

176. *The 3,4-Bisarenesulphonylfuroxans.*

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3,4-Bisarenesulphonylfuroxans are formed (a) by the action of nitric acid on arenesulphonylacetic acids and (b) by reaction between sulphinates and chloropicrin in concentrated aqueous solution.

THE reaction of (arythio)acetic acids with hypochlorite gives aryl trichloromethyl sulphones, usually in good yield.¹ A study has now been made of the reaction of (arythio)acetic acids with nitric acid, in the original expectation that the products might be the unknown aryl trinitromethyl sulphones. This proved not to be the case.

The first products of the reaction, under very mild conditions, were the arenesulphonylacetic acids, and it was found better in practice to use these as starting materials. Benzenesulphonylacetic acid gave good yields of a neutral substance, $C_{14}H_{10}N_2O_6S_2$; by analogy with the reaction of acetophenone with nitric acid to give 3,4-dibenzoylfuroxan,² this compound is believed to be 3,4-bisbenzenesulphonylfuroxan (I; $R = R' = Ph$). A similar compound was made from *p*-chlorobenzenesulphonylacetic acid (I; $R = R' = 4-ClC_6H_4$); but with toluene-*p*-sulphonylacetic acid nitration also occurred and the dinitro-compound (I; $R = R' = 4-Me,3-NO_2 \cdot C_6H_3$) was the only product. Nitration has also been observed in the preparation of dibenzoylfuroxan.³

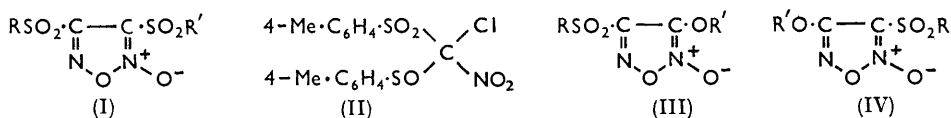
Even with benzenesulphonylacetic acid a mononitro-compound, m. p. 154—155° (I; $R = Ph$, $R' = 3-NO_2 \cdot C_6H_4$, or *vice versa*) could be obtained under more vigorous conditions. This is probably identical with a substance, m. p. 156—157°, described by

¹ Farrar, *J.*, 1956, 508.

² Holleman, *Ber.*, 1887, **20**, 3360; 1888, **21**, 2838.

³ Snyder and Boyer, *J. Amer. Chem. Soc.*, 1955, **77**, 4233.

Rössing⁴ from the same reaction, and given the unlikely formula $\text{PhSO}_2\cdot\text{NO}$. This incorrect empirical formula probably arose from the difficulties of analysis; the nitrated compounds especially tend to deflagrate in the combustion tube.



The 3,4-bisarenesulphonylfuroxans are also formed in what seems at first sight to be a very different reaction. Sodium toluene-*p*-sulphinic acid reacts slowly with chloropicrin in dilute aqueous solution to give mainly nitrobistoluene-*p*-sulphonylmethane (compare the reaction of chloropicrin with potassium sulphite to give potassium nitromethanesulphonate⁵). A minor by-product is the unexpected chloronitrotoluene-*p*-sulphonyltoluene-*p*-sulphonyl methane (II). In concentrated solution, however, the reaction is rapid and a neutral compound, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_6\text{S}_2$, is formed. This formula suggested that it was the furoxan (I; $\text{R} = \text{R}' = p\text{-Me}\cdot\text{C}_6\text{H}_4$), and this supposition was proved correct by showing that a similar product from sodium benzenesulphinic acid was identical with 3,4-bisbenzenesulphonylfuroxan.

The intermediate in both syntheses is probably the aryl nitromethyl sulphone. Little is known about the reactions of these substances,⁶ but they may lose water under the conditions of the reaction to form the (hypothetical) arenesulphonylnitrile oxide $\text{ArSO}_2\text{CN}^+\text{O}^-$; this would be expected to dimerise immediately to the furoxan.⁷ It is known that ω -nitroacetophenone will lose the elements of water under certain conditions to give dibenzoylfuroxan.⁸

Reduction of the 3,4-bisarenesulphonylfuroxans under a variety of conditions gave oils smelling of thiophenol; neither furazans nor 1,2-bisarenesulphonylethanes were isolated. The only reaction of interest so far discovered occurs with alcohols containing a trace of alkali; one of the arenesulphonyl groups is smoothly and quantitatively replaced by an alkoxy-group. It is not known whether the product has structure (III) or (IV). This reaction appears to have no analogue in the 3,4-diacylfuroxan series.

EXPERIMENTAL

Reaction of Arenesulphonylacetic Acids with Nitric Acid.—A mixture of the arenesulphonylacetic acid (12 g.), nitric acid (*d* 1.5; 27 g.), and acetic acid (35 c.c.) was refluxed for 30 min. The product was diluted with water, and the precipitate crystallised (solvent in parentheses). Yields were of the order 50–65%.

3,4-Bisbenzenesulphonylfuroxan (I; $\text{R} = \text{R}' = \text{Ph}$), m. p. 126–127° (ethanol) (Found: C, 46.2; H, 2.4; N, 7.2. $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_6\text{S}_2$ requires C, 46.0; H, 2.7; N, 7.6%).

*3,4-Bis-*p*-chlorobenzenesulphonylfuroxan* (I; $\text{R} = \text{R}' = 4\text{-ClC}_6\text{H}_4$), m. p. 178° (acetone) [Found: C, 38.5; H, 2.1; Cl, 16.9; N, 6.2; S, 14.35%; *M* (ebullioscopic in benzene), 420. $\text{C}_{14}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_6\text{S}_2$ requires C, 38.6; H, 1.85; Cl, 16.3; N, 6.35; S, 14.7%; *M*, 435).

3,4-Bis-4-methyl-3-nitrobenzenesulphonylfuroxan (I; $\text{R} = \text{R}' = 3\text{-NO}_2\text{-4-MeC}_6\text{H}_3$) (from toluene-*p*-sulphonylacetic acid), m. p. 195° (decomp.) (acetone) (Found: N, 11.0; S, 13.2. $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_{10}\text{S}_2$ requires N, 11.6; S, 13.2%). When the acetic acid was omitted from the reaction between benzenesulphonylacetic acid and nitric acid, the product was a complex mixture, from which a small amount of a *compound*, m. p. 154–155°, was isolated, probably (I; $\text{R} = \text{Ph}$, $\text{R}' = 3\text{-NO}_2\cdot\text{C}_6\text{H}_4$ or *vice versa*) (Found: C, 41.1; H, 2.4; N, 10.2; S, 15.4. $\text{C}_{14}\text{H}_8\text{N}_3\text{O}_8\text{S}_2$ requires C, 40.9; H, 2.2; N, 10.2; S, 15.6%).

*Reaction of Sodium Toluene-*p*-sulphinic acid with Chloropicrin.*—(a) *In concentrated solution.*

⁴ Rössing, *J. prakt. Chem.*, 1890, **41**, 369.

⁵ Backer, *Rec. Trav. chim.*, 1930, **49**, 1110.

⁶ Arndt and Rose, *J.*, 1935, 5.

⁷ Wieland and Semper, *Ber.*, 1906, **39**, 2523; Wieland, *ibid.*, 1907, **40**, 1671.

⁸ Alexander, Kinter, and McCollum, *J. Amer. Chem. Soc.*, 1950, **72**, 801.

A mixture of chloropicrin (5 g.), sodium toluene-*p*-sulphinate dihydrate (25 g.), and water (25 c.c.) was cautiously heated until an exothermic reaction began. When this was ended, heating was resumed for 2 hr. at 100°; dilution and filtration then gave crystals (4.5 g.) of 3,4-bistoluene-*p*-sulphonylfuroxan, m. p. 183° (from acetone) (Found: C, 48.7; H, 3.6; N, 7.0; S, 15.2. $C_{16}H_{14}N_2O_6S_2$ requires C, 48.7; H, 3.6; N, 7.1; S, 16.2%).

A similar experiment with sodium benzenesulphinate gave (I; R = R' = Ph), identical (mixed m. p.) with the product from benzenesulphonylacetic acid.

(b) *In dilute solution.* A mixture of chloropicrin (25 g.), sodium toluene-*p*-sulphinate dihydrate (100 g.), and water (600 c.c.) was refluxed for 2.5 hr. The product was washed by decantation, then taken up in warm, very dilute sodium hydroxide solution, leaving a small, semisolid residue. The alkaline extract, after acidification, gave nitrobistoluene-*p*-sulphonylmethane (17 g.), glassy prisms (from ethanol), m. p. 178—179° (Found: C, 49.3; H, 4.3; N, 3.9; S, 17.3. $C_{15}H_{15}NO_6S_2$ requires C, 48.8; H, 4.1; N, 3.8; S, 17.3%). This compound formed yellow solutions in sodium hydroxide, which readily deposited a sparingly soluble sodium salt.

The neutral, semisolid material crystallised from ethanol as needles, m. p. 149—150° (decomp.), of chloronitrotoluene-*p*-sulphinyltoluene-*p*-sulphonylmethane (II) (Found: C, 46.8; H, 3.7; N, 3.4; S, 16.5; Cl, 9.3. $C_{15}H_{14}ClNO_5S_2$ requires C, 46.5; H, 3.6; N, 3.6; S, 16.5; Cl, 9.2%).

4(or 3)-Benzenesulphonyl-3(or -4)-ethoxyfuroxan (III or IV; R = Ph, R' = Et). To a boiling suspension of 3,4-bisbenzenesulphonylfuroxan (0.2 g.) in ethanol (3 c.c.), aqueous sodium hydroxide (30%; 1 drop) was added. Addition of water then gave the compound as felted fine needles, m. p. 94—95°, in almost quantitative yield (Found: C, 44.0; H, 3.7; N, 10.7; S, 12.0. $C_{10}H_{10}N_2O_5S$ requires C, 44.4; H, 3.3; N, 10.4; S, 11.9%).

The toluene-*p*-sulphonyl derivative (III or IV; R' = Et, R = *p*-MeC₆H₄) was made similarly; it had m. p. 95° (from ethanol) (Found: C, 46.3; H, 4.0; N, 9.6. $C_{11}H_{12}N_2O_5S$ requires C, 46.5; H, 4.2; N, 9.9%).