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Interaction of hexafluoropropene trimers with ammonia and primary amines [1]

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Abstract

Hexafluoropropene trimers (HFPT) react with primary amines to form the corresponding enamines and enimines, i.e. products arising from the indirect substitution of fluorine atoms. The adduct with HFPT has been obtained for the first time in the reaction with ammonia. The intramolecular cyclization of the compounds synthesized to give azetines and azetidines has been studied. Specific features of the ^{19}F NMR spectra of the enimines obtained have been considered.

Keywords: Hexafluoropropene trimers; Ammonia; Primary amines; Synthesis; Cyclizations; IR spectroscopy; NMR spectroscopy; Mass spectrometry

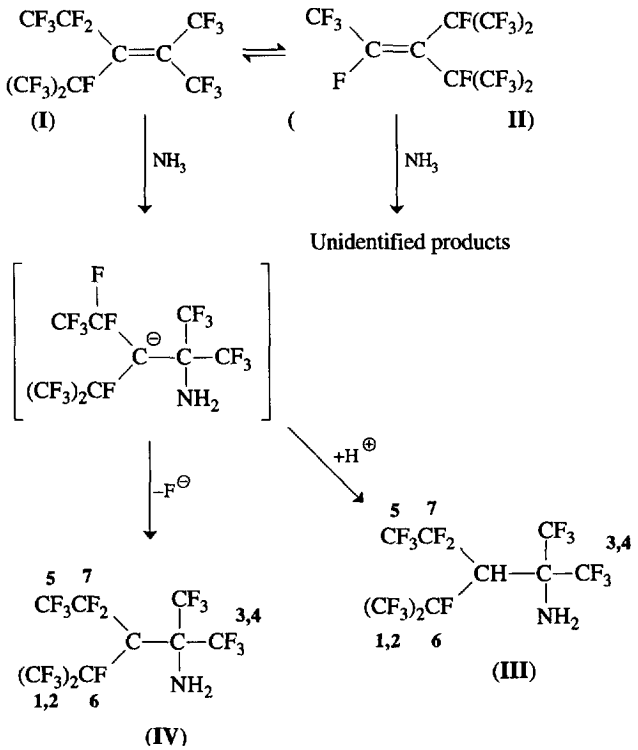
1. Introduction

Hexafluoropropene trimers (HFPT) are known to form the products arising from the substitution of one or several fluorine atoms when they interact with alcohols [1], thiols [2] and secondary amines [3].

2. Results and discussion

We have shown that, unlike secondary amines and alcohols, ammonia and primary amines reacted predominantly with the tetrasubstituted isomer of HFPT, perfluoro-2-methyl-3-isopropyl-2-pentane (**I**).

As a result of the interaction of a mixture of HFPT (**I** + **II**) with ammonia, we have obtained a mixture of 2-aminoperfluoro-2-methyl-3-isopropyl-3-hydropentane (**III**) – the adduct between ammonia and **I** – and 4-amino-perfluoro-4-methyl-3-isopropyl-2-pentane (**IV**) – the product of ammonia addition followed by elimination of a fluorine from the adjacent CF_2 group of **I**. We have not observed the products of the interaction of ammonia with HFPT (**II**). Such products are likely to undergo further conversions in the presence of NH_3 to result in an unidentified mixture of products. The formation of a compound which was similar to alkenylamine **IV** was observed in the reaction of aqueous ammonia with perfluoro-2-ethyl-3-methyl-2-pentene [4]. In the reactions of nucleophilic reagents with HFPT, the formation of addition products – adducts of type **III** – was never observed. This



fact has been explained by the high steric CH acidity of such adducts [5]. Our experimental data do not allow us to explain the relatively high stability of adduct **III**, which cannot be dehydrofluorinated by the action of the mild dehydrofluori-

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[1] In memory of the late Lev Solomonovich German.

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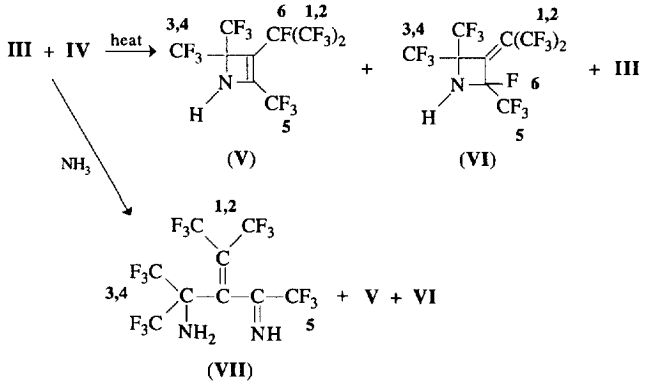
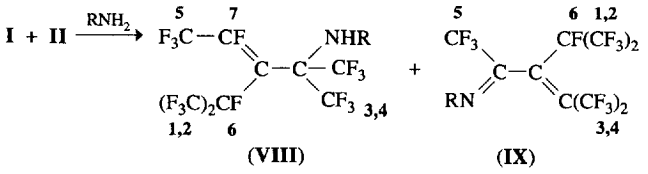
nating agent, $Et_3N \cdot BF_3$ in ether at room temperature. Judging from the ^{19}F NMR spectra, heating this mixture at 170 °C for 4 h leads to cyclization of the aminopentene **IV** affording two cyclic products, azetine **V** and azetidine **VI**; in this case, adduct **III** remained unchanged. At the same time, treatment of the mixture of **III** and **IV** with an excess of triethylamine (20 °C, 1 month, ^{19}F NMR analysis) gives azetidine **VI**. Further addition of excess ammonia to the mixture of **III** and **IV** results in 2,4-di(trifluoromethyl)-3(1′-imino-trifluoroethyl)-4-aminoperfluoro-2-pentane (**VII**) (similar to results reported in Ref. [6]). However, along with this process, intramolecular cyclization partially occurs involving substitution of the vinyl fluorine atom in **IV** and resulting in the formation of **V** and **VI**. Unfortunately, we failed to isolate these compounds. Identification was effected by ^{19}F NMR spectroscopic methods by analogy with products **X** and **XII**.



Primary amines react with the HFPT mixture to give reaction products arising from both isomers **I** and **II**. However, we failed to detect any addition products in this case, and the formation of products of substituting the fluorine atoms in isomer **I** via addition/elimination, i.e. enamines **VIII**, predominated.



[R = CH_3 (**a**); C_2H_5 (**b**); n-C_4H_9 (**c**)]

Unlike the 4-alkylaminoperfluoro-4-methyl-3-isopropyl-2-pentenes **VIIIa–c**, the 4-alkyliminoperfluoro-2-methyl-3-isopropyl-2-pentenes **IXa–c** formed from trimer **II** (not more than 20% yield) are not stable under the reaction conditions, and when an excess of amine was added they were converted to a mixture of products which could not be identified. We succeeded in isolating enimine **IXa** by preparative GLC; this is likely to be a mixture of isomers, i.e. the stable conformers [7,8]. Four possible patterns for such conformers are presented in Fig. 1.

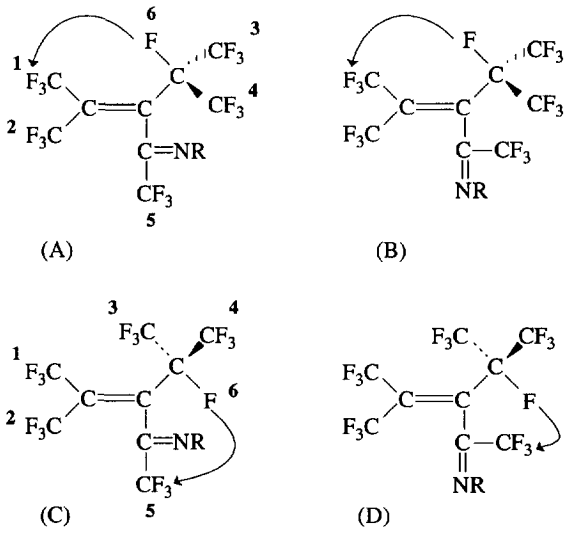


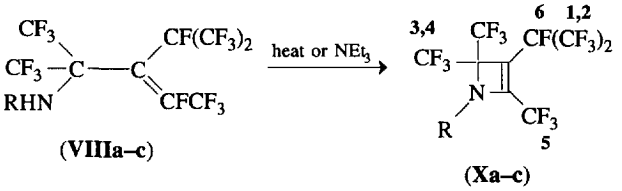
Fig. 1.

Complete interpretation of the ^{19}NMR spectrum of this mixture could not be made because all the signals of the trifluoromethyl groups are located in the region ranging from −21 ppm to +1 ppm. However, the signals of the fluorine atom (CF)[6] of the heptafluoroisopropyl group are very typical and informative. We observed four signals of different intensity, each corresponding to one of the conformers. This assumption is confirmed by the following: two of these signals are quartets occuring at 93 ppm and 87 ppm with coupling constants equal to 53 and 61 Hz, respectively, attributed to through-space interaction of this fluorine atom with the trifluoromethyl group. These signals have been assigned to conformers A and B. Similar doublet constants were observed in the signals of the trifluoromethyl group. Two other signals, quartets centred at 78.8 ppm and 77.5 ppm with coupling constants of ca. 12–14 Hz may be assigned to conformers C and D.

All other *N*-derivatives of THFP exist as one conformer.

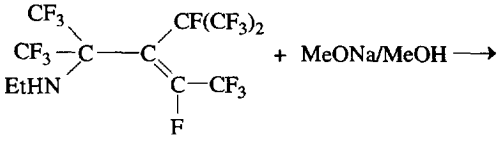
It is worth noting that the yield of enimines **IX** decreases as the bulk of the alkyl substituent in the primary amine molecule increases, and in contrast to this, the fraction of enamine **VIII** increases to a certain extent. In the reaction of HFPT with t-butylamine, we failed to detect the formation of both enamine **VIII** and enimine **IX**, and observed only unidentified products of their further interaction with t-butylamine.

On heating, the 4-alkylamino-perfluoro-4-methyl-3-isopropyl-2-pentenes **VIIIa–c**, like product **IV**, undergo intramolecular cyclization t form azetines **Xa–c** [9].

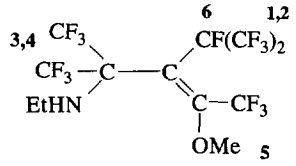


Additionally, we have demonstrated the substitution of the vinyl fluorine atom in enamines **VIII** in the reaction

of 4-ethylaminoperfluoro-4-methyl-3-isopropyl-2-pentene (**VIIIb**) with sodium methylate in methanol, leading to 2-methoxy-4-ethylaminoperfluoro-4-methyl-3-isopropyl-2-pentene (**XI**).



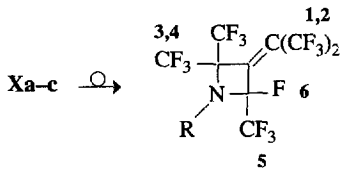
(**VIIIb**)



(**XI**)

A product (**XIa**) of this type was formed when the mixture of **III** and **IV** was treated with sodium methylate. However, only product **IV** reacted in this case, judging from the ^{19}F NMR spectra.

Azetines **Xa–c** isomerize to azetidines **XIIa–c** under the action of triethylamine or anhydrous CsF in acetonitrile.



(**XIIa–c**)

(R = Me; Et; ^{n}Bu)

3. Experimental details

^{1}H and ^{19}F NMR spectra were recorded on a Bruker AC-200 X instrument (200 MHz for ^{1}H and 188.3 MHz for ^{19}F), with TMS and CF_3COOH used, respectively, as references. Chemical shifts are given in ppm, using δ (^{1}H) and ϕ (^{19}F) scales; coupling constants, J, are given in Hz. Mass spectra were obtained on a VG 7070E spectrometer (ionizing electron energy 70 eV). IR spectra were recorded on a UR-20 instrument using thin layers.

3.1. Interaction of HFPT (I and II) with ammonia

Gaseous ammonia (4 g, 0.23 mol) was bubbled into a solution of a mixture of **I** + **II** (25 g, 0.055 mol) in dry ether (75 ml); the mixture was stirred at ca. 20 °C for 16 h, washed with water and dried over $MgSO_4$. After the ether was distilled off, the residue was distilled to give 9.4 g (36%) of a mixture (b.p. 74–78 °C) consisting of **III** (70%) and **IV** (30%).

Compound **III**: IR (ν, cm^{-1}): 3475 (NH_2). ^{1}H NMR δ: 2.65 (s, NH_2); 4.83 (d, CH, J_{H-F} = 20.0 Hz) ppm. ^{19}F NMR ϕ: −7.9 (br.d, CF_3); −6.3 (d m, CF_3); −5.0 (br.d, CF_3); 0.7 (br.d, CF_3); 3.9 (s, CF_3); 27.1 [AB, qh, $(CF_2)^7$, J_{A-B} = 302.5, $J_{F(A)-2CF_3}$ = 32.3, $J_{F(B)-2CF_3}$ = 26.9 Hz]; 86.7 [m, $(CF)^6$] ppm. MS [*m/z*, (intensity) (species)]: 448 (11) $(M-F)^+$; 428 (3) $(M-F-HF)^+$; 408 (6) $(M-F-2HF)^+$; 398 (100) $(M-CF_3)^+$; 378 (2) $(M-CF_3-HF)^+$; 358 (3) $(M-CF_3-2HF)^+$; 328 (4) $(M-C_2F_5-HF)^+$; 263 (8) $(M-C_3F_7NH-HF)^+$; 210 (18) $(M-C_2F_6-C_2F_5)^+$; 166 (60) $[(CF_3)_2C{=}NH_2]^+$; 160 (35) $(C_4H_3F_5N)^+$; 146 (13) $(C_4H_3F_5)^+$; 199 (22) $(C_2F_5)^+$; 96 (20) $(C_3H_3F_3)^+$; 69 (53) $(CF_3)^+$; 51 (19) $(CF_2H)^+$

Compound **IV**; IR (ν, cm^{-1}): 1640 (C=C); 3410 (NH_2). ^{1}H NMR δ: 2.55 (s, NH_2) ppm. ^{19}F NMR ϕ: −18.0 [s, $(CF_3)^5$]; −9.5 (m, $2CF_3$); −4.1 (m, $2CF_3$); −0.9 [dh, $(CF)^7$, J = 26.9 Hz]; 92.0 [dh, $(CF)^6$] ppm. MS [*m/z*, (intensity) (species)]: 428 (29) $(M-F)^+$; 408 (3) $(M-F-HF)^+$; 389 (2) $(M-2F-HF)^+$; 378 (100) $(M-CF_3)^+$; 358 (19) $(M-CF_3-HF)^+$; 338 (5) $(M-CF_3-2HF)$; 308 (40) $(M-C_2F_5-HF)^+$; 293 (9) $(M-C_2H_5NH-HF)^+$; 288 (5) $(M-C_2F_5-2HF)^+$; 243 (17) $(M-C_3F_7NH\text{-}HF)$; 220 (5) $(M-C_3HF_{10})^+$; 200 (18) $(C_4F_8)^+$; 143 (5) $(C_4F_5)^+$; 69 (59) $(CF_3)^+$; 51 (19) $(CF_2H)^+$

3.2. Transformations of the mixture of III and IV

Method a

The mixture of **III** and **IV** was heated in a sealed tube at 150 °C for 3 h and at 170 °C for 4 h. The reaction mixture consisted of 70% saturated amine **III**, 15% azetine **V** and 15% azetidine **VI** (according to ^{19}F NMR analysis).

Method b

To a solution of mixture **III** and **IV** in ether, an excess of triethylamine was added and the mixture obtained stored for 7 d at ca. 20 °C. The reaction mixture consisted of saturated amine **III** and azetidine **VI** (according to the ^{19}F NMR analysis).

The assignments of the signals related to azetine **V** and azetidine **VI** were achieved by analogy with the corresponding compounds **Xa–c** and **XIIa–c**.

3.3. Interaction of the mixture of III and IV with ammonia

Into a solution of the mixture of **III** + **IV** (3.2 g) in 15 ml of dry ether was bubbled 3 ml of ammonia with stirring and the resulting solution stored at room temperature for 48 h. The reaction mixture was washed with water and dried over $MgSO_4$. The ether was distilled off and the residue distilled to give 2,4-di(trifluoromethyl)-3(1′-iminotrifluoroethyl)-4-aminoperfluoro-2-pentene (**VII**) (1.2 g, 41%), b.p. 69–70 °C/20 Torr; m.p. 38–40 °C.

Compound **VII**: Analysis: Calc. for $C_9H_3F_{15}N_2$: C, 25.47; H, 0.71; F, 67.21; N, 6.60%. Found: C, 25.72; H, 0.78; F, 67.57; N, 6.88%. IR (ν, cm^{-1}): 1630 (C=C); 1720 (C=N);

3390, 3450 (NH). ^{1}H NMR δ: 2.6 (NH_2); 4.2 (NH) ppm. ^{19}F NMR ϕ: −17.0 [qq, $(CF_3)^1$]; −15.4 [qqq, $(CF_3)^2$]; −5.2 [qqq, $(CF_3)^3$]; −4.0 [qq, $(CF_3)^4$]; 3.0 [qq, $(CF_3)^5$] ppm; J_{1-2}=9.3, J_{1-5}=9.3, J_{2-5}=4.5, J_{2-3}=9.0, J_{3-4}=4.5 Hz. MS [*m/z*, (intensity) (species)]: 424 (2) M^+; 408 (3) $(M-NH_2)^+$; 405 (6) $(M-F)^+$; 388 (5) $(M-HF-NH_2)^+$; 385 (29) $(M-F-HF)^+$; 365 (16) $(M-F-2HF)^+$; 355 (100) $(M-CF_3)^+$; 293 (14) $(C_7F_{11})^+$; 190 (53) $[(CF_3)_2C{=}CHC{=}NH]^+$; 112 (19); 96 (26) $(C_2F_3NH)^+$; 69 (67) $(CF_3)^+$; 43 (39) $(CF{=}NH)^+$.

3.4. Reaction of HFPT with methylamine

Methylamine (12.4 g, 0.4 mol) was passed through a solution of HFPT mixture (**I**+**II**) (4.5 g, 0.1 mol) on 150 ml of dry ether. The reaction mixture was stirred at room temperature for 6 h and stored overnight. It was then washed with water and dried over $MgSO_4$. A mixture (29 g, 63%), b.p. 64–78 °C/40 Torr, containing 60% of 4-methylaminoperfluoro-4-methyl-3-isopropyl-2-pentene (**VIIIa**) and 40% of 4-methyliminoperfluoro-2-methyl-3-isopropyl-2-pentene (**IXa**) was obtained. Compounds **VIIIa** and **IXa** were isolated by preparative GLC.

Amine **VIIIa**: b.p. 77–78 °C/40 Torr. Analysis: Calc. for $C_{10}H_4F_{17}N$: C, 26.04; H, 0.86; F, 70.06; N, 3.04%. Found: C, 25.95; H, 0.94; F, 70.31; N, 3.50%. IR (ν, cm^{-1}): 1635 (C=C); 3410 (NH). ^{1}H NMR δ: 1.43 (q, NH, J_{H-CH_3}=5.7 Hz; 2.05 (d, CH_3, J_{CH_3-H}=5.7 Hz) ppm. ^{19}F NMR δ: −13.3 [h, $(CF_3)^5$]; −7.8 [br.d, $(2CF_3)^{3,4}$]; −3.8 [d, $(2CF_3)^{1,2}$]; 2.2 [dh, $(CF)^7$]; 92.3 [dh, $(CF)^6$] ppm; $J_{5-3,4}$=2–3, $J_{1,2-7}$=36.1, $J_{3,4-6}$=32.4, J_{6-7}=11.7 Hz. MS [*m/z*, (intensity) (species)]: 461 (0.8) $(M)^+$; 460 (7) $(M-H)^+$; 442 (24) $(M-F)^+$; 392 (100) $(M-CF_3)^+$; 372 (12) $(M-CF_3-HF)^+$; 322 (35) $(M-C_2F_5-HF)^+$; 254 (6) $(C_7H_4F_8N)^+$; 234 (5) $(C_7H_3F_7N)^+$; 180 (6) $(C_4H_4F_6N)^+$; 110 (15) $(C_3H_3F_3N)^+$; 69 (32) $(CF_3)^+$; 28 (7) $(CH_2N)^+$.

Imine **IXa**: inseparable mixture of conformers; b.p. 61–62 °C/40 Torr. Analysis: Calc. for $C_{10}H_3F_{16}N$: C, 27.21; H, 0.68; F, 68.93; N, 3.17%. Found: C, 26.89; H, 0.71; F, 68.68; N, 3.40%. IR (ν, cm^{-1}): 1630 (C=C); 1680 (C=N). ^{1}H NMR δ: 3.73 (s, CH_3); 3.78 (s, CH_3); 3.92 (s, CH_3) ppm. ^{19}F NMR ϕ: −21 [dm, $(CF_3)^{1a}$]; −20.3 [dm, $(CF_3)^{1b}$]; −19 to 1 (m, $18CF_3$); 77.5 [q, $(CF)^{6c}$]; 78.8 [q, $(CF)^{6d}$]; 86.7 [br.q, $(CF)^{6b}$]; 93.4 [br.q, $(CF)^{6a}$] ppm; J_{6a-1a}=56, J_{6b-1b}=52, $J_{6c,d-5c,d}$=13–14 Hz. MS [*m/z*, (intensity) (species)]: 441 (12) $(M)^+$; 422 (20) $(M-F)^+$; 372 (100) $(M-CF_3)^+$; 322 (4) $(M-C_2F_5)^+$; 284 (7) $(C_8H_3F_9N)^+$; 193 (9) $(C_5F_7)^+$; 143 (7) $(C_4F_5)^+$; 110 (20) $(C_3H_3F_3N)^+$; 69 (29) $(CF_3)^+$; 28 (6) $(CH_2N)^+$.

3.5. Reaction of HFPT with ethylamine

Ethylamine (9.6 g, 0.21 mol) was passed through a solution of HFPT mixture (**I**+**II**) (24 g, 0.053 mol) in 75 ml of dry ether. The reaction mixture was stirred at room temperature for 6 h and stored overnight. It was then washed with water and dried over $MgSO_4$. The ether was distilled off and the residue was distilled to give a mixture (19.3 g, 76%), b.p. 70–78 °C/22 Torr, containing 85% of 4-ethylaminoperfluoro-4-methyl-3-isopropyl-2-pentene (**VIIIb**) and 15% of isomeric 4-ethyliminoperfluoro-2-methyl-3-isopropyl-2-pentene (**IXb**). Distillation of the mixture gave ethylamine **VIIIb**, b.p. 71–72 °C/20 Torr.

Ethylamine **VIIIb**: Analysis: Calc. for $C_{11}H_6F_{17}N$: C, 27.78; H, 1.26; F, 68.00; N, 2.94%. Found: C, 28.04; H, 1.40; F, 68.00; N, 3.07%. IR (ν, cm^{-1}): 1635 (C=C); 3385 (NH). ^{1}H NMR δ: 1.54 (t, CH_3); 3.21 (q, CH_2, $J_{CH_2-CH_3}$=6.8 Hz); 1.92 (br.s, NH) ppm. ^{19}F NMR ϕ: −15.5 [qq, $(CF_3)^5$]; −9.8 [bd.d, $(2CF_3)^{1,2}$]; −6.0 [br.d, $(2CF_3)^{3,4}$]; 1.8 [dh, $(CF)^7$]; 91.3 [dh, $(CF)^6$] ppm; $J_{1,2-5}$=6.2, $J_{3,4-5}$=5.5, $J_{1,2-7}$=32, $J_{3,4-6}$=34, J_{6-7}=12 Hz. MS [*m/z*, (intensity) (species)]: 475 (0.6) $(M)^+$; 474 (4.5) $(M-H)^+$; 460 (11) $(M-CH_3)^+$; 456 (4) $(M-F)^+$; 428 (7) $(M-F-C_2H_4)^+$; 406 (48) $(M-CF_3)$; 378 (19) $(M-CF_3-C_2H_4)^+$; 336 (5) $(M-HF-C_2F_5)^+$; 322 (5) $(M-CH_3F-C_2F_5)^+$; 69 (22) $(CF_3)^+$; 29 (100) $C_2H_5^+$; 27 (10) $C_2H_3^+$.

Mixture of isomers **IXb**: ^{19}F NMR ϕ: −24 to +5 [m, $(5CF_3)$]; 78.0 [br.q, $(CF)^{6c,d}$, J=12.2 Hz]; 82.7 [br.q, $(CF)^{6c,d}$, J=39.9 Hz]; 83.7 [q, $(CF)^{6a}$, $J_{CF^{6a}-CF_3{}^{3,4}}$=41.7 Hz]; 93.6 [qm, $(CF)^{6b}$, $J_{CF^{6b}-CF_3{}^{3,4}}$=41.7 Hz] ppm.

3.6. Interaction of HFP trimers with butylamine

Under conditions similar to those described above, a mixture (8 g, 74%, b.p. 61–68/5 Torr) was obtained from THFP (9.6 g, 0.021 mol) and ^{n}BuNH$_2$ (6.2 g, 0.084 mol) in 30 ml of dry ether. The mixture obtained contained 85% of product **VIIIc** and 15% of **IXc**, b.p. 72–74 °C/7 Torr. Distillation of this mixture gave amine **VIIIc**.

Amine **VIIIc**: Analysis: Calc. for $C_{13}H_{10}F_{17}N$: C, 31.03; H, 1.98; F, 64.21; N, 2.78%. Found: C, 31.05; H, 2.06; F, 64.28; N, 2.85%. IR (ν, cm^{-1}): 1635 (C=C); 3390 (NH). ^{1}H NMR δ: 1.29 (m, CH_3); 1.78 (m, $2CH_2$); 3.06 (m, CH_2); 2.05 (br.s, NH) ppm. ^{19}F NMR ϕ: −15.5 [qq, $(CF_3)^5$]; −9.9 [br.d, $(2CF_3)^{1,2}$]; −6.0 [br.d, $(2CF_3)^{3,4}$]; 1.4 [dh, $(CF)^7$]; 91.1 [dh, $(CF)^6$] ppm. $J_{1,2-5}$=5.9, $J_{3,4-5}$=5.5, $J_{1,2-7}$=34, $J_{3,4-6}$=36, J_{6-7}=12.3 Hz. MS [*m/z*, (intensity) (species)]: 503 (0.2) $(M)^+$; 502 (1.4) $(M-H)^+$; 488 (0.5) $(M-CH_3)^+$; 484 (0.4) $(M-F)^+$; 474 (0.6) $(M-C_2H_5)^+$; 460 (3.8) $(M-C_3H_7)^+$; 440 (1.7) $(M-HF-C_3H_7)^+$; 434 (32) $(M-CF_3)^+$; 378 (7) $(M-CF_3-C_4H_8)^+$; 322 (10) $(M-2CF_3-C_3H_7)^+$; 69 (16) $(CF_3)^+$; 57 (100) $(C_4H_9)^+$; 41 (26) $(C_2H_3N)^+$; 29 (29) $(C_2H_5)^+$.

Mixture of isomers **IXc**: ^{19}F NMR ϕ: −22.2 [d, $(CF_3)^{1a}$]; −21.5 [d, $(CF_3)^{1b}$]; −20 to +5 (m, $4CF_3$); 75.5 [q, $(CF)^{6c,d}$]; 77.3 [[q, $(CF)^{6c,d}$]; 83.7 [br.q, $(CF)^{6b}$]; 92.0 [q, $(CF)^{6a}$] ppm; J_{1a-6a}=57.0; J_{1b-6b}=57.0, $J_{6c,d-5c,d}$=14.3 Hz. MS [*m/z*, (intensity) (species)]: 483 (0.1) M^+; 482 (0.2) $(M-H)^+$; 468 (0.5) $(M-CH_3)^+$; 464 (0.6)

$(M-F)^+$; 454 (0.5) $(M-C_2H_5)^+$; 440 (11) $(M-C_3H_7)^+$; 422 (1.4) $(9M-C_3H_6F)^+$; 414 (16) $(M-CF_3)^+$; 372 (13) $(M-CF_3-C_3H_6)^+$; 69 (12) CF_3^+; 57 (100) $C_4H_9^+$; 41 (27) $C_2H_5N^+$; 29 (30) $C_2H_5^+$; 28 (11) $C_2H_4^+$.

3.7. N-Methyl-perfluoro-2,4,4-trimethyl-3-isopropyl-2-azetine (Xa)

Product **VIIIa** (3 g) was heated for 5 h at 120–130 °C for 5 h. Distillation gave *N*-methylazetine **Xa** (2.5 g, 89%), b.p. 69–71 °C/60 Torr.

Compound **Xa**: Analysis: Calc. for $C_{10}H_3F_{16}N$: C, 27.21; H, 0.68; F, 68.93%. Found: C, 27.52; H, 0.65; F, 68.70%. IR (ν, cm^{-1}): 1680 (C=C). ^1H NMR δ: 3.67 (s, CH_3) ppm. ^{19}F NMR ϕ: −11.4 [dh, $(CF_3)^5$]; −8.2 [br.d, $(2CF_3)^{1,2}$]; −1.0 [m, $(2CF_3)^{3,4}$]; 102.0 [br.qh, $(CF)^6$] ppm; $J_{1,2-5}$ = 7.8, $J_{1,2-6}$ = 10.5, J_{5-6} = 4.3 Hz. MS [*m/z*, (intensity) (species)]: 441 (13) $(M)^+$; 422 (18) $(M-F)^+$; 372 (100) $(M-CF_3)^+$; 353 (2.2) $(M-F-CF_3)^+$; 334 (0.6) $(M-2F-CF_3)^+$; 322 (3.9) $(M-C_2F_5)^+$; 303 (1.7) $(M-C_2F_6)^+$; 293 (1.4) $(M-C_2F_5NCH_3)^+$; 284 (7.3) $(M-2F-C_2F_5)^+$; 193 (9) $(C_5F_7)^+$; 143 (6.7) $(C_4F_5)^+$; 110 (23) $(C_3H_3F_3N)^+$; 69 (32) $(CF_3)^+$.

3.8. N-Ethylperfluoro-2,4,4-trimethyl-3-isopropyl-2-azetine (Xb)

Amine **VIIIb** (7 g) was heated for 6 h at 130–150 °C. Distillation gave 5.5. g (82%) of azetine **Xb**, b.p. 72–73 °C/50 Torr.

Azetine **Xb**: Analysis: Calc. for $C_{11}H_5F_{16}N$: C, 29.01; H, 1.09; F, 66.81; N, 3.07%. Found: C, 29.00; H, 1.11; F, 66.96; N, 3.55%. IR (ν, cm^{-1}): 1675 (C=C). ^1H NMR δ: 1.63 (t, CH_3); 3.65 (q, CH_2, $J_{CH_3-CH_2}$ = 7.7 Hz) ppm. ^{19}F NMR ϕ: −11.7 [dh, $(CF_3)^5$]; −8.2 [dh, $(2CF_3)^{1,2}$]; −0.9 [m, $(2CF_3)^{3,4}$]; 101.6 [br.qh, $(CF)^6$] ppm. $J_{1,2-3,4}$ = 4.3, $J_{1,2-5}$ = 7.7, $J_{1,2-6}$ = 12.2, J_{5-6} = 4.0 Hz. MS [*m/z*, (intensity) (species)]: 455 (2.0) (M^+); 454 (6.2) $(m-H)^+$; 440 (71) $(M-CH_3)^+$; 436 (8) $(M-F)^+$; 408 (18) $(M-F-C_2H_4)^+$; 386 (78) $(M-CF_3)^+$; 371 (2.5) $(M-CF_3-CH_3)^+$; 358 (69) $(M-CF_3-C_2H_4)^+$; 270 (3.3) $(M-C_3F_7NH_2)^+$; 243 (7) $(C_4F_8NC_2H_5)^+$; 193 (10) $(C_5F_7)^+$; 143 (4.1) $(C_4F_5)^+$; 109 (6) $C_3H_2F_3N^+$; 69 (35) CF_3^+; 29 (100) $(C_2H_5)^+$; 28 (13) $(C_2H_4)^+$.

3.9. N-Butylperfluoro-2,4,4-trimethyl-3-isopropyl-2-azetine (Xc)

By the same procedure as that described above, 3.1 g of **VIIIc** yielded azetine **Xc**, b.p. 69–70 °C/8 Torr (2.7 *r*, 90%).

Azetine **Xc**: Analysis: Calc. for $C_{13}H_9F_{16}N$: C, 32.29; H, 1.86; F, 62.93; N, 2.89%. Found: C, 32.29; H, 1.98; F, 62.62; N, 3.28%. IR (ν, cm^{-1}): 1675 (C=C). ^1H NMR δ: 1.44 (t, CH_3); 1.70 (tq, CH_2); 1.96 (tt, CH_2); 3.53 (t, CH_2) ppm; $J_{CH_3-CH_2^1}$ = 7.3, $J_{CH_2^1-CH_2^2}$ = 14.6, $J_{CH_2^2-CH_2^3}$ = 7.7 Hz. ^{19}F NMR ϕ: −11.6 [dh, $(CF_3)^5$]; −8.5 [dh, $(2CF_3)^{1,2}$]; −1.1 [m, $(2CF_3)^{3,4}$]; 101.0 [br.qh, $(CF)^6$] ppm; $J_{1,2-3,4}$ = 2–3, $J_{1,2-5}$ = 8.0, $J_{1,2-6}$ = 12.0, J_{5-6} = 2.8 Hz. MS [*m/z*, (intensity) (species)]: 483 (9.3) M^+; 440 (77) $(M-C_3H_7)^+$; 422 (10) $(M-F-C_3H_6)^+$; 414 (4) $(M-CF_3)^+$; 371 (1.5) $(M-CF_3-C_3H_7)^+$; 302 (1.8) $(M-C_4F_7)^+$; 202 (1.7) $(M-C_5F_9)^+$; 109 (5.5) $(C_3H_2F_3N)^+$; 69 (14) $(CF_3)^+$; 57 (100) $(C_4H_9)^+$; 56 (22) $(C_4H_8)^+$; 55 (8) $(C_4H_7)^+$; 41 (35) $(C_3H_5)^+$; 29 (38) $(C_2H_5)^+$; 28 (12) $(C_2H_4)^+$.

3.10. 2-Methoxy-4-ethylaminoperfluoro-4-methyl-3-isopropyl-2-pentene (XI)

To a solution of ethylamine **VIIIb** (2 g, 0.004 mol) in 7 ml of dry methanol, KOH (0.35 g, 0.06 mol) in 5 ml of dry methanol was added dropwise with stirring and cooling with ice. The reaction mixture was stirred at room temperature for 30 min and diluted with water. The precipitate formed (1.7 g, 84%) was pentene **XI**, b.p. 75–76 °C/5 Torr; m.p. 50–56 °C.

Pentene **XI**: Analysis: Calc. for $C_{12}H_9F_{16}NO$: C, 29.56; H, 1.84; F, 62.42; N, 2.87%. Found: C, 29.76; H, 1.80; F, 62.44; N, 3.03%. IR (ν, cm^{-1}): 1600 (C=C); 3380 (NH). ^1H NMR δ: 1.43 (t, CH_3); 3.28 (dq, CH_2); 4.10 (s, CH_3O); 1.54 (t, NH) ppm. $J_{CH_3-CH_2}$ = 7.0, J_{CH_2NH} = 6.9 Hz. ^{19}F NMR ϕ: −18.7 [d, $(CF_3)^5$]; −11.0 [s, $(2CF_3)^{1,2}$]; −9.3 [s, $(2CF_3)^{3,4}$]; 77.2 [q, $(CF)^6$, J_{5-6} = 57.0 Hz] ppm. MS [*m/z*, (intensity) (species)]: 487 (1.7) $(M)^+$; 486 (1) $(M-H)^+$; 472 (1.2) $(M-CH_3)^+$; 468 (1.4) $(M-F)^+$; 443 (18) $(M-C_2H_5NH)^+$; 440 (5.4) $(M-HF-C_2H_3)^+$; 418 (100) $(M-CF_3)^+$; 390 (12) $(M-CF_3-C_2H_4)^+$; 370 (10) $(-CF_3-C_2H_5F)^+$; 359 (11) $(M-C_2F_4-C_2H_4)^+$; 194 (46) $(C_3F_6NHC_2H_5)^+$; 166 (29) $(C_3F_6O)^+$; 69 (35) $(CF_3)^+$; 29 (95) $(C_2H_5)^+$.

Pentene **XIa**: ^{19}F NMR ϕ: −18.4 [d, $(CF_3)^5$]; −7.8 [s, $(2CF_3)^{1,2}$]; −6.3 [s, $(2CF_3)^{3,4}$]; 82.0 [q, $(CF)^6$, J_{5-6} = 54.0 Hz] ppm.

3.11. N-Methylperfluoro-2,4,4-trimethyl-3-isopropenylazetidine (XIIa)

To 2.9 g of *N*-methylazetine **Xa**, 20 drops of Et_3N were added and the mixture kept at room temperature for 14 d. The reaction mixture was then diluted with ether, the etherial solution washed with dilute HCl, water and dried over $MgSO_4$. The ether was distilled off and the residue distilled to give 1.8 g (62%) of *N*-methylazetidine **XIIa**, b.p. 68–70 °C/60 Torr.

Azetidine **XIIa**: Analysis: Calc. for $C_{10}H_3F_{16}N$: C, 27.21; H, 0.68; F, 68.93; N, 3.17%. Found: C, 26.97; H, 0.76; F, 68.29; N, 3.18%. IR (ν, cm^{-1}): 1710 (C=C). ^1H NMR δ: 3.41 (s, CH_3) ppm. ^{19}F NMR ϕ: −16.9, −15.3 [m, $(2CF_3)^{1,2}$]; −8.1, −6.7 [m, $(2CF_3)^{3,4}$]; 0.3 [m, $(CF_3)^5$]; 52.5 [m, $(CF)^6$] ppm. MS [*m/z*, (intensity) (species)]: 441 (1.3) M^+; 440 (3.5) $(M-H)^+$; 422 (28) $(M-F)^+$; 372 (100) $(M-CF_3)^+$; 303 (3.3) $(M-C_2F_6)^+$; 293

(14.4) $(M-C_2F_5NCH_3)^+$; 284 (5.5) $(M-2F-C_2F_5)^+$; 243 (2.7) $(C_6F_9)^+$; 234 (3.1) $(C_7F_7H_3N)$; 193 (9) $(C_5F_7)^+$; 110 (19) $(C_3H_3F_3N)^+$; 69 (32) $(CF_3)^+$.

3.12. N-Ethylperfluoro-2,4,4-trimethyl-3-isopropenylazetidine (XIIb)

Method a

In a similar manner, *N*-ethylazetidine **XIIb** (1.6 g, 53%, b.p. 69–71 °C/35 Torr) was obtained from **Xb** (3 g) and 20 drops of NEt_3 within 25 d.

Azetidine **XIIb**: Analysis: Calc. for $C_{11}H_5F_{16}N$: C, 29.01; H, 1.09; F, 66.81; N, 3.07%. Found: C, 29.25; H, 1.19; F, 66.78; N, 3.01%. IR (ν, cm^{-1}): 1710 (C=C). ^1H NMR δ: 1.59 (t, CH_3); 3.65 (q, CH_2), $J_{CH_3-CH_2}=7.7$ Hz) ppm. ^{19}F NMR ϕ: −17.1, −15.7 [m, $(2CF_3)^{1,2}$]; −8.1, −7.7 [m, $(2CF_3)^{3,4}$]; −0.5 [m, $(CF_3)^5$]; 44.2 [m, $(CF)^6$] ppm. MS [*m/z*, (intensity) (species)]: 455 (2.9) $(M)^+$; 454 (5.5) $(M-H)^+$; 440 (70) $(M-CH_3)^+$; 436 (3.5) $(M-F)^+$; 408 (16) $(M-F-C_2H_4)^+$; 390 (7) $(M-CF_2-CH_3)$; 386 (52) $(M-CF_3)^+$; 358 (21) $(M-CF_3-C_2H_4)^+$; 338 (3.3) $(M-CF_3-C_2H_5F)$; 293 (19) $(M-C_2F_5-C_2H_5N)$; 243 (3.6) $(C_4F_8NC_2H_5)^+$; 109 (6) $(C_3H_2F_3)N^+$; 69 (31) $(CF_3)^+$; 29 (100) $(C_2H_5)^+$; 28 (13) $(C_2H_4)^+$.

Method b

N-ethylazetine **Xa** (1.7 g) was added to a suspension of dry CsF in 3 ml of anhydrous CH_3CN and the mixture was stirred at room temperature for 48 h. The reaction mixture was poured into water, the lower layer was separated and dissolved in ether, and dried over $MgSO_4$. The ether was distilled off and the residue distilled to afford *N*-ethylazetidine **XIIc** (1.2 g, 70%), b.p. 69–71 °C/35 Torr.

3.13. N-Butylperfluoro-2,4,4-trimethyl-3-isopropenylazetidine (XIIc)

Triethylamine (40 drops) was added to *N*-butylazetine **Xc** and the mixture stored at room temperature for 20 d. The reaction mixture was then diluted with ether, the etherial solution washed with dilute HCl and dried over $MgSO_4$. The ether was distilled off and the residue distilled to afford *N*-butylazetidine **XIIc** (0.8 g, 57%), b.p. 77–78 °C/15 Torr.

Azetidine **XIIc**: Analysis: Calc. for $C_{13}H_9F_{16}N$: C, 32.29; H, 1.86; F, 62.93%. Found: C, 32.17; H, 1.88; F, 62.99%. IR (ν, cm^{-1}): 1710 (C=C). ^1H NMR δ: 1.38 (t, CH_3); 1.65 (tq, CH_2); 1.96 (tt, CH_2); 3.53 (t, CH_2) ppm; $J_{CH_3-CH_2^1}=7.3$, $J_{CH_2^1-CH_2^2}=14.6$, $J_{CH_2^2-CH_2^3}=7.7$ Hz. ^{19}F NMR ϕ: −17.6, −16.1 [m, $(2CF_3)^{1,2}$]; −8.3 [m, $(2CF_3)^{3,4}$]; −1.2 [m, $(CF_3)^5$]; 43.1 [m, $(CF)^6$] ppm. MS [*m/z*, (intensity) (species)]: 483 (0.1) $(M)^+$; 440 (100) $(M-C_3H_7)^+$; 422 (5.5) $(M-F-C_3H_6)^+$; 414 (4.2) $(M-CF_3)^+$; 390 (4.4) $(M-CF_2-C_3H_7)$; 109 (3.3) $(C_3H_2F_3N)^+$; 69 (10) $(CF_3)^+$; 57 (45) $(C_4H_9)^+$; 56 (18) $(C_4H_9)^+$; 41 (15) $(C_3H_5N)^+$; 29 (16) $(C_2H_5)^+$; 28 (8) $(C_2H_4)^+$.

References

[1] K.N. Makarov, L.L. Gervits, Yu.A. Cheburkov and I.L. Knunyants, *J. Fluorine Chem., 10* (1977) 323.
[2] E.E. Nikolaeva, K.N. Makarov and V.F. Snegirev, *J. Fluorine Chem., 48* (1990) 133.
[3] A.A. Kadyrov, L.L. Gervits, L.F. Komarova and K.N. Makarov, *Izv. Akad. Nauk SSR, Ser. Khim.*, (1990) 1685.
[4] S. Bartlett, R.D. Chambers, A.A. Lindley and H.C. Fielding, *J. Chem. Soc., Perkin Trans. 1*, (1980) 1551.
[5] L.L. Gervits, S.V. Sereda, M.A. Antipin, K.N. Makarov and Yu.T. Struchkov, *J. Fluorine Chem., 45* (1989) 204.
[6] J.A. Olivier, R. Stephens, J.C. Tatlow and JR. Taylor, *J. Fluorine Chem., 7* (1976) 555.
[7] F. Cavaga and C. Shuman, *J. Magn. Reson., 22* (1976) 333.
[8] S.V. Sereda, M.A. Antipin, L.L. Gervits, K.N. Makarov and Yu.T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1989) 1549.
[9] Li-Fo Chen, *J. Fluorine Chem., 67* (1994) 95.