LI.—*Studies in the Naphthalene Series. Part IV. The Preparation and Properties of 2-Naphthol-3-sulphonic Acid.*

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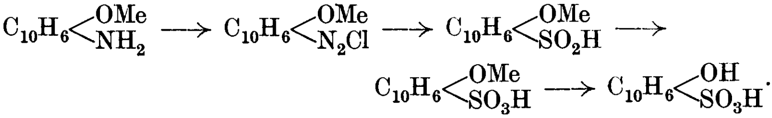
IN continuation of the investigation upon the 3-substituted derivatives of β-naphthol the preparation of *2-naphthol-3-sulphonic acid* has been effected, so all the possible isomeric monosulphonic acids of β-naphthol are now known.

For the production of the hitherto unknown 2 : 3-isomeride, direct sulphonation cannot be employed and the only practicable method available is indicated by the scheme :



$$C_{10}H_6{<}\begin{smallmatrix}OMe\\ NH_2\end{smallmatrix} \longrightarrow C_{10}H_6{<}\begin{smallmatrix}OMe\\ N_2Cl\end{smallmatrix} \longrightarrow C_{10}H_6{<}\begin{smallmatrix}OMe\\ SO_2H\end{smallmatrix} \longrightarrow C_{10}H_6{<}\begin{smallmatrix}OMe\\ SO_3H\end{smallmatrix} \longrightarrow C_{10}H_6{<}\begin{smallmatrix}OH\\ SO_3H\end{smallmatrix}.$$

The yields are good, the only difficulty being the preparation in quantity of 3-amino-2-naphthyl methyl ether (preceding paper).

The introduction of the sulphinic acid radical was effected by a modification of the Gattermann method. Oxidation of the 2-*methoxy*-3-*sulphinic acid* yielded the 2-*methoxy*-3-*sulphonic acid*, which was demethylated with surprising ease by dilute hydrochloric acid; with the more usual reagent, hydriodic acid, the sulpho-group was also removed, notable quantities of β-naphthol being produced (compare Meyer, *Ber.*, 1895, **28**, 1254).

2-Naphthol-3-sulphonic acid combined with diazotised bases to form azo-dyes of redder shade than the corresponding dyes from β-naphthol-6-sulphonic acid (compare *J. Soc. Dyers and Colourists*, 1930, **46**, 270).

From the new acid were obtained also 2-naphthol-3-sulphonamide and -3-sulphonanilide, but not in a pure state. The latter is of considerable interest from its close analogy with the important Naphthol AS (2-naphthol-3-carboxyanilide), and it combined with diazotised aniline to give a red insoluble colouring matter.

1-*Nitroso*-2-*naphthol*-3-*sulphonic acid* was also prepared and examined.

EXPERIMENTAL.

2-*Methoxynaphthalene*-3-*sulphinic Acid*.—Several methods for the replacement of the amino-group by the sulphinic acid radical have been described (compare G.P. 130119, Soc. of Chemical Industry in Bâle; Gattermann, *Ber.*, 1899, **32**, 1136), and numerous modifications were tested. The so-called "simplified" method, for instance, which consists in allowing a diazonium solution to flow into a suspension of copper powder in sulphurous acid, gave only 10% of the theoretical yield of the desired sulphinic acid. Satisfactory results were obtained, however, by the following method.

3-Amino-2-naphthyl methyl ether (14 g.) was dissolved in concentrated sulphuric acid (48 c.c.) and water (160 c.c.) and diazotised at 0° by the drop-wise addition of 2*N*-sodium nitrite solution (about 40 c.c.). Sulphur dioxide was passed into the diazo-solution until frothing became noticeable and 10 c.c. of liquid sulphur dioxide were then run in. To the clear orange diazo-solution, well cooled and stirred, was added *chemically prepared* copper powder (30 g.) in small quantities during 1 hour, a slow stream of sulphur dioxide being maintained, and the stirring continued until a test portion no longer gave a red coloration with alkaline β-naphthol solution. The mixture was filtered by suction, without delay, and the filter-cake extracted at once with 30% aqueous potassium carbonate (200—250 c.c.), the extract shaken with animal charcoal, filtered, and acidified with concentrated hydrochloric acid. The precipitated 2-*methoxynaphthalene*-3-*sulphinic acid* was filtered off, washed with a very little ice-water, and dried on a porous plate (yield, 16·0—16·5 g.; theoretical, 16·5 g.). After recrystallisation from ether, in which it was easily soluble, it formed colourless rosettes, m. p. 133—134° (Found : S, 14·2. $C_{11}H_{10}O_3S$ requires S, 14·4%).

The method gave uniformly good results, but when the precipitated copper was replaced by ether-washed "Ullmann" copper powder very poor yields were obtained.

2-*Methoxynaphthalene*-3-*sulphonic Acid*.—Finely powdered potassium permanganate (1·7 g.) was dusted into a well-stirred suspension of 2-methoxynaphthalene-3-sulphinic acid (2·2 g.) in acetone (150 c.c.) during ½ hour. The mixture was heated to ebullition for a few minutes and cooled, the liquid filtered, and the solid cake extracted with hot water. The extract, evaporated to dryness, left the pure *potassium* salt (2·5 g.; theoretical yield, 2·6 g.), which crystallised from boiling alcohol in colourless plates (Found : K, 14·1; S, 12·3. $C_{11}H_9O_4SK$ requires K, 14·1; S, 11·6%).

Oxidation was also effected in aqueous solution, but the yield was lower (75%) and the product was contaminated by coloured impurities, which remain in solution in the acetone method.

The salt in alkaline solution gave no coloration with diazotised 2 : 4-dinitroaniline, unlike the analogously constituted 2-methoxy-3-naphthoic acid, which couples readily with diazotised amines to form red azo-dyes from which the methyl group has been partly or completely removed (Jambuserwala, Holt, and Mason, *J. Soc. Dyers and Colourists*, 1930, **46**, 339). The presence of the 3-sulpho-group, therefore, inhibits all coupling with the methylated acid (compare Meyer, Irschik, and Schlosser, *Ber.*, 1914, **47**, 1741).

2-*Methoxynaphthalene*-3-*sulphonyl chloride* was prepared both by Thomas's method (J., 1909, **95**, 342) by treatment of the sulphonic acid with sodium hypochlorite in sodium carbonate solution, and by warming the potassium salt with phosphorus pentachloride or thionyl chloride. The colourless product had m. p. 137—138° after crystallisation from ether (Found : S, 12·4; Cl, 13·4. $C_{11}H_9O_3ClS$ requires S, 12·5; Cl, 13·8%).

2-Methoxynaphthalene-3-sulphonamide was prepared by Thomas's method (*loc. cit.*) from the sulphinic acid and also by the action of ammonium carbonate upon the sulphonyl chloride. It formed colourless plates, m. p. 113°, from alcohol.

2-*Methoxynaphthalene*-3-*sulphonanilide*, made by treating the acid chloride with excess of aniline in boiling ethereal solution, formed colourless crystals, m. p. 173—174°, from ether (Found : S, 10·2. $C_{17}H_{15}O_3NS$ requires S, 10·2%).

2 : 4-*Dinitrophenyl*-2-*methoxy*-3-*naphthylsulphone*,

$$OMe \cdot C_{10}H_6 \cdot SO_2 \cdot C_6H_3(NO_2)_2,$$

prepared by condensing 2-methoxynaphthalene-3-sulphinic acid with 2 : 4-dinitrochlorobenzene in warm alcoholic solution in presence of sodium acetate (Saunders and British Dyestuffs Corporation, Ltd., E.P. 245865), formed colourless plates, m. p. 213—214°, from alcohol (Found : S, 8·2. $C_{17}H_{12}O_7N_2S$ requires S, 8·2%).

2-*Naphthol*-3-*sulphonic Acid*.—Potassium 2-methoxynaphthalene-3-sulphonate (2·0 g.) was refluxed with hydrochloric acid (1 : 1; 20 c.c.) for 1 hour (yield, 1·3 g.; 93% of the theoretical). No β-naphthol could be detected in the product. The *sodium* salt crystallised from dilute alcohol in colourless plates containing $1H_2O$ (Found: C, 45·4; H, 3·5; S, 12·3; Na, 8·7. $C_{10}H_7O_4SNa,H_2O$ requires C, 45·5; H, 3·4; S, 12·1; Na, 8·7%).

A solution of the substance in aqueous ammonia or sodium carbonate shows a blue fluorescence similar to that shown by β-naphthol-3 : 6-disulphonic acid, and both the acid and its salts afford a deep blue coloration with ferric chloride.

The free *acid* was crystallised from concentrated hydrochloric acid (Found : C, 49·7; H, 4·3; S, 13·3. $C_{10}H_8O_4S,H_2O$ requires C, 49·2; H, 4·1; S, 13·2%). The aniline and the α-naphthylamine salt have m. p. 241—242° and 247—248° respectively.

The sulphonyl chloride was prepared by refluxing the dry sulphonic acid (3·3 g.) for 2 hours with phosphoryl chloride (10 c.c.) and phosphorus pentachloride (3 g.), and remained, after removal of the volatile liquids, as an amorphous product which could not be crystallised.

The sulphonamide was obtained as a yellow powder, m. p. 110°, on treatment of a benzene solution of the acid chloride with aqueous ammonia (*d* 0·880).

2-Naphthol-3-sulphonanilide was prepared by warming the acid chloride and aniline in benzene and evaporating the solution. The tarry product after three crystallisations from amyl alcohol formed a buff-coloured powder, m. p. 112° (decomp.), which became tarry on exposure to air. It was not obtained pure enough for analysis. It was soluble in cold dilute sodium hydroxide solution and was reprecipitated by dilute acetic acid.

1-*Nitroso-2-naphthol-3-sulphonic acid* was prepared by the action of nitrous acid upon 2-naphthol-3-sulphonic acid in the normal manner and formed a yellow crystalline powder which, after recrystallisation from water, decomposed sharply at 268° without melting (Found : S, 10·0. $C_{10}H_7O_5NS,4H_2O$ requires S, 9·9%). It formed a yellow aqueous solution and gave a deep brown colour with ferric chloride solution. On iron-mordanted cotton it afforded a tobacco-brown dyeing.

Azo-dyes from 2-Naphthol-3-sulphonic Acid.—Azo-dyes were prepared from the acid by combining it with diazotised amines in presence of sodium carbonate in the usual manner : from aniline, red needles with blue reflex (Found : S, 9·2; Na, 6·6.

$C_{16}H_{11}O_4N_2SNa$

requires S, 9·2; Na, 6·6%); from *p*-nitroaniline, red needles (Found : Na, 5·9. $C_{16}H_{10}O_6N_3SNa$ requires Na, 5·6%); from *m*-xylidine, red microcrystalline powder (Found : Na, 6·7. $C_{18}H_{15}O_4N_2SNa$ requires Na, 6·7%); from α-naphthylamine (Found : Na, 6·2. $C_{20}H_{15}O_4N_2SNa$ requires Na, 6·2%); from dianisidine (Found : Na, 7·5. $C_{34}H_{24}O_{10}N_4S_2Na_2$ requires Na, 7·2%).

Dyeings with the above dyes on wool were deeper in all cases than the corresponding shades obtained from Schaeffer acid. Aqueous solutions of the dyes were also examined with a Hilger–Nutting spectrophotometer, and the positions of the absorption bands measured :

Diazo component.	Peak of absorption curves (μμ).	
	Schaeffer (2 : 6) acid.	New (2 : 3) acid.
Aniline	515 (497)	520 (505)
m-Xylidine	490 (510)	500 (517)
α-Naphthylamine	505 (530)	520 (545)
Dianisidine	525 (485)	535 (500)

In general, the dyeing properties of the new dyes are similar to those of the corresponding Schaeffer acid dyes, but the relatively small amount of products obtained did not permit fuller tests being carried out as to fastness, etc.

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