Photolysis of Azidobenzo[*b*]thiophens in Secondary Amines

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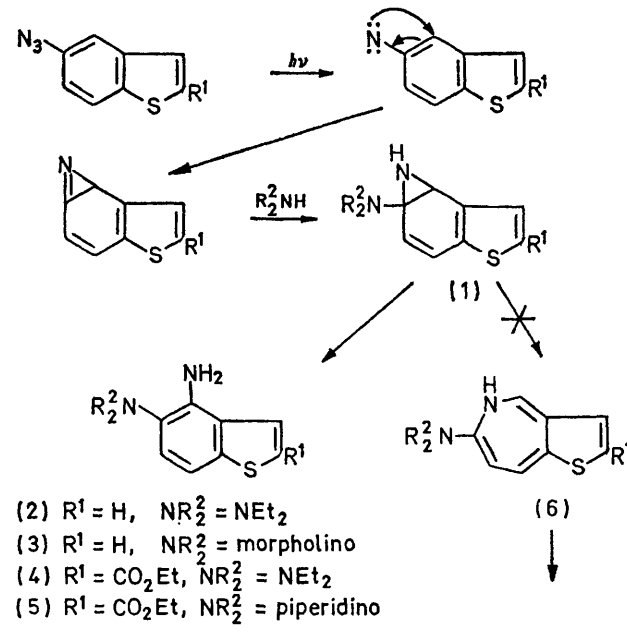
Summary Photolysis of various 5-azidobenzo[*b*]thiophens in secondary amines gave, unexpectedly, a 4-amino-5-*NN*-dialkylaminobenzo[*b*]thiophen, whilst 4-azidobenzo[*b*]-thiophen gave no rearranged products.

IN an attempt to prepare thieno-azepines by analogy with the photolytic ring-expansion of aryl azides in amines[1] we irradiated 4-azido-benzo[*b*]thiophen in an excess of diethylamine for 18 h. This gave starting material (40% recovery), 4-aminobenzo[*b*]thiophen[2] (35%), m.p. 51—52° and 4-(benzo[*b*]thien-4-yl) azobenzo[*b*]thiophen (20%), m.p 164—165°.† These products are analogous to those obtained by similar treatment of azidonaphthalenes[3] and suggest nitrene intermediacy.

In contrast, photolysis of 5-azidobenzo[*b*]thiophen for 18 h in an excess of diethylamine gave the benzo[*b*]thiophen (**2**) (24%) as the only isolable product,‡ b.p. 104—108° at 0·2 mmHg; diacetyl derivative (25%), m.p. 98—100°. Photolysis in morpholine similarly gave the benzo[*b*]-thiophen (**3**) (40%), m.p. 151—152°, whilst photolysis of ethyl 5-azidobenzo[*b*]thiophen-2-carboxylate in diethylamine or piperidine gave the benzo[*b*]thiophen (**4**) (43%), m.p. 73—74°, and benzo[*b*]thiophen (**5**) (12%), m.p. 115—116°, respectively.

Although the spectroscopic data for the diamines (**2**)—(**5**) are as expected, they do not differentiate between the 4-amino-5-*NN*-dialkylaminobenzo[*b*]thiophens (**2**)—(**5**) and their 5-amino-4-*NN*-dialkylamino-isomers. However, double irradiation of the amino-group protons of compound (**4**) at τ 5·30 resulted in a 12% increase in intensity of the signal assigned to 3-H at τ 1·87 owing to a nuclear Overhauser effect. The signal assigned to 6-H at τ 2·15 was unaffected. Double irradiation of both the methyl and methylene protons of this compound did not affect the signals assigned to 3-H and 6-H. These results confirm



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structure (**4**). Deamination of this compound *via* successive diazotisation and treatment of the diazonium compound with hypophosphorous acid gave ethyl 5-*NN*-diethylaminobenzo[*b*]thiophen-2-carboxylate (10%), b.p. 125—128° at 0·4 mmHg, with consistent spectra.

To account for the formation of the diamines (**2**)—(**5**) we propose the mechanism shown (Scheme): the azirine intermediate (**1**) ring-opens to give a diamine rather than

† All new compounds analysed correctly for C,H, and N.

‡ Isolated by chromatography; remainder of product was tar.

the corresponding thieno-azepine (**6**) presumably because the latter path would involve a considerable loss of resonance energy. For a similar reason the ring-expansion of aryl-nitrenes in amines to give a 2-amino-3*H*-azepine rather than an *o*-phenylenediamine derivative is really unexpected. The latter products could have escaped detection to date or, alternatively, they may decompose under the reaction conditions. As far as we are aware, the formation of an *o*-substituted diamine during the decomposition of an aryl azide has not been observed previously.

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