Reduction of Perfluoroacyl Halides with Organosilicon Hydrides. A Direct Synthesis of Fluorine Containing Esters and Lactones

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A method is described for the synthesis of fluorine containing esters of 1,1-dihydroperfluoroalkyl alcohols by a catalyzed organosilicon hydride reduction of perfluoroacyl halides. Using this technique, $CF_3CF_2OCF_2CF_2CO_2CH_2CF_2CF_2OCF_2CF_3$ (**1**) and $C_6F_{11}CO_2CH_2C_6F_{11}$ (**2**) were produced directly from perfluoroethoxypropionyl fluoride and perfluorocyclohexyl carbonyl fluoride, respectively. In addition, five- and six-membered lactones of hydroxy fluorocarbon carboxylic acids, compounds **3–5**, were obtained from the perfluorodiacyl halides: perfluorosuccinyl fluoride, perfluoroglutaryl fluoride, and perfluorooxydiacetyl chloride.

Synthesis of esters from highly fluorinated alcohols normally involves a number of synthetic steps,[1] including production of the necessary 1,1-dihydroperfluoroalkyl alcohols by reduction of a perfluoroalkyl carbonyl compound. A more convenient technique was sought for this transformation, based on the synthetic potential of organosilicon hydrides which have been exploited in the past to convert hydrocarbon acyl chlorides to aldehydes[2] and acyl fluorides to esters,[3] both conversions utilizing palladium on carbon as a catalyst. This paper describes the use of a catalyzed organosilicon hydride reduction to produce esters of 1,1-dihydroperfluoroalkyl alcohols, $R_FCO_2CH_2R_F$, and lactones of fluorine containing hydroxy acids in one step from perfluoroacyl halides and perfluorodiacyl halides, respectively.

The results of the organosilicon hydride reductions of various perfluoroacyl halides are summarized in Table I. In each case, trimethylsilane was heated with the perfluoroacyl halide to 160–210 °C in a Hoke stainless steel reactor in the presence of platinum on carbon, zinc chloride, and potassium fluoride. Thus, a mixture of trimethylsilane and perfluoroethoxypropionyl fluoride[4] was heated at 180 °C with platinum on charcoal, zinc chloride, and potassium fluoride to yield the ester, $CF_3CF_2OCF_2CF_2CO_2CH_2CF_2CF_2OCF_2CF_3$. A similar reaction with perfluorocyclohexyl carbonyl fluoride[5] also gave the corresponding ester **2**. In general, the product yields ranged from 10 to 30%.

With perfluorodiacyl halides, which are capable of ring closure to a five- or six-membered ring, lactones of the corresponding hydroxy fluorocarbon carboxylic acids were formed. Upon reaction with trimethylsilane, perfluorosuccinyl fluoride, perfluoroglutaryl fluoride, and perfluorooxydiacetyl chloride[6] gave the lactones, compounds **3–5**. The only reference to this type of fluorocarbon lactone is a patent[7] on the preparation of 5-hydroxy-2,2,3,3,4,4-hexafluorovaleric acid which suggested that the hydroxy acid may exist in equilibrium with its lactone but offered no confirming data.

All products were characterized on the basis of their elemental analyses and infrared and NMR spectra, with the results being summarized in the Experimental Section. The more complicated products gave NMR resonances which were broad or, at best, complex under high resolution. In these cases, the center of the resonance was taken as the chemical shift. However, the NMR pattern for compound **5a** could be analyzed by a first-order treatment owing to its asymmetrical nature. Results obtained for this compound are given in Table II.

In order to gain some insight into the reaction sequence, the following experiments were carried out. Excluding only the potassium fluoride from the reaction, perfluorocyclohexyl carbonyl fluoride was heated with trimethylsilane to yield [(perfluorocyclohexyl)methoxy]trimethylsilane (**6**). In addition, a sample of tetra(2,2,2-trifluoroethoxy)silane[8] and perfluorocyclohexyl carbonyl fluoride, heated in the presence of potassium fluoride, led to the isolation of trifluoroethyl perfluorocyclohexyl carboxylate (**7**). Citron[9] has also reported the formation of esters by reaction of acyl fluorides with alkoxy silanes. Finally, perfluorocyclohexyl carbonyl chloride (**8**) was characterized from a heated reaction of zinc chloride with perfluorocyclohexyl carbonyl fluoride.

No evidence was found for the presence of perfluoro-β-oxa-δ-valerolactone which was previously isolated from perfluorooxydiacetyl halide and potassium fluoride.[10] Formation of this lactone was rationalized by postulating a cyclization of a fluoroformyl-substituted perfluoroalkoxide formed by addition of a fluoride ion to one of the acyl fluoride end groups. A similar addition of fluoride ion to the aldehydic carbonyl of the $OHCCF_2OCF_2CFO$ intermediate thought to be present from the initial reaction of trimethylsilane and perfluorooxydiacetyl chloride could also be involved in the formation of compound **5a**. In accordance with the documented reduction by organosilicon hydrides of hydrocarbon acyl halides to the corresponding aldehyde,[2] an initial reduction of the perfluoroacyl halide to the aldehyde would be very likely here.

In summary, the use of catalyzed organosilicon hydride reactions with perfluoroacyl halides provides a convenient method for the synthesis of fluorine containing esters. In addition, certain lactones of fluorine containing hydroxy acids can be produced in a single synthetic step from perfluorodiacyl halides.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer using NaCl plates. The ^{19}F nuclear magnetic resonance measurements, made with a Varian V-4300-2 spectrometer operating at 40.0 MHz and utilizing an internal standard of $CFCl_3$ for the determination of chemical shifts, are reported as ϕ^* values.[11] ^1H NMR values were obtained from a Varian Model A-60 instrument with $CFCl_3$ as solvent and reported as τ values with tetramethylsilane as reference.[12] Finally, the GC unit used to trap analytical samples was a Perkin-Elmer Model 154 gas chromatograph employing 12 ft × 0.375 in. columns packed with either 33% FS-1265 or 25% SE-52 on Chromosorb P.

The 1% platinum on 28–150 mesh charcoal was purchased from Matheson Coleman and Bell. Perfluoroglutaryl chloride and perfluorosuccinic acid, both converted to the acyl fluorides by standard techniques, as well as trimethylsilane, were obtained from PCR, Inc.

Reaction of Perfluoroethoxypropionyl Fluoride with Trimethylsilane. A 150-ml Hoke stainless steel pressure reactor was loaded with 2.9 g of KF and evacuated, and 2.8 g of $C_2F_5OC_2F_4COF$[4] and 1.5 g of $(CH_3)_3SiH$ added. After the reactor was heated to 130 °C for 6 h, an ir spectrum indicated only starting materials. The reactor was cooled with liquid nitrogen, 1 g of 1% Pt/C and 0.2 g of $ZnCl_2$ added, the cooled reactor reevacuated, and the mixture reheated to 180 °C for 18 h. The products were allowed to vaporize into two evacuated traps connected in series, cooled to −40 and −196 °C, respectively, as the temperature of the reactor rose from −196 to 180 °C. This vacline separation led to the isolation of 1.8 g of $(CH_3)_3SiF$

Table I. Products from Acyl Halides and Silicon Hydrides

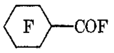
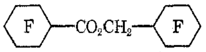
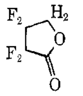
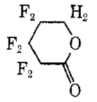
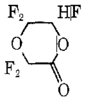
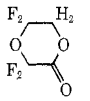
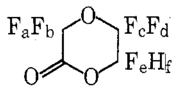
Registry no.	Acyl halide	Ester or lactone product	Compd	Registry no.
377-75-3	$CF_3CF_2OCF_2CF_2COF$	$CF_3CF_2OCF_2CF_2CO_2CH_2CF_2CF_2OCF_2CF_3$	**1**	58816-72-1
6588-63-2			**2**	58816-73-2
679-13-0	$FOC(CF_2)_2COF$		**3**	58816-74-3
678-78-4	$FOC(CF_2)_3COF$		**4**	58816-75-4
21297-62-1	$O(CF_2COCl)_2$		**5a**	58816-76-5
			**5b**	58816-77-6

Table II. Chemical Shift and Coupling Constants of 5a[a]



δ_a, δ_b 69.62, 70.54 ϕ^*		J_{ab} = 177.6 Hz
δ_c, δ_d 78.26, 89.51 ϕ^*		J_{cd} = 165.1 Hz
δ_e 135.58 ϕ^*	δ_f 3.95 τ	J_{ef} = 51.25 Hz
J_{ac} = 4.34 Hz	J_{bc} = 8.88 Hz	J_{ce} = 9.34 Hz
J_{ad} = 2.16 Hz	J_{bd} = 2.15 Hz	J_{cf} = 1.44 Hz
J_{ae} = 3.23 Hz	J_{be} = 8.02 Hz	J_{de} = 12.94 Hz
J_{af} = 0.50 Hz	J_{bf} = 0.15 Hz	J_{df} = 1.64 Hz

[a] The NMR spectrum was obtained using a Varian XL-100 spectrometer and the coupling constants given represent the average of two measured values.

and 0.5 g of $CF_3CF_2OCF_2CF_2CO_2CH_2CF_2CF_2OCF_2CF_3$ (**1**): ir (neat, 5.55 μ (C=O); NMR ($CFCl_3$) τ 5.25 (t, J = 12.0 Hz, CH_2), ϕ^* 87.3 (CF_3), 89.0 (CF_3CF_2), 86.6 (CF_2CF_2CO), 121.7 (CF_2CO), 124.0 (t, J = 12.0 Hz, CH_2CF_2), 85.8 ($CH_2CF_2CF_2$).

Anal. Calcd for $C_{10}H_2F_{18}O_4$: C, 22.7; F, 64.8. Found: C, 22.9; F, 65.0.

Reaction of Perfluorocyclohexyl Carbonyl Fluoride[5] with Trimethylsilane. Trimethylsilane (3.3 g), perfluorocyclohexyl carbonyl fluoride (6.6 g), 1% Pt/C (1 g), KF (3 g), and $ZnCl_2$ (100 mg) were heated together in a Hoke reactor to 160 °C for 18 h. The workup procedure consisted of a filtration, using $CHCl_3$ as a solvent, and a short-path distillation. Isolated was 1 g of [(perfluorocyclohexyl)methyl]perfluorocyclohexyl carboxylate (**2**): mp 86.5–88 °C; ir (neat) 5.58 μ (C=O); NMR ($CFCl_3$) τ 4.92 (d, J = 17.2 Hz, CH_2), ϕ^* 189.2 (complex, $CFCH_2$), 180.2 (complex, CFCO) plus complex absorptions between 115 and 150 (six AB quartets, J_{AB} 290 Hz, ring CF_2 groups).

Anal. Calcd for $C_{14}H_2F_{22}O_2$: C, 27.1; F, 67.4. Found: C, 26.8; F, 67.0.

Reaction of Perfluorosuccinyl Fluoride with Trimethylsilane. A Hoke reactor containing 2.9 g of KF, 1 g of 1% Pt/C, 0.2 g of $ZnCl_2$, 1.0 g of $FOC(CF_2)_2COF$, and 0.7 g of $(CH_3)_3SiH$ was heated at 170 °C for 15 h at 210 °C for 2 h. A vacline separation gave 0.2 g of the lactone of 4-hydroxy-2,2,3,3-tetrafluorobutyric acid (**3**): ir (gas) 5.40 μ (C=O); NMR ($CFCl_3$) τ 5.43 (t, J = 11.6 Hz, CH_2), ϕ^* 131.1 (t, J = 6.2 Hz, CF_2CO), 127.1 (t, t, CH_2CF_2).

Anal. Calcd for $C_4H_2F_4O_2$: C, 30.4; F, 48.1. Found: C, 30.2; F, 48.3.

Reaction of Perfluoroglutaryl Fluoride with Trimethylsilane. After a Hoke reactor containing 2.9 g of KF, 1 g of 1% Pt/C, 0.2 g of $ZnCl_2$, 2.4 g of $FOC(CF_2)_3COF$, and 1.5 g of $(CH_3)_3SiH$ was heated to 170 °C for 75 h, a vacline separation was carried out. Recovered was 0.4 g of starting material. Also isolated was 0.2 g of the lactone of 5-hydroxy-2,2,3,3,4,4-hexafluorovaleric acid (**4**): ir (neat, 5.54 μ (C=O); NMR ($CFCl_3$)τ 5.44 (t,t, J = 11.0 and 2.0 Hz, CH_2), ϕ^* 125.0 (complex, CF_2CH_2), 135.7 (complex, $CF_2CF_2CH_2$), 121.2 (complex, CF_2CO).

Anal. Calcd for $C_5H_2F_6O_2$: C, 28.9; F, 54.8. Found: C, 28.6; F, 54.4.

Reaction of Perfluorooxydiacetyl Chloride[6] with Trimethylsilane. A Hoke reactor was charged with 2.9 g of KF, 1 g of 1% Pt/C, 0.2 g of $ZnCl_2$, 3.6 g of $O(CF_2COCl)_2$, and 2.2 g of $(CH_3)_3SiH$ and heated to 160 °C for 48 h and 210 °C for 2 h. Two products were isolated from the −40 °C trap after a vacline separation. Found was 0.35 g of the lactone of 5-hydroxy-3-oxa-2,2,4,4,5-pentafluorovaleric acid (**5a**), ir (neat) 5.47 μ (C=O).

Anal. Calcd for $C_4HF_5O_3$: C, 25.0; F, 49.5. Found: C, 25.1, F, 50.1.

Also collected was 0.5 g of the lactone of 5-hydroxy-3-oxa-2,2,4,4-tetrafluorovaleric acid (**5b**): ir (neat) 5.50 μ (C=O); NMR ($CFCl_3$) τ 5.26 (complex, CH_2), ϕ^* 75.8 (complex, CF_2CH_2) and 76.3 (complex, CF_2CO).

Anal. Calcd for $C_4H_2F_4O_3$: C, 27.6; F, 43.7. Found: C, 27.4; F, 43.8.

Reaction of Perfluorocyclohexyl Carbonyl Fluoride with Trimethylsilane. A mixture of 1 g of 1% Pt/C, 0.2 g of $ZnCl_2$, 1.5 g of $(CH_3)_3SiH$, and 3.3 g of perfluorocyclohexyl carbonyl fluoride was heated in a Hoke reactor to 140 °C for 89 h. A vacline separation led to the recovery of 1.2 g of starting material. Pumping on the hot reactor gave 0.4 g of [(perfluorocyclohexyl)methoxy]trimethylsilane: NMR ($CFCl_3$) τ 9.84 (CH_3), 5.70 (d, J = 19.3 Hz, CH_2), ϕ^* 190.3 (complex, CF), 119.9 and 133.0, 123.5 and 140.4, 124.8 and 142.4 (three AB quartet patterns, J_{AB} = 290, 286, and 280 Hz, respectively, ring CF_2 groups).

Anal. Calcd for $C_{10}H_{11}F_{11}OSi$: C, 31.2; F, 54.4; H, 2.9. Found: C, 30.9; F, 55.0; H, 3.1.

This material was also prepared in much higher yield by the reaction of (perfluorocyclohexyl)methanol[13] and chlorotrimethylsilane.

Reaction of Perfluorocyclohexyl Carbonyl Fluoride with Tetra(2,2,2-trifluoroethoxy)silane.[8] A Hoke reactor was charged with 5.8 g of KF, 2.2 g of $Si(OCH_2CF_3)_4$, and 6.6 g of perfluorocyclohexyl carbonyl fluoride. After the reactor was heated to 160 °C for 18 h and 210 °C for 2 h, a vacline separation gave 8.5 g of 2,2,2-trifluoroethylperfluorocyclohexyl carboxylate (**7**): ir (neat) 5.58 μ (C=O); NMR ($CFCl_3$) τ 5.28 (q, J = 7.8 Hz, CH_2), ϕ^* 75.0 (t, J = 7.8 Hz, CF_3), 180.4 (complex, CF), 118.3 and 131.6, 123.4 and 139.2, 122.6 and 141.8 (three AB quartet patterns, J_{AB} quartet patterns, J_{AB} = 294, 283, and 286 Hz, respectively, ring CF_2 groups).

Anal. Calcd for $C_9H_2F_{14}O_2$: C, 26.5; F, 65.2. Found: C, 26.6; F, 65.4.

Reaction of Perfluorocyclohexyl Carbonyl Fluoride with Zinc Chloride. Isolated by a short-path distillation was 9.5 g of perfluorocyclohexyl carbonyl chloride after a Hoke reactor containing 6.6 g of perfluorocyclohexyl carbonyl fluoride and 2.7 g of $ZnCl_2$ was heated to 185 °C for 20 h. Perfluorocyclohexyl carbonyl chloride (**8**): ir (neat) 5.55 μ (C=O); NMR ($CFCl_3$) ϕ^* 167.0 (CF), 119.0 and 131.0, 123.5 and 138.9, 122.9 and 141.6 (three AB quartet patterns, J_{AB} = 294, 292, and 291 Hz, respectively, ring CF_2 groups).

Anal. Calcd for $C_7ClF_{11}O$: C, 24.4; F, 60.7. Found: C, 24.4; F, 61.1.

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Registry No.—**7**, 58816-78-7; **8**, 58816-79-8; trimethylsilane, 993-07-7; [(perfluorocyclohexyl)methoxy]trimethylsilane, 58816-80-1; tetra(2,2,2-trifluoroethoxy)silane, 338-39-6; zinc chloride, 7646-85-7.

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Controlled Substituent Exchange in Cyclopropenium Ions. Role of Counterion in Friedel–Crafts Reactions of the Trichlorocyclopropenium Ion

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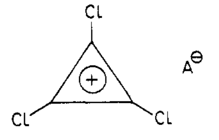
Friedel–Crafts reactions of the trichlorocyclopropenium cation ($C_3Cl_3^+$) with unsaturated substrates are very sensitive to the nature of its counterion. The triflate salt is ideal in Friedel–Crafts reactions with *nonactivated* aromatic substrates and permits facile synthesis of the corresponding triarylcyclopropenium systems. $SbCl_6^-$ is the counterion of choice in reactions of $C_3Cl_3^+$ with *olefinic and acetylenic bonds.* Thus usage of $C_3Cl_3^-SbCl_6^-$ opens up a synthetic pathway to representatives of the hitherto unknown di- and trivinylcyclopropenium salts. A mechanistic model is offered which accounts for the observed anion effects.

Owing to their multifunctional character and high internal energy[1] cyclopropenium ions (and derived cyclopropenes) should possess considerable potential as synthons. With this final aim in mind it is of interest to attach diverse structural units to the cyclopropenium system as a template and thus create molecular frameworks which are both synthetically useful and theoretically interesting.

Trichlorocyclopropenium salts 1 offer a good starting point for such an exercise because they are highly reactive and easily accessible on the basis of cheap starting materials.[2] Consequently, since the pioneering work of West[3] considerable efforts have been spent on replacing the chlorine atoms in 1 by various other substituents.[4] As a rule it was not generally possible to control the extent of substituent exchange and, in a number of cases, to avoid destruction of the highly strained cyclopropenium system. We now report that the course of such reactions can be controlled by two important independent factors: (a) selection of an appropriate counterion A^- in 1 and (b) choice of a selective exchange reagent. In this paper we focus on a, looking at Friedel-Crafts reactions of 1, while in subsequent papers[5] we shall deal with b.



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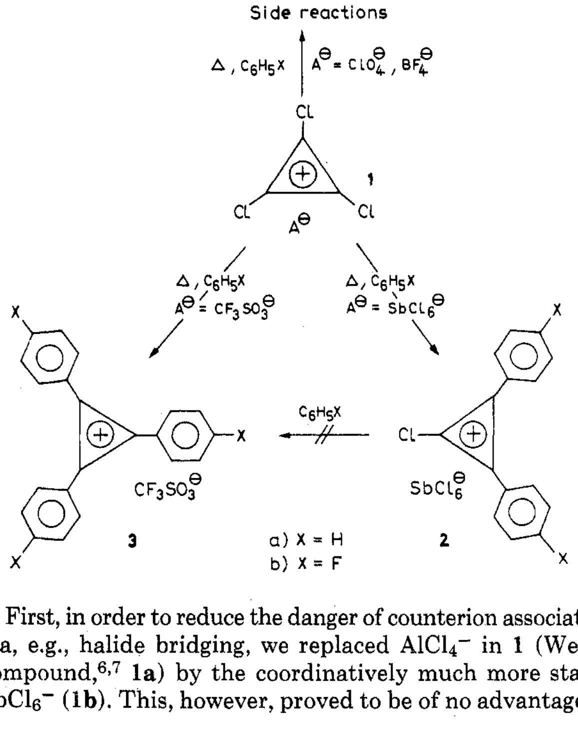
Results and Discussion

A. Reactions with Aromatic Substrates. Friedel–Crafts reactions of 1 with aromatic substrates were among the first things studied when this highly reactive species became known. Selective temperature-controlled mono- and disubstitutions of Cl atoms in 1 by phenyl and its weakly activated (*p*-alkyl-substituted) or deactivated (*p*-halo-substituted) derivatives were reported by West.[2,6] However, attempts to synthesize *triaryl*cyclopropenium systems via this route met with failure unless strongly activated substrates like phenols were used.[7] In this section we discuss reasons for this restriction and show how it can be relieved. It had occurred to us that in the earlier work one potentially important structural parameter had been neglected, namely the nature of counterion A^- in 1. For it is highly unlikely that the trichlorocyclopropenium ion and its partially arylated successor ions will exist in "free" form in the essentially nonpolar media (benzene and its derivatives) used.[2,6] Rather, these cations will be more or less tightly bound to their counterions A^-. Consequently, we tested the substitution behavior of various trichlorocyclopropenium salts in benzene and fluorobenzene as solvent and substrate, respectively, and indeed found a very pronounced counterion dependence of product distributions. Results are summarized in Scheme I.

Scheme I



First, in order to reduce the danger of counterion association via, e.g., halide bridging, we replaced $AlCl_4^-$ in 1 (West's compound,[6,7] **1a**) by the coordinatively much more stable $SbCl_6^-$ (**1b**). This, however, proved to be of no advantage as