formation has been obtained which suggests a possible reason for their formation. Reaction of 1.0 mol equiv of p-tolyllithium[20] with 1.0 mol equiv of **3a** in C_6D_6–ether gave 33% toluene, 37% p-tolyl sulfide, 5% 1-p-tolyl-2-thiochromene,[21] and a red-brown nonvolatile material that featured a broad absorption in the aromatic region of its ^{1}H nmr spectrum (δ 7.5–6.5).[22,23] Production of toluene was further investigated by the reaction of 2-thianapthalenium-*1,3,4-d₃* perchlorate (**8**)[24] with p-tolyllithium. In addition to the products previously noted, this reaction generated 31% toluene-d_1 (80% D).[21,26] Whether proton abstraction from **3a** occurs in an initial step[27] or whether **3b** is initially formed and proton abstraction ensues has not yet been determined. In any case, formation of both toluene and p-tolyl sulfide clearly indicates that the reaction of **3a** with aryllithium reagents results in extensive destruction of the sulfur ring system. It is not unreasonable to assume that the reactive species produced by proton abstraction and by formation of p-tolyl sulfide are responsible for the amorphous substances that are isolated.

It has been established that the stable red-brown amorphous materials which are isolated from the reactions of **1a–4a** with phenyllithium are not thiaarenes **1b–4b**. Actual properties of the class of compounds represented by **1b–4b** will be discussed in the following communication.[28]

Acknowledgment. We thank Professor Ronald H. Levin for the determination of the ^{13}C nmr spectrum.

(20) M. Schlosser and V. Ladenberger, *J. Organometal. Chem.*, **8**, 193 (1967).

(21) Yields were determined by glpc and are based on p-tolyllithium. Products were identified by coinjection with authentic compounds and by glpc–mass spectral analysis.

(22) The residue was obtained by removal of all volatile material by bulb-to-bulb distillation (80°, 5 × 10⁻⁶ Torr), the progress of which was monitored by ^{1}H nmr.

(23) Analogous products were also found for the reactions of **1a** and **2a** with p-tolyllithium.

(24) Prepared by α-deuterium exchange of 2-thiochromanone³ with NaOD–D₂O, followed by reduction with LiAlD₄ to the alcohol and dehydration with potassium pyrosulfate to the olefin. Successive hydride abstractions with trityl perchlorate²⁵ followed by LiAlD₄ reductions gave **8** with >95% deuterium incorporation at the 1-, 3-, and 4-positions, as determined by the ^{1}H nmr spectrum of the olefin obtained by LiAlD₄ reduction of **8**.

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

(26) Control experiments ruled out deuterium abstraction from benzene-d_6.

(27) Proton abstraction by weak base is known to occur in N-substituted pyridinium salts. See J. A. Zoltewicz and L. S. Helmick, *J. Amer. Chem. Soc.*, **92**, 7547 (1970).

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

G. H. Senkler, Jr., Joseph Stackhouse
Bruce E. Maryanoff, Kurt Mislow*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received March 8, 1974

# Thiabenzenes. II. Evidence for an Ylide Model[1]

Sir:

The preceding communication[2] presented evidence invalidating prior claims[3,4] for the syntheses of 1-

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

(2) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5648 (1974).

phenylthiabenzene, 1-phenyl-1-thianaphthalene, 2-phenyl-2-thianaphthalene, and 10-phenyl-10-thiaanthracene. Although it had been alleged that these compounds should be much more stable than other, more highly substituted thiabenzenes,[3–6] the present work establishes the contrary: the more highly substituted thiabenzenes (*e.g.*, 1,2,4,6-tetraphenylthiabenzene (**1**),[7] 1-methyl-3,5-diphenylthiabenzene (**2**),[8] and 1,2-diphenyl-2-thianaphthalene (**4a**)[5]) are, in fact, the more stable species. We also report on some of the chemical and physical properties that are characteristic of this class of compounds.

The deprotonation of **3a** by Price and Follweiler[5] to generate **4a** suggested a convenient method for the study of substituted thiabenzenes. Sulfonium salts **3a–e**[5,9] were deprotonated (eq 1) with dimsyl-d_5 sodium or

$$\text{3} \xrightarrow{\text{DMSO}^-} \text{4} \tag{1}$$
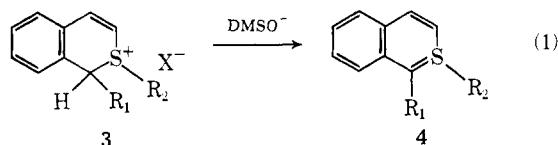
a, R_1 = phenyl; R_2 = phenyl
b, R_1 = phenyl; R_2 = methyl
c, R_1 = o-isopropylphenyl; R_2 = methyl
d, R_1 = pentafluorophenyl; R_2 = methyl
e, R_1 = H; R_2 = methyl
(**3a**, X = ClO₄⁻; **3b–e**, X = BF₄⁻)

lithium[12] in toluene-d_8 at −25° under a dry nitrogen atmosphere. The reaction mixtures obtained from **3a–d** were intensely colored and gave the ^{1}H nmr spectra summarized in Table I. These spectral data are con-

Table I. 60-MHz [1]H Nmr Spectral Data for 4a–d[a]

Compd	Aromatic H	3-H ($^3J_{HH}$, Hz)[b]	4-H[c]	S–CH₃
4a[d]	8.2–6.6 (m)	5.15 (d, 8)		
4b[e]	8.2–6.8 (m)	4.47 (d, 8)	6.72 (d)	0.92 (s)
4c[f]	7.4–6.9 (m)	4.53 (d, 8)	6.92 (d)	1.04 (s)
4d	7.3–6.7 (m)	4.76 (d, 8)	6.82 (d)	1.27 (s)

[a] Spectra run in benzene-d_6 at ambient probe temperature unless otherwise noted. [b] Assignment of the 3-H is based on the chemical shift observed for the 2,6-protons of **2** (δ 4.03, DMSO-d_6;[8] 3.91, benzene-d_6) and the assignment of the 3,5-protons of **1** (δ 7.72, benzene-d_6). [c] Assigned by irradiation of the 3-H. [d] A similar spectrum was observed for the purple solution obtained by reaction of 1-phenyl-2-thianaphthalenium perchlorate[5] with phenyllithium; it does not agree with the reported spectrum of **4a** (broad absorption at δ 7.8–6.6).[5] [e] Spectrum run at −35° in toluene-d_8–benzene-d_6 (2:1). [f] Spectrum run at 5° in toluene-d_8–benzene-d_6 (2:1); isopropyl group: δ 1.09 (pr of d, J = 7 Hz, $\Delta\nu$ = 4.4 Hz), 3.25 (m).

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

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

(5) C. C. Price and D. H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969); D. M. Follweiler, Ph.D. Thesis, University of Pennsylvania, 1968.

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

(7) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 1770 (1961); **84**, 2094 (1962).

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

(9) **3b–e** were synthesized by reaction of the corresponding sulfide with CH₃I–AgBF₄.[10,11]

(10) T. E. Young and R. Lazarus, *J. Org. Chem.*, **33**, 3770 (1968).

(11) Satisfactory elemental analyses were obtained for all new compounds.

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

sistent with the structures **4a–d**. The marked upfield shift noted for the 3-protons, similar to that found for **2**,[8] is a characteristic of protons in the ortho positions of thiabenzenes. Addition of acid to the solution of **4a–d** at −25° resulted in the regeneration of **3a–d**.

Solutions of **4a** (purple) and **4d** (red) could be warmed to ca. 40° with no observable change in color or nmr spectrum. However, when a solution of **4b** was allowed to warm to ca. 40°, its color changed from purple to light red, and the resulting nmr spectrum featured absorptions at δ 7.7–6.7 (m, 9 H, aromatic H), 6.30 (AB q, $^3J_{HH}$ = 9.5 Hz, $\Delta\nu_{AB}$ = 20.4 Hz, 2 H, olefinic H), 1.85 (s, 3 H, CH₃). 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**.[7]

(2)

4b   **5**
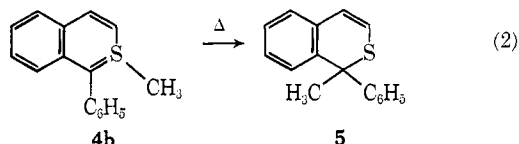
1-methyl-2,4,6-triphenylthiabenzene (**6**),[13] and 10-methyl-10-thiaanthracene,[2,14] and can be viewed as a formal extension of the Stevens rearrangement known to occur in sulfur ylides.[15] The deprotonation of **3e** differed from the others in that even at −65° it was not possible to obtain a stable 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**),[16] (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**.[8]

The remarkable stability of **4d** has permitted the isolation and characterization of this thiabenzene as a pure orange-red crystalline solid (mp 107–108°, dec). Elemental analysis, exact mass, solution molecular weight (osmometry in benzene), and nmr spectral data (¹H and ¹³C) 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. Hsü, *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.[13]

Table II. Thermal Stability of Thiabenzenes

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

[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 only *relative* thermal stability. [b] Generated by addition of phenyllithium to 2,4,6-triphenylthiopyrylium perchlorate. [c] Generated by addition of CH₃MgI to 2,4,6-triphenylthiopyrylium perchlorate. [d] Generated by deprotonation of the sulfonium salt with dimsyl anion. [e] Value is approximate due to spectral interference by decomposition products. [f] 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.[8] Specifically, the factors which should stabilize sulfonium ylides should also stabilize thiabenzenes. This view is contrary to the one proposed by Price, et al.,[6] 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.[17] 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.

Joseph Stackhouse, Bruce E. Maryanoff
G. H. Senkler, Jr., Kurt Mislow*
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Thiabenzenes. III. Pyramidal Stability at Sulfur[1]

Sir:

In the course of our studies on pyramidal inversion,[2] we had occasion to calculate the barrier to inversion at sulfur in 1-methylthiabenzene (**1**) by use of a specially parametrized semiempirical (CNDO/2) scheme.[3] 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).