403. *Preparation and Properties of Some Pentafluorosulphuroxy-aryl Compounds*, $ArO{\cdot}SF_5$.

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Bispentafluorosulphur peroxide reacts with benzene, toluene, or chlorobenzene to give compounds in which the pentafluorosulphuroxy-group ($F_5S{\cdot}O-$) * is a substituent in the aromatic ring. Some reactions of these compounds are described.

Bispentafluorosulphur peroxide [1] reacts with benzene at 150° to give pentafluorosulphuroxybenzene * in 50% yield:

$$C_6H_6 + SF_5{\cdot}O{\cdot}O{\cdot}SF_5 \longrightarrow C_6H_5{\cdot}O{\cdot}SF_5 + SOF_4 + HF$$

This reaction has also been carried out with toluene and chlorobenzene, but with compounds such as phenol, aniline, and anisole which are readily oxidised the only reaction observed even at 0° was violent oxidation which prevented substitution in the aromatic ring.

Reduction of pentafluorosulphuroxybenzene with sodium in ethanol gave phenol, and this reaction was used to establish the orientation of the products formed in the reactions of bispentafluorosulphur peroxide with toluene and chlorobenzene. Thus the product from the reaction with toluene, which was shown by gas chromatography to be a single compound, gave on reduction *p*-cresol and must therefore be *p*-pentafluorosulphuroxytoluene. The product from the reaction with chlorobenzene contained two isomers which were shown in a similar manner to be *o*- and *p*-chloropentafluorosulphuroxybenzene, in a ratio of ~1 : 10.

Although the pentafluorosulphuroxy-group is readily reduced it is stable to oxidation and hydrolysis, and a number of the standard aromatic substitutions can be carried out without removing it. Nitration gives a 94% yield of *p*-nitro(pentafluorosulphuroxy)-benzene, the orientation being established by alkaline hydrolysis to *p*-nitrophenol.

Attempts to reduce *p*-nitro(pentafluorosulphuroxy)benzene to the amine were unsuccessful, owing to simultaneous reduction of the pentafluorosulphuroxy-group, though reduction by zinc dust and hydrogen chloride in acetic anhydride afforded *p*-pentafluorosulphuroxyacetanilide.

p-Pentafluorosulphuroxytoluene readily gave 2-nitro-4-pentafluorosulphuroxytoluene, and this was readily reduced by iron and very dilute hydrochloric acid to the amine. The orientation of these compounds was established by nuclear magnetic resonance spectroscopy.[2]

Sulphonation of pentafluorosulphuroxybenzene gives a 50% yield of the *p*-sulphonic acid, and thence 3-nitro-4-pentafluorosulphuroxybenzenesulphonic acid in 64% yield. Attempts to reduce this to the amine under a variety of conditions gave only 3-amino-4-hydroxybenzenesulphonic acid, but this established the orientation in the series.

These differences in reactions of the pentafluorosulphuroxy-group with reducing agents may be due to the different orientations with respect to the nitro-group. For *ortho*- and *para*-compounds there is the possibility of ready decomposition through quinonoid intermediates, *e.g.*, $p\text{-}NH_2{\cdot}C_6H_4{\cdot}O{\cdot}SF_5 \longrightarrow H^+ + NH{:}C_6H_4{:}OSF_4 + F^-$.

Oxidation of *p*-pentafluorosulphuroxytoluene with chromium trioxide in glacial acetic acid and acetic anhydride proceeds smoothly, giving 88% of *p*-pentafluorosulphuroxybenzoic acid.

* The name " pentafluorosulphuroxy " for the group $F_5S{\cdot}O^-$ seems advisable, in preference to pentafluorothio-oxy (since thioxy has been used for –S–) or pentafluorosulphoxy (to avoid possible confusion with a sulphoxide). Ed.

[1] H. L. Roberts, *J.*, 1960, 2774.

[2] Imperial Chemical Industries Ltd., Dyestuffs Division, unpublished work.

p-Pentafluorosulphuroxybenzoic acid (K_a $9{\cdot}2 \times 10^{-6}$) is a stronger acid than benzoic acid (K_a $2{\cdot}1 \times 10^{-6}$) but weaker than *p*-nitrobenzoic acid (K_a $28{\cdot}2 \times 10^{-6}$). The pentafluorosulphuroxy-group attached to a benzene ring is seen above to direct an incoming electrophilic substituent predominantly to the *para*-position, the *ortho*-position presumaby being sterically blocked to a large extent. This indicates a $+E$ effect analogous to that exerted by halogen atoms. The acidity of the benzoic acid indicates a σ-value [3] of +0·44 for the *p*-SF_5·O group. This is much larger than that found [3] for *p*-F (+0·062) but comparable with that for the *p*-ethoxycarbonyl (0·45) and the *p*-acetylthio-group (0·44). As oxygen cannot exert a $-E$ effect the large positive σ-value must be due to the strong $-I$ effect of the SF_5·O substituent.

Experimental

Apparatus and Procedure.—The procedure for autoclave reactions and gas chromatography has been described.[4]

Reactions of Bispentafluorosulphur Peroxide.—(*a*) *With benzene.* Benzene (30 c.c.) and bispentafluorosulphur peroxide (19 g.) were heated in an autoclave to 150° for 15 hr. After cooling to room temperature the excess of pressure was released through a trap cooled in liquid air. This condensed a white solid (10 g.) which on warming melted and finally vaporised. An infrared spectrum of the gas showed strong absorption at 1379, 927, and 820 cm.$^{-1}$ characteristic of thionyl tetrafluoride [5] and at 1022 cm.$^{-1}$ due to silicon tetrafluoride (produced by the action of hydrogen fluoride on the glass trap). There remained in the autoclave a dark brown liquid (32 g.).

In a series of similar experiments bispentafluorosulphur peroxide (133 g.) was treated with benzene (160 c.c.), giving liquid products (225 g.) which were distilled to give: (1) b. p. up to 80°; (2) b. p. 80°—139° (5 g.); (3) b. p. 139° (47·5 g.), *pentafluorosulphuroxybenzene* (Found: C, 32·9; F, 43·1. $C_6H_5F_5OS$ requires C, 32·7; F, 43·2%), $\nu_{max.}$ 1590, 1485, 1195, 1155, 930—915—900vs, 845s, 775 cm.$^{-1}$. To a refluxing solution of the product (1·6 g.) in ethanol, sodium (0·8 g.) was added during ½ hr. The products were decanted into cold water and a few drops of a heavy lower layer rejected. Bromine water was added to the aqueous solution until a faint yellow colour persisted. The white precipitate (1 g.) was filtered off and recrystallised from aqueous ethanol. It had m. p. 94° alone or mixed with 2,4,6-tribromophenol.

(*b*) *With toluene.* Toluene (50 c.c.), trichlorofluoromethane (20 c.c.), and bispentafluorosulphur peroxide (38 g.) were heated in an autoclave at 90° for 10 hr. In similar reactions, the procedure given above afforded from 194 g. of bispentafluorosulphur peroxide a fraction, b. p. 60°/17 mm., 161°/760 mm. (85 g.), shown by gas chromatography to contain only one component, namely p-*pentafluorosulphuroxytoluene* (Found: C, 35·9; F, 40·7. $C_7H_7F_5OS$ requires C, 35·9; F, 40·7%). Reduction with sodium in ethanol gave *p*-cresol, identified as its benzoate.

(*c*) *With chlorobenzene.* Chlorobenzene (15 g.) with bispentafluorosulphur peroxide (20 g.) in an autoclave to 150° (15 hr.) gave a liquid product (21·5 g.) which after removal of unchanged chlorobenzene afforded a fraction, b. p. 58°/10 mm., shown by gas chromatography to contain two components in a ratio of about 10 : 1, namely, *p*- and *o*-chloro(pentafluorosulphuroxy)-benzene (Found: S, 12·3%; *M*, 255. Calc. for $C_6H_4ClF_5OS$: S, 12·6%; *M*, 254·5). Reduction followed by bromination gave 2,6-dibromo-4-chlorophenol as major product, m. p. and mixed m. p. 90°. The minor component had m. p. 75°, identical with that for 2,4-dibromo-6-chlorophenol.

Nitration of Pentafluorosulphuroxybenzene.—This compound (10 g.) was dissolved in glacial acetic acid (20 c.c.), and concentrated sulphuric acid (20 c.c.) added, followed slowly by concentrated nitric acid (20 c.c.), and the mixture was kept at 80° for 3 hr., all with stirring. The solution was then cooled and poured on ice. The crude product recrystallised from ligroin (b. p. 60—80°), giving p-*nitro*(*pentafluorosulphuroxy*)*benzene* (7·7 g.), m. p. 63·4° (Found: N, 5·5; S, 12·0; F, 36·2. $C_6H_4F_5O_3NS$ requires N, 5·3; S, 12·1; F, 35·8%). With potassium hydroxide in boiling aqueous ethanol (72 hr.) this gave *p*-nitrophenol, m. p. 114°.

p-*Pentasulphuroxyacetanilide.*—A solution of the preceding product (1 g.) in acetic anhydride

[3] Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[4] Case, Ray, and H. L. Roberts, *J.*, 1961, 2066.
[5] Goggin, H. L. Roberts, and Woodward, *Trans. Faraday Soc.*, 1961, **57**, 1877.

(10 c.c.) was saturated with hydrogen chloride. Zinc dust (5 g.) was then slowly added until a drop of the solution gave a solid precipitate when diluted with water. The solution was then filtered and run into water. The white solid was filtered off, dried (P_2O_5), and recrystallised from benzene, giving p-*pentafluorosulphuroxyacetanilide* as needles, m. p. 157° (decomp.) (Found: C, 35·0; H, 2·6; N, 5·3. $C_8H_8F_5NO_2S$ requires C, 34·7; H, 2·9; N, 5·1%).

2-*Nitro*-4-*pentafluorosulphuroxytoluene*.—*p*-Pentafluorosulphuroxytoluene (30 g.) was dissolved in concentrated sulphuric acid (60 c.c.) and then kept at 10° and stirred while nitric acid (*d* 1·4; 50 c.c.) was added during 30 min. The temperature was then raised to 40° and after 30 minutes' further stirring the mixture was cooled and poured on ice (300 g.). Extraction with ether (3 × 50 c.c.), drying ($MgSO_4$), removal of the solvent, and distillation gave 2-*nitro*-4-*pentafluorosulphuroxytoluene* (34 g., 95%), b. p. 122—124°/12 mm. (Found: C, 30·3; H, 2·1; N, 5·5; S, 11·0. F_5NO_3S requires C, 30·25; H, 2·15; N, 5·05; S, 11·45%.

Amino-4-*pentafluorosulphuroxytoluene*.—To a boiling, stirred mixture of ethanol (20 c.c.), concentrated hydrochloric acid (0·8 c.c.), and iron dust (6 g.) 2-nitro-4-pentafluorosulphuroxytoluene (5·6 g.) was added during 1 hr. The mixture was refluxed for a further 3½ hr., then rendered alkaline with ammonia, stirred for 15 min., and filtered. The solid was washed with hot ethanol (2 × 20 c.c.). After removal of the solvents from the combined filtrate and washings the residual oil was dissolved in ether and extracted with dilute hydrochloric acid. The acid extracts were made alkaline with sodium hydroxide solution and extracted with ether which removed the *amine* (3·2 g., 64%), b. p. 108—110°/12 mm. (Found: C, 33·8; H, 3·3; N, 5·5; S, 13·3. $C_7H_8F_5NOS$ requires C, 33·75; H, 3·25; N, 5·6; S, 12·85%).

Sulphonation of Pentafluorosulphuroxybenzene.—The fluoride (12·5 g.) was stirred with sulphuric acid (*d* 1·84; 5·0 c.c.) and a crystal of iodine at 110—115° for 7 hr., cooled, and poured into saturated brine (30 c.c.) at 0°. The crude product was filtered off, dissolved in water, and treated with potassium acetate. The precipitate of *potassium* p-*pentafluorosulphuroxybenzenesulphonate* (10·1 g., 50%) was washed with ethanol (Found: C, 20·4; H, 1·4; S, 18·4; sulphated ash, 26·4. $C_6H_4F_5KO_4S_2,H_2O$ requires C, 20·25; H, 1·7; S, 18·15; sulphated ash, 25·8%).

2-*Nitro*-4-*pentafluorosulphuroxybenzenesulphonic Acid*.—Potassium *p*-pentafluorosulphuroxybenzenesulphonate (2·0 g.), dissolved in concentrated sulphuric acid (5 c.c.), was cooled to 0·5°. Nitric acid (*d* 1·4; 7·5 c.c.) was added with stirring and the mixture was kept at 50° for 1 hr., cooled, and poured into ice-cold saturated brine (60 c.c.). The product was filtered off, crystallised repeatedly from potassium acetate, and finally washed with ethanol, to give *potassium* 2-*nitro*-4-*pentafluorosulphuroxybenzenesulphonate* (1·45 g., 64%) as colourless plates (Found: C, 18·4; H, 0·7; N, 3·9; S, 16·4. $C_6H_3F_5KNO_6S$ requires C, 18·75; H, 0·8; N, 3·65; S, 15·65%).

Reduction of 2-*Nitro*-4-*pentafluorosulphuroxybenzenesulphonic Acid*.—A mixture of water (150 c.c.), iron borings (20 g.), and potassium 2-nitro-4-pentafluorosulphuroxybenzenesulphonate (18·5 g.) was stirred at 65° while 85% formic acid (1 g.) in water (9 c.c.) was added in 10 portions at 15-min. intervals. Stirring was continued for a further 90 min. The mixture was then made slightly alkaline with potassium carbonate and filtered. The residues were washed with hot water (2 × 25 c.c.). After evaporation to small volume the combined filtrate and washings were acidified with hydrochloric acid and cooled. The precipitated 3-amino-4-hydroxybenzenesulphonic acid (6·5 g.) was filtered off, washed with a little water, and dried (Found: C, 36·1; H, 4·0; N, 6·9; S, 16·4. Calc. for $C_6H_7NO_4S,\frac{1}{2}H_2O$: C, 36·3; H, 4·05; N, 7·1; S, 16·15%).

Oxidation of p-*Pentafluorosulphuroxytoluene*.—To this compound (10 g.), acetic acid (64 c.c.), acetic anhydride (64 c.c.), and concentrated sulphuric acid (23 c.c.), stirred at 0—10°, chromium trioxide (15 g.) was added. Then the mixture was poured on ice. A solid that separated was dissolved in ether and combined with an ethereal extract of the aqueous layer. These ethereal solutions were extracted with sodium carbonate solution, and this extract was added to concentrated hydrochloric acid. The precipitate (10 g., 88%) recrystallised from benzene, to give p-*pentafluorosulphuroxybenzoic acid* as needles, m. p. 214° (Found: C, 32·0; H, 2·0; F, 35·9; S, 11·9%; equiv., 262. $C_7H_5F_5O_3S$ requires C, 31·8; H, 1·9; F, 36·0; S, 12·1%; equiv., 264).

Measurement of Apparent Ionization Constants and Evaluation of the σ-*Value for the* $SF_5{\cdot}O$ *Group*.—The method was essentially that described by J. D. Roberts *et al.*[6] Twice recrystallised samples of *p*-toluic, benzoic, *p*-nitrobenzoic, and *p*-pentafluorosulphuroxybenzoic acid (0·5—1·0 g.) were titrated in solutions (200 ml.) of 1 : 1 water–ethanol with carbonate-free aqueous

[6] J. D. Roberts, McElhill, and Armstrong, *J. Amer. Chem. Soc.*, 1949, **71**, 2923.

N-sodium hydroxide at 25° ± 0·2°, by means of an E.I.L. Titrimeter with a glass electrode and a saturated potassium chloride–calomel electrode. The half-neutralisation point acidities were obtained graphically. The results are summarised in the Table. K_R is an apparent dissociation constant calculated for unit activities and on the assumption that the readings of the pH-meter scale are equal to the logarithm of the reciprocal of the hydrogen-ion concentration at the half-point. The half-point readings on the pH scale of the titrimeter were calibrated for standard aqueous buffer solutions at half-neutralisation point without correction for liquid junction potentials. A plot of $\log_{10}(K_R/K_H)$ against the respective σ-value for the

R in *p*-R·C_6H_4·CO_2H	Me	H	SF_5·O	NO_2
Half-point reading	5·91	5·67	5·04	4·55
10^6K_R	1·2	2·1	9·2	28·2

substituents gave a straight line of slope ρ +1·43. The σ-values are taken from Jaffé's compilation,[3] which cites a value of ρ 1·423 for the ethanol–water system used here. Linear integration gives a value of σ +0·44 for the SF_5·O group.

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