A Novel Synthesis of the Indole Ring System

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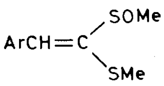
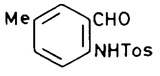
Intramolecular acid catalysed cyclisation of the ketene dithioacetal *S*-oxide (**3**) from the *o*-toluenesulphonamidobenzaldehyde (**2**) leads to two indole derivatives (**5**) and (**6**), the structure (**6**) being confirmed by *X*-ray crystallography.

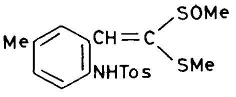
One of the established methods for the conversion of aromatic aldehydes into the corresponding arylacetic acids is by acid treatment of the derived ketene dithioacetal *S*-oxide (**1**).[1] In the course of a synthetic study we needed to carry out such a transformation on the aldehyde (**2**). Reaction between (**2**) and $MeSCH_2SOMe$, catalysed by Triton B,[1] gave (**3**) as desired (58%, m.p. 160—162 °C) but treatment of (**3**) with aqueous acid under a range of conditions failed to yield the desired acid (**4**). However, when (**3**) was stirred in dichloromethane containing 10 M HCl, two major products were isolated, to which we assign structures (**5**) [36%; oil; $\lambda_{max.}$ (EtOH) 263, 269, and 290 nm; δ_H ($CDCl_3$) 2.30 (3H, s), 2.37 (3H, s), 2.48



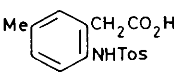
(**1**)



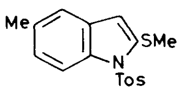
(**2**)



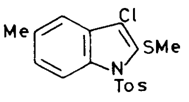
(**3**)



(**4**)



(**5**)



(**6**)

Tos = p-$MeC_6H_4SO_2$–

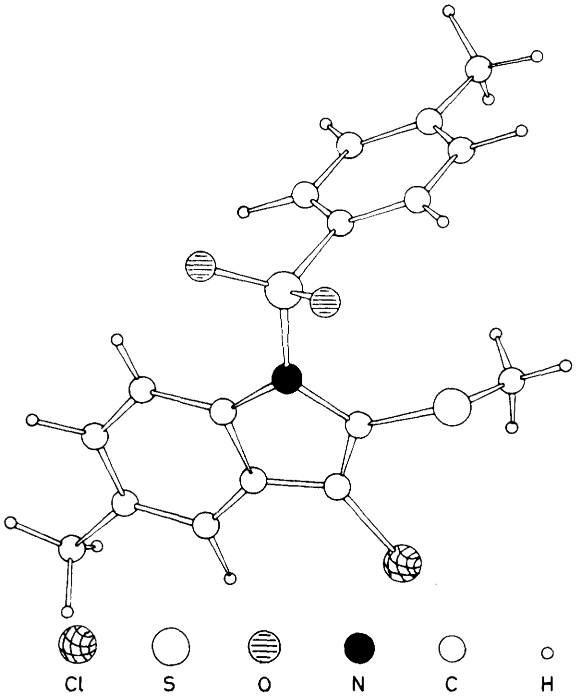
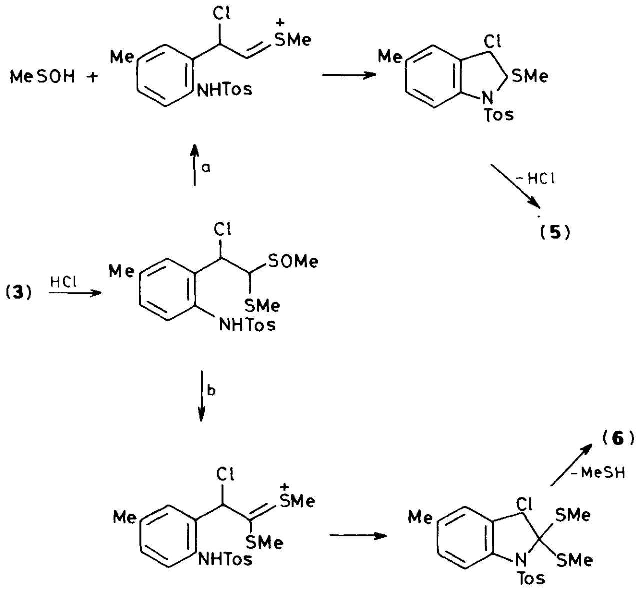


Figure 1. The *X*-ray structure of (**6**).

(3H, s), 6.26 (1H, s), 6.9—7.3 (4H, m), 7.8 (2H, d, *J* 8 Hz), and 8.03 (1H, d, *J* 8 Hz)] and (**6**) [38%; m.p. 118 °C; $\lambda_{max.}$ (EtOH) 262, 274, 284, and 288 nm; δ_H ($CDCl_3$) 2.34 (3H, s), 2.40 (3H, s), 2.45 (3H, s), 6.9—7.2 (4H, m,), 7.6 (2H, d, *J* 8 Hz), and 8.05 (1H, d, *J* 8 Hz)]. The structure (**6**) was confirmed by *X*-ray analysis (Figure 1).† Treatment of (**5**) with sulphuryl chloride in dichloromethane gave (**6**) (75%) thus confirming the structure of (**5**).



Scheme 1

The two products are thought to arise by initial addition of HCl to the highly electrophilic double bond of the ketene dithioacetal *S*-oxide. The adduct may then react (Scheme 1) by loss of methanesulphenic acid (path a) or by Pummerer rearrangement (path b). Related Pummerer reactions have been described.[2,3]

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References

1 K. Ogura, Y. Ito, and G. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2013.
2 M. Artico, F. Corelli, S. Massa, and G. Stefancich, *J. Heterocycl. Chem.*, 1982, **19**, 1493.
3 Jap. P. 61 159, 1979.
4 G. M. Sheldrick, 1976, SHELX—a Programme for crystal structure analysis, University of Cambridge, England.

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† *Crystal data:* $C_{17}H_{16}ClNO_2S_2$, $M = 365.9$, monoclinic, space group $P2_1/c$, $a = 8.732(2)$, $b = 19.392(6)$, $c = 10.186(3)$ Å, $\beta = 96.19(6)°$, $U = 1708.4$ Å^3, $Z = 4$, $D_c = 1.42$ g cm^{-3}, $F(000) = 760$ electrons, graphite-monochromated Mo-K_α *X*-radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 4.2 cm^{-1}; $R = 0.040$ for 1460 independent reflections having $I/\sigma(I) > 3.0$ collected on a Stöe Stadi 2 two-circle diffractometer. The structure was solved by direct and Fourier methods and refined by least squares calculations using SHELX.[4] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.