Reaction of 1-Methyl-1,2,2-trichloro-3,3-difluorobutane (7) with Triethylamine.—A 10-g sample of 1-methyl-1,2,2-trichloro-3,3-difluorocyclobutane was refluxed with 7.5 g of triethylamine for 91 hr. After washing with hydrochloric acid, separation, and drying, 4 g of starting material was recovered by distillation. Also isolated was 4 g of 1-methyl-3,3-difluoro-4,4-dichlorocyclobutene (9): bp 130° (629 mm); $n^{25}D$ 1.4261; d^{25} 1.34; molar refractivity, calcd 33.0, found, 32.9; ir 1645 cm^{-1} ($HC{=}CCH_3$).

Anal. Calcd for $C_5H_4Cl_2F_2$: C, 34.68; H, 2.31; Cl, 41.04; F, 21.96. Found: C, 34.79; H, 2.38; Cl, 41.09; F, 21.83.

Acknowledgments.—The authors wish to express their appreciation to Dr. J. J. McBrady and Dr. G. R. Sparrow of the 3M Co., St. Paul, Minn., for having run the ^{19}F nmr spectra and the mass spectrum reported in this paper. We also wish to thank AFOSR Chemical Division and the 3M Co., St. Paul, Minn., for their support of this work.

Registry No.—**1**, 356-58-1; **2**, 41785-17-5; **3**, 41785-18-6; **4**, 356-59-2; **5**, 41785-19-7; **6**, 41785-20-0; **7**, 41785-21-1; **8**, 41785-22-2; **9**, 41785-23-3; aluminum chloride, 7446-70-0; 2-chloropropene, 557-98-2; 1,1-dichloro-2,2-difluoroethylene, 79-35-6; 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene, 377-93-5; 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane, 336-50-5; zinc, 7740-66-6; triethylamine, 121-44-8.

Fluorinated Esters Stable to Fluoride Ion

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Some new fluorinated esters, $CF_3CO_2R_f$ [R_f = $(CF_3)_3C$, $C_2F_5(CF_3)_2C$, $(CF_3)_2(CH_3)C$, and $(CF_3)_2CH$], with substituents other than fluorine on the alkoxy α carbon have been prepared using the cesium fluoride catalyzed reactions of trifluoroacetyl fluoride with fluoro alcohols. Unlike the fluorinated esters with fluorine at the alkoxy α carbon atom, these esters are stable in the presence of fluoride ion at 25° or higher temperatures. Their ir, nmr, and mass spectra are reported.

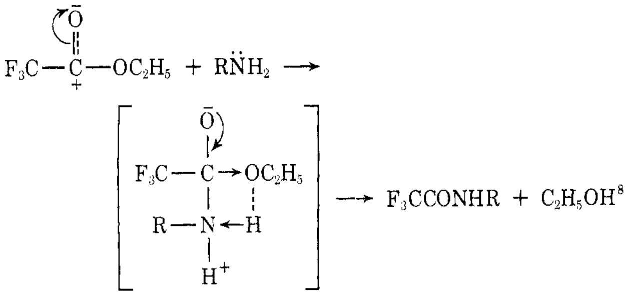
In our earlier studies,[1] we had observed that, while the totally fluorinated esters were stable at 25° and above when pure, they disproportionated readily at $> -78°$ in the presence of fluoride ions. Each of these esters contained a perfluoroalkoxy group with at least one fluorine atom bonded to the α carbon adjacent to the oxygen, $-OCR_f(R_f')F$ (R_f = CF_3, R_f' = F; R_f = R_f' = CF_3). We now have extended our study to a variety of other esters with different substituents on that carbon to determine their stabilities to attack by fluoride ions.

Contrary to the well-known reactions of acid chlorides with alcohols, the corresponding reactions of acid fluorides have neither been as popular nor as lucrative; *e.g.*, trifluoroacetyl fluoride with ethanol yielded a trace of ethyl trifluoroacetate, $CF_3CO_2C_2H_5$, accompanied by other products.[2] However, we found that a modification of this route provided a good general preparative method for esters.

Although some of the esters described in this paper have been previously reported,[3-7] little spectral characterization was included. Full details of infrared, mass, and ^1H and ^{19}F nmr spectra are given.

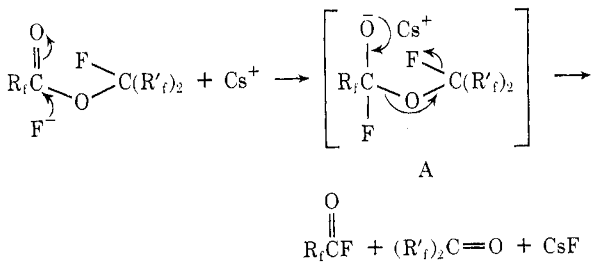
Results and Discussion

Fluorinated esters of the type $R_fCO_2CF(CF_3)_2$ which contain fluorine on the alkoxy α carbon are unstable in the presence of fluoride ion at −78° or above.[1] However, esters described in this paper that contain substituents other than fluorine at this carbon are very stable in the presence of fluoride ion even at higher temperatures. Since R_f is an electronegative group, it enhances the electrophilic character of the carbonyl carbon atom and thus promotes addition to the carbonyl double bond.



The fluoride ion, which is strongly nucleophilic, can readily attack at the positive carbon of the carbonyl group to form a similar intermediate which will then disproportionate to give the acid fluoride.

Owing to the very strong inductive effect of F, its departure as shown in eq 1 will be favored. However,



(1)

the inductive effects of CF_3 and particularly of H and CH_3 are very much less than that of fluorine.[8b] Thus, these moieties will not be good leaving groups in a complex like A. This explains the greater stability of the

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[1] R. A. De Marco, D. A. Couch, and J. M. Shreeve, *J. Org. Chem.*, **37**, 3332 (1972).

[2] W. T. Miller, Jr., and M. Prober, *J. Amer. Chem. Soc.*, **70**, 2602 (1948).

[3] F. J. Pavlik and P. E. Toren, *J. Org. Chem.*, **35**, 2054 (1970).

[4] E. Bergman, *J. Org. Chem.*, **23**, 476 (1958).

[5] B. L. Dyatkin and E. P. Mochalina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1035 (1965).

[6] E. T. McBee and D. L. Christman, *J. Amer. Chem. Soc.*, **77**, 755 (1955).

[7] G. Gorin, O. R. Pierce, and E. T. McBee, *J. Amer. Chem. Soc.*, **75**, 5622 (1953).

[8] (a) M. M. Joullie and A. R. Day, *J. Amer. Chem. Soc.*, **76**, 2990 (1954); (b) H. P. Braendlin and E. T. McBee, *Advan. Fluorine Chem.*, **3**, 2 (1963).

TABLE I

INFRARED SPECTRA OF $R_fCO_2R_f'$

Compd	Ir, cm^{-1}
$CF_3CO_2C_2H_5$	2985 m, 2950 sh, 2890 vw, 1790 vs, 1450 w, br, 1375 m, 1340 m, 1228 vs, 1180 s, 1145 s, 1015 w, 852 vs, 770 w, 725 m
$CF_3CO_2CH_2CF_3$	2985 w, 2960 w, 1810 vs, 1412 m, 1350 m, 1282 s, 1242 s, 1185 s, 975 m, 900 w, 770 w, 733 m, 650 w, 550 vw, 455 vw
$CF_3CO_2C(CF_3)_3$	1876 s, 1379 sh, 1346 w, 1295 vs, 1277 sh, 1261 sh, 1211 s, 1136 s, 1078 w, 1012 m, 995 m, 756 m, 733 m, 718 w, 671 w
$CF_3CO_2C_5F_{11}$	1858 s, 1330 m, 1265 sh, 1258 vs, 1235 sh, 1198 s, 1128 s, 1065 m, 1085 w, 1000 m, 985 sh, 925 sh, 905 sh, 895 m, 750 m, 735 m, 715 m, 665 w–m, 618 w–m, 540 w, 518 s, 445 w
$CF_3CO_2C(CF_3)_2H$	2975 m, 1825 sh, 1823 s, 1378 s, 1343 m, 1298 s, 1275 m, 1235 s, 1215 m, 1195 s, 1160 sh, 1125 s, 1024 m, 915 s, 824 w, 760 m, 744 m, 710 s, 688 s, 820 m, 474 w,
$CF_3CO_2C(CF_3)_2CH_3$	2950 w, br, 818 s, 1456 m, 1396 w, 1341 w, 1315 s, br, 1205 s, 1195 m, 1182 sh, 1141 s, 1125 sh, 1093 s, 891 w, 835 w, 760 w, 742 m, 693 m, 645 w, 520 br, w

fluorinated esters with groups other than fluorine on the alkoxy carbon.

The primary alcohols ethanol and trifluoroethanol reacted at 100° with trifluoroacetyl fluoride in the absence of cesium fluoride to give significant amounts of the respective trifluoroacetates. Secondary and tertiary alcohols, *e.g.*, hexafluoroisopropyl, hexafluoro-2-methylpropyl, perfluoro-*tert*-butyl, and perfluoroisoamyl alcohols, reacted only in the presence of cesium fluoride. Their order of reactivity is roughly represented by $(CF_3)_3COH > (CF_3)_2(C_2F_5)COH > (CF_3)_2C(CH_3)OH \approx (CF_3)_2CHOH$. This can be explained on the basis of the inductive effect of the fluorinated chains and thus the acidity of the alcohols, since the introduction of fluorine or of perfluoroalkyl groups increases the acidity of the alcohols.[9] Based on a comparative study of the pK_a values of the hydrogenated and fluoro alcohols, the secondary fluoro alcohols have the same order of acidity as phenol, and, whereas the primary alcohols are less acidic, the tertiary alcohols compare with carboxylic acids.[10,11] Since ethanol and trifluoroethanol are fairly basic (pK_a = 15.93 and 12.8, respectively),[10] their reactions with trifluoroacetyl fluoride are typical acid-base reactions. However, the other alcohols appear to react through the formation of an alkoxide intermediate. With increasing acidity

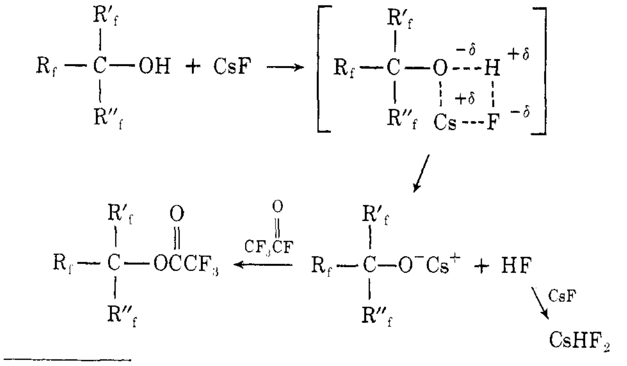

TABLE II

MASS SPECTRA OF $CF_3CO_2R_f$ (17 eV)

Registry no.	Compd	m/e (assignments, rel intensity)]
383-63-1	$CF_3CO_2C_2H_5$	142 (M, 4.8), 141 (M − H, 14.5), 140 (M − 2 H, 3.2), 127 (M − CH_3, 29), 113 (M − C_2H_5, 9.7), 99 ($C_2H_2F_3O$, 45.1), (C_2F_3O, 6.4), 73 (M − CF_3, 19.3), 69 (CF_3, 16.9), 30 (CH_2O, 9.7), 29 (C_2H_5, 100), 27 (C_2H_3, 11.3)
407-38-5	$CF_3CO_2CH_2CF_3$	177 (M − F, 27.2), 127 (M − CF_3, 100), 99 ($C_2H_2F_3O$, 22.8), 97 (C_2F_3O, 7.1), 83 ($C_2H_2F_3$, 79.6), 69 (CF_3, 17.0)
24165-10-4	$CF_3CO_2C(CF_3)_3$	313 (M − F, 12.5), 263 (M − CF_3, 73.9), 235 (M − CF_3CO, 17), 219 [$(CF_3)_3C$, 13.2], 200 (C_4F_8, 1.8), 166 (C_3F_6O, 2), 164 (?, 3), 162 (?, 4), 147 (C_3F_5O, 9.5), 131 (C_3F_5, 13), 97 (CF_3CO, 85.5), 87 (?, 3), 85 (CF_3O, 19.4), 69 (CF_3, 100)
42133-36-8	$CF_3CO_2C_5F_{11}$	363 (M − F, 4.4), 313 (M − CF_3, 4.4), 285 (M − CF_3CO, 0.8), 269 (M − CF_3CO_2, 0.8), 247 (C_5F_9O, 1), 181 (C_4F_7, 3.8), 131 (C_3F_5, 1.8), 119 (C_2F_5, 6.8), 100 (C_2F_4, 1.6), 97 (C_2F_3O, 28.8), 93 (C_3F_3, 2), 78 (C_2F_2O, 1.8), 69 (CF_3, 100), 50 (CF_2, 3.8), 47 (CFO, 1.1), 44 (CO_2, 1.1), 31 (CF, 2.8)
42031-15-2	$CF_3CO_2C(CF_3)_2H$	245 (M − F, 8.2), 226 (M − 2 F, 4.1), 225 (M − HF_2, 49.6), 195 (M − CF_3, 48.4), 175 ($C_4F_5O_2$, 1.9), 167 (C_3HF_6O, 13.2), 151 (C_3HF_6, 42.5), 132 (C_3HF_5, 1.9), 130 (C_3F_5, 2.8), 129 (C_3HF_4O, 2.5), 128 (C_3F_4O, 1.9), 113 ($C_2F_3O_2$, 5.7), 101 (C_2HF_4, 5.3), 100 (C_2F_4, 1.9), 98 (C_2HF_3O, 2.2), 97 (C_2F_3O, 52.2), 82 (C_2HF_3, 5.7), 79 (C_2HF_2O, 14.5), 78 (C_2F_2O, 9.1), 69 (CF_3, 4.1), 63 (C_2HF_2, 4.1), 51 (HCF_2, 28.9), 50 (CF_2, 17.9), 44 (CO_2, 6.3), 32 (HCF, 5.7), 31 (CF, 10.8), 29 (HCO, 16.4)
42031-16-3	$CF_3CO_2C(CF_3)_2CH_3$	278 (M, 1.3), 259 (M − F, 2.9), 258 (M − HF, 9.0), 239 [M − (2 F + H), 1.6], 209 (M − CF_3, 23.4), 181 (M − CF_3CO, 55.1), 165 (M − CF_3CO_2, 45.5), 164 ($C_4H_2F_6$, 7.4), 146 ($C_4H_3F_5$, 5.8), 145 ($C_4H_2F_5$, 100), 115 ($C_3H_3F_4$, 19.9), 113 (CF_3CO_2, 3.2), 97 (CF_3CO, 15.1), 95 ($C_3H_2F_3$, 14.4), 93 (C_3F_3, 14.4), 77 ($C_3H_3F_2$, 34.3), 69 (CF_3, 44.2), 45 (?, 4.2), 43 (CH_3CO, 72.4)

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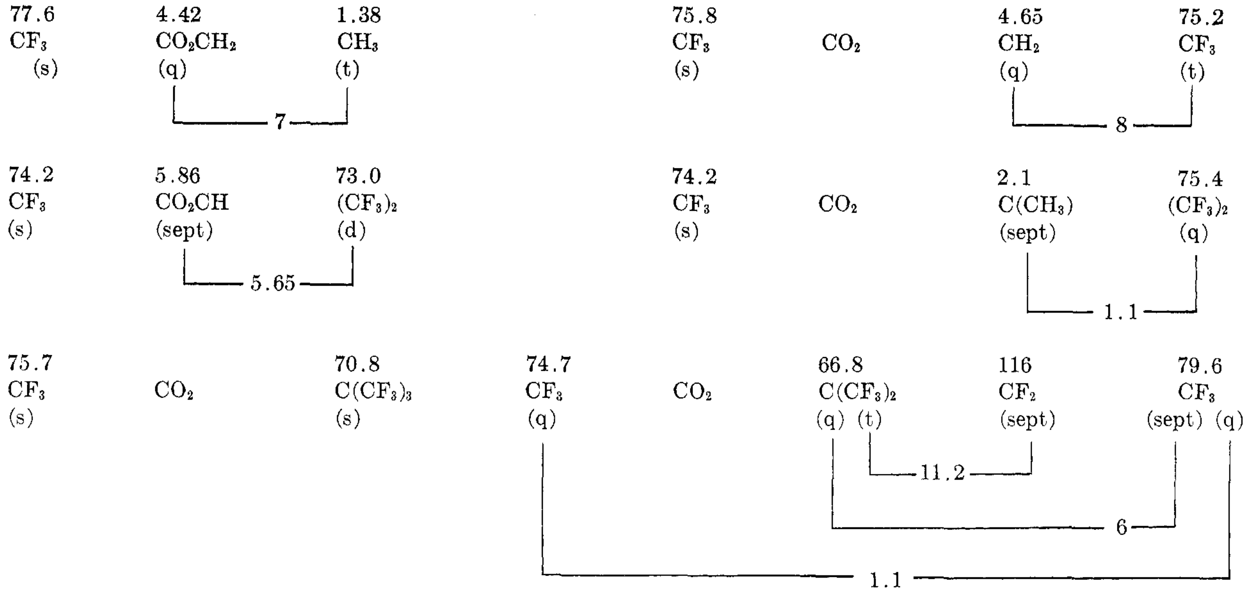
[9] F. Swarts, *Bull. Soc. Chim. Belg.*, **38**, 99 (1929).

[10] J. Murto, *Acta Chem. Scand.*, **18**, 1043 (1964).

[11] S. Kumar De and S. R. Palit, *Advan. Fluorine Chem.*, **6**, 73 (1970).

TABLE III

NMR SPECTRA[a]



77.6 CF_3 (s)	4.42 CO_2CH_2 (q)	1.38 CH_3 (t)		75.8 CF_3 (s)	CO_2	4.65 CH_2 (q)	75.2 CF_3 (t)
	7					8	
74.2 CF_3 (s)	5.86 CO_2CH (sept)	73.0 $(CF_3)_2$ (d)		74.2 CF_3 (s)	CO_2	2.1 $C(CH_3)$ (sept)	75.4 $(CF_3)_2$ (q)
	5.65					1.1	
75.7 CF_3 (s)	CO_2	70.8 $C(CF_3)_3$ (s)	74.7 CF_3 (q)	CO_2	66.8 $C(CF_3)_2$ (q) (t)	116 CF_2 (sept)	79.6 CF_3 (sept) (q)
					11.2 6 1.1		

[a] ^1H chemical shifts in parts per million (low field of Me_4Si); ^{19}F chemical shift upfield relative to CCl_3F both as internal indicators. Letters in parentheses: s, singlet; t, triplet; q, quartet; sept, septet. Relative areas of the signals correspond to the assignments in each case.

of the alcohols, the $[R_fCR_f'(R_f'')O^-]$ anion becomes more stable and thus alkoxide formation is favored. This is in line with observed reactivities.

Except for hexafluoroisopropyl trifluoroacetate, $CF_3CO_2CH(CF_3)_2$, all of the esters are stable toward hydrolysis by water at 25°, and all are hydrolyzed at $\leqslant 100°$. Since the proton on the alkoxy carbon of the hexafluoroisopropyl group is acidic, nucleophilic attack of water at this point should be very likely, which explains the rapid hydrolysis of this ester.

Infrared spectra of the fluorinated esters are given in Table I. As expected, the carbonyl stretching frequency of ethyl trifluoroacetate is the lowest, and agrees with the previously reported value.[6] Differences between the carbonyl stretching frequencies of $CF_3CH_2O_2CCF_3$, $(CF_3)_2C(CH_3)O_2CCF_3$, and $(CF_3)_2C(H)O_2CCF_3$ are not very large. The carbonyl frequencies for the $(CF_3)_2(C_2F_5)CO_2CCF_3$ and $(CF_3)_3CO_2CCF_3$ esters are significantly higher than for the other four esters. This again indicates that inductive effects of the fluoroalkyl group are more significant than their steric effect. Occurrence of strong bands in the region of 1100–1300 cm^{-1} for C–F stretching modes makes the assignments for $\nu_{C=O}$ difficult.

The mass spectra are given in Table II. Parent peaks were found only for ethyl trifluoroacetate and hexafluoro-2-methylpropyl trifluoroacetate-2. For all other esters, the highest peak observed corresponded to M − F. For the general ester $CF_3CO_2R_f$, a consistent cracking pattern was found. Fragments were observed for each ester corresponding to CF_3, CF_3CO, $(M - CF_3)$, R_f, and R_fO. This is consistent with the spectra of previously reported fluorinated esters.[1] It is significant to note that the CF_3CO_2 fragment is only observed for the esters $CF_3CO_2C_2H_5$, $CF_3CO_2C(H)(CF_3)_2$, and $CF_3CO_2C(CH_3)(CF_3)_2$. This is in line with the previous results.[1]

Nmr spectra of these esters are given in Table III. The spectra are first order and directly interpretable. No spin–spin coupling of the acyl CF_3 group with the fluoroalkyl CF_3 in $CF_3CO_2CH_2CF_3$ and $CF_3CO_2C(CF_3)_2R$ (R = H, CH_3, CF_3) occurs. However, consistent with $C_2F_5CO_2C(CF_3)_2F$ and $C_3F_7CO_2C(CF_3)_2F$,[1] the CF_3 of the perfluoroethyl group in $CF_3CO_2C(CF_3)_2C_2F_5$ is split by the acyl CF_3 group because of through-space coupling.

Experimental Section

General Procedures.—Standard vacuum line techniques were used throughout and rigorous precautions were taken to exclude moisture from all systems. In particular, all glassware was flamed out before each experiment. All reactions were carried out in 200-ml Pyrex bulbs fitted with Teflon (Quickfit) stopcocks. Pressures were measured with a Heise–Bourdon tube gauge. Amounts of volatile materials were determined by PVT measurements assuming ideal gas behavior. In general, the esters were readily separated from more volatile unreacted trifluoroacetyl fluoride by fractional condensation (low-temperature separation based on differences in volatility of components).

Infrared spectra were taken on a Perkin-Elmer 457 spectrometer using a 10-cm Pyrex glass cell equipped with KBr windows and were calibrated against known absorption bands in a polystyrene film. The ^{19}F nmr spectra were obtained on a Varian Model HA-100 spectrometer operating at 94.1 MHz using Freon-11 as an internal standard. The ^1H nmr were determined on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained using a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer at 17 and 70 eV. Molecular weights were determined by vapor density measurements. Vapor pressures were obtained by the method of Kellogg and Cady.[12] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data. Elemental analyses were performed by Laboratorium Beller, Göttingen, Germany.

Reagents.—Cesium fluoride (99%) was obtained from ROC/RIC Chemical Co. and was heated at 200° for 24 hr and then powdered. Before use, CsF was activated by forming the salt $(CF_3)_2CFO^-Cs^+$,[13] which was subsequently thermally decomposed at ~100° under dynamic vacuum. This gave a well-dried, finely divided powder. Anhydrous ethanol was obtained from Commercial Solvents Corp. All other chemicals were obtained from PCR, Inc., and used without further purification.

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(12) K. B. Kellogg and G. H. Cady, *J. Amer. Chem. Soc.*, **70**, 3986 (1948).

(13) C. T. Ratcliffe and J. M. Shreeve, *Chem. Commun.*, 674 (1966).

TABLE IV

REACTION CONDITIONS AND PRODUCT YIELDS[a]

CF_3COF, mmol	Alcohol (mmol)	Time, day	Ester (mmol)	Mol wt[b]
10.0	C_2H_5OH (4.0)	0.5	$CF_3CO_2C_2H_5$ (3.9)	142.8 (142.0)[c]
11.0	CF_3CH_2OH (4.0)	0.5	$CF_3CO_2CH_2CF_3$ (3.9)	195.6 (196.0)
7.0	$(CF_3)_2CHOH$ (4.0)	4.0	$CF_3CO_2C(CF_3)_2H$ (3.4)	263.1 (264.0)
6.0	$(CF_3)_2C(CH_3)OH$ (2.0)	4.0	$CF_3CO_2C(CF_3)_2CH_3$ (1.6)	279.3 (278.0)
5.0	$(CF_3)_3COH$ (1.1)	2.0	$CF_3CO_2C(CF_3)_3$ (1.1)	331.3 (332.0)
0.8	$(CF_3)_2C(C_2F_5)OH$ (0.6)	3.0	$CF_3CO_2C(CF_3)_2C_2F_5$ (0.6)	380.7 (382.0)

[a] All reactions were carried out in the presence of CsF at room temperature. [b] Vapor density determined assuming ideal gas behavior by Regnault's method. [c] Calculated value.

TABLE V

ELEMENTAL ANALYSIS AND THERMODYNAMIC DATA

	Elemental analysis, %			Bp,	ΔH_v,	ΔS_v,	Log $P_{mm} = a - b/T$	
Ester	C	H	F	°C	kcal/mol	eu	a	b
$CF_3CO_2C_2H_5$	33.8 (33.8)[a]	3.6 (3.5)	39.9 (40.1)	62	8.3	24.6	8.27	1809
$CF_3CO_2CH_2CF_3$	24.5 (24.5)	1.0 (1.0)	24.5 (24.5)	57	7.6	23.1	7.92	1663
$CF_3CO_2C(CF_3)_2H$	22.7 (22.7)	0.4 (0.4)	65.5 (64.8)	48	6.8	21.2	7.51	1487
$CF_3CO_2C(CF_3)_2CH_3$	25.9 (25.9)	1.1 (1.1)	62.0 (61.5)	65	8.0	23.6	8.04	1743
$CF_3CO_2C(CF_3)_3$	21.7 (21.7)		68.9 (68.7)	56	7.9	24.0	8.12	1724
$CF_3CO_2C(CF_3)_2C_2F_5$	21.9 (22.0)		69.7 (69.6)					

[a] Calculated value.

Preparative Procedure.—In a typical reaction a 2.5:1 excess of CF_3COF was condensed into a vessel which contained 4 mmol of the appropriate alcohol and about 5 g of activated CsF. The mixture was left at 25° until the band due to OH stretch (~3600 cm^{-1}) disappeared from the infrared spectrum of the mixture. The volatilities of all the esters prepared were much less than that of the trifluoroacetyl fluoride (CF_3COF), which facilitated the separation of the esters from the excess unreacted CF_3COF by fractional condensation. Except for hexafluoroisopropyl alcohol, $(CF_3)_2CHOH$, and hexafluoro-2-methylpropanol-2, $(CF_3)_2C(CH_3)OH$, reaction of CF_3COF with the other alcohols went to completion without any difficulty, giving pure esters. The cesium fluoride recovered from these reactions became increasingly more active. $(CF_3)_2CHOH$ and $(CF_3)_2C(CH_3)OH$ reacted more slowly. Some unreacted alcohol always remained in these latter cases and the complete separation from the ester was difficult. However, completion of the reaction could be achieved by condensing the impure ester onto fresh CsF in the presence of excess CF_3COF. The solid recovered from these latter reactions had a moist appearance and on heating at 100° evolved the parent alcohol. Reaction conditions and yields of products are given in Table IV. Elemental analyses and thermodynamic data are found in Table V.

Acknowledgment.—Fluorine research at the University of Idaho is supported by the National Science Foundation and the Office of Naval Research. We thank Mr. N. R. Zack for mass spectra and Mr. C. Srivanavit for nuclear magnetic resonance spectra. Dr. C. T. Ratcliffe provided samples of $(CF_3)_3COH$ and $(CF_3)_2(C_2F_5)COH$.

Halomethyl–Metal Compounds. LXV. Generation of Fluorocarboalkoxycarbenes *via* the Organomercury Route[1,2]

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Received June 29, 1973

The organomercurials $PhHgCFClCO_2R$ (R = CH_3 and C_2H_5) and $PhHgCFBrCO_2C_2H_5$ have been prepared by reaction of the respective alkyl dihaloacetate with potassium *tert*-butoxide and phenylmercuric chloride or by mercuration of the respective ethyl trihalovinyl ether with mercuric nitrate in ethanol, followed by redistribution of the mercuration product with diphenylmercury. These mercurials are $FCCO_2R$ transfer agents at temperatures above 125°, reacting with olefins to give *gem*-fluorocarboalkoxycyclopropanes and inserting $FCCO_2R$ into the Si–H bond of triethylsilane. Also described is $FCCO_2Et$ addition to the C=N bond of $PhN{=}CCl_2$.

In a previous investigation[3] we prepared $PhHgCCl_2CO_2CH_3$ and $PhHgCClBrCO_2CH_3$, both $ClCCO_2CH_3$ transfer agents, as well as $PhHgCBr_2CO_2CH_3$, a source of $BrCCO_2CH_3$. In view of our interest in organometallic routes to fluorinated carbenes,[4–9] we have extended these studies to mercury compounds of the type $PhHgCFXCO_2R$ (X = Cl, Br; R = CH_3 or C_2H_5). The divalent carbon transfer chemistry of the $PhHgCClXCO_2CH_3$ compounds and of $PhHgCBr_2CO_2CH_3$ required rather drastic conditions, but it was expected

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[1] Part LXIV: D. Seyferth and Y. M. Cheng, *J. Amer. Chem. Soc.*, **95**, 6763 (1973). (This paper is labeled part XIII by error.)

[2] Preliminary communication: D. Seyferth and R. A. Woodruff, *J. Fluorine Chem.*, **2**, 214 (1972).

[3] D. Seyferth, R. A. Woodruff, D. C. Mueller, and R. L. Lambert, Jr., *J. Organometal. Chem.*, **43**, 55 (1972).

[4] D. Seyferth and S. P. Hopper, *J. Org. Chem.*, **37**, 4070 (1972).

[5] D. Seyferth, H. Dertouzos, R. Suzuki, and J. Y.-P. Mui, *J. Org. Chem.*, **32**, 2980 (1967).

[6] D. Seyferth and K. V. Darragh, *J. Org. Chem.*, **35**, 1297 (1970).

[7] D. Seyferth and G. J. Murphy, *J. Organometal. Chem.*, **49**, 117 (1973).

[8] D. Seyferth and S. P. Hopper, *J. Organometal. Chem.*, **51**, 77 (1973).

[9] D. Seyferth and G. J. Murphy, *J. Organometal. Chem.*, **52**, C1 (1973).