Photochemical reactions of *N*-acylbenzoxazole-2-thiones

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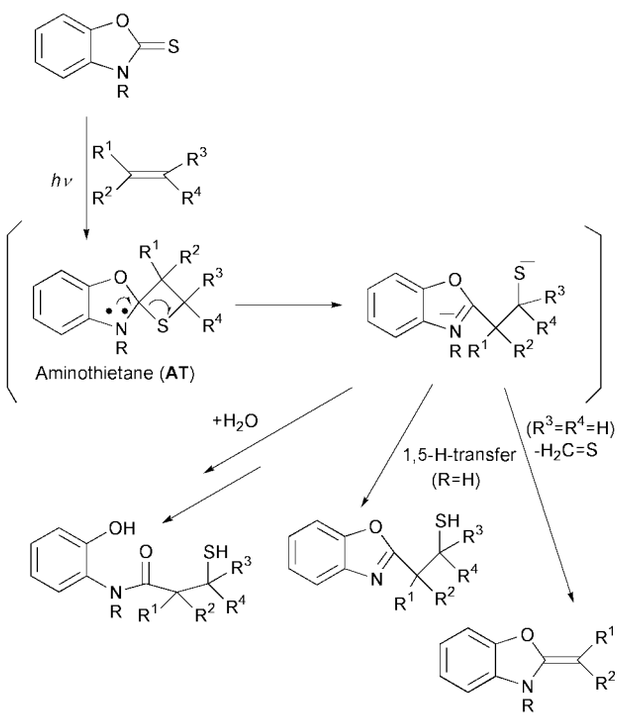
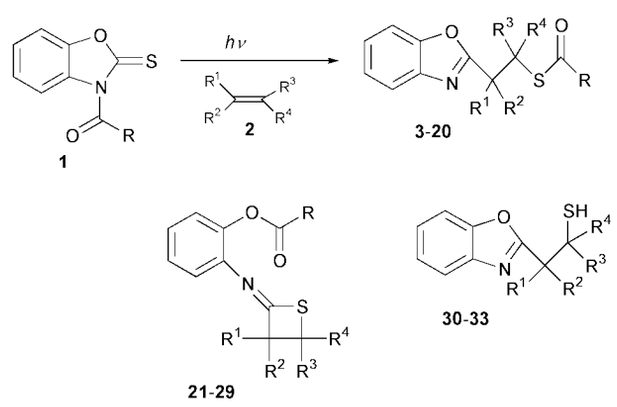
The photochemical reactions of *N*-acylbenzoxazole-2-thiones **1** are examined. Irradiation of *N*-acylbenzoxazole-2-thiones **1** in the presence of a variety of alkenes **2** yields 2-substituted benzoxazoles **3**–**20** and/or the unexpected products, iminothietanes **21**–**29** by intramolecular trapping of the acyl group by thiolate anion of the zwitterionic intermediate **I** and by the phenolate anion of the zwitterionic intermediate **II**, respectively, derived from the spirocyclic aminothietanes AT which are formed by regioselective [2+2] cycloaddition of the carbon–sulfur double bond of **1** to the alkene double bond.

Introduction

The photochemistry of thiocarbonyl compounds such as thioketones[1] and thioimides[1,2] has been of considerable synthetic and mechanistic interest and these compounds behave like carbonyl compounds in many respects. Thioamides are, however, photochemically much less reactive than these compounds and few reports have been published on their photochemical reactions.[1b,2b,3] In the course of our studies on the photochemistry of cyclic conjugated nitrogen-thiocarbonyl systems,[3,4] we have reported the photochemical behavior of the benzoxazole-2-thiones.[4b,e,f] For example, irradiation of the benzoxazole-2-thiones in the presence of alkenes gave 2-alkylated benzoxazoles, 2-alkylidenebenzoxazoles and the ring-opened products, amide derivatives, depending on the nature of substituents both on the N-atom of the benzoxazole and those present in the alkene. In these reactions, aminothietanes (AT) are believed to be intermediates. However, they are usually unstable, probably because the nitrogen lone pair electron-assisted cleavage of the C–S bond of the thietane ring facilitates the formation of a zwitterion (Scheme 1). We are interested in exploring the effect of substituents on the N-atom of benzoxazole-2-thiones **1** upon [2 + 2] photocycloaddition of species **1** with alkenes **2**. We now report the results of photoaddition reactions of *N*-acylbenzoxazole-2-thiones **1**, substituted with an electron-withdrawing group on the N-atom, and alkenes **2** yielding 2-substituted benzoxazoles **3**–**20** and/or the unexpected products, iminothietane derivatives **21**–**29** (Scheme 2).[4e]



Scheme 1



Scheme 2

Results and discussion

When a benzene solution of *N*-acetyl- and *N*-isobutyrylbenzoxazole-2-thione **1a** and **1b** was irradiated with a high-pressure mercury lamp through a Pyrex filter under argon, the starting material was recovered quantitatively. However, irradiation of *N*-acetylbenzoxazole-2-thione **1a** in benzene in the presence of 1,1-disubstituted alkenes such as 2-methylpropene **2a** and methacrylonitrile **2h** under the same conditions as described above gave 2-substituted benzoxazoles **3** and **6**, exclusively, which were 1 : 1-adducts of the reactants, in 59 and 63% isolated yield, respectively. Irradiation of **1a** in the presence of a 1,1,2-trisubstituted alkene, 2-methylbut-2-ene **2b**, and a 1,1,2,2-tetrasubstituted alkene, 2,3-dimethylbut-2-ene **2c**, gave 2-substituted benzoxazoles **4** and **5** and the unexpected products, imino-

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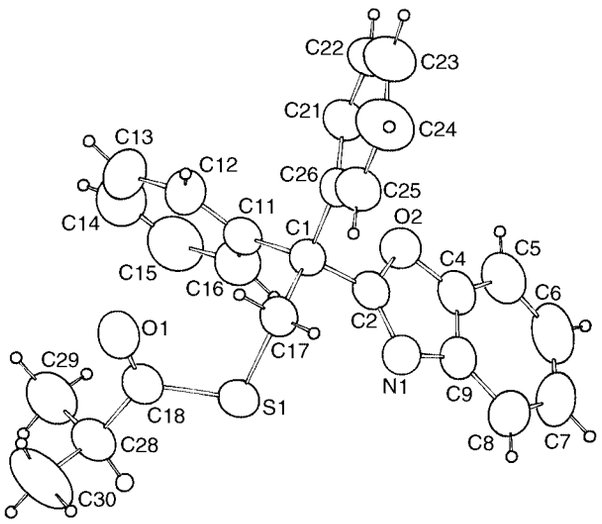


Fig. 1 ORTEP perspective view of *S*-2-(1,3-benzoxazol-2-yl)-2,2-diphenylethyl 2-methylpropanethioate **10** with crystallographic numbering scheme. Non-H-atoms are drawn at 50% probability level.

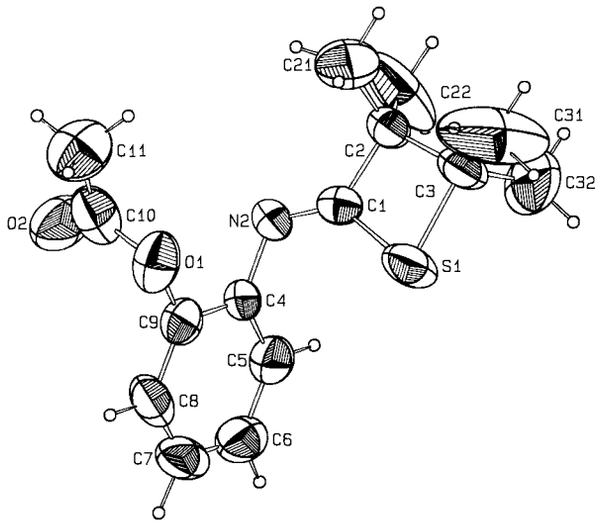


Fig. 2 ORTEP perspective view of *o*-acetoxy-*N*-(3,3,4,4-tetramethylthietan-2-ylidene)aniline **22** with crystallographic numbering scheme. Non-H-atoms are drawn at the 50% probability level.

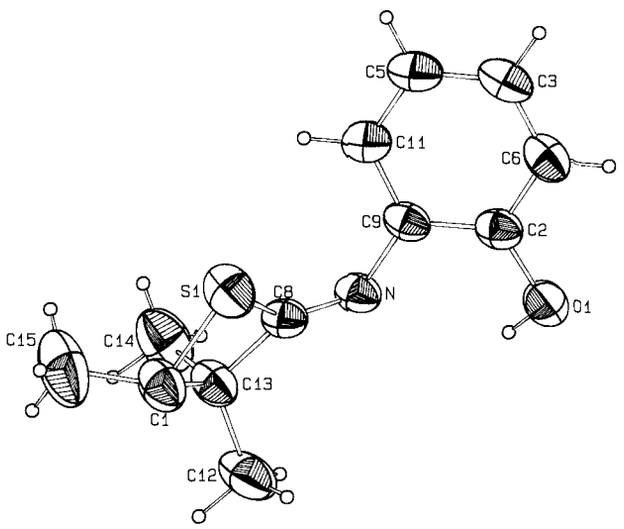


Fig. 3 ORTEP perspective view of *o*-hydroxy-*N*-(3,3,4-trimethylthietan-2-ylidene)aniline **37** with crystallographic numbering scheme. Non-H-atoms are drawn at the 50% probability level.

thietanes **21** and **22**. Photoreaction of **1a** and a diene such as 2,5-dimethylhexa-2,4-diene **2l** also proceeded smoothly to yield both products, the 2-substituted benzoxazole **7** and the iminothietane **23**. On the other hand, irradiation of **1a** in the presence of 1,2-disubstituted alkenes such as stilbene and 1,2-dicyanoethylene resulted in recovery of unchanged **1a**, while that of **1a** and but-2-ene **2d** gave the (2-mercaptoalkyl)benzoxazole **30** as the only isolable product. In contrast, irradiation of *N*-isobutyryl-, *N*-(3-methylbutanoyl)-, *N*-phenylacetyl-, and *N*-(2-phenylpropanoyl)-benzoxazole-2-thione **1b**–**1e** in benzene in the presence of alkenes **2** gave 2-substituted benzoxazoles **8**–**14**, **17**–**20** or iminothietanes **24**, **25**, **28**, **29**, exclusively, depending on the substitution pattern of the alkenes. Similar results were obtained when the benzoxazole-2-thiones **1** and alkenes **2** were irradiated in methanol and acetonitrile. In the cases of **1b** and **2e**,**f**, and **1d** and **2c**, the formation of 2-(2-mercaptoalkyl)benzoxazoles **31**–**33** was observed. Furthermore, irradiation of **1b** and 2,5-dimethylhexa-2,4-diene **2l**, and of **1b** and 2,3-dimethylbuta-1,3-diene **2m**, yielded both products, 2-substituted benzoxazoles **15** and **16**, and iminothietanes **26** and **27**. The structures of all new photoproducts **3**–**31** were elucidated on the basis of spectral data, analytical results and chemical evidence, and those of **32** and **33** were confirmed by direct comparison of their spectral properties with those of the known compounds.[4b] The IR spectra of 2-substituted benzoxazoles **3**–**20** showed the characteristic absorption of thioester carbonyls (1665–1700 cm^{-1}), while those of iminothietanes **21**–**29** showed absorptions characteristic of an ester group (1750–1775 cm^{-1}) and an imino group (1650–1675 cm^{-1}). The ^{13}C NMR spectra of 2-substituted benzoxazoles **3**–**20** exhibited the presence of a thioester carbonyl carbon (δ_C 185.1–204.8) and an imino carbon (δ_C 157.3–171.5) of the benzoxazole ring. Those of iminothietanes **21**–**29** exhibited the corresponding signals at δ_C 168.8–174.8 and δ_C 166.3–173.1, which were assigned to ester carbonyl and imino carbons, respectively. Finally, the structures of *S*-2-(1,3-benzoxazol-2-yl)-2,2-diphenylethyl 2-methylpropanethioate **10** and *N*-(3,3,4,4-tetramethylthietan-2-ylidene)-*o*-acetoxyaniline **22** were confirmed by X-ray structural analysis (Figs. 1 and 2). The photoproduct, 2-(1,3-benzoxazol-2-yl)-2-cyanopropyl 2-methylpropanethioate **11**, was hydrolyzed with sodium hydroxide in methanol to yield 2-(1,3-benzoxazol-2-yl)-2-cyanopropane-1-thiol **34**, whose structure was confirmed by spectral comparison with authentic material which was independently prepared by the photoaddition of benzoxazole-2-thione with methacrylonitrile,[4b] in 56% yield. Treatment of **11** with sodium ethoxide in ethanol also gave **34**, in quantitative yield. The iminothietanes **22**, **24**, **25** and **29** were treated with sodium methoxide in methanol to yield *o*-hydroxy-*N*-(thietan-2-ylidene)anilines **36** and **37** in high yields. Methyl 3-phenylpropionate was isolated in 43% yield as a by-product when **29** was treated with sodium methoxide. The structures of **36** and **37** were elucidated on the basis of spectral properties and elemental analysis, and finally the structure of *o*-hydroxy-*N*-(3,3,4-trimethylthietan-2-ylidene)aniline **37** was confirmed by X-ray structural analysis (Fig. 3). *o*-Hydroxy-*N*-(tetramethylthietan-2-ylidene)aniline **36** thus obtained was heated to reflux in toluene to yield the 2-(mercaptoalkyl)benzoxazole **33** quantitatively. The *o*-hydroxythietanylideneaniline **37** also gave a 2-(mercaptoalkyl)benzoxazole, **35**, when heated to reflux in toluene. Treatment of the *o*-acetoxy-*N*-(thietan-2-ylidene)aniline **22** with hydrochloric acid yielded **33** and **36**. The latter gave **33** by further treatment with hydrochloric acid. Reduction of the *o*-isobutyryloxy-*N*-(thietan-2-ylidene)aniline **25** with sodium borohydride in methanol gave 2-(mercaptoalkyl)benzoxazole **33** and the *o*-hydroxy-*N*-(thietan-2-ylidene)aniline **36**, while that of **25** with lithium aluminium hydride in diethyl ether gave **36**. The 2-(mercaptoalkyl)benzoxazole **36** was refluxed in acetic anhydride to yield two acetylated products, **22** and **5**. The *o*-acetoxy-*N*-(thietan-2-ylidene)aniline **22** was treated with *m*-chloroperbenzoic acid (MCPBA) to give a complex mixture

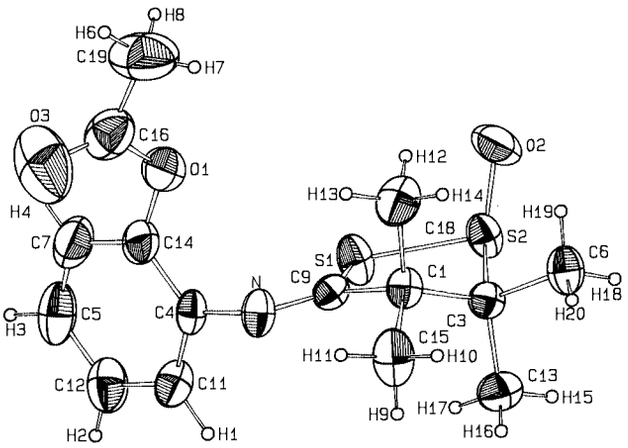


Fig. 4 ORTEP perspective view of 3-(*o*-acetoxyphenylimino)-4,4,5,5-tetramethyl-1,2-dithiolane 1-oxide **38** with crystallographic numbering scheme. Non-H-atoms are drawn at the 50% probability level.

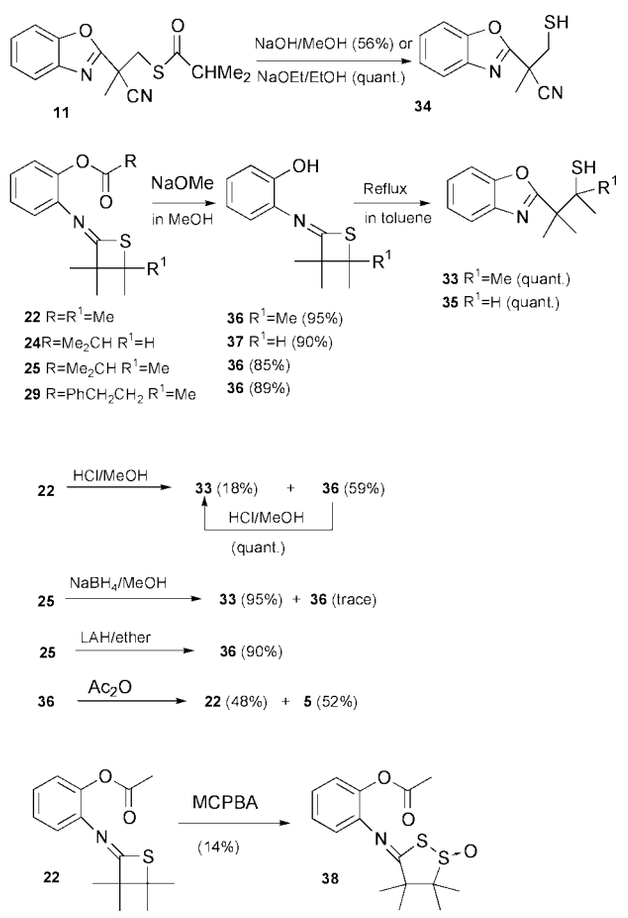
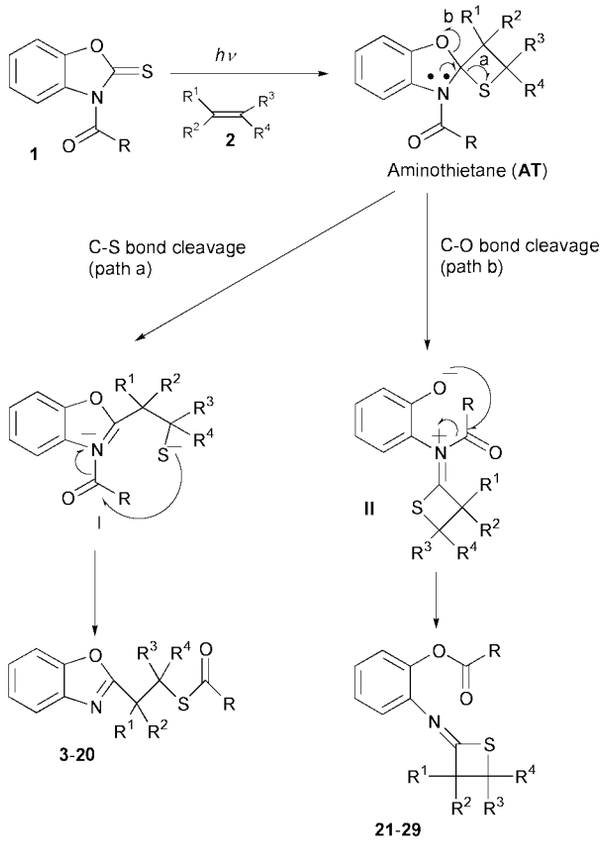


Chart 1

of products from which the 3-(*o*-acetoxyphenylimino)-4,4,5,5-tetramethyl-1,2-dithiolane 1-oxide **38** was isolated in low yield (14%) when the reaction mixture was purified through silica gel column chromatography (Chart 1). The structure of **38** was confirmed by X-ray structural analysis (Fig. 4).

The formation of 2-substituted benzoxazoles **3**–**20** and iminothietanes **21**–**29** in the photocycloaddition of *N*-acylbenzoxazole-2-thiones **1** and alkenes **2** can be rationalized by the mechanism shown in Scheme 3. The aminothietane AT was initially formed through the regioselective [2 + 2] photocycloaddition of the C=S double bond of **1** and the alkene double bond. The regiochemistry is in accord with the formation of the more stable diradical intermediate in the [2 + 2] photocycloaddition process.[1b,2b,3a] The aminothietane AT thus



Scheme 3

formed is unstable and undergoes C–S bond cleavage of the thietane ring or C–O bond cleavage of the oxazole ring assisted by the lone-pair electrons on nitrogen to yield the respective zwitterion **I** or **II**. Intramolecular nucleophilic attack of the thiolate anion of the zwitterion **I** (path a) and of the phenolate anion of the zwitterion **II** on the acyl group (path b) yielded the 2-substituted benzoxazoles **3**–**20** and the iminothietanes **21**–**29**, respectively. Irradiation of *N*-acylbenzoxazole-2-thiones **1** and alkenes **2** in methanol was carried out in the hope of trapping a zwitterion intermediate AT; however, this attempt was unsuccessful, and similar results were obtained as when the photoreaction of **1** and **2** was run in benzene (see Table 1). The two modes of cleavage in this proposed reaction intermediate, aminothietane AT, could be explained in terms of the stability of aminothietanes AT and zwitterions **I** and **II**: MO calculation suggests that the heat of formation of thietanes having substituents at C-2 adjacent to the S-atom is lower than that of thietanes having no substituents at C-2 by about 4 kcal mol^{-1}.† The zwitterion **II** substituted at the carbon adjacent to sulfur is more stable than the other zwitterion **II** having no substituents adjacent to sulfur by 10–15 kcal mol^{-1}, although there is only a small difference in the heat of formation of identically substituted zwitterions **I** (Table 2). The formation of 2-(mercaptoalkyl)benzoxazoles **30**–**33** can be interpreted in terms of the photoaddition of N-unsubstituted benzoxazole-2-thione, which was produced by hydrogen abstraction by the excited thiocarbonyl group of *N*-acylbenzoxazole-2-thiones **1**,[5] with alkenes.[4b]

The photoaddition reaction of *N*-acylbenzoxazole-2-thiones **1** to a variety of alkenes (electron-rich and -poor) proceeds smoothly to yield 2-substituted benzoxazoles **3**–**20** and/or iminothietanes **21**–**29**, depending on the nature of substituents present in the alkenes. Although a few syntheses of iminothietanes have been reported,[6] the photoreaction described here would be an efficient and novel method for their synthesis.

† 1 cal = 4.184 J.

Table 1 Yields of photoproducts **3**–**33**

Thione		Alkene							
	R		R^1	R^2	R^3	R^4	Yield (%)[a]		
1a	Me	**2a**	Me	Me	H	H	**3** (59)		
1a		**2b**	Me	Me	Me	H	**4** (61)	**21** (tr)	
1a		**2c**	Me	Me	Me	Me	**5** (7)	**22** (52)	
1a		**2d**	Me	H	Me	H			**30** (25)
1a		**2h**	Me	CN	H	H	**6** (63)		
1a		**2l**	Me	Me	H	$CH{=}CMe_2$	**7** (28)	**23** (31)	
1a[b]		**2l**					**7** (26)	**23** (38)	
1b	Me_2CH	**2b**	Me	Me	Me	H		**24** (53)	
1b[c]		**2b**						**24** (76)	
1b		**2c**	Me	Me	Me	Me		**25** (51)	
1b		**2e**	Ph	H	H	H	**8** (25)		**31** (18)
1b		**2f**	Ph	Me	H	H	**9** (38)		**32** (tr)
1b		**2g**	Ph	Ph	H	H	**10** (55)		
1b[b]		**2g**					**10** (94)		
1b		**2h**	Me	CN	H	H	**11** (54)		
1b[b]		**2h**					**11** (77)		
1b[c]		**2h**					**11** (59)		
1b		**2i**	CN	H	H	H	**12** (26)		
1b		**2j**	Me	CO_2Me	H	H	**13** (56)		
1b		**2k**	EtO	H	H	H	**14** (53)		
1b		**2l**	Me	Me	H	$CH{=}CMe_2$	**15** (5)	**26** (48)	
1b[b]		**2l**					**15** (21)	**26** (33)	
1b		**2m**	Me	$C(Me){=}CH_2$	H	H	**16** (50)	**27** (20)	
1c	Me_2CHCH_2	**2h**	Me	CN	H	H	**17** (64)		
1d	$PhCH_2$	**2c**	Me	Me	Me	Me		**28** (11)	**33** (55)
1d		**2h**	Me	CN	H	H	**18** (58)		
1e	$PhCH_2CH_2$	**2c**	Me	Me	Me	Me		**29** (63)	
1e		**2h**	Me	CN	H	H	**19** (63)		
1e		**2j**	Me	CO_2Me	H	H	**20** (63)		

[a] Isolated yield. [b] In MeOH. [c] In CH_3CN.

Table 2 Heat of formation of aminothietanes (AT) and zwitterions (**I** and **II**)[a]

	R	R^1	R^2	R^3	R^4	Heat of formation (kcal mol^{-1})
AT	Me	H	H	H	H	−21.3749
	Me	Me	Me	H	H	−27.9568
	Me	H	H	Me	Me	−31.6509
	Me	Me	Me	Me	H	−31.0276
	Me	Me	Me	Me	Me	−31.7902
I	Me	Me	Me	H	H	−28.0839
	Me	H	H	Me	Me	−27.2179
	Me	Me	Me	Me	H	−29.1132
	Me	Me	Me	Me	Me	−28.2083
II	Me	Me	Me	H	H	−26.6756
	Me	H	H	Me	Me	−33.1855
	Me	Me	Me	Me	H	−36.4227
	Me	Me	Me	Me	Me	−41.9096

[a] Calculated by PM3 (HyperChem) method.

Experimental

Mps and bps were measured on a Yanako micro melting point apparatus (MP-3J) and a Shibata tube oven distillation apparatus (GTO-350D), respectively and are uncorrected. IR spectra were recorded on a Hitachi 260-30 or JASCO FT/IR-300 spectrophotometer. ^1H and ^{13}C NMR spectra were run on JEOL FX 90Q (90 MHz) and JEOL JMN-EX-270 (270 MHz) spectrometers with $CDCl_3$ as solvent and tetramethylsilane as internal standard. *J*-Values are given in Hz. UV spectra were measured with a Shimadzu UV-3100PC spectrophotometer. An Eikosha HALos (500 W) high-pressure mercury lamp was used as the irradiation source.

General procedure for the photochemical reactions of the *N*-acylbenzoxazole-2-thiones 1 with the alkenes 2

UV spectra: **1a** λ_{max}(EtOH)/nm (ε) 258 (6.2×10^3) and 304 (2.07×10^4). **1b** λ_{max}(EtOH)/nm (ε) 211.5 (1.97×10^4), 259 (1.49×10^4) and 300 (4.26×10^4). **1c** λ_{max}(EtOH)/nm (ε) 259 (9.4×10^3), 300 (2.80×10^4) and 303.5 (2.81×10^4). **1d** λ_{max}(EtOH)/nm (ε) 259 (1.28×10^4), 300 (3.63×10^4) and 303.5 (3.64×10^4). **1e** 259 (6.0×10^3) and 304 (1.96×10^4).

A solution of **1** (1 mmol) and **2** (≈1 cm^3 or 2 equiv. for the alkenes **2f** and **2g**) in benzene (70 cm^3) was irradiated in a Pyrex vessel with the high-pressure mercury lamp (500 W) under argon for 10–20 h at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene (or toluene)–ethyl acetate (9 : 1–50 : 1) as eluent to yield the corresponding photoproducts (**3**–**33**). The structure of the photoproducts **32** and **33** was determined on the basis of our previous work.[4b]

***S*-2-(1,3-Benzoxazol-2-yl)-2-methylpropyl thioacetate 3.** Bp 180 °C/2 mmHg (Found: C, 62.5; H, 6.05; N, 5.6. $C_{13}H_{15}NO_2S$ requires C, 62.65; H, 6.05; N, 5.6%); ν_{max}(film)/cm^{-1} 1685; δ_H 1.53 (6H, s), 2.30 (3H, s), 3.44 (2H, s), 7.28–7.32 (2H, m), 7.48–7.52 (1H, m) and 7.68–7.73 (1H, m); δ_C 25.5 (q), 30.6 (q), 38.4 (s), 39.0 (t), 110.4 (d), 119.9 (d), 124.2 (d), 124.7 (d), 140.9 (s), 150.8 (s), 170.7 (s) and 194.8 (s).

***S*-3-(1,3-Benzoxazol-2-yl)-3-methylbutan-2-yl thioacetate 4.** Bp 170 °C/2 mmHg (Found: C, 63.55; H, 6.45; N, 5.35. $C_{14}H_{17}NO_2S$ requires C, 63.85; H, 6.5; N, 5.3%); ν_{max}(film)/cm^{-1} 1685; δ_H 1.27 (3H, d, *J* 6.9), 1.52 (3H, s), 1.54 (3H, s), 2.31 (3H, s), 4.19 (1H, q, *J* 6.9), 7.29–7.34 (2H, m), 7.49–7.54 (1H, m) and 7.69–7.74 (1H, m); δ_C 18.0 (q), 23.2 (q), 25.0 (q), 30.7 (q), 41.5 (s), 47.2 (d), 110.5 (d), 124.1 (d), 124.7 (d), 140.8 (s), 150.7 (s), 170.6 (s) and 194.6 (s).

***S*-3-(1,3-Benzoxazol-2-yl)-2,3-dimethylbutan-2-yl thioacetate 5.** Bp 180 °C/2 mmHg; mp 55–56 °C (Found: C, 65.05; H, 6.9; N, 5.05. $C_{15}H_{19}NO_2S$ requires C, 64.95; H, 6.9; N, 5.05%); λ_{max}(EtOH)/nm (ε) 235 (1.42×10^4), 272 (4.9×10^4) and 279 (4.2×10^4); ν_{max}(film)/cm^{-1} 1685; δ_H 1.61 (6H, s), 1.68 (6H, s),

2.21 (3H, s), 7.30–7.34 (2H, m), 7.50–7.55 (1H, m) and 7.72–7.76 (1H, m); δ_C 22.9 (q), 23.7 (q), 31.8 (q), 45.4 (s), 58.4 (s), 110.5 (d), 119.9 (d), 124.1 (d), 124.7 (d), 140.8 (s), 150.5 (s), 169.6 (s) and 185.1 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-cyanopropyl thioacetate 6.** Mp 67–68 °C (Found: C, 60.35; H, 4.7; N, 10.8. $C_{13}H_{12}N_2O_2S$ requires C, 60.0; H, 4.6; N, 10.75%); ν_{max}(KBr)/cm^{-1} 2240 and 1700; δ_H 1.94 (3H, s), 2.37 (3H, s), 3.74 (2H, dd, *J* 12.9, 15.5), 7.37–7.42 (2H, m), 7.56–7.60 (1H, m) and 7.74–7.78 (1H, m); δ_C 23.4 (q), 30.4 (q), 36.1 (t), 39.8 (s), 110.0 (d), 118.4 (s), 120.6 (d), 125.0 (d), 126.1 (d), 140.4 (s), 151.1 (s), 161.5 (s) and 192.8 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2,5-dimethylhex-4-en-3-yl thioacetate 7.** Bp 185 °C/2 mmHg (Found: C, 67.45; H, 7.0; N, 4.65. $C_{17}H_{21}NO_2S$ requires C, 67.3; H, 7.0; N, 4.6%); ν_{max}(film)/cm^{-1} 1680; δ_H 1.56 (3H, s), 1.62 (3H, s), 1.75 (3H, d, *J* 1.0), 1.79 (3H, d, *J* 1.3), 2.29 (3H, s), 4.85 (1H, d, *J* 10.6), 5.59 (1H, br d, *J* 10.6), 7.26–7.32 (2H, m), 7.48–7.52 (1H, m) and 7.69–7.73 (1H, m); δ_C 18.5 (q), 24.9 (q), 25.2 (q), 26.1 (q), 31.4 (q), 45.8 (d), 54.4 (s), 110.5 (d), 119.0 (d), 119.9 (d), 124.1 (d), 124.6 (d), 137.9 (s), 141.2 (s), 150.2 (s), 166.4 (s) and 196.6 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-phenylethyl 2-methylpropanethioate 8.** Bp 190 °C/2 mmHg (Found: C, 70.45; H, 5.8; N, 4.6. $C_{19}H_{19}NO_2S$ requires C, 70.15; H, 5.9; N, 4.3%); ν_{max}(film)/cm^{-1} 1680; δ_H 1.13 (3H, d, *J* 6.9), 1.14 (3H, d, *J* 6.9), 2.68 (1H, sep, *J* 6.9), 3.62 (1H, A of ABX, *J* 6.3, 13.5), 3.73 (1H, B of ABX, *J* 9.2, 13.5), 4.47 (1H, X of ABX, *J* 6.3, 9.2), 7.20–7.47 (8H, m) and 7.72–7.76 (1H, m); δ_C 19.2 (q), 19.3 (q), 32.6 (t), 43.0 (d), 46.3 (d), 110.6 (d), 120.0 (d), 124.2 (d), 124.9 (d), 127.9 (d), 128.9 (d), 138.4 (s), 141.0 (s), 150.8 (s), 166.3 (s) and 203.4 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-phenylpropyl 2-methylpropanethioate 9.** Bp 190 °C/2 mmHg (Found: C, 71.05; H, 6.3; N, 4.1. $C_{20}H_{21}NO_2S$ requires C, 70.8; H, 6.25; N, 4.15%); ν_{max}(film)/cm^{-1} 1680; δ_H 1.09 (3H, d, *J* 6.9), 1.11 (3H, d, *J* 6.9), 1.90 (3H, s), 2.68 (1H, sep, *J* 6.9), 3.86 (2H, s), 7.20–7.40 (8H, m) and 7.75–7.79 (1H, m); δ_C 19.3 (q), 23.1 (q), 38.1 (t), 43.1 (d), 46.3 (s), 110.7 (d), 120.1 (d), 124.3 (d), 124.9 (d), 126.2 (d), 127.4 (d), 128.6 (d), 169.5 (s) and 203.0 (s); MS 339 (M^+) and 268 ($M^+ - Me_2CHCHO$).

***S*-2-(1,3-Benzoxazol-2-yl)-2,2-diphenylethyl 2-methylpropanethioate 10.** Mp 93–94 °C (Found: C, 74.8; H, 5.85; N, 3.45. $C_{25}H_{23}NO_2S$ requires C, 74.8; H, 5.75; N, 3.5%); ν_{max}(KBr)/cm^{-1} 1685; δ_H 0.93 (6H, d, *J* 6.9), 2.53 (1H, sep, *J* 6.9), 4.34 (2H, s), 7.02–7.45 (13H, m) and 7.74–7.78 (1H, m); δ_C 19.2 (q), 37.2 (t), 42.8 (d), 55.8 (s), 110.8 (d), 120.4 (d), 124.3 (d), 125.0 (d), 126.9 (d), 127.4 (d), 128.0 (d), 128.5 (d), 128.9 (d), 140.7 (s), 141.7 (s), 151.0 (s), 168.3 (s) and 202.3 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-cyanopropyl 2-methylpropanethioate 11.** Mp 60–61 °C (Found: C, 62.3; H, 5.65; N, 9.55. $C_{15}H_{16}N_2O_2S$ requires C, 62.5; H, 5.6; N, 9.7%); ν_{max}(KBr)/cm^{-1} 2225 and 1680; δ_H 1.16 (3H, d, *J* 6.9), 1.17 (3H, d, *J* 6.9), 1.95 (3H, s), 2.66–2.83 (1H, m), 3.72 (2H, dd, *J* 13.8, 16.5), 7.34–7.44 (2H, m), 7.56–7.60 (1H, m) and 7.74–7.78 (1H, m); δ_C 19.1 (q), 19.2 (q), 23.4 (q), 35.4 (t), 40.0 (s), 43.2 (d), 110.0 (d), 118.5 (s), 120.6 (d), 125.0 (d), 126.1 (d), 140.4 (s), 151.1 (s), 161.6 (s) and 201.1 (s); MS 288 (M^+) and 217 ($M^+ - Me_2CHCHO$).

A solution of **11** (0.5 mmol) and NaOH powder (25 mg) in methanol (10 cm^3) was stirred under argon for 2 h at room temperature. Usual work-up gave 2-(benzoxazol-2-yl)-2-cyanopropane-1-thiol **34** (56%) whose structure was confirmed by direct comparison of IR and NMR spectra with those of an authentic sample.[4b] To a solution of sodium (15 mg) in EtOH (5 cm^3) was added dropwise a solution of **11** (0.5 mmol) in EtOH (10 cm^3) under argon and the mixture was then stirred for 15 min at room temperature. Usual work-up gave **34** quantitatively.

***S*-2-(1,3-Benzoxazol-2-yl)-2-cyanoethyl 2-methylpropanethioate 12.** Mp 73–74 °C (Found: C, 61.0; H, 5.1; N, 10.25. $C_{14}H_{14}N_2O_2S$ requires C, 61.3; H, 5.15; N, 10.2%); ν_{max}(KBr)/cm^{-1} 2200 and 1690; δ_H 1.20 (6H, d, *J* 6.9), 2.71–2.80 (1H, m), 3.53–3.63 (1H, A of ABX), 3.67–3.76 (1H, B of ABX), 4.52 (1H, X of ABX, *J* 6.6, 7.6), 7.23–7.44 (2H, m), 7.54–7.59 (1H, m) and 7.72–7.77 (1H, m); δ_C 19.1 (q), 29.2 (t), 32.8 (d), 43.2 (d), 110.0 (d), 115.2 (s), 120.6 (d), 125.1 (d), 126.1 (d), 140.5 (s), 151.1 (s), 157.3 (s) and 202.2 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-(methoxycarbonyl)propyl 2-methylpropanethioate 13.** Bp 210 °C/1 mmHg (Found: C, 60.1; H, 5.9; N, 4.35. $C_{16}H_{19}NO_4S$ requires C, 59.8; H, 5.95; N, 4.35%); ν_{max}(film)/cm^{-1} 1740 and 1690; δ_H 1.12 (3H, d, *J* 6.9), 1.13 (3H, d, *J* 6.9), 1.78 (3H, s), 2.62–2.76 (1H, m), 3.73 (3H, s), 3.77 (2H, s), 7.29–7.37 (2H, m), 7.48–7.53 (1H, m) and 7.71–7.76 (1H, m); δ_C 19.3 (q), 20.5 (q), 34.2 (t), 43.1 (d), 49.6 (s), 53.1 (q), 110.7 (d), 120.3 (d), 124.5 (d), 125.3 (d), 128.3 (d), 140.7 (s), 150.9 (s), 165.2 (s), 171.5 (s) and 202.4 (s); MS 321 (M^+) and 250 ($M^+ - Me_2CHCHO$).

***S*-2-(1,3-Benzoxazol-2-yl)-2-ethoxyethyl 2-methylpropanethioate 14.** Bp 200 °C/1 mmHg (Found: C, 61.15; H, 6.45; N, 4.7. $C_{15}H_{19}NO_3S$ requires C, 61.4; H, 6.55; N, 4.8%); ν_{max}(film)/cm^{-1} 1685; δ_H 1.16 (6H, d, *J* 6.9), 1.24 (3H, t, *J* 6.9), 2.72 (1H, sep, *J* 6.9), 3.51 (2H, d, *J* 6.9), 3.67 (2H, q, *J* 6.9), 4.68 (1H, t, *J* 6.9), 7.29–7.40 (2H, m), 7.52–7.59 (1H, m) and 7.71–7.77 (1H, m); δ_C 15.1 (q), 19.2 (q), 31.3 (t), 43.0 (d), 66.2 (t), 74.4 (d), 110.9 (d), 120.4 (d), 124.5 (d), 125.5 (d), 140.7 (s), 150.8 (s), 163.9 (s) and 203.0 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2,5-dimethylhex-4-en-3-yl 2-methylpropanethioate 15.** Bp 200 °C/2 mmHg (Found: C, 68.75; H, 7.4; N, 4.3. $C_{19}H_{25}NO_2S$ requires C, 68.85; H, 7.6; N, 4.25%); ν_{max}(film)/cm^{-1} 1665; δ_H 1.13 (6H, d, *J* 6.9), 1.55 (3H, s), 1.63 (3H, s), 1.76 (3H, s), 1.78 (3H, s), 2.60 (1H, sep, *J* 6.9), 4.98 (1H, q, *J* 10.6), 5.63 (1H, d, *J* 10.6), 7.27–7.33 (2H, m), 7.45–7.49 (1H, m) and 7.68–7.72 (1H, m); δ_C 18.6 (q), 19.2 (q), 19.6 (q), 24.8 (q), 25.6 (q), 26.0 (q), 43.4 (d), 53.8 (s), 110.4 (d), 119.2 (d), 119.8 (d), 124.1 (d), 124.5 (d), 137.6 (s), 137.6 (s), 141.2 (s), 150.1 (s), 166.7 (s) and 204.8 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2,3-dimethylbut-3-enyl 2-methylpropanethioate 16.** Bp 230 °C/1 mmHg (Found: C, 67.3; H, 6.9; N, 4.7. $C_{17}H_{21}NO_2S$ requires C, 67.3; H, 7.0; N, 4.6%); ν_{max}(film)/cm^{-1} 1685 and 1640; δ_H 1.13 (3H, d, *J* 6.9), 1.15 (3H, d, *J* 6.9), 1.63 (3H, s), 1.74 (3H, s), 2.72 (1H, sep, *J* 6.9), 3.67 (2H, dd, *J* 3.5, 7.2), 4.92 (1H, s), 5.05 (1H, s), 7.27–7.35 (2H, m), 7.46–7.52 (1H, m) and 7.71–7.77 (1H, m); δ_C 19.4 (q), 20.0 (q), 21.7 (q), 35.5 (t), 43.1 (d), 47.1 (s), 110.6 (d), 113.4 (t), 120.1 (d), 124.2 (d), 124.9 (d), 140.8 (s), 145.9 (s), 150.8 (s), 169.0 (s) and 203.1 (s); MS 303 (M^+), 232 ($M^+ - Me_2CHCO$), 200 ($M^+ - Me_2CHCOS$) and 186 ($M^+ - Me_2CHCOSCH_2$).

***S*-2-(1,3-Benzoxazol-2-yl)-2-cyanopropyl 3-methylbutanethioate 17.** Bp 235 °C/1 mmHg (Found: C, 63.5; H, 5.95; N, 9.5. $C_{16}H_{18}N_2O_2S$ requires C, 63.55; H, 6.0; N, 9.25%); ν_{max}(film)/cm^{-1} 1695; δ_H 0.92 (6H, d, *J* 6.6), 1.95 (3H, s), 2.02–2.18 (1H, m), 2.46 (2H, d, *J* 6.8), 3.74 (2H, dd, *J* 13.9, 15.8), 7.36–7.42 (2H, m), 7.55–7.60 (1H, m) and 7.72–7.78 (1H, m); δ_C 22.2 (q), 23.4 (q), 26.4 (d), 35.9 (t), 39.9 (s), 52.7 (t), 110.0 (d), 118.5 (s), 120.6 (d), 125.0 (d), 126.1 (d), 140.5 (s), 151.1 (s), 161.6 (s) and 195.9 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-cyanopropyl phenyl(thioacetate) 18.** Bp 230 °C/1 mmHg (Found: C, 68.05; H, 5.0; N, 8.45. $C_{19}H_{16}N_2O_2S$ requires C, 67.85; H, 4.8; N, 8.35%); ν_{max}(film)/

cm^{-1} 2240 and 1695; δ_H 1.87 (3H, s), 3.70 (2H, dd, *J* 13.9, 15.8), 3.83 (2H, s), 7.17–7.39 (7H, m), 7.49–7.54 (1H, m) and 7.70–7.75 (1H, m); δ_C 23.3 (q), 36.0 (t), 39.7 (s), 50.2 (t), 110.0 (d), 118.3 (s), 120.6 (d), 125.0 (d), 126.1 (d), 127.6 (d), 128.7 (d), 129.5 (d), 132.6 (s), 140.3 (s), 151.0 (s), 161.4 (s) and 194.5 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-cyanopropyl 2-phenylpropanethioate 19.** Bp 250 °C/1 mmHg (Found: C, 68.85; H, 5.4; N, 8.1. $C_{20}H_{18}N_2O_2S$ requires C, 68.55; H, 5.2; N, 8.0%); ν_{max}(film)/cm^{-1} 2240 and 1700; δ_H 1.89 (3H, s), 2.86–2.96 (4H, m), 3.73 (2H, t, *J* 14.5), 7.12–7.43 (7H, m), 7.54–7.58 (1H, m) and 7.73–7.77 (1H, m); δ_C 23.3 (q), 31.2 (t), 35.8 (t), 39.8 (s), 45.3 (t), 110.0 (d), 118.4 (s), 120.6 (d), 125.0 (d), 126.4 (d), 126.6 (d), 128.2 (d), 128.6 (d), 139.5 (s), 140.4 (s), 151.0 (s), 161.5 (s) and 195.6 (s).

***S*-2-(1,3-Benzoxazol-2-yl)-2-(methoxycarbonyl)propyl 2-phenylpropanethioate 20.** Bp 230 °C/1 mmHg (Found: C, 65.75; H, 5.6; N, 3.8. $C_{21}H_{21}NO_4S$ requires C, 65.8; H, 5.5; N, 3.65%); ν_{max}(film)/cm^{-1} 1730 and 1685; δ_H 1.74 (3H, s), 2.79–2.95 (4H, m), 3.71 (3H, s), 3.77 (2H, s), 7.11–7.36 (7H, m), 7.49–7.55 (1H, m) and 7.73–7.78 (1H, m); δ_C 20.4 (q), 31.4 (t), 34.6 (t), 45.3 (t), 49.5 (s), 53.1 (q), 110.7 (d), 120.3 (d), 124.5 (d), 126.4 (d), 128.2 (d), 128.5 (d), 139.7 (s), 140.7 (s), 150.9 (s), 165.1 (s), 171.4 (s) and 197.0 (s).

***o*-Acetoxy-*N*-(3,3,4-trimethylthietan-2-ylidene)aniline 21.** Oil; ν_{max}(film)/cm^{-1} 1775 and 1665; δ_H 1.35 (3H, s), 1.46 (3H, s), 1.47 (3H, d, *J* 6.9), 2.28 (3H, s), 3.50 (1H, q, *J* 6.9) and 6.99–7.27 (4H, m).

***o*-Acetoxy-*N*-(3,3,4,4-tetramethylthietan-2-ylidene)aniline 22.** Mp 63–64 °C (Found: C, 64.8; H, 6.85; N, 5.1. $C_{15}H_{19}NO_2S$ requires C, 64.95; H, 6.9; N, 5.05%); λ_{max}(EtOH)/nm (ε) 246 (1.17×10^4) and 286 (6.4×10^4); ν_{max}(KBr)/cm^{-1} 1760 and 1665; δ_H 1.43 (6H, s), 1.61 (6H, s), 2.28 (3H, s), 6.95–6.99 (1H, m) and 7.06–7.18 (3H, m); δ_C 20.7 (q), 22.8 (q), 27.7 (q), 52.1 (s), 62.4 (s), 120.5 (d), 122.5 (d), 125.5 (d), 126.4 (d), 140.4 (s), 142.8 (s), 168.9 (s) and 173.2 (s).

A solution of **22** (0.5 mmol) in methanol in the presence of a few drops of hydrochloric acid was stirred for 5 h at room temperature. Usual work-up gave the 2-substituted benzoxazole **33** (18%) and the *o*-hydroxy-*N*-thietanylideneaniline **36** (59%). A solution of **36** (0.5 mmol) thus produced, containing a few drops of hydrochloric acid, was kept for 15 h at room temperature and then usual work-up gave **33** quantitatively.

***o*-Acetoxy-*N*-[3,3-dimethyl-4-(2-methylprop-1-enyl)thietan-2-ylidene]aniline 23.** Bp 205 °C/2 mmHg (Found: C, 67.15; H, 7.1; N, 4.75. $C_{17}H_{21}NO_2S$ requires C, 67.3; H, 7.0; N, 4.6%); ν_{max}(film)/cm^{-1} 1760 and 1660; δ_H 1.54 (3H, s), 1.69 (3H, s), 1.75 (3H, s), 1.80 (3H, s), 2.29 (3H, s), 4.63 (1H, d, *J* 9.2), 5.45 (1H, br d, *J* 9.2) and 6.98–7.27 (4H, m); δ_C 18.7 (q), 20.8 (q), 25.8 (q), 27.7 (q), 32.4 (q), 51.4 (d), 66.2 (s), 119.3 (d), 120.5 (d), 122.6 (d), 125.6 (d), 126.4 (d), 137.4 (s), 140.4 (s), 142.9 (s), 166.9 (s) and 168.8 (s).

***o*-(2-Methylpropanoyl)-*N*-(3,3,4-trimethylthietan-2-ylidene)-aniline 24.** Bp 190 °C/1 mmHg (Found: C, 65.65; H, 7.3; N, 4.95. $C_{16}H_{21}NO_2S$ requires C, 65.95; H, 7.25; N, 4.8%); ν_{max}(film)/cm^{-1} 1755 and 1675; δ_H 1.32 (6H, d, *J* 6.9), 1.34 (3H, s), 1.45 (3H, s), 1.47 (3H, d, *J* 6.9), 2.81 (1H, sep, *J* 6.9), 3.50 (1H, q, *J* 6.9) and 6.90–7.20 (4H, m); δ_C 17.7 (q), 19.0 (q), 20.6 (q), 26.7 (q), 33.9 (d), 44.2 (d), 61.4 (s), 120.5 (d), 122.8 (d), 125.6 (d), 126.2 (d), 140.0 (s), 143.0 (s), 173.1 (s) and 174.6 (s); MS 291 (M^+).

***o*-(2-Methylpropanoyl)-*N*-(3,3,4,4-tetramethylthietan-2-ylidene)aniline 25.** Bp 200 °C/1 mmHg (Found: C, 65.65; H, 7.6; N, 4.65. $C_{17}H_{23}NO_2S$ requires C, 65.85; H, 7.6; N, 4.6%); ν_{max}(film)/cm^{-1} 1760 and 1665; δ_H 1.32 (6H, d, *J* 6.9), 1.41 (6H, s), 1.60 (6H, s), 2.81 (1H, sep, *J* 6.9) and 6.95–7.19 (4H, m); δ_C 19.0 (q), 23.0 (q), 27.7 (q), 33.9 (d), 52.0 (s), 62.5 (s), 120.5 (d), 122.7 (d), 125.5 (d), 126.2 (d), 140.4 (s), 143.0 (s), 172.8 (s) and 174.6 (s); MS 305 (M^+).

***N*-[3,3-Dimethyl-4-(2-methylprop-1-enyl)thietan-2-ylidene]-*o*-(2-methylpropanoyl)aniline 26.** Bp 180 °C/1 mmHg (Found: C, 68.9; H, 7.55; N, 4.45. $C_{19}H_{25}NO_2S$ requires C, 68.85; H, 7.6; N, 4.25%); ν_{max}(film)/cm^{-1} 1760 and 1660; δ_H 1.33 (6H, d, *J* 6.9), 1.54 (3H, s), 1.68 (3H, s), 1.73 (3H, s), 1.78 (3H, s), 2.81 (1H, sep, *J* 6.9), 4.61 (1H, d, *J* 9.2), 5.42 (1H, d, *J* 9.2) and 6.98–7.36 (4H, m); δ_C 18.6 (q), 19.0 (q), 25.7 (q), 27.9 (q), 32.4 (q), 34.0 (d), 51.2 (s), 66.3 (d), 119.4 (d), 120.5 (d), 122.7 (d), 125.6 (d), 126.2 (d), 137.3 (s), 140.5 (s), 143.1 (s), 166.3 (s) and 174.7 (s).

***N*-[3-Isopropenyl-3-methylthietan-2-ylidene]-*o*-(2-methylpropanoyl)aniline 27.** Bp 220 °C/1 mmHg (Found: C, 67.1; H, 6.95; N, 4.5. $C_{17}H_{21}NO_2S$ requires C, 67.3; H, 7.0; N, 4.6%); ν_{max}(film)/cm^{-1} 1750 and 1650; δ_H 1.30 (6H, d, *J* 6.9), 1.63 (3H, s), 1.93 (3H, s), 2.78 (1H, sep, *J* 6.9), 2.90 (1H, d, *J* 8.6), 3.24 (1H, d, *J* 8.6), 4.91 (1H, s), 5.12 (1H, s) and 7.04–7.26 (4H, m); δ_C 19.0 (q), 19.1 (q), 24.1 (q), 32.8 (t), 33.9 (d), 68.2 (s), 111.4 (t), 120.2 (d), 123.0 (d), 125.2 (d), 126.3 (d), 139.9 (s), 143.0 (s), 144.3 (s), 170.8 (s) and 174.8 (s); MS 303 (M^+).

***o*-Phenylacetoxy-*N*-(3,3,4,4-tetramethylthietan-2-ylidene)-aniline 28.** Bp 220 °C/1 mmHg (Found: C, 71.15; H, 6.65; N, 4.1. $C_{21}H_{23}NO_2S$ requires C, 71.35; H, 6.55; N, 3.95%); ν_{max}(film)/cm^{-1} 1760 and 1660; δ_H 1.33 (6H, s), 1.56 (6H, s), 3.87 (2H, s) and 6.95–7.42 (9H, m); δ_C 22.8 (q), 27.6 (q), 40.8 (t), 52.0 (s), 62.4 (s), 120.5 (d), 122.5 (d), 125.4 (d), 126.4 (d), 127.1 (d), 128.5 (d), 129.5 (d), 133.5 (s), 140.4 (s), 142.8 (s), 169.0 (s) and 173.0 (s); MS 353 (M^+).

***o*-(2-Phenylpropanoyl)-*N*-(3,3,4,4-tetramethylthietan-2-ylidene)aniline 29.** Bp 230 °C/1 mmHg (Found: C, 72.1; H, 6.85; N, 3.75. $C_{22}H_{25}NO_2S$ requires C, 71.9; H, 6.85; N, 3.8%); ν_{max}(film)/cm^{-1} 1760 and 1660; δ_H 1.39 (6H, s), 1.58 (6H, s), 2.83–2.90 (2H, m), 3.04–3.10 (2H, m) and 6.95–7.36 (9H, m); δ_C 22.9 (q), 27.7 (q), 30.9 (t), 35.7 (t), 52.1 (s), 62.4 (s), 120.5 (d), 122.6 (d), 125.5 (d), 126.3 (d), 128.4 (d), 128.5 (d), 140.3 (s), 142.8 (s), 170.4 (s) and 173.1 (s).

2-(3-Mercaptobutan-2-yl)benzoxazole 30. Bp 190 °C/2 mmHg (Found: C, 63.75; H, 6.3; N, 6.65. $C_{11}H_{13}NOS$ requires C, 63.75; H, 6.3; N, 6.75%); ν_{max}(film)/cm^{-1} 2560; δ_H 1.41 (3H, d, *J* 6.9), 1.53 (3H, d, *J* 6.9), 1.72 (1H, d, *J* 7.6), 3.22–3.36 (1H, m), 3.42–3.56 (1H, m), 7.29–7.35 (2H, m), 7.47–7.57 (1H, m) and 7.67–7.75 (1H, m); δ_C 14.7 (q), 21.8 (q), 38.3 (d), 42.7 (d), 110.3 (d), 119.7 (d), 124.1 (d), 124.5 (d), 140.9 (s), 150.4 (s) and 168.0 (s).

2-(2-Mercapto-1-phenylethyl)benzoxazole 31. Mp 61–62 °C (Found: C, 70.85; H, 5.3; N, 5.45. $C_{15}H_{13}NOS$ requires C, 70.6; H, 5.15; N, 5.5%); ν_{max}(KBr)/cm^{-1} 2560 and 1670; δ_H 1.68 (1H, t, *J* 8.6), 3.09–3.20 (1H, m), 3.43–3.56 (1H, m), 4.41 (1H, dd, *J* 6.9, 8.6), 7.13–7.46 (8H, m) and 7.71–7.75 (1H, m); δ_C 28.6 (t), 50.2 (d), 110.5 (d), 119.9 (d), 124.2 (d), 124.8 (d), 127.9 (d), 128.3 (d), 128.9 (d), 138.1 (s), 141.0 (s), 150.7 (s) and 166.1 (s).

Reaction of the *o*-acyloxythietan-2-ylideneanilines 22, 24, 25 and 29 with sodium methoxide

To a solution of sodium methoxide [Na (15 mg) in MeOH (5 cm^3)] was added dropwise a solution of an *o*-acyloxythietan-2-ylideneaniline (0.5 mmol) in methanol (10 cm^3) under argon with stirring. The mixture was stirred for 15 min at room temperature. Usual work-up yielded the corresponding *o*-hydroxy-

thietan-2-ylideneaniline **36** or **37**. A solution of **36** (or **37**) (0.5 mmol) in toluene (15 cm^3) was refluxed under argon for 5 h, then usual work-up gave the 2-substituted benzoxazole **33** (or **35**[4b]) in quantitative yield.

***o*-Hydroxy-*N*-(3,3,4,4-tetramethylthietan-2-ylidene)aniline 36.** Bp 165 °C/2 mmHg (Found: C, 66.4; H, 7.25; N, 5.9. $C_{13}H_{17}NOS$ requires C, 66.35; H, 7.3; N, 5.95%); ν_{max}(film)/cm^{-1} 3410 and 1645; δ_H 1.43 (6H, s), 1.64 (6H, s) and 6.81–7.07 (4H, m); δ_C 23.3 (q), 27.7 (q), 54.4 (s), 63.7 (s), 114.3 (d), 118.8 (d), 119.5 (d), 127.0 (d), 133.0 (s), 151.1 (s) and 170.7 (s).

***o*-Hydroxy-*N*-(3,3,4-trimethylthietan-2-ylidene)aniline 37.** Mp 78–79 °C (Found: C, 65.05; H, 6.85; N, 6.25. $C_{12}H_{15}NOS$ requires C, 65.15; H, 6.85; N, 6.3%); ν_{max}(KBr)/cm^{-1} 1630; δ_H 1.35 (3H, s), 1.45 (3H, s), 1.50 (3H, d, *J* 6.9), 3.62 (1H, q, *J* 6.9), 6.77–6.87 (2H, m) and 6.93–7.10 (2H, m); δ_C 17.7 (q), 20.8 (q), 27.0 (q), 46.4 (d), 62.5 (s), 114.3 (d), 118.8 (d), 119.5 (d), 127.0 (d), 132.9 (s), 151.1 (s) and 170.7 (s).

Oxidation of the *o*-acyloxythietan-2-ylideneaniline 22 with MCPBA

To a solution of **22** (1 mmol) in methylene dichloride (15 cm^3) was added a solution of MCPBA (1.2 equiv.) in methylene dichloride (15 cm^3) under argon at 0 °C (ice-bath) and then the mixture was stirred for 5 h at room temperature. Usual work-up yielded 3-(acetoxyphenylimino)-4,4,5,5-tetramethyl-1,2-dithiolane 1-oxide **38** (14%). With use of 3 equiv. of MCPBA, the oxide **38** was obtained in 10% yield.

3-(*o*-Acetoxyphenylimino)-4,4,5,5-tetramethyl-1,2-dithiolane 1-oxide 38. Mp 120–121 °C (Found: C, 55.4; H, 5.9; N, 4.25. $C_{15}H_{19}NO_3S_2$ requires C, 55.4; H, 5.9; N, 4.3%); ν_{max}(KBr)/cm^{-1} 1750, 1630, 1480, 1365, 1205, 1180, 1080, 985, 840 and 765; δ_H 1.18 (3H, s), 1.34 (3H, s), 1.57 (3H, s), 1.59 (3H, s), 2.20 (3H, s), 6.91–6.96 (1H, m) and 7.08–7.25 (3H, m); δ_C 17.7 (q), 20.5 (q), 20.6 (q), 23.6 (q), 25.3 (q), 55.5 (s), 71.0 (s), 120.3 (d), 122.9 (d), 126.4 (d), 126.6 (d), 140.9 (s), 142.0 (s), 168.3 (s) and 177.8 (s); MS 325 (M^+).

Reduction of the *o*-acyloxythietan-2-ylideneaniline 25

The mixture of **25** (0.5 mmol) and $NaBH_4$ (1 mmol) in MeOH (20 cm^3) was stirred under argon for 30 min at room temperature and then usual work-up gave 2-substituted benzoxazole **33** (95%) and the *o*-hydroxythietan-2-ylideneaniline **36** (trace). A mixture of **25** (0.5 mmol) and $LiAlH_4$ (1 mmol) in diethyl ether (30 cm^3) was stirred under argon for 1.5 h at room temperature. Usual work-up gave **36** (90%).

Acetylation of the *o*-hydroxythietan-2-ylideneaniline 36

A solution of **36** (0.5 mmol) in acetic anhydride (10 cm^3) was refluxed under argon for 1 h and then usual work-up gave the *o*-acetoxythietan-2-ylideneaniline **22** (48%) and the 2-substituted benzoxazole **5** (52%).

X-Ray crystal structure determination of *S*-2-(1,3-benzoxazol-2-yl)-2,2-diphenylethyl 2-methylpropanethioate 10‡

A crystal of **10** from chloroform–hexane, with approximate dimensions of 0.70 × 0.40 × 0.40 mm, was mounted on a glass fiber and used for the X-ray study.

Crystal data. $C_{25}H_{23}NO_2S$, $M = 401.52$. Monoclinic, space group $P2_1/c$, $a = 11.060(5)$, $b = 10.059(3)$, $c = 19.726(10)$ Å, $\beta = 92.26(3)°$, $V = 2192.9$ Å^3, $Z = 4$, $D_c = 1.22$ g cm^{-3}. Colorless rods. $F(000) = 816$. μ(Mo-Kα) 1.6 cm^{-1}.

‡ Tables of crystal data are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b002548h/

Data collection, structure solution and refinement. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.709 30 Å) using the ω–2θ scan technique in the range of $2\theta < 50.0°$. Out of 4221 total reflections, 2934 having intensities greater than 3.0 $\sigma(I)$ were used in the refinements. The data were corrected for Lorentz-polarization factors but no absorption corrections were made. The structure was solved by direct methods using the SPD/VAX (Enraf-Nonius & B. A. Frenz and Associates). Least-squares refinement including anisotropic thermal parameters for non-hydrogen atoms and isotropic refinement of hydrogen atoms located in difference Fourier Synthesis terminated at 0.044 (R_w 0.040).

X-Ray crystal structure determination of *o*-acetoxy-*N*-(3,3,4,4-tetramethylthietan-2-ylidene)aniline 22

A crystal of **22** from chloroform–hexane, with approximate dimensions of 0.30 × 0.30 × 0.40 mm, was used for the X-ray study.

Crystal data. $C_{15}H_{19}NO_2S$, $M = 277.39$. Orthorhombic, space group $P2_12_12_1$, $a = 6.577(2)$, $b = 12.604(1)$, $c = 18.742(3)$ Å, $V = 1553.6$ Å^3, $Z = 4$, $D_c = 1.19$ g cm^{-3}. Colorless rods. $F(000) = 592$. μ(Mo-Kα) 1.6 cm^{-1}.

Data collection, structure solution and refinement. Out of 1297 total reflections, 1176 having intensities greater than 3.0 $\sigma(I)$ were used in the refinements. Least-squares refinement terminated at 0.056 (R_w 0.054).

X-Ray crystal structure determination of *o*-hydroxy-*N*-(3,3,4-trimethylthietan-2-ylidene)aniline 37

A crystal of **37** from chloroform–hexane, with approximate dimensions of 0.30 × 0.40 × 0.20 mm, was used for the X-ray study.

Crystal data. $C_{12}H_{15}NOS$, $M = 221.22$. Orthorhombic, space group $Ccc2$, $a = 16.400(1)$, $b = 20.779(3)$, $c = 6.931(2)$ Å, $V = 2361.9$ Å^3, $Z = 8$, $D_c = 1.14$ g cm^{-3}. Colorless rods. $F(000) = 468$. μ(Mo-Kα) 1.2 cm^{-1}.

Data collection, structure solution and refinement. Out of 4352 total reflections, 3959 having intensities greater than 3.0 $\sigma(I)$ were used in the refinements. Least-squares refinement terminated at 0.036 (R_w 0.037).

X-Ray crystal structure determination of 3-(*o*-acetoxyphenylimino)-4,4,5,5-tetramethyl-1,2-dithiolane 1-oxide 38

A crystal of **38** from chloroform–hexane, with approximate dimensions of 0.40 × 0.30 × 0.60 mm, was used for the X-ray study.

Crystal data. $C_{15}H_{19}NO_3S_2$, $M = 325.44$. Monoclinic, space group $P2_1$, $a = 6.375(2)$, $b = 11.908(2)$, $c = 10.866(2)$ Å, $\beta = 98.39(1)$, $V = 816.0$ Å^3, $Z = 2$, $D_c = 1.32$ g cm^{-3}. Colorless rods. $F(000) = 344$. μ(Mo-Kα) 2.1 cm^{-1}.

Data collection, structure solution and refinement. Out of 1594 total reflections, 1474 having intensities greater than 3.0 $\sigma(I)$ were used in the refinements. Least-squares refinement terminated at 0.031 (R_w 0.039).

Atomic coordinates, bond lengths and angles and thermal parameters of X-ray crystal structures of **10**, **22**, **37** and **38** have been deposited with the Cambridge Crystallographic Data Centre.‡

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