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THE REACTION OF SECONDARY PERFLUOROALKYL IODIDES WITH ZINC

T.M. KELLER and PAUL TARRANT

Department of Chemistry, University of Florida, Gainesville,
Florida 32611

SUMMARY

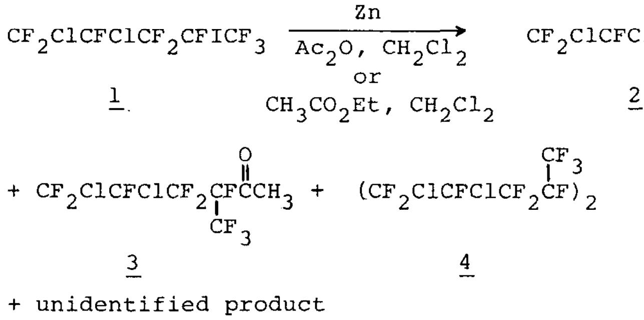
Evidence for the existence of two mechanistic pathways for the reaction of secondary perfluoroalkyl iodides with zinc has been obtained. At high concentration of secondary iodides, a bimolecular homolytic type reaction of the iodide on the zinc surface to yield dimers appears to be preferred. When the reaction is carried out under dilute conditions, an ionic type mechanism appears to predominate. This paper also shows that the substrate itself can influence the reaction route.

INTRODUCTION

In 1957 Miller et al. showed[1] that primary fluorocarbon iodides react with zinc to give olefin, organozinc iodide, hydride or the coupled product. That solvent plays a role in the reaction was indicated by the fact that no reaction occurred between n-heptafluoropropyl iodide and zinc in the absence of solvent or in the presence of non-donor solvents such as benzene, methylene chloride or ethyl heptafluorobutyrate whereas dioxane caused reaction at a lower temperature. Chambers et al. in 1961 found[2] that 1-heptafluoropropyl iodide gave a 96.5% yield of the coupled product when subjected to ultraviolet irradiation in the presence of mercury.

RESULTS AND DISCUSSION

During the reaction of 1,2-dichloro-4-iodoperfluoropentane 1[3] with zinc, five fluorine-containing compounds were formed. Four of these compounds were identified as 2-H-4, 5-dichloroperfluoropentane 2, 1,1,1-H,H,H-5, 6-dichloro-3-trifluoromethylperfluorohexan-2-one 3, d, l- and meso-1,2,7,8-tetrachloro-4, 5-bis (trifluoromethyl)-perfluorooctane 4.



$$\underset{\mathbf{1}}{CF_2ClCFClCF_2CFICF_3} \xrightarrow[\text{Ac}_2\text{O, CH}_2\text{Cl}_2 \text{ or } \text{CH}_3\text{CO}_2\text{Et, CH}_2\text{Cl}_2]{\text{Zn}} \underset{\mathbf{2}}{CF_2ClCFClCF_2CFHCF_3}$$

$$+ \underset{\mathbf{3}}{CF_2ClCFClCF_2\underset{CF_3}{C}F\overset{O}{\overset{\|}{C}}CH_3} + \underset{\mathbf{4}}{(CF_2ClCFClCF_2\overset{CF_3}{C}F)_2}$$

+ unidentified product

[eq. 1]

The yield of each compound was found to depend on the reaction conditions (see Table 1). At longer reaction times and higher

TABLE 1 Reaction of 1 with Zinc under Different Conditions (Relative Ratios)[a]

Conditions	2	3	4	Unidentified Product
Zn, Ac_2O, CH_2Cl_2 [b]	18	16	55	11
Zn, Ac_2O, CH_2Cl_2 [c]	25	31	32	12
Zn, CH_3CO_2Et, CH_2Cl_2 [c]	68	4	21	7

[a] Relative ratios are weight percentage obtained from integrated peaks using a thermal detector.

[b] Addition of 1 in one sum. [c] Addition of 1 dropwise.

temperatures, at least three other volatile compounds were formed, probably from the slow dehalogenation of the main components.

Besides spectral means, the identity of each product was proven by chemical means. The reaction of 1 and potassium hydroxide in hexamethylphosphoric triamide (HMPT) yielded 2 upon quenching in water.

$$\underline{1} \xrightarrow[\text{HMPT}]{\text{KOH}} CF_2ClCFClCF_2\overset{K^+}{\overset{-}{C}}FCF_3 \xrightarrow{H_2O} \underline{2} \qquad [\text{eq. } 2]$$

During the reaction of 1 with zinc, 3 was formed from two acetyl sources, acetic anhydride and ethyl acetate, but in different amounts (see Table 1). Apparently, the ethoxy anion, being a stronger base, is not as good a leaving group compared to the acetyloxy anion. The two coupled products 4 could not be separated by analytical means. However, reaction of 4 with zinc dust in refluxing dioxane yielded *d*-,*l*- and *meso*- 4, 5-bis (trifluoromethyl)-1,7-perfluorooctadiene 5 which could be separated on a glpc. The mass spectra of the two diasteromers were identical with the exception of the relative abundance of some of the molecular fragments. Moreover, the infrared and ^{19}F nmr spectra were slightly different.

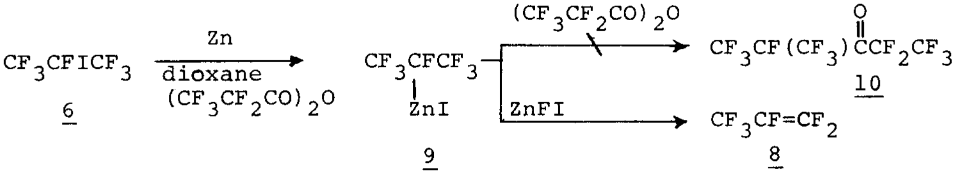
The results which were obtained during the reaction of 1 with zinc indicated that two mechanisms were probably operative. The coupled product 4 is almost certainly formed by a radical-type mechanism[1] since S_N2 reactions do not readily occur at a highly fluorinated carbon atom. The noncoupled products, 2 and 3, appear to be formed by an ionic mechanism (eq.3). Therefore, the two mechanisms

$$CF_2ClCFClCF_2CFICF_3 \xrightarrow{Zn} CF_2ClCFClCF_2CF(CF_3)ZnI \left| \begin{array}{l} \xrightarrow{Ac_2O} \underline{3} \\ \text{or} \\ CH_3CO_2Et \\ \xrightarrow{\text{dil. HCl}} \underline{2} \end{array} \right. \qquad [\text{eq. } 3]$$

are competitive, depending on the reaction conditions.

Since the ionic mechanism appears to predominate under dilute conditions, we decided to investigate the feasibility of synthesizing perfluoroketones from secondary perfluoroalkyl iodides. The reaction of 2-iodoperfluoropropane 6 with zinc in perfluoroacetic anhydride, perfluoroacetic anhydride-chloroform and perfluoropropionic anhydride proceeded very slowly to yield two unidentifiable, volatile compounds in an extremely low yield. Apparently, radical and ionic formations are highly unfavorable in the non-donor, perfluorinated solvents.[1]

An attempt to prepare 2-perfluoropropylzinc iodide 9 in dioxane-perfluoropropionic anhydride led to the rapid evolution of perfluoropropene 8. The fact that 9 does not react with perfluoropropionic anhydride to yield 2-trifluoromethylperfluoropentan-3-one 10 is surprising. The carbonyl



group in perfluoropropionic anhydride should be more electrophilic and thus more reactive toward 9 than acetic anhydride unless some other phenomenom is operative. Dioxane is a donor-type solvent and could solvate the carbonyl groups of the fluorinated anhydride to such an extent that its reactivity is greatly diminished relative to acetic anhydride.

Since the reaction of 6 with zinc in both perfluoroacetic and perfluoropropionic anhydrides was slow, we decided to repeat the reaction using ethyl trifluoroacetate, which was dried over molecular sieves, as the solvent. The reaction proceeded rapidly to yield 2-H-perfluoropropane 7 and 2, 3-bis (trifluoromethyl)-perfluorobutane 11 (see Table 2).

$$\underset{6}{CF_3CFICF_3} \xrightarrow[CF_3CO_2Et]{Zn} \underset{7}{CF_3CFHCF_3} + \underset{11}{[(CF_3)_2CF]_2}$$

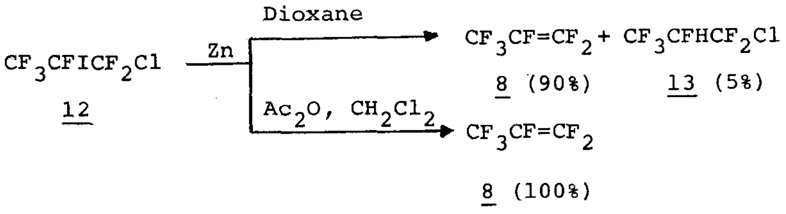
2, 3-Bis (trifluoromethyl)-perfluorobutane 11 has been prepared previously[2] by irradiating 6 in the presence of mercury.

TABLE 2 Reaction of 6 with Zinc in Ethyl Trifluoroacetate (Relative Ratios)

Conditions	7	11
Zn, $CO_3CF_2Et^a$	46	54
Zn, $CF_3CO_2Et^b$	77	23

[a]Reactant added in one sum. [b]Reactant added dropwise.

To shed more light on the reaction of secondary iodides with zinc, 1-chloro-2-iodoperfluoropropane 12 was synthesized[4] and treated with zinc in both dry dioxane and acetic anhydride-methylene chlorine. From acetic anhydride-methylene chloride perfluoropropene 8 was the sole product. When dioxane was used, 8 was again the main product but a second product, which was believed to be 1-chloro-2-H-perfluoropropane 13 from its infrared spectrum, was also formed in a small amount. The formation of 13 in dioxane is probably due to small amounts of peroxides.[1,5,6] Apparently, incorporation of the zinc



between the carbon-iodine bond is favored over the radical abstraction of iodine from two molecules of reactants by zinc to yield the coupled product.

The preferred ionic pathway for the reaction of 12 with zinc could be attributed to either electronic or steric effects. The reaction of 1,2-dichloroiodotrifluoroethane 14 with zinc yields 1,2,3,4-tetrachloroperfluorobutane 15,[7] and n-perfluoropropylzinc iodide has been shown to be inert except under extreme conditions,[1] indicating that the carbon-zinc bond is covalent for primary perfluoroalkyl iodides. The observed coupling of 14 which is in contrast to 12 supports the steric interaction concept. Moreover, the greater stability of secondary perfluoroalkyl anions relative to primary perfluoroalkyl anion is surely important.[8] Thus, when more than one mechanistic pathway is possible the concentration, the solvent and the substrate seem to determine which products will be formed.

EXPERIMENTAL

1,2-Dichloro-4-iodoperfluoropentane 1 was prepared by a literature procedure, B.P. 58-61 (20 mm); reported 58.5-60.5 (20 mm).[3]

The reaction of 1 with Zinc in Acetic Anhydride-Methylene Chloride. -To a 25 ml, three-necked flask was added 0.71 g (0.011 g. atom) of granular zinc, 3 ml of methylene chloride and 3 ml of acetic anhydride. Compound 1 (5.1 g, 0.011 mol) was added in one sum and the reaction mixture was heated at 40-

45° for 53 hours. After removing the unreacted zinc by filtration, dilute hydrochloric acid was slowly added and the resulting solution was allowed to stir overnight. The organic layer was washed with saturated sodium bicarbonate solution until neutral, with 10% sodium bisulfite, and was dried over anhydrous sodium sulfate. Analysis (glpc relative ratios) of the concentrated residue indicated that five fluorine-containing compounds had been formed.

The <u>first</u> component was identified as 2-H-4, 5-dichloroperfluoropentane (NC) <u>2</u> (18% relative ratio); ir (gas): 1375-1130 cm^{-1} (C-F;m/e 267 $[M^+(Cl^{35})-Cl^{35}]$; ^{19}F nmr ($CFCl_3$), external TFA ref): -14.1 (CF_2Cl, muliplet), -2.3 (CF_3, multiplet), 40.9 (CF_2, multiplet), 54.0 (CFCl, multiplet), 77.1 ppm (CFH, multiplet) This compound was extremely volatile, having a low heat of vaporization and elemental analyses could not be obtained; however, the infrared, mass and ^{19}F nmr spectra were consistent with the proposed structure. It was also made by an independent method as described below.

The <u>second</u> component was identified as 1,1,1-H,H,H-5,6-dichloro-3-trifluoromethylperfluorohexan-2-one <u>3</u> (NC) (16% relative ratio); ir (neat): 2930 (C-H), 1740 (C=O), 1300-1100 (C-F), 712, 665 cm^{-1} (C-Cl); m/e 309 $[M^+(Cl^{35})-Cl^{35}]$; ^{19}F nmr (neat, $CFCl_3$ ref): 72.3 (CF_2, multiplet), 63.3 (CF_2Cl, multiplet, 133 (CFCl, multiplet), 106.1 (CF_2, multiplet), 168.9 ppm (CF multiplet): ^1H nmr (neat, TMS ref): 2.46 (CH_3, doublet). The infrared, mass, proton, and ^{19}F nmr spectra were consistent with the proposed structure.

<u>Anal</u>. Calcd for $C_7H_3F_9Cl_2O$: C, 24.4; H,0.87; Cl, 20.6

Found: C, 23.98; H, 0.81; Cl, 20.40.

The third and fourth components were identified as d,l- and meso-1,2,7,8-tetrachloro-4,5-bis(trifluoromethyl)-perfluorooctane 4 (55% relative ratio); ir (neat): 1280-1120 (C-F), 690 cm^{-1} (C-Cl); m/e 567 [M$^+$(Cl^{35})-Cl^{35}]. Since the two compounds could not be separated, the ^{19}F nmr was not obtained.

Anal. Calcd, for $C_{10}F_{18}Cl_4$: Cl, 23.48
Found: Cl, 22.54

The fifth component (11%) was extremely volatile and was not identified. According to its infrared spectrum, it is a saturated compound.

A second reaction was carried out by placing 0.91 g (0.014 g. atom) of granular zinc, 5 ml of acetic anhydride and 20 ml of methylene chloride into a 50 ml, three-necked flask. The resulting mixture was heated to 43° (reflux) and 6.0 g (0.014 mol) of 1 was added dropwise over a period of 12 hours. After heating for 24 hours at 43° the reaction mixture was worked up by the same procedure as above. Analysis (glpc) of the concentrated product mixture indicated that the same components were formed but in different amount: 2 (25%), 3 (31%), 4 (32%) and unidentified product (12%).

The Reaction of 1 under Dilute Conditions with Zinc in Ethyl Acetate-Methylene Chloride. -To a 100 ml, three-necked flask containing 1.7 g (0.026 g. atom) of granular zinc, 30 ml of ethyl acetate and 30 ml of methylene chloride was added dropwise 10.2 g (0.023 mol) of 1 at 48-50°. The resulting mixture was heated at the above temperature for 24 hours and then at reflux (62°) for 24 hours. Workup and concentration was achieved in the usual manner. The same components as in the preceeding experiment were formed in the following relative ratios: 2 (68%), 3 (4%), 4 (21%) and unidentified product (7%).

The Reaction of 1 with Potassium Hydroxide in HMPT. -To a 100 ml, roundbottomed flask was added 15.7 g (0.036 mol) of 1, 50 ml of HMPT and 3.0 g (0.054 mol) of potassium hydroxide. The resulting solution was heated at 70-75° for 24 hours, cooled and poured into 100 ml of ice water. Distillation of the organic layer yielded 4.0 g (33%) of 2, b.p. 96-100°, along with some polymeric material. The infrared and mass spectra were identical to 2 which was produced during the reaction of 1 with zinc.

The Dechlorination of 4 with Zinc Dust. -To a 500 ml, three-necked flask was added 7.8 g (0.12 g. atom) of zinc dust and 150 ml of diglyme. To this hot solution was added dropwise 19.9 g (0.033 mol) of 4 and the resulting mixture was heated at 140° for 1 hour. The temperature was then increased and the product was distilled from the reaction vessel at 137-138°. The product (10g) was washed with water and was dried over anhydrous sodium sulfate. The product was separated into two components by glpc. These components were identified as d, l (5A) - and meso (5B)-4, 5- bis(trifluoromethyl)-1, 7-perfluorooctadiene. The assignments were made from the ^{19}F nmr due to the complexity of 5A and the simplicity of 5B.

Data for 5A (NC): ir (gas): 1770 (=CF_2), 1350-1250 cm^{-1} (C-F); m/e 462 (M^+Cl^{35});^{19}F nmr ($CFCl_3$, external TFA ref): -5.9 and -3.4 (CF_3, multiplets), 11.6 (F in = CF_2, quartet), 28.8 (CF_2 and F in = CF_2, complex multiplet), 108.4 ppm (2 CF, multiplet).

Anal. Calcd $C_{10}F_{18}$: F, 74.97
Found: F, 74.88

Data for 5B (NC): ir (gas): 1770 (=CF_2), 1350-1250 cm^{-1} (C-F); m/e 462 (M^+ Cl^{35}); ^{19}F nmr ($CFCl_3$, external TFA ref): -7.9 (CF_3, multiplet), 7.1 and 25.7 (=CF_2, triplet and multiplet), 28.8 (CF_2, multiplet), 97.3 (CF, multiplet), and 107.9 ppm (CF, multiplet). The infrared, mass and ^{19}F nmr spectra were consistent with the proposed structures.

Anal. Calcd $C_{10}F_{18}$: F, 74.97
Found: F, 74.94

The Treatment of 2-Iodoperfluoropropane 6 with Zinc in Perfluoroacetic Anhydride and Pentafluoropropionic Anhydride. -To a 100 ml, three-necked flask was added 3.43 g (0.053 g. atom) of granular zinc and 30 ml of perfluoroacetic anhydride. The heterogeneous mixture was heated to 39° (reflux) and 15.1 g. (0.051 mol) of 6 was slowly added over a period of 12 hours. The mixture was then stirred for an additional 12 hours. Analysis (glpc and IR) of the distillate, b.p. 36-39°, showed 6, perfluoroacetic anhydride, and trace amounts of two other compounds to be present.

This distillate was slowly added to a mixture of 3.2 g (0.049 g. atom) of granular zinc and 25 ml of dry chloroform. The reaction mixture was heated at reflux (38-39°) for 15 hours. Analysis showed again only trace amount of two new compounds.

Another reaction was attempted using 2.6 g (0.040 g. atom) of zinc dust and 13.2 g (0.024 mol) of pentafluoropropionic anhydride, a higher boiling solvent. The resulting heterogeneous mixture was heated to 60-65°, 7.2 g (0.024 mol) of 6 was slowly added; and the reaction mixture was then heated at reflux (57°) for 12 hours. Again, analysis of the reaction mixture indicated mostly starting materials to be present.

The Reaction of 2-Iodoperfluoropropane 6 with Zinc in Dioxane-Pentafluoropropionic Anhydride. -To a 25 ml, three-necked flask were added 2.6g (0.040 g. atom) of zinc dust, 30 ml of dry dioxane and 13.2 g (0.042 mol) of pentafluoropropionic anhydride. The resulting mixture was flushed with nitrogen, heated to 45-50°, and 6 was slowly added over a period of 4 hours. No reaction was observed. The temperature was then increased to 78-80° (reflux) for 10 hours. Most of the zinc dust had disappeared. Fractional distillation yielded only pentafluoropropionic anhydride and dioxane. Analysis of the trapped material showed mainly perfluoropropene 8 (99%) to be present.

The Reaction of 6 with Zinc in Ethyl Trifluoroacetate. -To a 100 ml, three-necked flask was added 3.3 g (0.051 g atom) of granular zinc and 20 ml of ethyl trifluoroacetate. The heterogeneous mixture was heated to 55-60° and 14.7 g (0.049 mol) of 6 was slowly added. After the addition was completed, the reaction content was heated at 55-60° for 20 hours. Ethyl trifluoroacetate was removed by distillation. During the reaction and distillation, volatile components were collected in a cold trap. Analysis by glpc indicated that two compounds had been formed.

The first compound was identified as 2-H-perfluoropropane 7 (77%); ir (gas): 2980 (C-H) 1380-1120 cm^{-1} (C-F). Compound 7 was also produced by treating 6 with n-butyllithium and by quenching 2-perfluoropropyllithium which was formed with water.

The second compound was identified as 2, 3-bis (trifluoromethyl)-perfluorobutane 11 (23%); ir (gas): 1270-1130 cm^{-1} (C-F); m/e 319 (M+-F); ^{19}F nmr ($CFCl_3$, external TFA ref.): -7.2 (CF_3, doublet) and 112.2 ppm (CF, multiplet). The ^{19}F nmr spectrum matches that of an authentic sample.[9]

A second reaction using 1.3 g (0.020 g atom) of granular zinc and 7 ml of ethyl trifluoroacetate was carried out. Compound 6 (5.0 g, 0.017 mol) was added in one sum and the resulting mixture was stirred at 52-54° for 35 hours. Analysis by glpc (relative ratios) of the trapped material indicated that 46% of 7 and 54% of 11 had been formed.

The Reaction of 12 with Zinc in Dioxane. -To a 50 ml, three-necked flask was added 6.5 g (0.11 g. atom) of granular zinc, 8 ml of dioxane and 30.6 g (0.096 mol) of 12, prepared by a known procedure.[4] The resulting heterogeneous mixture was stirred at room temperature for 20 minutes and was then heated at 40-50° for 10 hours. Analysis by glpc of the volatile material showed two components to be present. The first peak (~95%) was found to be perfluoropropene 8 by comparison of its IR spectrum with an authentic sample. The second peak (~5%) was believed to be 1-chloro-2-H-perfluoropropane 13 from its IR spectrum.

The Reaction of 12 with Zinc in Acetic Anhydride-Methylene Chloride. -To a 50 ml, three-necked flask was added 4.1 g (0.064 g atom) of granular zinc, 5 ml of acetic anhydride and 5 ml of methylene chloride. Compound 12 (20.1 g, 0.064 mol) was added in one sum. The temperature began to rise immediately but was kept at 25-30° for 20 hours by cooling in water. Workup was accomplished by the usual method. Analysis (IR and glpc) of the volatile material in the cold trap showed only perfluoropropene 8 to be present. No other organic component besides the solvent was present in the reaction vessel.

A second reaction was carried out using 5 ml of acetic anhydride, 5 ml of methylene chloride, and 2.1 g (0.032 g atom) of granular zinc. The resulting heterogeneous solution was cooled to -30 to -20° and 10.4 g (0.033 mol) of 12 was added. After 3 hours no observable reaction had occurred. The temperature was kept at this temperature for 4 hours. Most of the zinc had disappeared and the mixture was allowed to rise to room temperature. Perfluoropropene 8 was the only product which was formed.

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