# Photochemical δ-Hydrogen Abstraction from Acyclic and Semicyclic Monothioimides

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Photochemical δ-hydrogen abstraction from acyclic and semicyclic monothioimides have been studied. Photolysis of acyclic monothioimides possessing a benzylic hydrogen atom at the δ-position gave γ-lactams, *via* a 1,5-diradical intermediate, accompanied by thioamides were generated by γ-hydrogen abstraction. Irradiation of the five-membered semicyclic monothioimide, *N*-(3-phenylpropionyl)pyrrolidine-2-thione, yielded 5-mercapto-4-phenyl-1-azabicyclo[3.3.0]octan-2-one. For *N*-(3-phenylbutyryl)pyrrolidine-2-thione, disproportionation, involving 1,6-hydrogen migration, was the main path. Photolysis of the six-membered semicyclic monothioimide, *N*-(3-phenylbutyryl)piperidine-2-thione, gave an unsaturated thiol, *via* a 1,4-hydrogen shift of a 1,5-diradical intermediate, accompanied by cyclisation product and piperidine-2-thione.

Photochemical hydrogen abstraction from thioketones has been well studied.[1] P. de Mayo *et al.* reported that thioketones underwent photochemical hydrogen abstraction from the δ-position *via* π,π* singlet excited state ($S_2$) and that this process was preferred to γ-hydrogen abstraction.[2] Recently, the photochemistry of nitrogen-containing thiocarbonyl compounds has received much attention from the mechanistic and synthetic view points. Since these compounds show somewhat different photochemical behaviour from that of carbonyl compounds, their photochemistry may also lead to useful syntheses of some heterocycles.[3] We have already reported that the photolysis of acyclic monothioimides led to hydrogen abstraction from the β-position to produce thioketones *via* 2-mercaptoaziridines.[4] Furthermore, irradiation of acyclic and semicyclic monothioimides gave β-lactams by γ-hydrogen abstraction from the thiocarbonyl moiety.[5] We now report a synthesis of γ-lactams *via* δ-hydrogen abstraction from acyclic and semicyclic monothioimides.†

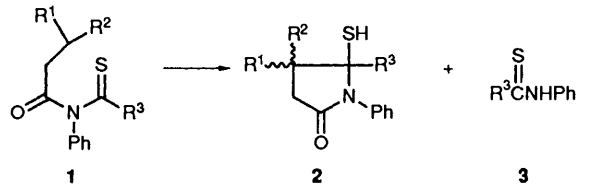
## Results and Discussion

All monothioimides **1a–1** were easily prepared from acid chlorides and the corresponding thioamides in the presence of triethylamine. *N*-Isovalerylthiobenzanilide **1a** was a red liquid whose UV spectrum exhibited maxima at 313 nm (ε 8600) and 500 nm (ε 160) derived from the n→π* region of the thiocarbonyl group. When the acyclic monothioimide **1a** was irradiated in benzene with a 1 kW high-pressure mercury lamp under argon until the starting material had disappeared, thiobenzanilide **3a** was obtained in 63% yield. Photolysis of the imide **1b** gave similar results. Irradiation of the monothioimide **1c** yielded 5-mercapto-1,4,5-triphenylpyrrolidin-2-one **2c** in 43% yield as a mixture of stereoisomers (major:minor 8:3) accompanied by thiobenzanilide **3c** (= **3a**) (45%) (Scheme 1). The structure of γ-lactam **2c** was deduced from its spectra. The IR spectrum (for solution in $CHCl_3$) exhibited a carbonyl frequency at 1700 $cm^{-1}$ characteristic of a five-membered lactam. The $^1H$ NMR spectrum of the major isomer showed signals at δ 1.60 for SH ($D_2O$-exchangeable) and three double doublets, coupled to each other, at δ 2.96 (1 H, dd, *J* 16.5 and 7.3 Hz), 3.27 (1 H, dd, *J* 16.5 and 9.5 Hz) and 4.04 (1 H, dd, *J* 9.5 and 7.3 Hz). In the $^{13}C$ NMR spectrum, the peak derived from the thiocarbonyl carbon did not appear, and new doublet and singlet peaks were shown at $\delta_C$ 55.3 (d) and 82.7 (s), assignable to C-4 and C-5, respectively. For other monothioimides **1d–1g** which have a benzylic hydrogen atom at the δ-position to the thiocarbonyl group, the corresponding 5-mercaptopyrrolidin-2-ones **2d–2g** were obtained as shown in Table 1, irrespective of the substituent on the thiobenzoyl ring.

**Table 1** Photolysis of acyclic monothioimides **1a–1g**

| | | | | Yield (%)[a] | |
|---|---|---|---|---|---|
| 1 | $R^1$ | $R^2$ | $R^3$ | 2 | 3 |
| **a** | Me | Me | Ph | 0 | 63 |
| **b** | MeO | H | Ph | 0 | 36 |
| **c** | Ph | H | Ph | 43 | 45 |
| **d** | Ph | Me | Ph | 53 | 15 |
| **e** | Ph | H | *p*-$MeOC_6H_4$ | 64 | 32 |
| **f** | Ph | H | *p*-$MeC_6H_4$ | 52 | 31 |
| **g** | Ph | H | *p*-$ClC_6H_4$ | 50 | 39 |

[a] Isolated yield.



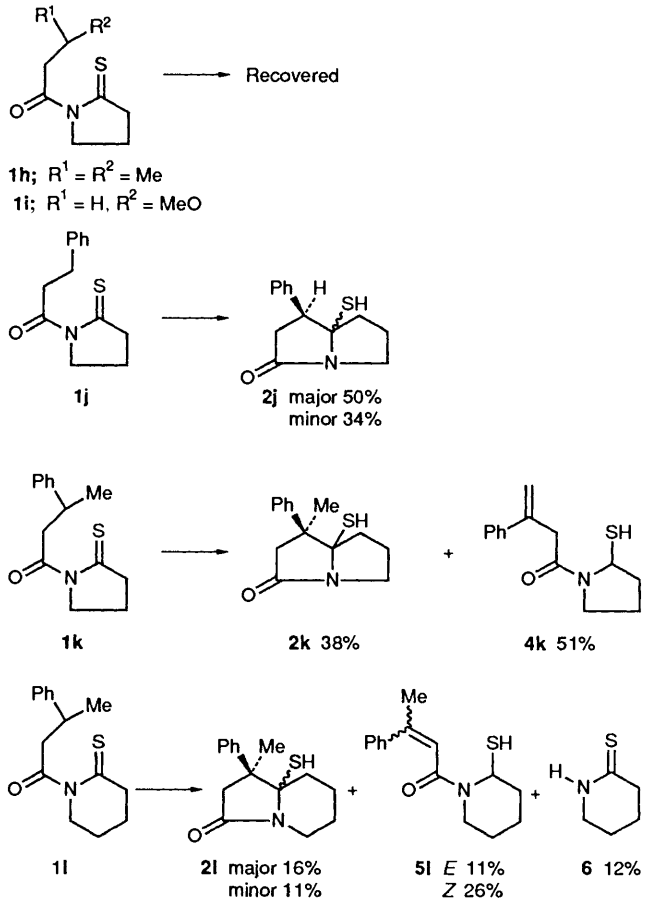

1 2 3

**Scheme 1** *Reaction conditions:* hν, benzene

Irradiation of the semicyclic monothioimide **1j** gave the bicyclic lactam 5-mercapto-4-phenyl-1-azabicyclo[3.3.0]octan-2-one (**2j**-major 50%, **2j**-minor 34%), while 1-isovaleryl- and 1-(3-methoxypropionyl)-pyrrolidine-2-thione **1h** and **1i** were inert toward photolysis as shown in Scheme 2.‡ The structure of compound **2j** was determined on the basis of elemental analyses and spectral data. The $^1H$ NMR spectrum of the major isomer exhibited a peak at δ 1.52, assignable to the mercapto group ($D_2O$-exchangeable), and three double doublets, which were coupled to each other, at δ 2.69 (1 H, dd, *J* 15.5 and 6.9 Hz), 3.38 (1 H, dd, *J* 15.5 and 12.8 Hz) and 3.74 (1 H, dd, *J* 12.8 and 6.9

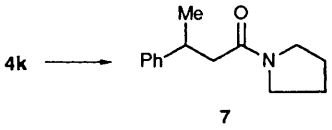
† We have already reported δ-hydrogen abstraction from thioimide-like compounds *N*-acyl- and *N*-thioacyl-thioureas; H. Aoyama, M. Sakamoto and Y. Omote, *Chem. Lett.*, 1983, 1397. Another group studies a similar reaction for cyclic thioimides; M. Machida, K. Oda, E. Yoshida and Y. Kanaoka, *J. Org. Chem.*, 1985, **50**, 1681.

‡ Prolonged irradiation of the imides **1h** and **1i** gave pyrrolidinethione.




**Scheme 2** *Reaction conditions:* hν, benzene

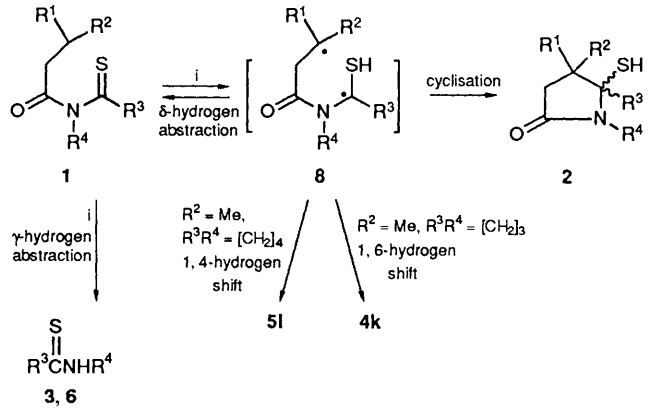
Hz). In the $^{13}C$ NMR spectra, the peak derived from the thiocarbonyl carbon did not appear and a new doublet and a singlet appeared at $\delta_C$ 54.5 (d) and 82.0 (s), assignable to C-4 and C-5, respectively. Mass spectra (SIMS) exhibited molecular-ion peaks at 234 (M + 1). For the imide **1k**, both of lactam **2k** (38%, one isomer was isolated) and 1-(3-phenylbut-3-enoyl)-pyrrolidine-2-thiol **4k** (51%) were obtained. The structute of compound **4k** was determined on the basis of its spectral data. Furthermore, it was supported by the fact that desulphurisation by Raney nickel (W-3) gave amide **7**, which was determined by comparison with an authentic sample prepared by acylation of pyrrolidine with 3-phenylbutyryl chloride as shown in Scheme 3. In the photolyses of the five-membered semicyclic imides **1j** and **1k**, pyrrolidinethione products were not detected at all.




**Scheme 3** *Reagents and conditions:* Raney nickel, MeOH

When six-membered semicyclic monothioimides **1l** was irradiated under the same conditions, α,β-unsaturated amide 1-(β-methylcinnamoyl)pyrrolidine-2-thiol (**5l**-*E* 11%, *Z* 26%) was obtained as the main product accompanied by bicyclic lactams **2l** and **6**, whereas photolysis of the imide **1k** gave 1-(β,γ-unsaturated alkanoyl)pyrrolidine-2-thiol **4k** (Scheme 2).

For the formation of γ-lactams **2c–2g** and **2j–2l**, photochemical δ-hydrogen abstraction followed by cyclisation is




**Scheme 4** *Reagents and conditions:* i, hν

postulated as shown in Scheme 4. The intermediacy of diradical **8** was supported by the fact that disproportionation took place in the photoreaction of semicyclic monothioimides **1k** and **1l**, since it is reasonable that the unsaturated photoproducts **4k** and **5l**, disproportionation products, are formed *via* diradical intermediate **8**. 1,4-Hydrogen shift in diradical **8** affords α,β-unsaturated amide **5l**, whereas β,γ-unsaturated amide **4k** is formed *via* 1,6-hydrogen shift. It seems that the difference in distance between the hydrogen atom and radical centre caused by the difference in conformation of the five-membered ring and that of the six-membered ring is reflected in the photoproducts. However, there is no satisfactory explanation at present. For the formation of thiolactams **3** and **6**, a Type-11 cleavage (γ-hydrogen abstraction) is postulated.[5]

The UV spectrum of *N*-(3-phenylpropionyl)pyrrolidine-2-thione **1j** exhibited maxima derived from the n→π* band of the thiocarbonyl moiety at 426 nm (ε 20). The photoreaction also proceeded when the imide **1j** was irradiated in the n→π* region (436 nm) selectively. The photocyclisation was sensitised by Michler's ketone ($E_T$ 62 kcal mol$^{-1}$)[6,*] and thioxanthone ($E_T$ 65.5 kcal mol$^{-1}$).[6] Though this photoreaction was not quenched by either (*E*)-stilbene ($E_T$ 50 kcal mol$^{-1}$)[6] or ferrocene ($E_T$ 35 kcal mol$^{-1}$),[3c] sensitisation experiments suggested that the cyclisation proceeds from the n→π* triplet excited state of the thiocarbonyl group.

In conclusion, photolysis of acyclic and semicyclic monothioimides possessing a benzylic hydrogen atom at the δ-position gave γ-lactams *via* a 1,5-diradical intermediate. Even a methoxy group attached to the δ-$CH_2$ group is not sufficient to direct the hydrogen abstraction to that position, but indeed a phenyl is needed. This is in contrast to the simple ketones studied by Wagner.[7] In some cases, *viz.* irradiation of semicyclic monothioimides, disproportionation took place and unsaturated thiols were obtained. Furthermore, the disproportionation involving 1,4-hydrogen shift appeared in five-membered semicyclic monothioimide, whereas six-membered semicyclic monothioimides gave the thermodynamically unstable olefin *via* 1,6-hydrogen shift. These photoreactions not only provide a useful synthesis of some δ-lactams, including pyrrolidine alkaloid analogues, but also yield important insight into hydrogen abstraction of thiocarbonyl compounds, since disproportionation to give unsaturated thiols is rare in ketone photochemistry.

## Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-420 spectrophotometer. $^1H$ and $^{13}C$ NMR spectra were recorded on Hitachi R-600 and JEOL GX-270 spectrometers with tetramethylsilane as internal standard, and

* 1 cal = 4.184 J.

$CDCl_3$ as solvent unless otherwise stated. UV spectra were measured on a Shimadzu UV-200A UV-VIS-NIR recording spectrophotometer. Eikohsya 1 kW and 500 W high-pressure mercury lamps were used as the irradiation source. Silica gel (Merk, Kieselgel 60; 230–400 mesh) was used for flash column chromatography.

*Preparation of Monothioimides.*—All monothioimides were prepared by condensation of thioamides with the corresponding acid chlorides. The preparation of *N*-isovalerylthiobenzanilide **1a** is given as an example. Triethylamine (300 mg, 3.0 mmol) was added dropwise to a solution of thiobenzanilide (600 mg, 2.8 mmol) and isovaleryl chloride (340 mg, 3.0 mmol) in dry benzene (30 $cm^3$) at room temperature under nitrogen and the reaction mixture was then stirred for 2 h. The precipitated triethylamine hydrochloride was removed by filtration through a Celite column, the filtrate was evaporated, and the residual mixture was subjected to flash column chromatography (eluent: benzene–hexane, 4:1). *N*-Isovalerylthiobenzanilide **1a** (770 mg, 92%) was isolated as a red liquid and purified by molecular distillation. All other monothioimides **1b–1l** were synthesized in the same manner. Crystalline monothioimides were recrystallised from chloroform–hexane.

*N-Isovalerylthiobenzanilide* **1a**. B.p. 80–85 °C/$10^{-2}$ mmHg; $\lambda_{max}$(c-$C_6H_{12}$)/nm 313 (ε 8600) and 500 (160); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 0.86 (6 H, d, *J* 6.6 Hz, 2 × Me), 1.8–2.4 [3 H, m, C(=O)$CH_2$ and C*H*$Me_2$] and 7.1–8.8 (10 H, m, ArH) (Found: C, 72.4; H, 6.4; N, 4.7. $C_{18}H_{19}NOS$ requires C, 72.69; H, 6.43; N, 4.70%).

*N-(3-Methoxypropionyl)thiobenzanilide* **1b**. M.p. 60–61 °C; $\lambda_{max}$(c-$C_6H_{12}$)/nm 313 (12 000) and 499 (180); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 2.65 [2 H, t, *J* 6.6 Hz, C(=O)$CH_2$], 3.32 (3 H, s, OMe), 3.65 (2 H, t, *J* 6.6 Hz, $CH_2O$) and 7.2–7.9 (10 H, m, ArH) (Found: C, 67.95; H, 5.7; N, 4.7. $C_{17}H_{17}NO_2S$ requires C, 68.20; H, 5.72; N, 4.67%).

*N-(3-Phenylpropionyl)thiobenzanilide* **1c**. M.p. 67–68 °C; $\lambda_{max}$(c-$C_6H_{12}$)/nm 313 (11 900) and 500 (190); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 2.77 [2 H, t, *J* 7.0 Hz, C(=O)$CH_2$], 2.89 (2 H, t, *J* 7.0 Hz, C$H_2$Ph) and 7.0–7.7 (15 H, m, ArH) (Found: C, 76.2; H, 5.6; N, 4.0. $C_{22}H_{19}NOS$ requires C, 76.49; H, 5.54; N, 4.05%).

*N-(3-Phenylbutyryl)thiobenzanilide* **1d**. M.p. 60–62 °C; $\lambda_{max}$(c-$C_6H_{12}$)/nm 315 (10 500) and 502 (150); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 1.21 (3 H, d, *J* 7.0 Hz, Me), 2.64 [2 H, t, *J* 4.2 Hz, C(=O)$CH_2$], 2.9–3.6 (1 H, m, C*H*Ph) and 6.7–7.6 (15 H, m, ArH) (Found: C, 76.6; H, 5.8; N, 3.9. $C_{23}H_{21}NOS$ requires C, 76.84; H, 5.88; N, 3.89%).

*p-Methoxy-N-(3-phenylpropionyl)thiobenzanilide* **1e**. M.p. 65–67 °C; $\lambda_{max}$(c-$C_6H_{12}$)/nm 343 (17 500) and 502 (260); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 2.75 [2 H, t, *J* 6.6 Hz, C(=O)$CH_2$], 2.87 (2 H, t, *J* 6.6 Hz, C$H_2$Ar), 3.73 (3 H, s, OMe) and 7.0–7.7 (14 H, m, ArH) (Found: C, 73.5; H, 5.5; N, 3.7. $C_{23}H_{21}NO_2S$ requires C, 73.57; H, 5.63; N, 3.73%).

*p-Methyl-N-(3-phenylpropionyl)thiobenzanilide* **1f**. M.p. 67–69 °C; $\lambda_{max}$(c-$C_6H_{12}$)/nm 322 (13 700) and 502 (200); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1705; $\delta_H$ 2.29 (3 H, s, Me), 2.79 [2 H, t, *J* 7.0 Hz, C(=O)$CH_2$], 2.87 (2 H, t, *J* 7.0 Hz, C$H_2$Ar) and 6.9–7.7 (14 H, m, ArH) (Found: C, 76.7; H, 5.8; N, 3.9. $C_{23}H_{21}NOS$ requires C, 76.84; H, 5.88; N, 3.89%).

*p-Chloro-N-(3-phenylpropionyl)thiobenzanilide* **1g**. M.p. 112–114 °C; $\lambda_{max}$(c-$C_6H_{12}$)/nm 319 (10 100) and 503 (230); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1710; $\delta_H$ 2.78 [2 H, t, *J* 7.0 Hz, C(=O)$CH_2$], 2.86 (2 H, t, *J* 7.0 Hz, C$H_2$Ar) and 7.0–7.7 (14 H, m, ArH) (Found: C, 69.5; H, 4.85; N, 3.7. $C_{22}H_{18}ClNOS$ requires C, 69.55; H, 4.77; N, 3.68%).

*N-Isovalerylpyrrolidine-2-thione* **1h**. B.p. 70–72 °C/5 mmHg; $\lambda_{max}$(c-$C_6H_{12}$)/nm 287 (12 500) and 426 (30); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1690; $\delta_H$ 0.99 (6 H, d, *J* 6.6 Hz, 2 × Me), 1.8–2.4 (3 H, m, C*H*$Me_2$ + $CH_2$), 3.19 [2 H, t, *J* 7.2 Hz, C(=S)$CH_2$], 3.20 [2 H, d, *J* 6.6 Hz, C(=O)$CH_2$] and 4.15 (2 H, t, *J* 7.2 Hz, $NCH_2$) (Found: C, 58.1; H, 8.1; N, 7.6. $C_9H_{15}NOS$ requires C, 58.34; H, 8.15; N, 7.55%).

*N-(3-Methoxypropionyl)pyrrolidine-2-thione* **1i**. B.p. 64–66 °C/2 mmHg; $\lambda_{max}$(c-$C_6H_{12}$)/nm 287 (10 500) and 423 (20); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1690; $\delta_H$ 1.7–2.3 (2 H, m, $CH_2$), 3.10 [2 H, t, *J* 7.2 Hz, C(=S)$CH_2$], 3.27 (3 H, s, OMe), 3.46 [2 H, t, *J* 7.8 Hz, C(=O)$CH_2$], 3.64 (2 H, t, *J* 7.8 Hz, $OCH_2$) and 4.06 (2 H, t, *J* 7.2 Hz, $NCH_2$) (Found: C, 51.15; H, 7.0; N, 7.4. $C_8H_{13}NO_2S$ requires C, 51.31; H, 6.99; N, 7.47%).

*N-(3-Phenylpropionyl)pyrrolidine-2-thione* **1j**. B.p. 59–60 °C/5 mmHg; $\lambda_{max}$(c-$C_6H_{12}$)/nm 287 (13 500) and 426 (30); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 1.7–2.3 (2 H, m, $CH_2$), 3.00 (2 H, t, *J* 6.6 Hz, C$H_2$Ph), 3.14 [2 H, t, *J* 7.2 Hz, C(=S)$CH_2$], 3.60 [2, H, t, *J* 6.6 Hz, C(=O)$CH_2$], 4.09 (2 H, t, *J* 7.2 Hz, $NCH_2$) and 7.21 (5 H, s, ArH) (Found: C, 66.7; H, 6.5; N, 5.9. $C_{13}H_{15}NOS$ requires C, 66.92; H, 6.47; N, 6.00%).

*N-(3-Phenylbutyryl)pyrrolidine-2-thione* **1k**. B.p. 104–106 °C/5 mmHg; $\lambda_{max}$(c-$C_6H_{12}$)/nm 289 (11 900) and 426 (20); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 1.32 (3 H, d, *J* 6.6 Hz, Me), 1.6–2.2 (2 H, m, $CH_2$), 3.12 [2 H, t, *J* 7.2 Hz, C(=S)$CH_2$], 3.3–3.8 (1 H, m, C*H*MePh), 3.72 [2 H, d, *J* 3.0 Hz, C(=O)$CH_2$], 4.01 (2 H, t, *J* 7.2 Hz, $NCH_2$) and 7.26 (5 H, s, ArH) (Found: C, 67.8; H, 6.9; N, 5.6. $C_{14}H_{17}NOS$ requires C, 67.98; H, 6.92; N, 5.66%).

*N-(3-Phenylbutyryl)piperidine-2-thione* **1l**. B.p. 105–110 °C/1 mmHg; $\lambda_{max}$(c-$C_6H_{12}$)/nm 305 (10 000) and 420 (40); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; $\delta_H$ 1.30 (3 H, d, *J* 6.0 Hz, Me), 1.5–1.8 (4 H, m, 2 × $CH_2$), 2.5–3.7 (7 H, m, C*H*Me + 3 × $CH_2$) and 7.25 (5 H, s, ArH) (Found: C, 68.7; H, 7.25; N, 5.35. $C_{15}H_{19}NOS$ requires C, 68.92; H, 7.32; N, 5.35%).

*General Procedure for the Photochemical Reaction of Monothioimides* **1a–1l**.—A benzene solution of the monothioimide was irradaiated with a 1 kW high-pressure mercury lamp under argon at room temperature until the starting material had disappeared (TLC). After evaporation of the solvent, the residual mixture was subjected to flash chromatography with benzene–ethyl acetate (10:1) as eluent. The crystalline photoproducts **2j** and **2k** were recrystallised from chloroform–hexane, whereas products **2c–2g**, **2l**, **4k** and **5l** were liquid and decomposed on attempted distillation.

*5-Mercapto-1,4,5-triphenylpyrrolidin-2-one* **2c**. This photoproduct was obtained as a mixture of two stereoisomers in the ratio 8:3. $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; *m/z* (CI) 346 (M + 1).

(Major isomer): $\delta_H$ 1.60 (1 H, s, SH), 2.96 (1 H, dd, *J* 16.6 and 7.5 Hz, 3-H), 3.27 (1 H, dd, *J* 16.6 and 9.6 Hz, 3-H), 4.04 (1 H, dd, *J* 9.6 and 7.5 Hz, 4-H) and 6.8–7.7 (15 H, m, ArH); $\delta_C$ 35.4 (t, C-3), 55.3 (d, C-4), 82.7 (s, C-5), 126.5 (d, Ph), 126.6 (d, Ph), 128.0 (d, Ph), 128.3 (d, Ph), 128.4 (d, Ph), 128.5 (d, Ph), 128.6 (d, Ph), 128.9 (d, Ph), 129.0 (d, Ph), 136.1 (s, Ph), 136.5 (s, Ph), 142.1 (s, Ph) and 174.0 (s).

(Minor isomer): $\delta_H$ 2.46 (1 H, s, SH), 2.83 (1 H, dd, *J* 16.8 and 8.2 Hz, 3-H), 3.04 (1 H, dd, *J* 16.8 and 7.3 Hz, 3-H), 4.05 (1 H, dd, *J* 8.2 and 7.3 Hz, 4-H) and 6.8–7.7 (15 H, m, ArH); $\delta_C$ 35.2 (t, C-3), 55.7 (d, C-4), 81.3 (s, C-5), 134.8 (s, Ph), 136.5 (s, Ph), 139.1 (s, Ph) and 172.8 (s).

*5-Mercapto-4-methyl-1,4,5-triphenylpyrrolidin-2-one* **2d**. This photoproduct was obtained as a mixture of two stereoisomers in the ratio 3:2. $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1700; *m/z* (CI) 360 (M + 1).

(Major isomer): $\delta_H$ 1.58 (1 H, s, SH), 1.87 (3 H, s, Me), 2.49 (1 H, d, *J* 16.0 Hz, 3-H), 3.40 (1 H, d, *J* 16.0 Hz, 3-H) and 7.0–7.5 (15 H, m, ArH); $\delta_C$ 26.2 (q, Me), 41.7 (t, C-3), 52.0 (s, C-4), 85.6 (s, C-5), 139.7 (s, Ph), 140.5 (s, Ph), 141.0 (s, Ph) and 174.3 (s, C=O).

(Minor isomer): $\delta_H$ 1.23 (3 H, s, Me), 2.14 (1 H, s, SH), 2.80 (1 H, d, *J* 15.9 Hz, 3-H), 3.28 (1 H, d, *J* 15.9 Hz, 3-H) and 7.0–7.5 (15 H, m, ArH); $\delta_C$ 25.1 (q, Me), 44.6 (t, C-3), 50.8 (s, C-4), 85.2

(s, C-5), 136.9 (s, Ph), 137.0 (s, Ph), 143.2 (s, Ph) and 173.3 (s, C=O).

5-*Mercapto*-5-(p-*methoxyphenyl*)-1,4-*diphenylpyrrolidin*-2-*one* **2e**. This photoproduct was obtained as a mixture of two stereoisomers in the ratio 3:1. $\nu_{max}(CHCl_3)/cm^{-1}$ 1700; *m/z* (CI) 376 (M + 1).

(Major isomer): $\delta_H$ 1.99 (1 H, s, SH), 2.94 (1 H, dd, *J* 16.6 and 7.5 Hz, 3-H), 3.29 (1 H, dd, *J* 16.6 and 10.2 Hz, 3-H), 3.82 (3 H, s, MeO), 4.05 (1 H, dd, *J* 10.2 and 7.5 Hz, 4-H) and 6.6–7.7 (14 H, m, ArH); $\delta_C$ 35.3 (t, C-3), 55.3 (q, MeO), 67.5 (d, C-4), 82.5 (s, C-5), 113.6 (d, Ph), 126.6 (d, Ph), 126.7 (d, Ph), 128.3 (d, Ph), 128.5 (d, Ph), 128.8 (d, Ph), 128.9 (d, Ph), 129.4 (d, Ph), 133.8 (s, Ph), 136.1 (s, Ph), 136.5 (s, Ph), 159.5 (s, Ph) and 174.0 (s, C=O).

(Minor isomer): $\delta_H$ 2.42 (1 H, s, SH), 2.82 (1 H, dd, *J* 16.8 and 8.1 Hz, 3-H), 2.98 (1 H, dd, *J* 16.8 and 4.3 Hz, 3-H), 3.78 (3 H, s, MeO), 4.05 (1 H, dd, *J* 8.1 and 4.3 Hz, 4-H) and 6.6–7.7 (14 H, m, ArH); $\delta_C$ 40.1 (t, C-3), 55.1 (q, MeO), 69.1 (d, C-4), 82.2 (s, C-5), 134.3 (s, Ph), 135.2 (s, Ph), 137.4 (s, Ph), 158.9 (s, Ph) and 170.0 (s, C=O).

5-*Mercapto*-1,4-*diphenyl*-5-(p-*tolyl*)*pyrrolidin*-2-*one* **2f**. This photoproduct was obtained as a mixture of two stereoisomers in the ratio 3:1. $\nu_{max}(CHCl_3)/cm^{-1}$ 1695; *m/z* (CI) 360 (M + 1).

(Major isomer): $\delta_H$ 1.60 (1 H, s, SH), 2.35 (3 H, s, Me), 2.95 (1 H, dd, *J* 16.5 and 7.3 Hz, 3-H), 3.26 (1 H, dd, *J* 16.5 and 9.5 Hz, 3-H), 4.03 (1 H, dd, *J* 9.5 and 7.3 Hz, 4-H) and 6.9–7.6 (14 H, m, ArH); $\delta_C$ 21.0 (q, Me), 35.4 (t, C-3), 55.3 (d, C-4), 82.7 (s, C-5), 126.6 (d, Ph), 127.8 (d, Ph), 128.2 (d, Ph), 128.3 (d, Ph), 128.5 (d, Ph), 128.6 (d, Ph), 128.9 (d, Ph), 129.1 (d, Ph), 136.3 (s, Ph), 136.5 (s, Ph), 138.2 (s, Ph), 139.1 (s, Ph) and 174.1 (s, C=O).

(Minor isomer): $\delta_H$ 2.20 (1 H, s, SH), 2.30 (3 H, s, Me), 2.81 (1 H, dd, *J* 16.8 and 7.9 Hz, 3-H), 2.99 (1 H, dd, *J* 16.8 and 12.6 Hz, 3-C), 4.00 (1 H, dd, *J* 12.6 and 7.9 Hz, 4-C) and 6.9–7.6 (14 H, m, ArH); $\delta_C$ 20.9 (q, Me), 35.3 (t, C-3), 55.7 (d, C-4), 81.4 (s, C-5), 132.5 (s, Ph), 134.7 (s, Ph), 136.2 (s, Ph), 136.7 (s, Ph) and 173.0 (s, C=O).

5-(p-*Chlorophenyl*)-5-*mercapto*-1,4-*diphenylpyrrolidin*-2-*one* **2g**. This photoproduct was obtained as a mixture of two stereoisomers in the ratio 3:1. $\nu_{max}(CHCl_3)/cm^{-1}$ 1695; *m/z* (CI) 380 (M + 1).

(Major isomer): $\delta_H$ 1.57 (1 H, s, SH), 2.94 (1 H, dd, *J* 16.5 and 7.4 Hz, 3-H), 3.31 (1 H, dd, *J* 16.5 and 10.3 Hz, 3-H), 3.99 (1 H, dd, *J* 10.3 and 7.4 Hz, 4-H) and 6.8–7.6 (14 H, m, ArH); $\delta_C$ 35.3 (t, C-3), 55.5 (d, C-4), 82.2 (s, C-5), 126.5 (d, Ph), 126.6 (d, Ph), 128.0 (d, Ph), 128.2 (d, Ph), 128.4 (d, Ph), 128.5 (d, Ph), 128.6 (d, Ph), 128.9 (d, Ph), 134.5 (s, Ph), 135.5 (s, Ph), 136.3 (s, Ph), 140.7 (s, Ph) and 174.0 (s, C=O).

(Minor isomer): $\delta_H$ 2.07 (1 H, s, SH), 2.86 (1 H, dd, *J* 16.8 and 8.2 Hz, 3-H), 3.01 (1 H, dd, *J* 16.8 and 6.4 Hz, 3-H), 4.02 (1 H, dd, *J* 8.2 and 6.4 Hz, 4-H) and 6.8–7.6 (14 H, m, ArH); $\delta_C$ 35.0 (t, C-3), 55.6 (d, C-4), 80.8 (s, C-5), 134.4 (s, Ph), 136.6 (s, Ph), 138.0 (s, Ph), 142.0 (s, Ph) and 172.6 (s, C=O).

5-*Mercapto*-4-*phenyl*-1-*azabicyclo*[3.3.0]*octan*-2-*one* **2j**. (*Major isomer*): m.p. 100–101 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1690; $\delta_H$ 1.52 (1 H, s, SH), 2.2–2.3 (1 H, m, 6-H), 2.3–2.4 (2 H, m, 6- and 7-H), 2.5–2.7 (1 H, m, 7-H), 2.69 (1 H, dd, *J* 15.5 and 6.9 Hz, 3-H), 3.3–3.4 (1 H, m, 8-H), 3.38 (1 H, dd, *J* 15.5 and 12.8 Hz, 3-H), 3.55–3.75 (1 H, m, 8-H), 3.74 (1 H, dd, *J* 12.8 and 6.9 Hz, 4-H) and 7.25–7.45 (5 H, m, ArH); $\delta_C$ 26.3 (t, C-7), 38.4 (t, C-3), 40.4 (t, C-8), 43.1 (t, C-6), 54.4 (d, C-4), 82.0 (s, C-5), 127.8 (d, Ph), 128.1 (d, Ph), 128.6 (d, Ph), 137.0 (s, Ph) and 171.1 (s, C=O); *m/z* (SIMS) 234 (M + 1) (Found: C, 66.7; H, 6.5; N, 5.9. $C_{13}H_{15}NOS$ requires C, 66.92; H, 6.47; N, 6.00%).

(*Minor isomer*): m.p. 71–73 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1690; $\delta_H$ 1.3–1.5 (1 H, m, 6-H), 1.5–1.7 (1 H, m, 6-H), 1.8–2.0 (1 H, m, 7-H), 2.2–2.4 (1 H, m, 7-H), 2.55 (1 H, s, SH), 2.71 (1 H, d, *J* 17.1 Hz, 3-H), 3.2–3.3 (1 H, m, 8-H), 3.4–3.5 (1 H, m, 8-H), 3.50 (1 H, dd, *J* 17.1 and 6.7 Hz, 3-H), 3.90 (1 H, d, *J* 6.7 Hz, 4-H) and 7.2–7.5 (5 H, m, ArH); $\delta_C$ 25.9 (t, C-7), 36.9 (t, C-3), 40.4 (t, C-8), 40.8 (t, C-6), 53.7 (d, C-4), 82.1 (s, C-5), 127.5 (d, Ph), 127.7 (d, Ph), 128.9 (d, Ph), 139.7 (s, Ph) and 172.3 (s, C=O); *m/z* (SIMS) 234 (M + 1) (Found: C, 66.8; H, 6.45; N, 6.0%).

5-*Mercapto*-4-*methyl*-4-*phenyl*-1-*azabicyclo*[3.3.0]*octan*-2-*one* **2k**. M.p. 105–107 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1680; $\delta_H$ 1.39 (3 H, s, Me), 1.62 (1 H, s, SH), 2.1–2.3 (1 H, m, 6-H), 2.3–2.4 (1 H, m, 6-H), 2.50 (1 H, d, *J* 15.2 Hz, 3-H), 2.5–2.7 (2 H, m, 7-$H_2$), 3.2–3.4 (1 H, m, 8-H), 3.4–3.6 (1 H, m, 8-H), 3.67 (1 H, d, *J* 15.2 Hz, 3-H) and 7.2–7.5 (5 H, m, ArH); $\delta_C$ 23.3 (t, C-7), 27.0 (q, Me), 36.5 (t, C-3), 40.2 (t, C-8), 46.6 (t, C-6), 52.9 (d, C-4), 85.0 (s, C-5), 126.4 (d, Ph), 127.1 (d, Ph), 128.7 (d, Ph), 144.2 (s, Ph) and 170.8 (s, C=O); *m/z* (CI) 248 (M + 1) (Found: C, 68.0; H, 6.9; N, 5.7. $C_{14}H_{17}NOS$ requires C, 67.97; H, 6.94; N, 5.66%).

N-(3′-*Phenylbut*-3′-*enoyl*)*pyrrolidine*-2-*thiol* **4k**. $\nu_{max}(CHCl_3)/cm^{-1}$ 1685 and 1635; $\delta_H$ 1.26 (1 H, s, SH), 1.6–2.2 (6 H, m, 3-, 4- and 2′-$H_2$), 2.8–3.2 (1 H, m, 5-H), 3.4–3.8 (2 H, m, 2- and 5-H), 5.19 (1 H, d, *J* 0.6 Hz, C=CH), 5.52 (1 H, d, *J* 0.6 Hz, C=CH) and 7.2–7.6 (5 H, m, ArH); $\delta_C$ 24.3 (t, C-4), 33.0 (t, C-H or -3), 42.0 (t, C-5), 46.6 (t, C-2′), 56.2 (d, C-2), 114.9 (t, C-4′), 125.7 (d, Ph), 127.8 (d, Ph), 128.4 (d, Ph), 140.2 (s, C-3′ or Ph), 141.2 (s, Ph or C-3′) and 168.9 (s, C=O); *m/z* (CI) 248 (M + 1).

6-*Mercapto*-7-*methyl*-7-*phenyl*-1-*azabicyclo*[4.3.0]*nonan*-9-*one* **2l**. (Major isomer): obtained in 16% yield, $\nu_{max}(CHCl_3)/cm^{-1}$ 1680; $\delta_H$ 1.2–1.5 (2 H, m, 3- or 4-$H_2$), 1.49 (3 H, s, Me), 1.57 (1 H, s, SH), 1.7–2.1 (2 H, m, 4- or 3-$H_2$), 2.1–2.25 (2 H, m, 5-$H_2$), 2.34 (1 H, d, *J* 15.9 Hz, 8-H), 2.7–2.9 (1 H, m, 2-H), 3.34 (1 H, d, *J* 15.9 Hz, 8-H), 4.0–4.1 (1 H, m, 2-H) and 7.2–7.4 (5 H, m, Ph); $\delta_C$ 20.2 (q, Me), 23.5 (t, C-3 or -4), 26.2 (t, C-4 or -3), 34.5 (t, C-5), 37.7 (t, C-8), 42.2 (t, C-2), 51.1 (s, C-7), 78.5 (s, C-6), 126.8 (d, Ph), 127.3 (d, Ph), 128.3 (d, Ph), 143.3 (s, Ph) and 172.6 (s, C=O); *m/z* (CI) 261 (M + 1).

(Minor isomer): 11% yield, $\nu_{max}(CHCl_3)/cm^{-1}$ 1670; $\delta_H$ 0.9–1.2 (2 H, m, 3- or 4-$H_2$), 1.4–1.7 (2 H, m, 4- or 3-Hz), 1.63 (3 H, s, Me), 1.7–2.0 (2 H, m, 5-$H_2$), 1.99 (1 H, s, SH), 2.64 (1 H, d, *J* 16.8 Hz, 8-H), 2.96 (1 H, *J* 16.5 Hz, 8-H), 3.6–3.7 (1 H, m, 2-H), 3.9–4.1 (1 H, m, 2-H) and 7.2–7.4 (5 H, m, ArH); $\delta_C$ 20.6 (q, Me), 23.7 (t, C-3 or -4), 26.5 (t, C-4 or -3), 35.3 (t, C-5), 37.6 (t, C-8), 44.0 (t, C-2), 48.0 (s, C-7), 78.0 (s, C-6), 125.8 (d, Ph), 127.0 (d, Ph), 128.4 (d, Ph), 143.3 (s, Ph) and 173.0 (s, C=O); *m/z* (CI) 261 (M + 1).

N-(β-*Methylcinnamoyl*)*piperidine*-2-*thiol* **5l**. [(*Z*)-isomer]: obtained in 26% yield, $\nu_{max}(CHCl_3)/cm^{-1}$ 1640; $\delta_H$ 1.2–2.1 (7 H, m, 3 × $CH_2$ + SH), 2.25 (3 H, s, Me), 2.3–2.4 (1 H, m), 3.4–3.9 (2 H, m), 6.21 (1 H, br s, C=CH), 7.1–7.5 (5 H, m, ArH); $\delta_C$ 17.9 (q, Me), 19.3 (t, C-3 or -4), 25.7 (t, C-4 or -3), 32.1 (t, C-5), 41.2 (t, C-2), 50.4 (d, C-6), 119.6 (d, C-α), 125.9 (d, Ph), 128.4 (d, Ph) 128.5 (d, Ph), 139.3 (s, Ph or C-β), 141.6 (s, C-β or Ph) and 167.8 (s, C=O); *m/z* (CI) 261 (M + 1).

[(*E*)-isomer]: 11% yield, $\nu_{max}(CHCl_3)/cm^{-1}$ 1640; $\delta_H$ 1.1–2.1 (6 H, m, 3 × $CH_2$), 2.18 (3 H, d, *J* 1.5 Hz, Me), 2.62 (1 H, s, SH), 3.0–3.2 (1 H, m), 3.5–3.7 (1 H, m), 4.2–4.4 (1 H, m), 5.88 (1 H, q, *J* 1.5 Hz, C=CH) and 7.2–7.6 (5 H, m, ArH); $\delta_C$ 19.0 (t, C-3 or 4-H), 24.3 (q, Me), 25.0 (t, C-4 or -3), 31.6 (t, C-5), 41.2 (t, C-2), 50.1 (d, C-6), 120.6 (d, C-α), 127.4 (d, Ph), 128.1 (d, Ph), 128.3 (d, Ph), 139.9 (s, Ph or C-β), 143.3 (s, C-β or Ph) and 167.9 (s, C=O); *m/z* (CI) 261 (M + 1).

*Sensitisation and Quenching of* N-(3-*Phenylpropionyl*)*pyrrolidine*-2-*thione* **1j**.—Five Pyrex tubes were irradiated at 365 nm with a 500 W high-pressure mercury lamp in a merry-go-round apparatus. The tubes contained starting material **1j** (0.02 mol $dm^{-3}$), **1j** and Michler's ketone, **1j** and thioxanthone, **1j** and stilbene, and **1j** and ferrocene, respectively. After removal of benzene the extent of reaction was determined by $^1H$ NMR spectroscopy. The 365 nm radiation was isolated by using a uranil glass filter. Concentration of each sensitiser was adjusted so that 5% or less of the incident light was absorbed

by the imide **1j** (in sensitisation) or by the sensitiser (in quenching).

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*Paper* 0/03096D
*Received* 9*th July* 1990
*Accepted* 29*th August* 1990