320. *5-Sulpho-3-nitro- and 5-Sulpho-3-hydroxy-benzoic Acid.*

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The structure assigned by van Dorssen (*Rec. trav. chim.*, 1910, **14**, 368) to the sulphonitrobenzoic acid obtained by Limpricht and Uslar (*Annalen*, 1858, **106**, 27) after successive sulphonation and nitration of benzoic acid is now confirmed, for the acid is not 3-sulpho-2-nitro- (Taverne, *Rec. trav. chim.*, 1906, **25**, 50), but 5-sulpho-3-nitro-benzoic acid. Our confirmation is based on the following considerations.

(1) The nitro-sulphonic acid was reduced to the corresponding amino-acid (Limpricht and Uslar, *loc. cit.*; Zürcher, *Ber.*, 1888, **21**, 180; van Dorssen, *loc. cit.*), and thence converted quantitatively into 5-sulpho-3-hydroxybenzoic acid.

(2) Methylation of the hydroxy-acid, and treatment of the *methyl ether* with phosphorus pentachloride afforded *5-chlorosulphonyl-3-methoxybenzoyl chloride*, which was converted into *5-chlorosulphonyl-3-methoxybenzoic acid* and *5-amidosulphonyl-3-methoxybenzamide*. The former when digested with ammonia, and the latter when hydrolysed with hydrochloric acid, yielded *5-amidosulphonyl-3-methoxybenzoic acid*, identical with the product of oxidation of 3-methoxytoluene-5-sulphonamide. A similar series of reactions was applied to the original nitro-acid, corresponding derivatives being obtained.

(3) 5-Sulpho-3-hydroxybenzoic acid and its methyl ether on fusion with alkali both gave α-resorcylic acid, and thence 3 : 5-dimethoxybenzoic acid was prepared. Further confirmation of orientation was obtained by converting 5-chlorosulphonyl-3-methoxybenzoic acid into 5-methylsulphonyl-3-methoxybenzoic acid (see following paper).

Experimental.

5-Sulpho-3-nitrobenzoic Acid.—Benzoic acid (20 g.) was heated with fuming sulphuric acid (20% SO_3; 50 g.) at 215° for 6 hours and then treated with fuming nitric acid (*d* 1·5; 15 c.c.), the mixture being finally kept at 50° for 1 hour. The mass was poured into water, and the acid isolated as its barium salt (50 g.), which separated in rectangular plates with $4H_2O$ [Found : Ba, 19·5; H_2O, 10·2; equiv., 349·2. Calc. for $(C_7H_4O_7NS)_2Ba,4H_2O$: Ba, 19·6; H_2O, 10·3%; equiv., 350·5] (compare Limpricht and Uslar, *loc. cit.*).

The *sodium hydrogen* salt crystallised in thick rhombic plates (Found : Na, 8·1; H_2O, 3·05; equiv., 279. $C_7H_4O_7NSNa,\frac{1}{2}H_2O$ requires Na, 8·3; H_2O, 3·2%; equiv., 278), and the *potassium hydrogen* salt in plates (Found : K, 12·8; H_2O, 5·6; equiv., 303·3. $C_7H_4O_7NSK,H_2O$ requires K, 12·9; H_2O, 5·9%; equiv., 303·1). The acid separated as monohydrate in needles, m. p. 70°; on desiccation the anhydrous acid, m. p. 152°, was obtained (Found, for hydrated acid : equiv., 133. Calc. for $C_7H_5O_7NS,H_2O$: equiv., 132·5. Found, for anhydrous acid : equiv., 123. Calc. for $C_7H_5O_7NS$: equiv., 123·5). The *ammonium hydrogen* salt crystallised in thick plates (Found : equiv., 263·2. $C_7H_8O_7N_2S$ requires equiv., 264).

5-Chlorosulphonyl-3-nitrobenzoic Acid.—Dry sodium or potassium hydrogen 5-sulpho-3-nitrobenzoate (10 g.) was heated with phosphorus pentachloride (25 g.) on a water-bath for 4 hours. The liquid mass was poured into ice-water, and the insoluble portion washed and dried (8 g.). The *acid chloride* dissolved freely in benzene or toluene, and moderately readily in carbon tetrachloride; it separated in clusters of small prisms, m. p. 64° (Found : S, 10·2; Cl, 24·9. $C_7H_3O_5NCl_2S$ requires S, 10·3; Cl, 25·0%). On hydrolysis by cold water (5 days), it yielded the chlorosulphonyl *acid*, m. p. 170°, which crystallised from benzene in needles (Found : S, 12·0; Cl, 13·25. $C_7H_4O_6NClS$ requires S, 12·1; Cl, 13·3%).

When the chloride was heated with excess of ammonia (*d* 0·88), it afforded *5-amidosulphonyl-3-nitrobenzamide*, slender needles, m. p. 226° (shrinking at 213°) (Found : S, 12·9; N, 17·0. $C_7H_7O_5N_3S$ requires S, 13·1; N, 17·1%), from water.

5-*Amidosulphonyl*-3-*nitrobenzoic Acid.*—(i) 5-Chlorosulphonyl-3-nitrobenzoic acid (1 g.) was boiled with ammonia until the excess was expelled, and the solution acidified; 5-amidosulphonyl-3-nitrobenzoic acid (1 g.), m. p. 230°, resulted. (ii) 5-Amidosulphonyl-3-nitrobenzamide (2 g.) was boiled under reflux with hydrochloric acid (25 c.c.) for 4 hours, and the liquid concentrated and cooled; the same acid (2 g.), m. p. 230°, was obtained. 5-*Amidosulphonyl*-3-*nitrobenzoic acid* was readily soluble in methyl alcohol, ethyl alcohol, acetone, moderately readily soluble in water, and almost insoluble in benzene and toluene; it crystallised in soft shining plates (Found : S, 12·8; equiv., 244·9. $C_7H_6O_6N_2S$ requires S, 13·0%; equiv., 246).

5-*Sulpho*-3-*aminobenzoic Acid.*—An ammoniacal solution of 5-sulpho-3-nitrobenzoic acid (40 g.) in water (160 c.c.) was treated with hydrogen sulphide for 2 hours, and then boiled; after removal of free sulphur, the solution was concentrated, acidified, and cooled. 5-Sulpho-3-aminobenzoic acid, obtained in quantitative yield, crystallised from hot water in needles (Found : S, 14·7; equiv., 110. Calc. for $C_7H_7O_5NS$: S, 14·7%; equiv., 108·5).

5-Amidosulphonyl-3-nitrobenzoic acid when similarly reduced gave 5-*amidosulphonyl*-3-*aminobenzoic acid*, clusters of long needles, m. p. 242° (decomp.) (Found : S, 14·7. $C_7H_8O_4N_2S$ requires S, 14·8%), from water.

5-*Sulpho*-3-*diazobenzoic Acid.*—Into a suspension of finely powdered 5-sulpho-3-aminobenzoic acid (10 g.) in water (50 c.c.), nitrous fumes were passed for 2 hours. A semi-solid mass separated at first but gradually redissolved, yielding the *diazo*-compound in thick square plates or cubes. These were cooled in a freezing mixture, separated, washed with a little alcohol, and dried (9 g.); decomp. 137° (Found : N, 12·1. $C_7H_4O_5N_2S$ requires N, 12·25%).

5-*Sulpho*-3-*hydroxybenzoic Acid.*—The above diazo-compound (10 g.) was boiled with water (400 c.c.) until nitrogen was no longer evolved; evaporation to dryness then gave 5-sulpho-3-hydroxybenzoic acid (9 g.), which crystallised in needles or plates of the dihydrate. This is stable in air and not hygroscopic; when heated, it softens from 70° upwards and does not show a sharp m. p. up to 140° (Found : equiv., 127·5. Calc. for $C_7H_6O_6S,2H_2O$: equiv., 127). Desiccation afforded the *monohydrate* as an opaque white mass, m. p. 142° (shrinking at 135°) (Found : equiv., 118·2. $C_7H_6O_6S,H_2O$ requires equiv., 118).

The normal *potassium* salt was obtained in prisms (Found : K, 22·4; H_2O, 15·3. $C_7H_4O_6SK_2,3H_2O$ requires K, 22·45; H_2O, 15·5%), the *sodium hydrogen* salt as microcrystals (Found, for anhydrous salt : Na, 9·5; equiv., 240·5. $C_7H_5O_6SNa$ requires Na, 9·6%; equiv., 240), and the *potassium hydrogen* salt in prisms or plates (Found : K, 13·7; H_2O, 9·9. $C_7H_5O_6SK,1\frac{1}{2}H_2O$ requires K, 13·8; H_2O, 9·5%). The *ammonium hydrogen* salt was highly crystalline (Found : equiv., 234. $C_7H_9O_6NS$ requires equiv., 235).

5-*Sulpho*-3-*methoxybenzoic Acid.*—The aqueous solution of the above acid (from 10 g. of diazo-compound) was methylated with 25% potassium hydroxide solution (250 c.c.) and methyl sulphate (30 c.c.). The alkaline mixture was heated to hydrolyse the ester formed, neutralised, concentrated, and cooled. The filtrate on acidification gave *potassium hydrogen* 5-*sulpho*-3-*methoxybenzoate* in clusters of needles or plates (Found : K, 13·7; H_2O, 6·1; equiv., 286·4. $C_8H_7O_6SK,H_2O$ requires K, 13·9; H_2O, 6·25%; equiv., 288·1). The *sodium hydrogen* salt separated from water in thick plates (Found, for anhydrous salt : Na, 8·8; equiv., 253·1. $C_8H_7O_6SNa$ requires Na, 9·05%; equiv., 254), and the *barium* salt in microscopic needles (Found : Ba, 37·25. $C_8H_6O_6SBa$ requires Ba, 37·4%). The *sulphonic acid*, obtained either from the barium salt or from 5-chlorosulphonyl-3-methoxybenzoic acid or its chloride (below), separated in long needles, m. p. 125° (Found : S, 12·0; equiv., 133. $C_8H_8O_6S,2H_2O$ requires S, 12·1%; equiv., 134).

5-*Chlorosulphonyl*-3-*methoxybenzoyl Chloride.*—The acid *chloride* (8 g.) was obtained from anhydrous potassium hydrogen 5-sulpho-3-methoxybenzoate (10 g.) by treatment with phosphorus pentachloride (30 g.); it dissolved freely in benzene or toluene, and moderately readily in carbon tetrachloride, crystallising in rhombohedra, m. p. 51·5° (Found : S, 11·8; Cl, 26·2. $C_8H_6O_4Cl_2S$ requires S, 11·9; Cl, 26·4%). It was converted on treatment with ammonia into 5-*amidosulphonyl*-3-*methoxybenzamide*, which separated from water in prismatic plates, m. p. 184° (Found : S, 13·8; N, 12·0. $C_8H_{10}O_4N_2S$ requires S, 13·9; N, 12·2%).

5-*Chlorosulphonyl*-3-*methoxybenzoic acid* was obtained (2·5 g.) by leaving its acid chloride (10 g.) in contact with water (500 c.c.) for 16 days; it crystallised from benzene and toluene in rectangular plates, m. p. 160° (Found : S, 12·55; Cl, 13·9. $C_8H_7O_5ClS$ requires S, 12·8; Cl, 14·2%).

5-*Amidosulphonyl*-3-*methoxybenzoic acid* was prepared in three ways : (i) 5-Chlorosulphonyl-3-methoxybenzoic acid (2 g.) was heated with ammonia, and the solution on acidification gave the required acid, m. p. 214°. (ii) 5-Amidosulphonyl-3-methoxybenzamide (2 g.) was boiled under reflux with hydrochloric acid (30 c.c.) for 6 hours; the solid that separated on cooling had m. p. 214°. (iii) 3-Methoxytoluene-5-sulphonamide, m. p. 119°, obtained from 3-methoxytoluene-5-sulphinic acid *via* 3-methoxytoluene-5-sulphonic acid and -5-sulphonyl chloride by Haworth and Lapworth's method (J., 1923, **123**, 2991), was oxidised with potassium permanganate, and the filtered liquid concentrated and acidified with hydrochloric acid. The product was identical (mixed m. p.) with those obtained in (i) and (ii).

The acid was readily soluble in methyl alcohol, ethyl alcohol, and acetone, moderately readily soluble in hot water, and almost insoluble in benzene and toluene. It crystallised in needles [Found: S, 13·6; equiv. (addition of excess of NaOH, and back titration), 114·8. $C_8H_9O_5NS$ requires S, 13·85%; equiv. (for hydrolysis of $\cdot SO_2\cdot NH_2$ group also), 115·5].

Fusion of 5-*Sulpho*-3-*hydroxybenzoic Acid and of its Methyl Ether with Alkali.*—Finely powdered potassium 5-sulpho-3-hydroxybenzoate or -3-methoxybenzoate (5 g.) was added to fused potassium hydroxide (70 g.) in a nickel crucible at 220°, and the mass well stirred. Considerable frothing occurred when the temperature was raised, and the liquid became clear at 290°, at which it was kept for 15 minutes. The fused mass was cooled, dissolved in water, neutralised, filtered, acidified, and extracted with ether. The extract left a residue of α-resorcylic (3 : 5-dihydroxybenzoic) acid, which crystallised in prisms with $1\frac{1}{2}H_2O$, m. p. 233° (3 g.) (Found: loss at 120°, 14·8. Calc. for $C_7H_6O_4,1\frac{1}{2}H_2O$: $1\frac{1}{2}H_2O$, 14·9%) (compare Bottinger, *Ber.*, 1875, **8**, 374).

The dihydroxybenzoic acid, on methylation with methyl sulphate, passed into 3 : 5-dimethoxybenzoic acid, m. p. 176°, which crystallised from alcohol in needles or plates (compare Tiemann and Streng, *Ber.*, 1881, **14**, 2003) (Found: equiv., 181·8. Calc. for $C_9H_{10}O_4$: equiv., 182).

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