Although this mechanism has been depicted as involving only two solvent molecules, it is possible that more than two are involved or, alternatively, that a single solvent molecule is involved in a cyclic transition state as suggested by Kornblum and Blackwood.[1d] In this case, too, the roles of the oxygen and nitrogen atoms of dimethylformamide may be reversed.[17] Also, the ion–dipole solvation bond to carbon may be from the front rather than the rear. In any case, the kinetics would be those observed.

Our results do not permit us to make a choice between these possibilities. It is clear that there may be solvolytic reactions in which the solvent functions in a purely electrophilic manner. It is equally probable that there are solvolytic mechanisms in which the action of the solvent is entirely nucleophilic. Between these two extremes there must be a broad range of mechanisms in which two or more solvent molecules are involved and in which the solvent acts both electrophilically and nucleophilically. These mechanisms, thus, reflect an equally broad and continuous spectrum of transition states differing in the configurations of the solvating solvent molecules and are best considered as differing in degree but not in kind.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Perfluoroalkylzinc Compounds. I. The Preparation and Properties of Perfluoroalkylzinc Halides[1,2]

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Convenient methods for the preparation of perfluoroalkylzinc compounds of the type R_FCF_2ZnI (solvated) are described together with the results of related work on the reactions of fluoroperhaloalkyl bromides and iodides with metallic zinc. The perfluoroalkylzinc iodides as exemplified by perfluoro-*n*-propylzinc iodide are shown to be thermally stable in solution and inert to carbon dioxide and to oxygen. They are strong Lewis acids, in contrast to the alkylzinc iodides. They are readily hydrolyzed, cleaved by halogen and converted into olefins by pyrolysis. They are unreactive with organic electrophiles, but under vigorous conditions in the presence of such compounds containing active hydrogen they tend to yield R_FCF_2H rather than addition products.

Introduction

Evidence for the existence of perhaloalkylzinc compounds was first obtained in attempting to dehalogenate fluoroperhalo compounds which do not contain halogens other than fluorine in the 1,2-relation to produce olefins. Reduced products were isolated by hydrolysis of reaction mixtures under conditions which suggested the intermediate formation of perhalo zinc compounds.[4] Efforts were then made to prepare perfluoroalkylzinc compounds, and it was found that perfluoro-*n*-propylzinc iodide could be obtained readily in dioxane solution.[5] The present paper presents work on the preparation and properties of solvated perfluoroalkylzinc compounds of the type R_FCF_2ZnX and on related reactions of fluoroperhaloalkyl iodides and bromides with metallic zinc.

The preparation of solutions of zinc and cadmium perfluoroalkyls from trifluoromethyl iodide and heptafluoro-*n*-propyl iodide has been reported independently by Haszeldine[6] with experimental work on heptafluoro-*n*-propylzinc iodide appearing more recently.[7] Earlier attempts by Emeléus and Haszeldine to prepare organozinc compounds from trifluoroiodomethane and pentafluoroiodoethane yielded only fluoroform and pentafluoroethane as organic products.[8]

Discussion and Results

In the present work all of the fluoroperhaloalkyl iodides and bromides tested were found to react with zinc dust in donor-type solvents such as aliphatic ethers and pyridine at or below reflux temperatures. Depending upon the structure of the perhaloalkyl halide and the choice of solvent and reaction conditions, one or more products of the type shown below were isolated. Organozinc compounds have been obtained only when Y is fluorine. When Y is chlorine intramolecular dehalogenation ordinarily occurs readily and always with great ease when Y is bromine or iodine.

$$\begin{array}{lrl} R_FCFYCF_2X + Zn \xrightarrow{\text{solvent}} & R_FCF{=}CF_2 & (I) \\ X = Br \text{ or } I & R_FCFYCF_2ZnX & (II) \\ Y = F \text{ or other halogen} & R_FCFYCHF_2 & (III) \\ & [R_FCFYCF_2{-}]_2 & (IV) \end{array}$$

Perfluoro-*n*-propyl iodide was found to react readily with zinc in dioxane to yield more than 75% perfluoro-*n*-propylzinc iodide (II) plus small amounts of heptafluoropropane (III). Perfluoro-*n*-propyl bromide reacted in 1,2-dimethoxyethane after a long induction period to yield 60% of the corresponding zinc compound (II). Perfluoro-*n*-pentyl iodide reacted sluggishly with zinc in dioxane to yield a mixture of perfluoro-*n*-pentylzinc iodide (II), undecafluoro-*n*-pentane (III) and perfluoro-*n*-decane (IV). The perhalomethanes failed to

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(1) Taken, in part, from a thesis submitted by Elliot Bergman to the Graduate School, Cornell University, Ithaca, N. Y., June, 1955.

(2) This research was supported in part by the Office of Naval Research.

(3) Procter and Gamble Fellow, 1953–1954.

(4) A. H. Fainberg and W. T. Miller, Jr., Abstracts of Papers, 120th Meeting, American Chemical Society, New York, N. Y., Sept., 1951, p. 7K; W. T. Miller, Jr., and J. M. Howald, unpublished work.

(5) W. T. Miller, Jr., A. H. Fainberg and E. Bergman, Abstracts of Papers, 122nd Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1952, p. 14-K.

(6) R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

(7) R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.*, 3606 (1953).

(8) H. J. Emeléus and R. N. Haszeldine, *ibid.*, 2948, 2953 (1949).

give detectable quantities of organozinc compounds under any of the conditions utilized. Trifluoroiodomethane was converted into fluoroform (III), dichlorofluoroiodomethane yielded dichlorofluoromethane (III) plus the dimer product (IV) and bromodichlorofluoromethane yielded condensed material in addition to undergoing general decomposition to form inorganic products. 1,2-Dichloro-1,2,2-trifluoroiodoethane yielded only its dehalogenation product, chlorotrifluoroethylene (I), under the experimental conditions utilized.[9]

The reactions between zinc and fluoroperhaloalkyl iodides and bromides were greatly facilitated by the presence of a donor-type solvent. In the absence of solvent or in the presence of non-donor type solvents such as benzene, methylene chloride and ethyl heptafluoro-*n*-butyrate, no reaction was observed with *n*-propyl iodide at temperatures up to 100°. Haszeldine and Walaschewski obtained somewhat similar results at moderate temperatures and have reported that perfluoro-*n*-propyl iodide and zinc react at 310° to yield perfluoro-*n*-hexane.[7] The behavior of perfluoroalkyl iodides with zinc differs from that of alkyl iodides, which yield dialkylzinc compounds at elevated temperatures in the absence of solvent.[10]

Perfluoro-*n*-propylzinc Iodide.—It was found that perfluoro-*n*-propylzinc iodide could be conveniently prepared in high yield by reaction of zinc with perfluoro-*n*-propyl iodide in dioxane or 1,2-dimethoxyethane solution at temperatures up to about 100°. Other donor-type solvents such as pyridine also could be utilized. Small amounts of heptafluoropropane always were formed during reaction of the perfluoroiodide with zinc, but once formed the zinc compound was stable in solution at reflux temperatures for prolonged periods and on storage at room temperature for more than a year. This thermal stability in solution, which is in striking contrast to the instability at relatively low temperatures exhibited by the corresponding magnesium[11,12] and lithium[13] compounds, suggests that the formation of monohydroperfluoroalkanes during the preparation of perfluoroalkylzinc compounds proceeds by free radical abstraction of a hydrogen atom from solvent rather than by removal of a proton by a perfluorocarbanion as previously suggested.[7] The low order of reactivity found with carbonyl compounds described below also argues against the availability of a reactive carbanion.[14]

Attempts to prepare perfluoro-*n*-propylzinc iodide in ethyl ether solution led to the rapid evolution of heptafluoropropane with the production of little, if any, zinc compound. This anomalous result in diethyl ether is attributed to small amounts of peroxide which were found to be present. Since typical free radical type inhibitors such as hydroquinone (quinone) were found to quench the reaction, these observations can be accounted for by an organic peroxide–zinc induced free radical chain reaction between the iodide and ether. Similarly, Emeléus and Haszeldine isolated only pentafluoroethane from the reaction of pentafluoroiodoethane with zinc–copper couple in ethyl ether.[8] However, Haszeldine and Walaschewski[7] subsequently reported no difficulty with this solvent. Pierce, McBee and Judd,[13] following up our preliminary report,[4] obtained only heptafluoropropane by reaction of perfluoro-*n*-propyl iodide with zinc in commercial dioxane, a solvent which readily forms peroxide on exposure to air. The choice and purity of solvent utilized for the preparation of perfluoroalkylzinc compounds is thus shown to be of primary importance. Peroxide-free dioxane and 1,2-dimethoxyethane were found to be effective and convenient solvents; 1,2-dimethoxyethane was especially advantageous in some instances because of greater solubility of its addition compounds.[15] The purity of the zinc metal utilized for reaction was not indicated as critical. All dry unoxidized samples of commercial zinc dust tested worked well. Similarly the reaction temperature did not exert a major effect upon the yield of perfluoro-*n*-propylzinc iodide over the range investigated (*ca.* 25–100°).

The concentration of heptafluoropropyl iodide in solution was found to be the most important variable in determining the relative yields of organozinc compound II and of dimer product IV. With dropwise addition of the iodide to zinc dust suspended in dioxane no perfluoro-*n*-hexane could be isolated. On the other hand, when a concentrated solution of iodide was employed in a sealed tube, a vigorous exothermic reaction occurred to form perfluorohexane as the major product. These observations suggest that the dimerization reaction proceeds by a bimolecular homolytic type reaction of the iodide on the zinc surface rather than by secondary reaction with perfluoropropylzinc iodide. This conclusion was supported by the observed failure of a filtered solution of perfluoropropylzinc iodide in dioxane to react with additional added iodide. Haszeldine and Walaschewski[7] obtained perfluoro-*n*-hexane in up to 45% yield by a sealed-tube reaction of perfluoro-*n*-propyl iodide with zinc in dioxane. Henne obtained 77% perfluoro-*n*-hexane by the same type reaction in refluxing acetic anhydride–methylene chloride.[16,17]

The chemical reactivity of the perfluoroalkylzinc compounds was found to lie between that of the stable relatively unreactive perfluoroalkylmercury compounds[8] and the unstable highly reactive perfluoroalkylmagnesium compounds.[5,11,12] The fol-

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(9) Some coupled product probably was formed also; see R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952); A. L. Henne, THIS JOURNAL, **77**, 2334 (1955).

(10) E. Frankland, *Ann.*, **71**, 171 (1849). Zinc–copper couple: C. R. Noller, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 184–187.

(11) R. N. Haszeldine, *J. Chem. Soc.*, 3423 (1952); 1748 (1953); 1273 (1954).

(12) A. L. Henne and W. C. Francis, THIS JOURNAL, **73**, 3518 (1951); **75**, 992 (1953).

(13) O. R. Pierce, E. T. McBee and G. F. Judd, *ibid.*, **76**, 474 (1954).

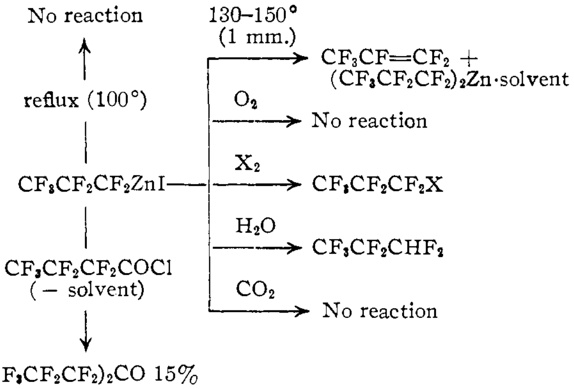
(14) The highly reactive heptafluoropropyllithium also does not yield heptafluoropropane in the absence of acidic hydrogen.[13]

(15) This solvent has been found especially suitable for the preparation of other organo-metallic compounds; H. L. Cohen and G. F. Wright, *J. Org. Chem.*, **18**, 432 (1953).

(16) A. L. Henne, THIS JOURNAL, **75**, 5750 (1953).

(17) Higher temperatures (100°) were found by Haszeldine and Walaschewski to favor the formation of coupled product (IV) under their reaction conditions.[7] Henne found a controlled low temperature essential (40–45°).[16]

lowing chart summarizes illustrative experimental results.



No reaction was observed with oxygen over long periods. Hydrolysis proceeded slowly with the addition of water at room temperature. The addition of aqueous acid or base increased the rate of hydrolysis markedly. Chlorinolysis and brominolysis occurred exothermally, but heating to 80–100° was required for rapid reaction with iodine. This behavior is in strong contrast to that of the lower alkyl zinc compounds which react vigorously with water at room temperature and ignite with the halogens and with oxygen.[18] The hydrolysis and halogenolysis reactions demonstrate the presence of the carbon–zinc bond.

An outstanding property of the perhaloalkylzinc halides is their strength as Lewis acids. Perfluoropropylzinc iodide exhibits a low order of reactivity with organic electrophilic systems. Attempts to carry out typical organo-metallic synthetic reactions in dioxane solution were unsuccessful. At low temperatures little reaction occurred. Perfluoropropylzinc iodide could be prepared in acetone solution. Carbon dioxide was without effect at 100°. Aldehydes, ketones, anhydrides and acid halides containing enolizable hydrogen were unreactive but yielded heptafluoropropane and condensation and solvent cleavage products on long refluxing. Less complete consumption of the zinc compound took place with reactants containing no α-hydrogen, but none of the desired addition products could be isolated.[19] By largely removing the dioxane solvent from perfluoro-*n*-propylzinc iodide at low pressure and treating the solid residue with perfluoro acid chlorides the corresponding perfluoro ketones were obtained in low yields. However, even under these conditions acetyl chloride and acetic anhydride, which contain enolizable hydrogen, yielded only heptafluoropropane.

The increase in acid strength of the perhaloalkylzinc halides over that of the alkylzinc compounds may be accounted for by the strong electron-attracting property of the perfluoropropyl group, which results in a more polar carbon–zinc bond and higher solvation energies. The high energies of solvation contribute to the ease of formation of the zinc compounds in donor-type solvents and to their stability once formed. Efforts to remove solvent completely without decomposition were unsuccessful.[21] As indicated above, removal of solvent *in vacuo* left a crystalline residue of solid perfluoropropylzinc iodide solvent complex. Sublimation of the solid dioxane complex yielded perfluoropropene and a very small amount of perfluoropropylzinc dioxanate. Pyrolysis of the corresponding 1,2-dimethoxyethane addition compound gave a higher yield (50%) of perfluorodi-*n*-propyl zinc as the etherate in addition to perfluoropropene.[22]

Experimental[23–25]

Starting Materials.—Perfluoroacids were purchased from the Minnesota Mining and Manufacturing Co. Silver salts of perfluoroacids were prepared by previously described procedures.[26] Pure, peroxide-free dioxane was prepared by the method of Fieser.[27] Other ethers were purified by refluxing with and distilling from sodium wire under dry nitrogen. They were stored in the dark over sodium under nitrogen. Baker and Adamson 90% zinc dust was used in all experiments.

Perfluoroalkyl Iodides.—Heptafluoro-*n*-propyl iodide was prepared in 92% yield by a procedure similar to that described by Hauptschein and Grosse.[26] Found: b.p. 39.3° (736 mm.), f.p. −95.3, f.p. dep. 0.1°, $n^{20}\text{D}$ 1.3281, d^{20}_4 2.0566, mol. wt. 295 and 299 (vapor density), $MR^{20}\text{D}$ 29.22; reported[26]: b.p. 41.2°, $n^{20}\text{D}$ 1.3272, d^{20}_4 2.0626; calculated for C_3F_7I: mol. wt. 296, $MR^{20}\text{D}$ 29.64.[28]

Perfluoro-*n*-amyl iodide was prepared in 65% yield by heating an intimate mixture of 108 g., 0.257 mole of dry silver perfluoro-*n*-hexanoate and 85 g., 0.334 mole, of iodine in a distilling flask with a free flame. Found: b.p. 94° (755 mm.), $n^{17}\text{D}$ 1.3310; reported[29]: b.p. 94°, $n^{31.5}\text{D}$ 1.3243.

Trifluoroiodomethane was prepared in 80% yield by the method of Henne.[30] It was washed with aqueous alkali, dried by passage through concentrated sulfuric acid or phosphorus pentoxide and used without further purification.

Bromodichlorofluoromethane was prepared by the vapor phase bromination of dichlorofluoromethane at 475° by the procedure of Miller and Howald.[31] Found: b.p. 50.4° at 727 mm., $n^{20}\text{D}$ 1.4308; reported[31]: b.p. 50.2° (734 mm.), $n^{20}\text{D}$ 1.4304.

Dichlorofluoroiodomethane was prepared in 44% yield by treating bromodichlorofluoromethane with sodium iodide in acetone for 3 hr. at 120°.[31] Found: b.p. 87–90° (735 mm.), reported[31] b.p. 90°.

Perfluoroacid Chlorides.—Perfluoroacid chlorides were prepared by the reaction of the corresponding acids with phosphorus pentachloride (10–20 mole per cent. excess) followed by distillation of the crude product from a small

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(18) E. Frankland, *Ann.*, **85**, 346 (1853); **95**, 28 (1855).

(19) Partial condensation of aldehydes and ketones by perfluoropropyllithium[13] and of acetone by heptafluoropropylmagnesium iodide[12] with formation of heptafluoropropane has been reported. Pawlow similarly obtained ethane and mesityl oxide by reaction of acetone with diethylzinc.[20]

(20) D. Pawlow, *Ann.*, **188**, 104 (1877)

(21) The isolation of small amounts of $CF_3CF_2CF_2ZnI$ by fractional vacuum sublimation has been reported by Haszeldine and Walaschewski.[7]

(22) W. T. Miller, Jr., and E. Bergman, Abstracts of Papers, 126th Meeting, American Chemical Society, New York, N. Y., Sept., 1954, p. 35M. In contrast, alkylzinc compounds are readily separated from ether solvents. See, for example: L. F. Hatch, G. Sutherland and W. J. Ross, *J. Org. Chem.*, **14**, 1130 (1949).

(23) Melting and boiling points are uncorrected unless otherwise indicated.

(24) Infrared spectra were measured on a Perkin-Elmer model 21, double-beam recording spectrophotometer.

(25) Freezing points were determined by a procedure similar to that described by A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

(26) M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

(27) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 368.

(28) A. H. Fainberg and W. T. Miller, Jr., unpublished work.

(29) M. Hauptschein, A. V. Grosse and R. L. Kinsman, THIS JOURNAL, **74**, 849 (1952).

(30) A. L. Henne and W. C. Finnegan, *ibid.*, **72**, 3806 (1950).

(31) J. M. Howald, Ph.D. Thesis, Cornell University, 1953.

amount of dimethylaniline. In this way trifluoroacetyl chloride, b.p. −20 to −19° (740 mm.), and perfluoro-*n*-butyryl chloride, b.p. 38–39° (740 mm.), were obtained in 76 and 89% yields, respectively.

Perfluoro-*n*-propylzinc Iodide.—The following preparative procedure gave consistently reproducible results. A 1-l. three-necked flask was fitted with a sealed stirrer, a dropping funnel and a reflux condenser in series with a Dry Ice trap and charged with 39.2 g., 0.60 gram-atom, of zinc dust. The apparatus was flushed with warm dry nitrogen and 120 ml. of dioxane added; 20 ml. of a solution of 88.8 g., 0.300 mole, of perfluoro-*n*-propyl iodide in 60 ml. of dioxane was added and the stirred solution warmed to 100°. The reaction started at about 60°.[32] The remainder of the solution was added without external heating at such a rate that gentle reflux was maintained. Shortly after this period of about 2 hr. reaction was complete, as evidenced by a drop in temperature. The Dry Ice trap contained 5.2 g., 10%, of 1,1,2,2,3,3,3-heptafluoropropane; 25 g. of water was added to the reaction flask, and the mixture refluxed for 4 hr. during which time 39 g., 77%, of heptafluoropropane was collected. Found: b.p. −17° (735 mm.), f.p. −148.5° without depression, mol. wt. 168 and 168, narrow carbon-hydrogen infrared absorption band at 3.36 μ; reported[33]: b.p. −18 to −17°; calculated for C_3HF_7, mol. wt., 170.

In order to demonstrate positively that the heptafluoropropane produced during the reaction could not be accounted for by hydrolysis of the zinc compound,[34] the reaction was run under rigorously anhydrous conditions in an all-glass apparatus. The zinc dust was introduced into the apparatus and dried with a stream of nitrogen while warming the flask. Dry dioxane, 158 g., was introduced under a blanket of nitrogen. The zinc was maintained in suspension by a magnetic stirrer and the dioxane refluxed. After 15 minutes a 15-ml. sample of dioxane was removed and a Karl Fischer titration[35] for water was found to be indistinguishable from a blank determination. Perfluoro-*n*-propyl iodide, 93.0 g., 0.314 mole, was added dropwise to the stirred zinc suspension at such a rate that the mixture remained at approximately 75°. A total of 6.8 g. (13%) of heptafluoropropane, free of perfluoropropene, and 6.2 g. (7%) of starting iodide were collected in the trap.[36] The reaction mixture was filtered free of zinc through a sintered glass filter and the residual zinc washed with 43 g. of dioxane. The combined filtrates were refluxed with 50 ml. of water to yield 36.3 g., 68%, of heptafluoropropane. One to two grams of an oil, b.p. >100°, remained in the hydrolyzate.

The above procedure was repeated using 1,2-dimethoxyethane as solvent. The reaction could be started at room temperature. A 0.240-mole run afforded 2.5 g., 6%, of perfluoropropane and 2 g., 3%, of starting iodide. Hydrolysis of the filtered solution yielded 33.5 g. which on redistillation gave 30.5 g., b.p. −19° (739 mm.), of heptafluoropropane corresponding to a 75% yield of zinc compound based on starting iodide.

Using 84 g. of pyridine and 42 g. of benzene as solvent and maintaining the reaction temperature at 60° by the rate of iodide addition, 71 g. of heptafluoro-*n*-propyl iodide yielded 5% heptafluoropropane, 10% recovered iodide and 42% zinc compound. The reaction mixture unlike those obtained with the above ether solvents was dark colored, tarry and difficult to filter.

The all-glass apparatus also was used as described above with ethyl ether as solvent. Upon addition of each portion of a total of 62 g. of iodide to 39 g. of zinc in 92 g. of ether, a deep red color appeared which gradually faded. A total of 37 g. of material was condensed in the cold trap. Distillation gave 15 g. of heptafluoropropane, b.p. −17° (734 mm.), and 22 g. of ether-soluble residue which contained iodine (sodium fusion). The residue reacted with zinc in ether to give a gas and was assumed to be unchanged iodide, 36%. Hydrolysis of the dark ethereal reaction mixture gave <1 g. of heptafluoropropane showing that little, if any, organozinc compound was present.

A similar reaction was carried out in acetone solution. To the stirred suspension of 10.4 g., 0.16 gram-atom, of zinc dust in 44 g. of dry acetone was added 39 g., 0.13 mole, of heptafluoropropyl iodide in 11 g. of acetone. The reaction was so mild at room temperature that all of the iodide solution was added over a 2-minute period. The temperature rose to 50° when the zinc was stirred very vigorously. After 0.5 hr. only 0.5 g. of material had distilled into the cold trap. The reaction mixture was refluxed for 8 hr. to yield 8.4 g. of volatile product which after bubbling through concentrated sulfuric acid consisted of 5.3 g., 24%, of heptafluoropropane. The reaction mixture was filtered and hydrolyzed to yield 7.0 g., 31%, of heptafluoropropane and 3.3 g. of an oil boiling over a wide range which appeared to be mainly condensation products of acetone.

Perfluoro-*n*-propylzinc Bromide.—A glass ampoule was charged with 5.0 g., 0.020 mole, of perfluoro-*n*-propyl bromide, 1.6 g., 0.025 gram-atom, of zinc dust and 10 ml. of 1,2-dimethoxyethane and rocked mechanically while heated up stepwise to 90° over a 73-hr. period. The zinc did not appear to react. The ampoule was set aside, and it was observed after 1.5 months that the zinc was etched and crystalline material had formed. No heptafluoropropane or starting material was found. Hydrolysis yielded 2.0 g. of heptafluoropropane corresponding to a 60% yield of heptafluoro-*n*-propyl zinc bromide.

Perfluoro-*n*-amylzinc Iodide.—A solution of 49.0 g., 0.124 mole, of perfluoro-*n*-amyl iodide in 50 ml. of dioxane was added dropwise to a stirred suspension of 9.2 g., 0.14 gram-atom, of zinc in 100 ml. of dioxane maintained at 65° by an oil-bath. The reaction was not exothermic. The second half of the iodide solution was added over a 0.5-hr. period with the temperature held at 85°. After stirring for an additional 5 hr. at 80–82° and standing overnight, 7.0 g. of undecafluoropentane was isolated which was identified by its infrared spectrum and its b.p. of 45° (755 mm.). Traces of unsaturated material were present as indicated by decolorization of acetone permanganate solution. A lower liquid layer separated out of the dioxane. This material, 8.0 g., b.p. 146–148° at 755 mm., $n^{20}D$ <1.3 and m.p. 32°, contained fluorine but no iodine; reported[37] for perfluoro-*n*-decane: b.p. 144°, m.p. 36°.

Hydrolysis of the reaction mixture yielded 9.5 g., 28% of undecafluoropentane, b.p. 45° and $n^{20}D$ <1.3. Calcd. for C_5HF_{11}: C, 22.23; mol. wt., 270. Found: C, 22.4; mol. wt., 271, 271.

Attempted Reaction of Perfluoro-*n*-propylzinc Iodide with Heptafluoro-*n*-propyl Iodide.—A filtered solution of 0.22 mole of heptafluoro-*n*-propylzinc iodide in 105 ml. of 1,2-dimethoxyethane was refluxed with 64.5 g., 0.218 mole of heptafluoro-*n*-propyl iodide for 24 hr. No insoluble material separated. Distillation yielded 51.5 g., b.p. 39–42°, n^{20}_D 1.3283, an 80% recovery of the propyl iodide. Similar reactions with dioxane solutions of perfluoropropylzinc iodide and *t*-butyl chloride, perfluoroallyl iodide and 1,2-dichlorotrifluoroiodoethane also failed to give coupled products.

Dimerization of Heptafluoro-*n*-propyl Iodide. Perfluoro-*n*-hexane.—The exact procedure of Henne[16] was repeated and found to yield 62% perfluoro-*n*-hexane and 13% heptafluoropropane. In a second run the acetic anhydride was replaced by 1,2-dimethoxyethane. Forty-eight grams, 0.162 mole, of heptafluoro-*n*-propyl iodide, 19.6 g. (0.298 gram-atom) of zinc dust, 16 ml. of 1,2-dimethoxyethane and 42 ml. of methylene chloride were sealed in a Pyrex ampoule at Dry Ice temperature. On warming to room temperature an exothermic reaction took place. After rocking one day at room temperature, it was observed that a new liquid layer had appeared. After eight days the ampoule was vented to yield 3 g., 11%, of heptafluoropropane. The residue was distilled *in vacuo* to yield a two-phase system. The lower layer, 19.8 g., after separation, yielded 17 g., b.p. 57.0°, 62%, of perfluoro-*n*-hexane; found: n^{20}_D <1.3, d. 1.71 (gravitometer), mol. wt. 336.

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(32) Induction periods of a few minutes were observed in only two out of more than fifty preparations.

(33) A. F. Benning and J. D. Park (1950), U. S. Patent 2,490,764.

(34) Since heptafluoropropane was evolved throughout the reaction period, it was considered unlikely that simple hydrolysis could explain its formation.

(35) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 120.

(36) Unless otherwise indicated trap materials were worked up as follows. The trap was immersed in an ice-bath and the material b.p. <0° was distilled into another trap. The crude fractions were identified by spectroscopic examination and chemical tests, *e.g.*, the unsaturation test with potassium permanganate.

(37) R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 3617 (1950).

and 344, immiscible with benzene or ether; reported[16]: n^{20}_{D} <1.3, d^{20}_{4} 1.6995, b.p. 57°., calcd. for C_6F_{14}: mol. wt. 338. The residual salts in the ampoule were hydrolyzed to yield 5.5 g., 20%, of heptafluoropropane.

The above procedure was repeated using only 1,2-dimethoxyethane as solvent. Heptafluoropropane, perfluoro-*n*-hexane and heptafluoro-*n*-propylzinc iodide were obtained in 15, 47 and 29% yields, respectively.

Attempted Preparation of Other Zinc Compounds.—Reactions between powdered zinc metal and the following compounds were carried out under conditions found favorable for the preparation of heptafluoro-*n*-propylzinc iodide.

Trifluoroiodomethane.—A 500-ml. three-necked flask which was fitted with a mechanical stirrer, a thermometer and a Dry Ice reflux condenser and connected in series with Dry Ice and liquid nitrogen traps was charged with 19.6 g., 0.30 gram-atom, of zinc and dried as described above; 14 g. of 1,2-dimethoxyethane and 21 g. of trifluoroiodomethane were added to the flask. Reaction started on warming with the palm of the hand but was quenched by adding 124 g. of additional solvent; 20 g. of additional iodide was added slowly to the flask through the Dry Ice condenser but reaction failed to start. On warming a sudden reaction caused the loss of some material, but now the remaining 35 g. of the total of 76 g., 0.39 mole, of iodide was added at such a rate that the reaction mixture remained at 60–65°. During the reaction 10 g., 39%, of fluoroform (infrared spectrum) was collected in the liquid nitrogen trap. Found: mol. wt., 70.8, 70.9. Calcd. for CHF_3: mol. wt., 70.0. Hydrolysis of the reaction mixture gave no fluoroform indicating that a stable zinc compound was not formed. Considerable fluoride ion was present in the reaction mixture.

Bromodichlorofluoromethane.—This reaction was carried out as described above for the preparation of heptafluoro-*n*-propylzinc iodide in dioxane in the all-glass apparatus; 36.4 g., 0.20 mole, of bromide was added to the stirred suspension of 16 g., 0.23 gram-atom, of zinc in 80 ml. of dioxane maintained at 50°. The mixture became dark in color and after stirring overnight at 55–60° was black. No material was collected in the cold trap on hydrolysis. The filtered solution yielded no low boiling material. Steam distillation yielded 2.1 g., n^{20}_{D} 1.4198, and a liquid residue of 11 g. The hydrolysis mixture gave strong tests for fluoride, chloride and bromide ions.

Dichlorofluoroiodomethane.—As described above, 92 g., 0.402 mole, of iodide and 41 g. of 1,2-dimethoxyethane were added to 57.6 g., 0.88 gram-atom, of zinc suspended in 199 g. of solvent at such a rate that the temperature was maintained at 30°. The reaction mixture was distilled to yield 21 g., b.p. up to 25°, and 18 g., 44%, of dichlorofluoromethane, b.p. 10–13°, identified by its infrared spectrum; reported[38] b.p. 8.9°. This material contained formaldehyde and methyl iodide in small amounts. A dinitrophenylhydrazone, m.p. 162–165°, was prepared; its infrared spectra was superimposable with that of authentic formaldehyde dinitrophenylhydrazone. Steam distillation of the reaction mixture gave no dichlorofluoromethane, showing that no zinc compound was present, but gave 10 g. of a liquid product. Redistillation yielded 5.7 g., b.p. 86–101°, n^{26}_{D} 1.4041 to 1.4118. This material contained fluorine and chlorine, and its infrared spectrum corresponded to that of *sym*-difluorotetrachloroethane n^{26}_{D} 1.4122, b.p. 91°. It corresponded to 14% of the starting material.

1,2-Dichlorotrifluoroiodoethane.—A solution of 21.1 g., 0.076 mole, of iodide in 34 ml. of dioxane was added to 6.5 g., 0.10 gram-atom of zinc, suspended in 24 ml. of dioxane during a 2-hr. period while maintaining the temperature at 15–20°. A total of 5.5 g., b.p. <0°, identified as chlorotrifluoroethylene (63%) by its infrared spectrum, was isolated. Hydrolysis of the reaction mixture yielded no hydrogen compounds.

Pyrolysis of Perfluoro-*n*-propylzinc Iodide.—An apparatus consisting of a 500-ml. round flask, with a 1-in. diameter neck 13 in. long was connected in series with two traps and charged with 78 ml. of dioxane solution containing 0.244 mole[39] of perfluoro-*n*-propylzinc iodide. The dioxane was removed *in vacuo* to the second trap by gradually warming the flask to 60° and lowering the pressure to 1 mm. With the pressure at 1 mm. the flask and first trap were isolated from the rest of the system by a stopcock, and the first trap was cooled in liquid nitrogen. The flask was immersed in a deep oil-bath, 3.5 in. of the neck of the flask was covered with oil and the temperature raised to 150–160°. Distillate was collected in the trap and small amounts of a white crystalline sublimate condensed on the cooler portion of the neck of the flask. After 15 hr. the reaction was stopped and the volatile material in the trap bubbled through concentrated sulfuric acid to remove dioxane. In this way 29 g., 79%, of perfluoropropene (infrared spectrum), b.p. less than 0°, was collected. Photochemical bromination of 8.1 g. (0.054 mole) of the propene distillate from a similar pyrolysis with 6.5 g. (0.041 mole) of bromine in a Pyrex ampoule yielded on simple distillation 11.7 g. of 1,2-dibromohexafluoropropane. Found: b.p. 70.0–72.0° (734 mm.), n^{20}_{D} 1.3588, d^{20}_{4} 2.163, MR_D 31.53, reported[40]: b.p. 72–73° at 740 mm., n^{20}_{D} 1.3588, d^{20}_{4} 2.1693; calcd. for $C_3Br_2F_6$: MR^{20}_{D} 31.50.[28]

The white hygroscopic sublimate (*ca.* 0.5 g.) contained traces of iodide which could be removed by resublimation. It reacted with water to give a gas, decomposed on heating to give perfluoropropene (infrared spectrum), reacted vigorously with bromine, gave a Tollens test and burned only when held in a flame. The reactions of this sublimate suggested that it was perfluorodi-*n*-propylzinc dioxanate.

Reactions of Perfluoro-*n*-propylzinc Iodide.—The following reactions were carried out with perfluoropropylzinc iodide prepared as described above. Solid dioxane solvate containing from one to two moles of dioxane per mole of perfluoro-*n*-propylzinc iodide was prepared by removing excess solvent under reduced pressure.

Iodine.—When 0.17 mole of zinc compound was treated with 50.8 g., 0.200 mole, of iodine in 90 ml. of diozane, no apparent reaction occurred until the mixture was warmed. The mixture was refluxed and perfluoro-*n*-propyl iodide distilled out. A total of 38.7 g., 77%, of product was thus obtained. Found: b.p. 39 to 41°, n^{20}_{D} 1.3281, mol. wt. 292 and 293.

Bromine.—Similarly to the reaction with iodine, 64 g., 0.40 mole, of bromine was added dropwise to 0.18 mole of zinc compound in 100 ml. of dioxane. The mixture turned iodine colored and the temperature rose to 80°. After approximately one-half of the bromine was added, refluxing occurred at the distillation head which was cooled by ice-water. The low boiling material, 33 g., was collected in a Dry Ice trap. Distillation yielded: (1) 26.8 g., b.p. 11.0–13.8° (740 mm.), mol. wt. 231 and 232; (2) 8 g., b.p. 25–45°, 2 g. of which b.p. 35–45°, n^{20}_{D} 1.3281. Fraction 1 was estimated by infrared spectrum and molecular weight, to be a mixture of heptafluoropropane and heptafluoropropyl bromide corresponding to yields of 23 and 44%. Redistillation of (1) yielded an end fraction, mol. wt. 246 and 247, f.p. −145.5 to −146.5°; found for perfluoro-*n*-propyl bromide prepared from silver perfluoro-*n*-butyrate and bromine: b.p. 12°, f.p. −144.0°; calcd. for C_3BrF_7: mol. wt. 249. Fraction 2 was principally perfluoro-*n*-propyl iodide, presumably formed by reaction of iodine with the zinc compound.

Chlorine.—Twenty-eight ml. of dioxane solution containing 0.029 mole of perfluoro-*n*-propylzinc iodide was placed in a two-necked flask fitted with a thermocouple extending into the solution and a Dry Ice reflux condenser in series with a trap. Chlorine, 19 g., 0.27 mole, was condensed into the flask; the temperature rose to 75° and the mixture turned iodine colored. The mixture was allowed to reflux for several hours and the volatile product then passed through a strongly basic sulfite solution to yield 5.5 g. of material identified as a mixture of heptafluoropropane, 46 mole per cent., and perfluoro-*n*-propyl chloride, 54 mole per cent., by infrared and molecular weight analysis; found: mol. wt. 189; calcd. for C_3ClF_7: mol. wt. 205. Ampoule-to-ampoule distillation yielded an end fraction, 0.5 g., with an infrared spectrum essentially identical with that of perfluoro-*n*-propyl chloride; found: mol. wt. 205, 207.

Hydrolysis of the reaction mixture gave no heptafluoropropane nor did any perfluoro-*n*-propyl iodide separate from

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(38) A. F. Benning and R. C. McHarness, *Ind. Eng. Chem.*, **31**, 912 (1939).

(39) For convenience the titers of the zinc compound solutions given are calculated from the moles of perfluoro-*n*-propyl iodide used to prepare the zinc compound minus the moles of heptafluoropropane and of unchanged iodide isolated during the preparation.

(40) W. T. Miller, Jr., Chap. 32, *Nat. Nuclear Energy Ser.*, Div. VII, I, "Prepn., Properties and Technol. of Fluorine and Org. Fluorine Compds.," McGraw-Hill Book Co., Inc., New York, N. Y., 1951.

the aqueous solution. The production of heptafluoropropane during the bromination and chlorination of perfluoro-*n*-propylzinc iodide presumably was due to reaction with hydrogen halide produced by the halogenation of dioxane at the reaction temperatures employed.[41]

Oxygen.—A solution of 0.114 mole of zinc compound in 90 ml. of dioxane failed to gain weight or show any positive signs of reaction when dry oxygen was bubbled into it at a rate of 0.5 mole per hour at room temperature. Likewise, at 90° after two days no evidence of reaction was observed. One gram, 5%, of heptafluoropropane was evolved during this period. Hydrolysis yielded 15 g. or a total of 16 g., 82%, of heptafluoropropane and the hydrolyzate was free of fluoride ion.[42]

In a parallel experiment with oxygen, 0.144 mole of zinc compound in dioxane was illuminated with eight G.E. 15 watt B.L. fluorescent bulbs placed concentrically around and one inch from the Pyrex reaction flask. No positive evidence of reaction was observed during 48 hr. with the solution at 35° and an oxygen flow of 0.5 mole per hour. The temperature was raised to 90–100° and the oxygen flow continued for five days during which time 18 g. of condensate collected in the Dry Ice trap. The system lost 9 g. in weight, presumably by oxygen entrainment. Separation of the trap material yielded 1.5 g., 6%, of heptafluoropropane, and 11 g., b.p. 40°, $n^{20}{}_D$ 1.3290, identified as perfluoro-*n*-propyl iodide, 26%. Hydrolysis of the reaction mixture, which gave a faint test for fluoride, yielded 3 g., 12%, of heptafluoropropane. Distillation of the hydrolysate from excess silver sulfate yielded only 1.4 meq. of acid.

Carbon Dioxide.—A solution of 0.261 mole of zinc compound was placed in a dry lecture cylinder and 70 g., 1.6 moles, of carbon dioxide was added with the cylinder cooled in Dry Ice. The cylinder was closed with a steel valve and heated in a reciprocating shaker at 106° for 110 hr. Carbon dioxide was vented through a sintered glass disk into 500 ml. of $14N$ caustic to yield 4 g. of heptafluoropropane, 9%, which was free of perfluoropropene as tested by infrared spectrum and acetone permanganate. Water, 50 ml., was added to the bomb which was then heated at 100° for 2 hr. to yield 30 g. of material, b.p. <0°, which on redistillation gave 25 g., 56%, of heptafluoropropane, b.p. −13.0 to −12.5° (740 mm.). No perfluorobutyric acid was obtained by distillation of the hydrolyzate from excess silver sulfate.

Carbonyl Compounds.—The essential technique in the reactions summarized below was to heat the reactants together under the conditions specified. The volatile products were isolated by distillation and the residual salts hydrolyzed in order to estimate the quantity of unchanged zinc compound. The percentage yields listed are regarded as approximate values. Water-insoluble products remaining in the hydrolyzate were partially investigated. Only in the case of perfluoro acid chlorides were detectable quantities of the desired products, ketones, produced. The reaction mixtures in which most of the zinc compound was consumed during the heating period were characteristically dark and tarry. The reaction mixtures in which most of the zinc compound was unchanged, despite the relatively high temperatures employed, remained fairly clean. Varying amounts of ester by-products were shown to be formed by cleavage of dioxane in the reactions with acid halides and anhydrides.

Illustrative results are summarized below. In each case following the name of the organic reagent is given: the number of moles organic reagent per mole of zinc compound, the reaction time and temperature, the percentage heptafluoropropane (I) evolved during the reaction period and the percentage unchanged zinc compound II and/or other products isolated. Percentages are based on the initial concentration of zinc compound.[39]

Perfluoro-*n*-propylzinc Iodide in Dioxane Solution.—*Paraformaldehyde:* 3.3, 5.5 days at 130°, 46% I (containing some formaldehyde), 42% II. *Benzophenone:* 0.82, 18 hr. at 80° plus 7 days at 115°, 8% I, 62% II. *Ethyl perfluoro-n-butyrate:* 1.1, 24 hr. at 80° plus 4 hr. at 105°. I and II were not determined quantitatively, but 75% ethyl perfluoro-*n*-butyrate was recovered. *Benzoyl chloride:* 0.84, 18 hr. at 90°, 14% I, 49% II (β-chloroethyl benzoate, ethylene glycol dibenzoate and possibly β-iodoethyl benzoate were shown to be present). *Perfluoro-n-butyryl chloride:* 1.5, 2 hr. at 60°, 8% I, 76% II. 1.4, 16 hr. at 110°, 63% I (containing some acid chloride), 31% II.

Perfluoro-*n*-propylzinc Iodide Solid Dioxane Solvate.—One to two moles of dioxane plus approximately 0.25 mole of zinc iodide were present per mole of organozinc compound. Complete conversion of the zinc compound took place in each case. *Acetic anhydride:* 5.6, 12 hr. at 110°, 56% I. *Acetyl chloride:* 4.4, 12 hr. at 90°, 78% I. *Benzoyl chloride:* 1.8, 12 hr. at 130–140°, 59% I, 17% heptafluoro-*n*-propyl iodide. *Trifluoroacetyl chloride:* 2.4 (plus chlorobenzene diluent), 15 hr. at 120°, compound I was mixed with trifluoroacetyl chloride and was not determined quantitatively, 6% perfluoro-2-pentanone. *Perfluoro-n-butyryl chloride:* 1.9, 65 hr. at 120°, compound I was mixed with perfluoro-*n*-butyryl chloride; 15% perfluoro-4-heptanone, b.p. 72–74° (738 mm.), yielded a solid ammonia adduct, m.p. 57.5–58.5°, phenylhydrazone, m.p. 35–37°, and formed a liquid hydrate; reported[43] for perfluoro-*n*-heptanone b.p. 75° (740 mm.).

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[41] C. L. Butler and L. H. Cretcher, THIS JOURNAL, **54**, 2987 (1932).

[42] The postulated product, $CF_3CF_2CF_2OZnI$, would be expected to break down to give perfluoropropionic acid and hydrogen fluoride.

[43] A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 991 (1953).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Preferential Replacement Reactions of Highly Fluorinated Alkyl Halides. I. Preparation of Certain Fluorinated Allyl Iodides[1,2]

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Certain fluorinated allyl chlorides, including 3-chloropentafluoropropene and 2,3-dichlorotetrafluoropropene, have been found to react readily with sodium iodide in anhydrous acetone to yield 3-iodopentafluoropropene and 2-chloro-3-iodotetrafluoropropene, respectively. Other compounds such as 1,1,2,3-tetrachlorodifluoropropene and 1,3-dichlorotetrafluoropropene were completely inert under more rigorous conditions. The resistance of the latter two compounds to substitution suggests that the ready reaction of the first two does not involve direct reaction at the α-carbon atom, but rather anionic attack by iodide ion on the γ-carbon atom, with allylic shift and elimination of chloride ion, an S_N2' mechanism.

As part of a general investigation of the reactivity of X in highly halogenated compounds of the type RCF_2X, $RCFXR'$ and $RR'R''CX$, where $X = Cl$, Br or I, a number of compounds containing the group $CClF_2$ in the allylic and benzylic positions have been prepared. Physical properties for these compounds, and for their precursors and derivatives, are listed in Table I. For the

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[1] Presented at the 119th Meeting of the American Chemical Society, Boston, Mass., April, 1951, Abstracts of Papers, p. 24-M. Based in part on the thesis submitted by Arnold H. Fainberg to the Graduate School of Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1950.

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