

CCCXXIII.—*Some Sulphur Derivatives of Substituted Benzaldehydes.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

PREVIOUS work on the mercaptobenzaldehydes appears to be limited to that of Friedländer and Lenk (*Ber.*, 1912, **45**, 2083), who prepared the *o*- and *p*-mercaptans and *o*- and *p*-thioethers of benzaldehyde itself. The present paper records the preparation of several substituted benzaldehydes containing sulphur, some of which exhibit remarkable properties.

The dioxime of 3 : 3'-dinitrodibenzaldehyde 4 : 4'-disulphide is a very stable yellow product which, unlike the corresponding 6 : 6'-disulphide dioxime, is converted by cold aqueous sodium hydroxide into what appears to be an isomeride of deeper shade, melting 30° lower, and decomposing with violence when heated rapidly, thereby resembling the second dioxime above. The conversion is accompanied by a gradual and remarkable series of colour changes.

Amino-derivatives of the benzaldehyde thioethers proved to be unstable, thus resembling the simple aminobenzaldehydes, although their solutions in acids may be diazotised normally.

The *p*-nitrophenylhydrazones of 3-chloro-4- and -6-methylthiolbenzaldehyde were scarlet and orange, respectively, and gave bluish-purple and reddish-purple colorations with alkaline hydroxides, thus showing the much more pronounced bathochromic effect of the methylthiol group when para than when ortho to the hydrazine group (compare the azo-group, Hodgson and Handley, *J.*, 1926, 542).

Bromine displaces the methylthiol group from 3-amino-6-methylthiolbenzaldoxime, forming 2 : 4 : 5 : 6-tetrabromo-3-aminobenzaldoxime, but it decomposes the 4-methylthiol isomeride.

E X P E R I M E N T A L.

3 : 3'-Dinitrodibenzaldehyde 6 : 6'-Disulphide.—This was prepared by gradually adding aqueous sodium disulphide (crystallised sodium sulphide, 48 g.; sulphur, 6 g.; water, 120 c.c.) to a solution in alcohol (300 c.c.) of 6-chloro-3-nitrobenzaldehyde (64 g.), and boiling for 2 hours; the disulphide separated quantitatively as a microcrystalline orange-brown powder, m. p. 230—234° (Found : N, 7.5; S, 20.5. $C_{14}H_8O_6N_2S_2$ requires N, 7.7; S, 17.6%); yield, 60 g. By extracting the crude product (10 g.) with boiling glacial acetic acid (two portions of 100 c.c.) its m. p. could be raised to 257° (8 g.) (Found : N, 7.5; S, 17.6%), and the first extract deposited on cooling a mixture of two kinds of crystals (0.7 g.) which were mechanically separated and proved to be sulphur and a

substance of m. p. 220°; this appears to be a mixture containing mainly the monosulphide (Found: N, 8.5; S, 12.2. Calc.: N, 8.4; S, 9.6%). The second extract also deposited this product, m. p. 220°. The first extract on dilution with water gave a pale straw-coloured substance (0.7 g.), m. p. 207—210° (Found: N, 8.0; S, 14.6%), probably impure monosulphide.

Dioxime. The disulphide (3.5 g.), suspended in alcohol (60 c.c.), was boiled under reflux for 1 hour during the gradual addition of a solution of hydroxylamine hydrochloride (1.6 g.) and sodium acetate (2.6 g.) in water (5 c.c.)—longer boiling produced an inferior product. The hot mixture was filtered, the residue extracted with hot alcohol, and the extract added to the filtrate. The *dioxime* separates from alcohol as a straw-coloured microcrystalline powder which does not melt but decomposes violently between 140° and 160° (yield, 50%) (Found: N, 14.0; S, 16.5. $C_{14}H_{10}O_6N_4S_2$ requires N, 14.2; S, 16.2%); it is insoluble in ether, but moderately soluble in acetic acid.

Di-p-nitrophenylhydrazone. The disulphide (0.36 g.), dissolved in hot glacial acetic acid (100 c.c.), was treated at 50—60° with a solution of *p*-nitrophenylhydrazine (0.36 g.) in glacial acetic acid (5 c.c.); the hydrazone was deposited very gradually, although quantitatively, as red micro-needles, m. p. 283—284° (decomp.) (Found: S, 9.8. $C_{26}H_{18}O_8N_8S_2$ requires S, 10.1%). Alkalis give an immediate reddish-purple colour.

3 : 3'-Dinitrodibenzaldehyde 4 : 4'-Disulphide.—This is prepared almost quantitatively as above from 4-chloro-3-nitrobenzaldehyde. The crude product is practically pure (m. p. 228—232°), and crystallises from glacial acetic acid in bright yellow needles, m. p. 237—238° (Found: N, 7.8; S, 17.7. $C_{14}H_8O_6N_2S_2$ requires N, 7.7; S, 17.6%).

Dioxime. Oximation as described above was complete in 15 minutes, as shown by the entire solubility of the product in aqueous sodium hydroxide. It is very sparingly soluble in all the usual solvents and crystallises from glacial acetic acid in fine, yellow needles, m. p. 260—261° (Found: N, 14.1; S, 16.3. $C_{14}H_{10}O_6N_4S_2$ requires N, 14.2; S, 16.2%).

Behaviour towards Aqueous Sodium Hydroxide.—The yellow solution of this dioxime in cold aqueous sodium hydroxide undergoes the following sequence of colour changes during 15—30 minutes: yellow, yellowish-green, olive-green, deep green, reddish-green, red. When the alkali is added to a hot aqueous suspension of the dioxime, the initial deep green colour rapidly turns to red. On acidification of the red solution with acetic or hydrochloric acid, a substance is precipitated (? isomeric dioxime) which possesses a

deeper yellow colour than the original and is more soluble in acetic acid, acetone, or methyl or ethyl alcohol. This product separates from alcohol in crystalline clusters, m. p. 230—232° (decomp.; shrinking at 160—170°) (Found: N, 14.0; S, 15.9. $C_{14}H_{10}O_6N_4S_2$ requires N, 14.2; S, 16.2%). The change at 160—170° increases in violence with the rate of heating, and becomes explosive if the m.p. tube is plunged in a bath at 170°. Probably this more labile substance is in a similar physical state to the dioxime of 3 : 3'-dinitrodibenzaldehyde 6 : 6'-disulphide above.

Di-p-nitrophenylhydrazone. This may be prepared as above, except that the disulphide is dissolved in only 30 c.c. of glacial acetic acid. The product separates immediately as a fine, orange-red, microcrystalline powder, m. p. 305—310° (decomp.) (Found: S, 10.0. $C_{26}H_{18}O_8N_8S_2$ requires S, 10.1%); it gives a claret colour with alkalis.

Preparation of Thioethers from the Disulphides.

3-Nitro-6-methylthiolbenzaldehyde.—The corresponding disulphide (10 g., m. p. 257°), suspended in alcohol (50 c.c.), was treated gradually with a solution of sodium hydroxide (12 g.) and crystallised sodium sulphide (5 g.) in water (60 c.c.). Dissolution rapidly ensued with rise of temperature, and after the dark red mixture had been kept at 50—60° for 15 minutes, it was cooled, diluted with water (100 c.c.), and vigorously stirred with methyl sulphate (10 c.c.). The granular product (8.8 g.) was extracted with hot 60% acetic acid and left a very sparingly soluble product (this contained an aldehyde group, but has not been identified). The *3-nitro-6-methylthiolbenzaldehyde* was precipitated by dilution of the acetic acid extract, and on recrystallisation from this acid it separated in pale straw-coloured needles, m. p. 159—160° (Found: N, 7.2; S, 16.3. $C_8H_7O_3NS$ requires N, 7.1; S, 16.2%). The by-product was always obtained in spite of many attempts to prevent its formation under different conditions; its production was minimised by the vigorous agitation.

The *oxime* crystallises from alcohol in colourless needles, m. p. 187° (Found: N, 13.4; S, 15.2. $C_8H_8O_3N_2S$ requires N, 13.2; S, 15.1%), and forms a pale yellow, sparingly soluble *sodium* salt. The *p-nitrophenylhydrazone* crystallises from glacial acetic acid in reddish-orange needles, m. p. 250—252° (Found: S, 9.8. $C_{14}H_{12}O_4N_4S$ requires S, 9.6%), and gives a claret colour with alkalis.

3-Nitro-4-methylthiolbenzaldehyde.—When 3 : 3'-dinitrodibenzaldehyde 4 : 4'-disulphide is reduced by the above procedure, it is essential that the time and temperature of reduction be rigidly

adhered to; methylation then gives a bright yellow, flocculent precipitate, which is very difficult to filter off and dry; dilution of the reaction mixture with three times its volume of water, however, facilitates the filtration (yield, 92%). Extraction with 60% acetic acid leaves almost pure 3-nitro-4-methylthiolbenzaldehyde, which crystallises from dilute acetic acid in yellow plates, m. p. 141—142° (Found: N, 7.3; S, 16.0. $C_8H_7O_3NS$ requires N, 7.1; S, 16.2%).

The acetic acid extract contained in addition to the above product a non-aldehydic substance which was separated by oximation as follows: The crude product (10 g.), suspended in alcohol (60 c.c.), was boiled for 2 hours under reflux with a solution of hydroxylamine hydrochloride (3.5 g.) and sodium acetate (6 g.) in water (5 c.c.); the mixture was diluted with water (100 c.c.), made alkaline with sodium hydroxide, and heated to 50°, whereby about 70% dissolved. On acidification of the filtered solution, 3-nitro-4-methylthiolbenzaldoxime was precipitated; it crystallised from alcohol in yellow needles, m. p. 210° (Found: N, 13.5; S, 15.2. $C_8H_8O_3N_2S$ requires N, 13.3; S, 15.1%). This product was totally insoluble in water, only sparingly soluble in the usual solvents, and formed an orange sodium salt which gave a red solution in water. 3-Nitro-4-methylthiolbenzaldehyde-*p*-nitrophenylhydrazone crystallises from glacial acetic acid as an orange, microcrystalline powder, m. p. 294—296° (decomp.) (Found: S, 9.7. $C_{14}H_{12}O_4N_4S$ requires S, 9.6%), and gives a claret colour with alkalis.

3-Nitroso-4-methylthiolbenzyl Alcohol (?).—The residue (3 g.) from the foregoing oximation separation crystallises from hot water in orange-yellow needles, m. p. 127°, and is moderately soluble in the usual solvents. The colours given with concentrated sulphuric acid and alcoholic potassium hydroxide are light cherry-red and deep reddish-orange, respectively, in contrast to the deep red and pale yellow given by 3-nitro-4-methylthiolbenzaldehyde. The product forms neither an oxime nor a *p*-nitrophenylhydrazone; it does not respond to Liebermann's nitrosoamine reaction, but when heated with hydriodic acid (*d* 1.7) it gives methyl iodide and a mercaptan. Further, it only gradually gives a silver mirror when warmed with ammoniacal silver nitrate, and is, in general, a less active reducing agent than the above thioether (Found: C, 52.2, 52.3, 52.3; H, 5.31, 5.26, 5.25; N, 7.72, 7.76, 7.7; S, 17.3, 17.3, 17.4; *M*, cryoscopic in naphthalene, 182, 182. $C_8H_9O_2NS$ requires C, 52.4; H, 4.9; N, 7.65; S, 17.4%; *M*, 183). On reduction with titanous sulphate, only 3 atoms of hydrogen were used, but 3-nitro-4-methylthiolbenzaldehyde consumed only 5 atoms instead of the anticipated 6. The data agree with those required for 3-nitroso-

4-methylthiolbenzyl alcohol, but this constitution is only tentatively adopted.

Reduction of the Nitrobenzaldehyde Thioethers and Preparation of the Chlorobenzaldehyde Thioethers.—The thioether (5 g.), suspended in water (80 c.c.), was reduced by adding sodium hyposulphite (18 g.) all at once (about 1 g. of an insoluble complex by-product was invariably formed). The resulting aminobenzaldehyde thioether could be precipitated by alkalis, but was almost unfilterable and resinified rapidly on keeping (compare *m*-aminobenzaldehyde); the reaction mixture was therefore acidified at 0–10° with hydrochloric acid, diazotised by solid nitrite (12 g.), and decomposed in the usual way with cuprous chloride, the chloro-compound being removed by distillation with steam.

3-Chloro-6-methylthiolbenzaldehyde is readily soluble in the usual solvents and crystallises from alcohol in colourless cubes, m. p. 65° (Found: Cl, 19.1. C_8H_7OClS requires Cl, 19.0%); yield, 1.6 g. Its *oxime* crystallises from alcohol in colourless needles, m. p. 114° (Found: Cl, 17.5. C_8H_8ONClS requires Cl, 17.6%), and its *p*-nitrophenylhydrazone from glacial acetic acid in orange needles, m. p. 246°, giving a reddish-purple colour with alkalis.

3-Chloro-4-methylthiolbenzaldehyde was obtained in much smaller yield than its isomeride, and was not so readily volatile in steam. It is soluble in the usual solvents and crystallises from alcohol in colourless needles, m. p. 58–59° (Found: Cl, 18.9%). Its *oxime* crystallises from alcohol in colourless needles, m. p. 134° (Found: Cl, 17.6%), and the *p*-nitrophenylhydrazone from glacial acetic acid in scarlet micro-needles, m. p. 222–223°, which give a bluish-purple colour with alkalis.

Reduction of the Oximes of 3-Nitro-4- and -6-methylthiolbenzaldehyde.—The oxime (2 g.), dissolved in 20% aqueous sodium hydroxide (4 c.c.), was added to a boiling solution of ferrous sulphate (18 g.; crystallised) in water (100 c.c.); ammonia was added periodically and the boiling continued for 1 hour. The hot mixture was filtered, and the aminomethylthiolbenzaldoxime separated in colourless needles on cooling; yield, 80%.

3-Amino-6-methylthiolbenzaldoxime, m. p. 140° (Found: N, 15.5. $C_8H_{10}ON_2S$ requires N, 15.4%), was treated with bromine water in hydrochloric acid solution at 0°, whereupon 2 : 4 : 5 : 6-tetrabromo-3-aminobenzaldoxime was formed; it crystallised in colourless needles, m. p. 202–203° (Found: Br, 70.0. $C_7H_4ON_2Br_4$ requires Br, 70.8%), from glacial acetic acid. This product contains no sulphur, is soluble in alkalis, and diazotises in concentrated sulphuric acid solution; the diluted diazo-solution couples with alkaline β -naphthol.

3-*Amino-4-methylthiolbenzaldoxime*, m. p. 100° (Found : N, 15·3%), is decomposed by bromine into a tarry complex substance insoluble in alkalis.

Analytical Note.—Estimations of sulphur by the Carius method in products containing the methylthiol group were without exception too low, but the oxidation method with sodium peroxide proved satisfactory.

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TECHNICAL COLLEGE, HUDDERSFIELD.

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