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3-THIETANONE 1,1-DIOXIDE

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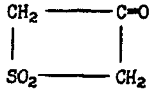
Considerable interest (2,3,4,5) has recently been directed toward the synthesis and properties of thietanes (thiacyclobutanes) and their derivatives. In particular, 3-thietanone has been prepared by two independent methods (4,5); however, the corresponding sulfone (I) has been more elusive and has escaped attempts at its synthesis. *A priori*, ketosulfone I would be expected to possess properties similar to those of the recently-reported 1,3-cyclobutanedione (6).



I

We now wish to report a convenient synthesis for 3-thietanone 1,1-dioxide (I). Recently (7) it was shown that when methanesulfonyl chloride

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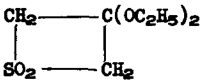
is added to ketene diethylacetal in the presence of triethylamine, II is obtained in good yield.



II

When II (0.03 mole) is dissolved in 40 ml. of conc. hydrochloric acid at 25°, I precipitates as a white crystalline solid after about fifteen minutes. More I is obtained by evaporation of the acid *in vacuo* (total yield, 90%). After one recrystallization from dioxane or sublimation at 100°/1.0 mm. the compound melts at 219-221° dec. *Anal*. Calcd. for $C_3H_4O_3S$: C, 29.99; H, 3.36; S, 26.69; M.W. 120.1. Found: C, 29.79; H, 3.30; S, 26.42; M.W, 121.2 (Osmometer).

Spectral studies support the structure in that a single unsplit peak occurs in the NMR spectrum at 4.22 δ in DMSO or at 4.92 δ in dioxane. The infrared spectrum (Nujol) exhibits a strong carbonyl absorbance at 5.62 μ with a weak side band at 5.45 μ and strong sulfone absorbances at 7.61 μ and 8.36 μ. Two other strong bands are prevalent at 8.86 μ and 13.84 μ. Compound I forms a very-insoluble, bright-yellow 2,4-dinitrophenylhydrazone (m.p. 241° dec.), which can be crystallized from dioxane, *Anal*. Calcd. for $C_9H_8N_4O_6S$: C, 36.00; H, 2.69; N, 18.66; S, 10.68. Found: C, 36.31; H, 2.91; N, 18.49; S, 10.81.

Acidic properties are exhibited by the ready solubility of the ketosulfone in 10% sodium hydroxide and vigorous effervescence with a sodium bicarbonate solution. The compound is nearly insoluble in the common organic solvents. Also, compound II was reduced in good yield by means of diborane (8) in dioxane to 3-hydroxythietane 1,1-dioxide, identical with an authentic sample (9).

Further studies concerning the chemistry of I are currently under investigation in these laboratories and will be elaborated on at a later date.

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