III.—3-*Nitro*-4-*amino- and the* 3 : 4-*Dihalogeno-benzaldehydes.*

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The substituted benzaldehydes described in this paper were required for an investigation of the colour and constitution of dyes of the triphenylmethane series. They were all prepared at first from 3-nitro-4-aminobenzaldehyde; later, however, by a modification of Erdmann's method (D.R.-P. 62180), the 4-halogeno-3-nitrobenzaldehydes were obtained from the 4-halogenobenzaldehydes by direct nitration.

The preparation of a mononitro-derivative of *p*-aminobenzaldehyde was patented by Kalle and Co. (D.R.-P. 89244), but Walther and Bretschneider (*J. pr. Chem.*, 1898, **57**, 535) were unable to reproduce their result. Cohn and Springer (*Monatsh.*, 1903, **24**, 87) obtained 3-nitro-4-acetamidobenzaldehyde by nitrating *p*-acetamidobenzaldehyde with a mixture of sulphuric and nitric acids, and converted it into 3-nitro-4-aminobenzaldehyde by hydrolysing it with concentrated hydrochloric acid. This method, however, gave in our hands a very poor yield of a mixture of products, and the nitration of *p*-acetamidobenzaldehyde was much improved by using diacetylorthonitric acid in acetic anhydride solution; in this case formation of *p*-acetamidobenzylidene diacetate preceded nitration. The acetate groups can be removed from 3-nitro-4-acetamidobenzylidene diacetate either separately or together.

The various melting points recorded by Cohn and Springer (*loc. cit.*) have been confirmed, and the constitutions of all the aldehydes described in this paper have been established by converting them into the corresponding benzoic acids by oxidation with neutral aqueous permanganate.

The yellow *leuco*-compound obtained by condensing 3-nitro-4-aminobenzaldehyde with diethylaniline in hydrochloric acid solution gives, on oxidation, a dye which imparts to wool a blue shade with a faint red tint. Since benzaldehyde, similarly treated, gives a brilliant green dye, the influence of substitution in the condensing aldehyde on the colour of the triphenylmethane dye appears to be pronounced and is being investigated.

EXPERIMENTAL.

3-*Nitro*-4-*aminobenzaldehyde*.

The initial material, *p*-aminobenzaldehyde, was prepared by Geigy's process (D.R.-P. 86874) from *p*-nitrotoluene (300 g.) and sodium disulphide in boiling alcohol. Three-quarters of the alcohol were recovered prior to steam distillation, which removed most (120 g.) of the *p*-toluidine simultaneously formed; the non-volatile *p*-aminobenzaldehyde was then extracted with ether.

The crude product was directly acetylated by suspension in water (200 c.c.) and treatment first with glacial acetic acid (200 c.c.), a red precipitate forming, and then gradually with acetic anhydride (160 c.c.); the reaction was completed by heating on the water-bath until the solid dissolved (30 min.). On pouring the mixture into ice-water (1500 c.c.) a yellow, crystalline solid separated, and more was obtained by making the filtrate just alkaline and adding sodium chloride. The total yield was 145 g. of a mixture of *p*-acetamidobenzaldehyde, aceto-*p*-toluidide, and a small quantity of *p*-aminobenzylidene-*p*-toluidine.

This mixture (135 g.) was heated slowly to 50° with 33% aqueous sodium bisulphite (400 c.c.) and water (200 c.c.) and cooled, the undissolved portion was well washed, and the combined filtrate and washings were treated with 20% aqueous sodium hydroxide as long as *p*-acetamidobenzaldehyde was precipitated. This substance was colourless when freshly prepared but became more and more yellow on keeping. It crystallised from water in prisms, m. p. 156° (Janse, *Rec. trav. chim.*, 1921, **40**, 285, gives m. p. 152°) (Found: N, 8·7. Calc.: N, 8·6%). The p-*nitrophenylhydrazone* separated from alcohol in deep orange needles, m. p. 264—265° (Found: N, 19·0. $C_{15}H_{14}O_3N_4$ requires N, 18·8%).

The insoluble portion of the above mixture, on fractional crystallisation from alcohol, gave p-*acetamidobenzylidene*-p-*toluidine* as the least soluble constituent; this was identified by comparison with a specimen, m. p. 187—188°, prepared from *p*-toluidine and *p*-acetamidobenzaldehyde (Found: N, 11·2. $C_{16}H_{16}ON_2$ requires N, 11·1%).

During the above operations, partial change of the *p*-aminobenzaldehyde into its amorphous, insoluble modification occurred, and this could only be acetylated by warming with acetic anhydride.

Nitration of p-*Acetamidobenzaldehyde.*—The aldehyde (30 g.) was obtained in small crystals by rapidly cooling a warm solution in acetic anhydride (75 c.c.) to 20°. Diacetylorthonitric acid (40 c.c.) was gradually added, the temperature not being allowed to exceed 40—50°. The crystals dissolved; after the addition of about 12 c.c. of diacetylorthonitric acid colourless plates of *p*-acetamidobenzylidene diacetate separated; these dissolved on further addition of the acid and remained in solution even on cooling. Nitration had not yet occurred, and numerous experiments have indicated the preliminary formation of this diacetate to be essential to smooth nitration. After the diacetylnitric acid had been added, the mixture was kept at 50° for 15 minutes, cooled, and poured into ice-water (400 c.c.) with vigorous stirring. After 2 hours, the 3-*nitro*-4-*acetamidobenzylidene diacetate* produced was filtered off, washed, and dried (yield, 45 g.). It gave no hydrazone and crystallised from alcohol in pale yellow leaflets, m. p. 114° (Found: N, 8·7. $C_{13}H_{14}O_7N_2$ requires N, 9·0%). It was easily soluble in alcohol or glacial acetic acid but sparingly soluble in chloroform.

Unlike *p*-acetamidobenzaldehyde, *p*-acetamidobenzylidene diacetate remains unchanged in colour on keeping. It melts at 170° (Blanksma, *Chem. Weekblad*, 1909, **6**, 899, gives m. p. 166°) (Found : N, 5·5. Calc.: N, 5·3%).

Hydrolysis of 3-*Nitro*-4-*acetamidobenzylidene Diacetate.*—The diacetate (10 g.) was heated on the water-bath for 15 minutes with concentrated hydrochloric acid (25 c.c.). Separation of 3-*nitro*-4-*aminobenzaldehyde* from the cherry-coloured solution then began and was completed by the addition of water. The product was only slightly soluble in concentrated or dilute hydrochloric acid, cold alcohol, or glacial acetic acid; it deepened in colour from yellow through orange to old-gold on prolonged contact with hot hydrochloric acid, and crystallised from alcohol or water in orange needles, m. p. 191° (Cohn and Springer, *loc. cit.*, give m. p. 190·5—191°) (Found : N, 17·0. Calc.: N, 16·9%).

3-Nitro-4-acetamidobenzaldehyde was obtained when the diacetate (2 g.) was triturated with concentrated hydrochloric acid (10 c.c.) and the mixture was heated gradually to 40° until solution occurred, and then cooled rapidly and thrown into cold water (yield, 1·3 g.). It crystallised from hot water in pale yellow needles, m. p. 155° (Cohn and Springer, *loc. cit.*, give m. p. 155°) (Found : N, 12·9. Calc.: N, 13·4%). The p-*nitrophenylhydrazone* crystallises from alcohol in deep orange needles, m. p. 289—290° (Found : N, 20·6. $C_{15}H_{13}O_5N_5$ requires N, 20·5%).

3-*Nitro*-4-*aminobenzaldehyde*-p-*nitrophenylhydrazone* crystallises from glacial acetic acid in dark maroon needles, m. p. 270—272° (Found : N, 23·1. $C_{13}H_{11}O_4N_5$ requires N, 23·3%).

3-*Nitro*-4-*aminobenzaldoxime* crystallises from dilute alcohol in orange needles, m. p. 207°, and gives a deep red solution in aqueous sodium hydroxide (Found : N, 23·05. $C_7H_7O_3N_3$ requires N, 23·2%).

3-*Nitrobenzaldehyde*-4-*azo*-β-*naphthol* crystallises from glacial acetic acid in fine, crimson needles, m. p. 271° (Found : N, 13·2. $C_{17}H_{11}O_4N_3$ requires N, 13·6%). It is very slightly soluble in all the usual solvents and gives an insoluble, brick-red sodium salt.

Diazotisation of 3-*Nitro*-4-*aminobenzaldehyde.*—A solution of the aldehyde (4 g.) in warm 80% acetic acid (30 c.c.) was cooled, and to the paste of fine crystals thus obtained 20% aqueous sodium nitrite (10 c.c.) was added, followed gradually by concentrated hydrochloric acid (10 c.c.), the temperature being kept just below 20°. (Diazotisation takes place more readily at *ca.* 20° than at 0°, and without loss of nitrogen.) After the excess of nitrous acid had been destroyed by carbamide, the 4-halogeno-3-nitrobenzaldehydes were obtained by the usual Sandmeyer processes. The

4-chloro-compound could be obtained only in about 30% yield, probably owing to the formation of a diphenyl derivative, but 4-bromo- and 4-iodo-3-nitrobenzaldehydes were isolated in nearly quantitative amounts and almost pure.

The p-*Nitrophenylhydrazones of the* 4-*Halogeno*-3-*nitro- and* 3 : 4-*Dihalogeno-benzaldehydes.*

The *p*-nitrophenylhydrazones of the 4-halogeno-3-nitrobenzaldehydes are very sparingly soluble in the usual solvents and the conditions for their preparation described below must be carefully observed if they are to be obtained crystalline. When heated, they exhibit a colour change from orange to red at *ca.* 160° which is not reversed on cooling (compare Chattaway and Walker, J., 1924, **125**, 1210). The *p*-nitrophenylhydrazones of the 3 : 4-dihalogenobenzaldehydes are much more soluble.

A solution of the aldehyde (0·1 g.) in cold alcohol (5 c.c.) is made faintly turbid by dilution with water and is then heated to boiling, and a solution of *p*-nitrophenylhydrazine (0·6 g.) in alcohol (3 c.c.) and glacial acetic acid (0·5 c.c.) at the same temperature is added. The crystalline product that separates immediately has a very sharp m. p. When the method of preparation described by Hodgson and Beard (J., 1925, **127**, 880) is used, the product is non-crystalline and very sparingly soluble and has an indefinite m. p.

The 4-*Halogeno*-3-*nitrobenzaldehydes.*

4-Chloro-3-nitrobenzaldehyde forms colourless needles, m. p. 64·5°, from dilute alcohol (Erdmann, *loc. cit.*, gives m. p. 64·5°) (Found : Cl, 18·9. Calc. : Cl, 19·1%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 278—279° (Found : Cl, 11·1. $C_{13}H_9O_4N_4Cl$ requires Cl, 11·1%) and the *oxime* crystallises from alcohol in pale yellow needles, m. p. 146° (Found : Cl, 17·6. $C_7H_5O_3N_2Cl$ requires Cl, 17·7%).

4-Chloro-3-nitrobenzoic acid crystallises from dilute acetic acid in colourless prisms, m. p. 180—181° (Hübner, *Z. Chem.*, 1866, **6**, 5, gives m. p. 178—180°) (Found : Cl, 17·5. Calc. : Cl, 17·6%).

4-Bromo-3-nitrobenzaldehyde separates from alcohol in pale yellow needles, m. p. 106° (Schöpff, *Ber.*, 1891, **24**, 3775, gives m. p. 103°) (Found : Br, 33·8. Calc. : Br, 34·0%), and is very volatile in steam. The p-*nitrophenylhydrazone* forms yellow, micro-crystalline needles, m. p. 282—283° (Found : Br, 21·8. $C_{13}H_9O_4N_4Br$ requires Br, 21·9%), and the oxime crystallises from dilute alcohol in orange needles, m. p. 154° (Schöpff, *loc. cit.*, gives m. p. 145—146°) (Found : Br, 32·3. Calc. : Br, 32·5%).

4-Bromo-3-nitrobenzoic acid crystallises from dilute acetic acid in colourless, fern-like masses, m. p. 203° (Hübner, Philipp, and Ohly, *Annalen*, 1867, **143**, 248, give m. p. 199°) (Found : Br, 32·3. Calc. : Br, 32·5%).

4-*Iodo*-3-*nitrobenzaldehyde* is only very slowly volatile in steam. It is sparingly soluble in cold alcohol and crystallises from a hot solution in deep yellow needles, m. p. 141° (Found : I, 45·4. $C_7H_4O_3NI$ requires I, 45·8%). The p-*nitrophenylhydrazone* forms yellow, microcrystalline needles, m. p. 277—278° (decomp.) (Found : I, 30·5. $C_{13}H_9O_4N_4I$ requires I, 30·8%). The *oxime* forms pale yellow needles, m. p. 157°, from alcohol (Found : I, 43·5. $C_7H_5O_3N_2I$ requires I, 43·5%).

4-Iodo-3-nitrobenzoic acid crystallises from alcohol in yellow prisms, m. p. 213° (Glassner, *Ber.*, 1875, **8**, 562, gives m. p. 210°) (Found : I, 43·0. Calc. : I, 43·3%).

Preparation of the 4-*Halogeno*-3-*nitrobenzaldehydes by Direct Nitration of the* 4-*Halogenobenzaldehydes*.—The aldehyde (10 g.) is added gradually to a mixture of sodium nitrate (5·5 g.) and concentrated sulphuric acid (60 g.) kept at 15—20°, and the whole is then heated at 70° for 15 minutes, cooled, and poured on to ice; the yield is almost quantitative (compare Erdmann, *loc. cit.*).

The 3 : 4-*Dihalogenobenzaldehydes.*

These aldehydes were prepared from the 4-halogeno-3-nitrobenzaldehydes by the method already described (*J. Soc. Chem. Ind.*, 1926, **45**, 91T).

3 : 4-Dichlorobenzaldehyde crystallises from alcohol in colourless needles, m. p. 44° (Erdmann and Schwechten, *Annalen*, 1890, **260**, 72, give m. p. 44°) (Found : Cl, 40·3. Calc. : Cl, 40·5%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 276—277° (Found : Cl, 22·7. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9%), and the *oxime* colourless needles, m. p. 118—119°, from dilute alcohol (E. and S., *loc. cit.*, give m. p. 114—115°) (Found : Cl, 37·1. Calc. : Cl, 37·3%).

3 : 4-Dichlorobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 201—202° (Beilstein and Kuhlberg, *Annalen*, 1869, **152**, 232, give m. p. 201—202°) (Found : Cl, 36·9. Calc. : Cl, 37·1%).

4-*Chloro*-3-*bromobenzaldehyde* forms colourless needles, m. p. 70°, from alcohol (0·1460 g.; 0·2232 g.; 0·2210 g.*). The p-*nitrophenylhydrazone* forms orange needles, m. p. 273—274° (Found : N, 12·0. $C_{13}H_9O_2N_3ClBr$ requires N, 11·8%), and the *oxime*

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* In this and in the other cases given later, the three quantities are, respectively, the weight of substance taken for analysis and the weights of mixed silver halides found and calculated.

crystallises from dilute alcohol in colourless needles, m. p. 131° (Found : N, 5·8. $C_7H_5ONClBr$ requires N, 5·5%).

4-Chloro-3-bromobenzoic acid separates from dilute acetic acid in colourless plates, m. p. 215—216° (Cohen and Raper, J., 1904, **85**, 1269, give m. p. 214°) (0·1180 g.; 0·1650 g.; 0·1657 g.).

4-*Chloro*-3-*iodobenzaldehyde* is very volatile in steam and separates from alcohol in colourless, spear-shaped crystals, m. p. 117° (0·1332 g.; 0·1846 g.; 0·1892 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 277—278° (decomp.) (Found : N, 10·6. $C_{13}H_9O_2N_3ClI$ requires N, 10·5%), and the *oxime* is obtained from dilute alcohol in colourless needles, m. p. 115—116° (Found : N, 5·1. C_7H_5ONClI requires N, 5·0%).

4-*Chloro*-3-*iodobenzoic acid* separates from dilute acetic acid in colourless plates, m. p. 216—217° (0·1412 g.; 0·1872 g.; 0·1892 g.).

3-*Chloro*-4-*bromobenzaldehyde* crystallises from alcohol in colourless needles, m. p. 52° (0·1098 g.; 0·1150 g.; 0·1157 g.). The p-*nitrophenylhydrazone* separates in orange needles, m. p. 272—273° (Found : N, 12·1. $C_{13}H_9O_2N_3ClBr$ requires N, 11·8%), and the *oxime* in colourless needles, m. p. 104°, from dilute alcohol (Found : N, 5·7. $C_7H_5ONClBr$ requires N, 5·5%).

3-Chloro-4-bromobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 219° (Cohen and Raper, J., 1904, **85**, 1262, give m. p. 218°) (0·1180 g.; 0·1652 g.; 0·1657 g.).

3 : 4-*Dibromobenzaldehyde* separates from alcohol in colourless needles, m. p. 75° (Found : Br, 60·7. $C_7H_4OBr_2$ requires Br, 60·6%). The p-*nitrophenylhydrazone* separates in orange needles, m. p. 270—274° (Found : Br, 39·9. $C_{13}H_9O_2N_3Br_2$ requires Br, 40·2%), and the *oxime* in colourless needles, m. p. 129°, from dilute alcohol (Found : Br, 57·1. $C_7H_5ONBr_2$ requires Br, 57·3%).

3 : 4-Dibromobenzoic acid crystallises from dilute acetic acid in colourless plates, m. p. 233—234° (Hübner, *Annalen*, 1884, **222**, 184, gives m. p. 232—235°) (Found : Br, 50·4. Calc. : Br, 50·7%).

4-*Bromo*-3-*iodobenzaldehyde* is obtained from alcohol in thick, colourless prisms, m. p. 127° (0·1555 g.; 0·2134 g.; 0·2115 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 265° (decomp.) (Found : N, 9·5. $C_{13}H_9O_2N_3BrI$ requires N, 9·4%), and the *oxime* colourless needles, m. p. 141°, from dilute alcohol (Found : N, 4·6. C_7H_5ONBrI requires N, 4·3%).

4-*Bromo*-3-*iodobenzoic acid* crystallises from dilute acetic acid in colourless needles, m. p. 243—244° (0·1082 g.; 0·1052 g.; 0·1060 g.).

3-*Chloro*-4-*iodobenzaldehyde* is very volatile in steam and separates from glacial acetic acid in colourless needles, m. p. 70·5° (0·1066 g.; 0·1482 g.; 0·1515 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 261—262° (decomp.), from dilute alcohol (Found : N, 10·7. $C_{13}H_9O_2N_3ClI$ requires N, 10·5%), and the *oxime* colourless needles, m. p. 129°, from alcohol (Found : N, 5·3. C_7H_5ONClI requires N, 5·0%).

3-*Chloro*-4-*iodobenzoic acid* crystallises from glacial acetic acid in colourless plates, m. p. 219° (0·1412 g.; 0·1862 g.; 0·1892 g.).

3-*Bromo*-4-*iodobenzaldehyde* crystallises from alcohol in colourless needles, m. p. 66° (0·1550 g.; 0·2140 g.; 0·2115 g.). The p-*nitrophenylhydrazone* forms orange needles, m. p. 260—261° (decomp.), from dilute alcohol (Found : N, 9·6. $C_{13}H_9O_2N_3BrI$ requires N, 9·4%), and the *oxime* colourless needles, m. p. 157—158°, from alcohol (Found : N, 4·5. C_7H_5ONBrI requires N, 4·3%).

3-*Bromo*-4-*iodobenzoic acid* crystallises from glacial acetic acid in colourless plates, m. p. 242—243° (0·1630 g.; 0·2062 g.; 0·2115 g.).

3 : 4-*Di-iodobenzaldehyde* crystallises from alcohol in colourless, micro-crystalline needles, m. p. 118° (Found : I, 71·0. $C_7H_4OI_2$ requires I, 70·95%). The p-*nitrophenylhydrazone* forms orange needles, m. p. 245—247° (decomp.), from dilute alcohol (Found : I, 51·3. $C_{13}H_9O_2N_3I_2$ requires I, 51·6%), and the *oxime* colourless needles, m. p. 177—178°, from alcohol (Found : I, 68·2. $C_7H_5ONI_2$ requires I, 68·1%).

3 : 4-Di-iodobenzoic acid crystallises from glacial acetic acid in colourless plates, m. p. 256—258° (Wheeler and Liddle, *Amer. Chem. J.*, 1909, 42, 444, give m. p. 257°) (Found : I, 67·7. Calc. : I, 67·9%).

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