

Reaction of 2-Nitrothiophen with Secondary Aliphatic Amines

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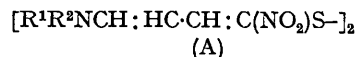
Summary The reaction between 2-nitrothiophen and secondary aliphatic amines has been investigated: the u.v. and ^1H n.m.r. spectra of the red crystalline products isolated suggest that the thiophen ring opening has occurred.

In relation to our studies in the thiophen series,¹ we report here results on the reaction of 2-nitrothiophen with a series of secondary aliphatic amines. When ethanolic diethylamine (1 mole) was added to 2-nitrothiophen (1 mole) also dissolved in ethanol, an intense red colour developed immediately. After 5 days at 0° red crystals were filtered off and recrystallized. Analytical data (C, H, N, O, and S, and molecular weight) corresponded to the formula $\text{C}_{16}\text{H}_{26}\text{N}_4\text{O}_4\text{S}_2$.

The structure of the compound was assigned on the basis of its ^1H n.m.r. [τ 1.76 (1H, d, J 12.3 Hz), 2.79 (1H, d, J 12.3 Hz), 4.33 (1H, t, J 12.3 Hz), 6.60 (4H, q, J 7.2 Hz, amine CH_2), and 8.73 (6H, t, J 7.2 Hz, amine Me)] and u.v. (λ_{max} 458 nm, $\log \epsilon$ 4.75) spectra. 2-Nitro-3-deuteriothiophen and

diethylamine gave a product with no doublet at τ 1.76, and a doublet (J 12.3 Hz) rather than a triplet at τ 4.33; the product from 2-nitro-5-deuteriothiophen showed no doublet at τ 2.79, and a doublet (J 12.3 Hz again) at τ 4.33. The remaining peaks in the spectra were unaffected upon deuteration. Similar compounds and analogous spectral data were obtained with various other aliphatic secondary amines (Me_2NH , Pr_2NH , piperidine, and morpholine).

On the basis of these spectral data, structure (A) is one possibility for these compounds. The reaction between 2-



nitrothiophen and secondary aliphatic amines thus seems to be of the 'nonbenzenoid' type² leading to products in which thiophen ring opening has occurred under very mild conditions.

An X-ray structural investigation is in progress.

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¹ G. Guanti, C. Dell'Erba, and P. Macera, *J. Heterocyclic Chem.*, 1971, 8, 537.

² S. Gronowitz, in 'Organosulfur Chemistry', ed. M. J. Janssen, Interscience, New York, 1967, pp. 119—141.