

399. Preparation of *m*-Dimethylaminobenzaldehyde. Part I.

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m-Dimethylaminobenzaldehyde has been conveniently prepared from *m*-aminobenzaldehyde by methylation of its acetal and distillation of the quaternary iodide.

p-DIMETHYLAMINO BENZALDEHYDE is readily prepared by a variety of technical processes (D.R.-PP. 105,103, 105,105, etc.) and the *o*-isomer is also easily obtained in 60% yield by the methylation of anthranil (Bamberger, *Ber.*, 1904, **37**, 973). The direct methylation of *o*-aminobenzaldehyde is, however, not as satisfactory (Bamberger, *loc. cit.*, p. 989). Attempts to methylate the supposed *m*-aminobenzaldehyde (anhydro-compound, C₇H₅N) by direct methods are futile and the materials remain unchanged, but the methylation of *m*-aminobenzaldehydediethylacetal by means of methyl iodide proceeds very smoothly. The acetalisation of the anhydro-compound is effected by means of a mixture of 5% alcoholic hydrogen chloride and ethyl orthoformate, the latter ensuring no loss of acetal by the presence of moisture in the reactants, since it is more readily decomposed by acid than the acetal (compare Claisen, *Ber.*, 1893, **26**, 2731; 1896, **29**, 1005, 2931; 1900, **33**, 3778; 1903, **36**, 3664; 1907, **40**, 3903; *Annalen*, 1894, **281**, 312; 1896, **291**, 43; 1897, **297**, 3). The yields of acetal by this method have been as high as 85%, which compare very favourably with the yields obtained by Haworth and Lapworth (J., 1922, **121**, 76) by the reduction of *m*-nitrobenzaldehydediethylacetal with sodium sulphide. During the methylation process deacetalisation takes place and the final product is the *quaternary salt* of the free aldehyde. This is the more interesting since deacetalisation in alkali is unusual. It is probable that it takes place before quaternary salt formation, as theoretically the acetal of the quaternary salt [CH(OEt)₂·C₆H₄·NMe₃I] should be as stable as that of *m*-nitrobenzaldehyde. The quaternary salt of the free aldehyde is, however, smoothly decomposed on distillation under reduced pressure into *m*-dimethylaminobenzaldehyde and a little of its hydriodide, the overall yields being about 35% on the anhydro-*m*-aminobenzaldehyde.

EXPERIMENTAL.

m-Aminobenzaldehydediethylacetal.—A mixture of commercial *m*-aminobenzaldehyde (25 g.), 5% alcoholic hydrogen chloride (175 g.), and ethyl orthoformate (75 g.) was kept in a stoppered

flask for 12 hours at room temperature, sodium ethoxide (prepared from 8 g. of sodium and 175 c.c. of alcohol) then added to the well-agitated mixture to remove the excess of hydrogen chloride, and the whole diluted with water (4—5 vols.). The precipitated pale yellow oil was extracted with ether in a continuous apparatus, dried (anhydrous potassium carbonate), and recovered (36 g.) on the water-bath at 60°; as a rule it was directly used for methylation experiments as described below. For analysis a sample was fractionally distilled in a vacuum, the portion, b. p. 137—139°/5 mm., being almost pure acetal (Found: C, 67.5; H, 8.7; N, 7.5. Calc. for $C_{11}H_{17}O_2N$: C, 67.7; H, 8.7; N, 7.2%). Its ready conversion into the free amino-aldehyde by warming with a trace of mineral acid establishes its identity (compare Haworth and Lapworth, *loc. cit.*). Although distillation of the acetal is described, this procedure is not to be recommended, as much decomposition takes place during the process and even during the removal of ether from an ethereal solution at temperatures above about 60°.

Methylation. The crude acetal (36 g.), suspended in 10% aqueous sodium carbonate (200 c.c.), was heated under reflux on the steam-bath with methyl iodide (91 g.; 1.16 mols.), added at intervals during 24 hours. The cooled mixture was diluted with water (200 c.c.) and extracted (continuous) with ether to remove unchanged acetal and methyl iodide. The liquid, containing deposited quaternary salt, was boiled with animal charcoal, filtered hot, and concentrated. Successive crops of quaternary salt were collected, each being washed with a little ice-cold water and dried; yield, 46.5 g. (66% on *m*-aminobenzaldehyde used); m. p. 180—200° (decomp.). Recrystallisation from water gave little improvement in m. p. (Found: C, 41.5; H, 5.1. $C_{10}H_{14}ONI$ requires C, 41.2; H, 4.8%). The crystals were poorly defined, but are probably flat, transparent prisms. Aqueous solutions immediately give silver iodide with silver nitrate. The view that the quaternary salt is that of the free aldehyde is supported by the facts that gentle boiling with hydriodic acid under reflux yielded no ethyl iodide and gentle heating with nitric acid or chromic acid and sulphuric acid yielded neither ethyl nitrite nor acetaldehyde.

m-Dimethylaminobenzaldehyde.—The quaternary iodide (20 g.) was heated under reduced pressure (10—15 mm.) in a Claisen flask immersed in an oil-bath at 150—160° and finally at 190—200° until distillation ceased. The yellow distillate was filtered from *m*-dimethylaminobenzaldehyde hydriodide (about 6% of the total weight) and consisted of almost pure *m*-dimethylaminobenzaldehyde (6.6 g.; 46% yield calc. on *m*-aminobenzaldehyde). On fractionation under reduced pressure it distilled at 137.5—138°/9 mm., giving a pale yellow oil with a strong basic odour, readily soluble in mineral acids, alcohol, ether and benzene (Found: C, 72.7; H, 7.5. $C_9H_{11}ON$ requires C, 72.5; H, 7.4%). The *oxime*,* prepared by standard methods in 97—99% yield, was deposited in long, transparent, colourless prisms from aqueous alcohol, m. p. 75—76° (Found: C, 65.7; H, 7.6. $C_9H_{12}ON_2$ requires C, 65.9; H, 7.3%). The *semicarbazone* was deposited in thin, shiny, colourless plates, m. p. 218—222° (slow heating) or 228—229° (instantaneous) (Found: C, 58.5; H, 6.8. $C_{10}H_{14}ON_4$ requires C, 58.2; H, 6.8%). The methiodide, obtained by gently warming the aldehyde with methyl iodide for a few minutes, was a pale yellow solid, m. p. 185—186° (decomp.), similar in all respects to the methiodide prepared as above (Found by titration: I, 45.7. Calc. for $C_{10}H_{14}ONI$: I, 43.6%). The *picrate*, prepared in alcohol, formed flat rectangular plates, soluble in hot benzene and hot water; m. p. 147—147.5° (Found: N, 14.8. $C_{15}H_{14}O_8N_4$ requires N, 14.8%).

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* Dr. Shoppee (J., 1932, 702) obtained the oxime from aldehyde prepared according to the method described above and recorded m. p. 75.5° (private communication).