[Contribution from the School of Chemistry of the University of Minnesota]

SYNTHESIS, NITRATION, AND OXIDATION OF 3-AZAFLUORANTHENE[1]

C. F. KOELSCH and ALFRED F. STEINHAUER

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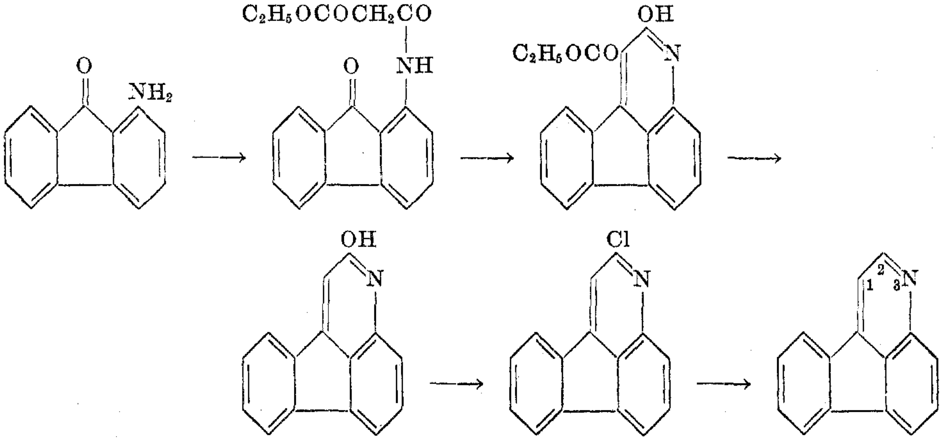
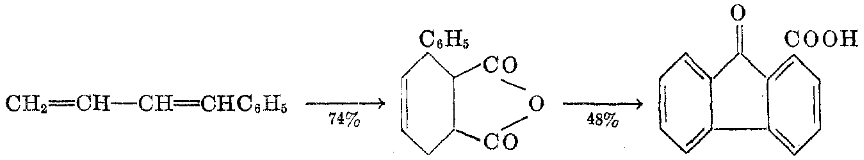
A substituted 4-phenyltetrahydroquinolinic acid is a key substance in a proposed morphine synthesis (1). The present work was undertaken to see if preparation of a possible precursor of the desired quinolinic acid might be achieved through synthesis and degradation of 3-azafluoranthene (I). The process was successful, but it involved too many steps to be a practical solution of the ultimate problem.

The following formulas indicate the route to 3-azafluoranthene.



The necessary 1-aminofluorenone was obtained through a Hoffmann degradation of the amide of fluorenone-1-carboxylic acid. Part of this acid was obtained in the usual way, and part was prepared by a new method, indicated in the following formulas.

$$CH_3CH{=}CHCHO + C_6H_5MgBr \xrightarrow[78\%]{} CH_3CH{=}CHCHOHC_6H_5 \xrightarrow[85\%]{}$$



Oxidation of 3-azafluoranthene with hot aqueous permanganate gave 2-azafluorenone-1-carboxylic acid (II) in 67% yield. The structure of the oxidation product was established by synthesis, shown below.

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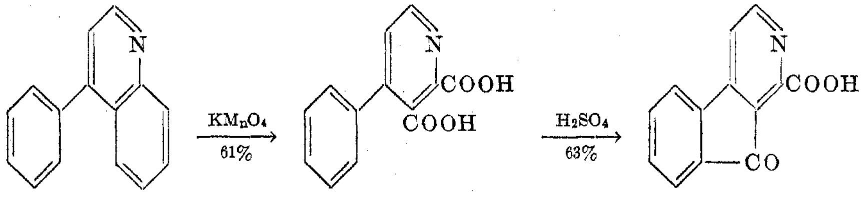
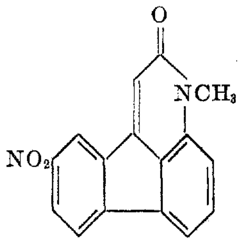
[1] From the Ph.D. thesis of A. F. Steinhauer, March 1950.

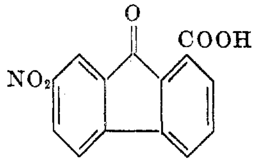


II

Nitration of 3-azafluoranthene gave 9-nitro-3-azafluoranthene in 70% yield. Orientation of the nitro group in the product could not be determined directly, because the nitro compound was resistant to oxidizing agents. However, the metho-*p*-toluenesulfonate of the nitro compound was oxidized by either alkaline permanganate or ferricyanide to the corresponding 3-methyl-9-nitro-3-aza-2-fluoranthone (III). The position of the nitro group in this substance was established by synthesis. 7-Nitrofluorenone-1-carboxylic acid (IV) was converted into 1-amino-7-nitrofluorenone, and a pyridone ring was built on this by the Camps reaction. Decarboxylation and methylation gave a product (III) identical with that obtained from 9-nitro-3-azafluoranthene.



III



IV

The 7-nitrofluorenone-1-carboxylic acid used was obtained by nitration of fluorenone-1-carboxylic acid. Decarboxylation of it yielded 2-nitrofluorenone, proving the nitro group to be in position 2 or 7. Reduction of the aminonitrofluorenone derived from the nitroacid gave a diamine which formed a diformyl derivative and not a glyoxaline with formic acid, showing that the two amino groups were not in the 1,2-positions. Thus they were in the 1,7-positions, and the nitro acid had the 1,7-orientation indicated above.[2]

EXPERIMENTAL

Fluorenone-1-carboxylic acid. (*A*). Oxidation of 400 g. of fluoranthene in 100-g. portions and purification through the barium salt according to the method of Fieser and Seligman (2) gave 237 g. (53%) of product, m.p. 185–190°.

(*B*). A solution of 290 g. of crotonaldehyde was added during 90 minutes to phenylmagnesium bromide prepared from 108 g. of magnesium in 1400 ml. of ether. The mixture was stirred for two hours and then decomposed with iced ammonium chloride. There was obtained 434–452 g. (71–77.5%) of α-phenyl-γ-methylallyl alcohol, b.p. 125° at 18 mm. The alcohol (886 g.) was added slowly from a dropping-funnel to 50 g. of potassium acid sulfate

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[2] Another proof of orientation of this acid has been published recently by Garascia, Fries, and Ching, *J. Org. Chem.*, **17**, 226 (1952).

in a one-liter Claisen flask set up for reduced pressure distillation and heated in an oil-bath at about 150°. 1-Phenylbutadiene and water distilled at 95–100° at 19 mm. Water was separated, and the crude diene (659 g., 85%) was dissolved in benzene and treated with 500 g. of maleic anhydride. The solution was boiled for 30 minutes, and then cooled, giving 850 g. (74%) of 3-phenyl-1,2,3,4-tetrahydrophthalic anhydride, m.p. 116–120°, reported 120° (3). A mixture of 200 g. of the anhydride with 120 g. of sulfur was stirred and heated at 215° for two hours. The melt was cooled somewhat, 600 ml. of concentrated sulfuric acid was added, and the whole was heated for ten minutes at 100° after complete solution had been effected. The solution was then poured on ice and the solid product was extracted with sodium carbonate. The impure acid (m.p. 175–200°) was extracted four times with boiling aqueous suspensions of barium carbonate (total 18 liters). Filtration and subsequent acidification with hydrochloric acid gave 43–48% of pure fluorenone-1-carboxylic acid.

1-Aminofluorenone. Fluorenone-1-carboxamide, m.p. 223–227°, yield 97%, was converted into 1-aminofluorenone, crude m.p. 107–114°, yield 47%, by the method of Huntress, Pfister, and Pfister (4). A similar procedure but using sodium hypochlorite gave a purer crude product, m.p. 113–117°, in the same yield.

1-Acetylaminofluorenone, m.p. 136–137° (reported m.p. 138–138.3°) could not be induced to undergo the Camps reaction with hot alcoholic sodium hydroxide or sodium ethoxide.

1-Carbethoxyacetamidofluorenone. (*A*). A solution of 65 g. of 1-aminofluorenone in 400 ml. of ethyl malonate was boiled for 30 minutes, and then most of the excess ethyl malonate was distilled under reduced pressure. The residue was stirred with 250 ml. of alcohol and cooled, giving 63.5 g. of crude product, m.p. 116–120°. Extraction with 1600 ml. of boiling alcohol left 5.5 g. of insoluble residue, m.p. 220–240°, and cooling the extract gave 54 g. (53%) of the desired product, yellow needles, m.p. 124–125.5°.

Anal. Calc'd for $C_{18}H_{15}NO_4$: C, 69.9; H. 4.9.

Found: C, 70.0; H, 4.9.

(*B*). A solution of 63 g. of 1-aminofluorenone and 52 g. of pyridine in 350 ml. of chloroform was treated with 70 g. of the acid chloride of ethyl hydrogen malonate (5) in 250 ml. of chloroform. The mixture was kept for three hours, and then the solid product was removed and washed with alcohol; yield 73 g., m.p. 119–125°. From the mother liquors there was recovered about 8 g. of aminofluorenone.

Ethyl 2-hydroxy-3-azafluoranthene-1-carboxylate. To a boiling solution of 94.3 g. of 1-carbethoxyacetamidofluorenone in 1600 ml. of absolute alcohol there was added a solution of 28 g. of sodium in 600 ml. of absolute alcohol. The mixture was boiled and stirred for 45 minutes, then cooled and filtered. The solid was suspended in 500 ml. of water and neutralized with hydrochloric acid. The resulting yellow crystalline product was washed with water and dried, giving 77.6 g. (87%) m.p. 251–256°. Recrystallization from nitrobenzene and dioxane gave yellow needles, m.p. 264–266°.

Anal. Calc'd for $C_{18}H_{13}NO_3$: C, 74.2; H, 4.5.

Found: C, 73.9; H, 4.8.

A mixture of 169 g. of ethyl 2-hydroxy-3-azafluoranthene-1-carboxylate and nine liters of 5% sodium hydroxide was boiled for three hours. The resulting solution was filtered and added dropwise and with mechanical stirring to boiling 1:1 hydrochloric acid; conc'd hydrochloric acid was added in portions to keep the mixture strongly acid. The precipitate was washed with water and dried giving 151 g. (98%) of *2-hydroxy-3-azafluoranthene-1-carboxylic acid*, m.p. 298–300° dec.

Crystallization from acetic acid gave orange needles containing solvent. These were boiled with water for 90 minutes giving a yellow-orange powder, m.p. 298–300° dec.

Anal. Calc'd for $C_{16}H_9NO_3$: C, 73.0; H, 3.5.

Found: C, 72.8; H, 3.4.

3-Azafluoranthol-2. The preceding acid (40.7 g.) was heated in a metal bath at 310° for 2.5 hours. The residue was ground, washed with dil. sodium hydroxide, and dried. Continued extraction with 400 ml. of boiling dioxane left a black tar, and cooling the extract gave 22.7 g. (66%) of yellow crystals, m.p. 275–277°. Sublimation and crystallization from acetic acid gave a pure product, m.p. 277–279°.

Anal. Calc'd for $C_{15}H_9NO$: C, 82.2; H, 4.1.

Found: C, 82.0; H, 4.1.

2-Chloro-3-azafluoranthene. (*A*). A solution of 6.4 g. of 3-azafluoranthol-2 in 20 ml. of phosphorus oxychloride was boiled for 30 minutes, then poured on ice and neutralized with sodium hydroxide. There was obtained 5.8 g. (83%) of product, yellow needles from ligroin and alcohol, m.p. 121–122°.

Anal. Calc'd for $C_{15}H_8ClN$: C, 75.8; H, 3.4.

Found: C, 76.1; H, 3.6.

(*B*). 2-Hydroxy-3-azafluoranthene-1-carboxylic acid (35 g.) was heated at 300° for one hour, and the melt was then spread in a thin layer by swirling the flask while it was cooled. There was added 100 ml. of phosphorus oxychloride, and the whole was boiled for one hour. The solution was poured on iced sodium hydroxide, and the resulting solid was dried (31.7 g.) and distilled rapidly, boiling point 265° at 17 mm. (Even the pure material decomposes partly when it is distilled.) There was obtained 25–29 g. (82–89%) of nearly pure 2-chloro-3-azafluoranthene.

When 2-chloro-3-azafluoranthene was boiled for four hours with excess alcoholic sodium ethoxide, it yielded *2-ethoxy-3-azafluoranthene*, flesh-colored needles from dilute alcohol, m.p. 76.5–77.5°.

Anal. Calc'd for $C_{17}H_{13}NO$: C, 82.6; H, 5.3.

Found: C, 82.8; H, 5.5.

3-Azafluoranthene. A solution of 15 g. of 2-chloro-3-azafluoranthene and 4.4 g. of potassium hydroxide in 1450 ml. of absolute alcohol was treated with 3 ml. of Raney nickel and shaken under hydrogen at atmospheric pressure for 11 hours. During this time, 2159 ml. of hydrogen was absorbed (calc'd 1593 ml.), but blank experiments indicated that 500–600 ml. of hydrogen was used to bring the alcohol into equilibrium with the hydrogen atmosphere. The solution was then filtered, acidified with hydrochloric acid, and distilled to dryness. The base was freed and converted into its *picrate*, which was washed with hot alcohol (24.3 g., m.p. 265–276°) and crystallized from four liters of nitromethane, giving 21.7 g. (79%) of deep orange needles, m.p. 275–276°.

Anal. Calc'd for $C_{21}H_{12}N_4O_7$: C, 58.3; H, 2.8.

Found: C, 58.6; H, 3.0.

The *free base* (9.1 g.) had b.p. 240–245° at 23 mm. and formed yellow needles from ligroin, m.p. 102–103°.

Anal. Calc'd for $C_{15}H_9N$: C, 88.7; H, 4.5.

Found: C, 88.9; H, 4.9.

A solution of 12 g. of 3-azafluoranthene in dilute nitric acid was evaporated, and the residue was crystallized from alcohol, giving 15.2 g. of the *nitrate*, orange needles, m.p. 175–189° dec.

Anal. Calc'd for $C_{15}H_9N + HNO_3$: C, 67.7; H, 3.8.

Found: C, 67.9; H, 4.0.

Oxidation of 3-azafluoranthene. A mixture of 2 g. of the base and 50 ml. of water was boiled and stirred while 3% potassium permanganate was added slowly. After six hours, 369 ml. (11.1 g., calc'd 8.3 g.) had been added, and decolorization became much slower. The mixture was filtered, concentrated to 125 ml., and made weakly acid with nitric acid, giving 1.5 g. (67%) of crude product, m.p. 184° dec., which could be purified only through its ester.

A solution of 0.4 g. of the crude acid and 0.5 ml. of sulfuric acid in 25 ml. of methanol was boiled for two hours, then concentrated and treated with aqueous soda. Crystallization from methanol gave 0.32 g. (76%) of *methyl 2-azafluorenone-1-carboxylate*, pale yellow needles, m.p. 114.5–115.5°, soluble in dil. HCl.

Anal. Calc'd for $C_{14}H_9NO_3$: C, 70.3; H, 3.8.

Found: C, 70.2; H, 3.9.

Saponification of the ester with 5% aqueous sodium hydroxide gave *2-azafluorenone-1-carboxylic acid,* yellow crystals from water, m.p. 191° dec.

Anal. Calc'd for $C_{13}H_7NO_3$: C, 69.3; H, 3.1.

Found: C, 69.7; H, 3.4.

Synthesis of the oxidation product. β-Chloropropiophenone (95 g.), aniline (110 g.), aniline hydrochloride (77 g.), alcohol (77 g.), and stannic chloride pentahydrate (198 g.) were heated and stirred together at 100° for one hour, and the mixture was then treated with excess potassium hydroxide (6). Fractional distillation of the precipitate gave 38.9 g., b.p. 160–195° at 3 mm., which furnished 41.1 g. of the yellow picrate of 4-phenylquinoline, m.p. 223–226° (reported 225°). Decomposition of the picrate with lithium hydroxide (7) gave 18.9 g. (16%) of 4-phenylquinoline as an oil, reported m.p. 61–62° (8), which formed a sulfate m.p. 192–194°, reported m.p. 195–196° (9) and a methiodide m.p. 220.5–221.5° dec., reported m.p. 222° dec. (9).

A mixture of 17.5 g. of 4-phenylquinoline and 300 ml. of water was boiled and stirred while powdered potassium permanganate was added in about 5-g. portions. After six hours 103 g. of oxidizing agent had been added (calc'd 81 g.), and decolorization became slow. The solution was filtered and concentrated to 175 ml., and 130 ml. of the concentrate was made distinctly acid with nitric acid. There was precipitated 9.4 g. (61%) of *4-phenylquinolinic acid,* colorless plates from water, m.p. 173–175° dec.

Anal. Calc'd for $C_{13}H_9NO_4$: C, 64.2; H, 3.7.

Found: C, 63.8; H, 3.9.

A solution of 0.5 g. of the acid in 2 ml. of sulfuric acid was heated at 100° for 20 hours, then diluted and neutralized with sodium hydroxide. There was obtained 0.3 g. (63%) of 2-azafluorenone-1-carboxylic acid, m.p. 182–185° dec. Esterification gave the methyl ester m.p. 114.5–115.5° alone or mixed with the product obtained from 3-azafluoranthene.

Nitration of 3-azafluoranthene. 3-Azafluoranthene nitrate (7.8 g.) was added slowly to 35 ml. of sulfuric acid, while the temperature was kept below 35°. The solution was kept at room temperature for 90 minutes, then warmed to 60° for 20 minutes. It was then poured into water, and the yellow precipitate was removed and boiled with dil. sodium carbonate. Boiling the residue with one liter of toluene left 0.9 g. of insoluble material, and cooling the toluene extract gave 4.36 g. (60%) of yellow plates, m.p. 264–268°. Concentration of the mother liquor gave 0.78 g. of slightly impure product. Crystallization from benzene gave pure *9-nitro-3-azafluoranthene,* yellow plates m.p. 264–266°.

Anal. Calc'd for $C_{15}H_8N_2O_2$: C, 72.6; H, 3.3.

Found: C, 72.5; H, 3.3.

The nitro compound was recovered unchanged after it had been boiled with 4% aqueous permanganate for one hour, and also after it had been heated at 95° with excess permanganate in pyridine.

Reduction of 0.8 g. of the nitro compound in 100 ml. of alcohol with platinum oxide and hydrogen at atmospheric pressure gave 0.51 g. (73%) of *9-amino-3-azafluoranthene,* red needles from alcohol, m.p. 263–266°.

Anal. Calc'd for $C_{15}H_{10}N_2$: C, 82.5; H, 4.6.

Found: C, 82.4; H, 4.6.

The amine was oxidized with hot 4% permanganate, but no useful product was obtained. It was diazotized in dil. sulfuric acid, but boiling this solution gave a red-brown solid, m.p. 280–300° that could not be crystallized. When it was heated with 1:1 hydrochloric acid at 240° for four hours, the amine was partly unchanged and partly resinified.

9-Nitro-3-azafluoranthene (0.5 g.) was warmed at 100° with excess methyl *p*-toluenesulfonate for 45 minutes. The mixture was extracted with hot benzene, leaving 0.87 g. (99%) of yellow crystals, m.p. 266–268° that could not be recrystallized. For analysis the salt was converted into *9-nitro-3-azafluoranthene methiodide* by precipitating its aqueous solution with potassium iodide; red needles from water, m.p. 280–282° dec.

Anal. Calc'd for $C_{16}H_{11}IN_2O_2$: C, 49.3; H, 2.8.

Found: C, 49.4; H, 3.1.

A solution of 0.93 g. of 9-nitro-3-azafluoranthene metho-*p*-toluenesulfonate in 270 ml. of water at 10–15° was added to 1.44 g. of potassium ferricyanide in 90 ml. of 5% sodium hydroxide. The mixture was stirred for 15 minutes while it was being cooled in an ice-bath, and the insoluble product (0.497 g.) was then removed and crystallized from boiling toluene. There was obtained 0.431 g. (72%) of *3-methyl-9-nitro-3-aza-2-fluoranthone*, yellow needles, m.p. 307–309°.

Anal. Calc'd for $C_{16}H_{10}N_2O_3$: C, 69.1; H, 3.6.

Found: C, 69.3; H, 4.0.

The fluoranthone (0.015 g.) was first obtained by oxidation of 0.085 g. of 9-nitro-3-azafluoranthene metho-*p*-toluenesulfonate in aqueous potassium hydroxide with 0.033 g. of potassium permanganate. It was resistant to further oxidation by chromic acid in acetic acid, and gave amorphous black material with potassium dichromate in sulfuric acid.

7-Nitrofluorenone-1-carboxylic acid. A solution of 18.9 g. of fluorenone-1-carboxylic acid in 50 ml. of conc'd sulfuric acid was stirred and kept below 30° while a solution of 7.5 g. of sodium nitrate in 45 ml. of sulfuric acid was added. After one hour, the mixture was poured into water, and the precipitate was removed and boiled with 300 ml. of 10% sodium hydroxide. The resulting solution was cooled and filtered; the filtrate contained an orange acidic substance, m.p. 160–185°; the residue was dissolved by boiling it with 10 g. of sodium hydroxide in 3500 ml. of water. Filtration then removed a dark impurity, and acidification gave a bright yellow solid, m.p. 237–242° (18.5 g., 82%). Recrystallization from alcohol gave yellow needles, m.p. 242–244°. This substance, reported m.p. 245–246° (10) has been analyzed but not recognized as the 7-nitro compound (however, see footnote 2).

When 7-nitrofluorenone-1-carboxylic acid was mixed with a little copper acetate and heated at 300–310° for 45 minutes, it gave a sublimate of 2-nitrofluorenone, m.p. 216–218° alone or mixed with an authentic sample.

7-Nitrofluorenone-1-carboxamide, obtained in 87% yield by treating the acid with thionyl chloride and then with conc'd aqueous ammonia, formed yellow crystals from acetic acid, m.p. 275–277°.

Anal. Calc'd for $C_{14}H_8N_2O_4$: C, 62.7; H, 3.0.

Found: C, 62.3; H, 3.0.

1-Amino-7-nitrofluorenone. A suspension of 16.5 g. of 7-nitrofluorenone-1-carboxamide in 30 ml. of water was treated with potassium hypobromite from 3.5 ml. of bromine, 275 ml. of ice-water, and 21 g. of potassium hydroxide. The mixture was stirred for 90 minutes, then mixed with 30 g. of potassium hydroxide and heated for one hour. The solid was removed and extracted with eight liters of boiling alcohol. Cooling the extract gave 7.4 g. (50%) of product, orange needles, m.p. 261–263°.

Anal. Calc'd for $C_{13}H_8N_2O_3$: C, 65.0; H, 3.4.

Found: C, 64.8; H, 3.8.

1,7-Diaminofluorenone. A suspension of 0.5 g. of 1-amino-7-nitrofluorenone and 1 g. of ammonium chloride in 200 ml. of alcohol was treated with 7.5 g. of $Na_2S \cdot 9H_2O$, boiled for two hours, and then distilled to a small volume. The product was washed with water and crystallized from alcohol giving bright red needles (0.38 g., 87%), m.p. 228–232°.

Anal. Calc'd for $C_{13}H_{10}N_2O$: C, 74.3; H, 4.8.

Found: C, 74.1; H, 5.0.

A solution of 0.35 g. of the diamine in 15 ml. of 85% formic acid was boiled for four hours and then cooled. The resulting *1,7-diformylaminofluorenone* (0.37 g., 82%) formed yellow orange needles from formic acid, m.p. 281–283°.

Anal. Calc'd for $C_{15}H_{10}N_2O_3$: C, 67.7; H, 3.8.

Found: C, 67.7; H, 4.0.

When the diformyl derivative was boiled for a few minutes with 1:1 hydrochloric acid, it was hydrolyzed to 1,7-diaminofluorenone, indicating that it was not a glyoxaline formate.

1-Carbethoxyacetamido-7-nitrofluorenone. A paste of 5 g. of 1-amino-7-nitrofluorenone and 6 g. of pyridine was treated slowly with 14 g. of the acid chloride of ethyl hydrogen malonate while it was stirred and cooled. The mixture was then extracted with 100 ml. of hot alcohol, and the residue was crystallized from acetic acid, giving 5 g. of bright yellow needles which sintered at 195–200°, then resolidified and did not melt below 300°.

Anal. Calc'd for $C_{18}H_{14}N_2O_6$: C, 60.9; H, 4.0.
Found: C, 60.7; H, 4.1.

Ethyl 2-hydroxy-9-nitro-3-azafluoranthene-1-carboxylate. A solution of 3.5 g. of the preceding compound in 1800 ml. of hot absolute alcohol was treated with a solution of 0.8 g. of sodium in 100 ml. of alcohol. The precipitate which formed rapidly was removed and boiled with dilute acetic acid. It was crystallized from glacial acetic acid and then boiled with water giving 1.8 g. (54%) of yellow needles, m.p. 305–307°.

Anal. Calc'd for $C_{18}H_{12}N_2O_5$: C, 64.3; H, 3.6.
Found: C, 64.4; H, 3.7.

2-Hydroxy-9-nitro-3-azafluoranthene-1-carboxylic acid. A mixture of 1.57 g. of the preceding ester with 25 ml. of 1:1 sulfuric acid was boiled for 45 minutes, then cooled and poured in water. The precipitate was crystallized from acetic acid and boiled with water, giving 1.35 g., m.p. 336–338° dec.

Anal. Calc'd for $C_{16}H_8N_2O_5 + CH_3COOH$: C, 58.7; H, 2.6.
Found: C, 58.7; H, 3.3.

9-Nitro-3-azafluoranthol-2. The preceding acid (0.3 g.) was heated at 345° and 3 mm. for several minutes, and then distilled. The distillate (0.17 g., 66%) was a yellow crystalline material that did not melt below 370°. It was recrystallized from acetic acid and boiled with water.

Anal. Calc'd for $C_{15}H_8N_2O_3$: C, 68.2; H, 3.1.
Found: C, 68.3; H, 3.5.

A solution of 0.03 g. of 9-nitro-3-azafluoranthol-2 in 30 ml. of hot methanol containing 0.5 g. of potassium hydroxide was mixed with 10 ml. of methyl iodide and boiled for one hour. Most of the solvent was distilled, and the product was precipitated with water and crystalized from toluene. It formed yellow needles, m.p. 307–309°, alone or mixed with the 3-methyl-9-nitro-3-aza-2-fluoranthone obtained by oxidation of 9-nitro-3-azafluoranthene metho-*p*-toluenesulfonate. The ultraviolet absorption spectra of the two samples in 95% alcohol were identical [λ_{max} (mμ), $\epsilon \times 10^{-4}$]: 375, 1.05; 300, 2.07; 235, 3.97.

SUMMARY

1-Aminofluorenone in the Camps pyridonation reaction yields a product which has been transformed by standard methods into 3-azafluoranthene. This new heterocyclic substance has been found to undergo nitration in position-9, and to be oxidized by permanganate with formation of 2-azafluorenone-1-carboxylic acid.

Fluorenone-1-carboxylic acid has been prepared by a new method, and its nitration product has been characterized as 7-nitrofluorenone-1-carboxylic acid.

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