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A DERIVATIVE OF [1,2,5]OXATHIAZOLO[2,3-b] [1,2,5] -OXATHIAZOLE-7-S^{IV}

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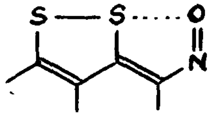
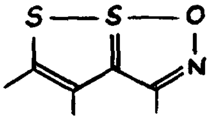
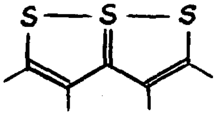
The close intramolecular 'contacts' (2.0 - 2.1Å) between oxygen and sulphur atoms in 3-nitrosomethylene-1,2-dithioles[1](I) suggest that these compounds should be formulated as bicyclic systems (II) with the central sulphur atom bonded as in 6a-thiathiophthens[2] (III). Similar bonding is indicated for selenium in compounds of type (IV) by recent spectroscopic and X-ray crystallographic studies[3]. Thus, the product obtained[4] by the action of selenium dioxide on dimedone dioxime has been found to have the symmetrical structure (V) with the Se-O distances shown.



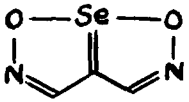
(I)



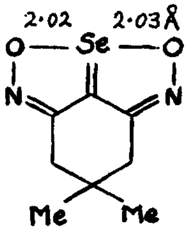
(II)



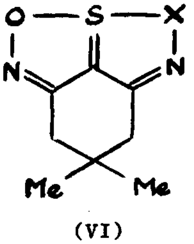
(III)



(IV)



(V)



(VI)

We now report the synthesis of the sulphur analogue of (V). Treatment of anhydrous dimedone dioxime (sublimed sample) with sulphur dichloride (SCl_2) in tetrahydrofuran, first at -70° and subsequently at room temperature yielded a dark red oil from which two components were isolated by chromatography on silica in light petroleum-diethyl ether. The first product eluted formed orange flattened prisms (30%) m.p. 66°, from light petroleum [Found: C, 48·6; H, 5·1; N, 14·0; S, 15·85%; M,[*] 198. $C_8H_{10}N_2O_2S$ requires C, 48·5; H, 5·1; N, 14·1; S, 16.2%; M, 198]. Further elution yielded a small amount (1·6%) of a second crystalline product, which formed very dark orange (in some samples, almost black) needles, m.p. 97° [Found: C, 44·9; H, 4·85; N, 12.85; S, 29·7%; M,[*] 214. $C_8H_{10}N_2OS_2$ requires C, 44·8: H, 4·7; N, 13·1; S, 29·9%; M, 214] .

The symmetrical structure (VI; X=O) is assigned to the product, m.p. 66°, on the basis of its N.M.R. spectrum [τ 8.82 (6H, singlet), 6.87 (4H, singlet); $CDCl_3$ solution] which closely resembles that of the selenium compound (V) [τ 8.92 (6H, singlet), 6.78 (4H, singlet)] . The second product, m.p. 97°, is formulated as (VI; X=S) [τ 8.82 (6H, singlet), 6.82 (2H, singlet), 6.73 (2H, singlet)] .

[*] by mass spectrometry

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