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SOME APPROACHES TO THE SYNTHESIS OF FLUORINATED ALCOHOLS AND ESTERS.

I. COMPLETELY FLUORINATED ESTERS FROM THE HUNSDIECKER REACTION OF SILVER F-ALKANOATES WITH IODINE

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SUMMARY

A completely fluorinated ester of the type $R_FCO_2CF_2R_F'$ was obtained from reaction of silver 3,6,9-trioxa-F-undecanoate and iodine with a diluent at 130°. This new substance resembled closely the previously prepared 1,1-dichloro-F-alkyl esters and was hydrolytically and thermally labile. Substitution products, R_FCOY (Y = nucleophile) and pyrolysis products, R_FCOF and $R_F'COF$ were isolated and characterized. It appears probable that the acyl hypoiodite and the iodo-F-alkane reacted by an S_Ei-type process to give the completely fluorinated ester.

INTRODUCTION

Reaction of silver F-alkanoates with iodine is often used to prepare iodo-F-alkanes. Indeed, Professor Miller used this reaction as a step in the synthesis of C_3F_7ZnI [1]. The mechanism of the Hunsdiecker reaction, as it is called, is known in most of its details [2,3]; the silver salt reacts with iodine to give an acyl hypoiodite that normally decomposes by a free radical process to $RCOO^\bullet$, and then to $R^\bullet$. Capture of the alkyl radical by iodine gives RI. The hypoiodite also has ionic properties; Henne and Zimmer [4] used $CF_3CO_2^-\ I^+$ to iodinate toluene in the ring. The intermediacy of RCO_2I has been confirmed by Barton, et al. in a different context [5]. While fluorinated acids provide iodo-F-alkanes in high yield (92-95%), unfluorinated silver alkanoates with iodine give significant amounts of esters RCOOR, by ionic displacement of $RCOO^-$ on RI;

this is known as the Simonini reaction [2,6]. However, Hauptschein and v. Grosse found that completely fluorinated esters were not obtained by heating of C_3F_7I and C_3F_7COOAg at 275-325°, but gave only $CF_3(CF_2)_4CF_3$. Thus, $C_3F_7^{\cdot}$ and $C_3F_7COO^{\cdot}$ do not couple under these conditions. No reaction occurred at 220° [7]. This has been attributed to the very weak nucleophilicity of R_FCOO^- and the inertness of $-CF_2I$ to S_N2 or S_N2-like displacement reactions [6]. Nevertheless, Hauptschein, et al [8] found that silver 1,5-pentanedioate with iodine gave the perfluorinated lactone, F-γ-butyrolactone (44-56 %) and a lesser amount of 1,3-diiodo-F-propane (10-18 %). Accordingly, it must not be supposed that oxygen substitution cannot take place at the $-CF_2I$ end of the molecule. It is the purpose of this paper to support this possibility.

Until recently, completely fluorinated esters had not been discovered [9,10]; of those derived from perfluorinated alcohols, only $CF_3CO_2CF_3$ was known [11]. Esters of fluoro-alcohols lacking alpha-fluorine atoms had been prepared [12,13,14], and with the recent isolation of the very instable CF_3OH [15], a new chapter on the subject can be written. However, back in 1962, the author obtained higher esters of the type $R_FCO_2R_F'$ as a product from the Hunsdiecker reaction, and it is now possible to disclose these previously unreported results [16]. Prior to this time Brace and McCormack reported the synthesis of quite analogous compounds of the structure $R_FCO_2CCl_2R_F'$ [17]; the similarity in structure and properties of these related compounds greatly facilitated the identification of the new 1,1-difluoro esters.

RESULTS AND DISCUSSION

To provide a basis for understanding the new 1,1-difluoro esters, the work with 1,1-dichloro esters will be briefly summarized. These 1,1-dichloro esters were formed by photochlorination of 1,1-dihydryl-F-alkyl esters. For example, $Cl(CF_2)_4CO_2CCl_2(CF_2)_4Cl$ was thus obtained in 97.6 % of theory. This ester was pyrolyzed at 214° in a spinning band column to give two moles of $Cl(CF_2)_4COCl$; a catalytic amount of NaF in tetramethylene sulone (TMS) lowered the temperature to 100°. Exchange of Cl by F occurred either by using two moles of NaF in TMS or by oxidative fluorination with CoF_3 at 150°. Reaction of 1,1-dichloro esters with nucleophiles gave an essentially quantitative yield of the corresponding acid derivatives, as summarized in Chart I.

Of special interest was the ester exchange of $\mathrm{Cl(CF_2)_4CO_2CCl_2(CF_2)_2CF_3}$ with $\mathrm{H(CF_2)_4CH_2OH}$ at 144-150°. The products, $\mathrm{Cl(CF_2)_4CO_2CH_2(CF_2)_4H}$ (87 %) and $\mathrm{CF_3(CF_2)_2COCl}$ (100 %), showed that carbonyl addition and displacement reaction, and not thermal decomposition followed by esterification had occurred. However, the transitory 1,1-dichloro alcohol, $\mathrm{CF_3(CF_2)_2CCl_2OH}$ decomposed to $\mathrm{CF_3(CF_2)_2COCl}$ and HCl, and could not be isolated under these conditions. In principle this would be possible if displacement can be done using a limited amount of a nucleophile at a lower temperature. It may be noted that ammonia reacted vigorously at 0°, water at 25° and ethanol at 62°. In these particular cases an excess of reagent was employed, and of course, reacted with the mole of acid chloride that was generated by decomposition of the 1,1-dichloro alcohol.

CHART I. Reactions of 1,1,ω-Trichloro-F-alkyl ω-chloro-F-alkanoates

$$\begin{array}{lll}
 & \xrightarrow{\text{Heat, 214°}} & 2\ \mathrm{Cl(CF_2)_nCOCl} \\
 & \xrightarrow{\text{NaF, TMS,100°}} & 2\ \mathrm{Cl(CF_2)_nCOCl} \\
 & \xrightarrow{\mathrm{NH_3,\ C_6H_6,\ 0°}} & 2\ \mathrm{Cl(CF_2)_nCONH_2} + 2\ \mathrm{NH_4Cl} \\
\mathrm{Cl(CF_2)_nCO_2CCl_2(CF_2)_nCl} & \xrightarrow{\mathrm{H_2O,\ 25°}} & 2\ \mathrm{Cl(CF_2)_nCO_2H} + 2\ \mathrm{HCl} \\
(n \doteq 4,6,8) & \xrightarrow{\text{EtOH, 62°}} & 2\ \mathrm{Cl(CF_2)_nCO_2Et} + 2\ \mathrm{HCl} \\
 & \xrightarrow[\text{4h}]{\text{CoF , 150°,}} & 2\ \mathrm{Cl(CF_2)_nCOF} + \mathrm{Cl_2} \\
 & \xrightarrow[\text{150°, 3 h}]{\text{NaF, TMS,}} & 2\ \mathrm{Cl(CF_2)_nCOF} + 2\ \mathrm{NaCl}
\end{array}$$

$$\begin{array}{lcl}
\mathrm{Cl(CF_2)_4CO_2CCl_2(CF_2)_2CF_3} & & \mathrm{Cl(CF_2)_4CO_2CH_2(CF_2)_4H}\ (87\ \%) \\
+ & \xrightarrow{\text{144-150°}} & \\
\mathrm{H(CF_2)_4CH_2OH} & & \mathrm{CF_3(CF_2)_2COCl}\ (100\%) + \mathrm{HCl}
\end{array}$$

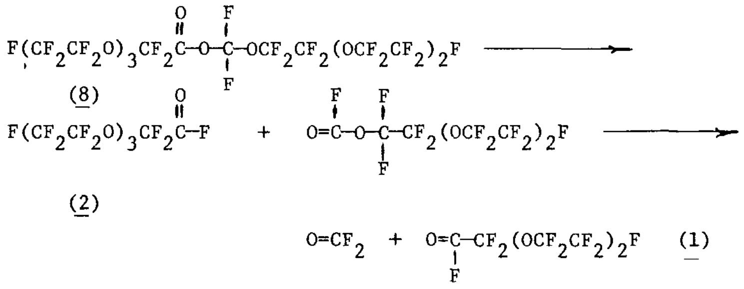
The important findings from this prior work were: 1) 1,1-dichloro esters were thermally labile above 140-200°; 2) the *alpha*-chlorine atoms were only indirectly substituted by nucleophiles; and 3) oxidative substitution of chlorine by fluorine did not give a stable (at 150°) 1,1- difluoro ester.

Hunsdiecker Reaction of Silver 3,6,9-Trioxa-F-undecanoate with Iodine.

In view of the many interesting reactions of 1-iodo-F-alkanes (R_FI), we wished to prepare the novel $F(CF_2CF_2O)_nCF_2I$ from the series of acids discovered by Warnell [18]. Telomerization of tetrafluoroethylene oxide with CF_3COF gave $F(CF_2CF_2O)_nCF_2COF$ (n = 1,2,3,4). The corresponding acids and their silver salts were synthesized. Heating of $F(CF_2CF_2O)_3$-CF_2CO_2Ag (5) with iodine at 150° (conditions that routinely gave 90-95 % of 1-iodo-F-alkanes), surprisingly, gave only 35 % conversion to $F(CF_2CF_2O)_3CF_2I$ [2,3]. The *acid*, $F(CF_2CF_2O)_3CF_2COOH$ (4), 30 % recovery, was obtained after work-up. The silver salt, of course, was not affected by water; thus, 4 had been formed in some obscure fashion. Heating of $F(CF_2CF_2O)_nCF_2COF$ with KI at 200-220° for 10 h gave no reaction [3, 19].

Subsequent experiments showed that 5 reacted with iodine at 25°, but gave no iodo-alkane 7. Passing of iodine vapors over 5 in a column at 150° gave a very vigorous reaction and produced a complex mixture of volatile products including $F(CF_2CF_2O)_2CF_2I$ (6), the homolog 7, $F(CF_2CF_2O)_2COF$ (1), $F(CF_2CF_2O)_3CF_2COF$ (2), and a new substance, the 1,1-difluoro ester, $F(CF_2CF_2O)_3CF_2CO_2CF_2O(CF_2CF_2O)_2CF_2CF_3$ (8). When a diluent was employed to moderate the reaction of 5 and iodine in a shaker tube at 130°, the desired iodo-F-alkane 7 was obtained in 67 % yield (using F-cyclobutane), or in 58 % yield (using 1,3-F-dimethylcyclobutane). In the latter case pyrolysis and hydrolysis products of 8 were isolated: 1, 10 % and 4, 12 %, besides 8, bp 65-66°/2.0 mm, 18 % yield. The 1,1-difluoro ester 8 was characterized by IR spectrum ($\nu C{=}O$, 1845 cm^{-1}), GC retention time (different from and longer than that of 1, 2, or 4), elemental analysis, and mass spectrum. The molecular ion (878) was beyond the operating range of the instrument, and injection was made into a manifold at about 200°. Under these conditions pyrolysis of 8 to acid fluorides 1 and 2 occurred and the mass spectrum was identical to that of these substances. Some characteristic IR carbonyl stretching frequencies are listed in Table I for substances of interest.

Thermal cleavage of 8 was analogous to that of 1,1-dichloro esters (Chart I, above). However, the oxadifluoro group *alpha* to the carbonyl of the acid fluoride obtained from the alkyl portion of ester 8 was itself susceptible to splitting off. Accordingly, pyrolysis products of 8 included two different acid fluorides, 1 and 2, and carbonyl fluoride. Each



$$F(CF_2CF_2O)_3CF_2\overset{O}{\overset{\|}{C}}{-}O{-}\underset{F}{\overset{F}{C}}{-}OCF_2CF_2(OCF_2CF_2)_2F \;(8) \longrightarrow$$

$$F(CF_2CF_2O)_3CF_2\overset{O}{\overset{\|}{C}}{-}F \;(2) + O{=}C{-}O{-}\underset{F}{\overset{F}{C}}{-}CF_2(OCF_2CF_2)_2F \longrightarrow$$

$$O{=}CF_2 + O{=}\underset{F}{C}{-}CF_2(OCF_2CF_2)_2F \;(1)$$

nucleophile similarly afforded three substances by reaction with the 1,1-difluoro ester 8. Thus, reaction with water gave $F(CF_2CF_2O)_2CF_2CO_2H$ (3), the acid 4, and carbonic acid. Methanol and 8 gave quantitatively $F(CF_2CF_2O)_2CF_2CO_2Me$ (10), $F(CF_2CF_2O)_3CF_2CO_2Me$ (11) and $(CH_3O)_2C{=}O$. Ammonia and 8 gave a mixture of amides that contained $F(CF_2CF_2O)_nCF_2CONH_2$ (n = 2,3) and urea. The pure amide n = 3 was prepared from the methyl ester 11 and ammonia and was suitably characterized as $F(CF_2CF_2O)_3CF_2CONH_2$ (12).

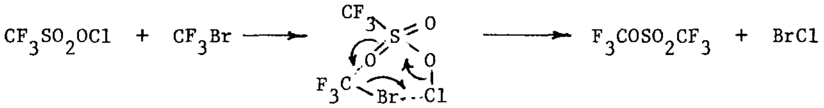
TABLE 1

Infrared Stretching Frequencies of 1,1-Difluoro Ester 8 and Other Compounds

Structure of Substance	Code No.	ν (C=O) Microns	cm^{-1}
$F(CF_2CF_2O)_3CF_2CO_2CF_2(OCF_2CF_2)_2OCF_2CF_3$	8	5.42	1845
$Cl(CF_2)_4CO_2CCl_2(CF_2)_4Cl$	--	5.45	1835
$F(CF_2CF_2O)_3CF_2COF$	2	5.26	1901
$F(CF_2CF_2O)_3CF_2COOH$	4	5.62	1779
$F(CF_2CF_2O)_3CF_2CO_2CH_3$	11	5.60	1786
$CF_3CO_2CCl_2CF_2Cl^a$	--	5.45	1836
$CF_3CF_2CF_2CO_2CF_2CF_2Cl^a$	--	5.45	1837

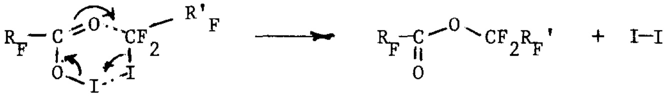
[a] See reference [9]

Mechanistic Considerations. Formation of a 1,1-difluoro ester in the reaction of R_FCOOAg and iodine logically could involve the acyl hypoiodite. The mechanism most likely to obtain is that recently proposed by Katsuhara and DesMarteau for similar reaction of CF_3SO_2OCl with F-alkyl bromides [20]. The 'positive' chlorine of the hypochlorite is transferred to "negative" halogen of the bromo-F-alkane in a concerted S_Ei-type process [20]. Tari



and DesMarteau [15] and Schack and Christe [10] have extended this concept to the addition of acyl hypochlorites to alkenes, including tetrafluoroethylene. These reactions afforded a large number of 1,1-difluoro esters and proved the generality of the postulated concerted polar addition mechanism. It has strong precedent in the well known Prevost reaction [2].

It is probable, therefore, that fluorinated acyl hypoiodite under proper conditions (lower reaction temperature, diluent present) reacted similarly to give the 1,1-difluoro ester. This point of view is consistent



with all prior facts and would account for the present results. It is hoped that future investigation will prove this to be a fruitful suggestion.

EXPERIMENTAL

2,5,8-Trioxa-1-Iodo-F-Decane (7) and 2,5,8-Trioxa-1-F-Decyl 3,6,9-Trioxa-F-Undecanoate (8) by the Hunsdiecker Reaction

(a) Preparation of 3,6-dioxa-F-octanoic acid (3) and 3,6,9-trioxa-F-undecanoic acid (4)

$F(CF_2CF_2O)_2CF_2COF$ (1), bp 66.5°, and $F(CF_2CF_2O)_3CF_2COF$ (2), bp 105-106°, distilled in a 3-ft platinum spinning band column (Column A), were obtained from the telomerization of tetrafluoroethylene oxide with trifluoroacetyl fluoride in $HCF_2CF_2CH_2Cl$ [18]. GC: 95-97.5% pure; IR: ν C=O 1887 cm^{-1}. Samples were stored in polyethylene bottles under nitrogen. Hydrolysis to acids 3 and 4 was conveniently done as follows: 1 (46.4 g, 0.10 mole) and water (1.8 g, 0.10 mole) were stirred at 0° by a "Teflon covered magnet bar in a polyethylene bottle, the HF purged with nitrogen to a 1-inch by 18-inch plastic cylinder containing 12 inches of sodium fluoride (1/8 inch pellets). The mixture was allowed to warm to 35° during

1 h. IR: ν C=0 1790 cm^{-1} only (COOH). 1,1,2-Trichloro-1,2,2-trifluoroethane ('F-113', 50 ml) and dry silica gel (10.0 g, 0.16 mole, 14-20 mesh size) were added (exotherm) and stirring continued for 3 h, with evolution of SiF_4 gas. Distillation (Column A) gave 4, bp 70°/5 mm or 85°/10 mm, d^{25}_{4}1.6915; 40.2 g, 90% of theory. A larger scale reaction gave 93% of 4. Analysis: Found: C, 20.8; H, 0.2; F, 62.0 %. $C_8F_{15}O_5H$ requires C, 20.8; H, 0.20; F, 61.7 %. $F(CF_2CF_2O)_2CF_2COOH$ (3), bp 64.5°/11 mm, d^{25}_{4}1.6675; 71% yield; and sodium 3,6-dioxa-F-octanoate (14 %), mp 76-79°, were obtained in similar fashion when sodium fluoride was used in place of silica gel to react with HF. Analysis: Found: C, 21.0; H, 0.29; F, 58.3 %. $C_6F_{11}O_4H$ requires C, 20.82; H, 0.29; F, 60.39 %.

(b) Silver 3,6,9-trioxa-F-undecanoate (5)

$F(CF_2CF_2O)_3CF_2COOH$ (4, 92.0 g, 0.200 mole) was added during 1.5 h at 40° to freshly precipitated Ag_2O (from 34.0g, 0.200 mole of silver nitrate and 8.0 g, 0.20 mole of sodium hydroxide in 200 ml of water and washed by decantation 10 times). After 2 h at 40-58°, 0.02 mole of Ag_2O and 1.4 g of 4 were added to bring the pH to 7. After 10 minutes at 60°, the mixture was cooled to 10°, and solid 5 was collected and washed 4 times with water on a Buchner funnel. 5 (nc) was dried for 2 days in a vacuum desiccator (P_2O_5) to give 110.8 g, 96% of theory; mp, sinter 165°, 169-173°. An ether solution of 5 was filtered and evaporated, then dried over P_2O_5; mp, sinter 127°, 157-166°. Analysis: Found: C,17.1; F, 50.1; Ag, 19.6 %. $C_8F_{15}O_5Ag$ requires C, 16.88; F, 50.09; Ag, 19.0 %.

(c) Hunsdiecker reaction of silver 3,6,9-trioxa-F-undecanoate (5)

A 'Hastelloy C'-lined 400 ml shaker tube was charged with 5 (60.0 g, 0.105 mole) and iodine (27.9 g, 0.110 mole) and heated to 150° while shaking for 15 h. The tube was vented at 25° and the solid slurry (68.2 g) rinsed out with "F-113" (25 ml). A preliminary distillation gave volatile products containing 2 and 7. The solid contained some fluoride. Analysis: Found: F, 1.34. Iodine in the distillate was washed out with 5 ml of 5% sodium bisulfite solution. The colorless liquid was dried ($MgSO_4$) and distilled (Column A): 7, (nc), bp 60°/85 mm, or bp 72°/108 mm, n^{25}_{D} less than 1.300; 18.9 g, 35% of theory; and acid 4 (probably from 2, by hydrolysis), bp 76°/8 mm, 14.0 g, 30 % recovery. Analysis: Found (7): C, 15.6; F, 52.5; I, 22.0 %. $C_7F_{15}O_3I$ requires C, 15.5; F, 52.4; I, 23.3 %.

Subsequent experiments showed that placing 5 and iodine in a jar and allowing the mixture to stand for 1 day at 25° caused extensive decomposition. Heating to 100° for 8 h and distillation gave no 7, but washing the residue with water gave the acid 4 (60% recovery). Passing iodine vapors over 5 in a column at 150° gave vigorous reaction and GC/MS analysis of the product mixture showed that $F(CF_2CF_2O)_2CF_2I$ (6), 7, $F(CF_2CF_2O)_2CF_2COF$ (1) $F(CF_2CF_2O)_3CF_2COF$ (2) and the new ester 8 were formed (see below for the isolation of 8).

(d) Hunsdiecker reaction of 5 with diluent present

Silver 3,6,9-trioxa-F-undecanoate (5, 28.7 g, 0.0500 mole, recrystallized twice from cyclohexane-benzene, mp, sinter 160°, 166-171.5°), iodine (13.3 g, 0.055 mole) and F-cyclobutane ("FC-318", 10.0 g) were charged to the shaker tube, heated at 130° for 5 h, and vented at 25° into a -70° trap. The liquid-solid slurry (37 g), rinsed out with "F-113", was distilled (no column) to give fraction I, bp 54-82°/103 mm, 15.4 g; and fraction II, bp 50-83°/ 10 mm, 4.8 g; leaving a residue, 10.0 g, of silver salts. Analysis: Found: Ag, 44.5; I, 54.1; F, 1.3 %. AgF requires Ag, 45.6; I, 54.0 %. Fraction I contained 7, 90 %; 1, 1.1 %; 2, 1.4 %; and ester 8, 1.6 %. IR: ν C=O 1901 and 1887 cm^{-1} (COF); 1845 cm^{-1}(ester, 8); 1779 cm^{-1} (COOH). II contained 7, 85.6 %; 1, 1.4 %; 2, 2.65 %; and 8, 9.9 %. Analysis was by GC/MS. The total yield of 7 was 67 % of theory, and of 8, 3.3 % of theory. The 1779 cm^{-1} band was likely formed during loading of the IR cell.

In a second experiment the shaker tube was charged with 5 (59.0 g, 0.10 mole), iodine (28.0 g, 0.11 mole) and 1,3-F-dimethylcyclobutane (20 g), purged with nitrogen, and heated to 130° for 5 h. Worked-up as above, the product mixture gave (distillation in Column A): 7, fractions II-VI, bp 68-69°/108 mm and 71-69°/98 mm, 31.2 g, 58 % of theory; 4, fractions VII and VIII, bp 71-74°/5.4 mm, 6.0 g, 12 % recovery; and 1,1-difluoro ester,8(nc), IX,bp 65-66°/2.0 mm, n^{25}_{D}less than 1.300, 8.2 g, 18 % of theory; hold-up in column, 0.4 g, mostly 8. The trap liquid and fraction I contained 1 (estimated 10 % of theory) and solvent. The residue was 3.1 g of heavy oil. IR: fraction IX, ν C=O 1845 cm^{-1} only. GC analysis of 1, 2 and 8 on the same column (Dow Corning Silicone oil 200, temperature programmed from 50-150°) gave: 1, retention time, 113 sec; 2, 188 sec; and 8, 398 sec. The mass spectrum of 8 showed only the same lines as in 1 and 2; the molecular ion (878) was beyond the range of the instrument under the operating conditions used. The sample was injected into a manifold at about 200° and was therefore pyrolyzed to the acid fluorides. These data support the structure $F(CF_2CF_2O)_3CF_2COOCF_2(OCF_2CF_2)_2OCF_2CF_3$ for 8. Analysis: Found: C, 20.8; F, 65.4; H, less than 0.1 %. $C_{15}F_{30}O_8$ requires C, 20.5; F, 64.9 %. 8 was hydrolytically and thermally unstable. A sample of 8 kept for two weeks in a vial showed both acid and ester carbonyl bands in the IR.

Nucleophilic substitution reactions of 1,1-difluoro ester 8

(a) Reaction with ammonia

In a 50-ml flask fitted with a gas inlet tube and drying tube was placed 8 (0.68 g, 0.40 ml, 0.77 mmole) and 20 ml of dry ether, while purging with nitrogen. When ammonia was admitted, white fumes appeared and the temperature rose from 25 to 31° during 10 minutes. Stirring was continued for 1 h at 22°; then ether was evaporated, the white solid extracted with water, and taken up in "F-113". Evaporation of "F-113" gave $F(CF_2CF_2O)_nCF_2$-$CONH_2$, n = 2,3; wt. 0.46 g, 75 % of theory; mp, sinter below 40°, 40-44° (dried over P_2O_5 in vacuo). $F(CF_2CF_2O)_3CF_2CONH_2$ (12) was prepared in similar manner from $F(CF_2CF_2O)_3CF_2COOCH_3$ (11, nc, 4.26 g), giving 12 (nc), 4.0 g, 96.9 % of theory, mp 58-59.5°. From a comparison of mp it was evident that the product from 8 was a mixture of amides. Analysis: Found (12): C, 21.0; H, 0.54; F, 63.3; N, (Kjeldahl), 2.0 %. $C_8F_{15}H_2NO_4$ requires C, 20.92; H, 0.42; F, 61.8; N, 3.0 %.

(b) Methanolysis

Ester 8 (1.18 g, 1.27 mmole) and methanol (0.081 g, 2.5 mmole) were shaken in a tightly closed vial and cooled. Etching of the glass and HF/SiF_4 fumes were observed. GC analysis: four substances present. Sodium fluoride (0.05 g) was added and the liquid removed by syringe. Analysis, using GC/MS and authentic compounds gave the results listed in Table 2.

TABLE 2

Methanolysis of Ester 8; Identification of Products

Substance	Code No.	Area, %	Ret. time, min.[a]
$F(CF_2CF_2O)_2CF_3COOCH_3$	10	39.0	2.45
CH_3OH		0.50	3.00
$F(CF_2CF_2O)_3CF_2COOCH_3$	11	53.0	3.45
$(CH_3O)_2C{=}O$		7.35	7.30

[a] GC analysis was done using a 2-meter polypropylene glycol column at 80°.

The ratio of areas (39:53:7.4) corresponds well to the mol. wt ratio (348:464:90), the expected stoichiometric ratio for quantitative reaction.

(c) Hydrolysis of alpha difluoro ester 8

8 (1.18 g, 1.34 mmole) and water (0.050 g, 2.8 mmole) were shaken in a vial; heat was evolved and the glass was etched. An infrared spectrum showed νOH, 3333 to 3030 cm^{-1} and νC=O, 1786 cm^{-1}; the spectrum appeared to be identical with that of $F(CF_2CF_2O)_nCF_2COOH$ (n = 2,3).

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