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A Novel Route to Indolines by Photochemical Desulphurization of Indoline-2-thiones

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Photochemical reactions of the indoline-2-thiones in the presence of amine produce the desulphurization products, indolines.

While there has been growing interest in the photochemistry of thiocarbonyl compounds¹ in recent years, relatively few reports have dealt with the photochemical properties of thioamides.^{2—10} The observed reactions of thioamides are [2 + 2] photocycloadditions of alkenes at the C=S double bond to form thietanes, which are often unstable and are transformed into fragmentation products. In our study of the photochemical reactions of cyclic conjugated nitrogen–thiocarbonyl systems,^{9,10} we found that on irradiation, indoline-2-thiones which have at least one hydrogen at 3-position produce the indoles,^{10a} while the indoline-2-thiones undergo [2 + 2] photocycloaddition with cyano-alkenes to give 2-alkylidene indoles.^{10b} We report here a new type of the photoreaction of indoline-2-thiones in the presence of amine, namely photodesulphurization.

I-Phenyl-3,3-dimethylindole-2-thione (1a) itself did not react on irradiation. However, when irradiated in the



presence of triethylamine (1 M, 10 equiv.) as an electron donor in benzene in a Pyrex vessel with a high-pressure mercury lamp (300 W) (under argon, 5 h, room temp.) the desulphurization product, 1-phenyl-3,3-dimethylindoline (**2a**), and *N*,*N*diethylthioacetamide (**3**) were produced in 45 and 43% isolated yields, respectively. (Scheme 1)[‡] The ¹³C n.m.r. spectra of (**2a**) showed a newly formed signal at 66.3 (t), which we assigned to the carbon at C-2, and no thiocarbonyl carbon signal.[‡] The structure of the photoproducts (**2a**) and (**3**) was further confirmed by direct comparison of their i.r. and n.m.r. spectra with those of authentic materials, which were independently prepared.§

Similarly, irradiation of the indoline-2-thiones (1b-f and h)in the presence of triethylamine gave the corresponding indolines (2b-f and h). The photoreaction of (1a) was examined in the presence of various amines and in various

 \ddagger ¹³C N.m.r. data for (**1a**): (CDCl₃) δ 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).

§ The indoline (2a) was prepared by the reduction of 1-phenyl-3,3dimethylindole-2-one with LiAlH₄, and the thioamide (3) by the thiation of N,N-diethylacetamide with Lawesson's reagent.

[†] Satisfactory elemental analyses were obtained for all new compounds. Data for (**2a**): m.p. 59—60 °C; i.r. (film) v 1595, 1500, 1480, 1460, 1395, 1380, 1335, 1290, 740, and 695 cm⁻¹; ¹H n.m.r. (CDCl₃) ð 1.34 (6H, s), 3.66 (2H, s), and 6.68—7.41 (9H, m); ¹³C n.m.r. (CDCl₃) ð 27.8(q), 39.8(s), 66.3(t), 108.1(d), 117.4(d), 119.0(d), 120.7(d), 122.2(d), 127.1(d), 129.1(d), 140.2(s), 144.1(s), and 145.5(s).

Table 1. Yields of the indolines (2).

	Indole-2-thione (1)			Amine		Yield of (2)
	R1	\mathbb{R}^2	R ³	(Ionization potential) ^a	Solvent	/% ^b
(1a)	Ph	Me	Me	Et ₃ N (7.50)	Benzene	45 (78)°
				Et ₃ N	MeCN	(65)
				Et ₃ N	MeOH	(0)
				Et ₂ NH (8.01)	Benzene	(17)
				Bu ⁿ ₃ N	Benzene	(62)
				$Bu_{2}^{n}NH(7.69)$	Benzene	` (9)
				$Bu^{n}NH_{2}(8.71)$	Benzene	ò
				$PhNMe_{2}(7.1)$	Benzene	(44)
				PhNEt ₂	Benzene	(22)
				PhNHĒt	Benzene	(22)
				$PhNH_{2}(7.71)$	Benzene	ົເຫົ
(1b)	Ph		(CH ₂)5	Et ₃ N	Benzene	48
(1c)	Ph	Me	Ph(CH ₂) ₃	Et ₃ N	Benzene	46
(1d)	PhCH ₂	Me	Me	Et ₃ N	Benzene	11
(1e)	Bu ⁿ	Me	Me	Et ₃ N	MeCN	32
(1f)	Me	Me	Me	Et ₃ N	Benzene	33
(1g)	Me	Ph	Ph	Et ₃ N	MeCN	d
(1h)	Н	Ph	Ph	Et ₃ N	MeCN	33

a Ref. 13. b Isolated yield. c Yields in parentheses determined by g.c. d (1g) in benzene gave an intractable mixture on irradiation.



solvents in the presence of triethylamine. The results are summarized in Table 1. The photoreaction proceeds smoothly in acetonitrile and in benzene, but does not proceed in methanol, probably owing to hydrogen bonding interactions between the amine and the alcohol, which suppress the electron transfer process.¹² Generally, amines with lower ionization potential and aliphatic tertiary amines are more favourable for the formation of indolines (2). Furthermore, the indolines were not formed when the photoreaction was carried out in the presence of hydrogen donating reagents such as xanthene and dihydroanthracene, or in hydrogen donating solvents such as ether and tetrahydrofuran.

From these results, we postulate that the formation of desulphurization products, indolines (2), involves the zwit-

terion intermediate (4) resulting from electron transfer from the amine to the excited indoline-2-thione (1) (Scheme 2).¶ The photoreactions described here could provide a convenient preparative route to indoline derivatives.

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¶ An analogous intermediate has been proposed in the photochemical amine- and phosphite-promoted coupling of 2-thioxo-1,3-dithioles.¹¹