CCLXXXVI.—*Aromatic Sulphonyl Fluorides. A Convenient Method of Preparation.*

By William Davies and John Henry Dick.

The only method so far described of preparing aromatic sulphonyl fluorides is that of Steinkopf and his collaborators (*J. pr. Chem.*, 1927, **117**, 1; 1930, **128**, 63), who heated the aromatic hydrocarbon and a sulphonate or a sulphonyl chloride with excess of fluorosulphonic acid. The inaccessibility of this substance and the use of metal apparatus considerably limit the utility of the process. It has now been found that mono-, di-, and tri-sulphonyl fluorides of benzene and its derivatives are readily produced in glass vessels, and in better yield, by boiling the corresponding chloride for a short time with a neutral aqueous solution of an inorganic fluoride. The excessively soluble potassium fluoride is the best salt for the purpose, but sodium, ammonium, and zinc fluorides (the last partly in suspension) may be used. The yields of the monosulphonyl fluorides of benzene and its derivatives are usually 60—80%, and less for the di- and tri-sulphonyl derivatives. The only case in which the method has failed is in the reaction of potassium fluoride with phenol-2 : 4 : 6-trisulphonyl chloride, and this is due to the fact that this substance is decomposed by cold water.

It is noteworthy that, at moderate temperatures at least, the presence of water appears necessary for the conversion of the chloride to the fluoride. For example, although *p*-toluenesulphonyl chloride is recovered unchanged after its benzene solution has been refluxed for five days with dry zinc fluoride, yet the addition of water or the passage of steam causes almost complete conversion to the fluoride in about an hour. The same phenomenon has been observed with many other aromatic sulphonyl chlorides, and may indicate that an ionising medium is advantageous.

The aromatic sulphonyl fluorides are much more stable to acid or neutral hydrolytic agents than the corresponding chlorides, thus enabling them to be purified by crystallisation from dilute alcohol or by distillation in steam. Their stability also makes them valuable for preparative work; *e.g.*, they can be nitrated without appreciable loss of the sulphonyl fluoride group. They are even more important from the analytical point of view, for, though so stable to neutral and acid media, the simpler sulphonyl fluorides are quantitatively converted into sodium fluoride and the corresponding sulphonate by hydrolysis with sodium hydroxide solution. In the absence of any trustworthy method of obtaining pure, soluble, solid inorganic fluorides (our experience confirms the necessity of a procedure such as that of Kurtenacker and Jurenka, *Z. anal. Chem.*, 1930, **82**, 214, for obtaining a definite fluorine-ion concentration), solid sulphonyl fluorides are the most convenient source of a definite concentration of ionisable fluorine for quantitative work. Further, the sulphonyl fluorides and their derivatives appear to have germicidal and insecticidal properties.

The study of the further reactions of sulphonyl fluorides and other organic fluorides is being continued.

EXPERIMENTAL.

Preparation of Aromatic Sulphonyl Fluorides.—The best method is to boil the mixture of sulphonyl chloride with 50% excess of neutral potassium fluoride solution (73 g. of KF in 100 c.c. of solution) for ¼—1 hour. When less than 3 g. of sulphonyl chloride are used, it is advisable to use a relatively larger proportion of potassium fluoride solution in order to ensure steady boiling and the safety of the flask. Potassium chloride separates during the reaction, the product is diluted with water, the sulphonyl fluoride is extracted and distilled (if a liquid) or crystallised from aqueous alcohol (if a solid). Only slight etching of the flask occurs, and it can be used repeatedly. However, when the b. p. of the potassium fluoride solution is below the m. p. of the chloride, the latter hydrolyses faster than substitution takes place. Addition of a high-boiling non-hydrolytic solvent minimises this disadvantage, but addition of acetone or sodium acetate is ineffective.

The weights of the sulphonyl chlorides taken have generally been small, larger yields of sulphonyl fluorides (especially when liquid) being obtained by using quantities of chlorides of the order of 50—100 g. The yields given refer to purified material. During the earlier experiments sodium fluoride was used, and also an aqueous suspension of zinc fluoride. In the latter case the sulphonyl fluoride was steam-distilled from the reaction mixture. When no inorganic fluoride is specified it is understood that potassium fluoride was used.

Analysis of Sulphonyl Fluorides.—The sulphonyl fluoride (0·5000 g.) is dissolved in sufficient alcohol (about 20 c.c.) to ensure a clear solution when the alkali (20 c.c. of 0·5N-sodium hydroxide) is added. The mixture is refluxed for 2 hours, most of the alcohol distilled off, and, without cooling, the excess of alkali is estimated by standard acid, phenolphthalein being the indicator. The "hydrolysis values" (H.V.) are thus deduced. The fluorine is estimated (compare Kurtenacker and Jurenka, *loc. cit.*) as follows : excess sodium chloride is added to the titrated neutral solution, after the addition of methyl-red the solution (containing undissolved sodium chloride) is brought to the boil, and neutral N-aluminium chloride solution is run in from a microburette. The end-point is indicated by the first permanent red colour. As the end-point is approached the solution should be again heated to boiling. The microburette accurately measures the amount of N-aluminium chloride solution (about 4 c.c.) required for the titration of the above weak fluoride solutions, which are about $N/5$ (Kurtenacker and Jurenka used N) : the end-point is accurate to one drop (0·03 c.c.).

Benzenesulphonyl fluoride. Yield 30 g. from 40 g. of chloride (82·7%). Time 1 hour. B. p. 207°; $n_D^{20°}$ 1·4922. (Steinkopf gives b. p. 203—204°, $n_D^{18°}$ 1·4932.)

o-*Toluenesulphonyl fluoride.* Yield 27·5 g. from 50 g. of chloride (60%). Time 1 hour, zinc fluoride being used. B. p. 223—225°; $n_D^{20°}$ 1·5007. (Steinkopf gives b. p. 146·2°/83 mm.)

p-*Toluenesulphonyl fluoride.* Yield 72·5 g. from 100 g. of chloride (80%). Time 1 hour. M. p. 41—42° (Steinkopf gives 43—44°)

(Found : H.V., 11·49 c.c.; F, 10·92. Calc. for $C_7H_7O_2FS$: 11·49 c.c.; F, 10·92%).

1 : 3-*Dimethylbenzene*-4-*sulphonyl fluoride.* Yield 12·5 g. from 25 g. of chloride (54%). Time 1 hour. B. p. 246°; $n_D^{20°}$ 1·5086. (Steinkopf gives b. p. 239—240°.)

p-*Chlorobenzenesulphonyl fluoride.* Yield 20 g. from 30 g. of chloride (72·5%). Time 1 hour (zinc fluoride). M. p. 47—48° (Found : H.V., 10·19 c.c. Calc. for $C_6H_4O_2ClFS$: 10·19 c.c.).

6-*Chloro*-o-*toluenesulphonyl fluoride.* Yield 14 g. from 20 g. of chloride (75·5%). Time 1 hour. M. p. 44—45° (Found : H.V., 9·61 c.c. Calc. for $C_7H_6O_2ClFS$: 9·59 c.c.).

2-*Chloro*-5-*nitro*-p-*toluenesulphonyl fluoride.* Yield 9·8 g. from 13·5 g. of chloride (77·5%). Time 2 hours (sodium fluoride). M. p. 84—85°. Boiling alkali gradually replaces the sulphonic by a hydroxyl group, as with the sulphonyl chloride (Davies, J., 1921, **119**, 866). The presence of the *o*-nitrophenol group does not, however, interfere with the end-point in the estimation of fluorine (Found : H.V., 8·0 c.c.; F, 7·54. $C_7H_5O_4NClFS$ requires 7·89 c.c.; F, 7·50%).

Benzenedisulphonyl fluoride. Yield 6 g. from 10 g. of chloride (68%). Time ½ hour. M. p. 38—39°, as recorded by Steinkopf (Found : H.V., 16·52 c.c.; F, 15·80. Calc. for $C_6H_4O_4F_2S_2$: 16·54 c.c.; F, 15·70%).

1 : 3-*Dimethylbenzene*-4 : 6-*disulphonyl fluoride.* Yield 5·5 g. from 10 g. of chloride of m. p. 130° (62%). Time 2 hours (zinc fluoride). M. p. 116—118° (Found : H.V., 14·82 c.c.; F, 14·10. Calc. for $C_8H_8O_4F_2S_2$: 14·82 c.c.; F, 14·08%). Steinkopf (*loc. cit.*, p. 42) calls the product (m. p. 116—117°) from *m*-xylene, 1 : 3-dimethylbenzene-2 : 4-disulphonyl fluoride, and gives similar formulæ for the chloride (m. p. 129°) and amide (m. p. 249°) derived from the compound. It has been proved by Pollak and Lustig (*Annalen*, 1923, **433**, 191) that disulphonation of *m*-xylene gives chiefly the 4 : 6-acid, m. p. of chloride 129°. As our chloride was made in the usual way and has the 4 : 6-formula, it is probable that Steinkopf was following the older literature in assigning the 2 : 4-structure to his compound.

Chlorobenzene-2 : 4-*disulphonyl fluoride.* Yield 3·35 g. from 5 g. of chloride (71·3%). Time 25 mins. M. p. 88—89° (Found : H.V., 14·52 c.c.; F, 14·01. $C_6H_3O_4ClF_2S_2$ requires 14·50 c.c.; F, 13·77%).

1 : 3-*Dichlorobenzene*-4 : 6-*disulphonyl fluoride.* Yield 3 g. from 7·25 g. of chloride (45·8%). Time 3 hrs. (sodium fluoride). M. p. 141—143° (Found : H.V., 12·78 c.c. $C_6H_2O_4Cl_2F_2S_2$ requires 12·85 c.c.).

1 : 3 : 5-*Trichlorobenzenedisulphonyl fluoride.* Yield 0·38 g. from

0·8 g. of chloride. Time ½ hour, xylene being added as solvent. M. p. 109—110°.

1 : 3-*Dimethoxy*-4 : 6-*disulphonyl fluoride.* Yield 2·25 g. from 4 g. of chloride (62·3%). Time 4¼ hours (sodium fluoride). M. p. 209—211° (Found: H.V., 13·11 c.c.; F, 12·38. $C_8H_8O_6F_2S_2$ requires 13·23 c.c.; F, 12·58%).

Benzene-1 : 3 : 5-*trisulphonyl fluoride.* Yield 2·0 g. from 5 g. of chloride (46%). Time ½ hour, 30 c.c. of xylene being added as solvent. M. p. 166—167° (Found: H.V., 18·50 c.c.; F, 17·8. $C_6H_3O_6F_3S_3$ requires 18·52 c.c.; F, 17·6%).

Chlorobenzene-2 : 3 : 6-*trisulphonyl fluoride.* Yield 1·4 g. from 4 g. of chloride (40%). Time ½ hour, 10 c.c. of xylene being added as solvent. M. p. 179—181° (Found: H.V., 16·80 c.c.; F, 15·95. $C_6H_2O_6F_3ClS_3$ requires 16·72 c.c.; F, 15·90%).

Naphthalene-β-*sulphonyl fluoride.* Yield 3·5 g. from 5 g. of chloride (75·6%). Time ½ hour. M. p. 86—88° (Steinkopf gives 87—88°).

Properties of the Aromatic Sulphonyl Fluorides.—The solid fluorides now described are crystalline and can be kept without change in stoppered bottles. They are more stable and more volatile than the corresponding chlorides. The fluorine atom is but feebly ionised at ordinary temperatures, and also at high temperatures in the absence of alkali. They are stable to pyridine at ordinary temperatures, *p*-toluenesulphonyl fluoride having been kept unchanged in this solvent for two months, whilst the corresponding chloride gives a crystalline compound in a few minutes. Pyridine or hot aqueous alcohol is the best crystallising medium when unchanged sulphonyl chloride is present. The sulphonyl fluorides are generally more soluble in organic solvents than the corresponding chlorides, and the liquid and low-melting monosulphonyl fluorides are even miscible in all proportions with light petroleum (b. p. 40—60°). The smell of the sulphonyl fluorides is less unpleasant than that of the analogous sulphonyl chlorides and often recalls that of the corresponding chloride, but when quite pure it is reminiscent of *p*-dichlorobenzene.

The sulphonyl fluorides are moderately readily hydrolysed by boiling alcoholic alkali, and amides and anilides can be made by prolonged treatment with the appropriate reagent. Steinkopf (*loc. cit.*) has shown that with aluminium chloride they regenerate the sulphonyl chloride, though often in poor yield. It is noteworthy that hydrogen chloride will not bring about this change, a stream of the dry gas at 110—140° for 2 hours leaving *o*-toluenesulphonyl fluoride completely unchanged. On the other hand, concentrated aqueous hydrofluoric acid has no appreciable action on an aromatic sulphonic acid.

Summary.

Aromatic sulphonyl fluorides are obtained in good yield by refluxing the corresponding chloride with an aqueous solution of an inorganic fluoride. The relatively stable nature of these sulphonic acid derivatives is discussed. Various mono-, di-, and tri-sulphonyl fluorides are described.

THE UNIVERSITY OF MELBOURNE. [*Received, June* 29*th,* 1931.]