Synthesis of Fluoroalkyl Iodides

C. G. KRESPAN

Contribution No. 725 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

Received November 15, 1961

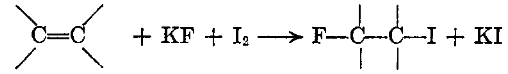
A new one-step route to fluoroalkyl iodides has been found in the reaction of fluoroolefins with potassium fluoride and iodine. Yields, which varied markedly with the structural type of the olefin, ranged from 60–70% for heptafluoroisopropyl iodide to 7% for pentafluoroethyl iodide.

Fluoroalkyl iodides are now recognized to be convenient sources of fluorinated free radicals, because the C—I bond in these compounds undergoes homolysis cleanly on heating, irradiation, or attack by another free radical. Since the pioneering work of Emeleus and co-workers,[1-3] directed mainly toward the preparation and use of trifluoromethyl iodide and pentafluoroethyl iodide, several generally useful synthetic routes to fluorinated iodides have appeared. One such method involves the reaction of the silver salt of a fluorinated carboxylic acid with iodine.[4] A subsequent method which requires a fluorinated acid as a starting material, but avoids use of a silver salt, is the interaction of a fluorinated acid chloride and potassium iodide.[5]

The preparation of pentafluoroethyl iodide from iodine pentafluoride and tetrafluoroethylene or tetrafluoroethylene diiodide[2,6] has recently been modified and extended to other olefins. It was found[7,8] that a mixture of iodine and iodine pentafluoride acts as though it is iodine monofluoride in its addition to a fluoroolefin, giving the saturated fluoroalkyl iodide in high yield. Addition occurs as $F^{\delta-}$—$I^{\delta+}$, so that terminal fluoroolefins give rise to secondary iodides. A similar polar addition of mercuric fluoride to fluoroethylenes provides a convenient route to some fluoroalkylmercurials,[9] hence also to some fluoroalkyl iodides by the known reaction of fluoroalkylmercury compounds with iodine.[10]

The present one-step synthesis of fluoroalkyl iodides from potassium fluoride, iodine, and fluoroolefins relies upon the susceptibility of fluoroolefins to nucleophilic attack by fluoride ion and the ability of the transient carbanion thus formed to react with iodine. This new method complements the earlier syntheses starting from fluorinated acids, since the available acids are generally straight chain and give primary iodides, while the olefin route leads to branched chain iodides. In this respect the potassium fluoride–iodine system resembles the recently developed I–F method, with, of course, the advantage that the reagent is more readily accessible.

In general terms, the new preparative method involves the interaction of potassium fluoride, iodine, and a fluoroolefin at 100–150° in an inert solvent such as acetonitrile to form a fluoroalkyl iodide by apparent addition of F^- and I^+ to the double bond.



$$>C{=}C< + KF + I_2 \longrightarrow F-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-I + KI$$

Several types of fluoroolefin have been used successfully, including chlorofluoro, internal, terminal with a long chain, and cyclic olefins. Depending upon the reactivity of the olefin, yields ranged from 7–70% in single experiments. Absence of a solvent lowered the yield markedly, as did the use of sodium fluoride in place of potassium fluoride. Fluorides of metals with large atomic radii, particularly cesium[11] and silver fluorides, should give improved yields.

Iodine does not add to most fluoroolefins, so that the reaction cannot proceed through a diiodide which subsequently exchanges an iodine atom for fluorine. In fact, tetrafluoroethylene reacts poorly with potassium fluoride–iodine in part because it does add iodine to form tetrafluoro-1,2-diiodoethane as a product as well as pentafluoroethyl iodide. On the other hand nucleophilic attack on fluoroolefins by anions such as fluoride[12] and alkoxide[13] is well established.

The intermediacy of a fluorocarbanion in many cases has been demonstrated by isolation of products formed by attack of the carbanion on carbonyl compounds,[14] on another molecule of fluoro-

---

(1) A. A. Banks, H. J. Emeleus, R. N. Haszeldine, and V. Kerrigan, *J. Chem. Soc.*, 2188 (1948).

(2) H. J. Emeleus and R. N. Haszeldine, *ibid.*, 2948 (1949).

(3) J. Banus, H. J. Emeleus, and R. N Haszeldine, *ibid.*, 3041 (1950).

(4) J. H. Simons and T. J. Brice in Simons, "Fluorine Chemistry," Vol. II, Academic Press, New York, 1954, p. 367, and references cited therein.

(5) C. G. Krespan, *J. Org. Chem.*, **23**, 2016 (1958).

(6) J. H. Simons and T. J. Brice, U. S. Patent 2,614,131 (1952).

(7) R. D. Chambers, W. K. R. Musgrave, and J. Savory, *Proc. Chem. Soc.*, 113 (1961).

(8) M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2383 (1961).

(9) C. G. Krespan, *J. Org. Chem.*, **25**, 105 (1960).

(10) H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2953 (1949).

(11) W. T. Miller, W. Frass, and P. R. Resnick, *J. Am. Chem. Soc.*, **83**, 1767 (1961).

(12) J. H. Fried and W. T. Miller, *J. Am. Chem. Soc.*, **81**, 2078 (1959).

(13) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, 1958, pp. 156–158.

(14) D. W. Wiley, U. S. Patent 2,988,537 (1961).

olefin,[15] and on compounds containing active hydrogen.[12] The potassium fluoride–iodine reagent in an unreactive solvent, then, generates fluorocarbanion by addition of fluoride ion to the fluoroolefin. In a more or less discrete second step, the carbanion then attacks iodine to form fluoroalkyl iodide and iodide ion.

Since fluoride ion tends to equilibrate terminal with internal fluoroolefin,[16] the preparation of nonafluoro-2-iodobutane from octafluoro-2-butene might be considered a result of isomerization to the 1-butene followed by conversion to the iodide. The preparation of heptafluorocyclobutyl iodide from hexafluorocyclobutene, however, provides a straightforward example of addition of "I—F" to an internal olefin.

Previous failure to add "I—F" to tetrachloroethylene and abnormal as well as normal addition of "I—F" to chlorotrifluoroethylene led to claims of instability of the $—CCl_2I$ group for steric reasons.[7] However, the preparation of 1,1-dichloro-2,2,2-trifluoroethyl iodide in the present work, as well as by Hauptschein and Braid,[8] indicates reasonable stability for $CX_3—CCl_2I$ unless the substituents X are too bulky.

Experimental[17]

Heptafluoroisopropyl Iodide.—A mixture of 30 g. (0.20 mole) of hexafluoropropylene, 23.2 g. (0.40 mole) of anhydrous potassium fluoride, 63.5 g. (0.25 mole) of iodine, and 80 ml. of acetonitrile was heated under autogenous pressure at 100° for 10 hr. in a 300-ml. shaker tube. Distillation of the reaction mixture, 150 g., gave 36.3 g. (61% yield) of heptafluoroisopropyl iodide, b.p. 39–41° (ref. 7 reports b.p. 38° and ref. 8 reports 40°). The product was identified by its NMR spectrum for F^{19}, which consisted of a septuplet centered at +4601 c.p.s. for C—F and a doublet centered at +513 c.p.s. for CF_3 ($J = 14$).

A similar reaction carried out at 150° without acetonitrile gave the iodide in 5% yield. Sodium fluoride rather than potassium fluoride gave at 150° only a 1% yield of heptafluoroisopropyl iodide.

Pentafluoroethyl Iodide.—A mixture of 19.8 g. (0.20 mole) of tetrafluoroethylene, 58.3 g. (0.23 mole) of iodine, 19.7 g. (0.34 mole) of anhydrous potassium fluoride, and 60 ml. of acetonitrile was heated at 150° for 10 hr. in a 240-ml. shaker tube under autogenous pressure. The gases from the reaction mixture that were condensible at −60° were shown by NMR to be composed of *ca.* 1.1 g. of CF_3CF_2I and 0.3 g. of octafluorocyclobutane (TFE dimer). Warming of the reaction mixture afforded an additional 2.1 g. of pentafluoroethyl iodide,[18] raising the total conversion to pentafluoroethyl iodide to 7% (3.2 g.). The NMR spectrum for fluorine showed the expected bands for CF_3 and CF_2 at +1079 and +11 c.p.s., respectively (3:2 ratio). Further distillation of the reaction mixture, after it had been washed with 1 l. of cold water and dried, afforded 27.2 g. (38%) of tetrafluoroethylene diiodide, b.p. 52–54° (100 mm.). This product was identified by comparison of its NMR spectrum with that of a known sample.

8-*H*-2-Iodoperfluorooctane.—8-*H*-Perfluoro-1-octene, b.p. 118–119°, was prepared by pyrolysis of the sodium salt of ω-*H*-perfluorononanoic acid at 280–300°.

A mixture of 57.3 g. (0.15 mole) of 8-*H*-perfluoro-1-octene, 17.4 g. (0.30 mole) of anhydrous potassium fluoride, 50.8 g. (0.20 mole) of iodine, and 80 ml. of acetonitrile was heated at 150° for 10 hr. under autogenous pressure in a 300-ml. shaker tube. The reaction mixture, 177 g., was distilled to give 34.1 g. of mixed fluorooctenes,[16] b.p. 45–49°/70 mm., and 10.5 g. (13% yield) of 8-*H*-2-iodoperfluorooctane, b.p. 59–60° (10 mm.). NMR confirmed the structure, $H(CF_2)_6CFICF_3$, in that the F^{19} spectrum contained a doublet for terminal CF_2 at +3955 c.p.s. ($J = 52$), bands for internal CF_2 groups at +3515, +3149, +3051, +2907, and +2238 c.p.s., CF_3 at +320 c.p.s. and a band for CF at +4338 c.p.s.

Anal. Calcd. for $C_8HF_{16}I$: F, 57.57; I, 24.04. Found: F, 57.75; I, 23.83.

Heptafluorocyclobutyl Iodide.—A mixture of 33 g. (0.20 mole) of hexafluorocyclobutene, 23.2 g. (0.40 mole) of anhydrous potassium fluoride, 63.5 g. (0.25 mole) of iodine, and 80 ml. of acetonitrile was heated at 150° for 10 hr. in a 300-ml. shaker tube. The reaction mixture, 158 g., was distilled to give 18.0 g. of crude product, b.p. 61–66°. Redistillation afforded 16.4 g. (27% yield) of heptafluorocyclobutyl iodide, b.p. 63–64°. A sample was washed with water, dried, and redistilled to remove any trace of acetonitrile before analysis. The structure was confirmed by the NMR spectrum, which exhibited two w-s-s-w groups for CF_2 in 2:1 ratio of intensities at +2231, +2454, +3568, and +3783 c.p.s., and +2997, +3225, +3579, and +3803 c.p.s., respectively, and CF resonance at +4612 c.p.s.

Anal. Calcd. for C_4F_7I: F, 43.19; I, 41.21. Found: F, 43.00; I, 41.06.

Nonafluoro-2-iodobutane.—A mixture of 40.0 g. (0.20 mole) of octafluoro-2-butene, 23.2 g. (0.40 mole) of anhydrous potassium fluoride, 63.5 g. (0.25 mole) of iodine, and 80 ml. of acetonitrile was heated at 150° for 10 hr. in a 300-ml. tube under autogenous pressure. The reaction mixture, 156 g., was distilled to give crude product, b.p. 60–75°. This distillate was washed with 500 ml. of water, dried over anhydrous calcium chloride, filtered, and redistilled to give 11.8 g. (17% yield) of nonafluoro-2-iodobutane, b.p. 65–67°; $n^{25}D$ 1.334.[19] NMR confirmed the structure in that the F^{19} spectrum displayed bands for CF_3 groups at +364 and +651 c.p.s., a w-s-s-w group for CF_2 (on an asymmetric carbon) at +2151, +2436, +2519, and +3097 c.p.s., and a band for CF at +4412 c.p.s.

1,1-Dichloro-2,2,2-trifluoroethyl Iodide.—A mixture of 27 g. (0.20 mole) of 1,1-dichloro-2,2-difluoroethylene, 23.2 g. (0.40 mole) of anhydrous potassium fluoride, 63.5 g. (0.25 mole) of iodine, and 80 ml. of acetonitrile was heated at 125° for 12 hr. under pressure. Addition to the reaction mixture of 1.5 l. of water gave a small lower layer, which was removed. The aqueous layer was extracted with 100 ml. of methylene chloride, and the organic layers were combined, washed with water, dried, and distilled. There was thus obtained 5.2 g. (9% yield) of 1,1-dichloro-2,2,2-trifluoroethyl iodide, b.p. 57–59° (200 mm.). A sample was shaken with mercury and redistilled, b.p. 58–59° (200 mm.), for analysis. NMR revealed the expected single resonance for CF_3 at +688 c.p.s.

Anal. Calcd. for $C_2Cl_2F_3I$: Cl, 25.43; I, 45.52. Found: Cl, 25.41; I, 45.12.

---

[15] W. J. Brehm, K. G. Bremer, H. S. Eleuterio, and R. W. Meschke, U. S. Patent 2,918,501 (1959).

[16] W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

[17] All boiling points are uncorrected. The NMR spectra were obtained by means of a high-resolution NMR spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 56.4 mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F^{19} resonance of 1,1,2,2-tetrachloro-1,2-difluoroethane. Negative frequency displacements indicate resonances occurring at lower field than the reference.

[18] M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 2461 (1951) report b.p. 12.5° for this compound.

[19] R. N. Haszeldine, *J. Chem. Soc.*, 3559 (1953) reports b.p. 65.5° and $n^{20}D$ 1.340 for this compound.