275. *Internuclear Cyclisation. Part III.* An Extension of the Pschorr Phenanthrene Synthesis to the Synthesis of Phenanthridones.*

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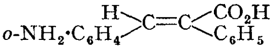
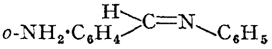
Diazonium salts prepared from *o*-amino-*N*-methylbenzanilide have been converted into *N*-methylphenanthridone by eight methods. *o*-Hydroxy-*N*-methylbenzanilide was frequently found as a by-product. Decomposition of the diazonium borofluoride in acetone in presence of copper proved to be a convenient method of preparation of the phenanthridone and this method was also applied successfully to the isomeric *o'*-amino-*N*-methylbenzanilide.

An investigation has been carried out into the extension of the well-known Pschorr reaction for the synthesis of derivatives of phenanthrene to include the synthesis of derivatives of phenanthridine. In order to achieve this object it is necessary to replace the intermediate symmetrical diarylethylene of type (I) by the system (II), but the ease of hydrolysis normally shown by Schiff's bases suggests that more successful results might result from



$o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}{=}\text{C}(\text{CO}_2\text{H})\cdot\text{C}_6\text{H}_5$

(I)



$o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}{=}\text{N}\cdot\text{C}_6\text{H}_5$

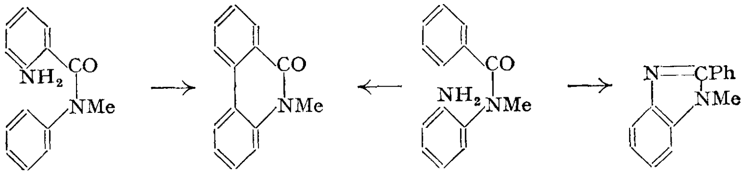
(II)

$o\text{-NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NR}\cdot\text{C}_6\text{H}_5$

(III)

the use of the saturated system (III), in which, to eliminate the formation on diazotisation of a triazolone, R should be an alkyl group. The use of compounds of type (III) also eliminates the necessity to consider the geometrical isomerism of the intermediate compound, which in the phenanthrene synthesis is known to be of vital importance. On the other hand, the two positions in the aromatic nuclei between which the new internuclear bond is to be formed are not as near to each other in space as they would be in the appropriate Schiff's base. The successful development of a general method of synthesis in this manner would provide a new and useful route to a variety of substituted phenanthridines, and in addition would enable a new approach to be made to the synthesis of alkaloids of the chelidonine–sanguinarine group. Such an 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 of the amine afforded only a brown tar. The failure of a similar reaction was reported at about the same time by Noller, Denyes, Gates, and Wasley (*J. Amer. Chem. Soc.*, 1937, **59**, 2079).

When this work was started it was known that Pictet and Gonset (*Arch. Sci. phys. nat. Genève*, 1897, **3**, 37) had reported the formation of *N*-methylphenanthridone (V) by heating



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

an aqueous solution of the diazonium chloride prepared from *o*-amino-*N*-methylbenzanilide (IV), but no yield was mentioned. In addition, Forrest, Haworth, Pinder, and Stevens (*J.*, 1949, 1311) had 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, although a similar reaction with the *N*-methylbenzo-α-naphthalide failed.

No further examples of the synthesis of the phenanthridine system by this route could be found, but during the course of this work it was learned that Mitsuhashi (*J. Pharm. Soc.*

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* Part II, *J.*, 1949, 3172.

Japan, 1943, **63**, 177; *Chem. Abstracts*, 1951, **45**, 628) had obtained *N*-benzylphenanthridone in 54% yield by the action of heat or of copper powder on an aqueous solution of the diazonium salt prepared from *o*-amino-*N*-benzylbenzanilide, and a *N*-benzyl-ethoxy- and a -methoxyphenanthridone were also prepared in similar manner. At the same time Chardonnens and Würmli (*Helv. Chim. Acta*, 1950, **33**, 1338) reported the formation of 1 : 3 : *N*-trimethylphenanthridone in 8% yield from the diazonium chloride prepared from *o*-amino-*N* : 2′ : 4′-trimethylbenzanilide.

As part of a programme of work devised to ascertain the scope and limitations of this synthetic approach to the phenanthridine system, the present communication is limited to a study of the formation of *N*-methylphenanthridone from both *o*-amino- and *o*′-amino-*N*-methylbenzanilide under a variety of experimental conditions with special reference to the yields obtained and the nature of any by-products formed.

The original observation by Pictet and Gonset has been confirmed and, by boiling an aqueous solution of the diazonium sulphate prepared from *o*-amino-*N*-methylbenzanilide, *N*-methylphenanthridone was obtained in 50% yield, together with *o*-hydroxy-*N*-methylbenzanilide in 40% yield. Seven modified procedures were then used, starting in each case with *o*-amino-*N*-methylbenzanilide, and the yields of *N*-methylphenanthridone and the nature of the by-products are shown in the table. The by-products consisted of either the phenol or the dimeride formed by the union of two molecules from which the amino-groups had been eliminated. The maximum yield of *N*-methylphenanthridone (53%) was obtained by the decomposition of the solid diazonium sulphate in acetone in presence of copper (see Hey and Osbond, *J.*, 1949, 3164). Of most interest is the reaction in which the diazonium fluoroborate of *o*-amino-*N*-methylbenzanilide was decomposed in acetone in presence of copper. This reaction, which is clean and easy to carry out, gave *N*-methylphenanthridone in 50% yield. Previous uses of fluoroborate for effecting the union of aryl nuclei have been reported by Nesmejanov and Makarova (*Bull. Acad. Sci. U.R.S.S.*, Classe Sci. Chim., 1947, 213; *Chem. Abstracts*, 1948, **42**, 5440), although in the few examples recorded only very small yields were obtained.

Ring-closure experiments with o-*amino*-N-*methylbenzanilide.*

	Experimental conditions	Yield, %, of *N*-methylphenanthridone	By-products
(*a*)	Heating aq. diazonium sulphate	50	*o*-Hydroxy-*N*-methylbenzanilide (40%)
(*b*)	,, ,, ,, with Cu	50	,, ,, ,, (4%)
(*c*)	,, ,, chloride ,, ...	29	,, ,, ,, (20%)
(*d*)	Addition of aq. NaOH to diazonium sulphate	11	—
(*e*)	Action of H_3PO_2 on diazonium sulphate in dioxan with Cu	40	Product, m. p. 220°, and dimeride
(*f*)	Solid diazonium sulphate in acetone with Cu...	53	*o*-Hydroxy-*N*-methylbenzanilide (3%)
(*g*)	Diazonium fluoroborate ,, ,, ...	50	Dimeride
(*h*)	,, ,, in boiling light petroleum (b. p. 80—100°)	17	—

The successful use of *o*-amino-*N*-methylbenzanilide (IV) for the synthesis of *N*-methylphenanthridone (V) outlined above suggested that the alternative approach through *o*′-amino-*N*-methylbenzanilide (VI) was worthy of attention. The ease with which monoacyl-*o*-phenylenediamines are known to be converted into benziminazoles indicates that *o*′-amino-*N*-methylbenzanilide might yield 1-methyl-2-phenylbenziminazole (VII), and in the preparation of the base (VI) from the corresponding nitro-compound by means of iron and acetic acid there was evidence that the benziminazole (VII) was in fact formed. Chardonnens and Würmli (*loc. cit.*) have also reported the ready formation of 2-(2 : 4-dimethylphenyl)-1-methylbenziminazole from *o*′-amino-*N* : 2 : 4-trimethylbenzanilide. The base (VI), however, was obtained in quantitative yield on catalytic hydrogenation of the corresponding nitro-compound, and when the diazonium fluoroborate was decomposed under acetone with copper powder, *N*-methylphenanthridone (V) was obtained in 31% yield. This route, however, is somewhat inferior to the former route, since the product is more highly coloured and the yield of phenanthridone is lower.

EXPERIMENTAL

N-*Methyl*-o-*nitrobenzanilide*.—(*a*) Methylaniline (60 c.c.) was slowly added to a boiling ethereal solution of *o*-nitrobenzoyl chloride (from 40 g. of acid). After being boiled under reflux for 4 hours, the suspension was filtered and the precipitate washed with water. The ethereal solution was washed with dilute hydrochloric acid and evaporated. The solid residue was combined with the precipitate, and crystallisation from benzene gave *N*-methyl-*o*-nitrobenzanilide (47 g.) in colourless needles, m. p. 94°.

(*b*) An ethereal solution of *o*-nitrobenzoyl chloride (from 40 g. of acid) was added slowly to a solution of methylaniline (25·6 g.) in pyridine (60 c.c.) The ether was evaporated and the clear pyridine solution was boiled for 5 minutes, cooled, and poured into water. Crystallisation from benzene (charcoal) of the solid which separated gave the anilide (45 g.) in colourless needles, m. p. 94°. Pictet and Gonset (*loc. cit.*) recorded m. p. 94·5° for this compound prepared by the Schotten–Baumann reaction (no yield quoted).

o-*Amino*-N-*methylbenzanilide*.—A suspension of iron filings (80 g.) in 5% aqueous acetic acid (100 c.c.) was heated on a steam-bath, with stirring, until no more hydrogen was evolved. *N*-Methyl-*o*-nitrobenzanilide (35 g.) was slowly added, and the mixture was stirred on the steam-bath for 1 hour. The solution was neutralised with aqueous sodium carbonate, and charcoal added to assist filtration. After filtration, both residue and filtrate were repeatedly extracted with hot benzene. The combined benzene extracts were concentrated, and *o*-amino-*N*-methylbenzanilide (26 g.) separated in white needles, m. p. 126—127°. Pictet and Gonset (*loc. cit.*) carried out the reduction with ammonium sulphide and recorded m. p. 127° but no yield. When the base was (*a*) heated with an excess of acetic anhydride for 30 minutes, or (*b*) left overnight at room temperature with acetic acid, acetic anhydride, and a few drops of concentrated sulphuric acid, only *N*-acetylanthranilic acid was isolated from the product. Acetyl chloride (5 c.c.) was slowly added to a stirred solution of *o*-amino-*N*-methylbenzanilide (6·2 g.) in pyridine (20 c.c.) at 0°. A vigorous reaction took place and the mixture was poured into a large excess of ice-water. The white solid which separated was recrystallised from benzene–light petroleum (b. p. 60—80°) and o-*acetamido*-N-*methylbenzanilide* (6·1 g.) separated in white cubic crystals, m. p. 124—125° (Found: C, 72·1; H, 5·8. $C_{16}H_{16}O_2N_2$ requires C, 71·6; H, 6·0%). Admixture with the starting material (m. p. 126—127°) resulted in a strong depression in m. p.

N-*Methylbenzanilide*-o-*diazonium Fluoroborate*.—*o*-Amino-*N*-methylbenzanilide (2·5 g.) was dissolved in concentrated sulphuric acid (20 c.c.) and water (40 c.c.) by warming, and after this had been cooled to 0° a solution of sodium nitrite (1 g.) in water (10 c.c.) was added. After being stirred for 1 hour at 0° the pale yellow-green solution was filtered, and a solution of sodium fluoroborate (5 g.) in water (20 c.c.) was slowly added to a stirred solution at 0°. The fluoroborate separated as a pale yellow solid (7·5 g.), m. p. 122·5° (decomp.), which was collected in a sintered-glass crucible and washed with a little ice-cold water. Purification was effected by dissolving the compound in boiling "AnalaR" acetone, quickly cooling the solution in an ice–salt freezing mixture, and precipitating the diazonium salt by addition of light petroleum (b. p. 40—60°). N-*Methylbenzanilide*-o-*diazonium fluoroborate* was obtained in very pale yellow needles, m. p. 125° (decomp.) (Found: C, 51·5; H, 4·0; N, 12·8. $C_{14}H_{12}ON_3BF_4$ requires C, 51·7; H, 3·7; N, 12·9%).

Preparation of N-*Methylphenanthridone*.—(*a*) *o*-Amino-*N*-methylbenzanilide (2·2 g.) was diazotised as described above in a mixture of concentrated sulphuric acid (5 c.c.) and water (100 c.c.) by addition at 0° of sodium nitrite (0·8 g.) in water (10 c.c.). The filtered solution was gently warmed on a water-bath to 70°, whereat decomposition commenced. The reaction was complete after about 1½ hours and much tar was formed. The mixture was extracted with chloroform, and the chloroform solution was repeatedly extracted with 10% aqueous sodium hydroxide to remove phenolic substances. Evaporation of the dried (Na_2SO_4) neutral extract left a light brown solid (1·3 g.), m. p. 96—98°. Recrystallisation from benzene–light petroleum (b. p. 60—80°) with charcoal gave *N*-methylphenanthridone (0·98 g.) in white needles, m. p. 104—105° (Found: C, 80·0; H, 5·0. Calc. for $C_{14}H_{11}ON$: C, 80·3; H, 5·2%). Pictet and Gonset (*loc. cit.*) quoted no yield but gave m. p. 109° for this compound. Acidification of the sodium hydroxide washings and extraction with ether gave a brown solid (0·96 g.), m. p. 102—108°, which on recrystallisation from aqueous alcohol (charcoal) afforded *o*-hydroxy-*N*-methylbenzanilide (0·8 g.), m. p. 112—113°, both alone and on admixture with an authentic specimen. Pictet and Gonset (*loc. cit.*) did not record the isolation of any phenolic compound.

(*b*) *o*-Amino-*N*-methylbenzanilide (3 g.) was diazotised as described above in a mixture of concentrated sulphuric acid (5 c.c.) and water (100 c.c.) by addition at 0° of sodium nitrite (1 g.) in water (10 c.c.). To the filtered solution copper powder * (3 g.) was slowly added, and nitrogen was evolved in the cold. The solution was stirred at room temperature for 24 hours, and then boiled. The resulting suspension was filtered, and both filtrate and residue were repeatedly extracted with hot chloroform. The chloroform solution was washed with 10% aqueous sodium hydroxide and concentrated, as in (*a*). A brown tar (2·6 g.) was obtained. Purification was effected by dissolving the tar in benzene–light petroleum (b. p. 60—80°) (4 : 1), adsorption on an alumina column (20 × 2 cm.), and washing the column with the same solvent. *N*-Methylphenanthridone (1·4 g.) was obtained in white needles, m. p. 109° [cf. reaction (*a*)]. When this was admixed with the product obtained from reaction (*a*) no depression in m. p. was observed, and on seeding of a solution of the compound, m. p. 105°, with a crystal of m. p. 109°, the resulting product had m. p. 108—109°. Further washing of the column with benzene and ether gave brown viscous oils of unidentified composition. The alkaline extract, treated as described above, gave a brown crystalline solid (0·05 g.) which on recrystallisation from aqueous alcohol afforded *o*-hydroxy-*N*-methylbenzanilide (0·03 g.) in white needles, m. p. 112°.

(*c*) *o*-Amino-*N*-methylbenzanilide (3 g.) was diazotised in a mixture of concentrated hydrochloric acid (5 c.c.) and water (100 c.c.) by addition at 0° of sodium nitrite (1 g.) in water (10 c.c.). To the filtered solution copper powder (3 g.) was slowly added and nitrogen was evolved. The suspension was stirred for 24 hours and then boiled. The product was worked up as described under reaction (*b*). The neutral extract yielded a brown solid (1·6 g.), m. p. 95—100°, which on recrystallisation from benzene–light petroleum (b. p. 60—80°) with charcoal gave *N*-methylphenanthridone (0·8 g.) in colourless needles, m. p. 105°. The alkaline extract yielded a brown solid, which on recrystallisation from aqueous alcohol (charcoal) gave *o*-hydroxy-*N*-methylbenzanilide (0·6 g.), m. p. 111—112°.

(*d*) *o*-Amino-*N*-methylbenzanilide (2 g.) was diazotised as described above in a mixture of concentrated sulphuric acid (5 c.c.) and water (50 c.c.) by the addition at 0° of sodium nitrite (0·8 g.) in water (10 c.c.) Aqueous sodium hydroxide (10%) was added dropwise to the filtered diazonium solution with stirring at 0° until the solution was just alkaline to phenolphthalein. The pale yellow solution became cloudy, but there was no change in colour or evolution of nitrogen. The solution was stirred at room temperature for 3 days, during which the colour of the suspension changed from pale yellow to deep orange and nitrogen was slowly evolved. The reaction was completed by warming to 70° on a water-bath, with stirring, for a further 3 hours. The solution and suspended tar were then extracted with chloroform. Evaporation of the chloroform extract left a red-brown tar (0·8 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (2 : 1) and adsorbed on an alumina column (25 × 2 cm.). When the column was washed with benzene–light petroleum (b. p. 60—80°) (4 : 1) (500 c.c.) a pale orange solid (0·25 g.), m. p. 100—108°, was obtained. Recrystallisation from light petroleum (b. p. 80—100°) with charcoal gave *N*-methylphenanthridone (0·2 g.), m. p. 109°, in colourless needles. Further washing of the column with benzene and with ether gave orange and red vitreous substances of unidentified composition. Acidification of the original alkaline-soluble reaction product and extraction with chloroform gave a brown tar from which no identifiable products were obtained.

(*e*) A solution of *o*-amino-*N*-methylbenzanilide (2 g.) in a mixture of dioxan (40 c.c.) and concentrated sulphuric acid (3 c.c.) was diazotised by slow addition of amyl nitrite (4 c.c.) at room temperature. The solution was stirred at room temperature for 2 hours to complete the reaction. The bright yellow solution was added dropwise to a stirred suspension of copper (4 g.) in a solution of sodium hypophosphite (18 g.) in water (20 c.c.) (cf. Cassaday and Bogert, *J. Amer. Chem. Soc.*, 1939, **61**, 2461, 3058). The mixture was stirred at 70—80° for 1 hour. The cooled suspension was filtered and both the filtrate and the residue were extracted with hot chloroform, and the chloroform extracts were washed with 10% aqueous sodium hydroxide. Concentration of the neutral extract left a red-brown solid (1·1 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) and adsorbed on an alumina column (24 × 2 cm.). On washing of the column with benzene–light petroleum (4 : 1) (600 c.c.) a white solid (0·9 g.), m. p. 102—104°, was obtained, which on crystallisation from light petroleum (b. p. 80—100°) yielded *N*-methylphenanthridone (0·75 g.), m. p. 109°, in colourless needles. On washing of the column with benzene–ether (1 : 1) a pale orange solid (0·2 g.), m. p. 210—220°, was obtained, which on recrystallisation from methanol gave crude 2 : 2′-bis-*N*-methylbenzamidodiphenyl (0·1 g.) in pale yellow prisms, m. p. 240—242° [cf. reaction (*g*)]. Further washing of the column

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* In all the reactions described in this paper the copper powder was prepared by precipitation from aqueous copper sulphate with zinc dust.

with the same solvent gave only orange glassy material of unidentified composition. Acidification of the alkaline washings gave a pale brown solid (1 g.), which on recrystallisation from methanol gave a product, m. p. 220° (Found : C, 70·5; H, 5·2%).

(*f*) A solution of *o*-amino-*N*-methylbenzanilide (2 g.) in glacial acetic acid (20 c.c.) was cooled to 0° with vigorous stirring and diazotised by addition of sodium nitrite (2 g.) in concentrated sulphuric acid (10 c.c.) (cf. Hodgson and Mahadevan, *J.*, **1947**, 325). The solution was allowed to warm to room temperature with stirring to complete the reaction, and dry ether was then added. The ethereal layer was decanted and the diazonium sulphate, obtained as a viscous gum, was dissolved in " AnalaR " acetone. Some sodium hydrogen sulphate which had separated was filtered off. Copper powder (3 g.) was added to the acetone solution and an immediate vigorous evolution of nitrogen took place. The reaction was complete in a few minutes. The acetone solution was filtered into water and the copper powder was extracted with hot acetone and washed with boiling water. The whole aqueous-acetone solution was extracted with chloroform, and the chloroform solution washed with 10% aqueous sodium hydroxide. Evaporation of the neutral chloroform extract yielded a brown tar (1·7 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (5 : 1) and adsorbed on an alumina column (25 × 2 cm.). On washing of the column with the same solvent (800 c.c.) a pale yellow solid (1·15 g.), m. p. 99—104°, was obtained. Recrystallisation from light petroleum (b. p. 80—100°) gave *N*-methylphenanthridone (0·97 g.), m. p. 105° [cf. reaction (*b*)] (Found : C, 80·3; H, 5·3. Calc. for $C_{14}H_{11}ON$: C, 80·3; H, 5·2%). Further washing of the column with benzene and benzene–ether mixtures gave a series of unidentifiable brown tars. The alkaline extract on acidification yielded a brown solid (0·08 g.), which on recrystallisation from aqueous alcohol (charcoal) gave *o*-hydroxy-*N*-methylbenzanilide (0·05 g.), m. p. 110—112°.

(*g*) Dry *N*-methylbenzanilide-*o*-diazonium borofluoride (2·5 g.), prepared as described above, was suspended in " AnalaR " acetone (50 c.c.), and on the addition of copper powder (3 g.) a vigorous evolution of nitrogen occurred. The reaction was complete within a few minutes and the solution was then filtered into an excess of cold water. The copper powder was washed with boiling water and hot acetone, and the whole aqueous-acetone solution extracted with chloroform. The chloroform extract was washed with 10% aqueous sodium hydroxide. Concentration of the neutral extract gave a light brown solid (2·0 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (1 : 1) and adsorbed on an alumina column (25 × 2 cm.). Washing of the column with benzene–light petroleum (b. p. 60—80°) (3 : 1) (500 c.c.) and (9 : 1) (500 c.c.) gave white and pale pink solids (0·9 g. and 0·1 g.), m. p. 96—99° and 90—100°, respectively. Recrystallisation of these combined fractions from light petroleum (b. p. 60—80°) with charcoal gave *N*-methylphenanthridone (0·84 g.), m. p. 105°. Further washing of the column with benzene (500 c.c.) and benzene–ether (500 c.c.) gave a yellow solid (0·9 g.), m. p. 203—210°. Recrystallisation from benzene and then from alcohol gave 2 : 2'-*bis*-N-*methylbenzamidodiphenyl* (0·4 g.) in colourless prisms, m. p. 248—249° (Found : C, 80·1; H, 5·8%; *M*, 402. $C_{28}H_{24}O_2N_2$ requires C, 80·0; H, 5·7%; *M*, 420). Acidification and subsequent extraction of the alkaline washing gave only a trace of a black tar.

(*h*) A suspension of *N*-methylbenzanilide-*o*-diazonium borofluoride (3 g.) in sodium-dried light petroleum (b. p. 80—100°) (150 c.c.) was boiled under reflux for 12 hours. A large amount of a dark red insoluble tar was formed from which the solution was decanted. The tar was extracted with benzene and the benzene extract and light petroleum solution were combined and concentrated. *N*-Methylphenanthridone (0·32 g.) was obtained in colourless needles, m. p. 109°.

N-*Methyl*-o'-*nitrobenzanilide*.—(*a*) A solution of *o'*-nitrobenzanilide (30 g.), prepared by the method of Fischer and Römer (*J. pr. Chem.*, 1906, **73**, 432), in acetone (30 c.c.) with potassium hydroxide (30 g.) was boiled under reflux while methyl sulphate (50 c.c.) was slowly added. When the vigorous reaction had subsided the mixture was cooled and added to an excess of ice-cold ammonia (*d* 0·88). The yellow oil, which separated, solidified. Recrystallisation from aqueous alcohol or from benzene–light petroleum (b. p. 60—80°) gave N-*methyl*-o'-*nitrobenzanilide* (18·4 g.) in pale yellow plates, m. p. 80—81° (Found : C, 65·6; H, 4·6. $C_{14}H_{12}O_3N_2$ requires C, 65·6; H, 4·7%).

(*b*) *N*-Methyl-*o*-nitroaniline (3·3 g.), prepared by the method of Usherwood and Whiteley (*J.*, **1923**, **123**, 1084), and benzoyl chloride (2·8 c.c.) were heated on the steam-bath for one hour. Trituration of the product with light petroleum (b. p. 40—60°) gave the crude benzoyl derivative, m. p. 75—78°. Recrystallisation from aqueous alcohol gave *N*-methyl-*o'*-nitrobenzanilide (3·2 g.) in pale yellow plates, m. p. 81°.

o'-*Amino*-N-*methylbenzanilide*.—A solution of *N*-methyl-*o'*-nitrobenzanilide (7 g.) in ethyl alcohol (200 c.c.) and a suspension of Raney nickel (7 g.) in ethyl alcohol was shaken with hydrogen at atmospheric pressure for 1½ hours. When 1800 c.c. of hydrogen had been absorbed the suspension was filtered, and the filtrate concentrated under reduced pressure. The resulting white solid was crystallised from dry benzene. o'-*Amino*-N-*methylbenzanilide* (5·6 g.) was obtained in needles, m. p. 125—126° (Found: C, 74·5; H, 6·1. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2%).

Conversion of o'-*Amino*-N-*methylbenzanilide into* N-*Methylphenanthridone*.—*o'*-Amino-*N*-methylbenzanilide (2·5 g.) in sulphuric acid (20 c.c.) and water (60 c.c.) was diazotised at 0—5° with sodium nitrite (2 g.) in water (10 c.c.). To the filtered solution of the diazonium sulphate at 0°, a solution of sodium fluoroborate (5 g.) in water (10 c.c.) was slowly added with stirring. After ½ hour the solid diazonium fluoroborate was filtered off and dried *in vacuo* (3·7 g.). Copper powder (3 g.) was added to a suspension of the borofluoride in "AnalaR" acetone (50 c.c.) and an immediate evolution of nitrogen ensued. After ½ hour the suspension was filtered into cold water and the residue was extracted with hot acetone and boiling water. The combined washings and filtrate were extracted with chloroform. After being washed with aqueous sodium hydroxide, the chloroform was evaporated and a brown tar (2·1 g.) remained. A solution in benzene–light petroleum (b. p. 60—80°) (3 : 1) was adsorbed on an alumina column (20 × 2 cm.). Elution with the same solvent gave *N*-methylphenanthridone (0·71 g.) in colourless needles, m. p. 105°.

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