

Under normal conditions all these lipids were retained on the Florisil columns but they appeared, for instance, in the effluent at overloading of the column. For a positive identification of the sulfolipids it was, therefore, necessary to apply as much material on the paper that with the cresyl violet stain a brown-red metachromatic spot was obtained.

Summary. A simple procedure is described for the chromatographic determination of small amounts of sulfatides in biological materials. As little as 0.2 μg of sulfatides can be detected and the optimal concentration for the analysis is 1–10 μg of sulfatides.

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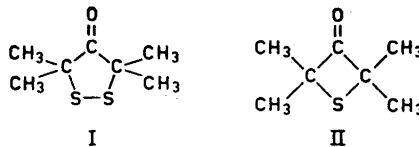
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The Preparation of 3,3,5,5-Tetramethyl-1,2-dithiolane-4-one

GÖRAN CLAEISSON and ARNE THALÉN

Research Department, AB Bofors, Nobelkrut, Bofors, Sweden, and Department of Organic Chemistry, Chemical Institute, University of Uppsala, Uppsala, Sweden

The unsubstituted 1,2-dithiolane-4-one (1,2-dithiacyclopentane-4-one) is too unstable to be isolated in the pure state. Schotte was, however, able to prepare its semicarbazone¹. We wish to report here the synthesis of the tetramethyl-



substituted ketodisulphide (I), where the methyl groups have stabilized the ring system making it possible to isolate the compound by distillation.

As the starting material for the synthesis we have used α,α' -dibromodiisopropylketone. This compound has been prepared from diisopropylketone, bromine and phosphorus pentabromide by Faworsky². We have simplified the synthesis and obtained the dibromoketone in a better yield by performing the bromination with bromine in hydrobromic acid.

At first we attempted to prepare the dimercapto compound corresponding to I by starting with α,α' -dibromodiisopropylketone and sodium hydrosulphide, but the only isolated product was the cyclic monosulphide II, 2,2,4,4-tetramethyl-3-thietanone³. However, the disulphide I could be obtained in a fairly good yield from the dibromoketone and sodium disulphide. It is a light yellow liquid (m.p. 13–14°) and shows a number of ultra-violet absorption peaks between 200 and 330 $m\mu$.

Further work is in progress on the cyclic ketodisulphides.

Experimental. α,α' -Dibromodiisopropylketone.

While stirring at room temperature, 80 g (0.5 mole) of bromine were added dropwise to 57 g (0.5 mole) of diisopropylketone mixed with 50 ml of hydrobromic acid (48 %). The mixture was heated to 55° and a further 80 g (0.5 mole) of bromine were added. The mixture was kept at this temperature with continued stirring for 3 h. The product was separated from the hydrobromic acid, washed with water, sodium bisulphite solution (10 %), sodium carbonate solution (5 %), water, and dried over anhydrous calcium chloride. The α,α' -dibromodiisopropylketone was collected at 84.5–86.5°/10 mm, n_D^{20} 1.5062. The yield was 109 g (80 %). α,α' -Dibromodiisopropylketone prepared according to Faworsky shows b.p. 84–85°/9 mm² and n_D^{20} 1.5062².

3,3,5,5-Tetramethyl-1,2-dithiolane-4-one. 18 g of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in a mixture of 200 ml of dimethyl sulphoxide and 30 ml of water were dissolved with stirring at 75°. 2.4 g of finely ground sulphur were then added, and heating

and stirring were continued until the sulphur had dissolved forming a brownish-red solution of sodium disulphide. The warm sodium disulphide solution was added dropwise with stirring, to a solution of 13.6 g (0.05 mole) of α, α' -dibromodiisopropylketone in 50 ml of dimethyl sulphoxide at room temperature. After the addition was complete, the reaction mixture was kept at 40° and stirred for 2 h; 500 ml of water were added and the mixture extracted ten times with ether. The ethereal extracts were dried over anhydrous magnesium sulphate, and the ether removed *in vacuo* leaving 8 g of a yellowish-red oil, containing a mixture of the mono-sulphide (II) and the disulphide (I) (identified through IR-spectra). The monosulphide together with some disulphide were removed by careful sublimation at 0.3 mm. The 3,3,5,5-tetramethyl-1,2-dithiolane-4-one was then collected at 37–39°/0.3 mm, n_D^{20} 1.5102, m.p. 13–14°. The yield was 3.1 g (35 %).

(Found: C 47.72; H 6.89; S 36.19. Calc. for $C_7H_{12}OS_2$ (176.31): C 47.69; H 6.86; S 36.38.)

Spectrochemical data: UV, $\lambda_{\max}^{\text{isoctane}}$ 230, 253, 275, 302, 312, and 325 m μ .

IR, carbonyl absorption at 1735 cm^{-1} (liq. phase).

NMR, a single peak at $\tau = 9.26$ ppm.

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Dimorphism of N,N-Diethyl-*p*-toluenesulphonamide

BODIL JERSLEV and E. JØLK
RAVN-JONSEN

Chemical Laboratory C, The Royal Danish School of Pharmacy, Copenhagen, Denmark

In performing the Hinsberg test on diethylamine, a reaction product was consistently obtained with m.p. 46° (in capillary tube) instead of as reported 60°¹. Subsequently, a number of students working in the same room reported either one or the other melting point, but after a few weeks melting points of 60° were invariably found.

The low-melting compound is an unstable modification of N,N-diethyl-*p*-toluenesulphonamide as apparent from the following observations: Kjeldahl analyses of a number of preparations dried in various ways gave results within 2% of the theoretical value. A sample of the low-melting compound enclosed in a sealed capillary tube showed m.p. 45.5–46° on a number of successive determinations; after heating to 62° and recrystallization the product melted at 59.5–60°. Melting point determination on a microscope hot-stage showed two different types of crystals; one melting at 45°, the other at 60°.

The low-melting modification is rapidly transformed in the presence of nuclei of the high-melting modification; thus in some cases melting point determinations performed on two successive days of a sample left openly in the laboratory revealed transformation. Only one example of N-*p*-toluenesulphonamide derivatives exhibiting dimorphism has been found in the literature, *viz.* that of N-butylaniline,² but in a number of cases inconsistent melting point data have been reported. These findings indicate, that polymorphism is a phenomenon that should not be overlooked, when *p*-toluenesulphonyl derivatives are used for the identification of amines.

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