 Bull. Chem. Soc. Jpn. Vol. 80, No. 8, 1611–1616 (2007)

Synthesis of Perfluorinated Ketones by Utilizing Liquid-Phase Direct Fluorination

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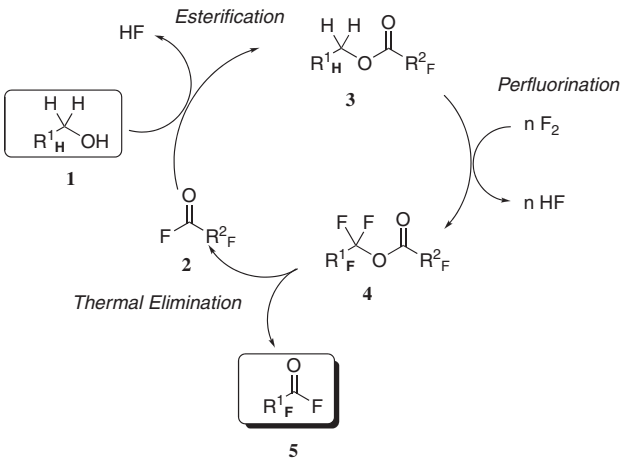
A new synthetic procedure for the preparation of perfluorinated ketones from nonfluorinated *sec*-alcohols was developed. A key step in the synthetic route was a liquid-phase direct fluorination reaction with elemental fluorine. Direct fluorination of a partially fluorinated ester, which was prepared from a nonfluorinated *sec*-alcohols and a perfluorinated acyl fluoride, followed by thermal elimination, gave a perfluorinated ketone and the starting perfluorinated acyl fluoride, which could be recycled. Application to the synthesis of a precursor polyfluoroketone for fluoropolymer resists for 157 nm microlithography was also established.

Perfluorinated compounds are important precursors for thermally and chemically resistant materials in industrial areas and recently for medical, IT, and electronics applications.[1,2] However, they are expensive, because they are usually prepared from fluorinated methane derivatives via multi-step reactions. Moreover, it has been difficult to synthesize new perfluorinated compounds for perfluorinated monomers and for perfluorinated building blocks, because the reactivity of fluorinated compounds is restricted.

Liquid-phase direct fluorination is a powerful tool to make perfluorinated compounds.[3,4] Especially, the Exfluor–Lagow elemental fluorine process is effective under mild conditions.[5,6] Lagow et al. have reported the direct fluorination of nonfluorinated compounds with relatively simple structures.[6] In our previous paper, the direct fluorination of small molecules, such as monomer precursors, has been examined; however, it is not easy.[7] In some cases, reaction in the vapor phase due to high volatility of the substrate partly takes place, leading to an explosion. In order to solve this problem, we have developed the PERFECT process (Scheme 1).[7] The name "PERFECT" stands for PERFluorination of an Esterified Compound then Thermal elimination. By employing a higher-molecular weight partially fluorinated ester **3**, which is synthesized from a nonfluorinated alcohol **1** and a perfluorinated acyl fluoride **2**, as the substrate for direct fluorination, any dangerous vapor-phase reactions can be avoided, and the solubility of the substrate in the solvent used in the liquid-phase fluorination is improved. This is in contrast to that of a nonfluorinated compound.

By using the PERFECT process, various perfluoroacyl fluorides have been synthesized. The synthesis of perfluorinated propyl vinyl ether (PPVE),[7] which is the monomer of perfluoroalkoxy copolymer (PFA), the synthesis of various perfluoroacyl fluorides,[8] the synthesis of perfluoroalkanesulfonyl fluorides,[9] and the synthesis of the carboxylic acid monomers for ion exchange membrane (Flemion®)[10] have been reported. Primary alcohols have been employed as the starting hydrocarbon components in each case.



Scheme 1. The "PERFECT" cycle.

On the other hand, the synthesis of perfluoroketones by direct fluorination[6,11] has so far been limited, because it has not been suitable for large-scale synthesis, especially using small molecular weight ketones. Lagow et al. have reported that secondary alkyl esters are perfluorinated and following transesterification in the presense of sodium fluoride give perfluoroketones.[6] Adcock and Luo have reported that ketones with adamantane structure can be perfluorinated using an aerosol to give perfluorinated ketones.[11]

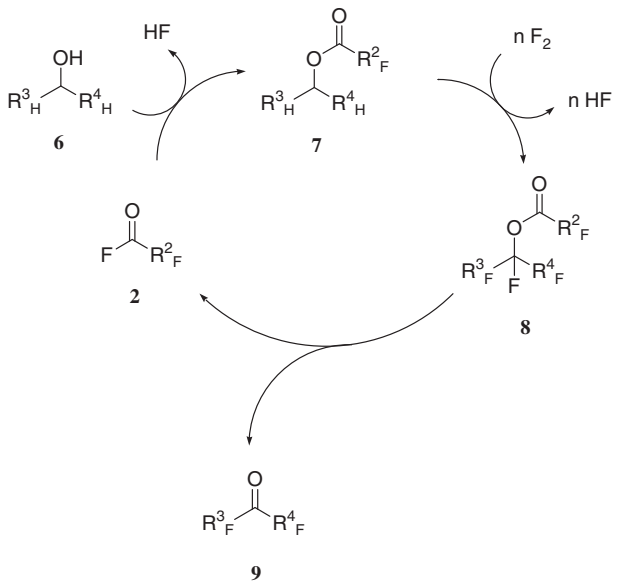
In this paper, we present a new application of the PERFECT process, that is, the preparation of perfluoroketones, using the corresponding secondary alcohols as the starting material, and this synthesis can be scaled up.

Published on the web August 10, 2007; doi:10.1246/bcsj.80.1611

Results and Discussion

The PERFECT Process for the Synthesis of Hexafluoroacetone. In the PERFECT process, perfluorination is achieved by direct fluorination of a partially fluorinated compound. In application of the PERFECT process for perfluoroketone synthesis, a nonfluorinated secondary alcohol was employed as the starting material (Scheme 2).

First, a small hydrocarbon component with the backbone structure of the desired ketone, secondary alcohol **6**, was synthesized by organic synthesis, when it was not available. Then, it was coupled with a perfluorinated moiety, perfluoroacyl fluoride **2** in a typical case, to be a large molecule, that is, partially fluorinated ester **7**. Perfluorination was achieved by liquid-phase direct fluorination with elemental fluorine to give the perfluorinated ester **8**. In the direct fluorination reaction, vapor-phase reaction was avoided since substrate **7** had a low vapor pressure and the solubility of the substrate in the perfluorinated solvent significantly increased. It has an advantage that various perfluorinated compounds other than CFCs can be used as the solvent. Typically, the perfluoroacyl fluoride **2** itself was employed. Final thermal elimination gave the starting perfluoroacyl fluoride **2** and the desired perfluorinated ketone **9**. Separation was achieved by distillation.



Scheme 2. The "PERFECT" process for the synthesis of a perfluoroketone.

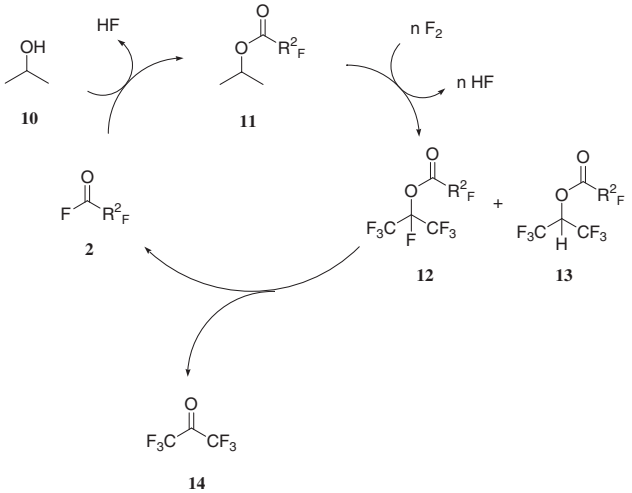
We first applied this methodology to the synthesis of hexafluoroacetone (HFA) (Scheme 3).

Esterification was carried out simply by mixing 2-propanol (**10**) and perfluoroacyl fluoride **2** while removing HF formed in the reaction system with a stream of nitrogen. Both perfluoroacyl fluorides, so-called HFPO dimer **2a** and trimer **2b**, gave the desired partially fluorinated esters **11**.

The next liquid-phase direct fluorination was carried out basically in a manner similar to the Exfluor–Lagow method.[6] In order to control the reaction, heat removal, use of inert solvent, appropriate dilution of both fluorine and the substrate, and excess amount of fluorine to replace all of the hydrogen atoms in the substrate at all times are essential as in the case of nonfluorinated substrates. Nevertheless, reaction in the vapor phase due to high volatility of the nonfluorinated substrate partly takes place and leads to an explosion in some cases.

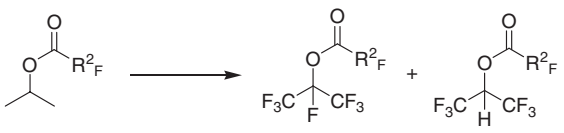
In the PERFECT process, however, the dangerous vapor-phase reaction was avoided by employing a higher-molecular weight partially fluorinated ester as the substrate. Thus, the reaction was carried out with 1.5–3.0 molar amounts of fluorine diluted to 20–50% in nitrogen to give the desired perfluorinated ester (Table 1).

Thus, the partially fluorinated ester **11a** derived from **2a** was perfluorinated with 20% F_2/N_2 in 1,1,2-trichloro-1,2,2-trifluoroethane (R113) as the solvent at room temperature (Run 1). The desired perfluorinated ester **12a** was obtained

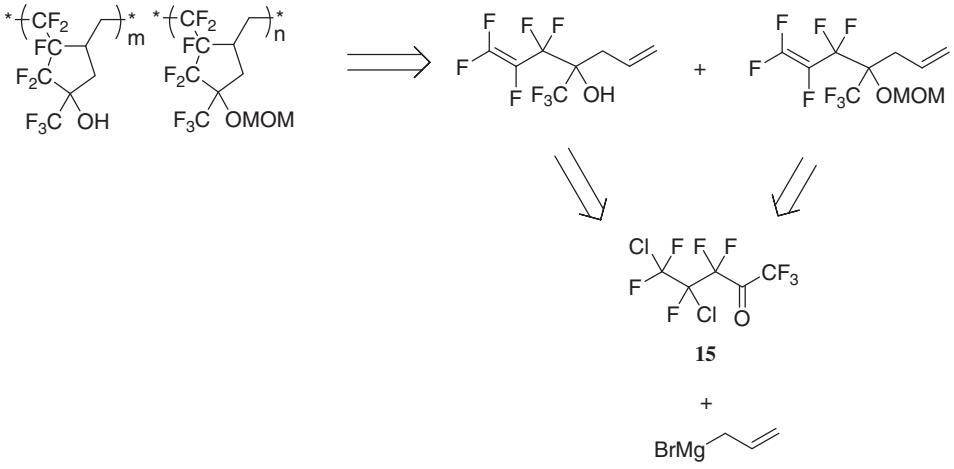


Scheme 3. The "PERFECT" process for the synthesis of HFA.

Table 1. Liquid-Phase Direct Fluorination of a Partially Fluorinated Ester **11**



Run	Substrate	R^2_F	Solvent	F_2/N_2	Temperature/°C	Yield/%	
						12	**13**
1	**11a**	$-CF(CF_3)OCF_2CF_2CF_3$	R113	20%	25	48	19
2	**11b**	$-CF(CF_3)OCF_2CF(CF_3)OCF_2CF_2CF_3$	R113	20%	25	52	42
3	**11b**	$-CF(CF_3)OCF_2CF(CF_3)OCF_2CF_2CF_3$	**2b**	50%	25	94	0



Scheme 4. Retrosynthetic analysis of the fluoropolymer resists for 157 nm microlithography.

in 48% yield, whereas the compound with sterically hindered C–H bonding remained compound **13a** was afforded in 19% yield. The 30% was lost probably because the substrate **11a** is still volatile. In the case of larger partially fluorinated ester **11b** derived from **2b** as the substrate, the material balance was improved; however, 42% of the C–H remained (Run 2). Longer reaction times were not effective at all. Although the addition of benzene to generate a lot of fresh fluorine radical[12] was effective to some extent, the reaction did not go to completion. A higher concentration of fluorine was effective, and 50% F_2/N_2 gave the disired perfluorinated ester **12b** in 94% yield (Run 3). In this case, R113 was not an appropriate solvent, because it partly reacts with 50% F_2/N_2. Therefore, **2b** was used as the solvent.

The next thermal elimination was carried out with potassium fluoride to give HFA (**14**) in excellent yield. Potassium fluoride works as the catalyst of the reaction.
In addition, **14** was reduced to give 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), which is an important material for a pharmaceutical intermediates[13] as well as a special solvent.[14]

The PERFECT Process for the Synthesis of a Polyfluoroketone for Fluoropolymer Resists. This methodology was applied to the synthesis of the compound for a fluoropolymer resist for 157 nm microlithography.[15]

The key material is the dichloropolyfluoropentanone **15**, which is reacted with allyl Grignard reagent, followed by dechlorination with zinc, to give the monomer, as shown in the retrosynthetic analysis (Scheme 4).

Dichloropolyfluoropentanone **15** is synthesized from an intermediate for CYTOP®, which is a transparent perfluorinated resin, according to the procedure reported by Dupont.[16] However, it included a hazardous oxidation step of an iodine containing compound with oleum. This problem was avoided by using the PERFECT process.

The structure of the target ketone had vicinal dichlorinated structure, and therefore, an alkenol, 4-penten-2-ol (**16**), was chosen as the starting material. It was esterified with a perfluoroacyl fluoride **2a** and chlorinated with chlorine before fluorination (Scheme 5).

The direct fluorination of **18** was carried out at first with 20% F_2/N_2 in R113 to afford **19** in 44% yield. Partially unreacted compound **20** remained again, and considerable amounts of by-products arising from Cl-atom migration formed. As in the case of the synthesis of HFA, the reaction with 50% F_2/N_2 in perfluoroacyl fluoride **2b** as the solvent was carried out. Although the C–H remaining compound **20** almost disappeared and yield was improved, the Cl-migrated products still formed. The final thermal elimination was carried out as usual in the presence of potassium fluoride to give the desired ketone **15** in 85% yield.

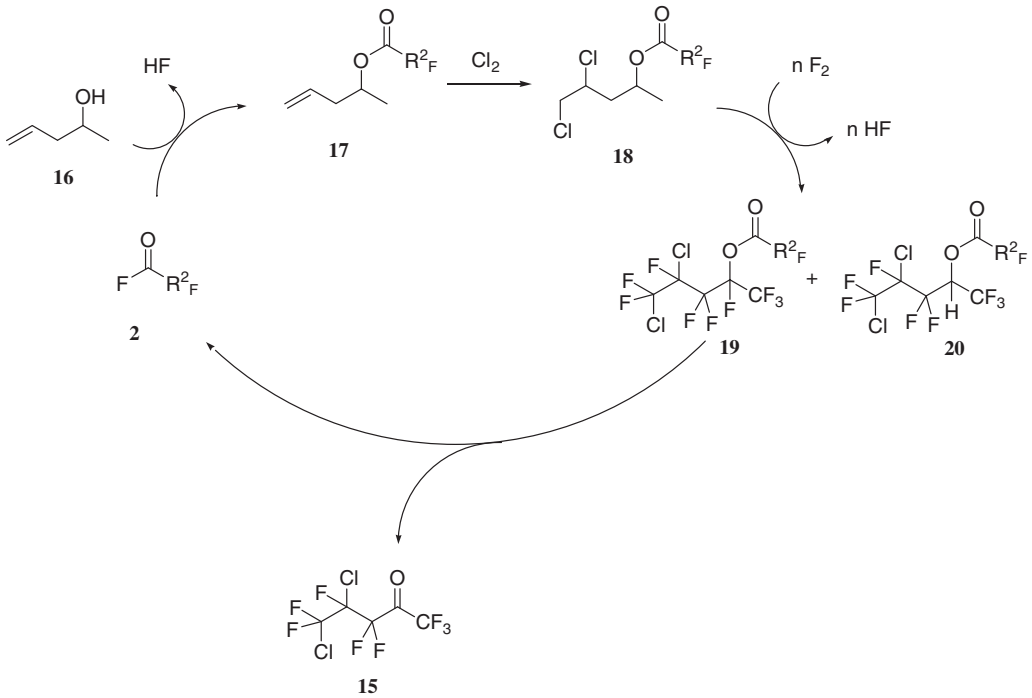
Conclusion

Perfluoroketones were synthesized by using the PERFECT process, which utilizes direct fluorination with elemental fluorine as a key step from the corresponding nonfluorinated secondary alcohols. Industrially useful **14** and a perfluoroketone, which is a precursor for fluoropolymer resist, were synthesized.

The PERFECT methodology does not require iodine, oleum or other hazardous reagents. It does also not require solvent other than the starting perfluoroacyl fluoride. Besides, HF, which can be electrolyzed to F_2 and H_2, is essentially the only by-product in the PERFECT cycle. Therefore, the PERFECT process is an industrially suitable process.

Experimental

General. NMR spectra were obtained on a JEOL EX-400 or AL-300 (tetramethylsilane as internal standard for ^{1}H, and trichlorofluoromethane for ^{19}F). High-resolution mass spectra were obtained on a JEOL SX-102A coupled to HP-5890 with a 60 m capillary column J&W DB-1 or DB-1301. A typical equipment for liquid-phase direct fluorination is described in the literature.[5] 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-trichloro-1,2,2-trifluoroethane (R113) is regulated, we will mention an experimental example with it in a small scale for convenience, because it is still much more cheaply available (Aldrich) than compound **2b**, which is obtained from manufacturing process,



Scheme 5. The "PERFECT" process for the synthesis of the fluoropolymer resists for 157 nm microlithography.

for use as a solvent. Care must be taken in order not to emit R113 to the environment by using, for example, a rotary evaporator with PTFE diaphragm-type vacuum pump and cooling trap. If enough of compound **2b** is obtained, it should be used instead of R113. In a large scale synthesis, it is strongly recommended. Other reagents were obtained from Kanto Chemicals (Japan) and used without purification.

Typical Procedure. Preparation of $(CH_3)_2CHOCOCF(CF_3)OCF_2CF_2CF_3$ (11a): While bubbling nitrogen gas, to a stirred 2-propanol (7.00 g, 116 mmol) was added perfluoroacyl fluoride **2a** (45.5 g, 137 mmol) dropwise at 25 to 30 °C over a period of 0.5 h. The mixture was stirred for 1 h at room temperature and quenched with a saturated aqueous sodium hydrogencarbonate (50 mL) at most 15 °C. The mixture was washed twice with water (50 mL), dried over magnesium sulfate and then filtered to obtain a crude liquid. Distillation (67–68 °C/10.7 kPa) gave the partially fluorinated ester **11a** (24.9 g, GC purity: 99%, 66.9 mmol, 58%). ^{1}H NMR (399.0 MHz, $CDCl_3$) δ: 1.33 (d, $J = 6.0$ Hz, 6H), 5.17 to 5.29 (m, 1H). ^{19}F NMR (376.0 MHz, $CDCl_3$) δ: −79.6 (1F), −81.4 (3F), −82.3 (3F), −86.5 (1F), −129.6 (2F), −131.6 (1F): HRMS (CI^+) $m/z = 373.0290$, calcd for $C_9H_8F_{11}O_3[M + H]^+$: $m/z = 373.0298$.

Preparation of $(CH_3)_2CHOCOCF(CF_3)OCF_2CF(CF_3)OCF_2CF_2CF_3$ (11b): A reaction was carried out in the same manner as the preparation of **11a** except that **2b** (61.0 g, 122 mmol) was used instead of **2a**. The reaction mixture was washed twice with water (50 mL), dried over magnesium sulfate and then filtered to obtain **11b** (64.0 g, GC purity: 98%, 116 mmol, 100%). ^{1}H NMR (399.0 MHz, $CDCl_3$) δ: 1.23 to 1.29 (m, 6H), 5.15 to 5.27 (m, 1H). ^{19}F NMR (376.0 MHz, $CDCl_3$) δ: −79.1 to −80.5 (4F), −81.8 (3F), −82.1 (2F), −82.7 (3F), −84.8 to −85.6 (1F), −130.1 (2F), −132.0 (1F), −145.6 (1F): HRMS (CI^+) $m/z =$ 539.0156, calcd for $C_{12}H_8F_{17}O_4[M + H]^+$: $m/z = 539.0156$.

Small-Scale Synthesis of $(CF_3)_2CFOCOCF(CF_3)OCF_2CF_2CF_3$ (12a): In a 500-mL autoclave made of nickel, R113 (312 g) was stirred at 25 °C. At the gas outlet of the autoclave, a cooler maintained at −15 °C was installed. After supplying nitrogen gas for 1 h, 20% F_2/N_2 was added for 1 h at a flow rate of 6.17 L h^{-1}, and the internal pressure of the reactor was maintained at 0.15 MPa. While maintaining the internal pressure of the reactor at 0.15 MPa and supplying 20% F_2/N_2 at the same flow rate, a solution of compound **11a** (4.99 g, 13.4 mmol) in R113 (100 g) was injected over a period of 5.3 h and then a solution of benzene in R113 (0.01 g mL^{-1}, 9 mL) was injected while raising the temperature from 25 to 40 °C. The 20% F_2/N_2 mixture was supplied at the same flow rate for another 0.5 h. Then, the above benzene solution (6 mL) was injected, and 20% F_2/N_2 was supplied at the same flow rate for 0.5 h. The same operation was repeated once, and then nitrogen gas was supplied for 3 h to remove volatile materials.

The yield of the perfluorinated ester **12a** determined by ^{19}F NMR was 48%, and partially unreacted compound **13a** was 19%. The product **12a** decomposed on silica-gel column and partly decomposed even in a distillation process.

12a: ^{19}F NMR (376.0 MHz, $CDCl_3$) δ: −79.4 (3F), −79.6 (3F), −79.9 (1F), −82.1 (3F), −82.2 (3F), −87.7 (1F), −130.4 (2F), −132.1 (1F), −143.4 (1F): HRMS (EI^+) $m/z = 478.9582$, calcd for $C_9F_{17}O_3[M - F]^+$: $m/z = 478.9576$.

13a: ^{1}H NMR (399.0 MHz, $CDCl_3$) δ: 5.80 (m, 1H). ^{19}F NMR (376.0 MHz, $CDCl_3$) δ: −74.0 (3F), −74.1 (3F), −79.9 (1F), −82.3 (3F), −82.5 (3F), −87.7 (1F), −130.4 (2F), −132.6 (1F).

Large-Scale Synthesis of $(CF_3)_2CFOCOCF(CF_3)OCF_2CF(CF_3)OCF_2CF_2CF_3$ (12b): In a 3-L autoclave made of nickel and having an external circulation tubular type reactor, **2b** (2534 g) was circulated and stirred at 25 °C. At the gas outlet of the autoclave, a cooler maintained at −10 °C was installed. After supplying nitrogen gas for 2 h, 50% F_2/N_2 was supplied for 2 h at a flow rate of 42.0 L h^{-1}. While supplying 50% F_2/N_2 at the same flow rate, **11b** (1440 g, 2.68 mol) was injected over 24 h. The reaction mixture (1700 g) was extracted from the reactor.

The same operation was repeated 6 times, then nitrogen gas was supplied for 2 h. The combined reaction mixture was concentrated to give the crude liquid. Then, the crude liquid (2500 g) was put into the above autoclave, circulated and stirred again at 25 °C. After supplying nitrogen gas for 2 h, 50% F_2/N_2 gas was supplied for 2 h at a flow rate of 42.0 L h^{-1}. Then, while supplying 50% F_2/N_2 at the same flow rate, **11b** (1440 g, 2.68 mol) was injected over a period of 24 h, and then nitrogen gas was supplied for 2 h. A crude liquid (4190 g) was obtained. The desired product was quantified by ^{19}F NMR (internal standard: C_6F_6), and the yield of **12b** was 94%. The product **12b** decomposed on silica-gel column and partly decomposed even in a distillation process so that the crude product was directly used for the next step. ^{19}F NMR (376.0 MHz, $CDCl_3$) δ: −78.5 to −80.0 (7F), −80.7 (3F), −81.9 to −82.8 (8F), −84.8 to −86.3 (1F), −130.2 (2F), −132.2 (1F), −143.1 (1F), −145.4 (1F): HRMS (EI^+) m/z = 644.9422, calcd for $C_{12}F_{23}O_4[M - F]^+$: m/z = 644.9429.

Synthesis of Hexafluoroacetone (HFA) (14): Into an Inconel column (inner diameter = 14 mm, length = 1 m), potassium fluoride (10–20 mesh, 50 g) was packed and set in a salt bath, and the internal temperature of the salt bath was adjusted to 200 °C. To this reactor, a mixture of **12b** and **13b** in a ratio of 8:2 obtained in the same manner as above was fed for 2 h at a rate of 60 g h^{-1} by means of a metering pump. At the outlet of the reactor, a reflux condenser at −20 °C was installed, and the mixture was separated into a gas sample and a liquid sample. The gas sample (23.2 g) was collected in a collecting container made of a fluorocarbon resin, and the liquid sample (95.8 g) was recovered in a glass trap. The gaseous sample was analyzed by GC-MS and found to be HFA (yield from **12b** was 97%). From the liquid sample, **2b** (69.5 g) was recovered by distillation.

Preparation of $CH_2ClCHClCH_2CH(CH_3)OCOCF(CF_3)OCF_2CF_2CF_3$ (18): 4-Penten-2-ol (**16**, 13.1 kg, 152 mol) was stirred, while bubbling nitrogen gas, and **2a** (54.3 kg, 164 mol) was charged over 5 h, while maintaining the internal temperature at from 25 to 30 °C. After completion of the charging, the reaction mixture was stirred for 70 h at from 30 to 50 °C, while bubbling nitrogen gas. The obtained crude liquid of **17** (58.3 kg) was used for the next step without purification. The purity by GC was 97%. ^{1}H NMR (300.4 MHz, $CDCl_3$) δ: 1.32 (d, J = 6.0 Hz, 3H), 2.30 to 2.50 (m, 2H), 5.07 to 5.21 (m, 3H), 5.61 to 5.76 (m, 1H). ^{19}F NMR (282.7 MHz, $CDCl_3$) δ: −79.6 (1F), −81.3 (3F), −82.0 (3F), −86.3 (1F), −129.4 (2F), −131.5 (1F).

Into a 5-L flask equipped with a reflux condenser adjusted at 20 °C, **17** (5000 g, 12.6 mol) obtained above was charged, and the reactor was cooled to −30 °C. Then, chlorine gas was continuously bubbled into the reaction solution, while maintaining the internal temperature at under 10 °C. When the reaction proceeded and no more heat generation was observed, the temperature of the reactor was raised to room temperature and nitrogen gas was bubbled in the reaction solution for 24 h to obtain a crude liquid (5900 g). The compound **18** was found to have formed in 95% yield by GC analysis. ^{1}H NMR (300.4 MHz, $CDCl_3$) δ: 1.42 (d, J = 6.3 Hz, 3H), 1.86 to 2.51 (m, 2H), 3.52 to 3.84 (m, 2H), 3.97 to 4.09 (m, 1H), 5.34 to 5.59 (m, 1H). ^{19}F NMR (282.7 MHz, $CDCl_3$) δ: −80.4 (1F), −81.9 (3F), −82.5 (3F), −86.7 (1F), −130.2 (2F), −132.3 (1F): HRMS (CI^+) m/z = 448.9772, calcd for $C_{11}H_9{}^{35}Cl_2F_{10}O_3[M - F]^+$: m/z = 448.9769.

Large-Scale Synthesis of $CF_2ClCFClCF_2CF(CF_3)OCOCF(CF_3)OCF_2CF_2CF_3$ (19): Into a 3-L autoclave made of nickel and having an external circulation tubular type reactor, **2b** (2510 g) was circulated and stirred at 25 °C. At the gas outlet of the autoclave, a cooler maintained at −10 °C was installed. After supplying nitrogen gas for 2 h, 50% F_2/N_2 was supplied for 2 h at a flow rate of 64.4 L h^{-1}. While supplying 50% F_2/N_2 at the same flow rate, **18** (1200 g, 2.56 mol) was injected over 24 h. The crude liquid (1400 g) was extracted from the reactor. The same operation was repeated 9 times, then nitrogen gas was supplied for 2 h. The combined reaction mixture was concentrated to give the crude liquid. Then, the crude liquid (2090 g) was put into the above autoclave, circulated and stirred again at 40 °C. After supplying nitrogen gas for 2 h, 50% F_2/N_2 was supplied for 2 h at a flow rate of 142 L h^{-1}. Then, while supplying 50% F_2/N_2 at the same flow rate, **18** (1200 g, 2.56 mol) was injected over a period of 24 h, and then nitrogen gas was supplied for 2 h. A liquid (3650 g) was obtained, and the yield of **19** determined by GC and NMR analysis was 83%. ^{19}F NMR (282.7 MHz, $CDCl_3$) δ: −63.1 to −65.0 (2F), −75.5 to −76.5 (3F), −79.0 to −80.5 (1F), −81.9 (3F), −82.1 (3F), −86.0 to −88.0 (1F), −110.0 to −115.5 (2F), −130.0 (2F), −130.5 to −133.5 (2F), −135.0 to −138.0 (1F). HRMS (CI^+) m/z = 610.8915, calcd for $C_{11}{}^{35}Cl_2F_{19}O_3[M - F]^+$: m/z = 610.8921.

Synthesis of $CF_2ClCFClCF_2COCF_3$ (15):[16] The crude dichloropolyfluoro ester **19** (24.8 g) obtained above and potassium fluoride powder (1.17 g) were heated at 130 °C for 2 h and at 140 °C for 1.5 h, while stirring vigorously. After cooling, a liquid sample (21.7 g) was recovered and analyzed by GC-MS. The yield of **15** from **19** was determined by GC and found to be 85%.

We would like to thank Professor Richard D. Chambers for helpful discussions.

References

1 a) T. Hiyama, *Organofluorine Compounds*, Springer, Berlin, **2000**. b) R. D. Chambers, *Fluorine in Organic Chemistry*, 2nd ed., Oxford, **2004**. c) P. Kirsh, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**.

2 a) J. H. Holloway, *J. Fluorine Chem.* **2000**, *104*, 3. b) W. R. Dolbier, Jr., *J. Fluorine Chem.* **2005**, *126*, 157.

3 a) S. Rosen, *Reactions of Fluorine in Inert Media* in *Methoden Org. Chem. (Houben-Weyl)*, 4th ed., ed. by B. Baasner, H. Hagemann, J. C. Tatlow, Georg Thieme Verlag, Stuttgart, **1999**, Vol. E10a, pp. 167–187. b) W. W. Schmiegel, *Organic Fluoropolymers* in *Chemistry of Organic Fluorine Compounds II*, ed. by M. Hudlicky, A. E. Pavlath, American Chemical Society, Washington, DC, **1995**, pp. 97–112.

4 J. Hutchinson, G. Sandford, *Top. Curr. Chem.* **1997**, *193*, 1.

5 R. J. Lagow, *Reactions of Fluorine in the Presence of Solvents*, in *Methoden Org. Chem. (Houben-Weyl)*, 4th ed., ed. by B. Baasner, H. Hagemann, J. C. Tatlow, Georg Thieme Verlag, Stuttgart, **1999**, Vol. E10a, pp. 194–200.

6 T. R. Bierschenk, T. Juhlke, H. Kawa, R. J. Lagow, U.S. Patent 5093432, **1992**.

7 T. Okazoe, K. Watanabe, M. Itoh, D. Shirakawa, H. Murofushi, H. Okamoto, S. Tatematsu, *Adv. Synth. Catal.* **2001**, *343*, 215.

8 T. Okazoe, K. Watanabe, M. Itoh, D. Shirakawa, H. Murofushi, H. Okamoto, S. Tatematsu, *J. Fluorine Chem.* **2001**, *112*, 109.

9 T. Okazoe, E. Murotani, K. Watanabe, M. Itoh, D. Shirakawa, K. Kawahara, I. Kaneko, S. Tatematsu, *J. Fluorine Chem.* **2004**, *125*, 1695.

10 T. Okazoe, K. Watanabe, M. Itoh, D. Shirakawa,

K. Kawahara, S. Tatematsu, *J. Fluorine Chem.* **2005**, *126*, 519.
11 J. L. Adcock, H. Luo, *J. Org. Chem.* **1993**, *58*, 1704.
12 T. Ono, *Chim. Oggi* **2003**, 39.
13 Y. Katsuhara, M. Aramaki, A. Ishii, T. Kume, C. Kawashima, S. Mitsumoto, *J. Fluorine Chem.* **2006**, *127*, 8.
14 S. Mori, T. Isemura, S. Yonemori, Japanese Patent 74892, **2000**.
15 a) M. Toriumi, N. Shida, H. Watanabe, T. Yamazaki, S. Ishikawa, T. Itani, *Proc. SPIE* **2002**, *4690*, 191. b) S. Kodama, I. Kaneko, Y. Takebe, S. Okada, Y. Kawaguchi, N. Shida, S. Ishikawa, M. Toriumi, T. Itani, *Proc. SPIE* **2002**, *4690*, 76. c) S. Ishikawa, S. Irie, T. Itani, Y. Kawaguchi, O. Yokokoji, S. Kodama, *Proc. SPIE* **2003**, *5039*, 580. d) S. Irie, S. Ishikawa, T. Hagiwara, T. Yamazaki, T. Furukawa, T. Itani, Y. Kawaguchi, O. Yokokoji, I. Kaneko, *Jpn. J. Appl. Phys.* **2003**, *42*, 3743.
16 B. C. Anderson, U.S. Patent 3391119, **1968**.