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

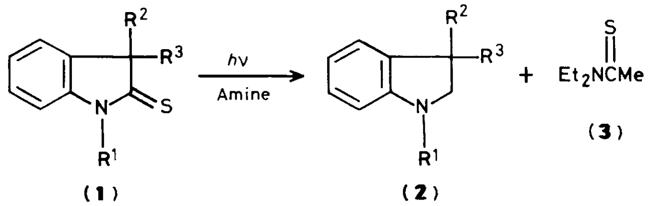
Takehiko Nishio,* Norikazu Okuda, Choji Kashima, and Yoshimori Omote

Department of Chemistry, University of Tsukuba, Tennodai, Tsukuba-shi, Ibaraki 305, Japan

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 compounds[1] 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.

1-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 ^{13}C 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.[§]



R^1 = H, alkyl, aryl.
R^2, R^3 = alkyl, aryl.

Scheme 1

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

---

[†] Satisfactory elemental analyses were obtained for all new compounds. Data for (**2a**): m.p. 59—60 °C; i.r. (film) ν 1595, 1500, 1480, 1460, 1395, 1380, 1335, 1290, 740, and 695 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.34 (6H, s), 3.66 (2H, s), and 6.68—7.41 (9H, m); ^{13}C n.m.r. ($CDCl_3$) δ 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).

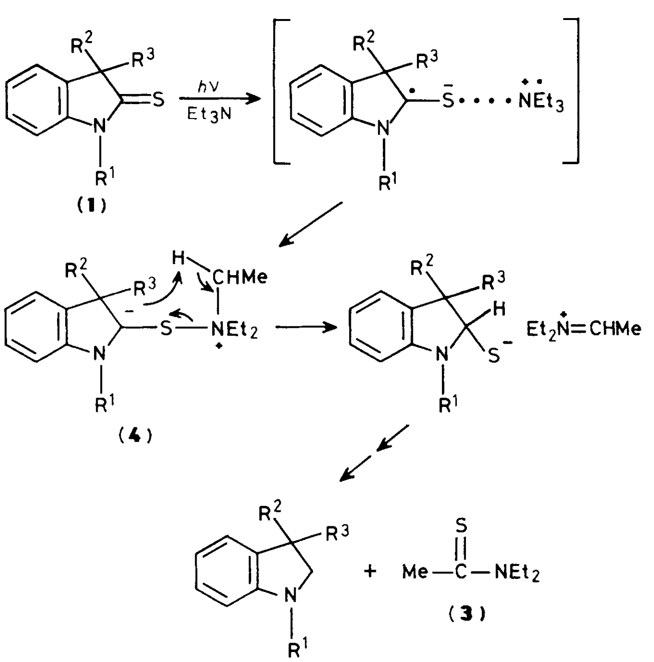
[‡] ^{13}C N.m.r. data for (**1a**): ($CDCl_3$) δ 28.5(q), 55.2(s), 110.5(d), 122.8(d), 124.2(d), 127.5(d), 127.6(d), 129.0(d), 139.6(s), 140.0(s), 144.8(s), and 213.5(s).

[§] The indoline (**2a**) was prepared by the reduction of 1-phenyl-3,3-dimethylindole-2-one with $LiAlH_4$, and the thioamide (**3**) by the thiation of *N*,*N*-diethylacetamide with Lawesson's reagent.

Table 1. Yields of the indolines (**2**).

	Indole-2-thione (**1**) R^1	R^2	R^3	Amine (Ionization potential)[a]	Solvent	Yield of (**2**) /%[b]
(**1a**)	Ph	Me	Me	Et_3N (7.50)	Benzene	45 (78)[c]
				Et_3N	MeCN	(65)
				Et_3N	MeOH	(0)
				Et_2NH (8.01)	Benzene	(17)
				$Bu^n{}_3N$	Benzene	(62)
				$Bu^n{}_2NH$ (7.69)	Benzene	(9)
				Bu^nNH_2 (8.71)	Benzene	(0)
				$PhNMe_2$ (7.1)	Benzene	(44)
				$PhNEt_2$	Benzene	(22)
				PhNHEt	Benzene	(22)
				$PhNH_2$ (7.71)	Benzene	(0)
(**1b**)	Ph	$-(CH_2)_5-$		Et_3N	Benzene	48
(**1c**)	Ph	Me	$Ph(CH_2)_3$	Et_3N	Benzene	46
(**1d**)	$PhCH_2$	Me	Me	Et_3N	Benzene	11
(**1e**)	Bu^n	Me	Me	Et_3N	MeCN	32
(**1f**)	Me	Me	Me	Et_3N	Benzene	33
(**1g**)	Me	Ph	Ph	Et_3N	MeCN	[d]
(**1h**)	H	Ph	Ph	Et_3N	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.



Scheme 2

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 zwitterion 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.

Received, 21st December 1987; Com. 1824

References

1 A. Ohno, *Int. J. Sulfur Chem. B*, 1971, **6**, 183; P. de Mayo, *Acc. Chem. Res.*, 1978, **9**, 52; J. D. Coyle, *Tetrahedron*, 1985, **41**, 5395; V. Ramamurthy, 'Organic Photochemistry,' ed. A. Padwa, Marcel Dekker, New York, 1985, vol. 7, p. 231.

2 K. H. Grellmann and E. Tauer, *Tetrahedron Lett.*, 1967, 1909; R. Paramasivn, P. Ralaniappan, and V. T. Ramakrishnan, *J. Chem. Soc., Chem. Commun.*, 1979, 260.

3 J. L. Fourrey, P. Jouin, and J. Moron, *Tetrahedron Lett.*, 1974, 3005; P. Jouin and J. L. Fourrey, *ibid.*, 1975, 1329, and references cited therein.

4 C. Marazano, J. L. Fourrey, and D. C. Das, *J. Chem. Soc., Chem. Commun.*, 1977, 724; D. C. Das, J. L. Fourrey, C. Marazano, A. Marrien, and J. Polonsky, *J. Chem. Res. C*, 1978, 370.

5 P. de Mayo, L. K. Sydnes, and G. Wenska, *J. Org. Chem.*, 1980, **45**, 1949.

6 A. Couture, A. Duniez, and A. Lablach-Combier, *J. Chem. Soc., Chem. Commun.*, 1982, 842; *J. Org. Chem.*, 1984, **49**, 714.

7 M. Machida, K. Oda, and Y. Kanaoka, *Tetrahedron Lett.*, 1984, **25**, 409.

8 E. Sato, M. Hasebe, and Y. Kanaoka, *Chem. Pharm. Bull.*, 1986, **34**, 3061; E. Sato, Y. Ikeda, and Y. Kanaoka, *ibid.*, 1987, **35**, 3641; *Chem. Lett.*, 1987, 273.

9 T. Nishio and Y. Omote, *Heterocycles*, 1985, **23**, 29; Synthesis, 1987, 54; T. Nishio, M. Fujisawa, and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2523.

10 (a) T. Nishio, *J. Org. Chem.*, in the press; (b) T. Nishio, N. Okuda, and Y. Omote, *J. Chem. Soc., Perkin Trans. 1*, in the press.

11 K. Tsujimoto, Y. Okeda, and M. Ohashi, *J. Chem. Soc., Chem. Commun.*, 1985, 1803.

12 S. Oh, Y. Shirota, H. Mikami, and S. Kusabayashi, *Chem. Lett.*, 1986, 2121.

13 D. W. Turner, 'Advances in Physical Organic Chemistry,' ed. V. Gold, Academic Press, London, 1966, vol. 4, p. 47.

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