Ring transformation of the adducts of the polar cycloadditions of 2-benzothiopyrylium salts

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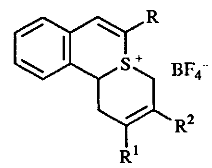
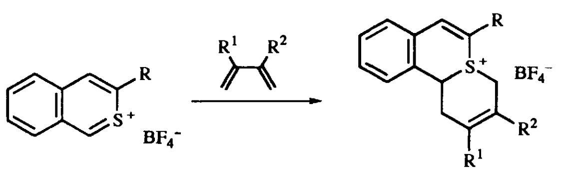
Ring transformation of the adducts **1** of the polar cycloadditions of 2-benzothiopyrylium salts induced by a variety of bases and reducing agents has been investigated. Treatment of the 9-unsubstituted cycloadducts **1a**, **b**, **c** with strong bases such as lithium diisopropylamide (LDA), sodium hydride and potassium carbonate afforded the vinylcyclopropane derivatives **2** and the 1,5-methano-2-benzothionines **3**. In contrast, treatment of compound **1a** with weak bases such as triethylamine, diethylamine and potassium acetate gave no compounds **2a** or **3a**, but only ring-opened compounds **4a** in high yields *via* S_N2-type processes. In these reactions, weak bases acted as nucleophiles. In contrast, the 9-benzoyl cycloadduct **1d** reacted with both weak and strong bases to afford, mainly, the similar ring-transformed product **2d**. Whilst the strong base LDA gave compound **3d** (as a minor product) in addition to compound **2d**, weak bases such as diethylamine and butylamine also acted as nucleophiles to give the corresponding ring-opened compounds **4d** as minor products. A mechanistic interpretation of the above reactions is presented. When heated at high temperature, the vinylcyclopropane **2d** was converted into the cyclopentene derivative **5**. Ring transformations of compounds **1** with reducing agents such as sodium borohydride and samarium diiodide are also described.

In our recent paper, we described the interesting [$2^+ + 4$] polar cycloaddition of 2-benzothiopyrylium salts **I** with various 1,3-dienes affording benzo-fused bicyclic sulfonium salts, 4b,5-dihydro-8*H*-8a-thioniaphenanthrenes **1**, having sulfur at a bridgehead position in excellent yields.[1] We thought it would be interesting to investigate the transformation of the cycloadducts **1** into compounds having new skeletons as a consequence of the sulfonium ion structures. In this paper, we describe the ring transformation of the cycloadducts **1** by treatment with a variety of bases and reducing agents.

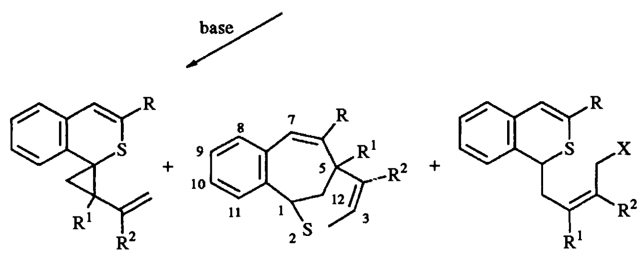


1a R = H, $R^1 = R^2$ = Me
b R = H, R^1 = Me, R^2 = H
c R = $R^1 = R^2$ = H
d R = Bz, $R^1 = R^2$ = Me



I 1

Scheme 1



2 3 4

Scheme 2

Results and discussion

The 9-unsubstituted compounds **1a–c** and 9-benzoyl-4b,5-dihydro-8*H*-8a-thioniaphenanthrene tetrafluoroboranuide **1d** reacted with the strong bases lithium diisopropylamide (LDA) NaH and K_2CO_3 and the weak bases Et_3N, Et_2NH, $BuNH_2$ and KOAc to afford three types of product: the vinylcyclopropane derivatives **2**, 1,5-methano-2-benzothionine **3**, and 1-(4-functionized but-2-enyl)-1*H*-2-benzothiopyrans **4** (see Scheme 2). The product distribution was found to depend upon the nature of the bases used and the substituent at the 9-position of the cycloadducts **1** (see Table 1). Treatment of the 9-unsubstituted cycloadducts **1a–c** with strong and non-nucleophilic bases such as LDA, NaH and K_2CO_3 afforded the compounds **2a–c** and **3a–c** (entries 1, 2 and 6–8), while upon treatment with weak and nucleophilic bases such as alkylamines and KOAc, the cycloadduct **1a** failed to give compounds **2a** or **3a** but, instead produced 1-(but-2-enyl)-2-benzothiopyrans $\mathbf{4a_1}$–$\mathbf{a_3}$ in high yields (entries 3–5). In contrast, the 9-benzoyl cycloadduct **1d** reacted with both weak and strong bases to afford the corresponding vinylcyclopropane derivative **2d** as a major product (entries 9–15). In particular, treatment with the strong base LDA yielded a small amount of compound **3d** as a by-product (entry 9). Furthermore, weak and nucleophilic bases such as diethylamine and butylamine also acted as nucleophiles to give the corresponding 1-(but-2-enyl)-2-benzothiopyrans $\mathbf{4d_1}$ and $\mathbf{4d_2}$ as minor products, respectively.

Structural identification of the above products was established mainly on the basis of spectroscopic evidence (see the Experimental section). For example, the structures of **2a**, **3c** and $\mathbf{4a_3}$ as typical compounds were elucidated as follows. Elemental analysis and mass spectral data [*m/z* 228(M^+)] indicate a molecular formula of $C_{15}H_{16}S$ for compound **2a**. The ^1H NMR spectrum ($CDCl_3$) of **2a** showed a singlet for the methyl group on the cyclopropane ring at δ 0.79, two doublets (*J* 6.4 Hz) for the methylene group of the cyclopropane ring at δ 1.30 and 1.63, a broad singlet for the vinylic methyl group at δ

Table 1 Reactions of the sulfonium salts **1** with various bases

Entry	Sulfonium salt	Base	Solvent	Temp (*T*/°C)	Products (% yield) 2	3	4
1	**1a**	LDA	THF	−78–0	**2a** (35)	**3a** (52)	
2	**1a**	NaH	DMF	0–RT	**2a** (28)	**3a** (70)	
3	**1a**	Et_3N	$(CH_2Cl)_2$	0–RT			$\mathbf{4a_1}$(88)[a]
4	**1a**	Et_2NH	$(CH_2Cl)_2$	RT			$\mathbf{4a_2}$(72)[b]
5	**1a**	AcOK	$(CH_2Cl)_2$	RT			$\mathbf{4a_3}$(91)[c]
6	**1a**	K_2CO_3	Acetone	RT	**2a** (21)	**3a** (20)	
7	**1b**	NaH	DMF	0	**2b** (44)	**3b** (45)	
8	**1c**	NaH	DMF	0	**2c** (46)	**3c** (45)	
9	**1d**	LDA	THF	−78–0	**2d** (57)	**3d** (7)	
10	**1d**	NaH	THF	0–RT	**2d** (75)		
11	**1d**	Et_3N	$(CH_2Cl)_2$	0–RT	**2d** (70)		
12	**1d**	Et_2NH	$(CH_2Cl)_2$	RT	**2d** (56)		$\mathbf{4d_1}$(22)[b]
13	**1d**	$BuNH_2$	$(CH_2Cl)_2$	RT	**2d** (45)		$\mathbf{4d_2}$(34)[d]
14	**1d**	AcOK	$(CH_2Cl)_2$	RT	**2d** (84)		
15	**1d**	K_2CO_3	Acetone	Reflux	**2d** (64)		

[a] X = NEt_3BF_4. [b] X = NEt_2. [c] X = OAc. [d] X = NHBu.

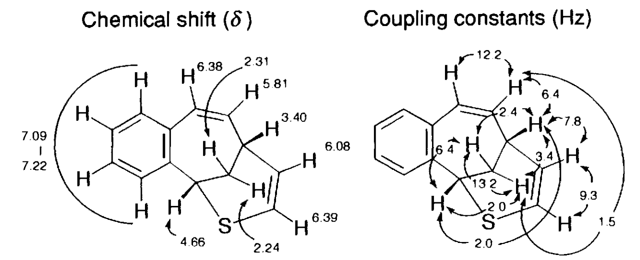
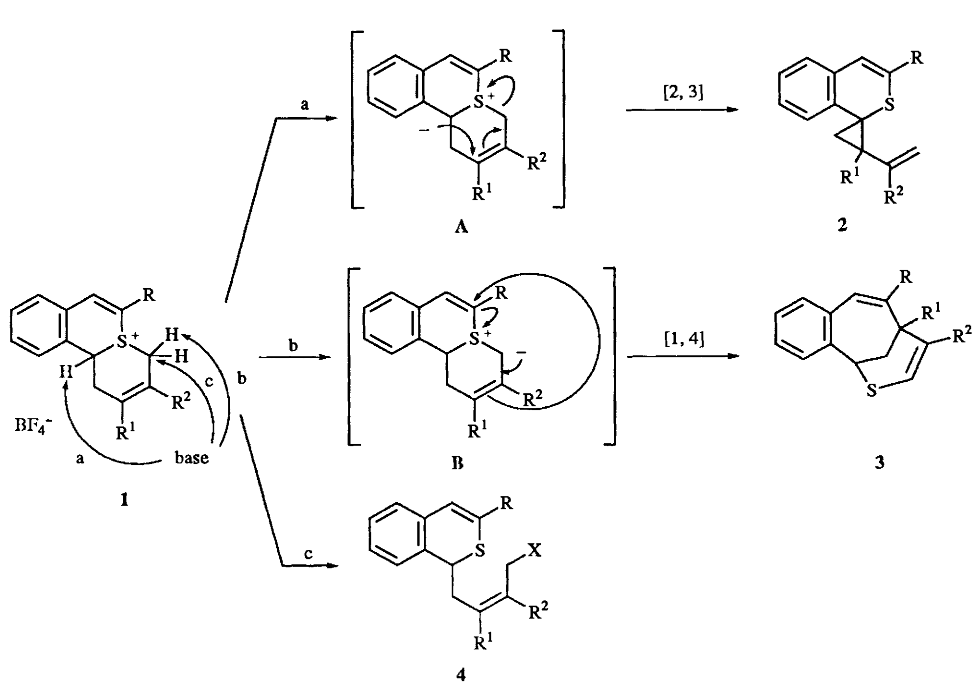


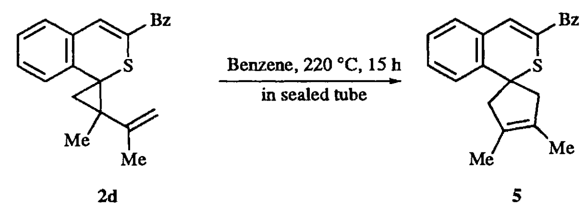
Fig. 1 ^1H NMR chemical shifts and coupling constants between the correlated protons of compound **3c**

1.79, two broad singlets for the vinylic methylene protons at δ 4.88 and 5.03, a doublet (*J* 9.8 Hz) for 3-H at δ 6.52, a doublet (*J* 9.8 Hz) for 4-H at δ 6.73, and a multiplet for the four aromatic protons at δ 7.05–7.28. The ^{13}C NMR spectrum ($CDCl_3$) of compound **2a** showed two methyl carbons at δ 18.8 and 20.9, an sp^3-secondary carbon at δ 19.1, an sp^2-secondary carbon at δ 114.0, two sp^3-quaternary carbons at δ 31.3 and 40.0, six sp^2-tertiary carbons and three sp^3-quaternary carbons at δ 130.1, 135.3 and 146.5. Elemental analysis and mass spectral data [*m/z* 200 (M^+)] indicate a molecular formula of $C_{13}H_{12}S$ for compound **3c**. Assignments for compound **3c** in the ^1H NMR spectrum ($CDCl_3$) were based on a ^1H-^1H COSY experiment. The assigned chemical shifts and coupling constants between the correlated protons are shown in Fig. 1. The ^{13}C NMR spectrum ($CDCl_3$) of compound **3c** exhibited a methylene carbon at δ 28.2, two methine carbons at δ 34.4 and 43.4, four sp^2-tertiary carbons of olefinic bonds, four sp^2-aromatic tertiary carbons, and two sp^2-quaternary carbons. For compound $\mathbf{4a_3}$, elemental analysis and mass spectral data [*m/z* 288 (M^+)] show a molecular formula of $C_{17}H_{20}O_2S$ for this compound. The IR spectrum exhibited an ester carbonyl band at 1730 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) revealed a singlet for two vinylic methyl groups at δ 6.3, a singlet for the acetoxy methyl group at δ 1.99, a doublet (*J* 7.8 Hz) for the methylene group at δ 2.57, a doublet of triplets (*J* 7.8 and 2.0 Hz) for the methine proton at δ 3.82, a doublet of doublets (*J* 9.3 and 2.0 Hz) for 3-H at δ 6.32, and a doublet (*J* 9.3 Hz) for 4-H at δ 6.74. ^{13}C NMR ($CDCl_3$) showed three methyl carbons at δ 16.5, 19.2, and 20.9, two methylene carbons at δ 39.5 and 64.6, an sp^3-tertiary carbon at δ 41.3 and an ester carbonyl carbon at δ 170.9. A plausible mechanistic rationalization for the ring transformation of cycloadduct **1** caused by various bases is based on the basic strength and nucleophilicity of the bases used. The reaction course might be divided into three paths, a, b and c as shown in Scheme 3. Path a in which the bases abstract the acidic benzylic proton of the sulfonium compound **1** leads to the ylide intermediate **A**. Intermediate **A** undergoes then a 2,3-sigmatropic rearrangement to construct the cyclopropane ring and afford compound **2**. The similar 2,3-sigmatropic rearrangement of other types of cyclic allyl sulfonium ylides into vinylcyclopropanes has been observed.[2-4] Path b in which the bases abstract a further acidic proton of the sulfonium compound **1** forms another ylidic intermediate **B**, which rearranges *via* a 1,4-rearrangement of the vinyl group to the allylic position along with cleavage of the vinyl–sulfur bond to give compound **3**. This easy migration of the vinyl group might be rationalized by the proximate position between the vinyl group and allylic group based upon the *cis* fused stereochemistry at positions 4b and 8a as reported in our previous paper.[1] Bases which nucleophilically attack the allylic carbon of the sulfonium compound **1** together with fission of the carbon–sulfur bond afford compound **4** as shown in Scheme 3. The product distribution in the above reaction was strongly influenced by the substituent at the 9-position of the sulfonium compound **1** and the nature of the bases as summarized in Table 1. These phenomena may be rationally explained as follows. In the case of the 9-unsubstituted compounds **1a–c**, all the bases with either low or no nucleophilicity abstract the highly acidic benzylic and allylic protons and produce the compounds **2** and **3** *via* paths a and b, respectively, while nucleophilic bases predominate the nucleophilic attack at the allylic carbon to afford only compound **4** by path c. In contrast, for the case of the 9-benzoyl substituted compound **1d**, all the bases with and without nucleophilicity predominantly abstract the most acidic protons activated by the electron-withdrawing group to mainly give compound **2d** *via* path a, and a strong base such as LDA also abstracts the allylic proton to afford **3d** in low yield, while highly nucleophilic amines also attack the allylic carbon to afford compound $\mathbf{4d_1}$ or $\mathbf{4d_2}$ as minor products by path c, respectively.

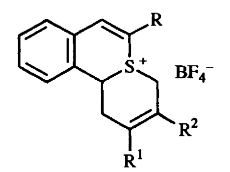
The thermal ring transformation of vinylcyclopropanes to cyclopentenes has been observed.[2-4] Therefore, we attempted the thermal reaction of the cyclopropane derivative **2d** we obtained. When the benzene solution was heated at 220 °C in a sealed tube, compound **2d** underwent rearrangement to give the expected spiro cyclopentene derivative **5** but in low yield (34%) (Scheme 4).



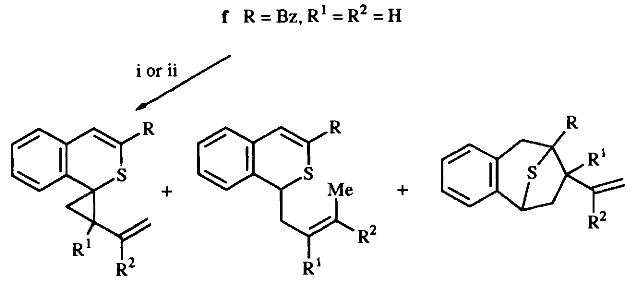
Scheme 3



Scheme 4



1a R = H, $R^1 = R^2$ = Me
d R = Bz, $R^1 = R^2$ = Me
e R = Bz, R^1 = Me, R^2 = H
f R = Bz, $R^1 = R^2$ = H



2 **6** **7**

Scheme 5 *Reagents and conditions*: i, $NaBH_4$, EtOH, room temp.; ii, $NaBH_3CN$, THF, room temp.

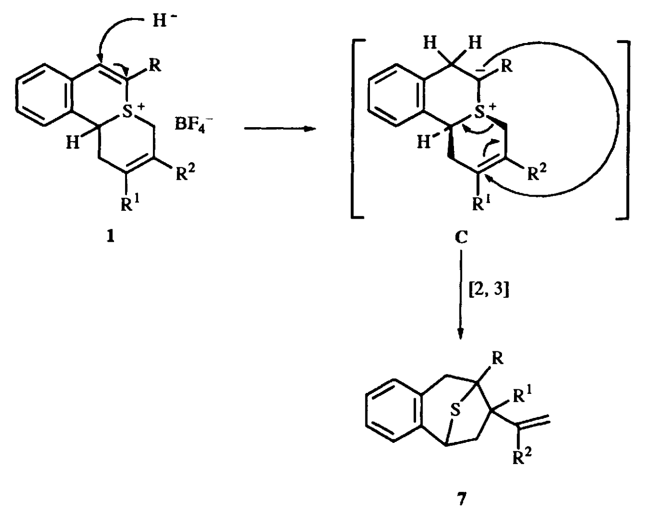
Because we have recently found that bicyclic sulfonium salts with a sulfur atom at a bridgehead are easily reduced to sulfur-containing, ten-membered rings,[5] we next investigated reduction of the cycloadducts **1** in the hope that their ring transformation was dependent on the sulfonium structure. Although treatment of the cycloadduct **1a** with sodium borohydride in ethanol afforded compound **6a** (84%) by attack of a hydride ion on the allylic carbon, the cycloadduct **1d** when treated similarly gave the epithiobenzocycloheptene **7d** (17%) and the vinyl spiro cyclopropane derivative **2d** (7%), but no compound **6a**. Similarly, reduction of the cycloadducts **1d**, **1e** and **1f** with sodium borocyanohydride in THF afforded compounds **7d**, **7e** and **7f** in 44, 36 and 36% yields, together with traces of compounds **2d**, **2e** and **2f**, respectively (Scheme 5 and Table 2). Structural identification of the above products was established on the basis of spectroscopic evidence (see the Experimental section). For example, the structural assignment of compound **7d** was made as follows. The IR spectrum revealed a benzoyl carbonyl band at 1665 cm^{-1}, the mass spectrum showed a molecular ion peak at *m/z* 334; the ^1H NMR spectrum ($CDCl_3$) revealed a doublet of doublets (*J* 13.2 and 6.4 Hz) for one of the 6-methylene protons at δ 2.82, a doublet (*J* 13.2 Hz) for another of the methylene protons at δ 2.11, a doublet (*J* 6.4 Hz) for a 5-methine proton at δ 4.20, two doublets with only geminal coupling (*J* 17.6 Hz) for the 9-methylene protons at δ 3.56 and 3.72, and two broad singlets for the vinylic methylene protons at δ 4.89 and 5.20. The ^{13}C NMR spectrum ($CDCl_3$) showed peaks for two sp^3 quaternary carbons at δ 55.7 and 73.6, two sp^3-secondary carbons at δ 42.7 and 56.2, a tertiary carbon at δ 49.0, and a carbonyl carbon at δ 204.0.

A plausible mechanism for the formation of compound **7** may be explained by postulating an intermediate **C**, derived from a Michael-type addition of the hydride ion to the vinylic carbon (C-10), because the carbon is strongly activated by benzoyl and sulfonio groups (Scheme 6), which then undergoes a 2,3-sigmatropic rearrangement to give compound **7**. The non-formation of **7** from compound **1a** may be rationalized in terms of the low stability of the intermediate **C**, and its reduced ability to act as a Michael acceptor of the vinylic carbon (C-10), because of the absence of an electron-withdrawing benzoyl group. The formation of compound **2** may be understood in terms of a hydride ion having acted as a base.

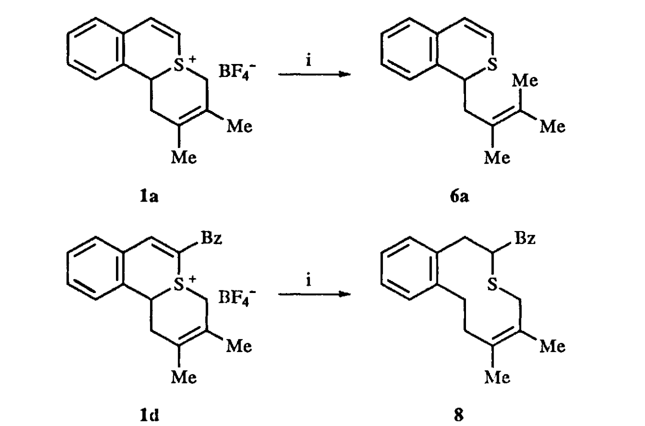
Finally, we investigated the reduction of compound **1a** with a single-electron transfer reducing agent, samarium diiodide (Scheme 7) in THF in the presence of methanol at room temperature. This afforded the ring-opened compound **6a** (63%), while compound **1d**, under similar conditions, gave the

Table 2 Hydride reductions of the sulfonium salts **1**

	Reactants		Conditions		Products (% yield)		
Entry	Salt	Reducing agent	Solvent	Time (min)	6	7	2
1	**1a**	$NaBH_4$	EtOH	10	**6a** (84)		
2	**1d**	$NaBH_4$	EtOH	15		**7d** (17)	**2d** (7)
3	**1d**	$NaBH_3CN$	THF	60		**7d** (44)	**2d** (trace)
4	**1e**	$NaBH_3CN$	THF	30		**7e** (36)	**2e** (trace)
5	**1f**	$NaBH_3CN$	THF	15		**7f** (36)	**2f** (trace)



Scheme 6



Scheme 7 *Reagents and conditions*: i, SmI_2, MeOH, THF, room temp.

ring-expanded product **8** along with a further reduction in one of the double bonds in 20% yield.

Experimental

Mps were determined using a Yanagimoto micromelting point apparatus, and are uncorrected. IR spectra were measured using a JASCO A-1 spectrophotometer and ^1H and ^{13}C NMR spectra were recorded on a JEOL GX-270 (270 MHz) and EX-400 (400 MHz) spectrometers with tetramethylsilane as the internal standard. The chemical shifts are given as δ values (ppm) with coupling constants in Hz. All ^{13}C data are quoted with ^1H multiplicities (off-resonance results in brackets), although this multiplicity was usually inferred from the DEPT experiment. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. High-resolution mass determination was conducted using a JMA 2000 on-line system. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Analytical and preparative TLC (PLC) were performed on Merck silica gel 60PF-254 plates.

General procedure for the reaction of the cycloadducts 1a–d with a variety of bases

The results including reaction conditions and yields are summarized in Table 1.

(a) With lithium diisopropylamide (LDA). Butyllithium (1.62 mol dm^{-3} solution in hexane; 1.2 mmol) was added with stirring to diisopropylamine (1.2 mmol) in dry THF (10 cm^3) at -30 °C under nitrogen. After 30 min, the cycloadducts **1** (1 mmol) were added in a stream of nitrogen at -78 °C to the mixture which was then stirred for 1 h before being allowed to warm to 0 °C. Aq. NH_4Cl was added to the reaction mixture which was then extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to afford a residue which was subjected to PLC on silica gel. The following products were obtained from the cycloadduct **1a** after PLC on silica gel with hexane–dichloromethane (6:1).

2′-Isopropenyl-2′-methylspiro[1*H*-2-benzothiopyran-1,1′-cyclopropane] **2a**; columns, mp 103–105 °C (from MeOH); $\delta_H(CDCl_3)$ 0.79 (3 H, s, Me), 1.30 and 1.63 (each 1 H, each d, *J* 6.4, cyclopropane CH_2), 1.79 (3 H, s, CH_2=C*Me*), 4.88–4.89 (1 H, m, =C*H*H), 5.02–5.03 (1 H, m, C=CH*H*), 6.52 (1 H, d, *J* 9.8, 3′-H), 6.73 (1 H, d, *J* 9.8, 4′-H), 7.05–7.08 (1 H, m, ArH), 7.11–7.14 (1 H, m, ArH) and 7.19–7.28 (2 H, m, ArH); $\delta_C(CDCl_3)$ 18.8 (q), 19.1 (t), 20.9 (q), 31.1 (s), 40.0 (s), 114.0 (t), 124.6 (d), 124.9 (d), 125.9 (d), 126.6 (d), 126.8 (d), 127.4 (d), 130.1 (s), 135.3 (s) and 146.5 (s); *m/z* 228 (M^+), 213 (base) (Found: C, 78.6; H, 7.2%; M^+, 228.0981. $C_{15}H_{16}S$ requires C, 78.90; H, 7.06%; *M*, 228.0973).

4,5-Dimethyl-1,5-methano-2-benzothionine **3a**; an oil; $\delta_H(CDCl_3)$ 1.32 (3 H, s, Me), 1.88 (3 H, d, *J* 1, CH=C*Me*), 2.12 (1 H, ddd, *J* 13.7, 6.8 and 2, C*H*H), 2.27 (1 H, dd, *J* 13.7 and 1.5, CH*H*), 4.54 (1 H, dd, *J* 6.8 and 1.5, 1-H), 5.62 (1 H, dd, *J* 12.2 and 2, 6-H), 6.05 (1 H, d, *J* 1, 3-H), 6.27 (1 H, d, *J* 12.2, 7-H), 7.05–7.12 (2 H, m, ArH) and 7.14–7.22 (2 H, m, ArH); $\delta_C(CDCl_3)$ 20.6 (q), 26.2 (q), 38.4 (t), 40.0 (s), 42.7 (d), 117.6 (d), 126.5 (d), 126.7 (d), 127.3 (d), 129.2 (d), 132.7 (d), 134.7 (s), 135.1 (s), 135.6 (d) and 142.8 (s); *m/z* 228 (M^+) and 116 (base) (Found: C, 78.6; H, 7.1%; M^+, 228.0956. $C_{15}H_{16}S$ requires C, 78.90; H, 7.06%; *M*, 228.0972).

From the cycloadduct **1d**, the following products were obtained after PLC on silica gel with hexane–ethyl acetate (6:1).

3-Benzoyl-2′-isopropenyl-2′-methylspiro[1*H*-2-benzothio-pyran-1,1′-cyclopropane] **2d**; yellow plates, mp 121–121.5 °C (from dichloromethane–hexane); $\nu_{max}(KBr)/cm^{-1}$ 1640 (CO); $\delta_H(CDCl_3)$ 0.83 (3 H, s, Me), 1.43 and 1.69 (each 1 H, each d, *J* 6.4; cyclopropane CH_2), 1.76 (3 H, s, =CMe), 4.93 and 5.02 (each 1 H, each br s, =CH_2), 7.14–7.28 (3 H, m, ArH), 7.37–7.61 (5 H, m, ArH and 4′-H) and 7.75–7.79 (2 H, m, ArH); $\delta_C(CDCl_3)$ 18.9 (s), 19.4 (t), 20.9 (q), 31.5 (s), 40.1 (s), 114.9 (t), 124.8 (d), 126.8 (d), 128.4 (d), 129.0 (d), 129.2 (d), 130.1 (d), 132.2 (d), 132.5 (s), 134.9 (s), 135.2 (d), 136.8 (s), 140.3 (s), 145.2

(s) and 193.3 (s); *m/z* 332 (M^+) (Found: C, 79.7; H, 6.1. $C_{22}H_{20}OS$ requires C, 79.48; H, 6.06%).

6-Benzoyl-4,5-dimethyl-1,5-methano-2-benzothionine **3d**; pale yellow plates, mp 135–135.5 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1} 1650 (CO); δ_H($CDCl_3$) 1.57 (3 H, s, Me), 1.92 (3 H, s, Me), 1.99 (1 H, dd, *J* 13.2 and 7.8, C*H*H), 2.34 (1 H, d, *J* 13.2, CH*H*), 4.49 (1 H, d, *J* 7.8, 1-H), 6.23 (1 H, s, 3-H), 6.74 (1 H, s, 7-H), 7.16–7.26 (4 H, m, ArH), 7.38–7.44 (2 H, m, ArH), 7.51–7.56 (1 H, m, ArH) and 7.85 (2 H, br d, *J* 7.8, ArH); δ_C($CDCl_3$) 21.5 (q), 24.7 (q), 42.2 (d), 43.0 (t), 43.0 (s), 119.3 (d), 127.5 (d), 127.9 (d), 133.2 (d), 133.9 (d), 135.6 (d), 139.0 (s), 139.1 (s), 141.8 (s), 144.6 (s) and 199.4 (s); *m/z* 332 (M^+) (Found: C, 79.3; H, 6.2. $C_{22}H_{20}OS$ requires C, 79.48; H, 6.06%).

(b) With sodium hydride. Sodium hydride (60% dispersion in mineral oil; 0.6 mmol) was added portionwise with stirring to an ice-cooled solution of the cycloadduct **1a-d** (0.5 mmol) in dry THF or DMF (5 cm^3) under nitrogen, and the mixture was stirred for 30 min. The reaction mixture was poured into ice–water and extracted with ethyl acetate. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residue was purified by PLC on silica gel. The following products were obtained from the cycloadduct **1b**.

2′-Methyl-2′-vinylspiro[1*H*-2-benzothiopyran-1,1′-cyclopropane] **2b**; a pale yellow oil, δ_H($CDCl_3$) 0.75 (3 H, s, Me), 1.30 and 1.71 (each 1 H, each d, *J* 6.8, CH_2), 5.07 (1 H, dd, *J* 17.1 and 1.0, CH=C*H*H), 5.13 (1 H, dd, *J* 10.7 and 1.0, CH=CH*H*), 6.16 (1 H, dd, *J* 17.1 and 10.7, C*H*=CH_2), 6.49 (1 H, d, *J* 9.8, 3-H′), 6.73 (1 H, d, *J* 9.8, 4-H′), 7.04–7.12 (2 H, m, ArH) and 7.18–7.25 (2 H, m, ArH); δ_C($CDCl_3$) 17.4 (q), 20.9 (t), 32.5 (s), 33.6 (s), 113.6 (t), 124.2 (d), 124.8 (d), 126.2 (d), 126.5 (d), 126.6 (d), 127.5 (d), 130.8 (s), 135.6 (s) and 141.8 (s); *m/z* 214 (M^+) and 199 (base) (Found: M^+, 214.0829. $C_{14}H_{14}S$ requires *M*, 214–0817).

5-Methyl-1,5-methano-2-benzothionine **3b**; an oil, δ_H($CDCl_3$) 1.30 (3 H, s, Me), 1.98 (1 H, ddd, *J* 13.2, 6.8 and 2.4, 12-H), 2.26 (1 H, br, d, *J* 13.2, 12-H), 4.60 (1 H, dd, *J* 6.8 and 1.5, 1-H), 5.49 (1 H, dd, *J* 12.7 and 2.4, 6-H), 5.84 (1 H, d, *J* 9.3, 4-H), 6.24 (1 H, d, *J* 12.7, 7-H), 6.43 (1 H, d, *J* 9.3, 3-H), 7.07–7.09 (2 H, m, ArH) and 7.13–7.18 (2 H, m, ArH); δ_C($CDCl_3$) 29.2 (q), 36.5 (t), 37.2 (s), 43.7 (d), 124.1 (d), 126.5 (d), 127.4 (d), 129.1 (d), 129.4 (d), 132.8 (d), 134.5 (s), 136.8 (d) and 142.7 (s); *m/z* 214 (M^+, base) (Found: C, 78.5; H, 6.7%; M^+, 214.0829. $C_{14}H_{14}S$ requires C, 78.46; H, 6.58%; *M*. 214.0816).

From the cycloadduct **1c**, the following products were obtained after PLC on silica gel. 2-Vinylspiro[1*H*-2-benzothiopyran-1,1′-cyclopropane] **2c**; a pale yellow oil, δ_C($CDCl_3$) 1.13 (1 H, dd, *J* 6.8 and 6.4, CHC*H*H), 1.58 (1 H, ddd, *J* 8.8, 8.3 and 6.8, C*H*CH_2), 1.87 (1 H, dd, *J* 8.8 and 6.4, CHCH*H*), 5.13 (1 H, br d, *J* 10.3, CH=C*H*H), 5.14 (1H, br d, *J* 17.1, CH=CH*H*), 5.88 (1H, ddd, *J* 17.1, 10.3 and 8.3, C*H*=CH_2), 6.43 (1 H, d, *J* 9.8, 3-H), 6.72 (1 H, d, *J* 9.8, 4-H), 6.92–6.96 (1 H, m, ArH) and 7.05–7.22 (3 H, m, ArH); δ_C($CDCl_3$) 17.9 (t), 29.0 (s), 34.9 (d), 116.4 (t), 121.0 (d), 123.6 (d), 125.9 (d), 126.7 (d), 126.9 (d), 128.4 (d), 133.9 (s), 134.6 (s) and 136.3 (d); *m/z* 200 (M^+) and 199 (base) (Found: M^+, 200.0673. $C_{13}H_{12}S$ requires *M*, 200.0661).

1,5-Methano-2-benzothionine **3c**; plates, mp 62–63 °C (from methanol); δ_H($CDCl_3$) 2.24 (1 H, dddd, *J* 13.2, 6.4, 3.4 and 1.5, 12-H), 2.31 (1 H, ddd, *J* 13.2, 2.4 and 2.0, 12-H), 3.40 (1 H, ddddd, *J* 7.8, 6.4, 3.4, 2.4 and 2.0, 5-H), 4.66 (1 H, dt, *J* 6.4 and 2.0, 1-H), 5.81 (1 H, ddd, *J* 12.2, 6.4 and 1.5, 6-H), 6.08 (1 H, dd, *J* 9.3 and 7.8, 4-H), 6.38 (1 H, d, *J* 12.2, 7-H), 6.39 (1 H, d, *J* 9.3, 3-H) and 7.09–7.22 (4 H, m, ArH); δ_C($CDCl_3$) 28.2 (t), 34.4 (d), 43.4 (d), 122.8 (d), 123.5 (d), 126.6 (d), 127.3 (d), 128.8 (d), 129.5 (d), 131.4 (d), 133.1 (d), 134.7 (s) and 143.0 (s); *m/z* 200 (M^+, base) (Found: C, 77.8, H, 6.1. $C_{13}H_{12}S$ requires C, 77.95; H, 6.04%).

(c) With triethylamine. The cycloadduct **1a** or **1d** (0.5 mmol) was added with stirring to an ice-cooled solution of triethylamine (1 mmol) in 1,2-dichloroethane (5 cm^3), and the mixture was stirred for 30 min. After this it was poured into water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC on silica gel with hexane–ethyl acetate (4:1).

2,3-Dimethyl-4-(1*H*-2-benzothiopyran-1-yl)but-2-enyl(triethyl)ammonium tetrafluoroboranuide **4a$_1$** from the cycloadduct **1a** after precipitation by addition of diethyl ether to the reaction mixture; leaflets, mp 138.5–139 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1080–1030 (BF_4^-); δ_H($CDCl_3$) 1.25 (9 H, t, *J* 6.8, 3 × CH_2*Me*), 1.79 (3 H, s, Me), 1.82 (3 H, s, Me), 2.54 and 2.55 (each 1 H, each dd, *J* 13.7 and 7.3, CHC*H*$_2$), 3.11 (3 H, dq, *J* 14.2 and 6.8, 3 × C*H*HMe), 3.14 (3 H, dq, *J* 14.2 and 6.8, 3 × CH*H*Me), 3.31 (2 H, s, C*H*$_2$$N^+Et_3$), 3.90 (1 H, dt, *J* 7.3 and 1.5, C*H*CH_2), 6.44 (1 H, dd, *J* 9.3 and 1.5, 3′-H), 6.81 (1H, d, *J* 9.3, 4′-H), 6.94–6.97 (1 H, m, ArH), 7.14–7.18 (1 H, m, ArH) and 7.20–7.31 (2 H, m, ArH); δ_C($CDCl_3$) 7.9 (q), 20.1 (q), 20.2 (q), 40.3 (d), 40.3 (t), 53.5 (t), 59.3 (t), 120.3 (d), 120.9 (s), 123.9 (d), 127.1 (d), 127.5 (d), 128.0 (d), 128.2 (d), 130.1 (s), 131.0 (s) and 141.5 (s) (Found: C, 60.2; H, 7.8; N, 3.3. $C_{21}H_{32}BF_4NS$ requires C, 60.44; H, 7.73; N, 3.36%).

(d) With diethylamine. A mixture of the cycloadduct **1a** or **1d** (0.5 mmol) and diethylamine (1 mmol) in 1,2-dichloroethane (5 cm^3) was stirred at room temperature for 10–20 min as above and worked up to afford a crude oil, which was subjected to PLC on silica gel with hexane–ethyl acetate (6:1).

1-(4-Diethylamino-2,3-dimethylbut-2-enyl)-1*H*-2-benzothiopyran **4a$_2$** from the cycloadduct **1a**: a pale yellow oil, δ_H($CDCl_3$) 0.92 (6 H, t, *J* 7.3, 2 × CH_2*Me*), 1.58 (3 H, s, Me), 1.62 (3 H, s, Me), 2.24–2.37 (4 H, m, 2 × C*H*$_2$Me), 2.40–2.67 (4 H, m, CHC*H*$_2$ and C*H*$_2$$NEt_2$), 3.38 (1 H, dt, *J* 7.3 and 2.0, C*H*CH_2), 6.33 (1 H, dd, *J* 9.8 and 2.0, 3-H), 6.72 (1 H, d, *J* 9.8, 4-H), 6.89–6.92 (1 H, m, ArH), 7.06–7.09 (1 H, m, ArH) and 7.13–7.24 (2 H, m, ArH); δ_C($CDCl_3$) 11.7 (q), 17.5 (q), 19.4 (q), 39.7 (t), 41.5 (d), 46.4 (t), 55.1 (t), 120.3 (d), 123.8 (d), 127.0 (d), 127.2 (s), 127.2 (d), 127.3 (d), 127.6 (d), 131.3 (s), 131.4 (s) and 131.7 (s); *m/z* 301 (M^+) (Found: C, 75.6; H, 9.1; N, 4.6%; M^+, 301.1891. $C_{19}H_{27}NS$ requires C, 75.59; H, 9.01; N, 4.64%; *M*, 301.1864).

3-Benzoyl-1-(4-diethylamino-2,3-dimethylbut-2-enyl)-1*H*-2-benzothiopyran **4d$_1$** from the cycloadduct **1d**; a yellow oil, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H($CDCl_3$) 0.91 (6 H, t, *J* 7.3, 2 × CH_2*Me*), 1,60 (3 H, s, Me), 1.63 (3 H, s, Me), 2.23–2.36 (4 H, m, 2 × C*H*$_2$Me), 2.47 and 2.65 (each 1 H, each d, *J* 13.2, C*H*$_2$$NEt_2$), 2.61 (2 H, d, *J* 7.8, CHC*H*$_2$), 4.07 (1 H, t, *J* 7.8, C*H*CH_2), 7.05 (1 H, br d, *J* 7.3, ArH), 7.20–7.42 (3 H, m, ArH), 7.47 (1 H, s, 4-H), 7.50–7.57 (2 H, m, ArH), 7.60–7.63 (1 H, m, ArH) and 7.78–7.81 (2 H, m, ArH); δ_C($CDCl_3$) 11.7 (q), 17.6 (q), 19.5 (q), 40.1 (t), 42.4 (d), 46.5 (t), 55.2 (t), 126.8 (s), 127.4 (d), 127.5 (d), 128.4 (d), 129.2 (d), 129.5 (d), 130.5 (d), 131.1 (s), 131.7 (s), 132.3 (d), 133.7 (s), 134.7 (d), 134.7 (s), 137.1 (s) and 194.1 (s); *m/z* 405 (M^+) (Found: M^+, 405.2159. $C_{26}H_{31}NOS$ requires *M*, 405.2126).

(e) With butylamine. A mixture of the cycloadduct **1d** (1 mmol) and butylamine (2.05 mmol) in 1,2-dichloroethane (10 cm^3) was stirred at room temperature for 15 min and worked up as above to give 3-benzoyl-1-(4-butylamino-2,3-dimethylbut-2-enyl)-1*H*-2-benzothiopyran **4d$_2$** (34%) and bis[4-(3-benzoyl-1*H*-2-benzothiopyran-1-yl)-2,3-dimethylbut-2-enyl]butylamine (13%) as an inseparable diastereoisomeric mixture in the ratio 1 : 1 along with the spiro compound **2d** (45%). Compound **4d$_2$**; a yellow gum, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H($CDCl_3$) 0.86 [3 H, t, *J* 7.3, N(CH_2)$_3$*Me*], 1.19–1.42 [4 H, m, CH_2(C*H*$_2$)$_2$Me], 1.63 (3 H, s, Me), 1.64 (3 H, s, Me), 2.37 [2 H, t, *J* 7.3, C*H*$_2$(CH_2)$_2$Me], 2.56 and 2.61 (each 1 H, each dd, *J* 13.2 and 7.8, CHC*H*$_2$), 2.79 and 2.85 (each 1 H, each d, *J* 12.7,

CH_2NHBu), 4.06 (1 H, t, *J* 7.8, C*H*CH_2), 7.05–7.07 (1 H, m, ArH), 7.19–7.37 (4 H, m, ArH), 7.41 (1 H, s, 4-H), 7.46–7.61 (3 H, m, ArH) and 7.77–7.80 (2 H, m, ArH); δ_C($CDCl_3$) 13.9 (q), 17.4 (q), 19.0 (q), 20.4 (t), 32.0 (t), 40.1 (t), 41.9 (d), 49.3 (t), 51.5 (t), 126.3 (s), 127.3 (d), 127.5 (d), 128.3 (d), 129.1 (d), 129.5 (d), 130.4 (d), 130.8 (s), 131.5 (s), 132.2 (d), 133.5 (s), 134.5 (d), 134.6 (s), 136.9 (s) and 193.9 (s); *m/z* 405 (M^+) and 251 (base). Bis-[4-(3-benzoyl-1*H*-2-benzothiopyran-1-yl)-2,3-dimethylbut-2-enyl]butylamine; a yellow gum, ν_{max}(KBr)/cm^{-1} 1640 (CO); δ_H($CDCl_3$) 0.73–0.80 [3 H, m, $(CH_2)_3$*Me*], 1.16–1.26 [4 H, m, $CH_2(CH_2)_2$Me], 1.53 (6 H, s, 2 × Me), 1.55 (6 H, s, 2 × Me), 1.94–1.96 [2 H, m, $CH_2(CH_2)_2$Me], 2.20–2.44 (4 H, m, 2 × CH_2NBu), 2.52 (4 H, t, *J* 7.8, 2 × CHCH_2), 3.96 (2 H, t, *J* 7.8, 2 × C*H*CH_2) and 6.89–7.78 (20 H, m, ArH and 4-H); *m/z* 737 (M^+).

(f) With potassium acetate. The cycloadduct **1a** or **1d** (0.5 mmol) was added to a stirred suspension of potassium acetate (1 mmol) in 1,2-dichloroethane (5 cm^3), and the mixture was stirred for 30 min. After dilution with water the reaction mixture was extracted with dichloromethane and the extract washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC on silica gel with hexane–ethyl acetate (6:1) or with hexane–dichloromethane (6:1).

1-(4-Acetoxy-2,3-dimethylbut-2-enyl)-1*H*-2-benzothiopyran **4a$_3$**, from the cycloadduct **1a**, an oil, ν_{max}(neat)/cm^{-1} 1730 (ester); δ_H($CDCl_3$) 1.63 (6 H, s, 2 × Me), 1.99 (3 H, s, OMe), 2.57 (2 H, d, *J* 7.8, CHCH_2), 3.82 (1 H, dt, *J* 7.8 and 2.0, C*H*CH_2), 4.12 and 4.28 (each 1 H, each d, *J* 12.2, CH_2OAc), 6.32 (1 H, dd, *J* 9.3 and 2.0, 3-H), 6.74 (1 H, d, *J* 9.3, 4-H), 6.91–6.94 (1 H, m, ArH), 7.08–7.15 (1 H, m, ArH) and 7.17–7.25 (2 H, m, ArH); δ_C($CDCl_3$) 16.5 (q), 19.2 (q), 20.9 (q), 39.5 (t), 41.3 (d), 64.6 (t), 119.8 (d), 124.1 (d), 127.1 (d), 127.2 (d), 127.3 (d), 127.5 (s), 127.6 (d), 130.8 (s), 130.9 (s), 131.4 (s) and 170.9 (s); *m/z* 288 (M^+) and 147 (base) (Found: C, 70.6; H, 7.0: $C_{17}H_{20}O_2S$ requires C, 70.80; H, 6.99%)

(g) With potassium carbonate. The cycloadduct **1a** or **1d** (0.5 mmol) was added to a stirred suspension of potassium carbonate (1 mmol) in acetone (5 cm^3), and the mixture was stirred under reflux for 10 min or at room temperature for 4 h. After dilution with water, the reaction mixture was extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC on silica gel with hexane–dichloromethane (6:1) or with hexane–ethyl acetate (6:1).

Thermal rearrangement of the spiro compound 2d

A solution of the spiro compound **2d** (332 mg, 1 mmol) in benzene (10 cm^3) was heated at 220 °C in a sealed tube for 15 h after which the reaction mixture was concentrated to dryness. The residue was subjected to PLC on silica gel with hexane–ethyl acetate (15:1) to give 3-benzoyl-3',4'-dimethylspirol[1*H*-2-benzothiopyran-1,1'-cyclopent-3-ene] **5** (114 mg, 34.3%); yellow needles, mp 128–130 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1} 1635 (CO); δ_H($CDCl_3$) 1.63 (6 H, s, 2 × Me), 2.90 (2 H, d, *J* 16.6, CH_2), 2.91 (2 H, d, *J* 16.6, CH_2), 7.22–7.28 (3 H, m, ArH), 7.35–7.42 (2 H, m, ArH and 4-H), 7.45–7.51 (2 H, m, ArH), 7.55–7.61 (1 H, m, ArH) and 7.77–7.81 (2 H, m, ArH); δ_C($CDCl_3$) 13.5 (q), 50.0 (s), 52.1 (t), 122.5 (d), 126.8 (d), 128.2 (s), 128.3 (d), 129.2 (d), 130.2 (d), 130.9 (d), 131.7 (s), 132.2 (d), 135.7 (d), 136.6 (s), 137.0 (s), 139.0 (s) and 194.2(s); *m/z* 332 (M^+) (Found: M^+, 332.1256. $C_{22}H_{20}OS$ requires *M*, 332.1236).

Hydride reduction of cycloadducts

(a) With sodium borohydride. Sodium borohydride (1 mmol) was added with stirring to a suspension of the cycloadduct **1** (1 mmol) in dry ethanol (10 cm^3) and the mixture was stirred for 10–15 min until dissolution occurred. After dilution with water, the reaction mixture was extracted with dichloromethane and the extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was subjected to PLC on silica gel with hexane–ethyl acetate (4:1). The results are summarized in Table 2. 1-(2,3-Dimethylbut-2-enyl)-1*H*-2-benzothiopyran **6a** from the cycloadduct **1a**; a pale yellow oil, δ_H($CDCl_3$) 1.33 (3 H, s, Me), 1.54 (3 H, s, Me), 1.57 (3 H, s, Me), 2.45 and 2.54 (each 1 H, each dd, *J* 13.7 and 7.8, CHC*H*$_2$), 3.82 (1 H, dt, *J* 7.8 and 1.5, C*H*CH_2), 6.33 (1 H, dd, *J* 9.3 and 1.5, 3-H), 6.71 (1 H, d, *J* 9.3, 4-H), 6.90–6.93 (1 H, m, ArH), 7.05–7.08 (1 H, m, ArH) and 7.13–7.23 (2 H, m, ArH); δ_C($CDCl_3$) 18.8 (q), 20.0 (q), 20.6 (q), 40.1 (t), 41.3 (d), 120.2 (d), 123.4 (s), 123.9 (d), 127.0 (d), 127.2 (d), 127.3 (d), 127.5 (d), 128.5 (s) and 131.6 (s); *m/z* 230 (M^+) and 147 (base) (Found: C, 78.1; H, 8.1. $C_{15}H_{18}S$ requires C, 78.21; H, 7.88%). 8-Benzoyl-7-isopropenyl-7-methyl-6,7-dihydro-5,8-epithio-9*H*-benzocycloheptene **7d** from the cycloadduct **1d**, needles, mp 111–112 °C (from methanol), ν_{max}(KBr)/cm^{-1} 1665 (CO); δ_H($CDCl_3$) 1.48 (3 H, s, Me), 1.80 (3 H, s, Me), 2.11 (1 H, d, *J* 13.2, 6-H), 2.82 (1 H, dd, *J* 13.2 and 6.4, 6-H), 3.56 and 3.72 (each 1 H, each d, *J* 17.6, 9-H), 4.20 (1 H, d, *J* 6.4, 5-H), 4.89 and 5.20 (each 1 H, each br s, =CH_2), 7.02–7.19 (4 H, m, ArH), 7.35–7.48 (3 H, m, ArH) and 7.78–7.81 (2 H, m, ArH); δ_C($CDCl_3$) 23.3 (q), 25.9 (q), 42.7 (t), 49.0 (d), 55.7 (s), 56.2 (t), 73.6 (s), 114.9 (t), 125.4 (d), 126.0 (d), 127.2 (d), 127.5 (d), 127.9 (d), 129.1 (d), 131.6 (d), 134.4 (s), 139.4 (s), 142.2 (s), 151.6 (s) and 204.0 (s); *m/z* 334 (M^+) (Found: C, 78.9; H, 6.7%; M^+, 334.1407. $C_{22}H_{22}OS$ requires C, 79.00; H, 6.63%; *M*, 334.1392).

(b) With sodium cyanoborohydride. Sodium cyanoborohydride (1 mmol) was added to a stirred suspension of the cycloadduct (1 mmol) in dry THF (10 cm^3) at room temperature, and the mixture was stirred for 15 min–1 h. Dil. hydrochloric acid (1 mol dm^{-3}) was added to the reaction mixture and the whole was extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residue was purified by PLC on silica gel with hexane–ethyl acetate (4:1) to give the products. The results are summarized in Table 2. 8-Benzoyl-7-methyl-7-vinyl-6,7-dihydro-5,8-epithio-9*H*-benzocycloheptene **7e**; needles, mp 92.5–93 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1665 (CO); δ_H($CDCl_3$) 1.43 (3 H, s, Me), 2.08 (1 H, d, *J* 13.2, 6-H), 2.53 (1 H, dd, *J* 13.2 and 6.4, 6-H), 3.50 and 3.78 (each 1 H, each d, *J* 18.1, CH_2), 4.13 (1 H, d, *J* 6.4, 5-H), 4.98 (1 H, d, *J* 10.3, CH=C*H*H), 5.01 (1 H, d, *J* 17.6, CH=CH*H*), 6.17 (1 H, dd, *J* 17.6 and 10.3, C*H*=CH_2), 7.00 (1 H, br d, *J* 7.3, ArH), 7.08–7.21 (3H, m, ArH), 7.35–7.50 (3 H, m, ArH) and 7.69–7.72 (2 H, m, ArH); δ_C($CDCl_3$) 22.1 (q), 41.0 (t), 48.9 (d), 54.2 (s), 55.0 (t), 73.1 (s), 111.9 (t), 125.1 (d), 126.0 (d), 127.1 (d), 127.3 (d), 127.9 (d), 129.5 (d), 131.4 (d), 133.8 (s), 139.9 (s), 142.4 (s), 145.8 (d) and 204.7 (s); *m/z* 320 (M^+) (Found: C, 78.7; H, 6.4. $C_{21}H_{20}OS$ requires C, 78.71; H, 6.29%).

8-Benzoyl-7-vinyl-6,7-dihydro-5,8-epithio-9*H*-benzocycloheptene **7f**; needles, mp 204.5–205 °C (from chloroform); ν_{max}(KBr)/cm^{-1} 1660 (CO); δ_H($CDCl_3$) 2.38 (1 H, ddd, *J* 12.7, 6.8 and 5.9, 6-H), 2.77 (1 H, dd, *J* 12.7 and 7.8, 6-H), 3.37–3.49 (2 H, m, 7-H and 9-H), 3.61 (1 H, d, *J* 17.1, 9-H), 4.19 (1 H, d, *J* 5.9, H-5), 4.76 (1 H, br d, *J* 10.3, CH=C*H*H), 5.00 (1 H, br d, *J* 17.1, CH=CH*H*), 5.75 (1 H, ddd, *J* 17.1, 10.3 and 6.8, C*H*=CH_2), 7.05–7.17 (4 H, m, ArH), 7.44–7.59 (3 H, m, ArH) and 7.95–7.97 (2 H, m, ArH); δ_C($CDCl_3$) 45.1 (t), 47.8 (d), 51.3 (t), 52.9 (d), 76.0 (s), 115.5 (t), 125.5 (d), 126.1 (d), 127.0 (d), 128.3 (d), 129.6 (d), 129.9 (d), 132.8 (d), 133.4 (s), 135.5 (s), 139.3 (d), 142.1 (s) and 199.0 (s); *m/z* 306 (M^+) (Found: C, 78.3; H, 5.9. $C_{20}H_{18}OS$ requires C, 78.40; H, 5.92%).

Reduction of the cycloadduct 1a with samarium diiodide

A mixture of samarium (1.504 g, 10 mmol) and 1,2-diiodoethane (1.409 g, 5 mmol) in dry THF (50 cm^3) was stirred and refluxed with under nitrogen for 30 min, after which stirring was continued overnight. This SmI_2 solution (20 cm^3, 2 mmol) was dropwise added to a stirred suspension of the cycloadduct **1a** (316 mg, 1 mmol) in dry THF (10 cm^3) at room temperature under nitrogen, and the mixture was stirred for 15 min. Dilute hydrochloric acid (1 mol dm^{-3}, 20 cm^3) was then added to the reaction mixture which was then extracted with diethyl ether. The extract was washed successively with sat. aq. $NaHCO_3$, water, 10% aqueous $Na_2S_2O_3$ and water, dried ($MgSO_4$) and evaporated. The residue was purified by PLC on silica gel with hexane–ethyl acetate (15:1) to give compound **6a** (145 mg, 63%), which was identical with the sample obtained by $NaBH_4$ reduction of **1a** in ethanol.

Reduction of the cycloadduct 1d with SmI_2

In a similar way to that described for the cycloadduct **1a**, the cycloadduct **1d** was reduced with SmI_2 to afford 2-benzoyl-5,6-dimethyl-1,2,7,8-tetrahydro-4*H*-3-benzothiecine **8** (20.2%) as a yellow oil, ν_{max}(neat)/cm^{-1} 1680 (CO); δ_H($CDCl_3$) 1.71 (3 H, s, Me), 1.75 (3 H, s, Me), 2.31–3.50 (8 H, m, 1-H, 4-H, 7-H and 8-H), 4.17 (1 H, dd, *J* 10.3 and 3.9, 2-H), 7.16–7.26 (3 H, m, ArH), 7.37–7.58 (4 H, m, ArH) and 7.96–7.99 (2 H, m, ArH); δ_C($CDCl_3$) 19.4 (q), 20.3 (q), 27.2 (t), 33.3 (t), 38.8 (d), 39.8 (t), 40.3 (t), 123.2 (s), 126.9 (d), 127.0 (d), 127.3 (d), 127.7 (s), 128.0 (d), 128.6 (d), 129.6 (d), 133.1 (d), 136.7 (s), 138.7 (s), 140.1 (s) and 199.2 (s); *m*/*z* 336 (M^+) (Found: M^+, 336.1530. $C_{22}H_{24}OS$ requires *M*, 336.1547).

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Paper 4/07751B
Received 20*th December* 1994
Accepted 16*th February* 1995