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Liquid-phase photofluorination with elemental fluorine. Part II. Synthesis of perfluorotertiary amines

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Abstract

The tertiary amines derived from hexafluoropropene dimers were subjected to liquid-phase photofluorination (LPPF). The corresponding perfluorotertiary amines, which were difficult to synthesize by the conventional fluorination methods such as electrochemical fluorination and indirect fluorination using high-valency metal fluorides, were obtained in good yields. Prepared by this method were *F*-(*N,N*-dimethyl-2-methylpentyl)amine **3**, *F*-(*N,N*-diethyl-2-methylpentyl)amine **4**, *F*-3-(1-pyrrolidino)-2-methylpentane **11**, *F*-(*N,N*-dimethyl-1,1-dimethylbutyl)amine **13**. Discussion on the regioselectivity in the reaction of *F*-2-methyl-2-pentene (D-II) with secondary amines is also included in connection with the necessity of preparing a regioselective adduct, 3-(1-pyrrolidino)-*F*-2-methyl-2-pentene, for the synthesis of **11**.

Keywords: Liquid-phase photofluorination; Perfluorotertiary amines; Perfluorochemicals; Synthesis

1. Introduction

Perfluorochemicals have many industrial applications [1]. One of the most important is in the medical field; for example, Fluosol DA® has been used as oxygen carrier in percutaneous transluminal coronary angioplasty (PTCA) [2]. Very necessary in the fine chemicals industries in this field is a sophisticated technology to enable us to synthesize tailor-made perfluorochemicals. Conventional synthetic methods are too vigorous to synthesize the designed perfluorochemicals in pure form (i.e. electrochemical fluorination and indirect fluorination using metal fluoride), or too time-consuming to obtain them in large quantity (i.e. conventional direct fluorination) [3]. Therefore, we have developed a new perfluorination method which we call liquid-phase photofluorination (LPPF). A previous report showed that this method was applicable for the synthesis of perfluoroethers [4]. This paper describes further application of the LPPF method to the synthesis of perfluorotertiary amines.

The present work was carried out in 1982–1984, and its original concept has already been reported in a patent [5]. This paper describes a part of the work in detail.

2. Results and discussion

2.1. Synthesis of the starting tertiary amines

Since, from a technical requirement for LPPF, the starting tertiary amines should be soluble in a perfluoro-solvent like perfluorohexane, we synthesized partly fluorinated tertiary amines utilizing a hexafluoropropene dimer, *F*-2-methyl-2-pentene (conventionally abbreviated as D-II) (Scheme 1).

Compound **1** was prepared by the reaction of D-II with bis(dimethyl-amino)methane in 67% yield. Compound **2** was synthesized by our method, which is superior to the literature methods [6]. Thus, **2** was obtained in an almost quantitative yield by reacting D-II with *N,N*-diethylaminotrimethylsilane. As in the cases of **1** and **2**, the reaction of D-II with aliphatic amines proceeds through an isomerized form in general. Thus D-II is isomerized to a terminal olefin by F^--catalyzed double-bond migration before reacting with the nucleophiles [7].

Conflicting results have been reported on the reaction of cyclic amines with D-II. For example, Flowers et al. referred to the formation of an inner enamine, 3-piperidino-*F*-2-

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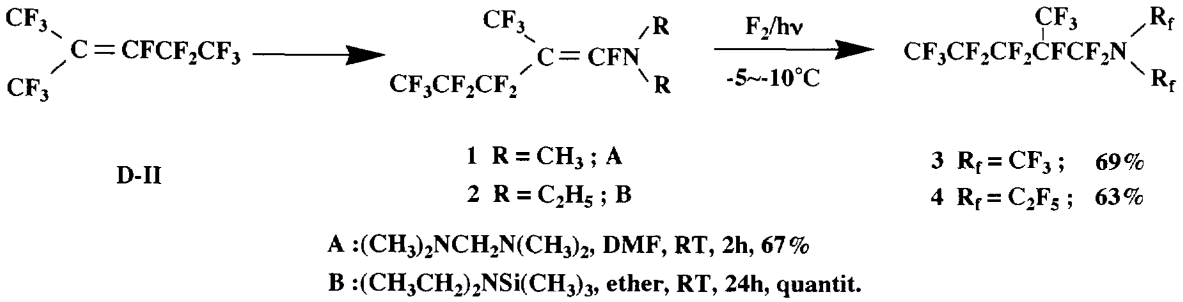
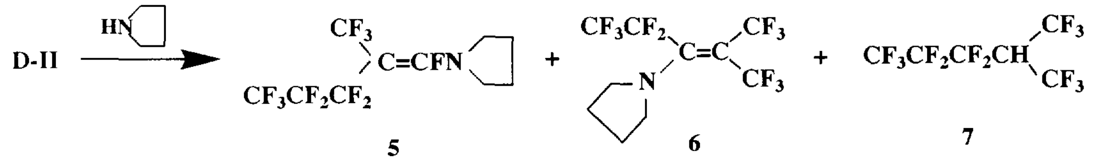


Scheme 1.



Scheme 2.

Table 1
Results of the reaction of D-II with pyrrolidine under various conditions

Run	D-II (eq.)	Pyrrolidine (eq.)	$Et_3N{:}BF_3$ (eq.)	$Et_2O{:}BF_3$ (eq.)	Solvent	Temperature (°C)	5 [a] (%)	6 [a] (%)	7 [a] (%)
1	1	2	–	–	Dioxane		80	20	–
2	1	2	1	–	Ether		70	30	–
3	1	1	2	–	Ether		70	30	–
4	1	1	4	–	DMF		70	30	–
5	1	2	–	1	Ether	−37	26	13	61
6	1	2	–	1	Ether	−78	6	34	60
7	1	0.5	–	–	Ether	−78	–	29	81
8	1	1	–	–	Ether	−78	–	33	67
9	1	2	–	–	Ether	−78	–	67	33

[a] NMR yields.

methyl-2-pentene in the reaction of D-II with piperidine without any experimental details [8], but England and Piecara reported that the inner enamine was accompanied as a minor product along with a terminal enamine, 1-piperidino-*F*-2-methyl-1-pentene [9]. Ishikawa's report said the terminal enamine was the sole product [6]. Our result of a similar reaction of D-II with pyrrolidine was comparable to the one reported by England and Piecara (Table 1, run 1).

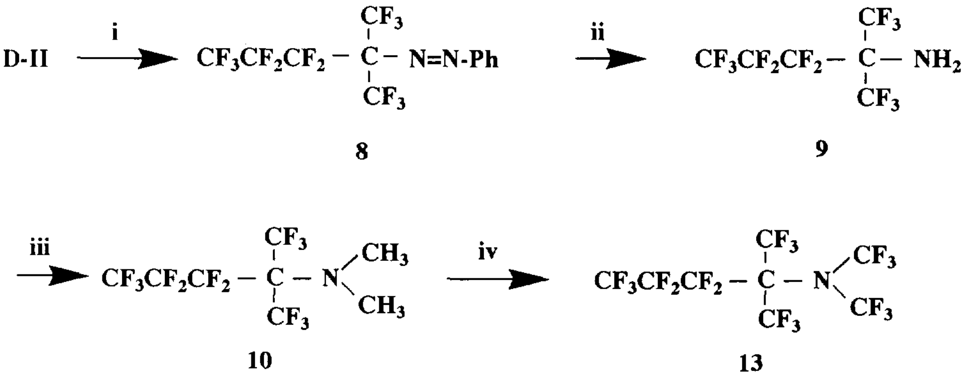
We were most interested in a more highly branched perfluorotertiary amine **6** than **5** as an oxygen carrier (Scheme 2). In this context, we sought the conditions for preparing **6** selectively. Double-bond migration of D-II is catalyzed by fluoride ions formed as the reaction proceeds. Therefore, with an excess of triethylamine-boron trifluoride complex ($Et_3N{:}BF_3$), which is known to be able to trap hydrogen fluoride, we expected that such double-bond migration would be suppressed to give **6** selectively. But, disappointingly, **5** was still obtained as a major compound (runs 2–4). Diethyl ether-boron trifluoride complex ($Et_2O{:}BF_3$) was not effective either (runs 5, 6). When the reaction temperature was lowered to −78 °C, the formation of **5** diminished to nil, and **6** formed as a major product with a concomitant formation of **7**. Separation of **6** and **7** was easily performed by simple distillation.

Compound **10** was synthesized as shown in Scheme 3. Thus, D-II was converted to a phenyldiazonium compound **8** by treatment with phenyldiazonium tetrafluoroborate, followed by Zn(Hg) reduction and methylation with methyl triflate in 48% overall yield [10].

2.2. Liquid-phase photofluorination

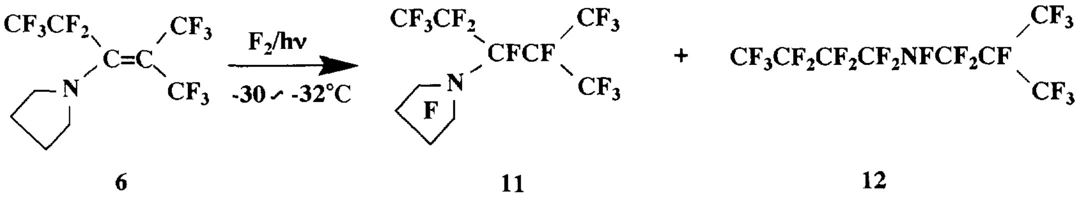
Electrochemical fluorination (ECF) seems to be the only practical method for preparing perfluorotertiary amines on an industrial scale. Even though several beneficial points exist in the ECF process, the spectrum of the application is narrowed by the disadvantages caused by rearrangement and degradation reactions, which lead to a complex mixture. Similar physicochemical properties of the isomer products make it difficult to purify the desired component. From our special interest, we applied LPPF to the synthesis of perfluorotertiary amines with highly branched structures.

The LPPF of the enamines **1** and **2** gave corresponding *F*-tertiary amines **3** and **4** in 69% and 63% isolated yields,



i: $PhN_2^+BF_4^-$, KF/DMF, 15 ~ 20°C, 30min., 70.3% ii: $Zn(Hg)/CF_3CO_2H$, RT, 7days, 93%
iii: CH_3OTf, 60°C, 5days, 70% iv: F_2/hv, -6°C, 61%

Scheme 3.



Scheme 4.

respectively. Both **3** and **4** were obtained in a very pure form by simple distillation.

Moldavsky et al. recently reported on the ECF of the same kind of enamine, *N*,*N*-dibutyl-*N*-(*F*-2-methyl-1-pentenyl)-amine, showing that a corresponding *F*-tertiary amine was obtained in 54% crude yield [11]. The yield is better than usual because the substrate has the perfluorinated moiety of D-II. There is no doubt a difficulty in the isolation of the desired perfluorochemicals in pure form from the crude mixture obtained by ECF. LPPF seems to be superior to ECF from this aspect.

The structures of **3** and **4** were confirmed by ^{19}F NMR and negative-chemical-ionization gas chromatography/mass spectrometry (NCI-GC–MS). Characteristic in both ^{19}F NMR spectra are AB systems, found in all CF_2 groups, caused by the asymmetric tertiary carbon.

The signal at about -180 ppm, which we assigned as a fluorine connected to the tertiary carbon adjacent to a nitrogen atom in **3** and **4**, was not consistent with the data of the homologues, *F*-(*N*,*N*-dipropyl-*N*-2-methylpentyl)amine and *F*-(*N*,*N*-dibutyl-*N*-2-methylpentyl)amine, which were reported by Moldavsky et al. Their chemical shift of the corresponding F atom was about -161 ppm, which, we think, is shifted too much down-field (for further supportive data for a similar grouping at -184 ppm, see Ref. [12]). The other signals are very similar to their reported data. Di-(*F*-alkyl)amino anions ($^{-}N(CF_3)_2$ and $^{-}N(C_2F_5)_2$) gave base peaks in both NCI-GC–MSs.

The superior results on LPPF of **1** and **2** encouraged us to step up to the highly congested enamine, **6** (Scheme 4). The desired product, **11** is highly congested (compare with a persistent *F*-alkyl radical, *F*-2,4-dimethyl-3-ethyl-3-pentyl, reported by Scherer et al. [13]), so that the fluorination was carried out at lower temperatures (about -30 °C) to prevent degradation reactions. Even operated at the lower temperature, the desired *F*-3-(1-pyrrolidino)-2-methylpentane **11** was accompanied by a degraded by-product, **12**, and other unknown by-products (92:7:1). The desired **11**, boiling at 140–143 °C, was fortunately separated in a pure form from the lower-boiling by-products, but the yield was slightly lowered to 43%.

The structures of **11** and **12** were determined by ^{19}F NMR and NCI-GC–MS. Trifluoromethyl groups of $CF(CF_3)_2$ moiety had different chemical shifts at -70.5 and -71.5 ppm. It is tempting to attribute the occurrence of two signals for the trifluoromethyl groups to a hindered rotation of the *F*-isopropyl group. Such behavior is well known for rotation about C–C bonds [14] [4]. Of two sets of the difluoromethylene groups of the pyrrolidyl ring, the one distant from the N atom showed an AB quartet at -133.9 and -140.4, but the other one, directly connected to the N atom, might be complicated by the hindered rotations, yielding a deformed AB-system-like signals between -84.3 and -97.4 ppm.

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[4] A referee offers another explanation: in compound **11** the tertiary carbon atom to which the *F*-isopropyl group is bound is an asymmetric one; owing to this, the two adjacent trifluoromethyl groups may no longer be equivalent.

We did not study the rotational barriers further owing to a lack of a temperature control unit for the NMR measurement. Two broad singlet signals at − 160.1 and − 175.6 were consistent with $=C\underline{F}–N=$ and $C\underline{F}(CF_3)_2$, respectively. The signal of **12** found at − 89.6 is characteristic for the $=N–F$ moiety. The existence of this moiety was futher confirmed by a reaction with a saturated KI acetone solution. NCI-GC–MS of **11** and **12** gave characteristic anion fragments $^-NC_4F_8$ and $^-NC_8F_{18}$ as base peaks, respectively. It should be mentioned that no appreciable amount of persistent *F*-alkyl radicals was formed under these reaction conditions.

The structure of **12** clearly shows a splitting-off of the pentafluoroethyl group through the fluorination reaction. This bond-breaking position is rather unexpected because the C(*tert*)–C(*tert*) bond between the adjacent tertiary carbons is weaker than the C(*sec*)–C(*tert*) bond [15].

The tertiary amine **10**, with a *F-tert*-hexyl group, was also successfuly fluorinated in the same manner to give the desired *F*-(*N*,*N*-dimethyl-*N*-1,1-dimethylbutyl)amine **13** in a good isolated yield (61%). The stable *F*-(dimethyl)amino anion, $(CF_3)_2N^-$, was the base peak in the NCI-GC–MS of **13**.

3. Experimental details

All the usual safety precautions should be taken when handling undiluted fluorine. D-II was prepared according to Ishikawa's method [6]. Benzenediazonium tetrafluoroborate was prepared by the reported procedure [16]. Elemental fluorine (98% technical grade) was purchased from Air Products and Chemicals Inc. and used after purification through sodium fluoride pellets. FC-72 (3M Co.) [5] was used as the solvent after refining by distillation (b.p. 55–57 °C).

IR spectra were obtained on a Perkin–Elmer 281 spectrometer. Mass spectra were run on a Hewlet–Packard 5980A GC–MS system using a 4.8 cm × 0.32 cm column packed with 10% OV-202 on 100–200 mesh Gas Chrom RZ. Nitrogen gas was used as a buffer gas for measuring mass spectra in the NCI mode. ^1H and ^{19}F NMR spectra were measured with a Varian T-60 (56.4 MHz) in neat liquids. Chemical shifts of ^{19}F NMR are reported on the δ scale, with $CFCl_3$ as an internal standard, and positive shifts to high frequency of the reference; those of ^1H NMR are expressed on the δ scale, using TMS as an external standard.

Experimental details on LPPF were shown in the previous report [4].

3.1.1. 1-Dimethylamino-F-2-methyl-1-pentene, 1 (nc)

A mixture of D-II (50 g, 0.17 mol) and bis(dimethylamino)methane (17.5 g, 0.17 mol) in 100 ml of dry DMF was stirred at room temperature for 2 h. The reaction mixture was poured into 300 ml of iced water. The lower layer was separated, washed with water, and dried over $CaCl_2$. Distillation gave a pale yellow liquid **1**, b.p. 73–74 °C (10 mmHg), 37 g (67%). ^{19}F NMR (neat): −52.7 (m, 3F), −57.6 (m, 1F), −81.4 (t, 3F), −102.2 (m, 2F), −124.6 (dq, 2F). ^1H NMR (neat): 2.46 (CH_3). IR (CCl_4): 2940 (CH), 1665 (C=C). Anal. Found: C, 29.88; H, 1.62; N, 4.91; F, 64.30. $C_8H_6NF_{11}$. Calc.: C, 29.55; H, 1.86; N, 4.31; F, 64.28.

3.1.2. 1-Diethylamino-F-2-methyl-1-pentene, 2

A mixture of D-II (16.3 g, 54 mmol) and diethylaminotrimethylsilane (7.2 g, 54 mmol) in 20 ml of dry ether was stirred at room temperature for 24 h. Ether was distilled off under reduced pressure. Distillation of the residue gave a pale yellow liquid **2**, b.p. 95–96 °C (30 mmHg), 18.6 g (97.6%), which was identified by comparison of its NMR spectra with those reported [6].

3.1.3. 3-(1-pyrrolidino)-F-2-methyl-2-pentene, 6 (nc)

To a mixture of D-II (159 g, 0.53 mol) and dioxane (80 ml) cooled in a dry-ice–acetone bath, a solution of pyrrolidine (75.8 g, 1.07 mol) in dioxane (70 ml) was added over 4 h, with vigorous stirring. The bath was taken away and the mixture was stirred at room temperature overnight. The reaction mixture was poured onto a mixture of 1,1,2-trichloro-1,2,2-trifluoroethane (F113, 200 ml) and 6N HCl (100 ml) and the whole was stirred vigorously at room temperature for 30 min. The Freon layer was washed with dilute HCl and water, then dried over anhydrous sodium sulfate. Distillation gave a pale yellow liquid **6**, b.p. 54–55 °C (5 mmHg), 33.3g (18.3%). ^{19}F NMR (neat): −53.4 (m, 3F), −58.9 (q, J = 8.5 Hz, 3F), −80.2 (q, J = 9.0 Hz, 3F), −106.0 (q, J = 15.8 Hz, 2F). ^1H NMR (neat): 1.68 (bs, 4H), 3.34 (bs, 4H). IR (CCl_4): 2952 (CH), 1660 (C=C).

3.1.4. 2-Amino-F-2-methylpentane, 9 (nc)

Into a mixture of dried DMF (400 ml), calcined KF (50 g, 0.86 mol), and D-II (100 ml, 0.5 mol) cooled at 15–20 °C was added benzenediazonium tetrafluoroborate (96 g, 0.5 mol) with vigorous stirring in small portions. After stirring for 30 min, the reaction mixture was filtered with suction and the filter cake (KBF_4 + KF) was washed with ether until the solids were almost white. 2N NaOH (500 ml) and ether (850 ml) were added to the filtrate and extracted. The etherial layer was separated, washed with 5% KOH, with 1N H_2SO_4, and with brine in this order, then dried over $CaCl_2$ overnight. Ether was evaporated and the residue was distilled in vacuo into a dry-ice-cooled receiver to give a orange-colored liquid **8**; b.p. 50 °C (3 mmHg); yield, 372.4 g (70.3%). Amalgamated zinc (130 g, 2.1 mol), trifluoroacetic acid (800 ml), and **8** (267 g, 0.63 mol) were placed in a 2 l flask and stirred for 8 days at room temperature. Water (650 ml) was added and the product **9** was obtained by steam distillation; b.p. 96–97 °C, d^{33} 1.718; yield, 93% (196 g). ^{19}F NMR (neat, int.

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[5] Nominal chemical structure is not released by the manufacturer, but FC-72 appears to be *F*-hexane, as a dominant component, by both its ^{19}F NMR spectrum and observed physical properties. Some physical data are available in Ref. [1b].

CF_3Cl_3): −71.8 (m, 6F), −81.2 (t, 3F), −113.2 (m, 2F), −123.0 (m, 2F). ^{1}H NMR (neat, ext. TMS) δ 2.1 (s, 2H).

*3.1.5. 2-Dimethylamino-F-2-methylpentane, **10** (nc)*

A solution of **9** (6.7 g, 20 mmol) in freshly prepared methyl triflate (7.2 g, 44 mmol) was heated at 60 °C for 24 h. Additional methyl triflate (3.6 g, 22 mmol) and powdered sodium chloride (5 g) were added on the first and the third day of the heating period (5 days). The reaction mixture was diluted with 150 ml of water and carefully made alkaline with aqeous KOH. The lower layer was separated, washed with water, dried over $CaCl_2$, and distilled to give a colorless liquid; b.p. 123–124 °C; yield, 5.1 g (70%). ^{19}F NMR (neat): −62.1 (tt, 6F), −80.9 (t, 3F), −106.3 (m, 2F), −123.7 (m, 2F). ^{1}H NMR (neat): 2.4 (s, 6H). IR (CCl_4) 2919, 2876, 2830, 1464. Anal. Found: C, 26.66; H, 1.38. $C_8H_6NF_{13}$. Calc.: C, 26.46; H, 1.67.

3.2. Liquid-phase photofluorination

*3.2.1. F-(N,N-Dimethyl-2-methylpentyl)amine, **3** (nc)*

The enamine **1** (16.0 g, 49 mmol) was pumped into the photoreactor [4] filled with F_2-saturated FC-72 at a rate of 5 mmol h^{-1} under UV irradiation. Undiluted fluorine gas was bubbled into the reaction mixture throughout the fluorination to keep the solution saturated. Temperature of the reaction mixture was maintained at −10 °C during the reaction. The reaction procedure followed the detail described in the previous report. Distillation of the resultant liquid using a vacuum-jacketed silver-lined glass column packed with stainless gauze (about 30 cm in length) gave a colorless liquid (99% purity by glc); b.p. 109–110 °C; yield, 16.0 g (69%). ^{19}F NMR ($CDCl_3$): −54.3 (t, J = 15.6 Hz, 6F), −72.9 (brs, 3F), −80.7, −87.3 (ABq., J = 252.2 Hz, 2F), −81.7 (t, J = 12.9 Hz, 3F), −116.5, −117.6 (ABq., J = 312.1 Hz, 2F), −125.8, −127.2 (ABq., J = 292.1 Hz, 2F), −180.0 (m, 1F). NCI-GC–MS: 452(M-F), 319, 300, 250, 200, 152 (base, $C_2F_6N^-$).

*3.2.2. F-(N,N-Diethyl-2-methylpentyl)amine, **4** (nc)*

The enamine **2** (82 g, 0.23 mol) was metered into the photoreactor at a rate of 8.4–12.5 mmol h^{-1}. Temperature of the reaction mixture was maintained at −20–22 °C during the reaction. Other experimental procedures are the same as before.

Distillation gave a colorless liquid; b.p. 147–148 °C; yield, 81.4 g (62%). ^{19}F NMR ($CDCl_3$): −72.4 (brs, 3F), −80.2 (s, 6F), −81.7 (t, J = 12.5 Hz, 3F), −82.3, −83.3 (ABq, J = 231 Hz, 2F), −88.8 (m, 2F), −90.4 (m, 2F), −115.6, −117.0 (ABq., J = 311 Hz, 2F), −125.1, −127.1 (ABq., J = 287.5 Hz, 2F), −180.6 (m, 1F). NCI-GC–MS: 452 (M-C_2F_5), 300, 252 (base, $C_4F_{10}N^-$), 250, 233, 200.

*3.2.3. F-3-(1-pyrrolidino)-2-methylpentane, **11** (nc)*

The enamine **6** (65 g) dissolved in an equal volume of FC-72 was metered into the photoreactor at a rate of 2 ml h^{-1} (4.4 mmol h^{-1}). Temperature of the reaction mixture was maintained at −30–32 °C during the reaction. Distillation gave a colorless liquid; b.p. 140–143 C; yield, 42.4 g (43%). ^{19}F NMR (neat): −70.5 (brs, 3F), −71.5 (brs, 3F), −80.9 (brs, 3F), −84.3–97.4 (brm, 4F), −120.5 (brs, 2F), −134.5, −137.5 (ABq., 248 Hz, 4F), −160.1 (brs, 1F), −175.6 (brs, 1F). MS: 514 (M-F, 2.4), 69 (base, CF_3). NCI-GC–MS: 495 (M-2F, 0.7), 214 (base, $C_4F_8N^-$). The fraction with a lower boiling range (62–140 °C) consisted of a major component, *F*-n-butyl-iso-butylnitrogen fluoride, 12 (nc), ^{19}F NMR (CCl_4) −74.8 (m, 6F), −83.0 (t, J = 20.3Hz, 3F), −89.6 (m, 1F), −103.2 (m, 2F), −106.9 (m, 2F), −125.0 (m, 2F), −129.2 (m, 2F), −188.1 (m, 1F), MS: 452 (M-F, 1.3), 219 (C_4F_9, base), NCI-GC–MS: 452 (M-F, base) and several minor components, two of which were estimated as *F*-n-butyl-n-propyl nitrogen fluoride and *F-n*-butyl-iso-propyl nitrogen fluoride. Since these minor components were superimposed in glc, their structures were only estimated by the following circumstantial evidence. The existence of an N–F bond was proved by treatment with a saturated KI acetone solution. NCI-GC–MS gave the fragment anion with m/z 402 as a base peak, which is considered to be M-F$^-$ from the analogy to the NCI-GC–MS of **12**. Positive-ion MS gave the fragment ion with m/z of 302, 252, 219 and 169 (base peak) which correspond to $CF_2{=}NFC_4F_9$, $CF_2{=}NFC_3F_7$, C_4F_9, and C_3F_7, respectively. ^{19}F NMR of the minor components was explainable by a convolution of these two nitrogen fluoride structures.

*3.2.4. F-(N,N-Dimethyl-1,1-dimethylbutyl)amine, **13** (nc)*

Neat liquid **10** (15 g, 41 mmol) was metered into the photoreactor cooled at −6 °C at a rate of 7.4 mmol h^{-1}. Distillation gave a colorless liquid with b.p. 110–111 °C; yield, 11.9 g (61%). ^{19}F NMR ($CDCl_3$): −46.6 (septet, 6F), −57.8 (tt, J = 10.8 Hz, 6F), −79.1 (t, J = 12.0 Hz, 3F), −101.9 (tm, J = 12.1 Hz, 2F), −120.0 (m, 2F). NCI-GC–MS: 319, 152 (base, $C_2F_6N^-$).

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