321. *Thiols derived from* o-, m-, *and* p-*Methoxy-toluenes and -benzoic Acids.*

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The present work was undertaken primarily because a knowledge of these substances and their derivatives was required in elucidating the constitutions of certain substituted benzenesulphonic acids.

Thiolmethoxytoluenes.—Of the ten isomeric mercaptans, three are known, *viz.*, 3-thiol-4-methoxy- (Gattermann, *Ber.*, 1899, **32**, 1149), 4-thiol-3-methoxy- (Shah, J., 1930, 1300), and 5-thiol-2-methoxy-toluene (Kolhatkar and Bokil, *J. Indian Chem. Soc.*, 1930, **7**, 849).

(A) The first and third of the above thiols and also the new 2-thiol-5-methoxytoluene have now been prepared by reduction of the corresponding sulphonyl chlorides, which were derived from the acids obtained by sulphonating the appropriate tolyl methyl ether.

(B) The sulphonic acids corresponding to 4-*thiol*-2-*methoxy*- and 2-*thiol*-4-*methoxytoluene* could not be prepared by direct sulphonation as in (A), but were obtained from *o*-nitrotoluene-4- and *p*-nitrotoluene-2-sulphonic acid *via* the toluidine- and cresol-sulphonic acids.

(C) The remaining thiols, *viz.*, 3- and 6-*thiol*-2-*methoxytoluene* and 2- and 5-*thiol*-3-*methoxytoluene* were derived from the corresponding nitromethoxytoluenes, which, with one exception, were obtained by methylating nitrocresols in xylene solution (Haworth and Lapworth, J., 1923, **123**, 2986); 6-nitro-2-methoxytoluene, however, was prepared from 3-nitro-2-methoxytoluene according to Simonsen and Nayak's method (J., 1915, **107**, 830). The nitromethoxytoluenes were reduced to the amino-compounds, and these were diazotised and converted by Gattermann's method (*loc. cit.*) into the corresponding sulphinic acids, which were reduced with tin and hydrochloric acid.

All the methoxytolyl mercaptans passed on methylation into the corresponding methylthiols, from which oxidation with alkaline permanganate afforded the methylsulphones; 6-methylthiol-2-methoxytoluene, however, underwent more extensive oxidation and failed to yield the methylsulphone.

Thiolmethoxybenzoic Acids.—The sulphomethoxybenzoic acids required as initial material for the preparation of these acids were prepared, when possible, by (*a*) sulphonation of methoxybenzoic acids, (*b*) methylation of sulphohydroxybenzoic acids, or (*c*) oxidation of methoxytoluenesulphonic acids.

(*a*) 2- and 4-Methoxybenzoic acids yielded on sulphonation 5-sulpho-2-methoxy- and 3-sulpho-4-methoxy-benzoic acid, as described by Meldrum and Shah (J., 1923, **123**, 1992) and Zervas (*Annalen*, 1857, **103**, 338) respectively.

(*b*) 5-Sulphosalicylic acid (Meldrum and Shah, *loc. cit.*), 4-sulphosalicylic acid (Hirwe and Jambhekar, *J. Indian Chem. Soc.*, 1933, **10**, 47), and 5-sulpho-3-hydroxybenzoic acid (see preceding paper) were methylated, and the sulphomethoxybenzoic acids, together with those described in (*a*), were identified with the products obtained on oxidation of the corresponding methoxytoluenesulphonic acids.

(*c*) 2-Sulpho-5- and 2-sulpho-4-methoxybenzoic acid were obtained on oxidation of 5-methoxytoluene-2-sulphonic acid and 4-methoxytoluene-2-sulphonic acid as described by Haworth and Lapworth (J., 1924, **125**, 1299) and Parks (*Amer. Chem. J.*, 1893, **15**, 320) respectively. 3-Methoxytoluene-2-sulphonic acid suffered too extensive oxidation, so the corresponding 2-thiol-3-methoxybenzoic acid is being obtained by other means.

Neither 6- nor 3-sulpho-2-methoxybenzoic acid could be synthesised, but other attempts are being made to prepare the corresponding thiol-2-methoxybenzoic acids.

All sulphomethoxybenzoic acids, except those having the SO_3H group in the vicinal position, on trituration with phosphorus pentachloride, afforded the corresponding chlorosulphonylmethoxybenzoyl chlorides. These were treated with water at room temperature with a view to obtain chlorosulphonylmethoxybenzoic acids; the results, however, showed that (1) 4- and 5-chlorosulphonyl-2-methoxybenzoyl chlorides, *i.e.*, the derivatives of salicylic acid, are completely hydrolysed within ½ hour; (2) with 5-chlorosulphonyl-3- and 3-*chlorosulphonyl-4-methoxybenzoyl chloride*, hydrolysis required 16 and 8 days respectively; (3) 2-chlorosulphonyl-5- and -4-methoxybenzoyl chloride are very resistant, but after more than a month, they were completely hydrolysed, both the SO_2Cl and the COCl group being affected.

The chlorosulphonylmethoxybenzoic acids described in (1) and (2) were reduced by Gattermann's method (*loc. cit.*) to the corresponding thiolmethoxybenzoic acids. These were successively methylated and oxidised, the resulting *methylsulphones* being identical with those derived from methoxytolylmercaptans.

EXPERIMENTAL.

In order to avoid repetition, three general methods adopted in the present work are first described.

Methylation.—(1) The nitrocresol (25 g.) was heated with xylene (125 c.c.) and anhydrous (fused) potassium carbonate (40 g.) under reflux, and methyl sulphate (30 g.) gradually added (compare Haworth and Lapworth, *loc. cit.*). After cooling, a 2% solution of sodium hydroxide was added to dissolve unchanged nitrocresol, and the xylene removed by distillation in steam.

(2) Cresolsulphonic acids, thiolmethoxy-toluenes and -benzoic acids were methylated with methyl sulphate (1 mol.) and 25% sodium hydroxide solution until a neutralised sample developed no coloration with ferric chloride. The solution was then neutralised, and (i) sodium salts of sulphonic acids were separated by fractional crystallisation, (ii) the methylthiolmethoxytoluenes extracted with ether, or (iii) the substituted benzoic acids precipitated by hydrochloric acid.

Conversion of Methoxytoluenesulphinic Acids, Chlorosulphonylmethoxy-toluenes and -benzoic Acids into the Corresponding Thiols.—This was accomplished essentially by Gattermann's method (*loc. cit.*), reduction of 10 g. of material by means of tin (30 g.) and hydrochloric acid (100 c.c.) being carried out first at room temperature for an hour, and then under reflux for 2 hours. The thiolmethoxytoluenes were isolated by distillation with steam and extraction with ether, but the thiolmethoxybenzoic acids separated on cooling, and were collected, washed, dried, and purified by repeated dissolution in sodium hydroxide and precipitation with hydrochloric acid.

From the thiolmethoxytoluenes, the mercury and lead mercaptides were prepared in alcoholic solution by treatment with mercuric chloride and lead acetate respectively; the benzoyl derivatives were prepared by the Schotten–Baumann method, and the disulphides by shaking an alkaline solution of the thiol with a solution of iodine in potassium iodide, both types of derivative being recrystallised from alcohol.

Conversion of Methylthiolmethoxy-toluenes and -benzoic Acids into Methylsulphonylmethoxy-benzoic Acids.—This was carried out by heating the methylthiol (5 g.) with a slight excess of 5% potassium permanganate solution in presence of a little potassium carbonate. After oxidation was complete (8—10 hours), excess permanganate was destroyed by addition of alcohol, manganese dioxide was removed, and the filtrate concentrated to small bulk and acidified; the required methylsulphone separated in a crystalline state. All methylsulphones were readily soluble in alcohol or acetone, moderately soluble in hot water, and almost insoluble in benzene, toluene, chloroform, or carbon tetrachloride.

Derivatives of o-*Methoxytoluene and* o-*Methoxybenzoic Acid.*

3-*Thiol*-2-*methoxytoluene.*—3-Nitro-*o*-cresol (20 g.; m. p. 69°) (Hofmann and Miller, *Ber.*, 1881, **14**, 568) was methylated by the procedure described above, and the methyl ether (20 g.) extracted by ether after removal of xylene; it distilled at 225°, and solidified in plates, m. p. 24°. On oxidation by permanganate, a sample afforded 3-nitro-2-methoxybenzoic acid, m. p. and mixed m. p. 196° (Simonsen and Rau, J., 1917, **111**, 220; Meldrum and Shah, *J. Indian Chem. Soc.*, 1931, **8**, 575).

3-*Amino*-2-*methoxytoluene.* The above methyl ether (45 g.) was heated with stannous chloride (200 g.) and hydrochloric acid (300 c.c.) under reflux for 3 hours; the mixture was cooled, basified, and distilled in steam. The ethereal extract of the distillate yielded 3-amino-2-methoxytoluene as a colourless oil, b. p. 253°; its acetyl derivative, m. p. 101°, was identical with that described by Simonsen and Nayak (*loc. cit.*). The benzoyl derivative crystallised from alcohol in long needles, m. p. 120°.

2-*Methoxytoluene*-3-*sulphinic acid.* The above amine (10 g.), in sulphuric acid (30 g.) and water (100 c.c.) at − 10°, was diazotised by sodium nitrite (5·25 g.) in water (25 c.c.); after an hour, a cooled mixture of sulphuric acid (40 g.) and water (40 c.c.) was added, and the solution saturated with sulphur dioxide for 2 hours, dry copper powder (15 g.; previously washed with alcohol and ether) being added in small portions with constant stirring, and the temperature being kept below 0°. After 12 hours, the mixture was extracted several times with ether, and the extract afforded the required acid (9 g.), as a thick yellow liquid.

2-*Methoxytoluene*-3-*sulphonyl chloride.* The foregoing acid (9 g.) was oxidised with 1% barium permanganate solution on a water-bath. Unchanged permanganate was destroyed by alcohol, manganese dioxide removed, and the solution treated with potassium carbonate. Potassium 2-methoxytoluene-3-sulphonate was collected, dried, and heated with phosphorus pentachloride (25 g.) for 2 hours. The mass, on treatment with ice, gave 2-*methoxytoluene*-3-*sulphonyl chloride* as an oil (7 g.) (Found: Cl, 16·0. $C_8H_9O_3SCl$ requires Cl, 16·1%). 2-*Methoxytoluene*-3-*sulphonamide* crystallised from hot water in needles, m. p. 143—144° (Found: S, 15·8. $C_8H_{11}O_3SN$ requires S, 15·9%).

3-*Thiol*-2-*methoxytoluene.* Reduction of the foregoing sulphinic acid or sulphonyl chloride according to the general procedure (p. 1376) afforded 3-thiol-2-methoxytoluene, b. p. 235—236°, which had a disagreeable odour and was soluble in alcohol and other organic solvents; it gave a white mercury mercaptide and a deep yellow *lead* mercaptide [Found: Pb, 39·9. $(C_8H_9OS)_2Pb$ requires Pb, 40·4%]; its *benzoyl* derivative crystallised in leaflets, m. p. 47° (Found: S, 12·1. $C_{15}H_{14}O_2S$ requires S, 12·4%). The disulphide separated as an oil. On methylation, it was converted into 3-*methylthiol*-2-*methoxytoluene*, b. p. 254° (Found: S, 18·9. $C_9H_{12}OS$ requires S, 19·0%), which had a fruity odour. The latter compound was oxidised to 3-*methylsulphonyl*-2-*methoxybenzoic acid*, prismatic plates, m. p. 166° (Found: S, 13·8; equiv., 229·4. $C_9H_{10}O_5S$ requires S, 13·9%; equiv., 230), from water.

4-*Thiol*-2-*methoxytoluene.*—*o*-Nitrotoluene-4-sulphonic acid (Beilstein and Kuhlberg, *Annalen*, 1870, **155**, 27; Bek, *Z. Chem.*, 1869, 210) [*barium* salt, rhombic plates (Found: Ba, 22·6; H_2O, 5·2. $C_{14}H_{12}O_{10}N_2S_2Ba,2H_2O$ requires Ba, 22·7; H_2O, 5·9%); *potassium* salt, needles (Found: K, 15·1. $C_7H_6O_5NSK$ requires K, 15·3%)] was reduced by aqueous ammonium sulphide to *o*-toluidine-4-sulphonic acid (Beilstein and Kuhlberg; Bek, *locc. cit.*), which was diazotised with nitrous fumes, the *diazo*-compound (decomp. 104°), being precipitated by alcohol at 0° (Found: N, 14·15. $C_7H_6O_3N_2S$ requires N, 14·1%). Decomposition of the latter with boiling water gave *o*-cresol-4-sulphonic acid (Engelhardt and Latschinow, *Z. Chem.*, 1869, 621; Hantke, *Ber.*, 1887, **20**, 3210; Hayduck, *Annalen*, 1874, **172**, 214; **1874**, **174**, 345); *barium* salt, small prisms [Found: Ba, 24·95; H_2O, 6·4. $(C_7H_7O_4S)_2Ba,2H_2O$ requires Ba, 25·1; H_2O, 6·6%].

2-*Methoxytoluene*-4-*sulphonic acid.* Methylation of the above cresolsulphonic acid gave the *sodium* salt of this acid (Found: Na, 9·4; H_2O, 7·7. $C_8H_9O_4SNa,H_2O$ requires Na, 9·5; H_2O, 7·4%). The *barium* salt was obtained in fine plates [Found: Ba, 23·9; H_2O, 4·9. $(C_8H_9O_4S)_2Ba,1\frac{1}{2}H_2O$ requires Ba, 24·3; H_2O, 4·8%]. The sulphonic acid, prepared from the latter, could not be induced to crystallise and was evidently different from 2-methoxytoluene-5-sulphonic acid (Meldrum and Shah, *loc. cit.*).

2-*Methoxytoluene*-4-*sulphonyl chloride.* Dry sodium 2-methoxytoluene-4-sulphonate (10 g.) was treated with phosphorus pentachloride (25 g.) as for the 3-sulphonate (above), and the resulting oil extracted with ether and dried (Found: Cl, 16·0. $C_8H_9O_3ClS$ requires Cl, 16·1%). It gave on treatment with ammonia 2-*methoxytoluene*-4-*sulphonamide*, which crystallised from alcohol in prismatic plates, m. p. 123° (Found: S, 15·8. $C_8H_{11}O_3NS$ requires S, 15·9%). On reducing the above sulphonyl chloride, 4-*thiol*-2-*methoxytoluene* was obtained as an oil with a disagreeable smell, b. p. 238—239° (Found: S, 20·7. $C_8H_{10}OS$ requires S, 20·8%). It formed a white mercury mercaptide and a yellow *lead* mercaptide [Found: Pb, 40·2. $(C_8H_9OS)_2Pb$ requires Pb, 40·4%]. The benzoyl derivative and the disulphide were oils.

4-*Methylthiol*-2-*methoxytoluene*, obtained on methylating the above thiol, had an aromatic odour and boiled at 255—256° (Found: S, 18·9. $C_9H_{12}OS$ requires S, 19·0%); when oxidised with permanganate, it afforded 4-*methylsulphonyl*-2-*methoxybenzoic acid*, which crystallised from water in small needles, m. p. 151° (Found: S, 13·8; equiv., 228·9. $C_9H_{10}O_5S$ requires S, 13·9%; equiv., 230).

4-*Thiol*-2-*methoxybenzoic Acid.*—4-*Sulpho*-2-*methoxybenzoic acid.* 4-Sulphosalicylic acid (10 g.; Hirwe and Jambhekar, *loc. cit.*) was methylated with methyl sulphate (30 c.c.) and 25% sodium hydroxide solution (300 c.c.), and the alkaline mixture heated to hydrolyse the ester formed. 4-*Sulpho*-2-*methoxybenzoic acid* was recovered in the usual way as sodium hydrogen salt, from which the normal *barium* salt was prepared as microcrystalline needles (Found: Ba, 37·7. $C_8H_6O_6SBa$ requires Ba, 37·2%). The acid obtained therefrom crystallised in deliquescent needles, m. p. 152° (Found: equiv., 125·4. $C_8H_8O_6S,H_2O$ requires equiv., 125).

4-*Chlorosulphonyl*-2-*methoxybenzoic acid.* This *acid*, prepared from the above sodium salt as for the corresponding toluene derivative, crystallised from benzene or toluene in rhombohedra, m. p. 149·5° (Found: Cl, 13·9. $C_8H_7O_5ClS$ requires Cl, 14·2%); it gave on treatment with ammonia 4-*amidosulphonyl*-2-*methoxybenzoic acid*, crystallising in woolly needles, m. p. 201°, identical (mixed m. p.) with the substance produced when 2-methoxytoluene-4-sulphonamide was oxidised with permanganate (Found: S, 13·72; equiv., 232·7. $C_8H_9O_5NS$ requires S, 13·85%; equiv., 231).

Reduction of the foregoing chlorosulphonyl acid (5 g.) afforded 3 g. of 4-*thiol*-2-*methoxybenzoic acid*, as thin plates, m. p. 95° (Found: S, 17·2. $C_8H_8O_3S$ requires S, 17·4%), readily soluble in organic solvents, but difficultly soluble in water. The disulphide could not be prepared by the method described on p. 1380.

4-*Methylthiol*-2-*methoxybenzoic acid* crystallised from alcohol in glossy needles, m. p. 112° (Found: S, 16·1; equiv., 197·8. $C_9H_{10}O_3S$ requires S, 16·2%; equiv., 198), and was oxidised to 4-methylsulphonyl-2-methoxybenzoic acid, m. p. 151° (Found: S, 13·8%), identical (mixed m. p.) with that derived from 4-thiol-2-methoxytoluene.

5-*Thiol*-2-*methoxytoluene.*—2-Methoxytoluene-5-sulphonic acid (Meldrum and Shah, *loc. cit.*) was converted into the sulphonyl chloride, and thence into amidosulphonyl-2-methoxytoluene, m. p. 137°. 5-Thiol-2-methoxytoluene, obtained by reducing the sulphonyl chloride, distilled at 234—235° and solidified to yellow plates, m. p. 40° (Kolhatkar and Bokil, *loc. cit.*, give 38°). The *benzoyl* derivative separated in prismatic plates, m. p. 80° (Found: S, 12·2. $C_{15}H_{14}O_2S$ requires S, 12·4%).

5-*Methylthiol*-2-*methoxytoluene*, prepared by methylating the above mercaptan, was a colourless oil with a fruity smell; b. p. 259° (Found: S, 18·9. $C_9H_{12}OS$ requires S, 19·0%). On oxidation, it afforded 5-*methylsulphonyl*-2-*methoxybenzoic acid*, shining needles, m. p. 190° (Found: S, 13·6; equiv., 232·1. $C_9H_{10}O_5S$ requires S, 13·9%; equiv., 230).

5-*Thiol*-2-*methoxybenzoic Acid.*—5-Sulpho-2-methoxybenzoic acid was converted into 5-chlorosulphonyl-2-methoxybenzoic acid, m. p. 148·5° (Meldrum and Shah, *loc. cit.*), which was reduced to 5-*thiol*-2-*methoxybenzoic acid*, flocculent woolly needles, m. p. 205° (Found: S, 17·2. $C_8H_8O_3S$ requires S, 17·4%). The disulphide could not be prepared.

5-*Methylthiol*-2-*methoxybenzoic acid* crystallised from alcohol in prismatic needles, m. p. 75° (Found: S, 16·0; equiv., 197·4. $C_9H_{10}O_3S$ requires S, 16·2%; equiv., 198); and the sulphone obtained therefrom, m. p. 190°, was identical (mixed m. p.) with the product of oxidation of the corresponding toluene (above) (Found: equiv., 228·8).

6-*Thiol-2-methoxytoluene.*—Considerable difficulty was experienced in the preparation of this thiol. 2-Nitrotoluene-6-sulphonic acid was synthesised from 4-nitrotoluene-2-sulphonic acid by nitration with fuming nitric acid, followed by partial reduction with aqueous ammonium sulphide and replacement of the amino-group by hydrogen (Cohen and McCandlish, J., 1905, **87**, 1270), but it could not be converted into the above thiol. Finally, the mercaptan was prepared from 6-nitro-2-methoxytoluene as follows. 3-Acetamido-2-methoxytoluene was nitrated and 6-nitro-3-amino-2-methoxytoluene, m. p. 103°, isolated according to the method of Simonsen and Nayak (*loc. cit.*). The amino-group was removed by the method described below; decomposition proceeded cleanly and the yield of 6-nitro-2-methoxytoluene, m. p. 52°, was better than that described by Simonsen and Nayak. Reduction then afforded 6-amino-2-methoxytoluene, which was converted into 2-methoxytoluene-6-sulphinic acid, and by oxidation of this acid with 1% barium permanganate, followed by treatment with potassium carbonate, *potassium* 2-*methoxytoluene*-6-*sulphonate* was prepared; thin plates (Found: K, 15·0; H_2O, 6·8. $C_8H_9O_4SK,H_2O$ requires K, 15·2; H_2O, 6·9%). Thence were obtained the *sulphonyl chloride* (Found: Cl, 15·8. $C_8H_9O_3ClS$ requires Cl, 16·1%), an oil, and 2-*methoxytoluene*-6-*sulphonamide*, long needles, m. p. 164° (Found: S, 16·1. $C_8H_{11}O_3NS$ requires S, 15·9%).

The above sulphinic acid was reduced to 6-*thiol*-2-*methoxytoluene*, b. p. 238°, which possessed the mercaptanic smell (Found: S, 20·6. $C_8H_{10}OS$ requires S, 20·8%). The benzoyl derivative crystallised in plates, m. p. 62°, and the disulphide was microcrystalline, m. p. 80°. It gave a white mercury mercaptide and a canary-yellow lead mercaptide.

On methylation the above mercaptan passed into 6-*methylthiol*-2-*methoxytoluene*, b. p. 256°, possessing a pleasant aromatic smell (Found: S, 18·8. $C_9H_{12}OS$ requires S, 19·0%), but this could not be oxidised to the sulphone.

Derivatives of m-*Methoxytoluene and* m-*Methoxybenzoic Acid.*

2-*Thiol*-3-*methoxytoluene.*—The methylation of 2-nitro-*m*-cresol (m. p. 41°; Gibson, J., 1923, **123**, 1269) and the conversion of the methyl ether, m. p. 49°, into 3-methoxytoluene-2-sulphinic acid, m. p. 94·5°, *via* 2-amino-*m*-tolyl methyl ether, m. p. 32°, were carried out according to Haworth and Lapworth's method (*loc. cit.*). In methylation, however, the distillation of xylene in a vacuum was not necessary, as the marked fall in the yield of nitro-methyl ether noted by these workers was not observed.

The sulphinic acid on reduction passed into 2-*thiol*-3-*methoxytoluene*, b. p. 256—257° (Found: S, 20·7. $C_8H_{10}OS$ requires S, 20·8%); the benzoyl derivative was an oil, but the *disulphide* crystallised in plates, m. p. 148° (Found: S, 20·8. $C_{16}H_{18}O_2S_2$ requires S, 20·9%).

2-*Methylthiol*-3-*methoxytoluene* was obtained from the above mercaptan on methylation in the usual way; it had a fruity odour and boiled at 269—270° (Found: S, 18·9. $C_9H_{12}OS$ requires S, 19·0%). Oxidation of this compound gave 2-*methylsulphonyl*-3-*methoxybenzoic acid*, m. p. 212°, which was more soluble than other sulphones described in this paper and crystallised in clusters of needles (Found: S, 13·8; equiv., 229. $C_9H_{10}O_5S$ requires S, 13·9%; equiv., 230).

5-*Thiol*-3-*methoxytoluene.*—3-Methoxytoluene-5-sulphinic acid was prepared essentially as described by Haworth and Lapworth (*loc. cit.*), but for the synthesis of 5-nitro-*m*-toluidine we followed the procedure of Brady, Day, and Rolt (J., 1922, **121**, 529). Further, for the replacement of the amino-group by hydrogen in 3 : 5-dinitro-*p*-toluidine, we modified Cohen and McCandlish's method as follows: a solution of 3 : 5-dinitro-*p*-toluidine (10 g.) in absolute alcohol (200 c.c.) was treated with sulphuric acid (50 c.c.), cooled, and diazotised at 0° by gradual addition of sodium nitrite (30 g.); the mixture was kept at 0° for 1 hour and then heated under reflux for 2 hours. Alcohol was then distilled over, and the concentrated mixture diluted with water; 3 : 5-dinitrotoluene, m. p. 92°, separated cleanly and free from tar.

5-*Thiol*-3-*methoxytoluene* was obtained from the above sulphinic acid by Gattermann's method; it was an oil of unpleasant thiophenolic odour, b. p. 251—252° (Found: S, 20·6. $C_8H_{10}OS$ requires S, 20·8%). It gave a white mercury mercaptide and a lemon-yellow lead mercaptide. The benzoyl derivative and the disulphide were also oils.

5-*Methylthiol*-3-*methoxytoluene*, b. p. 263°, was prepared in the usual manner; it had a fruity odour (Found: S, 19·0. $C_9H_{12}OS$ requires S, 19·0%). 5-*Methylsulphonyl*-3-*methoxybenzoic acid* crystallised in long needles, m. p. 195° (Found: S, 13·9; equiv., 229·4. $C_9H_{10}O_5S$ requires S, 13·9%; equiv., 230).

5-*Thiol*-3-*methoxybenzoic Acid.*—Reduction of 5-chlorosulphonyl-3-methoxybenzoic acid (preceding paper) afforded this *acid*, which formed microcrystals from alcohol, m. p. 162° (Found: S, 17·3. $C_8H_8O_3S$ requires S, 17·4%).

3-*Methoxybenzoic acid*-5-*disulphide.* A cold alcoholic solution of 5-chlorosulphonyl-3-methoxybenzoic acid (1 g.) was treated with zinc dust (1·5 g.) and hydrochloric acid (10 c.c.). The excess of zinc was removed, and the filtrate digested with solid ferric chloride in presence of hydrochloric acid. After one hour the *disulphide*, which separated on dilution with water, was filtered off, washed, dissolved in aqueous sodium carbonate solution, and precipitated with hydrochloric acid. It was obtained from alcohol as a fine white powder (0·9 g.), m. p. 228° (Found : S, 17·3; equiv., 183·1. $C_{16}H_{14}O_6S_2$ requires S, 17·5%; equiv., 183).

5-*Methylthiol*-3-*methoxybenzoic acid.* On methylating the above thiol-acid the *methylthiol* was obtained as a flocculent mass which crystallised from all organic solvents except chloroform and carbon tetrachloride in thin glossy plates, m. p. 155° (Found : S, 16·0; equiv., 196·6. $C_9H_{10}O_3S$ requires S, 16·2%; equiv., 198). It yielded on oxidation 5-methylsulphonyl-3-methoxybenzoic acid, needles, m. p. 195°, identical with that obtained from 5-thiol-3-methoxytoluene (Found : S, 13·87%).

2-*Thiol*-5-*methoxytoluene.*—Reduction of 5-methoxytoluene-2-sulphonyl chloride gave 2-thiol-5-methoxytoluene, b. p. 253—254°. The mercury and the lead salt were orange and white respectively. The disulphide was an oil, and the *benzoyl* derivative was obtained in needles, m. p. 84° (Found : S, 12·3. $C_{15}H_{14}O_2S$ requires S, 12·4%).

6-*Methylthiol*-3-*methoxytoluene* was obtained as a colourless, pleasant-smelling oil, b. p. 272° (Found : S, 19·0. $C_9H_{12}OS$ requires S, 19·0%); on oxidation it was converted into 6-*methylsulphonyl*-3-*methoxybenzoic acid,* rectangular plates, m. p. 180° (Found : S, 13·8; equiv., 229·0. $C_9H_{10}O_5S$ requires S, 13·9%; equiv., 230).

Derivatives of p-*Methoxytoluene and* p-*Methoxybenzoic Acid.*

2-*Thiol*-4-*methoxytoluene.*—4-Nitrotoluene-2-sulphonic acid (Beilstein and Kuhlberg, *loc. cit.*) was reduced to the amino-acid, which was converted *via* the diazo-compound (Jenssen, *Annalen*, 1874, **172**, 230; Remsen and Darshiell, *Amer. Chem. J.*, 1893, **15**, 108; Parks, *ibid.*, p. 320) into *p*-cresol-2-sulphonic acid, and thence into 4-methoxytoluene-2-sulphonic acid (Parks, *loc. cit.*). The sulphonyl chloride separated as a yellow oil, and the sulphonamide crystallised in prisms, m. p. 151°.

Reduction of the sulphonyl chloride gave 2-*thiol*-4-*methoxytoluene* as an oil, b. p. 253—254°, with the usual disagreeable smell (Found : S, 20·7. $C_8H_{10}OS$ requires S, 20·8%). It gave a lemon-yellow mercury mercaptide and a carmine-yellow lead salt. Its benzoyl derivative and the disulphide were syrups.

2-*Methylthiol*-4-*methoxytoluene* had b. p. 260—261° (Found : S, 19·0. $C_9H_{12}OS$ requires S, 19·0%), and 2-*methylsulphonyl*-4-*methoxybenzoic acid* crystallised in long needles, m. p. 180° (Found : S, 13·8; equiv., 230·6. $C_9H_{10}O_5S$ requires S, 13·9%; equiv., 230).

3-*Thiol*-4-*methoxytoluene.*—4-Methoxytoluene-3-sulphonic acid (Allemann, *Amer. Chem. J.*, 1904, **31**, 24), obtained by sulphonating *p*-tolyl methyl ether with 100% sulphuric acid or chlorosulphonic acid at 0—10°, was converted into the sulphonyl chloride and thence into 3-thiol-4-methoxytoluene, b. p. 252—253° (m. p. 36—37°); *benzoyl* derivative, prisms, m. p. 75° (Found : S, 12·1. $C_{15}H_{14}O_2S$ requires S, 12·4%); disulphide, microscopic needles, m. p. 74°. On methylation it was converted into 3-methylthiol-4-methoxytoluene, b. p. 262°. The thiol, disulphide and methylthiol are identical with those described by Gattermann (*loc. cit.*).

3-*Methylsulphonyl*-4-*methoxybenzoic acid,* produced in the usual way, crystallised in small needles, m. p. 215° (Found : S, 13·9. $C_9H_{10}O_5S$ requires S, 13·9%).

3-*Thiol*-4-*methoxybenzoic Acid.*—3-*Sulpho*-4-*methoxybenzoic* acid was prepared as its *potassium hydrogen* salt (Found : K, 12·8; H_2O, 11·7; equiv., 308·1. $C_8H_7O_6SK,2H_2O$ requires K, 12·7; H_2O, 11·8%; equiv., 306·1) by sulphonating anisic acid (Zervas, *loc. cit.*) and converting the resulting acid into the *barium* salt (plates) (Found : Ba, 34·3; H_2O, 8·9. $C_8H_6O_6SBa,2H_2O$ requires Ba, 34·1; H_2O, 9·3%) or by oxidising 4-methoxytoluene-3-sulphonic acid and proceeding as before. The acid was microcrystalline, m. p. 250—251° (Found : equiv., 133. $C_8H_8O_6S,2H_2O$ requires equiv., 134). Fusion of the potassium salt with potassium hydroxide yielded protocatechuic acid, m. p. 199°.

3-*Chlorosulphonyl*-4-*methoxybenzoyl chloride,* prepared as usual, crystallised from benzene or toluene in rhombic plates, m. p. 70° (Found : Cl, 26·3. $C_8H_6O_4Cl_2S$ requires Cl, 26·4%). 3-*Amidosulphonyl*-4-*methoxybenzamide* crystallised in needles, m. p. 262° (Found : S, 13·8. $C_8H_{10}O_4SN_2$ requires S, 13·9%).

3-*Chlorosulphonyl*-4-*methoxybenzoic acid.* The above chlorosulphonylmethoxybenzoyl chloride (3 g.) was shaken with water (200 c.c.) at room temperature. After 8 days the partial hydrolysis was complete, and the residue consisted solely of 3-*chlorosulphonyl*-4-*methoxybenzoic* *acid*, m. p. 178°. It crystallised from toluene in square plates (1·2 g.) (Found : Cl, 14·1. $C_8H_7O_5SCl$ requires Cl, 14·2%).

3-Amidosulphonyl-4-methoxybenzoic acid was prepared in three ways : (1) 3-Chlorosulphonyl-4-methoxybenzoic acid was heated with ammonia, and the solution acidified; (2) 3-amidosulphonyl-4-methoxybenzamide was boiled under reflux with hydrochloric acid for 2 days; (3) 4-methoxytoluene-3-sulphonamide, prepared from 3-chlorosulphonyl-4-methoxytoluene, was oxidised with potassium permanganate, and the filtered liquid was concentrated and acidified with hydrochloric acid. The three products were identical and crystallised in needles, m. p. 288° (Found : S, 13·8. Calc. : S, 13·8%) (compare Metcalf, *Amer. Chem. J.*, 1893, **15**, 301; Allemann, *loc. cit.*, p. 24).

3-*Thiol*-4-*methoxybenzoic acid*, obtained by reduction of the foregoing acid, was amorphous, m. p. 317° (decomp.) (Found : S, 17·3. $C_8H_8O_3S$ requires S, 17·4%). 3-*Methylthiol*-4-*methoxybenzoic acid* crystallised from alcohol in thin plates, m. p. 205° (Found : S, 16·1; equiv., 198. $C_9H_{10}O_3S$ requires S, 16·2%; equiv., 198). 3-Methylsulphonyl-4-methoxybenzoic acid, m. p. 215°, was identical with that derived from 3-thiol-4-methoxytoluene (Found : S, 13·85%).

2-Chlorosulphonyl-5-methoxy- and 2-chlorosulphonyl-4-methoxy-benzoyl chlorides were identified by conversion into the corresponding 3- and 4-methoxy-*o*-benzoic sulphinimides, m. p. 237° and 271° respectively (Haworth and Lapworth, *loc. cit.*; Parks, *loc. cit.*). Moreover, the potassium salt of 2-sulpho-4-methoxybenzoic acid when fused with alkali yielded β-resorcylic acid, m. p. 213°.

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