426. *Internuclear Cyclisation. Part V.* The Cyclisation of Derivatives of Diphenylmethane, Benzophenone, and* N-*Methyldiphenylamine.*

By D. H. Hey and R. D. Mulley.

Diazonium compounds prepared from 2-aminodiphenylmethane, 2-aminobenzophenone, 2-amino-2′-nitrobenzophenone, 2-amino-*N*-methyldiphenylamine, and 2-amino-*N*-methyl-2′-nitrodiphenylamine have been converted by a variety of methods into the fluorene, fluorenone, and *N*-methylcarbazole systems respectively. With the aid of chromatography the by-products formed in these reactions have been isolated and identified. Examples have been established in which the formation of the new internuclear bond involves the ejection from a nitrophenyl group of (*a*) nuclear hydrogen at the *meta*-position to the nitro-group, and (*b*) the nitro-group itself.

Fischer and Schmidt (*Ber.*, 1894, **27**, 2787) have shown that, when an aqueous solution of diphenylmethane-2-diazonium sulphate is heated, fluorene and 2-hydroxydiphenylmethane are formed. In similar manner Graebe and Ullmann (*ibid.*, p. 3484) showed that benzophenone-2-diazonium sulphate gave fluorenone and 2-hydroxybenzophenone, and several substituted fluorenones have also been prepared by this method (Ullmann and Mallet, *Ber.*, 1898, **31**, 1694; Ullmann and Bleier, *Ber.*, 1902, **35**, 4279; Miller and Bachman, *J. Amer. Chem. Soc.*, 1935, **57**, 2443). In an attempt to prepare carbazole in an analogous

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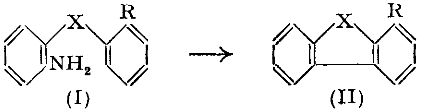
* Part IV, *J.*, 1952, 1513.

manner from diazotised 2-aminodiphenylamine Graebe and Ullmann (*Annalen*, 1896, **291**, 16) obtained 1-phenylbenzotriazole, but this, when heated at 360°, was converted into carbazole and nitrogen. Substituted carbazoles have been prepared in a similar manner (Ullmann, *Ber.*, 1898, **31**, 1697; *Annalen*, 1904, **332**, 82; Hunter and Darling, *J. Amer. Chem. Soc.*, 1931, **53**, 4183; Plant and Tomlinson, *J.*, 1932, 2188; Preston, Tucker, and Cameron, *J.*, 1942, 500; Coker, Plant, and Turner, *J.*, 1951, 110; Clifton and Plant, *ibid.*, p. 461; etc.). It has also been shown by Burton and Gibson (*J.*, 1924, 2501) that *N*-methylcarbazole can be obtained in high yield by decomposition of the aqueous diazonium chloride prepared from 2-amino-*N*-methyldiphenylamine-2′-carboxylic acid in the presence of alkali.

In Part I (*J.*, 1949, 3164) it was shown that the Pschorr phenanthrene synthesis could be carried out in a variety of new ways, and in Part III (*J.*, 1952, 1508) the use of diazonium fluoroborates was described for an analogous reaction. It therefore became of interest to investigate the application of these new techniques to the preparation of derivatives of fluorene (II; X = CH_2, R = H), fluorenone (II; X = CO, R = H), and *N*-methylcarbazole (II; X = NMe, R = H) from 2-amino-derivatives of diphenylmethane, benzophenone, and *N*-methyldiphenylamine respectively. For this purpose diazonium salts were prepared from the five bases, 2-aminodiphenylmethane (I; X = CH_2, R = H) 2-aminobenzophenone (I; X = CO, R = H), 2-amino-2′-nitrobenzophenone (I; X = CO, R = NO_2), 2-amino-*N*-methyldiphenylamine (I; X = NMe, R = H), and 2-amino-*N*-methyl-2′-nitrodiphenylamine (I; X = NMe, R = NO_2), and the reaction products obtained on elimination of nitrogen were investigated, in most examples with the aid of chromatography. The results, which showed wide variations, are summarised in the Table on p. 2278. In addition to the product of cyclisation, which was not invariably obtained, several reactions gave the phenol, the product resulting from deamination, the dimeride resulting from the union of two molecules at the position originally occupied by the amino-group, and in certain cases an azo-compound and a product in which a nitro-group had been eliminated. 2-Acetamidodiphenylmethane was converted into 2-nitrosoacetamidodiphenylmethane, the decomposition of which in hot benzene solution gave only 3-phenylindazole (in 88% yield). For purposes of comparison three of the standard techniques were also applied to *o*-amino-α-phenylcinnamic acid.



(I) (II)

In all the reactions investigated internuclear cyclisation was effected by the action either of heat or of copper powder on the aqueous solution of the diazonium salt. The high yields obtained with *o*-amino-α-phenylcinnamic acid (the Pschorr phenanthrene synthesis) were never reached in any of the reactions leading to the five-membered ring systems. In the latter systems carbazole formation proved to be rather easier than fluorenone formation and the fluorene system proved to be most resistant to ring formation. By means of atomic models and graphical representation, using known values for the interatomic distances and bond angles (Branch and Calvin, "The Theory of Organic Chemistry," Prentice Hall Inc., New York, 1941, Chap. V; Pauling, "The Nature of the Chemical Bond," 2nd. Edn., Cornell Univ. Press, Ithaca, N.Y., 1940, Chap. V), it is possible to calculate the following values for the distances in the unstrained molecules between which the new internuclear bonds are to be formed:

o-Amino-α-phenylcinnamic acid	1·5 Å	*o*-Aminodiphenylmethane	2·2 Å
o-Aminodiphenylamine *	2·0 Å	*o*-Aminobenzophenone	2·4 Å

* No figures are available for the *N*-methyldiphenylamine system.

From these figures it is evident that in none of the five-membered ring intermediates does the distance between the two positions involved in the formation of the new internuclear bond approach the value required for the new bond to the extent encountered in *o*-amino-α-phenylcinnamic acid. When the positions are not sufficiently near to each other in space, cyclisation in most cases appears to be replaced by deamination, which becomes the predominant reaction in non-aqueous solvents. In aqueous solvents a sluggish ring closure would be expected to be replaced by normal phenol formation. The unexpected formation of 2-hydroxydiphenylmethane in the action of copper powder on the diazonium fluoroborate in acetone is attributed to the adventitious intrusion of water into the reacting system, and it is noteworthy that in this reaction alone was an azo-compound found among the products.

		Ring closure				
Base	Method	Normal product yield (%)	Abnormal product	Deamination, yield (%)	Phenol, yield (%)	Other compounds
o-Amino-α-phenylcinnamic acid	B ii	86	—	—	—	—
,, ,,	A ii	60	—	—	8·5 as 3-phenylcoumarin	—
,, ,,	C	93·5	—	—	—	—
2-Aminodiphenylmethane	B i	—	—	43·5	5	—
,, ,,	A i	13	—	—	56	—
,, ,,	D in Et_2O	—	—	91	—	—
,, ,,	C	—	—	35	22	2 : 2′-Dibenzylazobenzene (23·5%)
2-Aminobenzophenone	A i	58·5	—	—	26·5	—
,, ,,	B i	—	—	—	—	Dimeride (25·5%) Chloro-compd. (48·5%)
,, ,,	D in Me_2CO	—	—	92	—	—
,, ,,	B ii	52·5	—	—	8	—
,, ,,	C	—	—	45·5	—	Dimeride (31·5%)
,, ,,	E	—	—	95·5	—	—
,, ,,	F	19·5	—	—	—	—
2-Amino-2′-nitrobenzophenone	A ii	8·5	Fluorenone (1·5%)	—	46	—
,, ,,	B ii	6·5	Fluorenone (13·5%)	Trace	21	Dimeride (4%)
,, ,,	C	—	—	57	—	Dimeride (18%)
2-Amino-*N*-methyldiphenylamine	A ii	60	—	—	—	—
,, ,,	B ii	66·5	—	—	—	—
,, ,,	C	42·5	—	23·5	—	—
2-Amino-*N*-methyl-2′-nitrodiphenylamine	B ii	8·5	*N*-Methylcarbazole (56%)	8·5	—	2 : 4′-Dinitrodiphenylamine (trace)
,, ,,	A ii	37·5	*N*-Methylcarbazole (6·5%) *N*-Methyl-3-nitrocarbazole (13%)	12	—	2 : 4′-Dinitrodiphenylamine (7%)
,, ,,	C	24	*N*-Methylcarbazole (40%) *N*-Methyl-3-nitrocarbazole (trace)	15	—	—

Methods.

A. Action of heat on aqueous diazonium salt (i, chloride; ii, sulphate). B. Action of copper powder on an aqueous diazonium salt (i, chloride; ii, sulphate). C. Action of copper powder on diazonium fluoroborate in acetone. D. Action of copper powder on solid diazonium chloride in an organic solvent. E. Action of hypophosphorous acid on the aqueous diazonium chloride. F. Action of aqueous sodium hydroxide on the aqueous diazonium sulphate.

Of particular interest are the reactions with 2-amino-2′-nitrobenzophenone (I; X = CO, R = NO_2) and 2-amino-*N*-methyl-2′-nitrodiphenylamine (I; NMe, R = NO_2) in which the formation of the new internuclear bond involves the ejection of nuclear hydrogen from a nitrophenyl group at a position *meta* to the nitro-group. In both series the yields obtained on straightforward ring closure were lower than with the corresponding unsubstituted compounds, but the reaction products contained in addition a ring-closed product from which the nitro-group had been eliminated. Thus, 2-amino-2′-nitrobenzophenone (I; X = CO, R = NO_2) gave both 1-nitrofluorenone (II; X = CO, R = NO_2) and fluorenone, and 2-amino-*N*-methyl-2′-nitrodiphenylamine (I; X = NMe, R = NO_2) gave both *N*-methyl-1-nitrocarbazole (II; X = NMe, R = NO_2) and *N*-methylcarbazole. In the carbazole series ring closure accompanied by the elimination of the nitro-group constituted the major reaction, so that the total ring closure in this instance approximated closely to the extent of ring closure in the unsubstituted 2-amino-*N*-methyldiphenylamine. In two of the reactions in the 2-amino-*N*-methyl-2′-nitrodiphenylamine series the product also contained some *N*-methyl-3-nitrocarbazole and, in one instance, some 2 : 4′-dinitrodiphenylamine as well. The formation of *N*-methyl-3-nitrocarbazole in addition to *N*-methyl-1-nitrocarbazole may be attributed to the elimination of the nitro-group during ring closure, possibly as nitrous acid, followed by nitration of the unsubstituted *N*-methylcarbazole. It is known that nitration of *N*-methylcarbazole under such conditions leads to *N*-methyl-3-nitrocarbazole (D.R.-P. 259,504). The elimination of the nitro-group in this manner is of special interest from the point of view of the mechanism of the process because Loebl, Stein, and Weiss (*J.*, 1950, 2704) have already shown that the action of hydroxyl radicals on nitrobenzene results in some elimination of the nitro-group as nitric acid. Nitro-groups attached to an aromatic nucleus can also be removed by electrolytic oxidation (Fichter and Bonhôte, *Helv. Chim. Acta*, 1920, **3**, 395) and possibly also by triphenylmethyl radicals (Hammond and Ravve, *J. Amer. Chem. Soc.*, 1951, **73**, 1891).

DeTar and Sagmanli (*ibid.*, 1950, **72**, 965) have carried out a number of similar reactions with 2-aminobenzophenone as well as with 2-aminodiphenyl ether, 2-aminodiphenyl sulphide, and 2-aminodiphenyl sulphone. They obtained fluorenone in 80% yield by heating an aqueous solution of the diazonium sulphate prepared from 2-aminobenzophenone, but under alkaline conditions the yields obtained were small or negligible. On the basis of these results these authors suggest that under alkaline conditions a free-radical mechanism is involved, since addition of benzene results in the normal Gomberg–Bachmann reaction leading to diaryl formation, but that under acid conditions an ionic mechanism is favoured which leads to high yields of fluorenone. It appears to be extremely doubtful if arguments on reaction mechanism based on observations relating to the internuclear bonding between two aromatic nuclei in *different* molecules, as in the Gomberg reaction, can be applied to internuclear bonding *within one molecule*, as in the Pschorr phenanthrene synthesis and in the reactions studied in this communication and that of DeTar and Sagmanli (*loc. cit.*) and *vice versa*. In many cases the best experimental conditions for a high yield in the intramolecular reaction are those which lead to a very poor or negligible yield in the intermolecular reaction. The conditions in the two series are, in fact, so fundamentally different that each requires separate treatment. For the intermolecular reaction the experimental facts and their interpretation are, for the most part, clear, but with the intramolecular reactions further investigation is called for, particularly on the influence of substituent atoms or groups on the ease of reaction with the substituted nucleus. The results already obtained in this series of papers provide some evidence of a homolytic mechanism in certain reactions but the heterolytic and homolytic mechanisms, both leading to the same end-product, may in some cases be delicately balanced.

2-Amino-2′-nitrobenzophenone (I; X = CO, R = NO_2) was prepared by the partial reduction of 2 : 2′-dinitrobenzophenone, which was obtained from the nitration of either benzophenone or 2-nitrobenzophenone. The latter was conveniently prepared by a low-temperature Grignard reaction between phenylmagnesium bromide and *o*-nitrobenzaldehyde at −70°, following the technique of Newman and Smith (*J. Org. Chem.*, 1948, **13**, 596), with the subsequent oxidation of the resulting *o*-nitrodiphenylmethyl alcohol. 2-Amino-*N*-methyl-2′-nitrodiphenylamine (I; X = NMe, R = NO_2) was prepared by two independent methods. Partial reduction of *N*-methyl-2 : 2′-dinitrodiphenylamine gave 2-amino-*N*-methyl-2′-nitrodiphenylamine together with 2-methylamino-2′-nitrodiphenylamine. In the second method 2-carbomethoxy-2′-nitrodiphenylamine was prepared from methyl anthranilate and *o*-bromonitrobenzene, and subsequent methylation and hydrolysis gave 2-carboxy-*N*-methyl-2′-nitrodiphenylamine. Conversion into the amide and subsequent treatment with aqueous sodium hypochlorite gave 2-amino-*N*-methyl-2′-nitrodiphenylamine, identical with one of the products obtained from the partial reduction of *N*-methyl-2 : 2′-dinitrodiphenylamine.

EXPERIMENTAL

(1) *Experiments with* o-*Amino-α-phenylcinnamic Acid.*—*o*-Amino-α-phenylcinnamic acid was obtained by the reduction with ferrous sulphate and ammonia of the corresponding nitro-compound prepared from *o*-nitrobenzaldehyde and sodium phenylacetate in acetic anhydride.

(a) *Action of copper powder on the diazonium sulphate in aqueous solution.* To a solution of *o*-amino-α-phenylcinnamic acid (3 g.) in concentrated sulphuric acid (3 c.c.) and water (200 c.c.) at 0° was added dropwise a solution of sodium nitrite (1·3 g.) in water (20 c.c.) with constant stirring. On the addition of copper powder * (3 g.), nitrogen was evolved; the mixture was then left overnight. For completion of the reaction, the mixture was warmed until a negative coupling reaction with alkaline β-naphthol was obtained. The precipitate was filtered off and extracted with dilute aqueous ammonia. Acidification of this extract gave phenanthrene-9-carboxylic acid, which crystallised from glacial acetic acid in colourless needles (2·4 g.), m. p. 250—252°.

(b) *Action of heat on the diazonium sulphate in aqueous solution.* *o*-Amino-α-phenylcinnamic acid (1·9 g.) was diazotised as described above in a mixture of concentrated sulphuric acid (2 c.c.) and water (100 c.c.) by the addition of sodium nitrite (0·9 g.) in water (20 c.c.) at 0°. The diazonium solution was heated at 50° for 5 hours, nitrogen being evolved. Crystallisation of the off-white precipitate (1·5 g.) from glacial acetic acid gave phenanthrene-9-carboxylic acid (1·06 g.), m. p. 250—252°. Dilution of the acetic acid mother-liquor with water gave a precipitate, which after crystallisation from aqueous alcohol gave 3-phenylcoumarin (0·15 g.) in colourless needles, m. p. 138—139° (Found: C, 81·0; H, 4·5. Calc. for $C_{15}H_{10}O_2$: C, 81·1; H, 4·5%). Stoermer and Prigge (*Annalen*, 1915, **409**, 24) do not give a yield.

(c) *Action of copper powder on the diazonium fluoroborate in acetone.* *o*-Amino-α-phenylcinnamic acid (2 g.) was diazotised, as described above, in a mixture of concentrated hydrochloric acid (10 c.c.) and water (10 c.c.) by the addition of sodium nitrite (1 g.) in water (5 c.c.). After complete diazotisation water (80 c.c.) was added to dissolve the suspended salt. Sodium fluoroborate (2·5 g.) in water (6 c.c.) was added slowly at 0° with stirring to the filtered diazonium chloride solution. The diazonium fluoroborate (2·2 g.) which separated was collected, washed with a minimum of cold water, and dried over concentrated sulphuric acid at 0°. The diazonium salt was transferred to a flask fitted with a calcium chloride guard tube, and "AnalaR" acetone (50 c.c.) added. Addition of copper powder (3 g.) caused an immediate evolution of nitrogen. Completion of the reaction was ensured by warming the suspension, which was then filtered free from copper powder into water. The copper powder itself was added to dilute hydrochloric acid and extracted with chloroform. The precipitated white solid and that obtained from the extract were combined and shown to be phenanthrene-9-carboxylic acid (1·35 g.), m. p. 250—252°.

(2) *Experiments with 2-Aminodiphenylmethane.*—2-Aminodiphenylmethane was prepared by reduction of 2-nitrodiphenylmethane with tin and hydrochloric acid. The nitro-compound was obtained by a Friedel–Crafts reaction with *o*-nitrobenzyl chloride and benzene.

(a) *Action of copper powder on the diazonium chloride in aqueous solution.* 2-Aminodiphenylmethane (3 g.) was diazotised in concentrated hydrochloric acid (7 c.c.) and water (80 c.c.) by the addition of sodium nitrite (1·2 g.) in water (20 c.c.). When copper powder (3 g.) was added to the diazonium solution, nitrogen was evolved and after an hour the solution was heated to 40° to complete the reaction. The mixture was distilled with steam and the distillate extracted with ether and washed with aqueous sodium hydroxide (10%). The alkali-soluble fraction gave *o*-hydroxydiphenylmethane (0·15 g.) as a light brown oil, which was converted into its phenylurethane, which separated from light petroleum (b. p. 60—80°) in long colourless plates, m. p. and mixed m. p. with an authentic specimen 116—117°. The neutral extract gave an oil (1·48 g.) which was collected at 130—140°/11 mm., to give diphenylmethane (1·2 g.), which was in turn oxidised to benzophenone, the 2 : 4-dinitrophenylhydrazone of which had m. p. 234—236° undepressed on admixture with an authetic specimen.

(b) *Action of heat on the diazonium chloride in aqueous solution.* 2-Aminodiphenylmethane (5 g.) was diazotised in concentrated hydrochloric acid (10 c.c.) and water (100 c.c.) by the

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* The copper powder used in all experiments was prepared by the addition of zinc dust to aqueous copper sulphate.

addition of sodium nitrite (2·2 g.) in water (20 c.c.). The diazonium solution was heated to 50°, whereupon evolution of nitrogen was noticeable, and the decomposition was finally completed by boiling. The mixture was distilled with steam and the products isolated as described above. The residue (2·8 g.) from the ethereal extract, which was partly solid, was crystallised from aqueous alcohol, to give fluorene (0·6 g.) in plates, m. p. and mixed m. p. with an authentic specimen 114°. The residual oil from the mother-liquor (2·0 g.) was added to the product obtained from the alkaline washings, and the whole (3 g.) on distillation at 169—172°/10 mm. gave *o*-hydroxydiphenylmethane (2·8 g.) (phenylurethane, m. p. and mixed m. p. 117—118°). Fischer and Schmidt (*loc. cit.*) do not give yields.

(c) *Action of copper powder on the diazonium fluoroborate in acetone.* 2-Aminodiphenylmethane (4·2 g.) was diazotised in concentrated sulphuric acid (4 c.c.) and water (4 c.c.) by the addition of sodium nitrite (1·8 g.) in water (10 c.c.). Sodium fluoroborate (4 g.) in water (8 c.c.) was added slowly with stirring to the diazonium solution at 0°. The yellow diazonium fluoroborate (6·31 g.) which separated was collected, washed with the minimum amount of cold water, and dried over sulphuric acid at 0°. To a suspension of the dry salt in " AnalaR " acetone (50 c.c.), copper powder (4 g.) was added. There was an immediate evolution of nitrogen on slight warming, and the reaction was complete in 10 minutes. The reaction mixture was filtered into water, the filtrate was extracted with ether, and the extract washed with aqueous sodium hydroxide. The residue from the ethereal extract, a deep-red oily solid (3·57 g.), was chromatographed in benzene solution on an alumina column (30 × 2 cm.). Continued elution with benzene brought down a red band, and crystallisation of the product from alcohol gave 2 : 2'-dibenzylazobenzene (0·95 g.) in red needles, which melted at 114—115°, then solidified and melted again at 122—123° (Found : C, 85·9; H, 6·2; N, 7·9. Calc. for $C_{26}H_{22}N_2$: C, 86·15; H, 6·1; N, 7·7%). Carré (*Compt. rend.*, 1909, **148**, 102) gives m. p.s of two forms as 116—117° and 124—125°. The alcoholic mother-liquors gave a red oil (1·4 g.) which on distillation at 142—144°/20 mm. gave diphenylmethane as a pale yellow oil (1·32 g.), which was oxidised to benzophenone and identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 235—236°. Elution with benzene–ether (1 : 1) gave a light brown oil (0·67 g.), which was added to the product obtained from the alkaline washings, and the whole (1·15 g.) was distilled at 141—143°/0·5 mm., to give *o*-hydroxydiphenylmethane (0·92 g.) (phenylurethane, m. p. 117—118°).

(d) *Preparation and decomposition of 2-nitrosoacetamidodiphenylmethane.* To a mixture of 2-acetamidodiphenylmethane (4 g.), freshly fused potassium acetate (5 g.), phosphoric oxide (0·5 g.), glacial acetic acid (40 c.c.), and acetic anhydride (30 c.c.) at 8° nitrosyl chloride (1·75 g.) in acetic anhydride (5·25 g.) was added dropwise with stirring. After the addition the orange-coloured solution was stirred for a further 45 minutes; it was then added, in portions, to ice-cold water (500 c.c.). The nitroso-compound, which was obtained as a yellow solid on scratching, was collected and dried over concentrated sulphuric acid at 0°. The solid (4·2 g.), m. p. 66—67° (decomp.), was dissolved in dry benzene and boiled under reflux for 16 hours. The benzene was removed under reduced pressure and the residual red oil was distilled at 161—163°/0·2 mm., to give a solid product (3·1 g.). Crystallisation from light petroleum (b. p. 60—80°) gave 3-phenylindazole (2·8 g.) in colourless needles, m. p. 107—108° (Found : C, 80·1; H, 5·4; N, 14·6. Calc. for $C_{13}H_{10}N_2$: C, 80·4; H, 5·2; N, 14·4%). Auwers and Hüttenes (*Ber.*, 1922, **55**, 1112) give m. p. 107—108° for the form crystallising in needles.

(e) *Action of copper powder on the diazonium chloride in ether.* Dry hydrogen chloride was passed into a solution of 2-aminodiphenylmethane (3 g.) in sodium-dried ether (25 c.c.) at 0° until the hydrochloride of the base was fully precipitated. To this suspension, at 0° under anhydrous conditions, amyl nitrite (2·6 c.c.) was added dropwise with shaking. As diazotisation took place the solid dissolved, and a deep-red solution resulted. Further dry ether (50 c.c.) was added, followed by copper powder (3 g.), whereupon an immediate vigorous evolution of nitrogen was observed. On completion of the reaction, the ether was removed and the resulting brown oil distilled with steam. Extraction of the distillate with ether, followed by distillation of the product at 134—140°/9 mm., gave diphenylmethane (2·5 g.) as a light yellow oil, identified by oxidation to benzophenone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 236—237°).

(3) *Experiments with 2-Aminobenzophenone.*—2-Aminobenzophenone was prepared by the Hofmann degradation of *o*-benzoylbenzamide by using sodium hypochlorite.

(a) *Action of heat on the diazonium chloride in aqueous solution* (cf. DeTar and Sagmanli, *loc. cit.*). To a solution of 2-aminobenzophenone (3 g.) in concentrated hydrochloric acid (10 c.c.) and water (100 c.c.) at 5° was added dropwise sodium nitrite (1·3 g.) in water (20 c.c.) with constant stirring. The diazonium solution was heated to 50° for 30 minutes and then boiled to complete the reaction. The yellow oil which separated was extracted with ether, and the extract was washed with aqueous sodium hydroxide (10%). The phenolic product (0·9 g.) on distillation at 180—182°/14 mm. gave 2-hydroxybenzophenone (0·8 g.) as a light yellow oil, which solidified and then had m. p. 36—38°. Crystallisation of the neutral product (2 g.) from aqueous alcohol gave fluorenone (1·6 g.) in yellow plates, m. p. and mixed m. p. with an authentic specimen 83—85°.

(b) *Action of copper powder on the diazonium chloride in aqueous solution.* 2-Aminobenzophenone (3 g.) was diazotised, as above, in concentrated hydrochloric acid (10 c.c.) and water (100 c.c.) by the addition of sodium nitrite (1·3 g.) in water (20 c.c.). When copper powder (3 g.) was added there was only a slight evolution of nitrogen, and the decomposition was carried out at 40° for 1 hour. The mixture was extracted with ether, and the copper removed by filtration. The extract was washed with aqueous sodium hydroxide as above, but the quantity of phenolic material obtained was negligible. The neutral residue (2·9 g.), which partly solidified, was extracted with cold ether, which left behind yellow prismatic crystals of 2 : 2′-dibenzoyldiphenyl (0·7 g.), which after repeated crystallisation from alcohol had m. p. 168—170° (Found : C, 85·7; H, 5·2. Calc. for $C_{26}H_{18}O_2$: C, 86·1; H, 5·0%). Tschitschibabin and Ssergejeff (*Ber.*, 1926, **59**, 657) give m. p. 172—173° for this compound. Concentration of the ethereal extract gave a dark-red oil which was collected at 180°/12 mm. 2-Chlorobenzophenone (1·6 g.) was obtained, which on solidification and crystallisation from light petroleum (b. p. 40—60°) gave light yellow prisms, m. p. 44—46°. Newton and Groggins (*Ind. Eng. Chem.*, 1935, **27**, 1398) record m. p. 45·5—46°.

(c) *Action of copper powder on the diazonium sulphate in aqueous solution.* A suspension of 2-aminobenzophenone (3 g.) in concentrated sulphuric acid (3·5 c.c.) and water (100 c.c.) was diazotised, as described above, by the addition of sodium nitrite (1·3 g.) in water (20 c.c.). Some unchanged amine (0·7 g.) was filtered off and on the addition of copper powder (3 g.) decomposition commenced, and this was completed at 40°. The mixture was extracted with ether, filtered from copper powder, and washed with aqueous sodium hydroxide (10%). The phenolic fraction (0·27 g.) on distillation at 170—172°/12 mm. gave 2-hydroxybenzophenone (0·18 g.), m. p. 37—38·5°. The neutral fraction (1·8 g.) on distillation at 106°/3 × 10^{-3} mm. gave fluorenone (1·1 g.), m. p. 80—82°, undepressed on admixture with an authentic specimen.

(d) *Action of copper powder on the diazonium chloride in acetone.* Dry hydrogen chloride was passed into a solution of 2-aminobenzophenone (3 g.) in sodium-dried ether (50 c.c.) at 0° until the hydrochloride was fully precipitated. To this suspension, under anhydrous conditions at 0°, was added amyl nitrite (2·8 c.c.) dropwise with shaking. The off-white crystalline diazonium salt was collected and washed with dry ether. To a solution of the dry diazonium salt in " AnalaR " acetone (100 c.c.) copper powder (3 g.) was added and there was an immediate vigorous evolution of nitrogen. The mixture was filtered into water and extracted with ether. The residual brown oil on distillation at 187—189°/24 mm. gave benzophenone (2·55 g.) as a light yellow oil (2 : 4-dinitrophenylhydrazone, m. p. 235—237°, both alone and on admixture with an authentic specimen).

(e) *Action of copper powder on the diazonium fluoroborate in acetone.* 2-Aminobenzophenone (3 g.) was diazotised in concentrated sulphuric acid (3 c.c.) and water (3 c.c.) by the addition of sodium nitrite (1·3 g.) in water (5 c.c.). Sodium fluoroborate (3 g.) in water (6 c.c.) was added slowly to the diazonium solution at 0° with stirring. The diazonium fluoroborate which separated was collected, washed with a minimum of cold water, and dried over sulphuric acid at 0°. To the solid diazonium salt (4·29 g.) in " AnalaR " acetone (50 c.c.), in which it partly dissolved, copper powder (3 g.) was added. Evolution of nitrogen commenced on warming and decomposition was complete in 10 minutes. The mixture was filtered into water, extracted with ether, and washed with aqueous sodium hydroxide (10%). The brown semi-solid residue (2·54 g.) obtained on concentration of the ethereal solution was chromatographed in benzene–light petroleum (b. p. 60—80°) (1 : 1) on a column (30 × 2 cm.) of activated alumina. Elution with benzene–light petroleum (b. p. 60—80°) gave a light yellow oil (1·22 g.), which on distillation at 174°/17 mm. gave benzophenone (1·2 g.) (2 : 4-dinitrophenylhydrazone, m. p. 236—238°). Further elution with the same mixed solvent gave 2 : 2′-dibenzoyldiphenyl (0·83 g.), m. p. 168—170°, both alone and on admixture with an authentic specimen.

(f) *Action of aqueous sodium hydroxide on the diazonium sulphate.* 2-Aminobenzophenone (2·5 g.) was diazotised in concentrated sulphuric acid (3 c.c.) and water (10 c.c.) by the addition of sodium nitrite (1·1 g.) in water (5 c.c.). The solution was diluted with water (100 c.c.) and made just alkaline to phenolphthalein by additon of aqueous sodium hydroxide, a brick-red precipitate being formed. This mixture was stirred overnight at room temperature and then boiled to complete the decomposition. The mixture was extracted with chloroform and washed with aqueous sodium hydroxide (10%). The neutral fraction (2·22 g.), a dark tar, was chromatographed in benzene on a column (30 × 2 cm.) of alumina. Elution with benzene gave an oily yellow solid, which on crystallisation from light petroleum (b. p. 60—80°) deposited fluorenone (0·45 g.) in yellow plates, m. p. 82—84°. The alkali-soluble fraction (0·23 g.) was chromatographed in benzene on a column (10 × 2 cm.) of silica gel. Elution with benzene gave light-brown needles, m. p. 114—117°, in minute yield. DeTar and Sagmanli (*loc. cit.*) record a yield of only 1% of steam-volatile material regarded as fluorenone from a similar reaction.

(g) *Action of hypophosphorous acid on the diazonium chloride in aqueous solution.* 2-Aminobenzophenone (2 g.) was diazotised in concentrated hydrochloric acid (6 c.c.) and water (12 c.c.) by the addition of sodium nitrite (0·9 g.) in water (7 c.c.). After complete diazotisation ice-cold 30% hypophosphorous acid (25 c.c.) was added to the cold solution and the mixture kept at 0° for 3 days. Nitrogen was slowly evolved and a light-yellow oil separated. The mixture was extracted with ether and washed with aqueous sodium hydroxide (10%). Concentration of the ethereal extract, followed by distillation at 172—174°/18 mm., gave benzophenone (1·76 g.) (2 : 4-dinitrophenylhydrazone, m. p. 236—238°).

(4) *Experiments with 2-Amino-2′-nitrobenzophenone.*—o-*Nitrodiphenylmethyl alcohol* (cf. Newman and Smith, *loc. cit.*). A solution of *o*-nitrobenzaldehyde (24 g.) in sodium-dried toluene (350 c.c.) was cooled to −70° in a solid carbon dioxide bath whilst a stream of dry nitrogen was passed in. To this solution phenylmagnesium bromide, prepared from bromobenzene (27·9 g.) and magnesium (4·3 g.) in sodium-dried ether (100 c.c.), was added dropwise during 2 hours with vigorous stirring. The temperature was kept at −70° for a further 2 hours and then allowed to rise. At −10°, alcohol (20 c.c.) was added to decompose any unchanged Grignard reagent. The solution was poured into ammonium chloride (30 g.) in ice-water (600 c.c.) and left overnight at 0°. Separation of the organic solvent layer, followed by concentration, gave a brown oil which was distilled. o-*Nitrodiphenylmethyl alcohol* (29·5 g.) was collected at 170—180°/0·74 mm. as a light yellow oil. On long storage it solidified, and crystallisation from light petroleum (b. p. 40—60°) gave plates, m. p. 59—60° (Found : C, 68·1; H, 4·9. $C_{13}H_{11}O_3N$ requires C, 68·1; H, 4·8%).

2-*Nitrobenzophenone* (cf. Newman and Smith, *loc. cit.*). To a boiling solution of the foregoing alcohol (29·5 g.) in glacial acetic acid (50 c.c.) was added dropwise during 30 minutes a hot solution of chromium trioxide (24 g.) in glacial acetic acid (90 c.c.). After boiling under reflux for a further 15 minutes the solution was poured into cold water (1000 c.c.). The 2-nitrobenzophenone (28·3 g.) which separated was collected, washed, and dried; it had m. p. 103—104° both alone and on admixture with an authentic specimen.

2-*Amino-2′-nitrobenzophenone* (cf. Purdie, *J. Amer. Chem. Soc.*, 1941, **63**, 2276). An aqueous solution of sodium polysulphide was added dropwise to a boiling suspension of 2 : 2′-dinitrobenzophenone (5 g.) in alcohol (150 c.c.). The sodium polysulphide was prepared by dissolving sodium sulphide (6 g.) and sulphur (1·5 g.) in water (40 c.c.). On completion of the addition the suspension was boiled for a further 3 hours, all of the 2 : 2′-dinitrobenzophenone dissolving. Most of the alcohol (100 c.c.) was removed by distillation and the residue was poured into water. The yellow solid which separated was collected, extracted several times with hot concentrated hydrochloric acid, and made alkaline with aqueous ammonia (*d* 0·880). The 2-amino-2′-nitrobenzophenone (3·4 g.) which separated crystallised from alcohol in brown-yellow needles, m. p. 149—150° (Found : C, 64·2; H, 4·3; N, 11·8. Calc. for $C_{13}H_{10}O_3N_2$: C, 64·5; H, 4·2; N, 11·6%). Heyl (*Ber.*, 1898, **31**, 3033) reports m. p. 149—150°.

(a) *Action of copper powder on the diazonium sulphate in aqueous solution.* A solution of 2-amino-2′-nitrobenzophenone (2·5 g.) in concentrated sulphuric acid (6 c.c.) and water (20 c.c.) at 5° was diazotised with sodium nitrite (1·2 g.) in water (5 c.c.). This diazonium solution was diluted with water (100 c.c.), and copper powder (3 g.) was added. After 2 days' stirring at room temperature, more copper powder (2 g.) was added and the suspension was heated to 70°. The mixture was extracted with chloroform and the copper removed by filtration. The extract was washed with 10% aqueous sodium hydroxide, and the washings were acidified and extracted with chloroform. The phenolic product, a brown gum (0·87 g.), was chromatographed in benzene on a column (10 × 2 cm.) of silica gel. Elution by benzene (400 c.c.), followed by crystallisation of the product from methyl alcohol, gave 2-*hydroxy-2′-nitrobenzophenone* (0·53 g.) in yellow leaflets m. p. 121—122° (Found : C, 64·0; H, 3·75; N, 5·35. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7; N, 5·8%). The neutral extract gave a brown oil (1·36 g.) which was chromatographed in benzene on activated alumina (30 × 2 cm.). Elution with benzene gave a yellow solid, which on crystallisation from light petroleum (b. p. 60—80°) deposited fluorenone (0·25 g.) in yellow plates, m. p. 83—84°, which showed no depression on admixture with an authentic specimen. Further elution with benzene gave (*a*) 2-nitrobenzophenone (0·01 g.) [needles from light petroleum (b. p. 60—80°)], m. p. and mixed m. p. with an authentic specimen 101—103°, and (*b*) 1-nitrofluorenone (0·15 g.) in small yellow plates (from benzene), m. p. and mixed m. p. with an authentic specimen (Chase and Hey, *J.*, 1952, 566) 187—189°. Elution with benzene–ether (9 : 1), followed by crystallisation of the product from benzene, gave 2 : 2′-*di*-o-*nitrobenzoyldiphenyl* (0·1 g.) in pale yellow prisms, m. p. 214—216° (Found: C, 69·4; H, 3·8; N, 6·2%; *M*, 450. $C_{26}H_{16}O_6N_2$ requires C, 69·05; H, 3·6; N, 6·2%; *M*, 452).

(b) *Action of heat on the diazonium sulphate in water.* 2-Amino-2′-nitrobenzophenone (2·5 g.) was diazotised as described above. After dilution with water (100 c.c.), the solution was stirred at room temperature overnight, after which it was decomposed by heating to 70°. The mixture was extracted with chloroform, and the extract washed with aqueous sodium hydroxide (10%). The phenolic product (1·54 g.) was chromatographed in benzene on a column (10 × 2 cm.) of silica gel. Elution with benzene, followed by crystallisation of the product from methyl alcohol, gave 2-hydroxy-2′-nitrobenzophenone (1·15 g.) in yellow leaflets, m. p. 121—122°, both alone and on admixture with an authentic specimen. The neutral product (0·83 g.) was chromatographed in benzene on a column (30 × 2 cm.) of alumina. Elution with benzene and crystallisation of the product from light petroleum (b. p. 60—80°) gave fluorenone (0·03 g.) in yellow plates, m. p. 79—81°. Further elution with benzene, followed by crystallisation from the same solvent, gave 1-nitrofluorenone (0·2 g.) in small yellow plates, m. p. 185—187°, both alone and on admixture with an authentic specimen.

(c) *Action of copper powder on the diazonium fluoroborate in acetone.* Sodium fluoroborate (3 g.) in water (6 c.c.) was added slowly at 0° with stirring to the diazonium solution prepared from 2-amino-2′-nitrobenzophenone (2·5 g.) in concentrated sulphuric acid (4 c.c.) and water (4 c.c.) by the addition of sodium nitrite (1·2 g.) in water (5 c.c.). The light-yellow diazonium fluoroborate (3·37 g.) was collected, washed with a minimum of cold water, and dried over sulphuric acid at 0°. Copper powder (3 g.) was added to the solid diazonium salt under "AnalaR" acetone (50 c.c.). Decomposition commenced on slight warming and was complete in 10 minutes. The reaction mixture was filtered into water and extracted with chloroform, and the chloroform extract was washed with aqueous sodium hydroxide (10%). The neutral product (2·47 g.), obtained on removal of the solvent, was chromatographed in benzene on alumina (30 × 2 cm.). Elution with benzene gave 2-nitrobenzophenone (1·28 g.) in white needles (from alcohol), m. p. 102—104°, both alone and on admixture with an authentic specimen. Elution with benzene–ether (9 : 1) gave 2 : 2′-di-*o*-nitrobenzoyldiphenyl (0·41 g.) in pale yellow needles (from benzene), m. p. 214—216° alone and on admixture with an authentic specimen.

(5) *Experiments with 2-Amino-*N*-methyldiphenylamine.*—*2-Amino-*N*-methyldiphenylamine* (cf. Kehrmann and Havas, *Ber.*, 1913, **46**, 341). *o*-Chloronitrobenzene (20 g.), methylaniline (34 g.), and powdered, freshly fused sodium acetate (11 g.) were heated for 10 hours at 210°. The mixture was distilled with steam to remove unchanged reactants, the residue being extracted with ether. The *N*-methyl-2-nitrodiphenylamine (12 g.) obtained on removal of the ether was collected at 203—207°/11 mm. and reduced with tin and hydrochloric acid.

(a) *Action of copper powder on the diazonium sulphate in aqueous solution.* A solution of sodium nitrite (1·3 g.) in water (20 c.c.) was added dropwise with stirring to a solution of 2-amino-*N*-methyldiphenylamine (3 g.) in concentrated sulphuric acid (3 c.c.) and water (100 c.c.) at 5°. Copper powder (3 g.) was added to the deep-red solution, which was stirred at room temperature for 30 minutes and finally heated to 50°. The reaction product was extracted with ether, and the copper powder removed by filtration. Washing the extract with 10% aqueous sodium hydroxide removed only a small quantity (0·08 g.) of tar. The neutral product (2·75 g.) distilled at 190—196°/11 mm. and gave a light yellow oil (2·15 g.) which rapidly solidified. Crystallisation from alcohol afforded *N*-methylcarbazole (1·83 g.) in needles, m. p. 88—90°. The picrate separated from alcohol in deep red needles, m. p. 145—146°. Graebe (*Annalen*, 1880, **202**, 23) gives m. p. 87° and m. p. 141° for *N*-methylcarbazole and its picrate.

(b) *Action of heat on the diazonium sulphate in water.* 2-Amino-*N*-methyldiphenylamine (2·05 g.) was diazotised, as described above, in concentrated sulphuric acid (2 c.c.) and water (70 c.c.) by the addition of sodium nitrite (1 g.) in water (10 c.c.). After being stirred at room temperature for 2 hours the deep red solution was boiled to complete the decomposition. The mixture was extracted with ether, and the extract was washed with 10% aqueous sodium hydroxide. Evaporation of the ether, followed by distillation at 190—196°/11 mm., gave a light yellow oil (1·45 g.) which solidified. Crystallisation from alcohol afforded *N*-methylcarbazole (1·12 g.) in needles, m. p. 88—89° alone and on admixture with an authentic specimen.

(c) *Action of copper powder on the diazonium fluoroborate under acetone.* 2-Amino-*N*-methyldiphenylamine (2·8 g.) was diazotised, as described above, in concentrated sulphuric acid (3 c.c.) and water (3 c.c.) by the addition of sodium nitrite (1·3 g.) in water (5 c.c.). Sodium fluoroborate (3 g.) in water (6 c.c.) was added slowly to the solution at 0° with stirring. The light-brown diazonium fluoroborate (3·77 g.) was collected, washed with a minimum of cold water, and dried over concentrated sulphuric acid at 0°. Copper powder (3 g.) was added to a suspension of the solid diazonium salt in " AnalaR " acetone (100 c.c.). No nitrogen was evolved until the acetone suspension was heated almost to boiling, whereupon decomposition was rapid. The reaction mixture was filtered from copper powder into water, extracted with chloroform, and washed with 10% aqueous sodium hydroxide. The brown semi-solid residue (2·23 g.) obtained on removal of the chloroform was separated by chromatography in benzene on alumina (30 × 2 cm.). Elution with benzene gave an orange semi-solid (1·66 g.) which, on crystallisation from methyl alcohol, gave *N*-methylcarbazole (0·98 g.) in needles, m. p. 85—87° alone and on admixture with an authentic specimen. The methyl alcohol mother-liquors on dilution with water gave a red oil (0·69 g.) which, on distillation at 162—166°/22 mm., gave *N*-methyldiphenylamine (0·54 g.) as a light yellow oil. The double salt of the hydrochloride of the base with zinc chloride, prepared in glacial acetic acid, had m. p. 181—185°. Craig (*J. Amer. Chem. Soc.*, 1933, **55**, 3727) records m. p. 186—188° for this salt.

(6) *Experiments with 2-Amino-*N*-methyl-2′-nitrodiphenylamine.*—N*-Methyl-2 : 2′-dinitrodiphenylamine* (cf. Storrie and Tucker, *J.*, 1931, 2261). Powdered potassium hydroxide (9 g.) was added to a solution of 2 : 2′-dinitrodiphenylamine (9·3 g.) in acetone (80 c.c.), and the suspension was heated to boiling. After the slow addition of methyl sulphate (15 c.c.), boiling under reflux was continued for 5 minutes, the violet colour being discharged. The suspension was poured into water and the yellow-orange precipitate collected. Crystallisation from alcohol gave N-*methyl*-2 : 2′-*dinitrodiphenylamine* (8·45 g.) in orange plates, m. p. 147·5—148·5° (Found : C, 57·3; H, 4·3. $C_{13}H_{11}O_4N_3$ requires C, 57·2; H, 4·1%).

Action of sodium polysulphide solution on N-*methyl-2 : 2′-dinitrodiphenylamine in alcohol* (cf. Purdie, *loc. cit.*). A hot aqueous solution of sodium polysulphide was added dropwise to a suspension of *N*-methyl-2 : 2′-dinitrodiphenylamine (14·4 g.) in alcohol (200 c.c.) boiling under reflux. The sodium polysulphide was prepared from sodium sulphide (15 g.), sulphur (3·8 g.), and water (50 c.c.). On completion of the addition the suspension was boiled for a further 3½ hours, solution then being complete. Most of the alcohol (150 c.c.) was distilled off and the residue poured into water. The oil which separated was dissolved in benzene and a small quantity of yellow insoluble material was filtered off. Concentration of the solution gave a red oil (11·73 g.) which was collected at 150—174°/0·3 mm., and rapidly solidified. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave a mixture of red prisms, m. p. 114—116°, and yellow-orange needles, m. p. 80—130°, which were separated by hand-picking. Crystallisation of the red prisms from alcohol gave 2-*amino*-N-*methyl*-2′-*nitrodiphenylamine* (3·5 g.), m. p. 118—119° (Found : C, 64·4; H, 5·45; N, 17·2. $C_{13}H_{13}O_2N_3$ requires C, 64·2; H, 5·4; N, 17·3%). The yellow-orange needles were extracted with hot light petroleum (b. p. 60—80°), which left behind unchanged starting material (1·9 g.), m. p. 142—146°. Concentration of the light petroleum solution gave 2-*methylamino*-2′-*nitrodiphenylamine* (4·2 g.) in yellow-orange needles, m. p. 99—100° (Found : C, 64·1; H, 5·3; N, 17·0. $C_{13}H_{13}O_2N_3$ requires C, 64·2; H, 5·4; N, 17·3%), identical with an authentic specimen prepared as described below.

2-*Methylamino-2′-nitrodiphenylamine* (cf. Ullmann, *Annalen*, 1907, **355**, 327). Hydrogenation of *N*-methyl-*o*-nitroaniline (5 g.) at atmospheric pressure in alcohol, with Raney nickel catalyst, gave *N*-methyl-*o*-phenylenediamine (3·13 g.), which, with *o*-bromonitrobenzene (5 g.), dry potassium carbonate (3 g.), and a trace of cuprous chloride was heated at 150—170° for 3 hours. The reaction product was extracted with chloroform, and the fraction of b. p. 154°/10^{-2} mm. collected. Crystallisation from light petroleum (b. p. 60—80°) gave 2-methylamino-2′-nitrodiphenylamine (0·6 g.) in orange-yellow needles, m. p. 98—100°.

2-*Carbomethoxy-2′-nitrodiphenylamine* (cf. Ullmann, *loc. cit.*). Methyl anthranilate (10 g.), *o*-bromonitrobenzene (15 g.), dry potassium carbonate (5 g.), and a trace of cuprous chloride were heated together at 170—190° for 3 hours. There was an initial rapid evolution of carbon dioxide. The solid product was extracted many times with boiling water. Crystallisation of the residue twice from glacial acetic acid gave 2-*carbomethoxy*-2′-*nitrodiphenylamine* (8 g.) in light brown plates, m. p. 159—160° (Found : C, 61·9; H, 4·4; N, 10·1. $C_{14}H_{12}O_4N_2$ requires C, 61·7; H, 4·4; N, 10·3%).

2-*Carbomethoxy*-N-*methyl-2′-nitrodiphenylamine* (cf. Storrie and Tucker, *loc. cit.*). A mixture of methyl sulphate (12 c.c.), powdered potassium hydroxide (8 g.), and 2-carbomethoxy-2′-

nitrodiphenylamine (8 g.) in acetone (100 c.c.) was boiled under reflux for 30 minutes. The colour was thereby discharged, and the mixture poured into water. The yellow precipitate was collected and dried. Crystallisation from light petroleum (b. p. 60—80°) gave *2-carbomethoxy-*N*-methyl-2'-nitrodiphenylamine* (7·5 g.) in thick yellow needles, m. p. 77—78° (Found : C, 63·1; H, 5·2. $C_{15}H_{14}O_4N_2$ requires C, 62·9; H, 4·9%).

*2-Carbamyl-*N*-methyl-2'-nitrodiphenylamine.* A suspension of 2-carbomethoxy-*N*-methyl-2'-nitrodiphenylamine (3 g.) in aqueous sodium hydroxide (50 c.c., 10%) was boiled under reflux until solution was complete. The deep red solution was cooled and made just acid with dilute acetic acid. The deep yellow precipitate was collected and dried. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave 2-carboxy-*N*-methyl-2'-nitrodiphenylamine (2·57 g.) as a mixture of yellow needles and red prisms, m. p. 122—130° (Found : C, 61·5; H, 4·5; N, 10·3. Calc. for $C_{14}H_{12}O_4N_2$: C, 61·7; H, 4·4; N, 10·3%). Neither recrystallisation nor purification by chromatography through alumina affected the melting-point range (cf. Burton and Gibson, *loc. cit.*). Thionyl chloride (3 c.c.) was added to a solution of the acid (4·89 g.) in dry chloroform (30 c.c.), and the reaction was completed by 2 hours' boiling under reflux. The chloroform and most of the excess of thionyl chloride were removed by distillation under reduced pressure, and the last traces of thionyl chloride by successive distillations under vacuum with dry benzene (2 × 20 c.c.). The acid chloride, obtained as a dark-red syrup, was dissolved in dry benzene (15 c.c.), and aqueous ammonia (10 c.c.; *d* 0·880) cautiously added, the solution being cooled and shaken. An orange solid separated, and crystallisation from methyl alcohol gave *2-carbamyl-*N*-methyl-2'-nitrodiphenylamine* (4·56 g.) in orange plates, m. p. 170—172° (Found : C, 62·2; H, 4·9. $C_{14}H_{13}O_3N_3$ requires C, 62·0; H, 4·8%).

*2-Amino-*N*-methyl-2'-nitrodiphenylamine.* To a suspension of finely powdered 2-carbamyl-*N*-methyl-2'-nitrodiphenylamine (8 g.) in aqueous sodium hydroxide (3·25 g. in 15 c.c.), cooled in ice, sodium hypochlorite solution was added slowly with vigorous stirring. The sodium hypochlorite solution was prepared by passing chlorine (2·2 g.) into sodium hydroxide (2·4 g.) in water (15 c.c.) cooled in ice. The suspension was then heated to 55—60° and kept at that temperature for 1 hour, whereafter solution was almost complete. Finally, it was boiled for ½ hour. On cooling, a dark-red solid (7·05 g.) was collected by filtration. It was crushed and extracted overnight in a Soxhlet apparatus with light petroleum (b. p. 60—80°), the insoluble residue (1·93 g.; m. p. 164—169°) being unchanged 2-carbamyl-*N*-methyl-2'-nitrodiphenylamine. The product, soluble in the light petroleum (b. p. 60—80°), was crystallised from the same solvent and then from light petroleum (b. p. 80—100°). 2-Amino-*N*-methyl-2'-nitrodiphenylamine (3·5 g.) was obtained in red prisms, m. p. 118—119°, not depressed on admixture with the base prepared as described above by the partial reduction of *N*-methyl-2 : 2'-dinitrodiphenylamine.

(a) *Action of copper powder on the diazonium sulphate in water.* A solution of 2-amino-*N*-methyl-2'-nitrodiphenylamine (1·8 g.) in concentrated sulphuric acid (3 c.c.) and water (100 c.c.) was diazotised at 5° with a solution of sodium nitrite (1·3 g.) in water (20 c.c.) added dropwise with constant stirring. Copper powder (3 g.) was added to the red solution, which was stirred at room temperature for 24 hours. For completion of the reaction the suspension was boiled after the addition of more copper powder (2 g.). The mixture was extracted with chloroform, filtered from the copper, and washed with aqueous 10% sodium hydroxide. No phenolic product was isolated. Evaporation of the chloroform extract gave a brown oil (1·47 g.), which was chromatographed in benzene–light petroleum (b. p. 60—80°) (2 : 1) on alumina (30 × 2 cm.). Elution with the same mixed solvent gave, first, *N*-methylcarbazole (0·75 g.) in white needles, m. p. 88—89°, from light petroleum (b. p. 60—80°), undepressed on admixture with an authentic specimen, and, secondly, a red partly solid material (0·29 g.), from which N*-methyl-1-nitrocarbazole* (0·14 g.) was obtained in yellow needles, m. p. 91—92°, from methyl alcohol (Found : C, 69·3; H, 4·7; N, 11·85. $C_{13}H_{10}O_2N_2$ requires C, 69·0; H, 4·5; N, 12·4%). A mixed m. p. with an authentic specimen, prepared as described below, showed no depression. The methyl alcohol mother-liquors, on dilution with water, afforded *N*-methyl-2-nitrodiphenylamine (0·14 g.), b. p. 230—234°/30 mm. This product, obtained as a red oil, was combined with the analogous fractions from reactions (*b*) and (*c*), and reduced and acetylated. The product melted at 86—87·5°, both alone and on admixture with an authentic specimen of 2-acetamido-*N*-methyldiphenylamine. Elution with benzene–ether (2 : 1) gave 2 : 4'-dinitrodiphenylamine, m. p. 210—215° (from ethyl alcohol), in very small yield. This product showed no depression in m. p. on admixture with an authentic specimen, m. p. 221—222°. Davis and Ashdown (*J. Amer. Chem. Soc.*, 1924, **46**, 1053) record m. p. 220—221·5° for this compound.

N*-Methyl-1-nitrocarbazole* (cf. Stevens and Tucker, *J.*, 1923, 2143). Methyl sulphate

(0·3 c.c.) was added to a solution of 1-nitrocarbazole (0·2 g.) in acetone (2 c.c.) and aqueous potassium hydroxide (0·3 c.c.; 66%). The mixture was shaken for a few seconds until the deep violet colour had been discharged; then warm water (4 c.c.) was added. The product solidified and was collected. Crystallisation from methyl alcohol gave *N*-methyl-1-nitrocarbazole in deep yellow needles (0·16 g.), m. p. 91·5—92·5°.

(b) *Action of copper powder on the diazonium fluoroborate under acetone.* 2-Amino-*N*-methyl-2′-nitrodiphenylamine (1·36 g.) was diazotised, as described above, in concentrated sulphuric acid (1·3 c.c.) and water (2 c.c.) by the addition of sodium nitrite (0·65 g.) in water (3 c.c.). Sodium fluoroborate (1·5 g.) in water (3 c.c.) was added slowly to the deep-red solution at 0° with stirring. The solid fluoroborate (1·89 g.) was collected, washed with a small amount of cold water, and dried over sulphuric acid at 0°. Copper powder (3 g.) was added to the dry diazonium salt in " AnalaR " acetone (100 c.c.). Very slight decomposition commenced on warming, and to complete the reaction it was necessary to boil the mixture under reflux for 2 hours. The mixture was filtered into water, extracted with chloroform, and washed with 10% aqueous sodium hydroxide. The dark-brown gum (1·20 g.) obtained on evaporation of the chloroform was separated by chromatography in benzene–light petroleum (b. p. 60—80°) (1 : 1) on alumina (30 × 2 cm.). Elution with the same mixed solvent gave *N*-methylcarbazole (0·4 g.) in needles, m. p. 88—89° [from light petroleum (b. p. 60—80°)]. A mixed m. p. with an authentic specimen showed no depression. Continued elution with benzene–light petroleum (b. p. 60—80°) (1 : 1) gave *N*-methyl-1-nitrocarbazole (0·3 g.) in deep yellow needles (from methyl alcohol), m. p. and mixed m. p. with an authentic specimen 89—91°. Dilution of the methyl alcohol mother-liquors with water gave *N*-methyl-2-nitrodiphenylamine (0·19 g.), b. p. 230—234°/30 mm., which was treated as described above. Elution with benzene gave a trace of *N*-methyl-3-nitrocarbazole as a yellow solid, m. p. 165—168°, from ethyl alcohol. A mixed m. p. with an authentic specimen showed no depression.

(c) *Action of heat on the diazonium sulphate in water.* 2-Amino-*N*-methyl-2′-nitrodiphenylamine (1·5 g.) was diazotised, as described above, in concentrated sulphuric acid (2·5 c.c.) and water (70 c.c.) by the addition of sodium nitrite (1 g.) in water (20 c.c.). After the whole had been stirred at room temperature overnight the reaction was completed by boiling. The mixture was extracted with chloroform, and the extract was washed with 10% aqueous sodium hydroxide. A small phenolic fraction (0·05 g.) was obtained as a dark-brown tar. Removal of the solvent from the neutral fraction gave a brown oily solid (1·34 g.), which was purified by chromatography in benzene–light petroleum (b. p. 60—80°) (2 : 1) through alumina (30 × 2 cm.). Elution with this mixed solvent gave (*a*) *N*-methylcarbazole (0·07 g.) in white needles from light petroleum (b. p. 60—80°), m. p. and mixed m. p. with an authentic specimen 87—89°, and (*b*) *N*-methyl-1-nitrocarbazole (0·52 g.) in deep yellow needles (from methyl alcohol), m. p. 91—92°, both alone and on admixture with an authentic specimen. *N*-Methyl-2-nitrodiphenylamine (0·17 g.), b. p. 230—234°/30 mm., was obtained as a red oil from the mother-liquors. Elution with benzene gave *N*-methyl-3-nitrocarbazole (0·18 g.) in light yellow needles (from ethyl alcohol), m. p. 170—172° (Found : C, 69·4; H, 4·6; N, 12·2%; *M*, 238. Calc. for $C_{13}H_{10}O_2N_2$: C, 69·0; H, 4·5; N, 12·4%; *M*, 226). Stevens and Tucker (*J.*, 1923, 2143) give m. p. 169—171°. Reduction, as described below, gave 3-amino-*N*-methylcarbazole, m. p. 171—173°, for which Lindemann (*Ber.*, 1924, **57**, 557) gives m. p. 174°. Elution with benzene–ether (9 : 1) gave 2 : 4′-dinitrodiphenylamine in small red needles (0·11 g.) (from ethyl alcohol), having m. p. and mixed m. p. with an authentic specimen 219—220° (Found : C, 55·9; H, 3·5; N, 17·1%; *M*, 272. Calc. for $C_{12}H_9O_4N_3$: C, 55·6; H, 3·5; N, 16·3%; *M*, 259).

3-*Amino*-N-*methylcarbazole.* A suspension of Raney nickel (0·6 g.) in alcohol (3 c.c.) was added to a solution of *N*-methyl-3-nitrocarbazole (0·03 g.) in sulphur-free benzene (30 c.c.). Hydrogenation was carried out at atmospheric pressure with rapid shaking. When the hydrogen absorbed reached a constant value the Raney nickel was filtered off, the strongly fluorescent solution concentrated, and light petroleum (b. p. 60—80°) added. White needles, m. p. 171—173°, of 3-amino-*N*-methylcarbazole separated. A mixed m. p. with the starting material showed a large depression.

Grateful acknowledgement is made to British Celanese Ltd. for the award of a Studentship to R. D. M. Thanks are also accorded to Dr. S. H. Tucker for the gift of a specimen of 1-nitrocarbazole.

King's College, University of London,
Strand, London, W.C.2.

[*Received, February 26th,* 1952.]