Reaction of 2-Nitrothiophen with Secondary Aliphatic Amines

By G. GUANTI, C. DELL'ERBA,* and G. LEANDRI

(*Istituto di Chimica Organica dell'Università, Via Pastore* 3, *Genova, Italy*, 16132)

Summary The reaction between 2-nitrothiophen and secondary aliphatic amines has been investigated: the u.v. and ^{1}H 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 $C_{16}H_{26}N_4O_4S_2$.

The structure of the compound was assigned on the basis of its ^{1}H 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 ϵ 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 deuteriation. 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-

$$[R^1R^2NCH:HC{\cdot}CH:C(NO_2)S-]_2$$
(A)

nitrothiophen and secondary aliphatic amines thus seems to be of the 'nonbenzenoid' type[2] leading to products in which thiophen ring opening has occurred under very mild conditions.

An X-ray structural investigation is in progress.

(*Received, 2nd May* 1972; *Com.* 749.)

[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.