Synthesis and reactions of lactam sulfonium salts with a sulfonio bridgehead. Part 1. 4,4a,5,6-Tetrahydro-5-oxo-1*H*-thiopyrano[1,2-*a*]-1,4-benzothiazinium perchlorates

Tadashi Kataoka,*[a] Yoshihide Nakamura,[a] Harutoshi Matsumoto,[a] Tetsuo Iwama,[a] Hirohito Kondo,[a] Hiroshi Shimizu,[a] Osamu Muraoka[a] and Genzoh Tanabe[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*

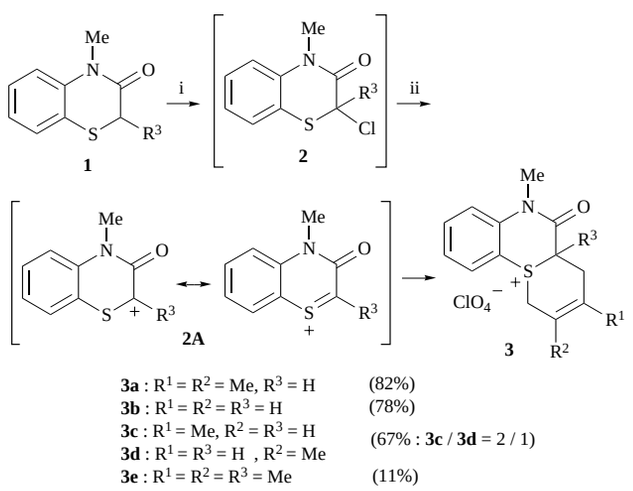
Tricyclic benzothiazinium salts 3 are prepared by [2⁺+4] polar cycloaddition of thionium intermediates 2A, generated from the corresponding α-chloro sulfides 2, and dienes in the presence of silver perchlorate. Ring transformation of benzothiazinium salts 3 with a reducing agent such as Mg, $NaBH_4$ and Zn–AcOH or with a base, furnishes spiro-vinylcyclopropane derivatives 4 in moderate to high yields. Electrolysis of 3a at −1.4 V *vs*. SCE in acetonitrile also affords vinylcyclopropane 4a (60%). These results indicate that both ionic and radical mechanisms may account for the vinylcyclopropane formation, although it is unclear as to the nature of the radical intermediate. The stereochemistry of 4a was determined by X-ray analysis showing that sulfur and the vinyl group are *cis*-orientated. Ten-membered lactam sulfides 6 are obtained as the major product of SmI_2 reduction of 3.

Introduction

Pharmacologically active benzothiazinone derivatives such as semotiadil, a Ca^{2+} antagonist,[1] or SPR-210, an aldose reductase inhibitor, have been synthesised.[2] Furthermore we earlier synthesised medium-sized cyclic sulfides both by reduction of bicyclic sulfonium salts bearing a bridgehead sulfur atom and by treatment of the salts with a base; we also applied such methods to bicyclic lactam sulfonium salts with a sulfonio bridgehead to give medium-sized lactam sulfides by cleavage of the cross-piece C–S bond.[3] It has been recently reported that α-chloro sulfides or thionium ions react with 1,3-dienes to form the bicyclic sulfonium salts, which undergo rearrangement on treatment with a base.[4,5] We planned to prepare tricyclic lactam sulfonium salts fused by a 5,6-dihydro-2*H*-thiopyran skeleton and to synthesise new lactam sulfides with unusual ring skeletons by transformation of the salts with a reducing agent or a base.[6] In this paper we describe the synthesis and ring transformation of benzothiazinium salts with a sulfonio bridgehead.

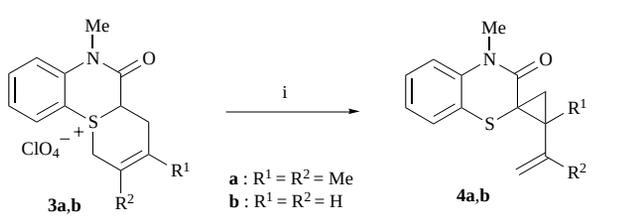
Synthesis of lactam sulfonium salts by [2⁺+4] polar cycloaddition

Benzothiazinones **1**, prepared according to the literature,[7] were treated with NCS (*N*-chlorosuccinimide). The resultant crude α-chloro sulfides **2** reacted with 1,3-dienes such as buta-1,3-diene, isoprene and 2,3-dimethylbuta-1,3-diene in the presence of silver perchlorate *via* an α-thiocarbocation **2A** to give benzothiazinium salts **3** in moderate to good yield (Scheme 1). Isoprene adducts **3c** and **3d** were obtained as a mixture of regioisomers (**3c**:**3d** = 2:1, calculated from the intensities of methyl groups in their ^{1}H NMR spectrum).



3a : $R^1 = R^2 = Me$, $R^3 = H$ (82%)
3b : $R^1 = R^2 = R^3 = H$ (78%)
3c : $R^1 = Me$, $R^2 = R^3 = H$
3d : $R^1 = R^3 = H$, $R^2 = Me$ (67% : **3c** / **3d** = 2 / 1)
3e : $R^1 = R^2 = R^3 = Me$ (11%)

Scheme 1 *Reagents and conditions:* i, NCS, CH_2Cl_2, 0 °C then room temp. 5 h; ii, diene, $AgClO_4$, CH_3CN, 0 °C then room temp. 30 min



a : $R^1 = R^2 = Me$
b : $R^1 = R^2 = H$

Scheme 2 *Reagents and conditions:* i, reducing reagent, room temp., 1 h–11 d, or electrolysis, MeCN, 1 h

Ring transformation of benzothiazinium salts

First, we reduced benzothiazinium salts **3** with magnesium, Zn–AcOH or $NaBH_4$ (Scheme 2, Table 1). Treatment of **3** with magnesium in tetrahydrofuran (THF) at room temperature gave spiro vinylcyclopropane derivatives **4** in moderate yield although the reactions were very slow (over 10 days) (entries 1 and 4). Use of Zn in AcOH or $NaBH_4$ in EtOH gave the spiro compounds **4** faster and in higher yield (entries 2, 3, 5 and 6). The structure of **4** was established from its ^{1}H NMR, ^{13}C NMR and IR spectra. In the ^{1}H NMR spectrum of **4a** (taken as a representative of vinylcyclopropanes **4**) the pair of doublets at δ 1.25 and 1.90 were assigned to the CH_2 protons of the cyclopropane ring, the small geminal coupling constant (J 6) of which suggested a similar structure. The ^{13}C NMR signal of the methylene carbon of the cyclopropane ring was observed at δ 20.9 and that of the terminal olefinic methylene carbon appeared at δ 114.2. The IR spectrum showed absorptions for

Table 1 Reactions of benzothiazinium salts **3** with reducing reagents

Entry	Sulfonium salt	Reducing agent	Solvent	Time	Product (% yield)
1	**3a**	Mg	THF	10 d	**4a** (58)
2	**3a**	$NaBH_4$	EtOH	1 h	**4a** (90)
3	**3a**	Zn	AcOH	2 h	**4a** (85)
4	**3b**	Mg	THF	11 d	**4b** (56)
5	**3b**	$NaBH_4$	EtOH	2 h	**4b** (88)
6	**3b**	Zn	AcOH	1 h	**4b** (88)

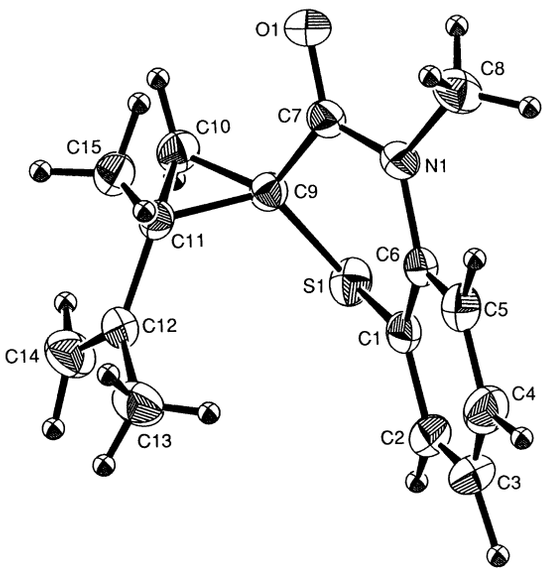
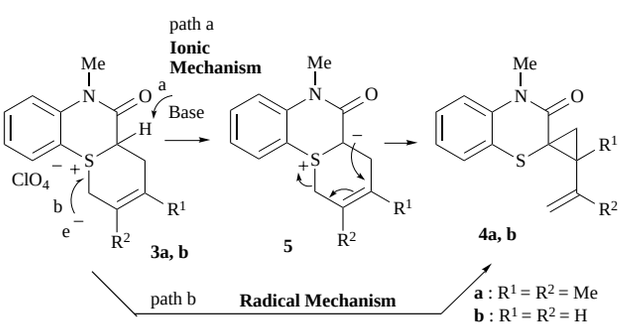


Fig. 1 ORTEP Drawing of spirovinylcyclopropane **4a**

the cyclopropyl CH at 3000 and 3080 cm^{-1}. The relative configuration of vinylcyclopropane **4a** was determined by X-ray crystallographic analysis (Fig. 1). All of the vinylcyclopropanes **4** gave satisfactory elemental analyses.

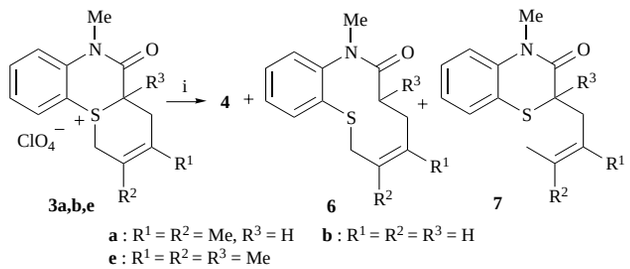
Two pathways, path a and path b, may explain the formation of vinylcyclopropanes **4** (see Scheme 3). The first is by way of



Scheme 3

an ionic mechanism (path a). Thus, abstraction of a bridgehead proton by a reducing reagent, which acts as a base, produces an ylide **5**. This then, by attack of the ylide carbanion on the olefinic carbon, undergoes ionic C–S bond cleavage to give **4**.[4,5] Since we earlier reported that sulfonium salts were reduced by magnesium or Grignard reagents *via* the single electron transfer (SET) process,[8] we subjected **3a** to electrolysis to confirm the radical mechanism. In such a way compound **4a** was obtained (60%) by electrolytic reduction of **3a** at −1.4 V *vs.* saturated calomel electrode (SCE) in acetonitrile for 1 h. This result suggests that the reactions of **3** with magnesium or Zn–AcOH probably proceed *via* path b although it is unclear which radical intermediates would be generated in the reaction system. However, the ionic mechanism may predominate in reactions with $NaBH_4$. We examined the reactions of **3** with a base in order to confirm that the ionic mechanism is also a reasonable pathway. Treatment of **3** with a variety of bases furnished vinylcyclopropanes **4** as summarised in Table 2. These experiments indicated that both radical and ionic mechanisms may be possible for the formation of vinylcyclopropanes.

We recently reported that the SET reduction of sulfonium salts with SmI_2 gave sulfides in high yield.[9] Therefore, we applied this method to the benzothiazinium salts **3** (Scheme 4,



Scheme 4 *Reagents and conditions:* i, SmI_2, THF, −60 °C to room temp., 2–15 h

Table 3). Thus, treatment of **3a** with SmI_2 (3.0 equiv.) in THF at room temperature under a nitrogen atmosphere provided the 2-allylbenzothiazinone derivative **7a** (50%) together with the ten-membered lactam sulfide **6a** (22%) (entry 1). At a lower reaction temperature (−60 °C), the yield of the lactam sulfide **6a** increased (55%) whilst vinylcyclopropane **4a** (4%) and **7a** (10%) were also produced (entry 2). SmI_2 reduction of **3b** at room temperature gave exclusively medium-sized lactam sulfide **6b** (91%) (entry 3). Reactions of 4a-methylbenzothiazinium salt **3e** lacking a 4a-hydrogen were also examined (entry 4). Treatment of **3e** with SmI_2 (3.0 equiv.) in THF at 0 °C under a nitrogen atmosphere provided ten-membered lactam sulfide **6e** (49% isolated yield) although reaction of **3e** with MeLi (1.5 equiv.) in diethyl ether at −20 °C gave a complex mixture.

The structures of **6** and **7** were determined from ^1H and ^{13}C NMR spectroscopic results. In the ^1H NMR spectrum of **6a**, a pair of doublets at δ 3.05 and 3.94 were assigned to the 10-CH_2 protons (J 13). The signals of three methylene carbons were observed at δ 30.7, 32.5 and 39.6 in the ^{13}C NMR spectrum. Compound **6a** gave an elemental analysis consistent with the proposed structure. The ^1H NMR spectrum of **7a** showed that a doublet of doublets at δ 3.57 (J 6.5 and 9.5, 2-methine proton) was coupled with a pair of doublet of doublets at δ 2.34 and 2.50 (J 9.5 and 14, 6.5 and 14, respectively, 1′-methylene protons) but showed no signal due to an olefinic proton. In the ^{13}C NMR spectrum two tetrasubstituted olefinic carbons appeared at δ 121.7 and 122.9, and three methyl carbons were observed at δ 18.2, 20.3 and 20.8.

Formation of **6** and **7** is also understandable in terms of a radical mechanism *via* a sulfuranyl radical **8** (see Scheme 5), generated by SET reduction of a sulfonium salt with SmI_2. Thus, SET reduction of **9** gives a samarium enolate **10** which is converted into lactam sulfide **6** by protonation (path a). By path b, allylic radicals **11** and **12** are formed by homolytic C–S bond cleavage of **8** to furnish 2-allylbenzothiazinone **7** and cyclopropyl derivative **4**, respectively. However, predominant formation of **6** rather than **4** and **7** may be explained by the mechanism shown in Scheme 6. A radical cation **13** is formed by the SET reduction of the carbonyl group which undergoes a further SET reduction with homolytic cleavage of the cross-piece C–S bond, followed by protonation to give lactam sulfide **6**. Both mechanisms would account for the formation of lactam sulfide **6**.

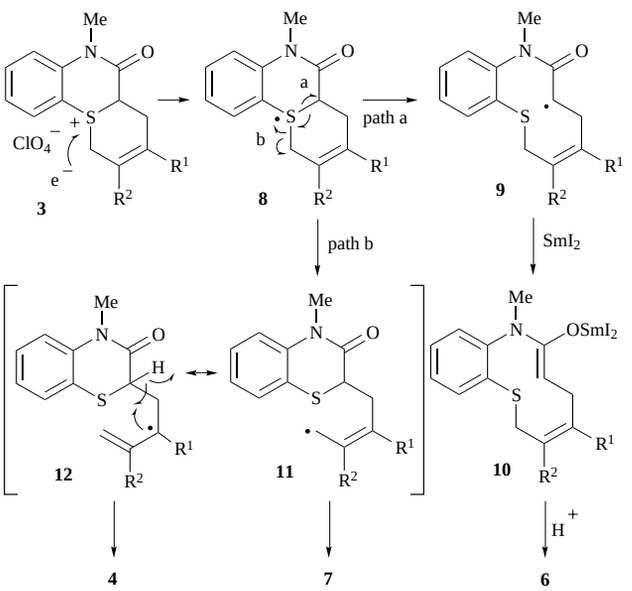
Next, we examined the reactions of benzothiazinium salt **3b** with nucleophiles such as PhSNa, PhSH, PhSeNa and KCl (Scheme 7, Table 4). Treatment of **3b** with PhSNa (prepared from PhSH and NaH) in DMF at 0 °C for 2 h provided vinyl-

Table 2 Reactions of benzothiazinium salts **3** with bases

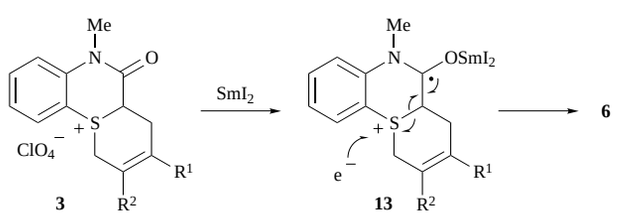
Entry	Sulfonium salt	Base	Solvent	*T*/°C	Time	Product (% yield)
1	**3a**	NaH	DMF	0	0.5 h	**4a** (98)
2	**3a**	$Mg(OH)_2$	THF	Room temp.	Overnight	**4a** (42)
3	**3a**	Et_3N	EtOH	0	1 h	**4a** (57)
4	**3a**	Pr^iNH_2	DMF	Room temp.	1 h	**4a** (94)
5	**3b**	NaH	DMF	0	0.5 h	**4b** (96)
6	**3b**	Et_3N	EtOH	0	1 h	**4b** (55)

Table 3 SmI_2 reduction of benzothiazinium salts **3**

Entry	Sulfonium salt	*t*/h	*T*/°C	Products (% yield) **4**	**6**	**7**
1	**3a**	2	Room temp.	—	22	50
2	**3a**	15	−60	4	55	10
3	**3b**	2	Room temp.	—	91	—
4	**3e**	3	Room temp.	—	49	—

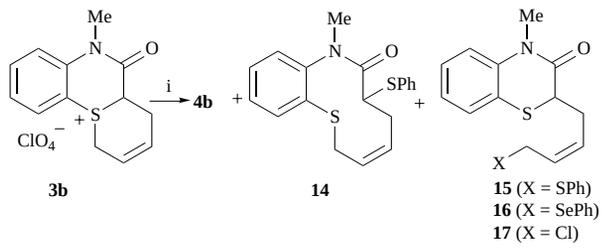


Scheme 5

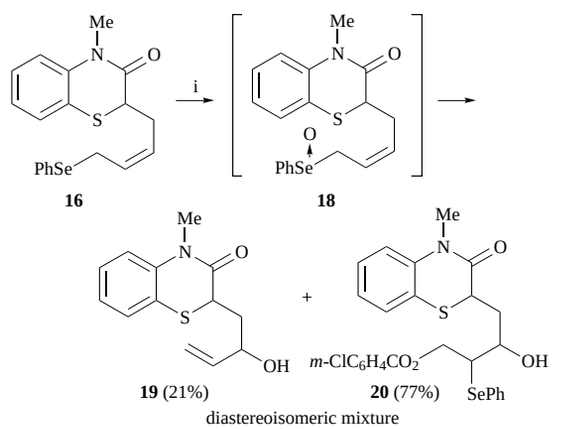


Scheme 6

cyclopropane **4b** (82%) together with ring-enlarged product **14** (1%) and ring-opened product **15** (11%) (entry 1). The ratio of **14** and **15** was reversed by use of PhSH as a nucleophile although yields of the two were much lower (entries 2 and 3). Reaction of **3b** with PhSeNa [prepared from $(PhSe)_2$ and $NaBH_4$] in EtOH at 0 °C afforded **4b** (42%) and **16** (31%) (entry 4). When the reaction was carried out at −20 °C and then warmed to room temperature the yield of **16** increased (94%) and a trace of **4b** was also formed (entry 5). Allyl chloride **17** was exclusively furnished by treatment of **3b** with KCl in acetone at room temperature for 12 h. All of the compounds **14**–**17** have *cis*-*J* values for *vic*-olefinic protons in their ^1H NMR spectra. In order to determine whether compounds **15**–**17** are the ring-opened products, we subjected compound **16** to MCPBA oxidation in CH_2Cl_2 (Scheme 8). A diastereoisomeric mixture



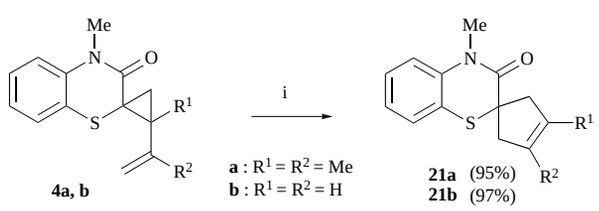
Scheme 7 *Reagents:* i, nucleophile



Scheme 8 *Reagents and conditions:* i, MCPBA, CH_2Cl_2, −20 °C, 12 h

of allyl alcohols **19** was obtained (21%) by [2,3]-sigmatropic rearrangement of the allyl selenoxide **18** together with selenide **20** (77%) as a diastereoisomeric mixture. The result indicates that the compound **16** has an allyl selenide moiety.

We also subjected vinylcyclopropanes **4a** and **4b** to thermal rearrangement.[10] Spirocyclopentene derivatives **21a** (95%) and **21b** (97%) were obtained by heating benzene solutions of **4a** and **4b** respectively at 230 °C in a sealed tube (Scheme 9).



Scheme 9 *Reagents and conditions:* i, sealed tube, benzene, 230 °C, 6 h

Conclusions

Lactam sulfonium salts bearing a dihydrothiopyran skeleton with a sulfonio bridgehead, and benzothiazinium salts, have been synthesised by the reaction of α-chloro sulfides with dienes in the presence of silver perchlorate by $[2^+ + 4]$ polar cycloaddition. Treatment of benzothiazinium salts with Mg, $NaBH_4$, Zn–AcOH or a base furnished benzothiazinone derivatives with a spirovinylcyclopropane ring. SmI_2 reduction of the salts afforded ten-membered lactam sulfides as the major products.

Table 4 Reactions of benzothiazinium salt **3b** with nucleophiles

Entry	Nucleophile	Conditions	Products (% yield)
1	PhSNa	DMF, 0 °C, 2 h	**4b** (82), **14** (1), **15** (11)
2	PhSH	DMF, room temp., 12 h	**14** (9), **15** (2)
3	PhSH	THF, reflux, 12 h	**14** (11), **15** (6)
4	PhSeNa	EtOH, 0 °C, 2 h	**4b** (42), **16** (31)
5	PhSeNa	EtOH, −20 °C to room temp., 5 h	**4b** (2), **16** (94)
6	KCl	Acetone, room temp., 12 h	**17** (100)

Thermal rearrangement of vinylcyclopropanes furnished spirocyclopentene derivatives. Since some benzothiazinones[1,2] possess potent pharmacological activity, all of the new compounds with unusual skeletons synthesised in this paper are of pharmacological interest.

Experimental

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR Spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR Spectra were recorded on a Hitachi R-20B (60 MHz), a JEOL GX-270 (270 MHz) or a JEOL EX-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR Spectra and NOE spectra were run on a JEOL EX-400 spectrometer. *J* Values are given in Hz. Mass spectra were recorded on a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed by a YANACO CHN CORDER MT-5. All chromatographic isolations were achieved either with Kieselgel 60 (70–230 mesh) for column chromatography or Kieselgel 60 PF_{254} containing gypsum for preparative TLC. Ether refers to diethyl ether.

Synthesis of 6-methyl-4,4a,5,6-tetrahydro-5-oxo-1*H*-thiopyrano-[1,2-*a*]-1,4-benzothiazinium perchlorates 3

General procedure. To a stirred solution of benzothiazinone **1** (5 mmol) in dry CH_2Cl_2 (25 cm^3) was added NCS (5 mmol) at 0 °C. After 5 h at room temperature, the mixture was evaporated and benzene was added to the residue. The precipitated succinimide was filtered off and rinsed with benzene. The filtrate was concentrated under reduced pressure to give the crude α-chloro sulfide **2**. A solution of the crude product **2** and a diene (10 mmol) in dry CH_3CN (25 cm^3) was treated with $AgClO_4$ (5 mmol) at 0 °C, and then stirred for 30 min at room temperature. The precipitate of AgCl was filtered off and washed with CH_3CN. The filtrate was evaporated and the resultant benzothiazinium salt **3** was purified by recrystallisation.

2,3,6-Trimethyl-4,4a,5,6-tetrahydro-5-oxo-1*H*-thiopyrano-[1,2-*a*]-1,4-benzothiazinium perchlorate 3a. Yield 82%, colourless prisms (CH_3CN–ether), mp 164–165 °C (Found: C, 49.9; H, 5.1; N, 4.0. $C_{15}H_{18}ClNO_5S$ requires C, 50.07; H, 5.04; N, 3.89%); ν_{max}(KBr)/cm^{-1} 1675 (C=O) and 1080 (ClO_4^-); δ_H(CD_3CN) 1.77 (3 H, s, Me), 1.80 (3 H, s, Me), 2.82 (1 H, br d, *J* 16, 4-H), 3.29 (1 H, br d, *J* 16, 4-H), 3.48 (3 H, s, NMe), 3.95 (1 H, d, *J* 15.6, 1-H), 4.12 (1 H, d, *J* 15.6, 1-H), 4.70 (1 H, dd, *J* 2 and 5, 4a-H), 7.41 (1 H, t, *J* 8, ArH), 7.49 (1 H, d, *J* 8, ArH), 7.87 (1 H, t, *J* 8, ArH) and 7.90 (1 H, d, *J* 8, ArH); δ_C(CD_3CN) 19.0 (q), 19.1 (q), 29.0 (t), 32.5 (q), 36.9 (t), 41.7 (d), 104.4 (s), 116.8 (s), 119.7 (d), 125.0 (d), 129.0 (s), 133.4 (d), 136.6 (d), 141.8 (s) and 160.2 (s).

6-Methyl-4,4a,5,6-tetrahydro-5-oxo-1*H*-thiopyrano[1,2-*a*]-1,4-benzothiazinium perchlorate 3b. Yield 78%, colourless prisms (CH_3CN–ether), mp 168–169 °C (Found: C, 46.8; H, 4.2; N, 4.2. $C_{13}H_{14}ClNO_5S$ requires C, 47.06; H, 4.25; N, 4.22%); ν_{max}(KBr)/cm^{-1} 1670 (C=O) and 1070 (ClO_4^-); δ_H(CD_3CN) 2.79 –2.92 (1 H, m, 4-H), 3.41 (1 H, ddd, *J* 2, 5 and 7, 4-H), 3.48 (3 H, s, NMe), 4.05–4.23 (2 H, m, 1-H), 4.75 (1 H, br d, *J* 5, 4a-H), 5.84 (1 H, ddd, *J* 2, 6 and 11, 3-H), 6.12 (1 H, ddd, *J* 2, 4 and 11, 2-H), 7.42 (1 H, t, *J* 8, ArH), 7.59 (1 H, d, *J* 8, ArH), 7.88 (1 H, t, *J* 8, ArH) and 7.92 (1 H, d, *J* 8, ArH); δ_C(CD_3CN) 24.5 (t), 33.6 (q), 34.6 (t), 42.9 (d), 105.3 (s), 116.8 (d), 120.8 (d), 126.0 (d), 130.0 (d), 134.4 (d), 137.7 (d), 142.9 (s) and 161.1 (s).

3,6-Dimethyl-4,4a,5,6-tetrahydro-5-oxo-1*H*-thiopyrano[1,2-*a*]-1,4-benzothiazinium perchlorate 3c and 2,6-dimethyl-4,4a,5,6-tetrahydro-5-oxo-1*H*-thiopyrano[1,2-*a*]-1,4-benzothiazinium perchlorate 3d. Yield 67% as a mixture of **3c** and **3d**, colourless prisms (CH_3CN–ether) (Found: C, 48.4; H, 4.7; N, 4.0. $C_{14}H_{16}ClNO_5S$ requires C, 48.63; H, 4.66; N, 4.05%); ν_{max}(KBr)/cm^{-1} 1670 (C=O) and 1080 (ClO_4^-); **3c** δ_H(CD_3CN) 1.88 (3 H, s, Me), 2.83 (1 H, dd, *J* 5 and 19, 4-H), 3.31 (1 H, dd, *J* 2 and 19, 4-H), 3.50 (3 H, s, NMe), 4.13 (1 H, br d, *J* 16, 1-H), 4.17 (1 H, dd, *J* 6 and 16, 1-H), 4.75 (1 H, dd, *J* 2 and 5, 4a-H), 5.58 (1 H, br d, *J* 6, 2-H), 7.38–7.50 (2 H, m, ArH) and 7.84–7.94 (2 H, m, ArH); δ_C(CD_3CN) 23.7 (q), 28.1 (t), 32.9 (q), 34.0 (t), 42.6 (d), 104.7 (s), 110.5 (d), 120.2 (d), 125.4 (d), 134.0 (d), 137.0 (d), 138.3 (s), 142.2 (s) and 160.6 (s); **3d** δ_H(CD_3CN) 1.84 (3 H, s, Me), 2.72–2.92 (1 H, m, 4-H), 3.25–3.35 (1 H, m, 4-H), 3.50 (3 H, s, NMe), 3.99 and 4.10 (each 1 H, br d, *J* 16, 1-H), 4.79 (1 H, dd, *J* 2 and 5, 4a-H), 5.82 (1 H, br s, 3-H), 7.38–7.50 (2 H, m, ArH) and 7.84–7.94 (2 H, m, ArH); δ_C(CD_3CN) 23.4 (q), 23.8 (t), 32.9 (q), 36.6 (t), 41.4 (d), 104.7 (s), 110.5 (d), 122.9 (d), 124.7 (s), 125.4 (d), 133.7 (d), 137.1 (d), 142.2 (s) and 160.5 (s).

2,3,4a,6-Tetramethyl-4,4a,5,6-tetrahydro-5-oxo-1*H*-thiopyrano[1,2-*a*]-1,4-benzothiazinium perchlorate 3e. This compound was synthesised from 2,4-dimethyl-2*H*-1,4-benzothiazin-3(4*H*)-one. Yield 11%, colourless prisms (acetone–ether), mp 179–180 °C (Found: C, 51.15; H, 5.4; N, 3.8. $C_{16}H_{20}ClNO_5S$ requires C, 51.40; H, 5.39; N, 3.74%); ν_{max}(KBr)/cm^{-1} 1690 (C=O) and 1070 (ClO_4^-); δ_H(CD_3CN) 1.57 (3 H, s, Me), 1.76 (3 H, s, Me), 1.78 (3 H, s, Me), 2.67 (1 H, d, *J* 18.6, 4-H), 3.38 (1 H, d, *J* 18.6, 4-H), 3.48 (3 H, s, NMe), 4.11 (2 H, br s, 1-H), 7.45 (1 H, t, *J* 8, ArH), 7.51 (1 H, d, *J* 8, ArH), 7.90 (1 H, t, *J* 8, ArH) and 7.94 (1 H, d, *J* 8, ArH); δ_C(CD_3CN) 19.4 (q), 19.9 (q), 21.4 (q), 33.7 (q), 38.6 (t), 40.5 (t), 50.6 (s), 103.7 (s), 117.6 (s), 120.8 (d), 126.4 (d), 130.1 (d), 135.2 (d), 137.8 (s), 142.0 (s) and 163.8 (s); *m*/*z* 289 (M^+, 83%) and 241 (100).

Reduction of benzothiazinium salts 3 with magnesium

General procedure. A mixture of benzothiazinium salt (1 mmol) and magnesium (73 mg, 3 mmol) in dry THF (20 cm^3) was stirred at room temperature for several days. Saturated aqueous NH_4Cl was added to the reaction mixture which was then stirred until the excess of magnesium had dissolved. The organic layer was separated and the water layer was extracted with ether. The organic layer and the extracts were combined, washed successively with water and saturated brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1 : 10). Reaction conditions and the results are summarised in Table 1.

2′-Isopropenyl-2′,4-dimethyl-2*H*-benzothiazine-2-spirocyclopropan-3(4*H*)-one 4a. Colourless prisms (CH_2Cl_2), mp 87–89 °C (Found: C, 69.7; H, 6.7; N, 5.4. $C_{15}H_{17}NOS$ requires C, 69.46; H, 6.61; N, 5.37%); ν_{max}(KBr)/cm^{-1} 3080 and 3000 (cyclopropane) and 1660 (C=O); δ_H($CDCl_3$) 1.14 (3 H, s, Me), 1.27 (3 H, s, Me), 1.25 (1 H, d, *J* 6, 3′-H), 1.90 (1 H, d, *J* 6, 3′-H), 3.49 (3 H, s, NMe), 4.71 (1 H, br s, olefinic H), 4.94 (1 H,

br s, olefinic H), 6.98 (1 H, t, *J* 8, ArH), 7.06 (1 H, d, *J* 8 ArH) and 7.20–7.27 (2 H, m, ArH); $\delta_C(CDCl_3)$ 18.1 (q), 20.8 (q), 20.9 (t), 32.4 (s), 33.0 (q), 38.6 (s), 114.2 (t), 117.3 (d), 123.0 (d), 125.0 (s), 126.8 (d), 127.8 (d), 139.6 (s), 144.1 (s) and 167.0 (s); *m*/*z* 259 (M^+, 18%) and 121 (100).

4-Methyl-2′-vinyl-2*H*-benzothiazine-2-spirocyclopropane-3(4*H*)-one 4b. Colourless prisms (CH_2Cl_2), mp 81–82 °C (Found: C, 73.35; H, 6.1; N, 6.6. $C_{13}H_{13}NOS$ requires C, 73.20; H, 6.14; N, 6.57%); ν_{max}(KBr)/cm^{-1} 3090 and 3000 (cyclopropane) and 1660 (C=O); $\delta_H(CDCl_3)$ 1.04 (1 H, dd, *J* 5.5 and 7, 3′-H), 1.98 (1 H, dd, *J* 5.5 and 9, 3′-H), 2.22 (1 H, ddd, *J* 7, 8.5 and 9, 2′-H), 3.41 (3 H, s, NMe), 5.11 (1 H, dd, *J* 1.5 and 10, CH=CH_2), 5.15 (1 H, dd, *J* 1.5 and 17, CH=CH_2), 5.56 (1 H, ddd, *J* 8.5, 10 and 17, 4′-H), 6.98–7.03 (2 H, m, ArH) and 7.21–7.29 (2 H, m, ArH); $\delta_C(CDCl_3)$ 19.5 (t), 29.4 (s), 29.8 (d), 32.7 (q), 116.8 (d), 118.1 (t), 122.3 (s), 123.3 (d), 127.2 (d), 128.1 (d), 133.8 (d), 139.9 (s) and 169.3 (s); *m*/*z* 231 (M^+, 20%) and 121 (100).

Reactions of benzothiazinium salts 3 with sodium borohydride

General procedure. To a suspension of benzothiazinium salt **3** (1 mmol) in EtOH (5 cm^3) was added $NaBH_4$ (1.0–1.1 mmol) at 0 °C. After the reaction mixture had been stirred at room temperature for several hours, it was diluted with water and extracted with CH_2Cl_2. The extracts were washed successively with water and saturated brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:10). Reaction conditions and the results are summarised in Table 1.

Reduction of benzothiazinium salts 3 with zinc in acetic acid

General procedure. To a solution of benzothiazinium salt **3** (1 mmol) in acetic acid was added activated Zn (washed successively with alcohol and ether, and dried under reduced pressure). After several hours, the inorganic materials were filtered off and ether was added to the filtrate. This was then washed successively with 5% aqueous NaOH and water. The alkaline and aqueous layers were combined and back-extracted with ether. The organic layer and extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:10). Reaction conditions and the results are summarised in Table 1.

Electrolysis of 3a

Electrolysis was performed under potentiostatic conditions with a three-electrode system consisting of a carbon working electrode, a saturated calomel reference electrode (SCE) and a Pt counter electrode. Benzothiazinium salt **3a** was dissolved in acetonitrile containing tetraethylammonium perchlorate (0.15 mol dm^{-3}) as a supporting electrolyte. The reduction was carried out at −1.4 V *vs*. SCE for 1 h after which the reaction mixture was diluted with water and extracted with CH_2Cl_2. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **4a** (60%).

Reactions of benzothiazinium salts 3 with sodium hydride

General procedure. To a stirred suspension of NaH (60% in paraffin oil; 1.1 mmol) in dry DMF (2 cm^3) was added benzothiazinium salt **3** (1 mmol) at 0 °C. After 30 min at room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5). Reaction conditions and the results are summarised in Table 2.

Reactions of benzothiazinium salts 3 with triethylamine

General procedure. To a stirred suspension of benzothiazinium salt **3** (0.5 mmol) in EtOH (5 cm^3) was added triethylamine (5 cm^3) at room temperature. After 1 h, 3 M hydrochloric acid was added to the reaction mixture which was then extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:10). Reaction conditions and the results are summarised in Table 2.

Reaction of benzothiazinium salt 3a with magnesium hydroxide

A suspension of **3a** (180 mg, 0.5 mmol) and $Mg(OH)_2$ (1 mmol) in dry THF (2 cm^3) was stirred at room temperature overnight after which it was diluted with water and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **4a** (55 mg, 42%).

Reaction of benzothiazinium salt 3a with isopropylamine

To a stirred solution of **3a** (180 mg, 0.5 mmol) in dry DMF was added isopropylamine (0.55 mmol) at room temperature. After 1 h the reaction mixture was diluted with water and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **4a** (122 mg, 94%).

Reduction of benzothiazinium salts 3 with samarium diiodide

General procedure. To a suspension of benzothiazinium salt **3** (1 mmol) in THF (5 cm^3) containing MeOH (0.6 cm^3) was added 0.1 M SmI_2 solution in THF[11] (30 cm^3, 3 mmol) at 0 °C under a nitrogen atmosphere. After 2 h at room temperature the reaction mixture was treated with conc. hydrochloric acid and extracted with ether. The extracts were washed successively with saturated aqueous $NaHCO_3$, 10% aqueous $Na_2S_2O_3$ and water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:10). Reaction conditions and the results are summarised in Table 3.

3,4,8-Trimethyl-5,6,7,8-tetrahydro-2*H*-benzo[*b*][1,4]-thiazecin-7-one 6a. Colourless prisms (CH_2Cl_2), mp 82 °C (Found: C, 68.8; H, 7.3; N, 5.4. $C_{15}H_{19}NOS$ requires C, 68.93; H, 7.33; N, 5.36%); ν_{max}(KBr)/cm^{-1} 1680 (C=O); $\delta_H(CDCl_3)$ 1.39 (3 H, s, Me), 1.64 (3 H, s, Me), 1.96 (1 H, ddd, *J* 3, 7 and 14, 5-H), 2.27 (1 H, ddd, *J* 3, 8 and 14, 6-H), 2.31 (1 H, ddd, *J* 3, 7 and 14, 6-H), 2.47 (1 H, ddd, *J* 3, 8 and 14, 5-H), 3.03 (1 H, d, *J* 13, 2-H), 3.31 (3 H, s, NMe), 3.94 (1 H, d, *J* 13, 2-H), 7.17 (1 H, dd, *J* 1.5 and 7, ArH), 7.25 (1 H, dt, *J* 1.5 and 7, ArH), 7.36 (1 H, dt, *J* 1.5 and 7, ArH) and 7.59 (1 H, dd, *J* 1.5 and 7, ArH); $\delta_C(CDCl_3)$ 17.9 (q), 19.6 (q), 30.7 (t), 32.5 (t), 36.3 (q), 39.6 (t), 125.6 (s), 128.3 (d), 129.1 (d), 130.0 (d), 132.8 (s), 133.3 (s), 138.3 (d), 147.9 (s) and 174.7 (s); *m*/*z* 261 (M^+, 30%) and 166 (100).

2-(2,3-Dimethylbut-2-enyl)-4-methyl-2*H*-1,4-benzothiazin-3-one 7a. Yellow oil (Found: C, 69.0; H, 7.3; N, 5.4. $C_{15}H_{19}NOS$ requires C, 68.93; H, 7.33; N, 5.36%); ν_{max}(NaCl)/cm^{-1} 1680 (C=O); $\delta_H(CDCl_3)$ 1.47 (3 H, s, Me), 1.65 (6 H, s, Me × 2), 2.34 (1 H, dd, *J* 9.5 and 14, 1′-H), 2.50 (1 H, dd, *J* 6.5 and 14, 1′-H), 3.44 (3 H, s, NMe), 3.57 (1 H, dd, *J* 6.5 and 9.5, 2-H), 6.99–7.07 (2 H, m, ArH) and 7.22–7.36 (2 H, m, ArH); $\delta_C(CDCl_3)$ 18.2 (q), 20.3 (q), 20.8 (q), 32.2 (q), 34.3 (t), 42.4 (d), 117.0 (d), 121.7 (s), 122.9 (s), 123.3 (d), 127.0 (d), 128.6 (s), 129.0 (d), 140.0 (s) and 167.3 (s); *m*/*z* 261 (M^+, 24%) and 179 (100).

8-Methyl-5,6,7,8-tetrahydro-2*H*-benzo[*b*][1,4]thiazecin-7-one 6b. Colourless prisms (CH_2Cl_2), mp 79–80 °C (Found: C, 66.7; H, 6.4; N, 6.0. $C_{13}H_{15}NOS$ requires C, 66.92; H, 6.48; N, 6.01%); ν_{max}(KBr)/cm^{-1} 1690 (C=O); $\delta_H(CDCl_3)$ 2.02–2.11 (1 H, m, 5-H), 2.21–2.41 [3 H, m, 6-H (2 H) and 5-H (1 H)], 3.10 (1 H, dd, *J* 5 and 13, 2-H), 3.32 (3 H, s, NMe), 3.77 (1 H, dd, *J* 10.5 and 13, 2-H), 5.41–5.51 (2 H, m, 4-H and 3-H), 7.18 (1 H, dd, *J* 1.5 and 7, ArH), 7.28 (1 H, dt, *J* 1.5 and 7, ArH), 7.36 (1 H,

dt, *J* 1.5 and 7, ArH) and 7.60 (1 H, dd, *J* 1.5 and 7, ArH); $\delta_C(CDCl_3)$ 23.1 (t), 31.9 (t), 36.2 (q), 53.6 (t), 128.2 (d), 128.5 (d), 129.1 (d), 129.8 (d), 131.1 (d), 132.6 (s), 137.7 (d), 146.8 (s) and 174.9 (s); *m*/*z* 233 (M^+, 23%) and 139 (100).

3,4,6,8-Tetramethyl-5,6,7,8-tetrahydro-2*H*-benzo[*b*][1,4]-thiazecin-7-one 6e. White powder, mp 93–96 °C (Found: 275.1362. $C_{16}H_{21}NOS$ requires 275.1344); ν_{max}(KBr)/cm^{-1} 1650 (C=O); $\delta_H(CDCl_3)$ 1.18 (3 H, d, *J* 6.8, 6-Me), 1.35 (3 H, s, Me), 1.50 (1 H, d, *J* 14.2, 5-H), 1.62 (3 H, s, Me), 2.38 (1 H, quintet, *J* 6.8, 6-H), 2.76 (1 H, dd, *J* 6.8 and 14.2, 5-H), 2.87 (1 H, d, *J* 12.7, 2-H), 3.33 (3 H, s, NMe), 4.11 (1 H, d, *J* 12.7, 2-H), 7.08 (1 H, d, *J* 7, ArH), 7.22 (1 H, t, *J* 7, ArH), 7.34 (1 H, t, *J* 7, ArH) and 7.54 (1 H, d, *J* 7, ArH); $\delta_C(CDCl_3)$ 17.4 (q), 20.2 (q), 20.9 (q), 35.7 (q), 36.0 (d), 38.7 (t), 40.2 (t), 124.1 (s), 128.0 (d), 129.1 (d), 129.7 (d), 131.8 (s), 133.5 (s), 137.9 (d), 147.6 (s) and 178.1 (s); *m*/*z* 275 (M^+, 14%) and 166 (100).

Reaction of benzothiazinium salt 3b with PhSNa

To a stirred solution of PhSNa [0.5 mmol; prepared from PhSH (55 mg) and NaH in paraffin oil (60%; 20 mg)] in DMF (1.5 cm^3) was added **3b** (166 mg, 0.5 mmol) at 0 °C. After 2 h, the reaction mixture was diluted with water (5 cm^3) and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **4b** (96 mg, 82%), (*Z*)-8-methyl-6-phenylthio-5,6,7,8-tetrahydro-2*H*-benzo[*b*][1,4]thiazecin-7-one **14** (2 mg, 1%) and (*Z*)-4-methyl-2-(4-phenylthiobut-2-enyl)-2*H*-benzothiazin-3(4*H*)-one **15** (18 mg, 11%).

Compound 14. Yellow oil (Found: 341.0890. $C_{19}H_{19}NOS_2$ requires 341.0908); ν_{max}(NaCl)/cm^{-1} 1665 (C=O); $\delta_H(CDCl_3)$ 2.25 (1 H, ddd, *J* 5, 9 and 15, 5-H), 2.52–2.58 (1 H, m, 5-H), 3.28 (1 H, dd, *J* 6 and 9, 6-H), 3.42 (3 H, s, NMe), 3.43 and 3.50 (each 1 H, dd, *J* 5 and 12, 2-H), 5.52 (1 H, dt, J_{cis} 10 and *J* 5, 3-H), 5.51–5.56 (1 H, m, 4-H), 7.00–7.07 (2 H, m, ArH), 7.13 (1 H, t, *J* 8, ArH), 7.20–7.27 (3 H, m, ArH) and 7.30–7.35 (3 H, m, ArH); $\delta_C(CDCl_3)$ 31.9 (t), 32.4 (q), 36.2 (t), 43.1 (d), 117.2 (d), 121.7 (s), 123.4 (d), 126.2 (d), 127.1 (d), 128.7 (d), 128.8 (d), 129.0 (d), 130.1 (d), 135.8 (s), 139.7 (s) and 137.0 (s); *m*/*z* 341 (M^+, 2%) and 232 (100).

Compound 15. Yellow oil (Found: 341.0932. $C_{19}H_{19}NOS_2$ requires 341.0908) ν_{max}(NaCl)/cm^{-1} 1660 (C=O); $\delta_H(CDCl_3)$ 2.22 (1 H, ddd, *J* 7.3, 8.8 and 15, 1′-H), 2.51 (1 H, ddd, *J* 6.3, 7.3 and 15, 1′-H), 3.22 (1 H, dd, *J* 6.3 and 8.8, 2-H), 3.42 (2 H, d, *J* 7.8, 4′-H), 3.43 (3 H, s, NMe), 5.55 (1 H, dt, J_{cis} 10 and 7.3, 2′-H), 5.67 (1 H, dt, J_{cis} 10 and 7.8, 3′-H), 7.01–7.07 (2 H, m, ArH), 7.13 (1 H, t, *J* 7, ArH) and 7.20–7.36 (6 H, m, ArH); $\delta_C(CDCl_3)$ 26.9 (t), 31.5 (t), 32.4 (q), 43.1 (d), 117.3 (d), 121.6 (s) 123.5 (d), 126.5 (d), 127.2 (d), 128.0 (d), 128.8 (d), 128.9 (d), 130.6 (d), 135.7 (s), 139.7 (s) and 166.9 (s); *m*/*z* 341 (M^+, 2%), 232 (M^+ − SPh, 100) and 109 (SPh, 52).

Reaction of benzothiazinium salt 3b with PhSH

Method A. To a stirred solution of PhSH (110 mg, 1 mmol) in DMF (1.5 cm^3) was added **3b** (166 mg, 0.5 mmol) at room temperature. After 12 h, the reaction mixture was diluted with water (5 cm^3) and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **14** (15 mg, 9%) and **15** (4 mg, 2%).

Method B. To a stirred solution of PhSH (110 mg, 1 mmol) in THF (2 cm^3) was added **3b** (166 mg, 0.5 mmol) at room temperature under a nitrogen atmosphere. The mixture was refluxed for 12 h after which it was cooled, diluted with water (5 cm^3) and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **14** (19 mg, 11%) and **15** (10 mg, 6%).

Reaction of benzothiazinium salt 3b with PhSeNa

Method A. To a stirred solution of PhSeNa [prepared from $(PhSe)_2$ (312 mg, 1 mmol) and $NaBH_4$ (10 mg, 0.26 mmol)] in EtOH (5 cm^3) was added **3b** (166 mg, 0.5 mmol) at 0 °C. After 2 h, the reaction mixture was diluted with water (10 cm^3) and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **4b** (48 mg, 42%) and (*Z*)-4-methyl-2-(4-phenylselenobut-2-enyl)-2*H*-benzothiazin-3(4*H*)-one **16** (61 mg, 31%).

Compound 16. Yellow oil (Found: C, 58.8; H, 5.0; N, 3.6. $C_{19}H_{19}NOSSe$ requires C, 58.76; H, 4.93; N, 3.61%); ν_{max}(NaCl)/cm^{-1} 1670 (C=O); $\delta_H(CDCl_3)$ 2.12 (1 H, ddd, *J* 7.3, 8.8 and 15, 1′-H), 2.40 (1 H, ddd, *J* 6.4, 7.3 and 15, 1′-H), 3.13 (1 H, dd, *J* 6.4 and 8.8, 2-H), 3.40 (2 H, d, *J* 7.3, 4′-H), 3.42 (3 H, s, NMe), 5.46 (1 H, dt, J_{cis} 11 and 7.3, olefinic H), 5.74 (1 H, dt, J_{cis} 11 and 7.3, olefinic H), 7.00–7.05 (2 H, m, ArH), 7.16–7.20 (3 H, m, ArH), 7.25 (1 H, t, *J* 7, ArH), 7.32 (1 H, d, *J* 6, ArH) and 7.41–7.44 (2 H, m, ArH); $\delta_C(CDCl_3)$ 24.6 (t), 26.5 (t), 32.3 (q), 42.9 (d), 117.2 (d), 121.6 (s), 123.4 (d), 127.1 (d), 127.3 (d), 128.5 (d), 128.7 (d), 128.8 (d), 129.6 (s), 134.0 (d), 139.7 (s) and 166.8 (s); *m*/*z* 389 (M^+), 232 (M^+ − SePh, 100%) and 157 (SePh, 5).

Method B. To a stirred solution of PhSeNa [prepared from $(PhSe)_2$ (312 mg, 1 mmol) and $NaBH_4$ (10 mg, 0.26 mmol)] in EtOH (5 cm^3) was added **3b** (166 mg, 0.5 mmol) at −20 °C. After 5 h at −20 °C, warming to room temperature, the reaction mixture was diluted with water (10 cm^3) and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:5) to give **4b** (2 mg, 2%) and **16** (183 mg, 94%).

Reaction of benzothiazinium salt 3b and KCl

To a stirred suspension of KCl (8 mg, 0.1 mmol) in acetone (3 cm^3) was added **3b** (33 mg, 0.1 mmol) at room temperature. After 12 h, the reaction mixture was diluted with water (10 cm^3) and extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:10) to give (*Z*)-2-(4-chloro-but-2-enyl)-4-methyl-2*H*-benzothiazin-3(4*H*)-one **17** (27 mg, 100%) as a colourless oil (Found: C, 58.8; H, 5.0; N, 3.6. $C_{13}H_{14}ClNOS$ requires C, 58.76; H, 4.93; N, 3.61%); ν_{max}(NaCl)/cm^{-1} 1660 (C=O); $\delta_H(CDCl_3)$ 2.42 (1 H, ddd, *J* 7, 8 and 15, 1′-H), 2.68 (1 H, dt, *J* 15 and 7, 1′-H), 3.45 (1 H, dd, *J* 7 and 8, 2-H), 3.45 (3 H, s, NMe), 3.94 (2 H, d, *J* 7, 4′-H), 5.66 and 5.79 (each 1 H, dt, J_{cis} 11 and 7, olefinic H), 7.02–7.10 (2 H, m, ArH) and 7.25–7.37 (2 H, m, ArH); $\delta_C(CDCl_3)$ 27.0 (t), 32.4 (q), 38.9 (t), 42.7 (d), 117.3 (d), 121.2 (s), 123.5 (d), 127.3 (d), 128.4 (d), 128.8 (d), 129.5 (d), 139.6 (s) and 166.6 (s); *m*/*z* 267 (M^+, 17%), 232 (M^+ − Cl, 98) and 150 (100).

MCPBA oxidation of allyl selenide 16

To a stirred solution of allyl selenide **16** (183 mg, 0.47 mmol) in CH_2Cl_2 (5 cm^3) with ice–NaCl cooling was added MCPBA (85% purity; 95 mg, 0.47 mmol) in several portions. After 12 h, saturated aqueous $NaHCO_3$ was added to the reaction mixture and the organic layer was separated, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:2) to give as the third fraction 2-(2-hydroxybut-3-enyl)-4-methyl-2*H*-benzothiazin-3(4*H*)-one **19** (25 mg, 21%), a light yellow oil as a mixture of diastereoisomers (Found: 249.0812. $C_{13}H_{15}NO_2S$ requires 249.0824); ν_{max}(NaCl)/cm^{-1} 3420 (OH) and 1655 (C=O); $\delta_H(CDCl_3)$ of major isomer 1.85 (1 H, ddd, *J* 5.9, 8 and 14, 1′-H), 2.13 (1 H, ddd, *J* 5, 8.8 and 14, 1′-H), 2.92 (1 H, br s, OH), 3.46 (3 H, s, NMe), 3.61 (1 H, dd, *J* 5.9 and 8.8, 2-H), 4.33 (1 H, br s, 2′-H), 5.12 (1 H, d, J_{cis} 10, 4′-H), 5.29 (1 H, d, J_{trans}

17, 4′-H), 5.81 (1 H, ddd, *J* 6, 10 and 17, 3′-H), 7.02–7.09 (2 H, m, ArH), 7.27 (1 H, t, *J* 8, ArH) and 7.36 (1 H, d, *J* 8, ArH); of minor isomer 1.70–1.80 (1 H, m, 1′-H), 2.06–2.15 (1 H, m, 1′-H), 2.67 (1 H, br s, OH), 3.44 (3 H, s, NMe), 3.67 (1 H, dd, *J* 7 and 8, 2-H), 4.32 (1 H, br s, 2′-H), 5.09 (1 H, d, J_{cis} 9, 4′-H), 5.25 (1 H, d, J_{trans} 17, 4′-H), 5.76–5.84 (1 H, m, 3′-H), 6.97–7.08 (2 H, m, ArH), 7.25 (1 H, t, *J* 7, ArH) and 7.52 (1 H, d, *J* 7, ArH); $\delta_C(CDCl_3)$ of major isomer 32.6 (q), 36.7 (t), 39.4 (d), 70.3 (d), 115.6 (t), 117.4 (d), 122.2 (s), 123.6 (d), 127.2 (d), 128.6 (d), 139.5 (s) and 168.0 (s); of minor isomer 32.6 (q), 36.4 (t), 40.3 (d), 70.0 (d), 114.9 (t), 117.4 (d), 123.4 (d), 123.5 (d), 127.2 (d), 128.6 (d), 140.2 (s) and 168.2 (s); *m*/*z* 249 (M^+, 100%). [3-(3-Chlorobenzoyloxy)-2-hydroxy-4-phenylselenobutyl]-4-methyl-2*H*-benzothiazin-3(4*H*)-one **20** was isolated as a mixture of diastereoisomers composing the first (129 mg, 49%) and the second (74 mg, 28%) fractions, respectively; the first fraction was a yellow oil (Found: 561.0266. $C_{26}H_{24}ClNO_4SSe$ requires 561.0280); ν_{max}(NaCl)/cm^{-1} 3450 (OH), 1730 (C=O) and 1665 (C=O); $\delta_H(CDCl_3)$ 2.11–2.16 (1 H, m, 1′-H), 2.18 (1 H, br s, OH), 2.32–2.39 (1 H, m, 1′-H), 3.39 (3 H, s, NMe), 3.61 (1 H, br m, 3′-H), 3.71 (1 H, dd, *J* 5 and 9, 2-H), 4.15 (1 H, br m, 2′-H), 4.60 (1 H, dd, *J* 5 and 11, 4′-H), 4.70 (1 H, d, *J* 9 and 11, 4′-H), 7.01–7.03 (2 H, m, ArH), 7.23 (4 H, br m, ArH), 7.30–7.36 (2 H, m, ArH), 7.50 (1 H, d, *J* 7, ArH), 7.52–7.57 (2 H, m, ArH), 7.82 (1 H, d, *J* 8, ArH), and 7.91 (1 H, s, ArH); $\delta_C(CDCl_3)$ 32.4 (q), 36.1 (t), 40.0 (d), 51.1 (d), 65.6 (t), 68.2 (d), 117.3 (d), 121.9 (s), 123.6 (d), 127.2 (d), 127.7 (d), 128.4 (s), 128.6 (d), 129.2 (d), 129.5 (d), 129.6 (d), 131.5 (s), 133.0 (d), 134.2 (d), 134.4 (s), 139.3 (s), 165.0 (s) and 167.5 (s); *m*/*z* 561 (M^+, 3%) and 139 (100); the second fraction was also a yellow oil (Found: 561.0273. $C_{26}H_{24}ClNO_4SSe$ requires 561.0279); ν_{max}(NaCl)/cm^{-1} 3430 (OH), 1720 (C=O) and 1660 (C=O); $\delta_H(CDCl_3)$ 1.85 (1 H, ddd, *J* 7, 8 and 12, 1′-H), 1.94 (1 H, br s, OH), 2.57 (1 H, ddd, *J* 7, 10 and 12, 1′-H), 3.44 (3 H, s, NMe), 3.67 (1 H, t, *J* 7, 2-H), 3.79 (1 H, br m, 3′-H), 4.21 (1 H, br m, 2′-H), 4.61 (1 H, dd, *J* 5 and 12, 4′-H), 4.71 (1 H, dd, *J* 9 and 12, 4′-H), 6.98 (1 H, t, *J* 7, ArH), 7.06 (1 H, d, *J* 8, ArH), 7.23–7.28 (5 H, m, ArH), 7.36 (1 H, t, *J* 8, ArH), 7.52 (1 H, d, *J* 8, ArH), 7.57–7.59 (2 H, m, ArH), 7.85 (1 H, d, *J* 7, ArH) and 7.93 (1 H, s, ArH); $\delta_C(CDCl_3)$ 32.9 (q), 35.5 (t), 41.2 (d), 51.9 (d), 65.9 (t), 68.5 (d), 117.7 (d), 122.1 (s), 123.9 (d), 127.6 (d), 128.1 (d), 128.7 (s), 128.8 (d), 129.5 (d), 129.9 (d), 130.0 (d), 131.8 (s), 133.4 (d), 134.6 (d), 134.8 (s), 139.8 (s), 165.4 (s) and 168.5 (s); *m*/*z* 561 (M^+, 6%) and 139 (100).

Thermal rearrangement of vinylcyclopropane derivatives 4

General procedure. A solution of vinylcyclopropane **4** (0.5 mmol) in benzene (5 cm^3) was heated at 230 °C in a sealed tube for 6 h. After cooling, the reaction mixture was evaporated and the residue was purified by preparative TLC eluting with ethyl acetate–hexane (1:10) to give 3′,4,4′-trimethyl-2*H*-benzothiazine-2-spirocyclopent-3′-en-3(4*H*)-one **21a** as colourless prisms, mp 84.5–86.0 °C (Found: C, 69.2; H, 6.6; N, 5.4. $C_{15}H_{17}NOS$ requires C, 69.46; H, 6.61; N, 5.40%); ν_{max}(KBr)/cm^{-1} 1660 (C=O); $\delta_H(CDCl_3)$ 1.57 (6 H, s, Me × 2), 2.30 (2 H, d, *J* 16, CH_2), 3.11 (2 H, d, *J* 16, CH_2), 3.46 (3 H, s, NMe), 6.99 (1 H, t, *J* 7, ArH), 7.04 (1 H, d, *J* 7, ArH), 7.20 (1 H, t, *J* 7, ArH) and 7.30 (1 H, d, *J* 7, ArH); $\delta_C(CDCl_3)$ 13.2 (q), 32.8 (q), 47.9 (t), 48.6 (s), 116.9 (d), 122.9 (d), 126.9 (d), 127.5 (s × 2), 128.8 (d), 140.2 (s) and 169.8 (s); *m*/*z* 259 (M^+, 38%) and 121 (100).

4-Methyl-2*H*-benzothiazine-2-spirocyclopent-3′-en-3(4*H*)-one **21b**, colourless prisms, mp 47–49 °C (Found: C, 67.4; H, 5.6; N, 6.1. $C_{13}H_{13}NOS$ requires C, 67.50; H, 5.67; N, 6.06%); ν_{max}(KBr)/cm^{-1} 1670 (C=O); $\delta_H(CDCl_3)$ 2.40 (2 H, d, *J* 16, CH_2), 3.15 (2 H, d, *J* 16, CH_2), 3.47 (3 H, s, NMe), 5.61 (2 H, br s, olefinic H), 7.00 (1 H, t, *J* 7, ArH), 7.06 (1 H, d, *J* 7, ArH), 7.25 (1 H, t, *J* 7, ArH) and 7.31 (1 H, d, *J* 7, ArH); $\delta_C(CDCl_3)$ 32.9 (q), 42.8 (t), 50.7 (s), 117.0 (d), 122.6 (s), 123.0 (d), 127.0 (d), 127.2 (d), 128.9 (d), 140.2 (s) and 169.4 (s); *m*/*z* 231 (M^+, 52%) and 139 (100).

X-Ray study of 2′-isopropenyl-2′,4-dimethyl-2*H*-benzothiazine-2-spirocyclopropan-3(4*H*)-one 4a

A colourless prism was mounted on a glass fibre and transferred to the diffractometer.

Crystal data. $C_{15}H_{17}NOS$, $M = 259.37$. Monoclinic, $a = 11.825(3)$, $b = 9.659(3)$, $c = 12.386(3)$ Å, $\beta = 103.79(2)°$, $V = 1373.9(5)$ $Å^3$ (from setting angles of 20 centred reflections with $20.1 \leq 2\theta \leq 26.4°$, $\lambda = 0.710\ 73$ Å, $T = 298$ K), space group $P2_1/a$ (alt $P2_1/c$, No. 14), $Z = 4$, $D_x = 1.254$ cm^3, colourless prism 0.2 × 0.2 × 0.1 mm, μ(Mo-Kα) = 0.213 mm^{-1}.

Data collection and processing. Rigaku AFC-5R four-circle diffractometer with 12 kW rotating anode generator, $\omega/2\theta$ scans with ω scan width $(1.52 + 0.30 \tan\theta)°$, graphite-monochromated Mo-Kα X-radiation; 3508 reflections measured to $2\theta_{max} = 55°$, 3354 unique (merging $R = 0.046$), giving 1443 with $F \geq 6\sigma(F)$ which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption.

Structure solution and refinement. Automatic direct methods[12] (all non-H atoms). Full-matrix least-squares refinement[13] with all non-H atoms anisotropic.

The weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. Final $R = 0.047$, $R_w = 0.051$, $S = 1.45$ for 163 refined parameters. The final ΔF synthesis showed no peaks above ± 0.20 e $Å^{-3}$.

Detailed crystallographic results for this study have been deposited with the Cambridge Crystallographic Data Centre. Any requests for this material should be accompanied by a full bibliographic citation together with the reference number CCDC 207/64. For details of this scheme, see Instructions for Authors (1997), *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.

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