

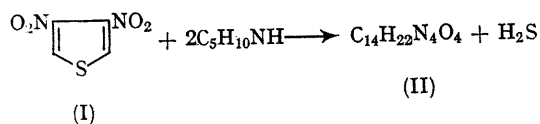
Ring-opening Reaction in the Thiophen Series: Reaction between 3,4-Dinitrothiophen and Secondary Amines†

By C. DELL'ERBA, D. SPINELLI,*† and G. LEANDRI

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

IN the course of our work¹ on nucleophilic substitution in the thiophen series we reported that 3,4-dinitrothiophen reacts with sodium thiophenoxide to give phenyl 2-(4-nitro)thienyl sulphide *via* a cinucleophilic substitution.²

We have now observed that 3,4-dinitrothiophen (I) reacts with piperidine in methanol at room temperature to give a yellow compound (II) (m.p. 200°) and H₂S. Analytical data (C, H, N; S absent; molecular weight) for compound (II) correspond to the formula C₁₄H₂₂N₄O₄. Yields of H₂S and (II) are consistent with reaction:



The ring-opening of 3,4-dinitrothiophen has no parallel in other aromatic systems. Compound (II) has been shown to be 1,4-dipiperidino-2,3-dinitrobutadiene C₅H₁₀N·CH:C(NO₂)·C(NO₂):CH·NC₅H₁₀ on the basis of n.m.r. spectral data (60 Mc./sec., CDCl₃), τ 1.45 (s, 1H), 6.48 (m, 4H), and 8.34 (m, 6H) and the u.v. absorption maximum (λ_{max} 360 nm., log ε 4.5) characteristic of a nitro-enamine group.³

3,4-Dinitrothiophen reacts in a similar way with various other secondary amines (see Table).

According to Gronowitz's nomenclature,⁴ the reaction is a "nonbenzoid" reaction of a thiophen compound.

Other instances of ring opening in the thiophen series are known, *e.g.*, decomposition of organolithium compounds,⁵ catalytic desulphurations,⁶ or a hydrolytic process in hindered thiophens by action of Derbyshire and Waters' reagent;⁷ *i.e.*, drastic conditions are necessary.

TABLE

XHC : C(NO ₂)·C(NO ₂) : CHX			
X		Colour	M.p.
Morpholino	Yellow	260°
NMe ₂	Yellow	207°
NEt ₂	Orange-yellow	154°
NPr ⁿ ₂	Orange-yellow	127°

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‡ Present address: Institute of Organic Chemistry, Faculty of Pharmacy, University of Sassari, Italy, 07100.

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² C. Dell'Erba, D. Spinelli, and G. Leandri, *Gazzetta*, in the press.

³ L. Marchetti and V. Passalacqua, *Ann. Chim. (Italy)*, 1967, **57**, 1266.

⁴ S. Gronowitz, in "Organosulfur Chemistry," ed. M. J. Janssen, Interscience, New York, 1967, pp. 119—141.

⁵ M. Rings, Dissertation, Universität Heidelberg, 1966, quoted in R. W. Hofmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, p. 290.

⁶ S. Gronowitz, *Adv. Heterocyclic Chem.*, 1963, **1**, 108, and references therein.

⁷ S. Gronowitz and G. L. Borgen, *Acta Chem. Scand.*, 1965, **19**, 1180.