effects upon the spontaneous and fluoride ion catalyzed hydrolysis of acetyl fluoride means that the ratios of the activity coefficients of the initial and transition states must be similar, and analogy with the behavior of acetic anhydride suggests that the salt effects upon the initial state are specific, and on the transition state nonspecific.

Electrophilic Catalysis.—The hydrolysis of benzoyl fluoride is catalyzed by acids in aqueous acetone,[26] although it was not known whether the catalysis was specific or general.

Our values of k_ψ vary linearly with $[\overset{+}{H}]$, and there is an appreciable acid-catalyzed hydrolysis even at pH 2. Acetyl fluoride is, therefore, very much more sensitive to acid than is acetic anhydride. The acid hydrolysis of acetic anhydride is relatively insignificant unless the acid concentration is >2 *M*. The value of k_H for the hydrolysis of acetic anhydride in aqueous sulfuric acid at 0° is *ca.* 1.2×10^{-3} l. mole^{-1} sec^{-1}, with some uncertainty because of the electrolyte effect of the acid upon the spontaneous hydrolysis,[27] and is very much less than that of 0.66 for acetyl fluoride, reflecting the strength of the hydrogen–fluorine relative to the hydrogen–oxygen bond. A reasonable mechanism involves protonation of acetyl fluoride followed by a rate-limiting attack of water upon the conjugate acid.

$$CH_3COF + \overset{+}{H} \rightleftharpoons CH_3CO\overset{+}{F}H \qquad \text{(fast)}$$

$$CH_3CO\overset{+}{F}H + H_2O \longrightarrow CH_3CO_2 + HF \qquad \text{(slow)}$$

These hydrolyses at low pH had a good first-order kinetic form, with no autocatalysis by the hydrogen fluoride produced, suggesting that general acids are not effective catalysts for this reaction.

Metallic cations will often coordinate with electronegative atoms, and so act as electrophilic catalysts,[28] but neither copper nor magnesium ions have other than a small salt effect on the hydrolysis of acetyl fluoride. These observations suggest that breaking of the carbon–fluorine bond has made much progress in the transition state, because one might expect a partially formed fluoride ion to interact strongly with a cation. It may be that other inorganic cations will catalyze the hydrolysis of acid fluorides in water, but the use of a pH-Stat restricts our choice of cation.

Acknowledgment.—Support by the National Science Foundation under G.P. 2889 is gratefully acknowledged.

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The Chemistry of Hexafluoropropene Epoxide

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Hexafluoropropene epoxide was treated with a number of organic and inorganic (protic) reagents resulting in the synthesis of a series of α-substituted perfluoropropionic acids and their derivatives. The structures of the products indicated that in all cases the opening of the epoxide ring was initiated by a nucleophilic attack on the secondary carbon atom. The ability of some organic bases to isomerize the epoxide to perfluoropropionyl fluoride was observed and discussed.

Very little information has appeared in the literature concerning the synthesis and the chemical behavior of halo-substituted epoxide rings. However, the epoxides of perfluorinated olefins have been recently described. Tetrafluoroethylene epoxide has been prepared by the oxidation of C_2F_4, induced by electromagnetic radiations;[1,2] hexafluoropropene epoxide, formerly obtained by electrochemical fluorination of epichlorohydrin,[3] more recently has been directly synthesized by chemical[4] or photochemical[2,5] oxidation of hexafluoropropene.

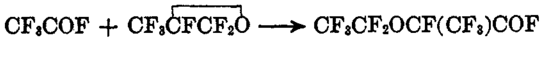
Unlike tetrafluoroethylene epoxide, which was found to isomerize spontaneously even below room temperature to CF_3COF,[1] hexafluoropropene epoxide is quite a stable compound, being thermally converted to perfluoropropionyl fluoride only at high temperature.[4]

As far as we know only a few reactions of hexafluoropropene epoxide have been described and these only in the patent literature. In addition to the above-mentioned thermal isomerization to the acyl fluoride, the epoxide was found to undergo another type of isomerization, yielding hexafluoroacetone under the catalytic action of antimony pentafluoride.[6]

Other known reactions of the epoxide can be summarized as follows: (1) oligomerization,[7] catalyzed by active carbon or by fluoride ion, which gives polyethers of the structure which is illustrated below;

$$CF_3CF_2CF_2O(\underset{CF_3}{CF}CF_2O)_n\underset{CF_3}{CF}COF$$

(2) addition to perfluorinated acid fluorides,[8] to give 2-perfluoroalkoxyperfluoropropionyl fluorides, as *e.g.*



$$CF_3COF + CF_3\overbrace{CFCF_2O} \longrightarrow CF_3CF_2OCF(CF_3)COF$$

(3) copyrolysis with halothiocarbonyl compounds,[9] to form fluorinated thiiranes.

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[1] V. Caglioti, A. Delle Site, M. Lenzi, and A. Mele, *J. Chem. Soc.*, 5430 (1964).

[2] E. I. du Pont de Nemours and Co., British Patent 931,587 (1963).

[3] E. A. Kauk and J. H. Simons, British Patent 672,720 (1952).

[4] E. I. du Pont de Nemours and Co., British Patent 904,877 (1960).

[5] D. Sianesi, A. Pasetti, and C. Corti, *Makromol. Chem.*, **86**, 308 (1965).

[6] D. E. Morin, U. S. Patent 3,213,134 (1965).

[7] E. P. Moore, A. Milian, and H. S. Eleuterio, Belgium Patent 616,756 (1962).

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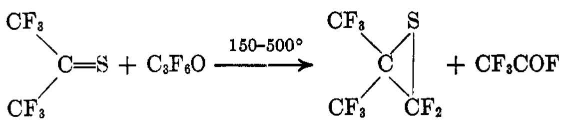
TABLE I

PRODUCTS FROM THE REACTIONS OF HEXAFLUOROPROPENE EPOXIDE WITH AN EXCESS OF EACH OF THE LISTED REAGENTS

Reagent	Reaction product[a]	Yield,[b] %	Bp, °C (mm)	Mp, °C (solvent)	Formula	Calcd, %					Found, %				
						C	H	F	N	Other	C	H	F	N	Other
H_2O	$CF_3C(OH)_2COOH$	68	Sublimes	118.5–119	$C_3H_3F_3O_4$	22.5	1.9	35.6	...	...	22.5	1.9	35.3	...	...
CH_3OH	$CF_3CF(OCH_3)COOCH_3$	96	40–41 (21)		$C_5H_6F_4O_3$	31.6	3.2	40.0	...	...	31.7	3.2	40.0	...	...
C_2H_5OH	$CF_3CF(OC_2H_5)COOC_2H_5$	66.6	50.5–51 (14)		$C_7H_{10}F_4O_3$	38.5	4.6	34.8	...	...	38.8	4.8	35.3	...	...
i-C_3H_7OH	$CF_3CF(OC_3H_7\text{-}i)COOC_3H_7\text{-}i$	52	73–74 (26)		$C_9H_{14}F_4O_3$	43.9	5.7	30.9	...	...	44.0	5.9	31.1	...	...
CH_2ClCH_2OH	$CF_3CF(OCH_2CH_2Cl)COOCH_2CH_2Cl$	41	119–120 (15)		$C_7H_8Cl_2F_4O_3$	29.3	2.8	26.5	...	Cl, 24.7	29.6	2.9	25.6	...	Cl, 24.8
$CF_2HCF_2CH_2OH$	$CF_3CF(OCH_2CF_2CF_2H)COOCH_2CF_2\text{-}CF_2H$	14	83 (15)		$C_9H_6F_{12}O_3$	27.7	1.5	58.4	...	...	27.5	1.6	58.3	...	...
$CH_2{=}CHCH_2OH$	$CF_3CF(OCH_2CH{=}CH_2)COOCH_2\text{-}CH{=}CH_2$	41	74 (15)		$C_9H_{10}F_4O_3$	44.6	4.2	31.4	...	...	44.6	4.2	31.8	...	...
C_6H_5OH	$CF_3CF(OC_6H_5)COOC_6H_5$	13	80–82 (0.1)	39.5–40	$C_{15}H_{10}F_4O_3$	57.3	3.2	24.2	...	...	57.3	3.3	23.9	...	...
C_2H_5SH	$CF_3CF(SC_2H_5)COSC_2H_5$	40	92–93 (15)		$C_7H_{10}F_4OS_2$	33.6	4.0	30.4	...	S, 25.6	33.5	4.1	30.0	...	S, 25.7
HCl, C_2H_5OH	$CF_3CFClCOOC_2H_5$	18	104–105 (755)		$C_5H_5ClF_4O_2$	28.8	2.4	36.4	...	Cl, 17.0	29.1	2.8	35.2	...	Cl, 17.5
HBr, C_2H_5OH	$CF_3CFBrCOOC_2H_5$	16	122–123 (755)		$C_5H_5BrF_4O_2$	23.7	2.0	30.0	...	Br, 31.6	24.0	1.9	29.4	...	Br, 32.0
NH_3	$CF_3C(NH_2)_2CONH_2$	41		110.5–111.5 (acetone)	$C_3H_6F_3N_3O$	23.0	3.8	36.3	26.7	...	23.2	4.0	35.5	26.5	...
$C_2H_5NH_2$	$CF_3C({=}NC_2H_5)CONHC_2H_5$	50	63–64 (0.2)	59–60 (petroleum ether)	$C_7H_{11}F_3N_2O$	42.8	5.6	29.0	14.3	...	42.9	5.8	29.6	14.2	...
$C_6H_5NH_2$	$CF_3C(NHC_6H_5)_2CONHC_6H_5$	70		179–180 (4:1 acetone/H_2O)	$C_{21}H_{18}F_3N_3O$	65.4	4.7	14.8	10.9	...	65.7	4.8	14.3	10.8	...
o-$ClC_6H_4NH_2$	$CF_3C(NHC_6H_4Cl\text{-}o)_2CONHC_6H_4Cl\text{-}o$	25		95–96 (ethanol)	$C_{21}H_{15}Cl_3F_3N_3O$	51.6	3.1	11.7	8.6	Cl, 21.8	51.8	3.2	11.8	8.6	Cl, 21.4
	$CF_3C({=}NC_6H_4Cl\text{-}o)CONHC_6H_4Cl\text{-}o$	5		89–90 (ethanol)	$C_{15}H_9Cl_2F_3N_2O$	49.9	2.5	15.8	7.8	Cl, 19.6	49.5	3.0	15.0	7.6	Cl, 19.5
m-$ClC_6H_4NH_2$	$CF_3C(NHC_6H_4Cl\text{-}m)_2CONHC_6H_4Cl\text{-}m$	64		107–108 (petroleum ether)	$C_{21}H_{15}Cl_3F_3N_3O$	51.6	3.1	11.7	8.6	Cl, 21.8	51.5	3.0	11.4	8.9	Cl, 21.7
p-$ClC_6H_4NH_2$	$CF_3C(NHC_6H_4Cl\text{-}p)_2CONHC_6H_4Cl\text{-}p$	70		155.5–156.5 (CCl_4)	$C_{21}H_{15}Cl_3F_3N_3O$	51.6	3.1	11.7	8.6	Cl, 21.8	50.7	3.1	11.3	8.3	Cl, 21.7
o-$CH_3C_6H_4NH_2$	$CF_3C({=}NC_6H_4CH_3\text{-}o)CONHC_6H_4\text{-}CH_3\text{-}o$	52		135–136 (benzene)	$C_{17}H_{15}F_3N_2O$	63.7	4.7	17.8	8.7	...	63.8	4.7	17.6	8.7	...
p-$CH_3C_6H_4NH_2$	$CF_3C(NHC_6H_4CH_3\text{-}p)_2CONHC_6H_4\text{-}CH_3\text{-}p$	69		182.5–183 (CCl_4)	$C_{24}H_{24}F_3N_3O$	67.4	5.7	13.3	9.8	...	67.1	5.7	13.1	9.8	...

[a] The spectroscopic (infrared and nmr) and chemical properties of all the new compounds supported the proposed structures and will be reported in detail in subsequent publications. [b] Yields are not maximal. Significant improvements may well be possible.



In conclusion, very little indeed was known of the chemical behavior of hexafluoropropene epoxide and the present study was initiated to examine the effect on the epoxide of a series of reagents containing active hydrogen.

The epoxide was found to react with a number of organic and inorganic reagents of this class; with some of them (lower alcohols, ammonia, and amines) the reaction was very fast even below room temperature. With some other reagents, such as phenol and higher alcohols, the reaction required longer time and occurred only at high temperature under pressure.

Table I shows the compounds which have been obtained by the reaction of the epoxide with an excess of each of the indicated reagents. In all instances these derivatives of α-substituted perfluoropropionic acids have been isolated as the main product of the reactions.

In some cases, other side products were formed, but no special attempts were made to isolate them or to improve their yields.

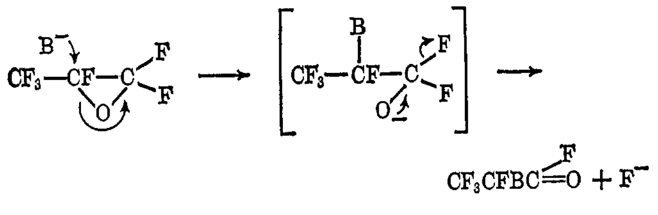
It will be observed that only in the case of the reaction of the epoxide with water the product could, *a priori*, result from the breaking of either of the two carbon–oxygen bonds, trifluoropyruvic acid hydrate being obviously the hydrolysis product of the unstable 1,2-glycol $CF_3CFOHCF_2OH$ intermediate.

In all of the other cases, the structure of the products clearly point to a common reaction mechanism in which the opening of the epoxide ring occurred through nucleophilic displacement at the central carbon atom.

There is probably involved a direct attack of the nucleophile on the secondary carbon atom; this S_N2 type of reaction at a fluoro-substituted saturated carbon is likely to be favored by the powerful electron-withdrawing CF_3 group and by the relieving of strain at the opening of the ring.

On the other hand, it should be considered that the known lack of basic properties of perfluorinated ethers[10] makes a prior protonation step of the oxygen atom most unlikely even in a strong acidic medium.

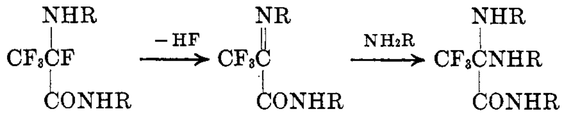
As illustrated in the following equation, the oxygen displacement by the basic reagent will give a 1,1-difluoroalkoxide ion as an unstable intermediate; this, losing a fluoride ion, will transform to the acyl fluoride.



Obviously, the final product (see Table I) will result from the further reaction of the acyl fluoride with the excess of the reagent BH or with some other reactive molecule present in the reaction medium.

The products isolated from the reaction of the epoxide with ammonia and primary amines can be explained on the basis of this simple reaction scheme by taking into account the great tendency of the intermediate amine to lose hydrogen fluoride from the tertiary fluorine atom and a proton on the adjacent nitrogen.

The thus resulting α-imino derivative might then be eventually converted by addition of another molecule of the amine to the corresponding α,α-disubstituted derivative.



$$CF_3\overset{\displaystyle NHR}{\underset{\displaystyle CONHR}{C}}F \xrightarrow{-HF} CF_3\overset{\displaystyle NR}{\underset{\displaystyle CONHR}{C}} \xrightarrow{NH_2R} CF_3\overset{\displaystyle NHR}{\underset{\displaystyle CONHR}{C}}NHR$$

As it resulted especially from the reactions of the epoxide with substituted anilines, the prevailing formation of the imino or diamino compound mostly depended from the steric requirement of the attacking group, the *gem*-diamino derivatives being formed by the less hindered amines.

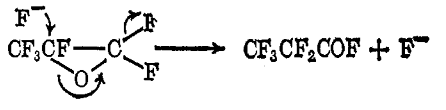
It is worthy of note that when the internal elimination of HF was not possible, as in the case of the ethers $CF_3CF(OR)COOR$, these compounds were found to be very stable, especially against alkaline hydrolysis.

A rather different course of reaction was experienced, however, when hexafluoropropene epoxide was treated with some secondary amines. These reactions yielded the corresponding perfluoropropionamides, thus indicating that isomerization of epoxide to acyl fluoride first occurred in the presence of the secondary amine.

$$CF_3CFCF_2O + NHRR' \longrightarrow CF_3CF_2CONRR'$$

(R = ethyl; R' = ethyl, phenyl)

One could suspect that in this case the true isomerizing agent was the fluoride ion, coming from the dissociation of the dialkylammonium fluoride (the latter arising as a side reaction product in the normal reaction).



In this connection the high order of nucleophilic reactivity toward fluoro olefins by fluoride ions (from the dissociation of tetraalkylammonium fluorides) is very well known.[11]

However, tertiary amines too were found to induce a fast isomerization of the epoxide to pentafluoropropionyl fluoride. This proved that organic bases display their own activity toward isomerization and suggested that isomerization of the epoxide to the acyl fluoride should have the same mechanism with both secondary and tertiary amines.

It is believed that the primary act in this base-catalyzed isomerization of the epoxide is the attack on the electrophilic carbon by the unshared electrons pair of the nitrogen atom of the amine.

As outlined below, this attack can be the driving force for the carbon–oxygen bond rupture, followed by an anionotropic rearrangement to the acid fluoride.

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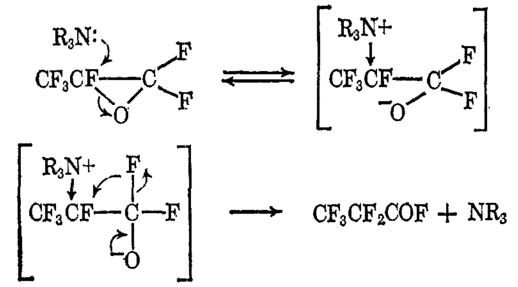
[10] J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press Inc., New York, N. Y., 1950, p 489.

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



The aforementioned results with ammonia or primary amines would indicate that, in this case, the faster displacement reaction which involves HF elimination prevails against the simple base-catalyzed isomerization.

Experimental Section

Hexafluoropropene Epoxide.—The preparation of the epoxide was carried out following a disclosed method[4] which was modified and improved in some detail.

A 3-l. four-neck flask fitted with thermometer, delivery tube, stirrer, addition funnel, and a solid carbon dioxide–ethanol-cooled condenser was charged with 85% potassium hydroxide (160 g), 150 ml of water, and 750 ml of methanol. The solution was then cooled to −50°, while 525 ml of 30% hydrogen peroxide was gradually added, followed by 135 g (0.9 mole) of hexafluoropropene. The oxidation was continued for a period of 1.5 hr at −50 to −40°. The temperature of the mixture was then slowly raised to room temperature; the escaping gases, washed with water and dried over granular calcium chloride, were condensed at −78° in a cylinder. On an average, 40 g of epoxide was thus obtained, which contained as main impurities CO_2 (3–4%) and C_3F_6 (1–2%) (yield *ca.* 25%). The epoxide, bp −28°, approaching 100% purity was obtained by careful distillation at low temperature, some difficulty being encountered in removing the last traces of hexafluoropropene (bp −29.4°).

The purity of the epoxide was checked by gas chromatography, with a 6-m Kel-F oil on chromosorb column at 40°.

2,2-Dihydroxytrifluoropropionic Acid.—Hexafluoropropene epoxide was allowed to react with water both in the absence and in the presence of some added solvent. Either procedure was satisfactory, but the use of a common solvent was preferred since its use accelerated the reaction.

A 200-cm^3 glass ampoule was charged with water (33 ml), dioxan (66 ml), and then, by vacuum distillation at −78°, with epoxide (32 g); the sealed tube was maintained for 8 hr at room temperature while gently shaking. At the end, the content was poured into 100 ml of water, exactly neutralized with 2 *N* potassium hydroxide, and then evaporated to dryness under vacuum. To the salts residue phosphoric acid 98% (150 ml) was added and the mixture was heated slightly >100° under 15 mm of pressure; a total of 21 g of $CF_3C(OH)_2COOH$ was obtained as a white sublimate: acidimetric equiv wt, 160.8 (calcd, 160.05).

The acid was found to be easily oxidized by permanganate solution and to be unstable in mildly alkaline solution, being quantitatively decomposed to CHF_3 and oxalate ion. Some attempts were made to dehydrate the compound in order to obtain trifluoropyruvic acid; the hydrate, however, was recovered unchanged after sublimation over phosphoric pentoxide and after prolonged boiling in a solution of thionyl chloride.

Methyl 2-Methoxytetrafluoropropionate.—Working in a closed system at atmospheric pressure, gaseous hexafluoropropene epoxide was bubbled through 300 ml of methanol maintained at room temperature by using intermittent cooling. In the period of 4 hr a total of 56.6 g of epoxide was absorbed with a mild exothermic reaction.

Water (1000 ml) was added to the alcoholic solution; the lower layer was separated, washed twice with water, dried (Na_2SO_4), and fractionated to give 62 g of $CF_3CF(OCH_3)COOCH_3$.

Starting from 32 g of the methyl ester, by saponification with an excess of boiling 2 *N* potassium hydroxide solution followed by acidification, ether extraction and fractionation, **2-methoxytetrafluoropropionic acid**, bp 71.5–72.5° (13 mm), was obtained in a yield of 22 g (74%). *Anal.* Calcd for $C_4H_4F_4O_3$: C, 27.3; H, 2.3; F, 43.2; acidimetric equiv wt, 176.1. Found: C, 27.8; H, 2.1; F, 42.5; acidimetric equiv wt, 176.0.

2-Methoxytetrafluoropropionamide was obtained in good yield by shaking the ester (5 g) for 2 hr at room temperature with 20 ml of concentrated ammonium hydroxide: crystallized twice from benzene, mp 109°. *Anal.* Calcd for $C_4H_5F_4NO_2$: C, 27.4; H, 2.9; F, 43.4; N, 8.0. Found: C, 27.3; H, 2.8; F, 43.1; N, 8.0.

Ethyl 2-Ethoxytetrafluoropropionate.—Hexafluoropropene epoxide (128 g) was treated with ethanol (500 ml) as in the previous experiment to give $CF_3CF(OC_2H_5)COOC_2H_5$ (112 g). From the ethyl ester with the usual methods have been prepared **2-ethoxytetrafluoropropionic acid**, bp 83–84° (13 mm) (*Anal.* Calcd for $C_5H_6F_4O_3$: C, 31.6; H, 3.2; F, 40.0; acidimetric equiv wt., 190.1 Found: C, 32.0; H, 3.3; F, 38.6; acidimetric equiv wt., 185.6.); **2-ethoxytetrafluoropropionamide**, crystallized from CCl_4, mp 82° (*Anal.* Calcd for $C_5H_7F_4NO_2$: C, 31.7; H, 3.7; F, 40.2; N, 7.4. Found: C, 31.5; H, 3.7; F, 39.8; N, 7.4).

Isopropyl 2-Isopropoxytetrafluoropropionate.—In a 25-cm^3 sealed glass tube, 2-propanol (12 g, 0.2 mole) and hexafluoropropene epoxide (8.3 g, 0.05 mole) reacted at room temperature for 10 days. The solution was then poured into 100 ml of water and extracted with 50 ml of chloroform. The organic layer was dried (Na_2SO_4) and vacuum fractionated to give $CF_3CF(O\text{-}i\text{-}C_3H_7)COO\text{-}i\text{-}C_3H_7$ (6.4 g).

2-Chloroethyl 2-(2-Chloroethoxy)tetrafluoropropionate.—C_3F_6O (10 g, 0.06 mole) and 2-chloroethanol (60 g) were treated for 5 days at room temperature in a 100-cm^3 glass tube. The product was then treated with excess of water; the organic layer was separated, washed with water, and dried (Na_2SO_4) (11.5 g of crude product). By vacuum distillation pure $CF_3CF(OCH_2CH_2Cl)COOCH_2CH_2Cl$ (7 g) was obtained.

Allyl 2-Allyloxytetrafluoropropionate.—As in the preceding case, from C_3F_6O (5 g, 0.03 mole) and allyl alcohol (20 ml), $CF_3CF(OCH_2CH{=}CH_2)COOCH_2CH{=}CH_2$ was obtained in a yield of 3 g.

2,2,3,3-Tetrafluoropropyl 2-(2,2,3,3-Tetrafluoropropoxy)tetrafluoropropionate.—$CF_2HCF_2CH_2OH$ (50 g, 0.38 mole) was charged into a 100-ml Hastelloy-lined pressure vessel. After cooling to −78° and evacuating, hexafluoropropene epoxide (30 g, 0.18 mole) was added and the reactants were heated at 80° for 5 days. The product was treated with excess sodium fluoride powder to remove hydrogen fluoride, suction filtered using a small amount of chloroform as a rinse, and fractionated; $CF_3CF(OCH_2CF_2CF_2H)COOCH_2CF_2CF_2H$ was obtained in a yield of 9.6 g.

Phenyl 2-Phenoxytetrafluoropropionate.—As in the previous experiment, phenol (30 g, 0.32 mole) and hexafluoropropene oxide (20 g, 0.12 mole) were treated at 100° for 4 days, to give 5 g of $CF_3CF(OC_6H_5)COOC_6H_5$.

Ethyl 2-Ethylmercaptotetrafluoropropionthiolate.—In a 50-cm^3 sealed glass tube C_3F_6O (11.5 g, 0.07 mole) was treated for 4 days at room temperature with ethyl mercaptan (25 g, 0.4 mole). The reaction mixture was added to an excess of water, the organic layer, dried over Na_2SO_4, was then vacuum fractionated to give a 7-g yield of $CF_3CF(SC_2H_5)COSC_2H_5$.

Ethyl 2-Chlorotetrafluoropropionate.—A 1-l. flask fitted with a carbon dioxide–ethanol cooled condenser was charged at −30° with ethanol (500 ml), anhydrous hydrogen chloride (40 g, 1.1 mole), and hexafluoropropene epoxide (60 g, 0.36 mole). The solution was allowed to boil at its own temperature until (after 9 hr) reflux was ceased at room temperature. The mixture was then poured into 1.5 l. of water, and the organic layer, washed with water and dried (Na_2SO_4), was carefully fractionated to give 13.4 g of $CF_3CFClCOOC_2H_5$.

Ammonolysis of the 2-chlorotetrafluoropropionic ester in ether solution at Dry Ice temperature yielded the crystalline **2-chlorotetrafluoropropionamide** in nearly quantitative yield: mp 92–92.5°, crystallized from CCl_4. *Anal.* Calcd for $C_3H_2ClF_4NO$: C, 20.1; H, 1.1; F, 42.3; Cl, 19.7; N, 7.8. Found: C, 20.4; H, 1.1; F, 42.1; Cl, 19.5; N, 7.8.

Ethyl 2-Bromotetrafluoropropionate.—Hexafluoropropene epoxide gas was bubbled at room temperature through a mixture of 48% HBr (100 ml) and ethanol (200 ml), until, after 7 hr, a total of 22 g (0.13 mole) was absorbed. The mixture was then diluted with water; the organic layer was separated, washed with water to neutral, dried, and fractionated. $CF_3CFBrCOOC_2H_5$ was obtained in a yield of 5.2 g. By adding an excess of dry ammonia to a cold solution of the ester in ethyl ether, **2-bromotetrafluoropropionamide** was obtained: crystallized from CCl_4, mp 86.5–87.5°

(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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