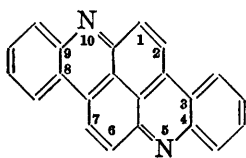


243. The Synthesis of 3 : 4 : 8 : 9-Dibenzo-5 : 10-diazapyrene.

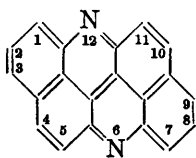
By G. R. CLEMO and E. C. DAWSON.

The synthesis of 3 : 4 : 8 : 9-dibenzo-5 : 10-diazapyrene (I) is described. A simple new method for the preparation of 2 : 2'-diamino-1 : 1'-dinaphthyl is described.

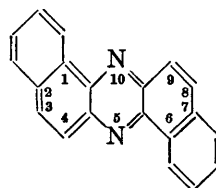
IN view of the present-day interest attaching to the phenazine system the preparation of the analogues 3 : 4 : 8 : 9-dibenzo-5 : 10-diazapyrene (I) and 6 : 12-diaza-anthanthrene (II) has been investigated. We were forestalled by I. G. Farbenindustrie (D.P. 659,881) in



(I.)



(II.)



(III.)

the preparation of the latter, but prepared the former by oxidation of the 1 : 5-dianilino-naphthalene with gaseous oxygen in the presence of aluminium chloride. A similar method was used by Vollmann and co-workers (*Annalen*, 1937, 531, 102) for the conversion of 2 : 6-dihydroxy-1 : 5-dibenzoylnaphthalene into 1 : 6-dihydroxy-3 : 4 : 8 : 9-dibenzopyrene-5 : 10-quinone.

3 : 4 : 8 : 9-Dibenzo-5 : 10-diazapyrene is a very stable compound, which sublimes, or crystallises from chlorobenzene, in chrome-yellow needles, and forms red salts. The analy-

tical figures do not definitely distinguish it from its 5 : 10-dihydro-derivative, but the latter is precipitated from acid solution by metals, and is reconverted into (I) by ferric chloride. Preliminary experiments have shown that (I) does not react with nitric acid or bromine, but is sulphonated by chlorosulphonic acid.

Attempts to synthesise 6 : 12-diaza-anthanthrene by the oxidation of β -naphthylamine were unsuccessful. Lead dioxide yielded 1 : 2 : 6 : 7-dibenzophenazine (III) [cf. its preparation by Claus and Jaeck (D.R.-P. 78,748) and by the K \ddot{o} chster Farbwendung (D.R.-P. 165,226) from β -naphthylamine by other methods] and a trace of a new compound, $C_{20}H_{14}N_2$, which may possibly be 5 : 10-dihydro-1 : 2 : 6 : 7-dibenzophenazine.

The preparation of 2 : 2'-diamino-1 : 1'-dinaphthyl by Meisenheimer and Witte (*Ber.*, 1903, 36, 4155) involved many stages and gave a poor yield. Fischer (*Annalen*, 1885, 232, 242) prepared β -naphthylhydrazine by the reaction between equimolecular amounts of β -naphthol and hydrazine hydrate, but we have found that by using two equivalents of β -naphthol, 2 : 2'-diamino-1 : 1'-dinaphthyl can be readily obtained in 45% yield. The intermediate $\beta\beta'$ -hydrazonaphthalene was not isolated, and it is uncertain whether the *o*-benzidine conversion took place during the main reaction, or in the subsequent extraction with hot acid. The latter seems more probable, however, as at reaction temperatures above 190° only β -naphthylamine was formed, and the diaminodinaphthyl is stable under these conditions.

The ring closure of diaminodinaphthyl was investigated by many methods with a view to preparing (II), but no success was obtained.

EXPERIMENTAL.

1 : 5-Dianilinonaphthalene.—1 : 5-Dihydroxynaphthalene (4 g.) and aniline (9 c.c.) were heated at 260° for 24 hours in a sealed tube. The product was stirred with cold dilute hydrochloric acid, washed successively with cold dilute hydrochloric acid, water, cold dilute sodium hydroxide solution, and water, and dried. The crude product thus obtained (yield, 40%), m. p. 205°, is satisfactory for the ring closure. The compound is insoluble in hydrochloric acid and sparingly soluble in most organic solvents, but crystallises from chlorobenzene in colourless prisms, m. p. 214° (Found : C, 85.0; H, 5.7. $C_{22}H_{16}N_2$ requires C, 85.1; H, 5.8%).

3 : 4 : 8 : 9-Dibenzo-5 : 10-diazapyrene.—Sodium chloride (7 g.) and aluminium chloride (33 g.) were ground together and fused in a metal-bath. 1 : 5-Dianilinonaphthalene (5 g.) was added, and the temperature gradually raised to 320—330°, where it was maintained while oxygen was blown through the mixture. After 8—9 hours the product, which had acquired the consistency of putty, was added while still hot to dilute hydrochloric acid (200 c.c.) and boiled for a few minutes. Ferric chloride (0.5 g.) was added to reduce the solubility of the material and reoxidise any dihydro-derivative formed by the action of the nickel spatula used for stirring. After cooling, the solid was collected, washed, stirred with dilute sodium hydroxide solution, kept overnight, then again filtered off, washed, and dried. The material was extracted from a Soxhlet thimble suspended in a wire cage under the reflux condenser in a flask of boiling chlorobenzene, and thus obtained in chrome-yellow needles, m. p. 362°. Yield, 60%, and a further 5% by evaporation of the solution (Found : C, 86.5; H, 4.1. $C_{22}H_{12}N_2$ requires C, 86.8; H, 4.0%). 3 : 4 : 8 : 9-Dibenzo-5 : 10-diazapyrene sublimes, is slightly soluble in organic solvents, and gives orange-red solutions in concentrated acids. The hydrochloride is bright red. Its 5 : 10-dihydro-derivative is thrown down from a hydrochloric acid solution of dibenzodiazapyrene by the action of zinc, tin, nickel, etc., as a flocculent brown precipitate, which does not sublime and is insoluble in organic solvents and acids.

Oxidation of β -Naphthylamine.— β -Naphthylamine (1 g.) and lead dioxide (4 g.) were intimately mixed and heated at 180° for 24 hours. The mass was extracted with pyridine and the products were precipitated with water, dried, and separated into an alcohol-soluble and an alcohol-insoluble fraction. The latter was 1 : 2 : 6 : 7-dibenzophenazine, crystallising from glacial acetic acid in yellow needles, m. p. 283° (Found : C, 85.9; H, 4.3. Calc. for $C_{20}H_{12}N_2$: C, 85.7; H, 4.3%). The alcohol-soluble material, which alternatively could be extracted directly from the reaction mass with hot alcohol, crystallised on cooling in pale yellow needles, m. p. 195°, sparingly soluble in organic solvents and insoluble in hydrochloric acid. It sublimes (Found : C, 85.5; H, 5.3. $C_{20}H_{14}N_2$ requires C, 85.1; H, 5.0%). Yield, 2%.

2 : 2'-Diamino-1 : 1'-dinaphthyl.—Hydrazine hydrate (5 c.c.) and β -naphthol (30 g.) were heated in a sealed tube at 170—180° for 48 hours, the tube opened and its contents remelted

in a water-bath, poured into hydrochloric acid (50—100 c.c. ; 1 : 1), and boiled for a few minutes with stirring. The liquid was allowed to stand just long enough to separate into two layers, and the upper aqueous layer was siphoned off. On cooling, it deposited crystals of diamino-dinaphthyl hydrochloride (the mother-liquor was used for several more extractions). The last extract was made into a paste with the crystals, excess of sodium carbonate solution added, and the mixture left overnight. The brown precipitate was washed with a little warm alcohol and dried. Yield 45%, m. p. 185—187°. Crystallisation from alcohol effected only a partial purification; benzene—light petroleum (3 : 1) gave a reduced yield of white material, m. p. 191°.

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