561. *Attempts to Prepare Optically Active Tervalent Nitrogen Compounds. Part III.* Attempted Resolution of* 6-*Substituted* 1 : 9-*Phenylenecarbazoles* (3-*Substituted Indolo*[3,2,1-jk]*carbazoles*).

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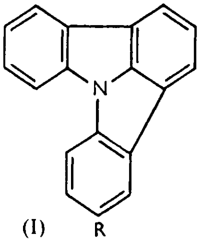
Improved methods for preparation of 6-carboxy-, 6-methoxycarbonyl-, and 6-methyl-1 : 9-phenylenecarbazole are submitted. Optical resolution of the acid by means of its alkaloidal salts, and of the 6-methoxycarbonyl and the 6-methyl compound by means of complexes with (−)-α-(2 : 4 : 5 : 7-tetranitro-9-fluorenylideneamino-oxy)propionic acid failed. 6-Methyl-1 : 9-phenylenecarbazole was examined for unstable optical activity by dissolution in ethyl (+)-tartrate, with negative results.

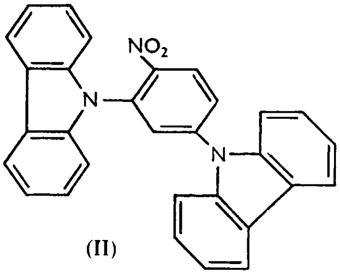
6-Bromo-1 : 9-phenylenecarbazole has been synthesised; the nature of a by-product is discussed.

Attempts at optical resolution of 1 : 9-phenylenecarbazole-3 : 6-dicarboxylic acid (indolo[3,2,1-*jk*]carbazole-6 : 9-dicarboxylic acid) by means of alkaloids failed owing to the instability of the salts in solution.[1] Similar results have now been obtained in attempts to form salts of 1 : 9-phenylenecarbazole-6-carboxylic acid (I; R = CO_2H).† The methohydroxides of alkaloids [2] similarly gave negative results. The methyl ester (I; R = CO_2Me) of the monocarboxylic acid and 6-methyl-1 : 9-phenylenecarbazole (I; R = Me) gave complexes with Newman and Lutz's compound, (—)-α-(2 : 4 : 5 : 7-tetranitro-9-fluorenylideneamino-oxy)propionic acid,[3] but no resolution could be effected. Crystallisation of 6-methyl-1 : 9-phenylenecarbazole from ethyl (+)-tartrate [4] also failed to disclose optical activity.

The 6-derivatives (I; R = Me, CO_2H, CO_2Me) have been prepared before,[1] † but in such poor yield that further work with them was impracticable. Improved methods starting from carbazole [1] and from 1-nitrocarbazole [5] are described in the Experimental section.



(I)



(II)

6-Bromo-1 : 9-phenylenecarbazole (I; R = Br) has been synthesised from carbazole, 2 : 5-dibromonitrobenzene, potassium carbonate, and copper bronze at 244°. When, however, one or more mols. of carbazole per mol. of 2 : 5-dibromonitrobenzene were used, a bromine-free by-product was obtained. It is suggested that this compound may be 2 : 4-dicarbazolyl-1-nitrobenzene (II), produced by nucleophilic attack by the 9-carbazolyl anion on the carbon atom *para* to the nitro-group in the initially formed 9-(4-bromo-2-nitrophenyl)carbazole, concomitant displacement of bromine by hydride ion taking

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* Part II, *J.*, 1943, 659.

† Previously [1] these compounds had been ambiguously named as 4′-derivatives.

[1] Dunlop and Tucker, *J.*, 1939, 1945.

[2] Major and Finkelstein, *J. Amer. Chem. Soc.*, 1941, **63**, 1368.

[3] Newman and Lutz, *ibid.*, 1956, **78**, 2469.

[4] Buchanan and Graham, *J.*, 1950, 500.

[5] Cf. Preston and Tucker, *J.*, 1943, 659.

place. This is analogous to the action of nitrobenzene on carbazole in the presence of caustic alkali.[6] The novel suggestion that such replacements may involve a benzyne intermediate [7] might apply here, but the directive influence of the nitro-group should then favour formation of the 1 : 4-dicarbazolyl-2-nitrobenzene. This compound (II) was also prepared (78% yield) by reaction of 9-(4-bromo-2-nitrophenyl)carbazole (assumed to be the intermediate above) and carbazole. Attempts to prepare it by heating carbazole and 9-*o*-nitrophenylcarbazole with potassium carbonate and a trace of copper at 244° for 5 hours or potassium hydroxide and a trace of copper at 155° for 1 hr. failed.

The ultraviolet absorption spectra are summarised in the Table. The complete curves of the 9-substituted carbazoles closely resemble one another; similarly, those graphs of the 6-substituted 1 : 9-phenylenecarbazoles are practically superposable. But, as would be expected, the two series exhibit marked differences, providing a decisive criterion of ring closure.

Ultraviolet absorption spectra (λ *in* mμ) *of ethanol solutions.*

1 : 9-*Phenylenecarbazoles.*								
Unsubst.	$\lambda_{max.}$	237	267	283	291	307	319	361
	log ε	4·78	4·53	4·56	3·96	3·84	3·91	3·95
6-Methyl	$\lambda_{max.}$	235	270	284	296	310	322	366
	log ε	4·78	4·58	4·46	3·95	3·89	3·92	3·82
6-Bromo	$\lambda_{max.}$	234[b]	273	285	297	309	322	368
	log ε	4·72	4·65	4·49	4·09	3·89	3·96	3·94
6-Methoxycarbonyl[a]	$\lambda_{max.}$	—	—	285	—	—	—	361
	log ε	—	—	3·71	—	—	—	3·25
6-Ethoxycarbonyl[a]	$\lambda_{max.}$	—	—	285	—	—	—	361
	log ε	—	—	3·68	—	—	—	3·26
Carbazoles.								
Unsubst.[c,d]	$\lambda_{max.}$	234	245	257	293	324	337	
	log ε	4·58	4·36	4·27	4·18	3·51	3·47	
9-Phenyl	$\lambda_{max.}$	239	—	—	292[e]	326	340	
	log ε	4·71	—	—	4·29	3·57	3·63	
9-$C_6H_4{\cdot}CO_2Et$-*p*	$\lambda_{max.}$	—	—	—	293	327	339	
	log ε	—	—	—	3·23	3·19	3·16	

[a] In $CHCl_3$ (measured by Mr. G. Ferguson). [b] Also an exceptional max. at 240 mμ (log 4·73). [c] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, New York, 1951, No. 293. [d] The 9-methyl, 9-*iso*propyl, 9-*p*-chlorophenyl, 3-chloro-, 3-bromo-, 3-bromo-9-methyl, 3-bromo-9-ethyl, and 3-iodo-9-methyl analogues had almost the same $\lambda_{max.}$ as the 9-phenyl compound and very similar ε. [e] Also an exceptional max. at 287 mμ (log ε 4·20).

Unsuccessful attempts have been made to condense carbazole with 2-chloro-1 : 3-benzene.[8]

This line of research has now been abandoned.

EXPERIMENTAL

Attempted Optical Resolutions.—1 : 9-Phenylenecarbazole-4′-carboxylic acid failed to form isolatable salts with (−)-brucine, (−)-quinine, (+)-cinchonine, or (+)-1-phenylethylamine in acetone. The acid appeared to form a salt with (−)-quinine methohydroxide,[2] since it dissolved readily in a warm aqueous-alcoholic solution of one equivalent of the base, but, on cooling, an uncrystallisable oil, presumably the salt, separated. Evaporation of the solution to dryness resulted in dissociation. Addition of dioxan or benzene to a solution of the salt in ethanol gave the acid, fractional precipitation yielding samples with zero rotation in pyridine. Similar results were obtained with the methohydroxides of (+)-cinchonine and (+)-quinidine.[2]

4′-Methyl-1 : 9-phenylenecarbazole and methyl 1 : 9-phenylenecarbazole-4′-carboxylate gave molecular complexes with (−)-α-(2 : 4 : 5 : 7-tetranitro-9-fluorenylideneamino-oxy)-propionic acid in acetic acid, but substances recovered from the complexes and from the acetic acid mother-liquors showed no rotation in chloroform.

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[6] G. and M. de Montmollin, *Helv. Chim. Acta*, 1923, **6**, 94; cf. Nelmes and Tucker, *J.*, 1933, 1523.

[7] Roberts, Simmons, Carlsmith, and Vaughan, *J. Amer. Chem. Soc.*, 1953, **75**, 3290; *Ann. Reports*, 1956, **53**, 192.

[8] Gunstone and Tucker, *J. Appl. Chem.*, 1952, **2**, 204.

4′-Methyl-1 : 9-phenylenecarbazole crystallised from ethyl (+)-tartrate in an inactive condition.

1-*Nitrocarbazole*.—To carbazole (8·35 g.) in acetic anhydride (50 ml.), a mixture of concentrated nitric acid (3·5 ml.) and acetic anhydride (5 ml.), cooled to 0°, was added, the temperature being kept at 10—15°. The mixture was heated to 80°, and there maintained for 10 min., then concentrated to half its bulk. A drop of concentrated sulphuric acid in acetic anhydride (1 ml.) was added, and the mixture boiled, with vigorous shaking, until solid separated. It was allowed to cool and crystallise. 9-Acetyl-3-nitrocarbazole was removed and washed with acetic acid or acetone, in which it is practically insoluble: crystallised from nitromethane, it had m. p. 237—238°. The filtrate was poured into hot water (300 ml.), the cold mixture was filtered, the solid dried and dissolved in benzene, and the solution distilled until all water had passed over, then chromatographed on alumina (10 × 2·5 cm.) previously heated to 300° for 3 hr.; the first eluate gave 1-nitrocarbazole (1·12 g., 9%), m. p. 187°. This method has no advantage over others.[9]

Synthesis of 6-*Methyl*-1 : 9-*phenylenecarbazole* (I; R = Me).—*Route A, from carbazole* (with N. C. KIRK). Carbazole (8·35 g.), 4-bromo-3-nitrotoluene (27 g., 150 % excess), potassium carbonate (8·4 g.), and copper bronze (0·15 g.) were heated at 244° (diethylene glycol vapour)[10] for 80 min., the melt was extracted with boiling benzene, the solution steam-distilled to remove benzene and excess of bromonitrotoluene, and the remaining tar extracted with ethanol; crystals grew therefrom very slowly. Recrystallisation from acetic acid gave orange prisms (*ca.* 60%), m. p. 93—94° (lit., 104—106°) of 9-(4-methyl-2-nitrophenyl)carbazole (Found: C, 75·6; H, 4·4; N, 9·1. Calc. for $C_{19}H_{14}O_2N_2$: C, 75·5; H, 4·7; N, 9·3%).

This nitro-compound (2·2 g.) was reduced by hydrogen and Raney nickel in ethanol (*ca.* 2 hr.) to give cream prisms (from ethanol), m. p. 116—118° (1·83 g., 90%), of the amine (Found: C, 83·8; H, 6·0. Calc. for $C_{19}H_{16}N_2$: C, 83·8; H, 5·9%). Final darker crops were best obtained by slow evaporation.

The amine (2·72 g.) dissolved in a hot mixture of acetic acid (10 ml.), concentrated sulphuric acid (12 ml.), and water (50 ml.). The solution after being quickly cooled, with shaking, to *ca.* 20° was treated, all at once, with sodium nitrite (0·76 g., 10% excess) in water (10 ml.). The deep red solution was diluted with water (80 ml.) and treated with sulphamic acid, copper bronze added, and the whole cautiously heated until effervescence was vigorous: it was then heated on a boiling-water bath, with occasional swirling, until the liquid portion was colourless (45 min.). After cooling, the salmon-coloured solid was removed, washed, and boiled with benzene, the solution filtered from copper, water removed by distillation in benzene, and the residual oil chromatographed in ligroin (b. p. 60—80°) on alumina (10 × 2 cm.). The colourless eluate (violet in ultraviolet light) gave 6-methyl-1 : 9-phenylenecarbazole, m. p. 110—112° (2·14 g., 84%), as needles having a faint violet fluorescence. No phenolic material could be detected in the benzene solution. Use of benzene in place of ligroin for chromatography gave a brown eluate. 6-Methyl-1 : 9-phenylenecarbazole gave a deep scarlet 2 : 4 : 7-*trinitrofluorenone complex* (from acetic acid), softening at 193°, melting at 200° (Found: C, 67·3; H, 3·1; N, 10·0. $C_{19}H_{13}N,C_{13}H_5O_7N_3$ requires C, 67·4; H, 3·2; N, 9·8%).

Route (*B*), *from* 1-*nitrocarbazole*. 1-Nitrocarbazole (0·8 g.), *p*-iodotoluene (6 g.), anhydrous potassium carbonate (0·8 g.), and copper bronze (0·01 g.) were heated under reflux for 6 hr.; the excess of *p*-iodotoluene was removed by distillation (3·5 g. recovered), the residue extracted with boiling acetone, the extract steam-distilled to remove the rest of the *p*-iodotoluene, the residue extracted with benzene, and the dried solution chromatographed on alumina (5 × 1·5 cm.). The eluate gave a yellow solid which after crystallisation from benzene (charcoal) and then from methyl acetate gave canary-yellow octahedra of 1-*nitro*-9-p-*tolylcarbazole*, m. p. 159—160° (0·74 g., 65%) (Found: C, 75·7; H, 4·6; N, 9·1. $C_{19}H_{14}O_2N_2$ requires C, 75·5; H, 4·7; N, 9·3%). When the reaction mixture was heated for only 3 hr., the yield was reduced to 58%.

The above nitro-compound (3·02 g.) was hydrogenated in benzene (50 ml.) in presence of Raney nickel (2 g.) and ethanol (10 ml.) until 820 ml. of hydrogen had been absorbed (theor., 672 ml.). The *amine* (2·38 g., 87%) was purified with difficulty, but by crystallisation from light petroleum (b. p. 80—100°), then from methanol and from ethanol; it was obtained in pale green needles, m. p. 131—132° (Found: C, 83·8; H, 6·0; N, 10·3. $C_{19}H_{16}N_2$ requires

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[9] Preston, Tucker, and Cameron, *J.*, 1942, 500.

[10] Tucker, *J. Chem. Educ.*, 1953, **30**, 634.

C, 83·8; H, 5·9; N, 10·3%). The *acetyl derivative*, m. p. 212—213° (formed by acetic anhydride in benzene), crystallised in pale brown stout prisms from acetic acid (Found: C, 80·0; H, 5·9; N, 8·7. $C_{21}H_{18}ON_2$ requires C, 80·2; H, 5·8; N, 8·9%).

Cyclisation of the above amine was accomplished in *ca.* 41% yield, as for the analogous cyclisation from 9-(2-amino-4-methylphenyl)carbazole to give, as before, 6-methyl-1 : 9-phenylenecarbazole, m. p. and mixed m. p. 110—112°.

Synthesis of 1 : 9-*Phenylenecarbazole*-6-*carboxylic Acid from* 1-*Nitrocarbazole*.—*Methyl* 1-*nitro*-9-*phenylcarbazole*-4′-*carboxylate* (with E. Thomson, B.Sc.). A mixture of 1-nitrocarbazole (2·12 g., 0·01 mole), methyl *p*-iodobenzoate (7·8 g., excess), anhydrous potassium carbonate (0·7 g.), and copper bronze (0·04 g.) were heated in the vapour of boiling methyl salicylate [10] (b. p. 223°) with continuous stirring with a spiral copper wire. After 2 hr. another addition of potassium carbonate (0·7 g.) and copper (0·04 g.) was made, and heating continued for 4 hr. The melt was extracted with hot water, the filtrate rendered acid with hydrochloric acid, and the precipitated *p*-iodobenzoic acid (1·14 g.; m. p. 264°) removed. A benzene extract of the original melt, on steam-distillation, gave benzene and methyl *p*-iodobenzoate (3·5 g.). The undistilled red residue was filtered, dried, dissolved in benzene, and chromatographed on alumina (20 × 1·5 cm.). On elution with benzene, a canary-yellow band developed: the first 300 ml. of eluate, after evaporation to dryness and crystallisation of the residue from ethanol, gave the main bulk (2·00 g.), but continued elution (750 ml.) gave more (0·46 g.) *methyl* 1-*nitro*-9-*phenylcarbazole*-4′-*carboxylate*, m. p. 170—171° (total, 2·46 g., 78%) (Found: C, 69·3; H, 4·3; N, 8·2. $C_{20}H_{14}O_4N_2$ requires C, 69·35; H, 4·1; N, 8·1%). When heating was for only 3 hr., unchanged 1-nitrocarbazole was recovered. It appeared as a deep red-brown band on the chromatogram and was eluted after methyl 1-nitro-9-phenylcarbazole-4′-carboxylate. Crystallisation of the crude 1-nitrocarbazole from benzene separated it from the much more soluble carboxylate. The reverse is true when ethanol is used. Methyl 1-nitro-9-phenylcarbazole-4′-carboxylate normally crystallises in stout pale yellow prisms, but these soon became superficially golden-yellow: long pale green needles often separated from cold solutions. The m. p. of the two forms, and of a mixture, was 170—171°. The needles slowly changed to the yellow prisms. The forms appear to be polymorphs.

Methyl 1-*amino*-9-*phenylcarbazole*-4′-*carboxylate*. The nitro-ester (2·08 g.) dissolved in benzene (20 ml., which had been stored over Raney nickel) was reduced by hydrogen in presence of Raney nickel (2 g. in 10 ml. of ethanolic suspension) in 2 hr. Hydrogen (462 ml.) was absorbed, in excess of that required by theory (402 ml.). The mixture was boiled and filtered, and the nickel extracted with boiling ethanol. The combined liquors were evaporated to small bulk, to give pale green needles (later crops, pale brown plates) of pure *methyl* 1-*amino*-9-*phenylcarbazole*-4′-*carboxylate*, m. p. 173—174° (1·81 g., 95%). Crystallisation from methanol gave a mixture of faintly yellow needles and stout yellow-ochre prisms. Both, and a mixture, had m. p. 173—174° (Found: C, 76·2; H, 5·0; N, 8·9. $C_{20}H_{16}O_2N_2$ requires C, 75·9; H, 5·1; N, 8·9%). The amine, when boiled with acetic anhydride in benzene, gave the *acetyl derivative* as thin rods (from ethanol), m. p. 202—204° (Found: C, 73·65; H, 5·1; N, 8·0. $C_{22}H_{18}O_3N_2$ requires C, 73·7; H, 5·1; N, 7·8%).

In one hydrogenation of methyl 1-nitro-9-phenylcarbazole-4′-carboxylate, with Raney nickel and ethanol but no benzene, absorption of hydrogen was less than the theoretical: yellow-ochre short prisms, m. p. 140—141°, were isolated from ethanol, consisting probably of *methyl* 1-*hydroxyamino*-9-*phenylcarbazole*-4′-*carboxylate* (Found: C, 72·1; H, 4·7; N, 8·9. $C_{20}H_{16}O_3N_2$ requires C, 72·3; H, 4·8; N, 8·4%).

Methyl 1 : 9-*Phenylenecarbazole*-6-*carboxylate* (I; R = CO_2Me). The amino-9-phenylcarbazole-4′-carboxylate (0·316 g.) in a mixture of concentrated sulphuric acid (2 ml.) and water (8 ml.) was diazotised by rapid addition of sodium nitrite (1·05 g., 50% excess) in water (15 ml.) without cooling. The deep red solution was diluted with water (15 ml.) (apparently necessary for completion of diazotisation), sulphamic acid was added to destroy excess of nitrite, then copper bronze, and the mixture boiled gently for 30 min. The hot suspension of red and yellow flocculent precipitates was extracted with benzene, copper was removed, and the benzene extract was shaken with 10% aqueous potassium hydroxide. The alkaline solution contained chiefly phenolic by-products: in only a few experiments could carboxylic acid be separated. The benzene extract was distilled until all the water had been carried over, and the concentrate was then chromatographed on alumina (8 × 1·5 cm.) and eluted with benzene. Various colours (in ultraviolet light) developed, but were due to impurities. After the first runnings (*ca.* 50 ml.) had been discarded, most of the *ester* was obtained in the next 250 ml. of eluate. Crystallisation from light petroleum (b. p. 80—100°) gave needles, m. p. 163—164° (0·10 g., 33%) (Found: C, 80·2; H, 4·1; N, 4·9. $C_{20}H_{13}O_2N$ requires C, 80·2; H, 4·4; N, 4·7%).

1 : 9-Phenylenecarbazole-6-carboxylic acid (I; R = CO_2H) was prepared by boiling this ester (1·05 g.) with 10% aqueous potassium hydroxide (25 ml.) and ethanol (30 ml.) for 1 hr. The clear liquor, poured into hot water (1 l.) (the potassium salt of the carboxylic acid is only slightly soluble), gave a nearly clear solution which with excess of concentrated hydrochloric acid gave a voluminous precipitate (*ca.* 100%). This acid crystallised from anisole in needles, softening at 335°, melting at 342° (Found: C, 79·8; H, 3·9; N, 4·9. Calc. for $C_{19}H_{11}O_2N$: C, 80·0; H, 3·9; N, 4·9%). The 2 : 4 : 7-*trinitrofluorenone complex*, orange crystals from acetic acid, softened at 280° and melted much higher: it dissociated on attempted crystallisation (Found: C, 63·7; H, 2·6; N, 9·2. $C_{19}H_{11}O_2N,C_{13}H_5O_7N_3$ requires C, 64·0; H, 2·7; N, 9·3%). Esterification with ethanolic hydrogen chloride gave the *ethyl ester* (I; R = CO_2Et), needles [from 1 : 1-benzene–light petroleum (b. p. 80—100°)], m. p. 173—174° (Found: C, 80·5; H, 4·9; N, 4·5. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8; N, 4·5%).

Oxidation of 6-*Methyl*-1 : 9-*phenylenecarbazole to* 1 : 9-*Phenylenecarbazole*-6-*carboxylic Acid*.—6-Methyl-1 : 9-phenylenecarbazole (0·43 g.) and potassium hydroxide (0·05 g.) in water (2 ml.) and pyridine (10 ml.) were treated at the b. p. with potassium permanganate (*ca.* 0·75 g.) in portions during 3 hr. Excess of dilute sulphuric acid containing sulphurous acid was added, and the white precipitate was filtered off, washed, dried, and extracted with ligroin (b. p. 60—80°) to remove unchanged methyl compound (0·05 g.). The residue was pure 1 : 9-phenylenecarbazole-6-carboxylic acid (0·41 g., 84%). A nearly theoretical yield was obtained by using relatively more (50%) of solvents and reagents, and heating for 7·5 hr. 6-Methyl-1 : 9-phenylenecarbazole was unaffected when boiled in acetone with potassium permanganate.

The acid was decarboxylated by copper bronze.[1] The benzene extract of the melt was chromatographed on alumina, and the product, isolated in the usual way, crystallised from methanol–acetone (2 : 1 v/v). The 1 : 9-phenylenecarbazole had m. p. and mixed m. p. 135—137°.

Synthesis of 6-*Bromo*-1 : 9-*phenylenecarbazole* (I; R = Br) (with J. M. COUPER, B.Sc.).—Carbazole (11·7 g., 0·07 mole), 2 : 5-dibromonitrobenzene (39·3 g., 0·14 mole), anhydrous potassium carbonate (20 g., 0·14 mole), and copper bronze (0·1 g.) were stirred together at 244° for 1 hr.[10] The product was extracted with boiling acetone, the concentrated solution poured into dilute hydrochloric acid, and the precipitated red oil washed with water, and crystallised by dissolving in a small amount of acetone and adding boiling methanol, as orange prisms of 9-(4-*bromo*-2-*nitrophenyl*)*carbazole* (12·8 g., 50%), m. p. 152—154° (Found: C, 59·0; H, 3·2; N, 7·8. $C_{18}H_{11}O_2N_2Br$ requires C, 58·9; H, 3·0; N, 7·6%). The yield was from 39% after 0·25 hour's heating to 54% after 6 hours.

When copper was omitted, a charred mass was obtained under various conditions.

The isolation of a compound, m. p. 220°, is described below.

The foregoing nitro-compound (2 g.) in boiling glacial acetic acid (100 ml.) was treated with activated zinc (6 g., activated with dilute hydrochloric acid). Colour was discharged in 10 min., but refluxing was continued for 1 hr. The liquid decanted from unused zinc, was poured into water, giving a white precipitate containing zinc; this was dissolved in acetic acid and poured into excess of diluted hydrochloric acid (1 part of concentrated acid and 10 parts by vol. of water). The precipitate, washed with water and dried, was pale brown and had m. p. 93—95° (1·3 g., 65%). Recrystallisation was extremely difficult, usually only oils being obtained. Ethanol, or ethanol containing a trace of water, gave the *amine* as rosettes of prisms, softening at 95°, melting at 100° (Found: C, 64·1; H, 3·9; N, 8·25. $C_{18}H_{13}N_2Br$ requires C, 64·1; H, 3·9; N, 8·3%).

Reduction with hydrogen in presence of Raney nickel in ethanol gave the amine but, again, the product could not be readily crystallised; there was evidence that it contained a bromine-free substance, possibly 9-*o*-aminophenylcarbazole (see below). Reduction in methanol gave a solid amine which could not be recrystallised. This product gave a 2 : 4 : 7-*trinitrofluorenone complex* as deep red prisms, m. p. 198—215°, but attempts to crystallise it from glacial acetic acid gave the trinitrofluorenone. The amine gave a *picrate*, softening at 80°, m. p. 99°, as orange prisms from methanol (Found: C, 45·4; H, 2·6; N, 14·25. $C_{18}H_{13}N_2Br,2C_6H_3O_7N_3$ requires C, 45·3; H, 2·4; N, 14·1%). Since the substance evidently dissociates the m. p. is unreliable. During crystallisation yellow and orange crystals separated. The amine with acetic anhydride and benzene gave the *acetyl derivative* as leaflets (from ethanol), m. p. 217—219° (Found: C, 63·2; H, 4·1. $C_{20}H_{15}ON_2Br$ requires C, 63·3; H, 4·0%). This was obtained also by reduction of the nitro-compound by zinc, acetic acid, and acetic anhydride. Reduction of the nitro-compound by zinc, ammonium chloride, and ethanol gave no useful result.

The oily amine (0·9 g.) obtained by hydrogen and Raney nickel in ethanol was treated in glacial acetic acid (10 ml.), concentrated sulphuric acid (5 ml.), and water (10 ml.) with sodium nitrite (2 g.) in water (2—3 ml.), without external cooling. The deep scarlet solution was diluted with water (10 ml.), sulphamic acid and then copper bronze were added, and the solution was slowly heated to the b. p. and kept thereat for 10 min. The black pasty mass obtained was dissolved in benzene, water removed by distilling off most of the benzene, and the dry solution chromatographed on alumina. After removal of a pale blue (ultraviolet light) band, elution (*ca.* 250 ml.) of a continuous purple zone gave, in the usual way, leaflets (from ethyl acetate containing a drop of ethanol) of 6-*bromo*-1 : 9-*phenylenecarbazole* (0·07 g.), m. p. 144—145° (Found: C, 67·7; H, 3·3; N, 4·3. $C_{18}H_{10}NBr$ requires C, 67·5; H, 3·15; N, 4·4%). It gave a scarlet 2 : 4 : 7-*trinitrofluorenone complex* (from acetic acid), m. p. 181—182° (Found: C, 58·45; H, 2·5; N, 8·7. $C_{18}H_{10}NBr,C_{13}H_5O_7N_3$ requires C, 58·6; H, 2·4; N, 8·8%). It also gave a 1 : 3 : 5-*trinitrobenzene complex* (from acetic acid), golden-yellow needles, m. p. 156—158° (Found: C, 54·3; H, 2·6. $C_{18}H_{10}NBr,C_6H_3O_6N_3$ requires C, 54·1; H, 2·45%). Filtrates after isolation of 6-bromo-1 : 9-phenylenecarbazole, when treated with picric acid, gave a small amount of a red picrate, softening at 140°, m. p. 165°, which contained no bromine, and appeared to be the picrate (m. p. 165—169°) of 1 : 9-phenylenecarbazole (Found: C, 61·0; H, 3·1; N, 12·0. Calc. for $C_{18}H_{11}N,C_6H_3O_7N_3$: C, 61·3; H, 3·0; N, 11·9%). The 1 : 9-phenylenecarbazole is probably derived from 9-*o*-aminophenylcarbazole produced during the preceding reduction. For comparison, the 2 : 4 : 7-*trinitrofluorenone complex* of 1 : 9-phenylenecarbazole was prepared in acetic acid forming scarlet needles, m. p. 198—199° (Found: C, 66·9; H, 2·8; N, 10·0. $C_{18}H_{11}N,C_{13}H_5O_7N_3$ requires C, 66·9; H, 2·9; N, 10·1%).

2 : 4-*Dicarbazolyl*-1-*nitrobenzene* (II).—When in the preparation of 9-(4-bromo-2-nitrophenyl)-carbazole, 1 mol. or more of carbazole to 2 : 5-dibromonitrobenzene was used at 244° during 6 hr., there were obtained at first (before removal of the dibromonitro-compound) from the acetone extract, scarlet plates, m. p. 220°. These were better prepared by the action of carbazole on 9-(4-bromo-2-nitrophenyl)carbazole: carbazole (1·0 g.), 9-(4-bromo-2-nitrophenyl)-carbazole (0·9 g.), anhydrous potassium carbonate (0·5 g.), and copper bronze (0·2 g.) were heated at 244° for 5 hr. The boiling acetone extract gave practically pure, scarlet diamond-shaped plates of 2 : 4-*dicarbazyl*-1-*nitrobenzene*, which, after chromatography in benzene on alumina and crystallisation from benzene, had m. p. 220° (0·87 g., 78%) (Found: C, 79·4; H, 4·0; N, 9·1. $C_{30}H_{19}O_2N_3$ requires C, 79·45; H, 4·2; N, 9·3%). When, in the above experiment, the amount of copper was doubled, the yield was reduced to 29%: it is difficult to understand why copper should thus influence the reaction.

9-p-*Bromophenylcarbazole*.—Carbazole (1·12 g.), *p*-bromoiodobenzene (2·83 g.), anhydrous potassium carbonate (1·5 g.), and copper bronze (0·01 g.) were heated at 244° for 6 hr. The acetone extract, poured into dilute hydrochloric acid, gave a brown solid which crystallised from benzene–ligroin (b. p. 60—80°) in thick rectangular plates, then from methyl cyanide in pale brown prisms, m. p. 146—147° (Found: C, 67·0; H, 3·9; N, 4·15. $C_{18}H_{12}NBr$ requires C, 67·1; H, 3·8; N, 4·35%). A mixture with 6-bromo-1 : 9-phenylenecarbazole had a greatly lowered m. p.

9-p-*Bromophenylcarbazole* gave a 2 : 4 : 7-*trinitrofluorenone complex* (from acetic acid) in plates which were scarlet by transmitted, but purple-black by reflected, light, m. p. 168—170° (Found: C, 58·2; H, 2·9; N, 8·8. $C_{18}H_{12}NBr,C_{13}H_5O_7N_3$ requires C, 58·4; H, 2·7; N, 8·8%).

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