10.95 (vinyl hydrogen), and 13.20 μ (four adjacent hydrogens on an aromatic ring). The NMR spectrum was in agreement with the assigned structure, *o*-divinylbenzene.

Cotrimerization of divinylacetylene and methylacetylene. To a dry 500-ml. reactor equipped with a mechanical stirrer, condenser, dropping funnel, gas addition tube (open-end type extended below liquid level) and a thermometer, there was added 200 ml. of toluene dried with calcium hydride. Triisobutylaluminum (5 ml.) was added to the reactor under nitrogen by means of a hypodermic syringe, followed by titanium tetrachloride (1.5 ml.). Methylacetylene, dried by passing it through a tower containing Drierite, was added at the rate of 1.2 moles per hour. Concurrently, a solution of 15.6 g. (0.2 mole) of divinylacetylene in 50 ml. of toluene was added dropwise over a period of 80 min. Throughout the reaction, the temperature was maintained between 9° and 16° by means of an ice bath. Ten minutes after completion of the addition of the divinylacetylene, the catalyst was deactivated by addition of 50 ml. of methanol. On distillation there was obtained 40 g. of a trimethylbenzene isomer mixture, b.p. 32°/2 mm., and 9 g. (28% yield) of dimethyl-*o*-divinylbenzene[12] isomer mixture, b.p. 50–51°/0.2 mm., n_D^{25} 1.5598 and $\lambda_{max}^{C_2H_5OH}$ 228 mμ (ϵ 23,200).

Anal. Calcd. for $C_{14}H_{16}$: C, 91.14; H, 8.86; mol. wt., 158. Found: C, 90.73; H, 9.13; mol. wt., 158 (by mass spectrometry).

Gas chromatographic analysis of the product using a 1-m. Perkin Elmer Column R at 168° (preheat 220°) with a helium flow of 75 ml./min. showed three components with retention times of 11.7 min., 14.2 min., and 17.2 min., representing approximately 5%, 85%, and 10%, respectively, of the total. The three isomers were not identified.

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WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE LABORATORY OF BIOCHEMISTRY, NATIONAL CANCER INSTITUTE[1]]

Replacement and Elimination of Bromine in Bromonitrofluorenones. The Preparation of 2,3- and 1,2,3-Substituted Fluorenes and Fluorenones

KAZUO SUZUKI,[2] ELIZABETH K. WEISBURGER, AND JOHN H. WEISBURGER

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The oxidation by peracetic acid of 2-amino-3-bromofluorene and 2-amino-3-bromofluorenone, and of 1,3-dibromo-2-fluorenamine furnished the corresponding nitro derivatives. In the nitrobromofluorenones the bromine was readily replaced by amino groups in ethanolic ammonia. Ethanolic potassium hydroxide introduced a hydroxyl group into these compounds, but in one case elimination of bromine in the 1-position with substitution by hydrogen occurred. Potassium hydroxide in pyridine substituted a hydroxyl for a bromine at the 3-, but not at the 1-position in 1,3-dibromo-2-nitrofluorenone. These replacement reactions led to the facile preparation of a number of new 2,3- and 1,2,3-substituted fluorenones, and fluorenes.

The recent description[3] of a procedure for the oxidation of a primary aromatic amine by peracetic acid to the corresponding nitro derivative has suggested its use for the purpose of activating halogens *ortho* to the nitro group, thereby permitting the selective replacement of the halogen by other functional groups. The present paper deals with the application of this method to the convenient preparation of a number of otherwise difficultly available 2,3- and 1,2,3-substituted fluorene and fluorenone derivatives.

Bromination of 2-aminofluorenone by bromine afforded the 3-bromo derivative. The use of *tert*-butyl bromide in dimethyl sulfoxide[4] in addition produced 2-amino-3-bromo-9-fluorenol. Reduction of 2-amino-3-bromofluorenone by the Wolff-Kishner reaction resulted in good yields of 3-bromo-2-fluorenamine, provided that the reaction was performed in the absence of alkali. If alkali was added, halogen elimination ensued so that the product was 2-fluorenamine.

The action of peracetic acid on the 2-amino-3-bromofluorene and 2-amino-3-bromofluorenone readily gave the nitro derivatives. In the resulting nitrobromofluorenone bromine was easily replaced by amino, or by hydroxyl to yield the corresponding 2-nitro-3-amino-9-fluorenone or 2-nitro-3-hydroxy-9-fluorenone. This latter material served as a good source for the otherwise difficultly prepared 2-amino-3-fluorenol.[5] In fact, this aminohydroxyfluorene could be made in a single sequence of operations directly from 2-nitro-3-bromo-9-fluorenone by first treating with alkali under mild conditions, followed by addition of hydrazine and raising the temperature, thus effecting the Wolff-Kishner reaction. This new, short sequence of steps would appear to be the procedure of choice for the preparation of 2-amino-3-fluorenol.

Attempts to replace the bromine by fluorine in 2-nitro-3-bromo-9-fluorenone in acetamide as solvent gave the expected elimination of bromine, but under these conditions fluorine did not enter

(1) National Institutes of Health, Public Health Service, Department of Health, Education and Welfare.

(2) Visiting Scientist, National Cancer Institute. On leave of absence from Yamaguchi University, Ube, Japan.

(3) W. L. Mosby and W. L. Berry, *Tetrahedron*, 5, 93 (1959).

(4) T. L. Fletcher and H. L. Pan, *J. Am. Chem. Soc.*, **78**, 4812 (1956). T. L. Fletcher, M. J. Namkung, and H. L. Pan, *Chem. and Ind.*, 660 (1957).

(5) E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, 19, 964 (1954).

the molecule. Instead, a hydroxyl group and an amino group were introduced, even though the reactants had been rigorously dried. The amino group possibly resulted from the partial dissociation of acetamide. Indeed, when dimethylsulfoxide was used under mild conditions, only the hydroxy compound was formed. In none of the many attempts could a fluorine-containing compound be detected.[6] Likewise, although the bromine atom was eliminated, there was no evidence for the formation of a bifluorene derivative in this reaction.

The authentic bifluorene was prepared in poor yield by the action of activated copper on 2-nitro-3-bromo-9-fluorenone. In this instance as well, loss of halogen with production of 2-nitrofluorenone was the main reaction. Dehalogenation during the Ullmann reaction has been observed by Longo and Pirona.[7]

Peracetic acid likewise smoothly oxidized 1,3-dibromo-2-fluorenamine to the nitro derivative. Some 1,3-dibromo-2-nitro-9-fluorenone was also produced. In the latter compound both halogens proved susceptible to replacement by amino groups, thus yielding a 1,2,3-nitrogen substituted fluorenone derivative. On the other hand, refluxing 1,3-dibromo-2-nitrofluorenone with aqueous ethanolic alkali did not give the expected dihydroxy compound, but furnished instead 2-nitro-3-hydroxy-9-fluorenone. The halogen at the 1-position was eliminated under the influence of alkali, just as in the case of the Wolff-Kishner reaction of 3-bromo-2-aminofluorenone in the presence of potassium hydroxide, discussed above. Performance of the reaction in pyridine and alkali, however, led to the replacement of the bromine at the 3- position only, giving 1-bromo-2-nitro-3-hydroxyfluorenone. This compound also lost the halogen under the influence of ethanolic alkali.

It was of some interest to investigate whether the replacement of halogen by other functions in these fluorenones was mediated as a result of activation by the nitro group, or whether the keto group played a major role.[8] To this end, exchange reactions of 1,3-dibromo-2-nitrofluorene with ethanolic ammonia and ethanolic potassium hydroxide were performed as described for the fluorenone derivative. In the case of ammonia, about 30% of the starting material was recovered, and in addition a small amount of 1,3-dibromo-3-nitro-9-fluorenone was also isolated. Silver bromide equivalent to a 13% replacement of halogen was found. The potassium hydroxide reaction gave only a trace of alkali-soluble product. In addition, a number of unidentified substances were observed in both reactions. All of these exhibited a band in the infrared which indicated the presence of a keto function, suggesting that the exchange of halogen for another substituent occurs only when the keto group is present. Apparently the single nitro group does not activate an *ortho* halogen sufficiently in the fluorene ring system. Bradley and Williams also noted the inertness of 2-nitrofluorene to the action of potassium hydroxide in pyridine under conditions where 2-nitrofluorenone reacted.[9]

EXPERIMENTAL

The melting points were determined in a capillary tube and are not corrected. In a few cases, high melting points were taken on a Kofler apparatus. The ultraviolet spectra were recorded by Mr. P. H. Grantham on a Cary recording spectrophotometer as $5 \times 10^{-5}M$ 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.

2-Amino-3-bromo-9-fluorenone. A. 2-Amino-9-fluorenone (12 g.) in 200 ml. acetic acid reacted with 3.16 ml. bromine at 20° to yield 2-amino-3-bromo-9-fluorenone (11.9 g., 71%), m.p. 210° (from ethanol) (lit.[4] m.p. 216°).

B. 2-Amino-9-fluorenone (7.6 g.) in 196 ml. dimethyl sulfoxide was treated with 4.45 ml. of *t*-butyl bromide at 105° for 1.5 hr. and poured into water.[4] Extraction of the product by refluxing benzene gave upon cooling 1.9 g. of brick-red 2-amino-3-bromo-9-fluorenone, m.p. 210°. Extraction of the benzene-insoluble material with hot 1*N* hydrochloric acid and subsequent neutralization gave 1.5 g. of *2-amino-3-bromo-9-fluorenol,*[10] m.p. 198° (raised to 205–206°, from ethanol and benzene). Thus, reduction of the keto function in a position *para-* to the entering bromo group was a concomitant reaction.

Anal. Calcd. for $C_{13}H_{10}BrNO$: C, 56.54; H, 3.65; N, 5.79; Br, 28.93. Found: C, 56.80; H, 3.74; N, 5.27; Br, 28.36.

3-Bromo-2-fluorenamine. A Wolff-Kishner reduction of 5.5 g. of 2-amino-3-bromo-9-fluorenone, 20 ml. of 85% hydrazine hydrate, and 40 ml. of diethylene glycol afforded in 2 hr. 4.8 g. (91%), of 3-bromo-2-fluorenamine, m.p. 137–139° (colorless plates from cyclohexane) (lit.[4] m.p. 142.5°).

In the presence of potassium hydroxide the only product isolated was 2-fluorenamine. Thus, 550 mg. of ketone, 2 ml. of hydrazine hydrate, 170 mg. of alkali, and 5 ml. of glycol gave 462 mg. of product, m.p. 115°, which was sublimed *in vacuo* and recrystallized from cyclohexane: 185 mg. (51%) of 2-fluorenamine, m.p. and mixed m.p. 124° (lit.[11] m.p. 127.5°).

2-Nitro-3-bromofluorene. 3-Bromo-2-fluorenamine (4.2 g.) in 60 ml. 40% peracetic acid was refluxed for 10 min. (color changes through green to brown) and cooled. The crude product was sublimed *in vacuo* at 130° and the sublimate crystallized from acetic acid: 2-Nitro-3-bromofluorene (1.6 g., 35%), m.p. 130–131°. From the sublimation residues and the mother liquors 1 g. (20%) of 2-nitro-3-bromofluorenone, m.p. 250° was isolated. λ_{max} 260 mμ (ϵ = 12,910); 307 (10,-180); λ_{min} 239 (8860), 275 (7000).

Anal. Calcd. for $C_{13}H_6BrNO_2$: C, 53.81; H, 2.78. Found: C, 54.15; H, 3.07.

(6) We are grateful to Dr. C. G. Finger, Illinois State Geological Survey, Urbana, Ill., for valuable discussions regarding the introduction of fluorine into aromatic compounds by exchange reactions.

(7) B. Longo and M. Pirona, *Gazz. chim. ital.*, **77**, 117 (1947).

(8) P. E. Fanta, *Chem. Revs.*, **38**, 139 (1946).

(9) W. Bradley and F. P. Williams, *J. Chem. Soc.*, 1205 (1959).

(10) Catalytic reduction of 2-amino-3-bromofluorenone over platinum oxide in ethanol also furnished the fluorenol, m.p. and mixed m.p. 205°.

(11) W. E. Kuhn, *Org. Syntheses*, **Coll. Vol. II**, 447 (1943).

2-Nitro-3-bromofluorenone. 2-Amino-3-bromo-9-fluorenone (5.05 g.) in 100 ml. of 40% peracetic acid was refluxed for 3 hr. (color change to dark yellow). A small amount of potassium bichromate was added and refluxing continued briefly to give upon cooling 5.3 g. of product, m.p. 254° (m.p. 255–257°, from benzene or acetic acid) λ_{max} 260 mμ (ϵ = 36,830); λ_{min} 226(9140).

Anal. Calcd. for $C_{13}H_6BrNO_3$: C, 51.34; H, 1.99. Found: C, 51.25; H, 2.37.

2-Nitro-3-amino-9-fluorenone. 2-Nitro-3-bromo-9-fluorenone (304 mg.) in 70 ml. of absolute ethanol, saturated at 0° with ammonia, was heated in a pressure bottle for 24 hr. at 60° (green solution) to give upon cooling 240 mg. of brownish yellow crystals, m.p. 312–313° (m.p. 313–314°, Kofler, from benzene) λ_{max} 236.5 mμ (ϵ 11,210); 273 (13,270), 307.5 (19,520); 402 (7770); λ_{min} 244 (7950), 281 (12, 170), 359 (4640).

Anal. Calcd. for $C_{13}H_8N_2O_3$: C, 65.00; H, 3.36; N, 11.66. Found: C, 64.92; H, 3.73; N, 11.40.

A Wolff-Kishner reduction of 312 mg. of this compound in 2.5 ml. of hydrazine hydrate and 5 ml. of diethylene glycol produced 122 mg. of *2,3-fluorenediamine,* m.p. and mixed m.p. 193° (lit.[12] m.p. 192°), (from cyclohexane and dilute ethanol).

Refluxing 240 mg. of 2-nitro-3-aminofluorenone in 50 ml. of acetic anhydride for 7 hr. yielded 210 mg. of *N-(2-nitro-9-oxo-3-fluorenyl) acetamide,* m.p. 187°, after chromatography on alumina in benzene and crystallization from ethanol, (m.p. 190–191°, from ethanol, or cyclohexane-ethanol), λ_{max} 255 mμ (ϵ 25,790), 303.5 (30,640), 363 (6160); λ_{min} 232 (12,710), 276.5 (18,600); 347.5 (5840).

Anal. Calcd. for $C_{15}H_{10}N_2O_4$: C, 63.82; H, 3.57; N, 9.93. Found: C, 63.55; H, 3.76; N, 9.65.

2-Nitro-3-hydroxy-9-fluorenone. 2-Nitro-3-bromo-9-fluorenone (912 mg.) in 30 ml. each of ethanol and 2*N* potassium hydroxide was refluxed for 1 hr. (color change from yellow to red). The solution was diluted with water, filtered, and acidified, giving 594 mg. (82%) of product, m.p. 245° [from benzene; 247–248° (lit.[9] 248–249°) from benzene and ethanol]. λ_{max} 247.5 mμ (ϵ = 28,010); 296.5 (31,920); 357.5 (9170); λ_{min} 266(15,950); 333.5 (7780)

2-Amino-3-fluorenol. A. A Wolff-Kishner reduction of 241 mg. of 2-nitro-3-hydroxy-9-fluorenone in 2 ml. of hydrazine hydrate and 4 ml. of diethylene glycol yielded 180 mg. (91%) of 2-amino-3-fluorenol, m.p. and mixed m.p. 211–212° (lit.[5] 209–210°), from benzene.

B. 2-Nitro-3-bromo-9-fluorenone (304 mg.) and 170 mg. of potassium hydroxide in 5 ml. of diethylene glycol was heated for 2 hr. on a steam bath. After cooling, 2 ml. of hydrazine hydrate was added and a Wolff-Kishner reaction performed: 2-amino-3-fluorenol (187 mg., 95%), m.p. 212–213°.

Reaction of 2-nitro-3-bromo-9-fluorenone with potassium fluoride. A. The fluorenone (4.86 g.), 50 g. of dry acetamide (sublimed and recrystallized), and 3.6 g. of oven-dried potassium fluoride was heated to 170–175° with stirring for 7.5 hr. Extraction of the brown product with water, acidification of the solution with nitric acid, and addition of silver nitrate precipitated 2.67 g. (89%) of silver bromide.

Extraction of the residue with hot sodium bicarbonate and acidification gave 0.88 g. of 2-nitro-3-hydroxyfluorenone, m.p. 249–250°. The residue was further extracted in a Soxhlet apparatus for 11 days with benzene. Extraction of the benzene solution with sodium bicarbonate furnished another 0.17 g., m.p. 248°.

Further extraction of the residue with ethanol for 3 days, and concentration of the ethanol solution produced 0.43 g. of brownish crystals, m.p. 280–300°, which yielded 0.25 g. of 2-nitro-3-aminofluorenone, m.p. 309–310° (from pyridine). The black residue, m.p. > 360°, weighed 2.14 g.[13]

B. In dimethyl sulfoxide. 2-Nitro-3-bromofluorenone (608 mg.), 354 mg. of oven-dried potassium fluoride in 50 ml. of vacuum-distilled dimethyl sulfoxide was stirred at 115° for 78 hr. and diluted with 200 ml. water to give a yellow precipitate (465 mg.), m.p. 238–242°. A chloroform solution of this material was extracted with sodium bicarbonate and the aqueous layer acidified to give 2-nitro-3-hydroxy-9-fluorenone (401 mg.), m.p. and mixed m.p. 248°. No evidence for the 3-fluorine-substituted material was found in the chloroform layer.

2,2'-Dinitro-3,3'-bifluoren-9-one. 2-Nitro-3-bromofluorenone (1.5 g.) in 70 ml. of dry xylene was refluxed for 20 hr. with 2 g. of iodine-activated copper powder.[14] The solution was filtered, and cooled to give a small amount of crystalline material, m.p. > 360°. The filtrate was chromatographed on alumina. A faster yellow band was extracted with benzene to give 2-nitrofluorenone (0.45 g.), m.p. and mixed m.p. 218°. A slower brown band extracted with pyridine furnished a solid, which was combined with a pyridine extract of the copper powder, and the high melting product above to give yellow 2,2'-dinitro-3,3'-bifluoren-9-one (69 mg.) m.p. >360°, from pyridine. λ_{max} 270 mμ (ϵ = 35,310); λ_{min} 226 (17,340); inflection pt. 360.

Anal. Calcd. for $C_{26}H_{12}N_2O_6$: C, 69.64; H, 2.70; N, 6.25. Found: C, 69.00; H, 3.08; N, 6.33.

3,3'-Bis-2,2'-fluorenamine. A Wolff-Kishner reduction of 896 mg. of dinitrobifluorenone, 150 ml. of diethylene glycol, and 60 ml. of hydrazine hydrate produced a gray precipitate. Chromatography on alumina in benzene and crystallization from ethyl acetate and pyridine left 450 mg. of yellow diamine, m.p. 314–316°. λ_{max} 270 mμ (ϵ = 48,360); 367 (26,630); 389 (23,930); λ_{min} 234 (20,220); 310 (10,010); 380 (22,030).

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.63; H, 5.59; N, 7.77. Found: C, 87.03; H, 4.66; N, 7.97.

The *diacetyl derivative* was prepared in benzene with acetic anhydride as pale yellow crystals, m.p. 284–285°, from ethyl acetate. λ_{max} 277 mμ (ϵ = 36,180); 304 (23,230); λ_{min} 235 (22,230); 302 (23,230); shoulder 258 mμ.

Anal. Calcd. for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 80.47; H, 5.39; N, 6.33.

1,3-Dibromo-2-nitrofluorene. 1,3-Dibromo-2-fluorenamine[4] (13.6 g.) was refluxed for 40 min. in 272 ml. of 40% peracetic acid and 120 ml. of acetic acid (color from green to red to golden yellow). The reaction was terminated at this point to avoid extensive oxidation to the fluorenone. Dilution with water gave a product which was chromatographed on alumina in benzene to give colorless 1,3-dibromo-2-nitrofluorene (8.5 g.) m.p. 163° (m.p. 164–165°, from cyclohexane or ethanol). This compound is sensitive to light in solution and in the solid state, being altered to a violet product. λ_{max} 270 mμ (ϵ = 15,760); 297 (7820); 307.5 (6300); λ_{min} 245 (8380); 295 (7760); 305 (5830).

Anal. Calcd. for $C_{13}H_7Br_2NO_2$: C, 42.31; H, 1.91; Br, 43.31. Found: C, 42.01; H, 2.06; Br, 43.26.

Elution of the alumina column, above, with 10% ethanol, in benzene gave 1.15 g. of 1,3-dibromo-2-nitrofluorenone, m.p. 248° (see below). The fluorene derivative could also be separated from the smaller amounts of the fluorenone compound by reason of the virtual insolubility of the latter compound in cyclohexane.

1,3-Dibromo-2-nitrofluorenone. 1,3-Dibromo-2-nitrofluorene (3.7 g.) and 3 g. of potassium bichromate in 110 ml. of acetic acid were refluxed for 5 hr. and poured into water to give 1,3-dibromo-2- nitrofluorenone (2.8 g., 82%), m.p. 251–252°, from benzene. A sample, chromatographed on alumina in benzene, was eluted with ethanol from the segment containing the yellow band to give material with m.p. 253–254°, from benzene and acetic acid. λ_{max} 269 mμ (ϵ = 7220); 306 (550); 321 (400); 335.5 (300); λ_{min} 233 (1250); 300.5 (460); 317 (390); 332 (295).

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

(13) The infrared spectrum of this material was unlike that of the bifluorene derivative described below, but exhibited instead some of the features of a 2,3-substituted fluorenone.

(14) E. C. Kleiderer and R. Adams, *J. Am. Chem. Soc.,* **55,** 4219 (1933).

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

KAZUO SUZUKI,[2] ELIZABETH K. WEISBURGER, AND JOHN H. WEISBURGER

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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

(1) National Institutes of Health, Public Health Service, Department of Health, Education and Welfare.

(2) Visiting Scientist, National Cancer Institute. On leave of absence from Yamaguchi University, Ube, Japan.

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