

## Photoreactions of Indoline-2-thiones with Cyanoalkenes

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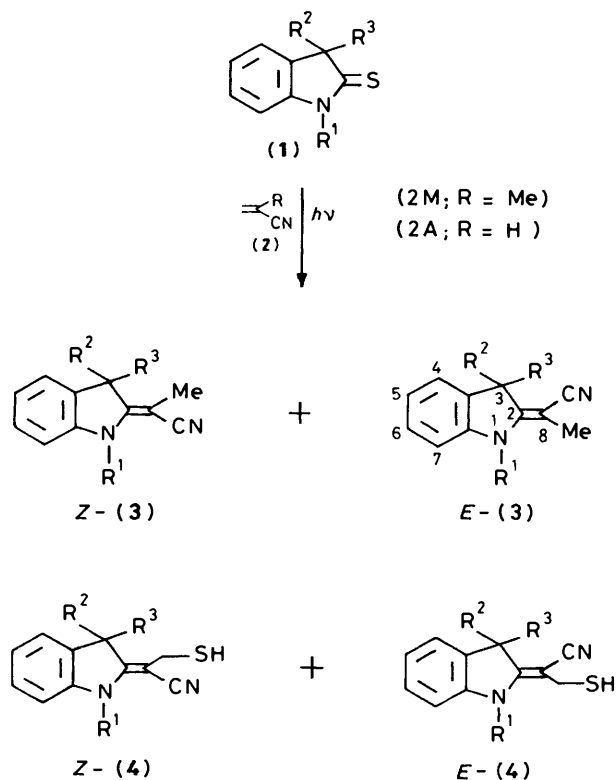
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The photochemical reactions of indoline-2-thiones with alkenes have been examined. Irradiation of indoline-2-thiones (**1**) in the presence of cyano olefins (**2**) gave (*E/Z*)-2-alkylideneindolines (**3**) and (**4**) through ring cleavage of thietanes, which were formed by [2 + 2] photocycloaddition of thiocarbonyl and olefin. Aminothietane (**6**), hitherto unknown, was first isolated in the photoreaction of 1,3,3-trimethylindoline-2-thione (**1a**) with isobutene.

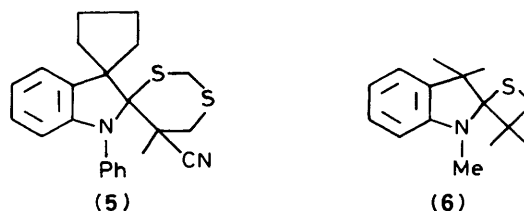
There has been a great deal of interest in the photochemistry of thiocarbonyl compounds over the past two decades.<sup>1-4</sup> As a result of differences in chemical reactivity and thermodynamic properties the observed photoreactions of thiocarbonyl compounds often follow a different course from those of analogous carbonyl compounds. On the other hand, relatively few reports have dealt with the photochemical properties of thioamides.<sup>5-12</sup> It has recently been reported that thioamides undergo intramolecular<sup>10</sup> or intermolecular<sup>12</sup> photochemical cycloaddition with alkenes. Of these reactions, the formation of aminothietanes was suggested as the intermediate although such a compound has not yet been isolated. However, in the photochemical reaction of *N*-(*o*-vinylphenyl)thioamides, de Mayo *et al.* confirmed the formation of an aminothietane by the low-temperature n.m.r. spectroscopy.<sup>10</sup> Das *et al.* have shown that indoline-2-thiones undergo photoinduced addition to methyl methacrylate to give a mixture of isomeric 2-substituted indoles,<sup>7,8</sup> in which one of the isomers has been employed as a key intermediate in a synthesis of desethylcatharanthine. In our exploration of the photochemical reactions of heteroaromatic thiones such as pyridinethiones,<sup>13a,b</sup> quinolinethiones,<sup>13a</sup> quinoxalinethiones,<sup>14</sup> and pyrimidinethiones,<sup>15</sup> we found that photoinduced addition of these thiones to alkenes provided a novel method for carbon-carbon bond formation in heterocyclic compounds. We now report both the photochemical reactions of indoline-2-thiones (**1**) with alkenes (**2**) which have potential in synthesis and also the first isolation of the aminothietane (**6**).

### Results and Discussion

The indoline-2-thiones (**1a-j**) are readily accessible by direct sulphuration of their oxygen analogues with the dimer of *p*-methoxyphenylthionophosphine (Lawesson's reagent) in reasonable yields. When a benzene solution of the indoline-2-thiones (**1a-c, i, j**) was irradiated with a high-pressure mercury lamp through a Pyrex filter under argon, unchanged starting material was recovered. However, irradiation of 1,3,3-trimethylindoline-2-thione (**1a**) in benzene in the presence of methacrylonitrile (**2M**) under the same conditions as described above for 5 h gave a mixture, inseparable by chromatography, of *E/Z*-isomers of 2-alkylideneindoline (**3a**) (59%) in a ratio of 13:7. The structure of (**3a**) was elucidated on the basis of spectroscopic properties and elemental analysis. Stereochemical assignments to the *E/Z*-isomers of (**3a**) were tentatively made as shown in the Figure on the basis of n.m.r. spectral results. The 1-methyl protons of the *E*-isomer appeared as a singlet at  $\delta$  3.43 (3 H) to higher field than those [ $\delta$  3.56 (3 H)] of the *Z*-isomer probably owing to the anisotropic effect of the cyano group.<sup>16</sup> On the other hand, the 3-methyl protons of the *E*-isomer [ $\delta$  1.65 (6 H)] were observed at lower field than those [ $\delta$  1.53 (6 H)] of the *Z*-isomer. Similarly, indoline-2-thiones (**1b-i**) reacted photochemically with methacrylonitrile (**2M**) to yield the 2-alkylideneindolines (**3b-i**) (40-90%). The structure of the



photoproducts was confirmed on the basis of spectral data and elemental analyses. The 2-alkylideneindoline (**3e**) was treated with ozone to give 3,3-dimethyl-1-phenylindolin-2-one (37%). The photoproduct (**3e**) was assigned an *E*-configuration on the basis of n.m.r. spectral results in which the 8-methyl protons [ $\delta$  1.29 (3 H)] appeared to higher field than the corresponding olefinic methyl protons adjacent to the cyano group ( $\delta$  around 2.00)<sup>16</sup> owing to the anisotropic effect of the phenyl group. By analogy the stereochemistry (*E/Z*) of other photoproducts was assigned from their n.m.r. spectra. Irradiation of the spiro indoline-2-thione (**1j**) in benzene in the presence of methacrylonitrile (**2M**) gave the 2-alkylideneindoline (**3j**) (26%) and the unexpected product (**5**) (43%). The structure of the latter was



**Table 1.** Yield of photoproducts (3)—(5)

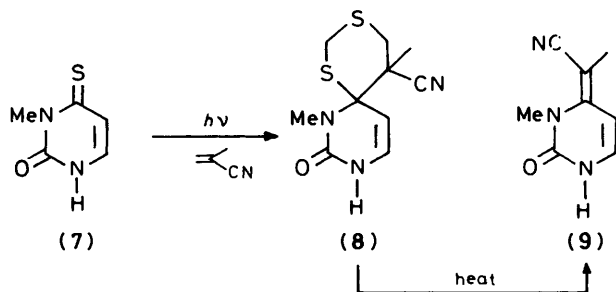
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield (%) <sup>a</sup> (E/Z) <sup>b</sup>			
				Olefin (2)	(3)	(4)	Recovered (1)
(1a)	Me	Me	Me	(2M)	59 (13:7)		5
(1a)	Me	Me	Me	(2A)		84 (1:0) <sup>c</sup>	13
(1b)	Me	Ph	Ph	(2M)	64 (1:0)		Trace
(1b)	Me	Ph	Ph	(2A)		81 (1:0)	Trace
(1c)	Bu	Me	Me	(2M)	87 (13:7)		Trace
(1c)	Bu	Me	Me	(2A)		76 (1:1)	Trace
(1d)	PhCH <sub>2</sub>	Me	Me	(2M)	83 (9:1)		Trace
(1d)	PhCH <sub>2</sub>	Me	Me	(2A)		80 (9:1)	Trace
(1e)	Ph	Me	Me	(2M)	90 (1:0)		7
(1e)	Ph	Me	Me	(2A)		94 (1:0)	5
(1f)	Ph	Me	Pent <sup>1</sup>	(2M)	56 (1:0)		Trace
(1g)	Ph	Me	<sup>E</sup> tO(CH <sub>2</sub> ) <sub>2</sub>	(2M)	49 (1:0)		15
(1h)	Ph	-(CH <sub>2</sub> ) <sub>5</sub> <sup>-</sup>		(2M)	56 (1:0)		Trace
(1h)	Ph	-(CH <sub>2</sub> ) <sub>5</sub> <sup>-</sup>		(2A)		99 (4:1) <sup>d</sup>	Trace
(1i)	Ph	-(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> <sup>-</sup>		(2M)	40 (1:0)		Trace
(1i)	Ph	-(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> <sup>-</sup>		(2A)		98 (10:1)	Trace
(1j)	Ph	-(CH <sub>2</sub> ) <sub>4</sub> <sup>-</sup>		(2M)	26 (1:0)		6
(1j)	Ph	-(CH <sub>2</sub> ) <sub>4</sub> <sup>-</sup>		(2A)		99 (13:7) <sup>d</sup>	Trace

<sup>a</sup> Isolated yield. <sup>b</sup> Ratio of E/Z-isomers determined by the n.m.r. spectrum. <sup>c</sup> The E-isomer isomerized gradually to Z-isomer in CDCl<sub>3</sub> solution (E/Z = 3:2). <sup>d</sup> Two isomers were separated by silica gel column chromatography.

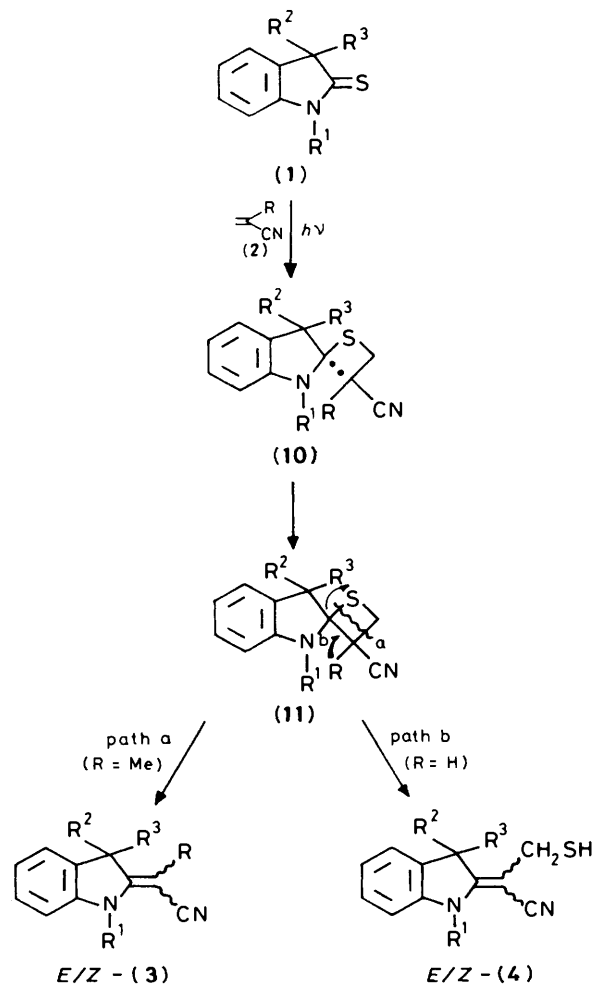
**Table 2.** Yield of the 2-alkylideneindoline (3e) in the photoreaction (366 nm)<sup>a</sup> of the indoline-2-thione (1e)<sup>b</sup>

Additive	Conversion (%)	Yield of (3e) (%) <sup>f</sup>
None	42	52
Thioxanthone <sup>d</sup>	48	81
Michler's ketone <sup>d</sup>	34	82
<i>trans</i> -Stilbene <sup>e</sup>	22	34
Cyclo-octatetraene	24	29

<sup>a</sup> The photoreaction was carried out in degassed benzene at room temperature. Irradiation time: 3 h. A Pyrex filter and methanol solution of naphthalene (5 g l<sup>-1</sup>) were used to isolate the 366 nm region. <sup>b</sup> U.v. spectrum of (1e) showed an end absorption until 380 nm (ε 250 at 366 nm). <sup>c</sup> Isolated yield. <sup>d</sup> A triplet sensitizer absorbed more than 95% incident light. <sup>e</sup> U.v. spectrum of *trans*-stilbene shows no absorption at 366 nm.

**Scheme 1.**

confirmed on the basis of spectral and elemental results. The methyl signal in the n.m.r. spectrum of compound (5) appeared at δ 1.52 and two AB systems centred at δ 2.42 and 3.00, and 3.27 and 3.76 were attributed to CH<sub>2</sub>S methylene protons. The mass spectrum of (5) showed a molecular ion peak at *m/z* 392 (*M*<sup>+</sup>) and two characteristic fragments at *m/z* 325 (*M*<sup>+</sup> - C<sub>4</sub>H<sub>5</sub>N) and 300 (*M*<sup>+</sup> - 2 × CH<sub>2</sub>S). Although the mechanism for the formation of (5) is unclear at present, formation of a similar photoproduct was reported in the photochemistry of thiouracil and methacrylonitrile by Jouin and Fourrey.<sup>6</sup> They also

**Scheme 2.**

reported that the spiro-1,3-dithiane (8) in refluxing pyridine yielded the 4-alkylidene-2-thiopyridine (9) (Scheme 1). However, the photoproduct (5) when heated to reflux in benzene or

Table 3. Physical properties of the photoproducts (3)—(6)

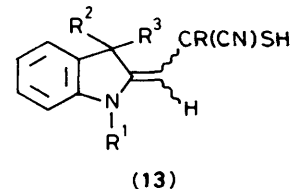
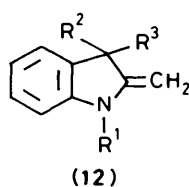
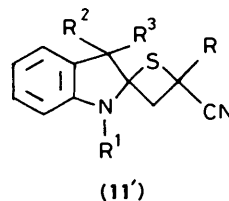
Compd.	$\nu_{\max.}/(\text{cm}^{-1})$	$\delta_{\text{H}}(\text{CDCl}_3)$	$\delta_{\text{C}}(\text{CDCl}_3)$
(3a)	(KBr) ( <i>E/Z</i> ) 2 170, 1 615, 1 585, 1 490, 1 340, 1 130, 750	( <i>E</i> ) 1.65 (6 H, s), 2.47 (3 H, s), 3.43 (3 H, s), 6.65 (1 H, br d), 6.82—7.28 (3 H, m)	17.0(q), 26.2(q), 34.0(q), 47.6(s), 69.5(s), 106.9(d), 121.2(d), 121.5(d), 123.9(s), 127.7(d), 138.1(s), 145.5(s), 167.8(s)
		( <i>Z</i> ) 1.53 (6 H, s), 2.14 (3 H, s), 3.56 (3 H, s), 6.65 (1 H, br d), 6.82—7.28 (3 H, m)	16.2(q), 25.7(q), 32.7(q), 47.6(s), 65.9(s), 106.7(d), 120.9(d), 121.5(d), 123.6(s), 127.9(d), 137.9(s), 145.2(s), 166.0(s)
(3b)	(KBr) ( <i>E</i> ) 2 160, 1 575, 1 475, 1 450, 1 330, 730, 690	( <i>E</i> ) 1.46 (3 H, s), 3.72 (3 H, s), 6.66—7.38 (14 H, m)	17.5(q), 33.2(q), 65.1(s), 73.1(s), 107.0(d), 121.5(d), 122.9(s), 124.2(d), 127.1(d), 128.3(d), 128.8(d), 129.3(s), 138.1(s), 139.9(s), 145.5(s), 164.5(s)
(3c)	(CDCl <sub>3</sub> ) ( <i>E/Z</i> ) 2 170, 1 580, 1 455, 1 335, 1 180, 1 130, 1 090	( <i>E</i> ) 0.97 (3 H, t), 1.21—1.99 (4 H, m), 1.65 (6 H, s), 2.12 (3 H, s), 3.77 (2 H, br t), 6.60—6.72 (1 H, m), 6.80—7.26 (3 H, m)	13.8(q), 16.8(q), 19.8(t), 26.2(q), 30.6(t), 43.8(t), 47.7(s), 69.3(s), 124.2(s), 166.6(s) in addition to aromatic carbon peaks
		( <i>Z</i> ) 0.97 (3 H, t), 1.21—1.99 (4 H, m), 1.52 (6 H, s), 2.16 (3 H, s), 4.02 (2 H, br t), 6.60—6.72 (1 H, m), 6.80—7.26 (3 H, m)	14.0(q), 16.6(q), 19.7(t), 25.7(q), 29.9(t), 44.9(t), 47.7(s), 69.3(s), 124.2(s), 164.3(s) in addition to aromatic carbon peaks
(3d)	(KBr) ( <i>E/Z</i> ) 2 180, 1 605, 1 570, 1 470, 1 330, 1 175, 740	( <i>E</i> ) 1.75 (6 H, s), 1.97 (3 H, s), 5.02 (2 H, s), 6.46—6.61 (1 H, m), 6.93—7.43 (8 H, m)	16.6(q), 26.5(q), 47.9(s), 49.4(t), 70.0(s), 107.6(d), 121.7(d), 121.8(d), 123.7(s), 125.5(d), 127.5(d), 127.8(d), 129.0(d), 137.0(s), 138.0(s), 145.0(s), 167.2(s)
		( <i>Z</i> ) 1.60 (6 H, s), 2.14 (3 H, s), 5.34 (2 H, s), 6.46—6.61 (1 H, m), 6.93—7.43 (8 H, m)	16.6(q), 26.5(q), 47.6(s), 72.6(s), 108.2(d), 121.9(d), 123.2(s), 127.5(d), 128.2(d), 128.4(d), 129.6(d), 137.6(s), 139.1(s), 145.8(s), 165.9(s)
(3e)	(KBr) ( <i>E</i> ) 2 210, 1 635, 1 605, 1 495, 1 305, 1 215, 765, 700	( <i>E</i> ) 1.29 (3 H, s), 1.79 (6 H, s), 6.34—6.42 (1 H, m), 6.88—7.60 (8 H, m)	16.6(q), 26.5(q), 47.6(s), 72.6(s), 108.2(d), 121.9(d), 123.2(s), 127.5(d), 128.2(d), 128.4(d), 129.6(d), 137.6(s), 139.1(s), 145.8(s), 165.9(s)
(3f)	(KBr) ( <i>E</i> ) 2 170, 16 160, 1 580, 1 445, 740	( <i>E</i> ) 0.82 (3 H, d, <i>J</i> 6.4 Hz), 0.87 (3 H, d, <i>J</i> 6.4 Hz), 0.52—2.07 (4 H, m), 1.31 (3 H, s), 1.76 (3 H, s), 2.53—2.84 (1 H, m), 6.30—6.39 (1 H, m), 6.81—7.61 (8 H, m)	16.7(q), 22.4(q), 26.7(q), 28.0(d), 33.2(t), 33.9(t), 51.7(s), 72.5(s), 108.0(d), 121.8(d), 123.1(s), 127.5(d), 128.2(d), 128.5(d), 129.6(d), 135.8(s), 139.2(s), 146.7(s), 164.3(s)
(3g)	(KBr) ( <i>E</i> ) 2 170, 1 615, 1 585, 755, 700	( <i>E</i> ) 1.04 (3 H, t, <i>J</i> 6.8 Hz), 1.30 (3 H, s), 1.79 (3 H, s), 2.03—2.33 (1 H, m), 2.87—3.50 (3 H, m), 3.33 (2 H, q, <i>J</i> 6.8 Hz), 6.30—6.39 (1 H, m), 6.86—7.61 (8 H, m)	15.1(q), 16.7(q), 27.0(q), 38.6(t), 50.0(s), 65.9(t), 67.2(t), 72.9(s), 108.1(d), 121.9(d), 122.1(d), 123.1(s), 127.7(d), 128.3(d), 128.5(d), 129.6(d), 135.3(s), 139.2(s), 146.5(s), 164.0(s)
(3h)	(KBr) ( <i>E</i> ) 2 175, 1 620, 1 585, 1 495, 1 460, 1 240, 745, 700	( <i>E</i> ) 1.30 (3 H, s), 1.60—2.05 (8 H, m), 2.50—2.90 (2 H, m), 6.40 (1 H, dd, <i>J</i> 1.0, 7.3 Hz), 6.84—7.60 (7 H, m), 7.65—7.75 (1 H, m)	17.4(q), 21.7(t), 24.1(t), 33.8(t), 51.1(s), 72.3(s), 108.6(d), 121.2(d), 123.6(s), 125.0(d), 127.3(d), 128.2(d), 128.6(d), 129.6(d), 136.4(s), 139.6(s), 146.2(s), 166.4(s)
(3i)	(KBr) ( <i>E</i> ) 2 170, 1 620, 1 585, 1 480, 1 460, 1 245, 840, 760, 700	( <i>E</i> ) 1.33 (3 H, s), 1.72 (2 H, br d), 2.88—3.21 (2 H, m), 4.06—4.29 (4 H, m), 6.43 (1 H, dd, <i>J</i> 1.5, 7.3 Hz), 6.88—7.69 (7 H, m), 7.82 (1 H, dd, <i>J</i> 1.5, 7.3 Hz)	17.3(q), 33.6(t), 48.4(s), 63.2(t), 73.4(s), 108.9(d), 121.6(d), 122.9(s), 124.7(d), 127.9(d), 128.4(d), 128.6(d), 129.8(d), 135.5(s), 139.3(s), 146.3(s), 164.7(s)
(3j)	(KBr) ( <i>E</i> ) 2 175, 1 620, 1 585, 1 480	( <i>E</i> ) 1.30 (3 H, m), 1.95—2.90 (8 H, m), 6.32—6.41 (1 H, m), 6.83—7.60 (8 H, m)	16.7(q), 27.2(t), 41.8(t), 57.6(s), 71.8(s), 108.0(d), 122.1(d), 123.1(d), 127.1(d), 128.2(d), 128.6(d), 129.6(d), 139.4(s), 140.3(s), 145.5(s), 166.7(s)
(4a)	(KBr) ( <i>E</i> ) 2 535, 2 175, 1 615, 1 580, 1 485, 1 340, 1 125, 735	( <i>E</i> ) 1.65 (6 H, s), 2.06 (1 H, t, <i>J</i> 6.3 Hz), 3.56 (3 H, s), 3.65 (2 H, dd, <i>J</i> 6.3 Hz), 6.74 (1 H, br d), 6.90—7.32 (3 H, m)	25.3(t), 26.1(q), 33.6(q), 48.0(s), 76.9(s), 107.3(d), 121.7(d), 121.7(s), 122.2(d), 127.8(d), 140.0(s), 145.0(s), 168.1(s)
		( <i>Z</i> ) 1.55 (6 H, s), 2.01 (1 H, t, <i>J</i> 7.3 Hz), 3.61 (3 H, s), 3.67 (2 H, d, <i>J</i> 7.3 Hz), 6.63 (1 H, br s), 6.87—7.31 (3 H, m)	25.4(t), 26.9(q), 32.6(q), 48.0(s), 76.9(s), 107.3(s), 121.2(d), 121.7(d), 121.7(s), 128.1(d), 140.0(s), 144.5(s), 166.0(s)
(4b)	(KBr) ( <i>E</i> ) 2 190, 1 615, 1 580, 1 490, 1 340, 1 100, 740, 730, 695	( <i>E</i> ) 0.67 (1 H, t, <i>J</i> 8.3 Hz), 3.02 (2 H, d, <i>J</i> 8.3 Hz), 3.76 (3 H, s), 6.70—6.88 (2 H, m), 7.02—7.77 (12 H, m)	26.9(t), 33.0(q), 65.1(s), 80.3(s), 107.4(d), 121.0(s), 122.0(d), 124.0(d), 127.4(d), 128.5(d), 128.5(d), 138.2(s), 139.8(s), 144.8(s), 163.6(s)
(4c)	(CDCl <sub>3</sub> ) ( <i>E/Z</i> ) 2 170, 1 570, 1 455, 1 350, 1 185	( <i>E</i> ) 1.00 (3 H, t), 1.66 (6 H, s), 2.03 (1 H, t, <i>J</i> 7.3 Hz), 1.25—2.00 (4 H, m), 3.68 (2 H, d, <i>J</i> 7.3 Hz), 4.07 (2 H, t), 6.67—7.29 (4 H, m)	
		( <i>Z</i> ) 1.01 (3 H, t), 1.55 (6 H, s), 1.25—2.00 (4 H, m), 2.02 (1 H, t, <i>J</i> 7.3 Hz), 3.56 (2 H, d, <i>J</i> 7.3 Hz), 3.85 (2 H, t), 6.67—7.29 (4 H, m)	
(4d)	(film) ( <i>E/Z</i> ) 2 535, 2 170, 1 555, 1 460, 1 435, 1 330, 1 165, 1 095, 730	( <i>E</i> ) 1.75 (6 H, s), 1.99 (1 H, t, <i>J</i> 6.3 Hz), 3.26 (2 H, d, <i>J</i> 6.3 Hz), 5.14 (2 H, s), 6.54—6.70 (1 H, m), 6.91—7.48 (8 H, m)	24.9(t), 26.2(q), 48.2(s), 49.6(t), 76.5(s), 125.3(s), 167.6(s) in addition to aromatic carbon peaks
		( <i>Z</i> ) 1.61 (6 H, s), 1.92 (1 H, d, <i>J</i> 6.4 Hz), 3.63 (2 H, d, <i>J</i> 6.4 Hz), 5.37 (2 H, s), 6.54—6.70 (7 H, m), 6.91—7.48 (8 H, m)	
(4e)	(KBr) ( <i>E</i> ) 2 550, 2 180, 1 620, 1 580, 1 480, 1 455, 1 365, 1 295, 1 205, 760, 700	( <i>E</i> ) 1.67 (1 H, t, <i>J</i> 7.8 Hz), 1.80 (6 H, s), 2.73 (2 H, d, <i>J</i> 7.8 Hz), 6.26—6.35 (1 H, m), 6.89—7.64 (8 H, m)	23.7(t), 26.2(q), 48.0(s), 79.3(s), 108.4(d), 121.5(s), 121.8(d), 122.4(d), 127.7(d), 128.0(d), 129.2(d), 130.3(d), 137.4(s), 138.4(s), 145.6(s), 165.8(s)

Table 3 (continued)

Compd.	$\nu_{\max.}/(\text{cm}^{-1})$	$\delta_{\text{H}}(\text{CDCl}_3)$	$\delta_{\text{C}}(\text{CDCl}_3)$
(4h)	(KBr) ( <i>E</i> ) 2 530, 2 180, 1 615, 1 590, 1 490, 1 455, 1 215, 745, 695	( <i>E</i> ) 1.68 (1 H, t, <i>J</i> 8.3 Hz), 1.50—2.20 (8 H, m), 2.42—2.95 (2 H, m), 2.76 (2 H, d, <i>J</i> 8.3 Hz), 6.28—6.38 (1 H, m), 6.87—7.66 (8 H, m)	21.6(t), 24.0(t), 24.5(t), 33.2(t), 51.7(s), 79.3(s), 108.9(d), 121.7(d), 121.9(s), 125.0(d), 127.5(d), 128.2(d), 129.2(d), 130.4(d), 136.4(d), 138.9(s), 146.1(s), 166.4(s)
	(KBr) ( <i>Z</i> ) 2 180, 1 615, 1 590, 1 490, 1 455, 1 215, 745, 695	( <i>Z</i> ) 1.59—2.65 (11 H, m), 3.75 (2 H, d, <i>J</i> 7.3 Hz), 6.28—6.38 (1 H, m), 6.80—7.70 (8 H, m)	21.3(t), 24.6(t), 26.0(t), 33.1(t), 51.6(s), 79.3(s), 128.7(s), 165.1(s) in addition to aromatic carbon peaks
(4i)	(KBr) ( <i>E/Z</i> ) 2 175, 1 590, 1 570, 1 480, 1 455, 1 240, 745, 700	( <i>E</i> ) 1.72 (1 H, t, <i>J</i> 7.8 Hz), 1.60—1.90 (2 H, m), 2.77 (2 H, d, <i>J</i> 7.8 Hz), 2.87—3.20 (2 H, m), 4.05—4.35 (4 H, m), 6.31—6.41 (1 H, m), 6.89—7.88 (8 H, m)	25.7(t), 33.3(t), 48.9(s), 63.1(t), 79.5(s), 121.2(s), 163.5(s), in addition to aromatic carbon peaks
		( <i>Z</i> ) 1.60—1.90 (2 H, m), 2.02 (1 H, t, <i>J</i> 6.8 Hz), 2.35—2.60 (2 H, m), 3.78 (2 H, d, <i>J</i> 7.8 Hz), 4.05—4.35 (4 H, m), 6.31—6.41 (1 H, m), 6.89—7.88 (8 H, m)	24.4(t), 33.1(t), 48.3(s), 63.6(t), 80.2(s), 118.4(s), 164.5(s) in addition to aromatic carbon peaks
(4j)	(KBr) ( <i>E</i> ) 2 180, 1 615, 1 580, 1 490, 1 475, 1 460, 1 365, 1 335, 1 200, 755, 700	( <i>E</i> ) 1.68 (1 H, t, <i>J</i> 7.8 Hz), 1.90—2.80 (8 H, m), 2.76 (2 H, d, <i>J</i> 7.8 Hz), 6.24—7.34 (1 H, m), 6.87—7.64 (8 H, m)	24.0(t), 27.2(t), 41.7(t), 58.4(s), 78.6(s), 108.3(d), 121.4(s), 122.0(d), 122.5(d), 127.2(d), 128.2(d), 129.2(d), 130.3(d), 138.7(s), 140.1(s), 145.4(s), 166.7(s)
	(KBr) ( <i>Z</i> ) 2 180, 1 615, 1 590, 1 575, 1 495, 1 475, 1 455, 1 375, 1 340, 1 205, 745, 700	( <i>Z</i> ) 2.01 (1 H, t, <i>J</i> 7.8 Hz), 1.93—2.42 (8 H, m), 3.51 (2 H, d, <i>J</i> 7.8 Hz), 6.26—6.35 (1 H, m), 6.84—7.63 (8H, m)	25.5(t), 27.3(t), 41.2(t), 57.6(s), 78.3(s), 108.2(d), 118.6(s), 121.5(d), 121.9(d), 127.6(d), 129.4(d), 129.9(d), 137.0(s), 140.3(s), 145.0(s), 165.9(s)
(5)	(KBr) 2 220, 1 585, 1 485, 1 470, 755, 705	1.52 (3 H, s), 1.58—2.96 (8 H, m), 2.42 (1 H, dd, <i>J</i> 2.0, 14.2 Hz), 3.00 (1 H, dd, <i>J</i> 2.0, 14.2 Hz), 3.27 (1 H, d, <i>J</i> 14.2 Hz), 3.76 (1 H, d, <i>J</i> 14.2 Hz), 6.15 (1 H, dd, <i>J</i> 1.0, 7.8 Hz), 6.65—7.07 (3 H, m), 7.31—7.45 (5 H, m)	21.6(t), 24.4(t), 26.4(q), 27.9(t), 31.7(t), 36.2(t), 38.5(t), 45.8(s), 64.4(s), 80.6(s), 109.2(d), 119.8(d), 121.4(d), 122.5(s), 127.6(d), 128.0(d), 129.6(d), 132.7(d), 138.4(s), 142.8(s), 150.4(s)
(6)	(CDCl <sub>3</sub> ) 1 600, 1 480, 1 455, 1 290, 1 015, 890	1.21 (3 H, s), 1.33 (3 H, s), 1.61 (3 H, s), 1.83 (3 H, s), 2.33 (1 H, d, <i>J</i> 8.8 Hz), 3.22 (3 H, s), 3.29 (1 H, d, <i>J</i> 8.8 Hz), 6.55—7.22 (4 H, m)	24.4(q), 25.2(q), 25.7(q), 28.8(q), 33.1(q), 36.5(t), 48.6(s), 51.1(s), 102.2(s), 109.0(d), 119.9(d), 120.2(d), 127.5(d), 138.6(s), 148.4(s)

toluene, gave only recovery of unchanged starting material as was also the case when it was irradiated in benzene. The photoreaction of the indoline-2-thione (**1e**) and methacrylonitrile (**2M**) was sensitized by the addition of triplet sensitizer such as thioxanthone ( $E_T = 65\text{--}66 \text{ kcal mol}^{-1}$ ) and Michler's ketone ( $E_T \sim 62 \text{ kcal mol}^{-1}$ ), and the addition of a triplet quencher such as *trans*-stilbene ( $E_T \sim 50 \text{ kcal mol}^{-1}$ ) or cyclooctatetraene ( $E_T \sim 40 \text{ kcal mol}^{-1}$ ) decreased the reaction rate and yield of 2-alkylideneindoline (**3e**) to ca. 30% (Table 2). Irradiation of (**1e**) and methacrylonitrile (**2M**) in benzene in the  $\pi\pi^*$  region using a halogen lamp under the same conditions as described above also gave the 2-alkylideneindoline (**3e**) (44%). These results suggest that the formation of 2-alkylideneindoline (**3e**) proceeds mainly *via* the  $\pi\pi^*$  triplet state of (**1e**) although the possibility of a  $\pi\pi^*$  singlet state cannot be ruled out completely. Irradiation of indoline-2-thiones (**1**) in benzene in the presence of acrylonitrile (**2A**) in a similar fashion gave (*E/Z*)-2-mercaptoalkylideneindolines (**4**) in excellent yields. The structure of the photoproducts was established on the basis of their spectroscopic properties and elemental analyses. Ozonolysis of 2-mercaptoalkylideneindoline (**4e**) gave 3,3-dimethyl-1-phenylindolin-2-one (54%). Characteristically, the mercapto and methylene protons of *Z*-(**4**) appeared upfield from the corresponding protons of *Z*-(**4**) as a triplet and doublet, respectively, in the n.m.r. spectra. The stereochemistry of the photoproducts (**4**) was tentatively assigned (see the Figure) by comparing the chemical shifts of (**4**) with those of 2-alkylideneindolines (**3**) in the n.m.r. spectra. To test the scope of the reaction, irradiations were carried out with a range of alkenes. Indoline-2-thione (**1e**) failed to react photochemically with electron-rich alkene (ethyl vinyl ether), electron-neutral alkenes (1,1-diphenylethylene, styrene, cyclohexene), and 1,2-disubstituted cyanoalkenes (crotononitrile, 1,2-dicyanoethylene, 2-methylbut-2-enenitrile) and was recovered in almost quantitative yield. When indoline-2-thiones (**1a,c,e**) in benzene

were irradiated in the presence of methyl methacrylate, several products were detected by t.l.c., but separation and isolation of pure components proved difficult. The formation of the 2-alkylideneindolines (**3**) and 2-mercaptoalkylideneindolines (**4**) can be best explained through the intermediacy of a spiro aminothietane (**11**), which is formed initially by the photochemical [2 + 2]cycloaddition of thiocarbonyl to alkenes, and then eliminates thioformaldehyde to yield the 2-alkylideneindolines (**3**) (path a in Scheme 2). The spiro aminothietane (**11**) undergoes ring cleavage of the thietane ring with a 1,3-hydrogen shift to yield 2-mercaptoalkylideneindolines (**4**)



(path b in Scheme 2). [2 + 2]Photocycloaddition of thiocarbonyl to alkenes proceeds in a regiospecific manner since alkylideneindolines (**12**), (**13**), derived from the alternate spiro aminothietane (**11'**), could not be detected. The regiospecificity is that expected with the formation of more stable diradical intermediate (**10**). Although neither of the spiro aminothietane

intermediates (**11**) could be isolated in the photoreactions of indoline-2-thiones (**1**) with cyanoalkenes (**2**), we finally succeeded in isolating them<sup>17</sup> by irradiation of a solution of 1,3,3-trimethylindoline-2-thione (**1a**) in the presence of an excess of isobutene. In this way the aminothietane (**6**), was isolated in low yield (8%), along with unchanged (**1a**) (85%). The <sup>1</sup>H n.m.r. spectrum of (**6**) showed five singlets at  $\delta$  1.21, 1.33, 1.61, 1.83, and 3.22 attributable to methyl and methylamino groups, two doublets at  $\delta$  2.33 (*J* 8.8 Hz) and 3.29 (*J* 8.8 Hz) due to methylene protons of the thietane ring, and multiplet at  $\delta$  6.55—7.22 assignable to aromatic protons. The <sup>13</sup>C n.m.r. spectrum of compound (**6**) showed peaks due to four methyl [ $\delta$  24.4(q), 25.2(q), 25.7(q), and 28.8(q)], *N*-methyl [ $\delta$  33.1(q)], methylene [ $\delta$  36.5(t)], and three quaternary carbons [ $\delta$  48.6(s), 51.1(s), and 102.2(s)] in addition to aromatic carbons. The mass spectrum of the aminothietane (**6**) showed a molecular ion peak at *m/z* 247 (*M*<sup>+</sup>) and displayed two characteristic fragments at *m/z* 201 (*M*<sup>+</sup> - CH<sub>2</sub>S) and 191 (*M*<sup>+</sup> - C<sub>4</sub>H<sub>8</sub>): this cleavage pattern points to the orientation of addition (head-to-head) as shown in (**6**), rather than that of the alternative mode (head-to-tail). Thus the reaction of indoline-2-thiones with alkenes is regioselective, like that of thioimides,<sup>17</sup> giving 2-aminothietanes, which undergo ring cleavage to yield alkylideneindolines.

## Experimental

**Starting Materials.**—Indoline-2-thiones (**1**) were prepared by the sulphuration of the corresponding indolin-2-ones<sup>18,19</sup> with Lawesson's reagent. A solution of the indolin-2-ones (0.01 mol) and Lawesson's reagent (5.5 mmol) in dimethoxyethane or toluene (100 ml) was refluxed for 0.5—3 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (50:1—19:1) to yield the corresponding indoline-2-thiones (**1**) in 47–92% yields. The properties of compounds (**1a**–**j**) are listed below. The n.m.r. spectra were measured in CDCl<sub>3</sub> as solvent using TMS as internal standard.

1,3,3-Trimethylindoline-2-thione (**1a**) (77%), b.p. 130 °C at 2 mmHg (lit.,<sup>19</sup> 137 °C at 2 mmHg);  $\nu_{\max}$  (film) 1 610, 1 460, 1 365, 1 305, 1 260, 1 105, and 750 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.44 (6 H, s), 3.65 (3 H, s), and 6.99—7.46 (4 H, m);  $\delta_{\text{C}}$  28.0(q), 31.4(q), 54.8(s), 109.5(d), 122.6(d), 127.8(d), 140.3(s), 143.8(s), and 211.8(s).

1-Methyl-3,3-diphenylindoline-2-thione (**1b**) (47%), m.p. 179—180 °C (Found: C, 79.85; H, 5.45; N, 4.65. C<sub>21</sub>H<sub>17</sub>NS requires C, 79.95; H, 5.45; N, 4.45%);  $\nu_{\max}$  (KBr) 1 600, 1 460, 1 360, 1 300, 1 115, 745, and 695 cm<sup>-1</sup>;  $\delta_{\text{H}}$  3.69 (3 H, s), 7.01—7.42 (14 H, m);  $\delta_{\text{C}}$  31.9(q), 72.4(s), 109.8(d), 124.5(d), 126.1(d), 127.2(d), 128.0(d), 128.3(d), 129.0(d), 138.2(s), 143.1(s), 144.1(s), and 207.9(s).

1-Butyl-3,3-dimethylindoline-2-thione (**1c**) (72%), b.p. 140 °C at 2 mmHg (Found: C, 72.25; H, 8.25; N, 6.0. C<sub>14</sub>H<sub>19</sub>NS requires C, 72.05; H, 8.2; N, 6.0%);  $\nu_{\max}$  (film) 1 605, 1 450, 1 380, 1 345, 1 125, 1 110, 740 cm<sup>-1</sup>;  $\delta_{\text{H}}$  0.97 (3 H, t), 1.21—1.86 (4 H, m), 1.43 (6 H, s), 4.22 (2 H, t), and 6.99—7.41 (4 H, m);  $\delta_{\text{C}}$  13.9(q), 20.2(t), 28.1(q), 28.5(t), 44.3(t), 54.8(s), 109.7(d), 122.7(d), 123.9(d), 127.6(d), 140.6(s), 143.2(s), and 211.3(s).

1-Benzyl-3,3-dimethylindoline-2-thione (**1d**) (82%), m.p. 94—95 °C (Found: C, 76.1; H, 6.4; N, 5.15. C<sub>17</sub>H<sub>17</sub>NS requires C, 76.35; H, 6.4; N, 5.25%);  $\nu_{\max}$  (KBr) 1 605, 1 595, 1 495, 1 455, 1 380, 1 225, 755, and 685 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.50 (6 H, s), 5.48 (2 H, s), 6.85—6.99 (1 H, m), 7.09—7.38 (8 H, m);  $\delta_{\text{C}}$  28.2(q), 47.9(t), 55.0(s), 110.3(d), 122.6(d), 124.1(d), 127.0(d), 127.6(d), 128.7(d), 134.8(s), 140.3(s), 143.0(s), and 212.7(s).

3,3-Dimethyl-1-phenylindoline-2-thione (**1e**) (79%), m.p. 105—106 °C (Found: C, 75.8; H, 5.95; N, 5.45. C<sub>16</sub>H<sub>15</sub>NS requires C, 75.85; H, 5.95; N, 5.5%);  $\lambda$ (EtOH) 226 (14 700), 294 (8 400), and 317 (13 900);  $\nu_{\max}$  (KBr) 1 610, 1 590, 1 450, 1 370, 1 300, 1 245, 755, and 695 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.56 (6 H, s), 6.59—

6.77 (1 H, m), and 7.09—7.69 (8 H, m);  $\delta_{\text{C}}$  28.5(q), 55.2(s), 110.5(d), 122.8(d), 124.2(d), 127.5(d), 127.6(d), 129.0(d), 139.6(s), 140.0(s), 144.8(s), and 213.5(s).

3-Isopentyl-3-methyl-1-phenylindoline-2-thione (**1f**) (50%), m.p. 105.5—106 °C (Found: C, 77.6; H, 7.6; N, 4.55. C<sub>20</sub>H<sub>23</sub>NS requires C, 77.6; H, 7.5; N, 4.5%);  $\nu_{\max}$  (KBr) 1 605, 1 585, 1 495, 1 455, 1 370, 1 340, 1 310, 1 295, 745, and 690 cm<sup>-1</sup>;  $\delta_{\text{H}}$  0.78 (3 H, d, *J* 6.4 Hz), 0.80 (3 H, d, *J* 6.4 Hz), 0.37—1.17 (2 H, m), 1.24—1.60 (1 H, m), 1.54 (3 H, s), 1.79—2.32 (2 H, m), 6.58—6.75 (1 H, m), and 7.07—7.70 (3 H, m);  $\delta_{\text{C}}$  22.4(q), 22.5(q), 28.0(q), 28.2(d), 33.1(t), 40.2(t), 59.2(s), 110.3(d), 122.9(d), 124.2(d), 127.6(d), 129.0(d), 129.8(d), 137.0(s), 138.4(s), 145.7(s), and 212.5(s).

3-Ethoxyethyl-3-methyl-1-phenylindoline-2-thione (**1g**) (92%), m.p. 79—80 °C (Found: C, 73.2; H, 6.75; N, 4.5. C<sub>19</sub>H<sub>20</sub>NOS requires C, 73.25; H, 6.8; N, 4.5%);  $\nu_{\max}$  (KBr) 1 610, 1 590, 1 495, 1 455, 1 375, 1 340, 1 315, 1 200, 750, and 695 cm<sup>-1</sup>;  $\delta_{\text{H}}$  0.99 (3 H, t), 1.56 (3 H, s), 2.11—2.62 (2 H, m), 2.91—3.05 (2 H, m), 3.25 (2 H, q), 6.61—6.76 (1 H, m), and 7.09—7.70 (8 H, m);  $\delta_{\text{C}}$  15.0 (q), 28.9(q), 41.1(t), 57.5(s), 65.9(t), 66.6(t), 110.4(d), 123.2(d), 124.1(d), 127.5(d), 127.7(d), 129.0(d), 129.8(d), 137.0(s), 137.9(s), 145.5(s), and 211.8(s).

The spiro indoline-2-thione (**1h**) (85%), m.p. 142—143 °C (Found: C, 77.9; H, 6.5; N, 4.8. C<sub>19</sub>H<sub>19</sub>NS requires C, 77.75; H, 6.5; N, 4.75%);  $\nu_{\max}$  (KBr) 1 605, 1 585, 1 495, 1 365, 1 195, 740, and 690 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.35—2.45 (10 H, m), 6.60—6.78 (1 H, m), and 7.05—7.86 (8 H, m);  $\delta_{\text{C}}$  21.5(t) 24.9(t), 36.9(t), 59.0(s), 110.7(d), 123.2(d), 125.1(d), 127.3(d), 127.7(d), 129.0(d), 129.8(d), 137.3(s), 139.3(s), 145.2(s), and 213.1(s).

The spiro indoline-2-thione (**1i**) (74%), m.p. 189.5—190 °C (Found: C, 73.4; H, 5.7; N, 4.65. C<sub>18</sub>H<sub>17</sub>NOS requires C, 73.2; H, 5.8; N, 4.75%);  $\nu_{\max}$  (KBr) 1 605, 1 585, 1 500, 1 460, 1 380, 1 315, 760, 750, and 700 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.55—1.71 (2 H, m), 2.36—2.67 (2 H, m), 3.95—4.38 (4 H, m), 6.62—6.80 (1 H, m), and 7.10—7.90 (8 H, m);  $\delta_{\text{C}}$  36.3(t), 55.8(s), 63.0(t), 110.9(d), 123.7(d), 124.4(d), 127.6(d), 127.9(d), 129.1(d), 129.9(d), 137.0(s), 138.2(s), 145.2(s), and 211.1(s).

The spiro indoline-2-thione (**1j**) (90%), b.p. 190 °C at 2 mmHg; m.p. 107.5—108 °C (Found: C, 77.35; H, 6.1; N, 5.0. C<sub>18</sub>H<sub>17</sub>NS requires C, 77.35; H, 6.15; N, 5.0%);  $\nu_{\max}$  (KBr) 1 615, 1 590, 1 455, 1 370, 1 305, 750, and 695 cm<sup>-1</sup>;  $\delta_{\text{H}}$  1.95—2.50 (8 H, m), 6.60—6.70 (1 H, m), and 7.05—7.69 (8 H, m);  $\delta_{\text{C}}$  27.1(t), 43.5(t), 65.6(s), 110.3(d), 122.6(d), 124.2(d), 127.2(d), 127.7(d), 129.8(d), 137.3(s), 141.7(s), 144.8(s), and 214.2(s).

**General Procedure for the Photochemical Reactions of the Indoline-2-thiones (1) in the Presence of Alkenes (2).**—A solution of the indoline-2-thione (**1**) (200 mg) and alkene (*ca.* 1 ml) in benzene (70 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp (300 or 450 W) under argon for 5 h at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column with benzene-hexane (4:1—9:1) or benzene-ethyl acetate (50:1) as eluant to give the photoproducts (**3**)—(**6**), along with recovered (**1**). The i.r. and n.m.r. spectra were shown in Table 3.

The 2-alkylideneindoline *E/Z*-(**3a**), m.p. 141—143 °C (Found: C, 79.0; H, 7.65; N, 13.1. C<sub>14</sub>H<sub>16</sub>N<sub>2</sub> requires C, 79.2; H, 7.6; N, 13.2%).

The 2-alkylideneindoline *E*-(**3b**), m.p. 211—213 °C (Found: C, 85.5; H, 6.0; N, 8.35. C<sub>24</sub>H<sub>20</sub>N<sub>2</sub> requires C, 85.7; H, 6.0; N, 8.3%).

The 2-alkylideneindoline *E/Z*-(**3c**), oil (Found: C, 80.05; H, 8.75; N, 10.9. C<sub>17</sub>H<sub>22</sub>N<sub>2</sub> requires C, 80.25; H, 8.7; N, 11.0%).

The 2-alkylideneindoline *E/Z*-(**3d**), m.p. 135 °C (Found: C, 83.2; H, 7.0; N, 9.7. C<sub>20</sub>H<sub>20</sub>N<sub>2</sub> requires C, 83.3; H, 7.0; N, 9.7%).

The 2-alkylideneindoline *E*-(**3e**), m.p. 151—153 °C (Found: C, 83.15; H, 6.6; N, 10.25. C<sub>19</sub>H<sub>18</sub>N<sub>2</sub> requires C, 83.15; H, 6.6; N, 10.2%).

The 2-alkylideneindoline *E*-(**3f**), m.p. 141–142 °C (Found: C, 83.3; H, 7.85; N, 8.3. C<sub>23</sub>H<sub>26</sub>N<sub>2</sub> requires C, 83.6; H, 7.95; N, 8.45%).

The 2-alkylideneindoline *E*-(**3g**), m.p. 169.5–171 °C (Found: C, 79.4; H, 7.15; N, 8.25. C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O requires C, 79.5; H, 7.3; N, 8.45%).

The 2-alkylideneindoline *E*-(**3h**), m.p. 169–170 °C (Found: C, 84.0; H, 7.05; N, 8.85. C<sub>22</sub>H<sub>22</sub>N<sub>2</sub> requires C, 84.05; H, 7.05; N, 8.9%).

The 2-alkylideneindoline *E*-(**3i**), m.p. 237–238 °C (Found: C, 79.55; H, 6.4; N, 8.8. C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O requires C, 79.7; H, 6.35; N, 8.85%).

The 2-alkylideneindoline *E*-(**3j**), m.p. 184–185 °C (Found: C, 83.7; H, 6.7; N, 9.3. C<sub>21</sub>H<sub>20</sub>N<sub>2</sub> requires C, 83.95; H, 6.7; N, 9.3%).

The 2-mercaptoalkylideneindoline *E*-(**4a**), m.p. 104–106 °C (Found: C, 68.85; H, 6.55; N, 11.45. C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>S requires C, 68.8; H, 6.6; N, 11.45%).

The 2-mercaptoalkylideneindoline *E*-(**4b**), m.p. 218–220 °C (Found: C, 78.05; H, 5.45; N, 7.55. C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>S requires C, 78.2; H, 5.45; N, 7.6%).

The 2-mercaptoalkylideneindoline *E/Z*-(**4c**), b.p. 80 °C at 10<sup>-4</sup> mmHg (Found: C, 71.6; H, 7.8; N, 9.7. C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>S requires C, 71.3; H, 7.75; N, 9.8%).

The 2-mercaptoalkylideneindoline *E/Z*-(**4d**), b.p. 160 °C at 2 mmHg (Found: C, 75.3; H, 6.35; N, 8.65. C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>S requires C, 75.0; H, 6.3; N, 8.75%).

The 2-mercaptoalkylideneindoline *E*-(**4e**), m.p. 127–128 °C (Found: C, 74.4; H, 5.95; N, 9.15. C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>S requires C, 74.45; H, 5.9; N, 9.15%).

The 2-mercaptoalkylideneindoline *E*-(**4h**), m.p. 98–99 °C (Found: C, 76.45; H, 6.4; N, 8.1. C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>S requires C, 76.25; H, 6.4; N, 8.1%).

The 2-mercaptoalkylideneindoline *Z*-(**4h**), m.p. 112–114 °C (Found: C, 76.45; H, 6.45; N, 8.1. C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>S requires C, 76.25; H, 6.4; N, 8.1%).

The 2-mercaptoalkylideneindoline *E/Z*-(**4i**), m.p. 169–170 °C (Found: C, 72.65; H, 5.85; N, 8.05. C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>OS requires C, 72.4; H, 5.8; N, 8.05%).

The 2-mercaptoalkylideneindoline *E*-(**4j**), m.p. 132.5–133.5 °C (Found: C, 76.0; H, 6.05; N, 8.45. C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>S requires 75.85; H, 6.05; N, 8.4%).

The 2-mercaptoalkylideneindoline *Z*-(**4j**), m.p. 142–144 °C (Found: C, 75.6; H, 6.0; N, 8.35. C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>S requires C, 75.85; H, 6.05; N, 8.4%).

The spiro-1,3-dithiane (**5**), m.p. 145–147 °C (Found: C, 70.55; H, 6.15; N, 7.15. C<sub>23</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub> requires C, 70.4; H, 6.15; N, 7.15%). *m/z* 392 (*M*<sup>+</sup>), 325 (*M*<sup>+</sup> – C<sub>4</sub>H<sub>5</sub>N), 300 (*M*<sup>+</sup> – C<sub>2</sub>H<sub>4</sub>S<sub>2</sub>), 285 (*M*<sup>+</sup> – C<sub>3</sub>H<sub>7</sub>S<sub>2</sub>), and 279 (*M*<sup>+</sup> – C<sub>5</sub>H<sub>7</sub>NS).

*Photoreaction of 1,3,3-Trimethylindoline-2-thione (1a) with Isobutene.*—A solution of (**1a**) (300 mg) and an excess of

isobutene (500 mg) in benzene (70 ml) was irradiated in a similar manner for 5 h. Work-up gave the aminothietane (**6**) (8%), along with recovered (**1a**) (85%). Prolonged irradiation (12 h) of (**1a**) and isobutene gave small amounts of inseparable mixtures, besides the aminothietane and recovered (**1a**). The aminothietane when heated in benzene at 80 °C gave an intractable mixture.

The aminothietane (**6**), b.p. 65 °C at 2 mmHg (decomp.) (Found: C, 72.75; H, 8.6; N, 5.6%; *M*, 247.139 69. C<sub>15</sub>H<sub>21</sub>NS requires C, 77.8; H, 8.5; N, 5.65%; *M*, 247.139 63); *m/z* 247 (*M*<sup>+</sup>), 201 (*M*<sup>+</sup> – CH<sub>2</sub>S), and 191 (*M*<sup>+</sup> – C<sub>4</sub>H<sub>8</sub>).

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