*Some Observations on the Synthesis of 3-Bromofluorenone**

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(Received July 30, 1963)

A synthetic pathway leading to 3-bromofluorenone by the following sequence has been investigated and found to result in a better yield than the method starting with 2-(4'-bromobenzoyl)-benzoic acid:[1] 2-Nitrofluorene→2-nitrofluorenone→2-aminofluorenone (I)→2-amino-3-bromofluorenone (II)→3-bromofluorenone.

The deamination reaction of II is the crucial step in this route. Fletcher and Pan[2] attemted this reaction, but have not yet reported on the yield.

In the present work the deamination of II was carried out in an 82% yield by diazotization and decomposition in concentrated sulfuric acid. 2-Nitrofluorene, 2-nitrofluorenone[3] and I[4] were obtained in good yields. The bromination of I by the action of 48% aqueous hydrogen bromide in dimethyl sulfoxide[2] resulted in an 80% yield. However, in the present experiments we re-examined[5] the bromination of the same base by the action of an equimolar quantity of bromine in acetic acid; the main product was II (60%), accompanied by a small amount of a new bromoketone, III (6%, m.p. 254°C).

The following experiments proved that the bromine atoms were indeed in the 1, 3-positions of III. The analytical results agreed with a dibromo compound. Reduction and acetylation gave 1, 3-dibromo-2-aminofluorene and its acetyl derivative;[2] deamination gave 1, 3-dibromofluorenone.

The electron-releasing substituent at carbon 2 of I makes carbons 1, 3, 5 and 7 susceptible to an electrophilic attack. This was illustrated by the attack of the second bromine atom at the 1-position of the same ring. The same compound (92%) was obtained by the bromination of II.

Experimental[6]

Bromination of 2-Aminofluorenone (I). — Into a solution of 128 g. of I in 2140 ml. of acetic acid, 32.8 ml. of bromine in 50 ml. of acetic acid were stirred drop by drop over a 1.5 hr. period at about 20°C. The precipitate was filtered and digested with a hot dilute alkali solution; then it was filtered and washed with water. The crude product was extracted several times with hot benzene. The first fraction was a mixture of I, II and III. On being heated with alcohol, it was separated into a soluble (I and II) and an insoluble part (III).

The insoluble part was recrystallized from benzene to give III; 12.3 g. (6%), m. p. 254°C.

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6) All melting points are uncorrected.

Found: C, 44.39; H, 2.20; N, 3.88; Br, 45.55%. Calcd. for $C_{13}H_7ONBr_2$: C, 44.23; H, 2.00; N, 3.97; Br, 45.27%.

IR: 3380, 3280 (ν N-H), 1710 (ν C=O), 1600 cm^{-1} (δ N-H).

III was acetylated, and the product was recrystallized from benzene, melting at 248~249°C.

Found: N, 3.37; Br, 40.46%; Calcd. for $C_{15}H_9O_2NBr_2$: N, 3.55; Br, 40.45%.

IR: 3175 (ν N-H), 1710 cm^{-1} (ν C=O).

The soluble part was evaporated to dryness, and the residue was extracted with hot dilute hydrochloric acid. Crude I (12.4 g.) was recovered by the addition of alkali. II (41 g.) was obtained from the acid-insoluble part.

A small amount of III was isolated from the benzene mother liquor by means of chromatography in benzene on alumina. On the other hand, the second and later benzene extractions contained II almost entirely; this was recrystallized from benzene to give 55.6 g. (total 96.6 g., 60%) (m. p. 215°C).

3-Bromofluorenone. — Finely-powdered sodium nitrite (13 g.) was stirred into a solution of 42.8 g. of II in 234 ml. of concentrated sulfuric acid over a period of 1 hr. at 10~15°C. Stirring was continued for an additional 30 min., and then the brown, diazotized solution was poured into 750 g. of ice, and 310 ml. of 50% hypophosphorous acid was added to the reaction mixture. Upon gradual heating, the vigorous evolution of nitrogen occurred at 60°C; after this stirring was continued at 80°C for 20 min.

The yellow precipitate was filtered and chromatographed in benzene on alumina. The crude product was recrystalized from benzene; weight, 33 g. (82%); m.p. 164~165°C, IR: 1703 cm^{-1} (ν C=O); this compound was identified by melting point and mixed melting point determination and by comparing its infrared absorption spectrum with an authentic sample of 3-bromofluorenone.

Deamination of III, the New Bromoketone (M.p. 254°C).—This deamination was carried out under the same conditions as in the case of II. 1,3-Dibromofluorenone was obtained from the mixture of 3 g. of III, 16.4 ml. of sulfuric acid, 0.87 g. of sodium nitrite and 21.9 ml. of hypophosphorous acid. The crude product was recrystallized from benzene to yield 2.3 g. (80%); m.p. 216~218°C (reported[7] m.p. 225°C), (Found: Br, 46.84%; Calcd. for $C_{13}H_6OBr_2$: Br, 47.28%; IR: 1710 cm^{-1} (ν C=O)).

Reduction of III.—a) A mixture of 0.5 g. of III in 6 ml. diethylene glycol, and 1 ml. of 50% hydrazine hydrate was heated under reflux at 160°C for 1 hr. and at 200°C for 2 hr. The reaction mixture was poured into water, and the product was filtered and recrystallized from cyclohexane to give 1,3-dibromo-2-aminofluoren (0.36 g. (74%), m. p. 183~185°C). (Found: Br, 47.58%; Calcd. for $C_{13}H_9NBr_2$: Br, 47.14%). IR: 3240 cm^{-1} (ν N-H), 1610 cm^{-1}, (δ N-H). This was identified with an authentic sample by mixed melting point determination and infrared spectrum comparison.

b) A mixture of 0.5 g. of the same sample, 31 ml. of acetic acid, 3 ml. of hydrogen iodide and 0.1 g. of red phosphorus was refluxed for 7 hr. When poured into cold water, 2-aminofluorene (m.p. 125.5~127.5°C; 0.12 g., 46%) was obtained.

Bromination of II.—A solution of 1.6 g. of bromine in 5 ml. of acetic acid was vigorously stirred into 274 g. of II in 200 ml. of acetic acid over a period of 20 min. at 20°C. The product deposited was filtered, washed with water, and then recrystallized from benzene to give III (m.p. 254°C, 1.6 g.). From the mother liquor, 1.4 g. of II was recovered (balance yield, 92%).

The authors wish to express their gratitude to Drs. John and Elizabeth Weisburger of the National Institutes of Health, U.S.A., for valuable information, and also to Dr. Moses J. Namkung and Dr. Nobuo Ishikawa of the University of Washington, Seattle, for furnishing helpful information on the diazotization of 2-amino-3-bromofluorenone.

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