Synthesis, Properties, and Reactions of New Perfluorinated Diketones

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(Trifluoromethyl)trimethylsilane reacts with diacyl fluorides $F(O)C(CF_2)_nC(O)F$ ($n = 2,3$) in the presence of excess KF in benzonitrile to give the cyclic alkoxides $CF_3(F)C(CF_2)_nCO(CF_3)O^-K^+$. The alkoxides are formed by the formal nucleophilic substitution of CF_3^- on F(O)C– followed by a rapid cyclization of the diketone by fluoride ion to give the observed alkoxides. The free diketones $CF_3(O)C(CF_2)_nC(O)CF_3$ are isolated by a 1,4- loss of KF from the alkoxide by heating the latter under dynamic vacuum. The new diketones exhibit a high reactivity with many nucleophiles resulting in a facile intramolecular cyclization. With water the novel cyclic diols $CF_3(HO)C(CF_2)_nCO(OH)CF_3$ are formed in high yield. The structures of the *cis*- ($n = 3$) and *trans*- ($n = 2$) diols were obtained by single-crystal X-ray diffraction.

Introduction

We have previously reported that $(CH_3)_3SiCF_3$ (TMS-CF_3) can be employed to generate tertiary alkoxides and alcohols by nucleophilic trifluoromethylation of a variety of fluoroketones and acid fluorides in the presence of metal fluorides.[1] As an extension of this chemistry, we have investigated the reactions of TMS-CF_3 with some diacyl fluorides. Our goal was to prepare fluorinated diols $(CF_3)_2C(OH)(CF_2)_nC(OH)(CF_3)_2$ of various chain lengths which would have useful solvent properties. Fluoroalcohols and their derivatives are attaining increasing importance in dyestuffs, plastics, pharmaceuticals, and surface coatings, as well as use in fluorine-containing polymers.

Work has appeared by Chen et al., in which highly fluorinated mono- and diketones have been prepared by the reaction of organolithium reagents with various fluorinated esters and perfluoroalkyl iodides.[2–4] Such reactions rely on the in situ generation of R_fLi compounds at −78 °C, which attack the fluorinated ester and upon hydrolysis yield the ketones.[5]

Herein we report that the reactions between TMS-CF_3 and diacyl fluorides $F(O)C(CF_2)_nC(O)F$ do not lead to formation of the expected diols. Instead we observe formation of new perfluorodiketones $CF_3(O)C(CF_2)_nC(O)CF_3$ ($n = 2, 3$) and decompostion of the starting diacyl fluoride when $n = 0$.[6] The diketones are extremely reactive owing to the electron-deficient carbonyl group and their ability to undergo an intramolecular cyclization. The synthesis of the diketones, their reaction with water to give cyclic diols, and the structures of these diols are discussed.

Experimental Section

Caution! Working with highly acidic alcohols is potentially hazardous since perfluoropinacol has been determined to be a highly toxic material, both from the standpoint of skin contact and inhalation, while other alcohols have been tested as fumigants.[7] Compounds **4** and **5** are quite similar to perfluoropinacol and should be treated as potentially highly toxic materials.

General Methods. Gases and volatile materials were handled in glass vacuum systems, equipped with glass–Teflon valves. Amounts of volatile compounds were determined by PVT measurements using a Wallace & Tiernan Series 1500 differential pressure gauge. All trap-to-trap fractionations were performed under dynamic vacuum. The reaction vessel for preparation of the diketones consisted of a 1000-mL Pyrex flask with a glass–Teflon valve attached through an Ace-Thred O-ring seal. The body of the flask was modified by the addition of a side arm fitted with a Teflon-faced silicone septum. Liquids could be added via syringe, without compromising the ability of the system to hold vacuum after removal of the syringe needle. The reactors contained a Teflon-coated magnetic stirbar.

Infrared spectra were recorded in a 10-cm glass cell fitted with KCl windows. NMR spectra were acquired at 200.13 MHz for ^1H, 188.31 MHz for ^{19}F, and 75.47 for ^{13}C. Chemical shifts are reported relative to $Si(CH_3)_4$ or $CFCl_3$ with shifts upfield from these designated as negative. Mass spectra were recorded on a Hewlett-Packard 5985B spectrometer at 70 eV for EI and CI (CH_4) with samples introduced by direct gas injection. Boiling points were determined by Siwoloboff's method[8] and are uncorrected.

Starting Materials. Perfluorosuccinyl chloride and perfluoroglutaryl chloride were obtained from PCR, Inc., and used as received. The corresponding diacyl fluorides were prepared by the reaction of the diacyl chloride with a large excess (1:24) of NaF in sulfolane at 90 °C for 15 h. (Trifluoromethyl)trimethylsilane was prepared by literature methods.[1,9] Active KF was prepared by fusion in a Pt dish followed by pulverization under very dry nitrogen in a porcelain mortar and then to a fine powder in a porcelain ball mill. Dry solid materials were handled inside an efficient drybox. Benzonitrile was dried over P_4O_{10} and stored over molecular sieves.

Preparation of $CF_3(O)C(CF_2)_2C(O)CF_3$ (1) from $F(O)C(CF_2)_2C(O)F$. Fused potassium fluoride (3.16 g, 54.4 mmol) was loaded into the reactor (see above), the reactor was partially evacuated, and 8.0 mL of benzonitrile was added by syringe. The reactor was cooled to −196 °C and evacuated. Perfluorosuccinyl fluoride (11.17 mmol) and TMS-CF_3 (23.54 mmol) were condensed into the reactor by vacuum transfer. The reactor was placed in a 0 °C bath, and stirring was begun as soon as the reaction mixture melted. After 16 h the volatiles were removed at 22 °C by vacuum pumping through a trap at −196 °C for 2 h. The contents of this trap were fractionated through traps at −33, −77, and −196 °C. The −196 °C trap contained 24.91 mmol of a mixture consisting mainly of TMS-F (94%) with some CF_3H (6%). Benzonitrile was retained in the −33 °C trap. The reactor was then heated to 120 °C for 30 min under dynamic vacuum, and the volatile compounds collected at -196 °C were

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fractionated through traps at −33, −77, and −196 °C. The −77 °C trap gave 7.98 mmol of **1**[e](71.4% yield).

The new compound **1** was characterized as follows: bp 59–61 °C at 742 mmHg; IR (4 Torr) 1785 (s), 1311 (s), 1287 (vs), 1246 (vs), 1200 (vs), 1090 (m), 1050 (m), 909 (m), 842 (s), 724 (vs) cm^{-1}; NMR ($CF_3{}^A$-$(O)CCF_2{}^B)_2$ ($CDCl_3$, 24 °C) $\delta(^{19}F)$ A −75.1 (6 F, m), B −119.5 (4 F, m) ppm; MS (EI) *m/e* 197 (6.6, $CF_3(O)CCF_2CF_2{}^+$), 100 (8.2, $CF_2CF_2{}^+$), 97 (15.9, $CF_3(O)C^+$), 69 (100, $CF_3{}^+$), 50 (23.7%, $CF_2{}^+$); (CI) *m/e* 295 (83.3, MH^+), 275 (79.0, ($MH - HF^+$), 225 (30.9, $M - CF_3{}^+$), 197 (100.0, $CF_3(O)CCF_2CF_2{}^+$), 147 (96.9, $CF_3(O)CCF_2{}^+$), 131 (50.0, $CF_3CCF_2{}^+$), 109 (88.9, $CF_3C_2O^+$), 100 (47.5, $C_2F_4{}^+$).

Preparation of $CF_3(O)C(CF_2)_3C(O)CF_3$ (2) from $F(O)C(CF_2)_3C(O)F$. Potassium fluoride (2.92 g, 50.3 mmol) and 11.0 mL of anhydrous benzonitrile, perfluoroglutaryl fluoride (11.32 mmol), and TMS-CF_3 (23.67 mmol) were combined and allowed to react for 14 h as with **1**. The volatile materials were then fractionated through traps at −28, −68, and −196 °C. The −196 °C trap contained 23.71 mmol of material which by ^{19}F NMR consisted of TMS-F and a trace of CF_3H. The solid material remaining in the reactor was then heated to 150 °C for 1.5 h under dynamic vacuum, and the volatile compounds collected at −196 °C were fractionated through traps at −21, −78, and −196 °C. The −78 °C trap gave 10.17 mmol of **2** (89.8% yield).

The new compound **2** was characterized as follows: bp 78 °C at 750 mmHg; IR (2 Torr) 1797 (s), 1251 (vs), 1198 (vs), 1098 (w), 1013 (m), 912 (m), 843 (m), 730 (m), 642 (m) cm^{-1}; NMR $[(CF_3{}^A(O)C(CF_2{}^B)]_2$-$CF_2{}^C$ ($CDCl_3$, 24 °C) $\delta(^{19}F)$ A -75.1 (6 F, m), B −118.1 (4 F, m), C −121.8 (2 F, m) ppm; MS (EI) *m/e* 247 (3.4, $CF_3(O)CCF_2CF_2CF_2{}^+$), 147 (3.3, $CF_3(O)CCF_2{}^+$), 131 (5.1, $CF_3CCF_2{}^+$), 100 (5.2, $CF_2CF_2{}^+$), 97 (35.3, $CF_3(O)C^+$), 69 (100.0%, $CF_3{}^+$); MS (CI) *m/e* 345 (100.0, MH^+), 325 (23.2, $MH - HF^+$), 275 (4.9, $M - CF_3{}^+$), 247 (57.6, $M - CF_3(O)C^+$), 231 (21.5 ($CF_3CCF_2CF_2CF_2{}^+$), 197 (10.7, $CF_3(O)CCF_2CF_2{}^+$), 147 (8.9, $CF_3(O)CCF_2{}^+$), 131 (12.6, $CF_3CCF_2{}^+$), 100 (12.3, $C_2F_4{}^+$).

Reaction of F(O)CC(O)F with TMS-CF_3. Potassium fluoride (0.50 g, 8.6 mmol), 3.0 mL of anhydrous benzonitrile, oxalyl fluoride (2.03 mmol), and TMS-CF_3 (4.32 mmol) were combined as above for **1**, for 14 h in a 250-mL reactor. The volatile products were removed by vacuum pumping for 1.5 h at 22 °C and fractionated through traps at −29, −130, and −196 °C. The −196 °C trap contained 1.14 mmol of material which by ^{19}F NMR consisted of (mol %) $CF_3C(O)F$ (52.1), COF_2 (43.6), and CF_3H (4.3). The −130 °C trap contained 4.53 mmol of a mixture of TMS-CF_3 and TMS-F. None of the expected diketone was isolated upon heating the solids remaining in the reactor at 150 °C under dynamic vacuum.

Reaction of the Intermediate to 2 with $(CH_3)_2SO_4$. Fused potassium fluoride (0.64 g, 11.0 mmol), 3.0 mL of anhydrous benzonitrile, perfluoroglutaryl fluoride (2.46 mmol), and TMS-CF_3 (5.30 mmol) were added to a 100-mL reactor and allowed to react for 18 h as with **1** above. The volatiles were then removed under dynamic vacuum at 22 °C for 45 min and fractionated through traps at −25 and -196 °C. They were shown by ^{19}F NMR to consist of TMS-F with a trace of CF_3H. Methyl iodide (1.2 mL, 19.3 mmol) was added to the reaction mixture and allowed to stand at 22 °C for 24 h. The volatiles were removed under dynamic vacuum and fractionated through traps at −26, −64, and −196 °C. The −196 °C trap contained an almost quantitative amount of unreacted CH_3I. Dimethyl sulfate (1.5 mL) was then added to the reactor, and an immediate exothermic reaction took place. The reactor was then heated to 110 °C under dynamic vacuum, and the volatiles were collected over 1 h in a −196 °C trap, followed by fractionation through traps at −25, −74, and -196 °C. The −74 °C trap contained 1.06 mmol (43.1%) of the methylated derivative $CF_3(F)C(CF_2)_3CO(OCH_3)CF_3$ (3) of the proposed intermediate alkoxide to **2** (see Discussion).

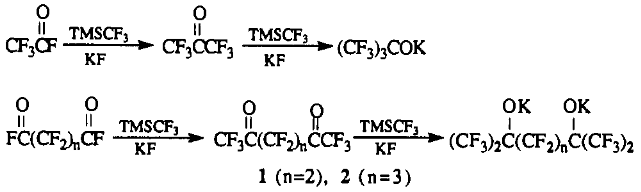
Compound 3 was characterized as follows: IR (2 Torr) 2971 (m), 2866 (m), 1334 (s), 1307 (vs), 1254 (vs), 1217 (vs), 1192 (s). 1168 (s), 1141 (s), 1113 (s), 1044 (s), 1027 (vs), 979 (s), 844 (m), 748 (m), 735 (m), 683 (m), 631 (m) cm^{-1}; NMR $CF_3{}^C(F)^DCCF^{A_1}F^{B_1}CF^{A_2}F^{B_2}CF^{A_3}$-$F^{B_3}CO(OCH_3)^ECF_3{}^F$ ($CDCl_3$, 24 °C) $\delta(^{19}F)$ C −80.4 (3 F, d, m), D −135.7 (1 F, q), A_1 −125.2, B_1 −132.1 (2 F, AB pattern), A_2 −122.3, B_2 −142.3 (2 F, AB pattern), A_3 −126.7, B_3 −130.7 (2 F, AB pattern), F −74.5 (3 F, m), $J_{A^1B^1}$ = 272.7, $J_{A^2B^2}$ = 276.1, $J_{A^3B^3}$ = 255.9 Hz; NMR $\delta(^1H)$ E 3.49 (3 H, s); MS (EI) *m/e* 359 (7.0, $M - F^+$), 347 (2.7, $M - OCH_3{}^+$), 309 (34.6, $M - CF_3{}^+$), 247 (4.2, $CF_3COCF_2CF_2CF_2{}^+$), 231 (6.2, $CF_3CCF_2CF_2CF_2{}^+$), 181 (11.9, $CF_3CCF_2CF_2{}^+$), 162 (17.8, $CF_2C(OCH_3)CF_3{}^+$), 150 (10.3, $CF_3CFCF_2{}^+$), 131 (17.7, $CF_3CCF_2{}^+$), 128 (9.6, $OC(OCH_3)CF_3{}^+$), 100 (26.4, $CF_2CF_2{}^+$), 97 (18.0, CF_3CO^+), 69 (100.0, $CF_3{}^+$), 59 (10.7%, $OCOCH_3{}^+$); MS (CI) *m/e* 379 (27.8, MH^+), 359 (100.0, $MH - HF^+$), 309 (15.0, $M - CF_3{}^+$).

Table I. Crystal Data

	compd	
	4	5
formula	$C_6H_2O_3F_{10}$	$C_7H_2O_3F_{12}$
fw	312.06	362.07
cryst syst	tetragonal	monoclinic
space group	$I\bar{4}2d$ (No. 122)	$C2/c$ (No. 15)
a, Å	15.728(2)	30.748(10)
b, Å		11.611(5)
c, Å	8.459(2)	19.465(8)
β, deg		104.73(3)
V, Å3	2092.3(8)	6721(5)
Z	8	24
D_{calc}, g cm^{-3}	1.98	2.15
μ, mm^{-1}	0.25	0.27
no. of obsd data ($I > 3\sigma(I)$)	342	2064
$R(F_o)$[a]	0.0557	0.1004
$R_w(F_o)$[b]	0.0592	0.1070

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $[\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Scheme I



Reaction of 2, TMS-CF_3, and KF. Potassium fluoride (0.58 g, 10.0 mmol), 2.0 mL of anhydrous benzonitrile, **2** (2.1 mmol), and TMS-CF_3 (4.10 mmol) were combined in a 100-mL reactor as in the preparation of **2**. After 20 h the volatiles were removed by vacuum pumping for 50 min and fractionated through traps at −25 and −196 °C. The contents of the −196 °C trap were further separated through traps at -75, −109, and −196 °C. Tetrafluoroethylene (0.70 mmol) stopped in the −196 °C trap, TMS-F (4.15 mmol) in the −109 °C trap, and the unreacted **2** (1.05 mmol, 52.5%) in the -75 °C trap. Reaction of the solid in the reactor with concentrated H_2SO_4 gave no evidence for the desired 2,6-diol, HO-$(CF_3)_2C(CF_2)_3C(CF_3)_2OH$.

Preparation of the Diol $CF_3(HO)C(CF_2)_2CO(OH)CF_3$ (4). Water (9 μL, 0.50 mmol) was added to a 50-mL flask fitted with a glass–Teflon valve. The flask was cooled to −196 °C and evacuated, and $CF_3(O)C$-$(CF_2)_2C(O)CF_3$ (0.56 mmol) was condensed into the flask by vacuum transfer. The flask was allowed to warm to 22 °C and a nearly quantitative yield of a white solid (**4**) was obtained after 1 h.

^{19}F NMR indicated that the new compound was a mixture of *cis* and *trans* isomers in the ratio of 55:45. NMR [($CD_3C(O)CD_3$, 24 °C)]: *cis*-$CF_3{}^C(HO)^DC(CF^AF^B)_2CO(OH)^DCF_3{}^C$ $\delta(^{19}F)$ C −80.4 (6 F, m), A −120.9, B −132.3 (4 F, AB pattern), J_{AB} = 245.2 Hz; *trans*-$CF_3{}^C(OH)^D$-$CCF^{A_2}F^{B_2}CF^{A_1}F^{B_1}CO(OH)^DCF_3{}^C$ $\delta(^{19}F)$ C −80.0 (6 F, 2 lines), A −126.2, B −130.5 (4 F, AB pattern), J_{AB} = 242.0 Hz. NMR $\delta(^1H)$ of mixture [$CDCl_3$, 24 °C]: D *cis* (2H, s) 4.87; *trans* (2H, s) 4.37. NMR $\delta(^1H)$ of mixture [$CD_3C(O)CD_3$, 24 °C]: D 8.98 (2 H, s). IR (solid/KCl): 3622 (m), 1329 (m), 1249 (vs), 1225 (vs), 1190 (m), 1152 (m), 1073 (m), 1040 (s), 941 (m), 860 (m), 762 (w), 744 (m), 709 (w), 635 (vw), 596 (w) cm^{-1}.

Preparation of the Diol $CF_3(HO)C(CF_2)_3CO(OH)CF_3$ (5). As with 3, 0.50 mmol of H_2O and $CF_3(O)C(CF_2)_3C(O)CF_3$ (0.56 mmol) were allowed to react for 1 h. A quantitative yield of a white solid (**5**) was obtained.

The new compound **5** was shown to exist only in *cis* form by X-ray crystallography and ^{19}F NMR: mp 61–63 °C; IR (solid/KCl) 3608 (m), 1306 (m), 1254 (vs), 1212 (vs), 1089 (s), 920 (m), 839 (w), 447 (w), 685 (w), 644 (w), 574 (w), 537 (w) cm^{-1}; NMR $CF_3{}^C(HO)^DCCF^{A_1}F^{B_1}CF^{A_2}F^{B_2}$-$CF^{A_1}F^{B_1}CO(OH)^DCF_3{}^C$ ($CDCl_3$, 24 °C) $\delta(^{19}F)$ C −81.5 (6 F, m), A_1 −127.4, B_1 -130.8 (4 F, AB pattern);,A_2 −120.2, B_2 −141.4 (2 F, AB

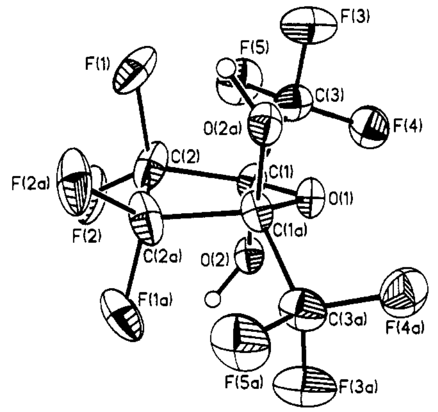


Figure 1. Thermal ellipsoid plot (35% probability) of $C_6H_2O_3F_{10}$ (4). Atoms labeled with "a" are related to unlettered atoms by the following symmetry operation: x, $1.5 - y$, $1.25 - z$.

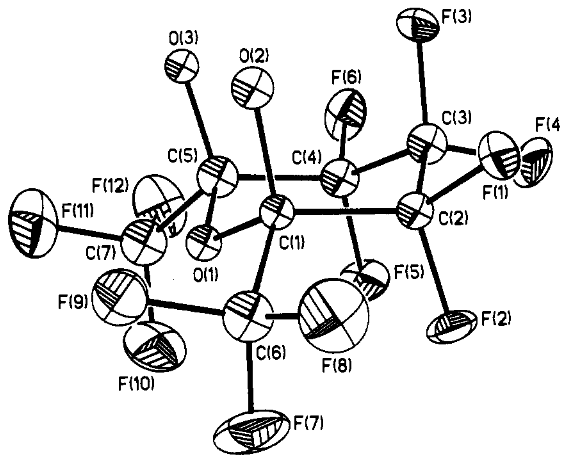
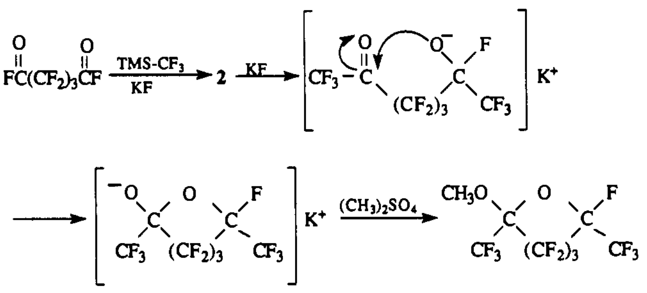
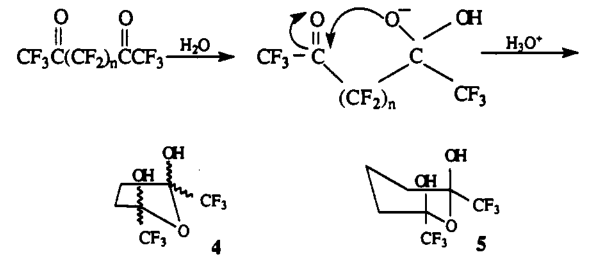


Figure 2. Thermal ellipsoid plot (35% probability) of $C_7H_2O_3F_{12}$ (5).

Scheme II



Scheme III



pattern); NMR $\delta(^1H)$ D 4.59 (2 H, s); $\delta(^{13}C)$ 119.4 (2 C, q $^1J_{F,C}$ = 288.4 Hz), 109.2 (2 C, d,d,t $^1J_{F,C}$ = 279.2, $^1J_{F,C}$ = 263.9, $^2J_{C,F}$ = 24.2 Hz), 107.7 (1 C, d,d,t $^1J_{F,C}$ = 280.7, $^1J_{F,C}$ = 261.5, $^2J_{C,F}$ = 24.4 Hz), 94.6 (2 C, m), $J_{A^1B^1}$ = 274.3, $J_{A^2B^2}$ = 281.1 Hz.

X-ray Crystallographic Analysis. Intensity data for both compounds were measured at -80 ± 1 °C using $\omega/2\theta$ scans ($2\theta_{max}$ = 48° for 4, 45° for 5) on a Nicolet R3mV diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Linear decay corrections were applied to the data for both compounds (15% for 4, 35% for 5). Lorentz and polarization corrections were also applied; however, no absorption correction was deemed necessary. The structures were solved by direct methods and refined by using full-matrix least-squares techniques. For 4, all non-hydrogen atoms were refined anisotropically; the hydroxyl hydrogen atom was placed in an optimized position (d_{O-H} = 0.85 Å), based on its location in a difference Fourier map. For 5, only the fluorine atoms were refined anisotropically, all other non-hydrogen atoms were refined with isotropic thermal parameters, and the hydrogen atoms were not located. The unusually high residual values obtained for 5 are most probably due to the significant crystal decomposition which occurred during the course of data collection. Structure solution, refinement, and the calculation of derived results were performed with the SHELXTL[10] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[11] and the real and imaginary anomalous dispersion corrections were those of Cromer.[12] Relevant crystallographic data are given in Table I.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å$^2 \times 10^3$) for 4

	x	y	z	U_{eq}[a]
F(1)	6396(3)	7644(4)	4217(6)	61(2)
F(2)	6793(3)	8472(3)	6130(9)	68(2)
F(3)	4841(5)	7992(4)	3196(6)	70(2)
F(4)	4158(3)	8909(4)	4601(6)	56(2)
F(5)	5426(4)	9200(3)	3775(8)	66(2)
O(1)	4807(4)	7500	6250	33(2)
O(2)	5284(3)	8828(3)	7023(6)	35(1)
C(1)	5300(4)	8227(4)	5840(8)	29(2)
C(2)	6222(6)	7893(5)	5729(11)	49(3)
C(3)	4921(7)	8588(5)	4325(9)	44(3)
H(1)	5610	8839	7823	86(44)

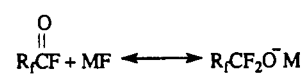
[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Synthesis of Diketones 1 and 2. Trifluoromethylation of diacyl fluorides with CF_3SiMe_3 was expected to proceed in the same ways as with the monofunctional acyl fluorides[1] as shown in Scheme I. We did not anticipate that the extraordinary reactivity of the diketones with fluoride ion and the resultant facile intramolecular cyclization would prohibit the full trifluoromethylation of the acyl fluorides. In the initial stages of this work, we observed that considerable unreacted TMS-CF_3 was present at the end of the reaction when 4 equiv of TMS-CF_3 was used.

Treatment of solid remaining in the reactor with H_2SO_4 as with monofunctional acyl fluorides gave no evidence for the expected diols $(CF_3)_2C(CF_2)_nC(OH)(CF_3)_2$. Subsequently it was recognized that the stoichiometry was 2:1 TMS-CF_3 to the diacyl fluoride and the solid product was probably a cyclic alkoxide which underwent some exchange process in solution. It was reasoned that the reactions of Scheme II were occurring. Support for this was obtained by trapping the intermediate alkoxide by methylation with dimethyl sulfate for n = 3.

For the isolation of the free ketones 1 and 2, heating under dynamic vacuum resulted in the formal 1,4-loss of KF from the alkoxide. In general, fluorinated alkoxides containing an α-fluorine on the alkoxide carbon are unstable and the equilibrium lies to the left depending on conditions.[13]



$$R_f\overset{O}{\overset{\|}{C}}F + MF \longleftrightarrow R_fCF_2O^-M^+$$

In this case, the alkoxide resembles tertiary perfluoroalkoxides,

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(10) Sheldrick, G. M. *SHELXTL, Crystallographic Computing System*; Nicolet Instruments Division: Madison, WI, 1986.

(11) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(12) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(13) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley Interscience: New York, 1973; p 223.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **5**

	x	y	z	U_{eq}[a]
F(1)	1767(4)	3057(9)	8495(5)	43(5)
F(2)	1417(4)	1488(10)	8029(5)	40(4)
F(3)	1027(4)	3942(9)	8719(5)	36(4)
F(4)	899(4)	3288(11)	7637(5)	52(5)
F(5)	501(4)	1433(11)	7946(5)	48(5)
F(6)	234(3)	3931(11)	8359(5)	47(5)
F(7)	1756(5)	−105(12)	9001(7)	70(6)
F(8)	2251(4)	1204(12)	9236(7)	62(6)
F(9)	1988(4)	510(11)	10062(6)	49(5)
F(10)	434(5)	−176(12)	8901(8)	75(7)
F(11)	466(5)	431(13)	9938(7)	72(6)
F(12)	−38(4)	1116(13)	9023(7)	72(6)
F(13)	613(3)	6452(10)	11039(5)	42(4)
F(14)	845(4)	7842(9)	10465(6)	40(4)
F(15)	1467(4)	7391(9)	11640(5)	41(5)
F(16)	1422(4)	5571(9)	11428(5)	33(4)
F(17)	2142(4)	6442(11)	11120(5)	47(5)
F(18)	1764(4)	7821(9)	10518(5)	37(4)
F(19)	456(4)	7325(10)	9099(6)	48(5)
F(20)	305(4)	5540(10)	8919(6)	46(5)
F(21)	59(3)	6444(12)	9692(6)	56(5)
F(22)	1835(4)	5459(11)	8986(5)	47(5)
F(23)	2334(3)	6326(11)	9794(6)	50(5)
F(24)	1778(4)	7278(9)	9169(6)	46(5)
F(25)	678(4)	969(10)	11537(7)	57(5)
F(26)	1113(4)	1138(11)	12606(5)	53(5)
F(27)	1479(5)	−261(10)	11822(6)	65(6)
F(28)	1343(4)	923(11)	10936(5)	51(5)
F(29)	2207(4)	989(10)	11653(6)	50(5)
F(30)	2025(4)	1137(11)	12657(5)	48(5)
F(31)	961(4)	3307(11)	12972(5)	49(5)
F(32)	709(4)	4428(10)	12080(6)	48(5)
F(33)	372(3)	2837(11)	12164(6)	52(5)
F(34)	2267(4)	4482(12)	12202(6)	58(5)
F(35)	2283(4)	3331(11)	13063(5)	48(5)
F(36)	2658(3)	2948(13)	12316(6)	64(6)
O(1)	1133(4)	1118(10)	9320(5)	23(3)
O(2)	1647(4)	2605(11)	9755(6)	28(3)
O(3)	696(4)	2564(10)	9672(5)	23(3)
O(4)	1182(4)	6145(10)	9642(5)	19(3)
O(5)	778(4)	4870(10)	10176(6)	25(3)
O(6)	1726(4)	4836(10)	10241(6)	23(3)
O(7)	1491(3)	3174(10)	12133(5)	20(3)
O(8)	900(4)	2998(11)	11139(6)	27(3)
O(9)	1843(4)	3026(10)	11196(5)	20(3)
C(1)	1516(6)	1714(15)	9259(8)	20(4)
C(2)	1436(6)	2299(16)	8526(9)	24(4)
C(3)	995(6)	2958(18)	8327(9)	32(5)
C(4)	594(6)	2281(18)	8439(9)	32(5)
C(5)	704(7)	1727(18)	9181(10)	35(5)
C(6)	1881(7)	820(19)	9373(10)	39(5)
C(7)	386(8)	745(21)	9231(11)	48(6)
C(8)	823(6)	5974(16)	9985(9)	25(4)
C(9)	918(6)	6726(17)	10665(9)	28(5)
C(10)	1379(7)	6572(19)	11107(10)	35(5)
C(11)	1744(7)	6754(18)	10703(10)	33(5)
C(12)	1628(6)	5965(16)	10014(8)	22(4)
C(13)	411(7)	6321(19)	9414(10)	39(5)
C(14)	1903(7)	6258(18)	9486(9)	30(4)
C(15)	1060(6)	2738(15)	11842(8)	18(4)
C(16)	1059(7)	1424(19)	11902(10)	38(5)
C(17)	1453(7)	791(18)	11651(10)	30(5)
C(18)	1884(7)	1443(19)	11962(10)	34(5)
C(19)	1871(6)	2729(16)	11895(8)	19(4)
C(20)	767(7)	3328(18)	12284(10)	35(5)
C(21)	2266(7)	3367(18)	12371(10)	33(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Bond Distances (Å) and Angles (deg) for **4**[a]

	Distances		
F(1)–C(2)	1.366(10)	F(2)–C(2)	1.324(9)
F(3)–C(3)	1.344(10)	F(4)–C(3)	1.323(12)
F(5)–C(3)	1.332(11)	O(1)–C(1)	1.424(7)
O(2)–C(1)	1.376(8)	C(1)–C(2)	1.545(11)
C(1)–C(3)	1.523(11)	C(2)–C(2A)	1.519(16)
	Angles		
C(1)–O(1)–C(1A)	114.1(7)	O(1)–C(1)–O(2)	111.3(5)
O(1)–C(1)–C(2)	104.7(5)	O(2)–C(1)–C(2)	107.1(6)
O(1)–C(1)–C(3)	106.9(6)	O(2)–C(1)–C(3)	110.4(6)
C(2)–C(1)–C(3)	116.3(7)	F(1)–C(2)–F(2)	107.5(7)
F(1)–C(2)–C(1)	110.1(7)	F(2)–C(2)–C(1)	112.9(6)
F(1)–C(2)–C(2A)	108.0(8)	F(2)–C(2)–C(2A)	114.3(7)
C(1)–C(2)–C(2A)	104.0(4)	F(3)–C(3)–F(4)	107.9(8)
F(3)–C(3)–F(5)	108.2(7)	F(4)–C(3)–F(5)	109.1(7)
F(3)–C(3)–C(1)	111.9(7)	F(4)–C(3)–C(1)	110.4(6)
F(5)–C(3)–C(1)	109.3(8)		

[a] Atoms labeled with "A" are generated by the following symmetry operation: x, $1.5 - y$, $1.25 - z$.

Table V. Bond Distances (Å) and Angles (deg) for **5**

	Distances		
F(1)–C(2)	1.357(22)	F(2)–C(2)	1.342(21)
F(3)–C(3)	1.362(22)	F(4)–C(3)	1.356(20)
F(5)–C(4)	1.353(22)	F(6)–C(4)	1.315(23)
F(7)–C(6)	1.297(25)	F(8)–C(6)	1.311(27)
F(9)–C(6)	1.347(22)	F(10)–C(7)	1.275(29)
F(11)–C(7)	1.382(25)	F(12)–C(7)	1.334(27)
O(1)–C(1)	1.398(21)	O(1)–C(5)	1.458(23)
O(2)–C(1)	1.402(20)	O(3)–C(5)	1.368(23)
C(1)–C(2)	1.542(23)	C(1)–C(6)	1.503(28)
C(2)–C(3)	1.521(26)	C(3)–C(4)	1.523(29)
C(4)–C(5)	1.538(26)	C(5)–C(7)	1.522(33)
	Angles		
C(1)–O(1)–C(5)	119.1(13)	O(1)–C(1)–O(2)	114.1(14)
O(1)–C(1)–C(2)	110.9(12)	O(2)–C(1)–C(2)	105.2(14)
O(1)–C(1)–C(6)	105.0(15)	O(2)–C(1)–C(6)	109.6(13)
C(2)–C(1)–C(6)	112.2(16)	F(1)–C(2)–F(2)	108.5(15)
F(1)–C(2)–C(1)	112.5(13)	F(2)–C(2)–C(1)	109.1(15)
F(1)–C(2)–C(3)	107.0(15)	F(2)–C(2)–C(3)	107.3(13)
C(1)–C(2)–C(3)	112.3(16)	F(3)–C(3)–F(4)	106.5(15)
F(3)–C(3)–C(2)	110.2(14)	F(4)–C(3)–C(2)	110.4(16)
F(3)–C(3)–C(4)	107.5(16)	F(4)–C(3)–C(4)	107.9(14)
C(2)–C(3)–C(4)	114.0(16)	F(5)–C(4)–F(6)	108.3(13)
F(5)–C(4)–C(3)	107.9(16)	F(6)–C(4)–C(3)	112.0(17)
F(5)–C(4)–C(5)	108.5(16)	F(6)–C(4)–C(5)	109.2(16)
C(3)–C(4)–C(5)	110.8(14)	O(1)–C(5)–O(3)	113.1(13)
O(1)–C(5)–C(4)	110.5(16)	O(3)–C(5)–C(4)	108.6(16)
O(1)–C(5)–C(7)	101.0(16)	O(3)–C(5)–C(7)	111.1(18)
C(4)–C(5)–C(7)	112.5(15)	F(7)–C(6)–F(8)	108.5(19)
F(7)–C(6)–F(9)	107.3(17)	F(8)–C(6)–F(9)	106.7(15)
F(7)–C(6)–C(1)	112.7(16)	F(8)–C(6)–C(1)	112.9(18)
F(9)–C(6)–C(1)	108.4(17)	F(10)–C(7)–F(11)	105.4(19)
F(10)–C(7)–F(12)	110.3(18)	F(11)–C(7)–F(12)	107.5(20)
F(10)–C(7)–C(5)	115.9(22)	F(11)–C(7)–C(5)	107.8(16)
F(12)–C(7)–C(5)	109.5(19)		

which are stable and highly covalent.[14] The observed 1,4-elimination of KF in this work can be viewed as a reversal of the formation process. The alkoxide is stable in the solid state, but for both $n = 2$ and 3, ^{19}F NMR in CH_3CN indicates an equilibrium in solution. Related cyclic alkoxides intermediates have been proposed by others involving diacyl fluorides,[15,16] but the presence of an α-fluorine on the alkoxide carbon in these cases renders these species much less stable than that observed here.

Reaction of 1 and 2 with H_2O. The very high reactivity of compounds **1** and **2** toward nucleophiles was further demonstrated by their reaction with water. The facile intramolecular cyclization leads to the cyclic 2,5- and 2,6-diols for **1** and **2**, respectively (Scheme III).

Compound **5** shows a single *cis* isomer in solutions by NMR, and **4** shows a 55:45 mixture of *cis/trans* isomers. The crystal

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structure of **5** confirms the *cis* isomer. For compound **4** the crystal selected for the structure determination was the *trans* isomer. This may have been due to chance, or perhaps only the *trans* isomer was present in the solid state. A crystal grown under the same conditions as that for the structure determination showed a 60:40 *trans* to *cis* ratio in $CDCl_3$ solution by ^{19}F NMR, which on standing for 12 h at 22 °C changed to a 40:60 ratio. This result may imply that *trans*-**4** is the thermodynamically favored stereoisomer in the solid state, but further work is needed to confirm this and the mechanism for the isomerization of **4**.

From the observed structures it can be seen that the *cis*(ee) isomer of **5** minimizes the repulsion between the CF_3 groups and the C-4 fluorines. In the *trans* isomer of **5** considerable steric repulsion would probably exist between an axial CF_3 group and an axial fluorine at C-4, which may account for the presence of only the *cis* isomer. In **4** the nearly planar five-membered ring can easily accommodate the CF_3 groups in both *cis* and *trans* confirmations.

As expected compounds **4** and **5** are very acidic. The chemical shift of the hydroxy protons for **5** in $CDCl_3$ is δ 4.59 compared to 3.4 and 3.7 for perfluorinated tertiary alcohols.[1,17] Titration of **5** with aqueous NaOH gave a pK_1 of 5.4, which is the same as that reported for $(CF_3)_3COH$[18] and more acidic than that for perfluoropinacol (5.93).[7] For **4** in $CDCl_3$ the δ(H) values are similar at 4.87 (*cis*) and 4.37 (*trans*) with assignments based on the relative areas compared with the isomer ratio determined from ^{19}F NMR. In acetone-d_6, both **4** and **5** show single broad peaks near $\delta(^1H)$ 9.0, indicating protonation of acetone by the diol and proton exchange.

Molecular Structures of 4 and 5. Thermal ellipsoid plots of **4** and **5** are shown in Figures 1 and 2, respectively. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables II and III; selected bond distances and angles for **4** are given in Table IV and for **5** are given in Table V. The *trans* isomer of **4** crystallizes in the tetragonal space group $I\bar{4}2d$ with eight molecules per unit cell. The asymmetric unit consists of one-half molecule, which is situated about a crystallographic 2-fold axis passing through the ring oxygen atom and the midpoint of the carbon–carbon bond. The crystal packing is dominated by hydrogen bonding between hydroxyl groups of adjacent molecules ($O(2)\cdots O(2')$ = 2.802(6) Å; $H(1)\cdots O(2')$ = 2.44 Å; $O(2)-H(1)\cdots O(2')$ = 106°). Spiral columns of H-bonded molecules run parallel to the *c*-axis; adjacent molecules in the spiral are related by $\bar{4}$ sites which lie between translationally related (*I*-centering) columns. Compound **5** crystallizes in the monoclinic space group with three molecules per asymmetric unit, for a total of 24 molecules per unit cell. These molecules are associated into a hydrogen-bonded trimer (Figure 3) involving the hydroxyl groups ($O\cdots O_{avg}$ = 2.79(4) Å). Although the trimer has local 3-fold symmetry, the trimers do not pack with this symmetry. The cavity formed at the center of each trimer is partially filled by a trifluoromethyl group from the trimer directly above it and by the trimer directly below it. This interaction prevents the 3-fold rotation axis passing through the center of each trimer from relating adjacent trimers, thus breaking the symmetry.

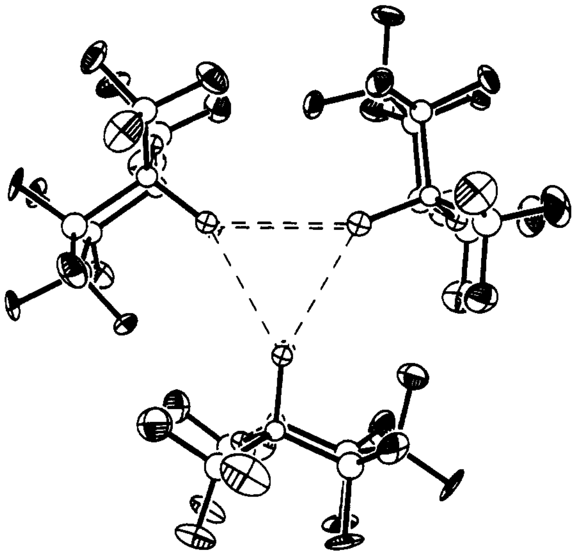

Figure 3. Hydrogen-bonded trimer of molecules of **5**.

Conclusion

The practical synthesis of new perfluorodiketones via nucleophilic trifluoromethylation of diacyl fluorides has been demonstrated. The high reactivity of these diketones with nucleophiles is evident by their reactions with KF and water. This high reactivity arises in part by the facile intramolecular cyclization of the intermediate to favorable five- and six-membered furan and pyran derivatives, respectively. Extension of these reactions to many other substrates of varying nucleophilicities is possible and this work is in progress.

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Supplementary Material Available: Complete listings for **4** and **5** of crystallographic data, bonding distances and angles, and anisotropic thermal parameters and figures showing packing diagrams and molecular plots (of molecules two and three for compound **5**) and observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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