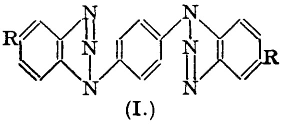
100. *Experiments on the Preparation of Indolocarbazoles. Part III.*

By P. V. CLIFTON and S. G. P. PLANT.

Investigations into the possibility of applying established synthetical methods in the carbazole group to the preparation of indolocarbazoles from derivatives of *p*-phenylenediamine, including 3-aminocarbazole and related substances, have culminated in the synthesis of 6-cyanoindolo(2′ : 3′-3 : 4)-carbazole.

THIS communication describes attempts to apply known methods for the synthesis of carbazoles to the preparation of indolocarbazoles from various derivatives of *p*-phenylenediamine. Manjunath (*J. Indian Chem. Soc.*, 1927, **4**, 271) was unable to obtain an indolocarbazole by heating the phenylenebistriazole (I; R = H), and we have confirmed his observations. The degree of success attending the Graebe–Ullmann reaction, however, can vary widely among closely related compounds, and it seemed desirable to investigate other substances of this type. Accordingly the bistriazoles (I; R = Cl, OMe, and CN) have been synthesised and then heated under a variety of conditions, but none gave the desired product.



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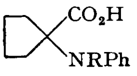

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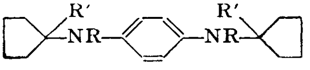
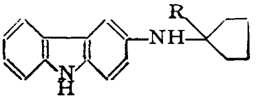


(III.)

Carbazole has been obtained from 1-anilino*cyclo*pentane-1-carboxylic acid (II; R = H), and the 1- and 3-methylcarbazoles from the corresponding toluidino-compounds, by heating them with potassium hydroxide, sometimes with the addition of sodium ethoxide (Plant and Facer, *J.*, 1925, **127**, 2037; Oakeshott and Plant, *J.*, 1926, 1210; 1927, 484), and it seemed possible that the same reaction might be applied to the acid (III; R = H, R′ = CO_2H) with the formation of an indolocarbazole. *NN*′-Di-(1-cyano*cyclo*pentyl)-*p*-phenylenediamine (III; R = H, R′ = CN) has been prepared by adding potassium cyanide to *p*-phenylenediamine and *cyclo*pentanone in acetic acid, and converted into the corresponding diamide. When the latter was fused with potassium hydroxide, a substantial amount of *p*-phenylenediamine was formed, and the fact that the alkali residue was completely soluble in water showed the absence of an indolocarbazole. In this respect the diamide behaves like the analogous compound derived from tolylene-2 : 4-diamine (Bond, Deegan, and Plant, *J.*, 1949, S160). Hydrolysis of the diamide led to the acid (III; R = H, R′ = CO_2H), which, on fusion with a mixture of potassium hydroxide and sodium ethoxide, gave 3-aminocarbazole. Evidently carbazole formation has proceeded in one half of the molecule, but fission of the type which characterises the diamide has ensued in the other, and the acid (IV; R = CO_2H) may be an intermediate stage in the process. In an attempt to prepare (IV; R = CO_2H), 3-(1-cyano*cyclo*pentylamino)carbazole (IV; R = CN) has been made, but hydrolysis to the acid has not been effected. Boiling hydrochloric acid gave 3-aminocarbazole, and the use of concentrated sulphuric acid to obtain the amide led to sulphonation.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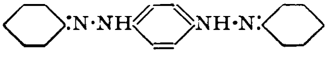
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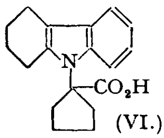
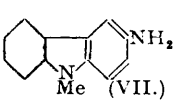

(VI.)

Several possibilities exist for the application of the Fischer indole synthesis to this problem in the *p*-phenylene series, and some of these have been examined. Unfortunately, we have been unable to eliminate $2NH_3$ from *N′N‴*-di*cyclo*hexylidene-*p*-phenylenedihydrazine (V), and we have been unsuccessful, as was Manjunath (*loc. cit.*), in attempts to obtain an *N*-methylated indolocarbazole from the bisnitrosamine from *NN′*-dimethyl-*p*-phenylenediamine by reduction with zinc in acetic acid in the presence of *cyclo*hexanone. Plant and Rippon (*J.*, 1928, 1906) reduced the nitrosamine (II; R = NO) in acetic acid containing *cyclo*hexanone and obtained 1-(tetrahydro-9-carbazolyl)*cyclo*pentane-1-carboxylic acid (VI), which decomposed to give tetrahydrocarbazole and *cyclo*pent-1-ene-1-carboxylic acid with hot 60% sulphuric acid, and in other ways. It therefore seemed possible that the bisnitrosamine (III; R = NO, R′ = CN) and the corresponding di*cyclo*hexyl compound might undergo similar conversion into octahydroindolocarbazoles containing 1-cyano*cyclo*alkyl substituents attached to the nitrogen atoms, which would have the advantage over the simpler methyl derivatives that the substituents might be very easily removed from the product. Unfortunately, neither bisnitrosamine could be made to give the substances envisaged.

The difficulty of effecting the above double cyclisation processes suggested the use of aminocarbazoles from which it would be necessary to form only one additional indole system. A convenient compound of this type seemed to be 6-amino-9-methylhexahydrocarbazole (VII) in which the orientation of *p*-phenylenediamine is maintained. This substance was prepared by reduction of the known tetrahydro-9-methyl-6-nitrocarbazole and also, less satisfactorily, from the product of nitrosating hexahydro-9-methylcarbazole. Both nitrogen atoms are basic, and it seemed desirable first to examine similar reactions with the closely related and more easily accessible *p*-aminodimethylaniline. The latter has accordingly been converted into 1-cyano-1-*p*-dimethylaminoanilino*cyclo*pentane, which was hydrolysed *via* the amide to the acid (VIII), but this gave no 3-dimethylaminocarbazole when its sodium salt was fused with sodium ethoxide and potassium hydroxide. An attempt to apply the Graebe–Ullmann reaction to 1-*p*-dimethylaminophenyl-5-nitrobenzotriazole (IX; R = NO_2) failed, but it is known that the reaction does not proceed well with nitrobenzotriazoles and that better results can be expected when the nitro-group is replaced by acyl or cyano- (see, *e.g.*, Preston, Tucker, and Cameron, *J.*, 1942, 500). The triazoles (IX; R = COMe, COPh, and CN) were accordingly prepared from *p*-aminodimethylaniline, but in no case could the Graebe–Ullmann reaction be successfully applied. This is surprising in view of the fact that the reaction has been used for making amino-, cyano-, and *C*-acyl-carbazoles. The results suggested that 6-aminohexahydro-9-methylcarbazole would be unlikely to give indolocarbazoles in similar reactions, and the use of 3-aminocarbazole in which the ring-nitrogen is non-basic seemed to be more promising. This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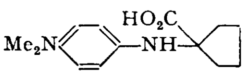
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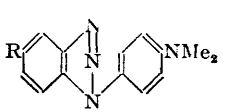
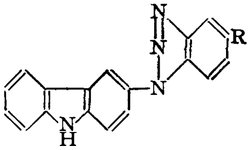

(IX.)

has been condensed with 4-chloro-3-nitrobenzonitrile and the product converted through the corresponding amine into 1-3′-carbazolyl-5-cyanobenzotriazole * (X; R = CN) and, when the latter was heated, nitrogen was eliminated with the formation of a cyanoindolocarbazole.



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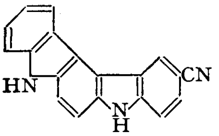

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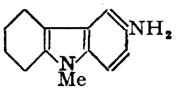

(XII.)

There are two possible structures, but a " linear " arrangement of the rings is less likely on general grounds, and the substance is regarded as 6-cyanoindolo(2′ : 3′-3 : 4)carbazole (XI). It seems probable that other substituted indolo(2′ : 3′-3 : 4)carbazoles could be obtained from 3-aminocarbazole by the Graebe–Ullmann method, but it must be noted that Manjunath (*loc. cit.*) was unable to effect the reaction with the two compounds (X; R = NO_2 and NH_2). In an attempt to carry out a parallel synthesis from 6-amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (XII), in which the ring-nitrogen is also non-basic, 6-(2-amino-4-cyanoanilino)-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole has been prepared, but it could not be converted into the requisite triazole.

EXPERIMENTAL.

p-*Di-(5-chlorobenzotriazol-1-yl)benzene* (I; R = Cl).—A mixture of 4-chloro-2-nitroaniline (47 g.), *p*-dibromobenzene (32 g.), and potassium carbonate (39 g.) was heated in nitrobenzene (190 c.c.) containing a little copper powder for 8 hours at 190—200° with mechanical stirring under a short air condenser. The whole was filtered while hot through glass-wool, and, on cooling, NN′-*di-(4-chloro-2-nitrophenyl)*-p-*phenylenediamine* separated from the solution in red prisms (19 g.). After being refluxed for a short time with ethanol (200 c.c.), it was recrystallised from nitrobenzene, and had m. p. 291—292° (Found: C, 51·7; H, 3·2. $C_{18}H_{12}O_4N_4Cl_2$ requires C, 51·6; H, 2·9%). A solution of sodium (6·5 g.) in ethanol (150 c.c.) was saturated with hydrogen sulphide, the above dinitro-compound (19 g.) added, and the mixture heated until a vigorous reaction set in. After this had subsided, the whole was refluxed for 12 hours, and, when cold, the colourless solid (8·5 g.) was collected, washed with water, and crystallised from xylene, from which NN′-*di-(2-amino-4-chlorophenyl)*-p-*phenylenediamine* separated in colourless needles, m. p. 202—203° (Found: N, 15·7. $C_{18}H_{16}N_4Cl_2$ requires N, 15·6%). Sodium nitrite (3·4 g.) in a little water was gradually added, with stirring, to the diamine (8·5 g.) in glacial acetic acid (100 c.c.) containing concentrated hydrochloric acid (6·6 c.c.) at 10°. After 2 hours, dilution with water precipitated p-*di-(5-chlorobenzotriazol-1-yl)benzene* (8·3 g.), which crystallised from nitrobenzene in colourless plates, m. p. 325° (decomp.) (Found: C, 56·4; H, 2·7. $C_{18}H_{10}N_6Cl_2$ requires C, 56·7; H, 2·6%).

p-*Di-(5-methoxybenzotriazol-1-yl)benzene* (I; R = OMe).—Prepared from 4-methoxy-2-nitroaniline by methods similar to those described above, NN′-*di-(4-methoxy-2-nitrophenyl)*-p-*phenylenediamine* (reaction temperature: 185°, for 6 hours) crystallised from nitrobenzene in dark violet needles, m. p. 220° (Found: C, 58·2; H, 4·5. $C_{20}H_{18}O_6N_4$ requires C, 58·5; H, 4·4%), NN′-*di-(2-amino-4-methoxyphenyl)*-p-*phenylenediamine* from xylene in colourless plates, m. p. 219° (Found: C, 68·5; H, 6·5. $C_{20}H_{22}O_2N_4$ requires C, 68·6; H, 6·3%), and p-*di-(5-methoxybenzotriazol-1-yl)benzene* from nitrobenzene in solvated colourless needles, m. p. 321—323° (Found: N, 20·1. $C_{20}H_{16}O_2N_6,C_6H_5O_2N$ requires N, 19·8%).

p-*Di-(5-cyanobenzotriazol-1-yl)benzene* (I; R = CN).—Powdered anhydrous sodium acetate (4·6 g.) was added to a molten mixture of *p*-phenylenediamine (2 g.) and 4-chloro-3-nitrobenzonitrile (6·1 g.), and the whole heated at 180° with stirring until it solidified. After the mixture had been boiled with ethanol and the residue crystallised from nitrobenzene, NN′-*di-(4-cyano-2-nitrophenyl)*-p-*phenylenediamine* was obtained in red prisms (3·3 g.), m. p. 317—318° (Found: C, 60·3; H, 3·1. $C_{20}H_{12}O_4N_6$ requires C, 60·0; H, 3·0%). A boiling solution of stannous chloride (20 g.) in concentrated hydrochloric acid (50 c.c.) was added to this substance (2·9 g.) in hot glacial acetic acid (250 c.c.), and the whole boiled for 20 minutes. When cold, the mixture was made alkaline with sodium hydroxide, the solid dissolved in acetic acid (60 c.c.) containing concentrated hydrochloric acid (4 c.c.) at 30°, and the solution treated with aqueous sodium nitrite (1·1 g.). The precipitated p-*di-(5-cyanobenzotriazol-1-yl)benzene* was washed with dilute hydrochloric acid and crystallised from nitrobenzene, from which it separated in colourless prisms, m. p. above 360° (Found: C, 66·2; H, 2·8. $C_{20}H_{10}N_8$ requires C, 66·3; H, 2·8%).

NN′-*Di-(1-cyano*cyclo*pentyl)*-p-*phenylenediamine* (III; R = H, R′ = CN).—Potassium cyanide (6·4 g.) in water (20 c.c.) was gradually added to *p*-phenylenediamine (5 g.) and *cyclo*pentanone (7·4 g.), in glacial acetic acid (50 c.c.) at room temperature, and after 24 hours the NN′-*di-(1-cyano*cyclo*pentyl)*-p-*phenylenediamine* (9·9 g.), m. p. 149°, which had separated was collected, washed with ethanol, and dried. It crystallised from ethanol in almost colourless needles, m. p. 151—152° (Found: C, 73·2; H, 7·5. $C_{18}H_{22}N_4$ requires C, 73·5; H, 7·5%). Its *bisnitrosamine*, which separated when the diamine was treated

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* Ring Index numbering.

with sodium nitrite in acetic acid–hydrochloric acid, crystallised from benzene in pale yellow plates, m. p. 151—152° (decomp.) (Found : C, 61·5; H, 5·8. $C_{18}H_{20}O_2N_6$ requires C, 61·4; H, 5·7%).

NN′-*Di*-(1-*carbamyl*cyclo*pentyl*)-p-*phenylenediamine* (III; R = H, R′ = $CO{\cdot}NH_2$).—A solution of the above dicyanide (5 g.) in concentrated sulphuric acid (50 c.c.) was kept for 2 days, poured on ice, and made alkaline with ice–concentrated aqueous ammonia. The precipitated NN′-*di*-(1-*carbamyl*cyclo*pentyl*)-p-*phenylenediamine* (4·8 g.) separated from ethanol in colourless plates, m. p. 290—292° (Found : C, 65·6; H, 7·9. $C_{18}H_{26}O_2N_4$ requires C, 65·5; H, 7·9%).

A mixture of the diamide (2·8 g.) and powdered potassium hydroxide (10 g.) was heated at 320° in a copper tube, and the volatile material was condensed and collected. When the distillate was dissolved in dilute acetic acid, the solution shaken with ether, and the aqueous layer shaken for 10 minutes with acetic anhydride (3 c.c.), *NN*′-diacetyl-*p*-phenylenediamine (0·5 g.), identified by mixed m. p. with an authentic specimen, gradually separated. No appreciable amount of insoluble material appeared when the alkali residue was dissolved in water.

NN′-*Di*-(1-*carboxy*cyclo*pentyl*)-p-*phenylenediamine* (III; R = H, R′ = CO_2H).—The above diamide (5 g.) was refluxed with concentrated hydrochloric acid (50 c.c.) for an hour, the whole evaporated to dryness on a steam-bath, the residue dissolved in dilute aqueous sodium hydroxide, and the filtered solution acidified with acetic acid. The *NN*′-di-(1-carboxy*cyclo*pentyl)-*p*-phenylenediamine (3 g.), m. p. 253° (decomp.), which separated, could not be satisfactorily recrystallised and was converted into its *diethyl* ester, almost colourless needles, m. p. 101° (from ethanol), by refluxing it with ethanolic hydrogen chloride for 5 hours (Found : C, 68·4; H, 8·0. $C_{22}H_{32}O_4N_2$ requires C, 68·0; H, 8·2%).

When the acid (12 g.) was heated with powdered potassium hydroxide (20 g.) and sodium ethoxide (20 g.) at 300° for an hour in a copper tube, no *p*-phenylenediamine could be detected in the distillate by the above method. After the alkali residue had been treated with water, the dark, insoluble material was dried and distilled under reduced pressure. The substance obtained was crystallised from ethanol in colourless plates, m. p. 250° (Found : C, 79·2; H, 5·5. Calc. for $C_{12}H_{10}N_2$: C, 79·1; H, 5·5%), and was shown to be 3-aminocarbazole by mixed m. p.

3-(1-*Cyano*cyclo*pentylamino*)*carbazole* (IV; R = CN).—Prepared from 3-aminocarbazole by a process similar to that described for *NN*′-di-(1-cyano*cyclo*pentyl)-*p*-phenylenediamine, this *carbazole* crystallised from ethanol in colourless plates, m. p. 138—139° (Found : C, 78·5; H, 6·2. $C_{18}H_{17}N_3$ requires C, 78·5; H, 6·2%). After the cyanide (3 g.) had been refluxed with concentrated hydrochloric acid (70 c.c.) for 5 hours, addition of alkali to the filtered solution precipitated 3-aminocarbazole, which separated from toluene in almost colourless plates (1 g.), m. p. and mixed m. p. 254°.

N′N‴-*Di*cyclo*hexylidene*-p-*phenylenedihydrazine* (V).—*p*-Phenylenedihydrazine dihydrochloride (3·4 g.; Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4545), *cyclo*hexanone (5 c.c.), and anhydrous sodium acetate (5 g.) were stirred in ethanol (50 c.c.) at 0°, and a mixture of equal volumes of ethanol and water (25 c.c.) was gradually added. After a further 40 minutes' stirring, the yellow solid was collected and quickly dissolved in hot ethanol (60 c.c.), and the filtered solution cooled. The *dihydrazone* was obtained in orange plates (3 g.), m. p. 172° (decomp.) (Found : C, 72·5; H, 8·9. $C_{18}H_{26}N_4$ requires C, 72·5; H, 8·7%), which gradually decomposed on being kept.

NN′-*Dimethyl*-p-*phenylenediamine*.—The following method for the preparation of this substance was found to be more convenient than that described by Willstätter and Pfannenstiel (*Ber.*, 1905, **38**, 2244). Methyl iodide (80 g.) and ethanolic potassium hydroxide (24 g. in 130 c.c.) were added at room temperature to *NN*′-diformyl-*p*-phenylenediamine (33 g.) in ethanol (400 c.c.) and, after being kept overnight, the mixture was heated at 50° for 24 hours. When cold, ethanol was distilled from the filtered solution, and the residue warmed for 2 hours on the steam-bath with concentrated hydrochloric acid (250 c.c.), and made alkaline. After the product had been extracted with ether, and the extract dried (K_2CO_3) and fractionated, *NN*′-dimethyl-*p*-phenylenediamine (15 g.) was collected at 146—148°/16 mm.

NN′-*Di*-(1-*cyano*cyclo*hexyl*)-p-*phenylenediamine*.—Prepared from *cyclo*hexanone by methods similar to those used for the analogous *cyclo*pentyl compounds, *NN*′-di-(1-cyano*cyclo*hexyl)-*p*-phenylenediamine crystallised from ethanol in colourless prisms, m. p. 194° (Found : C, 74·3; H, 8·2. Calc. for $C_{20}H_{26}N_4$: C, 74·5; H, 8·1%), and its *bisnitrosamine* from ethanol in brown prisms, m. p. 171—172° (decomp.) (Found : C, 63·0; H, 6·4. $C_{20}H_{24}O_2N_6$ requires C, 63·2; H, 6·3%). Bucherer and Fischbeck (*J. pr. Chem.*, 1934, **140**, 69) made the dicyanide by a different process, but give the m. p. 169° and no analysis.

6-*Aminohexahydro*-9-*methylcarbazole* (VII).—A mixture of tetrahydro-9-methyl-6-nitrocarbazole (20 g.; Perkin and Plant, *J.*, 1921, **119**, 1825), granulated tin (120 g.), ethanol (200 c.c.), and concentrated hydrochloric acid (200 c.c.) was refluxed for 24 hours, most of the ethanol distilled off, and the residue treated with an excess of aqueous sodium hydroxide. When the product was extracted with ether, the extract dried (K_2CO_3), the solvent removed, and the residue fractionated under reduced pressure, 6-*aminohexahydro*-9-*methylcarbazole* was collected as a pale yellow syrup (10 g.), b. p. 213—215°/16 mm. (Found : C, 77·6; H, 8·9. $C_{13}H_{18}N_2$ requires C, 77·2; H, 8·9%). 6-*Benzamidohexahydro*-9-*methylcarbazole*, obtained from the base by the action of benzoyl chloride and alkali in acetone, separated from ethanol in colourless needles, m. p. 230—231° (Found : C, 78·3; H, 6·9. $C_{20}H_{22}ON_2$ requires C, 78·4; H, 7·2%).

A mixture of the hydrochloride (7 g.) of 6-aminohexahydro-9-methylcarbazole (prepared by passing hydrogen chloride into the base in ether) and 1-chloro-2 : 4-dinitrobenzene (6 g.) in boiling ethanol was treated with a concentrated aqueous solution of sodium carbonate (3·2 g.). After a few minutes the mixture was cooled, and the dark solid was boiled in ethanol with charcoal. 6-(2 : 4-*Dinitroanilino*)-*hexahydro*-9-*methylcarbazole* crystallised from the filtered solution, on cooling, in red prisms (4 g.), m. p. 155—156° (Found : C, 62·2; H, 5·4. $C_{19}H_{20}O_4N_4$ requires C, 62·0; H, 5·4%).

1-p-*Dimethylaminoanilino*cyclo*pentane*-1-*carboxylic Acid* (VIII).—A solution of *p*-aminodimethylaniline (9 g.) and *cyclo*pentanone (6 c.c.) in glacial acetic acid (40 c.c.) was treated at 0° with aqueous potassium cyanide (4·5 g.), and after 4 hours the whole was made alkaline with ice–concentrated ammonia. When the solid was crystallised from aqueous ethanol, 1-p-*dimethylaminoanilino*-1-*cyano*cyclo*pentane* was obtained in colourless needles (8 g.), m. p. 83° (Found: C, 73·2; H, 8·5. $C_{14}H_{19}N_3$ requires C, 73·4; H, 8·3%). It was hydrolysed to the corresponding *amide*, colourless prisms, m. p. 193—194° (from ethanol), in almost theoretical yield by the usual sulphuric acid method (above) (Found: C, 68·4; H, 8·5. $C_{14}H_{21}ON_3$ requires C, 68·0; H, 8·5%). The amide (4 g.) was refluxed for an hour with concentrated hydrochloric acid (50 c.c.), the whole evaporated to a thick paste, the paste shaken with cold dilute aqueous sodium hydroxide, and the filtered solution treated with concentrated aqueous sodium hydroxide. 1-*p*-Dimethylaminoanilino*cyclo*pentane-1-carboxylic acid separated as its sodium salt which (2 g.) was refluxed with methanolic hydrogen chloride for 5 hours. After the methanol had been removed, the residue dissolved in water, and the filtered solution made alkaline, the *methyl* ester, colourless needles, m. p. 69—70° (from water), was precipitated (Found: C, 68·5; H, 8·5. $C_{15}H_{22}O_2N_2$ requires C, 68·7; H, 8·4%).

A mixture of the sodium salt (3 g.), sodium ethoxide (10 g.), and powdered potassium hydroxide (10 g.) was heated at 330° for an hour in a copper tube and, when the distillate was treated with dilute acetic acid and acetic anhydride, *p*-acetamidodimethylaniline (0·4 g.), m. p. and mixed m. p. 129—130°, was obtained. No 3-dimethylaminocarbazole was isolated from the material obtained by treating the alkali residue with water.

1-p-*Dimethylaminophenyl*-5-*nitrobenzotriazole* (IX; R = NO_2).—A boiling aqueous solution of hydrated sodium sulphide (9·3 g.) was added to 4′-dimethylamino-2 : 4-dinitrodiphenylamine (6·2 g.; Lellmann and Mack, *Ber.*, 1890, **23**, 2739) in hot ethanol (45 c.c.), and after the vigorous reaction had subsided the whole was boiled for 10 minutes, filtered whilst hot, and treated with water (100 c.c.). When the mixture was again boiled and allowed to cool, 2-*amino*-4′-*dimethylamino*-4-*nitrodiphenylamine*, golden-yellow prisms (5 g.), m. p. 185° (from ethanol), separated (Found: C, 61·9; H, 6·2. $C_{14}H_{16}O_2N_4$ requires C, 61·8; H, 5·9%). Sodium nitrite (1 g. in concentrated aqueous solution) was added to the amine (3·5 g.) in glacial acetic acid (20 c.c.), containing a molecular proportion of hydrochloric acid, at 5°. After the addition of more acetic acid (20 c.c.), the whole was warmed to 100°, allowed to cool, and the solid crystallised from ethanol, from which 1-p-*dimethylaminophenyl*-5-*nitrobenzotriazole* separated in yellow plates (2·8 g.), m. p. 231—232° (Found: C, 59·2; H, 4·9. $C_{14}H_{13}O_2N_5$ requires C, 59·4; H, 4·6%).

5-*Acetyl*-1-p-*dimethylaminophenylbenzotriazole* (IX; R = Ac).—Sodium carbonate (3 g. in concentrated aqueous solution) was gradually added to *p*-aminodimethylaniline dihydrochloride (4 g.) and 4-bromo-3-nitroacetophenone (4 g.) in boiling ethanol (40 c.c.), and the whole refluxed for ½ hour (compare Lellmann and Mack, *loc. cit.*). When the product (3·6 g.) which separated on cooling was recrystallised from ethanol, 4-*acetyl*-4′-*dimethylamino*-2-*nitrodiphenylamine* was obtained in chocolate coloured plates, m. p. 145—146° (Found: C, 64·5; H, 5·9. $C_{16}H_{17}O_3N_3$ requires C, 64·2; H, 5·7%). Stannous chloride (15 g.) in concentrated hydrochloric acid (40 c.c.) was added to the nitro-compound (3·2 g.) in hot glacial acetic acid (50 c.c.), and the whole boiled for a few minutes, cooled, and made alkaline with aqueous sodium hydroxide. After the solid had been crystallised from ethanol, 4-*acetyl*-2-*amino*-4′-*dimethylaminodiphenylamine* was isolated in yellow prisms (1·9 g.), m. p. 155—156° (Found: N, 15·5. $C_{16}H_{19}ON_3$ requires N, 15·6%). The amine (1·1 g.) in glacial acetic acid (20 c.c.) containing concentrated hydrochloric acid (2 c.c.) was treated at 5° with a slight excess of aqueous sodium nitrite, and, after 2 hours, the whole was made alkaline with ammonia. The precipitated 5-*acetyl*-1-p-*dimethylaminophenylbenzotriazole* crystallised from ethanol in yellow needles, m. p. 153—154° (Found: N, 20·2. $C_{16}H_{16}ON_4$ requires N, 20·0%). When the compound was purified by adsorption on alumina and then crystallised from toluene, a polymorphic form was obtained as pale yellow needles, m. p. 182—183° (Found: N, 20·2%). This seems to be an example of the stabilisation of the lower-melting form by a trace of impurity, observed for other compounds by Gorvin (*J.*, 1950, 407).

5-*Benzoyl*-1-p-*dimethylaminophenylbenzotriazole* (IX; R = COPh).—Prepared from 4-chloro-3-nitrobenzophenone like the analogous compounds from 4-bromo-3-nitroacetophenone, 4-*benzoyl*-4′-*dimethylamino*-2-*nitrodiphenylamine* crystallised from methanol in dark red needles, m. p. 159—161° (Found: C, 69·9; H, 5·4. $C_{21}H_{19}O_3N_3$ requires C, 69·8; H, 5·3%), 2-*amino*-4-*benzoyl*-4′-*dimethylaminodiphenylamine* from ethanol in yellow prisms, m. p. 208—210° (Found: N, 12·4. $C_{21}H_{21}ON_3$ requires N, 12·7%), and 5-*benzoyl*-1-p-*dimethylaminophenylbenzotriazole* from ethanol, after purification by adsorption on alumina, in pale yellow needles, m. p. 162—164° (Found: N, 16·2. $C_{21}H_{18}ON_4$ requires N, 16·4%).

5-*Cyano*-1-p-*dimethylaminophenylbenzotriazole* (IX; R = CN).—Prepared from 4-chloro-3-nitrobenzonitrile like the related compounds from 4-bromo-3-nitroacetophenone, 4-*cyano*-4′-*dimethylamino*-2-*nitrodiphenylamine* separated from ethanol in dark red plates, m. p. 156—157° (Found: C, 64·1; H, 5·2. $C_{15}H_{14}O_2N_4$ requires C, 63·8; H, 5·0%), 2-*amino*-4-*cyano*-4′-*dimethylaminodiphenylamine* from methanol in pale yellow prisms, m. p. 133—134° (Found: N, 22·2. $C_{15}H_{16}N_4$ requires N, 22·2%), and 5-*cyano*-1-p-*dimethylaminophenylbenzotriazole* from methanol in yellow needles, m. p. 218—220° (Found: N, 26·9. $C_{15}H_{13}N_5$ requires N, 26·6%).

6-*Cyanoindolo*(2′ : 3′-3 : 4)*carbazole* (XI).—After 3-aminocarbazole (8 g.), 4-chloro-3-nitrobenzonitrile (8 g.), and anhydrous sodium acetate (9 g.) had been refluxed for 6 hours in ethanol (300 c.c.), 3-(4-*cyano*-2-*nitroanilino*)*carbazole* separated on cooling, and, when recrystallised from acetic acid, it was obtained in red-brown prisms (9·5 g.), m. p. 190—191° (Found: C, 69·5; H, 3·9. $C_{19}H_{12}O_2N_4$ requires C, 69·5; H, 3·7%). The nitro-compound (9·5 g.) was reduced with stannous chloride as described above for similar substances, and 3-(2-*amino*-4-*cyanoanilino*)*carbazole* was isolated from amyl alcohol in colourless plates (4·3 g.), m. p. 267—269° (Found: N, 18·3. $C_{19}H_{14}N_4$ requires N, 18·8%). A solution of the amine (4 g.) in glacial acetic acid (90 c.c.) and concentrated hydrochloric acid (7 c.c.) was treated with the theoretical amount of sodium nitrite (0·93 g.) in water. Use of an excess of the reagent led to further reaction with formation of material difficult to remove from the product. 1-3'-*Carbazolyl*-5-*cyanobenzotriazole* (X ; R = CN) crystallised from acetic acid in colourless plates (2 g.), m. p. 279—280° (Found : N, 22·7. $C_{19}H_{11}N_5$ requires N, 22·7%). The triazole (1 g.) was heated at 360° until evolution of nitrogen ceased, the residue extracted with boiling ethanol (charcoal), and the filtered solution diluted with water. When the precipitate was crystallised from aqueous ethanol, 6-*cyanoindolo*(2' : 3'-3 : 4)-*carbazole* was obtained in pale brown prisms (0·2 g.), m. p. 310—312° (Found : C, 80·7 ; H, 4·1 ; N, 14·5. $C_{19}H_{11}N_3$ requires C, 81·1 ; H, 3·9 ; N, 14·9%). It dissolved in cold concentrated sulphuric acid to give a green solution, and it exhibited a blue fluorescence in ethanol.

6-(2-*Amino*-4-*cyanoanilino*)*tetrahydro*-9-*methylcarbazole*.—The following method was found to be more convenient than that described by Perkin and Plant (*loc. cit.*) for the preparation of 6-amino-tetrahydro-9-methylcarbazole. Molten hydrated sodium sulphide (80 g.) was poured slowly into a suspension of tetrahydro-9-methyl-6-nitrocarbazole (10 g.) in hot ethanol (100 c.c.), the whole refluxed for 5 hours, most of the ethanol distilled off, and the residue diluted with water. When the precipitate was crystallised from aqueous ethanol, the amine was obtained in colourless needles (5 g.), m. p. 105—106°. After a mixture of the amine (4·8 g.), 4-chloro-3-nitrobenzonitrile (4·3 g.), and anhydrous sodium acetate (2 g.) in ethanol (75 c.c.) had been heated on the steam-bath for ½ hour and allowed to cool, the dark red 6-(4-*cyano*-2-*nitroanilino*)*tetrahydro*-9-*methylcarbazole* (6 g.) which separated was recrystallised from benzene and obtained in red prisms, m. p. 197—198° (Found : C, 69·6 ; H, 5·2. $C_{20}H_{18}O_2N_4$ requires C, 69·4 ; H, 5·2%). When reduced with stannous chloride as described above for related nitro-compounds, it gave 6-(2-*amino*-4-*cyanoanilino*)*tetrahydro*-9-*methylcarbazole*, almost colourless prisms, m. p. 220—221° (from xylene) (Found : N, 17·5. $C_{20}H_{20}N_4$ requires N, 17·7%).

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