Ethanedisulphinic Anhydride and Ethanedisulphinic Acid

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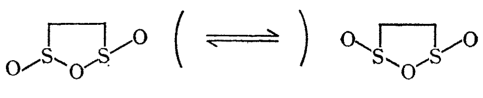
Summary The synthesis of the anhydride of ethanedisulphinic acid from the disulphinyl chloride and the subsequent formation of the acid from the anhydride is described.

THE first successful synthesis of a sulphinic anhydride was recently described.[1] The preparation of di-t-butylsulphinic anhydride (I) was accomplished *via* low-temperature metathesis of silver 2-methylpropane-2-sulphinate and 2-methylpropane-2-sulphinyl chloride. The absence of sulphone-like bands in the i.r. spectrum of the product provided compelling evidence against the isomeric sulphinyl sulphone (II). The authors also cited the sensitivity of hydrolysis of (I) to acid catalysis in their structural proof.

$Me_3CSO{\cdot}O{\cdot}SO{\cdot}CMe_3$ (I)

$Me_3CSO_2{\cdot}SO{\cdot}CMe_3$ (II)



(IIIa) (IIIb)

We report that carefully controlled hydrolysis of ethanebisdisulphinyl chloride[2] affords the novel heterocyclic anhydride (III) in good yield when carried out in tetrahydrofuran at room temperature.†

The sulphinyl sulphone (IV) is ruled out as the product since in its i.r. spectrum (run either as a KBr pellet or in chloroform solution) no bands appear in the 7·4—7·7 μm. region. Instead, a weak band at 7·15 μm. assignable to C-H bending is present in both media; in chloroform a broad triplet with maxima at 8·65, 8·87, and 9·30 μm. also appears. In the KBr disc a single medium band at 7·95 μm. and a strong broad band centred at 9·0 μm. were apparent.

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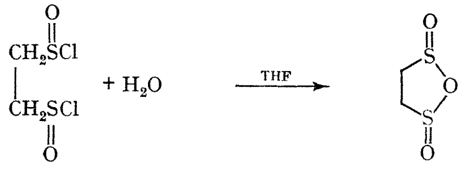
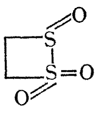
† The product, colourless crystals partially soluble in tetrahydrofuran, has m.p. 117—118° with decomposition. Microanalysis indicates the composition $C_2H_4S_2O_3$.

These 7·95—9·30 μm. absorptions are attributable to the sulphinic anhydride group.[1,3] In its n.m.r. spectrum ($CDCl_3$), (III) exhibits a close doublet of doublets (each split by 1·5 Hz.) falling at δ 3·64 and 3·70. It cannot at this time be ascertained whether (III) exists in solution as a *transoid* (IIIa) or a *cisoid* (IIIb) or rapidly interconverting isomers.



(III)



(IV)

Treatment of (III) with boiling water for 1 min. results in nearly quantitative conversion into ethane-1,2-disulphinic acid.‡ This ostensibly obvious observation clearly contradicts literature references to the lability of this compound (whenever attempts to prepare it *via* other routes usually involving reduction of a sulphonyl precursor were reported[4]).

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‡ This material, a colourless solid from the evaporated water, has m.p. 109—111° with gas evolution but no charring. Aqueous solutions of the crystals are acidic. It shows only a singlet in its n.m.r. (D_2O) at δ 3·11. A KBr pellet i.r. spectrum of the diacid has a strong doublet with maxima at 9·35 and 9·75 μm. (indicative of a sulphinic acid[4]) and no bands near 8·5 μm. Microanalysis indicates the composition $C_2H_6S_2O_4$.

[1] J. L. Kice and K. Ikura, *J. Amer. Chem. Soc.*, 1968, **90**, 7378.

[2] I. B. Douglass, B. A. Farah, and E. G. Thomas, *J. Org. Chem.*, 1961, **26**, 1996.

[3] H. Bredereck, A. Wagner, H. Beck, and R. J. Klein, *Chem. Ber.*, 1960, **93**, 2736.

[4] M. T. Beachem, J. T. Shaw, G. D. Sargent, R. T. Fortenbaugh, and J. M. Salsbury, *J. Amer. Chem. Soc.*, 1959, **81**, 5430, and references therein.