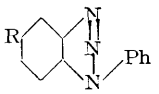
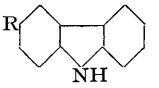
90. *The Graebe–Ullmann Synthesis of Carbazole Derivatives. Preparation and Synthesis of* 1-*Nitrocarbazole.*

By Robert W. G. Preston, S. Horwood Tucker, and (in part) James M. L. Cameron.

Carbazole derivatives containing unsaturated substituents, *e.g.*, nitro, acetyl, cyano, have, contrary to former experience, been obtained by pyrogenesis from the corresponding triazoles. In particular, 1-nitrocarbazole has been thus synthesised. Its preparation by nitration of carbazole, and separation from the 3-isomer by chromatographic analysis, are described. 1-Nitrocarbazole has also been synthesised from 3 : 6-bistrichloroacetylcarbazole—a process in which it is prepared free from 3-nitrocarbazole.

In the Graebe–Ullmann synthesis of carbazole (*Annalen*, 1896, **291**, 16) the last step is completed by heating 1-phenyl-1 : 2 : 3-benztriazole (I; R = H). The preparation of carbazole derivatives by this method proceeds

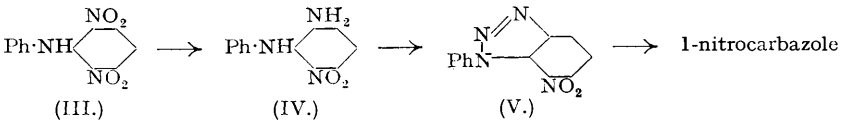
smoothly when the substituent is a saturated group, *e.g.*, amino or alkyl, but when an unsaturated group such as nitro, acetyl, or cyano is present in either benzene ring of the triazole, conversion into the corresponding

(I.)   (II.)

carbazole has not hitherto been accomplished (see *Arch. Sci. phys. nat.*, 1904, **17**, 88; *Annalen*, 1911, **379**, 168; *Ber.*, 1916, **49**, 2231, 2237; *Helv. Chim. Acta*, 1921, **4**, 1036; J., 1932, 2188; 1935, 741. On the other hand cf. *Annalen*, 1904, **332**, 82; *Arch. Sci. phys. nat.*, 1904, **17**, 78; *J. Amer. Chem. Soc.*, 1931, **53**, 4183; J., 1932, 2188).

We have been successful in bringing about the triazole ⟶ carbazole (I ⟶ II) reactions, where R = NO_2, COMe, CN, giving yields of a trace, 22% and 34% respectively. The synthesis of 3-acetylcarbazole by this unambiguous method confirms the work of Plant and Williams (J., 1934, 1142), who prepared 3-acetylcarbazole and settled its constitution by other methods.

The conversion of 7-nitro-1-phenyl-1 : 2 : 3-benztriazole into 1-nitrocarbazole (18%) by the Graebe–Ullmann method was effected as outlined below :

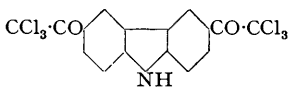
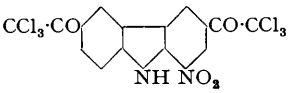


(III.) (IV.) (V.)

2 : 6-Dinitrodiphenylamine (III) was prepared by the action of 1-chloro-2 : 6-dinitrobenzene on aniline, and also by decarboxylation of 2 : 6-dinitrodiphenylamine-4-carboxylic acid. A deep red by-product, which is possibly 1-*nitrophenazine*, was isolated in the latter case.

The nitration of carbazole gives a mixture of 1-nitrocarbazole (4%) and 3-nitrocarbazole (75%) (Lindemann and Werther, *Ber.*, 1924, **57**, 555, 1316; Lindemann and Wessel, *ibid.*, 1925, **58**, 1221), the separation of which by Morgan and Mitchell's method (J., 1931, 3283) gave capricious results in our hands, but was easily accomplished by chromatographic analysis with benzene as solvent and elution reagent : 1-nitrocarbazole (6%) was eluted first and 3-nitrocarbazole (70%) followed very slowly. Three methods of nitration were adopted : (*a*) Ziersch's method (*Ber.*, 1909, **42**, 3797), (*b*) fuming nitric acid in acetic anhydride, (*c*) potassium nitrate in glacial acetic acid–acetic anhydride.

The following synthetic method provides 1-nitrocarbazole free from 3-nitrocarbazole : Carbazole was converted by the action of trichloroacetonitrile, anhydrous aluminium chloride, and hydrogen chloride in chlorobenzene, followed by acid hydrolysis, into 3 : 6-bistrichloroacetylcarbazole (VI) (Dunlop and Tucker, J., 1939, 1954; and this paper). Nitration by concentrated nitric acid in glacial acetic acid gave the 1-*nitro*-derivative (VII), which by alkaline hydrolysis afforded 1-*nitrocarbazole*-3 : 6-*dicarboxylic acid*. Decarboxylation in quinoline–copper gave 1-nitrocarbazole.

(VI.)   (VII.)

1-Nitrocarbazole was also prepared by the conversion of 3 : 6-bistrichloroacetylcarbazole (VI) into ethyl carbazole-3 : 6-dicarboxylate by treatment with sodium in ethyl alcohol (Houben and Fischer, *Ber.*, 1931, **64**, 240, 2636), this method, contrary to Houben and Fischer's general finding, being preferable to the use of potassium acetate in alcohol. The ester on nitration gave *ethyl* 1-*nitrocarbazole*-3 : 6-*dicarboxylate*, which on hydrolysis and decarboxylation gave 1-nitrocarbazole.

3-*Cyano*- and 3 : 6-*dicyano-carbazole* have been prepared from carbazole by the Houben–Fischer method (*Ber.*, 1930, **63**, 2464; 1933, **66**, 339. See Dunlop and Tucker, *loc. cit.*, p. 1949).

Experimental.

Graebe–Ullmann Syntheses.

3-*Nitrocarbazole*.—2 : 4-Dinitrodiphenylamine, m. p. 153°, was prepared by heating 1-chloro-2 : 4-dinitrobenzene (20 g.; 1 mol.) with aniline (10 g.; 1·1 mols.) until the vigorous reaction which set in had subsided, then raising the temperature to the b. p. The product, after crystallisation from glacial acetic acid (yield, 100%) (cf. Reissert and Goll, *Ber.*, 1905, **38**, 93), was reduced to 4-nitro-2-aminodiphenylamine (Ullmann, *Annalen*, 1904, **332**, 98). Diazotisation to give 5-nitro-1-phenyl-1 : 2 : 3-benztriazole was accomplished by means of excess of sodium nitrite in excess of hot glacial acetic acid—the method adopted for all triazoles subsequently described (cf. Nietzki, *Ber.*, 1895, **28**, 2971). The triazole, in portions, was carefully heated over a free flame. The product, dissolved in glycol methyl ether, gave unchanged triazole and, on standing and scratching, a trace of 3-nitrocarbazole, m. p. 213°.

3-*Acetylcarbazole*.—4-Bromo-3-nitroacetophenone (Borsche *et al.*, *Ber.*, 1916, **49**, 2235) was prepared by dissolving *p*-bromoacetophenone (20 g.) in fuming nitric acid (*d* 1·52; 150 ml.) at 0° (yield, 19 g.; 78%). When nitric acid, *d* 1·50, was used, *p*-bromoacetophenone was recovered unchanged, unless the temperature was allowed to rise during nitration; a substance, m. p. 175—176°, was then obtained which was probably 4-*bromo*-3 : 5-*dinitroacetophenone* (Found : N, 9·8. $C_8H_5O_5N_2Br$ requires N, 9·7%).

4-Bromo-3-nitroacetophenone (6 g.), aniline (20 g.), and anhydrous potassium carbonate (2 g.) were heated together

(15 minutes), the product treated with dilute hydrochloric acid, and the residue crystallised from alcohol, giving 2-nitro-4-acetyldiphenylamine (5 g.; yield, 89%).

2-Amino-4-acetyldiphenylamine was prepared by reduction of the above nitro-compound by stannous chloride, glacial acetic acid, and hydrochloric acid (yield, 68%). Diazotisation gave 5-acetyl-1-phenyl-1 : 2 : 3-benztriazole (yield, 62%). The triazole (1 g.) was heated over a free flame until a slight explosion ensued. The solid, extracted with alcohol (charcoal), crystallised from toluene in straw-coloured laminæ, m. p. 165—167°, of 3-acetylcarbazole (0·2 g.; yield, 22%) (Found: N, 6·5. Calc.: N, 6·7%).

3-*Cyanocarbazole*.—2-Nitro-4-cyanodiphenylamine (Schöpff, *Ber.*, 1890, **23**, 3442; Borsche *et al.*, *loc. cit.*) was prepared by heating equimolecular quantities of aniline and 4-chloro-3-nitrobenzonitrile (Dunlop, Macrae, and Tucker, J., 1934, 1676) to the b. p. (yield, 78%). Reduction (stannous chloride, glacial acetic acid, hydrochloric acid) gave 2-amino-4-cyanodiphenylamine (yield, 78%), diazotisation of which gave 5-cyano-1-phenyl-1 : 2 : 3-benztriazole (yield, 65%). The triazole (1 g.) was heated (metal bath) until evolution of nitrogen ceased. Extraction with ethanol (charcoal) and crystallisation from toluene gave 3-*cyanocarbazole* in colourless needles, m. p. 184—185° (0·3 g.; yield, 35%) (Found: C, 81·2; H, 4·0; N, 14·5. $C_{13}H_8N_2$ requires C, 81·25; H, 4·2; N, 14·6%).

3-Cyanocarbazole was also prepared by the Houben–Fischer method (*Ber.*, 1930, **63**, 1933): carbazole was treated with trichloroacetonitrile as for the preparation of carbazole-3-carboxylic acid (Dunlop and Tucker, *loc. cit.*, p. 1953; this paper, later), but the reaction mixture was not treated with acid; instead, more chlorobenzene was added, and dry ammonia passed to precipitate aluminium. The liquid was filtered, and the residue extracted with hot chlorobenzene and finally with ether. The united filtrates were shaken with potassium hydroxide (dry powder). The brown precipitate, mixed with the excess of potassium hydroxide, when treated with water and then with dilute hydrochloric acid, gave 3-cyanocarbazole. A small amount was obtained from the chlorobenzene–ether solution.

Similarly, by using the quantities given for the preparation of carbazole-3 : 6-dicarboxylic acid by the improved method described on p. 503, 3 : 6-*dicyanocarbazole* was obtained in colourless microcrystals from nitrobenzene (followed by sublimation), unmelted at 360° (Found: C, 77·4; H, 3·3; N, 19·3. $C_{14}H_7N_3$ requires C, 77·4; H, 3·2; N, 19·35%).

3-*Cyano*-9-*acetylcarbazole*, obtained by heating 3-cyanocarbazole with acetic anhydride in presence of a trace of concentrated sulphuric acid, crystallised from glacial acetic acid in silky needles, m. p. 197—199° (Found: C, 76·7; H, 3·9; N, 11·7. $C_{15}H_{10}ON_2$ requires C, 76·9; H, 4·3; N, 12·0%).

1-*Nitrocarbazole* (*Graebe–Ullmann Synthesis*).—1-Chloro-2 : 6-dinitrobenzene (13·8 g.) and excess of aniline (13 g.) were heated on the boiling water-bath with shaking until (about 1 min.) the mixture became solid; the temperature was then raised just to the b. p. The product was extracted by grinding with hot dilute hydrochloric acid, and the residue crystallised from glacial acetic acid, giving 2 : 6-dinitrodiphenylamine, m. p. 107—108° (16 g.; yield, 94%) (cf. Borsche and Rantscheff, *Annalen*, 1911, **379**, 167).

A mixture of 2 : 6-dinitrodiphenylamine (5 g.), ethanol (25 ml.), and concentrated aqueous ammonia (7·5 ml.) was warmed, and hydrogen sulphide passed in until the scarlet crystals dissolved (30 mins.). The solution was boiled, filtered from sulphur, and excess of dilute hydrochloric acid added. The black precipitate, after crystallisation from alcohol, gave black-red crystals of 6-nitro-2-aminodiphenylamine, m. p. 101°, in excellent yield (cf. Borsche and Rantscheff, *loc. cit.*, p. 168).

Diazotisation with excess of sodium nitrite in glacial acetic acid (cf. Borsche and Rantscheff, *loc. cit.*) gave, from acetic acid, 7-nitro-1-phenylbenztriazole, m. p. 152°. This triazole can be sublimed; but gentle boiling of it (2·5 g.) with copper bronze (0·5 g.) over a free flame until nitrogen evolution ceased, followed by extraction with benzene, gave bronze-yellow needles of 1-nitrocarbazole (0·39 g.; yield, 18%).

Attempts were made to prepare 7-nitro-1-phenyl-1 : 2 : 3-benztriazole by the route: 2 : 6-dinitrodiphenylamine-4-carboxylic acid ⟶ 6-nitro-2-aminodiphenylamine-4-carboxylic acid ⟶ 7-nitro-1-phenyl-1 : 2 : 3-benztriazole-5-carboxylic acid; but the last could not be converted into 1-nitrocarbazole.

2 : 6-Dinitrodiphenylamine-4-carboxylic acid (Jackson and Ittner, *Amer. Chem. J.*, 1897, **19**, 18) was prepared from 4-chloro-3 : 5-dinitrobenzoic acid and aniline in boiling ethanol (yield, 96%).

2 : 6-*Dinitrodiphenylamine and* 1-*Nitrophenazine*.—The above carboxylic acid (1 g.) was boiled (15 mins.) with quinoline–copper, the solution poured into dilute hydrochloric acid, and the precipitate extracted successively with dilute aqueous ammonia and benzene (charcoal; 1 hour). The residue obtained on evaporation separated from glacial acetic acid, on dilution with a drop of water, in dark red crystals of what may be 1-*nitrophenazine*, m. p. 192—195° (Found: C, 63·7; H, 3·2; N, 18·5. $C_{12}H_7O_2N_3$ requires C, 64·0; H, 3·1; N, 18·7%). The acetic acid filtrate, on scratching, deposited scarlet crystals of 2 : 6-dinitrodiphenylamine (0·1 g.; yield, 11%).

6-*Nitro*-2-*aminodiphenylamine*-4-*carboxylic Acid* (cf. Lindemann and Wessel, *Ber.*, 1925, **58**, 1229, 1230).—Sodium sulphide ($Na_2S,9H_2O$) (7·5 g.), sulphur (2 g.), and ethanol (1 ml.) were warmed to give a clear brown solution, which was added to a solution of 2 : 6-dinitrodiphenylamine-4-carboxylic acid (9·5 g.) in ethanol (300 ml.) and water (200 ml.) containing sodium hydroxide (1·26 g.). After 3 hours' boiling, the solution was filtered, concentrated to 400 ml., again filtered, and treated with hydrochloric acid until turbid. On cooling there separated scarlet 6-nitro-2-aminodiphenylamine-4-carboxylic acid, which, after crystallisation from ethanol, had m. p. 239° (5·7 g.; yield, 67%) (Found: C, 56·9; H, 4·2; N, 15·5. Calc. for $C_{13}H_{11}O_4N_3$: C, 57·1; H, 4·0; N, 15·4%). In absence of sodium hydroxide and water, used above, the yield was reduced to 37%.

Diazotisation and crystallisation from ethyl acetate gave colourless 7-nitro-1-phenyl-1 : 2 : 3-benztriazole-5-carboxylic acid (yield, 67%) (Found: N, 19·5. Calc. for $C_{13}H_8O_4N_4$: N, 19·7%).

Nitration of Carbazole.—(a) (Ziersch, *Ber.*, 1909, **42**, 3797; cf. Morgan and Mitchell, *loc. cit.*, p. 3284, footnote). Nitric acid (*d* 1·42; 2·3 ml., theo. 1·9 ml.) in glacial acetic acid (5 ml.) was added dropwise in 15 mins. to a shaken mixture of carbazole (5 g.) and glacial acetic acid (40 ml.) maintained at 80°. The solution was poured into water, and the yellow precipitate crystallised several times from xylene, giving 3-nitrocarbazole. The evaporated filtrates gave more of this and finally a residue, which was dissolved in benzene and chromatographed (alumina, 30 × 1·5 cm.). The first portion of the benzene eluate on evaporation gave pure 1-nitrocarbazole, and later a mixture of 1- and 3-nitrocarbazole. The mixture, crystallised from glycol methyl ether–ethanol (1 : 1), gave 1-nitrocarbazole (total, 0·43 g.; yield, 6%) and, on scratching, 3-nitrocarbazole. An upper yellow band in the chromatogram was extracted with acetone and gave more 3-nitrocarbazole (total yield, approx. 70%). A small amount of 3 : 6-dinitrocarbazole was also obtained.

(b) 1-Nitrocarbazole (6%) was obtained by the action of fuming nitric acid in acetic anhydride on carbazole at 10—15°.

Nitration of 9-acetylcarbazole gave no useful results.

1-*Nitro*-9-*acetylcarbazole*.—1-Nitrocarbazole (0·2 g.) and potassium hydroxide powder (0·4 g.) in acetone (5 ml.) were heated on the boiling water-bath, and acetic anhydride added drop by drop until the purple particles changed to yellow. After 1 hour water was added, and the precipitate crystallised from methanol (wood charcoal, ½ hour), forming long, golden-yellow, square-ended prisms of 1-*nitro*-9-*acetylcarbazole*, m. p. 172—174° (yield, 100%) (Found: C, 66·3; H, 3·8; N, 11·3. $C_{14}H_{10}O_3N_2$ requires C, 66·1; H, 3·9; N, 11·0%).

1-Nitrocarbazole could not be acetylated by boiling with acetic anhydride containing a trace of sulphuric acid.

Synthesis of 1-*Nitrocarbazole.*—3 : 6-Bistrichloroacetylcarbazole (VI) (Dunlop and Tucker, *loc. cit.*) was prepared by the following slightly modified method and isolated : A mixture of carbazole (8·4 g.; 1 mol.), chlorobenzene (80 ml.), trichloroacetonitrile (12 ml.; 2·4 mols.), and anhydrous aluminium chloride (16 g.; 2·4 mols.) was treated with dry hydrogen chloride for 45 minutes. Throughout this and subsequent operations the mixture was violently shaken at frequent intervals. The colour of the solid changed from tomato-red to brown and finally the mixture became mobile. It was heated at 60° for ½ hour and at the b. p. for ½ hour, a black-green solid being obtained. Concentrated hydrochloric acid was added and, after the vigorous reaction had subsided, the chlorobenzene was removed in steam. To ensure hydrolysis, the green residue was ground, thoroughly boiled with concentrated hydrochloric acid, and again treated with steam; after washing with water the light green product (yield, 100%) was sufficiently pure for further use. [It gave no insoluble residue (carbazole) after being boiled with dilute potassium hydroxide solution.] It separated from glacial acetic acid (deep red solution) (charcoal; 1 hr.) in pale green crystals, but from a solution in acetic acid, subsequently diluted with water, in silver-grey, stellate clusters of needles, giving 3 : 6-bistrichloroacetylcarbazole, m. p. 193—195° (bottle-green melt) (Found : C, 41·8; H, 1·7; Cl, 46·3. Calc. for $C_{16}H_7O_2NCl_6$: C, 41·9; H, 1·5; Cl, 46·5%) (yield, 18·5 g.; 81%). Evaporation of the acetic acid filtrate, followed by dilution with water, sometimes yielded a small amount of 3-trichloroacetylcarbazole.

Purification of 3 : 6-bistrichloroacetylcarbazole was facilitated by boiling with acetic acid and sodium dichromate, but addition of concentrated sulphuric acid to this boiling mixture effected oxidation : a product was isolated and is being investigated.

3 : 6-Bistrichloroacetylcarbazole appeared to combine with acetic anhydride, but it could not be acetylated by boiling with the anhydride in presence of a trace of concentrated sulphuric acid. When boiled with dilute potassium hydroxide solution, it evolved chloroform and dissolved completely. The acidified solution gave carbazole-3 : 6-dicarboxylic acid (yield, 75%).

3-Trichloroacetylcarbazole was prepared (yield, 85%) by a similar procedure, the quantities formerly given (Dunlop and Tucker, *loc. cit.*, p. 1953) being used.

1-*Nitro*-3 : 6-*bistrichloroacetylcarbazole* (VII). 3 : 6-Bistrichloroacetylcarbazole (7 g.), dissolved in hot glacial acetic acid (70 ml.), was treated with concentrated nitric acid (21 ml.), and the mixture heated to the b. p. When the vigorous reaction had subsided, the mixture was boiled for 1 min.; a yellow crystalline precipitate separated from the boiling solution, which was then allowed to cool. Practically pure product (6·5 g.; yield, 83%) separated. 1-*Nitro*-3 : 6-*bistrichloroacetylcarbazole* separated from acetic anhydride in pale yellow crystals, which slowly lost acetic anhydride of crystallisation on standing or on treatment with acetic acid and became bright yellow, m. p. 247—249° (red melt) (Found : N, 5·4; Cl, 42·5. $C_{16}H_6O_4N_2Cl_6$ requires N, 5·6; Cl, 42·35%).

The filtrate from the above reaction mixture after removal of 1-nitro-3 : 6-bistrichloroacetylcarbazole gave with water a nearly colourless precipitate, which turned scarlet when treated with any of the usual solvents. When boiled with glacial acetic acid, it gave nitrous fumes (possibly from the >N·NO group) and, exposed to air, the scarlet solution deposited a red solid continuously during several months. Recrystallised, this gave scarlet nodules, m. p. 220—237° (Found : C, 38·9; H, 1·6; N, 6·4%). It dissolved in boiling potassium hydroxide solution. Addition of acetic acid and crystallisation of the precipitate from pyridine diluted with a small amount of water gave ill-defined crystals, unmelted at 300° (Found : N, 12·9. $C_{14}H_7O_7N_3$ requires N, 12·8%).

1-*Nitrocarbazole*-3 : 6-*dicarboxylic acid.* 1-Nitro-3 : 6-bistrichloroacetylcarbazole was boiled with excess of dilute potassium hydroxide solution until no more chloroform was evolved. The deep scarlet solution, treated hot with excess of hot glacial acetic acid, gave a canary-yellow precipitate, which separated from acetic anhydride in yellow micro-crystals of 1-*nitrocarbazole*-3 : 6-*dicarboxylic acid*, m. p. >300° (yield, 100%) (Found for a sample dried at 120°/1 hour : C, 55·9; H, 2·8; N, 9·2. $C_{14}H_8O_6N_2$ requires C, 56·0; H, 2·7; N, 9·3%).

1-*Nitrocarbazole.* 1-Nitrocarbazole-3 : 6-dicarboxylic acid (3·5 g.) was boiled with pure quinoline (35 ml.) and copper bronze (0·1 g.) for 2 hours. The mixture was steam-distilled to remove quinoline, and the black residue ground, boiled with dilute hydrochloric acid, washed with water, and extracted with aqueous ammonia to remove unchanged acid (0·05 g.). A benzene extract of the insoluble residue was passed through alumina (5 cm.) and eluted with benzene to give 1-nitrocarbazole, m. p. and mixed m. p. 187° (0·94 g.; yield, 38%). Charring occurred when 1-nitrocarbazole-3 : 6-dicarboxylic acid was heated alone. Attempts to remove quinoline by means of dilute acid, without steam-distillation, resulted in complete loss of 1-nitrocarbazole.

Ethyl Carbazole-3 : 6-*dicarboxylate.*—3 : 6-Bistrichloroacetylcarbazole (2 g.) was mixed with absolute ethanol (6 ml.) and a solution of sodium (0·1 g.) in absolute ethanol (4 ml.), occasionally shaken, and left for 5 hours (better, 2—3 days). The usual procedure gave carbazole-3 : 6-dicarboxylic acid (0·15 g.; yield, 13%) and pale cream prisms (from toluene–charcoal) of ethyl carbazole-3 : 6-dicarboxylate; the m. p. of the latter and that of a mixture with material prepared by esterifying carbazole-3 : 6-dicarboxylic acid (Dunlop and Tucker, *loc. cit.*, p. 1955) was 206° (corr.) (0·9 g.; yield, 67%).

Similarly, 3-trichloroacetylcarbazole gave ethyl carbazole-3-carboxylate, which, crystallised from ethanol, had m. p. and mixed m. p. 165—167° (yield, 80%).

Ethyl 1-*Nitrocarbazole*-3 : 6-*dicarboxylate.*—Ethyl carbazole-3 : 6-dicarboxylate (7 g.), dissolved in glacial acetic acid (100 ml.), was cooled to room temperature, a solution of concentrated nitric acid (15 ml.) in glacial acetic acid (20 ml.) added all at once, and the mixture left for 15 minutes, heated to the b. p., and filtered after standing. The crystalline precipitate, washed with very dilute aqueous ammonia and dried, gave *ethyl* 1-*nitrocarbazole*-3 : 6-*dicarboxylate* which separated from acetic anhydride in yellow micro-crystals, m. p. 257—261°. The filtrate, treated with water, gave material which, when boiled with acetic anhydride, gave a copious evolution of nitrous fumes and, on cooling, a further crop of the above (total 7·1 g.; yield, 90%) (Found : C, 60·9; H, 4·4; N, 7·9. $C_{18}H_{16}O_6N_2$ requires C, 60·7; H, 4·5; N, 7·9%).

Hydrolysis of this ester was readily effected by boiling (5 mins.) with alcoholic-aqueous potassium hydroxide solution. Addition of hot glacial acetic acid gave 1-nitrocarbazole-3 : 6-dicarboxylic acid, m. p. >300° (6 g.; yield, 100%). Decarboxylation of this material gave 1-nitrocarbazole.

The following reference compounds were also prepared.

9-Toluene-*p*-sulphonylcarbazole (cf. Stevens and Tucker, J., 1923, **123**, 2147) was prepared free from carbazole thus : Carbazole (20 g.), toluene-*p*-sulphonyl chloride (40 g.), and acetone (200 ml.) were warmed to effect solution, and potassium hydroxide powder (33 g.) added. After precipitation by water and crystallisation from ethanol the product (23 g.) was suspended in glacial acetic acid (120 ml.), concentrated nitric acid (10 ml.) added, and the mixture shaken for 1 minute and poured into a large volume of water. The green precipitate, extracted with and crystallised from ethanol (charcoal), gave 9-toluene-*p*-sulphonylcarbazole (7 g.), m. p. 127—128°.

3-*Nitro*-9-*toluene*-p-*sulphonylcarbazole.* A mixture of 3-nitrocarbazole (2 g.), toluene-*p*-sulphonyl chloride (2 g.), and potassium hydroxide powder (1 g.) in acetone (20 ml.) was shaken for 10 minutes on the boiling water-bath and then poured into water. The precipitate crystallised from glacial acetic acid in yellow needles. Recrystallisation from glycol methyl ether gave colourless crystals of 3-*nitro*-9-*toluene*-p-*sulphonylcarbazole* (2·3 g.), m. p. 208—211° (yield, 65%) Found : C, 62·1; H, 3·8; N, 7·7. $C_{19}H_{14}O_4N_2S$ requires C, 62·3; H, 3·8; N, 7·7%).

An attempt to prepare the corresponding derivative of 1-nitrocarbazole failed.

9-(2′-*Nitrotoluene*-4′-*sulphonyl*)*carbazole*, prepared as above, 2-nitrotoluene-4-sulphonyl chloride being used, crystallised from alcohol in colourless needles, m. p. 164° (yield, 33%) (Found: N, 7·7. $C_{19}H_{14}O_4N_2S$ requires N, 7·7%).

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