

THE NABAM OXIDATION PRODUCT
SYNTHESIS OF SOME IMIDAZO-1,2,4-DITHIAZOLE DERIVATIVES

R.J.S. Beer^{*} and A. Naylor

The Robert Robinson Laboratories, University of Liverpool

(Received in UK 24 May 1973; accepted for publication 7 June 1973)

The highly active fungicidal compound obtained by oxidation of disodium ethylene bisdithiocarbamate (nabam), originally thought to be ethylenethiuram monosulphide (I), has been reformulated as the 1,2,4-dithiazole-3-thione derivative (II)¹. The revised structure has been supported in a recent note² describing ¹³C n.m.r. studies, and the formation of ethylenethiourea by electrochemical reduction.

We wish to report two syntheses of the nabam oxidation product, both of which use ethylenethiourea as starting material, and provide further evidence supporting structure (II).

Oxidation of mixtures of thiourea and a variety of thiols with hydrogen peroxide in the presence of hydrochloric acid has been shown³ to lead to S-alkylthioisothiuronium chlorides. This method, applied to ethylenethiourea and benzyl mercaptan, gave the S-benzylthioisothiuronium salt (III), in approximately 50% yield. A suspension of the salt in carbon disulphide was stirred vigorously with aqueous sodium hydrogen carbonate, when a red voluminous precipitate slowly formed. The red product corresponds to the unstable carbon disulphide adduct (IVa) described by Pluijgers, Vonk, and Thorn¹; extraction with warm chloroform, followed by chromatography on silica

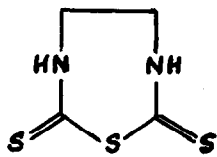
(elution with ethylacetate/chloroform, 1:1), gave a yellow product, m.p. 125^o, in 30% yield (λ max. in EtOH 280 nm., ϵ 18,000; n.m.r. spectrum in CDCl₃, triplets at τ 5.53, 6.13) identical with a sample prepared by oxidation of nabam.⁴

An alternative route to the thione (II) involved treatment of a solution of the isothiuronium salt (III) and phenyl isothiocyanate in methanol with aqueous sodium hydrogen carbonate. The yellow product, which formed needles (33%), m.p. 163^o, from benzene-light petroleum [Found: C, 54.9; H, 3.9; N, 15.3. C₁₇H₁₄N₄S₃ requires C, 55.1; H, 3.8; N, 15.1% : λ max. in CH₂Cl₂ 259, 309 nm, ϵ 44,400, 16,400] , has a symmetrical structure, since the four methylene protons appear as a singlet (τ 5.53, CDCl₃) in the n.m.r. spectrum. We provisionally assign the tricyclic structure (V) to this product, although the alternative structure (VI) is not entirely excluded.

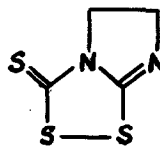
When the tricyclic compound (V) [or (VI)] was heated under reflux with carbon disulphide containing sulphur for 20 hours, conditions reported⁵ to be effective in converting certain heterocyclic anils to the corresponding thiones, the red complex (IV) was again obtained in 65% yield.

The formation of the thione (II) [as its easily dissociated carbon disulphide complex (IVa) or (IVb)] from the tricyclic compound is evidently reversible, the latter compound being regenerated when the thione is treated with phenyl isothiocyanate in benzene solution at room temperature.

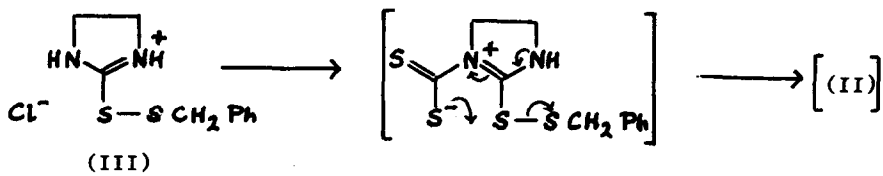
Our results support the view expressed by Pluijgers et al that the structure of their carbon disulphide adduct resembles those of 6a-thiathiophthens (trithiapentalenes) and related compounds. Structures (IVb), (V), and (VI), however, differ from the "aromatic" thiathiophthen-type systems in bond distribution, in particular, in having two exocyclic double bonds. The determination of bond lengths in the stable and crystalline compound which we regard as (V) is therefore a matter of considerable interest.⁶



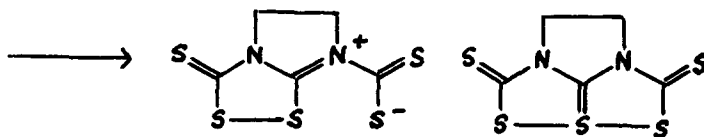
(I)



(II)

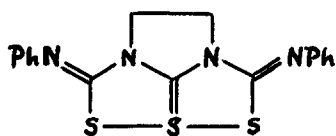


(III)

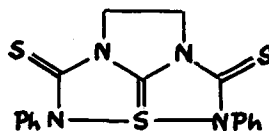


(IVa)

(IVb)



(V)



(VI)

References

1. C.W. Pluijgers, J.W. Vonk, and G.D. Thorn, Tetrahedron Letters, 1317, (1971).
2. M. Alvarez, R.W. Creekmore, and R.T. Rosen, Tetrahedron Letters, 939, (1973).
3. K. Sirakawa, O. Aki, T. Tsujikawa, and T. Tsuda, Chem. Pharm. Bull., 18, 235, (1970).
4. G.D. Thorn and R.A. Ludwig, J. Appl. Chem., 12, 90, (1962).
5. W. Ried, R. Oxenius, and W. Merkel, Angew. Chem. Int. Edn., 11, 511, (1972).
6. Dr. Iain Paul, of the University of Illinois, has kindly agreed to make a detailed crystallographic study of this compound.