217. *The Catalytic Phenylation of α-Naphthylamine.*

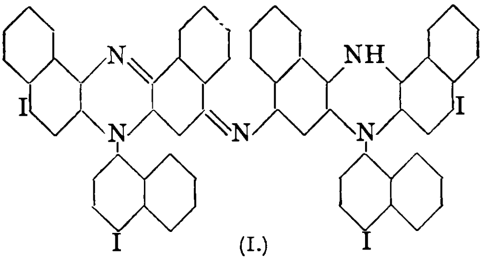
By HERBERT H. HODGSON and EWART MARSDEN.

Ammonium iodide, hydrogen iodide, and iodine catalyse the phenylation of α-naphthylamine in decreasing order of efficiency, the first giving the maximum yield of a product almost free from the aposafranine-like *dyes* (I) and (II). Compounds of these types are normal products of the oxidation of amines by iodine.

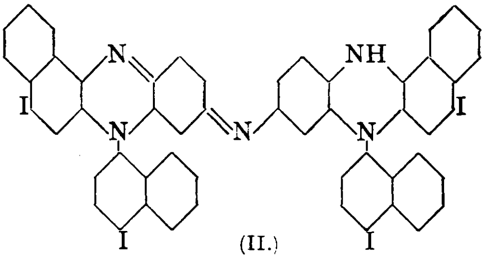
IODINE as a catalyst for the phenylation of α-naphthylamine and related amines was first used by Knoll and Co. (G.P. 241,853). A preliminary investigation of the mechanism of the reaction by the present authors (J., 1937, 1365) dealt with the interaction of iodine and aniline alone, wherein it was established that the products first formed were *p*-iodoaniline and aniline hydriodide. In the actual phenylation process, therefore, hydrogen iodide would appear to play the essential rôle, becoming ammonium iodide intermediately; this would decompose at the reaction temperature with the evolution of ammonia and regeneration of hydrogen iodide. In fact, when ammonium iodide is used as the catalyst, oxidation to highly coloured, aposafranine-like compounds, which occurs when iodine is used, is minimised and the products are much less coloured.

Nine comparative experiments on phenylation, *p*-tolylation, and α-naphthylation with iodine, hydrogen iodide, and ammonium iodide as catalysts proved definitely that the last was the most efficient, inasmuch as the yields were greater by *ca.* 1% and the crude products purer (freezing points *ca.* 2° higher) than those afforded by the other two catalysts, of which iodine was the less efficient. That phenylation is the main reaction, however, is indicated by the very sluggish action of aniline hydriodide on aniline itself.

As in the case of aniline (*loc. cit.*), iodine reacts with α-naphthylamine to give a *dye* of probable constitution (I), and *p*-iodoaniline reacts to form two dyes, *viz.*, a small quantity of (I), which doubtless arises from the action of liberated iodine on α-naphthylamine, and a larger amount of (II). These dyes are separated by hot glacial acetic acid, in which (I) alone is insoluble.



(I.)



(II.)

EXPERIMENTAL.

The Reaction between Aniline Hydriodide and α-Naphthylamine in Aniline Solution.—A mixture of the three compounds (0·493 g., 28·6 g., and 27·9 g., respectively) was heated for 12 hours under reflux; the temperature rose from 180° to 230° and ammonia was evolved continuously. The phenyl-α-naphthylamine formed (31·2 g.), after being washed with boiling 10% hydrochloric acid and water, had f. p. 52·6°, raised to 59° by one crystallisation from ligroin (f. p. of an authentic specimen, 59°).

The Reaction between α-Naphthylamine Hydriodide and α-Naphthylamine in Aniline Solution.—With respective quantities of 0·61 g., 28·6 g., and 27·9 g., the yield of crude phenyl-α-naphthylamine was 31 g. of f. p. 53°, raised to 59° by one crystallisation from ligroin.

Comparison of Methods for the Preparation of Phenyl-α-naphthylamine.—(a) *With iodine as catalyst.* Aniline (210 g.), α-naphthylamine (221 g.), and iodine (2·21 g.) were boiled under reflux for 12 hours, the temperature rising from 180° to 230°. The cooled product was poured into boiling water (500 c.c.) and just acidified with concentrated hydrochloric acid and the heavy oil of phenyl-α-naphthylamine was washed with water and dried at 120°. The very dark, crude product (308 g.; yield, *ca.* 94%) had f. p. 52·6° (pure product 59°) and the following compounds were isolated from it: phenyl-β-naphthylamine (0·5%, arising from β-naphthylamine in the α-naphthylamine used), dye (I) (0·5%), dye (II) (0·7%), and diphenylamine (3·5%); the amount of phenyl-α-naphthylamine was 94·8% (by difference).

(b) *With ammonium iodide* (1·25 *g.*) *as catalyst.* With quantities and procedure as in (a) the yield of crude product was 312 g. (95·2%) and f. p. 55·2°. Phenyl-β-naphthylamine (0·5%) and diphenylamine (3·5%) were isolated, the quantity of the dyes was negligible, and the amount of phenyl-α-naphthylamine was 96·0% (by difference).

The Action of Aniline Hydriodide on Aniline.—Aniline (46·5 g.) was refluxed with aniline hydriodide (0·493 g.) for 30 hours; ammonia was very slowly evolved and the temperature rose to 198°. The yield of diphenylamine was 3·2 g.; m. p. 54° after recrystallisation from alcohol.

The Action of α-Naphthylamine Hydriodide on α-Naphthylamine.—α-Naphthylamine (57·2 g.) was heated to 50°, α-naphthylamine hydriodide (1·0 g.) added, and the heating continued until evolution of ammonia had ceased (15 hours); the temperature was then 250°. The αα'-dinaphthylamine (42·3 g.) formed, after one crystallisation from ligroin, had m. p. 110° (lit. 111°) (Found: N, 5·3. Calc.: N, 5·2%). When ammonium iodide was used as catalyst, the yield of crude αα'-dinaphthylamine was 51·5 g.

p-*Tolylation of α-Naphthylamine.*—α-Naphthylamine (44·2 g.), *p*-toluidine (42·0 g.), and ammonium iodide (0·25 g.) were heated for 12 hours under reflux, the temperature rising to 230°. The crude product was steam-distilled to remove unchanged amines; the yield was 58·8 g., f. p. 70°, and after one recrystallisation from ligroin, m. p. 78° (lit. 78°).

The Action of p-*Iodoaniline on α-Naphthylamine.*—When these compounds in equimolecular proportion were gradually heated, reaction began with explosive violence at 40—50°, aniline, iodine, and ammonia were evolved, and a purple dye produced. When, however, an excess of α-naphthylamine was used (5 : 1) and the mixture was heated at 100° for 24 hours, two dyes were formed, *viz.*, (I) (0·02 pt.) and (II) (0·65 pt.), which were separated by extraction with glacial acetic acid, in which (II) alone was soluble. *Dye* (I) crystallised from monochlorodimethyl ether in purple micro-plates [Found: N, 5·2; I, 37·9; *M*, cryoscopic in phenyl-α-naphthylamine (constant, 85), 1342. $C_{60}H_{33}N_5I_4$ requires N, 5·25; I, 38·1%; *M*, 1331]. It decomposed at *ca.* 260°, giving α-naphthylamine and αβ-dinaphthazine [yellow needles, m. p. 280° (lit. 283°)] (Found: N, 10·2. Calc.: N, 10%), formed a deep green solution in cold concentrated sulphuric acid, and appeared to be identical in all respects with the product (below) obtained by the action of iodine on α-naphthylamine. *Dye* (II) crystallised from glacial acetic acid in purple microplates, decomp. *ca.* 280° (Found: N, 5·8; I, 41·1; *M*, cryoscopic in phenyl-α-naphthylamine, 1221. $C_{52}H_{29}N_5I_4$ requires N, 5·7; I, 41·3%; *M*, 1231). It was only very slightly soluble in alcohol, but dissolved readily in aniline; in cold concentrated sulphuric acid it formed a blue-green solution intermediate in shade between those of the aposafranine-like products obtained by the action of iodine on aniline and α-naphthylamine. On distillation with zinc dust, dye (II) gave ammonia, carbylamine, α-naphthylamine, and naphthaphenazine [yellow needles, m. p. 142° (lit. 142°). Found: N, 12·4. Calc.: N, 12·2%].

Dyes (I) and (II) were precipitated from their solutions in concentrated sulphuric acid on dilution with water, and unmordanted wool immersed in their suspensions was dyed in fugitive purple-blue shades [(I) bluer than (II)], which were stripped by boiling alcohol or 10% acetic acid, and discharged on treatment with zinc dust and acetic acid but returned on subsequent exposure to air.

The Action of Iodine on α-Naphthylamine.—α-Naphthylamine (5·0 g.) was heated to 50°, and iodine (2·6 g.) added between 50° and 55° during 20 minutes with continuous stirring. The mixture rapidly darkened to deep red and became solid during the next 30 minutes; it was cooled, powdered, and extracted with 10% sulphuric acid until free from α-naphthylamine, then with water, alcohol, and benzene to remove any unchanged iodine (none found). The dark residue (2 g.) of dye (I) crystallised from monochlorodimethyl ether in dark purple microplates, which decomposed with evolution of iodine when heated (Found: N, 5·2; I, 37·8%; *M*, cryoscopic in phenyl-α-naphthylamine, 1321).

The Action of Iodine on β-Naphthylamine.—A vigorous reaction occurred at the m. p. of β-naphthylamine when it (5 g.) was heated with iodine (2·6 g.); β-naphthylamine hydriodide (2·9 g.) was isolated from the mixture. The remainder (3·7 g.) was an uncrystallisable brown tar, insoluble in benzene but very soluble in alcohol; it could not be acetylated or benzoylated and was decomposed by concentrated sulphuric acid with evolution of iodine.

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