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1. *Internuclear Cyclisation. Part VII.* The Synthesis of Some Nitro-N-methylphenanthridones.*

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Methods for the preparation of *o*-amino-*N*-methylnitrobenzanilides have been investigated. Unambiguous methods have been used for the synthesis of *o*-amino-*N*-methyl-*o*′-nitro-, -*p*′-nitro-, and -3′ : 5′-dinitro-benzanilide, and the decomposition of the diazonium fluoroborates prepared from these bases gave *N*-methyl-1-nitro-, *N*-methyl-3-nitro-, and *N*-methyl-2 : 4-dinitrophenanthridone respectively.

IN Part III (*J.*, 1952, 1508) methods were described for the conversion of *o*-amino-*N*-methylbenzanilide into *N*-methylphenanthridone, and in Part VI * these methods were successfully applied to the synthesis of some methyl-, halogeno-, and carbomethoxy-*N*-methylphenanthridones. In order further to ascertain the scope and limitations of these reactions and to obtain information on the mechanism of the internuclear cyclisation process the conversion by similar methods of three *o*-amino-*N*-methylnitrobenzanilides into *N*-methylnitrophenanthridones has been investigated. These reactions are of special interest because they involve the formation of a new internuclear bond in two instances at a position *meta* with respect to a nitro-group and in one instance at a position which is both *ortho* and *para* with respect to a nitro-group.

Three methods were investigated for the preparation of the required *o*-amino-*N*-methylnitrobenzanilides. In the first a series of five dinitrobenzanilides was prepared by the interaction of a nitrobenzoyl chloride with a nitroaniline, at least one of the two components being an *ortho*-isomeride, and the products were methylated with methyl sulphate in aqueous acetone. Two of these *N*-methyldinitrobenzanilides were subjected to partial reduction with sodium disulphide in an attempt to obtain the required amino-*N*-methylnitrobenzanilide. With *N*-methyl-*o*′*p*-dinitrobenzanilide (I) the product proved to be, not *o*′-amino-*N*-methyl-*p*-nitrobenzanilide, but *p*-amino-*N*-methyl-*o*′-nitrobenzanilide (II), the identity of which was established by deamination to *N*-methyl-*o*′-nitrobenzanilide. A similar method of reduction applied to *N*-methyl-*oo*′-dinitrobenzanilide (III) gave *o*′-amino-*N*-methyl-*o*-nitrobenzanilide (IV), the constitution of which was established by its non-identity with an authentic specimen of the isomeric *o*-amino-*N*-methyl-*o*′-nitrobenzanilide (VI), prepared as described below.

$$\underset{\text{(I)}}{o\text{-}NO_2\cdot C_6H_4\cdot NMe\cdot CO\cdot C_6H_4\cdot NO_2\text{-}p} \longrightarrow \underset{\text{(II)}}{o\text{-}NO_2\cdot C_6H_4\cdot NMe\cdot CO\cdot C_6H_4\cdot NH_2\text{-}p}$$

$$\underset{\text{(III)}}{o\text{-}NO_2\cdot C_6H_4\cdot NMe\cdot CO\cdot C_6H_4\cdot NO_2\text{-}o} \longrightarrow \underset{\text{(IV)}}{o\text{-}NH_2\cdot C_6H_4\cdot NMe\cdot CO\cdot C_6H_4\cdot NO_2\text{-}o}$$

$$\underset{\text{(V)}}{o\text{-}NO_2\cdot C_6H_4\cdot NMe\cdot CO\cdot C_6H_4\cdot CO_2H\text{-}o} \xrightarrow[\text{or azide}]{\textit{via}\text{ amide}} \underset{\text{(VI)}}{o\text{-}NO_2\cdot C_6H_4\cdot NMe\cdot CO\cdot C_6H_4\cdot NH_2\text{-}o} \xleftarrow[H_2SO_4]{\text{Conc.}} \underset{\text{(VII)}}{o\text{-}NO_2\cdot C_6H_4\cdot NMe\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2Ph\text{-}o}$$

The second method of preparation is illustrated by the conversion of the known *o*′-nitrophthalanilic acid into *N*-methyl-*o*′-nitrophthalanilic acid (V), and thence into either the

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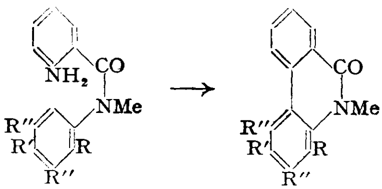
* Part VI, *J.*, 1952, 4059.

amide or the azide. By means of the Hofmann and the Curtius degradation respectively the latter were converted into *o*-amino-*N*-methyl-*o*′-nitrobenzanilide (VI). The third method involves condensation of benzenesulphonylanthraniloyl chloride with a nitromethylaniline followed by removal of the benzenesulphonyl group from the *o*-benzenesulphonamido-*N*-methyl-*o*′-nitrobenzanilide (*e.g.*, VII) on long storage at room temperature in the presence of concentrated sulphuric acid by the procedure due to Schroeter and Eisleb (*Annalen*, 1909, **367**, 101). In this manner *o*-amino-*N*-methyl-*o*′-nitro- (VI), -*p*′-nitro- and -3′ : 5′-dinitro-benzanilide were obtained. No constitutional ambiguity is involved in the second and the third method.

Diazonium fluoroborates were prepared from *o*-amino-*N*-methyl-*o*′-nitro- (VIII; $R = NO_2$, $R' = R'' = H$), -*p*′-nitro- (VIII; $R' = NO_2$, $R = R'' = H$), and -3′ : 5′-dinitro-benzanilide (VIII; $R'' = NO_2$, $R = R' = H$), and were decomposed in suspension in dry acetone by the addition of copper powder. In this manner 10-methyl-1-nitro- (IX; $R = NO_2$, $R' = R'' = H$), 10-methyl-3-nitro- (IX; $R' = NO_2$, $R = R'' = H$), and 10-methyl-2 : 4-dinitro-phenanthridone (IX; $R'' = NO_2$, $R = R' = H$) were obtained in yields of 21·5%, 28·5%, and 34·5% respectively. No hydroxy-*N*-methylnitrobenzanilides were isolated in these reactions. 10-Methyl-1-nitrophenanthridone (IX; $R = NO_2$, $R' = R'' = H$) was also obtained in 12% yield by the thermal decomposition in aqueous solution of the diazonium sulphate prepared from *o*-amino-*N*-methyl-*o*′-nitrobenzanilide (VIII; $R = NO_2$, $R' = R'' = H$), which reaction also gave *o*-hydroxy-*N*-methyl-*o*′-nitrobenzanilide in 9% yield. The decomposition of the diazonium fluoroborate prepared from *p*-amino-*N*-methyl-*o*′-nitrobenzanilide, which cannot give a phenanthridone, gave *N*-methyl-*o*′-nitrobenzanilide by deamination and *p*-hydroxy-*N*-methyl-*o*′-nitrobenzanilide, the latter being formed presumably as a result of the adventitious presence of moisture.

(VIII)



(IX)

The yields of *N*-methylphenanthridones obtained in the decomposition of the diazonium fluoroborates prepared from *o*-amino-*N*-methylbenzanilides with substituent atoms or groups in the methylaniline nucleus show little relation to the electronic character of the substituent.

EXPERIMENTAL

N-*Methyldinitrobenzanilides*.—The nitroaniline (1 mol.) and nitrobenzoyl chloride (prepared from ~1 mol. of acid) in pyridine were boiled for 5 minutes, cooled, and poured into water. The dinitrobenzanilide crystallised from aqueous alcohol with charcoal. *o*-Nitrobenzoyl chloride (Böetius and Römisch, *Ber.*, 1935, **68**, 1924) was used in solution in dry ether which was filtered before use. An excess of methyl sulphate (~3 mols.) was added slowly to a boiling and vigorously stirred mixture of the dinitrobenzanilide (1 mol.) in a mixture of equal volumes of acetone and 20% aqueous sodium hydroxide. The colour of the acetone layer changed from deep orange to pale yellow, after which the mixture was cooled and added to an excess of 20% aqueous sodium hydroxide and ice. The yellow oil which separated, solidified and was recrystallised from aqueous alcohol with charcoal. The results obtained are tabulated on p. 5.

Partial Reduction of N-*Methyl*-o′p- *and of* N-*Methyl*-oo′-*dinitrobenzanilide*.—A solution of sodium disulphide, prepared by boiling sodium sulphide ($Na_2S,9H_2O$, 8 g.) in water (100 c.c.) with sulphur (2 g.) until a clear solution was obtained, was added to a stirred boiling suspension of *N*-methyl-*o*′*p*-dinitrobenzanilide (8 g.) in alcohol (50 c.c.) and water (150 c.c.). After being boiled under reflux for 20 hours the mixture was cooled to 0° and the yellow solid which separated was collected. The filtrate was extracted with benzene and concentration of the dried (Na_2SO_4) extract gave a brown solid. The combined solids were recrystallised several times from benzene and gave p-*amino*-N-*methyl*-o′-*nitrobenzanilide* (6 g.) in orange needles, m. p. 148—149° (Found :

C, 62·6; H, 4·9. $C_{14}H_{13}O_3N_3$ requires C, 62·0; H, 4·8%). The application of the same procedure to *N*-methyl-*oo*′-dinitrobenzanilide (8 g.) gave on crystallisation from alcohol the unchanged *N*-methyldinitrobenzanilide (2·5 g.; m. p. 117—119° undepressed on admixture with the starting material), and on further concentration o′-*amino*-N-*methyl*-o-*nitrobenzanilide*, which separated from benzene–light petroleum (b. p. 80—100°) in orange plates (2 g.), m. p. 174—176° (Found: C, 62·0; H, 4·8%).

Preparation of N-*methyldinitrobenzanilides.*

Nitroaniline (g.)	Nitrobenzoic acid (g.)	Dinitrobenzanilide		Dinitrobenzanilide taken (g.)	Me_2SO_4 (c.c.)	Acetone (c.c.)	20% NaOH (c.c.)	*N*-Methyldinitrobenzanilide	
		yield (g.)	m. p.					yield (g.)	m. p.
o- 25	*p*- 25 *	2′ : 4- 29	222—223° [a]	24	50	100	100	22	126° [f]
o- 25	*m*- 25	2′ : 3- 38	137—138 [b]	36	75	150	150	28	110—111 [g]
o- 25	*o*- 25	2 : 2′- 33	155—157 [c]	30	50	125	125	26·5	124—125 [h]
m- 20	*o*- 20	2 : 3′- 26	192 [d]	16	50	70	70	16	137—138 [i]
p- 30	*o*- 30	2 : 4′- 34	210—212 [e]	30	70	120	120	30·5	149—150 [j]

* Acid chloride.

[a] Miklaszewski and Niementowski (*Ber.*, 1901, **34**, 2959) recorded m. p. 216°. [b] Witjens (*Rec. Trav. chim.*, 1943, **62**, 523) recorded m. p. 139—140°. [c] Niementowski (*Ber.*, 1899, **32**, 1463) recorded m. p. 167—168°, which fell to 133—136° on exposure to light. [d] Needles from benzene–acetone (Found: C, 54·5; H, 3·0. $C_{13}H_9O_5N_3$ requires C, 54·4; H, 3·2%). [e] Witjens (*loc. cit.*) recorded m. p. 219—220°. [f] Prisms from benzene–light petroleum (b. p. 80—100°) (Found: C, 56·2; H, 3·6. $C_{14}H_{11}O_5N_3$ requires C, 55·8; H, 3·8%). [g] Needles from aqueous alcohol (Found: C, 55·5; H, 3·6. $C_{14}H_{11}O_5N_3$ requires C, 55·8; H, 3·8%). [h] Prisms from benzene–light petroleum (b. p. 80—100°) (Found: C, 56·0; H, 3·6%). [i] Prisms from aqueous alcohol (Found: C, 56·0; H, 3·6%). [j] Plates from aqueous alcohol (Found: C, 56·0; H, 3·6%). (The dinitroanilides are pale yellow. The previous preparations were by different methods.)

Methylation of o′-*Nitrophthalanilic Acid.*—(*a*) Methyl sulphate (50 c.c.) was added slowly to a solution of *o*′-nitrophthalanilic acid (33 g.) (Meyer and Maier, *Annalen*, 1903, **327**, 55) in 10% aqueous sodium hydroxide (100 c.c.) at 70°. When the vigorous reaction had subsided the mixture was cooled by the addition of ice, and an excess of aqueous sodium hydroxide was added. The oil, which had separated, solidified and crystallisation from aqueous alcohol with charcoal gave *methyl* N-*methyl*-o′-*nitrophthalanilate* (10·7 g.) in yellow plates, m. p. 126—127° (Found: C, 61·1; H, 4·4. $C_{16}H_{14}O_5N_2$ requires C, 61·2; H, 4·5%). Crystallisation from benzene–light petroleum (b. p. 80—100°) gave yellow prisms, m. p. 127°. Acidification of the cold alkaline solution precipitated, overnight, N-*methyl*-o′-*nitrophthalanilic acid* (13·7 g.), which crystallised from alcohol in pale yellow prisms, m. p. 177° (Found: C, 60·3; H, 4·1. $C_{15}H_{12}O_5N_2$ requires C, 60·0; H, 4·0%). The ester was hydrolysed quantitatively to the acid by boiling it under reflux for 20 minutes with 4% aqueous sodium hydroxide. (*b*) In a second preparation conducted as above, but with *o*′-nitrophthalanilic acid (40 g.), 10% aqueous sodium hydroxide (150 c.c.), and methyl sulphate (100 c.c.), the products were methyl *N*-methyl-*o*′-nitrophthalanilate (30 g.), m. p. 126—127°, and *N*-methyl-*o*′-nitrophthalanilic acid (8 g.), m. p. 176—177°. (*c*) Methyl sulphate (4·5 c.c.) was shaken with a suspension of *o*′-nitrophthalanilic acid (10 g.) in 4% aqueous sodium hydroxide (100 c.c.) at room temperature for ½ hour. Acidification of the filtered solution gave *N*-methyl-*o*′-nitrophthalanilic acid (8·2 g.), pale yellow prisms (from aqueous alcohol), m. p. 175—176°.

N-*Methyl*-o′-*nitrophthalanilamide.*—A solution of *N*-methyl-*o*′-nitrophthalaniloyl chloride, prepared as a yellow gum from the acid (14 g.) by boiling thionyl chloride, in dry benzene (200 c.c.) at 0° was saturated with dry ammonia. The yellow solid which separated was filtered off and washed with water. The filtrate was washed with aqueous ammonia. The residue obtained on evaporation of the benzene solution was combined with the precipitate and crystallisation of the whole from ethyl alcohol gave N-*methyl*-o′-*nitrophthalanilamide* (12·5 g.) in yellow needles, m. p. 183—184° (Found: C, 60·5; H, 4·6. $C_{15}H_{13}O_4N_3$ requires C, 60·2; H, 4·7%).

N-*Methyl*-o′-*nitrophthalanilazide.*—Sodium azide (1·2 g.) in water (5 c.c.) was added with shaking to *N*-methyl-*o*′-nitrophthalaniloyl chloride (prepared as described above, from 5 g. of acid) in acetone (30 c.c.) at 0°. The mixture was shaken for 15 minutes and then poured into water (300 c.c.). The yellow oil, which separated, solidified. The solid was collected and washed with concentrated aqueous ammonia. N-*Methyl*-o′-*nitrophthalanilazide* (1 g.) was obtained as a yellow powder, m. p. 110—112° (decomp.) (Found: C, 55·5; H, 3·3. $C_{15}H_{11}O_4N_5$

requires C, 55·4; H, 3·4%). Acidification of the ammoniacal washings gave the unchanged acid (3 g.), m. p. 175—176°.

o-*Amino*-N-*methyl*-o'-*nitrobenzanilide*.—(a) *From* N-*methyl*-o'-*nitrophthalanilamide*. A suspension of the amide (5 g.) in a solution of bromine (8 g.) in 5·6% aqueous potassium hydroxide (200 c.c.) was stirred at 0° for 1 hour and then filtered. The orange-coloured filtrate was heated at 80° for 15 minutes, then extracted with ether. Evaporation of the solvent gave a red tar but subsequent crystallisation from benzene–light petroleum (b. p. 80—100°) gave o-*amino*-N-*methyl*-o'-*nitrobenzanilide* (1·5 g.) in orange plates, m. p. 104—105° (Found: C, 62·0; H, 4·9. $C_{14}H_{13}O_3N_3$ requires C, 62·0; H, 4·8%).

(b) *From* N-*methyl*-o'-*nitrophthalanilazide*. A suspension of the azide (1 g.) in dry benzene (40 c.c.) was heated on a steam-bath. The solid dissolved slowly with evolution of nitrogen, to give a yellow solution. The solution was boiled under reflux to complete the reaction. After the addition of 50% aqueous sodium hydroxide (40 c.c.) the mixture was boiled under reflux for a further 3 hours. The benzene layer was separated, dried (Na_2SO_4), and concentrated. *o*-Amino-*N*-methyl-*o'*-nitrobenzanilide (0·3 g.) separated in orange plates, m. p. 103—104°, undepressed on admixture with the specimen prepared by method (*a*) above.

N-*Methyl*-o-, N-*Methyl*-p-, *and* N-*Methyl*-3 : 5-*di-nitroaniline*.—*N*-Methyl-*o*-nitroaniline was prepared by Usherwood and Whiteley's method (*J.*, 1923, 1084). *N*-Methyl-*p*-nitroaniline was prepared by Halberkann's method (*Ber.*, 1921, **54**, 1833), with Usherwood and Whiteley's method for the hydrolysis of the methylsulphonanilide. 3 : 5-Dinitroaniline was prepared from 3 : 5-dinitrobenzoic acid according to Blanksma and Verberg (*Rec. Trav. chim.*, 1934, **53**, 988). A solution of 3 : 5-dinitroaniline (2 g.) and phthalic anhydride (3 g.) in ethyl acetate (30 c.c.) was boiled under reflux for 3 hours. 3 : 5-*Dinitrophthalanilic acid* (0·6 g.) separated and on recrystallisation from alcohol gave pale yellow plates, m. p. 208° (Found: C, 50·9; H, 2·7. $C_{14}H_9O_7N_3$ requires C, 50·6; H, 3·0%). To a solution of 3 : 5-dinitroaniline (28 g.) in pyridine (100 c.c.) toluene-*p*-sulphonyl chloride (26 g.) was slowly added. The solution was boiled for 5 minutes and poured into water. Crystallisation of the separated solid from acetic acid or alcohol gave 3 : 5-*dinitro*-N-*toluene*-p-*sulphonanilide* (20 g.), needles, m. p. 221—222° (Found: C, 46·0; H, 3·3. $C_{13}H_{11}O_6N_3S$ requires C, 46·3; H, 3·3%). Methyl sulphate (18 c.c.) was added with caution to a heated suspension of the sulphonanilide (20 g.) in 20% aqueous sodium hydroxide (100 c.c.). The mixture was kept alkaline and recrystallisation of the solid which separated gave N-*methyl*-3 : 5-*dinitro*-N-*toluene*-p-*sulphonanilide* (18 g.) in needles, m. p. 162° (Found: C, 48·2; H, 3·8. $C_{14}H_{13}O_6N_3S$ requires C, 47·9; H, 3·7%). A solution of this (18 g.) in concentrated sulphuric (30 c.c.) and acetic acid (15 c.c.) was heated on a steam-bath for 1 hour. When cold the mixture was poured into an excess of aqueous ammonia and ice. Crystallisation of the orange precipitate from methyl alcohol gave N-*methyl*-3 : 5-*dinitroaniline* (7·6 g.), orange plates, m. p. 158—159° (Found: C, 42·9; H, 3·6. $C_7H_7O_4N_3$ requires C, 42·6; H, 3·5%). Benzoylation (in boiling pyridine; 5 minutes) gave N-*methyl*-3' : 5'-*dinitrobenzanilide*, pale yellow prisms, m. p. 124—125°, from benzene–light petroleum (b. p. 80—100°) (Found: C, 55·9; H, 3·7. $C_{14}H_{11}O_5N_3$ requires C, 55·8; H, 3·8%).

Preparation of o-*Amino*-N-*methylnitrobenzanilides* (cf. Schroeter and Eisleb, *loc. cit.*).—The *N*-methylnitroaniline and benzenesulphonylanthraniloyl chloride (Schroeter, *Ber.*, 1907, **40**, 1610) were boiled under reflux in benzene, after which the solvent was removed by distillation and the residual *o*-benzenesulphonamido-*N*-methylnitrobenzanilide crystallised. Subsequent hydrolysis was effected at room temperature in concentrated sulphuric acid for 4 or 5 days, after which the solution was poured slowly into an excess of ice and aqueous ammonia. The yellow solid which separated was adsorbed on alumina (20 × 2 cm.) from benzene or benzene–light petroleum (b. p. 60—80°) and elution with the same solvent gave the pure *o*-amino-*N*-methylnitrobenzanilide. The results obtained are summarised below:

o-*Benzenesulphonamido*-N-*methylnitrobenzanilides*.

N-Methylaniline: cpd.	g.	*N*-Benzenesulphonyl-anthraniloyl chloride (g.)	Time of reflux (hr.)	*o*-Benzenesulphonamido-*N*-methyl-nitrobenzanilide: g.	m. p.
o-Nitro	10	10	6	10	115—116° [a]
p-Nitro	6·5	11	20	13	170—171 [b]
3 : 5-Dinitro	7·6	10·8	44	12·8	190 [c]

[a] Pale yellow prisms from alcohol–light petroleum (b. p. 80—100°) (Found: C, 58·4; H, 4·0; N, 9·9. $C_{20}H_{17}O_5N_3S$ requires C, 58·4; H, 4·1; N, 10·1%). [b] Pale yellow prisms from benzene (Found: C, 58·5; H, 4·1; N, 9·8%). [c] Pale yellow prisms from aqueous acetic acid (Found: C, 52·8; H, 3·3; N, 12·0. $C_{20}H_{16}O_7N_4S$ requires C, 52·6; H, 3·3; N, 12·3%).

o-*Amino*-N-*methylnitrobenzanilides.*

o-Benzenesulphonamido-*N*-methylbenzanilide : cpd.	g.	Sulphuric acid (c.c.)	Time (days)	*o*-Amino-*N*-methylnitrobenzanilide : g.	m. p.
o'-Nitro	10	50	4	4·0	103—104° [d]
p'-Nitro	13	70	4	5·0	160—161 [e]
3' : 5'-Dinitro	11	70	5	3·5	188—189 [f]

[d] 2·5 G. of unchanged starting material were recovered from the solution in benzene–light petroleum (b. p. 60—80°) (4 : 1) before adsorption. The product did not depress the m. p. of the compound prepared by Hofmann or Curtius degradation described above. [e] 2·5 G. of unchanged starting material were recovered from the solution in benzene–light petroleum (b. p. 60—80°) (3 : 1) before adsorption. The *product* separated from benzene–light petroleum (b. p. 80—100°) in yellow prisms (Found : C, 62·0; H, 4·9. $C_{14}H_{13}O_3N_3$ requires C, 62·0; H, 4·8%). [f] Elution was by benzene. The *product* separated from benzene in yellow needles (Found : C, 52·8; H, 3·6. $C_{14}H_{12}O_5N_4$ requires C, 53·2; H, 3·8%).

Decomposition of the Diazonium Fluoroborate prepared from p-*Amino*-N-*methyl*-o-*nitrobenzanilide*.—A suspension of this anilide (3 g.) in concentrated sulphuric acid (10 c.c.) and water (30 c.c.) was diazotised at 0° with a solution of sodium nitrite (1 g.) in water (10 c.c.). After being stirred for 1 hour at 0—5° the solution was filtered and sodium fluoroborate (5 g.) in water (10 c.c.) was added at 0°. The diazonium fluoroborate was collected, dried under reduced pressure, and suspended in " AnalaR " acetone (50 c.c.) to which copper powder (3 g.), prepared from zinc dust and aqueous copper sulphate, was added. On warming, nitrogen was freely evolved. When the reaction was complete, as shown by a negative coupling reaction with alkaline β-naphthol, the mixture was filtered into an excess of cold water. The residue was washed with boiling water and hot acetone, and the combined aqueous acetone solution was extracted with chloroform and the extract washed with 10% aqueous sodium hydroxide. Concentration of the dried (Na_2SO_4) neutral extract gave a red oil (3·2 g.), which was adsorbed from benzene–light petroleum (b. p. 60—80°) (3 : 1) on alumina (20 × 2 cm.). Elution with the same solvent (600 c.c.) and then with benzene (700 c.c.) gave *N*-methyl-*o'*-nitrobenzanilide (1·7 g.), which separated from benzene–light petroleum (b. p. 80—100°) in yellow needles, m. p. 81°, both alone and on admixture with an authentic specimen. Further elution gave a series of tars. Acidification of the alkaline washings and subsequent extraction with chloroform gave, on evaporation, p-*hydroxy*-N-*methyl*-o'-*nitrobenzanilide* (0·42 g.), which crystallised from methyl alcohol in yellow needles, m. p. 209° (Found : C, 62·2; H, 4·5; N, 10·1. $C_{14}H_{12}O_4N_2$ requires C, 61·8; H, 4·3; N, 10·3%).

Decomposition of the Diazonium Sulphate prepared from o-*Amino*-N-*methyl*-o'-*nitrobenzanilide*.—A solution of the *o*-amino-*N*-methyl-*o'*-nitrobenzanilide (2 g.) in sulphuric acid (7 c.c.) and water (100 c.c.) was diazotised at 0° with a solution of sodium nitrite (0·8 g.) in water (10 c.c.). After being stirred at 0° for 1 hour, the filtered solution was heated at 70° for 1 hour. Much tar was formed and the mixture was extracted with chloroform and the extract repeatedly washed with 10% aqueous sodium hydroxide. Evaporation of the dried (Na_2SO_4) chloroform solution gave a brown gum (1·0 g.), which was adsorbed from benzene on alumina (2 × 20 cm.). Elution with benzene (500 c.c.) gave 10-*methyl*-1-*nitrophenanthridone* (0·2 g.), which separated from light petroleum (b. p. 80—100°) in yellow needles, 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%). Subsequent elution with benzene and then with benzene–ether (3 : 1) gave small quantities of yellow needles, m. p. 160—165° and colourless needles, m. p. 155—158° (mixed m. p. 135—142°). Acidification of the alkaline washings and extraction with chloroform gave on evaporation a brown tar (1·0 g.), which was adsorbed from benzene on silica gel (10 × 1 cm.). Elution with benzene (600 c.c.) gave o-*hydroxy*-N-*methyl*-o'-*nitrobenzanilide* (0·18 g.), yellow needles (from methyl alcohol), m. p. 157—158° (Found : C, 61·7; H, 4·2. $C_{14}H_{12}O_4N_2$ requires C, 61·8; H, 4·3%).

Decomposition of the Diazonium Fluoroborate prepared from o-*Amino*-N-*methyl*-o'-*nitrobenzanilide*.—The diazonium fluoroborate, prepared from the anilide (1·5 g.) as described above for the isomeric *p*-amino-compound, was allowed to decompose in " AnalaR " acetone (50 c.c.) with the addition of copper powder (2 g.). The reaction products were isolated and purified as described above. The neutral chloroform extract gave an orange-coloured solid (0·42 g.), which was adsorbed from benzene–light petroleum (b. p. 60—80°) (2 : 1) on alumina (2 × 20 cm.). Elution with the same solvent (400 c.c.) gave 10-methyl-1-nitrophenanthridone (0·3 g.), which crystallised from light petroleum (b. p. 80—100°) in yellow needles, m. p. 92—93°, undepressed on admixture with the compound prepared as above from decomposition of the diazonium sulphate in aqueous solution. Further elution afforded only orange-coloured gums. The alkaline washings, on acidification, extraction, and evaporation, gave only a trace of a black tar.

Decomposition of the Diazonium Fluoroborate prepared from o-*Amino*-N-*methyl*-p′-*nitrobenzanilide*.—In similar manner this anilide (3·0 g.) was converted into the diazonium fluoroborate and decomposed. The neutral chloroform extract gave a dark-red solid (2·8 g.), which was purified by adsorption on alumina and afforded 10-*methyl*-3-*nitrophenanthridone* (0·8 g.), yellow needles (from benzene), m. p. 249° (Found : C, 66·0; H, 3·8%). Further elution of the column gave needles (0·4 g.), m. p. 178—180° (Found : C, 65·5; H, 4·5; N, 11·0%; *M*, 248). The alkaline washings yielded only a trace of a brown tar.

Decomposition of the Diazonium Fluoroborate prepared from o-*Amino*-N-*methyl*-3′ : 5′-*dinitrobenzanilide*.—This reaction was carried out as described for the preceding examples, but with *o*-amino-*N*-methyl-3 : 5-dinitrobenzanilide (3·2 g.) in sulphuric acid (10 c.c.) and water (100 c.c.). Five hours were allowed for the completion of the diazotisation. The neutral chloroform extract gave a red solid (1·7 g.), which on chromatographic purification afforded 10-*methyl*-2 : 4-*dinitrophenanthridone* (0·75 g.), yellow needles (from aqueous acetic acid), m. p. 281° (Found : C, 56·2; H, 3·1. $C_{14}H_9O_5N_3$ requires C, 56·2; H, 3·0%), and on further elution a second compound which crystallised from the same solvent in buff-coloured plates (0·5 g.), m. p. 244—246° (Found : C, 55·7; H, 3·3; N, 14·0%; *M*, 262). The alkaline extract afforded only a small quantity of a red tar.

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