733. *Triazaphenanthrenes. Part II.* Derivatives of 10-Phenyl-1 : 2 : 9-triazaphenanthrene.*

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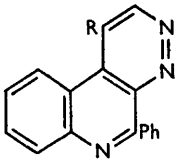
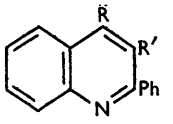
A preparative route to 4-acetyl-3-amino-2-phenylquinoline has been developed. Diazotisation of the amino-ketone in hydrochloric acid and subsequent cyclisation gave mainly 4-acetyl-3-chloro-2-phenylquinoline, with 10% of the hydroxytriazaphenanthrene (I; R = OH); an 80% yield of the latter was obtained by cyclisation in an alkaline medium. 4-Amino-10-phenyl-1 : 2 : 9-triazaphenanthrene formed a monomethiodide which was biologically inactive.

Preparation of the amino-ketone (II; R = Ac, R′ = NH_2) for conversion into the triazaphenanthrene (I; R = OH) was unexpectedly difficult. No useful result was attained by condensation of ethyl 2-phenyl-3-phthalimidoquinoline-4-carboxylate (formed only *via* the acid chloride) with ethyl acetate (cf. ref. 1) and hydrolysis of the product. Likewise, reaction of the acid chloride with ethyl sodiomalonate gave a crystalline product in good yield, but hydrolysis to the amino-ketone could not be achieved. Heating the condensation product under reflux with 35% sulphuric acid gave 4-acetyl-2-phenyl-3-phthalimidoquinoline [II; R = Ac, R′ = $N(CO)_2C_6H_4$] and several variations in the strength of the acid or the duration of boiling yielded only the phthalimido-acid [II; R = CO_2H, R′ = $N(CO)_2C_6H_4$] or the amine (II; R = H, R′ = NH_2), the latter being also



(I)



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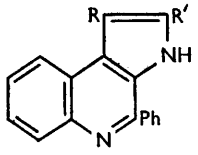

(III)

formed by hydrolysis of the acetyl group from the phthalimido-ketone. Treatment of either the condensation product or the phthalimido-ketone with hydrazine in acetic acid yielded the hydrazone [II; R = CMe:N·NH_2, R′ = $N(CO)_2C_6H_4$], but the free amine could not be obtained, nor was it possible to regenerate the ketone. An attempt to carry out a similar malonic ester synthesis starting from the amino-acid (II; R = CO_2H, R′ = NH_2) failed since the latter, on treatment with thionyl chloride under reflux, gave a sticky red solid which lost sulphur dioxide when kept and yielded 3-amino-4-chloro-2-phenylquinoline on digestion with cold hydrochloric acid. Similar treatment of 3-acetamido-2-phenylquinoline-4-carboxylic acid provided an unstable intermediate (containing sulphur and chlorine) which gave no useful product.

An alternative route to the amino-ketone involved oxidation of the condensed pyrrole (III; R = R′ = Me), but although this derivative was readily prepared *via* the hydrazine (II; R = H, R′ = NH·NH_2), oxidation to a useful product with chromic acid or ozone was unsuccessful, as was the attempted oxidation of the compound (III; R = Me, R′ = Ph). These results were surprising in view of the beneficial effects of a *Bz*-nitro-group or a 2-phenyl group on the oxidation of indoles.[2]

The amino-ketone (II; R = Ac, R′ = NH_2) was eventually synthesised by a Grignard reaction with the amino-amide (II; R = CO·NH_2, R′ = NH_2) or amino-nitrile, the intermediate ketimide being remarkably stable to cold hydrochloric acid but readily decomposed by hot acid or alkali or slowly by contact with alumina. Diazotisation of the amino-ketone in concentrated hydrochloric acid and subsequent heating, to cause ring-closure as in the

* Part I, preceding paper.

[1] Campbell, *J. Amer. Chem. Soc.*, 1946, **68**, 1837.
[2] Schofield, *J.*, 1950, 1505; Atkinson, Simpson, and Taylor, *J.*, 1954, 1381.

Borsche reaction,[3] gave approximately 10% of the required 4-hydroxy-10-phenyl-1 : 2 : 9-triazaphenanthrene (I; R = OH) and 50% of 4-acetyl-3-chloro-2-phenylquinoline (II; R = Ac, R′ = Cl). However, diazotisation as before and ring-closure in a strongly alkaline medium at room temperature gave the desired product in 80% yield. This result was as unexpected as that obtained in concentrated acid, since the beneficial effect of the latter conditions has been emphasised by Schofield and Simpson.[3] These workers have stressed the importance of acid-catalysed enolisation of the ketone grouping as a prelude to ring closure, but in the present work such catalysis is largely nullified by salt formation at the ring nitrogen atom. It appears, therefore, that the mechanism of ring closure in this case is more correctly represented as an intramolecular coupling of the diazonium cation with the enolate anion,[4] the latter stabilised in an alkaline environment; experiments are in hand to test this hypothesis.

4-Hydroxy-10-phenyl-1 : 2 : 9-triazaphenanthrene (I; R = OH) readily yielded the chloro-compound (I; R = Cl) on treatment with phosphorus pentachloride and oxychloride under reflux, and the phenoxy-derivative (I; R = OPh) was obtained by standard methods. 4-Amino-10-phenyl-1 : 2 : 9-triazaphenanthrene (I; R = NH_2) formed a monomethiodide, but the site of quaternisation has not been determined. This salt was tested for biological activity by arrangement with Dr. F. Hawking, of the National Institute for Medical Research, and was found to be inactive against the organisms listed in the preceding paper.

As was expected, treatment of the hydroxy-compound (I; R = OH) with methyl sulphate yielded the *N*-methyl derivative, distinct from the *O*-methyl isomer prepared from the chloro-compound and sodium methoxide.

Experimental

3-Amino-2-phenylquinoline.—2-Phenyl-3-phthalimidoquinoline-4-carboxylic acid (40 g.) was heated under reflux with 50% v/v sulphuric acid (400 c.c.) for ½ hr. and the mixture was cooled, diluted to twice its volume, partially neutralised, and filtered (with filter-aid) to remove tar. The cold filtrate was basified with aqueous ammonia (*d* 0·880) and extracted three times with chloroform, to yield practically pure 3-amino-2-phenylquinoline (15 g.) as a pale yellow powder, m. p. not depressed on admixture with a sample, m. p. 119°, prepared by the method of Petrow *et al.*[5] Neutralisation of the mother-liquors and re-extraction with chloroform yielded the amino-acid (1 g.), m. p. and mixed m. p. 224°.

The amine was also formed by similar treatment of 2-phenyl-3-phthalimidoquinoline (see below).

The phthalimido-acid was recovered after 2 hours' heating with 20% or 75% sodium hydroxide solution.

2-Phenyl-3-phthalimidoquinoline.—The phthalimido-acid (2·5 g.) and phosphoric acid (15 c.c.; *d* 1·75) were heated at 215° ± 5° for 1 hr. Water (75 c.c.) was added and the pale yellow precipitate (2 g.) was collected and recrystallised repeatedly from benzene, to yield *2-phenyl-3-phthalimidoquinoline*, m. p. 249—250° (Found: C, 78·95; H, 4·25; N, 8·0. $C_{23}H_{14}O_2N_2$ requires C, 78·8; H, 4·0; N, 8·0%). Presence of 3-amino-2-phenylquinoline in the aqueous mother-liquor was indicated by its green fluorescence and by the sublimate of phthalic anhydride in the condenser.

3-Hydrazino-2-phenylquinoline Hydrochloride.—A solution of 3-amino-2-phenylquinoline (18 g.) in water (45 c.c.) and concentrated hydrochloric acid (75 c.c.) was diazotised at 0° with sodium nitrite (6 g. in 200 c.c. of water). The resultant solution was added at 0° to stannous chloride (54 g.) in concentrated hydrochloric acid (54 c.c.) and water (100 c.c.). The mixture was kept at 0° for ½ hr., allowed to reach room-temperature overnight, then diluted to 1500 c.c. and partially neutralised with sodium hydroxide solution (25 g. in 50 c.c.). Tin salts were removed as the sulphide, and the precipitate (collected with a filter-aid) was digested with boiling water (2 × 400 c.c.), the combined filtrates being concentrated to 350 c.c. and then

[3] Borsche and Herbert, *Annalen*, 1941, **546**, 293; Schofield and Simpson, *J.*, 1948, 1170.
[4] Leonard, *Chem. Rev.*, 1945, **37**, 269.
[5] Petrow, Stack, and Wragg, *J.*, 1943, 316.

cooled in ice. The hydrazine hydrochloride (14·8 g.) separated as a yellow powder, m. p. 255° (decomp.).

The *hydrazone* of ethyl methyl ketone (16 c.c.) was prepared from this hydrochloride (10 g.) under reflux with sodium acetate (16 g.) in water (16 c.c.) and ethanol (25 c.c.) for 5 min. The derivative (9·3 g.) separated on cooling and formed light brown needles, m. p. 123°, from aqueous ethanol (Found: C, 78·9; H, 6·7; N, 14·8. $C_{19}H_{19}N_3$ requires C, 78·9; H, 6·6; N, 14·5%).

The derivative from propiophenone, prepared by the same method, was a sticky solid which could not be recrystallised.

4′ : 5′-Dimethyl-2-phenylpyrrolo(2′ : 3′-3 : 4)quinoline.—Ethyl methyl ketone 2-phenyl-3-quinolylhydrazone (9·3 g.) was heated on a steam-bath with concentrated hydrochloric acid (80 c.c.) for 6 hr. The precipitate (8·2 g.) was collected, washed with 50% hydrochloric acid, dissolved in the minimum volume of hot water, and recrystallised by cooling followed by the addition of concentrated hydrochloric acid, to give the pure *hydrochloride* (5·9 g.), m. p. ~300° (variable) (Found: C, 73·6; H, 5·7; N, 9·3; Cl, 10·0. $C_{19}H_{16}N_2$,HCl requires C, 73·9; H, 5·55; N, 9·1; Cl, 11·5%).

The *base*, m. p. 304—305°, obtained by making alkaline (ammonia) a solution of the hydrochloride, separated from benzene in colourless needles (Found: C, 83·8; H, 6·0; N, 10·5. $C_{19}H_{16}N_2$ requires C, 83·8; H, 5·9; N, 10·3%). This compound was recovered unchanged after 4½ hours' heating with either acetyl chloride or acetic anhydride.

4′-Methyl-2 : 5′-diphenylpyrrolo(2′ : 3′-3 : 4)quinoline Hydrochloride.—Crude propiophenone 2-phenyl-3-quinolylhydrazone (2·8 g.) was heated on a steam-bath with concentrated hydrochloric acid (30 c.c.) for 6 hr. The precipitate was collected, washed with concentrated hydrochloric acid, and recrystallised three times from diluted hydrochloric acid and finally from water, to yield the *hydrochloride*, m. p. ~300° (variable) (Found: C, 73·2; H, 5·3; N, 7·2; Cl, 9·0. $C_{24}H_{18}N_2$,HCl,H_2O requires C, 74·2; H, 5·4; N, 7·2; Cl, 9·15%).

Ethyl 2-Phenyl-3-phthalimidoquinoline-4-carboxylate.—The acid (10 g.) was heated under reflux with thionyl chloride (30 c.c.) for ½ hr. and the cold mixture was treated with ethanol (50 c.c.) and then heated for a further ½ hr. Volatile products were removed under reduced pressure and the residue was recrystallised from ethanol, to provide colourless leaflets of the *ester*, m. p. 192—193° (Found: C, 73·3; H, 4·4; N, 6·9. $C_{26}H_{18}O_4N_2$ requires C, 73·9; H, 4·3; N, 6·6%).

4-Acetyl-2-phenyl-3-phthalimidoquinoline.—The acid (50 g.) was heated under reflux for ½ hr. with thionyl chloride (75 c.c.), the excess of thionyl chloride was removed under reduced pressure (finally with dry benzene), and the acid chloride was suspended in dry benzene (400 c.c.). This suspension was added to a hot stirred suspension of sodiomalonic ester prepared in the usual way from diethyl malonate (24 c.c.), powdered sodium (4·2 g.), and benzene (200 c.c.); the mixture was stirred for 18 hr., heated under reflux for 5 hr., stirred at room temperature for 18 hr., heated to *ca.* 60° and stirred for ¼ hr. with diluted hydrochloric acid (60 c.c. of concentrated acid in 100 c.c. of water). The aqueous layer was extracted with benzene, and the original layer and combined extracts were washed, dried (Na_2SO_4), and evaporated to about 50 c.c. to yield crystals of the condensation product (*ca.* 35 g.), m. p. 184°. This substance (15 g.) was added to 35% v/v sulphuric acid (210 c.c.), and the suspension heated under reflux, with occasional shaking, for 10 min., cooled, and poured into water (300 c.c.). The solid (10 g.), m. p. 232°, furnished the pure *ketone*, m. p. 240—241°, on recrystallisation from ethanol (Found: C, 76·5; H, 4·2; N, 7·4. $C_{25}H_{16}O_3N_2$ requires C, 76·5; H, 4·1; N, 7·1%). The *oxime*, m. p. 240° (decomp.), separated from methanol as cream-coloured needles (Found: C, 72·6; H, 4·4; N, 10·0. $C_{25}H_{17}O_3N_3$ requires C, 73·7; H, 4·2; N, 10·3%).

On heating this ketone (3 g.) under reflux with acetic acid (20 c.c.) and 100% hydrazine hydrate (3 c.c.) for 4 hr. and recrystallising the product (2·3 g., m. p. 160—165°) from benzene–light petroleum (b. p. 60—80°) the *hydrazone* was obtained as an orange powder, m. p. 196° (decomp.) (Found: C, 73·6; H, 4·3; N, 13·2. $C_{25}H_{18}O_2N_4$ requires C, 73·9; H, 4·5; N, 13·8%).

When the ketone (0·5 g.) was heated under reflux with 48% hydrobromic acid (8 c.c.) for 3½ hr. and the solution was cooled, diluted, and filtered to remove a small amount of solid, basification of the filtrate yielded a pale yellow solid (0·25 g.) which crystallised from light petroleum (b. p. 80—100°) in needles, m. p. 117—118° not depressed on admixture with 3-amino-2-phenylquinoline.

Action of Thionyl Chloride on 3-Amino-2-phenylquinoline-4-carboxylic Acid.—The amino-acid (2 g.) was heated under reflux for 30 min. with thionyl chloride (5 c.c.), the excess of thionyl

chloride removed under reduced pressure, and the red residue left at room temperature with 15% hydrochloric acid (20 c.c.) for a few hours and then filtered. The filtrate was made alkaline with aqueous ammonia, and the resultant sticky solid (1·5 g.) was dried and digested with boiling light petroleum (b. p. 80—100°); this provided *3-amino-4-chloro-2-phenylquinoline* (0·9 g.) as pale yellow needles, m. p. 126° (Found: C, 70·8; H, 4·6; N, 11·3; Cl, 12·6. $C_{15}H_{11}N_2Cl$ requires C, 70·7; H, 4·3; N, 11·0; Cl, 13·95%). The *acetyl derivative* formed colourless needles, m. p. 195°, from benzene (Found: C, 68·7; H, 4·4; N, 8·6; Cl, 11·6. $C_{17}H_{13}ON_2Cl$ requires C, 68·6; H, 4·4; N, 9·5; Cl, 11·95%). An identical experiment, in which the treatment with hydrochloric acid was omitted, yielded by digestion with light petroleum only a small quantity of an orange solid which became sticky on contact with air and spontaneously decomposed with evolution of sulphur dioxide. The compound, m. p. 126°, was unchanged after 2 hours' heating under reflux with 18% v/v sulphuric acid, but with 55% acid for 1 hr. gave a pale yellow solid, m. p. *ca.* 210°, on basification with aqueous ammonia. This provided, by recrystallisation from ethyl acetate–methanol, *3-amino-4-hydroxy-2-phenylquinoline*, m. p. 251° (decomp.) (Found: C, 75·9; H, 5·25; N, 12·1. $C_{15}H_{12}ON_2$ requires C, 76·25; H, 5·1; N, 11·9%).

3-Amino-4-phenoxy-2-phenylquinoline.—A solution of 3-amino-4-chloro-2-phenylquinoline (0·5 g.) in phenol (*ca.* 7 g.) was treated with a stream of dry ammonia for 1·5 hr. at 195° ±15°. The cold mixture was treated with water (*ca.* 100 c.c.) and sodium hydroxide solution to dissolve phenol. Recrystallisation of the crude product from methanol gave pale yellow blades of the *phenoxy-compound* (0·3 g.), m. p. 175° (Found: C, 80·5; H, 5·4; N, 10·5. $C_{21}H_{16}ON_2$ requires C, 80·7; H, 5·1; N, 9·0%). Treatment of the chloro-compound with phenol and potassium hydroxide at 100° failed to provide the phenoxy-compound. Attempts to convert this compound into the 4-amino-derivative, by heating in ammonium acetate at 140°, failed.

4-Acetyl-3-amino-2-phenylquinoline.—(*a*) 3-Amino-4-cyano-2-phenylquinoline (24 g.) was added during ½ hr. to a Grignard reagent prepared from magnesium (7·2 g.) and methyl iodide (20 c.c.) in ether (150 c.c.) and benzene (450 c.c.). The solution was heated under reflux for *ca.* 20 hr., cooled, and stirred with ice (1400 g.) and concentrated hydrochloric acid (360 c.c.) for 3½ hr. The organic layer was extracted with 5N-hydrochloric acid (2 × 150 c.c.) and the acid solution was then basified and extracted with benzene (3 × 300 c.c.). Evaporation of the washed and dried ($MgSO_4$) extract yielded a sticky solid which gave an almost pure product (22·4 g.; m. p. 130—133°) when washed with ether. The *ketimide*, m. p. 133—134°, formed almost colourless crystals from benzene–light petroleum (b. p. 80—100°) (Found: C, 77·8; H, 5·55; N, 15·1. $C_{17}H_{15}N_3$ requires C, 78·1; H, 5·8; N, 16·1%). The ketone (13·8 g.) was best prepared by heating the ketimide (15 g.) under reflux with water and concentrated hydrochloric acid (120 c.c.; 2 : 1 v/v) for 1 hr. For isolation, the reaction mixture was basified and extracted with ether, and the residue from evaporation of the washed and dried (Na_2SO_4) extract was recrystallised from *n*-hexane; the pure *ketone*, m. p. 93—94°, separated as pale yellow needles or blades (Found: C, 77·7; H, 5·3; N, 10·1. $C_{17}H_{14}ON_2$ requires C, 77·8; H, 5·4; N, 10·7%).

(*b*) 3-Amino-2-phenylquinoline-4-carboxyamide (35 g.) was added with stirring during 15 min. to a Grignard reagent prepared from magnesium (18 g.) and methyl iodide (54 c.c.) in ether (225 c.c.) and benzene (600 c.c.). The mixture was heated under reflux for 3½ hr., then cooled, and the ketimide (29 g.) was isolated as before and hydrolysed to give the almost pure ketone (25 g.).

Action of Nitrous Acid on 4-Acetyl-3-amino-2-phenylquinoline.—(*a*) A hot solution of the amino-ketone (12 g.) in concentrated hydrochloric acid (30 c.c.) and water (120 c.c.) was cooled to −5° and the finely divided suspension was treated below 0° with sodium nitrite (3·1 g.) in water (60 c.c.) during 5 min. The mixture was stirred below 0° and treated with 6N-sodium hydroxide (120 c.c.), then set aside at room temperature for 2 hr., filtered, and neutralised. The precipitate of *4-hydroxy-10-phenyl-1 : 2 : 9-triazaphenanthrene* (10·2 g.) formed plates, m. p. 262°, from ethanol (Found: C, 74·5; H, 4·0; N, 14·8. $C_{17}H_{11}ON_3$ requires C, 74·7; H, 4·1; N, 15·4%).

(*b*) The ketone (1 g.) was treated in concentrated hydrochloric acid (25 c.c.) at 0° with sodium nitrite (0·3 g.) in water (2 c.c.) during 5 min. After a few minutes, concentrated hydrochloric acid (75 c.c.) was added, and the mixture heated at 60° for 4 hr. Excess of acid was removed under reduced pressure and the residue neutralised with a concentrated solution of sodium acetate. The sticky solid (1 g.) was collected and recrystallised (charcoal) from ethanol, to provide crystals (0·6 g.), m. p. 98°; digestion with *n*-hexane gave an insoluble fraction (90 mg.; m. p. 253—255°) identical with the hydroxy-compound, m. p. 262°, and a soluble fraction,

m. p. 100—101°, identified as 4-*acetyl*-3-*chloro*-2-*phenylquinoline* (Found: C, 73·0; H, 4·6; N, 4·8; Cl, 12·0. $C_{17}H_{12}ONCl$ requires C, 72·5; H, 4·3; N, 5·0; Cl, 12·6%).

4-*Chloro*-10-*phenyl*-1 : 2 : 9-*triazaphenanthrene*.—The 4-hydroxy-compound (11 g.), phosphorus pentachloride (17 g.), and phosphoryl chloride (85 c.c.) were heated under reflux for 2½ hr. The phosphoryl chloride was distilled off under reduced pressure and the residue was shaken with benzene (100 c.c.), ice (150 g.), and 3N-sodium hydroxide (100 c.c.) for 20 min. The benzene layer, combined with further benzene extracts, was dried ($MgSO_4$) and evaporated to yield material (9·4 g.), m. p. 183°. The pure *chloro-compound*, m. p. 186°, separated as pale yellow blades from ethyl acetate (Found: C, 69·6; H, 3·35; N, 14·9; Cl, 12·5. $C_{17}H_{10}N_3Cl$ requires C, 69·9; H, 3·45; N, 14·4; Cl, 12·1%).

4-*Phenoxy*-10-*phenyl*-1 : 2 : 9-*triazaphenanthrane*.—(*a*) A stream of dry ammonia was passed through a solution of the foregoing chloro-compound (0·4 g.) in phenol (2 g.) at 180°. The stirred mixture was heated on a steam-bath with sodium hydroxide solution (4 g. in 30 c.c.) for 15 min., then cooled, and the product was collected and washed with 3N-sodium hydroxide, then with water. The product (0·4 g.; m. p. *ca.* 200°) crystallised from methyl acetate to provide pale pink needles of the *phenoxy-compound*, m. p. 221° (Found: C, 78·5; H, 3·9; N, 10·4. $C_{23}H_{15}ON_3$ requires C, 79·1; H, 4·3; N, 12·0%).

(*b*) The chloro-compound (6 g.) was heated on a steam-bath for 1½ hr. with potassium hydroxide (2 g.) in phenol (30 g.), the product cooled, and digested with warm 1·5N-sodium hydroxide (350 c.c.), and the phenoxy-compound (8 g.), m. p. and mixed m. p. 219—220°, was collected.

4-*Amino*-10-*phenyl*-1 : 2 : 9-*triazaphenanthrene*.—(*a*) The phenoxy-compound (1 g.) was heated in an open tube with ammonium acetate (*ca.* 10 g.) at 180—200° (bath) for 3 hr., the ammonium acetate being renewed as necessary. The cold mixture was digested with dilute sodium hydroxide solution, and the well-washed crude product (0·45 g.), m. p. *ca.* 255°, recrystallised from nitromethane to provide colourless needles, m. p. 276°, of the pure *amine* (Found: C, 74·9; H, 4·6; N, 18·15. $C_{17}H_{12}N_4$ requires C, 75·0; H, 4·4; N, 20·6%).

(*b*) A stream of dry ammonia was passed for ½ hr. into a solution of the phenoxy-compound (0·5 g.) in acetamide (5 g.) at 175° ± 5°. The mixture was cooled and diluted with water, and the product, m. p. *ca.* 210°, was collected and washed: this material could be separated into a portion (0·3 g.; m. p. 219—220°) insoluble in warm dilute hydrochloric acid and a soluble fraction (50 mg.; m. p. 269—270°) shown to be the phenoxy- and the amino-compound respectively.

4-*Acetamido*-10-*phenyl*-1 : 2 : 9-*triazaphenanthrene*.—The amine (0·09 g.) was heated under reflux with acetic anhydride (1·5 c.c.) for 5 min. and then for 15 min. on a steam-bath; the cold mixture was shaken with water and a little ethanol, and the product (90 mg.) was collected. Recrystallisation from acetic acid furnished the *acetyl derivative* as needles, m. p. 287—289° (Found: C, 71·0; H, 4·9; N, 17·7. $C_{18}H_{14}ON_4$ requires C, 71·5; H, 4·7; N, 18·5%).

4-*Amino*-10-*phenyl*-1 : 2 : 9-*triazaphenanthrene Methiodide*.—The amine (1·2 g., m. p. *ca.* 270°) was heated under reflux with methyl iodide (10 c.c.) in methanol (10 c.c.) for 2 hr., then cooled, and the product (1·5 g.) recrystallised from methanol, to give golden-yellow needles (0·9 g.) of the *salt*, m. p. 285° (decomp.) (Found: C, 52·15; H, 4·1; N, 13·3; I, 30·5. $C_{18}H_{15}N_4I$ requires C, 52·1; H, 3·65; N, 13·5; I, 30·7%).

N′-*Methyl*-4-*oxo*-10-*phenyl*-1 : 2 : 9-*triazaphenanthrene*.—A cold solution of the hydroxy-compound (1 g.) in 3N-sodium hydroxide (10 c.c.) was treated with dimethyl sulphate (1 c.c.), and the suspension was heated at *ca.* 55° for 5 min. The product (0·7 g.), m. p. 270°, was collected cold and recrystallised from ethyl alcohol and from *n*-butyl alcohol, to provide the *derivative*, m. p. 280—281°, as pale yellow leaflets (Found: C, 75·2; H, 4·4; N, 14·9. $C_{18}H_{13}ON_3$ requires C, 75·2; H, 4·6; N, 14·6%).

4-*Methoxy*-10-*phenyl*-1 : 2 : 9-*triazaphenanthrene*.—The 4-chloro-compound (0·6 g.) was heated under reflux for 2 hr. with methanolic sodium methoxide, prepared from sodium (0·25 g.) and methanol (15 c.c.). The mixture was evaporated to half-volume, then cooled, and the crystals (0·6 g.) were recrystallised from ethyl alcohol, to provide colourless needles of the *methoxy-compound*, m. p. 194—198° (Found: C, 75·3; H, 4·0; N, 14·6. $C_{18}H_{13}ON_3$ requires C, 75·2; H, 4·6; N, 14·6%).

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