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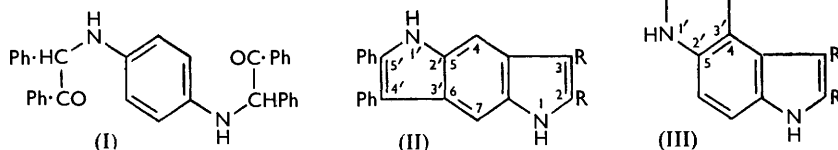
1. *The Synthesis and Structure of Some Pyrroloindoles.*

By D. A. KINSLEY and (the late) S. G. P. PLANT.

Benzoin has been condensed with *p*-phenylenediamine to give a mixture containing two tetraphenylpyrroloindoles, the structures of which have been determined by degradation of the "linear" 2 : 3 : 4' : 5'-tetraphenylpyrrolo-(2' : 3'-5 : 6)indole to *p*-dibenzoylbenzene. The structures of the products obtained by analogous condensations with 5-amino-2 : 3-dimethylindole are discussed. The preparation of other aminoindoles and their condensation products is described.

IN recent papers^{1,2} it has been shown that the Japp-Murray synthesis³ of indoles by which an aromatic amine is condensed with an α -hydroxy-ketone such as benzoin or 2-hydroxycyclohexanone⁴ is a promising method for the preparation of pyrroloindoles and this communication describes the synthesis of some pyrroloindoles derived formally from *o*- and *p*-phenylenediamine. Similar compounds derived from *m*-phenylenediamine have been synthesised by Ruggli and his co-workers.⁵

Japp and Meldrum⁶ prepared *NN'*-didesyl-*p*-phenylenediamine (I) from benzoin and *p*-phenylenediamine and stated that, when the compound was heated with zinc chloride, two substances, m. p. 318° and 335° respectively, were obtained but no further practical details were given. In the present investigation, the mixture obtained by repeating this reaction was separated into 2 : 3 : 4' : 5'-tetraphenylpyrrolo(2' : 3'-5 : 6)-indole (II; R = Ph) which was the major product and its isomer, 2 : 3 : 4' : 5'-tetraphenylpyrrolo(3' : 2'-4 : 5)indole (III; R = Ph).



The "linear" structure of the pyrroloindole (II; R = Ph) was established by degradation. Oxidation with chromic anhydride^{7,8} in acetic acid gave 1 : 4-dibenzamido-2 : 5-dibenzoylbenzene (IV; R = Bz) from which 1 : 4-diamino-2 : 5-dibenzoylbenzene (IV; R = H) was obtained by hydrolysis with sulphuric acid. Tetrazotisation of this amine followed by treatment with hypophosphorous acid⁹ provided *p*-dibenzoylbenzene

¹ Swindells and Tomlinson, *J.*, 1956, 1135.

² Carter, Katritzky, and Plant, *J.*, 1955, 337.

³ Japp and Murray, *J.*, 1894, **65**, 889.

⁴ Jones and Tomlinson, *J.*, 1953, 4114.

⁵ Ruggli and Straub, *Helv. Chim. Acta*, 1938, **21**, 1084, and previous papers.

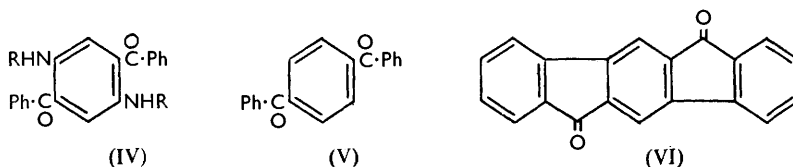
⁶ Japp and Meldrum, *J.*, 1899, **75**, 1043.

⁷ Gaudion, Hook, and Plant, *J.*, 1947, 1631.

⁸ Schofield and Theobald, *J.*, 1949, 796.

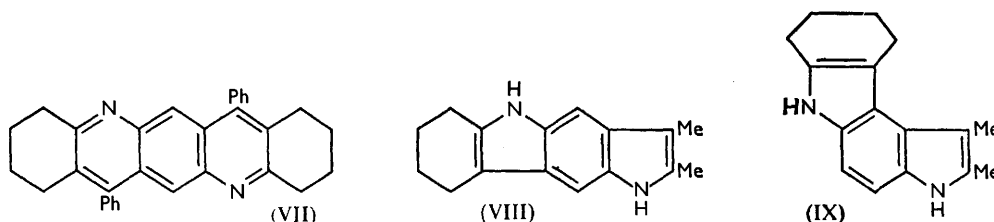
⁹ Cf. Kornblum in Adams, "Organic Reactions," John Wiley and Sons, New York, 1944, Vol. II, p. 262.

(V) identical (mixed m. p.) with a synthetic specimen. When the tetrazo-compound was heated at 100°, ring closure occurred giving 9:1'-dioxoindeno(3':2'-2:3)fluorene (VI), the properties of which agreed with those given by Deuschel.¹⁰



The amine (IV; R = H) has also been condensed with *cyclohexanone*, giving 6:7:8:9:5':6':7':8'-octahydro-5:4'-diphenylquinolino(3':2'-2:3)acridine (VII), aniline hydrochloride being used as a catalyst instead of alkali which is the usual catalyst in such reactions.¹¹

It then seemed interesting to investigate the preparation of pyrroloindoles, analogous to those described above, by the interaction of benzoin with various aminoindoles. Accordingly, 5-amino-2:3-dimethylindole was heated with benzoin in the presence of a little hydrochloric acid. The mixture which was isolated was separated into 2:3-dimethyl-4':5'-diphenyl-pyrrolo(2':3'-5:6)indole (II; R = Me) and -pyrrolo(3':2'-4:5)-indole (III; R = Me). Similarly, the product of the reaction between 5-amino-2:3-dimethylindole and 2-hydroxycyclohexanone in the presence of aniline hydrobromide¹² gave 5:6:7:8-tetrahydro-4':5'-dimethylpyrrolo(3':2'-2:3)carbazole (VIII) and its "angular" isomer (IX).



These pyrroloindoles were markedly prone to oxidation and their solutions darkened in air, presumably owing to the formation of peroxides. Their structures were assigned by comparing their ultraviolet absorption spectra with those of the tetraphenylpyrroloindoles (II and III; R = Ph). These spectra are shown in the Figure. "Linear" isomers absorb more light at the longer wavelengths than the "angular" ones, and possess a characteristic absorption maximum at 2300—2500 Å.

The formation of both "linear" and "angular" isomers during these cyclisations is unusual since related reactions usually give "angular" products in preference to "linear" ones.^{4,13} In the above "angular" products, however, there is probably considerable repulsion between the groups, phenyl or methyl, attached to the 3- and 4'-positions of the pyrroloindole (III; R = Ph or Me) or between the corresponding methyl and methylene groups in the pyrrolo-carbazole (IX) and this will favour the formation of the linear products (II) and (VIII). An analogous situation occurs in 4:5-disubstituted phenanthrenes such as (X) in which hindrance between the methyl groups in the 4- and the 5-position causes asymmetry which has been demonstrated by resolution of the compound into optically active forms.¹⁴ Bendas and Djerassi¹⁵ have shown that the

¹⁰ Deuschel, *Helv. Chim. Acta*, 1951, **34**, 2403.

¹¹ Cf. Albert, "The Acridines," Edward Arnold and Co., London, 1951, p. 62.

¹² Cf. Crowther, Mann, and Purdie, *J.*, 1943, 58.

¹³ See, e.g., Smith, *J. Amer. Chem. Soc.*, 1930, **52**, 397; Kulke and Manske, *Canad. J. Chem.*, 1952, **30**, 711.

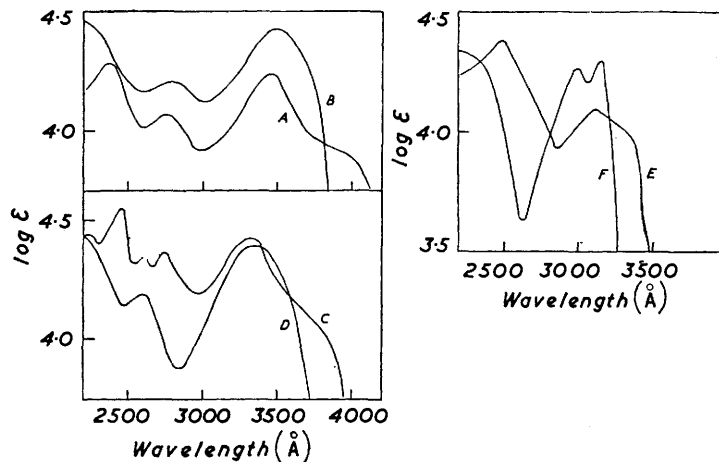
¹⁴ Newman and Hussey, *J. Amer. Chem. Soc.*, 1947, **69**, 3023.

¹⁵ Bendas and Djerassi, *ibid.*, 1956, **78**, 2474.

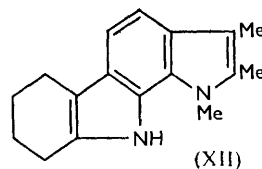
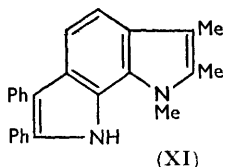
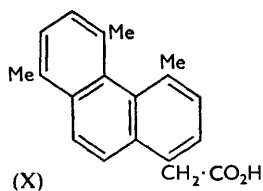
unexpected production of the anthracene nucleus in cyclisations which usually lead to the formation of phenanthrenes can be attributed to steric hindrance of this nature.

To extend these investigations to other aminoindoles, 4-, 5-, and 6-amino-2:3-diphenylindole were prepared by reduction of the corresponding nitro-compounds with dithionite, using the technique of Shaw and Woolley.¹⁶ These amines were stable when

Absorption spectra of (A) 2:3:4':5'-tetraphenylpyrrolo(2':3'-5:6)indole (II; R = Ph), (B) 2:3:4':5'-tetraphenylpyrrolo(3':2'-4:5)indole (III; R = Ph), (C) 2:3-dimethyl-4':5'-diphenylpyrrolo(2':3'-5:6)indole (II; R = Me), (D) 2:3-dimethyl-4':5'-diphenylpyrrolo(3':2'-4:5)indole (III; R = Me), (E) 5:6:7:8-tetrahydro-4':5'-dimethylpyrrolo(3':2'-2:3)carbazole (VIII), and (F) 5:6:7:8-tetrahydro-4':5'-dimethylpyrrolo(2':3'-3:4)carbazole (IX) (A, B, C, and D in MeOH; E and F in EtOH).



dry but, when wet with solvents, they underwent oxidation in air and became discoloured, the melting points being lowered. By reaction with ethyl acetoacetate, 5-amino-2:3-diphenylindole was converted into the corresponding indolylaminocrotonate, and with



benzaldehyde it yielded a Schiff's base which has been reduced catalytically to 5-benzylamino-2:3-diphenylindole. With benzoin a mixture was obtained from which the tetraphenylpyrroloindole (II; R = Ph) was isolated. When 6-amino-2:3-diphenylindole reacted with benzoin, 2:3:4':5'-tetraphenylpyrrolo(2':3'-4:5)indole, identical with the compound prepared by Japp and Meldrum⁶ from *m*-phenylenediamine, was obtained. Although the reaction between benzoin and 4-amino-2:3-dimethylindole afforded 2:3-dimethyl-4':5'-diphenylpyrrolo(2':3'-4:5)indole, no product could be isolated from the analogous reaction with 6-amino-2:3-dimethylindole.

Although many nitroindoles can be conveniently reduced to amines with dithionite, this method was not satisfactory for the preparation of 7-amino-2:3-dimethylindole and 7-amino-1:2:3-trimethylindole, probably because these bases were particularly liable to oxidation during their isolation. Brown and Nelson¹⁷ used Raney nickel and hydrazine

¹⁶ Shaw and Woolley, *J. Amer. Chem. Soc.*, 1953, **75**, 1877.

¹⁷ Brown and Nelson, *ibid.*, 1954, **76**, 5149.

to prepare 6-aminoindole and in the present work this elegant technique gave the required 7-aminoindoles in yields of 50—75%.

When 7-amino-2 : 3-dimethylindole was heated with benzoin, and aniline hydrobromide as catalyst, no product could be isolated. Under the same conditions, however, 7-amino-1 : 2 : 3-trimethylindole gave the pyrroloindole (XI). In a similar way, 5 : 6 : 7 : 8-tetrahydro-1' : 4' : 5'-trimethylpyrrolo(2' : 3'-1 : 2)carbazole (XII) was obtained when the amine was heated with 2-hydroxycyclohexanone.

EXPERIMENTAL

NN'-Didesyl-p-phenylenediamine.⁶—*p*-Phenylenediamine (12 g.) and benzoin (48 g.) were melted together at 140°, and hydrochloric acid (0.5 c.c.) was added. A vigorous reaction took place, and the mass solidified. The crude product (44 g.) was used directly in the following synthesis. It crystallised from cyclohexanone as yellow rhombs, m. p. 250—257° (rapid heating).

2 : 3 : 4' : 5'-*Tetraphenyl-pyrrolo*(2' : 3'-5 : 6)*indole* and *-pyrrolo*(3' : 2'-4 : 5)*indole*.—*NN'*-Didesyl-*p*-phenylenediamine (44 g.) and zinc chloride (27 g.) were ground together and heated at 200—210°, until the vigorous reaction had subsided. When cold, the solid was triturated with hot ethanol and then boiled with aqueous ethanol. The crude product (22 g.; m. p. 280—320°) crystallised from cyclohexanone (300 c.c.), giving 2 : 3 : 4' : 5'-*tetraphenylpyrrolo*(2' : 3'-5 : 6)*indole* (9 g.), m. p. 330°, which separated from pyridine as colourless needles, m. p. 331—333° (rapid heating), becoming yellow in air (Found: C, 88.5; H, 5.2; N, 5.8. C₃₄H₂₄N₂ requires C, 88.7; H, 5.2; N, 6.1%).

*cyclo*Hexanone, from the mother-liquors of the crystallisation described above, was removed in steam, and the residue was extracted with hot ethanol and crystallised three times from pyridine. 2 : 3 : 4' : 5'-*Tetraphenylpyrrolo*(3' : 2'-4 : 5)*indole* (1.4 g.) was obtained as needles, m. p. 310—312° (Found: C, 88.6; H, 5.4; N, 6.2%).

1 : 4-*Dibenzamido*-2 : 5-*dibenzoylbenzene*.—Finely powdered 2 : 3 : 4' : 5'-*tetraphenylpyrrolo*(2' : 3'-5 : 6)*indole* (5.8 g.), suspended in acetic acid (160 c.c.), was treated with chromic anhydride (3.6 g. in a little water), and the whole was stirred and heated on a water-bath for 2 hr. When cold, the solid residue of 1 : 4-*dibenzamido*-2 : 5-*dibenzoylbenzene* (1.7 g.), m. p. 293—296°, was washed with acetic acid and crystallised from pyridine, giving orange needles, m. p. 298° (Found: C, 77.6; H, 4.6; N, 5.3. C₃₄H₂₄O₄N₂ requires C, 77.9; H, 4.6; N, 5.3%).

1 : 4-*Diamino*-2 : 5-*dibenzoylbenzene*.—Sulphuric acid (48 c.c.) in water (32 c.c.) and 1 : 4-*dibenzamido*-2 : 5-*dibenzoylbenzene* (3.5 g.) were refluxed for 20 min. The hot solution was filtered (sintered-glass funnel), cooled, and after careful dilution with water was made alkaline with ammonia. The product (1.8 g.; m. p. 190—200°) separated from ethanol as crimson prisms, m. p. 204—206° with previous sintering, of 1 : 4-*diamino*-2 : 5-*dibenzoylbenzene* (1 g.) (Found: C, 75.9; H, 5.0. C₂₀H₁₆O₂N₂ requires C, 76.0; H, 5.1%). Treatment of this amine with benzoyl chloride in pyridine regenerated its benzoyl derivative.

Conversion of 1 : 4-Diamino-2 : 5-*dibenzoylbenzene into p-Dibenzoylbenzene*.—A stirred suspension of 1 : 4-*diamino*-2 : 5-*dibenzoylbenzene* (1 g.) in sulphuric acid (3.3 c.c.) and acetic acid (10 c.c.) was tetrazotised at 0—10° with sodium nitrite (0.5 g.). After hypophosphorous acid (6 g.) in water (16 c.c.) had been added, the whole was corked loosely and kept at 0° for 40 hr. The mass was extracted with benzene (300 c.c.)—ether (100 c.c.) and, after the extract had been washed successively with 2*N*-hydrochloric acid (2 × 50 c.c.), dilute ammonia (50 c.c.) and aqueous sodium carbonate (50 c.c.), it was dried (MgSO₄) and evaporated. The sticky residue was taken up in benzene and passed down a column of alumina (30 g.) and eluted with benzene. From the first eluate (175 c.c.), crude *p*-*dibenzoylbenzene*, m. p. 155—160°, was obtained by evaporation. The second fraction (475 c.c.) gave a mixture containing 9 : 1'-*dioxoindeno*(3' : 2'-2 : 3)*fluorene*, which was purified by washing with a little benzene, a further quantity of *p*-*dibenzoylbenzene*, m. p. 147—157°, being recovered from the washings. The combined yield of *p*-*dibenzoylbenzene* (0.2 g.) crystallised from acetic acid in needles, m. p. 158—160°, not depressed by admixture with an authentic specimen prepared from terephthalic acid.¹⁸

9 : 1'-*Dioxoindeno*(3' : 2'-2 : 3)*fluorene*.—The mixture obtained by tetrazotisation of 1 : 4-*diamino*-2 : 5-*dibenzoylbenzene* (0.8 g.) as described above was heated on a water-bath for $\frac{1}{2}$ hr.,

¹⁸ Munchmeyer, *Ber.*, 1886, 19, 1845.

until effervescence had ceased. After 12 hr. the precipitate was triturated with hot ammonia and taken up in benzene (500 c.c.). The solution was passed through alumina (15 g.) and was eluted with benzene. Evaporation of the first fraction gave a residue (0.06 g., m. p. 315—330°) which separated from acetic acid in violet needles of 9 : 1'-dioxoindeno(3' : 2'-2 : 3)fluorene, m. p. 338—340° (Found: C, 84.8; H, 3.9. Calc. for C₂₀H₁₀O₂: C, 85.1; H, 3.5%). Deuschel¹⁰ gives m. p. 345—346°.

6 : 7 : 8 : 9 : 5' : 6' : 7' : 8'-Octahydro-5 : 4'-diphenylquinolino(3' : 2'-2 : 3)acridine.—When 1 : 4-diamino-2 : 5-dibenzoylbenzene (1 g.), cyclohexanone (0.8 g.), and a catalytic amount of aniline hydrochloride were heated together at 135°, steam was evolved and the mass solidified. After the solid had been washed with hot ethanol, the quinolinoacridine (0.5 g.), m. p. 380—390°, was obtained by crystallisation from anisole. Further crystallisation from anisole gave yellow prisms, m. p. 382—390° (black liquid), which for analysis were dried at 200° *in vacuo* (Found: C, 87.9, 87.9; H, 6.2, 6.4; N, 6.0, 6.0. C₃₂H₂₈N₂ requires C, 87.3; H, 6.4; N, 6.4%).

2 : 3-Dimethyl-4' : 5'-diphenyl-pyrrolo(2' : 3'-5 : 6)indole and -pyrrolo(3' : 2'-4 : 5)indole. 5-Amino-2 : 3-dimethylindole¹⁶ (7 g.), benzoin (9 g.), and hydrochloric acid (4 drops) were heated together at 205° until the melt solidified. After trituration with ethanol the crude mixture (9 g.), m. p. 235—245°, was crystallised three times from anisole, giving 2 : 3-dimethyl-4' : 5'-diphenyl-pyrrolo(2' : 3'-5 : 6)indole (0.9 g.) as plates, m. p. 285—287° (Found: C, 85.6; H, 6.1. C₂₄H₂₀N₂ requires C, 85.7; H, 6.0; N, 8.3%). After the anisole mother-liquors from the first of the above crystallisations had been boiled down almost to dryness, the material which separated was crystallised three times from anisole, and 2 : 3-dimethyl-4' : 5'-diphenylpyrrolo(3' : 2'-4 : 5)-indole (0.5 g.) was obtained as needles, m. p. 269—271° (rapid heating) (Found: C, 85.6; H, 6.2; N, 8.1%).

5 : 6 : 7 : 8-Tetrahydro-4' : 5'-dimethyl-pyrrolo(3' : 2'-2 : 3)carbazole and -pyrrolo(2' : 3'-3 : 4)-carbazole.—After 5-amino-2 : 3-dimethylindole (3.4 g.) and 2-hydroxycyclohexanone (2.4 g.) had been heated together at 140° until evolution of water had subsided, aniline hydrobromide (0.05 g.) was added, and the melt heated to 200° until it solidified. The solid was ground with ethanol, and the crude mixture (1.9 g.), m. p. 240—280°, was crystallised from anisole giving 5 : 6 : 7 : 8-tetrahydro-4' : 5'-dimethylpyrrolo(3' : 2'-2 : 3)carbazole (0.8 g.) as prisms, m. p. 356—360° (rapid heating) (Found: C, 80.7; H, 7.8; N, 11.6. C₁₆H₁₈N₂ requires C, 80.7; H, 7.6; N, 11.8%). The anisole mother-liquors were rapidly evaporated to small bulk, and light petroleum (b. p. 40—60°) was added. The precipitated solid (1.1 g.), m. p. 225—255°, was crystallised twice from anisole. To minimise decomposition each crystallisation was carried out rapidly and the crystals were washed well with ethanol before being dried for a short time at 100°. 5 : 6 : 7 : 8-Tetrahydro-4' : 5'-dimethylpyrrolo(2' : 3'-3 : 4)carbazole (0.3 g.) separated as needles, m. p. 261—265°. Sublimation at 200°/2 × 10⁻⁴ mm. for 3½ hr. gave microcrystalline material, m. p. 263—267° (rapid heating) (Found: C, 80.4; H, 7.9%).

Nitro-2 : 3-diphenylindoles.—5-Nitro-2 : 3-diphenylindole,^{19, 20} prepared from deoxybenzoin *p*-nitrophenylhydrazone, was obtained after purification (alumina) as prisms,²⁰ m. p. 200° (from ethanol), or needles,¹⁹ m. p. 210° (from acetic acid). 4- and 6-Nitro-2 : 3-diphenylindole were prepared by separating the mixture obtained by the cyclisation of deoxybenzoin *m*-nitrophenylhydrazone.^{19, 20}

6-Nitro-2 : 3-diphenylindole was more conveniently obtained by nitration.²¹ Nitric acid (4 c.c.; *d* 1.5) in acetic acid (16 c.c.) was cautiously added to a hot solution of 2 : 3-diphenylindole (27 g.) in acetic acid (60 c.c.). The whole was boiled for 5 min. and the product (8 g.; m. p. 220—225°) which separated was collected. It crystallised from acetic acid in orange needles, m. p. 225—227°.

4- and 6-Amino-2 : 3-diphenylindole.—These were obtained in 70% yield by reduction of the corresponding nitroindoles with alkaline dithionite.¹⁶ 4-Amino-2 : 3-diphenylindole crystallised from ethanol in plates, m. p. 202° (Found: C, 84.1; H, 5.6; N, 10.0. C₂₀H₁₆N₂ requires C, 84.5; H, 5.6; N, 9.9%). Its *acetyl derivative*, m. p. 197°, was obtained as rhombs (from ethanol) on treatment of the amine with acetic anhydride (Found: C, 80.9; H, 5.5. C₂₂H₁₈ON₂ requires C, 81.0; H, 5.5; N, 8.6%). 6-Amino-2 : 3-diphenylindole formed needles (from aqueous ethanol), m. p. 177° (Found: C, 84.3; H, 5.6; N, 9.7%), and its *acetyl derivative* crystallised from aqueous acetic acid in needles, m. p. 269° (Found: C, 80.9; H, 5.6%).

¹⁹ Fennell and Plant, *J.*, 1932, 2872.

²⁰ Schofield and Theobald, *J.*, 1950, 1505.

²¹ Bannister, B.A. Thesis, Oxford, 1947.

5-Amino-2 : 3-diphenylindole.—A hot solution of 5-nitro-2 : 3-diphenylindole (11 g.) in ethanol (750 c.c.) and *N*-sodium hydroxide (150 c.c.) was treated with sodium dithionite (55 g.) in 0.5*N*-sodium hydroxide (220 c.c.). The light red solution was poured into water, and the crude product (8.5 g., m. p. 193—196°) was collected. For purification, it was distilled under reduced pressure and then crystallised from ethanol, giving *5-amino-2 : 3-diphenylindole* as plates, m. p. 202° (Found: C, 84.6; H, 5.7; N, 9.8%). The *hydrochloride* separated from ethanol in needles, m. p. 330° (Found: N, 9.1; Cl, 11.3. $C_{20}H_{17}N_2Cl$ requires N, 8.7; Cl, 11.1%). The *acetyl derivative* separated from aqueous ethanol in plates, m. p. 236° (Found: C, 81.1; H, 5.8; N, 8.5%).

5-Amino-2 : 3-diphenylindole (0.5 g.), ethyl acetoacetate (0.3 g.), and concentrated hydrochloric acid (1 drop) were ground together. After 12 hr., the solid (0.5 g.; m. p. 141°) obtained by trituration with ethanol crystallised from benzene–light petroleum, giving *ethyl β-(2 : 3-diphenylindol-5-yl)aminocrotonate* as needles, m. p. 142° (Found: C, 78.7; H, 6.0; N, 7.2. $C_{26}H_{24}O_2N_2$ requires C, 78.8; H, 6.1; N, 7.1%).

5-Benzylidene- and 5-Benzyl-amino-2 : 3-diphenylindole.—After *5-amino-2 : 3-diphenylindole* (0.95 g.) and benzaldehyde (0.35 g.) had been heated to 120° for 10 min., crystallisation of the solid from methanol gave yellow needles (0.9 g.; m. p. 85—95°) containing solvent of crystallisation which was removed by drying first at 60° and then at 135° *in vacuo* for 10 hr., *5-benzylideneamino-2 : 3-diphenylindole* being obtained as brown rhombs, m. p. 158° (previous sintering) (Found: C, 86.9; H, 5.5. $C_{27}H_{20}N_2$ requires C, 87.1; H, 5.4%).

This compound (0.9 g., containing methanol of crystallisation) in methanol (150 c.c.) was shaken with hydrogen in the presence of 1% palladium–strontium carbonate (0.4 g.) until absorption ceased (5 hr., 88 c.c.; H_2 requires 54 c.c.). After the solution had been boiled, filtered whilst hot, and evaporated, the residue separated from ethanol in plates, m. p. 153°, of *5-benzylamino-2 : 3-diphenylindole* (0.2 g.) (Found: C, 86.3; H, 6.0. $C_{27}H_{22}N_2$ requires C, 86.6; H, 5.9%).

Treatment of this amine with acetic anhydride in benzene gave the *acetyl derivative*, which separated from ethanol in needles. These were dried at 210° *in vacuo* leaving the solvent-free derivative, m. p. 233° (Found: C, 83.3; H, 5.9. $C_{29}H_{24}ON_2$ requires C, 83.7; H, 5.8%).

Condensations with Benzoin.—(a) After *6-amino-2 : 3-diphenylindole* (0.6 g.), benzoin (0.4 g.), and hydrochloric acid (1 drop) had been heated at 210° until the melt solidified, the solid was washed with ethanol, and the crude product (0.65 g., m. p. 271—279°) was crystallised three times from anisole, giving *2 : 3 : 4' : 5'-tetraphenylpyrrolo(2' : 3'-4 : 5)indole* in needles, m. p. 282°, identical (mixed m. p.) with an authentic sample prepared from *m*-phenylenediamine.^{4, 6}

(b) *5-Amino-2 : 3-diphenylindole* (0.6 g.) and benzoin (0.4 g.) were condensed in the same way and the product (0.5 g.), m. p. 280—315°, was crystallised first from cyclohexanone and then twice from pyridine, giving yellow needles of *2 : 3 : 4' : 5'-tetraphenylpyrrolo(2' : 3'-5 : 6)indole*, m. p. 333°, not depressed by admixture with a specimen prepared (see above) from *NN'*-didesyl-*p*-phenylenediamine.

(c) *4-Amino-2 : 3-dimethylindole*^{8, 16} (0.4 g.), benzoin (0.5 g.), and a catalytic quantity of aniline hydrobromide¹² were condensed together at 215°. The product (0.35 g.; m. p. 247—251°) obtained by trituration with ethanol was crystallised from anisole, to give *2 : 3-dimethyl-4' : 5'-diphenylpyrrolo(2' : 3'-4 : 5)indole*, m. p. 250°, which for analysis was sublimed at 180°/3 × 10⁻⁴ mm. (Found: N, 8.2. $C_{24}H_{20}N_2$ requires N, 8.3%).

7-Amino-2 : 3-dimethylindole.—*2 : 3-Dimethyl-7-nitroindole* (1 g.) in warm methanol (60 c.c.) was treated alternately with small portions of Raney nickel and aqueous hydrazine (60%), so that gas was continuously evolved from the mixture, which was boiled occasionally. After ½ hr., when the yellow colour had been discharged, the solution was boiled to remove any excess of hydrazine, and was filtered. The filtrate was evaporated and the residue dried in a desiccator over potassium hydroxide. The *amine* then separated from carbon tetrachloride in needles (0.55 g.), m. p. 125—129°. Sublimation at 120°/4 × 10⁻² mm. provided needles, m. p. 127—129° [Blackhall and Thomson²² give m. p. 126° (decomp)] (Found: C, 74.7; H, 7.4. Calc. for $C_{10}H_{12}N_2$: C, 75.0; H, 7.5%). Treatment of the amine with acetic anhydride afforded the *acetyl derivative* as needles, m. p. 167° (from ethanol) (Found: C, 71.5; H, 7.1. $C_{12}H_{14}ON_2$ requires C, 71.3; H, 6.9%).

1 : 2 : 3-Trimethyl-7-nitroindole.—After *2 : 3-dimethyl-7-nitroindole*⁸ (17.5 g.), potassium hydroxide (44 g.) in water (14 c.c.), dimethyl sulphate (40 c.c.), and acetone (300 c.c.) had been

²² Blackhall and Thomson, *J.*, 1954, 3916.

refluxed together for $\frac{1}{2}$ hr., addition of water precipitated 1 : 2 : 3-trimethyl-7-nitroindole (18.5 g.; m. p. 89—93°) which separated from ethanol in yellow prisms, m. p. 93° (Found: C, 64.7; H, 5.8. $C_{11}H_{12}O_2N_2$ requires C, 64.7; H, 5.9%).

7-Amino-1 : 2 : 3-trimethylindole.—1 : 2 : 3-Trimethyl-7-nitroindole (3 g.) in methanol (40 c.c.) was reduced with Raney nickel and hydrazine, by the technique described above. The residue obtained by evaporation of the methanol was dried over potassium hydroxide and triturated with a little ether, giving the crude product (1.2 g.; m. p. 139—143°). Sublimation at $110^\circ/4 \times 10^{-2}$ mm. gave the *amine* as needles, m. p. 146° (previous sintering) (Found: C, 75.9; H, 8.2. $C_{11}H_{14}N_2$ requires C, 75.9; H, 8.1%). Its *acetyl derivative* crystallised from methanol in needles, m. p. 189° (Found: C, 71.9; H, 7.2. $C_{13}H_{16}ON_2$ requires C, 72.2; H, 7.4%).

1 : 2 : 3-Trimethyl-4' : 5'-diphenylpyrrolo(3' : 2'-6 : 7)indole.—After 7-amino-1 : 2 : 3-trimethylindole (0.35 g.) and benzoin (0.4 g.) had been condensed together at 200° with aniline hydrobromide as catalyst, the solid was washed with ethanol, and the product (0.55 g.; m. p. 243—250°) was crystallised twice from anisole, giving the *pyrroloindole* as prisms, m. p. 256° (previous sintering) (Found: C, 85.4; H, 6.5. $C_{25}H_{22}N_2$ requires C, 85.7; H, 6.3%).

5 : 6 : 7 : 8-Tetrahydro-1' : 4' : 5'-trimethylpyrrolo(2' : 3'-1 : 2)carbazole.—7-Amino-1 : 2 : 3-trimethylindole (1.2 g.) was heated with 2-hydroxycyclohexanone (0.8 g.) and aniline hydrobromide. At 165°, the melt solidified and the product (1.4 g.) was crystallised from anisole, and was then sublimed at $180^\circ/8 \times 10^{-2}$ mm., giving the *carbazole* as needles, m. p. 242—244° (Found: C, 80.8; H, 7.8. $C_{17}H_{20}N_2$ requires C, 81.0; H, 7.9%).

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