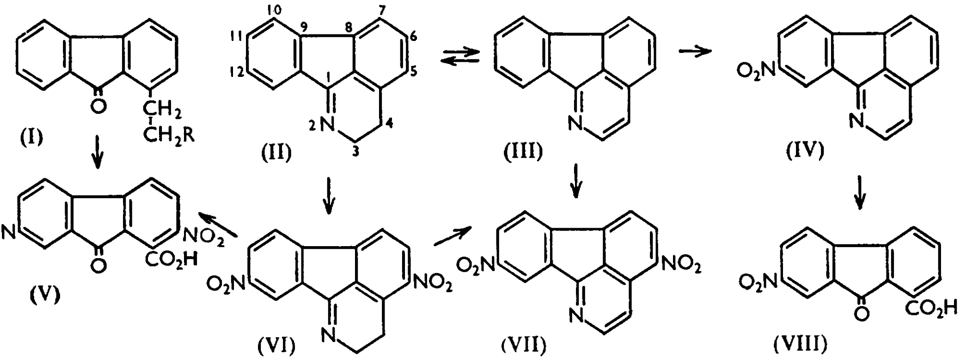
956. *The Synthesis and Properties of 2-Azafluoranthene.*

By Neil Campbell and Kenneth F. Reid.

The syntheses of 3 : 4-dihydro-2-azafluoranthene and 2-azafluoranthene are described. The latter substance is reduced to the former by sodium amalgam and ethanol and on nitration yields 12-nitro- and 5 : 12-dinitro-2-azafluoranthene.

2-Azafluoranthene (III) has been isolated from coal tar.[1] We have synthesised it by applying the Curtius reaction to β-(9-oxo-1-fluorenyl)propionic acid (I; R = CO_2H) to give the substituted ethylamine (I; R = NH_2), which with alkali affords 3 : 4-dihydro-2-azafluoranthene (II). This on dehydrogenation with palladised charcoal yields 2-azafluoranthene (III).



The amide (I; R = $CO{\cdot}NH_2$) undergoes the Hofmann reaction to yield directly impure dihydro-2-azafluoranthene (II), identified as the hydrochloride, methiodide, and picrate. Nitration of 2-azafluoranthene yields 12-nitro- (IV) and 5 : 12-dinitro-2-azafluoranthene (VII). The constitution of the mononitro-compound follows from oxidation of its methiodide to 7-nitrofluorenone-1-carboxylic acid (VIII). The dinitroazafluoranthene was orientated by its preparation by the dehydrogenation of 3 : 4-dihydro-5 : 12-dinitro-2-azafluoranthene (VI) (obtained by nitration of 3 : 4-dihydro-2-azafluoranthene), whose constitution is established by its oxidation to 2 : 7-dinitrofluorenone-1-carboxylic acid[2] (V). The structure of this acid was established by decarboxylation to 2 : 7-dinitrofluorenone.[3] The formation of 12-nitro-2-azafluoranthene is not unexpected since 4-azafluoranthene also undergoes nitration at position 12.[4]

Reduction of 2-azafluoranthene with 5% sodium amalgam and ethanol yields 3 : 4-dihydro-2-azafluoranthene, a somewhat surprising result since 3 : 4-dihydro-products

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[1] Kruber, *Chem. Ber.*, 1949, **82**, 199; Oberkobusch, *ibid.*, 1953, **86**, 975.

[2] Garascia, Fries, and Ching, *J. Org. Chem.*, 1952, **17**, 226.

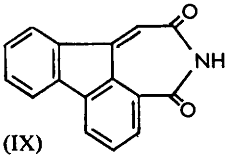
[3] Campbell and Stafford, *J.*, 1952, 299; A. Temple, Thesis, Edinburgh, 1954.

[4] Koelsch and Steinhauer, *J. Org. Chem.*, 1953, **18**, 1516; Campbell and Keir, *J.*, 1955, 1233.

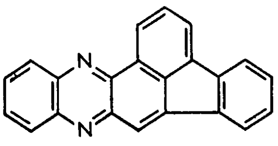
arising from the reduction of fluoranthene, quinoline, or *iso*quinoline have not been reported.[5] Reduction of 2-azafluoranthene or its dihydro-derivative with tin and hydrochloric acid yields 1 : 2 : 3 : 4-tetrahydro-2-azafluoranthene.

The absorption spectrum of 2-azafluoranthene contains three groups of bands and closely resembles that of fluoranthene.[6]

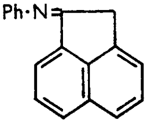
It was hoped that fluoranthene-3 : 4-quinone would react with hydrazoic acid to give 3-hydroxy-4-aza- or 4-hydroxy-3-aza-fluoranthene,[7] but the product was the imide (IX), whose structure was proved by hydrolytic degradation to fluorene-1-carboxylic acid. 1-Carboxylfluorenylideneacrylic acid is presumably an intermediate since fluorenylideneacrylic acid undergoes alkaline hydrolysis to fluorene. Our results emphasise the highly specific nature of the reaction of hydrazoic acid with *o*-quinones, since 1 : 2-naphthaquinone yields 4-amino-1 : 2-naphthaquinone, phenanthraquinone affords phenanthridone, and acenaphthenequinone yields naphthalic anhydride (probably *via* the imide).[8] Fluoranthenequinone reacts with *o*-phenylenediamine, giving 9 : 14-diazanaphtho[2 : 3-*b*]fluoranthene (X).



(IX)



(X)



(XI)

Acenaphthenone with hydrazoic acid in benzene gives the anil (XI).

EXPERIMENTAL

Chromatographic separations were effected on alumina, and ultraviolet spectra were measured by means of a Unicam SP. 500 spectrophotometer.

Synthesis of 2-Azafluoranthene.—Activated sodium azide [9] (2·6 g.) was added to β-(9-oxo-1-fluorenyl)propionyl chloride (from 10 g. of acid) in dry benzene (50 ml.) and the whole was heated for 20 hr. The filtered solution, when heated for 4 hr. with concentrated hydrochloric acid (50 ml.), deposited β-(9-*oxo*-1-*fluorenyl*)*ethylamine hydrochloride*, greenish-yellow plates (from dioxan), m. p. 210—211° (Found: C, 69·2; H, 5·4; N, 5·5; Cl, 13·6. $C_{15}H_{14}ONCl$ requires C, 69·4; H, 5·4; N, 5·4; Cl, 13·7%), which with alkali gave 3 : 4-dihydro-2-azafluoranthene [*hydrochloride*, orange needles (from ethanol–light petroleum), m. p. 193—194° (Found: N, 5·5. $C_{15}H_{12}NCl$ requires N, 5·8%; *methiodide*, orange-red needles (from ethanol), m. p. 252—253 (Found: I, 36·2. $C_{16}H_{14}NI$ requires I, 36·6%); *picrate*, orange needles (from ethanol), m. p. 229—230° (decomp.) (Found: N, 12·6. $C_{21}H_{14}O_7N_4$ requires N, 12·9%)]. The dihydroazafluoranthene was obtained in 40% yield by the action of sodium hypobromite on β-(9-*oxo*-1-*fluorenyl*)*propionamide*, yellow needles (from aqueous ethanol), m. p. 193—194° (Found: C, 76·5; H, 5·4; N, 5·4. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·2; N, 5·6%).

5% Sodium amalgam (40 g.) was added in small portions to 2-azafluoranthene (2 g.) in boiling ethanol (80 ml.), the solution boiled for 2 hr., the volume reduced to 50 ml., and the residue neutralised with concentrated hydrochloric acid and poured into water (400 ml.). The suspension was extracted with ether, and the extract dried (Na_2SO_4) and evaporated. The residual oil was chromatographed with light petroleum as solvent and developer. Elution yielded first 3 : 4-dihydro-2-azafluoranthene (1·14 g.), characterised as the picrate and methiodide, and then starting material (0·28 g.).

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[5] Knowles and Watt, *J. Amer. Chem. Soc.*, 1943, **65**, 410; Bohlmann, *Chem. Ber.*, 1952, **85**, 390; Jackman and Packham, *Chem. and Ind.*, 1955, 360.

[6] Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727; Clar, Stubbs, and Tucker, *Nature*, 1950, **166**, 1075.

[7] Cf. Badger and Seidler, *J.*, 1954, 2329.

[8] Wolff, "Organic Reactions," John Wiley and Son, Inc., New York, 1947, Vol. III, p. 320; Stephenson, *J.*, 1949, 2620; Edwards and Petrow, *J.*, 1948, 1713.

[9] Nelles, *Ber.*, 1932, **65**, 1345.

2-*Azafluoranthene.*—Dihydroazafluoranthene (0·3 g.) was boiled for 3 hr. in 1-methylnaphthalene (5 ml.) with 20% palladised charcoal (0·05 g.) in an atmosphere of carbon dioxide. The mixture was filtered and the catalyst washed with benzene. The combined filtrate and washings were extracted with concentrated hydrochloric acid, and the acid layer was made alkaline. The precipitate, dissolved in ether, was washed with water and dried (Na_2SO_4). Evaporation of the ether yielded 2-azafluoranthene (0·285 g.), pale yellow needles, m. p. 91—92° (lit., 83°, 91—92°), $\lambda_{max.}$ 233, 254, 258, 280, 287, 308, 349, 355, and 365 mμ (log ε 4·4, 3·93, 3·95, 4·05, 4·0, 3·05, 3·70, 3·75, 3·80 respectively), $\lambda_{min.}$ 219, 250, 256, 262, 282, 306, 310, 350, 359 mμ (log ε 4·05, 3·87, 3·9, 3·9, 4·0, 3·03, 2·97, 3·69, 3·65) in *cyclo*hexane. This compound formed a *methiodide*, orange needles (from ethanol), m. p. 273° (decomp.) (Found: N, 4·0; I, 36·6. $C_{16}H_{12}NI$ requires N, 4·1; I, 36·8%), *trinitrobenzene complex*, pale yellow needles (from ethanol), m. p. 126—127° (Found: N, 12·8. $C_{21}H_{12}O_6N_4$ requires N, 13·5%), and *hydrochloride*, yellow needles, m. p. 208—209° (from ethanol–light petroleum) (Found: N, 5·6; Cl, 12·5. $C_{15}H_{10}NCl$ requires N, 5·9; Cl, 14·8%). The picrate is recorded [1] as having m. p. 222° but we found m. p. 239°.

2-Azafluoranthene (0·5 g.) or 3 : 4-dihydro-2-azafluoranthene hydrochloride (0·5 g.) was boiled with concentrated hydrochloric acid (20 ml.) and tin (10 g.) until the solution was nearly colourless. More acid (5 ml.) was added and the whole was heated until a colourless solution resulted. The cooled solution was decanted, made alkaline, and extracted several times with ether. The combined extracts were washed with water and dried (Na_2SO_4). Evaporation yielded 1 : 2 : 3 : 4-tetrahydro-2-azafluoranthene (0·2 g.), colourless needles (from light petroleum), m. p. 74—76°. It decomposed when dried and formed a *hydrochloride*, prisms (from light petroleum), m. p. 258—260° (decomp.) (Found: N, 5·6; Cl, 14·2. $C_{15}H_{14}NCl$ requires N, 5·8; Cl, 14·6%), and a *picrate*, yellow needles (from ethanol), m. p. 225—228° (decomp.) (Found: N, 12·8. $C_{21}H_{16}O_7N_4$ requires N, 12·8%).

5 : 12-*Dinitro*-2-*azafluoranthene.*—Dihydro-2-azafluoranthene (1 g.) was kept for 17 hr. in nitric acid (*d* 1·5; 8 ml.) at room temperature. It was poured into a stirred solution of potassium carbonate, and the resulting 3 : 4-*dihydro*-5 : 12-*dinitro*-2-*azafluoranthene* crystallised from toluene–light petroleum in brownish-yellow needles (0·7 g.), m. p. 278—284° (decomp.), the m. p. depending on the rate of heating (Found: C, 61·4; H, 2·9; N, 13·8. $C_{15}H_9O_4N_3$ requires C, 61·0; H, 3·1; N, 14·2%).

Chromic anhydride (1·2 g.) in acetic acid (5 ml.) and water (5 ml.) was added to the dihydrodinitro-2-azafluoranthene (0·9 g.) in boiling acetic acid (25 ml.) and the whole poured into water. The precipitate in benzene–chlorobenzene was chromatographed and development with this mixture gave 5 : 12-*dinitro*-2-*azafluoranthene*, yellow needles (from toluene–chlorobenzene), m. p. 300—301°, undepressed when admixed with the dinitro-2-azafluoranthene described below (Found: C, 61·2; H, 2·2; N, 14·0. $C_{15}H_7O_4N_3$ requires C, 61·4; H, 2·5; N, 14·3%). The same product was obtained by keeping 2-azafluoranthene (0·5 g.) for 20 hr. in nitric acid (*d* 1·5; 5 ml.) at room temperature or by nitration with concentrated nitric acid in acetic acid or potassium nitrate and concentrated sulphuric acid.

The dihydrodinitro-2-azafluoranthene (0·75 g.), 30% sulphuric acid (75 ml.), and potassium permanganate (2 g.) were boiled until the permanganate was decolorised. The mixture was then treated with sulphurous acid. The precipitate was extracted with chloroform, most of the solvent distilled off, and light petroleum added to precipitate 2 : 7-dinitrofluorenone-1-carboxylic acid, yellow needles (from chlorobenzene–light petroleum), m. p. and mixed m. p. 265—268°, yielding 2 : 7-dinitrofluorenone, m. p. 292°, when decarboxylated in quinoline at 180° in presence of a trace of copper.

12-*Nitro*-2-*azafluoranthene.*—2-Azafluoranthene and dilute acid gave the *nitrate*, yellow needles (from ethanol), m. p. 179° (Found: 67·8; H, 3·8; N, 11·2. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·8; N, 10·5%). The nitrate (3·6 g.) was added slowly to concentrated sulphuric acid (18 ml.) with cooling and kept at room temperature for 1½ hr., then heated for 20 min. at 60° and poured into water. 12-*Nitro*-2-*azafluoranthene* separated, and was boiled with potassium carbonate solution, dried, and crystallised from benzene in yellow needles (1·8 g.), m. p. 250—252° (Found: C, 71·7; H, 3·4; N, 11·0. $C_{15}H_8O_2N_2$ requires C, 72·6; H, 3·2; N, 11·3%). The nitro-compound (0·8 g.) was heated for 1 hr. in excess of methyl toluene-*p*-sulphonate at 100°. The mixture was extracted twice with hot benzene and once with ether. The metho-toluene-*p*-sulphonate, yellow needles (1 g.), m. p. 218—220°, was converted by precipitation with potassium iodide into the more readily crystallisable *methiodide* which separated from aqueous ethanol in reddish-violet needles, m. p. 254—255° (Found: N, 7·1; I, 32·1. $C_{16}H_{11}O_2N_2I$ requires N, 7·2; I, 32·6%). Potassium permanganate (2 g.) in water (100 ml.) was added dropwise (4 hr.) to the methiodide (0·9 g.) in 10% potassium hydroxide solution (32 g.) at 60° and the solution having been kept at room temperature (1 hr.) was boiled and filtered. The manganese dioxide was extracted with boiling water, and the combined filtrates were acidified. The precipitate in chloroform was washed with water, dried (Na_2SO_4), evaporated to 1—2 ml. and when treated with light petroleum yielded 7-nitrofluorenone-1-carboxylic acid (0·05 g.), yellow needles (from acetic acid), m. p. and mixed m. p. 245—247°.

Fluoranthene-3 : 4-*quinone*.—The scant recorded description [10] of the preparation of the quinone requires supplementation. Chromic acid anhydride (15 g.) in water (10 ml.) and acetic acid (10 ml.) was added to fluoranthene (10 g.) in acetic acid (150 ml.) so that the temperature did not exceed 50°. The mixture was heated for 18 hr. on the water-bath, then poured into water (1·5 l.), and the brown-red precipitate was washed thoroughly with hot water. The precipitate in chloroform was extracted twice with 10% aqueous sodium carbonate, which on acidification gave fluorenone-1-carboxylic acid (4 g.), and the chloroform solution was reduced in volume and chromatographed. Development first with benzene and then benzene–chloroform (1 : 1 v/v) gave first fluoranthene (2 g.) and then the quinone (1·5 g.), red needles, m. p. 194° (lit., 188—189°), giving with *o*-phenylenediamine in acetic acid 9 : 14-*diazanaphtho*-[2 : 3-b]*fluoranthene*, yellow needles (from acetic acid), m. p. 229° (Found: C, 86·6; H, 3·8; N, 8·9. $C_{22}H_{12}N_2$ requires C, 86·8; H, 4·0; N, 9·2%).

Sodium azide (1·2 g., 0·018 mole) was added gradually to the quinone (1·4 g., 0·006 mole) in trichloroacetic acid (20 g.) at 60° with stirring, and heating was continued for 1 hr. Pouring into water (70 ml.) gave after several hours the *imide* (IX) (0·35 g.), subliming at 190—200°/0·1—0·5 mm. in yellow needles, m. p. 256° (Found: C, 77·5; H, 3·8; N, 6·1. $C_{16}H_9O_2N$ requires C, 77·7; H, 3·7; N, 5·7%). The imide (0·2 g.) was not hydrolysed by sulphuric or hydrochloric acid, but when boiled for 17 hr. with 20% sodium hydroxide solution (14 ml.) and acidified yielded fluorene-1-carboxylic acid (0·1 g.), m. p. and mixed m. p. 246—249°.

Fission of β-*Fluorenylidenenacrylic acid*.—Ethyl fluorenyl-9-glyoxylate, m. p. 85—87° (lit., 74—76°), α-hydroxy-9-fluorenylacetic acid, m. p. 205—206° (lit., 194—195°), and fluorenylideneacrylic acid, m. p. 228—229° (lit., 222—223°), were prepared by Wislicenus and Weitemeyer's method.[11] The acrylic acid (0·2 g.) was boiled for 6 hr. with sodium hydroxide (2·0 g.) in water (20 ml.). Fluorene (0·05 g.), m. p. and mixed m. p. 115°, collected in the condenser, and from the reaction mixture unchanged fluorenylideneacrylic acid (0·12 g.) was recovered.

Schmidt Reaction on Acenaphthenone.—Acenaphthenone yields a 2 : 4-*dinitrophenylhydrazone*, red needles (from xylene), m. p. 259—260° (Found: N, 15·9. $C_{18}H_{12}O_4N_4$ requires N, 16·1%). Hydrazoic acid (from 3·2 g. of sodium azide) in benzene was added to acenaphthenone (2·5 g.) in benzene (20 ml.) and concentrated sulphuric acid (4 ml.) and gave the *anil*, prisms (from ethanol), m. p. 93°, after chromatographic purification, blue fluorescence in solution (Found: C, 89·1; H, 5·6; N, 5·5. $C_{18}H_{13}N$ requires C, 88·9; H, 5·4; N, 5·8%).

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[10] Goldschmiedt, *Ber.*, 1877, **10**, 2029.
[11] Wislicenus and Weitemeyer, *Annalen*, 1924, **436**, 1.