solution of the chloride was shaken with silver carbonate.

The yellow picrate precipitated when picric acid, dissolved in alcohol, was added to an aqueous solution of the chloride.

All of the arsonium salts mentioned above are soluble in water with the exception of the picrate.

Experimental Part

General Procedures. (a) **Arsines and Methyl Iodide.**—The arsine was dissolved in the least possible amount of methyl iodide and the mixture refluxed. The precipitated product[4] was filtered, washed with ether and recrystallized.

For the preparation of compound 1 (Table I) the mixture of arsine and iodide was heated for one hour, for compound 3, twenty-four hours, and for compounds 4 and 6, seventy hours.

(b) **Arsine Oxides and Grignard Reagents.**—One-tenth mole of the arsine oxide, dissolved in warm, dry benzene,[5] was added, slowly, with agitation to 0.3 mole of the Grignard reagent and the mixture refluxed for two hours. The solvents were decanted, the residue treated with 40 cc. of water followed by 15 cc. of constant boiling hydrobromic acid. The arsonium bromide separated in crystalline form when the mixture was cooled.

Thermal Decompositions.—A very slow stream of dry nitrogen was passed through a distillation flask which contained 4.6 g. of tetraphenylarsonium bromide and which was heated in a metal bath at 315–335° for fifteen minutes. The distillate, bromobenzene, weighed 1.4 g. and was identified by conversion into phenylmagnesium bromide. Upon addition of benzophenone to the latter triphenylcarbinol was obtained. The residue of triphenylarsine in the distillation flask was dissolved in absolute ether and treated with mercuric chloride, dissolved in the same solvent. There was obtained 4.5 g. of $(C_6H_5)_3As\cdot HgCl_2$; m. p. 245–246°[6] after recrystallization from acetic acid.

When 4.5 g. of methyltriphenylarsonium iodide was heated at 175–200° there was obtained 1.2 g. of methyl iodide and 5.2 g. of $(C_6H_5)_3As\cdot HgCl_2$. In order to identify the methyl iodide it was dissolved in 10 cc. of absolute alcohol and heated for one hour with 5.5 g. of the silver salt of 2-methyl-3,5-dinitrobenzoic acid. After removal of the solvent and extraction of the residue with 25 cc. of benzene there was obtained 1.0 g. of methyl 2-methyl-3,5-dinitrobenzoate; mixed m. p. 73–74°[7] after recrystallization from acetic acid.

From 4.5 g. of cyclohexyltriphenylarsonium bromide, heated at 185–270° over a fifteen-minute period, there was produced 1.3 g. of bromocyclohexane and 4.5 g. of $(C_6H_5)_3As\cdot HgCl_2$. The refractive index of the bromide obtained was $n^{27.5}$ 1.4937; the index of a known specimen was $n^{27.5}$ 1.4939.

Summary

A number of new arsonium halides have been prepared from a tertiary arsine and methyl iodide and by interaction of a tertiary arsine oxide with a Grignard reagent. In addition tetraphenylarsonium nitrate, sulfate, acetate, bicarbonate and picrate have been described.

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(4) In some instances it was necessary to remove partially the methyl iodide.

(5) Anisole was used for the preparation of compound 9.

(6) Blicke and Smith, THIS JOURNAL, **51**, 1561 (1929).

(7) Racine, *Ann.*, **239**, 77 (1887).

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 20, 1937

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

A Further Study of the Bromination of the Nitrodiphenyls

BY FRANCIS H. CASE

It was stated by Guglialmelli and Franco[1] that as a result of the bromination of 4-nitrodiphenyl, in addition to large amounts of 4-bromo-4′-nitrodiphenyl, a compound A was obtained, m. p. 102°, which they believed to be 2-bromo-4′-nitrodiphenyl. On reduction A yielded an amine, B, m. p. 120,° which was converted to an acetyl derivative, C, m. p. 155–156°. B when subjected to the Sandmeyer reaction yielded a dibromide, D, m. p. 109°. All these derivatives, they believed to belong to the 2,4′-system.

Finzi and Bellavita[2] pointed out that the true 2-bromo-4′-nitrodiphenyl, m. p. 82.5°, had already been synthesized by Scarborough and Waters[3] by the nitration of 2-acetaminodiphenyl, followed by hydrolysis and replacement of amino by bromine. Since Guglialmelli and Franco's compound A could not be 2-bromo-4′-nitrodiphenyl, and since it yielded on oxidation 4-nitrobenzoic acid, Finzi and Bellavita reasoned that compound A was probably 3-bromo-4′-nitrodiphenyl and that the corresponding derivatives, B, C, and D belonged to the 3,4′-system.

In order to settle this question definitely, the synthesis of 3-bromo-4′-nitrodiphenyl was effected in this Laboratory in the following manner

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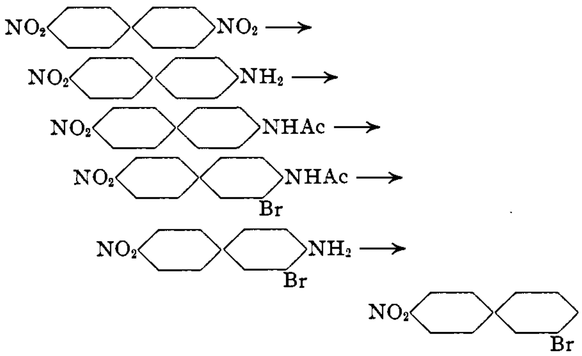
(1) Guglialmelli and Franco, *Anal. asoc. quim. argentina*, **20**, 8 (1932).

(2) Finzi and Bellavita, *Gazz. chim. ital.*, **64**, 335 (1934).

(3) Scarborough and Waters, *J. Chem. Soc.*, 96 (1927).



The proof of structure of the nitrobromodiphenyl was that on reduction and subsequent oxidation by chromic anhydride it yielded *m*-bromobenzoic acid. The 3-bromo-4′-nitrodiphenyl thus prepared melts at 94–95°, and is identical with the product prepared from diazotized *m*-bromoaniline and nitrobenzene by the reaction of Gomberg and Pernert.[4] (These authors mention the para-orienting influence of nitro groups in this reaction.) On reduction it yields a base, m. p. 64–65°, whose acetyl derivative melts at 182–183°. By deaminization of 3,4′-dibromo-4-aminodiphenyl[5] was obtained 3,4′-dibromodiphenyl, a liquid, b. p. 175–177° (3 mm.).

The bromination of 4-nitrodiphenyl now has been repeated both in glacial acetic acid and in an aqueous medium. The reaction product in each case, after removal of 4-bromo-4′-nitrodiphenyl, has been worked up by repeated fractional distillation and crystallization, and the only substances found present were 2-bromo-4′-nitrodiphenyl and unchanged 4-nitrodiphenyl. We are therefore forced to conclude that Guglialmelli and Franco's "compound," m. p. 102°, also obtained by Finzi and Bellavita, is a constant melting mixture, perhaps of 2-bromo-4′-nitrodiphenyl and 4-nitrodiphenyl.

In order to complete the series of 2,4′-derivatives, 2-bromo-4′-nitrodiphenyl has been reduced to the corresponding base, a liquid, b. p. 190–195° (3 mm.); acetyl derivative, m. p. 155–156° (same m. p. as compound C of Guglialmelli and Franco). 2-Bromo-4′-aminodiphenyl yields the known 2,4′-dibromodiphenyl, m.p. 55–56°.[2]

The description of the bromination of 3-nitrodiphenyl in the literature[6] makes no mention of the formation of 2-bromo-3′-nitrodiphenyl as a by-product. This substance now has been isolated in small yield and its identity established by mixed melting point with the product obtained by the action of copper on a mixture of *o*-bromoiodobenzene and *m*-nitroiodobenzene. The base and acetyl derivative corresponding to 2-bromo-3′-nitrodiphenyl also have been prepared.

The bromination of 2-nitrodiphenyl has failed to yield any 2-bromo-2′-nitrodiphenyl although the reaction product has been separated by vacuum distillation into numerous fractions and seeded with 2-bromo-2′-nitrodiphenyl prepared by Ullmann's reaction.[7]

Experimental

Bromination of 4-Nitrodiphenyl

(A) **In Acetic Acid.**—The procedure of Le Fèvre and Turner[8] was followed: *i. e.*, 4-nitrodiphenyl (90 g.), dissolved in 180 cc. of glacial acetic acid, was treated with 45 cc. of bromine and 1 g. of ferric chloride. The mixture was heated for twelve hours on the steam-bath, cooled, poured into water and filtered. The precipitate was extracted with hot alcohol. The insoluble portion, which was recrystallized from glacial acetic acid, was 4-bromo-4′-nitrodiphenyl, m. p. 176°; total yield, 68 g. The alcohol-soluble fraction was evaporated to dryness and fractionally distilled *in vacuo*. By repeated distillation and crystallization from methanol 8 g. of 2-bromo-4′-nitrodiphenyl, identical with that prepared by the method of Scarborough and Waters,[3] was obtained and a small amount of unchanged 4-nitrodiphenyl. No other products were found.

(B) **In Presence of Water.**—The procedure of Le Fèvre and Turner[8] for the bromination of 2-nitrodiphenyl was used; a mixture of 67.5 g. of 4-nitrodiphenyl, 24 cc. of bromine, 3 g. of ferric chloride and 75 cc. of water was well stirred and allowed to stand overnight. The excess bromine was removed by sodium carbonate solution, and the precipitate filtered and extracted with hot alcohol. The alcohol-insoluble material yielded 26.5 g. of 4-bromo-4′-nitrodiphenyl. From the hot alcohol solution a precipitate (13 g.) settled, which after purification melted constantly at 107°, but was separated by vacuum distillation into two portions which after crystallization from methanol yielded unchanged 4-nitrodiphenyl and 4-bromo-4′-nitrodiphenyl, respectively. The alcohol-soluble material was worked up as in the acetic acid procedure, and again only unchanged 4-nitrodiphenyl and 2-bromo-4′-nitrodiphenyl were obtained. In this case, the amount of unchanged material was relatively larger.

4-Amino-4′-nitrodiphenyl.—For the preparation of this compound, the method of Marler and Turner[9] was found to be the most satisfactory. The separation of the base from sulfur was facilitated by repeated extraction with hot dilute acetic, rather than hydrochloric, acid.

3-Bromo-4-acetamino-4′-nitrodiphenyl.—4-Nitro-4′-acetaminodiphenyl (24 g.) and 28 g. of anhydrous sodium

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[4] Gomberg and Pernert, THIS JOURNAL, **48**, 1372 (1926).

[5] Case and Sloviter, *ibid.*, **59**, 2381 (1937).

[6] Blakey and Scarborough, *J. Chem. Soc.*, 3004 (1927).

[7] Ullmann, *Ann.*, **332**, 38 (1904).

[8] Le Fèvre and Turner, *J. Chem. Soc.*, 2043 (1926).

[9] Marler and Turner, *ibid.*, 1359 (1931).

acetate were dissolved in 600 cc. of hot glacial acetic acid, and the mixture allowed to cool rapidly. Bromine (12 cc.) was added, followed by twelve hours of heating on the steam-bath. The reaction product was then poured into water and crystallized from glacial acetic acid: yield, 22.5 g. of material; m. p. 235–236°. The pure product melts at 236–237°.

Anal. Calcd. for $C_{14}H_{11}N_2O_3Br$: Br, 23.85. Found: Br, 24.00.

3-Bromo-4-amino-4'-nitrodiphenyl.—The above acetamino compound, on hydrolysis with alcoholic hydrobromic acid, yielded the free base, crystallized from benzene–petroleum ether, m. p. 118–119°.

Anal. Calcd. for $C_{12}H_9N_2O_2Br$: Br, 27.28. Found: Br, 27.27.

3-Bromo-4'-nitrodiphenyl.—3 - Bromo-4-amino-4'-nitrodiphenyl (13 g.) was dissolved in 200 cc. of alcohol, treated with 50 cc. of dilute sulfuric acid (1–1), and warmed on the steam-bath. A solution of 6 g. of sodium nitrite then was added gradually, and the mixture refluxed for one and one-half hours. After cooling the 3-bromo-4'-nitrodiphenyl was filtered off and recrystallized from methanol: yield 7.5 g.; m. p. 94–95°.

Anal. Calcd. for $C_{12}H_8NO_2Br$: Br, 28.75. Found: Br, 28.98.

This compound also was prepared by the method of Gomberg and Pernert[4] as follows: *m*-bromoaniline (51.3 g.) was treated with 56 cc. of concentrated hydrochloric acid and enough ice to make a paste. Diazotization was effected with 23 g. of sodium nitrite in saturated solution. The diazonium solution, mixed with 250 cc. of nitrobenzene, was treated with 64 cc. of 5 *N* sodium hydroxide, the temperature being kept below 5°, and then allowed to stand overnight. After removal of the nitrobenzene *in vacuo*, the resulting tar was extracted repeatedly with petroleum ether. The extract was fractionated *in vacuo* and from the higher fraction was obtained 1 g. of product melting at 94–95° and unchanged when mixed with 3-bromo-4'-nitrodiphenyl prepared as above.

3-Bromo-4'-acetaminodiphenyl.—To a solution of 46.5 g. of $SnCl_2 \cdot 2H_2O$ in 300 cc. of absolute alcohol was added 18.5 g. of 3-bromo-4'-nitrodiphenyl and the mixture refluxed twelve hours. After removal of the alcohol, decomposition of the tin compound by sodium hydroxide, and extraction with ether, 17 g. of crude base was obtained. On acetylation, this yielded 10 g. of 3-bromo-4'-acetaminodiphenyl, crystallized from methanol, m. p. 182–183°.

Anal. Calcd. for $C_{14}H_{12}ONBr$: Br, 27.56. Found: Br, 27.85.

3-Bromo-4'-aminodiphenyl.—On hydrolysis of the above acetamino compound with alcoholic hydrobromic acid, the free base was obtained, m. p. 64–65°. It was crystallized from ether–petroleum ether.

Anal. Calcd. for $C_{12}H_{10}NBr$: Br, 32.26. Found: Br, 32.25.

On oxidation with chromic acid in glacial acetic acid, *p*-bromobenzoic acid was obtained.

3,4'-Dibromodiphenyl.—This was prepared by the deaminization of 3,4'-dibromo-4-aminodiphenyl by a method analogous to the deaminization of 3-bromo-4-amino-4'-nitrodiphenyl, described above. After removal of the alcohol, the crude dibromodiphenyl first obtained by distillation *in vacuo*, was dissolved in absolute ether and freed of unchanged amine by passing in dry hydrogen bromide and filtering off the precipitate. The pure product boiled at 175–177° (3 mm.).

Anal. Calcd. for $C_{12}H_8Br_2$: Br, 51.28. Found: Br, 51.47.

On oxidation with chromic acid, *p*-bromobenzoic acid was formed.

2-Bromo-4'-acetaminodiphenyl.—This was prepared by reduction of 2-bromo-4'-nitrodiphenyl (prepared by the method of Scarborough and Waters)[3] by the theoretical amount of stannous chloride in alcohol solution, followed by acetylation of the crude base. Pure 2-bromo-4'-acetaminodiphenyl, crystallized from benzene, melts at 155–156°.

Anal. Calcd. for $C_{14}H_{12}ONBr$: Br, 27.56. Found: Br, 27.21.

2-Bromo-4'-aminodiphenyl.—This was prepared from the above acetamino compound by hydrolysis with hydrobromic acid in alcoholic solution. It is a liquid boiling at 183–185° (3 mm.).

Anal. Calcd. for $C_{12}H_{10}NBr$: Br, 32.26. Found: Br, 32.26.

2,4'-Dibromodiphenyl.—This was prepared from the above base by the Gattermann reaction. It crystallizes from petroleum ether, m. p. 55–56°. It was prepared previously by Finzi and Bellavita[2] by the deaminization of 2,4'-dibromo-4-aminodiphenyl.

2-Bromo-3'-nitrodiphenyl.—A mixture of *o*-bromoiodobenzene (28 g.), *m*-nitroiodobenzene (26 g.), and 16 g. of copper powder was heated at 250° for one hour. The mixture was then taken up in ether, the ether removed, and the residue distilled *in vacuo*. By means of petroleum ether it was separated into two portions, the insoluble part yielding a very small amount of 3,3'-dinitrodiphenyl. The soluble part, after fractional distillation *in vacuo*, yielded 2.7 g. of 2-bromo-3'-nitrodiphenyl, m. p. 78–79°.

Anal. Calcd. for $C_{12}H_8NO_2Br$: Br, 28.75. Found: Br, 28.91.

2-Bromo-3'-acetaminodiphenyl.—This was prepared by the reduction of 2-bromo-3'-nitrodiphenyl in alcohol with the theoretical quantity of $SnCl_2 \cdot 2H_2O$, followed by acetylation of the crude base. The acetylated base was crystallized from benzene–petroleum ether, m. p. 135°.

Anal. Calcd. for $C_{14}H_{12}ONBr$: Br, 27.56. Found: Br, 27.84.

2-Bromo-3'-aminodiphenyl.—This was prepared by the hydrolysis of the acetamino derivative by alcoholic hydrobromic acid. It was crystallized from ether–petroleum ether, m. p. 57°.

Anal. Calcd. for $C_{12}H_{10}NBr$: Br, 32.26. Found: Br, 32.25.

Bromination of 3-Nitrodiphenyl.—The directions were the same as those of Le Fèvre and Turner (acetic acid method)[8] for the bromination of 4-nitrodiphenyl, using 45 g. of 3-nitrodiphenyl. The precipitate, obtained by pouring the acetic acid solution into water, was recrystallized from alcohol, yielding 49 g. of 4-bromo-3'-nitrodiphenyl, m. p. 95°. From the alcoholic filtrate, evaporated to dryness, was obtained after fractional distillation *in vacuo* and several crystallizations from methanol, 4 g. of a product, m. p. 79°, and unchanged when mixed with 2-bromo-3′-nitrodiphenyl, prepared by Ullmann's method.

Bromination of 2-Nitrodiphenyl.—The same directions were used as for the meta isomer. The reaction product was separated by fractional distillation into nine fractions from which 28 g. of crude 4-bromo-2′-nitrodiphenyl was obtained, and 5 g. of unchanged 2-nitrodiphenyl. The intermediate fractions remained liquid, even though seeded with 2-bromo-2′-nitrodiphenyl prepared by the method of Ullmann.

Summary

1. The bromination of 4-nitrodiphenyl has been shown to yield small amounts of the 2′-bromo derivative (in addition to the 4′-compound chiefly formed), but none of the 3′-bromo derivative as has been suggested elsewhere.

2. 3-Bromo-4′-nitrodiphenyl and its amino and acetamino derivatives have been synthesized.

3. 2-Bromo-4′-aminodiphenyl and its acetamino derivative have been synthesized.

4. The 2′-bromo derivative of 3-nitrodiphenyl has been isolated from its bromination products. The corresponding amino and acetamino derivatives are described.

PHILADELPHIA, PENNA. RECEIVED DECEMBER 20, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine Upon Organic Compounds. V[1]

BY NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

An earlier report from this Laboratory[2] has described the direct fluorination of hexachlorobenzene in carbon tetrachloride solution, leading to the isolation of two definite, solid addition compounds, having the empirical formulas $C_6Cl_6F_4$ and $C_6Cl_6F_6$. In the present work, we have attacked the problem from a different angle, by carrying out the reaction in the vapor phase, in presence of a copper gauze catalyst, somewhat similar to that described before.[3] The reaction took place very smoothly, with the formation of a highly reactive liquid, which was presumably an addition product. This was reduced with iron in glacial acetic acid solution, in order to form if possible stable compounds, having no stereoisomers, which would be crystalline in nature and more tractable. The results were gratifying, since we have been able to isolate from the reduced product no less than twelve distinct compounds; two of which were white crystalline solids, and the other ten colorless liquids, most of which became crystalline at −80°. The characteristics of these substances, together with the quantities obtained of each, are listed in Table I.

The liquids were separated by fractionation from a precision still, and were cut from flat plateaus in the distillation curve, which was itself readily reproducible. Also, the fractions which crystallized on cooling yielded freezing curves with flat inflections. The solids were isolated by repeated fractional crystallization, and had sharp melting points. As shown above, the results of the analyses indicated that the atomic ratio of Cl:F in each of these compounds was very closely that of simple whole numbers. These facts, taken together, leave no reasonable doubt that the products must be considered as definite chemical individuals.

The elucidation of the structures of these substances will require much further investigation, which is now in progress in this Laboratory. The above results are nevertheless presented as representing the first instance to be described of a series of definite compounds, crystalline in nature, resulting from the action of elementary fluorine on the aromatic organic nucleus.

Experimental Part

The apparatus used for the vapor phase fluorination was quite simple, and is illustrated to scale in Fig. 1. Fluorine was admitted through F by means of a copper tube, perforated at the lower end and wrapped with a 20-mesh copper gauze roll C. The sample was simultaneously sublimed into the reaction chamber from the wide side-arm A, heated by the metal jacket B, the liquid products condensed being collected in the flask D. Cork stoppers covered with copper foil were used, and the tube E was left open.

In a typical run, the apparatus was swept out with fluorine which continued to flow at the rate of about 2 liters per hour. Hexachlorobenzene was packed loosely in the side-arm, which was gradually heated, and maintained at 180–195°. The charge was in this way sublimed into the reaction chamber, where a perfectly quiet, con-

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[1] Presented in part before the Organic Division at the Chapel Hill meeting of the American Chemical Society, April 13, 1937.

[2] Bigelow and Pearson, THIS JOURNAL, **56**, 2773 (1934).

[3] Miller, Calfee and Bigelow, *ibid.*, **59**, 198 (1937).