30 cc. of 2B ethanol. Then an additional 3 g. of paraformaldehyde was added, the reaction mixture refluxed for 15 minutes and filtered hot. The product separated from the cooled filtrate, yield 4 g., m.p. 193–194° after recrystallization from ethanol–acetone.

Anal. Calcd. for $C_{14}H_{19}O_3N_2Cl$: N, 9.38. Found: N, 9.64.

***p*-Nitro-ω-dimethylaminopropiophenone Hydrochloride.**—To a refluxing solution of 40.75 g. of dimethylamine hydrochloride, 22.5 g. of paraformaldehyde, 1.5 cc. of concentrated hydrochloric acid in 200 cc. of 2B ethanol, 82.5 g. of *p*-nitroacetophenone was added portionwise over a period of 1 hour. The reaction mixture was refluxed an additional 15 minutes, cooled and the keto base filtered, yield 20 g., m.p. 190–191° after recrystallization from ethanol–ether.

Anal. Calcd. for $C_{11}H_{15}O_3N_2Cl$: N, 10.83. Found: N, 10.86.

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Some Notes on the Chemistry of Arsafluorinic Acid[1]

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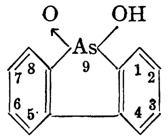
Arsafluorinic acid (I) has been the object of only scant attention. Aeschlimann, *et al.*,[2] were the first to report its preparation from ring closure of biphenyl-2-arsonic acid.



I

The chemistry of the system was somewhat extended by Cookson and Mann[3] who prepared several 9-substituted arsafluorenes. Recently, Feitelson and Petrow[4] reported a more varied series of compounds obtained by ring-closure methods and by direct substitution. This last publication appeared when we were in the final stages of some research in the same field. Though our efforts were not so extensive as those of Feitelson and Petrow, many of the compounds reported by them had been prepared by us, and agreement on the data concerning these was, in general, very good. There were some points of difference, however, and some new material which may be of interest in view of the paucity of information pertaining to the system.

The parent compound, arsafluorinic acid, was synthesized according to the method of Aeschlimann by treating biphenyl-2-arsonic acid with concentrated sulfuric acid for ten minutes at 100°. The compound obtained, however, had consistently a melting point of 327–328°. Since Cookson and Mann had reported a melting point of 299°, the product was submitted to further examination. Conversion to 9-chloro- and 9-iodoarsafluorene gave products melting at described temperatures.[2] The neutral equivalent, determined by titration with standard alkali in an alcohol–water medium using phenolphthalein indicator, gave values (260, 259) close to the calculated molecular weight of the compound. Arsenic analysis gave results consistent with the calculated content. Finally, hydrolysis and oxidation of 9-chloroarsafluorene by addition of 30% hydrogen peroxide to the suspension of the compound in hot potassium hydroxide solution gave, on acidification, arsafluorinic acid melting at 328–328.2°. The purity of the compound was then confirmed. Feitelson and Petrow indicate the melting temperature to be above 300°.

A simpler method for preparing the 9-chloro derivative was discovered. It consists in suspending arsafluorinic acid in glacial acetic acid, heating to 80° and adding phosphorus trichloride dropwise with stirring until the arsinic acid dissolves. Cooling effects the separation of 9-chloroarsafluorene in good yield and purity. This procedure was also applied, using chloroform as a solvent and phosphorus tribromide, to prepare for the first time 9-bromoarsafluorene, melting at 178°. Nitration of arsafluorinic acid to give the 2-nitro compound was accomplished by a method very similar to that described by Feitelson and Petrow,[4] but these authors do not comment on the surprising ease of nitration. The reaction is carried out at 5° with little more than the calculated quantity of nitric acid. This facility for nitration is unexpected in view of the electronegativity of the arsinic acid grouping. Dinitration is imminent and is, indeed, readily accomplished under mild conditions.

From the nitroarsinic acid, 2-nitro-9-chloroarsafluorene was prepared by the action of phosphorus trichloride. These haloarsines are useful compounds for purification and characterization since they represent soluble, crystallizable materials with good melting points. In the same way, 3-nitroarsafluorinic acid, obtained by ring closure of 5-nitrobiphenyl-2-arsonic acid, was converted to 3-nitro-9-chloroarsafluorene. Similarly, in the case of intermediates used in ring closing attempts, 5-nitrobiphenyl-2-dichloroarsine and 4′-nitrobiphenyl-2-dichloroarsine were prepared.

Reduction of the 2-nitro compound to the amine was accomplished with alkaline ferrous hydroxide in a manner similar to that already described[4] except that boiling-water temperature was used in the final stage. This amine decomposed without melting and had a clean yellow color instead of the pink color described for it. We suggest that the pink color of the material obtained by Feitelson and Petrow was due to the presence of some dinitroarsafluorinic acid in the starting material since we have obtained a light red product from attempts to reduce the dinitro compound with hot alkaline ferrous hydroxide. In the latter case evidence is incomplete, but our observations are at variance with those of Feitelson and Petrow who claim to have been unable to effect reduction of the dinitro-arsinic acid either with ferrous hydroxide or catalytic hydrogenation. Our light red material is probably not the diamine, but represents at least a partially reduced stage, perhaps the nitroamine.

Experimental

Preparation of Haloarsines. General Procedure.—Approximately 2 g. of the arsonic or arsinic acid was suspended

[1] Abstracted from a thesis presented by I. Victor Mattei in partial fulfillment of the requirements for the Master of Science degree at Xavier University.

[2] J. A. Aeschlimann, N. D. Lees, N. P. McLeland and G. N. Nicklin, *J. Chem. Soc.*, **127**, 66 (1925).

[3] G. H. Cookson and F. G. Mann, *ibid.*, 2888 (1949).

[4] B. N. Feitelson and V. Petrow, *ibid.*, 2279 (1951).

in 10 ml. of either glacial acetic acid or chloroform. The mixture was heated on a water-bath and the appropriate phosphorus trihalide (1–2 ml.) was added dropwise with shaking until the suspension completely dissolved. The solution was warmed 10–15 minutes on the water-bath, filtered, and allowed to cool. The crystalline material depositing was recrystallized, usually from chloroform. In this manner were prepared 9-chloroarsafluorene (I), 9-bromoarsafluorene (II), 2-nitro-9-chloroarsafluorene (III), 3-nitro-9-chloroarsafluorene (IV), 5-nitrobiphenyl-2-dichloroarsine (V) and 4′-nitrobiphenyl-2-dichloroarsine (VI). Details are given in Table I. Melting points were obtained with an aluminum block using a calibrated thermometer. Arsenic analysis was accomplished according to the procedure of Robertson.[5]

TABLE I

PREPARATION OF SOME HALOARSINES

Compound	Reaction solvent[b]	Recrystn. solvent[b]	Yield, %[a]	M.p., °C.	Arsenic, % Calcd.	Arsenic, % Found
I	A	B	43.2	160–161	...	...
II	B	B	65.1	174–175	24.48	25.55
III	A	B	79.3	186–187	24.43	24.36
IV	A	B	80.1	199–200	24.43	24.47
V	A	B	70.9	105–106	21.84	21.78
VI	B	C	76.5	81–82	21.84	21.35

[a] Yield calculated from weight of recrystallized product. [b] Key to solvents: A, glacial acetic acid; B, chloroform; C, benzene–petroleum ether.

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[5] G. R. Robertson, THIS JOURNAL, **43**, 182 (1921).

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The Preparation of Two Fluorinated *p*-Dihalobenzenes[1]

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A number of benzene derivatives containing fluorine and other halogens have been reported in the literature.[2] None of these compounds, however, contain two halogen atoms, other than fluorine, in positions para to each other. More recently Finger and co-workers[3] prepared 1,4-dichloro-2,5-difluorobenzene and 1,4-dibromo-2,5-difluorobenzene as the first compounds of this type to be made.

In this paper two new compounds of this series are reported containing one and four fluorine atoms, respectively. They are 1,4-dichloro-2-fluorobenzene, which was prepared from 2,5-dichloroaniline by the Schiemann reaction,[2] and 1,4-dibromo-2,3,-5,6-tetrafluorobenzene, which was obtained by brominating *sym*-tetrafluorobenzene. Finger and his associates had prepared this tetrafluorobenzene but found it relatively resistant to further substitution such as nitration and chlorination.[3] Our attempts to brominate this compound failed under mild conditions, but by using fuming sulfuric acid as a solvent, a good yield of the desired product was obtained. The identity of both new compounds was established by chemical analysis and by their ultraviolet absorption spectra.

The ultraviolet absorption data of the two new fluorinated *p*-dihalobenzenes and their non-fluorinated analogs are presented in Table I. The shapes of the ultraviolet absorption curves for these new compounds agree with those generally found for aromatic compounds.[4] It is evident from these data that the introduction of fluorine atoms does not affect the main absorption bands appreciably. The secondary bands appear to be intensified in the fluorinated compounds, but they do not show any significant shifts. More detailed data on the ultraviolet absorption spectra of these and other fluorinated benzenes will be published at a later date.

TABLE I

ULTRAVIOLET ABSORPTION DATA

Compound	Primary band Wave length, Å.	Primary band Molar absorbance	Secondary band Wave length, Å.	Secondary band Molar absorbance
1,4-Dichlorobenzene	2248	12,900	2650 2728 2805	300 390 330
1,4-Dichloro-2-fluorobenzene	2240	11,400	2665 2718 2795	780 1080 1030
1,4-Dibromobenzene	2278	15,500	2655 2733 2821	290 300 195
1,4-Dibromo-2,3,5,6-tetrafluorobenzene	2275	18,400	2480 2700	1750 1100

Experimental

1. **1,4-Dibromo-2,3,5,6-tetrafluorobenzene.**—The bromination was performed in a 100-ml. three-neck flask equipped with a mercury-sealed stirrer, condenser and a dropping funnel. Into this flask 14 ml. of bromine, 15 ml. of 60% fuming sulfuric acid and 0.5 g. of aluminum bromide were introduced. The mixture was stirred and 10 g. of 1,2,4,5-tetrafluorobenzene was added dropwise. An exothermic reaction occurred with the evolution of white fumes. After the addition was completed, the flask was heated in a water-bath at 50–60° for 4 hours. The contents were then carefully poured over cracked ice. The product settled out as a brownish solid which was filtered and washed successively with sodium carbonate, sodium bisulfite and water. It was then recrystallized from a methanol–water mixture and dried at room temperature; yield 16 g. (78%), m.p. 76–77°.

Anal. Calcd. for $C_6F_4Br_2$: F, 24.68; Br, 51.91; mol. wt., 307.9. Found: F, 24.7; Br, 51.7; mol. wt., 296.

2. **1,4-Dichloro-2-fluorobenzene.**—A suspension of 49.6 g. of 2,5-dichloroaniline hydrochloride in 40 ml. of concentrated hydrochloric acid and 80 ml. of water was stirred and cooled to −5°. A solution of 19.7 g. of sodium nitrite in 60 ml. of water was added dropwise while the temperature was maintained at −5°. After the addition was completed, the solution was stirred for 5 minutes. Any solid that remained at this point was removed by filtration at 0°. To the clear filtrate 42 ml. of 40% fluoboric acid was added rapidly. The resulting suspension of the diazonium fluoborate was stirred vigorously at about 5° for 30 minutes and filtered. The precipitate was washed with 25-ml. portions of 5% fluoboric acid, methanol and ether. The salt was then spread out on a large filter paper and dried in air; yield 46.6 g. (72%).

The diazonium fluoborate was decomposed in a system containing two flasks connected by a bent tube of large bore. The salt was introduced into one flask and the other was cooled in an ice-bath. The receiving flask was connected to a trap, cooled in ice, which had an outlet to the hood. The decomposition was performed by intermittent heating with a Bunsen burner until no more white fumes were given

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[1] This paper is based on work sponsored by the Ordnance Corps, United States Department of the Army.

[2] For references up to 1946 see A. Roe, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 193–228.

[3] G. C. Finger, F. H. Reed, D. M. Burness, D. M. Fort and R. R. Blough, THIS JOURNAL, **73**, 145 (1951).

[4] L. Doub and J. M. Vandenbelt, *ibid.*, **69**, 2714 (1947).