218. *Derivatives of 1-Azanthraquinone. Part I.*

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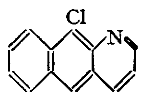
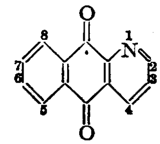
1-Azanthraquinone (II) and 9-chloro-1-azanthracene (I) have been prepared by the method of E.P. 427,485 involving a Skraup reaction on 1-chloro-2-naphthylamine and their nitration and bromination studied. 9 : 10-*Dichloro-1-azanthracene* is readily prepared by chlorination of I. The 5- and 6-*bromo-1-azanthraquinones* have been synthesised but attempts to prepare 8-bromo- and 5-, 6-, and 8-nitro-1-azanthraquinones failed.

Although 1-azanthraquinone (II) has been known since 1894, except for two I.G. Farbenindustrie patents (G.P. 597,833 and E.P. 427,485) which give few details of physical constants, no detailed examination of its properties has been made. Several syntheses have been recorded (Philips, *Ber.*, 1894, **27**, 1923; Braun and

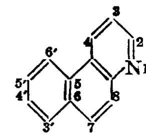
Gruber, *Ber.*, 1922, **55**, 1710; I.G. Farbenindustrie, *loc. cit.*; Braun and Nelles, *Ber.*, 1937, **70**, 1760) but only the I.G. Farbenindustrie method, for which no yield is recorded, appears suitable for the preparation of a quantity of the base.



(I.)



(II.)



(III.)

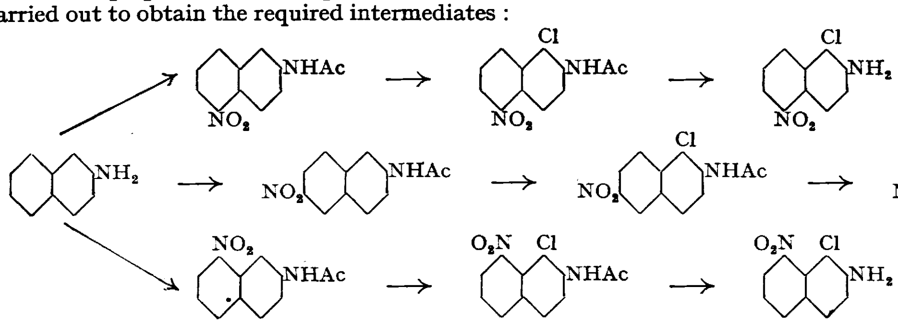
A 25% yield of 9-*chloro*-1-*azanthracene* (I) has been obtained by the present authors by this method from 1-chloro-2-naphthylamine together with about an equal amount of 5 : 6-benzquinoline (III) which is formed by elimination of the chlorine atom during the Skraup reaction. Oxidation of 9-chloro-1-azanthracene to 1-azanthraquinone takes place quantitatively with chromic anhydride in acetic acid solution.

9-Chloro-1-azanthracene is brominated and chlorinated in the 10-position giving dihalogeno compounds, the identity of these being proved by oxidation to 1-azanthraquinone. Further chlorination could not be induced, but vigorous bromination gives a *dibromo-derivative* of 9-chloro-1-azanthracene which oxidised to a *monobromo-derivative* of 1-azanthraquinone identical with the product obtained by the direct bromination of 1-azanthraquinone.

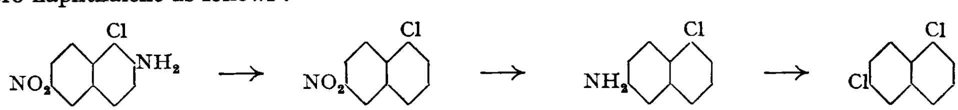
9-Chloro-1-azanthracene is readily nitrated in glacial acetic acid to give 9-*chloro*-10-*nitro*-1-*azanthracene*, the identity of which was proved by oxidation to 1-azanthraquinone. Under more vigorous conditions of nitration a *mononitro-derivative* of 1-azanthraquinone was formed.

Nitration of 1-azanthraquinone under mild conditions gave a *mononitro-derivative* of 1-azanthraquinone, m. p. 215—218°, identical with that obtained by nitrating 9-chloro-1-azanthracene. Nitration of 1-azanthraquinone under vigorous conditions gave a mononitro compound, m. p. 180—181°, and traces of another, m. p. 215—217°. On acid reduction the nitro compounds gave amino-1-azanthrones while 1-azanthraquinone gave 1-*azanthrone*, and with sodium sulphide *amino*-1-*azanthraquinones* were obtained in good yield.

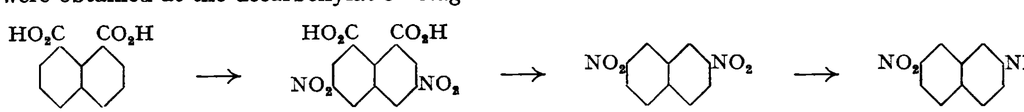
In order to prepare 1-azanthraquinone derivatives of known orientation the following series of reactions was carried out to obtain the required intermediates :



Proof that chlorination had taken place in the 1-position was obtained in the case of the 5- and 8-nitro-1-chloro-2-naphthylamines by de-amination to the corresponding nitro-1-chloro-naphthalenes both of which are known, and in the case of 6-nitro-1-chloro-2-naphthylamine the compound was converted to the known 1 : 6-dichloro-naphthalene as follows :



An attempt to prepare 7-nitro-2-naphthylamine by the following series of reactons was abandoned as poor yields were obtained at the decarboxylation stage :—

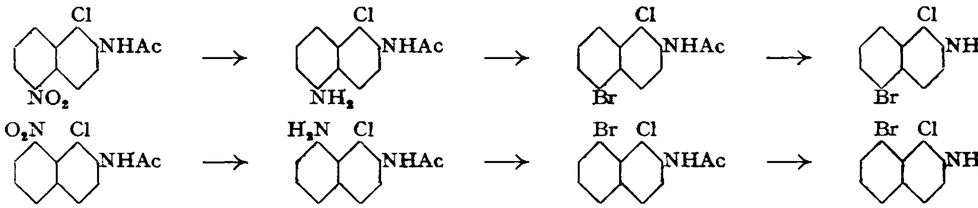


Of the three nitro-1-chloro-2-naphthylamines prepared, only the 6-nitro compound however gave any of the required 9-chloro-1-azanthracene derivative by the Skraup reaction and the 9-*chloro*-6-*nitro*-1-*azanthracene* thus obtained could not be oxidised to 6-nitro-1-azanthraquinone.

Since the completion of this work Gerhardt and Hamilton (*J. Amer. Chem. Soc.*, 1944, **66**, 479) have described the preparation of 9-chloro-1-azanthracene by the same method as the present authors (U.S.P. 2,093,596 is

8-nitro-compounds, these are not described here. The method of orientation differs from that of the present authors and it is claimed that 9-chloro-5-nitro-, 9-chloro-6-nitro-, and 9-chloro-8-nitro-1-azanthracenes were obtained from these intermediates; but attempts by the present authors to repeat this in the case of the 5- and 8- isomers have failed. In addition, Gerhardt and Hamilton (*loc. cit.*) describe the nitration of 9-chloro-1-azanthracene in nitric acid at −18° as taking place in the 5- and 8-positions and not in the *meso*-position. Thus three different nitration products of 9-chloro-1-azanthracene, *viz.*, the 5-nitro-, the 8-nitro-, and the 10-nitro-derivative, as well as a mononitro-derivative of 1-azanthraquinone, are obtained (see below).

As the nitro-derivatives of 1-chloro-2-naphthylamine are liable to reduction in the course of the Skramp reaction (giving diamino-derivatives of 1-chloronaphthalene and hence undesirable by-products) it was considered that the corresponding bromo-derivatives of 1-chloro-2-naphthylamine would be more suitable intermediates for the preparation of substituted 1-azanthraquinones of known constitution. 1-*Chloro*-6-*bromo*-2-*naphthylamine* was prepared by bromination of 1-chloro-2-naphthylamine (Armstrong and Rossiter, *Chem. News*, **63**, 137) and it gave a 5% yield of 9-chloro-6-bromo-1-azanthracene which oxidised readily to 6-bromo-1-azanthraquinone (G.P. 597,833). The 5- and 8-bromo-derivatives of 1-chloro-2-naphthylamine were obtained as follows:



The reduction of the nitro compounds without hydrolysis of the acetamido group was accomplished by the use of etched iron in neutral solution. 1-Chloro-5-bromo-2-naphthylamine gave 9-*chloro*-5-*bromo*-1-*azanthracene* by the Skraup reaction and this was oxidised to 5-*bromo*-1-*azanthraquinone*, but 1-chloro-8-bromo-2-naphthylamine gave only 6′-bromo-5 : 6-benzquinoline.

EXPERIMENTAL.

9-Chloro-1-azanthracene was prepared by the method of E.P. 427,485 and the crude material fractionated under reduced pressure, giving 9-chloro-1-azanthracene, b. p. 190—195°/2 mm., as almost colourless plates, m. p. 141° from ligroin (Found: C, 73·8; H, 3·7. Calc. for $C_{13}H_8NCl$: C, 73·2; H, 3·7%). Its picrate crystallised in yellow prisms from alcohol, m. p. 206° (Found: C, 51·3; H, 3·1. Calc. for $C_{19}H_{11}O_7N_4Cl$: C, 51·5; H, 2·5%). 5 : 6-Benzquinoline (III) had b. p. 170—172°/2 mm., m. p. 94°, and its picrate had m. p. 251—252°. 1-Azanthraquinone was obtained in theoretical yield, by oxidation of 9-chloro-1-azanthracene (E.P. 427,485) with chromic oxide in acetic acid, as pale yellow needles, m. p. 276°, from ethanol or chlorobenzene (Found: C, 75·1; H, 3·7; N, 6·4. Calc. for $C_{13}H_7O_2N$: C, 74·6; H, 3·4; N, 6·7%).

Nitration of 9-*Chloro*-1-*azanthracene*.—(a) 9-*Chloro*-10-*nitro*-1-*azanthracene*. 9-Chloro-1-azanthracene (0·5 g.) in glacial acetic acid (4 c.c.) was treated with nitric acid (0·2 c.c., *d* 1·42) and warmed on a water bath at 100° for 2 hours. The solution was poured into ice water and made alkaline with sodium hydroxide. The precipitated solid was filtered off, washed with water, dried and crystallised from acetic acid giving a yellow solid (0·42 g., 70%), m. p. 201—203°, which sublimed under reduced pressure to give bright yellow needles having the same m. p. (Found: C, 60·3; H, 3·0. $C_{13}H_7O_2N_2Cl$ requires C, 60·3; H, 2·7%); on oxidation with chromic anhydride in acetic acid solution it was converted into 1-azanthraquinone, thus proving the orientation of the compound. (b) 9-Chloro-1-azanthracene (1 g.) was refluxed with nitric acid (10 c.c., *d* 1·5) for 20—24 hours. Excess nitric acid was then distilled off and the liquid diluted with water and made alkaline. The precipitated nitro compound was filtered off, washed with water, dried and recrystallised from chloroform or dilute acetic acid and sublimed under reduced pressure giving a red powder (40%), m. p. 215—218° (Found: C, 61·5; H, 2·8. Calc. for $C_{13}H_6O_4N_2$: C, 61·4; H, 2·4%).

9-*Chloro*-10-*bromo*-1-*azanthracene*.—9-Chloro-1-azanthracene (0·5 g.) was dissolved in carbon tetrachloride (15 c.c.) and bromine (0·1 c.c.) in carbon tetrachloride (1·25 c.c.) added. After refluxing gently for an hour the liquid was cooled and the separated solid (0·3 g., 43%) collected and recrystallised from alcohol, changing from red to yellow. It had m. p. 190° (Found: total halogen, 39·2. $C_{13}H_7NClBr$ requires 39·5%). The compound was oxidised readily with chromic anhydride in acetic acid solution being converted into 1-azanthraquinone, thus proving it to be substituted only in the *meso* positions.

9-*Chloro*-10 : ?-*dibromo*-1-*azanthracene*.—9-Chloro-1-azanthracene (1 g.) was dissolved in carbon tetrachloride (30 c.c.) and bromine (1·5 g.) in carbon tetrachloride (5 c.c.) added. A bright red solid was precipitated and, after being heated on a water-bath for 1 hour and cooled, this was separated and recrystallised from alcohol giving yellow needles which sublimed under reduced pressure as bright yellow needles, m. p. 224—227° (1·3 g., 74%) (Found: C, 42·1; H, 1·9. $C_{13}H_6NClBr_2$ requires C, 42·0; H, 1·6%).

9 : 10-*Dichloro*-1-*azanthracene*.—9-Chloro-1-azanthracene (0·8 g.) was dissolved in glacial acetic acid (5 c.c.) and warmed to 50°. Chlorine was passed into the solution until two equivalents (0·53 g.) had been absorbed. The solution was poured into water, the yellow solid collected, washed with water and dried (46%). After crystallising twice from alcohol it had m. p. 204° and sublimed in a vacuum as yellow needles, m. p. 208° (Found: C, 62·8; H, 2·8. Calc. for $C_{13}H_7NCl_2$: C, 63·0; H, 2·8%) (Gerhardt and Hamilton, *loc. cit.*, give m. p. 213—215°). The identity of the compound was proved by oxidation to 1-azanthraquinone.

Nitration of 1-*Azanthraquinone*.—(a) *Under mild conditions*. 1-Azanthraquinone (1 g.) was dissolved in sulphuric acid (10 c.c., 100%) and warmed on a water bath to about 80° and nitric acid (2 c.c., *d* 1·4) dropped in during a few minutes. After heating for a further two hours the mixture was poured into ice water and basified; the mononitro compound separated as a red powder (80%). This was filtered off, dried, and recrystallised from alcohol, xylene or dilute acetic acid, giving a pale red compound, m. p. 215—218° (Found: C, 61·1; H, 2·5; N, 11·7. Calc. for $C_{13}H_6O_4N_2$: C, 61·4; H, 2·4; N, 11·0%). A mixed m. p. with the compound obtained by nitration of 9-chloro-1-azanthracene proved that these compounds were identical. (b) *Under vigorous conditions*. 1-Azanthraquinone (1 g.) was refluxed with a mixture of nitric acid (10 c.c., *d* 1·5), sulphuric acid (5 c.c., 98%) and potassium nitrate (5 g.) for 20—24 hours; the mixture was cooled, diluted with water and made alkaline. The crude nitro compounds were filtered off as a brown powder in 75% yield. By fractional crystallisation from xylene two mono-nitro compounds were obtained: a red solid, m. p. 180—181° (Found: C, 61·1; H, 2·8%), and a small amount of a buff coloured solid, m. p. 215—217° (Found: C, 61·1; H, 2·9. $C_{13}H_6O_4N_2$ requires C, 61·4; H, 2·4%). A mixture of the nitro compound, m. p. 215—217°, with that having m. p. 215—218° (from the mild nitration) had m. p. 200—204°. All three compounds gave a violet "vat" on warming with alkaline hydrosulphite solution.

*Amino-*1*-azanthraquinones*.—The *nitro* compound (0·5 g.) was boiled with sodium sulphide solution (5 c.c. 4%) for 20 minutes and the deep purple solution cooled in ice for half an hour. The solid was filtered off and recrystallised from xylene. Both nitro-1-azanthraquinones (m. p.'s 215—218° and 180—181°) gave light red *amines*, m. p.'s 274° and 262°, respectively (Found: C, 69·2; H, 3·8; and C, 69·0; H, 3·7. $C_{13}H_8O_2N_2$ requires C, 69·6; H, 3·6%).

The amino-1-azanthraquinones were highly crystalline solids which, unlike the nitro compounds, were readily purified. They were sparingly soluble in most organic solvents and in dilute mineral acids. Attempts to diazotise them failed.

1-*Azanthrone*.—1-Azanthraquinone (0·5 g.) was dissolved in hydrochloric acid (20 c.c., 10%) and granulated tin (1 g.) added in small pieces. The solution was refluxed for 3 hours during which the colour of the solution changed to deep red and then became paler. After cooling the mixture was made alkaline, the resulting solid collected and recrystallised from alcohol giving 1-*azanthrone* as a red brown powder, m. p. 274° (Found: C, 79·4; H, 5·1. $C_{13}H_9ON$ requires C, 80·0; H, 4·6%).

*Monobromo-*1*-azanthraquinone*.—(a) *By direct bromination.* 1-Azanthraquinone (1 g.) was heated in a sealed tube with bromine (3 c.c.) and a trace of iodine at 180° for 24 hours. The tube was opened, excess bromine boiled off and the solid washed with water, filtered and dried. After recrystallising from 50% acetic acid it sublimed at 1 mm. as bright yellow needles (0·4 g., m. p. 242°) (Found: C, 54·0; H, 2·0. $C_{13}H_6O_2NBr$ requires C, 54·2; H, 2·1%). (b) *From* 9*-chloro-*10 : ?*-dibromo-*1*-azanthracene*. The compound (0·15 g.) was added to glacial acetic acid (5 c.c.), warmed to 60° and chromic anhydride (0·1 g.) added slowly. After heating at 100° for 3 hours the solution was poured into water, the yellow solid filtered off, recrystallised from alcohol and sublimed in a vacuum giving bright yellow needles (0·06 g.), m. p. 241°, identical with that obtained above (Found: Br, 27·5. $C_{13}H_6O_2NBr$ requires Br, 27·8%).

5*-Bromo-*1*-azanthraquinone*.—(a) 1*-Chloro-*5*-nitro-*2*-naphthylamine*, prepared by chlorination of 5-nitro-2-acetamido-naphthalene (Gerhardt and Hamilton, *loc. cit.*) followed by hydrolysis with alcoholic hydrogen chloride, crystallised from alcohol in bright orange needles (m. p. 164°) from alcohol (Found: C, 53·9; H, 3·4. $C_{10}H_7O_2N_2Cl$ requires C, 53·9; H, 3·1%).

(b) 1*-Chloro-*5*-amino-*2*-acetamido-naphthalene*. Iron filings (60 g.) in alcohol (100 c.c.) were vigorously stirred and hydrochloric acid (20 c.c., *d* 1·18) added. After half an hour the alcohol was refluxed gently for a further 15 minutes and then decanted and the etched filings washed twice with water. 1-Chloro-5-nitro-2-acetamido-naphthalene (15 g.), dissolved in hot alcohol (450 c.c.), was then added to the wet filings and the solution refluxed with vigorous stirring for 3 hours and filtered. On cooling, the filtrate deposited colourless needles of 1*-chloro-*5*-amino-*2*-acetamidonaphthalene* (10·9 g., 81%; m. p. 193°) (Found: C, 60·8; H, 3·9; N, 11·5. $C_{12}H_{11}ON_2Cl$ requires C, 61·4; H, 4·7; N, 11·9%).

(c) 1*-Chloro-*5*-bromo-*2*-acetamidonaphthalene*. 1-Chloro-5-amino-2-acetamidonaphthalene (10·5 g.) was dissolved in acetic acid (120 c.c.) by warming and then cooled rapidly with stirring to 5°. Sodium nitrite (3·15 g.) was finely powdered and added slowly to well cooled sulphuric acid (20 c.c., *d* 1·84) with stirring and then warmed to 70° until the nitrite had dissolved. This solution was also cooled to 5° and the solution of the amine gradually added to it with vigorous stirring at 5°. The solution was allowed to stand at room temperature for ½ hour, and added to a solution of cuprous bromide (8·6 g.) in hydrobromic acid (15 c.c., *d* 1·5). The resulting mixture was warmed on a water-bath for half an hour, nitrogen being evolved. Most of the acetic acid was then removed under reduced pressure at 100° and the residue poured into water (200 c.c.). 1*-Chloro-*5*-bromo-*2*-acetamidonaphthalene* was precipitated as a white solid, separated, washed with water and crystallised from alcohol (charcoal) giving white plates (5·8 g., m. p. 185°) (Found: C, 48·9; H, 2·7; N, 5·0. $C_{12}H_9ONClBr$ requires C, 48·3; H, 3·0; N, 4·7%).

(d) 1*-Chloro-*5*-bromo-*2*-naphthylamine*. The acetyl compound (5·8 g.) was hydrolysed by boiling with alcohol (90 c.c.) and hydrochloric acid (12·5 c.c., *d* 1·18) for 1½ hours. The solution was then made alkaline and half the alcohol removed. On cooling, the free *amine* separated as white needles (4·75 g., m. p. 136°) (Found: C, 46·7; H, 2·6; N, 5·9. $C_{10}H_7NClBr$ requires C, 46·8; H, 2·7; N, 5·5%).

(e) 5*-Bromo-*1*-azanthraquinone*. 1-Chloro-5-bromo-2-naphthylamine (2·5 g.) was dissolved in sulphuric acid (25 c.c., 66%) by heating and glycerol (2·5 g.) added. Sodium *m*-nitrobenzenesulphonate (3·7 g.) was added in portions over ½ hour to the gently boiling solution which was then boiled for a further 5 hours, poured into water and made alkaline. The black tar was separated, washed, dried and extracted with ligroin (b. p. 80—100°). After removal of most of the solvent brown plates (0·5 g.) were deposited on cooling. These were dissolved in acetic acid (10 c.c.), chromic anhydride (1 g.) added and the solution heated at 100° for 2 hours. The yellow precipitate obtained on pouring into water was separated and crystallised from alcohol giving pale brown crystals which separated into two fractions on sublimation in a vacuum, bright yellow needles of 5*-bromo-*1*-azanthraquinone* (0·1 g.; m. p. 268°) (Found: C, 54·6; H, 2·2; N, 5·2. $C_{13}H_6O_2NBr$ requires: C, 54·2; H, 2·1; N, 4·9%) and colourless crystals (0·3 g., m. p. 122°) of 3′*-bromo-*5 : 6*-benzquinoline* (Found: C, 60·2; H, 3·2; N, 5·4. $C_{13}H_8NBr$ requires C, 60·4; H, 3·1; N, 5·4%).

9*-Chloro-*6*-nitro-*1*-azanthracene*. 1*-Chloro-*6*-nitro-*2*-naphthylamine*, obtained by chlorination of 6-nitro-2-naphthylamine (Gerhardt and Hamilton, *loc. cit.*) followed by hydrolysis with alcoholic hydrogen chloride, crystallised from alcohol in orange-red needles, m. p. 220° (Found: C, 53·4; H, 2·8. $C_{10}H_7O_2N_2Cl$ requires C, 53·9; H, 3·1%). Under the same conditions as for the preparation of 5-bromo-1-azanthraquinone the amine gave a trace of 9*-chloro-*6*-nitro-*1*-azanthracene* subliming under reduced pressure in yellow needles, m. p. 240° (Found: C, 60·4; H, 3·2. $C_{13}H_7O_2N_2Cl$ requires C, 60·3; H, 2·7%). This could not be oxidised to the corresponding quinone.

6-Bromo-1-azanthraquinone (E.P. 427,485; Example 4) was obtained in yellow needles (6%), m. p. 259° (Found: C, 53·2; H, 2·2; N, 5·1. Calc. for $C_{13}H_6O_2NBr$: C, 54·2; H, 2·1; N, 4·9%) from 1-chloro-6-bromo-2-naphthylamine. 9*-Chloro-*6*-bromo-*1*-azanthracene* (not isolated in E.P. 427,485) was obtained as pale yellow plates from ligroin (b. p. 80—100°), m. p. 178° (Found: C, 53·7; H, 2·4. $C_{13}H_7NClBr$ requires C, 53·3; H, 2·4%).

Attempted Preparation of 8*-Bromo-*1*-azanthraquinone*.—(a) 8*-Nitro-*1*-chloro-*2*-naphthylamine* was prepared by the same method as the 5-nitro isomer and crystallised from methanol in orange needles (8·3 g., m. p. 147°) (Found: C, 53·3; H, 3·3. $C_{10}H_7O_2N_2Cl$ requires C, 53·9; H, 3·1%). The acetyl derivative was reduced by the method given above to 1*-chloro-*8*-amino-*2*-acetamido-naphthalene* in 82% yield; colourless needles, m. p. 160°, from alcohol (Found: C, 61·8; H, 5·1; N, 12·1. $C_{12}H_{11}ON_2Cl$ requires C, 61·4; H, 4·7; N, 11·9%).

(b) 1*-Chloro-*8*-bromo-*2*-acetamidonaphthalene*. 1-Chloro-8-amino-2-acetamidonaphthalene (15 g.) was suspended in a solution of hydrobromic acid (17·7 c.c., 48%) in water (64 c.c.) and cooled to 0° with stirring. A solution of sodium nitrite (4·6 g.) in water (10 c.c.) was then added slowly until the solution gave a permanent blue coloration with starch iodide paper. The thick precipitate of the diazonium bromide which separated was stirred for a further hour at 0° and then quickly run into a suspension of cuprous bromide (19·3 g.) in hydrobromic acid (53 c.c., 48%) in water (127 c.c.) and the whole stirred at 0° until a sample no longer gave any colour with alkaline "H acid" solution. The whole was then stirred overnight until evolution of nitrogen had ceased. The precipitated bromo-compound was filtered off, washed and dried. Extraction with boiling methanol gave 1-*chloro*-8-*bromo*-2-*acetamidonaphthalene* as pale straw coloured needles, m. p. 147°, in 41% yield (Found : C, 48·8; H, 2·9; N, 5·1. $C_{12}H_9ONClBr$ requires C, 48·3; H, 3·0; N, 4·7%).

By hydrolysis, this compound was converted into 1-*chloro*-8-*bromo*-2-*naphthylamine* (90%), crystallising in colourless needles, m. p. 85°, from methanol (Found : C, 46·9; H, 2·9; N, 5·5. $C_{10}H_7NClBr$ requires C, 46·8; H, 2·7; N, 5·5%).

A Skraup reaction under the above conditions on the amine (5·8 g.) gave 6′-*bromo*-5 : 6-*benzquinoline* (2·2 g.) crystallising in pale yellow needles, m. p. 165°, from ethanol (Found : C, 60·9; H, 3·5. $C_{13}H_8NBr$ requires C, 60·5; H, 3·1%). There was no trace of 9-chloro-8-bromo-1-azanthracene in the product.

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