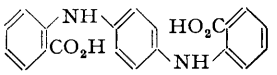
344. *Polynuclear Heterocyclic Systems. Part V.** 5 : 8-*Diazapentaphene.*

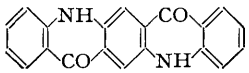
By G. M. Badger and R. Pettit.

Cyclisation of *p*-phenylenedianthranilic acid (I) has been shown to give the angular quinacridone (III). The aza-hydrocarbon prepared from this is 5 : 8-diazapentaphene (VIII) and not the linear compound (IV), from (II), as originally supposed by Ullmann and Maag (*Ber.*, 1907, **40**, 2515). Oxidation of diazapentaphene (VIII) with selenium dioxide gave 2 : 3-6 : 7-dibenzo-1 : 8-diazafluorenone (XII).

In 1907, Ullmann and Maag (*Ber.*, 1907, **40**, 2515; see also *Ber.*, 1906, **39**, 1693) described the preparation of *NN'-p*-phenylenedianthranilic acid (I) and its cyclisation to a "quinacridone." The direction of cyclisation was not established, but the linear structure (II) was favoured rather than the alternative angular compound (III). The supposed (II) was reduced to a red dihydro-compound, and on mild oxidation this gave an aromatic aza-hydrocarbon which was thought to be the linear pentacyclic compound (IV). On the other hand, by treating *p*-benzoquinone with anthranilic acid, followed by cyclisation of



(I)



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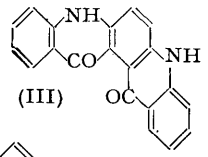
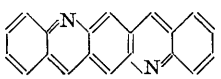
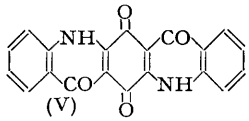


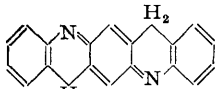
(III)



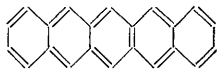
(IV)



(V)



(VI)



(VII)

the product, Leśniański (*Ber.*, 1918, **51**, 695) obtained a compound having the structure (V). On zinc-dust distillation, this gave a very small amount of a dark red dihydro-compound (presumably VI †) which was not identical with Ullmann and Maag's dihydro-derivative.

* Part IV, 1951, 3211.

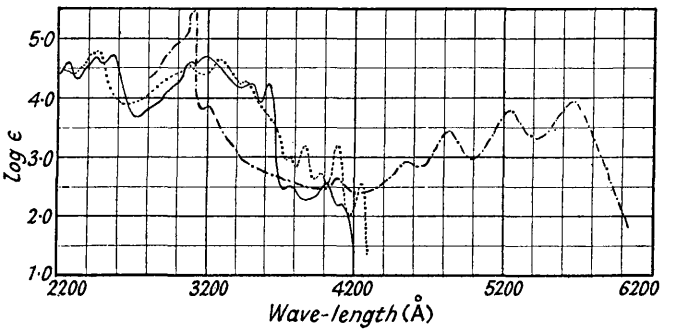
† The red colour of this compound indicates that it must have a completely conjugated quinonoid structure (cf. Badger and Pettit, *J.*, 1951, 3211). The alternative structure favoured by Leśniański would have an acridine-like spectrum and would be yellow.

He therefore suggested that the compound obtained by Ullmann and Maag must have an angular structure. Furthermore, by cyclisation of 2 : 5-dianilinoterephthalic acid, Liebermann (*Annalen*, 1935, **518**, 245) prepared authentic linear quinacridone (II) and found it to be different from the quinacridone obtained by Ullmann and Maag.

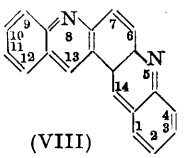
In view of these discrepancies, it seemed certain that Ullmann and Maag's aza-hydrocarbon could not have the structure (IV), and this conclusion is supported by other evidence. It has been shown (Badger, Pearce, and Pettit, *J.*, 1951, 3199) that the absorption spectra of aromatic heterocyclic compounds closely resemble those of their carbocyclic analogues. This means that the colour of an unknown aromatic heterocyclic compound can be predicted with reasonable certainty provided the analogous hydrocarbon is known. It is therefore significant that, although the aromatic hydrocarbon pentacene (VII) is deep blue, Ullmann and Maag's aromatic heterocylic compound is pale yellow.

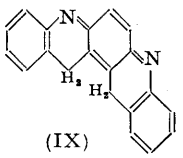
It has now been found that cyclisation of *p*-phenylenedianthranilic acid (I) gives the angular quinacridone (III), and that the aromatic compound derived from it is 5 : 8-diazapentaphene (VIII). Its absorption spectrum (Fig. 1) resembles that of the analogous

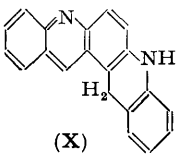
FIG. 1. *Absorption spectra of* 5 : 8-*diazapentaphene* (– – – – –), *of pentaphene* (———), *and of pentacene* (· — · — · —), *all in ethanol. The spectra of the two hydrocarbons are taken from Clar* (Ber., 1932, **65**, 503; "*Aromatische Kohlenwassertsoffe*," *Springer-Verlag*, 1941, *p.* 182).



hydrocarbon, pentaphene, very closely indeed, and such differences as are found are in the direction expected (cf. Badger, Pearce, and Pettit, *loc. cit.*). On the other hand, the spectrum differs widely from that of the linear hydrocarbon, pentacene (VII). The red

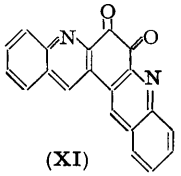

(VIII)

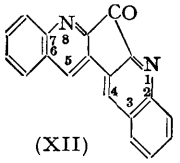

(IX)

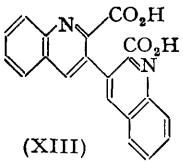

(X)

colour of the intermediate dihydro-compound indicates that this substance must have a completely conjugated quinonoid structure (IX), and not the alternative form (X).

It was hoped to confirm the structure of the diazapentaphene (VIII) by oxidation to the *o*-quinone (XI) and subsequent condensation with *o*-phenylenediamine. Unfortunately


(XI)


(XII)


(XIII)

the aza-hydrocarbon proved very resistant to oxidation, even to chromic acid in concentrated sulphuric acid, and the desired quinone could not be obtained.

With selenium dioxide in a sealed tube, oxidation proceeded readily. However, the

analysis and absorption spectrum of the product indicate that it must be 1 : 8-diaza-2 : 3-6 : 7-dibenzofluorenone (XII), and it seems likely that this is formed from the aza-hydrocarbon (VIII) by oxidation to the quinone (XI), then to the dicarboxylic acid (XIII), and subsequent loss of carbon dioxide and water. Fig. 2 shows the absorption spectrum of 1 : 8-diaza-2 : 3-6 : 7-dibenzofluoreneone and that of the " parent " substance, 2 : 3-6 : 7-dibenzofluorenone, which was prepared by Martin's method (*J.*, 1941, 679). Diazabenzofluorenone (XII) could only arise by oxidation of the angular aza-hydrocarbon (VIII), and this fact confirms this assignment of structure to the compound originally prepared by Ullmann and Maag.

Little difficulty was experienced in repeating Ullmann and Maag's synthesis; but some improvements are recorded in the Experimental section. The reduction of the quinacridone (III) with sodium and alcohol gave the dihydro-compound (IX) together with a colourless product (also noted by the original workers) which has been identified as acridan. The presence of this material is due to the incomplete removal of *N*-*p*-bromophenylanthranilic acid from the *p*-phenylenedianthranilic acid (I) before cyclisation. This leads to the presence of 3-bromoacridone in the quinacridone, and on reduction this yields

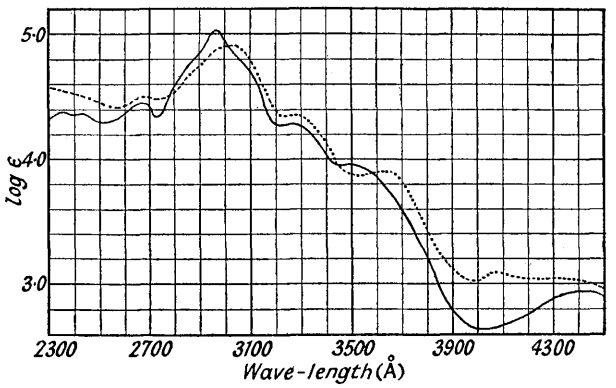


FIG. 2. *Absorption spectra of* 2 : 3-6 : 7-*dibenzofluorenone* (———), *and of* 1 : 8-*diaza*-2 : 3-6 : 7-*dibenzofluorenone* (– – – – –), *both in ethanol.*

acridan. This impurity was largely eliminated by using a large excess of anthranilic acid in the preparation of *p*-phenylenedianthranilic acid.

EXPERIMENTAL

NN'-p-*Phenylenedianthranilic Acid* (I).—A mixture of anthranilic acid (140 g.), potassium carbonate (100 g.), *p*-dibromobenzene (70 g.), cuprous chloride (2·7 g.), copper bronze (1·8 g.), and *iso*amyl alcohol (120 c.c.) was heated in an oil-bath at 150° for 3½ hours. After steam-distillation, the mixture was filtered and acidified with hydrochloric acid, and the precipitate collected. After extraction with boiling ethanol (6 × 300 c.c.) the *p*-phenylenedianthranilic acid (90 g.) was obtained as pale greenish-yellow crystals, m. p. 290—292° (Ullmann and Maag give m. p. 286°).

From the alcoholic liquors, *N*-*p*-bromophenylanthranilic acid (15 g.) was obtained as colourless plates, m. p. 182—183°.

13 : 14-*Dihydro*-5 : 8-*diazapentaphene.*—Cyclisation of the above *p*-phenylenedianthranilic acid (60 g.) was carried out essentially as described by Ullmann and Maag (*loc. cit.*), and yielded the quinacridone (III) (32 g.) as pale yellow needles, m. p. 412—414° (Ullmann and Maag give m. p. 394°). For the reduction, the quinacridone (8 g.) in boiling absolute alcohol (240 c.c.) was treated with sodium (24 g.) in small pieces. The mixture was then evaporated on a steam-bath, with constant stirring, to a thick red paste. This paste was added to a mixture of 10N-hydrochloric acid (120 c.c.) and water (200 c.c.), and the dark blue precipitate of the hydrochloride was collected and washed. The free base (4·0 g.) was obtained by addition to aqueous ammonia, and on recrystallisation from alcohol, the 13 : 14-dihydro-5 : 8-diazapentaphene formed deep-red needles, m. p. 243°. Solutions of this compound were oxidised in air to the aromatic substance.

5 : 8-*Diazapentaphene.*—This was obtained by oxidation of the above dihydro-compound

with nitric acid in acetic acid. It crystallised from alcohol in pale yellow needles, m. p. 245°, in agreement with Ullmann and Maag.

Acridan.—Cyclisation of *N*-*p*-bromophenylanthranilic acid (10 g.) with sulphuric acid in the same manner as for *p*-phenylenedianthranilic acid, gave 3-bromoacridone (6 g.), which formed yellow needles, m. p. 389° (decomp.), from acetic acid. Reduction of this compound (2 g.) with sodium and boiling alcohol gave a colourless product (1·4 g.) which, after recrystallisation from alcohol, formed colourless needles, m. p. 167—168° alone or mixed with an authentic specimen of acridan. Its identification was completed by oxidation, with potassium dichromate in acetic acid, to acridine, m. p. and mixed m. p. 111—112°.

1 : 8-*Diaza*-2 : 3-6 : 7-*Dibenzofluorenone.*—A mixture of 5 : 8-diazapentaphene (2·0 g.), selenium dioxide (4·0 g.), and water (15 c.c.) was heated in a sealed tube at 230—240° for 4 hours. After the mixture had cooled, the product was collected, washed well with water, and dried. The resulting yellow powder was first heated at 180°/0·01 mm. for 30 minutes to remove selenium; the residue was then sublimed at 240—250°/0·01 mm., the sublimate being collected. 1 : 8-*Diaza*-2 : 3-6 : 7-*dibenzofluorenone* (1·0 g.) was recrystallised from pyridine, and formed beautiful orange needles, m. p. 374—376° (Found: C, 81·1; H, 3·75; N, 9·8. $C_{19}H_{10}ON_2$ requires C, 80·8; H, 3·6; N, 9·9%).

2 : 3-6 : 7-*Dibenzofluorenone.*—Prepared by Martin's method (*loc. cit.*), this had m. p. 277—278°.

Absorption Spectra.—These were determined with a Hilger Uvispek spectrophotometer.

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