

Photoaddition Reactions of Benzoxazole-2(3*H*)-thiones to Cycloalkenes and Heteroaromatics

by Takehiko Nishio^{a)}, Kiyoko Shiwa^{a)}, and Masami Sakamoto^{b)}

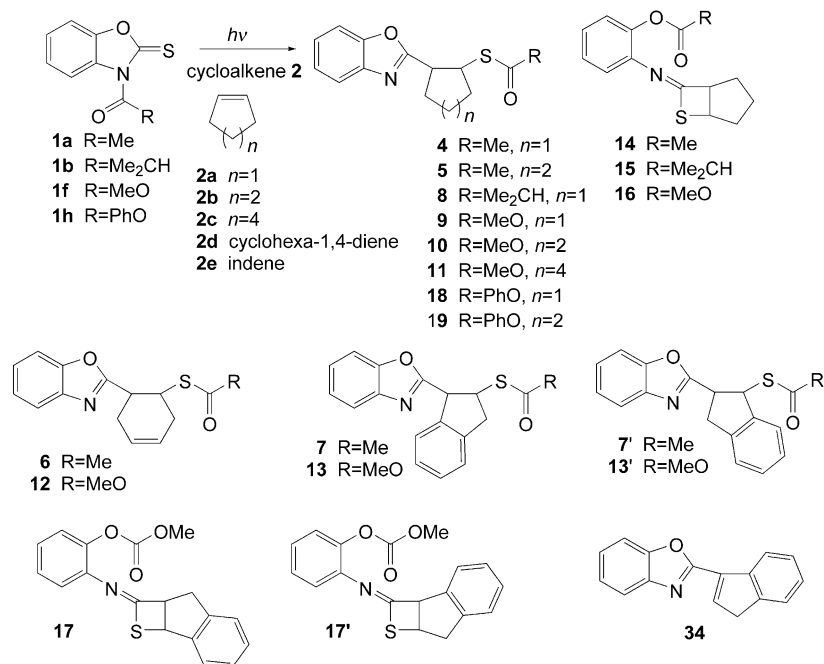
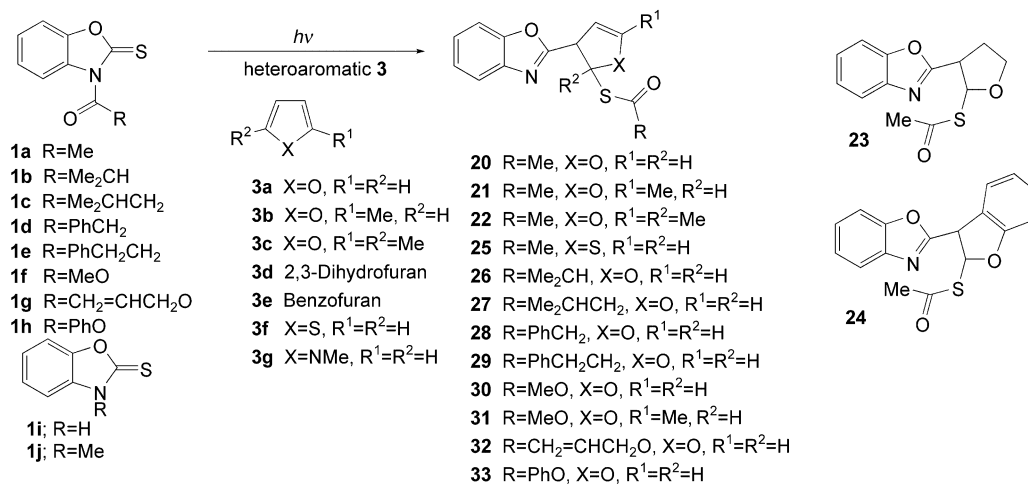
^{a)} Department of Chemistry, University of Tsukuba, Tsukuba-shi, Ibaraki, 305-8571 Japan

^{b)} Department of Materials Technology, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba, 263-8522 Japan

Photoaddition reactions of benzoxazole-2-thiones **1** with cycloalkenes **2** and heteroaromatics **3** were examined. Irradiation of *N*-acylbenzoxazole-2-thiones **1a** and **1b**, and 3-(methoxycarbonyl)- and 3-(phenoxycarbonyl)benzoxazole-2(3*H*)-thiones (**1f** and **1h**, resp.) in the presence of cycloalkenes **2a–2c**, cyclohexa-1,4-diene (**2d**), and indene (**2e**) yielded 2-substituted benzoxazoles **4–13**, **18** and **19**, and iminothietanes **14–17**, by intramolecular trapping of the acyl or MeOCO and PhOCO groups by thiolate anion of the zwitterionic intermediate **I** and by the phenolate anion of the zwitterionic intermediate **II**, respectively, derived from the spirocyclic amino-thietanes **AT** formed by [2 + 2] cycloaddition of the C=S bond of **1** and C=C bond of **2**. Irradiation of **1** in the presence of heteroaromatics **3** gave the 2-substituted benzoxazoles **20–33** exclusively.

1. Introduction. – The photochemistry of thiocarbonyl compounds such as thioketones [1a–c][1e,f], thioimides, and thioamides [1d][1g–m] has been of considerable synthetic and mechanistic interest. These compounds behave like carbonyl compounds in many respects. In the course of our studies on the photochemistry of cyclic conjugated nitrogen-thiocarbonyl systems [1j–m][2][3], we have reported the photoaddition reactions of the benzoxazole-2-thiones [2] and benzothiazole-2-thiones [3] with alkenes. For example, irradiation of *N*-acylbenzoxazole-2-thiones, in the presence of alkenes gave 2-alkylated benzoxazoles and/or iminothietanes, *via* the [2 + 2] cycloaddition intermediates, spirocyclic amino-thietanes [2b], depending on the nature of substituents present in the alkenes, while that of *N*-(alkoxycarbonyl)- and *N*-(aryloxycarbonyl)-benzoxazole-2-thiones, in the presence of alkenes, gave [2 + 2] cycloadducts, spirocyclic amino-thietanes [2c]. To investigate the scope and limitation of the photocycloaddition of benzoxazole-2(3*H*)-thiones **1** and alkenes, we examined the photoreactions of **1** and cycloalkenes **2a–2c**, cyclohexa-1,4-diene (**2d**) and indene (**2e**), and heteroaromatics **3**, and our results are described in this paper (*Schemes 1* and *2*).

2. Results and Discussion. – When a solution of 3-acetylbenzoxazole-2(3*H*)-thione (**1a**) in MeOH was irradiated in the presence of cyclopentene (**2a**) with a high-pressure Hg lamp through a Pyrex filter under Ar at room temperature, 2-substituted benzoxazole, *S*-[2-(benzoxazol-2-yl)cyclopentyl] thioacetate (**4**), and iminothietane, 2-[(6-thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl acetate (**14**), were obtained, which were 1:1 adducts of **1a** and **2a**, in 34 and 25% isolated yields, respectively. A similar result was obtained when benzene was used as solvent. The structures of photoproducts **4** and **14** were elucidated on the basis of spectral data and elemental

Scheme 1. Photoaddition of Benzoxazole-2(3H)-thiones **1a**, **1b**, **1f**, and **1h**, and Cyclic Alkenes **2**Scheme 2. Photoaddition of Benzoxazole-2(3H)-thiones **1a–1h** and Heteroaromatics **3**

analyses. The *cis* relationship between the two substituents, benzoxazolyl and thioacetyl groups at C(2) and C(1), respectively, of the cyclopentane ring in **4** was established by an X-ray structure determination (*Fig.*). The configuration of the cyclopentane ring in **4** is predictable on the basis of mechanistic considerations, where are initially formed

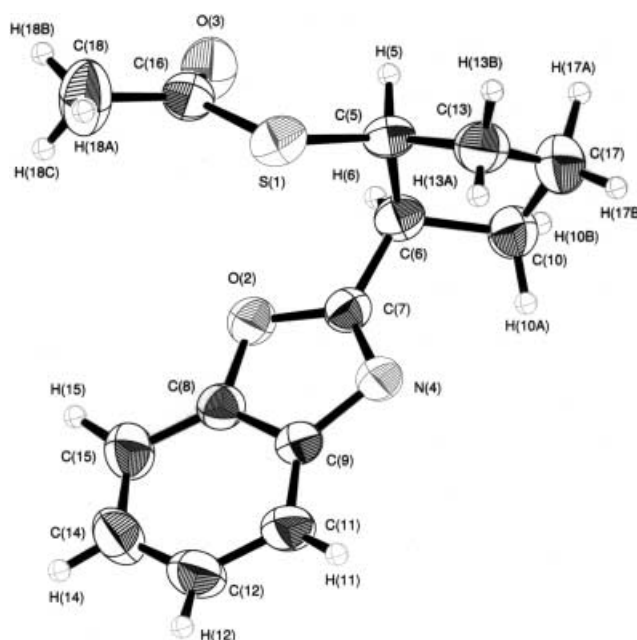


Figure. ORTEP View of S-[2-(benzoxazol-2-yl)cyclopentyl] thioacetate (**4**) with crystallographic numbering scheme

amino-thietane **AT** by [2 + 2] cycloaddition of the C=S bond of **1a** and C=C bond of **2a** (cf. Scheme 4). Irradiation of **1b** and **1f** in the presence of cyclopentene (**2a**), and **1f** in the presence of indene (**2e**) gave 2-substituted benzoxazoles **8** and **9**, **13**, respectively, and iminothietanes **15**–**17**. Irradiation of **1a**, **1f**, and **1h** in the presence of cyclic alkenes **2b** and **2c**, cyclohexa-1,4-diene (**2d**), and indene (**2e**) afforded 2-substituted benzoxazoles **5**–**7**, **10**–**12**, and **18** and **19**, respectively, as the sole products (Table 1). For the

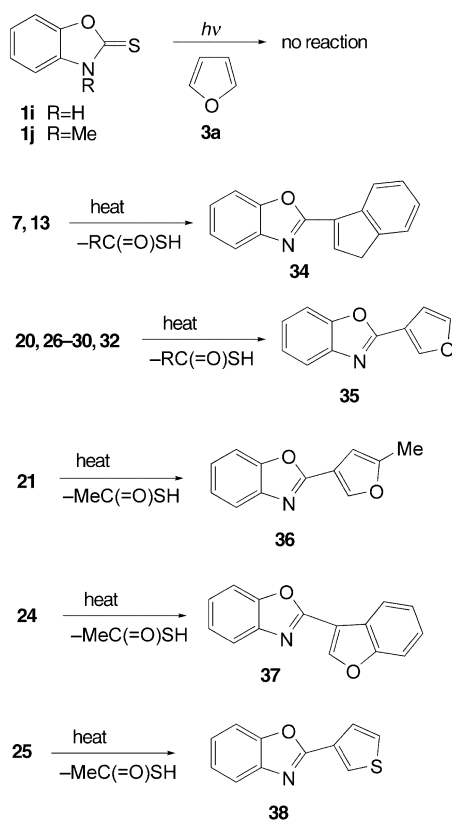
Table 1. Yields of the Photoproducts **4**–**19**

	R	Cycloalkene	Solvent	Product (Yield [%] ^a)
1a	Me	2a	MeOH	4 (34), 14 (25)
1a	Me	2b	MeOH	5 (84)
1a	Me	2d	MeOH	6 (37)
1a	Me	2e	Benzene	7 (63)
1a	Me	2e	Benzene ^b)	7 (trace)
1a	Me	2e	MeOH	7 (91)
1b	Me ₂ CH	2a	MeOH	8 (32), 15 (46), 1i (20)
1f	MeO	2a	Benzene	9 (61), 16 (trace)
1f	MeO	2b	MeOH	10 (78)
1f	MeO	2c	MeOH	11 (52)
1f	MeO	2d	MeOH	12 (43)
1f	MeO	2e	MeOH	13 (43), 17 (21)
1h	PhO	2a	MeOH	18 (69)
1h	PhO	2b	MeOH	19 (67)

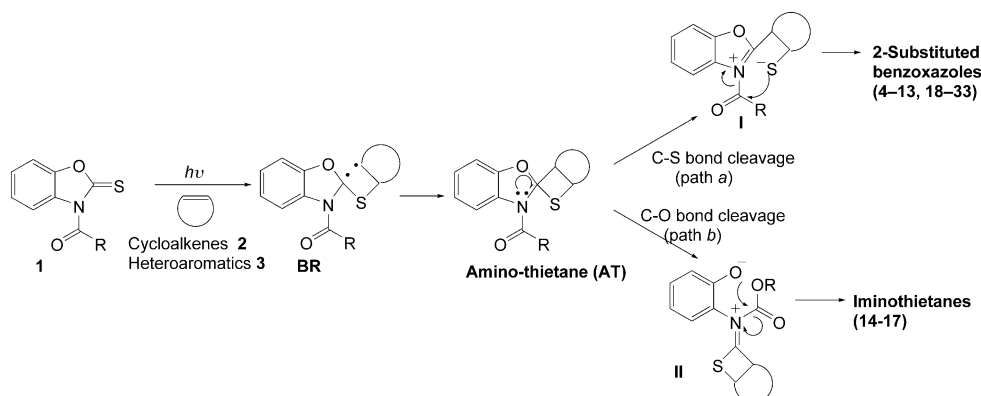
^a) Isolated yield. ^b) Under an O₂ atmosphere

1:1 adducts, 2-substituted benzoxazoles derived from **1a** and **1f** and indene **2e**, and imino-thietane derived from **1f** and **2e**, the formation of two regioisomers (*i.e.*, **7** and **7'**, **13** and **13'**, and **17** and **17'**) is to be expected, in principle. The regioisomers of these photoproducts could not be determined from their spectral data. However, the structures of these compounds were tentatively assigned as **7**, **13**, and **17** from the following evidence. 2-Substituted benzoxazole **7** was converted gradually at room temperature or easily on distillation to 2-(1*H*-inden-3-yl)benzoxazole (**34**) by the elimination of MeCOSH (*Scheme 3*). 2-Substituted benzoxazole **13** was also heated to reflux in toluene for 10 h to yield **34** in 50% yield. In the ¹H-NMR spectrum of **34**, the signal of the CH₂ H-atoms appeared as *doublet* with a coupling constant of 2.3 Hz [4], indicating that the compound **34** is to be 3-substituted 1*H*-indene. The regiochemistry of **7**, **13**, and **17** is reasonably explained by a mechanism in that the photoexcited thioamide **1** initially attacks the C(2)-atom of indene (**2e**) to give the stabilized intermediate biradical **BR** (*cf. Scheme 4*). The two modes of cleavage in this reaction intermediate **AT** might be explained in terms of the stability of zwitterions **I** and **II** affected by a ring-size effect [2b]. In the photoreaction of 3-isobutyrylbenzoxazole-2(3*H*)-thione **1b** and **2a**, the deacylation product, benzoxazole-2(3*H*)-thione **1i**, was

Scheme 3



Scheme 4



obtained in 20% yield, accompanied by 2-substituted benzoxazole **8** (32%) and iminothietane **15** (46%). Probably, compound **1i** arises from the γ -H abstraction by the excited thioamide S-atom, followed by elimination of ketene. Analogous γ -H abstractions were observed in the photolysis of *N*-acylthiazolidine-2-thiones [5] and *N*-acylindoline-2-thiones [6]. The 1:1 adduct **7** was not formed when a benzene solution of **1a** and indene **2e** was irradiated under an O_2 atmosphere.

Irradiation of *N*-acylbenzoxazole-2-thiones **1a–1e** in the presence of heteroaromatics such as furan derivatives **3a–3e** and thiophene (**3f**) in MeOH (or benzene) under the same conditions as described above gave 1:1 adducts of **1** and **3**, 2-substituted benzoxazoles **20–29**, along with a deacylation product, benzoxazole-2(3*H*)-thione (**1i**; Scheme 2 and Table 2).

Table 2. Yields of the Products **20–33**

	R	Heteroaromatic	Solvent	Product (Yield [%] ^a)
1a	Me	3a	MeOH	20 (75)
1a	Me	3a	MeOH ^b)	20 (6)
1a	Me	3b	MeOH	21 (20) 1i (27)
1a	Me	3c	Benzene	22 (47)
1a	Me	3d	MeOH	23 (30)
1a	Me	3e	Benzene	24 (35)
1a	Me	3f	MeOH	25 (20)
1a	Me	3g	Benzene	– ^c)
1b	Me ₂ CH	3a	MeOH	26 (55) 1i (40)
1c	Me ₂ CHCH ₂	3a	Benzene	27 (67) 1i (30)
1d	PhCH ₂	3a	Benzene	28 (13) 1i (50)
1e	PhCH ₂ CH ₂	3a	Benzene	29 (65) 1i (25)
1f	MeO	3a	MeOH	30 (69)
1f	MeO	3b	MeOH	31 (39)
1g	CH ₂ =CHCH ₂ O	3a	Benzene	32 (53)
1h	PhO	3a	MeOH	33 (59)

^a) Isolated yield. ^b) Under an O_2 atmosphere. ^c) No reaction.

The formation of **1i** can be explained in terms of the pathway involving γ -H abstraction by the excited thioamide S-atom as already described above. In contrast, when a benzene solution of **1a** and an excess of 1-methyl-1*H*-pyrrole (**3g**) was irradiated, no photoproducts were obtained, and unchanged starting material **1a** was recovered quantitatively. Irradiation of 3-(alkoxycarbonyl)- and 3-(aryloxy carbonyl)-benzoxazole-2(3*H*)-thiones (**1f–1h**) gave in the presence of furans **3a** and **3b** 1:1 adducts of **1** and **3**, 2-substituted benzoxazoles **30–33**. Irradiation of **1a** and furan **3a** in MeOH under an O₂ atmosphere gave the 1:1 adduct **20** (6%), but in low yield. The structures of photoproducts **20–33** were elucidated on the basis of their spectral properties and chemical evidence (see *Exper. Part*). The 1:1 adducts **20** and **21**, **24–30**, and **32** are not stable and converted gradually at room temperature and easily on distillation into 2-(furan-3-yl)benzoxazole derivatives **35–37**, and 2-(thiophen-3-yl)benzoxazole **38** by elimination of the corresponding alkanethioic S-acid or *O*-alkyl hydrogen thiocarbonate (*Scheme 3*). Irradiation of the parent benzoxazole-2(3*H*)-thione (**1i**) and 3-methylbenzoxazole-2(3*H*)-thione (**1j**) in benzene in the presence of furan (**3a**) resulted in recovery of unchanged starting materials **1i** and **1j**.

The mechanism for the formation of 2-substituted benzoxazoles **4–13**, **18–33**, and iminothietane derivatives **14–17** in the photoaddition reaction of 3-acylbenzoxazole-2(3*H*)-thiones (**1a–1e**), and 3-(alkoxycarbonyl)- and 3-(aryloxy carbonyl)benzoxazole-2(3*H*)-thiones (**1f–1h**, resp.) with cycloalkenes **2a–2c**, cyclohexa-1,4-diene (**2d**), and indene (**2e**), and heteroaromatics **3** could be understood in terms of the pathways shown in *Scheme 4*, which we had proposed for the photoreactions of thioamides and alkenes [2][3][5]. The spirocyclic amino-thietanes **AT** were formed initially through the regioselective [2 + 2] photocycloaddition of the C=S bond of **1** and C=C bond of **2** or **3**. The regiochemistry of the addition of **1** to heteroaromatics **3** could be explained by the thietane formation in the first step, where the photo-excited **1** initially attacks C(2) of the heteroaromatics **3**. This addition mechanism is similar to that proposed by *Oda* and *Machida* for the photoaddition reaction of arenecarbothioamides and furans [7]. The chemoselectivity in the addition of **1** to **3** seems to reflect the steric effect of an α -substituent on an unsymmetrically substituted furan **3b** [7]. Amino-thietane **AT** then underwent C–S bond cleavage of the thietane ring or C–O bond cleavage of oxazole ring assisted by the lone-pair electrons on the N-atom to yield the zwitterions **I** or **II**. Intramolecular trapping of acyl group by the thiolate (path *a*) or phenolate moiety (path *b*) of the zwitterions gave the 2-substituted benzoxazoles **3–13**, **18–33**, and iminothietanes **14–17** [2c].

Experimental Part

General. M.p. and b.p.: *Yanako* micro melting-point apparatus (*MP-3J*) and a *Shibata* glass-tube oven-distillation apparatus (*GTO-350RD*), resp.; uncorrected. Flash chromatography (FC): silica gel *Wakogel C-300* and *Merck 60*. IR Spectra: *JASCO FT/IR-300* spectrophotometer, in cm⁻¹. ¹H- and ¹³C-NMR spectra: *JEOL-JNM-EX270* (270 MHz) spectrometer; in CDCl₃, with Me₄Si as internal standard; δ in ppm, *J* in Hz. Irradiation: *Eikosha HALos* (500 W) high-pressure Hg lamp.

General Procedure for the Photochemical Reactions of the Benzoxazole-2(3H)-thiones 1 and Cycloalkenes 2 or Heteroaromatics 3. A soln. of **1** (1 mmol) and **2** (or **3**) (ca. 0.5 ml) in MeOH (or benzene) (70 ml) was irradiated in a *Pyrex* vessel with the high-pressure Hg lamp under Ar for 5–15 h at r. t. After removal of the solvent, the residual oil was chromatographed on a silica-gel column with toluene/AcOEt 50:1–9:1 to yield the 2-substituted benzoxazoles **4–13**, **18–33**, and iminothietanes **14–17**. For yields, cf. *Tables 1* and *2*.

S-[2-(Benzoxazol-2-yl)cyclopentyl] Thioacetate (**4**). M.p. 55–56°. IR (CHCl₃): 1685, 1610. ¹H-NMR: 1.76–2.34 (m, 6 H); 2.17 (s, 3 H); 3.87 (dd, *J* = 7.6, 14.9, 1 H); 4.23 (dd, *J* = 7.6, 14.9, 1 H); 7.27–7.34 (m, 2 H); 7.45–7.52 (m, 1 H); 7.66–7.73 (m, 1 H). ¹³C-NMR: 23.3; 29.4; 30.5; 32.4; 42.8; 46.6; 110.4; 119.8; 124.1; 124.6; 141.0; 150.6; 167.3; 195.2. Anal. calc. for C₁₄H₁₅NO₂S (261.27): C 64.36, H 5.79, N 5.36; found: C 64.49, H 5.82, N 5.33.

2-[6-(Thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl Acetate (**14**). B.p. 200°/3 Torr. IR (CHCl₃): 1760, 1670. ¹H-NMR: 1.58–2.38 (m, 6 H); 2.29 (s, 3 H); 4.00 (t, *J* = 5.9, 1 H); 4.39 (dd, *J* = 5.9, 8.6, 1 H); 6.98–7.26 (m, 4 H). ¹³C-NMR: 20.7; 23.0; 31.4; 32.8; 41.3; 63.6; 120.4; 122.8; 125.6; 126.5; 140.3; 142.8; 168.4; 168.9. Anal. calc. for C₁₄H₁₅NO₂S (261.27): C 64.36, H 5.79, N 5.36; found C 64.25, H 5.85, N 5.63.

S-[2-(Benzoxazol-2-yl)cyclohexyl] Thioacetate (**5**). M.p. 62–63°. IR (CHCl₃): 1690, 1610. ¹H-NMR: 1.43–1.54 (m, 1 H); 1.63–2.18 (m, 7 H); 2.17 (s, 3 H); 3.42–3.49 (m, 1 H); 4.21–4.38 (m, 1 H); 7.26–7.33 (m, 2 H); 7.46–7.51 (m, 1 H); 7.56–7.73 (m, 1 H). ¹³C-NMR: 23.2; 23.7; 30.7; 31.2; 40.9; 44.2; 110.4; 119.9; 124.0; 124.7; 141.0; 150.5; 167.0; 194.5. Anal. calc. for C₁₅H₁₇NO₂S (275.29): C 65.44, H 6.22, N 5.09; found C 65.29, H 6.27 N 4.97.

S-[6-(Benzoxazol-2-yl)cyclohex-3-enyl] Thioacetate (**6**). M.p. 107–108°. IR (KBr): 1685. ¹H-NMR: 2.21 (s, 3 H); 2.41–2.85 (m, 4 H); 3.58–3.65 (m, 1 H); 4.45–4.55 (m, 1 H); 5.70–5.85 (m, 2 H); 7.26–7.34 (m, 2 H); 7.48–7.53 (m, 1 H); 7.68–7.73 (m, 1 H). ¹³C-NMR: 26.5; 30.7; 31.7; 37.4; 41.0; 110.4; 119.9; 124.1; 124.7; 125.1; 141.0; 150.8; 166.5; 194.9.

S-[1-(Benzoxazol-2-yl)-2,3-dihydro-1H-inden-3-yl] Thioacetate (**7**). B.p. > 250°/2 Torr (dec.). IR (CHCl₃): 1690. ¹H-NMR: 2.22 (s, 3 H); 3.37–3.45 (m, 2 H); 4.73 (dd, *J* = 8.3, 17.5, 1 H); 5.06 (d, *J* = 8.3, 1 H); 7.17–7.34 (m, 6 H); 7.40–7.46 (m, 1 H); 7.67–7.72 (m, 1 H). ¹³C-NMR: 30.4; 38.1; 45.7; 48.8; 110.5; 120.0; 124.2; 124.8; 125.1; 127.2; 128.3; 140.1; 140.9; 141.8; 150.7; 165.4; 195.1. The photoproduct **7** was gradually converted to **34** at r.t.

2-(1H-Inden-3-yl)benzoxazole (**34**). M.p. 93–94°. IR: 1630, 1515, 1450, 1380, 1240, 1145, 985, 955, 745. ¹H-NMR: 3.63 (d, *J* = 2.3, 2 H); 7.28–7.59 (m, 7 H); 7.78–7.84 (m, 1 H); 8.47 (d, *J* = 7.6, 1 H). ¹³C-NMR: 38.9; 110.3; 120.3; 122.6; 123.8; 124.4; 125.3; 125.8; 126.7; 132.1; 139.3; 140.5; 141.9; 143.5; 150.0; 159.6. Anal. calc. for C₁₆H₁₁NO (233.26): C 82.38, H 4.75, N 6.01; found C 82.44, H 4.84, N 5.73.

S-[2-(Benzoxazol-2-yl)cyclopentyl] 2-Methylpropanethioate (**8**). B.p. 205°/2 Torr. IR (CHCl₃): 1680, 1615. ¹H-NMR: 0.96 (d, *J* = 6.9, 3 H); 1.04 (d, *J* = 6.9, 3 H); 1.70–2.42 (m, 6 H); 2.53 (sept., *J* = 6.9, 1 H); 3.86 (dd, *J* = 7.6, 14.8, 1 H); 4.22 (dd, *J* = 7.6, 14.8, 1 H); 7.25–7.35 (m, 2 H); 7.43–7.53 (m, 1 H); 7.65–7.74 (m, 1 H). ¹³C-NMR: 19.1; 19.2; 22.8; 29.3; 32.3; 42.9; 46.0; 110.3; 119.7; 124.0; 141.0; 150.6; 167.4; 203.4. Anal. calc. for C₁₆H₁₉NO₂S (289.32): C 66.41, H 6.62, N 4.84; found C 66.02, H 6.29, N 4.62.

2-[6-(Thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl 2-Methylpropanoate (**15**). B.p. 200°/3 Torr. IR (film): 1755, 1670. ¹H-NMR: 1.32 (d, *J* = 6.9, 6 H); 1.54–2.37 (m, 6 H); 2.84 (sept., *J* = 6.9, 1 H); 3.97 (t, *J* = 5.9, 1 H); 4.32–4.39 (m, 1 H); 6.99–7.20 (m, 4 H). ¹³C-NMR: 19.0; 19.1; 22.9; 31.3; 32.8; 33.9; 41.1; 63.6; 120.3; 122.8; 125.6; 126.3; 140.3; 142.9; 168.0; 174.8. Anal. calc. for C₁₆H₁₉NO₂S (289.32): C 66.41, H 6.62, N 4.84; found C 66.26, H 6.73, N 4.84.

S-[2-(Benzoxazol-2-yl)cyclopentyl] O-Methyl Thiocarbonate (**9**) and Methyl 2-[6-(Thiabicyclo[3.2.0]heptan-7-ylidene)amino]phenyl Carbonate (**16**). Compounds **9** and **16** could not be separated completely. B.p. (a mixture of **9** and **16**) 200°/3 Torr. IR (film; a mixture of **9** and **16**): 1750, 1705, 1605. ¹H-NMR of **9**: 1.76–1.88 (m, 1 H); 2.01–2.38 (m, 5 H); 3.70 (s, 3 H); 3.85 (dd, *J* = 7.3, 14.2, 1 H); 4.12 (dd, *J* = 7.3, 14.2, 1 H); 7.26–7.32 (m, 2 H); 7.45–7.51 (m, 1 H); 7.66–7.72 (m, 1 H). ¹³C-NMR of **9**: 23.1; 29.3; 32.4; 43.1; 48.6; 54.0; 110.4; 119.8; 124.1; 124.6; 141.0; 150.7; 167.0; 170.8. ¹H-NMR of **16**: 1.68–2.35 (m, 6 H); 3.31–3.40 (m, 1 H); 3.68–3.77 (m, 1 H); 3.75 (s, 3 H); 7.04–7.09 (m, 1 H); 7.23–7.36 (m, 2 H); 8.12–8.16 (m, 1 H). ¹³C-NMR of **16**: 22.8; 26.5; 36.6; 41.3; 51.3; 52.4; 154.0; 171.2 in addition to the signals of aromatic C-atoms. Anal. calc. for C₁₄H₁₅NO₃S (277.27; a mixture of **9** and **16**): C 60.63, H 5.45, N 5.05; found C 60.29, H 5.45, N 5.10.

S-[2-(Benzoxazol-2-yl)cyclohexyl] O-Methyl Carbonate (**10**). M.p. 74–75°. IR (CHCl₃): 1710. ¹H-NMR: 1.41–1.59 (m, 1 H); 1.61–1.85 (m, 3 H); 1.93–2.27 (m, 4 H); 3.47–3.55 (m, 1 H); 3.65 (s, 3 H); 4.19–4.25 (m, 1 H); 7.26–7.36 (m, 2 H); 7.45–7.53 (m, 1 H); 7.63–7.73 (m, 1 H). ¹³C-NMR: 23.0; 23.7; 27.1; 31.3; 41.1; 46.7; 54.0; 110.4; 119.9; 124.1; 124.7; 141.1; 150.6; 166.8; 170.7. Anal. calc. for C₁₅H₁₇NO₃S (291.29): C 61.85, H 5.88, N 4.81; found C 61.45, H 5.90, N 4.75.

S-[2-(Benzoxazol-2-yl)cyclooctyl] O-Methyl Carbonate (**11**). B.p. 210°/3 Torr. IR (film): 1730, 1610. ¹H-NMR: 1.55–2.25 (m, 12 H); 3.26–3.33 (m, 1 H); 3.67–3.74 (m, 1 H); 3.75 (s, 3 H); 7.05 (d, *J* = 4.3, 1 H); 7.13–7.27 (m, 1 H); 7.42 (br. s, 1 H); 8.12 (br. d, *J* = 8.3, 1 H). ¹³C-NMR: 24.1; 25.9; 26.4; 27.6; 35.8; 40.8; 47.9; 52.4; 120.5; 122.2; 123.3; 126.7; 130.6; 139.9; 154.0; 172.4. Anal. calc. for C₁₇H₂₁NO₃S (319.35): C 63.93, H 6.63, N 4.39; found C 64.16, H 6.76, N 4.12.

S-[6-(Benzoxazol-2-yl)cyclohex-3-enyl] O-Methyl Carbonate (**12**). B.p. 220°/3 Torr. IR (film): 1710, 1615. ¹H-NMR: 2.52–2.81 (m, 3 H); 3.65 (s, 3 H); 4.30–4.36 (m, 1 H); 5.71–5.90 (m, 2 H); 7.26–7.33 (m, 2 H); 7.46–7.51 (m, 1 H); 7.68–7.72 (m, 1 H). ¹³C-NMR: 23.6; 31.8; 37.7; 43.3; 54.0; 110.4; 119.9; 124.1; 124.7; 124.8; 125.0; 141.1; 150.7; 166.7; 170.8. Anal. calc. for C₁₅H₁₅NO₃S (289.28): C 62.28, H 5.23, N 4.84; found C 62.22, H 5.28, N 4.82.

S-[2-(Benzoxazol-2-yl)-2,3-dihydro-1H-inden-1-yl] O-Methyl Thiocarbonate (**13**). Oil. IR (CHCl₃): 1710. ¹H-NMR: 3.39–3.51 (m, 2 H); 3.76 (s, 3 H); 4.63 (dd, *J* = 8.3, 17.8, 1 H); 5.11 (d, *J* = 7.9, 1 H); 7.20–7.47 (m, 7 H); 7.66–7.71 (m, 1 H). ¹³C-NMR: 30.3; 47.5; 49.1; 57.4; 110.4; 122.0; 124.2; 124.8; 125.1; 127.3; 128.4; 140.1; 141.6; 150.8; 165.2; 170.5. Anal. calc. for C₁₈H₁₅NO₃S (325.31): C 66.45, H 4.65, N 4.32; found C 66.75, H 4.81, N 4.03.

Methyl 2-[1,2a,3,7b-Tetrahydroindeno[2,1-b]thiet-1-yl]amino]phenyl Carbonate (**17**). M.p. 129–130°. IR (CHCl₃): 1735, 1615. ¹H-NMR: 2.18 (d, *J* = 9.2, 1 H); 3.26 (dd, *J* = 7.6, 15.8, 1 H); 3.75 (s, 3 H); 4.06 (dd, *J* = 7.6, 18.9, 1 H); 4.51 (d, *J* = 7.6, 1 H); 7.02–7.08 (m, 2 H); 7.18–7.30 (m, 5 H); 7.70 (br. d, *J* = 3.3, 1 H). ¹³C-NMR: 40.8; 42.6; 52.1; 57.4; 122.1; 123.1; 124.8; 125.3; 126.8; 127.4; 128.5; 130.5; 138.3; 142.2; 153.8; 169.1. Anal. calc. for C₁₈H₁₅NO₃S (325.31): C 66.45, H 4.65, N 4.32; found C 66.24, H 4.61, N 4.08.

S-[2-(Benzoxazol-2-yl)cyclopentyl] O-Phenyl Thiocarbonate (**18**). B.p. 220°/3 Torr. IR (film): 1725. ¹H-NMR: 1.80–2.47 (m, 6 H); 3.92 (dd, *J* = 7.3, 14.2, 1 H); 4.18 (dd, *J* = 7.3, 14.2, 1 H); 6.95–7.00 (m, 2 H); 7.21–7.36 (m, 5 H); 7.47–7.54 (m, 1 H); 7.72–7.77 (m, 1 H). ¹³C-NMR: 23.3; 29.2; 32.2; 43.1; 48.9; 110.5; 119.9; 121.2; 124.2; 124.7; 128.3; 129.4; 141.1; 151.1; 167.0. Anal. calc. for C₁₉H₁₇NO₃S (339.33): C 67.25, H 5.05, N 4.13; found C 67.08, H 5.34, N 4.41.

S-[2-(Benzoxazol-2-yl)cyclohexyl] O-Phenyl Thiocarbonate (**19**). M.p. 97–98°. IR (KBr): 1720, 1615. ¹H-NMR: 1.39–1.59 (m, 1 H); 1.62–1.85 (m, 3 H); 1.93–2.15 (m, 3 H); 2.23–2.35 (m, 1 H); 3.50–3.57 (m, 1 H); 4.24–4.30 (m, 1 H); 6.88–6.95 (m, 2 H); 7.11–7.34 (m, 5 H); 7.45–7.52 (m, 1 H); 7.70–7.77 (m, 1 H). ¹³C-NMR: 23.2; 23.6; 27.1; 31.1; 41.0; 47.1; 110.5; 119.9; 121.1; 124.1; 124.7; 125.9; 128.3; 129.3; 141.1; 151.1; 166.7. Anal. calc. for C₂₀H₁₉NO₃S (353.36): C 67.98, H 5.42, N 3.96; found C 67.67, H 5.49, N 3.85.

2-[2-(Acetylsulfanyl)-2,3-dihydrofuran-3-yl]benzoxazole (**20**). B.p. 175–180°/3 Torr (dec.). IR (film): 1695, 1605. ¹H-NMR: 2.24 (s, 3 H); 4.95 (dt, *J* = 2.3, 9.9, 1 H); 5.40 (dd, *J* = 2.3, 2.6, 1 H); 6.63 (t, *J* = 2.6, 1 H); 6.73 (d, *J* = 9.9, 1 H); 7.32–7.40 (m, 2 H); 7.51–7.56 (m, 1 H); 7.73–7.77 (m, 1 H). ¹³C-NMR: 31.0; 46.4; 86.0; 101.0; 110.8; 120.3; 124.6; 125.4; 140.9; 147.8; 150.8; 163.5; 192.9. Anal. calc. for C₁₃H₁₁NO₃S (261.23): C 59.77, H 4.24, N 5.36; found C 60.08, H 4.04, N 5.44. The photoadduct **20** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

2-(Furan-3-yl)benzoxazole (**35**). M.p. 88–89°. IR (CHCl₃): 1645. ¹H-NMR: 7.03 (dd, *J* = 1.0, 2.0, 1 H); 7.26–7.36 (m, 2 H); 7.40–7.56 (m, 2 H); 8.22 (dd, *J* = 1.0, 1.7, 1 H). ¹³C-NMR: 108.8; 110.2; 115.2; 119.5; 124.3; 124.7; 141.6; 144.1; 150.0; 158.1. Anal. calc. for C₁₁H₇NO₂ (185.17): C 71.35, H 3.81, N 7.56; found C 71.36, H 3.71, N 7.52.

2-[2-(Acetylsulfanyl)-2,3-dihydro-5-methylfuran-3-yl]benzoxazole (**21**). B.p. 185°/3 Torr (dec.). IR (CHCl₃): 1715. ¹H-NMR: 1.95 (s, 3 H); 2.23 (s, 3 H); 4.96 (dt, *J* = 2.0, 9.9, 1 H); 5.02 (dd, *J* = 1.3, 2.0, 1 H); 6.27 (d, *J* = 9.9, 1 H); 7.31–7.39 (m, 2 H); 7.49–7.55 (m, 1 H); 7.73–7.77 (m, 1 H). ¹³C-NMR: 13.7; 30.9; 47.4; 85.9; 95.7; 110.7; 120.2; 124.5; 125.2; 140.8; 150.8; 157.6; 164.2; 193.1. The photoadduct **21** was unstable at r.t. and converted gradually or easily on distillation (185–190°/3 Torr) to **36**.

2-(5-Methylfuran-3-yl)benzoxazole (**36**). M.p. 75–76°. IR (CHCl₃): 1645. ¹H-NMR: 2.34 (d, *J* = 1.0, 3 H); 6.59 (t, *J* = 1.0, 1 H); 7.25–7.32 (m, 2 H); 7.44–7.52 (m, 1 H); 7.65–7.77 (m, 1 H); 8.05 (d, *J* = 0.7, 1 H). ¹³C-NMR: 13.3; 104.6; 110.2; 115.8; 119.4; 124.3; 124.6; 141.7; 142.7; 150.0; 154.1; 158.5. Anal. calc. for C₁₂H₉NO₂ (199.20): C 72.35, H 4.55, N 7.03; found C 72.39, H 4.51, N 6.93.

2-[2-(Acetylsulfanyl)-2,3-dihydro-2,5-dimethylfuran-3-yl]benzoxazole (**22**). M.p. 72–73°. IR (film): 1695, 1610. ¹H-NMR: 1.94 (d, *J* = 2.0, 3 H); 2.07 (s, 3 H); 2.32 (s, 3 H); 4.60 (q, *J* = 2.0, 1 H); 5.06 (s, 1 H); 7.28–7.38 (m, 2 H); 7.52–7.56 (m, 1 H); 7.73–7.78 (m, 1 H). ¹³C-NMR: 14.0; 27.6; 31.3; 56.1; 96.1; 99.0; 110.7; 120.2; 124.5; 125.0; 141.0; 150.8; 156.6; 163.5; 193.5. Anal. calc. for C₁₅H₁₃NO₃S (289.28): C 62.28, H 5.23, N 4.84; found C 62.14, H 5.21, N 4.75.

2-[2-(Acetylsulfanyl)-2,3,4,5-tetrahydrofuran-3-yl]benzoxazole (**23**). B.p. 19°/3 Torr. IR (CHCl₃): 1695, 1615. ¹H-NMR: 2.21 (s, 3 H); 2.33–2.56 (m, 2 H); 4.08 (dd, *J* = 8.2, 15.2, 1 H); 4.35–4.44 (m, 2 H); 5.52 (d, *J* = 7.3, 1 H); 7.29–7.36 (m, 2 H); 7.50–7.55 (m, 1 H); 7.71–7.76 (m, 1 H). ¹³C-NMR: 30.2; 31.2; 44.0; 68.1; 76.0; 110.7; 120.3; 124.3; 125.2; 140.5; 150.3; 163.7; 194.2. Anal. calc. for C₁₃H₁₃NO₃S (263.24): C 59.31, H 4.98, N 5.32; found C 59.08, H 4.99, N 5.36.

2-[2-(Acetylsulfanyl)-2,3-dihydrobenzofuran-3-yl]benzoxazole (**24**). Oil. IR (CHCl₃): 1705. ¹H-NMR: 2.25 (s, 3 H); 5.45 (d, *J* = 9.2, 1 H); 6.94–7.05 (m, 3 H); 7.24–7.40 (m, 4 H); 7.50–7.54 (m, 1 H); 7.74–7.99 (m, 1 H).

^{13}C -NMR: 30.3; 46.2; 87.4; 110.9; 120.4; 122.3; 124.1; 124.6; 125.5; 125.6; 130.0; 140.8; 150.9; 158.4; 162.5; 192.8. The photoadduct **24** was unstable at r.t. and gradually converted to **37**.

2-(Benzofuran-3-yl)benzoxazole (**37**). M.p. 128–130°. IR (CHCl_3): 1645. ^1H -NMR: 7.26–7.47 (*m*, 4 H); 7.53–7.59 (*m*, 2 H); 7.75–7.83 (*m*, 1 H); 8.35–8.43 (*m*, 2 H). ^{13}C -NMR: 110.3; 111.1; 111.7; 119.8; 122.2; 124.1; 124.5; 125.0; 125.6; 141.9; 147.0; 150.0; 155.6; 158.0. Anal. calc. for $\text{C}_{15}\text{H}_9\text{NO}_2$ (235.23): C 75.58, H 3.86, N 5.95; found C, 75.89, H 3.78, N 5.88.

2-[2-(Acetylsulfanyl)-2,3-dihydrothiophen-3-yl]benzoxazole (**25**). Oil. ^1H -NMR: 2.15 (*s*, 3 H); 4.95 (*td*, *J* = 2.3, 7.9, 1 H); 5.81 (*d*, *J* = 7.9, 1 H); 6.03 (*dd*, *J* = 2.3, 6.3, 1 H); 6.58 (*dd*, *J* = 3.0, 6.3, 1 H); 7.31–7.39 (*m*, 3 H); 7.51–7.56 (*m*, 1 H); 7.73–7.81 (*m*, 2 H). ^{13}C -NMR: 30.5; 51.8; 55.3; 110.7; 120.2; 120.4; 124.6; 125.4; 129.0; 140.8; 150.8; 163.0; 193.9. The photoadduct **25** was unstable at r.t. and converted to **38**.

2-(Thiophen-3-yl)benzoxazole (**38**). M.p. 139–140°. IR (KBr): 1620. ^1H -NMR: 7.29–7.37 (*m*, 2 H); 7.41–7.45 (*m*, 1 H); 7.50–7.56 (*m*, 1 H); 7.72–7.80 (*m*, 2 H); 8.17–8.20 (*m*, 1 H). ^{13}C -NMR: 110.4; 119.9; 124.5; 125.0; 126.6; 127.0; 128.0; 129.2; 141.9; 150.3; 159.7. Anal. calc. for $\text{C}_{11}\text{H}_7\text{NOS}$ (201.17): C 65.67, H 3.51, N 6.96; found C 65.67, H 3.46, N 6.87.

2-[2,3-Dihydro-2-[(2-methylpropanoyl)sulfanyl]furan-3-yl]benzoxazole (**26**). B.p. 175°/3 Torr (dec.). IR (CHCl_3): 1695, 1620. ^1H -NMR: 1.02 (*d*, *J* = 6.9, 3 H); 1.09 (*d*, *J* = 6.9, 3 H); 2.56 (*sept.*, *J* = 6.9, 1 H); 4.97 (*td*, *J* = 2.3, 9.9, 1 H); 5.40 (*t*, *J* = 2.3, 1 H); 6.64 (*t*, *J* = 2.6, 1 H); 6.71 (*d*, *J* = 9.9, 1 H); 7.31–7.39 (*m*, 2 H); 7.49–7.55 (*m*, 1 H); 7.72–7.77 (*m*, 1 H). ^{13}C -NMR: 18.9; 19.0; 43.5; 46.6; 85.7; 100.9; 110.7; 120.2; 124.5; 125.2; 140.8; 147.8; 150.8; 163.6; 201.1. Anal. calc. for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$ (289.28): C 62.28, H 5.23, N 4.84; found 62.49, H 4.94, N 4.66. The photoadduct **26** was unstable at r.t. and converted to **35**.

2-[2,3-Dihydro-2-[(3-methylbutanoyl)sulfanyl]furan-3-yl]benzoxazole (**27**). B.p. 180°/3 Torr (dec.). IR (CHCl_3): 1700, 1620, 1610. ^1H -NMR: 0.82 (*d*, *J* = 6.6, 3 H); 0.86 (*d*, *J* = 6.6, 3 H); 1.95–2.09 (*m*, 1 H); 2.23–2.39 (*m*, 2 H); 4.96 (*td*, *J* = 2.3, 9.9, 1 H); 5.36–5.41 (*m*, 1 H); 6.63 (*t*, *J* = 2.3, 1 H); 6.74 (*d*, *J* = 9.9, 1 H); 7.31–7.39 (*m*, 2 H); 7.48–7.56 (*m*, 1 H); 7.70–7.76 (*m*, 1 H). ^{13}C -NMR: 22.0, 22.1; 26.1; 46.6; 53.1; 85.8; 100.9; 110.7; 120.3; 124.5; 125.2; 140.9; 147.8; 150.8; 163.6; 195.9. The photoadduct **27** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

2-[2,3-Dihydro-2-[(2-phenylethanoyl)sulfanyl]furan-3-yl]benzoxazole (**28**). Oil. IR (CHCl_3): 1700, 1645, 1610. ^1H -NMR: 3.67 (*s*, 2 H); 4.97 (*td*, *J* = 2.3, 9.9, 1 H); 5.37 (*t*, *J* = 2.3, 1 H); 6.59 (*t*, *J* = 2.6, 1 H); 6.70 (*d*, *J* = 9.9, 1 H); 7.01–9.07 (*m*, 2 H); 7.12–7.19 (*m*, 2 H); 7.26–7.41 (*m*, 3 H); 7.44–7.52 (*m*, 1 H); 7.69–7.78 (*m*, 1 H). ^{13}C -NMR: 46.6; 50.5; 86.0; 100.9; 110.7; 120.2; 124.5; 152.2; 127.4; 128.5; 129.4; 132.3; 140.7; 147.7; 150.7; 163.4; 194.5. The photoadduct **28** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

2-[2,3-Dihydro-2-[(3-phenylpropanoyl)sulfanyl]furan-3-yl]benzoxazole (**29**). Oil. IR (CHCl_3): 1700, 1645. ^1H -NMR: 2.63–3.05 (*m*, 4 H); 4.95 (*td*, *J* = 2.3, 9.9, 1 H); 5.39 (*t*, *J* = 2.3, 1 H); 6.62 (*t*, *J* = 2.5, 1 H); 6.76 (*d*, *J* = 9.9, 1 H); 7.02–7.40 (*m*, 4 H); 7.48–7.55 (*m*, 1 H); 7.69–7.78 (*m*, 1 H). ^{13}C -NMR: 30.8, 45.8; 46.5; 85.8; 101.0; 110.7; 120.3; 124.5; 125.3; 126.3; 128.1; 128.4; 139.5; 140.8; 147.7; 150.8; 163.5; 195.6. The photoadduct **29** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

S-[3-(Benzoxazol-2-yl)-2,3-dihydrofuran-2-yl] O-Methyl Thiocarbonate (**30**). Oil. IR (CHCl_3): 1720, 1610. ^1H -NMR: 3.78 (*s*, 3 H); 4.98 (*dt*, *J* = 2.3, 9.6, 1 H); 5.41 (*t*, *J* = 2.3, 1 H); 6.63 (*t*, *J* = 2.3, 1 H); 6.70 (*d*, *J* = 9.6, 1 H); 7.27–7.39 (*m*, 2 H); 7.51–7.55 (*m*, 1 H); 7.70–7.76 (*m*, 1 H). ^{13}C -NMR: 46.4; 54.6; 88.3; 101.1; 110.7; 120.2; 124.5; 125.3; 140.7; 147.5; 150.7; 163.0; 168.8. The photoadduct **30** was unstable at r.t. and converted gradually or easily on distillation (175–100°/3 Torr) to **35**.

S-[3-(Benzoxazol-2-yl)-2,3-dihydro-5-methylfuran-2-yl] O-Methyl Thiocarbonate (**31**). B.p. 190°/3 Torr (dec.). IR (CHCl_3): 1720, 1610. ^1H -NMR: 1.95 (*dd*, *J* = 1.3, 2.3, 3 H); 2.35 (*s*, 3 H); 3.62 (*s*, 3 H); 4.63 (*t*, *J* = 2.3, 1 H); 5.09 (*br. s*, 1 H); 7.28–7.37 (*m*, 2 H); 7.49–7.55 (*m*, 1 H); 7.72–7.76 (*m*, 1 H). ^{13}C -NMR: 13.9; 27.9; 53.5; 55.9; 96.2; 98.7; 110.6; 120.1; 124.4; 125.2; 140.8; 150.7; 156.5; 163.0; 167.9. The result of the elemental analysis of **31** was not in agreement with the calculated values, since **31** decomposed on distillation.

S-[3-(Benzoxazol-2-yl)-2,3-dihydrofuran-2-yl] O-(Prop-2-enyl) Thiocarbonate (**32**). Oil. IR (CHCl_3): 1720, 1610. ^1H -NMR: 4.66 (*m*, 2 H); 4.98 (*td*, *J* = 2.3, 9.9, 1 H); 5.20–5.31 (*m*, 2 H); 5.41 (*t*, *J* = 2.3, 1 H); 5.76–5.91 (*m*, 1 H); 6.63 (*t*, *J* = 2.6, 1 H); 6.69 (*d*, *J* = 9.9, 1 H); 7.30–7.40 (*m*, 2 H); 7.48–7.55 (*m*, 1 H); 7.72–7.77 (*m*, 1 H). ^{13}C -NMR: 46.5; 68.4; 88.3; 101.2; 110.7; 119.5; 120.3; 124.6; 125.4; 130.9; 140.8; 147.5; 150.8; 163.1; 168.1. The photoadduct **32** was unstable at r.t. and converted gradually or easily on distillation (175–180°/3 Torr) to **35**.

S-[3-(Benzoxazol-2-yl)-2,3-dihydrofuran-2-yl] O-Phenyl Thiocarbonate (**33**). M.p. 112–113°. IR (KBr): 1725, 1625, 1610. ^1H -NMR: 5.03 (*dt*, *J* = 2.3, 9.9, 1 H); 5.44 (*t*, *J* = 3.0, 1 H); 6.65 (*t*, *J* = 3.0, 1 H); 6.74 (*d*, *J* = 9.9, 1 H); 7.02–7.08 (*m*, 2 H); 7.17–7.41 (*m*, 5 H); 7.53–7.58 (*m*, 1 H); 7.73–7.80 (*m*, 1 H). ^{13}C -NMR: 46.7; 88.5;

101.3; 110.8; 120.4; 121.0; 124.7; 125.6; 126.4; 128.3; 129.5; 140.8; 147.6; 150.9; 163.0; 167.5. Anal. calc. for $C_{18}H_{13}NO_4S$ (339.29): C 63.72, H 3.86, N 4.13; found C 63.95, H 3.71, N 4.10.

X-Ray Crystal-Structure Determination of 4. The crystal of **4** from $CHCl_3$ /hexane (approximate dimensions of $0.30 \times 0.35 \times 0.20$ mm) was mounted on a glass fiber and used for the X-ray study.

Crystal Data. $C_{18}H_{13}NO_4S$, M_r 261.343, monoclinic, space group $P2_1/c$, $a = 12.054(3)$, $b = 5.564(2)$, $c = 20.413(5)$ Å, $\alpha = 90.00^\circ$, $\beta = 104.36(2)^\circ$, $\gamma = 90.00^\circ$, $V = 1326.2(7)$ Å³, $Z = 4$, $D_x = 1.309$ g cm⁻³, colorless rod, $F(000) = 552$, $\mu(CuK\alpha) = 2.12$ mm⁻¹.

Data Collection, Structure Solution, and Refinement. The intensity data were collected in a *Mac Science MXC 18* diffractometer with graphite-monochromated $CuK\alpha$ radiation (λ 1.54 Å) by means of ω - 2θ scan technique in the range $2\theta < 70.00^\circ$. Out of 2892 total reflections, 2274 reflections with intensities greater than $3.0 \sigma(I)$ 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 0.055 and R_w 0.265 (F^2).

Tables of crystal data are available as supplementary data. Atomic coordinates, bond lengths and angles, and thermal parameters of X-ray crystal structure of **4** (CCDC-208836) 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 CB21EZ, UK (fax: +44-1223/336-033; e-mail: deposit@ccdc.scan.ac.uk).

REFERENCES

- [1] a) A. Ohno, *Int. J. Sulfur Chem., Part B* **1971**, 6, 183; b) A. Ohno, in 'Organic Chemistry of Sulfur', Ed. S. Oae, Plenum, New York, 1977, p. 189; c) J. Coyle, *Chem. Soc. Rev.* **1975**, 4, 523; d) J. Coyle, *Tetrahedron* **1985**, 42, 5393; e) P. de Mayo, *Acc. Chem. Res.* **1976**, 9, 52; f) N. Turro, V. Ramamurthy, W. Cherry, W. Farneth, *Chem. Rev.* **1978**, 78, 125; g) V. Ramamurthy, in 'Organic Photochemistry', Ed. A. Padwa, Marcel Dekker, New York, 1985, p. 231; h) M. Machida, K. Oda, E. Sato, Y. Kanaoka, *J. Synth. Org. Chem. Jpn. (Yuki Gosei Kagaku Kyokai-shi)* **1986**, 44, 1071; i) V. P. Rao, *Sulfur Reports* **1992**, 12, 359; j) M. Sakamoto, T. Fujita, S. Watanabe, T. Nishio, *J. Synth. Org. Chem. Jpn. (Yuki Gosei Kagaku Kyokai-shi)* **1994**, 52, 685; k) T. Nishio, M. Sakamoto, *Rev. Heteroat. Chem.* **1995**, 12, 23; l) M. Sakamoto, T. Nishio, *Rev. Heteroat. Chem.* **1995**, 12, 53; m) M. Sakamoto, T. Nishio, *Heterocycles*, **2003**, 59, 399.
- [2] a) T. Nishio, Y. Mori, I. Iida, A. Hosomi, *J. Chem. Soc., Perkin Trans. 1* **1996**, 921; b) T. Nishio, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1007; T. Nishio, I. Iida, K. Sugiyama, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 3039; c) T. Nishio, *J. Chem. Soc., Perkin Trans. 1* **1999**, 1151; T. Nishio, K. Shiwa, M. Sakamoto, *Helv. Chim. Acta* **2002**, 85, 2383.
- [3] a) T. Nishio, Y. Mori, I. Iida, A. Hosomi, *J. Chem. Soc. Perkin Trans. 1* **1993**, 2197; b) T. Nishio, Y. Mori, I. Iida, A. Hosomi, *Helv. Chim. Acta* **1994**, 77, 981.
- [4] E. Pretsch, W. Simon, J. Seibl, T. Clerc, 'Table of Spectral Data for Structure Determination of Organic Compounds', Springer-Verlag, Berlin, 1989, p. H240.
- [5] L. P. Burton, J. D. White, *Tetrahedron Lett.* **1980**, 21, 3147.
- [6] T. Nishio, M. Oka, *Helv. Chim. Acta* **1997**, 80, 388.
- [7] K. Oda, Machida, *Tetrahedron Lett.* **1989**, 30, 4421; K. Oda, H. Tsujita, K. Ohno, M. Machida, *J. Chem. Soc., Perkin Trans. 1* **1995**, 2931.

Received May 13, 2003