Dicyclohexenyl-1,1′, b. p. 133–135° (23 mm.) was prepared in 68% yields by dehydrating dicyclohexanediol-1,1′[7] using an analogous procedure. The latter compound was prepared in poor yields by following the procedure given in "Organic Syntheses," Coll. Vol. I, p. 448, for pinacol hydrate. This was found to be superior to the sodium reduction method of Zelinsky.[8]

Tetrahydrodiphenyl was prepared by the procedure of Bamberger and Lodter.[3]

Ozonation and Decomposition of the Ozonides.—Oxygen containing 4–5% ozone was passed into a solution of the compound in glacial acetic acid until a sample no longer decolorized a solution of bromine in carbon tetrachloride. To the acetic acid solution of the ozonide was added 25 cc. of water and the solution refluxed for one hour. The acetic acid and water were distilled under reduced pressure and the residue poured into an evaporating dish to solidify. In the cases of phenylcyclohexene and tetrahydrodiphenyl the products were crystallized from ether and melted at 77–78°; the semicarbazones melted at 191–192° and mixed melting points showed no depression. Auwers and Treppmann[9] report the melting point of δ-benzoyl-*n*-valeric acid as 77–78° and the semicarbazone as 187°.

The crude product of the decomposition of the ozonide of dicyclohexenyl-1,1′ was crystallized from ethyl acetate, when it melted at 152–153° and had a neutralization equivalent of 74.6. Adipic acid melts at 153–153.5° and has a neutralization equivalent of 73. A mixed melting point showed no depression.

Summary

1. 1-Phenylcyclohexene-1 adds one mole of ozone to the double bond in the cyclohexene ring and dicyclohexenyl-1,1′ adds ozone to both double bonds. This indicates that steric hindrance in the 1 and 1′ positions is not the factor involved in the failure of diphenyl to form a hexaozonide.

2. Tetrahydrodiphenyl prepared by reducing diphenyl with sodium and amyl alcohol is chiefly 1-phenylcyclohexene-1.

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[7] Wallach and Pauly, *Ann.*, **381**, 112 (1911).

[8] Zelinsky, *Ber.*, **34**, 2801 (1901).

[9] K. v. Auwers and W. Treppmann, *ibid.*, **48**, 1217 (1915).

STANFORD UNIVERSITY, CALIF.

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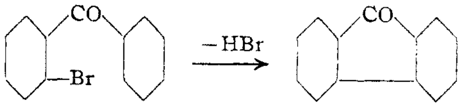
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Higher Benzenoid Hydrocarbons. II. The Isomeric Bromofluorenones[1]

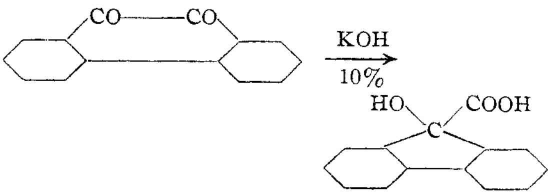
BY HARRY F. MILLER AND G. BRYANT BACHMAN

Of the four possible monobromofluorenones, 2-bromofluorenone is the only one readily available. The preparation of the 4-isomer has never been recorded and the 1- and 3-isomers have been prepared in small quantities only and by way of difficultly accessible intermediates.[2] As a part of our program to elucidate the fundamental chemistry of some of the polycyclic coal tar hydrocarbons it was decided to devise nuclear syntheses for the 3- and 4-bromofluorenones which would make them more readily available and which would serve to establish definitely their structure.

There are five general methods which have been used for the preparation of substituted fluorenones. (1) *Direct substitution.* This serves very well for the preparation of 2-bromo and 2,7-dibromofluorenones. Apparently, however, no other isomers arise in the bromination of either fluorenone or fluorene.[3] (2) *Elimination of hydrogen bromide from substituted o-bromobenzophenones.*



Although this method was used by Montagne to prepare 1- and 3-bromofluorenones, the yields are small and the intermediates difficult to prepare. Furthermore, in view of the high temperatures employed to effect condensation, there is always to be considered the danger of an intramolecular rearrangement. (3) *The rearrangement of phenanthraquinone derivatives.* This is an application of the benzil–benzilic acid rearrangement.



The diphenyleneglycolic acid formed decomposes in the presence of boiling water liberating fluorenone. The method has been used successfully in the preparation of certain nitrofluorenes[4] and of a

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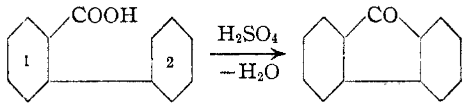
[1] First paper in this series, THIS JOURNAL, **57**, 766 (1935).

[2] Montagne and Van Charante, *Rec. trav. chim.*, **32**, 164 (1913).

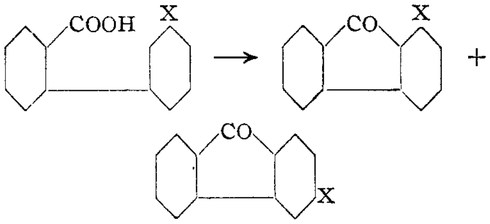
[3] Courtot and Vignati, *Bull. soc. chim.*, [4] **41**, 58 (1927).

[4] Schmidt, *et al.*, *Ber.*, **38**, 3737 (1905); **41**, 3679 (1908).

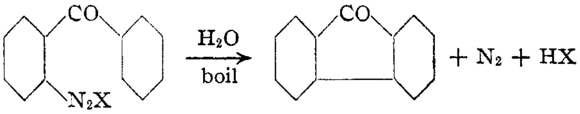
few other fluorene derivatives, but its broader application awaits the further development of phenanthrene chemistry, since in many cases the necessary phenanthraquinones are unknown. The isomeric bromophenanthraquinones have not yet been thoroughly studied. (4) *The dehydration of o-carboxydiphenyl derivatives.* This method is



of particular value in that it gives very high yields as a rule. Applied to the synthesis of substituted fluorenones however it will be noted that the method suffers certain disadvantages if the substituent group is located in the meta position of ring 2. In such cases either one or both of two different isomers may result upon ring closure



Where establishment of structure is being attempted such a mixture might lead to confusion and should be avoided. Furthermore, it has been our experience that mixtures of bromofluorenones are not easily separable. Substituents in ring 1 and in the ortho or para position of ring 2 lead to but one product, however, and since this method is otherwise quite general in its application and relatively simple to apply, it is to be recommended. The above arguments apply to all nuclear fluorenone syntheses in which ring closure of this type occurs. These include methods (2), (4) and (5). *Method* (5) consists in the coupling of diazotized *o*-aminobenzophenone derivatives.[5]



For the present work methods (4) and (5) have been used since they seemed to be most satisfactory from the standpoints of yield, cost, and generality of application. The flow diagram shown in Table I indicates the various steps used for the synthesis of 3- and 4-bromofluorenones. For 3-bromofluorenone the over-all yield from phthalic anhydride (5 steps) was 55%, from anthranilic acid (4 steps) 21%. The 4-bromofluorenone was obtained from bromophthalic anhydride (5 steps) in 25% yield, from *o*-iodobromobenzene and methyl *o*-iodobenzoate (2 steps) in 14% yield. The difficulty of preparing the last two intermediates makes this last synthesis of little practical value. Fortunately 4-bromofluorenone may be obtained more readily by the oxidation of the easily prepared 4-bromofluorene whose synthesis will be described in the succeeding paper.

It should be pointed out that by combinations of the two general methods here used some of the heteronuclear dibromofluorenones could also be prepared. The conversion of the bromofluorenones into the corresponding bromofluorenols and bromofluorenes is described in the succeeding paper.

The Synthesis of 3-Bromofluorenone

2-(4-Bromobenzoyl)-benzoyl Chloride.—The condensation of phthalic anhydride with bromobenzene in the presence of aluminum chloride according to Ullmann and Sone[6] yielded 2-(4-bromobenzoyl)-benzoic acid, m. p. 171–172°, in 83% yields (above authors report 86%). Fifty-three grams of this product, 37 g. of phosphorus pentachloride and 200 cc. of benzene were refluxed until no more hydrogen chloride was evolved. On cooling, the acid chloride separated as white opaque needles; yield 92% theoretical, m. p. 162–163°.

Anal. Calcd. for $C_{14}H_8O_2BrCl$: Br and Cl, 35.66. Found: Br and Cl, 35.48.

2-(4-Bromobenzoyl)-benzamide.—Twenty-five grams of finely powdered acid chloride was added in small portions to 200 cc. of liquid ammonia in a Dewar tube. The mixture was stirred by a stream of air bubbles from a capillary at the bottom of the tube. After the ammonia had evaporated water was added and the residue separated and recrystallized from a mixture of 500 cc. of xylene and 50 cc. of acetone. The amide formed feathery white needles, m. p. 184.5–185.0°, and was obtained in 95% yields.

Anal. Calcd. for $C_{14}H_{10}O_2NBr$: Br, 26.20. Found: Br, 26.05.

2-(4-Toluenesulfonamido)-benzoyl Chloride.—Anthranilic acid was converted into its *p*-toluenesulfonanilide (yield 86%, m. p. 217–218°)[5b] and then into the corresponding acid chloride[7] with phosphorus pentachloride (yield 96%, m. p. 129°). In this latter reaction it was found simplest to use no solvent since the acid is but slightly soluble in benzene and other inert solvents.

2-(4-Bromobenzoyl)-aniline. First Procedure.—Ten grams of 2-(4-bromobenzoyl)-benzamide and 30 cc. of 10% sodium hydroxide solution were made into a thin paste in a mortar. A sodium hypobromite solution was prepared from 15 g. of sodium hydroxide, 13 g. of bromine

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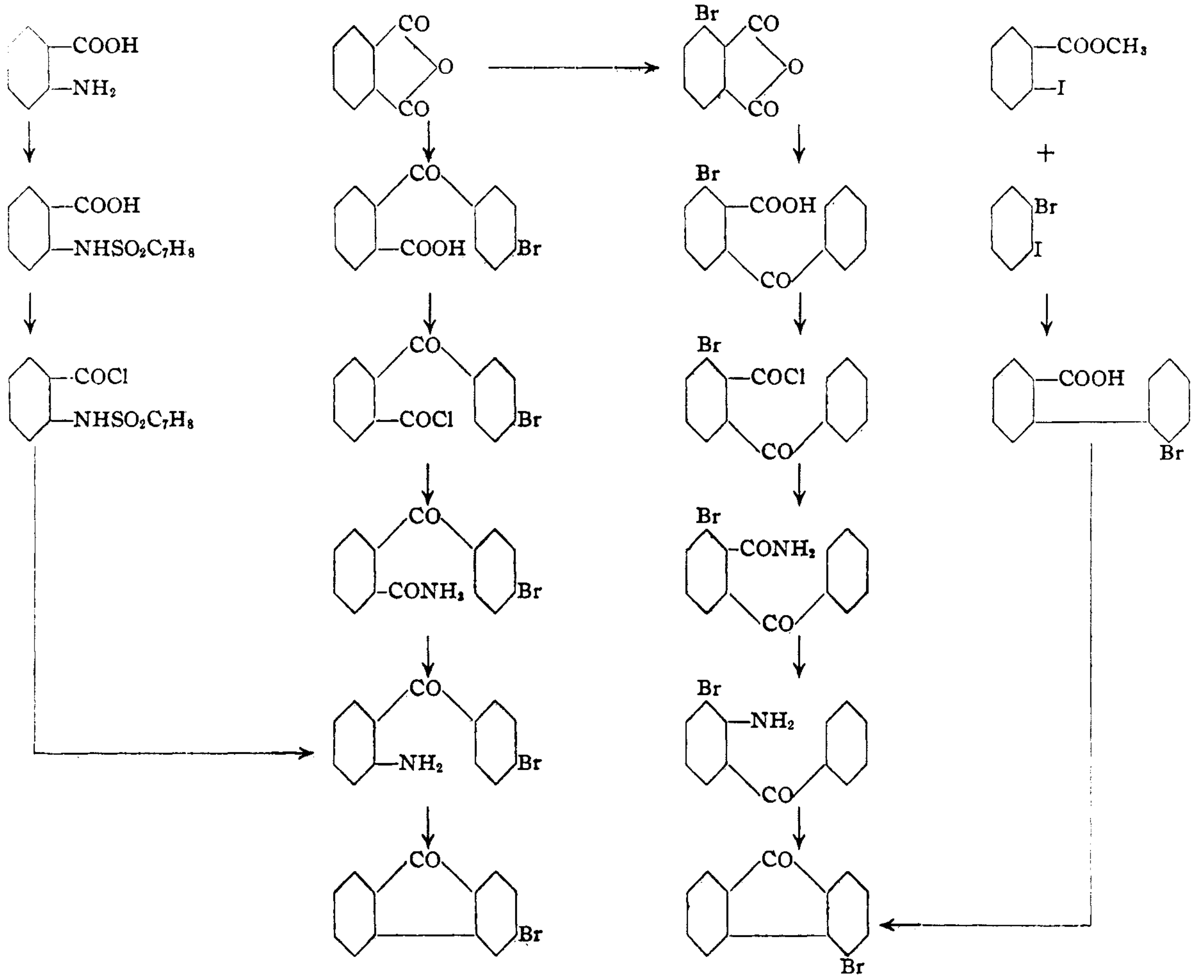
[5] (a) Ullmann and Mallett, *Ber.*, **31**, 1694 (1898); (b) Ullmann and Bleier, *ibid.*, **35**, 4273 (1902).

[6] Ullmann and Sone, *Ann.*, **380**, 337 (1911).

[7] Schroeter and Eisleb, *ibid.*, **367**, 111 (1909).

TABLE I

SYNTHESIS OF 3- AND 4-BROMOFLUORENONES



and 100 cc. of water. The mixture was cooled in an ice-bath and the amide paste added in small portions with vigorous stirring. Most of it dissolved. After standing for one hour in the cold, the solution was filtered, 5 cc. of ethanol added, and the mixture then boiled for one-half hour and allowed to stand for one day. The yellow amine crystallized in a cake and was filtered and dried. It melted at 107–108° and was pure enough for further synthesis. The filtrate was boiled with 20 cc. of saturated sodium bisulfite solution and on cooling deposited 1.5 g. of unchanged amide. On acidification, the second filtrate precipitated 3.9 g. of 2-(4-bromobenzoyl)-benzoic acid. The total yield of amine was 3.8 g. (82.5%, based on the amide used).

Second Procedure.—Fifty-three grams of 2-(4-toluenesulfonamido)-benzoyl chloride was refluxed with 100 g. of bromobenzene until solution took place. One hundred grams of anhydrous aluminum chloride was added to the cooled solution and the mixture warmed on the water-bath, gently at first, and then at the boiling point for eight hours. The mass was cooled, decomposed with ice, water and hydrochloric acid, the water layer decanted, and the pitch-like solid steam distilled to remove excess bromobenzene. The remaining dark solid sulfonamide was too insoluble to be purified by solution in alkali, therefore it was converted directly to the amine. This was done by dissolving the crude product in a mixture of 300 cc. of 90% sulfuric acid and 150 cc. of glacial acetic acid, heating for three hours on the water-bath, and then allowing to stand overnight. The solution was poured into 3 liters of water and filtered. The clear filtrate was neutralized cautiously with concentrated sodium hydroxide. On cooling, bright yellow needles of the amine, melting at 108°, formed. By treating the residue once more with sulfuric acid, as above, a further quantity of amine was obtained; total yield 12.9 g. (28% of theoretical).

Third Procedure. The Oesterlin Reaction.—Oesterlin[8] has proposed a general method for the conversion of carboxy acids into amines directly. In applying this reaction to 2-(4-bromobenzoyl)-benzoic acid the expected synthesis occurred to a very small extent only and the dimorph of the original acid was obtained as the principal product. Eight and seven-tenths grams of acid dissolved in 50 cc. of chloroform was treated with 50 cc. of concd. sulfuric acid, the temperature being maintained at 40–45°. To the mixture was then added in small portions 1.8 g. of

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(8) Oesterlin, *Z. angew. Chem.*, **45**, 536 (1932).

sodium azide. There was a vigorous gas evolution after each addition. The mixture was held at 40° for one hour and then poured into 600 cc. of cold water. The white solid which precipitated was filtered and dried. It weighed 7.3 g., melted at 158°, and proved to be the dimorph of the original acid. After resolidification it melted at 173° and was identical with the original acid. The yellow-colored filtrate was made alkaline with 10% sodium hydroxide. On standing 0.15 g. of 2-(4-bromobenzoyl)-aniline precipitated; yield 1.9%, m. p. 106–107°.

Anal. Calcd. for $C_{13}H_{10}OBrN$: Br, 28.95. Found: Br, 28.77.

3-Bromofluorenone.—To 5 g. of 2-amino-4-bromobenzophenone suspended in 50 cc. of water was added 4 cc. of concentrated sulfuric acid. The amine dissolved in the hot solution, but the amine sulfate quickly precipitated as a fine suspension. This suspension was cooled to 10° and diazotized with 1.3 g. of sodium nitrite in 3 cc. of water. The sulfate first dissolved and the solid diazo compound on warming gradually took on the yellow color characteristic of fluorenones, and, after standing for three hours, was filtered by suction, washed with water and then warmed with 5% sodium hydroxide solution in a beaker, with stirring. The solid was again filtered, washed well with water and air dried. Recrystallization from benzene gave light yellow needles, melting at 162°; total yield 4.3 g. (92% of theoretical).

Anal. Calcd. for $C_{13}H_7OBr$: Br, 30.73. Found: Br, 30.67.

The Synthesis of 4-Bromofluorenone

2-Benzoyl-6-bromobenzoyl Chloride.—To 7.8 g. of 2-benzoyl-6-bromobenzoic acid, prepared from bromophthalic anhydride, benzene and aluminum chloride according to the directions of Stephens,[9] were added 5.5 g. of phosphorus pentachloride and 25 cc. of benzene. The mixture was refluxed for forty-five minutes, then cooled, and 25 cc. of ligroin added. Light brown prisms of the acid chloride, m. p. 119–120°, separated; yield 7.1 g., 85.9%.

Anal. Calcd. for $C_{14}H_8O_2ClBr$: Br and Cl, 35.66. Found: Br and Cl, 35.70.

2-Bromo-6-benzoylbenzamide.—A mixture of 5 g. of 2-benzoyl-6-bromobenzoyl chloride and 15 g. of finely powdered ammonium carbonate was heated until gas evolution began. It was maintained at this temperature with stirring for ten minutes and then cooled. Water was added and the insoluble residue separated, dried and recrystallized from 150 cc. of xylene. The amide formed white matted needles, m. p. 135–140°; yield 4.2 g., 87%.

Anal. Calcd. for $C_{14}H_{10}O_2BrN$: Br, 26.20. Found: Br, 26.09.

2-Bromo-6-benzoylaniline.—Three grams of 2-bromo-6-benzoylbenzamide was subjected to the Hofmann degradation in a manner similar to that used in the preparation of 2-(4-bromobenzoyl)-anilines. On heating to boiling an oily yellow liquid separated which solidified on cooling. Recrystallization from alcohol gave 1.6 g. of the amine, m. p. 128–130°, a 57% yield. Acidification of the filtrate gave 0.8 g. of 2-bromo-6-benzoylbenzoic acid, formed by the hydrolysis of part of the amide.

Anal. Calcd. for $C_{13}H_{10}OBrN$: Br, 28.95. Found: Br, 28.76.

2-Bromo-2′-carboxydiphenyl.—A 500-cc., three-necked flask was fitted with a stirrer, an air condenser, and a 400° thermometer. Fifty-three grams of methyl-*o*-iodobenzoate and 56 g. of *o*-bromoiodobenzene were placed in the flask and the mixture heated to 260° in a Woods metal bath. Sixty grams of copper powder which had been treated as recommended by Kleiderer and Adams[10] was then added over a one-hour period to the vigorously stirred mixture, after which the temperature was raised to 290°, kept there for a further half hour, and then allowed to cool. The voluminous precipitate of copper iodide was extracted with two 150-cc. portions of boiling ethanol, which were combined and evaporated to 100 cc. This solution then was refluxed for eight hours with 500 cc. of 10% sodium hydroxide solution, and cooled. The water layer was filtered and acidified slowly with dilute acetic acid. A precipitate formed on standing which was filtered, redissolved in sodium hydroxide solution, and again precipitated as above with acetic acid. The product so obtained was recrystallized from 80% acetic acid to give 5.7 g. (14% yield) of 2-bromo-2′-carboxydiphenyl, white clumps, which darkened on standing, and melted at 186–187°.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.84. Found: Br, 28.61.

The combined filtrates, on acidification with dilute hydrochloric acid, gave 15.6 g. of diphenic acid, m. p. 227°.

4-Bromofluorenone. First Procedure.—Two grams of 2-bromo-6-benzoylaniline was added with stirring to 20 cc. of 25% sulfuric acid. The amine sulfate immediately precipitated in a finely divided form. After cooling to 10° diazotization was effected with 1 g. of sodium nitrite dissolved in 3 cc. of water. The precipitate slowly changed to a lighter shade of color. The solution was allowed to warm up to room temperature, and after five hours' standing was heated to boiling. As soon as the precipitate clumped together and turned yellow, the mixture was cooled and the yellow solid filtered, and stirred into 50 cc. of 10% sodium hydroxide solution. The undissolved solid was filtered, washed with water several times, and dried. When recrystallized from benzene, 1.3 g. of 4-bromofluorenone, m. p. 185–187°, was obtained in the form of light yellow clumps. This corresponded to a 70% yield.

Second Procedure.—One gram of 2-bromo-2′-carboxydiphenyl was heated on a steam-bath with 40 cc. of concentrated sulfuric acid for one-half hour. The hot mixture was poured onto 500 cc. of ice and allowed to stand an hour with occasional stirring, after which the yellow solid was filtered with suction and air-dried. Recrystallization from benzene gave light yellow needles, melting at 190–191°; yield quantitative.

Anal. Calcd. for $C_{13}H_7OBr$: Br, 30.73. Found: Br, 30.61.

Summary

1. 3- and 4-bromofluorenones have been prepared by nuclear syntheses and their properties described.

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(9) Stephens, THIS JOURNAL, 43, 1950 (1921).

(10) Kleiderer and Adams, *ibid.*, 55, 4225 (1933).