Journal of Fluorine Chemistry, 63 (1993) 193–201

Partially fluorinated enamines and their electrochemical fluorination

D. D. Moldavsky, G. I. Kaurova, T. A. Bispen
Institute Applied Chemistry, St. Petersburg 197198 (Russian Federation)
G. G. Furin*
Institute of Organic Chemistry, Novosibirsk 630090 (Russian Federation)

(Received May 1, 1992; accepted November 3, 1992)

Abstract

The reactions of hexafluoropropylene, its dimers and trimers, and perfluoro-1-ethylcyclohex-1-ene with secondary amines (dipropylamine, dibutylamine and diallylamine) have been shown to form enamines. The enamines were electrochemically fluorinated in anhydrous hydrogen fluoride. This paper reports the electrochemical fluorination data for the fluorination of tripropylamine, tributylamine, triamylamine and the partially fluorinated enamines. The structures of the products have been confirmed by ^{19}F NMR and GC–MS methods.

Introduction

Perfluorinated trialkylamines have found extensive use as inert liquid dielectrics, special liquids for microelectronics, synthetic blood components and refrigerants [1]. They are generally obtained by electrochemical fluorination (ECF) of the appropriate hydrocarbon amines [2]. The main demerits of this method involve the low yield of desired product (7–12%) and the destruction of the hydrocarbon framework of the starting compound [3, 4]. The destruction of hydrocarbon radicals leads to various products and irreversible changes in the electrolyte, electrode destruction and tar products, reducing the electrolysis time. With long hydrocarbon radicals, the hydrocarbon framework also undergoes isomerization, making electrochemical fluorination unacceptable for such compounds. In the present work, we have investigated the possibility of synthesizing perfluorinated trialkylamines (C_9–C_{15}) from partially fluorinated enamines and have compared the ECF data with those of trialkylamines. The favourable influence of the preliminary fluorination of the starting molecules by ECF on the yield of the desired

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*To whom all correspondence should be addressed.

product has been demonstrated by reference to 2-fluoropyridine [5] and 2,2,3,3-tetrafluoropropanol [6]. The starting enamine compounds were synthesized by the reactions of hexafluoropropylene, its dimers and trimers and perfluoro-1-methylcyclohex-1-ene with secondary amines.

The behaviour of the hexafluoropropylene dimer in nucleophilic substitution reactions has been studied using different nucleophiles [7, 8]. With secondary amines, these reactions are not well known. Those which have been investigated include the reactions of hexafluoropropylene dimers with diethylamine [9], piperidine and pyrrolidine [10, 11]. The authors of these works have shown that the reactions of the hexafluoropropylene dimers **A** and **B** proceed with substitution of a terminal rather than an internal fluorine atom to form enamines. This was explained by isomerization of the isomeric olefins **A** and **B** to olefin **C**. The rate of nucleophilic substitution of the terminal fluorine atom in **C** is known to be much higher than that of the internal ones and, despite the low concentration of olefin **C**, the reaction with secondary amines proceeds via this isomer.

$(CF_3)_2C{=}CFC_2F_5$ **(A)** $(CF_3)_2CFCF{=}CFCF_3$ **(B)** $F_2C{=}C(CF_3)CF_2CF_2CF_3$ **(C)**

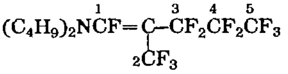
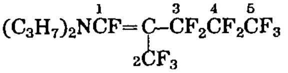
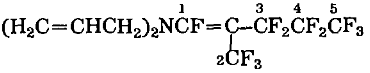
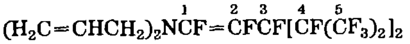
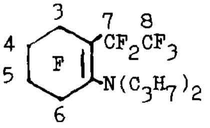
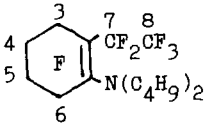
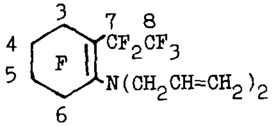
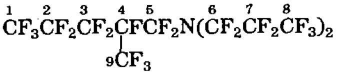
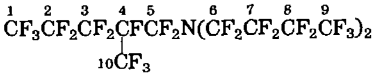
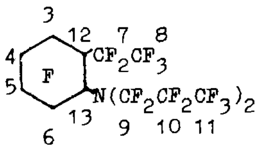
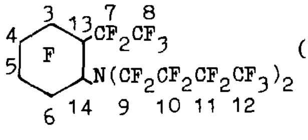
Results and discussion

We have shown that perfluoro-2-methylpent-2-ene (**A**) reacts with dibutylamine in acetonitrile at 40–50 °C to give 1-(*N*,*N*-dibutylamino)-undecafluoro-2-methylpent-1-ene (**1**) rather than the product of fluorine substitution at the double bond in substrate **A** (Table 1). Dipropylamine and diallylamine gave, with **A**, analogous products (enamines **2** and **3**, respectively). No products of addition at a multiple bond have been found, as opposed to the reaction of hexafluoropropylene with secondary dialkylamines for which earlier authors [12] reported the formation of the product of fluorine addition at a double bond along with that of substitution. The structures of the products have been identified by elemental analysis (Table 2) and by ^{19}F NMR data (Table 1).

The reaction demands one extra mole of secondary amine in order to scavenge the hydrogen fluoride liberated, but instead of the secondary amine we have used triethylamine and pyridine for that purpose. The latter amines were found to produce a catalytic effect in this reaction and as a result the reaction temperature and time were reduced. Without a solvent and excess triethylamine, the reaction was very sluggish. We have investigated different solvents (dioxan, CH_3CN, diethyl ether, ethanol, DMF, etc.) and found that the best yields of the desired product are obtained in dipolar aprotic solvents, particularly acetonitrile. It should be noted that the stirring rate is also relevant because the limited solubility of perfluoro-2-methylpent-2-ene in acetonitrile makes the process heterogeneous.

TABLE 1

Structures and ^{19}F NMR spectral data for partially fluorinated enamines and perfluorotrialkylamines (reference compound C_6F_6)

Compound	^{19}F NMR δ (ppm)
 $(C_4H_9)_2N\overset{1}{C}F{=}\underset{{}_{2}CF_3}{C}{-}\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_3$ (**1**)	110.6 ($1F^1$); 110.6 ($3F^2$); 61.2 ($2F^3$); 39.7 ($2F^4$); 83.0 ($3F^5$)
 $(C_3H_7)_2N\overset{1}{C}F{=}\underset{{}_{2}CF_3}{C}{-}\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_3$ (**2**)	110.2 ($1F^1$); 110.5 ($3F^2$); 61.4 ($2F^3$); 39.8 ($2F^4$); 83.0 ($3F^5$)
 $(H_2C{=}CHCH_2)_2N\overset{1}{C}F{=}\underset{{}_{2}CF_3}{C}{-}\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_3$ (**3**)	111.0 ($1F^1$); 102.5 ($3F^2$); 52.0 ($2F^3$); 39.1 ($2F^4$); 83.0 ($3F^5$)
 $(H_2C{=}CHCH_2)_2N\overset{1}{C}F{=}\overset{2}{C}F\overset{3}{C}F[\overset{4}{C}F(\overset{5}{C}F_3)_2]_2$ (**4**)	110.7 ($1F^1$); 96.3 ($1F^2$); 90.7 ($12F^5$); 1.1 ($1F^3$); −12.6 ($2F^4$)
 (**5**)	111.0 ($3F^8$); 83.0 ($2F^7$); 59.6 ($2F^3$); 55.8 ($2F^6$); 59.6 ($2F^3$)
 (**6**)	100.9 ($3F^8$); 82.4 ($2F^7$); 59.7 ($2F^3$); 56.0 ($2F^6$); 31.9 ($2F^5$); 28.9 ($2F^4$)
 (**7**)	100.8 ($3F^8$); 83.2 ($2F^7$); 59.2 ($2F^3$); 55.1 ($2F^6$); 30.7 ($2F^5$); 29.3 ($2F^5$)
 $\overset{1}{C}F_3\overset{2}{C}F_2\overset{3}{C}F_2\underset{{}_{9}CF_3}{\overset{4}{C}}F\overset{5}{C}F_2N(\overset{6}{C}F_2\overset{7}{C}F_2\overset{8}{C}F_3)_2$ (**8**)	80.6 ($3F^1$); 35.6 ($2F^2$); 38.8 ($2F^3$); 2.1 ($1F^4$); 74.2 ($2F^5$); 74.8 ($2F^6$); 41.9 ($2F^7$); 80.7 ($3F^8$); 86.1 ($3F^9$)
 $\overset{1}{C}F_3\overset{2}{C}F_2\overset{3}{C}F_2\underset{{}_{10}CF_3}{\overset{4}{C}}F\overset{5}{C}F_2N(\overset{6}{C}F_2\overset{7}{C}F_2\overset{8}{C}F_2\overset{9}{C}F_3)_2$ (**9**)	93.3; 81.8 ($2F^5$, AB system, $J_{FF}=256$ Hz); 91.4 ($3F^{10}$); 81.4 ($3F^1$); 80.5 ($6F^9$); 74 ($4F^6$); 48.5 ($2F^3$); 40.9 ($4F^7$); 37.8 (2F); 35.2 ($4F^8$); 2.1 ($1F^4$)
 (**10**)	75.2 ($4F^9$); 59.6 ($2F^3$); 55.7 ($2F^6$); 40.3 ($4F^{10}$); 31.9 ($2F^5$); 29.1 ($2F^4$); 2.9 ($1F^{12}$); −3.0 ($1F^{13}$); 110.9 ($3F^8$); 83.4 ($2F^7$); 80.7 ($6F^{11}$)
 (**11**)	74.9 ($4F^9$); 41.2 ($4F^{10}$); 34.9 ($4F^{11}$); 80.6 ($6F^{12}$); 2.8 ($1F^{13}$); −3.4 ($1F^{14}$); 59.5 ($2F^3$); 29.0 ($2F^4$); 32.0 ($2F^5$); 55.9 ($2F^6$); 83.5 ($2F^7$); 110.7 ($3F^8$)

(continued)

TABLE 1 (*continued*)

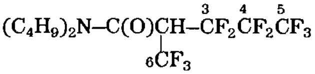
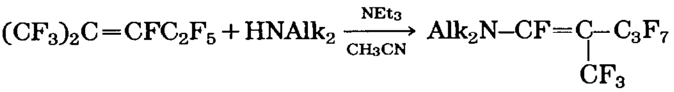
Compound		^{19}F NMR δ (ppm)
$(\overset{1}{C}F_3\overset{2}{C}F_2\overset{3}{C}F_2)_2N\overset{4}{C}F_2\overset{5}{C}F_2\overset{6}{C}F[\overset{7}{C}F(\overset{8}{C}F_3)_2]_2$	**(12)**	90.8 ($12F^8$); 80.6 ($6F^1$); 74.8 ($4F^3$); 74.2 ($2F^4$); 41.6 ($2F^5$); 40.2 ($4F^2$); 1.1 ($1F^6$); −12.6 ($2F^7$)
 $(C_4H_9)_2N{-}C(O)\underset{\underset{6}{}CF_3}{CH}{-}\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}F_3$	**(13)**	120.2 ($3F^6$); 83.5 ($3F^5$); 53.0, 48.9 ($2F^3$, AB system, J_{FF}=280 Hz); 42.2 ($2F^4$)

TABLE 2

Analytical data for partially fluorinated enamines and perfluorotrialkylamines

Compound	Yield (%)	B.p. (°C/mmHg)	Found (%)				Formula	Calc. (%)			
			C	H	F	N		C	H	F	N
1	51	106–108/5	42.0 41.7	4.41 4.20	50.4 50.9	3.40	$C_{14}H_{18}F_{11}N$	41.1	4.40	51.1	3.42
2	64	89–92/5	37.4 37.5	3.50 3.48	54.6 54.5	3.52	$C_{12}H_{14}F_{11}N$	37.8	3.67	54.9	3.67
3	53	83–84/5	38.0 37.9	2.54 2.50	55.2 55.2		$C_{12}H_{10}F_{11}N$	38.2	2.65	55.4	3.71
4	43	124–125/5	34.1 33.9	1.80 1.90	61.0 61.1	2.71	$C_{15}H_{10}F_{17}N$	34.2	1.90	61.3	2.66
5	56	73–75/2	38.0 38.2	3.20 3.10	55.6 55.3	3.29	$C_{14}H_{14}F_{13}N$	37.9	3.16	55.8	3.16
6	67	81–82/2	40.6 40.5	3.89 3.82	52.2 52.0	3.02	$C_{16}H_{18}F_{13}N$	40.8	3.82	52.4	2.97
7	53	70–71/2	38.4 38.1	2.34 2.19	55.9 55.7	3.20	$C_{14}H_{10}F_{13}N$	38.3	2.28	56.3	3.19
8	19	177–178	21.1 21.6		76.2 76.6	2.36	$C_{12}F_{27}N$	21.5		76.5	2.09
9	38	203–204	21.7 21.4		76.3 76.0	1.90	$C_{14}F_{31}N$	21.8		76.4	1.82
10	35	204–205	23.1 22.8		75.2 75.4	2.03	$C_{14}F_{29}N$	22.9		75.2	1.91
11	32	230–231	23.1 23.3		75.4 75.7	1.56	$C_{16}F_{33}N$	23.1		75.3	1.68
12	26	217–218	21.7 21.8		76.0 76.1	1.64	$C_{15}F_{33}N$	21.9		76.4	1.71
13	87	86–88/3	41.0	4.53	46.2	3.37	$C_{14}H_{19}F_{10}NO$	41.3	4.67	46.7	3.44



$$(CF_3)_2C{=}CFC_2F_5 + HNAlk_2 \xrightarrow[CH_3CN]{NEt_3} Alk_2N{-}CF{=}\underset{\displaystyle CF_3}{\underset{|}{C}}{-}C_3F_7$$

(**1**) Alk = C_4H_9; (**2**) Alk = C_3H_7; (**3**) Alk = $CH_2{-}CH{=}CH_2$

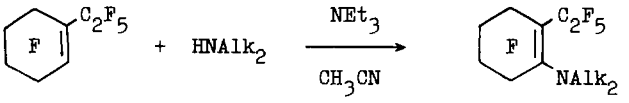
The reactions of perfluoro-4-methylpent-2-ene (**B**) with these dialkylamines in the presence of triethylamine also form enamines **1–3**, apparently as a result of isomerization of this compound to olefin **C** induced by triethylamine. In this case, the reaction time was about three times longer than for olefin **A**. The reaction of a mixture of hexafluoropropylene trimers with diallylamine under the same conditions led to enamine **4** being formed.

$$CF_3CF{=}C[CF(CF_3)_2]_2 + HN(CH_2CH{=}CH_2)_2 \xrightarrow[CH_3CN]{NEt_3}$$

$$(CH_2{=}CHCH_2)_2NCF{=}CF{-}CF[CF(CF_3)_2]_2$$

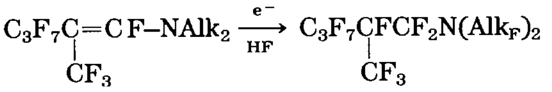
(**4**)

However, dipropylamine, dibutylamine or diallylamine reacted with perfluoro-1-ethylcyclohex-1-ene with substitution of the multiple bond fluorine to give 1-*N*,*N*-dipropylperfluoro-2-ethylcyclohex-1-ene (**5**), enamine **6** and enamine **7**, respectively (Tables 1 and 2).



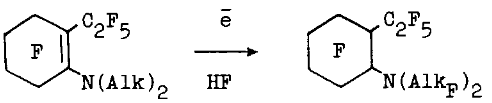
Alk = C_3H_7 (**5**); Alk = C_4H_9 (**6**); Alk = $CH_2CH{=}CH_2$ (**7**)

Enamines **1–7** were subjected to exhaustive electrochemical fluorination in anhydrous hydrogen fluoride; the ^{19}F NMR and analytical data for the perfluorinated trialkylamines are listed in Tables 1 and 2.



$$C_3F_7\underset{\displaystyle CF_3}{\underset{|}{C}}{=}CF{-}NAlk_2 \xrightarrow[HF]{e^-} C_3F_7\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2N(Alk_F)_2$$

Alk = C_3H_7, $CH_2CH{=}CH_2$, C_4H_9; (**8**) $Alk_F = C_3F_7$; (**9**) $Alk_F = C_4F_9$



Alk = C_3H_7, $CH_2CH{=}CH_2$, C_4H_9; (**10**) $Alk_F = C_3F_7$; (**11**) $Alk_F = C_4F_9$

$$\underset{(\mathbf{4})}{(CH_2{=}CHCH_2)_2NCF{=}CF{-}CF[CF(CF_3)_2]_2} \xrightarrow[HF]{e^-}$$

$$(C_3F_7)_2NCF_2CF_2CF[CF(CF_3)_2]_2$$

(**12**)

The reaction mixtures were distilled and analyzed by GC–MS and ^{19}F NMR methods in a similar fashion to that reported in ref. 13. As expected, the reaction gave not only the perfluorinated amines **8** and **12** but also some by-products formed as a result of the destruction of carbon radicals and transformations of the intermediate radical species. Among the by-products were tertiary amines with shorter carbon radicals, heterocyclic nitrogen-containing compounds and perfluoroparaffins.

It has been shown earlier that in ECF the yield of the crude product changes with time depending on the quantity of electricity passed through the electrolyte [14]. The crude product appears only after 150–250 A h^{-1} has been passed, its yield being low (5–20%). During the process of electrolysis the yield of the crude product increases, reaching a maximum value after the passage of 2000–3500 A h^{-1}. Then, if the electrolyte is transformed to a tar with time, the yield of crude product decreases. This was also observed in the ECF of tripropylamine, tributylamine, triallylamine and triamylamine. For this reason, the ECF data for trialkylamines were compared with those for the enamines obtained in this work for the passage of the same quantity of electricity (Table 3).

As seen from the data in Table 3, the yield of crude product in the ECF of tributylamine after 1640 A h l^{-1} of electricity had been passed was 37%, the content of perfluorotributylamine being 50%. When the same quantity of electricity was passed through the solution of compound **3** in anhydrous HF, the yield of product **8** was 62%, with the content of **8** in the crude product being 81%. The total theoretical yield in the former case was 12% and in the latter case 50%. Another advantage of ECF of partially fluorinated products is the higher electrochemical equivalent in the latter case relative to the former. This is the reason for the higher output of crude product per unit time or per unit quantity of electricity passed. It should be noted that a limitation on electrolysis is the slow rate of the process (the current density is 0.01–0.04 A cm^{-2} and cannot be increased to any great extent). Hence it is important to increase the current efficiency, i.e. the output of the crude product per unit quantity of electricity passed. In our examples, this quantity is 0.20 g of perfluorotributylamine and 0.64 g of compound **8** per 1 A h^{-1} of electricity passed. As seen from Table 3, this general tendency also holds for other products irrespective of the length of the fluorinated carbon units.

Experimental

^{19}F NMR spectra were recorded on a Bruker WP200 SY spectrometer at frequencies of 188 and 28 MHz (internal standards C_6F_6 and TMS). The GLC analysis was performed on an LkhM 72 chromatograph (15% SE-30, SKTFV-803 or QF-1 on Chromosorb W, 4000 mm column, diam. 4 mm), mass spectra on a VG 707 OE instrument, ionizing beam energy 70 eV. 1-*N*,*N*-Dipropylaminopentafluoropropylene (**14**) was prepared according to ref. 12 by treatment of hexafluoropropylene with dipropylamine.

TABLE 3

ECF data for partially fluorinated enamines and trialkylamines

Starting material	Desired product	Strength of current (A/cm^2)	Mass per cent substrate (%)	Voltage (V)	Quantity of electricity passed (A h l^{-1})	Yield per 1 A h^{-1} (g)	Yield of crude product (%)	Product content	
								Found (%)	Theory (%)
$(C_3H_7)_3N$	$(C_3F_7)_3N$	5/0.02	6.4	5.4–6.1	1030	71	12	55	7
14	$(C_3F_7)_3N$	8.4/0.02	10	4.6–6.1	1000	154	34	65	22
$(C_4H_9)_3N$	$(C_4F_9)_3N$	12.6/0.03	6.5	5.1–6.1	1640	194	37	50	12
3	**8**	4.6/0.02	10	4.5–5.1	1640	262	62	81	50
$(C_5H_{11})_3N$	$(C_5F_{11})_3N$	7.0/0.03	8	5.7–6.3	1390	352	23	60	7
4	**12**	12/0.03	15	4.8–6.2	1310	256	32	81	26
1	**9**	8.4/0.02	8	4.6–6.1	2200	512	54	74	25
5	**10**	8.4/0.02	6.5	6.0–6.6	1500		70	80	56
6	**11**	8.6/0.02	6.8	6.0–6.6	1670		75	78	58

Interaction of perfluoro-olefins with secondary amines

In a 5 l capacity flask, equipped with a reflux condenser, an effective stirrer and a dropping funnel, was placed 1000 g (615 ml, 3.38 mmol) of perfluoro-2-methylpent-2-ene and 1000 ml of CH_3CN. After the mixture had been stirred at 30 °C for 2.5 h, a mixture of 430 g (565 ml, 3.33 mmol) of dibutylamine and 336 g (475 ml, 3.33 mmol) of triethylamine (or pyridine) was added. The end of the process was distinguished by the formation of a homogeneous, slightly yellowish solution. The reaction mixture was poured into 3 l of water, the bottom organic layer separated on a separating funnel, washed with 10% HCl to pH ~5–6, then washed with water and distilled *in vacuo* without preliminary drying to remove traces of water. This gave 700 g (51%) of compound **1**. The analytical data for this compound and other products obtained under similar conditions are given in Table 2; ^{19}F NMR data are listed in Table 1. Attempted removal of residual moisture by drying the compounds over $CaCl_2$ or $MgSO_4$, by passing them through adsorbents (SiO_2, Al_2O_3) or by azeotropic drying with toluene resulted in a vigorous reaction accompanied by the liberation of hydrogen fluoride and a sharp increase of temperature. This produced α-hydroperfluoro-1-methylpentanoic acid dibutylamide $(C_4H_9)_2NC(O)CH(CF_3)CF_2CF_2CF_3$ (**13**). Hydrogen fluoride possibly acts as a catalyst promoting the transformation of compound **1** to the amide of fatty acid **13**.

Electrochemical fluorination of enamines 1–7

The ECF studies were performed on a laboratory apparatus for electrochemical fluorination with currents ranging from 4.6 A to 17.0 A. A batch electrolyzer consisting of alternating anode and cathode nickel plates was used. The current density in the ECF was 0.015–0.03 A cm^{-2}, electrolyte temperature 20–25 °C, refrigerant temperature at the outlet −40 °C. Tables 1 and 2 give the data for the perfluorinated amines obtained in the electrochemical fluorination. Perfluorotripropylamine had the same data as given in ref. 15, perfluorotriamylamine as in ref. 16.

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