

57. *Aliphatic Sulphonyl Fluorides.*

By WILLIAM DAVIES and JOHN HENRY DICK.

ATTEMPTS to prepare any aliphatic sulphonyl fluoride have hitherto been unsuccessful. For example, Steinkopf and his collaborators (*J. pr. Chem.*, 1927, **117**, 13) showed that ethanesulphonyl fluoride is not obtained from the corresponding sulphonate or sulphonyl chloride by the action of fluorosulphonic acid, nor from the action of arsenic trifluoride on ethanesulphonyl chloride. It has now been found that the method of preparing aromatic sulphonyl fluorides by heating the corresponding chloride with an aqueous solution of potassium fluoride (Davies and Dick, *J.*, 1931, 2104) is also successful in the aliphatic series. *Methane-*, *ethane-*, *α -chloroethane-*, *cyclohexane-*, and *ω -toluene-sulphonyl fluorides* have thus been readily prepared. In the case of methanesulphonyl fluoride, owing to the ease of hydrolysis of the corresponding chloride, a better yield can be obtained by simply heating the chloride in a metal flask with zinc fluoride. This method is slow and not so useful as the one mentioned above, but it can also be successfully employed in the aromatic series, as a 17½% yield of *p*-toluenesulphonyl fluoride is obtained from the chloride by heating it at 200° for 14 hours with excess of dry zinc fluoride (contrast Davies and Dick, *loc. cit.*, p. 2105).

The purely aliphatic sulphonyl fluorides are colourless liquids with the odour of saturated alkyl halides, and they can be distilled and kept in glass vessels without appreciable change. They are much less reactive than the corresponding chlorides. The fluorides do not lose sulphur dioxide so readily as the aliphatic sulphonyl chlorides, when heated in the presence of compounds such as aluminium chloride and zinc chloride. Ethanesulphonyl fluoride, like the aromatic sulphonyl fluorides, does not react with cold pyridine over a period of weeks, but benzylsulphonyl fluoride does slowly react with it. Aliphatic sulphonyl fluorides do not react readily in the cold with amines and even boiling water only hydrolyses the fluorides relatively slowly. Boiling the sulphonyl fluorides with excess of alkali, however, results in their complete hydrolysis to the

corresponding sulphonate and sodium fluoride, and this was the method of analysis adopted. The difference between the chlorides and the fluorides is only one of degree, higher temperatures or more prolonged action in the latter case resulting in the same condensation products as those readily obtained from the chlorides.

The most satisfactory way of preparing some of the rather inaccessible aliphatic sulphonyl chlorides required is by the action of alkyl halides on sodium sulphite.

EXPERIMENTAL.

Preparation of Aliphatic Sulphonyl Chlorides.—Methane-, ethane- and cyclohexane-sulphonyl chlorides are prepared in poor yield by the method of Böeseke and van Ockenburg (*Rec. trav. chim.*, 1914, **33**, 319).

The best way of preparing ethane- and ω -toluene-sulphonates is to heat at about 37°, with frequent shaking, the corresponding halides (ethyl iodide and benzyl chloride) with sodium sulphite (1 g.-mol.) in aqueous alcohol (compare the action of sodium sulphite on halides; Sprung, *J. Amer. Chem. Soc.*, 1930, **52**, 1644). After about 6 days little organic halide is left; the mixture is then refluxed for an hour, the alcohol distilled off, and the dried residual salts freed from sodium iodide by means of acetone. Residual sodium chloride from benzyl chloride does not interfere with the action of phosphorus pentachloride. *cyclo*Hexanesulphonate can be made in this way from *cyclo*hexyl bromide, but the reaction requires many weeks at 37°. The dry sodium sulphonates are treated, with efficient cooling, with 5% excess of phosphorus pentachloride in the presence of a large amount of chloroform. In the case of sodium ω -toluene-sulphonate the use of chloroform can be dispensed with, provided the reaction mixture is kept cold; otherwise the presence of phosphorus compounds brings about the production of sulphur dioxide and benzyl chloride. The chlorides are worked up in the usual way and overall yields of 50% of ethanesulphonyl chloride (b. p. 95–98°/50 mm.) and 85% of ω -toluenesulphonyl chloride (m. p. 93°) are obtained from the original organic halides.

α -Chloroethanesulphonyl chloride (b. p. 180°/20 mm.) is obtained after the method of Müller and Randenbusch (*Ber.*, 1931, **64**, 94), in about 32% yield when the preparation is carried out on a large scale (44 g. of trithioacetaldehyde).

Methanesulphonyl fluoride is best made in the dry way as follows. The corresponding chloride (15.5 g., b. p. 161°/730 mm.) is poured on dry zinc fluoride (10.5 g.; twice the theoretical quantity) in an inclined platinum distilling flask connected to a copper water-condenser by a rubber stopper. The flask is heated, with frequent

shaking, in an oil-bath for 18 hours, the temperature gradually rising from 100° to 160°; it is then cooled, a further 5 g. of zinc fluoride added, and the liquid gently refluxed (oil-bath at 165—170°) for a further 6 hours. The liquid is then distilled from the platinum flask, almost all of it coming over at 123—124°, and by redistillation from a glass flask a yield of more than 80% of pure fluoride is obtained. The preliminary gradual heating from 100—160° is essential: another experiment in which the chloride was straightway heated at 160—170° for 6 hours gave a purely inorganic residue in the flask, the chloride apparently having decomposed into gases (compare Böeseken and van Ockenburg, *loc. cit.*). Methanesulphonyl fluoride has b. p. 124.2°/754 mm., n_D^{20} 1.3596 [Found: H.V. (see Davies and Dick, *loc. cit.*, p. 2106), 20.22 c.c.; F, 19.2. $\text{CH}_3\text{O}_2\text{FS}$ requires H.V., 20.40 c.c.; F, 19.4%]. It has a smell reminiscent of chloroform, and when cold is not lachrymatory like the chloride. It reacts with warm piperidine, the *piperidide* being formed in plates very soluble in organic solvents, m. p. 48°, b. p. 167—168°/4 mm. (Found: C, 44.0; H, 8.1. $\text{C}_6\text{H}_{13}\text{O}_2\text{NS}$ requires C, 44.2; H, 8.0%). This piperidide is at once formed in the cold from methanesulphonyl chloride.

Ethanesulphonyl Fluoride.—Ethanesulphonyl chloride (30 g.) is heated, with almost continuous shaking, in a glass flask on the water-bath for 20 minutes with 70% potassium fluoride solution (30 c.c.). The mixture is cooled, diluted, and extracted with ether, and the ether removed; the residual oil is chlorine-free. The yield is 66.8% (17.5 g.).

Ethanesulphonyl fluoride is chemically similar to the methyl compound, and has b. p. 134—135°, n_D^{15} 1.3757 (Found: H.V., 17.70 c.c.; F, 16.9. $\text{C}_2\text{H}_5\text{O}_2\text{FS}$ requires H.V., 17.86 c.c.; F, 17.0%). It can also be prepared, but less expeditiously, in the dry way described above.

α -Chloroethanesulphonyl fluoride is made in the wet way precisely as the ethanesulphonyl fluoride, 20 g. of chloride yielding 12 g. of fluoride (67% yield). B. p. 138—139°, n_D^{20} 1.4070 (Found: H.V., 13.30 c.c.; F, 12.9. $\text{C}_2\text{H}_4\text{O}_2\text{ClFS}$ requires H.V., 12.27 c.c.; F, 13.0%). The high hydrolysis figure indicates the slow hydrolysis of the chlorine atom, the total H.V. for both sulphonyl fluoride group and chlorine atom being 18.40 c.c. α -Chloroethanesulphonyl fluoride does not react appreciably with cold aniline over a period of several weeks, whereas the original chloride forms α -chloroethanesulphanilide almost instantly under the same conditions.

cycloHexanesulphonyl Fluoride.—The chloride (4.4 g.) is boiled with 5 c.c. of potassium fluoride solution (70%) for 13 minutes. The *fluoride*, isolated in the usual way (2.2 g.; 55% yield), has b. p.

218° (Found : H.V., 12.04 c.c. ; F, 11.5. $C_6H_{11}O_2FS$ requires H.V., 12.05 c.c. ; F, 11.4%).

ω-Toluenesulphonyl Fluoride.—The chloride (10 g.) is dissolved in xylene (10 c.c.) and refluxed with potassium fluoride solution (10 c.c. of 70%) for 1 hour. The mixture is then cooled and diluted with water, and the *fluoride*, which crystallises from the xylene, is collected. Recrystallised from light petroleum (b. p. 60—80°), it forms colourless needles, m. p. 90—91° (7 g. ; 76% yield) (Found : H.V., 11.41 c.c. ; F, 10.8. $C_7H_7O_2FS$ requires H.V., 11.48 c.c. ; F, 10.9%).

The authors gratefully acknowledge a grant from the Trustees of the Commonwealth Science and Industry Endowment Fund towards the expenses of both this research and the previously described work on aromatic sulphonyl fluorides.

THE UNIVERSITY OF MELBOURNE.

[Received, December 28th, 1931.]
