Pummerer reaction of 2-vinylcyclopropyl sulfoxides: generation and reactions of butadienylthionium ion intermediates

Tetsuo Iwama,[a] Harutoshi Matsumoto,[a] Hiroshi Shimizu,[a] Tadashi Kataoka,*[,a] Osamu Muraoka[b] and Genzoh Tanabe[b]

[a] *Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-chome, Gifu 502-8585, Japan*
[b] *Kinki University, Faculty of Pharmaceutical Sciences, 3-4-1, Kowakae, Higashi-osaka, Osaka 577-0818, Japan*

Generation of butadienylthionium ions in the Pummerer reactions of 2-vinylcyclopropyl sulfoxides has been investigated. Although the Pummerer reactions of 2-vinylcyclopropyl sulfoxides 1 are complicated, benzothiazinone derivatives 10 smoothly react with trifluoroacetic anhydride to give 1,3-dienes in good yields. The reactions proceed *via* butadienylthionium ions by proton abstraction from the 2′-methyl group or the cyclopropane ring. Reactions of disubstituted benzothiazinones 10e–h provided cyclic dienes while treatment of mono- or un-substituted derivatives gave acyclic conjugated dienes 11a–d. 2-Vinylcyclopropyl sulfoxides 1 and 10 were prepared by MCPBA oxidation of the corresponding 2-vinylcyclopropyl sulfides 19 and 23, respectively, which were obtained by cyclopropanation of α-chloro sulfides with 1,3-dienes *via* the 5,6-dihydro-2*H*-thiopyranium intermediate 22.

Introduction

Butadienylthionium ions[1] are versatile intermediates for the synthesis of functionalised conjugated dienes. The Pummerer reaction of sulfoxides has been much studied[2] and the general mechanism of the reaction is believed to consist of four sequential steps, involving a thionium ion intermediate.[3] Generation of vinylthionium ions has been widely investigated in the Pummerer reactions of allyl sulfoxides,[4] in the vinylogous Pummerer reactions of vinyl sulfoxides[4c,f,5] and in various reactions of other types of compounds.[6] In contrast, little attention has been paid to the generation of butadienylthionium ions in the Pummerer reactions of sulfoxides.[7] The abnormal Pummerer reaction, involving sulfenic acid derivatives, proceeds when sulfoxides lacking an α-hydrogen, but possessing β-hydrogens, are treated with proton acids, acid anhydrides *etc.*[8] We previously reported that treatment of 2-vinylcyclopropyl sulfoxides without an α-hydrogen with acid anhydrides generated a butadienylthionium ion *via* the destruction of the cyclopropyl ring.[9] In this paper we describe extensive studies on this Pummerer reaction of various 2-vinylcyclopropyl sulfoxides and its limitations.

Pummerer reactions of 2-vinylcyclopropyl sulfoxides 1

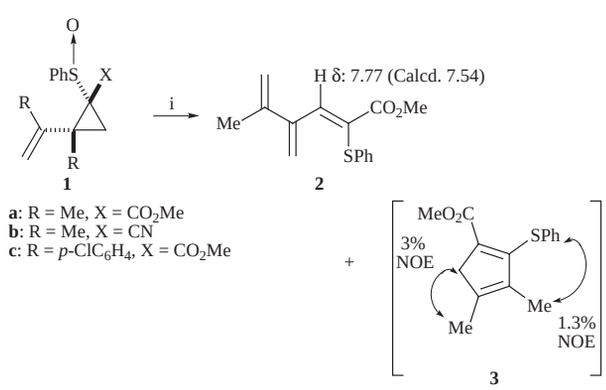
The sulfoxides **1** were treated under Pummerer conditions (Scheme 1, Table 1). Treatment of the sulfoxide **1a** with Ac_2O in the presence of a catalytic amount of *p*-$MeC_6H_4SO_3H$ in benzene at 85 °C in a sealed tube for 12 h gave only the partly isomerised starting sulfoxide (entry 1). The reaction with trifluoroacetic anhydride (TFAA) (2.1 equiv.) in CH_2Cl_2 at room temperature for 24 h provided triene **2** (3%), an unknown compound **3** (17%) and the partly isomerised starting sulfoxide (43%) (entry 2). The geometry of the double bond of the triene **2** was determined as being (*Z*) by applying the additive rule in the ^1H NMR spectrum.[10c] The structure of compound **3** is proposed as shown in Scheme 1.† The ^{13}C NMR spectrum of compound **3** shows four quaternary olefinic carbons except for an aromatic carbon and one alkyl methylene carbon. High resolution mass spectroscopy suggests that the molecular formula is $C_{15}H_{16}O_2S$. NOE measurements show slight enhancements of the signals as shown in Scheme 1. Use of 10 equiv. of TFAA gave the compounds **2** and **3** in poor yields (entries 3 and 4). Reactions of sulfoxides **1b**,**c** resulted in recovery of the starting sulfoxides or complex mixtures, and no products could be identified.

A proposed mechanism for formation of the compounds **2** and **3** is described in Scheme 2. An oxysulfonium salt **4** is

Table 1 Reactions of sulfoxides **1** under Pummerer conditions

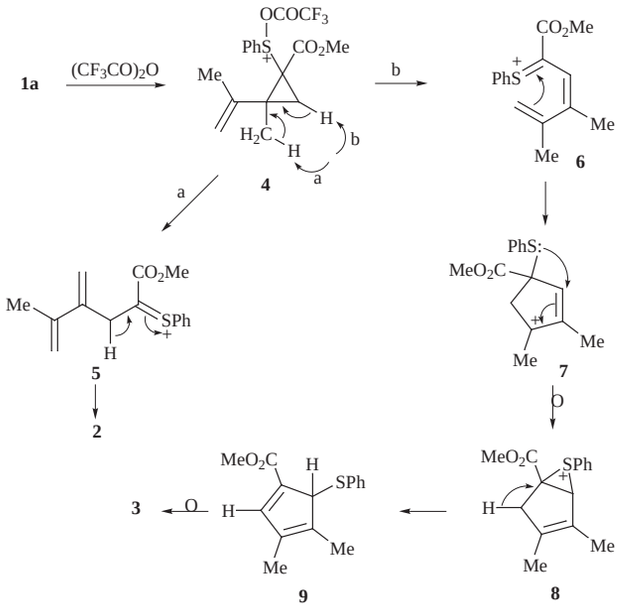
Entry	Sulfoxide	Conditions (equiv.)	Products (% yield)
1	**1a**[a]	Ac_2O (1), *p*-TsOH (0.1), PhH, sealed tube, 85 °C, 12 h	No reaction[b]
2	**1a**[a]	TFAA (2.1), CH_2Cl_2, rt, 24 h	**1a**[c] (43), **2** (3), **3** (17)
3	**1a**[a]	TFAA (10), CH_2Cl_2, rt, 2 h	**2** (11), **3** (23)
4	**1a**[a]	TFAA (10), no solvent, rt, 2 h	**2** (15), **3** (11)
5	**1b**	TFAA (5), CH_2Cl_2, rt, 48 h	No reaction[b]
6	**1b**	TMSOTf (4), CH_2Cl_2, rt, 25 h	No reaction[b]
7	**1b**	TFAA (10), no solvent, rt, 16 h	Complex mixture
8	**1c**[a]	TFAA (10), CH_2Cl_2, rt, 12 h	Complex mixture

[a] One of the two isomers was used. [b] Isomerisation of the sulfoxide moiety was observed. [c] Isomerisation of the sulfoxide moiety was observed. The starting sulfoxide and its isomer were isolated in 30 and 13% yield, respectively.



Scheme 1 *Reagents and conditions:* i, Ac_2O or TFAA or TMSOTf

† Compound **3** was very unstable and gradually decomposed during standing at room temperature. We failed in trapping the diene **3** with tetracyanoethylene by a Diels–Alder reaction, and only a complicated mixture was obtained from the reaction.

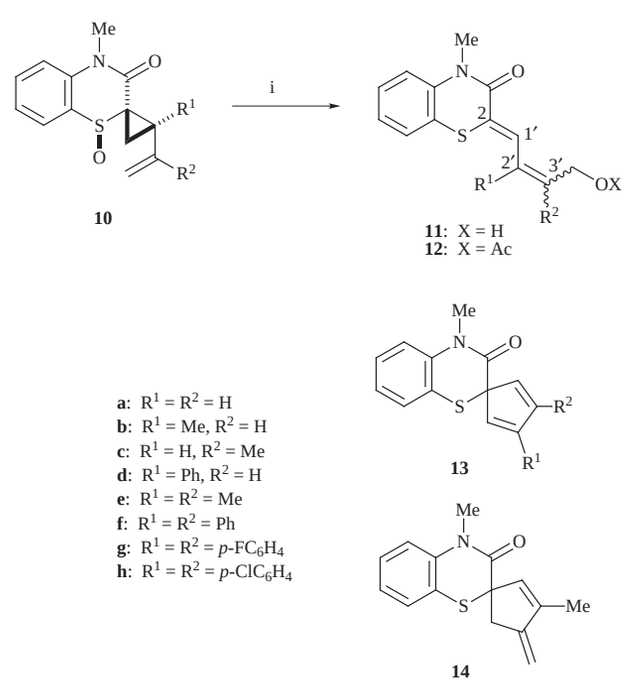


Scheme 2

formed by the reaction of a sulfoxide **1** with TFAA. Deprotonation of a C(2)-methyl proton (process **a**) gives an acyclic thionium intermediate **5**, which is converted to the triene **2**. A butadienylthionium ion **6**, which is generated by the ring-opening of the cyclopropyl ring with the elimination of a ring proton (process **b**), undergoes olefinic cyclisation to form a cyclic cation **7**.[11] 1,2-Sulfenyl rearrangement of the cation **7** *via* an episulfonium intermediate **8** produces an allylic sulfide **9**.[12] Compound **3** is formed by isomerisation of the sulfide **9** under acidic conditions.

Pummerer reactions of benzothiazinone 1-oxides 10 with a spiro vinylcyclopropane ring

Benzothiazinone 1-oxides **10** were treated by two methods: Method A, 2 equiv. of TFAA in CH_2Cl_2 at room temperature for 2 h; Method B: 5 equiv. of Ac_2O and a catalytic amount of *p*-$MeC_6H_4SO_3H$ in benzene at 85 °C in a sealed tube for 24 h (Scheme 3, Table 2). Acyclic dienols **11a**–**d** were formed in good



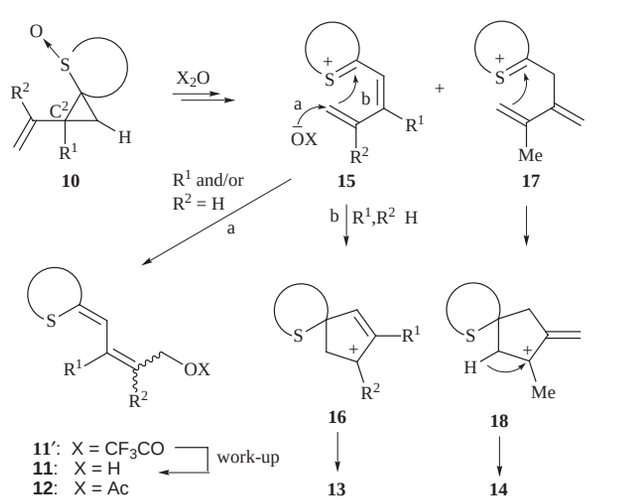
Scheme 3 *Reagents and conditions:* i, Method A: TFAA (2 equiv.), CH_2Cl_2, rt, 2 h; Method B: Ac_2O (5 equiv.), *p*-$MeC_6H_4SO_3H$ (cat.), benzene, 85 °C, sealed tube, 24 h

Table 2 Reactions of 2-vinylcyclopropyl sulfoxides **10** with acid anhydrides

Entry	Sulfoxide	Method[a]	Products (% yield)[b]
1	**10a**	A	**11a** (2′-*E*, 81)[d]
2	**10a**	B	**12a** (2′-*E*, 39)[d]
3	**10b**	A	**11b** (2′-*E*:2′-*Z* = 1:1, 73)[e]
4	**10b**,**c**[c]	A	**11b** (2′-*E*:2′-*Z* = 1:1, 79)[e,f] **11c** (2′-*E*, 78)[f,g]
5	**10d**	A	**11d** (2′-*E*:2′-*Z* = 1:1, 79)[e]
6	**10e**	A	**13e** (25), **14** (46)
7	**10e**	B	**13e** (21), **14** (19)
8	**10f**	A	**13f** (79)
9	**10g**	A	**13g** (72)
10	**10h**	A	**13h** (75)

[a] A: TFAA (2 equiv.), CH_2Cl_2, rt, 2 h; B: Ac_2O (5 equiv.), *p*-$MeC_6H_4SO_3H$ (cat.), benzene, 85 °C, sealed tube, 24 h. [b] Isolated yield. [c] **b**:**c** = 2:1. [d] The geometry of the 2′,3′-double bond was determined from the coupling constant in the ^1H NMR spectra. [e] An inseparable mixture of geometrical isomers. Assignment of the ^1H NMR signals and the geometry of the 2′,3′-double bond were determined by NOE experiments and the ratio was estimated from the ^1H NMR spectrum. [f] Yield based on the corresponding sulfoxide. [g] The geometry of the 2′,3′-double bond was determined by NOE experiments.

yields from un- or mono-substituted sulfoxides **10a**–**d**, respectively, by Method A (entries 1, 3–5). Treatment of the sulfoxide **10a** by Method B provided dienol ester **12a** in 39% yield. On the other hand, dimethyl-substituted sulfoxide **10e** (R^1 = R^2 = Me) furnished two types of cyclic dienes **13e** and **14** (entries 6 and 7). Other disubstituted sulfoxides **10f**–**h** gave cyclic dienes **10f**–**h**, respectively, as a sole product in good yields (entries 8–10). The geometry of the C(2′)–C(3′) double bond of the compounds **11a** and **12a** was determined from the coupling constant of 2′-H and 3′-H (**11a**: *J* 15, **12a**: *J* 15) in the ^1H NMR spectrum. The geometry of the other dienols **11b**–**d** and the assignment of their ^1H NMR signals were determined by NOE experiments.‡ The geometry of the C(2)–C(1′) double bond was determined as being (*Z*) by applying the additive rule in the ^1H NMR spectrum.[10c] A plausible mechanism for the Pummerer reaction is described in Scheme 4. A butadienylthionium ion **15**



Scheme 4

is formed by a similar process to that described in Scheme 2. In the cases of R^1 and/or R^2 = H, nucleophilic attack of XO^- at the ε-carbon of the cation **15** (process **a**) provides a trifluoro-

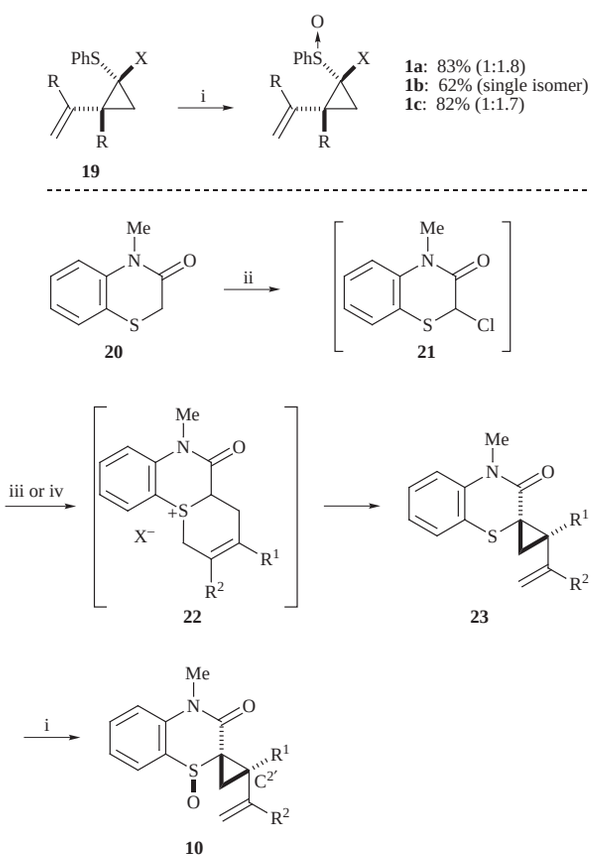
‡ For example, 5% and 3% NOEs were observed between the 1′- and 3′-hydrogens and between the 2′-methyl and 4′-methylene groups, respectively, in the case of dienol (**2′-*E*)-11b**. In the case of (**2′-*E*)-11c** 14% and 7% NOEs were observed between the 1′-hydrogen and the 3′-methyl group and between the 2′-hydrogen and the 4′-methylene group, respectively.

acetate **11′** or an acetate **12**. The ester **11′** is hydrolyzed to the corresponding dienol **11** during work-up. When neither of the substituents R^1 and R^2 are hydrogens, the thionium ion **15** causes olefinic cyclisation[11] to form a cation **16** (process **b**) owing to the stabilisation from R^2. Deprotonation of an α-ring proton then gives a cyclic diene **13**. In the case of $R^1 = R^2 = Me$, another butadienylthionium ion **17** is generated by abstraction of the C(2)-methyl proton in a similar way as for **5** and it then undergoes olefinic cyclisation to give a diene **14** *via* an intermediate **18**. This pathway to the diene **14** is more plausible than that involving deprotonation of an α-methyl hydrogen since formation of the less-substituted exocyclic double bond is disfavored.

The difference in reactivity between phenyl sulfoxides **1** and benzothiazinone 1-oxides **10** may be explained as follows: the cyclopropane ring of benzothiazinone 1-oxides **10** easily opens owing to increased distortion of the ring by the fixed spiro structure. The flexibility of the sulfoxides **1** lowers the reactivity of the cyclopropane ring. In conclusion, this Pummerer reaction of 2-vinylcyclopropyl sulfoxides lacking an α-hydrogen should be useful for the preparation of sulfur-heterocycles, with a butadienyl group or a spiro-bound cyclopentadiene moiety, which can then lead to biologically active compounds.

Synthesis of 2-vinylcyclopropyl sulfoxides 1 and 10

We prepared 2-vinylcyclopropyl sulfoxides **1** by *m*-chloroperbenzoic acid (MCPBA) oxidation of the corresponding sulfides **19**[10a,b] (Scheme 5). Ester derivatives **1a**,**c** were obtained as a



Scheme 5 *Reagents and conditions:* i, MCPBA, CH_2Cl_2, 0 °C; ii, NCS, CCl_4, rt; iii, diene, $SnCl_4$, CH_2Cl_2, −20 °C followed by Et_3N, −20 °C–rt; iv, isoprene, $AgClO_4$, acetone, rt followed by NaH, DMF, 0 °C–rt

mixture of diastereomers, whereas cyano derivative **1b** was obtained as a single isomer probably due to the difference in steric hindrance between a sulfenyl group and an ester group or a cyano group. Benzothiazinone 1-oxides **10** were synthesised from 4-methyl-1,4-benzothiazin-3-one **20**[13] by vinylcyclopropanation[14] followed by MCPBA oxidation (Table 3). Treatment of an α-chloro sulfide **21** with dienes in the presence of $SnCl_4$ followed by Et_3N gave vinylcyclopropanes **23** (Method A in Table 3).[14] Use of isoprene as a diene gave the vinylcyclopropane **23b** as almost a single regiosiomer.§ On the other hand, a mixture of regioisomers (**23b**:**23c** = 2:1, estimated by ^1H NMR spectroscopy) was obtained by use of $AgClO_4$ followed by NaH.[15] The difference is attributable to the nature of the α-thio carbocation (thionium ion). The thionium ion, generated from the chloride **21** and $AgClO_4$, would be a considerably harder cation and the reaction with isoprene proceeds with poor regioselectivity. In contrast, the soft thionium ion, formed from the chloride **21** and $SnCl_4$, regioselectively reacts with isoprene to give a sulfonium salt **22b** *via* the more stable carbocation **25** than the other cationic intermediate **24**. MCPBA oxidation of compounds **22** gave benzothiazinone 1-oxides **10** as single stereoisomers except for **10a**. The stereochemistry of sulfoxide **10e**, as a representative example, was determined by X-ray crystallographic analysis (Fig. 1), and the ORTEP draw-

Table 3 Synthesis of vinylcyclopropyl sulfides **23** and sulfoxides **10**

Entry	Sulfide	Method[a]	% Yield[b]	Sulfoxide[c]	% Yield[b]
1	**23a**	A	76	**10a**[d]	95
2	**23b**[e]	A	61	**10b**	91
3	**23b**,**c**[f]	B	66	**10b**,**c**[f]	89
4	**23d**	A	72	**10d**	86
5	**23e**	A	66	**10e**	93
6	**23f**	A	64	**10f**	90
7	**23g**	A	56	**10g**	88
8	**23h**	A	65	**10h**	92

[a] A: α-Chloro sulfide was treated with a diene and $SnCl_4$ followed by Et_3N; B: α-chloro sulfide was treated with a diene and $AgClO_4$ followed by NaH. [b] Isolated yield. [c] Single isomer unless otherwise mentioned. [d] A mixture of diastereomers at the sulfoxide moiety (2:1, estimated from the ^1H NMR spectrum). [e] A small amount of sulfide **23c** was detected in the ^1H NMR spectrum. [f] **b**:**c** = 2:1. The ratio was determined from the ^1H NMR spectra.

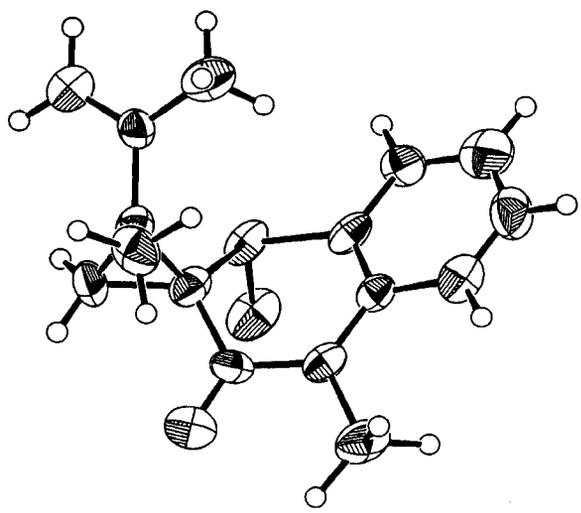
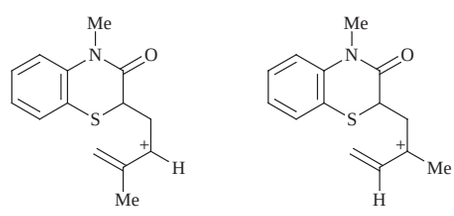


Fig. 1 ORTEP drawing of sulfoxide **10e**



§ A small amount of regioisomer **23c** was detected in the ^1H NMR spectrum of compound **23b**.

ing shows that the sulfoxide oxygen exists in an *anti*-form against C(2′) of the cyclopropane ring.¶

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 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 experiments were obtained on a JEOL EX-400 spectrometer. The *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 accomplished with either Kieselgel 60 (Merck) or BW-127ZH (Fuji Silysia) for column chromatography or Kieselgel 60 PF_{254} containing gypsum (Merck) for PLC.

The Pummerer reactions of 2-vinylcyclopropyl sulfoxides 1 and 10

Method A: general procedure. To a solution of the 2-vinylcyclopropyl sulfoxide **10** (0.5 mmol) in dry CH_2Cl_2 (5 cm^3) was added TFAA (210 mg, 1.0 mmol) at room temperature. After 2 h, saturated aqueous $NaHCO_3$ was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 cm^3). The organic layer and the extracts were combined, dried ($MgSO_4$) and then concentrated. The residue was purified by PLC on silica gel eluting with hexane–ethyl acetate (4:1, v/v) to give the conjugated dienes as shown in Table 1 and Table 2.

Method B: general procedure. A mixture of the sulfoxide **10** (0.5 mmol), Ac_2O (255 mg, 2.5 mmol) and *p*-TsOH·H_2O (10 mg, 0.05 mmol) in benzene (10 cm^3) was heated at 85 °C in a sealed tube for 24 h. The reaction mixture was cooled and concentrated. The residue was purified by PLC on silica gel eluting with hexane–ethyl acetate (4:1, v/v) to give **13** and **14** or **12** as shown in Table 2.

Methyl 5-methyl-4-methylene-2-phenylsulfanylhexa-2,5-dienoate 2. Yellow *oil* (Found: 260.0860. $C_{15}H_{16}O_2S$ requires 260.0871); ν_{max}(NaCl)/cm^{-1}: 1730 (C=O) and 1235 (C–O); δ_H(400 MHz; $CDCl_3$) 1.97 (3 H, s, 5-Me), 3.62 (3 H, s, OMe), 5.07, 5.09, 5.26 and 5.52 (each 1 H, s, 6-H and 4-CH_2), 7.18–7.25 (5 H, m, ArH) and 7.77 (1 H, s, 3-H); δ_C(400 MHz; $CDCl_3$) 20.4 (q), 52.7 (q), 115.6 (t), 118.0 (t), 126.5 (d), 128.7 (d), 128.9 (d), 129.2 (s), 135.5 (s), 141.5 (s), 142.8 (s), 145.3 (d) and 166.0 (s); *m*/*z* 260 (5%, M$^+$) and 97 (100).

Methyl 3,4-dimethyl-2-phenylsulfanylcyclopenta-1,3-diene-1-carboxylate 3. Yellow *oil* (Found: 260.0865. $C_{15}H_{16}O_2S$ requires 260.0871); ν_{max}(NaCl)/cm^{-1}: 1705 (C=O) and 1245 (C–O); δ_H(400 MHz; $CDCl_3$) 1.49 and 1.97 (each 3 H, s, 3- and 4-Me), 3.34 (2 H, s, 5-H), 3.74 (3 H, s, OMe) and 7.16–7.29 (5 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 11.7 (q), 14.3 (q), 45.9 (t), 51.1 (q), 126.4 (d), 128.9 (d), 129.7 (d), 132.3 (s), 135.4 (s), 137.8 (s), 143.8 (s), 150.0 (s) and 164.2 (s); *m*/*z* 260 (100%, M$^+$).

(2,1′*Z*)-2-[(2*E*)-4-Hydroxybut-2-enylidene]-4-methyl-3,4-dihydro-2*H*-1,4-benzothiazin-3-one 11a. Orange *prisms* (from CH_2Cl_2–diethyl ether), mp 102–103 °C (Found: C, 63.0; H, 5.4; N, 5.6. $C_{13}H_{13}NO_2S$ requires C, 63.14; H, 5.30; N, 5.66%); ν_{max}(KBr)/cm^{-1} 3200 (OH) and 1655 (C=O); δ_H(270 MHz; $CDCl_3$) 2.63 (1 H, br s, OH), 3.51 (3 H, s, NMe), 4.34 (2 H, d, *J* 4, 4′-H), 6.27 (1 H, dt, J_{trans} 15 and *J* 4, 3′-H), 6.76 (1 H, dd, J_{trans} 15 and *J* 11, 2′-H), 7.01–7.07 (2 H, m, ArH), 7.21–7.27 (2 H, m, ArH) and 7.36 (1 H, d, *J* 11, 1′-H); δ_C(270 MHz; $CDCl_3$) 32.4 (q), 62.9 (t), 116.6 (d), 119.6 (s), 120.5 (s), 123.3 (d), 124.5 (d), 126.3 (d), 126.8 (d), 134.0 (d), 137.8 (s), 140.7 (d) and 162.5 (s); *m*/*z* 247 (100%, M$^+$).

(2,1′*Z*)-2-[(2*E*)-4-Acetoxybut-2-enylidene]-4-methyl-3,4-dihydro-2*H*-1,4-benzothiazin-3-one 12a. Pale yellow *oil* (Found: 289.0788. $C_{15}H_{15}NO_3S$ requires 289.0773); ν_{max}(NaCl)/cm^{-1}: 1740 (C=O), 1650 (C=O) and 1255 (C–O); δ_H(270 MHz; $CDCl_3$) 2.11 (3 H, s, CH_3CO), 3.50 (3 H, s, NMe), 4.72 (2 H, d, *J* 6, 4′-H), 6.15 (1 H, dt, J_{trans} 15 and *J* 6, 3′-H), 6.73 (1 H, dd, J_{trans} 15 and *J* 11, 2′-H), 7.01–7.06 (2 H, m, ArH), 7.21–7.28 (2 H, m, ArH) and 7.34 (1 H, d, *J* 11, 1′-H); δ_C(270 MHz; $CDCl_3$) 21.1 (q), 32.6 (q), 64.8 (t), 116.9 (d), 119.5 (s), 122.3 (s), 123.6 (d), 126.5 (d), 127.2 (d), 127.8 (d), 133.3 (d), 134.4 (d), 138.1 (s), 162.3 (s) and 170.8 (s); *m*/*z* 289 (100%, M$^+$).

(2,1′*Z*)-2-[(2*Z*)- and (2*E*)-4-Hydroxy-2-methylbut-2-enylidene]-4-methyl-3,4-dihydro-2*H*-1,4-benzothiazin-3-one 11b. Pale yellow *oil* as a 1:1 mixture of geometrical isomers (Found: 261.0815. $C_{14}H_{15}NO_2S$ requires 261.0823); ν_{max}(NaCl)/cm^{-1}: 3400 (OH) and 1645 (C=O); δ_H(270 MHz; $CDCl_3$) 1.95 [3 H, s, (*Z*)-2′-Me], 1.99 [3 H, s, (*E*)-2′-Me], 2.68 (total 2 H, br s, OH), 3.51 [3 H, s, (*Z*)-NMe], 3.51 [3 H, s, (*E*)-NMe], 4.12 [2 H, d, *J* 7, (*Z*)-4′-H], 4.37 [2 H, d, *J* 6, (*E*)-4′-H], 5.75 [1 H, t, *J* 7, (*Z*)-3′-H], 5.85 [1 H, t, *J* 6, (*E*)-3′-H], 7.00–7.06 (total 4 H, m, ArH), 7.21–7.25 (total 4 H, m, ArH), 7.32 [1 H, s, (*E*)-1′-H] and 7.41 [1 H, s, (*Z*)-1′-H]; δ_C(270 MHz; $CDCl_3$): 16.8 (q), 22.4 (q), 32.6 (q), 32.7 (q), 59.6 (t), 60.1 (t), 116.5 (d), 116.6 (d), 119.5 (s), 119.7 (s), 112.0 (s), 122.3 (s), 123.3 (d), 123.7 (d), 123.4 (d), 126.2 (d), 126.3 (d), 126.9 (d), 132.0 (d), 133.2 (s), 133.4 (s), 133.8 (d), 135.8 (d), 137.0 (s), 137.4 (s), 137.9 (d), 161.8 (s) and 162.2 (s); *m*/*z* 261 (60%, M$^+$), 230 (100).

(2,1′*Z*)-2-[(2*E*)-4-Hydroxy-3-methylbut-2-enylidene]-4-methyl-3,4-dihydro-2*H*-1,4-benzothiazin-3-one 11c. Pale yellow *oil* (Found: 261.0816. $C_{12}H_{15}NO_2S$ requires 261.0823); ν_{max}(NaCl)/cm^{-1}: 3400 (OH) and 1640 (C=O); δ_H(270 MHz; $CDCl_3$) 1.90 (3 H, s, 3′-Me), 2.19 (1 H, br s, OH), 3.50 (3 H, s, NMe), 4.19 (2 H, s, 4′-H), 6.57 (1 H, d, *J* 12, 2′-H), 6.99–7.04 (2 H, m, ArH), 7.19–7.27 (2 H, m, ArH) and 7.61 (1 H, d, *J* 12, 1′-H); δ_C(270 MHz; $CDCl_3$) 14.9 (q), 32.4 (q), 67.7 (t), 116.5 (d), 118.7 (d), 119.8 (s), 119.9 (s), 123.3 (d), 126.3 (d), 126.8 (d), 130.3 (d), 137.9 (s), 146.8 (s) and 162.8 (s); *m*/*z* 261 (100%, M$^+$).

(2,1′*Z*)-2-[(2*E*)- and (2*Z*)-4-Hydroxy-2-phenylbut-2-enylidene]-4-methyl-3,4-dihydro-2*H*-1,4-benzothiazin-3-one 11d. Yellow *oil* as a 1:1 mixture of geometrical isomers (Found: C, 70.65; H, 5.4; N, 4.3. $C_{19}H_{17}NO_2S$ requires C, 70.56; H, 5.30; N, 4.33%); ν_{max}(NaCl)/cm^{-1}: 3450 (OH) and 1660 (C=O); δ_H(400 MHz, $CDCl_3$) 2.51 (total 2 H, br s, OH), 3.47 [3 H, s, (*E*)-NMe], 3.51 [3 H, s, (*Z*)-NMe], 4.25 [2 H, d, *J* 6.8, (*E*)-4′-H], 4.29 [2 H, dd, *J* 6.8, (*Z*)-4′-H], 6.15 [1 H, t, *J* 6.8, (*E*)-3′-H], 6.24 [1 H, dt, *J* 1 and 6.8, (*Z*)-3′-H], 6.92–7.32 (total 18 H, m, ArH), 7.51 [1 H, s, (*E*)-1′-H] and 7.63 [1 H, d, *J* 1, (*Z*)-1′-H]; δ_C(400 MHz; $CDCl_3$) 32.5 (q), 32.6 (q), 60.1 (t), 60.5 (t), 116.3 (d), 116.6 (d), 119.3 (s), 119.8 (s), 121.6 (s), 123.2 (d), 123.4 (d), 125.3 (s), 126.1 (d), 126.2 (d), 126.7 (d), 126.7 (d), 126.8 (d), 127.3 (s), 127.8 (d), 127.9 (d), 128.2 (s), 128.3 (d), 128.5 (d), 128.9 (d), 131.9 (d), 132.1 (d), 135.7 (d), 136.4 (s), 137.0 (s), 137.2 (d), 138.3 (s), 138.6 (s), 161.0 (s) and 162.2 (s); *m*/*z* 323 (33%, M$^+$) and 179 (100).

3′,4,4′-Trimethyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2′-spiro-1′-cyclopenta-2′,4′-diene 13e. Pale yellow *prisms* (from CH_2Cl_2–diethyl ether), mp 103–104 °C (Found: 257.0889. $C_{15}H_{15}NOS$ requires 257.0874); ν_{max}(KBr)/cm^{-1}: 1660 (C=O); δ_H(270 MHz; $CDCl_3$) 1.90 (6 H, d, *J* 1, 3′- and 4′-Me), 3.46 (3 H, s, NMe), 5.92 (2 H, q, *J* 1, 2′- and 5′-H), 7.00–7.11 (2 H, m, ArH) and 7.25–7.35 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 13.8 (q), 32.8 (q), 51.7 (s), 117.3 (d), 123.2 (d), 123.9 (s), 127.1

¶ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/201.

(d), 128.1 (d), 129.5 (d), 140.3 (s), 145.9 (s) and 166.2 (s); *m*/*z* 257 (100%, M^+).

3′,4-Dimethyl-4′-methylene-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2′-spiro-1′-cyclopent-2′-ene 14. Pale yellow *prisms* (from CH_2Cl_2–diethyl ether), mp 88–89 °C (Found: C, 69.7; H, 6.1; N, 5.2. $C_{15}H_{15}NOS$ requires C, 70.01; H, 5.88; N, 5.44%); ν_{max}(KBr)/cm^{-1}: 1660 (C=O); δ_H(270 MHz; $CDCl_3$) 1.79 (3 H, d, *J* 1, 3′-Me), 2.60 and 3.45 (each 1 H, d, *J* 17, 5′-H), 3.48 (3 H, s, NMe), 4.92 and 4.96 (each 1 H, br s, CH_2=C), 5.68 (1 H, br s, 2′-H), 7.00–7.10 (2 H, m, ArH) and 7.24–7.35 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 12.6 (q), 33.1 (q), 40.1 (t), 54.6 (s), 104.7 (t), 117.2 (d), 122.8 (s), 123.3 (d), 127.1 (d), 128.8 (d), 131.2 (d), 139.9 (s), 144.4 (s), 150.6 (s), 168.0 (s); *m*/*z* 257 (100%, M^+).

4-Methyl-3′,4′-diphenyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2′-spiro-1′-cyclopenta-2′,4′-diene 13f. Orange *prisms* (from CH_2Cl_2–diethyl ether), mp 139–140 °C (Found: C, 78.5; H, 5.2; N, 3.61. $C_{25}H_{19}NOS$ requires C, 78.71; H, 5.02; N, 3.67%); ν_{max}(KBr)/cm^{-1}: 1660 (C=O); δ_H(270 MHz; $CDCl_3$) 3.50 (3 H, s, NMe), 6.37 (2 H, s, 2′- and 5′-H) and 6.90–7.37 (14 H, m, ArH); δ_C(270 MHz; $CDCl_3$) 32.8 (q), 57.5 (s), 117.5 (d), 123.1 (s), 123.4 (d), 127.3 (d), 127.7 (d), 127.8 (d), 128.1 (d), 128.2 (d), 132.6 (d), 134.4 (s), 140.1 (s), 148.1 (s) and 165.0 (s); *m*/*z* 381 (100%, M^+).

3′,4′-Bis(*p*-fluorophenyl)-4-methyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2′-spiro-1′-cyclopenta-2′,4′-diene 13g. Yellow *oil* (Found: 417.0982. $C_{25}H_{17}F_2NOS$ requires 417.0999); ν_{max}(NaCl)/cm^{-1}: 1660 (C=O); δ_H(270 MHz; $CDCl_3$) 3.51 (3 H, s, NMe), 6.35 (2 H, s, 2′- and 5′-H), 6.91 (4 H, t, $J_{H(o)} = J_{F(o)}$ 9, ArH), 7.08 (4 H, dd, $J_{F(m)}$ 5 and $J_{H(o)}$ 8, ArH), 7.03–7.11 (2 H, m, ArH) and 7.26–7.38 (2 H, m, ArH); δ_C(270 MHz; $CDCl_3$) 32.7 (q), 57.4 (s), 114.9 (d, $^2J_{CF}$ 20), 117.5 (d), 122.8 (s), 123.4 (d), 127.4 (d), 128.1 (d), 129.9 (d, $^3J_{CF}$ 9), 130.3 (s), 132.6 (d), 140.0 (s), 146.8 (s), 162.4 (s, $^1J_{CF}$ 248) and 164.7 (s); *m*/*z* 417 (100%, M^+).

3′,4′-Bis(*p*-chlorophenyl)-4-methyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2′-spiro-1′-cyclopenta-2′,4′-diene 13h. Yellow *oil* (Found: 449.0391. $C_{25}H_{17}Cl_2NOS$ requires 449.0408); ν_{max}(NaCl)/cm^{-1}: 1660 (C=O); δ_H(400 MHz; $CDCl_3$) 3.51 (3 H, s, NMe), 6.37 (2 H, s, 2′- and 5′-H), 7.04 (4 H, d, *J* 8, ArH), 7.06 (1 H, t, *J* 8, ArH), 7.15 (1 H, d, *J* 8, ArH), 7.20 (4 H, d, *J* 8, ArH), 7.32 (1 H, t, *J* 8, ArH) and 7.36 (1 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 32.9 (q), 57.7 (s), 117.6 (d), 122.8 (s), 123.6 (d), 127.6 (d), 128.3 (d), 129.6 (d), 132.7 (s), 133.3 (d), 134.1 (s), 140.1 (s), 146.7 (s) and 164.7 (s); *m*/*z* 449 (37%, M^+) and 179 (100).

Synthesis of 2-vinylcyclopropyl sulfides 23

Method A: general procedure. To a stirred solution of benzothiazinone **20** (1.9 g, 10 mmol) in dry CCl_4 (20 cm^3) was added NCS (1.34 g, 10 mmol) in portions at room temperature. After 2 h, the precipitate of succinimide was filtered off and the filtrate was evaporated under reduced pressure. $SnCl_4$ (1.35 cm^3, 11.5 mmol) was added to a solution of the resultant α-chloro sulfide **2** in CH_2Cl_2 (30 cm^3) in the presence of a diene (12 mmol) at −20 °C under nitrogen. After 45 min, Et_3N (7.0 cm^3, 50 mmol) was added to the reaction mixture at −20 °C which was stirred for 30 min at room temperature. Et_2O (30 cm^3) was added and the precipitate was filtered off through Celite. The filtrate was evaporated under reduced pressure (if needed, filtration was carried out two or three times) and the residue was purified by silica gel column chromatography eluting with ethyl acetate–hexane (1 : 5, v/v) to give a vinylcyclopropyl sulfide **23**.

2′,4-Dimethyl-2′-vinyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 23b. Yield 61%, light yellow *oil* (Found: 245.0881. $C_{14}H_{15}NOS$ requires 245.0874); ν_{max}(NaCl)/cm^{-1}: 1655 (C=O); δ_H(400 MHz; $CDCl_3$) 1.08 (3 H, s, 2′-Me), 1.21 and 1.97 (each 1 H, d, *J* 5.8, 3′-H), 3.47 (3 H, s, NMe), 4.91 (1 H, d, J_{trans} 17, CH=CH_2), 5.06 (1 H, d, J_{cis} 11, CH=CH_2), 5.83 (1 H, dd, *J* 11 and 17, C*H*=CH_2), 7.69–7.05 (2 H, m, ArH) and 7.21–7.28 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 16.3 (q), 22.2 (t), 31.6 (s), 32.8 (q), 34.3 (s), 115.2 (t), 117.1 (d), 123.0 (d), 124.1 (s), 127.1 (d), 128.0 (d), 138.7 (d), 140.1 (s) and 167.1 (s); *m*/*z* 245 (86%, M^+) and 107 (100).

4-Methyl-2′-phenyl-2′-vinyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 23d. Yield 72%, *prisms* (from EtOAc–hexane), mp 116–124 °C (Found: C, 74.4; H, 5.6; N, 4.6. $C_{19}H_{17}NOS$ requires C, 74.24; H, 5.57; N, 4.56%); ν_{max}(KBr)/cm^{-1}: 1660 (C=O); δ_H(400 MHz; $CDCl_3$) 1.51 and 2.71 (each 1 H, d, *J* 6, 3′-H), 3.17 (3 H, s, NMe), 4.58 (1 H, d, J_{trans} 17.1, CH=CH_2), 5.06 (1 H, d, J_{cis} 11.7, CH=CH_2), 6.05 (1 H, dd, *J* 11.7 and 17.1, C*H*=CH_2), 6.82 (2 H, d, *J* 8, ArH), 7.06–7.09 (2 H, m, ArH), 7.18–7.19 (3 H, m, ArH), 7.34 (1 H, t, *J* 8, ArH) and 7.39 (1 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 20.5 (t), 32.4 (q), 35.8 (s), 42.7 (s), 116.9 (d), 117.3 (t), 123.2 (d), 123.4 (s), 127.2 (d), 127.6 (d), 128.0 (d), 128.3 (d), 129.9, (d), 137.1 (s), 138.4 (d), 140.0 (s) and 166.1 (s); *m*/*z* 307 (47%, M^+) and 169 (100).

4-Methyl-2′-phenyl-2′-(1-phenylvinyl)-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 23f. Yield 64%, *needles* (from CH_2Cl_2–hexane), mp 130–131 °C (Found: C, 78.35; H, 5.5; N, 3.8. $C_{25}H_{17}NOS$ requires C, 78.30; H, 5.52; N, 3.65%); ν_{max}(KBr)/cm^{-1}: 1665 (C=O); δ_H(400 MHz; $CDCl_3$) 1.40 and 2.72 (each 1 H, d, *J* 6, 3′-H), 3.25 (3 H, s, NMe), 4.89 and 5.37 (each 1 H, s, olefinic H), 7.04–7.24 (12 H, m, ArH) and 7.30–7.36 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 21.4 (t), 32.8 (q), 35.3 (s), 46.7 (s), 117.2 (d), 119.1 (t), 123.3 (d), 124.0 (s), 127.0 (d), 127.1 (d), 127.3 (d), 127.8 (d), 128.1 (d), 128.4 (d), 129.2 (d), 139.6 (s), 139.9 (s), 141.4 (s), 146.4 (s) and 165.4 (s); *m*/*z* 383 (46%, M^+) and 245 (100).

2′-*p*-Fluorophenyl-2′-[1-(*p*-fluorophenyl)vinyl]-4-methyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 23g. Yield 56%, *needles* (from CH_2Cl_2–hexane), mp 115–116 °C (Found: C, 71.5; H, 4.6; N, 3.4. $C_{25}H_{19}F_2NOS$ requires C, 71.58; H, 4.57; N, 3.34%); ν_{max}(KBr)/cm^{-1}: 1645 (C=O); δ_H(400 MHz; $CDCl_3$) 1.43 and 2.67 (each 1 H, d, *J* 6, 3′-H), 3.28 (3 H, s, NMe), 4.94 and 5.34 (each 1 H, s, olefinic H), 6.80 (2 H, t, $J_{H(o)} = J_{F(o)}$ 8, ArH), 6.86 (2 H, t, $J_{H(o)} = J_{F(o)}$ 8, ArH), 7.01 (2 H, dd, $J_{F(m)}$ 5 and $J_{H(o)}$ 8, ArH), 7.06 (2 H, dd, $J_{F(m)}$ 5 and $J_{H(o)}$ 8, ArH), 7.08 (1 H, t, *J* 8, ArH), 7.13 (1 H, d, *J* 8, ArH), 7.28 (1 H, t, *J* 8, ArH) and 7.35 (1 H, t, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 21.4 (t), 32.9 (q), 35.5 (s), 46.2 (s), 114.7 (d, $^2J_{CF}$ 22), 115.0 (d, $^2J_{CF}$ 22), 117.3 (d), 119.1 (t), 123.4 (d), 123.9 (s), 127.5 (d), 128.4 (d), 129.0 (d, $^3J_{CF}$ 9), 130.8 (d, $^3J_{CF}$ 9), 135.1 (s), 137.1 (s), 139.7 (s), 145.5 (s), 161.6 (s, $^1J_{CF}$ 246), 162.0 (s, $^1J_{CF}$ 246) and 165.1 (s); *m*/*z* 419 (36%, M^+) and 281 (100).

2′-*p*-Chlorophenyl-2′-[1-(*p*-chlorophenyl)vinyl]-4-methyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 23h. Yield 65%, *needles* (from CH_2Cl_2–hexane), mp 138–139 °C (Found: C, 66.5; H, 4.3; N, 3.1. $C_{25}H_{19}Cl_2NOS$ requires C, 66.37; H, 4.23; N, 3.10%); ν_{max}(KBr)/cm^{-1}: 1655 (C=O); δ_H(400 MHz; $CDCl_3$) 1.43 and 2.67 (each 1 H, d, *J* 6, 3′-H), 3.29 (3 H, s, NMe), 4.98 and 5.38 (each 1 H, s, olefinic H), 6.96–7.15 (10 H, m, ArH), 7.24 (1 H, d, *J* 8, ArH) and 7.35 (1 H, d, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 21.5 (t), 33.0 (q), 35.5 (s), 46.1 (s), 117.3 (d), 119.6 (t), 123.5 (d), 123.7 (s), 127.5 (d), 128.0 (d), 128.4 (d), 128.6 (d), 130.5 (d), 133.0 (s), 133.1 (s), 137.7 (s), 139.4 (s), 139.6 (s), 145.3 (s) and 165.0 (s); *m*/*z* 451 (49%, M^+) and 313 (100).

Method B. To a stirred solution of benzothiazinone **20** (896 mg, 5 mmol) in dry CCl_4 (25 cm^3) was added NCS (668 mg, 5 mmol) at 0 °C. After 2 h at room temperature, the solvent 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 a crude α-chloro sulfide **21**. A solution of the crude **21** and isoprene (1.0 cm^3, 10 mmol) in dry acetone (25 cm^3) was treated with $AgClO_4$ (1.07 g, 97% purity, 5 mmol) at 0 °C, and then stirred for 30 min at room temperature. The precipitate of AgCl was filtered off and washed with hot CH_3CN. The filtrate was evaporated and

the residue was solved in dry DMF (20 cm^3). NaH (220 mg, 60% in paraffin oil, 5.5 mmol) was added to the solution in portions at 0 °C. After 30 min at room temperature, water was added to the reaction mixture and the whole was extracted with ethyl acetate. The extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by silica gel column chromatography eluting with ethyl acetate–hexane (1:5, v/v) to give 862 mg (66%) of vinylcyclopropyl sulfides **23b** and **23c** as an inseparable mixture.

2′,4-Dimethyl-2′-vinyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 23b and 2′-isopropenyl-4-methyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 23c. Yield 66%, light yellow *oil* as a mixture of **23b** and **23c** (2:1, estimated by the ^1H NMR spectrum) (Found: 245.0867. $C_{14}H_{15}NOS$ requires 245.0874); ν_{max}(NaCl)/cm^{-1}: 1655 (C=O); δ_H(400 MHz; $CDCl_3$) 1.08 (3 H, s, **23b**-2′-Me), 1.16 (1 H, dd, *J* 5.4 and 7.8, **23c**-3′-H), 1.21 and 1.97 (each 1 H, d, *J* 5.8, **23b**-3′-H), 1.46 (3 H, s, **23c**-Me), 1.94 (1 H, dd, *J* 5.4 and 8.8, **23c**-3′-H), 2.14 (1 H, dd, *J* 8.8 and 7.8, **23c**-2′-H), 3.44 (3 H, s, **23c**-NMe), 3.47 (3 H, s, **23b**-NMe), 4.72 and 5.02 (each 1 H, s, **23c**-C=CH_2), 4.91 (1 H, d, J_{trans} 17, **23b**-CH=CH_2), 5.06 (1 H, d, J_{cis} 11, **23b**-CH=CH_2), 5.83 (1 H, dd, *J* 11 and 17, **23b**-C*H*=CH_2), 6.96–7.05 (total 4 H, m, ArH) and 7.21–7.28 (total 4 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 16.3 (q, **23b**), 16.8 (t, **23c**), 22.2 (t, **23b**), 23.3 (q, **23c**), 28.8 (s, **23c**), 31.6 (s, **23b**), 32.8 (q, **23b** and **23c**), 33.9 (d, **23c**), 34.3 (s, **23b**), 114.1 (t, **23c**), 115.2 (t, **23b**), 116.8 (d, **23c**), 117.1 (d, **23b**), 123.0 (d, **23b**), 123.2 (d, **23c**), 124.1 (s, **23b**), 127.1 (d, **23b** and **23c**), 128.0 (d, **23b**), 128.1 (d, **23c**), 138.7 (d, **23b**), 139.4 (s, **23c**), 139.7 (s, **23c**), 140.1 (s, **23b**), 167.1 (s, **23c**) and 167.1 (s, **23b**); *m*/*z* 245 (86%, M^+) and 107 (100).

Synthesis of 2-vinylcyclopropyl sulfoxides 1 and 10

General procedure. To a stirred solution of sulfide **19** or **23**[10a] (1 mmol) in dry CH_2Cl_2 (5 cm^3) was added MCPBA (85% purity, 203 mg, 1 mmol) in several portions at 0 °C. After 1 h, saturated aqueous $NaHCO_3$ was added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 cm^3). The organic layer and the extracts were combined, washed with saturated aqueous NaCl, dried ($MgSO_4$) and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluting with hexane–ethyl acetate (4:1–1:1, v/v) to give 2-vinylcyclopropyl sulfoxide **1** or **10**.

Methyl 2-isopropenyl-2-methyl-1-phenylsulfinylcyclopropane-1-carboxylate 1a. Fraction 1, 53%, *prisms* (from EtOAc–hexane), mp 97–98 °C (decomp.) (Found: C, 64.45; H, 6.5. $C_{15}H_{18}O_3S$ requires C, 64.72; H, 6.52%); ν_{max}(KBr)/cm^{-1}: 1725 (C=O), 1240 (C–O) and 1060 (S–O); δ_H(400 MHz; $CDCl_3$) 1.27 (3 H, s, 2-Me), 1.39 and 2.24 (each 1 H, d, *J* 5.9, 3-H), 1.89 (3 H, s, Me), 3.40 (3 H, s, OMe), 5.14 (2 H, br s, C=CH_2), 7.43–7.49 (3 H, m, ArH) and 7.66 (2 H, d, *J* 6.8, ArH); δ_C(400 MHz; $CDCl_3$) 14.0 (t), 21.0 (q), 22.2 (q), 35.3 (s), 52.0 (q), 55.7 (s), 115.4 (t), 126.3 (d), 128.8 (d), 131.9 (d), 142.9 (s), 143.6 (s) and 167.1 (s); *m*/*z* 278 (2%, M^+) and 93 (100). Fraction 2, 30%, *prisms* (from EtOAc–hexane), mp 110–111 °C (decomp.) (Found: C, 64.95; H, 6.6. $C_{15}H_{18}O_3S$ requires C, 64.72; H, 6.52%); ν_{max}(KBr)/cm^{-1}: 1715 (C=O), 1250 (C–O) and 1055 (S–O); δ_H(400 MHz; $CDCl_3$) 1.32 (3 H, s, 2-Me), 1.67 and 1.88 (each 1 H, d, *J* 5.9, 3-H), 2.10 (3 H, s, Me), 3.51 (3 H, s, OMe), 5.12 and 5.17 (each 1 H, s, C=CH_2), 7.45–7.50 (3 H, m, ArH) and 7.59 (2 H, dd, *J* 7.3 and 1.5, ArH); δ_C(400 MHz; $CDCl_3$) 20.0 (q), 21.3 (q), 21.8 (t), 37.8 (s), 52.3 (q), 55.1 (s), 115.6 (t), 124.1 (d), 128.8 (d), 130.7 (d), 142.6 (s), 143.0 (s) and 166.9 (s); *m*/*z* 278 (3%, M^+) and 93 (100).

2-Isopropenyl-2-methyl-1-phenylsulfinylcyclopropane-1-carbonitrile 1b. 62%, *prisms* (from EtOAc–hexane), mp 130–132 °C (decomp.) (Found: C, 68.5; H, 6.2; N, 5.7. $C_{14}H_{15}NOS$ requires C, 68.54; H, 6.16; N, 5.76%); ν_{max}(KBr)/cm^{-1}: 2235 (CN) and 1055 (S–O); δ_H(400 MHz; $CDCl_3$) 1.47 and 1.80 (each 1 H, d, *J* 6.4, 3-H), 1.58 (3 H, s, 2-Me), 2.08 (3 H, s, Me), 5.11 and 5.21 (each 1 H, s, C=CH_2), 7.57–7.58 (3 H, m, ArH) and 7.72–7.74 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 20.9 (q), 22.2 (q), 24.0 (t), 39.5 (s), 44.8 (s), 114.4 (s), 116.8 (t), 124.5 (d), 129.4 (d), 132.1 (d), 141.4 (s) and 141.9 (s); *m*/*z* 229 (10%, M^+) and 120 (100).

Methyl 2-*p*-chlorophenyl-2-[1-(*p*-chlorophenyl)vinyl]-1-phenylsulfinylcyclopropane-1-carboxylate 1c. Fraction 1, 52%, *prisms* (from EtOAc–hexane), mp 155–159 °C (Found: C, 63.9; H, 4.3. $C_{25}H_{20}Cl_2O_3S$ requires C, 63.70; H, 4.28%); ν_{max}(KBr)/cm^{-1}: 1755 (C=O), 1260 (C–O) and 1055 (S–O); δ_H(400 MHz; $CDCl_3$) 2.21 and 2.37 (each 1 H, d, *J* 6.3, 3-H), 3.12 (3 H, s, OMe), 5.77 and 5.92 (each 1 H, s, C=CH_2), 7.23–7.26 (4 H, m, ArH), 7.33 (2 H, d, *J* 8, ArH), 7.40–7.47 (5 H, m, ArH) and 7.65 (2 H, dd, *J* 8 and 1, ArH); δ_C(400 MHz; $CDCl_3$) 12.3 (t), 41.7 (s), 52.0 (q), 58.8 (s), 119.3 (t), 126.3 (d), 128.3 (d), 128.5 (d), 128.9 (d), 130.0 (d), 132.1 (d), 133.6 (d), 137.0 (s), 138.3 (s), 142.7 (s), 144.0 (s) and 165.4 (s); *m*/*z* 470 (3%, M^+) and 344 (100). Fraction 2, 30%, *prisms* (from EtOAc–hexane), mp 158–161 °C (Found: C, 63.6; H, 4.3. $C_{25}H_{20}Cl_2O_3S$ requires C, 63.70; H, 4.28%); ν_{max}(KBr)/cm^{-1}: 1725 (C=O), 1260 (C–O) and 1050 (S–O); δ_H(400 MHz; $CDCl_3$) 1.86 and 2.38 (each 1 H, d, *J* 6.3, 3-H), 3.32 (3 H, s, OMe), 5.90 and 6.20 (each 1 H, s, C=CH_2), 7.20 (2 H, d, *J* 8, ArH), 7.27 (2 H, d, *J* 8, ArH), 7.34 (2 H, d, *J* 8, ArH), 7.39 (2 H, d, *J* 8, ArH), 7.46–7.48 (3 H, m, ArH) and 7.62–7.65 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 20.0 (t), 45.4 (s), 52.8 (q), 57.5 (s), 121.5 (t), 124.7 (d), 128.7 (d), 128.8 (d), 128.9 (d), 129.4 (d), 130.4 (d), 131.5 (d), 134.2 (s), 136.5 (s), 138.4 (s), 141.8 (s), 143.8 (s) and 165.2 (s); *m*/*z* 470 (3%, M^+) and 215 (100).

4-Methyl-2′-vinyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10a. Yield 95%, *prisms* as a 2:1 mixture of diastereomers at the sulfoxide moiety (from CH_2Cl_2–diethyl ether) (Found: C, 62.9; H, 5.3; N, 5.65. $C_{13}H_{13}NO_2S$ requires C, 63.14; H, 5.30; N, 5.66%); ν_{max}(KBr)/cm^{-1}: 1660 (CO) and 1030 (SO); δ_H(270 MHz; $CDCl_3$) isomer$_{major}$: 1.99 (1 H, dd, J_{trans} 7 and J_{AB} 5, 3′-H), 2.37 (1 H, dt, *J* 7 and 8, 2′-H), 2.59 (1 H, dd, J_{cis} 8 and J_{AB} 5, 3′-H), 3.51 (3 H, s, NMe), 5.10 (1 H, d, J_{cis} 10, CH=CH_2), 5.15 (1 H, d, J_{trans} 17, CH=CH_2), 5.88 (1 H, ddd, *J* 17, 10 and 8, C*H*=CH_2), 7.21–7.29 (2 H, m, ArH) and 7.59–7.66 (2 H, m, ArH); isomer$_{minor}$: 1.47 (1 H, dd, J_{trans} 8 and J_{AB} 5, 3′-H), 1.50 (1 H, dd, J_{cis} 10 and J_{AB} 5, 3′-H), 3.37–3.46 (1 H, m, 2′-H), 3.52 (3 H, s, NMe), 5.45 (1 H, d, J_{cis} 10, CH=CH_2), 5.49 (1 H, d, J_{trans} 15, CH=CH_2), 6.14 (1 H, ddd, *J* 15, 10 and 6, C*H*=CH_2), 7.23–7.28 (2 H, m, ArH) and 7.59–7.72 (2 H, m, ArH); δ_C(270 MHz; $CDCl_3$) isomer$_{major}$: 19.1 (t), 31.8 (q), 33.8 (d), 44.2 (s), 117.1 (d), 119.8 (t), 123.6 (d), 124.9 (t), 129.7 (d), 131.5 (d), 133.7 (s), 138.5 (s), 163.8 (s); isomer$_{minor}$: 19.1 (t), 28.0 (d), 31.9 (q), 44.5 (s), 117.2 (d), 120.4 (t), 123.6 (d), 125.0 (t), 129.9 (d), 131.6 (d), 133.7 (s), 138.9 (s) and 163.7 (s); *m*/*z* 247 (9%, M^+) and 184 (100).

2′,4-Dimethyl-2′-vinyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10b. Yield 91%, *prisms* (from CH_2Cl_2–diethyl ether), mp 135–136 °C (decomp.) (Found: C, 64.3; H, 5.8; N, 5.5. $C_{14}H_{15}NO_2S$ requires C, 64.34; H, 5.79; N, 5.36%); ν_{max}(KBr)/cm^{-1}: 1660 (C=O) and 1040 (SO); δ_H(270 MHz; $CDCl_3$) 1.12 (3 H, s, 2′-Me), 2.05 and 2.43 (each 1 H, d, *J* 6, 3′-H), 3.57 (3 H, s, NMe), 4.98 (1 H, d, J_{trans} 17, CH=CH_2), 5.08 (1 H, d, J_{cis} 10, CH=CH_2), 5.61 (1 H, dd, *J* 10 and 17, C*H*=CH_2), 7.18–7.27 (2 H, m, ArH) and 7.57–7.62 (2 H, m, ArH); δ_C(270 MHz; $CDCl_3$) 16.4 (q), 24.5 (t), 32.2 (q), 35.1 (s), 49.9 (s), 117.5 (t), 117.6 (d), 123.6 (d), 126.5 (s), 129.6 (d), 133.6 (d), 136.8 (d), 139.1 (s) and 162.5 (s); *m*/*z* 261 (9%, M^+) and 198 (100).

2′,4-Dimethyl-2′-vinyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10b and 2′-isopropenyl-4-methyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10c. Yield 89%, *prisms* as a mixture of **10b** and **10c** (2:1, estimated by the ^1H NMR spectrum) (Found: C, 63.95; H, 5.8; N, 5.2. $C_{14}H_{15}NO_2S$ requires C, 64.34; H, 5.79; N, 5.36%); ν_{max}(KBr)/cm^{-1}: 1655 (C=O) and 1035 (SO); δ_H(400

MHz; $CDCl_3$) 1.11 (3 H, s, **10b**-2′-Me), 1.75 (3 H, s, **10c**-Me), 2.06 and 2.43 (each 1 H, d, *J* 6, **10b**-3′-H), 2.17 (1 H, dd, *J* 5.9 and 7.8, **10c**-3′-H), 2.31 (1 H, dd, *J* 7.8 and 8.3, **10c**-2′H), 2.52 (1 H, dd, *J* 5.9 and 8.3, **10c**-3′-H), 3.53 (3 H, s, **10c**-NMe), 3.57 (3 H, s, **10b**-NMe), 4.91 and 4.96 (each 1 H, s, **10c**-C=CH_2), 4.98 (1 H, d, J_{trans} 17, **10b**-CH=CH_2), 5.19 (1 H, d, J_{cis} 11, **10b**-CH=CH_2), 5.61 (1 H, dd, *J* 11 and 17, **10b**-C*H*=CH_2), 7.18–7.26 (total 4 H, m, ArH) and 7.57–7.66 (total 4 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 16.4 (q, **10b**), 17.8 (t, **10c**), 23.2 (q, **10c**), 24.5 (t, **10b**), 32.2 (q, **10b**), 32.2 (q, **10c**), 35.1 (s, **10b**), 37.8 (d, **10c**), 43.9 (s, **10c**), 49.9 (s, **10b**), 115.4 (t, **10c**), 117.3 (d, **10c**), 117.5 (t, **10b**), 117.6 (d, **10b**), 123.6 (d, **10b**), 123.8 (d, **10c**), 126.1 (s, **10c**), 126.5 (s, **10b**), 129.6 (d, **10b**), 130.3 (d, **10c**), 133.6 (d, **10b**), 133.9 (d, **10c**), 136.8 (d, **10b**), 137.5 (s, **10c**), 138.7 (s, **10c**), 139.1 (s, **10b**), 162.5 (s, **10b**) and 164.8 (s, **10c**); *m*/*z* 261 (8%, M^+) and 198 (100).

4-Methyl-2′-phenyl-2′-vinyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10d. Yield 86%, *prisms* (from EtOAc–hexane), mp 182–186 °C (decomp.) (Found: C, 70.5; H, 5.3; N, 4.3. $C_{19}H_{17}NO_2S$ requires C, 70.56; H, 5.30; N, 4.33%); ν_{max}(KBr)/cm^{-1}: 1665 (C=O) and 1045 (SO); δ_H(400 MHz; $CDCl_3$) 2.37 and 3.07 (each 1 H, d, *J* 6.4, 3′-H), 3.26 (3 H, s, NMe), 4.74 (1 H, d, J_{trans} 17, CH=CH_2), 5.09 (1 H, d, J_{cis} 10, CH=CH_2), 5.82 (1 H, dd, *J* 10 and 17, C*H*=CH_2), 6.74–6.76 (2 H, m, ArH), 7.18–7.31 (5 H, m, ArH) and 7.67–7.73 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 22.5 (t), 31.9 (q), 45.1 (s), 50.7 (s), 117.3 (d), 119.1 (t), 123.7 (d), 126.2 (s), 127.9 (d), 128.4 (d), 128.8 (d), 129.9 (d), 134.2 (d), 135.7 (s), 136.1 (d), 139.3 (s) and 161.2 (s); *m*/*z* 323 (7%, M^+) and 169 (100).

2′-Isopropenyl-2′,4-dimethyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10e. Yield 93%, *prisms* (from CH_2Cl_2–diethyl ether), mp 168–169 °C (decomp.) (Found: C, 65.3; H, 6.2; N, 5.1. $C_{15}H_{17}NO_2S$ requires C, 65.42; H, 6.22; N, 5.09%); ν_{max}(KBr)/cm^{-1}: 1665 (C=O) and 1035 (SO); δ_H(270 MHz; $CDCl_3$) 1.19 and 1.23 (each 3 H, s, Me), 2.21 and 2.36 (each 1 H, d, *J* 6, 3′-H), 3.58 (3 H, s, NMe), 4.81 and 4.91 (each 1 H, s, olefinic H), 7.19–7.30 (2 H, m, ArH) and 7.35–7.65 (2 H, m, ArH); δ_C(270 MHz; $CDCl_3$) 18.2 (q), 21.0 (q), 23.6 (t), 32.1 (q), 40.7 (s), 48.7 (s), 114.9 (t), 117.5 (d), 123.4 (d), 126.7 (s), 129.9 (d), 136.6 (d), 138.7 (s), 142.1 (s) and 162.5 (s); *m*/*z* 275 (16%, M^+) and 212 (100).

4-Methyl-2′-phenyl-2′-(1-phenylvinyl)-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10f. Yield 90%, *prisms* (from CH_2Cl_2–diethyl ether), mp 157 °C (decomp.) (Found: C, 75.1; H, 5.3; N, 3.5. $C_{25}H_{21}NO_2S$ requires C, 75.16; H, 5.30; N, 3.51%); ν_{max}(KBr)/cm^{-1}: 1655 (C=O) and 1055 (SO); δ_H(400 MHz; $CDCl_3$) 2.19 and 3.04 (each 1 H, d, *J* 6, 3′-H), 3.35 (3 H, s, NMe), 4.91 and 5.31 (each 1 H, s, olefinic H), 7.11–7.34 (12 H, m, ArH) and 7.63–7.71 (2 H, m, ArH); δ_C(400 MHz; $CDCl_3$) 23.8 (t), 32.2 (q), 47.7 (s), 50.2 (s), 117.6 (d), 119.7 (t), 123.7 (d), 125.8 (s), 127.3 (d), 127.7 (d), 127.9 (d), 128.2 (d), 128.4 (d), 128.6 (d), 130.5 (d), 134.0 (d), 138.7 (s), 139.5 (s), 140.1 (s), 146.4 (s) and 161.3 (s); *m*/*z* 399 (2%, M^+) and 245 (100).

2′-*p*-Fluorophenyl-2′-[1-(*p*-fluorophenyl)vinyl]-4-methyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10g. Yield 88%, *prisms* (from CH_2Cl_2–diethyl ether), mp 157 °C (decomp.) (Found: C, 68.8; H, 4.5; N, 3.3. $C_{25}H_{19}F_2NO_2S$ requires C, 68.95; H, 4.40; N, 3.22%); ν_{max}(KBr)/cm^{-1}: 1665 (C=O) and 1050 (SO); δ_H(400 MHz; $CDCl_3$) 2.20 and 3.01 (each 1 H, d, *J* 6, 3′-H), 3.37 (3 H, s, NMe), 4.93 and 5.30 (each 1 H, s, olefinic H), 6.90 (2 H, t, $J_{H(o)} = J_{F(o)}$ 8, ArH), 6.91 (2 H, t, $J_{H(o)} = J_{F(o)}$ 8, ArH), 7.07 (2 H, dd, $J_{F(m)}$ 5 and $J_{H(o)}$ 8, ArH), 7.14 (2 H, dd, $J_{F(m)}$ 5 and $J_{H(o)}$ 8, ArH), 7.28 (1 H, t, *J* 8, ArH), 7.32 (1 H, d, *J* 8, ArH), 7.62 (1 H, t, *J* 8, ArH) and 7.69 (1 H, t, *J* 8, ArH); δ_C(400 MHz; $CDCl_3$) 23.8 (t), 32.2 (q), 47.2 (s), 50.3 (s), 115.1 (d, $^2J_{CF}$ 22), 115.4 (d, $^2J_{CF}$ 20), 117.7 (d), 119.5 (t), 123.8 (d), 125.8 (s), 128.9 (d, $^3J_{CF}$ 9), 130.3 (d), 130.4 (d, $^3J_{CF}$ 9), 134.0 (s), 134.2 (d), 135.9 (s), 139.3 (s), 145.4 (s), 161.1 (s), 162.0 (s, $^1J_{CF}$ 248) and 162.5 (s, $^1J_{CF}$ 248); *m*/*z* 435 (2%, M^+) and 281 (100).

2′-*p*-Chlorophenyl-2′-[1-(*p*-chlorophenyl)vinyl]-4-methyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10h. Yield 92%, *prisms* (from CH_2Cl_2–diethyl ether), mp 215 °C (decomp.) (Found: C, 63.8; H, 4.2; N, 3.0. $C_{25}H_{19}Cl_2NO_2S$ requires C, 64.11; H, 4.09; N, 3.00%); ν_{max}(KBr)/cm^{-1}: 1670 (C=O) and 1055 (SO); δ_H(400 MHz; $CDCl_3$) 2.21 and 3.00 (each 1 H, d, *J* 6, 3′-H), 3.37 (3 H, s, NMe), 4.98 and 5.35 (each 1 H, s, olefinic H), 7.01–7.32 (10 H, m, ArH), 7.58 (1 H, d, *J* 7, ArH) and 7.69 (1 H, t, *J* 7, ArH); δ_C(400 MHz; $CDCl_3$) 24.1 (t), 32.7 (q), 47.4 (s), 50.6 (s), 118.0 (d), 120.3 (t), 124.2 (d), 126.1 (s), 128.7 (d), 129.0 (d), 130.3 (d), 130.7 (d), 134.2 (s), 134.3 (s), 134.5 (d), 136.9 (s), 138.4 (s), 139.6 (s), 145.5 (s) and 161.3 (s); *m*/*z* 467 (3%, M^+) and 313 (100).

X-Ray study of 2′-isopropenyl-2′,4-dimethyl-1-oxido-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine-2-spiro-1′-cyclopropane 10e

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

Crystal data. $C_{15}H_{17}NO_2S$, $M = 275.36$, orthorhombic, $a = 13.067(6)$, $b = 13.094(2)$, $c = 8.299(1)$ Å, $V = 1420.0(6)$ Å^3 (from setting angles of 25 centred reflections with $20.64 < 2\theta < 32.15°$; $\lambda = 0.710\,69$ Å, $T = 296$ K), space group $P2_12_12_1$ (# 19), $Z = 4$, $D_c = 1.288$ g cm^{-3}, colourless needles $0.10 \times 0.20 \times 0.20$ mm, μ(Mo-Kα) = 2.15 cm^{-1}.

Data collection and processing. Rigaku AFC-5R four-circle diffractometer with 12 kW rotating anode generator, $\bar{\omega}/2\theta$ scans with $\bar{\omega}$ scan width $(1.21 + 0.30 \tan \theta)°$, graphite-monochromated Mo-Kα X-radiation; 1887 reflections measured to $2\theta_{max} = 55°$, giving 1158 which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption.

Structure solution and refinement. Automatic direct method [16] (all non-H atoms). Full-matrix least-squares refinement [17] with all non-H atoms anisotropic. The weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. Final $R = 0.050$, $R_w = 0.067$, $S = 2.16$ for 172 refined parameters. The final ΔF synthesis showed no peaks above ±0.21 e Å^{-3}.

Acknowledgements

This work was supported in part by a grant from the Ministry of Education, Science, Sports and Culture.

References

1 K. Ogura, N. Yahata, T. Fujimori and M. Fujita, *Tetrahedron Lett.*, 1990, **31**, 4621.

2 For reviews see: G. A. Russell and G. I. Mikol, in *Mechanisms of Molecular Migrations*, ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1968, **1**, 15; T. Durst, *Adv. Org. Chem.*, 1969, **6**, 285; J. P. Marino, in *Topics in Sulfur Chemistry*, ed. A. Senning, George Thieme, Stuttgart, 1976, **1**, 1; S. Oae, in *Organic Chemistry of Sulfur*, Plenum Press, New York, 1977, 406; T. Numata and S. Oae, *Yuki Gosei Kagaku Kyokaishi*, 1977, **35**, 726 (*Chem. Abstr.*, 1978, **88**, 5639s); T. Numata, *Yuki Gosei Kagaku Kyokaishi*, 1978, **36**, 845 (*Chem. Abstr.*, 1979, **90**, 13 6847x); S. Oae and T. Numata, in *Isotopes in Organic Chemistry*, ed. E. Buncel and C. C. Lee, Elsevier, New York, 1980, **5**, 45; S. Oae, T. Numata and T. Yoshimura, in *The Chemistry of the Sulfonium Group*, ed. C. J. M. Stirling and S. Patai, Wiley, New York, 1981, **2**, 571; O. D. Lucchi, U. Miotti and G. Modena, *Org. React.*, 1991, **40**, 157.

3 C. R. Johnson, J. C. Sharp and W. G. Phillips, *Tetrahedron Lett.*, 1967, 5299.

4 (*a*) G. A. Koppel and L. J. McShane, *J. Am. Chem. Soc.*, 1978, **100**, 288; (*b*) I. Cutting and P. J. Parsons, *Tetrahedron Lett.*, 1981, **22**, 2021; (*c*) R. D. Miller and D. R. McKean, *Tetrahedron Lett.*, 1983, **24**, 2619; (*d*) C. U. Kim, P. F. Misco, U. J. Haynes and D. N. McGregor, *J. Med. Chem.*, 1984, **27**, 1225; (*e*) R. D. Miller and R. Hässig, *Tetrahedron Lett.*, 1984, **25**, 5351; (*f*) R. Hunter and C. D. Simon, *Tetrahedron Lett.*, 1986, **27**, 1385; (*g*) Y. Kita, O. Tamura, F. Itoh, H. Yasuda, T. Miki and Y. Tamura, *Chem. Pharm. Bull.*, 1987, **35**, 562; (*h*) T. Ishihara, T. Shinozaki and

M. Kuroboshi, *Chem. Lett.*, 1989, 1369; (*i*) R. Hunter, L. Carlton, P. F. Cirillo, J. P. Michael, C. D. Simon and D. S. Walter, *J. Chem. Soc.*, *Perkin Trans. 1*, 1989, 1631; (*j*) R. Hunter, J. P. Michael, C. D. Simon and D. S. Walter, *Tetrahedron*, 1994, **50**, 9365.

5 H. Kosugi, H. Uda and S. Yamagiwa, *J. Chem. Soc.*, *Chem. Commun.*, 1975, 192; S. Yamagiwa, H. Sato, N. Hoshi, H. Kosugi and H. Uda, *J. Chem. Soc.*, *Perkin Trans. 1*, 1979, 570.

6 Y. Hashimoto and T. Mukaiyama, *Chem. Lett.*, 1986, 755; Y. Hashimoto, H. Sugumi, T. Okauchi and T. Mukaiyama, *Chem. Lett.*, 1987, 1691; T. Takeda, A. Nakamura, T. Furukawa and T. Fujiwara, *Tetrahedron Lett.*, 1990, **31**, 6685; R. Brückner and R. Huisgen, *J. Org. Chem.*, 1991, **56**, 1677; M. Harmata, V. R. Fletcher and R. J. Claassen II, *J. Am. Chem. Soc.*, 1991, **113**, 9861; R. Hunter, J. P. Michael and D. S. Walter, *Tetrahedron*, 1994, **50**, 9377.

7 E. J. Corey and D. J. Hoover, *Tetrahedron Lett.*, 1982, **23**, 3463.

8 R. B. Morin, D. O. Spry and R. A. Mueller, *Tetrahedron Lett.*, 1969, 849; R. B. Morin and D. O. Spry, *J. Chem. Soc.*, *Chem. Commun.*, 1970, 335; F. Chioccara, L. Oliva and G. Prota, *Synthesis*, 1978, 744; M. Hori, T. Kataoka, H. Shimizu and Y. Imai, *Chem. Pharm. Bull.*, 1979, **27**, 1982; M. Hori, T. Kataoka, H. Shimizu and N. Ueda, *Tetrahedron Lett.*, 1981, **22**, 1701; H. Shimizu, N. Ueda, T. Kataoka and M. Hori, *Chem. Pharm. Bull.*, 1984, **32**, 2571.

9 T. Kataoka, H. Matsumoto, T. Iwama, T. Ito and H. Shimizu, *J. Chem. Soc.*, *Perkin Trans. 1*, 1995, 737.

10 (*a*) T. Iwama, H. Matsumoto and T. Kataoka, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 835; (*b*) T. Kataoka, H. Matsumoto, T. Iwama and H. Shimizu, *Chem. Lett.*, 1995, 459; (*c*) E. Pretsch, T. Clerc, J. Seibl and W. Simon, translated by Biemann, in *Tables of Spectral Data for Structure Determination of Organic Compounds*, ed. W. Fresenius, J. F. K. Huber, E. Pungor, G. A. Rechnits, W. Simon and T. S. West, Springer-Verlag, New York, 1989, H215.

11 Y. Tamura, H. Maeda, S. Akai, K. Ishiyama and H. Ishibashi, *Tetrahedron Lett.*, 1981, **22**, 4301; L. N. Mander and P. H. C. Mundill, *Synthesis*, 1981, 620; Y. Tamura, H. Maeda, S. Akai and H. Ishibashi, *Tetrahedron Lett.*, 1982, **23**, 2209; H, Ishibashi, M. Okada, H. Komatsu, M. Ikeda and Y. Tamura, *Synthesis*, 1985, 643; H. Ishibashi, H. Ozeki and M. Ikeda, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 654; H. Ishibashi, S. Harada, M. Okada, M. Ikeda, K. Ishiyama, H. Yamashita and Y. Tamura, *Synthesis*, 1986, 847.

12 P. Brownbridge and S. Warren, *J. Chem. Soc.*, *Chem. Commun.*, 1975, 820; P. Brownbridge and S. Warren, *J. Chem. Soc.*, *Perkin Trans. 1*, 1977, 1131.

13 H. Tawada, Y. Sugiyama, H. Ikeda, Y. Yamamoto and K. Meguro, *Chem. Pharm. Bull.*, 1990, **38**, 1238.

14 H. Ishibashi, Y. Kitano, K. Nakatani, M. Okada, M. Ikeda, M. Okura and Y. Tamura, *Tetrahedron Lett.*, 1984, **25**, 4231; H. Ishibashi, M. Okada, H. Nakatani and M. Ikeda, *J. Chem. Soc.*, *Perkin Trans. 1*, 1986, 1763.

15 T Kataoka, Y. Nakamura, H. Matsumoto, T. Iwama, H. Kondo, H. Shimizu, O. Muraoka and G. Tanabe, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 309.

16 Structure Solution Methods: MITHRIL; C. J. Gilmore, MITHRIL—an integrated direct methods computer program, Univ. of Glasgow, Scotland, *J. Appl. Crystallogr.*, 1984, **17**, 42; DIRDIF: P. T. Beurskens, DIRDIF: Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed. Nijmegen, Netherlands.

17 D. T. Cromer and J. T. Waber, Table 2.2A in *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, 1974, vol. 4.

Paper 7/08724A
Received 3rd *December* 1997
Accepted 24th *February* 1998