82. *The Reaction between* o-*Toluidine and Sulphur.*

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Gattermann (*Ber.*, 1889, **22**, 422) found that *o*-toluidine resembled the *p*-isomeride in its behaviour towards sulphur, the product being a thiazole: the constitution of this, however, he did not determine, neither did he mention any other product. As it has been shown (Hodgson, J., 1912, **101**, 1693; Hodgson and France, J., 1932, 1987) that the presence of *o*-toluidine hydrochloride in the reaction mixture causes the production of 2 : 2′-diamino-5 : 5′-ditolyl trisulphide almost entirely, it was anticipated that 2 : 2′-*diamino*-3 : 3′- and -5 : 5′-*ditolyl disulphides* should also be formed, in addition to the thiazole, in the above reaction. This anticipation has been verified, and the thiazole has been identified as 2′-*amino*-1-*phenyl*-3-*methylbenzthiazole* by its synthesis from the *o*-nitrobenzoyl derivative of the above 3 : 3′-disulphide: the synthesis also establishes the constitution of the 3 : 3′-disulphide, additional evidence being its conversion into 2-*diazotoluene* 3-*sulphide* by nitrous acid.

The presence of a little water in the reaction mixture, besides controlling the temperature, promotes the formation of 2 : 2′-diamino-5 : 5′-ditolyl disulphide: in the absence of water, only a little 5 : 5′-disulphide is produced, the 3 : 3′-isomeride predominating. These reactions appear to support Peacock's suggestion (*Nature*, 1932, **129**, 57) that some kind of co-ordination occurs between the methyl and the amino-group in *o*-toluidine, with consequent diminution in anionoid activity of the 5-carbon atom, since such co-ordination is inhibited, completely when hydrochloric acid is present and partly when water is present, 5-carbon reactivity being predominant in the former case (since thiazole formation does not occur) and considerably strengthened in the latter. These results are in accord with the general experience that the combined effect of two *op*-directing groups in ortho-positions is manifested at the para-position to the more powerful group. Further evidence in support of Peacock's view is afforded by the ready solubility of 2 : 2′-diamino-3 : 3′-ditolyl disulphide in light petroleum in contrast to the very sparing solubility of the 5 : 5′-isomeride. In alkaline solution, 2-aminotolyl-5-mercaptan is more readily oxidised by air than the 3-mercaptan, since in mixtures the 5 : 5′-disulphide is always found in the initial precipitation; this result is in accord with deduction from current electronic theory, since the 3-SH group will be much less acidic (*i.e.*, more anionoid) than the 5-SH group, owing to the nearer proximity of the 2-amino-1-methyl *op*-directing combination.

EXPERIMENTAL.

Sulphuration of o-*Toluidine*.—(a) An anhydr. mixture of *o*-toluidine (100 g.) and S (32 g.) was refluxed at 180—190° for 4 hr., the product neutralised and steam-distilled (60 g. unchanged amine), and the residue extracted with hot 10% HCl aq. (3 × 100 c.c.). On cooling, the extract deposited 5 g. of product; the filtered liquor, after treatment with Zn dust, was added to excess of 10% NaOH aq., again filtered, and finally oxidised by passage of air.

(b) The above procedure was repeated with the addition of 0·5 c.c. of H_2O to the refluxion, whereby the temp. remained between 180° and 185°: 10 g. of product crystallised from the acid extract.

Disulphides were removed from deposit (a) by extraction, after basification, with hot Na_2S aq., and the residue of 2′-amino-1-phenyl-3-methylbenzthiazole crystallised from 50% aq. EtOH (m. p. 122°). The aq. Na_2S extract contained a very small amount of admixed 2-aminotolyl-3- and -5-mercaptans, which was isolated by oxidation to disulphide. Deposit (b) contained mainly thiazole with a small amount of the 5 : 5′-disulphide [though larger than in (a)] and scarcely any 3 : 3′-disulphide.

The ppt. from the alkaline liquor (a) was removed at intervals and tested by diazotisation and coupling with β-naphthol, the 5 : 5′-disulphide giving an azo-compound (0·4 g., approx., in all), and the 3 : 3′-disulphide a non-coupling diazo-sulphide. Only the initial deposits contained the 5 : 5′-disulphide, the bulk of the deposit (3—4 g.) being the 3 : 3′-isomeride. The ppt. from the alkaline liquor (b) was almost entirely the 5 : 5′-disulphide (5 g.).

2′-*Amino*-1-*phenyl*-3-*methylbenzthiazole* is only moderately sol. in hot 50% aq. EtOH and light petroleum, from which it crystallises in pale yellow parallelepipeds, m. p. 125° (Gattermann, *loc. cit.*, gives m. p. 120°) (Found: N, 11·8; S, 13·4. $C_{14}H_{12}N_2S$ requires N, 11·7; S, 13·3%). The yellow diazonium chloride, which is sparingly sol. in HCl of moderate concn. but sol. in H_2O, gives an *azo*-β-*naphthol* derivative, scarlet micro-needles, m. p. 165°, from AcOH (Found: S, 8·1. $C_{24}H_{17}ON_3S$ requires S, 8·1%), and affords with conc. H_2SO_4 a beautiful $KMnO_4$-violet colour, which becomes scarlet on addition of H_2O. *Hydrochloride*, short, almost colourless needles, m. p. 203° (Found: Cl, 12·7; S, 11·8. $C_{14}H_{12}N_2S,HCl$ requires Cl, 12·8; S, 11·6%); *picrate*, sparingly sol. in EtOH, yellow micro-needles, m. p. 208° (Found: N, 15·2. $C_{14}H_{12}N_2S,C_6H_3O_7N_3$ requires N, 14·9%); *acetyl* derivative, colourless needles, m. p. 122° (depressed to 87° by admixture with the thiazole), from 50% aq. EtOH (Found: S, 11·5. $C_{16}H_{14}ON_2S$ requires S, 11·3%); *benzoyl* derivative, colourless parallelepipeds, m. p. 127°, from EtOH (Found: S, 9·5. $C_{21}H_{16}ON_2S$ requires S, 9·3%).

2 : 2′-*Diamino*-3 : 3′-*ditolyl disulphide* forms long, pale yellow needles from light petroleum, m. p. 84° (Found: S, 23·3. $C_{14}H_{16}N_2S_2$ requires S, 23·2%), which with HNO_2 gives 2-*diazotoluene* 3-*sulphide*, an oil at 0° (Found: S, 21·1. $C_7H_6N_2S$ requires S, 21·3%) which has a strong odour similar to that of phenyldiazosulphide; *dihydrochloride*, almost colourless micro-plates, m. p. 197°, from conc. HCl (Found: Cl, 20·3; S, 18·0. $C_{14}H_{16}N_2S_2,2HCl$ requires Cl, 20·3; S, 18·3%), very sol. in H_2O and dil. HCl; *dipicrate*; orange-yellow plates, m. p. 134°, from aq. EtOH or H_2O (Found: S, 9·0. $C_{14}H_{16}N_2S_2,2C_6H_3O_7N_3$ requires S, 8·7%); *dipicrate of* 2 : 2′-*diaminodiphenyl disulphide*, orange-yellow needles, m. p. 141° (Found: S, 9·2. $C_{12}H_{12}N_2S_2,2C_6H_3O_7N_3$ requires S, 9·1%).

Synthesis of 2′-*Amino*-1-*phenyl*-3-*methylbenzthiazole*.—2 : 2′-Diamino-3 : 3′-ditolyl disulphide was converted by the Schotten–Baumann reaction into the di-*o*-nitrobenzoyl derivative, colourless micro-plates, m. p. 217—220°, from EtOH, which on reduction with Fe and dil. HCl gave a product identical with the thiazole above (comparison of hydrochloride, picrate, and azo-β-naphthol derivative).

2 : 2′-Diamino-5 : 5′-ditolyl disulphide, obtained in reactions (a) and (b) above, crystallised from 50% aq. alcohol in long colourless rhombs, m. p. 112° (Found: S, 23·3. Calc.: S, 23·2%), identical with an authentic specimen, gave a *dipicrate*, deep orange-red plates, m. p. 179°, from H_2O or aq. EtOH (Found: S, 8·8. $C_{14}H_{16}N_2S_2,2C_6H_3O_7N_3$ requires S, 8·7%), and a *di*-o-*nitrobenzoyl* derivative, which was sparingly sol. in most solvents but crystallised from $PhNO_2$ in colourless micro-plates, m. p. 240° (Found: N, 10·0. $C_{28}H_{22}O_6N_4S_2$ requires N, 9·7%). The latter product was readily formed by addition of *o*-nitrobenzoyl chloride to a dry ether or benzene solution of the amine, but this reaction did not proceed with the 3 : 3′-isomeride, which required the presence of alkali. Acetylation of the 5 : 5′-disulphide readily occurs by the usual procedure (*loc. cit.*), which fails with the 3 : 3′-isomeride.

The authors thank Imperial Chemical Industries, Ltd., for various gifts.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December* 16*th*, 1932.]
