Synthesis of a Dithieno[2,3-*b*:3',2'-*e*][1,4]thiazine and of Di-3-thienylamine

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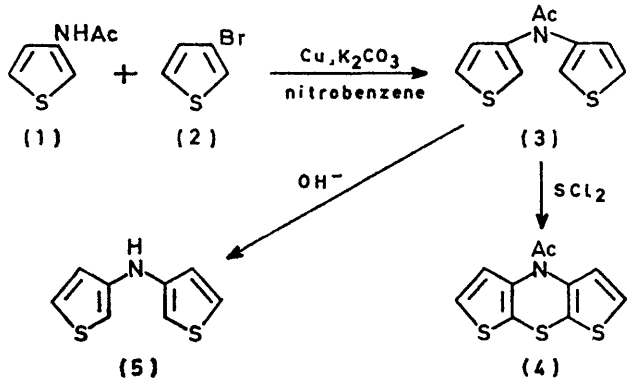
4-Acetyldithieno[2,3-*b*;3',2'-*e*][1,4]thiazine has been synthesized by direct sulphuration of *N*-acetyldi-3-thienylamine with sulphur dichloride. Hydrolysis of the latter amide afforded di-3-thienylamine, which was not present in the imino-form as shown by ^{1}H n.m.r. spectroscopy.

We have previously [1] described the preparation of the first dithienothiazine, as a result of our studies on the synthesis of thiophen analogues of phenothiazines.



Because of the length of this synthesis we have been searching for a more direct way of preparing some additional derivatives of this new heterocyclic system. The simplest way to the dithienothiazines seemed to be sulphuration of an *NN*-dithienylacetamide or of the corresponding dithienylamine, and we therefore investigated the sulphuration of *N*-acetyldi-3-thienylamine, with two equivalent α-positions.

A coupling reaction [2] with 3-acetamidothiophen (1), synthesized from thiophen-3-carboxamide [3] by a Hofmann rearrangement, and 3-bromothiophen (2) gave the amide (3), which converted directly into the dithienothiazine (4) with sulphur dichloride in benzene.

The dithienothiazine (4) was not hydrolysed to the unsubstituted thiazine by acid or base. Hydrolysis of the *N*-acetyldithienylamine with ethanolic potassium hydroxide gave the amine (5), $\nu_{max.}$ 3400 cm^{-1}, δ 5·7 (NH), indicating that at room temperature it is not present in the imino-form.[4]

EXPERIMENTAL

The Experimental section is available as Supplementary Publication No. SUP 21350 (4 pp.).†

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† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1974, Index issue.

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[4] A. R. Katrizky and J. M. Lagowski, *Adv. Heterocyclic Chem.*, 1964, **2**, ch. 1.