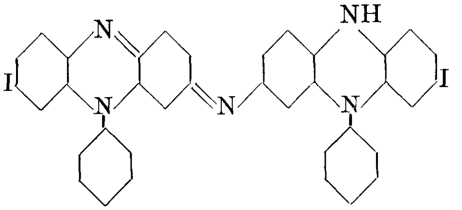
278. *The Reaction between Aniline and Iodine.*

By HERBERT H. HODGSON and EWART MARSDEN.

The present study has indicated that temperature plays an important part in the reaction between iodine and aniline. Below 150° iodination alone occurs, whereas above 150° the oxidising rôle of the iodine appears and proceeds with increasing intensity until from 180° to 230° appreciable amounts of a dark blue product are formed. This coloured compound is regarded as possessing the formula inset below, and has been alternatively prepared by heating *p*-iodoaniline with aniline at 220—230°.

FRITZSCHE (*J. pr. Chem.*, 1840, **20**, 454; 1843, **28**, 202) and Hofmann (*Annalen*, 1848, **67**, 65) have previously studied the reaction between aniline and iodine, and among the products have identified aniline hydriodide and a monoiodoaniline. Subsequent investigators, however, intent on the preparation of *p*-iodoaniline in good yield, have all utilised a third substance to decompose the hydrogen iodide liberated (cf. "Organic Syntheses," Vol. XI, New York, 1931, p. 62). In view of the oxidising rôle which the iodine may fulfil, the present investigation has been undertaken to elucidate the mechanism of direct iodination.

Various amounts of aniline and iodine were heated together at temperatures ranging from 20° to 230° (see table), and it was found that from 20° to 150° the main products were *p*-iodoaniline and aniline hydriodide, if molecular quantities were taken, but that 2 : 4-di-iodoaniline occurred with increasing amounts of iodine. At higher temperatures, a dark blue product was formed, which was identified as a single substance with a probable aposafranine formula (inset). This coloured compound, which has vat dye properties, has been alternatively synthesised by heating *p*-iodoaniline with aniline, but when carefully purified *p*-iodoaniline was heated alone, there resulted only 2 : 4-di-iodoaniline and free iodine.



The mechanism of the reaction at the higher temperatures would thus appear to be the initial formation of *p*-iodoaniline with subsequent oxidation in presence of aniline to an iodohydroaposafranine, two molecules of which condense with diarylamine formation and final oxidation to the complex indamine.

EXPERIMENTAL.

General Iodination Procedure.—Iodine was added gradually to vigorously stirred aniline during 20 minutes, the mixture being maintained at a constant temperature, and the agitation continued for 30 minutes after complete dissolution of the iodine had occurred. When cold, the product was washed 12 times with cold water (400 c.c. per time) to remove aniline hydriodide, then dissolved in hot (80°) concentrated hydrochloric acid (*d* 1·16) in sufficient amount for the solution to give a distinctly acid reaction with Congo-red paper. After filtration, the hot filtrate was chilled rapidly to 5—10°, whereupon a greenish crystalline mixture of the hydrochlorides of the iodoanilines separated, and was filtered off.

The insoluble tarry matter was dried, dissolved in aniline, and recovered in a more workable condition by removal of the aniline by dilute hydrochloric acid.

The crude hydrochlorides above were stirred with hot water at 80° (500 c.c. per 0·5 g. of iodine originally used); the *p*-iodoaniline hydrochloride dissolved, the solution was filtered, and the filtrate treated with sulphuric acid, whereby *p*-iodoaniline sulphate separated on cooling to 5—10°, and, on basification by trituration with hot dilute sodium carbonate, afforded *p*-iodoaniline, which crystallised from alcohol in colourless needles, m. p. 63° (lit. 63°) (Found : N, 6·4. Calc. for C_6H_6NI : N, 6·4%). The solubility of *p*-iodoaniline in water at 12° is 0·65%. The oily residue of 2 : 4-di-iodoaniline left after the water extraction was crystallised from 80% aqueous acetic acid, and obtained in pale yellow needles, m. p. 95° (Found : N, 4·0; *M*, by nitrite titration, 335. Calc. for $C_6H_5NI_2$: N, 4·1% ; *M*, 345). If the amount of 2 : 4-di-iodoaniline is very small, the glacial acetic acid extract of the oily residue above is diluted with an equal volume of water, and the base salted out by addition of sodium acetate. Since free iodine was always present in the *p*-iodoaniline thus obtained, notwithstanding variations in the amount of iodine employed, and also since its amount increased with time, it was necessary to perform the above operations as rapidly as possible.

Table of Results.

Expt.	NH_2Ph, g.	I, g.	Mol. ratio, NH_2Ph/I.	Temp.	*p*-Iodo-aniline, g.	2 : 4-Di-iodo-aniline, g.	NH_2Ph,HI, g.
1	10·0	6·85	2·0	40°	5·7	0·10	5·8
2	21·5	15·75	1·86	60	10·2	3·50	15·7
3	20·0	27·3	1·00	80—100	Nil	22·50	19·2
4	10·0	13·5	1·01	20—40	10·6	0·03	11·9
5	20·0	6·5	4·2	27—32	4·8	0·27	5·2
6	20·1	6·0	4·6	30—35	4·7	0·37	5·2
7	19·99	6·0	4·55	40—45	4·9	0·26	5·2
8	20·1	6·0	4·6	50—55	4·9	0·07	5·1
9	20·05	6·0	4·58	90—95	4·8	0·14	5·0
10 *	10·0	6·0	2·28	130—150	4·9	0·14	5·2
11 †	10·0	6·0	2·28	180—230	Nil	Nil	12·0

* In this experiment, 0·004 g. of a red, insoluble residue was obtained.

† 2·75 G. of a blue insoluble residue were obtained.

Discussion.—(1) All the experiments except Nos. 2, 3, and 11 give data in conformity with the equation

$$2C_6H_5{\cdot}NH_2 + I_2 = I{\cdot}C_6H_4{\cdot}NH_2 + C_6H_5{\cdot}NH_2{,}HI.$$

Expt. 10 appears to indicate aposafranine formation.

(2) Expt. 3 is represented by the equation

$$3C_6H_5{\cdot}NH_2 + 2I_2 = C_6H_3I_2{\cdot}NH_2 + 2C_6H_5{\cdot}NH_2{,}HI$$

and expt. 2 is represented by a combination of both equations. The total weight of insoluble matter recovered from all the experiments 1—10 was only 0·034 g.

The Dyestuff from Experiment 11.—The dark blue residue was thoroughly washed with water, dried, and found to be very insoluble in all the ordinary solvents; it was moderately soluble, however, in α-naphthylamine, cellosolve, and aniline, giving indigo-blue solutions, from the last of which it crystallised in violet-blue micro-crystals which decomposed on heating [Found : N, 8·9; I, 32·4; *M*, cryoscopic in α-naphthylamine (constant 89·5), 758. $C_{36}H_{23}N_5I_2$ requires N, 9·0; I, 32·6% ; *M*, 779]. This *product* dissolved in cold concentrated sulphuric acid to give a deep blue solution which was not diazotised by nitrous acid and did not become red on dilution, as in the case of safranine; the colour was precipitated as a fine suspension on dilution, and unmordanted wool immersed in this suspension was dyed in fugitive blue shades which were discharged on treatment with zinc dust and acetic acid but returned on subsequent exposure to air. Dry distillation with zinc dust produced ammonia, carbylamine, aniline, and a sublimate (0·5 g. from 3 g. of dye) of yellow crystals of phenazine, m. p. 170·5° (Found : N, 15·7. Calc. for $C_{12}H_8N_2$: N, 15·5%).

Synthesis of the Above Dye from p-*Iodoaniline and Aniline.*—A mixture of *p*-iodoaniline (2·0 g.) and aniline (0·1 g.) was heated under the reflux for 30 minutes at 220—230°. The liquid gradually darkened, and the dark blue product obtained on cooling was washed with hot dilute sulphuric acid to remove unchanged amine (none detected) and aniline hydriodide (0·0954 g.), then with hot glacial acetic acid to remove 2 : 4-di-iodoaniline (1·32 g.) and free iodine (0·15 g.), and finally recrystallised from aniline. It proved to be identical with the product above from direct iodination (Found : N, 9·0; I, 32·5% ; *M*, 762).

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TECHNICAL COLLEGE, HUDDERSFIELD.

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