reached. This highest concentration of tetra-*n*-butylammonium taurinate was 2.88×10^{-2} M and it gave a molar absorptivity for *p*-nitrophenoxide of 25 048 L mol^{-1}.

The equilibrium constant, K_3, was calculated from the expression

$$K_3 = \frac{A/\epsilon}{[\mathrm{PNP} - A/\epsilon][\mathrm{TBAT} - A/\epsilon]}$$

The equilibrium constant, K_4, was calculated by using the expression

$$K_4 = \frac{A/\epsilon}{[(\mathrm{PNP} - A/\epsilon)1/2]^{1/2}[\mathrm{TBAT} - A/\epsilon]}$$

Acknowledgment. This work was supported in part by a grant from the PSC-CUNY Research Award Program of the City University of New York.

Registry No. Tetra-*n*-butylammonium bromide, 1643-19-2; tetra-*n*-butylammonium hydroxide, 2052-49-5; *tetra-n*-butylammonium taurinate, 91900-05-9; taurine, 107-35-7; *p*-nitrophenol, 100-02-7; benzylamine, 100-46-9.

S-Substituted Thiacyclobutenium Salts[1]

James R. Bodwell,[2] Bhalchandra H. Patwardhan, and Donald C. Dittmer*

Department of Chemistry, Syracuse University, Syracuse, New York 13210

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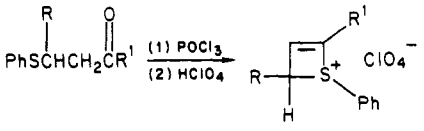
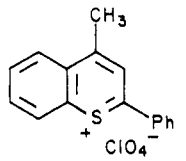
Treatment of 3-phenyl- or 3-(2-naphthyl)-2*H*-thietes with trimethyl- or triethyloxonium tetrafluoroborate or with methyl trifluoromethanesulfonate yields colorless *S*-alkylthiacyclobutenium salts. They react with cyanide ion to give both ring opened and dealkylated products. Repetition of previously reported syntheses of 4-methyl-1,2-diphenylthiacyclobutenium perchlorate and 2-methyl-1,4-diphenylthiacyclobutenium perchlorate gave instead 4-methyl-2-phenylbenzo-1-thiopyrylium perchlorate and 2-methyl-4-phenylbenzo-1-thiopyrylium perchlorate, respectively. These thiopyrylium salts also were synthesized independently.

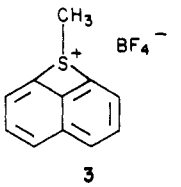
The synthesis of S-substituted thiacyclobutenium salts **1a** and **1b** by cyclization of β-phenylthio ketones has been described.[3] The purported salt **1a** had a melting or decomposition point (212 °C) identical with that reported for the thiopyrylium salt **2**.[4,5] In the reported ^{1}H NMR



1a, R = Ph; R^1 = CH_3
1b, R = CH_3; R^1 = Ph



2

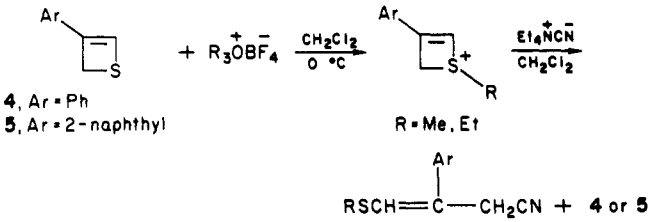


3

spectra of **1a** and **1b** in trifluoroacetic acid, the absorption of the methine proton on carbon-2 was not observed. Moreover, the ultraviolet spectrum attributed to **1a** was essentially identical with that reported for **2**.[4,5] The only other thiacyclobutenium salt reported previously is **3**, in which the carbon–carbon double bond is part of an aromatic system.[6] Several thiacyclobutenium structures, however, have been suggested as intermediates.[5,7]

Results and Discussion

Alkylation of Thietes. A different method than that used for the synthesis of the alleged structures **1a** and **1b** was adopted as a general way of preparing thiacyclobutenium salts. 3-Arylthietes, e.g., **4** and **5**, are much more stable[8] than alkyl-substituted thietes or the unsubstituted thiete,[9] and they can be alkylated with triethyl- or trimethyloxonium tetrafluoroborate in methylene chloride at 0 °C. The sulfonium salts obtained are hygroscopic and difficult to isolate. They yield ring opened and dealkylated products on treatment with tetraethylammonium cyanide. The ring-opened 4-(methylthio)- or 4-(ethylthio)-3-butenonitriles were obtained in about 25% yield and the dealkylated products, thietes **4** and **5**, were obtained in about 50% yield.



4, Ar = Ph
5, Ar = 2-naphthyl

R = Me, Et

The trifluoromethanesulfonate (triflate) salts, **6** and **7**, prepared by alkylation with methyl triflate, were less hy-

(1) Presented in part at the 186th National Meeting, American Chemical Society, Washington, D.C., Sept, 1983, Abstract ORGN 248. Taken in part from the Ph.D. Thesis of James R. Bodwell, Syracuse University, 1984.
(2) Syracuse University Fellow, 1982–1983.
(3) Tilak, B. D.; Gogte, V. N.; Devdhar, R. S. *Tetrahedron Lett.* **1974**, *45*, 3911.
(4) Tilak, B. D.; Panse, G. T. *Indian J. Chem.* **1969**, *7*, 191.
(5) Devdhar, R. S.; Gogte, V. N.; Tilak, B. D. *Indian J. Chem. Sect. B* **1980**, *19B*, 1014.
(6) Meinwald, J.; Knapp, S.; Obendorf, S. K., Hughes, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 6643.
(7) Engelhard, N.; Kolb, A. *Liebigs Ann. Chem.* **1964**, *673*, 136. Tilak, B. D.; Jindal, S. L. *Indian J. Chem.* **1969**, *7*, 737.
(8) Patwardhan, B. H.; Parker, E. J.; Dittmer, D. C. *Phosphorus Sulfur* **1979**, *7*, 5.
(9) Dittmer, D. C.; Chang, P.-L.; Davis, F. A.; Iwanami, M.; Stamos, I. K.; Takahashi, K. *J. Org. Chem.* **1972**, *37*, 1111.

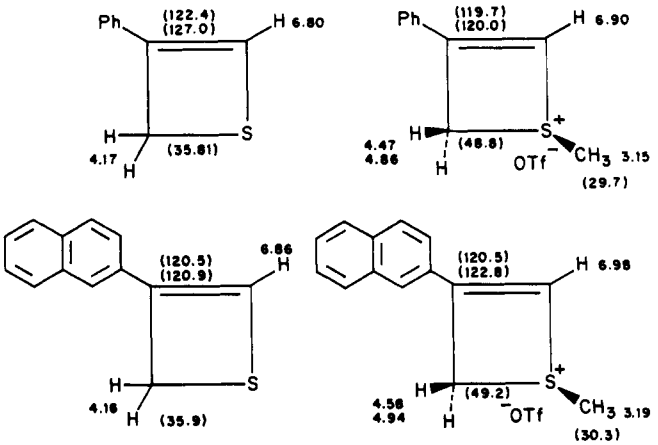
0022-3263/84/1949-4192$01.50/0

Table I. Comparison of Properties of Purported 1,2-Diphenyl-2*H*-4-methylthiacyclobutenium Perchlorate (1a) with 4-Methyl-2-phenylbenzo-1-thiopyrylium Perchlorate (2)

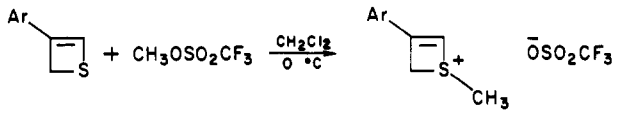
	"1a"[a]	"1a"[b]	2[c]	2[d]
mp, °C	212	210–212	212	209–211
UV (λ_{max}, nm, log ϵ)	268 (3.99)[e]	261 (4.36)[f]	264 (3.43)[e]	264 (4.36)[f]
	297 (3.24)	296 (4.00)	296 (3.99)	292 (4.00)
	391 (3.72)	389 (4.22)	390 (3.39)	389 (4.22)
^{1}H NMR, δ	3.5 (s, 3 H)[g]	3.3 (s, 3 H)[h]		3.3 (s, 3 H)[h]
	7.6–8.4 (s, 11 H)	7.7–9.1 (m, 10 H)		7.7–9.0 (m, 10 H)
^{13}C NMR, δ[g]		24.5, 129.6, 130.0		25.0, 129.9, 130.1
		131.3, 131.4, 131.7		131.5, 132.0, 132.4
		132.1, 134.2, 135.9		132.7, 132.9, 135.3
		136.0, 143.2, 168.4		135.4, 136.9, 143.7
		176.3		168.6, 178.2

[a] Data from ref 3. [b] Prepared according to the procedure in ref 3. [c] Data from ref 4 and 5. [d] Prepared according to Scheme I. [e] Solvent 1% $HClO_4$–HOAc. [f] Solvent MeCN. [g] Solvent CF_3CO_2H. Not all aromatic carbon resonances are necessarily resolved. [h] Solvent CD_3CN.

Chart I. Proton and Carbon-13 (in Parentheses) Chemical Shifts (δ, Me_4Si Reference)



groscopic and could be characterized spectroscopically, chemically, and by analysis for carbon and hydrogen. They are stable in air at room temperature for at least 30 min. Their mass spectra show the free thiacyclobutenium ions.

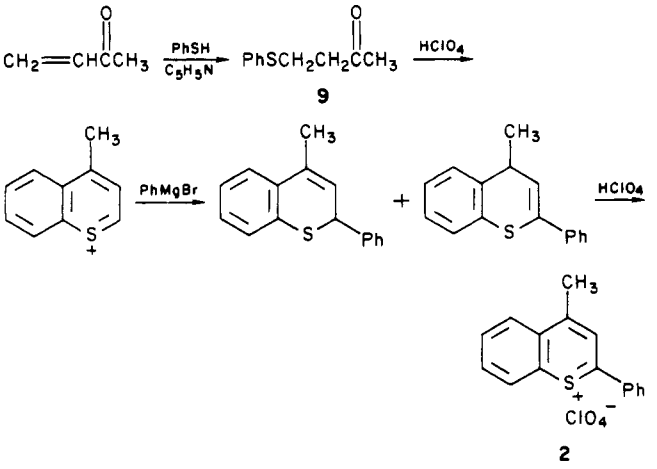


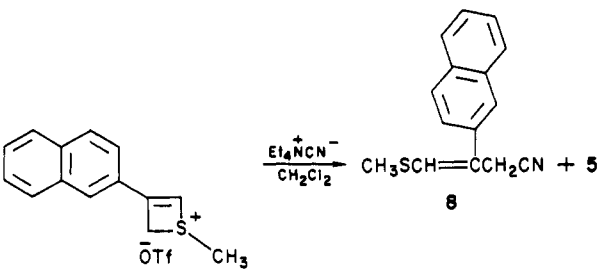
6, Ar = Ph
7, Ar = 2-naphthyl

The ^{1}H NMR spectra at 360 MHz of **6** and **7** show the methylene protons as a pair of doublets which indicate that the two protons are nonequivalent (diastereotopic), one being cis and the other trans to the methyl group on the tetrahedral sulfur atom which is chiral. In **6**, the two doublets are centered at δ 4.47 and 4.86 and each doublet is separated by 14.2 Hz; in **7** they are centered at δ 4.58 and 4.94 and are separated by 13.5 Hz. In the saturated S-alkylthietanium salts the α-methylene protons appear at δ 3.50–3.80 and the *S*-methyl protons at δ 3.25.[10] The ^{1}H and ^{13}C NMR data of both starting materials and salts are summarized in Chart I.

Treatment of triflate **7**, the more stable of the two triflate salts, with tetraethylammonium cyanide gives 4-(methylthio)-3-(2-naphthyl)-3-butenonitrile (**8**) and 3-naphthylthiete (**5**), the same result as with the tetrafluoroborate salt except that the ring opened product, the nitrile, is obtained in 75% yield and the dealkylated product, **5**, in 21% yield. The smaller amount of dealkylation with the triflate salt relative to the tetrafluoroborate is believed to be due to incomplete alkylation of the thiete **5** with trimethyloxonium tetrafluoroborate so that the tetrafluoroborate salt, which was not isolated because of its hygroscopic nature, was contaminated with the unreacted thiete.

Scheme I





Cyclization of β-Phenylthio Ketones. The previous claim of the synthesis of thiacyclobutenium salts, **1a** and **1b**, was examined by repeating the described procedure.[3] Treatment of 4-phenyl-4-(phenylthio)-2-butanone with phosphorus oxychloride and perchloric acid as set forth in the original report[3] gave thiopyrylium salt **2**. These same products have been obtained from the β-phenylthio ketone and perchloric acid alone.[4,5] The structure of thiopyrylium salt **2** was established by an independent synthesis outlined in Scheme I. The reaction of thiapyrylium salts with Grignard reagents and the dehydrogenation of 2*H*- and 4*H*-1-benzothiopyrans are well-known reactions.[11] Table I compares the properties observed for this independently synthesized sample of **2** with (1) the properties reported for **1a**,[3] (2) the properties of the salt

(10) Barbarella, G.; Garbesi, A.; Fava, A. *Helv. Chim. Acta* **1971**, *54*, 2297.

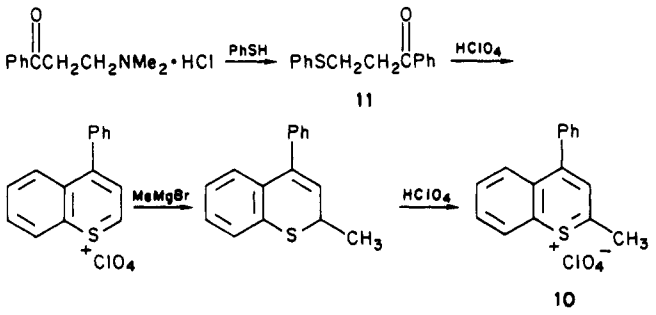
(11) For a review of cyclic sulfonium salts including thiapyrylium salts, see: Dittmer, D. C.; Patwardhan, B. H. In "The Chemistry of the Sulphonium Group"; Stirling, C. J. M., Patai, S., Eds.; John Wiley and Sons, Ltd.: Chichester, 1981; Chapter 13.

Table II. Comparison of Properties of Purported 2*H*-2-Methyl-1,4-diphenylthiacyclobutenium Perchlorate (1b) with 2-Methyl-4-phenylbenzo-1-thiopyrylium Perchlorate (10)

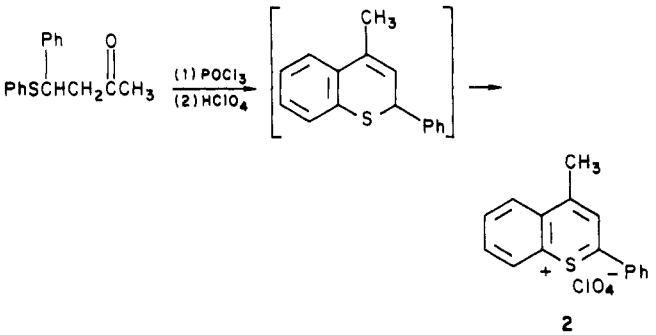
	"1b"[a]	"1b"[b]	10[c]	10[d]
mp, °C	229	190–220 dec	242	160–220 dec
UV (λ_{max}, nm, log ϵ)	276 (3.80)[e]	261 (4.41)[f]	264,[g] 343	264 (4.40),[f] 343 (3.94), 396 (4.26)
	394 (4.03)	389 (4.25)		
^{1}H NMR	2.9 (d, 3 H)[h]	3.3 (s, 3 H)[i]		3.3 (s, 3 H)[i]
	7.5–8.4 (m, 11 H)	7.7 (s, 5 H)		7.7 (s, 5 H)
		8.0–8.75 (m, 5 H)		8.0–8.8 (m, 5 H)
^{13}C NMR[h]		25.3, 128.3, 130.2		25.4, 128.2, 129.9
		130.3, 131.1, 133.0		130.2, 130.8, 132.7
		133.7, 134.1, 134.2		133.5, 133.8, 133.9
		135.8, 136.8, 145.0		135.5, 136.5, 144.7
		168.3, 179.0		167.8, 178.8

[a] Data from ref 3. [b] Prepared according to the procedure in ref 3. [c] Data from ref 5. [d] Prepared according to Scheme II. [e] Solvent 1% $HClO_4$–HOAc. [f] Solvent MeCN. [g] Solvent HOAc. [h] Solvent CF_3CO_2H. [i] Solvent CD_3CN.

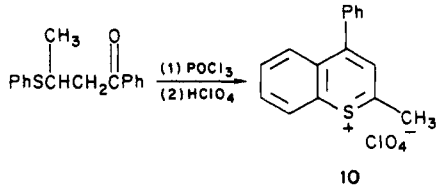
Scheme II



obtained by repeating the previous procedure said to give **1a**, and (3) the properties reported earlier for **2**.[4,5]



Repetition of the reaction of 1-phenyl-3-(phenylthio)-1-butanone with phosphorus oxychloride-perchloric acid described previously as giving **1b**[3] instead gave a thiopyrylium salt, **10**, isomeric with **2**. The salt, 2-methyl-4-phenylbenzo-1-thiopyrylium perchlorate, was prepared by the independent synthesis outlined in Scheme II. Incidentally, the absorption of the methylene protons in the ^{1}H NMR spectra ($CDCl_3$) of the two intermediates **9** and **11** are different. In **9** the absorption appears as a multiplet and in **11** as a singlet due to the slight difference in the environments of the protons which constitute an AA'BB' system.[12] The methylene proton absorption in **11** previously was reported as a singlet in $CDCl_3$ but as a multiplet in C_6D_6.[13]

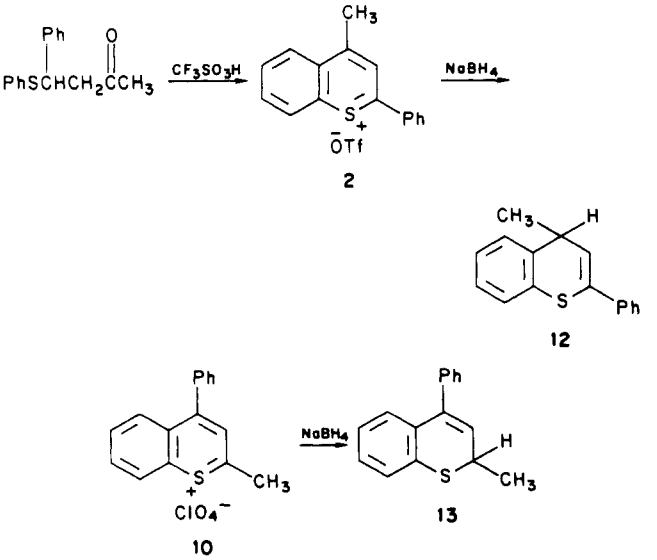


The properties of thiopyrylium salt **10** are compared in Table II with those attributed to thiacyclobutenium salt, **1b**. The ^{13}C NMR spectra given in Tables I and II are inconsistent with thiacyclobutenium structures **1a** and **1b** for which a maximum of 24 absorptions should be observed, including those for two aliphatic carbon atoms.

The "melting points" given in Tables I and II are really decomposition points. The salts darken over a range of temperatures before decomposing to black tarry material. This is especially apparent for 2-methyl-4-phenylbenzo-1-thiopyrylium perchlorate.

In the synthesis of 2-methyl-4-phenylbenzo-1-thiopyrylium perchlorate, **10**, by treatment of 1-phenyl-3-(phenylthio)-1-butanone with phosphorus oxychloride–perchloric acid as reported previously,[3] a new yellow perchlorate salt, mp 200–240 °C dec, was obtained on three occasions. The spectroscopic properties of this unknown salt are inconsistent with structure **1b**.

Cyclization of 4-phenyl-4-(phenylthio)-2-butanone also may be accomplished by the use of trifluoromethanesulfonic acid instead of perchloric acid. The two isomeric thiopyrylium ions, **2** (as the triflate) and **10**, undergo reduction with sodium borohydride to give 2*H*- or 4*H*-1-benzothiopyrans (**12** and **13**) in which the 2- or 4-phenyl group is conjugated with the double bond.



Treatment of salts alleged to be **1a** and **1b** with sodium hydride was said to give a green thiacyclobutadiene which on reprotonation gave exclusively **1a**.[3] No experimental details were given and the reported results could not be reproduced. The methyl protons in the thiapyrylium salts are acidic and exchange with ethanol-d_1 at low temperature. Also, colored dimers have been reported on treat-

(12) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; John Wiley and Sons: New York, 1981; p 203.
(13) Suzuki, K.; Sekiya, M. *Synthesis* **1981**, 297.

ment of methyl-substituted thiopyrylium salts with bases.[14] Indeed, treatment of 2-phenyl-4-methylbenzo-1-thiopyrylium perchlorate, **2**, with pyridine gave the previously reported green dimer, 4,4′-(1,2-ethanediylidene)-2,2′-diphenylbis(4*H*-benzo-1-thiopyran).[14]

Conclusion

The products obtained by treatment of 4-phenyl-4-(phenylthio)-2-butanone or 1-phenyl-3-(phenylthio)-1-butanone with phosphorus oxychloride–perchloric acid are benzothiopyrylium salts and not thiacyclobutenium salts, **1a** and **1b**.[15] The first synthesis of thiacyclobutenium salts, e.g., **6** and **7**, which do not involve an aromatic ring fused to the thiete, was accomplished by alkylation of thietes.

Experimental Section

Elemental analyses were performed at Microanalysis, Inc., Wilmington, DE or locally. Proton and ^{13}C NMR spectra were recorded on either a Varian T60, Varian CFT-20, or a Bruker WM-360 spectrometer. In some cases, particularly with the CFT-20 spectrometer, not all of closely spaced carbon resonances could be resolved. Chemical shifts are reported in ppm downfield from Me_4Si. Infrared spectra were recorded on a Perkin Elmer 710B spectrometer and ultraviolet spectra were recorded on a Cary 219 spectrometer. Mass spectra were obtained on a Finnigan 4000 GC/MS Mass Spectrometer Data System (electron impact) at 70 eV. Melting points were recorded on a Mel-Temp apparatus and are uncorrected.

Treatment of Thietes with Trimethyl- or Triethyloxonium Tetrafluoroborates Followed by Tetraethylammonium Cyanide. 3-(2-Naphthyl)-2*H*-thiete, **5**, (0.20 g, 1.0 mmol) in dichloromethane (10 mL) was added rapidly to trimethyloxonium tetrafluoroborate (0.20 g, 1.3 mmol) in a nitrogen atmosphere in dry dichloromethane (10 mL). The solution was stirred at 0 °C for 2 h, and a solution of tetraethylammonium cyanide (0.30 g, 1.9 mmol) in dichloromethane (10 mL) was added. Stirring was continued for 1 h at room temperature. The dichloromethane solution was washed with water (4 × 50 mL) and dried ($MgSO_4$). Removal of solvent gave a yellow oil which was chromatographed on Florisil (20 g). Elution with pentane gave 3-(2-naphthyl)-2*H*-thiete, **5** (0.10 g, 0.50 mmol, 50%), and elution with ether gave a 4-(methylthio)-3-(2-naphthyl)-3-butenenitrile, **8** (0.05 g, 0.25 mmol, 25%): ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 3.63 (s, 2 H), 6.60 (s, 1 H), 7.54 (m, 7 H); IR (neat) 2230 (m), 1590 (m) cm^{-1}; MS, *m/e* (relative intensity) 239 (65) (M^+), 184 (75) ($M^+ - CH_3 - CH_2CN$). Anal. Calcd for $C_{15}H_{13}NS$: C, 75.27; H, 5.47. Found: C, 74.81; H, 5.88.

In a similar manner, naphthylthiete, **5** (0.70 g, 3.6 mmol), was treated with triethyloxonium tetrafluoroborate (0.70 g, 3.6 mmol) and tetraethylammonium cyanide (0.70 g, 4. 4 mmol) to give **5** (0.39 g, 2.0 mmol, 56%) and 4-(ethylthio)-3-(2-naphthyl)-3-butenenitrile (0.20 g, 1.0 mmol, 28%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 1.4 (t, 3 H), 2.9 (q, 2 H), 3.75 (s, 2 H), 6.8 (s, 1 H), 7.4 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 15.7, 20.0, 28.7, 123.3, 124.0, 126.3, 126.6, 127.6, 128.2, 129.5, 130.0, 135.8; IR (neat) 2225 (m), 1595 (m) cm^{-1}. This compound was more difficult to purify than the preceding one and a completely satisfactory elemental analysis was not obtained. Anal. Calcd for $C_{16}H_{15}NS$: C, 75.85; H, 5.97. Found: C, 74.54, H, 5.89.

Treatment of 3-phenyl-2*H*-thiete (0.60 g, 4.0 mmol) with triethyloxonium tetrafluoroborate (0.70 g, 3.6 mmol) and tetraethylammonium cyanide (1.0 g, 6.4 mmol) gave thiete **4** (0.30 g, 2.0 mmol, 50%) and 4-(ethylthio)-3-phenyl-3-butenenitrile (0.20 g, 1.0 mmol, 25%): ^1H NMR ($CDCl_3$) δ 1.3 (t, 3 H), 2.8 (q, 2 H), 3.4 (s, 2 H), 6.5 (s, 1 H), 7.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 15.5, 19.9, 28.4, 123.3, 124.0, 126.3, 126.6, 127.6, 128.2, 128.5, 130.0, 135.8; IR (neat) 2225 (m), 1590 (m) cm^{-1}.

***S*-Methyl-3-phenylthiacyclobutenium Trifluoromethanesulfonate (6).** Methyl trifluoromethanesulfonate (0.46 g, 2.8 mmol) was added via syringe through a syringe cap to a solution at −30 °C of 3-phenyl-2*H*-thiete, **4** (0.20 g, 1.4 mmol), in dichloromethane (10 mL) under nitrogen. The reaction mixture was allowed to stand for 2 days at −30 °C. White crystals of **6** were separated by filtration and washed with pentane (0.25 g, 0.80 mmol, 59%): mp 63–69 °C dec; ^1H NMR (CD_3CN) δ 3.15 (s, 3 H), 4.47 (d, 1 H, *J* = 14.2 Hz), 4.86 (d, 1 H, *J* = 14.2 Hz), 6.90 (s, 1 H), 7.56 (s, 5 H); ^{13}C NMR (CD_3CN) δ 29.7, 48.8, 119.7, 120.0, 126.7, 129.7, 131.2, 132.8. Anal. Calcd for $C_{11}H_{11}F_3O_3S_2$: C, 42.30; H, 3.55. Found: C, 41.89; H, 3.76.

***S*-Methyl-3-(2-naphthyl)thiacyclobutenium Trifluoromethanesulfonate (7).** Treatment of 3-(2-naphthyl)-2*H*-thiete, **5** (0.50 g, 2.5 mmol), with methyl trifluoromethanesulfonate as described above gave white crystals of **7** (0.85 g, 2.3 mmol, 94%): mp 50–100 °C dec; ^1H NMR (CD_3CN) δ 3.19 (s, 3 H), 4.58 (d, 1 H, *J* = 13.5 Hz), 4.94 (d, 1 H, *J* = 13.5 Hz), 6.98 (s, 1 H), 7.62–8.10 (m, 7 H); ^{13}C NMR (CD_3CN) δ 30.3, 49.2, 120.5, 122.8, 128.2, 128.4, 128.6, 129.0, 129.5, 129.8, 129.9, 133.5, 135.5; IR(KBr) 3120 (m), 3050 (w), 1595 (w), 1320 (m), 1275 (vs), 1175 (vs), 1040 (vs), 870 (m), 810 (m), 760 (m) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 253 (4.25), 262 (4.25), 277 (4.03), 291 (4.02), 302 (4.05) nm; MS, *m/e* (relative intensity) 213 (16.5) ($M - CF_3SO_3$), 197 (65.1) ($M - CF_3SO_3 - CH_3 - H$), 165 (100) ($M - CF_3SO_3 - CH_3SH$), 152 (59.2) ($M - CF_3SO_3 - CH_2SCH_3$). Anal. Calcd for $C_{15}H_{13}F_3O_3S_2$: C, 49.71; H, 3.62. Found: C, 49.46; H, 3.57.

Treatment of a suspension of **7** (0.100 g, 0.280 mmol) with tetraethylammonium cyanide (0.080 g, 0.800 mmol) in dichloromethane (10 mL) resulted in a solution from which naphthylthiete **5** (0.013 g, 0.060 mmol, 21%) and 4-(methylthio)-3-(2-naphthyl)-3-butenenitrile, **8** (0.50 g, 0.209 mmol, 75%), were obtained. The properties of the latter were identical with those of the product obtained from the S-methyl tetrafluoroborate salt.

4-Phenyl-4-(phenylthio)-2-butanone was prepared as described previously:[4] mp 55–57 °C; (lit[4] mp 60 °C); ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 3.1 (d, 2 H, *J* = 7 Hz), 4.7 (t, 1 H, *J* = 7 Hz), 7.0–7.3 (s, 10 H); ^{13}C NMR ($CDCl_3$) δ 30.6, 48.0, 49.5, 127.4, 127.7, 128.5, 128.8, 132.9, 134.1, 141.0, 186.6.

Treatment of 4-Phenyl-4-(phenylthio)-2-butanone with Phosphorus Oxychloride–Perchloric Acid. Treatment of 4-phenyl-4-(phenylthio)-2-butanone (1.2 g, 4.7 mmol) with phosphorus oxychloride (3.0 g, 20 mmol) at temperatures ranging from 0 to 60 °C for 1–48 h followed by treatment with 70% perchloric acid at temperatures ranging from ice bath temperature to room temperature for 1–24 h invariably gave 4-methyl-2-phenylbenzo-1-thiopyrylium perchlorate (24–80%) with no sign of any other salt. The solutions were cooled to 0 °C and treated with an excess of ether to precipitate the salt: mp 210–212 °C dec (lit[4] mp 212 °C); ^1H NMR, ^{13}C NMR, and UV, see Table I; IR (KBr) 1100 (s, ClO_4^-) cm^{-1}; MS, *m/e* (relative intensity) 236 (100) ($M - HClO_4$). The aqueous ether mixture remaining after precipitation of the thiopyrylium salt was extracted with benzene (3 × 20 mL). The benzene extract was washed with a saturated solution of sodium bicarbonate (3 × 20 mL) and dried ($MgSO_4$) and the benzene removed to give an oil apparently containing *cis*- and *trans*-3,4-dihydro-4-methyl-2-phenyl-2*H*-1-benzothiopyran: ^1H NMR ($CDCl_3$) δ 1.4 (m, 3 H), 2.0 (m, 2 H), 3.7 (m, 1 H), 4.3 (m, 1 H), 7.2–7.6 (m, 6 H) [lit.[5] ^1H NMR (CCl_4) cis 1.39 (d), 4.5 (t); trans 1.42 (d), 3.80 (t), 4.40 (t)]. The thiopyrylium salt also was obtained by treating 4-phenyl-4-(phenylthio)-2-butanone with 70% perchloric acid alone. The trifluoromethanesulfonate salt was obtained by similar treatment of the keto sulfide with trifluoromethanesulfonic acid: mp 143–144 °C; ^1H NMR (CD_3CN) δ 3.2 (s, 3 H), 7.6–8.8 (m, 10 H); IR (KBr) 1290 (vs), 1270 (vs), 1160 (s), 1150 (s), 1040 (s) cm^{-1}; ^{13}C NMR (CD_2Cl_2) δ 24.3, 128.8, 129.1, 130.1, 130.7, 130.9, 131.3, 133.4, 133.9, 135.0, 135.3, 141.9, 167.0, 175.4; UV (CH_3CN) λ_{max} (log ε) 261 (4.45), 2.89 (4.08), 389 nm (4.30); MS, *m/e* (relative intensity) 236 (100) ($M - CF_3SO_3H$).

Independent Synthesis of 4-Methyl-2-phenylbenzo-1-thiopyrylium Perchlorate (2). 4-(Phenylthio)-2-butanone (**9**) was obtained as an oil in 82% yield by treatment of 3-buten-2-one with thiophenol and piperidine as previously described:[4,16] ^1H

(14) Reynolds, G. A.; Van Allen, J. A. *J. Heterocycl. Chem.* **1969**, *6*, 623.
(15) Professor Kurt Mislow has kindly informed us that his co-worker, Dennis Dougherty, also was unable to reproduce the work described in ref 3.
(16) Kuwajima, I.; Murofushi, T.; Nakamura, E. *Synthesis* **1976**, 602.

NMR ($CDCl_3$) δ 2.2 (s, 3 H), 2.6–3.3 (m, 4 H), 7.2 (m, 5 H).

4-(Phenylthio)-2-butanone (**9**) (1.2 g, 6.6 mmol) and 70% perchloric acid (2.0 mL) were stirred at room temperature for 20 min. The solution was cooled in an ice bath and ether was added to precipitate 4-methylbenzo-1-thiopyrylium (0.40 g, 1.5 mmol, 47%): mp 119–124 °C dec (lit.[17] mp 119–123 °C); ^1H NMR (CD_3CN) δ 3.3 (s, 3 H), 8.1–9.4 (m, 5 H), 10.2 (d, 1 H, J = 9 Hz) [lit.[17] ^1H NMR (CF_3CO_2D) δ 3.41 (s, 3 H), 8.32–9.10 (m, 5 H), 10.23 (d, 1 H)]; UV (CH_3CN) λ_{max} (log ε) 256 (4.29), 334 (3.68), 376 nm (3.60) [lit.[11] UV (1% $HClO_4$–CH_3CN) 257 (4.60), 333 (3.71), 380 (3.65), 580 (2.72) sh, 616 (3.09) nm]; IR (KBr) 1100 (s, ClO_4^-) cm^{-1}.

4-Methylbenzo-1-thiopyrylium perchlorate (0.20 g, 0.76 mmol) was added to freshly prepared phenylmagnesium bromide (4.0 mmol) in ether (30 mL) at 0 °C. The salt slowly dissolved. The solution was stirred for 40 min and poured into saturated aqueous ammonium chloride (20 mL). The solution was extracted with ether (100 mL) and the ether extract was washed with water (4 × 20 mL) and dried ($MgSO_4$), and the solvent was removed to yield an oil which appeared to be a mixture of 2*H*- and 4*H*-2-phenyl-4-methyl-1-benzothiopyran:[5] ^1H NMR (CCl_4) δ 1.3 (m), 2.1 (m), 3.4 (m), 4.7 (m), 5.8 (m), 6.8–8.00 (m).

The mixture of benzothiopyrans was added to 70% perchloric acid (1.0 mL) and the mixture was stirred at room temperature for 20 min. It was cooled in an ice bath, and ether (15 mL) was added with stirring. The precipitate was filtered to yield 4-methyl-2-phenylbenzo-1-thiopyrylium perchlorate, **2** (0.10 g, 0.29 mmol, 76% based on 4-methylbenzo-1-thiopyrylium perchlorate): mp 209–211 °C dec (lit.[4] mp 212 °C); ^1H NMR, ^{13}C NMR, and UV, see Table I; MS, m/e (relative intensity) 237 (18) (M^+ for cation), 236 (100).

Refluxing a mixture of **2** (0.20 g, 0.60 mmol) and pyridine (2 mL) for 10 min gave green crystals of 4,4′-(1,2-ethanediylidene)-2,2-diphenylbis(4*H*-benzo-1-thiopyran) (0.026 g, 0.055 mmol, 9.2%): mp 280–281 °C dec [lit.[14] mp 278–279 °C].

Reduction of either the perchlorate salt or trifluoromethanesulfonate salt of **2** with sodium borohydride in ethanol gave 4*H*-4-methyl-2-phenylbenzo-1-thiopyran **12**, as an oil in 80–88% yield: ^1H NMR (CCl_4) δ 1.4 (d, 3 H, J = 7 Hz), 3.5 (m, 1 H), 6.1 (d, 1 H, J = 6 Hz), 6.9–7.6 (m, 9 H) [lit.[5] ^1H NMR (CCl_4) δ 1.25 (d, 3 H), 3.6 (d, 1 H), 6.1 (d, 1 H), 7.0–7.9 (m, 9 H)]; ^{13}C NMR ($CDCl_3$) δ 18.9, 37.3, 124.4, 126.6, 126.7, 126.8, 127.0, 127.7, 128.2, 128.4, 128.6, 138.2.

Independent Synthesis of 2-Methyl-4-phenylbenzo-1-thiopyrylium Perchlorate (10). 1-Phenyl-3-(phenylthio)-1-propanone,[4,18] was obtained in 70% yield from β-(*N*,*N*-dimethylamino)propiophenone and thiophenol as previously described:[4] ^1H NMR (CCl_4) δ 3.2 (s, 4 H), 7.0–7.9 (m, 10 H).

1-Phenyl-3-(phenylthio)-1-propanone (1.2 g, 5.0 mmol) was added to 70% perchloric acid (3.0 mL) at 60 °C and the mixture was stirred for 10 min. The solution was cooled and extracted with benzene (3 × 20 mL). Ether (20 mL) was added to the ice cold acid solution to give a yellow precipitate of 4-phenylbenzo-1-thiopyrylium perchlorate (0.57 g, 1.8 mmol, 72%): mp 138 °C dec [lit.[4,19] mp 138 °C dec]; ^1H NMR (CD_3CN) δ 7.8 (s, 5 H), 8.7 (d, 1 H, J = 9 Hz), 8.2–9.0 (m, 4 H), 10.2 (d, 1 H, J = 9 Hz) [lit.[20] ^1H NMR (CF_3CO_2D) δ 7.90 (m, 5 H, Ph), 8.93 (d, 1 H, J = 10 Hz), 8.36–9.04 (m, 4 H), 10.43 (d, 1 H, J = 10 Hz)]; IR (KBr) 1100 cm^{-1} (s, ClO_4^-); UV (CH_3CN) λ_{max} (log ε) 262 (4.44), 347 (3.88), 408 nm (3.95) [lit.[4] UV (1% $HClO_4$–AcOH) 262 (4.54), 344 (3.94), 404 nm (4.04).

4-Phenylbenzo-1-thiopyrylium perchlorate (0.40 g, 1.2 mmol) was added to a freshly prepared methylmagnesium bromide solution (2.0 mmol) at 0 °C in ether. The salt dissolved quickly. The solution was stirred at room temperature for 30 min and was poured into saturated aqueous ammonium chloride (30 mL). Extraction with ether (100 mL), washing with water (5 × 15 mL), drying ($MgSO_4$), and evaporation gave 2*H*-2-methyl-4-phenyl-1-benzothiopyran[5] as an oil (0.40 g, 1.7 mmol, 85%): ^1H NMR ($CDCl_3$), δ 1.4 (d, 3 H, J = 6.0 Hz), 3.7 (m, 1 H), 5.9 (d, 1 H, J = 6.0 Hz), 6.9–7.4 (m, 4 H), 7.2 (s, 5 H).

2*H*-2-Methyl-4-phenyl-1-benzothiopyran (0.20 g, 0.85 mmol) was added to 70% perchloric acid (1.5 mL) at 60 °C and the mixture was stirred for 10 min. The solution was cooled in an ice bath and ether (15 mL) was added. No precipitate formed initially but precipitation of 2-methyl-4-phenylbenzo-1-thiopyrylium perchlorate, **10** (0.10 g, 0.29 mmol, 68%), was induced at −30 °C: mp 160–220 °C dec (lit.[5] mp 242 °C); ^1H NMR, ^{13}C NMR, and UV, see Table II; IR (KBr) 1100 (s, ClO_4^-) cm^{-1}.

Reduction of **10** with sodium borohydride in ethanol gave 2*H*-2-methyl-4-phenyl-1-benzothiopyran, **13** in 75% yield: ^1H NMR ($CDCl_3$) δ 1.4 (d, 3 H, J = 9 Hz), 3.8 (m, 1 H), 5.9 (d, 1 H, J = 6 Hz), 6.9–7.4 (m, 9 H) [lit.[5] ^1H NMR (CCl_4) δ 1.40 (d, 3 H), 3.65 (m, 1 H), 5.8 (d, 1 H), 6.8–7.4 (m, 9 H)].

Treatment of 1-Phenyl-3-(phenylthio)-1-butanone with Phosphorus Oxychloride–Perchloric Acid. 1-Phenyl-3-(phenylthio)-1-butanone was treated with phosphorus oxychloride followed by 70% perchloric acid as described previously.[3] 2-Methyl-4-phenylbenzo-1-thiopyrylium perchlorate, **10** (20–60%), was obtained. Its properties were essentially identical with those of the salt obtained in the independent synthesis described above (see Table II). The same thiopyrylium salt was obtained by treatment of the keto sulfide with 70% perchloric acid, the step involving phosphorus oxychloride being omitted. After precipitation of salts by addition of ether, the remaining mixture was extracted with benzene as described for the reaction of 4-phenyl-4-(phenylthio)-2-butanone with $POCl_3$–$HClO_4$ to give apparently a mixture of *cis*- and *trans*-3,4-dihydro-2-methyl-4-phenylbenzo-2*H*-1-thiopyran: ^1H NMR ($CDCl_3$) δ 1.3 (m, 3 H), 2.0 (dd, 2 H), 3.3 (m, 1 H), 4.0 (m, 1 H), 7.0–8.0 (m, 9 H) [lit.[5] ^1H NMR (CCl_4) δ 1.32 (d), 3.40 (m), 4.10 (t)].

In three cases, a yellow, higher molecular weight, salt-like substance of unknown composition was formed: mp 200–240 °C; ^1H NMR (CF_3CO_2H) 2.9 (s, 1 H), 7.7–8.4 (m, 5 H); IR (KBr) 1100 (s) (ClO_4^-); ^{13}C NMR (CF_3CO_2H) δ 23.8, 119.6, 128.4, 128.8, 131.0, 136.9, 172.4, 174.5; MS, m/e (relative intensity) 460 (3), 245 (14), 215 (19), 214 (22), 213 (57), 185 (13), 111 (100).

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(17) Young, T. E.; Ohnmacht, C. J. *J. Org. Chem.* **1967**, *32*, 1558.
(18) Thomas, P. J.; Marshall, D. R.; Stirling, C. J. M. *J. Chem. Soc., Perkin Trans 2* **1977**, 1914.
(19) Lüttringhaus, A.; Engelhard, N.; Kolb, A. *Liebigs Ann. Chem.* **1962**, *654*, 189.
(20) Degani, I.; Fochi, R.; Spunta, G. *Ann. Chim. (Rome)* **1973**, *63*, 527.