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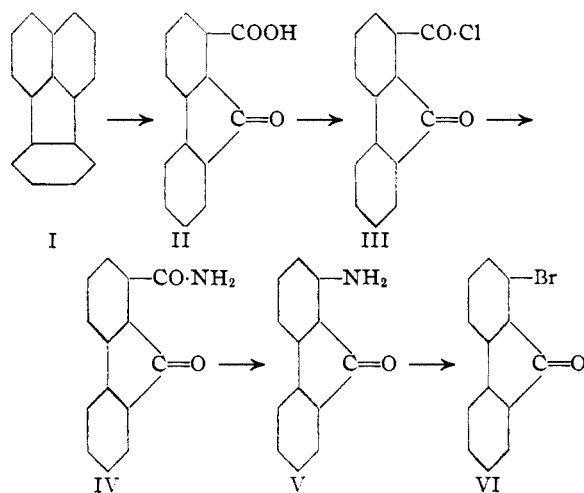
## Fluorenones and Diphenic Acids. IX.<sup>1</sup> Establishment of Authentic 1-Bromo- and 4-Bromofluorenones

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Of the four isomeric monobromofluorenones predicted by the structure theory, the 2-bromofluorenone<sup>3</sup> and 3-bromofluorenone<sup>3b,4</sup> have been well established. Data regarding the other two isomers, however, are inadequate for 1-bromofluorenone and contradictory for the 4-bromofluorenone. The present paper confirms and expands our knowledge of the first, and resolves the prior contradictions for the second.

Previous to this work, 1-bromofluorenone had been reported only once.<sup>4a</sup> It had been obtained by debromination of 2,6-dibromobenzophenone under conditions so drastic (heating at its boiling point for several days) as to leave some doubt as to the ultimate location of the residual bromine atom, particularly in view of previously unsuccessful attempts in this Laboratory to repeat this method of preparation and of the alleged existence of two 4-bromofluorenones discussed later in this paper.

We have, therefore, prepared authentic 1-bromofluorenone by an independent sequence of conventional reactions not involving drastic conditions. This sequence is diagrammed as follows



(1) For Article VIII of this series see Huntress and Seikel, *THIS JOURNAL*, **61**, 1358-1364 (1939).

(2) This paper is in part constructed from a thesis submitted in May, 1940, by K. Pfister to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Bachelor of Science.

(3) (a) Courtot, *Ann. chim.*, [10] **14**, 59-62 (1930); (b) Heilbron, Hey and Wilkinson, *J. Chem. Soc.*, 113 (1938).

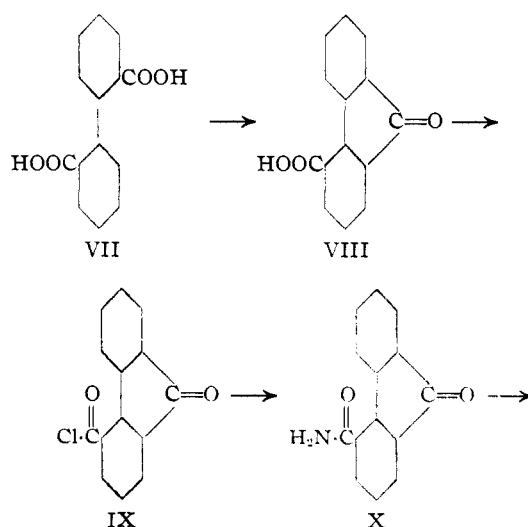
(4) (a) Montagne and van Charante, *Rec. trav. chim.*, **32**, 164-173 (1913); (b) Miller and G. B. Bachman, *THIS JOURNAL*, **57**, 2443-2446 (1935); (c) **57**, 2447-2450 (1935).

The properties of the resultant 1-bromofluorenone are in excellent agreement with those described for the original method<sup>4a</sup> and this result provides for the first time not only convincing evidence of the stability of the bromoketone toward heat but also a much improved method of preparation.

The structure of our product is supported not only by analysis, but also by conversion of its precursor (1-aminofluorenone) to 1-cyanofluorenone and thence to fluorenone-1-carboxylic acid whose structure has already been definitely established.<sup>5</sup>

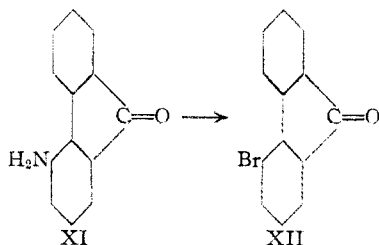
Two distinctly different compounds both claimed to be 4-bromofluorenones are recorded. The higher melting compound was reported<sup>4b,c</sup> as the product of three independent processes. The lower melting substance was independently obtained<sup>6</sup> by a fourth method. Despite the marked difference of their product from that originally described by Miller and Bachman<sup>4b,c</sup> these authors made no reference in their paper to any of the preceding work.

We have prepared 4-bromofluorenone by a different series of reactions as follows



(5) (a) Mayer and Freitag, *Ber.*, **54**, 347 (1921); (b) Sieglitz, *ibid.*, **57**, 316 (1924); (c) von Braun and Anton, *ibid.*, **62**, 145 (1929).

(6) France, Heilbron and Hey, *J. Chem. Soc.*, 1364 (1938).

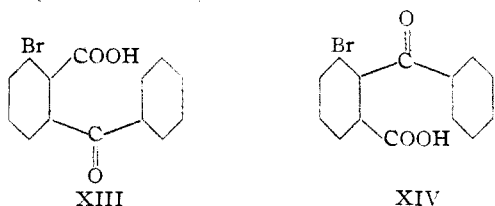


By this sequence the position of the bromine in the ultimate ketone is unequivocally established since there can be no ambiguity regarding the structure of fluorenone-4-carboxylic acid (VIII). The melting point of our 4-bromofluorenone so prepared proved to be in accord with that observed by France, Heilbron and Hey<sup>6</sup> and confirms the identity of their product. Since the numerical magnitude of this melting point is not very different from that of 1-bromofluorenone we have also shown that the melting point of a mixture of authentic 1-bromofluorenone with authentic 4-bromofluorenone is substantially depressed.

The results described above left seriously in doubt the identity of the bromofluorenone originally reported by Miller and Bachman as the 4-bromo isomer. We have, therefore, attempted to repeat their three syntheses. We were unable, however, to duplicate their results by the method starting with methyl *o*-iodobenzoate and made several unsuccessful efforts to employ their oxidation<sup>4c</sup> of supposed 4-bromofluorene from the mercuriation of fluorene. Extensive experimentation with their method from 3-bromophthalic anhydride, however, led to the discovery that it yielded to us 1-bromofluorenone identical with our authentic material described above and definitely depressing the melting point of the true 4-bromofluorenone.

The error into which the American workers fell in this last case is attributable to their acceptance without further corroboration of the structure assigned by Stephens<sup>7</sup> to an acid resulting from the interaction of 3-bromophthalic anhydride with benzene in the presence of aluminum chloride.

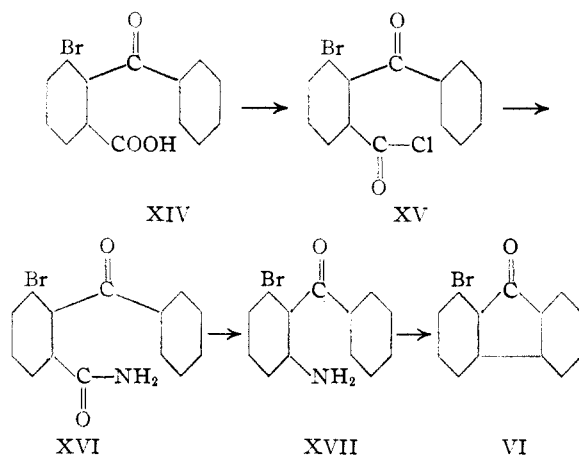
From its method of preparation Stephens' acid could have had only one or the other of two structures (XIII or XIV).



(7) Stephens, *THIS JOURNAL*, **43**, 1950-1956 (1921).

Upon what now seems like extremely meager evidence Stephens assigned to his product structure XIII. This evidence consisted of the observation that when his product was subjected to fusion with potassium hydroxide benzoic acid and *o*-bromobenzoic acid were isolated. Stephens appears not to have considered the possibility that both of these products might equally well have resulted from structure XIV by loss of carbon dioxide and fission of the resultant *o*-bromobenzophenone in both possible senses.

We have prepared Stephens' acid and carried it through the Miller and Bachman series of reactions to the resultant bromofluorenone. Contrary



to the results of Miller and Bachman this turned out to be 1-bromofluorenone identical with the authentic product prepared by us by a series of reactions starting with fluorenone. This work thus serves not only to correct the errors of Miller and Bachman, but also establishes the structure of Stephens' acid and represents a third and independent preparation of 1-bromofluorenone.

### Experimental Work

The melting points reported below were taken with a 360° rod form melting point thermometer by the Berl-Kullmann copper block method and are uncorrected.

**Fluorenone-1-carboxylic Acid (II).**—Pure fluorenone (m. p. 109-110°) was oxidized to fluorenone-1-carboxylic acid substantially according to the directions of Fieser and Seligman<sup>8</sup>; yield 55%, m. p. 188.5-190.5°. Repeated recrystallization from dilute alcohol gave long orange-red needles, m. p. 191-192°.

**Fluorenone-1-carboxylic Acid Amide (IV).**—The acid was converted to the acid chloride by brief boiling with twice its weight of thionyl chloride. After cooling the clear light-red solution the precipitated yellow solid was filtered off and washed with petroleum ether (b. p. 35-60°). The finely powdered acid chloride was then allowed to

(8) Fieser and Seligman, *ibid.*, **57**, 2175 (1935).

stand overnight with excess concentrated ammonium hydroxide, the resultant amide filtered off, washed with water and dried; yield 95%, m. p. 222.5–225°. Recrystallization of the acid chloride from petroleum ether prior to ammonia treatment gave a crude amide of m. p. 224.5–227°. Recrystallization of the amide from 95% alcohol yielded long deep yellow needles, m. p. 226.5–227°.

**Fluorenoneanil-1-carboxylic Acid Anilide.**—This product was obtained from fluorenone-1-carboxylic acid chloride by warming for a few minutes with aniline. Evaporation of excess amine left a brown residue which upon recrystallization from 95% alcohol gave long yellow needles, m. p. 184.7–185°.

*Anal.* Calcd. for the anil-anilide ( $C_{26}H_{18}ON_2$ ): N, 7.50. Found: N, 7.62. (Calcd. for fluorenone-1-carboxylic acid anilide ( $C_{20}H_{18}O_2N$ ): N, 4.68.)

**1-Aminofluorenone (V).**—To fluorenone-1-carboxylic acid amide (2.0 g. = 0.009 mole) finely powdered in water (3 ml.) was added in one batch the hypobromite solution prepared by adding bromine (1.4 g. = 0.009 mole) to water (15 ml.) and then adding dropwise an ice-cold solution of potassium hydroxide (3.0 g. = 0.054 mole) in water (25 ml.). The resultant mixture was warmed gently for a few minutes until a homogeneous brown gel had formed, then allowed to stand for two hours. Finally the mixture was heated for half an hour at 100°, a solution of potassium hydroxide (4.5 g. = 0.08 mole) in water (4.5 ml.) added and heating at 100° continued for forty-five more minutes. After cooling, the resultant yellow-brown solid was filtered off and extracted four successive times with 25-ml. portions of boiling 6 *N* hydrochloric acid, refluxing fifteen minutes with each portion before filtration. The amine hydrochloride which separated from these extracts on cooling was collected, washed with 6 *N* hydrochloric acid and converted to 1-aminofluorenone with concentrated ammonium hydroxide. The resultant 1-aminofluorenone, m. p. 114.5–116.5°, was obtained in 56% yield. After vacuum sublimation (140–150° at 2 mm. bath temperature) and several recrystallizations from dilute alcohol the aminoketone formed beautiful long yellow needles, m. p. 118–118.5° (only previously recorded<sup>9</sup> m. p. 110°).

**1-Acetylaminofluorenone.**—1-Aminofluorenone boiled for one minute with acetic anhydride and a trace of concd. sulfuric acid gave on cooling a solid, which after recrystallization from 95% alcohol and from ligroin (b. p. 90–100°) separated as yellow needles (75% yield) m. p. 138–138.3°.

*Anal.* Calcd. for  $C_{18}H_{11}O_2N$ : N, 5.90. Found: N, 6.13, 6.28.

**1-Benzoylaminofluorenone.**—1-Aminofluorenone dissolved in pyridine and shaken with equivalent benzoyl chloride, then diluted with water gave a yellow precipitate of benzoyl derivative. After washing with water, dilute aqueous sodium carbonate and recrystallization from 95% alcohol and from ligroin, it was obtained (75% yield) as long silky yellow needles, m. p. 149–149.8°.

*Anal.* Calcd. for  $C_{20}H_{13}O_2N$ : N, 4.68. Found: N, 4.75.

**1-Chlorofluorenone.**—To 1-aminofluorenone (0.976 g. = 0.005 mole) was added concentrated hydrochloric acid (2.92 ml. = 0.035 mole) and from the resultant solution

the free base was reprecipitated in finely divided form by addition of water (25 ml.) and cooling to 10–15°. The resulting suspension was diazotized by addition of sodium nitrite (0.35 g. = 0.005 mole) in water (10 ml.), stirring for ten minutes. After removing excess nitrous acid by addition of urea, the filtered solution was added in a fine stream to a boiling solution of cuprous chloride (0.6 g. = 0.006 mole) in 6 *N* hydrochloric acid (30 ml.). Five minutes at 100° served to coagulate the yellow precipitate which was filtered off after standing for several hours. This crude product was washed with 1 *N* sodium hydroxide, then extracted with hot glacial acetic acid (15 ml.) and the crude 1-chlorofluorenone precipitated from the filtrate by addition of water. Distillation under reduced pressure (2 mm. at 175–185° bath temperature) gave 40% yield, m. p. 134.0–135.5°; two recrystallizations from 95% alcohol raised the melting point of the yellow needles to 137–137.8°.

*Anal.* Calcd. for  $C_{13}H_7OCl$ : Cl, 16.52; Found: Cl, 16.5, 16.3.

**1-Bromofluorenone (from 1-Aminofluorenone).**—To 1-aminofluorenone (0.976 g. = 0.005 mole) was added 40% hydrobromic acid (5.13 ml. = 0.035 mole) and the diazotization carried through as for the preceding case. The cold diazonium solution was added in a thin stream to a gently boiling solution of cuprous bromide (0.86 g. = 0.006 mole) in 40% hydrobromic acid (50 ml.). After ten minutes digestion at 100° the reaction product was cooled, the solid filtered off and washed with 1 *N* sodium hydroxide, extracted with hot alcohol, and reprecipitated by dilution. After being dried and vacuum distilled (2 mm. at 170–180° bath temperature) the yield of 1-bromofluorenone was 42%. Two recrystallizations from 95% alcohol gave stubby yellow needles, m. p. 134–134.3°. (The only other recorded value is 135°. <sup>4a</sup>)

*Anal.* Calcd. for  $C_{13}H_7OBr$ : C, 60.26; H, 2.73; Br, 30.84. Found: C, 60.1, 60.2; H, 2.85, 2.92; Br, 29.8, 30.0.

**1-Iodofluorenone.**—1-Aminofluorenone hydrochloride (1.16 g. = 0.005 mole) in a mixture of concentrated hydrochloric acid (2.5 ml. = 0.030 mole) with water (25 ml.) was diazotized as above. Particular care that every trace of excess nitrous acid should be removed by the urea treatment was found essential. To the cold filtered diazonium solution was added potassium iodide (1.0 g. = 0.006 mole) in water (15 ml.) and after heating at 100° for five minutes, the resulting suspension stood several hours. After the usual alkali washing and vacuum distillation (2 mm. at 180–190° bath temperature) the 1-iodofluorenone was obtained (48% yield) as yellow needles, m. p. 144–145°. Two recrystallizations from 95% alcohol raised the value to 146.5–147°.

*Anal.* Calcd. for  $C_{13}H_7OI$ : I, 41.46. Found: I, 41.4, 41.2.

**1-Cyanofluorenone.**—The diazotized solution prepared from 1-aminofluorenone exactly as for 1-chlorofluorenone (above) was added in a fine stream to the hot solution from copper sulfate crystals (1.25 g. = 0.005 mole) and potassium cyanide (1.40 g. = 0.020 mole) in water (15 ml.). After standing several hours, the solid was filtered off, washed with alkali, dried and distilled (2 mm. at bath temperature of 220°). After recrystallization from alco-

(9) Goldschmiedt, *Monatsh.*, **23**, 893–895 (1902).

hol, the resulting 1-cyanofluorenone (14% yield) melted at 174–175.5°.

This nitrile was also obtained from fluorenone-1-carboxylic acid amide (0.25 g. = 0.0011 mole) by warming with phosphorus pentachloride (0.23 g. = 0.0011 mole). After the initial rapid reaction the mixture was heated at 200° for one and one-half hours (48% yield). One recrystallization from dilute acetic acid gave a product of m. p. 172–173.2°. Since this material did not depress the melting point of the product from the Sandmeyer method, all the corresponding materials were combined and several times recrystallized from dilute acetic acid. The 1-cyanofluorenone was then obtained in short deep yellow rods, m. p. 177.2–177.8°.

*Anal.* Calcd. for  $C_{14}H_7ON$ : N, 6.83. Found: N, 6.74.

Further confirmation of the identity of this nitrile was obtained by its hydrolysis with hot 50% sulfuric acid to fluorenone-1-carboxylic acid. After crystallization from 95% alcohol the small orange-red needles (80% yield) showed m. p. 190–192° and did not depress the melting point of an authentic sample (m. p. 191–192°) from the oxidation of fluoranthene.

**Fluorenone-4-carboxylic Acid (VIII).**—Diphenic acid (5 g. = 0.021 mole) was added to concentrated sulfuric acid (23 g. = 0.45 mole) during the two minutes required to bring the mixture to  $140 \pm 5^\circ$ . The red solution was held at this temperature with constant shaking for twelve minutes, then poured into water (150 ml.). The yellow precipitate was boiled gently for an hour, then filtered hot and washed with a large volume of hot water. The yield of crude keto acid was 82%; m. p. 216–218°. After recrystallization from 50% alcohol it was obtained in yellow needles, m. p. 220–221°.

**Fluorenone-4-carboxylic Acid Amide (X).**—The keto acid (1.0 g.) was added slowly to thionyl chloride (5 ml.). After refluxing the clear but dark colored solution for a few minutes, the excess thionyl chloride was evaporated in a dry air blast and the crude dry keto acid chloride allowed to stand for an hour in excess (5 ml.) concentrated ammonium hydroxide. The solid was then filtered, washed with water and recrystallized from 95% alcohol from which on cooling beautiful cream-colored needles, m. p. 223–224°, separated in 82% yield.

**4-Aminofluorenone (XI).**—Fluorenone-4-carboxylic acid amide (1 g. = 0.0045 mole) ground to a fine slurry with water (15 ml.) was added to an alkaline hypobromite solution prepared by adding to bromine (0.7 g. = 0.0045 mole) in water (5 ml.) at 0° a solution of potassium hydroxide (1.5 g. = 0.027 mole) in water (10 ml.). The amide dissolved almost immediately and the resultant orange solution was left at room temperature for two hours. After removing a dark colored high melting residue by suction filtration, the filtrate was heated at 100° for seventy-five minutes to cause precipitation of the aminoketone. After cooling the orange needles were filtered, washed with ice water and dried, yield 74%, m. p. 138–139°.

**4-Bromofluorenone (XII).**—The above 4-aminofluorenone (1 g. = 0.005 mole) was diazotized in the usual way using 40% hydrobromic acid (5.25 ml. = 0.036 mole), sodium nitrite (0.36 g. = 0.005 mole) and a total of 35 ml. of water. The resultant filtered solution was poured in a fine stream into a boiling solution of cuprous bromide

(0.88 g. = 0.06 mole) in 40% hydrobromic acid (50 ml.). After heating at 100° for five to ten minutes the resultant light orange precipitate was filtered off, ground up with excess 1 *N* sodium hydroxide solution, filtered and washed. The undissolved bromoketone was then distilled at reduced pressure (2 mm. at bath temperature of 105–115°) giving 45% yield, m. p. 124.5–125.5°. Recrystallization from dilute acetic acid and from 95% alcohol gave 4-bromofluorenone as small yellow needles, m. p. 125–126°.

*Anal.* Calcd. for  $C_{13}H_7OBr$ : Br, 30.84. Found: Br, 30.7, 30.8.

The melting point of a mixture of this 4-bromofluorenone with authentic 1-bromofluorenone was depressed more than 25°.

**2-Benzoyl-3-bromobenzoic Acid (XIV) (Stephens' Acid).**—This compound was prepared from 3-bromophthalic anhydride, benzene and aluminum chloride precisely according to Stephens' directions; yield 83%, m. p. 226–227°. After recrystallization from 50% aqueous acetone our melting point was 227–228° (Stephens gave 231.5° but did not state whether this value was corrected or not).

*Anal.* Calcd. for  $C_{14}H_9O_3Br$ : neut. eq., 305.1; C, 55.11; H, 2.97; Br, 26.19. Found: neut. eq., 304.0, 304.7; C, 55.1, 54.9; H, 3.00, 3.12; Br, 26.0, 26.0.

**Methyl 2-Benzoyl-3-bromobenzoate.**—This ester (not previously recorded) was prepared via the diazomethane method. It formed colorless flat rectangular prisms, m. p. 136.7–137.5°.

*Anal.* Calcd. for  $C_{15}H_{11}O_3Br$ : Br, 25.04. Found: Br, 25.0, 24.9.

**2-Benzoyl-3-bromobenzoyl Chloride (XV).**—The above acid (Stephens') was converted to the acid chloride with phosphorus pentachloride in benzene precisely according to Miller and Bachman,<sup>4c</sup> except that not until the amount of benzene had been reduced to one-half their quantity and petroleum ether substituted for their ligroin did we obtain their yield. They described their acid chloride as light brown prisms, m. p. 119–120°. Our product, however, was perfectly white and showed m. p. 121–122°.

**2-Benzoyl-3-bromobenzamide (XVI).**—Many attempts to follow the Miller and Bachman procedure for conversion of the acid chloride from Stephens' acid to the corresponding amide gave only mixtures of compounds which obstinately resisted separation. By the following modification, however, we obtained the amide easily and in good yields.

A citrate of magnesia bottle was charged with two dozen small quartz pebbles and concentrated ammonium hydroxide (120 ml.) and chilled in an icebox overnight. To it was then added freshly prepared 2-benzoyl-3-bromobenzoyl chloride (14.5 g. = 0.045 mole) and the mixture tumbled for six hours. The flask contents were then diluted with water, the pebbles screened out, the solid filtered off with suction, washed thoroughly with dilute ammonium hydroxide (1 volume concd.  $NH_4OH$ : 2 water), and dried. The yield was 12.7 g. (93%). Recrystallization from toluene gave m. p. 202–202.5° (somewhat higher melting points were, however, sometimes obtained).

*Anal.* Calcd. for  $C_{14}H_{10}O_2NBr$ : N, 4.61; Br, 26.28. Found: N, 4.64, 4.66; Br, 26.2, 26.3.

In one experiment where the flask containing both crystals and mother liquor was allowed to stand for several

days the bulky needles were replaced by an entirely different appearing mass of intensely glittering prisms. These, however, showed the same melting point as the usual needles, and reverted to the latter upon recrystallization.

**2-Benzoyl-3-bromoaniline (XVII).**—The above amide (7.5 g. = 0.025 mole) was added to an alkaline hypobromite solution prepared from bromine (1.3 ml.) and potassium hydroxide solution (12.5 ml. of 1:1 solution plus 20 ml. water) and the mixture kept at 0° for half an hour with occasional stirring. The resulting white pulp was dissolved in water (60 ml.) and poured into a boiling mixture of water (400 ml.) and alcohol (50 ml.). After refluxing for an hour most of the alcohol was distilled off.

A heavy brown oil which had then separated was solidified by transferring it to a mortar, washing with a little 5% potassium hydroxide solution and then triturating with 5% hydrochloric acid (50 ml.). The resultant brown powder was filtered off, washed, dried, dissolved in ether (50 ml.), the ether solution filtered and treated with 72% perchloric acid (2.5 ml.). The amine perchlorate precipitated leaving the colored impurities behind in the mother liquor. After washing the perchlorate salt with ether it was decomposed with dilute ammonium hydroxide and the free amine washed and dried. The yield was 3.2 g. (46%). For further purification it was dissolved in ligroin (250 ml. of b. p. 60–90°), boiled with Norit, filtered and cooled. The amine separated as clusters of yellowish prisms, m. p. 84.5–85.5°.

*Anal.* Calcd. for  $C_{13}H_{10}ONBr$ : N, 5.07; Br, 28.94. Found: N, 5.45, 5.51; Br, 28.9, 29.1.

The aqueous alkaline solution decanted from the above amine (original crude oil) gave upon acidification an ample white precipitate indicating considerable hydrolysis of the original amine back to its acid as is often the case in Hofmann reactions.

**1-Bromofluorenone (VI) from 2-Benzoyl-3-bromoaniline (XVII).**—Preliminary experiments showed that this very weakly basic aminoketone does not readily lend itself to ring closure by elimination of the amino group *via* decomposition of the diazonium salt. The reaction tends to take a more complicated course leading largely to mixtures of resinous matter and amorphous dark-colored pigments. There is also formed a considerable amount of an alkali soluble product. However, a satisfactory result was finally obtained by the following procedure.

The aminoketone (3.5 g. = 0.0127 mole) dissolved in concentrated sulfuric acid (28 ml.) at 0° was treated at one time with finely powdered 97% sodium nitrite (0.014 mole) with constant shaking. As soon as a clear solution resulted, it was mixed with anhydrous sodium sulfate (100 g.), transferred to a large porcelain dish resting on a boiling water-bath, and constantly stirred for twenty minutes. After treatment with alkali (80 ml. 40° Baumé sodium hydroxide plus 1000 ml. water) the undissolved residue was filtered, washed and dried: weight 1.5 g.

This greyish-brown solid was mixed with Norit (3 g.), then refluxed with ligroin (400 ml., b. p. 60–90°) for one hour. After cooling and filtering, evaporation of the solvent yielded 0.4 g. of long lemon-yellow spears, m. p. 134.5–135°. From the Norit a second lot (0.4 g.) of equally pure material was obtained. The total yield was approximately 25% of the theoretical.

*Anal.* Calcd. for  $C_{13}H_7OBr$ : C, 60.26; H, 2.73; Br, 30.84. Found: C, 60.3, 60.0; H, 2.90, 3.15; Br, 30.8, 31.1.

This product (m. p. 134.5–135°) did not depress the melting point (134.0–134.3°) of 1-bromofluorenone prepared from fluorenone-1-carboxylic acid, but did depress that (125–126°) of 4-bromofluorenone obtained from fluorenone-4-carboxylic acid.

### Summary

1. 1-Bromofluorenone has been prepared from fluorenone-1-carboxylic acid by a series of reactions leaving no doubt as to its structure. Our results confirm the work of Montagne and van Charante, who prepared it by another method.

2. 4-Bromofluorenone has been prepared from fluorenone-4-carboxylic acid by a series of reactions leaving no doubt as to its structure. Our product confirms the properties previously reported by France, Heilbron and Hey.

3. The series of reactions by which Miller and Bachman reported to have obtained from 3-bromophthalic anhydride a product claimed to be 4-bromofluorenone yielded in our hands only authentic 1-bromofluorenone. This discovery resolves the serious contradictions in the previous literature of this compound.

4. As a result of the establishment of the true 1-bromo- and 4-bromofluorenone it was found that the bromobenzoylbenzoic acid resulting from the reaction of 3-bromophthalic anhydride with benzene in the presence of aluminum chloride is in fact 2-benzoyl-3-bromobenzoic acid and not the alternative 2-benzoyl-6-bromobenzoic acid erroneously inferred by previous workers.

5. The above discoveries bring in question the true nature of the Miller and Bachman supposed "4-bromofluorene" and "4-bromofluorene," the mercuration of fluorene in the 4-position, and their supposed "4-bromo-9-chlorofluorene" and "4,9-dibromofluorene." They also render very doubtful the structure proposed by Stephens for the diphenyl bromophthalide prepared from 3-bromophthalic anhydride.

6. During the course of the above work the following previously unreported compounds were characterized: 1-chloro-, 1-iodo-, 1-cyano-, 1-acetamino-, and 1-benzoylamino fluorenes; 2-benzoyl-3-bromobenzoic acid, methyl 2-benzoyl-3-bromobenzoate, 2-benzoyl-3-bromobenzoyl chloride, 2-benzoyl-3-bromobenzamide, 2-benzoyl-3-bromoaniline, and fluorenone-anil-1-carboxylic acid anilide.