775. *Internuclear Cyclisation. Part VI.* The Synthesis of Some Methyl-, Halogeno-, and Carbomethoxy-*N*-methylphenanthridones.*

By R. A. Heacock and D. H. Hey.

2-Amino-*N*-methylbenzo-*p*- and -*o*-toluidide, and 2-amino-4′-bromo-, 2-amino-4′-chloro-, 2-amino-2′-chloro-, and 2-amino-4-carbomethoxy-*N*-methylbenzanilide have been prepared. These six bases have been diazotised and the decomposition of the diazonium sulphates in aqueous solution and of the diazonium fluoroborates in acetone suspension has been studied. Substituted *N*-methylphenanthridones were obtained in each case except with 2-amino-2′-chloro-*N*-methylbenzanilide. The corresponding phenols accompanied the *N*-methylphenanthridones from the decomposition of the diazonium sulphates.

In Part III (*J.*, 1952, 1508) methods were described by which *N*-methylphenanthridone could be obtained from *o*-amino-*N*-methylbenzanilide by successive diazotisation and elimination of nitrogen. The present communication describes the application of these methods to the preparation of certain methyl-, halogeno-, and carbomethoxy-*N*-methylphenanthridones, and an examination by chromatographic adsorption of the products formed in these reactions, undertaken to ascertain the scope and limitations of this synthetical approach to the phenanthridine system and to obtain information on the mechanism of the internuclear cyclisation process.

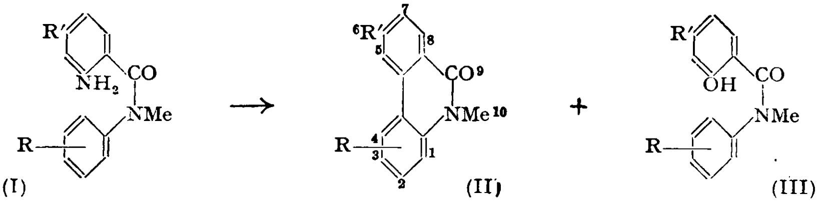
2-Amino-*N*-methylbenzo-*p*-toluidide (I; R = *p*-Me, R′ = H) was prepared by the reduction of *N*-methyl-2-nitrobenzo-*p*-toluidide, which was obtained both by the action of *o*-nitrobenzoyl chloride on methyl-*p*-toluidine and by the methylation of 2-nitrobenzo-*p*-toluidide. When an aqueous solution of the diazonium sulphate prepared from 2-amino-*N*-methylbenzo-*p*-toluidide was heated, nitrogen was evolved, and both 3 : 10-dimethylphenanthridone (II; R = 3-Me, R′ = H) and 2-hydroxy-*N*-methylbenzo-*p*-toluidide (III; R = *p*-Me, R′ = H) were formed. 3 : 10-Dimethylphenanthridone was also formed by the action of copper powder on the diazonium fluoroborate, prepared from 2-amino-*N*-methylbenzo-*p*-toluidide, together with a second compound, m. p. 193°. In similar manner 2-amino-*N*-methylbenzo-*o*-toluidide (I; R = *o*-Me, R′ = H) was prepared by the reduction of the corresponding nitro-compound, which was obtained by the two procedures outlined

---

* Part V, *J.*, 1952, 2276.

above for the isomeric benzo-*p*-toluidide. The action of heat on an aqueous solution of the diazonium sulphate gave 1 : 10-dimethylphenanthridone (II; R = 1-Me, R′ = H) and 2-hydroxy-*N*-methylbenzo-*o*-toluidide (III; R = *o*-Me, R′ = H); the former was also obtained by the action of copper powder on the diazonium fluoroborate in acetone.

Similarly both 4′-bromo- and 4′-chloro-*N*-methyl-2-nitrobenzanilide were converted into the corresponding amines (I; R = *p*-Br, R′ = H; and R = *p*-Cl, R′ = H), and decomposition of their diazonium fluoroborates in acetone gave 3-bromo- (II; R = 3-Br, R′ = H) and 3-chloro-10-methylphenanthridone (II; R = 3-Cl, R′ = H), respectively. The 4′-halogeno-*N*-methyl-2-nitrobenzanilides were prepared by the methylation of the corresponding 4′-halogeno-2-nitrobenzanilides obtained from the action of *o*-nitrobenzoyl chloride on *p*-bromo- and *p*-chloro-aniline. 2′-Chloro-*N*-methyl-2-nitrobenzanilide, prepared both by the methylation of 2′-chloro-2-nitrobenzanilide and by the action of *o*-nitrobenzoyl chloride on *o*-chloro-*N*-methylaniline, gave on reduction the amine (I; R = *o*-Cl, R′ = H), which on diazotisation and subsequent heating gave only 2′-chloro-2-hydroxy-*N*-methylbenzanilide (III; R = *o*-Cl, R′ = H) and unidentified products.



4-Carbomethoxy-*N*-methyl-2-nitrobenzanilide was prepared by the action of 4-carbomethoxy-2-nitrobenzoyl chloride on methylaniline. Reduction to the corresponding base (I; R = H, R′ = CO_2Me), followed by diazotisation and the action of heat on the diazonium solution, gave both 6-carbomethoxy-10-methylphenanthridone (II; R = H, R′ = CO_2Me) and 4-carbomethoxy-2-hydroxy-*N*-methylbenzanilide (III; R = H, R′ = CO_2Me). Decomposition of the diazonium fluoroborate in acetone suspension by the addition of copper powder also gave 6-carbomethoxy-10-methylphenanthridone, but not the phenol.

With the limited range of substituted *o*-amino-*N*-methylbenzanilides so far used for the preparation of *N*-methylphenanthridones, it is not possible to discern any marked influence of the substituent atom or group on the yield in the cyclisation reaction apart from an indication of a low yield when the presence of an *ortho*-substituent limits the number of positions at which internuclear cyclisation can occur from two to one. The results so far reported are summarised below. Further discussion of the possible implications of these results must await investigations in which the nature and position of the substituent R is further varied.

Yields of the N-*methylphenanthridone obtained from* o-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}NMe{\cdot}C_6H_4R$.

R	Diazonium sulphate method, %	Fluoroborate method, %
H	50	50
p-Me	50	49
o-Me	12	22
p-Br	—	33
p-Cl	—	44
o-Cl	0	—

EXPERIMENTAL

Dimethylphenanthridones.

N-*Methyl-2-nitrobenzo*-p-*toluidide*.—(*a*) To a solution of methyl-*p*-toluidine (10 g.) (Halberkann, *Ber.*, 1921, **54**, 1833) in pyridine (50 c.c.) was added slowly an ethereal solution of *o*-nitrobenzoyl chloride, prepared from the acid (12·2 g.) by Boëtius and Römisch's method (*Ber.*, 1935, **68**, 1924.) After removal of the ether, the solution was boiled for 5 minutes, cooled, and poured into water. The solid which separated was crystallised from benzene–light petroleum (b. p. 80—100°) and gave N-*methyl-2-nitrobenzo*-p-*toluidide* (15 g.) in hexagonal flat prisms, m. p. 105° (Found: C, 66·7; H, 5·3. $C_{15}H_{14}O_3N_2$ requires C, 66·7; H, 5·2%). (*b*) By the procedure outlined above *o*-nitrobenzoyl chloride (from 20 g. of acid) and *p*-toluidine (12·9 g.) gave 2-nitrobenzo-*p*-toluidide (25·3 g.) in glistening plates, m. p. 147°, from aqueous alcohol (cf. Bellavita, *Gazzetta*, 1940, **70**, 584). A solution of the amide (20 g.) in a mixture of acetone (100 c.c.) and 20% aqueous sodium hydroxide (100 c.c.) was boiled under reflux with vigorous stirring, and methyl sulphate (40 c.c.) was added slowly. The mixture was then cooled and added to ice-water which was kept alkaline with 20% aqueous sodium hydroxide. An oil separated and solidified. Recrystallisation from benzene–light petroleum (b. p. 80—100°) gave *N*-methyl-2-nitrobenzo-*p*-toluidide (17·1) g. in prisms, m. p. 105—106°, identical with the product prepared by method (*a*).

N-*Methyl-2-nitrobenzo*-o-*toluidide*.—(*a*) A solution of toluene-*p*-sulphon-*o*′-toluidide (33·6 g.), prepared by Reverdin and Crepieux's method (*Ber.*, 1902, **35**, 1440), in 16% aqueous sodium hydroxide was warmed and methyl sulphate (25 c.c.) added. The mixture was kept alkaline with 16% aqueous sodium hydroxide. An oil separated and solidified. Recrystallisation from alcohol gave *N*-methyltoluene-*p*-sulphon-*o*′-toluidide (27 g.) in needles, m. p. 87°. Witt and Uerményi (*Ber.*, 1913, **46**, 302) recorded m. p. 119—120° for this compound, prepared by the action of toluene-*p*-sulphonyl chloride on methyl-*o*-toluidine, but Young (*J. Amer. Chem. Soc.*, 1934, **56**, 2783) gave m. p. 87—87·5° for the compound prepared by methylation of the sulphonanilide. Hydrolysis of *N*-methyltoluene-*p*-sulphon-*o*′-toluidide (26 g.) with concentrated sulphuric acid (30 c.c.) and acetic acid (15 c.c.), by the method used by Usherwood and Whiteley (*J.*, 1923, 1084) for the preparation of methyl-*o*-nitroaniline, gave methyl-*o*-toluidine (10·1 g.), b. p. 205—207°/760 mm. By the procedure described above for the corresponding derivative of *p*-toluidine, methyl-*o*-toluidine (10·1 g.) and *o*-nitrobenzoyl chloride (from 16·7 g. of acid) gave N-*methyl-2-nitrobenzo*-o-*toluidide* (8 g.) in prisms, m. p. 121—122°, from benzene–light petroleum (b. p. 80—100°) (Found: C, 66·5; H, 5·4%). (*b*) By the method used above with *p*-toluidine, *o*-nitrobenzoyl chloride (from 16·7 g. of acid) and *o*-toluidine (10·7 g.) gave 2-*nitrobenzo*-o-*toluidide* (21 g.) in needles, m. p. 174°, from alcohol (Found: C, 65·8; H, 4·5. $C_{14}H_{12}O_3N_2$ requires C, 65·6; H, 4·7%). Methylation of the nitrobenzotoluidide (20 g.), as in the preceding example, gave *N*-methyl-2-nitrobenzo-*o*-toluidide (18 g.) in needles, m. p. 122°, identical with the product prepared by method (*a*).

2-*Amino*-N-*methylbenzo*-p-*toluidide*.—A solution of the nitro-compound (10 g.) in alcohol (100 c.c.) and a suspension of Raney nickel (10 g.) in the same solvent were shaken with hydrogen at atmospheric pressure until the required quantity of hydrogen had been absorbed (2 hours). The suspension was filtered and the filtrate concentrated under reduced pressure. Recrystallisation of the solid which separated gave 2-*amino*-N-*methylbenzo*-p-*toluidide* (7·6 g.) in elongated prisms, m. p. 64—65°, from light petroleum (b. p. 40—60°) (Found: C, 75·2; H, 6·4. $C_{15}H_{16}ON_2$ requires C, 75·0; H, 6·7%).

2-*Amino*-N-*methylbenzo*-o-*toluidide*.—In similar manner the corresponding nitro-compound (10 g.) gave 2-*amino*-N-*methylbenzo*-o-*toluidide* (8 g.), which separated from benzene–light petroleum (b. p. 80—100°) in prisms, m. p. 99—100° (Found: C, 74·7; H, 6·7%).

Decomposition of the Diazonium Sulphate prepared from 2-*Amino*-N-*methylbenzo*-p-*toluidide*.—The amine (2·5 g.) was diazotised in concentrated sulphuric acid (10 c.c.) and water (100 c.c.) by the addition of sodium nitrite (1 g.) in water (10 c.c.), and after filtration the solution was heated on a boiling-water bath for 1 hour. The cold mixture was extracted with chloroform, and the extract was washed several times with 10% aqueous sodium hydroxide. Concentration of the dried (Na_2SO_4) chloroform extract gave a brown tar (1·5 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (3 : 1) and adsorbed on an alumina column (20 × 2 cm.). Washing of the column with the same mixed solvent (1000 c.c.) gave a yellow solid, which on recrystallisation gave 3 : 10-*dimethylphenanthridone* (1·11 g.) in long prisms, m. p. 136—137°, from benzene–light petroleum (b. p. 80—100°) (Found: C, 80·7; H, 5·7. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8%). Subsequent successive elution with benzene, benzene–ether, and ether gave, first, a yellow solid (0·1 g.), m. p. 120—140°, and then brown tars. Acidification of the alkaline extract liberated a brown tar (1·1 g.) which was dissolved in benzene and adsorbed on a column of silica gel (10 × 2 cm.). Elution with benzene (400 c.c.) gave a white solid, which yielded 2-*hydroxy*-N-*methylbenzo*-p-*toluidide* (0·5 g.) in needles, m. p. 90—91°, from light petroleum (b. p. 80—100°) (Found: C, 74·7; H, 6·3. $C_{15}H_{15}O_2N$ requires C, 74·5; H, 6·2%).

Decomposition of the Diazonium Fluoroborate prepared from 2-*Amino*-N-*methylbenzo*-p-*toluidide*.—The amine (2 g.) was diazotised in concentrated sulphuric acid (10 c.c.) and water (30 c.c.) with sodium nitrite (1 g.) in water (10 c.c.), and to the filtered solution, cooled to 0°, sodium fluoroborate (5 g.) in water (10 c.c.) was added slowly with stirring. After ½ hour the yellow diazonium fluoroborate, which had separated, was collected and dried *in vacuo*. To a suspension of the dry fluoroborate in " AnalaR " acetone (50 c.c.) copper powder * (2 g.) was added. There was a vigorous evolution of nitrogen, and the reaction was complete within ½ hour. The mixture was filtered into cold water, the residue being extracted successively 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 yellow solid (2 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (3 : 1) and adsorbed on an alumina column (20 × 2 cm.). Elution with the same solvent and then with benzene (900 c.c.) gave 3 : 10-dimethylphenanthridone (0·9 g.) in prisms, m. p. 136—137°, from benzene–light petroleum (b. p. 80—100°). There was no depression in m. p. on admixture of the specimen with the corresponding product prepared from the diazonium sulphate. Further elution with benzene–ether (3 : 1) (1000 c.c.) gave another *substance* as pale yellow prisms (0·6 g.), m. p. 193°, from benzene (Found : C, 79·7; H, 6·4; N, 6·4%; *M*, 244), and finally a brown tar. Acidification of the alkaline extract gave only a trace of a black tar.

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-*N*-methylbenzo-*o*-toluidide.*—The amine (3·5 g.) was diazotised in sulphuric acid, the solution was heated, and the products were worked up and purified as described above for the corresponding reaction with the benzo-*p*-toluidide. The brown tar (1·1) g. from the neutral chloroform extract gave 1 : 10-*dimethylphenanthridone* (0·4 g.) in needles, m. p. 141—142°, from light petroleum (b. p. 80—100°) (Found : C, 80·3; H, 6·1%). Further elution with benzene (2500 c.c.) gave a *substance* as pale yellow prisms (0·3 g.), m. p. 165° [from benzene–light petroleum (b. p. 80—100°)] (Found : C, 75·3; H, 5·7; N, 5·9%; *M*, 224). Acidification and extraction of the alkaline washings gave, by the procedure described above, 2-*hydroxy-*N*-methylbenzo-*o*-toluidide* (0·52 g.) in needles, m. p. 99° (Found : C, 74·5; H, 6·6%).

*Decomposition of the Diazonium Fluoroborate prepared from 2-Amino-*N*-methylbenzo-*o*-toluidide.*—The diazonium fluoroborate, prepared from the amine (3·5 g.), was decomposed and the product worked up as described above for the corresponding reaction with the benzo-*p*-toluidide. The orange gum (3·4 g.), obtained from the neutral chloroform solution, was adsorbed on alumina from benzene–light petroleum (b. p. 60—80°) (1 : 1). Elution with benzene–light petroleum (b. p. 60—80°) (2 : 1) (2000 c.c.) gave 1 : 10-dimethylphenanthridone (0·75 g.) in needles, m. p. 141—142°, from light petroleum (b. p. 80—100°), identical with the product obtained from the diazonium sulphate. Further elution with various solvents gave only unidentified tars. Acidification of the alkaline washings gave only a trace of a brown gum.

*Halogeno-*N*-methylphenanthridones.*

Halogeno-2-nitrobenzanilides.—An ethereal solution of *o*-nitrobenzoyl chloride (prepared from 20 g. of the acid) was added slowly with cooling to a solution of *p*-bromoaniline (20 g.) in pyridine (100 c.c.). The ether was evaporated and the pyridine solution was boiled for 5 minutes, cooled, and poured into water. Crystallisation of the separated solid from alcohol–acetone gave 4′-*bromo-2-nitrobenzanilide* (29 g.) in needles, m. p. 200—201° (Found : C, 48·7; H, 3·1. $C_{13}H_9O_3N_2Br$ requires C, 48·6; H, 3·1%). In similar manner *o*-nitrobenzoyl chloride (from 20 g. of acid) and *p*-chloroaniline (15·4 g.) gave 4′-*chloro-2-nitrobenzanilide* (27 g.), which separated from alcohol in needles, m. p. 182—183° (Found : C, 56·5; H, 3·4. $C_{13}H_9O_3N_2Cl$ requires C, 56·5; H, 3·3%). From *o*-chloroaniline (15·4 g.) in place of *p*-chloroaniline, 2′-*chloro-2-nitrobenzanilide* (14 g.) was obtained in needles, m. p. 190—192°, from benzene–acetone (Found: C, 56·5; H, 3·2%).

*Halogeno-*N*-methyl-2-nitrobenzanilides.*—A solution of 4′-bromo-2-nitrobenzanilide (30 g.) in acetone (200 c.c.) and 20% aqueous sodium hydroxide (200 c.c.) was boiled under reflux with stirring, and methyl sulphate (60 c.c.) was slowly added. When cold, the mixture was diluted with ice-water, and an oil separated which solidified. Recrystallisation from alcohol gave 4′-*bromo-*N*-methyl-2-nitrobenzanilide* (29 g.) in needles, m. p. 118—119° (Found: C, 49·9; H, 3·5. $C_{14}H_{11}O_3N_2Br$ requires C, 50·2; H, 3·3%). In similar manner 4′-chloro-2-nitrobenzanilide (20 g.) gave 4′-*chloro-*N*-methyl-2-nitrobenzanilide* (18 g.) in prisms, m. p. 112—113°, from alcohol (Found: C, 58·1; H, 3·9. $C_{14}H_{11}O_3N_2Cl$ requires C, 57·9; H, 3·8%), and 2′-chloro-2-nitrobenzanilide (10 g.) gave 2′-*chloro-*N*-methyl-2-nitrobenzanilide* (9 g.) in prisms, m. p. 127—128°, from alcohol (Found : C, 58·2; H, 4·2%). The latter compound was also prepared by the *o*-nitrobenzoylation of *o*-chloro-*N*-methylaniline. To 2-chlorotoluene-*p*-sulphonanilide (m. p.

---

* The copper powder used in this and subsequent experiments was prepared from zinc dust and aqueous copper sulphate.

104—105°; 18·4 g.) in warm 16% aqueous sodium hydroxide, methyl sulphate (10 c.c.) was slowly added. The oil which separated solidified and when crystallised from benzene-light petroleum (b. p. 80—100°) gave *2-chloro-*N*-methyltoluene-*p*-sulphonanilide* (17 g.) in needles, m. p. 97—98° (Found : C, 56·8; H, 5·1. $C_{14}H_{14}O_2NSCl$ requires C, 57·1; H, 4·7%). Hydrolysis of the latter (15 g.) with 60% sulphuric acid (100 c.c.) at 110° for 1 hour, followed by pouring into an excess of ice-cold aqueous ammonia, gave *o*-chloro-*N*-methylaniline (5 g.), which was extracted with ether and collected at 126°/20 mm. *o*-Nitrobenzoyl chloride (from 6 g. of acid) in ether was added to the base (5 g.) in pyridine (30 c.c.), and after removal of the ether the mixture was boiled for 5 minutes. When cold the whole was added to water, 2′-chloro-*N*-methyl-2-nitrobenzanilide (8·1 g.) separating, which crystallised from alcohol in prisms, m. p. 128°, identical with the sample prepared above.

*Decomposition of the Diazonium Fluoroborates prepared from 2-Amino-4′-bromo- and 2-Amino-4′-chloro-*N*-methylbenzanilide.*—A suspension of iron filings (30 g.) in 5% aqueous acetic acid (50 c.c.) was heated on a steam-bath with stirring until no more hydrogen was evolved, then 4′-bromo-*N*-methyl-2-nitrobenzanilide (12 g.) was added slowly. After 1 hour on the steam-bath the mixture was neutralised with aqueous sodium carbonate, and charcoal was added to assist filtration. Both filtrate and residue were repeatedly extracted with hot benzene. The combined extracts on evaporation gave the base as an oil (8·4 g.), which charred on attempted distillation under reduced pressure. It was therefore diazotised in concentrated sulphuric acid (40 c.c.) and water (100 c.c.) with sodium nitrite (3 g.) in water (15 c.c.). A solution of sodium fluoroborate (15 g.) in water (30 c.c.) was added slowly with stirring to the filtered diazonium salt solution cooled to 0°. The diazonium fluoroborate separated as an orange solid. Crystallisation from acetone–light petroleum (b. p. 40—60°) gave *4′-bromo-*N*-methylbenzanilide-2-diazonium fluoroborate* (7 g.) in yellow-orange prisms, m. p. 112° (decomp.) (Found : C, 41·3; H, 2·5. $C_{14}H_{11}ON_3Br,BF_4$ requires C, 41·6; H, 2·7%). In similar manner 4′-chloro-*N*-methyl-2-nitrobenzanilide (12 g.) gave the base (9·1 g.) from which *4′-chloro-*N*-methylbenzanilide-2-diazonium fluoroborate* (10 g.) was obtained in yellow-orange prisms, m. p. 107° (decomp.) (Found : C, 46·8; H, 3·4. $C_{14}H_{11}ON_3Cl,BF_4$ requires C, 46·8; H, 3·1%). The 4′-bromo-*N*-methylbenzanilide-2-diazonium fluoroborate (6·4 g.) in acetone suspension was decomposed by the addition of copper powder as described above for the benzotoluidide-diazonium fluoroborates. Concentration of the alkali-washed and dried chloroform solution gave an orange solid (4·2 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (4 : 1) and adsorbed on an alumina column (30 × 2 cm.). Elution with the same mixed solvent (800 c.c.) gave *3-bromo-10-methylphenanthridone* (1·5 g.), which crystallised from benzene-light petroleum (b. p. 80—100°) in needles, m. p. 188—189° (Found: C, 58·6; H, 3·6. $C_{14}H_{10}ONBr$ requires C, 58·3; H, 3·6%). Further elution with the mixed solvent and then with benzene (800 c.c.) gave a second *substance* (0·4 g.) in buff plates, m. p. 235°, from aqueous acetic acid (Found : C, 76·3; H, 5·2; N, 6·6%). Subsequent elution with various solvents gave only gums. Acidification of the original alkaline washings gave only a trace of brown gum. In a similar manner 4-′chloro-*N*-methylbenzanilide-2-diazonium fluoroborate (9·4 g.) gave *3-chloro-10-methylphenanthridone* (2·8 g.), which crystallised from methanol in needles, m. p. 192° (Found : C, 68·8; H, 4·2. $C_{14}H_{10}ONCl$ requires C, 69·0; H, 4·2%), and a second *substance* (0·7 g.) in plates, m. p. 208—210°, from aqueous acetic acid (Found : C, 73·5; H, 5·6; N, 6·3%). Again, acidification of the alkaline washings gave only a trace of a dark gum.

*2-Amino-2′-chloro-*N*-methylbenzanilide.*—(*a*) Reduction of the nitro-compound (7 g.) with iron and acetic acid as described above for the *p*-halogeno-compounds gave, on evaporation of the benzene extracts, a solid which on crystallisation from benzene–light petroleum (b. p. 80—100°) afforded *2-amino-2′-chloro-*N*-methylbenzanilide* (4·1 g.) in needles, m. p. 109—110·5° (Found : C, 64·9; H, 5·3. $C_{14}H_{13}ON_2Cl$ requires C, 64·5; H, 5·0%). (*b*) A solution of the nitro-compound (5 g.) in ethanol (100 c.c.) was shaken with Raney nickel (5 g.) and hydrogen at atmospheric pressure for 1½ hours. When 1150 c.c. of hydrogen had been absorbed the suspension was filtered and the filtrate concentrated under reduced pressure. Crystallisation of the solid residue from benzene–light petroleum (b. p. 80—100°) gave 2-amino-2′-chloro-*N*-methylbenzanilide (3·3 g.) in needles, m. p. 113—115° undepressed on admixture with the product prepared by method (*a*) (Found : C, 64·0; H, 5·3%).

*2′-Chloro-*N*-methylbenzanilide-2-diazonium Fluoroborate.*—The amine (4 g.) in concentrated sulphuric acid (20 c.c.) and water (40 c.c.) was diazotised with sodium nitrite (1·5 g.) in water (10 c.c.) and to the filtered solution at 0° a solution of sodium fluoroborate (7 g.) in water (10 c.c.) was added slowly with stirring. Crystallisation of the separated solid from acetone–light petroleum (b. p. 40—60°) gave *2′-chloro-*N*-methylbenzanilide-2-diazonium fluoroborate*

(4·2 g.) in pale yellow prisms, m. p. 119° (decomp.) (Found : C, 46·9; H, 3·3. $C_{14}H_{11}ON_3Cl,BF_4$ requires C, 46·8; H, 3·1%).

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-2′-chloro-*N*-methylbenzanilide.*—The amine (3 g.) was diazotised as described above and the filtered diazonium sulphate solution was heated for 1 hour on a boiling-water bath. When cold the mixture was extracted with chloroform. Evaporation of the alkali-washed chloroform extract gave a dark gum (2 g.), but adsorption from benzene solution on an alumina column and subsequent elution with the same solvent gave only a waxy *substance* (0·7 g.), m. p. 70—75°, from methanol (Found: C, 67·4; H, 4·1; Cl, 15·2%), a red oil, and a pale yellow *substance* (0·3 g.), m. p. 246—250°, from methanol (Found : C, 60·9; H, 4·0; Cl, 13·5%). Acidification of the alkaline extract gave a dark solid (1·2 g.), which was adsorbed from benzene solution on a silica-gel column (10 × 1 cm.). Elution with the same solvent gave a white solid, which crystallised from aqueous methanol as needles of *2′-chloro-2-hydroxy-*N*-methylbenzanilide* (0·2 g.), m. p. 92° (Found: C, 64·4; H, 4·7. $C_{14}H_{12}O_2NCl$ requires C, 64·3; H, 4·6%).

*Carbomethoxy-*N*-methylphenanthridone.*

*4-Carbomethoxy-*N*-methyl-2-nitrobenzanilide.*—Methyl 4-carboxy-3-nitrobenzoate (15 g.), kindly provided by Dr. B. H. Chase, was boiled under reflux for 2 hours with an excess of thionyl chloride (50 c.c.). The crude acid chloride, obtained on removal of the excess of thionyl chloride, in ether, was added slowly to a solution of methylaniline (30 c.c.) in pyridine (50 c.c.). The ether was evaporated and the pyridine solution was boiled for 5 minutes, cooled, and added to cold dilute hydrochloric acid. The brown oil solidified. Recrystallisation from aqueous alcohol (charcoal) or benzene–light petroleum (b. p. 80—100°) gave *4-carbomethoxy-*N*-methyl-2-nitrobenzanilide* (12·6 g.) in needles, m. p. 124—125°, which became coloured on exposure to light (Found : C, 61·2; H, 4·4. $C_{16}H_{14}O_5N_2$ requires C, 61·3; H, 4·5%).

*2-Amino-4-carbomethoxy-*N*-methylbenzanilide.*—The nitro-compound (12 g.) was added slowly to a suspension of iron filings (50 g.) in 5% aqueous acetic acid (100 c.c.) which had been heated on a steam-bath with stirring until no more hydrogen was evolved. After 1 hour's further stirring on the steam-bath the solution was neutralised with aqueous sodium carbonate and filtered with added charcoal. Both filtrate and residue were well extracted with hot benzene, and concentration of the combined extracts gave *2-amino-4-carbomethoxy-*N*-methylbenzanilide* (9·1 g.) in prisms, m. p. 138° (Found: C, 67·8; H, 5·8. $C_{16}H_{16}O_3N_2$ requires C, 67·6; H, 5·6%).

*Decomposition of the Diazonium Sulphate prepared from 2-Amino-4-carbomethoxy-*N*-methylbenzanilide.*—The amine (3 g.) was diazotised in sulphuric acid (5 c.c.) and water (100 c.c.) by the addition of sodium nitrite (1 g.) in water (10 c.c.). The filtered solution was decomposed and the products worked up as described above for the benzotoluidide-diazonium sulphates. Evaporation of the alkali-washed chloroform solution left a brown solid (1·82 g.), which was adsorbed on an alumina column (20 × 2 cm.) from benzene–light petroleum (b. p. 60—80°) (4 : 1). Elution with benzene (800 c.c.) gave a white solid, which crystallised from benzene–light petroleum (b. p. 80—100°) in needles of *6-carbomethoxy-10-methylphenanthridone* (1 g.), m. p. 165° (Found : C, 71·9; H, 5·1. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9%). Further elution with benzene–ether (3 : 1) (450 c.c.) gave a second *substance* in pale yellow needles, m p. 151—152°, from benzene–light petroleum (b. p. 80—100°) (Found : C, 67·1; H, 5·0%; *M*, 285). Acidification and extraction of the alkaline washings gave a brown tar (1·73 g.), which was adsorbed from benzene on a column of silica gel (10 × 2 cm.). Elution with the same solvent (350 c.c.) gave *4-carbomethoxy-2-hydroxy-*N*-methylbenzanilide* (0·46 g.) in needles, m. p. 181° (Found : C, 67·4; H, 5·0. $C_{16}H_{15}O_4N$ requires C, 67·4; H, 5·3%).

*Decomposition of the Diazonium Fluoroborate prepared from 2-Amino-4-carbomethoxy-*N*-methylbenzanilide.*—The diazonium fluoroborate, prepared from the amine (3 g.), was decomposed and the products were worked up as in the examples given above. Evaporation of the alkali-washed chloroform extract left a pale brown solid (2·85 g.), which was dissolved in benzene–light petroleum (b. p. 60—80°) (4 : 1) and purified by adsorption on alumina. In this manner 6-carbomethoxy-10-methylphenanthridone (1·1 g.) was again obtained in needles, m. p. 164—165°. In addition to brown gums, a small quantity of a second compound, m. p. 240—245°, was obtained on further elution with benzene. Acidification and extraction of the alkaline washings gave only a minute quantity of a red tar.

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

[*Received, June 19th,* 1952.]