

82. *The Coupling of m-Halogenophenols with Diazotised Aniline, and the Existence of Chromoisomerism among the 3-Halogeno-4-benzeneazophenols.*

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In contrast with *m*-fluorophenol, which forms only 3-fluoro-4-benzeneazophenol, the other three *m*-halogenophenols couple in mild alkaline solution with one equivalent of diazotised aniline to form the 3-halogeno-4-benzeneazophenols, and with two equivalents to form the 3-halogeno-2 : 4-bisbenzeneazophenols. No trisazo-compounds appear to be formed. When caustic alkali is present, the tendency to form bisazo-compounds is paramount. Boiling aqueous potassium hydroxide decomposes 3-bromo- and 3-iodo-2 : 4-bisbenzeneazophenols

* All analyses are micro.

to form 2 : 4-bisbenzeneazoresorcinol, but the chloro-analogue resists such replacement. The 3-halogeno-4-benzeneazophenols exist in fairly stable, chromoisomeric forms.

DIAZOTISED aniline, even in great excess, couples with 3-fluorophenol in sodium hydroxide solution to form only 3-fluoro-4-benzeneazophenol (Hodgson and Nicholson, J., 1941, 470). 3-Chloro-, 3-bromo- and 3-iodophenol give first a 3-halogeno-4-benzeneazophenol and then a 3-halogeno-2 : 4-bisbenzeneazophenol; trisazo-compounds are not formed. The bisazo-dyes cannot be readily halogenated in the 6-position.

Monocoupling is best carried out in sodium carbonate solution; when sodium hydroxide is present, dicoupling occurs even when equivalent quantities of phenol and diazotised aniline are present; coupling does not take place in sodium acetate solution. That monocoupling first takes place in the 4-position follows from reduction of the 3-halogeno-4-benzeneazophenol to the 3-halogeno-4-aminophenol, oxidisable to the corresponding 2-halogenobenzoquinone. That the second coupling is in the 2-position has been established for 3-bromo- and 3-iodo-2 : 4-bisbenzeneazophenols by their conversion into 2 : 4-bisbenzeneazoresorcinol by boiling aqueous potassium hydroxide. The chlorine atom in 3-chloro-2 : 4-bisbenzeneazophenol resisted replacement by hydroxyl even after several hours' boiling with aqueous alkali, but aniline was gradually expelled, some hydroxyl at the azo-groups being thereby indicated. 3-Chloro-2 : 4-bisbenzeneazophenol was, however, readily reduced in aqueous sodium carbonate suspension by sodium hyposulphite to 3-chloro-2 : 4-diaminophenol, and this diamine, after tetrazotisation by Hodgson and Walker's method (J., 1933, 1620; 1935, 530); was converted by the Sandmeyer reaction into 2 : 3 : 4-trichlorophenol. For comparison 3-chloro-4 : 6-dinitrophenol was reduced by zinc dust in ethyl-alcoholic hydrochloric acid solution to 3-chloro-4 : 6-diaminophenol; this was not isolated owing to experimental difficulties, but was converted into the *dibenzoyl* derivative, which differed from the *dibenzoyl* derivative of 3-chloro-2 : 4-diaminophenol.

3-Chloro-, 3-bromo- and 3-iodo-4-benzeneazophenol exhibit chromoisomerism, since stable orange-yellow and orange-red forms have been isolated in each case which differ appreciably in m. p. The literature only records the existence of the orange-red 3-chloro-4-benzeneazophenol, m. p. 114° (Wohlleben, *Ber.*, 1909, 42, 4372). The orange-red forms are obtained in the presence of hydrochloric acid fumes; an ammonia environment transforms them into the orange-yellow variety. A fairly stable, pink form of 3-chloro-4-benzeneazophenol has also been isolated.

These results indicate that the 3-halogeno-4-benzeneazophenols behave like the very similar 4-benzeneazoresorcinol, and that Baker's explanation (J., 1934, 1684) for the 2 : 4-dicoupling of resorcinol will also hold for the 2 : 4-dicoupling of 3-chloro-, 3-bromo- and 3-iodo-phenol.

EXPERIMENTAL.

The colour produced by concentrated sulphuric acid and an azo-compound is given immediately after the m. p. of the latter.

Coupling of Diazotised Aniline with m-Chlorophenol.—Aniline (2 g.) was diazotised in hydrochloric acid (7 c.c., *d* 1.16) and water (20 c.c.), the excess of nitrous acid destroyed by urea, and the solution divided into four equal parts, three of which were treated with three different solutions of *m*-chlorophenol, and the fourth with one of 3-chloro-4-benzeneazophenol at 0°, as follows:

(a) *m*-Chlorophenol (0.6 g.) was suspended in a solution of sodium acetate (6 g.) in water (20 c.c.) to which a little ethyl alcohol had been added. Stirring was continued for 1 hour after addition of the diazotised aniline, but no coupling took place.

(b) *m*-Chlorophenol (0.6 g.) was dissolved in water (30 c.c.) containing sodium carbonate (6 g.). After 1 hour's stirring, the precipitate of 3-chloro-4-benzeneazophenol was collected and crystallised from 25% aqueous acetic acid, forming orange-yellow needles, m. p. 95° (deep yellow) (Found: N, 12.2; Cl, 15.1. Calc.: N, 12.0; Cl, 15.2%); after fusion, followed by slow cooling, the m. p. became 114°. The orange-yellow form (m. p. 95°), on drying over concentrated sulphuric acid in a vacuum desiccator, changed to a pink variety, m. p. 104° (deep yellow) (Found: N, 12.1; Cl, 15.1%), and when it was kept warm near a Bunsen burner for 2 hours its colour changed to orange-red and the m. p. to 114° (deep yellow) (Found: N, 12.1; Cl, 15.1%). The orange-yellow form (m. p. 95°) on exposure to hydrochloric acid fumes or when washed with dilute hydrochloric acid, followed by water, prior to drying, changed into the orange-red form (m. p. 114°). The orange-red form was changed by ammonia fumes into the orange-yellow variety. M. p.'s of 101° and 108° were found for mixtures of the two forms and when a small quantity of the orange-red was mixed with a large quantity of the orange-yellow form (m. p. 95°) a m. p. of 94° was obtained. The three mixtures were allowed to cool slowly after fusion; they then all had m. p. 114°. Recrystallisation of the orange-red and the pink variety from 25% aqueous acetic acid gave orange-yellow needles, m. p. 95°. All the forms were stable when kept in corked test-tubes, but when exposed to the atmosphere the orange-yellow slowly changed into the orange-red variety.

(c) *m*-Chlorophenol (0.6 g.) was dissolved in water (30 c.c.) containing sodium bicarbonate (6 g.) and a little ethyl alcohol. A longer stirring period (*ca.* 2 hours) was required than in (b) before the 3-chloro-4-benzeneazophenol was completely precipitated.

(d) 3-Chloro-4-benzeneazophenol (1 g.) was dissolved in 20% aqueous sodium hydroxide (10 c.c.), to which saturated aqueous sodium carbonate (3 c.c.) had been added, and the fourth portion of diazotised aniline was gradually stirred in. 3-Chloro-2 : 4-bisbenzeneazophenol, collected after 15 mins., crystallised from 90% aqueous pyridine in dark red-brown needles, m. p. 181° (yellow-brown) (Found: N, 16.7; Cl, 10.4. $C_{13}H_{13}ON_4Cl$ requires N, 16.6; Cl, 10.5%).

Coupling of Diazotised Aniline with m-Chlorophenol in Presence of Sodium Hydroxide.—Four solutions of *m*-chlorophenol (0.6 g.; 0.005 g.-mol.) in water (60 c.c.) containing 20% aqueous sodium hydroxide (2 c.c.) and sodium carbonate (12 g.) were severally treated with 1, 2, 3 and 4 equivs. of diazotised aniline. In all four cases the product was 3-chloro-2 : 4-bisbenzeneazophenol (red-brown needles from 90% aqueous pyridine, m. p. and mixed m. p. 181°) and neither mono- nor tris-azo-dyes appeared to be formed. With less than 1 equiv. of diazotised aniline, some 3-chloro-4-benzeneazophenol was formed; it was extracted from the bisazo-compound with 10% aqueous sodium hydroxide and crystallised from 25% aqueous acetic acid, forming orange-yellow needles, m. p. 95° (Found: N, 12.1%). The procedure described for the preparation of 3-fluoro-4-benzeneazophenol (Hodgson and Nicholson, *loc. cit.*), when used with *m*-chlorophenol, always gave the bisazo-compound.

Coupling of Diazotised Aniline with m-Bromo- and m-Iodo-phenol.—Procedure (b) above with a slight excess of *m*-bromophenol gave 3-bromo-4-benzeneazophenol, which crystallised from 25% aqueous acetic acid in orange-yellow needles, m. p. 128° (unchanged on fusion a second time after slow cooling) (deep yellow) (Found : N, 10.2; Br, 28.7. $C_{12}H_9ON_2Br$ requires N, 10.1; Br, 28.8%). When exposed to hydrochloric acid fumes and then gently heated to remove adherent acid, the orange-yellow changed into orange-red needles, m. p. 161—163° (deep yellow) (Found : N, 10.2; Br, 28.6%); these were reconverted into the orange-yellow needles by ammonia fumes. Mixed m. p.'s of 125°, 132° and 134° were obtained for different mixtures of the two forms. When dried over concentrated sulphuric acid in a vacuum desiccator, the orange-red form changed into the orange-yellow variety.

When sodium hydroxide was present in the coupling solution, even with equivalent amounts of diazotised aniline and *m*-bromophenol, 3-bromo-2 : 4-bisbenzeneazophenol was formed, which crystallised from 90% aqueous pyridine in red-brown needles, m. p. 175° (yellow-brown, redder than the colour given by the chloro-analogue) (Found : N, 14.8; Br, 20.8. $C_{18}H_{13}ON_4Br$ requires N, 14.7; Br, 21.0%). This compound was also the only one formed when *m*-bromophenol was treated in alkaline (mild or caustic) solution with 4 equivs. of diazotised aniline, or when 3-bromo-4-benzeneazophenol was treated in like manner. The bisazo-compound was dissolved in an excess of alcoholic potassium hydroxide, to which water was subsequently added, and the mixture refluxed so that the alcohol was gradually removed; the solution after filtration and acidification yielded 2 : 4-bisbenzeneazoresorcinol, m. p. and mixed m. p. with an authentic specimen, 221° (deep orange-red; 4 : 6-bisbenzeneazoresorcinol, m. p. 213—215°, gives a characteristic bluish-red colour with concentrated sulphuric acid) (Found : N, 17.7. Calc. : N, 17.6%).

3-Iodo-4-benzeneazophenol, prepared by procedure (b) above but with a 50% excess of *m*-iodophenol, crystallised from 25% aqueous acetic acid in orange-yellow needles, m. p. 145° (unchanged when repeated after solidification) (deep reddish-yellow) (Found : N, 8.7; I, 39.0. $C_{12}H_9ON_2I$ requires N, 8.6; I, 39.2%). The orange-red form, obtained by exposure of the orange-yellow variety to hydrochloric acid fumes and gentle heating to remove adherent acid, had m. p. 138° (deep reddish-yellow) (Found : N, 8.8; I, 39.0%). Mixed m. p.'s of 137° and 141° were obtained with suitable mixtures to establish depressions. The orange-red variety, recrystallised from 25% aqueous acetic acid or kept in a vacuum over concentrated sulphuric acid, changed into the orange-yellow form, m. p. 145°.

3-Iodo-2 : 4-bisbenzeneazophenol was even more readily formed than the chloro- and bromo-analogues under like conditions, and was present when equivalent amounts of diazotised aniline and 3-iodophenol reacted in aqueous sodium carbonate solution; it crystallised from 90% aqueous pyridine in red-brown needles, m. p. 187° (yellow-brown, redder than the colours given by the chloro- and bromo-analogues) (Found : N, 13.2; I, 29.5. $C_{18}H_{13}ON_4I$ requires N, 13.1; I, 29.7%), and was converted into 2 : 4-bisbenzeneazoresorcinol by the ethyl-alcoholic potassium hydroxide procedure described for the bromo-analogue.

3-Chloro-2 : 4-diaminophenol.—3-Chloro-2 : 4-bisbenzeneazophenol (3 g.) was suspended in a solution of sodium carbonate (6 g.) and water (30 c.c.) and boiled during the gradual addition of sodium hyposulphite ("hydros," ca. 10 g.) until the reduction product passed into solution, which became almost colourless. The liberated aniline was removed by steam-distillation, and the hot residual liquor filtered; 3-chloro-2 : 4-diaminophenol (0.7 g.), which separated on cooling, crystallised from benzene in colourless needles, m. p. 200° (Found : Cl, 22.2. $C_8H_7ON_2Cl$ requires Cl, 22.4%). The *dibenzoyl* derivative, prepared by the Schotten-Baumann method, crystallised from aqueous alcohol in colourless needles, m. p. 192° (Found : Cl, 9.7. $C_{20}H_{15}O_3N_2Cl$ requires Cl, 9.7%). 3-Chloro-2 : 4-diaminophenol was tetrazotised by nitrosylsulphuric acid in glacial acetic acid, and the solution added to cuprous chloride dissolved in concentrated hydrochloric acid (method of Hodgson and Walker, *loc. cit.*); steam-distillation then removed 2 : 3 : 4-trichlorophenol, m. p. 80—81° (Found : Cl, 53.8. Calc. : Cl, 54.0%), which formed a benzoate, m. p. 143° (Found : Cl, 35.3. Calc. : Cl, 35.3%) (Groves, Turner, and Sharp, J., 1929, 522, give the same m. p.'s).

A solution of 3-chloro-4 : 6-dinitrophenol (1 g.) in ethyl alcohol (20 c.c.) and hydrochloric acid (10 c.c., *d* 1.16) was treated with zinc dust until the red colour disappeared. The liquid, after filtration, was shaken with benzoyl chloride (2 c.c.) and 2*N*-sodium hydroxide (50 c.c.), giving the *dibenzoyl* derivative of 3-chloro-4 : 6-diaminophenol, which crystallised from aqueous alcohol in colourless needles, m. p. 215° (Found : Cl, 9.6. $C_{20}H_{15}O_3N_2Cl$ requires Cl, 9.7%). Reduction of 3-chloro-4 : 6-dinitrophenol with sodium hyposulphite gave unsatisfactory results.

The authors thank Imperial Chemical Industries (Dyestuffs) Ltd. for gifts of chemicals, and Dr. D. E. Nicholson for some micro-analyses.

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[Received, March 7th, 1942.]