Reactions of Organic Azides. Part III. The Synthesis of Phenanthridines by the Interaction of Fluoren-9-ols with Hydrazoic and Sulphuric Acids, and the Mechanism of the Rearrangement of the Intermediate Azides.*

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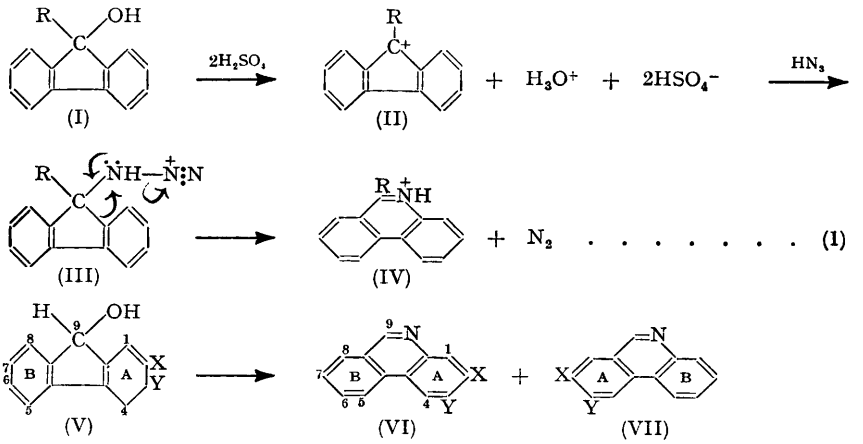
On reaction with hydrazoic and sulphuric acids, 2-, 3-, and 9-substituted fluoren-9-ols (also 9-benzylidenefluorene) yield phenanthridines. Evidence is presented that reaction proceeds by the formation and intramolecular rearrangement of a protonated azide.

An unsymmetrically substituted fluorenol yields a mixture of two isomeric phenanthridines. The rates of migration of the two rings of the fluorenol are proportional to the yields of the resultant phenanthridines; the ratios of these yields have been found to be directly related to the capacities of the rings for electron-release at their point of attachment to $C_{(9)}$.

Reactions of phenanthridine-6- and -7-diazonium sulphates, and of 7-hydroxyphenanthridine, and syntheses (other than *via* azides) of 2- and 3-nitrophenanthridines, are recorded.

It has been found (Part I *) that the interaction of fluoren-9-ol with hydrazoic acid in the presence of sulphuric acid yields phenanthridine. A number of substituted fluoren-9-ols have been prepared (*J.*, 1954, 3977), and their conversion into phenanthridines by the above reaction is now reported (for a preliminary note see *Chem. and Ind.*, 1953, 995). Results which bear on the reaction mechanism have been obtained by ascertaining the course of the reaction when groups of different electronic character are present as substituents in the fluorenols.



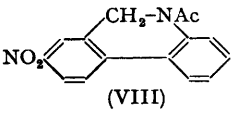
The reaction is carried out by addition of the fluorenol, with vigorous stirring at 25°, to a solution of hydrazoic acid in chloroform together with sulphuric acid. Reaction is considered (Part I) to proceed by the following mechanism: the fluorenol (I) reacts with the sulphuric acid to yield a carbonium ion (II); the latter combines with hydrazoic acid to give the proton-adduct of the azide (III), which rearranges with loss of nitrogen to yield the phenanthridinium ion (IV); electronic sharing between the carbon atom of the migrating ring and the CR–NH fragment is continuous during the rearrangement.

2-, 3-, 6-, 7-*Substituted Phenanthridines and their Orientation.*—Six fluoren-9-ols (V), substituted in positions 2- or 3-, have been converted into phenanthridines; from a

* The papers by Arcus and Mesley and by Arcus and Coombs (*J.*, 1953, 178, 3698) are regarded as Parts I and II.

2-substituted fluorenol there can potentially arise a pair of phenanthridines substituted in positions 2 and 7 (VI and VII; Y = H) and a 3-substituted fluorenol similarly yields 3- and 6-substituted phenanthridines (VI and VII; X = H). Each pair of isomers is formed by the rearrangement of a common precursor, the protonated azide (as III), whence the relative rates with which the substituted and unsubstituted rings migrate from bonding with $C_{(9)}$ to bonding with N is directly given by the ratio of the yields of the isomeric phenanthridines (VI) and (VII). The results obtained are summarised in the Table.

The reaction with 2-nitrofluoren-9-ol gave a mixture of 2- and 7-nitrophenanthridines in high yield. Fractional crystallisation of this mixture yielded a principal product (*A*), m. p. 180°, and another, m. p. 159°, in small amount. Nitrophenanthridines having each of these m. p.s are described in the literature as the 7-isomer: Ritchie (*J. Proc. Roy. Soc. N.S.W.*, 1945, **78**, 183) nitrated 10-acetyl-9 : 10-dihydrophenanthridine, and by "oxidative hydrolysis" of the 7-nitro-derivative (VIII) obtained 7-nitrophenanthridine having m. p. 178°. Caldwell and Walls (*J.*, 1952, 2156) isolated a nitrophenanthridine, m. p. 158°, from the mixture of isomers obtained by the nitration of phenanthridine. Ritchie had no definite proof of the orientation of his compound, but argued that it was probably the 7-isomer because 2-acetamidodiphenyl, under the same conditions of nitration, yields 2-acetamido-4'-nitrodiphenyl. On the other hand, Caldwell and Walls isolated 7-nitrophenanthridone on oxidation of their substance, and, from its reduction product, 7-aminophenanthridine identical with that obtained by an unambiguous synthetic route. Nevertheless, the results described below show that the substance, m. p. 159°, is a 1 : 1 complex of 2- and 7-nitrophenanthridine, and that the compound *A*, m. p. 180°, is 7-nitrophenanthridine. It is concluded that Caldwell and Walls's procedures for oxidation and reduction, together with subsequent purifications (no yields are stated), result in the preferential separation of, respectively, 7-nitrophenanthridone and 7-aminophenanthridine.



(VIII)

(i) On oxidation with acid permanganate, the material *A* gave 7-nitrophenanthridone (60%); it was converted into 9-chloro-7-nitrophenanthridine. The product obtained by Caldwell and Walls had m. p. 285—305° (*i.e.*, approximately that of the complex of 2- and 7-nitrophenanthridones discovered by Nunn, Schofield, and Theobald, *J.*, 1952, 2797); 7-nitrophenanthridone was isolated chromatographically from this material. (ii) Oxidation of the material *A* with alkaline permanganate gave no phthalic acid; the product was an unidentified nitrogen-containing acid. Huntress and Moore (*J. Amer. Chem. Soc.*, 1927, **49**, 1324) have shown that, under these conditions, 2-nitrophenanthridone yields phthalic acid. (iii) The material *A*, on reduction, yielded 7-aminophenanthridine (83%), from which was prepared 7-ethoxycarbonylaminophenanthridine. (iv) When equal weights of 2-nitrophenanthridine (m. p. 196—197°, synthesis below) and of *A* (m. p. 180°) crystallised together from ethanol, the substance of m. p. 159° (88%) was obtained.

A mixture of 3- and 6-nitrophenanthridine was obtained in good yield from the hydrazoic–sulphuric acid reaction with 3-nitrofluoren-9-ol. Fractional crystallisation yielded as principal product 6-nitrophenanthridine, which was orientated by reduction to the known 6-aminophenanthridine; 3-nitrophenanthridine, not completely freed from the 6-isomer, was also isolated, and was characterised by its m. p. when mixed with authentic 3-nitrophenanthridine (synthesis below).

From the product of the reaction with 2-aminofluoren-9-ol, there was isolated only 7-aminophenanthridine.

The mixture of 2- and 7-methoxyphenanthridine obtained from the reaction with 2-methoxyfluoren-9-ol was separated by fractional crystallisation. On demethylation, the isomer having m. p. 90° yielded 7-hydroxyphenanthridine, m. p. 282°, identical with that prepared (below) from the known 7-aminophenanthridine. The other methoxyphenanthridine, m. p. 58°, and the hydroxyphenanthridine, m. p. 245°, derived from it, are, it is concluded, the 2-isomers.

The reaction with 3-methoxyfluoren-9-ol gave 5% yields of base from which, by short-path distillation, a mixture of methoxyphenanthridines was obtained. The quantity was

insufficient to permit quantitative separation but they are probably 3- and 6-methoxyphenanthridine.

Fluorenol derivative	Total yield, %, of phenanthridines	Phenanthridines formed	Percentage of total yield
2-Nitro	92	2-Nitro	3
		7-Nitro	97
3-Nitro	88	3-Nitro	6
		6-Nitro	94
2-Amino	33	7-Amino	—
2-Methoxy	32	2-Methoxy	32
		7-Methoxy	68
3-Methoxy	5	(3- and 6-)Methoxy (not separated)	—
2-Methyl	81	2-Methyl	53
		7-Methyl	47
3-Methyl	68	3-Methyl	80
9-Phenyl	94	9-Phenyl	—
9-Methyl	47	9-Methyl	—
9-Benzyl	40	9-Benzyl	—
9-Benzylidenefluorene	49	9-Benzyl	—

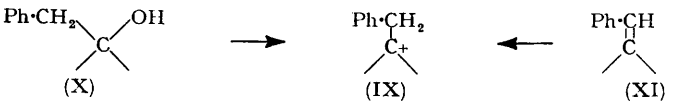
2- and 7-Methylphenanthridines were obtained in good yield from 2-methylfluoren-9-ol and were separated by fractional crystallisation of the mixture and of its picrate. The total yield of components separated by fractional crystallisation of the phenanthridines from 2-nitro-, 3-nitro-, and 2-methoxy-fluoren-9-ols was in each instance over 80%. The weights of 2- and 7-methylphenanthridine were comparatively small; the relative proportions of these compounds in the original product were determined by the use of a mixed melting point curve of the pure isomers and found to be 53 : 47.

Fractional crystallisation of the mixture of methylphenanthridines from the reaction with 3-methylfluoren-9-ol yielded only the principal product, 3-methylphenanthridine.

9-*Substituted Phenanthridines.*—The fluorenols, above, are all secondary alcohols. It has been found (Part I) that triphenylmethanol, on reaction with hydrazoic and sulphuric acids as above, yields azidotriphenylmethane; this azide, which is known to be exceptionally stable, undergoes no appreciable rearrangement under the conditions of the reaction. However, the related tertiary alcohol, 9-phenylfluoren-9-ol, gave 9-phenylphenanthridine in high yield, indicating the great tendency for ring expansion with 9-azidofluorenes.

The reaction with 9-methylfluoren-9-ol gave 9-methylphenanthridine and, in considerable yield, a compound $C_{28}H_{21}N$; this formed a 1 : 1 picrate and is probably a methylfluorenylmethylphenanthridine.

9-Benzylfluoren-9-ol yielded 9-benzylphenanthridine. The cation (IX), derived from 9-benzylfluoren-9-ol (X), can also be formed by the addition of a proton to 9-benzylidenefluorene (XI) and this, on reaction with hydrazoic and sulphuric acids, gave 9-benzylphenanthridine, the yield not differing substantially from that given by 9-benzylfluoren-9-ol.



9-Benzylidene-2-nitrofluorene was not converted into a phenanthridine; presumably the $-I$ effect of the nitro-group so constricts the π-electrons of the 9-double bond that protonation, leading to the formation of a carbonium ion, does not occur.

Reaction Mechanism.—The formation of 9-benzylphenanthridine from both 9-benzylfluoren-9-ol and 9-benzylidenefluorene constitutes further evidence for the ionic mechanism.

9-Azido-2-methoxyfluorene was readily prepared from 9-chloro-2-methoxyfluorene and sodium azide; it exists in three forms, melting at 44°, 56—58°, and 65—66° respectively. The azidofluorene was allowed to react with sulphuric acid under conditions simulating those of the hydrazoic–sulphuric acid reaction; there was obtained, in 54% yield, a mixture of 2- and 7-methoxyphenanthridines from which, by fractional crystallisation, the isomers were isolated in the ratio 34 : 66. The similarity of this ratio to that found for the hydrazoic–sulphuric acid reaction with 2-methoxyfluoren-9-ol indicates that it is the proton-adduct of the azide, which may be formed both by combination of a carbonium

ion with hydrazoic acid and by direct protonation of an azide, which rearranges with loss of nitrogen to yield the phenanthridinium ion.

When 9-chloro-2-nitrofluorene was heated with sodium azide in methanol (the method for the preparation of 9-azido-2-methoxyfluorene) 9-imino-2-nitrofluorene was obtained in high yield. It has been found (Part I) that 9-azidofluorene, on storage or on heating above its m. p. (45°), yields 9-iminofluorene, and the formation of 9-imino-2-nitrofluorene is attributed to a similar breakdown of the (unprotonated) azide under the conditions used for its preparation.

For the Schmidt reaction with ketones, Smith and his co-workers (*J. Amer. Chem. Soc.*, 1948, **70**, 320; 1950, **72**, 2503, 3718) have proposed an oxime-like intermediate (XII), formed by the elimination of water from the adduct of hydrazoic acid and the protonated ketone. The preponderating isomer is that in which the group having the greater bulk in the neighbourhood of the C=N group is *anti* to the $-N^+{:}N$ group; nitrogen separates and this group, R, migrates. These authors proposed the mechanism in order to account for the following observations: (*a*) In the reaction with *p*-substituted and *pp'*-disubstituted benzophenones, the migratory aptitudes of all groups are approximately equal; the groups differed widely in electronic character, but had essentially the same bulk in the neighbourhood of the carbonyl group. (*b*) In a series of alkyl phenyl ketones, the relative extent of migration of the alkyl group increases in the order Me < Et < Pr^i < Bu^t. Schlechter and Kirk (*ibid.*, 1951, **73**, 3087) found that, in general, the substituted carbon atom migrates preferentially during the reaction with 2-substituted *cyclo*pentanones and *cyclo*hexanones, a result which accords with Smith's mechanism. However, there is no correlation of migratory aptitude with size for *o*-substituted phenyl (and related) groups in the Schmidt reaction with aryl phenyl ketones (Smith, *ibid.*, 1954, **76**, 431; Badger, Howard, and Simons, *J.*, 1952, 2849; Dice and Smith, *J. Org. Chem.*, 1949, **14**, 179).

R–C(R′)=N–$N^+{:}N$ (XII)

The mechanism above is inapplicable to the reaction with alcohols and olefins because the doubly-bonded intermediate (XII) cannot be formed by dehydration of, *e.g.*, (III). There is no consistent relation between bulk and migratory aptitude for the rings in 2- and 3-substituted fluoren-9-ols: it is seen (Table) that in two instances the substituted and in four the unsubstituted ring migrates to the preponderating extent.

Models show that the 2- and the 3-substituents used in the present work offer no steric hindrance to the free rotation of the $-NH-N^+{:}N$ group about the $C_{(9)}$–N bond. It is considered that the $-N^+{:}N$ group is readily able to take up a configuration *anti* to the migrant group, which becomes attached to the nitrogen atom at the face opposite to that from which the N_2 molecule departs. This molecule incorporates the electrons of the N–N bond, and the migrating group functions as an electron donor. It is concluded (below) that the factor having the greatest influence on the migratory aptitudes of the rings is their capacity for electron-release at the point of attachment to $C_{(9)}$.

For a number of *p*- and *m*-substituted phenyl groups in the reaction of 1 : 1-diarylethylenes with hydrazoic and sulphuric acids:

$$CH_2{:}C(C_6H_5)\cdot C_6H_4R \xrightarrow{HN_3\text{–}H_2SO_4} C_6H_4R\cdot N{:}C(CH_3)\cdot C_6H_5 + C_6H_5\cdot N{:}C(CH_3)\cdot C_6H_4R$$

McEwen and Mehta (*J. Amer. Chem. Soc.*, 1952, **74**, 526) found the migratory aptitude to be directly related to the electron-release of the group as measured by $\log(K_{C_6H_5\cdot CO_2H}/K_{C_6H_4R\cdot CO_2H})$. A similar relation has been found by Ege and Sherk (*ibid.*, 1953, **75**, 354) for the migratory aptitudes of *p*-substituted phenyl groups during the acid-catalysed decomposition of 1 : 1-diarylazidoethanes.

The results given in the Table have been correlated with the properties of the substituents in the fluoren-9-ols. The electronic characteristics of substituents in aromatic systems have been discussed by Ingold ("Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, pp. 231—269, 738—743); the dissociation constants of acids quoted below are those selected by Dippy (*Chem. Reviews*, 1939, **25**, 151). The permanent (*I*, *M*) effects appear to take part in the present reaction, as do the $+E$ effects evoked at reaction time; $-E$ effects would not be expected to arise during a reaction dependent on electron-release. With regard to the protonated azide derived from (V), a

substituent in position 3 is *para* to the bond from ring A to $C_{(9)}$ (abbreviated to A–$C_{(9)}$ hereafter); a conjugated system is therefore available for the transmission of tautomeric, as well as inductive, electron-displacements. No such system is available between position 3 and B–$C_{(9)}$, and effects can be transmitted only inductively over this relatively long route. With the nitro-group ($-I$, $-M$) in the 3-position in fluoren-9-ol, the product is largely 6-nitrophenanthridine; when the methyl group ($+I$, and hyperconjugative electron-release) is in this position, the reaction yields mainly 3-methylphenanthridine; it is thus the ring having the greater electron-release (respectively the unsubstituted and substituted ring) which migrates.

A substituent in position 2 is *meta* to A–$C_{(9)}$, whence effects are relayed inductively to this bond; there is, however, a conjugated system (XIII) connecting position 3 to B–$C_{(9)}$, whereby tautomeric electron-displacements may be relayed to this point. The transmission of inductive effects may be less effective, owing to the length of the system. Berliner and Blommers (*J. Amer. Chem. Soc.*, 1951, **73**, 2479) have concluded from a study of the dissociation constants of 4′-substituted diphenyl-4-carboxylic acids that electron-displacements are transmitted through this diphenyl system about one-third as effectively as from position 1 to position 4 in a benzene ring.

(XIII)

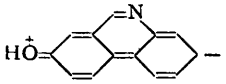
The principal product from the reaction with 2-nitrofluoren-9-ol is 7-nitrophenanthridine, the unsubstituted ring migrating. The dissociation constants of benzoic, *m*-nitrobenzoic, and *p*-nitrobenzoic acid, 6·27, 32·1, 37·6 × 10^{-5}, respectively, indicate a large part of the electron-attraction of the nitro-group to be inductive, and, from the above result, this component appears to be more effectively exerted at A–$C_{(9)}$ than it, together with the $-M$ effect, is transmitted to B–$C_{(9)}$.

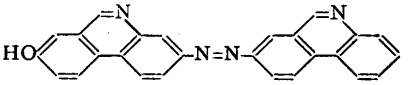
The amino-group in 2-aminofluoren-9-ol will, in the presence of concentrated sulphuric acid, exist almost entirely as the ammonium ion, which exerts a considerable $-I$ effect. The effect would be expected to constrict electrons to a greater extent at an adjacent *meta*-position than at the relatively remote B–$C_{(9)}$ bond; the formation of 7-aminophenanthridine as the sole isolated product is in accordance with the unsubstituted ring's having the greater electron-release.

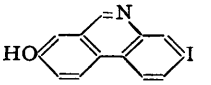
The dissociation constants of *m*-toluic and *p*-toluic acid are 5·35 and 4·24 × 10^{-5} respectively, whence, in 2-methylfluoren-9-ol, inductive electron-release is to be expected at A–$C_{(9)}$; further, the conjugated system (XIII) permits electron-release at B–$C_{(9)}$ by hyperconjugation ($+M$ and $+E$) with the methyl group; 2- and 7-methylphenanthridines were formed in ratio 53 : 47, and it is inferred that the two routes for electron-release are approximately equally effective. The dissociation constants for *m*- and *p*-methoxybenzoic acid, 8·17 and 3·38 × 10^{-5}, indicate the methoxy-group to exert inductive withdrawal of electrons at a *meta*-position, and mesomeric electron-release (which outweighs the $-I$ effect) at a *para*-position. In 2-methoxyfluoren-9-ol there would be expected an inductive withdrawal of electrons from A–$C_{(9)}$, and relay by (XIII) of electron-release ($+M$ and $+E$) to B–$C_{(9)}$. The experimental result, that unsubstituted and substituted rings migrate in ratio 68 : 32, accords with this assignment of electronic effects.

Other Reactions relating to Phenanthridines.—Phenanthridine-7-diazonium sulphate, when boiled with methanol, was reduced to phenanthridine. The heterocyclic nitrogen atom may be regarded as a deactivating attachment to the ring bearing the diazonium group, and reduction, rather than replacement by methoxyl, is general with diazonium salts which contain deactivating substituents (Hodgson and Foster, *J.*, 1942, 581; Houben-Weyl, " Die Methoden der Organische Chemie," G. Thieme, Leipzig, 1924, Vol. IV, p. 615). An aqueous solution of phenanthridine-7-diazonium sulphate, when heated, gave 7-hydroxyphenanthridine, but in small yield; the major product was a red compound which gave analyses approximating to those for the azo-compound formed by coupling of the diazonium ion with 7-hydroxyphenanthridine. Such coupling in acid solution is unusual and indicates that the phenol is susceptible to electrophilic attack (Saunders, " The Aromatic Diazo Compounds," E. Arnold and Co., London, 1949, pp. 195, 196, 230). In contrast, phenanthridine-6-diazonium sulphate gave 6-hydroxyphenanthridine in good

yield. 7-Hydroxyphenanthridine, on being heated with hydriodic acid containing iodine, gave a monoiodo-derivative, the ease of substitution perhaps being due to the contribution of a quinonoid form (XIV) to the total structure. Such a *para*-quinonoid form cannot be postulated for 6-hydroxyphenanthridine. Electrophilic attack appears most probable, therefore, at position 2, and structures (XV) and (XVI) are assigned to the above azo- and iodo-compounds.


(XIV)


(XV)


(XVI)

6-Nitrophenanthridine was oxidised with acid permanganate to 6-nitrophenanthridone, which on reaction with phosphorus oxychloride yielded 9-chloro-6-nitrophenanthridine.

2-Formamido-5-nitrodiphenyl, on being heated with stannic chloride and phosphorus oxychloride (a method of cyclisation due to Ockenden and Schofield, *J.*, 1953, 717), gave 3-nitrophenanthridine in 10% yield. Similar treatment of 2-formamido-4′-nitrodiphenyl gave no 7-nitrophenanthridine. Cyclisation probably involves an electrophilic attack by the group $-N{:}CH^+$ on the second ring of the diphenyl (Theobald and Schofield, *Chem. Reviews*, 1950, **46**, 178); it is concluded that the presence of a nitro-group in this ring so deactivates it that reaction does not take place, and that substantial deactivation is also caused by the presence of a nitro-group in the other diphenyl ring.

9-Chloro-2-nitrophenanthridine was condensed with toluene-*p*-sulphonhydrazide; the sulphonhydrazide, on being heated with alkali, yielded 2-nitrophenanthridine. This reaction was first used in the phenanthridine series by Badger, Seidler, and Thomson (*J.*, 1951, 3210) who converted 9-chlorophenanthridine into the parent base; the method is particularly useful when nitro-groups are present in the molecule and more usual reductive methods cannot, therefore, be employed.

Experimental

M. p.s are corrected.

The Hydrazoic Acid–Sulphuric Acid Reaction.—To a suspension of sodium azide in chloroform, cooled in ice, sulphuric acid (98%) was added dropwise, with stirring which was continued for 10 minutes at 0°. There were used, alternatively: (*A*) 1·5 mols. of sodium azide, with 15 ml. of chloroform and 4 ml. of sulphuric acid per g. of sodium azide; (*B*) 1·75 mols. of sodium azide, with 4 ml. of chloroform and 2·5 ml. of sulphuric acid per g. of sodium azide. The ice was replaced by a water-bath maintained at 25°, and the fluorene was added, as the powdered solid or as a solution or suspension in chloroform, to the vigorously stirred mixture during 1 hr. Stirring was continued for a further hour; the product was then poured on ice (40 g. per ml. of sulphuric acid) and the whole was shaken. From the aqueous acidic solution, and from the sulphate which frequently separated, the base was liberated by addition of 2N-sodium hydroxide. The nitro-, amino-, and 9-substituted phenanthridines were filtered off, washed, and dried; the other phenanthridines were extracted with ether, and the extracts were washed, dried (Na_2SO_4), and evaporated.

2-*Nitrofluoren*-9-*ol.* The reaction (*A*) with 2-nitrofluoren-9-ol (28·7 g.) yielded a base (26·0 g.), m. p. 145—170°, which was separated into two components by fractional crystallisation from benzene. There were obtained: 7-nitrophenanthridine (19·7 g.), m. p. 171—176°, which on further recrystallisation from benzene formed orange leaflets (11·8 g.), m. p. 180° (Found: C, 70·1; H, 3·6; N, 12·9. Calc. for $C_{13}H_8O_2N_2$: C, 69·65; H, 3·6; N, 12·5%); and the complex of 2- and 7-nitrophenanthridines (1·45 g.), m. p. 155—160°, which, after recrystallisation from ethanol, formed yellow needles (1·1 g.), m. p. 158—160° (Found: C, 69·6; H, 3·7; N, 12·2%).

When 2-nitrophenanthridine, m. p. 196—197° (0·6 g.), and 7-nitrophenanthridine, m. p. 180° (0·6 g.), were allowed to crystallise together from ethanol (100 ml.), the first crop (*a*, 0·3 g.) melted at 161—162°, and the second and third crops (*b*, *c*; 0·75 g.) at 156—158°. The m. p. of a mixture of *a* with *bc*, or of a mixture of either with the analysed complex, m. p. 158—160°, above, was 159—160°.

To a solution of 7-nitrophenanthridine (1·0 g.) in boiling 2N-sulphuric acid (60 ml.), potassium permanganate (2·0 g.) was added during 15 min. Extraction of the brown

precipitate with boiling pyridine (40 ml.) and dilution of the extract with water gave a solid (0·6 g.), m. p. 325—328°, which, on recrystallisation from pyridine or acetic acid, yielded 7-nitrophenanthridone, yellow needles, m. p. 329° alone or when mixed with an authentic specimen, m. p. 328°, kindly supplied by Dr. K. Schofield (Found: C, 65·0; H, 3·5. Calc. for $C_{13}H_8O_3N_2$: C, 65·0; H, 3·35%). 7-Nitrophenanthridone (0·3 g.) was heated under reflux for 4 hr. with phosphorus oxychloride (3 ml.); the precipitate formed when the product was poured on ice yielded 9-chloro-7-nitrophenanthridine (0·2 g., from benzene), needles, m. p. 207—208°. Nunn, Schofield, and Theobald (*loc. cit.*) record m. p. 204—205°.

7-Nitrophenanthridine (1·0 g.) was cautiously heated with potassium permanganate (8·5 g.) and water (80 ml.); the mixture was finally boiled under reflux for 3 hr., and filtered. The filtrate was concentrated to 10 ml. and acidified with hydrochloric acid: there separated a nitrogen-containing acid (0·4 g.), m. p. 255° (decomp.).

A suspension of 7-nitrophenanthridine (5·0 g.) and iron powder (10 g.) in 0·06N-acetic acid (250 ml.) was heated under reflux for 5 hr. The black solid was collected, dried, and extracted with hot benzene. The extract yielded 7-aminophenanthridine (3·6 g.), m. p. 201—203°, which on recrystallisation from aqueous methanol formed needles, m. p. 202—203° (Found: C, 80·2; H, 5·0; N, 14·5. Calc. for $C_{13}H_{10}N_2$: C, 80·35; H, 5·25; N, 14·45%). Ethyl chloroformate (1·5 ml.) was added dropwise to a solution of 7-aminophenanthridine (2·5 g.) and diethylaniline (3 ml.) in boiling ethanol (99%; 40 ml.). The solution was heated under reflux for ½ hr.; on cooling it yielded 7-ethoxycarbonylaminophenanthridine, which after recrystallisation from methanol formed buff needles (0·75 g.), m. p. 206—207° (Found: C, 72·5; H, 5·35; N, 10·8. Calc. for $C_{16}H_{14}O_2N_2$: C, 72·2; H, 5·3; N, 10·5%). The ethanolic mother-liquor deposited a *substance* as needles (1·4 g., from ethanol), m. p. 152—153° (Found: C, 71·0; H, 6·3; N, 9·25%). Caldwell and Walls (*loc. cit.*) record m. p. 203—204° for the amine and m. p. 205—206° for its ethoxycarbonyl derivative.

3-*Nitrofluoren*-9-*ol*. The acidic aqueous solution and the base sulphate from the reaction (*A*) with 3-nitrofluoren-9-ol (5·0 g.) yielded 1·6 g. of base, m. p. 185—189°; a further 2·35 g., m. p. 180—190°, was obtained from the chloroform solution. The combined base, on fractional crystallisation from benzene, gave 6-*nitrophenanthridine* (3·3 g.), m. p. 192—194°, golden needles having m. p. 194° after further recrystallisations (Found: C, 69·75; H, 3·65; N, 12·4%). A second substance (0·25 g.), m. p. 225—245°, was obtained which, after two recrystallisations from benzene, yielded 3-nitrophenanthridine, orange needles, m. p. 256—259° alone, and 262—264° when mixed with an authentic specimen (below) having m. p. 268°. In a second experiment the fluorenol (10·0 g.) gave base (9·5 g.), m. p. 184—188°, which yielded 6-nitrophenanthridine (7·5 g.), m. p. 191—193°, and crude 3-nitrophenanthridine (0·45 g.), m. p. 225—235°.

Reduction of 6-nitrophenanthridine (1·0 g.), by the method described for the 7-isomer, yielded 6-aminophenanthridine (0·75 g., from benzene), needles, m. p. 194—195° (Found: C, 80·45; H, 5·4; N, 14·35%). Caldwell and Walls (*ibid.*, p. 2160) record m. p. 192—194°.

2-*Aminofluoren*-9-*ol*. The resinous product from the reaction (*B*) with 2-aminofluoren-9-ol (9·25 g., added in 40 ml. of chloroform) was extracted with boiling benzene (2 × 300 ml.) from which, on cooling, 2-aminofluoren-9-ol (1·9 g.) separated. Progressive concentration of the filtrate yielded six crops (total 3·0 g.), m. p.s in the range 165—197°, which, combined and recrystallised from aqueous methanol, yielded 7-aminophenanthridine, needles, m. p. 202° alone and when mixed with the analysed specimen above.

2-*Methoxyfluoren*-9-*ol*. This compound [(i), (ii) 5·0 g., (iii) 10·0 g.; added in chloroform, 2 ml. to 1 g.] was allowed to react by method *B*; when the reaction mixture was poured on ice a non-basic product separated. It was amorphous, infusible, and insoluble in dilute acid and alkali, and in all common organic solvents, and contained nitrogen and sulphur. The yields of base [(i) 2·00, (ii) 1·43, (iii) 2·59 g.] were not constant; a similar variation in yield has been experienced in the conversion of fluoren-9-ol into phenanthridine (Part I, *loc. cit.*). The average of the yields is recorded in the Table. A preparation (iv), as (i) but with twice the quantities of chloroform, gave 1·30 g. of base, and a similar experiment (v), which was allowed to proceed at 0°, yielded 1·00 g. base. The base from each of experiments (i)—(v) had m. p. 55—75°.

A solution of oxalic acid (dihydrate; 3·75 g.) in ethanol (20 ml.) was added to the total base (6·2 g.) from (ii)—(v) dissolved in ethanol (10 ml.); there separated buff needles (7·2 g.), m. p. 160—167°. Fractional crystallisation did not lead to separation of the isomers: five crops, m. p.s in the range 160—169°, were obtained; 2- and 7-*methoxyphenanthridine hydrogen oxalate*, thrice recrystallised from ethanol, had m. p. 169° (Found: C, 64·35; H, 4·3; N,

4·65. $C_{16}H_{13}O_5N$ requires C, 64·25; H, 4·4; N, 4·7%). On being shaken with ether and 2N-sodium hydroxide, the hydrogen oxalate (6·25 g.) yielded the base (4·45 g.), which was fractionally crystallised from light petroleum (b. p. 100—110°). The first crop (2·5 g.), leaflets, m. p. 86—88°, after two recrystallisations gave *7-methoxyphenanthridine* (1·95 g.), m. p. 90° (Found: C, 80·6; H, 5·35; N, 6·6. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3; N, 6·7%). Three further crops (1·2 g.), m. p. 56—58°, were twice recrystallised, and yielded *2-methoxyphenanthridine* (0·24 g.), plates, m. p. 57—58° (Found: C, 80·8; H, 5·2; N, 6·6%). Fractional crystallisation of the base (2·0 g.) from (i) yielded 7-methoxyphenanthridine (0·7 g.), m. p. 89°, and 2-methoxyphenanthridine (0·35 g.), m. p. 57—59°.

A solution of 7-methoxyphenanthridine (0·5 g.) in hydrobromic acid (48%; 25 ml.) was heated under reflux for 3 hr. in a current of carbon dioxide. The solution was made alkaline with sodium hydroxide solution, then just acidified with acetic acid; a precipitate separated, which was washed with water and dried. On recrystallisation from ethanol it yielded 7-hydroxyphenanthridine (0·3 g.), m. p. 281—282° alone and when mixed with an authentic specimen (below). Similar demethylation of 2-methoxyphenanthridine (0·5 g.) gave 2-hydroxyphenanthridine (0·2 g., from aqueous ethanol), leaflets, m. p. 245° (Found: C, 79·6; H, 4·9; N, 7·1. $C_{13}H_9ON$ requires C, 79·95; H, 4·65; N, 7·2%).

3-Methoxyfluoren-9-ol. The reaction (*B*) with 3-methoxyfluoren-9-ol [(i), (ii) 4·25 g., added in 15 ml. of chloroform] gave considerable non-basic amorphous material which contained nitrogen and sulphur. The basic product was extracted with boiling light petroleum (b. p. 60—80°; 100 ml.), which on evaporation gave a semi-solid base [(i) 0·20, (ii) 0·23 g.]. Short-path distillation of the combined base at 130°/0·1 mm. yielded (3- and 6-)methoxyphenanthridines, needles, m. p. 70—78° (Found: C, 78·8; H, 5·15; N, 6·35%).

2-Methylfluoren-9-ol. The basic product from the reaction (*A*) with 2-methylfluoren-9-ol [(i) 1·95, (ii) 3·9 g.] was extracted with boiling light petroleum (b. p. 40—60°; 100 ml.), which yielded methylphenanthridines [(i) 1·6 g., m. p. 42—53°; (ii) 3·05 g., m. p. 45—55°]. The combined base was fractionally crystallised from this solvent: the first four crops (0·95 g.) melted within the range 72—80°, and after three recrystallisations yielded 7-methylphenanthridine (0·38 g.), needles, m. p. 87·5—88° (Found: C, 87·2; H, 5·75; N, 7·15. Calc. for $C_{14}H_{11}N$: C, 87·0; H, 5·75; N, 7·25%). Kenner, Ritchie, and Statham (*J.*, 1937, 1169) record m. p. 88°. The picrate (6·95 g.) prepared from the four most soluble crops (3·35 g.) was repeatedly recrystallised from dioxan; it (4·15 g.) was reconverted into the base (1·75 g.), m. p. 70—75°, which after four recrystallisations from light petroleum yielded 2-methylphenanthridine (0·70 g.), needles, m. p. 80° (Found: C, 86·9; H, 5·95; N, 6·9%). Ritchie (*loc. cit.*) records m. p. 81°.

A m. p.–composition curve was constructed as follows: mixtures of 2- and 7-methylphenanthridine were intimately mixed by grinding; the mixtures were heated in tubes of 2-mm. diameter at 1° per minute, the temperature at which the last solid disappeared being recorded. The curve has a simple form with a eutectic at the equimolar point.

7-Methylphenanthridine (%)	20	40	50	60	80
M. p. { (i)	73°	64°	59°	64°	80°
M. p. { (ii)	73°	65°	58°	63°	81°

Three portions of base were recovered: (*a*) material from the mother-liquors of 7-methylphenanthridine (0·55 g.), m. p. 72°; (*b*) material from the mother-liquors of 2-methylphenanthridine (0·50 g.), m. p. 73°; (*c*) material from intermediate mother-liquors (1·40 g.), m. p. 67°. The percentages of 2-methylphenanthridine in (*a*), (*b*), (*c*) were found, from the m. p.–composition curve, to be 35, 80, 42% respectively. That (*c*) is on the branch of the curve leading to the 7-isomer is shown by the fact that its m. p. was lowered (to 61°) by the addition of 2-methylphenanthridine, and raised (to 75°) by the addition of 7-methylphenanthridine. From these analyses, together with the weights of isomers isolated, the yields of 2- and 7-methylphenanthridine are found to be 1·88 and 1·65 g. respectively.

3-Methylfluoren-9-ol. Reaction with 3-methylfluoren-9-ol [(i) 1·95 g., (ii) 5·85 g.], as described for the 2-isomer, yielded methylphenanthridines [(i) 1·7 g., m. p. 65—76°; (ii) 2·75 g., m. p. 62—76°]. The combined base was fractionally crystallised from light petroleum (b. p. 40—60°); the first eight crops (3·3 g.), melting within the range 79—86°, after four recrystallisations gave 3-methylphenanthridine (0·45 g.), leaflets, m. p. 89—89·5° (Found: C, 86·9; H, 5·7; N, 7·25%) [picrate, yellow needles (from dioxan), m. p. 271—272° (Found: N, 13·15. Calc. for $C_{20}H_{14}O_7N_4$: N, 13·25%)]. Kenner *et al.* (*loc. cit.*) record m. p. 89° for the base and m. p. 266° for the picrate. From the succeeding four crops, melting in the range 45—75°,

there was isolated only 3-methylphenanthridine (0·25 g.), m. p. 84—86° and m. p. 86—89° when mixed with the pure compound.

9-*Phenylfluoren*-9-*ol*. This compound [m. p. 85°; (i), (ii) 2·6 g., added in 10 ml. of chloroform], on reaction by method *A* (the chloroform layer was twice extracted with 10N-sulphuric acid), yielded 9-phenylphenanthridine [(i) 2·5, (ii) 2·35 g.; m. p.s 104—106°] which on recrystallisation from ethanol or from light petroleum formed leaflets, m. p. 106°, unaltered by repeated recrystallisation from ethanol (Found: C, 89·8; H, 5·2; N, 5·6. Calc. for $C_{19}H_{13}N$: C, 89·35; H, 5·15; N, 5·5%) [picrate, yellow needles (from acetic acid), m. p. 251° (decomp.) (Found: N, 11·15. Calc. for $C_{25}H_{16}O_7N_4$: N, 11·55%)]. Pictet and Hubert (*Ber.*, **1896**, **29**, 1184) record m. p. 109° for the base, and m. p. 242° (decomp.) for the picrate.

9-*Methylfluoren*-9-*ol*. The base from the reaction (*A*) with 9-methylfluoren-9-ol [(i), (ii) 4·9 g., (iii) 13·7 g.] was extracted with boiling light petroleum (b. p. 60—80°); the extract yielded 9-methylphenanthridine [(i) 1·85, (ii) 2·15, (iii) 7·75 g., m. p.s 80—84°], which on recrystallisation formed needles, m. p. 85° (Found: C, 86·9; H, 5·9; N, 7·2%) [picrate, yellow needles (from dioxan), m. p. 249° (decomp.) (Found: N, 12·9%)]. Pictet and Hubert (*loc. cit.*) record m. p. 85° for the base, and m. p. 233° (decomp.) for the picrate.

On evaporation, the chloroform solution from (iii) yielded a *substance* (3·5 g.), m. p. 148—153°, which after two recrystallisations from ethanol formed needles, m. p. 157° (Found: C, 90·3; H, 5·8; N, 4·0. $C_{28}H_{21}N$ requires C, 90·5; H, 5·7; N, 3·8%) [*picrate*, yellow needles (from ethanol), m. p. 266—268° (Found: N, 9·55. $C_{34}H_{24}O_7N_4$ requires N, 9·35%)].

9-*Benzylfluoren*-9-*ol*. The reaction (*A*) with 9-benzylfluoren-9-ol (2·0 g., added in 20 ml. of chloroform) yielded 9-benzylphenanthridine (0·8 g.), m. p. 105—107°, which, after recrystallisation from ethanol and short-path distillation at 130°/0·4 mm., formed needles, m. p. 112° (Found: C, 88 7; H, 5·7; N, 5·15. Calc. for $C_{20}H_{15}N$: C, 89·2; H, 5·6; N, 5·2%) [picrate, yellow needles (from butanol), m. p. 200—202° (decomp.) (Found: N, 11·1. Calc. for $C_{26}H_{18}O_7N_4$: N, 11·25%)]. Ritchie (*J. Proc. Roy. Soc. N.S.W.*, 1945, **78**, 155) records m. p. 112° for the base, and m. p. 190° (decomp.) for the picrate.

9-*Benzylidenefluorene*. The reaction (*A*) with 9-benzylidenefluorene [(i), (ii) 3·8 g.; m. p. 75°; Thiele, *Ber.*, 1900, **33**, 852] yielded 9-benzylphenanthridine [(i) 2·1, (ii) 1·85 g.; m. p.s 100—105°], which after purification as above had m. p. 112° alone and when mixed with the analysed specimen. Similar treatment of 9-benzylidene-2-nitrofluorene (m. p. 147—149°; Loevenich and Loeser, *J. pr. Chem.*, 1927, **116**, 325) gave a negligible quantity of base, and 83% of the olefin was recovered.

9-*Azido*-2-*methoxyfluorene*.—9-Chloro-2-methoxyfluorene (2·0 g.), sodium azide (1·0 g.), and methanol (15 ml.) were heated under reflux for 3 hr.; the solution was then poured into water. The product (1·9 g.), m. p. 36—38°, yielded, after two crystallisations from light petroleum (b. p. 40—60°), 9-*azido*-2-*methoxyfluorene*, needles (Found: C, 71·1; H, 4·65; N, 17·45. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·65; N, 17·7%). The analysed specimen melted at 43·5—44·5°; it then resolidified and remelted at 56—58°. When this melt was chilled, the crystalline solid obtained usually had m. p. 65—66°, but one such specimen had the original m. p. 44°.

A mixture of sulphuric acid (98%, 2 ml.) and chloroform (10 ml.) was vigorously stirred at 25° during the dropwise addition (30 min.) of a solution of 9-azido-2-methoxyfluorene [(i) 1·0, (ii) 0·90 g.] in chloroform (5 ml.); thereafter the product was treated as in the hydrazoic–sulphuric acid reaction with 2-methoxyfluoren-9-ol. A non-basic solid was formed which contained nitrogen and sulphur, and resembled that from the latter reaction; it was extracted with boiling N-hydrochloric acid. The reaction yielded methoxyphenanthridines [(i) 0·50 g., m. p. 58—75°; (ii) 0·40 g., m. p. 60—74°]; fractional crystallisation of the base (i) from light petroleum (b. p. 100—110°) gave 7-methoxyphenanthridine (0·23 g.) having m. p. 85—88°, and m. p. 87—89° when mixed with the pure compound of m. p. 90°, and 2-methoxyphenanthridine (0·12 g.), m. p. 55—57° and m. p. 56—58° when mixed with the pure compound of m. p. 58°.

9-Chloro-2-nitrofluorene (2·0 g.), sodium azide (1·0 g.), and methanol (40 ml.) were heated under reflux for 4 hr., and allowed to cool. The solid product was collected, washed with water, dried, and recrystallised from benzene; it yielded 9-*imino*-2-*nitrofluorene* (1·4 g.), orange needles, m. p. 209° (Found: C, 69·75; H, 3·55; N, 12·3. $C_{13}H_8O_2N_2$ requires C, 69·65; H, 3·6; N, 12·5%). This compound (0·5 g.), when boiled for ¾ hr. with 12N-sulphuric acid (15 ml.), yielded 2-nitrofluorenone (0·5 g.), yellow flocks, m. p. 222° alone and when mixed with an authentic specimen. Attempts to effect reaction between 9-chloro-2-nitrofluorene and sodium azide under milder conditions than those described led to the formation of lower-melting, chlorine-containing mixtures.

Reactions of Phenanthridine-7-diazonium Sulphate.—Amyl nitrite (2·0 g.) was added to a

suspension of 7-aminophenanthridine sulphate, formed by the dropwise addition of sulphuric acid (98%; 2 ml.) to a solution of the base (2·0 g.) in ethanol (99%; 40 ml.). The suspension was kept at 25°, with shaking, for 2½ hr.; the solid was collected, washed with ethanol and with ether, and suspended in methanol (distilled from calcium oxide; 100 ml.) which was then boiled for 1 hr. Nitrogen was evolved. The solution was evaporated to 10 ml. and added to N-hydrochloric acid (150 ml.); this solution, separated from some tar, was made alkaline with sodium hydroxide solution and thrice extracted with ether. The extract was dried (Na_2SO_4) and evaporated, yielding a base which was repeatedly extracted with boiling light petroleum (b. p. 40—60°). Evaporation of the extracts gave a product which, after distillation at 120°/2 mm., yielded phenanthridine (0·45 g.), needles, m. p. 103—104° (picrate, yellow needles, m. p. 244—245°). M. p. 106—107° and m. p. 245° have been recorded (Part I) for phenanthridine and its picrate.

A hot solution of 7-aminophenanthridine (1·8 g.) in 1·5N-sulphuric acid (20 ml.) was cooled, with stirring; the suspension of the sulphate was diazotised at 0° with a solution of sodium nitrite (0·7 g.) in water (3 ml.). After ¼ hr., the solution was filtered and heated on a steam-bath, nitrogen being evolved, for ½ hr.; it was cooled, made alkaline with sodium hydroxide solution, and filtered from a red azo-compound (1·05 g.). Neutralisation of the filtrate with N-sulphuric acid gave a precipitate which was dissolved in hot 3N-hydrochloric acid; from this solution, at 0°, there separated orange needles (0·65 g.); the base, m. p. 279—281°, obtained by decomposition of this hydrochloride with one equivalent of sodium hydroxide solution, on crystallisation from ethanol yielded 7-*hydroxyphenanthridine* (0·3 g.), a microcrystalline powder, m. p. 282—283° (Found: C, 79·55; H, 4·9; N, 7·3. $C_{13}H_9ON$ requires C, 79·95; H, 4·65; N, 7·2%). The *azo*-compound was thrice recrystallised from hot acetic acid, from which it separated as bright red needles, m. p. 295° (decomp.) (Found: C, 76·55; H, 4·05; N, 13·0. $C_{26}H_{16}ON_4$ requires C, 78·0; H, 4·05; N, 14·0%).

7-*Hydroxy*-2-*iodophenanthridine*.—7-Methoxyphenanthridine (0·5 g.) was heated under reflux for 3 hr. with hydriodic acid (25 ml.; freshly distilled, b. p. 126°, containing some iodine); the violet, crystalline hydriodide which separated was dissolved in dilute sodium hydroxide, and the solution was then just acidified with acetic acid. The precipitate (0·64 g.), m. p. 230—235°, after two recrystallisations from dioxan yielded 7-*hydroxy*-2-*iodophenanthridine* (0·25 g.), yellow tablets, m. p. 235° (Found: I, 39·2. $C_{13}H_8ONI$ requires I, 39·5%). It was soluble both in 0·5N-sodium hydroxide and in warm dilute hydrochloric acid which, on cooling, deposited yellow needles of the hydrochloride. 7-Hydroxy-2-iodophenanthridine was also obtained by the interaction, as above, of 7-hydroxyphenanthridine with hydriodic acid.

6-*Hydroxyphenanthridine*.—A solution of 6-aminophenanthridine (1·7 g.) in 4N-sulphuric acid (50 ml.) was diazotised as described for the 7-isomer; urea was then added and the solution was boiled until nitrogen ceased to be evolved (10 min.). The solution was cooled, made alkaline with sodium hydroxide solution, filtered from a trace of red solid, and made just acid with acetic acid. The precipitate was collected, washed with water, and dried; it (1·55 g.), m. p. 264—267°, yielded, on recrystallisation from ethanol, 6-*hydroxyphenanthridine* (0·9 g.), leaflets, m. p. 271—272° (Found: C, 80·2; H, 4·7; N, 7·2%).

6-*Nitrophenanthridone*.—6-Nitrophenanthridine (1·0 g.), on oxidation with acid permanganate as described for the 7-isomer, yielded 6-*nitrophenanthridone* (0·6 g.), yellow needles, m. p. 368° (uncorrected) (Found: C, 65·2; H, 3·3; N, 11·6. $C_{13}H_8O_3N_2$ requires C, 65·0; H, 3·35; N, 11·65%). It (1·0 g.) yielded, by the method used for the 7-isomer, 9-*chloro*-6-*nitrophenanthridine* (0·7 g., from benzene), yellow needles, m. p. 218° (Found: C, 60·95; H, 2·85; N, 10·75; Cl, 13·35. $C_{13}H_7O_2N_2Cl$ requires C, 60·35; H, 2·75; N, 10·85; Cl, 13·7%).

3-*Nitrophenanthridine*.—2-Amino-5-nitrodiphenyl (5·0 g.) was heated under reflux for 1 hr. with formic acid (90%; 50 ml.); the solution was poured into water and gave a precipitate which, on recrystallisation from ethanol, yielded 2-*formamido*-5-*nitrodiphenyl* (3·7 g.), buff needles, m. p. 145—146° (Found: C, 64·25; H, 4·15; N, 11·6. $C_{13}H_{10}O_3N_2$ requires C, 64·45; H, 4·15; N, 11·55%). The deep violet solution formed by the addition of stannic chloride (0·9 g.) to 2-formamido-5-nitrodiphenyl (2·0 g.), phosphorus oxychloride (10 ml.) and nitrobenzene (20 ml.) was heated under reflux for 4 hr., cooled, and poured on ice. The mixture was shaken mechanically for 2 hr., and the nitrobenzene was distilled off in steam; there remained a solution and a non-basic solid which was filtered off and extracted with hot 5N-hydrochloric acid. The combined acidic solutions were made alkaline with sodium hydroxide solution, and there separated a base which, on crystallisation from benzene, yielded 3-nitrophenanthridine (0·2 g.), yellow needles, m. p. 268° (Found: C, 69·5; H, 3·6; N, 12·6. Calc. for $C_{13}H_8O_2N_2$: C, 69·65; H, 3·6; N, 12·5%).

2-Amino-4′-nitrodiphenyl (9·3 g.; m. p. 157—158°; Waters and Scarborough, *J.*, 1927, 87) was converted, by the procedure described above, into 2-*formamido*-4′-*nitrodiphenyl* (6·9 g.), needles, m. p. 176° (Found : C, 64·1; H, 4·2; N, 11·55%). From an attempted cyclisation, by the method given above, there was isolated only 2-amino-4′-nitrodiphenyl.

2-*Nitrophenanthridine*.—2-Nitrophenanthridone (10·0 g.; m. p. 358—359°), on reaction with phosphorus oxychloride as described for the 7-isomer, yielded 9-chloro-2-nitrophenanthridine (9·6 g.), which on crystallisation from benzene formed needles, m. p. 209° (Found : C, 60·8; H, 2·4; N, 10·8; Cl, 14·0%). Nunn, Schofield, and Theobald (*loc. cit.*) record m. p. 204—205°, but m. p. 214—215° after chromatographic purification of the specimen. This compound (2·6 g.), toluene-*p*-sulphonhydrazide (2·0 g.), and chloroform (135 ml.) were heated under reflux for 21 hr.; the precipitate (3·4 g.) was then collected and dissolved in 0·5N-sodium hydroxide (400 ml.). The red solution was heated at 80° with stirring for 1½ hr. : the colour was discharged with evolution of nitrogen and the separation of a brown solid. The latter was filtered off and extracted with boiling 5N-hydrochloric acid, and the extract was poured into excess of 5N-sodium hydroxide. The precipitate yielded 2-nitrophenanthridine (0·5 g., from benzene), yellow needles, m. p. 196—197° (Found : C, 69·8; H, 3·7; N, 12·4%). For 2- and 3-nitrophenanthridine, isolated from the nitration products of phenanthridine, Caldwell and Walls (*J.*, 1952, 2156) record m. p. 196—197° and m. p. 266—267°.

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