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Structure and Novel Reactivity of a New Heterocyclic Bridged Ring System

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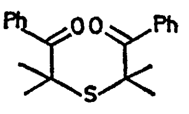
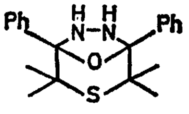
Summary Reaction of the diketo-sulphide (I) with anhydrous hydrazine in pyridine leads to the formation of (II), whose hitherto unknown ring system has been structurally elucidated by spectroscopic and *X*-ray crystallographic methods; (II) is stable in the crystal, but in benzene solution in the presence of oxygen undergoes a remarkable transformation into the ozonide sulphide (III) in effectively quantitative yield.

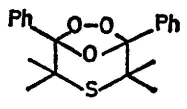
We report the formation of a new bridged heterocyclic ring system discovered on treatment of the highly hindered diketo-sulphide (I) with anhydrous hydrazine (3 mol equiv.) in pyridine at room temperature. After 20 days, needles (14%) of a compound $C_{20}H_{24}N_2OS$, m.p. 219—221 °C (from MeOH, evacuated sealed capillary) were isolated: satisfactory microanalysis, mass spectrum *m/e* 340, and osmometric M 338; requires 340.



(I)



(II)



(III)

The i.r. spectrum (KBr disc) of this compound shows two sharp bands at 3303m cm^{-1} and 3275m cm^{-1}, indicative of ν(NH) absorption. This together with the ^{1}H n.m.r. spectrum (τ, $CDCl_3$): 8·77 (6H, s), 8·45 (6H, s), 5·06 (2H, broad), and *ca.* 2·3—2·8 (10H, complex) and the u.v. spectrum (no conjugation to phenyl groups) allowed us to assign to compound (II) the structure formulated.

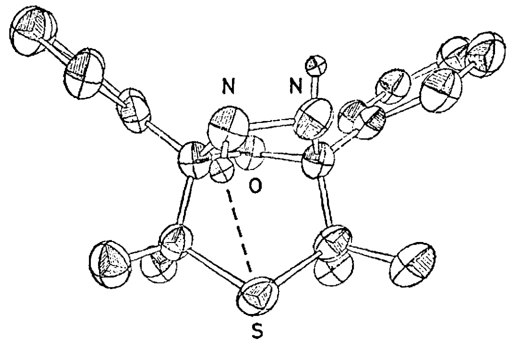


FIGURE. *An ORTEP drawing showing a general view of the molecular structure of* (II) *in the crystal.* (*Only the hydrogen atoms attached to nitrogen are included, and the intramolecular hydrogen bond involving one of these is denoted by a broken line*).

Since (II) embodies the first example of the 8-oxa-3-thia-6,7-diazabicyclo[3,2,1]octane ring system, we have carried out a single-crystal *X*-ray diffraction analysis of this compound. *Crystal data:* M = 340·5. Triclinic, a = 9·911(6), b = 15·297(10), c = 6·257(4) Å, α = 103°1′ (±3′), β = 106°9′ (±4′), γ = 81°10′ (±3′), U = 883·7 Å^3, D_m = 1·24, D_c = 1·27 g/cm^3, Z = 2, $F(000)$ = 364, space group $P\bar{1}$. Mo-K_α radiation, λ = 0·7107 Å, μ(Mo-K_α) = 1·9 cm^{-1}. Data were collected on a Hilger-Watts automatic diffractometer and the structure was solved by Patterson and

Fourier methods: the final R value was 7·7%. During the course of the analysis, all 24 hydrogen atoms were located in a difference electron-density distribution. The Figure shows a general view of the structure of (II) in the crystal (for clarity all hydrogen atoms have been omitted except those bonded to nitrogen). The seven-membered ring has a boat conformation, and an intramolecular hydrogen bond of the type $N\text{–}H \cdots S$ is present, involving one bridge nitrogen atom and its hydrogen, as shown. The six-membered 1,4-oxathian ring is present as a chair, though a pronounced "flattening" of its four ring carbons and sulphur† is found; this may be due in part at least, to an inverse reflex effect[1] corresponding to that found in the bridged carbocycle.

Compound (II) is stable in air in the crystalline state and shows no significant decomposition in a sealed tube at 200 °C for 20 min in a degassed solvent, such as tetrahydropyran. However, stirring a benzene solution of (II) under oxygen at room temperature for 2 days produces as the only isolable product a compound, m.p. 182—185 °C (decomp.), $C_{20}H_{22}O_3S$, (III) in a smooth reaction apparently unaffected by light or dark. Compound (III) gave an osmometric M of 347 ($C_{20}H_{22}O_3S$ requires 342), a u.v. spectrum rather similar to that of (II), and an i.r. spectrum (KBr disc) which, apart from the absence of ν(NH) absorption, resembles that of (II), and shows no hydroxy, carbonyl, sulphoxide, or sulphone absorption. On this basis, and the ^1H n.m.r. spectrum: 8·73 (6H, s), 8·41 (6H, s), and *ca.* 2·4—2·8 (10H, m), one may assign the formulated structure to compound (III). Consistent with this, stirring (III) for 2 days with excess of zinc in acetic acid was found to give a quantitative yield of the diketo-sulphide (I).

The mechanism of the ready conversion of (II) into (III), which may involve intermediate azo-compound formation‡ is under investigation, as are other reactions of (II) and (III) and related compounds.

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† A detailed description of the structure of (II) will be given later.

‡ The reaction of the azo-compound corresponding to (II) with oxygen to give (III) would find a possible analogy in the high yield conversion of 1,1′-dihydroxyazocyclohexane into 1,1′-dihydroxydicyclohexyl peroxide in the presence of air (see ref. 2).

[1] C. W. Jefford, A. Baretta, J. Fournier, and B. Waegell, *Helv. Chim. Acta*, 1970, **53**, 1180.

[2] E. Schmitz, R. Ohme, and S. Schramm, *Annalen*, 1967, **702**, 131.