243. *Thio-*o*-toluidine. Its Preparation by Synthesis and by the Action of Sulphur on* o*-Toluidine in the Presence of Litharge.*

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SULPHUR reacts with aniline alone to form 2 : 2′-diaminodiphenyl disulphide (Hofmann, *Ber.*, 1894, **27**, 2807), but when litharge is present the main product is 4 : 4′-diaminodiphenyl sulphide (Merz and Weith, *Ber.*, 1871, **4**, 384; Hodgson, J., 1924, **125**, 1855). Similarly *o*-toluidine reacts with sulphur (though very tardily) to give a small amount of 2 : 2′-diamino-3 : 3′-ditolyl disulphide together with a relatively large quantity of 2′-amino-1-phenyl-3-methylbenzthiazole, presumably derived from the first product, and some 5 : 5′-disulphide (particularly if a little water be present) (Hodgson and France, J., 1933, 296).

It appeared of interest, therefore, to ascertain what influence litharge would exert in the reaction of *o*-toluidine with sulphur, and again the analogy with aniline was found to be followed, an excellent yield being obtained of 2 : 2′-*diamino*-5 : 5′-*ditolyl sulphide* (*thio*-o-*toluidine*). To prevent the formation of highly coloured by-products, however, the temperature of reaction must be kept as low as possible, and some of the *o*-toluidine should remain unaffected.

The constitution of this compound was confirmed by its preparation from 2′-*nitro*-2-*amino*-5 : 5′-*ditolyl sulphide*, which, in turn, was obtained by the interaction of 5-bromo-2-nitrotoluene with the sodium salt of 2-amino-5-tolylmercaptan.

It is noteworthy that the *bisazo*-derivative with β-naphthol gives a fine blue colour with concentrated sulphuric acid in contrast with the usual violet-blues obtained from similar products.

When 5-bromo-2-nitrotoluene is boiled with excess of aqueous sodium sulphide, about 3% is reduced directly to 5-bromo-*o*-toluidine, and approximately 20% is converted into a monosulphide, whilst the remainder (77%) reacts to form a mercaptan which is subsequently reduced to the sodium salt of 2-amino-5-tolylmercaptan.

EXPERIMENTAL.

Sulphuration of o*-Toluidine in Presence of Litharge.*—A mixture of *o*-toluidine (107 g.) and sulphur (32 g.) was vigorously stirred at 135° while litharge (160 g.) was added portionwise (5½ hours), the temperature throughout not being allowed to exceed 145°. After a further 30 minutes' stirring, the mixture was cooled, treated with 30 c.c. of 20% aqueous sodium hydroxide, and steam distilled, 20 g. of *o*-toluidine passing over. The dark blue residue was extracted 4 times with boiling benzene (800 c.c. in all), and the filtered extract treated with a slow stream of dry hydrogen chloride until precipitation commenced; the initial highly coloured products were then filtered off, the substance in solution being finally precipitated as a hydrochloride; yield, 70 g. If the reaction temperature exceeded 150° for any length of time, no unchanged *o*-toluidine was found, but the yield of highly coloured products was greatly increased.

2 : 2′-*Diamino*-5 : 5′-*ditolyl Sulphide.*—The above hydrochloride was redissolved in very dilute hydrochloric acid and fractionally precipitated by means of 1% aqueous sodium hydroxide until the products were only faintly coloured; the whole of the *base* was then precipitated, washed free from alkali, and crystallised from 25% aqueous ethyl alcohol (charcoal); long colourless needles, m. p. 96° (Found : N, 11·6; S, 13·2. $C_{14}H_{16}N_2S$ requires N, 11·5; S, 13·1%), sparingly soluble in hot water but readily in the usual organic solvents. The *dihydrochloride* crystallised from hot dilute hydrochloric acid in silvery white plates, m. p. 248—249° (Found : Cl, 22·3; S, 10·3. $C_{14}H_{16}N_2S,2HCl$ requires Cl, 22·4; S, 10·1%); the *dipicrate*

crystallised from water or 25% aqueous alcohol in small rectangular plates, m. p. 186° (Found : S, 4·6. $C_{14}H_{16}N_2S,2C_6H_3O_7N_3$ requires S, 4·6%); the *diacetyl* derivative from dilute ethyl alcohol in colourless micro-needles, m. p. 220° (Found : S, 9·9. $C_{18}H_{20}O_2N_2S$ requires S, 9·8%), and the *dibenzoyl* derivative from methyl or ethyl alcohol in colourless needles, m. p. 233° (Found : S, 7·3. $C_{28}H_{24}O_2N_2S$ requires S, 7·1%). The base readily diazotises and couples with alkaline β-naphthol to give a *bisazo*-compound, which crystallises from benzene or ethylene dichloride in maroon micro-plates, m. p. 258° (Found : N, 10·3. $C_{34}H_{26}O_2N_4S$ requires N, 10·1%), and gives the characteristic colour reaction noted above.

Synthesis.—A suspension of 5-bromo-2-nitrotoluene (5 g.) in a solution of sodium sulphide crystals (20 g.) and water (100 c.c.) was boiled for 4 hours under reflux, steam-distilled to remove volatile 5-bromo-*o*-toluidine (0·25 g., as determined by diazotisation and coupling with β-naphthol), and the residual liquor filtered (filtrate A) to remove insoluble product (0·8 g.). This was boiled 3 times with great excess of 10% aqueous hydrochloric acid to remove nitro-amine, and the insoluble 2 : 2'-*dinitro*-5 : 5'-*ditolyl sulphide* crystallised from glacial acetic acid; pale straw-coloured parallelepipeds, m. p. 164° (Found : N, 9·3; S, 10·7. $C_{14}H_{12}O_4N_2S$ requires N, 9·2; S, 10·5%), insoluble in boiling aqueous sodium mono- or di-sulphide.

The filtrate A from the foregoing compound was treated with a current of air, whereby the 2-amino-5-tolylmercaptan was converted into the insoluble 2 : 2'-diamino-5 : 5'-ditolyl disulphide (2·2 g.).

2 : 2'-*Dinitro*-5 : 5'-*ditolyl disulphide*, prepared by the action of sodium disulphide on 5-bromo-2-nitrotoluene dissolved in alcohol, crystallises from glacial acetic acid in colourless plates, m. p. 163° (depressed to 140° by the monosulphide above) (Found : N, 8·5; S, 19·3. $C_{14}H_{12}O_4N_2S_2$ requires N, 8·3; S, 19·0%), soluble in boiling aqueous sodium sulphide.

5-*Bromotoluene*-2-*azo*-β-*naphthol* crystallises from dilute acetic acid in scarlet needles, m. p. 172° (Found : Br, 23·3. $C_{17}H_{13}ON_2Br$ requires Br, 23·5%), which give a beautiful permanganate colour with concentrated sulphuric acid, turning scarlet on dilution.

2'-*Nitro*-2-*amino*-5 : 5'-*ditolyl Sulphide.*—The zinc salt of 2-amino-5-tolylmercaptan (10 g.), prepared by reducing 2 : 2'-diamino-5 : 5'-ditolyl disulphide with zinc dust and aqueous hydrochloric acid and precipitating it by addition of sodium acetate, was suspended in ethyl alcohol (100 c.c.) and first treated with sodium (1·5 g.) to convert it into the sodium salt, after which 5-bromo-2-nitrotoluene (7 g.) was added, and the mixture heated under reflux for 6 hours. On cooling, almost pure 2'-*nitro*-2-*amino*-5 : 5'-*ditolyl sulphide* (4·5 g., m. p. 101°) separated, and a further 1·5 g. (m. p. 98°) were obtained by concentration. It was almost insoluble in light petroleum, fairly soluble in ethylene dichloride, and crystallised from 50% aqueous alcohol in yellow rhombs, m. p. 104° (Found : N, 10·3; S, 11·9. $C_{14}H_{14}O_2N_2S$ requires N, 10·2; S, 11·7%), which give a vivid orange-red colour with concentrated sulphuric acid. The *hydrochloride* crystallised from hot dilute hydrochloric acid in colourless plates, m. p. 187° (Found : Cl, 11·2. $C_{14}H_{14}O_2N_2S,HCl$ requires Cl, 11·4%), and was moderately soluble in ethyl alcohol; the *acetyl* derivative crystallised from dilute methyl alcohol in pale straw-coloured needles, m. p. 143° (Found : S, 10·2. $C_{16}H_{16}O_3N_2S$ requires S, 10·1%); the *benzoyl* derivative from methyl alcohol in long, pale straw-coloured needles, m. p. 119° (Found : S, 8·6. $C_{21}H_{18}O_3N_2S$ requires S, 8·5%); and the *azo*-β-*naphthol* derivative separated from glacial acetic acid, in which it is sparingly soluble, in deep maroon micro-plates, m. p. 194° (Found : N, 10·0. $C_{24}H_{19}O_3N_3S$ requires N, 9·8%), which are moderately soluble in ethylene dichloride, and give a violet-blue colour with concentrated sulphuric acid which turns scarlet on dilution.

2 : 2'-Diamino-5 : 5'-ditolyl sulphide was prepared from the above nitro-amine by reduction with iron dust and very dilute hydrochloric acid in the usual way. The product so obtained, together with its five derivatives, were identical with the compound and its corresponding derivatives described above.

When 2 : 2'-diamino-5 : 5'-ditolyl disulphide was boiled for several hours with *o*-toluidine it was recovered unchanged, and the addition of litharge to the boiling mixture failed to produce the monosulphide.

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