Photocycloaddition Reactions of Alkyl and Aryl 2-Thioxo-3*H*-benzoxazole-3-carboxylates to Alkenes

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The photochemical reactions of alkyl and aryl 2-thioxo-3*H*-benzoxazole-3-carboxylates **1** have been examined. Irradiation of **1** in the presence of tetra- and trisubstituted alkenes **2a** and **2b**, 2-methylprop-2-ene nitrile **2e**, and dienes **2f** and **2g** gave [2+2] cycloadducts of the C=S bond of 2-thioxobenzoxazoles and the C=C bond of alkenes, spiro[benzoxazole-thietanes] **3**, **4**, **8**–**13**, **15**, **18**, **20**, **23**–**26** in moderate-to-good yields. The photoaddition reactions proceed in a regiospecific manner. The spirocyclic compounds obtained are indefinitely stable at room temperature. Irradiation of **1a** in the presence of 1,1- and 1,2-disubstituted alkenes **2c** and **2d** yielded the products **5**–**7** of oxazole-ring cleavage. Compound **1d** also underwent photoaddition with alkenes to yield spiro[benzoxazole-thietanes] and/or 2-substituted benzoxazoles and/or iminothietanes, depending on the nature of the substituents present in the alkenes. On intramolecular [2+2] photoadduct, tetracyclic **27**, was obtained, when ethenyl 2-thioxobenzoxazole-3-carboxylate **1e** was irradiated.

1. Introduction. – The photochemistry of thiocarbonyl compounds, including thioimides and thioamides, has been of considerable synthetic and mechanistic interest [1–4], and these compounds behave like carbonyl compounds in many respects. In the course of our studies on the photochemistry of cyclic conjugated nitrogen-thiocarbonyl systems [1i–k] [2][3], we have reported the photoaddition reactions of the benzoxazole-2-thiones [2] and benzothiazole-2-thiones [3] with alkenes. In these reactions, [2+2] cycloadducts, aminothietanes are believed to be primary photoproducts. However, they are usually unstable, probably because the N-atom lone-pair-electron-assisted cleavage of either the C–S bond of the thietane ring or the C–O bond of the oxazole ring facilitates the formation of zwitterions. In contrast, thietanes have been isolated from photochemical cycloaddition of alkenes and thioimides, which have a cross-conjugated C=O system [1a][1h][1j][4]. This has been explained in terms of difference between the π-electron-donating effects of N-atoms of thioamides and those of thioimides. We are interested in exploring the effect of the substituents at the N-atom of thioamides upon photocycloaddition of thioamides and alkenes. Here[1]), we describe the results of photochemical reactions of alkyl and aryl 2-thioxobenzoxazole-3-carboxylates **1**, substituted with an electron-withdrawing group at the N-atom, with alkenes **2**, yielding the stable isolable spirocyclic aminothietanes.

2. Results and Discussion. – Irradiation of a benzene solution of methyl 2-thioxo-3*H*-benzoxazole-3-carboxylate (**1a**; λ_{max} (EtOH)/nm (ε) 213.5 (1.19×10^4) and 300

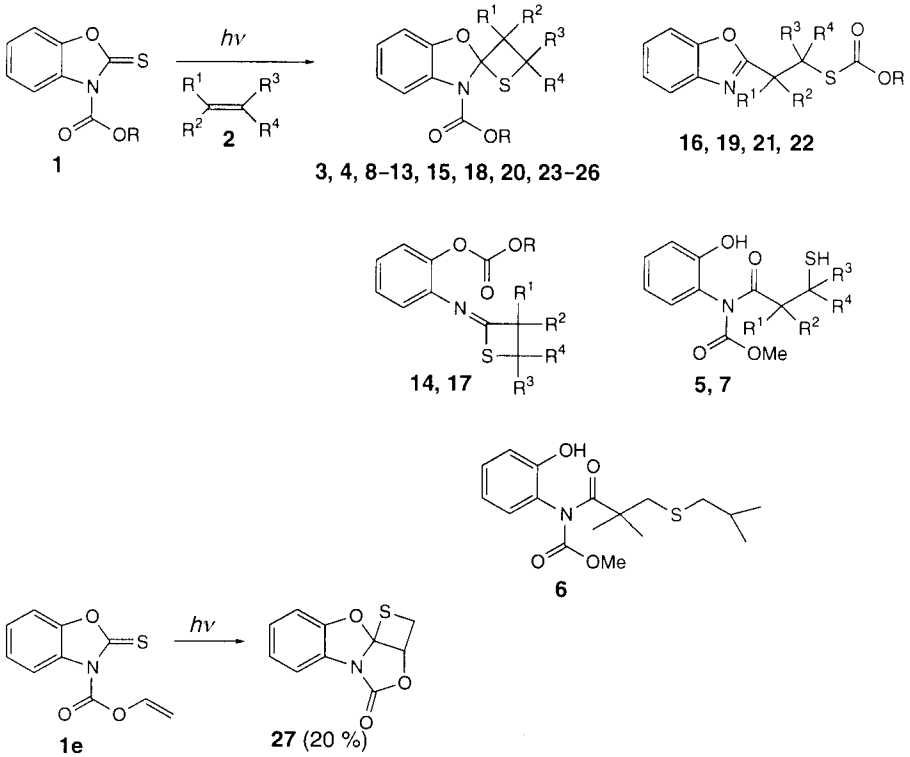
[1]) For a preliminary report of part of this work, see [2c].

(2.18×10^4)) with a high-pressure Hg lamp through a *Pyrex* filter under Ar resulted in the recovery of unchanged starting material **1a**. However, when a solution of **1a** in benzene was irradiated in the presence of 2,3-dimethylbut-2-ene (**2a**) under the same conditions as described above, a 1:1 adduct of **1a** and **2a**, spirocyclic aminothietane **3**, was obtained in 50% yield (*Scheme 1*). The structure of **3** was confirmed on the basis of spectroscopic data, elemental analysis, and chemical evidence. The ^{1}H-NMR spectrum of spirocyclic aminothietane **3** showed four *singlets* (δ 1.10–1.71 ppm) and one *singlet* (δ 3.91 ppm) assignable to Me and MeO, and aromatic H-atom signals. The ^{13}C-NMR spectrum of **3** showed four signals for Me C-atoms, one for MeO C-atom, four for quaternary C-atoms, C=O C-atoms, and aromatic ^{13}C signals. The C=S ^{13}C signal (δ 176.7 ppm) disappeared. Treatment of spirocyclic thietane **3** with 2 equiv. of *m*-chloroperbenzoic acid (MCPBA) yielded the sultine **37** (*cf. Scheme 2*) in 54% yield, the structure of which was confirmed by X-ray crystal-structure analysis (*Fig.*).

Spirocyclic aminothietane **3** was treated with MeONa in MeOH to yield 2-substituted benzoxazole **38a** and iminothietane **39** (*Scheme 2*). The later was acylated with Ac_2O anhydride to give 2-[(3,3,4,4-tetramethylthietan-2-ylidene)amino]phenyl acetate (**40**) and *S*-[3-(1,3-benzoxazol-2-yl)-2,3-dimethylbut-2-yl] thioacetate (**41**) [2b].

In a similar manner, irradiation of **1a–c** and a tetrasubstituted alkene such as 2,3-dimethylbut-2-ene (**2a**), 1,1,3-trisubstituted alkenes such as 2-methylbut-2-ene (**2b**) and

Scheme 1



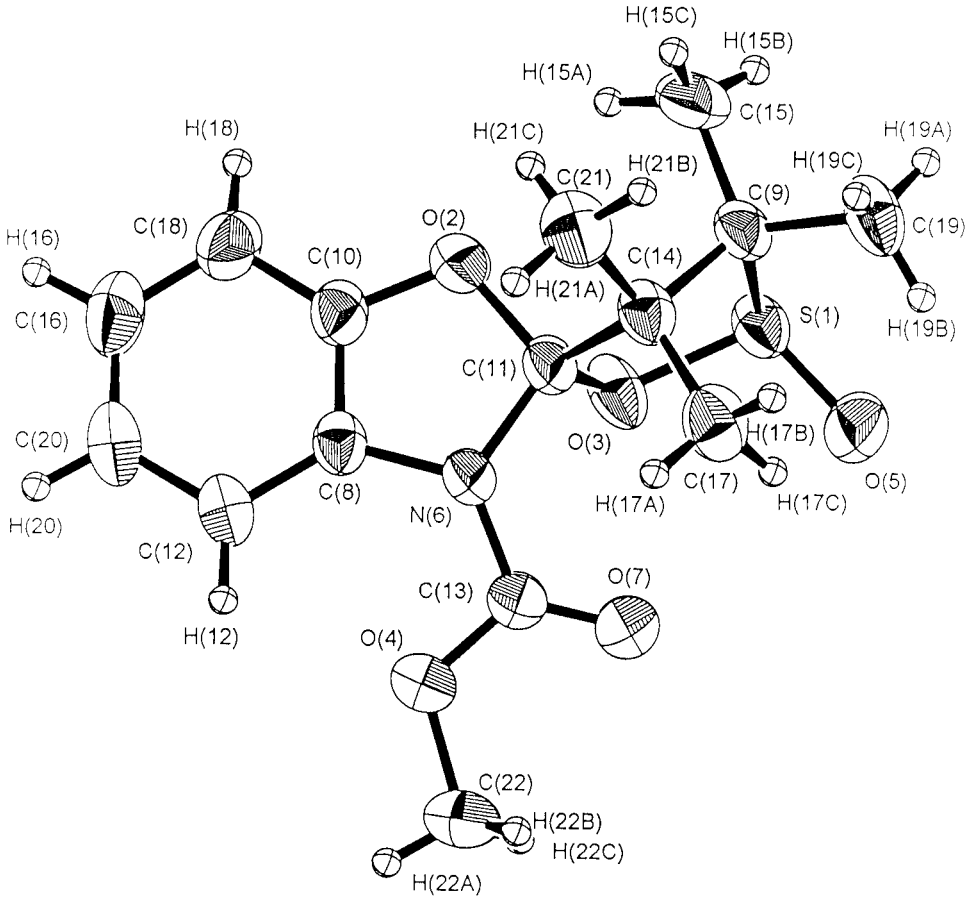
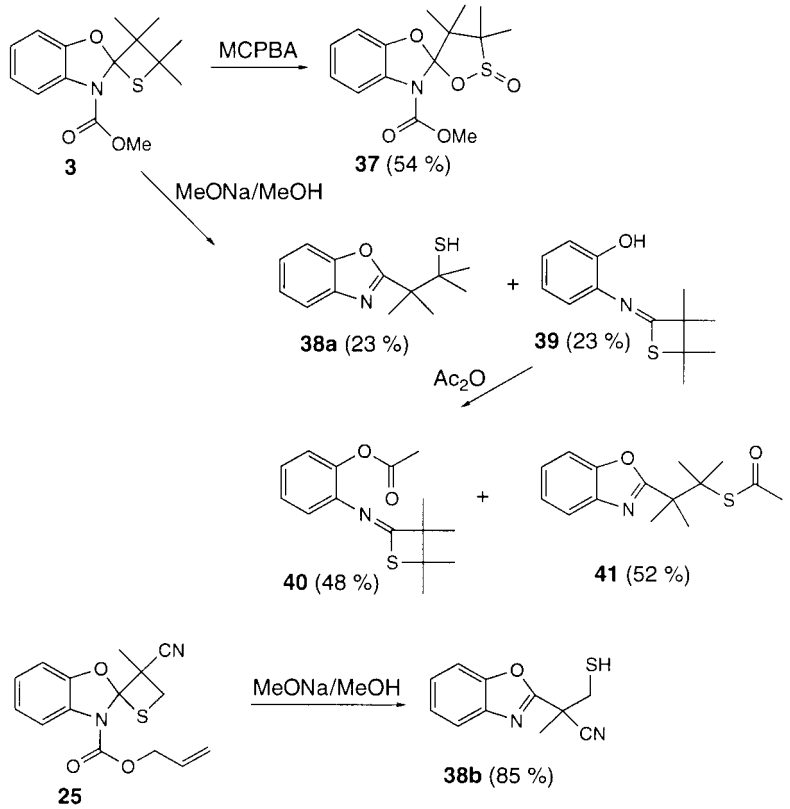


Figure. *ORTEP Perspective view of the sultine* **37** *with crystallographic numbering scheme*

2,5-dimethylhexa-2,4-diene (**2f**), and a 1,1-disubstituted alkene such as 2-methylprop-2-enenitrile (**2e**) in benzene gave the corresponding spirocyclic aminothietanes **4** and **8**–**12**, exclusively, in fair-to-high yields. In the photoaddition reaction of **1** to **2e**, spirocyclic aminothietanes **8** and **11** were obtained as a mixture of two stereoisomers, the assignment of which was ambiguous from spectral analysis. The photocycloaddition leading to spirocyclic aminothietanes is regiospecific, and the orientation of addition of thiones **1** to alkenes **2** can be predicted from consideration of the most-stable diradical intermediate in the [2 + 2] photocycloaddition process [1a][1i–k][2–4]. The formation of spirocyclic aminothietane **9** from **1a** and the conjugated diene 2,5-dimethylhexa-2,4-diene **2f** indicated that the spirocyclic aminothietanes are formed through the excited singlet state of the 2-thioxo-3*H*-benzoxazole-3-carboxylates **1**. On the other hand, irradiation of **1a** in benzene in the presence of 1,1-disubstituted alkene such as 2-methylprop-2-ene (**2c**) and 1,2-disubstituted alkenes such as (*Z*)- and (*E*)-but-2-ene (**2d**) yielded the products of oxazole-ring cleavage, *i.e.*, *N*-acylcarbamate derivatives

Scheme 2



5–**7**. The carbamate **7** was formed as a mixture of two isomers [2a]. Analogous ring-opening reactions have been observed in the photoaddition of *N*-alkylbenzoxazole-2-thiones to alkenes [2a]. Irradiation of phenyl 2-thioxo-3*H*-benzoxazole-3-carboxylate (**1d**: λ_{max} (EtOH)/nm (ε) 225 (1.17×10^4) and 300 (1.60×10^4)) in benzene in the presence of alkenes **2a**, **2b**, and **2e**–**g** under the same conditions gave spirocyclic aminothietanes **13**, **15**, **18**, and **20**, and/or 2-substituted benzoxazoles **16**, **19**, **21**, and **22** and/or iminothietanes **14** and **17**, depending on the substitution pattern of the alkenes (*Table 1*). The structures of photoproducts were elucidated on the basis of their spectral and analytical data.

As described above, in principle, alkyl and aryl 2-thioxo-3*H*-benzoxazole-3-carboxylates **1a**–**d** undergo efficient intermolecular photocycloaddition with alkenes **2** to yield stable spirocyclic aminothietanes. To assess the generality of this photoreaction, we investigated the alkenyl 2-thioxo-3*H*-benzoxazole-3-carboxylates **1e**–**g**. Irradiation of vinyl benzoxazole-carboxylate **1e** in benzene under the same conditions as described above gave the intramolecular [2 + 2] cycloadduct, multifused thietane **27** in 20% yield, while that of **1f**–**g** resulted in the recovery of unchanged starting materials. However, the intermolecular [2 + 2] photocycloaddition reaction of **1e**–**g** to

Table 1. *Yields of Photoproducts* **3**–**26**

2-Thioxo-3*H*-benzoxazole-3-carboxylates		Alkene					Product (Yield [%][a]))		
	R		R^1	R^2	R^3	R^4			
1a	Me	**2a**	Me	Me	Me	Me	**3** (50)		
1a	Me	**2b**	Me	Me	Me	H	**4** (75)		
1a	Me	**2c**	Me	Me	H	H		**5** (64)	**6** (23)
1a	Me	(*E*)-**2d**	Me	H	H	Me		**7** (62)[b])	
1a	Me	(*Z*)-**2d**	Me	H	Me	H		**7** (68)[b])	
1a	Me	**2e**	Me	CN	H	H	**8** (98)[b])		
1a	Me	**2f**	Me	Me	H	Me_2C=CH	**9** (50)		
1b	Et	**2a**	Me	Me	Me	Me	**10** (73)		
1b	Et	**2e**	Me	CN	H	H	**11** (96)[b])		
1c	$PhCH_2$	**2a**	Me	Me	Me	Me	**12** (43)		
1d	Ph	**2a**	Me	Me	Me	Me	**13** (68)		**14** (18)
1d	Ph	**2b**	Me	Me	Me	H	**15** (28)	**16** (17)	**17** (28)
1d	Ph	**2e**	Me	CN	H	H	**18** (67)[b])	**19** (15)	
1d	Ph	**2f**	Me	Me	H	Me_2C=CH	**20** (16)	**21** (20)	
1d	Ph	**2g**	CH_2=C(Me)	Me	H	H		**22** (41)	
1e	CH_2=CH	**2e**	Me	CN	H	H	**23** (67)[b])		
1f	CH_2=$CHCH_2$	**2a**	Me	Me	Me	Me	**24** (24)		
1f	CH_2=$CHCH_2$	**2e**	Me	CN	H	H	**25** (82)[b])		
1g	CH_2=$CH(CH_2)_2$	**2e**	Me	CN	H	H	**26** (61)[b])		

[a]) Yield of isolated product. [b]) A mixture of two stereoisomers.

2,3-dimethylbut-2-ene (**2a**) and 2-methyl prop-2-ene-2-carbonitrile **2e** proceeds smoothly to yield spirocyclic aminothietanes **23**–**26**. The structures of **23**–**26** were elucidated on the basis of their spectral and analytical data. Spirocyclic aminothietane **25** was treated with MeONa in MeOH to afford 2-(1,3-benzoxazol-2-yl)-2-methyl-3-sulfanylpropanenitrile (**38b**) in 85% yield.

The spirocyclic aminothietanes thus obtained by photocycloaddition of the benzoxazole-3-carboxylates **1** and alkenes **2** are indefinitely stable at room temperature. However, upon heating to reflux in toluene, spirocyclic aminothietanes **3**, **4**, **8**, **9**, **12**, **13**, **15**, **18**, **20** and **23**–**25** were transformed into 2-substituted benzoxazoles **16**, **19**, **21**, **29**, **31**–**34**, and **36** and/or iminothietanes **14**, **28**, **30**, and **35** in good yields (*Scheme 3* and *Table 2*). Conversion of the spirocyclic aminothietanes to iminothietanes and 2-substituted benzoxazoles is thought to arise by thermally induced cleavage of the oxazole or the thietane ring to zwitterions, which then undergo intramolecular trapping of the acyl group by the thiolate or phenolate moiety of the zwitterions. An analogous

Scheme 3

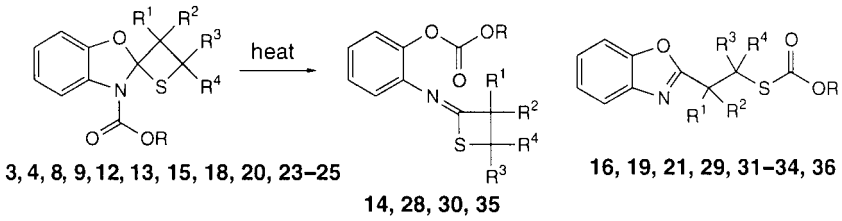


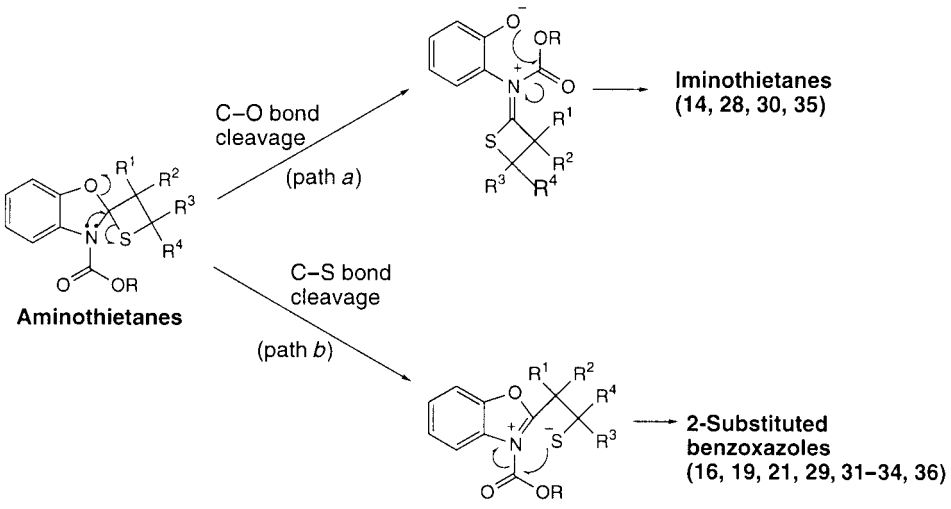
Table 2. *Yields of Benzoxazoles and Iminothietanes Derived from Spirocyclic Aminothietanes*

Spiro[benzoxazole-thietanes]						Product (Yield [%][a]))	
	R	R^1	R^2	R^3	R^4	Benzoxazole	Iminothietane
3	Me	Me	Me	Me	Me		**28** (quant.)
4	Me	Me	Me	Me	H	**29** (72)	**30** (25)
8	Me	Me	CN	H	H	**31** (quant.)	
9	Me	Me	Me	H	$Me_2C=CH$	**32** (quant.)	
12	$PhCH_2$	Me	Me	Me	Me	**33** (quant.)	
13	Ph	Me	Me	Me	Me		**14** (90)
15	Ph	Me	Me	Me	H	**16** (90)	
18	Ph	Me	CN	H	H	**19** (quant.)	
20	Ph	Me	Me	H	$Me_2C=CH$	**21** (quant.)	
23	$CH_2=CH$	Me	CN	H	H	**34** (95)	
24	$CH_2=CHCH_2$	Me	Me	Me	Me		**35** (quant.)
25	$CH_2=CHCH_2$	Me	CN	H	H	**36** (quant.)	

[a]) Yield of isolated product.

mechanism in the photoaddition reactions of *N*-acylbenzoxazole-2-thiones to alkenes was presented previously by us (*Scheme 4*) [2b]. The stability of spirocyclic aminothietanes described here can be rationalized in terms of the lesser participation of N-atom lone-pairs, which facilitate the ring cleavage of the thietane or the oxazole rings through conjugation of the electron-withdrawing substituent, the alkoxy or aryloxycarbonyl group[2]).

Scheme 4



[2]) Aminothietanes have not been isolated with one exception: 2,3-dihydro-1,3,3,3′,3′-pentamethylspiro[1*H*-indole-2,2′-thietane] from the photocycloaddition of 1,3,3-trimethyl-1*H*-indole-2-thione and 2-methylprop-2-ene, in only 8% yield [5].

Experimental Part

1. *General*. M.p. and b.p.: *Yanaco* micro melting-point apparatus (*MP-J3*) and a *Shibata* glass-tube-oven-distillation apparatus (*GTO-350RD*), resp.; uncorrected. IR Spectra: *Hitachi 260-30 or JASCO FT/IR-300* spectrophotometers; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *JEOL 90Q* (90 MHz) or *JEOL JNM-EX-270* (270 MHz) spectrometers; in $CDCl_3$ with Me_4Si as an internal standard; δ in ppm, J in Hz. Flash chromatography (FC): silica gel *Wakogel C-300* and *Merck 60*.

2. *Photochemical Reactions of the 2-Thioxo-3*H*-benzoxazole-3-carboxylates* **1** *with Alkenes* **2**: *General Procedure*. A soln. of **1** (1 mmol) and **2** (*ca*. 0.5 ml) in benzene (70 ml) was irradiated in a *Pyrex* tube with a high-pressure Hg lamp (500 W) under Ar for 6–15 h at r.t. After removal of the solvent, the residual oil was chromatographed on a silica-gel column with toluene/AcOEt 50:1 to 4:1 to yield the corresponding photoproducts **3**–**27**. For yields, *cf. Table 1*.

*Methyl 3′,3′,4′,4′-Tetramethylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**3**). M.p. 67–68°. IR (KBr): 1725, 1620. ^1H-NMR: 1.10 (*m*, 3 H); 1.39 (*s*, 3 H); 1.55 (*s*, 3 H); 1.71 (*s*, 3 H); 3.91 (*s*, 3 H); 6.80–6.96 (*m*, 3 H); 7.37–7.43 (*m*, 1 H). ^{13}C-NMR: 21.3; 22.1; 26.3; 29.8; 48.0; 52.9; 62.9; 108.2; 109.8; 115.4; 121.1; 123.9; 129.8; 148.2; 152.5. Anal. calc. for $C_{15}H_{19}NO_3S$ (293.3): C 61.41, H 6.53, N 4.77; found: C 61.62, H 6.50, N 4.80.

*Methyl 3′,3′,4′-Trimethylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**4**). B.p. 180°/2 Torr. IR (film): 1720, 1620. ^1H-NMR: 1.16 (*s*, 3 H); 1.31 (*d*, $J = 6.6$, 3 H); 1.41 (*s*, 3 H); 3.99 (*s*, 3 H); 4.01 (*q*, $J = 6.6$, 1 H); 6.78–6.93 (*m*, 3 H); 7.41–7.46 (*m*, 1 H). ^{13}C-NMR: 15.7; 21.4; 23.3; 40.0; 53.1; 60.4; 108.3; 110.9; 114.7; 121.5; 123.5; 128.9; 147.4; 152.2. Anal. calc. for $C_{14}H_{17}NO_3S$ (279.3): C 60.20, H 6.14, N 5.02; found: C 59.98, H 6.26, N 4.90.

Methyl N-*(2,2-Dimethyl-3-sulfanylpropanoyl)*-N-*(2-hydroxyphenyl)carbamate* (**5**). B.p. 225°/2 Torr. IR (film): 3345, 2575, 1740, 1610. ^1H-NMR: 1.43 (*s*, 6 H); 1.73 (*t*, $J = 8.4$, 1 H); 2.85 (*d*, $J = 8.4$, 2 H); 3.75 (*s*, 3 H); 6.99–7.07 (*m*, 2 H); 7.20–7.27 (*m*, 2 H); 8.07–8.11 (br. *s*, 1 H). ^{13}C-NMR: 24.4; 34.3; 45.4; 52.4; 120.7; 123.4; 126.7; 130.4; 153.9; 174.1. Anal. calc. for $C_{13}H_{17}NO_4S$ (283.3): C 55.12, H 6.05, N 4.95; found: C 54.99, H 5.80, N 5.01.

Methyl N-*{2,2-Dimethyl-3-[(2-methylpropyl)sulfanyl]propanoyl}*-N-*(2-hydroxyphenyl)carbamate* (**6**). B.p. 210°/2 Torr. IR ($CHCl_3$): 3300, 1735, 1615. ^1H-NMR: 1.00 (*d*, $J = 6.9$, 6 H); 1.43 (*s*, 6 H); 1.80–1.87 (*m*, 1 H); 2.52 (*d*, $J = 6.9$, 2 H); 2.88 (*s*, 2 H); 3.74 (*s*, 3 H); 6.97–7.05 (*m*, 2 H); 7.19–7.27 (*m*, 2 H). ^{13}C-NMR: 21.9; 25.3; 28.7; 43.5; 43.6; 44.8; 52.1; 120.1; 121.9; 123.0; 126.6; 130.8; 139.3; 153.9; 174.4. Anal. calc. for $C_{17}H_{25}NO_4S$ (339.4): C 60.16, H 7.43, N 4.13; found: C 59.87, H 7.15, N 4.31.

Methyl N-*(2-Hydroxyphenyl)*-N-*(2-methyl-3-sulfanylbutanoyl)carbamate* (**7**; mixture of two isomers (7:10)). B.p. 220°/2 Torr. IR (film): 3335, 1735, 1610. ^1H-NMR: (major product): 1.40 (*d*, $J = 6.9$, 3 H); 1.50 (*d*, $J = 6.9$, 3 H); 1.88 (*d*, $J = 8.6$, 1 H); 2.77–2.84 (*m*, 1 H); 3.13–3.20 (*m*, 1 H); 3.75 (*s*, 3 H); 7.04–7.08 (*m*, 2 H); 7.19–7.31 (*m*, 2 H); 8.11 (br. *s*, 1 H). ^{13}C-NMR (major product): 15.9; 23.0; 37.5; 50.0; 52.4; 153.9; 172.8 in addition to arom.-C signals. ^1H-NMR: (minor product) 1.37 (*d*, $J = 6.9$, 6 H); 1.48 (*d*, $J = 6.9$, 3 H); 1.76 (*d*, $J = 7.9$, 1 H); 2.95–3.01 (*m*, 1 H); 3.13–3.20 (*m*, 1 H); 3.76 (*s*, 3 H); 7.04–7.08 (*m*, 2 H); 7.19–7.31 (*m*, 2 H); 8.11 (br. *s*, 1 H). ^{13}C-NMR (minor product): 12.0; 23.0; 37.2; 47.0; 52.4; 153.9; 172.0 in addition to arom.-C signals. Anal. calc. for $C_{13}H_{17}NO_4S$ (283.3) (a mixture of two isomers): C 55.12, H 6.05, N 4.95; found: C 54.93, H 5.84, N 5.01.

*Methyl 3′-Cyano-3′-methylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**8**; mixture of two stereoisomers). B.p. 205°/3 Torr. M.p. 82–85°. IR (KBr): 2230, 1730, 1625. ^1H-NMR (isomer 1): 1.99 (*s*, 3 H); 2.70 (*d*, $J = 7.9$, 1 H); 3.91–3.96 (*m*, 1 H); 4.08 (*s*, 3 H); 6.86–7.02 (*m*, 3 H); 7.40–7.60 (*m*, 1 H). ^{13}C-NMR (isomer 1): 106.7 (C(2)); 151.9 (CO). ^1H-NMR (isomer 2): 1.64 (*s*, 3 H); 3.24 (*d*, $J = 7.9$, 1 H); 3.63 (*d*, $J = 7.9$, 1 H); 6.86–7.02 (*m*, 3 H); 7.40–7.60 (*m*, 1 H). ^{13}C-NMR (isomer 2): 106.3 (C(2)); 151.2 (CO). Anal. calc. for $C_{13}H_{12}N_2O_3S$ (276.2) (a mixture of two stereoisomers): C 56.52,H 4.38, N 10.14; found: C 56.65, H 4.35, N 10.15.

*Methyl 3′,3′-Dimethyl-4′-(2-methylprop-1-enyl)spiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**9**). M.p. 104–105°. IR (KBr): 1715, 1625. ^1H-NMR: 1.65 (*s*, 3 H); 1.66 (*s*, 3 H); 1.68 (*s*, 3 H); 1.72 (*s*, 3 H); 3.98 (*s*, 3 H); 5.06 (br. *s*, 2 H); 6.89–6.94 (*m*, 3 H); 7.39–7.43 (*m*, 1 H). ^{13}C-NMR: 18.7; 26.0; 28.4; 32.0; 45.8; 53.0; 59.0; 107.9; 109.4; 114.4; 117.9; 121.6; 123.8; 137.8; 147.2; 151.5. Anal. calc. for $C_{17}H_{21}NO_3S$ (319.6): C 63.93, H 6.63, N 4.39; found: C 64.15, H 6.60, N 4.38.

*Ethyl 3′,3′,4′,4′-Tetramethylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**10**). B.p. 210°/3 Torr. IR (film): 1725, 1620. ^1H-NMR: 1.09 (*s*, 3 H); 1.41 (*s*, 3 H); 1.43 (*t*, $J = 7.3$, 3 H); 1.54 (*s*, 3 H); 1.71 (*s*, 3 H); 4.33–4.43 (*m*, 2 H); 6.81–6.96 (*m*, 3 H); 7.35–7.44 (*m*, 1 H). ^{13}C-NMR: 14.3; 21.4; 22.1; 26.2; 29.8; 48.0; 62.3; 62.9; 108.1; 109.8; 115.4; 121.0; 123.7; 129.9; 148.2; 151.9. Anal. calc. for $C_{16}H_{21}NO_3S$ (307.3): C 62.52, H 6.88, N 4.56; found: C 62.77, H 6.91, N 4.57.

*Ethyl 3′-Cyano-3′-methylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**11**; mixture of two stereoisomers). B.p. 200°/3 Torr. IR (film): 2230, 1720, 1625. ^{1}H-NMR (isomer 1): 1.51 (*t*, *J* = 7.3, 3 H); 1.99 (*s*, 3 H); 2.69 (*d*, *J* = 6.9, 1 H); 3.95 (br. *d*, 1 H); 4.39 – 4.61 (*m*, 2 H); 6.84 – 7.05 (*m*, 3 H); 7.38 – 7.60 (*m*, 1 H). ^{13}C-NMR (isomer 1): 14.3; 23.5; 28.9; 53.8; 63.4; 106.8; 108.7; 114.6; 118.6; 122.7; 123.8; 128.2; 146.5; 150.9. ^{1}H-NMR (isomer 2): 1.48 (*t*, *J* = 7.6, 3 H); 1.64 (*s*, 3 H); 3.24 (*d*, *J* = 8.3, 1 H); 3.62 (*d*, *J* = 8.3, 1 H); 4.39 – 4.61 (*m*, 2 H); 6.84 – 7.05 (*m*, 3 H); 7.38 – 7.60 (*m*, 1 H). ^{13}C-NMR (isomer 2): 107.5 (C(2)); 150.3 (CO). Anal. calc. for $C_{14}H_{14}N_2O_3S$ (290.3) (a mixture of two stereoisomers): C 57.95, H 4.86, N 9.65; found: C 58.23, H 4.85, N 9.65.

*Benzyl 3′,3′,4′,4′-Tetramethylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**12**). B.p. 210°/2 Torr. IR (film): 1730, 1625. ^{1}H-NMR: 1.07 (*s*, 3 H); 1.36 (*s*, 3 H); 1.48 (*s*, 3 H); 1.71 (*s*, 3 H); 3.34 (*AB*, *q*, *J* = 12.5, 23.1, 2 H); 6.77 – 6.95 (*m*, 2 H); 7.14 – 7.49 (*m*, 7 H). ^{13}C-NMR: 21.3; 22.1; 26.1; 29.8; 36.5; 48.2; 62.8; 68.1; 108.2; 151.8; and arom.-C signals. Anal. calc. for $C_{21}H_{23}NO_3S$ (369.4): C 68.28, H 6.28, N 3.79; found: C 68.40, H 6.32, N 3.38.

*Phenyl 3′,3′,4′,4′-Tetramethylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**13**). B.p. 155°/2 Torr. IR (film): 1745. ^{1}H-NMR: 1.15 (*s*, 3 H); 1.49 (*s*, 3 H); 1.52 (*s*, 3 H); 1.73 (*s*, 3 H); 6.85 – 7.04 (*m*, 2 H); 7.22 – 7.49 (*m*, 6 H); 7.54 – 7.58 (*m*, 1 H). ^{13}C-NMR: 21.4; 22.2; 26.2; 29.8; 48.1; 62.8; 108.4; 150.2; and arom.-C signals. Anal. calc. for $C_{20}H_{21}NO_3S$ (355.4): C 67.59, H 5.96, N 3.94; found: C 67.62, H 6.02, N 3.95.

Phenyl 2-[(3,3,4,4-Tetramethylthietan-2-ylidene)amino]phenyl Carbonate (**14**). B.p. 155°/3 Torr. IR (film): 1780, 1665. ^{1}H-NMR: 1.44 (*s*, 6 H); 1.59 (*s*, 6 H); 7.01 – 7.04 (*m*, 1 H); 7.10 – 7.42 (*m*, 8 H). ^{13}C-NMR: 23.0; 27.7; 52.3; 62.6; 151.3; 173.9; and arom.-C signals. Anal. calc. for $C_{20}H_{21}NO_3S$ (355.4): C 67.59, H 5.96, N 3.96; found: C 67.69, H 6.06, N 3.95.

*Phenyl 3′,3′,4′-Trimethylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**15**). B.p. 210°/3 Torr. IR (film): 1735. ^{1}H-NMR: 1.26 (*s*, 3 H); 1.29 (*d*, *J* = 6.9, 3 H); 1.44 (*s*, 3 H); 4.03 (*q*, *J* = 6.9, 1 H); 6.84 – 7.02 (*m*, 3 H); 7.20 – 7.33 (*m*, 3 H); 7.42 – 7.50 (*m*, 2 H); 7.57 – 7.61 (*m*, 1 H). ^{13}C-NMR: 15.7; 16.7; 21.5; 23.4; 40.1; 60.4; 108.6; 150.2; and arom.-C signals. Anal. calc. for $C_{19}H_{19}NO_3S$ (341.4): C 66.85, H 5.61, N 4.10; found: C 66.67, H 5.75, N 4.02.

S-*[2-(Benzoxazol-2-yl)-1,2-dimethylpropyl]* O-*Phenyl Thiocarbonate* (**16**). B.p. 210°/2 Torr. IR (film): 1730. ^{1}H-NMR: 1.41 (*d*, *J* = 7.3, 3 H); 1.59 (*s*, 3 H); 1.63 (*s*, 3 H); 4.12 (*q*, *J* = 7.3, 1 H); 7.09 (*d*, *J* = 7.6, 2 H); 7.19 – 7.37 (*m*, 5 H); 7.47 – 7.53 (*m*, 1 H); 7.70 – 7.76 (*m*, 1 H). ^{13}C-NMR: 18.3; 23.3; 24.9; 41.9; 50.4; 110.6; 120.0; 121.2; 124.3; 124.8; 126.1; 129.4; 140.9; 150.8; 151.2; 169.7; 170.3. Anal. calc. for $C_{19}H_{19}NO_3S$ (341.4): C 66.85, H 5.61, N 4.10; found: C 66.85, H 5.65, N 4.08.

Phenyl 2-[(3,4,4-Trimethylthietan-2-ylidene)amino]phenyl Carbonate (**17**). B.p. 220°/3 Torr. IR (film): 1755, 1610. ^{1}H-NMR: 1.38 (*s*, 3 H); 1.45 (*s*, 3 H); 1.45 (*d*, *J* = 6.9, 3 H); 3.50 (*q*, *J* = 6.9, 1 H); 7.02 – 7.47 (*m*, 7 H); 7.69 – 7.74 (*m*, 1 H); 8.12 – 8.16 (*m*, 1 H). ^{13}C-NMR: 19.0; 20.4; 24.3; 42.0; 48.9; 150.6; 174.7; and arom.-C signals. Anal. calc. for $C_{19}H_{19}NO_3S$ (341.4): C 66.85, H 5.61, N 4.10; found: C 66.75, H 5.82, N 4.31.

*Phenyl 3′-Cyano-3′-methylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**18**, mixture of two stereoisomers). M.p. 139 – 141°. IR (KBr): 2235, 1735, 1625. ^{1}H-NMR (isomer 1): 2.08 (*s*, 3 H); 2.65 (*d*, *J* = 5.6, 1 H); 3.92 (br. *s*, 1 H); 6.91 – 7.06 (*m*, 3 H); 7.26 – 7.51 (*m*, 6 H). ^{1}H-NMR (isomer 2): 1.71 (*s*, 3 H); 3.23 (*d*, *J* = 8.5, 1 H); 3.60 (*d*, *J* = 8.3, 1 H); 6.91 – 7.06 (*m*, 3 H); 7.26 – 7.51 (*m*, 6 H). Anal. calc. for $C_{18}H_{14}N_2O_3S$ (338.3) (a mixture of two stereoisomers): C 63.90, H 4.17, N 8.23; found: C 63.94, H 4.26, N 8.03.

S-*[2-(Benzoxazol-2-yl)-2-cyanopropyl]* O-*Phenyl Thiocarbonate* (**19**). B.p. 210°/3 Torr. IR (film): 1735. ^{1}H-NMR: 2.02 (*m*, 3 H); 3.91 (*AB*, *q*, *J* = 14.2, 21.1, 2 H); 7.05 – 7.09 (*m*, 2 H); 7.20 – 7.50 (*m*, 5 H); 7.55 – 7.61 (*m*, 1 H); 7.74 – 7.80 (*m*, 1 H). ^{13}C-NMR: 23.5; 38.8; 40.1; 111.1; 118.2; 120.7; 121.0; 126.2; 126.4; 126.5; 129.5; 140.4; 151.5; 161.2; 168.5. Anal. calc. for $C_{16}H_{21}NO_3S$ (307.3): C 62.52, H 6.88, N 4.56; found: C 62.77, H 6.91, N 4.57.

*Phenyl 3′,3′-Dimethyl-4′-(2-methylprop-1-enyl)spiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**20**). B.p. 180°/2 Torr. IR (film): 1735. ^{1}H-NMR: 1.64 (*s*, 3 H); 1.68 (*s*, 3 H); 1.75 (*s*, 3 H); 1.76 (*s*, 3 H); 5.64 (br. *s*, 2 H); 6.86 – 7.05 (*m*, 3 H); 7.13 – 7.57 (*m*, 7 H). Anal. calc. for $C_{16}H_{21}NO_3S$ (307.3): C 62.52, H 6.88, N 4.56; found: C 62.77, H 6.91, N 4.57.

S-*{1-[1-(Benzoxazol-2-yl)-1-methylethyl]-3-methylbut-2-enyl}* O-*Phenyl Thiocarbonate* (**21**). B.p. 180°/2 Torr. IR (film): 1725. ^{1}H-NMR: 1.63 (*s*, 3 H); 1.69 (*s*, 3 H); 1.76 (*d*, *J* = 1.0, 3 H); 1.85 (*s*, 3 H); 4.89 (*d*, *J* = 10.6, 1 H); 5.67 (br. *d*, *J* = 10.6, 1 H); 7.12 – 7.41 (*m*, 7 H); 7.47 – 7.53 (*m*, 1 H); 7.69 – 7.76 (*m*, 1 H). ^{13}C-NMR: 18.5; 25.0; 25.5; 26.1; 45.8; 54.2; 110.5; 118.9; 119.9; 121.4; 124.2; 124.7; 129.5; 138.1; 141.2; 150.2; 150.8; 166.2; 168.8. Anal. calc. for $C_{22}H_{23}NO_3S$ (381.4): C 69.27, H 6.08, N 3.67; found: C 69.16, H 6.29, N 3.87.

S-*[2-(Benzoxazol-2-yl)-2,3-dimethylbut-3-enyl]* O-*Phenyl Thiocarbonate* (**22**). B.p. 150°/2. IR (film): 1730. ^{1}H-NMR: 1.74 (*s*, 6 H); 3.69 (*d*, *J* = 13.5, 1 H); 3.80 (*d*, *J* = 13.5, 1 H); 4.95 (br. *s*, 1 H); 5.09 (br. *s*, 1 H); 7.06 – 7.16 (*m*, 2 H); 7.20 – 7.54 (*m*, 6 H); 7.71 – 7.78 (*m*, 1 H). ^{13}C-NMR: 19.9; 21.7; 38.8; 47.2; 110.6; 113.9; 120.1; 121.1;

124.3; 125.0; 126.1; 129.5; 140.8; 145.4; 150.9; 151.2; 168.6; 170.2. Anal. calc. for $C_{20}H_{19}NO_3S$ (353.4): C 62.52, H 6.88, N 4.56; found: C 62.77, H 6.91, N 4.57.

*Ethenyl 3′-Cyano-3′-methylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**23**; mixture of two stereoisomers). B.p. 210°/2 Torr. IR (film): 2240, 1735, 1645. ^{1}H-NMR (isomer 1): 1.65 (*s*, 3 H); 3.26 (*d*, *J* = 8.2, 1 H); 3.62 (*d*, *J* = 8.2, 1 H); 4.78–4.83 (*m*, 1 H); 5.09–5.17 (*m*, 1 H); 6.87–7.06 (*m*, 3 H); 7.03–7.74 (*m*, 2 H). ^{13}C-NMR (isomer 1): 106.1 (C(2)); 148.6 (CO). ^{1}H-NMR (isomer 2): 2.00 (*s*, 3 H); 2.71 (*d*, *J* = 7.9, 1 H); 3.97 (br. *s*, 1 H); 4.78–4.83 (*m*, 1 H); 5.09–5.17 (*m*, 1 H); 6.87–7.06 (*m*, 3 H); 7.03–7.74 (*m*, 2 H). ^{13}C-NMR (isomer 2): 106.6 (C(2)); 148.0 (CO). Anal. calc. for $C_{14}H_{12}N_2O_3S$ (288.3) (a mixture of two stereoisomers): C 58.32, H 4.19, N 9.72; found: C 58.37, H 4.15, N 9.63.

*Prop-2-enyl 3′,3′,4′,4′-Tetramethylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**24**). B.p. 230°/2 Torr. IR (film): 1725, 1645, 1620. ^{1}H-NMR: 1.09 (*s*, 3 H); 1.40 (*s*, 3 H); 1.54 (*s*, 3 H); 1.72 (*s*, 3 H); 4.72–4.90 (*m*, 2 H); 5.31 (*dd*, *J* = 1.0, 10.2, 1 H); 5.45 (*dd*, *J* = 1.0, 17.2, 1 H); 5.98–6.11 (*m*, 1 H); 6.82–6.97 (*m*, 3 H); 7.44 (*d*, *J* = 7.9, 1 H). ^{13}C-NMR: 21.3; 22.2; 26.2; 29.8; 48.1; 62.9; 66.9; 108.2; 109.8; 115.5; 119.0; 121.1; 123.9; 129.8; 131.8; 148.3; 151.7. Anal. calc. for $C_{17}H_{21}NO_3S$ (343.4): C 63.93, H 6.63, N 4.39; found: C 63.82, H 6.58, N 4.35.

*Prop-2-enyl 3′-Cyano-3′-methylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**25**; mixture of two stereoisomers). B.p. 210°/2 Torr. IR (film): 2230, 1725, 1625. ^{1}H-NMR (isomer 1): 1.64 (*s*, 3 H); 3.23 (*d*, *J* = 8.3, 1 H); 3.61 (*d*, *J* = 8.3, 1 H); 4.85–5.06 (*m*, 2 H); 5.33–5.55 (*m*, 2 H); 6.02–6.20 (*m*, 1 H); 6.85–7.02 (*m*, 3 H); 7.40–7.60 (*m*, 1 H). ^{13}C-NMR (isomer 1): 29.1 (C(2′)); 59.3 (C(3′)); 106.7 (C(2)); 151.2 (CO). ^{1}H-NMR (isomer 2): 1.98 (*s*, 3 H); 2.68 (*d*, *J* = 7.9, 1 H); 3.93 (br. *s*, 1 H); 4.85–5.06 (*m*, 2 H); 5.33–5.55 (*m*, 2 H); 6.02–6.20 (*m*, 1 H); 6.85–7.02 (*m*, 3 H); 7.40–7.60 (*m*, 1 H). ^{13}C-NMR (isomer 2): 28.9 (C(2′)); 53.7 (C(3′)); 106.7 (C(2)); 150.6 (CO). Anal. calc. for $C_{15}H_{14}N_2O_3S$ (302.3) (a mixture of two stereoisomers): C 59.60, H 4.67, N 9.27; found: C 59.35, H 4.49, N 9.08.

*But-3-enyl 3′-Cyano-3′-methylspiro[3*H*-benzoxazole-2,2′-thietane]-3-carboxylate* (**26**; mixture of two stereoisomers). B.p. 210°/2 Torr. IR (film): 2220, 1720, 1625. ^{1}H-NMR (isomer 1): 1.64 (*s*, 3 H); 2.56–2.70 (*m*, 2 H); 3.23 (*d*, *J* = 8.3, 1 H); 3.63 (*d*, *J* = 8.3, 1 H); 4.42–4.65 (*m*, 2 H); 5.13–5.28 (*m*, 2 H); 5.80–5.96 (*m*, 1 H); 6.85–7.24 (*m*, 3 H); 7.31–7.59 (*m*, 1 H). ^{13}C-NMR (isomer 1): 106.9 (C(2)); 150.9 (CO). ^{1}H-NMR (isomer 2): 1.98 (*s*, 3 H); 2.56–2.70 (*m*, 2 H); 2.68 (*d*, *J* = 7.9, 1 H); 3.97 (br. *s*, 1 H); 4.42–4.65 (*m*, 2 H); 5.13–5.28 (*m*, 2 H); 5.80–5.96 (*m*, 1 H); 6.85–7.24 (*m*, 3 H); 7.31–7.59 (*m*, 1 H). ^{13}C-NMR (isomer 2): 105.4 (C(2)); 151.5 (CO). Anal. calc. for $C_{16}H_{16}N_2O_3S$ (316.3) (a mixture of two stereoisomers): C 60.75, H 5.10, N 8.86; found: C 61.10, H 5.09, N 8.85.

*2,2a-Dihydrothieto[2′,3′:4,5]oxazolo[4,3-*b*]benzoxazol-4-one* (**27**). M.p. 105–106°. IR (KBr): 1800, 1775, 1610. ^{1}H-NMR: 3.22 (*dd*, *J* = 3.6, 10.6, 1 H); 3.56 (*dd*, *J* = 7.3, 10.6, 1 H); 5.94 (*dd*, *J* = 3.6, 7.3, 1 H); 6.93–7.27 (*m*, 3 H); 7.48 (*dd*, *J* = 1.3, 7.6, 1 H). ^{13}C-NMR: 25.6; 87.3; 108.5; 109.8; 116.8; 123.2; 126.8; 127.5; 149.9; 156.6. Anal. calc. for $C_{10}H_7NO_3S$ (221.2): C 54.29, H 3.19, N 6.33; found: C 54.62, H 3.39, N 6.13.

3. *Thermal Reactions of the Spirocyclic Aminothietanes* **3**, **4**, **8**, **9**, **12**, **13**, **15**, **18**, **20**, and **23**–**25**. *General Procedure.* A soln. of the aminothietane (100 mg) in toluene (30 ml) was heated to reflux under Ar for 2–5 h. After removal of the solvent, the residual oil was purified by FC to give the iminothietanes **14**, **28**, **30**, and **35**, and/or the benzoxazoles **16**, **19**, **21**, **29**, **31**–**34**, and **36**. For yields, *cf. Table 2*.

Methyl 2-[(3,3,4,4-Tetramethylthietan-2-ylidene)amino]phenyl Carbonate (**28**). B.p. 200°/2 Torr. IR (film): 1760, 1660. ^{1}H-NMR: 1.43 (*s*, 6 H); 1.62 (*s*, 6 H); 3.87 (*s*, 3 H); 6.96–7.00 (*m*, 1 H); 7.10–7.20 (*m*, 3 H). ^{13}C-NMR: 22.8; 27.7; 52.1; 55.3; 62.5; 120.7; 122.1; 125.4; 126.6; 140.4; 142.9; 153.6; 173.5. Anal. calc. for $C_{15}H_{19}NO_3S$ (293.3): C 61.41, H 6.53, N 4.77; found: C 61.53, H 6.36, N 4.97.

S-*[2-(Benzoxazol-2-yl)-1,2-dimethylpropyl]* O-*Methyl Thiocarbonate* (**29**). B.p. 195°/2 Torr. M.p. 39–40°. IR (KBr): 1715, 1610. ^{1}H-NMR: 1.35 (*d*, *J* = 6.9, 3 H); 1.54 (*s*, 3 H); 1.58 (*s*, 3 H); 3.79 (*s*, 3 H); 4.07 (*q*, *J* = 6.9, 1 H); 7.27–7.35 (*m*, 2 H); 7.49–7.55 (*m*, 1 H); 7.69–7.74 (*m*, 1 H). ^{13}C-NMR: 18.5; 23.0; 25.0; 41.8; 49.9; 53.4; 110.5; 119.9; 124.2; 124.8; 140.9; 150.7; 170.5; 171.0. Anal. calc. for $C_{14}H_{17}NO_3S$ (279.3): C 60.19, H 6.13, N 5.01; found: C 60.41, H 5.94, N 5.12.

Methyl 2-[(3,4,4-Trimethylthietan-2-ylidene)amino]phenyl Carbonate (**30**). B.p. 200°/2 Torr. IR (film): 1765, 1655. ^{1}H-NMR: 1.35 (*s*, 3 H); 1.45 (*s*, 3 H); 1.47 (*d*, *J* = 6.9, 3 H); 3.51 (*q*, *J* = 6.9, 1 H); 3.86 (*s*, 3 H); 6.99–7.03 (*m*, 1 H); 7.10–7.22 (*m*, 3 H). ^{13}C-NMR: 17.8; 20.4; 26.5; 44.2; 55.3; 61.4; 120.6; 122.1; 125.5; 126.7; 140.2; 143.0; 153.6; 173.5. Anal. calc. for $C_{14}H_{17}NO_3S$ (279.3): C 60.19, H 6.13, N 5.01; found: C 59.98, H 6.16, N 5.09.

S-*[2-(Benzoxazol-2-yl)-2-cyanopropyl]* O-*Methyl Thiocarbonate* (**31**). M.p. 72–73°. IR (KBr): 2230, 1715. ^{1}H-NMR: 1.98 (*s*, 3 H); 3.75 (*AB*, *q*, *J* = 14.2, 21.8, 2 H); 3.81 (*s*, 3 H); 7.27–7.45 (*m*, 2 H); 7.56–7.60 (*m*, 1 H); 7.74–7.78 (*m*, 1 H). ^{13}C-NMR: 23.3; 38.6; 40.0; 55.0; 110.0; 118.2; 120.6; 125.1; 126.1; 140.4; 151.1; 161.3; 169.6. Anal. calc. for $C_{13}H_{12}N_2O_3S$ (276.4): C 56.51, H 4.38, N 10.14; found: C 56.63, H 4.37, N 10.16.

S-*[1-[1-(Benzoxazol-2-yl)-1-methylethyl]-3-methylbut-2-enyl]* O-*Methyl Thiocarbonate* (**32**). B.p. 190°/2 Torr. IR (film): 1710, 1610. ^{1}H-NMR: 1.58 (*s*, 3 H); 1.64 (*s*, 3 H); 1.75 (*d*, *J* = 1.3, 3 H); 1.79 (*d*, *J* = 1.3, 3 H); 3.78 (*s*, 3 H); 4.85 (*d*, *J* = 10.6, 1 H); 5.63 (*dd*, *J* = 1.3, 10.6, 1 H); 7.26–7.33 (*m*, 2 H); 7.46–7.50 (*m*, 1 H); 7.67–7.74 (*m*, 1 H). ^{13}C-NMR: 18.3; 25.2; 25.5; 26.0; 45.9; 53.3; 53.9; 110.4; 119.0; 119.8; 124.0; 124.5; 137.8; 141.1; 150.2; 166.2; 170.2. Anal. calc. for $C_{17}H_{21}NO_3S$ (319.4): C 63.93, H 6.63, N 4.39; found: C 64.15, H 6.71, N 4.46.

S-*[2-(Benzoxazo-2-yl)-1,1,2-trimethylpropyl]* O-*Benzyl Thiocarbonate* (**33**). B.p. 210°/3 Torr. IR (film): 1765, 1665. ^{1}H-NMR: 1.33 (*s*, 6 H); 1.51 (*s*, 6 H); 5.24 (*s*, 2 H); 6.96–7.00 (*m*, 1 H); 7.09–7.18 (*m*, 3 H); 7.30–7.45 (*m*, 5 H). ^{13}C-NMR: 22.8; 27.7; 52.2; 62.5; 70.2; 120.8; 122.2; 125.4; 126.7; 128.6; 130.5; 140.5; 142.9; 153.1; 173.4. Anal. calc. for $C_{21}H_{23}NO_3S$ (369.4): C 68.28, H 6.28, N 3.79; found: C 68.40, H 6.32, N 3.82.

S-*[2-(Benzoxazol-2-yl)-2-cyanopropyl]* O-*Ethenyl Thiocarbonate* (**34**). B.p. 210°/2 Torr. IR (film): 2220, 1720, 1640. ^{1}H-NMR: 1.99 (*s*, 3 H); 3.78 (*AB*, *q*, *J* = 4.2, 19.8, 2 H); 4.63 (*dd*, *J* = 1.3, 6.3, 1 H); 4.93 (*dd*, *J* = 1.3, 13.9, 1 H); 7.19 (*dd*, *J* = 6.3, 13.9, 1 H); 7.35–7.45 (*m*, 2 H); 7.56–7.61 (*m*, 1 H); 7.74–7.79 (*m*, 1 H). ^{13}C-NMR: 23.3; 38.3; 39.8; 98.8; 110.0; 118.0; 120.6; 125.0; 126.1; 140.2; 141.5; 151.1; 161.8; 167.2. Anal. calc. for $C_{14}H_{12}N_2O_3S$ (288.3): C 58.33, H 4.20, N 9.72; found: C 58.26, H 4.13, N 9.99.

Prop-2-enyl 2-[(3,3,4,4-Tetramethylthietan-2-ylidene)amino]phenyl Carbonate (**35**). B.p. 230°/2 Torr. IR (film): 1760, 1660. ^{1}H-NMR: 1.42 (*s*, 6 H); 1.61 (*s*, 6 H); 4.70 (*dt*, *J* = 1.3, 5.9, 2 H); 5.29 (*dq*, *J* = 1.3, 10.6, 1 H); 5.42 (*dq*, *J* = 1.3, 15.2, 1 H); 5.92–6.00 (*m*, 1 H); 6.96–7.00 (*m*, 1 H); 7.10–7.26 (*m*, 3 H). ^{13}C-NMR: 22.9; 27.7; 52.1; 62.5; 69.0; 119.2; 120.7; 122.7; 125.4; 126.6; 131.3; 140.5; 142.9; 152.9; 173.4. Anal. calc. for $C_{17}H_{21}NO_3S$ (319.4): C 63.93, H 6.63, N 4.39; found: C 63.82, H 6.58, N 4.35.

S-*[2-(Benzoxazol-2-yl)-2-cyanopropyl]* O-*Prop-2-enyl Thiocarbonate* (**36**). M.p. 89–91°. IR (KBr): 2230, 1715, 1640. ^{1}H-NMR: 1.98 (*s*, 3 H); 3.75 (*AB*, *q*, *J* = 14.2, 21.4, 2 H); 4.66–4.70 (*m*, 2 H); 5.23–5.35 (*m*, 2 H); 5.78–5.91 (*m*, 1 H); 7.35–7.44 (*m*, 2 H); 7.54–7.60 (*m*, 1 H); 7.73–7.78 (*m*, 1 H). ^{13}C-NMR: 23.3; 38.6; 40.0; 68.8; 111.0; 118.3; 119.6; 120.6; 125.1; 126.1; 130.9; 140.4; 151.1; 161.3; 168.9. Anal. calc. for $C_{15}H_{14}N_2O_3S$ (302.3): C 59.60, H 4.67, N 9.27; found: C 59.49, H 4.61, N 9.35.

3. *Oxidation of* **3** *with* m-*Chloroperbenzoic Acid (MCPBA)*. A mixture *of* ***3*** (100 mg) and 2 equiv. of MCPBA (118 mg) in CH_2Cl_2 (30 ml) was stirred under Ar for 2 h at r.t. Usual workup gave **37** (54%).

*Methyl 3′,3′,4′,4′-Tetramethyl-2′-oxospiro[3*H*-benzoxazole-2,5′-oxathiolane]-2-carboxylate* (**37**). M.p. 111–112°. IR (KBr): 1745, 1620, 1480, 1425, 1305, 1250, 1145, 1125, 1055, 760, 740, 700. ^{1}H-NMR: 0.97 (*s*, 3 H); 1.36 (*s*, 3 H); 1.42 (*s*, 3 H); 1.53 (*s*, 3 H); 3.85 (*s*, 3 H); 6.77–6.82 (*m*, 1 H); 6.90–6.98 (*m*, 2 H); 7.58–7.63 (*m*, 1 H). ^{13}C-NMR: 18.3; 19.7; 20.1; 22.7; 52.0; 52.9; 67.7; 107.7; 115.1; 121.7; 123.7; 129.6; 131.2; 146.3; 151.9. Anal. calc. for $C_{15}H_{19}NO_5S$ (325.3): C 55.38, H 5.89, N 4.31; found: C 55.45, H 5.90, N 4.22.

X-Ray Crystal-Structure Determination of **37**. The crytsal **37** from $CHCl_3$/hexane, with approximate dimension of 0.50 × 0.50 × 0.60 mm, was mounted on a glass fiber and used for the X-ray study.

Crystal data: $C_{15}H_{19}NO_5S$, M_r 325.383, triclinic, space group $P\bar{1}$, $a = 6.741(4)$, $b = 11.090(3)$, $c = 11.096(5)$ Å, $\alpha = 96.24(3)°$, $\beta = 101.21(4)°$, $\gamma = 106.03(4)°$, $V = 770.3(6)$ Å^3, $Z = 2$, $D_m = 1.57$ g cm^{-3}, colorless rod, $F(000) = 344$, $\mu(CuK_\alpha)$ 2.08 cm^{-1}.

Data collection, structure solution, and refinement: The intensity data were collected in a *Mac Science MXC 18* diffractometer with graphite-monochromated CuK_α radiation (λ 1.54 Å) by means of the ω-2θ scan technique in the range $2\theta < 69.99°$. Out of 2927 total reflections, 2651 reflections having intensities greater than 3.0 σ (*I*) were used, but no absorption correction was made. The structure was solved by direct methods with maXus. Least-squares refinement including anisotropic thermal parameters for non-H-atoms and isotropic refinement of H-atoms located in difference *Fourier* synthesis terminated at *R* 0.057 (R_w2 0.147).

Tables of crystal data are available as supplementary data. Atomic coordinates bond lengths and angles and thermal parameters of X-ray crystal structure of **37** (CCDC-175876) have been deposited with *Cambridge Crystallographic Data Centre*. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.scan.ac.uk].

4. *Reaction of* **3** *and* **25** *with MeONa.* To a soln. of MeONa (from Na 230 mg in MeOH (20 ml)) in MeOH was added dropwise a soln. of **3** or **25** (1 mmol) in MeOH (30 ml) under Ar at 0° (ice-bath), and then the mixture was stirred for 2 h at r.t. Usual workup yielded *3-(benzoxazol-2-yl)-2,3-dimethylbutane-2-thiol* and *2-(benzoxazol-2-yl)-2-(sulfanylmethyl)propanenitrile* (**38a** and **38b** [2a], resp.) or *2-[(3,3,4,4-Tetramethylthietan-2-ylidene)amino]phenol* (**39**). For yields, *cf. Scheme 2*. The structures of **38a** and **38b**, and **39** [2b] were confirmed by comparison with their spectral data with those of previously described samples.

5. *Acylation of* **39**. A soln. of (**39**) (1 mmol) in Ac_2O (20 ml) was refluxed for 1 h. Usual workup gave *2-[(3,3,4,4-tetramethylthietan-2-ylidene)amino]phenyl acetate* (**40**, 48%), S-*[2-(benzoxazol-2-yl)-1,1,2-trimethylpropyl] thioacetate* and (**41**; 52%). The structures of **40** and **41** were confirmed by comparison of their spectral data with those of previously described samples [2b].

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Received April 16, 2002