

**Ring-Expansion of Fused Bicyclic Aromatic Azides; Synthesis of  
8*H*-thieno[2,3-*c*]azepines by Photolysis of 6-Azidobenzo[*b*]thiophens  
in Diethylamine**

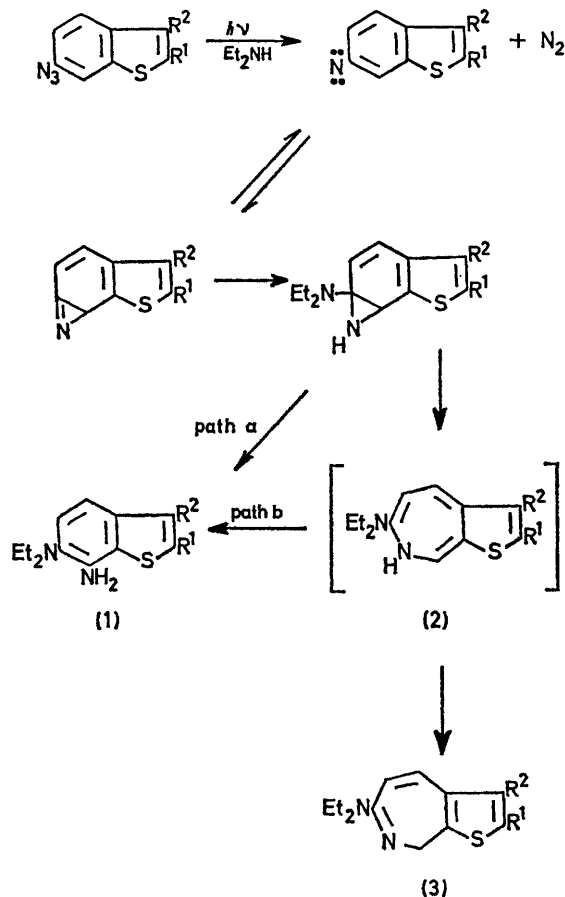
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*Summary* Photolysis of certain 6-azidobenzo[*b*]thiophens in an excess of diethylamine gave a mixture of a 7-amino-6-diethylaminobenzo[*b*]thiophen and a 6-diethylamino-8*H*-thieno[2,3-*c*]azepine, or either of these compounds depending on the reaction conditions.

We have recently shown that photolysis of 4-azidobenzo[*b*]thiophen in diethylamine for 24 h gives 4-aminobenzo[*b*]thiophen and 4,4'-azobenzo[*b*]thiophen, while 5-azidobenzo[*b*]thiophen yields 4-amino-5-*NN*-diethylaminobenzo[*b*]thiophen.<sup>1</sup>

We have now observed that photolysis (with a high pressure mercury vapour lamp through a Pyrex filter) of 6-azido-2,3-dibromobenzo[*b*]thiophen for 18 h in an excess of diethylamine under nitrogen yields 7-amino-2,3-dibromo-6-diethylaminobenzo[*b*]thiophen (**1**;  $R^1 = R^2 = \text{Br}$ ) (13%), b.p. 148–150° at 3.0 mmHg, and a trace of 2,3-dibromo-6-diethylamino-8*H*-thieno[2,3-*c*]azepine (**3**;  $R^1 = R^2 = \text{Br}$ ).



SCHEME

Irradiation for only 9 h gives a trace of (**1**;  $R^1 = R^2 = \text{Br}$ ) and the thienoazepine (**3**;  $R^1 = R^2 = \text{Br}$ ) (12%), m.p.

110–112°,  $\nu_{\text{max}}$  (Nujol) 1630,  $\text{cm}^{-1}$  ( $\text{C}=\text{N}$ ),  $\tau(\text{CDCl}_3)$  2.89 (1H, d,  $J$  12.0 Hz, 4- or 5-H) 3.31 (1H, d,  $J$  12.0 Hz, 4- or 5-H), 5.80 (2H, s, 8- $\text{CH}_2$ ), 6.69 (2H, q,  $J$  7.0 Hz,  $\text{CH}_2$ ), and 8.89 (3H, t,  $J$  7.0 Hz, Me). Addition of pyrene to the reaction mixture and irradiation for 18 h gives (**3**;  $R^1 = R^2 = \text{Br}$ ) as the only isolable product in a significantly increased yield (22%). In the same way methyl 6-azido-benzo[*b*]thiophen-2-carboxylate gives methyl 6-diethylamino-8*H*-thieno[2,3-*c*]azepine-2-carboxylate (**3**;  $R^1 = \text{CO}_2\text{Me}$ ,  $R^2 = \text{H}$ ) (34%), m.p. 66–68°,  $\nu_{\text{max}}$  (Nujol) 1630 ( $\text{C}=\text{N}$ ) and 1710  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ),  $\tau(\text{CDCl}_3)$  2.30 (1H, s, 3-H), 2.82 (1H, d,  $J$  12.0 Hz, 4- or 5-H), 3.40 (1H, d,  $J$  12.0 Hz, 4- or 5-H), 5.75 (2H, s, 8- $\text{CH}_2$ ), 6.12 (3H, s, Me), 6.69 (2H, q,  $J$  7.0 Hz,  $\text{CH}_2$ ), and 8.90 (3H, t,  $J$  7.0 Hz, Me),  $m/e$  278 ( $M^+$ ); tartrate, m.p. 209–210° (decomp.),  $\nu_{\text{max}}$  (Nujol) 1710  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).

A mechanism which accounts for the formation of the 8*H*-thieno[2,3-*c*]azepines (**3**) as well as the diamine (**1**;  $R^1 = R^2 = \text{Br}$ ) is shown in the Scheme. The increased yield of the thienoazepine (**3**;  $R^1 = R^2 = \text{Br}$ ) in the presence of pyrene suggests that singlet nitrenes participate in the formation of these compounds. Formation of the diamine (**1**;  $R^1 = R^2 = \text{Br}$ ) is more difficult to rationalise; two pathways (*a* and *b*) are shown in the Scheme (see also ref. 1). The apparent increased yield (< 5% to 13%) of this diamine with increased reaction time (9 to 18 h) suggests that it may be a product of thermodynamic control while the thienoazepine (**3**;  $R^1 = R^2 = \text{Br}$ ) may be one of kinetic control.<sup>2</sup> Irradiation of the thienoazepine (**3**;  $R^1 = R^2 = \text{Br}$ ) in an excess of diethylamine for 9 h did not cause conversion into the diamine. The key intermediate, however, is probably the unstable thienoazepine (**2**).

Our preliminary results appear to be the first photochemically initiated ring-expansions of fused bicyclic aromatic azides to azepines. Decomposition of azidonaphthalenes, for example, does not give benzazepines.<sup>3</sup> Also, compounds (**3**;  $R^1 = R^2 = \text{Br}$ ) and (**3**;  $R^1 = \text{CO}_2\text{Me}$ ,  $R^2 = \text{H}$ ) are the first derivatives of the 8*H*-thieno[2,3-*c*]azepine ring system.

The new compounds analysed correctly for C, H and N. We thank the Nicholas Research Institute Ltd., Slough, for a research studentship (to M.W.P.) and Dr. R. T. Parfitt and his colleagues for useful discussions.

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<sup>1</sup> B. Iddon, H. Suschitzky, and D. S. Taylor, *J.C.S. Chem. Comm.*, 1972, 879; *J.C.S. Perkin I*, 1974, 579.

<sup>2</sup> R. A. Abramovitch, S. R. Challand, and E. F. V. Scriven, *J. Amer. Chem. Soc.*, 1972, **94**, 1374.

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