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Synthesis and thermal transformation of stable monocyclic λ^4-thiabenzenes

Hiroshi Shimizu,* Noriaki Kudo, Tadashi Kataoka and Mikio Hori

Gifu Pharmaceutical University, 5-6-1, Mitahora-higashi, Gifu 502-8585, Japan

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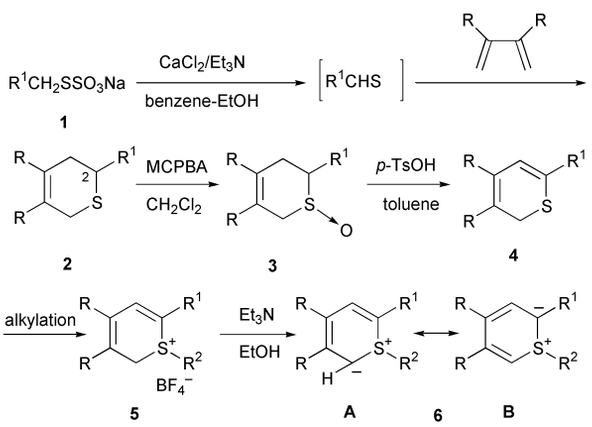
The stable monocyclic λ^4-thiabenzenes **6a**–**e**, which are stabilized with electron-withdrawing substituents such as benzoyl, cyano and alkoxycarbonyl groups, are synthesized in high yields by proton abstraction from the corresponding thiopyranium salts **5a**–**e** with triethylamine in ethanol. The ylidic properties of the λ^4-thiabenzenes are established based on spectral and chemical evidence. Thermal decomposition of the λ^4-thiabenzenes affords alkyl-rearranged products **7**, **8**, and **9**, thienofuran derivatives **10** (from benzoyl-substituted λ^4-thiabenzenes), and thiophene derivatives **11**. A plausible mechanism for the formation of those products is also discussed.

We have reported a series of cyclic sulfur ylides, so-called 'thiabenzenes', in which a sulfur ylide bond participates as part of a cyclic conjugated ring system having six π-electrons. However, all of these thiabenzenes are benzo-fused derivatives, 1-[1] and 2-thianaphthalenes,[2] 9-thiaanthracenes,[3] and 9-thiaphenanthrenes.[4] It is of more interest to synthesize monocyclic thiabenzenes in order to investigate in detail the chemistry of the thiabenzene skeleton itself. Attempts for the preparation of monocyclic thiabenzenes have been made by Price[5] and Hortmann,[6] but their compounds were too unstable to be isolated. Weber succeeded in stabilization of thiabenzenes as ligands of metal complexes.[7] Thus, there is no report on the successful isolation of monocyclic thiabenzenes.

We have planned to stabilize the thiabenzenes with an electron-withdrawing group such as a cyano or carbonyl group on the basis of our previous knowledge for the isolation of other benzo-fused thiabenzenes synthesized so far. We report here in detail the synthesis of stable monocyclic thiabenzenes together with their thermal reactions affording some rearranged products including ring contracted ones with an interesting thienofuran skeleton.[8]



a; R = H, R^1 = *p*-BrC_6H_4CO, R^2 = Me
b; R = R^2 = Me, R^1 = *p*-BrC_6H_4CO
b'; R = Me, R^1 = *p*-BrC_6H_4CO, R^2 = Et
c; R = R^2 = Me, R^1=PhCO
d; R = R^2 = Me, R^1=CN
e; R = R^2 = Me, R^1=CO_2Me

Scheme 1

Results and discussion

The synthesis of monocyclic thiabenzenes **6** was achieved as illustrated in Scheme 1. Dihydrothiopyrans **2b**–**e** were prepared by the hetero-Diels–Alder reaction of various thioaldehydes, generated *in situ* from the corresponding Bunte salts and base, with 2,3-dimethylbuta-1,3-dienes according to the procedure of Kirby *et al.*[9] The above cycloaddition reaction using buta-1,3-diene gas as diene from a cylinder for the synthesis of thiopyran **2a** with no alkyl substituents on the hetero ring resulted in a very low yield (14%) of desired product. Therefore, we tried this synthesis using buta-1,3-diene[10] generated *in situ* from the thermolysis of sulfolene in xylene–butanol under an N_2 atmosphere to obtain a rather higher yield (63%) of the thiopyran **2a**.

The dihydrothiopyrans **2** were oxidized with *m*-chloroperbenzoic acid (MCPBA) in a cooled dichloromethane solution to afford the corresponding sulfoxides **3** in high yields. All of these dihydrothiopyran sulfoxides were obtained as a mixture of *cis* and *trans* diastereomers pertaining to the 2-substituent and sulfoxide oxygen. The structures of *cis* and *trans* isomers were assigned by means of ^{1}H NMR spectroscopy, according to the ordinarily accepted view that relative configuration of the substituents at the 1- and 2-position can be established by assuming that the inductive and deshielding effect of the sulfoxide function on the proton at the 2-position is larger in the *trans* isomer than in the *cis* isomer and consequently this proton absorbs at lower field.[11,12]

On refluxing in toluene in the presence of toluene-*p*-sulfonic acid (*p*-TsOH) catalyst, the dihydrothiopyrans were dehydrated to give the corresponding 2*H*-thiopyrans **4** in 68–78% yield. Alkylation of 6-aroyl(thiopyrans) **4a**–**c** with alkyl iodide in the presence of silver tetrafluoroborate or with dialkoxycarbenium tetrafluoroborate in dichloromethane proceeded smoothly to give the corresponding 1-alkylthiopyranium tetrafluoroborates **5a**–**c** in high yield. Methylation of 6-cyano- **4d** and 6-methoxycarbonyl(thiopyrans) **4e** was accomplished with methyl trifluoromethanesulfonate to give methylthiopyranium salts **5d** and **5e** in high yield, respectively, although their alkylation with the combination of methyl iodide and silver tetrafluoroborate proceeded in low yields. Deprotonation of thiopyranium salts **5** with triethylamine in ethanol yielded the corresponding

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Table 1 Thermal reactions of thiabenzenes **6**

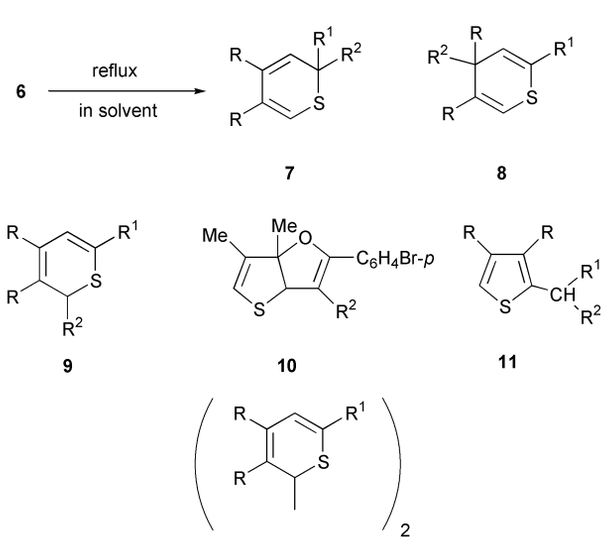
Entry	Compd.	Solvent	Time (*t*/h)	Products (% yield)					
				7	**8**	**9**	**10**	**11**	**12**
1	**6b**	Benzene	1.7	25	15	20	5		
2	**6b**	EtOH	10		8	4	11	12	
3	**6b**	MeCN	4	7	13	14	11	5	
4	**6b′**	Benzene	1	24	13	15	3		
5	**6b′**	EtOH	8		17	19	22	13	
6	**6d**	Benzene	0.8	5	5			7	3
7	**6d**	EtOH	1	10	4			11	18

monocyclic thiabenzenes **6** as orange to yellow compounds in 57–100% yield. These compounds are stable even on exposure to air at room temperature.

The structures of these thiabenzenes were established on the basis of spectral and chemical evidence. The IR spectra of compound **6a** shows a strong carbonyl absorption at 1535 cm^{-1}, a lower wavenumber than that of an ordinary aroyl group (1620–1690 cm^{-1}). This indicates the delocalization of the carbanion electron through the carbonyl group. The ^1H NMR spectrum ($CDCl_3$) of **6a** shows a singlet signal at δ 2.17 assignable to S-Me, two doublets at δ 5.20 and 6.90 which are attributed to H-6 and H-3, respectively, and two doublets of doublets at δ 5.58 and 6.98 attributable to H-4 and H-5, respectively. The ^{13}C NMR spectrum ($CDCl_3$) of **6a** shows signals at δ_C 65.7 and 85.0 attributable to C-2 and C-6, respectively. These two ^{13}C signals are assigned to sp^3 carbons and therefore suggest that a resonance form **6B**, in which the ylide carbanion is located on the C-2 position, is an important contributor to the electronic distribution in **6a**, as well as a resonance form **6A**.

The thiabenzene **6a** was treated with tetrafluoroboric acid in ether to give **5a** as the sole product in 84% yield. This indicates that **6a** reacted with acid in the resonance form **6A** rather than in the resonance form **6B**. The spectral and chemical observations described above show that the thiabenzene **6a** has ylidic character. Similar spectral and chemical behaviour was observed for the other thiabenzenes **6b**, **6b′**, **6c**, **6d**, and **6e** (Experimental section).

Thiabenzenes are very soluble in several solvents such as benzene, ethanol and acetonitrile and can be stored without decomposition at room temperature for several days. We next investigated a thermal reaction of thiabenzenes **6b**, **6b′**, and **6d** in refluxing solvents. The results are summarized in Scheme 2 and Table 1.



Scheme 2

Thermal decomposition of thiabenzenes proceeded faster in benzene compared with that in acetonitrile and ethanol. This is probably explained by solvation of the polar ylidic structure of thiabenzenes by polar solvents. 2-Aroylthiabenzenes **6b** and **6b′** in the non-polar solvent benzene underwent thermal rearrangement of 1-alkyl substituents to give three possible products **7**, **8**, and **9**, and thienofuran derivative **10** (entries 1 and 4). In contrast, they decomposed in the protic solvent ethanol to afford ring-contracted products **11** as well as two alkyl-migrated products **8** and **9**, and thienofuran **10** (entries 2 and 5). Interestingly, **6b** afforded all of the above five products on refluxing in the polar aprotic solvent acetonitrile for 4 h (entry 3). 6-Cyano-substituted thiabenzene **6d** is less stable than 6-aroyl-substituted ones and was decomposed on refluxing in solvent within 1 h to give two S-methyl migrated products **7d** and **8d**, **11d**, and dimerized product **12d** in low yield.

The structures of the above products were easily elucidated on the basis of their spectral evidence. For example, structure determination of three methyl-migrated products was made on the basis of ^1H NMR spectra which showed allylic coupling (J 1.7 Hz) between each methyl group and olefinic proton for the compound **7b**, and a singlet signal of two methyl groups at the 4-position at δ 1.22 and allyl coupling between the 5-methyl and 6-olefinic proton at δ 1.87 for the compound **8b**, and a doublet (J 6.8 Hz) of the 6-methyl group at δ 1.28 for compound **9b**.

The structure of **10b** was also elucidated on the basis of spectral data: the ^1H NMR spectrum showing a doublet (δ 1.83, J 1.7 Hz) of the 6-methyl group coupled with the olefinic proton (δ 5.80, J 1.7 Hz), and a doublet (δ 1.86, J 1.3 Hz) of the 6a-methyl group with a long-range coupling with 3a-methine proton (δ 4.64, J 1.3 Hz), as well as a lack of both IR absorption and ^{13}C NMR signal due to a carbonyl group in the molecule.

High-resolution mass spectral data indicated a molecular formula of $C_{15}H_{15}BrOS$ for compound **11b**. The IR spectrum of compound **11b** showed a characteristic absorption band at 1690 cm^{-1} for the benzoyl group. The ^1H NMR spectrum of compound **11b** showed a characteristic singlet at δ 6.76 for the thiophene ring proton, and in the phenacyl substituent a methyl doublet (J 6.8 Hz) at δ 1.53 coupled with a methine proton appearing at δ 4.83.

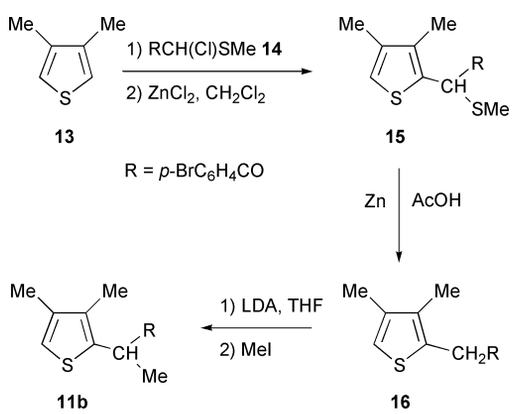
The complete structure determination of compound **11b** was made by comparison with an authentic sample prepared by the route depicted in Scheme 3. The Friedel–Crafts reaction of 3,4-dimethylthiophene **13** in the presence of anhydrous $ZnCl_2$ with α-chloro-4-bromophenacyl methyl sulfide **14** prepared by chlorination of 4-bromophenacyl methyl sulfide[13] with NCS afforded 2-substituted 3,4-dimethylthiophene **15** in 39% yield. Treatment of **15** with Zn in acetic acid led to the reduction product **16** in 27% yield, according to the method of Tamura *et al.*[14] Deprotonation of **16** with LDA in THF, followed by addition of methyl iodide, gave the expected compound **11b** in 48% yield.

Finally, we discuss the mechanism for the formation of compounds **10**, **11**, and **12**. The thienofuran **10b** was found to

isomerize to the thiophene derivative **11b** on storage at room temperature for about one week. The rearranged product **7b** was also isomerized partly to the thiophene **11b** on storage at room temperature for more than one month. In addition, the isolated product **7b** was subjected to further thermolysis under conditions of refluxing in ethanol for 2.5 h to give **10b** in 11% yield.

Taking account of the above results, the products **10** and **11** are considered to be formed by decomposition of the rearranged products **7**. In considering the mechanism for the formation of products **10** and **11**, we propose the formation of the common intermediate **C** as a key intermediate from the thiopyran **7** as shown in Scheme 4.

The attack of the lone-pair electrons of sulfur of **7** at the olefinic carbon at the 3-position generates episulfonium ylide intermediate **A** (path a). The three-membered ring of the intermediate **A** is opened to give intermediate **C**. Enolate ion of the intermediate **C** attacks at the 3-position to afford the corresponding compound **10**. The enolate ion abstracts the acidic proton at the 2-position activated by the adjacent sulfonium ion, followed by tautomerization to furnish the corresponding compound **11**. The intermediate **C** might be generated by an alternative mechanism involving the thermally provoked electrocyclic ring-opening of the thiopyran **7** to the thiocarbonyl intermediate **B** (path b), followed by Michael addition of the sulfur atom at an electron-deficient olefinic carbon.



Scheme 3

In order to get information pertaining to the formation of the thiocarbonyl intermediate **B**, we attempted to trap such a highly reactive thioaldehyde intermediate by the hetero-Diels–Alder reaction with 2,3-dimethylbuta-1,3-diene. However, we could not detect any cycloaddition product. This result suggests the low possibility of path b. In addition, higher yields of products **10** and **11** were obtained in polar solvents such as ethanol and acetonitrile than in non-polar solvents as described above, suggesting the preferred formation of polar ylidic intermediate **A** in path a.

Porter and co-workers also discussed the two plausible intermediates, an episulfonium ylide intermediate and a thiocarbonyl one for the similar thermal ring contraction of 1,2-bis(alkoxycarbonyl)-2*H*-thiopyran derivatives to thiophenes, and they ruled out the thiocarbonyl intermediate based on the failure of trapping such an intermediate.[15] We also discussed the similar episulfonium ylide intermediate in the mechanism for the ring contraction of 2-benzothiopyran derivatives to benzothiophenes in our previous report.[16]

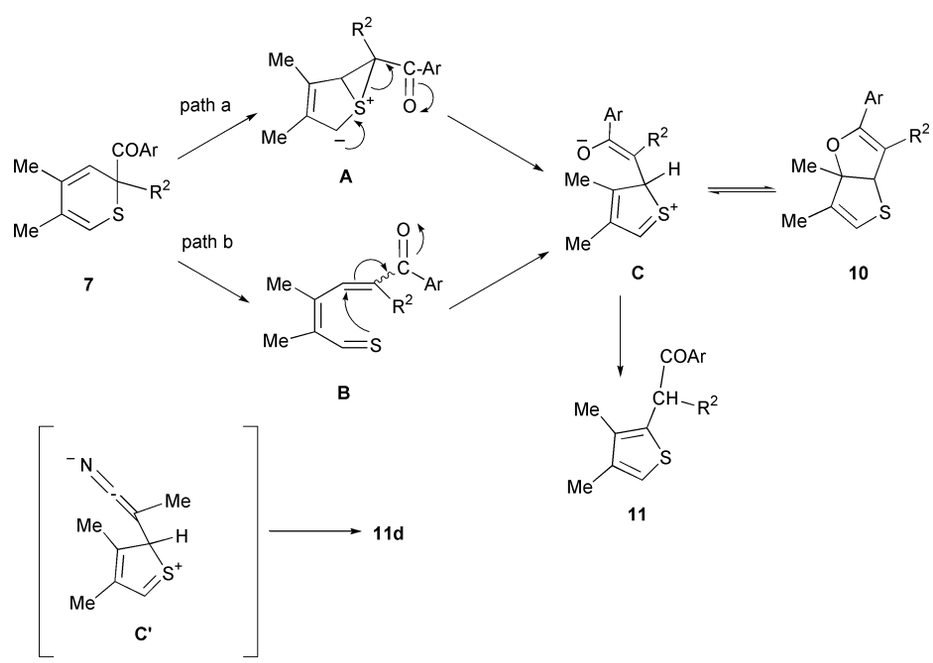
Thermal equilibration between the intermediate **C** and compound **10** explains the transformation of **10** to the compound **11**.

Similar thermal decomposition of 2-cyano-substituted derivative **7d** forms the corresponding intermediate **C′**, which isomerizes only to compound **11d**, with no cyclization to the bicyclic product corresponding to compound **10**, probably because of the linear structure of the heterocummulene moiety of the estimated intermediate **C′**.

The formation of product **12** might be explained by a mechanism involving self-coupling of the thiopyranyl radical intermediate formed by homolytic demethylation of the thiabenzene **6d**. Such a homolytic dealkylation has been often observed in the thermal decomposition of sulfonium salts.[17]

Experimental

Mps were determined on a Yanagimoto micro melting-point apparatus, and are uncorrected. IR spectra were measured on a JASCO IRA-100 spectrophotometer. NMR spectra were recorded on a JEOL JNM GX-270 spectrometer at 270 MHz (^{1}H) and 67.5 MHz (^{13}C) or a JEOL JNM GX-400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). Chemical shifts were measured in ppm on the δ-scale downfield from tetramethylsilane as internal standard; *J*-values are recorded in Hz.



Scheme 4

^{13}C Data are quoted with ^{1}H multiplicity (off-resonance results in parentheses), although this multiplicity was usually inferred from a DEPT experiment. Mass spectra were obtained by electron impact at 70 eV on a JEOL JMS-D300 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Analytical and preparative TLC (PLC) were carried out on E. M. Merck silica gel 60PF-254 plates. Spots were visualized with a UV hand lamp.

2-(4-Bromobenzoyl)-3,6-dihydro-2*H*-thiopyran 2a

A solution of triethylamine (7.3 g, 72.1 mmmol) in xylene (a mixture of *o*-, *m*- and *p*-isomers) (40 cm^3) was added dropwise under nitrogen atmosphere to a stirred mixture of sodium *S*-4-bromophenacyl thiosulfate **1a** (5.01 g, 15.04 mmol), 2,5-dihydrothiophene *S*,*S*-dioxide (sulfolene) (15.1 g, 0.13 mol) and $CaCl_2 \cdot 2H_2O$ (2.9 g, 19.5 mmol) in a mixture of butan-1-ol (40 cm^3) and xylene (a mixture of *o*-, *m*- and *p*-isomers) (80 cm^3) with reflux over a period of 50 min. The mixture was then refluxed for an additional 2.5 h. After cooling, the reaction mixture was acidified with 10% aq. HCl and extracted with chloroform. The chloroform layer was washed successively with 10% aq. HCl, 10% aq. NaOH, and water, and dried ($MgSO_4$). Evaporation of the mixture gave an oil, which was chromatographed on silica gel with hexane–ethyl acetate (40 : 1) to afford *the thiopyran* **2a** (2.68 g, 62.9%) as colourless columns, mp 99–102 °C (from dichloromethane–hexane); ν_{max} (KBr)/cm^{-1} 1670 (CO); δ_H ($CDCl_3$) 2.47–2.66 (2H, m, 3-H), 2.99–3.15 (2H, m, 6-H), 4.44 (1H, t, *J* 5.1, 2-H), 5.85–5.97 (2H, m, 4-, 5-H) and 7.59 and 7.87 (each 2H, d, *J* 8.8, ArH); δ_C ($CDCl_3$) 24.2 (t), 25.7 (t), 40.3 (d), 122.6 (d), 126.9 (d), 128.1 (s), 130.2 (d), 131.8 (d), 133.7 (s) and 194.1 (s); *m*/*z* 282 (M^+) (Found: C, 50.78; H, 3.95. $C_{12}H_{11}BrOS$ requires C, 50.90; H, 3.92%).

General procedure for the preparation of 3,6-dihydro-4,5-dimethyl-2*H*-thiopyrans 2b–e

2-(4-Bromobenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran 2b. A solution of triethylamine (4.87 g, 48.2 mmol) in benzene (60 cm^3) was added dropwise to a stirred mixture of the 4-bromophenacyl thiosulfate **1a** (16.04 g, 48.2 mmol), 2,3-dimethylbuta-1,3-diene (4.75 g, 57.8 mmol) and $CaCl_2 \cdot 2H_2O$ (7.08 g, 48.1 mmol) in a mixture of ethanol (60 cm^3) and benzene (120 cm^3) with reflux over a period of 30 min. The mixture was then refluxed with stirring for an additional 4.5 h. After having cooled to room temperature, the reaction mixture was acidified by 10% aq. HCl, and extracted with chloroform. The extract was washed successively with 10% aq. HCl, 10% aq. NaOH, and water, and dried ($MgSO_4$). The solvent was evaporated off to leave a crude oil, which was subjected to column chromatography on silica gel with hexane–ethyl acetate (40 : 1) to afford *the thiopyran* **2b** (10.7 g, 71.6%) as colourless prisms, mp 38 °C (from dichloromethane–hexane); ν_{max} (KBr)/cm^{-1} 1675 (CO); δ_H ($CDCl_3$) 1.73 and 1.74 (each 3H, s, Me), 2.42 (1H, dd, *J* 16.8 and 3.9, 3-H), 2.52 (1H, dd, *J* 16.8 and 3.8, 3-H), 2.96 (2H, br s, 6-H), 4.41 (1H, dd, *J* 3.9 and 3.8, 2-H) and 7.58 and 7.85 (each 2H, d, *J* 8.6, ArH); δ_C ($CDCl_3$) 19.5 (q), 20.0 (q), 29.7 (t), 32.4 (t), 41.7 (d), 122.5 (s), 126.1 (s), 128.0 (s), 130.1 (d), 131.7 (d), 133.9 (s) and 194.4 (s); *m*/*z* 310 (M^+) (Found: C, 54.27; H, 4.87. $C_{14}H_{15}BrOS$ requires C, 54.03; H, 4.86%).

The following 3,6-dihydro-2*H*-thiopyrans were prepared from the proper thiosulfates **1** in a similar manner to that described above.

2-Benzoyl-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran 2c. Yield 63.5%, a *pale yellow oil* from sodium phenacyl thiosulfate **1c** after refluxing for 4 h; ν_{max} (neat)/cm^{-1} 1670 (CO); δ_H ($CDCl_3$) 1.74 (6H, s, 2 × Me), 2.43 (1H, dd, *J* 16.7 and 4.1, 3-H), 2.53 (1H, dd, *J* 16.7 and 5.6, 3-H), 2.98 and 3.00 (each 1H, d, *J* 17.5, 6-H), 4.49 (1H, dd, *J* 5.6 and 4.1, 2-H), 7.41–7.57 (3H, m, ArH) and 7.97–8.01 (2H, m, ArH); δ_C ($CDCl_3$) 19.5 (q), 20.0 (q), 29.9 (t), 32.7 (t), 41.9 (d), 122.6 (s), 126.3 (s), 128.5 (d), 128.6 (d), 133.0 (d), 135.2 (s) and 195.7 (s); *m*/*z* 232 (M^+) (Found: M^+, 232.0931. $C_{14}H_{16}OS$ requires *M*, 232.0922).

2-Cyano-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran 2d. Yield 68.3%, a *pale yellow oil* from sodium cyanomethyl thiosulfate **1d** after refluxing for 5 h; ν_{max} (neat)/cm^{-1} 2240 (CN); δ_H ($CDCl_3$) 1.71 and 1.77 (each 3H, s, Me), 2.42 and 2.60 (each 1H, dd, *J* 17.1 and 4.4, 3-H), 2.96 and 3.51 (each 1H, d, *J* 17.1, 6-H) and 3.79 (1H, t, *J* 4.4, 2-H); δ_C ($CDCl_3$) 19.3 (q), 19.7 (q), 25.5 (d), 28.7 (t), 34.6 (t), 118.7 (s), 123.2 (s) and 123.5 (s); *m*/*z* 153 (M^+, base) (Found: M^+, 153.0612. $C_8H_{11}NS$ requires *M*, 153.0612).

3,6-Dihydro-2-methoxycarbonyl-4,5-dimethyl-2*H*-thiopyran 2e. Yield 72.5%, a *pale yellow oil* from sodium methoxycarbonylmethyl thiosulfate **1e** after refluxing for 10 h in methanol; ν_{max} (neat)/cm^{-1} 1735 (ester); δ_H ($CDCl_3$) 1.70 and 1.73 (each 3H, s, Me), 2.46 (2H, br d, *J* 6.3, 3-H_2), 3.05 and 3.12 (each 1H, d, *J* 16.4, 6-H), 3.64 (1H, t, *J* 6.3, 2-H) and 3.73 (3H, s, OMe); δ_C ($CDCl_3$) 19.5 (q), 20.1 (q), 30.7 (t), 34.2 (t), 41.0 (d), 52.4 (q), 123.2 (s), 125.8 (s) and 172.3 (s); *m*/*z* 186 (M^+) (Found: M^+, 186.0720. $C_9H_{14}O_2S$ requires *M*, 186.0716).

General procedure for the preparation of thiopyran 1-oxides 3a–e

2-(4-Bromobenzoyl)-3,6-dihydro-2*H*-thiopyran 1-oxide 3a. MCPBA (85% purity; 1.95 g, 9.62 mmol) was added to an ice-cooled solution of **2a** (2.67 g, 9.4 mmol) in dichloromethane (100 cm^3) and the mixture was stirred for 3.5 h. Aq. $NaHCO_3$ was added to the reaction mixture, and the dichloromethane layer was separated, washed with water, and dried ($MgSO_4$). The solvent was evaporated off under reduced pressure to give a residue, which was triturated with diethyl ether to give an inseparable mixture of *cis* and *trans* diastereomers of the thiopyran oxide **3a** (2.73 g, 97.0%) as crystals in the ratio 1 : 3.4 judging from the integration of the 2-H signal in the ^{1}H NMR spectrum. Data for the diastereomeric mixture of **3a**: *colourless needles*, mp 148–165 °C (from chloroform–diethyl ether); *m*/*z* 298 (M^+) (Found: C, 47.95; H, 3.72. $C_{12}H_{11}BrO_2S$ requires C, 48.18; H, 3.71%); ***cis*-3a**: δ_H ($CDCl_3$) 2.50 (1H, br d, *J* 19.0, 3-H), 3.05–3.13 (1H, m, 3-H), 3.46–3.52 (2H, m, 6-H_2), 4.51 (1H, dd, *J* 10.0 and 4.6, 2-H), 5.63–5.70 (1H, m, 5-H), 6.06–6.10 (1H, m, 4-H) and 7.65 and 7.81 (each 2H, d, *J* 8.8, ArH); δ_C ($CDCl_3$) 20.4 (t), 46.9 (t), 58.2 (d), 115.7 (d), 128.0 (d), 129.2 (s), 130.3 (d), 132.0 (d), 134.2 (s) and 193.5 (s); ***trans*-3a**: δ_H ($CDCl_3$) 2.77 (2H, br s, 3-H_2), 3.46–3.52 (1H, m, 6-H), 3.78 (1H, ddd, *J* 16.6, 5.4 and 1.5, 6-H), 4.87 (1H, t, *J* 7.1, 2-H), 5.63–5.70 (1H, m, 5-H), 5.91–5.95 (1H, m, 4-H), 7.66 and 7.90 (each 2H, d, *J* 8.8, ArH); δ_C ($CDCl_3$) 26.4 (t), 48.6 (t), 63.9 (d), 117.4 (d), 127.7 (d), 129.6 (s), 130.4 (d), 132.1 (d), 134.7 (s) and 194.5 (s).

The following thiopyran 1-oxides were prepared from the corresponding thiopyrans **2** in a similar manner to that described above. 2-Benzoyl-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran **3c** was also synthesized by this method. However, since compound **3c** is a known compound prepared by Zwanenburg and co-workers,[12] we give no description for it here.

2-(4-Bromobenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran 1-oxide 3b. A mixture of *cis* and *trans* forms (93.5%) in the ratio 1 : 3 was subjected to fractional recrystallization from dichloromethane–hexane to afford pure *cis* and *trans* isomers. ***cis*-3b**: *colourless needles*, mp 148–165 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1675 (CO) and 1035 (SO); δ_H ($CDCl_3$) 1.77 and 1.79 (each 3H, s, Me), 2.27 and 2.33 (each 1H, br s, 3-H), 3.33 and 3.51 (each 1H, d, *J* 17.1, 6-H), 4.46 (1H, dd, *J* 9.6 and 4.7, 2-H), 7.61 and 7.80 (each 2H, d, *J* 8.1, ArH); δ_C ($CDCl_3$) 19.5 (q), 19.7 (q), 26.0 (t), 52.1 (t), 59.0 (d), 115.3 (s), 127.3 (s), 129.0 (s), 130.2 (d),

131.9 (d), 134.2 (s) and 193.5 (s); *m/z* 326 (M^+) (Found: C, 51.16; H, 4.60. $C_{14}H_{15}BrO_2S$ requires C, 51.39; H, 4.62%). ***trans*-3b**: *pale yellow columns*, mp 154–169 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1680 (CO) and 1035 (SO); δ_H ($CDCl_3$) 1.71 and 1.75 (each 3H, s, Me), 2.65 (2H, br s, 3-H_2), 3.48 and 3.58 (each 1H, d, *J* 15.8, 6-H), 4.74 (1H, dd, *J* 6.4 and 5.0, 2-H) and 7.62 and 7.87 (each 2H, d, *J* 7.3, ArH); δ_C ($CDCl_3$) 19.1 (q), 19.8 (q), 32.3 (t), 54.0 (t), 65.5 (d), 117.7 (s), 127.7 (s), 129.4 (d), 130.3 (d), 132.0 (d), 134.7 (s) and 194.6 (s); *m/z* 326 (M^+) (Found: C, 51.53; H, 4.62. $C_{14}H_{15}BrO_2S$ requires C, 51.39; H, 4.62%).

2-Cyano-3,6-dihydro-4,5-dimethyl-2*H*-thiopyran 1-oxide 3d. An inseparable mixture of *cis* and *trans* forms (96%) in the ratio 1 : 1, data for a diastereomeric mixture of **3d**: ν_{max} (neat)/cm^{-1} 2250 (CN) and 1065 (SO); δ_H ($CDCl_3$) 3.97 (t, *J* 4.9, 2-H for the *cis* form) and 4.09 (t, *J* 5.6, 2-H for the *trans* form); *m/z* 169 (M^+) (Found: M^+, 169.0547. $C_8H_{11}NOS$ requires *M*, 169.0561).

3,6-Dihydro-2-methoxycarbonyl-4,5-dimethyl-2*H*-thiopyran 1-oxide 3e. An inseparable mixture of *cis* and *trans* forms (99%) in the ratio 1 : 5, data for the diastereomeric mixture of **3e**: ν_{max} (neat)/cm^{-1} 1740 (ester) and 1060 (SO); δ_H ($CDCl_3$) 1.79 (6H, br s, 2 × Me of the *cis* form) and 1.74 (6H, br s, 2 × Me of the *trans* form); *m/z* 202 (M^+) (Found: M^+, 202.0659. $C_9H_{14}O_3S$ requires *M*, 202.0663).

General procedure for the preparation of 2*H*-thiopyrans 4a–e

6-(4-Bromobenzoyl)-2*H*-thiopyran 4a. A mixture of **3a** (3.93 g, 13.14 mmol) and *p*-TsOH monohydrate (100 mg) in toluene (170 cm^3) was refluxed with stirring for 3 h. Evaporation of the mixture left a crude oil, which was subjected to column chromatography on silica gel using hexane–ethyl acetate (10 : 1) to afford *the thiopyran* **4a** (2.51 g, 67.8%) as pale brown needles after recrystallization from dichloromethane–hexane, mp 95–96 °C; ν_{max} (KBr)/cm^{-1} 1630 (CO); δ_H ($CDCl_3$) 3.37 (2H, dd, *J* 5.4 and 1.5, 2-H_2), 5.96 (1H, dt, *J* 9.3 and 5.4, 3-H), 6.20 (1H, ddt, *J* 9.3, 6.4 and 1.5, 4-H), 6.80 (1H, d, *J* 6.4, 5-H) and 7.59 (4H, s, ArH); δ_C ($CDCl_3$) 24.6 (t), 122.3 (s), 126.4 (s), 127.0 (s), 130.5 (d), 131.5 (d), 132.9 (d), 135.4 (s), 136.9 (s) and 192.5 (s); *m/z* 280 (M^+) (Found: C, 51.05; H, 3.24. $C_{12}H_9BrOS$ requires C, 51.26; H, 3.23%).

The following thiopyrans were prepared from the corresponding thiopyran 1-oxides **3** in a similar manner to that described above.

6-(4-Bromobenzoyl)-3,4-dimethyl-2*H*-thiopyran 4b. Yield 67.5%, *colourless needles*, mp 71–73 °C (from dichloromethane–hexane); ν_{max} (KBr)/cm^{-1} 1630 (CO); δ_H ($CDCl_3$) 1.81 and 1.98 (each 3H, br s, Me), 3.29 (2H, br s, 2-H_2), 6.69 (1H, s, 5-H) and 7.57 and 7.59 (each 2H, d, *J* 9, ArH); δ_C ($CDCl_3$) 17.9 (q), 20.1 (q), 31.4 (t), 126.7 (s), 127.7 (s), 128.4 (s), 130.5 (d), 131.6 (d), 133.7 (s), 135.9 (s), 139.0 (s) and 192.7 (s); *m/z* 308 (M^+) (Found: C, 54.29; H, 4.27. $C_{14}H_{13}BrOS$ requires C, 54.38; H, 4.24%).

6-Benzoyl-3,4-dimethyl-2*H*-thiopyran 4c. Yield 78.3%, a *yellow oil*; ν_{max} (neat)/cm^{-1} 1630 (CO); δ_H ($CDCl_3$) 1.79 and 1.96 (each 3H, q, *J* 1.3, Me), 3.28 (2H, br s, 2-H_2), 6.73 (1H, s, 5-H), 7.41–7.57 (3H, m, ArH) and 7.67–7.71 (2H, m, ArH); δ_C ($CDCl_3$) 17.8 (q), 20.0 (q), 31.3 (t), 127.6 (s), 128.0 (s), 128.2 (d), 128.8 (d), 131.8 (d), 133.9 (s), 137.1 (s), 138.9 (d) and 193.7 (s); *m/z* 230 (M^+) (Found: M^+, 230.0757. $C_{14}H_{14}OS$ requires *M*, 230.0765).

6-Cyano-3,4-dimethyl-2*H*-thiopyran 4d. Yield 73.7%, a *yellow oil* after refluxing for 8 h; ν_{max} (neat)/cm^{-1} 2225 (CN); δ_H ($CDCl_3$) 1.82 and 1.94 (each 3H, br s, Me), 3.28 (2H, br s, 2-H_2), 6.71 (1H, s, 5-H); δ_C ($CDCl_3$) 17.1 (q), 19.6 (q), 30.9 (t), 101.7 (s), 116.2 (s), 126.4 (s), 126.8 (s) and 140.0 (d); *m/z* 151 (M^+) (Found: M^+, 151.0460. C_8H_9NS requires *M*, 151.0456).

6-Methoxycarbonyl-3,4-dimethyl-2*H*-thiopyran 4e. Yield 73.7%, a *pale yellow oil* after refluxing for 9 h; ν_{max} (neat)/cm^{-1} 1710 (ester); δ_H ($CDCl_3$) 1.84 and 1.98 (each 3H, s, Me), 3.22 (2H, s, 2-H_2), 3.80 (3H, s, OMe) and 7.09 (1H, s, 5-H); δ_C ($CDCl_3$) 17.4 (q), 19.5 (q), 31.2 (t), 51.8 (q), 123.4 (s), 125.7 (s), 127.2 (s), 135.3 (d) and 164.9 (s); *m/z* 184 (M^+) (Found: M^+, 184.0569. $C_9H_{12}O_2S$ requires *M*, 184.0598).

General procedure for the preparation of thiopyranium salts 5

6-(4-Bromobenzoyl)-1-methyl-2*H*-thiopyranium tetrafluoroborate 5a. Silver tetrafluoroborate (1.05 g, 4.85 mmol) was added portionwise with ice-cooling to a stirred solution of **4a** (840 mg, 2.97 mmol) and methyl iodide (4.34 g, 30.59 mmol) in dichloromethane (50 cm^3) and the mixture was stirred for 5 h at room temperature. The precipitated silver iodide was filtered off and the filtrate was diluted with diethyl ether. The white precipitate was collected and recrystallized from acetone–diethyl ether to give the *thiopyranium salt* **5a** (1.16 g, quant.) as white needles, mp 117–118 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1635 (CO) and 1090–1025 (BF_4^-); δ_H (CD_3CN + $CDCl_3$) 2.84 (3H, s, SMe), 4.27 (2H, dd, *J* 4.5 and 1.5, 2-H_2), 6.62 (1H, dt, *J* 9.8 and 4.5, 3-H), 6.76 (1H, ddt, *J* 9.8, 6.8 and 1.5, 4-H), 7.64 (1H, d, *J* 6.8, 5-H) and 7.70 and 7.76 (each 2H, d, *J* 8.8, ArH); δ_C (CD_3CN + $CDCl_3$) 21.1 (q), 32.2 (t), 121.0 (s), 124.3 (d), 126.8 (d), 128.4 (s), 130.9 (d), 132.0 (d), 132.4 (s), 143.3 (d) and 188.9 (s) (Found: C, 40.77; H, 3.21. $C_{13}H_{12}BBrF_4OS$ requires C, 40.77; H, 3.16%).

6-(4-Bromobenzoyl)-1,3,4-trimethyl-2*H*-thiopyranium tetrafluoroborate 5b. By a similar method to that described for **5a**, the *thiopyranium salt* **5b** was obtained in 96.2% yield as colourless needles after recrystallization from acetone–diethyl ether, mp 135–136 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1640 (CO) and 1120–1040 (BF_4^-); δ_H (CD_3CN + $CDCl_3$) 2.01 and 2.16 (each 3H, s, Me), 2.78 (3H, s, SMe), 4.00 and 4.26 (each 1H, d, *J* 18.1, 2-H), 7.50 (1H, s, 5-H) and 7.69 and 7.75 (each 2H, d, *J* 8.8, ArH); δ_C (CD_3CN + $CDCl_3$) 17.2 (q), 20.0 (q), 20.5 (q), 36.4 (t), 117.8 (s), 127.4 (s), 127.9 (s), 130.8 (d), 131.8 (d), 132.6 (s), 133.0 (s), 148.7 (d) and 188.9 (s) (Found: C, 43.61; H, 3.79. $C_{15}H_{16}BBrF_4OS$ requires C, 43.83; H, 3.92%).

6-(4-Bromobenzoyl)-1-ethyl-3,4-dimethyl-2*H*-thiopyranium tetrafluoroborate 5b′. By the same method as that described for **5a** except using ethyl iodide as alkylating agent instead of methyl iodide, the *thiopyranium salt* **5b′** was obtained in 58.1% yield as colourless needles after recrystallization from acetone–diethyl ether, mp 120–121 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1630 (CO) and 1080–1010 (BF_4^-); δ_H (CD_3CN + $CDCl_3$) 1.39 (3H, t, *J* 7.6, SCH_2CH_3), 2.00 and 2.16 (each 3H, s, Me), 3.28–3.41 (2H, m, SCH_2Me), 4.04 and 4.31 (each 1H, d, *J* 18.3, 2-H), 7.53 (1H, s, 5-H), 7.68 and 7.74 (each 2H, d, *J* 8.8, ArH); δ_C (CD_3CN + $CDCl_3$) 8.4 (q), 16.9 (q), 19.7 (q), 33.5 (t), 34.7 (t), 127.3 (s), 127.5 (s), 130.4 (d), 131.5 (d), 132.5 (s), 133.4 (s), 149.2 (d) and 188.9 (s) (Found: C, 44.98; H, 4.38. $C_{16}H_{18}BBrF_4OS$ requires C, 45.21; H, 4.27%).

6-Benzoyl-1,3,4-trimethyl-2*H*-thiopyranium tetrafluoroborate 5c. By a similar method to that described for **5a**, the *thiopyranium salt* **5c** was obtained in 88% yield as colourless needles after recrystallization from acetone–diethyl ether, mp 138–139 °C (decomp.); ν_{max} (KBr)/cm^{-1} 1630 (CO) and 1120–1040 (BF_4^-); δ_H (CD_3CN + $CDCl_3$) 2.00 and 2.15 (each 3H, s, Me), 2.79 (3H, s, SMe), 4.02 and 4.26 (each 1H, d, *J* 18.1, 2-H), 7.50 (1H, s, 5-H) and 7.57–7.81 (5H, m, ArH); δ_C (CD_3CN + $CDCl_3$) 16.7 (q), 19.5 (q), 20.1 (q), 35.9 (t), 117.7 (s), 126.9 (s), 128.1 (d), 128.6 (d), 132.2 (s), 133.0 (d), 133.1 (s), 148.0 (d) and

189.2 (s) (Found: C, 54.08; H, 5.16. $C_{15}H_{17}BF_4OS$ requires C, 54.24; H, 5.16%).

6-Cyano-1,3,4-trimethyl-2*H*-thiopyranium triflate 5d. A mixture of **4d** (1 g, 6.61 mmol) and methyl trifluoromethanesulfonate (0.94 cm^3, 8.27 mmol) was stirred at room temperature for 1 h, during which time solid materials appeared gradually and finally the whole of the mixture solidified. Diethyl ether was added to the solids, which were then pulverized to afford *thiopyranium salt* **5d** (1.98 g, 95%). Recrystallization from acetone–diethyl ether gave pale grey needles, mp 119–120 °C (decomp.); ν_{max} (KBr)/cm^{-1} 2230 (CN) and 1250 and 1030 (SO_2); δ_H (CD_3CN + $CDCl_3$) 2.03 and 2.12 (each 3H, s, Me), 2.97 (3H, s, SMe), 4.13 and 4.47 (each 1H, d, *J* 18.3, 2-H) and 7.67 (1H, s, 5-H); δ_C (CD_3CN + $CDCl_3$) 16.2 (q), 19.3 (q), 20.3 (q), 37.1 (t), 87.8 (s), 111.9 (s), 127.0 (s), 132.1 (s) and 152.7 (d) (Found: C, 38.08; H, 3.75; N, 4.43. $C_{10}H_{12}F_3NO_3S_2$ requires C, 38.09; H, 3.84; N, 4.44%).

6-Methoxycarbonyl-1,3,4-trimethyl-2*H*-thiopyranium triflate 5e. By a similar method to that for **5d**, the *thiopyranium salt* **5e** was obtained in 93% yield as colourless leaflets after recrystallization from dichloromethane–diethyl ether, mp 99–102 °C; ν_{max} (KBr)/cm^{-1} 1705 (ester), 1260 and 1030 (SO_2); δ_H ($CDCl_3$) 2.09 and 2.17 (each 3H, s, Me), 2.88 (3H, s, SMe), 3.93 (3H, s, OMe), 4.38 (2H, br s, 2-H_2) and 7.73 (1H, s, 5-H); δ_C ($CDCl_3$) 18.2 (q), 20.7 (q), 21.2 (q), 37.3 (t), 53.7 (q), 110.0 (s), 126.9 (s), 132.2 (s), 147.1 (d) and 161.5 (s) (Found: C, 37.90; H, 4.33. $C_{11}H_{15}F_3O_5S_2$ requires C, 37.93; H, 4.34%).

General procedure for the preparation of 1-alkyl-λ⁴-thiabenzenes 6

2-(4-Bromobenzoyl)-1-methyl-1-thiabenzen-1-ium-2-ide 6a. Triethylamine (2.3 g, 22.7 mmol) was added to a stirred suspension of **5a** (2.12 g, 5.5 mmol) in ethanol (90 cm^3) with ice-cooling and the mixture was stirred for 4 h, poured into water, and extracted with dichloromethane. The extract was washed with water and dried ($MgSO_4$). Evaporation of the mixture *in vacuo* gave a crude residue, which was recrystallized from diethyl ether to afford the *λ⁴-thiabenzene* **6a** (0.75 g, 45.7%) as light brown crystals, mp 90–92 °C; ν_{max} (KBr)/cm^{-1} 1535 (CO); δ_H ($CDCl_3$) 2.17 (3H, s, SMe), 5.20 (1H, d, *J* 7.8, 6-H), 5.58 (1H, dd, *J* 7.6 and 8.3, 4-H), 6.90 (1H, d, *J* 8.3, 3-H), 6.98 (1H, dd, *J* 7.6 and 7.8, 5-H) and 7.52 and 7.58 (each 2H, d, *J* 8.5, ArH); δ_C ($CDCl_3$) 28.5 (q), 65.7 (s), 85.1 (d), 105.0 (s), 124.5 (s), 130.6 (d), 131.1 (d), 132.6 (d), 137.0 (s), 138.1 (s) and 184.8 (s); *m*/*z* 294 (M^+) (Found: C, 52.82; H, 3.86. $C_{13}H_{11}BrOS$ requires C, 52.90; H, 3.76%).

The following 1-alkyl-λ⁴-thiabenzenes were synthesized by the same general method.

2-(4-Bromobenzoyl)-1,4,5-trimethyl-1-thiabenzen-1-ium-2-ide 6b. Yield 89%, *dark red needles*, mp 123–125 °C (decomp., from diethyl ether); ν_{max} (KBr)/cm^{-1} 1545 (CO); δ_H ($CDCl_3$) 1.90 and 2.08 (each 3H, br s, Me), 2.05 (3H, s, SMe), 5.06 (1H, s, 6-H), 6.53 (1H, br s, 3-H) and 7.45 and 7.52 (each 2H, d, *J* 9.0, ArH); δ_C ($CDCl_3$) 19.3 (q), 21.4 (q), 29.1 (q), 76.6 (s), 84.1 (d), 114.1 (s), 124.0 (s), 129.7 (d), 130.6 (d), 130.9 (d), 138.5 (s), 149.0 (s) and 183.1 (s); *m*/*z* 322 (M^+) (Found: C, 55.50; H, 4.69. $C_{15}H_{15}BrOS$ requires C, 55.74; H, 4.68%).

2-(4-Bromobenzoyl)-1-ethyl-4,5-dimethyl-1-thiabenzen-1-ium-2-ide 6b′. Yield 57.5%, a *dark red oil* after column chromatography on silica gel with ethyl acetate; ν_{max} (KBr)/cm^{-1} 1530 (CO); δ_H ($CDCl_3$) 1.12 (3H, t, *J* 7.3, CH_2CH_3), 1.87 (3H, br s, Me), 2.05 (3H, s, Me), 2.34–2.62 (2H, m, CH_2Me), 5.04 (1H, s, 6-H), 6.55 (1H, br s, 3-H) and 7.44 and 7.52 (each 2H, d, *J* 8.5, ArH); δ_C ($CDCl_3$) 6.7 (q), 19.4 (q), 21.5 (q), 39.3 (t), 76.0 (s), 82.5 (d), 114.3 (s), 123.8 (s), 130.5 (d), 131.0 (d), 131.1 (d), 138.9 (s), 149.6 (s) and 183.7 (s); *m*/*z* 336 (M^+) (Found: M^+, 336.0199. $C_{16}H_{17}BrOS$ requires *M*, 336.0184).

2-Benzoyl-1,4,5-trimethyl-1-thiabenzen-1-ium-2-ide 6c. Yield 98%, a *red oil*; ν_{max} (neat)/cm^{-1} 1535 (CO); δ_H ($CDCl_3$) 1.89 and 2.07 (each 3H, br s, Me), 2.04 (3H, s, SMe), 5.03 (1H, s, 6-H), 6.59 (1H, br s, 3-H) and 7.36–7.58 (5H, m, ArH); δ_C ($CDCl_3$) 19.3 (q), 21.4 (q), 29.2 (q), 53.3 (s), 83.5 (d), 113.7 (s), 127.8 (d), 128.9 (d), 129.6 (d), 130.4 (d), 139.7 (d), 148.9 (d) and 184.7 (s); *m*/*z* 244 (M^+) (Found: M^+, 244.0899. $C_{15}H_{16}OS$ requires *M*, 244.0921).

2-Cyano-1,4,5-trimethyl-1-thiabenzen-1-ium-2-ide 6d. Yield 76.3%, *orange prisms*, mp 68–69 °C (decomp., from diethyl ether); ν_{max} (KBr)/cm^{-1} 2170 (CN); δ_H ($CDCl_3$) 1.89 and 1.98 (each 3H, s, Me), 2.04 (3H, s, SMe), 4.68 (1H, br s, 6-H), 6.54 (1H, br s, 3-H); δ_C ($CDCl_3$) 18.6 (q), 20.5 (q), 28.9 (q), 31.9 (s), 74.0 (d), 115.2 (s), 121.4 (s), 130.2 (d) and 145.8 (s); *m*/*z* 165 (M^+) (Found: C, 65.16; H, 6.78; N, 8.51. $C_9H_{11}NS$ requires C, 65.41; H, 6.71; N, 8.48%).

2-Methoxycarbonyl-1,4,5-trimethyl-1-thiabenzen-1-ium-2-ide 6e. Yield 92.3%, a *red oil*; ν_{max} (neat)/cm^{-1} 1655 (ester); δ_H ($CDCl_3$) 1.89 and 1.97 (each 3H, br s, Me), 2.01 (3H, br s, SMe), 3.07 (3H, s, OMe), 4.75 (1H, s, 6-H) and 6.98 (1H, br s, 3-H); δ_C ($CDCl_3$) 18.8 (q), 20.7 (q), 28.9 (q), 45.5 (s), 50.4 (q), 77.9 (d), 113.2 (s), 129.8 (d), 147.3 (d) and 165.5 (s); *m*/*z* 198 (M^+) (Found: M^+, 198.0699. $C_{10}H_{14}O_2S$ requires *M*, 198.0714).

General procedure for thermolysis of thiabenzenes 6

A solution of **6** (1.5 mmol) in an appropriate solvent (35 cm^3) was refluxed with stirring and the reaction was followed by TLC until completion. After evaporation of the mixture, the residue was subjected to PLC on silica gel using an appropriate solvent. The results, including reaction conditions and yields, are summarized in Table 1.

From the thiabenzene **6b**, the following products were obtained after PLC with hexane–ethyl acetate (10 : 1) as solvent.

2-(4-Bromobenzoyl)-2,4,5-trimethyl-2*H*-thiopyran 7b. A *yellow oil*; ν_{max} (neat)/cm^{-1} 1680 (CO); δ_H ($CDCl_3$) 1.65 (3H, s, Me), 1.88 and 1.89 (each 3H, d, *J* 1.7, Me), 5.45 and 5.92 (each 1H, br s, olefinic H) and 7.54 and 8.01 (each 2H, d, *J* 8.6, ArH); δ_C ($CDCl_3$) 20.3 (q), 20.6 (q), 25.2 (q), 52.3 (s), 113.5 (d), 120.2 (d), 127.2 (s), 130.3 (s), 131.1 (d), 131.8 (d), 133.8 (s), 134.5 (s) and 197.9 (s); *m*/*z* 322 (M^+) (Found: M^+, 322.0001. $C_{15}H_{15}BrOS$ requires *M*, 322.0027).

2-(4-Bromobenzoyl)-4,4,5-trimethyl-4*H*-thiopyran 8b. *Colourless plates*, mp 84–85 °C (from ethanol); ν_{max} (KBr)/cm^{-1} 1650 (CO); δ_H ($CDCl_3$) 1.22 (6H, s, 2 × Me), 1.87 (3H, s, *J* 1.3, Me), 5.91 (1H, q, *J* 1.3, 6-H), 6.15 (1H, s, 3-H) and 7.58 and 7.60 (each 2H, d, *J* 9.0, ArH); δ_C ($CDCl_3$) 19.8 (q), 26.8 (q), 37.0 (s), 111.6 (d), 127.2 (s), 130.9 (d), 131.6 (d), 133.0 (s), 134.0 (s), 135.6 (s), 143.4 (d) and 192.0 (s); *m*/*z* 322 (M^+) (Found: C, 55.71; H, 4.72. $C_{15}H_{15}BrOS$ requires C, 55.74; H, 4.68%).

6-(4-Bromobenzoyl)-2,3,4-trimethyl-2*H*-thiopyran 9b. *Colourless prisms*, mp 102–103 °C (from dichloromethane–hexane); ν_{max} (KBr)/cm^{-1} 1620 (CO); δ_H ($CDCl_3$) 1.28 (3H, d, *J* 6.8, Me), 1.84 and 1.98 (each 3H, br s, Me), 3.29 (1H, q, *J* 6.8, 2-H), 6.70 (1H, s, 5-H) and 7.56 and 7.59 (each 2H, d, *J* 9.0, ArH); δ_C ($CDCl_3$) 18.4 (q), 19.1 (q), 19.2 (q), 38.9 (d), 125.6 (s), 126.7 (s), 130.0 (s), 130.6 (d), 131.6 (d), 134.7 (s), 136.3 (s), 137.1 (d) and 193.2 (s); *m*/*z* 322 (M^+) (Found: C, 55.66; H, 4.70. $C_{15}H_{15}BrOS$ requires C, 55.74; H, 4.68%).

2-(4-Bromophenyl)-3a,6a-dihydro-3,6,6a-trimethylthieno[3,2-*b*]furan 10b. An *orange oil*; δ_H ($CDCl_3$) 1.57 (3H, s, Me), 1.83 (3H, d, *J* 1.7, Me), 1.86 (3H, d, *J* 1.3, Me), 4.64 (1H, q, *J* 1.3, 3a-H), 5.80 (1H, q, *J* 1.7, olefinic H) and 7.39 and 7.47 (each 2H, d, *J* 8.6, ArH); δ_C ($CDCl_3$) 11.9 (q), 13.0 (q), 22.8 (q), 66.6 (d), 97.6 (s), 107.0 (s), 119.1 (d), 122.0 (s), 128.9 (d), 130.5 (s), 131.2 (d), 133.8 (s) and 146.6 (s); *m*/*z* 322 (M^+).

2-[1-(4-Bromobenzoyl)ethyl]-3,4-dimethylthiophene 11b. A *colourless oil*; ν_{max} (neat)/cm^{-1} 1690 (CO); δ_H ($CDCl_3$) 1.53 (3H, d, *J* 6.8, Me), 2.10 and 2.11 (each 3H, s, Me), 4.83 (1H, q, *J* 6.8, CH), 6.76 (1H, s, thiophene ring-H) and 7.54 and 7.78 (each 2H, d, *J* 8.6, ArH); δ_C ($CDCl_3$) 12.3 (q), 15.3 (q), 19.0 (q), 41.9 (d), 119.0 (d), 128.0 (s), 130.0 (d), 131.8 (d), 132.9 (s), 135.0 (s), 136.7 (s), 138.0 (s) and 198.5 (s); *m*/*z* 322 (M^+) (Found: M^+, 322.0011. $C_{15}H_{15}BrOS$ requires *M*, 322.0027).

From the thiabenzene **6b′**, the following products were obtained after PLC on silica gel with hexane–dichloromethane (3 : 2).

2-(4-Bromobenzoyl)-2-ethyl-4,5-dimethyl-2*H*-thiopyran 7b′. A *yellow oil*; ν_{max} (neat)/cm^{-1} 1680 (CO); δ_H ($CDCl_3$) 0.91 (3H, t, *J* 7.3, CH_2CH_3), 1.85 and 1.88 (each 3H, s, Me), 2.00–2.16 (2H, m, CH_2CH_3), 5.46 and 5.92 (each 1H, br s, olefinic H) and 7.53 and 7.91 (each 2H, d, *J* 8.5, ArH); δ_C ($CDCl_3$) 8.8 (q), 20.1 (q), 20.7 (q), 31.2 (t), 57.4 (s), 113.9 (d), 118.4 (d), 126.8 (s), 130.3 (s), 131.12 (d), 131.14 (d), 134.6 (s), 135.2 (s) and 197.7 (s); *m*/*z* 336 (M^+) (Found: M^+, 336.0173. $C_{16}H_{17}BrOS$ requires *M*, 336.0183).

2-(4-Bromobenzoyl)-4-ethyl-4,5-dimethyl-4*H*-thiopyran 8b′. A *colourless oil*; ν_{max} (neat)/cm^{-1} 1655 (CO); δ_H ($CDCl_3$) 0.91 (3H, t, *J* 7.3, CH_2CH_3), 1.22 (3H, s, Me), 1.72–1.78 (2H, m, CH_2CH_3), 1.81 (3H, d, *J* 1.5, Me), 5.93 (1H, q, *J* 1.5, 6-H), 5.99 (1H, s, 3-H), 7.57 and 7.60 (each 2H, d, *J* 8.8, ArH); δ_C ($CDCl_3$) 10.0 (q), 19.8 (q), 27.1 (q), 33.3 (t), 41.6 (s), 112.5 (d), 127.1 (s), 130.8 (d), 131.2 (s), 131.6 (d), 133.4 (s), 135.6 (s), 142.5 (d) and 192.0 (s); *m*/*z* 336 (M^+) (Found: M^+, 336.0194. $C_{16}H_{17}BrOS$ requires *M*, 336.0184).

6-(4-Bromobenzoyl)-2-ethyl-3,4-dimethyl-2*H*-thiopyran 9b′. A *colourless oil*; ν_{max} (neat)/cm^{-1} 1640 (CO); δ_H ($CDCl_3$) 0.97 (3H, t, *J* 7.3, CH_2CH_3), 1.60 (2H, quint, *J* 7.3, CH_2CH_3), 1.83 and 1.99 (each 3H, br s, Me), 3.04 (1H, t, *J* 7.3, 2-H), 6.70 (1H, s, 5-H), 7.55 and 7.59 (each 2H, d, *J* 8.8, ArH); δ_C ($CDCl_3$) 11.0 (q), 18.4 (q), 20.2 (q), 25.3 (t), 46.6 (d), 126.0 (s), 130.3 (s), 130.5 (d), 131.5 (d), 133.6 (s), 136.2 (s), 137.5 (d) and 193.0 (s); *m*/*z* 336 (M^+) (Found: M^+, 336.0158. $C_{16}H_{17}BrOS$ requires *M*, 336.0184).

2-(4-Bromophenyl)-3-ethyl-3a,6a-dihydro-6,6a-dimethylthieno[3,2-*b*]furan 10b′. A *colourless oil*; δ_H ($CDCl_3$) 1.10 (3H, t, *J* 7.6, CH_2CH_3), 1.56 (3H, s, Me), 1.83 (3H, d, *J* 1.5, Me), 2.17–2.46 (2H, m, CH_2CH_3), 4.76 (1H, br s, 3a-H), 5.82 (1H, q, *J* 1.5, 5-H) and 7.36 and 7.47 (each 2H, d, *J* 8.6, ArH); δ_C ($CDCl_3$) 12.7 (q), 13.0 (q), 19.1 (t), 22.8 (q), 64.0 (d), 97.8 (s), 112.8 (s), 119.5 (d), 122.2 (s), 128.9 (d), 130.6 (s), 131.3 (d), 133.5 (s) and 146.6 (s); *m*/*z* 336 (M^+).

2-[1-(4-Bromobenzoyl)propyl]-3,4-dimethylthiophene 11b′. A *yellow oil*; ν_{max} (neat)/cm^{-1} 1680 (CO); δ_H ($CDCl_3$) 0.93 (3H, t, *J* 7.6, CH_2CH_3), 1.75–1.95 and 2.12–2.22 (each 1H, m, CH_2CH_3), 2.10 (3H, d, *J* 1.0, Me), 2.13 (3H, s, Me), 4.64 (1H, t, *J* 7.3, CHCO), 6.76 (1H, s, 5-H) and 7.54 and 7.79 (each 2H, d, *J* 8.5, ArH); δ_C ($CDCl_3$) 12.1 (q), 12.7 (q), 15.3 (q), 27.4 (t), 49.0 (d), 119.3 (d), 128.0 (s), 129.9 (d), 131.9 (d), 133.6 (s), 135.2 (s), 135.6 (s), 137.8 (s) and 198.4 (s); *m*/*z* 336 (M^+) (Found: M^+, 336.0195. $C_{16}H_{17}BrOS$ requires *M*, 336.0184).

From the thiabenzene **6d**, the following compounds were obtained after PLC on silica gel with hexane–ether (2 : 1).

2-Cyano-2,4,5-trimethyl-2*H*-thiopyran 7d and 2-(1-cyanoethyl)-3,4-dimethylthiophene 11d. An inseparable mixture, as a yellow oil; ν_{max} (neat)/cm^{-1} 2220 (CN); *m*/*z* 165 (M^+) (Found: M^+, 165.0619. $C_9H_{11}NS$ requires *M*, 165.0612); δ_H ($CDCl_3$) assigned to **7d**: 1.78 (3H, s, Me), 1.88 and 1.98 (each 3H, d, *J* 1.5, Me) and 5.23 and 6.08 (each 1H, br s, olefinic H); δ_H ($CDCl_3$) assigned to **11d**: 1.25 (3H, d, *J* 6.8, Me), 1.84 and 1.93 (each 3H, s, Me), 3.17 (1H, q, *J* 6.8, CHCN) and 6.71 (1H, s, 5-H).

2-Cyano-4,4,5-trimethyl-4*H*-thiopyran 8d. A *pale orange oil*; ν_{max} (neat)/cm^{-1} 2230 (CN); δ_H ($CDCl_3$) 1.20 (6H, s, 2 × Me), 1.85 (3H, d, *J* 1.5, Me), 5.80 (1H, q, *J* 1.5, 6-H), 6.21 (1H, s, 3-H); *m*/*z* 165 (M^+) (Found: M^+, 165.0611. $C_9H_{11}NS$ requires *M*, 165.0612).

Bis(6-cyano-3,4-dimethyl-2*H*-thiopyran-2-yl) 12d. *Yellow prisms*, mp 189–190 °C (from ethanol); ν_{max} (KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$) 1.82 and 1.87 (each 6H, s, 2 × Me), 3.27 (2H, s, 2-H), 6.83 (2H, s, olefinic H); δ_C ($CDCl_3$) 18.2 (q), 21.8 (q), 44.8 (d), 100.7 (s), 116.4 (s), 128.1 (s), 129.1 (s) and 138.0 (d); *m*/*z* 150 (base, M^+/2) (Found: C, 63.97; H, 5.37; N, 9.32. $C_{16}H_{16}N_2S_2$ requires C, 63.88; H, 5.39; N, 9.26%).

2-[4-Bromobenzoyl(methylsulfanyl)methyl]-3,4-dimethylthiophene 15

NCS (452 mg, 3.38 mmol) was added to an ice-cooled solution of 4-bromophenacyl methyl sulfide[13] (798 mg, 3.26 mmol) in tetrachloromethane (15 cm^3) with stirring. The mixture was stirred for 2 h and the precipitate was filtered off. The filtrate was concentrated under reduced pressure and dichloromethane (8 cm^3) and 3,4-dimethylthiophene[18] **13** (1.83 g, 16.3 mmol) were added to the residue. This mixture was ice-cooled and zinc chloride (311 mg, 2.28 mmol) was added with stirring. After the reaction mixture had been stirred for 40 min, water was added and the organic layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the mixture gave a crude oil, which was chromatographed on silica gel with hexane–ethyl acetate (100 : 1) to afford **15** (448 mg, 38.7%) as a *pale yellow oil*; ν_{max} (neat)/cm^{-1} 1675 (CO); δ_H ($CDCl_3$) 2.05, 2.12 and 2.15 (each 3H, s, Me) and 5.67 (1H, s, CH), 6.89 (1H, br s, 5-H) and 7.58 and 7.87 (each 2H, d, *J* 8.5, ArH); δ_C ($CDCl_3$) 12.9 (q), 13.6 (q), 15.1 (q), 47.7 (d), 121.3 (d), 128.4 (s), 130.2 (d), 130.7 (s), 131.9 (d), 134.2 (s), 135.2 (s), 137.5 (s) and 191.4 (s); *m*/*z* 354 (M^+) (Found: M^+, 353.9728. $C_{15}H_{15}BrOS_2$ requires *M*, 353.9747).

2-(4-Bromophenacyl)-3,4-dimethylthiophene 16

Zinc dust (1.4 g, 21 mmol) was added to a solution of **15** (350 mg, 0.99 mmol) in acetic acid (5 cm^3) and the mixture was stirred at 100 °C for 1 h. The cooled reaction mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The oily residue was purified by PLC on silica gel with hexane–ethyl acetate (40 : 1) to afford **16** (81 mg, 27%) as a *pale orange oil*; ν_{max} (neat)/cm^{-1} 1690 (CO); δ_H ($CDCl_3$) 2.04 (3H, s, Me), 2.06 (3H, br s, Me), 4.32 (2H, s, CH_2), 6.79 (1H, s, 5-H) and 7.60 and 7.86 (each 2H, d, *J* 8.5, ArH); δ_C ($CDCl_3$) 12.5 (q), 15.3 (q), 38.3 (t), 118.9 (d), 128.3 (s), 128.4 (s), 130.0 (d), 131.9 (d), 135.0 (s), 135.2 (s), 137.9 (s) and 195.0 (s); *m*/*z* 308 (M^+) (Found: M^+, 307.9845. $C_{14}H_{13}BrOS$ requires *M*, 307.9870).

2-[1-(4-Bromobenzoyl)ethyl]-3,4-dimethylthiophene 11b

Butyllithium (1.62 mol dm^{-3} solution in hexane; 0.25 cm^3, 0.41 mmol) was added with stirring to a solution of diisopropylamine (0.1 cm^3, 0.41 mmol) in dry THF (5 cm^3) at −30 °C under nitrogen. After 30 min, a solution of **16** (58 mg, 0.19 mmol) in dry THF (2 cm^3) was added in a stream of nitrogen to

the above solution at −70 °C. After the mixture had been stirred for 50 min at the same temperature, methyl iodide (0.1 cm^3, 1.6 mmol) was added and the mixture was allowed to warm to room temperature. Saturated aq. NH_4Cl was added and the mixture was extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residual oil was subjected to PLC on silica gel with hexane–ethyl acetate (13 : 1) to afford **11b** (29 mg, 48%) as a *colourless oil*. This compound showed the same spectral properties as those of compound **11b** obtained from thermolysis of **6b**.

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