## 256. *Some Syntheses in the Benzquinoline, Benzacridine, and Phenanthridine Series.*

By Adrien Albert, D. J. Brown, and Heinz Duewell.

A number of amines in the benzquinoline, benzacridine, phenanthridine, and phenanthroline series have been prepared by the action of ammonia on the corresponding chloro-compounds; the best conditions were found to be those required by simpler ring systems halogenated in the same positions relative to the ring-nitrogen.

Two linear aminobenzacridines made in this way rapidly underwent photopolymerisation in sunlight, an effect not previously described in that series.

Difficulty in synthesising 4-*chloro*-6 : 7-*benzquinoline* for the above work was surmounted by treating *ethyl* 3-*acetamido*-2-*naphthoate* (VIII) with phosphorus oxychloride, followed by a stepwise degradation of the resulting 4-*hydroxy*-2-*methyl*-6 : 7-*benzquinoline*-3-*carboxy*-(2′-*carboxy*-3′-*naphthyl*)*amide* (IX).

4-*Chloro*-3-*nitro*-6 : 7-*benzquinoline*, which has an easily hydrolysed chlorine atom, has been dehalogenated to 3-*nitro*-6 : 7-*benzquinoline* by a new method.

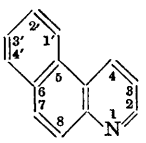
A new preparative route to phenanthridine was found in the reductive dehalogenation of 9-bromophenanthridine, and provides the first practicable method for passing from the phenanthridone to the phenanthridine series.

A hitherto unsuspected need for a trace of copper in the usual synthesis of acetoacet-α-naphthalide has been found.

It has been shown that antibacterial activity in the acridine series is proportional to the extent of kationic ionization at pH 7 (Albert, Rubbo, Goldacre, Davey, and Stone, *Brit. J. Exp. Path.*, 1945, **26**, 160). In the course of demonstrating that this same relationship holds in the benzquinoline, benzacridine, and phenanthridine series, a number of amino-derivatives of these nuclei (I—VII) were prepared. Particular attention was paid to amines obtainable by the replacement of activated chlorine, as it was expected that these would have electronic configurations favouring ionic resonance (Albert and Goldacre, *J.*, 1943, 454) and hence be stronger bases than their isomerides; this proved to be so (Albert, Goldacre, and Phillips, to be published).

Previously, 4-aminobenzquinolines had been obtained only by sealed-tube techniques, but the 4-chloro-derivatives of 5 : 6-, 6 : 7-, and 7 : 8-benzquinoline (I, II, and III) have now been converted into the corresponding 4-amino-compounds by passing a stream of ammonia through

their solutions in phenol at 180°, a method which Backeberg and Marais (*J.*, 1942, 381) used to aminate γ-chloroquinolines. The transformation of only one substance (4-chloro-2-methyl-5 : 6-benzquinoline) became arrested at the intermediate phenyl ether stage, but, when the phenolic catalyst was replaced by copper and an inert solvent, the desired amine was quantitatively obtained.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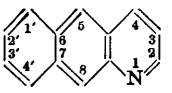
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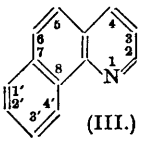
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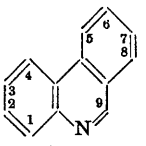
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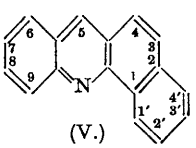
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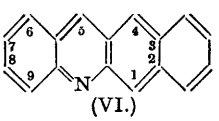
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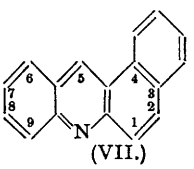
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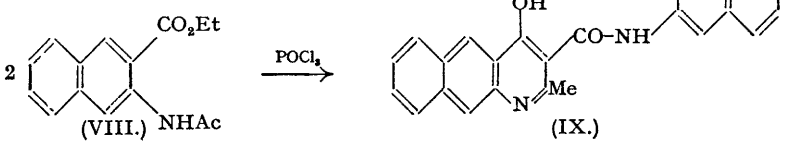
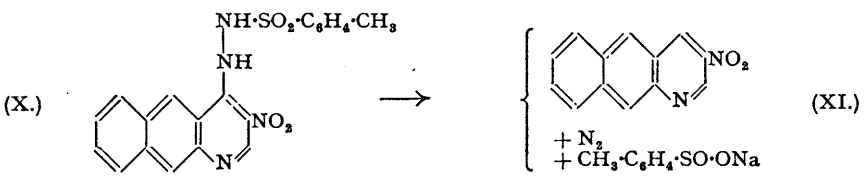

(VIII.) (IX.)


(X.) (XI.)

The 2-chlorobenzquinolines could not be aminated in phenol, as the reaction ceased at the phenyl ether stage. Moreover copper did not induce amination in an inert solvent. However, good results were obtained when the chloro-compound was heated with zinc chloride diammine at *ca.* 240° in a sealed tube, *i.e.*, the conditions found necessary for α-chloroquinolines by Backeberg and Marais (*loc. cit.*).

1-Chloro-*p*-phenanthroline, which is a γ-chloroquinoline derivative, was readily aminated by ammonia in phenols, whereas 9-*chloro*-2 : 7-*dinitrophenanthridine* (cf. IV), which is an α-chloroquinoline derivative, gave only the phenyl ether by this method; it was readily aminated by zinc chloride diammine.

Although the facile amination of 5-chloroacridines (which are γ-chloroquinolines) by ammonium carbonate in phenol at *ca.* 120° (Albert and Ritchie, *J. Soc. Chem. Ind.*, 1941, **60**, 120; Albert and Gledhill, *ibid.*, 1945, **64**, 169) could not be duplicated in the benzquinoline series, it was readily performed on the 5-chloro-derivatives of 1 : 2-, 2 : 3-, and 3 : 4-benzacridines (V, VI, and VII).

None of these α- or γ-amino-compounds could be diazotised in aqueous solution. They are all stable to boiling N-sodium hydroxide, but some of them (notably 5-amino-2 : 3-benzacridine) evolve ammonia when boiled with dilute alcohol.

5-*Amino*-2 : 3-*benzacridine* and its 6 : 7 : 8 : 9-*tetrahydro*-derivative were rapidly decomposed in sunlight even under anærobic conditions. There was no change in ultimate composition, suggesting that polymerisation had taken place. The very poor general solubility of the products and their instability to heat prevented accurate molecular-weight determination, but they appeared to be dimeric. 5-Amino-2 : 3-benzacridine is regenerated from its transformation product when touched with a hot wire. It is known that 5-aminoacridine is not altered by even three months' exposure to light under the same conditions (Falk and Thomas, *Pharm. J.*, 1944, **153**, 158); 5-*amino*-1 : 2- and -3 : 4-*benzacridine* were found not to be greatly affected by light,

and 2 : 3-benzacridine was decomposed only slowly. Solutions of the hydrochlorides in water were used in each case.

Photopolymerisation has not previously been recorded in the benzacridine series. The kinetics of the reversible photodimerism of anthracene have been carefully studied (Weigert, *Naturwiss.*, 1927, **15**, 124), and Linebarger's formula, in which two molecules of anthracene are linked by both 9- and 10- positions (*Amer. Chem. J.*, 1892, **14**, 597), is generally accepted. Phenanthrene does not photodimerise, but a similar effect is given by acridine (Orndorff and Cameron, *Amer. Chem. J.*, 1895, **17**, 658) and 6 : 7-benzquinoline (Étienne, *Compt. rend.*, 1944, **218**, 841).

The preparation of linear benzquinolines (II) presents special difficulties, because most quinoline reactions give angular products when applied to the benzquinoline series. In the endeavour to obtain 4-hydroxy-6 : 7-benzquinoline (or the corresponding chloro- or amino-analogue) the following reactions were tried without success: (i) diazotisation of 3 : 4-diamino- (also 3-amino-4-hydroxy- and 3-amino-4-methoxy-) 6 : 7-benzquinoline followed by reaction with alcohol or hypophosphorous acid, (ii) reduction of 4-*chloro*-3-*nitro*-6 : 7-*benzquinoline* with stannous chloride in cold glacial acetic acid followed by diazotisation of the product, (iii) reaction of ethyl 3-amino-2-naphthoate with ethyl formylacetate. In addition, methyl anthranilate was used as a model to attempt to discover new quinoline reactions in which sufficient of the pyridine ring is pre-formed for ring-closure to take place in the correct position. This substance was heated with acetal at 180° in a sealed tube; also its azomethine with acetaldoxime was (i) refluxed with sodium methoxide in ether or toluene, (ii) heated with acetic anhydride and sodium acetate, and (iii) pyrolysed at 250° in paraffin. In no case was 4-hydroxyquinoline obtained. Attempts to obtain 3-amino-2-acetonaphthone, for a Camps's synthesis, were unsuccessful.

Success was finally obtained by treating *ethyl* 3-*acetamido*-2-*naphthoate* (VIII) with phosphorus oxychloride, in analogy with a reaction similarly performed on ethyl acetylanthranilate by Anschütz and Schmidt (*Ber.*, 1902, **35**, 3473) and interpreted by Heller and Grundmann (*Ber.*, 1923, **56**, 200). The product, 4-*hydroxy*-2-*methyl*-6 : 7-*benzquinoline*-3-*carboxy*-(2′-*carboxy*-3′-*naphthyl*)*amide* (IX) was simultaneously hydrolysed and decarboxylated by sulphuric acid giving 4-*hydroxy*-2-*methyl*-6 : 7-*benzquinoline*. The demethylation of this compound was explored by the method devised by Späth (*Monatsh.*, 1919, **40**, 109) for 4-hydroxy-6 : 8-dimethylquinoline, *viz.*, the hydroxyl group was etherified so that the 2-methyl group could be condensed with benzaldehyde; the styryl group was then oxidised, and the product was decarboxylated to 4-*hydroxy*-6 : 7-*benzquinoline* which was readily converted into the desired 4-*amino*-6 : 7-*benzquinoline*. However, much better yields were obtained in a new reaction sequence, *viz.*, by condensing 4-*amino*-2-*methyl*-6 : 7-*benzquinoline* (from the hydroxy-analogue) with acetic anhydride and benzaldehyde to 4-*acetamido*-2-*styryl*-6 : 7-*benzquinoline* which was, in turn, oxidised to the carboxylic acid, deacetylated, and decarboxylated to 4-amino-6 : 7-benzquinoline. This reaction has proved useful also for the removal of α-methyl groups in 4-amino-derivatives of quinoline and pyridine (Mr. Richard Royer, private communication.

No satisfactory method has been described for passing from the phenanthridone to the phenanthridine series. Distillation with zinc dust does not go smoothly and the yields are poor. Reduction with sodium in alcohol, which goes so well with acridone (Albert and Willis, *J. Soc. Chem. Ind.*, 1946, **65**, 26), gives octahydrophenanthridine (Kruber, *Ber.*, 1939, **72**, 771), and sodium amalgam gives a compound agreeing in composition with *hexahydrophenanthridone*. However, the desired transformation has been achieved by the catalytic debromination of 9-bromophenanthridine (readily prepared from phenanthridone) with hydrogen and Raney nickel, giving a 95% yield of phenanthridine (the corresponding reaction with 9-chloro-phenanthridine was sluggish). Hydrogenation usually ceased abruptly when 2H had been taken up. On one occasion, using freshly prepared catalyst, 9 : 10-dihydrophenanthridine (=4H) was produced, but this was readily oxidised back to phenanthridine by the method of Pictet and Ankerschmit (*Annalen*, 1891, **266**, 151).

Although reductive dehalogenations of this type seem to be general in heterocyclic series, they are not usually suitable when nitro-groups are also present because of the tendency for the latter to be reduced first, leading to a catalysed self-condensation. This has been found in the acridine series (Albert and Willis, *loc. cit.*), and occurred again in the attempted production of 3-*amino*-6 : 7-*benzquinoline* from 4-chloro-3-nitro-6 : 7-benzquinoline. Equally ineffective, because of condensation or hydrolysis, were (i) palladium dehydrogenations under acid, alkaline, or neutral conditions, (ii) boiling with zinc dust and dilute ammonia, and (iii) refluxing with

copper-bronze and calcium carbonate in dilute alcohol. Reduction of 3-nitro-4-hydroxy-6 : 7-benzquinoline with sodium amalgam in aqueous alcohol was also unsuccessful.

The problem was finally overcome by condensing the chloronitrobenzquinoline with *p*-toluenesulphonhydrazide and warming the product (X) with aqueous alkali which gave (XI) [cf. the similar reaction for converting acid chlorides into aldehydes (McFadyen and Stevens, *J.*, 1936, 584)]. The yields of 3-*nitro*-6 : 7-*benzquinoline* with 0·25N-, 0·5N-, N-, and 2N-sodium hydroxide were 50, 60, 50, and 35% respectively, based on the chloro-compound. N-Sodium carbonate gave only 40%.

2 : 3-Benzacridone could be prepared in only 20, 1, and 10% yields by the methods described by Schöpff (*Ber.*, 1893, **26**, 2589), *viz.*, by heating 3-anilino-2-naphthoic acid, or its anilide, at 180° with hydrochloric acid, and by fusing 3-hydroxy-2-naphthanilide with zinc chloride. It was found that sulphuric acid sulphonated 3-anilino-2-naphthoic acid too readily to be of use, but that phosphorus oxychloride cyclised it quantitatively.

Great difficulty in preparing acetoacet-α-naphthylamide from ethyl acetoacetate and α-naphthylamine was experienced by Gibson, Hariharan, Menon, and Simonsen (*J.*, 1926, 2247). In the present work the yield actually fell to zero when the starting materials were rigorously purified. It was recalled that copper catalyses many reactions of amines, and hence a trace was added to the reaction mixture, with the result that a 70% yield of pure material was obtained repeatedly. However, the formation of the β-isomeride did not require copper catalysis.

These naphthylamides were cyclised in a new way, *viz.*, by heating them with concentrated hydrochloric acid for 15 minutes. Previously this acid had been used only at room temperature, ring-closure then taking several weeks, and sulphuric acid gave low yields because of sulphonation.

Apart from the α- and γ-amino-derivatives, with which this paper is principally concerned, a number of other amino-benzquinolines and -benzacridines were prepared.

Comparison of the linear amines (and parent substances) with their angular analogues showed that in each case the linear compound absorbed at a longer wave-length just as would be predicted from the theory connecting colour with the amplitude of charge oscillation in the long axis of a molecule (Lewis and Calvin, *Chem. Reviews*, 1939, **25**, 273; Craig, *Proc. Roy. Soc. N.S.W.*, 1945, **79**, 160).

## Experimental.

### (i) *Preparation of γ-Aminoquinoline Analogues.*

*General Method.*—The chloro-compound (2 g.) and either phenol or *p*-cresol (6 to 10 g.) were heated for 4 hours under reflux in a bath at 180° while ammonia was passed in at the rate of 2 bubbles a second. The product was made alkaline to orange-II paper with sodium hydroxide. The material which remained undissolved was repeatedly extracted with dilute acetic acid. The combined extracts were brought to about pH 6 to precipitate feebly basic substances, and filtered. The filtrate was made strongly alkaline, thus precipitating the required amine which was filtered off, washed, and dried at 120°. Except where otherwise stated both hydrochloride and base are white, and neither fluoresces.

4-Amino-5 : 6-benzquinoline, prepared in this way in 75% yield from the chlorine analogue (Mueller and Hamilton, *J. Amer. Chem. Soc.*, 1943, **65**, 1017), was recrystallised from alcohol. It melted at 150—151° and gave no depression with a specimen, m. p. 149—150°, kindly supplied by Professor C. S. Hamilton, which had been prepared by a Curtius degradation of the corresponding acid (Barnum and Hamilton, *J. Amer. Chem. Soc.*, 1942, **64**, 540).

4-Amino-7 : 8-benzquinoline, similarly prepared in 75% yield from the chlorine analogue (Foster, Lipscomb, Thompson, and Hamilton, *J. Amer. Chem. Soc.*, 1946, **68**, 1327), melted at 173—174° after recrystallisation from alcohol (Found : C, 80·5; H, 5·1; N, 14·4. Calc. for $C_{13}H_{10}N_2$ : C, 80·4; H, 5·2; N, 14·4%). Foster *et al.* prepared this compound in 66% yield by heating the chloro-compound with ammonia and copper under pressure.

4-*Amino*-2-*methyl*-5 : 6-*benzquinoline*.—4-Hydroxy-2-methyl-5 : 6-benzquinoline (2 g.) and phosphorus oxychloride (6 ml.) were refluxed for an hour in a bath at 130°, and the excess reagent was removed under reduced pressure. The sticky residue was stirred into ice and ammonia, the mixture never being allowed to become acid. Stirring was continued until the product became a fine powder. The 4-*chloro*-2-*methyl*-5 : 6-*benzquinoline* formed white crystals from light petroleum, m. p. 99—100° (85% yield) (Found : C, 73·2; H, 4·2; N, 6·3. $C_{14}H_{10}NCl$ requires C, 73·8; H, 4·4; N, 6·15%). When the amination of this substance was attempted by the general method, 4-p-*tolyloxy*-2-*methyl*-5 : 6-*benzquinoline* was obtained as white crystals from dilute alcohol, m. p. 137° (95% yield) (Found : C, 83·7; H, 5·7. $C_{21}H_{17}ON$ requires C, 84·2; H, 5·7%). However, when ammonia was bubbled through a mixture of the chloro-compound (5 g.), diphenyl ether (20 g.), and anhydrous copper sulphate (0·5 g.) kept in a bath at 200° for 4 hours, and the product extracted with ether (rejected) and worked up as above, a 90% yield of 4-*amino*-2-*methyl*-5 : 6-*benzquinoline* was obtained, m. p. 161° (164° corr.) from 4 parts of alcohol or 12 parts of benzene (Found : C, 80·3; H, 5·6; N, 13·6. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·5%). The hydrochloride is not readily precipitated by chloride ions.

4-*Amino*-2-*methyl*-6 : 7-*benzquinoline*.—Ethyl 3-amino-2-naphthoate (35 g.; m. p. 109°) was stirred with acetic anhydride (70 ml.) for 10 minutes at 90°, cooled, and diluted with water. The precipitate

was recrystallised from a little alcohol and then from *cyclo*hexane giving cream-coloured crystals (36 g.) of *ethyl 3-acetamido-2-naphthoate* (VIII), m. p. 123—124° (Found: C, 69·6; H, 5·85; N, 5·5. $C_{15}H_{15}O_3N$ requires C, 70·0; H, 5·9; N, 5·45%).

This ester (25 g.) and phosphorus oxychloride (25 ml.) were heated under reflux in an oil-bath at 75° until dissolved (*ca.* ½ hour). The temperature of the bath was then slowly increased to 125° during 90 minutes (the reaction began at about 90°, clouds of hydrogen chloride and some ethanol being evolved). The product was slowly stirred into water (100 ml.), and the mixture was heated in a boiling water-bath for 5 hours, cooled, and filtered. For preparative purposes the crude acid (IX) was air-dried to constant weight and submitted to combined hydrolysis and decarboxylation by mechanical stirring under water-reflux with a mixture of sulphuric acid (75 ml.) and water (75 ml.) for 3 hours in a bath kept at 210°. The mixture was then cooled, diluted with water (150 ml.), and cooled in ice for 5 hours, and filtered. The precipitate of 4-hydroxy-2-methyl-6 : 7-benzquinoline sulphate was extracted with boiling water (150 ml.) and then, in portions, with 0·5N-hydrochloric acid (100 ml.). (The insoluble material was an anhydride of 3-amino-2-naphthoic acid, into which it was transformed on longer hydrolysis.) Ammonia was added to the filtrate until a faint precipitate formed. The mixture was then treated at the boil with sodium carbonate until faintly alkaline (phenolphthalein). The precipitate was filtered off and purified by dissolution and re-precipitation followed by recrystallisation from dilute alcohol, giving 5·9 g. (60% yield) of *4-hydroxy-2-methyl-6 : 7-benzquinoline* as buff crystals, m. p. 296—298° (sealed). It was sparingly soluble in boiling water (intense violet fluorescence) and N-sodium carbonate, moderately soluble in boiling alcohol to a pale yellow solution with intense violet fluorescence, and very soluble in pyridine (yellow solution with violet fluorescence) (Found: C, 79·6; H, 5·3; N, 6·75. $C_{14}H_{11}ON$ requires C, 80·3; H, 5·3; N, 6·7%). The solutions in 2N-hydrochloric acid and glacial acetic acid are yellow with a green fluorescence. The solution in N-sodium hydroxide is yellow with a green fluorescence.

The filtrate from which this substance was precipitated gave, when faintly acidified (methyl-orange), 13·5 g. (80% recovery) of 3-amino-2-naphthoic acid, m. p. 212° (lit. 214°).

The product of the action of phosphorus oxychloride on ethyl 3-acetamido-2-naphthoate was examined more closely, using another batch of the same size. After the 5 hours' heating with water at 97°, which was found to make the material more homogeneous by hydrolysing ester and labile chlorine groups, the solid was filtered off, dried, refluxed with alcohol (250 ml.) for ½ hour, and filtered. The residue, which formed 65% by weight of the total solids, yielded nothing further to alcohol. Extraction, in alternation, with N-sodium carbonate and water showed that it consisted of two fractions, (*a*) acidic and (*b*) non-acidic. The latter represented only 10% of the total solids. Both (*a*) and (*b*) gave good yields of 4-hydroxy-2-methyl-6 : 7-benzquinoline and 3-amino-2-naphthoic acid on acid hydrolysis at 210°. Evidently fraction (*b*), which was not further investigated because of its insoluble and colloidal nature, is closely related to (*a*). The alcoholic filtrate (above) gave a slimy orange acidic substance (*c*), m. p. *ca.* 190° (decomp.), on evaporation. This yielded only 3-amino-2-naphthoic acid and acetic acid on acid hydrolysis at 210°. The solid (*c*) is apparently an anhydride of 3-acetamido-2-naphthoic acid probably related to the 3-*o*-carboxyphenyl-2-methyl-4-quinazolone which Anschütz and Schmidt (*Ber.*, 1902, **35**, 3473) obtained by a similar procedure from acetylanthranilic acid and which broke down entirely to anthranilic and acetic acids on hydrolysis.

Fraction (*a*) was purified through its sodium salt which was taken up in hot 50% alcohol, filtered, precipitated with acetic acid, and dried at 100°, giving *4-hydroxy-2-methyl-6 : 7-benzquinoline-3-carboxy-(2′-carboxy-3′-naphthyl)amide* (IX) in 55% yield as a pale yellow amorphous solid, insoluble in most common solvents, soluble in pyridine with salt formation and in ethylene glycol with decarboxylation (Found: C, 72·5; H, 4·6; N, 6·4; loss at 130° in a vacuum, 2·0. $C_{26}H_{18}O_4N_2,0{\cdot}5H_2O$ requires C, 72·4; H, 4·4; N, 6·5; $H_2O$, 2·1%). The sodium salt is readily precipitated from aqueous solution by sodium ions.

4-Hydroxy-2-methyl-6 : 7-benzquinoline (5 g.) and phosphorus oxychloride (50 ml.; a large excess was used because of poor solubility) were heated in a bath at 125° for an hour, and as much as possible of the excess reagent removed in a vacuum. The product was slowly stirred into a mixture of ice and ammonia which was never allowed to become acid, filtered, and the solid dried in a vacuum. A quantitative yield of the crude chloro-analogue, m. p. 130° (decomp.), was obtained. It formed a pale yellow solid, very soluble in chloroform, much less soluble in light petroleum.

This chloro-compound was aminated, and the product recrystallised from 30 parts of benzene, giving *4-amino-2-methyl-6 : 7-benzquinoline* as pale yellow crystals, m. p. 180°. It was very soluble in alcohol or acetone to a yellow solution with intense blue fluorescence attributable to the kation because it is removed by sodium hydroxide (Found: C, 80·2; H, 5·85; N, 13·4. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·5%).

The hydrochloride is the same colour as the base, and is salted out by *ca.* 2N-concentration of chloride ions. Dilute aqueous solutions fluoresce intensely blue. The acetate is more soluble than the hydrochloride in water.

*4-Amino-2-methyl-7 : 8-benzquinoline.*—The 4-chloro-analogue (Limpach, *Ber.*, 1931, **64**, 969; Gibson, Hariharan, Menon, and Simonsen, *J.*, 1926, 2247) when aminated by the general method gave *4-amino-2-methyl-7 : 8-benzquinoline*, crystals from dilute alcohol, m. p. 149—150° (70% yield) (Found: C, 81·0; H, 5·6; N, 13·4. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·5%).

*3-Nitro-4-aminoquinoline.*—This compound was synthesised as a model for the 6 : 7-benzquinoline analogue (see later). 3-Nitro-4-hydroxyquinoline (3·45 g.; Musajo, *Gazzetta*, 1937, **67**, 222) was refluxed for 2 hours with phosphorus oxychloride (20 ml.) in a bath kept at 125°. The product was worked up as in analogous cases (see above), and the dry solid extracted with chloroform which was evaporated to small bulk, cooled, and diluted with light petroleum (b. p. 40—60°) until a precipitate appeared; it was then warmed until dissolution occurred. On cooling, long cream-coloured crystals of *4-chloro-3-nitroquinoline* separated, m. p. 119—120° (Found: C, 51·4; H, 2·4; N, 13·45. $C_9H_5O_2N_2Cl$ requires C, 51·8; H, 2·4; N, 13·4%). This compound was not produced when phosphorus oxychloride

was allowed to act on the *N* : *β*-nitroethylideneanthranilic acid from which the nitrohydroxyquinoline had been prepared by ring-closure with acetic anhydride.

When this chloro-compound was aminated, and the product recrystallised from alcohol, 3-*nitro*-4-*aminoquinoline*, m. p. 261—262°, was produced in 90% yield. It forms long bright yellow crystals, soluble in acetone and almost insoluble in ether (Found : C, 57·2; H, 3·7; N, 22·0. $C_9H_7O_2N_3$ requires C, 57·1; H, 3·7; N, 22·2%). It gives colourless and greenish-yellow solutions in mineral acids and 2N-acetic acid, respectively.

3-*Nitro*-4-*amino*-6 : 7-*benzquinoline*.—3-Amino-2-naphthoic acid (9·17 g.) and N-hydrochloric acid (275 ml.) were boiled, cooled to 60°, and stirred vigorously while a solution of sodium methazonate (made from 6·03 g. of nitromethane; Steinkopf, *Ber.*, 1909, **42**, 2031) freshly acidified with 5N-hydrochloric acid (25 ml.) was added during 2 minutes. Stirring was continued until the temperature fell to 20°. The next day, the precipitate (m. p. 209—210°; 85% yield) was collected, washed, dried at 110°, and recrystallised from alcohol, giving yellow crystals of 3-*β*-*nitroethylideneamino*-2-*naphthoic acid*, m. p. 213° (decomp.) (Found : C, 60·2; H, 3·9; N, 10·9. $C_{13}H_{10}O_4N_2$ requires C, 60·5; H, 3·9; N, 10·85%). D.R.-P. 347,375 (Badische, 1921) gives m. p. 212°.

This acid (5 g.), acetic anhydride (50 ml.), and anhydrous sodium acetate (2·5 g.) were boiled for 3 minutes, cooled in ice, and filtered, giving 3-nitro-4-hydroxy-6 : 7-benzquinoline as a yellow, sparingly soluble solid, m. p. > 300° (decomp.), in 50% yield. The same yield was obtained when the heating was prolonged for several hours and more sodium acetate used than in D.R.-P. 347,375.

This hydroxy-compound (2·4 g.) was chlorinated with phosphorus oxychloride (20 ml.). The solid, recrystallised from 100 parts of benzene, gave orange crystals of 4-*chloro*-3-*nitro*-6 : 7-*benzquinoline*, m. p. 237° (decomp.), in 90% yield (Found : C, 60·4; H, 2·75; N, 10·8. $C_{13}H_7O_2N_2Cl$ requires C, 60·3; H, 2·7; N, 10·8%).

This chloro-compound was aminated by the general method, and the product (m. p. 280—282°; 95% yield) recrystallised from alcohol giving orange crystals of 3-*nitro*-4-*amino*-6 : 7-*benzquinoline*, m. p. 282—283°. It is soluble in about 700 parts of alcohol (at 0°) and 800 parts of acetone (at 20°) (Found : C, 65·1; H, 3·8; N, 17·6. $C_{13}H_9O_2N_3$ requires C, 65·2; H, 3·8; N, 17·6%). The salts are yellow and dissolve only sparingly in cold water, the hydrochloride being less soluble than 1 in 5000.

3 : 4-*Diamino*-6 : 7-*benzquinoline*.—The nitro-amine (6·4 g.), stannous chloride crystals (23·3 g.; 30% excess), concentrated hydrochloric acid (45 ml.), water (15 ml.), and alcohol (100 ml.) were refluxed for 2 hours with vigorous stirring. The suspension was poured into excess of sodium hydroxide (orange-II) and the pale yellow precipitate of 3 : 4-diamino-6 : 7-benzquinoline, m. p. 212° (decomp.), was dried in a vacuum (90% yield). It was soluble in alcohol with an intense green fluorescence. As it readily oxidised in the air, it was dissolved in a little dilute acetic acid, made neutral to litmus, filtered from debris, and precipitated as the hydrochloride with 10N-hydrochloric acid. The dihydrochloride was recrystallised from 2N-hydrochloric acid until ashless, and dried over calcium chloride in a vacuum. 3 : 4-*Diamino*-6 : 7-*benzquinoline hydrochloride* forms fluffy, bright yellow crystals, m. p. *ca.* 310° (decomp.), very soluble in water to an orange solution with an intense green fluorescence on dilution (Found : C, 49·3; H, 5·3; N, 13·3. $C_{13}H_{11}N_3,2HCl,2H_2O$ requires C, 49·0; H, 5·4; N, 13·2%). It was partly decomposed at 120°. Phenanthraquinone gave an azine, m. p. *ca.* 370° after recrystallisation from benzene, which produced an intense green colour with sulphuric acid.

3 : 4-Diamino-6 : 7-benzquinoline dihydrochloride (0·56 g.) in water (5 ml.) was stirred with 10N-hydrochloric acid (5 ml.) at − 5°. Sodium nitrite (0·15 g.) in water (5 ml.) was added during 5 minutes. The mixture was stirred at − 5° for ½ hour, made alkaline with ammonia, and filtered from a trace of insoluble material. The filtrate, treated with acetic acid, gave a precipitate of 3 : 4-*triazolo*-6 : 7-*benzquinoline* in 80% yield. It was recrystallised from supersaturated solutions in acetone and then alcohol, giving cream-coloured crystals, m. p. *ca.* 290° (decomp.) (sealed tube), sparingly soluble in water and soluble in *ca.* 300 parts of boiling alcohol (Found : C, 70·3; H, 3·7; N, 25·2. $C_{13}H_8N_4$ requires C, 70·8; H, 3·7; N, 25·5%). The yellow solution in dilute hydrochloric acid has a green fluorescence, whereas the solution in concentrated sulphuric acid is blood-red. It is not soluble in boiling 10% acetic acid.

8-*Chloro*-4-*amino*-2-*methyl*-6 : 7-*benzquinoline*.—1-Chloro-2-naphthylamine (1 mol.) and ethyl acetoacetate (1 mol.) were left in a vacuum desiccator over sulphuric acid for 5 days. The ethyl *β*-(1-chloro-2-naphthylamino)crotonate crystallised out in 90% yield on chilling. This ester (15 g.) was slowly added to stirred liquid paraffin at 270° and kept there for 15 minutes. After cooling, the pale grey solid was filtered off, washed with light petroleum, and dried at 115°, giving white crystals of 8-*chloro*-4-*hydroxy*-2-*methyl*-6 : 7-*benzquinoline* (m. p. > 350°) in 55% yield. Being sparingly soluble in common solvents it was twice recrystallised from aniline (Found : C, 69·1; H, 4·2; N, 5·85. $C_{14}H_{10}ONCl$ requires C, 69·0; H, 4·1; N, 5·8%). It is insoluble in boiling 5N-sodium hydroxide.

This hydroxy-compound (1·2 g.) was chlorinated with phosphorus oxychloride (20 ml.), giving a quantitative yield of a pale yellow solid, m. p. 159—161°, which was unexpectedly stable to boiling 0·1N-hydrochloric acid.

This chloro-compound was aminated, and the product was recrystallised from alcohol, giving brownish-yellow crystals of 8-*chloro*-4-*amino*-2-*methyl*-6 : 7-*benzquinoline*, m. p. 179—180° (65% yield), very soluble in alcohol (slight blue fluorescence) (Found : C, 69·3; H, 4·6; N, 11·75. $C_{14}H_{11}N_2Cl$ requires C, 69·3; H, 4·6; N, 11·5%). The hydrochloride is faintly yellow and is easily precipitated by chloride ions.

1-*Amino*-p-*phenanthroline* [1-amino-4 : 7-phenanthroline; 4-amino(3′ : 2′ : 5 : 6)pyridoquinoline].—4-Quinolinol (Albert and Magrath, *Biochem. J.*, 1947, **41**, 534) was nitrated by the method used by Kermack and Weatherhead (*J.*, 1939, 563) for nitrating 2-methyl-4-quinolinol, and the product reduced with stannous chloride in boiling hydrochloric acid and poured into excess of sodium hydroxide solution. The precipitate was extracted with alcohol, and the solvent concentrated until it began to deposit white crystals, m. p. 242° (decomp.), of 6-*amino*-4-*quinolinol* (Found : N, 17·6. $C_9H_8ON_2$ requires N, 17·5%) which Kermack and Weatherhead (*J.*, 1940, 1164) had obtained only as a brown oil by a different

synthetic approach. However, the m. p.s, fluorescences, and solubilities of the dihydrochloride and sulphate agreed with those given by these authors.

1-Hydroxy-*p*-phenanthroline was prepared from this by the method of Kermack and Weatherhead (1940, *loc. cit.*). It was also prepared, in smaller yield, by interaction of 6-aminoquinoline and ethyl oxaloacetate. No depression of m. p. occurred on mixing the two specimens, thus confirming the orientation of the product of nitration of 4-quinolinol. The hydroxyphenanthroline was chlorinated, and the 1-chloro-*p*-phenanthroline (1·13 g.) aminated. Addition of dried acetamide (1·1 g.) to the mixture before amination gave a cleaner product. The reaction mixture was best worked up by pouring it into N-hydrochloric acid and shaking out with ether (rejected). The aqueous layer was concentrated and made alkaline. On cooling, it deposited buff crystals of 1-*amino*-p-*phenanthroline*, m. p. 204° unchanged by recrystallisation from 10 parts of boiling water, in 85% yield. Cold aqueous solutions of the base are rather viscous, and it would appear that micelles are formed by attraction between the negatively charged ring-nitrogen in the 7-position and the positively charged primary amino-group. The base is very soluble in alcohol but less soluble in acetone and benzene (Found: C, 73·6; H, 4·7; N, 21·5. $C_{12}H_9N_3$ requires C, 73·8; H, 4·65; N, 21·5%). It does not evolve ammonia when boiled with N-sodium hydroxide. The hydrochloride is pale yellow. It does not diazotise and couple in aqueous solution.

5-*Amino*-6 : 7 : 8 : 9-*tetrahydro*-2 : 3-*benzacridine* (4-amino-2 : 3-tetramethylene-6 : 7-benzquinoline).—3-Amino-2-naphthoic acid (8 g.) and *cyclo*hexanone (8 g.) were slowly heated to 210° during ½ hour under air-reflux and kept at 210—220° for 1½ hours more. The mixture was then refluxed with benzene (60 ml.) for ½ hour and the residue washed well with benzene (100 ml.) and then ether (60 ml.). The insoluble material was recrystallised from pyridine, giving yellow crystals of 5-*hydroxy*-6 : 7 : 8 : 9-*tetrahydro*-2 : 3-*benzacridine*, m. p. 315° (sealed tube), in 50% yield (Found: N, 5·65. $C_{17}H_{15}ON$ requires N, 5·6%).

This hydroxy-compound (4 g.) was chlorinated with phosphorus oxychloride (25 ml.), and the product recrystallised from acetone, giving cream-coloured crystals of 5-*chloro*-6 : 7 : 8 : 9-*tetrahydro*-2 : 3-*benzacridine*, m. p. 141—142°, in 85% yield (Found: N, 5·2. $C_{17}H_{14}NCl$ requires N, 5·2%).

The chloro-compound was aminated, and the product recrystallised from toluene, giving a 75% yield of orange-yellow crystals of 5-*amino*-6 : 7 : 8 : 9-*tetrahydro*-2 : 3-*benzacridine*, m. p. 236—238° (not sharp as polymerisation appears to begin slowly about 200°). It is soluble in 55 parts of boiling (and 400 parts of ice-cold) toluene, moderately soluble in warm alcohol (with an intense blue fluorescence) (Found: C, 82·0; H, 6·5; N, 11·2. $C_{17}H_{16}N_2$ requires C, 82·2; H, 6·5; N, 11·3%). The hydrochloride dissolves in about 500 parts of cold water to a pale yellow solution (blue fluorescence), and is readily precipitated by chloride ions. Solutions are quite stable in the dark.

*Photo-polymer of* 5-*Amino*-6 : 7 : 8 : 9-*tetrahydro*-2 : 3-*benzacridine*.—A 0·2% aqueous solution of the hydrochloride of the monomer was exposed to direct Spring sunlight at sea-level, Lat. 34° S. A white powder began to separate almost at once, and the deposition was complete in 2 days. The colourless filtrate gave no precipitate with sodium hydroxide. The powder was washed well with boiling water and then stirred with 0·3N-sodium hydroxide (200 ml.) to liberate the base which was filtered off, dissolved in dilute acetic acid, reprecipitated with alkali, and recrystallised from aniline, giving white crystals of the *polymer*, m. p. 265° (95% yield) [Found, for material dried at 120° in a vacuum over phosphoric oxide: C, 82·1; H, 6·5; N, 11·3. $(C_{17}H_{16}N_2)_n$ requires C, 82·2; H, 6·5; N, 11·3%]. The polymerisation was not reversed by irradiation with light of (mainly) 3650 A.

5-*Amino*-1 : 2-*benzacridine*.—5-Chloro-1 : 2-benzacridine (11 g.; Bachman and Picha, *J. Amer. Chem. Soc.*, 1946, **68**, 1599) was dissolved at 70° in phenol (54 g.). Finely powdered ammonium carbonate (6 g.) was added during 5 minutes while stirring. The temperature was then raised to 120° and kept there for ½ hour. The melt was poured into excess of sodium hydroxide solution and the base was collected, washed with water and extracted with N-acetic acid (300 ml.). After adjustment of the pH to about 6 and removal of the weakly basic material which had precipitated, excess of sodium hydroxide was added. The precipitate was recrystallised from 21 parts of toluene, giving yellow crystals of 5-*amino*-1 : 2-*benzacridine*, m. p. 196—197°, in 90% yield. The solution in alcohol is pale yellow with an intense violet fluorescence (Found: C, 83·5; H, 4·9; N, 11·6. $C_{17}H_{12}N_2$ requires C, 83·6; H, 5·0; N, 11·5%).

Von Braun (*Annalen*, 1926, **451**, 1) ascribed this constitution to a substance, m. p. 94—98°, which he obtained in poor yield by a Hofmann degradation of 1 : 2-benzacridine-5-carboxyamide, but the only analytical figure was for Cl in the hydrochloride.

The hydrochloride derived from our base was pale yellow and gave a faintly coloured solution in water with a faint green fluorescence which changed to intense violet on dilution. It was soluble in 150 parts of cold water and was readily precipitated by chloride ions.

5-*Amino*-2 : 3-*benzacridine*.—Details in the literature for the preparation of 3-anilino-2-naphthoic acid (Schöpff, *Ber.*, 1892, **25**, 2741) being inadequate, the following method was evolved. 3-Hydroxy-2-naphthoic acid (120 g.) was refluxed with aniline (120 ml.) for 10 hours in a bath at 200°. The product was poured while hot into N-hydrochloric acid (800 ml.), stirred at 100° for 5 minutes, and filtered hot to remove aniline hydrochloride. The cake was washed with 0·2N-hydrochloric acid (200 ml.). The undried solid was boiled for 10 minutes with 0·5N-sodium carbonate (2 l.), with mechanical stirring, and filtered from the cake of anilides. The red filtrate was treated dropwise with 5N-hydrochloric acid (*ca.* 45 ml.) with mechanical stirring until all the 3-anilino-2-naphthoic acid (yellow) had been precipitated, avoiding excess which would precipitate the 3-hydroxy-2-naphthoic acid (almost white). The beginning of precipitation of the latter was marked by the evolution of carbon dioxide, and bromothymol-blue paper was turned light green. The anilinonaphthoic acid, dried at 110° and recrystallised from alcohol, gave yellow crystals, m. p. 229°, in 14% yield (28%, allowing for recovered 3-hydroxy-2-naphthoic acid; on this basis the yield of 3-hydroxy-2-naphthanilide was 52% and of 3-anilino-2-naphthanilide, 16%).

3-Anilino-2-naphthoic acid (5 g.), chlorinated with phosphorus oxychloride (30 ml.), gave a 97% yield of 5-chloro-2 : 3-benzacridine, having the properties described by Schöpff (*Ber.*, 1893, **26**, 2589). It was

quantitatively hydrolysed to 2 : 3-benzacridone (m. p. 303°) when refluxed with 3N-hydrochloric acid for an hour.

This chloro-compound was aminated, care being taken to exclude daylight throughout (the light of a 100-watt incandescent lamp proved non-injurious). The product, dried in a vacuum and recrystallised from toluene, gave scarlet crystals of *5-amino-2 : 3-benzacridine*, m. p. 231—232° (sealed tube), in 75% yield. It is soluble in 17 parts of alcohol with an orange fluorescence (Found : C, 83·6; H, 4·8; N, 11·5. $C_{17}H_{12}N_2$ requires C, 83·6; H, 5·0; N, 11·5%). The hydrochloride, which decomposes at *ca.* 360°, has the same colour and fluorescence as the base. It is readily precipitated by chloride ions but the acetate is more soluble. Solutions are quite stable in the dark.

The base (0·3 g.) and acetic anhydride (5 ml.) were heated, with stirring and exclusion of daylight, at 105° for an hour. The product was evaporated to dryness under reduced pressure and the residue suspended in dilute ammonia, filtered off, and dried in a vacuum. The solid was extracted with toluene (5 ml., discarded) and then recrystallised from alcohol, giving hygroscopic orange crystals (0·15 g.) of *5-acetamido-2 : 3-benzacridine*, m. p. *ca.* 230° (decomp.). The orange solution in alcohol has a slight green fluorescence (Found : C, 78·2; H, 5·1; N, 9·5. $C_{19}H_{14}ON_2,0{\cdot}25H_2O$ requires C, 78·45; H, 5·0; N, 9·6%). It dissolved in N-sodium hydroxide (scarlet) and 2N-acetic acid (purple).

*Photo-polymer of 5-Amino-2 : 3-benzacridine.*—The monomer (0·244 g.; 0·001 mole), N-hydrochloric acid (1 ml.), and water (200 ml.) were boiled for 5 minutes in the dark, filtered, cooled, and exposed to direct Spring sunlight at sea-level, Lat. 34° S. Precipitation of a buff solid began in 5 minutes and was almost complete in 8 hours. The precipitate was filtered off, leaving a colourless liquid which gave no precipitate with alkalis or silver nitrate and did not evolve ammonia when boiled with sodium hydroxide. The precipitate of the polymer hydrochloride was repeatedly extracted with boiling water (filtrates discarded), recrystallised from dilute alcohol, and dried to constant weight in a vacuum over phosphoric oxide [Found : C, 69·4; H, 5·0; N, 9·25. $(C_{17}H_{12}N_2,HCl,0{\cdot}75H_2O)_n$ requires C, 69·4; H, 5·0; N, 9·45%]. When stirred for a day with N-sodium hydroxide, the chlorine-free base was obtained as an ivory-coloured powder which, introduced into a bath at 240°, melted sharply at 310° and turned bright red. It could be recrystallised from aniline (poor recovery), but was in general poorly soluble. The acetate is moderately soluble in water to a colourless solution.

*5-Amino-3 : 4-benzacridine.*—5-Chloro-3 : 4-benzacridine (Bachman and Picha, *loc. cit.*) was aminated. The solid, recrystallized from 65 parts of toluene, gave golden crystals of *5-amino-3 : 4-benzacridine*, m. p. 236—237°, in 80% yield. It is moderately soluble in alcohol to a pale yellow solution (with a green fluorescence that becomes intense violet on dilution) and readily soluble in acetone (Found : C, 83·4; H, 4·9; N, 11·4. $C_{17}H_{12}N_2$ requires C, 83·6; H, 5·0; N, 11·5%). The hydrochloride is cream-coloured and dissolves in 400 parts of cold water to a light yellow solution (with a violet fluorescence when dilute). It is not so readily precipitated by chloride ions as its 1 : 2-isomeride.

*4′ : 5-Diamino-1 : 2-benzacridine.*—5-Nitro-1-naphthylamine (4 g.; Vorozhtzov, *Chem. Abs.*, 1929, **23**, 3697), potassium *o*-chlorobenzoate (8 g.; excess), catalytic copper (0·1 g.), anhydrous potassium carbonate (1·5 g.), and *cyclo*hexanol (40 ml.) were heated in a bath at 160—170° for 7 hours. During steam-distillation the volume of the residual solution was adjusted to 300 ml., filtered hot, and potassium carbonate (30 g.) added. The whole was chilled overnight, and the required potassium salt filtered off, dissolved in 40 ml. of boiling water, and acidified with acetic acid. The precipitate was dried at 110° and recrystallised from 25 parts of chlorobenzene, giving light brown crystals of *2-(5′-nitro-α-naphthylamino)-benzoic acid*, m. p. 239°, in 21% yield. It is sparingly soluble in hot alcohol (Found : N, 9·1. $C_{17}H_{12}O_4N_2$ requires N, 9·1%).

This acid (1·4 g.) was converted into 5-chloro-4′-nitro-1 : 2-benzacridine with phosphorus oxychloride (14 g.), and a 95% yield of product obtained, m. p. 233°.

This chloro-compound (1·4 g.) was aminated, and the product was recrystallised from 35 parts of chlorobenzene, giving red crystals of *4′-nitro-5-amino-1 : 2-benzacridine*, m. p. 250—252° (decomp.), in 85% yield. It is soluble in about 120 parts of cold acetone, and in *ca.* 500 parts of chlorobenzene at 0° (Found : C, 70·6; H, 3·85; N, 14·5. $C_{17}H_{11}O_2N_3$ requires C, 70·6; H, 3·8; N, 14·5%). The hydrochloride is yellow and is practically insoluble in boiling water, whereas the acetate readily dissolves in cold water.

This nitro-compound (1 g.) was hydrogenated in acetone (150 ml.) at atmospheric temperature and pressure using Raney nickel catalyst. When the theoretical amount of hydrogen had been absorbed, the uptake fell sharply. The nickel was filtered off and washed with hot acetone (100 ml.), and the combined filtrates were taken to dryness. The yellow powder was made into a paste with water and left in the air on a glazed slab for 24 hours (to compensate for over-reduction), and then dried at 110° Crystallisation from 50 parts of chlorobenzene gave orange-yellow needles of *4′ : 5-diamino-1 : 2-benzacridine*, m. p. 225—226°, in 85% yield. It is slightly soluble in water but more soluble in alcohol and acetone (yellow solutions with yellow-green fluorescence), and soluble in *ca.* 1000 parts of chlorobenzene at 0° (Found : C, 78·8; H, 5·0; N, 16·2. $C_{17}H_{13}N_3$ requires C, 78·7; H, 5·1; N, 16·2%). The base is stable to boiling with N-sodium hydroxide. The monohydrochloride is orange and the dihydrochloride pale yellow. Both are very soluble in water with very little fluorescence, and resist hydrolysis on boiling with dilute hydrochloric acid for 2 hours. The brown diazo-solution couples with β-naphthol (purple-red).

(ii) *Preparation of α-Aminoquinoline Analogues.*

*General Method.*—The chloro-compound (3 g.), zinc chloride diammine (15 g.; Merz and Müller, *Ber.*, 1886, **19**, 2902), and ammonium chloride (3 g.) were heated in an open test-tube, contained in a sealed mild steel tube almost immersed in an oil-bath at 220—240°, for 6 hours. The product was dissolved in hydrochloric acid and precipitated with ammonia, in alternation, until free from zinc. It was then extracted with N-acetic acid and the filtrate was taken to about pH 5 to precipitate unchanged chloro-compound. The base was liberated from the filtrate with sodium hydroxide and recrystallised. Unless otherwise stated, both hydrochloride and base are white and neither fluoresces.

*2-Amino-4-methyl-5 : 6-benzquinoline.*—Acetoacet-β-naphthalide, prepared in 70% yield in the

same way as the α-analogue (see later), formed white crystals from benzene, m. p. 102°, or water, m. p. 92°. Only the low-melting form has been described (Knorr, *Ber.*, 1884, **17**, 540) (Found for the high-melting form: C, 73·3; H, 5·8; N, 6·1. Calc. for $C_{14}H_{13}O_2N$: C, 74·0; H, 5·8; N, 6·1%).

Both forms cyclise quantitatively to 2-hydroxy-4-methyl-5 : 6-benzquinoline when stirred with 9 parts of concentrated hydrochloric acid in a boiling water-bath for 15 minutes. Sulphuric acid, which has been used previously, gave poor yields because of sulphonation.

This hydroxy-compound was chlorinated with phosphorus oxychloride, giving 2-chloro-4-methyl-5 : 6-benzquinoline, m. p. 153—154°, in 95% yield. Benson and Hamilton who used phosphorus pentachloride obtained only 50%.

The chloro-compound was aminated. The product (m. p. 219—221°; 60% yield), recrystallised from alcohol and then from acetone, gave crystals of 2-*amino*-4-*methyl*-5 : 6-*benzquinoline*, m. p. 224—225° (Found: C, 80·1; H, 5·5; N, 13·1. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·5%). The hydrochloride is easily salted out by excess of chloride ions.

2-*Amino*-4-*methyl*-7 : 8-*benzquinoline*.—Ethyl acetoacetate (18 ml., freshly distilled) and cupric acetate (0·025 g.) were heated to 160° over a flame. Freshly distilled α-naphthylamine (5 g.) was added with vigorous stirring. After 15 minutes at 160°, the source of heat was removed and the mixture left over-night. After removal of the excess of ester under reduced pressure, the solid was ground under water (100 ml.), and then under just enough ether to cover it. After filtration, the cake was washed with ether–light petroleum (1 : 1) and finally with light petroleum alone, giving acetoacet-α-naphthalide, m. p. 115—117° (70% yield). Crystallisation from benzene gives the form, m. p. 106—107°, obtained by Gibson *et al.* (*loc. cit.*).

This ester was cyclised, giving an 85% yield of 2-hydroxy-4-methyl-7 : 8-benzquinoline, m. p. 294—295° (Gibson *et al.* give m. p. 292°).

The hydroxy-compound was chlorinated with phosphorus oxychloride, giving a 95% yield of 2-chloro-4-methyl-7 : 8-benzquinoline as white crystals from alcohol, m. p. 136—137° (Gibson *et al.* give m. p. 134—135°).

This chloro-compound was aminated, and the product purified through the sparingly soluble white hydrochloride and recrystallised from 35% alcohol, giving a 40% yield of 2-*amino*-4-*methyl*-7 : 8-*benzquinoline* as needles, m. p. 133—134°. It is very soluble in alcohol and benzene but sparingly soluble in ether (Found: C, 80·2; H, 5·6; N, 13·2. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·45%). The acetate is very soluble in cold water.

*Attempted Synthesis of* 2 : 4-*Diamino*-7 : 8-*benzquinoline*.—Baumgarten and Kärgel (*Ber.*, 1927, **60**, 841) described the preparation of 2 : 4-dihydroxy-7 : 8-benzquinoline, m. p. 320°, in 80% yield by heating α-naphthylamine and malonic ester at 200—230°, but we could obtain only a 30% yield by this method. It was found better to stir α-naphthylamine (7·3 g.; 0·05 mole) into ethyl malonate (32 g.; 0·2 mole) pre-heated to 180°. After 15 minutes at 180° the mixture was cooled and left overnight. After filtration from crystals of the dinaphthalide the product was freed from ethyl malonate under reduced pressure. The crude ethyl malonate mono-α-naphthalide (which could be obtained as white crystals from ethyl acetate, m. p. 227°) was added to liquid paraffin (100 ml.) at 260—280°, and kept there, with stirring, for 15 minutes. The product was cooled and filtered. The crystals were washed with heavy petroleum and then with benzene. The crude product was dissolved in N-sodium hydroxide, filtered from insoluble matter, precipitated with acetic acid, and recrystallised from alcohol, giving 2 : 4-dihydroxy-7 : 8-benzquinoline, m. p. 320°, in 50% yield.

The dihydroxy-compound (5 g.) was chlorinated by refluxing it for 2½ hours with phosphorus oxychloride (50 ml.) and the product worked up as in previous cases. Recrystallisation from 50 parts of alcohol gave white crystals of 2 : 4-*dichloro*-7 : 8-*benzquinoline*, m. p. 133° (80% yield) (Found: C, 62·6; H, 3·0; N, 5·6. $C_{13}H_7NCl_2$ requires C, 62·9; H, 2·85; N, 5·65%). This compound could not be aminated by any of the methods described above.

2 : 7 : 9-*Triaminophenanthridine*.—2 : 7-Dinitrophenanthridone (5 g.; Walls, *J.*, 1935, 1405) and phosphorus oxychloride (50 ml.) were refluxed for 5 hours and worked up as were the chlorobenzquinolines. The product (m. p. 222—223°; 97% yield), recrystallised from 300 ml. of chloroform, gave cream-coloured crystals of 9-*chloro*-2 : 7-*dinitrophenanthridine*, m. p. 225° (Found: C, 51·6; H, 2·0; N, 13·8. $C_{13}H_6O_4N_3Cl$ requires C, 51·4; H, 2·0; N, 13·8%).

This chloro-compound was aminated, the crude product was boiled for 10 minutes with 2N-hydrochloric acid and filtered, and the cake of insoluble hydrochloride was suspended in N-sodium carbonate. The base was collected, washed, and dried at 120°. Recrystallisation from aniline gave yellow crystals of 2 : 7-dinitro-9-aminophenanthridine, m. p. 321—322°, in 85% yield. It was insoluble in low-boiling solvents and in dilute acids.

The above nitro-compound (1·9 g.) was added in small portions to a solution of stannous chloride (13 g.) in concentrated hydrochloric acid (14 ml.) at 100°, heated for 1 hour, and poured into excess of sodium hydroxide. The filter-cake was extracted with 2N-acetic acid, and the base precipitated with sodium hydroxide. After recrystallisation from 20% alcohol, 2 : 7 : 9-*triaminophenanthridine* was obtained as cream-coloured crystals, m. p. 200° (70% yield). It is soluble in alcohol to a yellow solution with intense green fluorescence, attributed to the mono-ion as it vanished on addition of alkali. It is sparingly soluble in acetone, ether, and benzene (Found: C, 69·2; H, 5·35; N, 25·05. $C_{13}H_{12}N_4$ requires C, 69·6; H, 5·4; N, 25·0%). The acetate dissolves in water with a pale yellow colour and intense green fluorescence; the solution in 3N-hydrochloric acid is colourless (? di-ion) and without fluorescence, and is not readily precipitated by chloride ions. It diazotises to an orange solution which couples (purple) with β-naphthol. The nitrate and sulphate are sparingly soluble.

(iii) *Miscellaneous.*

*Demethylation of* 4-*Amino*-2-*methyl*-6 : 7-*benzquinoline*.—This substance (5·01 g.; 0·025 mole) and acetic anhydride (8·4 ml.; 0·075 mole) were refluxed for 5 minutes at 155°. Benzaldehyde (8·4 ml.; 0·075 mole) was added, and heating at 155° continued for 3 hours. The mixture was steam-distilled and

the residue filtered off and powdered under methanol (20 ml.). The suspension was diluted with water (200 ml.) and filtered. Recrystallisation from methanol gave yellow, hygroscopic crystals of 4-*acetamido*-2-*styryl*-6 : 7-*benzquinoline*, m. p. 244° (90% yield) (Found for material dried in a vacuum to constant weight : C, 80·0; H, 5·5; N, 8·1; loss at 130°, 2·5. $C_{23}H_{18}ON_2,\frac{1}{2}H_2O$ requires C, 79·5; H, 5·5; N, 8·1; $H_2O$, 2·6%).

The above styryl compound (4·2 g.) was dissolved in a mixture of dried pyridine (80 ml.) and water (16 ml.). Finely powdered potassium permanganate (5·3 g.; 2·7 mols.) was added during an hour to the mechanically stirred mixture which was kept below 20°. Water (30 ml. in all) was added steadily throughout the reaction to keep salts in solution. After a further hour, the mixture was diluted with water (100 ml.), made alkaline to phenolphthalein, and filtered from manganese dioxide (the use of sulphur dioxide instead of alkali gave a lower yield). The cake was repeatedly boiled with water. The combined filtrates (*ca.* 250 ml.) were steam-distilled, the volume being kept constant. Sodium hydroxide (10 g.) was then added, and the whole refluxed for 2 hours to hydrolyse the acetyl group. The filtrate from the product was made faintly acid to litmus, giving bright yellow micro-crystals of 4-amino-6 : 7-benzquinoline-2-carboxylic acid (70% yield) which was decarboxylated at 290° when heated slowly. The substance was poorly soluble in all solvents tried.

This acid (1 g.) was added to stirred liquid paraffin (60 ml.) kept at 280° ± 2° for exactly 3 minutes. The cooled mixture was extracted (liquid and solid phases separately) with N-acetic acid. The combined filtrates were brought to *ca.* pH 6, filtered from impurities, and poured into excess of 5N-sodium hydroxide. The precipitate, recrystallised from toluene (180 parts) and then from acetone (70 parts), gave bright yellow, greasy crystals of 4-*amino*-6 : 7-*benzquinoline*, m. p. 233° (sealed tube), in 50% yield. It is sparingly soluble in ether but moderately soluble in alcohol to a yellow solution with blue fluorescence (Found : C, 79·8; H, 5·2; N, 14·5. $C_{13}H_{10}N_2$ requires C, 80·4; H, 5·2; N, 14·4%). The hydrochloride is not readily precipitated by chloride ions (distinction from the isomeric 5-aminoacridine), but can be recrystallised from a little 3N-hydrochloric acid. There is little difference in colour between ion and base, but the latter has the more vivid fluorescence. The yellow solution of the base in sulphuric acid (*d* 1·84) is turned green by a crystal of sodium nitrite.

Alternatively, 4-chloro-2-methyl-6 : 7-benzquinoline (1·14 g.; 0·005 mole) was added to a solution of sodium (0·23 g.; 0·01 mole) in methanol dried over calcium carbide (15 ml.). The mixture was refluxed for 2 hours, cooled, filtered from sodium chloride, and evaporated to dryness. The residue, recrystallised from dilute methanol and dried in a vacuum, gave yellow crystals of 4-*methoxy*-2-*methyl*-6 : 7-*benzquinoline*, m. p. 103—105°, in 90% yield (Found : N, 6·3. $C_{15}H_{13}ON$ requires N, 6·3%).

This methoxy-compound (1 g.), benzaldehyde (2 ml.), and finely powdered zinc chloride (0·05 g.) were heated at 135—140° for an hour. More zinc chloride (0·05 g.) was added and the heating continued for 1 hour more. The solid remaining after steam distillation was extracted with N-sodium hydroxide and dried in a vacuum. The yellow, crude 4-methoxy-2-styryl-6 : 7-benzquinoline (1·3 g.; m. p. 128°), was oxidised as in the previous example. The combined filtrates from the cake of manganese dioxide, when made just acid to methyl-orange, precipitated 4-methoxy-6 : 7-benzquinoline-2-carboxylic acid as a yellow powder, m. p. 255° (decomp.), poorly soluble in organic solvents. It was demethylated by refluxing it with a mixture of sulphuric acid (3 ml.) and water (3 ml.) in a bath at 210° for 3 hours. The 4-hydroxy-6 : 7-benzquinoline-2-carboxylic acid was dried and stirred with liquid paraffin at 270° for 3 minutes. The precipitate was extracted with boiling 0·5N-hydrochloric acid, and the filtrate was boiled with excess of 2N-sodium carbonate. The precipitate was recrystallised (as the salt) from 0·5N-hydrochloric acid, and the base from alcohol and then from dilute alcohol, giving 0·2 g. of 4-*hydroxy*-6 : 7-*benzquinoline* as cream-coloured crystals, m. p. 272—273° (sealed), sparingly soluble in water (violet fluorescence), hot N-sodium carbonate, ether, or chlorobenzene; very soluble in pyridine with a violet fluorescence (Found : C, 79·45; H, 4·6; N, 7·1. $C_{13}H_9ON$ requires C, 80·0; H, 4·65; N, 7·2%). The solutions in hydrochloric acid and N-sodium hydroxide are yellow with green fluorescences.

This hydroxy-compound was converted through the chloro-derivative into 4-amino-6 : 7-benzquinoline (mixed m. p.).

*Dechlorination of* 4-*Chloro*-3-*nitro*-6 : 7-*benzquinoline*.—To a saturated solution of this substance in chloroform (3 g. in 600 ml.) was added a slight excess of *p*-toluenesulphonhydrazide (2 g.; Freudenberg and Blümmel, *Annalen*, 1924, **440**, 45) in chloroform (90 ml.). After 24 hours, the precipitated 3-nitro-6 : 7-benzquinolyl(*p*-toluenesulphon)hydrazide (decomp. *ca.* 170°) was filtered off, dissolved in 0·5N-sodium hydroxide (450 ml.), and kept at 80° for 1½ hours (nitrogen was evolved during the first hour). The product was filtered off and extracted with boiling 5N-hydrochloric acid (300 ml.). The filtrate was poured into 10N-sodium hydroxide, giving 3-*nitro*-6 : 7-*benzquinoline* which formed orange crystals from alcohol or benzene, m. p. 206° (60% yield) (Found : C, 69·0; H, 3·8; N, 12·3. $C_{13}H_8O_2N_2$ requires C, 69·6; H, 3·6; N, 12·5%).

As with other nitrobenzquinolines, complete combustion in the Dumas nitrogen micro-determination required the use of potassium chlorate. The base is almost insoluble in N-hydrochloric acid.

3-Nitro-6 : 7-benzquinoline was reduced (similarly to 3-nitro-4-amino-6 : 7-benzquinoline, *q.v.*). The resulting solution was poured into excess of 5N-sodium hydroxide (orange-II paper) and the precipitate was collected and extracted with alcohol. When the extract was concentrated and the crystals recrystallised from toluene, yellow-brown crystals of 3-*amino*-6 : 7-*benzquinoline* were obtained, m. p. 240—241°, in 85% yield. They were soluble in about 30 parts of boiling alcohol, an intense green fluorescence being seen on dilution. Solubility in light petroleum was slight (Found : C, 79·8; H, 5·2; N, 14·3. $C_{13}H_{10}N_2$ requires C, 80·4; H, 5·2; N, 14·4%). The hydrochloride gave an orange solution in water with a slight fluorescence.

*Dehalogenation of* 9-*Bromophenanthridine*.—9-Bromophenanthridine (1 g.) in alcohol (30 ml.) and a large excess of Raney nickel catalyst (*ca.* 3 g.) were added to a solution of potassium hydroxide (0·5 g.) in alcohol (10 ml.) and the whole was shaken with hydrogen at room temperature and pressure until the theoretical quantity (2H) of hydrogen had been absorbed. The filtrate was concentrated to 15 ml., and

hot water added until crystallisation began. The yield of phenanthridine was 95%, m. p. 105—106°, raised to 107—108° after one recrystallisation from dilute alcohol, not depressed by material obtained from 2-formamidodiphenyl. 23 Ml. of the alcohol could be replaced by 8 ml. of pyridine which had previously been refluxed for 4 hours with some Raney nickel catalyst.

*Reduction of Phenanthridone.*—Phenanthridone (2 g.) was dissolved in alcohol (150 ml.) containing sodium hydroxide (0·9 g.). Water (50 ml.) was added. While a temperature of 85° and vigorous stirring were maintained, sodium amalgam (200 g.; 2·5%) was added during 1½ hours, a stream of carbon dioxide being led through the mixture at the same time. The mixture was then heated in a bath at 100° for 1½ hours. The alcohol was then recovered, and the solid, freed from mercury, was extracted with ether. The extract was evaporated to dryness and the white solid recrystallised from petroleum (b. p. 90—110°), giving white crystals (1 g.), m. p. 176—178° (Found for material dried over phosphoric oxide in a vacuum at 120° for 2 hours: C, 77·8; H, 7·3; N, 6·8. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5; N, 7·0%), corresponding to a *hexahydrophenanthridone*.

7-*Amino*-1 : 2-*benzacridine*.—Although this could not be prepared from α-naphthol by the method used for the 3 : 4-isomeride (*q.v.*), the following was successful. 5-Nitro-2-(α-naphthylamino)benzoic acid (9·7 g.), prepared according to Lesnianski (*Bull. Acad. Polon. Sci.*, 1929, *A*, 81) but with *cyclo*hexanol, which greatly improved the yield (55%), instead of glycerol, was cyclised by phosphorus oxychloride and worked up as in analogous cases. The product was refluxed for 5 hours with 2N-hydrochloric acid (350 ml.) and the yellow, poorly soluble 7-nitro-1 : 2-benzacridone filtered off, washed, and dried at 120° (yield, 95%).

This nitro-compound (2·9 g.; 0·01 mole) was dissolved in boiling alcohol (150 ml.) with the aid of sodium hydroxide (0·9 g.). Hot water (150 ml.) was then added. With vigorous mechanical stirring and a bath-temperature of 85°, sodium amalgam (200 g.; 2·5%) was added to the red solution during 2 hours while a brisk stream of carbon dioxide was passed in. Stirring, heating, and the passage of carbon dioxide were continued for 2 hours more, and then the alcohol was recovered. The residue, freed from mercury, was extracted with boiling 1·5N-hydrochloric acid (200 ml.). Air was blown at 95° for 4 hours through the extract which was then filtered into 2·5N-sodium hydroxide (150 ml.). The precipitate, recrystallised from a little alcohol and then from 8 parts of toluene, gave light brown crystals of 7-*amino*-1 : 2-*benzacridine*, m. p. 165° (50% yield, falling to 25% when alcohol was omitted). It is sparingly soluble in water and in light petroleum (violet fluorescence). The fluorescence in alcohol is green (Found: C, 83·3; H, 4·9; N, 11·5. $C_{17}H_{12}N_2$ requires C, 83·6; H, 5·0; N, 11·5%). The monohydrochloride is red and is soluble in water with a green fluorescence. It diazotises and couples normally. The dihydrochloride is yellow.

7-*Amino*-2 : 3-*benzacridine*.—3-Amino-2-naphthoic acid (9 g.), *p*-bromonitrobenzene (15 g.), anhydrous potassium carbonate (7·5 g.), catalytic copper (0·3 g.), and nitrobenzene (45 ml.) were heated at 150° for 1½ hours and then at 180° for 2 hours. After steam-distillation the solution was filtered hot and refrigerated overnight. Next day, the red crystals were filtered off, dissolved in hot water, and acidified. The precipitate was recrystallised from benzene, giving yellow crystals of 3-(p-*nitroanilino*)-2-*naphthoic acid*, m. p. 260° (60% yield). It is very soluble in amyl alcohol (Found: N, 9·0. $C_{17}H_{12}O_4N_2$ requires N, 9·1%).

This acid was cyclised with phosphorus oxychloride and hydrolysed with hydrochloric acid, giving 7-*nitro*-2 : 3-*benzacridone* (95% yield) as yellow-brown solvated crystals from 100 parts of pyridine. It does not melt below 360° and is insoluble in many common solvents (Found for material dried at 120° to constant weight: N, 10·6. $C_{17}H_{10}O_3N_2,0{\cdot}5C_5H_5N$ requires N, 10·6%).

This substance was reduced with sodium amalgam, giving bright red crystals of 7-*amino*-2 : 3-*benzacridine* (from 70 parts of 30% aqueous pyridine), m. p. 285—286°, in 60% yield. It is soluble in 300 parts of alcohol, hot or cold, with an intense orange fluorescence, and sparingly soluble in benzene with a brilliant green fluorescence (Found: C, 83·0; H, 4·9; N, 11·5. $C_{17}H_{12}N_2$ requires C, 83·6; H, 5·0; N, 11·5%). It is stable to boiling N-sodium hydroxide. The monohydrochloride is soluble in about 20 parts of water to a red solution without fluorescence. It diazotises and couples normally. The base gives a purple solution of the di-ion in concentrated hydrochloric acid, and a green solution (? the true mono-ion) in alcohol containing a trace of acetic or hydrochloric acid. All the foregoing solutions were monochroic, but the base dissolved in glacial acetic acid to a red solution that appeared green in thin layers, or on dilution; the same dichroism was found in N-acetic acid. It is thought that the red colour is due to association which is reversed by alcohol.

3-Chloro-2-naphthoic acid (2·1 g.), dehydrated potassium carbonate (2·8 g.; 2 mol.), amyl alcohol (25 ml.), and catalytic copper (0·1 g.) were heated until the temperature of the vapour became 128°. *m*-Nitroaniline (2·1 g.; 1·5 mols.) was added, and the whole heated in a bath at 140° for 18 hours and then steam distilled. 3-(m-*Nitroanilino*)-2-*naphthoic acid*, purified through its sparingly soluble potassium salt, gave yellow needles from chlorobenzene, m. p. 226—227° (yield, 15%) (Found: N, 9·0. $C_{17}H_{12}O_4N_2$ requires N, 9·1%). This isomeride was not converted into a benzacridine.

7-*Amino*-3 : 4-*benzacridine*.—β-Naphthol (12 g.) and N-methylenebis-*p*-aminoacetanilide (5 g.) were heated in a test-tube at 170° for an hour. The melt was extracted 4 times with boiling 0·2N-sodium hydroxide (discarded) giving 7-acetamido-3 : 4-benzacridine as pale yellow crystals from alcohol, m. p. 272°. Ullmann gave 255° for material similarly obtained [D.R.-P. 123,260 (1899); "Friedländer", **6**, 463].

This substance (2 g.) was refluxed with alcohol (60 ml.) and concentrated hydrochloric acid (25 ml.) for 2 hours. The product was cooled to 0°, and the yellow crystals collected and basified with dilute ammonia, giving a 70% yield of 7-amino-3 : 4-benzacridine. This formed yellow crystals from 25 parts of chlorobenzene, m. p. 237—238°, as described by Saftien (*Ber.*, 1925, **58**, 1958) who obtained it from benzocoumaranedione. It is soluble in alcohol with a strong green fluorescence. The red monohydrochloride does not fluoresce in solution. It diazotises normally.

2 : 3-*Benzacridine*.—Distillation of 2 : 3-benzacridone with zinc dust as recommended by Schöpff (*Ber.*, 1894, **27**, 2840) gave only a 15% yield of 2 : 3-benzacridine which resisted purification. Reduction

with sodium in amyl alcohol produced an unidentified compound of high m. p. (probably a bisbenzacridyl). On the other hand, reduction with sodium amalgam, condemned as ineffective by Schöpff (*loc. cit.*), actually gave a 70% yield when carried out as in the preparation of 7-amino-1 : 2-benzacridine (*q.v.*) and with the same proportion of sodium even though no nitro-group is present. After separation of the mercury, the white solid (7 : 8-benzacridan) was suspended in a solution of ferric chloride hexahydrate (6·1 g.) in 1·5N-hydrochloric acid (2·5 l.) and boiled, while stirring, for 2 hours. The purple solution was filtered hot and refrigerated overnight. The violet benzacridine hydrochloride was dissolved in boiling N/30-hydrochloric acid (2 l.) and precipitated with ammonia. The 2 : 3-benzacridine was recrystallised from 100 parts of alcohol to give orange crystals, m. p. 223°, as obtained by von Braun, in small yield, from octahydrobenzacridine by way of tetrahydronaphthisatin (*Annalen*, 1926, **451**, 31). It is soluble in about 30 parts of boiling benzene and in 500 parts of alcohol at 0°. The alcoholic solution has a green fluorescence. The ion is magenta in all solvents and is never dichroic.

6 : 7-*Benzquinoline*.—This has previously been prepared only by distilling 1′ : 2′ : 3′ : 4′-tetrahydro-6 : 7-benzquinoline over litharge at 700° (von Braun and Gruber, *Ber.*, 1922, **55**, 1710). Dehydrogenation with iodine, chloranil, and sulphur proving unsuccessful, the tetrahydro-compound (1 g.) was heated with diphenyl ether (5 ml.) and 10% palladised charcoal (0·5 g.; hydrogen-reduced) in a bath at 270° for 3 hours, carbon dioxide being bubbled through the mixture. Precipitation was effected through the nitrate which is sparingly soluble in 2·5N-nitric acid at 0°. The yield was 15% of cream-coloured crystals, m. p. 116°. The base fluoresces violet in dilute, and green in concentrated, solution (distinction from angular isomerides which do not fluoresce). The salts do not fluoresce in solution (distinction from acridine).

6-*Amino*-2-*methyl*-7 : 8-*benzquinoline*.—4-Nitro-1-naphthylamine (7·9 g.), concentrated hydrochloric acid (17 ml.), and paraldehyde (6·8 ml.) were refluxed in a boiling water-bath for 1 hour, diluted with 0·3N-hydrochloric acid (1·5 l.), boiled for ½ hour, and filtered at the boil. The residue was extracted with 3 more portions (1·5 l. each) of acid. The base, precipitated by ammonia from the filtrates, was boiled for exactly 15 minutes with 0·3N-nitric acid (6 l.), filtered at the boil, and immediately reprecipitated with ammonia. The base, taken up in 4 volumes of boiling benzene to which 30 volumes of light petroleum (b. p. 60—90°) were then added, gave light yellow crystals of 6-*nitro*-2-*methyl*-7 : 8-*benzquinoline*, m. p. 141—142° (sealed tube), in 35% yield (Found : N, 11·75. $C_{14}H_{10}O_2N_2$ requires N, 11·8%).

This nitro-compound (2·5 g.) was hydrogenated in acetone (150 ml.) at atmospheric temperature and pressure, and in the presence of Raney nickel catalyst, until the yellow colour almost disappeared (= 6H). The residue left on evaporation of the filtered product was recrystallised from a mixture of chlorobenzene (2 parts) and petroleum (3 parts), giving buff crystals, m. p. 128—129° (sealed tube), of 6-*amino*-2-*methyl*-7 : 8-*benzquinoline* in 90% yield. It was readily soluble in alcohol (weak blue fluorescence) (Found : C, 79·9; H, 5·8; N, 13·1. $C_{14}H_{12}N_2$ requires C, 80·7; H, 5·8; N, 13·5%). The mono-salts are intense yellow in solution and do not fluoresce : they diazotise and couple normally. The di-salts are colourless.

Starting from 5-nitro-1-naphthylamine, 1′-*nitro*-2-*methyl*-7 : 8-*benzquinoline* was similarly prepared in 30% yield, recrystallisation from alcohol replacing the nitric acid treatment. It formed white crystals, m. p. 153°, soluble in 50 parts of cold acetone (Found : C, 70·1; H, 4·2; N, 11·7. $C_{14}H_{10}O_2N_2$ requires C, 70·55; H, 4·2; N, 11·8%). It was reduced, as above, to 1′-*amino*-2-*methyl*-7 : 8-*benzquinoline* (90% yield) which formed buff crystals from chlorobenzene–petroleum, m. p. 141·5°, readily soluble in alcohol to a pale yellow solution with a faint green fluorescence (Found : C, 80·0; H, 5·8; N, 13·1%). The mono- and di-salts resemble those of the isomeride.

Skraup reactions, carried out on the above nitronaphthylamines, led to their complete destruction.

6-Nitro-2-methyl-7 : 8-benzquinoline (3·1 g.), condensed with benzaldehyde similarly to 4-methoxy-2-methyl-6 : 7-benzquinoline (*q.v.*), gave a 50% yield of yellow crystals of 6-*nitro*-2-*styryl*-7 : 8-*benzquinoline*, m. p. 142—143°, from 12 parts of *iso*amyl alcohol (Found : N, 8·6. $C_{21}H_{14}O_2N_2$ requires N, 8·6%).

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