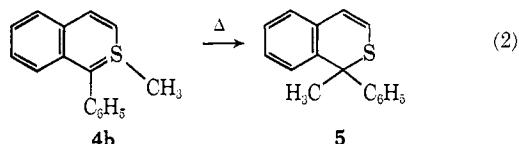


sistent with the structures **4a-d**. The marked upfield shift noted for the 3-protons, similar to that found for **2**,<sup>8</sup> is a characteristic of protons in the ortho positions of thiabenzenes. Addition of acid to the solution of **4a-d** at  $-25^\circ$  resulted in the regeneration of **3a-d**.

Solutions of **4a** (purple) and **4d** (red) could be warmed to *ca.*  $40^\circ$  with no observable change in color or nmr spectrum. However, when a solution of **4b** was allowed to warm to *ca.*  $40^\circ$ , its color changed from purple to light red, and the resulting nmr spectrum featured absorptions at  $\delta$  7.7–6.7 (m, 9 H, aromatic H), 6.30 (AB q,  $^3J_{\text{HH}} = 9.5$  Hz,  $\Delta\nu_{\text{AB}} = 20.4$  Hz, 2 H, olefinic H), 1.85 (s, 3 H,  $\text{CH}_3$ ). Identification of the product as 1-phenyl-1-methyl-2-thiochromene (**5**) was confirmed by an independent synthesis. The observed rearrangement (eq 2) is analogous to those found for **1**,<sup>7</sup>



1-methyl-2,4,6-triphenylthiabenzenesulfonium salt (**6**),<sup>13</sup> and 10-methyl-10-thiaanthracene,<sup>2,14</sup> and can be viewed as a formal extension of the Stevens rearrangement known to occur in sulfur ylides.<sup>15</sup> The deprotonation of **3e** differed from the others in that even at  $-65^\circ$  it was not possible to obtain a stable solution of **4e**. Analysis of the reaction mixture by glpc-mass spectroscopy permitted identification of the principal rearrangement products as 1-methyl-2-thiochromene and 2-thiochromene. This result indicates that **4e** is formed under the condition of the deprotonation but that it is an extremely unstable species.

The behavior noted on deprotonation of **3a-e** suggests that delocalization of charge is an important factor in determining the stability of thiabenzenes. To gain further information on this point, the visible spectra of the thiabenzenes in Table II were monitored under standard conditions as a function of time. The relative thermal stabilities of the thiabenzenes are reflected in the length of their first half-lives (*i.e.*, the time for 50% decomposition). The data show (a) that thiabenzenes are stabilized by *S*-phenyl substitution as compared to *S*-methyl substitution (*cf.* **1** vs. **6**; **4a** vs. **4b**),<sup>16</sup> (b) that particular stability results from substitution of a strongly electron withdrawing group (*e.g.*, pentafluorophenyl) on the thiabenzene skeleton (*cf.* **4d** vs. **4b**), and (c) that increased stability seems to go hand in hand with increasing solvent polarity (*cf.* entry for **4b**), a point that was previously mentioned by Hortmann and Harris in discussing the properties of **2**.<sup>8</sup>

The remarkable stability of **4d** has permitted the isolation and characterization of this thiabenzene as a pure orange-red crystalline solid (mp  $107$ – $108^\circ$ , dec). Elemental analysis, exact mass, solution molecular weight (osmometry in benzene), and nmr spectral data ( $^1\text{H}$  and  $^{13}\text{C}$ ) are all consistent with the assigned structure. The crystallinity of **4d** was confirmed by the X-ray powder pattern of the solid.

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

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

(15) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, 3646 (1969), and references cited therein.

(16) This has been previously noted for **1** and **6** by Suld and Price.<sup>13</sup>

Table II. Thermal Stability of Thiabenzenes

Compd ( $\lambda_{\text{max}}$ , nm)	Time (hr) for 50% decomposition <sup>a</sup> ( $^\circ\text{C}$ , solvent)
<b>1</b> (524) <sup>b</sup>	8.2 (22, benzene)
(521) <sup>b</sup>	3.5 (23, isooctane)
<b>6</b> (527) <sup>c</sup>	0.35 (21, benzene)
<b>2</b> (439) <sup>d,e</sup>	<i>ca.</i> 4 (22, benzene)
<b>4a</b> (518) <sup>d</sup>	3.9 (21, benzene)
(519) <sup>d</sup>	1.5 (23, isooctane)
<b>4b</b> (511) <sup>d</sup>	0.83 (27, dimethyl sulfoxide)
(519) <sup>d</sup>	0.39 (22, benzene)
(–) <sup>d,f</sup>	<0.1 (25, isooctane)
<b>4d</b> (485) <sup>d</sup>	65 (20, benzene)
(480) <sup>d</sup>	249 (23, dimethylsulfoxide)

<sup>a</sup> 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 only relative thermal stability. <sup>b</sup> Generated by addition of phenyllithium to 2,4,6-triphenylthiopyrylium perchlorate. <sup>c</sup> Generated by addition of  $\text{CH}_3\text{MgI}$  to 2,4,6-triphenylthiopyrylium perchlorate. <sup>d</sup> Generated by deprotonation of the sulfonium salt with dimsyl anion. <sup>e</sup> Value is approximate due to spectral interference by decomposition products. <sup>f</sup> Decomposition was too fast to allow monitoring of the solution by this method.

The foregoing observations furnish convincing evidence for the ylide-like nature of thiabenzenes.<sup>8</sup> Specifically, the factors which should stabilize sulfonium ylides should also stabilize thiabenzenes. This view is contrary to the one proposed by Price, *et al.*,<sup>6</sup> in which a continuous (*i.e.*, through-sulfur) delocalization of electrons, permitting a cyclic aromatic ring current, is declared responsible for stabilization in this class of compounds. However, while our experimental data support an ylide-like model, they provide no insight into the possible involvement of d orbital participation in the bonding of thiabenzenes.<sup>17</sup> Further discussion on this point is reserved for a subsequent, detailed paper.

(17) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 430–436, for a discussion of the possible role of d orbitals in thiabenzenes.

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### Thiabenzenes. III. Pyramidal Stability at Sulfur<sup>1</sup>

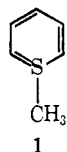
Sir:

In the course of our studies on pyramidal inversion,<sup>2</sup> we had occasion to calculate the barrier to inversion at sulfur in 1-methylthiabenzenes (**1**) by use of a specially parametrized semiempirical (CNDO/2) scheme.<sup>3</sup> Our conclusion, that **1** is pyramidal with a high barrier to inversion (42.5 kcal/mol), was in conflict with the view advanced by Price and coworkers that unhindered

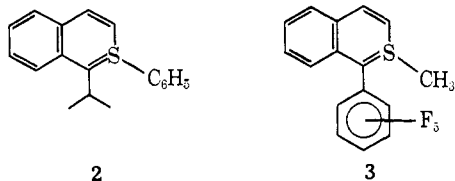
(1) This work was supported by the National Science Foundation (GP-30257).

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

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



thiabenzene should be planar or have a very low bending barrier at sulfur,<sup>4-7</sup> and with related Hückel calculations on 2-phenyl-2-thianaphthalene which predict a planar structure with a barrier to out-of-plane bending at the S-phenyl bond of less than 5.0 kcal/mol.<sup>8</sup> We now wish to report our finding that 2-thianaphthalenes **2** and **3** are in fact stably pyramidal at



sulfur, with *lower limits* for the barrier to pyramidal inversion of 16.8 and 22.3 kcal/mol, respectively. These findings are consistent with our previously stated view<sup>9</sup> that thiabenzene is best described by an ylide-like model.<sup>10</sup>

Thiabenzene **2** was prepared by addition of purified phenyllithium to 1-isopropyl-2-thianaphthalenium perchlorate<sup>11</sup> under a dry nitrogen atmosphere in benzene-*d*<sub>6</sub>. The <sup>1</sup>H nmr spectrum of the purple solution thus obtained at 37° displayed a well-resolved pair of isopropyl methyl doublets ( $\delta$  1.35, 1.42;  $J$  = 6.5 Hz), as well as a doublet at  $\delta$  5.00 ( $J$  = 8 Hz) which is characteristic 3-proton signal of the 2-thianaphthalene ring.<sup>9</sup> On standing at 37° these absorptions disappeared and the purple color changed to light brown. The thermal decomposition mixture did not contain 1-phenyl-1-isopropyl-2-thio-3-chromene, a possible rearrangement product, which was prepared by an independent synthesis.<sup>12</sup>

The sharp diastereotopic isopropyl methyl signals in **2** demonstrate that inversion at pyramidal sulfur is slow on the nmr time scale.<sup>13</sup> This diastereotopicity ( $\Delta\nu$  = 4 Hz (60 MHz), 37°) requires a minimum barrier to pyramidal inversion of 16.8 kcal/mol. Heating the sample of **2** to *ca.* 60° results in rapid decomposition, and we were thus unable to raise the value of the lower limit by this method.

Since the calculated barrier to pyramidal inversion for **1** exceeds the limits of dnmr, an alternative approach to the problem lies in the preparation of an op-

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

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

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

(7) C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971).

(8) C. K. Miao, M.S. Thesis, University of Pennsylvania, 1967. We thank Professor Charles C. Price for bringing this work to our attention.

(9) J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5650 (1974).

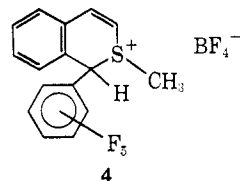
(10) See also A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

(11) Prepared by analogy with the reported synthesis of 1-*tert*-butyl-2-thianaphthalenium perchlorate.<sup>6</sup>

(12) In contrast to the thermal decomposition of 1-phenyl-2-methyl-2-thianaphthalene,<sup>9</sup> the decomposition of **2** does not entail migration (Stevens rearrangement) of the S-substituent to the 1-position.

(13) Pyramidal sulfur is the only reasonable element of chirality in **2** on this time scale of observation.

tically active thiabenzene. It had previously been shown<sup>9</sup> that **3** possesses a markedly enhanced thermal stability resulting from incorporation of the strongly electron withdrawing pentafluorophenyl group; therefore this compound was chosen for the present study. Optically active **3** was prepared by partial deprotonation of 0.050 mmol of **4**<sup>9,14</sup> with 0.028 mmol of brucine



in anhydrous dimethyl sulfoxide (5.0 ml) under a dry nitrogen atmosphere. The optical activity of the orange solution of **3** thus generated was detected by circular dichroism (CD)<sup>15</sup> in the region of the characteristic thiabenzene absorption band ( $\lambda_{\text{max}}$  480 nm, DMSO). The Cotton effect is positive, with the maximum at 480 nm,  $\theta$  = +0.0112  $\pm$  0.0008° ( $l$  1.0 cm),<sup>16</sup> and with  $\theta$  = 0.0000  $\pm$  0.0008° at 540 and at 400 nm.<sup>17</sup> The observation of optical activity (less than a 20% change in optical activity on standing at 27° for 10 min) assures that the barrier to pyramidal inversion in **3** must be at least 22.3 kcal/mol. The CD band decreases in rotational strength with time, and ultimately vanishes, paralleling a similar decrease in the intensity of the characteristic absorption in the visible region.<sup>18</sup>

Prior studies have established a pyramidal structure for the sulfur center in acyclic sulfonium ylides,<sup>19,20</sup> and the pyramidal inversion barrier for ethylmethylsulfonium phenacylide (**5**) has been determined to be 23.3 kcal/mol.<sup>20</sup> Our estimate of a lower limit for pyramidal inversion in **2** of 16.8 kcal/mol and in **3** of 22.3 kcal/mol is therefore consistent with the view that thiabenzene is ylide-like in character.<sup>9,10</sup>

(14) Although two diastereomers (*cis* and *trans*) are possible for this compound, <sup>1</sup>H nmr spectroscopic evidence suggests that one predominates to the virtual exclusion of the other in recrystallized **4**.

(15) By employing CD, interference from other optically active substances which do not have absorptions in the visible region is precluded.

(16) Assuming a quantitative yield (0.028 mmol) of thiabenzene, one obtains  $[\theta]_{480}^{20} + 204$ .

(17) In a control experiment, racemic **3** was generated by deprotonation of **4** with dimethyl lithium. Addition of brucine did not yield the observed Cotton effect.

(18) A detailed discussion is reserved for the full account of this work.

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

(20) D. Darwish and R. L. Tomlinson, *J. Amer. Chem. Soc.*, **90**, 5938 (1968).

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*Received May 4, 1974*

### Fixation of a Spin Labeled Organic Ion to Ion Exchangers

Sir:

It is generally considered that the affinity and fixation of ions, both inorganic and organic, in aqueous