[CONTRIBUTION FROM THE BAKER CHEMISTRY LABORATORY OF CORNELL UNIVERSITY]

The Action of Fluorine upon some Simple Aliphatic Chlorinated Hydrocarbons

BY WILLIAM T. MILLER

In beginning an investigation of the reactions of elementary fluorine with organic compounds it was observed that fluorine prepared without especial precautions may contain considerable amounts of oxygen due to the presence of water in the electrolyte.[1] Such a gaseous mixture is unsuitable for reacting with organic compounds because of its very great oxidizing action. To avoid this difficulty a carefully standardized method of preparation was developed and shown by analysis to yield nearly pure fluorine.[2]

The present paper describes a simple technique for bringing fluorine into reaction with organic compounds,[3] and reports the reactions of some chlorinated hydrocarbons with undiluted fluorine obtained using this procedure. This work is part of a research program designed to establish and investigate the general type reactions of fluorine with organic compounds.

Earlier work with the chlorinated hydrocarbons is rather limited. Humiston[4] found that the reaction between chloroform vapor and fluorine over fluorspar sand yielded free chlorine, phosgene (O_2 present?) and unidentified carbon fluorides as well as considerable carbon and tarry material. Similarly, pure fluorine containing compounds could not be isolated from the reaction between fluorine and tetrachloroethylene in carbon tetrachloride solution. Bockemüller,[5] however, has successfully carried out the fluorination of tetrachloroethylene at −80° in difluorodichloromethane solution and at 0° in carbon tetrachloride using fluorine diluted with carbon dioxide. At −80° difluorotetrachloroethane, fluoropentachloroethane and difluoroöctachlorobutane (characterized only as a liquid b. p. 139–142° at 13 mm.) were obtained as reaction products. At 0° no difluorotetrachloroethane was isolatable and only small amounts of fluoropentachloroethane and difluoroöctachlorobutane were found.

Experimental Results

Materials.—Fluorine was obtained by essentially the procedure previously described.[2]

The chlorinated hydrocarbons were obtained by refractionating C. P. grade materials through a 50 × 1 cm. column packed with glass helices after suitable washing. Fractions with a boiling point range of 0.2° or less were utilized. Boiling points are uncorrected unless otherwise noted.

Samples for halogen analysis were decomposed by fusion with sodium peroxide. Chlorine was then determined gravimetrically and fluorine by titrating aliquots of the carefully neutralized fusion mixture with cerium nitrate solution using a procedure modeled after that of Kurtenacker and Jereuka[6] as modified by Scott and Henne.[7]

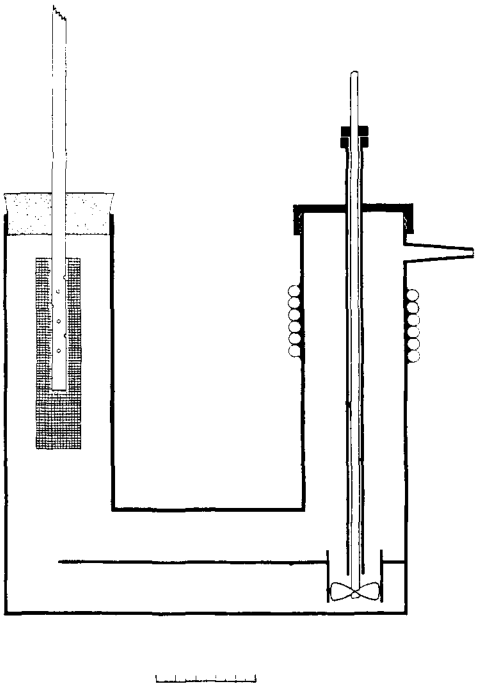

Fig. 1.—Reaction vessel.

General Method.—Reactions were carried out in apparatus of the design shown in Fig. 1, which was constructed from brass tubing with silver soldered joints. One arm of the U-shaped vessel was closed by a rubber stopper which supported the fluorine inlet tube, and the other by a threaded cap which was fitted with a stirrer as indicated in the drawing. The rubber stopper was protected on the inside by a covering of thin copper foil, and in case of a too sudden reaction functioned as a safety

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[1] For other observations see: Cuthbertson and Prideaux, *Trans. Roy. Soc. (London)*, **A205**, 395 (1906); Fredenhagen and Krefft, *Z. Elektrochem.*, **35**, 671 (1929); Ruff and Miltschitzky, *Z. anorg. Chem.*, **221**, 155 (1934).

[2] Miller and Bigelow, THIS JOURNAL, **58**, 1585 (1936).

[3] Compare: U. S. 2,013,030 and 2,013,035; *C. A.*, **29**, 6900 (1935).

[4] Humiston, *J. Phys. Chem.*, **23**, 572 (1919).

[5] Bockemüller, *Ann.*, **506**, 20 (1933).

[6] Kurtenacker and Jereuka, *Z. anal. Chem.*, **82**, 210 (1930).

[7] Scott and Henne, *Ind. Eng. Chem., Anal. Ed.*, **7**, 299 (1935).

valve. In use the vessels were filled up to the horizontal division. The stirrer then acted as a pump to force a rapid counter-current flow of liquid along the horizontal section which divided the lower part of the vessel. Fluorine was passed in at a 5 amp. rate through a roll of copper gauze[8] and temperature control was obtained by surrounding the reaction vessel with a suitable bath.

Chloroform.—The inertness and high vapor pressure of chloroform make reaction in a suitably packed tube[9] preferable to the procedure used in this work. Small puffs due to sudden reaction occurred at regular intervals. From 150 g. of chloroform which was caused to react for three hours at 0°, 149.5 g. of washed and dried water-white product was obtained. Distillation yielded 21.0 g., b. p. 23–59°, and 0.8 g. of crystalline residue after removal of the main chloroform fraction. Redistillation yielded 8.5 g. of fluorotrichloromethane, b. p. 23.0–25.0° (reported 24.1°).[10] The purified crystalline residue (m. p. 184° subl.) was shown to be hexachloroethane.

Pentachloroethane.—This compound may be heated sufficiently to bring about smooth reaction without at the same time obtaining a too great vapor concentration. From 350 g. of pentachloroethane which was caused to react for ten hours at 90 ± 3°, 297 g. of partially crystalline (at 0°) product was obtained.

Preliminary distillation yielded the following fractions: (1) 7.6 g., b. p. 88–100°; (2) 28.5 g., b. p. 100–130°; (3) 57.4 g., b. p. 130–140° (solid); (4) 11.8 g., b. p. 140–148°; (5) 12.9 g., b. p. 148–156°; (6) 91.6 g., b. p. 156–159°; (7) 45.2 g., oily semi-solid residue. Small amounts of hydrogen chloride gas were evolved during this first distillation. By repeated fractionation the following products were isolated.

sym.-Difluorotetrachloroethane.—5.0 g.: b. p. 91.0–92.0°; n^{25}_{D} 1.4133; m. p. 22–24°. Previously reported: m. p. 24.65°; b. p. 92.8°; n^{25}_{D} 1.4130.[11]

Tetrachloroethylene.—15.6 g.: b. p. 117.5–118.0°. Chlorination in sunlight yielded only hexachloroethane.

Fluoropentachloroethane.—83.1 g.: b. p. 137.0–139.0°. A redistilled sample melted at 99.8–100.0° in a sealed tube. Previously reported: m. p. 101.3°; b. p. 137.9°.[11]

Pentachloroethane.—93.4 g.: b. p. 159.0–160.0°.

Hexachloroethane.—28.5 g.: m. p. 174–181° subl. A recrystallized sample melted 183.0–184.0° subl.; shown to be hexachloroethane.

Decachlorobutane.—Distillation of the residue (8.4 g.), remaining from the above separations, at 2.0 mm. pressure, yielded 4.2 g. of mobile oil, b. p. 100–116°, from which no pure products were isolated. However, by extracting the still residue with hot alcohol and evaporating the filtered extract, 1.9 g. of oily crystalline material was obtained of m. p. 61–69°. This substance was extremely soluble in usual organic solvents but only slightly soluble in glacial formic acid. Three recrystallizations by slow evaporation of its solution in 1:1 glacial formic and acetic acids yielded 0.1 g., m. p. 80.0–81.0°. Calcd. for C_4Cl_{10}: C, 11.92; Cl, 88.07; H, 0.0; mol. wt., 403. Found: C, 12.1; Cl, 88.0; H, 0.11; mol. wt., 397.[12]

Considerably improved recovery was found possible in subsequent runs for which, however, complete separations were not carried out. For example, 343 g. of crude material was obtained from a similar ten-hour reaction starting with 365 g. of pentachloroethane.

Tetrachloroethane.—From 327 g. of tetrachloroethane which was caused to react at 50 ± 2° for fourteen hours, 310 g. of washed and dried product was recovered. Preliminary distillation yielded the following fractions: (1) 7.9 g. to b. p. 90°; (2) 18.4 g., b. p. 90–95°; (3) 5.8 g., b. p. 93–113°; (4) 75.3 g., b. p. 113–118°; (5) 11.4 g., b. p. 118–142°; (6) 168.3 g., b. p. 142–150°; (7) 21.2 g. residue. Continued fractionation yielded:

Trichloroethylene and sym-Difluorotetrachloroethane.—Separation of these substances cannot be accomplished by distillation; however, trichloroethylene was shown to be present and separated by preparing its mercury salt Hg($CCl{=}CCl_2$)$_2$, m. p. 82–83°.[13] Difluorotetrachloroethane was obtained slightly impure; m. p. 19–23°, b. p. 92–93°.

Fluorotetrachloroethane.—($CHCl_2CFCl_2$), 67.8 g., b. p. 115.5–116.5°, was obtained from fraction (4). For a redistilled sample of constant b. p. 115.7°: d^{20}_{4} 1.6218; n^{20}_{D} 1.4487. Previously reported: b. p. 116.6°; d^{20}_{4} 1.6223; n^{20}_{D} 1.4487.[14]

Tetrachloroethane.—Fraction (6) was principally unreacted tetrachloroethane.

Pentachloroethane.—11.2 g. was obtained from fraction (7); b. p. 159.0–160.0°. No hexachloroethane could be isolated.

Tetrachloroethylene.—From 335 g. of tetrachloroethylene which was caused to react at 0° for twelve hours, 354 g. of washed and dried product was recovered. Complete absorption of the fluorine occurred.

Preliminary distillation yielded the following fractions: (1) 15.4 g., b. p. 40–80°; (2) 58.5 g., b. p. 80–115°; (3) 30.6 g., b. p. 115–120° (the distillation was interrupted at this point because of decomposition to yield some free chlorine, and then continued under reduced pressure without a fractionating column); (4) 138.4 g. to b. p. 125° at 35 mm.; (5) 6.1 g., b. p. 125–155° at 35 mm.; (6) 88.7 g., b. p. 155–173° at 35 mm.; (7) 11.5 g. residue. Careful fractionation yielded the following pure products:

sym-Difluorotetrachloroethane.—55.0 g., b. p. 89–94°. Redistillation yielded 42.7 g., b. p. 92.0–93.0°. A redistilled sample of constant b. p. 92.3° melted at 24.43–24.73° corr.

Fluoropentachloroethane.—49.7 g., b. p. 136.0–138.0°. A redistilled sample melted at 99.0–99.5° in a sealed tube. The yield of fluoropentachloroethane varied considerably between runs and in one case a minimum of 18.0 g. was obtained together with 40.0 g. $C_2F_2Cl_4$ and 50.5 g. $C_4F_2Cl_8$.

Difluoroöctachlorobutane.—(Presumably 1,4-), 66.0 g., m. p. 4.0–5.0°; b. p. 152.5° at 20.0 mm.; n^{20}_{D} 1.5256; d^{20}_{4} 1.9272: Calcd. for $C_4Cl_8F_2$: Cl, 76.7%; MR_D 59.39.[15] Found: Cl, 76.6%; MR_D 58.86.

A residue of 11.1 g. remained from the above separations, b. p. principally 102–130° at 1 mm.

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(8) Fredenhagen and Cadenbach, *Ber.*, **67**, 928 (1934).

(9) Miller, Calfee and Bigelow, THIS JOURNAL, **59**, 198 (1937).

(10) Ruff and Keim, *Z. anorg. Chem.*, **201**, 245 (1931).

(11) Locke, Brode and Henne, THIS JOURNAL, **56**, 1726 (1934).

(12) In fluoropentachloroethane solution; unpublished work.

(13) Schmalguss and Werner, *Z. anal. Chem.*, **97**, 314 (1934).

(14) Henne and Ladd, THIS JOURNAL, **58**, 403 (1936).

(15) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Company, New York, N. Y., 1931, pp. 152–153.

Tetrachloroethylene in Trifluorotrichloroethane Solution.—Sixty-five grams of tetrachloroethlyene dissolved in 150 cc. of trifluorotrichloroethane[16] was caused to react with a slight excess of fluorine at 0°. Careful fractionation of two such reaction products yielded: 46.9 g. of *difluorotetrachloroethane*, b. p. 91–93°; 10.1 g. of *fluoropentachloroethane*, b. p. 137–138°; 49.5 g. of *difluorooctachlorobutane*, b. p. 152–153° at 20 mm. *Hexachloroethane* also was identified, but was present only as a trace.

Trichloroethylene.—From 340 g. of trichloroethylene which was caused to react at 0° for ten hours, 347 g. of washed and dried product was obtained. Preliminary distillation yielded: (1) Approximately 5 cc. of liquid uncondensed by 11° cooling water but retained by a dry-ice cooled trap; (2) 10.0 g., b. p. 32–40°; (3) 4.6 g., b. p. 40–65°; (4) 40.5 g., b. p. 65–85.5°; (5) 153.9 g., b. p. 85.5–86.5°; (6) 15.6 g., b. p. 86.5–114.0° (mostly 113–114°); (7) 17.7 g., b. p. 48–80° at 93 mm.; (8) 11.6 g., to b. p. 123° at 25 mm.; (9) 48.0 g., b. p. 123–125.5° at 25 mm.; (10) 13.4 g. brown viscous residue.

Fractions (1) and (2) were brominated in sunlight. Distillation of the product yielded 3 g., b. p. 31.0–32.0°, n^{20}_D 1.338; an intermediate fraction of 3.5 g. to b. p. 160°; and 0.9 g., b. p. 160–162°, n^{23}_D 1.5194, which contained bromine. Reported for fluoro-1,2-dichloro-1,2-dibromoethane: b. p. 163.5°; n^{23}_D 1.5160.[14]

Refractionation of samples (4) to (7) inclusive yielded:

1,2-Difluoro-1,2,2-trichloroethane and fluorotrichloroethylene, 14.9 g., b. p. 71.5–73.0°. Redistilled sample: b. p. 72.3–72.6°; n^{20}_D 1.3967; d^{20}_4 1.5555. Previously reported for $CHClF—CCl_2F$: b. p. 72.5; d^{20}_4 1.5587; n^{20}_D 1.3942;[14] for $CFCl{=}CCl_2$: b. p. 72.1°; d^{20}_4 1.5541; n^{20}_D 1.4360.[11] Chlorination of this product yielded *sym*-difluorotetrachloroethane principally (b. p. 92.0–92.3°, m. p. 22–24°, n^{25}_D 1.4135) and a small residue of fluoropentachloroethane (m. p. 75–82°, b. p. 135°).

Fluorotetrachloroethanes.—$CHFCl—CCl_3$ and $CHCl_2—CFCl_2$, 18.7 g.: b. p. 114.0–116.0°. Redistilled sample, b. p. 115.9–116.0°; n^{20}_D 1.4488; d^{20}_4 1.6192. Previously reported for $CHFCl—CCl_3$: b. p. 117.0°; n^{20}_D 1.4525;[14] d^{20}_4 1.6253. For $CFCl_2—CHCl_2$, see above. Chlorination yielded only fluoropentachloroethane (m. p. 96.0–98.0°).

Hexachlorobutene.—Distillation of sample (9) combined with the residue from the lower boiling fractions yielded: (11) 8.9 g., b. p. 70–122° at 25 mm.; (12) 42.4 g., b. p. 122.0–125.5° at 25 mm.; (13) 5 g. residue. Crystallization of (12) from 30–60° b. p. petroleum ether yielded 20.6 g. of white crystalline material (m. p. 6–9°). Several recrystallizations yielded: 6 g., m. p. 9.5–11.0°; b. p. 125.5° at 25 mm.; n^{20}_D 1.5442; d^{20}_4 1.6880. It contained no fluorine. Calcd. for $C_4H_2Cl_6$: C, 18.28; H, 0.76; Cl, 80.94; mol. wt., 262.8; MR_D 50.61. Found: C, 18.3; H, 0.73; Cl, 81.0; mol. wt. (Rast), 261; MR_D 49.17. This substance did not add bromine or chlorine in sunlight, and differs in properties from 1,1,2,3,4,4-hexachlorobutene-2.[17]

The lower melting fraction from sample (12) contained fluorine as well as chlorine.

Octachlorobutane.—Sample (13) partially solidified on cooling to 0° and 2.5 g. of material melting above room temperature was obtained. Several recrystallizations from petroleum ether and from methyl alcohol yielded 1.2 g. of white crystals, m. p. 75.0–76.0°. This compound did not contain fluorine and had no noticeable odor. Calcd. for $C_4H_2Cl_8$: C, 14.40; H, 0.60; Cl, 84.98. Found: C, 14.5; H, 0.65; Cl, 84.7. This substance appeared to have a structure other than 1,1,2,2,3,3,4,4-octachlorobutane.[18]

Trichloroethylene in Trifluorotrichloroethane Solution.—Fifty-five grams of trichloroethylene was dissolved in 160 cc. of trichlorotrifluoroethane[16] and caused to react at 0° for six and one-half hours. The products from three duplicate reactions were combined for distillation which yielded after removal of the solvent to b. p. 50°: (1) 2.9 g., b. p. 50–72°; (2) 29.0 g., b. p. 72–75°; (3) 15.4 g., b. p. 75–114°; (4) 20.9 g., b. p. 114–116°; (5) still residue.

Difluorohexachlorobutane.—Crystallization of sample (5) from 30–60° b. p. petroleum ether with dry-ice cooling yielded 14.6 g. of white crystals, m. p. 47–52°. Several recrystallizations from this solvent and from methyl alcohol yielded 2.5 g., m. p. 55–56°. Calcd. for $C_4H_2F_2Cl_6$: C, 16.01; H, 0.67; F, 12.63; Cl, 70.74. Found: C, 16.0; H, 0.67; F, 12.8; Cl, 70.8.

Lower melting isomers of difluorohexachlorobutane were indicated as being present in the soluble residue from the above separation by distillation, determination of molecular refraction and analysis.

Discussion

The physical as well as chemical properties of fluorine must be taken into account in considering actual reaction conditions. It has been found to be insoluble in carbon tetrachloride within the limit of measurement[19] and in general a slight solubility for fluorine in compounds of this type may be expected from its low boiling point (−188°). Consequently, the reactions observed in this work occur principally in the gas phase and at the liquid surface under essentially "non-ionic" conditions,[20] and radical type mechanisms in which the fluorine molecule is split symmetrically are considered to be of greatest importance. It is suggested that some of the observed differences of kind between the reactions of fluorine with organic compounds and the reactions of the other halogens may be found in this direction.

In addition to the expected substitution products which were obtained from chloroform and pentachloroethane, hexachloroethane and dodecachlorobutane were isolated in small amounts. This converse of the Wurtz–Fittig type of reaction has also been observed to occur when fluoroform reacts by sparking with fluorine.[21]

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[16] "Freon 113" Kinetic Chemicals Inc., Carney's Point, N. J.

[17] Müller and Hüther, *Ber.*, **64**, 589 (1931).

[18] Müller and Luber, *ibid.*, **65**, 285 (1932).

[19] William T. Miller, unpublished work.

[20] Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1937, p. 84.

[21] Ruff and Bretschneider, *Ber.*, **69**, 299 (1936).

With olefins the dimerization observed by Bockemüller[5] in the case of tetrachloroethylene was confirmed and also established for trichloroethylene. The products obtained may be termed *dimer addition products*, and it is assumed that in compounds of this type the fluorine atoms are in the 1,4-positions. Chlorine fluoride was formed in the reaction mixtures and substitution and addition products resulting from its action were isolated. Chlorine fluoride seems to add normally to ethylenic compounds without the formation of dimers since no monofluorobutane derivatives were found. In fact, the formation of dimer addition products from simple olefins appears to be a type of reaction peculiar to fluorine among the halogens.

Summary

The reactions of some simple chlorinated aliphatic organic compounds with fluorine have been studied. Using pure fluorine, charring was not observed in any case and reactions were easily controlled. The types of reaction observed were: substitution of hydrogen attached to saturated carbon; substitution of hydrogen attached to double bonded carbon; addition to ethylenic bonds; dimerization of saturated molecules by removal of two hydrogens; dimerization of ethylene derivatives accompanied by the addition of two fluorine atoms; secondary reactions due to the presence of chlorine fluoride.

The reaction conditions used and results obtained are discussed briefly. Essentially "nonionic" conditions prevailed and the hypothesis was advanced that radical type mechanisms of reaction in which the fluorine molecule is split symmetrically are of greatest significance.

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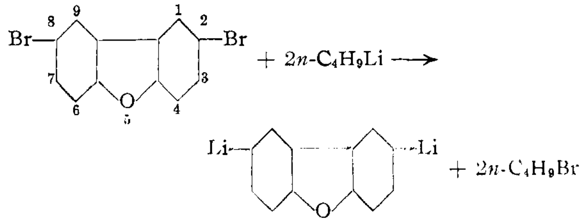
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

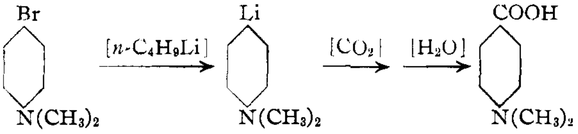
Halogen–Metal Interconversion with *m*- and *p*-Bromodimethylanilines[1]

BY HENRY GILMAN AND IRVING BANNER

The two chief transformations which resulted when an organolithium compound reacted with a nuclear-brominated aryl-alkyl or diaryl ether were: (1) metalation or replacement of a nuclear hydrogen by lithium[2] and (2) halogen–metal interconversion or the replacement of nuclear halogen by lithium.[2,3] The metalation occurred when the halogen was *para* to the ether linkage; and halogen–metal interconversion took place when the halogen was *ortho* to the ether linkage. Subsequently[4] it was shown that it was not necessary to have bromine *ortho* to an ether linkage to have a halogen–metal interconversion, for 2,8-dibromodibenzofuran and *n*-butyllithium gave an excellent yield of 2,8-dibenzodifurylenedilithium. When bromine is *meta* to the ether linkage as in 3-bromodibenzofuran, both metalation and interconversion probably occur, for the acids isolated subsequent to carbonation were 3-dibenzofurancarboxylic acid and 4-dibenzofurancarboxylic acid.[4] The reaction with 1-bromodibenzofuran, in which the bromine is also *meta* to the ether linkage, is exclusively interconversion.[5] Actually, as the accompanying paper[6] on methoxy-halogenodibenzofurans illustrates, interconversion is the predominant reaction of bromo ethers.



We are reporting at this time the reaction of *n*-butyllithium with *m*- and *p*-bromodimethylanilines. Reaction was to be expected because of the related activating effects of dialkylamino and alkoxy groups. In each case a halogen–metal interconversion took place.



Unlike the case with *p*-bromoanisole, there was

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(1) This is paper XXVIII in the series of relative reactivities of organometallic compounds. The preceding paper is THIS JOURNAL, **61**, 1513 (1939).

(2) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Wittig and co-workers, *Ber.*, **71**, 1903 (1938), and **72**, 89 (1939); Gilman, Langham and Jacoby, THIS JOURNAL, **61**, 106 939).

(3) Gilman, Cheney and Willis, *ibid.*, **61**, 951 (1939).

(4) Gilman, Willis and Swislowsky, *ibid.*, **61**, 1371 (1939).

(5) Unpublished studies.

(6) Gilman, Swislowsky and Brown, THIS JOURNAL, **62**, 348 (1940).