

197. *The Nitration of Benz-1-thia-2 : 3-diazole and the Synthesis of 7-Nitro-, 5-Methyl-, and 7-Nitro-5-methyl-benz-1-thia-2 : 3-diazole, with Improved Preparations of 1-Chloro-2 : 6-dinitrobenzene and 2-Chloro-3-nitroaniline.*

By HERBERT H. HODGSON and DOUGLAS P. DODGSON.

The synthesis of 7-nitrobenz-1-thia-2 : 3-diazole from 2-chloro-3-nitroaniline by thiolation and subsequent treatment with nitrous acid, has enabled the mononitration products of benz-1-thia-2 : 3-diazole to be identified as the 4- and the 7-nitro-isomeride. The 5-methyl and 7-nitro-5-methyl compounds have been prepared from 4-chloro-3-nitrotoluene and 4-chloro-5-nitro-*m*-toluidine respectively as initial substances. Improved preparations of 1-chloro-2 : 6-dinitrobenzene and 2-chloro-3-nitroaniline are described.

THE nitration of benz-1-thia-2 : 3-diazole had been carried out by Fries and Reitz (*Annalen*, 1936, **527**, 38), who isolated two compounds of m. p. 95° and 104°, the former predominating. Since 5- and 6-nitrobenz-1-thia-2 : 3-diazoles were known already, Fries and Reitz assumed the product of m. p. 95° to be the 4-isomeride, but they neither established its identity nor gave any opinion as to the structure of the product of m. p. 104°, since an attempted synthesis of 4-nitrobenz-1-thia-2 : 3-diazole from 2-nitrothioacetanilide was unsuccessful. In the present work, 7-nitrobenz-1-thia-2 : 3-diazole has been synthesised by thiolation of 2-chloro-3-nitroaniline

with aqueous sodium sulphide in the presence of sodium hydrogen carbonate (cf. Hodgson and Birtwell, *J.*, 1944, 75), and the resulting 2-nitro-6-aminothiophenol converted by nitrous acid into 7-nitrobenz-1-thia-2 : 3-diazole which had m. p. 105°, and was identical with the product prepared according to Fries and Reitz's directions (*loc. cit.*). The compound of m. p. 95° must therefore, by exclusion, have been the 4-nitrobenz-1-thia-2 : 3-diazole, thus confirming their assumption that nitration of benz-1-thia-2 : 3-diazole occurs in the 4- and 7-positions.

The resistance of the thiadiazole ring towards concentrated nitric acid affords further evidence of the great stability of the $\text{-}\ddot{\text{N}}=\ddot{\text{N}}\text{-S-}$ grouping, and the solubility of such compounds in strong mineral acids, thereby indicating the salt-forming character of the group, must be ascribed to the lone pairs of electrons present. The possibility of a diazonium structure (I) being produced by the acid would follow on analogy with the diazo-oxides, but this is ruled out by the fact that 5-aminobenz-1-thia-2 : 3-diazole on diazotisation followed by the Sandmeyer reaction gives a 5-halogenobenz-1-thia-2 : 3-diazole (cf. Hodgson and Dodgson, this vol., p. 870) and not a dihalogeno-compound such as a bis-diazonium compound would be expected to provide.

Benz-1-thia-2 : 3-diazole in many respects is similar to naphthalene but differs from it in the severe conditions required for its nitration and also in the intense violet-blue colour given with concentrated sulphuric acid; the latter suggests salt-formation of the type (II).



The preparation of 1-chloro-2 : 6-dinitrobenzene was necessary for the synthesis of 7-nitrobenz-1-thia-2 : 3-diazole, and for this purpose Borsche and Rantscheff's method (*Annalen*, 1911, 279, 152) was modified by the use of potassium xanthate in place of sodium acetoacetic ester, whereby a pure product was obtained by a simplified technique, since the xanthate only reacts with the 1-chloro-2 : 4-dinitrobenzene in the mixture of the 2 : 4- and 2 : 6-isomerides obtained in the nitration of 1-chloro-2-nitrobenzene. Alternatively, the 1-chloro-2 : 6-dinitrobenzene was obtained from 2 : 6-dinitrosulphanilic acid (Lindemann and Wessel, *Ber.*, 1925, 58, 1221) by desulphonation, diazotisation (Hodgson and Walker, *J.*, 1933, 1620), and finally the Sandmeyer reaction.

Reduction of 1-chloro-2 : 6-dinitrobenzene was readily effected by stannous chloride in glacial acetic acid solution to give 2-chloro-3-nitroaniline.

2 : 2'-Dinitro-4 : 4'-dimethyldiphenyl disulphide was prepared in 48% yield by the action of sodium disulphide on 4-chloro-3-nitrotoluene, and converted by reduction into 3-nitrothio-*p*-cresol, which, on diazotisation, afforded 5-methylbenz-1-thia-2 : 3-diazole. This compound somewhat resembled the parent substance in giving a blue colour with concentrated sulphuric acid. 7-Nitro-5-methylbenz-1-thia-2 : 3-diazole has likewise been obtained from 4-chloro-3 : 5-dinitrotoluene by a similar process to that used for the synthesis of 7-nitrobenz-1-thia-2 : 3-diazole, *viz.*, reduction to 4-chloro-5-nitro-*m*-toluidine with subsequent thiolation and diazotisation.

Unlike 2-chloro-5-nitroaniline, both 2-chloro-3-nitroaniline and 4-chloro-5-nitro-*m*-toluidine yield a considerable amount of brown by-product on thiolation; this appears to indicate some reduction of the second nitro-group, since diazotisation produces Bismarck-brown-like products.

Whereas 2-chloro-5-nitroaniline readily thiolates and on diazotisation gives a cream-coloured product which is fairly pure (Hodgson and Dodgson, *loc. cit.*), a similar treatment of 2-chloro-3-nitroaniline afforded a much browner product from which the thiadiazole had to be purified by sublimation. Working with the similar compound, 4-chloro-5-nitro-*m*-toluidine, the brown product and the thiadiazole could be separated by extraction of the latter with hot 20% hydrochloric acid. It is suggested that in the cases of brown product formation, the second nitro-group which is also adjacent to the chlorine has been partially reduced by the sulphide with some resulting diamine, which, in the subsequent diazotisation, has yielded Bismarck-brown-like compounds.

In attempts to find a rapid method for the preparation of 1-chloro-2 : 6-dinitrobenzene, the mixture of 1-chloro-2 : 4-dinitro- and 1-chloro-2 : 6-dinitro-benzenes, obtained by the nitration of 1-chloro-2-nitrobenzene, was first treated with potassium phthalimide in boiling ethanol without result; when the reactants were fused together some reaction occurred at about 120° but was incomplete and could not be used for the separation (cf. Schmidt, *Ber.*, 1889, 22, 3249, for the reaction of picryl chloride with potassium phthalimide which takes place at 70°). In

the case of the reaction with potassium xanthate above, only mixtures of m. p. $< 43^\circ$ could be used, otherwise no 1-chloro-2 : 6-dinitrobenzene could be isolated.

EXPERIMENTAL.

Preparation of Benz-1-thia-2 : 3-diazole.—A mixture of aniline (93 g., 1 g.-mol.) and sulphur (64 g., 2 g.-mols.) was refluxed at $180\text{--}190^\circ$ for 12 hours, and the cooled melt extracted with 2% aqueous hydrochloric acid to remove unchanged aniline. The residue, consisting mainly of *oo'*-dithioaniline, was suspended in hot 15% aqueous hydrochloric acid (500 c.c.) and saturated with hydrogen sulphide, after which the stirred mixture was cooled below 5° , treated with sodium nitrite (70 g.) dissolved in water (250 c.c.), kept for one hour, and then steam distilled; benz-1-thia-2 : 3-diazole passed over and was purified by steam distillation from 5% aqueous sodium hydroxide. Yield, 27 g. (20%); m. p. 35° (Jacobson, *Annalen*, 1893, **277**, 209, gives m. p. 35°) (Found : S, 23.6. Calc. for $C_6H_4N_2S$: S, 23.5%).

Nitration of Benz-1-thia-2 : 3-diazole.—The violet solution of the compound (13.6 g.) in sulphuric acid (60 c.c., *d* 1.84) was stirred gradually at room temperature with finely powdered potassium nitrate (12 g.); the colour changed to red and thence to pale yellow-brown, accompanied by a temperature rise of ca. 16° (precipitation experiments at this point indicated that nitration had not taken place). On being heated gradually to 100° , the solution turned brown, and was then cooled, poured on ice, and the precipitated mixture of the 4- and 7-nitrobenzthiadiazoles filtered off. This mixture contained no steam-volatile constituent, and recrystallisation from methanol and subsequently from toluene afforded needles of m. p. $70\text{--}80^\circ$ raised to $87\text{--}92^\circ$ when sublimed under reduced pressure at 140° . Fractional crystallisation of the sublimate from ethanol, and recrystallisation of the fractions, gave products of m. p. 95° (Found : S, 18.0. Calc. for $C_6H_3O_2N_2S$: S, 17.7%) and 105° (Found : S, 18%), respectively; Fries and Reitz (*loc. cit.*) give m. p.s 95° and 104° .

Nitration of 1-Chloro-2-nitrobenzene.—Nitric acid (31.5 g., *d* 1.4) was stirred gradually into a solution of 1-chloro-2-nitrobenzene (31.5 g.) in sulphuric acid (130 c.c., *d* 1.84), and the reaction mixture heated on the water-bath to 100° , cooled to room temperature, poured on ice, and the precipitated 1-chloro-2 : 4- and -2 : 6-dinitrobenzene removed as a white solid, washed with water, and dried. Slow crystallisation from their solution in ethanol afforded fractions whose m. p.s varied from 38° to 50° , the lower ones consisting mainly of needles and the higher of rhombic plates which were almost pure 1-chloro-2 : 4-dinitrobenzene. The former fractions containing the highest proportion of 1-chloro-2 : 6-dinitrobenzene were worked up as follows : A fraction (10 g.), of m. p. 43° or less, was dissolved in ethanol (100 c.c.), treated with potassium xanthate (4 g.), and the volume concentrated to 30 c.c. Ether (50 c.c.) was added, and the red colour, which was produced initially, had by this time given place to a yellow precipitate which consisted mainly of the monosulphides from the chlorodinitrobenzenes; it was filtered off, washed with ether, and the combined ethereal filtrates extracted with 2% aqueous sodium hydroxide, followed by water until the washings were colourless. The ether was allowed to evaporate gradually; 1-chloro-2 : 6-dinitrobenzene crystallised out (aided by scratching) and was filtered off and washed with ether-ligroin (1 : 1) to remove the xanthic ester also produced and finally with ligroin; yield, 1.7 g. On crystallisation from methanol, it had m. p. 88° (Borsche and Rantscheff, *Annalen*, 1914, **406**, 101, give m. p. 88°) (Found : Cl, 17.2. Calc. for $C_6H_3O_4N_2Cl$: Cl, 17.5%). Attempts to separate 1-chloro-2 : 6-dinitrobenzene from the crude mixture itself did not succeed, and it became necessary to fractionate as above; similarly, an attempted separation by reaction with potassium phthalimide also failed, since on using 80% of the theoretical amount of this reagent, no reaction took place even after refluxing in ethanol for 6 hours, while fusion of the reactants at 120° only brought about a partial reaction, in contrast to the ready reaction of picryl chloride with potassium phthalimide (cf. Schmidt, *Ber.*, 1889, **22**, 3249) which ensues at 70° .

Alternative Preparation of 1-Chloro-2 : 6-dinitrobenzene.—4-Chloro-3 : 5-dinitrobenzenesulphonic acid was obtained when a mixture of chlorobenzene (45 c.c.), 20% oleum (90 c.c.), sulphuric acid (830 c.c., *d* 1.84), and potassium nitrate (225 g.) was heated on a boiling water-bath for 16 hours, cooled, and poured on ice (5 kg.). The product was filtered off, washed with ether (50 c.c.) to remove chlorodinitrobenzenes, and crystallised from hot water, forming colourless plates, m.p. 293° (Ullmann and Kuhn, *Annalen*, 1909, **366**, 102, give m. p. 293°) (Found : S, 11.5. Calc. for $C_6H_3O_7N_2ClS$: S, 11.3%). The above sulphonic acid (20 g.) was suspended in ammonia (50 c.c., *d* 0.88), the mixture heated to boiling under reflux, cooled, and the yellow 2 : 6-dinitrosulphanilic acid which had been formed was filtered off, and washed with water (20 c.c.), and then crystallised from hot water in yellow needles which exploded at 360° (Found : S, 12.2. Calc. for $C_6H_3O_4N_2S$: S, 12.2%). Desulphonation was effected when this sulphonic acid was refluxed for 3 hours with sulphuric acid (120 c.c., *d* 1.84) and water (80 c.c.); on cooling, yellow plates (5 g.) of 2 : 6-dinitroaniline separated which when recrystallised from methanol had m. p. 139° (Welsh, *J. Amer. Chem. Soc.*, 1941, **63**, 3276, gives m. p. 139°) (Found : N, 23.2. Calc. for $C_6H_5O_4N_3$: N, 22.9%). A solution of this amine (4.5 g.) in sulphuric acid (20 c.c., *d* 1.84) was stirred into one of sodium nitrite (2 g.) in sulphuric acid (10 c.c., *d* 1.84), and glacial acetic acid (30 c.c.) was then added with stirring; after 30 minutes, the mixture was poured into a cold solution of cuprous chloride (10 g.) in hydrochloric acid (100 c.c., *d* 1.18) and kept until evolution of nitrogen had ceased. On dilution with water (50 c.c.), crude 1-chloro-2 : 6-dinitrobenzene separated and was filtered off, extracted with ether (100 c.c.), and the filtered extract washed first with 2% aqueous sodium hydroxide until the washings were colourless, then with water; finally the ether was allowed to evaporate gradually, whereupon 1-chloro-2 : 6-dinitrobenzene separated (3.5 g., 70% yield) and was recrystallised from methanol; m. p. 88° .

Reduction of 1-Chloro-2 : 6-dinitrobenzene.—Reduction of this compound (2.025 g.) to 2-chloro-3-nitroaniline was effected by dissolving it in glacial acetic acid (4 c.c.) and treating it with crystallised stannous chloride (6.8 g.) added in small portions to the hot solution. After 5 mins. refluxing, water (20 c.c.) was added, followed by 20% aqueous sodium hydroxide (30 c.c.), and the mixture was steam-distilled.

The distillate (3 l.) was cooled in ice, yellow needles of 2-chloro-3-nitroaniline (0.9 g., 53% yield) separating, a further 0.2 g. being obtained on concentration of the filtrate to 100 c.c.; it recrystallised from methanol in yellow needles, m. p. 96° (Wallach and Wibaut, *Rec. Trav. chim.*, 1936, **55**, 1075, give m. p. 95—96°) (Found: Cl, 20.9. Calc. for $C_6H_5O_2N_2Cl$: Cl, 20.6%).

Synthesis of 7-Nitrobenz-1-thia-2:3-diazole.—A solution of 2-chloro-3-nitroaniline (1.725 g.) in ethanol (25 c.c.) was treated gradually with one of crystalline sodium sulphide (3.6 g.) and sodium hydrogen carbonate (1.26 g.) in water (10 c.c.). The mixture was then heated on the water-bath for 2 hours, cooled, and water (65 c.c.) containing 20% aqueous sodium hydroxide (1 c.c.) added; the solution was then cooled in ice, filtered, sodium nitrite (1 g.) dissolved in it, and the whole stirred into sulphuric acid (25 c.c., *d* 1.84) mixed with ice (25 g.). After one hour, the brown precipitate of 7-nitrobenz-1-thia-2:3-diazole (0.4 g., 22% yield) was collected and purified by sublimation under reduced pressure; subsequent recrystallisation from methanol gave crystals with m. p. and mixed m. p. with a sample of Fries and Reitz's unidentified nitration compound, 105°; cooled and remelted, m. p. 105° (Found: N, 13.4. $C_6H_3O_2N_3S$ requires N, 13.2%).

Synthesis of 5-Methylbenz-1-thia-2:3-diazole.—2:2'-Dinitro-4'-dimethyldiphenyl disulphide was obtained when a solution of 4-chloro-3-nitrotoluene (13.72 g.) in ethanol (200 c.c.) was treated with one of sodium sulphide nonahydrate (9.6 g.) and sulphur (1.28 g.) in water (25 c.c.) and the mixture refluxed for 3 hours, after which the yellow disulphide (6.4 g., 48% yield) was filtered off and crystallised from 80% aqueous acetic acid (charcoal), forming yellow needles, m. p. 176° (Zincke and Röse, *Annalen*, 1914, **405**, 108, give m. p. 176°) (Found: S, 19.4. Calc. for $C_{14}H_{12}O_4N_2S_2$: S, 19.1%). This disulphide (3.36 g.) was suspended in 90% aqueous acetic acid (100 c.c.) with zinc dust (7 g.), and the mixture heated under reflux for one hour, filtered hot, the filtrate cooled to 10°, then stirred into a solution of sodium nitrite (1.5 g.) in sulphuric acid (10 c.c., *d* 1.84). The mixture was then poured on ice (100 g.), kept for one hour, made alkaline, and steam-distilled, whereupon the 5-methylbenz-1-thia-2:3-diazole came over as an oil which solidified on cooling; it was dissolved in boiling methanol (charcoal) from which it separated, when the methanol was gradually evaporated under reduced pressure, in clusters of small rods, m. p. 26° (Found: N, 18.9. $C_7H_6N_3S$ requires N, 18.7%), which gave a grey-blue solution in concentrated sulphuric acid, from which the thiadiazole was precipitated unchanged on dilution with water.

Synthesis of 7-Nitro-5-methylbenz-1-thia-2:3-diazole.—A solution of sodium nitrite (10 g.) in sulphuric acid (70 c.c., *d* 1.84) was stirred into one of 3:5-dinitro-*p*-toluidine (19.7 g.) in sulphuric acid (30 c.c., *d* 1.84) followed by glacial acetic acid (150 c.c.), the temperature being kept below 30° and the stirring continued for one hour. The mixture was then stirred into a solution of cuprous chloride (40 g.) in hydrochloric acid (150 c.c., *d* 1.18), kept until evolution of nitrogen had ceased (30 mins.), and poured on ice (1 kg.); the precipitate was filtered off, washed with water at the pump, extracted twice with boiling ethanol (2 × 100 c.c.), the extract filtered, the filtrate poured into ice-water (1 l.), aqueous 4% sodium hydroxide added (100 c.c.), and the precipitate (17 g., 78.5% yield) of crude 4-chloro-3:5-dinitrotoluene crystallised from ethanol in yellow needles, m. p. 116° (Borsche and Fiedler, *Ber.*, 1913, **46**, 2121, give m. p. 115—116°). A solution of this compound (21.65 g.) in hot glacial acetic (100 c.c.) was treated with powdered crystalline stannous chloride (67.8 g.) added in portions just sufficient to maintain ebullition, and when the addition was complete (2—3 mins.) the mixture was boiled for a further 5 minutes, diluted with water (100 c.c.), and poured into 10% sodium hydroxide in ice-water (1200 g., 1:1); when the precipitate had coagulated, it was filtered off, washed with water, dissolved in hot 20% hydrochloric acid (150 c.c.), the solution filtered hot, and the filtrate cooled, and neutralised with ammonia; the 4-chloro-5-nitro-3-aminotoluene (4-chloro-5-nitro-*m*-toluidine) was filtered off and steam-distilled, and the distillate cooled to 0°, affording the pure product, which crystallised from methanol in yellow needles, m. p. 95° (Found: N, 15.3. $C_7H_7O_2N_2Cl$ requires N, 15.0%). 4-Chloro-5-nitro-3-aceto-*m*-toluidide, prepared by the usual acetylation procedure, crystallised from ethanol in pale cream needles, m. p. 147° (Found: N, 12.5. $C_9H_9O_3N_2Cl$ requires N, 12.25%).

*Thiolation of 4-Chloro-5-nitro-*m*-toluidine.*—A mixture of a solution of the compound (9.325 g.) in ethanol (125 c.c.) with one of sodium sulphide nonahydrate (18 g.) and sodium hydrogen carbonate (6.3 g.) in water (50 c.c.), was refluxed on the water-bath for an hour, 20% aqueous sodium hydroxide (10 c.c.) added, and the whole poured into ice-water (400 c.c.), filtered, and the residue washed with a little water and dried to give unchanged material (2.9 g., 31% of that taken). Sodium nitrite (4 g.) was dissolved in the filtrate, which was then stirred at 0° into sulphuric acid (12.5 c.c., *d* 1.84) which had been diluted with ice-water (125 c.c.). After one hour, the crude brown product was extracted thrice with boiling 20% aqueous hydrochloric acid (3 × 50 c.c.), and from the solution the 7-nitro-5-methylbenz-1-thia-2:3-diazole was precipitated by addition of ice-water (150 c.c.) (yield, 0.5 g., m. p. 130—150°); it sublimed in minute yellow needles, m. p. 149° (Found: N, 21.8. $C_7H_5O_2N_3S$ requires N, 21.5%), which were dissolved in concentrated sulphuric acid to give a colourless solution from which the thiadiazole was precipitated unchanged on dilution with water. The residue (3.2 g.) from the above hydrochloric acid extraction was readily soluble in ethanol, but attempts at identification were unsuccessful.

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