulfide featured absorptions at δ 1.22 [d, 3 H, J = 6.5 Hz, $CH(CH_3)_2$], 1.28 [d, 3 H, J = 6.5 Hz, $CH(CH_3)_2$], 3.26 [m, 1 H, $CH(CH_3)_2$], 5.70 (s, 1 H, 1-H), 6.38 and 6.75 (AB q, 2 H, J = 10 Hz, 3,4-H), 7.0–7.5 (m, 8 H, aromatic H). This vinyl sulfide (266 mg, 1 mmol) was methylated with $AgBF_4$ (196 mg, 1 mmol) and methyl iodide (5 ml) using the procedure described for the synthesis of **32a**.[52] The crude salt was recrystallized twice from acetonitrile–ether to give **32b** (289 mg, 78%) as colorless needles, mp 162–163° dec. The ^{1}H NMR spectrum of **32b** featured absorptions at $\delta_{\mathrm{Me_2SO}\text{-}d_6}$ (Me_4Si) 1.36 [d, 3 H, J = 6.5 Hz, $CH(CH_3)_2$], 1.39 [d, 3 H, J = 6.5 Hz, $CH(CH_3)_2$], 3.10 (s, 3 H, S–CH_3), 3.65 [m, 1 H, $CH(CH_3)_2$], 6.65 (d, 1 H, J = 9 Hz, 3-H), 6.78 (br s, 1 H, 1-H), 7.0–7.9 (m, 8 H, aromatic H), 8.02 (d, 1 H, J = 9 Hz, 4-H).

Anal. Calcd for $C_{19}H_{21}SF_4B$: C, 61.97; H, 5.75; S, 20.64. Found: C, 62.25; H, 5.67; S, 21.35.

1-Pentafluorophenyl-2-methyl-2-thiochromenium Tetrafluoroborate (32c). Addition of freshly prepared pentafluorophenylmagnesium bromide[99] (62 mmol) in ether to a stirred suspension of **23** (5.0 g, 20 mmol) in anhydrous ether furnished a brown oil, after reaction work-up in the manner described above. Kugelrohr distillation [145–155° (0.15 mm)] gave a yellow oil which crystallized on standing. Recrystallization from hexane at −78° gave 1-pentafluorophenyl-2-thio-3-chromene (2.88 g, 46%) as yellow needles, mp 65–67°. The ^{1}H NMR spectrum of this sulfide featured absorptions at δ 5.91 (br s, 1 H, 1-H), 6.42 and 6.74 (AB q, 2 H, J = 10 Hz, 3,4-H), 6.7–7.5 (m, 4 H, aromatic H). Mass spectrum: *m/e* (rel intensity, %) 315 (11, P + 1), 314 (48, P), 313 (13), 293 (9), 148 (15), and 147 (100). Methylation of this sulfide (1.0 g, 3.2 mmol) was accomplished with $AgBF_4$ (0.62 g, 3.1 mmol) and methyl iodide (5 ml) using the method employed in the synthesis of **32a**.[52] The crude salt was recrystallized from acetonitrile–ether to give **32c** (60), mp 166–168° dec. The ^{1}H NMR spectrum of this product featured absorptions at δ_{CD_3CN} 3.08 (s, 3 H, S–CH_3), 6.63 (br s, 1 H, 1-H), 6.65 (d, 1 H, J = 9 Hz, 3-H), 7.30–7.75 (m, 4 H, aromatic H), 7.80 (d, 1 H, J = 9 Hz, 4-H) (all signals are referenced to the center of the CHD_2CN multiplet at δ 1.96).

Anal. Calcd for $C_{16}H_{10}SF_9B$: C, 46.18; H, 2.42; S, 7.71; F, 41.09. Found: C, 46.24; H, 2.55; S, 7.94; F, 41.31.

2-Methyl-2-thiochromenium Tetrafluoroborate (32d). 2-Thio-3-chromene[6] (1.0 g, 6.8 mmol) was methylated by the same method employed in the synthesis of **32a** with $AgBF_4$ (1.3 g, 6.5 mmol) and methyl iodide (5 ml).[52] Recrystallization from acetonitrile–ether gave **32d** (350 mg, 20%), mp 95–96°. The ^{1}H NMR spectrum of this product featured absorptions at δ_{CD_3CN} (Me_4Si) 2.68 (s, 3 H, S–CH_3), 4.60 (m, 2 H, 1-H), 6.57 (m, 1 H, 3-H), 7.6 (m, 4 H, aromatic H), 7.72 (d, 1 H, J = 10 Hz, 4-H).

Anal. Calcd for $C_{10}H_{11}SF_4B$: C, 48.03; H, 4.43; S, 12.82; F, 30.39; B, 4.32. Found: C, 48.25; H, 4.63; S, 13.07; F, 30.29; B, 4.46.

Generation of 1-Phenyl-2-methyl-2-thianaphthalene (33a) by Deprotonation of 32a. The procedure used was basically the same as that employed in the generation of **4b** from **4a**. The major modification was the use of a toluene-d_8–benzene-d_6 (2:1) solvent system to permit the deprotonation reaction to be carried out below ca. −20°. The purple reaction mixture was centrifuged, and the ^{1}H NMR spectrum (−35°) of the clear purple supernate featured the absorptions recorded in Table III.[93b]

As the solution was allowed to warm to ca. 40°, the signals due to **33a** disappeared, and those of **34** grew in.[67,93b] These spectral changes were accompanied by a color change from bright purple to pale red-brown. GLC analysis of the rearrangement mixture (5 ft × 0.25 in. 10% OV-1 on Chromosorb W), with thioxanthene added as an internal standard, revealed that 40 ± 3% of **34** was present in addition to ca. 5% 1-phenyl-2-thio-3-chromene (detector-response factors were determined with authentic compounds). The above rearrangement was examined several times, and the yield of **34** was consistently in the range of 40–50%, based on the initial amount of **32a** employed.

Reprotonation of **33a** could be accomplished by addition of fluoroboric acid (48%, ca. 1 mol equiv) to a solution of **33a** freshly generated at ca. 15° in dimethyl-d_6 sulfoxide. Immediately on addition of the acid, the color was discharged, and the ^{1}H NMR spectrum of the slightly yellow solution featured signals assignable to **32a**.

Generation of 1-(*o*-Isopropylphenyl)-2-methyl-2-thianaphthalene (33b) by Deprotonation of 32b. The procedure used for this deprotonation experiment was modeled on that described for the generation of **4b**. The solvent mixture of toluene-d_8–benzene-d_6 was chosen to allow the deprotonation to be carried out at a low temperature (ca. 0°). The deeply purple reaction mixture was centrifuged, and the ^{1}H NMR spectrum (5°) featured the absorptions recorded in Table III. Reprotonation of **33c** was accomplished by the addition of fluoroboric acid (48%) to a freshly generated solution of **33b** in dimethyl-d_6 sulfoxide. The color was immediately discharged, and the ^{1}H NMR spectrum of the slightly yellow solution featured absorptions assignable to **32b**.

Generation of 1-Pentafluorophenyl-2-methyl-2-thianaphthalene (33c) by Deprotonation of 32c. Following the procedure described for the deprotonation of **4a**, **32c** was deprotonated in benzene-d_6 to give a wine-red solution of **33c**. The ^{1}H NMR spectrum (40°) of the clear red supernate obtained after centrifugation featured the absorptions recorded in Table III.[93b] Addition of 1.0 mol equiv of *d*-camphorsulfonic acid to a freshly prepared solution of crystalline **33c** resulted in the immediate decolorization of the sample. Dilution of this solution with ether gave a solid whose ^{1}H NMR spectrum featured signals assignable to **32c** (camphorsulfonate salt).

The thermal stability of **33c** permitted its isolation and characterization as a crystalline solid. The thiochromenium salt **32c** (303.9 mg, 0.74 mmol) and freshly prepared $NaOCH_3$ (47.5 mg, 0.88 mmol) were weighed into a dry centrifuge tube, and anhydrous benzene (4 ml) was added (all solvents were nitrogen purged). The tube was purged with a stream of dry nitrogen and sealed with a rubber septum cap. The mixture was frozen in an acetone–Dry Ice bath, and methanol (0.5 ml) was added. The reaction was initiated by allowing the mixture to warm to ca. 10° with vigorous shaking. Anhydrous benzene (6 ml) was added, the resulting red reaction mixture was centrifuged, and the clear red supernate was transferred by syringe to a dry, nitrogen filled Schlenk flask. The solvent was removed under reduced pressure leaving a red powder which was dissolved in anhydrous dichloromethane (0.5–1.0 ml). This solution was diluted with hexane (20 ml) and seeded with a small amount of the initially formed red powder. Solvent was slowly blown off under a stream of dry nitrogen with exclusion of light and crystals formed. When the solution volume had been reduced to ca. 1 ml, the nitrogen flow was stopped and the supernatant liquid transferred by syringe to a second flask. The crystals were washed two times with hexane and dried under vacuum (90 mg, 37%). Alternatively, the initially formed powder was dissolved in dichloromethane or chloroform (0.5–1.0 ml) and the solution diluted with isooctane (20–30 ml, degassed by bubbling a stream of dry nitrogen through the solvent). The red solution was placed in a refrigerator at ca. −20° (protected from light), and crystals formed. The red crystalline solid could be stored for extended periods of time under a dry nitrogen atmosphere in the dark at ca. 0°. This material had mp 107–108° dec (sealed tube), and its ^{1}H NMR spectrum was identical with that obtained for the initially generated solution.

Anal. Calcd for $C_{16}H_9SF_5$ (mol wt 328): C, 58.53; H, 2.76; S, 9.77; F, 28.93. Found [mol wt 353 (osmometry in benzene)]: C, 58.67; H, 3.33; S, 9.67; F, 28.91.

The mass spectrum (90° inlet) of **33c** exhibited peaks at *m/e* (rel intensity, %) 328 (11, P), 315 (11), 314 (34), 313 (100), 293 (19), and 147 (12). Exact mass (calcd, 328.0345): 328.0346. The uv absorption spectrum (Me$_2$SO, nitrogen atmosphere) had absorptions at λ_{max} (log ϵ) 480 nm (3.87), 350 (3.85) and 275 (4.25). No change in these values was detected over a period of 1 hr. The crystallinity of **33c** was confirmed by an X-ray powder diagram which exhibited sharp, well-defined bands.

Deprotonation of 32d. Following the procedure used in the deprotonation of **6e** to give **7e** at low temperature, **32d** was deprotonated with dimsyl-d_5-lithium in toluene-d_8-dimethoxyethane (80:20). The initially produced orange reaction mixture, containing some dark precipitate, was centrifuged at ca. −75° to give a clear orange supernate, whose ^{1}H NMR spectrum did not feature any signals that could be assigned to **33d**; the only clear feature in the spectrum was an AB quartet centered at δ 6.4 which is typical of 2-thio-3-chromene derivatives. The sample was warmed to room temperature, and a known amount of napththalene was added as an internal standard. GLC analysis (5 ft × 0.25 in. OV-1 column, 10% on Chromosorb W) showed that 10 ± 3% of **35** was formed in addition to ca. 1–2% of 2-thio-3-chromene. Detector-response factors were determined on authentic compounds. Product identification was accomplished by coinjection with known compounds and GLC–mass spectrometric analysis.

1-Methyl-1-thio-3-chromenium Tetrafluoroborate. 1-Thio-3-chromene[111b] (2.0 g, 13.5 mmol) was methylated with AgBF$_4$ (2.6 g, 13.0 mmol) and methyl iodide (5 ml) in a manner identical with that employed in the preparation of **32a**.[52] Recrystallization from acetonitrile-ether gave the desired salt (2.0 g, 61%), mp 91–92° dec. The ^{1}H NMR spectrum of this product featured absorptions at δ_{CD_3CN} (Me$_4$Si) 2.92 (s, 3 H, S-CH$_3$), 4.25 (m, 2 H, 2-H), 6.28 [m, 1 H, 3-H (?)], 7.08 [m, 1 H, 4-H (?)], and 7.4–8.0 (m, 4 H, aromatic H).

Anal. Calcd for $C_{10}H_{11}SF_4B$: C, 48.03; H, 4.43; S, 12.82; F, 30.39; B, 4.32. Found: C, 48.03; H, 4.56; S, 12.99; F, 30.61; B, 4.49.

Deprotonation of this salt under the same conditions used for the deprotonation of **32d** gave qualitatively similar results. Analysis of the warmed reaction mixture by GLC–mass spectrometry was consistent with the qualitative presence of 2-methyl-1-thio-3-chromene, 4-methyl-1-thio-2-chromene, and 1-thio-3-chromene, in addition to at least three other unidentified volatile products. Product identification was further established by coinjection with authentic compounds.

1-Methyl-2-thio-3-chromene (35). Methylmagnesium bromide (10 mmol, 2 *M* solution in tetrahydrofuran–benzene) was added to a stirred suspension of **23** (1.0 g, 4.1 mmol) in anhydrous ether under a dry nitrogen atmosphere. After 0.5 hr of stirring, the reaction mixture was quenched with a saturated aqueous NH$_4$Cl solution. The organic layer was separated, washed with water, dried over anhydrous MgSO$_4$, and evaporated under reduced pressure to give a yellow oil. Kugelrohr distillation [bp 85–95° (0.5 mm)] furnished **35** (0.6 g, 90%). The ^{1}H NMR spectrum of the product featured absorptions at δ 1.50 (s, 3 H, CH$_3$), 4.00 (m, 1 H, 1-H), 6.40 and 6.75 (AB q, 2 H, *J* = 9.5 Hz, 3,4-H), 7.0–7.5 (m, 4 H, aromatic H).

1-Methyl-1-phenyl-2-thio-3-chromene (34). Methylmagnesium bromide (10 mmol, 2 *M* solution in tetrahydrofuran–benzene) was added to a stirred suspension of **30** (0.3 g, 0.9 mmol) in anhydrous ether under a dry nitrogen atmosphere. The reaction mixture was stirred for 1 hr and hydrolyzed with an ice-cold saturated aqueous NH$_4$Cl solution. The organic layer was separated, washed with water, dried over anhydrous MgSO$_4$, and evaporated under reduced pressure to give a yellow oil. Kugelrohr distillation [115–120° (0.01 mm)] gave **34** (0.15 g, 70%) as a pale yellow oil. The ^{1}H NMR spectrum of the product featured absorptions at $\delta_{C_6D_6}$ (Me$_4$Si) 1.88 (s, 3 H, CH$_3$), 6.14 and 6.50 (AB q, 2 H, *J* = 10 Hz, 3,4-H), 6.8–7.7 (m, 9 H, aromatic H).

Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45. Found: C, 80.73; H, 6.14; S, 13.64.

General Procedure for Determination of the First Half-Lives of Thermal Decomposition for Diverse Thiabenzenes. Deprotonation. The sulfonium salt (ca. 10 μmol) was placed in a flask under a dry nitrogen atmosphere, protected from light and cooled in an ice bath. Benzene (0.5 ml) was added, followed by dimethyl sulfoxide (ca. 1.8 μl.). The reaction was initiated by addition of *n*-butyllithium (ca. 5.3 μl., 1.9 *M* solution in hexane) to the frozen mixture, followed by warming. This furnished a highly colored solution which was transferred by syringe (ca. 50–100 μl.) under dim light into a nitrogen-purged glove bag. The sample was prepared by addition of the thiabenzene solution to 5 ml of the desired degassed solvent. The cuvette was then filled and sealed with a glass stopper; the sample was protected from light during periods when measurements were not being recorded. The sample was kept at the specified temperature (±2°), and spectra were recorded at periodic time intervals.

Addition. The thiopyrylium perchlorate salt (10 μmol) was suspended in benzene (0.5 ml) under a dry nitrogen atmosphere, and phenyllithium (10 μmol, benzene-ether) or methyllithium (10 μmol, ether) was added. Following the above procedure, the desired sample was prepared, and spectral data were recorded.

The first half-lives thus obtained are recorded in Table IV.

Reaction of 9 with *p*-Dimethylaminophenyllithium. Generation of 1-(*p*-Dimethylaminophenyl)-2,4,6-triphenylthiabenzene. Powdered **9** (120 mg, 0.283 mmol) and purified *p*-dimethylaminophenyllithium[118] (36.2 mg, 0.285 mmol) were placed in an NMR tube under a dry nitrogen atmosphere, and the tube was sealed with a rubber septum cap. The tube was immersed in a liquid nitrogen bath, and anhydrous ether (0.5 ml) was added. The reaction was initiated by warming the mixture to ca. −50°, the temperature being maintained by mixing-cooling cycles. The purple mixture was centrifuged, and the clear supernate was transferred by syringe to another nitrogen-purged NMR tube capped with a rubber septum cap. A stream of dry nitrogen was used to evaporate most of the ether, and anhydrous benzene-d_6 (0.5 ml) was added to the residue. The ^{1}H NMR spectrum of the clear purple solution featured absorptions at δ 2.30 (s, N-CH$_3$ of thiabenzene), 2.55 (s, N-CH$_3$ of thiopyran), 6.15 [d, *J* = 9 Hz, aromatic H (*p*-dimethylaminophenyl group of thiabenzene)], 6.65 [d, *J* = 9 Hz, aromatic H (*p*-dimethylaminophenyl group of thiopyran)], 6.8–7.9 (m, aromatic H), 7.91 (s, 3,5-H of thiabenzene). The integrated areas of the aromatic and aliphatic regions were consistent with a mixture of thiabenzene and thiopyran. The ratio of thiabenzene to thiopyran was ca. 4:1 as estimated from the peak areas of the *N*-methyl singlets. Similar results were obtained by following the general procedure described above using other solvent systems and reaction temperatures (solvent, temperature, ratio of thiabenzene to thiopyran): benzene-d_6–ether, 0–5°, ca. 1:1; toluene-d_8–tetrahydrofuran-d_8, ca. −0°, ca. 1:1; tetrahydrofuran-d_8, ca. −50°. 1:5.

The thermal decomposition of the intially formed mixtures of thiabenzene–thiopyran was monitored by ^{1}H NMR spectroscopy. Cyclohexane was added to the reaction mixtures as an internal standard, the tubes were heated at ca. 78° (protected from light) and, at periodic intervals, the ^{1}H NMR spectra of the reaction mixtures were recorded. In each case, the signals assigned to the thiabenzene disappeared as the purple color faded; however, no change in intensity was observed for the *N*-methyl singlet assigned to the thiopyran, and no new, major, distinct *N*-methyl signal appeared. Instead, a broadly structured absorption gradually appeared in the *N*-methyl region (δ 2.2–2.7). The doublet at δ 6.65 was unchanged, and the aromatic region became broadened and poorly resolved. These observations do not support the reported[21] rearrangement.

Crossover Experiment. Finely powdered **6a** (38 mg, 0.1 mmol) and **6c** (87 mg, 0.2 mmol)[119] were placed in an NMR tube, and the materials were thoroughly mixed. Benzene-d_6 (0.4 ml) was added, and the tube was flushed with nitrogen, capped with a rubber septum, and cooled in an acetone–Dry Ice bath. Dimsyllithium was generated in the tube by introducing dimethyl sulfoxide (23 μl.) followed by purified phenyllithium (26.0 mg, 0.31 mmol), previously weighed into a tared, nitrogen-filled, cutoff NMR tube. The tube was removed from the bath, the Me$_2$SO and phenyllithium were allowed to react by selectively warming the top of the contents, and the mixture was shaken vigorously until the reaction began to occur. The temperature was controlled by cooling–mixing cycles. The deeply purple reaction mixture was then allowed to warm to room temperature where the color faded. When the color was discharged, the tube was centrifuged and the ^{1}H NMR spectrum of the mixture recorded. We observed signals for **7a** and **7c**, but no signals were evident for the crossover product **7b** (as determined by comparison with the spectra of authentic compounds). GLC analysis (5 ft × 0.25 in. 10% OV-1 on Chromosorb W), in which the absence of **7b** was verified by coinjection of authentic samples, provided further evidence that **7a** and **7c** were present, and crossover product **7b** was absent (ca. <3%), testifying to the predominant intramolecularity of this rearrangement. Tlc examination of the product mixture reinforced this result. The reaction was also carried out with a 1:1 molar ratio of **6a** to **6c**. An acetone solution of **6a** (0.1 mmol) and **6c** (0.1 mmol) was evaporated under reduced pressure to give a fused mixture of the salts. The dried salt mixture was suspended in anhydrous benzene (0.5 ml) under a dry nitrogen atmosphere. Treatment of this suspension with dimsyl sodium (0.2 mmol, 2.5 *M* solution in Me_2SO) gave a deeply purple reaction mixture that faded to pale red. TLC analysis indicated the presence of **7a** and **7c** and the absence of crossover product **7b**. GLC analysis (thioxanthene used as internal standard) revealed that **7a** was formed in 82 ± 3% yield, and that **7c** was formed in ca. 70–80% yield.

1-Isopropyl-2-thianaphthalenium Perchlorate (38). Isopropylmagnesium chloride (20 mmol, 3 *M* solution in tetrahydrofuran) was added to a stirred suspension of **23** (3.0 g, 11.1 mmol) in anhydrous ether under a dry nitrogen atmosphere. The salt disappeared, and the reaction mixture turned red-brown. After 0.5 hr, the mixture was cautiously quenched with a saturated aqueous NH_4Cl solution (15 ml). The red organic layer was separated, washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give a red-brown oil. Kugelrohr distillation [110° (0.3 mm)] gave a pale-yellow oil (1.75 g) which was shown to be an approximately 80:20 mixture of 1-isopropyl-2-thio-3-chromene and 2-thio-3-chromene. Fractional distillation (6-cm Vigreux) gave, after some forerun, an oil (1.13 g), bp 117–119° (5 mm), containing ca. 90% of the desired isopropyl compound. The oil (960 mg) was dissolved in acetonitrile (10 ml), and trityl perchlorate[96] (1.71 g, 5 mmol) was added. The reaction mixture was heated to reflux under a dry nitrogen atmosphere and then allowed to cool. Anhydrous ether was added until the mixture became cloudy and, on cooling to 0°, yellow needles were deposited (1.07 g). Recrystallization from acetonitrile–ether gave a first crop of straw-yellow needles (0.7 g), mp 126–127° dec. A second crop (190 mg) was also obtained. The ^{1}H NMR spectrum of **38** featured absorptions at δ_{CD_3CN} (Me_4Si) 1.74 [d, 6 H, J = 7 Hz, $CH(CH_3)_2$], 4.80 [septet, 1 H, J = 7 Hz, $CH(CH_3)_2$], 8.15–8.90 (m, 6 H, aromatic H).

Anal. Calcd for $C_{12}H_{13}O_4SCl$: C, 49.91; H, 4.54. Found: C, 49.11; H, 4.47.

Reaction of 38 with Phenyllithium. Generation of 1-Isopropyl-2-phenyl-2-thianaphthalene (39). Two methods of generation were used to prepare solutions of **39**. (A) Finely powdered **38** (35 mg, 0.121 mmol) was suspended in anhydrous benzene-d_6 in an NMR tube under a dry nitrogen atmosphere, and the tube was sealed with a rubber septum cap. The suspension was cooled in an ice-bath, and phenyllithium (0.121 mmol, 1.35 *M* solution in benzene; trace of ether also present) was added. The reaction was allowed to proceed with mixing–cooling cycles, assuring that the temperature was maintained below ca. 15°. The NMR tube was then centrifuged, and the ^{1}H NMR spectrum (37°) of the clear, deep-purple supernate featured absorptions at $\delta_{C_6D_6}$ (Me_4Si) 1.35 [d, J = 6.5 Hz, $CH(CH_3)_2$], 1.42 [d, J = 6.5 Hz, $CH(CH_3)_2$], 3.47 [m, $CH(CH_3)_2$], 4.98 (d, J = 8 Hz, 3-H), in addition to the signals due to the solvent system. Evaporation of this purple solution under reduced pressure discharged the purple color. (B) Finely powdered **38** (56 mg, 0.194 mmol) was combined with purified phenyllithium (16.3 mg, 0.195 mmol) in an NMR tube under a dry nitrogen atmosphere. (*Caution:* on one occasion this procedure resulted in a mild explosion.) The NMR tube was sealed with a rubber septum cap and then cooled in an ice bath. Benzene-d_6 (0.45 ml) was carefully added to the tube, and the reaction was allowed to proceed with mixing–cooling cycles. The purple reaction mixture was centrifuged, and the ^{1}H NMR spectrum (37°) of the clear supernate featured absorptions at $\delta_{C_6D_6}$ (Me_4Si) 1.35 [d, J = 6.5 Hz, $CH(CH_3)_2$], 1.42 [d, J = 6.5 Hz, $CH(CH_3)_2$], 3.48 [m, $CH(CH_3)_2$], 5.00 (d, J = 8 Hz, 3-H), 6.8–7.7 (m, aromatic H + 4-H).[93b] A sharp singlet in the aromatic region at ca. δ 7.2, assigned to benzene, indicated that some proton abstraction had occurred during the synthesis of **39**. On warming the sample to 60°, the purple color was discharged, and the ^{1}H NMR spectrum (60°) of the brown reaction mixture showed that the pair of doublets at ca. δ 1.37 and the doublet at δ 5.00 were absent; decomposition of the sample was indicated by a broadly structured, uninterpretable multiplet in the upfield portion of the spectrum (δ 0.8–1.5).

Generation of Optically Active 33c. Dropwise addition of a solution of anhydrous brucine (11.0 mg, 0.028 mmol) in anhydrous dimethyl sulfoxide (2 ml) to a stirred solution of **32c** (20.8 mg, 0.05 mmol) in anhydrous dimethyl sulfoxide (3 ml) under a dry nitrogen atmosphere gave an orange solution. The electronic (isotropic) spectrum in the visible region for this solution (Figure 1) was identical with that for racemic **33c** prepared as described above. The CD spectrum was recorded from 600 to 400 nm, and a positive Cotton effect, centered around 480 nm (Figure 1), was observed. The uv and CD absorption maxima were monitored with time, and it was noted that the rate of decrease of intensity was coincident for the two observations. indicating that racemization was occurring *no faster* than decomposition (Figure 2). The rate of thermal decomposition was markedly faster for **33c** generated by deprotonation with brucine than for **33c** generated by deprotonation with dimsyl anion. It was also observed that **33c** in dimethyl sulfoxide, generated with dimsyl anion, underwent a similarly rapid thermal decomposition on addition of brucine hydrofluoroborate.[120] Thus the initially generated optically active **33c** (generated by brucine deprotonation in dimethyl sulfoxide) was stabilized by addition of anhydrous $NaOCH_3$, furnishing solutions with stability comparable to those generated by dimsyl anion deprotonation. The uv and CD spectra of such a stabilized solution were monitored for 200 min with no detectable loss of intensity of the uv absorption or loss of optical activity within the limits of experimental detection (see text).

In a control experiment, **33c**, generated by dimsyl anion deprotonation (Me_2SO), was treated with 2.5 mol equiv of brucine. The previously observed positive Cotton effect was not in evidence.

1-Phenyl-1-isopropyl-2-thio-3-chromene (40). Powdered **30** (323 mg, 1.0 mmol) was suspended in anhydrous ether (10 ml) under a dry nitrogen atmosphere, and isopropylmagnesium chloride (3.0 mmol, solution in ether) was added dropwise with stirring. The salt dissolved after ca. 15 min, and the reaction was quenched with aqueous NH_4Cl. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to give a residue that was a mixture of **40** and suspected 1-phenyl-2-thio-3-chromene (as determined by NMR and GLC). The mixture was chromatographed on a thick-layer silica gel plate (PQ4F 1000, Quantum Laboratories) using two hexane developments. The uv-absorbing band was divided into six fractions, and each fraction was extracted with chloroform. It was found that the faster moving fractions were enriched in the desired product. Fraction 2 crystallized and was used to seed fraction 3 (55 mg). Two recrystallizations from 90% aqueous methanol gave **40** as colorless prisms, mp 86–87.5°. The ^{1}H NMR spectrum of this product featured absorptions at δ 0.92 [d, 2.7 H, J = 7 Hz, $CH(CH_3)_2$], 1.25 [d, 2.7 H, J = 7 Hz, $CH(CH_3)_2$], 2.76 [septet, 0.9 H, J = 7 Hz, $CH(CH_3)_2$], 6.23 (m, 1.8 H, vinylic H), 6.8–7.5 (m, 9 H, aromatic H). The mass spectrum [*m/e* (rel intensity, %) 266 (5, P), 224 (22), 223 (100)] is characterized by the ready loss of an *m/e* 43 fragment (C_3H_7) from the molecular ion, as expected. Exact mass (calcd for P − 43, 223.052621) 223.052777.

Generation of Thiabenzenes in a Mass Spectrometer by Deprotonation. Mass Spectra of Thiabenzenes. The appropriate sulfonium salt was pulverized and mixed well with ground anhydrous sodium hydroxide. This powdered mixture was placed on the probe insert of the mass spectrometer, and heating the sample to ca. 70° produced sufficient thiabenzene to obtain a spectrum. This method was checked by noting that the mass spectrum obtained for **33c** generated in the above manner corresponded well with that obtained for pure, crystalline **33c**. The data obtained by this method are recorded below.

33c (70° inlet): *m/e* (rel intensity, %) 328 (6, P), 315 (9), 314

(35), 313 (60), 293 (20), 148 (11), 147 (100), 122 (11), and 121 (10).

4b (110° inlet): *m/e* (rel intensity, %) 301 (16, P + 1), 300 (34, P), 223 (12), 218 (10), 207 (34), 193 (10), 192 (48), 191 (100), 189 (23), 178 (10), 165 (12), 110 (22), 109 (18), 78 (11), 77 (14), 65 (13), and 51 (12).

5b (70° inlet): *m/e* (rel intensity, %) 264 (33, P), 250 (27), 249 (100), 218 (17), 217 (14), 215 (11), 115 (10), 100 (10), 68 (18), 57 (18), and 55 (11).

33a (80° inlet): *m/e* (rel intensity, %) 239 (12, P + 1), 238 (57, P), 225 (13), 224 (44), 223 (100), 221 (17), 208 (10), 207 (43), 189 (10), 178 (15), 161 (56), 147 (35), 128 (11), 115 (10), 111 (10), 89 (10), 78 (16), and 51 (10).

References and Notes

(1) This work was supported by the National Science Foundation (MPS74-18161).

(2) (a) Portions of this work have appeared in preliminary form: G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 5648 (1974); J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *ibid.*, **96**, 5650 (1974); B. E. Maryanoff, G. H. Senkler, Jr., J. Stackhouse, and K. Mislow, *ibid.*, **96**, 5651 (1974). (b) The interested reader is also directed to an account of this work presented at the VIth International Symposium on Organic Sulfur Chemistry, Bangor, Wales, July 1974 (G. H. Senkler, Jr., B. E. Maryanoff, J. Stackhouse, J. D. Andose, and K. Mislow in "Organic Sulphur Chemistry—Structure, Mechanism and Synthesis", C. J. M. Stirling, Ed., Butterworths, London, 1975).

(3) K. Mislow, *Trans, N.Y. Acad. Sci.*, **35**, 227 (1973).

(4) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6507 (1971).

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

(6) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Am. Chem. Soc.*, **85**, 2278 (1963).

(7) C. C. Price and D. H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).

(8) (a) C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971); (b) C. C. Price, M. Siskin, and C. K. Miao, *ibid.*, **36**, 794 (1971).

(9) Throughout this paper, the term *thiabenzene* is used not only to describe the parent system but also as a generic term for the whole class of thiaarenes which include thiabenzenes, thianaphthalenes, thiaanthracenes, etc.

(10) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **84**, 2090 (1962).

(11) The method used for the synthesis of 2-methylthiopyrylium perchlorate [I. Degani and C. Vincenzi, *Boll. Sci. Fac. Chim. Ind. Bologna*, **25**, 51 (1967)] was adapted for the synthesis of **3a.**

(12) A. G. Hortmann and R. L. Harris, *J. Am. Chem. Soc.*, **92**, 1803 (1970).

(13) (a) M. Hori, T Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.*, **21**, 1692 (1973); (b) M. Hori, T. Kataoka, H. Shimizu, and C.-F. Hsü, *Chem. Lett.*, 391 (1973).

(14) K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, **35**, 706 (1970).

(15) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).

(16) A purple color was obtained when R = aryl, and an orange color when R = methyl. Intense colors have repeatedly been associated with the presence of thiabenzenes.[7,8,10,12]

(17) (a) The instability of 10-thiaanthracenes is also suggested by the recent work of Ternay and coworkers in which 9,9-dideuteriothioxanthene was dissolved in an HF–SbF$_5$–SO$_2$ mixture at −50° to give the S-protonated species with no evidence of proton exchange at the 9 position. In a related observation, it was noted that thioxanthen-9-ol 10-oxide dehydrates in 96% H$_2$SO$_4$ with no evidence for the formation of 9,10-dihydroxy-10-thiaanthracene. See: A. L. Ternay, Jr., D. Deavenport, and S. A. Evans, Abstracts of the VIth Symposium on Organic Sulfur Chemistry, Bangor, Wales, 1974; D. W. Chasar, A. L. Ternay, Jr., L. Hughes, and H. J. Shine, submitted for publication. We thank Professor Ternay for bringing this work to our attention. (b) This has now been put on a quantitative basis. For example, we find that 10-phenyl-10-thiaanthracene rearranges in Me$_2$SO at 25° to 9-phenylthioxanthene with a half-life of 50 ± 14 sec (W. D. Hounshell and W. J. Richter, unpublished results). See also ref 37.

(18) A. W. Johnson, "Ylid Chemistry", Academic Press, New York, N.Y., 1966, pp 354–356; D. H. Reid in "Organic Compounds of Sulfur, Selenium, and Tellurium", Vol. 1, The Chemical Society, London, 1970, pp 309–312; Vol. 2, pp 341–344; P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971, pp 127–128; W. G. Salmond, *Q. Rev., Chem. Soc.*, **22**, 253 (1968).

(19) (a) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); (b) *ibid.*, **84**, 2094 (1962).

(20) The reported elemental analysis was adjusted to include an otherwise unverified 0.5 mol equiv of ethyl ether.

(21) C. C. Price and H. Pirelahi, *J. Org. Chem.*, **37**, 1718 (1972).

(22) G. Suld, Ph.D. Thesis, University of Pennsylvania, 1960.

(23) The ^{1}H NMR spectrum (CCl$_4$) of the isolated purple material had been described[6] as ". . . a single sharp band at 2.66 τ".

(24) Inspection of the reaction mixtures immediately after combining the reagents was expected to offer the best opportunity for detecting the products formed directly (in situ); in this way, products derived from secondary reactions (heat, air, or light induced) would be held to a minimum.

(25) For a detailed description, see the Experimental Section.

(26) Our original reason for wanting to prepare **14c** derived from the problem of pyramidal inversion; we had hoped to employ the isopropyl groups of **14c** as a DNMR probe for the interconversion between C_s (pyramidal) and C_{2v} (planar) structures. However, this approach was foiled by our inability to prepare **14c** free of side products.

(27) Apparently, the signal for the other ring proton of **19b** is buried beneath the signal from **19a** at δ 5.86 (CCl$_4$): δ 5.88 (C$_6$D$_6$–Et$_2$O).

(28) The term "*stable thiabenzenes*" is used throughout this discussion to describe the red-brown amorphous solids that were characterized by Price and coworkers[5,6] as stable representatives of ". . . the new 'aromatic' thiabenzene ring system . . .".[6] These materials were ". . .all much more stable to heat, to light, and to oxygen [than **10**] . . .",[6] and ". . . could be boiled in acetic acid with no loss of color and no conversion to the isomeric thiopyran . . .".[6] Further, these substances ". . . proved very resistant to desulfurization (compared to thiopyrans studied earlier) but after extensive reflux, small yields [3–5%] of the expected products were obtained".[6]

(29) (a) M. Polk, Ph.D. Thesis, University of Pennsylvania, 1964; (b) M. Siskin, Ph.D. Thesis, University of Pennsylvania, 1968; (c) C. K. Miao, M.S. Thesis, University of Pennsylvania, 1967.

(30) The term *oligomeric* is used throughout this paper to emphasize the fact that these amorphous materials of undetermined structure and composition gave average molecular weights significantly greater than expected for the monomer (i.e., **2**, **8**, **24**, and **25**). However, *we distinctly do not mean to imply that a simple polymerization of monomeric thiabenzenes is necessarily responsible for the formation of the observed materials* (see discussion on the actual reactions that occur on addition of phenyllithium to **20–23**); our major point here is that these higher molecular weight substances are not thiabenzenes.

(31) The choice of the Rast method[5,29a] for determining molecular weights of unknown compounds is questionable in light of the substantial variation in the molal depression constant with concentration reported for camphor.[32]

(32) W. B. Meldrum, L. P. Saxer, and T. O. Jones, *J. Am. Chem. Soc.*, **65**, 2023 (1943).

(33) As will be demonstrated by the data reported in the section dealing with the thermal stability of thiabenzenes, all authentic thiabenzenes have distinct absorption maxima in the visible region.

(34) Differential thermal analyses on samples of material obtained on reaction of **21** and **23** with phenyllithium did not show any true melting behavior, although the material obtained from **21** did on occasion exhibit a decomposition exotherm at 105°, and the material obtained from **23** did show a glass transition temperature of 81°.[25]

(35) Peaks at *m/e* values higher than those expected for monomers were also observed for these materials in our hands.[25]

(36) (a) M. Hori and H. Fujimura, Japan Patent 70 20,905 [see *Chem. Abstr.*, **73**, 87796t (1970)]; M. Hori and T. Kataoka, *Kagaku* (*Kyoto*), **25**, 838 (1970), and references cited therein; M. Hori, M. Nozaki, and T. Kataoka, *Yakugaku Zasshi*, **94**, 466 (1974); see also ref 13a; (b) M. Hori, T. Kataoka, and H. Shimizu, *Chem. Lett.*, 1073 (1974).

(37) Most recently, Hori et al.[36b] obtained a product, mp 149° dec, from the reaction of phenyllithium with 9-phenylthioxanthene 10-oxide (10% yield) which they characterized as "9,10-diphenyl-10-thiaanthracene" and thus identified with the "stable brown powder", *mp 143–146°* (also described[8a] as "softening at 142–145° "), previously obtained[6] by reaction of phenyllithium with 9-phenylthioxanthylium perchlorate. On the basis of mass spectral measurements, Hori et al. concluded that this substance was monomeric. In point of fact, 9,10-diphenyl-10-thiaanthracene, like other 10-thiaanthracenes, is an extremely unstable compound which rearranges at 25° in Me$_2$SO to 9,9-diphenylthioxanthene, identified by comparison with authentic material[6] and isolated in better than 80% yield. The half-life for the rearrangement in Me$_2$SO is 10 ± 1 sec (W. D. Hounshell and W. J. Richter, unpublished results). We find that reaction of an excess of phenyllithium with 9-phenylthioxanthylium perchlorate under the previously described[6] conditions yields an amorphous solid whose properties are substantially identical with those reported[6,8a] for the "stable brown powder", except for solution (average) molecular weight [(calcd 350) found 757 by osmometry in benzene].[25] Since this substance "could be boiled in acetic acid with no loss of color and no conversion to the isomeric [thioxanthene]",[6] its properties are obviously inconsistent with those of authentic 9,10-diphenyl-10-thiaanthracene. With reference to the claim[36b] that this brown solid is monomeric, we note that the sample may contain occluded 9,9-diphenylthioxanthene. For the mass spectrum of this thioxanthene (70 eV), we find *m/e* (% rel intensity) 350 (44, M$^+$) and 273 (100), the latter peak being due to loss of phenyl. All other peaks are of relative intensity less that 5 or 10% for inlet temperatures of 75 or 200°, respectively. The same two peaks are also in evidence in the "brown powder".[8a] Alternatively, the 350 mass peak may correspond to a cleavage product if the "brown powder" is largely a dimer of 9,10-diphenyl-10-thiaanthracene, as suggested by the mass spectrum[8a] and solution molecular weight. Neither we nor the previous workers[8a] have observed an intense peak at *m/e* 213, the base peak reported[36b] for the "monomer". It is therefore interesting to note that the mass spectrum of a likely contaminant, 9-phenylthioxanthen-9-ol, has a base peak at *m/e* 213.

(38) (a) M. Hori, T. Kataoka, and C.-F. Hsü, *Chem. Pharm. Bull.*, **22**, 15 (1974); M. Hori, T. Kataoka, H. Shimizu, C.-F. Hsü, Y. Asahi, and E. Mizuta, *ibid.*, **22**, 32 (1974); (b) J. Stackhouse, G. H. Senkler, Jr., B. E. Maryanoff, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 7835 (1974).

(39) M. S. B. Munson, *J. Am. Chem. Soc.*, **87**, 5313 (1965), and references cited therein.

(40) The composition of each distillate, as determined by ^{1}H NMR spectroscopy, was the same as that previously noted for the volatile materials in each crude reaction mixture (Table II), indicative of neglible thermal decomposition during the distillation.[25]

(41) It should be noted that the reaction conditions employed are equivalent to or milder than those used by Price and coworkers.[5,6]

(42) Control experiments ruled out deuterium abstraction from the solvent.[25]

(43) (a) An accurate account of the relative site preference for abstraction is precluded by the anticipated H(D) kinetic isotope effect. (b) This scheme is necessarily nonexclusive of other reasonable processes, such as electron-transfer reactions, which might well be taking place but for which we have no direct evidence, and which are therefore not included in our discussion.

(44) J. A. Zoltewicz and R. E. Cross, *J. Chem. Soc., Perkin Trans. 2*, 1363, 1368 (1974), and references cited therein.

(45) (a) P. Haake and W. B. Miller, *J. Am. Chem. Soc.*, **85**, 4044 (1963), and references cited therein; (b) J. E. Baldwin and J. A. Walker, *ibid.*, **96**, 596 (1974), and references cited therein; (c) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem., Int. Ed. Engl.*, **4**, 435 (1965).

(46) Theoretical descriptions of systems in which a carbene is adjacent to sulfur (or nitrogen) atoms have been presented by H. C. Sorensen and L. L. Ingraham, *J. Heterocycl. Chem.*, **8**, 551 (1971). For examples of dithiocarbenes, see: J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 354 (1972); H. D. Hartzler, *J. Am. Chem. Soc.*, **92**, 1412 (1970).

(47) Decomposition of σ-sulfuranes into Ar_2S and Ar_2 has been reported; see: G. Wittig and H. Fritz, *Justus Liebigs Ann. Chem.*, **577**, 39 (1952); D. Harrington, J. Weston, J. Jacobus, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 1079 (1972); B. M. Trost and H. C. Arndt, *J. Am. Chem. Soc.*, **95**, 5288 (1973); B. K. Ackerman, K. K. Andersen, I. Karup-Nielsen, N. B. Peynircioglu, and S. A. Yeager, *J. Org. Chem.*, **39**, 964 (1974).

(48) D. M. Follweiler, Ph.D. Thesis, University of Pennsylvania, 1968.

(49) Additional support for these assignments is provided below in the discussion on thermal stability of thiabenzenes.

(50) R. L. Harris, Ph.D. Thesis, Washington University, 1970; see also ref 54.

(51) Simply substituted thiabenzenes are conspicuously unstable to heat, light, air, and acids. We have experienced that even momentary exposure of solutions to air strongly accelerates the rate of decomposition. (a) Note Added in Proof. The results presented in this paper also invalidate the recent claims for air-stable isolable 1- and 2-thianaphthalenes advanced by M. Hori *et al.*, *Chem. Pharm. Bull.*, **22**, 2485, 2752, 2754 (1974).

(52) T. E. Young and R. A. Lazarus, *J. Org. Chem.*, **33**, 3770 (1968). (a) Note Added in Proof. An upfield shift similar to that observed for the C-3 proton of 1-aryl-2-methyl-2-thianaphthalenes (Table III) has been reported for 1-cyano- and 1-benzoyl-2-methyl-2-thianaphthalene (M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, and A. Aoki, *Chem. Lett.*, 1101 (1974)).

(53) The reactivity toward aqueous HBF_4 precluded the regeneration of **32c** from **33c**. Reprotonation of **33c** could be achieved by the use of *d*-camphorsulfonic acid.

(54) The overall conversion of **32a** → **33a** → **34** occurs in ca. 40–50% yield with ca. 5% 1-phenyl-2-thio-3-chromene also being formed (yields determined by GLC). The synthesis of **33a** and its subsequent rearrangement have been the subject of an independent investigation: A. G. Hortmann, R. L. Harris, and J. A. Miles *J. Am. Chem. Soc.*, **96**, 6119 (1974). We thank Professor Hortmann for bringing this work to our attention prior to publication.

(55) Low temperature (−65°) deprotonation of 1-methyl-1-thio-3-chromenium tetrafluoroborate also generated products (2-methyl-1-thio-3-chromene, 4-methyl-1-thio-2-chromene, and 1-thio-3-chromene) indicative of the initial formation of 1-methyl-1-thianaphthalene, which evidently is also extremely unstable.

(56) Price and coworkers stated that "stable thiabenzenes" (e.g., **2**, **8**, **24**, and **25**) have electronic spectra that ". . . seem to resemble closely the analogous carbon aromatic systems, superimposed on a long 'tail' out into the visible which gives these compounds their color".[5] As we now know (see above), the compounds referred to are not the alleged thiabenzenes. In point of fact, every thiabenzene that we have studied displays a distinctive absorption band in the visible region; it is this which is responsible for their color.

(57) This contrast has been previously noted for **10** vs. **14f** by Suld and Price.[10]

(58) Price and coworkers[8a,21] reported that 1-(*p*-dimethylaminophenyl)-2,4,6-triphenylthiabenzene could be isolated in crystalline form. They further suggested that this thiabenzene readily underwent thermal and/or photochemical rearrangement to give a mixture of the isomeric thiopyrans [2-(*p*-dimethylaminophenyl)- and 4-(*p*-dimethylaminophenyl)-2,4,6-triphenylthiopyran (the 2 and 4 adduct, respectively)][21] with only the presence of the 4 adduct definitively demonstrated. A reexamination of this system using the NMR technique[25] has revealed that the addition of *p*-dimethylaminophenyllithium to **9** under a variety of reaction conditions produces a purple mixture featuring absorptions in the ^1H NMR that could reasonably be assigned to the thiabenzene and a thiopyran, presumably the **4** adduct, formed by direct attack on carbon (Scheme I, pathway c). Our observations made on this reaction mixture do not support the reported[21] rearrangement since no increase was observed in the intensity of the *N*-methyl signal because of the initially present thiopyran, and no *new*, major *N*-methyl signal appeared as the *N*-methyl signal for the thiabenzene disappeared. Thus, the reported[21] products which are derived from the 4 adduct, present in the thermal decomposition mixture, appear to arise from the initial formation of this thiopyran, and not from rearrangement. In light of these observations, the question remains open whether 1-(*p*-dimethylaminophenyl)-2,4,6-triphenylthiabenzene is stable enough to permit isolation as a crystalline solid. As an interesting aside, we have observed red-violet crystals on the walls of sealed tubes containing $CDCl_3$ solutions of **10**. Evidence for crystallinity of the particles rests on their ability to extinguish plane polarized light (microscopy).

(59) We would like to acknowledge the assistance of Professor R. Levin in obtaining the ^{13}C NMR spectra reported in this paper.

(60) R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Am. Chem. Soc.*, **95**, 926 (1973).

(61) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 5092 (1973); *ibid.*, **95**, 7736 (1973).

(62) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

(63) Yields of this isomer, the only product to be isolated, were in the range of 20–40%,[8a,19] inadequately accounting for the material balance. Although all genuine thiabenzenes that have been studied thus far readily suffer thermal decomposition, such decomposition is not always uniquely associated with rearrangement to thiopyrans. For example, in the thermal decomposition of **4b**, discussed previously, we have not discovered any evidence pointing to rearrangement, i.e., to formation of 1,1-diphenyl-2-thio-3-chromene. The specific factors which determine the course of thermal decomposition [i.e., rearrangement (as in **16**)], decomposition without rearrangement (as in **4b**), or a combination of these two pathways (as is apparently the case in **10**)] remains yet to be determined.

(64) The mixture of rearrangement products was examined by ^1H NMR spectroscopy, GLC, and TLC; these experimental techniques ensure that less than 3% of crossover product **7b** was present in this mixture. Subsequent rate studies (W. D. Hounshell, unpublished work) have revealed that rearrangement of 10-phenyl-10-thiaanthracene in Me_2SO at 25° proceeds 11 times as fast as that of 2-chloro-10-(2,5-xylyl)-10-thiaanthracene. However, on the assumption that the rates of random recombination of the fragments in an *intermolecular* process are the same, and that recombination is much faster than dissociation, 10.5% of each crossover product (e.g., **7b**) would still be formed, well above the threshold of detection. (a) Note Added in Proof. The intramolecularity of this rearrangement has been independently confirmed in a crossover experiment reported by M. Hori, T. Kataoka, and H. Shimizu, *Chem. Lett.*, 1117 (1974).

(65) Ample discussion has been provided dealing with a variety of mechanistic possibilities for analogous carbanionic rearrangements.[82,88]

(66) T. S. Stevens and W. E. Watts, "Selected Molecular Rearrangements", Van Nostrand, London, 1973, pp 82–83, 101–108; T. L. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry", Cambridge University Press, London, 1972, pp 238–240; R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1971, pp 114–132.

(67) In a preliminary experiment, we observed ^1H NMR emission and enhanced absorption in the rearrangement of **33a**. The origin of this CIDNP effect could not be assigned to rearrangement-product (**34**) polarization and may be attributable to scavenging reactions caused by radicals escaping from an intimate cage. Nevertheless, the observation implies that the rearrangement involves some radical-pair process and under the proper conditions[68] should be amenable to a CIDNP investigation.

(68) An extensive discussion of this topic has recently appeared: A. R. Lepley in "Chemically Induced Magnetic Polarization", A. R. Lepley and G. L. Closs, Ed., Wiley, New York, N.Y., 1973, pp 323–384.

(69) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

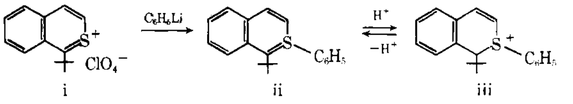
(70) W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *J. Chem. Soc., Chem. Commun.*, 654 (1973).

(71) J. A. Berson, *Acc. Chem. Res.*, **5**, 406 (1972); J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *ibid.*, **5**, 402 (1972).

(72) M. J. S. Dewar and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 1839 (1974).

(73) Another possible mechanism for the formation of these products from deprotonation of *S*-methyl substituted sulfonium salts (e.g., **6e**, **6f**, **32a**, and **32d**) is attack of base at the methyl group on sulfur to give the sulfonium methylide, which could then decompose to a carbene and the corresponding sulfide.

(74) Price and Follweiler[7,48] were able to generate purple solutions either by reaction of i with phenyllithium or phenylmagnesium bromide or by deprotonation of iii. These results may be taken as evidence for the in situ formation of ii. On the basis of a description of thiabenzenes as sulfonium ylides (see discussion on thermal stability above), we would predict that **25** should be no less stable than either **39** or ii. Yet, as we have previously discussed, **25** cannot be observed on the addition of phenyllithium to **23**, while thianaphthalenes are formed on addition of phenyllithium to **38** and i. In our discussion of the actual reactions that occur on addition of phenyllithium to **20**, **22**, and **23**, we emphasized that it is the accessibility of pathways leading to the destruction of initially formed thiabenzene which precludes the direct observation of thiabenzenes in these reactions, while, contrariwise, it is the inhibition of these pathways which permits the observation of thiabenzenes such as **39** and ii, even though their thermal stability would be expected to be less than that of **25**. The ^1H NMR spectrum of the solution of **39** (eq 13) did show that the product was not entirely free of contaminants, possibly because of some α-proton abstraction.



(75) Pyramidal sulfur is the only reasonable element of chirality in **39** on the NMR time scale of observation.

(76) This value derives from the observed diastereotopicity at 37° of 4.0 Hz (60 MHz). By assuming a coalescence temperature of 37°, an approx-

imate rate constant can be calculated using the Gutowsky–Holm equation,[77] which, on substitution into the Eyring equation (assuming a transmission coefficient of unity), gives the reported lower limit for the barrier to pyramidal inversion in **39**.

(77) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(78) Although two diastereomers (cis and trans) are possible for this compound, ^{1}H NMR spectroscopic evidence suggests that one predominates to the virtual exclusion of the other in recrystallized **32c**.

(79) By employing CD, it was possible to prevent interference from other optically active substances that do not have absorptions in the visible region.

(80) In a control experiment, racemic **33c** was generated by deprotonation with dimsyl anion. Addition of brucine did not yield the observed Cotton effect. Furthermore, racemic **33c** could be generated by deprotonation of **32c** with triethylamine in Me_2SO.

(81) By assuming that a 10% change in optical activity had occurred over the 200-min period of observation, a rate constant was estimated from which the lower limit was calculated from the Eyring equation (assuming a transmission coefficient of unity).

(82) A. Hochrainer and W. Silhan, *Monatsh. Chem.*, **97**, 1477 (1966); K. W. Ratts, *Tetrahedron Lett.*, 4707 (1966); H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, **23**, 4279 (1967); A. F. Cook and J. G. Moffatt, *J. Am. Chem. Soc.*, **90**, 740 (1968); B. M. Trost and R. F. Hammen, *ibid.*, **95**, 962 (1973).

(83) D. Darwish and R. L. Tomilson, *J. Am. Chem. Soc.*, **90**, 5938 (1968); see also S. J. Campbell and D. Darwish, *Can. J. Chem.*, **52**, 2953 (1974).

(84) W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6205 (1971); J. D. Andose, A. Rauk, and K. Mislow, *ibid.*, **96**, 6904 (1974).

(85) D. P. Craig and N. L. Paddock, *Nature (London)*, **181**, 1052 (1958); D. P. Craig in "Theoretical Organic Chemistry (Kekule Symposium)", Butterworths Press, London, 1959, p 20; D. P. Craig, M. L. Heffernan, R. Mason, and N. L. Paddock, *J. Chem. Soc.*, 1376 (1961); C. A. Coulson, *Nature (London)*, **221**, 1106 (1969).

(86) (a) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960); (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, pp 430–436.

(87) Preliminary calculations have been performed at the semiempirical (CNDO/2) level of approximation.[88] While a meaningful assessment of the bonding in thiabenzenes can be achieved only through high quality, nonempirical molecular orbital calculations, these results may provide some insight into this problem.[89] All calculations (both sp and spd basis sets) show sulfur as pyramidal with a substantial (40–60 kcal/mol) barrier to inversion.[4,88] They further show that the net atomic-charge distributions are consistent with an ylide-like bonding model, i.e., concentration of positive charge on sulfur with concomitant build-up of negative charge on the 2, 4, and 6 ring positions.

(88) J. D. Andose, unpublished results; see also ref 2b.

(89) Due to the minimal nature of the CNDO/2 basis set, this method overestimates the importance of d orbitals; see D. T. Clark, *Tetrahedron*, **24**, 2663 (1968); D. T. Clark and D. R. Armstrong, *Chem. Commun.*, 319 (1970).

(90) A. G. Hortmann, *J. Am. Chem. Soc.*, **87**, 4972 (1965); A. G. Hortmann and R. L. Harris, *ibid.*, **93**, 2471 (1971).

(91) The enhanced thermal stability of thiabenzene 1-oxides compared with thiabenzenes is analogous to the well-established thermal stability of dimethylsulfoxonium methylide as compared with dimethylsulfonium methylide.[92]

(92) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

(93) (a) Elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Differential thermal analyses were performed by DeBell and Richardson Testing Institute, Enfield, Conn. Unless otherwise noted, ^{1}H NMR spectra were recorded on a Varian A-60A spectrometer and refer to ca. 10% solutions in deuteriochloroform, with tetramethylsilane (Me_4Si) as an internal reference. Chemical shifts are reported in parts per million downfield from Me_4Si. Ultraviolet absorption spectra were recorded on a Cary 14 spectrometer (those of authentic thiabenzenes are collected in Table IV), infrared spectra were recorded on a Perkin-Elmer 237B spectrometer, and circular dichroism measurements were recorded on a Cary 6001 circular dichrograph. Mass spectra (peaks reported $\geq$10% rel intensity unless otherwise noted) were obtained on an AEI MS-9 high-resolution mass spectrometer at an ionizing potential of 70 eV unless otherwise indicated. GLC–mass spectral analyses were carried out on a Du Pont 21-490 mass spectrometer with an ionizing potential of 70 eV. Melting points were determined on a Thomas-Hoover apparatus and are corrected. (b) Full NMR and uv spectral displays of several key substances will be found in ref 2b, as indicated in the appropriate section below.

(94) M. Schlosser and V. Ladenberger, *J. Organomet. Chem.*, **8**, 193 (1967).

(95) P. J. C. Fierens, *Bull. Soc. Chim. Belg.*, **64**, 772 (1955).

(96) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(97) No attempt was made to maximize the yield from this reaction sequence.

(98) G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc. C*, 659 (1968).

(99) N. N. Vorozhtsov, Jr., V. A. Barkhash, N. G. Ivanova, S. A. Anichkina, and O. I. Andreevskaya, *Dokl. Akad. Nauk SSSR*, **159**, 125 (1964).

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(101) A. L. Ternay, Jr., L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 940 (1969).

(102) R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).

(103) R. Wizinger, S. Losinger, and P. Ulrich, *Helv. Chim. Acta*, **39**, 5 (1956).

(104) In a number of preparations, the product obtained was consistently contaminated with 5–15% starting material. Recrystallizations from glacial acetic acid or acetone–water were ineffective in purifying **9** and occasionally resulted in an enhancement of the pyrylium salt content. Although recrystallization from glacial acetic acid did not remove the pyrylium salt impurity, it did raise the mp to 215–215.5°. It was found that recrystallization from dichloromethane–pentane left mother liquors that on dilution with hexane gave crystalline solids which were enriched in the desired thiopyrylium salt. This method was chosen for the purification of **9** and other thiopyrylium salts.

(105) Prepared in a manner analogous to the method of C. R. Hauser, W. J. Humphlett, and M. J. Weiss, *J. Am. Chem. Soc.*, **70**, 426 (1948).

(106) W. Dilthey, *J. Prakt. Chem.*, **94**, 53 (1916).

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

(108) J. Strating, J. H. Keijer, E. Molenaar, and L. Brandsma, *Angew. Chem.*, **74**, 465 (1962). A detailed description of this procedure can be found in ref 29b.

(109) The uv spectrum reported here for **21** agrees well with the values reported by Young and Ohnmacht:[110] 278 (4.97), 380 (4.36), 485 (3.50), and 510 (3.42) nm. The log ϵ values do not agree with those reported by Price et al.:[8] 276 (3.76), 377 (3.21), 480 (1.39), and 506 nm (1.32).

(110) T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, **32**, 444 (1967).

(111) (a) W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959); (b) *Chem. Ind. (London)* 1192 (1960).

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

(113) A Mechrolab vapor-pressure osmometer (Model 301A) was employed[93a] in the determination of all the solution number average molecular weights reported in this paper. For a discussion of this method of molecular weight determination, see J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959); W. I. Higuchi, M. A. Schwartz, E. G. Ripple, and T. Higuchi, *J. Phys. Chem.*, **63**, 996 (1959); A. Wilson, L. Bini, and R. Hofstader, *Anal. Chem.*, **33**, 135 (1961). This method has given consistently reliable results (see, for example, the molecular weight determinations reported for **7a** and **33c**) and, in several cases, the identical sample of oligomeric material was submitted twice to ascertain the reproducibility of the determination. For these samples, the deviation between determinations was at most 6%. It should be noted further that the reactions in which oligomeric materials were formed were repeated several times and comparable results were obtained in each instance.

(114) It is important to note that the reported spectra[29a,b] for "**2**" also contain the broad absorption at ca. δ 6.2, although the low amplitude and low signal-to-noise ratio employed during the recording of these spectra may have caused this absorption to be overlooked.

(115) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Atlas of Mass Spectral Data", Vol. 2, Interscience, New York, N.Y., 1969, p 928.

(116) In one reaction series, water (100 μl., degassed) was added at this point to quench the reaction. A second NMR spectrum was then recorded.

(117) Total area of the absorptions at δ 5.78 and 5.84 is 2 H; separate integration is not possible because of superposition of the signals.

(118) The reagent was prepared as previously described [H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933)] from *p*-dimethylaminobromobenzene and lithium metal in anhydrous ether. The solution was evaporated under reduced pressure, and the resulting tan solid was warmed with hexane (dried over sodium) under a dry nitrogen atmosphere. The hexane was removed by syringe, and the process was repeated two times. The resulting tan solid was vacuum dried.

(119) In earlier experiments, it had been noted that the intense purple color initially generated on deprotonation of **6a** was discharged appreciably faster than that generated on deprotonation of **6c**, and 2 mol equiv of **6c** was thus used. Subsequent rate studies (see ref 64) have borne out this qualitative observation.

(120) E. Wilke-Dörfurt and G. Balz, *Chem. Ber.*, **60B**, 115 (1927).