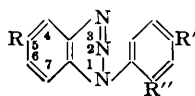


25. Experiments on the Preparation of Indolocarbazoles. Part II. Some Observations on the Graebe-Ullmann Carbazole Synthesis.

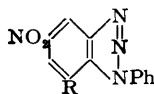
By G. G. COKER, S. G. P. PLANT, and P. B. TURNER.

3- and 1-Chloro-6-nitro-, 1-chloro-3-nitro-, 6-cyano-3-methyl-, 6-cyano-1-methyl-, 3- and 1-chloro-6-cyano-, and 6-cyano-1-methyl-3-nitro-carbazole have been prepared by the Graebe-Ullmann reaction, but attempts to obtain carbazoles from certain other 5-nitro-1-phenylbenzotriazoles failed. The investigations have formed the basis for experiments designed to obtain indolocarbazoles from bistriazoles. Some structural problems in the polynitro-diphenylamines required as intermediates have been elucidated.

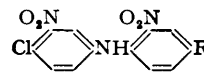
APPLICATIONS of the Graebe-Ullmann synthesis of carbazole derivatives (*Annalen*, 1896, **291**, 16) usually involve the preparation of a 2-nitrodiphenylamine and its conversion through the corresponding 2-amino-compound into a 1-phenylbenzotriazole, from which nitrogen is finally eliminated. Although the reactions have been applied to a number of compounds, information regarding the effect of different substituents in the various positions of the triazole molecule on the yield of the carbazole is still relatively meagre. During studies which are in progress in this laboratory into the synthesis and reactions of indolocarbazoles (*J.*, 1949, S 160 is regarded as Part I of this series) the possibility of applying the Graebe-Ullmann reaction to suitable bistriazoles as in the examples below is being investigated. The facile preparation of the requisite diphenylamines in most cases necessitates the condensation of a feebly-basic substituted



(I.)



(II.)



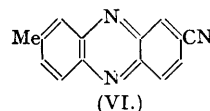
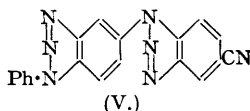
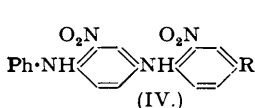
(III.)

aniline with an *o*-halogenonitrobenzene containing an additional activating substituent, such as nitro- or cyano- *para* to the halogen. Earlier attempts to prepare carbazoles from the simplest analogues of the corresponding triazoles have been mainly disappointing. Thus, although Preston, Tucker, and Cameron (*J.*, 1942, 500) obtained a 34% yield of 3-cyanocarbazole from the triazole (I; R = CN, R' = R'' = H), only a trace of 3-nitrocarbazole resulted from (I; R = NO₂, R' = R'' = H). Again, Blom (*Helv. Chim. Acta*, 1921, **4**, 1036) failed to obtain carbazoles from the triazoles (I; R = NO₂, R' = Cl or EtO, R'' = H). It therefore seemed desirable to investigate more fully the application of the reaction to some simpler substances related to the intermediates in the projected indolocarbazole syntheses.

We have confirmed the observation that only a trace of 3-nitrocarbazole is formed in this

way, and have been unable to obtain the corresponding carbazoles from the closely related 5-nitro-1-*p*-tolyl- (I; R = NO₂, R' = Me, R'' = H), 5-nitro-1-*o*-tolyl (I; R = NO₂, R' = H, R'' = Me), 7-methyl-5-nitro-1-phenyl- (II; R = Me), 1-(2-methyl-4-nitrophenyl)-5-nitro- (I; R = R' = NO₂, R'' = Me), and 1-(2-chloro-4-nitrophenyl)-5-nitro-benzotriazole (I; R = R' = NO₂, R'' = Cl). Other 5-nitro-1-phenylbenzotriazoles have given better results, and the yields of the corresponding carbazoles shown in parentheses have been obtained from 1-*p*-chlorophenyl-5-nitro- (I; R = NO₂; R' = Cl; R'' = H) (7%; contrast Blom's observation), 1-*o*-chlorophenyl-5-nitro- (I; R = NO₂; R' = H; R'' = Cl) (14%), and 7-chloro-5-nitro-1-phenyl-benzotriazole (II; R = Cl) (28%). Evidently the presence of chlorine, unlike that of methyl, in the 7-, 1-*o*-, or 1-*p*-position facilitates the reaction in this group. As found by Preston, Tucker, and Cameron in the simplest case, the use of 5-cyano-1-phenylbenzotriazoles has given much more satisfactory products, and carbazoles have been prepared from 5-cyano-1-*p*-tolyl- (I; R = CN, R' = Me, R'' = H) (57%), 5-cyano-1-*o*-tolyl- (I; R = CN, R' = H, R'' = Me) (71%), 1-*p*-chlorophenyl-5-cyano- (I; R = CN, R' = Cl, R'' = H) (22%), 1-*o*-chlorophenyl-5-cyano- (I; R = CN, R' = H, R'' = Cl) (15%), and 5-cyano-1-(2-methyl-4-nitrophenyl)benzotriazole (I; R = CN, R' = NO₂, R'' = Me) (8%). It is noteworthy, however, that in this series the presence of methyl rather than chlorine as a substituent in the 1-phenyl group leads to increased yields.

In first attempts to prepare substituted indolocarbazoles, 4-chloro-3-nitroaniline has been condensed with 1-chloro-2 : 4-dinitrobenzene and with 4-chloro-3-nitrobenzotriazole; the products (III; R = NO₂ or CN) condensed with aniline to give the anilindiphenylamines (IV; R = NO₂ or CN), but efforts to reduce the former to a diamine which could be converted into a bistriazole failed. The latter, however, was transformed in this way into 5-(5-cyanobenzotriazol-1-yl)-1-phenylbenzotriazole (V), but attempts to effect a double Graebe-Ullmann change with the formation of a cyanoindolocarbazole were unsuccessful.



Some observations incidental to the preparation of the intermediates described in the Experimental section need comment. Reverdin and Crépieux (*Ber.*, 1903, **36**, 29; *Bull. Soc. chim.*, 1903, **29**, 235) heated 2-methyl-2' : 4'-dinitrodiphenylamine with nitric acid (*d* 1.2) on a steam-bath for an hour and obtained a trinitro- (m. p. 158°) and a tetranitro-compound (m. p. 190°), but the structures were not determined. More satisfactory conditions have now been developed for the preparation of each of these substances, and the former has been shown to be 2-methyl-4 : 2' : 4'-trinitrodiphenylamine by synthesis from 5-nitro-*o*-toluidine and 1-chloro-2 : 4-dinitrobenzene. The latter has also been obtained by the nitration of 2-methyl-4 : 6-dinitrodiphenylamine and so must be the 2-methyl-4 : 6 : 2' : 4'-tetranitro-compound. The same authors were unable to isolate a pure substance from the nitration of the isomeric 3-methyl-2' : 4'-dinitrodiphenylamine under similar conditions. It has been found, however, that the action of concentrated nitric acid on this dinitro-compound in glacial acetic acid at room temperature leads to a mixture containing 3-methyl-4 : 2' : 4'-trinitrodiphenylamine, also synthesised from 6-nitro-*m*-toluidine. More vigorous conditions gave 3-methyl-4 : 6 : 2' : 4'-tetranitrodiphenylamine, the structure of which was established by its preparation from 3-methyl-4 : 6-dinitrodiphenylamine. The nitration of the last was modified to give 3-methyl-4 : 6 : 4'-trinitrodiphenylamine, also obtained from *p*-nitroaniline and 1-chloro-3-methyl-4 : 6-dinitrobenzene.

Nitro-groups were readily introduced into the 2- and the 6-position of 4'-cyano-4-methyl-2'-nitrodiphenylamine, the orientation being established by the preparation of the same substance by nitrating the product of condensing 4-methyl-2 : 6-dinitrophenyltoluene-*p*-sulphonate with *p*-aminobenzonitrile. The intermediate compound, 4'-cyano-4-methyl-2 : 2'-dinitrodiphenylamine, was more conveniently obtained synthetically from 3-nitro-*p*-toluidine and 4-chloro-3-nitrobenzotriazole and, when reduced with sodium sulphide under conditions used to obtain most of the 2-aminodiphenylamines described below, it gave 2-cyano-7-methylphenazine (VI). 7-Chloro-2-cyanophenazine was similarly obtained from the analogous 4-chloro-compound. The introduction of one nitro-group, in the 4-position, into the isomeric 4'-cyano-2-methyl-2'-nitrodiphenylamine proceeded readily, however, the identity of the product being confirmed by synthesis from 5-nitro-*o*-toluidine. Further nitration gave 4'-cyano-2-methyl-4 : 6 : 2'-trinitrodiphenylamine.

Reverdin and Crépieux (*loc. cit.*) stated that a product, m. p. 182—183°, obtained by nitrating 4-chloro-2' : 4'-dinitrodiphenylamine is a tetranitro-compound, but they did not establish its structure and relied solely on a nitrogen analysis for its composition. It has now been proved that this substance is 4-chloro-2 : 2' : 4'-trinitrodiphenylamine, identical with a sample prepared synthetically from 4-chloro-2-nitroaniline. The tetranitro-compound obtained on further nitration was found to melt at 215° and has been shown to have the additional substituent in the 6-position.

It has already been shown by Reverdin and Crépieux that mononitration of 2-chloro-2' : 4'-dinitrodiphenylamine involves substitution at the 4-position by the fact that they obtained the same product by chlorinating the requisite trinitro-compound. Further nitration has now been found to give the expected 2-chloro-4 : 6 : 2' : 4'-tetranitrodiphenylamine.

EXPERIMENTAL.

2-Methyl-4 : 2' : 4'-trinitrodiphenylamine.—(a) After 2-methyl-2' : 4'-dinitrodiphenylamine (2 g.) had been shaken with glacial acetic acid (30 c.c.) containing nitric acid (7 c.c.; *d* 1.42), and the mixture left at room temperature overnight, the solid was crystallised from aqueous acetic acid, and 2-methyl-4 : 2' : 4'-trinitrodiphenylamine obtained in orange prisms (1.2 g.), m. p. 159° (Found : C, 49.2; H, 3.2. $C_{13}H_{10}O_6N_4$ requires C, 49.1; H, 3.1%). (b) A mixture of 1-chloro-2 : 4-dinitrobenzene (2 g.), 5-nitro-*o*-toluidine (1.6 g.), and potassium carbonate (3 g.) was heated for 2 hours at 165°, and the product extracted with boiling glacial acetic acid (100 c.c.). The filtered solution was boiled with charcoal, again filtered, and poured into water, and the gummy material boiled with acetone (1 c.c.). When cold, the solid trinitro-compound (1.4 g.) was collected, recrystallised from acetic acid, and obtained in prisms, m. p. 159°, identical (mixed m. p.) with the substance described above.

1-(2-Methyl-4-nitrophenyl)-5-nitrobenzotriazole.—A mixture of the above trinitro-compound (15 g.) and alcohol (40 c.c.) was heated on the steam-bath in a 3-l. flask, crystalline sodium sulphide (21 g.) in water (20 c.c.) added, and the whole shaken. After the violent reaction had subsided, hot water was added, and the mixture boiled, and filtered while still hot. When the solid was extracted with hot acetone, and the extract boiled with charcoal and evaporated to small bulk, 2'-amino-2-methyl-4 : 4'-dinitrodiphenylamine (5.5 g.), dark red needles, m. p. 229° (from dimethylaniline), separated (Found : C, 54.1; H, 4.1. $C_{13}H_{12}O_4N_4$ requires C, 54.2; H, 4.2%). The amine (1 g.) was dissolved in hot glacial acetic acid (15 c.c.) containing concentrated hydrochloric acid (1 c.c.), and, with stirring, the mixture was cooled and treated with concentrated aqueous sodium nitrite (0.5 g.). After dilution with water, the solid was crystallised from alcohol, and 1-(2-methyl-4-nitrophenyl)-5-nitrobenzotriazole (1 g.) obtained in yellow prisms, m. p. 185° (Found : C, 52.2; H, 2.9. $C_{13}H_9O_4N_5$ requires C, 52.1; H, 3.0%).

Unless otherwise stated, the analogous 2-aminodiphenylamines and derived 1-phenylbenzotriazoles described below were prepared by methods similar to those given above.

2-Methyl-4 : 6 : 2' : 4'-tetranitrodiphenylamine.—(a) 2-Methyl-2' : 4'-dinitrodiphenylamine (2 g.) was heated on the steam-bath with glacial acetic acid (30 c.c.) and nitric acid (10 c.c.; *d* 1.42) until a straw-coloured solution was obtained (about $\frac{1}{2}$ hour). When the solid which separated when the mixture was cooled and kept for a day was crystallised from acetic acid, 2-methyl-4 : 6 : 2' : 4'-tetranitrodiphenylamine was isolated in yellow needles (1.4 g.), m. p. 190° (Found : C, 42.9; H, 2.7. $C_{13}H_9O_8N_5$ requires C, 43.0; H, 2.5%). The same substance was obtained by similar treatment of 2-methyl-4 : 2' : 4'-trinitrodiphenylamine. (b) After a mixture of 2-methyl-4 : 6-dinitrophenyl toluene-*p*-sulphonate (29 g.) and aniline (30 g.) had been heated first near the b. p. for $\frac{1}{4}$ hour and then on the steam-bath for an hour, red crystals separated overnight. The mixture was stirred with glacial acetic acid (60 c.c.), then diluted with water, and the solid crystallised from acetic acid, from which 2-methyl-4 : 6-dinitrodiphenylamine was obtained in orange-red prisms (15 g.), m. p. 169°, identical with a specimen prepared from 2-chloro-3 : 5-dinitrotoluene as described by Nietzki and Rehe (*Ber.*, 1892, 25, 3005). After the product (1 g.) had been set aside for a short time at room temperature with nitric acid (15 c.c.; *d* 1.42), addition of water precipitated the tetranitro-compound, identical (mixed m. p.) with the substance described above.

7-Methyl-5-nitro-1-phenylbenzotriazole.—Prepared from 2-methyl-4 : 6-dinitrodiphenylamine through the requisite amine which was not completely purified, this substance crystallised from ethanol in yellow plates, m. p. 198° (Found : C, 61.2; H, 3.8. $C_{13}H_{10}O_2N_4$ requires C, 61.4; H, 3.9%).

5-Nitro-1-*m*-tolylbenzotriazole.—3-Methyl-2' : 4'-dinitrodiphenylamine was converted into 2'-amino-3-methyl-4'-nitrodiphenylamine, red plates (Found : C, 64.2; H, 5.5. $C_{13}H_{13}O_2N_3$ requires C, 64.2; H, 5.3%), m. p. 117° (from aqueous ethanol), and thence into 5-nitro-1-*m*-tolylbenzotriazole, colourless plates, m. p. 151° (from ethanol) (Found : C, 61.4; H, 4.1. $C_{13}H_{10}O_2N_4$ requires C, 61.4; H, 3.9%).

3-Methyl-4 : 2' : 4'-trinitrodiphenylamine.—After a mixture of 1-chloro-2 : 4-dinitrobenzene (5 g.), 6-nitro-*m*-toluidine (4 g.), and anhydrous sodium acetate (4 g.) had been heated for an hour at 190° and the product extracted with hot glacial acetic acid (100 c.c.), the filtered solution was poured into dilute hydrochloric acid, and 3-methyl-4 : 2' : 4'-trinitrodiphenylamine, red prisms (4 g.), m. p. 171—172° (from acetic acid), was precipitated (Found : C, 49.3; H, 3.5%). A mixture was obtained by leaving 3-methyl-2' : 4'-dinitrodiphenylamine at room temperature with glacial acetic acid and nitric acid (*d* 1.42) for several hours, but adsorption of the product on alumina led to the isolation of some of the above trinitro-compound together with an isomeride, probably 3-methyl-6 : 2' : 4'-trinitrodiphenylamine, which separated from chloroform in yellow prisms (Found : C, 49.4; H, 3.4%) and changed to a red polymorphic form, m. p. 183°, on heating.

3-Methyl-4 : 6 : 2' : 4'-tetranitrodiphenylamine.—(a) 3-Methyl-2' : 4'-dinitrodiphenylamine (5 g.) was heated on the steam-bath with concentrated sulphuric acid (10 c.c.) and nitric acid (20 c.c.; *d* 1.42) until the solution became pale yellow (about $\frac{1}{2}$ hour). When cold, the mixture was poured on ice, and the precipitated 3-methyl-4 : 6 : 2' : 4'-tetranitrodiphenylamine separated from acetic acid in yellow plates (2.5 g.), m. p. 208—209° (Found : C, 43.7; H, 2.6%). (b) 3-Methyl-4 : 6-dinitrodiphenylamine (0.5 g.; Borsche and Fiedler, *Ber.*, 1913, 46, 2117) was kept for a few minutes with nitric acid (5 c.c.; *d* 1.42), the whole heated for 20 minutes on the steam-bath, then poured on ice, and the solid crystallised from acetic acid; the same tetranitro-compound (0.5 g.) was obtained.

3-Methyl-4 : 6 : 4'-trinitrodiphenylamine.—After 3-methyl-4 : 6-dinitrodiphenylamine (0.5 g.) had been left with nitric acid (5 c.c.; *d* 1.42) at room temperature for 5 minutes and the whole poured on ice, 3-methyl-4 : 6 : 4'-trinitrodiphenylamine, yellow needles (0.5 g.), m. p. 207° (from acetic acid), was precipitated (Found : C, 49.4; H, 2.9%). The same compound (2 g.) was obtained when a mixture of 1-chloro-3-methyl-4 : 6-dinitrobenzene (2.2 g.), *p*-nitroaniline (1.5 g.), and diethylaniline (5 c.c.) was heated at 190° for 2 hours and then extracted with hot glacial acetic acid (15 c.c.), the solution poured into dilute hydrochloric acid, and the product crystallised from acetic acid.

6-Cyano-3-methylcarbazole.—A hot solution of stannous chloride (45 g.) in concentrated hydrochloric acid (100 c.c.) was added to 4'-cyano-4-methyl-2'-nitrodiphenylamine (9 g.; Mattaar, *Rec. Trav. chim.*, 1922, 41, 24) in boiling glacial acetic acid, and the whole boiled until the colour became deep yellow (about 5 minutes). When cold, the mixture was made alkaline with aqueous sodium hydroxide, and the solid filtered off and crystallised from ethanol (200 c.c.), from which 2'-amino-4'-cyano-4-methyldiphenylamine separated in colourless plates (6 g.), m. p. 162—163° (Found : C, 75.0; H, 6.0. $C_{14}H_{13}N_3$ requires C, 75.3; H, 5.8%). The derived 5-cyano-1-*p*-tolylbenzotriazole crystallised from ethanol in colourless needles, m. p. 199° (Found : C, 71.7; H, 4.4. $C_{14}H_{10}N_4$ requires C, 71.8; H, 4.3%). This substance (3 g.) was heated gradually from 320° to 380°, the residue was twice extracted with hot ethanol (60 c.c.), the united extracts were boiled with charcoal, and the product was precipitated from the filtered solution by dilution with water (in the preparation of all the substituted carbazoles described below the reaction product was similarly treated before crystallisation). 6-Cyano-3-methylcarbazole crystallised from ethanol in colourless plates (1.5 g.), m. p. 183—184° (Found : C, 81.5; H, 4.8. $C_{14}H_{10}N_2$ requires C, 81.6; H, 4.9%).

4'-Cyano-4-methyl-2 : 6 : 2'-trinitrodiphenylamine.—(a) When 4'-cyano-4-methyl-2'-nitrodiphenylamine (10 g.) was heated for several hours on the steam-bath with nitric acid (100 c.c.; *d* 1.3) and the solid obtained by dilution with water was crystallised from ethanol, 4'-cyano-4-methyl-2 : 6 : 2'-trinitrodiphenylamine was obtained in yellow needles (6 g.), m. p. 188° (Found : C, 48.9; H, 2.5. $C_{14}H_9O_6N_5$ requires C, 49.0; H, 2.6%). (b) After a mixture of 4-methyl-2 : 6-dinitrophenyl toluene-*p*-sulphonate (2 g.) and *p*-aminobenzonitrile (2 g.) had been heated at 180° for 20 minutes and then crystallised from ethanol, 4'-cyano-4-methyl-2 : 6-dinitrodiphenylamine was isolated in red prisms (0.5 g.), m. p. 156—158° (Found : C, 56.2; H, 3.4. $C_{14}H_{10}O_4N_4$ requires C, 56.4; H, 3.4%). When this substance (0.3 g.) was heated with nitric acid (3 c.c.; *d* 1.42) at 90° for 2 minutes, the whole poured into water, and the product crystallised from ethanol, the trinitro-compound (0.25 g.), identical (mixed m. p.) with the above material, was obtained.

2-Cyano-7-methylphenazine.—After a mixture of 3-nitro-*p*-toluidine (5 g.), 4-chloro-3-nitrobenzonitrile (5.5 g.), and potassium carbonate (4 g.) had been heated at 170° for $\frac{1}{2}$ hour and then ground with dilute hydrochloric acid, and the product crystallised from ethanol (charcoal), 4'-cyano-4-methyl-2 : 2'-dinitrodiphenylamine was obtained in orange needles (3 g.), m. p. 244° (Found : C, 56.0; H, 3.4%). When reduced with sodium sulphide as described for 2-methyl-4 : 2' : 4'-trinitrodiphenylamine, this substance gave 2-cyano-7-methylphenazine, which separated from ethanol in pale yellow plates, m. p. 248° (Found : C, 76.4; H, 4.1. $C_{14}H_9N_3$ requires C, 76.7; H, 4.1%).

6-Cyano-1-methylcarbazole.—Prepared from 4'-cyano-2-methyl-2'-nitrodiphenylamine (m. p. 121°; compare Mattaar, *loc. cit.*) like the isomerides described above, 2'-amino-4'-cyano-2-methyldiphenylamine separated from ethanol in colourless needles, m. p. 154° (Found : C, 75.0; H, 6.0%), and 5-cyano-1-*o*-tolylbenzotriazole from aqueous ethanol in colourless plates, m. p. 100° (Found : C, 71.7; H, 4.4%). The latter (2 g.) was heated from 290° to 340° during $\frac{1}{2}$ hour, and the 6-cyano-1-methylcarbazole obtained from aqueous ethanol in pale yellow needles (1.25 g.), m. p. 230° (Found : C, 81.4; H, 5.1%).

6-Cyano-1-methyl-3-nitrocarbazole.—When nitric acid (25 c.c.; *d* 1.42) was added below 20° to 4'-cyano-2-methyl-2'-nitrodiphenylamine (8 g.) in glacial acetic acid (150 c.c.), 4'-cyano-2-methyl-4 : 2'-dinitrodiphenylamine (7.5 g.), m. p. 231—232°, gradually separated in red plates. The same compound (4 g.) was obtained when the product of heating a mixture of 5-nitro-*o*-toluidine (7 g.), 4-chloro-3-nitrobenzonitrile (7.5 g.), and potassium carbonate (6 g.) at 150—160° was ground with dilute hydrochloric acid and crystallised from acetic acid (Found : C, 56.3; H, 3.5%). It was converted into 2'-amino-4'-cyano-2-methyl-4-nitrodiphenylamine, orange-yellow needles, m. p. 210—211° (from ethanol) (Found : C, 62.7; H, 4.4. $C_{14}H_{12}O_2N_4$ requires C, 62.7; H, 4.5%), and 5-cyano-1-(2-methyl-4-nitrophenyl)benzotriazole, orange prisms, m. p. 220—221° (from ethanol) (Found : C, 60.2; H, 3.1. $C_{14}H_9O_2N_5$ requires C, 60.2; H, 3.2%). The latter (2 g.) was heated gradually from 280° to 310°; when the product, isolated as before, was crystallised from benzene-light petroleum (b. p. 60—80°), 6-cyano-1-methyl-3-nitrocarbazole was obtained in pale yellow needles (0.15 g.), m. p. 348—350° (Found : C, 66.4; H, 3.6. $C_{14}H_9O_2N_3$ requires C, 66.9; H, 3.6%).

4'-Cyano-2-methyl-4 : 6 : 2'-trinitrodiphenylamine.—This compound was obtained when a mixture of the above dinitro-compound (2 g.; m. p. 231—232°), glacial acetic acid (50 c.c.), and nitric acid (15 c.c.; *d* 1.42) was heated on the steam-bath until a clear yellow solution resulted, and then poured into water; it crystallised from acetic acid in pale yellow prisms (2 g.), m. p. 221° (Found : C, 48.7; H, 2.6%).

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3-Chloro-6-nitrocarbazole.—Two portions of 1-*p*-chlorophenyl-5-nitrobenzotriazole (each 1.5 g., prepared as described by Blom, *loc. cit.*) were heated separately at 350° (metal-bath) for 10 minutes in a flask with a long neck, the sublimate of unchanged triazole being decomposed with a free flame. 3-Chloro-6-nitrocarbazole was obtained from benzene in pale yellow needles (0.2 g.), m. p. 284° (Found: C, 58.8; H, 2.8. Calc. for $C_{12}H_8O_2N_4Cl$: C, 58.4; H, 2.8%). The use of larger quantities of material, or higher temperatures, led to explosions. This substance has been prepared in other ways (Lamberti-Zanardi, *Gazzetta*, 1896, **26**, 289; D.R.-P. 295,817, *Chem. Zentr.*, 1917, **1**, 295).

4-Chloro-2 : 2' : 4'-trinitrodiphenylamine.—(a) When 4-chloro-2' : 4'-dinitrodiphenylamine (8 g.) was treated with nitric acid (70 c.c.; *d* 1.23) for $\frac{1}{2}$ hour at 90°, the red colour of the suspended solid became yellow. After dilution with water, the product was crystallised from acetic acid, and 4-chloro-2 : 2' : 4'-trinitrodiphenylamine obtained in orange-yellow needles (7.5 g.), m. p. 186° (Found: C, 42.7; H, 2.1. $C_{12}H_8O_6N_4Cl$ requires C, 42.5; H, 2.1%). (b) When a mixture of 4-chloro-2-nitroaniline (1.7 g.), 1-chloro-2 : 4-dinitrobenzene (2 g.), and potassium carbonate (2 g.) was heated at 180° for an hour and the product was washed with hot dilute hydrochloric acid and crystallised from acetic acid, the same trinitro-compound (mixed m. p.) was isolated in golden-yellow needles (1.5 g.), m. p. 185°.

4-Chloro-2 : 6 : 2' : 4'-tetranitrodiphenylamine.—The above trinitro-compound (1 g.) dissolved when heated on the steam-bath with nitric acid (30 c.c.; *d* 1.42), and, after dilution with water, the precipitated 4-chloro-2 : 6 : 2' : 4'-tetranitrodiphenylamine crystallised from acetic acid in lemon-yellow needles (1 g.), m. p. 215° (Found: C, 37.4; H, 1.8. $C_{12}H_8O_8N_4Cl$ requires C, 37.5; H, 1.6%). The same compound (m. p. and mixed m. p. 215°) was isolated when 4-chloro-2 : 6-dinitrodiphenylamine (Ullmann and Sané, *loc. cit.*) was nitrated under similar conditions.

4-Chloro-3 : 2' : 4'-trinitrodiphenylamine.—After 4-chloro-3-nitroaniline (1.7 g.), 1-chloro-2 : 4-dinitrobenzene (2 g.), and anhydrous sodium acetate (1 g.) had been heated together at 180° for an hour and the product extracted with hot acetic acid, 4-chloro-3 : 2' : 4'-trinitrodiphenylamine, yellow needles (1.5 g.), m. p. 179—180° (from ethanol), separated on cooling (Found: C, 42.7; H, 2.3%). The derived 2'-amino-4-chloro-3 : 4'-dinitrodiphenylamine was extracted from the crude reduction product (dried at 100°) with boiling benzene (charcoal) and recovered by the addition of light petroleum (b. p. 60—80°); it separated from benzene-light petroleum in dark red needles, m. p. 194° (Found: C, 46.7; H, 3.0. $C_{12}H_8O_4N_4Cl$ requires C, 46.7; H, 2.9%). After the trinitro-compound (1 g.) had been refluxed with aniline (10 c.c.) for 3 hours and the mixture treated with dilute hydrochloric acid, the solid was washed with a little ethanol and twice recrystallised from acetic acid; 4-anilino-3 : 2' : 4'-trinitrodiphenylamine was obtained in red plates (0.5 g.), m. p. 197—198° (Found: C, 54.0; H, 3.3. $C_{18}H_{18}O_6N_6$ requires C, 54.7; H, 3.3%).

1-Chloro-6-nitrocarbazole.—Prepared from 2-chloro-2' : 4'-dinitrodiphenylamine, 2'-amino-2-chloro-4'-nitrodiphenylamine crystallised from ethanol in red prisms, m. p. 112° [compare Fries (*Annalen*, 1927, **454**, 206), who gives m. p. 117°; a polymorphic form (orange needles) melted at 90° and resolidified to the red form], and 1-*o*-chlorophenyl-5-nitrobenzotriazole from ethanol in colourless needles, m. p. 130° (Found: C, 52.6; H, 2.6. $C_{12}H_8O_2N_4Cl$ requires C, 52.5; H, 2.6%). When the latter (4 g.) was heated in two portions, evolution of nitrogen began at 310—320° and was complete after a short time at 360°. 1-Chloro-6-nitrocarbazole crystallised from benzene (charcoal) in golden yellow prisms (0.5 g.), m. p. 254° (Found: C, 58.4; H, 3.0%).

1-(2-Chloro-4-nitrophenyl)-5-nitrobenzotriazole.—Prepared from 2-chloro-4 : 2' : 4'-trinitrodiphenylamine (7 g.; Reverdin and Crépieux, *loc. cit.*), the crude 2'-amino-2-chloro-4 : 4'-dinitrodiphenylamine was dried and extracted with boiling benzene, and the extract boiled with charcoal, filtered, and treated while still boiling with light petroleum until crystallisation began. The amine was recrystallised from benzene-light petroleum and obtained in brown prisms (4 g.), which changed at 180° to a yellow form, m. p. 210° (Found: C, 46.8; H, 2.8%). 1-(2-Chloro-4-nitrophenyl)-5-nitrobenzotriazole crystallised from ethanol in colourless plates, m. p. 149° (Found: C, 45.0; H, 1.8. $C_{12}H_8O_4N_5Cl$ requires C, 45.1; H, 1.9%).

2-Chloro-4 : 6 : 2' : 4'-tetranitrodiphenylamine.—(a) After 2-chloro-4 : 2' : 4'-trinitrodiphenylamine (2 g.) had been heated on a steam-bath for an hour with nitric acid (50 c.c.; *d* 1.42), addition of water precipitated 2-chloro-4 : 6 : 2' : 4'-tetranitrodiphenylamine, yellow needles (2 g.), m. p. 191° (from acetic acid) (Found: C, 38.0; H, 1.6%). (b) Anhydrous sodium carbonate (12 g.) was gradually added to a mixture of 2-chloro-4 : 6-dinitrophenol (22 g.), toluene-*p*-sulphonyl chloride (20 g.), and water (40 c.c.) heated on a steam-bath, and after $\frac{1}{2}$ hour the whole was extracted several times with warm dilute sodium carbonate solution (cf. Ullmann and Sané, *loc. cit.*). The residue was twice recrystallised from benzene, and 2-chloro-4 : 6-dinitrophenyl toluene-*p*-sulphonate obtained in colourless needles (25 g.), m. p. 155° (Found: C, 42.4; H, 2.7. $C_{15}H_8O_6N_2ClS$ requires C, 41.9; H, 2.4%). After this compound, (3 g.) had been heated with aniline (15 c.c.) at 90° for 2 hours, an equal volume of ethanol was added, and the whole poured into an excess of dilute hydrochloric acid. The precipitated 2-chloro-4 : 6-dinitrodiphenylamine separated from ethanol in orange plates (1.5 g.), m. p. 140° (Found: C, 49.4; H, 3.0. Calc. for $C_{12}H_8O_2N_4Cl$: C, 49.1; H, 2.7%). Ullmann and Sané (*loc. cit.*) made this substance from aniline and 1 : 2-dichloro-4 : 6-dinitrobenzene, but gave no m. p. The compound (1 g.) rapidly dissolved in nitric acid (30 c.c.; *d* 1.42) at 90°, and water then precipitated the above tetranitro-derivative (1 g.).

1-Chloro-3-nitrocarbazole.—Prepared from 2-chloro-4 : 6-dinitrodiphenylamine, 6-amino-2-chloro-4-nitrodiphenylamine separated from aqueous ethanol in brown plates, m. p. 122—124°, and was converted without further purification into 7-chloro-5-nitro-1-phenylbenzotriazole pale brown prisms, m. p. 209° (from ethanol) (Found: C, 53.0; H, 2.7%). This compound (1 g.) was heated at 320° until effervescence ceased, and, after crystallisation twice from toluene and then from aqueous ethanol, 1-chloro-3-nitrocarbazole was obtained in pale yellow needles (0.25 g.), m. p. 206° (Found: C, 58.8; H, 2.5%).

3-Chloro-6-cyanocarbazole.—After a mixture of *p*-chloroaniline (10 g.), 4-chloro-3-nitrobenzonitrile (10 g.), and anhydrous sodium acetate (7 g.) had been heated at 165° for $\frac{1}{2}$ hour and the product extracted

with boiling ethanol, 4-chloro-4'-cyano-2'-nitrodiphenylamine crystallised from the solution, on cooling, in orange-red needles (14 g.), m. p. 165° (Found: C, 57.2; H, 3.4. $C_{13}H_8O_2N_3Cl$ requires C, 57.0; H, 2.9%). A hot solution of stannous chloride (10 g.) in concentrated hydrochloric acid (20 c.c.) was added to a boiling solution of this compound (2 g.) in glacial acetic acid, and after a few minutes the mixture was cooled and made strongly alkaline with concentrated aqueous sodium hydroxide. The solid was extracted with boiling ethanol, and the product which separated from the extract on cooling yielded 2'-amino-4-chloro-4'-cyanodiphenylamine, almost colourless needles (1.5 g.), m. p. 209° (from ethanol) (Found: C, 64.7; H, 4.3. $C_{13}H_{10}N_3Cl$ requires C, 64.1; H, 4.1%). The derived 1-p-chlorophenyl-5-cyanobenzotriazole crystallised from acetic acid in colourless needles, m. p. 298° (Found: C, 61.5; H, 2.9. $C_{13}H_7N_4Cl$ requires C, 61.3; H, 2.8%). The triazole (1 g.) was heated at 380° for 20 minutes. When the material extracted as before was crystallised from a little ethanol, unchanged triazole separated, and, after this had been removed, 3-chloro-6-cyanocarbazole was obtained by the addition of water. The latter process was repeated and the substance was finally isolated from aqueous ethanol in colourless needles (0.2 g.) m. p. 250° (Found: C, 68.5; H, 3.4. $C_{13}H_7N_2Cl$ requires C, 68.9; H, 3.1%).

7-Chloro-2-cyanophenazine.—After 4-chloro-4'-cyano-2'-nitrodiphenylamine (10 g.) had been heated on a steam-bath with nitric acid (100 c.c.; d 1.23) for an hour, water precipitated 4-chloro-4'-cyano-2':2'-dinitrodiphenylamine, orange-red needles (10 g.), m. p. 241° (from acetic acid) (Found: C, 49.3; H, 2.1. $C_{13}H_8O_4N_4Cl$ requires C, 49.0; H, 2.2%). When reduced with sodium sulphide as described for 2-methyl-4':2':4'-trinitrodiphenylamine, it gave 7-chloro-2-cyanophenazine, pale yellow needles, m. p. 317° (from amyl alcohol) (Found: C, 65.2; H, 2.6. $C_{13}H_8N_3Cl$ requires C, 65.1; H, 2.5%).

5-(5-Cyanobenzotriazol-1-yl)-1-phenylbenzotriazole.—A mixture of 4-chloro-3-nitroaniline (8 g.), 4-chloro-3-nitrobenzotrile (8 g.), and potassium carbonate (6 g.) was heated at 160° with stirring for 20 minutes and then extracted with warm dilute hydrochloric acid, and the residue crystallised from acetic acid (charcoal); 4-chloro-4'-cyano-3':2'-dinitrodiphenylamine separated in orange needles (4 g.), m. p. 224° (Found: C, 49.2; H, 2.5%). After this substance (4 g.) had been treated with aniline as described for 4-anilino-3':2':4'-trinitrodiphenylamine, 4-anilino-4'-cyano-3':2'-dinitrodiphenylamine, red plates (2 g.), m. p. 215° (from acetic acid), was obtained (Found: C, 60.2; H, 4.0. $C_{19}H_{13}O_4N_5$ requires C, 60.8; H, 3.5%). Stannous chloride (10 g.) in concentrated hydrochloric acid (30 c.c.) was added to a hot solution of the anilino-compound (2 g.) in glacial acetic acid (100 c.c.), and the mixture was boiled for 5 minutes, cooled, and immediately treated with aqueous sodium nitrite (1.5 g.). Addition of dilute hydrochloric acid precipitated 5-(5-cyanobenzotriazol-1-yl)-1-phenylbenzotriazole, almost colourless prisms (1 g.), m. p. 310—312° [from acetic acid (charcoal)] (Found: C, 67.2; H, 3.3. $C_{19}H_{11}N_7$ requires C, 67.7; H, 3.3%).

1-Chloro-6-cyanocarbazole.—After a mixture of *o*-chloroaniline (15 c.c.), 4-chloro-3-nitrobenzotrile (10 g.), and anhydrous sodium acetate (7 g.) had been heated at 205° for 2 hours, ethanol (50 c.c.) added, and the whole poured into dilute hydrochloric acid, 2-chloro-4'-cyano-2'-nitrodiphenylamine, orange-yellow needles (6 g.), m. p. 164—165° (from ethanol), was precipitated (Found: C, 57.4; H, 2.8%). Prepared like the isomeride described above, 2'-amino-2-chloro-4'-cyanodiphenylamine separated from ethanol in colourless needles, m. p. 151° (Found: C, 64.2; H, 4.3%), and the derived 1-*o*-chlorophenyl-5-cyanobenzotriazole crystallised from ethanol in colourless prisms, m. p. 138° (Found: C, 61.4; H, 2.9%). The triazole (1.5 g.) was heated at 350° until evolution of nitrogen ceased, and 1-chloro-6-cyanocarbazole, pale brown prisms (0.2 g.), m. p. 247° (from aqueous ethanol), was obtained (Found: C, 69.3; H, 3.2%).

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