

SHORT COMMUNICATIONS

PREPARATION OF AROMATIC SULPHONYL HALIDES*

By F. E. JENKINS† and A. N. HAMBLY†

In connection with a study now being made of the properties of sulphonyl halides (Jenkins 1952 ; Ham and Hambly 1953*a*, 1953*b*) a variety of aromatic sulphonyl chlorides and fluorides was required. One possible route for their synthesis involved the conversion of a substituted amine via the sulphinic acid to the sulphonyl chloride or fluoride.

The usual technique for the conversion of aromatic amines to sulphinic acids is that of Gattermann (1899), in which the amine (1 part) in dilute sulphuric acid solution is diazotized, the solution saturated with sulphur dioxide and then 5 to 6 parts of copper powder added with stirring. Several workers have recorded difficulties with this reaction in preparing *m*-substituted sulphinic acids.

Tröger and Hille (1903) found that the saturation of the solution of diazotized *m*-toluidine with sulphur dioxide gave a red precipitate, and practically no sulphinic acid on the addition of copper powder. Silvester and Wynne (1936) obtained a similar red by-product from 2,6-dichloro-*m*-toluidine while Todd and Shriner (1934) obtained only a 21 per cent. yield of *m*-chlorobenzenesulphinic acid, from *m*-chloraniline, compared with an 86 per cent. yield of the corresponding *o*-acid.

Gattermann in his original paper suggested a modification of the above procedure as especially suitable for naphthalene derivatives. We find that this modification, which differs from the preceding merely in the addition of the diazonium sulphate solution to a suspension of copper powder in dilute sulphuric acid, which is kept saturated with sulphur dioxide, overcomes the difficulties met by the above workers. The sulphinic acid is readily separated as its insoluble ferric salt, which can then be converted to the sodium salt and halogenated to yield the sulphonyl chloride, bromide, or iodide (Thomas 1909).

The conversion of aromatic sulphonyl chlorides to fluorides by refluxing with excess of a saturated aqueous solution of potassium fluoride (Davies and Dick 1931, 1932) usually gives good yields without special precautions. However, the rate of hydrolysis of the product becomes more rapid when there are electron attracting substituents present (Walker 1950), and a series of experiments in the preparation of *p*-nitrobenzene sulphonyl fluoride showed that an optimum yield of 65 per cent. was obtained after 30 min. For the conversion of high

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† Chemistry Department, University of Melbourne.

melting point, sparingly soluble, sulphonyl chlorides such as *p*-acetamidobenzene sulphonyl chloride to the corresponding fluoride the addition of dioxan to the reaction mixture is advantageous.

Experimental

(a) *Preparation of Sulphonyl Chlorides.*—(i) *m*-Toluene Sulphonyl Chloride. Freshly distilled *m*-toluidine (20 g) in sulphuric acid (40 ml H_2SO_4 , 200 ml H_2O) was diazotized at 0 °C with sodium nitrite (16 g) in water (80 ml). Copper powder (40 g) was suspended in sulphuric acid (50 ml H_2SO_4 , 200 ml H_2O), the mixture saturated with sulphur dioxide, and then the diazonium solution added with vigorous stirring while maintaining a current of sulphur dioxide.

The product was filtered, the insoluble residue washed three times with concentrated ammonia and the washings added to the filtrate which was made just acid to Congo red. Concentrated ferric chloride was then added until no more orange precipitate was formed, the ferric sulphinate filtered off and washed with a little alcohol. In a series of experiments in which the quantity of copper powder was varied from 20–80 g the yield of ferric sulphinate remained between 70 and 79% of the theoretical quantity.

TABLE I

Substituted Benzene Sulphonyl Fluoride	Physical Constants	Yield (%)	Molecular Weight		
			Calculated	From Hydrolysis*	From Fluoride Estimation†
<i>o</i> -Methoxy- ..	M.p. 39–40 °C	42	190.2	190.1	190.7
<i>m</i> -Methyl- ..	B.p. 78.5–79 °C/1.4 mm, n_D^{25} 1.4909	85	174.3	174.2	173.7
<i>p</i> -Acetamido-‡	M.p. 176 °C	47	217.2	—	218.4
<i>m</i> -Chloro- ..	B.p. 69–70 °C/0.8 mm, n_D^{25} 1.5114	63	194.7	194.0	194.5
<i>m</i> -Bromo- ..	B.p. 90 °C/1 mm, n_D^{25} 1.5358	63	239.1	236.0	238.6
<i>p</i> -Nitro- ..	M.p. 77.5–78.5 °C (corr.)	65	205.2	203.2	204.8

* By back titration after hydrolysis with excess alkali in aqueous dioxan.

† By titration at pH 3 with thorium nitrate of solution from alkaline hydrolysis.

‡ Using aqueous dioxan (40 : 60) as solvent.

The orange precipitate was treated with excess sodium hydroxide solution (2N), the black hydrated iron oxide filtered off (with the aid of "Filtercel") and the filtrate just neutralized with hydrochloric acid (2N). Chlorine was passed into this solution until no more oily sulphonyl chloride separated, the product was extracted with carbon tetrachloride and the extracts, after washing with water, dried over anhydrous CaCl_2 . After the removal of the solvent on the water-bath the crude sulphonyl chloride was distilled under reduced pressure to yield *m*-toluene sulphonyl chloride (17.8 g, 50% based on *m*-toluidine), b.p. 77–78 °C/0.3 mm Hg (Found : S, 16.8 ; Cl, 18.7%. Calc. for $\text{C}_7\text{H}_7\text{O}_2\text{SCl}$: S, 16.8 ; Cl, 18.6%).

Treatment with concentrated ammonia gave *m*-toluene sulphonamide, m.p. 108.5–109.5 °C (cf. Hollemann and Caland 1911) (Found : N, 8.5 ; S, 18.4%. Calc. for $\text{C}_7\text{H}_7\text{O}_2\text{NS}$: N, 8.2 ; S, 18.7%).

(ii) Using the above general method, *o*-methoxybenzene sulphonyl chloride, m.p. 53·5–55 °C, 51% yield; *m*-chlorobenzene sulphonyl chloride, b.p. 143–144 °C/12 mm Hg, 50% yield; and *m*-bromobenzene sulphonyl chloride, b.p. 164 °C/14 mm Hg, 54% yield, were prepared.

(b) *Preparation of Sulphonyl Fluorides.*—(i) *By the Method of Davies and Dick.* The sulphonyl fluorides shown in Table I were prepared by refluxing the corresponding sulphonyl chloride with 100% excess of saturated potassium fluoride solution. The first three compounds have not been reported previously while *m*-chloro- and *m*-bromobenzene sulphonyl fluorides have been prepared only by the Sandmeyer reaction with *m*-aminobenzene sulphonyl fluoride (Steinkopf and Hübner 1934).

(ii) *p*-Aminobenzene Sulphonyl Fluoride.—*p*-Nitrobenzene sulphonyl fluoride (30 g) was reduced with granulated tin (40 g) and concentrated hydrochloric acid (200 ml), the latter being added slowly and the temperature being kept below 50 °C. When all the acid had been added the mixture was kept at 40–45 °C for 30 min and then decanted from residual tin. To the cold solution was added hydrated sodium acetate (450 g), the white precipitate filtered off and extracted with hot alcohol. The sulphonyl fluoride was precipitated from the alcoholic solution by addition of water and crystallized from light petroleum/chloroform as colourless needles, m.p. 72–73 °C (45%).

Acetylation with acetic anhydride in glacial acetic acid gave *p*-acetamidobenzene sulphonyl fluoride identical in m.p. and mixed m.p. with the product from *p*-acetamidobenzene sulphonyl chloride and potassium fluoride.

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