

# Photochemical synthesis of pyrrole derivatives by desulfurization of 2,5-dihydro-1*H*-pyrrole-2-thiones and [2 + 2] cycloaddition of 2,5-dihydro-1*H*-pyrrole-2-thiones with alkenes

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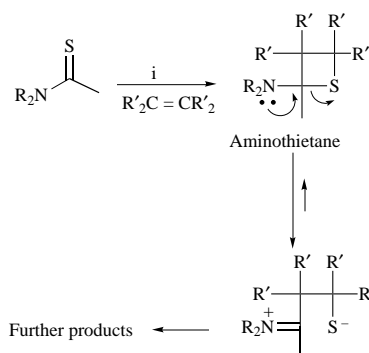
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The photochemical reactions of the 2,5-dihydro-1*H*-pyrrole-2-thiones **2** have been examined. Irradiation of 2,5-dihydro-1*H*-pyrrole-2-thiones **2** in the presence of triethylamine gives desulfurization products, the pyrroles **3**, or reduction products, the pyrrolidine-2-thiones **4**, depending on the substituent on the nitrogen atom of thione **2**. This reaction can be explained by a sequential electron/proton-transfer mechanism from the amine to the excited pyrrolethione. Irradiation of thiones **2** in the presence of alkenes **5** gives 2-alkylated pyrroles **6–14**. The formation of these photoproducts can be explained in terms of the intermediacy of spiroaminothietanes, which are derived by [2 + 2] photocycloaddition of the C=S bond of thione **2** and the C=C bond of alkene **5**.

## Introduction

The photochemistry of thiocarbonyl compounds has received much attention from both synthetic and mechanistic viewpoints,<sup>1</sup> and these compounds behave like carbonyl compounds in many respects. In particular, the [2 + 2] photocycloaddition with alkenes affords thietanes as primary products, which are often unstable and are transformed into fragmentation products. Thioamides also undergo both inter- and intra-molecular photocycloaddition with alkenes.<sup>1*b*,2–4</sup> Aminothietanes are believed to be intermediates in these reactions, although they have not yet been isolated,<sup>5</sup> probably because the nitrogen lone-pair electron-assisted cleavage of the C–S bond of the thietane ring facilitates the formation of a zwitterion (Scheme 1). In con-



Scheme 1 Conditions: i, *hν*

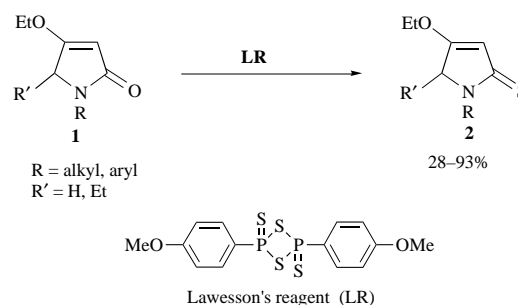
tinuation of our work on the photochemistry of cyclic conjugated nitrogen–thiocarbonyl systems,<sup>3*d–g*,4</sup> we found that the photochemically induced addition of these thioamide compounds to alkenes provides a simple and novel method for C–C bond formation in nitrogen-containing heterocycles. We now report the photochemical desulfurization of 2,5-dihydro-1*H*-pyrrole-2-thiones **2** and the photoaddition reactions of compounds **2** with alkenes, which have potential in the synthesis of 2-substituted pyrroles.

## Results and discussion

### Photochemical reaction of 2,5-dihydro-1*H*-pyrrole-2-thiones **2** in the presence of triethylamine

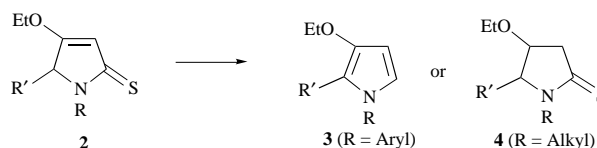
The 2,5-dihydro-1*H*-pyrrole-2-thiones **2** are readily access-

ible by direct sulfuration of their oxygen analogues with Lawesson's reagent [LR: 2,4-bis(*p*-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide] in 28–93% yield (Scheme 2).



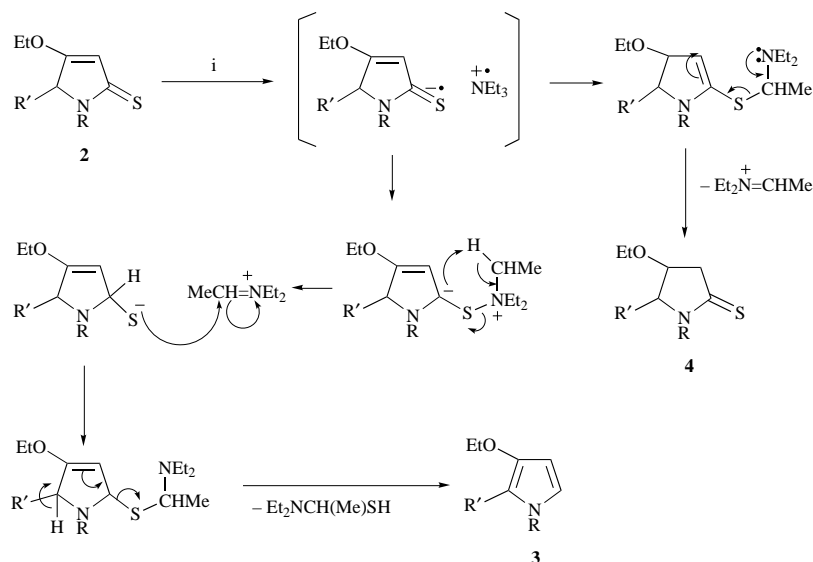
Scheme 2 Compounds **1**, **2** are defined in Table 1

When a benzene solution of 4-ethoxy-1-phenyl-2,5-dihydro-1*H*-pyrrole-2-thione **2a** was irradiated with a high-pressure mercury lamp through a Pyrex filter under argon, the starting material was recovered (> 80%) with a small amount of several inseparable by-products. However, irradiation of compound **2a** in benzene in the presence of triethylamine for 3 h, under the same conditions as described above, gave the desulfurization product, 3-ethoxy-1-phenylpyrrole **3a** in 53% yield (Scheme 3,



Scheme 3 Reagents and conditions: Et<sub>3</sub>N, PhH, *hν*

Table 1). The structure of product **3a** was confirmed by direct comparison of its IR and NMR spectra with that of authentic material.<sup>6</sup> In a similar manner, irradiation of 1-aryl-2,5-dihydro-1*H*-pyrrole-2-thiones **2b–d** in the presence of triethylamine yielded 1-aryl-3-ethoxypyrroles **3b–d** in 40–67% yield. In contrast, irradiation of 1-alkyl-2,5-dihydro-1*H*-pyrrole-2-thiones **2e,f** in the presence of triethylamine gave the reduction products, 1-alkyl-4-ethoxypyrrolidine-2-thiones **4e,f** in 30–32% yield. The structure of the photoproducts **3b–d** and **4e,f** was elucidated on the basis of their spectroscopic properties and



**Scheme 4** Reagents and conditions: i, Et<sub>3</sub>N, *hν*

**Table 1** Yields of the photoproducts **3** and **4**

|           | Pyrrole-2-thione <b>2</b>                 |    | Yield (%) |          |
|-----------|---|----|-----------|----------|
|           | R   | R' | <b>3</b>  | <b>4</b> |
| <b>2a</b> | Ph  | H  | 53        |          |
| <b>2b</b> | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> | H  | 43        |          |
| <b>2c</b> | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> | H  | 40        |          |
| <b>2d</b> | Ph  | Et | 67        |          |
| <b>2e</b> | Me  | H  |           | 30       |
| <b>2f</b> | PhCH <sub>2</sub>                         | H  |           | 32       |

elemental analyses. In accordance with the results obtained earlier, namely the photochemical desulfurization of the indoline-2-thiones to indolines in the presence of amines,<sup>4d</sup> we propose a plausible mechanism for the formation of desulfurization products **3** and reduction products **4**, which involves the zwitterionic intermediates resulting from electron transfer from the amine to the excited pyrrolothione, followed by proton transfer and electron redistribution (see Scheme 4). An analogous mechanism has been proposed in the photochemical amine- or phosphite-promoted coupling of 2-thioxo-1,3-dithioles.<sup>7</sup>

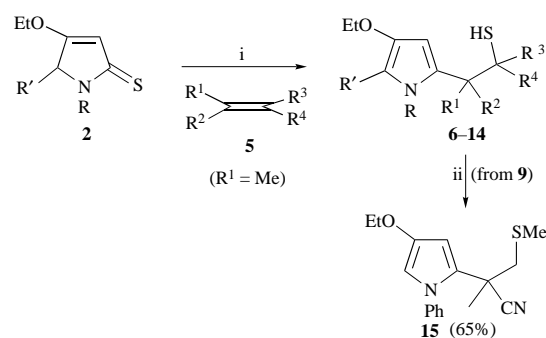
#### Photocycloaddition of 2,5-dihydro-1*H*-pyrrole-2-thiones **2** to alkenes **5**

Irradiation of 4-ethoxy-1-phenyl-2,5-dihydro-1*H*-pyrrole-2-thione **2a** in benzene in the presence of a large excess of electron-rich alkenes such as 2,3-dimethylbut-2-ene **5a**, 2-methylbut-2-ene **5b** and 2-methylprop-2-ene **5c** and an electron-poor alkene such as methacrylonitrile **5d** under the same conditions as described above gave good yields (66–83%) of 2-(mercaptoalkyl)pyrroles **6–9**, which are the 1:1-adducts of **2a** and alkenes **5** (see Scheme 5 and Table 2). The structure of products **6–9** was confirmed on the basis of their spectral data and elemental analyses. The IR spectrum of 2-(mercaptoalkyl)pyrroles **6–9** shows a characteristic thiol absorption around 2550 cm<sup>-1</sup> and in the <sup>1</sup>H NMR spectrum the signal at δ 1.12–1.60 is assignable to the thiol proton. Treatment of the 2-(mercaptoalkyl)pyrrole **9** with MeI gave the corresponding sulfide (*e.g.* **15** in 65% yield). The photocycloaddition reaction of substrates **2a** and **5a** also proceeds in methanol but with low efficiency. The photochemical formation of product **6** was weakly quenched by the addition of stilbene (*E<sub>T</sub>* = 209 kJ mol<sup>-1</sup>) and almost completely quenched by the addition of azulene (*E<sub>T</sub>* = 129 kJ mol<sup>-1</sup>), suggesting that the photoaddition of **2a** to **5a** proceeded *via* an *n*-π\* triplet state. Similarly, irradi-

**Table 2** Yields of the photoproducts **6–14**

| Pyrrole-2-thione <b>2</b> | Alkene <b>5</b>                           |    |  | Product and yield (%) <sup>a</sup> |
|---------------------------|---|----|--|------------------------------------|
|                           | R   | R' | R <sup>2</sup> R <sup>3</sup> R <sup>4</sup> |                                    |
| <b>2a</b>                 | Ph  | H  | <b>5a</b> Me Me Me                           | <b>6</b> 68                        |
| <b>2a<sup>b</sup></b>     |   |    | <b>5a</b>                                    | <b>6</b> 14                        |
| <b>2a<sup>c</sup></b>     |   |    | <b>5a</b>                                    | <b>6</b> 63                        |
| <b>2a<sup>c,d</sup></b>   |   |    | <b>5a</b>                                    | <b>6</b> 20                        |
| <b>2a<sup>c,e</sup></b>   |   |    | <b>5a</b>                                    | <b>6</b> 7                         |
| <b>2a</b>                 |   |    | <b>5b</b> Me Me H                            | <b>7</b> 66                        |
| <b>2a</b>                 |   |    | <b>5c</b> Me H H                             | <b>8</b> 78                        |
| <b>2a</b>                 |   |    | <b>5d</b> CN H H                             | <b>9</b> 83                        |
| <b>2b</b>                 | <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> | H  | <b>5a</b>                                    | <b>10</b> 53                       |
| <b>2c</b>                 | <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> | H  | <b>5a</b>                                    | <b>11</b> 71                       |
| <b>2d</b>                 | Ph  | Et | <b>5a</b>                                    | <b>12</b> 37                       |
| <b>2e</b>                 | Me  | H  | <b>5a</b>                                    | <b>13</b> 36                       |
| <b>2f</b>                 | PhCH <sub>2</sub>                         | H  | <b>5a</b>                                    | <b>14</b> 70                       |

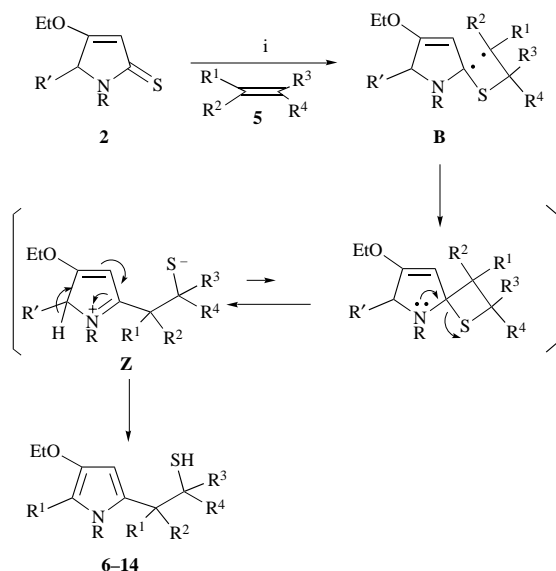
<sup>a</sup> Isolated yield. <sup>b</sup> In MeOH. <sup>c</sup> Photoreaction was carried out at 366 nm. <sup>d</sup> In the presence of stilbene (3 mol equiv.). <sup>e</sup> In the presence of azulene (2 mol equiv.).



**Scheme 5** Reagents and conditions: i, **5** (R' = Me), *hν*; ii, MeI. Structures **5a–d** and **6–14** are defined in Table 2.

ation of the 2,5-dihydro-1*H*-pyrrole-2-thiones **2b–f** in the presence of 2,3-dimethylbut-2-ene **5a** yielded the corresponding 2-(mercaptoalkyl)pyrroles **10–14** in 36–71% yield.

A plausible mechanism for the formation of the 2-(mercaptoalkyl)pyrroles **6–14** is presented in Scheme 6. In this mechanism, a spiroaminothietane is initially formed in a regio-specific manner through the photochemical [2 + 2] cycloaddition of the C=S bond of pyrrole-2-thiones **2** and the C=C bond of alkenes **5**. The regiochemistry is in accord with the formation of the more stable diradical intermediate **B** in the [2 + 2] photocycloaddition process.<sup>3,4,8–10</sup> The spiroaminothietanes thus



Scheme 6 Conditions: i, hv

formed are unstable owing to the participation of the lone-pair electrons on the nitrogen atom and they undergo thietane ring cleavage to yield the zwitterion **Z**. Subsequent 1,7-hydrogen transfer from C-5 to sulfur gives 2-(mercaptoalkyl)pyrroles **6-14**. The observed regioselective photoaddition reaction of 2,5-dihydro-1H-pyrrole-2-thiones **2** with alkenes **5** represents a ready mode of C–C bond formation and provides an efficient and novel method of alkylation of the pyrrole ring.

## Experimental

Mps and bps were measured with a Yanaco micro melting point apparatus (MP-J3) and a Büchi Kugelrohr distillation apparatus (KR-3), respectively, and are uncorrected. IR Spectra were recorded on a Hitachi 260-30 spectrophotometer. <sup>1</sup>H And <sup>13</sup>C NMR spectra were run on JEOL FX 100 (100 MHz) or JEOL-JNM-EX-270 (270 MHz) spectrometers with CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard. *J* Values are given in Hz.

### Materials

The 2,5-dihydro-1H-pyrrole-2-ones<sup>11</sup> **1a,b** and **e** and the 2,5-dihydro-1H-pyrrole-2-thiones<sup>6</sup> **2a,b** and **e** were prepared according to the methods previously described in the literature, and the 2,5-dihydro-1H-pyrrole-2-ones **1c,d** and **f** and -thiones **2c,d** and **f** were prepared by a modification of these methods. The thionation of compounds **1c,d** and **f** with Lawesson's reagent was carried out in 1,2-dimethoxyethane under reflux to yield the corresponding thiones **2c,d** and **f** exclusively.

**1-(*p*-Chlorophenyl)-4-ethoxy-2,5-dihydro-1H-pyrrole-2-one 1c** (35%). Mp 136–138 °C (Found: C, 60.55; H, 5.05; N, 6.0. C<sub>12</sub>H<sub>12</sub>ClNO<sub>2</sub> requires C, 60.65; H, 5.1; N, 5.9%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 1670 (CO) and 1625 (C=C);  $\delta_{\text{H}}$  1.41 (3 H, t, *J* 6.8), 4.04 (2 H, q, *J* 6.8), 4.18 (2 H, d), 5.09 (1 H, s), 7.18–7.35 (2 H, m) and 7.48–7.62 (2 H, m);  $\delta_{\text{C}}$  14.0 (q), 50.6 (t), 67.3 (t), 95.4 (d), 119.1 (d), 127.9 (s), 128.8 (d), 137.9 (s), 170.7 (s) and 171.7 (s).

**4-Ethoxy-5-ethyl-1-phenyl-2,5-dihydro-1H-pyrrole-2-one 1d** (47%). Mp 97–98 °C (Found: C, 72.55; H, 7.4; N, 6.05. C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub> requires C, 72.7; H, 7.4; N, 6.05%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 1670 (CO) and 1610 (C=C);  $\delta_{\text{H}}$  0.66 (3 H, t, *J* 6.8), 1.42 (3 H, t, *J* 6.8), 1.81 (2 H, dq, *J* 3.9 and 6.8), 4.04 (2 H, q, *J* 6.8), 4.68 (1 H, t, *J* 3.9), 5.15 (1 H, s) and 7.02–7.51 (5 H, m);  $\delta_{\text{C}}$  6.0 (q), 14.1 (q), 21.1 (t), 60.7 (t), 67.0 (d), 95.0 (d), 122.2 (d), 124.1 (d), 128.8 (d), 136.9 (s), 170.5 (s) and 174.1 (s).

**1-Benzyl-4-ethoxy-2,5-dihydro-1H-pyrrole-2-one 1f** (72%). Bp 175 °C/3 mmHg; mp 59–60 °C (Found: C, 71.75; H, 7.0; N, 6.45. C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub> requires C, 71.85; H, 6.95; N, 6.45%);  $\nu_{\max}$ (KBr)/

cm<sup>-1</sup> 1675 (CO) and 1615 (C=C);  $\delta_{\text{H}}$  1.35 (3 H, t, *J* 6.8), 3.77 (2 H, s), 4.04 (2 H, q, *J* 6.8), 4.56 (2 H, s), 5.06 (1 H, s) and 7.13–7.43 (5 H, m);  $\delta_{\text{C}}$  13.9 (q), 45.2 (t), 49.9 (t), 66.8 (t), 94.1 (d), 127.3 (d), 127.7 (d), 128.5 (d), 137.4 (s), 172.1 (s) and 172.2 (s).

**1-(*p*-Chlorophenyl)-4-ethoxy-2,5-dihydro-1H-pyrrole-2-thione 2c** (47%). Mp 134–135.5 °C (Found: C, 56.8; H, 4.8; N, 5.5. C<sub>12</sub>H<sub>12</sub>ClNOS requires C, 56.8; H, 4.75; N, 5.5%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 1600, 1495, 1340, 1205, 1136, 1020, 865, 825, 800 and 700;  $\delta_{\text{H}}$  1.43 (3 H, t, *J* 6.8), 4.06 (2 H, q, *J* 6.8), 4.53 (2 H, s), 5.77 (1 H, s), 7.28–7.44 (2 H, m) and 7.52–7.67 (2 H, m);  $\delta_{\text{C}}$  14.2 (q), 59.6 (t), 67.8 (t), 108.5 (d), 126.1 (d), 129.6 (d), 132.3 (s), 137.9 (s), 171.5 (s) and 198.0 (s).

**4-Ethoxy-5-ethyl-1-phenyl-2,5-dihydro-1H-pyrrole-2-thione 2d** (93%). Mp 94–95 °C (Found: C, 67.65; H, 6.85; N, 5.55. C<sub>14</sub>H<sub>17</sub>NOS requires C, 68.0; H, 6.95; N, 5.65%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 1585, 1490, 1330, 1325, 1200, 1140, 1025, 885, 805, 755 and 700;  $\delta_{\text{H}}$  0.71 (3 H, t, *J* 7.3), 1.43 (3 H, t, *J* 7.3), 1.58–1.87 (2 H, m), 4.07 (2 H, q, *J* 7.3), 4.78 (1 H, t, *J* 4.4), 5.78 (1 H, s) and 7.20–7.48 (5 H, m);  $\delta_{\text{C}}$  6.4 (q), 14.0 (q), 21.8 (t), 67.3 (t), 69.7 (d), 107.3 (d), 126.6 (d), 127.1 (d), 128.8 (d), 137.7 (s), 173.6 (s) and 197.2 (s).

**1-Benzyl-4-ethoxy-2,5-dihydro-1H-pyrrole-2-thione 2f** (83%). Mp 82–83 °C (Found: C, 66.5; H, 6.5; N, 5.95. C<sub>13</sub>H<sub>15</sub>NOS requires C, 66.9; H, 6.5; N, 6.0%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 1585, 1460, 1440, 1340, 1180, 1130, 1025, 875, 730 and 695;  $\delta_{\text{H}}$  1.33 (3 H, t, *J* 6.8), 3.93 (2 H, q, *J* 6.8), 3.96 (2 H, s), 5.03 (2 H, s), 5.64 (1 H, s) and 7.21–7.34 (5 H, m);  $\delta_{\text{C}}$  13.8 (q), 49.1 (t), 56.2 (t), 67.2 (t), 106.1 (d), 127.5 (d), 127.9 (d), 128.6 (d), 136.3 (s), 171.8 (s) and 197.5 (s).

### General procedure for the photochemical reactions of 2,5-dihydro-1H-pyrrole-2-thiones **2** in the presence of triethylamine

A solution of the thione **2** (200 mg) in benzene (70 cm<sup>3</sup>) in the presence of an excess of triethylamine (~1 cm<sup>3</sup>) was irradiated in a Pyrex vessel under argon with a high-pressure mercury lamp (Eikosha EHP-300 W) for 3–5 h at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column (Wakogel C-300 for flash chromatography) with benzene–hexane (4:1) as eluent to give the pyrroles **3** or the pyrrolidine-2-thiones **4**. The structure of pyrroles **3a,b** was confirmed by direct comparison of their IR and NMR spectra with those of authentic samples.<sup>6</sup>

**1-(*p*-Chlorophenyl)-3-ethoxypyrrole 3c**. Bp 160 °C/3 mmHg (Found: C, 65.0; H, 5.55; N, 6.25. C<sub>12</sub>H<sub>12</sub>ClNO requires C, 65.0; H, 5.45; N, 6.3%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1595, 1585, 1560, 1500, 1370, 1340, 1240, 1090, 1050, 820 and 730;  $\delta_{\text{H}}$  1.38 (3 H, t, *J* 6.8), 3.94 (2 H, q, *J* 6.8), 6.02–6.07 (1 H, m), 6.55–6.60 (1 H, m), 6.81 (1 H, t, *J* 3.4) and 7.14–7.40 (4 H, m);  $\delta_{\text{C}}$  14.9 (q), 66.1 (t), 101.2 (d), 117.0 (d), 120.4 (d), 129.5 (d), 130.1 (s), 139.3 (s) and 149.8 (s).

**3-Ethoxy-2-ethyl-1-phenylpyrrole 3d**. Bp 135 °C/3 mmHg (Found: C, 78.1; H, 7.9; N, 6.45. C<sub>14</sub>H<sub>17</sub>NO requires C, 78.1; H, 7.95; N, 6.5%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1600, 1580, 1500, 1370, 1350, 1240, 1175, 1145, 760 and 695;  $\delta_{\text{H}}$  0.96 (3 H, t, *J* 7.3), 1.36 (3 H, t, *J* 6.8), 2.60 (2 H, q, *J* 7.3), 3.99 (2 H, q, *J* 6.8), 6.01 (1 H, d, *J* 2.9), 6.50 (1 H, d, *J* 2.9) and 7.18–7.51 (5 H, m);  $\delta_{\text{C}}$  14.1 (q), 15.4 (q), 16.7 (t), 67.3 (t), 98.2 (d), 117.4 (d), 120.2 (s), 125.6 (d), 126.7 (d), 129.0 (d), 140.8 (s) and 143.9 (s).

**4-Ethoxy-1-methylpyrrolidine-2-thione 4e**. Bp 145 °C/3 mmHg (Found: C, 52.6; H, 8.35; N, 8.7. C<sub>7</sub>H<sub>13</sub>NOS requires C, 52.8; H, 8.25; N, 8.8%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1525, 1325 and 1085;  $\delta_{\text{H}}$  1.91 (3 H, t, *J* 6.8), 3.11–3.17 (2 H, m), 3.27 (3 H, s), 3.47 (2 H, dq, *J* 2.0 and 6.8), 3.62–3.98 (2 H, m) and 4.02–4.24 (1 H, m);  $\delta_{\text{C}}$  15.0 (q), 35.1 (q), 50.9 (t), 62.9 (t), 64.2 (t), 72.1 (d) and 198.9 (s).

**1-Benzyl-4-ethoxypyrrolidine-2-thione 4f**. Bp 180 °C/3 mmHg (Found: C, 66.25; H, 7.45; N, 5.95. C<sub>13</sub>H<sub>17</sub>NOS requires C, 66.35; H, 7.3; N, 5.95%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1605, 1500, 1445, 1335, 1265, 1120, 1095, 740 and 700;  $\delta_{\text{H}}$  1.13 (3 H, t, *J* 6.8), 3.18 (2 H, d, *J* 4.4), 3.39 (2 H, dq, *J* 2.4 and 6.8), 3.58–3.70 (2 H, m),

4.01–4.19 (1 H, m), 5.00 (2 H, s) and 7.31 (5 H, s);  $\delta_C$  14.9 (q), 50.9 (t), 51.1 (t), 59.4 (t), 64.0 (d), 72.1 (t), 127.7 (d), 127.8 (d), 128.5 (d), 134.4 (s) and 199.4 (s).

#### General procedure for the photochemical reactions of 2,5-dihydro-1H-pyrrole-2-thiones **2** in the presence of alkenes **5**

A solution of the thione **2** (200 mg) in benzene (70 cm<sup>3</sup>) in the presence of an excess of alkene **5** (~1 cm<sup>3</sup>) was irradiated, under the same conditions as described above, for 15–20 h. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene–hexane (4:1) to give the corresponding pyrrole derivatives **6–14**.

**4-Ethoxy-2-(2'-mercapto-2',3'-dimethylbutan-3'-yl)-1-phenylpyrrole 6.** Mp 103–104 °C (Found: C, 71.35; H, 8.4; N, 4.6. C<sub>18</sub>H<sub>25</sub>NOS requires C, 71.25; H, 8.3; N, 4.6%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2550, 1575, 1485, 1370, 1350, 1095, 1045, 780, 760, 705 and 695;  $\delta_H$  1.20 (6 H, s), 1.36 (6 H, s), 1.36 (3 H, t, *J* 6.8), 1.60 (1 H, s), 3.82 (2 H, q, *J* 6.8), 6.01 (2 H, br s) and 7.34 (5 H, s);  $\delta_C$  15.0 (q), 26.9 (q), 30.3 (q), 45.1 (s), 52.9 (s), 65.5 (t), 101.4 (d), 107.9 (d), 127.9 (d), 129.6 (d), 136.0 (s), 143.6 (s) and 145.9 (s).

**4-Ethoxy-2-(2'-mercapto-3'-methylbutan-3'-yl)-1-phenylpyrrole 7.** Bp 170 °C/3 mmHg (Found: C, 70.5; H, 8.05; N, 4.9. C<sub>17</sub>H<sub>23</sub>NOS requires C, 70.55; H, 8.0; N, 4.85%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2550, 1635, 1575, 1500, 1370, 1350, 1050, 775 and 700;  $\delta_H$  1.11 (3 H, d, *J* 6.8), 1.18 (3 H, s), 1.20 (3 H, s), 1.28 (1 H, d, *J* 5.4), 1.36 (3 H, t, *J* 6.8), 2.97–3.24 (1 H, m), 3.86 (2 H, q, *J* 6.8), 5.86 (1 H, s), 6.11 (1 H, br s) and 7.35–7.40 (5 H, m);  $\delta_C$  15.5 (q), 19.9 (q), 24.1 (q), 25.2 (q), 40.7 (s), 43.8 (d), 65.5 (t), 98.5 (d), 107.4 (d), 128.3 (d), 128.5 (d), 129.0 (d), 138.6 (s), 142.6 (s) and 146.2 (s).

**4-Ethoxy-2-(1'-mercapto-2'-methylpropan-2'-yl)-1-phenylpyrrole 8.** Mp 87–89 °C (Found: C, 69.45; H, 7.8; N, 5.0. C<sub>16</sub>H<sub>21</sub>NOS requires C, 69.8; H, 7.7; N, 5.1%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2550, 1635, 1575, 1495, 1375, 1350, 1045, 775 and 700;  $\delta_H$  1.12 (1 H, t, *J* 7.8), 1.21 (6 H, s), 1.36 (3 H, t, *J* 6.8), 2.45 (2 H, d, *J* 7.8), 3.87 (2 H, q, *J* 6.8), 5.86 (1 H, d, *J* 2.0), 6.14 (1 H, d, *J* 2.0) and 7.39 (5 H, s);  $\delta_C$  15.0 (q), 28.3 (q), 37.1 (t), 37.9 (s), 65.5 (t), 98.8 (d), 107.4 (d), 128.4 (d), 128.5 (d), 128.9 (d), 136.8 (s), 142.3 (s) and 146.2 (s).

**2-(2'-Cyano-1'-mercapto-2'-yl)-4-ethoxy-1-phenylpyrrole 9.** Bp 160 °C/3 mmHg (Found: C, 67.35; H, 6.35; N, 9.65. C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O requires C, 67.1; H, 6.35; N, 9.8%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2560, 2230, 1640, 1580, 1500, 1380, 1360, 1055, 775 and 700;  $\delta_H$  1.37 (3 H, t, *J* 6.8), 1.39 (1 H, X of ABX), 1.68 (3 H, s), 2.66 (1 H, A of ABX, *J* 8.3 and 13.7), 2.75 (1 H, B of ABX, *J* 9.3 and 13.7), 3.89 (2 H, q, *J* 6.8), 6.02 (1 H, d, *J* 1.9), 6.29 (1 H, *J* 1.9) and 7.25–7.46 (5 H, m);  $\delta_C$  14.9 (q), 24.6 (q), 34.0 (t), 38.5 (s), 65.9 (t), 100.4 (d), 109.2 (d), 121.6 (s), 126.7 (s), 128.2 (d), 128.5 (d), 129.1 (d), 139.7 (s) and 146.5 (s).

A solution of compound **9** (152 mg), sodium hydride (30 mg) and methyl iodide (213 mg) in benzene (20 cm<sup>3</sup>) was heated to reflux for 3 h under argon. Usual work-up gave the sulfide **15** in 65% yield.

**2-Cyano-2-(4'-ethoxy-N-phenylpyrrol-2'-yl)propyl methyl sulfide 15.** Bp 180 °C/3 mmHg;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2210, 1645, 1595, 1580, 1500, 1375, 1340, 1185, 1115, 1055, 780 and 700;  $\delta_H$  1.37 (3 H, t, *J* 6.9), 1.70 (3 H, s), 1.98 (3 H, s), 2.72 (2 H, AB q), 3.89 (2 H, q, *J* 6.9), 6.01 (1 H, d, *J* 1.9), 6.20 (1 H, d, *J* 1.9) and 7.35–7.50 (5 H, m);  $\delta_C$  15.0 (q), 17.5 (q), 25.4 (q), 37.4 (s), 44.2 (t), 65.9 (t), 99.7 (d), 109.0 (d), 122.4 (s), 126.0 (d), 127.2 (s), 128.9 (d), 129.0 (d), 139.9 (s) and 146.6 (s).

**4-Ethoxy-2-(2'-mercapto-2',3'-dimethylbutan-3'-yl)-1-(p-tolyl)pyrrole 10.** Bp 160 °C/3 mmHg (Found: C, 71.7; H, 8.6; N, 4.4. C<sub>19</sub>H<sub>27</sub>NOS requires C, 71.9; H, 8.55; N, 4.4%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2550, 1575, 1500, 1450, 1370, 1445, 1085, 1045, 830, 780 and 695;  $\delta_H$  1.21 (6 H, s), 1.35 (6 H, s), 1.35 (3 H, t, *J* 7.3), 1.60 (1 H, s), 2.38 (3 H, s), 3.86 (2 H, q, *J* 7.3), 6.00 (2 H, br s) and 7.06–7.36 (4 H, m);  $\delta_C$  15.0 (q), 21.1 (q), 27.0 (q), 30.3 (q), 45.1 (s), 53.0 (s), 65.5 (t), 101.2 (d), 107.9 (d), 128.5 (d), 129.3 (d), 136.0 (s), 137.7 (s), 141.0 (s) and 145.7 (s).

**1-(p-Chlorophenyl)-4-ethoxy-2-(2'-mercapto-2',3'-dimethylbutan-3'-yl)-pyrrole 11.** Mp 138–139 °C (Found: C, 63.8; H, 7.25; N, 4.15. C<sub>18</sub>H<sub>24</sub>ClNOS requires C, 64.0; H, 7.15; N, 4.15%);  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 2550, 1575, 1490, 1380, 1355, 1090, 1055, 845, 790, 775 and 690;  $\delta_H$  1.20 (6 H, s), 1.35 (6 H, s), 1.35 (3 H, t, *J* 6.8), 1.57 (1 H, s), 3.85 (2 H, q, *J* 6.8), 6.00 (2 H, s) and 7.30 (4 H, s);  $\delta_C$  15.0 (q), 27.0 (q), 30.2 (q), 45.1 (s), 52.8 (s), 65.5 (t), 101.8 (d), 107.8 (d), 128.1 (d), 130.9 (d), 133.7 (s), 136.3 (s), 142.2 (s) and 146.1 (s).

**4-Ethoxy-5-ethyl-2-(2'-mercapto-2',3'-dimethylbutan-3'-yl)-1-phenylpyrrole 12.** Bp 160 °C/3 mmHg (Found: C, 72.35; H, 8.65; N, 4.45. C<sub>20</sub>H<sub>29</sub>NOS requires C, 72.45; H, 8.8; N, 4.35%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2550, 1600, 1500, 1370, 1350, 1155, 1105, 1050, 760 and 700;  $\delta_H$  0.82 (3 H, t, *J* 7.3), 1.16 (6 H, s), 1.35 (6 H, s), 1.35 (3 H, t, *J* 6.8), 1.60 (1 H, s), 2.15 (2 H, q, *J* 7.3), 3.99 (2 H, q, *J* 6.8), 6.03 (1 H, s) and 7.19–7.44 (5 H, s);  $\delta_C$  14.6 (q), 15.4 (q), 16.9 (t), 27.0 (q), 30.4 (q), 45.0 (s), 53.2 (s), 67.1 (t), 100.9 (d), 122.4 (s), 127.8 (d), 128.5 (d), 130.9 (d), 132.8 (s), 141.1 (s) and 141.3.

**4-Ethoxy-2-(2'-mercapto-2',3'-dimethylbutan-3'-yl)-1-methylpyrrole 13.** Bp 140 °C/3 mmHg (Found: C, 64.55; H, 9.6; N, 5.85. C<sub>13</sub>H<sub>23</sub>NOS requires C, 64.7; H, 9.6; N, 5.8%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2550, 1575, 1460, 1370, 1325 and 1055;  $\delta_H$  1.34 (3 H, t, *J* 6.8), 1.41 (6 H, s), 1.48 (6 H, s), 1.57 (1 H, s), 3.72 (3 H, s), 3.85 (2 H, q, *J* 6.8), 5.81 (1 H, s) and 5.89 (1 H, br s);  $\delta_C$  15.0 (q), 26.5 (q), 29.6 (q), 38.7 (q), 44.6 (s), 53.4 (s), 65.6 (t), 100.4 (d), 106.1 (d), 134.3 (s) and 145.2 (s).

**1-Benzyl-4-ethoxy-2-(2'-mercapto-2',3'-dimethylbutan-3'-yl)pyrrole 14.** Bp 190 °C/3 mmHg (Found: C, 71.95; H, 8.45; N, 4.6. C<sub>19</sub>H<sub>27</sub>NOS requires C, 71.9; H, 8.55; N, 4.6%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2560, 1580, 1495, 1450, 1375, 1330, 1115, 1060, 780, 725 and 695;  $\delta_H$  1.33 (3 H, t, *J* 7.3), 1.37 (6 H, s), 1.42 (6 H, s), 1.53 (1 H, s), 3.83 (2 H, q, *J* 7.3), 5.30 (2 H, s), 5.85 (1 H, d, *J* 1.5), 6.01 (1 H, br s), 6.85–7.00 (1 H, m) and 7.01–7.38 (4 H, m);  $\delta_C$  14.9 (q), 21.1 (q), 29.4 (q), 44.5 (s), 52.9 (s), 53.9 (t), 65.4 (t), 100.9 (d), 105.4 (d), 125.6 (d), 126.7 (d), 128.4 (d), 134.6 (s), 140.1 (s) and 145.5 (s).

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