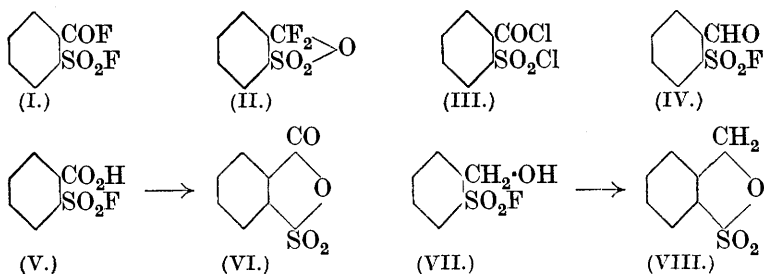


285. *Benzenesulphonyl Fluoride Derivatives.*

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IN an unsuccessful attempt to prepare *o*-fluorosulphonylbenzoyl fluoride (I) with the view of investigating the possibility of the change into (II), the juxtaposition of the sulphonyl fluoride group and an *o*-substituent has been observed to cause one or other of the groups to exhibit anomalous behaviour.

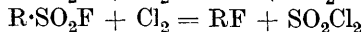
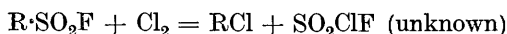
The dichloride (III), when treated with an inorganic fluoride



under conditions which transform the COCl and the SO₂Cl group, present separately, into the corresponding fluoride (J., 1931, 2104), is unchanged or converted into *o*-sulphobenzoic anhydride. The *p*-acid dichloride reacts with aqueous potassium fluoride to give a 44% yield of *p*-fluorosulphonylbenzoic acid. A still more pronounced difference in behaviour is shown in the oxidation of *o*- and *p*-toluenesulphonyl fluorides in non-alkaline media: a good yield of *p*-fluorosulphonylbenzoic acid is obtained, but the *o*-compound is destroyed or recovered unchanged. So great is the selective action of oxidising agents that a mere trace of the *p*-isomeride in *o*-toluenesulphonyl chloride is detected by conversion into the

fluoride and oxidation of the product; the high-melting *p*-fluoro-sulphonylbenzoic acid is then obtained.

To facilitate the oxidation of the side chain *o*-toluenesulphonyl fluoride has been chlorinated. Unlike the *p*-compound, it loses weight on chlorination owing to elimination of the sulphonyl group. The following reactions probably take place, the methyl group being simultaneously chlorinated :



These two equations are supported (p. 2044) by the isolation of a mixture of *o*-chlorobenzylidene chloride and a compound containing fluorine in the nucleus. (*o*-Toluenesulphonyl chloride also readily loses its sulphonyl group on chlorination at a high temperature, and the method has been used to produce *o*-chlorobenzylidene chloride in 73.5% yield.) By chlorinating *o*-toluenesulphonyl fluoride very rapidly at a high temperature, a moderate yield of *ω*-chloro-*o*-toluenesulphonyl fluoride is obtained, which is converted (via the iodo-fluoride) into *ω*-hydroxy-*o*-toluenesulphonyl fluoride (VII). This alcohol cannot be oxidised to give (V), as the aromatic sulphonyl fluoride group which is normally so unreactive (Davies and Dick, *loc. cit.*) readily loses its fluorine to form the *sultone* (VIII).

Benzaldehyde-o-sulphonyl fluoride (IV), obtained in a moderately pure condition by the action of chromylchloride on *o*-toluenesulphonyl fluoride, is oxidised by exposure to the atmosphere to (V). This compound, however, has not been isolated in the pure state because under the above conditions it loses hydrogen fluoride to form (VI), the latter being then converted into *o*-sulphobenzoic acid. The surprising activity of the fluorine atom is here also doubtless due to the tendency to ring formation in the ortho-position.

o-Cyanobenzenesulphonyl fluoride also has anomalous properties. The cyano-group is not attacked or hydrolysed by cold acid hydrolytic reagents, and in ether it is not affected by dry hydrogen chloride, bromide or iodide, whereas benzonitrile is immediately attacked even by hydrogen chloride.

In order to ascertain whether the unexpected reactions of the *o*-compounds are due to the proximity of the two groups, the corresponding *p*-compounds have been prepared in certain cases for comparative purposes. The *p*-analogues of (V) and (VII) are stable compounds, the sulphonyl group showing the usual inertness and not interfering with the normal reactions of the other group present. It is evident from this that the tendency to form a stable ring (in the *o*-position) can modify profoundly the properties of one of the groups responsible for such ring formation.

E X P E R I M E N T A L.

o- and *p*-Chlorosulphonylbenzoyl Chlorides.—In each case the toluenesulphonyl chloride is hydrolysed with KOH aq. and oxidised with alkaline KMnO_4 aq. to potassium sulphobenzoate. Acidification with HCl aq. and evaporation to dryness gives a mixture of KCl and potassium sulphobenzoate, which is dried at 150° and heated with a 20% excess of PCl_5 on the water-bath for 2 hrs., the product being poured on ice and worked up as follows :

Ortho. The oil is extracted and dried (Na_2SO_4) in C_6H_6 and distilled at 2 mm. : 5 g. of *o*-chlorobenzoyl chloride (b. p. $228\text{--}236^\circ/760$ mm.) are obtained and then 100 g. of (III), b. p. $187\text{--}188^\circ/2$ mm., m. p. 40° (Scheiber and Knothe, *Ber.*, 1912, 45, 2254).

Para. The solid dichloride is dried in Et_2O and recryst. from light petroleum ; m. p. $55\text{--}57^\circ$: about 10% of the product does not dissolve in this solvent, has m. p. 242° after several recrystns. from anisole, and has not been identified.

Treatment of the Dichlorides with Zinc Fluoride.—When a solution of the *o*-dichloride in dry C_6H_6 or light petroleum (b. p. $60\text{--}80^\circ$ or $80\text{--}100^\circ$) is heated with dry ZnF_2 for 5—18 hrs., a small amount of *o*-sulphobenzoic anhydride only is obtained [m. p. $124\text{--}125^\circ$. Found : H.V. (see Davies and Dick, *loc. cit.*), 10.82 c.c. $\text{C}_7\text{H}_4\text{O}_4\text{S}$ requires 10.87 c.c.] apart from unchanged chloride. Nothing further is produced when no solvent is used, either at room temp. or at 100° , or when NaF or AgF is substituted for ZnF_2 .

When the *p*-dichloride (20 g.) is refluxed for 48 hrs. in C_6H_6 with excess of ZnF_2 (or ZnCl_2), unchanged chloride (10 g.) and *pp'*-bischlorosulphonylbenzoic anhydride (4 g.), plates, m. p. 197° , from anisole or xylene [Found : Cl, 16.8 ; S, 15.5 ; *M* (Rast), 418 ; H.V., 14.31 c.c. $\text{C}_{14}\text{H}_8\text{O}_7\text{Cl}_2\text{S}_2$ requires Cl, 16.8 ; S, 15.1% ; *M*, 423 ; H.V., 14.24 c.c.], are obtained.

Treatment of the Dichlorides with 70% Potassium Fluoride Solution.—The *o*-dichloride is completely hydrolysed after 12 mins. by boiling KF aq.

When the *p*-dichloride (10 g.) is refluxed with KF aq. (10 c.c.) for 8 min., and the liquid is diluted and filtered, *p*-fluorosulphonylbenzoic acid is obtained (3.75 g., m. p. 271° after recrystn. from H_2O) (Steinkopf, *J. pr. Chem.*, 1927, 117, 28).

Chlorination of o-Toluenesulphonyl Fluoride.—174 G., chlorinated at $140\text{--}175^\circ$, first lose wt. and then after 57 hrs. gain 16.5 g., HCl and a gas forming H_2SO_4 still being produced. A cryst. mixture (48 g.) of ω -mono- and dichloro-*o*-toluenesulphonyl fluorides is formed and the filtrate, on distillation at 20 mm., gives a fraction (97 g.) at $115\text{--}147^\circ$. From this, at $224\text{--}232^\circ$ /ord. press., a substance is obtained which contains no S, etches the glass when heated with fuming HNO_3 in a sealed tube at $150\text{--}200^\circ$ for 2 days, and when boiled with alc. NaOH for 18 hrs. (Found : H.V., 10.72 c.c. $\text{C}_6\text{H}_4\text{F}\cdot\text{CHCl}_2$ requires 11.18 c.c. $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHCl}_2$ requires 10.12 c.c.) gives a product which is oxidised by KMnO_4 to *o*-chlorobenzoic acid, m. p., and mixed m. p. $137\text{--}139^\circ$.

*ω -Chloro-*o*-toluenesulphonyl fluoride*, colourless lachrymatory prisms, m. p. 69° , after crystn. from light petroleum, is obtained (70 g.) when *o*-toluenesulphonyl fluoride (174 g.) is chlorinated at $180\text{--}200^\circ$ for 11 hrs., the process after $5\frac{1}{2}$ hrs. and again 3 hrs. later being interrupted, the product cooled, the crystals collected, and the filtrate rechlorinated [Found : F, 9.0 ; H.V., 14.41 c.c. $\text{C}_7\text{H}_6\text{O}_2\text{ClFS}$ requires F, 9.1% ; H.V. (for both Cl and F), 14.38 c.c.].

*ω -Iodo-*o*-toluenesulphonyl fluoride*, quant. made by boiling ω -chloro-*o*-

toluenesulphonyl fluoride with NaI in Me₂CO for 30 mins., forms very lachrymatory, colourless plates, m. p. 85—86° [Found: F, 6.4; H.V., 9.84 c.c. C₇H₆O₂IFS requires F, 6.3%; H.V. (for both I and F), 10.00 c.c.].

Chlorination of o-Toluenesulphonyl Chloride.—After an initial loss of wt., *o*-toluenesulphonyl chloride (95½ g.), when chlorinated at 92—93° for 36 hrs., gives *o*-chlorobenzylidene chloride (72 g.), b. p. 225—232°, *n*_D¹⁶ 1.5670.

Chlorination of 95½ g. for 5½ hrs. at 110—130° in presence of a trace of PCl₃ gives a product (91 g.) which contains *o*-chlorotoluene (11%), *o*-chlorobenzyl chloride (20%), unchanged *o*-toluenesulphonyl chloride (25%), and *ω*-chloro-*o*-toluenesulphonyl chloride (7 g.; 6% yield), b. p. about 175°/22 mm., needles, m. p. 46°, from light petroleum [Found: H.V., 13.27 c.c. C₇H₆O₂Cl₂S requires (for both Cl's) H.V., 13.34 c.c.]. The last substance is converted into *ω*-chloro-*o*-toluenesulphonyl fluoride, m. p. 69°, by KF aq.

Chlorination of p-Toluenesulphonyl Fluoride.—Side-chain chlorination here takes place without much loss of the sulphonyl group. *p*-Toluenesulphonyl fluoride (174 g.), chlorinated at 160—210° for 7 hrs. until it gains 32 g. (theoretical, 34.5 g.), gives *ω*-chloro-*p*-toluenesulphonyl fluoride, b. p. 148—152°/20 mm., in 62.4% yield (130 g.). This forms long plates, m. p. 56°, from light petroleum and is only very slightly lachrymatory (Found: F, 9.2; H.V., 14.54 c.c. C₇H₆O₂ClFS requires F, 9.1%; H.V., 14.38 c.c.).

ω-Iodo-*p*-toluenesulphonyl fluoride, made in the same way as the *o*-isomeride, crystallises from light petroleum in long plates, m. p. 106°. This again is not nearly so lachrymatory as the *o*-compound (Found: F, 6.4%; H.V., 9.78 c.c. C₇H₆O₂IFS requires F, 6.3%; H.V., 10.00 c.c.).

Preparation of ω-Hydroxytoluenesulphonyl Fluorides.—When *ω*-chloro-*o*-toluenesulphonyl fluoride is boiled with aq.-alc. Ag₂O suspension, or Ag₂SO₄ aq., hydrolysis of the SO₂F occurs more readily than removal of Cl and consequently, although AgCl is pptd., no *ω*-hydroxy-*o*-toluenesulphonyl fluoride is produced. Further, in contrast to most aromatic monosulphonyl fluorides, this compound is hydrolysed about 50% when boiled with H₂O for 3 hrs.

ω-Hydroxy-*o*-toluenesulphonyl fluoride is, however, prepared in 10 mins. by heating *ω*-iodo-*o*-toluenesulphonyl fluoride (30 g.) in aq. EtOH with Ag₂O. After filtration from AgI and dilution with H₂O, an oil (11 g.) is obtained, and also the *sultone* of *ω*-hydroxy-*o*-toluenesulphonic acid as a white cryst. solid (4.2 g.), m. p. 112—113° (Found: H.V., 5.92 c.c. C₇H₆O₃S requires H.V., 5.88 c.c.). The oil has b. p. 128—130°/1 mm. (9.5 g.) (Found: F, 9.4; H.V., 9.84 c.c. C₇H₇O₃FS requires F, 10.0%; H.V., 10.52 c.c.): the discrepancy is due to *sultone* from which it could not be further purified by distillation.

ω-Hydroxy-*p*-toluenesulphonyl fluoride is prepared in a similar manner to the *o*-compound: 34 g. of the iodo-derivative give 14.2 g. (60% yield) of product, and on distillation 6.7 g. have b. p. 157—160°/1 mm., the remainder boiling slightly higher (Found: H.V., 10.53 c.c.; F, 9.9%).

The use of AgNO₃ instead of Ag₂O in these two preps. gives products containing HNO₃ which is not readily removed.

Oxidation of ω-Hydroxytoluenesulphonyl Fluorides.—50% of the *o*-compound is recovered after treatment with CrO₃ in AcOH. When 150% excess of AgMnO₄ is used, 1.6 g. (from 3.9 g.) are recovered unchanged and pptn. of the Ag in the aq. solution indicates the hydrolysis of 1.8 g.

The *p*-compound is readily oxidised by CrO₃-AcOH to *p*-fluorosulphonylbenzoic acid.

Benzaldehyde-o-sulphonyl Fluoride (IV).—A mixture of *o*-toluenesulphonyl fluoride (20 g.) and CrO_2Cl_2 (20 c.c.) is kept cool for 14 days, and the solid broken up, washed with CS_2 , and decomposed with H_2O . Somewhat impure *benzaldehyde-o-sulphonyl fluoride* separates as an oil which, after drying in C_6H_6 over Na_2SO_4 , distils at $143\text{--}155^\circ/1$ mm. (8.8 g.) (Found: F, 9.9; H.V., 11.24 c.c. $\text{C}_7\text{H}_5\text{O}_3\text{FS}$ requires F, 10.1%; H.V., 10.64 c.c.). The red 2 : 4-dinitrophenylhydrazone, prepared by Brady's method (J., 1931, 756), has m. p. $216\text{--}218^\circ$ after recrystn. from xylene [Found (micro-Dumas): N, 15.2. $\text{C}_{13}\text{H}_9\text{O}_6\text{N}_4\text{FS}$ requires N, 15.2%]. (*o*-Toluenesulphonyl fluoride gives no hydrazide when heated with a H_2SO_4 solution of 2 : 4-dinitrophenylhydrazine and kept for several days.)

Benzaldehyde-o-sulphonyl fluoride, exposed to the atmosphere in a thin layer for a week, is converted into a cryst. material, m. p. 65° with subsequent efferv. This material is quickly converted entirely into *o*-sulphobenzoic acid (m. p. 68°) by ice-cold H_2O . The dry material contains 3.4% F, *i.e.*, probably about one-third remains as *o*-fluorosulphonyl benzoic acid at the time of analysis; this probability is supported to some extent by the effervescence just after melting.

Oxidation of the aldehyde by the ordinary methods always results in the hydrolysis of the SO_2F group.

o-Cyanobenzenesulphonyl Fluoride.—Saccharin (44 g.) is heated at $120\text{--}130^\circ$ for $1\frac{1}{2}$ hrs. with PCl_5 (100 g.), and the mixture poured into H_2O . The dried product weighs 49 g. A portion of this (7 g.) is insol. in Et_2O and is saccharin according to Walker and Smith (J., 1906, 89, 350). It, however, has m. p. $135\text{--}139^\circ$ after several recrystallns. from C_6H_6 , contains Cl, and on solution in alkali and reprecip. with acid gives saccharin. This indicates pseudo-saccharin chloride, which has m. p. 149° and is known to be formed when the above reaction is carried out at a higher temperature (see Jesurun, *Ber.*, 1893, 26, 2294; Fritsch, *Ber.*, 1896, 29, 2295). After recrystallising several times from light petroleum, the *o*-cyanobenzenesulphonyl chloride has m. p. $65\text{--}68^\circ$ (W. & S. give 67.5°).

A solution of *o*-cyanobenzenesulphonyl chloride (4.8 g.) in xylene (5 c.c.), heated on the water-bath for $\frac{1}{2}$ hr. with 70% KF aq. (5 c.c.) and cooled, gives *o*-cyanobenzenesulphonyl fluoride (3 g.), m. p. $88\text{--}89^\circ$ after recrystn. from EtOH and light petroleum; this crystallises unchanged from H_2O [Found: F, 10.3; N, (Kjeldahl), 7.6; H.V., 10.62 c.c. after 3 hrs.' hydrolysis, 10.92 c.c. after $7\frac{1}{2}$ hrs. $\text{C}_7\text{H}_4\text{O}_2\text{NFS}$ requires F, 10.3; N, 7.6%; H.V. (both CN and F), 16.22 c.c.]. The discrepancy in H.V. is due to the difficulty of hydrolysis of the cyano-group, the sulphonyl fluoride group, alone, requiring 10.81 c.c.

o-Nitrobenzenesulphonyl Fluoride.—*o*-Nitrobenzenesulphonyl chloride (6 g.) is refluxed for 15 mins. with 70% KF aq. (6 c.c.). After cooling and dilution with H_2O the fluoride is removed and recrystallised from EtOH and light petroleum; 3.1 g. (56.5% yield), m. p. 60° (Found: F, 9.2; H.V., 9.76 c.c. $\text{C}_6\text{H}_4\text{O}_4\text{NFS}$ requires F, 9.3%; H.V., 9.75 c.c.).

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