# Photoaddition of benzoxazole-2-thiones with alkenes

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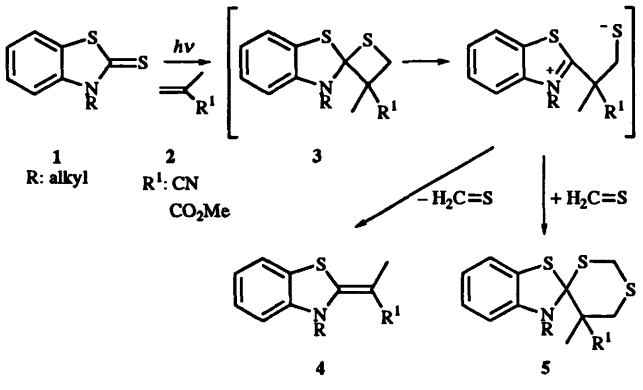
**The photochemical reactions of the benzoxazole-2-thiones 6 have been examined. Irradiation of 3-unsubstituted benzoxazole-2-thione 6a in the presence of alkenes 2 gave 2-alkylated benzoxazoles 7, 9–15 and 8 (in the case of 2a). Irradiation of 3-substituted benzoxazole-2-thiones 6b–e and acrylonitrile 2f yielded the 2-alkylidenebenzoxazoles 17, 22 and 24–25. Irradiation of 6b–e in the presence of 1,1-di- and tetra-substituted alkenes 2a,c and e gave the amide derivatives 18–20, 23 and 26. The 3-(alk-ω-enyl)-benzoxazole-2-thiones 6g–i gave the lactam derivatives 28g–i upon irradiation. The formation of these photoproducts can be explained in terms of the intermediacy of amino spiro-thietanes, which are derived by [2 + 2] photocycloaddition of the C=S bond of benzoxazole-2-thiones and the C=C bond of alkenes.**

The photochemistry of thiocarbonyl compounds has been of considerable synthetic and mechanistic interest.[1] Some reports have dealt with photochemical reactions involving the C=S group of thioamides and thioimides.[1b,e,2] In the course of our studies of the photochemistry of cyclic conjugated nitrogen–thiocarbonyl systems,[3] we have reported the photochemical behaviour of benzothiazole-2-thiones.[3k,l] For, example, irradiation of 3-alkylbenzothiazole-2-thiones **1** in the presence of electron-deficient alkenes **2** such as methacrylonitrile and methyl methacrylate gave 2-alkylidenebenzothiazole **4** and spiro-1,3-dithianes **5** (see Scheme 1).




Scheme 1

Although the aminothietanes **3** are believed to be intermediates in these reactions, except for one example,[3f] they have not been isolated, probably because the nitrogen-lone-pair-electron-assisted cleavage of the C–S bond of the thietane ring facilitates formation of a zwitterion. The present investigation was aimed at extending this photoaddition to benzoxazole-2-thiones **6**, which although in some respects is analogous to that of benzothiazole-2-thiones **1**, also shows significant differences.

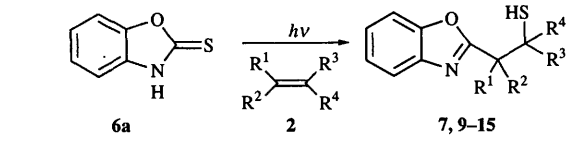
## Results and discussion

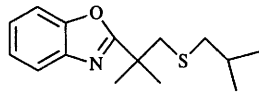
### Intermolecular photocycloaddition of benzoxazole-2-thione 6a–e with alkenes

The benzoxazole-2-thiones **6a–e** were photochemically unreactive when they were irradiated alone in solution under an inert atmosphere. However, 3-unsubstituted benzoxazole-2-thione **6a** in benzene–dimethoxyethane (DME) in the presence of a large excess of isobutene **2a** when irradiated with a high-pressure mercury lamp through a Pyrex filter gave 2-(2′-mercaptoalkyl)benzoxazole **7** (68%) and the sulfide **8** (10%), the 1:2-adducts of **6a** and **2a**, respectively (Scheme 2, Table 1). The latter product **8** was also produced when a solution of **7** in benzene–DME saturated with isobutene **2a** was irradiated. 2-(2′-Mercaptoalkyl)benzoxazoles **9–15** were exclusively obtained when benzoxazole-2-thione **6a** was irradiated in the presence of electron-rich alkenes such as 3-methylbut-2-ene **2b**, 2,3-dimethylbut-2-ene **2c** and ethyl vinyl

**Table 1** Yields of the photoproducts **7–15**

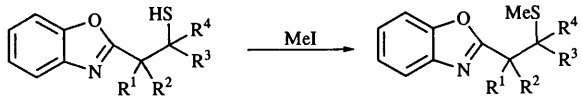
| | Alkene **2** | | | | Yield of products (%) |
|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | |
| **2a** | Me | Me | H | H | **7** (68) **8** (10) |
| **2b** | Me | Me | Me | H | **9** (28) |
| **2c** | Me | Me | Me | Me | **10** (26) |
| **2d** | EtO | H | H | H | **11** (4) |
| **2e** | Me | CN | H | H | **12** (76) |
| **2g** | Me | $CO_2Me$ | H | H | **13** (47) |
| **2h** | Ph | Me | H | H | **14** (45) |
| **2i** | Ph | Ph | H | H | **15** (60) |



8

7 —hν, 2a→ 8 (quant.)




**16b**: $R^1 = R^2 = Me$, $R^3 = R^4 = H$(68%)
**16c**: $R^1 = R^2 = R^3 = R^4 = Me$(quant.)
**16e**: $R^1 = R^2 = Ph$, $R^3 = R^4 = H$(75%)

Scheme 2

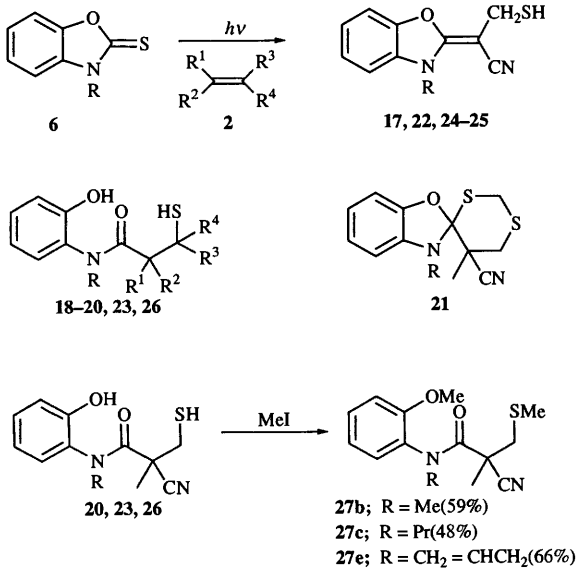
ether **2d**, electron-deficient alkenes such as methacrylonitrile **2e** and methyl methacrylate **2g**, and arylalkenes such as 2-phenylpropene **2h** and 1,1-diphenylethylene **2i**. The structures of photoproducts were elucidated on the basis of their spectral and analytical data. Methylation of 2-(2′-mercaptoalkyl)benzoxazoles **7**, **10** and **15** thus obtained with methyl iodide gave 2-(2′-methylsulfanylalkyl)benzoxazoles **16b–c** and **e** in good yields.

Irradiation of 3-substituted benzoxazole-2-thiones **6b–d** in the presence of the mono-substituted alkene, acrylonitrile **2f**, gave 2-mercaptoalkylidenebenzoxazoles **17**, **22** and **24–25** in 14–33% yields (Scheme 3, Table 2). The $^1$H NMR spectra of these photoproducts showed the presence of an SH group by a signal at *ca.* $\delta$ 2.00 (1 H, t) and the IR spectra exhibited characteristic thiol absorption at *ca.* 2550 cm$^{-1}$. In contrast, irradiation of a solution of 3-substituted benzoxazole-2-thiones **6b–c** and **e** and 1,1-di- or tetra-substituted alkenes **2a,c** and **e** in benzene yielded the products of oxazole ring-cleavage, the amide derivatives **18** and **19** as the sole isomer, and **20**, **23** and **26** as a mixture of two isomers. In the case of 3-methylbenzoxazole-2-thione **6b** and methacrylonitrile **2e**, a small amount of the spiro-1,3-dithiane **21** was isolated. The formation of spiro-1,3-dithianes was observed in the photoaddition of benzothiazole-2-thiones **1** and electron-deficient alkenes.[3k] The structures of these photoproducts were confirmed on the basis of spectral and elemental analyses. The $^1$H and $^{13}$C NMR spectra of compounds **20**, **23** and **26** showed the presence of two isomers at room temperature as a result of intramolecular hydrogen bonding between the SH and CO or between the OH and CO groups, or *cis–trans* isomerization resulting from resonance of the amide group. At 50 °C the $^1$H and $^{13}$C NMR spectra of **20** showed that it was a single isomer (see Experimental section). The photoproducts **20**, **23** and **26** were treated with methyl iodide to give the *O*,*S*-dimethylated products **27b–c** and **e**, whose NMR spectra also showed the presence of two isomers. These results suggest that the two isomers of the photoproducts **20**, **23** and **26** and the dimethylated products **27b,c** and **e** result from *cis-trans* isomerization caused by resonance of the amide group (Scheme 4). The photoproducts **7–15** and **17–26**, thus formed by cycloaddition of benzoxazole-2-thiones **6a–e** and the alkenes **2**, are influenced both by the two substituents on the nitrogen of benzoxazole-2-thiones and the nature of the alkenes (*e.g.* mono-, di-, tri- and tetra-substituted alkenes).

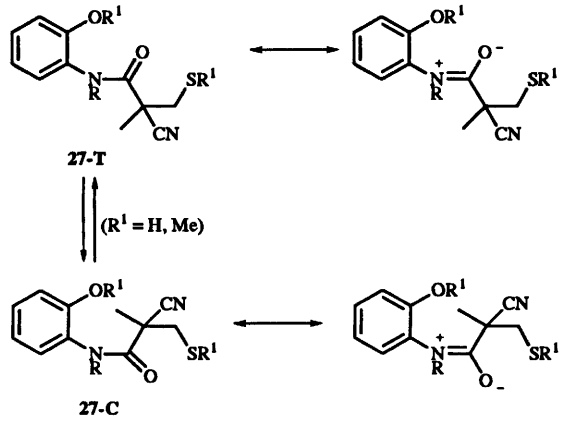
**Table 2** Yields of the photoproducts **17–26**

| | Thione **6** | | Alkene **2** | | | | |
|---|---|---|---|---|---|---|---|
| | R | | R$^1$ | R$^2$ | R$^3$ | R$^4$ | Yield of product (%) |
| **6b** | Me | **2f** | H | CN | H | H | **17** (33) |
| **6b** | | **2a** | Me | Me | H | H | **18** (33) |
| **6b** | | **2c** | Me | Me | Me | Me | **19** (14) |
| **6b** | | **2e** | Me | CN | H | H | **20** (40) **21** (6) |
| **6b**[a] | | **2e** | | | | | **20** (30) |
| **6b**[b] | | **2e** | | | | | **20** (38) |
| **6b**[c] | | **2e** | | | | | **20** (40) |
| **6c** | Pr | **2f** | H | CN | H | H | **22** (14) |
| **6c** | | **2e** | Me | CN | H | H | **23** (76) |
| **6d** | $PhCH_2CH_2$ | **2f** | H | CN | H | H | **24** (22) |
| **6e** | $CH_2$=$CHCH_2$ | **2f** | H | CN | H | H | **25** (23) |
| **6e** | | **2e** | Me | CN | H | H | **26** (66) |

[a] Molecular sieve. [b] Saturated water. [c] In MeOH.




**Scheme 3**

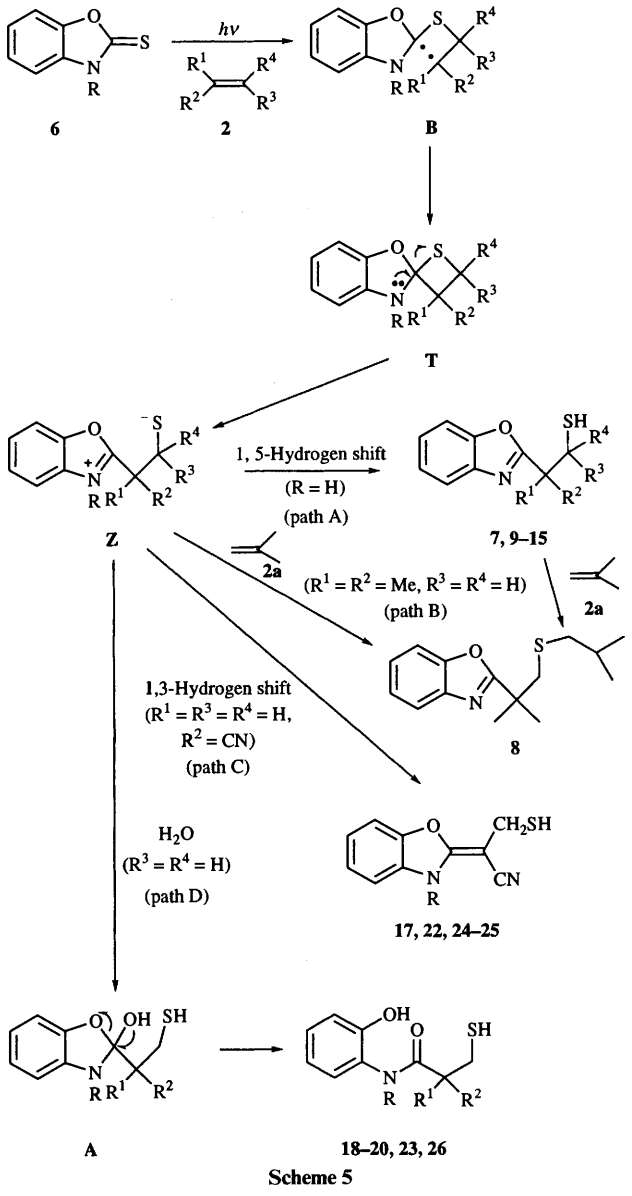



**Scheme 4**

A reasonable mechanism for the formation of 2-alkylbenzoxazoles **7–15**, 2-alkylidenebenzoxazoles **17**, **22** and **24–25** and the amide derivatives **18–20**, **23** and **26** is presented in Scheme 5. The amino-thietane **T** was formed initially through the regioselective [2+2] photocycloaddition of the C=S bond of the thioamides **6** and the C=C bond of the alkenes **2**. The regiochemistry is in accord with the formation of the more stable diradical **B** in the [2+2] photocycloaddition process.[2,3] Subsequent heterolytic cleavage of the C–S bond of the aminothietane **T** owing to the participation of the lone-pair electrons on the nitrogen atom afforded the zwitterion **Z**.[3j–m] 1,5-Hydrogen transfer from nitrogen to sulfur gave 2-alkylbenzoxazoles **7** and **9–15** (path A), while 1,3-hydrogen transfer from carbon in the side chain to sulfur yielded 2-alkylidenebenzoxazoles **17**, **22** and **24–25** (path C). Addition of a second molecule of isobutene **2a** to the zwitterion **Z**, in which the sulfide-anion site is less hindered (R$^3$ = R$^4$ = H) gave the sulfide **8** (path B). A similar photochemical addition was reported for aza-aromatic thiones and **2a**.[3l,4] The zwitterion **Z** was trapped with a trace of water in the solvent to yield, *via* the adduct **A**, the amide derivatives **18–20**, **23** and **26** (path D). To remove traces of water in the solvent, the photoreaction of the benzoxazole-2-thione **6b** and methacrylonitrile **2e** was performed in the presence of molecular sieve; the latter, however, had little effect, a closely similar result to that in its absence being obtained (Table 2). Irradiation of **6b** and **2e** in water-saturated benzene gave a similar yield (38%) of the amide derivative **20**. An attempt to trap the zwitterion **Z** with methanol was unsuccessful and irradiation of **6b** in methanol in the presence of **2e** gave **20** exclusively in 40% yield.

### Intramolecular photocycloaddition of *N*-(alk-ω-enyl)-benzoxazole-2-thiones 6f–j

As described above, in principle, the benzoxazole-2-thiones undergo efficient intermolecular photocycloaddition with alkenes to yield amino spiro-thietanes as the primary products;



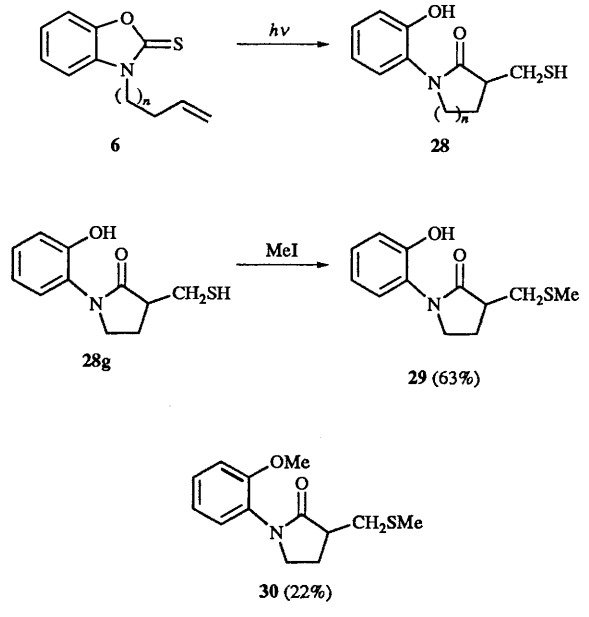

Scheme 5

these were unstable owing to participation of the lone-pair electrons on the nitrogen atom and were further transformed into the final products. In order to assess the generality of this reaction process, we subjected the 3-(alk-ω-enyl)benzoxazole-2-thiones **6f–j** to intramolecular photocycloaddition. Benzene solutions of 3-allyl- **6f** or 3-(oct-7-enyl)-benzoxazole-2-thione **6j** when irradiated for 15 h under the same conditions as described above, gave quantitative recovery of unchanged starting material. However, irradiation of 3-(but-3-enyl)- **6g**, 3-(pent-4-enyl)- **6h** and 3-(hex-5-enyl)-benzoxazole-2-thiones **6i** in benzene gave the lactam derivatives **28g–i** (Scheme 6, Table 3). The structures of **28g–i** were elucidated on the basis of their spectral properties and elemental analyses. The IR spectra of **28g–i** showed absorption at 3150–3240, 2555–2565 and 1610–1650 $cm^{-1}$ attributable to hydroxy, thiol and amide carbonyl groups, respectively and their $^1H$ NMR spectra showed a thiol group signal at $\delta$ 1.26–1.56 (1 H, t). Methylation of **28g** with methyl iodide yielded the *S*-methylated and *S,O*-dimethylated products, **29** (63%) and **30** (22%), respectively. The structure of **28g** was finally confirmed by X-ray structural analysis (Fig. 1). The photoreaction of 3-(but-3-enyl)benzoxazole-2-thione **6g** in benzene under oxygen decreased both the reaction rate and the yield of the lactam **28g**, whereas for a reaction with **6g** carried out in the presence of a triplet quencher such as 2,5-dimethylhexa-2,4-diene ($E_T$ = 59 kcal $mol^{-1}$) there was no quenching effect. Nor was the photoreaction of **6g** affected by the

**Table 3** Yields of the photoproducts **28**

| Thione **6** | Solvent | Yield (%) |
|---|---|---|
| **6f** $n$ = 0 | Benzene | —(100)[a] |
| **6g** $n$ = 1 | Benzene | **28g** 63 (10) |
| **6g**[b] | Benzene | **28g** 22 (62) |
| **6g**[c] | Benzene | **28g** 58 (11) |
| **6g**[d] | Benzene | **28g** tr. (88) |
| **6g**[e] | Benzene | **28g** tr. (90) |
| **6g**[f] | Benzene | **28g** tr. (34) |
| **6g** | MeOH | **28g** 25 (45) |
| **6g**[g] | MeOH | **28g** 22 (44) |
| **6h** $n$ = 2 | Benzene | **28h** 50 (49) |
| **6i** $n$ = 3 | Benzene | **28i** 10 (80) |
| **6j** $n$ = 5 | Benzene | —(100) |

Irradiation was carried out at wavelength >300 nm; tr = trace. [a] Recovered **6**. [b] Under $O_2$. [c] In the presence of 2,5-dimethylhexa-2,4-diene. [d] Halogen lamp (λ > 400 nm) was used as an irradiation source. [e] Wavelength λ = 366 nm. [f] Wavelength λ = 366 nm, in the presence of xanthone. [g] In the presence of molecular sieve.




Scheme 6

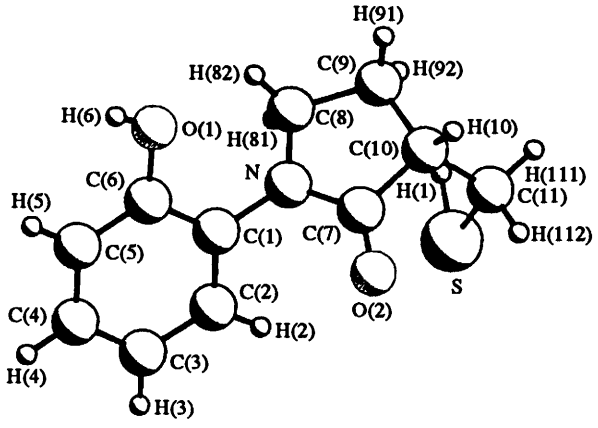
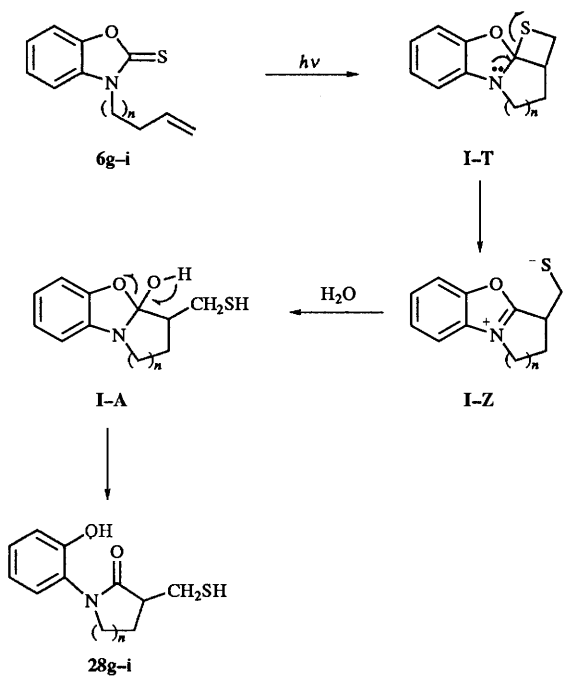



**Fig. 1** Crystal structure of *N*-(*o*-hydroxyphenyl)-3-sulfanylmethyl-pyrrolidin-2-one **28g**. Arbitrary numbering

addition of the triplet sensitizer, xanthone ($E_T$ 74 kcal $mol^{-1}$). Irradiation of **6g** in benzene in the n-π* region with a halogen lamp under conditions similar to those described failed to give the lactam **28g** (Table 3). These results suggest that formation of the lactam **28g** proceeds *via* the π-π* singlet state of **6g**.

A plausible pathway for the formation of the lactams **28g–i** also involves initial intramolecular [2+2] cycloaddition of the




Scheme 7

C=S bond and the C=C bond of the benzoxazole-2-thiones **6g–i** to give a multi-fused amino-thietane intermediate **I-T** (Scheme 7). Subsequent heterolytic cleavage of the C–S bond of **I-T** gives the zwitterion **I-Z**, which is trapped by a trace of water in the solvent to yield the lactams **28g–i** *via* the adduct **I-A**. An attempt to trap the zwitterion **I-Z** with methanol was also unsuccessful; irradiation of 3-(but-3-enyl)benzoxazole-2-thione **6g** in methanol yielded the lactam **28g** in 25% yield, whilst in the presence of molecular sieve to remove water in the solvent, the product yield was 22%. Inertness of photochemical [2+2] cycloaddition of 3-allyl- **6f** and 3-(oct-7-enyl)-benzoxazole-2-thione **6j** can be explained in terms of the lack of orbital overlap between the thione and alkene functions because of steric hindrance and the flexibility of the alkenyl substituent.

## Experimental

Mps and bps are uncorrected. IR spectra were recorded on a Hitachi 260-30 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were run on JEOL FX 90Q (90 MHz) or JEOL-JNM-EX-270 (270 MHz) spectrometers with $CDCl_3$ as solvent unless otherwise noted and tetramethylsilane as an internal standard. *J* Values are given in Hz.

### General procedure for the photochemical reactions of the benzoxazole-2-thiones 6 with the alkenes 2

A solution of **6** (200 mg) and **2** (*ca.* 1 $cm^3$ or 2 mol equiv. for **2h**,i) in benzene (60 $cm^3$)–dimethoxyethane (10 $cm^3$) (for **6a**) (or MeOH, benzene, acetonitrile for **6b–j**) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (300 or 500 W) under argon for 12–20 h at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–ethyl acetate (9 : 1–50 : 1) as eluent to yield the corresponding photoproducts (**7–15**, **17–26** and **28**).

**2-(1′,1′-Dimethyl-2′-sulfanylethyl)benzoxazole 7.** Bp 185 °C/3 Torr (Found: C, 63.6; H, 6.35; N, 6.9. $C_{11}H_{13}NOS$ requires C, 63.75; H, 6.3; N, 6.75%); $\nu_{max}$(film)/$cm^{-1}$ 2550; $\delta_H$ 1.41 (1 H, t, *J* 8.9), 1.54 (6 H, s), 2.97 (2 H, d, *J* 8.9), 7.25–7.33 (2 H, m), 7.46–7.51 (1 H, m) and 7.69–7.73 (1 H, m); $\delta_C$ 25.3 (q), 35.7 (t), 39.6 (s), 110.4 (d), 119.8 (d), 124.1 (d), 124.6 (d), 141.0 (s), 150.7 (s) and 170.8 (s).

**2-(Benzoxazol-2′-yl)-2-methylpropyl isobutyl sulfide 8.** Bp 210 °C/3 Torr (Found: C, 68.5; H, 8.1; N, 5.35. $C_{15}H_{21}NOS$ requires C, 68.4; H, 8.05; N, 5.5%); $\nu_{max}$(film)/$cm^{-1}$ 1605, 1560, 1455, 1380, 1365, 1245, 995, 925, 800, 765 and 745; $\delta_H$ 0.88 (6 H, d, *J* 6.6), 1.56 (6 H, s), 1.65–1.80 (1 H, m), 2.29 (2 H, d, *J* 6.0), 3.01 (2 H, s), 7.26–7.31 (2 H, m), 7.45–7.52 (1 H, m) and 7.69–7.73 (1 H, m); $\delta_C$ 21.8 (q), 25.9 (q), 28.6 (d), 39.2 (s), 43.3 (t), 44.7 (t), 110.4 (d), 119.8 (d), 124.1 (d), 124.6 (d), 141.6 (s), 150.7 (s) and 171.5 (s).

**2-(1′,1′-Dimethyl-2′-sulfanylpropyl)benzoxazole 9.** Bp 200 °C/2 Torr (Found: C, 65.2; H, 6.9; N, 6.1. $C_{12}H_{15}NOS$ requires C, 65.15; H, 6.85; N, 6.35%); $\nu_{max}$(film)/$cm^{-1}$ 2550; $\delta_H$ 1.31 (3 H, d, *J* 6.9), 1.49 (1 H, d, *J* 7.6), 1.52 (3 H, s), 1.55 (3 H, s), 3.51–3.62 (1 H, m), 7.26–7.34 (2 H, m), 7.46–7.52 (1 H, m) and 7.69–7.73 (1 H, m); $\delta_C$ 10.6 (q), 22.1 (q), 23.5 (q), 42.7 (s), 43.6 (d), 110.4 (d), 119.8 (d), 124.1 (d), 124.6 (d), 140.9 (s), 150.5 (s) and 171.4 (s).

**2-(2′-Methyl-3′-sulfanylbutan-2′-yl)benzoxazole 10.** Mp 88–89 °C (Found: C, 66.35; H, 7.15; N, 5.85. $C_{13}H_{17}NOS$ requires C, 66.35; H, 7.3; N, 5.95%); $\nu_{max}$(KBr)/$cm^{-1}$ 2540; $\delta_H$ 1.49 (6 H, s), 1.64 (6 H, s), 1.87 (1 H, s), 7.29–7.33 (2 H, m), 7.47–7.53 (1 H, m) and 7.71–7.75 (1 H, m); $\delta_C$ 23.4 (q), 29.5 (q), 45.6 (s), 51.0 (s), 110.4 (d), 119.9 (d), 124.1 (d), 124.6 (d), 140.9 (s), 150.3 (s) and 170.6 (s).

**2-(1′-Ethoxy-2′-sulfanylethyl)benzoxazole 11.** Bp 185 °C/3 Torr (Found: C, 59.2; H, 5.9; N, 6.25. $C_{11}H_{13}NO_2S$ requires C, 59.15; H, 5.85; N, 6.25%); $\nu_{max}$(film)/$cm^{-1}$ 2540; $\delta_H$ 1.26 (3 H, t, *J* 6.9), 1.75 (1 H, X of ABX, *J* 7.6, 9.5), 2.98–3.21 (2 H, m), 3.60–3.73 (2 H, m), 4.69 (1 H, t, *J* 7.3), 7.32–7.40 (2 H, m), 7.52–7.57 (1 H, m) and 7.73–7.77 (1 H, m); $\delta_C$ 15.1 (q), 27.7 (t), 66.3 (t), 77.1 (d), 110.9 (d), 120.4 (d), 124.6 (d), 125.5 (d), 140.7 (s), 150.7 (s) and 164.1 (s).

**2-(2′-Cyano-3′-sulfanylpropan-2′-yl)benzoxazole 12.** Bp 135 °C/2 Torr (Found: C, 60.35; H, 4.65; N, 12.7. $C_{11}H_{10}N_2OS$ requires C, 60.55; H, 4.6; N, 12.85%); $\nu_{max}$(film)/$cm^{-1}$ 2560 and 2240; $\delta_H$ 1.91 (1 H, t, *J* 9.3), 1.98 (3 H, s), 3.28 (2 H, AB of ABX, *J* 8.3, 9.3) and 7.27–7.84 (4 H, m); $\delta_H$ 23.4 (q), 33.2 (t), 42.1 (s), 110.9 (d), 118.6 (s), 120.5 (d), 125.0 (d), 125.9 (d), 140.4 (s), 150.8 (s) and 161.6 (s).

**2-(2′-Methoxycarbonyl-3′-sulfanylpropan-2′-yl)benzoxazole 13.** Mp 41–42 °C (Found: C, 57.25; H, 5.2; N, 5.55. $C_{12}H_{13}NO_3S$ requires C, 57.35; H, 5.2; N, 5.6%); $\nu_{max}$(KBr)/$cm^{-1}$ 2530 and 1730; $\delta_H$ 1.65 (1 H, t, *J* 9.3), 1.85 (3 H, s), 3.32 (2 H, d, *J* 9.3), 3.74 (3 H, s), 7.23–7.57 (3 H, m) and 7.65–7.80 (1 H, m); $\delta_C$ 20.5 (q), 31.6 (t), 51.0 (s), 53.0 (q), 110.7 (d), 120.2 (d), 124.4 (d), 125.2 (d), 140.7 (s), 150.8 (S), 165.1 (s) and 171.5 (s).

**2-(2′-Phenyl-3′-sulfanylpropan-2′-yl)benzoxazole 14.** Bp 205 °C/3 Torr (Found: C 71.7; H, 5.6; N, 5.25. $C_{16}H_{15}NOS$ requires C, 71.35; H, 5.6; N, 5.2%); $\nu_{max}$(film)/$cm^{-1}$ 2560; $\delta_H$ 1.45 (1 H, X of ABX, *J* 8.9), 2.00 (3 H, s), 3.27 (1 H, A of ABX, *J* 8.3, 11.6), 3.54 (1 H, B of ABX, *J* 8.3, 11.6), 7.23–7.36 (7 H, m), 7.42–7.47 (1 H, m) and 7.74–7.81 (1 H, m); $\delta_C$ 22.7 (q), 35.6 (t), 47.1 (s), 110.6 (d), 120.1 (d), 124.3 (d), 124.9 (d), 126.3 (d), 127.4 (d), 128.7 (d), 140.8 (s), 142.6 (s), 150.8 (s) and 169.4 (s).

**2-(1′,1′-Diphenyl-2′-sulfanylethyl)benzoxazole 15.** Bp 250 °C/2 Torr (Found: C, 75.85; H, 5.2; N, 4.25. $C_{21}H_{17}NOS$ requires C, 76.1; N, 5.15; N, 4.25%); $\nu_{max}$(film)/$cm^{-1}$ 2575; $\delta_H$ 1.47 (1 H, t, *J* 8.6), 3.89 (2 H, d, *J* 8.6), 7.16–7.47 (12 H, m) and 7.72–7.79 (2 H, m); $\delta_C$ 34.6 (t), 56.8 (s), 110.7 (d), 120.2 (d), 124.3 (d), 125.0 (d), 127.4 (d), 128.1 (d), 129.1 (d), 140.8 (s), 141.7 (s), 150.8 (s) and 167.9 (s).

A solution of each of the benzoxazoles **7**, **10** and **15** (1 mmol) in acetone in the presence of potassium carbonate (2.2 mmol) was treated with methyl iodide (2 mmol) under argon for 2 h at room temperature. Work-up gave the corresponding sulfides **16b**,**c** and **e**.

**2-(Benzoxazol-2′-yl)-2-methylpropan-2-yl methyl sulfide 16b.** Bp 185 °C/3 Torr (Found: C, 65.45; H, 7.0; N, 6.35. $C_{12}H_{15}NOS$ requires C, 65.15; H, 6.85; N, 6.35%); $\nu_{max}$(film)/$cm^{-1}$ 1605, 1555, 1450, 1240, 1090, 800, 760 and 745; $\delta_H$ 1.57 (6 H, s), 2.00 (3 H, s), 3.01 (2 H, s), 7.27–7.32 (2 H, m), 7.46–7.52 (1 H, m) and 7.69–7.73 (1 H, m); $\delta_C$ 17.7 (q), 25.8 (q),

39.3 (s), 46.5 (t), 110.4 (d), 119.9 (d), 121.1 (d), 124.6 (d), 141.1 (s), 150.7 (s) and 171.3 (s).

**3-(Benzoxazol-2′-yl)-2,3,-dimethylbutan-2-yl methyl sulfide 16c.** Bp 200 °C/3 Torr (Found: C, 67.15; H, 7.7; N, 5.7. $C_{14}H_{19}NOS$ requires C, 67.45; H, 7.7; N, 5.6%); $\nu_{max}$(film)/cm$^{-1}$ 1610, 1550, 1460, 1385, 1245, 1090, 765, 750 and 740; $\delta_H$ 1.41 (6 H, s), 1.64 (6 H, s), 1.94 (3 H, s), 7.26–7.33 (2 H, m), 7.51–7.56 (1 H, m) and 7.73–7.76 (1 H, m); $\delta_C$ 12.3 (q), 23.3 (q), 25.1 (q), 45.6 (s), 50.6 (s), 110.5 (d), 119.9 (d), 124.1 (d), 124.6 (d), 141.0 (s), 150.4 (s) and 170.8 (s).

**2-(Benzoxazol-2′-yl)-2,2-diphenylethyl methyl sulfide 16e.** Bp 230 °C/2 Torr (Found: C, 76.35; H, 5.55; N, 3.95. $C_{22}H_{19}NOS$ requires C, 76.5; H, 5.55; N, 4.05%); $\nu_{max}$(film)/cm$^{-1}$ 1600, 1550, 1495, 1455, 1240, 760, 745 and 700; $\delta_H$ 1.66 (3 H, s), 3.92 (2 H, s), 7.22–7.47 (12 H, m) and 7.73–7.79 (2 H, m); $\delta_C$ 15.6 (q), 44.9 (t), 56.2 (s), 110.7 (d), 120.2 (d), 124.2 (d), 124.9 (d), 127.3 (d), 128.0 (d), 129.1 (d), 140.8 (s), 141.9 (s), 150.8 (s) and 168.5 (s).

**2-(1′-Cyano-2′-sulfanylethylidene)-3-methylbenzoxazole 17.** Mp 116–117 °C (Found: C, 60.5; H, 4.6; N, 12.85. $C_{11}H_{10}N_2OS$ requires C, 60.5; H, 4.75; N, 12.85%); $\nu_{max}$(KBr)/cm$^{-1}$ 2540, 2170 and 1640; $\delta_H$ 2.00 (1 H, t, *J* 7.8), 3.58 (2 H, d, *J* 7.8), 3.69 (3 H, s) and 6.86–7.30 (4 H, m); $\delta_C$ 23.8 (t), 31.0 (q), 57.7 (s), 107.6 (d), 109.4 (d), 120.9 (s), 122.2 (d), 124.5 (d), 133.6 (s), 145.9 (s) and 161.2 (s).

***N*-(*o*-Hydroxyphenyl)-*N*-methyl-2,2-dimethyl-3-sulfanylpropanamide 18.** Mp 107–108 °C (Found: C, 60.3; H, 7.25; N, 5.75. $C_{12}H_{12}NO_2S$ requires C, 60.25; H, 7.15; N, 5.85%); $\nu_{max}$(KBr)/cm$^{-1}$ 3200, 2515 and 1610; $\delta_H$ 1.08 (6 H, br s), 1.58 (1 H, t, *J* 8.8), 2.56–2.79 (2 H, m), 3.21 (3 H, s), 6.72–6.91 (1 H, m) and 7.05–7.29 (3 H, m); $\delta_C$ 25.7 (q), 37.3 (t), 39.9 (q), 46.5 (s), 117.0 (d), 120.4 (d), 129.1 (d), 129.9 (d), 131.3 (s), 152.5 (s) and 177.1 (s).

***N*-(*o*-Hydroxyphenyl)-*N*-methyl-2,2,3-trimethyl-3-sulfanylbutanamide 19.** Mp 129–130 °C (Found: C, 62.85; H, 7.6; N, 5.2. $C_{14}H_{21}NO_2S$ requires C, 62.9; H, 7.9; N, 5.25%); $\nu_{max}$ (KBr)/cm$^{-1}$ 3155, 2550 and 1610; $\delta_H$1.10 (6 H, s), 1.52 (6 H, s), 2.07 (1 H, s), 3.17 (3 H, s), 6.84–7.02 (2 H, m) and 7.10–7.25 (2 H, m); $\delta_C$ 23.7 (q), 30.1 (q), 41.0 (q), 51.9 (s), 52.7 (s), 116.9 (d), 120.5 (d), 128.4 (d), 129.4 (d), 133.1 (s), 151.9 (s) and 177.6 (s).

**2-Cyano-*N*-(*o*-hydroxyphenyl)-2,*N*-dimethyl-3-sulfanylpropanamide 20.** A mixture of two isomers: mp 151–152 °C (Found: C, 57.45; H, 5.6; N, 11.15. $C_{12}H_{14}N_2O_2S$ requires C, 57.6; H, 5.65; N, 11.2%); $\nu_{max}$(KBr)/cm$^{-1}$ 3335, 2565, 2250 and 1645; $\delta_H$($CD_3OD$) 1.64 and 1.65 (3 H, s), 2.74 (1 H, br d, *J* 13.7), 3.25 (1 H, br d, *J* 13.7), 3.27 (3 H, br s), 6.83–6.98 (2 H, m) and 7.14–7.39 (2 H, m); $\delta_C$($CD_3OD$) 24.7, 25.0 (q), 34.1 and 35.0 (t), 39.0 and 39.4 (q), 46.5 (s), 116.8 and 117.4 (d), 118.5 and 119.0 (s), 120.1 and 120.5 (d), 128.9 (s), 129.7 (d), 131.2 (d), 154.3 and 154.5 (s) and 167.7 and 168.0 (s). At 50 °C the NMR spectrum of **20**, as a single isomer, was obtained: $\delta_H$ 1.63 (3 H, s), 2.75 (1 H, d, *J* 13.7), 3.24 (1 H, d, *J* 13.7), 3.26 (3 H, s), 6.80–6.97 (2 H, m) and 7.20–7.38 (2 H, m); $\delta_C$ 25.0 (q), 35.3 (t), 39.7 (q), 47.7 (s), 117.9 (d), 121.2 (d), 130.5 (s), 131.2 (d), 132.0 (d), 155.6 (s) and 169.2 (s).

**5′-Cyano-3,5′-dimethylspiro[benzoxazole-2,4′-(1′,3′-dithiane)] 21.** Mp 167–169 °C (Found: C, 55.9; H, 5.05; N, 10.0. $C_{13}H_{14}N_2OS_2$ requires C, 56.05; H, 5.05; N, 10.05%); $\nu_{max}$(KBr)/cm$^{-1}$ 2200, 1620, 1595, 1485, 1220, 1205, 1045, 805, 740 and 725; $\delta_H$ 1.56 (3 H, s), 2.92 (1 H, dd, *J* 2.4, 14.2), 3.10 (3 H, s), 3.49 (1 H, dd, *J* 2.4, 13.7), 3.66 (1 H, d, *J* 14.2), 4.52 (1 H, d, *J* 13.7), 6.54 (1 H, d, *J* 6.8) and 6.73–7.01 (3 H, m); $\delta_C$ 22.3 (q), 31.1 (t), 31.8 (q), 38.5 (t), 44.8 (s), 107.1 (d), 108.9 (d), 110.0 (s), 119.8 (d), 120.5 (s), 122.8 (d), 139.0 (s) and 146.1 (s).

**2-(1′-Cyano-2′-sulfanylethylidene)-3-propyl-2,3-dihydrobenzoxazole 22.** Mp 84–85 °C (Found: C, 63.25; H, 5.7; N, 11.3. $C_{13}H_{14}N_2OS$ requires C, 63.4; H, 5.85; N, 11.4%); $\nu_{max}$ (KBr)/cm$^{-1}$ 2550, 2175 and 1640; $\delta_H$ 1.04 (3 H, t, *J* 7.8), 1.85 (1 H, t, *J* 7.3), 1.99 (2 H, t, *J* 7.8), 3.59 (2 H, d, *J* 7.8), 4.07 (2 H, t, *J* 7.3) and 6.79–7.28 (4 H, m); $\delta_C$ 10.8 (q), 21.7 (t), 24.0 (t), 45.4 (t), 57.4 (s), 107.7 (d), 109.4 (d), 120.7 (s), 122.0 (d), 124.4 (d), 133.2 (s), 145.9 (s) and 160.5 (s).

***N*-(*o*-Hydroxyphenyl)-*N*-propyl-2-cyano-2-methyl-3-sulfanylpropanamide 23.** A mixture of two isomers: bp 165 °C/3 Torr (decomp.); mp 86–87 °C (Found: C, 60.2; H, 6.5; N, 9.95. $C_{14}H_{18}N_2O_2S$ requires C, 60.5; H, 6.5; N, 10.05%); $\nu_{max}$(KBr)/cm$^{-1}$ 3300, 2575, 2240, 1650 and 1625; $\delta_H$ 0.90 (3 H, t, *J* 7.3), 1.66 (3 H, br s), 1.25–2.03 (3 H, m), 2.64–2.88 (1 H, m), 3.07–3.58 (2 H, m), 3.75–4.19 (1 H, m) and 6.85–7.41 (4 H, m); $\delta_C$ 11.2 (q), 20.4 (t), 25.1 (q), 34.6 and 35.0 (t), 46.0 (s), 52.7 and 53.4 (t), 117.6 (d), 120.5 (d), 127.1 (s), 130.3 (d), 131.2 (d), 153.7 (s) and 167.4 (s).

**2-(1′-Cyano-2′-sulfanylethylidene)-3-phenethylbenzoxazole 24.** Mp 85–87 °C (Found: C, 69.9; H, 5.25; N, 9.1. $C_{18}H_{16}N_2OS$ requires C, 70.1; H, 5.25; N, 9.1%); $\nu_{max}$(KBr)/cm$^{-1}$ 2560, 2170 and 1640; $\delta_H$ 1.99 (1 H, t, *J* 7.8), 3.12 (2 H, t, *J* 8.3), 3.59 (2 H, d, *J* 7.8), 4.30 (2 H, t, *J* 8.3), 6.65–6.80 (1 H, m) and 6.90–7.33 (8 H, m); $\delta_C$ 23.9 (t), 34.5 (t), 45.8 (t), 57.8 (s), 107.7 (d), 109.4 (d), 120.8 (s), 122.1 (d), 124.3 (d), 126.9 (d), 128.8 (d), 129.0 (d), 132.9 (s), 137.0 (s), 145.8 (s) and 160.3 (s).

**3-Allyl-2-(1′-cyano-2′-sulfanylethylidene)benzoxazole 25.** Mp 95–96 °C (Found: C, 63.7; H, 5.1; N, 11.4. $C_{13}H_{12}N_2OS$ requires C, 63.9; H, 4.95; N, 11.45%); $\nu_{max}$(KBr)/cm$^{-1}$ 2560, 2175 and 1640; $\delta_H$ 1.99 (1 H, t, *J* 7.8), 3.58 (2 H, d, *J* 7.8), 4.71–4.79 (2 H, m), 5.20–5.39 (2 H, m), 5.80–6.18 (1 H, m) and 6.87–7.28 (4 H, m); $\delta_C$ 23.8 (t), 46.1 (t), 58.0 (s), 108.0 (d), 109.4 (d), 118.8 (t), 120.4 (s), 122.3 (d), 124.5 (d), 129.9 (d), 132.9 (s), 145.9 (s) and 160.3 (s).

***N*-Allyl-2-cyano-*N*-(*o*-hydroxyphenyl)-2-methyl-3-sulfanylpropanamide 26.** A mixture of two isomers: mp 87–88 °C (Found: C, 60.5; H, 5.85; N, 9.9. $C_{14}H_{15}N_2O_2S$ requires C, 60.85; H, 5.85; N, 10.15%); $\nu_{max}$(KBr) 3370, 2570, 2240 and 1645; $\delta_H$ 1.67 (3 H, br s), 1.83–2.02 (1 H, m), 2.69–2.89 (1 H, m), 3.16–3.42 (1 H, m), 3.77–4.02 (1 H, m), 4.47–4.82 (1 H, m), 5.00–5.21 (2 H, m), 5.71–6.12 (1 H, m) and 6.82–7.40 (4 H, m); $\delta_C$ 25.0 (q), 34.6 and 35.0 (t), 46.6 (s), 54.1 and 54.7 (t), 116.9 and 117.5 (d), 119.0 (t), 120.3 (d), 127.0 (s), 131.4 (d), 131.9 (d), 153.7 (s) and 167.4 (s). At 50 °C the $^1$H NMR spectrum of **26** was obtained as the sole product: $\delta_H$ 1.65 (3 H, s), 1.87 (1 H, br t, *J* 9.3), 2.77 (1 H, dd, *J* 9.3, 13.7), 3.27 (1 H, dd, *J* 9.3, 13.7), 4.00–4.57 (2 H, m), 5.40–5.21 (2 H, m), 5.72–6.12 (1 H, m) and 6.84–7.40 (4 H, m).

A solution of each of the amide derivatives **20**, **23** and **26** (1 mmol) in acetone (20 cm$^3$) under argon was treated in the presence of potassium carbonate (4.2 mmol) with methyl iodide (4 mmol) for 2 h at room temperature. Work-up gave the corresponding sulfides **27b,c** and **e**.

**2-Cyano-*N*-(*o*-methoxyphenyl)-*N*,2-dimethyl-3-methylsulfanylpropanamide 27b.** A mixture of two isomers: bp 80 °C/10$^{-2}$ Torr (Found: C, 60.75; H, 6.45; N, 10.1. $C_{14}H_{18}N_2O_2S$ requires C, 60.4; H, 6.5; N, 10.05%); $\nu_{max}$(film)/cm$^{-1}$ 2230 and 1650; $\delta_H$ 1.59 and 1.62 (3 H, s), 2.22 (3 H, s), 2.73–2.82 (1 H, m), 3.21–3.31 (1 H, m), 3.22 and 3.24 (3 H, s), 3.87 and 3.91 (3 H, s), 6.95–7.06 (2 H, m) and 7.21–7.47 (2 H, m); $\delta_C$ 17.6 (q), 25.5 and 25.8 (q), 39.1 and 39.4 (q), 43.9 and 44.9 (t), 44.0 (s), 55.4 and 55.6 (q), 11.8 and 112.4 (d), 120.8 and 121.2 (d), 128.3 and 129.9 (d), 131.1 (d), 131.3 (d), 156.3 and 156.6 (s) and 167.4 and 167.5 (s). At 70 °C the $^1$H NMR spectrum of **27b**, as a single isomer, was obtained: $\delta_H$ 1.46 (3 H, s), 2.00 (3 H, s), 2.66 (1 H, d, *J* 13.7), 3.13 (3 H, s), 3.20 (1 H, d, *J* 13.7), 3.42 (3 H, s), 6.54–6.84 (2 H, m) and 7.03–7.21 (2 H, m).

**2-Cyano-*N*-(*o*-methoxyphenyl)-2-methyl-3-methylsulfanyl-*N*-propylpropanamide 27c.** A mixture of two isomers: bp 250 °C/3 Torr (Found: C, 63.0; H, 7.3; N, 9.2. $C_{16}H_{22}N_2O_2S$ requires C, 62.7; H, 7.25; N, 9.15%); $\nu_{max}$(film) 2220 and 1645; $\delta_H$ 0.85–0.94 (3 H, m), 1.59 and 1.61 (3 H, s), 1.50–1.71 (2 H, m), 2.22 (3 H, s), 2.72–2.81 (1 H, m), 3.08–3.33 (2 H, m), 3.84–4.04 (1 H, m), 3.87 and 3.91 (3 H, s), 6.95–7.06 (2 H, m) and 7.16–7.48 (2 H, m); $\delta_C$ 11.2 and 11.3 (q), 17.6 and 17.7 (q), 20.5 (t), 25.8 and 26.0 (q), 44.0 and 45.1 (t), 44.4 and 44.7 (s), 52.8 and 53.4 (s), 55.3 and 55.5 (q), 118.2 and 112.4 (d), 120.4 and 120.8 (d), 129.1 (s), 130.9 (s), 131.0 (d), 131.2 (d), 132.4 (d), 156.6 and 156.8 (s) and 167.2 (s).

***N*-Allyl-2-cyano-*N*-(*o*-methoxyphenyl)-2-methyl-3-methylsulfanylpropanamide 27e.** A mixture of two isomers: bp 80 °C/$10^{-2}$ Torr (Found: C, 63.15; H, 6.65; N, 9.25. $C_{16}H_{20}N_2O_2S$ requires C, 63.15; H, 6.6; N, 9.2%); $\nu_{max}$(film)/cm$^{-1}$ 2230 and 1650; $\delta_H$ 1.61 and 1.64 (3 H, s), 2.22 (3 H, s), 2.77 (1 H, dd, *J* 2.9, 13.7), 3.29 (1 H, dd, *J* 2.4, 13.7), 3.86 and 3.90 (3 H, s), 3.58–3.92 (1 H, m), 4.44–4.79 (1 H, m), 4.97–5.16 (2 H, m), 5.63–6.09 (1 H, m) and 6.84–7.57 (4 H, m); $\delta_C$ 17.7 (q), 25.6 and 25.8 (q), 44.4 and 44.7 (s), 43.9 and 45.0 (t), 54.1 and 54.6 (t), 55.4 (q), 111.8 and 112.3 (d), 118.3 and 118.4 (d), 119.6 and 119.9 (s), 120.4 and 120.7 (d), 128.9 (s), 131.1 (d), 132.1 (d), 132.5 (d), 156.5 and 156.7 (s) and 167.1 (s).

**1-(*o*-Hydroxyphenyl)-3-sulfanylmethylpyrrolidin-2-one 28g.** Mp 118–120 °C (Found: C, 59.05; H, 5.85; N, 6.25. $C_{11}H_{13}NO_2S$ requires C, 59.15; H, 5.85, N, 6.25%); $\nu_{max}$(KBr)/cm$^{-1}$ 3150, 2565 and 1650; $\delta_H$ 1.56 (1 H, t, *J* 8.8), 2.07–2.57 (2 H, m), 2.70–3.17 (3 H, m), 3.65–4.04 (2 H, m), 6.81–7.26 (4 H, m) and 8.41 (1 H, s); $\delta_C$ 24.1 (t), 25.4 (t), 45.3 (d), 48.7 (t), 120.5 (d), 121.5 (d), 127.4 (s), 127.9 (d), 150.1 (s) and 175.4 (s).

**1-(*o*-Hydroxyphenyl)-3-sulfanylmethylpiperidin-2-one 28h.** Mp 121–122 °C (Found: C, 60.65; H, 6.3; N, 5.8. $C_{12}H_{15}NO_2S$ requires C, 60.75; H, 6.35; N, 5.9%); $\nu_{max}$(KBr)/cm$^{-1}$ 3180, 2555 and 1610; $\delta_H$ 1.63 (1 H, t, *J* 8.8), 1.78–2.20 (4 H, m), 2.62–3.27 (3 H, m), 3.53–3.92 (2 H, m) and 6.81–7.36 (4 H, m); $\delta_C$ 22.9 (t), 25.0 (t), 26.9 (t), 44.5 (d), 51.8 (t), 119.4 (d), 120.9 (d), 125.3 (d), 128.5 (d), 131.5 (s), 151.2 (s) and 172.1 (s).

**1-(*o*-Hydroxyphenyl)-3-sulfanylmethylazepin-2-one 28i.** An oil (Found: C, 61.9; H, 6.8; N, 5.5. $C_{13}H_{17}NO_2S$ requires C, 62.1; H, 6.8; N, 5.55%); $\nu_{max}$(film)/cm$^{-1}$ 3240, 2560 and 1625; $\delta_H$ 1.26 (1 H, t, *J* 3.4), 1.47–2.14 (7 H, m), 2.30–2.62 (1 H, m), 2.85–3.25 (1 H, m), 3.55–3.80 (1 H, m), 3.90–4.22 (1 H, m) and 6.81–7.36 (4 H, m); $\delta_C$ 27.1 (t), 28.1 (t), 28.7 (t), 29.7 (t), 49.0 (d), 53.2 (t), 119.9 (d), 121.3 (d), 124.8 (d), 128.1 (d), 133.2 (s), 151.0 (s) and 176.5 (s).

A solution of compound **28g** (1 mmol) and potassium carbonate (4.4 mmol) in acetone (20 cm$^3$) under argon was treated with methyl iodide (4 mmol) for 2 h at room temperature. Work-up yielded compounds **29** and **30**.

**1-(*o*-Hydroxyphenyl)-3-methylsulfanylmethylpyrrolidin-2-one 29.** Mp 76–77 °C (Found: C, 60.8; H, 6.4; N, 5.85. $C_{12}H_{15}NO_2S$ requires C, 60.75; H, 6.35; N, 5.9%); $\nu_{max}$(KBr) 1645, 1585, 1460 and 745; $\delta_H$ 2.14 (3 H, s), 2.06–2.18 (1 H, m), 2.38–2.47 (1 H, m), 2.66–2.77 (1 H, m), 2.91–3.07 (2 H, m), 3.73–3.88 (1 H, m), 3.92–4.09 (1 H, m), 6.87–6.96 (1 H, m), 7.01–7.35 (3 H, m) and 8.48 (1 H, s); $\delta_C$ 16.2 (q), 25.3 (t), 35.5 (t), 43.1 (d), 48.8 (t), 120.5 (d), 121.5 (d), 127.5 (s), 127.8 (d), 150.2 (s) and 176.2 (s).

**1-(*o*-Methoxyphenyl)-3-methylsulfanylmethylpyrrolidin-2-one 30.** Bp 210 °C/2 Torr (Found: C, 62.35; H, 6.95; N, 5.5. $C_{13}H_{17}NO_2S$ requires C, 62.1; H, 6.8; N, 5.55%); $\nu_{max}$ (film)/cm$^{-1}$ 1685, 1590, 1500 and 750; $\delta_H$ 2.01–2.17 (1 H, m), 2.16 (3 H, s), 2.33–2.43 (1 H, m), 2.65–2.74 (1 H, m), 2.80–2.91 (1 H, m), 3.09 (1 H, dd, *J* 3.6, 12.9), 3.69–3.79 (2 H, m), 3.81 (3 H, s), 6.93–7.00 (2 H, m) and 7.21–7.36 (2 H, m); $\delta_C$ 15.8 (q), 24.9 (t), 35.6 (t), 41.9 (d), 47.8 (t), 55.4 (q), 111.8 (d), 120.6 (d), 127.0 (s), 128.3 (d), 128.5 (d), 154.6 (s) and 174.8 (s).

**X-Ray analysis of compound 28g**

A colourless rod-shaped crystal of dimensions 0.3 × 0.20 × 0.15 mm was used for X-ray crystallography. Formula $C_{11}H_{13}NO_2S$, mol. wt. 223.30; monoclinic space group $P2_1/N$; cell parameters: $a$ = 6.355(2), $b$ = 17.572(2), $c$ = 10.026(2) Å, $\beta$ = 105.33(1)°, $V$ = 1079.8 Å$^3$, $Z$ = 4, $D_c$ = 1.37 g cm$^{-3}$. Intensitites were measured at 23 °C with an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo-K$\alpha$, $\lambda$ = 0.709 30 Å). Of the 1439 reflections with $2\theta_{max}$ = 50.0°, 1176 with $I > 3.0\sigma(I)$ were used in the refinement. The structure was solved by direct method [5] and refined by full-matrix least-square analysis. The refinement coverged at $R$ = 0.043, $R_w$ = 0.043. Full crystallographic details for the structure determination have been deposited with the Cambridge Crystallographic Data Centre.†

† See Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1.

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