

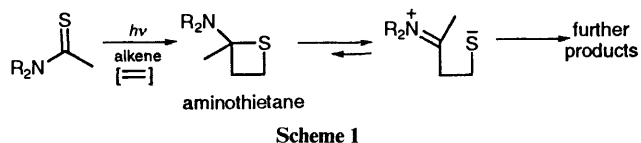
Photochemical Reactions of Benzothiazole-2-thiones

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The photochemical reactions of benzothiazole-2-thiones in the presence of alkenes have been examined. Irradiation of *N*-unsubstituted benzothiazole-2-thione in the presence of electron-poor alkenes gave 2-substituted benzothiazoles. Irradiation of *N*-substituted benzothiazole-2-thiones and electron-poor alkenes yielded 2-alkylidenebenzothiazoles and the unexpected spiro-1,3-dithianes. The formation of these photoproducts can be explained in terms of the intermediacy of amino-spirothietanes, which are derived by [2 + 2] photocycloaddition of the C=S bond of benzothiazole-2-thiones to the C=C bond of alkenes.

The photochemistry of thiocarbonyl compounds is well documented¹ and these compounds behave like carbonyl compounds in many respects. In particular, they give, by [2 + 2] photocycloaddition with alkenes, thietanes as primary products, which are often unstable and transformed into fragmentation products. Thioamides also undergo both inter- and intra-molecular photocycloaddition with alkenes.^{1d,2} Amino-thietanes are suggested as intermediates in these reactions, although such compounds have not been isolated except for one example.³ This may be ascribed to the participation of the lone-pair electrons on the nitrogen atom, which facilitate the C-S bond cleavage in the thietane ring leading to the formation of the zwitterion (Scheme 1). Meanwhile, thietanes are products

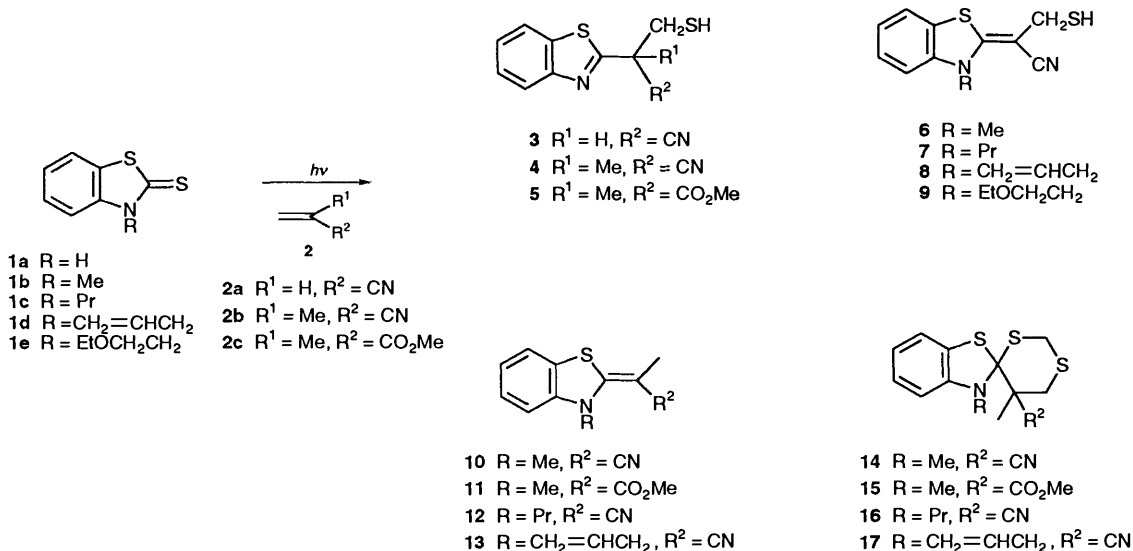


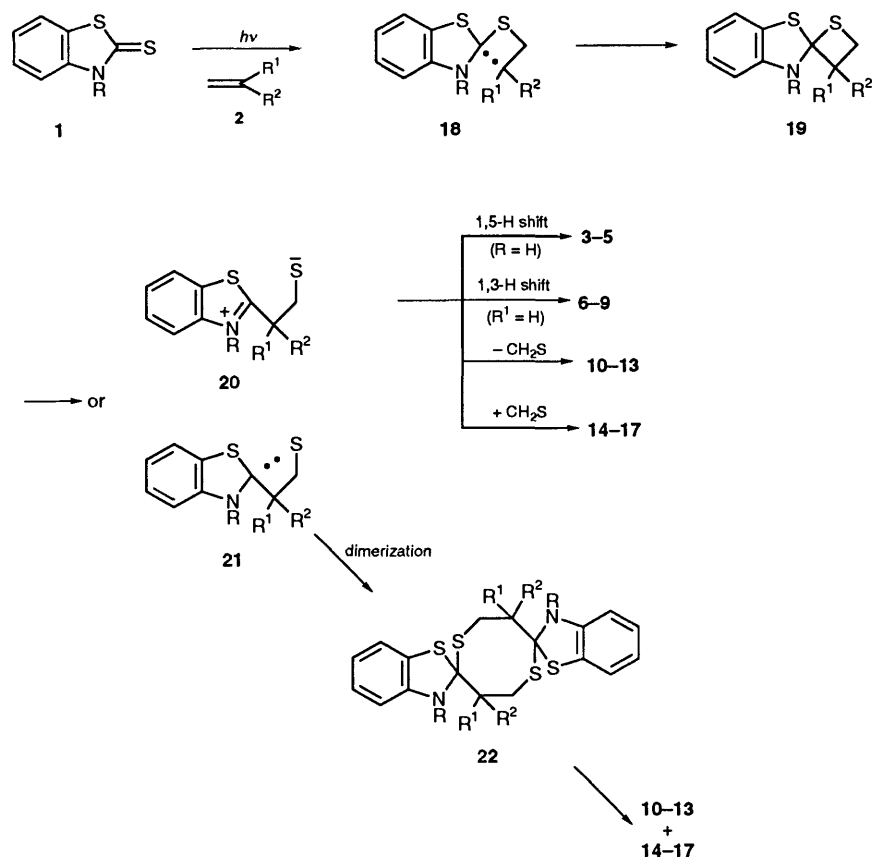
resulting from the [2 + 2] photocycloaddition of thioimides,⁴ thiouracils⁵ and 2-thioparabanic acids⁶ to alkenes, in which the effect of the lone-pair electrons on the nitrogen atom is reduced by conjugation with the second carbonyl group. We now present the results of photochemical reactions between benzothiazole-2-thiones **1** and electron-poor alkenes **2**, which yield 2-substituted benzothiazoles **3-5**, 2-alkylidenebenzothi-

azoles **6-13** and the rather unexpected spiro 1,3-dithiane derivatives **14-17**.

Results and Discussion

When a benzene or 1,2-dimethoxyethane (DME) solution of the benzothiazole-2-thiones **1** was irradiated with a high-pressure mercury lamp through a Pyrex filter under argon, unchanged starting material was recovered. However, irradiation of *N*-unsubstituted benzothiazole-2-thione **1a** in DME in the presence of electron-poor alkenes such as acrylonitrile **2a**, methacrylonitrile **2b** and methyl methacrylate **2c** gave 2-substituted benzothiazoles **3-5**, probably derived from the amino-thietane intermediate. The structures of photoproducts **3-5** were determined on the basis of their spectral and analytical data. Irradiation of *N*-substituted benzothiazole-2-thiones **1b-e** and acrylonitrile **2a** in benzene gave 2-mercaptoethylidenebenzothiazoles **6-9**. The ¹H NMR spectra of photoproducts **6-9** showed the presence of a mercaptomethyl group [δ 2.01-2.03 (1 H, t, SH) and 3.43-3.48 (2 H, d, CH₂)]. The IR spectra showed an absorption characteristic of thiol (2530-2560 cm⁻¹). In contrast, irradiation of 3-methylbenzothiazole-2-thione **1b** in benzene in the presence of methacrylonitrile **2b** yielded 2-ethylidenebenzothiazole **10** and the unexpected spiro-1,3-dithiane **14** both in 40% yield. The structures of **10** and **14** were confirmed on the basis of spectral and elemental results. In the ¹H NMR spectrum of the latter, two AB systems attributed to two CH₂S





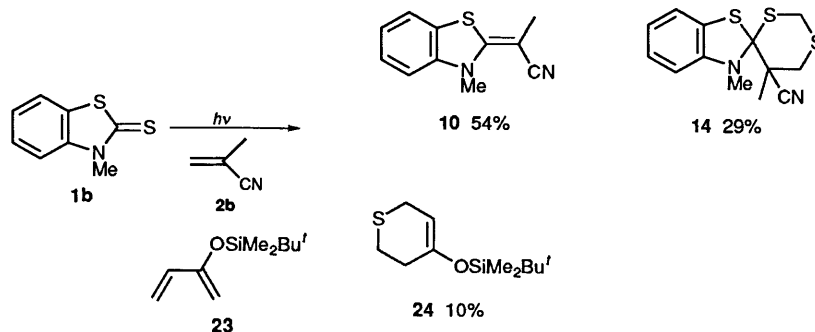
methylene protons appeared. The ^{13}C NMR spectrum of **14** showed a methyl carbon, two CH_2S methylene carbons, a quaternary carbon and *N*-methyl and aromatic carbons. In a similar manner, 2-alkylidenebenzothiazoles **11–13** and spiro-1,3-dithianes **15–17** were obtained in reasonable yields when benzothiazole-2-thiones **1c–e** were irradiated in the presence of 1,1-disubstituted electron-poor alkenes such as methacrylonitrile **2b** and methyl methacrylate **2c**.

A plausible mechanism for the formation of the photoproducts **3–17** is presented in Scheme 2. In this mechanism, an aminothietane **19** is formed regioselectively through the photochemical [2 + 2] cycloaddition of the C=S bond of **1** to C=C bond of **2**. The regiochemistry is in accord with the formation of the more stable diradical intermediate **18** in the [2 + 2] photocycloaddition process.^{2,4–6} The aminothietane thus formed is unstable owing to the participation of the lone-pair electrons on the nitrogen atom and then undergoes thietane ring cleavage to yield the zwitterion **20**. 1,5-Hydrogen transfer from nitrogen to sulfur gave 2-substituted benzothiazoles **3–5**, while 1,3-hydrogen transfer from carbon to sulfur yielded 2-mercaptoethylidenebenzothiazoles **6–9**. The elimination of thioformaldehyde from **20** gave 2-ethylidenebenzothiazoles **10–13** and the thioformaldehyde thus formed was trapped with zwitterion **20** to yield spiro-1,3-dithianes **14–17**. Homolytic cleavage of the aminothietane ring involving diradical **21** would also be possible. The diradical **21** dimerized to produce the eight-membered compound **22**, which then decomposed by disproportionation yielding an equimolar amount of 2-ethylidenebenzothiazole and spiro-1,3-dithiane. Formation of similar photoproducts was reported in the photochemistry of thiouracil and methacrylonitrile by Jouin and Fourrey.^{5b} They reported the formation of an eight-membered intermediate produced by the dimerization of biradical species, of which formation was confirmed from the mass spectrum. In the

photoreaction of *N*-allylbenzothiazole **1d** and methacrylonitrile **2b**, 2-alkylidenebenzothiazole **13** and spiro-1,3-dithiane **17** were produced in 54 and 40% yields, respectively, suggesting that the photochemical pathway for the formation of **13** and **17** proceeds *via* zwitterion intermediate **20**. If the formation of photoproducts **13** and **17** proceeds *via* diradical intermediate **21** followed by dimerization and decomposition with disproportionation, an equimolar amount of photoproducts **13** and **17** must be formed (yields of each photoproduct do not exceed 50%). The spiro-1,3-dithiane **14** decomposed thermally to give alkylidenebenzothiazole **10** and photochemical decomposition of **14** to **10** was not observed. Furthermore, an attempt to detect the formation of thioformaldehyde was made using 2-(*tert*-butyldimethylsiloxy)butadiene **23**.⁷ Irradiation of 3-methylbenzothiazole-2-thione **1b** in the presence of both methacrylonitrile **2b** and siloxydiene **23** under the same conditions as described above gave alkylidenebenzothiazole **10**, spiro-1,3-dithiane **14**, and the silyl enol ether of tetrahydrothiopyran **24**. The formation of **24** can be best explained in terms of [2 + 4] cycloaddition of siloxydiene **23** and thioformaldehyde, which was eliminated from zwitterion intermediate **20**. These findings support the idea that the zwitterion **20** is an intermediate in the reaction of photoexcited benzothiazole-2-thiones **1** with electron-poor alkenes **2**.

Experimental

M.p.s and b.p.s are uncorrected. IR spectra were measured using a Hitachi 260–30 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q (90 MHz) or an FX 100 (100 MHz) spectrometer using CDCl_3 as solvent and tetramethylsilane as internal standard. *J* Values are given in Hz. Yields of photoproducts are given in Table 1.

**Table 1** Yield of the photoproducts 3–17

Run	Thione	Alkene	Yield (%)
1	1a	2a	3 (27)
2	1a	2b	4 (64)
3	1a	2c	5 (92)
4	1b	2a	6 (21)
5	1b	2b	10 (40), 14 (40)
6	1b	2c	11 (14), 15 (16)
7	1c	2a	7 (26)
8	1c	2b	12 (33), 16 (28)
9	1d	2a	8 (34)
10	1d	2b	13 (54), 17 (44)
11	1e	2a	9 (41)

Preparation of Benzothiazole-2-thiones 1.—Benzothiazole-2-thiones **1a, b** are commercially available. Benzothiazole-2-thiones **1c–e** were prepared by the thionation of the corresponding benzothiazol-2-ones with 2,4-bis(*p*-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-dithione (Lawesson reagent: LR). A solution of the benzothiazol-2-ones **1** (10 mmol) and LR (5.5 mmol) in toluene (70 cm³) was refluxed under argon for 1–3 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–hexane (4:1–20:1) to yield the benzothiazole-2-thiones **1**.

3-Propylbenzothiazole-2-thione 1c. M.p. 76–76.5 °C (Found: C, 57.3; H, 5.3; N, 6.7. C₁₀H₁₁NS₂ requires C, 57.4; H, 5.3; N, 6.7%); ν_{\max} (KBr)/cm⁻¹ 1595, 1505, 1460, 1375, 1320 and 1225; δ_{H} 1.03 (3 H, t, *J* 7.3), 1.64–2.03 (2 H, m), 4.35 (2 H, t, *J* 7.8) and 7.15–7.50 (4 H, m); δ_{C} 11.3 (q), 20.2 (t), 47.6 (t), 112.3 (d), 121.2 (d), 124.5 (d), 126.8 (d), 127.5 (s), 141.3 (s) and 188.6 (s).

3-Allylbenzothiazole-2-thione 1d. M.p. 67.5–68 °C (Found: C, 58.1; H, 4.35; N, 6.75. C₁₀H₉NS₂ requires C, 57.95; H, 4.35; N, 6.75%); ν_{\max} (KBr)/cm⁻¹ 1630, 1455, 1370, 1310, 1255 and 1210; δ_{H} 5.06–5.18 (2 H, m), 5.20–5.35 (2 H, m), 5.73–6.11 (1 H, m) and 7.13–7.53 (4 H, m); δ_{C} 48.3 (t), 112.8 (d), 118.8 (t), 121.3 (d), 124.8 (d), 126.9 (d), 127.5 (s), 129.5 (d), 141.3 (s) and 189.3 (s).

3-Ethoxyethylbenzothiazole-2-thione 1e. M.p. 50–51 °C (Found: C, 54.95; H, 5.5; N, 5.75. C₁₁H₁₃NS₂ requires C, 55.2; H, 5.45; N, 5.85%); ν_{\max} (KBr)/cm⁻¹ 1450, 1375, 1320, 1255 and 1210; δ_{H} 1.10 (3 H, t, *J* 7.3), 3.46 (2 H, q, *J* 7.3), 3.83 (2 H, t, *J* 5.8), 4.62 (2 H, t, *J* 5.8) and 7.17–7.51 (4 H, m); δ_{C} 15.0 (q), 46.7 (t), 66.8 (t), 66.9 (t), 113.5 (d), 120.8 (d), 124.5 (d), 126.6 (d), 127.3 (s), 142.3 (s) and 189.1 (s).

General Procedure for the Photochemical Reaction of Benzothiazole-2-thiones 1 with Alkenes 2.—A solution of **1** (200 mg) and **2** (ca. 1 cm³) in 1,2-dimethoxyethane (70 cm³) (for **1a**) or benzene (70 cm³) (for **1b–e**) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (300 W) under argon for 6–15 h at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–ethyl acetate (30:1–5:1) as eluent to give the corresponding photoproducts **3–17** along with unchanged **1**.

2-(1-Cyano-2-mercaptoethyl)benzothiazole 3. B.p. 160 °C/2 mmHg (decomp.) (Found: C, 54.7; H, 3.5; N, 13.0. C₁₀H₈N₂S₂ requires C, 54.5; H, 3.65; N, 12.7%); ν_{\max} (film)/cm⁻¹ 2550 and 2240; δ_{H} 1.98 (1 H, t, *J* 9.3), 3.27 (2 H, dd, *J* 6.3, 9.3), 4.59 (1 H, t, *J* 6.3), 7.26–7.58 (2 H, m) and 7.76–8.12 (2 H, m); δ_{C} 27.7 (t), 40.5 (d), 117.1 (s), 121.7 (d), 123.4 (d), 126.0 (d), 126.6 (d), 135.0 (s), 152.6 (s) and 161.8 (s).

2-(1-Cyano-1-mercaptomethyl)ethylbenzothiazole 4. B.p. 148 °C/2 mmHg (Found: C, 56.65; H, 4.35; N, 12.0. C₁₁H₁₀N₂S₂ requires C, 56.4; H, 4.3; N, 11.95%); ν_{\max} (film)/cm⁻¹ 2560 and 2230; δ_{H} 1.84 (1 H, X of ABX, *J* 9.3), 1.95 (3 H, s), 3.12 (1 H, A of ABX, *J* 9.3, 14.2), 3.36 (1 H, B of ABX, *J* 9.3, 14.2), 7.27–7.57 (2 H, m) and 7.81–8.06 (2 H, m); δ_{C} 25.5 (q), 34.8 (t), 45.7 (s), 120.2 (s), 121.6 (d), 123.3 (d), 125.8 (d), 126.5 (d), 134.7 (s) and 167.7 (s).

2-(1-Methoxycarbonyl-1-mercaptomethyl)ethylbenzothiazole 5. B.p. 80 °C/10⁻² mmHg (Found: C, 54.05; H, 4.9; N, 5.3. C₁₂H₁₃NO₂S₂ requires C, 53.9; H, 4.9; N, 5.25%); ν_{\max} (film)/cm⁻¹ 2560 and 1730; δ_{H} 1.59 (1 H, X of ABX, *J* 8.8), 1.86 (3 H, s), 3.24 (1 H, A of ABX, *J* 9.3, 14.2), 3.41 (1 H, B of ABX, *J* 9.3, 14.2), 3.75 (3 H, s), 7.25–7.54 (2 H, m) and 7.80–8.07 (2 H, m); δ_{C} 22.8 (q), 33.3 (t), 52.7 (q), 54.3 (s), 121.3 (d), 123.1 (d), 125.1 (d), 125.9 (d), 135.0 (s), 152.4 (s), 171.3 (s) and 172.4 (s).

2-(1-Cyano-2-mercapto)ethylidene-3-methylbenzothiazole 6. M.p. 114–115 °C (Found: C, 56.35; H, 4.3; N, 11.9. C₁₁H₁₀N₂S₂ requires C, 56.4; H, 4.25; N, 11.95%); ν_{\max} (KBr)/cm⁻¹ 2530 and 2160; δ_{H} 2.01 (1 H, t, *J* 7.8), 3.43 (2 H, d, *J* 7.8), 3.74 (3 H, s) and 6.89–7.43 (4 H, m); δ_{C} 29.5 (t), 34.0 (q), 67.6 (s), 109.9 (d), 120.8 (s), 121.4 (d), 122.4 (d), 126.8 (d), 128.2 (s), 143.1 (s) and 159.8 (s).

2-(1-Cyano-2-mercapto)ethylidene-3-propylbenzothiazole 7. M.p. 65–66 °C (Found: C, 59.55; H, 5.45; N, 10.6. C₁₃H₁₄N₂S₂ requires C, 59.5; H, 5.35; N, 10.65%); ν_{\max} (KBr)/cm⁻¹ 2540 and 2160; δ_{H} 1.06 (3 H, t, *J* 7.8), 1.69–2.02 (2 H, m), 2.02 (1 H, t, *J* 7.3), 3.47 (2 H, d, *J* 7.3), 4.18 (2 H, t, *J* 7.3) and 6.93–7.46 (4 H, m); δ_{C} 10.5 (q), 21.4 (t), 29.9 (t), 47.4 (t), 67.8 (s), 110.0 (d), 120.5 (s), 121.4 (d), 122.2 (d), 123.6 (s), 126.8 (d), 142.7 (s) and 158.1 (s).

2-(1-Cyano-2-mercapto)ethylidene-3-allylbenzothiazole 8. M.p. 97–98 °C (Found: C, 59.9; H, 4.75; N, 10.7. C₁₃H₁₂N₂S₂ requires C, 59.95; H, 4.65; N, 10.75%); ν_{\max} (KBr)/cm⁻¹ 2550 and 2170; δ_{H} 2.01 (1 H, t, *J* 7.8), 3.46 (2 H, d, *J* 7.8), 4.72–4.93 (2 H, m), 5.27–5.38 (2 H, m), 5.88–6.21 (1 H, m) and 6.82–7.47 (4 H, m); δ_{C} 29.7 (t), 48.2 (t), 68.7 (s), 110.3 (d), 117.8 (d), 120.3 (s), 121.4 (d), 122.6 (d), 123.5 (s), 126.9 (d), 130.4 (d), 142.7 (s) and 158.0 (s).

2-(1-Cyano-2-mercapto)ethylidene-3-ethoxyethylbenzothiazole 9. M.p. 50–51 °C (Found: C, 57.2; H, 5.5; N, 9.5. C₁₃H₁₆NOS₂ requires C, 57.5; H, 5.5; N, 9.6%); ν_{\max} (KBr)/cm⁻¹ 2560 and 2160; δ_{H} 1.13 (3 H, t, *J* 6.8), 2.03 (1 H, t, *J* 7.3), 3.40–3.61 (2 H, m), 3.48 (2 H, d, *J* 7.3), 3.88 (2 H, t, *J* 5.3), 4.43 (2 H, t, *J* 5.3) and 6.98–7.41 (4 H, m); δ_{C} 15.1 (q), 29.8 (t), 42.0 (t), 66.9 (t), 68.0 (s), 69.1 (t), 111.6 (d), 120.6 (s), 121.0 (d), 122.4 (d), 132.2 (s), 126.6 (d), 143.5 (s) and 158.6 (s).

2-(1-Cyano)ethylidene-3-methylbenzothiazole 10. M.p. 134–135 °C (Found: C, 65.25; H, 4.95; N, 13.85. C₁₁H₁₀N₂S requires C, 65.35; H, 4.95; N, 13.85%); ν_{\max} (KBr)/cm⁻¹ 2160; δ_{H} 1.88 (3 H, s), 3.73 (3 H, s) and 6.91–7.38 (4 H, m); δ_{C} 19.0 (q), 33.8 (q), 61.6

(s), 109.3 (d), 121.1 (s), 122.6 (d), 123.6 (d), 126.5 (d), 143.6 (s) and 158.0 (s).

2-(1-Methoxycarbonyl)ethylidene-3-methylbenzothiazole 11. M.p. 131–132 °C (Found: C, 61.25; H, 5.6; N, 5.95. $C_{12}H_{13}NO_2S$ requires C, 61.25; H, 5.55; N, 5.95%); $\nu_{max}(KBr)/cm^{-1}$ 1740; δ_H 2.21 (3 H, s), 3.63 (3 H, s), 3.77 (3 H, s) and 6.88–7.42 (4 H, m); δ_C 14.6 (q), 37.9 (q), 51.1 (q), 88.0 (s), 109.6 (d), 120.8 (d), 121.9 (d), 125.5 (d), 127.5 (s), 143.1 (s), 159.7 (s) and 167.0 (s).

2-(1-Cyano)ethylidene-3-propylbenzothiazole 12. M.p. 73–74 °C (Found: C, 67.4; H, 6.1; N, 12.1. $C_{13}H_{14}N_2S$ requires C, 67.8; H, 6.15; N, 12.15%); $\nu_{max}(KBr)/cm^{-1}$ 2150; δ_H 1.05 (3 H, t, *J* 6.8), 1.69–2.00 (2 H, m), 1.90 (3 H, s), 4.07–4.24 (2 H, m) and 6.85–7.40 (4 H, m); δ_C 10.5 (q), 19.3 (q), 21.4 (t), 47.2 (t), 60.7 (s), 109.4 (d), 121.2 (d), 121.6 (d), 122.0 (s), 123.8 (s), 126.5 (d), 143.3 (s) and 157.1 (s).

2-(1-Cyano)ethylidene-3-allylbenzothiazole 13. M.p. 98–99 °C (Found: C, 68.05; H, 5.5; N, 12.25. $C_{13}H_{12}N_2S$ requires C, 68.4; H, 5.3; N, 12.25%); $\nu_{max}(KBr)/cm^{-1}$ 2150; δ_H 1.90 (3 H, s), 4.82–4.91 (2 H, m), 5.21–5.36 (2 H, m), 5.83–6.21 (1 H, m) and 6.82–7.41 (4 H, m); δ_C 17.2 (q), 48.0 (t), 61.5 (s), 109.7 (d), 121.1 (d), 121.7 (s), 121.9 (d), 123.6 (s), 126.6 (d), 130.8 (d), 143.3 (s) and 156.9 (s).

5'-Cyano-3,5'-dimethylbenzothiazole-2-spiro-4'-(1',3'-dithiane) 14. M.p. 125–126 °C (Found: C, 53.1; H, 4.8; N, 9.5. $C_{13}H_{14}N_2S_3$ requires C, 53.0; H, 4.8; N, 9.5%); $\nu_{max}(KBr)/cm^{-1}$ 2220; δ_H 1.71 (3 H, s), 2.92 (1 H, dd, *J* 2.4, 14.7), 3.20 (3 H, s), 3.25 (1 H, d, *J* 14.7), 3.59 (1 H, dd, *J* 2.4, 14.2), 4.52 (1 H, d, *J* 14.2), 6.45–6.55 (1 H, m), 6.76–6.86 (1 H, m) and 6.98–7.16 (2 H, m); δ_C 24.7 (q), 32.1 (t), 41.0 (q), 32.7 (t), 46.0 (s), 95.9 (s), 108.4 (d), 120.0 (s), 121.0 (s), 126.3 (d) and 147.4 (s).

5'-Methoxycarbonyl-3,5'-dimethylbenzothiazole-2-spiro-4'-(1',3'-dithiane) 15. B.p. 130 °C/2 mmHg (decomp.); $\nu_{max}(\text{film})/cm^{-1}$ 1720; δ_H 1.93 (3 H, s), 2.87 (1 H, dd, *J* 2.4, 15.1), 3.07 (3 H, s), 3.51 (3 H, s), 3.52 (1 H, dd, *J* 2.4, 14.2), 3.72 (1 H, d, *J* 15.1), 4.39 (1 H, m), *J* 14.2), 6.30–6.45 (1 H, m), 6.59–6.77 (1 H, m) and 6.90–7.15 (2 H, m); δ_C 21.7 (q), 32.8 (t), 33.8 (q), 40.5 (t), 52.5 (q), 53.1 (s), 95.7 (s), 107.3 (d), 118.8 (d), 120.6 (d), 122.1 (s), 125.8 (d), 147.5 (s) and 172.9 (s) (Found: M^+ , 327.0404. Calc. for $C_{14}H_{17}NO_2S_3$, *M*, 327.0421).

5'-Cyano-5'-methyl-3-propylbenzothiazole-2-spiro-4'-(1',3'-dithiane) 16. M.p. 172–173 °C (Found: C, 55.6; H, 5.65; N, 8.65. $C_{15}H_{18}N_2S_3$ requires C, 55.85; H, 5.6; N, 8.7%); $\nu_{max}(KBr)/cm^{-1}$ 2240; δ_H 1.01 (3 H, s), 1.65–2.05 (2 H, m), 1.76 (3 H, s), 3.00 (1 H, dd, *J* 2.4, 15.1), 3.23 (1 H, d, *J* 15.1), 3.51–4.06 (2 H, m), 3.60 (1 H, dd, *J* 2.4, 14.2), 4.51 (1 H, d, *J* 14.2), 6.49 (1 H, br s) and 6.70–7.16 (3 H, m); δ_C 11.0 (q), 21.8 (t), 25.2 (q), 33.0 (t), 41.3 (t), 46.3 (s), 48.3 (t), 95.5 (s), 108.5 (d), 119.8 (d), 120.5 (s), 120.8 (s), 121.3 (d), 126.3 (d) and 147.1 (s).

3-Allyl-5'-cyano-5'-methylbenzothiazole-2-spiro-4'-(1',3'-dithiane) 17. M.p. 137–138 °C (Found: C, 56.2; H, 5.2; N, 8.65. $C_{15}H_{16}N_2S_3$ requires C, 56.2; H, 5.05; N, 8.75%); $\nu_{max}(KBr)/cm^{-1}$ 2240 and 1640; δ_H 1.77 (3 H, s), 2.97 (1 H, dd, *J* 2.4, 15.1), 3.27 (1 H, d, *J* 15.1), 3.60 (1 H, dd, *J* 2.4, 14.6), 3.86–4.38 (1 H, m), 4.53 (1 H, d, *J* 14.6), 4.48–4.84 (1 H, m), 5.22–5.67 (2 H,

m), 5.76–6.16 (1 H, m) and 6.50–7.25 (4 H, m); δ_C 25.2 (q), 33.0 (t), 41.3 (t), 46.4 (s), 48.6 (t), 95.6 (s), 109.6 (d), 117.9 (t), 120.2 (d), 120.6 (s), 121.2 (d), 126.3 (d), 131.9 (d), 132.9 (s) and 147.1 (s).

Photoreaction of 3-Methylbenzothiazole-2-thione 1b and Methacrylonitrile 2b in the presence of 2-(tert-Butyldimethylsiloxy)buta-1,3-diene 23.—A solution of **1b** (300 mg, 1.65 mmol) and **2b** (ca. 1 cm³) in benzene (70 cm³) was irradiated in the presence of **23** (528 mg, 2.85 mmol) in a similar manner as described above for 6 h. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–hexane (1 : 10) to give the ethylidenebenzothiazole **10**, spiro-dithiane **14**, and thiopyran **24**.

5,6-Dihydro-4-(tert-butyldimethylsiloxy)-2H-thiopyran 24. Oil; $\nu_{max}(\text{film})/cm^{-1}$ 1665; δ_H 0.15 (6 H, s), 0.92 (9 H, s), 2.18–2.38 (2 H, m), 2.77 (2 H, t, *J* 6.3), 3.11–3.19 (2 H, m) and 4.98–5.13 (1 H, m); δ_C –4.3 (q), 18.0 (s), 25.5 (t), 25.7 (t), 25.7 (q), 31.2 (t), 102.2 (d) and 151.5 (s); *m/z* 230 (M^+).

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Paper 3/02074F

Received 13th April 1993

Accepted 8th June 1993