

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

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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 β -sultone (**6**).

No simple compounds containing both a chlorosulphonyl group and a primary or secondary alcohol function appear to have been reported.[†] One might expect, however, from the comparative sluggishness of the uncatalysed reaction of sulphonyl halides with alcohols,[‡] 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 cm^{-1} (neat film, KBr plates); the ^{13}C n.m.r. spectrum showed peaks at δ 67.6 and 56.9 p.p.m., while the ^1H n.m.r. spectrum displayed a symmetrical pattern of perturbed 'triplets' (4H, central peaks at δ 3.98 and 4.28) plus a singlet (1H) at δ 2.8. Confirmation of the structure was provided by the reactions shown in Scheme 1. Acetyl chloride gave 2-acetoxyethanesulphonyl chloride⁴ (**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 sulphone⁵ (**3**) with ethyl iodide.¶ A neat sample of (**1**) was *ca.* 50% de-

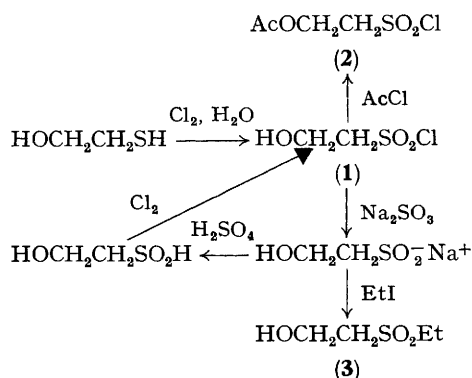
[†] Hydroxyarenesulphonyl chlorides are well known.¹ The only report of a hydroxyalkanesulphonyl chloride that we are aware of is Schroeter's alleged preparation of 2-hydroxypropane-2-sulphonyl chloride.² It has been noted, however, that those compounds of the general formula RSO_2Z , wherein Z is a good leaving group and the derived cation R^+ relatively stable, are difficult to prepare and, when made, are easily desulphonylated;³ reinvestigation of Schroeter's work by modern methods would seem to be required.

[‡] 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).

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

[¶] 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 elsewhere⁶ (M. Aslam, personal communication); (**8**) and (**9**) from reaction of Me_3N 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.

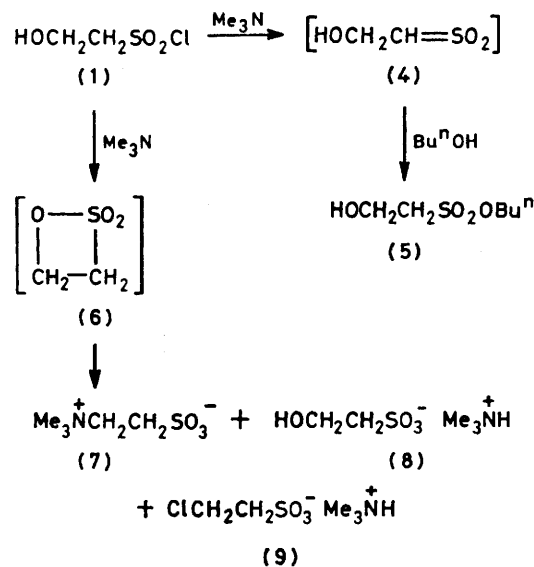
composed when kept at room temperature for one month; during the same time a dilute solution in CDCl_3 or a neat sample kept at -20°C showed no significant decomposition as judged from ^1H n.m.r. spectra.



SCHEME 1.

The action of tertiary amines on (1) evidently follows two pathways, one *via* the sulphene (thioaldehyde 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 betaine⁷ (7) (45%) plus small amounts (*ca.* 5% each) of the 2-hydroxy- and 2-chloro-ethanesulphonates (8) and (9), respectively.

^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.⁸

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¹ 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.

² G. Schroeter, *Ber.*, 1928, **61**, 1616.

³ 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.

⁴ R. Anschütz, *Liebigs Ann. Chem.*, 1918, **415**, 64.

⁵ J. v. Braun and K. Weissbach, *Ber.*, 1930, **63**, 2836.

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

⁷ 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.

⁸ 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.