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PERFLUOROETHYL AMINES FROM THE ELECTROCHEMICAL FLUORINATION OF TRIMETHYLAMINE. NMR AND VIBRATIONAL SPECTRA OF NEW FLUOROALKYL AMINES

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SUMMARY

The perfluoroethyl amines $C_2F_5N(CF_3)_2$, $C_2F_5N(CF_3)CHF_2$, and $C_2F_5N(CHF_2)_2$ have been isolated from the electrofluorination of $N(CH_3)_3$ as well as $C_2H_5N(CH_3)_2$. Evidence is presented that, in the former case, the C_2F_5 compounds are formed by $\cdot CF_3$ attack on partly fluorinated trimethylamines $NC_3F_{9-n}H_n$, n = 1 to 3. The compounds have been characterized by analytical, nmr and vibrational spectroscopic methods.

INTRODUCTION

The electrochemical fluorination of $N(CH_3)_3$ is the most convenient synthesis for perfluorotrimethylamine, $N(CF_3)_3$. The yield however is moderate and several hydrogen-containing species of the series $C_3H_nF_{9-n}N$, n = 1 to 3, have been isolated from the crude electrofluorination products [1]. While the claim has been made that the electrochemical fluorination of alkylamines leads to alkyl chain-length growth [2], no convincing evidence for such growth or the composition of the resulting compounds could be presented.

Obviously the detection and characterization of such species, e.g. of perfluoroethyl derivatives generated from $N(CH_3)_3$, will be a valuable key to the understanding of the electrofluorination process. We therefore decided to search for such compounds in the volatile products of the $N(CH_3)_3$

electrofluorination [1], to identify these species and, if necessary, to synthesize them independently. The following contribution describes the identification, isolation and characterization of the perfluoroethylamines $C_2F_5N(CF_3)_n(CHF_2)_{2-n}$ (n = 0, 1, 2). Particular attention is given to the analysis of their nmr and vibrational spectra.

ELECTROFLUORINATION OF $N(CH_3)_3$ AND $C_2H_5N(CH_3)_2$

The electrochemical fluorination of $N(CH_3)_3$ under previously described conditions [1] had yielded $N(CF_3)_3$ (I), $CHF_2N(CF_3)_2$ (II), $(CHF_2)_2NCF_3$ (III) and $N(CHF_2)_3$ (IV) in a relative ratio of 100 : 20 : 5 : 1. The residue of the fractional distillation which had afforded I and II was mainly composed of III and IV, but components were detected by ^{19}F nmr spectroscopy which obviously contained C_2F_5N groups. The compounds III, IV as well as VII, which was identified as $C_2F_5N(CHF_2)_2$ by ^{19}F and ^1H spectroscopy, were separated by preparative glc while all other material was collected and combined. Two components, $C_2F_5N(CF_3)_2$ (V) [3] and $C_2F_5N(CF_3)(CHF_2)$ (VI), were identified by ^{19}F nmr investigations of the combined fractions. The ^{19}F nmr spectrum of V has already been reported [4] while VI and VII, to our knowledge, have not yet been described. The quantity of VI as generated proved to be too small for separation and characterization. Therefore, we decided to synthesize VI by electrochemical fluorination of $C_2H_5N(CH_3)_2$ under conditions similar to those described previously [1].

After removal of the products volatile in vacuo at -114° (mainly NF_3, CHF_3 and CF_4), the residue was subjected to a fractional distillation at normal pressure over a 30" spinning band column. A fraction consisting of ~ 80% V and ~ 20% I came over at 21° C which could not be separated by repeated distillation and which probably represents an azeotropic mixture of I and V. Isolation of V was achieved by glc employing a 1/4" SE 30 column at 35° C.

The residue of the fractional distillation mainly consisted of V, VI and VII. Of these VI and VII were isolated by the same glc techniques.

Distribution of products

The distribution of I to VII in the crude reaction products obtained from the electrofluorination of $N(CH_3)_3$ and $C_2H_5N(CH_3)_2$ is given in Table 1. While the total yield is much higher in the latter case the ratios I : II : III and V : VI : VII are similar. The comparability of the ratio V : VI : VII irrespective of the alkylamine used should be noted. One can assume that V, VI and VII are formed both by attack of $\cdot CF_3$ on II, III and IV (eqn. 1) and by subsequent fluorination (eqn. 2).

TABLE 1

Typical yields (% wt.) of fluoroalkyl amines

Starting material	I	II	III	IV	V	VI	VII
$N(CH_3)_3$	11	2	0.5	0.1	0.2	0.02	0.005
$C_2H_5N(CH_3)_2$	5	0.3	0.05	-	41	1.5	0.5

$$>N\text{-}CHF_2 \xrightarrow{\circ F,\ \cdot CF_3} >N\text{-}CF_2\text{-}CF_3 + HF \qquad (1)$$

$$(IV \rightarrow VII,\ III \rightarrow VI,\ II \rightarrow V)$$

$$C_2F_5>N\text{-}CHF_2 \xrightarrow{2\ \cdot F} C_2F_5>N\text{-}CF_3 + HF \qquad (2)$$

$$(VI \rightarrow V,\ VII \rightarrow VI)$$

Though a trimethylamine has not yet been detected which contains less fluorine than IV, attack of a $\cdot CF_3$ radical might occur in an earlier stage of the fluorination process. Such precursors of the general formula $C_3H_nF_{9-n}N$, $n > 3$, obviously only exist in contact with the anode. Their existence is however supported by detecting $CF_3CHFN(CHF_2)_2$ ($< 0.01\,\%$) in the volatile products of the $N(CH_3)_3$ electrofluorination, a species which has not been found in the electrofluorination of $C_2H_5N(CH_3)_2$ [5]. Eqn. (3) accounts for its formation.

$$(CHF_2)_2N\text{-}CH_2F \xrightarrow{\cdot F,\ \cdot CF_3} (CHF_2)_2N\text{-}CHF\text{-}CF_3 + HF \qquad (3)$$

To ensure that V to VII were really formed by alkyl growth, careful verification was made of the absence of C_2H_5 containing impurities in the $N(CH_3)_3$.

PROPERTIES OF THE PERFLUOROETHYL AMINES

The amines V to VII are volatile, colourless liquids. While V is insoluble in C_6H_6, CCl_4 and $(CH_3)_2CO$, VI and VII dissolve readily in these solvents. V is however miscible with other perfluoroalkyl amines like I to IV.

The physical properties of V to VII are listed in Table 2.

TABLE 2

Properties of the compounds V to VII

	V	VI	VII
Formula	$C_4F_{11}N$	$C_4HF_{10}N$	$C_4H_2F_9N$
MW calc.	271.03	253.04	235.05
obs.	271.4 [a]	251.2	233.4
mp [°C]	-119	-99	-93.5
bp_{760} [°C]	19.3 [a]	32.6	43.1
log p [Torr] = -A/T + B			
A	1480	1498	1807
B	7.941	7.780	8.594
ΔH_v [Kcal·mole^{-1}]	6.768	6.850	8.263
$\Delta H_v/T$ [cal·mole^{-1}K^{-1}]	23.1	22.4	26.1

[a] Ref. [6] MW obs. 268-272, bp_{760} 20.5 [°C].

The enhanced value of the vaporization entropy of VII is indicative of hydrogen bonding. A similar behaviour was observed for IV for which the same value was found.

The constitution of V to VII follows from their vapour densities and vibrational and nmr spectra, which are described in the following sections.

NMR SPECTRA

The ^1H and ^{19}F nmr spectra of V, VI and VII demonstrate the strongly-coupled, multispin nature of these compounds. The spin systems may be designated as $A_2M_3X_6$, $A_2M_2P_3Q_3X$ and $A_2A_2'M_2P_3XX'$ respectively. For the most part, the near first-order character of the spectra greatly facilitated their interpretation. Several general features should be noted.

TABLE 3

^1H and ^{19}F nmr spectra

		V[a]	VI	VII	II[1]
δ(H)[ppm][b]			6.46(2)	6.51(2)	6.49(2)
^2J (HF) [Hz]			56.1(5)	57.3(5)	57.0(5)
^4J (HF) [Hz]	$\underline{H}CNC\underline{F}_3$		1.2(1)		0.67(3)
	$\underline{H}CNC\underline{F}_2H$			1.3(2)	
δ(F)[ppm][c]	$C\underline{F}_3N$	-53.0(2)	-52.9(2)		-56.3(2)
	$C\underline{F}_3C$	-85.0(2)	-86.3(2)	-86.6(2)	
	$C\underline{F}_2C$	-96.0(2)	-99.2(2)	-99.5(2)	
	$C\underline{F}_2H$		-96.5(2)	-95.5(2)	-98.0(2)
^2J (FH) [Hz]			56.0(5)	58.1(5)	56.4(5)
^4J (FH) [Hz]	$C\underline{F}_3NC\underline{H}F_2$		1.1(1)		
^3J (FF) [Hz]		0.70(5)	<1	<0.7	
^4J (FF) [Hz]	$CC\underline{F}_2NC\underline{F}_3$	15.8(2)	13.0(2)		
	$CC\underline{F}_2NC\underline{F}_2H$		8.3(2)	9.6(2)	
	$C\underline{F}_3NC\underline{F}_2H$		9.6(2)		8.00(5)
	$CH\underline{F}_2NCH\underline{F}_2$			5.2(2)[d]	
^5J (FF) [Hz]	$C\underline{F}_3CNC\underline{F}_3$	5.8(2)	4.8(2)		
	$C\underline{F}_3CNC\underline{F}_2H$		3.1(2)	3.9(1)	

[a] Ref. [4] : δ(F) CF_3N -23.1, CF_3C 8.5, CF_2 19.9 [ppm] from external CF_3COOH, $^3J(FF) \leq 1$[Hz], $^4J(FF)$ 16[Hz], $^5J(FF)$ 6[Hz]. [b] From internal TMS. [c] From internal $CFCl_3$, positive sign = high frequency. [d] From simulation of the ^1H spectrum.

The chemical shifts of the fluorinated dimethylamino parts are similar to those of the corresponding fluorotrimethylamine species I to IV [1]. As expected [7, 8], the C_2F_5 parts are characterized by well-separated resonances of the CF_3 and CF_2 groups with small values of $^3J(FF)$. Contrastingly, long-range, through-space couplings $^4J(FF)$ are substantial.

The nmr data are given by Table 3 and compared with respective results obtained for compound II [1].

^1H nmr spectra. Due to geminal CF coupling, the spectrum of VI exhibits a triplet which is further split into quartets by coupling with the NCF_3 group. $^4J(HF)$ is twice as large as was observed in II. δ CH and $^2J(HF)$ do not differ significantly for II, VI and VII. The ^1H spectrum of VII, however, is of higher order, the fine structure of the triplet being mainly caused by the 5.2 [Hz] coupling constant $^4J(FF)$ between the magnetically nonequivalent fluorine nuclei. Fig. 1 shows the experimental spectrum (A) and the simulation (B), which neglects further coupling with the C_2F_5 group.

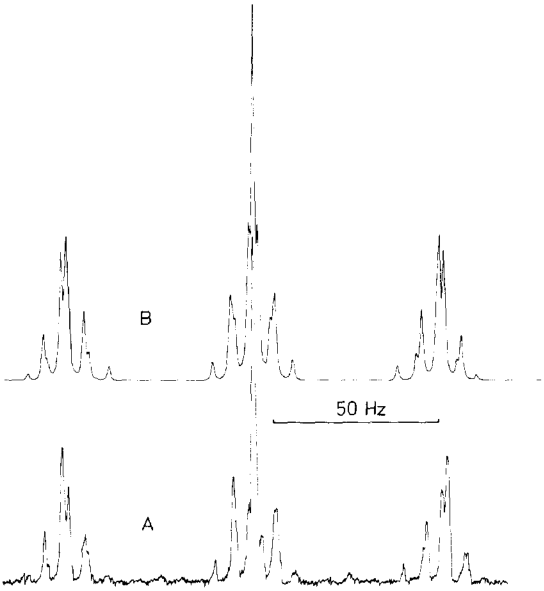

Fig. 1 ^1H nmr spectrum of VII. A : Observed, B : Computed

^{19}F nmr spectra. The ^{19}F nmr spectrum of V is consistent with that reported in the literature, but chemical shifts and coupling constants are now determined more precisely. While the NCF_3 fluorines exhibit a triplet of quartets, both the CF_3 and CF_2 fluorine resonances of the C_2F_5 group appear as septets with a fine structure due to $^3J(FF)$. Similarly, the C_2F_5 groups of VI and VII appear as quartets of triplets and as quintets, respectively, due to coupling with the NCF fluorines. No long-range coupling has been observed between C_2F_5 fluorines and the H atoms. For VI, the NCF_3 group is coupled with three different fluorines and with the hydrogen to yield a triplet of triplets of quartets of doublets. The CHF_2 fluorines of VI appear as a doublet of quartets of triplets of quartets. The fine structure of the signal was elucidated by decoupling experiments.

In VII the CHF_2 group looks like a doublet of triplets of quartets. Although this spectrum is clearly not first order, simulation experiments did not significantly improve the parameters which were obtained from a first order analysis.

VIBRATIONAL SPECTRA

The compounds V to VII have been investigated by infrared and Raman spectroscopy in the gaseous and liquid state respectively. The complete list of observed vibrational frequencies is deposited in Ref. [5] and available from the first author on request. The spectra were assigned by comparison with I for which a vibrational analysis has been performed [9] and with II to IV, all having increments in common with V to VII.

The considerable information now available may be useful for the identification and characterization of related compounds, and though it is a common feature of fluoroalkyl compounds that many vibrations are strongly coupled, several diagnostic vibrations could be detected and assigned for the series of fluoroalkyl amines I to VII. These are supposed to originate from one of the molecular fragments, the CF_3, CF_2H, C_2F_5 and $NC_3(F_n)$ groups. Table 4 summarizes several of these

TABLE 4

Characteristic vibrations of the compounds I to VII, intensities (IR/Ra) and their assignments

I	II	III	IV	V	VI	VII	Assignment
				188 /w	187 /w	182 /w	$\delta(\mathrm{CNC-C_2F_5})$
210 /w	210 /w	203 /w	197 /w	217 /w	208 /w	207 /w	$\delta(\mathrm{CNC-CF_3})$
				235 /w	235 /w	233 /w	$\delta(\mathrm{CNC-C_2F_5})$
329 /sp	336 /sp	340 /sp	340 /sp	308 /sp	306 /sp	312 /sp	"ν_s"(NC_3), see[9]
358 /sp	355 /mp 364 /w	360 /mp		343 /mp 354 /s	350 /mp		$\rho(\mathrm{CF_3-N})$
				385 /mp	376 /mp	374 /mp	$\rho(\mathrm{CF_3-C})$
				745s/	751m/sp	751s/mp	$\delta_s(\mathrm{CF_3-C})$
735vs/ 793 /vsp	676s/ 755 /sp	676m/		682m/ 780 /sp	774 /mp		$\delta_s(\mathrm{CF_3-N})$
	813s/sp	762s/ 832 /vsp	727s/ 915 /vsp		807 /vsp	797s/ 798 /vsp	$\delta_s(\mathrm{CF_2-H})$
1306 /mp 1370vs/	1265 /wp 1365vs/	1290vs/wp		1317 /wp 1345vs/	1297vs/		$\nu_s(\mathrm{CF_3-N})$
				1374s/	1374s/	1373s/	$\nu_s(\mathrm{CF_3-C})$
	1355vs/ 1455s/	1348s/ 1450s/	1342m/ 1440s/		1340vs/ 1450s/	1350s/ 1450s/	$\delta(\mathrm{HCF})$
	3053w/wp	3048w/wp	3045w/wp		3067w/wp	3047w/wp 3057w/wp	$\nu(\mathrm{CH})$

characteristic frequencies. It should be noted that the CH stretching vibrations ν(CH) are accidently degenerate in III and IV while VII exhibits two polarized Raman lines due to the influence of the C_2F_5 group.

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EXPERIMENTAL

Glc : Varian 3700, TCD.
^{1}H nmr : Varian EM 390, neat liquids, internal TMS.
^{19}F nmr : Varian EM 390, 84.67 MHz, neat liquids, internal $CFCl_3$. Positive chemical shifts refer to high field.
IR : Perkin-Elmer 580 B, Beckman IR 12, Nicolet 7199, 4000 - 400 cm^{-1}, ± 2 cm^{-1}; 10 cm gas cells, KBr windows.
Raman : Cary 82, Kr^+ 647.1 nm, 1 mm i.d. capillaries.

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