(lit.[12] 89.5–90.5°). *Anal.* Calcd for $C_3H_2BrF_4NO$: C, 16.1; H, 0.9; Br, 35.7; F, 33.9; N, 6.2. Found: C, 16.3; H, 0.9; Br, 36.0, F, 33.5; N, 6.3.

2,2-Diaminotrifluoropropionamide.—A 100-cm^3 flask fitted with a solid carbon dioxide–ethanol condenser was charged with ethyl ether (50 ml) and dry ammonia (13 g, 0.76 mole); through a dipping tube, hexafluoropropene epoxide (11.5 g, 0.07 mole) was then slowly introduced into the solution cooled to *ca.* −30°. The reaction was immediate and very exothermic, a white solid being formed; the mixture was evaporated to dryness under slight vacuum, and the residue was extracted with boiling acetone. By further crystallizations from acetone, pure $CF_3C(NH_2)_2CONH_2$ was obtained in a yield of 3.7 g.

N-Ethyl-2-(N-Ethylimino)trifluoropropionamide.—As in the preceeding case, hexafluoropropene epoxide (20 g, 0.12 mole) was treated for 4 hr. at *ca.* 0° with ethylamine (35 g, 0.78 mole) in a solution of ethyl ether (200 ml). The ethereal solution was then washed with water, dried, and distilled to yield 11.6 g of $CF_3C(=NC_2H_5)CONHC_2H_5$ as an oily material which solidified on standing and was purified by crystallization from petroleum ether.

2,2-Di(N-phenylamino)trifluoropropionanilide.—Using a 100-cm^3 flask fitted with a Dry Ice–ethanol condenser, hexafluoropropene epoxide (10 g, 0.06 mole) was treated for 4 hr with aniline (37 g, 0.4 mole) in ethyl ether (200 ml). The ether solution was washed with diluted HCl, then with water, and dried (Na_2SO_4); the solvent was evaporated under slight vacuum. The residue was repeatedly crystallized from acetone–water mixture (4:1) yielding 16 g of $CF_3C(NHC_6H_5)_2COONHC_6H_5$.

All the substituted anilides listed in Table I were prepared in a similar manner, by treating the epoxide in ether solution for 4 hr with a sixfold molar amount of the corresponding anilines.

N-Diethylpentafluoropropionamide.—Hexafluoropropene epoxide (20 g, 0.12 mole) was treated in 100 ml of ethyl ether with diethylamine (40 g, 0.55 mole). With a mild exothermic reaction $CF_3CF_2CON(C_2H_5)_2$ was produced in a yield of 15.7 g (60%), bp 67–69° (25 mm). *Anal.* Calcd for $C_7H_{10}F_5NO$: C, 38.4; H, 4.6; F, 43.3; N, 6.4. Found: C, 38.6; H, 4.6; F, 42.7; N, 6.4.

N-Ethyl-N-phenylpentafluoropropionamide was obtained (36%) in a similar way, by treating the epoxide with N-ethylaniline: bp 48–50° (0.1 mm). *Anal.* Calcd for $C_{11}H_{10}F_5NO$: C, 49.4; H, 3.8; F, 35.5; N, 5.2. Found: C, 49.6; H, 3.6; F, 35.1; N, 5.3.

Pentafluoropropionamide.—Epoxide (10 g, 0.06 mole) was introduced at −30° into a solution of triethylamine (10 g) in ethyl ether (100 ml). After a period of 4 hr, dry ammonia (4 g, 0.24 mole) was added to the solution which was then immediately poured into an excess of water. The ether layer was then dried and evaporated under slight vacuum; the residue was crystallized from chloroform to give 5.6 g (58%) of $CF_3CF_2CONH_2$, mp 95° (lit.[13] 94–95°). *Anal.* Calcd for $C_3H_2F_5NO$: C, 22.1; H, 1.2; F, 58.3; N, 8.6. Found: C, 22.0; H, 1.3; F, 57.6; N, 8.6. A similar result was obtained by using pyridine (10 g) instead of triethylamine to induce the isomerization of the epoxide.

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Fluoro Ketone–Metal Fluoride Adducts as Fluorinating Agents in the Preparation of Fluorosilanes and Fluorinated Acyl Fluorides

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A convenient method is described for the preparation of fluorosilanes and perfluoroacyl fluorides. The reaction involves the addition of a chloro- or bromosilane, or a perfluoroacyl chloride, to the 1:1 addition product of a perhalo ketone and a metal fluoride. A reaction occurs immediately at room temperature with the formation of a fluorosilane or perfluoroacyl fluoride and the regenerated perhalo ketone. A possible reaction mechanism involving intramolecular fluorine transfer on an intermediate, unstable, fluoroalkoxysilane or perfluoro ester is discussed.

We have previously described the preparation of fluoroalkyl acrylate and methacrylate esters by the reaction of acryloyl or methacryloyl chloride with fluoro ketone–metal fluoride adducts.[2–4] A by-product in this reaction, acryloyl or methacryloyl fluoride, is formed in varying amounts depending partly on the solvent employed. In bis(2-methoxyethyl)ether (diglyme) or N,N-dimethylformamide (DMF) the product generally contained less than 10% of the acid fluoride whereas in acetone or acetonitrile the amount of acid fluoride in the product increased to 35%.[4]

We have now found that, when a perfluoro acid chloride is treated with the adduct of hexafluoroacetone–potassium fluoride, the corresponding perfluoro acid fluoride and regenerated hexafluoroacetone are formed immediately with no evidence for perfluoro ester formation.

The fluoro ketone–metal fluoride adducts are also useful fluorinating agents in the preparation of fluorosilanes. In attempts to prepare fluoroalkoxy silanes by the reaction of chlorosilanes with fluoro ketone–metal fluoride adducts, the only products obtained were fluorosilanes, metal chloride, and regenerated fluoro ketone. The reaction can be described by the following equation. As in the case of perfluoro acid

$$\equiv SiCl + (R_F)_2CFO^- K^+ \longrightarrow \equiv SiF + (R_F)_2C{=}O + KCl$$

chlorides, fluorination takes place immediately in high yields at room temperature and the fluorinated ketone can easily be recovered. This represents one of the more convenient methods for the conversion of a chlorosilane to a fluorosilane. Other methods previously reported for replacing chlorine with fluorine on a silicon atom include the use of SbF_3,[5] anhydrous zinc

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(1) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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fluoride,[6] anhydrous HF,[7] aqueous HF,[8] and sodium fluoroborate.[9]

The reaction was carried out successfully on a number of chlorosilanes and on a bromosilane (Table I) using hexafluoroacetone and potassium fluoride. When the boiling point differential between the product fluorosilane and the regenerated hexafluoroacetone is small, ketones other than hexafluoroacetone can be utilized. For example, we found that triethylchlorosilane was converted to triethylfluorosilane when either the adduct of hexafluoroacetone–potassium fluoride or the adduct of *sym*-dichlorotetrafluoroacetone–potassium fluoride was used. We were unable to obtain good yields of monosubstituted products when the silane contained more than one chlorine atom. The major product was always the completely fluoro-substituted silane.

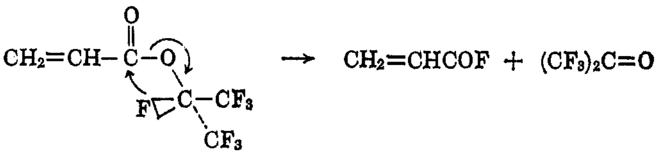
TABLE I

PREPARATION OF SOME FLUOROSILANES USING HEXAFLUOROACETONE–POTASSIUM FLUORIDE ADDUCT

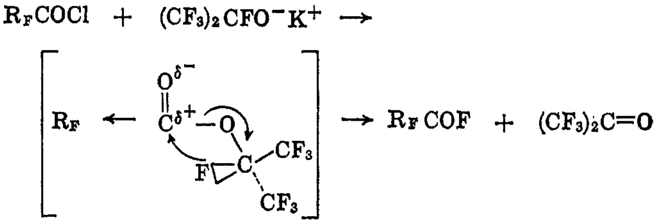
Starting halosilane	Product[a]	Yield,[b] %
Et_3SiCl	Et_3SiF	90
Et_3SiBr	Et_3SiF	69
Et_2SiCl_2	Et_2SiF_2[c]	72
Phenyl-$SiCl_3$	Phenyl-SiF_3[d]	43

[a] Identity of products were confirmed by comparison with authentic samples. [b] No attempt was made to optimize product yields. Yields are based on purified product obtained by distillation from reaction mixture. [c] A 2-mole equiv of the hexafluoroacetone–KF adduct per mole of diethyldichlorosilane was used. [d] A 3-mole equiv of the hexafluoroacetone–KF adduct per mole of phenyltrichlorosilane was used.

In the reaction of the hexafluoroacetone–potassium fluoride adduct with acryloyl or methacryloyl chloride we have suggested that the acid fluoride is formed by a breakdown of the ester *via* an intramolecular fluorine shift.[4] Evidence was presented which indicates that



the formation of acid fluoride does not take place by the reaction of free fluoride ion with either the acid chloride or the fluoroalkyl ester.[4] We found that, although the heptafluoroisopropyl acrylate and methacrylate esters are stable compounds, the saturated ester, heptafluoroisopropyl propionate, was comparatively unstable and undergoes acid-catalyzed decomposition to propionyl fluoride and hexafluoroacetone. An examination of a Fisher–Hirschfelder model of heptafluoroisopropyl propionate revealed considerable hindrance to the free rotation of the isopropyl group due to the steric requirements of the CH_3CH_2 group. The unsaturated ethylenic group of the acrylate or methacrylate esters does not interfere with the free rotation of this group to an appreciable extent. Further, in the less hindered conformations of the heptafluoroisopropyl propionate ester, the fluorine atom on the secondary carbon of the isopropyl group is in position for a backside attack on the carbonyl carbon.[4] Free rotation of the perfluoroisopropyl group in a completely fluorinated ester is also greatly restricted by the fluorine atoms of the perfluoroacyl segment. In addition, the increased electrophilicity of the carbonyl carbon in a perfluoro ester should increase the ease with which an intramolecular fluorine shift occurs. Steric factors could also



account for the presumed instability of the heptafluoroisopropoxysilanes and their conversion to fluorosilanes. An examination of a Fisher–Hirschfelder model of heptafluoroisopropoxytrimethylsilane showed that there is virtually no free rotation of the perfluoroisopropyl group about the oxygen atom. The only conformation relatively free of fluorine–hydrogen nonbonded interaction places the fluorine atom on the secondary carbon of the isopropyl group in an excellent position for an intramolecular transfer to the silicon atom. We therefore favor a mechanism involving intramolecular fluorine transfer rather than ones which would require attack by free fluoride ion. Fluorina-

$$\equiv SiCl + F^- \longrightarrow \equiv SiF + Cl^-$$

$$\equiv SiOCF(CF_3)_2 + F^- \longrightarrow \equiv SiF + OCF(CF_3)_2^-$$

tion of chlorosilanes or perfluoro acid chlorides with potassium fluoride in diglyme was found to be a sluggish reaction even at elevated temperatures. Reaction of fluoride ion with the preformed perfluoro ester or fluoroalkoxysilane could occur; however, the production of the required fluoride ion through equilibration of the fluoro ketone–potassium fluoride adduct does not seem likely at room temperature. At room tem-

$$(CF_3)_2CFO^- \rightleftarrows (CF_3)_2C{=}O + F^-$$

perature the equilibrium is apparently shifted completely to the left. We have been unable to demonstrate the presence of free hexafluoroacetone in a solution of the hexafluoroacetone–potassium fluoride adduct by removal under vacuum at 24°.[4]

Experimental Section

Fluorosilanes were obtained from Pierce Chemical Co.[10] Chlorosilanes were obtained from Pierce Chemical Co. and Union Carbide Corp. Hexafluoroacetone and *sym*-dichlorotetrafluoroacetone were obtained from General Chemical Division, Allied Chemical Corp., and were used without further purification. Fluorinated acid chlorides were obtained from Peninsular Chemical Research, Inc.

Gas chromatographic studies were carried out with an Aerograph Autoprep Model A-700 having a 20-ft column ($^3/_8$-in. o.d.) packed with 30% silicone gum rubber on Chromosorb P, 60–80 mesh, which had been acid washed and pretreated with dimethyldichlorosilane.

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(10) Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

Reaction mixtures were analyzed by gas chromatography, and in some cases yields were calculated from peak areas of gas chromatograms.

Preparation of Triethylfluorosilane Using Hexafluoroacetone.—A 250-ml flask equipped with a stirring bar, Dry Ice condenser, gas inlet, and rubber septum was charged with 5.8 g (0.1 mole) of anhydrous KF. The flask was placed under vacuum and heated with a burner to remove moisture. After the flask came to room temperature, nitrogen was bled into the system and then 45 ml of anhydrous diglyme was introduced. The condenser was filled with Dry Ice, and 16.6 g (0.1 mole) of hexafluoroacetone was introduced slowly through the gas inlet. Then the contents of the flask was stirred until no more dispersed KF was evident in the flask and there was no more condensation of free hexafluoroacetone. At this point, the Dry Ice condenser was replaced with a water condenser which was then connected to a Dry Ice trap. Triethylchlorosilane (15 g, 0.1 mole) was added slowly with a syringe to the stirred solution. Upon addition of the chlorosilane, KCl precipitated immediately and hexafluoroacetone was evolved. The mixture was stirred for an additional 30 min at 35–40°, and then the product, plus some diglyme, was removed from the slurry by vacuum distillation. Redistillation yielded 12 g (90%) of triethylfluorosilane, bp 108–109° (760 mm) (lit.[9] bp 109°). The infrared spectrum and gas chromatographic retention time were found to be identical with those of an authentic sample of triethylfluorosilane. Thirteen and one-half grams of hexafluoroacetone was recovered in the Dry Ice trap.

The reaction was repeated with anhydrous acetone used as the solvent in place of diglyme. The resulting solution was not distilled but was filtered free of KCl and analyzed by gas chromatography. The chromatogram of the solution revealed (excluding the solvent) the presence of 94.2% triethylfluorosilane and 5.8% of an unidentified lower boiling component. There was no indication of unreacted triethylchlorosilane.

Preparation of Triethylfluorosilane Using *sym*-Dichlorotetrafluoroacetone.—A 250-ml, three-necked flask equipped with a water condenser, magnetic stirring bar, and dropping funnel was charged with 11.6 g (0.2 mole) of KF and dried under vacuum. Dry diglyme (180 ml) was introduced then 40 g (0.2 mole) of *sym*-dichlorotetrafluoroacetone was added slowly. After adduct formation was complete, as evidenced by the disappearance of dispersed KF, 30 g (0.2 mole) of triethylchlorosilane was added slowly to the stirred solution. As in the preceding example, KCl precipitated immediately upon addition of the chlorosilane. Product and solvent were removed from the salt slurry by vacuum distillation and collected in a flask cooled by Dry Ice. Redistillation yielded 27 g *sym*-dichlorotetrafluoroacetone, bp 45°, and 24.5 g of a fraction with bp 109–120°. This fraction was analyzed by gas chromatography and found to contain 91.1% triethylfluorosilane and 8.9% diglyme.

Perfluorooctanoyl Fluoride.—A 50-ml three-necked flask equipped with magnetic stirring bar, Dry Ice condenser, gas inlet, and an inlet capped with a rubber septum was charged with 1.65 g (0.028 mole) of anhydrous KF and dried under vacuum. After the flask had been cooled under a nitrogen blanket, 20 ml of anhydrous diglyme was introduced, followed by 4.65 g (0.028 mole) of hexafluoroacetone. The mixture was stirred until a clear solution of the soluble adduct was obtained, as evidenced by the absence of free hexafluoroacetone on the Dry Ice condenser. The Dry Ice condenser was replaced with a water condenser which was in turn connected to a Dry Ice trap. Perfluorooctanoyl chloride (12.1 g, 0.028 mole) was added slowly to the stirred diglyme solution by means of a syringe. Immediately upon addition of the acid chloride, a white precipitate formed and the contents of the flask became cool as a result of the evolution of hexafluoroacetone. After all the acid chloride had been added, the mixture was stirred for an additional 30 min and heated to 40°. The Dry Ice trap contained 2.5 g of hexafluoroacetone. A Claisen head was connected to the flask. The receiver was cooled by Dry Ice. The system was placed under vacuum, and a lower fluorocarbon layer was collected, followed by a lighter fraction consisting mostly of diglyme. The lower layer consisted of 10.5 g (90% crude yield) of a product which contained 97% perfluorooctanoyl fluoride and 3% unreacted perfluorooctanoyl chloride as determined by gas chromatographic analysis. The perfluorooctanoyl fluoride formed by this reaction was identical with a sample prepared independently by refluxing a mixture of perfluorooctanoyl chloride and potassium fluoride in tetramethylene sulfone.

Perfluoroglutaryl Fluoride.—The adduct of hexafluoroacetone–KF was prepared as in the preceding example; 78 g (0.47 mole) of hexafluoroacetone, 27.3 g (0.47 mole) of anhydrous KF, and 300 ml of anhydrous diglyme were used. Perfluoroglutaryl chloride (59.2 g, 0.2 mole) was added from a dropping funnel to the stirred solution over a 30-min period. During the addition, KCl precipitated and hexafluoroacetone was evolved. The gaseous hexafluoroacetone was collected in an attached Dry Ice trap. After the addition the mixture was stirred for an additional 30-min at room temperature. The product and some diglyme were removed from the slurry by vacuum distillation and then redistilled on a short Vigreux column. Twenty-nine grams (58% yield) of perfluoroglutaryl fluoride, bp 47–48° (767 mm) (lit.[11] bp 47–49°), was obtained. Sixty-five grams (0.39 mole) of hexafluoroacetone was recovered in the Dry Ice trap.

Reaction of Potassium Fluoride with Triethylchlorosilane and Perfluoroglutaryl Chloride. Equimolar quantities of anhydrous potassium fluoride and triethylchlorosilane were heated at 90° in diglyme (3 ml of solvent per gram of chlorosilane) for 3 hr. After this time, gas chromatographic analysis of the solution showed the presence of triethylfluorosilane and triethylchlorosilane in the ratio 1:4.5.

A 2-mole quantity of anhydrous potassium fluoride and perfluoroglutaryl chloride was also heated at 90° in diglyme (3 ml of solvent per gram of acid chloride) for 3 hr. After this time, the product ratio of $(CF_2)_3(COF)(COCl)$ to $(CF_2)_3(COF)_2$ to $(CF_2)_3(COCl)_2$ was 1:1.7:6.8 by gas chromatographic analysis.

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