ppm are observed between the protonated and nonprotonated forms of these compounds.[12] Given the relatively great magnitude of these chemical shift differences and the small chemical shift range observed over the 500-fold concentration range measured, it seems reasonable to conclude that intramolecular hydrogen bonding does not significantly influence the measured ^{19}F chemical shifts in the solvents utilized here.

It is clear from these data that this SCS-based additivity method effectively predicts ^{19}F chemical shifts in fluoroaromatic compounds. The extent to which this method would apply to other types of fluoroorganic compounds has yet to be determined, but is clearly an area for future investigation.

Registry No. *o*-Difluorobenzene, 367-11-3; *m*-difluorobenzene, 372-18-9; *p*-difluorobenzene, 540-36-3; *o*-fluoroacetanilide, 399-31-5; *m*-fluoroacetanilide, 351-28-0; *p*-fluoroacetanilide, 351-83-7; *o*-fluoroacetophenone, 445-27-2; *m*-fluoroacetophenone, 455-36-7; *p*-fluoroacetophenone, 403-42-9; *o*-fluoraniline, 348-54-9; *m*-fluoroaniline, 372-19-0; *p*-fluoroaniline, 371-40-4; *o*-fluoroanisole, 321-28-8; *m*-fluoroanisole, 456-49-5; *p*-fluoroanisole, 459-60-9; *o*-fluorobenzaldehyde, 446-52-6; *m*-fluorobenzaldehyde, 456-48-4; *p*-fluorobenzaldehyde, 459-57-4; *o*-fluorobenzamide, 445-28-3; *m*-fluorobenzamide, 455-37-8; *p*-fluorobenzamide, 824-75-9; *o*-fluorobenzoic acid, 445-29-4; *m*-fluorobenzoic acid, 455-38-9; *p*-fluorobenzoic acid, 456-22-4; *o*-fluorobenzoyl chloride, 393-52-2; *m*-fluorobenzoyl chloride, 1711-07-5; *p*-fluorobenzoyl chloride, 403-43-0; *o*-fluorobenzonitrile, 394-47-8; *m*-fluorobenzonitrile, 403-54-3; *p*-fluorobenzonitrile, 1194-02-1; *o*-fluorobenzotrifluoride, 392-85-8; *m*-fluorobenzotrifluoride, 401-80-9; *p*-fluorobenzotrifluoride, 402-44-8; *o*-fluorobromobenzene, 1072-85-1; *m*-fluorobromobenzene, 1073-06-9; *p*-fluorobromobenzene, 460-00-4; *o*-fluorochlorobenzene, 348-51-6; *m*-fluorochlorobenzene, 625-98-9; *p*-fluorochlorobenzene, 352-33-0; *o*-fluoroiodobenzene, 348-52-7; *m*-fluoroiodobenzene, 1121-86-4; *p*-fluoroiodobenzene, 352-34-1; *N*-(*o*-fluorophenyl)methanesulfonamide, 98611-90-6; *N*-(*m*-fluorophenyl)methanesulfonamide, 35980-20-2; *N*-(*p*-fluorophenyl)methanesulfonamide, 35980-24-6; *N*-(*o*-fluorophenyl)-trifluoroacetamide, 61984-68-7; *N*-(*m*-fluorophenyl)trifluoroacetamide, 35980-21-3; *N*-(*p*-fluorophenyl)trifluoroacetamide, 35980-25-7; *N*-(*o*-fluorophenyl)trifluoromethanesulfonamide, 23383-98-4; *N*-(*m*-fluorophenyl)trifluoromethanesulfonamide, 23384-01-2; *N*-(*p*-fluorophenyl)trifluoromethanesulfonamide, 23384-00-1; *o*-fluoronitrobenzene, 1493-27-2; *m*-fluoronitrobenzene, 402-67-5; *p*-fluoronitrobenzene, 350-46-9; *o*-fluorophenol, 367-12-4; *m*-fluorophenol, 372-20-3; *p*-fluorophenol, 371-41-5; *o*-fluorotoluene, 95-52-3; *m*-fluorotoluene, 352-70-5; *p*-fluorotoluene, 352-32-9; *o*-fluorophenyl isocyanate, 16744-98-2; *m*-fluorophenyl isocyanate, 404-71-7; *p*-fluorophenyl isocyanate, 1195-45-5; *N*-(*o*-fluorophenyl)phthalimide, 568-95-6; *N*-(*m*-fluorophenyl)-phthalimide, 19357-20-1; 4-chloro-2-fluoroacetanilide, 59280-70-5; (2,4-difluorophenyl)acetanilide, 399-36-0; (3,4-difluorophenyl)-acetanilide, 458-11-7; 2,5-difluoroaniline, 367-30-6; 2,6-difluoroaniline, 5509-65-9; 2-amino-3-fluorobenzoic acid, 825-22-9; 2,6-difluorobenzonitrile, 1897-52-5; 3-amino-5-fluorobenzotrifluoride, 393-39-5; 3-amino-4-fluorobenzotrifluoride, 535-52-4; 4-amino-3-fluorobenzotrifluoride, 69409-98-9; 5-amino-2-fluorobenzotrifluoride, 2357-47-3; 3-chloro-4-fluorobenzotrifluoride, 78068-85-6; 4-fluoro-3,5-dinitrobenzotrifluoride, 393-76-0; 2,3-dimethylfluorobenzene, 443-82-3; 3,4-dimethylfluorobenzene, 452-64-2; 1-bromo-2,5-difluorobenzene, 399-94-0; 2,4-difluorophenol, 367-27-1; 4,5-difluorophthalic anhydride, 18959-30-3; *N*-(2,6-difluorophenyl)phthalimide, 120371-26-8; 5-fluorosalicyclic acid, 345-16-4; *N*-(2,4-difluorophenyl)methanesulfonamide, 98611-91-7; *N*-(2,4-difluorophenyl)(trifluoromethyl)acetanilide, 98651-71-9; *N*-(2,6-difluorophenyl)(trifluoromethyl)acetanilide, 98634-00-5; *N*-(2,4-difluorophenyl)trifluoromethanesulfonamide, 23384-22-7; *N*-(2,6-difluorophenyl)trifluoromethanesulfonamide, 98611-93-9; 2-cyano-2-fluoroacetanilide, 829-81-2; 2-fluoro-4-(trifluoromethyl)acetanilide, 88288-14-6; (2,5-difluorophenyl)acetanilide, 398-90-3; 3-fluoro-4-methylacetanilide, 458-10-6; 2-fluoro-4-nitroacetanilide, 348-19-6; 3-fluoroanthranilic acid, 825-22-9; 4,5-difluoroanthranilic acid, 83506-93-8; 4-chloro-2-fluoroaniline, 57946-56-2; 2-carboxamido-4,5-difluorobenzoic acid, 83506-92-7; 2-chloro-4-fluorobenzotrifluoride, 94444-58-3; 3-chloro-4,5-difluorobenzotrifluoride, 77227-99-7; 1-bromo-2,6-difluorobenzene, 64248-56-2; 1,4-dibromo-2-fluorobenzene, 1435-52-5; 2,5-difluoronitrobenzene, 364-74-9; 5-fluoro-2-nitrotoluene, 446-33-3; 2-chloro-4-fluorophenol, 1996-41-4; 4,5-difluorophthalic acid, 18959-31-4; tetrafluorophthalic acid, 652-03-9; 3,6-difluorophthalic anhydride, 652-40-4.

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Perfluoro- and Polyfluorosulfonic Acids. 21. Synthesis of Difluoromethyl Esters Using Fluorosulfonyldifluoroacetic Acid as a Difluorocarbene Precursor

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Difluoromethyl alkanoates **5** and fluorinated and nonfluorinated alkanesulfonates **9** were synthesized in moderate yields by the reaction of alkali metal salts of acids with fluorosulfonyldifluoroacetic acid (**3**) in acetonitrile under mild conditions. The presumed intermediate anion $FO_2SCF_2CO_2^-$ generates CF_2: by elimination of SO_2, CO_2, and F^-. The esters are formed by insertion of CF_2: into the O–H of the acid, whereas HCF_3 is formed by the competing capture of F^-. Organic acids can be used indirectly in the reaction in the presence of inorganic salts such as Na_2SO_4 and KCl, with comparable yields of difluoromethyl esters.

Introduction

Difluorocarbene is a useful intermediate for synthesizing organofluorine compounds.[1] Although several methods for generating CF_2: are known,[2] there is a need for more readily available CF_2: precursors. In our study of the synthesis and reactions of perfluoro- and polyfluoroalkanesulfonic acids, we have discovered a new series of

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difluorocarbene precursors. Thus treatment of HCF_2SO_2Z (Z = F, OC_6H_5, $OCH_2CF_2CF_2H$, OC_6F_5, HCF_2O, $NCH_3C_6H_5$)[3,4] with alkoxide (EtO^-, $C_6H_5O^-$) generates CF_2: by abstracting the hydrogen and eliminating Z^- and SO_2, except for $HCF_2SO_2N(CH_3)C_6H_5$, which extrudes $C_6H_5N(CH_3)SO_2^-$. Difluorocarbene can also be prepared by nucleophilic attack of LiCl, KBr, KCNS, or an amine on the methoxy carbon of $CH_3O_2CCF_2SO_2Y$ (Y = F,[5] OC_6H_5, $HCF_2CF_2CH_2O$[3]) in an aprotic solvent.[5] Also, CF_2: can be produced under strongly acidic conditions from HCF_2SO_2W (W = OH, OCF_2H, OC_6H_5).[3-6] Difluoromethyl esters **1** are formed by heating a mixture of HCF_2SO_3H and a perfluoroalkanesulfonic acid in the presence of P_2O_5, $POCl_3$, or $SOCl_2$.[6]

$$HCF_2SO_3H + R_FSO_3H \xrightarrow{100\text{–}120\ ^\circ C} HCF_2SO_3CF_2H + R_FSO_3CF_2H$$
$$\mathbf{1}$$

R_F = CF_3, $I(CF_2)_2O(CF_2)_2$, $Cl(CF_2)_2O(CF_2)_2$, $Cl(CF_2)_4O(CF_2)_2$

Similarly, $R_FCO_2CF_2H$ (**2**) is obtained, although in lower yields, when perfluorocarboxylic acids are used in this reaction.[6]

The starting material for all of these routes to CF_2: is the readily available FO_2SCF_2COF, which is one of the starting materials for producing the commercial ion-exchange resins Nafion-H.[7]

Difluoromethyl esters **1** and **2** are useful intermediates because they have three reactive sites: the hydrogen, the methoxy carbon, and the sulfonyl sulfur (or carbonyl carbon). The reaction of **1** with nucleophiles has been shown to be more complicated[8] than those of $R_FSO_3CF_2R_F$ and $R_FSO_3CH_2R_F$, the former undergoing only S–O cleavage[9] and the latter undergong predominantly C–O scission.[10] In our studies of such esters, we sought a more readily available and convenient difluorocarbene precursor than HCF_2SO_3H for preparing them. We have found that $FO_2SCF_2CO_2H$ (**3**) is a suitable carbene source that is quite thermally stable and easily handled and can be readily obtained by hydrolysis of the acid fluoride. Herein we present a novel method for synthesizing difluoromethyl esters **1** and **2** using the acid **3** as a difluorocarbene precursor.

Results and Discussion

A few compounds **1** (R = CF_3), **5** (R = CH_3, n-C_6H_{13}, C_6H_5), and **2** (R_F = CF_3, n-C_3F_7) have been prepared by the insertion of CF_2: generated by photolysis of CF_2N_2, into the O–H of an acid. Owing to the unavailability of CF_2N_2, this method is seriously limited.[11] We have found that treatment of potassium or sodium alkanoates **4** with **3** in acetonitrile at ambient temperature for 1–2 h gives difluoromethyl alkanoates **5** in 40–70% yields.

Table I. Effect of Temperature on the Reaction of 3 with 4e in CH_3CN

temp, °C	time, h	conversn,[a] %	products (%) 5	6
−80	5	0	0	0
−20	5	45	60	35
0	3	100	56	40
20	1	100	54	40
100	momentary	100	21	70

[a] Determined by ^{19}F NMR.

$$FO_2SCF_2CO_2H + RCO_2M \xrightarrow{CH_3CN} RCO_2CF_2H + HCF_3 + SO_2 + CO_2 + MF$$
$$\mathbf{3} \qquad \mathbf{4} \qquad \mathbf{5} \qquad \mathbf{6}$$

The reaction does not proceed at −80 °C, and above +20 °C the yield of **5** decreases with increasing temperature, probably because of slight thermal decomposition of **3** (Table I). The results with a variety of acid salts are shown in Table II.

Fluoroform (**6**) is the only organic byproduct. Aprotic polar solvents such as dimethyl sulfoxide, diglyme, glyme, and tetrahydrofuran could not be used because DMSO reacts with **3** and the last three cause side reactions. Dimethylformamide is known to react with CF_2:,[12] but acetonitrile is inert to **3**. Acetonitrile must be thoroughly dry: the yield of **5e** decreased from 54% to 12%, and 4–10% of HCF_2SO_2F was formed, when the acetonitrile contained 3% v/v of water.

Attempts to prepare difluoromethyl polyfluoroalkanoates by reaction of **3** with salts of R_FCO_2M [**7**, M = K, Na; R_F = $H(CF_2)_6$ (**a**), CF_3 (**b**), $C_3F_7OCF(CF_3)$] under similar conditions gave only HCF_3 and unchanged salt.

Reaction of **3** with RSO_3M (**8**) gives difluoromethyl sulfonates **9**. The yield of **9** is also sensitive to the presence of water, and the reaction requires slightly higher temperatures than the reaction with RCO_2M (Table III). The results are shown in Table IV.

$$RSO_3M + 3 \rightarrow R_FSO_3CF_2H + 6$$
$$\mathbf{8} \qquad \mathbf{9}$$

Sodium diethyldithiocarbamate reacts with **3** in a similar fashion to give the corresponding difluoromethyl ester in 74% yield.

$$Et_2NC(S)SNa + 3 \rightarrow Et_2NC(S)SCF_2H + HCF_3$$
$$\mathbf{10} \qquad \mathbf{11}$$

Treatment of sodium benzenesulfinate with **3** in CH_3CN affords difluoromethyl phenyl sulfone, which was previously obtained by a two-step process from difluorochloromethane and benzenethiol.[13]

$$C_6H_5SO_2Na + 3 \rightarrow [C_6H_5S(O)OCF_2H] \rightarrow C_6H_5S(O_2)CF_2H$$
$$\mathbf{12} \qquad \mathbf{13}$$

The presumed intermediate, difluoromethyl phenylsulfinate, is known to rearrange to the sulfone **13**.[14]

Reaction of potassium dialkoxyphosphate **14** with **3** at 60 °C for 0.5 h gave two products in 78% conversion by

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Table II. Reaction of 3 with RCO_2M^a (4) in CH_3CN^b

salt	R	4:3	temp, °C	time, h	products (%)[c] 5	6
4a	CH_3	2.5	20	1	52	40
4b	n-C_6H_{13}	2.2	20	1.5	52	33
4c	n-$C_8H_{17}CH{=}CH(CH_2)_7$	1.8	50	2	42	49
4d	$C_6H_5CH_2$	2.0	20	1	64	30
4e	C_6H_5	2.5	20	1	54	20
4f	p-$CH_3OC_6H_4$	2.5	20	1	70	20
4g	p-$CH_3C_6H_4$	2.6	40	1	49	40
4h	2-furyl	2.5	50	1	42	47
4i	p-FC_6H_4	2.0	20	1.5	40	48
4j	p-IC_6H_4	1.7	20	2	43	51
4k	p-NCC_6H_4	2.3	20	2.5	50	42
4l	o-$CH_3CO_6H_4$	2.4	20	1.5	44	42
4m	o-FC_6H_4	2.0	20	1.5	40	49

[a] M = K or Na. [b] All reactions were run to 100% conversion. [c] Isolated yields.

Table III. Effect of Temperature on the Reaction of 3 with 8c in CH_3CN

temp, °C	time, h	conversn,[a] %	products (%) 9	6
−20	3	0	0	0
0	3	10	64	30
50	1	100	59	30
90	momentary	100	28	63

[a] Determined by ^{19}F NMR.

^{19}F NMR spectroscopy, showing two doublets (+3.2 and +0.2 ppm) in a ratio of 5:1. From ^1H, ^{19}F, MS, and IR data, the two products were identified as the phosphinic ester **15** and the phosphoryl fluoride **16**.

$$(i\text{-}C_8H_{17}O)_2P(O)OK + \underset{14}{3} \rightarrow (i\text{-}C_8H_{17}O)_2P(O)CF_2H + \underset{15}{(i\text{-}C_8H_{17}O)_2P(O)F}$$
$$\underset{16}{}$$

When the reaction was carried out under the same conditions for 3 h, the signal at 3.2 ppm disappeared and that at 0.2 ppm increased, indicating that **15** is thermally unstable and decomposes to **16**.

In the above reactions, potassium and sodium salts were prepared from the acids and aqueous alkali, followed by filtration and thorough drying. This inconvenience prompted us to try to use the acids directly. We found that both carboxylic and sulfonic acids react with **3** in the presence of sodium sulfate or potassium chloride to give the difluoromethyl esters in yields comparable to those obtained with the organic salts.

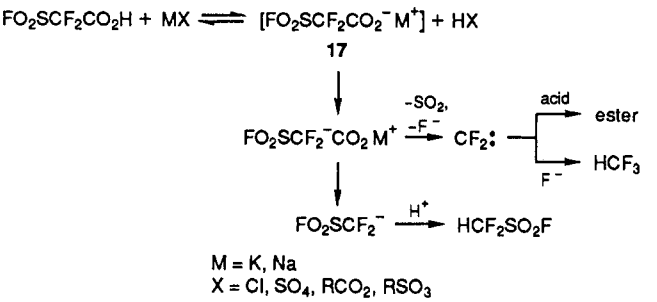
$$C_6H_5CO_2H + Na_2SO_4 + 3 \rightarrow \mathbf{5e} + \mathbf{6}$$

$$CF_3SO_3H + Na_2SO_4 + 3 \rightarrow \mathbf{9d} + \mathbf{6}$$

$$p\text{-}IC_6H_4CO_2H + KCl + 3 \rightarrow \mathbf{5j} + \mathbf{6} + HCF_2Cl$$

The products of these reactions, difluoromethyl ester, fluoroform, and sometimes HCF_2SO_2F, seems to indicate

Scheme I



that the first step of the reaction involves the conversion of **3** to sodium or potassium fluorosulfonyldifluoroacetate (**17**) with either organic or inorganic salts. Compound **17** is quite unstable and decomposes readily to generate CF_2: with simultaneous elimination of SO_2 and F^- (Scheme I). This behavior is similar to that of $FO_2SCF_2CO_2Li$, obtained from the reaction system of $FO_2SCF_2CO_2CH_3$/LiCl in HMPA–THF at 0 °C.[5] The resulting difluorocarbene either inserts into the acid to give the difluoromethyl ester or captures F^- to give CF_3^- and then CF_3H. The formation of HCF_2SO_2F in the presence of water-containing solvent can be rationalized as due to the presence of the relatively stable anion $FSO_2CF_2^-$. A similar result is observed with $FO_2SCF_2CO_2Me$/LiCl in an aqueous organic solvent.[5]

Once small amounts of inorganic or organic acid are formed, the equilibrium shifts to right with formation of **17**. The presence of CF_2: intermediate was confirmed by a trapping experiment with 2,3-dimethyl-2-butene. Treatment of **3** with the olefin and sodium chloride in CH_3CN at 60 °C for 6 h gave the expected 1,1-difluoro-2,2,3,3-tetramethylcyclopropane.

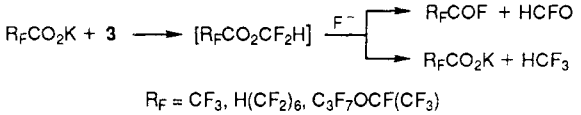
The mechanism of Scheme I raises questions about our failure to obtain $R_FCO_2CF_2H$ from **3** and R_FCO_2M and the formation of HCF_3 in this reaction. We had not expected to obtain $R_FCO_2CF_2H$ by this method, because they should be similar to the fully fluorinated carboxylic ester

Table IV. Reaction of 3 with RSO_3M^a (8) in CH_3CN^b

salt	R	8:3	temp, °C	time, h	products (%)[c] 9	6
8a	p-$CH_3C_6H_4$	2	50	2	59	32
8b	m-$O_2NC_6H_4$	2	60	2	52	37
8c	C_6H_5	3	50	1.5	58	30
8d	CF_3	3.5	100	2	42	47
8e	HCF_2	2.2	50	1.5	44	42
8f	$I(CF_2)_2O(CF_2)_2$	2	75	2	48	47
8g	dl-10-camphoryl	2	60	2	52	40
8h	n-$C_{12}H_{25}$	2.5	50	2	51	40

[a] M = K, Na. [b] All reactions were carried out to 100% conversion. [c] Isolated yields.

$R_FCO_2CF_2R_F$, which is known to be unstable in the presence of fluoride ion.[15]



$R_F = CF_3$, $H(CF_2)_6$, $C_3F_7OCF(CF_3)$

However, if the mechanism was operative, an acyl fluoride should be observed as in the reaction with sodium dialkylphosphate. The facts that the salt remained unchanged and HCFO was not detected, and that fluoroform was not formed in the absence of salt, seem to indicate the presence of $R_FCO_2CF_2H$. Subsequent attack by fluoride ion on the difluoromethoxy carbon, not the carbonyl carbon, could explain the formation of fluoroform. An alternative explanation is that the rate of insertion of CF_2: into the O–H of a polyfluoroalkanoic acid is much slower than that of capture by F^- leading to fluoroform; $R_FCO_2CF_2H$ would not be formed in this situation.

Nucleophiles react with difluoromethyl alkanoates by attack only on the carbonyl carbon to displace the CF_2H group.

$$\underset{\mathbf{5}}{RCO_2CF_2H} + \underset{\mathbf{18}}{Nu^-} \rightarrow \underset{\mathbf{19}}{RCONu} + HCONu + F^-$$

R = *p*-$CH_3C_6H_4$ (**g**), *o*-$CH_3OC_6H_4$ (**l**)

Nu = F (**a**), OH (**b**), OEt (**c**), CH_3CO_2 (**d**)

Experimental Section

Melting and boiling points are uncorrected. GC spectra were measured on a Shanghai Model 120 instrument packed with Porapak-Q. IR spectra were measured on a Shimadzu IR-440 spectrometer. NMR spectra were recorded on an EM-360 NMR spectrometer at 60 MHz. Chemical shifts are in parts per million from external TMS for ^1H and from external TFA for ^{19}F, positive for upfield shifts. Mass spectra were taken on an MS-4021 spectrometer.

All solvents and reagents were purified and dried prior to use. Compound **3** was prepared according to the literature.[16]

Typical Procedure for Synthesis of a Difluoromethyl Alkanoate. Sodium benzoate (7.2 g, 50 mmol) and CH_3CN (30 mL) were placed in a 100-mL three-necked, round-bottomed flask fitted with a magnetic stirrer, dropping funnel, and reflux condenser connected to a dry-ice trap. Compound **3** (3.6 g, 20 mmol) was added with stirring at 20 °C, and the mixture was stirred for 1 h at this temperature. The ^{19}F NMR spectrum showed that reaction was complete. The gas collected (550 mL) was passed into sodium hydroxide solution. HCF_3 (90 mL, 20%) was identified by GC–MS. Sulfur dioxide was collected in the cold trap and characterized by $KMnO_4$, I_2–starch, and $Ba(OH)_2$ tests. The reaction mixture was poured into water, the aqueous layer was extracted three times with ether, and the combined extracts were washed with water and dried over Na_2SO_4. After distillation of the ether, distillation in vacuo gave **5e** (1.9 g, 54%): bp 82–86 °C/16 mm (lit.[11] bp 75 °C/15 mm); ^1H NMR δ 7.2–7.9 (m, 5 H), 7.01 (t, 1 H); ^{19}F NMR δ 13.3 (d, J_{H-F} = 71) (lit.[11] ^{19}F NMR ϕ_{CFCl_3} 91.9, J_{H-F} = 70.7).

5c: bp 130–132 °C/2.0 mm. Found: C, 68.43; H, 10.50; F, 11.40. $C_{19}H_{34}O_2F_2$ requires C, 68.62; H, 10.32; F, 11.34. IR: ν_{max} (film) 3230, 2950, 1475, 1370, 1040–1160, 730, 670 cm^{-1}. MS: *m/e* (rel intensity) 332 (4.48), 307 (2.88), 265 (11.24), 57 (100.0), 51 (12.62), 43 (62.33). ^1H NMR: δ 6.91 (t, 1 H), 0.83–5.17 (m, 33 H). ^{19}F NMR: δ 13.5 (d, J_{H-F} = 72).

5d: bp 64–66 °C/3.0 mm. Found: C, 57.78; H, 4.30; F, 20.47. $C_9H_8O_2F_2$ requires C, 58.06; H, 4.34; F, 20.41. IR: ν_{max} (film) 3050, 1740, 1620, 1470, 1225, 1040–1160, 770, 690 cm^{-1}. MS: *m/e* (rel intensity) 186 (20.76), 118 (5.540), 91 (100), 51 (4.43). ^1H NMR: δ 7.11 (s, 5 H), 6.81 (t, 1 H), 3.46 (s, 2 H). ^{19}F NMR: δ 13.5 (d, J_{H-F} = 71).

5f: bp 94 °C/2.0 mm. Found: C, 53.69; H, 4.00; F, 18.25. $C_9H_8O_3F_2$ requires C, 53.46; H, 4.00; F, 18.80. IR: ν_{max} (film) 3030, 1750, 1620, 1510, 1270, 1020–1150, 850 cm^{-1}. MS: *m/e* (rel intensity) 202 (48.09), 135 (100), 107 (9.50), 92 (17.48), 77 (16.11), 51 (10.75). ^1H NMR: δ 7.03 (t, 1 H), 7.22 (m, 4 H), 3.71 (s, 3 H). ^{19}F NMR: δ 12.8 (d, J_{H-F} = 71).

5g: bp 70–72 °C/8.0 mm. Found: C, 58.26; H, 4.45; F, 19.79. $C_9H_8O_2F_2$ requires C, 58.06; H, 4.34; F, 20.41. IR: ν_{max} (film) 3020, 1750, 1610, 1510, 1260, 1040–1160, 840 cm^{-1}. MS: *m/e* (rel intensity) 186 (5.18), 120 (100), 91 (23.94), 76 (0.29), 51 (0.91). ^1H NMR: δ 7.13 (t, 1 H), 7.55 (m, 4 H), 2.33 (s, 3 H). ^{19}F NMR: δ 12.5 (d, J_{H-F} = 72).

5h: bp 47–49 °C/1.5 mm. Found: C, 44.54; H, 20.49; F, 23.42. $C_6H_4O_3F_2$ requires C, 44.45; H, 2.49; F, 23.78. IR: ν_{max} (film) 3140, 1750, 1610, 1470, 1380, 1230, 1040–1180, 770 cm^{-1}. MS: *m/e* (rel intensity) 162 (37.06), 112 (5.44), 96 (100), 68 (4.82), 51 (2.35). ^1H NMR: δ 7.17 (t, 1 H), 6.51–7.65 (m, 3 H). ^{19}F NMR: δ 12.6 (d, J_{H-F} = 71).

5i: bp 42 °C/8.0 mm. Found: C, 50.53; H, 2.53; F, 29.52. $C_8H_5O_2F_3$ requires C, 50.53; H, 2.66; F, 29.98. IR: ν_{max} (film) 3090, 1760, 1640, 1550, 1420, 1260, 1040–1160, 860 cm^{-1}. MS: *m/e* (rel intensity) 190 (34.18), 123 (100), 95 (32.21), 75 (17.28), 51 (20.65). ^1H NMR: δ 7.13 (t, 3 H), 7.03–7.95 (m, 3 H). ^{19}F NMR: δ 13.2 (d, J_{H-F} = 70, 2 F), 23.9 (s, 1 F).

5j: mp 74–76 °C. Found: C, 54.51; H, 2.42; N, 6.88; F, 19.32. $C_9H_5NO_2F_2$ requires C, 54.82; H, 2.56; N, 7.10; F, 19.2. IR: ν_{max} (film) 3080, 2250, 1770, 1620, 1420, 1270, 1040–1120, 880 cm^{-1}. MS: *m/e* (rel intensity) 197 (45.84), 131 (100), 102 (27.58), 75 (14.99), 51 (30.77). ^1H NMR: δ 7.25 (t, 1 H), 7.92 (m, 4 H). ^{19}F NMR: δ 12.7 (d, J_{H-F} = 70).

5k: bp 94–96 °C/5 mm. Found: C, 53.55; H, 3.94; F, 18.61. $C_9H_8O_3F_2$ requires C, 53.33; H, 4.00; F, 18.80. IR: ν_{max} (film) 3035, 1760, 1605, 1490, 1260, 1040–1140, 760 cm^{-1}. MS: *m/e* (rel intensity) 202 (26.70), 135 (100), 105 (12.92), 77 (11.38), 51 (10.79). ^1H NMR: δ 7.45 (t, 1 H), 6.68–7.73 (m, 4 H), 3.85 (s, 3 H). ^{19}F NMR: δ 13.0 (d, J_{H-F} = 71).

5l: bp 52–54 °C/2 mm. Found: C, 50.69; H, 2.61; F, 29.62. $C_8H_5O_2F_3$ requires C, 50.53; H, 2.66; F, 29.98. IR: ν_{max} (film) 3050, 1760, 1610, 1490, 1240, 1020–1160, 760. MS: *m/e* (rel intensity) 190 (34.32), 123 (100), 95 (25.21), 75 (13.13), 51 (16.16). ^1H NMR: δ 7.13 (t, 3 H), 6.83–7.95 (m, 4 H). ^{19}F NMR: δ 13.1 (d, J_{H-F} = 71, 2 F), 26.9 (s, 1 F).

Reaction of 3 with 4e in Aqueous CH_3CN. **4e** (7.2 g, 0.04 mol), CH_3CN (50 mL), and H_2O (1.5 g, 0.083 mol) were placed in a 100-mL three-necked round-bottomed flask fitted with a magnetic stirrer, a dropping funnel, and a reflux condenser connected with a dry-ice trap. **3** (3.6 g, 0.02 mol) was added with stirring for 2 h at room temperature. ^{19}F NMR showed that the reaction was complete. **5e** (0.4 g, 12%), HCF_2SO_2F (0.38 g, 14%, identified by ^1H and ^{19}F NMR[3b]), and **6** (28 mL, 54%) were obtained. In the absence of water under the same reaction conditions, the yield of **5e** was 54%.

Reaction of 3 with 7a. The procedure was similar to the above. The mixture of **3** (3.6 g, 0.02 mol) and **7a** (7.7 g, 0.02 mol) in CH_3CN (50 mL) was heated at 40 °C for 2 h. ^{19}F NMR showed that the reaction was complete. Sulfur dioxide (0.8 g, 64%) was obtained in the cold trap. The gas mixture was passed into the solution of sodium hydroxide. After elimination of CO_2, the gas remaining was identified as HCF_3 (394 mL, 88%) by GC–MS spectroscopy. **7a** was recovered completely. Similar procedures for the reactions of **3** with **7b** and **7c** gave fluoroform in 90% and 82% yields, respectively.

Synthesis of Difluoromethyl Alkanesulfonate. Typical Procedure. **8a** (9.2 g, 0.04 mol) and CH_3CN (30 mL) were placed in a 100-mL three-necked round-bottomed flask fitted with a magnetic stirrer, a dropping funnel, and a refluxing condenser. **3** (3 g, 0.02 mol) was added with stirring at 50 °C. After addition, the mixture was further stirred for 2 h at this temperature. ^{19}F NMR showed that the reaction was complete. The reaction mixture was poured into water. The aqueous layer was extracted with ether three times. The combined extracts were washed with water and dried over Na_2SO_4, and ether was distilled off. Distillation in vacuo gave **9a** (2.6 g, 59%): bp 68–70 °C/0.2 mm.

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Found: C, 42.76; H, 3.71; F, 17.00; S, 14.12. $C_8H_8O_3F_2S$ requires C, 43.20; H, 3.64; F, 17.10; S, 14.40. IR: ν_{max} (film) 3010, 1600, 1400, 1010–1070, 820 cm^{-1}. MS: *m/e* (rel intensity) 222 (40.99), 172 (10.40), 155 (100), 91 (87.44), 51 (15.58). ^1H NMR: δ 6.67 (t, 1 H), 7.47) (m, 4 H), 2.42 (s, 3 H). ^{19}F NMR: δ 5.8 (d, J_{H-F} = 71).

9b: bp 74–76 °C/0.6 mm. Found: C, 33.12; H, 1.92; N, 5.76; F, 14.78; S, 12.84. $C_7H_5NO_5F_2S$ requires C, 33.24; H, 1.99; N, 5.53; F, 15.03; S, 12.64. IR: ν_{max} (film) 3038, 1605, 1540, 1400, 1010–1160, 880 cm^{-1}. MS: *m/e* (rel intensity) 253 (94.60), 207 (18.32), 186 (100), 139 (7.26), 122 (16.81), 51 (52.76). ^1H NMR: δ 7.70–8.71 (m, 4 H), 6.90 (t, 1 H). ^{19}F NMR: δ 5.8 (d, J_{H-F} = 71).

9c: bp 74–76 °C/1 mm. Found: C, 40.44; H, 2.87; F, 18.45; S, 15.68. $C_7H_6O_3F_2S$ requires C, 40.39; H, 2.91; F, 18.26; S, 15.38. IR: ν_{max} (film) 3080, 1590, 1450, 1400, 1200, 1000–1060, 850 cm^{-1}. MS: *m/e* (rel intensity) 208 (52.99), 141 (100), 77 (91.95), 51 (50.95). ^1H NMR: δ 6.75 (t, 1 H), 7.47–7.96 (m, 5 H). ^{19}F NMR: δ 5.7 (d, J_{H-F} = 71).

9g: bp 127 °C/1 mm. Found: C, 47.10; H, 5.76; F, 12.95; S, 11.50. $C_{11}H_{16}O_4F_2S$ requires C, 46.76; H, 5.72; F, 13.46; S, 11.36. IR: ν_{max} (film) 2940, 1745, 1390, 1050 cm^{-1}. MS: *m/e* (rel intensity) 282 (5.40), 151 (54.49), 123 (41.96), 109 (100), 51 (12.91). ^1H NMR: δ 6.85 (t, 15 H), 1.03–3.95 (m, 15 H). ^{19}F NMR: δ 5.7 (d, J_{H-F} = 72).

9h: bp 128 °C/2 mm. Found: C, 52.30; H, 8.89; F, 11.97; S, 11.34. $C_{13}H_{26}O_3F_2S$ requires C, 51.98; H, 8.74; F, 12.65; S, 10.76. IR: ν_{max} (film) 2970 (s), 1410 (s), 1000–1070 (s). MS: *m/e* (rel intensity) 299 (1.36), 203 (42.50), 168 (100), 51 (0.69). ^1H NMR: δ 6.73 (t, 1 H), 0.84–3.17 (m, 25 H). ^{19}F NMR: δ 5.7 (d, J_{H-F} = 72).

Reaction of 3 with 10. The procedure was similar to the above. Mixing **3** (3.6 g, 0.02 mol) with **10** (6.9 g, 0.04 mol) in CH_3CN (30 mL) at room temperature for 1 h gave **11** (2.94 g, 74%).

11: bp 145 °C/2.5 mm. Found: C, 36.20; H, 5.81; N, 7.20; F, 19.78; S, 31.61. $C_6H_{11}NF_2S_2$ requires C, 36.16; H, 5.58; N, 7.03; F, 19.10; S, 32.16. IR: ν_{max} (film) 2980, 1480, 1430, 1060–1090. MS: *m/e* (rel intensity) 199 (100), 148 (46.63), 72 (53.67), 51 (17.58). ^1H NMR: δ 7.53 (t, 1 H), 3.47 (q, 4 H), 1.1 (t, 6 H). ^{19}F NMR: δ 21 (d, J_{H-F} = 51).

Reaction of 3 with 12. To a solution of **12** (7.9 g, 0.04 mol) and CH_3CN (30 mL) was added **3** (3.6 g, 0.02 mol) at room temperature for 1 h. ^{19}F NMR showed that the conversion was complete. **13** (2.5 g, 65%) was obtained.

13: bp 118–12 °C/7 mm (lit.[13] bp 115–120 °C/7 mm). ^1H NMR: δ 7.56–8.14 (m, 5 H), 6.15 (t, 1 H). ^{19}F NMR: δ 43.0 (d, J_{H-F} = 61).

Reaction of 3 with 14. A mixture of **3** (3.6 g, 0.02 mol) and **14** (10 g, 0.03 mol) in CH_3CN (50 mL) was heated at 60 °C for 0.5 h. ^{19}F NMR showed that the conversion was 78%. **16** (0.5 g, 10%) and **15** (2.78 g, 50%) were obtained. If the contents were further stirred for 3 h at 60 °C, ^{19}F NMR showed that the conversion was complete and only **16** (3.9 g, 60%) was obtained.

15: ^1H NMR: δ 6.52 (t, 1 H), 3.88 (q, 4 H), 0.90–1.4 (m, 30 H). ^{19}F NMR: δ 3.2 (d, J_{H-F} = 72).

16: bp 148–150 °C/1.5 mm. Found: C, 58.88; H, 11.10; F, 5.65. $C_{16}H_{34}O_3FP$ requires C, 59.21; H, 10.58; F, 5.86. IR: ν_{max} (film) 2700–2950, 1450, 1290–1320. MS: *m/e* (rel intensity) 325 (8.66), 257 (0.59), 213 (27.70), 113 (100), 101 (36.43), 59 (94.74). ^1H NMR: δ 4.0 (t, 4 H), 0.95–1.35 (m, 30 H). ^{19}F NMR: δ 0.20 (d, J_{P-F} = 936).

Reaction of 3 with 4e (M = H) in the Presence of Na_2SO_4. To a mixture of Na_2SO_4 (2.8 g, 0.02 mol), **4e** (M = H) (4.9 g, 0.04 mol), and CH_3CN (30 mL) was added **3** (3.6 g, 0.02 mol) at 60 °C for 2 h. ^{19}F NMR showed that the conversion was complete. The reaction mixture was poured into water, the aqueous layer was extracted with ether three times, the combined extracts were washed with water and dried over Na_2SO_4, and ether was distilled off. Distillation in vacuo gave **5e** (1.88 g, 56%).

Reaction of 3 with 4j (M = H) in the Presence of KCl. KCl (1.5 g, 0.04 mol), **4j** (M = H) (8.5 g, 0.034 mol), and CH_3CN (50 mL) were placed in a 100-mL three-necked round-bottomed flask fitted with a magnetic stirrer, a dropping funnel, and a refluxing condenser connected with a dry-ice trap. **3** (3.6 g, 0.02 mol) was added with stirring at 50 °C for 2.5 h. ^{19}F NMR showed that the reaction was complete. **5j** (2.7 g, 45%) was obtained. Sulfur dioxide and HCF_2Cl were collected in the cold trap and characterized by GC–MS spectroscopy. At the end of the trap a gas mixture was passed into $AgNO_3$ solution, and white deposition (4.3 g) was obtained. After acidification with dilute HNO_3, AgCl (2.1 g, 74%) was obtained.

Reaction of 3 with 2,3-Dimethyl-2-butene in the Presence of Na_2SO_4. To a mixture of Na_2SO_4 (2.8 g, 0.02 mol), 2,3-dimethyl-2-butene (6.8 g, 0.08 mol), and CH_3CN (30 mL) was added **3** (3.6 g, 0.02 mol) at 60 °C for 2 h. ^{19}F NMR showed that the conversion was complete. 1,1-Difluoro-2,2,3,3-tetramethylcyclopropane (1.4 g, 53%) was obtained: bp 90–92 °C (lit.[17] bp 90–91 °C). ^{19}F NMR: δ 71.0 (m). ^1H NMR: δ 1.0 (t).

Reaction of 5g with 18a. A solution of KF (0.6 g, 0.01 mol) and **5g** (0.04 g, 2.2×10^{-3} mol) in dioxane (5 mL) was heated at 110 °C for 10 h. ^{19}F NMR showed that the conversion was 85%. The gas (38 mL, 83%) was collected and was identified as HC(O)F by GC–MS spectroscopy. **19a** (0.25 g, 96%) was obtained. Similar reactions were carried out for **5g** or **5l** with **18b**, **18c**, and **18d** to give **19b**, **19c**, and **19d** in 95%, 85%, and 100% yields, respectively.

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Registry No. **3**, 1717-59-5; **4a** (M = Na), 127-09-3; **4b** (M = Na), 10051-45-3; **4c** (M = Na), 16558-02-4; **4d** (M = Na), 114-70-5; **4e** (M = Na), 532-32-1; **4e** (M = H), 65-85-0; **4f** (M = Na), 536-45-8; **4g** (M = Na), 17264-54-9; **4h** (M = Na), 57273-36-6; **4i** (M = Na), 499-90-1; **4j** (M = Na), 1005-30-7; **4j** (M = H), 619-58-9; **4k** (M = Na), 17264-66-3; **4l** (M = Na), 17264-78-7; **4m** (M = Na), 490-97-1; **5a**, 105198-13-8; **5b**, 120608-81-3; **5c**, 120608-82-4; **5d**, 120608-83-5; **5e**, 1885-09-2; **5f**, 120608-84-6; **5g**, 120608-85-7; **5h**, 14001-27-5; **5i**, 120608-86-8; **5j**, 120608-87-9; **5k**, 120608-88-0; **5l**, 120608-89-1; **5m**, 120608-90-4; **6**, 75-46-7; **7a** (M = Na), 2264-25-7; **7b** (M = Na), 2923-18-4; **7c** (M = Na), 67963-75-1; **8a** (M = Na), 657-84-1; **8b** (M = Na), 127-68-4; **8c** (M = Na), 515-42-4; **8d** (M = Na), 2926-30-9; **8e** (M = Na), 2795-52-0; **8f** (M = Na), 89740-21-6; **8g** (M = Na), 34850-66-3; **8h** (M = Na), 2386-53-0; **9a**, 14277-20-4; **9b**, 120608-91-5; **9c**, 120608-92-6; **9d**, 1885-46-7; **9e**, 101817-80-5; **9f**, 101817-81-6; **9g**, 120608-93-7; **9h**, 120608-94-8; **10**, 148-18-5; **11**, 120608-95-9; **12**, 515-42-4; **13**, 1535-65-5; **14**, 27708-64-1; **15**, 120636-82-0; **16**, 120608-96-0; **19a**, 1493-02-3; **19b**, 64-18-6; **19c**, 109-94-4; **19d**, 922-68-9; CF_2:, 2154-59-8; Na_2SO_4, 7757-82-6; KCl, 7447-40-7; sulfur dioxide, 7446-09-5; 2,3-dimethyl-2-butene, 563-79-1; 1,1-difluoro-2,2,3,3-tetramethylcyclopropane, 823-25-6.

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