91. Photocycloaddition of Benzothiazole-2-thiones to Alkenes

by **Takehiko Nishio***, **Yo-ichi Mori**, **Ikuo Iida**, and **Akira Hosomi**

Department of Chemistry, University of Tsukuba, Tsukuba-shi, Ibaraki, 305 Japan

(21.I.94)

The photocycloaddition of benzothiazole-2-thiones to electron-rich and aryl-substituted alkenes are described. Irradiation of *N*-unsubstituted benzothiazole-2-thione (**1**) in the presence of alkenes **3** gave 2-(2′-mercaptoalkyl)benzothiazoles **4**, and 2-substituted benzothiazoles **5** and **6** (in the case of **3a** and **3h**, resp.) through the ring cleavage of an intermediate 2-aminothietane (*Schemes 1* and *3*). The latter was formed by [2+2] cycloaddition of the C=S bond of **1** and the C=C bond of **3**. Irradiation of *N*-methylbenzothiazole-2-thione (**2**) and 2-methylpropene (**3a**) gave the spiro-1,3-dithiane **8**, 1,2,6-benzodithiazocin-5-one **9**, and disulfide **10**. The structure of **9** was established by X-ray crystal-structure analysis.

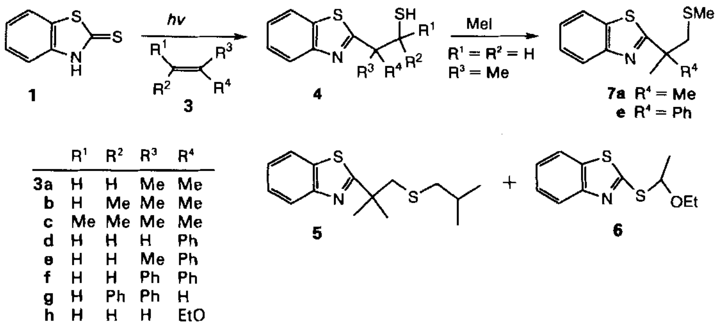
1. Introduction. – The photochemistry of thiocarbonyl compounds has been extensively studied over the past two decades [1–5]. The observed photoreactions of thiocarbonyl compounds often follow a different course from those of analogous carbonyl compounds. A majority of those reported involving thioketones undergo [2+2] cycloaddition to alkenes, alkynes, imines, *etc.*, inter- and intramolecular H-abstraction, and photooxidation [1–5]. Some reports deal with the photochemical reactions involving the C=S group of thioamides [6]. In particular, they give, by [2+2] photocycloaddition with alkenes, aminothietanes as primary products, which are usually unstable and transformed into fragmentation products. This may be ascribed to the participation of the lone-pair electrons of the N-atom, which facilitate the C–S bond cleavage of the thietane ring [6q]. On the other hand, thietanes are products resulting from the [2+2] photocycloaddition of thioimides, in which the effect of lone-pair electrons on the N-atom is reduced by conjugation with the second carbonyl group, to alkenes [7].

We recently reported that the photocycloaddition of benzothiazole-2-thiones with electron-poor alkenes yielded 2-substituted benzothiazoles, 2-alkylidenebenzothiazoles, and spiro-1,3-dithianes [8]. In the present paper, we describe the results of the photocycloaddition of benzothiazole-2-thiones **1** and **2** to electron-rich and aryl-substituted alkenes **3**.

2. Photochemical Reactions of Benzothiazole-2-thiones. – When a benzene or 1,2-dimethoxyethane (DME) solution of the benzothiazole-2-thiones **1** or **2** was irradiated with a high-pressure mercury lamp through a *Pyrex* filter under Ar, unchanged starting material was recovered. However, the 2-(2′-mercaptoalkyl)benzothiazoles **4a–c** and **4h** were formed when *N*-unsubstituted benzothiazole-2-thione **1** was irradiated in DME in the presence of excess of the electron-rich alkenes 2-methylpropene (**3a**), 2-methylbut-2-ene (**3b**), 2,3-dimethylbut-2-ene (**3c**), and ethyl vinyl ether (**3h**; *Scheme 1*). Sulfide **5**, the 1:2 adduct of **1** and **3a**, can be formed only from **3a** and 2-(ethylthio)benzothiazole **6** from **3h**. Irradiation of **1** in the presence of arylalkenes **3d–f** under the same conditions gave

2-(mercaptoalkyl)benzothiazoles **4d–f**. In contrast, irradiation of **1** in the presence of a 1,2-diarylalkene, *trans*-stilbene (**3g**), resulted in recovery of the unchanged thione **1**. Treatment of **4a** and **4e** with MeI yielded the sulfide **7a** and **7e**, respectively, in almost quantitative yield.

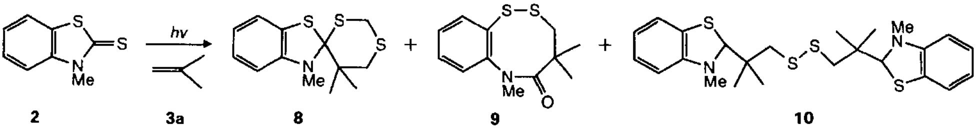
Scheme 1



	R¹	R²	R³	R⁴
3a	H	H	Me	Me
b	H	Me	Me	Me
c	Me	Me	Me	Me
d	H	H	H	Ph
e	H	H	Me	Ph
f	H	H	Ph	Ph
g	H	Ph	Ph	H
h	H	H	H	EtO

Irradiation of **2** in the presence of excess **3a** in benzene under Ar (66% conversion) gave the spiro-1,3-dithiane **8** (6%), 1,2,6-benzodithiazocin-5-one **9** (7%), and disulfide **10** (11%) (*Scheme 2*). Similar results were obtained in non-degassed benzene (66% conversion: **8** (3%), **9** (9%), and **10** (21%)). Irradiation of **2** in the presence of other electron-rich and aryl-substituted alkenes such as **3c**, **3d**, and **3e** resulted in recovery of the unchanged starting material **2**.

Scheme 2



3. Structure of the Photoproducts. – The structures of all new photoproducts were elucidated on the basis of their spectral and analytical data (see *Exper. Part*). Only the most relevant data are discussed below. The structure of **9** was confirmed by X-ray crystal-structure analysis (see *Fig.*).

The ^{1}H-NMR spectra of **4** showed the presence of a SH group at δ 1.30–1.95, and the IR spectra exhibited a characteristic thiol absorption around 2550 cm^{-1}.

The structure of **8** was confirmed by comparison of its spectra with those of previously described analogues [8].

The ^{13}C-NMR spectrum of **9** showed 3 Me groups at δ 23.2, 32.2, and 42.1, a CH_2 group at δ 47.8, a quaternary C-atom at δ 45.7, and a carbonyl C-atom at δ 177.6. In the IR spectrum, an absorption at 1630 cm^{-1} was assigned to the amide carbonyl group.

The MS of **10** showed a molecular peak at m/z 476. The ^{1}H-NMR spectrum displayed five *s* at δ 0.99 (6 H), 1.00 (6 H), 3.00 (6 H), 2.92 (4 H), and 4.83 (2 H) assignable to 3 Me, a CH_2, and a CH group and the ^{13}C-NMR spectrum a *t* at δ 49.8 (CH_2) and a *d* at δ 82.8 (CH).

X-Ray Analysis of **9**: Formula $C_{12}H_{15}NOS_2$, mol. wt. 253.39; monoclinic space group $P2_{1/c}$; cell parameters: $a = 9.303(3)$ Å, $b = 11.127(4)$ Å, $c = 24.278(9)$ Å, $\beta = 90.349(2)°$, $V = 2512.9$ Å^3, $Z = 8$, $d_{\text{calc.}} = 1.34$ g/cm^3.

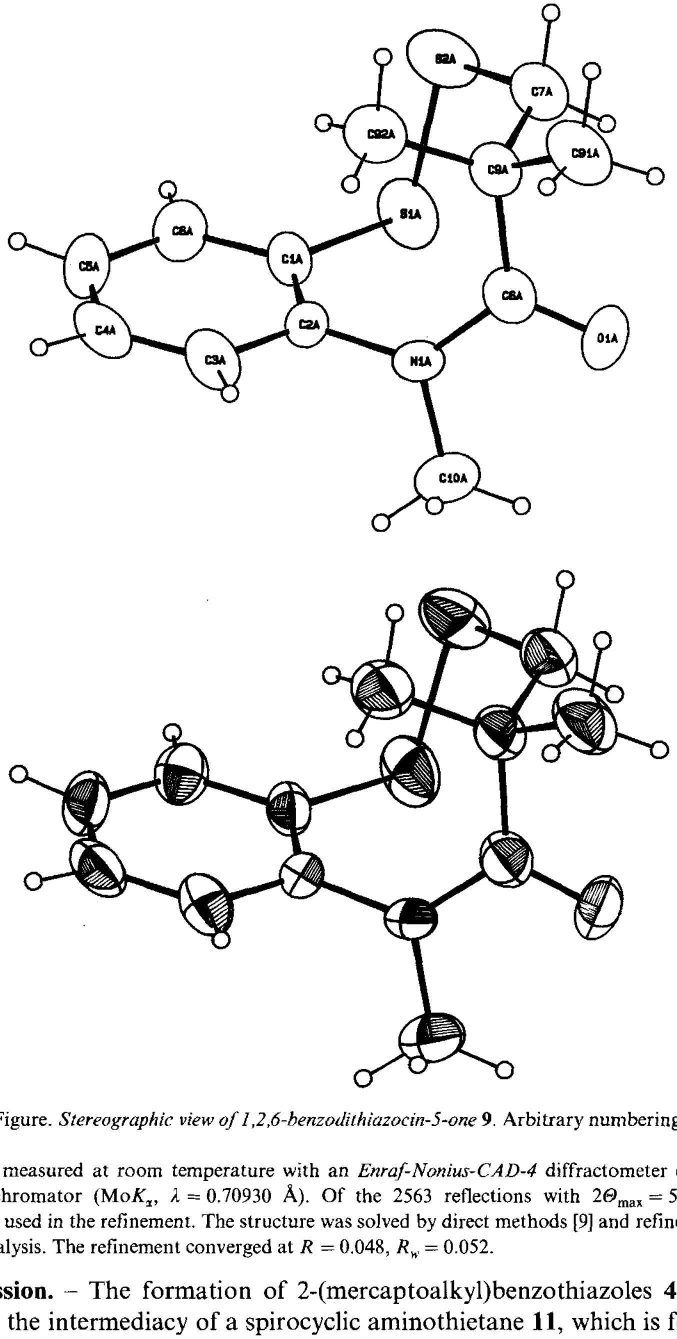
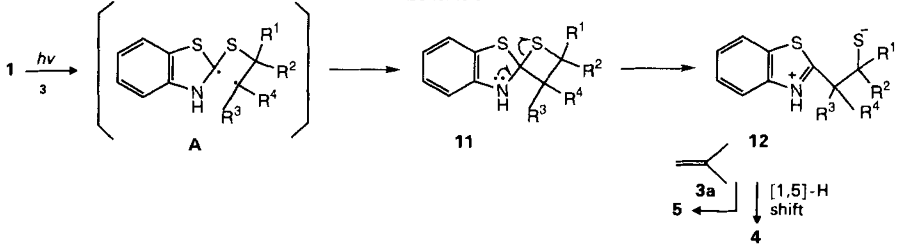


Figure. *Stereographic view of 1,2,6-benzodithiazocin-5-one* **9**. Arbitrary numbering.

Intensities were measured at room temperature with an *Enraf-Nonius-CAD-4* diffractometer equipped with a graphite monochromator (MoK_α, $\lambda = 0.70930$ Å). Of the 2563 reflections with $2\Theta_{max} = 50.0°$, 1176 with $I > 3.0\sigma(I)$ were used in the refinement. The structure was solved by direct methods [9] and refined by full-matrix least-squares analysis. The refinement converged at $R = 0.048$, $R_w = 0.052$.

4. Discussion. – The formation of 2-(mercaptoalkyl)benzothiazoles **4** can be best explained by the intermediacy of a spirocyclic aminothietane **11**, which is formed regioselectively by photochemical [2+2] cycloaddition of the C=S bond of benzothiazole-2-thione **1** and the C=C bond of alkene **3** *via* the more stable biradical intermediate **A** [6–8] (*Scheme 3*). Owing to the participation of the lone-pair electrons of the N-atom, **11** and undergoes thietane-ring cleavage to yield the zwitterion **12**, and [1,5]-H shift finally gives **4**. Addition of a second molecule of **3a** to zwitterion **12**, in which the sulfide-anion site is less hindered ($R^1=R^2=H$), affords the 1:2 adduct **5**. A similar photoaddition was reported for aza-aromatic thiones and **3a** [6j].

Scheme 3



A plausible pathway for the formation of the photoproducts **8**–**10** also involves initial [2+2] cycloaddition of thioamide **2** and **3a** giving a common aminothietane intermediate **13** (*Scheme 4*). Subsequent heterolytic cleavage of **13** (*Path A*) gives zwitterion **14**, which leads to spiro-1,3-dithiane **8** through a pathway similar to the one described for the photoreaction of *N*-substituted benzothiazole-2-thiones and electron-poor alkenes [8]. Alternatively, zwitterion **14** is trapped by a trace of H_2O in the solvent yielding *via* **15**, benzenethiol **16** which is oxidized by air to the 1,2,6-benzodithiazocin-5-one **9**. The formation of disulfide **10** may involve a sulfide radical **17** derived from the homolytic cleavage of the common intermediate **13** (*Path B*). H-Abstraction from **3a** by **17** (→**18**) and subsequent air oxidation affords then **10**. A similar photochemical formation of disulfides was observed in the photoadditions of aza-aromatic thiones and alkenes by *Kanaoka et al.* [6j]. If the photoreaction of **2** and **3a** was carried out in THF as H-donor solvent or in benzene saturated with H_2O, however, drastic changes in the distribution of products were not observed. Attemps to trap the zwitterion intermediate **14** with MeOH were also unsuccessful: Irradiation of **2** in the presence of **3a** in MeOH under Ar gave spiro-1,3-dithiane **8** and 1,2,6-dithiazocin-5-one **9** (*Table*). When the photoreaction of **2** and **3a** was carried out in non-degassed benzene, the disulfide **10** (21%) was obtained as the main product together with **8** (3%) and **9** (9%). Therefore, these results suggest that the photoaddition of **2** and **3a** proceeds through both pathways, *A* and *B*.

Scheme 4

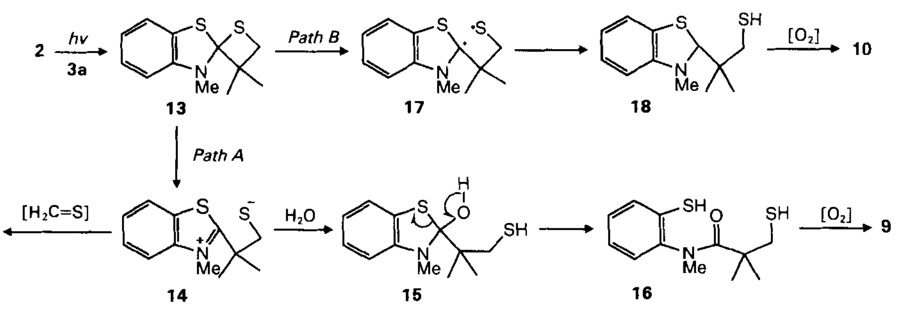


Table. *Yield of Photoproducts* **4–6** *and* **8–10**

Thiazole-2-thione	Alkene	Yield [%][a])					
		4	**5**	**6**	**8**	**9**	**10**
1	**3a**	33	27				
1	**b**	56					
1	**c**	29					
1	**d**	21					
1	**e**	85					
1	**f**	28					
1	**g**	–[b])					
1	**h**	5		9			
2	**a**				6	7	11
2[c])	**a**				7	7	trace
2[d])	**a**				3	9	21

[a]) Isolated yield. [b]) No reaction. Thiazole-2-thione **1** was recovered quantitatively. [c]) MeOH was used as solvent. [d]) The photoreaction was carried out in non-degassed benzene.

Experimental Part

General. Chromatography: silica gel *Merck 60* and *Wakogel C-300* for flash chromatography. M.p. and b.p.: uncorrected. IR Spectra: *Hitachi-260-30* photospectrometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Jeol-FX-100* (100 MHz) and *Jeol-JNM-EX-270* (270 MHz) spectrometers; in $CDCl_3$ using $SiMe_4$ as an internal standard; δ in ppm, J in Hz. Mass spectra: *Jeol-JMS-DX-300* spectrometer; direct insertion of the probe at 70 eV and 30 µA.

Photocycloaddition of Benzothiazol-2-ones **1** *or* **2** *to Alkenes* **3**: *General Procedure.* A soln. of **1** or **2** (300 mg) in 1,2-dimethoxyethane (70 ml; for **1**) or benzene (70 ml; for **2**) in the presence of an excess of alkene **3** (*ca.* 1 ml for **3a–c** and **3h**, 2 mol-equiv. for **3d–g**) in a *Pyrex* vessel under Ar was irradiated with a high-pressure mercury lamp (*HaLos EHP 300 W, Eikosha*) for 15–24 h at r.t. After removal of the solvent, the residue was chromatographed (silica gel, benzene/AcOEt 19:1 to 4:1) to yield products **4–6** and **8–10**, resp. (*Table*).

2-(Benzothiazol-2-yl)-2-methylpropane-1-thiol (**4a**) could not be purified completely. Oil. IR (film): 2550 (SH). ^{1}H-NMR: 1.39 (*t*, $J = 8.9$, 1 H); 1.56 (*s*, 6 H); 3.00 (*d*, $J = 8.9$, 2 H); 7.23–7.48 (*m*, 2 H); 7.82–7.87 (*m*, 1 H); 7.98–8.02 (*m*, 1 H). ^{13}C-NMR: 27.5 (*q*); 37.4 (*t*); 42.7 (*s*); 121.5 (*d*); 122.8 (*d*); 124.7 (*d*); 125.9 (*d*); 134.8 (*s*); 153.2 (*s*); 178.7 (*s*).

3-(Benzothiazol-2-yl)-3-methylbutane-2-thiol (**4b**): B.p. 185°/3 Torr. IR (film): 2550 (SH). ^{1}H-NMR: 1.30 (*d*, $J = 6.9$, 3 H); 1.51 (*d*, $J = 7.3$, 1 H); 1.53 (*s*, 3 H); 1.58 (*s*, 3 H); 3.58–3.70 (*m*, 1 H); 7.31–7.37 (*m*, 1 H); 7.41–7.48 (*m*, 1 H); 7.83–7.87 (*m*, 1 H); 7.97–8.01 (*m*, 1 H). ^{13}C-NMR: 20.4 (*q*); 24.1 (*q*); 26.0 (*q*); 45.4 (*d*); 45.9 (*s*); 121.4 (*d*); 122.8 (*d*); 124.7 (*d*); 125.9 (*d*); 134.6 (*s*); 153.0 (*s*); 179.6 (*s*). Anal. calc. for $C_{12}H_{15}NS_2$ (237.39): C 60.57, H 6.37, N 5.90; found: C 60.86, H 6.43, N 5.79.

3-(Benzothiazol-2-yl)-2,3-dimethylbutane-2-thiol (**4c**): B.p. 200°/3 Torr. IR (film): 2550 (SH). ^{1}H-NMR: 1.51 (*s*, 6 H); 1.67 (*s*, 6 H); 1.95 (*s*, 1 H); 7.33–7.38 (*m*, 1 H); 7.40–7.45 (*m*, 1 H); 7.83–7.87 (*m*, 1 H); 8.00–8.04 (*m*, 1 H). ^{13}C-NMR: 25.6 (*q*); 29.6 (*q*); 48.5 (*s*); 51.2 (*s*); 121.1 (*d*); 122.9 (*d*); 124.7 (*d*); 125.7 (*d*); 134.9 (*s*); 152.7 (*s*); 177.6 (*s*). Anal. calc. for $C_{13}H_{17}NS_2$ (251.416): C 62.11, H 6.82, N 5.57; found: C 62.30, H 6.72, N 5.59.

2-(Benzothiazol-2-yl)-2-phenylethanethiol (**4d**): B.p. 200°/2 Torr (dec.). IR (film): 2550 (SH). ^{1}H-NMR: 1.62 (*t*, $J = 8.9$, 1 H); 3.17–3.29 (*m*, 1 H); 3.53–3.66 (*m*, 1 H); 4.55 (*t*, $J = 7.6$, 1 H); 7.23–7.49 (*m*, 7 H); 7.76–7.80 (*m*, 1 H); 8.01–8.05 (*m*, 1 H). ^{13}C-NMR: 29.8 (*t*); 54.5 (*d*); 121.5 (*d*); 123.1 (*d*); 125.0 (*d*); 126.0 (*d*); 127.9 (*d*); 128.2 (*d*); 129.0 (*d*); 135 (*s*); 140.0 (*s*); 153.0 (*s*); 172.5 (*s*). MS: 271 (M^+), 238 ($[M - SH]^+$), 225 ($[M - H_2C{=}S]^+$), 167 ($[M - C_8H_8]^+$).

2-(Benzothiazol-2-yl)-2-phenylpropane-1-thiol (**4e**): B.p. 220°/2 Torr. IR (film): 2560 (SH). ^{1}H-NMR: 1.36 (*dd*, $J = 8.6, 9.2$, 1 H); 2.01 (*s*, 3 H); 3.39 (*dd*, $J = 8.6, 13.8$, 1 H); 3.60 (*dd*, $J = 9.2, 13.8$, 1 H); 7.22–7.49 (*m*, 7 H); 7.77 (*d*, $J = 8.3$, 1 H); 8.04 (*d*, $J = 8.3$, 1 H). ^{13}C-NMR: 25.4 (*q*); 36.8 (*t*); 50.1 (*s*); 121.5 (*d*); 123.1 (*d*); 125.0 (*d*); 125.9 (*d*); 126.9 (*d*); 127.3 (*d*); 128.5 (*d*); 135.5 (*s*); 144.0 (*s*); 152.7 (*s*); 178.2 (*s*). Anal. calc. for $C_{16}H_{15}NS_2$ (285.43): C 67.37, H 5.30, N 4.91; found: C 67.58, H 5.56, N 4.78.

2-(Benzothiazol-2-yl)-2,2-diphenylethanethiol (**4f**): M.p. 138–139°. IR (KBr): 2560 (SH). ^{1}H-NMR: 1.64 (*t*, J = 8.6, 1 H); 3.94 (*d*, J = 8.6, 2 H); 7.28–7.48 (*m*, 12 H); 7.73–7.76 (*m*, 1 H); 8.03–8.07 (*m*, 1 H). ^{13}C-NMR: 35.9 (*t*); 59.5 (*s*); 121.3 (*d*); 123.4 (*d*); 125.1 (*d*); 125.9 (*d*); 127.4 (*d*); 128.1 (*d*); 129.4 (*d*); 135.8 (*s*); 143.7 (*s*); 152.6 (*s*); 177.1 (*s*). Anal. calc. for $C_{21}H_{17}NS_2$ (347.496): C 72.59, H 4.93, N 4.03; found: C 72.52, H 4.86, N 3.90.

2-(Benzothiazol-2-yl)-2-ethoxyethanethiol (**4h**): B.p. 210°/3 Torr. IR (film): 2550 (SH). ^{1}H-NMR: 1.30 (*t*, J = 6.9, 3 H); 1.82 (*t*, J = 8.6, 1 H); 2.98–3.06 (*m*, 2 H); 3.64–3.76 (*m*, 2 H); 4.81 (*t*, J = 6.9, 1 H); 7.24–7.51 (*m*, 2 H); 7.87–7.91 (*m*, 1 H); 7.97–8.03 (*m*, 1 H). ^{13}C-NMR: 15.2 (*q*); 30.6 (*t*); 66.6 (*t*); 81.0 (*d*); 121.9 (*d*); 123.1 (*d*); 125.2 (*d*); 126.1 (*d*); 134.8 (*s*); 153.2 (*s*); 173.5 (*s*). MS: 239 (M^+), 238 ($[M - H]^+$), 206 ($[M - SH]^+$), 192 ($[M - CH_2SH]^+$). Anal. calc. for $C_{11}H_{13}NOS_2$ (239.364): C 55.20, H 5.47, N 5.85; found: C 55.33, H 5.33, N 5.70.

2-(Benzothiazol-2-yl)-2-methylpropyl 2-Methylpropyl Sulfide (**5**): B.p. 190°/3 Torr. IR (film): 1500, 1455, 1440, 1380, 1360, 1030, 760, 725. ^{1}H-NMR: 0.89 (*d*, J = 6.6, 6 H); 1.65 (*s*, 6 H); 1.66–1.78 (*m*, 1 H); 2.30 (*d*, J = 6.9, 2 H); 3.02 (*s*, 2 H); 7.23–7.37 (*m*, 1 H); 7.40–7.47 (*m*, 1 H); 7.88–7.87 (*m*, 1 H); 7.29–8.01 (*m*, 1 H). ^{13}C-NMR: 21.9 (*q*); 27.9 (*q*); 28.7 (*d*); 42.8 (*s*); 43.5 (*t*); 46.7 (*t*); 121.5 (*d*); 122.7 (*d*); 124.6 (*d*); 125.8 (*d*); 134.9 (*s*); 153.2 (*s*); 179.5 (*s*). Anal. calc. for $C_{15}H_{21}NS_2$ (279.468): C 64.72, H 7.57, N 5.01; found: C 64.62, H 7.41, N 5.01.

2-(1′-Ethoxyethylthio)benzothiazole (**6**): B.p. 190°/3 Torr. IR (film): 1580, 1455, 1390, 1310, 1260, 1120, 950, 745, 720. ^{1}H-NMR: 1.17 (*t*, J = 6.9, 3 H); 1.70 (*d*, J = 6.3, 3 H); 3.22–3.50 (*m*, 1 H); 3.51–3.64 (*m*, 1 H); 6.83 (*q*, J = 6.3, 1 H); 7.25–7.38 (*m*, 3 H); 7.44–7.49 (*m*, 1 H); 7.93–7.97 (*m*, 1 H). ^{13}C-NMR: 14.8 (*q*); 18.8 (*q*); 64.7 (*t*); 86.3 (*d*); 114.4 (*d*); 121.0 (*d*); 124.5 (*d*); 126.5 (*d*); 127.2 (*s*); 139.7 (*s*); 189.5 (*s*). Anal. calc. for $C_{11}H_{13}NOS_2$ (239.364): C 55.20, H 5.47, N 5.85; found: C 55.58, H 5.37, N 5.84.

*3,5,5′-Trimethylspiro[benzothiazole-2(3*H*),4′-[1,3]dithiane]* (**8**): M.p. 137–138°. IR (KBr): 1585, 1575, 1470, 1380, 1335, 1295, 1205, 1125, 1110, 1010, 740. ^{1}H-NMR: 1.35 (*s*, 3 H); 1.69 (*s*, 3 H); 2.48 (*dd*, J = 2.4, 14.6, 1 H); 3.01 (*s*, 3 H); 3.20 (br. *d*, J = 14.6, 1 H); 3.58 (*dd*, J = 2.4, 14.6, 1 H); 4,46 (*d*, J = 14.4, 1 H); 6.36–6.46 (*m*, 1 H); 6.54–6.80 (*m*, 2 H); 6.92–7.24 (*m*, 1 H). ^{13}C-NMR: 25.3 (*q*); 27.7 (*q*); 32.9 (*t*); 34.6 (*q*); 41.6 (*s*); 45.0 (*t*); 100.8 (*s*); 108.2 (*d*); 119.2 (*d*); 120.7 (*d*); 122.9 (*s*); 125.5 (*d*); 148.5 (*s*). Anal. calc. for $C_{13}H_{17}NS_3$ (283.486): C 55.08, H 6.04, N 4.94; found: C 55.25, H 6.15, N 4.90.

4,4,6-Trimethyl-1,2,6-benzodithiazocin-5-one (**9**): M.p. 130–131°. IR (KBr): 1630 (C=O), 1580, 1475, 1350, 1295, 1235, 1120, 1110, 775. ^{1}H-NMR: 0.62 (*s*, 3 H); 1.44 (*s*, 3 H); 2.23 (*d*, J = 13.7, 1 H); 3.18 (*s*, 3 H); 3.58 (*d*, J = 13.7, 1 H); 7.24–7.54 (*m*, 3 H); 7.71–7.81 (*m*, 1 H). ^{13}C-NMR: 23.2 (*q*); 32.2 (*q*); 42.1 (*q*); 45.7 (*s*); 47.8 (*t*); 126.9 (*d*); 128.9 (*d*); 131.6 (*d*); 134.9 (*s*); 137.1 (*d*); 148.3 (*s*); 177.6 (*s*). Anal. calc. for $C_{12}H_{15}NOS_2$ (253.39): C 56.88, H 5.97, N 5.53; found: C 57.12, H 6.18, N 5.57.

Bis[2-methyl-2-(3-methylbenzothiazol-2-yl)propyl] Disulfide (**10**): B.p. 140°/10^{-3} Torr (dec.). IR (film): 1590, 1475, 1425, 1390, 1360, 1295, 1220, 1125, 1105, 1025, 990, 740. ^{1}H-NMR: 0.99 (*s*, 6 H); 1.00 (*s*, 6 H); 2.92 (*s*, 4 H); 3.00 (*s*, 6 H); 4.83 (*s*, 2 H); 6.51–7.07 (*m*, 8 H). ^{13}C-NMR: 22.2 (*q*); 22.3 (*q*); 43.4 (*q*); 44.1 (*s*); 49.8 (*t*); 82.8 (*d*); 111.7 (*d*); 120.5 (*d*); 125.0 (*d*); 129.1 (*s*); 150.6 (*s*). HR-MS: 476.1425 ($C_{24}H_{32}N_2S_4^+$, calc. 476.1448).

2-(Benzothiazol-1-yl)-2-methylpropyl Methyl Sulfide (**7a**). A soln. of **4a** (1 mmol), MeI (1.5 mmol), and K_2CO_3 (1.2 mmol) in acetone was stirred under Ar for 5 h at r.t. Usual workup gave **7a** almost quantitatively. B.p. 185°/3 Torr. IR (film): 1500, 1450, 1435, 1380, 1360, 1025, 755, 720. ^{1}H-NMR: 1.59 (*s*, 6 H); 2.01 (*s*, 3 H); 3.03 (*s*. 2 H); 7.29–7.44 (*m*, 2 H); 7.82–7.86 (*m*, 1 H); 7.97–8.01 (*m*, 1 H). ^{13}C-NMR: 18.0 (*q*); 27.9 (*q*); 42.0 (*s*); 48.5 (*t*); 121.5 (*d*); 122.8 (*d*); 124.7 (*d*); 125.8 (*d*); 134.9 (*s*); 153.1 (*s*); 179.4 (*s*). Anal. calc. for $C_{12}H_{15}NS_2$ (237.39): C 60.72, H 6.37, N 5.97; found: C 60.97, H 6.45, N 5.83.

2-(Benzothiazol-2-yl)-2-phenylpropyl Methyl Sulfide (**7e**). As described for **7a**, with **4e**. Yield 100%. B.p. 230°/2 Torr. IR (film): 1595, 1485, 1435, 1000, 760, 725, 700. ^{1}H-NMR: 1.92 (*s*, 3 H); 2.03 (*s*, 3 H); 3.56 (*dd*, J = 13.2, 22.4, 2 H); 7.23–7.49 (*m*, 7 H); 7.76–7.80 (*m*, 1 H); 8.02–8.06 (*m*, 1 H). ^{13}C-NMR: 17.8 (*q*); 26.2 (*q*); 47.4 (*t*); 49.9 (*s*); 121.5 (*d*); 123.1 (*d*); 124.9 (*d*); 125.8 (*d*); 127.0 (*d*); 127.3 (*d*); 128.4 (*d*); 135.5 (*s*); 144.4 (*s*); 152.7 (*s*); 179.0 (*s*). Anal. calc. for $C_{17}H_{17}NS_2$ (299.456): C 68.19, H 5.72, N 4.68; found: C 67.94, H 5.42, N 4.85.

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