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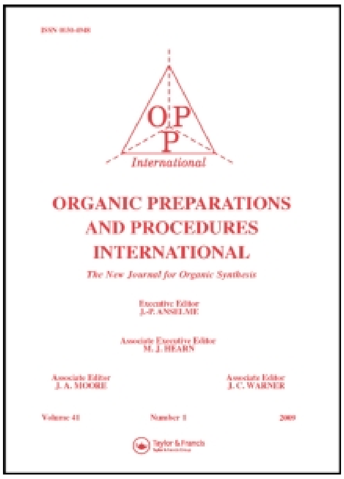

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THE PRODUCTS OF DEHYDRATION OF 2,4-DI-TERT-BUTYL-3,4-DIHYDROXYTETRAHYDROTHIOPHENE-1,1-DIOXIDE: A CORRECTION

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ORGANIC PREPARATIONS AND PROCEDURES 1(2), 91-96 (1969)

THE PRODUCTS OF DEHYDRATION OF 2,4-DI-TERT-BUTYL-3,4-DIHYDROXYTETRAHYDROTHIOPHENE-1,1-DIOXIDE

A CORRECTION

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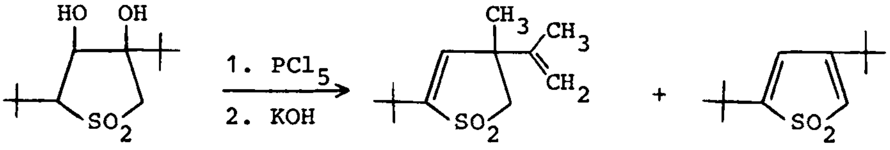
We have re-examined the dehydration of the diol I as described by Backer and Strating[1]. From the reaction now two products, II (m.p. 53-53.5°) and III (m.p. 135-136°), were isolated, whereas originally only the former isomer was obtained.

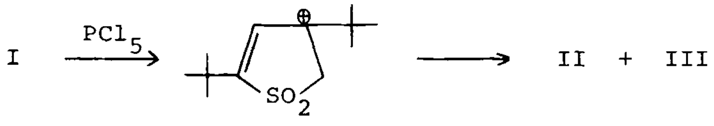


I II III

In 1937 Backer and Strating[1] described their dehydration product (m.p. 53-53.5°) as 2,4-di-t-butylthiophene-1,1-dioxide[2] (structure III). However, comparison with an authentic sample of this sulfone III prepared recently in 83% yield by the action of hydrogen peroxide on 2,4-di-t-butylthiophene[4] has shown that this is identical in all respects with the second product (m.p. 135-136°) now isolated from the reaction mixture obtained by Backer and Strating's procedure.

The structure of III was established unambiguously via elemental analysis which was correct for $C_{12}H_{20}O_2S$ and its PMR spectrum which exhibited two singlets of the t-butyl groups at δ 1.20 (9 H) and 1.36 ppm (9 H) and two doublets (J = 1.5 cps) at δ 6.00 (1 H) and 6.28 ppm (1 H) of the ring protons.

Compound II, elementary analysis correct for $C_{12}H_{20}O_2S$, showed infrared absorptions at 1642 and 1620 (sh) cm^{-1} (C=C) and at 1140 and 1292 cm^{-1} (SO_2). The PMR spectrum showed a singlet at δ 6.06 ppm (1 H), a broadened singlet at δ 4.86 ppm (2 H), two doublets (J = 13 cps) at δ 3.08 and 3.00 ppm (2 H), a broadened singlet at δ 1.78 ppm (3 H) and two singlets at δ 1.40 (3 H) and 1.32 ppm (9 H) respectively. These spectral data are consistent with those expected for 5-t-butyl-3-isopropenyl-3-methyl-2,3-dihydrothiophene-1,1-dioxide (II), presumably formed through a Wagner-Meerwein type rearrangement. Whether this occurs from IV or from a carbonium ion in which the first double bond is not yet introduced, is not known.



IV

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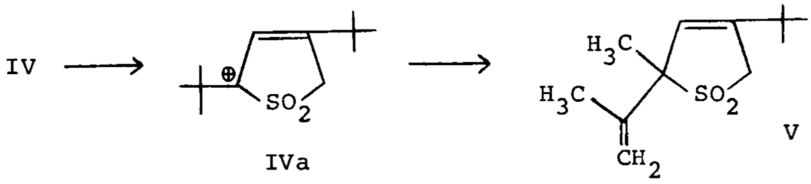
As alternative rearrangement product of IV, structure V can be envisaged occurring through the ion IVa.



IVa

V

This can be excluded on the basis of the following evidence.

(i) The signal of the α-sulfonyl methylene group in the PMR spectrum of II was found at δ 3.1 ppm. In V, the corresponding methylene group is also flanked by a double bond and is therefore expected to be more deshielded. The methylene groups in 3-*t*-butyl-2,5-dihydrothiophene-1,1-dioxide, for example, absorp at δ 3.8 ppm.

(ii) The ultraviolet spectrum of II exhibited a considerable end absorption (ε = 532 at 224 mμ) as consistent for an α,β-unsaturated sulfone[5]. A much lower extinction at this wavelength is expected for a β,γ-unsaturated sulfone such as V[6].

(iii) Pyrolysis of II started only at about 200°, i.e. 150° above its m.p. Decomposition at lower temperatures is expected for β,γ-unsaturated five membered cyclic sulfones because of the possibility of a *retro*-Diels-Alder reaction[7].

As expected[7,8], the internal double bond of II is very unreactive in addition reactions, likely due to steric hindrance by the sulfonyl and *t*-butyl groups. Hydrogenation as well as the addition of bromine failed under the usual conditions. Saturation of the isopropenyl side chain of II can readily be achieved by catalytic hydrogenation or by addition of bromine.

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EXPERIMENTAL

The PMR spectra were taken on a Varian Associates A-60 instrument, using CCl_4 as solvent (10% $^w/v$). The infrared spectra were run from KBr pellets, or CCl_4 solutions on a Perkin-Elmer 125 grating spectrometer.

Elementary analyses were performed in the Microanalytical Department of our laboratory under supervision of Mr. W.M. Hazenberg. In the described experiments Mr. G. Zuidema gave valuable and skilled assistance.

Dehydration of the diol I.

The diol I (3.58 g, 0.013 mole) dissolved in 70 ml of chloroform, was treated with 12.2 g of phosphorous pentachloride. After refluxing for 0.5 hr the mixture was cooled and extracted eight times with 35 ml of ice-water, once with saturated sodium bicarbonate solution and then again with water. The work-up of these combined water layers is described below.

Drying of the chloroform layer over sodium sulfate and subsequent removal of the solvent gave 1.2 g of a white solid (0.75 g, m.p. 119-122°, after crystallization from petroleum-ether, b.p. 80-100°). The latter compound was added to a solution of 2.5 g of potassium hydroxide pellets in 50 ml of absolute ethanol. After refluxing the mixture for one hr, 40 ml of ethanol was distilled off and 100 ml of water was added. Acidification and extraction with ether yielded a light-yellow oil which was, according to its PMR spectrum, almost

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pure II (0.45 g, 15%). Crystallization from 5 ml of petroleum-ether (b.p. 40-60°) at low temperature (-50°) gave 0.26 g of II, m.p. 26-29°; chromatography over alumina with benzene as eluent did not change this m.p. However, after seeding with a crystal of the original product of Backer and Strating which was still present in the store room of our laboratory, the m.p. raised[9] to 53-53.5°.

The combined water layers were concentrated in vacuo to 100 ml and then 17 g of KOH were added. After refluxing for one hr, this solution was extracted with methylene chloride. The solid obtained by removal of the solvent was crystallized from 6 ml of ether, giving 0.41 g of 2,4-di-t-butylthiophene-1,1-dioxide (m.p. 135.5-137°). To the aqueous layer, remaining from the methylene chloride extraction, more KOH (12 g) was added. This solution was refluxed for one hr and worked-up as described above, affording 0.76 g of the sulfone III (total yield 1.17 g, 38%).

Oxidation of 2,4-Di-t-butylthiophene (U.E. Wiersum).

A mixture of 1.96 g (0.01 mole) of 2,4-di-t-butylthiophene[10] and 4 ml of hydrogen peroxide (30%) in 40 ml of glacial acetic acid was stirred for 40 min. at 95-100°. After cooling, the mixture was poured into 120 ml of ice-water. The white precipitate was filtered off, dried over $CaCl_2$ in vacuo and chromatographed over alumina (active neutral) with pentane/ether (2:1) as eluent, yielding 1.9 g (83%) of the sulfone III, m.p. 131-133°. Crystallization from pentane/ether (2:1) at low temperature (- 20°) afforded analytically pure 2,4-di-t-butylthiophene-1,1-dioxide, m.p. 135-136°.

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