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THE SYNTHESIS OF PERFLUORO(N,N-DIALKYLCARBAMOYL FLUORIDES) BY THE REACTION OF PERFLUORO(N,N-DIALKYLMETHYLAMINES) WITH OLEUM

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SUMMARY

A convenient one-step preparation of new perfluoro(N,N-dialkylcarbamoyl fluorides)[dialkyl groups: $R_f=R_f'=C_2F_5$ (1b); $R_f=C_2F_5$, $R_f'=n-C_3F_7$ (2b); $R_f=R_f'=n-C_3F_7$ (3b); $R_f=n-C_3F_7, R_f'=n-C_4F_9$ (4b); $R_f=n-C_3F_7, R_f'=n-C_5F_{11}$ (5b); $R_f=R_f'=n-C_4F_9$ (6b); $R_f=n-C_3F_7, R_f'=CF_3$ (7b); $R_f=n-C_4F_9, R_f'=CF_3$ (8b); $R_f=n-C_5F_{11}, R_f'=CF_3$ (9b)] is described: the corresponding perfluoro(N,N-dialkylmethylamines) are treated with oleum. Catalysts ($HgSO_4$ and $MoCl_5$) improved the yields and the purity of the products obtained. Conditions for the preparation of nine new perfluorocarbamoyl fluorides and their properties are described: several reactions using 1b and 9b were conducted.

INTRODUCTION

The perfluorotertiaryamines are potentially useful compounds in numerous applications due to their unique physicochemical and chemical properties such as low surface energy, high volatility and thermal and chemical stabilities [1].

These compounds might also be useful synthetically if functional groups can be introduced into their skeletons.

We have recently shown that the treatment of several kinds of perfluoro(N-alkyl cyclic amines) with oleum provides a straightforward route to various perfluorolactams [2]. The present investigation offers further information on the reactions of perfluorotertiaryamines with oleum.

As far as perfluoro(N,N-dialkylcarbamoyl fluorides) are concerned, to our knowledge, very few synthetic approaches have so far been reported: they involve (1) the electrochemical flu-

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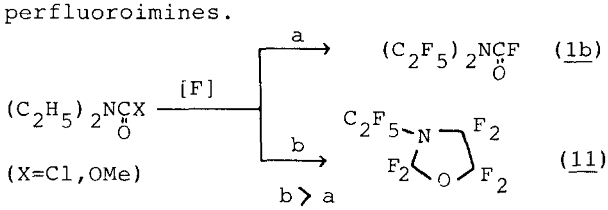
orination of several kinds of N,N-dialkylcarbamoyl chlorides [3], and (2) the addition of COF_2 to perfluoro(2-azapropene) in the presence of CsF to give $(CF_3)_2NC(O)F$ (10) [4].

However, the first method cannot be applied to the preparation of higher homologues beyond 10 because a competing cyclization occurs during fluorination of N,N-dialkylcarbamoyl chlorides [$(C_nH_{2n+1})_2NC(O)Cl$; $n \geq 2$] which gives perfluorooxazolines predominantly (Scheme 1, and also see the experimental section), and the second method has been limited so far to the preparation of 10 due to the difficulty in obtaining other kinds of requisite perfluoroimines.



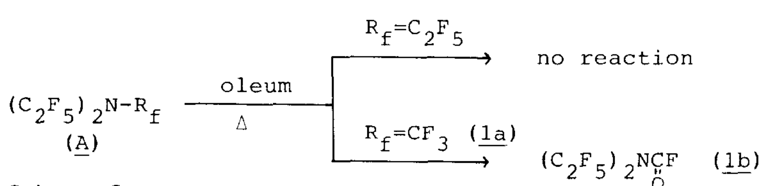
Scheme 1

In this paper, we report the reaction of aliphatic perfluoro(N,N-dialkylmethylamines)(A) with oleum to give a series of new perfluoro(N,N-dialkylcarbamoyl fluorides)(B) (Scheme 3) in fair yields and also several reactions using perfluoro(N,N-diethylcarbamoyl fluoride)(1b) and perfluoro(N-methyl,N-n-pentylcarbamoyl fluoride)(9b).

RESULTS AND DISCUSSION

Synthesis of perfluoro(N,N-dialkylcarbamoyl fluorides)(B)

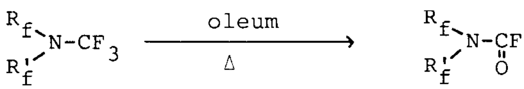
Although perfluoro(triethylamine) did not react with oleum (30%) at temperatures as high as 130∼170 °C, it was found that perfluoro(N,N-diethylmethylamine)(1a) underwent hydrolytic reaction under comparative reaction conditions giving perfluoro-(N,N-diethylcarbamoyl fluoride)(1b) in a fair yield.



Scheme 2

The result obtained was in contrast to that of the reaction with perfluoro(N-methyl cyclic amines) such as perfluoro(N-methyl pyrrolidine), perfluoro(N-methyl morpholine) and perfluoro(N-methyl piperidine), which reacted regiospecifically at the site of the α-CF_2 of the cyclic amine (but not at $>N-CF_3$ group) giving perfluorolactams exclusively [2].

Thus, the extension of this reaction to several aliphatic tertiary perfluoroamines having at least one $CF_3-N<$ group in the molecule was examined and the expected new perfluoro(N,N-dialkylcarbamoyl fluorides)(B) were obtained in fair yields successfully.



(A) (B)

1: $R_f=R'_f=C_2F_5$, 2: $R_f=C_2F_5, R'_f=n-C_3F_7$, 3: $R_f=R'_f=n-C_3F_7$, 4: $R_f=n-C_3F_7, R'_f=n-C_4F_9$, 5: $R_f=n-C_3F_7, R'_f=n-C_5F_{11}$, 6: $R_f=R'_f=n-C_4F_9$, 7: $R_f=n-C_3F_7, R'_f=CF_3$, 8: $R_f=n-C_4F_9$, $R'_f=CF_3$, 9: $R_f=n-C_5F_{11}, R'_f=CF_3$

Scheme 3

Initially, we examined the reaction using $(C_2F_5)_2NCF_3$ (1a) as a model compound to test the efficacy of the use of catalysts like $HgSO_4$, $MoCl_5$, $SnCl_2$, P_2O_5 and PCl_5, and the results are summarized in Table 1. Although a fair yield of perfluoro(N,N-diethylcarbamoyl fluoride)(1b) was obtained from 1a even without catalyst (Run 1), it was found that the addition of small amounts of $HgSO_4$ or $MoCl_5$ improved the yield and the purity of 1b considerably under the following reaction conditions: temp; 130 °C, time; 24 hrs, and mol ratio; 1a/SO_3 = 1 : 3.3~3.6 (Runs 2,3 and 5). However, when the reaction was carried out at 170 °C for 5 hrs, the addition of $HgSO_4$ as a catalyst brought about the adverse effect, lowering the yield of 1b from 42.9% in Run 2 to 27.8% (Run 8). From these results it appeared that the addition of the catalyst ($HgSO_4$ or $MoCl_5$) under relativley mild reaction conditions optimized the yields of the perfluorocarbamoyl fluorides (B). So, for the reactions of other perfluoro(N,N-di-

TABLE 1

Reactions of perfluoro(N,N-diethylmethylamine)(1a) with oleum using various kinds of catalysts[a)]

Run	Sample(1a) (mmol)	Catalyst	Yield of 1b (%)	Sample(1a) recovered (%)
1	5.23		21.0	31.6
2	5.11	$HgSO_4$	42.9	35.4
3[b)]	5.23	$HgSO_4$	44.9	31.6
4	5.23	PCl_5	22.4	48.8
5	5.23	$MoCl_5$	43.5	31.0
6	5.23	$SnCl_2$	30.3	34.6
7[c)]	5.27		40.7	73.2
8[c)]	5.36	$HgSO_4$	27.8	43.7
9[c)]	5.11	P_2O_5	30.3	45.8
10[c)]	5.20	PCl_5	26.2	41.3

[a] Reactions were conducted in the presence of small amount of catalyst (ca. 0.1 g) under the following conditions unless otherwise stated; amine/SO_3 ratio; 1 : 3.3∼3.6, reaction temp; 130 °C, and reaction time; 24 hrs.

[b] The amine/SO_3 ratio was 1 : 1.77.

[c] The reaction temperature; 170 °C and reaction time; 5 hrs were employed.

alkylmethylamines)(A), $MoCl_5$ was selected as a catalyst employing the reaction temperature of 150∼170 °C and the reaction time of 24 hrs. The results obtained are summarized in Table 2.

From such amines as 7a, 8a and 9a, which have two CF_3 group attached directly to the nitrogen atom in the molecule, the formation of perfluoro[N,N-bis(fluorocarbonyl)alkylamines](C) was expected by the further hydrolytic reaction of CF_3-N< of the perfluoro[N-methyl,N-alkylcarbamoyl fluorides](7b, 8b and 9b) formed. However, compounds (C) were not formed and 7b, 8b and 9b were obtained as the sole hydrolytic reaction products from 7a, 8a

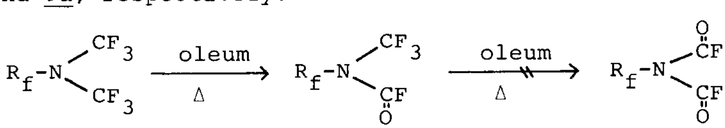
TABLE 2

Summary of reactions of perfluoro(N,N-dialkylmethylamines)(2a ~ 9a) with oleum[a)]

Sample (mmol)	Reaction temp (°C)	Carbamoyl fluoride (Yield %)	Sample recovered (%)
2a (3.82)	140	2b (54.9)	38.7
2a (3.91)	150	2b (39.0)	24.0
3a (4.09)	130	3b (59.2)	81.2
3a (4.16)	150	3b (62.0	66.3
3a (4.16)	170	3b (0)	0
4a (3.76)	160	4b (37.8)	40.2
5a (3.49)	170	5b (42.0)	31.8
6a (3.42)	150	6b (53.3)	78.1
6a (3.55)	170	6b (41.5)	44.2
7a (5.76)	130	7b (38.6)	44.4
8a (4.58)	140	8b (39.3)	34.1
9a (4.09)	130	9b (57.0)	77.3
9a (4.18)	150	9b (46.2)	46.7
9a (4.11)	170	9b (0)	0

[a] Reactions were conducted in the presence of small amounts of $MoCl_5$ (ca. 0.1 g) as a catalyst under the following conditions: amine/SO_3 ratio; 1 : 3.8 ~ 5.3, reaction time; 24 hrs, and reaction temperature indicated.

and 9a, respectively.



(7a, 8a and 9a) (7b, 8b and 9b) (C)

Scheme 4

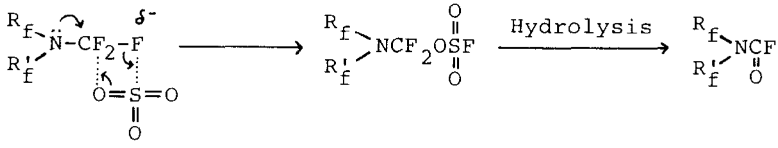
TABLE 3

Physical properties of perfluoro(N,N-dialkylcarbamoyl fluorides)(B)

Carbamoyl fluorides	Bp (°C)[a)]	n_D^{20}	d_4^{20}	Elemental analysis/C(%)
1b	58.5~59.0	<1.28	1.7002	19.97 (20.02)[b)]
2b	79.0~79.5	<1.28	1.7306	20.67 (20.65)
3b	99.0~99.5	1.2815	1.7557	21.09 (21.07)
4b	116.5~117.5	1.2886	1.7856	21.30 (21.40)
5b	134.0~134.5	1.2911	1.8113	21.68 (21.66)
6b	134.5~135.0	1.2908	1.8115	21.61 (21.66)
7b	58.0~59.5	<1.28	1.6890	20.07 (20.08)
8b	82.0~83.0	<1.28	1.7380	20.60 (20.65)
9b	105.0~106.0	1.2846	1.7730	21.06 (21.07)

a Boiling points are not corrected.
b Calculated values in parentheses.

Although the mechanism for the reactions between amines (A) and oleum seems to be rather complex and has not been clarified yet, the conversion of >N-CF_3 of A into >N-C(O)F of B can be explained if fluorosulfato-compounds are formed first and then undergo successive hydrolytic reactions to form the products B.



Scheme 5

Some chemistry of perfluoro(N,N-dialkylcarbamoyl fluorides)(B)

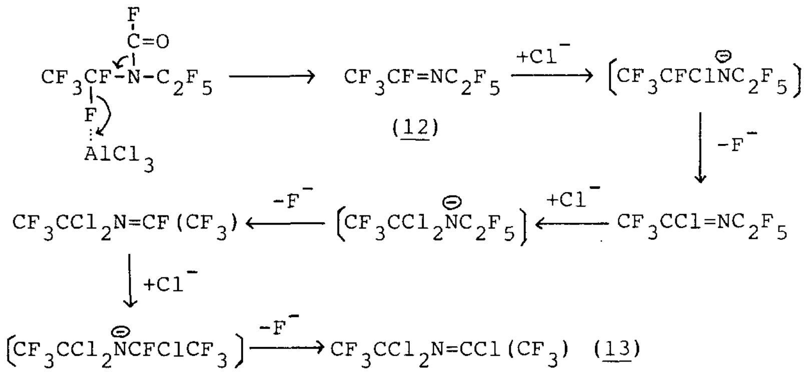
It has been shown that 10 exhibits an interesting chemical behavior towards water and the Lewis acids like $AlCl_3$, $SnCl_4$ or $SiCl_4$, which is considerably different from that expected for usual perfluoroacid fluorides. It resists facile hydrolysis by water and does not undergo simple halogen exchange with the Lewis acids. On pyrolysis, it affords perfluoro(2-azapropene) by splitting out of COF_2 from the molecule [3].

So, it was of interest to investigate several reactions using $(C_2F_5)_2NC(O)F$ (1b) and n-$C_5F_{11}(CF_3)NC(O)F$ (9b) similarly, as various kinds of perfluoro(N,N-dialkylcarbamoyl fluorides)(B) were readily available.

The chemical properties of 1b appeared to be very similar to those reported for 10 in terms of inertness toward several nucleophiles and thermolysis. 1b did not react on contacting with water at ambient temperature for a week and the methyl ester of 1b was not obtained by the reaction with CH_3ONa. When 1b was treated with $(CH_3)_2NLi$, perfluoro(3-azapentene-2)(12) was obtained in 91% yield. Thermolysis of 1b in the presence or absence of NaF at 350 °C afforded 12 in yields of 63% and 93%, respectively. When 1b was treated with $AlCl_3$ at 100 °C for 5 hrs, perfluoro(2,4,4-trichloro-3-azapentene-2)(13) was obtained in a yield of 39%. This reaction is considered to proceed via perfluoroimine, $C_2F_5N{=}CF(CF_3)$ (12), as an intermediate which is formed at the first stage by an abstraction of F^- from α-CF_2 by $AlCl_3$, followed by release of a fluoroacylinium ion in a concerted manner. Perhaps, this step may be the rate-determining one. Then the chlorination may proceed by an addition-elimination mechanism via a nitranion intermediate as shown in Scheme 6.

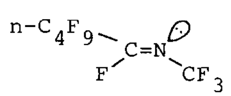
In a similar manner, perfluoro(3-chloro-2-azaheptene-2)(14) was obtained by the reaction of 9b with $AlCl_3$ in a low yield (12%). Although other polychlorinated imines might be also produced as the high-boiling products, they could not be isolated by means of vacuum line techniques.

Thermolysis of 9b in the presence of NaF was found to afford perfluoro(2-azaheptene-2)(15)(Y=73%) as the major product accompanied by perfluoro(N,N-dimethyl-n-pentylamine)(Y=15%).

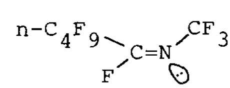


Scheme 6

In the ^{19}F nmr spectrum of 15, two absorption peaks due to $-\overset{|}{C}=N-CF_3$ appeared separately at ϕ-57.5 and ϕ-58.4 in a ratio of 6.5 : 1, each of which was split into a doublet with a coupling constant of 13.2 Hz and 2.5 Hz, respectively [Fig. 1]. These couplings are considered to be induced by the directly attached fluorine atom on the imino group (-CF=N-). Furthermore, absorption peaks due to $-CF_2-C=N-$ appeared at ϕ-118.3 and ϕ-120.7 in the same ratio as that due to $>C=N-CF_3$. Based on the detailed investigation of the integration of other peaks, it was determined that 15 consisted of a mixture of two isomeric forms (syn- and anti-forms).



15 (anti-form)



15 (syn-form)

Muller *et al.* who studied the ^{19}F nmr of perfluoro(2-aza-hexene-2), which is one of the homologous series of imines of the type of 15, could not determine its stereochemistry conclusively [5]. However, our ^{19}F nmr data of 15 provide some useful information that perfluoroimines having the structure $R_f(F)C=NCF_3$ (at least where R_f=n-C_4F_9) can exist in both anti- and syn-structures, and the interconversion between them does not occur at ambient temperature. In view of the large cou-

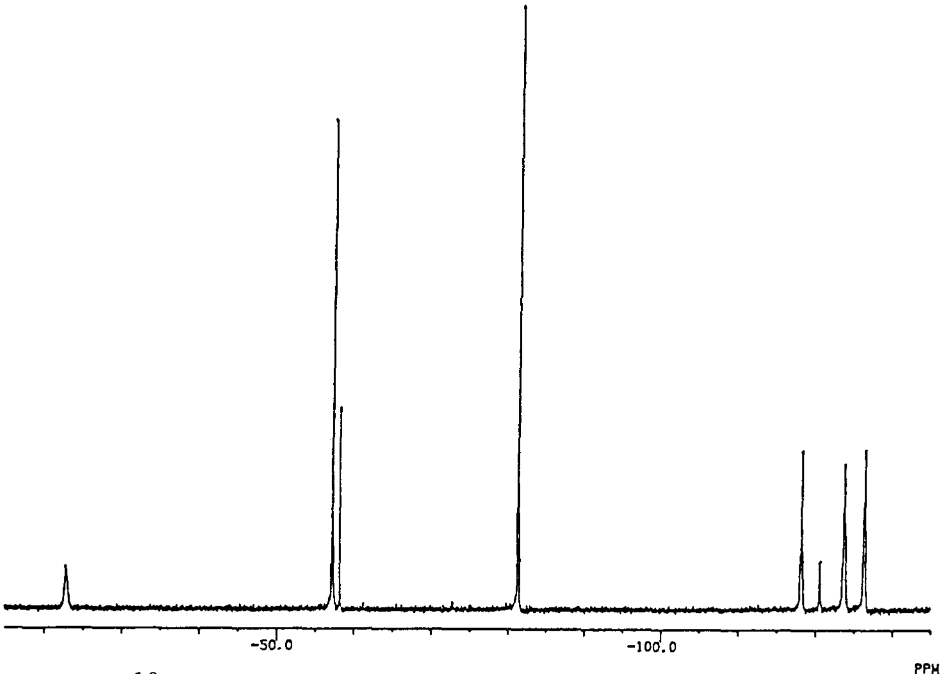


Fig. 1. ^{19}F nmr spectrum of perfluoro(2-azaheptene-2)(15)

pling constant (13.2 Hz) between -CF=N- and -C=NCF$_3$ nuclei observed at the peak of ϕ-57.5, compared with a smaller value (2.5 Hz) at that of ϕ-58.4, the anti-form seems to be most probable for the major component of 15. However, for a convincing assignment concerning its stereochemistry, the data still do not suffice and a further extensive ^{19}F nmr study on 15 and related compounds will be needed.

EXPERIMENTAL

Starting materials and apparatus

The aliphatic perfluorotertiaryamines except perfluoro-(N-methyl-N-ethyl-n-propylamine)(2a) used in this work were all made by the electrochemical fluorination of corresponding tertiary amines [6]. 2a was prepared by the fluorination of 1-methylhexahydro-1,4-diazepine [7]. They were purified by a preparative GLC before use.

Oleum (fuming sulfuric acid) (30%) [Nakarai Chemicals Ltd], mercury sulfate [Wako Chemicals Ltd], molybdenium pentachloride [Nakarai Chemicals Ltd], phosphorous pentachloride [Nakarai Chemicals Ltd], stannous chloride [Nakarai Chemicals Ltd] and phosphorous pentoxide [Wako Chemicals Ltd] were used as received.

Methyl N,N-diethylcarbamate (bp 103∼104 °C / 125 mmHg) which was subjected to electrochemical fluorination was prepared by the reaction of diethylamine and methyl chloroformate according to the method described in the literature [8].

A Pyrex vacuum line equipped with a Heise burdon tube gauge was used for handling the volatile compounds in the reactions of perfluoro(N,N-diethylcarbamoyl fluoride)(1b) and perfluoro-(N-methyl,N-n-pentylcarbamoyl fluoride)(9b).

Analytical GLC work was carried out with a Shimadzu GC-2C gas chromatograph using stainless columns (3 mm dia) packed with 30% 1,6-bis(1,1,12-trihydroperfluorododecyloxy)hexane on Chromosorb PAW (6.4 m) and 26% Kel F #90 on Chromosorb PAW (3.8 m). For a semi-preparative work, a Shimadzu GC-1C gas chromatograph was used employing stainless columns (10 mm dia) packed with 30% Fluorolube HG 1200 on Chromosorb PAW (4.1 m). The carrier gas was helium in all cases.

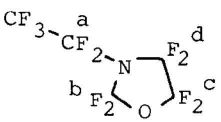
^{19}F nmr spectra were recorded on a Hitachi R-20 spectrometer at 56.4 MHz using $CFCl_3$ as an internal standard. IR spectra were measured on a Hitachi EPI-G3 spectrometer using a gas cell equipped with KBr optics and mass spectra on a Shimadzu GC/MS-7000 instrument at 70 eV.

Fluorination of methyl N,N-diethylcarbamate

Methyl N,N-diethylcarbamate (40.8 g, 0.311 mol) was charged into the cell which contained 450 ml electrically purified anhydrous hydrogen fluoride, and the solution was subjected to fluorination with an anodic current density of 3.5 A/dm^2, a cell voltage of 6.0∼6.1 V until it rose to 6.6 V over a period of 590 min (260 Ahr).

The effluent gases from the cell were passed over NaF pellets, a cold trap at -78 °C, and then bubbled through two consecutive bottles containing water and an alkaline solution of potassium sulfite, respectively.

The compounds (21.6 g) condensed in the -78 °C trap consisted primarily of perfluoro(3-ethyloxazoline)(11)(8.8 g), the cyclization product, and minor components like perfluoro(N,N-dimethylcarbamoyl fluoride)(10)(0.5 g), perfluoro(N,N-diethylcarbamoyl fluoride)(1b)(1.6 g) and unidentified (10.7 g). The yields of 11 and 1b were 9.4% and 1.7%, respectively. 11 was a known compound [3,5], which was identified on the basis of the following ^{19}F nmr data:



^{19}F nmr: $\phi(CF_3)$ -85.2 (pentet) [$J(CF_3-CF_2{}^b)=J(CF_3-CF_2{}^d)$=6.5 Hz], $\phi(CF_2{}^a)$ -98.8 (pentet) [$J(CF_2{}^a-CF_2{}^b)=J(CF_2{}^a-CF_2{}^b)$=9.9 Hz], $\phi(CF_2{}^b)$ -55.5, $\phi(CF_2{}^c)$ -86.7, $\phi(CF_2{}^d)$ -91.0.

1b was confirmed by its IR spectrum by comparison with that of an authentic sample prepared by the reaction of 1a with oleum. 10 showed the following absorption peaks in its IR spectrum: 1889 ν(C=O) (s), 1377 (vs), 1321 (vs), 1239 (vs), 1187 (w), 1092 (w), 1036 (m), 1003 (s), 924 (w), 727 (w), 714 (w).

General procedures of the reaction of perfluoro(N,N-dialkylmethyl amines) with oleum

To illustrate the general procedure of this reaction, the reaction of 1a with oleum will be described.

Reaction of 1a with oleum

In a Pyrex ampule, a mixture of 1.70 g(5.30 mmol) of 1a, 4.8 g of oleum (30%) and $MoCl_5$(0.08 g) was held at 130 °C for 24 hrs.

The products consisted of two layers, an upper transparent clear liquid and a lower transparent blue oily viscous liquid. The upper layer consisting of fluorocarbons was carefully separated from the lower one using a small separating funnel. Gas chromatographic separation of the upper layer (1.00 g) yielded unreacted 1a (0.52 g) and 1b (0.48 g). The yield of 1b was 43.5% based on the amine consumed.

Perfluoro(N,N-diethylcarbamoyl fluoride)(1b)(nc) had bp 58.5 ~59.0 °C, $n_D^{20} < 1.28$ and d_4^{20}1.7002. IR (gas): 1879 ν(C=O)(s), 1326 (vs), 1271 (vs), 1196 (w), 1171 (w), 1122 (vs), 1074 (w), 981 (m), 884 (ms), 754 (m), 727 (m), 712 (m), 671 (w), 546 (w), Mass: 280 $[M-F]^+$(4.4), 262 $C_6F_{10}^+$(3.0), 252 $C_4F_{10}N^+$(3.0), 230 $C_4F_8O^+$(63.0), 214 $C_4F_8N^+$(96.5), 164 $C_3F_6N^+$(31.7), 142 $C_3F_4NO^+$ (10.4), 119 $C_2F_5^+$(100), 114 $C_2F_4N^+$(26.0), 100 $C_2F_4^+$(4.7), 92 $C_2F_2NO^+$(6.2), 69 CF_3^+(71.0). Found: C, 20.05%. Calculated for $C_5F_{11}NO$: C, 20.02%. Its ^{19}F nmr data are given in Table 4.

Other perfluoro(N,N-dialkylcarbamoyl fluorides)(B) synthesized in this work were all new compounds. Physical properties and ^{19}F nmr data of these carbamoyl fluorides (2b ~ 9b) are shown in Table 3 and Table 4, respectively. The IR and Mass spectral data characterizing these new carbamoyl fluorides are given below

Perfluoro(N-ethyl,N-n-propylcarbamoyl fluoride)(2b): IR (gas): 1878 ν(C=O)(s), 1350 (vs), 1300 (vs), 1235 (vs), 1164 (ms), 1140 (s), 1052 (w), 1020 (m), 1006 (ms), 901 (w), 868 (s), 757 (m), 728 (ms), 714 (m). Mass: 330 $[M-F]^+$(0.7), 280 $C_5F_{10}NO^+$ (3.9), 192 $C_4F_6NO^+$(6.1), 169 $C_3F_7^+$(35.4), 164 $C_3F_6N^+$(8.6), 131 $C_3F_5^+$(4.9), 119 $C_2F_5^+$(51.2), 114 $C_2F_4N^+$(13.4), 100 $C_2F_4^+$(10.1), 92 $C_2F_2NO^+$(36.6), 69 CF_3^+(100), 47 CFO^+(34.1).

Perfluoro(N,N-di-n-propylcarbamoyl fluoride)(3b): IR (capillary film): 1870 ν(C=O)(vs), 1350 (s,sh), 1319 (vs), 1301 (s), 1269 (s), 1221 (vs), 1141 (s), 1051 (s), 1023 (m), 1011 (w), 910 (m), 831 (s), 753 (s), 728 (m), 719 (m), 612 (w), 553 (w). Mass: 380 $[M-F]^+$(0.3), 314 $C_6F_{12}N^+$(2.1), 280 $C_5F_{10}NO^+$ (14.2), 214 $C_4F_8N^+$(7.4), 192 $C_4F_6NO^+$(9.5), 169 $C_3F_7^+$(94.7), 119 $C_2F_5^+$(12.6), 114 $C_2F_4N^+$(7.9), 100 $C_2F_4^+$(15.2), 92 $C_2F_2NO^+$(31.6), 69 CF_3^+(100), 47 CFO^+(18.4).

Perfluoro(N-n-propyl,N-n-butylcarbamoyl fluoride)(4b): IR (capillary film): 1872 ν(C=O)(s), 1353 (m,sh), 1329 (vs), 1302 (s), 1263 (s,sh), 1220 (vs), 1144 (s), 1081 (w), 1069 (w), 1046 (m), 1024 (w), 1001 (m), 980 (w), 901 (w), 881 (w), 872 (m), 822 (w), 809 (m), 751 (m), 723 (m), 649 (w), 542 (w). Mass: 430 $[M-F]^+$(0.3), 364 $C_7F_{14}N^+$(10.3), 330 $C_6F_{12}NO^+$(2.6), 280 $C_5F_{10}NO^+$(6.5), 264 $C_5F_{10}N^+$(2.4), 219 $C_4F_9^+$(9.1), 214 $C_4F_8N^+$(3.0), 169 $C_3F_7^+$(35.3), 131 $C_3F_5^+$(13.4), 119 $C_2F_5^+$(10.3), 114 $C_2F_4N^+$ (6.0), 100 $C_2F_4^+$(12.1), 92 $C_2F_2NO^+$(25.4), 69 CF_3^+(100), 47 CFO^+ (13.8).

Perfluoro(N-n-propyl,N-n-pentylcarbamoyl fluoride)(5b): IR (capillary film): 1868 ν(C=O)(s), 1356 (ms,sh), 1329 (vs), 1296 (s), 1203 1236 (vs), 1156 (s,sh), 1142 (s), 1119 (m), 1055 (w), 1040 (w), 1025 (w), 956 (w), 942 (w), 873 (w), 860 (w), 818 (w), 794 (w), 785 (m), 757 (m), 746 (m), 721 (m), 712 (m), 662 (m), 611 (w), 581 (w), 540 (w). Mass: 480 $[M-F]^+$(0.5), 414 $C_8F_{16}N^+$(1.8), 380 $C_7F_{14}NO^+$(2.5), 314 $C_6F_{12}N^+$(2.6), 292 $C_6F_{10}NO^+$(3.1), 280 $C_5F_{10}NO^+$(15.3), 269 $C_5F_{11}^+$(6.1), 214 $C_4F_8N^+$ (5.5), 181 $C_4F_7^+$(6.7), 169 $C_3F_7^+$(46.6), 131 $C_3F_5^+$(9.8), 119 $C_2F_5^+$(20.9), 114 $C_2F_4N^+$(6.1), 100 $C_2F_4^+$(12.9), 92 $C_2F_2NO^+$(25.8), 69 CF_3^+(100), 47 CFO^+(11.7).

Perfluoro(N,N-di-n-butylcarbamoyl fluoride)(6b): IR (capillary film): 1872 ν(C=O)(s), 1357 (m,sh), 1326 (vs), 1302 (s), 1220∼1242 (vs), 1193 (s), 1155 (s), 1142 (vs), 1104 (w), 1083 (w), 1070 (w), 1059 (w), 1009 (w), 962 (w), 858 (w), 836 (m), 800 (m), 751 (s), 722 (s), 648 (w), 594 (w), 540 (w), Mass: 480 $[M-F]^+$(0.6), 414 $C_8F_{16}N^+$(2.5), 330 $C_6F_{12}NO^+$(8.2), 264 $C_5F_{10}N^+$(0.6), 242 $C_5F_8NO^+$(4.4), 219 $C_4F_9^+$(27.8), 131 $C_3F_5^+$(24.1), 119 $C_2F_5^+$(9.5), 100 $C_2F_4^+$(10.8), 92 $C_2F_2NO^+$(22.2), 69 CF_3^+(100), 47 CFO^+(8.9).

Perfluoro(N-methyl,N-n-propylcarbamoyl fluoride)(7b): IR (gas): 1879 ν(C=O)(s), 1350 (vs), 1300 (vs), 1235 (vs), 1164 (ms), 1140 (s), 1052 (w), 1020 (m), 1006 (ms), 901 (w), 868 (s), 757 (m), 728 (ms), 714 (m). Mass: 280 $[M-F]^+$(0.4), 214 $C_4F_8N^+$ (1.3), 192 $C_4F_6NO^+$(4.4), 187 $C_3F_6NO^+$(13.5), 169 $C_3F_7^+$(11.5), 119 $C_2F_5^+$(3.6), 114 $C_2F_4^+$(5.6), 92 $C_2F_2NO^+$(30.1), 69 CF_3^+(100), 47 CFO^+(23.8).

Perfluoro(N-methyl,N-n-butylcarbamoyl fluoride)(8b): IR (gas): 1882 ν(C=O)(s), 1351 (vs), 1309 (s,sh), 1306 (s), 1252 (vs), 1231 (vs), 1207 (m), 1150 (m), 1102 (w), 1031 (w), 1016 (w), 862 (w), 824 (m), 773 (w), 753 (m), 721 (m), 650 (w), 534 (w). Mass: 330 $[M-F]^+$(0.3), 242 $C_5F_8NO^+$(2.9), 219 $C_4F_9^+$(3.3), 180 $C_3F_6NO^+$(9.5), 131 $C_3F_5^+$(5.4), 119 $C_2F_5^+$(4.1), 114 $C_2F_4N^+$ (12.4), 100 $C_2F_4^+$(5.8), 92 $C_2F_2NO^+$(27.3), 69 CF_3^+(100), 47 CFO^+ (19.0).

Perfluoro(N-methyl,N-n-pentylcarbamoyl fluoride)(9b): IR (capillary film): 1872 ν(C=O)(s), 1347 (s), 1294 (ms), 1242 (s,sh), 1216 (vs), 1144 (ms), 1121 (m), 1052 (w), 1029 (m), 1008 (m), 846 (w), 811 (w), 796 (w), 772 (m), 749 (m), 734 (w), 712 (ms), 663 (m), 580 (w), 538 (w). Mass: 380 $[M-F]^+$(0.1),

TABLE 4

^{19}F nmr spectra of perfluorocarbamoyl fluorides

Compd	Formula	Chemical shift[a,b]		J (Hz)[b]
1b	$(\overset{a}{CF_3}\overset{b}{CF_2})_2NC(=O)\overset{c}{F}$	a	-83.3	b-c=19.7
		b	-94.0	
		c	6.1	
2b	$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}N(C(=O)\overset{f}{F})\overset{d}{CF_2}\overset{e}{CF_3}$	a	-18.9	a-c=10.2
		b	-123.7	b-d=14.1
		c	-89.1	b-f=12.4
		d	-93.1	e-c=8.2
		e	-83.0	e-f=9.3
		f	6.6	
3b	$(\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2})_2NC(=O)\overset{d}{F}$	a	-81.8	
		b	-123.5	
		c	-88.7	
		d	6.4	
4b	$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}N(C(=O)\overset{h}{F})\overset{e}{CF_2}\overset{f}{CF_2}\overset{g}{CF_3}$	a	-81.0	a-c=10.4
		b	-126.4	
		c	-123.0	
		d	-88.0	
		e	-88.0	
		f	-119.8	
		g	-81.4	
		h	6.8	
5b	$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF_2}N(C(=O)\overset{i}{F})\overset{f}{CF_2}\overset{g}{CF_2}\overset{h}{CF_3}$	a	-81.4	a-c=7.3
		b	-126.1	
		c	-122.7	
		d	-122.7	
		e	-87.8	
		f	-87.8	
		g	-118.9	
		h	-81.1	
		i	6.9	

TABLE 4 (cont.)

6b	$(\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2})_2NC(=O)\overset{e}{F}$	a	-81.0	a-c=10.7
		b	-126.5	
		c	-119.5	
		d	-87.6	
		f	7.2	
7b	$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}N(\overset{d}{CF_3})C(=O)\overset{e}{F}$	a	-81.9	a-c=10.2
		b	-125.3	d-b=7.6
		c	-96.9	d-c=16.9
		d	-54.7	d-e=17.8
		e	5.7	
8b	$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}N(\overset{e}{CF_3})C(=O)\overset{f}{F}$	a	-81.4	a-c=11.3
		b	-127.0	e-c=8.5
		c	-121.7	e-d=17.8
		d	-90.2	e-f=17.8
		e	-54.2	
		f	5.9	
9b	$\overset{a}{CF_3}\overset{b}{CF_2}\overset{c}{CF_2}\overset{d}{CF_2}\overset{e}{CF_2}N(\overset{f}{CF_3})C(=O)\overset{g}{F}$	a	-81.5	a-c=10.7
		b	-126.6	f-d=8.5
		c	-123.4	f-e=16.9
		d	-121.0	f-g=17.8
		e	-90.3	
		f	-54.4	
		g	5.9	

a ^{19}F chemical shifts in ppm relative to internal CCl_3F (negative shifts are upfield).

b Only obvious chemical shifts and coupling constants are given.

314 $C_6F_{12}N^+$(2.8), 292 $C_6F_{10}NO^+$(2.8), 269 $C_5F_{11}^+$(1.4), 180 $C_3F_6NO^+$(17.1), 131 $C_3F_5^+$(4.8), 119 $C_2F_5^+$(10.0), 114 $C_2F_4N^+$(18.1), 100 $C_2F_4^+$(7.6), 92 $C_2F_2NO^+$(35.2), 69 CF_3^+(100), 47 CFO^+(16.2).

Several reactions of 1b

With H_2O

Into a 5 ml conical reaction vial, 1.68 g of 1b and 2 ml of water were placed and agitated at ambient temperature for 2 hrs. However, reaction did not occur, as evidenced by the unchanged amount of the fluorocarbon lower layer. The reaction mixture was further left standing for a week, but 1b was recovered unchanged.

With CH_3ONa

Into a 50 ml reaction vessel which contained 0.19 g (3.52 mmol) of CH_3ONa, 1b (3.74 mmol) was condensed at -196 °C and warmed gradually to room temperature. After 46 min, purification was conducted by trap-to-trap distillation using traps at -78 °C and -196 °C. The compound remaining at -196 °C was mainly composed of CO_2 (0.83 mmol). The compound at -78 °C was unreacted 1b (0.81 g, 2.71 mmol).

With $(CH_3)_2NLi$

In an anlogous manner, 3.52 mmol of 1b was condensed at -196 °C onto 3.80 mmol of $(CH_3)_2NLi$ in the 50 ml reaction vessel and gradually warmed to room temperature. After 19 hrs, trap-to-trap distillation of the products afforded 1.29 mmol of COF_2 at -196 °C, 1.11 mmol of $C_2F_5N{=}CF(CF_3)$ (12) at -116 °C and 2.06 mmol of 12 at -40 °C, respectively. Yield of 12 was 90.5% based on the 1b fed. Its IR spectral data were identical with that reported in the literature [9].

With $AlCl_3$

In a 30 ml Hoke cylinder, a mixture of 1b (1.68 g, 5.62 mmol) and $AlCl_3$ (1.1 g) was held at 100 °C for 100 hrs. Purification was initially conducted by trap-to-trap distillation using traps at -196 °C, -116 °C and -78 °C, respectively. The compound at -116 °C was mainly $COCl_2$. Gas chromatographic separation of the products (1.10 g) at -78 °C yielded the following compounds: $COCl_2$ (0.02 g), 1b (0.56 g), CCl_4 (0.03 g), $CF_3CCl_2N{=}CCl(CF_3)$ (13) (0.41 g, 38.7% Yield) and unidentified (0.08 g).

Perfluoro(2,4,4-trichloro-3-azapentene-2)(13)(nc) had bp 102.0~102.5 °C, $n_D^{20} < 1.28$ and d_4^{20}1.6435. IR (gas): 1705 ν(N=C)(m), 1306 (m), 1270 (ms), 1228 (vs), 1190 (s), 1063 (m), 986 (ms), 863 (m), 738 (m), 631 (w), 523 (w). Mass: 146 $[M-Cl^{35}]^+$(100), 211 $[M-CF_3]^+$(39.3), 151 $CF_3CCl_2^{35+}$(58.1), 69 CF_3^+ (70.5). In addition to the fragments which contain Cl^{35}, ions containing Cl^{37} were observed in an appropriate isotope ratio. Found: C, 16.95%. Calculated for $C_4F_6Cl_3N$: C, 16.99%.

$\overset{a}{CF_3}CCl_2N{=}C(Cl)\overset{b}{CF_3}$ ^{19}F nmr: $\phi(CF_3^a)$ -82.8, $\phi(CF_3^b)$ -72.4.

Thermolysis of 1b

In a 30 ml Hoke cylinder, 3.10 mmol of 1b was held at 350 °C for 5 hrs. Separation of the reaction mixture by trap-to-tra- distillation resulted in the collection of COF_2(1.02 mmol), 12 (1.21 mmol) at -78 °C trap, and unreacted 1b (0.54 g, 0.81 mmol), respectively. Yield of 12 was 93.1% based on the 1b consumed.

Thermolysis of 1b in the presence of NaF

In almost the same reaction conditions but for the presence of dry NaF (2.0 g), 3.40 g of 1b was similarly treated. In this case, 1.63 mmol of COF_2 and 1.63 mmol of 12 (62.5% Yield) was obtained together with unreacted 1b (0.13 g, 0.43 mmol) and traces of $(C_2F_5)_2NCF_3$.

Reaction of 9b with $AlCl_3$

In a 30 ml Hoke cylinder, a mixture of 9b (3.83 g, 8.47 mmol) and $AlCl_3$ (1.3 g) was held at 100 °C for 20 hrs. Trap-to-trap distillation of the products afforded the following products: CO_2 + $COCl_2$ (0.25 mmol) at -196 °C trap, $COCl_2$ (0.81 mmol) at -116 °C trap, and 0.55 g of clear liquids at -78 °C trap. Gas chromatographic separation of the products at -78 °C yielded the following compounds: $COCl_2$ (trace), CCl_4 (trace), n-$C_4F_9(Cl)C{=}NCF_3$ (14) (0.32 g) and 9b (0.18 g). Yield of 14 was 11.5% based on 9b consumed.

Perfluoro(3-chloro-2-azaheptene-2) (14) (nc) had a vapor pressure of 16 torr at 13 °C. Its structure was determined by following spectroscopic evidence. IR (gas): 1701~1704 ν(C=N) (m), 1359 (w), 1253 (vs), 1212 (s), 1143 (m), 958 (w), 881 (w), 828 (w), 798 (w), 740~749 (w), Mass: 330 $[M-F]^+$(4.1), 314 $[M-Cl^{35}]^+$(4.8), 130 $[M-C_4F_9]^+$(30.3), 100 $C_2F_4^+$(4.6), 69 CF_3^+ (100). In addition to the fragments which contain Cl^{35}, ions containing Cl^{37} were observed in a ratio of 1 : 3.

$$CF_3\overset{a}{CF_2}\overset{b}{CF_2}\overset{c}{CF_2}\overset{Cl}{\overset{|}{C}}{=}NCF_3$$

^{19}F nmr: $\phi(CF_3)$ -81.3 (triplet) $[J(CF_3-CF_2^c)$ =10.7 Hz], $\phi(CF_2^a)$ -125.6, $\phi(CF_2^b)$ -121.5, $\phi(CF_2^c)$ -111.1 (triplet) $[J(CF_2^c-CF_2^a)=$ 13.8 Hz], $\phi(CF_3-N)$ -61.4.

Thermolysis of 9b in the presence of NaF

In a 30 ml Hoke cyclinder which contained 2.0 g of dry NaF, 9b (1.34 g, 3.36 mmol) was condensed and held at 350 °C for 5 hrs, similarly. Separation was conducted by a complex use of trap-to-trap distillation and GLC, which yielded n-$C_4F_9(F)C{=}NCF_3$ (15) (0.70 g, 72.9% Yield) and n-$C_5F_{11}N(CF_3)_2$ (0.18 g, 14.9% Yield).

Perfluoro(2-azaheptene-2) (15) (nc) had bp 64.0~64.5 °C. Its structure was determined by spectroscopic evidence: IR (gas): 1776 ν(C=N) (ms), 1218~1258 (vs), 1146 (ms), 1030 (w), 895 (m), 821 (w), 808 (w), 750 (m), 657 (w). Mass: 314 $[M-F]^+$ (14.7), 264 $[M-CF_3]^+$(3.3), 226 $C_5F_8N^+$(8.5), 169 $C_3F_7^+$(7.7), 164 $C_3F_6N^+$(17.4), 145 $C_3F_5N^+$(6.4), 131 $C_3F_5^+$(4.0), 119 $C_2F_5^+$(10.0), $C_2F_4N^+$(57.5), 69 CF_3^+(100).

$$CF_3\overset{a}{CF_2}\overset{b}{CF_2}\overset{c}{CF_2}\overset{F}{\overset{|}{C}}{=}NCF_3$$

^{19}F nmr: $\phi(CF_3)$ -81.5 (triplet) $[J(CF_3-CF_2^b)=9.5$ Hz], $\phi(CF_2^a)$ -126.4, $\phi(CF_2^b)$ -123.8, $\phi(CF_2^c)$ -118.3 and -120.7, $\phi(CF)$ -22.9, $\phi(CF_3-N)$ -57.5 (doublet) $[J(CF_3-CF)=13.2$ Hz] and -58.4 (doublet) $[J(CF_3-CF)=2.5$ Hz]. Its ^{19}F nmr spectrum is shown in Fig. 1.

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