ness, 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

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[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).

TABLE I

CHARACTERISTICS OF THE COMPOUNDS RESULTING FROM THE REDUCTION OF FLUORINATED HEXACHLOROBENZENE

| Cpd., g. | B. p. (11 mm.), °C. | M. p. °C. | Cl, % | | F, % | | Ratio, Cl:F |
|---|---|---|---|---|---|---|---|
| 3.6 | 32 | Glass | 33.4 | 33.5 | 44.2 | 44.2 | 2:4.94 |
| 1.2 | 37 | −41 | 34.4 | 34.4 | 41.2 | 41.2 | 4:8.96 |
| 2.1 | 41 | Glass | 35.5 | 35.5 | 38.0 | 38.0 | 1:2.00 |
| 3.5 | 45 | −56 | 38.5 | 38.5[a] | 31.2 | 31.2[a] | 2:3.02 |
| 3.0 | 52 | Glass | 40.5 | 40.4 | 36.2 | 36.0 | 3:5.01 |
| 5.1 | 56 | Glass | 41.9 | 41.8 | 37.4 | 37.4 | 3:5.01 |
| 1.6 | 64 | −44 | 44.2 | 44.4 | 36.1 | 35.9 | 2:3.02 |
| 2.2 | 68 | − 5 | 45.6 | 45.5 | 30.7 | 30.5 | 4:5.04 |
| 4.7 | 72 | 0 | 44.9 | 44.9 | 29.0 | 28.9 | 5:6.05 |
| 5.8 | 75 | − 9 | 47.3 | 47.3[a] | 12.6 | 12.7[a] | 2:1.00 |
| ... | .. | 69–70 | 56.4 | 56.4[b] | 18.0 | 18.0[b] | 5:2.98 |
| ... | .. | 142–143 | 68.0 | | 9.2 | | 4:1.01 |

[a] Analyses by Dr. Rose M. Davis, using the unmodified Willard and Winter method. [b] Sample analyzed melted at 69–71°.

tinuous reaction took place. The temperature in the large flask did not rise above 55° during the process, and the product, which was a heavy yellow oil, condensed and was collected below, at the rate of about 8 g. per hour. The charge was renewed progressively, and for each 25 g. of hexachlorobenzene consumed, approximately 27 g. of the oil was formed, indicating that addition had taken place at least in part. Altogether 507 g. of the crude addition product was prepared. It contained roughly 53% Cl, 13% F, and was essentially inert to fluorine when the gas was bubbled through it.

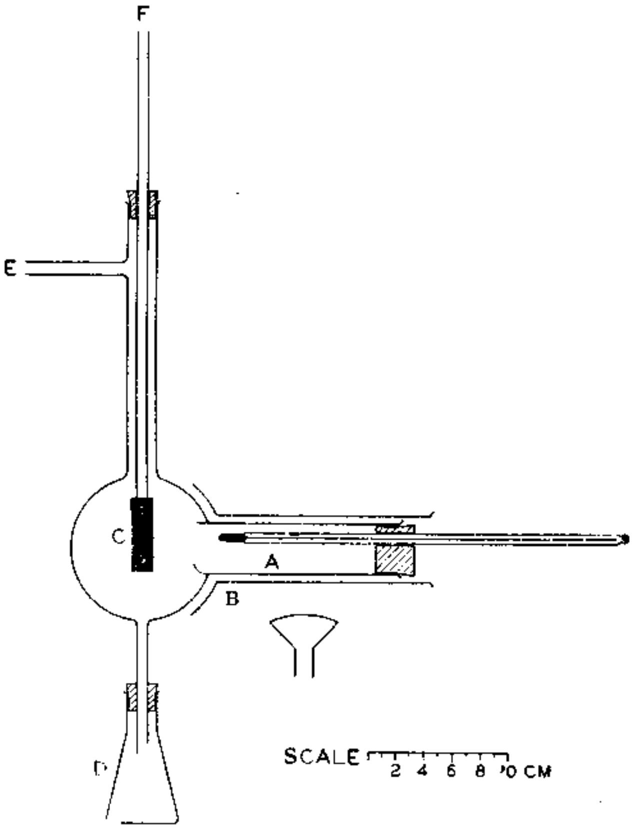

Fig. 1.—Apparatus for the fluorination of hexachlorobenzene.

As an example of the reduction process, 50.2 g. of crude oil was dissolved in 100 cc. of glacial acetic acid, and 12 g. of iron powder added in portions, with agitation, keeping the initial reaction moderate. Then the mixture was refluxed for about ten hours, poured into 200 cc. of water, and 100 cc. of concentrated hydrochloric acid added, in order to dissolve the iron. The dark oily layer which separated was steam distilled, changing receivers at the first appearance of crystalline material. The yield of oil was 14.4 g., and of solid 2.1 g. Altogether 127 g. of oil and 33 g. of crystals were prepared.

The oil was washed with 2% alkali solution, dried and distilled. The product weighed 82 g. and boiled at 38–70° at 5 mm. The yellowish solid residue weighed 10.5 g. The colorless liquid was then fractionated at 11 mm. in a Podbielniak still, yielding ten constant boiling fractions, the characteristics of which have been tabulated above. About 15 g. of the solid was fractionally crystallized some seventy times from methyl and ethyl alcohols, yielding finally small samples of white crystalline solids, melting at 142–143° and 69–71°, which were analyzed. One selected sample of oil, distilled through the Podbielniak still, yielded crystals, which after purification melted sharply at 69–70°. There were no other solid products present melting above room temperature.

The values for fluorine given in the table were obtained using the Hoskins and Ferris[4] modification of the Willard and Winter method, after decomposing the sample in a Parr bomb, and the chlorine was determined as silver chloride. Our procedure was checked by analyzing compounds of known fluorine content. With the exception of the two highest melting points, all temperatures recorded in the table were measured by means of carefully calibrated thermocouples, and the other melting points were determined from freezing curves. Attempts to determine the molecular weights of the compounds by three standard methods failed to yield concordant results, although checks were readily obtained.

The writers are glad to give due acknowledgment to Dr. William T. Miller, Jr., who first carried out preliminary work on the vapor phase fluorination of hexachlorobenzene in this Laboratory, several years ago.

## Summary

Hexachlorobenzene has been fluorinated with elementary fluorine in the vapor phase, using a

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[4] Hoskins and Ferris, *Ind. Eng. Chem., Anal. Ed.*, **8**, 6 (1936).

copper gauze catalyst, and by a continuous process. The product has been reduced and fractionated, yielding twelve definite chemical individuals, the characteristics of which are reported.

DURHAM, N. C. RECEIVED AUGUST 2, 1937

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

# Iodine Monochloride. II. Reactions with Salts

BY JACOB CORNOG, H. W. HORRABIN AND R. A. KARGES

In an earlier publication[1] Cornog and Karges report that potassium nitrate is converted quantitatively to potassium chloride if a mixture of potassium nitrate with iodine monochloride in excess is evaporated to dryness. This observation raises a question as to what becomes of both the iodine and the nitrate in this particular reaction, also the more general question, "What are the reactions between salts and iodine monochloride?" These questions have prompted the exploratory investigation here reported.

1. **Chlorides.**—Chloride salts, in excess quantity, were placed in iodine monochloride at 50°, the resulting mixtures were kept in a thermostat at 40° for two or more hours, the material remaining undissolved was removed by filtration, the excess iodine monochloride was removed by evaporation, and the residue was weighed and identified.

From such experiments we learned that the residue products thus obtained from 100 g. of iodine monochloride solution were always chlorides and weighed less than 0.6 g. This statement includes the chlorides of sodium, lithium, silver, cupric, and barium. The residues obtained from the chlorides of potassium, ammonium, rubidium, and cesium merit special mention. Data concerning them are shown in Table I.

TABLE I

| Chloride | Salt diss. by 100 g. ICl | Residue | |
|---|---|---|---|
| | | Formula | Stability, °C. |
| $KCl$ | 5.80 | $KCl\cdot ICl$ | 0 |
| $NH_4Cl$ | 6.27 | $NH_4Cl\cdot ICl$ | 25 |
| $RbCl$ | 14.10 | $RbCl\cdot ICl$ | 110 |
| $CsCl$ | 19.9 | $CsCl\cdot ICl$ | 180 |

The residues indicated in Column 3, Table I, are all bright golden yellow crystalline powders. These compounds also may be formed with iodine monochloride vapor by placing the corresponding chlorides within a desiccator which also contains iodine monochloride in a separate beaker. While the method of preparation differs, the general properties of these compounds resemble the compounds of similar formulas reported by Wells[2] and co-workers. Wells states that the compound represented by $KCl\cdot ICl$ decomposes at 215° while we noted slow decomposition of this compound even at 0°.

These data indicate that the chloride salts investigated are sparingly soluble in iodine monochloride, with the exception of the chlorides of potassium, ammonium, rubidium, and cesium.

2. **Nitrates and Sulfates.**—The nitrates and sulfates of sodium and potassium are completely converted to the corresponding chlorides, if portions of these salts are submerged in excess iodine monochloride and the resulting mixtures are evaporated to dryness. However, if these nitrate and sulfate salts are submitted to the treatment described for chlorides, the residues obtained by evaporation of the filtrate weigh less than 0.1 g. per 100 g. of iodine monochloride used. These residues are pure chlorides.

3. **Cyanides, Cyanates, and Thiocyanates.**—Qualitative experiments showed that these salts react vigorously with iodine monochloride. The final products obtained from such reactions are easily separated and identified. See illustrative equations, 1, 2, and 3.

$$NH_4CN + ICl = NH_4Cl + ICN \quad (1)$$

$$3KCNO + 3ICl + 3KCl + I(CNO)_3 + I_2 \quad (2)$$

$$3KCNS + 3ICl = 3KCl + I(CNS)_3 + I_2 \quad (3)$$

Iodine tricyanate and iodine trithiocyanate appear to be new compounds; further, all of the reactions between iodine monochloride and cyanide, cyanate, and thiocyanate salts appear to be new reactions. Both the new compounds and new reactions are described in the following text.

The quantitative experiments with cyanide, cyanate, and thiocyanate salts were executed in

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(1) I, Cornog and Karges, THIS JOURNAL, **54**, 1882 (1932).

(2) Wells, *Z. anorg. Chem.*, **1**, 85 (1892).