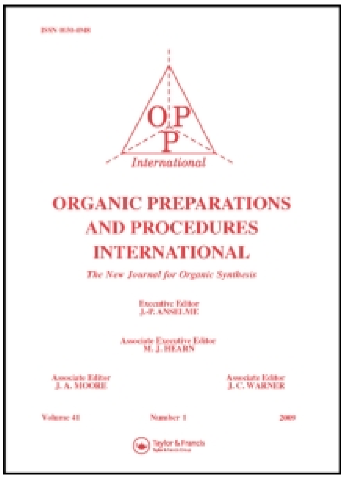

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1,2,5-THIADIAZOLID-3,4-DIONE-1-OXIDE

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1,2,5-THIADIAZOLID-3,4-DIONE-1-OXIDE

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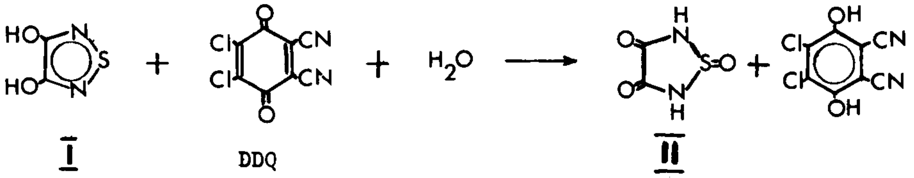
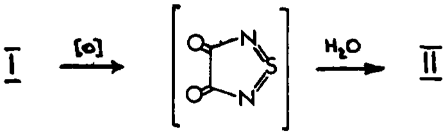
Although open-chain *secondary*-thionyldiamides (R-NH-SO-NH-R) are unknown, several examples of fused ring systems containing this grouping have recently been isolated as reaction intermediates in the preparation of benzo-2,1,3-thiadiazoles and naphtho-1,2,6-thiadiazines[1,2,3].

We now wish to report the synthesis of a monocyclic, five-membered thionyldiamide by the following oxidation reaction:



Apart from being the first example of the parent 1,2,5-thiadiazolidine-1-oxide nucleus[4], interest in the reaction also centers on the possible intermediacy of a tetravalent sulfur species of the type shown below.



The existance of hetero-tetravalent-sulfur intermediates has recently been demonstrated by their isolation as maleimide adducts[5,6,7]. The source of the mole of water required in the subsequent addition step was not investigated, but is presumed to be adventitious presence in the solvent, dioxane, which was not rigorously dried.

The starting material, 3,4-dihydroxy-1,2,5-thiadiazole (I), was prepared by $AlCl_3$-mediated alkyl group cleavage of the corresponding diethoxy derivative which has previously been reported[8,9].

The title compound, II, is readily hydrolysed in water to oxamide and behaves as a dibasic acid with pK's 2.62, 6.58. The monoanion displays a green fluorescence.

EXPERIMENTAL

3,4-Dihydroxy-1,2,5-thiadiazole[8] *(I)*

Anhydrous aluminum trichloride (45 gm.) was ground to a powder under dry benzene and the suspension placed in a 2-liter 3-necked flask equipped with stirrer, condenser and dropping funnel. The volume of benzene was made up to 750 ml. and a dried solution of 3,4-diethoxy-1,2,5-thiadiazole[8,9] (23 gm.) in benzene (300 ml.) was added dropwise under vigorous stirring. The mixture was heated under reflux and gentle stirring for 8 hr. and then poured onto cracked ice (500 gm.) mixed with concentrated hydrochloric acid (300 ml.). The suspension was extracted five times with ether (200 ml. portions) and the combined extracts dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* leaving an oily solid which was readily purified by trituration with benzene followed by suction filtration.[11] Final purification was effected by vacuum sublimation at 140 - 150° (0.2 mm Hg) which yielded 10.5 gm. (68%) of pure product, m.p. 228 - 230° (dec).

$\lambda_{max}^{H_2O}$ 282 mμ (log ε 3.83); γ_{max}^{KBr} 3130 cm^{-1} (broad and shouldered, OH). pKa_1 = 4.68, pKa_2 = 7.50 (18°). Equivalent weight by titration, 61 (Theory 59).

Anal.

Calc. for $C_2H_2N_2O_2S$: C, 20.3; H, 1.8; N, 23.7; S, 27.1%. Found: C, 19.9; H, 2.0; N, 24.0; S, 26.7%.

1,2,5-Thiadiazolid-3,4-dione-1-oxide (II)

3,4-Dihydroxy-1,2,5-thiadiazole (1.2 gm.) in dioxane (20 ml.) was rapidly added to a solution of 2,3-dicyano-5,6-dichloroquinone (2.3 gm.) in dioxane (50 ml.). After standing for several minutes, the combined solution turned an intense transitory red colour, and dichlorodicyanohydroquinone was rapidly deposited. After suction filtration, the volume was reduced *in vacuo* to the point where crystallization commenced and the solution was then stored in a refrigerator overnight. The product was recrystallized from tetrahydrofuran/hexane and gave m.p. 175° (decomp.) with a yield of 1.2 gm. (90%).

λ_{max}^{EtOH} 307 mμ (log ε 2.2); γ_{max}^{KBr} (cm^{-1}) 3450, 3300 (NH); 1760, 1720, 1710 (H-bonded CO); 1150 (S = O); n.m.r. (acetone-d_6) broad low-intensity peak at τ 5.85. pKa_1 2.62, pKa_2 6.58 (20°).

Anal.

Calc. for $C_2H_2N_2O_3S$: C, 17.9; H, 1.5; N, 20.9; S, 23.9%; MW, 134. Found: C, 18.1; H, 1.5; N, 20.9; S, 23.7; MW (osmometer), 133.

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10. Alternative common nomenclature would be cyclo-N,N'-thionyloxamide.
11. The benzene extract was found to contain ethyl benzene, 3-hydroxy-4-ethoxy-1,2,5-thiadiazole and unchanged starting material.

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