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# A NEW SYNTHETIC APPROACH TO PERFLUOROCHEMICALS: LIQUID PHASE PHOTOFLUORINATION WITH ELEMENTAL FLUORINE. PART I

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## SUMMARY

This paper describes a novel, safe, effective technique, with a new reactor design, for the synthesis of perfluorochemicals. This method, the liquid-phase photofluorination with undiluted fluorine, is applicable to the preparative-scale synthesis of isomerically-pure branched F-alkanes, F-ethers and F-tert-amines which are difficult to prepare by the classical fluorination methods (i.e. electrochemical or $CoF_3$). The technique is based on the controlled inverse addition of the materials to be fluorinated to a well-stirred $F_2$-saturated inert solvent, with simultaneous UV irradiation. The application of this method to the synthesis of F-ethers is described: the following were made by this method, F-2-propoxy-2-methylpentane, F-2-isobutoxy-2-methylpentane, F-n-heptylpropylether, F-2-pentoxy-2-methoxypropane, F-3-propoxy-2-methylpentane, F-2-ethyl-2-isopropyltetrahydrofuran, F-3-isobutoxy-2-methylpentane, F-2-methoxy-4-ethyl-4-methylhexane, and F-2-methyl-(1-ethyl-1-methylpropyl)oxetane.

## INTRODUCTION

Perfluorochemicals have become an interesting class of chemical substances with regard to both synthesis and biochemical applications [1]. Although there are several methods available for the synthesis of

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perfluorochemicals, some of them are so drastic that various kinds of degraded or rearranged by-products are usually formed as well and the others require a long reaction time with a rather sophisticated and big apparatus. Of particular interest is a structural variety of perfluorochemicals, the preparations of which is a prerequisite for the intensive study of perfluorochemical emulsions as candidate for potential oxygen carrying agents. The preparation of perfluorochemicals with complex structures on a preparative scale seems to be more than a challenge to the conventional processes. Consideration of the above has led us to develop a new technique for the synthesis of such perfluorochemicals which is simple, safe, and suitable for commercial scale-up.

The present work was carried out in 1979-1984 and its original concept has already been reported in a patent [2]. This paper describes a part of the work in detail.

## RESULTS AND DISCUSSION

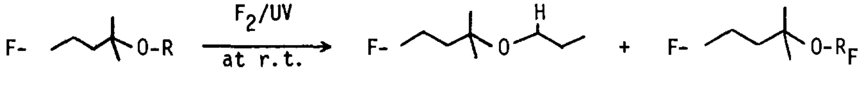
### Methodology

Since the precedent work [cf.3], the development of the liquid-phase direct perfluorination of organic compounds with elemental fluorine has been undoubtedly hindered, presumably owing to the occasional violence of the reaction [4] and its tendency to give oligomers [5]. The first requirement for the development of the liquid-phase direct fluorination is a sufficiently inert solvent which efficiently dissolves substrates to be fluorinated. The best for inertness would be an unstrained F-alkane which is kinetically stable in excess fluorine to high temperatures [6]. Such materials, however, normally exhibit very poor solubility for hydrocarbons [7]. This antinomy on solubility and inertness is intrinsic in F-alkane solvents so that the substrates had to be modified to be dissolved in them. For that purpose we selected partly fluorinated substrates since partial fluorination of hydrocarbons greatly improves solubility, for example, benzotrifluoride is completely miscible with F-hexane at 25°C, but toluene is not. The inescapable characteristic of direct fluorination is the great exothermicity of the reaction as described elsewhere [8]. Required in this regard is to tame the fluorination reaction to avoid violent explosions. To respond to this problem, many workers have passed highly diluted fluorine into or over a neat or diluted liquid substrate at moderate temperatures.

Sufficient dilution of the fluorine adequately controls the exothermicity of the reaction, but leads to extensive polymerization of the materials being fluorinated, because the intermediate carbon radicals combine themselves before encountering a molecule of fluorine or a fluorine radical. Conditions that we selected to overcome these problems here were an inverse addition of the substrates into an F-alkane solvent saturated with undiluted fluorine gas, under ultra violet irradiation. The substrate is slowly metered into the well stirred F-alkane solvent saturated with undiluted fluorine gas which is constantly introduced at the bottom of the reaction vessel. Fluorine, with low polarizability and a boiling point of -188.3 °C [9], can be expected to have a satisfactory solubility in perfluorochemicals. Solubility of fluorine gas in F-hexane at an atmospheric pressure was determined spectrophotometrically using a fused saphire cell to give a value of 0.02 M at 25°C. We believe that the value is much higher at low temperatures. With vigorous stirring, it should be possible to maintain the concentration of fluorine in solution well above the concentration of unreacted substrate present, provided that the rates of fluorine consumption and substrate are monitored and controlled. As a result, the substrate concentration is always low enough so that the intermediate radical can react with a fluorine molecule or a fluorine radical nearby in the environment to give the desired F-chemicals but not the oligomers.

## Synthesis of perfluoroethers

We have focused our attention on the synthesis of perfluorochemicals containing eight to ten carbons with the hope that they will be of value as oxygen carrying agents. Perfluorination of ether 3a which was derived from F-2-methyl-2-pentanol [10] and 1-iodopropane at ambient temperature, gave



3a, R = $n\text{-}C_3H_7$

3b, R = $CH_2C(CH_3)=CH_2$

4

5a

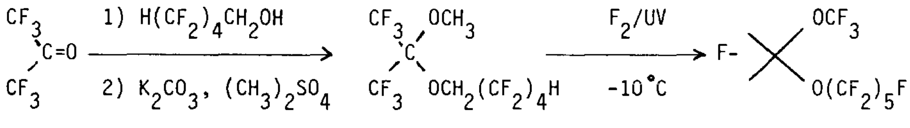
$$\begin{matrix}\underline{3a}\\ \underline{3b}\end{matrix} \xrightarrow[-5\ -7^{\circ}C]{F_2/UV} \begin{matrix}\underline{5a},\ R_F = n\text{-}C_3F_7\\ \underline{5b},\ R_F = i\text{-}C_4F_9\end{matrix}$$

the desired F-ether 5a in as low as 0.5% yield, along with incompletely fluorinated ether 4 in 39.3% yield. This suggested that there might take place considerable fragmentations giving F-isohexane 6 which is an isomer of the solvent used. Another run at lower temperatures (-5 -7°C) gave 5a in about 60% yield without the accompanying formation of high boiling compounds and 4. Analogous to 3a, 3b gave 5b in 51% yield. The use of low temperatures apparently minimized the fragmentation, and no high boiling residue was found in the distillation of the reaction mixture implying that the by-products formed in this process are probably more volatile compounds with fewer carbons rather than oligomers. Unlike compound 3, partly fluorinated ether 7 was smoothly fluorinated at room temperature to give the corresponding F-ether 8 in 55% yield. As all reactions described here were carried out at as high a temperature as possible with the aim of producing perfluorochemicals in at least 50% yield, we did not try this reaction at lower temperatures than room temperature but we believe that low temperature fluorination of 7 will provide much better yields of 8.

$$H(CF_2)_6CH_2OCH_2CH_2CH_3 \xrightarrow[\text{at r.t.}]{F_2/UV} F(CF_2)_7OCF_2CF_2CF_3$$

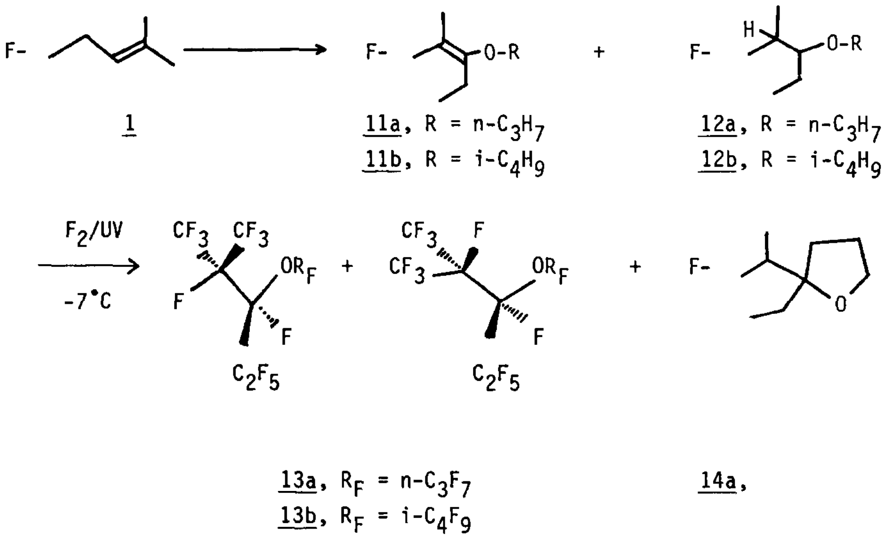
7 8

Similarly, ketal 9, which was obtained by the reaction of hexafluoroacetone 2 with 1H,1H,5H-F-pentan-1-ol followed by methylation with dimethylsulfate, was perfluorinated to give perfluoroketal 10 in 71% yield with ease. The fluorination of such an acid sensitive compound in solution is also of interest because 1 molecule of hydrogen fluoride is produced for every hydrogen substituted in the photofluorination process and the use of low temperatures will maintain the by-product HF as a liquid phase with a low vapor pressure. The photofluorination of the acid-sensitive ketal 9 shows no indication of HF solvolysis, as evidenced by the high yield.



2 9 10

Reaction of F-1-methyl-2-pentene 1 with aliphatic alcohols in the presence of an equimolar amount of triethylamine gave a mixture of 11 and 12 in high yields. Fluorination of the mixture at a rate of 20 mmol/hr on average at -7°C afforded a perfluorinated product mixture in fairly good yields. The double bond was situated in a position suitable for cyclization



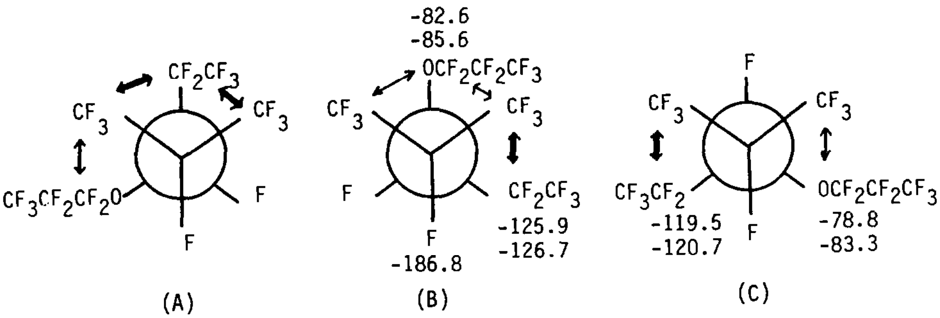
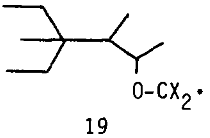


Fig.1. Newman Projections of Three possible gauche conformations of 13a.

through radical mechanism so that some cyclized by-product was formed [11]. The $^{19}$F-NMR of 13a measured at room temperature suggested that there were two components at the ratio of 5 to 2, but on raising the temperature (273 K to 373 K) of the measurement, some signals of both components (shown in Fig.1) coalesced and became consistent with $^{19}$F-NMR of the pure 13a. Newman projections along C2-C3 were drawn for three possible gauche conformations of 13a, (A), (B), and (C). Steric repulsions between $CF_3$ and $CF_2CF_3$ or between $CF_3$ and $OCF_2CF_2CF_3$ at gauche positions (shown by arrows) can account for the observed phenomenon as the existence of the rotamers. It is very likely that the repulsion of the former set of bulky groups is larger than the latter. Considering this, the integrated steric hindrance decreased in the order of (A), (B), and (C). Only two components were observed in $^{19}$F-NMR spectrum suggested that the rotamer (A) was too sterically hindered to exist. (B) and (C) are most likely to be the components of 13a with the population determined by the thermodynamic and kinetic factors.

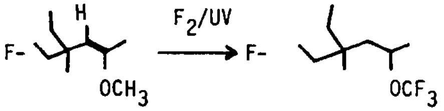
Perfluorination of ether 15, which was derived from tetrafluoroethylene pentamer 22, afforded the corresponding F-ether together with both degraded and cyclized by-products, 17 and 18, in a ratio of approximately 4:4:1. We expected that this reaction would provide the highest yield at moderately low temperatures in the experiments reported herein, because the fluorine content in 15 represents the highest case (as much as 68.4%) among the precursors synthesized for the study. The formation of 17 can be explained by both the steric effect and the instability of the intermediate radical 19.



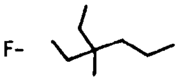
X = H or F

19

Because the photofluorination process reported herein is predominantly a radical process, complications do not seem to occur through rearrangements but do through degradation or cyclization in systems having bulky groups or double bonds. Radical recombinations leading to oligomer formation have been minimized in this liquid-phase photofluorination method but some fragmentations occurred regardless of the fluorine content of the substrate being fluorinated.



15 16



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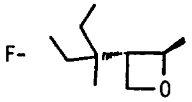

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In our liquid-phase photofluorination method, hydrogen atoms of the substrate are replaced with fluorine atoms at the rate of 140 (for 5a) to 280 mmol (for 13a) per hour per vessel (640 ml volume). The reaction conditions are not optimized and the reaction efficacy may be improved to some extent, perhaps by keeping the reaction temperature much lower or using F-alkanes with fewer carbon atoms in which much more fluorine gas is able to dissolve. But this is not the case for the sparingly soluble substrate because the low temperature makes the solubility situations worse. We have not enough experience on the fluorination of suspensions of the substrates, but it might be difficult to control the reaction precisely.

In our experience of the electrochemical fluorination process using a 1.5-L reactor cell, about 100 mmol exchange of hydrogen atoms per hour per 640 ml reactor volume was a conventional rate for the best substrates. Although further improvement of this new method is needed, the efficacy of the liquid-phase photofluorination reactor is already comparable to those reported in the electrochemical fluorination reactors of a similar size (*ca.* 300 mmol H per hour per 640 ml cell volume) [12].

La-Mar or Aerosol direct fluorination methods are well known as prior arts for preparing perfluorochemicals [cf. 3b]. Each method has its own characteristic. A wide scope of the application, for instance (even polymer can be fluorinated) is an advantage for the La-Mar method, but the long reaction time and the requirement of the large sophisticated reactor is a disadvantage. The Aerosol direct fluorination method is rather simple, but its efficacy is still not high (*ca.* 30 mmol H atom/h/1.4-L reactor) compared to our method [13].

We believe our simple and efficacious method will have an important place in this field of technology in the future.

## EXPERIMENTAL

All usual safety precautions should be taken when handling undiluted fluorine. F-2-Methyl-2-pentene 1 was prepared by the reported procedure [10], while 1H,1H,7H-F-1-heptanol 20 and 1H,1H,5H-F-1-pentanol 21 were purchased from PCR Research Chemicals, Inc., and used as received. FC-72 [14] (3M Co.)* was used as the solvent after refining by distillation (bp 55-57°C). Tetrafluoroethylene pentamer 22 (ICI Mond Division) and hexafluoroacetone 2 (Daikin Kogyo) were gifts and were used as received. Elemental fluorine (98% technical grade) was purchased from Air Products and Chemicals Inc. and used after purification through sodium fluoride pellets. Percentage yields of products are expressed as the isolated yield unless otherwise stated. All fluorinations were carried out at as high a temperature as possible where at least 50% yields can be obtained, repeated at least twice, but further investigation to obtain better yields was not tried in most cases.

IR spectra were obtained on a Perkin-Elmer 281 spectrophotometer. Mass spectra (negative chemical ionization = NCI) were run on a Hewlet-Packard 5980A GC/MS system using 4.8 x 0.32 cm columns packed with 10% OV-202 on 100-200 mesh Gas Chrom RZ. $^{1}$H- and $^{19}$F-NMR spectra of compounds other than perfluorochemical products were obtained with a Varian T-60 (56.4 MHz) in neat liquids and those of perfluorochemical products with a Bruker WM500 (470.6 MHz) (Southern California Regional NMR Facility, Pasadena, CA) in $CDCl_3$ solutions, unless otherwise stated; all chemical shifts in cases of $^{19}$F-NMR are reported on the $\phi$ scale, with $CFCl_3$ as an internal standard and positive shifts to high frequency of the reference; those in cases of $^{1}$H-NMR are expressed on the $\delta$ scale using TMS as an external standard. Known products were confirmed on the basis of spectral data of authentic samples. $^{19}$F- and $^{1}$H-NMR or NCI-MS spectra of the new compounds were consistent with their structures.

### Apparatus

A typical fluorine-handling apparatus used is shown in Fig. 2. It consisted of (1) needle valves to the regulate fluorine gas flow rate, (2) an HF

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* Nominal chemical structure is not released by the manufacturer, but FC72 appears to be F-hexane, as a dominant component, by both its $^{19}$F-NMR spectrum and observed physical properties.

trap, (3) a Matheson mass flowmeter and a Model H-500MX transducer for measuring the fluorine flow rate, (4) the reaction vessel, (5) motors for stirring magnetic bars, (6) a refrigerator to cool the reaction mixture, (7) a micro-metering pump, (8) a container for the substrate to be fluorinated, (9) a condenser cooled by dry ice, (10) a trap for both solvent and volatile products, (11) a gas bubbler, and (12) a nitrogen purge line to prevent moisture and oxygen from diffusing into the reactor. Addition of the substrate with a micro-metering pump avoids the accumulation of unreacted substrate, with careful observation of the reactor temperatures and fluorine uptake.

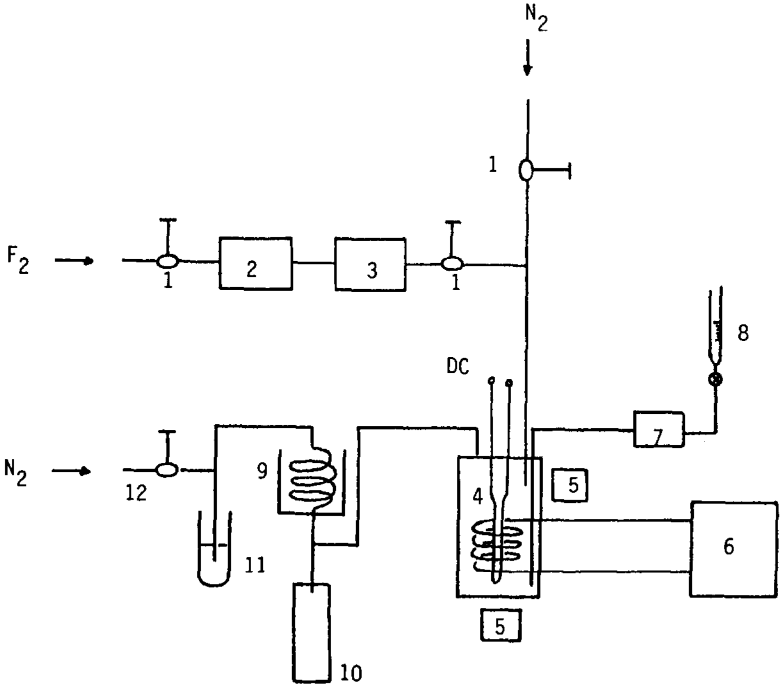

Fig.2. Diagram of Fluorination Apparatus.

Perfluorinations were conducted in the reaction vessel made of Teflon shown in Fig. 3. The reactor with a useful liquid capacity of 640 ml (25 °C) mainly consisted of a refrigeration spiral filled with 425 g of Freon 22 (A), a sapphire immersion well fitted with a mercury arc (B), an $F_2(N_2)$ inlet tube (C), a substrate inlet tube (D), a sample drain (E), a thermometer well (G), and an outlet connected to the trap and a nitrogen purge line (H). Stirring was carried out vigorously with two magnetic bars

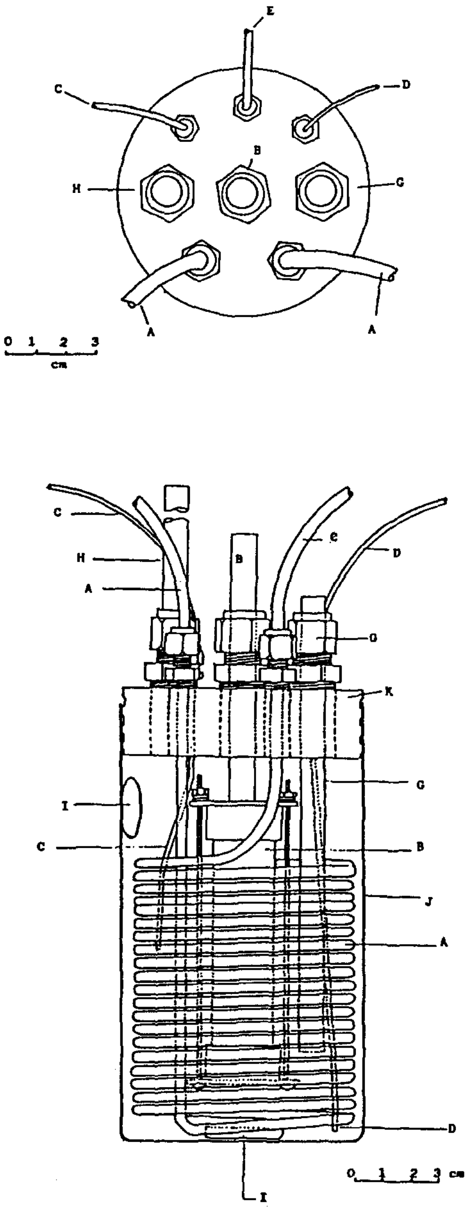

Fig.3. Reaction vessel for the direct liquid-phase photofluorination.

(I) at the bottom of and at the flank side of the vessel. The use of a 1-l Teflon bottle (Nalgen) (J), the top portion of which was cut off so that the rest can be fitted to the brass plate (K), made the entire mixture visible unless frosts gathered on the surface of the vessel. The immersion lamp system, details of which are shown in Fig. 4, was made of brass and a fused sapphire tube (6 cm long 2.4 cm o.d.) (M) which was held firmly between the two Teflon-sealed brass supporters (N, P). Medium-pressure mercury arcs (100 W, Hanovia) (Q) were used after removing its original ballast and jacket and reassembling wiring so as to be easily placed in the well. The entire arc immersion well equipped with a Pyrex filter (R) was placed in the center of the reaction vessel so that the maximum possible intensity of the light can be obtained.

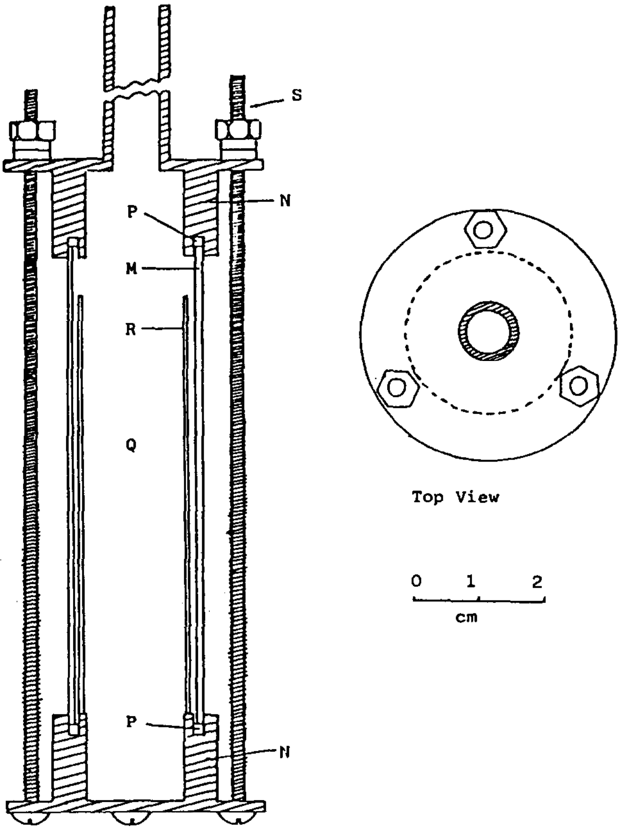

Fig.4. Detail of Sapphire Immersion Well.

## General procedure

The reaction vessel was filled with FC72 and connected to the brass lid. Nitrogen gas was bubbled into the vessel with vigorous stirring to purge the air inside the reaction system for at least 1 h, then replaced by undiluted fluorine gas. The substrate to be fluorinated was metered into the fluorine-saturated solvent by a micro-metering pump under UV irradiation at appropriate temperatures. Fluorine gas was introduced into the reaction mixture in a stoichiometric excess at all times. After the completion of the addition of the substrate, fluorine gas was continually introduced at the minimum controllable rate for 12-24h with the other conditions unchanged. The UV lamp was turned off and fluorine gas was purged out with a stream of nitrogen gas. The reaction mixture was washed with an aqueous saturated sodium bicarbonate solution and water, and dried over anhydrous $CaCl_2$. FC72 was removed by distillation and the residue obtained was distilled using a vaccum-jacketed silver-lined glass column packed with stainless gauze. If not purified in the distillation, the distillation fraction was subjected to preparative scale gas chromatography.

### 2-Propoxy-F-2-methylpentane (3a)(nc)

Dimethyl sulfoxide (110 ml), F-2-methyl-2-pentanol [10] (25.0 g, 0.074 mol), 85.7% KOH pellets (9.9 g, 0.15 mol) and 1-iodopropane (17.0 g, 0.10 mol) were combined and stirred at room temperature for 3 days. At the end of the reaction period the mixture was poured into _ca._ 300 ml of iced water and the crude lower layer which separated was dried over solid KOH. Distillation of the crude product at an atmospheric pressure gave 24 g of _3a_, 85% yield/ bp 124-125°C. Anal. for $C_9H_7OF_{13}$: C, 28.59; H, 1.87; Found: C, 28.64, H, 1.79.

### F-2-(1H-Propoxy)-2-methylpentane (4)(nc)

Ether _3a_ ( 20.7 g, 55 mM) was metered at room temperature over 3hr into F-hexane saturated with undiluted $F_2$, irradiated with the UV lamp and stirred vigorously. Distillation gave 10.5 g of colorless liquid _4_ (39.3%) bp 121-122°C [and 1.4 g (0.5%) of _5a_]. $^{19}$F-NMR ($CDCl_3$), -68.2 (octet, 6F), -81.8, (t, J=11.4 Hz, 3F), -83.0 (d, J=9.5 Hz, 3F), -114.7 (m, 2F), -125.7 (m, 2F), -129.1, -132.5 (AB q, J=285.8 Hz, 2F), -19.8 (d, J=53.3, 1F).

$^1$H-NMR (neat), 5.8 (d of t, J=53.0 Hz, 4.4 Hz, 1H). IR ( F-hexane ), 3055 cm$^{-1}$(CH). NCI-GC/MS, 319 (base,$C_6F_{13}^-$), 167 ($CF_3CF_2CFH^-$).

### F-2-Propoxy-2-methylpropane (5a)(nc), low temperature fluorination of 3a

Into $F_2$-saturated FC72 cooled at -6 ± 1°C was metered 126.5 g (0.335 mol) of 3a at a rate of 16 $\pm$ 3 mmol/h, under UV irradiation. After charging 3a the reaction mixture was bubbled continually with $F_2$ (15 ml/min.) at the same temperature range for 12 h. Distillation gave a colorless liquid 5a, 101.9 g (60.3%). bp 121.5-122 °C. $^{19}$F-NMR ($CDCl_3$), -68.9 (tt, J = 12.3 Hz, 6F),-82.0 (t, J = 12.4 Hz, 3F), -82.3 (br.s, 2F), -82.6 (br. s, 3F), -113.9 (septet, 2F), -125.4 (br. s, 2F), -130.5 (s, 2F).

### 2-Methylallyl-F-2-methylpentane (3b)(nc)

F-2-methyl-2-pentanol (67.2 g, 0.20 mol), 3-chloro-2-methylpropene (25.7 g, 0.30 mol), sodium iodide (1.5 g), and 150 mL dry dimethyl sulfoxide were placed in a 500-ml flask and stirred at room temperature for one week. The reaction mixture was poured into 300 ml of water. A lower layer was separated and dried over KOH pellets. Distillation under reduced pressure gave 42.7 g of a colorless liquid 3b in 55 % yield, bp 67-68 °C/80 mmHg. $^{19}$F-NMR (neat), -67.5 (tt, 6F), -81.3 (t, 3F), -112.1 (m, 2F), -123.0 (m, 2F). $^1$H-NMR (neat, $\delta$), 1.4 (m, 3H), 4.0 (m, 2H), 4.6 (m, 2H). IR ($CCl_4$), 3000, 2970, 2939 (CH), 1658 (C=C).

### F-2-Isobutoxy-2-methylpentane (5b)(nc)

Ether 3b (158 g, 0.405 mol) was metered at a rate of 19 mmol/hr at reaction temperatures controlled at -5 $\pm$ 2°C. After feeding, the entire mixture was bubbled with undiluted $F_2$ for 8 hr under the same conditions, then with dry $N_2$ for 50 min. Distillation gave 148 g of a colorless liquid 5b, bp 138.5-139.5°C in 66 % yield. $^{19}$F-NMR ($CDCl_3$), -68.6 (tt, J = 11 Hz, 6F), -74.3 (br. s, 2F), -74.6 (d, J = 1.2 Hz, 6F), -81.9 (t, J = 12.2 Hz, 3F), -113.3 (octet, J = 12.2 Hz, 2F), -125.7 (br. s, 2F), -186.8 (m, 1F). NCI-GC/MS, 554 ($M^-$), 335($C_6F_{13}O^-$), 300($C_6F_{12}^-$), 235 ( base, $C_4F_9O^-$).

### 1-Propoxy-1H,1H,7H-F-heptane (7)(nc)

Distilled propyl iodide (20.4 g, 0.12 mol) was added in portions to a stirred solution of 20 (33 g, 0.10 mol) and 85.7% KOH pellets (6.6 g, ca. 0.12 mol) in 50 ml of dimethyl sulfoxide at 5 to 10 °C. After 48 hr stirring at room temperature, propyl iodide (10.2 g, 0.06 mol) and KOH pellets (3.3 g, ca. 0.06 mol) were further added to the reaction mixture. The entire mixture was allowed to stir at room temperature for additional 24 hr and then poured into 200 ml of iced water. The lower layer was washed with an aqueous KOH solution, dried over KOH pellets, and distilled to give 29.7 g (79.4 %) of 7, bp 171-172°C. $^{19}$F-NMR (neat), -117.8 (quintet, J = 13.0 Hz , 2F), -120.1(m,2F), -121.5 (m, 4F), -127.9 (m, 2F), -135.9 (d, J = 54.5 Hz, 2F). $^{1}$H-NMR (neat), 0.75 (t, J = 6.5 Hz, 3H), 1.40 (q, J = 6.5 Hz, 2H), 3.40 (t, J = 6.5 Hz, 2H), 3.76 (t, J = 14.0 Hz, 2H), 5.96 ( tt, J = 5.0 and 54.5 Hz, 1H). IR ($CCl_4$), 2967, 2925, 2877 (CH).

### F-Heptylpropylether (8)(nc)

Distilled 7 (112.2 g, 0.30 mol) was metered at a rate of 4 mmol/hr at room temperature. After feeding, the entire reaction mixture was bubbled with undiluted $F_2$ for 12h under the same conditions, then with dry $N_2$ for 1h. Distillation gave 152.5 g (55.1%) of a colorless liquid , bp 136-137 C. $^{19}$F-NMR ($CDCl_3$ ), -82.1 (t, J = 10.5 Hz, 3F), -82.7 (t, J = 7.5 Hz, 3F), -84.3 (q, J = 13.0 Hz, 2F), -85.6 (octet, J = 6.5 Hz, 2F), -123.4 (m, 2F), -123.6 (m, 2F), -124.1 (m, 2F), -126.8 (m, 2F), -127.5 (m, 2F), -131.2 (s, 2F), NCI-GC/MS, 385($C_7F_{15}O^-$), 366($C_7F_{14}O^-$), 300($C_6F_{12}^-$), 185 (base, $C_3F_7O^-$), 166($C_3F_6O^-$).

### 2-Methoxy-F-2-(1H, 1H, 5H-pentoxy)propane (9)(nc)

Hexafluoroacetone 2 (22 ml at -78°C, ca. 0.21 mol) was slowly distilled into a stirred solution of 21 (48.9 g, 0.21 mol) in acetonitrile (50 ml). The entire mixture was stirred at room temperature overnight. The resulting hemiacetal was treated with dimethyl sulfate (29.3 g, 0.23 mol) followed by anhydrous potassium carbonate (24 g) which was added in small portions over 1 hr. After being stirred overnight the mixture was poured into water. The lower layer was separated, washed with an aqueous KOH solution then with water, and dried over $CaCl_2$. Distillation gave 40 g (46%) of 9 as a colorless liquid, bp 155-156°C. $^{19}$F-NMR (neat), -75.6 (s, 6F), -119.9 (quintet, J = 10.2 Hz, 2F), -124.8 (m, 2F), -129.9 (m, 2F),

-137.6 (dm, 2F). $^1$H-NMR (neat, $\delta$), 3.4 (s, 3H), 3.9 (t, 2H), 5.7 (tt, 1H). IR ($CCl_4$): 3015, 2971, 2856 (CH).

### F-2-Pentoxy-2-methoxypropane (10)(nc)

Ketal 9 (127.0 g, 0.308 mol), was fluorinated at -10 °C with a feeding rate of 4 mmol/hr. Distillation gave 113.7 g (71 %) of 10 as a colorless liquid, bp 123-124 °C, $^{19}$F-NMR ($CDCl_3$, $\phi$), -55.7 (s, 3F), -77.4 (dq, J = 7.5 Hz, 6F), -82.2 (t, J = 9.5 Hz, 3F), -83.9 (br.s, 2F), -124.6 (sextet, 2F), -126.8 (m, 2F), -127.7 (t, J = 13.9 Hz, 2F), NCI-GC/MS, 285 (base, $C_5F_{11}O^-$), 266($C_5F_{10}O^-$), 200($C_4F_8^-$), 185($C_3F_7O^-$)

### 3-Propoxy-F-2-methyl-2-pentene (11a)(nc) and 3-propoxy-F-2-methyl-2H-pentane (12a)(nc)

To a mixture of 1 (292.7 g, 0.98 mol) and propanol (59.0 g, 0.98 mol) was added dropwise triethylamine (98.5 g, 0.97 mol) over 6 hr at 0 to 5 °C. The entire mixture was stirred at room temperature overnight and poured into 300 ml of iced water. A lower layer was separated, washed with dilute HCl then with water and dried over $CaCl_2$. Distillation gave a colorless liquid (289.3 g), bp 120-124 °C, which was identified as a mixture of 11a (71 %) and 12a (29 %) by $^{19}$F-NMR. $^{19}$F-NMR (11a, neat), -56.3 (m, 3F), -59.3 (q, J = 9.1 Hz, 3F), -80.9 (q, J = 3.2 Hz, 3F), -110.0 (q, J = 19.4 Hz, 2F). IR ($CCl_4$ cm$^{-1}$), 1638 (C=C), 2980 (CH). $^1$H-NMR (neat, $\delta$), 0.72 (t, 3H), 1.42 (sextet, 2H), 4.0 (t, 2H); $^{19}$F-NMR (12a, neat), -61.0 (m, 6F), -80.5 (d, J = 12.4 Hz, 3F), -123.1 (m, 2F), -126.7 (m, 1F). $^1$H-NMR (neat, $\delta$ ), 0.72 (t, J = 7.0 Hz, 3H), 1.42 (sextet, J = 7.0 Hz, 2H), 3.82 (m, 1H), 3.74 (t, J = 7.0 Hz, 2H). IR ($CCl_4$, cm$^{-1}$), 2985 (C-H)

### F-3-Propoxy-2-methylpentane (13a)(nc) and F-2-ethyl-2-isopropyltetrahydrofuran (14a)(nc)

The mixture (11a/12a = 71/29) was charged at -6 ± 1 °C at a rate of 17 mmol/hr with a maximum of 40 mmol/hr. Distillation gave a colorless liquid (bp 100-129 °C, 216.4 g) containing two main components, which were separated by distillation followed by preparative scale gas chromatography (40 °C, OV 202): yields were calculated by analytical scale gas chromatography, giving 13a (51.1 %), bp 121-122 C, NCI-GC/MS: 466 ($M-F_2$), 335 ($C_6F_{13}O^-$), 300($C_6F_{12}^-$), 250($C_5F_{10}^-$), 216($C_5F_{10}O^-$), 185 (base, $C_3F_7O^-$) and

14a (7.8 %), $^{19}$F-NMR ($CDCl_3$,$\phi$), -69.7 (m, 6F), -78.5, -79.8 (ABq, J = 140 Hz, 2F), -80.8 (d, J = 15 Hz, 3F), -121.5, -122.6 (ABq, J = 250 Hz, 2F), -127.3, -127.9 (Abq, J = 92.5 Hz, 2F), -171.6 (m, 1F), NCI-GC/MS: 466 ($M^-$), 400 (base, $C_8F_{16}^-$), 397, 362, 347, 297. The NMR spectrum of 13a indicated a mixture of rotational isomers in the ratio of 5 : 2. On raising the temperature (273 K - 373 K), signals assigned to 2, 4, and 1-Fs showed broadening and coalescence. $^{19}$F signals were tentatively assigned to the two isomers at room temperature as follows: For major component, -72.0 (m,3F), -73.1 (m, 3F), -78.8, -83.3 (ABq, J = 144 Hz, 2F(1-Fs)), -81.2 (q, J = 11.9 Hz, 3F), -82.7 (t, J = 8.5 Hz, 3F), -119.5, -120.7 (ABq, J = 289 Hz, 2F (4-Fs)), -130.2, -130.9 (ABq, J = 283.0 Hz, 2F), -134.9 (m, 1F), -182.8 (dm, 1F (2-F)); for minor component, -72.7 (octet, 3F), -76.1 (m, 3F), -81.8 (t, J = 10.9 Hz, 3F), -82.6 (q, 3F), -85.6 (m, 2F, (1-Fs)), -116.4 (m, 1F), -125.9, -126.7 (ABq, J = 285 Hz, 2F, (4-Fs)), -131.2 (s, 2F), -186.8 (m, 1F, (2-F)).

### 3-Isobutoxy-F-2-methylpentene (11b) and 3-isobutoxy-F-2-methyl-2H-pentane (12b)

The reaction was carried out by the same way as described on 11a using isobutyl alcohol. A mixture of 11b and 11a was obtained in *ca.* 85% yield, in a ratio of 4 :1 determined by $^{19}$F-NMR. Separation of these compounds was not attempted, and the mixture was used for the fluorination. $^{19}$F-NMR (11b, neat), -54.7 (m, 3F), -57.6 (q, J = 9.4 Hz, 3F), -79.6 (q, 3F), -110.2 (q, J = 19.6 Hz, 2F). $^1$H-NMR (neat), 0.82 (d, 6H), 1.80 (septet, 1H), 3.9 (d, 2H). IR ($CCl_4$, $cm^{-1}$), 2990 (CH), 1639 (C=C), $^{19}$F-NMR (12b, neat), -59.9 (m, 6F), -79.1 (d, 3F), -118.8 (m, 2F), -122.3 (m, 1F). $^1$H-NMR; 12b (neat) 0.80 (d, J = 7.0 Hz, 6H), 1.80 (m, 1H), 3.60(m,1H), 3.80 (m, 3H), bp 134-138 C.

### F-3-Isobutoxy-2-methylpentane (13b)

The mixture obtained above (11b/12b = 4/1, 179.7 g) was charged at a rate of 17 mmol/h at -5 °C. Distillation gave a colorless liquid (bp 108-142 °C, 183.1 g) containing two main components, separated by distillation followed by preparative scale gas chromatography (40 °C, OV202):yields were calculated by analytical scale gas chromatography, giving 13b (45.6%), bp 136-137 °C, NCI-GC/MS: 335($C_6F_{13}O^-$), 300($C_6F_{12}^-$), 250($C_5F_{10}^-$), 235 (base, $C_4F_9O^-$), 216. The $^{19}$F-NMR of this fraction also indicated a mixture of conformational isomers in the ratio of 7 :2. $^{19}$F-NMR (major component, $CDCl_3$), -72.66, (ABq, J = 154.0 Hz, 1F), -78.41 (ABq, J = 148.0 Hz, 1F), -73.65 (m, 3F), -75.09 (m, 3F), -76.57 (br.s, 6F), -83.29 (q, J = 13.3 Hz, 3F), -119.75, -121.77 (ABq, J = 293, 284 Hz, 2F), -137.16 (m, 1F), -184.21 (dm, 1F), -189.33(s, 1F); (minor component, $CDCl_3$), -74.9 (m, 3F), -76.84 (m, 6F), -80.07 (m, 3F), -83.88 (t, J = 10.0 Hz, 3F), -84.43 (m, 2F), -128.06 , -128.83 (ABq, J = 295 Hz, 2F), -130.22 (s, 1F), -188.78 (m, 1F), -190.47 (m, 1F): the unknown original minor component(18.2 %), NCI-GC/MS: 516 ($M^-$, $C_{10}F_{20}O^-$), 450 ($C_9F_{18}$), 412($C_9F_{16}$), 397($C_8F_{15}O^-$), 347 (base, $C_7F_{13}O^-$), 281($C_6F_{11}^-$), 262($C_6F_{10}^-$)

### 3H-2-Methoxy-F-4-ethyl-4-methyl-2-hexene (15)(nc)

3H, 3H-F-4-ethyl-4-methyl-2-hexanone which was derived by the reaction of tetrafluoroethylene pentamer 22 with aqueous sodium hydroxide followed by acidification of the reaction product (43 g, 0.1 mol) [14], 100 mL of 1.2M KOH and methyl sulfate (13 g, 0.1 mol) were combined and stirred at room temperature for 18 hr. At the end of the reaction period a lower layer which formed was separated, washed with aqueous KOH solution and water, dried over $CaCl_2$ and distilled to give the ether 15, bp 136.5-137°C, 30.2 g (68 %). $^{19}$F-NMR (neat), -59.6 (m, 3F), -67.4 (s, 3F), -79.5 (s, 6F), -111.2 (m, 4F). $^1$H-NMR (neat), 3.6 (d, 3H), 5.2 (m, 1H). IR ($CCl_4$, $cm^{-1}$), 3007, 2961, 2884 (CH), 1677 (C=C).

### F-2-Methoxy-4-ethyl-4-methylhexane (16)(nc), F-3-ethyl-3-methylhexane (17) and F-2-methyl-3-(1-ethyl-1-methylpropyl)oxetane (18)(nc)

Distilled 15 (142.7 g, 0.321 mol) was perfluorinated by introducing it into the reaction vessel at a rate of 4 mmol/h at 0°C. Distillation gave a colorless liquid (bp 105-149°C, 158.5 g) containing three main components, isolated by redistillation followed by preparative-scale gas chromatography (40 °C, OV202); yields were calculated by analytical scale gas chromatography giving 16 (40.9%), bp 145-146°C, $^{19}$F-NMR ($CDCl_3$), -55.2 (t, J = 13.9 Hz, 3F), -57.4 (s, 3F), -77.0 (octet, J = 10.0 Hz, 3F), -79.0 (m, 6F), -96.8, -99.7 (ABq, J = 302 Hz, 2F), -103.1 (m, 4F), -133.1 (m, 1F), 17 (40.8%), bp 130-132°C, $^{19}$F-NMR ($CDCl_3$), -59.0 (octet, J = 10.9 Hz, 3F), -78.9 (m, 6F), -81.4 (t, J = 14.2 Hz, 3F), -104.1 (s, 4F), -110.5 (q, J =

10.9 Hz, 2F), -122.2 (sextet, J = 18.7 Hz, 2F) and 18 (10.9%) $^{19}$F-NMR ($CDCl_3$), -59.9 (octet, J = 10.9 Hz, 3F), -77.1, -79.1 (ABq, J = 235 Hz, 2F), -78.8 (m, 6F), -79.3 (br.s, 3F), -103.3, -105.5 (ABq, J = 315.4 Hz, 2F), -103.8, -104.8 (ABq, J = 300.5, 306.5 Hz, 2F), -117.2 (q, J = 6.5 Hz, 1F), -153.9 (m, 1F), NCI-GC/MS, 447 (M-$CF_3$), 397 (base, $C_8F_{15}O^-$), 319 ($C_6F_{13}^-$), 312($C_7F_{12}^-$), 300($C_6F_{12}^-$), 262($C_6F_{10}^-$).

## Solubility of fluorine gas in FC72

A sapphire-windowed UV cell made of brass with 10 cm of a light path was used for the measurement of UV spectra. The cell was filled with FC72 and the absorption spectrum was measured in the range of 250 to 550 nm using air as a reference and the absorbance at 285 nm was used as a blank (0.130). FC72 filled in the cell was saturated with fluorine gas by bubbling it through the cell for over 30 min at room temperature (25°C) and the absorption spectrum was measured in the same manner as before. Maximum absorption of fluorine gas dissolved in FC72 was found at 285 nm (1.361) as is the same for the fluorine gas itself [15]. According to the Beer's law, the fluorine gas solubility in FC72 was calculated as 0.02 M using the reported value of the molecular extinction coefficient (6.00 l $mole^{-1}$ $cm^{-1}$) of fluorine gas [15].

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