336. *Internuclear Cyclisation. Part XII.* The Synthesis of Some Benzophenanthridones. Abnormal Reaction of 1-Amino-N-methyl-2-naphthanilide.*

By R. A. Abramovitch, D. H. Hey, and R. A. J. Long.

Decomposition of the diazonium chloride from 1-amino-*N*-methyl-2-naphthanilide gave the deaminated and demethylated product, 2-naphthanilide, but no 10-methyl-5 : 6-benzophenanthridone which, however, was obtained from *N*-methyl-*N*-β-naphthoyl-*o*-phenylenediamine. 10-Methyl-6 : 7-benzophenanthridone was obtained from 3-amino-*N*-methyl-2-naphthanilide. Phosphorous tri-(*N*-methylanilide) can be used to prepare *N*-methylanilides not readily available by other methods. When 2-naphthoic and benzoic acid were condensed with *N*-methyl-*o*-nitroaniline in the presence of polyphosphoric acid 4-methylamino-3-nitrophenyl β-naphthyl ketone and 4-methylamino-3-nitrobenzophenone respectively were obtained. The latter was also obtained by heating *N*-methyl-*o*'-nitrobenzanilide with polyphosphoric acid.

In Part IX [1] it was shown that the decomposition of the diazonium salt from 2-amino-*N*-methylbenzo-1'-naphthalide gave rise to demethylation and deamination instead of to the expected cyclisation, this abnormal reaction being common to 2-amino-*N*-methylbenzanilides containing *ortho*-substituents in the anilide ring. On the other hand, 2-amino-*N*-methylbenzo-2'-naphthalide gave the corresponding *N*-methylbenzophenanthridone, cyclisation taking place at the 1'-position of the naphthalene ring. In the further application of this phenanthridone synthesis to the naphthalene series, a new abnormal reaction has now been disclosed in the attempted cyclisation of 1-amino-*N*-methyl-2-naphthanilide (V). Instead of the expected benzophenanthridone (IX), the only identifiable product was the demethylated and deaminated compound, 2-naphthanilide, which was formed together with two crystalline products, m. p. 137° and 185°, thought to be products

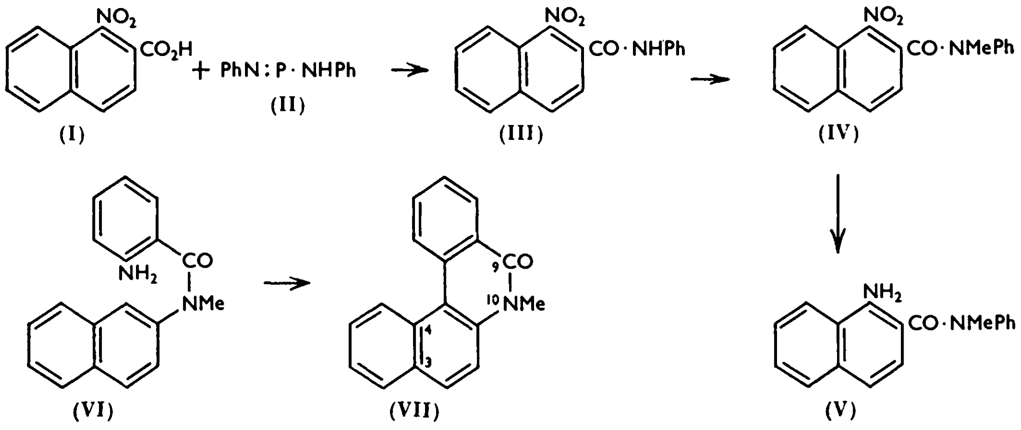
---

* Part XI, *J.*, 1954, 4263.

[1] Hey and Turpin, *J.*, 1954, 2471.

of rearrangement of the deaminated compounds. From this result it seems that a second group *ortho to the diazonium group*, as well as groups *ortho* to the anilide-nitrogen atom, can prevent normal cyclisation. This observation is being examined in greater detail.

In the synthesis of 1-amino-*N*-methyl-2-naphthanilide (V) the usual route to the amide from the acid by means of the acid chloride gave inconsistent results. 1-Nitro-2-naphthoic acid (I) can be obtained in poor yield from 2-methyl-1-nitronaphthalene by conversion into the pyruvic acid followed by oxidation with permanganate.[2] The conditions of the first stage were modified to give a better yield of the pyruvic acid. In attempts to find a better route to the naphthoic acid the oxidation of 2-methyl-1-nitronaphthalene with chromic acid was examined, but this method gave a yellow product which exhibited quinonoid properties and gave a derivative with 2 : 4-dinitrophenylhydrazine. These facts, in conjunction with the analytical data, lead us to formulate this product as 7-methyl-8-nitro-1 : 4-naphthaquinone. Oxidation with permanganate also failed to give the required acid. The unexpected stability of the methyl group, unlike that in *o*-nitrotoluene, was further demonstrated by its resistance to attack by *N*-bromosuccinimide, whereas *o*-nitrotoluene, 2-methylnaphthalene, and 1-bromo-2-methylnaphthalene[3] give the bromomethyl compounds. 1-Nitro-2-naphthoyl chloride, prepared under mild conditions, reacted with aniline and *N*-methylaniline, to give the corresponding amides, but these reactions were unreliable and could not be reproduced. Another route to the amides was therefore adopted which did not involve the formation of the acid chloride. The acid (I) was condensed with the phosphazo-compound (II) from aniline[4] to give 1-nitro-2-naphthanilide (III), which was methylated and then reduced to the amine (V). Diazotisation followed by decomposition in aqueous solution gave 2-naphthanilide but no 10-methyl-5 : 6-benzophenanthridone (IX).



The alternative route to 10-methyl-5 : 6-benzophenanthridone (IX) from *N*-methyl-*N*-β-naphthoyl-*o*-phenylenediamine (VIII), in which the diazonium group is now present in the benzene ring, was next examined. The amine was obtained from 2-naphthoyl chloride by condensation with *o*-nitroaniline followed by methylation and reduction. The diazotisation of the amine was carried out in dilute hydrochloric acid at 0° in order to obviate as far as possible the formation of the benziminazole, although this could not be completely avoided. Decomposition of the cold aqueous diazonium solution with copper powder gave a benzophenanthridone, the structure of which, however, was ambiguous because of the possibility of cyclisation at the 1- or the 3-position of the naphthalene ring. Hey and

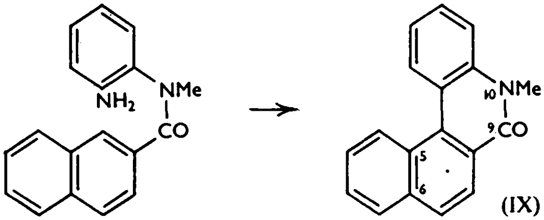
---

[2] Mayer and Oppenheimer, *Ber.*, 1916, **49**, 2137.

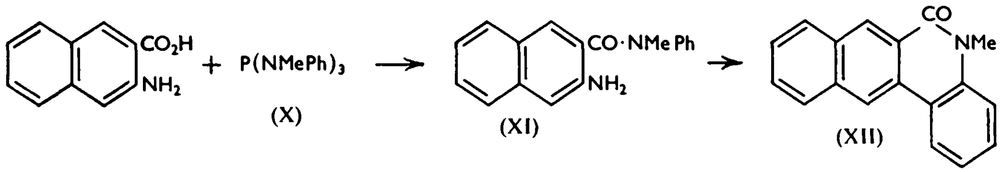
[3] Bergmann and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1951, **73**, 5153; Chapman and Williams, *J.*, 1952, 5044.

[4] Grimmel, Guenther, and Morgan, *J. Amer. Chem. Soc.*, 1946, **68**, 539.

Turpin[1] showed that 2-amino-*N*-methylbenzo-2′-naphthalide (VI) gave 10-methyl-3 : 4-benzophenanthridone (VII), but on the other hand, although Weitzenböck and Lieb,[5] and also Mayer and Oppenheimer,[6] claimed to have obtained a benzophenanthroic acid from 2-amino-α-2′-naphthylcinnamic acid, Cook[7] showed that their product was in reality a mixture of two acids in which cyclisation had taken place at the 1- and the 3-position in the naphthalene nucleus.



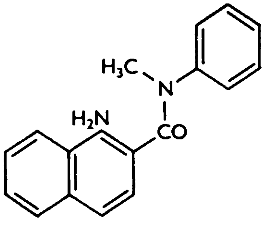
(VIII) (IX)



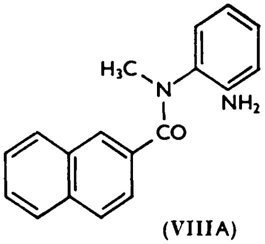
(X) (XI) (XII)

In order to eliminate the possibility that the cyclisation product from *N*-methyl-*N*-β-naphthoyl-*o*-phenylenediamine (VIII) was 10-methyl-6 : 7-benzophenanthridone (XII), the latter was synthesised unambiguously from 3-amino-*N*-methyl-2-naphthanilide (XI), which was conveniently obtained from 3-amino-2-naphthoic acid in one stage by an extension of the phosphazo-method[4] to secondary amines. This seems to be the first time that this method has been used for the synthesis of *NN*-disubstituted amides, and it has the advantage that it can be used in cases where the amide, such as this one, would have been difficult to obtain by other methods. The reaction of phosphorus trichloride with methylaniline in hot toluene gave a product assumed to be the tri-(*N*-methylanilide) (X).[8] With anthranilic acid this gave smoothly the known 2-amino-*N*-methylbenzanilide;[9, 11] similarly with 3-amino-2-naphthoic acid it gave the required amine (XI) in moderate yield. Cyclisation of the latter gave 10-methyl-6 : 7-benzophenanthridone (XII), which was different from the product obtained from *N*-methyl-*N*-β-naphthoyl-*o*-phenylenediamine which must therefore be the 5 : 6-benzophenanthridone (IX).

The phenomenon that, in apparently very similar reactions, demethylation and deamination take place in one case and cyclisation in the other may have steric causes. The amines (V and VIII), from which the diazonium salts are prepared, will favour the *anti*-relation for the naphthyl and phenyl groups as shown in (VA and VIIIA). The nuclear position at which the diazonium group is eliminated is thus in close proximity to the methyl



(VA)



(VIIIA)

---

[5] Weitzenböck and Lieb, *Monatsh.*, 1912, **33**, 549.

[6] Mayer and Oppenheimer, *Ber.*, 1918, **51**, 510.

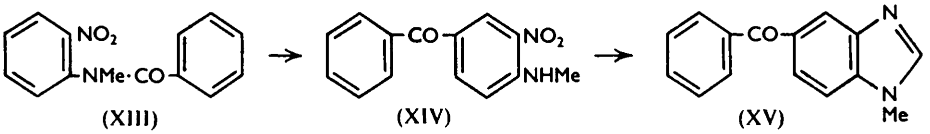
[7] Cook, *J.*, 1931, 2524.

[8] Kosolapoff, " Organophosphorus Compounds," John Wiley & Sons, New York, 1950, p. 278.

[9] Pictet and Gonset, *Arch. Sci. phys. nat. Genève*, 1897, **3**, 37.

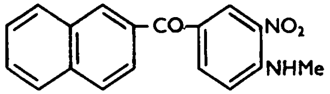
group in (VA), whereas in the isomeric amine (VIIIA) the same relation does not hold and free rotation about the N–CO bond (after elimination of the diazonium group and leading to cyclisation) is possible without impaction of the methyl group.

During this work the preparation of *N*-methyl-2′-nitro-2-naphthanilide by the direct condensation of 2-naphthoic acid and *N*-methyl-*o*-nitroaniline was investigated. Snyder and Elston [10] showed that polyphosphoric acid effected the condensation of weakly basic aromatic amines, *e.g.*, *o*-nitroaniline, with aromatic acids to give the amides. However 2-naphthoic acid and *N*-methyl-*o*-nitroaniline in polyphosphoric acid at 160° gave, in poor yield, a product isomeric with the naphthanilide obtained previously by reaction of 2-naphthoyl chloride and *o*-nitroaniline followed by methylation. A similar reaction with benzoic acid in place of 2-naphthoic acid gave, not the expected *N*-methyl-2′-nitrobenzanilide, but the isomeric 4-methylamino-3-nitrobenzophenone (XIV), which was further formed when *N*-methyl-2′-nitrobenzanilide (XIII) was heated with polyphosphoric acid. The benzophenone was identified by infrared spectroscopy, by formation of a 2 : 4-dinitrophenylhydrazone, and by conversion by boiling concentrated aqueous sodium hydroxide into 4-hydroxy-3-nitrobenzophenone; further, reduction followed by boiling with formic acid gave the benziminazole (XV), proving that the methylamino- and the nitro-group are adjacent. By analogy, the product obtained from *N*-methyl-*o*-nitroaniline and 2-naphthoic acid is formulated as 4-methylamino-3-nitrophenyl 2-naphthyl ketone (XVI).



(XIII) (XIV) (XV)

(XVI)



It is possible, but not necessary, that in these reactions the amide is first formed and then undergoes rearrangement to the ketone intermolecularly. This is suggested by the sublimation of benzoic acid from the reaction mixture when the pure *N*-methyl-2′-nitrobenzanilide (XIII) is used. A direct Friedel–Crafts aroylation is also possible. Similar rearrangements have been observed by Chattaway,[12] and by Dippy and his co-workers [13] when acyl, benzoyl, and dibenzoylanilides are caused to undergo rearrangement under different conditions with zinc or aluminium chlorides to the corresponding ketones. Dippy and Moss [13] postulate an intermolecular mechanism for this rearrangement. It is interesting that these authors did not obtain any identifiable products from nitroanilines under their conditions.

EXPERIMENTAL

Infrared measurements were carried out on a Grubb-Parsons S4 spectrometer with Nujol mulls of the compounds.

7-*Methyl*-8-*nitro*-1 : 4-*naphthaquinone*.—A solution of 2-methyl-1-nitronaphthalene (10 g.) in acetic acid (100 ml.) containing sulphuric acid (2 drops) was cooled in ice and treated with chromium trioxide (11 g.) during 2 hr. with stirring. The green solution was diluted with water, and the yellow solid (3·1 g.) was collected. Recrystallisation from light petroleum (b. p. 60—80°) gave 7-*methyl*-8-*nitro*-1 : 4-*naphthaquinone* in yellow needles, m. p. 138° (Found: C, 60·8; H, 3·2. $C_{11}H_7O_4N$ requires C, 60·8; H, 3·2%). The product obtained on reduction gave a positve β-naphthol coupling test for a primary amine. The compound dissolved in alkali to a

---

[10] Snyder and Elston, *J. Amer. Chem. Soc.*, 1954, **76**, 3039.
[11] Heacock and Hey, *J.*, 1952, 1508.
[12] Chattaway, *J.*, 1904, 395.
[13] Dippy and Wood, *J.*, 1949, 2719; Dippy and Moss, *J.*, 1952, 2205.

brown solution and in mineral acid to a red solution. It formed a 2 : 4-*dinitrophenylhydrazone*, m. p. 260° (Found : N, 17·1. $C_{17}H_{11}O_7N_5$ requires N, 17·6%).

1-*Nitro*-2-*naphthylpyruvic Acid* (cf. ref. 2).—Ethyl oxalate (100 g.) was added slowly with stirring to a solution of potassium (25 g.) in absolute methanol (200 ml.) at 0°. 2-Methyl-1-nitronaphthalene (40 g.) was then added portion-wise to the stirred solution, which was allowed to reach room temperature and then stirred overnight. The suspension was heated for 1 hr. at 45° and then boiled under reflux for a further hour. To the dark-red solution cooled in ice were added water (110 ml.) and 2N-sodium hydroxide (50 ml.). The solution was filtered, the residue washed with aqueous sodium hydroxide solution, and the combined filtrates were acidified carefully with hydrochloric acid. The oil which separated solidified. The mixture was kept in the refrigerator overnight and the pyruvic acid (59 g.) collected, which, after a further purification by precipitation from alkaline solution, had m. p. 199°. Mayer (*loc. cit.*) gives m. p. 207° (decomp. 199°).

1-*Nitro*-2-*naphthanilide*.—(i) To 1-nitro-2-naphthoic acid [3] (3·3 g.) in dry acetone (50 ml.), thionyl chloride (10 g.) was added and the solution boiled under reflux for 1 hr. The acetone and excess of thionyl chloride were removed under reduced pressure and the residue was kept in a vacuum-desiccator overnight. A portion of the solid acid chloride, on recrystallisation from ether, gave needles, m. p. 120°. To the crude acid chloride in cold pyridine (50 ml.) was added aniline (1·8 ml.), and the solution was heated on a steam-bath for 3 hr. and then poured into ice-water. The solid was filtered off and recrystallisation from aqueous ethanol gave 1-*nitro*-2-*naphthanilide* (1·8 g.), m. p. 182—183° (Found : C, 69·4; H, 4·1. $C_{17}H_{12}O_3N_2$ requires C, 69·8; N, 4·1%). Various attempts to repeat this experiment failed.

(ii) The phosphazo-compound [4] (1·5 g.), prepared from aniline and phosphorus trichloride in dry toluene, and 1-nitro-2-naphthoic acid (3 g.) in dry toluene (40 ml.) were boiled under reflux for 2 hr. The hot solution was filtered and the solid, which separated on cooling, crystallised from benzene–light petroleum (b. p. 60—80°) to give the anilide (2·1 g.), m. p. 182°, undepressed on admixture with a sample obtained by method (i). Steam-distillation of the toluene mother-liquors, after treatment with aqueous sodium carbonate, gave a further quantity of the crude anilide.

N-*Methyl*-1-*nitro*-2-*naphthanilide*.—(i) *N*-Methylaniline (2 ml.) in dry acetone (50 ml.) was added to 1-nitro-2-naphthoyl chloride (from 0·5 g. of acid), and the solution boiled under reflux for 1 hr. and then poured on ice. Recrystallisation of the solid from benzene–light petroleum (b. p. 60—80°) gave N-*methyl*-1-*nitro*-2-*naphthanilide* (0·32 g.) in plates, m. p. 135—136° (Found : C, 70·8; H, 4·7. $C_{18}H_{14}O_3N_2$ requires C, 70·6; H, 4·6%). Attempts to repeat this preparation were abortive.

(ii) 1-Nitro-2-naphthanilide (1·5 g.) in acetone (10 ml.) containing 20% aqueous sodium hydroxide (10 ml.) was boiled under reflux with rapid stirring while dimethyl sulphate (2·5 ml.) was added dropwise. After boiling for 20 min. the solution was poured into ice-water; the anilide recrystallised from benzene–light petroleum (b. p. 60—80°) as plates (1·4 g.), m. p. and mixed m. p. 136°. This substance can be obtained in rigid needles, prisms (both yellow), or colourless, fluffy needles.

1-*Amino*-N-*methyl*-2-*naphthanilide*.—A solution of *N*-methyl-1-nitro-2-naphthanilide (0·7 g.) in ethanol containing 5% palladium–charcoal (0·5 g.) was hydrogenated at room temperature and pressure. The catalyst was filtered off and the solvent removed *in vacuo*. The residual colourless oil, in ether, was saturated with dry hydrogen chloride to give 1-*amino*-N-*methyl*-2-*naphthanilide hydrochloride* (0·55 g.), m. p. 170—171° after recrystallisation from ethanol–ether saturated with dry hydrogen chloride (Found : C, 68·7; H, 5·6. $C_{18}H_{16}ON_2,HCl$ requires C, 69·2; H, 5·5%).

Decomposition of the Diazonium Chloride prepared from 1-*Amino*-N-*methyl*-2-*naphthanilide Hydrochloride*.—A suspension of the amine hydrochloride (1·56 g.) in ice-cold concentrated hydrochloric acid (14 ml.) and water (60 ml.) was diazotised at 0—5° with sodium nitrite (2 g.) in water (20 ml.). After being stirred for 1 hr. at 0° the mixture was diluted with water (150 ml.), treated with urea (2 g.) and then with copper powder, and stirred at room temperature overnight. A brown solid separated, and this and the mother-liquor were extracted with chloroform, the extracts being washed with alkali and dried (Na_2SO_4). The residue (1·1 g.) obtained on removal of the chloroform was chromatographed in benzene on alumina (30 × 2 cm.). Elution with benzene (600 ml.) gave a wax (0·05 g.). Benzene–ether (1 : 1) (200 ml.), followed by ether (150 ml.), gave a yellow gum (0·25 g.), which crystallised from ethanol to give 2-naphthanilide (0·18 g.) in plates, m. p. and mixed m. p. 170—171° (Found: C, 82·0; H, 5·5. Calc. for $C_{17}H_{13}ON$: C, 82·4; H, 5·3%). Vieth[14] gives m. p. 170°. Further elution with ether (250 ml.) gave a yellow gum (0·09 g.), which on crystallisation from benzene–light petroleum gave pale yellow prisms, m. p. 137° (Found: C, 83·2; H, 5·3%). This analysis approximates to that required for *N*-methyl-2-naphthanilide (C, 82·8; H, 5·75%), but the latter, as shown below, has m. p. 95—96°. The infrared spectrum (in Nujol mull) showed the following peaks: 3472 (broad), 1639 (s), 1608, 1585, 1560 (w), 1504 (w), 1466, 1414 (w), 1376, 1351, 1333, 1307 (m), 1101 (m), 838, 802 (w), 772 (m), and 760 cm.$^{-1}$ (s). No bands for a mono-substituted phenyl ring are present, and the analysis, spectrum, and colour seem to indicate a methylaminonaphthophenone structure. Further elution with ether (250 ml.) gave a yellow gum (0·1 g.), which did not crystallise, whereas more ether (250 ml.) gave a yellow gum (0·08 g.), which crystallised from benzene–light petroleum (b. p. 40—60°) in yellow needles, m. p. 185° (Found: C, 82·5; H, 5·7%), infrared max. (in Nujol mull) at 1689 (s), 1600 (w), 1468, 1420 (w), 1389, 1042, 1031, 1015, 905, 877, 837, 816, 803, 763 (m), 729, 686 cm.$^{-1}$ (m).

2′-Nitro-2-naphthanilide.—2-Naphthoic acid (5 g.) was boiled under reflux with an excess of thionyl chloride (10 ml.) for 1 hr. The excess of thionyl chloride was collected under reduced pressure, and the last traces removed by addition of dry benzene and vacuum-distillation. Ice-cold pyridine (10 ml.) was added to the acid chloride, and the solution treated with a solution of *o*-nitroaniline (4 g.) in pyridine (10 ml.). The orange solution was kept at room temperature overnight, heated on a boiling-water bath for 1 hr., and poured into ice-water (200 ml.). *2′-Nitro-2-naphthanilide* (7·0 g.) crystallised from ethanol in pale yellow needles, m. p. 138—139° (Found: C, 69·4; H, 3·95. $C_{17}H_{12}O_3N_2$ requires C, 69·9; H, 4·1%).

N-*Methyl-2′-nitro-2-naphthanilide.*—A suspension of 2′-nitro-2-naphthanilide (3·0 g.) in acetone (25 ml.) and 10% aqueous sodium hydroxide (30 ml.) was stirred and boiled under reflux. Dimethyl sulphate (4 ml.) was added dropwise and the orange solution became pale yellow. The cooled mixture was poured into ice-water, and the oil, which solidified on trituration, was washed with water. Recrystallisation from ethanol gave N-*methyl-2′-nitro-2-naphthanilide* (2·2 g.) in pale yellow plates, m. p. 124—125° (Found: C, 70·7; H, 4·55. $C_{18}H_{14}O_3N_2$ requires C, 70·6; H, 4·6%).

N-*Methyl*-N-*2-naphthoyl*-o-*phenylenediamine.*—The nitro-compound (3·0 g.) in warm methanol (200 ml.) was reduced with hydrogen in the presence of 5% palladium–charcoal at atmospheric temperature and pressure. The catalyst was filtered off and the solution evaporated to a small volume *in vacuo* at as low a temperature as possible. The solid which separated was washed with methanol–light petroleum, and recrystallisation from methanol gave N-*methyl*-N-*2-naphthoyl*-o-*phenylenediamine* (2·1 g.) in colourless prisms, m. p. 163—165° (Found: C, 77·9; H, 5·9. $C_{18}H_{16}ON_2$ requires C, 78·3; H, 5·8%).

Decomposition of the Diazonium Chloride prepared from N-*Methyl*-N-*2-naphthoyl*-o-*phenylenediamine.*—To the amine (2·1 g.) in methanol (150 ml.) at 0° was added a solution of concentrated hydrochloric acid (14 ml.) in methanol (20 ml.). Pentyl nitrite (4 ml.) was then added dropwise to the cooled stirred solution. After 4 hours' stirring at 0° copper powder (3·0 g.) was added and the mixture stirred for 18 hr., after which the evolution of nitrogen had ceased. The copper powder was filtered off and washed with hot methanol; the combined methanol solution was then evaporated to dryness under reduced pressure and the residual gum in a small volume of ethanol was adsorbed on alumina (80 g.). Elution with benzene gave a colourless gum, which crystallised from ethanol containing a few drops of benzene to give N-*methyl-5 : 6-benzophenanthridone* (0·20 g.) in fluffy needles, m. p. 158—159° (Found: C, 83·1; H, 5·2. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·0%), $\lambda_{max.}$ 228, 231, 238, 271 mμ ($10^{-3}\varepsilon$ 45·64, 45·8, 44·91, 72·65). The m. p. was depressed to 135° on admixture with the starting amine. Elution with benzene–ether (400 ml.; 3 : 5) gave a white solid which, on crystallisation from dilute methanol, gave 1-*methyl-2-2′-naphthylbenziminazole* (0·16 g.) in fine needles, m. p. 128° (Found: C, 84·4; H, 5·5. $C_{18}H_{14}N_2$ requires C, 83·8; H, 5·4%).

N-*Methyl-2-naphthanilide.*—The acid chloride from 2-naphthoic acid (1·0 g.) and *N*-methylaniline (0·56 g.) in dry benzene (10 ml.) were boiled under reflux for 2 hr. The solution was evaporated almost to dryness and light petroleum (b. p. 60—80°) was added until a turbidity appeared. The *anilide* separated gradually and crystallised from alcohol–light petroleum (b. p. 60—80°) in prisms (0·98 g.), m. p. 95—96° (Found: C, 82·5; H, 6·05. $C_{18}H_{15}ON$ requires C, 82·8; H, 5·75%).

---

[14] Vieth, *Annalen*, 1876, **180**, 305.

*2-Amino-*N*-methylbenzanilide.*—Phosphorus trichloride (9·2 g.) in dry toluene (20 ml.) was added dropwise to a stirred solution of *N*-methylaniline (42·8 g.) in dry toluene (50 ml.). The amine hydrochloride separated almost immediately. After 1 hour's stirring the mixture was heated at 100° for ½ hr., the solid dissolving. The cooled mixture was filtered and the solid washed with cold alcohol. Part of it dissolved and the insoluble residue was collected and dried. The filtrate was evaporated to dryness *in vacuo* and the solid residue washed with alcohol and combined with the first residue. The total weight of crude phosphorous tri-(*N*-methylanilide) was 16·6 g. This compound (1·18 g.), which is unstable, in dry toluene (20 ml.) was boiled under reflux for 3 hr. with anthranilic acid (1·5 g.). The hot solution was filtered from the gummy metaphosphorous acid and on concentration gave 2-amino-*N*-methylbenzanilide (0·5 g.), which crystallised from benzene in needles, m. p. 125° (Found : C, 74·4; H, 6·5. Calc. for $C_{14}H_{14}ON_2$: C, 74·6; H, 6·2%). Heacock and Hey [11] give m. p. 126—127° for this anilide prepared from *N*-methyl-2-nitrobenzanilide by reduction.

*3-Amino-*N*-methyl-2-naphthanilide* (XI).—Phosphorous tri-(*N*-methylanilide) (15 g.) in toluene (150 ml.) was boiled under reflux for 3 hr. with 3-amino-2-naphthoic acid (24 g.). The hot solution was filtered, washed with 2N-sodium hydroxide, and evaporated under diminished pressure. The residue, on crystallisation from methanol, gave the *anilide* (8·2 g.) in yellow needles, m. p. 163° (Found : C, 78·2; H, 5·5. $C_{18}H_{16}ON_2$ requires C, 78·2; H, 5·8%). It gave a positive diazo-coupling test for a primary amine and exhibited a strong absorption at 1639 cm.$^{-1}$, characteristic of the amide-carbonyl group.

*Decomposition of the Diazonium Chloride prepared from 3-Amino-*N*-methyl-2-naphthanilide.*—A suspension of the amine (1·0 g.) in concentrated hydrochloric acid (3 ml.) and water (10 ml.) was diazotised at 0° with sodium nitrite (0·5 g.) in water (10 ml.). After several hours' stirring at 0° water (200 ml.) was added and then urea (0·5 g.). The solution was treated with copper powder (1·0 g.) and stirred at room temperature for 24 hr. and then filtered. The residue and the filtrate were extracted separately with chloroform, and the combined extracts washed with alkali, dried (Na_2SO_4), and evaporated. The residual gum in benzene was chromatographed on alumina (90 g.). Elution with benzene (250 ml.) gave a gum. Elution with benzene–ether (1 : 1 v/v; 350 ml.) gave *10-methyl-6 : 7-benzophenanthridone* (0·1 g.) in fluffy needles, m. p. 180° (from methanol) (Found : C, 82·9; H, 5·5. $C_{18}H_{13}ON$ requires C, 83·4; H, 5·0%), $\lambda_{max.}$ 220, 264, 272 mμ ($10^{-3}\varepsilon$ 42·38, 62·0, 95·76). Further elution with benzene–ether (1 : 1) gave a yellow solid (0·07 g.) in fine yellow needles (from alcohol), m. p. 229° (Found : C, 77·7; H, 5·3%).

4-Methylamino-3-nitrophenyl 2-Naphthyl Ketone.—A mixture of 2-naphthoic acid (2 g.), *N*-methyl-*o*-nitroaniline (1·9 g.), and polyphosphoric acid (70 g.) was stirred while the temperature was slowly raised to 160° during 20 min. The colour changed from yellow to deep brown. The hot solution was then poured into cold water (600 ml.) and set aside overnight. The brown solid was filtered off. Crystallisation from alcohol gave the *naphthophenone* (0·2 g.) in yellow needles, m. p. 195° (Found : C, 69·8; H, 4·4. $C_{18}H_{14}O_3N_2$ requires C, 70·6; H, 4·6%), infrared max. (main peaks) at 3448, 1650 (m), 1634 (s), 1582, 1524, 1372, 1302, 1282, 758 cm.$^{-1}$.

4-Methylamino-3-nitrobenzophenone.—(i) A mixture of benzoic acid (5·1 g.), *N*-methyl-*o*-nitroaniline (6·0 g.), and polyphosphoric acid (50 g.) was stirred, heated, and worked up as in the previous preparation. Recrystallisation of the brown solid from alcohol gave the *benzophenone* (1·1 g.), m. p. 197° (Found : C, 65·4; H, 4·9. $C_{14}H_{12}O_3N_2$ requires C, 65·7; H, 4·7%), infrared max. (main peaks) at 3425, 1653 (m), 1626 (s), 1577, 1527, 1370, 1330, 1290, 1231, 766, 735, 693 cm.$^{-1}$). The 2 : *4-dinitrophenylhydrazone* had m. p. 257° (from ethanol) (Found : C, 55·7; H, 3·7. $C_{20}H_{16}O_6N_6$ requires C, 55·0; H, 3·7%).

(ii) *N*-Methyl-2-nitrobenzanilide (5·0 g.) was stirred and heated with polyphosphoric acid (50 g.) as described above. The resulting benzophenone (0·8 g.) had m. p. 197°, undepressed on admixture with the product prepared as described in method (i) above.

4-Hydroxy-3-nitrobenzophenone.—4-Methylamino-3-nitrobenzophenone (0·1 g.) was boiled with 10N-sodium hydroxide (50 ml.) for 48 hr., a clear solution being obtained. This was cooled, acidified, and extracted with ether. Evaporation of the dried (Na_2SO_4) ether gave 4-hydroxy-3-nitrobenzophenone (0·05 g.) in needles, m. p. 90° (from methanol) (Found : C, 63·7; H, 3·9; N, 5·35. Calc. for $C_{13}H_9O_4N$: C, 64·2; H, 3·7; N, 5·8%), infrared max. (main peaks) at 3378, 3125, 1678 (s), 1626 (s), 1587, 1543 (s), 1342, 1258, 1162, 743, 703 cm.$^{-1}$. The m. p. was undepressed on admixture with a sample prepared by the method of Blakey, Jones, and Scarborough [15] (who give m. p. 94°). The 2 : *4-dinitrophenylhydrazone* had m. p. and mixed

---

[15] Blakey, Jones, and Scarborough, *J.*, 1927, 2870.

m. p. 262° [from benzene–light petroleum (b. p. 40—60°)] (Found: C, 53·9; H, 3·1. $C_{19}H_{13}O_7N_5$ requires C, 53·9; H, 3·2%). The *semicarbazone*, m. p. and mixed m. p. 178°, separated from alcohol (Found: C, 55·2; H, 3·9. $C_{14}H_{12}O_4N_4$ requires C, 55·9; H, 4·0%).

3-*Amino*-4-*methylaminobenzophenone*.—4-Methylamino-3-nitrobenzophenone (0·2 g.) was treated with the stannous chloride reagent [16] (2 ml.), heated on a water-bath for 5 min., and then left at room temperature overnight. The complex was decomposed with an excess of alkali, and the solution extracted with ether. Evaporation of the dried ethereal extract gave the *diamine*, which separated from benzene–light petroleum (b. p. 40—60°) as a yellow solid (0·12 g.), m. p. 121° (Found: C, 74·3; H, 6·0. $C_{14}H_{14}ON_2$ requires C, 74·4; H, 6·2%). It diazotised normally, but the diazonium solution did not give a positive β-naphthol coupling test, probably owing to triazole formation. The diamine (0·2 g.) was boiled under reflux with 90% formic acid (10 ml.) for 2 hr. The excess of formic acid was then removed under reduced pressure and the residue kept on a water-bath in 4N-hydrochloric acid for 1 hr. The solution was concentrated, made alkaline, and extracted with chloroform. To the dried chloroform extract light petroleum (b. p. 40—60°) was added until a slight turbidity was obtained. 5-*Benzoyl*-1-*methylbenziminazole*, m. p. 97°, crystallised in white cubes and was recrystallised from chloroform–light petroleum (b. p. 40—60°) (Found: C, 76·2; H, 5·3. $C_{15}H_{12}ON_2$ requires C, 76·3; H, 5·1%).

This work was carried out during the tenure of an Imperial Chemical Industries Fellowship (R. A. A.) and a Hampshire County Major Scholarship (R. A. J. L.).

KING'S COLLEGE (UNIVERSITY OF LONDON),
STRAND, LONDON, W.C.2.

[*Received, November 21st*, 1956.]

---

[16] Abramovitch and Hey, *J.*, 1954, 1700.