238. *Syntheses of Some Derivatives of 4-Aza- and of 2 : 4-Diaza-fluoranthene.*

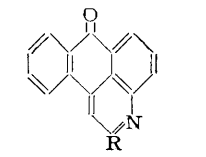
By J. W. Cook and J. S. Moffatt.

Derivatives of 4-azafluoranthene (III) have been prepared by cyclisation of appropriate acyl derivatives of 1-aminofluorenone. Derivatives of 2 : 4-diazafluoranthene (IV) have been obtained by reaction of 1-aminofluorenone with aryl cyanides or formamide, or by cyclisation of 1-carbamidofluorenone (IX; $R_1 = NH_2$, $R_2 = H$). Nitration of 1-carbethoxyaminofluorenone (IX; $R_1 = OEt$, $R_2 = H$) has given a mixture of products from which the 4- and 2-nitro-derivatives have been separated. 4-Nitro-1-aminofluorenone has been utilised as an intermediate for the preparation of certain 4-aza- and 2 : 4-diaza-fluoranthenes containing an amino-group in the 7-position of the azafluoranthene nucleus. Certain basic derivatives and quaternary ammonium salts of these two new heterocyclic systems have been examined for biological action, in particular in experimental trypanosomiasis and also in *E. histolytica* and *P. gallinaceum* infections. None showed any very marked activity.

In a series of patents (summarised in Houben and Fischer, "Das Anthracen und die Anthrachinone," Thieme, Leipzig, 1929, pp. 643, 650) granted to I.G. Farbenindustrie, there are outlined methods of preparation of derivatives of so-called "anthrapyridine" (I; R = H) and "anthrapyrimidine" (II; R = H). According to these patents (*e.g.*, D.R.-PP. 192,201, 203,752, 209,033, 250,885) and other publications (*e.g.*, Dupont, *Bull Soc. chim. Belg.*, 1943, **52**, 7), 1-acetamidoanthraquinone and certain of its derivatives undergo cyclisation under the influence of, *inter alia*, alkali hydroxide solutions, to give anthrapyridone (I; R = OH) and its derivatives. Derivatives of anthrapyrimidine (II; R = H, Me, Ph, etc.) are reported to be formed by reaction of 1-aminoanthraquinone and its derivatives with, for example, carboxylic

acid amides (B.P. 401,731), *N*-alkylbenzimino halides (B.P. 386,861), or aryl cyanides at high temperatures, and in presence of condensing agents (B.P. 415,069).

The object of the present work was to study the possibility of preparing basic derivatives of the hitherto undescribed nitrogenous ring systems, 4-aza- (III; $R_1 = R_2 = R_3 = H$) and 2 : 4-diaza-fluoranthene (IV; $R_1 = R_2 = R_3 = H$) by application of analogous series of reactions to 1-aminofluorenone and its derivatives. The aminofluorenone was conveniently prepared by application of the Curtius reaction (cf. Goldschmiedt, *Monatsh.*, 1902, **23**, 886; Huntress, Pfister, and Pfister, *J. Amer. Chem. Soc.*, 1942, **64**, 2845) to fluorenone-1-carboxylic acid (Fieser and Seligman, *J. Amer. Chem. Soc.*, 1935, **57**, 2174). Application of the conditions of the Schmidt reaction to this acid did not yield the desired amino-ketone, but gave a mixture from which two products, one acidic and the other neutral, were isolated. From their analyses, these are considered to be 9-*phenanthridone-1-carboxylic acid* (V), and 9-*hydroxyphenanthridine-8-carboxylic acid lactone* (VI) respectively, although the alternative structures, 9-phenanthridone-8-carboxylic acid (VII), and 9-phenanthridone-1-carboxylic acid lactam (VIII), cannot be excluded. In contrast to previously reported facile cyclisations of 1-acetamidoanthraquinone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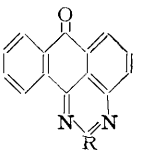
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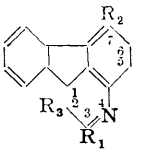
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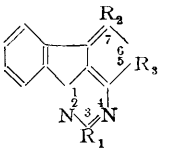
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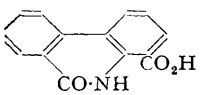
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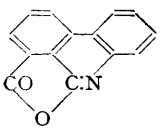
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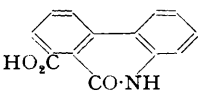
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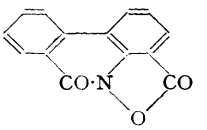
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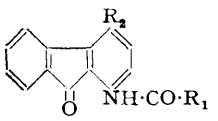
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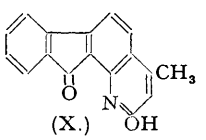
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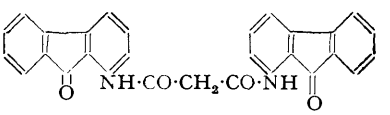
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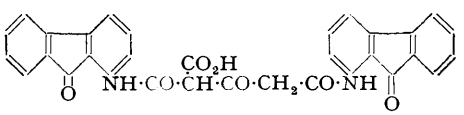
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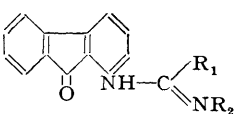

(XIII.)

and its derivatives by boiling aqueous or alcoholic alkalis (*e.g.*, D.R.-P. 192,201; Dupont, *loc. cit.*), 1-acetamidofluorenone (IX; $R_1 = Me$, $R_2 = H$) on being heated with, *inter alia*, methyl-alcoholic sodium methoxide solution or a suspension of sodium methoxide in nitrobenzene, under various conditions, was either unaffected or suffered hydrolysis to give the free amine. It was considered that cyclisation experiments with acyl derivatives in which the methylene group of the side chain is activated by the juxtaposition of a substituent possessing powerful electron-attractive properties might offer better prospects of success. Accordingly, 1-*acetoacetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CO{\cdot}CH_3$, $R_2 = H$) was prepared from 1-aminofluorenone and ethyl acetoacetate, and this with sodium methoxide in nitrobenzene at 140° gave a cyclisation *product* which, from its method of formation, is probably 3-hydroxy-2-acetyl-4-azafluoranthene (III; $R_1 = OH$, $R_2 = H$, $R_3 = CO{\cdot}CH_3$). However, it is conceivable that cyclisation may have taken place in the alternative direction to give the isomeric lepidone derivative (X). Attempts to prepare (X) by heating (IX; $R_1 = CH_2{\cdot}CO{\cdot}CH_3$, $R_2 = H$) with concentrated sulphuric acid at 65° (cf. Misani and Bogert, *J. Org. Chem.*, 1945, **10**, 347) merely resulted in hydrolysis to 1-aminofluorenone, and further investigation was not carried out. In order to obtain derivatives of (III; $R_1 = OH$, $R_2 = H$) where R_3 represents groups which might subsequently be readily eliminated, the preparation of (IX; $R_1 = CH_2{\cdot}CN$, $R_2 = H$)

and (IX; $R_1 = CH_2{\cdot}CO_2Et$, $R_2 = H$) was then investigated. 1-Aminofluorenone and ethyl cyanoacetate at 190° gave a low yield of 1-*cyanoacetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CN$, $R_2 = H$), together with much NN′-*di*(*fluorenon*-1-*yl*)*malonamide* (XI). Somewhat improved yields of the former product were obtained by interaction of *fluorenon*-1-*yl* iso*cyanate* and cyanoacetic acid. However, satisfactory yields of 1-*carbethoxyacetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CO_2Et$, $R_2 = H$) were obtained either by condensation of 1-aminofluorenone with ethyl malonate at 190°, which gave only small quantities of the accompanying malonamide derivative (XI), or by interaction of fluorenon-1-yl *iso*cyanate and ethyl hydrogen malonate. Attempted cyclisation of (IX; $R_1 = CH_2{\cdot}CO_2Et$, $R_2 = H$) by approximately one equivalent of dilute sodium hydroxide solution gave mainly 1-aminofluorenone, together with a low yield of a *carboxylic acid* whose behaviour on heating and analyses suggested the structure of the β-ketonic acid (XII). Cyclisation was eventually effected by heating the carbethoxyacetamido-derivative with sodium methoxide in nitrobenzene at 140°, which gave, after hydrolysis, 3-*hydroxy*-4-*azafluoranthene*-2-*carboxylic acid* (III; $R_1 = OH$, $R_3 = CO_2H$, $R_2 = H$). The acid was decarboxylated to give 3-*hydroxy*-4-*azafluoranthene* (III; $R_1 = OH$, $R_2 = R_3 = H$), which with phosphoryl chloride gave 3-*chloro*-4-*azafluoranthene* (III; $R_1 = Cl$, $R_2 = R_3 = H$). The chloro-compound was condensed with ammonia and a variety of amines to give 4-*azafluoranthenes* (III; $R_2 = R_3 = H$) in which $R_1 = NH_2$, NEt_2, $NH{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$, $NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$, and $NH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$.

For the preparation of derivatives of 4-azafluoranthene containing an amino- or substituted amino-substituent in the fluorene part of the nucleus, the required intermediate mononitro-1-aminofluorenones were obtained by nitration of 1-*carbethoxyaminofluorenone* (IX; $R_1 = OEt$, $R_2 = H$), which was conveniently prepared by heating *fluorenone*-1-*carboxylic acid azide* with ethanol. The resulting mixed products were separated into two isomeric nitro-1-carbethoxy-aminofluorenones, one having m. p. 210—211°, and the other m. p. 171—172°. The higher-melting *isomer*, which was formed in greater yield (47%), was the 4-nitro-derivative, since diazotisation, followed by hypophosphorous acid reduction of its hydrolysis product, 4-*nitro*-1-*aminofluorenone*, gave a mononitrofluorenone whose m. p. (174—175°) corresponds with that of the known 4-nitrofluorenone (Schmidt and Bauer, *Ber.*, 1905, **38**, 3737), and is clearly distinct from those of the known 2-nitro- and 3-nitro-fluorenones (see Ray and Barrick, *J. Amer. Chem. Soc.*, 1948, **70**, 1492). The *isomer*, m. p. 171—172°, which was formed in smaller amount (27%), was shown to be the 2-nitro-derivative by the following evidence. Hydrolysis, followed by hypophosphorous acid reduction of the diazonium sulphate from the resulting 2-*nitro*-1-*amino-fluorenone*, yielded 2-nitrofluorenone (Diels, *Ber.*, 1901, **34**, 1758). Moreover, catalytic hydrogenation of the nitroaminofluorenone gave the corresponding diamino-ketone which, since with phenanthraquinone it gave a *quinoxaline* derivative, must be 1 : 2-*diaminofluorenone*. It should perhaps be pointed out that the orientation of the 4-nitro-1-carbethoxyaminofluorenone depends on the reasonable assumption that on nitration of the carbethoxyamino-compound, the nitro-group enters the ring which contains the substituted amino-group. The proof of structure of the 2-nitro-derivative is, of course, independent of such an assumption.

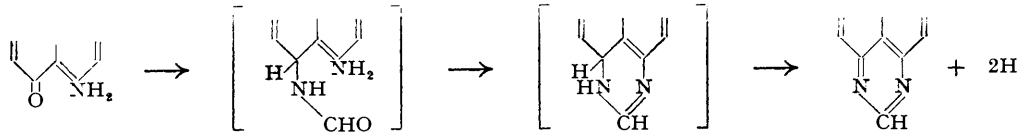
Condensation of 4-nitro-1-aminofluorenone with ethyl malonate yielded 4-*nitro*-1-*carbethoxy-acetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CO_2Et$, $R_2 = NO_2$) which cyclised on being heated with sodium methoxide in nitrobenzene, to give 7-*nitro*-3-*hydroxy*-2-*carbethoxy*-4-*azafluoranthene* (III; $R_1 = OH$, $R_2 = NO_2$, $R_3 = CO_2Et$). This, on hydrolysis, gave the free *acid* which, on decarboxylation, yielded 7-*nitro*-3-*hydroxy*-4-*azafluoranthene* (III; $R_1 = OH$, $R_2 = NO_2$, $R_3 = H$). Condensation of the corresponding *chloro*-compound with alcoholic ammonia gave 7-*nitro*-3-*amino*-4-*azafluoranthene* (III; $R_1 = NH_2$, $R_2 = NO_2$, $R_3 = H$). Condensation of the chloro-compound with 3-diethylaminopropylamine gave an oil which was reduced to 7-amino-3-(3-diethylaminopropylamino)-4-azafluoranthene (III; $R_1 = NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$, $R_2 = NH_2$, $R_3 = H$), characterised as its crystalline *dipicrate*. Similar transformations of 2-nitro-1-aminofluorenone could not be carried out because this intermediate failed to condense with ethyl malonate.

Derivatives of 2 : 4-*Diazafluoranthene*.—Condensation of 1-aminofluorenone with phenyl, *p*-chlorophenyl, and *p*-nitrophenyl cyanide in presence of hydrogen chloride at *ca.* 190° gave respectively, 3-*phenyl*- (IV; $R_1 = Ph$, $R_2 = R_3 = H$), 3-p-*chlorophenyl*- (IV; $R_1 = p$-C_6H_4Cl, $R_2 = R_3 = H$), and 3-p-*nitrophenyl*-2 : 4-*diazafluoranthene* (IV; $R_1 = p$-$NO_2{\cdot}C_6H_4$, $R_2 = R_3 = H$). Reduction of the nitro-compound with iron powder afforded the 3-p-*amino-phenyl* derivative. Presumably, *N*-substituted amidines (*e.g.*, XIII; $R_1 = Ph$, $R_2 = H$) are intermediates in the formation of these products, and indeed it was found that N-(*fluorenon*-

1-*yl*)-N′-*methylbenzamidine* (XIII; R_1 = Ph, R_2 = Me), which was prepared by condensation of 1-aminofluorenone with *N*-methylbenzimino chloride, undergoes cyclisation under the influence of sodium methoxide in nitrobenzene at 140° to give (IV; R_1 = Ph, R_2 = R_3 = H). Reaction of 4-nitro-1-aminofluorenone with phenyl cyanide failed to give any diazafluoranthene, the only products isolated being 4-*nitro*-1-*benzamidofluorenone* (IX; R_1 = Ph, R_2 = NO_2) and a *compound* ($C_{20}H_{12}O_2N_2$) whose constitution was not determined. Only a trace of a *product* having the composition of 5-nitro-3-phenyl-2 : 4-diazafluoranthene (IV; R_1 = Ph, R_2 = H, R_3 = NO_2) could be obtained from 2-nitro-1-aminofluorenone and phenyl cyanide. The nitro-amino-ketone failed to condense with *N*-methylbenzimino chloride.

Reaction between fluorenon-1-yl *iso*cyanate and anhydrous ammonia yielded 1-*carbamidofluorenone* (IX; R_1 = NH_2, R_2 = H) which cyclised on being treated with sodium methoxide in nitrobenzene at 190°, to give 3-*hydroxy*-2 : 4-*diazafluoranthene* (IV; R_1 = OH, R_2 = R_3 = H). The latter product with phosphoryl chloride afforded 3-*chloro*-2 : 4-*diazafluoranthene* which was condensed with ammonia and 3-diethylaminopropylamine to give 3-*amino*- (IV; R_1 = NH_2, R_2 = R_3 = H), and 3-(3-*diethylaminopropylamino*)-2 : 4-*diazafluoranthene* (IV; R_1 = $NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2$, R_2 = R_3 = H).

Interaction of 1-aminofluorenone and boiling formamide gave a low yield of 2 : 4-*diazafluoranthene* (IV; R_1 = R_2 = R_3 = H). 4-Nitro-1-aminofluorenone, on similar treatment, yielded 7-*amino*-2 : 4-*diazafluoranthene* (IV; R_2 = NH_2, R_1 = R_3 = H), together with its *formyl* derivative. This reduction of an aromatic nitro-group to an amino-group during treatment with boiling formamide was unexpected since such groups are not reduced under the conditions of the Leuckart reaction (Ingersoll *et al.*, *J. Amer. Chem. Soc.*, 1936, **58**, 1808; Rogers, *J.*, 1943, 590). Reduction, in the present case, probably occurs as a result of intramolecular disproportionation which may be represented in terms of the following intermediate stages of the reaction (XIV ⟶ XV) :



(XIV.) (XV.)

The susceptibility of the 2 : 4-diazafluoranthene ring system to hydrolytic fission by mineral acids was demonstrated by the behaviour of (IV; R_2 = NH_2, R_1 = R_3 = H) which was converted by hot dilute hydrochloric acid into 1 : 4-*diaminofluorenone*. A similar result was observed on boiling (IV; R_1 = *p*-$NH_2{\cdot}C_6H_4$, R_2 = R_3 = H) with alcoholic hydrogen chloride solution, which yielded a *product* having the composition of a *p*-aminobenzamidofluorenone hydrochloride.

Quaternary Ammonium Salts.—3-Amino-4-azafluoranthene (III; R_1 = NH_2, R_2 = R_3 = H), on treatment with methyl iodide in 2-methoxyethanol at 100°, formed a *monomethiodide* which was presumed to be methylated on the ring-nitrogen by analogy with the known behaviour of 4-aminoquinoline (Claus and Frobenius, *J. prakt. Chem.*, 1897, **56**, 181) and of 5-aminoacridine (Albert and Ritchie, *J.*, 1943, 458). Similarly, 3-amino-2 : 4-diazafluoranthene (IV; R_1 = NH_2, R_2 = R_3 = H) gave a *monomethiodide* which is presumably methylated on one of the ring-nitrogens. 7-Nitro-3-amino-4-azafluoranthene (III; R_1 = NH_2, R_2 = NO_2, R_3 = H) afforded a *monomethiodide* which, on reduction with iron powder, yielded 3 : 7-*diamino*-4-*azafluoranthene monomethiodide*. Attempts to methylate 3-phenyl- (IV; R_1 = Ph, R_2 = R_3 = H) and 3-*p*-chlorophenyl-2 : 4-diazafluoranthene (IV; R_1 = *p*-C_6H_4Cl, R_2 = R_3 = H) by methyl sulphate or methyl toluene-*p*-sulphonate under a variety of conditions were unsuccessful. The 3-phenyl derivative however, with methyl idodide at 100°, gave a *monomethiodide*; the 3-*p*-chlorophenyl derivative was unaffected under these conditions. The feebly basic nature of both of these tertiary bases was shown by the fact that the *monohydrochloride* of the former and the *hemihydrochloride* of the latter could be prepared only under anhydrous conditions, and were decomposed by warm water to give the corresponding free bases.

Note on Results of Biological Examination.—The following summarises the constitution of each compound examined and the toxicity data.

Compound no.	Derivatives of 4-azafluoranthene.	Approximate M.T.D.[1] (in mg. per 20-g. mouse; administered subcutaneously).
5	3-Amino-, monohydrochloride monohydrate	0·2
8	3-Acetamido-	10 [2,3]
16	3-Amino-, monomethoidide	0·8
4	3-Diethylamino-, monohydrochloride trihydrate	10 [3]
7	3-(2-Diethylaminoethylamino)-, monohydrochloride	2
6	3-(3-Diethylaminopropylamino)-, monohydrochloride	4
9	3-(4-Diethylamino-1-methylbutylamino)-, monohydrochloride	2
20	3 : 7-Diamino-, monomethiodide	1
19	7-Amino-3-(3-diethylaminopropylamino)-, monohydrochloride	1
	Derivatives of 2 : 4-diazafluoranthene.	
2	3-Phenyl-, monohydrochloride	2 [2]
17	3-Phenyl-, monomethiodide monohydrate	10 [2,3]
3	3-*p*-Chlorophenyl-, hemihydrochloride	2 [2,3]
10	3-*p*-Aminophenyl-, monohydrochloride monohydrate	4
11	3-*p*-Acetamidophenyl-	20 [2,3]
13	3-Amino-, monohydrochloride	10 [2,3]
15	3-Amino-, monomethiodide	0·8
14	3-(3-Diethylaminopropylamino)-, monohydrochloride	2
18	7-Amino-	10 [2,3]

[1] M.T.D. = maximum tolerated dose. [2] The substance was administered in the form of a suspension. [3] Largest amount tested.

Each of the above compounds was examined for chemotherapeutic trypanocidal activity against *Trypanosoma brucei* and *T. congolense* in mice. In addition, Nos. 5, 4, 7, and 6 were tested against *T. cruzi*. None showed any chemotherapeutic activity. The authors are indebted to Miss H. Adamson, B.Sc., working with the support of the Medical Research Council in the Bacteriology Department under Professor C. H. Browning, F.R.S., who furnished these data. They are further indebted to the late Dr. F. H. S. Curd and to Dr. S. Ellingworth of Imperial Chemical Pharmaceuticals Ltd., who supplied the information that Nos. 7, 6, 9, and 18, on examination for amœbicidal activity by the method of Jones (*Ann. Trop. Med. Parasit.*, 1946, **40**, 130), showed some activity of a low order, and that Nos. 7, 6, and 9 showed no activity against *Plasmodium gallinaceum* in chicks. Dr. J. D. Fulton reported that Nos. 20 and 19 show about one-tenth of the activity of emetine, tested under parallel conditions, against *Entamœba histolytica, in vitro*, in the presence of a mixed bacterial flora. No. 19, tested on *E. histolytica* in presence of a single bacterial species (*Bacterium coli*), was amœbicidal at a dilution of 1 in 10^{-4}. At the same dilution, No. 20 killed the *B. coli*.

Experimental.

Action of Hydrazoic Acid on Fluorenone-1-carboxylic Acid.—Sodium azide (0·72 g.) was added, in small portions, to a mechanically stirred mixture, heated at 45°, of the keto-acid (2·24 g; Fieser and Seligman, *loc. cit.*), concentrated sulphuric acid (5 c.c.), and chloroform (30 c.c.). A steady evolution of gas occurred while the mixture was stirred at 45° for 20 minutes. After being kept at room temperature for 2 hours the mixture was diluted with chloroform (120 c.c.), treated with crushed ice, and then basified by the addition of concentrated sodium hydroxide solution. The chloroform layer was separated, washed with water, and evaporated. The residue, on crystallisation from benzene, gave light-orange needles (0·8 g.), m. p. 223—224°, of *9-hydroxyphenanthridine-8-carboxylic acid lactone* or 9-phenanthridone-1-carboxylic acid lactam (VI or VIII) (Found: C, 76·2; H, 2·8; N, 6·4. $C_{14}H_7O_2N$ requires C, 76·0; H, 3·2; N, 6·3%). Acidification, with hydrochloric acid, of the aqueous-alkaline layer gave an orange-red solid (1·2 g.) which was separated by fractional crystallisation from ethanol followed by extraction with benzene, into unchanged starting material (0·2 g.), as more soluble product, and, as less soluble product, *9-phenanthridone-1(or 8)-carboxylic acid* (V or VII), which crystallised from glacial acetic acid in short, yellow needles (0·3 g.), m. p. 299° (decomp.) (Found: C, 70·5; H, 3·7; N, 5·9. $C_{14}H_9O_3N$ requires C, 70·3; H, 3·8; N, 5·9%).

New Synthesis of 1-Aminofluorenone.—Fluorenone-1-carboxylic acid (20 g.) was boiled under reflux with thionyl chloride (40 c.c.) for 30 minutes. Excess of thionyl chloride was removed by distillation under reduced pressure on a water-bath, and the residual solid freed from the last traces by repeated evaporation with anhydrous benzene. The residue of acid chloride was dissolved in dry acetone (440 c.c.). The solution was cooled to 0—5° and treated dropwise, with mechanical stirring, with a solution of sodium azide (8·5 g.) in water (25 c.c.). After being stirred at 0—5° for another 30 minutes, the mixture was treated with water (960 c.c.). The precipitated *fluorenone-1-carboxylic acid azide* formed a yellow, crystalline solid (20·8 g., 94%), m. p. 90—91° (decomp.) [0·206 g., heated in toluene, evolved 18·5 c.c. of nitrogen, measured at N.T.P. $(C_{13}H_7O)CO{\cdot}N_3$ requires 18·6 c.c.]. The azide was cautiously heated under reflux with concentrated hydrochloric acid (500 c.c.), until evolution of gas had ceased. The mixture was then boiled under reflux for 3 hours, diluted with water (400 c.c.), boiled again for 1 hour, and then filtered hot. The solid which separated from the filtrate on cooling gave, on treatment with dilute aqueous ammonia, a crude product (9·7 g.; m. p. 116—117°) which, on

recrystallisation from aqueous ethanol, formed yellow-orange leaflets (8·8 g.), m. p. 118—119° (Goldschmiedt, *loc. cit.*, gives m. p. 110°; Huntress, Pfister, and Pfister, *loc. cit.*, give m. p. 118—118·5° for 1-aminofluorenone).

Fluorenon-1-yl iso*Cyanate.*—The aforementioned azide (2·8 g.) was heated on a water-bath with anhydrous toluene (15 c.c.) for 30 minutes. The iso*cyanate* formed clusters of orange rhombs (2 g.), m. p. 144—146°, from the same solvent (Found : N, 6·2. $C_{14}H_7O_2N$ requires N, 6·3%). It reacted with water to give NN′-*di*(*fluorenon-1-yl*)*urea*, which formed yellow needles (from pyridine), m. p. 264° (Found : C, 77·6; H, 3·8; N, 6·5. $C_{27}H_{16}O_3N_2$ requires C, 77·9; H, 3·9; N, 6·7%).

1-*Carbethoxyaminofluorenone.*—The azide (26 g.) was cautiously heated with anhydrous ethanol (260 c.c.) under reflux on a water-bath. When the vigorous evolution of gas had ceased, the resulting solution was boiled under reflux for 3 hours and then filtered while hot. The *ester* separated from the filtrate in light-red rhombs (24 g.), m. p. 111—112° (Found : C, 71·8; H, 4·8; N, 5·1. $C_{16}H_{13}O_3N$ requires C, 71·9; H, 4·9; N, 5·2%).

1-*Carbamidofluorenone.*—The solution of fluorenon-1-yl *iso*cyanate, which was obtained on heating fluorenone-1-carboxylic acid azide (20 g.) with anhydrous toluene (200 c.c.) under reflux, was cooled to 30—40° and then treated with a stream of dry, gaseous ammonia during 2 hours. The resulting yellow precipitate, on recrystallisation (charcoal) from glacial acetic acid, gave yellow needles (10 g.) of the *amide*, m. p. 251° (Found : C, 70·4; H, 4·0; N, 11·5. $C_{14}H_{10}O_2N_2$ requires C, 70·6; H, 4·2; N, 11·8%). The *oxime*, prepared in pyridine, formed yellow needles (from aqueous ethanol), m. p. 214—215° with previous sintering at 190° (Found : N, 16·8. $C_{14}H_{11}O_2N_3$ requires N, 16·6%).

1-*Acetoacetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CO{\cdot}CH_3$, $R_2 = H$).—1-Aminofluorenone (5 g.) was added, in small portions, during 30 minutes, to ethyl acetoacetate (25 c.c.) heated to 160—165°. The mixture was heated at that temperature for 20 minutes longer. It was then distilled under reduced pressure on a water-bath to remove excess of ethyl acetoacetate. The residual gum, on trituration with light petroleum (b. p. 60—80°), gave a red solid. This was extracted with boiling ethanol (175 c.c.), and the extract concentrated to small bulk to give a crystalline solid (3·3 g.; m. p. 134—136°), which, on recrystallisation from ethanol, gave 1-*acetoacetamidofluorenone* as orange needles (3 g.), m. p. 139—140° (Found : C, 73·3; H, 4·6; N, 5·2. $C_{17}H_{13}O_3N$ requires C, 73·1; H. 4·7; N, 5·0%). The insoluble residue was a yellow solid (0·15 g.) which was hydrolysed by boiling under reflux with aqueous acetic acid containing a few drops of concentrated hydrochloric acid. The resulting gum was dissolved in benzene, and the solution percolated through a column of alumina. Elution of the lower, orange band with 1% methanol in benzene, gave 1-aminofluorenone (20 mg.). Elution, with 10% methanol in benzene. of the more strongly adsorbed yellow band, gave a few crystals. m. p. 264—267°, identified by m. p. and mixed m. p. as the compound described below as 3-hydroxy-2-acetyl-4-azafluoranthene.

1-*Cyanoacetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CN$, $R_2 = H$).—(i) *By condensation of* 1-*amino-fluorenone with ethyl cyanoacetate.* The amino-ketone (5 g.) was added, in small portions, to the cyano-ester (25 c.c.) heated to 170°. The temperature of the mixture was then raised to 190° and maintained at 190—195° for 30 minutes longer. Excess of ethyl cyanoacetate was removed by distillation under reduced pressure in an oil-bath at 100—120°. The residual gum was separated by treatment with warm acetone (40 c.c.) into an insoluble, solid fraction (0·66 g.), which formed minute, yellow prisms (from acetic acid), m. p. 233°, of NN′-*di*(*fluorenon-1-yl*)*malonamide* (XI) (Found : C, 75·8; H, 3·9; N, 6·0. $C_{29}H_{18}O_4N_2$ requires C, 76·0; H, 3·9; N, 6·1%), and a soluble, gummy fraction which, on treatment with ethanol followed by fractional crystallisation from this solvent, yielded unchanged 1-aminofluorenone (1·8 g.) and a solid (0·4 g.) which, on recrystallisation from glacial acetic acid followed by repeated recrystallisation from ethanol, gave 1-*cyanoacetamidofluorenone* as yellow needles, m. p. 203° (Found : C, 73·2; H, 3·7; N, 10·9. $C_{16}H_{10}O_2N_2$ requires C, 73·3; H, 3·8; N, 10·7%).

(ii) *By interaction of fluorenon-1-yl* iso*cyanate and cyanoacetic acid.* A mixture of the *iso*cyanate (0·5 g.), anhydrous cyanoacetic acid (0·4 g.; Phelps and Tillotson, *Chem. Abst.*, 1909, **3**, 1533), and anhydrous toluene (5 c.c.) was boiled under reflux for 16 hours. The mixture was treated with water and then filtered. The residue was extracted with ethanol and the extracts concentrated to small bulk to give yellow needles (0·32 g.), m. p. 200—202°, of 1-cyanoacetamidofluorenone.

1-*Carbethoxyacetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CO_2Et$, $R_2 = H$).—(i) *By condensation of* 1-*amino-fluorenone with ethyl malonate.* The amino-ketone (6 g.) was heated under an air-condenser with the ester (30 c.c.) at 190—200° for 17 hours. The mixture was then distilled under reduced pressure from an oil-bath at 110—130° so as to remove excess of ethyl malonate. The residual gum was triturated with light petroleum (b. p. 60—80°) and then separated, by extraction with warm acetone, into a sparingly soluble solid (0·6 g.) which, on recrystallisation from glacial acetic acid, gave yellow prisms, m. p. 233°, of *NN′*-di(fluorenon-1-yl)malonamide, and a more soluble fraction which, on recrystallisation from ethanol, gave orange, prismatic needles (7·8 g.), m. p. 126°, consisting of 1-*carbethoxyacetamidofluorenone* (Found : C, 70·2; H, 4·6; N, 4·4. $C_{18}H_{15}O_4N$ requires C, 69·9; H, 4·9; N, 4·5%).

(ii) *By interaction of fluorenon-1-yl* iso*cyanate and ethyl hydrogen malonate.* A mixture of the *iso*cyanate (0·89 g.), the anhydrous acid (1·2 g.; Marguery, *Bull. Soc. chim.*, 1905, **33** 544), and anhydrous toluene (10 c.c.) was heated under reflux on a water-bath for 3 hours, boiled under reflux for a further 2 hours, and then filtered hot. The material (0·2 g.), which crystallised from the filtrate on cooling, consisted of *NN′*-di(fluorenon-1-yl)urea. The mother-liquors were washed with water and then evaporated. Crystallisation of the residue from ethanol yielded orange, prismatic needles (0·34 g.), m. p. 122—125°, of 1-carbethoxyacetamidofluorenone.

3-*Hydroxy-2-acetyl-4-azafluoranthene* (III; $R_1 = OH$, $R_2 = H$, $R_3 = CO{\cdot}CH_3$).—A solution of 1-acetoacetamidofluorenone (1 g.) in anhydrous nitrobenzene (10 c.c.) was heated to 100° and then treated with powdered sodium methoxide (0·21 g.). The mixture was then heated at 135—140° for 4 hours. After being cooled, it was treated with 2N-hydrochloric acid (10 c.c.) and then distilled in steam. The residual gum, on trituration with chloroform, gave a solid which, on recrystallisation (charcoal) from glacial acetic acid, yielded yellow needles (0·45 g.), m. p. 265—268°, of 3-*hydroxy*-2-*acetyl-4-azafluoranthene* (Found : C, 78·2; H, 4·2; N, 5·4. $C_{17}H_{11}O_2N$ requires C, 78·2; H, 4·2; N, 5·4%).

Action of Dilute Sodium Hydroxide on 1-Carbethoxyacetamidofluorenone.—The finely powdered compound (390 mg.) was boiled under reflux with 1·02N-sodium hydroxide (1·85 c.c., 1·5 mols.) for 2·5 hours. The mixture was extracted with chloroform. Evaporation of the extract and crystallisation of the residue from aqueous ethanol gave 1-aminofluorenone (180 mg.). Acidification, with dilute hydrochloric acid, of the aqueous layer gave a crystalline precipitate (80 mg.), which on recrystallisation from glacial acetic acid and then from ethanol, gave faintly yellow needles, m. p. 155—156° (with evolution of gas), of an *acid* which is probably 2-keto-1-carboxy-*NN'*-di(fluorenon-1-yl)propane-1 : 3-dicarboxyamide (XII) (Found : C, 70·2; H, 3·7; N, 5·6. $C_{32}H_{20}O_7N_2$ requires C, 70·6; H, 3·7; N, 5·2%).

3-*Hydroxy*-4-*azafluoranthene*-2-*carboxylic Acid* (III; $R_1 = OH$, $R_2 = H$, $R_3 = CO_2H$).—A mechanically stirred solution of 1-carbethoxyacetamidofluorenone (5 g.) in anhydrous nitrobenzene (50 c.c.) was treated with powdered sodium methoxide (0·96 g.) and then heated at 135—140° for 11 hours. After being cooled, the mixture was treated with concentrated hydrochloric acid (2 c.c.), set aside for several hours, and then filtered. The orange crystalline residue was washed with benzene, and then boiled under reflux with N-sodium hydroxide (50 c.c.) for 3 hours. The resulting solution was filtered while hot. Acidification, with concentrated hydrochloric acid, of the hot filtrate gave a precipitate (3·4 g.) which, on recrystallisation from glacial acetic acid, gave orange needles, m. p. 310° (decomp.), of the required *acid* (III; $R_1 = OH$, $R_2 = H$, $R_3 = CO_2H$) (Found : C, 72·9; H, 3·6; N, 5·3. $C_{16}H_9O_3N$ requires C, 73·0; H, 3·4; N, 5·3%)

3-*Hydroxy*-4-*azafluoranthene* (III; $R_1 = OH$, $R_2 = R_3 = H$).—A solution of the above carboxylic acid (3·96 g.) in quinoline (15 c.c.) was treated, at 230°, portionwise with basic copper carbonate (0·3 g.). The mixture was maintained at the b. p. for a further 15 minutes, allowed to cool somewhat, and then poured into 2N-hydrochloric acid. Crystallisation of the product from glacial acetic acid gave yellow needles of *hydroxyazafluoranthene* (3 g.), m. p. 288—290° (Found : C, 82·1; H, 4·2; N, 6·4. $C_{15}H_9ON$ requires C, 82·2; H, 4·1; N, 6·4%).

3-*Chloro*-4-*azafluoranthene* (III; $R_1 = Cl$, $R_2 = R_3 = H$).—The above hydroxy-compound (3·3 g.) was boiled under reflux with phosphoryl chloride (33 c.c.) for 3·5 hours. Excess of phosphoryl chloride was removed under reduced pressure on a water-bath. The residue was treated with crushed ice and dilute aqueous ammonia and extracted with chloroform. The extract was washed with water, treated with charcoal, and evaporated. Recrystallisation of the residue from ethanol gave the *chloro*-compound as yellow needles (3·2 g.), m. p. 120—121° (Found : Cl, 15·1. $C_{15}H_8NCl$ requires Cl, 15·0%).

3-*Amino*-4-*azafluoranthene* (III; $R_1 = NH_2$, $R_2 = R_3 = H$).—The above chloro-compound (0·5 g.) was heated with saturated ethanolic ammonia (5 c.c.) at 185—190° for 17 hours in a sealed tube. The reaction mixture was evaporated on a water-bath. The residue was treated with dilute ammonia solution and extracted with chloroform. Chromatography of the washed and dried chloroform solution on alumina, followed by elution of the main yellow band with 1% methanol–chloroform, and recrystallisation from benzene, gave the *amine* as yellow needles (0·3 g.), m. p. 209—211° (Found : C, 82·7; H, 4·6; N, 12·8. $C_{15}H_{10}N_2$ requires C, 82·6; H, 4·6; N, 12·8%). It gave an *acetyl* derivative which formed pale buff needles (from methanol), m. p. 233° (Found : C, 78·3; H, 4·6. $C_{17}H_{12}ON_2$ requires C, 78·5; H, 4·6%), and a *monopicrate* which formed yellow needles (from acetone–ethanol), m. p. 268—270° (decomp.) (Found : C, 56·4; H, 3·0. $C_{15}H_{10}N_2,C_6H_3O_7N_3$ requires C, 56·4; H, 2·9%). The *monohydrochloride monohydrate* was obtained on passing hydrogen chloride into a solution of the base in (moist) chloroform. It formed stout, yellow rhombs which were reconverted into the free base when heated at 120—150° (Found : C, 66·0; H, 4·7. $C_{15}H_{10}N_2,HCl,H_2O$ requires C, 66·1; H, 4·8%).

3-*Diethylamino*-4-*azafluoranthene.*—The corresponding chloro-compound (III; $R_1 = Cl$, $R_2 = R_3 = H$) (0·5 g.) was heated with anhydrous diethylamine (5 c.c.) at 190—200° for 16 hours in a sealed tube. The resinous product gave a *monopicrate* which formed yellow needles (from acetone–ethanol), m. p. 210—212° (decomp.) (Found : C, 59·8; H, 4·3; N, 13·8. $C_{19}H_{18}N_2,C_6H_3O_7N_3$ requires C, 59·6; H, 4·2; N, 13·9%). The free base, on regeneration from the purified picrate by dilute sodium hydroxide, was a light-yellow gum; treatment of its (moist) ethereal solution with hydrogen chloride gave yellow crystals, m. p. 65—68° (decomp.), of the *monohydrochloride trihydrate* (Found : C, 62·3; H, 6·6; Cl, 9·9. $C_{19}H_{18}N_2,HCl,3H_2O$ requires C, 62·5; H, 6·9; Cl, 9·7%).

3-(2-*Diethylaminoethylamino*)-4-*azafluoranthene.*—The chloro-compound (0·5 g.) was heated with 2-diethylaminoethylamine (0·98 g.) and benzene (1·5 c.c.) at 185—190° for 12 hours in a sealed tube. The reaction mixture was treated with dilute aqueous sodium hydroxide and extracted with ether. The benzene–ethereal layer, after being washed several times with water, was extracted with 0·5N-hydrochloric acid. The extract was basified with dilute sodium hydroxide solution and extracted with ether. Evaporation of the ethereal solution gave an oil which yielded a *dipicrate*, which formed yellow prisms (1·0 g.) (from 2-methoxyethanol), m. p. 235—237° (decomp.) (Found : C, 51·1; H, 3·7; N, 16·3. $C_{21}H_{23}N_3,2C_6H_3O_7N_3$ requires C, 51·1; H, 3·7; N, 16·3%). The free *base* regenerated from the purified picrate was a yellow viscous oil (Found : C, 79·1; H, 7·0. $C_{21}H_{23}N_3$ requires C, 79·5; H, 7·2%). Attempted distillation under 1 mm. resulted in decomposition. The base dissolved in one equivalent of 0·1N-hydrochloric acid to give a solution neutral to litmus.

3-(3-*Diethylaminopropylamino*)-4-*azafluoranthene.*—Prepared in a similar manner, by condensation of the chloro-compound with 3-diethylaminopropylamine, the product was purified through its *dipicrate*, which formed yellow needles (from 2-methoxyethanol), m. p. 204—205° (Found : C, 51·8; H, 3·9; N, 16·1. $C_{22}H_{25}N_3,2C_6H_3O_7N_3$ requires C, 51·7; H, 3·9; N, 16·0%). The free *base* regenerated from the purified picrate, was a yellow-brown fluorescent oil (Found : C, 79·7; H, 7·7. $C_{22}H_{25}N_3$ requires C, 79·8; H, 7·6%), which dissolved in one equivalent of 0·1N-hydrochloric acid to give a neutral solution.

3-(4-*Diethylamino*-1-*methylbutylamino*)-4-*azafluoranthene* was similarly prepared by condensation of the chloro-compound with 4-diethylamino-1-methylbutylamine. It was purified through its *dipicrate*, which formed stout, golden rhombs (from acetone–ethanol) m. p. 184—185° (Found : C, 53·0; H, 4·2; N, 15·4. $C_{24}H_{29}N_3,2C_6H_3O_7N_3$ requires C, 52·9; H, 4·3; N, 15·4%). The free *base* was a golden, viscous oil (Found : C, 80·1; H, 8·1. $C_{24}H_{29}N_3$ requires C, 80·2; H, 8·1%) which dissolved in one equivalent of 0·1N-hydrochloric acid.

Nitration of 1-*Carbethoxyaminofluorenone.*—The finely powdered urethane (20 g.) was mechanically stirred with 15N-nitric acid (520 c.c.) at room temperature for 48 hours. The mixture was filtered. The residue was washed with water and then recrystallised from ethyl acetate to give pale yellow needles (10·1 g.), m. p. 210—211°, of 4-*nitro*-1-*carbethoxyaminofluorenone* (Found : C, 61·4; H, 3·9; N, 9·2. $C_{16}H_{12}O_5N_2$ requires C, 61·5; H, 3·9; N, 9·0%). The filtrate was poured into water, and the yellow solid (m. p. 148—155°; 11·5 g.) which separated was collected and washed with water. This was separated, by a process of fractional crystallisation from ethyl acetate coupled with chromatography, on alumina, of benzene solutions of the various fractions recovered from the ethyl acetate mother-liquors, into a further small quantity of the 4-nitro-isomer (less soluble, less strongly adsorbed; 0·5—1 g.), and 2-*nitro*-1-*carbethoxyaminofluorenone* (more soluble, more strongly adsorbed; 6·3 g.), which formed yellow needles (from ethanol), m. p. 171—172° (Found : C, 61·2; H, 3·5; N, 9·0. $C_{16}H_{12}O_5N_2$ requires C, 61·5; H, 3·9; N, 9·0%).

4-*Nitro*-1-*aminofluorenone.*—The above isomer, m. p. 210—211° (10 g.) was heated with sulphuric acid (95% v/v; 100 c.c.) on a water-bath for 2 hours, by which time evolution of carbon dioxide had ceased. After being cooled, the solution was poured into dilute aqueous ammonia. The resulting precipitated 4-*nitro*-1-*aminofluorenone* (m. p. 212—214°; 6·9 g.) formed orange needles (from ethanol), m. p. 213—214° (Found : C, 65·2; H, 3·3; N, 11·5. $C_{13}H_8O_3N_2$ requires C, 65·0; H, 3·4; N, 11·7%). With benzoyl chloride in pyridine this yielded 4-*nitro*-1-*benzamidofluorenone*, yellow needles (from glacial acetic acid), m. p. 226—227° (Found : C, 69·4; H, 3·5; N, 8·2. $C_{20}H_{12}O_4N_2$ requires C, 69·8; H, 3·5; N, 8·1%).

4-*Amino*-1-*benzamidofluorenone* was obtained on boiling the last-mentioned nitro-compound (50 mg.) under reflux with a mixture of iron powder (60 mg.), ethanol (5 c.c.), and N-hydrochloric acid (0·2 c.c.). It formed minute, crimson rhombs (from ethanol), m. p. 226° (Found : C, 76·3; H, 4·4; N, 9·3. $C_{20}H_{14}O_2N_2$ requires C, 76·4; H, 4·5; N, 8·9%). Acetylation of the primary amine with acetic anhydride in boiling benzene, yielded 4-*acetamido*-1-*benzamidofluorenone* which formed yellow needles (from glacial acetic acid), m. p. 307—308° (Found : C, 74·2; H, 4·7; N, 8·1. $C_{22}H_{16}O_3N_2$ requires C, 74·1; H, 4·5; N, 7·9%).

1 : 4-*Diaminofluorenone.*—A suspension of 4-nitro-1-aminofluorenone (100 mg.) in ethanol (50 c.c.) was shaken with a platinic oxide catalyst (10 mg.) in an atmosphere of hydrogen. Uptake ceased when 3 moles had been absorbed. The *diamine* formed crimson needles (64 mg.) (from ethanol), m. p. 232—234° (Found : C, 74·7; H, 5·0; N, 12·9. $C_{13}H_{10}ON_2$ requires C, 74·3; H, 4·8; N, 13·3%). Addition of acetic anhydride to its solution in boiling ethanol gave 1 : 4-*diacetamidofluorenone*, which formed yellow needles (from glacial acetic acid), m. p. 319—321° (Found : C, 69·3; H, 4·5; N, 9·9. $C_{17}H_{14}O_3N_2$ requires C, 69·4; H, 4·8; N, 9·5%).

Deamination of 4-*Nitro*-1-*aminofluorenone.*—A solution of the nitroamino-ketone (0·158 g.) in concentrated sulphuric acid (2·5 c.c.) was treated with glacial acetic acid (0·5 c.c.). The resulting suspension of fine crystals was cooled in an ice–salt bath and treated with small portions of finely powdered sodium nitrite (0·15 g.), followed by cold hypophosphorous acid solution (30%; 1·5 c.c.). The mixture was stirred for 30 minutes, kept at 0° for 20 hours longer, and then poured into water. The precipitate was collected and then sublimed at 130—140°/0·4 mm. The lemon-yellow sublimate was purified by adsorption from light petroleum (b. p. 60—80°) solution on to a column of alumina, followed by elution with benzene. Repeated recrystallisation of the eluate from ethanol gave faintly yellow needles (90 mg.), m. p. 174—175°, of 4-nitrofluorenone (Found : N, 6·1. Calc. for $C_{13}H_7O_3N$: N, 6·2%) (Schmidt and Bauer, *loc. cit.*, give m. p. 173—174°).

2-*Nitro*-1-*aminofluorenone.*—Hydrolysis, with sulphuric acid, of the isomer, m. p. 171—172°, obtained by nitration of 1-carbethoxyaminofluorenone, gave 2-*nitro*-1-*aminofluorenone* (yield nearly quantitative), which formed orange needles (from benzene), m. p. 198° (Found : C, 65·2; H, 3·6; N, 11·9. $C_{13}H_8O_3N_2$ requires C, 65·0; H, 3·4; N, 11·7%).

Deamination of the base in a way similar to that described above for the 4-nitro-isomer, gave 2-nitrofluorenone which formed yellow needles (from glacial acetic acid), m. p. 216—218° (Found : N, 6·3. Calc. for $C_{13}H_7O_3N$: N, 6·2%). Its m. p. was not depressed on admixture with an authentic sample, prepared by oxidation of 2-nitrofluorene (Diels, *loc. cit.*).

1 : 2-*Diaminofluorenone.*—A suspension of 2-nitro-1-aminofluorenone (100 mg.) in ethanol (20 c.c.) was shaken with hydrogen in presence of a platinic oxide catalyst (15 mg.) until uptake ceased (15 minutes). The catalyst was filtered off and the filtrate evaporated. Recrystallisation of the residue from benzene yielded crimson rhombs, m. p. 188—190° (Found : C, 74·2; H, 4·8; N, 13·0. $C_{13}H_{10}ON_2$ requires C, 74·3; H, 4·8; N, 13·3%). Heating the *diamine* under reflux with a solution of phenanthraquinone in ethanol yielded a *quinoxaline* derivative, which formed orange needles (from tetrachloroethane), m. p. 325° (Found : C, 85·3; H, 3·8; N, 7·5. $C_{27}H_{14}ON_2$ requires C, 84·8; H, 3·7; N, 7·3%).

4-*Nitro*-1-*carbethoxyacetamidofluorenone* (IX; $R_1 = CH_2{\cdot}CO_2Et$, $R_2 = NO_2$).—This was prepared by condensation of ethyl malonate with 4-nitro-1-aminofluorenone at 190—200°; the *product* (yield 68%) formed pale-yellow needles (from glacial acetic acid), m. p. 192—194° (Found : C, 61·0; H, 3·9; N, 8·2. $C_{18}H_{14}O_6N_2$ requires C, 61·0; H, 4·0; N, 7·9%).

7-*Nitro*-3-*hydroxy*-2-*carbethoxy*-4-*azafluoranthene* (III; $R_1 = OH$, $R_2 = NO_2$, $R_3 = CO_2Et$).—Cyclisation of the above ester by heating it with sodium methoxide in nitrobenzene at 130—135° for 10 hours gave, as principal product, the tetracyclic *ethyl* ester which formed lemon-yellow needles (from glacial acetic acid), m. p. 290—291° (Found : C, 64·7; H, 3·7; N, 8·4. $C_{16}H_{12}O_5N_2$ requires C, 64·3; H, 3·6; N, 8·3%). It was accompanied by, and gave on hydrolysis with boiling 2N-sodium hydroxide solution, 7-*nitro*-3-*hydroxy*-4-*azafluoranthene*-2-*carboxylic acid* which formed bronze needles (from glacial acetic acid), m. p. 340—345° (decomp.) (Found : C, 62·6; H, 2·5; N, 9·2. $C_{16}H_8O_5N_2$ requires C, 62·3; H, 2·6; N, 9·1%).

7-*Nitro*-3-*hydroxy*-4-*azafluoranthene.*—This was obtained by addition of basic copper carbonate (0·25 g.) to a solution, heated to 235—240°, of the above carboxylic acid (2·5 g.) in quinoline (15 c.c.); the *product* (1·7 g.) formed tan-coloured needles (from pyridine) which did not melt below 350° (Found : C, 68·6; H, 3·1; N, 10·6. $C_{15}H_8O_3N_2$ requires C, 68·2; H, 3·1; N, 10·6%).

3-*Chloro*-7-*nitro*-4-*azafluoranthene*.—The above hydroxy-compound (1·7 g.) was boiled under reflux with phosphory lchloride (20 c.c.) for 2 hours. Isolated in the usual way, the *chloro*-compound (1·3 g.) formed yellow-green needles (from 2-methoxyethanol), m. p. 249—250° (Found: C, 63·8; H, 2·6; N, 10·2. $C_{15}H_7O_2N_2Cl$ requires C, 63·7; H, 2·5; N, 9·9%).

7-*Nitro*-3-*amino*-4-*azafluoranthene*.—The above chloro-compound (0·5 g.) was heated in a sealed tube at 155—160° for 4·5 hours with 2-methoxyethanol (20 c.c.) which had previously been saturated at 0° with anhydrous ammonia. The *nitro-amine* crystallised from the reaction mixture on cooling, and on recrystallisation from 2-methoxyethanol formed copper needles (0·35 g.), m. p. 316—318° (Found: N, 16·1. $C_{15}H_9O_2N_3$ requires N, 16·0%).

7-*Nitro*-3-*amino*-4-*azafluoranthene Monomethiodide*.—The above nitro-amine (0·35 g.) was heated with methyl iodide (2 c.c.) and 2-methoxyethanol (10 c.c.) at 100° for 2·5 hours in a sealed tube; the *methiodide* formed yellow needles (from 2-methoxyethanol) (yield 0·36 g.), m. p. 304—306° (decomp.) (Found: C, 47·2; H, 3·3; N, 11·0. $C_{16}H_{12}O_2N_3I$ requires C, 47·4; H, 3·0; N, 10·4%).

3 : 7-*Diamino*-4-*azafluoranthene Monomethiodide*.—A mixture of iron powder (0·35 g.), 0·1N-hydrochloric acid (3 c.c.), and ethanol (50 c.c.) was heated under reflux on a water-bath and then treated with the nitro-methiodide described in the previous paragraph (0·35 g.). The mixture was boiled under reflux for 2 hours, diluted with ethanol (20 c.c.), and filtered while hot. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in warm water (50 c.c.), and the solution filtered. Dropwise addition of potassium iodide solution (50%) to the filtrate gave a precipitate which on recrystallisation from methanol gave microscopic, red needles (0·21 g.), m. p. 235—237° (decomp.) (Found: C, 51·2; H, 3·6; N, 11·4. $C_{16}H_{14}N_3I$ requires C, 51·2; H, 3·8; N, 11·2%).

7-*Amino*-3-(3-*diethylaminopropylamino*)-4-*azafluoranthene*.—A mixture of 3-chloro-7-nitro-4-azafluoranthene (0·5 g.), 3-diethylaminopropylamine (1·4 g.), and 2-methoxyethanol (10 c.c.) was heated at 155—165° for 4·5 hours in a sealed tube. The condensation product, isolated in the usual way, was a dark brown oil. It was dissolved in 0·1N-hydrochloric acid (36 c.c.). The solution was heated on a water-bath, mechanically stirred, and treated portionwise with iron powder (0·6 g.). The mixture was heated on the water-bath for 2 hours longer and filtered, and the residue washed with hot water. Addition of dilute aqueous sodium hydroxide to the combined filtrates caused the separation of an oil which was then extracted into chloroform. The extract was washed with water and evaporated. The residual viscous oil, on treatment with a solution of picric acid in ethanol, yielded a *dipicrate* which, on repeated recrystallisation from 2-methoxyethanol, formed red needles (0·7 g.), m. p. 209—212° (Found: C, 50·6; H, 4·0; N, 17·1. $C_{22}H_{26}N_4,2C_6H_3O_7N_3$ requires C, 50·7; H, 4·0; N, 17·4%). The free base, regenerated from the purified picrate by treatment with lithium hydroxide solution (Burger, *J. Amer. Chem. Soc.*, 1945, **67**, 1615), formed a yellow-brown oil, solutions of which in ethanol or chloroform showed a brilliant green fluorescence. It dissolved in one equivalent of 0·1N-hydrochloric acid to give a red solution which was neutral to litmus.

3-*Phenyl*-2 : 4-*diazafluoranthene* (IV; R_1 = Ph, R_2 = R_3 = H).—(i) *By interaction of* 1-*amino-fluorenone and benzonitrile*. Dry hydrogen chloride was passed into a mixture, heated at 180—185°, of the amino-ketone (1 g.) and benzonitrile (5 c.c.) during 11 hours. The reaction mixture was distilled in steam. The residue was treated with dilute sodium hydroxide solution and extracted with chloroform. The extract was washed with water, treated with charcoal, filtered, and evaporated. The residual brown gum was dissolved in benzene, and the solution percolated through a column of alumina. The column was repeatedly washed with benzene until the main faintly-yellow band had passed into the filtrate. Evaporation of the latter gave a crystalline residue which, on recrystallisation from ethanol, gave 3-*phenyl*-2 : 4-*diazafluoranthene* as lemon-yellow needles (0·9 g.), m. p. 130—131° (Found: C, 85·8; H, 4·2; N, 9·9. $C_{20}H_{12}N_2$ requires C, 85·7; H, 4·3; N, 10·0%).

(ii) *By cyclisation of* N-(*fluorenon*-1-*yl*)-N′-*methylbenzamidine* (XIII; R_1 = Ph, R_2 = Me). A solution of 1-aminofluorenone (1·24 g.) in anhydrous benzene (20 c.c.) was boiled under reflux and treated dropwise, during 20 minutes, with a solution of *N*-methylbenzimino chloride (von Pechmann, *Ber.*, 1895, **28**, 2362; 1·2 g.) in anhydrous benzene (5 c.c.). The mixture was boiled under reflux for 5 hours longer and then cooled, and the red crystalline solid which had separated was filtered off. It was shaken with ether and 2N-sodium hydroxide. The ethereal layer was washed with water and evaporated. The residue was dissolved in boiling N-hydrochloric acid (120 c.c.), and the solution filtered while hot. N-(*Fluorenon*-1-*yl*)-N′-*methylbenzamidine monohydrochloride dihydrate* separated from the filtrate in elongated, yellow prisms (1·92 g.), m. p. 230—231° (decomp.) with previous sintering at 130° and a colour change from yellow to orange at 150—200° (Found: C, 65·9; H, 5·5; N, 6·8. $C_{21}H_{16}ON_2,HCl,2H_2O$ requires C, 65·5; H, 5·5; N, 7·3%). A solution of the free base (from 0·278 g. of the hydrochloride dihydrate by treatment with dilute sodium hydroxide solution and isolation by means of ether) in anhydrous nitrobenzene (5 c.c.) was treated with powdered sodium methoxide (50 mg.). The mixture was heated at 185—195° for 4·5 hours. After being cooled and acidified with glacial acetic acid, it was distilled in steam. The product, isolated by means of chromatography as described in (i) above, formed lemon-yellow needles (0·12 g.) (from ethanol), m. p. 130—131°. It showed no m. p. depression on admixture with a sample of the product as described in (i). Passing dry hydrogen chloride into a solution of the base in benzene gave a *monohydrochloride* which formed orange crystals, m. p. 151—152° (Found: C, 76·0; H, 3·9. $C_{20}H_{12}N_2,HCl$ requires C, 75·8; H, 4·1%), which when heated with water were transformed into the free base.

Attempted Preparation of a Methosulphate.—A solution of the aforesaid base (300 mg.) in anhydrous xylene (3 c.c.) was heated to 140° and then treated with methyl sulphate (1·6 g.). The solution became pink and after a few minutes a red oil separated. The mixture was cooled and then distilled in steam. The aqueous phase was filtered while hot from an insoluble gum, and on evaporation under reduced pressure left no appreciable residue. The gum, on treatment with ethanol, gave a crystalline *product* (100 mg.; m. p. 150—152°) which, on repeated recrystallisation from ethanol, gave long, yellow needles, m. p. 153—154°, which contained no sulphur. Its analysis results suggested a benzamido-fluorenone (Found: C, 80·6; H, 4·6; N, 4·6. $C_{20}H_{13}O_2N$ requires C, 80·3; H, 4·4; N, 4·7%), but it showed a marked mixed-m. p. depression on admixture with an authentic sample (m. p. 150—152°) of

1-benzamidofluorenone prepared by benzoylation of 1-aminofluorenone (Huntress, Pfister, and Pfister, *loc. cit.*). It showed a marked m. p. depression also, on admixture with a sample of 1-*benzamidofluorenol*, which was prepared by Meerwein–Ponndorf reduction of 1-benzamidofluorenone. This carbinol formed elongated, faintly-yellow prisms (from benzene), m. p. 163—165° (Found : C, 79·6; H, 5·1; N, 5·0. $C_{20}H_{15}O_2N$ requires C, 79·7; H, 5·0; N, 4·7%). The same compound, of unascertained constitution, was obtained by treatment of the starting material, in nitrobenzene at 165—170°, with methyl sulphate.

3-*Phenyl*-2 : 4-*diazafluoranthene Monomethiodide Monohydrate.*—This was prepared by heating a solution of the base (0·4 g.) in methyl iodide (4 c.c.) at 100° for 12 hours. The *product* crystallised from the reaction mixture and was filtered off and washed with ether and water. It formed bright red needles (0·3 g.), m. p. 196—197° (Found : C, 56·8; H, 3·6; N, 6·4. $C_{21}H_{15}N_2I,H_2O$ requires C, 57·2; H, 3·9; N, 6·4%).

3-p-*Chlorophenyl*-2 : 4-*diazafluoranthene.*—Hydrogen chloride was passed into a solution, heated at 180—190°, of 1-aminofluorenone (1 g.) and *p*-chlorobenzonitrile (2·2 g.) in anhydrous nitrobenzene (3 c.c.); the *product*, purified by chromatography on alumina from benzene solution, formed yellow needles (from ethyl acetate; yield, 60%), m. p. 189° (Found : C, 76·6; H, 3·6; N, 8·9. $C_{20}H_{11}N_2Cl$ requires C, 76·3; H, 3·5; N, 8·9%). Passing hydrogen chloride into a solution of the base in benzene caused the precipitation of a *hemihydrochloride*, which separated as orange crystals which decomposed to give the free base either when heated to 160—170°, or when heated with water (Found : C, 72·0; H, 3·6; N, 8·5. $C_{20}H_{11}N_2Cl,\frac{1}{2}HCl$ requires C, 72·1; H, 3·5; N, 8·4%). The base was recovered unchanged after being heated with methyl iodide at 100° for several hours in a sealed tube.

3-p-*Nitrophenyl*-2 : 4-*diazafluoranthene.*—This was prepared by passing hydrogen chloride into a mixture, heated at 180—190°, of 1-aminofluorenone (2 g.), *p*-nitrobenzonitrile (Bogert and Kohnstamm, *J. Amer. Chem. Soc.*, 1903, **25**, 479; 1·7 g.), and anhydrous nitrobenzene (5 c.c.) for 10 hours; the *nitro*-compound could not be purified by chromatography owing to its sparing solubility in the common organic solvents. It formed tan-coloured needles (from xylene; yield, 27%), m. p. 275° (Found : C, 74·0; H, 3·4; N, 12·8. $C_{20}H_{11}O_2N_3$ requires C, 73·8; H, 3·4; N, 12·9%). Reduction, with iron powder, of a suspension of the nitro-compound in boiling acidulated ethanol yielded 3-p-*aminophenyl*-2 : 4-*diazafluoranthene* which separated from ethanol as orange-red needles (87%), m. p. 211° (Found : C, 81·3; H, 4·4; N, 14·1. $C_{20}H_{13}N_3$ requires C, 81·4; H, 4·4; N, 14·2%). Addition of 2N-hydrochloric acid to a solution of the base in ethanol precipitated minute, purple needles, m. p. 258—260°, of the *hydrochloride monohydrate* (Found : C, 66·9; H, 4·3; N, 12·1; Cl, 12·0. $C_{20}H_{13}N_3,1\frac{1}{2}HCl,H_2O$ requires C, 66·9; H, 4·5; N, 11·7; Cl, 12·4%) which could not be satisfactorily recrystallised owing to its insoluble nature. A dilute solution of the hydrochloride in saturated alcoholic hydrogen chloride, on being boiled under reflux for a short time, lost its originally deep-purple colour. The product which was obtained on evaporation of the resulting light-yellow solution formed minute, yellow crystals (from ethanol containing hydrogen chloride), m. p. 231—232°. Analysis indicated that this substance was the *hydrochloride* of a *p*-aminobenzamidofluorenone (Found : C, 68·6; H, 4·4; N, 8·4. $C_{20}H_{14}O_2N_2,HCl$ requires C, 68·5; H, 4·3; N, 8·0%); its nature was not further investigated.

3-p-*Acetamidophenyl*-2 : 4-*diazafluoranthene.*—A suspension of the primary amine (430 mg.) in benzene (13 c.c.) containing acetic anhydride (0·3 c.c) was boiled under reflux; the *acetyl* derivative formed orange needles (from ethanol; yield, 450 mg.), m. p. 244° (Found : C, 78·2; H, 4·4; N, 12·6. $C_{22}H_{15}ON_3$ requires C, 78·3; H, 4·5; N, 12·5%).

Reaction of 4-*Nitro*-1-*aminofluorenone with Benzonitrile.*—Treatment of a solution, heated at 190—200°, of the nitro-amino-ketone (5 g.) in benzonitrile (60 c.c.) with hydrogen chloride during 46 hours, followed by distillation in steam, yielded a solid (5·2 g.), which was separated by chromatography of a benzene solution on alumina into unchanged 4-nitro-1-aminofluorenone (more strongly adsorbed; 2·3 g.) and a mixture of crystalline solids (2·5 g.). The latter was separated by fractional crystallisation from benzene into 4-nitro-1-benzamidofluorenone (0·43 g.) which formed yellow needles, m. p. 225—226°, identified by comparison with an authentic specimen, and a crystalline mixture (1·8 g.; m. p. 165—175°) which, on repeated recrystallisation from benzene and then glacial acetic acid gave a fraction (0·5 g.), of constant m. p. 179—181°. This was still obviously heterogeneous but could not be further resolved by crystallisation or by chromatography of a benzene solution on alumina. However, reduction, with iron powder in acidulated ethanol, of the mixture (1·8 g.) recovered from the various mother-liquors gave a product which, by chromatography of a benzene solution on alumina, was readily separated into 4-amino-1-benzamidofluorenone (0·5 g.), as more strongly adsorbed fraction, and, as more weakly adsorbed fraction, a *substance*, which formed microscopic, yellow needles (0·9 g.; from glacial acetic acid), m. p. 198—199° [Found : C, 76·8; H, 3·6; N, 8·6%; *M* (Rast), 340. $C_{20}H_{12}O_2N_2$ requires C, 76·9; H, 3·9; N, 9·0%; *M*, 312]. Its m. p. was not depressed on admixture with a specimen of the above fraction of constant m. p. 179—181°, which indicates that this component of the original mixture had not undergone alteration under the conditions used for reduction.

Reaction of 2-*Nitro*-1-*aminofluorenone with Benzonitrile.*—Treatment of a solution, heated to 190—200°, of the nitro-amino-ketone (0·5 g.) in benzonitrile (10 c.c.) with hydrogen chloride during 24 hours gave a product which was isolated in the usual way and separated by crystallisation from benzene, followed by chromatography, on alumina, of a solution in the same solvent, into unchanged nitro-amino-ketone (0·4 g.) (more strongly adsorbed) and 5-*nitro*-3-*phenyl*-2 : 4-*diazafluoranthene* which formed yellow needles (10 mg.; from benzene), m. p. 221—222° (Found : C, 74·3; H, 3·4; N, 13·0. $C_{20}H_{11}O_2N_3$ requires C, 73·8; H, 3·4; N, 12·9%).

3-*Hydroxy*-2 : 4-*diazafluoranthene* (IV; R_1 = OH, R_2 = R_3 = H).—A mechanically stirred suspension of 1-carbamidofluorenone (9 g.) in anhydrous nitrobenzene (210 c.c.) was treated portionwise with powdered sodium methoxide (2·3 g.). The mixture was gradually heated to 190—195° and maintained at that temperature for 6 hours. It was cooled, treated with concentrated hydrochloric acid (4·8 c.c.), and then set aside for several hours. The 3-*hydroxy*-2 : 4-*diazafluoranthene* which crystallised was filtered off and washed with benzene and then with water. It (4·6 g.; m. p. 286—291°) was sufficiently pure for the next stage. A sample recrystallised from ethanol formed microscopic, yellow needles, m. p. 296—297° (Found : C, 76·5; H, 3·8; N, 12·9. $C_{14}H_8ON_2$ requires C, 76·3; H, 3·7; N, 12·7%).

3-*Chloro*-2 : 4-*diazafluoranthene*.—The foregoing hydroxy-compound (4·6 g.) was boiled under reflux with phosphoryl chloride (50 c.c.) for 2 hours. Excess of phosphoryl chloride was removed under reduced pressure. The residue was treated with crushed ice and dilute ammonia solution and then extracted with chloroform. Evaporation of the chloroform solution and crystallisation of the residue from ethanol yielded lemon-yellow needles (4·3 g.) of the *chloro*-compound, m. p. 167° (Found : C, 70·7; H, 3·0; N, 11·7. $C_{14}H_7N_2Cl$ requires C, 70·4; H, 3·0; N, 11·7%).

3-*Amino*-2 : 4-*diazafluoranthene*.—The foreging chloro-compound (2 g.) was heated with saturated, alcoholic ammonia (25 c.c.) at 180—185° for 6·5 hours in a sealed tube. The reaction mixture was evaporated to dryness, and the residue was treated with dilute sodium hydroxide solution and then extracted with chloroform. The extract was treated with charcoal, filtered, and evaporated. The residue, on repeated recrystallisation from ethanol, gave the *amine* as yellow needles (1·5 g.), m. p. 208° with previous sintering (Found : C, 76·5; H, 4·2; N, 19·0. $C_{14}H_9N_3$ requires C, 76·7; H, 4·1; N, 19·2%). The *monohydrochloride*, which was obtained by treatment of a solution of the base in chloroform with hydrogen chloride, formed orange prisms, m. p. 250—251° with previous sintering (Found : C, 65·7; H, 4·0. $C_{14}H_9N_3$,HCl requires C, 65·8; H, 3·9%). The *monomethiodide* was prepared by heating, under reflux on a water-bath, a mixture of the base (0·2 g.), methyl iodide (0·2 c.c.), and 2-methoxyethanol (2 c.c.) for 3 hours. The product crystallised from the reaction mixture on cooling, and formed prismatic, orange needles (from ethanol), m. p. 241—253° (decomp.) (Found : C, 49·8; H, 3·5; N, 11·6. $C_{15}H_{12}N_3I$ requires C, 49·9; H, 3·4; N, 11·6%).

3-(3-*Diethylaminopropylamino*)-2 : 4-*diazafluoranthene*.—The corresponding chloro-compound (0·5 g.) was heated with 3-diethylaminopropylamine (1·6 g.) and benzene (2 c.c.) at 170—175° for 6 hours in a sealed tube. The condensation product, isolated in the usual way, was a light-brown oil which could not be rendered crystalline. It gave a *dipicrate* which formed stout, golden rhombs (1 g.; from 2-methoxyethanol), which decomposed at 224—226° (Found : C, 50·3; H, 4·0; N, 18·0. $C_{21}H_{24}N_4,2C_6H_3O_7N_3$ requires C, 50·1; H, 3·8; N, 17·7%). Decomposition of the dipicrate with dilute sodium hydroxide solution yielded the free *base* which was a golden, viscous oil (Found : C, 75·8; H, 7·2. $C_{21}H_{24}N_4$ requires C, 75·9; H, 7·3%). It dissolved in approximately one equivalent of 0·2N-hydrochloric acid to give a solution neutral to litmus.

2 : 4-*Diazafluoranthene* (IV; $R_1 = R_2 = R_3 = H$).—1-Aminofluorenone (0·5 g.) was heated with formamide (redistilled; 5 c.c.) at 180—185° (air-condenser) for 18 hours. Trituration of the reaction mixture with water, followed by extraction of the resulting brittle gum with warm acetone, gave a sparingly soluble solid (50 mg.), which on repeated sublimation at 200—210°/0·2 mm. gave soft white needles which charred on heating to *ca.* 230° (Found : N, 13·7. $C_{14}H_8N_2$ requires N, 13·7%).

Reaction of 4-*Nitro*-1-*aminofluorenone with Formamide*.—The nitro-amino-ketone (2 g.) was heated (air-condenser; under nitrogen) with formamide (redistilled; 20 c.c.) at 190—195° for 2·5 hours. The mixture was distilled from an oil-bath at 120°, under reduced pressure, in order to remove excess of formamide. The residual tarry material was extracted with portions of warm methanol (250 c.c.). The combined extracts were treated with charcoal, filtered, and then concentrated (to *ca.* 60 c.c.). The material which crystallised on storage (0·4 g.; m. p. 238—240°) was filtered off. It gave, on repeated recrystallisation from methanol, clusters of tan-coloured needles, m. p. 250—252°, of 7-*formamido*-2 : 4-*diazafluoranthene* (Found : C, 73·1; H, 4·0; N, 16·8. $C_{15}H_9ON_3$ requires C, 72·9; H, 3·7; N, 17·0%). The first methanol mother-liquors were evaporated to dryness. Trituration of the residue with a small quantity of methanol gave an orange solid (0·6 g.) which, on crystallisation from methanol followed by repeated recrystallisation from glacial acetic acid, gave orange needles (0·4 g.), m. p. 282—284°, of 7-*amino*-2 : 4-*diazafluoranthene* (Found : C, 76·8; H, 4·3; N, 18·6. $C_{14}H_9N_3$ requires C, 76·7; H, 4·1; N, 19·2%) which was found to contain a diazotisable amino-group (β-naphthol test).

The free amine, on dissolution in 2N-hydrochloric acid gave a dark purple solution. The formamido-compound gave a pale straw-coloured solution. When either of these solutions was heated to its b. p., the original colour rapidly changed to blood-red, and then to that of pale straw. Basification of the resulting solutions caused the precipitation of crimson needles, m. p. 232—234°, of 1 : 4-diamino-fluorenone.

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