

# Photocycloaddition of *N*-alkoxycarbonylbenzoxazole-2-thiones to alkenes: isolation of stable aminothietanes

Takehiko Nishio

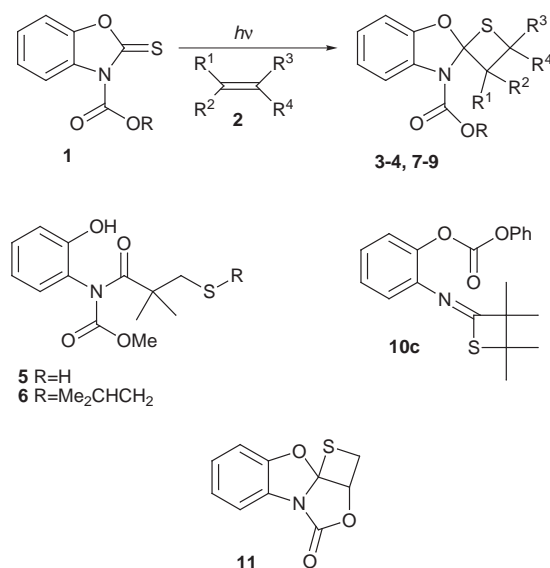
Department of Chemistry, University of Tsukuba, Tsukuba-shi, Ibaraki, 305-8571 Japan

Received (in Cambridge) 26th January 1999, Accepted 11th March 1999

*N*-Alkoxy- and *N*-aryloxy carbonylbenzoxazole-2-thiones **1** undergo photocycloaddition with alkenes **2** in a regio-specific manner to yield stable spirocyclic aminothietanes **3–4**, **7–9** and **11** in fair to high yields.

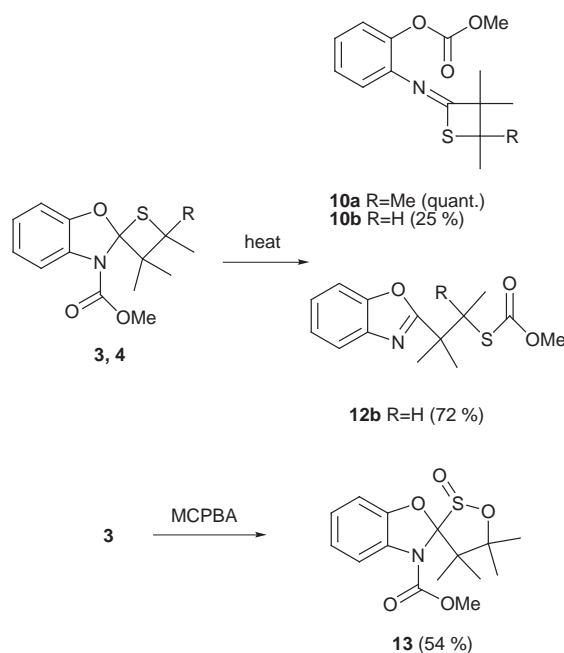
The photochemistry of thioamides has been of considerable synthetic and mechanistic interest.<sup>1,2</sup> In particular, they undergo both intra- and intermolecular [2 + 2] photocycloaddition with alkenes to yield aminothietanes as primary products,<sup>3</sup> which are usually unstable and transformed into fragmentation products. This probably occurs by the nitrogen lone-pair-assisted cleavage of the C–S bond of the thietane ring. In contrast, thietanes have been isolated from photochemical cycloaddition of alkenes and thioimides, which have a cross-conjugated carbanoyl system.<sup>1e,2</sup> We recently reported that photocycloaddition of *N*-acylbenzoxazole-2-thiones and alkenes yielded 2-substituted benzoxazoles and the unexpected iminothietanes. The formation of these products can be explained in terms of intramolecular trapping of zwitterion intermediates, derived from [2 + 2] cycloadducts, spirocyclic aminothietanes, although we were unable to isolate and characterize them.<sup>1f</sup> In the present paper, we describe the results of photochemical reactions of *N*-alkoxy- and aryloxy carbonylbenzoxazole-2-thiones **1** with alkenes **2** yielding the stable isolable aminothietanes **3–4**, **7–9** and **11**.

The *N*-methoxy- (**1a**) and *N*-phenoxycarbonylbenzoxazole-2-thiones (**1b**) were unreactive when they were irradiated alone in solution under an inert atmosphere. However, irradiation of a benzene solution of *N*-methoxycarbonylbenzoxazole-2-thione (**1a**) and electron-rich alkenes such as 2,3-dimethylbut-2-ene (**2a**) and 2-methylbut-2-ene (**2b**), or an electron-deficient alkene such as methacrylonitrile (**2d**), in a Pyrex vessel with a high-pressure mercury lamp under argon gave 1 : 1 adducts of **1a** and **2** in fair to high yields (Table 1). These were identified as the spirocyclic aminothietanes **3–4** and **7** (Scheme 1). The photocycloaddition leading to spirocyclic aminothietanes is regio-



Scheme 1

specific. The orientation of addition of thiones **1a** and alkenes **2** can be predicted from consideration of the most stable diradical intermediate in the [2 + 2] photocycloaddition process.<sup>1a,b,e,f</sup> Spirocyclic aminothietanes **3–4** and **7** thus obtained were stable at room temperature, however upon heating (reflux in toluene) **3–4** were transformed into iminothietanes **10** and/or 2-substituted benzoxazole **12b** (Scheme 2). On the other hand, irradi-



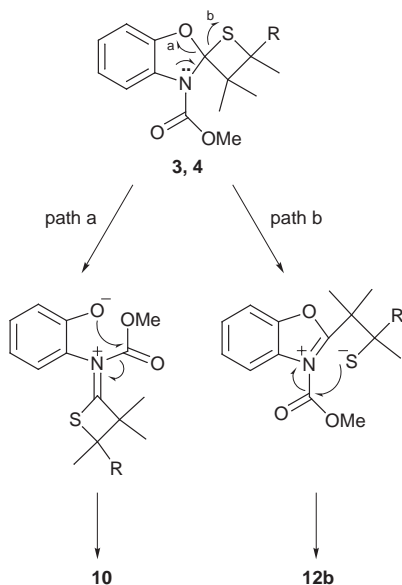
Scheme 2

ation of **1a** in the presence of 2-methylpropene (**2c**) gave the products of oxazole ring-cleavage, acylcarbamate derivatives **5** and **6**. Similar photochemical oxazole ring-cleavage has been observed in the photocycloaddition of *N*-alkylbenzoxazole-2-thiones and alkenes.<sup>1e</sup> As for the formation of **10** and **12b**, an analogous mechanism involving the C–S bond cleavage of thietane ring yielding a zwitterion intermediate was previously presented (Scheme 3).<sup>1f</sup> Treatment of spirocyclic thietane **3** with 2 equiv. of *m*-chloroperbenzoic acid (MCPBA) yielded the sultine **13** in 54% yield. Spirocyclic aminothietane **8** was also obtained as the sole product in 50% yield when **1a** was irradiated in the presence of the conjugated diene 2,5-dimethylhexa-2,4-diene (**2e**), suggesting the spirocyclic aminothietanes are formed through the excited singlet state of the benzoxazole-2-thiones **1a**. Irradiation of *N*-phenoxycarbonylbenzoxazole-2-thione (**1b**) in the presence of 2,3-dimethylbut-2-ene (**2a**) gave spirocyclic aminothietane **9** and the oxazole ring-cleavage product, iminothietane **10c** in 68 and 10% yields, respectively. Irradiation of a solution of *N*-vinyloxy carbonylbenzoxazole-2-thione (**1c**) in benzene under the same conditions gave the intramolecular [2 + 2] cycloadduct, multifused thietane **11**. The structures of all new photoproducts **3–11**, and **12b** and **13** were confirmed on the basis of spectral data and elemental analyses.<sup>4</sup> The <sup>13</sup>C NMR spectra of spirocyclic aminothietanes **3–4** and

**Table 1** Yields of photoproducts (3–11)

	Thione (1)		Alkene (2)				Product (% yield) <sup>a</sup>	
		R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>		
	<b>1a</b>	Me	<b>2a</b>	Me	Me	Me	Me	<b>3</b> (50)
	<b>1a</b>		<b>2b</b>	Me	Me	Me	H	<b>4</b> (75)
	<b>1a</b>		<b>2c</b>	Me	Me	H	H	<b>5</b> (64) <b>6</b> (23)
	<b>1a</b>		<b>2d</b>	Me	CN	H	H	<b>7</b> (98) <sup>b</sup>
	<b>1a</b>		<b>2e</b>	Me	Me	H	CH=CMe <sub>2</sub>	<b>8</b> (50)
	<b>1b</b>	Ph	<b>2a</b>	Me	Me	Me	Me	<b>9</b> (68) <b>10c</b> (18)
	<b>1c</b>	CH=CH <sub>2</sub>						<b>11</b> (20)

<sup>a</sup> Isolated yield. <sup>b</sup> Mixture of two stereoisomers.

**Scheme 3**

**7–9** exhibited a characteristic quaternal carbon peak at C-2 around  $\delta$  106.3–110.9 and other carbon peaks in the expected regions. The stability of spirocyclic aminothietanes described here can be rationalized in terms of the lower participation of nitrogen atom lone-pair electrons which facilitate the ring

cleavage of the thietane, by conjugation with the electron-withdrawing substituents, alkoxy- or aryloxycarbonyl groups.

## References

- (a) M. Sakamoto, T. Fujita, S. Watanabe and T. Nishio, *Yuki Gousei Kagaku Kyokaiishi*, 1995, **52**, 658; (b) T. Nishio and M. Sakamoto, in *Reviews on Heteroatom Chemistry*, ed. S. Oae, MYU, Tokyo, 1995, vol. 12, p. 23 and references cited therein; (c) M. Sakamoto and T. Nishio, in *Reviews on Heteroatom Chemistry*, ed. S. Oae, MYU, Tokyo, vol. 12, p. 53 and references cited therein; (d) T. Nishio, Y. Mori, I. Iida and A. Hosomi, *Helv. Chim. Acta*, 1994, **77**, 981; (e) T. Nishio, Y. Mori, I. Iida and A. Hosomi, *J. Chem. Soc., Perkin Trans. 1*, 1996, 921; (f) T. Nishio, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1007.
- J. D. Coyle, *Tetrahedron*, 1985, **41**, 539; M. Machida, K. Oda, E. Sato and Y. Kanaoka, *Yuki Gosei Kagaku Kyokaisi*, 1986, **44**, 1071; J. D. Coyle and P. A. Rapley, *J. Chem. Soc., Perkin Trans. 1*, 1986, 2273.
- Aminothietanes have not been isolated except for one example by us. By the photochemical cycloaddition of 1,3,3-trimethylindole-2-thione and 2-methylpropene, 1,3,3,3',3'-pentamethyl-2,3-dihydro-spiro[indole-2,2'-thietane] was isolated, though in only 8% yield; T. Nishio, N. Okuda and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1663.
- For example, spirocyclic aminothietane **3**: IR (KBr) 1725 and 1620  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}$  1.10 (3H, s), 1.39 (3H, s), 1.55 (3H, s), 1.71 (3H, s), 3.91 (3H, s), 6.80–6.96 (3H, m) and 7.37–7.43 (1H, m);  $\delta_{\text{C}}$  21.5 (q), 22.1 (q), 26.3 (q), 29.8 (q), 48.0 (s), 52.9 (q), 62.9 (s), 108.2 (d), 109.8 (s), 115.4 (d), 121.1 (d), 123.9 (d), 129.8 (s), 148.2 (s) and 152.5 (s). The structure of the sultine **13** was finally confirmed by X-ray structural analysis. Details will be reported elsewhere.

Communication 9/00699K