Internuclear Cyclisation. Part IX. Abnormal Reactions of 2-Amino-*N*-methylbenzanilides containing* ortho-*Substituents.*

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Decomposition of diazonium salts prepared from 2-amino-*N*-methylbenzanilides which contain a substituent atom or group at the *meta*- or *para*-position with reference to the nitrogen atom gives rise to *N*-methylphenanthridones, but with a substituent atom or group at the *ortho*-position the reaction gives a substituted benzanilide by a process of deamination and demethylation. *N*-Methylphenanthridones have been prepared from 2-amino-*N*-methylbenzo-2′-naphthalide, 2-amino-4′-methoxycarbonyl-*N*-methylbenzanilide, and 2-amino-3′-carboxy-*N*-methylbenzanilide, but deamination and demethylation took place with 2-amino-*N*-methylbenzo-1′-naphthalide, 2-amino-2′-methoxycarbonyl-*N*-methylbenzanilide, 2-amino-2′-carboxy-*N*-methylbenzanilide, 2-amino-*N*-methylbenzo-*o*-toluidide, 2-amino-2′-chloro-*N*-methylbenzanilide, 2-amino-*N*-methyl-2′-nitrobenzanilide, 2-amino-2′ : 4′ : *N*-trimethylbenzanilide, and 2-amino-2′-ethyl-*N*-methyl-4 : 5-methylenedioxybenzanilide.

It has been shown in Parts III, VI, and VII (*J.*, 1952, 1508, 4059; 1953, 3) that diazonium salts of *o*-amino-*N*-methylbenzanilides can be readily converted into *N*-methylphenanthridones. The success so far achieved suggested that similar reactions on appropriate derivatives of benzo-1-naphthalide might provide a new approach to the synthesis of alkaloids of the chelidonine–sanguinarine group, which contain the 1 : 2-benzophenanthridine system. A somewhat similar approach was envisaged by Richardson, Robinson, and Seijo (*J.*, 1937, 835), who attempted to apply a Pschorr-type ring closure to the reduction product of the Schiff base prepared from 6-nitropiperonaldehyde and α-naphthylamine, but diazotisation afforded only a brown tar. The failure of a similar reaction was reported by Noller, Denyes, Gates, and Wasley (*J. Amer. Chem. Soc.*, 1937, **59**, 2079). Forrest, Haworth, Pinder, and Stevens (*J.*, 1949, **1311**) were unable to obtain any product from diazotised 2-amino-*N*-methyl-4 : 5-methylenedioxybenzo-1′-naphthalide, although they reported the formation of *N*-methyl-6 : 7-methylenedioxyphenanthridone in more than 50% yield by heating the diazonium sulphate prepared from 2-amino-*N*-methyl-4 : 5-methylenedioxybenzanilide.

N-Methyl-2-nitrobenzo-1′-naphthalide has now been prepared from (*a*) α-naphthylamine and *o*-nitrobenzoyl chloride with subsequent methylation and (*b*) *N*-methyl-α-naphthylamine and *o*-nitrobenzoyl chloride, and reduced catalytically to 2-amino-*N*-methylbenzo-1′-naphthalide (I). This amine was converted into the diazonium fluoroborate (cf. Part III, *loc. cit.*), which was decomposed in suspension in acetone by the addition of copper powder. From this reaction there were obtained (*a*) benzo-1-naphthalide (II), (*b*) a compound, m. p. 178—179°, and (*c*) a compound, m. p. 255—256°. In a similar decomposition of the diazonium sulphate the same three products were obtained, thus showing that the fluoroborate anion had no major influence on the products formed. Neither compound (*b*) nor compound (*c*) corresponded with the expected *N*-methyl-1 : 2-benzophenanthridone (III).

The non-formation of the phenanthridone and the unexpected appearance of benzo-1-naphthalide (II), the product of deamination and demethylation of the original 2-amino-*N*-methylbenzo-1′-naphthalide (I), suggested that a similar series of reactions on the corresponding derivatives of β-naphthylamine would be of interest. Accordingly, 2-amino-*N*-methylbenzo-2′-naphthalide (IV) was prepared in the same ways as its isomer. Decomposition of the diazonium fluoroborate prepared from it gave *N*-methyl-3 : 4-benzophenanthridone (V), together with a small amount of a compound, m. p. 180—181°.

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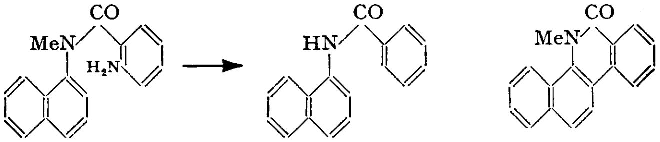
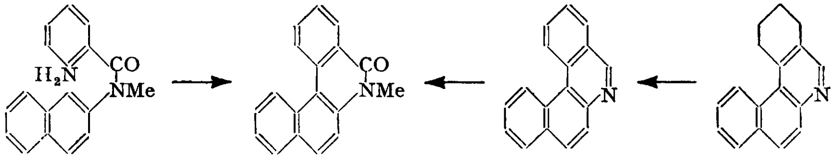
* Part VIII, *J.*, 1954, 1697.

Theoretically, this ring closure could give *N*-methyl-3 : 4- or -2 : 3-benzophenanthridone (or a mixture of both), but the identity of the product as the former was demonstrated by an independent synthesis from 5 : 6 : 7 : 8-tetrahydro-3 : 4-benzophenanthridine (VI). This compound, which had been prepared by Hollingsworth and Petrow (*J.*, 1948, 1540), was dehydrogenated to give 3 : 4-benzophenanthridine (VII), converted into its methiodide and then oxidised with potassium ferricyanide to *N*-methyl-3 : 4-benzophenanthridone (V).



(I) (II) (III)



(IV) (V) (VII) (VI)

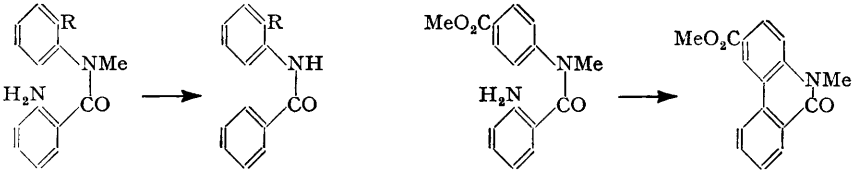
A parallel series of reactions was carried out on 2-amino-*N*-methylbenzanilides with a carboxy- or methoxycarbonyl group in the aniline nucleus. 2′-, 3′-, and 4′-Methoxycarbonyl-2-nitrobenzanilide (VIII), prepared from *o*-nitrobenzoyl chloride and the methyl ester of the appropriate aminobenzoic acid, on alkaline hydrolysis gave the corresponding carboxy-2-nitrobenzanilides (IX). The same acids were obtained from *o*-nitrobenzoyl chloride and the appropriate aminobenzoic acids (cf. Schroeter and Eisleb, ***Annalen***, 1909, **367**, 128). Methylation of the carboxynitrobenzanilides (IX) with methyl sulphate gave the corresponding carboxy-*N*-methyl-2-nitrobenzanilides (X). 2′- and 4′-Carboxy-*N*-methyl-2-nitrobenzanilide in turn were esterified with methanol and hydrogen chloride to give 2′- and 4′-methoxycarbonyl-*N*-methyl-2-nitrobenzanilide (XI). Catalytic reduction of these two esters gave 2-amino-2′- and 2-amino-4′-methoxycarbonyl-*N*-methylbenzanilide (XII). Reduction of 2′-carboxy-*N*-methyl-2-nitrobenzanilide with ammoniacal ferrous sulphate gave either 2-amino-2′-carboxy-*N*-methylbenzanilide or 2′-carboxy-2-methylaminobenzanilide, depending on the experimental conditions used. The former is converted into the latter when heated above its melting point (182°). Catalytic reduction of 4′-carboxy-*N*-methyl-2-nitrobenzanilide gave 2-amino-4′-carboxy-*N*-methylbenzanilide.

Decomposition with copper powder of the aqueous diazonium sulphate prepared from 2-amino-2′-methoxycarbonyl-*N*-methylbenzanilide (XIII; R = CO_2Me) gave (*a*) methyl *N*-benzoylanthranilate (XIV; R = CO_2Me), (*b*) a compound, m. p. 259° (decomp.), and (*c*) a compound, m. p. 197°. On the other hand, a similar reaction on 2-amino-4′-methoxycarbonyl-*N*-methylbenzanilide (XV) gave 3-methoxycarbonyl-*N*-methylphenanthridone (XVI) and a trace of a compound of m. p. 232—234°. The application of the same reaction to 2-amino-2′-carboxy-*N*-methylbenzanilide (XIII; R = CO_2H), as the diazonium chloride or sulphate, gave *N*-benzoylanthranilic acid (XIV; R = CO_2H) and a compound, m. p. 303—304°. The latter product was also obtained on hydrolysis of the compound, m. p. 197°, obtained above in the corresponding reaction with the diazonium sulphate from 2-amino-2′-methoxycarbonyl-*N*-methylbenzanilide. Decomposition of the diazonium sulphate prepared from 2-amino-4′-carboxy-*N*-methylbenzanilide gave only a highly insoluble product, m. p. 341—343°, whereas decomposition of the diazonium chloride prepared from the reduction product of 3′-carboxy-*N*-methyl-2-nitrobenzanilide gave a mixture of 2- and 4-carboxy-*N*-methylphenanthridone, together with a second compound, m. p. 320—322°.

The results thus obtained in the decomposition of the diazonium salts prepared from the carboxy- and methoxycarbonyl derivatives of 2-amino-*N*-methylbenzanilide show that when the substituent is at the *ortho*-position with reference to the nitrogen atom an abnormal reaction results which consists of a process of deamination and demethylation.

When, however, the substituent is attached to either the *meta*- or the *para*-position the normal reaction leading to phenanthridone formation takes place. These results are analogous to those reported above with derivatives of α- and β-naphthylamine.

$$\begin{tikzcd}
\underset{\text{(VIII)}}{o\text{-}NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Me} \arrow[r] & \underset{\text{(IX)}}{o\text{-}NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H} \arrow[d] \\
\underset{\text{(XI)}}{o\text{-}NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NMe{\cdot}C_6H_4{\cdot}CO_2Me} \arrow[d] & \underset{\text{(X)}}{o\text{-}NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NMe{\cdot}C_6H_4{\cdot}CO_2H} \arrow[l] \\
\underset{\text{(XII)}}{o\text{-}NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NMe{\cdot}C_6H_4{\cdot}CO_2Me} &
\end{tikzcd}$$



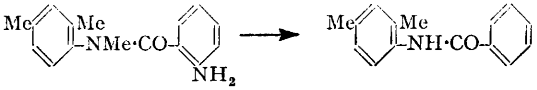
(XIII) (XIV) (XV) (XVI)

The occurrence of this abnormal reaction with *ortho*-substituted 2-amino-*N*-methylbenzanilides made it necessary to re-examine the three reactions reported in Parts VI and VII (*loc. cit.*) in which *ortho*-substituted benzanilides were used. The relevant bases are 2-amino-*N*-methylbenzo-*o*-toluidide (XIII; R = Me), 2-amino-2′-chloro-*N*-methylbenzanilide (XIII; R = Cl), and 2-amino-*N*-methyl-2′-nitrobenzanilide (XIII; R = NO_2). With the derivatives of *o*-toluidine and *o*-nitroaniline it was reported that the products were 1 : 10-dimethylphenanthridone, m. p. 141—142° (Found : C, 80·3; H, 6·1. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8%), and 10-methyl-1-nitrophenanthridone, m. p. 92—93° (Found : C, 65·5; H, 4·2. $C_{14}H_{10}O_3N_2$ requires C, 66·1; H, 3·9%) respectively. It is now shown that these two compounds are in fact benzo-*o*-toluidide (XIV; R = Me), m. p. 142—143° ($C_{14}H_{13}ON$ requires C, 79·6; H, 6·2%), and *o*-nitrobenzanilide (XIV; R = NO_2), m. p. 94° ($C_{13}H_{10}O_3N_2$ requires C, 64·5; H, 4·1%), respectively. In the decomposition of the diazonium sulphate from 2-amino-2′-chloro-*N*-methylbenzanilide (XIII; R = Cl) no phenanthridone formation was reported, but an unidentified compound, m. p. 70—75° (Found : C, 67·4; H, 4·1; Cl, 15·3%), was isolated which would now appear to be impure *o*-chlorobenzanilide (XIV; R = Cl), m. p. 99° ($C_{13}H_{10}ONCl$ requires C, 67·4; H, 4·3; Cl, 15·2%). On the other hand, the products obtained from 2-amino-*N*-methylbenzanilide substituted at the *meta*- and the *para*-positions are phenanthridones.

The apparent general character of the abnormal reaction for 2-amino-*N*-methylbenzanilides substituted at the *ortho*-position with respect to the nitrogen atom made it necessary to reinvestigate two further reactions reported by other workers. First, Chardonnens and Würmli (*Helv. Chim. Acta*, **1950**, **33**, 1340) have reported the formation of 1 : 3 : 10-trimethylphenanthridone, m. p. 194°, from the diazonium chloride prepared from 2-amino-2′ : 4′ : *N*-trimethylbenzanilide (XVII). This reaction has now been repeated and is found to give 2 : 4-dimethylbenzanilide (XVIII), m. p. 193—194°. No phenanthridone was obtained. Secondly, Kelly, Taylor, and Wiesner (*J.*, **1953**, 2094) have reported the preparation of 1-ethyl-10-methyl-6 : 7-methylenedioxyphenanthridone, in crude form as a yellow wax, from the decomposition of the diazonium sulphate prepared from 2-amino-2′-ethyl-*N*-methyl-4 : 5-methylenedioxybenzanilide (XIX). The crude phenanthridone was reduced with lithium aluminium hydride to 1-ethyl-9 : 10-dihydro-10-methyl-6 : 7-methylenedioxyphenanthridine, which gave a picrate, m. p. 175°, and was stated to be identical with dihydrolycorineanhydromethine. This reaction has been repeated, following closely the experimental conditions described by Kelly, Taylor, and Wiesner (*loc. cit.*). The sole crystalline product isolated from this reaction was 2′-ethyl-3 : 4-methylenedioxybenzanilide (XX), m. p. 143—144°, identical with an authentic specimen prepared from *o*-ethylaniline and 3 : 4-methylenedioxybenzoyl chloride. Reduction of this anilide with lithium aluminium hydride gave 2′-ethyl-3 : 4-methylenedioxybenzylaniline as an oil, which formed a picrate, m. p. 125°.

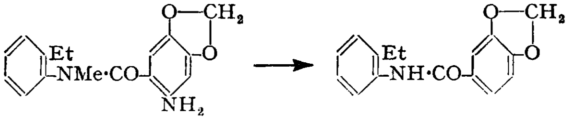
It is difficult to provide a satisfactory explanation for these two conflicting results with 2-amino-2′-ethyl-*N*-methyl-4 : 5-methylenedioxybenzanilide. In both reactions the product is isolated in small yield and much material remains unaccounted for. The 2′-ethyl-3 : 4-methylenedioxybenzanilide isolated by us sublimes unchanged at 130—150°/0·1 mm., which are the conditions used by Kelly, Taylor, and Wiesner for the isolation of 1-ethyl-10-methyl-6 : 7-methylenedioxyphenanthridone.

(XVII)



(XVIII)

(XIX)



(XX)

The conclusions reached from these investigations indicate that in the decomposition of diazonium salts prepared from 2-amino-*N*-methylbenzanilides substituted at the *ortho*-position, the normal cyclisation process leading to an *N*-methylphenanthridone is replaced by a reaction involving ***simultaneous deamination and demethylation.*** The eight substituents studied are Me, Cl, NO_2, CO_2H, CO_2Me, 2 : 4-Me_2, Et, and α-naphthyl. It is of interest that this abnormal reaction appears to be substantially independent of both the polar character of the *ortho*-substituent and the experimental conditions of the decomposition, at least as far as these have been studied. The fundamental reason for the anomalous course of the reaction with *ortho*-substituents is considered to be steric. The enforced proximity of the *N*-methyl group to the diazonium group results in the replacement of the latter by hydrogen supplied by the methyl group. Relevant to these considerations appears to be the mobility of the methyl group (*a*) in the reduction of 2′-carboxy-*N*-methyl-2-nitrobenzanilide to 2′-carboxy-2-methylaminobenzanilide reported above, (*b*) the reduction of *N*-methyl-2 : 2′-dinitrodiphenylamine to 2-methylamino-2′-nitrodiphenylamine (Hey and Mulley, *J.*, 1952, 2287), and (*c*) the formation of 2 : 4′-dinitrodiphenylamine as one of the products of decomposition of the diazonium sulphate prepared from 2-amino-*N*-methyl-2′-nitrodiphenylamine. In the last-named reaction deamination and demethylation take place, accompanied by incidental nitration at the 4′-position arising from the presence of a nitrating entity in the reaction system. None of these observations is found in the absence of a substituent group at the *ortho*-position with reference to the nitrogen atom.

EXPERIMENTAL

N-*Methyl*-2-*nitrobenzo*-1′-*naphthalide*.—(*a*) An ethereal solution of *o*-nitrobenzoyl chloride, prepared from the acid (10 g.) by Boëtius and Romisch's method (*Ber.*, 1935, **68**, 1924), was added slowly to a solution of 1-naphthylamine (10 g.) in pyridine (15 c.c.) and dry ether (40 c.c.), and the solution was boiled under reflux for 1 hr. After removal of the ether, the mixture was poured into water. Recrystallisation from alcohol (charcoal) of the brown solid which separated gave 2-*nitrobenzo*-1′-*naphthalide* (14·6 g.) in fluffy needles, m. p. 206° (Found : C, 70·0; H, 4·1. $C_{17}H_{12}O_3N_2$ requires C, 69·9; H, 4·1%). A solution of this compound (14·6 g.) in a mixture of acetone (90 c.c.) and 10% aqueous sodium hydroxide (90 c.c.) was boiled under reflux and methyl sulphate (25 c.c.) was added dropwise. The mixture was cooled and poured into 5% aqueous sodium hydroxide (600 c.c.). The solid which separated was recrystallised from benzene–light petroleum (b. p. 60—80°), to give *N*-methyl-2-nitrobenzo-1′-naphthalide (12·6 g.) in pale yellow diamond-shaped plates, m. p. 182—183° (Found : C, 70·9; H, 4·8. $C_{18}H_{14}O_3N_2$ requires C, 70·6; H, 4·6%). (*b*) *N*-Methyl-1-naphthylamine (0·5 g.) (Fischer, *Annalen*, 1895, **286**, 159) and *o*-nitrobenzoyl chloride (0·5 g.) in dry ether (40 c.c.), to which anhydrous potassium carbonate (1·5 g.) was added, were boiled under reflux for 10 min. and the ether removed. Addition of water gave a yellow solid, which on crystallisation from benzene–light petroleum

(b. p. 60—80°) gave *N*-methyl-2-nitrobenzo-1′-naphthalide (0·6 g.), m. p. 182—183°, identical with the compound prepared by method (*a*).

N-*Methyl-2-nitrobenzo-2′-naphthalide*.—(*a*) By the procedure (*a*) described above, 2-naphthylamine (10 g.) and *o*-nitrobenzoyl chloride (from 10 g. of acid) gave *2-nitrobenzo-2′-naphthalide* (12·5 g.) in needles, m. p. 178—179°, from alcohol (charcoal) (Found: C, 70·0; H, 4·1%). Methylation of this compound (10·8 g.), as in the preceding example, gave N-*methyl-2-nitrobenzo-2′-naphthalide* (7·1 g.) in pale yellow prisms, m. p. 110—111°, from benzene–light petroleum (b. p. 40—60°), which darkened on exposure to light (Found: C, 70·6; H, 4·7%). (*b*) A solution of *N*-toluene-*p*-sulphon-2-naphthalide (21·3 g.) (Morgan and Micklethwait, *J.*, 1912, **101**, 148) in 5% aqueous sodium hydroxide (400 c.c.) was heated to 70—80° and methyl sulphate (28 c.c.) was added in small portions to the solution which was heated for a further 15 min. A solid separated, which crystallised from alcohol to give *N*-methyl-*N*-toluene-*p*-sulphon-2-naphthalide (20·5 g.) in small needles, m. p. 72—77°. Morgan and Micklethwait (*loc. cit.*) recorded m. p. 77—78° for this compound, prepared by the action of methyl iodide on *N*-toluene-*p*-sulphon-2-naphthalide in alcoholic potassium hydroxide. The sulphonamide (20·5 g.) was warmed for 1 hr. with a mixture of concentrated sulphuric acid (25 c.c.) and glacial acetic acid (15 c.c.), cooled, and poured into water. The addition of aqueous sodium hydroxide gave a brown oil, which was extracted with benzene, and hydrogen chloride was passed into the dried ($CaCl_2$) solution. A solid separated, which on recrystallisation from alcohol saturated with hydrogen chloride, gave *N*-methyl-2-naphthylamine hydrochloride (8 g.), m. p. 176—180°. Pschorr and Karo (*Ber.*, 1906, **39**, 3141) recorded m. p. 182—183°. An ethereal solution of *o*-nitrobenzoyl chloride (from 2 g. of acid) was added slowly to *N*-methyl-2-naphthylamine hydrochloride (2 g.) dissolved in pyridine (10 c.c.) to which sodium acetate (1 g.) had been added, and the mixture was boiled under reflux for 30 min. Removal of the ether and addition of water gave a viscous red oil, which was dissolved in chloroform and washed with hydrochloric acid, water, and finally aqueous sodium carbonate. Removal of the chloroform left an oil, which was dissolved in benzene and allowed to stand. *N*-Methyl-2-nitrobenzo-2′-naphthalide (2·3 g.) separated, having m. p. 110°, identical with the compound prepared by method (*a*) above.

2-*Amino*-N-*methylbenzo-1′-naphthalide*.—A solution of *N*-methyl-2-nitrobenzo-1′-naphthalide (8·6 g.) in benzene (400 c.c.) and a suspension of Raney nickel (9 g.) in the same solvent were shaken with hydrogen at atmospheric pressure until the required quantity of hydrogen had been absorbed. Removal of the Raney nickel by filtration, and concentration of the filtrate, gave a solid, which on crystallisation from benzene–light petroleum (b. p. 60—80°) gave 2-*amino*-N-*methylbenzo-1′-naphthalide* (6·6 g.) in rectangular prisms, m. p. 144° (Found: C, 78·1; H, 5·8. $C_{18}H_{16}ON_2$ requires C, 78·3; H, 5·8%).

2-*Amino*-N-*methylbenzo-2′-naphthalide*.—A suspension of iron filings (50 g.) in 5% aqueous acetic acid (110 c.c.) was heated and stirred until hydrogen ceased to be evolved. The nitro-compound (11·5 g.) was added slowly and the mixture boiled for 1 hr. It was made alkaline with aqueous sodium carbonate, a little animal charcoal added, and the solution filtered whilst hot. Both filtrate and residue were repeatedly extracted with hot benzene. The combined extracts were concentrated, and crystallisation of the product from benzene–light petroleum (b. p. 60—80°) gave 2-*amino*-N-*methylbenzo-2′-naphthalide* (7·7 g.) in prisms, m. p. 108° (Found: C, 78·7; H, 5·9%).

Decomposition of the Diazonium Fluoroborate prepared from 2-*Amino*-N-*methylbenzo-1′-naphthalide*.—The amine (3·5 g.) was diazotised in concentrated hydrochloric acid (15 c.c.) and water (30 c.c.) with sodium nitrite (4 g.) in water (15 c.c.). The diazonium chloride separated as an orange solid, and was redissolved by the addition of water (250 c.c.). To the filtered solution, cooled to 0°, sodium fluoroborate (5 g.) in water (15 c.c.) was added slowly with stirring, and the yellow diazonium fluoroborate which separated was collected and dried *in vacuo* overnight. Copper powder (4 g.) was added to a suspension of the dry fluoroborate (4·6 g.) in "AnalaR" acetone (200 c.c.). There was an immediate evolution of nitrogen, and the mixture was allowed to stand for 2 hr. and then warmed on a water-bath. The mixture was filtered into water, and the residue extracted with hot acetone and boiling water. The combined aqueous and acetone solutions were extracted with chloroform, and the extract was washed with 10% aqueous sodium hydroxide. Concentration of the dried (Na_2SO_4) chloroform solution gave a brown glass-like resin (3·2 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (1 : 1) and adsorbed on an alumina column (90 g.). Elution with the same solvent (430 c.c.) gave benzo-1-naphthalide (0·23 g.) in fluffy needles, m. p. 161°, from alcohol. There was no depression of m. p. on admixture with an authentic specimen. Further elution with the same solvent (360 c.c.) gave a second product in rectangular plates (0·18 g.), m. p. 178—179°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 78·5, 78·9; H, 4·7, 4·8; N, 6·5%; *M*, 209). Elution with benzene–light petroleum (2 : 1) (1300 c.c.) and then with benzene–light petroleum (4 : 1) (300 c.c.) gave a third product in plates (0·4 g.), m. p. 255—256°, from benzene (Found: C, 84·0; H, 5·7; N, 6·5%; *M*, 352, 401). Further elution with benzene, benzene–ether (1 : 1), and then ether (180 c.c.) gave a yellow solid resin (1·3 g.) which could not be recrystallised. Acidification of the alkaline extract gave only a trace of tar.

Decomposition of the Diazonium Sulphate prepared from 2-*Amino*-N-*methylbenzo*-1′-*naphthalide*.—A solution of the amine (2·5 g.) in acetic acid (25 c.c.) was diazotised with nitrososulphuric acid made by the addition of sodium nitrite (3 g.) to concentrated sulphuric acid (15 c.c.) and subsequent removal of sodium hydrogen sulphate by filtration through glass wool (Hodgson and Mahadevan, *J.*, 1947, 325). The mixture was poured into ice-cold ether (400 c.c.); the diazonium sulphate separated as a yellow solid, which was washed with acetic acid–ether, and then with ether. The diazonium sulphate was decomposed under "AnalaR" acetone (200 c.c.) with copper powder (3 g.), and the products were worked up as described above. A brown resin (1·7 g.) was obtained from the chloroform extract, which was dissolved in benzene–light petroleum (3 : 1) (200 c.c.) and adsorbed on alumina (60 g.). Elution with the same solvent (510 c.c.) gave benzo-1-naphthalide (0·09 g.) in needles, m. p. 161°, from alcohol. Further elution with the same solvent (390 c.c.) gave a second product in rectangular plates (0·06 g.), m. p. 178—179°, from benzene–light petroleum, identical with the compound, m. p. 178—179°, isolated above. Elution with benzene–light petroleum (3 : 1) (200 c.c.) and then with benzene–ether (3 : 1) (180 c.c.) gave a third product in plates (0·1 g.), m. p. 255—256°, from benzene, identical with the compound, m. p. 255—256°, previously isolated. Further elution with benzene–ether mixtures and finally with ether yielded only brown tars. A trace of tar was obtained on acidification of the alkaline extract.

Decomposition of the Diazonium Fluoroborate prepared from 2-*Amino*-N-*methylbenzo*-2′-*naphthalide*.—The amine (4 g.) was diazotised in a mixture of concentrated hydrochloric acid (20 c.c.) and water (60 c.c.) with sodium nitrite (4 g.) in water (15 c.c.). Addition of sodium fluoroborate (4 g.) in water (20 c.c.) gave the solid yellow diazonium fluoroborate, which was unstable and began to redden on being washed with water. It was therefore immediately decomposed under "AnalaR" acetone (150 c.c.) with copper powder (4 g.), and the products were worked up as described above. A brown gum (3·6 g.) was obtained from the chloroform extract, which was dissolved in benzene–light petroleum (1 : 1) (200 c.c.) and adsorbed on alumina (90 g.). Elution with benzene–light petroleum (1 : 1) (200 c.c.), (2 : 1) (180 c.c.), and (3 : 1) (400 c.c.) gave a product as rectangular prisms (0·08 g.), m. p. 180—181°, from benzene (Found: C, 71·0; H, 4·8%). Elution with benzene (500 c.c.) gave N-*methyl*-3 : 4-*benzophenanthridone* (0·2 g.) in fluffy needles, m. p. 198—199°, from alcohol (Found: C, 83·0; H, 5·2. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·0%). Further elution with benzene–ether (1 : 1) (520 c.c.) gave tars. Acidification of the alkaline extract gave a small amount of tar.

3 : 4-*Benzophenanthridine*.—(*a*) 5 : 6 : 7 : 8-Tetrahydro-3 : 4-benzophenanthridine (1·5 g.), prepared by the method of Hollingsworth and Petrow (*J.*, 1948, 1540), was heated with selenium powder (1·5 g.) for 6 hr. at 280—310°. The product was extracted with benzene, passed through an alumina column (50 g.), and eluted with benzene (400 c.c.). Removal of the benzene gave a brown oil from which crystals gradually separated. Recrystallisation of the solid from light petroleum (b. p. 60—80°) (charcoal) afforded 3 : 4-*benzophenanthridine* (0·2 g.) in needles, m. p. 110° (Found: C, 89·1; H, 4·8. $C_{17}H_{11}N$ requires C, 88·8; H, 4·9%). Kenner, Ritchie, and Wain (*J.*, 1937, 1526), who incorrectly described this compound as 3 : 4-benzacridine, recorded m. p. 106°. (*b*) 5 : 6 : 7 : 8-Tetrahydro-3 : 4-benzophenanthridine (0·5 g.) was heated with a platinum–charcoal catalyst (0·1 g.) at 280° for 2 hr. Extraction with benzene and purification as described above gave 3 : 4-benzophenanthridine (0·2 g.) in needles, m. p. 110°, identical with the specimen prepared by method (*a*).

N-*Methyl*-3 : 4-*benzophenanthridone*.—3 : 4-Benzophenanthridine (0·2 g.) and an excess of methyl iodide gave 3 : 4-benzophenanthridine methiodide (0·3 g.) as a yellow powder. To a suspension of the methiodide in a mixture of methanol (20 c.c.) and 10% aqueous sodium hydroxide (20 c.c.), an excess of alkaline potassium ferricyanide solution was added and the mixture was boiled for 20 min. and cooled. The suspended solid was collected. Extraction with alcohol left a yellow solid, m. p. 230—240°. From the alcoholic extract *N*-methyl-3 : 4-benzophenanthridone, m. p. 195—198°, was obtained, which showed no depression on admixture with the compound prepared as above from the diazonium fluoroborate prepared from 2-amino-*N*-methylbenzo-2′-naphthalide.

2′-*Methoxycarbonyl*-2-*nitrobenzanilide*.—By the procedure described above for the preparation of 2-nitrobenzo-1′-naphthalide, methyl anthranilate (13·7 g.) and *o*-nitrobenzoyl chloride (from 14 g. of acid) in the presence of pyridine (10 g.) and ether (150 c.c.) gave 2′-*methoxycarbonyl*-2-*nitrobenzanilide* (20·5 g.) in prisms, m. p. 160°, from benzene (Found: C, 59·8; H, 4·3. $C_{15}H_{12}O_5N_2$ requires C, 60·0; H, 4·0%).

3′-*Methoxycarbonyl*-2-*nitrobenzanilide*.—By the same procedure methyl *m*-aminobenzoate (9·8 g.) and *o*-nitrobenzoyl chloride (from 10 g. of acid) gave 3′-*methoxycarbonyl*-2-*nitrobenzanilide* (13·6 g.) in shining plates, m. p. 175—176°, from methanol (charcoal) (Found: C, 59·9; H, 4·1%).

4′-*Methoxycarbonyl*-2-*nitrobenzanilide* was similarly obtained from methyl *p*-aminobenzoate (9·5 g.) and *o*-nitrobenzoyl chloride (from 10 g. of acid) in needles (14·7 g.), m. p. 166—167°, from methanol (Found: C, 59·7; H, 3·9%).

2′-*Carboxy*-2-*nitrobenzanilide*.—(*a*) Anthranilic acid (15 g.), dissolved in 2N-aqueous sodium hydroxide (150 c.c.), and *o*-nitrobenzoyl chloride (from 18·4 g. of acid) in ether (75 c.c.) gave, by Schroeter and Eisleb's method (*Annalen*, 1909, **367**, 101), 2′-carboxy-2-nitrobenzanilide (14·5 g.) in prisms, m. p. 238—239°, from alcohol. Schroeter and Eisleb (*loc. cit.*) record m. p. 234°. (*b*) 2′-Methoxycarbonyl-2-nitrobenzanilide (28 g.) was boiled under reflux for 2 hr. with 4% aqueous sodium hydroxide (200 c.c.). Acidification gave a white solid which on crystallisation from alcohol afforded 2′-carboxy-2-nitrobenzanilide (25·2 g.) in prisms, m. p. 238—239°, identical with the product prepared by method (*a*).

3′-*Carboxy*-2-*nitrobenzanilide*.—(*a*) In similar manner *m*-aminobenzoic acid (10 g.) in 2N-aqueous sodium hydroxide (100 c.c.) and *o*-nitrobenzoyl chloride (from 12·3 g. of acid) in ether (50 c.c.) gave 3′-*carboxy*-2-*nitrobenzanilide* (10·5 g.) in fluffy needles, m. p. 262—264°, from alcohol (Found: C, 58·4; H, 3·9. $C_{14}H_{10}O_5N_2$ requires C, 58·7; H, 3·7%). (*b*) 3′-Methoxycarbonyl-2-nitrobenzanilide (5 g.) was hydrolysed with 4% aqueous sodium hydroxide (100 c.c.) to 3′-carboxy-2-nitrobenzanilide (4·2 g.), m. p. 262—264°, identical with the specimen prepared by method (*a*).

4′-*Carboxy*-2-*nitrobenzanilide*.—(*a*) Similarly *p*-aminobenzoic acid (27 g.) and *o*-nitrobenzoyl chloride (from 33 g. of acid) gave 4′-*carboxy*-2-*nitrobenzanilide* (25 g.) in small shining plates, m. p. 303—304°, from nitrobenzene (Found: C, 58·9; H, 3·3%). (*b*) Hydrolysis of 4′-methoxycarbonyl-2-nitrobenzanilide (20 g.) gave the same acid (16·5 g.), m. p. 303—304°.

2′-*Carboxy*-N-*methyl*-2-*nitrobenzanilide*.—A solution of 2′-carboxy-2-nitrobenzanilide (22 g.) in 8% aqueous sodium hydroxide (200 c.c.) was allowed to stand with methyl sulphate (18 g.) at room temperature for 30 hr. with occasional shaking. Acidification precipitated 2′-carboxy-*N*-methyl-2-nitrobenzanilide (18·5 g.), which separated from alcohol in needles, m. p. 217—218°. Schroeter and Eisleb (*loc. cit.*) recorded m. p. 216°.

3′-*Carboxy*-N-*methyl*-2-*nitrobenzanilide*.—Methylation of 3′-carboxy-2-nitrobenzanilide (10 g.), as described in the preceding reaction, gave 3′-*carboxy*-N-*methyl*-2-*nitrobenzanilide* (5·5 g.) in yellow prisms, m. p. 176—177°, from ethyl acetate (charcoal) (Found: C, 59·7; H, 4·0. $C_{15}H_{12}O_5N_2$ requires C, 60·0; H, 4·0%).

4′-*Carboxy*-N-*methyl*-2-*nitrobenzanilide*.—On methylation 4′-carboxy-2-nitrobenzanilide (15 g.) gave 4′-*carboxy*-N-*methyl*-2-*nitrobenzanilide* (10 g.) in small fluffy needles, m. p. 227°, from alcohol (Found: C, 60·2; H, 4·0%).

2′-*Methoxycarbonyl*-N-*methyl*-2-*nitrobenzanilide*.—2′-Carboxy-*N*-methyl-2-nitrobenzanilide (16 g.) in methanol (80 c.c.), saturated with dry hydrogen chloride, was boiled under reflux for 2 hr. The mixture was cooled and poured into water (400 c.c.). The solid obtained was washed with sodium carbonate solution, and recrystallised from methanol to give 2′-methoxycarbonyl-*N*-methyl-2-nitrobenzanilide (13·4 g.) in clusters of stout needles, m. p. 116—117°. Schroeter and Eisleb (*loc. cit.*) recorded m. p. 117°.

4′-*Methoxycarbonyl*-N-*methyl*-2-*nitrobenzanilide*, similarly prepared from the acid (15 g.), formed colourless prisms (10·2 g.), m. p. 93—94°, from methanol (charcoal) (Found: C, 61·1; H, 4·6. $C_{16}H_{14}O_5N_2$ requires C, 61·1; H, 4·5%).

2-*Amino*-2′-*methoxycarbonyl*-N-*methylbenzanilide*.—A solution of 2′-methoxycarbonyl-*N*-methyl-2-nitrobenzanilide (7 g.) in benzene (150 c.c.) and a suspension of Raney nickel (7 g.) in the same solvent were shaken with hydrogen at atmospheric pressure until the required quantity of hydrogen had been absorbed. The Raney nickel was removed by filtration, and the solution concentrated. Addition of light petroleum (b. p. 40—60°) gave 2-*amino*-2′-*methoxycarbonyl*-N-*methylbenzanilide* (5·0 g.), which crystallised from benzene–light petroleum (b. p. 60—80°) in clusters of needles m. p. 88—89° (Found: C, 67·5; H, 5·9. $C_{16}H_{16}O_3N_2$ requires C, 67·6; H, 5·6%).

*2-Amino-4′-methoxycarbonyl-*N*-methylbenzanilide.*—4′-Methoxycarbonyl-*N*-methyl-2-nitrobenzanilide (6·7 g.) was reduced in benzene (150 c.c.) with Raney nickel as described above. *2-Amino-4′-methoxycarbonyl-*N*-methylbenzanilide* (6·5 g.) crystallised from benzene–light petroleum (b. p. 60—80°) in clusters of needles, m. p. 103—104°, which contain half a molecule of benzene of crystallisation (Found: C, 70·4; H, 6·0. $C_{16}H_{16}O_3N_2,\frac{1}{2}C_6H_6$ requires C, 70·6; H, 5·9%). The benzene of crystallisation can be removed by a recrystallisation from methyl alcohol without any change in m. p.

*Reduction of 2′-Carboxy-*N*-methyl-2-nitrobenzanilide.*—(*a*) A solution of 2′-carboxy-*N*-methyl-2-nitrobenzanilide (1·5 g.) in an excess of aqueous ammonia was added to a boiling solution of ferrous sulphate (10 g.) in water (100 c.c.) with vigorous stirring. Ammonia (90 c.c.; *d* 0·88) was added slowly while the mixture was boiled for 20 min. The mixture was filtered hot, and acidified with acetic acid to give a clear solution, a portion of which gave a brilliant red dye when diazotised and coupled with alkaline β-naphthol. Evaporation of the solution almost to dryness gave a yellow solid, which afforded a compound regarded as *2′-carboxy-2-methylaminobenzanilide* (0·9 g.) in yellow diamond-shaped prisms, m. p. 234—235° (decomp.), from alcohol (Found: C, 66·3; H, 5·0. $C_{15}H_{14}O_3N_2$ requires C, 66·7; H, 5·2%). (*b*) 2′-Carboxy-*N*-methyl-2-nitrobenzanilide (1·5 g.) was reduced as described above. After filtration, the solution was made strongly alkaline with ammonia, and the ammoniacal solution evaporated almost to dryness. Addition of acetic acid gave a light-brown solid which on crystallisation from alcohol (charcoal) gave *2-amino-2′-carboxy-*N*-methylbenzanilide* (0·8 g.) in prisms, m. p. 182° (decomp.) (Found: C, 66·4; H, 5·3. $C_{15}H_{14}O_3N_2$ requires C, 66·7; H, 5·2%). The compound melts at 182° and then resolidifies to a yellow solid, m. p. 229—234°, which on recrystallisation from alcohol gives the product prepared by method (*a*) above (m. p. 234—235°). Schroeter and Eisleb (*loc. cit.*) prepared 2-amino-2′-carboxy-*N*-methylbenzanilide by the hydrolysis of 2-benzenesulphonamido-2′-carboxy-*N*-methylbenzanilide, and record yellowish crystals (from alcohol) which melt at 170° when heated quickly. They state incorrectly that the amine decomposes into methyldianthranilide, m. p. 259°. (*c*) 2′-Carboxy-*N*-methyl-2-nitrobenzanilide (2 g.) was reduced as described above. The filtered solution was acidified with acetic acid, and an excess of aqueous copper sulphate was added. The copper salt of the amino-acid separated in small green needles (1·5 g.), which were stirred with sodium hydroxide (0·5 g.) in water (10 c.c.); the cupric hydroxide was then removed by filtration. Addition of acetic acid to the filtrate gave 2-amino-2′-carboxy-*N*-methylbenzanilide (1 g.), m. p. 182° (decomp.), from alcohol.

*2-Amino-4′-carboxy-*N*-methylbenzanilide.*—4′-Carboxy-*N*-methyl-2-nitrobenzanilide (4·5 g.) was suspended in ethyl acetate (150 c.c.) and the minimum amount of alcohol to dissolve it was added. A suspension of Raney nickel (5 g.) in ethyl acetate was added, and the mixture was shaken with hydrogen at atmospheric pressure until the required quantity of hydrogen had been absorbed. Removal of the Raney nickel and concentration of the solution gave a yellow residue, which on recrystallisation from ethyl acetate afforded *2-amino-4′-carboxy-*N*-methylbenzanilide* (1·8 g.) in prisms, m. p. 195—196° (Found: C, 66·4; H, 5·1%).

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-2′-methoxycarbonyl-*N*-methylbenzanilide.*—The amine (6·65 g.) in a mixture of concentrated sulphuric acid (6 c.c.) and water (100 c.c.) was diazotised with sodium nitrite (2 g.) in water (20 c.c.). The solution was diluted with water (280 c.c.), copper powder (7 g.) added, and the mixture stirred for 36 hr. at room temperature. Nitrogen was freely evolved. The mixture was filtered, and both filtrate and residue repeatedly extracted with hot chloroform. Removal of the chloroform from the dried (Na_2SO_4) extract left a brown gum (6·0 g.) which was extracted with benzene (200 c.c.). A buff powder (1·15 g.) remained undissolved, which on recrystallisation from a large volume of methanol (charcoal) gave small prisms (0·72 g.), m. p. 259° (decomp.) (Found: C, 63·1; H, 4·8%). The benzene solution was concentrated and adsorbed on an alumina column (35 × 2 cm.). Elution with the same solvent (200 c.c.) gave needles (0·92 g.), which on crystallisation from light petroleum (b. p. 60—80°) gave methyl *N*-benzoylanthranilate (0·76 g.) in clusters of needles, m. p. and mixed m. p. 101° (Found: C, 70·7; H, 5·1; N, 5·6. Calc. for $C_{15}H_{13}O_3N$: C, 70·6; H, 5·1; N, 5·5%). Further elution with benzene (1080 c.c.) gave yellow gums. Elution with benzene–ether (1 : 1) (220 c.c.), ether (250 c.c.), and methanol (300 c.c.) gave a yellow product (1·52 g.), which crystallised from methanol in almost colourless prisms (1·08 g.), m. p. 197° (Found: C, 69·2; H, 5·5%; *M*, 392).

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-4′-methoxycarbonyl-*N*-methylbenzanilide.*—The amine (4·8 g.) was diazotised in a mixture of concentrated sulphuric acid (6 c.c.) and water (150 c.c.) with sodium nitrite (2 g.) in water (20 c.c.). The solution was diluted with water (330 c.c.), and the decomposition effected at room temperature with copper powder

(7 g.). The reaction mixture, worked up as in the previous experiment, gave a brown gum (4·56 g.), which was extracted with hot benzene (200 c.c.) and adsorbed on alumina (33 × 2 cm.). Elution with the same solvent (195 c.c.) gave a yellow gum. Further elution with benzene (475 c.c.) gave a solid (1·02 g.), which on recrystallisation from benzene gave 3-*methoxycarbonyl*-N-*methylphenanthridone* (0·72 g.) in needles, m. p. 223—224° (Found: C, 71·8; H, 4·7. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9%). Further elution with benzene (300 c.c.) and then benzene–ether (3 : 1) (320 c.c.) gave yellow gums. Elution with methanol (405 c.c.) gave a dark red gum (1·1 g.), which crystallised from chloroform–acetone in fine needles (0·09 g.), m. p. 232—234°.

*Decomposition of the Diazonium Chloride prepared from 2-Amino-2′-carboxy-*N*-methylbenzanilide.*—A solution of the amine (2·4 g.) in concentrated hydrochloric acid (6 c.c.) and water (30 c.c.) was diazotised with sodium nitrite (2·5 g.) in water (15 c.c.). Urea (2·0 g.) was added to decompose the excess of nitrous acid, and the solution diluted with water (255 c.c.). Copper powder (3 g.) was added and the mixture stirred for 48 hr. at room temperature. The green organic copper salt which had separated was decomposed by the addition of an excess of aqueous sodium hydroxide. Cupric hydroxide and copper powder were removed from the mixture by filtration, and the residue on extraction with chloroform yielded no organic material. Acidification of the filtrate with hydrochloric acid gave a light-brown solid (1·51 g.), extraction of which with alcohol left a yellow powder (0·87 g.), m. p. 295—298° (decomp.), which was almost insoluble in all organic solvents. The solid was dissolved in aqueous sodium hydroxide, filtered, reprecipitated with acetic acid, and washed with several solvents. The product was obtained as a pale yellow powder (0·53 g.), which melted at 303—304° and immediately resolidified in long needles, which did not melt below 350° (Found: C, 69·3, 69·0; H, 4·9, 4·8%). The alcohol was removed from the extract, and the residue dissolved in light petroleum (b. p. 60—80°)–alcohol (3 : 1) and adsorbed on silica gel (10 × 2 cm.; 15 g.). Elution with the same solvent (120 c.c.) gave a brown gum (0·4 g.), which crystallised from ethyl acetate–light petroleum (b. p. 60—80°) to give *N*-benzoylanthranilic acid (0·07 g.) in needles, m. p. and mixed m. p. 183—184° (Found: C, 69·4; H, 4·8. Calc. for $C_{14}H_{11}O_3N$: C, 69·7; H, 4·6%). Further elution gave tars.

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-2′-carboxy-*N*-methylbenzanilide.*—A solution of the amine (2·4 g.) in concentrated sulphuric acid (5 c.c.) and water (30 c.c.) was diazotised with sodium nitrite (0·9 g.) in water (10 c.c.). The decomposition and purification of the products was carried out as described above for the diazonium chloride. *N*-Benzoylanthranilic acid, m. p. 183—184° (0·05 g.), was obtained. A pale yellow acidic substance (0·56 g.) was also obtained, m. p. 303—304° (decomp.), identical with the product isolated above. Hydrolysis of the compound of m. p. 197°, obtained in the decomposition of the diazonium sulphate from 2-amino-2′-methoxycarbonyl-*N*-methylbenzanilide (see above), gave a product, m. p. 303—304° (decomp.), identical with the acid, m. p. 303—304° (decomp.).

*Decomposition of the Diazonium Chloride prepared from the Reduction Product of 3′-Carboxy-*N*-methyl-2-nitrobenzanilide.*—A solution of 3′-carboxy-*N*-methyl-2-nitrobenzanilide (7 g.) in ethyl acetate and a suspension of Raney nickel (8 g.) under the same solvent were shaken with hydrogen until the theoretical quantity had been absorbed. Removal of the Raney nickel and concentration of the solution left an oil. Addition of light petroleum (b. p. 60—80°) gave a semi-solid (5 g.), which could not be recrystallised but gave a brilliant red dye on diazotisation and coupling with alkaline β-naphthol. The impure amine (5·0 g.) was diazotised in a mixture of concentrated hydrochloric acid (7 c.c.) and water (30 c.c.) with sodium nitrite (3·5 g.) in water (15 c.c.). A solid (1·0 g.) remained undissolved, which was removed by filtration and shown to be 3′-carboxy-*N*-methyl-2-nitrobenzanilide. The diazonium chloride solution was diluted with water (350 c.c.), and urea (3 g.) was added. The decomposition was effected by stirring the solution with copper powder (4 g.) for 48 hr. at room temperature. An excess of aqueous sodium hydroxide was added, and the mixture filtered. Acidification of the filtrate gave a brown solid, which was thoroughly extracted with light petroleum (b. p. 60—80°)–alcohol (4 : 1) (150 c.c.). A dark brown substance (0·43 g.) remained, which on recrystallisation from glacial acetic acid gave needles (0·21 g.) which shrank at 316° and melted at 320—322° (Found: C, 70·0, 70·1; H, 4·5, 4·5%). The light petroleum–alcohol solution was passed on to a silica gel column (25 × 2 cm.). Elution with the same solvent (150 c.c.) gave a brown solid (0·41 g.) which could not be purified. Further elution with the same solvent (230 c.c.) gave a buff solid (1·28 g.), which crystallised from glacial acetic acid to give a mixture of 2- and 4-carboxy-*N*-methylphenanthridone (0·72 g.) in needles, m. p. 260—272° (Found: C, 70·6; H, 4·4. Calc. for $C_{15}H_{11}O_3N$: C, 71·1; H, 4·4%).

Decomposition of the Diazonium Sulphate prepared from 2-*Amino*-4′-*carboxy*-N-*methylbenzanilide*.—A solution of the amine (2·36 g.) in concentrated sulphuric acid (5 c.c.) and water (30 c.c.) was diazotised with sodium nitrite (1 g.) in water (10 c.c.). The decomposition was carried out with copper powder (3 g.) as described above for the 2′-isomer, and the products were worked up in the same manner. An off-white solid (1·81 g.) was obtained from the acidified filtrate. Extraction of the solid with alcohol left a brown residue (0·51 g.). This *product* crystallised from nitrobenzene in needles (0·37 g.), which decomposed about 290° without melting and melted at 341—343° [Found: C, 70·7; H, 4·3; N, 5·3. $C_{30}H_{24}O_6N_2$ (dimeride) requires C, 70·9; H, 4·7; N, 5·5%]. The alcohol was removed from the filtrate and the residue dissolved in light petroleum–alcohol (4 : 1) (200 c.c.) and adsorbed on silica gel (28 × 2 cm.). Elution with light petroleum–alcohol mixtures gave no pure products.

2′ : 4′ : N-*Trimethyl*-2-*nitrobenzanilide*.—A solution of 2 : 4-dimethylaniline (11 g.) in pyridine (15 c.c.) and ether (150 c.c.) was condensed with *o*-nitrobenzoyl chloride (from 15 g. of acid) in ether (100 c.c.) to give 2′ : 4′-*dimethyl*-2-*nitrobenzanilide* (14·8 g.) in white rosettes, m. p. 163—164°, from alcohol (charcoal) (Found: C, 66·9; H, 5·2. $C_{15}H_{14}O_3N_2$ requires C, 66·7; H, 5·2%). A solution of 2′ : 4′-dimethyl-2-nitrobenzanilide (7·5 g.) in a mixture of acetone (100 c.c.) and 10% aqueous sodium hydroxide (100 c.c.) was methylated with methyl sulphate (15 g.) as described above for *N*-methyl-2-nitrobenzo-1′-naphthalide to give 2 : 4′ : N-*trimethyl*-2-*nitrobenzanilide* (5·5 g.) in needles, m. p. 126—127° after recrystallisation from benzene–light petroleum (b. p. 60—80°) (Found: C, 68·0; H, 5·6. $C_{16}H_{16}O_3N_2$ requires C, 68·2; H, 5·6%).

2-*Amino*-2′ : 4′ : N-*trimethylbenzanilide*.—A solution of the nitro-compound (4·5 g.) in benzene (150 c.c.) and a supension of Raney nickel (5 g.) in the same solvent (50 c.c.) were shaken with hydrogen until the required quantity had been absorbed. The Raney nickel was removed by filtration, and tbe benzene solution extracted with concentrated hydrochloric acid (50 c.c.). Evaporation of the hydrochloric acid extract to small bulk gave 2-amino-2′ : 4′ : *N*-trimethylbenzanilide hydrochloride in shining plates, m. p. 120—130° (Found: Cl, 12·1; N, 9·9. Calc. for $C_{15}H_{18}ON_2$,HCl: Cl, 12·2; N, 9·6%). Chardonnens and Würmli (*Helv. Chim. Acta*, 1950, **33**, 1344), who prepared this compound by hydrolysis of the toluene-*p*-sulphonyl derivative and treatment of the product with hydrochloric acid, recorded an indefinite m. p.

Decomposition of the Diazonium Chloride prepared from 2-*Amino*-2′ : 4′ : N-*trimethylbenzanilide*.—The amine hydrochloride (3·5 g.) in concentrated hydrochloric acid (5 c.c.) and water (35 c.c.) was diazotised with sodium nitrite (0·75 g.) in water (15 c.c.). Copper powder (3 g.) was added and the mixture was stirred at room temperature overnight. The mixture was filtered, and both residue and filtrate were repeatedly extracted with chloroform. The chloroform extracts were washed with 5% aqueous sodium hydroxide and dried (Na_2SO_4). Removal of the chloroform left a brown gum, which was dissolved in benzene (60 c.c.) and adsorbed on alumina (20 × 2 cm.). Elution with benzene (600 c.c.) gave 2′ : 4′-dimethylbenzanilide (0·24 g.) in shining needles (from alcohol), m. p. and mixed m. p. 193—194° (Found: C, 80·0; H, 6·7. Calc. for $C_{15}H_{15}ON$: C, 80·0; H, 6·7%). Chardonnens and Würmli (*loc. cit.*), who described this compound as 1 : 3 : 10(*N*)-trimethylphenanthridone, reported m. p. 194°. Further elution with different solvents gave gums which could not be crystallised.

2-*Amino*-2′-*ethyl*-N-*methyl*-4 : 5-*methylenedioxybenzanilide*.—*o*-Ethyl-*N*-methylaniline (3·5 g.), prepared from *o*-ethylformanilide (Kelly, Taylor, and Wiesner, *J.*, 1953, 2094), in ether (150 c.c.), was boiled under reflux for 2 hr. with 4 : 5-methylenedioxy-2-nitrobenzoyl chloride (from 5·5 g. of acid) in the presence of anhydrous potassium carbonate (6 g.). Removal of the ether and addition of water gave a brown solid, which was dissolved in benzene and purified on an alumina column by elution with benzene. A pale yellow solid was obtained, which on crystallisation from benzene–light petroleum (b. p. 60—80°) gave 2′-ethyl-*N*-methyl-4 : 5-methylenedioxy-2-nitrobenzanilide (5·6 g.) in pale yellow needles, m. p. 97—98°. Kelly, Taylor, and Wiesner (*loc. cit.*) recorded m. p. 106°. A solution of the nitro-compound (5·2 g.) in benzene (60 c.c.) was reduced with Raney nickel (5 g.) under benzene (100 c.c.) by shaking the mixture with hydrogen to give 2-amino-2′-ethyl-*N*-methyl-4 : 5-methylenedioxybenzanilide (4·1 g.) in shining plates, m. p. 121°, from benzene–light petroleum (b. p. 60—80°). Kelly, Taylor, and Wiesner (*loc. cit.*) recorded m. p. 121°.

2′-*Ethyl*-3 : 4-*methylenedioxybenzanilide*.—A solution of *o*-ethylaniline (3·6 g.) in ether (200 c.c.) and pyridine (10 c.c.) was condensed with 3 : 4-methylenedioxybenzoyl chloride (4·6 g.) to give 2′-*ethyl*-3 : 4-*methylenedioxybenzanilide* (5·8 g.) in shining needles, m. p. 143—144°, from alcohol–light petroleum (b. p. 60—80°) (Found: C, 71·8; H, 5·5. $C_{16}H_{15}O_3N$ requires C, 71·4; H, 5·6%).

Decomposition of the Diazonium Sulphate prepared from 2-*Amino*-2′-*ethyl*-N-*methyl*-4 : 5-*methylenedioxybenzanilide* (cf. Kelly, Taylor, and Wiesner, *loc. cit.*).—The amine (4·1 g.) in 5% sulphuric acid (150 c.c.) was diazotised with sodium nitrite (1·5 g.) in water (10 c.c.). The clear yellow solution was heated slowly to 75° and kept at this temperature for 2 hr. during the evolution of nitrogen, and finally boiled for 2½ hr. The tarry product was extracted with chloroform and washed with 10% aqueous sodium hydroxide (200 c.c.). Removal of the chloroform from the dried (Na_2SO_4) solution left a brown gum, which was dissolved in benzene (60 c.c.) and adsorbed on alumina (30 × 2 cm.). Elution with the same solvent (520 c.c.) and crystallisation of the product from alcohol–light petroleum (b. p. 60—80°) gave 2′-ethyl-3 : 4-methylenedioxybenzanilide (0·13 g.) in shining needles, m. p. 143—144°. On admixture with the authentic specimen, prepared above, there was no depression of m. p. Further elution with benzene (600 c.c.) and then ether (1110 c.c.) gave a series of gums. Heating of the combined gums at 130—200°/0·1 mm. gave no sublimate. Elution with alcohol (60 c.c.) gave a dark red residue, which was sublimed at 130—200°/0·1 mm. A trace of sublimate, m. p. 94—96°, was obtained, which was insufficient for further investigation. It was shown that 2′-ethyl-3 : 4-methylenedioxybenzanilide sublimes unchanged at 130—150°/0·1 mm. No pure product could be isolated from the alkaline extract.

Reduction of 2′-*Ethyl*-3 : 4-*methylenedioxybenzanilide*.—2′-Ethyl-3 : 4-methylenedioxybenzanilide (1·4 g.) was boiled under reflux for 6 hr. with lithium aluminium hydride (6 g.) in anhydrous ether (300 c.c.). The pale yellow oil thus obtained formed a picrate from benzene, which on recrystallisation from the same solvent gave 2′-*ethyl*-3 : 4-*methylenedioxybenzylaniline picrate* (1·41 g.) in yellow prisms, m. p. 124—125° (decomp.) (Found: C, 54·9; H, 4·3. $C_{16}H_{17}O_2N,C_6H_3O_7N_3$ requires C, 54·5; H, 4·1%).

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