

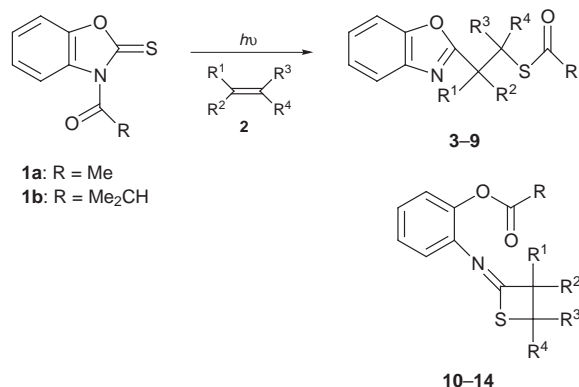
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N-Acylbenzoxazole-2-thiones **1** undergo photoaddition with alkenes **2** in a regioselective manner to yield benzoxazole derivatives **3–9** and/or the unexpected, iminothietanes **10–14** via spirocyclic aminothietane intermediates, depending on the nature of the substituents both on the N-atom of **1** and those present in the alkenes **2**.

Thiocarbonyl compounds are known to undergo photocycloaddition to a variety of alkenes.¹ Thioamides also undergo both inter- and intra-molecular photocycloaddition with alkenes.² Aminothietanes are believed to be intermediates in these reactions. However, such products have not been isolated except for one example,³ probably because the nitrogen lone-pair electron-assisted cleavage of the C–S bond of the thietane ring facilitates the formation of a zwitterion.² We are interested in exploring the effect of the substituents on the nitrogen atom of thioamides upon [2 + 2] photocycloaddition of thioamides with alkenes. We recently reported that the photocycloaddition of *N*-unsubstituted benzoxazole-2-thiones to alkenes gave 1:1-adducts of the reactants, 2-alkylated benzoxazoles, and that of *N*-alkylbenzoxazole-2-thiones to alkenes gave the ring-opened products, amide derivatives, which were derived from the addition of water to 1:1-adducts of the reactants.^{2e} We now report the results of photoreaction of *N*-acylbenzoxazole-2-thiones **1**, substituted with an electron-withdrawing group on the nitrogen atom, and alkenes **2** yielding 2-substituted benzoxazoles **3–9** and the unexpected products, iminothietanes **10–14**: these are formed by intramolecular trapping of zwitterion intermediates, derived from [2 + 2] cycloadducts, spirocyclic aminothietanes, of **1** and **2**.

Irradiation of a benzene solution of *N*-acetylbenzoxazole-2-thione **1a** and 1,1-disubstituted alkenes such as 2-methylprop-2-ene **2a** and methacrylonitrile **2g** in a Pyrex vessel with a high-pressure mercury lamp under argon gave 2-substituted benzoxazoles **3** and **7**, exclusively, which were 1:1-adducts of the reactants, in 59 and 63% isolated yields, respectively. Irradiation of **1a** in benzene in the presence of 1,1,2-trisubstituted alkenes, 2-methylbut-2-ene **2b** and 2,5-dimethylhexa-2,4-diene **2d** and the 1,1,2,2-tetrasubstituted alkene, 2,3-dimethylbut-2-ene **2c** under the same conditions gave 2-



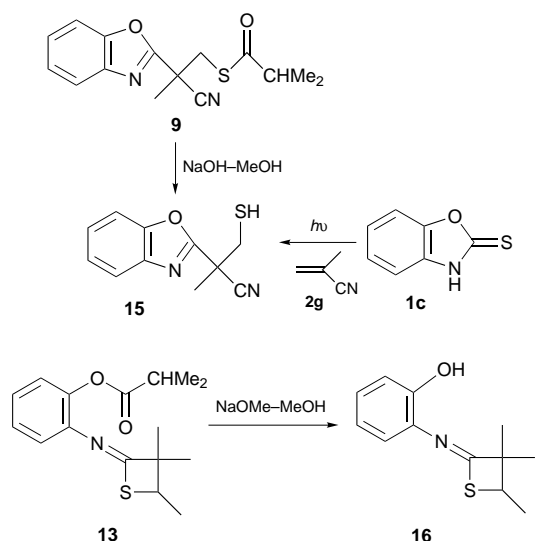
Scheme 1

Table 1 Yields of photoproducts (**3–14**)

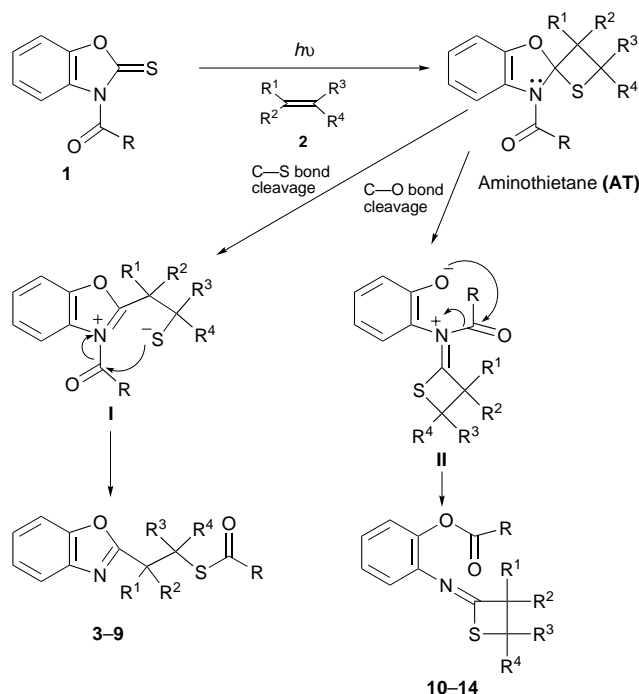
Thione (1)	Alkene (2)					Product (yield, %) ^a	
	R	R ¹	R ²	R ³	R ⁴		
1a	Me	2a	Me	Me	H	H	3 (59)
1a		2b	Me	Me	Me	H	4 (61) 10 (tr.)
1a		2c	Me	Me	Me	Me	5 (7) 11 (52)
1a		2d	Me	Me	H	CH=Me ₂	6 (28) 12 (31)
1a		2e	Ph	H	H	Ph	— ^b
1a		2g	Me	CN	H	H	7 (63)
1b	Me ₂ CH	2b	Me	Me	Me	H	13 (53)
1b		2c	Me	Me	Me	Me	14 (51)
1b		2f	Ph	Ph	H	H	8 (55)
1b		2g	Me	CN	H	H	9 (54)
1b^c		2g					9 (77)
1b^d		2g					9 (59)

^a Isolated yield. ^b Recovered **1a** (88%). ^c In MeOH. ^d In CH₃CN.

substituted benzoxazoles **4–6** and the unexpected products, iminothietanes **10–12**. On the other hand, irradiation of **1a** in the presence of 1,2-disubstituted alkenes such as stilbene **2e** resulted in recovery of unchanged **1a**. The structures of all new photoproducts **3–9** and **10–12** were confirmed on the basis of spectral data and analytical results. The IR spectra of 2-substituted benzoxazoles **3–7** showed the characteristic absorption of thioester carbonyls (1675–1700 cm⁻¹), while those of iminothietanes **10–12** showed absorptions characteristic of an ester group (1755–1760 cm⁻¹). The ¹³C NMR spectra of 2-substituted benzoxazoles **3–7** exhibited the presence of a thioester carbonyl carbon (δ 192.8–196.6) and an imino carbon (δ 161.5–170.7) of a benzoxazole ring. Those of iminothietanes **10–12** exhibited the signals at δ 168.8–173.2 and at δ 166.9–168.9, which were assigned to ester carbonyl and imino carbons, respectively. In contrast, irradiation of *N*-2-methylpropanoylbenzoxazole-2-thione **1b** in benzene in the presence of alkenes **2** gave 2-substituted benzoxazoles **8–9** or iminothietanes **13–14**, exclusively, depending on the substitution pattern of the alkenes. Similar results were obtained when **1b** was irradiated in methanol and acetonitrile in the presence of alkene **2g**. The structures of the photoproducts were elucidated on the basis of analytical results, spectral data and chemical evidence. The photoproduct, 2-(1,3-benzoxazol-2-yl)-2-cyanopropyl 2-methylpropanethioate **9**, was hydrolyzed with sodium hydroxide in methanol to give 2-(1,3-benzoxazol-2-yl)-2-cyanopropanethiol **15**. The structure of **15** was confirmed by spectral comparison with an authentic sample which was independently prepared by the photoaddition of benzoxazole **1c** with methacrylonitrile **2g**.^{2e} Treatment of iminothietane **13** with sodium methoxide in methanol gave *N*-(3,3,4-trimethyl-2-thietanylidene)-*o*-hydroxyaniline **16**. The structure of **16** was elucidated on the basis of its spectral properties and elemental analysis.⁴ The formation of 2-substituted benzoxazoles **3–9** and iminothietanes **10–14** in the photocycloaddition of *N*-acylbenzoxazole-2-thiones **1** with alkenes **2** could be explained in terms of the pathways shown in Scheme 3. The amino-



Scheme 2



Scheme 3

thietane **AT** was formed initially through the regioselective [2 + 2] photocycloaddition of the C=S bond of **1** and C=C bond of **2**. The regiochemistry is in accord with the formation

of the more stable diradical intermediate in the [2 + 2] photocycloaddition process.^{2a,b,5} The aminothietane thus formed is unstable owing to the participation of the lone-pair electrons on the nitrogen atom and then undergoes C-S bond cleavage of the thietane ring or C-O bond cleavage of the oxazole ring to yield the zwitterions **I** or **II**. Finally, intramolecular nucleophilic attack of the thiolate anion of the zwitterion **I** or the phenolate anion of the zwitterion **II** on the acyl group yields 2-substituted benzoxazoles **3-9** and iminothietanes **10-14**. The two modes of cleavage in this proposed reaction intermediate (**AT**) could be explained in terms of the stability of the thietanes: MO calculation suggests that the heat of formation of thietanes having substituents at C-2 adjacent to S is lower than that of thietanes having no substituents at C-2 by 4-15 kcal mol⁻¹.⁶ The photoaddition reaction of *N*-acylbenzoxazole-2-thiones to alkenes described here provides an efficient and novel method for the synthesis of iminothietanes, although a few syntheses of iminothietanes have been reported.⁷

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- The structure of **16** was finally confirmed by X-ray structural analysis. Details will be reported elsewhere.
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