Polar cycloaddition of 1-benzothiopyrylium salts with conjugated dienes and some transformations of the cycloadducts

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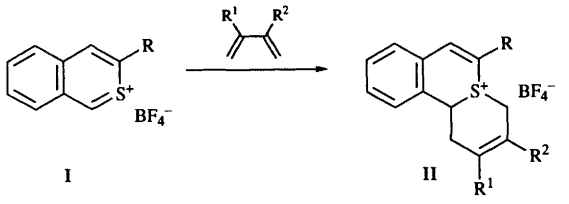
Polar cycloaddition of 1-benzothiopyrylium salts 2 with conjugated dienes proceeds regio- and stereo-specifically to afford the corresponding benzo-fused bicyclic sulfonium salts 4 in good yields. Reaction of the cycloadducts 4 with nucleophiles such as methanol or water causes ring opening to give 2-(but-2-enyl)- and 2-(but-3-enyl)-substituted 2*H*-1-benzothiopyrans 5 and 6, respectively. Treatment of the cycloadduct 4hA with a variety of bases affords the spirocyclopentene derivative 7 and the spiro-1,2-dioxolane derivative 8. A mechanism involving a biradical intermediate is discussed for the formation of the above products 7 and 8 on the basis of chemical evidence. Reduction of the cycloadduct 4hA with sodium borohydride or sodium cyanoborohydride is also described.

We have recently reported the first example of a [2$^+$ + 4]-type cationic polar cycloaddition of 2-benzothiopyrylium salts **I** with various 1,3-dienes giving benzo-fused bicyclic sulfonium salts **II** in high yield (Scheme 1)[1] and also the interesting ring



Scheme 1

transformation of the cycloadducts.[2] As part of continuing work on the development of thiopyrylium ions as new dienophiles, we investigated the polar cycloaddition of 1-benzothiopyrylium salts. In this paper, we describe the details of our findings that various 1-benzothiopyrylium salts **2** readily underwent a [2$^+$ + 4]polar cycloaddition with several 1,3-dienes to afford the benzo-fused bicyclic sulfonium salts **4**, and that the cycloadducts underwent a ring transformation on treatment with nucleophiles, bases or reducing agents.[3]

Results and discussion

The 1-benzothiopyrylium tetrafluoroboranuides **2** used for the present studies were prepared from the corresponding 2*H*-1-benzothiopyrans **1** (synthesized by the literature methods except for **1h**), using triphenylcarbenium tetrafluoroboranuide. 4-Cyano-1-benzothiopyran **1h** was prepared in 84% yield by reaction of 2,3-dihydro-1-benzothiopyran-4-one with trimethylsilyl cyanide in the presence of triethylamine, followed by treatment with excess phosphorus pentoxide in refluxing benzene.[4] Addition of 1-benzothiopyrylium tetrafluoroboranuides **2** to 2 mol equiv. of 2,3-dimethylbuta-1,3-diene **3A**, isoprene **3B**, 2-phenylbuta-1,3-diene **3C**, or buta-1,3-diene **3D** in dry 1,2-dichloroethane at room temperature and stirring of the mixture for 5–30 min afforded the corresponding cycloadducts **4** in fairly good yields, indicating that the salts **2** are effective dienophiles (Scheme 2). The reaction conditions and product yields are summarized in Table 1.

Cycloaddition of unsymmetrical 1,3-dienes such as isoprene **3B** or 2-phenylbuta-1,3-diene **3C** proceeded regiospecifically to give only a single regioisomer (entries 2, 4, 9, 12 and 13). The structural assignment of the cycloadducts was based on the spectroscopic evidence (see Experimental section). The

Table 1 Cycloadditions of 1-benzothiopyrylium salts **2** with 1,3-dienes **3**

	Reactants		Time	Product	
Entry	Salt	1,3-Diene	(*t*/min)	Compound	Yield (%)
1	**2a**	**3A**	30	**4aA**	70
2	**2a**	**3B**	30	**4aB**	66
3	**2b**	**3A**	20	**4bA**	89
4	**2b**	**3B**	20	**4bB**	66
5	**2c**	**3A**	20	**4cA**	81
6	**2d**	**3A**	20	**4dA**	87
7	**2e**	**3A**	20	**4eA**	94
8	**2f**	**3A**	30	**4fA**	58
9	**2f**	**3B**	30	**4fB**	65
10	**2g**	**3A**	30	**4gA**	78
11	**2h**	**3A**	5	**4hA**	94
12	**2h**	**3B**	5	**4hB**	89
13	**2h**	**3C**	5	**4hC**	71
14	**2h**	**3D**	20	**4hD**	79

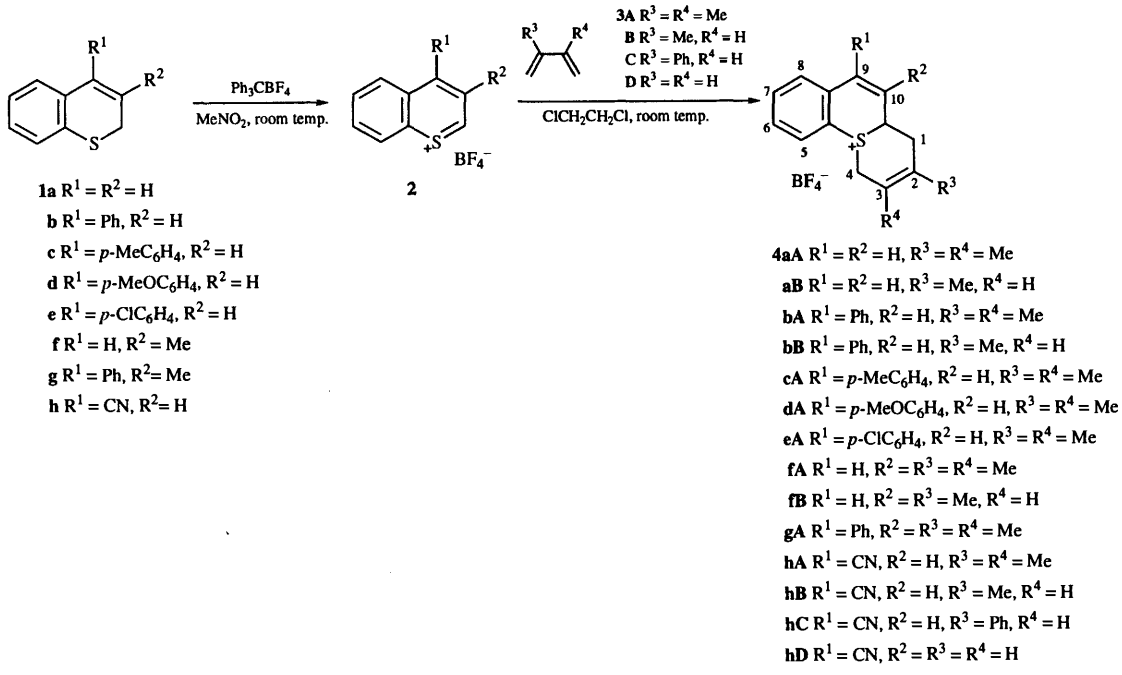
regiostructure of the 4a,10a-buteno moieties in the cycloadducts **4aB**, **4bB**, **4fB**, **4hB** and **4hC** was determined mainly from the ^{1}H NMR spectra which showed no coupling between the methylene protons of the allylic group attached to C-10a and the olefinic proton. The yields of the cycloadducts of 4-aryl substituted benzothiopyrylium salts **2b**,**c**,**d**,e were better than those of the 4-unsubstituted ones **2a**. The 4-cyano substituted benzothiopyrylium salt **2h** reacted more rapidly with 1,3-dienes to afford the cycloadducts in even better yields than the other benzothiopyrylium salts (entries 11–13). Furthermore, buta-1,3-diene **3D** reacted only with the salt **2h** to give the corresponding cycloadduct in reasonable yield (entry 14). The higher reactivity of the salt **2h** is probably due to lowering of the LUMO energy level of **2h** by the electron-withdrawing group on the hetero-ring. A 3-methyl group on the thiopyrylium ring generally decreases the reaction rate and the yield of the cycloadducts, probably because of steric interference to the attack of 1,3-dienes on the 2-position (entries 8–10).

We next turned our attention to an investigation of the reactivity of the cycloadducts obtained above in the hope of observing a new ring transformation, because the cycloadducts have reactive sulfonium ion structures. First, we performed the reaction with weak nucleophiles such as methanol or water. The reaction results are summarized in Scheme 3 and Table 2. The cycloadduct **4** underwent an easy cleavage of the sulfur–carbon bond on attack by the nucleophiles to give two types of ring-opened products, **5** and **6**. The latter compounds **6** were

Table 2 Reactions of cycloadducts **4** with nucleophiles

	Reactants		Conditions		Products				
Entry	Salt	Nucleophile	Solvent	Temp.	X	**5**	Yield (%)	**6**	Yield (%) (diastereoisomeric ratio)[a]
1	**4aA**	MeOH	none	reflux	OMe	**5a**	61	**6a**	10 (1 : 1.3)
2	**4bA**	MeOH	none	reflux	OMe	**5b**	49	**6b**	15 (1 : 1.5)
3	**4fA**	MeOH	none	reflux	OMe	**5c**	59	**6c**	5 (1 : 1.0)
4	**4hA**	MeOH	none	reflux	OMe	**5d**	77	**6d**	21 (1 : 2.6)
5	**4hA**	H_2O	acetone	room temp.	OH	**5e**	24	**6e**	6 (1 : 3.0)

[a] Determined by ^1H NMR spectroscopy.

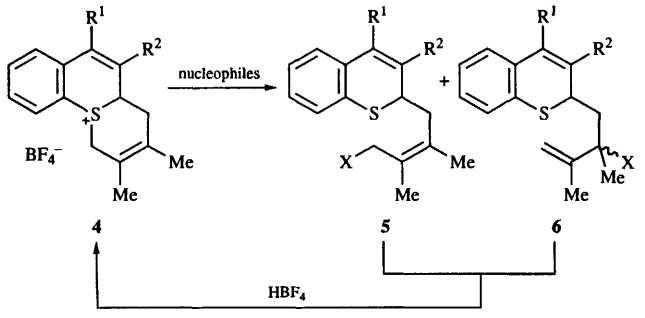


1a $R^1 = R^2 = H$
b R^1 = Ph, $R^2 = H$
c $R^1 = p$-MeC_6H_4, $R^2 = H$
d $R^1 = p$-$MeOC_6H_4$, $R^2 = H$
e $R^1 = p$-ClC_6H_4, $R^2 = H$
f $R^1 = H$, R^2 = Me
g R^1 = Ph, R^2 = Me
h R^1 = CN, R^2 = H

2

4aA $R^1 = R^2 = H$, $R^3 = R^4$ = Me
aB $R^1 = R^2 = H$, R^3 = Me, $R^4 = H$
bA R^1 = Ph, $R^2 = H$, $R^3 = R^4$ = Me
bB R^1 = Ph, $R^2 = H$, R^3 = Me, $R^4 = H$
cA $R^1 = p$-MeC_6H_4, $R^2 = H$, $R^3 = R^4$ = Me
dA $R^1 = p$-$MeOC_6H_4$, $R^2 = H$, $R^3 = R^4$ = Me
eA $R^1 = p$-ClC_6H_4, $R^2 = H$, $R^3 = R^4$ = Me
fA $R^1 = H$, $R^2 = R^3 = R^4$ = Me
fB $R^1 = H$, $R^2 = R^3$ = Me, $R^4 = H$
gA R^1 = Ph, $R^2 = R^3 = R^4$ = Me
hA R^1 = CN, $R^2 = H$, $R^3 = R^4$ = Me
hB R^1 = CN, $R^2 = H$, R^3 = Me, $R^4 = H$
hC R^1 = CN, $R^2 = H$, R^3 = Ph, $R^4 = H$
hD R^1 = CN, $R^2 = R^3 = R^4 = H$

Scheme 2



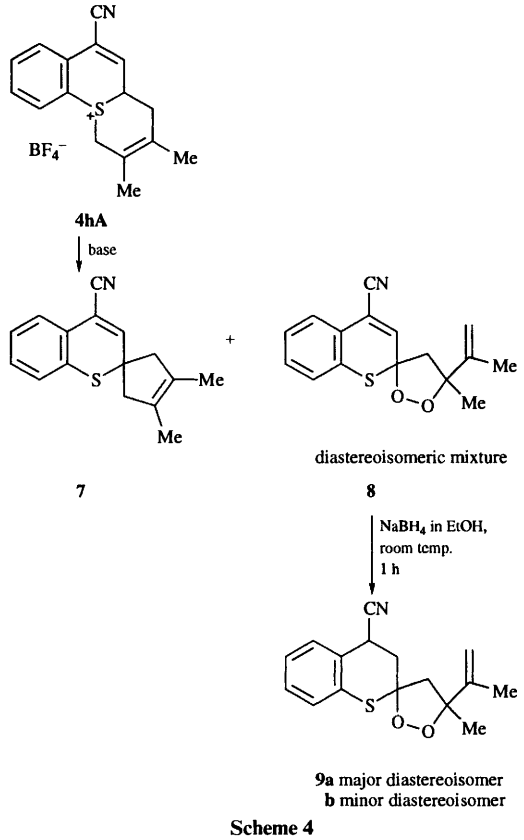
Scheme 3

obtained as inseparable diastereoisomeric mixtures in the ratios shown in Table 2. The structures were determined on the basis of spectroscopic data (see Experimental section). Both ring-opened products **5d** and **6d** were converted into the sulfonium salt **4hA** by treatment with tetrafluoroboric acid. We next performed the reaction of the cycloadduct **4hA** with various bases with a view to its transformation. Both strong and weak bases caused the same ring transformation to afford the spirocyclopentene derivative **7** and spiro-1,2-dioxolane derivative **8** as shown in Scheme 4. The latter compound **8** was obtained as an inseparable mixture of diastereoisomers. The results are summarized in Table 3. Structural identification of the above products was established mainly on the basis of spectroscopic evidence. Elemental analysis and mass spectral data [*m/z* 253 (M^+)] indicate a molecular formula of $C_{16}H_{15}NS$ for compound **7**. The ^1H NMR spectrum ($CDCl_3$) of **7** showed a broad singlet for the two methylene groups at δ 2.67 and a singlet for the olefinic proton (3-H) at δ 6.76. The ^{13}C NMR spectrum ($CDCl_3$) of compound **7** showed an sp^3-quaternary carbon at δ 47.3, and two sp^3-secondary carbon at δ 52.9. For compound **8**, elemental analysis and mass spectral data [*m/z* 285 (M^+)] showed a molecular formula of $C_{16}H_{15}NO_2S$ for this compound. The ^1H NMR spectrum ($CDCl_3$) of the major isomer of compound **8** showed a singlet for the methyl group at δ 1.49, a singlet for the vinylic methyl group at δ 1.88, two doublets (*J* 13.7 Hz) for the methylene group at δ 2.91 and 2.96, two broad singlets for the vinylic methylene protons at δ 5.01 and 5.09, and a singlet for the 3-H at δ 6.64. The ^{13}C NMR spectrum ($CDCl_3$) showed two methyl carbons at δ 18.4 and 25.4, a methylene carbon at δ 59.4, two sp^3-quaternary carbons at δ 87.5 and 88.4, and an sp^2-secondary carbon at δ 113.0. The ^1H NMR spectrum of the minor isomer of compound **8** showed a singlet for the methyl group at δ 1.56, a singlet for the vinylic methyl group at δ 1.83, two doublets (*J* 13.7 Hz) for the methylene group at δ 2.68 and 3.40, two broad singlets for the vinylic methylene protons at δ 5.01 and 5.09, and a singlet for the 3-H at δ 6.56. The ^{13}C NMR spectrum ($CDCl_3$) showed two methyl carbons at δ 19.1 and 22.8, a methylene carbon at δ 58.2, two sp^3-quaternary carbons at δ 87.7 and 88.8, and an sp^2-secondary carbon at δ 111.8. The structure of compound **8** was further confirmed by chemical transformation. Reduction of compound **8** with sodium borohydride in ethanol resulted in the formation of two diastereoisomeric hydrogenated compounds **9a** and **9b** which were successfully separated by PLC, and the structures were determined based on the spectroscopic data (see Experimental section).

Table 3 Reactions of cycloadduct **4hA** with various bases

Entry	Base	Solvent	Temp.	Products: 7 Yield (%)	Products: 8 Yield (%) (diastereoisomeric ratio)[a]
1	LDA	THF, N_2	−78 °C–0 °C	48	31 (1 : 1.4)
2	NaH	DMF, N_2	0 °C	42	31 (1 : 1.2)
3	Et_3N	EtOH	0 °C	51 [7][b]	28 (1 : 1.2) [73][b]
4	Et_2NH	$(CH_2Cl)_2$	room temp.	54	30 (1 : 1.1)
5	AcOK	$(CH_2Cl)_2$	room temp.	45	27 (1 : 1.1)
6	K_2CO_3	acetone	room temp.	34	35 (1 : 1.1)

[a] Determined by ^1H NMR spectroscopy. [b] The yield from the reaction carried out with bubbling oxygen.



Scheme 4

In order to determine a plausible mechanism for the formation of compound **8**, we carried out the above reaction with bubbling oxygen under the conditions of entry 3 and obtained the spirodioxolane derivative **8** in 73% yield and the spirocyclopentene derivative **7** in 7% yield, suggesting the formation of a common intermediate labile to oxygen. However, as shown in Table 3, even when the reaction was performed in carefully degassed solvent under an N_2 atmosphere (entries 1 and 2), the spirodioxolane **8** was formed in a similar yield to that obtained under an air atmosphere. This suggests that the spirodioxolane might be formed during work-up by oxygen capture of the rather unstable intermediate product. Indeed, the ^1H NMR spectrum of a mixture of the cycloadduct **4hA** and base (potassium acetate) in $CDCl_3$ in an N_2 atmospheric NMR tube revealed the existence of the presumed intermediate compound **B** (Scheme 5) as a mixture of diastereoisomers: two doublets (J 5.4 Hz) for the cyclopropane ring protons at δ 1.08 and 1.62, a singlet for the methyl group on the cyclopropane ring at δ 1.39, a singlet for the vinylic methyl group at δ 1.64, a multiplet for one of vinylic methylene protons at δ 4.81–4.83, a multiplet for another of the vinylic methylene protons at δ 4.93–4.94, and a singlet for the 3-H at δ 6.34, which are assignable to the major isomer of the intermediate compound **B**; two doublets (J 5.9 Hz) for the cyclopropane ring protons at δ 1.22 and 1.48, a singlet for the methyl group on the cyclopropane ring at δ 1.28, a singlet for the vinylic methyl group at δ 1.61, a multiplet for one of the vinylic methylene protons at δ 4.81–4.83, a broad singlet for another of the vinylic methylene protons at δ 5.01, and a singlet for 3-H at δ 6.53, which are assignable to the minor isomer of the intermediate compound **B**. It was also observed that the intermediate **B** gradually decomposed under an N_2 atmosphere in an NMR tube to give the spirocyclopentene derivative **7**.

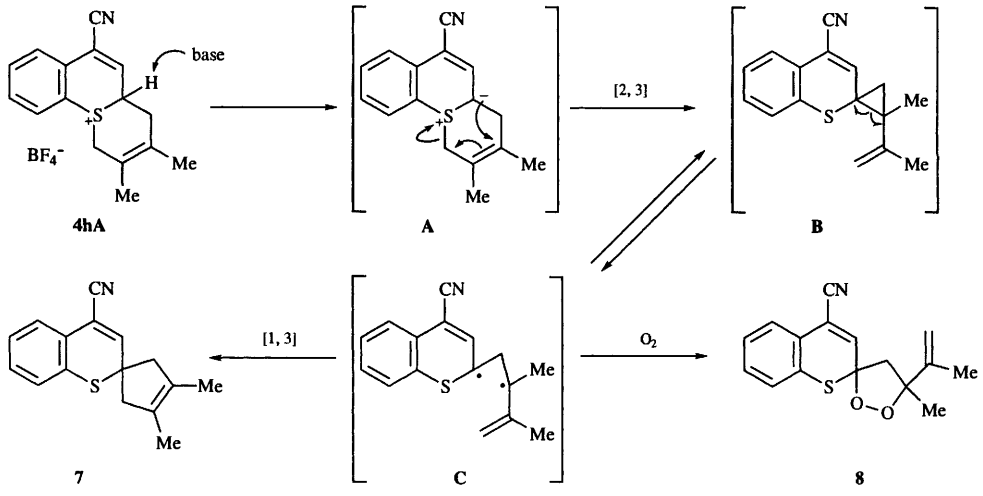
The above observation supports the following mechanism for the transformation of the cycloadduct **4hA** into spiro compounds **7** and **8** by treatment with bases (Scheme 5). The most acidic proton adjacent to sulfur in **4hA** is deprotonated with base to form the intermediate **A**, which subsequently undergoes 2,3-sigmatropic rearrangement to give the cyclopropane intemediate **B**. Homolytic cleavage of the cyclopropane ring of the intermediate **B** leads to the formation of biradical intermediate **C**, presumably because of stabilization of each of the biradicals by captodative substituents (sulfur and conjugated cyano group), and by allyl resonance, respectively. This type of radical fission of a cyclopropane ring has been observed in the *cis–trans*-isomerization of captodatively substituted cyclopropanes.[5,6] The intermediate **B** was observed by ^1H NMR spectroscopy as described above to be a mixture of diastereoisomers. Generally speaking, the Woodward–Hoffman rules do not permit the formation of two isomers in the intermediate **C** produced by 2,3-sigmatropic rearrangement. This conflict would be reasonably resolved by postulating an equilibrium between the intermediates **B** and **C**. The biradical intermediate **C** then recyclizes *via* the terminal methylene carbon to furnish the compound **7**, or is trapped with oxygen to afford the dioxolane **8**.

Finally, we have investigated the reduction of the cycloadduct **4hA** with sodium borohydride and sodium borocyanohydride expecting the formation of a sulfur-containing, ten-membered ring by the reductive cleavage of the $S–C_{10a}$ bond. However, the reducing agents attacked on the 4-position of **4hA** to give ring-opened compounds **10** or **12**, the former compound with further reduction in an activated double bond, and also acted as bases for deprotonation of the acidic proton at the 10a-position, followed by rearrangement as observed above to afford spiro compounds **7** and **11**, the latter compound with reduction of the activated double bond as shown in Scheme 6.

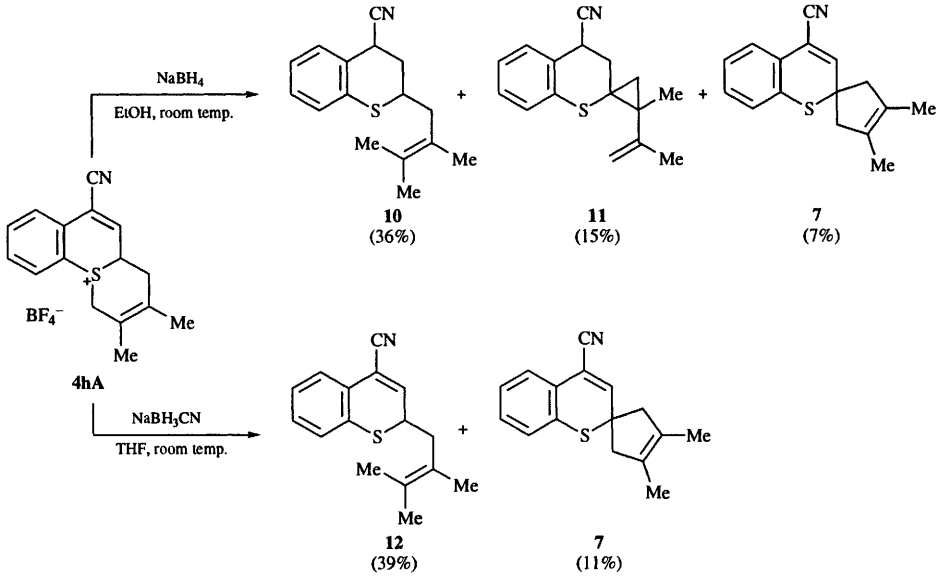
Experimental

General details

Mps were determined using a Yanagimoto micromelting point apparatus, and are uncorrected. IR Spectra were measured using a JASCO A-1 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on JEOL GX-270 (270 MHz) and EX-400 (400 MHz) spectrometers with tetramethylsilane as the internal standard. The chemical shifts (δ) are given in ppm with



Scheme 5



Scheme 6

coupling constants (J) in Hz. All ^{13}C data are quoted with ^{1}H 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.

A variety of substituted and unsubstituted 2*H*-1-benzothiopyrans (**1**), precursors of 1-benzothiopyrylium salts (**2**) were prepared by the practical methods reported in the literature.[7-10]

4-Cyano-2*H*-1-benzothiopyran 1h

Triethylamine (0.6 cm^3, 4.3 mmol) was added with stirring to an ice-cooled solution of 2,3-dihydro-1-benzothiopyran-4-one (1.64 g, 10 mmol) and trimethylsilyl cyanide (1.05 g, 10 mmol) in dichloromethane (40 cm^3) and the mixture was stirred for 2 h with ice-cooling, then for 15 h at room temperature. After evaporation of the solvent, P_2O_5 (3 g, 21 mmol), Hyflo Super Cel (1 g), and benzene (30 cm^3) were added to the residue, and the mixture was vigorously stirred with reflux for 30 min. The reaction mixture was poured into water, and extracted with dichloromethane. The organic layer was washed twice with water, dried ($MgSO_4$) and evaporated. The residual oil was chromatographed on a silica gel column and eluted with hexane-ethyl acetate (20:1) to afford the title compound **1h** (1.47 g, 84%) as a yellow oil; ν_{max}(neat)/cm^{-1} 2240 (CN); $\delta_H(CDCl_3)$ 3.52 (2 H, d, J 5.9, CH_2), 6.76 (1 H, t, J 5.9, olefinic H), 7.19–7.29 (3 H, m, ArH) and 7.50–7.55 (1 H, m, ArH); $\delta_C(CDCl_3)$ 25.0 (t), 116.0 (s), 126.4 (d), 127.0 (d), 127.6 (d), 128.0 (s), 129.9 (d), 131.8 (s) and 135.9 (d); m/z 173 (M^+, 77%) and 172 (100) (Found: M^+, 173.0291. $C_{10}H_{17}NS$ requires M, 173.0298).

General procedure for the preparation of 1-benzothiopyrylium tetrafluoroboranuides 2a–h

1-Benzothiopyrylium tetrafluoroboranuide 2a. Triphenylcarbenium tetrafluoroboranuide (7.065 g, 21.4 mmol) was added to a stirred solution of the 2*H*-1-benzothiopyran **1a** (3.019 g, 20.38 mmol) in dry nitromethane (30 cm^3) and the mixture was stirred for 4 h at room temperature. To the reaction mixture was added diethyl ether to precipitate the title tetrafluoroboranuide **2a** (3.986 g, 83.6%) as pale green rods; mp 137–139 °C (from acetonitrile–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H (CD_3CN) 8.26–8.38 (2 H, m, ArH), 8.71–8.79 (2 H, m, ArH), 8.79 (1 H, t, J 8.8, 3-H), 9.60 (1 H, d, J 8.8, 4-H) and 10.43 (1 H, d, J 8.8, 2-H); $\delta_C(CD_3CN)$ 129.4 (d), 131.34 (d), 133.6 (s), 134.7 (d), 136.0 (d), 136.5 (d), 145.8 (s), 154.8 (d) and 164.2 (d) (Found: C, 46.1; H, 3.1. $C_9H_7BF_4S$ requires C, 46.19; H, 3.02%).

The following 1-benzothiopyrylium tetrafluoroboranuides

were prepared from the corresponding 2*H*-1-benzothiopyrans **1** in a similar manner to that described above.

4-Phenyl-1-benzothiopyrylium tetrafluoroboranuide 2b. Yellow rods (85.9%) from 4-phenyl-2*H*-1-benzothiopyran **1b**; mp 123–125 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H(CD_3CN) 7.71–7.77 (5 H, m, ArH), 8.21 (1 H, dt, *J* 7.8 and 1.0, ArH), 8.32 (1 H, dt, *J* 7.8 and 1.5, ArH), 8.58 (1 H, dd, *J* 7.8 and 1.5, ArH), 8.69 (1 H, d, *J* 8.8, 3-H), 8.71 (1 H, br d, *J* 7.8, ArH) and 10.30 (1 H, d, *J* 8.8, 2-H); δ_C(CD_3CN) 130.0 (d), 130.2 (d), 131.3 (d), 132.6 (s), 132.7 (d), 133.1 (d), 134.0 (d), 134.7 (d), 135.7 (d), 137.6 (s), 146.3 (s), 161.3 (d) and 166.7 (s) (Found: C, 57.9; H, 3.6. $C_{15}H_{11}BF_4S$ requires C, 58.10; H, 3.58%).

4-(*p*-Tolyl)-1-benzothiopyrylium tetrafluoroboranuide 2c. Yellow needles (86.5%) from 4-(*p*-tolyl)-2*H*-1-benzothiopyran **1c**; mp 184–187 °C (decomp.) (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H(CD_3CN) 2.52 (3 H, s, Me), 7.54 and 7.64 (each 2 H, each d, *J* 7.8, ArH), 8.20 (1 H, dt, *J* 8.3 and 1.0, ArH), 8.30 (1 H, dt, *J* 8.3 and 1.0, ArH), 8.62 (1 H, br d, *J* 8.3, ArH) and 10.22 (1 H, d, *J* 8.8, 2-H); δ_C(CD_3CN) 21.6 (q), 130.0 (d), 131.0 (d), 131.7 (d), 132.5 (s), 133.0 (d), 134.2 (d), 134.6 (d), 134.9 (s), 135.7 (d), 144.2 (s), 146.2 (s), 160.7 (d) and 167.0 (s) (Found: C, 59.2; H, 4.1. $C_{16}H_{13}BF_4S$ requires C, 59.29; H, 4.04%).

4-(4-Methoxyphenyl)-1-benzothiopyrylium tetrafluoroboranuide 2d. Orange needles (86.3%) from 4-(4-methoxyphenyl)-2*H*-1-benzothiopyran **1d**; mp 158–162 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1040 (BF_4^-); δ_H(CD_3CN) 3.95 (3 H, s, OMe), 7.24 and 7.75 (each 2 H, each dt, *J* 8.8 and 2.0, ArH), 8.18 (1 H, dt, *J* 8.3 and 1.0, ArH), 8.28 (1 H, dt, *J* 8.3 and 1.0, ArH), 8.65 (1 H, dd, *J* 8.3 and 1.0, ArH), 8.65 (1 H, d, *J* 8.8, 3-H), 8.71 (1 H, dd, *J* 8.3 and 1.0, ArH) and 10.09 (1 H, d, *J* 8.8, 2-H); δ_C(CD_3CN) 56.7 (q), 116.2 (d), 129.9 (d), 130.0 (s), 132.3 (s), 132.7 (d), 134.3 (d), 134.4 (d), 135.5 (d), 146.0 (s), 159.3 (d), 164.5 (s) and 166.5 (s) (Found: C, 56.2; H, 3.9. $C_{16}H_{13}BF_4OS$ requires C, 56.50; H, 3.85%).

4-(4-Chlorophenyl)-1-benzothiopyrylium tetrafluoroboranuide 2e. Yellow needles (92.8%) from 4-(4-chlorophenyl)-2*H*-1-benzothiopyran **1e**; mp 132–135 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1040 (BF_4^-); δ_H(CD_3CN) 7.72 (4 H, br s, ArH), 8.21 (1 H, dt, *J* 8.3 and 1.0, ArH), 8.33 (1 H, dt, *J* 8.3 and 1.0, ArH), 8.56 (1 H, br d, *J* 8.3, ArH), 8.68 (1 H, d, *J* 8.8, 3-H), 8.82 (1 H, br d, *J* 8.3, ArH) and 10.31 (1 H, d, *J* 8.8, 2-H); δ_C(CD_3CN) 130.1 (d), 130.4 (d), 132.5 (s), 132.9 (d), 133.0 (d), 133.8 (d), 134.9 (d), 135.8 (d), 136.2 (s), 138.6 (s), 146.4 (s), 161.4 (s), 161.7 (d) and 165.3 (s) (Found: C, 52.05; H, 3.0. $C_{15}H_{10}BClF_4S$ requires C, 52.29; H, 2.93%).

3-Methyl-1-benzothiopyrylium tetrafluoroboranuide 2f. Pale green needles (91%) from 3-methyl-2*H*-1-benzothiopyran **1f**; mp 110.5–112.5 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1120–1030 (BF_4^-); δ_H(CD_3CN) 2.92 (3 H, s, Me), 8.21–8.30 (2 H, m, ArH), 8.59–8.63 (1 H, m, ArH), 8.70–8.73 (1 H, m, ArH), 9.41 (1 H, br s, 4-H) and 10.17 (1 H, br s, 2-H); δ_C(CD_3CN) 22.8 (q), 129.8 (d), 134.2 (s), 134.6 (d), 135.3 (d), 135.7 (d), 143.0 (s), 144.2 (s), 155.5 (d) and 162.4 (d) (Found: C, 48.15; H, 3.7. $C_{10}H_9BF_4S$ requires C, 48.42; H, 3.66%).

3-Methyl-4-phenyl-1-benzothiopyrylium tetrafluoroboranuide 2g. Pale green needles (91.9%) from 3-methyl-4-phenyl-2*H*-1-benzothiopyran **1g**; mp 153.5–157.5 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1110–1030 (BF_4^-); δ_H(CD_3CN) 2.56 (3 H, s, Me), 7.38–7.44 (2 H, m, ArH), 7.69–7.76 (3 H, m, ArH), 8.01–8.11 (2 H, m, ArH), 8.23 (1 H, dt, *J* 8.3 and 2.0, ArH), 8.76 (1 H, br d, *J* 8.3, ArH) and 10.24 (1 H, s, 2-H); δ_C(CD_3CN) 23.5 (q), 128.6 (d), 129.4 (d), 130.1 (d), 130.9 (d), 133.5 (d), 134.3 (s), 134.7 (d), 136.3 (s), 142.3 (s), 144.6 (s), 162.0 (d) and 166.5 (s) (Found: C, 59.4; H, 4.1. $C_{16}H_{13}BF_4S$ requires C, 59.29; H, 4.04%).

4-Cyano-1-benzothiopyrylium tetrafluoroboranuide 2h. Green crystals (90.1%), not sufficiently stable to be recrystallized, δ_H(CD_3CN) 8.45–8.55 (2 H, m, ArH), 8.92–9.00 (2 H, m, ArH), 9.06 (1 H, d, *J* 8.8, 3-H) and 10.66 (1 H, d, *J* 8.8, 2-H); δ_C(CD_3CN) 115.3 (s), 130.9 (d), 132.1 (d), 132.8 (s), 134.7 (d), 137.3 (d), 137.5 (d), 146.5 (s), 165.4 (d) and 165.4 (s).

General procedure for the reaction of 1-benzothiopyrylium salts 2 with substituted buta-1,3-dienes

The appropriate 1-benzothiopyrylium salt **2a–2h** (1 mmol) was added to a stirred solution of the appropriate substituted buta-1,3-diene **3A–3C** (2 mmol) in 1,2-dichloroethane (10 cm^3) at room temperature, and the mixture was stirred for an appropriate time. In the case of buta-1,3-diene, the butadiene gas was bubbled into a stirred suspension of benzothiopyrylium salt **2h** (1 mmol) in 1,2-dichloroethane (10 cm^3) for 5 min at room temperature, and the mixture was stirred for 20 min. Methanol (1 cm^3) was added to the reaction mixture, and then diethyl ether was added to precipitate the products. The reaction time and yields of the products are summarized in Table 1.

2,3-Dimethyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4aA. Plates, mp 108.5–109.5 °C (from acetonitrile–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H(CD_3CN) 1.79 (3 H, s, Me), 1.82 (3 H, Me), 2.70 and 3.13 (each 1 H, each br d, *J* 19.1, CHCH_2), 3.73 and 3.92 (each 1 H, each d, *J* 15.1, S^+–CH_2), 4.83 (1 H, br d, *J* 2.4, C*H*CH_2), 5.88 (1 H, dd, *J* 10.3 and 2.4, olefinic H), 6.89 (1 H, d, *J* 10.3, olefinic H), 7.45 (1 H, br d, *J* 7.3, ArH), 7.51 (1 H, dt, *J* 7.8 and 1.5, ArH), 7.69 (1 H, ddd, *J* 7.8, 7.3 and 1.5, ArH) and 8.02 (1 H, br d, *J* 7.8, ArH); δ_C(CD_3CN) 19.9 (q), 20.1 (q), 33.9 (t), 38.2 (t), 41.2 (d), 115.6 (s), 122.5 (s), 126.3 (d), 129.1 (d), 129.9 (s), 131.2 (d), 132.3 (s), 133.6 (d) and 136.3 (d) (Found: C, 56.9; H, 5.5. $C_{15}H_{17}BF_4S$ requires C, 56.98; H, 5.42%).

2,3-Dimethyl-9-phenyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4bA. Needles, mp 136.5–137.5 °C (from acetonitrile–diethyl ether); ν_{max}(KBr)/cm^{-1} 1120–1030 (BF_4^-); δ_H(CD_3CN) 1.77 and 1.79 (each 3 H, each s, 2 × Me), 2.78 and 3.03 (each 1 H, each br d, *J* 18.6, CHCH_2), 3.93 (2 H, br s, S^+–CH_2), 4.83 (1 H, br d, *J* 2.4, C*H*CH_2), 5.94 (1 H, d, *J* 2.4, olefinic H), 7.34–7.49 (6 H, m, ArH), 7.59–7.65 (1 H, m, ArH), 7.71–7.76 (1 H, m, ArH) and 7.98–8.01 (1 H, m, ArH); δ_C(CD_3CN) 20.2 (q), 20.3 (q), 34.2 (t), 37.3 (t), 41.2 (d), 117.2 (s), 122.3 (s), 124.7 (d), 129.7 (d), 129.8 (d), 129.9 (s), 129.9 (d), 130.8 (d), 131.3 (d), 134.0 (s), 134.4 (d), 136.3 (d), 138.5 (s) and 141.7 (s) (Found: C, 64.0; H, 5.3. $C_{21}H_{21}BF_4S$ requires C, 64.30; H, 5.40%).

2,3-Dimethyl-9-(*p*-tolyl)-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4cA. Prisms, mp 106–108 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H(CD_3CN) 1.77 and 1.79 (each 3 H, each s, 2 × Me), 2.39 (3 H, s, Ar-*Me*), 2.77 and 3.03 (each 1 H, each br d, *J* 18.6, CHCH_2), 3.92 (2 H, br s, S^+–CH_2), 4.81 (1 H, br s, C*H*CH_2), 5.90 (1 H, br s, olefinic H), 7.23 (4 H, br s, ArH), 7.36–7.38 (1 H, m, ArH), 7.59–7.64 (1 H, m, ArH), 7.70–7.76 (1 H, m, ArH) and 7.98–8.01 (1 H, m, ArH); δ_C(CD_3CN) 20.1 (q), 20.2 (q), 21.3 (q), 34.2 (t), 37.3 (t), 41.2 (d), 117.2 (s), 122.3 (s), 124.1 (d), 129.7 (d), 129.9 (s), 130.3 (d), 130.8 (d), 131.2 (d), 134.1 (s), 134.4 (d), 135.5 (s), 136.3 (d), 140.1 (s) and 141.7 (s) (Found: C, 64.8; H, 5.6. $C_{22}H_{23}BF_4S$ requires C, 65.04; H, 5.71%).

9-(4-Methoxyphenyl)-2,3-dimethyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4dA. Needles, mp 94–98 °C (decomp.) (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1120–1030 (BF_4^-); δ_H(CD_3CN) 1.77 and 1.80 (each 3 H, each s, 2 × Me), 2.77 and 3.03 (each 1 H, each br d, *J* 18.7, CHCH_2), 3.84 (3 H, s, OMe), 3.91 (2 H, br s, S^+–CH_2), 4.79–4.81 (1 H, m, C*H*CH_2), 5.88 (1 H, d, *J* 2.4, olefinic H), 7.01 and 7.33 (each 2 H, each d, *J* 8.8, ArH), 7.39–7.41 (1 H, m, ArH), 7.59–7.64 (1 H, m, ArH), 7.71–7.77 (1 H, m, ArH) and 7.97–8.00 (1 H, m, ArH); δ_C(CD_3CN) 20.1 (q), 20.2 (q), 34.2 (t), 37.2 (t), 41.2 (d), 56.1 (q), 115.0 (d), 117.2 (s), 122.2 (s), 123.5 (d), 129.9 (s), 130.6 (s), 130.9 (d), 131.2 (d), 134.2 (s), 134.3 (d), 136.3

(d), 141.4 (s) and 161.2 (s) (Found: C, 57.9; H, 5.2. $C_{22}H_{23}BF_4OS{\cdot}0.5CH_2Cl_2$ requires C, 58.15; H, 5.21%).

9-(4-Chlorophenyl)-2,3-dimethyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4eA. Prisms, mp 102–105 °C (decomp.) (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1030 (BF_4^-); δ_H(CD_3CN) 1.77 and 1.80 (each 3 H, each s, 2 × Me), 2.78 and 2.99 (each 1 H, each br d, *J* 19.0, CHC*H*$_2$), 3.92 (2 H, br s, S$^+$–C*H*$_2$), 4.81–4.85 (1 H, m, C*H*CH$_2$), 5.95 (1 H, d, *J* 2.9, olefinic H), 7.33–7.41 (3 H, m, ArH), 7.46–7.50 (2 H, m, ArH), 7.60–7.66 (1 H, m, ArH), 7.71–7.78 (1 H, m, ArH) and 7.98–8.02 (1 H, m, ArH); δ_C(CD_3CN) 20.2 (q), 20.3 (q), 34.1 (t), 37.3 (t), 41.2 (d), 117.1 (s), 122.3 (s), 125.2 (d), 129.8 (d), 129.9 (s), 130.7 (d), 131.4 (d), 131.5 (d), 133.7 (s), 134.4 (d), 135.4 (s), 136.3 (d), 137.2 (s) and 140.6 (s) (Found: C, 58.9; H, 5.1; N, 0.55. $C_{21}H_{20}BClF_4S{\cdot}0.25CH_3CN$ requires C, 59.10; H, 4.79; N, 0.80%).

2,3,10-Trimethyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4fA. Prisms, mp 94–95 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1030 (BF_4^-); δ_H(CD_3CN) 1.74, 1.80 and 2.04 (each 3 H, each s, 3 × Me), 2.87 (2 H, br s, CHC*H*$_2$), 3.85 and 3.94 (each 1 H, each d, *J* 15.6, S$^+$–C*H*$_2$), 4.69 (1 H, br s, C*H*CH$_2$), 6.75 (1 H, s, olefinic H), 7.45–7.54 (2 H, m, ArH), 7.70–7.75 (1 H, m, ArH) and 7.80–7.82 (1 H, m, ArH); δ_C(CD_3CN) 19.6 (q), 19.9 (q), 21.1 (q), 30.9 (t), 38.7 (t), 44.0 (d), 114.9 (s), 121.4 (s), 125.5 (d), 129.7 (s), 130.3 (d), 130.4 (d), 132.3 (d), 133.8 (s), 134.0 (s) and 136.0 (d) (Found: C, 58.0; H, 5.7. $C_{16}H_{19}BF_4S$ requires C, 58.20; H, 5.80%).

2,3,10-Trimethyl-9-phenyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4gA. Rods, mp 97.5–99 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H(CD_3CN) 1.75, 1.83 and 1.84 (each 3 H, each s, 3 × Me), 2.70 (1 H, dd, *J* 18.1 and 5.9, CHC*H*H), 2.88 (1 H, br d, *J* 18.1, CHCH*H*), 4.09 and 4.25 (each 1 H, each d, *J* 16.6, S$^+$–CH$_2$), 4.60 (1 H, t, *J* 5.9, C*H*CH$_2$), 6.83–6.86 (1 H, m, ArH), 7.20–7.23 (2 H, m, ArH), 7.43–7.57 (5 H, m, ArH) and 7.79–7.82 (1 H, m, ArH); δ_C(CD_3CN) 19.4 (q), 19.5 (q), 20.0 (q), 31.0 (t), 37.0 (t), 43.8 (d), 115.1 (s), 119.5 (s), 129.1 (d), 129.9 (d), 130.0 (s), 130.4 (d), 130.6 (d), 130.9 (s), 131.0 (d), 134.9 (d), 136.4 (s), 136.7 (s) and 138.4 (s) (Found: C, 64.8; H, 5.65. $C_{22}H_{23}BF_4S$ requires C, 65.04; H, 5.71%).

9-Cyano-2,3-dimethyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4hA. Rods, mp 153–155 °C (decomp.) (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1100–1030 (BF_4^-); δ_H(CD_3CN) 1.77 and 1.83 (each 3 H, each s, 2 × Me), 2.83 and 3.02 (each 1 H, each br d, *J* 19.0, CHC*H*$_2$), 3.88 (2 H, br s, S$^+$–CH$_2$), 4.96 (1 H, br d, *J* 2.4, C*H*CH$_2$), 6.88 (2 H, d, *J* 2.4, olefinic H), 7.70–7.77 (1 H, m, ArH) and 7.89–8.00 (3 H, m, ArH); δ_C(CD_3CN) 20.0 (q), 20.1 (q), 33.4 (t), 39.1 (t), 41.5 (d), 115.5 (s), 115.9 (s), 116.0 (s), 123.1 (s), 128.1 (s), 129.7 (d), 129.9 (s), 133.1 (d), 134.5 (d), 137.0 (d) and 140.7 (d) (Found: C, 56.1; H, 4.7; N, 4.1. $C_{16}H_{16}BF_4NS$ requires C, 56.33; H, 4.73; N, 4.11%).

2-Methyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4aB. Rods, mp 104.5–105.5 °C (from acetonitrile–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H(CD_3CN) 1.87 (3 H, s, Me), 2.76 and 3.00 (each 1 H, each br d, *J* 18.6, CHC*H*$_2$), 3.76 (1 H, br d, *J* 15.6, S$^+$–C*H*H), 3.97 (1 H, dd, *J* 15.6 and 6.4, S$^+$–CH*H*), 4.82 (1 H, br d, *J* 2.9, C*H*CH$_2$), 5.75 (1 H, br d, *J* 6.4, S$^+$–CH$_2$C*H*=CMe–), 5.97 (1 H, dd, *J* 10.3 and 2.4, olefinic H), 6.99 (1 H, dd, *J* 10.3 and 2.9, olefinic H), 7.54–7.60 (2 H, m, ArH), 7.78 (1 H, dt, *J* 7.8 and 1.5, ArH) and 7.89 (1 H, br d, *J* 7.8, ArH); δ_C(CD_3CN) 24.7 (q), 32.5 (t), 34.5 (t), 41.5 (d), 115.5 (d), 115.8 (d), 126.3 (d), 129.6 (d), 131.3 (d), 132.3 (s), 134.0 (s), 136.5 (d) and 138.3 (s) (Found: C, 55.6; H, 5.05. $C_{14}H_{15}BF_4S$ requires C, 55.65; H, 5.00%).

2-Methyl-9-phenyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4bB. Needles, mp 131.5–132 °C (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1120–1020 (BF_4^-); δ_H(CD_3CN) 1.85 (3 H, s, Me), 2.77 and 3.04 (each 1 H, each br d, *J* 18.6, CHC*H*$_2$), 3.91 (1 H, br d, *J* 15.6, S$^+$–C*H*H), 4.10 (1 H, dd, *J* 15.6 and 5.9, S$^+$–CH*H*), 4.88 (1 H, br s, C*H*CH$_2$), 5.75 (1 H, br d, *J* 5.9, S$^+$–CH$_2$C*H*=CMe–), 5.98 (1 H, d, *J* 2.4, olefinic H), 7.33–7.49 (6 H, m, ArH), 7.59–7.65 (1 H, m, ArH), 7.71–7.76 (1 H, m, ArH) and 8.01–8.04 (1 H, m, ArH); δ_C(CD_3CN) 24.6 (q), 32.7 (t), 34.0 (t), 41.7 (d), 115.6 (d), 117.0 (s), 124.5 (d), 129.7 (d), 129.9 (d), 130.7 (d), 131.2 (d), 134.1 (s), 134.5 (d), 136.3 (d), 138.4 (s) and 141.9 (s) (Found: C, 63.5; H, 5.1. $C_{20}H_{19}BF_4S$ requires C, 63.51; H, 5.06%).

2,10-Dimethyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4fB. Rods, mp 115–117.5 °C (decomp.) (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1030 (BF_4^-); δ_H(CD_3CN) 1.85 and 2.06 (each 3 H, each s, 2 × Me), 2.81 and 2.90 (each 1 H, each br d, *J* 19.0, CHC*H*$_2$), 3.97 (2 H, br s, S$^+$–CH$_2$), 4.74 (1 H, br s, C*H*CH$_2$), 5.68 (1 H, br s, S$^+$–CH$_2$C*H*=CMe–), 6.79 (1 H, s, olefinic H), 7.46–7.54 (2 H, m, ArH) and 7.70–7.83 (2 H, m, ArH); δ_C(CD_3CN) 21.0 (q), 24.3 (q), 29.1 (t), 34.6 (t), 43.9 (d), 114.4 (d), 114.6 (s), 125.9 (d), 130.3 (d), 130.4 (d), 132.5 (d), 134.1 (s), 136.0 (d) and 137.9 (s) (Found: C, 56.7; H, 5.4. $C_{15}H_{17}BF_4S$ requires C, 56.98; H, 5.42%).

9-Cyano-2-methyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4hB. Needles, mp 153 °C (decomp.) (from dichloromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1100–1030 (BF_4^-); δ_H(CD_3CN) 1.88 (3 H, s, Me), 2.83 and 3.03 (each 1 H, each br d, *J* 19.0, CHC*H*$_2$), 3.84 (1 H, br d, *J* 15.6, S$^+$–C*H*H), 4.07 (1 H, dd, *J* 15.6 and 5.9, S$^+$–CH*H*), 5.00 (1 H, br d, *J* 2.4, C*H*CH$_2$), 5.78 (1 H, br s, S$^+$–CH$_2$C*H*=CMe–), 6.92 (1 H, d, *J* 2.4, olefinic H), 7.71–7.77 (1 H, m, ArH) and 7.89–8.03 (3 H, m, ArH); δ_C(CD_3CN) 24.5 (q), 31.9 (t), 35.4 (t), 41.7 (d), 115.5 (s), 115.7 (s), 115.9 (d), 116.2 (s), 128.3 (s), 129.7 (d), 133.1 (d), 134.9 (d), 137.1 (d), 138.2 (s) and 140.6 (d) (Found: C, 54.85; H, 4.3; N, 4.3. $C_{15}H_{14}BF_4NS$ requires C, 55.07; H, 4.31; N, 4.28%).

9-Cyano-2-phenyl-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4hC. Leaflets, mp 140–145 °C (decomp.) (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 2230 (CN) and 1110–1030 (BF_4^-); δ_H(CD_3CN) 3.38 and 3.42 (each 1 H, each br d, *J* 19.0, CHC*H*$_2$), 4.06 (1 H, dd, *J* 16.6 and 2.0, S$^+$–C*H*H), 4.32 (1 H, dd, *J* 16.6 and 5.9, S$^+$–CH*H*), 5.19 (1 H, br s, C*H*CH$_2$), 6.33 (1 H, dd, *J* 5.9 and 2.0, S$^+$–CH$_2$C*H*=CPh–), 7.03 (1 H, d, *J* 2.4, olefinic H), 7.37–7.46 (5 H, m, ArH), 7.73–7.79 (1 H, m, ArH), 7.91–7.99 (2 H, m, ArH) and 8.06 (1 H, br d, *J* 8.3, ArH); δ_C(CD_3CN) 30.3 (t), 36.1 (t), 41.9 (d), 115.5 (s), 115.7 (s), 116.3 (s), 119.0 (d), 126.6 (d), 128.1 (s), 129.6 (d), 129.7 (d), 133.1 (d), 134.9 (d), 137.1 (d), 139.5 (s), 140.4 (d) and 140.4 (s) (Found: C, 61.6; H, 4.2; N, 3.8. $C_{20}H_{16}BF_4NS$ requires C, 61.72; H, 4.14; N, 3.60%).

9-Cyano-1,10a-dihydro-4*H*-4a-thioniaphenanthrene tetrafluoroboranuide 4hD. Needles, mp 175 °C (decomp.) (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 2240 (CN) and 1100–1030 (BF_4^-); δ_H(CD_3CN) 2.90–3.09 (2 H, m, CHC*H*$_2$), 3.85–3.92 (1 H, m, S$^+$–C*H*H), 4.07–4.15 (1 H, m, S$^+$–CH*H*), 4.99–5.01 (1 H, m, C*H*CH$_2$), 6.01–6.08 (1 H, m, S$^+$–CH$_2$–C*H*=CH–), 6.16–6.21 (1 H, m, S$^+$–CH$_2$CH=C*H*–), 6.91 (1 H, d, *J* 2.9, olefinic H), 7.17–7.78 (1 H, m, ArH) and 7.91–8.02 (3 H, m, ArH); δ_C(CD_3CN) 27.7 (t), 35.3 (t), 41.4 (d), 115.5 (s), 115.8 (s), 116.7 (s), 121.7 (d), 128.4 (s), 129.1 (d), 129.8 (d), 133.2 (d), 134.8 (d), 137.3 (d) and 140.9 (d) (Found: C, 53.4; H, 3.9; N, 4.5. $C_{14}H_{12}BF_4NS$ requires C, 53.70; H, 3.86; N, 4.47%).

Reactions of cycloadducts 4 with nucleophiles

(a) With methanol. A mixture of **4** (3 mmol) and dry methanol (30 cm^3) was refluxed for 5 min. To the reaction mixture was added sat. aqueous $NaHCO_3$ and the mixture was extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residual oil was subjected to PLC on silica gel with hexane–ethyl acetate (10:1) to afford two products **5** and **6** (X = OMe). The latter compounds were obtained as an inseparable mixture of diastereoisomers. The

reaction conditions and yields of the products including a diastereoisomeric ratio of the products **6** are summarized in Table 2.

2-(4-*Methoxy*-2,3-*dimethylbut*-2-*enyl*)-2H-1-*benzothiopyran* **5a**.—Yellow prisms (61%), from the cycloadduct **4aA**, mp 43.5–45 °C (from hexane); δ_H($CDCl_3$) 1.70 and 1.73 (each 3 H, each s, 2 × Me), 2.46 (2 H, d, *J* 7.3, CHCH_2), 3.18 (3 H, s, OMe), 3.64 (1 H, dd, *J* 7.3 and 5.9, C*H*CH_2), 3.77 and 3.82 (each 1 H, each d, *J* 11.2, CH_2OMe), 5.90 (1 H, dd, *J* 10.3 and 5.9, SCHC*H*=CH–), 6.48 (1 H, d, *J* 10.3, SCHCH=C*H*–), 7.08–7.14 (3 H, m, ArH) and 7.20–7.25 (1 H, m, ArH); δ_C($CDCl_3$) 16.8 (q), 18.8 (q), 37.5 (d), 39.6 (t), 57.7 (q), 72.9 (t), 125.4 (d), 126.8 (d), 127.5 (d), 127.8 (d), 127.9 (d), 128.0 (d), 129.1 (s), 129.6 (s), 130.6 (s) and 131.7 (s); *m*/*z* 258 (M^+ − 2, 0.7%) and 147 (100) (Found: C, 73.6; H, 7.8. $C_{16}H_{20}OS$ requires C, 73.80; H, 7.74%).

2-(2-*Methoxy*-2,3-*dimethylbut*-3-*enyl*)-2H-1-*benzothiopyran* **6a**.—Yellow oil (10%), inseparable mixture of diastereoisomers in the ratio 1:1.3 from the cycloadduct **4aA**. Data for the major isomer of **6a**: δ_H($CDCl_3$) 1.32 (3 H, s, Me), 1.70 (3 H, s, CH_2=C*Me*), 1.94–2.17 (2 H, m, CHCH_2), 3.07 (3 H, s, OMe), 3.57–3.71 (1 H, m, C*H*CH_2), 4.95–5.01 (2 H, m, C=CH_2), 6.00 (1 H, dd, *J* 10.3 and 5.9, SCHC*H*=CH–), 6.42 (1 H, d, *J* 10.3, SCHCH=C*H*–), 7.05–7.13 (3 H, m, ArH) and 7.20–7.22 (1 H, m, ArH); δ_C($CDCl_3$) 18.8 (q), 21.6 (q), 34.0 (d), 45.7 (t), 49.9 (q), 79.0 (s), 113.5 (t), 125.4 (d), 126.9 (d), 127.3 (d), 127.7 (d), 128.5 (d), 131.1 (s), 131.8 (s) and 146.7 (s); *m*/*z* 260 (M^+, 1.3%) and 147 (100) (Found: M^+, 260.1210. $C_{16}H_{20}OS$ requires *M*, 260.1234). Data for the minor isomer of **6a**: δ_H($CDCl_3$) 1.32 (3 H, s, Me), 1.70 (3 H, s, CH_2=C*Me*), 1.94–2.17 (2 H, m, CHCH_2), 3.09 (3 H, s, OMe), 3.57–3.71 (1 H, m, C*H*CH_2), 4.95–5.01 (2 H, m, C=CH_2), 5.98 (1 H, dd, *J* 10.3 and 5.9, SCHC*H*=CH–), 6.42 (1 H, d, *J* 10.3, SCHCH=C*H*–), 7.05–7.13 (3 H, m, ArH) and 7.20–7.22 (1 H, m, ArH); δ_C($CDCl_3$) 19.0 (q), 21.8 (q), 34.1 (d), 45.6 (t), 49.9 (q), 79.2 (s), 113.7 (t), 125.4 (d), 127.0 (d), 127.3 (d), 127.7 (d), 128.5 (d), 131.1 (s), 131.8 (s) and 147.2 (s).

2-(4-*Methoxy*-2,3-*dimethylbut*-2-*enyl*)-4-*phenyl*-2H-1-*benzothiopyran* **5b**.—Pale yellow needles (49%), from the cycloadduct **4bA**, mp 70–71 °C (from dichloromethane–hexane); δ_H($CDCl_3$) 1.74 and 1.76 (each 3 H, each s, 2 × Me), 2.51 (2 H, d, *J* 7.8, CHCH_2), 3.41 (3 H, s, OMe), 3.70 (1 H, dd, *J* 7.8 and 6.4, C*H*CH_2), 3.78 (2 H, br s, CH_2OMe), 5.97 (1 H, d, *J* 6.4, SCHC*H*=CAr–), 7.02–7.04 (2 H, m, ArH), 7.10–7.17 (1 H, m, ArH), 7.23–7.27 (2 H, m, ArH) and 7.30–7.38 (4 H, m, ArH); δ_C($CDCl_3$) 16.9 (q), 18.8 (q), 37.3 (d), 38.5 (t), 57.8 (q), 72.9 (t), 125.1 (d), 126.1 (d), 127.5 (d), 127.7 (d), 128.1 (d), 128.2 (d), 129.0 (d), 129.4 (s), 129.5 (s), 132.4 (s), 133.7 (s), 140.1 (s) and 140.8 (s); *m*/*z* 334 (M^+ − 2, 0.1%) and 223 (100) (Found: C, 78.6; H, 7.2. $C_{22}H_{24}OS$ requires C, 78.53; H, 7.19%).

2-(2-*Methoxy*-2,3-*dimethylbut*-3-enyl)-4-*phenyl*-2H-1-*benzothiopyran* **6b**.—Yellow oil (15%), inseparable mixture of diastereoisomers in the ratio 1:1.5 from the cycloadduct **4bA**. Data for the major isomer of **6b**: δ_H([$^2H_6$]benzene) 1.10 and 1.56 (each 3 H, each s, 2 × Me), 2.02 (1 H, dd, *J* 14.2 and 4.9, CHC*H*H), 2.20 (1 H, dd, *J* 14.2 and 7.8, CHCH*H*), 2.90 (3 H, s, OMe), 3.74 (1 H, ddd, *J* 7.8, 6.4 and 5.4, C*H*CH_2), 6.11 (1 H, d, *J* 6.4, SCHC*H*=CAr–), 6.77–6.91 (2 H, m, ArH), 7.09–7.19 (4 H, m, ArH), 7.23–7.29 (2 H, m, ArH) and 7.37–7.41 (2 H, m, ArH); δ_C($CDCl_3$) 19.0 (q), 21.7 (q), 34.0 (d), 44.4 (t), 49.9 (q), 79.1 (s) and 113.5 (t); *m*/*z* 336 (M^+, 1.1%) and 223 (100) (Found: M^+, 336.1527. $C_{22}H_{24}OS$ requires *M*, 336.1547). Data for the minor isomer of **6b**: 1.10 and 1.56 (each 3 H, each s, 2 × Me), 2.06 (1 H, dd, *J* 14.6 and 5.4, CHC*H*H), 2.25 (1 H, dd, *J* 14.6 and 7.8, CHCH*H*), 2.92 (3 H, s, OMe), 3.68 (1 H, ddd, *J* 7.8, 6.4 and 5.4, C*H*CH_2), 4.85–4.93 (2 H, m, C=CH_2), 6.06 (1 H, d, *J* 6.4, SCHC*H*=CAr–), 6.77–6.91 (2 H, m, ArH), 7.09–7.19 (4 H, m, ArH), 7.23–7.29 (2 H, m, ArH) and 7.37–7.41 (2 H, m, ArH); δ_C($CDCl_3$) 19.0 (q), 21.7 (q), 34.1 (d), 44.4 (t), 49.8 (q), 79.1 (s) and 113.8 (t).

2-(4-*Methoxy*-2,3-*dimethylbut*-2-*enyl*)-3-*methyl*-2H-1-*benzothiopyran* **5c**.—Yellow oil (59%), from the cycloadduct **4fA**, δ_H($CDCl_3$) 1.71 and 1.72 (each 3 H, each s, 2 × Me), 1.98 (3 H, d, *J* 1.5, SCHC*Me*=CH–), 2.31 (1 H, dd, *J* 13.7 and 6.4, CHC*H*H), 2.33 (1 H, dd, *J* 13.7 and 8.8, CHCH*H*), 3.11 (3 H, s, OMe), 3.15 (1 H, dd, *J* 8.8 and 6.4, C*H*CH_2), 3.72 (2 H, br s, CH_2OMe), 6.28 (1 H, br s, SCHCMe=C*H*–), 7.03–7.10 (3 H, m, ArH) and 7.20–7.24 (1 H, m, ArH); δ_C($CDCl_3$) 16.7 (q), 19.0 (q), 23.2 (q), 34.7 (t), 42.2 (d), 57.6 (q), 72.9 (t), 123.3 (d), 125.4 (d), 126.9 (d), 127.1 (d), 127.5 (d), 128.2 (s), 129.4 (s), 129.7 (s), 132.6 (s) and 136.4 (s); *m*/*z* 274 (M^+, 0.01%) and 161 (100) (Found: C, 74.25; H, 8.1. $C_{17}H_{22}OS$ requires C, 74.41; H, 8.08%).

2-(2-*Methoxy*-2,3-*dimethylbut*-3-*enyl*)-3-*methyl*-2H-1-*benzothiopyran* **6c**.—Yellow oil (5%), inseparable mixture of diastereoisomers in the ratio 1:1 from the cycloadduct **4fA**. Data for the diastereoisomeric mixture of **6c**: δ_H($CDCl_3$) 1.37, 1.38, 1.68 and 1.72 (each 3 H, each s, 2 × CH_2=C*Me* and 2 × Me), 1.73–1.79 (1 H, m, CHC*H*H), 1.95–2.06 (4 H, m, 3-Me and CHCH*H*), 3.04–3.23 (4 H, m, OMe and C*H*CH_2), 4.91 (1 H, br s, C=C*H*H), 4.97–4.98 (1 H, m, C=C*H*H), 5.00 (1 H, br s, C=CH*H*), 5.06–5.07 (1 H, m, C=CH*H*), 6.23 (1 H, br s, SCHCMe=C*H*–), 7.01–7.08 (3 H, m, ArH) and 7.21–7.26 (1 H, m, ArH); δ_C($CDCl_3$) 18.9 (q), 19.1 (q), 21.1 (q), 22.0 (q), 22.7 (q), 38.0 (t), 38.3 (t), 41.6 (d), 42.4 (d), 49.8 (q), 49.9 (q), 78.8 (s), 79.2 (s), 113.7 (t), 114.3 (t), 123.1 (d), 123.2 (d), 125.4 (d), 126.9 (d), 127.6 (d), 127.7 (d), 128.5 (s), 128.6 (s), 133.1 (s), 133.2 (s), 137.1 (s), 137.2 (s), 146.2 (s) and 147.8 (s); *m*/*z* 274 (M^+, 0.2%) and 161 (100). The high-resolution mass spectrum could not be recorded because of the very weak molecular ion peak.

4-*Cyano*-2-(4-*methoxy*-2,3-*dimethylbut*-2-*enyl*)-2H-1-*benzothiopyran* **5d**.—Yellow oil (77%), from the cycloadduct **4hA**, ν_{max}(neat)/cm^{-1} 2230 (CN); δ_H($CDCl_3$) 1.70 and 1.74 (each 3 H, each s, 3 × Me), 2.43 (1 H, dd, *J* 14.2 and 8.3, CHC*H*H), 2.51 (1 H, dd, *J* 14.2 and 7.8, CHCH*H*), 3.20 (3 H, s, OMe), 3.68–3.78 (3 H, m, C*H*CH_2 and CH_2OMe), 6.74 (1 H, d, *J* 6.8, SCHC*H*=CCN–), 7.19–7.31 (3 H, m, ArH) and 7.54–7.60 (1 H, m, ArH); δ_C($CDCl_3$) 17.0 (q), 18.6 (q), 36.9 (d), 37.8 (t), 57.8 (q), 72.7 (t), 114.4 (s), 116.8 (s), 126.1 (d), 126.5 (d), 127.5 (s), 127.7 (s), 127.9 (d), 129.8 (d), 130.7 (s), 130.8 (s) and 140.4 (d); *m*/*z* 285 (M^+, 0.02%) and 172 (100) (Found: C, 71.3; H, 6.8; N, 4.8. $C_{17}H_{19}NOS$ requires C, 71.54; H, 6.71; N, 4.91%).

4-*Cyano*-2-(2-*methoxy*-2,3-*dimethylbut*-3-*enyl*)-2H-1-*benzothiopyran* **6d**.—Yellow oil (21%), inseparable mixture of diastereoisomers in the ratio 1:2.6 from the cycloadduct **4hA**, ν_{max}(neat)/cm^{-1} 2230 (CN); *m*/*z* 285 (M^+, 0.4%) and 94 (100) (Found: M^+, 285.1211. $C_{17}H_{19}NOS$ requires *M*, 285.1188). Data for the major isomer of **6d**: δ_H($CDCl_3$) 1.30 and 1.67 (each 3 H, each s, 2 × Me), 1.88 (1 H, dd, *J* 14.2 and 4.4, CHC*H*H), 2.18 (1 H, dd, *J* 14.2 and 8.3, CHCH*H*), 3.08 (3 H, s, OMe), 3.78 (1 H, ddd, *J* 8.3, 6.4 and 4.4, C*H*CH_2), 6.88 (1 H, d, *J* 6.4, SCHC*H*=CCN–), 7.21–7.31 (3 H, m, ArH) and 7.51–7.57 (1 H, m, ArH); δ_C($CDCl_3$) 18.7 (q), 21.3 (q), 33.9 (d), 44.8 (t), 50.0 (q), 78.7 (s), 113.3 (s), 113.6 (t), 117.2 (s), 126.2 (d), 126.6 (d), 127.7 (s), 127.9 (d), 129.6 (d), 131.1 (s), 142.3 (d) and 146.8 (s). Data for the minor isomer of **6d**: δ_H($CDCl_3$) 1.27 and 1.67 (each 3 H, each s, 2 × Me), 1.94 (1 H, dd, *J* 14.2 and 4.4, CHC*H*H), 2.12 (1 H, dd, *J* 14.2 and 8.3, CHCH*H*), 3.10 (3 H, s, OMe), 3.66 (1 H, ddd, *J* 8.3, 6.4 and 4.4, C*H*CH_2), 6.87 (1 H, d. *J* 6.4, SCHC*H*=CCN–), 7.12–7.31 (3 H, m, ArH) and 7.51–7.57 (1 H, m, ArH); δ_C($CDCl_3$) 19.1 (q), 21.8 (q), 33.9 (d), 44.7 (t), 49.9 (q), 79.0 (s), 113.1 (s), 113.7 (t), 117.2 (s), 126.2 (d), 126.6 (d), 127.7 (s), 127.9 (d), 129.6 (d), 131.1 (s), 142.3 (d) and 145.8 (s).

(b) With water. A mixture of cycloadduct **4hA** (341 mg, 1 mmol) and water (0.5 cm^3) in acetone (10 cm^3) was stirred at room temperature for 20 min. The reaction mixture was diluted with water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residual oil was subjected to PLC on silica gel with hexane–ethyl acetate (10:1) to afford the following two products.

4-*Cyano*-2-(4-*hydroxy*-2,3-*dimethylbut*-2-*enyl*)-2H-1-*benzothiopyran* **5e**.—Yellow oil (24%); ν_{max}(neat)/cm^{-1} 3500–3300 (OH) and 2230 (CN); δ_H($CDCl_3$) 1.69 (3 H, s, Me), 1.79 (3 H, s, Me), 2.49 (1 H, dd, *J* 13.7 and 6.4, CHC*H*H), 2.54 (1 H, dd, *J* 13.7 and 9.3, CHCH*H*), 3.69 (1 H, dt, *J* 9.3 and 6.4, C*H*CH_2), 3.88 and 3.98 (each 1 H, each d, *J* 11.2, CH_2OH), 6.76 (1 H, d, *J* 6.4, SCHC*H*=CCN–), 7.21–7.31 (3 H, m, ArH) and 7.55–7.59 (1 H, m, ArH); δ_C($CDCl_3$) 16.9 (q), 18.7 (q), 37.0 (d), 37.5 (t), 63.0 (t), 114.6 (s), 116.9 (s), 126.5 (d), 126.8 (d), 127.4 (s), 128.1 (d), 130.0 (s), 130.1 (d), 133.3 (s) and 140.3 (d); *m*/*z* 271 (M^+, 0.05%) and 172 (100). The high resolution mass spectrum could not be recorded because of a very weak molecular ion peak.

4-*Cyano*-2-(2-*hydroxy*-2,3-*dimethylbut*-3-*enyl*)-2H-1-*benzothiopyran* **6e**.—Yellow oil (5.5%) inseparable mixture of diastereoisomers, ν_{max}(neat)/cm^{-1} 3600–3300 (OH) and 2230 (CN); *m*/*z* 271 (M^+, 16%) and 172 (100) (Found: M^+, 271.1022. $C_{16}H_{17}NOS$ requires *M*, 271.1030); δ_H($CDCl_3$) for the major isomer of **6e**: 1.28 (3 H, s, Me), 1.60 (1 H, br s, OH), 1.71 (3 H, s, Me), 1.94 (1 H, dd, *J* 14.7 and 6.4, CHC*H*H), 2.13 (1 H, dd, *J* 14.7 and 6.8, CHCH*H*), 3.74 (1 H, dt, *J* 6.8 and 6.4, C*H*CH_2), 4.94 (1 H, br s, C=C*H*H), 5.15 (1 H, br s, C=CH*H*), 6.81 (1 H, d, *J* 6.8, SCHC*H*=CCN–), 7.19–7.34 (3 H, m, ArH) and 7.53–7.59 (1 H, m, ArH); δ_H($CDCl_3$) for the minor isomer of **6e**: 1.31 (3 H, s, Me), 1.60 (1 H, br s, OH), 1.75 (3 H, s, Me), 2.00 (1 H, dd, *J* 13.7 and 4.9, CHC*H*H), 2.05 (1 H, dd, *J* 13.7 and 8.3, CHCH*H*), 3.65 (1 H, ddd, *J* 8.3, 6.4 and 4.9, C*H*CH_2), 4.94 (1 H, br s, C=C*H*H), 5.12 (1 H, br s, C=CH*H*), 6.98 (1 H, d, *J* 6.4, SCHC*H*=CCN–), 7.19–7.34 (3 H, m, ArH) and 7.53–7.59 (1 H, m, ArH).

Cyclization of compounds 5d and 6d by treatment with tetrafluoroboric acid

To a stirred, ice-cooled solution of compound **5d** or **6d** (100 mg) in diethyl ether (7 cm^3) was added 42% tetrafluoroboric acid (0.4 cm^3), and the mixture was stirred for 10 h at room temperature to precipitate the sulfonium salt **4hA** as crystals in 81.5% or 59.7% yield, respectively, which was completely identical with the cycloadduct **4hA** in all respects.

Reaction of the cycloadduct 4hA with a variety of bases

(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 (distilled over sodium and benzophenone, 10 cm^3) at −30 °C under nitrogen. After 30 min, the cycloadduct **4hA** (341 mg, 1 mmol) was added under nitrogen at −78 °C to the LDA solution prepared above, and the mixture was 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. The residual oil was subjected to PLC on silica gel with hexane–ethyl acetate (10:1) to afford the following products.

4-*Cyano*-3′,4′-*dimethylspiro*[2H-[1]*benzothiopyran*-2,1′-*cyclopent*-3′-*ene*] **7**.—An oil (122 mg, 48.2%); ν_{max}(neat)/cm^{-1} 2230 (CN); δ_H($CDCl_3$) 1.60 (6 H, br s, 2 × Me), 2.67 (4 H, br s, 2 × CH_2), 6.76 (1 H, s, olefinic H), 7.18–7.28 (3 H, m, ArH) and 7.55–7.59 (1 H, m, ArH); δ_C($CDCl_3$) 13.4 (q), 47.3 (s), 52.9 (t), 113.2 (s), 117.1 (s), 126.0 (d), 126.5 (d), 127.3 (s), 127.6 (d), 128.2 (s), 129.5 (d), 131.8 (s) and 147.5 (d); *m*/*z* 253 (M^+, 44%), 94 (100) (Found: C, 76.0; H, 6.0; N, 5.5; M^+, 253.0908. $C_{16}H_{15}NS$ requires C, 75.85; H, 5.97; N, 5.53%; *M*, 253.0925).

4-*Cyano*-5′-*isopropenyl*-5′-*methylspiro*[2H-[1]*benzothiopyran*-2,3′-[1,2]*dioxolane*] **8**.—Rods (88 mg, 31%), an inseparable mixture of diastereoisomers, mp 85–97.5 °C (from hexane–dichloromethane), ν_{max}(KBr)/cm^{-1} 2240 (CN); *m*/*z* 253 (M^+, 33%) and 159 (100) (Found: C, 67.5; H, 5.3; N, 5.0. $C_{16}H_{15}NO_2S$ requires C, 67.34; H, 5.30; N, 4.91%); δ_H($CDCl_3$) for the major isomer: 1.49 and 1.88 (each 3 H, each s, 2 × Me), 2.91 and 2.96 (each 1 H, each d, *J* 13.7, CH_2), 5.01 (1 H, br s, C=C*H*H), 5.09 (1 H, br s, C=CH*H*), 6.64 (1 H, s, olefinic H), 7.26–7.40 (3 H, m, ArH) and 7.71–7.77 (1 H, m, ArH); δ_H($CDCl_3$) for the minor isomer 1.56 and 1.83 (each 3 H, each s, 2 × Me), 2.68 and 3.40 (each 1 H, each d, *J* 13.7, CH_2), 5.01 (1 H, br s, C=C*H*H), 5.09 (1 H, br s, C=CH*H*), 6.56 (1 H, s, olefinic H), 7.29–7.40 (3 H, m, ArH) and 7.71–7.77 (1 H, m, ArH); δ_C($CDCl_3$) for the major isomer 18.4 (q), 25.4 (q), 59.4 (t), 87.5 (s), 88.4 (s), 113.0 (t), 116.2 (s), 118.1 (s), 124.9 (s), 126.3 (d), 127.2 (d), 127.6 (d), 130.3 (d), 130.9 (s), 132.4 (d) and 144.1 (s); δ_C($CDCl_3$) for the minor isomer 19.1 (q), 22.8 (q), 58.2 (t), 87.7 (s), 88.8 (s), 111.8 (t), 116.2 (s), 117.3 (s), 125.0 (s), 126.4 (d), 127.2 (d), 127.6 (d), 130.2 (d), 130.9 (s), 132.2 (d) and 146.9 (s).

(b) With sodium hydride. Sodium hydride (60% dispersion in mineral oil, 48 mg, 1.20 mmol) was added portionwise with stirring to an ice-cooled solution of the cycloadduct **4hA** (341 mg, 1 mmol) in dry DMF (carefully degassed before using, 10 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 residual oil was subjected to PLC on silica gel to afford compounds **7** and **8** in 41.9 and 31% yields, respectively.

(c) With triethylamine. Cycloadduct **4hA** (341 mg, 1 mmol) was added with stirring to an ice-cooled solution of triethylamine (202 mg, 2 mmol) in ethanol (10 cm^3), and the mixture was stirred for 30 min. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC on silica gel to give compounds **7** and **8** in 51.4 and 28% yields, respectively.

(d) With diethylamine. Cycloadduct **4hA** (341 mg, 1 mmol) was added to a solution of diethylamine (146 mg, 2 mmol) in 1,2-dichloroethane (10 cm^3) and the mixture was stirred at room temperature for 20 min and worked up as above to afford compounds **7** and **8** in 53.8 and 30% yields, respectively.

(e) With potassium acetate. A mixture of the cycloadduct **4hA** (341 mg, 1 mmol) and potassium acetate (196 mg, 2 mmol) in 1,2-dichloroethane (10 cm^3) was stirred for 30 min. After dilution with water (30 cm^3), the reaction mixture was extracted with dichloromethane and the extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC on silica gel to give compounds **7** and **8** in 45 and 27% yields, respectively.

(f) With potassium carbonate. Cycloadduct **4hA** (341 mg, 1 mmol) was added to a stirred suspension of potassium carbonate (276 mg, 2 mmol) in acetone (10 cm^3), and the mixture was stirred for 30 min at room temperature. Work up as above afforded compounds **7** and **8** in 34 and 35% yields, respectively.

Reduction of the compound 8 with sodium borohydride †

Sodium borohydride (19 mg, 0.5 mmol) was added portionwise to a stirred solution of compound **8** (127 mg, 0.45 mmol) in ethanol (5 cm^3) and the mixture was then stirred for 1 h at room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was subjected to PLC on silica gel with hexane–ethyl acetate (6:1) to afford the following two diastereoisomeric compounds **9a** and **9b**.

4-Cyano-5′-isopropenyl-5′-methylspiro[3,4-dihydro-2*H*-[1]-benzothiopyran-2,3′-[1,2]dioxolane] 9a. Major isomer, (47%) needles, mp 72–72.5 °C (from hexane); ν_{max}(KBr)/cm^{-1} 2250 (CN); δ_H($CDCl_3$) 1.50 and 1.87 (each 3 H, each s, 2 × Me), 2.37 (1 H, dd, *J* 13.2 and 12.7, CHC*H*H), 2.67 and 3.04 (each 1 H, each d, *J* 13.7, CH_2), 2.96 (1 H, dd, *J* 13.2 and 3.4, CHCH*H*), 4.32 (1 H, dd, *J* 12.7 and 3.4, C*H*CH_2), 5.00 and 5.11 (each 1 H, each br s, C=CH_2), 7.06–7.09 (1 H, m, ArH), 7.14–7.26 (2 H, m,

† The IUPAC name for sodium borohydride is sodium boranuide.

ArH) and 7.56–7.59 (1 H, m, ArH); δ_C($CDCl_3$) 18.7 (q), 24.0 (q), 29.5 (d), 37.8 (t), 57.2 (t), 88.4 (s), 90.0 (s), 112.0 (t), 119.7 (s), 125.6 (d), 125.6 (s), 126.2 (d), 128.0 (d), 128.7 (d), 131.0 (s) and 146.1 (s); *m/z* 287 (M^+, 0.3%) and 162 (100) (Found: C, 67.1; H, 6.0; N, 4.9. $C_{16}H_{17}NO_2S$ requires C, 66.87; H, 5.96; N, 4.87%). Minor isomer **9b**: (22%), rods, mp 91.5–92.5 °C (from hexane); ν_{max}(KBr)/cm^{-1} 2250 (CN); δ_H($CDCl_3$) 1.54 and 1.84 (each 3 H, s, 2 × Me), 2.37 (1 H, dd, *J* 13.2 and 12.7, CHC*H*H), 2.64 and 3.01 (each 1 H, each d, *J* 13.7, CH_2), 2.85 (1 H, dd, *J* 13.2 and 3.4, CHCH*H*), 4.27 (1 H, dd, *J* 12.7 and 3.4, C*H*CH_2), 4.97 and 5.06 (each 1 H, each br s, C=CH_2), 7.08–7.26 (3 H, m, ArH) and 7.55–7.58 (1 H, m, ArH); δ_C($CDCl_3$) 19.0 (q), 24.4 (q), 29.5 (d), 37.2 (t), 57.0 (t), 88.3 (s), 90.1 (s), 111.7 (t), 119.8 (s), 125.5 (s), 125.7 (d), 126.4 (d), 128.2 (d), 128.7 (d), 131.2 (s) and 145.9 (s); *m/z* 287 (M^+, 8.9%) and 43 (100) (Found: C, 66.9; H, 6.0; N, 4.9. $C_{16}H_{17}NO_2S$ requires C, 66.87; H, 5.96; N, 4.87%).

Reduction of the cycloadduct 4hA with sodium borohydride
Sodium borohydride (38 mg, 1 mmol) was added portionwise to a stirred suspension of the cycloadduct **4hA** (341 mg, 1 mmol) in dry ethanol (10 cm^3) and the mixture was stirred for 15 min. Water was added to the reaction mixture and then the mixture was extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to give an oil which was subjected to PLC on silica gel with hexane–ethyl acetate (20:1) to afford three compounds, **10**, **11** and **7** (6.7%).

4-Cyano-2-(2,3-dimethylbut-2-enyl)-3,4-dihydro-2*H*-1-benzothiopyran 10. Pale yellow oil (36.2%); ν_{max}(neat)/cm^{-1} 2250 (CN); δ_H($CDCl_3$) 1.72 (9 H, s, 3 × Me), 1.98 [1 H, ddd, *J* 14.7, 10.7 and 4.4, –(CN)CHC*H*H–], 2.38–2.45 [1 H, m, –(CN)CHCH*H*–], 2.44 (2 H, d, *J* 7.3, SCHC*H*$_2$), 3.71 (1 H, ddd, *J* 10.7, 7.3 and 4.4, SC*H*CH_2), 4.06 [1 H, t, *J* 4.4, –(CN)C*H*CH_2–] and 7.03–7.25 (4 H, m, ArH); δ_C($CDCl_3$) 18.3 (q), 20.8 (q), 31.2 (d), 32.5 (t), 37.2 (d), 39.8 (t), 120.1 (s), 123.1 (s), 124.7 (d), 126.6 (s), 127.1 (d), 128.5 (s), 128.6 (d), 129.7 (d) and 134.1 (s); *m/z* 257 (M^+, 22%) and 174 (100) (Found: M^+, 257.1218. $C_{16}H_{19}NS$ requires *M*, 257.1237).

4-Cyano-2′-isopropenyl-2′-methylspiro[3,4-dihydro-2*H*-[1]-benzothiopyran-2,1′-cyclopropane] 11. Plates (15%), mp 97–98 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1} 2250 (CN); δ_H($CDCl_3$) 0.97 (1 H, dd, *J* 5.4 and 1.0, C*H*H of cyclopropane ring), 1.05 (1 H, d, *J* 5.4, CH*H* of cyclopropane ring), 1.41 (3 H, s, Me), 1.75 (3 H, br s, CH=CMe), 2.07 [1 H, dd, *J* 13.2 and 4.4, –(CN)CHC*H*H–], 2.42 [1 H, ddd, *J* 13.2, 12.2 and 1.0, –(CN)CHCH*H*–], 4.00 [1 H, dd, *J* 12.2 and 4.4, –(CN)C*H*CH_2–], 4.79 and 4.96 (each 1 H, each br s, C=CH_2), 7.11–7.20 (3 H, m, ArH) and 7.54–7.57 (1 H, m, ArH); δ_C($CDCl_3$) 20.0 (q), 20.9 (q), 28.6 (t), 31.2 (s), 32.6 (d), 34.5 (t), 34.6 (s), 113.6 (t), 120.4 (s), 125.0 (d), 127.2 (d), 128.2 (d), 128.6 (d), 134.0 (s) and 145.4 (s); *m/z* 255 (M^+, 4.4%) and 107 (100) (Found: C, 75.3; H, 6.7; N, 5.5. $C_{16}H_{17}NS$ requires C, 75.25; H, 6.71; N, 5.48%).

Reduction of the cycloadduct 4hA with sodium cyanoborohydride
Sodium cyanoborohydride‡ (43 mg, 1 mmol) was added to a stirred suspension of the cycloadduct **4hA** (220 mg, 0.65 mmol) in dry THF (7 cm^3) at room temperature, and the mixture was stirred for 1.5 h. Dilute hydrochloric acid (1 mol dm^{-3}, 7 cm^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 subjected to PLC on silica gel with hexane–ethyl acetate (10:1) to afford compounds **7** (11.2%) and **12** (39.2%).

4-Cyano-2-(2,3-dimethylbut-2-enyl)-2*H*-1-benzothiopyran 12. A yellow oil, ν_{max}(neat)/cm^{-1} 2250 (CN); δ_H($CDCl_3$) 1.57, 1.64 and 1.68 (each 3 H, each s, 3 × Me), 2.35 and 2.49 (each 1 H, each dd, *J* 13.2 and 7.8, CHCH_2), 3.75 (1 H, dt, *J* 7.8 and 5.9, C*H*CH_2), 6.70 (1 H, d, *J* 5.9, olefinic H), 7.18–7.31 (3 H, m, ArH) and 7.54–7.59 (1 H, m, ArH); δ_C($CDCl_3$) 18.4 (q), 20.6 (q), 20.8 (q), 37.0 (d), 38.4 (t), 114.5 (s), 117.0 (s), 122.0 (s), 126.1 (d), 126.6 (d), 127.6 (s), 128.0 (d), 129.4 (s), 129.8 (d), 131.1 (s) and 140.9 (d); *m/z* 255 (M^+, 0.2%) and 172 (100) (Found: M^+, 255.1074. $C_{16}H_{17}NS$ requires *M*, 255.1103).

‡ The IUPAC name for sodium cyanoborohydride is sodium cyanoboranuide.

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