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A new route to perfluorinated vinyl ether monomers: synthesis of perfluoro(alkoxyalkanoyl) fluorides from non-fluorinated compounds

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Abstract

A new synthetic procedure for the preparation of various perfluoro(alkoxyalkanoyl) fluorides, which are precursors to perfluorinated vinyl ether monomers, from non-fluorinated alkoxyalcohols has been developed. Available perfluoro(alkoxyalkanoyl) fluorides such as perfluoro(2-propoxypropionyl) fluoride, so-called HFPO dimer, can be multiplied by the use of the hydrocarbon counterpart alcohols and fluorine gas as raw materials. In the case that the desired perfluoro(alkoxyalkanoyl) fluoride is not readily available, it can be obtained from its hydrocarbon counterpart alcohol and an available perfluoroacyl fluoride.

Keywords: Acyl fluorides; Direct fluorination; Fluorine; Perfluoropolymers; Synthesis

1. Introduction

Perfluoro(2-alkoxyalkanoyl) fluorides are important intermediates for fluororesins, such as PFA (perfluoroalkoxy copolymer). PFA is one of the most important perfluorinated polymers that is used as both thermally and chemically resistant material with melt processibility for industrial purpose [1–6]. One of its monomers, perfluoro(propyl vinyl ether) (PPVE), has been prepared via dimerization of hexafluoropropylene oxide (HFPO) [7] (Scheme 1). Although the HFPO chemistry is well established, it is specific to the propoxyl group as the side chain in the polymer in this case, because HFPO itself is employed as the precursor of the perfluoroalkoxide to react with HFPO. In the case of the perfluoro(alkyl vinyl ethers) other than PPVE, the preparation of the precursor perfluoro(2-alkoxyalkanoyl) fluoride is costly [8–10].

Recent perfluorinated hypofluorite chemistry [11] and the fluorination method of partially-fluorinated 1,2-dichloroethyl ethers [12] can give perfluoro(alkyl vinyl ethers) other than PPVE. However, these methods are still costly, because they require expensive (per)fluorinated starting materials.

On the other hand, a process for converting perfluorinated esters to perfluorinated acyl fluorides with a nucleophile in a solvent has been reported [13]. However, it has not been applied to the synthesis of the precursor to perfluorinated polymers.

Herein we present an essentially different synthesis. Our new synthetic route starts from non-fluorinated counterparts and utilizes liquid-phase direct fluorination [14] as a key step. Although Lagow and co-workers reported liquid-phase direct fluorination of non-fluorinated compounds [14], they just adopted it to molecules with simple structure, such as octyl octanoate. We considered that it could be applied to the synthesis of industrially important compounds, such as perfluorinated alkyl vinyl ethers, if we could make the corresponding hydrocarbon counterparts.

2. Results and discussion

2.1. Synthesis of the precursors to PPVE

We chose PPVE as our first target molecule, because it has a relatively simple structure. PPVE can be made either by thermal elimination of perfluoro(2-propoxypropionyl) fluoride (**1**) or by dechlorination of perfluoro(1,2-dichloroethyl propyl ether) (**2**). The dichloroether (**2**) could be obtained by direct fluorination of the corresponding hydrocarbon 1,2-dichloroethyl propyl ether (**3**), which is obtained from inexpensive propyl vinyl ether in only one step [15,16]. Because it seemed relatively easy, this route was selected as our first trial [17].

The dichloroethyl ether (**3**) was unstable, and it was difficult to purify by distillation or even by chromatography.

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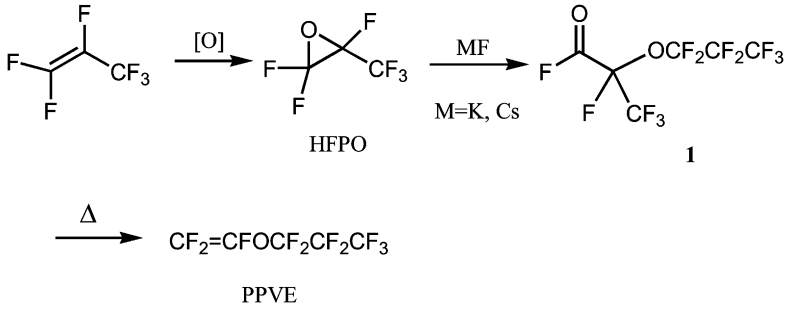
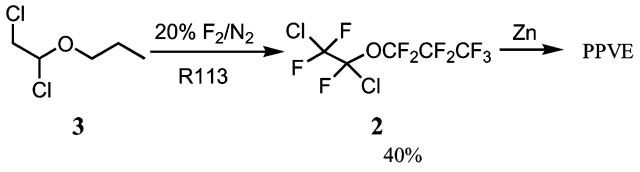
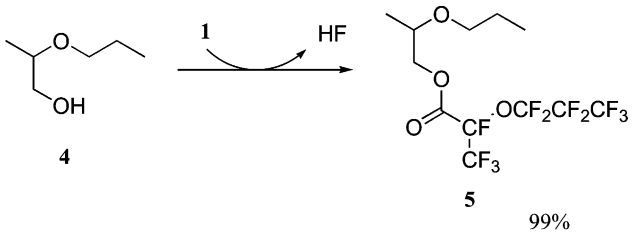


Scheme 1. Conventional synthesis of PPVE.



Scheme 2.



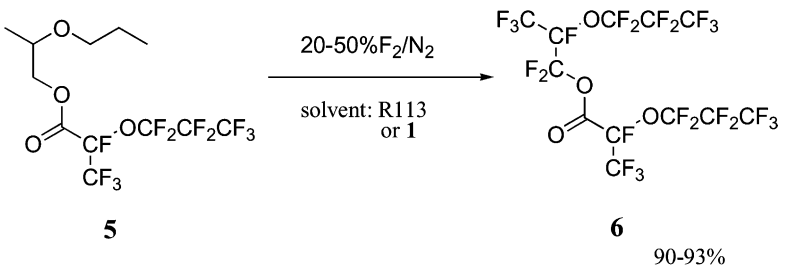
Scheme 3.

Therefore, the direct fluorination without purification of the substrate was carried out, basically applying Lagow's method. The direct fluorination was conducted with 20% fluorine gas diluted in nitrogen gas, and proceeded as we had intended (Scheme 2). However, it was limited by migration of chlorine atoms and formation of considerable amounts of by-products arising from C–C and C–O bond cleavage. The cause of this was probably some reaction in the vapor-phase, due to high volatility of the substrate, and the yield was only 40% at best. This suggested that compounds with low volatility are desirable for the liquid-phase reaction.

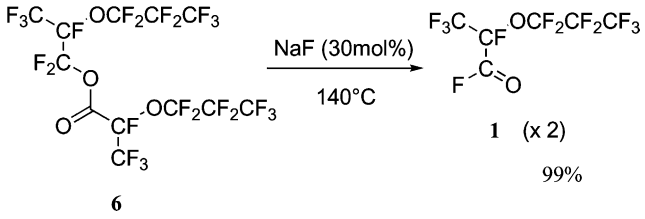
Then we examined the synthesis of the perfluoroacyl fluoride **1** [17]. This compound could be derived from alkoxyalcohol **4** as the precursor, however, direct fluorination of it seemed to be dangerous, because formation of unstable hypofluorite would likely to occur first [18]. As a result, protection of the OH group was essential in this route. The protecting group, in this case, should be a perfluorinated group for inactivity against fluorination, of large molecular weight for low volatility and removable after fluorination. Considering these demands, –COCF(CF_3)$OCF_2CF_2CF_3$ seemed to be most attractive, because the corresponding acyl fluoride is available as the intermediate to PPVE in the conventional manufacturing process, and, it could give the same acyl fluoride from perfluorinated hydrocarbon moiety, after addition of fluoride ion followed by elimination.

The actual synthesis was carried out as follows. The starting non-fluorinated alcohol **4** was synthesized from inexpensive propylene oxide and 1-propanol in the presence of an acid catalyst in one step [19–21]. Esterification (Scheme 3) was carried out simply by mixing the non-fluorinated alcohol **4** and the perfluoroacyl fluoride **1** from the conventional manufacturing route, with removal of HF formed during the reaction in a stream of nitrogen, to give the partially-fluorinated ester **5** in 99% yield.

The next liquid-phase direct fluorination was carried out basically in manner similar to Prof. Lagow's method (Scheme 4). Cooling was required in order to control the reaction together with use of an inert solvent, and appropriate dilution of both fluorine and the substrate. However, an excess of fluorine to replace all of the hydrogen atoms in the substrate was essential at all times as in the case of the non-fluorinated substrates that are described in the literature [14,22]. In our method, however, a potentially dangerous vapor-phase reaction was avoided by employing a higher



Scheme 4.



Scheme 5.

molecular weight partially-fluorinated ester as the substrate. A further benefit is that the solubility of the substrate in the perfluorinated solvent increased [23]. This is in contrast to that of a non-fluorinated compound. Moreover, it was found that the starting acyl fluoride itself is a good solvent for this fluorination. Thus, the direct fluorination of the partially-fluorinated ester **5** was carried out with 1.5–3.0 equivalent of fluorine diluted to 20–50% in nitrogen to give the desired perfluoroester **6** in over 90% yield. In the case that conversion was not enough, addition of benzene was effective in order to initiate the formation of fluorine atoms to complete the fluorination process.

The perfluorinated ester **6** obtained was converted to the desired acyl fluoride **1** with 30 mol% of sodium fluoride as a catalyst (Scheme 5). This thermal elimination reaction gave 2 mol of the desired acyl fluoride in 99% yield at lower temperature, compared to the reaction without catalyst [24].

The total process to a perfluorinated vinyl ether is shown in Scheme 6. We named this process ''PERFECT'', that is, the abbreviation of perfluorination of an esterified compound then thermal elimination. For the case of the synthesis of PPVE, the overall yield of the acyl fluoride **1a** from the one we started with was 180% per cycle. By repeating the cycle, the acyl fluoride **1a** will increase in geometric progression. In this sense, the cycle is a multiplication of the acyl fluoride.

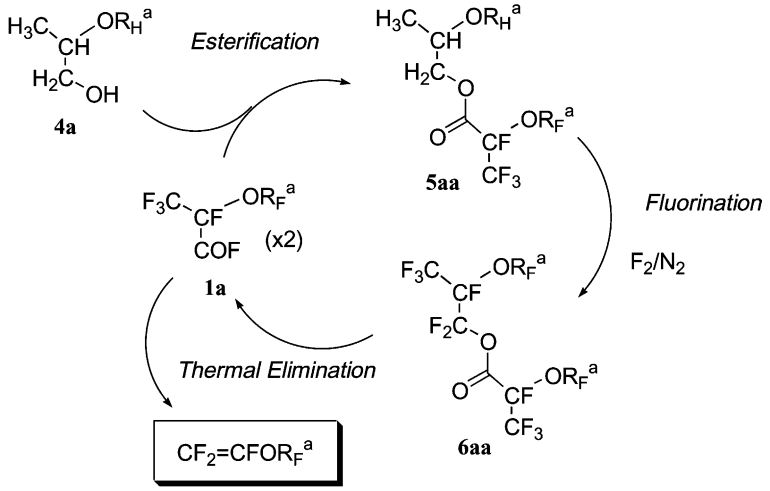
2.2. Synthesis of perfluoro(alkoxyalkanoyl) fluorides via perfluorinated mixed esters

In cases where the desired perfluoroacyl fluoride is available, it can be multiplied by the method shown above, but in many cases, the desired acyl fluorides are not readily available. In such situations, the hydrocarbon counterpart alcohol **4a** with the structure corresponding to the desired acyl fluoride **1a** is reacted with an available acyl fluoride **1b** (Scheme 7). The resulting mixed ester **5ab** is fluorinated to give the perfluoroester **6ab**, and the following thermal elimination gives the desired acyl fluoride **1a** and the recovered starting one **1b**. Once the desired acyl fluoride **1a** is obtained, then it can be multiplied by synthesizing the homoester **5aa** and applying the PERFECT process. Thus, liquid-phase direct fluorination followed by thermal elimination gives 2 mol of the desired acyl fluoride **1a**.

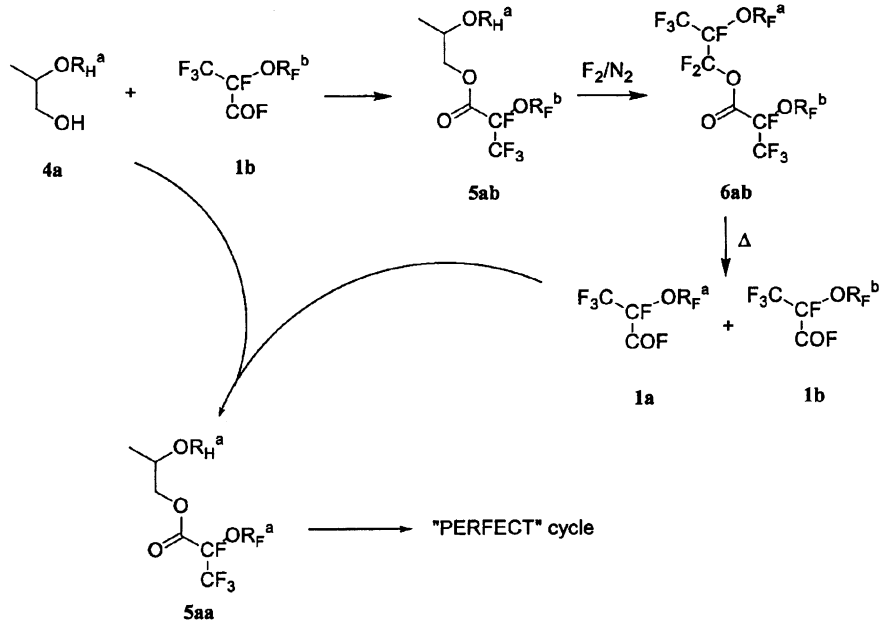
According to this methodology, various perfluoroacyl fluorides were synthesized.

When the hydrocarbon counterpart alkoxyalcohol **10** is not commercially available, it was synthesized from inexpensive 2-chloropropionyl chloride in three steps as shown in Scheme 8. The reaction of the alcohol **7**, which is corresponding to alkoxy moiety, with 2-chloropropionyl chloride gave propionate ester **8**. Nucleophilic substitution with alkoxide [25,26] of the alcohol **7** gave 2-alkoxypropionate **9**. Reduction with sodium bis(2-methoxyethoxy)-aluminum hydride in toluene gave the desired alkoxyalcohol **10**. Esterification with the available acyl fluoride **1**, the precursor of PPVE in the conventional manufacturing process, gave the substrate partially-fluorinated ester **11** for the liquid-phase direct fluorination.

When the substrate for the direct fluorination has a dioxolane unit, the desired counterpart-alcohol **13** was synthesized as shown in Scheme 9. Esterification with the available acyl fluoride **1** gave the substrate partially-fluorinated ester **14** for the liquid-phase direct fluorination.

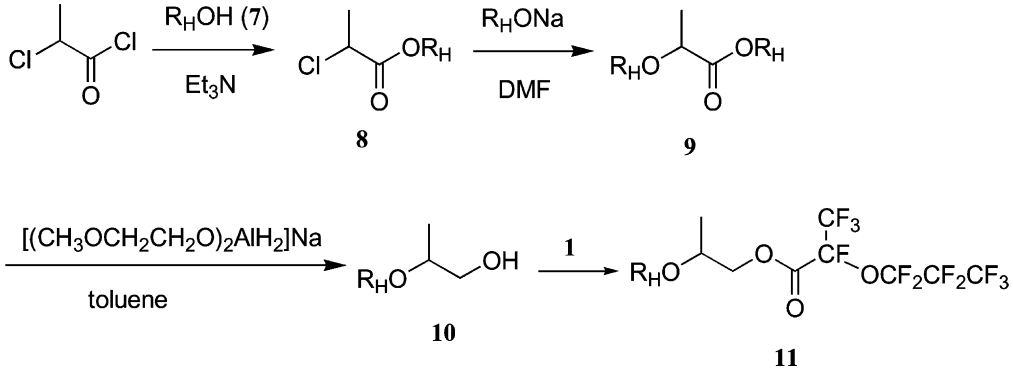


Scheme 6. The ''PERFECT'' cycle.

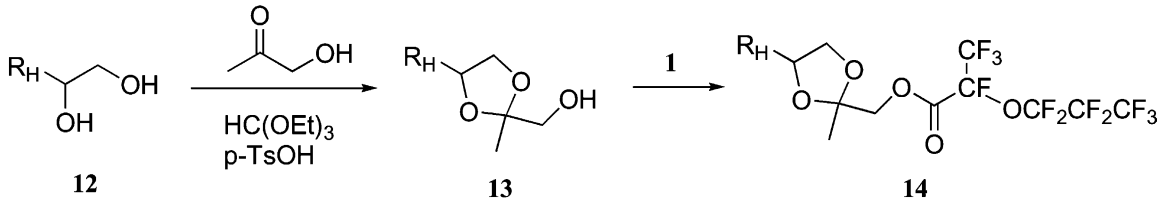


Scheme 7.

The partially-fluorinated esters were perfluorinated by the liquid-phase direct fluorination. A 5.0 g of the substrate (5% solution in 1,1,2-trichlorotrifluoroethane (R113)) was continuously introduced to R113 (200 ml) at 25°C with blowing 20% F_2/N_2 at a flow rate controlled at a ratio of $F_2/H = 3.0$–4.5 (3.0–4.5 equivalent excess to replace all of the hydrogen atoms in the substrate). Then 0.01% benzene (0.010–0.036 equivalent) in R113 was intermittently introduced as continued blowing 20% F_2/N_2 with raising temperature up to 40°C at 0–0.2 MPa. The results are summarized in Table 1. Both acyclic and cyclic partially-fluorinated esters were perfluorinated in good yields (runs 1 and 2). The yield of the compound with longer alkyl chain was a little lower, because some C–C bond cleavage took place (run 1). Dioxolane derivatives were also fluorinated in good yields (runs 3 and 4). Compounds with an aromatic moiety were also fluorinated, but the yields were quite low (runs 5 and 6). For example, although direct fluorination of the substrate

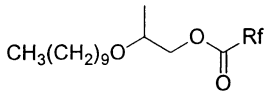
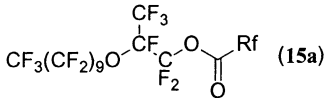
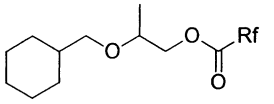
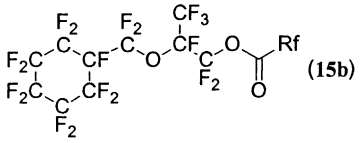
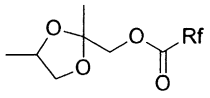
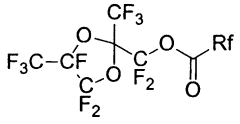
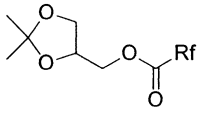
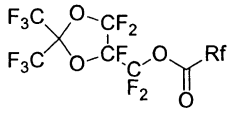
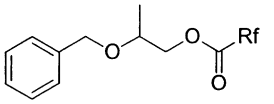
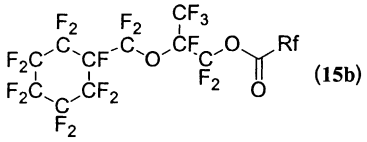
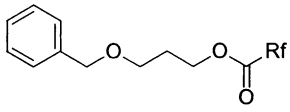
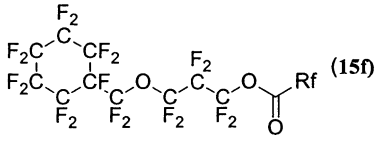
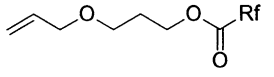
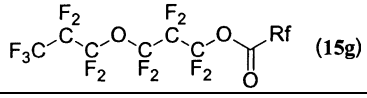


Scheme 8.



Scheme 9.

Table 1
Liquid-phase direct fluorination of partially-fluorinated esters[a]

Run	Substrate	Product	Yield
1	 (11a)	 (15a)	69
2	 (11b)	 (15b)	75
3	 (11c)	 (15c)	87
4	 (11d)	 (15d)	78
5	 (11e)	 (15b)	21
6	 (11f)	 (15f)	25
7	 (11g)	 (15g)	86

[a] Rf: $-CF(CF_3)OCF_2CF_2CF_3$.

with a phenyl moiety (run 5) gave the same product as the one from the cyclohexyl derivative (run 2), the yield was only 21%. Formation of a lot of C–C bond dissociation products was observed. This was probably due to too much radicals generated from the reaction of F_2 and the phenyl moiety. On the other hand, fluorination with a simple vinyl moiety gave the desired product in good yield (run 7).

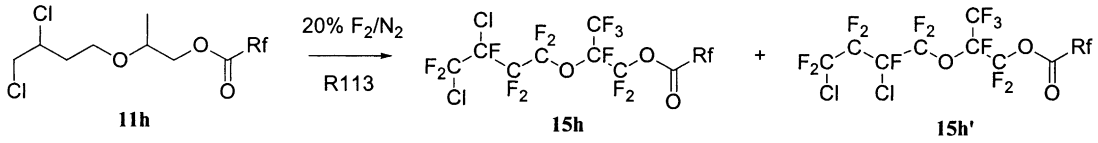
In order to obtain an intermediate for the transparent fluororesin, the compound with vicinal dichloro moiety was perfluorinated (Table 2). When the fluorination was carried out as usual at temperature of 25–40°C, chlorine migration [27,28] took place partially (run 1). It was found that this chlorine migration depended on reaction temperature. When most of the fluorination was carried out at −10°C and the last part of fluorination for remaining hydrogen atoms was carried out at 40°C, the migration was suppressed (run 2). This suggested that the chlorine migration did not take place even at 40°C after most of the hydrogen atoms were substituted by fluorine atoms.

Thermal elimination of the obtained perfluoroesters with a catalytic amount of sodium fluoride gave the desired acyl fluorides with the recovery of the starting acyl fluoride **1**. The results are shown in Table 3.

The perfluorinated acyl fluoride **1a** can be converted to the desired perfluoro(alkyl vinyl) ethers as described in the literature [29].

Thus, general organic synthesis, liquid-phase direct fluorination, and thermal elimination in fluorine chemistry are

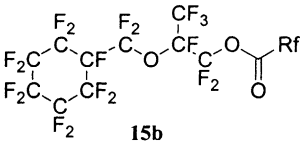
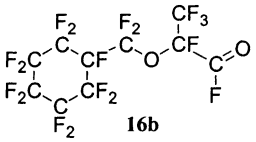
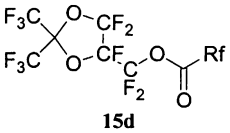
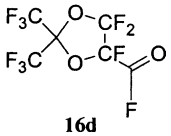
Table 2
Liquid-phase direct fluorination of a chlorine-containing partially-fluorinated ester[a]



Run	Temperature (°C)	Yield (%)	
1	25–40	63	32
2	−10–40	58	3

[a] Rf: $-CF(CF_3)OCF_2CF_2CF_3$.

Table 3
Thermal elimination of perfluoroesters[a]

Substrate	Product	Amount NaF (mol%)	Temperature (°C)	Yield (%)
 15b	 16b	18	120	66
 15d	 16d	20	120	73

[a] Rf: $-CF(CF_3)OCF_2CF_2CF_3$.

united to afford a new methodology to synthesize various perfluoro(alkyl vinyl) ethers. Scale-up of this process is under investigation.

3. Conclusions

The synthetic method of various perfluoro(alkoxyalkanoyl) fluorides utilizing liquid-phase direct fluorination with elemental fluorine was investigated. Direct fluorination of a partially-fluorinated ester synthesized from a non-fluorinated alkoxyalcohol and perfluorinated acid fluoride (**1**) was achieved in high yield. Degradation of the resulting perfluoroester gave the desired acid fluoride. It has advantages over known direct fluorination methods as follows.

1. It avoids vapor-phase reaction by employing a substrate with low vapor pressure.
2. It significantly increases the solubility of the substrate in the perfluorinated solvent used for fluorination, compared to non-fluorinated ester.
3. It is easy to synthesize the partially-fluorinated substrate because perfluorinated acyl fluoride (**1**) is available.
4. Various perfluoroacyl fluorides can be synthesized, because its carbon backbone is synthesized in hydrocarbon compounds by ordinary organic synthesis.

The raw materials are inexpensive hydrocarbon compounds and fluorine gas. Therefore, this method is expected to provide useful perfluorinated compounds in reasonable price.

4. Experimental

4.1. General

NMR spectra were obtained on a JEOL EX-400 (tetramethylsilane as internal standard for ^1H, and trichlorofluoromethane for ^{19}F). High resolution mass spectra were obtained on JEOL SX-102A coupled to HP-5890 with a 60 m capillary column J&W DB-1 or DB-1301.[1] Elemental fluorine was generated by Fluorodec™ 30, Fluoro Gas (UK). Elemental fluorine is highly toxic and corrosive gas, and may cause explosion when it meets organics in the vapor-phase. Extreme care must be taken when handling it! Both the liquid and vapor of hydrogen fluoride (bp 19.5°C) evolved during the reaction are also highly corrosive and cause severe burns when in contact. Care must be taken! Prior to use, all hydrocarbon greases must be removed and the apparatus must be gradually passivated with elemental fluorine. Although the use of 1,1,2-trichlorotrifluoroethane (R113) is regulated, we will mention experimental examples with it for convenience,

[1] Details of the analytic method will be reported separately.

because it is still much more cheaply available (Aldrich) than compound (**1**) for use as solvent. Care must be taken in order not to emit it to the environment by using, for example, a rotary evaporator with PTFE diaphragm type vacuum pump and cooling trap. Once enough of the compound (**1**) is obtained in the cycle, it should be used instead of R113. Other reagents were obtained from Kanto Chemicals (Japan) and used without purification.

4.2. Typical procedure

4.2.1. (2,2-Dimethyl-1,3-dioxolan-4-yl)methyl perfluoro(2-propoxypropionate) (**11d**)

Acyl fluoride **1** (40.0 g, 120 mmol) was added dropwise to solketal (2,2-dimethyl-1,3-dioxolane-4-methanol, 15.0 g, 113 mmol) over a period of 30 min while bubbling nitrogen gas to strip off hydrogen fluoride evolved, and maintaining the internal temperature between 25 and 30°C. After the addition, stirring was continued at room temperature for 3 h, and an aqueous saturated sodium hydrogen carbonate solution was added at an internal temperature of not higher than 15°C. The organic layer was washed twice with water (50 ml), dried over magnesium sulfate and then subjected to filtration. The crude liquid obtained was evaporated under reduced pressure to obtain compound **11d** (11.3 g, 26.4 mmol, 23% yield, 99% purity by GC); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 1.36 and 1.42 (s, 6H), 3.78 and 4.10 (dt, $^3J = 8.8$ Hz, $^4J = 5.2$ Hz; dd, $^3J = 8.8$ Hz, $^4J = 6.4$ Hz, 2H), 4.31–4.51 (m, 3H); ^{19}F NMR (376.2 MHz, $CDCl_3$) −80.3 (1F, OCF_2), −81.8 (3F, C(=O)CF(CF_3)O), −82.6 (3F, $OCF_2CF_2CF_3$), −87.0 (1F, OCF_2), −130.2 (2F, $OCF_2CF_2CF_3$), −132.2 (1F, C(=O)-CF(CF_3)O); high resolution mass spectrum (CI^+) 445.0537 ($[M + H]^+$, calculated for $C_{12}H_{12}F_{11}O_5$: 445.0509).

4.2.2. Perfluoro[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-propoxypropionate] (**15d**)

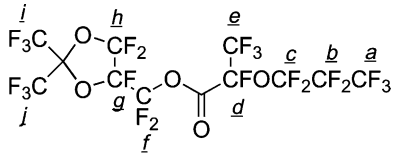
In a 500 ml autoclave made of nickel, equipped with a condenser maintained at 20°C, an NaF pellet packed layer, and a condenser maintained at −10°C in series at the gas outlet of the autoclave, as well as a liquid returning line in order to return the condensed liquid from the condenser maintained at −10°C, R113 (312 g) was stirred and maintained at 25°C. Nitrogen gas was blown into the system for 1.0 h, and then, fluorine gas diluted to 20% with nitrogen gas was blown into the mixture for 1 h at a flow rate of 7.71 l/h at atmospheric pressure. While blowing the 20% fluorine/nitrogen at the same rate, a solution of **11d** (5.01 g, 11.7 mmol) in R113 (100 g) was injected over a period of 5.6 h. Then, while blowing the 20% fluorine/nitrogen at the same rate, a solution of benzene in R113 (0.01 g/ml) was injected in an amount of 9 ml while raising the temperature from 25 to 40°C. Then, the inlet for benzene injection was closed, and the outlet valve of the autoclave was closed. When the pressure reached 0.20 MPa, the fluorine gas inlet valve of the autoclave was closed, and stirring was continued for 0.9 h. During this time, the pressure dropped slightly. Then, the pressure was adjusted to atmospheric pressure, and while maintaining the internal temperature of the reactor at 40°C, another portion of benzene solution (6 ml) was injected. The same operation was repeated four times. The total amount of benzene injected was 0.340 g (4.35 mmol), and the total amount of R113 injected was 33 ml. Further, nitrogen gas was blown into the mixture for 1.5 h. The desired product was quantitatively analyzed by ^{19}F NMR. The yield of **15d** was 78%; ^{19}F NMR (376.2 MHz, $CDCl_3$) −77.9 (1F, *h*), −79.6 to −80.8 (1F, *c*), −81.1 (3F, *i*), −81.2 (3F, *j*), −81.8 to −82.6 (3F of *a*, 3F of *e* and 1F of *h*), −85.9 to −88.0 (1F of *c* and 2F of *f*), −122.6 (1F, *g*), −130.4 (2F, *b*), −132.4 and −132.5 (1F, *d*); high resolution mass spectrum (EI^+) 622.9418 ($[M - F]^+$, calculated for $C_{12}F_{21}O_5$: 622.9410) (Fig. 1).

4.2.3. 2,2-Bis(trifluoromethyl)-4,5,5-trifluoro-1,3-dioxolane-4-carbonyl fluoride (**16d**)

In a 50 ml flask with reflux condenser adjusted at 20°C, a suspension of **15d** (1.8 g, 2.8 mmol) and NaF powder (0.02 g, 0.5 mmol) was heated at 120°C for 12 h with vigorous stirring. After cooling, a liquid obtained (1.6 g) was confirmed to be the mixture of **1** and **16d**. The NMR spectrum of **16d** obtained corresponded with the literature [30]. The yield of **16d** was determined by an internal standard (C_6F_6) and found to be 73%.

4.2.4. 2-(3,4-Dichlorobutoxy)propyl perfluoro-(2-propoxypropionate) (**11h**)

2-(3-Butenyloxy)-1-propanol (19.2 g, 98% purity, 145 mmol) was stirred while bubbling nitrogen gas. Calcium chloride (2.2 g, 20 mmol) and water (3.6 g) were added, followed by cooling to 10°C. Chlorine gas was blown into for 2 h at a supply rate of about 4 g/h. Then, consumption of the starting material was confirmed by GC, and diethyl ether (200 ml) and water (200 ml) were added. The organic layer was dried over magnesium sulfate. Then, the solvent was distilled off. The crude product was put into a flask and stirred while bubbling nitrogen gas. Acyl fluoride **1** (50 g, 150 mmol) was added dropwise over 1 h while maintaining the internal temperature at 25–30°C. After completion of the dropwise addition, stirring was continued at room temperature for 3 h and saturated aqueous sodium hydrogen carbonate solution (80 ml) was added at the internal temperature of not higher than 15°C. Water (50 ml) and chloroform (100 ml) were added. The organic layer was washed with water (100 ml) twice, dried over magnesium sulfate and



15d

Fig. 1.

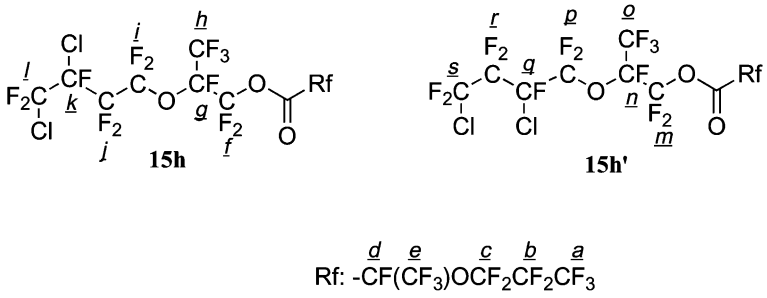


Fig. 2.

subjected to filtration to obtain a crude liquid. The crude liquid was concentrated and purified by a silica gel column chromatography (eluent: hexane/ethyl acetate = 4/1), followed by purification again by a silica gel column chromatography (eluent: AK-225) to obtain **11h** (37 g, 72 mmol, 50%yield, 99% purity by GC); ^{1}H NMR (399.8 MHz, $CDCl_3$) δ 1.21 (dd, $^3J = 6.3$ Hz, $^4J = 1.3$ Hz, 3H), 1.81–1.93 (m, 1H), 2.19–2.26 (m, 1H), 3.59–3.65 (m, 1H), 3.68–3.80 (m, 4H), 4.20–4.46 (m, 3H); ^{19}F NMR (376.2 MHz, $CDCl_3$) −80.3 (1F, OCF_2), −81.6 (3F, $C(=O)CF(CF_3)O$), −82.4 (3F, $OCF_2CF_2CF_3$), −86.7 (1F, OCF_2), −130.0 (2F, $OCF_2CF_2CF_3$), −132.0 (1F, $C(=O)CF(CF_3)O$); high resolution mass spectrum (CI^+) 513.0112 ($[M + H]^+$, calculated for $C_{13}H_{14}{}^{35}Cl_2F_{11}O_4$: 513.0094).

4.2.5. Perfluoro[2-(3,4-dichlorobutoxy)propyl 2-propoxypropionate] (*15h*) and perfluoro[2-(2,4-dichlorobutoxy)propyl 2-propoxypropionate] (*15h′*)

Fluorination of **11h** was carried out in manner similar to the synthesis of **15d**. The product was quantitatively analyzed by ^{19}F NMR (376.2 MHz, $CDCl_3$); **15h** (63%): −64.7 (2F, *l*), −76.5 to −80.0 (1F, *i*), −80.0 to −81.0 (3F of *h* and 1F of *c*), −82.2 (3F, *a*), −82.5 (3F, *e*), −82.0 to −82.9 (1F, *i*), −86.4 to −88.1 (2F of *f* and 1F of *c*), −117.0 to −119.7 (2F, *j*), −130.4 (2F, *b*), −131.9 (1F, *k*), −132.3 (1F, *d*), −145.9 (1F, *g*); **15h′** (32%): −65.7 to −67.2 (2F, *s*), −76.5 to −80.0 (2F, *p*), −81.0 to −81.3 (3F of *o* and 1F of *c*), −82.0 to −83.0 (6F, *a* and *e*), −86.5 to −88.5 (2F of *m* and 1F of *c*), −112.5 to −116.0 (2F, *r*), −130.5 (2F, *b*), −131.9 to −132.4 (1F, *d*), −136.5 (1F, *q*), −145.9 (1F, *n*); high resolution mass spectrum (EI^+) 726.8797 (M − F, calculated for $C_{13}{}^{35}Cl_2F_{23}O_4$: 726.8806) (Fig. 2).

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