# **399.** *Attempts to prepare Optically Active Tervalent Nitrogen Compounds. Part I. Syntheses of* 1 : 9-*Phenylenecarbazole and Derivatives.**

By Helen G. Dunlop and S. Horwood Tucker.

1 : 9-*Phenylenecarbazole* and its 4′-*methyl* and 4′-*carboxy*-derivatives have been prepared from carbazole by a method which has been standardised for the necessary five-membered ring closure. Carbazole-3-carboxylic and -3 : 6-dicarboxylic acids have

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* The major part of this work was incorporated in a thesis submitted (by H. G. D.) for the degree of Doctor of Philosophy of the University of Glasgow in May, 1936. Owing to experimental difficulties (described in this paper) we were unable to test the resolvability of our synthesised products. The work is still in progress, but the publication of a paper by Barger and Dyer (*J. Amer. Chem. Soc.*, 1938, **60**, 2414) and a letter by Lions and Ritchie (*ibid.*, 1939, **61**, 1927) necessitates the publication of our synthetic work.

been prepared by use of trichloroacetonitrile, and converted, by the above method of ring closure, into 1 : 9-*phenylenecarbazole*-3-*carboxylic* and -3 : 6-*dicarboxylic acids* respectively. 1 : 9-Phenylenecarbazole-3-carboxylic acid has also been produced by the reaction of trichloroacetonitrile with 1 : 9-phenylenecarbazole.

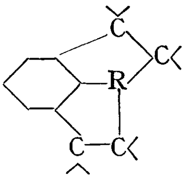
Attempts to resolve 1 : 9-phenylenecarbazole-3 : 6-dicarboxylic acid into optically active antipodes by means of alkaloids were impracticable owing to the instability of the salts in solvents.

NUMEROUS attempts have been made to prepare optically active isomers of nitrogen compounds whose activity was due to asymmetry of the tervalent nitrogen atom, but without success (*e.g.*, Jackson and Kenner, J., 1928, 573; Meisenheimer, *Ber.*, 1924, **57**, 1744; 1933, **66**, 985; Mumm and Ludwig, *Annalen*, 1934, **514**, 34; Schreiber and Schriner, *J. Amer. Chem. Soc.*, 1935, **57**, 1306; Kenner and Statham, *Ber.*, 1936, **69**, 187).

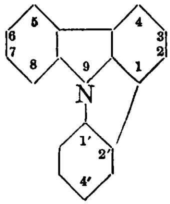
Compounds containing nitrogen linked to three different groups have been resolved into optical antipodes, but in all cases activity is due not to asymmetry of the nitrogen atom but to molecular dissymmetry dependent on restriction of rotation about a single bond (Mills and Elliott, J., 1928, 1291; Mills and Breckenridge, J., 1932, 2209; Bock and Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 374; Chang and Adams, *ibid.*, p. 2353; Jamison and Turner, J., 1938, 1646). 3-Nitro-9-phenylcarbazole-2′-carboxylic acid [*o*-(3-nitrocarbazyl)benzoic acid; Patterson and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 1069] was resolvable for the same reason. The statement of those authors that "in *o*-*N*-carbazylbenzoic acid there is a symmetrical substitution of the pyrrole ring, and therefore the compound should be resolvable only if the nitrogen atom retains a more or less fixed tetrahedral structure" is surely untenable, since, provided the plausible assumption is made that the third nitrogen bond is symmetrically placed in relation to the other two (pyrrole ring) bonds, the molecule will have a plane of symmetry whether the three bonds are planar or non-planar.

The negative * results obtained by Jackson and Kenner (*loc. cit.*) in their attempts to prepare systems containing a benzene ring and two five-membered rings, fused as shown in (*A*), supported, they considered, their contention that "two five-membered rings associated with a benzene nucleus in the manner contemplated must be co-planar."

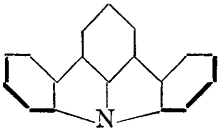
We have been fortunate in being able to synthesise compounds analogous to those sought by Jackson and Kenner, *viz.*, 1 : 9-*phenylenecarbazole* (I) and its derivatives.



(*A*; R = N or CH.)



(I.)



(II.)

Consideration of models shows that, if the whole molecule is planar, the nitrogen bonds, which are normally inclined at 120° to one another, are strained; but that this condition is partially relieved if the nitrogen atom adopts a position out of the plane of the benzene rings, *i.e.*, if it assumes a tetrahedral configuration, an exaggerated perspective view of such a structure being given by the "butterfly" formula (II), the thickened lines representing the portions of the benzene rings nearest to the observer. In such a structure the replacement by any atom or group of any hydrogen atom, other than that attached to the central benzene nucleus, and para to the nitrogen atom, will give rise to an asymmetric molecule

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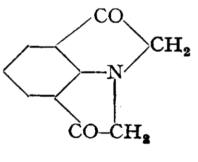
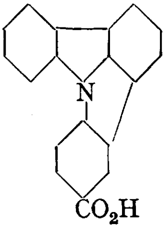
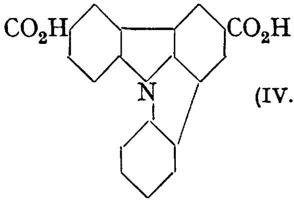


* The claim (*loc. cit.*, p. 576) that "small quantities of a compound of the desired composition were obtained" cannot be upheld, since the desired compound, represented by the annexed formula, has the molecular formula $C_{10}H_7O_2N$, whereas the compound isolated (*loc. cit.*, p. 581)—by the fusion of sodium indoxylacetate with sodamide, followed by treatment with methyl sulphate—gave an analysis in agreement with $C_{10}H_{10}O_2N_2$. Private communications from Professor Kenner and from Dr. Jackson admit, but do not elucidate, this discrepancy.

whose asymmetry is conditioned by the non-planar orientation of the tervalent nitrogen bonds. Thus with the above notation (I), derivatives of 1 : 9-phenylenecarbazole having the 3-position, and it only, substituted will be symmetrical, but 4′ (equivalent to 6)-derivatives, *e.g.*, will be asymmetric; and, if the molecule is sufficiently rigid to prevent the nitrogen atom moving into the planar configuration, such derivatives should be resolvable into optically active forms.

(III.)

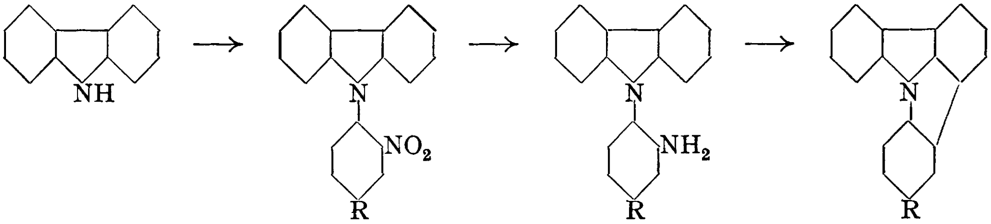




(IV.)

1 : 9-*Phenylenecarbazole*-4′-*carboxylic acid* (III) has been synthesised, but in insufficient quantity for resolution experiments. 1 : 9-*Phenylenecarbazole*-3 : 6-*dicarboxylic acid* (IV) has also been synthesised, and gave salts with brucine, quinine, morphine, and ephedrine, but on attempting crystallisation these dissociated: the recovered acid was inactive. The results are inconclusive; the work is being continued along other lines.

1 : 9-Phenylenecarbazole (I) was synthesised by condensation of carbazole (V) with *o*-chloronitrobenzene in presence of potassium carbonate and copper bronze to give 9-(2′-nitrophenyl)carbazole (VI, R = H). Reduction by means of stannous chloride in glacial acetic acid saturated with dry hydrogen chloride gave 9-(2′-*aminophenyl*)*carbazole* (VII, R = H), which, by diazotisation with an aqueous solution of sodium nitrite in a mixture of glacial acetic and concentrated sulphuric acids, followed by boiling, gave 1 : 9-phenylenecarbazole (VIII, R = H).

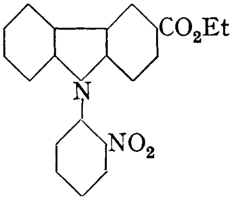


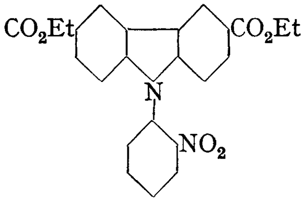
(V.) (VI.) (VII.) (VIII.)

Condensations (V—VI) were effected in like manner with carbazole and 1-chloro-2-nitrobenzenes containing a methyl, cyano-, chloro-, or nitro-group in position 4, giving rise to compounds represented by (VI), but when R = acetyl, no condensation product could be isolated.

Condensations were also readily effected likewise between substituted carbazoles and *o*-chloronitrobenzene. Thus ethyl carbazole-3-carboxylate and -3 : 6-dicarboxylate combined readily with *o*-chloronitrobenzene to give *ethyl* 9-(2′-*nitrophenyl*)*carbazole*-3-*carboxylate* (IX) -3 : 6-*dicarboxylate* (X) respectively.

(IX.)





(X.)

The effect of the addition of copper on the condensation of carbazole (+ potassium carbonate) with compounds of the formula 1-chloro-2-nitro-4-R-benzene is remarkable:

| R. | Temp. | Time (hrs.). | Yield (%). | |
|---|---|---|---|---|
| | | | Without Cu. | With Cu. |
| H | 240—250° | 3 | 10 | 50—60 |
| Me | 220—230 | 3 | 10 | 35 |
| Cl | 220—230 | 3 | 0 | 35 |
| | 230—240 | 7 | 10 | — |
| $NO_2$ | 170—180 | 12 | 50 | 50 |
| CN | 180—190 | 12 | 40 | 15 |

Similarly for carbazole (+ potassium carbonate) and the following three substances:

| | | | | |
|---|---|---|---|---|
| *p*-Iodotoluene | 180—200 | 6 | 40 | 66 |
| *p*-Chloroiodobenzene | 200 | 6 | 17 | 70 |
| Ethyl *p*-iodobenzoate | 220—230 | 6 | 0 | 80 |

Reduction (VI ⟶ VII) gave the corresponding amine (VII) except when $R = NO_2$. In this case, reduction by means of sodium sulphide of 9-(2′ : 4′-dinitrophenyl)carbazole (VI, $R = NO_2$) gave 9-(2′-nitro-4′-aminophenyl)carbazole (VI, $R = NH_2$) instead of the required 9-(2′-amino-4′-nitrophenyl)carbazole (VII, $R = NO_2$). That the 4′- and not the 2′-nitro-group had been reduced was proved by replacement of the amino-group by hydrogen and subsequent isolation of 9-(2′-nitrophenyl)carbazole. This result was not unexpected, however, since it has been found (Storrie and Tucker, J., 1931, 2255) that in the partial reduction of 2 : 4-dinitro-*N*-methyl(or ethyl)diphenylamine the 4-nitro-group is reduced, whereas with the unalkylated compound, 2 : 4-dinitrodiphenylamine, the 2-nitro-group is preferentially reduced.

Cyclisation (VII ⟶ VIII) was readily effected with compounds in which R = H or Me; but when R = Cl or CN, small amounts of unidentified products were obtained. Hydrolysis of 9-(4′-cyano-2′-aminophenyl)carbazole (VII, R = CN) gave 9-(2′-aminophenyl)-carbazole-4′-carboxylic acid (VII, $R = CO_2H$), which then cyclised to 1 : 9-phenylene-carbazole-4′-carboxylic acid (III) but only when nitrobenzene was present in the diazotisation mixture. *Ethyl* 9-(2′-*aminophenyl*)*carbazole*-3-*carboxylate* (from IX) gave ethyl 1 : 9-phenylenecarbazole-3-carboxylate, and *ethyl* 9-(2′-*aminophenyl*)*carbazole*-3 : 6-*dicarboxylate* (from X) gave *ethyl* 1 : 9-*phenylenecarbazole*-3 : 6-*dicarboxylate*.

Cyclisation (VII ⟶ VIII) to give 1 : 9-phenylenecarbazole could not be effected under any other conditions than those given. Thus (a) when the acetic acid was replaced by methyl alcohol, 9-phenylcarbazole resulted [cf. the conversion, under these conditions, of 9-(2′-aminobenzoyl)carbazole into 19-ketophenanthridinocoline; Plant and Tomlinson, J., 1932, 2188].

Similarly 9-(2′-amino-4′-cyanophenyl)carbazole gave 9-(4′-cyanophenyl)carbazole.

(b) When the diazonium sulphate solution obtained from 9-(2′-aminophenyl)carbazole was treated with sodium hydroxide solution, an unworkable product was obtained. 9-(2′-Amino-4′-cyanophenyl)carbazole behaved similarly (cf. the conversion, under these conditions, of *o*-amino-*N*-methyldiphenylamine into 9-methylcarbazole; Storrie and Tucker, J., 1931, 2262).

(c) Aluminium chloride in various solvents had no effect on 9-phenylcarbazole.

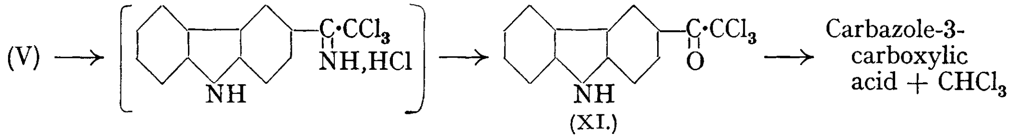
(d) Fusion of 9-p-*tolylcarbazole* with potassium hydroxide effected neither ring closure nor oxidation of the methyl to the carboxyl group.

Neither 1 : 9-(4′-*methylphenylene*)*carbazole* nor 9-*p*-tolylcarbazole could be oxidised to the corresponding 4′-carboxylic acid. It is significant that no method of oxidising a methylcarbazole to a carbazole carboxylic acid is known.

For comparison purposes 9-phenylcarbazole and its derivatives were prepared by condensing iodobenzene and the *p*-iodo-derivatives of toluene, chlorobenzene, and ethyl benzoate with carbazole in presence of anhydrous potassium carbonate and a trace of copper bronze. They were quite different from 1 : 9-phenylenecarbazole and its synthesised derivatives.

9-Benzoylcarbazole, whose preparation has hitherto proved capricious (Mazzara, *Ber.*, 1891, **24**, 278; Tucker and Stevens, J., 1923, **123**, 3146; Tucker, J., 1926, 548, footnote), can readily be prepared by this method.

*Preparation of Carboxy-derivatives of Carbazole and of* 1 : 9-*Phenylenecarbazole.*—The carboxy-derivatives of carbazole are not easily available, although various methods for the preparation of carbazole-1-, -2-, and -3-carboxylic acids are described in the literature (see Briscoe and Plant, J., 1928, 1990; Plant and Williams, J., 1934, 1142; Gilman and Kirby, *J. Org. Chem.*, 1936, **1**, 146). We have found that Houben and Fischer's methods of preparing carboxy- and cyano-derivatives of hydrocarbons (Houben and Fischer, *J. pr. Chem.*, 1929, **123**, 313; Houben, *Ber.*, 1930, **63**, 2455. Cyano-derivatives, Houben and Fischer, *ibid.*, p. 2464; 1933, **66**, 339) can be used for the preparation of these derivatives of carbazole. For instance, the action of trichloroacetonitrile on carbazole in chlorobenzene in the presence of anhydrous aluminium chloride and dry hydrogen chloride, followed by hydrolysis with concentrated hydrochloric acid, gave 3-*trichloroacetylcarbazole* (XI), which by alkaline hydrolysis gave carbazole-3-carboxylic acid:



(XI.)

*Carbazole-3:6-dicarboxylic acid* was similarly obtained. It was alleged to have been obtained (Meister, Lucius, and Brüning, D.R.-P. 263,150) by a process analogous to that by which carbazole-3-carboxylic acid was alleged to have been prepared (I. G. Farbenind. Akt.-Ges., D.R.-P. 442,609), but its constitution was not established until it had been prepared by potassium hydroxide fusion of 3 : 6-dibenzoylcarbazole and identified as its ethyl ester (Mitchell and Plant, J., 1936, 1296).

3-Cyano- and 3 : 6-dicyano-carbazole were prepared by the Houben–Fischer method (*loc. cit.*) and will be described in another communication. 1 : 9-Phenylenecarbazole was carboxylated by this method and gave a monocarboxylic acid, m. p. 305°, which was shown to be 1 : 9-*phenylenecarbazole*-3-*carboxylic acid* as follows: By our standard method of condensation with *o*-chloronitrobenzene, followed by reduction, ring closure, and hydrolysis, ethyl carbazole-3-carboxylate gave a phenylenecarbazolecarboxylic acid, m. p. 305°, which was identical with that obtained from 1 : 9-phenylenecarbazole. Now carbazole-3-carboxylic acid can theoretically give either 1 : 9-phenylenecarbazole-3-carboxylic acid or 1 : 9-phenylenecarbazole-4′-carboxylic acid (III). Since the last acid has been synthesised by an unambiguous process, above described, and found to melt at 340°, the carboxylic acid, m. p. 305°, derived both from carbazole-3-carboxylic acid and from 1 : 9-phenylenecarbazole is 1 : 9-phenylenecarbazole-3-carboxylic acid.

These results were unfortunate, since the last acid has a symmetric structure. The introduction of a single atom or group into any position in this molecule would have rendered it asymmetric (according to our theory), but this line was not tried, since carbazole-3 : 6-dicarboxylic acid by our standard method gave 1 : 9-phenylenecarbazole-3 : 6-dicarboxylic acid, which (according to our theory) might be asymmetric; but, as already mentioned, attempts at resolution were fruitless.

1 : 9-Phenylenecarbazole is a neutral substance. It forms a picrate and a trinitrobenzene derivative. It is relatively stable, since it sublimes unchanged at 230°/15 mm., and is unaffected by chlorine in chloroform or boiling glacial acetic acid; but with iodine and nitric acid in glacial acetic acid (Datta and Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 292) it gives a *monoiodotrinitro*-derivative. Regulated bromination gave rise to a monobromo- and a *dibromo*-derivative. Since, by the Houben–Fischer reaction with trichloroacetonitrile, substitution has been shown to take place in the 3-position of 1 : 9-phenylenecarbazole, we suggest that the monobromo-derivative is 3-*bromo*-1 : 9-*phenylenecarbazole*. It would not react with activated magnesium (Gilman and Kirby, *Rec. Trav. chim.*, 1935, 577) in amyl ether (it is practically insoluble in ethyl ether) or in xylene. Heating it with magnesium powder in an inert atmosphere (Gilman and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 3330) resulted in decomposition.

## EXPERIMENTAL.

Microanalyses were carried out by Mr. J. M. L. Cameron, Glasgow, and by Dr. Schoeller, Berlin.

*Synthesis of* 1 : 9-*Phenylenecarbazole* (I).—A mixture of carbazole (20 g.), *o*-chloronitrobenzene (40 g.), anhydrous potassium carbonate (20 g.), and copper bronze (0·2—0·3 g.) was boiled, with frequent shaking, for 3 hours, then steam-distilled to remove the excess of *o*-chloronitrobenzene. The brown residue was extracted with glacial acetic acid (250 c.c.; charcoal), the solution evaporated, and the product therefrom extracted several times with alcohol. The first extract contained a small amount of carbazole. 9-(2′-Nitrophenyl)carbazole crystallised from the other extracts in yellow needles (15—18 g.), m. p. 156° (corr.) (yield, 50—60%). The improved yield (Nelmes and Tucker, J., 1933, 1525, obtained 3 g.; yield, 10%) is due to addition of copper bronze. Replacement of potassium carbonate by copper bronze (1 g.) gave an unworkable tarry product. The optimum period of heating is 3 hours: after 2 hours' heating, much unchanged carbazole was recovered; after 4 hours, the product was tarry.

9-(2′-Nitrophenyl)carbazole (10 g.), stannous chloride (40 g.), and glacial acetic acid (150 c.c.) saturated with hydrogen chloride were boiled together. The solution, which almost immediately became green, was poured into a large excess of hot, fairly concentrated sodium hydroxide solution and, after settling, the precipitate was filtered off and extracted with benzene. The dried extract, on concentration almost to dryness, gave crystals which after recrystallisation from alcohol (charcoal) afforded colourless crystals of 9-(2′-*aminophenyl*)-*carbazole* (7 g.), m. p. 119—121° (corr.) (yield, 75%) (Found: N, 10·7. $C_{18}H_{14}N_2$ requires N, 10·85%). Nelmes and Tucker (*loc. cit.*) obtained this substance by the reduction with tin and hydrochloric acid—a much slower method—but failed to crystallise it. They obtained the acetyl derivative, 9-(2′-acetamidophenyl)carbazole, m. p. 150° (corr.).

Reduction with tin, hydrochloric acid, and glacial acetic acid gave a lower yield of amine (50%).

9-(2′-Aminophenyl)carbazole (5 g.) was dissolved in glacial acetic acid (50 c.c.), concentrated sulphuric acid (11 c.c.) added, and the solution diazotised at 0° with sodium nitrite (1·35 g. in 30 c.c. of water). After a short time the deep red solution was boiled for ½ hour. The reddish-brown crystalline solid obtained, recrystallised from alcohol (charcoal) or methyl alcohol, gave 1 : 9-*phenylenecarbazole* in colourless, silky needles (2·6 g.), m. p. 136·5—138·5° (corr.) (yield, 56%) (Found: C, 89·7; H, 4·7; N, 6·0; *M*, Rast, 248. $C_{18}H_{11}N$ requires C, 89·6; H, 4·6; N, 5·8%; *M*, 241).

The use of excess of sodium nitrite gave a lower yield. Heating may be carried out on the water-bath, but the reaction is slower, and the yield not improved. Vigorous boiling causes tarring. A quicker and more efficient way of purifying small quantities of 1 : 9-phenylenecarbazole is that of sublimation (250°/15 mm.). The substance is very soluble in cold benzene and in carbon tetrachloride, sparingly soluble in petroleum. The *picrate*, obtained from ethereal solutions of the components, crystallised from glacial acetic acid in red needles, m. p. 165—169° (Found: C, 61·3; H, 3·0; N, 11·7. $C_{18}H_{11}N,C_6H_3O_7N_3$ requires C, 61·3; H, 3·0; N, 11·9%). The s.-*trinitrobenzene* compound, prepared in alcoholic solution, crystallised from glacial acetic acid in long, yellow needles, m. p. 192—194° (Found: C, 63·5; H, 3·2; N, 12·4. $C_{18}H_{11}N,C_6H_3O_6N_3$ requires C, 63·4; H, 3·1; N, 12·3%).

9-*Phenylcarbazole*.—A mixture of carbazole (5 g.), iodobenzene (12 g.), anhydrous potassium carbonate (5 g.), and copper bronze (0·3 g.) was heated at 190—200° for 6 hours. After cooling, the product was washed with warm water, and the residue crystallised three times from alcohol, forming colourless crystals (4·5 g.), m. p. 91—93° (yield, 65%) (Found: C, 88·7; H, 5·6; N, 5·55. Calc.: C, 88·9; H, 5·35; N, 5·8%). Cassella (D.R.-P. 224,951) gives m. p. 82—84°; Eckert, Seidel, and Endler (*J. pr. Chem.*, 1922, **104**, 87) give m. p. 87—89°; *Organic Syntheses*, 1928, **8**, 119, gives m. p. 88—89° and 88% yield. The *picrate* formed scarlet needles, m. p. 126—129° (Found: C, 60·9; H, 3·6; N, 11·8. $C_{18}H_{13}N,C_6H_3O_7N_3$ requires C, 61·0; H, 3·4; N, 11·9%).

The s.-*trinitrobenzene* compound, prepared in alcohol, crystallised from alcohol and then from glacial acetic acid in orange needles, m. p. 132—134° (Found: N, 12·1. $C_{18}H_{13}N,C_6H_3O_6N_3$ requires N, 12·3%).

*Synthesis of* 1 : 9-(4′-*Methylphenylene*)*carbazole* (VIII, R = Me).—Carbazole (10 g.), 4-chloro-3-nitrotoluene (22 g.) (Gattermann, *Ber.*, 1885, **18**, 1483; Gattermann and Kaiser, *ibid.*, p. 2600), anhydrous potassium carbonate (10 g.), and copper bronze (0·1—0·2 g.) were heated together at 220—230° for 3 hours, the excess of 4-chloro-3-nitrotoluene removed by steam-distillation, and the residue dissolved in glacial acetic acid (charcoal). The solution, decanted from the brown tar which separated on cooling, gave 9-(2′-*nitro*-4′-*methylphenyl*)*carbazole*; a further quantity was obtained by extracting the tar with alcohol. It crystallised from alcohol in yellow needles, m. p. 104—106° (6 g.; yield, 35%) (Found: N, 9·4. $C_{19}H_{14}O_2N_2$ requires N, 9·3%).

No condensation occurred when barium carbonate replaced potassium carbonate (cf. Macrae and Tucker, J., 1933, 1521).

The above nitro-compound (5 g.), stannous chloride (25 g.), and glacial acetic acid (100 c.c.) saturated with hydrogen chloride were boiled together for ½ hour while hydrogen chloride was passed in. Further quantities of stannous chloride (10 g.) and acetic acid (25 c.c.) were added, and boiling continued until a white solid separated. The mixture was then poured into a large excess of sodium hydroxide solution and, after filtration, the solid was extracted with cold benzene. From the extract, concentrated almost to dryness, 9-(2'-*amino-4'-methylphenyl*)-*carbazole* separated; it crystallised from alcohol in colourless prisms, m. p. 117—119° (3 g.; yield, 75%) (Found: N, 10·3. $C_{19}H_{16}N_2$ requires N, 10·3%).

The above amine (5 g.) in glacial acetic acid (45 c.c.) and concentrated sulphuric acid (10 c.c.) was diazotised at 0° (1·3 g. of sodium nitrite in 30 c.c. of water), and the mixture boiled for 10 minutes. The black tar obtained solidified when cooled in ice. Extraction with alcohol and precipitation of the extracts with water yielded a brownish-white solid. Crystallisation from alcohol, followed by sublimation (210—270°/15 mm.), gave a soft, white sublimate, which slowly became brittle. Crystallisation from petroleum, methyl alcohol or glacial acetic acid gave tufts of long, colourless needles which on drying matted together like felt. 1 : 9-(4'-*Methylphenylene*)*carbazole* had m. p. 109—111° (corr.) (Found: C, 89·4; H, 5·1. $C_{19}H_{13}N$ requires C, 89·4; H, 5·1%). Its solutions in the usual organic solvents exhibited a faint violet fluorescence. The *picrate* crystallised from alcohol in red needles, m. p. 145—150° (Found: C, 62·0; H, 3·4; N, 11·5. $C_{19}H_{13}N,C_6H_3O_7N_3$ requires C, 62·0; H, 3·3; N, 11·6%), and the s.-*trinitrobenzene* compound from glacial acetic acid in yellow needles, m. p. 170—172° (Found: C, 63·9; H, 3·4; N, 12·0. $C_{19}H_{13}N,C_6H_3O_6N_3$ requires C, 64·1; H, 3·4; N, 12·0%).

9-p-*Tolylcarbazole*, prepared by means of *p*-iodotoluene (15 g.) in the same way as its phenyl analogue, formed colourless needles (5 g.), m. p. 105—107°, from alcohol (yield, 66%) (Found: N, 5·6. $C_{19}H_{15}N$ requires N, 5·45%). The s.-*trinitrobenzene* compound crystallised from alcohol in long red needles (yellow when powdered), m. p. 106—108° (Found: N, 12·1. $C_{19}H_{15}N,C_6H_3O_6N_3$ requires N, 11·9%).

*Attempted Synthesis of* 1 : 9-(4'-*Chlorophenylene*)*carbazole* (VIII, R = Cl).—A mixture of carbazole (10 g.), 1 : 4-dichloro-2-nitrobenzene (22 g.), anhydrous potassium carbonate (10 g.), and copper bronze (0·2 g.) was heated at 220—230° for 4 hours, the brown mass steam-distilled to remove the excess of 1 : 4-dichloro-2-nitrobenzene, and the residue crystallised from alcohol (charcoal); orange-yellow prisms of 9-(4'-*chloro-2'-nitrophenyl*)*carbazole* (VI, R = Cl), m. p. 134—136°, were obtained (6·6 g.; yield, 35%) (Found: Cl, 10·9. $C_{18}H_{11}O_2N_2Cl$ requires Cl, 11·0%).

The above nitro-compound (5 g.), stannous chloride (25 g.), and glacial acetic acid (100 c.c.) saturated with dry hydrogen chloride were boiled together for a few minutes until the colour of the solution was pale yellowish-green. 9-(4'-*Chloro-2'-aminophenyl*)*carbazole* (VII, R = Cl) was precipitated as previously described for analogous compounds. The dried benzene extract was concentrated, dry hydrogen chloride passed in, and the hydrochloride of the base precipitated by addition of petroleum (b. p. 60—80°). The hydrochloride was decomposed with ammonia, and the amine crystallised from methyl alcohol. An oil separated first, but from the mother-liquor crystals separated, m. p. 84—86° (4 g. of hydrochloride; yield, 80%) (Found: N, 9·5. $C_{18}H_{13}N_2Cl$ requires N, 9·6%).

The hydrochloride (2·5 g.) in glacial acetic acid (20 c.c.) and concentrated sulphuric acid (4·4 c.c.) was diazotised at 0° (0·54 g. of sodium nitrite in 12 c.c. of water) and after 10 minutes the crimson solution was heated at 80° for ½ hour. A black tar, which solidified readily on cooling, was obtained. It was sublimed (230—250°/15 mm.); the yellowish-white product crystallised from alcohol or acetic acid in colourless needles, m. p. 138—140°.

9-(4'-*Chlorophenyl*)*carbazole*.—A mixture of carbazole (5 g.), *p*-chloroiodobenzene (Gomberg and Cone, *Ber.*, 1906, **39**, 3281) (14 g.), anhydrous potassium carbonate (5 g.), and copper bronze (0·2 g.) was heated at 200° for 6 hours with frequent shaking. The excess of *p*-chloroiodobenzene was removed by steam-distillation; the residual brownish-white solid crystallised from ethyl acetate in colourless prisms, m. p. 140—143° (6 g.; yield, 70%) (Found: Cl, 13·0. Calc. for $C_{18}H_{12}NCl$: Cl, 12·8%). Guillaume and Marcel de Montmollin (*Helv. Chim. Acta*, 1923, **6**, 98) give m. p. 146°.

In the absence of copper bronze the solid which crystallised from the ethyl acetate extract was carbazole; 9-(4'-chlorophenyl)carbazole, mixed with carbazole, was isolated from the mother-liquor (1·5 g.; yield, 17%).

A mixture of 9-(4'-chlorophenyl)carbazole (m. p. 140—143°) with the alleged 9-(4'-chlorophenylene)carbazole (m. p. 138—140°) melted at 120°.

9-(2′-*Nitro*-4′-*aminophenyl*)*carbazole* (VI, R = $NH_2$).—Sodium sulphide (7·5 g.), sulphur (2 g.), and rectified spirit (0·5 c.c.) were heated together and added to 9-(2′ : 4′-dinitrophenyl)-carbazole (Dunlop, Macrae, and Tucker, *loc. cit.*, p. 1675) (9 g.) in methylated spirit (50 c.c.). The solution was boiled for 2 hours, filtered hot, and allowed to crystallise. The red solid obtained was converted into the hydrochloride by hydrogen chloride in dry benzene. The hydrochloride on treatment with ammonia gave the amine, which crystallised from alcohol in long red needles, m. p. 164—166° after softening at 145°. When boiled with acetic anhydride for a few minutes, it gave the *acetyl* derivative, which was recrystallised from acetic acid; m. p. 261—263° (Found : N, 12·1. $C_{20}H_{15}O_3N_3$ requires N, 12·2%).

9-(2′-Nitro-4′-aminophenyl)carbazole (2 g.) was heated with dilute sulphuric acid (5 c.c. of concentrated acid and 25 c.c. of water), cooled in ice, and diazotised (0·6 g. of sodium nitrite in water). The solution, containing a dark red solid, was poured into alcohol and heated on a water-bath until effervescence ceased. The liquid was filtered hot and the yellow solid which separated on cooling was crystallised several times from alcohol, giving long yellow needles of 9-(2′-nitrophenyl)carbazole, m. p. and mixed m. p. 151—153°.

9-(2′ : 4′-*Diaminophenyl*)*carbazole* (VII, R = $NH_2$).—9-(2′ : 4′-Dinitrophenyl)carbazole (2 g.) was boiled with stannous chloride (20 g.) and glacial acetic acid (100 c.c.) saturated with hydrogen chloride, until only a faint yellow colour persisted, and the product worked up as in analogous preparations. The dried benzene extract was concentrated, and the *diamine* precipitated with petroleum and thrice crystallised from aqueous alcohol; it formed tufts of colourlesss needles, m. p. 128—130° (1 g.; yield, 63%) (Found : N, 15·0. $C_{18}H_{15}N_3$ requires N, 15·3%).

9-(2′ : 4′-*Diacetamidophenyl*)*carbazole*, prepared by boiling the diamine for a few minutes with acetic anhydride, crystallised from aqueous alcohol in colourless plates, m. p. 230—235° (Found : N, 11·5. $C_{22}H_{19}O_2N_3$ requires N, 11·8%).

9-(2′-*Amino*-4′-*acetamidophenyl*)*carbazole*.—9-(2′-Nitro-4′-acetamidophenyl)carbazole (2 g.) and stannous chloride (10 g.) were boiled for a few minutes with glacial acetic acid (50 c.c.) saturated with hydrogen chloride and the hot solution was poured into concentrated sodium hydroxide solution. The grey solid obtained crystallised from aqueous alcohol in colourless plates, m. p. 235—245° (1·4 g.; yield, 75%). Attempts to effect ring closure by the diazotisation process already described failed.

Attempts to condense carbazole with either 4-chloro-, 4-bromo- or 4-iodo-3-nitroacetophenone also failed (*Organic Syntheses*, 1925, **5**, 17; Le Fèvre, J., 1932, 1991).

4-*Iodo*-3-*nitroacetophenone*.—*p*-Iodoacetophenone (1 g.) (Evans, Morgan, and Watson, J., 1935, 1172) was slowly added to nitric acid (6 c.c., *d* 1·5) cooled in ice. After 5 minutes the solution was poured into water. The product crystallised from alcohol in pale yellow needles, m. p. 112—115° (Found : N, 4·8; I, 44·2. $C_8H_6O_3NI$ requires N, 4·8; I, 43·6%).

*Synthesis of* 1 : 9-*Phenylenecarbazole*-4′-*carboxylic Acid* (III).—A mixture of carbazole (10 g.), 4-chloro-3-nitrobenzonitrile (25 g.) (Dunlop, Macrae, and Tucker, J., 1934, 1675), and anhydrous potassium carbonate (10 g.) was heated at 180—190° for 12 hours with frequent shaking. The cold mixture was extracted with glacial acetic acid (charcoal), from which a product crystallised containing carbazole and 4-chloro-3-nitrobenzonitrile. The latter was removed by washing with warm alcohol, and most of the former by crystallisation from xylene and then from acetic anhydride. 9-(2′-*Nitro*-4′-*cyanophenyl*)*carbazole* (VI, R = CN) crystallised from acetic anhydride or anisole in clusters of yellow needles, m. p. 172—174° (7·5 g.; yield, 40%) (Found : C, 72·9; H, 3·4; N, 13·3. $C_{19}H_{11}O_2N_3$ requires C, 72·5; H, 3·5; N, 13·4%).

No condensation took place when potassium carbonate was replaced by barium carbonate (cf. Macrae and Tucker, *loc. cit.*). Above 200°, or after 18 hours' heating, the reaction gave a charred mass.

The above nitro-compound (5 g.) was reduced as in analogous preparations. 9-(2′-*Amino*-4′-*cyanophenyl*)*carbazole* (VII, R = CN) crystallised from alcohol in colourless plates, m. p. 186—188° (3 g.; yield, 70%) (Found : N, 14·7. $C_{19}H_{13}N_3$ requires N, 14·8%). The acetyl derivative crystallised from methyl alcohol in nacreous plates, m. p. 241—243°.

The amine (4·2 g.) was boiled for 1 hour with a mixture of glacial acetic acid (30 c.c.) and concentrated hydrochloric acid (75 c.c.). The hot solution deposited 9-(2′-amino-4′-carboxyphenyl)carbazole hydrochloride, m. p. 210—220° (5 g.; yield, theoretical). This dissolved in a weakly acid solution, was precipitated therefrom by sodium hydroxide solution, and dissolved in excess of alkali. It could not be further purified.

The method usually adopted to effect ring closure having failed, the process was modified merely by addition of nitrobenzene thus : The above hydrochloride (3 g.) in glacial acetic acid

(25 c.c.) and concentrated sulphuric acid (6 c.c.) was diazotised at 0° (0·6 g. of sodium nitrite in 15 c.c. of water), redistilled nitrobenzene (25 c.c.) added, and the mixture heated for 10 minutes and allowed to cool. The pale brown, crystalline solid obtained (0·45 g.; yield, 18%) was sublimed at 300—350°/15 mm., and subsequent crystallisation yielded pink prisms of 1 : 9-*phenylenecarbazole*-4′-*carboxylic acid*, m. p. 340° after blackening at 320° (Found: C, 80·0; H, 3·9. $C_{19}H_{11}O_2N$ requires C, 80·0; H, 3·9%). The methyl ester, prepared from the acid and methyl-alcoholic hydrogen chloride, separated from aqueous dioxan in pink crystals, m. p. 155—162°.

The acid was heated with copper bronze until decomposition set in. The product, sublimed, and crystallised from alcohol, proved to be 1 : 9-phenylenecarbazole, identified by mixed m. p. and by formation of the trinitrobenzene compound. The acid was not decarboxylated by heating with copper in boiling quinoline, or with copper at 300°.

*Attempted Preparation of* 1 : 9-(4′-*Cyanophenylene*)*carbazole* (VIII, R = CN).—9-(2′-*Amino*-4′-*cyanophenyl*)*carbazole* (1 g.) in methyl alcohol (120 c.c.) and concentrated sulphuric acid (2 c.c.) was diazotised at 0° (0·25 g. of sodium nitrite in 5 c.c. of water), and the solution boiled and concentrated. The reddish crystalline product, recrystallised from alcohol and then from acetic anhydride, gave colourless 9-(4′-cyanophenyl)carbazole, m. p. 175—177° alone or mixed with a sample prepared from 9-(4′-nitrophenyl)carbazole (Guillaume and de Montmollin, *loc. cit.*, p. 94; Nelmes and Tucker, *loc. cit.*, p. 1524).

*Synthesis of* 9-*Phenylcarbazole*-4′-*carboxylic Acid*.—A mixture of *p*-iodotoluene (35 g.), glacial acetic acid (300 c.c.), concentrated sulphuric acid (50 c.c.), and water (50 c.c.) was boiled, and a solution of sodium dichromate (60 g.) in water (100 c.c.) added during ½ hour with frequent shaking. On cooling, *p*-iodobenzoic acid separated. After being washed with water, it was crystallised from glacial acetic acid; m. p. 265—266° (25 g.; yield, 63%) (cf. Hoffmann, *Annalen*, 1891, **264**, 166; Koopal, *Rec. Trav. chim.*, 1915, **34**, 151; Dunlop, Macrae, and Tucker, *loc. cit.*). The acid was esterified by boiling for 12 hours in absolute alcohol with hydrogen chloride (Schmidt and Schultz, *Annalen*, 1881, **207**, 334). The ethyl ester had b. p. 157°/24 mm.

A mixture of carbazole (4 g.), ethyl *p*-iodobenzoate (13 g.), anhydrous potassium carbonate (4 g.), and copper bronze (0·15 g.) was heated at 220—230° for 6 hours with frequent shaking, and the excess of ethyl *p*-iodobenzoate then removed by steam-distillation. The residue gave *ethyl* 9-*phenylcarbazole*-4′-*carboxylate*, which crystallised from alcohol in colourless plates, m. p. 97—100° (6 g.; yield, 80%) (Found: C, 80·0; H, 5·4; N, 4·5. $C_{21}H_{17}O_2N$ requires C, 80·0; H, 5·4; N, 4·4%). This ester was boiled with alcoholic potassium hydroxide for 20 minutes, and the mixture poured into dilute hydrochloric acid. The precipitated 9-*phenylcarbazole*-4′-*carboxylic acid* crystallised from glacial acetic acid in colourless prisms, m. p. 215—219°. It dissolved completely in aqueous ammonia (Found: C, 79·3; H, 4·5; N, 4·8. $C_{19}H_{13}O_2N$ requires C, 79·4; H, 4·5; N, 4·9%). When decarboxylated as in the case of 1 : 9-phenylenecarbazole-4′-carboxylic acid, it gave 9-phenylcarbazole, m. p. and mixed m. p. 91—93°. Decarboxylation could not be effected by boiling with copper in quinoline for 1 hour or by heating with copper at 300° for 15 minutes (cf. decarboxylation of 9-phenylcarbazole-2′-carboxylic acid; Eckert, Seidel, and Endler, *J. pr. Chem.*, 1922, **104**, 87).

*Carbazole*-3-*carboxylic Acid*.—Dry hydrogen chloride was passed into a cooled solution of trichloroacetic acid (1 mol.) in alcohol (1 mol.) until two layers appeared (5 hours). The ester was worked up in the usual way (yield, 90%; cf. Spiegel, *Ber.*, 1907, **40**, 1734, who obtained 50—60%) and converted by concentrated aqueous ammonia into trichloroacetamide (yield, 60%) (Clermont, *Compt. rend.*, 1901, **133**, 738). A mixture of trichloroacetamide (50 g.) and phosphoric oxide (70 g.) was heated until liquid trichloroacetonitrile appeared in the neck of the flask; the pasty mass was then submitted to distillation. Usually no amide distilled and the nitrile was pure; but to ensure purity, especially after storing, it was redistilled before use, b. p. 85—86° (38 g.; yield, 80%). Bisschopinck (*Ber.*, 1873, **6**, 732), Bauer (*Annalen*, 1885, **229**, 166), and Steinkopf (*Ber.*, 1908, **41**, 2540) employed vacuum distillation, but this is wasteful of product. Houben and Fischer (*Ber.*, 1927, **60**, 1765) heated the mixture under pressure (½ atm. excess) and distilled the nitrile in a vacuum.

Carbazole (4·2 g.; 1 mol.), chlorobenzene (40 c.c.), trichloroacetonitrile (3 c.c.; 1·2 mols.), and aluminium chloride (4 g.; 1·2 mols.) were mixed, saturated with hydrogen chloride, heated from 40° to 100° during 1 hour, and maintained at 100° for 1 hour; the mixture was shaken at frequent intervals. The hot brown-red product was treated with excess of concentrated hydrochloric acid, and the chlorobenzene removed in a vacuum. The pale green solid that eventually separated from the aqueous acid portion was retreated with hydrochloric acid and crystallised from glacial acetic acid, giving matted yellow needles of 3-*trichloroacetylcarbazole*,

m. p. 206—208° (7·5 g.; yield, 84%) (Found: C, 53·7; H, 2·6. $C_{14}H_8ONCl_3$ requires C, 53·8; H, 2·6%). The *acetyl* derivative was prepared by boiling with acetic anhydride containing a trace of concentrated sulphuric acid for 1 minute; dilution with acetic acid, then water, gave pale brown nodules, which separated from alcohol in cream crystals, m. p. 120—125° (Found: C, 54·1; H, 3·0. $C_{16}H_{10}O_2NCl_3$ requires C, 54·2; H, 2·8%).

When 3-trichloroacetylcarbazole was warmed with sodium hydroxide solution, chloroform was produced. The alkaline solution on addition of concentrated hydrochloric acid gave a gelatinous white precipitate, which crystallised from glacial acetic acid in colourless plates of carbazole-3-carboxylic acid, m. p. 270° after softening at 260° (Plant and Williams, *loc. cit.*, p. 1143, give 276—278°). It contained acetic acid of crystallisation (Found: $C_2H_4O_2$, 21·8. Calc. for $C_{13}H_9O_2N,C_2H_4O_2$: $C_2H_4O_2$, 22·1%. Found for vacuum-dried material: C, 73·7; H, 4·3; N, 6·5. Calc.: C, 73·9; H, 4·3; N, 6·6%). Usually, however, in preparing carbazole-3-carboxylic acid, 3-trichloroacetylcarbazole was not recrystallised but added directly to the sodium hydroxide solution. A small amount of brown insoluble matter was removed, and the filtrate worked up as above (4·6 g.; yield, 92%). The ethyl ester, m. p. 165—167°, was prepared by boiling the acid with absolute alcohol (20 c.c.) and concentrated sulphuric acid (1 c.c.) for 6 hours (Found: C, 75·3; H, 5·5; N, 5·9. Calc.: C, 75·3; H, 5·4; N, 5·9%). Both the acid and the ethyl ester were prepared by Plant and Williams' methods (*loc. cit.*) and found to be identical with the above. We are grateful to Dr. Plant for specimens.

Attempts to convert ethyl carbazole-9-carboxylate (Oddo, *Gazzetta*, 1911, **41**, I, 256) into the 3-carboxylate by means of aluminium chloride in nitrobenzene failed.

*Synthesis of* 1 : 9-*Phenylenecarbazole*-3-*carboxylic Acid*.—A mixture of ethyl carbazole-3-carboxylate (5 g.), *o*-chloronitrobenzene (10 g.), potassium carbonate (5 g.), and copper bronze (0·2 g.) was heated at 200—210° for 5 hours, the excess of *o*-chloronitrobenzene removed in steam, the residue dissolved in acetic acid (charcoal), the solution poured into water, and the resulting solid crystallised from methyl alcohol; small yellow needles of *ethyl* 9-(2'-*nitrophenyl*)-*carbazole*-3-*carboxylate* (IX), m. p. 120—122°, were obtained (5 g.; yield, 60%) (Found: N, 7·9. $C_{21}H_{16}O_4N_2$ requires N, 7·8%).

The above nitro-compound (4 g.), stannous chloride (10 g.), and glacial acetic acid (40 c.c.) saturated with dry hydrogen chloride were boiled together for a few minutes until the colour of the solution was greenish-yellow. The amine was obtained as usual, and the dried, concentrated benzene extract precipitated by the addition of ligroin. *Ethyl* 9-(2'-*aminophenyl*)-*carbazole*-3-*carboxylate* separated from methyl alcohol in colourless prisms, m. p. 140—142° (2·4 g.; yield, 70%) (Found: N, 8·3. $C_{21}H_{18}O_2N_2$ requires N, 8·5%).

Diazotisation of the amine (1·5 g.) in the usual way (glacial acetic acid, 12 c.c.; concentrated sulphuric acid, 2·7 c.c.; sodium nitrite, 0·3 g., in 12 c.c. of water) and subsequent heating gave a black tar, which solidified on cooling. A solution of it in dioxan was poured into water, the yellow precipitate boiled for ½ hour with alcoholic potassium hydroxide, the product poured into dilute hydrochloric acid, and the resulting solid dried and sublimed at 300°/15 mm. The white sublimate separated from acetic anhydride–nitrobenzene in micro-crystals of 1 : 9-*phenylenecarbazole*-3-*carboxylic acid*, m. p. 305° after softening at 240° (Found: C, 80·0; H, 3·9; N, 5·1. $C_{19}H_{11}O_2N$ requires C, 80·0; H, 3·9; N, 4·9%). Decarboxylation in boiling quinoline containing copper bronze for ¾ hour gave 1 : 9-phenylenecarbazole.

The same acid was also prepared as follows: Dry hydrogen chloride was passed into a solution of 1 : 9-phenylenecarbazole (2 g.), trichloroacetonitrile (1 c.c.), and aluminium chloride (4 g.) in chlorobenzene (5 c.c.), and the mixture kept for 3 weeks. On treatment with water the red mass became yellow. The insoluble matter was boiled for 1 minute with potassium hydroxide solution and then filtered off. The solid which separated from the filtrate (probably the potassium salt of the acid) was soluble in hot water, and on acidification a gelatinous precipitate was obtained. Filtration yielded a brown solid, which was purified as described above, and shown by m. p. and mixed m. p. to be 1 : 9-phenylenecarbazole-3-carboxylic acid.

*Carbazole*-3 : 6-*dicarboxylic Acid*.—A mixture of carbazole (4·2 g.; 1 mol.), chlorobenzene (40 c.c.), trichloroacetonitrile (6 c.c.; 2·4 mols.), and anhydrous aluminium chloride (8 g.; 2·4 mols.) was heated during 1 hour from 40° to 100° and maintained at 100° for 1 hour, the whole being frequently shaken. The black product was boiled with concentrated hydrochloric acid, and the chlorobenzene removed in a vacuum. The residual pale green solid, on being warmed with potassium hydroxide solution, turned brown. The insoluble residue (trace) was separated, and the filtrate acidified. The green gelatinous precipitate when dried became almost colourless (yield, > 70%). Extraction with glacial acetic acid failed to remove any carbazole-3-carboxylic acid. Crystallisation of *carbazole*-3 : 6-*dicarboxylic acid* presented unusual difficulty, since it was practically insoluble in neutral solvents. It dissolved in much glycol monomethyl ether but did not separate on cooling; the solution was therefore concentrated to half bulk and boiling water (2 vols.) added. The pale brown needles which separated were unmelted at 360° (2·7 g.; yield, 44%). The acid was obtained in pale green needles by boiling a solution in pyridine with 10—20 vols. of glacial acetic acid and adding sufficient water to produce a turbidity (Found: C, 65·9; H, 3·4; N, 5·6. $C_{14}H_9O_4N$ requires C, 65·9; H, 3·5; N, 5·5%).

The ethyl ester was prepared by boiling the acid with absolute alcohol containing concentrated sulphuric acid (1 c.c. of concentrated acid to 20 c.c. of alcohol) for 6 hours. The product was poured into water, unchanged acid washed out with aqueous ammonia, and the residual solid crystallised from acetic acid or alcohol; it formed pale yellow prisms, m. p. 206—207° (corr.) (Found: C, 69·6; H, 5·45; N, 4·5. Calc.: C, 69·45; H, 5·5; N, 4·5%) (Mitchell and Plant, *loc. cit.*).

*Synthesis of* 1 : 9-*Phenylenecarbazole*-3 : 6-*dicarboxylic Acid* (IV).—Treatment of a mixture of ethyl carbazole-3 : 6-dicarboxylate (5 g.), *o*-chloronitrobenzene (9 g.), anhydrous potassium carbonate (5 g.), and a trace of copper bronze (5 hours at 180°) in the usual way and removal of the excess of *o*-chloronitrobenzene left a residue, which crystallised from glacial acetic acid (charcoal) in clusters of pale yellow prisms of *ethyl* 9-(2′-*nitrophenyl*)*carbazole*-3 : 6-*dicarboxylate*, m. p. 202—203° (4·5 g.; yield, 70%) (Found: C, 66·9; H, 4·8; N, 6·5. $C_{24}H_{20}O_6N_2$ requires C, 66·7; H, 4·6; N, 6·5%). Reduction by the usual process (nitro-compound, 6 g.; stannous chloride, 24 g.; glacial acetic acid, 100 c.c., saturated with dry hydrogen chloride) gave *ethyl* 9-(2′-*aminophenyl*)*carbazole*-3 : 6-*dicarboxylate*, which was crystallised from benzene and then from acetic acid; it formed colourless prisms, m. p. 175—177° (5 g.; yield, 80%) (Found: N, 7·0. $C_{24}H_{22}O_4N_2$ requires N, 7·0%). Diazotisation (ester, 4·5 g.; glacial acetic acid, 30 c.c.; concentrated sulphuric acid, 6·6 c.c.; sodium nitrite, 0·8 g., in 18 c.c. of water) and subsequent heating on a water-bath for ½ hour gave a yellow solid, which was washed with alcohol to remove the colour, and crystallised from glacial acetic acid and then from aqueous dioxan. *Ethyl* 1 : 9-*phenylenecarbazole*-3 : 6-*dicarboxylate* had m. p. 185—187° (turbid melt up to 220°) (2 g.; yield, 46%) (Found: C, 74·65; H, 5·2. $C_{24}H_{19}O_4N$ requires C, 74·8; H, 4·9%). Hydrolysis of the ester with alcoholic potassium hydroxide solution gave the acid. This dissolved readily in cold pyridine, but, on warming, a white precipitate separated (pyridinium salt?) which dissolved in boiling pyridine. Addition of boiling glacial acetic acid to this solution caused, on standing, a slow deposition of colourless micro-crystals of 1 : 9-*phenylenecarbazole*-3 : 6-*dicarboxylic acid*, m. p. > 360° (Found: C, 72·8; H, 3·5; N, 4·3. $C_{20}H_{11}O_4N$ requires C, 72·9; H, 3·3; N, 4·25%).

*Ethyl* 9-*Phenylcarbazole*-3 : 6-*dicarboxylate*.—Ethyl carbazole-3 : 6-dicarboxylate (1 g.), anhydrous potassium carbonate (1 g.), iodobenzene (2 g.), and copper bronze (a trace) were heated together at 200° for 6 hours. The product, after being washed with water and dilute hydrochloric acid, crystallised from methyl alcohol in long colourless needles, m. p. 139—141° (Found: C, 74·3; H, 5·4; N, 3·7. $C_{24}H_{21}O_4N$ requires C, 74·4; H, 5·4; N, 3·6%).

3(?)-*Bromo*-1 : 9-*phenylenecarbazole*.—A solution of 1 : 9-phenylenecarbazole (4·5 g.) in chloroform (75 c.c.) at 0° was mechanically stirred while bromine (1 c.c.) in chloroform (30 c.c.) was added during 3 hours. The solid which separated was removed, and the filtrate evaporated to dryness. The residue contained some unchanged material, which was washed out with hot alcohol. The combined solids were repeatedly crystallised from amyl ether and from acetic acid, giving colourless needles, m. p. 205—210° (Found: Br, 25·4. $C_{18}H_{10}NBr$ requires Br, 25·0%).

3 : 6(?)-*Dibromo*-1 : 9-*phenylenecarbazole*.—1 : 9-Phenylenecarbazole (1·5 g.) was dissolved in warm chloroform (10 c.c.), and bromine (0·66 c.c.) in chloroform (6 c.c.) added. A vigorous evolution of hydrogen bromide took place and a white solid separated. The mixture was boiled for a few minutes, then cooled in ice, and the separated solid was washed with hot alcohol and a little hot acetic acid to remove unchanged material and crystallised from glacial acetic acid and then from glycol monomethyl ether; the product had m. p. 202—209° (turbid melt clearing at 214°) (Found: Br, 41·2. $C_{18}H_9NBr_2$ requires Br, 40·1%). Attempts to purify it by sublimation were unsuccessful. The *dibromo*-compound was also prepared by boiling the monobromo-compound (0·5 g.) and bromine (0·25 c.c.) in chloroform (20 c.c.) for ½ hour.

*Iodotrinitro*-1 : 9-*phenylenecarbazole*.—1 : 9-Phenylenecarbazole (2 g.), iodine (1 g.), and glacial acetic acid (50 c.c.) were boiled together while concentrated nitric acid (6 c.c.) was added drop by drop. The violet colour changed to red and a solid separated. After being washed with sodium bisulphite solution, this was crystallised from ethyl benzoate. The product did not melt below 340° (Found: I, 24·8, 24·8. $C_{18}H_7O_6N_4I$ requires I, 25·3%).

9-*Benzoylcarbazole.*—Carbazole (5 g.), anhydrous potassium carbonate (5 g.), and benzoyl chloride (10 g.) were heated together at 140—160° for 1 hour. The greenish solid product was washed with water to remove potassium carbonate and the excess of benzoyl chloride. The residue was extracted with alcohol, and 9-benzoylcarbazole crystallised (5 g.; yield, 60%). Concentration of the alcoholic residues yielded carbazole.

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