320. *Triazaphenanthrenes. Part V.* The Site of Quaternisation in Some Triazaphenanthrene Methiodides.*

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The site of quaternisation in the monomethiodides of 10-phenyl- (I; R = H) and 4-amino-10-phenyl-1,3,9-triazaphenanthrene (I; R = NH_2) is shown to be N^3. Evidence is presented to support the view that in salts of 4-amino-10-phenyl-1,2,9-triazaphenanthrene the quaternary atom is N^2.

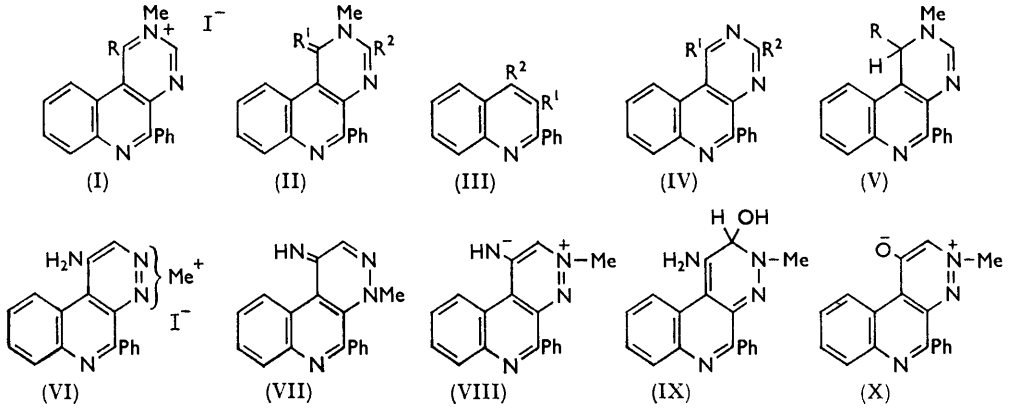
To determine the site of quaternisation in 4-amino-10-phenyl-1,3,9-triazaphenanthrene methiodide,[1] hydrolytic degradation was employed. When the quaternary salt (I; R = NH_2) was heated with soda-lime, 3-amino-2-phenylquinoline was isolated; thus N^9 was not methylated. On treatment with aqueous sodium hydroxide under a variety of conditions, the methiodide was converted into 3,4-dihydro-4-imino-3-methyl-10-phenyl-1,3,9-triazaphenanthrene (II; R^1 = NH, R^2 = H); surprisingly, this was stable to alkali, but with hot 50% aqueous sulphuric acid it yielded the 4-oxo-derivative (II; R^1 = O, R^2 = H), identical with that previously obtained [1] by methylation of 4-hydroxy-10-phenyl-1,3,9-triazaphenanthrene. This oxo-compound was completely stable to both acid and alkaline hydrolysis (cf. the easy hydrolysis of 3,4-dihydro-3-methyl-6-nitro-4-oxoquinazoline [2]) but with soda-lime it yielded 3-amino-2-phenylquinoline and methylamine. The structure (II; R^1 = O, R^2 = H) was confirmed by the following synthesis: 2-phenyl-3-phthalimidoquinoline-4-carboxylic acid was converted through the acid chloride into the 4-methylamide [III; $R^1 = N(CO)_2C_6H_4$, R^2 = CO·NHMe], the phthaloyl group was removed, and the amine (III; $R^1 = NH_2$, R^2 = CO·NHMe) was heated with formic acid to provide compound (II; R^1 = O, R^2 = H). Treatment of the 4-imino-derivative (II; R^1 = NH, R^2 = H) or the quaternary salt (I; R = NH_2) with 12% hydrochloric acid gave only a glass, which, we suggest, consists mainly of 3-amino-4-(*N*-methylamidino)-2-phenylquinoline [III; $R^1 = NH_2$, $R^2 = -C(:NH)\cdot NHMe$]. Evidence in favour of this formulation is (*a*) a green fluorescence in acid solution which was quenched by nitrous acid, a property which we have observed in many 3-amino-2-phenylquinolines, and

* Part IV, Atkinson and Rodway, *J.*, 1959, 6.

[1] Atkinson and Mattocks, *J.*, 1957, 3718.

[2] Morley and Simpson, *J.*, 1948, 360.

(*b*) reaction with hot formic acid, to give 4-methylamino-10-phenyl-1,3,9-triazaphenanthrene (IV; R^1 = NHMe, R^2 = H), identical with that synthesised from 4-chloro-10-phenyl-1,3,9-triazaphenanthrene (IV; R^1 = Cl, R^2 = H) and methylamine.



Degradation of 10-phenyl-1,3,9-triazaphenanthrene methiodide (I; R = H) followed a different pattern; heating it with soda-lime yielded methylamine and 3-amino-2-phenylquinoline, showing N^3 to be the quaternary centre. If the methiodide was treated with 2N-sodium hydroxide below 5° for a few minutes and the solution then neutralised, 3,4-dihydro-4-hydroxy-3-methyl-10-phenyl-1,3,9-triazaphenanthrene (V; R = OH) was obtained. This base was also prepared by treating 10-phenyl-1,3,9-triazaphenanthrene (IV; $R^1 = R^2$ = H) with methyl sulphate in aqueous alkali; its formulation rests on the ready formation of an ethyl ether (V; R = OEt) when heated in ethanol [3] and on its oxidation with hydrogen peroxide to the amide (II; R^1 = O, R^2 = H); prolonged oxidation gave the 2-hydroxy-derivative (II; R^1 = O, R^2 = OH). The last compound was also prepared by methylation of 2,4-dihydroxy-10-phenyl-1,3,9-triazaphenanthrene (IV; $R^1 = R^2$ = OH), obtained by oxidation of 4-hydroxy-10-phenyl-1,3,9-triazaphenanthrene.[1]

When the methiodide (I; R = H) was boiled with 50% sulphuric acid, presumably only the methosulphate was formed (iodine being driven off), since treatment of the cooled liquor with alkali yielded only the base (V; R = OH). In contrast, both the latter and the salt (I; R = H) were rapidly degraded by hot aqueous sodium hydroxide to methylamine and 3-amino-4-formyl-2-phenylquinoline (III; $R^1 = NH_2$, R^2 = CHO) which formed an oxime, was hydrolysed to 3-amino-2-phenylquinoline by boiling sulphuric acid, and was oxidised by nitric acid to 3-amino-2-phenylquinoline-4-carboxylic acid.

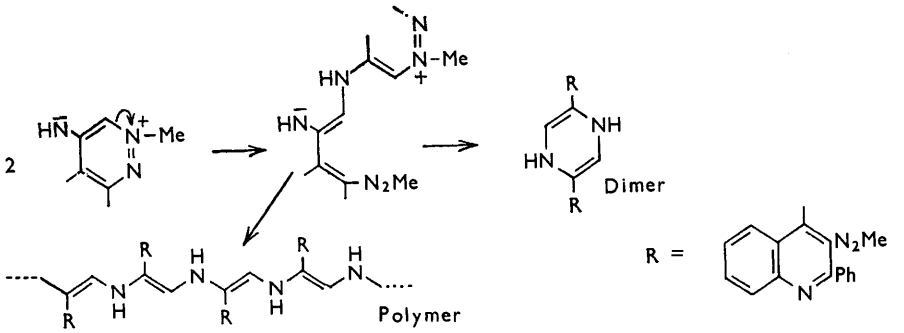
The site of quaternisation in 4-amino-10-phenyl-1,2,9-triazaphenanthrene methiodide [4] (VI) was much more difficult to determine because hydrolysis could not be used to separate the two adjacent nitrogen atoms. Simpson [5] found that when a similar compound, 4-amino-6-chlorocinnoline methiodide, was treated with aqueous alkali, the main product was a base that was stable at room temperature but in hot alkaline solution decomposed to ammonia and 6-chloro-1-methyl-4-cinnolone. He concluded [5,6] that the basic nitrogen in all cinnolines was probably N^1. In the present case strong, but not conclusive evidence has been obtained in favour of N^2 as the methylated atom. This does not necessarily mean that N^2 is the more basic centre, since in this case the ease of methylation at N^1 is decreased by steric hindrance.

As expected, treatment of the methiodide (VI) with various hydrolytic agents failed to

[3] Sidgwick, " Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937, p. 525.
[4] Atkinson and Mattocks, *J.*, 1957, 3722.
[5] Simpson, *J.*, 1947, 1653.
[6] Atkinson and Simpson, *J.*, 1947, 808.

open the pyridazine ring. With cold aqueous sodium hydroxide, a labile compound " A " was formed without loss of volatile bases; when heated with soda-lime, this yielded 3-amino-2-phenylquinoline, showing that neither N^9 nor N^1 was the site of quaternisation. The methiodide was readily regained from compound " A " by using cold dilute hydriodic acid and potassium iodide. Treatment of the methiodide with hot dilute hydrochloric or sulphuric acid gave, respectively, a chloride and a sulphate which yielded compound " A " on basification.

Analysis showed that compound " A " was not a stable pseudo-base or quaternary hydroxide but had a molecular formula represented by (VII) or (VIII). The latter is preferred since (VII) is analogous to the imine (II; $R^1 = NH$, $R^2 = H$) which could not be converted into the salt (I). Furthermore, compound " A," whilst fairly stable when dry or in aqueous suspension, polymerised to a dark green or brown material when dissolved in many organic solvents. This polymerisation was fastest in very dry solvents and was accelerated by sunlight. It is difficult to see why a compound (VII) should behave in this way, but (VIII) could dimerise or polymerise in the absence of a stabilising polar solvent:



In water (in which compound " A " is very slightly soluble), a material (VIII) could be stabilised by formation of a methohydroxide or α-amino-alcohol (IX).

When the methiodide (VI) was boiled with 70% sulphuric acid, it was partially converted into ammonia and a compound identical with that formerly obtained [4] by *N*-methylation of 4-hydroxy-10-phenyl-1,2,9-triazaphenanthrene, and at that time assigned the structure *N*-methyl-4-oxo-10-phenyl-1,2,9-triazaphenanthrene. If we exclude migration of the methyl group (under the drastic conditions) this should have structure (X). Like its 1,3,9-triaza-counterpart (II; $R^1 = O$, $R^2 = H$), this compound was completely resistant to both acid and alkaline hydrolysis, but fusing it with soda-lime gave 3-amino-2-phenylquinoline in over 50% yield, together with ammonia and methylamine. This is consistent with methylation at N^2, but it is not conclusive owing to the formation of appreciable amounts of ammonia. However, when 3-amino-2-phenylquinoline itself was heated with soda-lime, some ammonia was produced. When compound (X) was treated with reducing agents in aqueous solution, both ammonia and methylamine were produced; unfortunately no recognisable derivatives of 3-aminoquinoline could be isolated.

Experimental

Reactions of 4-Amino-10-phenyl-1,3,9-triazaphenanthrene Methiodide.—(a) *With soda-lime.* A mixture of the methiodide (0·5 g.) and powdered soda-lime (5·0 g.) was heated in a dry test tube over a small flame. There were produced a gas containing ammonia, an aqueous distillate, and a yellow oily distillate which yielded a non-crystalline solid on cooling. This solid recrystallised (charcoal) from light petroleum (b. p. 80—100°), to provide colourless needles of 3-amino-2-phenylquinoline, m. p. and mixed m. p. 113—114°.

(b) *With sodium hydroxide.* (i) The methiodide (0·2 g.) was treated with 2N-sodium hydroxide (5 ml.) at *ca.* 20° for 1 hr. The pale yellow solid became colourless in the first few

minutes. The halogen-free product (0·14 g.), m. p. 178—180°, was washed with water and dried *in vacuo*. The substance dissolved readily in cold dilute acids to give a very pale yellow solution and was reprecipitated on basification. Three recrystallisations from ethanol gave colourless needles, m. p. 185°, of *3,4-dihydro-4-imino-3-methyl-10-phenyl-1,3,9-triazaphenanthrene* (Found: C, 75·4; H, 4·8; N, 20·2. $C_{18}H_{14}N_4$ requires C, 75·5; H, 4·9; N, 19·6%). The alkaline mother-liquor yielded no ammonia or methylamine on being heated.

(ii) The methiodide (0·1 g.) was heated under reflux with 6N-sodium hydroxide (4·0 ml.) for 35 min., cooled, and diluted with water (8·0 ml.). The solid (50 mg.) was collected and recrystallised from ethanol, giving colourless needles, m. p. 183—184° not depressed by the product described under (i).

(c) *With sulphuric acid.* The methiodide (0·2 g.) and 50% v/v sulphuric acid (4 ml.) were heated in an open vessel for 5 min. to drive off all liberated iodine. Water was added to restore the original volume and the solution was heated under reflux for 30 min. Water (5 ml.) and 6N-sodium hydroxide were added and the white precipitate, which separated *before* neutrality was reached, was extracted with chloroform (2 × 10 ml.) to give material (0·1 g.), m. p. 167°. (The basified mother-liquor, when heated, yielded much ammonia.) The product recrystallised from ethyl acetate and from benzene–light petroleum (b. p. 80—100°) as needles, m. p. 171° not depressed when mixed with authentic 3,4-dihydro-3-methyl-4-oxo-10-phenyl-1,3,9-triazaphenanthrene [1] (m. p. 171—172°).

(d) *With hydrochloric acid.* (i) The methiodide (0·4 g.), concentrated hydrochloric acid (6 ml.), and water (12 ml.) were heated under reflux for 30 min. The cooled yellow solution, which showed a green fluorescence, was basified with sodium hydroxide and extracted with chloroform (the aqueous mother-liquor containing ammonium and iodide ions). The dried ($MgSO_4$) extract yielded a cream-coloured solid (0·22 g.), m. p. 75—110° (decomp.), which was very soluble in ether and in light petroleum. The methiodide was unchanged when heated under reflux for 1 hr. with 50% v/v sulphuric acid. The fluorescence of an acid solution was discharged by sodium nitrite but no dye was formed with β-naphthol.

(ii) The same cream-coloured material was formed when 3,4-dihydro-4-imino-3-methyl-10-phenyl-1,3,9-triazaphenanthrene (0·15 g.) was heated under reflux with concentrated hydrochloric acid (3 ml.) and water (5 ml.) for 2 hr.

Action of Formic Acid on the Product of Reaction (d).—The crude substance (50 mg.), m. p. 75—110°, was boiled under reflux with 95% formic acid (2·0 ml.) for 2 hr. After cooling, the solution was basified with aqueous ammonia, the solid was extracted with benzene, and the dried ($MgSO_4$) extract was concentrated under reduced pressure to dryness. The product (30 mg.) was twice recrystallised from absolute ethanol, yielding colourless blades, m. p. 210—212° not depressed when mixed with 4-methylamino-10-phenyl-1,3,9-triazaphenanthrene.

4-Methylamino-10-phenyl-1,3,9-triazaphenanthrene.—Methylamine was passed into a solution of 4-chloro-10-phenyl-1,3,9-triazaphenanthrene (0·2 g.) in phenol (2·0 g.) at 180—190° for 20 min. The solution was cooled and poured into cold 3N-sodium hydroxide (15 ml.). The precipitate (0·2 g.), m. p. 60—70°, was washed with 3N-sodium hydroxide, then copiously with water, and dried *in vacuo*. Successive recrystallisations from ethanol and from ethyl acetate yielded colourless needles, m. p. 216°, of the *methylamino-derivative* (Found: C, 75·3; H, 5·4; N, 19·2. $C_{18}H_{14}N_4$ requires C, 75·5; H, 4·9; N, 19·6%).

Degradation of 3,4-Dihydro-3-methyl-4-oxo-10-phenyl-1,3,9-triazaphenanthrene with Soda-lime.—An intimate mixture of the compound (0·5 g.) with powdered soda-lime (5·0 g.) was heated, gently at first, in a hard-glass tube. There were obtained an aqueous distillate and a yellow oil (0·3 g.); the latter, when crystallised successively from light petroleum (b. p. 80—100°) and hexane, yielded pale yellow needles, m. p. 115—116° not depressed when mixed with 3-amino-2-phenylquinoline. Distillation of the aqueous liquor yielded methylamine, isolated as its picrate, m. p. and mixed m. p. 205—206°.

The oxo-compound was recovered unchanged after 30 minutes' boiling with 12% aqueous hydrochloric acid or 50% v/v sulphuric acid.

4-N-Methylcarbamoyl-2-phenyl-3-phthalimidoquinoline.—2-Phenyl-3-phthalimidoquinoline-4-carboxylic acid (20 g.) and thionyl chloride (35 ml.) were heated under reflux for 20 min., the excess of reagent was removed under reduced pressure, and the residue washed with benzene and dried *in vacuo*, to provide the acid chloride (14 g.), m. p. 217°.

Into a stirred solution of the crude acid chloride (5 g.) in warm dry benzene (75 ml.) was passed methylamine [from the hydrochloride (4 g.) and warm 6N-sodium hydroxide (8 ml.)],

for 10 min.; the white solid (5 g.), m. p. 289°, was washed with benzene. Recrystallisation from aqueous acetic acid yielded rectangular prisms of the *methylamide*, m. p. 298° (Found: C, 73·1; H, 4·2; N, 9·7. $C_{25}H_{17}N_3O_3$ requires C, 73·7; H, 4·2; N, 10·3%).

3-Amino-4-N-methylcarbamoyl-2-phenylquinoline.—The preceding phthalimido-compound (1·5 g.), pyridine (6 ml.), and 100% hydrazine hydrate (3 ml.) were heated under reflux for 90 min., then poured into water (50 ml.), and the colourless crystals (0·85 g.), m. p. 188—189°, were washed and were dried at 100°. Recrystallisation from ethyl acetate and from ligroin yielded needles of the *amine*, m. p. 189° (Found: C, 73·3; H, 6·1; N, 14·95. $C_{17}H_{15}N_3O$ requires C, 73·6; H, 5·4; N, 15·15%). The *acetyl derivative*, prepared by use of acetic anhydride at 100° for 30 min., formed needles, m. p. 252° (decomp.) from ethanol (Found: C, 70·9; H, 5·15; N, 12·4. $C_{19}H_{17}N_3O_2$ requires C, 71·5; H, 5·3; N, 13·1%).

3,4-Dihydro-3-methyl-4-oxo-10-phenyl-1,3,9-triazaphenanthrene.—3-Amino-4-*N*-methylcarbamoyl-2-phenylquinoline (0·2 g.) and 95% formic acid (2·0 ml.) were boiled under reflux for 1 hr. The cooled solution was diluted with water (3 ml.) and partially neutralised with a few drops of aqueous ammonia (*d* 0·880). Colourless crystals (30 mg.), m. p. 170°, separated from the acid solution. [Basification of the mother-liquor yielded unchanged starting material (150 mg.).] The product separated from ethanol in blades, m. p. 173°, not depressed when mixed with the 3,4-dihydro-3-methyl-4-oxo-10-phenyl-1,3,9-triazaphenanthrene previously prepared.[1]

Paper Chromatography of 3-Amino-2-phenylquinoline and Related Compounds.—Ascending and descending chromatograms were run on Whatman No. 1 paper. The solvent was freshly prepared by saturating water with (1) butan-1-ol or (2) isobutyl alcohol at 20°. For descending chromatograms, runs were usually ~25 cm. (4—5 hr.). Spots were made visible by treating the dried paper with gaseous hydrogen chloride or by viewing the paper in ultraviolet light. R_F values for 4-substituted 3-amino-2-phenylquinolines were as follows (4-substituent given first). Ascending solvent (1): H, 0·56; CO_2H, 0·90; $CO{\cdot}NH_2$, 0·58; CO·NHMe, 0·70; CN, 0·00; Ac, 0·59; CHO, 0·38; C(:NH)·NHMe, 0·75. Descending solvent (2). H, 0·53; CO_2H, 0·90; CO·NHMe, 0·68; $CO{\cdot}NH{\cdot}NH_2$, 0·57; Ac, 0·59; CHO, 0·38; CMe:NH, 0·68; Cl, 0·00.

Experiments on the Degradation of 10-Phenyl-1,3,9-triazaphenanthrene Methiodide.—(a) *Action of soda-lime.* The methiodide (0·5 g.) was intimately mixed with soda-lime (5·0 g.) in a hard-glass tube and heated, gently at first. The aqueous distillate and alkaline vapour were led into saturated aqueous picric acid, to provide yellow needles of methylamine picrate, m. p. and mixed m. p. 206°. A yellow oil which also condensed was found, on paper chromatography, to give a single spot, R_F 0·56, with the same characteristics as one of 3-amino-2-phenylquinoline.

(b) *Action of sodium hydroxide.* (i) The methiodide (0·6 g.) was dissolved in 2N-sodium hydroxide (30 ml.) at 0—5°, and the pH of the pale yellow solution adjusted to 7 by addition of dilute hydrochloric acid below 5°. The white precipitate (0·3 g.), m. p. 160—180°, was washed, and dried at room temperature *in vacuo*. The mother-liquor contained no methylamine or ammonia. A further product (120 mg.), m. p. 206° (decomp.), was obtained when the *neutral* mother-liquor was boiled. Recrystallisation of either product from alcohol-free ethyl acetate yielded colourless diamond-shaped plates, m. p. 212° (decomp.), of *3,4-dihydro-4-hydroxy-3-methyl-10-phenyl-1,3,9-triazaphenanthrene* (Found: C, 75·0; H, 5·7; N, 15·0. $C_{18}H_{15}N_3O$ requires C, 74·8; H, 5·2; N, 14·5%).

When this compound was recrystallised from pure ethanol, the *O-ethyl derivative* was obtained, forming colourless platelets and blades, m. p. 175° (Found: C, 75·5; H, 6·1; N, 13·2. $C_{20}H_{19}N_3O$ requires C, 75·7; H, 6·0; N, 13·3%).

(ii) When the hydroxy-compound described above was boiled with aqueous sodium hydroxide, methylamine was evolved and there separated a yellow precipitate, shown by mixed m. p. and paper chromatography to be identical with the product of experiment (iii) (below).

(iii) The methiodide (0·6 g.) was dissolved in N-sodium hydroxide (25 ml.), 6N-sodium hydroxide (20 ml.) was added, and the solution was heated at 95—100° for 40 min. Methylamine was liberated (picrate, m. p., and mixed m. p., 207—208°); no ammonia was detected (Nessler test). Extraction with ether yielded yellow sticky material (0·35 g.), m. p. <100°. Recrystallisation successively from light petroleum (b. p. 80—100°), hexane, ethanol, and again from light petroleum furnished bright yellow needles, m. p. 135°, of *3-amino-4-formyl-2-phenylquinoline* (Found: C, 77·5; H, 4·85; N, 10·3. $C_{16}H_{12}N_2O$ requires C, 77·5; H, 4·8; N, 11·3%). This aldehyde gave in dilute acids a yellow, non-fluorescent solution, the colour of which was discharged by nitrous acid; no dye was formed with β-naphthol. In ethanolic solution it

showed a marked blue-green fluorescence. When the aldehyde was boiled under reflux with 60% v/v sulphuric acid for 15 min. and the green-fluorescent solution was basified with sodium hydroxide and extracted with ether, paper chromatography of the residue gave a single spot with characteristics identical with those of 3-amino-2-phenylquinoline.

A solution of the aldehyde in 2N-nitric acid, after being kept at room temperature for one week, developed a green fluorescence. The solution was carefully neutralised with sodium hydroxide, then extracted with ether, and the residue obtained on evaporation of the ether was subjected to paper chromatography. The chromatogram showed 2 spots, identical in R_F value and appearance with the starting material (R_F 0·38) and 3-amino-2-phenylquinoline-4-carboxylic acid (R_F 0·90). In confirmation it was shown that the fluorescent material in the original solution was not extracted by ether from an alkaline solution.

The *oxime*, prepared in acetic acid, crystallised from aqueous ethanol in orange-yellow needles, m. p. 170° (decomp.) (Found: C, 67·4; H, 5·0; N, 14·9. $C_{16}H_{13}N_3O,H_2O$ requires C, 68·3; H, 5·3; N, 15·0%).

(iv) The methiodide (0·1 g.) was treated with 2N-sodium hydroxide (3·0 ml.) for 3 weeks at room temperature. Methylamine was produced and crystals of the above hydroxy-compound (i) (33 mg.) and of the above aldehyde (iii) (33 mg.) were deposited. In a similar experiment in which the mixture was kept for 3 months, only the aldehyde (50 mg.) was obtained.

(c) *Action of sulphuric acid.* The methiodide (0·1 g.) was heated with 50% v/v sulphuric acid (3 ml.) in an open vessel for a few minutes to drive off liberated iodine. The volume was adjusted to 3 ml. by adding water and the solution was heated under reflux for 35 min., cooled, diluted, and adjusted to pH 7—8 with sodium hydroxide below 10°. The white precipitate (60 mg.), m. p. 130°, was dried at room temperature and, recrystallised from pure ethyl acetate, had m. p. 200° (decomp.), not depressed by 3,4-dihydro-4-hydroxy-3-methyl-10-phenyl-1,3,9-triazaphenanthrene.

(d) *Hydrolysis and oxidation.* The methiodide (0·2 g.) was dissolved in 3N-sodium hydroxide (2·5 ml.) at room temperature, and 1 min. later, acetic acid (4 ml.) was added, followed by 30% hydrogen peroxide (4 ml.). Iodine was removed by one extraction with carbon tetrachloride (10 ml.), and the solution was heated at 100° for 10 min., during which colourless needles (70 mg.), m. p. 156°, separated. Recrystallisation from ethanol gave needles, m. p. 171°, not depressed when mixed with 3,4-dihydro-3-methyl-4-oxo-10-phenyl-1,3,9-triazaphenanthrene. This was also formed when 3,4-dihydro-4-hydroxy-3-methyl-10-phenyl-1,3,9-triazaphenanthrene was oxidised under the same conditions.

Methylation of 10-*Phenyl*-1,3,9-*triazaphenanthrene.*—The base (1·0 g.) was shaken for 15 min. with dimethyl sulphate (10 ml.) and 3N-sodium hydroxide (25 ml.), further 6N-sodium hydroxide (total, 40 ml.) being added in portions to maintain alkalinity. After a further 15 min. the mixture was extracted with ether to yield a dark brown sticky residue. Recrystallisation from benzene (charcoal) yielded ill-defined crystals (100 mg.), m. p. 200—201° (decomp.), not depressed when mixed with 3,4-dihydro-4-hydroxy-3-methyl-1,3,9-triazaphenanthrene. For oxidation, the methylated base (70 mg.), acetic acid (2 ml.), and 30% hydrogen peroxide (1 ml.) were heated together at 100° for 80 min. and concentrated to *ca.* one-third the volume under reduced pressure. Colourless needles (50 mg.) separated on cooling and were recrystallised from ethanol containing a little acetic acid to provide needles, m. p. 275—276°, not depressed when mixed with the following compound.

3,4-*Dihydro*-2-*hydroxy*-3-*methyl*-4-*oxo*-10-*phenyl*-1,3,9-*triazaphenanthrene.*—3,4-Dihydro-3-methyl-4-oxo-10-phenyl-1,3,9-triazaphenanthrene (10 g.) was dissolved in warm acetic acid (10 ml.), 30% hydrogen peroxide (5 ml.) added, and the mixture was heated at 100° for 80 min. Colourless needles (0·9 g.) which separated on dilution recrystallised from acetic acid, to give the 2-*hydroxy-derivative*, m. p. 279—280° (Found: C, 71·3; H, 4·5; N, 14·9. $C_{18}H_{13}N_3O_2$ requires C, 71·3; H, 4·3; N, 13·9%), insoluble in dilute mineral acids and in aqueous sodium hydroxide.

Methylation of 2,4-*Dihydroxy*-10-*phenyl*-1,3,9-*triazaphenanthrene.*—The dihydroxy-compound [1] (0·5 g.) was shaken in 3N-sodium hydroxide (5 ml.) for 5 min. with dimethyl sulphate (0·5 ml.). After a further 20 min. the product (0·5 g.) was washed with water, dried, and recrystallised from acetic acid, to give colourless needles, m. p. and mixed m. p. with the foregoing compound, 279—280°.

Action of Reagents on 4-*Amino*-10-*phenyl*-1,2,9-*triazaphenanthrene Methiodide.*—(a) *Sodium hydroxide.* The pure methiodide (0·1 g.) was treated with 2N-sodium hydroxide (3 ml.) for 70 min. at room temperature. The yellow product (65 mg.), m. p. 185° (decomp.), was washed

with water and dried *in vacuo*. The colourless mother-liquor contained iodide but no ammonia (Nessler test) and did not give basic vapour when heated. The product, recrystallised from ethanol, gave yellow-green needles, m. p. 196° (decomp.), of compound " A," which did not contain halogen (Lassaigne's test). In a further attempt to recrystallise it from ethyl acetate, the solution was left at room temperature; the compound changed to dark-green material and later to a black acid-insoluble substance. A similar rapid change was observed in benzene solution within a few hours and, more slowly, in ethanol. The change occurred in the dark but was more rapid in daylight.

After 6 weeks' storage in a vacuum-desiccator, crude compound " A " still had a clean, medium-yellow colour, but the m. p. had dropped to 172° (decomp.) with darkening from 150°; the m. p. was restored to 195° (decomp.) on recrystallisation from ethanol (charcoal) if the whole operation was completed within 15 min. Two recrystallisations of fresh material from ethanol gave yellow-green platelets, m. p. 196° (decomp.) (Found: C, 75·2; H, 5·0; N, 19·5. $C_{18}H_{14}N_4$ requires C, 75·5; H, 4·9; N, 19·6%).

(b) *Hydrochloric acid.* The methiodide (25 mg.) was heated under reflux with concentrated hydrochloric acid (0·5 ml.) and water (1·0 ml.) for 1½ hr. The cooled yellow solution was partially neutralised with sodium hydroxide solution, and the pale yellow needles, m. p. 282° (decomp.), were collected. The mother-liquor contained iodide but no ammonia or methylamine. The product crystallised from water in needles; the aqueous solution contained chloride, and when basified (sodium hydroxide) gave yellow-green needles, m. p. 187° (decomp.), not depressed by compound " A."

(c) 50% *Sulphuric acid.* The methiodide (0·15 g.) was heated for 2 min. with 50% v/v sulphuric acid (4 ml.) in an open flask to drive off the liberated iodine. After cooling, the remaining iodine was removed by a single extraction with carbon tetrachloride (2 ml.), and the aqueous layer was readjusted to 4 ml. with water and boiled under reflux for 30 min. The yellow liquor was diluted to 30 ml. with water, and 6N-sodium hydroxide was slowly added. Colourless plates (0·1 g.), m. p. 300° (decomp.), separated from the still acid solution and were collected and washed with a little water. The mother-liquor did not contain ammonia or methylamine. The product gave in water an acid solution (which contained sulphate) and yielded a yellow precipitate, m. p. and mixed m. p. 198° (decomp.), of compound " A " when basified with sodium hydroxide.

(d) 70% *Sulphuric acid.* The methiodide (0·4 g.) was heated with 70% v/v sulphuric acid (5 ml.) in an open vessel to drive off liberated iodine, then boiled under reflux for 2 hr., cooled, diluted with water, and partially neutralised with sodium hydroxide. The pale brown solid (0·2 g.) was collected and boiled with water, and the brown insoluble material (50 mg.), m. p. 266°, was collected. Two recrystallisations from ethanol (charcoal) gave almost colourless plates of *N*-methyl-4-oxo-10-phenyl-1,2,9-triazaphenanthrene, m. p. and mixed m. p. 273° (decomp.).

On basification of the aqueous filtrate, crude compound " A " was obtained. The mother-liquor from the initial reaction was basified and distilled, yielding ammonia, identified as the picrate; no methylamine was detected.

Regeneration of the Methiodide from Compound " A ".—Freshly prepared compound " A " was dissolved in warm dilute hydriodic acid, and an excess of potassium iodide was added. On cooling, yellow-brown needles were obtained; they recrystallised from methanol to give 4-amino-10-phenyl-1,2,9-triazaphenanthrene methiodide, m. p. and mixed m. p. 283° (decomp.).

Action of Soda-lime on Compound " A ".—The compound (50 mg.) was heated with powdered soda-lime (0·5 g.) in a dry tube. The aqueous distillate was redistilled into picric acid solution, yielding ammonium picrate. A pale brown oil was also formed and was extracted with ether and subjected to paper chromatography; the main component had R_F 0·56, identical with that of 3-amino-2-phenylquinoline.

Reactions of N-*Methyl*-4-*oxo*-10-*phenyl*-1,2,9-*triazaphenanthrene.*—(a) *With acids.* The oxo-compound was recovered unchanged after 1 hour's boiling with 50% sulphuric or 12% hydrochloric acid.

(b) *With soda-lime.* The pure compound (0·5 g.) was heated with powdered soda-lime (5 g.) in a dry tube, gently at first. A dark yellow oil (0·23 g.) which appeared in the cooler parts of the tube was collected with ether and recrystallised from light petroleum (b. p. 80—100°) (charcoal), to give 3-amino-2-phenylquinoline, m. p. and mixed m. p. 111°. The aqueous distillate contained ammonia (Nessler test). When 3-amino-2-phenylquinoline was heated

with soda-lime in a dry tube, a small amount of ammonia was formed but most of the amine distilled unchanged.

(c) *With reducing agents.* Portions (0·2 g.) of the pure oxo-compound were reduced and the liquor made alkaline with 6N-sodium hydroxide and distilled for 15 min. into 0·1N-hydrochloric acid (20. ml.) in a Kjeldahl apparatus. Methylamine and ammonia were estimated as previously.[7] (i) Reduction with granular zinc and 18% hydrochloric acid for 3 hr. at 95—100° gave methylamine (35% of theoretical maximum) and ammonia (73%). Pure quinoline under the same conditions did not give ammonia, and 3-amino-2-phenylquinoline gave 47% of ammonia. (ii) Reduction with zinc dust and glacial acetic acid under reflux for 3 hr. gave 36% of methylamine and 63% of ammonia. (iii) Reduction with red phosphorus and 45% hydriodic acid under reflux for 3 hr. gave 26% of methylamine and 26% of ammonia. (iv) Heating with butanol and sodium under reflux for 1 hr gave 26% of methylamine and 23% of ammonia.

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[7] Atkinson and Taylor, *J.*, 1955, 4241.