Polar Cycloaddition of 2-Benzothiopyrylium Salts with Conjugated Dienes

Hiroshi Shimizu,*[a] Shojiro Miyazaki,[a] Tadashi Kataoka,[a] Mikio Hori[a] and Osamu Muraoka[b]
[a] *Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan*
[b] *Kinki University, Faculty of Pharmaceutical Sciences, 3-4-1, Kowakae, Higashi-Osaka, Osaka 577, Japan*

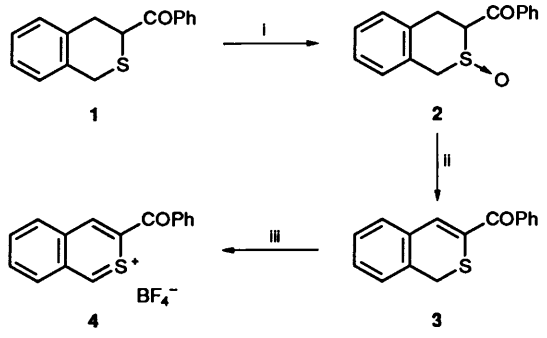
2-Benzothiopyrylium salts **4** and **6** underwent polar cycloaddition with conjugated dienes to afford benzo-fused bicyclic sulfonium salts **7** and **8**, respectively, having sulfur at a bridgehead position, in good yields. The salt **4** bearing an electron-withdrawing group at the 3-position was much more reactive than was the salt **6**. The structures of the cycloadducts have been established by X-ray crystallography of compound **7a**, indicating a *cis*-fused configuration. In contrast, attempted reaction of the salt **4** with furan as a heterocyclic diene resulted in the electrophilic substitution of the furan by the salt, giving compound **9**. The cycloadducts **7** underwent retro-addition to generate 2-benzothiopyrylium ion **4**, which was easily trapped with other dienes or active methyl compounds to give the corresponding adduct **7** or 1-alkylated 1*H*-2-benzothiopyran **5**, respectively. Reactions of the cycloadducts **7** with a variety of nucleophiles caused ring opening to afford 1-allyl- **12** and 1-homoallyl-substituted 1*H*-2-benzothiopyrans **13** in good yields. On the other hand, the cycloadduct **8**, when treated with nucleophiles, underwent a novel ring transformation along with nucleophilic ring-opening.

The Hetero-Diels–Alder reaction is a potentially effective tool for the construction of various six-membered heterocyclic compounds.[1] A number of novel heterodienes or heterodienophiles have been developed to achieve the synthesis of target heterocyclic compounds by this excellent reaction. Among these heterodienophiles, thiocarbonyl compounds, thioesters and sulfines are most generally known and have been intensively investigated as C–S heterodienophiles and utilized for the preparation of sulfur-containing heterocyclic compounds. Thienium ion (α-thiocarbocation) was first recognized as a C–S heterodienophile in the [2$^+$ + 4]-type cationic polar cycloaddition by Corey's group in 1972.[2] They found that the reaction of 1,3-dithienium tetrafluoroboranuide with conjugated dienes gave the [2$^+$ + 4] cycloadducts, which were elaborated to cyclopentenones. After that, this interesting reaction has not been explored. Recently, a [2$^+$ + 4]-type polar cycloaddition of a thienium ion intermediate generated *in situ* has been reported. Ishibashi *et al.* reported the reaction of a thienium ion intermediate, generated from the action of tin(IV) chloride on the corresponding α-chloro sulfide, with 1,3-dienes.[3] Fuji *et al.* reported the reaction of a thienium ion intermediate, generated from the action of aluminium chloride on the corresponding β-nitrovinyl sulfide, with 1,3-dienes.[4]

We have planned to examine the reaction of quasi-aromatic ring compounds, thiopyrylium ions, with 1,3-dienes in the hope that a [2$^+$ + 4]cycloaddition might occur, because these cations have the thienium ion structure. In this paper, we present our findings that 3-benzoyl-2-benzothiopyrylium salt **4** and 2-benzothiopyrylium salt **6** underwent readily a [2$^+$ + 4] polar cycloaddition with several types of 1,3-dienes to afford the benzo-fused bicyclic sulfonium salts bearing the sulfur atom at a bridgehead as isolable compounds, and that the cycloadducts were ring-transformed by treatment with various nucleophiles.[5]

Results and Discussion

Synthesis of 3-Benzoyl-2-benzothiopyrylium Tetrafluoroboranuide **4** *and its High Reactivity.*—At the start of this investigation, we selected 3-benzoyl-2-benzothiopyrylium tetrafluoroboranuide **4** and 2-benzothiopyrylium tetrafluoroboranuide **6** as thiopyrylium ion derivatives with a thienium ion structure. The former compound **4** was chosen since an electron-withdrawing substituent lowers the LUMO energy level of dienophiles; consequently such dienophiles can interact more effectively with electron-rich dienes to accelerate the rate of the reaction, and enhance the observed regioselectivity of the cycloaddition. Electron-withdrawing-group-substituted thiopyrylium ion derivatives are not well known so far,[6] probably because of their instability. We have achieved the preparation of the salt **4** as shown in Scheme 1. Oxidation of 3-benzoyl-3,4-dihydro-1*H*-2-benzothiopyran



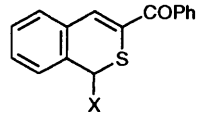
Scheme 1 *Reagents and conditions:* i, MCPBA, CH_2Cl_2, 0 °C; ii, PTSA, toluene, reflux; iii, Ph_3C^+ BF_4^-, $MeNO_2$, room temp.

1[7] with 1 mole equivalent of *m*-chloroperbenzoic acid (MCPBA) afforded the sulfoxide **2** in 91% yield. The sulfoxide **2** was dehydrated by being refluxed in toluene in the presence of a catalytic amount of toluene-*p*-sulfonic acid (PTSA) to give 3-benzoyl-1*H*-2-benzothiopyran **3** (94%), which was then treated with triphenylcarbenium tetrafluoroboranuide to afford the desired 3-benzoyl-2-benzothiopyrylium tetrafluoroboranuide **4** as pale green needles in 96% yield. The salt **4** was, as expected, more reactive than was the salt **6**, and easily decomposed on contact with water or alcohol. Furthermore, on dissolution of the salt **4** in dry acetone for the purpose of recrystallization, the salt was easily decomposed to form

Table 1 Reactions of 3-benzoyl-2-benzothiopyranylium salt **4** with active methylene compounds

Entry	Active methylene compound	Reaction conditions			Product		
		Solvent	Temp.	Time (t/h)	5	X	Yield (%)
1	MeCOMe	none	room temp.	3	**5a**	CH_2COMe	52
2	$CH_2(CO_2Me)_2$	$(CH_2Cl)_2$	reflux	3	**5b**	$CH(CO_2Me)_2$	29
3	$CH_2(COMe)_2$	$(CH_2Cl)_2$	room temp.	10	**5c**	$CH(COMe)_2$	73
4	$CH_2(COPh)_2$	$(CH_2Cl)_2$	room temp.	96	**5d**	$CH(COPh)_2$	87
5	$CH_2(COMe)CO_2Et$	$(CH_2Cl)_2$	room temp.	10	**5e**	$CH(COMe)CO_2Et$	82[a]
6	$MeCO_2Et$	none	reflux	240			
7	$CH_2(CN)CO_2Me$	$(CH_2Cl)_2$	reflux	28			

[a] The product **5e** was obtained as an inseparable mixture of diastereoisomers in the ratio 1:1.4 (determined by ^1H NMR spectroscopy).

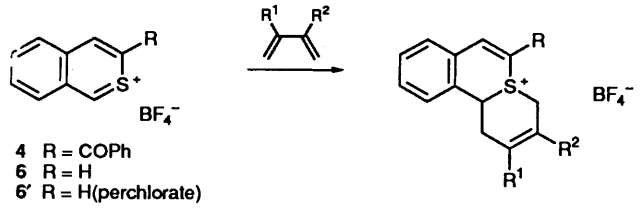


5 a X = CH_2COMe
b X = $CH(CO_2Me)_2$
c X = $CH(COMe)_2$
d X = $CH(COPh)_2$
e X = $CH(COMe)CO_2Et$

1-acetonyl-3-benzoyl-1*H*-2-benzothiopyran **5a** in 52% yield. This indicates that acetone acted as an active methyl compound. It is well known that thiopyrylium ions are reactive to active methylene compounds in the presence of a base.[8] Therefore, this is a quite rare case in which thiopyrylium ions react with active methylene compounds without base, suggesting the high activity of the salt **4**. Consequently, we investigated extensively the reaction of the salt **4** with other active methylene compounds. The results are summarized in Table 1. Dimethyl malonate was less reactive and needed to be refluxed to make the reaction proceed, but even then the yield was very low (29%) (entry 2). Ethyl acetate and methyl cyanoacetate did not react even on refluxing (entries 6 and 7), indicating that the above reaction is possible only within the limits imposed by the nature of the active methyl or methylene compounds.

Polar Cycloaddition of 2-Benzothiopyrylium Salts **4** *and* **6** *with Conjugated Dienes.*—Addition of 2-benzothiopyrylium tetrafluoroboranuide **6**[9] to 2 mole equivalents of 2,3-dimethylbuta-1,3-diene, isoprene, or buta-1,3-diene in dry 1,2-dichloroethane at room temperature and stirring of the mixture for 10–60 min afforded the cycloadducts **8** in fairly good yields (Scheme 2). The reaction conditions and product yields are summarized in Table 2.

A change of counter-ion for the 2-benzothiopyrylium salt **6** from tetrafluoroboranuide to perchlorate **6'** had no significant effect on the reactivity of the thiopyrylium ion (compare entries 1 and 2). Prolonged reaction time caused a decrease in yield of the cycloadduct (entry 3), and stirring of the reaction mixture for 30 h did not afford the cycloadduct at all (entry 4), giving an undetermined complex mixture, probably because of decomposition of the cycloadduct in the reaction medium or further reaction of the cycloadduct with any remaining excess of 1,3-diene. Cycloaddition of isoprene proceeded regiospecifically to give only a single adduct **8b** (entry 5). The reaction with buta-1,3-diene was rather slow and needed more reaction time (60 min) to give a satisfactory yield (entry 6). In expectation of raising the yield of cycloadducts, we next investigated the reaction of 3-benzoyl-2-benzothiopyrylium tetrafluoroboranuide **4** which is believed to be activated by an electron-withdrawing group at the 3-position. Indeed, the



4 R = COPh
6 R = H
6' R = H(perchlorate)

7a R = COPh, $R^1 = R^2$ = Me
b R = COPh, R^1 = Me, R^2 = H
c R = COPh, R^1 = Ph, R^2 = H
d R = COPh, $R^1 = R^2$ = H

8a R = H, $R^1 = R^2$ = Me
a' R = H, $R^1 = R^2$ = Me(perchlorate)
b R = H, R^1 = Me, R^2 = H
c R = H, $R^1 = R^2$ = H

Scheme 2

cycloaddition of the salt **4** with several 1,3-dienes including 2-phenylbuta-1,3-diene in addition to the above 1,3-dienes proceeded more rapidly to give the corresponding cycloadducts **7a–d** in more excellent yields (Table 2). Cycloaddition of isoprene or 2-phenylbuta-1,3-diene proceeded regiospecifically to afford only single isomer **7b** or **7c**, respectively. When the above reactions were performed in acetonitrile, the product yields were decreased by ~10% (entries 8, 10 and 13). The structural assignment of the cycloadducts was based on spectroscopic evidence (see the Experimental section). In particular, the regiochemistry of the 1,2-buteno moieties in the cycloadducts **7b**, **7c** and **8b** was readily determined on the basis of the lack of coupling between the methylene protons of the allyl group attached to C-1 and the olefinic proton in the ^1H NMR spectra. Single-crystal X-ray analysis of the cycloadduct **7a** revealed the stereochemistry with a *cis*-condensed six-membered ring as shown in Fig. 1. Atomic co-ordinates, bond lengths and angles have been deposited with the CCDC.*

We next examined the cycloaddition of the salt **4** with furan which is widely used as a reactive diene. However, the expected cycloadduct similar to the above was not obtained, but instead furan-ring-substituted 1*H*-2-benzothiopyrans **9** and **10** were obtained in 16 and 61% yield, respectively (Scheme 3). As one rational explanation for the formation of the products **9** and **10**, we think that a cycloadduct **A** is primarily formed by a [2^+ + 4] cycloaddition of 2-benzothiopyranylium salt **4** with furan, and that then the adduct **A** undergoes cleavage of the indicated carbon–sulfur bond (driving force: rearomatization to furan *via* deprotonation) to provide the product **9**, and that the furan

* See 'Instructions for Authors', in the January issue.

Table 2 Polar cycloadditions of 2-benzothiopyrylium salts **4** and **6** with several 1,3-dienes

	Reactants			Reaction conditions		Product	
		1,3-Diene					
Entry	Salt	R^1	R^2	Solvent	Time (*t*/min)	Compound	Yield (%)
1	**6**	Me	Me	$(CH_2Cl)_2$	10	**8a**	79
2	**6'**	Me	Me	$(CH_2Cl)_2$	10	**8a**	71
3	**6**	Me	Me	$(CH_2Cl)_2$	40	**8a**	41
4	**6**	Me	Me	$(CH_2Cl)_2$	1800 (30 h)	**8a**	
5	**6**	Me	H	$(CH_2Cl)_2$	10	**8b**	80
6	**6**	H	H	$(CH_2Cl)_2$	60	**8c**	79
7	**4**	Me	Me	$(CH_2Cl)_2$	15	**7a**	98
8	**4**	Me	Me	MeCN	15	**7a**	87
9	**4**	Me	H	$(CH_2Cl)_2$	15	**7b**	96
10	**4**	Me	H	MeCN	15	**7b**	82
11	**4**	Ph	H	$(CH_2Cl)_2$	15	**7c**	66
12	**4**	H	H	$(CH_2Cl)_2$	30	**7d**	88
13	**4**	H	H	MeCN	30	**7d**	82

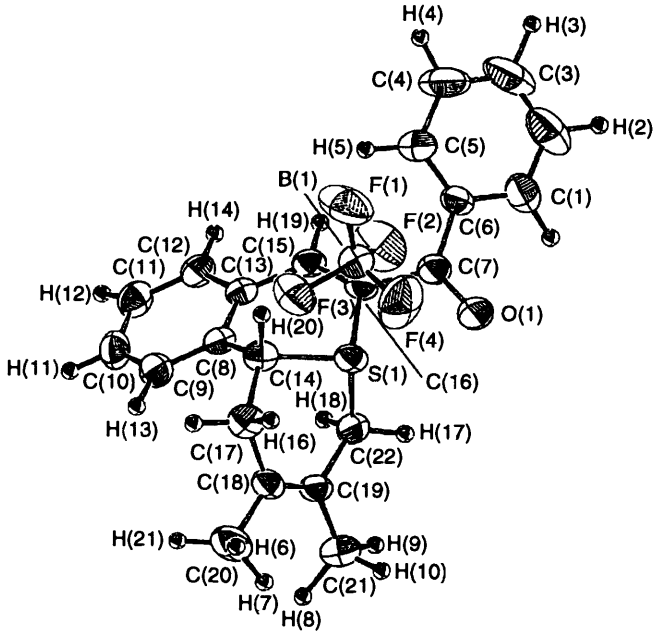
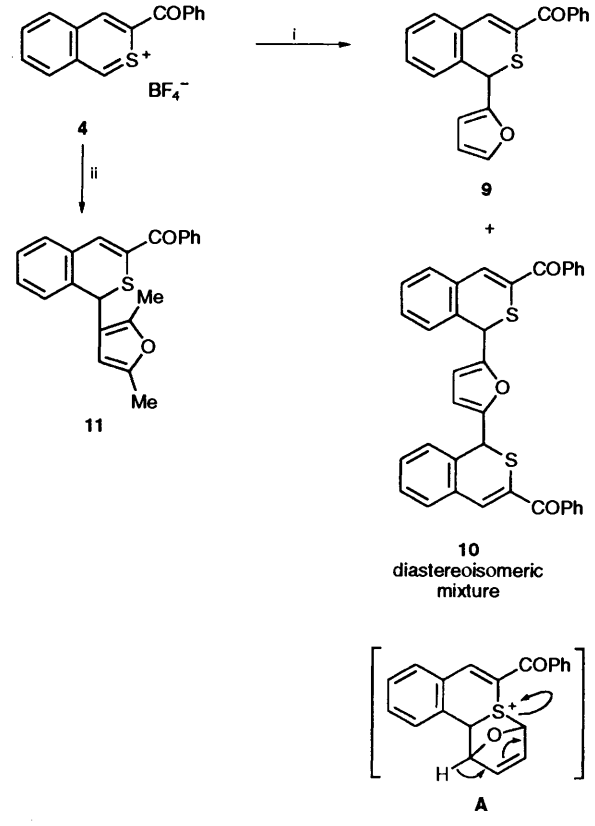


Fig. 1 X-Ray molecular structure of compound **7a**

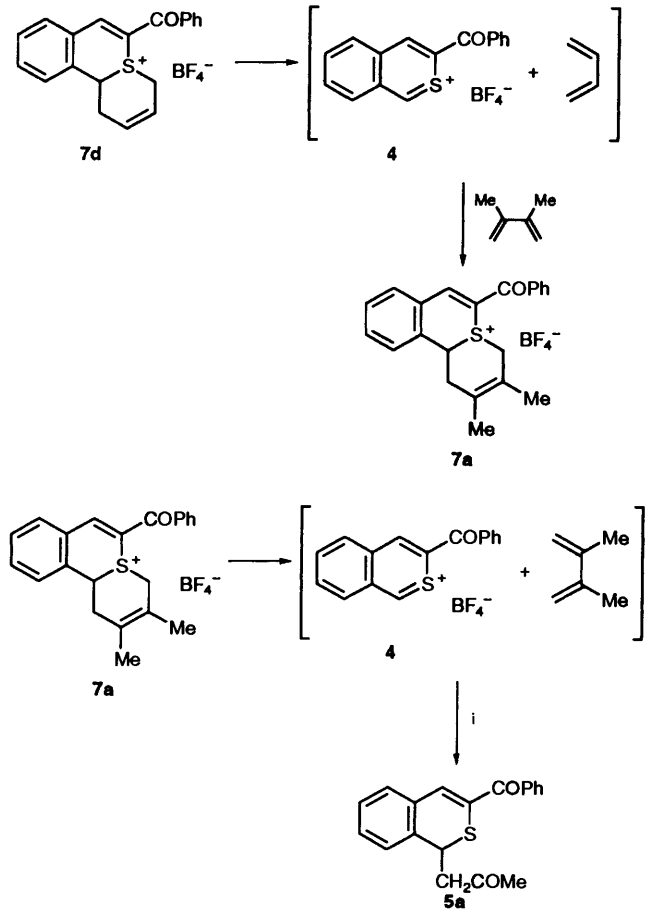


Scheme 3 *Reagents and conditions:* i, furan, $(CH_2Cl)_2$, room temp.; ii, 2,5-dimethylfuran, $(CH_2Cl)_2$, room temp.

ring of the product **9** again reacts with a second molecule of the salt **4** in a similar fashion to afford the product **10**. However, when 2,5-dimethylfuran, in which the 2- and 4-position are blocked with methyl groups, thus preventing rearomatization by deprotonation, was allowed to react with the salt **4**, the furan reacted at the 3-position to afford 1-furan-ring-substituted 1*H*-2-benzothiopyran **11** in 31% yield. These results might be rationalized in terms of electrophilic substitution of the furan ring with the 2-benzothiopyrylium salt rather than the cycloaddition mechanism. Reaction of the salt **6** with furan afforded no cycloadducts or furan-ring-substituted products as above, but instead gave complex mixtures. We also attempted cycloaddition of 1-substituted 2-benzothiopyrylium salts, 1-methyl- or 1-phenyl-2-benzothiopyrylium salts, with 1,3-dienes, but the former gave a complex mixture of products, and reaction of the latter did not proceed, starting material being recovered unchanged. Furthermore, other 1,3-dienes such as cyclopentadiene, penta-1,3-diene, 2-methoxybuta-1,3-diene, and 2-(trimethylsiloxy)buta-1,3-diene, which have been widely used in Diels–Alder reactions to date, gave undetermined complex mixtures. 1,4-Diphenylbuta-1,3-diene or anthracene did not react with the salt **4**, starting materials being recovered unchanged. These results show the scope and some limitations of the cycloaddition, such that substituents at the 1-position of 2-benzothiopyrylium salts prevent the reaction and, furthermore, 1- and/or 4-substituted 1,3-dienes and oxy-substituted dienes give no desired products.

The retro-Diels–Alder cleavage reactions of heterocycloaddition products have been well documented.[10] However, to our knowledge, there are no reports on retro-cycloaddition of cycloadducts derived from a thienium ion and dienes. Consequently, our attention was directed to the thermal behaviour of the cycloadducts obtained above. On refluxing in 1,2-dichloroethane with 2 mole equivalents of 2,3-dimethylbuta-1,3-diene for 10 min, a part of compound **7d** was converted into compound **7a**, which was detected by ^1H NMR spectroscopy

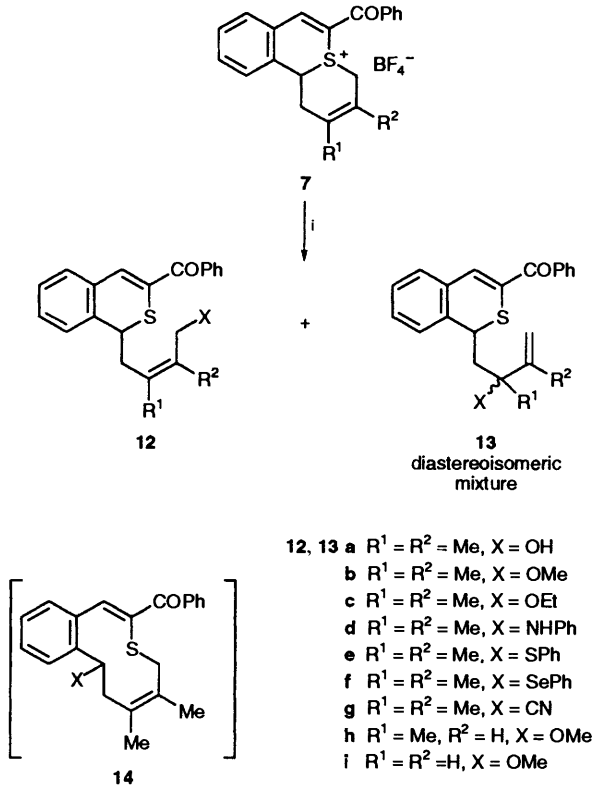
of the reaction mixture, but was difficult to separate from compound **7d** (Scheme 4).



Scheme 4 *Reagent:* i, acetone

Prolonged reaction time unfortunately resulted in the formation of an undetermined complex mixture. Therefore, we next tried the thermal reaction of compound **7a** in refluxing acetone. When refluxed in acetone for 10 h, compound **7a** was degraded and afforded 1-acetonyl-3-benzoyl-2-benzothiopyran **5a** in 74% yield. The formation of compound **5a** can be rationalized in terms of the generation of the intermediary 2-benzothiopyrylium ion **4** which was then nucleophilically attacked by acetone as described above. These results show an apparent occurrence of retro-cycloaddition of the cycloadduct **7**, as shown in Scheme 4.

We next paid attention to an investigation of the reactivity of the cycloadducts obtained above in the hope of observing formation of novel sulfur-containing heterocyclic compounds, because the cycloadducts have reactive sulfonium ion structures. We conducted the reaction with a variety of nucleophiles to cleave the sulfur–carbon bond of the sulfonium structure. The reaction results are summarized in Scheme 5 and Table 3. The cycloadducts **7** underwent easy cleavage of the sulfur–carbon bond by attack of the nucleophiles to afford two types of ring-opened products, **12** (major) and **13** (minor). The latter compounds **13** were obtained as an inseparable diastereoisomeric mixture in the ratios summarized in Table 3. The structural assignment of the products **12** and **13** was based on spectroscopic evidence (see the Experimental section). In particular, the structure of the products **12** was further confirmed by chemical transformations, because the differentiation between structure **12** and another possible ring-cleaved structure **14**, which might be derived from the attack of nucleophiles at the benzylic position of the sulfonium



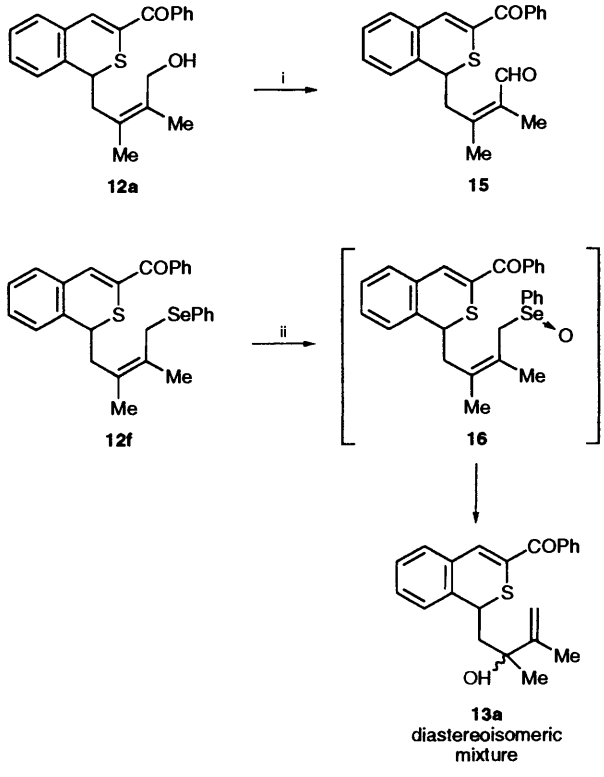
Scheme 5 *Reagent:* i, nucleophile

compound **7**, was unclear when based only on spectroscopic evidence. The hydroxy group of compound **12a** was selectively oxidized with pyridinium chlorochromate (PCC) in dichloromethane to give the corresponding aldehyde **15** in 58% yield, but no formation of ketone which would be expected from structure **14** having a secondary alcohol group; this indicated that structure **12a** is a primary alcohol (Scheme 6). The IR spectrum of compound **15** revealed a characteristic absorption band due to the aldehyde group at 2750 cm^{-1}, the ^1H NMR spectrum ($CDCl_3$) showed an aldehyde proton singlet (1 H) at δ 9.46 and the ^{13}C NMR spectrum ($CDCl_3$) showed a doublet signal attributable to an aldehyde carbon at δ_C 189.4 in an off-resonance technique. Furthermore, compound **12f** was carefully oxidized site-selectively with MCPBA to afford the allyl alcohol **13a** in 85% yield as an inseparable diastereoisomeric mixture in the ratio 1:1.6 on the basis of ^1H NMR spectroscopy. Compound **13a** might be formed *via* allyl rearrangement of intermediary selenoxide **16**. These chemical transformations of compounds **12a** and **12f** revealed that the structure of compounds **12** is not like that of bicycles **14**, but is a 1-allyl-substituted 1*H*-2-benzothiopyran structure. The formation of products **12** and **13** is explained by an S_N2 and S_N2' process with nucleophiles, respectively. In contrast to the above ring-cleavage reactions, treatment of cycloadduct **8a** with trimethylsilyl cyanide in the presence of tetrabutylammonium fluoride (TBAF) afforded 1,4-ethylene-bridged 2-benzothiopyran **17a** (41%) together with ring-opened compound **18a** (25%) (Scheme 7). Similarly, compound **8a** was allowed to react with boiling methanol to afford 1,4-ethylene-bridged 2-benzothiopyran **17b** (65%) and ring-opened compound **18b** (trace). The structure of the compounds **18a, b** was determined by comparison of spectroscopic data with those of compounds **12b, g** with similar structure. The structure of compounds **17a, b** was estimated mainly on the basis of spectral evidence. For example, elemental analysis and mass spectral data [*m*/*z* 255

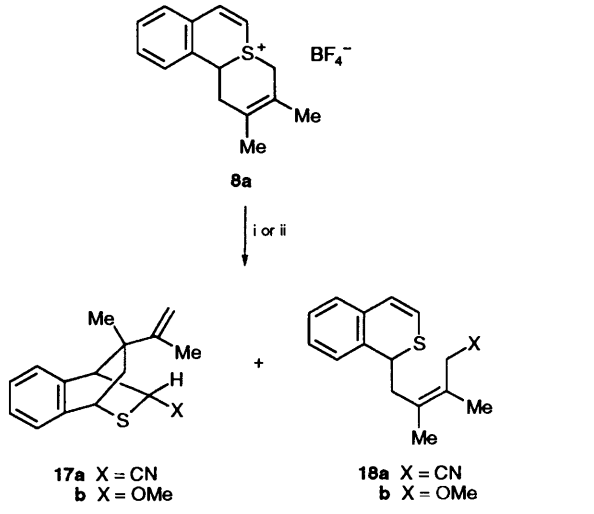
Table 3 Reactions of cycloadducts **7** with several nucleophiles

	Reactants		Conditions			Products				
Entry	Salt	Nucleophile	Solvent	Temp.	Time (min)	X	**12**	Yield (%)	**13**	Yield (%) (diastereoisomeric ratio)[a]
1	**7a**	Water	acetone	reflux	5	OH	**12a**	74	**13a**	25 (1:4.3)
2	**7a**	MeOH	none	reflux	5	OMe	**12b**	87	**13b**	12 (1:1.7)
3	**7a**	EtOH	none	reflux	5	OEt	**12c**	83	**13c**	7 (1:1.8)
4	**7a**	$PhNH_2$	$(CH_2Cl)_2$	room temp.	120	NHPh	**12d**	85		
5	**7a**	PhSNa	EtOH	room temp.	30	SPh	**12e**	96		
6	**7a**	PhSeLi	THF–diethyl ether	−40 °C–room temp.	24 h	SePh	**12f**	80		
7	**7a**	Me_3SiCN[b]	$(CH_2Cl)_2$	−30 °C–room temp.	24 h	CN	**12g**	54		
8	**7b**	MeOH	none	reflux	5	OMe	**12h**	85	**13h**	14 (1:1.8)
9	**7d**	MeOH	none	reflux	5	OMe	**12i**	73	**13i**	2[c]

[a] Determined by ^1H NMR spectroscopy. [b] In the presence of TBAF. [c] Diastereoisomeric ratio could not be determined because of the small amount of compound **13i** available.



Scheme 6 *Reagents and conditions:* i, PCC, CH_2Cl_2, room temp.; ii, MCPBA, CH_2Cl_2, 0 °C



Scheme 7 *Reagents and conditions:* i, Me_3SiCN, TBAF, $(CH_2Cl)_2$, −30 °C ⟶ room temp., N_2; ii, MeOH, reflux

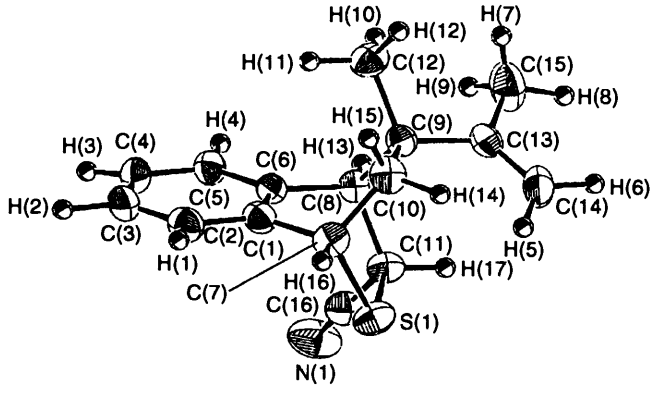


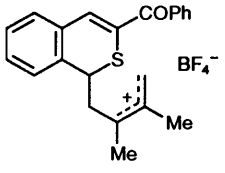
Fig. 2 X-Ray molecular structure of compound **17a**

(M^+)] indicate a molecular formula of $C_{16}H_{17}NS$ for compound **17a**. The IR spectrum of compound **17a** showed a characteristic absorption band at 2230 cm^{-1} for the cyano group. The ^1H NMR spectrum ($CDCl_3$) exhibited a vinylic methyl doublet (J 1 Hz) at δ 1.90 coupled with two broad singlets due to vinylic protons at δ 5.13 and 5.24, a methyl singlet at δ 0.76, a doublet of doublets (J 13.7, 3.4 Hz) due to one of the methylene protons at δ 1.51 coupled with a methine proton (1-H) at δ 4.05 (doublet, J 3.4 Hz), a doublet of doublets (J 13.7, 2.9 Hz) attributable to the other methylene protons, at δ 2.82, which is coupled with the methine proton (1-H), and a doublet (J 2.9 Hz) due to 4-H at δ 3.48 which is coupled with 3-H at δ 4.36. The structural determination of compounds **17** was finally carried out by an X-ray analysis of compound **17a** (see the Experimental section for crystal data and other information). The molecular structure of compound **17a** is illustrated in Fig. 2.

The mechanism for the formation of compounds **17** is not clear at present and is now under investigation.

Finally, our attention was directed towards the mechanism of the cycloaddition between 2-benzothiopyrylium salts and 1,3-dienes. As described above, the cycloaddition proceeded regiospecifically (as in the reaction with isoprene) and stereoselectively to afford only a single, *cis*-fused isomer. This

seems to suggest that the reaction proceeded *via* a concerted, one-step mechanism as in the normal Diels–Alder reaction. We performed the following reaction in order to obtain some information about whether the cycloaddition proceeded concertedly or in a stepwise manner. Treatment of compounds **12b** and **13b**, obtained from the reaction of the salt **7a** with methanol as described above, with tetrafluoroboric acid afforded cyclized product **7a** as a single isomer in high yield, possible *via* the common intermediate **19**. A similar result was



19

obtained by treating compound **12b** with triphenylcarbenium tetrafluoroboranuide. Taking account of this, the present polar cycloaddition might have proceeded in a stepwise manner *via* an intermediate similar to **19** at first derived from addition of diene to the positively charged 1-position of 2-benzothiopyrylium ion. The exclusive formation of a single regioisomer might be rationalized in terms of the difference in the stabilities of the intermediary carbenium ions (tertiary *vs.* secondary); the ion **7** (as an α-thiocarbocation) predominantly attacks one of the double bonds in the diene in the direction of formation of a more stable tertiary carbenium ion intermediate similar to intermediate **19**, followed by attack of sulfur on the conjugated allyl cation, resulting in ring closure. A similar stepwise mechanism was also proposed for the [$2^+ + 4$] cycloaddition of thienium ions, generated by the action of Lewis acid on α-chloro sulfides, with dienes, on the basis of the isolation of the alkene product derived from the deprotonation of intermediary carbenium ion similar to species **19**.[3]

Experimental

M.p.s were determined on a Yanagimoto micro melting point apparatus, and are uncorrected. IR spectra were measured on a JASCO A-1 spectrophotometer. NMR spectra were recorded on a Hitachi R-20B machine at 60 MHz (^{1}H), or a JEOL GX-270 spectrometer at 270 MHz (^{1}H) and 67.5 MHz (^{13}C). Chemical shifts were measured in ppm on the δ-scale downfield from tetramethylsilane as internal standard; *J*-values are recorded in Hz. All ^{13}C data are quoted with ^{1}H multiplicities (off-resonance results in brackets), although this multiplicity was usually inferred from a distortionless enhancement by polarization transfer (DEPT) experiment. Mass spectra were obtained by electron impact at 70 eV on a JEOL JMS-D300 spectrometer. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Analytical and preparative TLC (PLC) were carried out on E. M. Merck silica gel 60PF-254 plates. Spots were visualized with a UV hand lamp.

3-Benzoyl-3,4-dihydro-1H-2-benzothiopyran 2-Oxide **2**.—MCPBA (85% purity; 5.18 g) was added to an ice-cooled solution of 3-benzoyl-3,4-dihydro-1*H*-2-benzothiopyran **1** (6.49 g, 25.5 mmol) in dichloromethane (270 cm^3), and the mixture was stirred for 1 h before being washed successively with aq. $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated under reduced pressure. The residual oil was triturated with diethyl ether to give a mixture of *cis* and *trans* diastereoisomers of the *title compound* **2** (6.28 g, 91.1%) as pale orange crystals in the ratio 1:1.3 judging from the integration of 3-H signal in the ^{1}H NMR spectrum. Recrystallization from dichloromethane–diethyl ether afforded pure *cis* and *trans* isomers. *cis*-Isomer: orange columns, m.p. 157–165.5 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1670 (CO) and 1035 (SO); δ_H($CDCl_3$) 3.11 (1 H, dd, *J* 16.6 and 3.9, 4-H), 3.81 (1 H, dd, *J* 16.6 and 11.2, 4-H), 3.98 and 4.32 (each 1 H, d, *J* 15.1, 1-H), 4.62 (1 H, dd, *J* 11.2 and 3.9, 3-H), 7.16–7.31 (4 H, m, ArH), 7.44–7.66 (3 H, m, ArH) and 7.96–8.05 (2 H, m, ArH); δ_C($CDCl_3$) 25.3 (t), 53.1 (t), 60.9 (d), 126.3 (s), 127.2 (d), 128.1 (d), 128.5 (d), 128.8 (d), 129.9 (d), 133.8 (d), 135.2 (s), 135.7 (s) and 193.2 (s); *m*/*z* 270 (M^+), 252 ($M^+ - H_2O$) and 105 (base) (Found: C, 70.8; H, 5.2. $C_{16}H_{14}O_2S$ requires C, 71.08; H, 5.22%).

trans-Isomer: pale orange needles, m.p. 152.5–159.5 °C; ν_{max}(KBr)/cm^{-1} 1670 (CO) and 1035 (SO); δ_H($CDCl_3$) 3.20 (1 H, dd, *J* 15.6 and 9.3, 4-H), 3.36 (1 H, dd, *J* 15.6 and 5.4, 4-H), 3.94 and 4.15 (each 1 H, each d, *J* 14.2, 1-H), 4.55 (1 H, dd, *J* 9.3 and 5.4, 3-H), 7.16–7.31 (4 H, m, ArH), 7.44–7.66 (3 H, m, ArH) and 7.96–8.05 (2 H, m, ArH); δ_C($CDCl_3$) 29.9 (t), 52.2 (t), 69.5 (d), 126.8 (s), 127.6 (d), 128.4 (d), 128.8 (d), 128.9 (d), 130.3 (d), 134.2 (d), 135.2 (s) and 195.3 (s); *m*/*z* 270 (M^+), 252 ($M^+ - H_2O$) and 105 (base) (Found: C, 70.8; H, 5.2%).

3-Benzoyl-1H-2-benzothiopyran **3**.—A mixture of the sulfoxide **2** (6.54 g, 24.19 mmol) and a catalytic amount of PTSA monohydrate (15 mg) in toluene (240 cm^3) was refluxed for 30 min. The solvent was evaporated off and the residual oil was chromatographed on a silica gel column and eluted with dichloromethane–hexane (2:1) to afford the *title compound* **3** (5.76 g, 94.4%). Recrystallization from hexane–dichloromethane gave the pure compound as yellow columns, m.p. 122–123 °C; ν_{max}(KBr)/cm^{-1} 1630 (CO); δ_H($CDCl_3$) 3.94 (2 H, s, 1-H_2), 7.12–7.60 (8 H, m, ArH and 4-H) and 7.77 (2 H, d, *J* 7.3, ArH); δ_C($CDCl_3$) 30.5 (t), 127.0 (d), 127.7 (d), 128.4 (d), 129.0 (d), 129.1 (d), 129.4 (s), 130.8 (d), 132.2 (d), 132.3 (s), 136.0 (d), 136.7 (s), 137.9 (s) and 193.9 (s); *m*/*z* 252 (M^+) and 105 (base) (Found: C, 76.0; H, 4.8. $C_{16}H_{12}OS$ requires C, 76.16; H, 4.79%).

3-Benzoyl-2-benzothiopyrylium Tetrafluoroboranuide **4**.—Triphenylcarbenium tetrafluoroboranuide (2.09 g, 6.34 mmol) was added in one portion to a stirred solution of the 2-benzothiopyran **3** (1.45 g, 5.76 mmol) in dry nitromethane (40 cm^3) and the mixture was stirred for 2 h at room temperature. The solution was then reduced to one-third of its initial volume and dry diethyl ether was added to precipitate the *title tetrafluoroboranuide* **4** (1.87 g, 95.8%). Recrystallization from acetic acid containing a small amount of acetic anhydride afforded pale green needles, m.p. 128–129 °C; ν_{max}(KBr)/cm^{-1} 1640 (CO) and 1080–1030 (BF_4^-); δ_H(CD_3CN) 7.65–7.71 (2 H, m, ArH), 7.81–7.87 (1 H, m, ArH), 7.97–8.00 (2 H, m, ArH), 8.37–8.43 (1 H, m, ArH), 8.58–8.65 (2 H, m, ArH), 8.78 (1 H, d, *J* 8.3, ArH), 9.50 (1 H, s, 4-H) and 11.29 (1 H, s, 1-H); δ_C(CD_3CN) 131.0 (d), 131.4 (d), 134.2 (d), 134.8 (d), 134.9 (s), 135.6 (d), 136.1 (s), 139.2 (s), 142.1 (d), 143.2 (d), 147.0 (s), 174.1 (d) and 190.3 (s) (Found: C, 56.6; H, 3.4. $C_{16}H_{11}BF_4OS$ requires C, 56.76; H, 3.27%).

General Procedure for the Reaction of Benzothiopyrylium Salt **4** *with Active Methyl and Methylene Compounds.*—Benzothiopyrylium salt **4** (338 mg, 1.00 mmol) was added portionwise to a stirred solution of an active methyl or methylene compound (2 mmol) in dichloromethane (10 cm^3) or to a stirred active methylene compound without solvent, and the mixture was further stirred at room temperature for an appropriate time. Water was added to the reaction mixture, which was then stirred for a while, and organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated

under reduced pressure. The residue was purified by PLC on silica gel to afford 1-substituted 3-benzoyl-1*H*-2-benzothiopyrans **5**. The above results are summarized in Table 1, including active methyl and methylene compounds used, reaction conditions, and yields.

1-*Acetonyl*-3-*benzoyl*-1H-2-*benzothiopyran* **5a**, yellow columns, m.p. 149–150 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1} 1700 (COMe) and 1630 (COPh); δ_H($CDCl_3$) 2.06 (3 H, s, Me), 2.83 (1 H, dd, *J* 17.6 and 6.4, C*H*HCO), 3.10 (1 H, dd, *J* 17.6 and 7.3, CH*H*CO), 4.59 (1 H, dd, *J* 7.3 and 6.4, 1-H), 7.21–7.60 (8 H, m, ArH and 4-H) and 7.76–7.79 (2 H, m, ArH); δ_C($CDCl_3$) 30.7 (q), 37.6 (d), 49.4 (t), 127.2 (d), 127.9 (d), 128.4 (d), 129.1 (d), 129.6 (d), 130.8 (s), 131.1 (d), 132.4 (d), 132.6 (s), 134.4 (s), 134.5 (d), 136.7 (s), 193.9 (s) and 205.0 (s); *m*/*z* 308 (M^+) and 251 (base) (Found: C, 73.9; H, 5.3. $C_{19}H_{16}O_2S$ requires C, 74.00; H, 5.23%).

Dimethyl 3-*benzoyl*-1H-2-*benzothiopyran*-1-*yl*)*malonate* **5b**, yellow plates, m.p. 137–138 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1}1740 (ester) and 1640 (CO); δ_H($CDCl_3$) 3.46 (3 H, s, Me), 3.77 (3 H, s, Me), 3.97 [1 H, d, *J* 11.2, C*H*(CO_2Me)$_2$], 4.77 (1 H, d, *J* 11.2, 1-H), 7.23–7.64 (8 H, m, ArH and 4-H) and 7.79 (2 H, br d, *J* 6.8, ArH); δ_C($CDCl_3$) 41.8 (d), 52.5 (q), 52.8 (q), 55.9 (d), 127.9 (d), 128.4 (d), 128.5 (d), 129.1 (d), 129.2 (s), 129.6 (d), 130.7 (d), 131.1 (s), 132.5 (d), 134.2 (s), 134.5 (d), 136.5 (s), 166.6 (s), 166.8 (s) and 193.7 (s); *m*/*z* 382 (M^+) and 251 (base) (Found: C, 66.1; H, 4.7. $C_{21}H_{18}O_5S$ requires C, 65.95; H, 4.74%).

3-(3-*Benzoyl*-1H-2-*benzothiopyran*-1-*yl*)*pentane*-2,4-*dione* **5c**, yellow needles, m.p. 168–170 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1} 1730 (COMe) and 1630 (COPh); δ_H($CDCl_3$) 1.81 (3 H, s, Me), 2.27 (3 H, s, Me), 4.40 [1 H, d, *J* 11.2, C*H*(COMe)$_2$], 4.82 (1 H, d, *J* 11.2, 1-H), 7.20–7.40 (4 H, m, ArH), 7.46–7.64 (4 H, m, ArH and 4-H) and 7.78–7.81 (2 H, m, ArH); δ_C($CDCl_3$) 29.7 (q), 31.4 (q), 41.7 (d), 70.7 (d), 128.2 (d), 128.5 (d), 128.6 (d), 129.2 (d), 129.4 (s), 129.8 (d), 131.1 (s), 131.1 (d), 132.7 (d), 134.2 (s), 134.3 (d), 136.5 (s), 193.5 (s), 200.3 (s) and 201.2 (s); *m*/*z* 350 (M^+) and 251 (base) (Found: C, 72.2; H, 5.15. $C_{21}H_{18}O_3S$ requires C, 71.98; H, 5.18%).

3-*Benzoyl*-1-*dibenzoylmethyl*-1H-2-*benzothiopyran* **5d**, yellow needles, m.p. 155–156 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1} 1690 (CO) and 1640 (CO); δ_H($CDCl_3$) 5.43 (1 H, d, *J* 10.5, 1-H), 6.17 [1 H, d, *J* 10.5, C*H*(COPh)$_2$], 7.16–7.74 (16 H, m, ArH and 4-H), 7.88 (2 H, m, ArH) and 8.10–8.13 (2 H, m ArH); δ_C($CDCl_3$) 43.3 (d), 59.1 (d), 128.2 (d), 128.4 (d), 128.5 (d), 128.8 (d), 128.9 (d), 129.0 (d), 129.1 (d), 129.3 (s), 129.5 (d), 130.9 (d), 131.6 (s), 131.8 (s), 132.6 (d), 133.5 (d), 133.6 (d), 133.8 (d), 134.8 (s), 135.3 (d), 136.3 (s), 136.4 (s), 136.7 (s), 192.3 (s), 192.8 (s) and 193.2 (s); *m*/*z* 474 (M^+) and 105 (base) (Found: C, 78.3; H, 4.65. $C_{31}H_{22}O_3S$ requires C, 78.46; H, 4.67%).

Ethyl 2-(3-*benzoyl*-1H-2-*benzothiopyran*-1-*yl*)-3-*oxobutanoate* (diastereoisomeric mixture) **5e**, yellow oil, ν_{max}(neat)/cm^{-1} 1740–1720 and 1300–1270 (MeCO and ester) and 1640 (COPh); δ_H($CDCl_3$) 1.02 (3 H, t, *J* 7.3, CH_2*Me*), 1.25 (3 H, t, *J* 7.3, CH_2*Me*), 1.85 (3 H, s, COMe), 2.28 (3 H, s, COMe), 3.90 (2 H, q, *J* 7.3, C*H*$_2$Me), 4.15 (1 H, d, *J* 11.2, CH), 4.23 (2 H, q, *J* 7.3, C*H*$_2$Me), 4.79 (1 H, d, *J* 11.2, 1-H), 7.23–7.63 (6 H, m, ArH and 4-H) and 7.78–7.82 (2 H, m, ArH); δ_C($CDCl_3$) 13.7 (q), 14.0 (q), 30.3 (q), 30.8 (q), 41.0 (d), 41.5 (d), 61.6 (t), 61.9 (t), 62.5 (d), 62.7 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 129.1 (d), 129.2 (s), 129.5 (d), 130.7 (d), 130.8 (d), 131.0 (s), 131.3 (s), 132.5 (d), 132.6 (d), 133.9 (d), 134.0 (d), 134.7 (d), 136.5 (s), 136.6 (s), 166.2 (s), 166.3 (s), 193.5 (s), 193.7 (s), 199.5 (s) and 200.2 (s); *m*/*z* 380 (M^+) and 251 (base) (Found: M^+, 380.1108. $C_{22}H_{20}O_4S$ requires M, 380.1082).

General Procedure for the Reaction of Benzothiopyrylium Salts **4** *and* **6** *with Substituted Buta*-1,3-*dienes*.—Benzothiopyrylium salt **4** or **6** (1.00 mmol) was added portionwise to a stirred solution of an appropriate substituted buta-1,3-diene (2 mmol) in 1,2-dichloroethane or acetonitrile (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 (1 mmol) in 1,2-dichloroethane or acetonitrile (10 cm^3) for 5 min at room temperature, and the mixture was stirred for an appropriate time. Methanol (1 cm^3) was added to the reaction mixture, and then diethyl ether was added to precipitate the product as a fine powder. The reaction conditions and yields of the products are summarized in Table 2.

9-*Benzoyl*-6,7-*dimethyl*-4b,5-*dihydro*-8H-8a-*thioniaphenanthrene tetrafluoroboranuide* **7a**, leaflets, m.p. 147.5–148 °C (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1640 (CO) and 1090–1030 (BF_4^-); δ_H(CD_3CN) 1.68 (3 H, s, Me), 1.89 (3 H, s, Me), 3.11 (1 H, br d, *J* 18.1, CHC*H*H), 3.22 (1 H, br d, *J* 18.1, CHCH*H*), 3.52 (1 H, d, *J* 15.1, S^+C*H*H), 3.86 (1 H, d, *J* 15.1, S^+CH*H*), 5.17 (1 H, br s, C*H*CH_2), 7.58–7.82 (7 H, m, ArH), 7.91–7.94 (2 H, m, ArH) and 8.19 (1 H, s, olefinic H) (Found: C, 62.6; H, 5.0. $C_{22}H_{21}BF_4OS$ requires C, 62.87; H, 5.04%).

9-*Benzoyl*-6-*methyl*-4b,5-*dihydro*-8H-8a-*thioniaphenanthrene tetrafluoroboranuide* **7b**, leaflets, m.p. 166–167 °C (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1640 (CO) and 1080–1030 (BF_4^-); δ_H(CD_3CN) 1.95 (3 H, s, Me), 3.13 (1 H, br d, *J* 15.5, CHC*H*H), 3.34 (1 H, br d, *J* 15.9, CHCH*H*), 3.48 (1 H, br d, *J* 16.1, S^+C*H*HCH=C), 3.97 (1 H, dd, *J* 16.1 and 5.4, S^+CH*H*CH=C), 5.23 (1 H, br s, C*H*CH_2), 5.60 (1 H, br d, *J* 5.4, S^+CH_2C*H*=C), 7.58–7.82 (7 H, m, ArH), 7.92–7.95 (2 H, m, ArH) and 8.20 (1 H, s, olefinic H) (Found: C, 62.1; H, 4.7. $C_{21}H_{19}BF_4OS$ requires C, 62.09; H, 4.71%).

9-*Benzoyl*-6-*phenyl*-4b,5-*dihydro*-8H,8a-*thioniaphenanthrene tetrafluoroboranuide* **7c**, leaflets, m.p. 147–148 °C (decomp.) (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1640 (CO) and 1120–1030 (BF_4^-); δ_H(CD_3CN) 3.57 (1 H, br d, *J* 18.6, CHC*H*H), 3.75 (1 H, br d, *J* 16.6, S^+C*H*H), 3.82 (1 H, dd, *J* 18.6 and 3.9, CHCH*H*), 4.24 (1 H, dd, *J* 16.6 and 5.9, S^+CH*H*), 5.39 (1 H, br d, *J* 3.9, C*H*CH_2), 6.15 (1 H, dd, *J* 5.9 and 2.4, S^+CH_2C*H*=C), 7.43–7.51 (5 H, m, ArH), 7.60–7.83 (7 H, m, ArH), 7.95 (2 H, br d, *J* 7.3, ArH) and 8.24 (1 H, s, olefinic H) (Found: C, 66.5; H, 4.6. $C_{26}H_{21}BF_4OS$ requires C, 66.68; H, 4.51%).

9-*Benzoyl*-4b,5-*dihydro*-8H-8a-*thioniaphenanthrene tetrafluoroboranuide* **7d**, prisms, m.p. 148–149 °C (decomp.) (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1640 (CO) and 1080–1030 (BF_4^-); δ_H(CD_3N) 3.10–3.17 (1 H, m, CHC*H*H), 3.48–3.56 (2 H, m, CHCH*H* and S^+C*H*H), 4.01 (1 H, br d, *J* 5.4, S^+CH*H*), 5.24 (1 H, br s, C*H*CH_2), 5.83–5.86 (1 H, m, S^+CH_2CH=C*H*), 6.22–6.25 (1 H, m, S^+CH_2C*H*=CH), 7.58–7.82 (7 H, m, ArH), 7.93–7.96 (2 H, m, ArH) and 8.22 (1 H, s, olefinic H); δ_C(CD_3CN) 24.7 (t), 33.6 (t), 43.2 (d), 120.1 (d), 122.9 (s), 128.2 (d), 128.8 (d), 129.3 (s), 130.1 (d), 130.7 (d), 131.0 (d), 134.5 (s), 135.2 (d), 135.4 (d), 136.2 (d), 149.4 (d) and 190.8 (s) (Found: C, 61.0; H, 4.3. $C_{20}H_{17}BF_4OS$ requires C, 61.25; H, 4.37%).

6,7-*Dimethyl*-4b,5-*dihydro*-8H-8a-*thioniaphenanthrene tetrafluoroboranuide* **8a**, prisms, m.p. 87–89 °C (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1020 (BF_4^-); δ_H(CD_3CN) 1.75 (3 H, s, Me), 1.79 (3 H, s, Me), 2.80 (1 H, br d, *J* 18.1, CHC*H*H), 3.01 (1 H, dd, *J* 18.1 and 5.9, CHCH*H*), 3.66 (1 H, d, *J* 16.1, S^+C*H*H), 3.89 (1 H, d, *J* 6.1, S^+CH*H*), 4.85 (1 H, t, *J* 5.9, C*H*CH_2), 6.34 (1 H, d, *J* 9.3, olefinic H) and 7.44–7.57 (5 H, m, ArH and olefinic H); δ_C(CD_3CN) 19.6 (q), 20.2 (q), 32.8 (t), 37.9 (t), 43.4 (d), 107.8 (d), 120.1 (s), 128.5 (d), 128.9 (s), 129.1 (s), 130.6 (s), 130.9 (d), 132.0 (d), 133.2 (d) and 141.1 (d) (Found: C, 56.9; H, 5.4. $C_{15}H_{17}BF_4S$ requires C, 56.98; H, 5.24%).

6,7-*Dimethyl*-4b,5-*dihydro*-8H-8a-*thioniaphenanthrene perchlorate* **8a'**, prisms, m.p. 70–73 °C (decomp.) (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1140–1020 (ClO_4^-) (Found: C, 54.9; H, 5.3. $C_{15}H_{17}ClO_4S$ requires C, 54.79; H, 5.21%).

6-*Methyl*-4b,5-*dihydro*-8H-8a-*thioniaphenanthrene tetrafluoroboranuide* **8b**, columns, m.p. 108–109.5 °C (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1030 (BF_4^-); δ_H(CD_3CN) 1.87 (3 H, s, Me), 2.80 (1 H, br d, *J* 19.0, CHC*H*H), 2.99 (1 H, dd, *J* 19.0 and 5.9, CHCH*H*), 3.66 (1 H, br d, *J* 15.6, $S^+CHHCH{=}C$), 4.00 (1 H, br d, *J* 15.6, $S^+CHHCH{=}C$), 4.85 (1 H, t, *J* 5.9, $CHCH_2$), 5.63 (1 H, br s, $S^+CH_2CH{=}C$), 6.36 (1 H, d, *J* 9.3, olefinic H) and 7.48–7.57 (5 H, m, ArH and olefinic H); δ_C(CD_3CN) 24.7 (q), 30.1 (t), 33.8 (t), 43.3 (d), 108.4 (d), 113.2 (d), 128.4 (d), 128.7 (s), 129.6 (s), 131.2 (d), 132.1 (d), 133.3 (d), 138.1 (s) and 141.6 (d) (Found: C, 55.9; H, 5.05. $C_{14}H_{15}BF_4S$ requires C, 55.65; H, 5.00%).

4b,5-*Dihydro*-8H-8a-*thioniaphenanthrene tetrafluoroboranuide* **8c**, prisms, m.p. 101–103.5 °C (decomp.) (from nitromethane–diethyl ether); ν_{max}(KBr)/cm^{-1} 1100–1030 (BF_4^-); δ_H(CD_3CN) 2.83–2.90 (1 H, m, CHC*H*H), 3.04–3.12 (1 H, m, CHCH*H*), 3.67–3.73 (1 H, m, S^+CHH), 4.00–4.06 (1 H, m, S^+CHH), 4.83 (1 H, t, *J* 5.9, $CHCH_2$), 5.88–5.91 (1 H, m, $S^+CH_2CH{=}CH$), 6.17–6.20 (1 H, m, $S^+CH_2CH{=}CH$) and 7.51–7.59 (5 H, m, ArH and olefinic H); δ_C(CD_3CN) 25.3 (t), 33.3 (t), 42.8 (d), 108.6 (d), 119.0 (d), 128.6 (d), 128.7 (s), 129.2 (d), 129.8 (s), 131.4 (d), 132.1 (d), 133.3 (d) and 141.8 (d) (Found: C, 54.1; H, 4.6. $C_{13}H_{13}BF_4S$ requires C, 54.20; H, 4.55%).

Reactions of Benzothiopyrylium Salt **4** *with Furans.*—A mixture of tetrafluoroboranuide **4** (338 mg, 1 mmol) and furan (136 mg, 2 mmol) in 1,2-dichloroethane (10 cm^3) was stirred for 3 h at room temperature. The reaction mixture was treated with water and extracted with dichloromethane; the extract was washed twice with water, dried ($MgSO_4$), and evaporated. The residual oil was submitted to PLC on silica gel with hexane–ethyl acetate (2:1) to afford 2-(3'-*benzoyl*-1'H-2'-*benzothiopyran*-1'-*yl*)*furan* **9** (51 mg, 16.3%) and 2,5-*bis*-(3'-*benzoyl*-1'H-2'-*benzothiopyran*-1'-*yl*)*furan* **10** (205 mg, 60.6%) as diastereoisomeric mitures (1:1). Compound **9**, a yellow oil, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H($CDCl_3$) 5.33 (1 H, s, 1'-H), 5.83 (1 H, br d, *J* 2.9, 3-H), 6.24 (1 H, br s, 4-H), 7.22–7.48 (9 H, m, ArH, 4'-H and 5-H) and 7.68–7.70 (2 H, m, ArH); δ_C($CDCl_3$) 40.4 (d), 108.6 (d), 110.3 (d), 127.6 (d), 128.3 (d), 129.3 (d), 129.6 (d), 130.0 (s), 131.0 (d) 131.8 (s), 132.3 (d), 134.5 (s), 134.8 (d), 136.8 (s), 142.6 (d), 152.5 (s) and 193.9 (s); *m*/*z* 318 (M^+) and 105 (base) (Found: M^+, 318.0726. $C_{20}H_{14}OS$ requires M, 318.0715).

Compound **10**: pale brown powder, m.p. 99–102 °C (from dichloromethane–hexane); ν_{max}(KBr)/cm^{-1} 1640 (CO); δ_H($CDCl_3$) 5.25 and 5.32 (each 1 H, each s, 1'-H), 5.56 and 5.83 (each 1 H, each s, 3- and 4-H), 7.17–7.70 (20 H, m, ArH and 4'-H); δ_C($CDCl_3$) 40.3 (d), 40.5 (d), 109.3 (d), 109.5 (d), 127.6 (d), 127.8 (d), 128.2 (d), 128.3 (d), 128.4 (d), 129.3 (d), 129.5 (d), 129.6 (d), 130.1 (s), 131.0 (d), 131.1 (d), 131.7 (s), 131.8 (s), 132.3 (d), 132.4 (d), 134.3 (s), 134.6 (s), 134.8 (d), 134.9 (s), 136.7 (s), 136.8 (s), 152.5 (s), 152.6 (s), 193.8 (s) and 193.9 (s); *m*/*z* 568 (M^+) and 105 (base) (Found: C, 75.8; H, 4.6. $C_{36}H_{24}O_3S_2$ requires C, 76.03; H, 4.25%).

The above reaction was performed using 2,5-dimethylfuran instead of furan to give 3-benzoyl-1*H*-2-benzothiopyran **3** (31%) and 3-(3'-benzoyl-1'*H*-2'-benzothiopyran-1'-yl)-2,5-dimethylfuran **11** (31%) as an inseparable mixture. Compound **11**: δ_H($CDCl_3$) 2.21 (3 H, s, Me), 2.22 (3 H, s, Me), 5.24 (1 H, s, 1'-H), 5.89 (1 H, s, 4-H), 7.12–7.58 (8 H, m, ArH and 4'-H) and 7.77–7.79 (2 H, m, ArH); δ_C($CDCl_3$) 11.8 (q), 13.5 (q), 39.3 (d), 106.6 (d), 117.7 (s), 126.4 (d), 127.6 (d), 128.4 (d), 129.2 (d), 129.4 (d), 131.1 (d), 132.3 (d), 132.5 (s), 132.8 (s), 135.1 (d), 136.9 (s), 137.0 (s), 147.0 (s) 150.1 (s) and 193.9 (s); *m*/*z* 346 (M^+) and 105 (base).

Reaction of Cycloadduct **7d** *with* 2,3-*Dimethylbuta*-1,3-*diene.*—A stirred mixture of the cycloadduct **7d** (196 mg, 0.5 mmol) and 2,3-dimethyl-1,3-butadiene (84 mg, 1 mmol) in 1,2-dichloroethane (10 cm^3) was refluxed for 10 min. After the mixture had cooled, diethyl ether was added to precipitate crystals (37 mg), which were an inseparable mixture of starting material **7d** and cycloadduct **7a** in the ratio 1:2.7 based on ^{1}H NMR measurements.

Reaction of 2-*Benzothiopyrylium Salt* **4** *with a Mixture of Buta*-1,3-*diene and* 2,3-*Dimethylbuta*-1,3-*diene.*—Buta-1,3-diene gas was bubbled into a stirred solution of 2,3-dimethylbuta-1,3-diene (420 mg, 5 mmol) in 1,2-dichloroethane (10 cm^3) for 5 min, and to this was added the salt **4** (338 mg, 1 mmol) portionwise within 5 min, and stirring of the mixture was continued for another 30 min. Diethyl ether was added to the reaction mixture to precipitate cycloadduct **7a** (393 mg) as crystals.

Reaction of Cycloadduct **7a** *with Acetone.*—A stirred solution of the cycloadduct **7a** (210 mg, 0.5 mmol) in dry acetone (5 cm^3) was refluxed for 10 h. After cooling, the reaction mixture was poured into water and extracted with dichloromethane, washed twice with water, and dried ($MgSO_4$). The solvent was evaporated off to give the residue, which was purified by PLC on silica gel with hexane–ethyl acetate (4:1) to afford the 1-acetonyl-2-benzothiopyran **5a** (114 mg, 74%).

Reactions of Cycloadduct **7a** *with Nucleophiles.*—(a) *With water.* A mixture of cycloadduct **7a** (210 mg, 0.5 mmol) and water (0.5 cm^3) in acetone (5 cm^3) was refluxed for 5 min. After the mixture had cooled, water was added 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 (4:1) to afford the following three products: 4-(3-*benzoyl*-1H-2-*benzothiopyran*-1-*yl*)-2,3-*dimethylbut*-2-*en*-1-*ol* **12a** (129 mg, 73.7%) as a yellow oil, ν_{max}(KBr)/cm^{-1} 3500–3400 (OH) and 1635 (CO); δ_H($CDCl_3$) 1.69 (6 H, br s, 2 × Me), 2.48 (1 H, dd, *J* 13.7 and 7.8, CHC*H*H), 2.62 (1 H, dd, *J* 13.7 and 7.8, CHCH*H*), 3.62 (1 H, d, *J* 11.7, C*H*HOH), 3.82 (1 H, d, *J* 11.7, CH*H*OH), 4.04 (1 H, t, *J* 7.8, $CHCH_2$), 7.09–7.51 (2 H, m, ArH), 7.22–7.40 (4 H, m, ArH and 4-H), 7.46–7.51 (2 H, m ArH), 7.56–7.61 (1 H, m, ArH) and 7.75–7.78 (2 H, m, ArH); δ_C($CDCl_3$) 16.5 (q), 18.9 (q), 40.0 (t), 41.8 (d), 62.7 (t), 126.9 (s), 127.4 (d), 127.6 (d), 128.4 (d), 129.2 (d), 129.7 (d), 130.5 (d), 130.7 (s), 132.3 (d), 133.0 (s), 133.6 (s), 134.3 (s), 134.6 (d), 136.8 (s) and 194.2 (s); *m*/*z* 350 (M^+) (Found: C, 75.1; H, 6.35. $C_{22}H_{22}O_2S$ requires C, 75.40; H, 6.33%); 1-(3-*benzoyl*-1H-2-*benzothiopyran*-1-*yl*)-2,3-*dimethylbut*-3-*en*-2-*ol* **13a** (35 mg, 20%) as a yellow gum, ν_{max}(neat)/cm^{-1} 3500–3400 (OH) and 1640 (CO); δ_H($CDCl_3$) 1.23 (3 H, s, Me), 1.78 (3 H, s, Me), 1.83 (1 H, dd, *J* 15.1 and 2.9, CHC*H*H), 2.26 (1 H, dd, *J* 15.1 and 10.7, CHCH*H*), 3.46 (1 H, s, OH), 4.08 (1 H, dd, *J* 10.7 and 2.9, $CHCH_2$), 5.03 and 5.28 (each 1 H, each br s, $C{=}CH_2$), 7.13 (1 H, br d, *J* 7.3, ArH), 7.20–7.31 (2 H, m, ArH), 7.37–7.63 (5 H, m, ArH and 4-H) and 7.79 (2 H, br d, *J* 7.3, ArH); δ_C($CDCl_3$) 19.8 (q), 28.7 (q), 39.8 (d), 43.6 (t), 76.0 (s), 118.2 (t), 126.4 (d), 127.7 (d), 128.4 (d), 129.3 (d), 129.7 (d), 131.0 (d), 131.4 (s), 132.4 (d), 133.2 (s), 134.2 (s), 136.3 (d), 136.8 (s), 148.5 (s) and 193.7 (s); *m*/*z* 350 (M^+) and 251 (base) (Found: C, 75.2; H, 6.3%); a diastereoisomer of compound **13a** (8 mg, 4.6%) as a yellow gum, ν_{max}(neat)/cm^{-1} 3500–3400 (OH) and 1640 (CO); δ_H($CDCl_3$) 1.29 (3 H, s, Me),

1.80 (3 H, s, Me), 1.62 (1 H, br s, OH), 2.04 (1 H, dd, *J* 14.7 and 5.9, CHC*H*H), 2.32 (1 H, dd, *J* 14.7 and 6.4, CHCH*H*), 4.14 (1 H, dd, *J* 6.4 and 5.9, C*H*CH$_2$), 5.12 and 5.30 (each 1 H, each br s, C=CH$_2$), 7.21–7.31 (3 H, m, ArH), 7.37–7.42 (2 H, m, ArH and 4-H), 7.46–7.61 (3 H, m, ArH) and 7.77–7.80 (2 H, m, ArH); δ_C(CDCl$_3$) 19.9 (q), 28.5 (q), 39.0 (d), 46.0 (t), 75.3 (s), 110.8 (t), 126.8 (d), 127.6 (d), 128.5 (d), 129.3 (d), 129.7 (d), 131.1 (d), 131.3 (s), 132.4 (d), 134.6 (s), 134.8 (s), 135.3 (d), 137.0 (s), 149.8 (s) and 194.2 (s); *m*/*z* 350 (M^+) and 251 (base).

(b) *With methanol.* A mixture of the cycloadduct **7a** (1.26 g, 3 mmol) and dry methanol (30 cm^3) was refluxed for 5 min. To the reaction mixture was added saturated aq. NaHCO$_3$ and the mixture was extracted with dichloromethane. The organic layer was washed twice with water, dried (MgSO$_4$), and evaporated. The residue was subjected to PLC on silica gel with hexane–ethyl acetate (10:1) to afford 3-*benzoyl*-1-(4-*methoxy*-2,3-*dimethylbut*-2-*enyl*)-1H-2-*benzothiopyran* **12b** (952 mg, 87%) and 3-*benzoyl*-1-(2-*methoxy*-2,3-*dimethylbut*-3-*enyl*)-1H-2-*benzothiopyran* **13b** (133 mg, 12.2%) as an inseparable 1.7:1 mixture of diastereoisomers. Compound **12b** was a yellow oil, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H(CDCl$_3$) 1.61 (3 H, s, Me), 1.65 (3 H, s, Me), 2.55 and 2.64 (each 1 H, each dd, *J* 13.7 and 7.8, CHC*H*$_2$), 3.14 (3 H, s, OMe), 3.49 and 3.57 (each 1 H, each d, *J* 10.7, C*H*$_2$OMe), 4.03 (1 H, t, *J* 7.8, C*H*CH$_2$), 7.05–7.08 (1 H, m, ArH), 7.19–7.61 (7 H, m, ArH and 4-H) and 7.78—7.80 (2 H, m, ArH); δ_C(CDCl$_3$) 16.6 (q), 19.2 (q), 40.0 (t), 42.3 (d), 57.5 (q), 72.2 (t), 127.2 (d), 127.5 (d), 128.3 (d), 128.9 (s), 129.1 (d), 129.5 (d), 130.1 (s), 130.5 (d), 130.8 (s), 132.2 (d), 133.4 (s), 134.5 (d), 134.5 (s), 136.9 (s) and 193.9 (s); *m*/*z* 364 (M^+) and 251 (base) (Found: C, 75.5; H, 6.95. $C_{23}H_{24}O_2S$ requires C, 75.79; H, 6.64%). Data for the diastereoisomeric mixture of compound **13b**: a yellow oil, ν_{max}(neat)/cm^{-1} 1640; δ_H(CDCl$_3$) 1.29 (3 H, br s, Me), 1.64 (3 H, s, Me, major isomer), 1.66 (3 H, s, Me, minor isomer), 2.00 (1 H, dd, *J* 14.6 and 5.4, CHC*H*H, minor isomer), 2.02 (1 H, dd, *J* 14.6 and 5.4, CHC*H*H, major isomer), 2.27 (1 H, dd, *J* 14.6 and 6.4, CHCH*H*, minor isomer), 2.30 (1 H, dd, *J* 14.6 and 7.8, CHCH*H*, major isomer), 3.01 (3 H, s, OMe, minor isomer), 3.02 (3 H, s, OMe, major isomer), 3.99 (1 H, dd, *J* 6.4 and 5.4, C*H*CH$_2$, minor isomer), 4.11 (1 H, dd, *J* 7.8 and 5.4, C*H*CH$_2$, major isomer), 4.95 and 5.02 (each 1 H, each br s, C=CH$_2$, major isomer), 5.06 and 5.09 (each 1 H, each br s, C=CH$_2$, minor isomer), 7.17–7.26 (3 H, m, ArH), 7.33–7.60 (5 H, m, ArH and 4-H) and 7.76–7.79 (2 H, m, ArH); δ_C(CDCl$_3$) 18.7 (q, major isomer), 18.9 (q, minor isomer), 21.4 (q, major isomer), 21.6 (q, minor isomer), 38.5 (d, major isomer), 38.7 (d, minor isomer), 44.4 (t, minor isomer), 44.6 (t, major isomer), 49.5 (q, minor isomer), 49.7 (q, major isomer), 78.9 (s, major isomer), 79.3 (s, minor isomer), 114.0 (t, major isomer), 114.5 (t, minor isomer), 126.7 (d), 127.2 (d), 128.3 (d), 129.1 (d), 129.2 (d, minor isomer), 129.3 (d, major isomer), 130.8 (d, 131.1 (s), 132.2 (d), 134.8 (s), 134.8 (s, major isomer), 134.9 (s, minor isomer), 135.0 (d, major isomer), 135.2 (d, minor isomer), 136.9 (s), 146.4 (s, minor isomer), 147.0 (s, major isomer) and 194.2 (s); *m*/*z* 364 (M^+) (Found: C, 75.5; H, 6.8%).

Similar reactions of the cycloadducts **7b** and **7d** with methanol as above afforded a pair of the corresponding benzothiopyrans **12h** and **13h**, and **12i** and **13i**, respectively.

3-*Benzoyl*-1-(4-*methoxy*-2-*methylbut*-2-*enyl*)-1H-2-*benzothiopyran* **12h** (85%) from the cycloadduct **7b** was a yellow gum, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H(CDCl$_3$) 1.69 (3 H, s, Me), 2.49 and 2.60 (each 1 H, each dd, *J* 13.7 and 7.8, CHC*H*$_2$), 3.16 (3 H, s, OMe), 3.46 and 3.63 (each 1 H, each dd, *J* 11.2 and 6.8, C*H*$_2$OMe), 4.05 (1 H, t, *J* 7.8, C*H*CH$_2$), 5.44 (1 H, br t, *J* 6.8, C=C*H*CH$_2$OMe), 7.13 (1 H, br d, *J* 7.3, ArH), 7.20–7.61 (7 H, m, ArH and 4-H) and 7.77–7.80 (2 H, m, ArH); δ_C(CDCl$_3$) 23.7 (q), 38.1 (t), 41.7 (d), 57.6 (q), 68.2 (t), 125.8 (d), 127.2 (d), 127.6 (d), 128.3 (d), 129.0 (d), 129.5 (d), 130.6 (d), 130.7 (s), 132.2 (d), 133.2 (s), 134.2 (s), 134.4 (d), 135.1 (s), 136.8 (s) and 193.8 (s); *m*/*z* 350 (M^+) and 251 (base) (Found: C, 74.8; H, 6.3. $C_{22}H_{22}O_2S$ requires C, 75.40; H, 6.33%).

3-*Benzoyl*-1-(2-*methoxy*-2-*methylbut*-3-*enyl*)-1H-2-*benzothiopyran* **13h** (14.3%) was an inseparable mixture of diastereoisomers in the ratio 1:1.8 from the cycloadduct **7b**. Data for the diastereoisomeric mixture **13h**: a yellow gum, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H(CDCl$_3$) 1.19 (3 H, s, Me, minor isomer), 1.32 (3 H, s, Me, major isomer), 2.00 (1 H, dd, *J* 14.7 and 5.4, CHC*H*H, major isomer), 2.05 (1 H, dd, *J* 14.7 and 5.4, CHC*H*H, minor isomer), 2.21 (1 H, dd, *J* 14.7 and 6.4, CHCH*H*, minor isomer), 2.25 (1 H, dd, *J* 14.7 and 6.4, CHCH*H*, major isomer), 3.06 (3 H, s, OMe, minor isomer), 3.11 (3 H, s, OMe, major isomer), 4.18 (1 H, dd, *J* 6.4 and 5.4, C*H*CH$_2$, minor isomer), 4.25 (1 H, dd, *J* 6.4 and 5.4 C*H*CH$_2$, major isomer), 5.07–5.29 (2 H, m, CH=C*H*$_2$), 5.57–5.68 (1 H, m, C*H*=CH$_2$, major isomer), 5.81–5.91 (1 H, m, C*H*=CH$_2$, minor isomer), 7.18–7.29 (3 H, m, ArH), 7.35–7.41 (2 H, m, ArH and 4-H), 7.47–7.52 (2 H, m, ArH), 7.56–7.62 (1 H, m, ArH) and 7.77–7.80 (2 H, m, ArH); δ_C(CDCl$_3$) 22.2 (q, two isomers), 38.3 (d, major isomer), 38.5 (d, minor isomer), 46.1 (t, major isomer), 46.4 (t, minor isomer), 49.9 (q, minor isomer), 50.1 (q, major isomer), 76.9 (s), 115.1 (t, major isomer), 115.3 (t, minor isomer), 127.0 (d, major isomer), 127.1 (d, minor isomer), 127.3 (d), 128.4 (d), 129.3 (d), 130.8 (d, minor isomer), 130.9 (d, major isomer), 131.2 (s), 132.3 (d), 134.8 (s), 134.9 (s), 135.1 (d), 137.0 (s), 142.3 (d, minor isomer), 142.6 (d, major isomer) and 194.3 (s); *m*/*z* 350 (M^+) (Found: M^+, 350.1317. $C_{22}H_{22}OS$ requires M, 350.1340).

3-*Benzoyl*-1-(4-*methoxybut*-2-*enyl*)-1H-2-*benzothiopyran* **12i** (73.3%) from the cycloadduct **7d**, was a yellow oil, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H(CDCl$_3$) 2.48–2.68 (2 H, m, CHC*H*$_2$), 3.20 (3 H, s, OMe), 3.67–3.83 (2 H, m, C*H*$_2$OMe), 3.95 (1 H, t, *J* 7.3, C*H*CH$_2$), 5.52–5.68 (2 H, m, CH=C*H*CH$_2$OMe), 7.15–7.31 (3 H, m, ArH), 7.36–7.40 (2 H, m, ArH and 4-H), 7.47–7.52 (2 H, m, ArH), 7.57–7.62 (1 H, m, ArH) and 7.76–7.79 (2 H, m, ArH); δ_C(CDCl$_3$) 33.9 (t), 43.3 (d), 58.7 (q), 67.8 (t), 127.3 (d), 127.7 (d), 128.4 (d), 128.5 (d), 129.1 (d), 129.4 (d), 129.7 (d), 130.7 (d), 130.8 (s), 132.3 (d), 133.0 (s), 134.3 (s), 134.7 (d), 136.8 (s) and 193.9 (s); *m*/*z* 336 (M^+) and 251 (base) (Found: C, 74.7; H, 6.0. $C_{21}H_{20}O_2S$ requires C, 74.97; H, 5.99%).

3-Benzoyl-1-(2-methoxybut-3-enyl)-1*H*-2-benzothiopyran **13i** (2%) was an inseparable mixture of diastereoisomers; a yellow oil, δ_H(CDCl$_3$) 1.88–2.11 (2 H, m, CHC*H*$_2$), 3.20–3.32 (4 H, m, CHOMe), 4.17–4.34 (1 H, m, C*H*CH$_2$), 5.03–5.09 (2 H, m, CH=C*H*$_2$), 5.51–5.64 (1 H, m, C*H*=CH$_2$), 7.21–7.63 (8 H, m, ArH and 4-H) and 7.76–7.79 (2 H, m, ArH); *m*/*z* 336 (M^+).

(c) *With ethanol.* A similar reaction and work-up as with methanol afforded 3-benzoyl-1-(4-ethoxy-2,3-dimethylbut-2-enyl)-1*H*-2-benzothiopyran **12c** (82.5%), and 3-*benzoyl*-1-(2-*ethoxy*-2,3-*dimethylbut*-3-*enyl*)-1H-2-*benzothiopyran* **13c** (6.9%) as an inseparable mixture of diastereoisomers in the ratio 1.8:1. Compound **12c**: a yellow gum, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H(CDCl$_3$) 1.13 (3 H, t, *J* 6.8, OCH$_2$*Me*), 1.60 (3 H, s, Me), 1.66 (3 H, s, Me), 2.56 and 2.64 (each 1 H, each dd, *J* 13.7 and 7.8, CHC*H*$_2$), 3.27 (2 H, q, *J* 6.8, OC*H*$_2$Me), 3.50 and 3.61 (each 1 H, each d, *J* 10.7, C*H*$_2$OEt), 4.03 (1 H, t, *J* 7.8, C*H*CH$_2$), 7.05–7.08 (1 H, m, ArH), 7.19–7.37 (3 H, m, ArH), 7.42–7.61 (4 H, m, ArH and 4-H) and 7.77–7.80 (2 H, m, ArH); δ_C(CDCl$_3$) 15.1 (q), 16.7 (q), 19.2 (q), 40.0 (t), 42.3 (d), 65.1 (t), 70.2 (t), 127.2 (d), 127.5 (d), 128.3 (d), 128.5 (s), 129.0 (d), 129.5 (d), 130.4 (s), 130.4 (d), 130.8 (s), 132.2 (d), 133.4 (s), 134.4 (d), 134.5 (s), 136.9 (s) and 193.9 (s); *m*/*z* 378 (M^+) and 251 (base).

Data for the diastereoisomeric mixture **13c**: a yellow gum, ν_{max}(KBr)/cm^{-1} 1640 (CO); δ_H(CDCl$_3$) 1.11 (3 H, t, *J* 6.8, OCH$_2$*Me*, minor isomer), 1.12 (3 H, t, *J* 6.8, OCH$_2$*Me*, major isomer), 1.30 (3 H, s, Me, major isomer), 1.33 (3 H, s, Me, minor isomer), 1.65 (3 H, s, Me, major isomer), 1.67 (3 H, s, Me, minor

isomer), 1.98 (1 H, dd, *J* 14.2 and 4.9, CHC*H*H, major isomer), 2.04 (1 H, dd, *J* 14.2, and 4.9, CHC*H*H, minor isomer), 2.29 (1 H, dd, *J* 14.2 and 6.8, CHCH*H*, minor isomer), 2.30 (1 H, dd, *J* 14.2 and 6.4, CHCH*H*, major isomer), 3.07–3.30 (2 H, m, OCH_2Me), 4.01 (1 H, dd, *J* 6.8 and 4.9, $CHCH_2$, minor isomer), 4.13 (1 H, dd, *J* 6.4 and 4.9, $CHCH_2$, major isomer), 4.95 and 5.00 (each 1 H, each br s, $C{=}CH_2$, major isomer), 5.05 and 5.08 (each 1 H, each br s, $C{=}CH_2$, minor isomer), 7.18–7.26 (3 H, m, ArH), 7.34–7.47 (2 H, m, ArH and 4-H), 7.50–7.53 (2 H, m, ArH), 7.57–7.63 (1 H, m, ArH) and 7.78–7.80 (2 H, m, ArH); *m/z* 378 (M^+) (Found: M^+, 378.1681. $C_{24}H_{26}O_2S$ requires M, 378.1664.

(d) *With aniline.* The cycloadduct **7a** (210 mg, 0.5 mmol) was added portionwise to a stirred solution of aniline (106 mg, 1.14 mmol) in 1,2-dichloroethane (5 cm^3) at room temperature, and the mixture was stirred for a further 2 h. Water was added to the reaction mixture, which was then 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 afford 1-(4-*anilino*-2,3-*dimethylbut*-2-*enyl*)-3-*benzoyl*-1H-2-*benzothiopyran* **12d** (182 mg, 85.4%) as a yellow gum, ν_{max}(KBr)/cm^{-1} 3350 (NH) and 1640 (CO); δ_H($CDCl_3$) 1.68 (3 H, s, Me), 1.74 (3 H, s, Me), 2.63 (2 H, br d, *J* 6.8, $CHCH_2$), 3.16 (1 H, br s, NH), 3.23 and 3.32 (each 1 H, each d, *J* 11.7, CH_2NHPh), 4.10 (1 H, t, *J* 6.8, $CHCH_2$), 6.41–6.44 (2 H, m, ArH), 6.60–6.65 (1 H, m, ArH), 7.05–7.53 (10 H, m, ArH and 4-H) and 7.63–7.66 (2 H, m, ArH); δ_C($CDCl_3$) 17.7 (q), 18.8 (q), 40.2 (t), 41.8 (d), 46.2 (t), 112.5 (d), 117.0 (d), 127.4 (d), 127.6 (d), 127.7 (s), 128.3 (d), 129.0 (d), 129.2 (d), 129.7 (d), 130.5 (d), 130.6 (s), 131.0 (s), 132.1 (d), 133.5 (s), 134.7 (s), 134.9 (d), 136.8 (s), 148.5 (s) and 194.1 (s); *m/z* 425 (M^+) and 251 (base) (Found: C, 78.8; H, 6.4; N, 3.3. $C_{28}H_{27}NOS$ requires C, 79.02; H, 6.39; N, 3.29%).

(e) *With sodium benzenethiolate.* Benzenethiol (107 mg, 0.97 mmol) was added to a solution of sodium ethoxide (66 mg, 0.97 mmol) in ethanol (10 cm^3) and to this stirred solution was added the cycloadduct **7a** (408 mg, 0.97 mmol). After being stirred for 30 min at room temperature the reaction mixture was poured into water, and extracted with dichloromethane. The organic layer was washed successively with aq. NaOH (1 mol dm^{-3}) and water, dried ($MgSO_4$), and evaporated. The residual oil was purified by PLC on silica gel with hexane–ethyl acetate (4:1) to give 3-*benzoyl*-1-[2,3-*dimethyl*-4-(*phenylsulfanyl*)*but*-2-*enyl*]-1H-2-*benzothiopyran* **12e** (410 mg, 95.6%) as a yellow oil, ν_{max}(KBr)/cm^{-1} 1640; δ_H($CDCl_3$) 1.60 (3 H, s, Me), 1.74 (3 H, s, Me), 2.42 and 2.49 (each 1 H, each dd, *J* 13.7 and 7.3, $CHCH_2$), 3.19 and 3.24 (each 1 H, each d, *J* 12.2, CH_2SPh), 4.02 (1 H, t, *J* 7.3, $CHCH_2$), 7.05 (1 H, br d, *J* 7.3, ArH), 7.10–7.43 (11 H, m, ArH and 4-H), 7.52–7.57 (1 H, m, ArH) and 7.70–7.73 (2 H, m, ArH); δ_C($CDCl_3$) 18.5 (q), 19.2 (q), 38.1 (t), 40.1 (t), 41.9 (d), 126.0 (d), 127.3 (d), 127.6 (d), 127.7 (s), 128.4 (d), 128.7 (d), 129.0 (s), 129.2 (d), 129.5 (d), 129.6 (d), 130.6 (d), 130.9 (s), 132.2 (d), 133.5 (s), 134.7 (s), 134.7 (d), 136.9 (s), 137.1 (s) and 194.1 (s); *m/z* 442 (M^+) and 251 (base) (Found: C, 75.6; H, 6.05. $C_{28}H_{26}OS_2$ requires C, 75.98; H, 5.92%).

(f) *With lithium benzeneselenolate.* A solution of diphenyl diselenide (644 mg, 2 mmol) in dry tetrahydrofuran (THF) (10 cm^3) was slowly added to a stirred suspension of $LiAlH_4$ (72 mg, 1.9 mmol) in dry diethyl ether (10 cm^3) under argon at −78 °C, and the mixture was stirred for 3 h, during which time the temperature was gradually raised to 0 °C. To this was added the cycloadduct **7a** (841 mg, 2 mmol) at −40 °C and the mixture was stirred for 2 h during which time the temperature was gradually raised to ambient. The reaction mixture was poured into water, and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on a silica gel column and eluted with hexane–dichloromethane (2:1) ⟶ hexane–ethyl acetate (1:1) to afford 3-benzoyl-1-[2,3-dimethyl-4-(phenylselanyl)but-2-enyl]-1*H*-2-benzothiopyran **12f** (781 mg, 79.8%) as a yellow gum, ν_{max}(neat)/cm^{-1} 1640 (CO); δ_H($CDCl_3$) 1.56 (3 H, s, Me), 1.73 (3 H, s, Me), 2.35 (2 H, br d, *J* 7.3, $CHCH_2$), 3.25 (2 H, br s, CH_2SePh), 3.98 (1 H, t, *J* 7.3, $CHCH_2$), 7.01–7.04 (1 H, m, ArH), 7.16–7.56 (12 H, m, ArH and 4-H) and 7.72–7.75 (2 H, m, ArH); δ_C($CDCl_3$) 18.7 (q), 19.3 (q), 32.5 (t), 40.1 (t), 41.7 (d), 127.0 (d), 127.2 (d), 127.6 (d), 128.2 (s), 128.4 (d), 128.7 (s), 128.8 (d), 129.2 (d), 129.5 (d), 130.5 (d), 130.8 (s), 130.9 (s), 132.2 (d), 133.3 (d), 133.5 (s), 134.6 (d), 134.7 (s), 136.9 (s) and 194.0 (s); *m/z* 490 (M^+) and 251 (base).

(g) *With trimethylsilyl cyanide.* The cycloadduct **7a** (420 mg, 1 mmol) was added to a stirred solution of trimethylsilyl cyanide (522 mg, 5 mmol) in 1,2-dichloroethane (10 cm^3) at −30 °C under N_2, and the mixture was stirred for 30 min. To this was added a catalytic amount of TBAF, and the mixture was stirred at −30 °C for 1.5 h, then at 0 °C overnight, and at room temperature for a further 1 day. The reaction mixture was poured into water, and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue was chromatographed on a column of silica gel and eluted with hexane–ethyl acetate (8:1) to give 5-(3-*benzoyl*-1H-2-*benzothiopyran*-1-*yl*)-3,4-*dimethylpent*-3-*enonitrile* **12g** (193 mg, 53.7%) as yellow prisms after recrystallization from dichloromethane–hexane, m.p. 139–140 °C; ν_{max}(KBr)/cm^{-1} 2210 (CN) and 1665 (CO); δ_H($CDCl_3$) 1.72 (3 H, s, Me), 1.74 (3 H, s, Me), 2.44 (1 H, br d, *J* 16.6, CHC*H*H), 2.65–2.69 (1 H, m, CHCH*H*), 2.89 and 3.43 (each 1 H, each d, *J* 17, CH_2CN), 4.18 (1 H, dd, *J* 10.3 and 3.9, $CHCH_2$), 7.26–7.68 (7 H, m, ArH), 7.89 (1 H, s, 4-H) and 8.06–8.09 (2 H, m, ArH); δ_C($CDCl_3$) 19.3 (q), 20.3 (q), 33.2 (t), 39.3 (t), 39.7 (d), 116.7 (s), 122.9 (s), 123.3 (s), 127.6 (s), 127.9 (d), 128.2 (d), 128.8 (d), 129.1 (d), 129.4 (d), 130.7 (d), 133.5 (s), 134.3 (d), 136.3 (s), 139.1 (d), 140.4 (s) and 186.6 (s); *m/z* 359 (M^+) (Found: C, 76.6; H, 5.9; N, 3.8. $C_{23}H_{21}NOS$ requires C, 76.85; H, 5.89; N, 3.90%).

Oxidation of Compound **12a** *with PCC.*—A solution of compound **12a** (93 mg, 0.27 mmol) in dichloromethane (1 cm^3) was added in one portion to a stirred suspension of PCC (83 mg, 0.38 mmol) in dry dichloromethane (1 cm^3) and the mixture was stirred at room temperature for 2 h. Dry diethyl ether (10 cm^3) was added to the reaction mixture to extract organic materials and the extract was separated, passed through Celite, and evaporated. The residue was submitted to PLC on silica gel with hexane–ethyl acetate (2:1) to afford 4-(3-*benzoyl*-1H-2-*benzothiopyran*-1-*yl*)-2,3-*dimethylbut*-2-*enal* **15** (53 mg, 57.6%) as a yellow gum, ν_{max}(KBr)/cm^{-1} 2750 (CHO) and 1660–1635 (CHO and PhCO); δ_H($CDCl_3$) 1.65 (3 H, s, Me), 1.92 (3 H, s, Me), 2.89 (1 H, dd, *J* 13.2 and 6.4, CHC*H*H), 3.25 (1 H, dd, *J* 13.2 and 8.8, CHCH*H*), 4.13 (1 H, dd, *J* 8.8 and 6.4, $CHCH_2$), 6.97 (1 H, br d, *J* 6.4, ArH), 7.23–7.36 (3 H, m, ArH), 7.43–7.64 (4 H, m, ArH and 4-H), 7.78 (2 H, br d, *J* 6.8, ArH) and 9.46 (1 H, s, CHO); δ_C($CDCl_3$) 11.1 (q), 22.2 (q), 38.7 (t), 43.2 (d), 127.3 (d), 128.2 (d), 128.5 (d), 129.1 (d), 130.0 (d), 130.5 (s), 130.7 (d), 131.7 (s), 132.4 (d), 134.3 (s), 134.4 (d), 135.5 (s), 136.7 (s), 152.0 (s), 189.4 (d) and 193.7 (s); *m/z* 348 (M^+) and 251 (base) (Found: M^+, 348.1211. $C_{22}H_{20}O_2S$ requires M, 348.1185).

Selective Oxidation of the Selenium Atom of the Compound **12f** *with MCPBA.*—MCPBA (85% purity; 324 mg, 1.6 mmol) was added slowly to an ice-cooled and stirred solution of compound **12f** (781 mg, 1.6 mmol) in dichloromethane (15 cm^3), and the mixture was stirred for 15 min. The reaction mixture was basified by addition of aq. $NaHCO_3$ and the organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC on silica gel with

hexane–ethyl acetate (2:1) to afford the alcohol **13a** (477 mg, 85.2%) as an inseparable mixture of diastereoisomers in the ratio 1:1.5.

Reaction of the Cycloadduct **8a** *with Trimethylsilyl Cyanide.*—A similar reaction of the cycloadduct **8a** with trimethylsilyl cyanide and work-up as in the case of the cycloadduct **7a** afforded 5-(1*H*-2-benzothiopyran-1-yl)-3,4-dimethylpent-3-enonitrile **18a** (25%) and *9-isopropenyl-9-methyl-3,4-dihydro-*1H-1,4-*ethano-2-benzothiopyran-3-carbonitrile* **17a** (40.5%) which were an inseparable mixture. Compound **18a**: a yellow oil with compound **17a**, $\delta_H(CDCl_3)$ 1.68 (3 H, s, Me), 1.74 (3 H, s, Me), 2.47 (2 H, d, *J* 7.8, $CHCH_2$), 2.49 and 2.78 (each 1 H, each d, *J* 17.6, CH_2CN), 3.84 (1 H, dt, *J* 7.8 and 2.0, $CHCH_2$), 6.35 (1 H, dd, *J* 9.3 and 2.0, 3-H), 6.76 (1 H, d, *J* 9.3, 4-H), 6.91–6.94 (1 H, m, ArH), 7.10–7.13 (1 H, m, ArH) and 7.17–7.25 (2 H, m, ArH); $\delta_C(CDCl_3)$ 18.3 (q), 18.9 (q), 21.7 (t), 39.9 (t), 40.7 (d), 118.1 (s), 120.0 (d), 121.7 (s), 124.0 (d), 127.2 (d), 127.3 (d), 127.7 (d), 127.9 (d), 129.5 (s), 130.7 (s) and 131.2 (s); *m/z* 255 (M^+) and 147 (base). Fortunately, a part of compound **17a** crystallized on storage at room temperature. Recrystallization from dichloromethane–hexane afforded pure compound **17a** as yellow prisms, m.p. 114–116 °C; ν_{max}(KBr)/cm^{-1} 2230 (CN); $\delta_H(CDCl_3)$ 0.76 (3 H, s, Me), 1.51 (1 H, dd, *J* 13.7 and 3.4, CHC*H*H), 1.90 (3 H, d, *J* 1, CH_2=C*Me*), 2.82 (1 H, dd, *J* 13.7 and 2.9, CHCH*H*), 3.48 (1 H, d, *J* 2.9, 4-H), 4.05 (1 H, dd, *J* 3.4 and 2.9, 1-H), 4.36 (1 H, d, *J* 2.9, 3-H), 5.13 and 5.24 (each 1 H, each br s, C=CH_2), 7.20–7.25 (1 H, m, ArH) and 7.33–7.40 (3 H, m, ArH); $\delta_C(CDCl_3)$ 20.7 (q), 30.2 (q), 30.3 (d), 39.4 (d), 40.2 (t), 41.1 (s), 46.4 (d), 113.1 (t), 119.8 (s), 122.2 (d), 127.5 (d), 128.4 (d), 128.5 (d), 134.6 (s), 140.3 (s) and 147.6 (s); *m/z* 255 (M^+) and 172 (base) (Found: C, 75.1; H, 6.7; N, 5.4. $C_{16}H_{17}NS$ requires C, 75.25; H, 6.71; N, 5.48%).

Reaction of the Cycloadduct **8a** *with Methanol.*—Refluxing of the cycloadduct **8a** in methanol and work-up as in the case of compound **7a** afforded 1-(4-methoxy-2,3-dimethylbut-2-enyl)-1*H*-2-benzothiopyran **18b** (trace, determined by ^{1}H NMR spectroscopy) and *9-isopropenyl-3-methoxy-9-methyl-*1H-1,4-*ethano-2-benzothiopyran* **17b** (65.4%), a yellow oil; $\delta_H(CDCl_3)$ 0.76 (3 H, s, Me), 1.42 (1 H, dd, *J* 13.7 and 3.4, CHC*H*H), 1.94 (3 H, d, CH_2=C*Me*), 2.73 (1 H, dd, *J* 13.7 and 2.9, CHCH*H*), 3.11 (3 H, s, OMe), 3.54 (1 H, d, *J* 3.4, 4-H), 4.06 (1 H, dd, *J* 3.4 and 2.9, 1-H), 5.04 and 5.16 (each 1 H, each br s, C=CH_2), 5.18 (1 H, d, *J* 3.4, 3-H), 7.15–7.19 (1 H, m, ArH) and 7.22–7.27 (3 H, m, ArH); $\delta_C(CDCl_3)$ 20.9 (q), 30.5 (q), 39.9 (d), 40.4 (t), 40.8 (s), 49.9 (d), 55.7 (q), 85.9 (d), 112.0 (t), 121.7 (d), 126.7 (d), 127.2 (d), 128.9 (d), 136.1 (s), 140.8 (s) and 148.8 (s); *m/z* 260 (M^+) and 147 (base) (Found: M^+, 260.1215. $C_{16}H_{20}OS$ requires M, 260.1234).

Cyclization of Compounds **12a** *and* **13a** *to the Sulfonium Salt* **7a**.—(a) *With tetrafluoroboric acid.* To a stirred, ice-cooled solution of compound **12a** (70 mg, 0.19 mmol) in diethyl ether (5 cm^3) was added 42% tetrafluoroboric acid (0.3 cm^3), and the mixture was stirred for a further 12 h at room temperature to precipitate the sulfonium salt **7a** (71 mg, 88%) as crystals, which were completely identical with the cycloadduct **7a** in all respects. In a similar manner, compound **13a** was treated with tetrafluoroboric acid to give the sulfonium salt **7a** in 76.6% yield.

(b) *With triphenylcarbenium tetrafluoroboranuide.* Triphenylcarbenium tetrafluoroboranuide (354 mg, 1.07 mmol) was added to a stirred solution of compound **12a** (356 mg, 0.98 mmol) in nitromethane (10 cm^3) at room temperature and the mixture was stirred for 3 h. To the reaction mixture was added diethyl ether to precipitate the sulfonium salt **7a** (321 mg, 78.1%) as crystals.

X-Ray Study of 9-*Benzoyl-6,7-dimethyl-*4b,5-*dihydro-*8H-8a-*thioniaphenanthrene Tetrafluoroboranuide* **7a**.—*Crystal data.* $C_{22}H_{21}BF_4OS$, M = 420.27, triclinic, *a* = 10.707(4), *b* = 11.955(4), *c* = 8.675(3) Å, α = 105.78(3), β = 97.96(4), γ = 68.59 (3)°, *V* = 993.9(7) Å^3, *Z* = 2, D_c = 1.404 g cm^{-3}, space group $P\bar{1}$ (#2), *F*(000) = 436, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 2.01 cm^{-1}. A yellow needle crystal of the title compound having approximate dimensions of 0.200 × 0.200 × 0.100 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range 24.77 < 2θ < 36.35°, corresponded to a triclinic cell. The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ-value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.32° with a take-off angle of 6.0°. Scans of (1.57 + 0.30 tan θ)° were made at a speed of 8.0°/min (in omega). The weak reflections [$I < 10.0\,\sigma(I)$] were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal-to-detector distance was 40 cm.

Data reduction. Of the 4811 reflections which were collected, 4566 were unique (R_{int} = 0.018). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by direct methods.[11] The non-hydrogen atoms were refined either anisotropically or isotropically. The final cycle of full-matrix least-squares refinement was based on 2502 observed reflections [$I > 3.00\sigma(I)$] and 262 variable parameters and converged (largest parameter shift was 0.02 times its esd) with unweighted and weighted agreement factors of: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.050$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.057$. The standard deviation of an observation of unit weight was 1.67. The weighting scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.22 and −0.27 e$^-$ Å^{-3}, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.[12] Anomalous dispersion effects were included in F_{calc};[13] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[14] All calculations were performed using the TEXSAN[15] crystallographic software package from Molecular Structure Corporation.

X-Ray Study of 9-*Isopropenyl-9-methyl-*3,4-*dihydro-*1H-1,4-*ethano-2-benzothiopyran-3-carbonitrile* **17a**.—*Crystal data.* $C_{16}H_{17}NS$, M = 255.38, monoclinic, *a* = 7.000(1), *b* = 11.436(2), *c* = 16.918(1) Å, β = 98.64(1)°, *V* = 1338.9(3) Å^3, *Z* = 4, D_c = 1.267 g cm^{-3}, space group $P2_1/n$ (#14), *F*(000) = 544, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 2.13 cm^{-1}.

A prism crystal of the title compound having approximate dimensions of 0.200 × 0.200 × 0.200 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R

diffractometer with graphite-monochromated Mo-Kα radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centred reflections in the range $24.26 < 2\theta < 33.32°$, corresponded to a monoclinic cell. The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ-value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a take-off angle of 6.0°. Scans of $(1.31 + 0.30 \tan \theta)°$ were made at a speed of 8.0°/min (in omega). The weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal-to-detector distance was 40 cm.

Data reduction. Of the 3484 reflections which were collected, 3231 were unique ($R_{int} = 0.053$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by direct methods.[11] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1717 observed reflections $[I > 3.00\sigma(I)]$ and 163 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.043$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.049$. The standard deviation of an observation of unit weight was 1.48. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.26 and -0.18 e$^-$ Å^{-3}, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.[12] Anomalous dispersion effects were included in F_{calc};[13] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[14] All calculations were performed using the TEXSAN[15] crystallographic software package from Molecular Structure Corporation.

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