Anal. Calcd. for $C_{13}H_5Br_2NO_3$: C, 40.76; H, 1.32; N, 3.66; Br, 41.73. Found: C, 40.99; H, 1.46; N, 3.39; Br, 41.67.

1,3-Diamino-2-nitrofluorenone. A suspension of 0.57 g. of finely powdered 1,3-dibromo-2-nitrofluorenone in 90 ml. of absolute ethanol was saturated with gaseous ammonia at 0°, heated in a pressure bottle to 60° for 48 hr. and cooled to give orange needles, 0.28 g., m.p. 205° (Kofler block), from benzene or ethanol. λ_{max} 248 mμ (ϵ = 15,750); 264 (14,890); 292 (17,450); 304 (16,010); 355 (22,930); 455.5 (4790); λ_{min} 225 (11,070); 255 (14,100); 273.5 (12,860); 301 (15,850); 330 (9110); 417 (3110).

Anal. Calcd. for $C_{13}H_9N_3O_3$: C, 61.17; H, 3.56; N, 16.46. Found: C, 61.05; H, 3.76; N, 16.37.

The diacetyl derivative, *N, N'(2-nitro-9-oxo-1,3-fluorenylene) bisacetamide*, 102 mg., m.p. 325°, was prepared by refluxing 100 mg. of the amine for 8 hr. with 10 ml. each of acetic acid and acetic anhydride. Chromatography in benzene on alumina, and recrystallization from a mixture of benzene and ethanol, or from acetic acid gave colorless needles, m.p. 328° (Kofler). λ_{max} 265.5 mμ (ϵ = 25,970); λ_{min} 235 (14,310).

Anal. Calcd. for $C_{17}H_{13}N_3O_5$: C, 60.18; H, 3.86; N, 12.38. Found: C, 59.75; H, 4.24; N, 12.37.

1,2,3-Triacetylaminofluorene. 1,3-Diamino-2-nitro-9-fluorenone (0.8 g.) was subjected to a Wolff-Kishner reaction with 24 ml. of hydrazine hydrate and 40 ml. of diethylene glycol in a nitrogen atmosphere. Dilution with 100 ml. of oxygen-free water gave a precipitate which dissolved in 1*N* hydrochloric acid and reprecipitated by hydrazine hydrate yielded 530 mg. of crude 1,2,3-fluorenetriamine, m.p. 204°. This somewhat unstable compound was immediately acetylated by acetic anhydride in benzene to give a white triacetyl derivative (400 mg.), m.p. 285–287°, from acetic acid and benzene. λ_{max} 217 mμ(ϵ=34,890), 244 (31,340), 272.5 (23,160); λ_{min} 231 (22,260); 259 (18,270); shoulder 310 mμ (7310).

Anal. Calcd. for $C_{19}H_{19}N_3O_3$: C, 67.64; H, 5.68; N, 12.46. Found: C, 67.37; H, 5.82; N, 12.41.

Reaction of 1,3-dibromo-2-nitro-9-fluorenone with ethanolic alkali. A suspension of 497 mg. of 1,3-dibromo-2-nitrofluorenone in 70 ml. each of ethanol and 2*N* aqueous potassium hydroxide was refluxed for 35 hr. giving a red solution, which was diluted with water and acidified. The precipitate was dissolved in alkali (Norit) and reprecipitated with acid to give yellow 2-nitro-3-hydroxy-9-fluorenone (284 mg., 91%), m.p. and mixed m.p. 247°, from ethanol and benzene.

Anal. Calcd. for $C_{13}H_7NO_4$: C, 64.73; H, 2.93; N, 5.81. Found: C, 64.86; H, 3.33; N, 5.36.

1-Bromo-2-nitro-3-hydroxy-9-fluorenone. 1,3-Dibromo-2-nitrofluorenone (1.1 g.) in 35 ml. each of pyridine and 1*N* aqueous potassium hydroxide was refluxed for 1 hr. (color dark green), poured into water, acidified, and extracted with ether. The ether layer was shaken with bicarbonate and the aqueous layer acidified to give 1-bromo-2-nitro-3-hydroxyfluorenone (0.5 g.), m.p. 257° (raised to 257–258°, from benzene, acetic acid, ethanol, and dilute ethanol), positive Beilstein test. λ_{max} 258 mμ (ϵ = 30,630); 263 (30,710); 299 (31,030); 410 (2900); λ_{min} 228 (12,180); 260 (30,610); 296 (9800); 387 (2700).

Anal. Calcd. for $C_{13}H_6BrNO_4$: C, 48.77; H, 1.89; Br, 24.97. Found: C, 48.99; H, 2.13; Br, 25.67.

Further refluxing of this compound for 5.5 hr. in equal volumes of pyridine and 4*N* potassium hydroxide resulted in the recovery of the starting material. However, when 0.5 g. of compound was refluxed for 2 hr. in 25 ml. each of ethanol and 6*N* aqueous potassium hydroxide, 346 mg. (92%) of 2-nitro-3-hydroxyfluorenone, m.p. and mixed m.p. 248° was obtained.

Bethesda 14, Md.

[Contribution from the Laboratory of Biochemistry, National Cancer Institute[1]]

Derivatives of 3-Fluorofluorene by the Pschorr Synthesis

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The reaction of *p*-fluorophenylmagnesium iodide with 6-oxo-2-methyl-4,5-benz-1,3-oxazine (from acetic anhydride and anthranilic acid) gave 2-(4'-fluorobenzoyl)acetanilide, which was hydrolyzed to the amine. A Pschorr reaction on the latter afforded 3-fluorofluorenone, which in turn was readily reduced to 3-fluorofluorene. The intermediate aminofluorobenzophenone was also prepared by a Hofmann reaction on the corresponding amide. A Curtius reaction on *o*-benzoylbenzoic acid in the presence of pyridine yielded moderate amounts of 2-aminobenzophenone, but without pyridine the main product was *N*-phenylphthalimide. From the dinitration of 3-fluorofluorene the 2,7-dinitro derivative was obtained in good yield. Reduction of this compound by hydrogen sulfide gave a mixture of amines from which 3-fluoro-7-nitro-2-fluorenamine was isolated and characterized.

In connection with the preparation of fluorinated derivatives of the carcinogen *N*-2-fluorenylacetamide, a number of approaches to the synthesis of the required intermediates, especially 3-fluorofluorene, were explored. In a previous publication[3] the preparation of this compound from 3-fluorenamine was described. The present paper deals with two other routes giving 3-fluorofluorene from commercially available starting material. In addition, the dinitration of 3-fluorofluorene, and products related thereto will be described. Furthermore, some observations bearing on the chemistry of *ortho*-substituted benzophenones will be discussed.

One method leading to 3-fluorofluorenone consisted in the inverse addition of a Grignard reagent from *p*-fluoroiodobenzene to 6-oxo-2-methyl-4,5-benz-1,3-oxazine, itself readily available from acetic anhydride and anthranilic acid. The product, 2-(4'-fluorobenzoyl)acetanilide was converted to the corresponding amine, 2-amino-4'-fluorobenzophenone, which in turn was subjected to a Pschorr reaction with production of 3-fluorofluorenone. This

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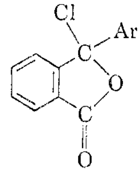
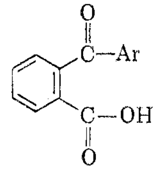
[3] K. Suzuki, E. K. Weisburger, and J. H. Weisburger, *J. Org. Chem.*, **24**, 1511 (1959).

compound was reduced in good yield to the fluorene derivative by a Wolff-Kishner reaction.

Another path to the intermediate 2-amino-4′-fluorobenzophenone involved a Hofmann reaction[4] on 2-(4′-fluorobenzoyl)benzamide. This amide was prepared from the acid *via* the ethyl ester. It could not be made *via* the acid[5] chloride, presumably because of the predominance of the pseudo form of the acid chloride, indicated by an infrared peak at 5.58 μ.[6] In contrast, the acid, ester, and amide existed primarily in the normal form, as evidenced by the similarity of their infrared peaks of 5.90 and 5.97, 5.86 and 5.99, and 5.86 and 6.01 μ, respectively.



Pseudo form



Normal form

Further evidence for the existence of normal and pseudo forms of certain derivatives of *o*-benzoylbenzoic acid was provided by the attempts to obtain 2-amino-4′-fluorobenzophenone from the corresponding acid by means of a modified Curtius reaction, successfully used in a number of other such conversions.[7] Thus, preparation of the azide, *via* the acid chloride, yielded an oil which when decomposed in the presence of acetic anhydride led mainly to *N*-(4′-fluorophenyl)phthalimide, and also gave small amounts of other, not precisely identified materials. Some parallel studies with *o*-benzoylbenzoic acid itself entirely confirmed the findings of Bhatt, of Arcus and associates, and of Badger *et al.*[8] who reported benzoylanthranilic acid, 6-oxo-2-phenyl-4,5-benzo-1,3-oxazine and chiefly *N*-phenylphthalimide as products of the Schmidt reaction on this acid. We have observed, however, that decomposition of the azide in a Curtius reaction in the presence of pyridine also led to moderate yields of the expected 2-aminobenzophenone, in addition to the above materials.

Another route to 3-fluorofluorene was by way of the corresponding diphenylmethane derivatives. The crucial intermediate 2-(4′-fluorobenzyl)benzoic acid,[9] m.p. 124°, was prepared best in two steps from the benzophenone derivative: (*1*) A reduction to the lactone, 3-(*p*-fluorophenyl)phthalide, m.p. 101°, with zinc and ammonia, (*2*) a reduction of this compound with phosphorus and hydrogen iodide. The use of the latter step alone on the benzophenone derivative yielded the dilactone, and only 50% of the desired acid. Likewise, a Wolff-Kishner reduction was unsuitable, for ring closure with production of 1-(2H)-2-(4′-fluorophenyl)-phthalazinone was the preponderant reaction taking place.

The modified Curtius reaction on 2-(4′-fluorobenzyl)benzoic acid gave excellent yields of the expected amine, 2-(4′-fluorobenzyl)aniline, *via* the intermediate acetyl and diacetyl derivatives, in contrast to the behavior in the benzophenone series. However, the Pschorr reaction on this amine afforded only traces of the fluorene derivatives, probably because of steric factors in the diphenylmethane derivative. Owing to the tetrahedral nature of the configuration around the methylene carbon, the phenyl rings are not coplanar and ring closure is thus not favored. On the other hand, benzophenones are coplanar, and ring closure is generally facile.[10]

The dinitration of 3-fluorofluorene, not previously studied, in acetic acid with fuming nitric acid led to the 2,7-dinitro derivative, in analogy with the reaction of fluorene. A mixture of amines was obtained by the action of hydrogen sulfide on this compound. The pure compound isolated from this reduction was 3-fluoro-7-nitro-2-fluorenamine, as proved by the isolation of 3-fluoro-7-nitrofluorene upon deamination.

EXPERIMENTAL

The melting points were determined in a capillary tube and are not corrected. The ultraviolet spectra were recorded by Mr. P. H. Grantham on a Cary recording spectrophotometer as 5×10^{-5} *M* solutions in ethanol and the infrared spectra on a Perkin-Elmer spectrophotometer, model 21, as solids in potassium bromide disks. We are indebted to the staff of the NIH Microanalytical Laboratory for the analyses.

Ethyl 2-(4′-fluorobenzoyl)benzoate. 2-(4′-Fluorobenzoyl)-benzoic acid[5] (84.7 g.), m.p. 138–139°, and 3 ml. of concd. sulfuric acid in 230 ml. of absolute ethanol was refluxed for 6 hr. Dilution with water gave 76.5 g. of the ester, m.p. 78–80°, from cyclohexane (lit.[5] m.p. 80°). λ_{max} 246.5 mμ (ϵ = 6990); λ_{min} 228 (5600).

Anal. Calcd. for $C_{16}H_{13}FO_3$: C, 70.58; H, 4.81. Found: C, 70.48; H, 5.01.

2-(4′-Fluorobenzoyl)benzamide. Ethyl 2-(4-fluorobenzoyl)-benzoate (12.8 g.) in 70 ml. of absolute ethanol, saturated

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(4) K. Suzuki, S. Kajigaeshi, and M. Sano, *Yûki Gôsei Kagaku Kyôkai Shi,* 16, 82 (1959).

(5) F. C. Hahn and E. E. Reid, *J. Am. Chem. Soc.*, **46**, 1645 (1924).

(6) W. Graf, E. Girod, E. Schmid, and W. G. Stoll, *Helv. Chim. Acta*, **42**, 1085 (1959).

(7) E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, **23**, 1193 (1958).

(8) M. V. Bhatt, *Chem. and Ind.*, 1390 (1956); C. L. Arcus and M. M. Coombs, *J. Chem. Soc.*, 3698 (1953); C. L. Arcus and R. E. Marks, *J. Chem. Soc.*, 1627 (1956); G. M. Badger, R. T. Howard, and A. Simons, *J. Chem. Soc.*, 2849 (1952).

(9) Hahn and Reid[5] reported a m.p. of 148–149° for this compound, prepared by reducing the benzophenone derivative with copper sulfate activated zinc dust in aqueous ammonium hydroxide or sodium hydroxide. The discrepancy in the melting point is not clear. The single analysis for fluorine shown by Hahn and Reid for this substance exhibits a larger deviation from theoretical (found 7.78%, calcd. 8.26%) than any of the other compounds listed in their paper. In our hands the use of ethanolic ammonium hydroxide and ordinary zinc dust led to the lactone, m.p. 101°.

(10) D. F. DeTar, *Org. Reactions*, 9, 409 (1957).

with ammonia gas at 0°, was heated in a pressure bottle for 24 hr. at 50°, and the solvent evaporated. The residue extracted with dilute sodium hydroxide gave a recovery of 1.5 g. of 2-(4′-fluorobenzoyl)benzoic acid. The alkali-insoluble part recrystallized from benzene yielded 8.3 g. of the amide, m.p. 174° (raised to 177–178°). λ_{max} 270 mμ (ϵ = 1230); 285 (450); λ_{min} 268 (1140); general absorption below 260 mμ.

Anal. Calcd. for $C_{14}H_{10}FNO_2$: C, 69.13; H, 4.14. Found: C, 69.36; H, 4.22.

2-Amino-4′-fluorobenzophenone. To an ice-cold solution of 0.7 g. of bromine and 1.5 g. of potassium hydroxide in 20 ml. of water, 1.09 g. of powdered amide was added slowly with stirring. After 2 hr., 2.25 g. of potassium hydroxide in 2.25 ml. of water was introduced and the mixture was heated at 100° for 45 min. to give a light yellow amine (0.57 g., 59%), m.p. 124–125° (raised to 127–128°), from cyclohexane. λ_{max} 234 mμ (ϵ = 13,660); 375 (5600).

Anal. Calcd. for $C_{13}H_{10}FNO$: C, 72.69; H, 4.92. Found: C, 72.40; H, 4.77.

The hydrochloride melted at 187–188° dec. Acetylation of the amine in benzene with acetic anhydride gave *2-(4′-fluorobenzoyl)acetanilide,* m.p. 98–100°, from methanol, identical with the material described below.

3-Fluorofluorenone. Finely powdered sodium nitrite (1.77 g.) was stirred into an ice-cold solution of 4.73 g. of the amine in 440 ml. of 50% sulfuric acid over 1 hr. After 2–3 hr. at 25°, and 0.5 hr. at 100° the mixture was cooled. An ether extract was washed with sodium bicarbonate and the ether was evaporated. The residue was sublimed *in vacuo* to give yellow 3-fluorofluorenone (3.72 g., 85%) m.p. 124–126° (raised to 128–129°), from cyclohexane. λ_{max} 249 mμ (ϵ = 46,770); 257 (65,560); 280 (2700); 290.5 (3970); 309 (1430); λ_{min} 250 (46,140); 272.5 (1740); 286.5 (2380); 305 (1190).

Anal. Calcd. for $C_{13}H_7FO$; C, 78.77; H, 3.56. Found: C, 79.29; H, 4.09.

Acidification of the bicarbonate extract in some runs gave a precipitate of *4′-fluoro-2-hydroxy-3(or 5)-nitrobenzophenone,* m.p. 99–100°. This compound presumably is the result of the action of excess nitrite on the phenol produced initially. λ_{max} 250 mμ (ϵ = 14,790); λ_{min} 225 (11,400).

Anal. Calcd. for $C_{13}H_8FNO_4$: C, 59.77; H, 3.09; N, 5.36. Found: C, 60.30; H, 3.79; N, 5.40.

3-Fluorofluorene. 3-Fluorofluorenone (3.6 g.) and 11 ml. of 85% hydrazine hydrate in 25 ml. of diethylene glycol was refluxed for 1.5 hr. The condenser was removed until the temperature rose to 185°, then refluxing was continued for 2 hr. The product collected on dilution with water was sublimed *in vacuo* and chromatographed on alumina in benzene: 3-Fluorofluorene (2.5 g., 75%), m.p. 80°, from cyclohexane, (lit.[3] m.p. 77–78°).

2-(4′-Fluorobenzoyl)acetanilide. This method was based on that of Lothrop and Goodwin.[11] A benzoxazine, m.p. 77–80°, was isolated from the reaction of acetic anhydride on anthranilic acid. A filtered Grignard reagent, from 13 g. of *p*-fluoroiodobenzene, 1.52 g. of magnesium, and 35 ml. of ether, was dropped into a cold solution of 9.4 g. of the benzoxazine in 216 ml. of dry benzene during 1.5 hr., and stirred 1 hr. more. After 15 hr. the reaction mixture was decomposed with 150 ml. of 3*N* sulfuric acid, the upper layer washed with water, the solvents evaporated, and the product chromatographed on alumina in benzene to give colorless needles (8.5 g., 57%), m.p. 96–97° (raised to 99–101°), from methanol. λ_{max} 235 mμ (ϵ = 21,900); 324 (2400) λ_{min} 220.5 (15,600), 294 (1700).

Anal. Calcd. for $C_{15}H_{12}FNO_2$: C, 70.03; H, 4.70. Found: C, 70.26; H, 4.93.

Hydrolysis of 0.5 g. of the acetylamino derivative in 1.5 ml. of 12*N* hydrochloric acid and 5 ml. of ethanol, and neutralization gave 0.38 g. (90%) of amine, m.p. 124–126° (from ethanol), undepressed by admixture of the amine obtained in the Hofmann reaction.

2-(4′-Fluorobenzyl)benzoic acid. A. The following is the preferred procedure. 2-(4′-Fluorobenzoyl)benzoic acid (9.7 g.) in 120 ml. of ethanol and 50 ml. of ammonium hydroxide was refluxed for 2 hr. with 25 g. of zinc dust. After removal of the zinc and concentration, 8.95 g. of the *lactone* (4-fluorophenyl)phthalide, m.p. 100–101°, crystallized. λ_{max} 264 mμ (ϵ = 1240); 270 (1420); 281 (1300); λ_{min} 248 (500), 267.5 (1160), 278 (1100); general absorption below 230 mμ.

Anal. Calcd. for $C_{14}H_9FO_2$: C, 73.68; H, 3.97. Found: C, 73.67; H, 4.21.

The lactone (8.95 g.) was refluxed for 5 hr. in 80 ml. of acetic acid and 15 ml. of hydriodic acid with 3 g. red phosphorus and diluted with water. Solution in bicarbonate and reprecipitation with acid gave 8.6 g. (over-all yield 93%) of *2-(4′-fluorobenzyl)benzoic acid,* m.p. 122–124°, from cyclohexane. λ_{max} 266.5 mμ (ϵ = 1940); 273 (2010); λ_{min} 254 (1250); 270 (1520); general absorption below 240 mμ.

Anal. Calcd. for $C_{14}H_{11}FO_2$: C, 73.03; H, 4.82. Found: C, 72.79; H, 5.09.

B. 2-(4′-Fluorobenzoyl)benzoic acid (18 g.) was refluxed in 100 ml. of acetic acid, 40 ml. of 50% hydroiodic acid, and 1 g. of red phosphorus for 9 hr. Dilution with water gave a precipitate extracted with bicarbonate. Acidification produced 8.9 g. (52%) of 2-(4′-fluorobenzyl)benzoic acid, m.p. 123°. The portion insoluble in bicarbonate was the *dilactone,* bis-(4-fluorophenyl)phthalide, 7.9 g. m.p. 272–273°, from benzene. λ_{max} 265 mμ (ϵ = 2920); 269.5 (3100); 277(3400); 284 (3660); λ_{min} 255 (2320), 267 (2900), 273 (3000), 281 (3300); general absorption below 240 mμ.

Anal. Calcd. for $C_{28}H_{16}F_2O_4$: C, 74.00; H, 3.55. Found: C, 73.60; H, 3.60.

The dilactone was converted in about 50% yield to the phthalide derivative, m.p. 100°, by refluxing for 1 hr. in ethanolic potassium hydroxide.

1(2H)-4-(4′-Fluorophenyl)phthalazinone. A white precipitate increasing with time appeared as 2.4 g. of 2-(4′-fluorobenzoyl)benzoic acid, 11 ml. of hydrazine hydrate, and 25 ml. of diethylene glycol was refluxed for 1 hr. Dilution with water gave 2.4 g. of compound, m.p. 257–264° (raised to 267–268.5°), from acetic acid, ethyl acetate, or *n*-butyl alcohol. λ_{max} 292.5 mμ (7900); λ_{min} 269 (5600).

Anal. Calcd. for $C_{14}H_9FN_2O$: C, 69.99; H, 3.78; N, 11.66. Found: C, 69.76; H, 4.00; N, 11.63.

Modified Curtius reaction on 2-(4′-fluorobenzyl)benzoic acid. The finely powdered acid (11.5 g.) stood 18 hr. in 100 ml. of thionyl chloride at 25°. The excess thionyl chloride was distilled *in vacuo* and traces removed by three further codistillations with petroleum ether. Sodium azide (4 g.) in 4 ml. of water was added to the residual acid chloride, m.p. 36–38°, in 100 ml. of dry acetone at −40°. After 2 hr. the mixture was poured into cold water and extracted with benzene. The dry (calcium chloride at 5°) benzene layer was distilled *in vacuo* leaving the azide as a light yellow oil.

The oil in 100 ml. of acetic anhydride was heated until gas evolution stopped, then poured into ice water. Extraction of the product with ether, and evaporation of the solvent yielded 10.6 g. (75%) of colorless *2″-(4‴-fluorobenzyl)diacetanilide* or 2-diacetylamino-4′-fluorodiphenylmethane, m.p. 67–69°, from petroleum ether. λ_{max} 260.5 mμ (ϵ = 1220); 266 (1510); 272 (1350); λ_{min} 247 (800), 262 (1200), 270 (850).

Anal. Calcd. for $C_{17}H_{16}FNO_2$: C, 71.56; H, 5.65; N, 4.91. Found: C, 71.74; H, 5.59; N, 4.80.

The ether-insoluble portion, 2.1 g. (17%), m.p. 152–154°, was *2-(4′-fluorobenzyl)acetanilide,* m.p. 155–156°, from benzene.

Anal. Calcd. for $C_{15}H_{14}FNO$: C, 74.05; H, 5.80; N, 5.76. Found: C, 73.68; H, 5.85; N, 5.87.

Both mono- and diacetylamino derivatives were hydrolyzed to 2-(4′-fluorobenzyl)aniline, m.p. 56–57°, from cyclohexane, in 85–90% yields by refluxing for 1.5 hr. in 12*N*

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[11] W. C. Lothrop and P. A. Goodwin, *J. Am. Chem. Soc.,* **65**, 363 (1943); *cf.* A. Mustafa, *et al., J. Am. Chem. Soc.,* **77**, 1612 (1955); A. Morrison and T. P. C. Mulholland, *J. Chem. Soc.,* 2702 (1958); E. D. Bergmann and R. Barshai, *J. Am. Chem. Soc.,* **81**, 5641 (1959).

hydrochloric acid, followed by neutralization. Direct hydrolysis of the crude mixture of mono- and diacetyl derivatives gave an over-all yield of 93% of amine. λ_{max} 235 mμ (ϵ = 7250); 266.5 (1900); 272.5 (2200); 287 (2280) λ_{min} 225 (6170), 262 (1500), 269 (1560), 276.5 (1800).

Anal. Calcd. for $C_{13}H_{12}FN$: C, 77.58; H, 6.01; N, 6.96. Found: C, 77.41; H, 6.16; N, 7.14.

Direct hydrolysis of the azide was not so useful. Thus, the azide from 2.3 g. of acid was refluxed for 1 hr. with 12*N* hydrochloric acid. The acid-soluble product yielded 220 mg. (11%) of amine, m.p. 56°. The acid-insoluble material was *sym-di[2-(4'-fluorobenzyl)phenyl]urea,* 0.49 g., m.p. 229–230° from benzene. λ_{max} 247 mμ (ϵ = 17,000), 272 (5600); λ_{min} 230 (10,600), 270.5 (5400).

Anal. Calcd. for $C_{27}H_{22}F_2N_2O$: C, 75.68; H, 5.18; N, 6.54. Found: C, 76.08; H, 5.50; N, 6.68.

The amine (200 mg.) in 500 ml. of ice-cold 60% sulfuric acid was diazotized with 100 mg. of sodium nitrite during 1.5 hr., refluxed 40 min., diluted with water, and extracted with benzene. The benzene solution was washed with 1*N* potassium hydroxide, evaporated, and the residue sublimed *in vacuo* giving 10 mg. of 3-fluorofluorene, m.p. 69–71° (raised to m.p. and mixed m.p. 74°, from petroleum ether).

Attempted Curtius reaction on 2-(4'-fluorobenzoyl)benzoic acid. The acid chloride, from 34.2 g. acid and 100 ml. of thionyl chloride, in 300 ml. cold, dry acetone was treated with 11 g. of sodium azide in 30 ml. water. The azide, extracted into cold benzene after dilution with ice water, was freed of solvent. After refluxing in 250 ml. of acetic anhydride for 3 hr. the solution was poured into water. The oily product was dissolved in 250 ml. of hot ethanol and the solution concentrated to give white felt-like *4'-fluorophenylphthalimide* (11.9 g.), m.p. 180–181.5°, from ethanol.

Anal. Calcd. for $C_{14}H_8FNO_2$: C, 69.71; H, 3.34. Found: C, 69.90; H, 3.42.

Modified Curtius reaction on benzophenone-2-carboxylic acid. The acid chloride, from 22.6 g. of acid and thionyl chloride at 25°, reacted in 300 ml. of cold acetone and 10 ml. of pyridine with 8 g. of sodium azide in 20 ml. of water. The azide was extracted into benzene, freed of solvent *in vacuo,* and refluxed with 150 ml. of acetic anhydride for 1.5 hr. *N-Phenylphthalimide* (6 g.) m.p. 199–201°, formed upon addition of water.

The filtrate taken to *p*H 6 with bicarbonate gave an oily precipitate, which was dissolved in ether. The solution extracted with bicarbonate and the latter acidified gave 1 g. of *N-benzoylanthranilic acid,* m.p. 185–188°. The ether solution, evaporated and the residue chromatographed in benzene on alumina, gave 6.7 g. of oily material which was refluxed for 3 hr. with equal volumes of 12*N* hydrochloric acid and ethanol. Neutralization and dilution with water gave 4.5 g. of *2-aminobenzophenone,* m.p. 102°. 2-Aminobenzophenone could not be isolated if pyridine was omitted during the formation and decomposition of the azide.

2,7-Dinitro-3-fluorofluorene. Powdered 3-fluorofluorene (9.2 g.) was vigorously stirred into 75 ml. of acetic and 75 ml. of fuming nitric acid (d = 1.5) over 15 min. The temperature rose to 55°. Upon cooling, 9.0 g. (66%) of yellow 2,7-dinitro-3-fluorofluorene, m.p. 274° (raised to 278–279°), from acetic acid, was collected. λ_{max} 329 mμ (ϵ = 24,980); λ_{min} 255 (3800).

Anal. Calcd. for $C_{13}H_7FN_2O_4$: C, 56.93; H, 2.57. Found: C, 56.63; H, 2.73.

In addition, 93 mg. of 7-nitro-3-fluorofluorene, m.p. and mixed m.p. 197° was isolated from the mother liquor.

3-Fluoro-2,7-fluorenediamine. Low-pressure catalytic reduction of 548 mg. of the dinitro compound over platinum oxide in 80 ml. of ethanol gave 310 mg. of diamine, m.p. 178° (raised to 181–182°), from cyclohexane. λ_{max} 293.6 mμ (ϵ = 23,840); 337 (9350); λ_{min} 247 (2660), 325 (8390).

Anal. Calcd. for $C_{13}H_{11}FN_2$: N, 13.08. Found: N, 12.81.

3-Fluoro-7-nitro-2-fluorenamine. A hot suspension of 8.3 g. of 2,7-dinitro-3-fluorofluorene in 400 ml. of ethanol and 140 ml. of 15*N* ammonium hydroxide was treated with hydrogen sulfide over 160 min. Dilution with water and repeated extraction of the resulting precipitate with 2900 ml. of 0.5*N* hydrochloric acid gave 4.6 g. of a crude mixture of amines. Orange 3-fluoro-7-nitro-2-fluorenamine (0.9 g.), m.p. 240° (raised to 242–243°) was obtained after crystallization from benzene, and from acetic acid as the acid sulfate[12]; λ_{max} 253 mμ (ϵ = 11,350), 390 (18,620); λ_{min} 227.5 (6610); 298 (2380).

Anal. Calcd. for $C_{13}H_9FN_2O_2$: C, 63.93; H, 3.71. Found: C, 64.07; H, 3.91.

Deamination of this compound (0.66 g.) by 3.8 ml. of hypophosphorous acid, after diazotization in 13 ml. of acetic acid, 1.4 ml. of water, and 0.5 ml. of sulfuric acid with 0.18 g. of sodium nitrite in 0.4 ml. of water, gave a crude product (0.62 g.) m.p. 192°. Vacuum sublimation at 160° gave 0.47 g. (75%) of 7-nitro-3-fluorofluorene (2-nitro-6-fluorofluorene), m.p. and mixed m.p. 197°, from acetic acid. Thus, the amino group in the compound, m.p. 243° described above, was in the 2- position.

2,7-Dinitro-3-fluoro-9-fluorenone. 2,7-Dinitro-3-fluorofluorene (5 g.) in 350 ml. of acetic acid was refluxed for 12 hr. while 57 ml. of red fuming nitric acid was added dropwise. Dilution with water gave 3.8 g. of yellow needles, m.p. 235–236°, from acetic acid. λ_{max} 281.5 mμ (ϵ = 35,020); 325.5 (8300); 340 (8170); λ_{min} 231.5 (13,450); 319 (7970); 334 (7550).

Anal. Calcd. for $C_{13}H_5FN_2O_5$: C, 54.18; H, 1.75; N, 9.72. Found: C, 53.93; H, 2.01; N, 9.63.

The same compound was also obtained by addition of 1 ml. of fuming nitric acid to a cooled solution of 0.9 g. of 7-nitro-3-fluorofluorenone in 12 ml. of concd. sulfuric acid. After 1 hr. the mixture was poured onto ice to give needles (0.6 g.), m.p. and mixed m.p. with the product above, 235–236°, from acetic acid.

6-Fluoro-2-amino-9-fluorenone. Hydrogen sulfide and 1.2 g. of 7-nitro-3-fluorofluorenone in 100 ml. of boiling ethanol and 60 ml. of ammonium hydroxide for 1 hr. followed by extraction of the crude product with dilute hydrochloric acid gave 0.52 g. of violet needles, m.p. 200° (raised to 210–211°, from benzene). λ_{max} 277 mμ (ϵ = 44,320); 327 (7270); λ_{min} 230 (6390); 315 (6740).

Anal. Calcd. for $C_{13}H_8FNO$: C, 73.23; H, 3.78; Found: C, 73.42; H, 3.99.

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[12] J. H. Weisburger and E. K. Weisburger, *J. Org. Chem.,* **21,** 514 (1956).