140. *A Preparation of* m-*Dimethylaminobenzaldehyde. Part II.*

By Wesley Cocker, J. O. Harris, and (in part) J. V. Loach.

The method used by Bottomley, Cocker, and Nanney (J., 1937, 1891) for the preparation of *m*-dimethylaminobenzaldehyde has been superseded by a method in which *m*-nitrobenzaldehyde dimethylacetal is reduced in aqueous solution with sodium sulphide to *m*-aminobenzaldehyde dimethylacetal and then methylated with methyl sulphate. The quaternary salt is decomposed by hot caustic potash solution, and *m*-dimethylaminobenzaldehyde obtained in yields exceeding 70%, calculated on the *m*-nitrobenzaldehyde used.

The preparation of the acetal of *m*-aminobenzaldehyde previously described (*loc. cit.*) required the use of somewhat costly materials. It has now been found simpler to reduce *m*-nitrobenzaldehyde dimethylacetal with aqueous sodium sulphide (compare Haworth and Lapworth, J., 1922, **121**, 76), since this acetal can be obtained in almost theoretical yield by the method of Voss and Blanke (*Annalen*, 1931, **485**, 271). No trace of *m*-dimethylaminobenzaldehyde dimethylacetal was found at any stage of the reaction, nor have we been able to prepare it by any of the known methods from *m*-dimethylaminobenzaldehyde, and it appears that even in alkaline solution it is incapable of existence.

Unlike the acetal of *m*-aminobenzaldehyde, *m*-nitrobenzaldehyde dimethylacetal is stable for short periods even in presence of mineral acid. This is not in disharmony with the known order of electron-releasing effects of NMe_2, NH_2, and NO_2 and the accepted mechanism of the decomposition of acetals, even though the acetal group be in the *m*-position to these groups.

m-Dimethylaminobenzaldehyde is unaffected even by prolonged boiling with concentrated caustic potash solution (compare Clemo and Smith, J., 1928, 2423, on *p*-dimethylaminobenzaldehyde). Attempts to prepare a " benzoin " from it have been futile, nor was it possible to prepare a " mixed benzoin " with piperonal, although Buck and Ide (*J. Amer. Chem. Soc.*, 1931, **53**, 2353) record the preparation of similar compounds from *p*-dimethylaminobenzaldehyde. In all our experiments along these lines the aldehyde was recovered quantitatively unchanged. In addition we have been unable to form a bisulphite compound. This evidence points to the feeble additive power of the carbonyl groups for anionoidal reagents.

o-Dimethylaminobenzaldehyde was similarly obtained from *o*-nitrobenzaldehyde, but the yields were only about 40% of the theoretical. Deacetalisation took place during methylation, but in addition, although a considerable excess of methyl sulphate over the theoretical quantity required for quaternary salt formation was used, the methylation apparently stopped at the tertiary amine stage. Possibly the presence of the *o*-aldehydo-group is responsible for this.

Experimental.

m-*Nitrobenzaldehyde Dimethylacetal.*—A mixture of *m*-nitrobenzaldehyde (76 g.), methyl sulphite (60 g.), and methyl alcohol (60 c.c.) was treated with a trace of dry hydrogen chloride and refluxed on the water-bath for 8 hours, sulphur dioxide being evolved as acetalisation took place. The homogeneous mixture was poured into a solution of sodium methoxide (sodium, 2 g.; methyl alcohol, 40 c.c.) to neutralise free acid present, and the excess of methyl sulphite decomposed by shaking for ½ hour with 15% sodium hydroxide solution (200 c.c.). The mixture was diluted to 1000 c.c. with water, and the acetal extracted with ether and washed with water. After removal of solvent the acetal was normally reduced without purification, but it may be purified by drying over sodium sulphate and distillation in a vacuum; b. p. 159°/20 mm. Yield, 96—98 g. or 97% of the theoretical (compare Claisen, *Ber.*, 1898, **31**, 1016; Haworth and Lapworth, *loc. cit.*).

m-*Aminobenzaldehyde Dimethylacetal.*—The above acetal was reduced by a modification of a method of Haworth and Lapworth. It was slowly poured down a condenser into a hot agitated mixture prepared from crystalline sodium sulphide (300 g. in 300 c.c. of water) and concentrated hydrochloric acid (125 g.). Reaction commenced almost immediately and was completed by boiling for a further 8 hours. The crude acetal was extracted with ether and washed with water.

Methylation. The ethereal extracts from the above, containing about 70 g. of crude acetal, were shaken with 300 c.c. of 7% sodium carbonate solution and 20 g. of methyl sulphate for 8 hours, and the process continued by the addition at 8-hour intervals of further similar quantities of methyl sulphate and sodium carbonate until 220 g. of methyl sulphate (1·7 mols.) had been added. The ethereal layer was separated, and the alkaline layer concentrated to about 500 c.c. It was then treated with 500 g. of solid caustic potash, with cooling to prevent loss of *m*-dimethylaminobenzaldehyde, which separated as an upper oily layer as the potash dissolved. The mixture was distilled, water being added to keep the volume constant. The aldehyde was extracted from the distillate with ether, dried (anhydrous potassium carbonate), and distilled in a vacuum. The yield was 46 g. (74% of the theoretical, calc. on the *m*-nitrobenzaldehyde); b. p. 112°/7 mm. The aldehyde thus prepared corresponded in all its properties with that prepared bv the method described in Part I (*loc. cit.*). It gave a semicarbazone, m. p. 228—229° (Found: N, 27·0. Calc. for $C_{10}H_{14}ON_4$: N, 27·2%), and an oxime, m. p. 75—76° (Found: C, 65·9; H, 7·2; N, 17·1. Calc. for $C_9H_{12}ON_2$: C, 65·85; H, 7·3; N, 17·1%). The 2 : 4-*dinitrophenylhydrazone hydrochloride* formed scarlet, ill-defined crystals, m. p. 231° (decomp.), from 25% hydrochloric acid (Found: N, 18·6; Cl, 9·4. $C_{15}H_{15}O_4N_5$,HCl requires N, 19·15; Cl, 9·7%). When heated with water, this rapidly lost hydrogen chloride and became oily, possibly yielding the free 2 : 4-dinitrophenylhydrazone and some free aldehyde. The *chloroplatinate* was deposited from hot water in transparent red-yellow needles, m. p. 167—168° (decomp. on rapid heating) (Found: C, 29·2; H, 3·75; Pt, 26·3. $2C_9H_{11}ON,H_2PtCl_6,2H_2O$ requires C, 29·1; H,3·2; Pt, 26·3%).

3 : 3′-*Bisdimethylaminobenzylideneazine.*—A mixture of *m*-dimethylaminobenzaldehyde (1 g.), hydrazine sulphate (2 g.), and alcohol (5 c.c.) was refluxed for 15 minutes, cooled, and treated with 15% caustic soda solution to remove sulphuric acid. The yellow precipitate, recrystallised from alcohol, formed large, transparent, flat, square plates, m. p. 153—154° (Found: N, 19·1. $C_{18}H_{22}N_4$ requires N, 19·2%).

m-*Dimethylaminobenzylideneacetophenone*, obtained from the aldehyde (1 g.), acetophenone (0·8 g.), alcohol (10 c.c.) and 15% caustic soda solution (1 c.c.) after 24 hours at room temperature, gave tufts of bright orange, rectangular plates, m. p. 108—109°, from 95% alcohol, readily soluble in benzene (Found: C, 81·4; H, 6·6; N, 5·8. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%).

6-*Nitroso*-m-*dimethylaminobenzaldehyde*, obtained by addition of sodium nitrite solution to an ice-cold solution of *m*-dimethylaminobenzaldehyde in N-hydrochloric acid, formed masses of bright yellow needles, m. p. 129·5—130°, from 95% alcohol (Found: N, 15·6. $C_9H_{10}O_2N_2$ requires N, 15·7%). It had a peppery odour and was readily soluble in concentrated hydrochloric acid, from which caustic soda precipitated it. The fact that the nitroso-group is in the *p*-position to the dimethylamino-group was confirmed by conversion into the corresponding "methylene-blue."

Crystal-violet Analogue.—*m*-Dimethylaminobenzaldehyde (2 g.), dimethylaniline (3·3 g.), and anhydrous zinc chloride (3·3 g.) were heated with stirring in an open dish for 5½ hours. The excess of volatile reagents was removed in steam, and the residual brown-yellow solid washed with water, dried, and recrystallised from absolute alcohol. The *leuco-base* (3·1 g.; 62% of the theoretical yield) formed long, green-yellow, transparent prisms, m. p. 149—149·5° (Found: C, 80·1; H, 8·2; N, 11·3. $C_{25}H_{31}N_3$ requires C, 80·4; H, 8·3; N, 11·3%). It was readily oxidised by lead peroxide to the colour base, which was intermediate in colour between malachite-green and crystal-violet.

The leuco-base prepared from diethylaniline and *m*-dimethylaminobenzaldehyde was obtained from alcohol as green-yellow, transparent prisms, m. p. 72—73·5°. It was readily oxidised to the deep green-violet colour base.

Attempted "Benzoin" Formation.—1. A mixture of *m*-dimethylaminobenzaldehyde (6 g.), potassium cyanide (3 g.), and alcohol (20 c.c.) was refluxed for 3 hours, cooled, and kept for 2 days. No crystals were deposited. Water was then added, and the precipitated oil extracted with ether. Yield, 7 g. Converted into semicarbazone, it gave an 80% yield of almost pure *m*-dimethylaminobenzaldehydesemicarbazone, indicating almost complete recovery of aldehyde.

2. A mixture of the aldehyde (3 g.), piperonal (3 g.), potassium cyanide (2 g.), and alcohol (15 c.c.) was refluxed for 3 hours. After 3 days the deposit was collected (0·9 g., m. p. 118—119°). It gave no depression of m. p. with piperoin. The alcoholic residue was diluted with water, and the oil extracted with ether. The extract, washed with hydrochloric acid, yielded 1·2 g. of piperonal and 2·5 g. of the aldehyde. Similar results were obtained when *m*-dimethylaminobenzaldehyde, benzoin, and potassium cyanide were heated together in alcohol. All the

reactants were recovered unchanged (compare Buck and Ide, *J. Amer. Chem. Soc.*, **1931**, **53**, 2785).

Experiments on the Preparation of o-*Dimethylaminobenzaldehyde.*—Using *o*-nitrobenzaldehyde (38 g.), methyl sulphite (30 g.), and methyl alcohol (30 c.c.) with a trace of dry hydrogen chloride as catalyst, we obtained the acetal in a yield of 45 g. (92% of the theoretical), b. p. 141—144°/15 mm. (compare Fischer, *Ber.*, 1897, **30**, 3053; 1898, **31**, 345). On reduction as described previously, 30 g. of *o*-aminobenzaldehyde dimethylacetal were obtained as a pale yellow liquid, which readily reverted to the free aldehyde even in the absence of acid (compare Freundler and De Laborderie, *Bull. Soc. chim.*, 1907, **1**, 234).

The methylation was carried out with methyl sulphate (115 g.; 1·7 mols.). After 2 days the ethereal layer was removed and distilled in steam, yielding crude *o*-dimethylaminobenzaldehyde. On distillation in a vacuum it yielded 12 g. (37% of the theoretical) of a pale yellow oil, b. p. 132°/25 mm. This was almost pure aldehyde. The aqueous layer from the methylation was concentrated to about 300 c.c., treated with 300 g. of solid caustic potash, and distilled. No oil passed over, but the aqueous distillate gave about 1 g. of aldehyde on continuous extraction with ether. Similarly the strongly alkaline solution yielded only a trace of oil.

o-Dimethylaminobenzaldehyde yielded a bisulphite compound after 2 hours' shaking with saturated sodium bisulphite. This yielded pure aldehyde on distillation with sodium carbonate solution. The *semicarbazone* crystallised from a large amount of alcohol in clusters of colourless transparent prisms, m. p. 224—225° (decomp.) (Found: N, 27·2. $C_{10}H_{14}ON_4$ requires N, 27·2%). The aldehyde yielded 2 : 2′-bisdimethylaminobenzylideneazine, m. p. 148—149° (Cohn, *Monatsh.*, 1904, **25**, 371) (Found: N, 18·9. Calc. for $C_{18}H_{22}N_4$: N, 19·0%).

o-*Dimethylaminobenzylideneacetophenone* separated from 95% alcohol in yellow, six-sided, pointed prisms, m. p. 66—67° (Found: N, 5·9. $C_{17}H_{17}ON$ requires N, 5·6%).

The authors express their thanks to Professor A. Lapworth, F.R.S., for his interest in the investigation and to the Chemical Society for a grant.

UNIVERSITY COLLEGE, EXETER.
UNIVERSITY OF MANCHESTER.

[*Received, March* 29*th*, 1938.]