

## Thietane-fused $\beta$ -Lactams *via* Photochemical Cycloaddition Reaction of $N$ -( $\alpha$ , $\beta$ -Unsaturated Carbonyl)thioamides

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Photolysis of  $N$ -( $\alpha$ ,  $\beta$ -unsaturated carbonyl)thioamides gave thietane-fused  $\beta$ -lactams in good yields, whereas some of the thioimides formed thiones *via*  $\beta$ -hydrogen abstraction of the thiocarbonyl group. Substituents at the  $\alpha$ -position to the carbonyl carbon lead to a preference for [2 + 2]-cyclisation over  $\beta$ -hydrogen abstraction. From a sensitisation experiment this reaction was shown to proceed *via* an  $n\pi^*$  triplet excited state.

Recently the photochemistry of nitrogen-containing thiocarbonyl compounds has attracted much attention, since it provides an important route to various heterocycles. The Paterno-Büchi reaction of thioamides<sup>1</sup> and cyclic thioimides<sup>2</sup> are examples of this. In this connection, new methods for constructing the four-membered lactam ring continue to be of interest as a route to the analogues of naturally occurring antibiotics: a number of preparative methods for the  $\beta$ -lactams including photochemical routes have been reported.<sup>3</sup> In relation to our previous studies of the photochemistry of acyclic and semicyclic thioimide systems,<sup>4</sup> we now report a synthesis of thietane-fused  $\beta$ -lactams *via* photochemical reaction of ( $\alpha$ ,  $\beta$ -unsaturated carbonyl)thioamides<sup>5</sup>.

### Results and Discussion

$N$ -( $\alpha$ ,  $\beta$ -Unsaturated carbonyl)thiobenzamides **1** were prepared easily and almost quantitatively by the reaction of the corresponding thioamides with  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid chlorides in the presence of base. The UV spectrum of  $N$ -benzyl- $N$ -methacryloylthiobenzamide **1d** exhibited maxima at 298 nm ( $\epsilon$  9100), 322 nm ( $\epsilon$  9900) and 462 nm ( $\epsilon$  190) derived from the  $n\pi^*$  band of the thiocarbonyl moiety. When monothioimides **1a–e** were irradiated with a 1000-W high-pressure mercury lamp under argon, the corresponding 4-methyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-ones **2a–e** were obtained in high yields (see Table 1). The structures of the thietane-fused  $\beta$ -lactams were determined on the basis of elemental analyses and spectral data. The fact that the photoproducts were structural isomers of the starting material **1** was supported by a molecular weight determination and the mass spectra. The <sup>1</sup>H NMR spectra showed a new ABq peak arising from 5-CH<sub>2</sub> and the absence of an olefinic proton. The <sup>13</sup>C NMR spectra exhibited two new singlets (1-C and 4-C) and a new triplet (5-C); the absence of the thiocarbonyl carbon was also suggested.

Photolysis of (*E*)-2-methylbut-2-enylamide derivatives **1f–h** gave similar results and the  $\beta$ -lactams **2f–h** were obtained. For the thioimide **1g** ( $R^3 = \text{Pr}^i$ ), (2-methylbut-2-enylamino)thioisobutyrophenone **3g** was obtained as the main photoproduct accompanied by the  $\beta$ -lactam **2g**.

In the photoreaction of the thioimides **1i–o** under the same conditions, tricyclic  $\beta$ -lactams were obtained. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra indicate that these tricyclic  $\beta$ -lactams were obtained as single stereoisomers.

In the photoreaction of the thioimides **1p–v** which had no substituents at the  $\alpha$ -position to the carbonyl groups, the yields of the  $\beta$ -lactams were lower except that of **1t**. The thione **3s** formed in the photolysis of thioamides **1s**, was isolated as *trans*

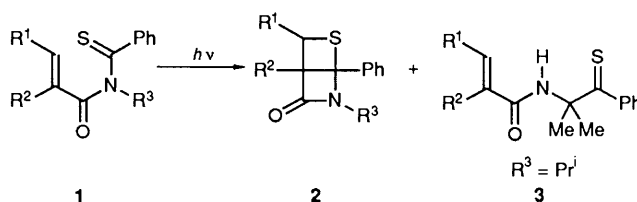
Table 1 Photolysis of monothioimides **1**

<b>1</b>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield of <b>2</b> (%) <sup>a</sup>
<b>a</b>	H	Me	Me	55 <sup>c</sup>
<b>b</b>	H	Me	Et	96 <sup>c</sup>
<b>c</b>	H	Me	Pr <sup>i</sup>	73
<b>d</b>	H	Me	CH <sub>2</sub> Ph	95
<b>e</b>	H	Me	Ph	77
<b>f</b>	Me	Me	Me	62 <sup>d</sup>
<b>g</b>	Me	Me	Pr <sup>i</sup>	80 <sup>d</sup> (17) <sup>b</sup>
<b>h</b>	Me	Me	Ph	80 <sup>d</sup>
<b>i</b>	-(CH <sub>2</sub> ) <sub>3</sub> -		Pr <sup>i</sup>	96
<b>j</b>	-(CH <sub>2</sub> ) <sub>3</sub> -		CH <sub>2</sub> Ph	83
<b>k</b>	-(CH <sub>2</sub> ) <sub>3</sub> -		Ph	96
<b>l</b>	-(CH <sub>2</sub> ) <sub>4</sub> -		Me	67
<b>m</b>	-(CH <sub>2</sub> ) <sub>4</sub> -		Pr <sup>i</sup>	99
<b>n</b>	-(CH <sub>2</sub> ) <sub>4</sub> -		CH <sub>2</sub> Ph	87
<b>o</b>	-(CH <sub>2</sub> ) <sub>4</sub> -		Ph	91
<b>p</b>	H	H	Pr <sup>i</sup>	9(38) <sup>b</sup>
<b>q</b>	H	H	CH <sub>2</sub> Ph	13 <sup>c</sup>
<b>r</b>	H	H	Ph	47
<b>s</b>	Me	H	Pr <sup>i</sup>	13 <sup>d</sup> (75) <sup>b</sup>
<b>t</b>	Me	H	Ph	73 <sup>d</sup>
<b>u</b>	Ph	H	Pr <sup>i</sup>	0(71) <sup>b</sup>
<b>v</b>	Ph	H	Ph	0 <sup>e</sup>

<sup>a</sup> Isolated yield. <sup>b</sup> Yield of the thioketones **3**. <sup>c</sup> Yield determined on the basis of the amount of thioamides. <sup>d</sup> Mixture of stereoisomers. <sup>e</sup> Recovered.

and *cis* isomers in 52 and 23% yield, respectively. Photolysis of the imide **1t** gave only the *trans*-thione **3t** in 71% yield. The imide **1g**, gave only a low yield of the  $\beta$ -lactam **2g**,  $\beta$ -hydrogen abstraction leading to a thione which was too unstable to be isolated; it is known that thiones having an  $\alpha$ -hydrogen atom are usually unstable. The  $\beta$ -lactams **2f–i** and **2s** were isolated as mixtures of stereoisomers but their separation by column chromatography or distillation was unsuccessful.

The mechanism for the formation of  $\beta$ -lactams is explicable in terms of the intermediacy diradical **4** as shown in Scheme 1.



Scheme 1

Thiones are formed by ring-opening reaction of the aziridine **6** which is produced by cyclisation of 1,3-diradical intermediate **5**. We have already reported the abstraction of the  $\beta$ -hydrogen to the thiocarbonyl group of acyclic monothioimide. This mechanism is supported by a trapping experiment. Thus, low temperature photolysis followed by addition of acetyl chloride and triethylamine gave acetylthioaziridine.<sup>4b</sup>

The conformation of ketones has been shown to be important in their photoreactions and conformational factors are expected to be even more important in the photochemistry of thioimides. Four possible conformations of acyclic monothioimides are shown in Fig. 1. Steric demands of substituents and dipole-

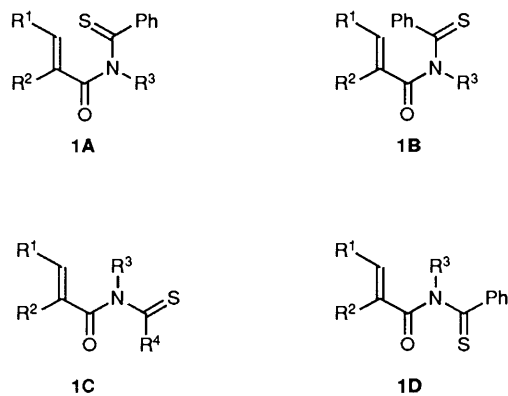


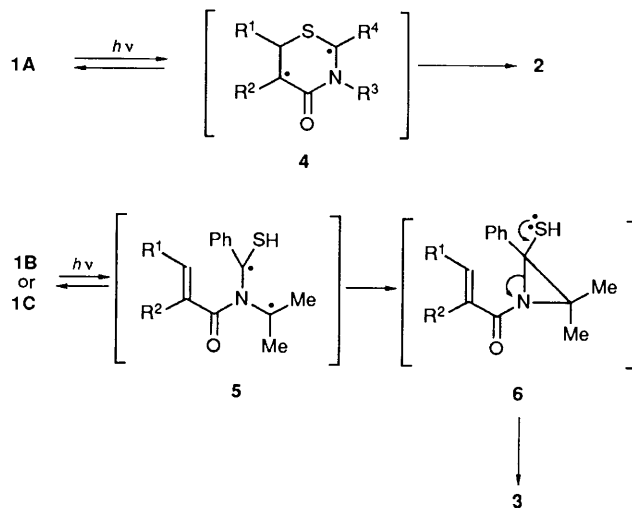
Fig. 1

dipole interactions define the conformer distribution and it is concluded that  $\beta$ -lactams are formed from conformer **A** and conformers **B** and **C** give thiones. It seems that this distribution is one of the important factors which determine the product ratio.

Substituents ( $R^2$ ) at the  $\alpha$ -position to the carbonyl carbon also influence the product ratio. Such a substituent makes a [2 + 2]cyclisation reaction more favourable since the intermediate 1,4-diradicals **4** are stabilised by it. For the photoreaction of the imide **1s**, two stereoisomeric thiones were isolated. Irradiation of the thiones **3s-trans** and **3s-cis** irradiated independently under identical conditions, showed that they were inert toward photolysis; furthermore, *cis-trans* isomerisation was absent. It is concluded that *cis-trans* isomerisation of the thioimide **1** leads to the formation of stereomixtures of thiones **3g** and **3s** and  $\beta$ -lactams **2f-h**, **2s** and **2t**. However, indirect isomerisation involving a back reaction from the 1,4-diradical intermediate **4** cannot be excluded. Three types of reactions, *cis-trans* isomerisation, intramolecular [2 + 2]cyclisation and  $\beta$ -hydrogen abstraction, occurs competitively in this photoreaction.

The quantum yield of the imide **1d** for the formation of  $\beta$ -lactams **2d** was 0.18. The photoreaction also proceeded when the imide **1d** was selectively irradiated in the  $n\pi^*$  region of the thiocarbonyl group (436 nm). The photocyclisation was sensitised by Michler's ketone ( $E_T = 62 \text{ kcal mol}^{-1}$ )<sup>6</sup> and thioxanthone ( $E_T = 65.5 \text{ kcal mol}^{-1}$ )<sup>6</sup>. Although this reaction was not quenched by ferrocene ( $E_T = 35 \text{ kcal mol}^{-1}$ )<sup>1c</sup> and *trans*-stilbene ( $E_T = 50 \text{ kcal mol}^{-1}$ )<sup>6</sup>, the sensitisation experiment suggests that the cyclisation proceeds from the  $n\pi^*$  triplet excited state of the thiocarbonyl group.

In conclusion, photochemical reactions of *N*-( $\alpha$ ,  $\beta$ -unsaturated carbonyl)thioamides **1** gave thietane-fused  $\beta$ -lactams **2** in good yields. The substituent at the  $\alpha$ -position to the carbonyl group was preferred in this photoreaction since the diradical intermediate **4** is stabilised by the substituent. When the thioimides possessing no substituents at the  $\alpha$ -position to the carbonyl group were irradiated,  $\beta$ -hydrogen abstraction by the thiocarbonyl function proceeded to give thiones as the major product. Intramolecular [2 + 2]photocyclisation to produce  $\beta$ -



Scheme 2

lactams proceeds from a  $n\pi^*$  triplet excited state as shown by the sensitisation experiment. This is interesting in that intermolecular photocycloaddition of *O*-vinylthioanilide proceeds with a singlet excited state.<sup>1c</sup> Furthermore, the  $\beta$ -lactams obtained by the photoreaction of *N*-( $\alpha$ ,  $\beta$ -unsaturated)thioamides have the interesting structural feature of a sulphur atom adjacent to the  $\beta$ -lactam ring. Since thietanes are known as reactive and useful intermediates in synthesis, it was expected the thietane-fused  $\beta$ -lactams would be versatile intermediates in a variety of reactions. Since the starting materials are easily obtained by acylation of thioamides, this reaction provides a useful synthesis of  $\beta$ -lactams.<sup>7</sup>

## Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus, and were uncorrected. IR spectra were measured on a Jasco IRA-1 spectrophotometer. <sup>1</sup>H- and <sup>13</sup>C NMR spectra were recorded on Hitachi R-600, JEOL-100 and Jasco GSX500 spectrometers using tetramethylsilane as an internal standard. The chemical shifts are recorded as  $\delta$  values with coupling constants in Hz; CDCl<sub>3</sub> was used as a solvent unless otherwise stated. UV spectra were measured on a Shimadzu UV-365 UV-VIS-NIR recording spectrophotometer. Eikohsya 1000-W and 500-W high-pressure mercury lamps were used as irradiation source. A Corona Model-117 molecular weight apparatus was used for molecular weight determination. Silica gel (Merk, Kieselgel 60, 230-400 mesh) was used for flash column chromatography.

*Preparation of Monothioimides.*—All monothioimides were prepared by the reaction of *N*-substituted thioamides with acid chlorides. The preparation of *N*-methacryloylthiobenzanilide **1e** is given as a sample. Triethylamine (300 mg, 3.0 mmol) was added dropwise to a solution of thiobenzanilide (600 mg, 2.8 mmol) and methacryloyl chloride (300 mg, 3.0 mmol) in dry benzene (30 ml) at room temperature under nitrogen and the reaction mixture was then stirred for 2 h. The precipitated triethylamine hydrochloride was removed by filtration through Celite, the benzene was evaporated off, and the residual mixture was subjected to chromatography on silica gel (eluent: benzene-hexane). *N*-Methacryloylthiobenzanilide (750 mg, 95%) was isolated as a red liquid. This monothioimide **1e** was unstable and used as soon as possible without further purifications. Most of monothioimides **1c**, **1e-p** and **1r-v** were synthesised in the same manner. The monothioimides **1a**, **1b**, **1d** and **1q** were however unstable and they could not be isolated even by flash

chromatography. Thus the reaction mixture was evaporated, hexane was added, and the precipitate was filtered off. The crude product was used for the photochemical step and the yields of  $\beta$ -lactams were determined on the basis of the amount of corresponding amides. Some monothioimides **1g**, **1h**, **1t** and **1v** were obtained as stable crystalline solids.

*N*-Methacryloyl-*N*-methylthiobenzamide **1a**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1625 and 1685;  $\delta(\text{CDCl}_3)$  1.48 (d, *J* 1, 1 H, C=CMe), 3.65 (s, 3 H, *N*-Me), 5.10 (m, 1 H, C=CH), 5.28 (m, 1 H, C=CH) and 6.9–7.4 (m, 5 H, ArH).

*N*-Methacryloyl-*N*-ethylthiobenzamide **1b**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1625 and 1680;  $\delta(\text{CDCl}_3)$  1.32 (d, *J* 7, 3 H, Et), 1.45 (d, *J* 1, 3 H, C=CMe), 4.30 (q, *J* 7, 2 H, Et), 5.03 (m, 1 H, C=CH), 5.27 (m, 1 H, C=CH) and 7.0–7.4 (m, 5 H, ArH).

*N*-Isopropyl-*N*-methacryloylthiobenzamide **1c**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1625 and 1680;  $\delta(\text{CDCl}_3)$  1.41 (d, *J* 1, 3 H, C=CMe), 1.47 (d, *J* 7, 6 H, CMe<sub>2</sub>), 5.39 (m, 1 H, C=CH), 5.45 (sep, *J* 7, 1 H, NCH), 5.53 (m, 1 H, C=CH) and 7.2–7.5 (m, 5 H, ArH).

*N*-Benzyl-*N*-methacryloylthiobenzamide **1d**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1625 and 1680;  $\delta(\text{CDCl}_3)$  1.38 (d, *J* 1, 3 H, C=CMe), 5.23 (m, 1 H, C=CH), 5.40 (s, 2 H, *N*-CH<sub>2</sub>), 5.48 (m, 1 H, C=CH) and 7.1–7.5 (m, 10 H, ArH).

*N*-Methacryloylthiobenzanilide **1e**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1625 and 1685;  $\delta(\text{CDCl}_3)$  1.79 (d, *J* 1, 3 H, C=CMe), 5.38 (m, 1 H, C=CH), 5.85 (m, 1 H, C=CH) and 6.9–7.6 (m, 10 H, ArH).

*N*-Methyl-*N*-[(*E*)-2-methylbut-2-enoyl]thiobenzamide **1f**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1635 and 1675;  $\delta(\text{CDCl}_3)$  1.3–1.45 (m, 3 H, C=CMe), 1.50 (dq, *J* 7 and 1, 3 H, C=CHMe), 3.73 (s, 3 H, *N*-Me), 6.03 (qq, *J* 7 and 1, 1 H, C=CH) and 7.2–7.4 (m, 5 H, ArH).

*N*-Isopropyl-*N*-[(*E*)-2-methylbut-2-enoyl]thiobenzamide **1g**. M.p. 64.5–66 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1635 and 1675;  $\delta(\text{CDCl}_3)$  1.2–1.35 (m, 3 H, C=CMe), 1.48 (d, *J* 7, 6 H, CMe<sub>2</sub>), 1.55 (dq, *J* 7 and 1, 3 H, C=CHMe), 5.68 (sep, *J* 7, 1 H, *N*-CH), 6.23 (qq, *J* 7 and 1, 1 H, C=CH) and 7.2–7.4 (m, 5 H, ArH) (Found: C, 68.95; H, 7.35; N, 5.3. C<sub>13</sub>H<sub>15</sub>NOS requires C, 68.92; H, 7.32; N, 5.35%).

*N*-[(*E*)-2-Methylbut-2-enoyl]thiobenzanilide **1h**. M.p. 96–98 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1635 and 1680;  $\delta(\text{CDCl}_3)$  1.6–1.7 (br s, 3 H, C=CMe), 1.68 (br d, *J* 7, 3 H, C=CHMe), 6.68 (br q, *J* 7, 1 H, C=CH) and 7.1–7.8 (m, 10 H, ArH) (Found: C, 73.25; H, 5.8; N, 4.7. C<sub>18</sub>H<sub>17</sub>NOS requires C, 73.18; H, 5.80; N, 4.74%).

*N*-(Cyclopent-1-enoyl)-*N*-isopropylthiobenzamide **1i**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1610 and 1680;  $\delta(\text{CDCl}_3)$  1.2–1.7 (m, 2 H, CH<sub>2</sub>), 1.43 (d, *J* 6, 6 H, CMe<sub>2</sub>), 1.8–2.4 (m, 4 H, CH<sub>2</sub> × 2), 5.58 (sep, *J* 6, 1 H, *N*-CH), 6.17 (br, 1 H, C=CH) and 7.1–7.3 (m, 5 H, ArH).

*N*-Benzyl-*N*-(cyclopent-1-enoyl)thiobenzamide **1j**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1675;  $\delta(\text{CDCl}_3)$  1.3–1.7 (m, 2 H, CH<sub>2</sub>), 1.9–2.3 (m, 4 H, CH<sub>2</sub> × 2), 5.45 (s, 2 H, *N*-CH<sub>2</sub>), 6.05 (br, 1 H, C=CH) and 7.1–7.4 (m, 10 H, ArH).

*N*-(Cyclopent-1-enoyl)thiobenzanilide **1k**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1675;  $\delta(\text{CDCl}_3)$  1.2–2.4 (m, 6 H, CH<sub>2</sub> × 2), 6.15 (br, 1 H, C=CH) and 7.0–7.5 (m, 10 H, ArH).

*N*-(Cyclohex-1-enoyl)-*N*-methylthiobenzamide **1l**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1675;  $\delta(\text{CDCl}_3)$  1.1–1.4 (m, 4 H, CH<sub>2</sub> × 2), 1.6–2.1 (m, 4 H, CH<sub>2</sub> × 2), 3.70 (s, 3 H, *N*-Me), 6.12 (br, 1 H, C=CH) and 7.1–7.3 (m, 5 H, ArH).

*N*-(Cyclohex-1-enoyl)-*N*-isopropylthiobenzamide **1m**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1680;  $\delta(\text{CDCl}_3)$  0.7–2.1 (m, 8 H, CH<sub>2</sub> × 4), 1.47 (d, *J* 7, 6 H, CMe<sub>2</sub>), 5.65 (sep, *J* 7, 1 H, *N*-CH), 6.3 (br, 1 H, C=CH) and 7.2–7.4 (m, 5 H, ArH).

*N*-Benzyl-*N*-(cyclohex-1-enoyl)thiobenzamide **1n**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1675;  $\delta(\text{CDCl}_3)$  1.0–1.3 (m, 4 H, CH<sub>2</sub> × 2), 1.6–2.0 (m, 4 H, CH<sub>2</sub> × 2), 5.38 (s, 2 H, *N*-CH<sub>2</sub>), 5.93 (br, 1 H, C=CH) and 7.0–7.4 (m, 10 H, ArH).

*N*-(Cyclohex-1-enoyl)thiobenzanilide **1o**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1675;  $\delta(\text{CDCl}_3)$  0.8–2.0 (m, 8 H, CH<sub>2</sub> × 2), 6.2 (br, 1 H, C=CH) and 7.0–7.5 (m, 10 H, ArH).

*N*-Acryloyl-*N*-isopropylthiobenzamide **1p**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1610 and 1685;  $\delta(\text{CDCl}_3)$  1.51 (d, *J* 7, 6 H, CH<sub>2</sub> × 3), 5.1–5.7 (m, 2 H, *N*-CH + CH=C), 5.8–6.1 (m, 2 H, C=CH<sub>2</sub>) and 7.0–7.6 (m, 5 H, ArH).

*N*-Acryloyl-*N*-benzylthiobenzamide **1q**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1615 and 1680;  $\delta(\text{CDCl}_3)$  5.0–5.2 (m, 1 H, CH=C), 5.40 (s, 2 H, *N*-CH<sub>2</sub>), 5.7–6.1 (m, 2 H, C=CH<sub>2</sub>) and 6.9–7.5 (m, 10 H, ArH).

*N*-Acryloylthiobenzanilide **1r**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1615 and 1690;  $\delta(\text{CDCl}_3)$  5.3–5.5 (m, 1 H, CH=C), 6.0–6.3 (m, 2 H, C=CH<sub>2</sub>) and 6.8–7.7 (m, 10 H, ArH).

*N*-Crotonoyl-*N*-isopropylthiobenzamide **1s**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1630 and 1685;  $\delta(\text{CDCl}_3)$  1.43 (d, *J* 7, 6 H, CMe<sub>2</sub>), 1.50 (dd, *J* 6 and 2, 3 H, C=CMe), 5.47 (m, 2 H, NCH + CH=C), 6.45 (dq, *J* 15 and 6, 1 H, C=CHMe) and 7.1–7.6 (m, 5 H, ArH).

*N*-Crotonoylthiobenzanilide **1t**. M.p. 116–117 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1635 and 1680;  $\delta(\text{CDCl}_3)$  1.50 (dd, *J* 6 and 2, 3 H, C=CMe), 5.4 (m, 1 H, CH=C), 6.00 (dq, *J* 15 and 6, 1 H, C=CHMe) and 7.1–7.6 (m, 10 H, ArH) (Found: C, 72.55; H, 5.4; N, 4.95. C<sub>17</sub>H<sub>15</sub>NOS requires C, 72.55; H, 5.37; N, 4.97%).

*N*-Cinnamoyl-*N*-isopropylthiobenzamide **1u**.  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1610 and 1690 cm<sup>-1</sup>;  $\delta(\text{CDCl}_3)$  1.48 (d, *J* 7, 6 H, CMe<sub>2</sub>), 5.55 (sep, *J* 7, 1 H, NCH), 6.50 (d, *J* 15, 1 H, CH=CPh) and 7.0–7.6 (m, 11 H, C=CHPh + ArH).

*N*-Cinnamoyl-*N*-phenylthiobenzamide **1v**. M.p. 106–108 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1605 and 1700;  $\delta(\text{CDCl}_3)$  6.57 (d, *J* 15, 1 H, CH=CPh) and 7.0–8.0 (m, 16 H, C=CHPh + ArH) (Found: C, 76.85; H, 4.95; N, 4.0. C<sub>22</sub>H<sub>17</sub>NOS requires C, 76.93; H, 4.98; N, 4.07%).

*General Procedure for the Photochemical Reaction of N*-( $\alpha,\beta$ -Unsaturated carbonyl)thioamides **1a–v**.—A benzene solution of the monothioimide was irradiated with a 1000-W high pressure mercury lamp under argon at room temperature until the starting material had disappeared. After evaporation of the solvent, the residual mixture was subjected to chromatography on silica gel, using benzene–ethyl acetate as eluent. The crystalline products were recrystallized from chloroform–hexane.

*2,4*-Dimethyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one **2a**. M.p. 103–104.5 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1745;  $\delta(\text{CDCl}_3)$  1.02 (s, 3H, 4-Me), 2.83 (s, 3 H, *N*-Me), 3.07 and 3.27 (ABq, *J* 10, 2 H, 5-CH<sub>2</sub>) and 7.1–7.5 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.7 (q, 4-Me), 25.5 (q, *N*-Me), 29.2 (t, 5-C), 68.6 (s, 4-C), 76.5 (s, 1-C), 128.3 (d, Ar), 128.8 (d, Ar), 128.8 (d, Ar), 134.2 (s, Ar) and 171.5 (s, C=O) (Found: C, 65.45; H, 5.95; N, 6.35. C<sub>12</sub>H<sub>13</sub>NOS requires C, 65.72; H, 5.97; N, 6.38%).

*2*-Ethyl-4-methyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one **2b**. B.p. 65–70 °C/10<sup>-3</sup> mmHg;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1745;  $\delta(\text{CDCl}_3)$  1.02 (s, 3 H, 4-Me), 1.24 (t, *J* 7, 3 H, *N*-Et), 3.03 and 3.30 (ABq, *J* 10, 2 H, 5-CH<sub>2</sub>) and 3.33 (q, *J* 7, 2 H, *N*Et) and 7.1–7.6 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  12.9 (q, Et), 14.7 (q, 4-Me), 28.9 (t, 5-C), 36.3 (t, Et), 68.0 (s, 4-C), 75.8 (s, 1-C), 128.5 (d, Ar), 128.6 (d, Ar), 128.8 (d, Ar), 134.7 (s, Ar) and 171.5 (s, C=O) (Found: C, 67.2; H, 6.5; N, 5.95. C<sub>13</sub>H<sub>15</sub>NOS requires C, 66.91; H, 6.48; N, 6.00%).

*2*-Isopropyl-4-methyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one **2c**. M.p. 82–83 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1740;  $\delta(\text{CDCl}_3)$  1.00 (s, 3 H, 4-Me) 1.33 (d, *J* 7, 3 H, CHMe), 1.35 (d, *J* 7, 3H, CHMe), 2.94 and 3.34 (ABq, *J* 10, 2 H, 5-CH<sub>2</sub>), 3.60 (sep, *J* 7, 1 H, NCH) and 7.0–7.4 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.8 (q, 4-Me), 20.6 (q, Pr<sup>i</sup>), 21.1 (q, Pr<sup>i</sup>), 28.7 (t, 5-C), 47.0 (d, Pr<sup>i</sup>), 67.0 (s, 4-C), 75.4 (s, 1-C), 128.5 (d, Ar), 128.6 (d, Ar), 128.6 (d, Ar), 135.5 (s, Ar) and 171.3 (s, C=O) (Found: C, 67.85; H, 7.0; N, 5.6. C<sub>14</sub>H<sub>17</sub>NOS requires C, 67.98; H, 6.92; N, 5.66%).

*2*-Benzyl-4-methyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one **2d**. M.p. 81–82 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1750;  $\delta(\text{CDCl}_3)$  1.02 (s, 3 H, 4-Me), 3.00 and 3.30 (ABq, *J* 10, 2 H, 5-CH<sub>2</sub>), 4.37 (s,

2 H, NCH<sub>2</sub>) and 7.0–7.4 (m, 10 H, Ar);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.9 (q, 4-Me), 29.2 (t, 5-C), 45.5 (t, N-CH<sub>2</sub>), 68.3 (s, 4-C), 76.5 (s, 1-C), 127.7 (d, Ar), 128.4 (d, Ar), 128.5 (d, Ar), 128.6 (d, Ar), 128.7 (d, Ar), 129.3 (d, Ar), 134.2 (s, Ar), 135.0 (s, Ar) and 171.5 (s, C=O) (Found: C, 72.95; H, 5.8; N, 4.7. C<sub>18</sub>H<sub>17</sub>NOS requires C, 73.19; H, 5.80; N, 4.74%).

**4-Methyl-1,2-diphenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2e.** M.p. 103–104 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1750;  $\delta(\text{CDCl}_3)$  1.08 (s, 3 H, 4-Me), 3.16 and 3.47 (ABq, *J* 10 Hz, 2 H, 5-CH<sub>2</sub>) and 6.8–7.5 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.9 (q, 4-Me), 30.3 (t, 5-C), 67.3 (s, 4-C), 73.7 (s, 1-C), 118.0 (d, Ar), 124.6 (d, Ar), 128.4 (d, Ar), 128.8 (d, Ar), 128.9 (d, Ar), 129.2 (d, Ar), 134.0 (s, Ar), 136.0 (s, Ar) and 168.3 (s, C=O) (Found: C, 72.6; H, 5.5; N, 4.9. C<sub>17</sub>H<sub>15</sub>NOS requires C, 72.56; H, 5.37; N, 4.97%).

**2,4,5-Trimethyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2f.** This  $\beta$ -lactam was obtained as a mixture of two stereoisomers (the ratio of them determined by NMR spectra was 60:40). B.p. 70–75 °C/10<sup>-3</sup> mmHg;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1750; (major isomer):  $\delta(\text{CDCl}_3)$  1.02 (s, 3 H, 4-Me), 1.51 (d, *J* 7, 3 H, 5-Me), 2.85 (s, 3 H, N-Me), 3.74 (q, *J* 7, 1 H, 5-CH) and 7.2–7.6 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  9.5 (q, Me), 20.1 (q, Me), 25.7 (q, NMe), 37.3 (d, 5-C), 72.8 (s, 1 or 4-CH<sub>2</sub>), 74.9 (s, 1- or 4-CH<sub>2</sub>), 128.2 (d, Ph), 128.3 (d, Ph), 128.6 (d, Ph), 134.0 (s, Ph) and 172.7 (s, C=O); minor isomer:  $\delta(\text{CDCl}_3)$  0.97 (s, 3 H, 4-Me), 1.48 (d, *J* 7, 3 H, 5-Me), 2.83 (s, 3 H, N-Me), 3.81 (q, *J* 7, 1 H, 5-CH) and 7.2–7.4 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.2 (q, Me), 20.3 (q, Me), 25.0 (q, N-Me), 40.9 (d, 5-C), 71.2 (s, 1- or 4-C), 71.9 (s, 1- or 4-C), 134.5 (s, Ph) and 169.7 (s, C=O) (Found: C, 67.2; H, 6.5; N, 6.0. C<sub>13</sub>H<sub>15</sub>NOS requires C, 66.91; H, 6.48; N, 6.00%).

**2-Isopropyl-4,5-dimethyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2g.** This  $\beta$ -lactam was obtained as a mixture of two stereoisomers (the ratio of them determined from NMR spectra was 60:40). M.p. 88–93 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1750; major isomer:  $\delta(\text{CDCl}_3)$  1.03 (s, 3 H, 4-Me), 1.39 (d, *J* 7, 6 H, CMe<sub>2</sub>), 1.59 (d, *J* 7, 3 H, 5-Me), 3.64 (q, *J* 7, 1 H, 5-CH), 3.72 (sep, *J* 7, 1 H, NCH) and 7.3–7.6 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  14.4 (q, Me), 20.5 (q, Me), 20.9 (q, Me), 21.3 (q, Me), 40.4 (d, 5-C), 46.9 (d, N-C), 70.2 (s, 1 or 4-C), 71.6 (s, 1 or 4-C), 128.4 (d, Ph), 128.5 (d, Ph), 128.6 (d, Ph), 135.3 (s, Ph) and 169.6 (s, C=O); minor isomer:  $\delta(\text{CDCl}_3)$  0.98 (s, 3 H, 4-Me), 1.36 (d, *J* 7, 6 H, CMe<sub>2</sub>), 1.48 (d, *J* 7, 3 H, 5-Me), 3.69 (q, *J* 7, 1 H, 5-CH), 3.90 (sep, *J* 7, 1 H, NCH) and 7.3–7.4 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  9.5 (q, Me), 19.9 (q, Me), 20.53 (q, Me), 21.0 (q, Me), 36.8 (d, 5-C), 47.0 (d, NC), 69.6 (s, 1 or 4-C), 73.8 (s, 1 or 4-C), 128.3 (s, Ph), 128.5 (d, Ph), 135.8 (s, Ph) and 172.6 (s, C=O) (Found: C, 69.0; H, 7.35; N, 5.35. C<sub>15</sub>H<sub>19</sub>NOS requires C, 68.92; H, 7.32; N, 5.35%).

**(2-Methylbut-2-enylamino)thioisobutyrophenone 3g.** *Z* isomer: yield 12%; M.p. 162–163 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  3400, 3300 and 1660;  $\delta(\text{CDCl}_3)$  1.73 (d, *J* 7, 3 H, C=CHMe), 1.75 (s, 3 H, C=CMe), 1.85 (s, 6 H, CMe<sub>2</sub>), 5.57 (dq, *J* 7 and 1.3, 1 H, C=CH), 6.85 (br s, 1 H, NH), 7.2–7.5 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  15.0 (q, Me), 20.6 (q, Me), 20.6 (q, Me), 28.4 (q, Me), 68.2 (s, N-C), 126.0 (d), 127.4 (d), 127.7 (d), 129.1 (d), 133.0 (s, Ph), 148.6 (s, C=C), 168.6 (s, C=O) and 255.9 (s, C=S) (Found: C, 68.95; H, 7.35; N, 5.3. C<sub>15</sub>H<sub>19</sub>NOS requires C, 68.92; H, 7.32; N, 5.35%).

*E* isomer: yield 5%;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  3400, 3300 and 1660;  $\delta(\text{CDCl}_3)$  1.73 (dq, *J* 7 and 1.1, 3 H, C=CHMe), 1.79 (d, *J* 1.1, 3 H, C=CMe), 1.83 (s, 6 H, CMe<sub>2</sub>), 6.37 (qd, *J* 7 and 1.1, 1 H, C=CH), 7.19 (br s, 1 H, NH), 7.3–7.6 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  13.9 (q, Me), 20.9 (q, Me), 27.8 (q, Me), 68.1 (s, N-C), 125.8 (d), 127.4 (d), 128.3 (d), 129.0 (d), 132.5 (s, Ph), 148.5 (s, C=C), 168.1 (s, C=O) and 256.3 (s, C=S).

**4,5-Dimethyl-1,2-diphenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2h.** This  $\beta$ -lactam was obtained as a mixture of two stereoisomers (the ratio of them determined from the NMR spectra was 70:30). M.p. 103–108 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1755;

major isomer:  $\delta(\text{CDCl}_3)$  1.07 (s, 3 H, 4-Me), 1.53 (d, *J* 7, 3 H, 5-Me), 3.89 (q, *J* 7, 1 H, 5-CH) and 7.0–7.7 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  9.5 (q, Me), 14.4 (q, Me), 20.5 (q, Me), 42.3 (d, 5-C), 70.2 (s, 1 or 4-C), 70.8 (s, 1 or 4-C), 118.0 (d, Ph), 124.4 (d, Ph), 128.3 (d, Ph), 128.5 (d, Ph), 128.8 (d, Ph), 129.1 (d, Ph), 133.9 (s, Ph), 135.8 (s, Ph) and 166.7 (s, C=O); minor isomer:  $\delta(\text{CDCl}_3)$  1.02 (s, 3 H, 4-Me), 1.56 (d, *J* 7, 3 H, 5-Me), 3.93 (q, *J* 7, 1 H, 5-CH) and 7.0–7.4 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  9.6 (q, Me), 20.2 (q, Me), 38.4 (d, 5-C), 70.0 (s, 1 or 4-C), 72.2 (s, 1 or 4-C), 134.4 (s, Ph), 136.3 (s, Ph) and 169.3 (s, C=O) (Found: C, 73.3; H, 5.85; N, 4.7. C<sub>18</sub>H<sub>17</sub>NOS requires C, 73.19; H, 5.80; N, 4.74%).

**3-Isopropyl-4-phenyl-5-thia-3-azabicyclo[4.3.0.0<sup>1,4</sup>]nonan-2-one 2i.** M.p. 115–116 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1740; <sup>1</sup>H  $\delta(\text{CDCl}_3)$  1.3–2.3 (m, 6 H, 7, 8 and 9-CH<sub>2</sub>), 1.31 (d, *J* 7, 3 H, Me), 1.33 (d, *J* 7, 3 H, Me), 3.70 (sep, *J* 7, 1 H, NCH), 4.05 (br, 1 H, 6-CH), 7.1–7.5 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  20.4 (q, Pr<sup>i</sup>), 21.2 (q, Pr<sup>i</sup>), 24.6 (t, 7-, 8- or 9-C), 26.8 (t, 7-, 8- or 9-C), 33.9 (7-, 8- or 9-C), 43.0 (d, 6-C), 47.0 (d, Pr<sup>i</sup>), 71.8 (s, 1 or 4-C), 77.7 (1 or 4-C), 128.5 (d, Ar), 128.5 (d, Ar), 128.6 (d, Ar), 135.5 (s, Ar) and 167.0 (s, C=O) (Found: C, 70.35; H, 7.05; N, 5.0. C<sub>16</sub>H<sub>19</sub>NOS requires C, 70.29; H, 7.00; N, 5.12%).

**3-Benzyl-4-phenyl-5-thia-3-azabicyclo[4.3.0.0<sup>1,4</sup>]nonan-2-one 2j.** M.p. 99–100 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1740;  $\delta(\text{CDCl}_3)$  1.5–2.2 (m, 6 H, 7-, 8- and 9-CH<sub>2</sub>), 3.93 (t, *J* 7, 1 H, 6-CH), 4.30 (s, 2 H, NCH<sub>2</sub>) and 6.9–7.1 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  24.7 (t, CH<sub>2</sub>), 26.9 (t, CH<sub>2</sub>), 34.1 (t, CH<sub>2</sub>), 43.5 (d, 6-C), 45.5 (t, N-CH<sub>2</sub>), 73.0 (s, 1 or 4-C), 79.0 (s, 1 or 4-C), 127.6 (d, Ph), 128.4 (d, Ph), 128.5 (d, Ph), 128.7 (d, Ph), 129.3 (d, Ph), 134.2 (s, Ph), 134.9 (s, Ph) and 169.8 (s, C=O) (Found: C, 74.55; H, 6.0; N, 4.3. C<sub>20</sub>H<sub>19</sub>NOS requires C, 74.37; H, 5.95; N, 4.35%).

**3,4-Diphenyl-5-thia-3-azabicyclo[4.3.0.0<sup>1,4</sup>]nonan-2-one 2k.** M.p. 160–161 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1745;  $\delta(\text{CDCl}_3)$  1.3–2.3 (m, 6 H, 7-, 8- and 9-CH<sub>2</sub>), 4.1–4.3 (m, 1 H, 6-CH) and 7.0–7.7 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  25.0 (t, CH<sub>2</sub>), 26.9 (t, CH<sub>2</sub>), 34.3 (t, CH<sub>2</sub>), 45.2 (d, 6-C), 70.9 (s, 1- or 4-C), 78.1 (s, 1- or 4-C), 117.7 (d, Ph), 124.4 (d, Ph), 128.5 (d, Ph), 128.8 (d, Ph), 128.9 (d, Ph), 129.1 (d, Ph), 134.0 (s, Ph), 136.3 (s, Ph) and 167.0 (s, C=O) (Found: C, 74.25; H, 5.6; N, 4.5. C<sub>19</sub>H<sub>17</sub>NOS requires C, 74.23; H, 5.57; N, 4.55%).

**3-Methyl-4-phenyl-5-thia-3-azabicyclo[4.4.0.0<sup>1,4</sup>]decan-2-one 2l.** M.p. 92–93 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1740;  $\delta(\text{CDCl}_3)$  1.3–1.8 (m, 8 H, 7, 8, 9 and 10-CH<sub>2</sub>), 2.75 (s, 3 H, N-Me), 3.64 (t, *J* 7, 1 H, 6-CH) and 7.2–7.6 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  19.6 (t, CH<sub>2</sub>), 20.5 (t, CH<sub>2</sub>), 21.5 (t, CH<sub>2</sub>), 25.5 (q, N-Me), 33.5 (t, CH<sub>2</sub>), 38.2 (d, 6-C), 71.1 (s, 1 or 4-C), 77.2 (s, 1 or 4-C), 128.4 (d, Ph), 128.7 (d, Ph), 128.8 (d, Ph), 134.2 (s, Ph) and 172.8 (s, C=O) (Found: C, 69.7; H, 6.65; N, 5.4. C<sub>15</sub>H<sub>17</sub>NOS requires C, 69.46; H, 6.60; N, 5.40%).

**3-Isopropyl-4-phenyl-5-thia-3-azabicyclo[4.4.0.0<sup>1,4</sup>]decan-2-one 2m.** M.p. 94.5–95 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1735;  $\delta_{\text{C}}(\text{CDCl}_3)$  0.5–2.5 (m, 8 H, 7, 8, 9 and 10-CH<sub>2</sub>), 1.28 (d, *J* 7, 3 H, Me), 1.37 (d, *J* 7, 3 H, Me), 3.63 (sep, *J* 7, 1 H, NCH), 3.78 (t, *J* 6, 1 H, 6-CH) and 7.1–7.7 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  18.9 (t, CH<sub>2</sub>), 19.6 (t, CH<sub>2</sub>), 20.6 (q, Me), 20.9 (t, CH<sub>2</sub>), 21.2 (q, Me), 32.2 (t, CH<sub>2</sub>), 37.8 (d, 6-C), 46.9 (d, N-C), 69.6 (s, 1 or 4-C), 75.7 (s, 1 or 4-C), 128.5 (d, Ph), 128.5 (d, Ph), 135.8 (s, CH<sub>2</sub>) and 172.5 (s, C=O) (Found: C, 71.2; H, 7.45; N, 4.85. C<sub>17</sub>H<sub>21</sub>NOS requires C, 71.04; H, 7.36; N, 4.87%).

**3-Benzyl-4-phenyl-5-thia-3-azabicyclo[4.4.0.0<sup>1,4</sup>]decan-2-one 2n.** M.p. 89–90 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1745;  $\delta(\text{CDCl}_3)$  0.5–2.5 (m, 8 H, 7-, 8-, 9- and 10-CH<sub>2</sub>), 3.80 (t, *J* 7, 1 H, 6-CH), 4.40 (s, 2 H, NCH<sub>2</sub>) and 7.0–7.5 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  19.3 (t, CH<sub>2</sub>), 20.0 (t, CH<sub>2</sub>), 21.3 (t, CH<sub>2</sub>), 32.9 (t, CH<sub>2</sub>), 38.2 (d, 6-C), 45.6 (t, CH<sub>2</sub>), 70.8 (s, 1 or 4-C), 77.0 (s, 1 or 4-C), 127.5 (d, Ph), 128.4 (d, Ph), 128.7 (d, Ph), 129.3 (d, Ph), 134.4 (s, Ph), 135.0 (s, Ph) and 172.8 (s, C=O) (Found: C, 74.85; H, 6.3; N, 4.15. C<sub>21</sub>H<sub>21</sub>NOS requires C, 75.18; H, 6.31; N, 4.17%).

**3,4-Diphenyl-5-thia-3-azabicyclo[4.4.0.0<sup>1,4</sup>]decan-2-one 2o.**

M.p. 143–145 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1750;  $\delta(\text{CDCl}_3)$  0.5–2.5 (m, 8 H, 7, 8, 9 and 10-CH<sub>2</sub>), 3.85 (t, *J* 7, 1 H, 6-CH) and 6.9–7.6 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  19.2 (t, CH<sub>2</sub>), 20.0 (t, CH<sub>2</sub>), 21.3 (t, CH<sub>2</sub>), 32.9 (t, CH<sub>2</sub>), 39.2 (d, 6-C), 69.6 (s, 1 or 4-C), 74.3 (s, 1 or 4-C), 118.0 (d, Ph), 124.4 (d, Ph), 128.3 (d, Ph), 128.8 (d, Ph), 128.9 (d, Ph), 129.1 (d, Ph), 134.1 (s, Ph), 136.0 (s, Ph) and 169.6 (s, C=O) (Found: C, 74.7; H, 6.05; N, 4.35. C<sub>20</sub>H<sub>19</sub>NOS requires C, 74.37; H, 5.95; N, 4.35%).

**2-Isopropyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2p.** M.p. 88–93 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1750;  $\delta(\text{CDCl}_3)$  1.29 (d, *J* 7, 3 H, Me), 1.30 (d, *J* 7, 3 H, Me), 3.24 (dd, *J* 3 and 10, 1 H, 5-CH), 3.48 (dd, *J* 9 and 10, 1 H, 5-CH), 3.72 (sep, *J* 7, 1 H, NCH), 4.11 (dd, *J* 3 and 9, 1 H, 4-CH) and 7.0–7.6 (m, 5 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  20.8 (q, Me), 21.1 (q, Me), 21.3 (t, CH<sub>2</sub>), 46.7 (d, NC), 61.6 (d, 4-C), 70.5 (s, 1-C), 126.4 (d, Ph), 128.3 (s, Ph), 137.4 (s, Ph) and 167.5 (s, C=O) (Found: C, 67.05; H, 6.6; N, 5.8. C<sub>13</sub>H<sub>15</sub>NOS requires C, 66.98; H, 6.58; N, 5.85%).

**(Acryloylamino)thioisobutyrophenone 3p.** M.p. 103–104 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1670 and 3320;  $\delta(\text{CDCl}_3)$  1.82 (s, 6 H, Me × 2), 5.43 (t, *J* 6, 1 H, CH=C), 6.07 (d, *J* 6 2, H, C=CH<sub>2</sub>), 7.1–7.6 (m, 5 H, ArH) and 7.85 (br, 1 H, NH) (Found: C, 66.9; H, 6.5; N, 6.0. C<sub>13</sub>H<sub>15</sub>NOS requires C, 66.98; H, 6.58; N, 5.85%).

**2-Benzyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2q.** M.p. 98–102 °C/10<sup>-2</sup> mmHg;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1750;  $\delta(\text{CDCl}_3)$  3.18 (dd, *J* 3 and 10, 1 H, 5-CH), 3.46 (dd, *J* 9 and 10, 1 H, 5-CH), 4.13 (dd, *J* 3 and 9, 1 H, 4-CH), 4.16 (s, 2 H, NCH<sub>2</sub>), and 7.0–7.4 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  21.7 (t, 5-C), 45.3 (t, NC), 62.3 (d, 4-C), 71.7 (s, 1-C), 126.5 (d, Ph), 126.6 (d, Ph), 127.3 (d, Ph), 128.2 (d, Ph), 128.5 (d, Ph), 128.8 (d, Ph), 134.2 (s, Ph), 136.0 (s, Ph) and 167.8 (s, C=O) (Found: C, 72.75; H, 5.4; N, 4.95. C<sub>17</sub>H<sub>15</sub>NOS requires C, 72.56; H, 5.37; N, 4.97%).

**1,2-Diphenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2r.** M.p. 119–120 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1755;  $\delta(\text{CDCl}_3)$  3.28 (dd, *J* 3 and 10, 1 H, 5-CH), 3.62 (dd, *J* 9 and 10, 1 H, 5-CH), 4.17 (dd, *J* 3 and 9, 1 H, 4-CH) and 7.1–7.6 (m, 10 H, ArH) (Found: C, 71.9; H, 5.0; N, 5.25. C<sub>16</sub>H<sub>13</sub>NOS requires C, 71.88; H, 4.90; N, 5.23%).

**2-Isopropyl-5-methyl-1-phenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2s.** This compound was obtained as a mixture of two stereoisomers. They could not be separated by column chromatography or distillation; b.p. 75–80 °C/10<sup>-2</sup> mmHg;  $\nu_{\max}(\text{CDCl}_3)/\text{cm}^{-1}$  1740;  $\delta(\text{CDCl}_3)$  1.29 and 1.31 (each d, *J* 6.7, total 6 H, Me × 2), 1.59 (d, *J* 6.7, 3 H, 5-Me), 3.6–4.2 (m, 3 H, NCH + 4-CH and 5-CH) and 7.2–7.6 (m, 5 H, ArH); major isomer:  $\delta(\text{CDCl}_3)$  20.2 (q, Me), 21.1 (q, Me), 25.3 (q, Me), 34.1 (d, 5-C), 47.0 (d, N-C), 68.8 (d, 4-C), 71.1 (s, 1-C), 126.8 (d, Ph), 128.5 (d, Ph), 128.6 (d, Ph), 138.4 (s, Ph) and 167.9 (s, C=O); minor isomer:  $\delta(\text{CDCl}_3)$  20.6 (q, Me), 21.0 (q, Me), 21.2 (q, Me), 32.7 (d, 5-C), 46.9 (d, N-C), 65.8 (d, 4-C), 68.3 (s, 1-C), 137.8 (s, Ph) and 165.9 (s, C=O). (Found: C, 68.3; H, 7.0; N, 5.5. C<sub>14</sub>H<sub>17</sub>NOS requires C, 67.98; H, 6.92; N, 5.66%).

**(But-2-enoylamino)thioisobutyrophenone 3s.** *E* Isomer: m.p. 125–126 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  3430, 3320, 1665 and 1635;  $\delta(\text{CDCl}_3)$  1.50 (dd, *J* 6, 3 H, C=CMe), 1.80 (s, 6 H, Me × 2), 5.45 (m, 1 H, CH=C), 6.20 (dq, *J* 15 and 1, 1 H, CH=C) and 7.1–7.7 (m, 5 H, ArH) (Found: C, 67.95; H, 6.9; N, 5.65. C<sub>14</sub>H<sub>17</sub>NOS requires C, 67.98; H, 6.92; N, 5.66%); *Z* Isomer: m.p. 102–103 °C;  $\nu_{\max}(\text{CHCl}_3)$  3430, 3320, 1675 and 1640 cm<sup>-1</sup>;  $\delta(\text{CDCl}_3)$  1.72 (s, 6 H, Me × 2), 1.90 (br d, *J* 6, 3 H, C=CMe), 5.50 (br d, *J* 12, 1 H, CH=C), 5.81 (dq, *J* 12 and 6, 1 H, C=CH) and 7.1–7.4 (m, 5 H, ArH) (Found: C, 67.85; H, 6.9; N, 5.65. C<sub>14</sub>H<sub>17</sub>NOS requires C, 67.98; H, 6.92; N, 5.66%).

**5-Methyl-1,2-diphenyl-6-thia-2-azabicyclo[2.2.0]hexan-3-one 2t.** This compound was obtained as a mixture of two stereoisomers (70:30). They could not be separated by column chromatography or distillation; b.p. 95–100 °C/10<sup>-3</sup> mmHg;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1750; major isomer:  $\delta(\text{CDCl}_3)$  1.73 (d, *J* 6.7,

3 H, 5-Me), 3.8–4.0 (m, 2 H, 4-CH<sub>2</sub>) and 7.0–7.7 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  25.4 (q, Me), 35.4 (d, 5-C), 66.6 (d, 4-C), 69.3 (d, 1-C), 117.8 (d, Ph), 127.1 (d, Ph), 127.2 (d, Ph), 128.8 (d, Ph), 128.9 (d, Ph), 129.1 (d, Ph), 136.3 (s, Ph), 136.9 (s, Ph) and 164.9 (s, C=O); minor isomer:  $\delta(\text{CDCl}_3)$  1.60 (d, *J* 6.7 (3 H, 5-Me), 4.1–4.5 (m, 2 H, 4-CH and 5-CH) and 7.0–7.7 (m, 10 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$ : 21.1 (q, Me), 34.1 (d, 5-C), 65.8 (d, 4-C), 67.6 (s, 1-C), 135.9 (s, Ph), 136.4 (s, Ph) and 163.4 (s, C=O) (Found: C, 72.75; H, 5.45; N, 4.95. C<sub>17</sub>H<sub>15</sub>NOS requires C, 72.56; H, 5.37; N, 4.97%).

**(Cinnamoylamino)thioisobutyrophenone 3u.** *trans* Isomer: m.p. 102–103 °C;  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  3430, 3310, 1665 and 1625;  $\delta(\text{CDCl}_3)$  6.87 (d, *J* 15, 1 H, CH=CPh), 7.0–7.5 (m, 11 H, C=CHPh + ArH) and 7.8 (br, 1 H, NH) (Found: C, 73.9; H, 6.25; N, 4.55. C<sub>19</sub>H<sub>19</sub>NOS requires C, 73.75; H, 6.18; N, 4.52%).

**Sensitisation and Quenching of N-Benzylmethacryloylthio-benzamide 1d.**—Five Pyrex tubes were irradiated at 365 nm with a 500-W high pressure mercury lamp in a merry-go-round apparatus. Each includes starting material **1d** (0.02 mol dm<sup>-3</sup>); **1d** and Michler's ketone; **1d** and thioxantone; **1d** and stilbene; and **1e** and ferrocene. After removal of the solvent, the degree of the reaction was determined by <sup>1</sup>H NMR spectroscopy. The 365 nm line was isolated by using a Uranil glass filter. Concentration of sensitisers were adjusted so that 5% or less of the incident light was absorbed by **1d** (in sensitisation), or sensitisers (in quenching). Sensitisation and quenching experiment of **1e** gave similar results to those of **1d**.

**Quantum Yield Determination for the Formation of the β-Lactam 2d.**—Benzophenone-benzhydrol actinometry was used for the quantum yield determination. Samples (0.02 mol dm<sup>-3</sup> in benzene) in Pyrex tubes were degassed to ca. 10<sup>-3</sup> mmHg in four-thaw cycles and sealed. These samples were irradiated at 365 nm in a merry-go-round apparatus. Photolyses were carried out to 20–25% conversion. The extent of the reaction was determined by <sup>1</sup>H NMR spectroscopy.

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