

## 2-Hydroxyethanesulphonyl Chloride: a Sulphonyl Chloride with a Primary Hydroxy-group

By JAMES F. KING\* and JOHN H. HILLHOUSE

(Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7, Canada)

**Summary** The preparation of 2-hydroxyethanesulphonyl chloride (**1**), the first example of a compound containing both sulphonyl chloride and primary alcohol functions, is described; reaction of (**1**) with base gives products evidently derived from the sulphene (**4**) and the  $\beta$ -sultone (**6**).

No simple compounds containing both a chlorosulphonyl group and a primary or secondary alcohol function appear to have been reported.<sup>†</sup> One might expect, however, from the comparative sluggishness of the uncatalysed reaction of sulphonyl halides with alcohols,<sup>‡</sup> that such compounds should be sufficiently long-lived to allow their isolation. We now describe the preparation and properties of 2-hydroxyethanesulphonyl chloride (**1**).

Excess of chlorine was bubbled rapidly for 10 min into an aqueous solution of 2-mercaptoethanol cooled in an ice-bath (initial and final temperatures, 3 and *ca.* 40 °C). The mixture was worked up by (a) washing with methylene dichloride which removes the 2-chloroethanesulphonyl

chloride§ co-product (*ca.* 10% yield) together with some of the required product (**1**), and (b) saturation of the aqueous layer with potassium chloride, followed by extraction with methylene dichloride. Evaporation of the extract gave (**1**) in 10–30% yield as a colourless syrup. In agreement with the proposed structure (**1**), this material gave correct elemental analyses (C, H, S, and Cl) and showed strong i.r. bands at 3550, 3370, 1365, 1165, 1060, 705, 590, 535, and 495  $\text{cm}^{-1}$  (neat film, KBr plates); the <sup>13</sup>C n.m.r. spectrum showed peaks at  $\delta$  67.6 and 56.9 p.p.m., while the <sup>1</sup>H n.m.r. spectrum displayed a symmetrical pattern of perturbed 'triplets' (4H, central peaks at  $\delta$  3.98 and 4.28) plus a singlet (1H) at  $\delta$  2.8. Confirmation of the structure was provided by the reactions shown in Scheme 1. Acetyl chloride gave 2-acetoxyethanesulphonyl chloride<sup>4</sup> (**2**) (83% yield), and reduction with sodium sulphite yielded the sulphinate salt, which was converted (a) back into (**1**) *via* chlorination of the sulphinic acid and (b) into ethyl 2-hydroxyethyl sulphone<sup>5</sup> (**3**) with ethyl iodide.¶ A neat sample of (**1**) was *ca.* 50% de-

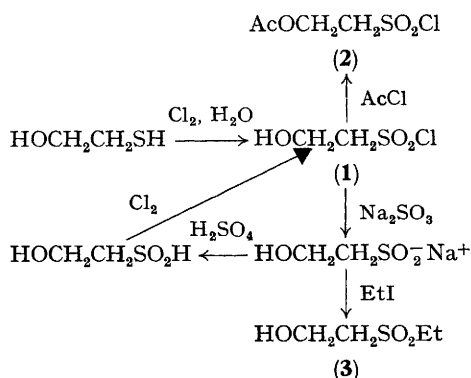
<sup>†</sup> Hydroxyarenesulphonyl chlorides are well known.<sup>1</sup> The only report of a hydroxyalkanesulphonyl chloride that we are aware of is Schroeter's alleged preparation of 2-hydroxypropane-2-sulphonyl chloride.<sup>2</sup> It has been noted, however, that those compounds of the general formula  $\text{RSO}_2\text{Z}$ , wherein Z is a good leaving group and the derived cation  $\text{R}^+$  relatively stable, are difficult to prepare and, when made, are easily desulphonylated;<sup>3</sup> reinvestigation of Schroeter's work by modern methods would seem to be required.

<sup>‡</sup> For example, previous work indicates a half-life of about 27 h for a solution of propane-1-sulphonyl chloride in butan-1-ol at 25 °C (G. Geiseler and P. Laue, *Chem. Ber.*, 1962, **95**, 867).

<sup>§</sup> This product is reportedly formed from 2-mercaptoethanol in 94% yield under somewhat different conditions: E. E. Gilbert, *Synthesis*, 1969, **3**.

<sup>¶</sup> Reaction products in the Schemes were identified by direct comparison with authentic specimens made either as described in the reference given or as follows: (**5**) by refluxing an equimolar mixture of butyl [2-(dimethylamino)ethanesulphonate and 2-hydroxyethanesulphonic acid in toluene following the general method given elsewhere<sup>6</sup> (M. Aslam, personal communication); (**8**) and (**9**) from reaction of  $\text{Me}_3\text{N}$  with  $\text{HOCH}_2\text{CH}_2\text{SO}_3\text{H}$  and  $\text{ClCH}_2\text{CH}_2\text{SO}_3\text{H}$ , respectively.

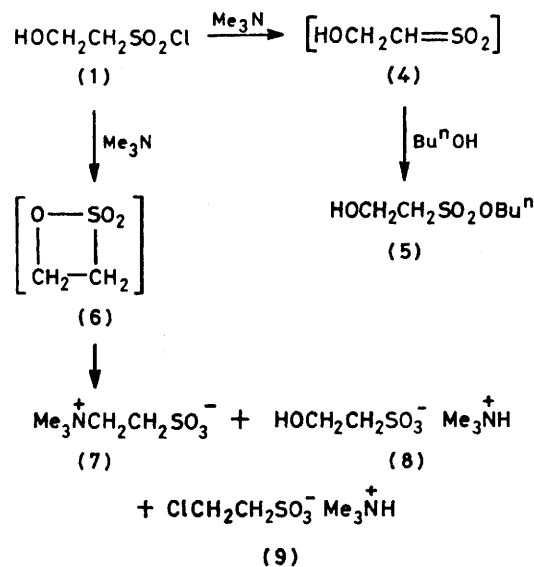
composed when kept at room temperature for one month; during the same time a dilute solution in  $\text{CDCl}_3$  or a neat sample kept at  $-20^\circ\text{C}$  showed no significant decomposition as judged from  $^1\text{H}$  n.m.r. spectra.



SCHEME 1.

The action of tertiary amines on (1) evidently follows two pathways, one *via* the sulphene (thioaldehyde  $\text{SS}$ -dioxide) (4), the other by way of the sultone (6) (Scheme 2). Trimethylamine and butan-1-ol gave the ester (5) (30%) and the betaine<sup>7</sup> (7) (45%) plus small amounts (*ca.* 5% each) of the 2-hydroxy- and 2-chloro-ethanesulphonates (8) and (9), respectively.

$[\text{^2H}]$ Butan-1-ol gave the monodeuteriated ester,  $\text{HOCH}_2\text{-CHDSO}_2\text{OBu}^n$ , but no deuterium was detected in (7), (8), or (9). With pyridine the yield of the ester (5) dropped to 5–10% while the amounts of the pyridine analogues of



SCHEME 2.

(7), (8), and (9) totalled about 90%. The result is in accord with previous observations of an increase in the importance of the general base-assisted displacement at sulphur, with a corresponding decrease in sulphene formation, as the basicity of the tertiary amine decreases.<sup>8</sup>

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

(Received, 23rd December 1980; Com. 1371.)

<sup>1</sup> T. Zincke and W. Glahn, *Ber.*, 1907, **40**, 3039; see also R. W. Campbell and H. W. Hill, Jr., *J. Org. Chem.*, 1973, **38**, 1047; R. J. Cremlyn and T. Cronje, *Phosphorus Sulfur*, 1979, **6**, 413.

<sup>2</sup> G. Schroeter, *Ber.*, 1928, **61**, 1616.

<sup>3</sup> J. F. King and M. Aslam, *Can. J. Chem.*, 1979, **57**, 3278; H. O. Fong, W. R. Hardstaff, D. G. Kay, R. F. Langler, R. H. Morse, and D. N. Sandoval, *Can. J. Chem.*, 1979, **57**, 1206 and references cited therein.

<sup>4</sup> R. Anschütz, *Liebigs Ann. Chem.*, 1918, **415**, 64.

<sup>5</sup> J. v. Braun and K. Weissbach, *Ber.*, 1930, **63**, 2836.

<sup>6</sup> J. F. King, S. M. Loosmore, J. D. Lock, and M. Aslam, *J. Am. Chem. Soc.*, 1978, **100**, 1637.

<sup>7</sup> P. Blumbergs, A. B. Ash, F. A. Daniher, C. L. Stevens, H. O. Michel, B. E. Hackley, Jr., and J. Epstein, *J. Org. Chem.*, 1969, **34**, 4065.

<sup>8</sup> J. F. King and Y. I. Kang, *J. Chem. Soc., Chem. Commun.*, 1975, 52; Y. G. Skrypnik, V. P. Besrodney, and S. N. Baranov, *Phosphorus Sulfur*, 1979, **6**, 285.