RADICAL ADDITION OF TRIETHYLAMINE AND 1-METHYLPIPERIDINE TO TETRAFLUOROETHENE

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Dedicated to Professor Milan Kratochvil on the occasion of his 70th birthday.

The radical addition of triethylamine (*I*) and 1-methylpiperidine (*II*) to tetrafluoroethene (*III*) initiated by UV and γ-^{60}Co radiation produces tertiary amines containing 1,1,2,2-tetrafluoroethyl group at α-position (1 : 1 adducts) and/or at α,α′-positions (1 : 2 adducts). 1 : 2 Telomers, 1 : 3 adducts, and products formed by recombination of 1 : 1 adduct radicals represent minor products.

From radical additions of tertiary amines to chlorotrifluoroethene we isolated[1–3] tertiary amines carrying 2-chloro-1,1,2-trifluoroethyl group at α-position (1 : 1 adducts) and at α,α′-positions (1 : 2 adducts) as the main products and 1 : 2 telomers as minor products. On the other hand, Podkhalyuzhin[4] reported 1 : 1 adducts and 1 : 2 telomers to be the main products obtained from the radiation-initiated addition of triethylamine (*I*) to tetrafluoroethene (*III*).

Therefore, in the present work we have focused our attention to studies of the addition of triethylamine (*I*) and 1-methylpiperidine (*II*) to tetrafluoroethene (*III*) initiated by UV or γ-^{60}Co radiation. In the former case ethene *III* was bubbled through a reaction vessel of photochemical reactor charged with the amines with simultaneous irradiation with a medium-pressure mercury discharge lamp. In the latter case, sealed ampoules containing the amine and ethene *III* in a chosen ratio were exposed to a radiation field of ^{60}Co. In the latter case the ethene *III* concentrations attained were higher than those in the former case.

EXPERIMENTAL

The temperature data were not corrected. The ^{1}H NMR and ^{19}F NMR spectra were measured in deuteriochloroform using tetramethylsilane and trichlorofluoromethane, respectively, as the internal standards, and a Varian XL-100-15 apparatus (Palo Alto) at the frequency of 100 MHz. The chemical shifts are given in ppm, the *J* spin–spin coupling constants in Hz. The mass spectra were measured with a JEOL JMS-D 300 mass spectrometer (Tokyo) with electron ionization (the electron energy of

70 eV), chromatographical inlet via a 25 m quartz capillary column with Carbowax 20M stationary phase, helium as the carrier gas. The infrared spectra (cm^{-1}) were measured in tetrachloromethane solutions using a Perkin–Elmer 325 apparatus (Bodenseewerk). The gas chromatographical analyses were performed on a Chrom 3 apparatus (Laboratorní pristroje Prague, The Czech Republic) with flame ionization detection, using poly(propanediol) sebacate on Chromosorb N-AW-DMCS as the stationary phase and nitrogen as the carrier gas. The calibration of the response of substances in the flame ionization detector was not carried out, the mixture composition being calculated as the ratio of the peak areas found by triangulation. The preparation-scale gas chromatography was performed on a Chrom 2 apparatus (Laboratorni pristroje Prague, The Czech Republic) using the same detection and stationary phase as above.

Chemicals

Tetrafluoroethene (*III*) was prepared by dehalogenation of 1,2-dibromotetrafluoroethane with zinc[5]; it was collected in a gas holder with water and introduced from there into the reaction mixture (see below) through a drying tower with molecular sieves (Potasit 4A). Triethylamine (Lachema Brno, The Czech Republic) was dried with solid sodium hydroxide and then rectified in the presence of sodium (2 g/l). The fraction with b.p. 89.0 – 89.5 °C (99.9% purity by GLC) was collected. 1-Methylpiperidine was prepared by methylation of piperidine with formaldehyde and formic acid[6]. The product was dried with solid sodium hydroxide and then rectified in the presence of sodium (4 g/l). The fraction with b.p. 106 – 107 °C (99.9% purity by GLC) was collected.

Addition of Triethylamine (*I*) and 1-Methylpiperidine (*II*) to Tetrafluoroethene (*III*)

A. The photochemically initiated additions were carried out in an immersion water-cooled photochemical reactor[7]. In all the cases the radiation source was a 125 W medium-pressure mercury discharge lamp Tesla RVK 125. Before the reaction, the apparatus was scavenged with nitrogen 15 min. The temperature of outlet water from the lamp cooling was maintained at 20 – 25 °C throughout the reaction period. Tetrafluoroethene (*III*) was introduced into the amines *I* and *II* at the rates of 0.6 l/h for 3 h and 1.0 l/h for 2 h, respectively. The amounts of educts and yields of products are presented in Tables I and II.

B. The radiation-initiated additions were carried out in nitrogen atmosphere in sealed glass ampoules of ca 180 ml volume. The way of filling was described elsewhere[1,2]; tetrafluoroethene (*III*) was condensed by cooling with liquid nitrogen. The radiation reactions were initiated in a Gammacell 220 apparatus (AEC Canada Ltd.). The source of γ photons was a ^{60}Co sample producing photons of average energy 1.25 MeV. The dose power input at the irradiation position varied in the interval of 1.29 – 0.80 Gy s^{-1}. The reaction mixtures were irradiated by doses of $3.45 \cdot 10^4$ Gy.

The amounts of educts, conversion of ethene *III*, and the main products are presented in Table I. The composition of resulting reaction mixtures is presented in Tables II and III.

Amines *IV* – *VIII*

Combined reaction mixtures from the individual additions were rectified on a 120 mm column packed with 4 mm Berl saddles, with evacuated jacket. The amine *IV* of 99.3% purity (GC) was obtained from the fraction boiling in the interval of 55 – 56 °C/2.7 kPa. The amines *Va*, *Vb*, *VI* – *VIII* were obtained by preparative GC from the fraction distilling at 60 – 92 °C/2.7 kPa.

3-Ethyl-5,5,6,6-tetrafluoro-4-methyl-3-azahexane (IV): For $C_8H_{15}F_4N$ (201.2) calculated: 47.76% C, 7.51% H, 37.77% F, 6.96% N; found: 47.98% C, 7.47% H, 37.40% F, 7.02% N. Mass spectrum, *m/z* (rel. int., %): 201 (2), 186 (8), 158 (5), 101 (3), 100 (100), 72 (3), 56 (3), 51 (2), 44 (5), 42 (4).

TABLE I
Amounts of reactants and conversion of ethene *III* to main addition products

Reaction	Amine g (mol)	CF_2=CF_2 g (mol)	Initiation	Conversion of CF_2=CF_2, %	
				1 : 1 adducts	1 : 2 adducts
	I				
1	21.0 (0.208)	7.5 (0.075)	UV	12	2
	I				
2	61.0 (0.603)	2.2 (0.022)	^{60}Co	38	46
	I				
3	61.0 (0.603)	4.3 (0.043)	^{60}Co	37	44
	I				
4	61.0 (0.603)	7.9 (0.079)	^{60}Co	37	48
	II				
5	25.0 (0.252)	8.3 (0.083)	UV	12	1
	II				
6	55.8 (0.562)	2.9 (0.029)	^{60}Co	89	9
	II				
7	55.4 (0.558)	6.8 (0.068)	^{60}Co	84	13
	II				
8	112.1 (1.130)	25.6 (0.256)	^{60}Co	83	13

TABLE II
Composition of reaction mixtures (%) in addition of amine *I* to CF_2=CF_2 (by GC)

Reaction	Proportions of amines in reaction mixture[a,b]							
	I	*IV*	*Va*	*Vb*	*VI*	*VII*	*VIII*	Nonidentified
1	91.9	6.6	0.3	0.4	–	0.8	–	–
2	92.8	3.1	1.3	1.5	0.3	0.7	0.1	0.2
3	84.4	6.4	2.7	3.1	1.0	1.4	0.4	0.6
4	75.7	10.5	4.8	5.2	1.9	0.8	0.6	0.5

[a] See Table I. [b] Determined by the method of proportions of peak areas without calibration of the FID response.

^{1}H NMR spectrum: 1.04 t, 6 H, *J*(H,H) = 7 (CH_3); 1.15 d, 3 H, *J*(H,H) = 7 (CH_3); 2.2 – 2.8 m, 4 H (CH_2NCH_2); 3.0 – 3.5 m, 1 H (CF_2CH); 6.18 ddd, 1 H, *J*(H,F) = 56, *J*(H,F) = 52, *J*(H,F) = 11 (CHF_2). ^{19}F NMR spectrum: –127.00 ddt, *J*(F,F) = 266, *J*(H,F) = 11, *J*(F,F) = 11 (CF–F); –130.23 ddd, *J*(F,F) = 266, *J*(H,F) = 24, *J*(F,F) = 11 (CF–F); –137.14 ddd, *J*(F,F) = 291, *J*(H,F) = 52, *J*(F,F) = 11 (CHF–F); –147.05 ddt, *J*(F,F) = 291, *J*(H,F) = 56, *J*(F,F) = 11 (CHF–F). IR spectrum: 994 m, 1 034 w, 1 055 wsh, 1 068 msh, 1 077 msh, 1 096 s, 1 104 ssh, 1 184 wsh, 1 198 msh, 1 298 w, 1 324 w, 1 363 wsh, 1 374 msh, 1 389 m, 1 452 w, 1 471 w, 1 712 w, 1 754 w, 2 830 m, 2 885 w, 2 940 m, 2 980 s.

4-Ethyl-1,1,2,2,6,6,7,7-octafluoro-3,5-dimethyl-4-azaheptane (Va): Mass spectrum, *m*/*z* (rel. int., %): 301 (1), 300 (1), 286 (6), 201 (4), 200 (100), 172 (9), 170 (2), 158 (2), 109 (2), 71 (1), 70 (2), 56 (4), 51 (2), 44 (3), 42 (3). ^{1}H NMR spectrum: 1.06 t, 3 H, *J*(H,H) = 7 (CH_3); 1.28 d, 6 H, *J*(H,H) = 7 (CH_3); 2.4 – 3.0 m, 2 H (NCH_2); 3.1 – 3.7 m, 2 H (CF_2CH); 6.01 tt, 2 H, *J*(H,F) = 54, *J*(H,F) = 5 (CHF_2). ^{19}F NMR spectrum: –125.76 m, 4 F (2 × CF_2); –137.14 ddm, 2 F, *J*(F,F) = 298, *J*(H,F) = 54 (CHF–F); –141.25 ddm, 2 F, *J*(F,F) = 298, *J*(H,F) = 54 (CHF–F). IR spectrum: 918 w, 1 036 m, 1 098 s, 1 113 ssh, 1 133 ssh, 1 166 w, 1 199 msh, 1 303 w, 1 318 s, 1 364 w, 1 391 m, 1 430 wsh, 1 457 wsh, 1 466 w, 2 850 w, 2 945 w, 2 945 wsh, 2 995 msh, 3 005 m.

4-Ethyl-1,1,2,2,6,6,7,7-octafluoro-3,5-dimethyl-4-azaheptane (Vb): Mass spectrum, *m*/*z* (rel. int., %): 301 (1), 300 (1), 286 (9), 201 (3), 200 (100), 172 (10), 170 (3), 158 (2), 109 (2), 71 (1), 70 (2), 56 (4), 51 (1), 44 (3), 42 (3). ^{1}H NMR spectrum: 1.04 t, 3 H, *J*(H,H) = 7 (CH_3); 1.28 d, 6 H, *J*(H,H) = 7 (CH_3); 2.82 qa, 2 H, *J*(H,H) = 7 (NCH_2); 3.2 – 3.8 m, 2 H (CF_2CH); 5.89 tt, 2 H, *J*(H,F) = 54, *J*(H,F) = 5 (CHF_2). ^{19}F NMR spectrum: –123.52 ddm, 2 F (*J*(F,F) = 272, *J*(H,F) = 14 (CF–F); –125.39 ddm, 2 F, *J*(F,F) = 272, *J*(H,F) = 12 (CF–F); –136.72 ddd, 2 F, *J*(F,F) = 300, *J*(H,F) = 54, *J*(F,F) = 5 (CHF–F); –139.27 ddt, 2 F, *J*(F,F) = 300, *J*(H,F) = 54, *J*(F,F) = 5 (CHF–F). IR spectrum: 918 w, 1 036 m, 1 098 s, 1 113 ssh, 1 133 ssh, 1 166 w, 1 199 msh, 1 303 w, 1 318 s, 1 364 w, 1 391 m, 1 430 wsh, 1 457 wsh, 1 466 w, 2 850 w, 2 945 w, 2 945 wsh, 2 995 msh, 3 005 m.

3-Ethyl-5,5,6,6,7,7,8,8-octafluoro-4-methyl-3-azaoctane (VI): Mass spectrum, *m*/*z* (rel. int., %): 301 (2), 300 (2), 286 (9), 272 (2), 258 (5), 101 (2), 100 (100), 72 (2), 56 (3), 51 (2), 44 (4), 42 (4). ^{1}H NMR spectrum: 1.01 t, 6 H, *J*(H,H) = 7 (CH_3); 1.20 d, 3 H, *J*(H,H) = 7 (CH_3); 2.3 – 2.9 m, 4 H (CH_2NCH_2); 3.2 – 3.7 m, 1 H (CF_2CHN); 6.03 tt, 1 H, *J*(H,F) = 52, *J*(H,F) = 5 (CHF_2). ^{19}F NMR spectrum: –113.54 dm, 1 F, *J*(F,F) = 280 (C(5)F–F); –121.17 dm, 1 F, *J*(F,F) = 280 (C(5)F–F);

TABLE III
Composition of reaction mixtures (%) in addition of amine *II* to CF_2=CF_2 (by GC)

Reaction	Proportions of amines in reaction mixture[a,b]						
	II	*IX*	*X*	*XI*	*XII*	*XIII*	Nonidentified
5	92.1	0.9	5.7	0.3	<0.1	–	0.9
6	91.5	1.0	0.3	0.5	0.1	0.1	0.3
7	81.3	2.6	1.0	1.6	0.3	0.3	0.6
8	68.5	4.1	1.9	2.9	0.4	0.9	0.2

[a] See Table I. [b] Determined by the method of proportions of peak areas without calibration of the FID response.

–121.65 dm, 1 F, *J*(F,F) = 298 (C(6)F–F); –125.44 dm, 1 F, *J*(F,F) = 298 (C(6)F–F); –130.8 m, 2 F (C(7)F2); –137.76 dm, 2 F, *J*(H,F) = 52 (CHF_2).

3,8-Diethyl-5,5,6,6,10,10,11,11-octafluoro-4,7,9-trimethyl-3,8-diazaundecane (VII). For $C_{16}H_{28}F_8N_2$ (400.4) calculated: 48.00% C, 7.05% H, 37.96% F, 7.00% N; found: 48.95% C, 7.40% H, 37.33% F, 6.99% N. In GC/MS compound *VII* was separated into two peaks with the following mass spectra, *m*/*z* (rel. int., %): 399 (0.2), 385 (0.1), 360 (1), 328 (2), 314 (3), 101 (67), 100 (100), 72 (2), 70 (2), 56 (3), and 399 (0.2), 385 (0.1), 360 (2), 328 (2), 314 (4), 101 (4), 100 (100), 72 (2), 70 (2), 56 (2). ^{1}H NMR spectrum: 1.02 t, *J*(H,H) = 7 (CH_3); 1.04 t, *J*(H,H) = 7 (CH_3); 1.18 d, 9 H, *J*(H,H) = 7 (CH_3); 2.2 – 2.9 m, 6 H (3 × NCH_2); 3.0 – 3.9 m, 3 H (3 × NCH); 6.21 ddd, 1 H, *J*(H,F) = 56, *J*(H,F) = 52, *J*(H,F) = 11 (CHF_2). ^{19}F NMR spectrum cannot be interpreted because amine *VII* represents a mixture of 4 diastereoisomeric racemates. IR spectrum: 903 wsh, 907 w, 917 wsh, 1 029 msh, 1 047 ssh, 1 066 ssh, 1 074 ssh, 1 092 s, 1 101 ssh, 1 175 m, 1 188 msh, 1 267 wsh, 1 299 w, 1 360 wsh, 1 377 msh, 1 386 m, 1 431 wsh, 1 451 m, 1 468 m, 2 835 m, 2 885 m, 2 945 m, 2 985 s.

1,1,2,2,6,6,7,7-Octafluoro-3,5-dimethyl-4-(2,2,3,3-tetrafluoro-1-methylpropyl)-4-azaheptane (VIII). Mass spectrum, *m*/*z* (rel. int., %): 401 (0.5), 400 (0.2), 386 (0.6), 382 (0.6), 301 (5), 300 (100), 258 (2), 172 (8), 109 (3), 70 (4), 51 (3), 44 (2), 42 (2).

Amines *IX – XIII*

Combined reaction mixtures from individual addition reactions were submitted to rectification. Amines *IX* and *X* were obtained by preparation-scale GC from the fraction distilling in the interval of 55 – 62 °C/2.0 kPa. Amines *XI – XIII* were obtained similarly from the fraction distilling in the interval of 51 – 60 °C/0.08 kPa.

1-(2,2,3,3-Tetrafluoropropyl)piperidine (IX). Mass spectrum, *m*/*z* (rel. int., %): 199 (4), 198 (4), 142 (2), 99 (5), 98 (100), 70 (2), 69 (3), 55 (7), 51 (2), 44 (2), 43 (9), 42 (6). ^{1}H NMR spectrum: 1.3 – 1.7 m, 6 H ((CH_2)$_3$); 2.54 t, 4 H, *J*(H,H) = 5 (CH_2NCH_2); 2.81 t, 2 H, *J*(H,F) = 14 (NCH_2CF_2); 5.99 tt, 1 H, *J*(H,F) = 54, *J*(H,F) = 5 (CHF_2). ^{19}F NMR spectrum: –121.65 ttd, 2 F, *J*(H,F) = 14, *J*(F,F) = *J*(H,F) = 5 (CF_2); –141.04 dt, 2 F, *J*(H,F) = 54, *J*(F,F) = 5 (HCF_2). IR spectrum: 1 007 wsh, 1 039 w, 1 054 m, 1 087 m, 1 106 s, 1 113 s, 1 124 s, 1 160 m, 1 182 m, 1 235 wsh, 1 306 w, 1 440 w, 1 453 w, 1 473 w, 1 485 wsh, 1 500 – 1 570 w, 2 200 – 2 400 w, 2 450 wsh, 2 485 m, 2 510 msh, 2 570 m, 2 625 m, 2 790 w, 2 885 w, 2 950 w.

1-Methyl-2-(1,1,2,2-tetrafluoroethyl)piperidine (X). Mass spectrum, *m*/*z* (rel. int., %): 199 (3), 198 (2), 99 (5), 98 (100), 97 (2), 96 (2), 70 (10), 55 (5), 51 (2), 44 (2), 43 (10), 42 (2). ^{1}H NMR spectrum: 1.3 – 1.9 m, 6 H ((CH_2)$_3$); 2.3 – 3.0 m ($CHNCH_2$); 2.41 s (NCH_3); 5.97 tt, 1 H, *J*(H,F) = 54, *J*(H,F) = 5 (CHF_2). ^{19}F NMR spectrum: –118.28 ddt, 1 F, *J*(F,F) = 271, *J*(H,F) = 13, *J*(F,F) = 7 (CF–F); –121.93 ddm, 1 F, *J*(F,F) = 271, *J*(H,F) = 18 (CF–F); –138.76 ddm, 1 F, *J*(F,F) = 294, *J*(H,F) = 54, *J*(F,F) = 7 (CHF–F); –140.10 ddt, 1 F, *J*(F,F) = 294, *J*(H,F) = 54, *J*(F,F) = 7 (CHF–F). IR spectrum: 919 w, 949 w, 959 wsh, 988 m, 1 029 s, 1 046 s, 1 058 msh, 1 063 m, 1 077 ssh, 1 082 s, 1 093 ssh, 1 108 s, 1 126 s, 1 150 s, 1 156 msh, 1 173 s, 1 181 msh, 1 211 m, 1 231 msh, 1 238 m, 1 261 m, 1 277 m, 1 308 m, 1 318 w, 1 332 wsh, 1 340 w, 1 348 wsh, 1 359 w, 1 379 m, 1 399 w, 1 408 wsh, 1 431 w, 1 442 m, 1 465 msh, 2 300 – 2 400 w, 2 455 wsh, 2 480 w, 2 510 w, 2 570 w, 2 595 w, 2 625 w, 2 650 wsh, 2 705 wsh, 2 725 w, 2 800 m, 2 820 msh, 2 870 m, 2 905 msh, 2 955 s, 3 020 m.

2-(1,1,2,2-Tetrafluoroethyl)-1-(2,2,3,3-tetrafluoropropyl)piperidine (XI). Mass spectrum, *m*/*z* (rel. int., %): 299 (0.5), 298 (0.5), 280 (2), 199 (5), 198 (100), 170 (4), 144 (2), 142 (5), 67 (2), 55 (10), 51 (3), 43 (2), 42 (3). ^{1}H NMR spectrum: 1.4 – 1.9 m, 6 H ((CH_2)$_3$); 2.5 – 3.4 m, 5H ($CHN(CH_2)_2$); 5.84 tt, 1 H, *J*(H,F) = 54, *J*(H,F) = 5 (CHF_2-(2)); 5.98 tt, 1H, *J*(H,F) = 54, *J*(H,F) = 5 (CHF_2-(1)). ^{19}F NMR spectrum: –119.87 dm, 2 F, *J*(H,F) = 14 ($CHCF_2$); –122.84 tm, 2 F, *J*(H,F) = 14 (CH_2CF_2); –137.92 ddm, 1 F, *J*(F,F) = 298, *J*(H,F) = 54 (CHF–F(2)); –140.02 ddm, 1 F, *J*(F,F) =

298, *J*(H,F) = 54 (CHF–F(2)); –136.52 ddm, 1 F, *J*(F,F) = 293, *J*(H,F) = 54 (CHF–F(1)); –142.66 ddt, 1 F, *J*(F,F) = 293, *J*(H,F) = 54, *J*(F,F) = 5 (CHF–F(1)). IR spectrum: 912 w, 978 m, 1 011 w, 1 030 msh, 1 040 s, 1 056 s, 1 087 ssh, 1 103 s, 1 110 ssh, 1 146 msh, 1 163 m, 1 175 msh, 1 183 m, 1 207 m, 1 273 w, 1 293 w, 1 308 w, 1 326 w, 1 348 w, 1 362 w, 1 394 w, 1 407 wsh, 1 437 w, 1 448 w, 1 458 w, 1 470 wsh, 1 484 wsh, 2 300 – 2 400 w, 2 465 wsh, 2 490 w, 2 520 w, 2 580 w, 2 600 w, 2 630 wsh, 2 870 w, 2 890 w, 2 930 msh, 2 960 m, 3 010 m.

1-Methyl-2,6-bis(1,1,2,2-tetrafluoroethyl)piperidine (XII). Mass spectrum, *m*/*z* (rel. int., %): 299 (0.4), 280 (2), 199 (4), 198 (100), 97 (7), 96 (2), 82 (3), 55 (6), 43 (6). ^{1}H NMR spectrum: 1.5 – 2.1 m, 6 H ($(CH_2)_3$); 3.0 – 3.6 m, 2 H (CHNCH); 2.38 s, 3 H (NCH_3); 5.89 tt, 2 H, *J*(H,F) = 54, *J*(H,F) = 5 (CHF_2). ^{19}F NMR spectrum: –123.55 m, 4 F (CF_2); –136,32 ddm, 2 F, *J*(F,F) = 300, *J*(H,F) = 54 (CHCF–F); –143.35 ddt, 2 F, *J*(F,F) = 300, *J*(H,F) = 54, *J*(F,F) = 12 (CHCF–F). IR spectrum: 927 w, 932 wsh, 958 w, 1 030 s, 1 038 s, 1 048 s, 1 056 m, 1 084 msh, 1 101 ssh, 1 114 s, 1 120 ssh, 1 148 m, 1 169 s, 1 182 s, 1 208 m, 1 277 m, 1 306 m, 1 311 wsh, 1 342 w, 1 399 w, 1 419 w, 1 437 wsh, 1 451 m, 1 469 w, 1 653 wsh, 1 672 m, 1 690 wsh, 2 280 – 2 400 w, 2 410 wsh, 2 485 w, 2 510 wsh, 2 580 wsh, 2 600 w, 2 630 w, 2 840 w, 2 870 w, 2 925 wsh, 2 965 m, 3 010 wsh.

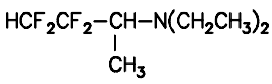
1-Methyl-2-(1,1,2,2,3,3,4,4-octafluorobutyl)piperidine (XIII). Mass spectrum, *m*/*z* (rel. int., %): 298 (1), 99 (3), 98 (100), 70 (8), 55 (4), 43 (7). ^{1}H NMR spectrum: 1.4 – 1.9 m, 6 H ($(CH_2)_3$); 2.4 – 3.2 m ($CHNCH_2$); 2.50 s (NCH_3); 6.03 tt, 1 H, *J*(H,F) = 52, *J*(H,F) = 5 (CHF_2). ^{19}F NMR spectrum: –111.92 dm, 1 F, *J*(F,F) = 278 (C(1)F–F); –113.52 dm, 1 F, *J*(F,F) = 278 (C(1)F–F); –124.6 m, 2 F ($C(3)F_2$); –131.1 m, 2 F ($C(2)F_2$); –137.97 dm, 2 F, *J*(H,F) = 52 (CHF_2). IR spectrum: 904 wsh, 917 w, 937 w, 948 w, 987 w, 1 006 w, 1 024 msh, 1 034 m, 1 057 msh, 1 070 msh, 1 076 s, 1 096 s, 1 120 ssh, 1 129 s, 1 143 s, 1 168 s, 1 174 ssh, 1 198 ssh, 1 228 m, 1 265 msh, 1 274 m, 1 291 msh, 1 314 wsh, 1 323 wsh, 1 334 w, 1 359 w, 1 386 w, 1 401 m, 1 430 w, 1 443 m, 1 458 m, 1 469 m, 1 485 wsh, 2 280 – 2 400 w, 2 480 w, 2 510 w, 2 570 w, 2 595 w, 2 620 w, 2 670 wsh, 2 710 w, 2 795 m, 2 820 m, 2 865 m, 2 885 m, 2 905 msh, 2 950 s, 3 010 wsh.

RESULTS AND DISCUSSION

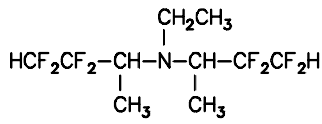
From the reaction mixture after the addition of triethylamine (*I*) to tetrafluoroethene (*III*) it was possible to isolate the 1 : 1 adduct 3-ethyl-5,5,6,6-tetrafluoro-4-methyl-3-azahexane (*IV*), the 1 : 2 adduct 4-ethyl-1,1,2,2,6,6,7,7-octafluoro-3,5-dimethyl-4-azaheptane (*V*) (both the *meso*-form *Va* and racemate *Vb* were isolated), the 1 : 2 telomer 3-ethyl-5,5,6,6,7,7,8,8-octafluoro-4-methyl-3-azaoctane (*VI*), and 3,8-diethyl-5,5,6,6,10,10,11,11-octafluoro-4,7,9-trimethyl-3,8-diazaundecane (*VII*). Besides the compounds *IV* – *VII* also the tritopic 1 : 3 adduct 1,1,2,2,6,6,7,7-octafluoro-3,5-dimethyl-4-(2,2,3,3-tetrafluoro-1-methylpropyl)-4-azaheptane (*VIII*) was detected in the reaction mixture by means of GC/MS.

From among the addition products of 1-methylpiperidine (*II*) and tetrafluoroethene (*III*) we isolated both 1 : 1 adducts, i.e. 1-(2,2,3,3-tetrafluoropropopyl)piperidine (*IX*) and 1-methyl-2-(1,1,2,2-tetrafluoroethyl)piperidine (*X*), both 1 : 2 adducts, i.e. 2-(1,1,2,2-tetrafluoroethyl)-1-(2,2,3,3-tetrafluoropropyl)piperidine (*XI*) and 1-methyl-2,6-bis(1,1,2,2-tetrafluoroethyl)piperidine (*XII*), and the 1 : 2 telomer 1-methyl-2-(1,1,2,2,3,3,4,4-octafluorobutyl)piperidine (*XIII*).

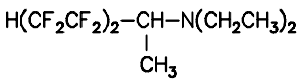
The formation of all the reaction products obtained in the addition reaction of triethylamine (*I*) and ethene *III* can be explained by conversions of 1 : 1 adduct radical *XV* produced by the addition of solvent radical *XIV* to alkene *III*.



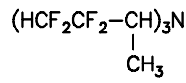
IV



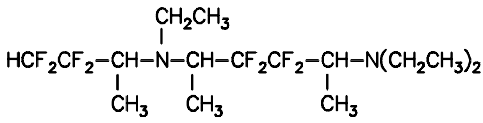
V



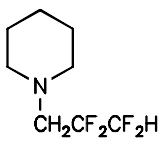
VI



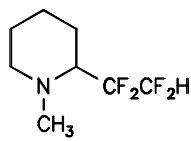
VIII



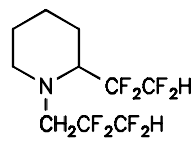
VII



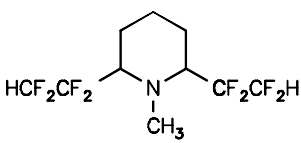
IX



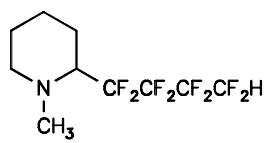
X



XI



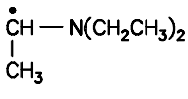
XII



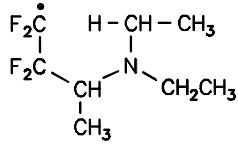
XIII

The chain transfer from radical *XV* to amine *I* produces the 1 : 1 adduct *IV* and a new solvent radical *XIV*. The relatively higher proportion of 1 : 2 adduct as compared with 1 : 2 telomer indicates that the radical *XV* prefers the intramolecular 1,5-shift of hydrogen[8] (giving radical *XVI*) to its addition to a further molecule of ethene *III* (giving the 1 : 2 telomer *VI*). The addition of radical *XVI* to ethene *III* produces the 1 : 2 adduct radical *XVII* which then gives the 1 : 2 adduct *V* by the chain transfer to amine *I*. The

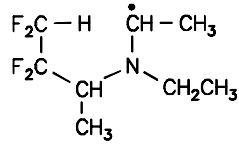
presence of 1 : 3 adduct *VIII* indicates that also the radical *XVII* rearranges via intramolecular 1,5-shift of hydrogen atom. The radical *XVIII* thus formed adds to ethene *III* to give the 1 : 3 adduct radical *XIX* which forms the 1 : 3 adduct *VIII* via a chain transfer to amine *I*.



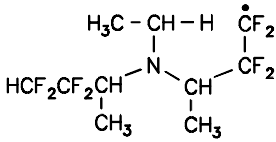
XIV



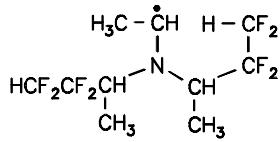
XV



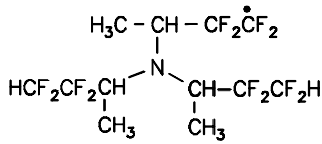
XVI



XVII



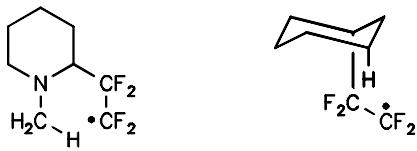
XVIII



XIX

The preference of intramolecular 1,5-shift of hydrogen in radical *XV* is due to the fact that this radical can assume a conformation suitable for the rearrangement and also to its lowered reactivity in oligomerization reactions: trialkylamines are used as inhibitors of polymerization of fluoroalkenes[9]. The fact that Podkhalyuzhin[4] only reported the formation of 1 : 2 telomer could be explained by his using different reaction conditions: he performed the reaction with a 6.5 mol excess of ethene *III*, i.e. the telomerization could dominate. It is, however, more likely that he incorrectly interpreted the ^{1}H NMR spectra. In the 1 : 2 telomer *VI*, both methylene groups appear as a single multiplet with the shift of 2.62 δ. On the other hand, the two diastereoisomers of 1 : 2 adduct *Va* and *Vb* differ in the chemical shift of methylene protons in ethyl group (the multiplet 2.70 δ and quartet 2.99 δ, respectively). Two signals of methylene groups with the difference of 0.14 δ in chemical shifts are also reported by Podkhalyuzhin[4], but they are

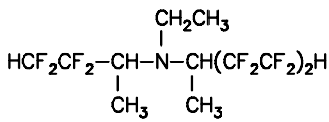
assigned to the 1 : 2 telomer *VI*. Amine *VII* can be formed by recombination of 1 : 2 adduct radical *XVII* with solvent radical *XIV* and/or by recombination of 1 : 1 adduct radical *XV* with radical *XVI*. Similarly it is possible to explain the formation of fluoroalkylamines in the addition of 1-methylpiperidine (*II*) to ethene *III*. The presence of 1 : 2 adducts *XI* and *XII* indicates the fact that in the 1 : 1 adduct radical *XX* there takes place a 1,5-shift of hydrogen both from methyl group and from 6-position of piperidine nucleus.



XX

The results of experiments are summarized in Tables I – III. The fact that it was impossible to detect the presence of any minor products (1 : 2 telomers *VI* and *XIII* and 1 : 3 adduct *VIII*) in the photochemically initiated addition reactions is probably caused by the low concentration of ethene *III* attainable in the flow arrangement of the experiment.

The structures of products were confirmed by ^{1}H and ^{19}F NMR spectra, IR spectra and mass spectra. The ^{1}H NMR spectrum of diamine *VII* indicates that the fluoroalkyl groups are attached to α carbon atoms with regard to nitrogen (the doublets with chemical shift 1.18 δ and coupling constant 7 Hz correspond to the methyl protons in the grouping $CF_2CH(CH_3)N$) and that the compound contains only one difluoromethyl group. The gas chromatography on capillary column separated compound *VII* into two pairs of diastereoisomers with similar mass spectra. The relative mass 100 of the basic ion in spectrum indicates the presence of $CH_3CHN(CH_2CH_3)_2$ grouping. The molecular ion (*m*/*z* 400) was not observed in the spectrum but the fragments [M – 1] and [M – 15] produced therefrom by splitting off of hydrogen and methyl radicals, respectively, (rel. mass 399 and 385, respectively) were found.



XXI

The structure of tritopic 1 : 3 adduct *VIII* has only been derived from the mass spectrum. The relative mass of the molecular ion is 401. Splitting off of methyl and tetrafluoroethyl radicals ([M − 15] and [M − 101], respectively) produces ions with relative masses of 386 and 300, respectively, the latter being the basic ion of the spectrum. As it was impossible to find the ion with *m*/*z* 200 in the spectrum, the structure of isomeric amine *XXI* (formed by telomerization of 1 : 2 adduct radical *XVII*) can be excluded.

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