Azothiophens Formed by a Diazonium Coupling Reaction with a Deactivated Thiophen Ring

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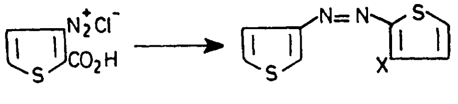
Summary 2-Carboxythiophen-3-diazonium chloride undergoes self-coupling to give substituted azothiophens.

ARYL diazonium salts are known to couple with thiophens to give azo compounds[1] but until recently a strongly activating substituent such as acetamido[2] was thought to be essential. It has now been shown, however, that weakly activating groups such as methyl or t-butyl also will suffice, although in some cases side-chain attack to give arylhydrazones predominates.[3] We now report the first example of a coupling reaction in which a deactivating group is present on the thiophen ring which is attacked.



(I)

(II)a; X = Cl
b; X = OEt

3-Aminothiophen-2-carboxylic acid[4] reacts with isopentyl nitrite and HCl to give the diazonium chloride (I)† in 85% yield, m.p. 150°. On heating a mixture of (I) and propylene oxide in chloroform under reflux for 1—3 h (potential aryne-producing conditions),[5] two new compounds were isolated. The first was obtained as yellow needles, m.p. 63—64°, (17% yield), and from its analytical† and spectral data was assigned structure (IIa). The second was obtained as a yellow oil (8% yield) and was assigned structure (IIb) based on its spectral properties.

That the ethoxy group of (IIb) originates from the 0·5% EtOH present in commercial CHCl_3 was clearly shown by repeating the reaction in ethanol-free CH_2Cl_2 [only (IIa) formed] and in CHCl_3–5% EtOH [only (IIb) formed]. This observation, taken with the failure to detect any 3-chloro or 3-ethoxythiophen in the reaction mixtures, strongly suggests ionic replacement of the diazonium group[6] after coupling has occurred. Although the exact nature and sequence of this coupling and the decarboxylations‡ remains to be specified, the net result of this reaction is to join, *via* an azo linkage, two thiophen rings neither of which need contain an activating group and at least one of which may contain a deactivating group.

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† Satisfactory microanalyses were obtained.

‡ Analogous to decarboxylative azo coupling to electron-rich aromatic acids (ref. 6, p. 239).

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