45. *New Syntheses of Heterocyclic Compounds. Part XIV.* Some New Derivatives of* 1 : 3-*Dimethyl-2-azafluorene.*

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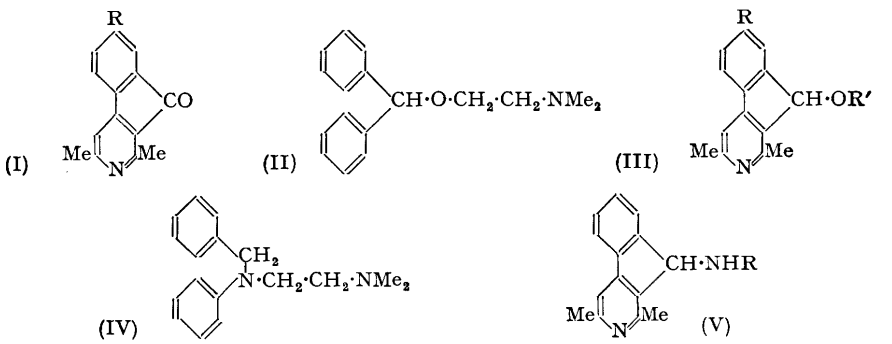
In the course of studies on the evaluation of the biological potentialities of 2-azafluorene, some 2-dialkylaminoalkyl ethers of 1 : 3-dimethyl-2-azafluorenol (III; R = H), and some *N*-substituted derivatives of 9-amino-1 : 3-dimethyl-2-azafluorene (V; R = H), have been prepared. Attempts to convert 1 : 3-dimethyl-2-azafluorene into the 9-carboxylic acid failed.

The present investigation arose from the observation recorded by Kahn, Petrow, Rewald, and Sturgeon (*J.*, 1949, 2128) that 1 : 3-dimethyl-2-azafluorenone (I; R = H) shows more pronounced spasmolytic properties than does papaverine. As musculotropic function had not hitherto been associated with this compound, an evaluation of the wider potentialities of the basic ring system assumed importance. We have therefore prepared selected derivatives of 1 : 3-dimethyl-2-azafluorene and now report some compounds with structural analogies to drugs of established pharmacological potency.



Initial experiments were directed towards the preparation of analogues of " Benadryl " (2-dimethylaminoethyl diphenylmethyl ether) (II), which has both antihistaminic and spasmolytic properties. 1 : 3-Dimethyl-2-azafluorenol (III; R = R′ = H) (Kahn *et al.*, *loc. cit.*) and 2-dimethylaminoethyl chloride, in the presence of sodamide, gave 1 : 3-dimethyl-9-2′-dimethylaminoethoxy-2-azafluorene (III; R = H, R′ = $CH_2 \cdot CH_2 \cdot NMe_2$) in low yield, as an oil which contained appreciable quantities of 1 : 3-dimethyl-2-azafluorenone, presumably formed from (III; R = R′ = H) by disproportionation (disproportionation was frequently encountered during the present investigation). The diethylamino-compound was similarly prepared. 7-Methoxy-1 : 3-dimethyl-2-azafluorenol, obtained by reduction of 1 : 3-dimethyl-7-methoxy-2-azafluorenone (Borsche and Hahn, *Annalen*,

* Part XIII, Courts and Petrow, *J.*, 1952, 1.

1939, **537**, 219) with zinc dust and ethanolic ammonia, furnished the corresponding 9-2′-diethylaminoethoxy-7-methoxy-1 : 3-dimethyl-2-azafluorene (III; R = OMe; R′ = $CH_2 \cdot CH_2 \cdot NEt_2$).

Attention was next directed to the preparation of compounds with structural features similar to the antihistaminic drug "Antergan" (IV). 9-Amino-1 : 3-dimethyl-2-azafluorene (V; R = H) (Kahn *et al.*, *loc. cit.*) with 2-diethylaminoethyl chloride in the presence of sodamide furnished 9-2′-diethylaminoethylamino-1 : 3-dimethyl-2-azafluorene (V; R = $CH_2 \cdot CH_2 \cdot NEt_2$) in low yield. Attempts to prepare other types, however, proved disappointing. *E.g.*, application of the Leuckart reaction to (I; R = H) failed. Reaction of (I; R = H) with formamide gave 9-formamido-1 : 3-dimethyl-2-azafluorene (V; R = CHO), but this could not be hydrolysed. Reductive acetylation of 7-methoxy-1 : 3-dimethyl-2-azafluorenone oxime led to 9-acetamido-7-methoxy-1 : 3-dimethyl-2-azafluorene in 54% yield, but its hydrolysis, when ultimately enforced, gave only a mixture of (I; R = H), some oil, and ammonium salts. The instability of the 9-amino-group in this series of compounds was further illustrated by the reaction of (V; R = H) with 1 : 5-dibromopentane, 1 : 3-dimethyl-2-azafluorenone being again the only product isolated.

Attempts to prepare 1 : 3-dimethyl-2-azafluorene-9-carboxylic acid, for conversion into an analogue of "Trasentin" (2-diethylaminoethyl diphenylacetate), failed: (i) 9-Chloro-1 : 3-dimethyl-2-azafluorene could not be prepared by methods used in the fluorene series (Schlenk and Bergmann, *Annalen*, 1928, **463**, 192; Courtot and Pierron, *Bull. Soc. chim.*, 1929, **45**, 290), but was readily obtained as the hydrochloride by treating 1 : 3-dimethyl-2-azafluorenol with thionyl chloride in chloroform. Careful treatment with aqueous ammonia gave the free base, which proved to be stable to boiling ethanol. The corresponding 9-bromofluorene hydrobromide was formed in high yield by refluxing the fluorenol with hydrobromic acid in acetic acid solution (cf. Ingold and Jessup, *J.*, 1929, 2357), and passed smoothly into the free bromo-compound on basification. The constitution assigned to these two compounds followed from their facile conversion into 1 : 3-dimethyl-9-piperidino-2-azafluorene. Reaction of 9-chloro- or 9-bromo-1 : 3-dimethyl-2-azafluorene with potassium cyanide in aqueous ethanol furnished an unidentified product, $C_{28}H_{23}N_3$, m. p. 202°; this was recovered unchanged after being heated with 50% sulphuric acid in aqueous or ethanolic solution, and attempted hydrolysis with alkali caused resinification. (ii) An alternative route to the 9-nitrile, whereby a 9-formylfluorene is converted into the oxime which is subsequently dehydrated (Von and Wagner, *J. Org. Chem.*, 1944, **9**, 162), was not successful in the present instance. Reaction of 1 : 3-dimethyl-2-azafluorene with ethyl formate in the presence of potassium methoxide gave a mixture from which an oxime could not be isolated. Hydrolysis with alkali led to the formation of a small quantity of (I; R = H). The 1 : 3-dimethyl-2-azafluorene was conveniently prepared by reduction of the fluorenone by the Huang-Minlon (*J. Amer. Chem. Soc.*, 1945, **67**, 1435) modification of the Wolf–Kishner method. (iii) 9-Chloro-1 : 3-dimethyl-2-azafluorene failed to react with magnesium. The corresponding bromo-compound, in contrast, readily did so under the usual experimental conditions. Carboxylation, as recommended by Gilman and Kirby (*J. Amer. Chem. Soc.*, 1926, **48**, 1735), failed to give the required acid. 9-Fluorenylmagnesium bromide gives only an 18% yield of the 9-carboxylic acid under these conditions (Campbell and Tucker, *J.*, 1949, 50). (iv) 1 : 3-Dimethyl-2-aza-9-fluorenyl-lithium was prepared by a halogen–metal interchange between the 9-bromo-base and butyl-lithium. Its carboxylation with solid carbon dioxide appeared to take place in the usual way, but the required 9-carboxylic acid could not be isolated. (v) Campbell and Tucker (*ibid.*, p. 2623) obtained fluorene-9-carboxylic acid in 75% yield by condensation of fluorene with methyl oxalate, followed by acid hydrolysis of the product. In our hands, 1 : 3-dimethyl-2-azafluorene gave a white crystalline product, $C_{16}H_{15}O_5N$, m. p. 216° (decomp.), of unknown constitution. As its formation may have involved reaction of one of the active methyl groups of the parent base with methyl oxalate, attempts were made to obtain 2-azafluorene for parallel study. Although we have improved Mills, Palmer, and Tomkinson's method (*J.*, 1924, 2365) for the preparation of 2-azafluorene, the yield was nevertheless too low to warrant condensation studies.

Reaction of 9-amino-1 : 3-dimethyl-2-azafluorene (V; R = H) with nicotinoyl chloride hydrochloride led to 1 : 3-dimethyl-9-nicotinamido-2-azafluorene. This may be regarded as a derivative of 3-nicotinamidomethylpyridine, which is claimed to produce a large and protracted lowering of the blood pressure (Roche Products Ltd., B.P. 639,246/1950). Treatment of 1 : 3-dimethyl-2-azafluorenone-4-carboxylic acid with 2-diethylaminoethyl chloride in *iso*propanol gave the corresponding ester.

Experimental

M. p.s are uncorrected.

1 : 3-*Dimethyl*-9-2′-*dimethylaminoethoxy*-2-*azafluorene*.—2-Dimethylaminoethyl chloride (from 7 g. of the hydrochloride) in benzene was added to sodamide (1·5 g.), 1 : 3-dimethyl-2-azafluorenol (7·03 g.), and benzene (80 ml.), and the mixture stirred under reflux for 4—4½ hours. After cooling somewhat and removal of precipitated sodium chloride, light petroleum was added and the solution set aside. 1 : 3-Dimethyl-2-azafluorenone (2·7 g.) separated and was removed. The mother-liquors were taken to dryness, the residue dissolved in absolute ethanol, and dry hydrogen chloride passed through the solution. 1 : 3-*Dimethyl*-9-2′-*dimethylaminoethoxy*-2-*azafluorene dihydrochloride dihydrate* was obtained (3·6 g.), having m. p. 266—267°, from alcohol (Found : C, 56·3; H, 6·9; N, 7·2; Cl, 18·2. $C_{18}H_{22}ON_2,2HCl,2H_2O$ requires C, 55·3; H, 7·2; N, 7·2; Cl, 18·1%). The *picrate* separated from ethanol–acetone in yellow crystals, m. p. 204° (Found : C, 48·2; H, 3·7; N, 14·6. $C_{18}H_{22}ON_2,2C_6H_3O_7N_3$ requires C, 48·7; H, 3·8; N, 15·1%).

9-2′-*Diethylaminoethoxy*-1 : 3-*dimethyl*-2-*azafluorene*.—2-Diethylaminoethyl chloride (5·7 g.), sodamide (1·9 g.), 1 : 3-dimethyl-2-azafluorenol (8·9 g.) and benzene (40 ml.) were heated under reflux with stirring for 4 hours, after which water (25 ml.) was added and the benzene layer extracted with 20% hydrochloric acid (25 ml.). Basification, followed by extraction with light petroleum, gave an oil which deposited 1 : 3-dimethyl-2-azafluorenone (500 mg.). The latter was removed, the residue dissolved in ethanol, and dry hydrogen chloride passed through the solution. 9-2′-*Diethylaminoethoxy*-1 : 3-*dimethyl*-2-*azafluorene dihydrochloride dihydrate* was obtained (22%) from ethanol, having m. p. 226—228° (Found : C, 58·7; H, 7·7; N, 6·5; Cl, 16·8. $C_{20}H_{26}ON_2,2HCl,2H_2O$ requires C, 58·4; H, 7·6; N, 6·5; Cl, 16·5%). The *picrate* formed needles, m. p. 169°, from ethanol–acetone (Found : C, 49·9; H, 4·2; N, 13·8. $C_{20}H_{26}ON_2,2C_6H_3O_7N_3$ requires C, 49·9; H, 4·2; N, 14·6%).

7-*Methoxy*-1 : 3-*dimethyl*-2-*azafluorenol*.—7-Methoxy-1 : 3-dimethyl-2-azafluorenone (11·5 g.), aqueous ammonia (250 ml.; *d* 0·880), zinc dust (80 g.), and ethanol (50 ml.) were heated under gentle reflux with stirring for 3 hours. The mixture was filtered hot and the solids were extracted 3 times with boiling ethanol. Concentration of the combined filtrates gave 7-*methoxy*-1 : 3-*dimethyl*-2-*azafluorenol* (10 g.), felted white needles (from benzene), m. p. 205° (Found : C, 74·4; H, 6·0; N, 6·0. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2; N, 5·8%). The *picrate* formed needles (from ethanol–acetone), m. p. 187° (Found : C, 53·8; H, 3·7; N, 11·9. $C_{15}H_{15}O_2N,C_6H_3O_7N_3$ requires C, 53·6; H, 3·8; N, 11·9%).

7-*Methoxy*-1 : 3-*dimethyl*-9-2′-*dimethylaminoethoxy*-2-*azafluorene dihydrochloride dihydrate* formed yellow crystals (15%), m. p. 250—251°, from ethanol–ether (Found : C, 54·1; H, 7·3; N, 7·2; Cl, 16·9. $C_{19}H_{24}O_2N_2,2HCl,2H_2O$ requires C, 54·2; H, 7·2; N, 6·7; Cl, 17·9%).

9-2′-*Diethylaminoethylamino*-1 : 3-*dimethyl*-2-*azafluorene*.—A mixture of 9-amino-1 : 3-dimethyl-2-azafluorene (5·2 g.) and sodamide (1·0 g.) in benzene (20 ml.) was gently heated with stirring under reflux for 1½ hours. 2-Diethylaminoethyl chloride (from 7 g. of the hydrochloride) in benzene was then added and heating continued for a further 6 hours. After removal of solids the liquors were taken to dryness, and the residue was dissolved in ethanol and treated with dry hydrogen chloride. 9-2′-*Diethylaminoethylamino*-1 : 3-*dimethyl*-2-*azafluorene trihydrochloride* was obtained (24%), having m. p. 280—281° (Found : C, 56·8; H, 7·0. $C_{20}H_{27}N_3,3HCl$ requires C, 57·3; H, 6·5%), from absolute ethanol. The *picrate* (from 2-ethoxyethanol) had m. p. 152° (Found : N, 16·8. $C_{20}H_{27}N_3,3C_6H_3O_7N_3$ requires N, 16·9%).

9-*Formamido*-1 : 3-*dimethyl*-2-*azafluorene*.—1 : 3-Dimethyl-2-azafluorenone (20 g.) and formamide (100 ml.) were heated under reflux for 30 minutes and the product was precipitated by addition to alkali. Crystallisation from benzene–light petroleum and finally from ethyl acetate furnished 9-*formamido*-1 : 3-*dimethyl*-2-*azafluorene*, needles, m. p. 236—237° (Found : C, 75·4; H, 5·9; N, 11·8. $C_{15}H_{14}ON_2$ requires C, 75·6; H, 5·9; N, 11·8%).

9-*Acetamido*-7-*methoxy*-1 : 3-*dimethyl*-2-*azafluorene*.—7-*Methoxy*-1 : 3-*dimethyl*-2-*azafluorenone*

oxime (83% yield) had m. p. 284° (from aqueous pyridine) (Found: C, 71·0; H, 5·5; N, 10·9. $C_{15}H_{14}O_2N_2$ requires C, 70·9; H, 5·5; N, 11·0%). This (5 g.), anhydrous sodium acetate (5 g.), and acetic anhydride (180 ml.) were heated under reflux, and treated with zinc dust (10 g.) portionwise, and refluxing was then continued for a further 1 hour. The mixture was filtered hot and poured into water (300 ml.), and the product precipitated by addition of aqueous ammonia. Purification from alcohol gave 9-*acetamido*-7-*methoxy*-1 : 3-*dimethyl*-2-*azafluorene*, m. p. 278° (Found: C, 72·4; H, 6·4; N, 9·6. $C_{17}H_{18}O_2N_2$ requires C, 72·4; H, 6·4; N, 9·9%). The mother-liquors yielded 7-methoxy-1 : 3-dimethyl-2-azafluorenone, identified as the *picrate*, needles (from ethanol–acetone), m. p. 224—225° (Found: C, 54·4; H, 3·4; N, 11·9. $C_{17}H_{18}O_2N_2,C_6H_3O_7N_3$ requires C, 53·9; H, 3·4; N, 12·0%).

9-*Chloro*-1 : 3-*dimethyl*-2-*azafluorene*.—1 : 3-Dimethyl-2-azafluorenol (2·1 g.) was heated under reflux with excess of thionyl chloride for 2 hours. Removal of excess of thionyl chloride gave 9-*chloro*-1 : 3-*dimethyl*-2-*azafluorene hydrochloride* (80%), m. p. >300° (from chloroform) (Found: C, 62·7; H, 4·8; N, 5·2; Cl, 26·3. $C_{14}H_{12}NCl,HCl$ requires C, 63·2; H, 4·9; N, 5·3; Cl, 26·7%). Treatment of an aqueous solution of the salt with dilute aqueous ammonia (to pH 7), followed by rapid cooling, gave 9-*chloro*-1 : 3-*dimethyl*-2-*azafluorene* as needles (from light petroleum), m. p. 117° (Found: C, 74·1; H, 5·2; N, 5·8; Cl, 15·1. $C_{14}H_{12}NCl$ requires C, 73·2; H, 5·2; N, 6·1; Cl, 15·4%). This gave (I; R = H) on several hours' contact with aqueous ammonia.

9-*Bromo*-1 : 3-*dimethyl*-2-*azafluorene*.—1 : 3-Dimethyl-2-azafluorenol (65 g.), acetic acid (250 ml.), and a solution of hydrobromic acid in acetic acid (225 ml. of 50%) were heated under reflux for 2½ hours. Next morning 9-*bromo*-1 : 3-*dimethyl*-2-*azafluorene hydrobromide* (94%) was collected; it had m. p. >300° (Found: C, 47·5; H, 3·7; N, 3·9; Br, 44·0. $C_{14}H_{12}NBr,HBr$ requires C, 47·3; H, 3·7; N, 3·9; Br, 45·0%). The free *base* formed needles from benzene–light petroleum, having m. p. 140—141° (Found: C, 60·9; H, 4·5; N, 5·3; Br, 28·3. $C_{14}H_{12}NBr$ requires C, 61·3; H, 4·4; N, 5·1; Br, 29·1%).

1 : 3-*Dimethyl*-9-*piperidino*-2-*azafluorene*.—(*a*) 9-Chloro-1 : 3-dimethyl-2-azafluorene hydrochloride (2·66 g.), piperidine (2·6 g.), and ethanol (10 ml.) were heated under reflux for 2 hours. The product, steam-distilled for removal of unchanged piperidine, was crystallised from light petroleum, to give 1 : 3-*dimethyl*-9-*piperidino*-2-*azafluorene*, large octagonal prisms (50%), m. p. 120° (Found: N, 9·7. $C_{19}H_{22}N_2$ requires N, 10·1%). The *picrate*, from 2-ethoxyethanol, formed needles, m. p. 214° (Found: C, 51·0; H, 3·8; N, 14·7. $C_{19}H_{22}N_2,2C_6H_3O_7N_3$ requires C, 50·5; H, 3·8; N, 15·2%).

(*b*) The foregoing compounds were likewise prepared from 9-bromo-1 : 3-dimethyl-2-azafluorene.

(*c*) An attempt to prepare the piperidino-compound by heating 9-amino-1 : 3-dimethyl-2-azafluorene (2·1 g.) with 1 : 5-dibromopentane (2·5 g.) for 2 hours on the steam-bath gave a crystalline yellow product which, after basification, afforded 1 : 3-dimethyl-2-azafluorenone, m. p. 158—160°, alone or on admixture with an authentic specimen.

Reaction of 9-*Bromo*-1 : 3-*dimethyl*-2-*azafluorene with Potassium Cyanide*.—The bromo-compound (7·35 g.) in ethanol (45 ml.) was treated with potassium cyanide (1·8 g.) dissolved in the minimum quantity of water, and the mixture heated under reflux for 1½ hours. After addition of water and removal of ethanol under reduced pressure, the product was extraced with chloroform, the extract washed with a little dilute acetic acid, then water, and the solvent removed. Crystallisation from light petroleum (b. p. 80—100°) gave a *substance* (3·6 g.), m. p. 202° (Found: C, 83·5; H, 5·8; N, 10·7. $C_{28}H_{23}N_3$ requires C, 83·6; H, 5·7; N, 10·5%). The same product was obtained from 9-chloro-1 : 3-dimethyl-2-azafluorene.

1 : 3-*Dimethyl*-2-*azafluorene*.—1 : 3-Dimethyl-2-azafluorenone (10·45 g.), potassium hydroxide (9·5 g.), diethylene glycol (70 ml.), and 100% hydrazine hydrate (5·7 ml.) were heated under reflux at 150° for 1½ hours. The temperature was then raised to 180—190° as rapidly as excessive foaming allowed, and kept there for 4 hours, whereafter evolution of nitrogen had ceased. Next morning the mixture was poured into water (500 ml.), and the precipitated solids were collected and crystallised from light petroleum, to give 1 : 3-dimethyl-2-azafluorene, pale yellow needles (75%), m. p. 93—94° alone or on admixture with an authentic specimen.

Attempted Preparation of 9-*Formyl*-1 : 3-*dimethyl*-2-*azafluorene*.—1 : 3-Dimethyl-2-azafluorene (7·25 g.) was treated with ethyl formate in ether in the presence of potassium methoxide, as described for fluorene by Von and Wagner (*loc. cit.*). The reaction mixture was poured into water and extracted with ether, and the aqueous layer brought to pH 7 by addition of dilute hydrochloric acid. The precipitated gelatinous solid (4·2 g.) was treated with hydroxylamine hydrochloride–sodium acetate in ethanol, giving pale yellow prisms (2·8 g.), m. p. >300°

(Found : C, 51·5; H, 4·0; N, 4·0; Cl, 38·8. 9-Formyl-1 : 3-dimethyl-2-azafluorenone oxime, $C_{15}H_{14}ON_2$, requires C, 75·6; H, 5·9; N, 11·8%). Treatment with alkali furnished a small quantity of 1 : 3-dimethyl-2-azafluorene.

The original product (5·1 g.) was heated with methanol under reflux. The cooled solution deposited yellow needles (1·3 g.), m. p. *ca.* 320° (Found : C, 82·7; H, 6·6; N, 7·4%).

Attempted Preparation of 1 : 3-*Dimethyl*-2-*azafluorene*-9-*carboxylic Acid.*—1 : 3-Dimethyl-azafluorene (4·88 g.) was condensed with methyl oxalate in the presence of potassium methoxide, as described for fluorene by Campbell and Tucker (*loc. cit.*). The *substance* formed prismatic needles (4·1 g.), m. p. 215° (decomp.) (Found : C, 64·2; H, 5·7; N, 4·7. $C_{16}H_{15}O_5N$ requires C, 63·8; H, 5·0; N, 4·7%). It was insoluble in cold dilute alkali, and, on warming, passed into an oil. Dissolution in dilute hydrochloric acid, followed by basification, led to an oil. Melting was accompanied by rapid evolution of gas. Treatment with picric acid gave yellow needles (from ethanol), m. p. 248—249° (Found : C, 56·8; H, 3·9; N, 12·0%). Pyrolysis in liquid paraffin at 200° gave 1 : 3-dimethyl-2-azafluorene, m. p. 88—90°, alone or on admixture with an authentic specimen.

1 : 3-*Distyryl*-2-*azafluorenone.*—1 : 3-Dimethyl-2-azafluorenone (20·9 g.), benzaldehyde (63·6 g.), and acetic anhydride (61·2 g.) were heated under reflux for 7½ hours. After being kept overnight the separated solids were collected and crystallised from chloroform–light petroleum, to give 1 : 3-*distyryl*-2-*azafluorenone*, bright yellow needles (29·5 g.), m. p. 202° (Found : C, 87·1; H, 5·0; N, 3·7. $C_{28}H_{19}ON$ requires C, 87·3; H, 4·9; N, 3·6%).

2-*Azafluorenone*-1 : 3-*dicarboxylic Acid.*—The foregoing compound (9·6 g.) in pure pyridine (150 ml.) was kept at 55° whilst a warm solution of potassium permanganate (22·5 g.) in water (150 ml.) was slowly added with vigorous stirring during 30—45 minutes. Only gentle external heating was required during the addition. After a further 30 minutes at 55° the precipitated solids were collected and extracted three times with hot water. The bulked filtrate and extracts were evaporated to *ca.* 30 ml. under reduced pressure and then brought to pH 1—2 by addition of concentrated hydrochloric acid. After the mixture had cooled, the precipitated solids were collected, washed free from benzoic acid with water and ether, and crystallised from methanol. 2-*Azafluorenone*-1 : 3-*dicarboxylic acid* (84%) formed yellow needles, m. p. 217° (decomp.) (Found : C, 61·8; H, 3·1; N, 5·3. $C_{14}H_7O_5N$ requires C, 62·4; H, 2·6; N, 5·2%). The *di-silver* salt formed a yellow powder (Found : N, 2·9; Ag, 44·0. $C_{14}H_5O_5NAg_2$ requires N, 3·2; Ag, 44·7%).

2-*Azafluorene.*—Decarboxylation of the foregoing acid by pyrolysis at 20 mm. could only be effected on a 1-g. scale, to give 2-*azafluorenone*, yellow plates (30%) (from aqueous ethanol), m. p. 156—158° (Found : C, 79·5; H, 3·6; N, 7·6. $C_{12}H_7ON$ requires C, 79·6; H, 3·9; N, 7·7%). Reduction gave 2-azafluorene (Mills *et al.*, *loc. cit.*).

1 : 3-*Dimethyl*-9-*nicotinamido*-2-*azafluorene*, feathery needles (from aqueous ethanol), m. p. 271° (Found : C, 72·4; H, 5·6; N, 12·6. $C_{20}H_{17}ON_3,H_2O$ requires C, 72·1; H, 5·7; N, 12·6%), was obtained by treating 9-amino-1 : 3-dimethyl-2-azafluorene (4·2 g.) in pyridine (10 ml.) with nicotinoyl chloride hydrochloride (from 3 g. of nicotinic acid) in pyridine (5 ml.) with external cooling, followed by short heating on a water-bath. The *dihydrochloride* formed feathery crystals (from ethanol–ether), m. p. 325° (Found : C, 61·2; H, 5·0; N, 10·8; Cl, 18·5. $C_{20}H_{17}ON_3,2HCl$ requires C, 61·8; H, 4·9; N, 10·8; Cl, 18·3%).

2-*Diethylaminoethyl* 1 : 3-*dimethyl*-2-*azafluorenone*-4-*carboxylate* separated on cooling a mixture of 1 : 3-dimethyl-2-azafluorenone-4-carboxylic acid (5·0 g.), propan-2-ol (100 ml.), and 2-diethylaminoethyl chloride (3·5 g.) which had been refluxed for 2 hours. It formed crystals, m. p. 58—60°, from water (Found : C, 70·9; H, 6·8; N, 8·2. $C_{21}H_{24}O_3N_2$ requires C, 71·6; H, 6·8; N, 8·0%). The *hydrochloride* formed pale yellow crystals, m. p. 190° (Found : C, 64·9; H, 6·6; N, 7·2; Cl, 9·3. $C_{21}H_{24}O_3N_2,HCl$ requires C, 64·8; H, 6·4; N, 7·2; Cl, 9·1%).

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