RADICAL ADDITIONS OF TERTIARY AMINES TO CHLOROTRIFLUOROETHYLENE

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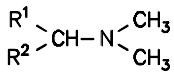
Radical addition of ethyldimethylamine, cyclohexyldimethylamine, 1-methylpyrrolidine, 1-methylpiperidine, 1-methylperhydroazepine and 1-methylmorpholine to chlorotrifluoroethylene afforded 1 : 1 and 1 : 2 adducts containing 2-chloro-1,1,2-trifluoroethyl groups in the α- or α,α′-positions. Further reaction products were 1 : 2 telomers and secondary products arising by reduction of the chlorine atom in CHFCl groups by tertiary amines. The reaction course and mass and NMR spectra of the products are discussed.

In our preceding communications of this series we described the addition of isopropyldimethylamine[1], trimethylamine and triethylamine[2] to chlorotrifluoroethylene, initiated by UV and ^{60}Co-γ radiation. The principal reaction products are tertiary amines containing a 2-chloro-1,1,2-trifluoroethyl group in α- or α,α′-positions to the nitrogen atom. It was of interest to study the chemoselectivity of addition of ethyldimethylamine (*I*), cyclohexyldimethylamine (*II*), 1-methylpyrrolidine (*IIIa*), 1-methylpiperidine (*IIIb*), 1-methylperhydroazepine (*IIIc*) and 1-methylmorpholine (*IIId*) to chlorotrifluoroethylene, initiated by UV, and in the case of 1-methylpiperidine (*IIIb*) also by ^{60}Co radiation.

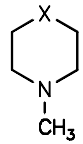
In the addition of ethyldimethylamine (*I*) both the methyl and ethyl groups are alkylated. Whereas both the 1 : 1 adducts, i.e. 6-chloro-5,5,6-trifluoro-3-methyl-3-azahexane (*IV*) and 5-chloro-4,4,5-trifluoro-2,3-dimethyl-2-azapentane (*V*), arise in an approximately 1 : 1 ratio, the principal 1 : 2 adduct is 1,7-dichloro-1,2,2,6,6,7-hexafluoro-3,4-dimethyl-4-azaheptane (*VI*) which is accompanied by about 3% of 1,7-dichloro-4-ethyl-1,2,2,6,6,7-hexafluoro-4-azaheptane (*VII*). Amines *IV*, *V* and *VI* were isolated from the individual distillation fractions by preparative gas-liquid chromatography (GLC). The presence of amine *VII* was indicated only by signals of ethyl group in the ^{1}H NMR spectrum of amine *VI*.

Similarly to isopropyldimethylamine[1], cyclohexyldimethylamine (*II*) is chlorotrifluoroethylated on the methyl group under formation of 5-chloro-2-cyclohexyl-4,4,5-



I, $R^1 = H$; $R^2 = CH_3$

II, R^1, $R^2 = (CH_2)_5$

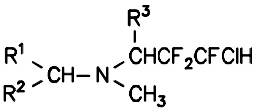


IIIa, X = $(CH_2)_0$

IIIb, X = CH_2

IIIc, X = $(CH_2)_2$

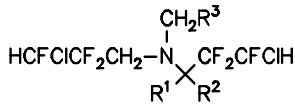
IIId, X = O



IV, $R^1 = CH_3$; $R^2 = R^3 = H$

V, $R^1 = R^2 = H$; $R^3 = CH_3$

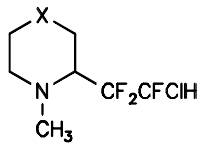
VIII, R^1, $R^2 = (CH_2)_5$; $R^3 = H$



VI, $R^1 = CH_3$; $R^2 = R^3 = H$

VII, $R^1 = R^2 = H$; $R^3 = CH_3$

IX, $R^1 = R^2 = (CH_2)_5$; $R^3 = H$

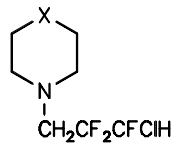


Xa, X = $(CH_2)_0$

Xb, X = CH_2

Xc, X = $(CH_2)_2$

Xd, X = O

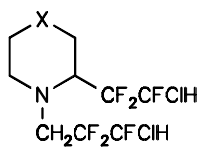


XIa, X = $(CH_2)_0$

XIb, X = CH_2

XIc, X = $(CH_2)_2$

XId, X = O

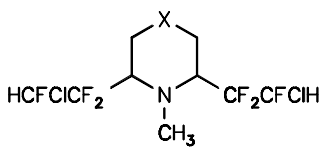


XIIa, X = $(CH_2)_0$

XIIb, X = CH_2

XIIc, X = $(CH_2)_2$

XIId, X = O



XIIIb, X = CH_2

XIIId, X = O

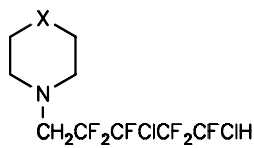
trifluoro-2-azapentane (*VIII*); as 1 : 2 adduct we isolated 1,7-dichloro-1,2,2,6,6,7-hexafluoro-4-methyl-3,3-pentamethylene-4-azaheptane (*IX*).

Addition of cyclic *N*-methylamines *IIIa – IIId* results predominantly in chlorotrifluoroethylation in the α-position of the ring under formation of the corresponding 2-(chlorotrifluoroethyl)perhydro heterocycles, i.e. 2-(2-chloro-1,1,2-trifluoroethyl)-1-methylpyrrolidine (*Xa*), -piperidine (*Xb*), -perhydroazepine (*Xc*) and -morpholine (*Xd*).

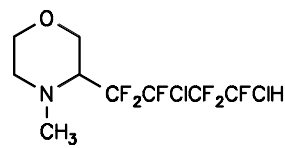
Hydrogen atoms of the *N*-methyl group are less reactive and therefore the yields of the corresponding 1-(chlorotrifluoropropyl)amines (1-(3-chloro-2,2,3-trifluoropropyl)-pyrrolidine (*XIa*), -piperidine (*XIb*), -perhydroazepine (*XIc*) and -morpholine (*XId*)) are 3 – 10 times lower (Table I).

In the 1 : 2 adducts, the chlorotrifluoroethyl groups are located on the *N*-methyl carbon atom and in the α-position of the ring, the products being 2-(2-chloro-1,1,2-trifluoroethyl)-1-(3-chloro-2,2,3-trifluoropropyl)pyrrolidine (*XIIa*), -piperidine (*XIIb*), -perhydroazepine (*XIIc*) and -morpholine (*XIId*). Only in the case of 1-methylpiperidine (*IIIb*) and 1-methylmorpholine (*IIId*) we detected further ditopic derivatives: 2,6-bis-(2-chloro-1,1,2-trifluoroethyl)-1-methylpiperidine (*XIIIb*) and -morpholine (*XIIId*), respectively.

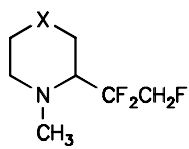
As primary products in the addition of amines *IIIa – IIId* we also isolated the 1 : 2 telomers, i.e. 1-(3,5-dichloro-2,2,3,4,4,5-hexafluoropentyl)pyrrolidine (*XIVa*), -perhydroazepine (*XIVc*), -morpholine (*XIVd*) and 2-(2,4-dichloro-1,1,2,3,3,4-hexafluorobutyl)-



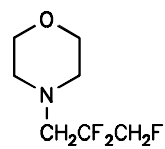
XIVa, X = $(CH_2)_0$
XIVc, X = $(CH_2)_2$
XIVd, X = O



XV



XVIa, X = $(CH_2)_0$
XVIc, X = $(CH_2)_2$
XVId, X = O



XVII

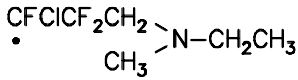
1-methylmorpholine (*XV*). All these compounds were formed in only minor quantities and their yields did not exceed 1% (Table I).

The addition of amines *IIIa – IIId* gave further minor products: 1-methyl-2-(1,1,2-trifluoroethyl)pyrrolidine (*XVIa*), -perhydroazepine (*XVIc*), -morpholine (*XVId*) and 1-(2,2,3-trifluoropropyl)morpholine (*XVII*). Amines *XVI* and *XVII* arise as secondary products by photochemically initiated reduction of the chlorine atoms in groups CHClF (refs[2,3]) of adducts *X* and *XI* with the corresponding tertiary amine.

We assume that all the corresponding minor products, i.e. 1 : 2 telomers and reduction products, are present also in the reaction mixtures arising from addition of amines *I*, *II* and *IIIb*, similarly as in the case of additions of trimethylamine and triethylamine[2], however, in our present study they were not identified closer and in Table I they are included among the unidentified products.

The formation of primary addition products (1 : 1 and 1 : 2 adducts and 1 : 2 telomers) is explained by a radical chain mechanism[2] (Scheme 1). On irradiation, the C–H bond in the tertiary amine is homolytically cleaved. The arising solvent radical is added to the difluoromethylene group of the alkene and affords 1 : 1 adduct radical. Reactions of 1 : 1 radicals can explain the formation of all the primary reaction products. Their addition to further alkene molecule leads to 1 : 2 telomer radicals. In a suitable conformational arrangement of 1 : 1 adduct radicals, 1,5-transfer[4] of the α′-hydrogen gives rise to isomeric 1 : 1 adduct radicals which on addition to another alkene molecule afford 1 : 2 adduct radicals. Transfer of hydrogen from the solvent (tertiary amine) to 1 : 1 and 1 : 2 adduct radicals and 1 : 2 telomer radicals gives rise to the corresponding 1 : 1 and 1 : 2 adducts, 1 : 2 telomers and new solvent radicals.

In the reaction of isopropyldimethylamine[1] and cyclohexyldimethylamine (*II*), the 1 : 1 adducts arise exclusively by chlorotrifluoroethylation of the methyl group. The higher reactivity of the methine group in isopropyl or cyclohexyl groups is manifested only in the formation of 1 : 2 adducts; the 1,5-hydrogen transfer in the 1 : 1 adduct radical starts exclusively from the methine group. Ethyldimethylamine (*I*) is chlorotrifluoroethylated both on the methyl and ethyl groups. Also the methylene group in amine *I* is more reactive only in the formation of 1 : 2 adducts; in the 1 : 1 adduct radical *XVIII* the hydrogen atom is transferred predominantly from this group. The product, arising by transfer from the methyl group, is formed only in negligible amount.



XVIII

The higher relative amount of 2-(chlorotrifluoroethyl)amines *Xa – Xd* than of 1-(chlorotrifluoropropyl)amines *XIa – XId* in the chlorotrifluoroethylation of cyclic

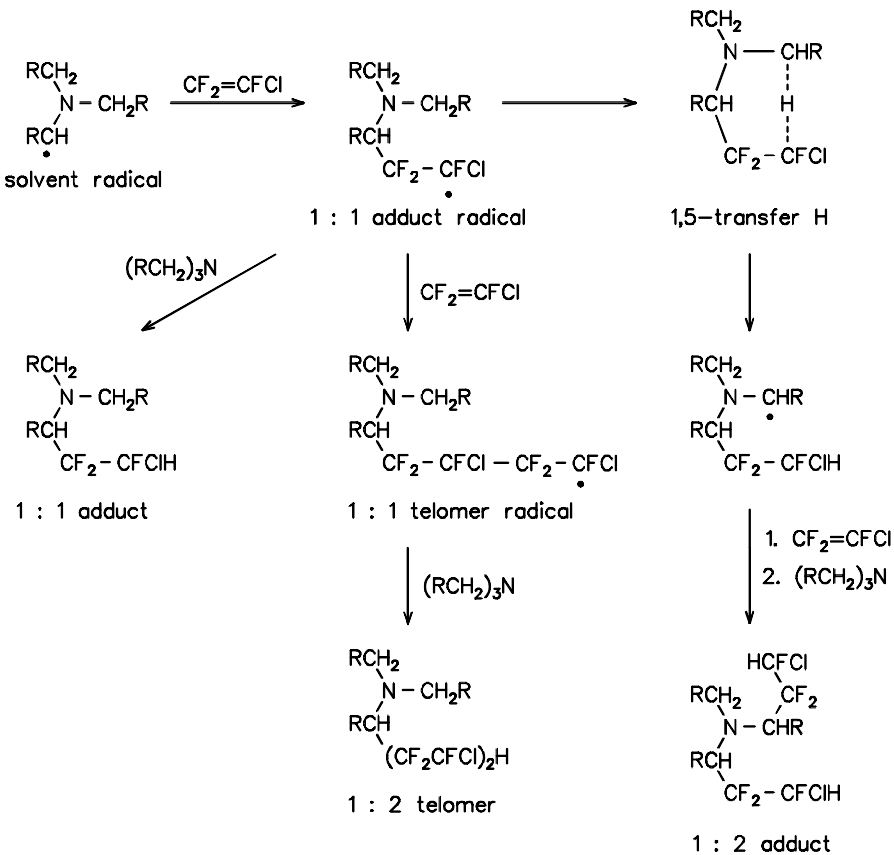
TABLE I
Reaction conditions and yields in addition reactions of amines *I* – *III* to CF_2=CFCl

Amine g (mol)	CF_2=CFCl g (mol)	Reaction time h	Yields of products, g (%)			Reduction products, g	Unidentified products, g
			1 : 1 adducts	1 : 2 adducts	1 : 2 telomers		
I			*IV*	*VI*			
106.5 (1.456)	51.7 (0.444)	7	33.0 (39.2)	13.1 (19.3)	–	–	8.0
			V	*VII*			
			33.0 (39.2)	0.4 (0.6)			
II			*VIII*	*IX*			
118.3 (0.932)	19.1 (0.164)	12	9.6 (24.1)	4.5 (15.1)	–	–	0.8
IIIa			*Xa*	*XIIa*	*XIVa*	*XVIa*	
101.1 (1.186)	34.0 (0.292)	30	32.1 (54.5)	2.8 (6.0)	0.3 (0.6)	0.3 (0.7)	0.2
			XIa				
			2.6 (4.4)				
IIIb			*Xb*	*XIIb*			
142.1 (1.432)	24.7 (0.212)	8	17.2 (37.6)	7.3 (20.6)	–	–	0.4
			*XI*b	*XIIIb*			
			5.3 (11.5)	0.2 (0.6)			
IIIb		portion	*Xb*	*XIIb*			
127.3 (1.283)	23.0 (0.198)	3.45 . 10^4 Gy	21.2 (49.7)	10.6 (32.2)	–	–	0.8
			XIb	*XIIIb*			
			5.4 (12.6)	0.3 (1.0)			
IIIc			*Xc*	*XIIc*	*XIVc*	*XVIc*	
101.0 (0.892)	44.0 (0.378)	30	45.7 (52.7)	6.8 (10.4)	0.2 (0.3)	0.4 (0.6)	0.9
			XIc				
			8.8 (10.1)				
IIId			*Xd*	*XIId*	*XIVd*	*XVId*	
136.0 (1.345)	32.6 (0.280)	30	9.3 (15.3)	2.6 (5.6)	0.3 (0.6)	0.7 (1.4)	0.4
			XId	*XIIId*	*XV*	*XVII*	
			5.1 (8.3)	0.9 (1.9)	0.4 (0.8)	0.3 (0.6)	

amines *IIIa – IIId* indicates that hydrogen atoms of the α-methylene are more reactive than those of the *N*-methyl group.

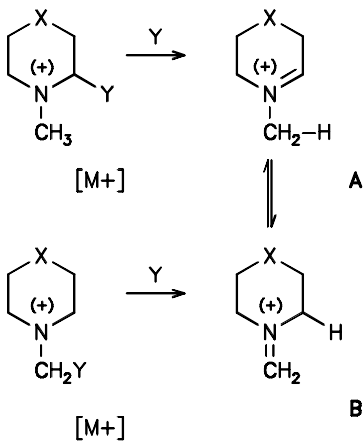
In additions of cyclic amines *IIIa – IIId* to chlorotrifluoroethylene, the formation of 1,2-adducts with chlorotrifluoromethyl groups in both the α- and α′-positions was observed only in the case of 1-methylpiperidine (*IIIb*) and 1-methylmorpholine (*IIId*). Apparently, only a six-membered ring enables the 1 : 1 adduct radical to assume a conformation suitable for 1,5-hydrogen transfer from position 6 to the chlorotrifluoroethyl group with unpaired electron in position 2.

Theoretically, in the addition to chlorotrifluoroethylene, 1-methylmorpholine (*IIId*) can also react as an ether, i.e., one could assume an alkylation in α-positions relative to the oxygen atom[5,6]. However, no corresponding products were found in the reaction mixture.



SCHEME 1

The structure of the products was confirmed by ^{1}H NMR and mass spectra. The presence of signals due to the CHClF group in the ^{1}H NMR spectra (doublets of doublets of doublets, or doublets of multiplets with coupling constants 45 – 50 Hz) proves regioselectivity of the addition to chlorotrifluoroethylene. Gas chromatography–mass spectra of the 1 : 1 adducts *Xa – Xd* and the 1 : 2 adducts *XIIa – XIId*, *XIIIb* and *XIIId*, whose structure was confirmed by ^{1}H NMR spectra, enabled us to identify even minor reaction products, amines *XIV – XVII*. From the number and intensity ratios of isotopic peaks M^+ we determined the number of chlorine atoms in the molecule and consequently the number of chlorotrifluoroethyl groups in the amine[7]. The distinction between 1 : 2 adduct and 1 : 2 telomer was based on the very characteristic fragmentation, involving cleavage of fluoroalkyl group from the molecular ion. In the case of 1 : 1 adducts *X* and *XI* and of 1 : 2 adducts *XII* and *XIII*, the most abundant are $(M - 117)^+$ ions, in the case of 1 : 2 telomers *XIV* and *XV* $(M - 233)^+$ ions, and in the case of amines *XVI* and *XVII*, devoid of the chlorine atom, the base peaks are $(M - 83)^+$. On the basis of mass spectra alone it is difficult to decide whether the alkylation took place at the *N*-methyl group or the C-2 carbon atom. The molecular ions of isomeric monotopic fluoroalkylamines (Scheme 2) give rise to ions A and B of the same relative mass but different structure. Both ions can be interconverted by hydrogen migration and in the spectra of 1 : 1 adducts we observe the same ionic species. The relative intensities of peaks in the molecular ion region are higher for 1 : 1 adducts *XI*, alkylated on the *N*-methyl group, than for 1 : 1 adducts *X*, bearing the chlorotrifluoroethyl group on C-2.



SCHEME 2

EXPERIMENTAL

Apparatus: The temperature data are uncorrected. ^{1}H NMR spectra were taken in deuteriochloroform with tetramethylsilane as internal standard on a Tesla BS 447 (60 MHz) or a Varian XL-100 (100 MHz) instrument. The chemical shifts are given in ppm, the coupling constants *J* in Hz. Mass spectra were obtained with an LKB 9000 spectrometer (electron ionization, electron energy 70 eV),

chromatographic inlet through a 2.5 m × 2.3 mm column packed with Carbowax 20 M and Apiezon L on Chromosorb or Celite, carrier gas helium, and a JEOL JMS-D300 instrument (electron ionization, electron energy 70 eV), chromatographic inlet through a 25 m capillary quartz column coated with Carbowax 20 M, carrier gas helium. The gas-liquid analyses were performed on a chromatograph Griffin & George, Ltd., model MK II B and on a Chrom 3 instrument (Laboratorni pristroje, Prague), both with flame-ionization detector. Analyses were performed on 2.5 m × 4 mm or 2.5 m × 6 mm columns packed with 20 or 15% poly(propanediol sebacate) on Celite 545 or on Chromaton N-AW-DMCS (0.150 – 0.200 mm). Preparative gas-liquid chromatography was carried out on a Chrom 2 instrument (Laboratorni pristroje, Prague) with flame-ionization detector. Columns: 15% Reoplex 400 on Chromaton N-AW-DMCS (0.200 – 0.250 mm) and 15% poly(propanediol sebacate) on Chromaton N-AW-DMCS (0.200 – 0.250 mm), length 3 m, diameter 8 mm. Carrier gas nitrogen.

Chemicals: Technical chlorotrifluoroethylene (Spolek pro chemickou a hutni vyrobu Usti nad Labem, The Czech Republic) was passed through a calcium chloride drying tube. Ethyldimethylamine (*I*), cyclohexyldimethylamine (*II*), 1-methylpiperidine (*IIIb*) and 1-methylmorpholine (*IIId*) were prepared by methylation of ethylamine, cyclohexylamine, piperidine and morpholine with formaldehyde and formic acid[8]. 1-Methylperhydroazepine (*IIIc*) was obtained by reduction of 2-perhydroazepinone with lithium aluminium hydride[7] and subsequent methylation[8]. 1-Methylpyrrolidine (*IIIa*) ("pure") was a Fluka product. Amines *I* – *III* were dried over solid potassium hydroxide and then distilled from sodium. Their purity (minimum 99.9%) was checked by GLC (area measurement).

Photochemically induced additions were performed in a water-cooled photochemical reactor[9]. In all cases, the mixtures were irradiated with a 125 W high-pressure mercury lamp Tesla RVK 125. Prior to the reaction, the reactor was flushed with nitrogen for at least 15 min. The temperature of the outgoing cooling water was kept at 20 – 25 °C throughout the whole reaction period. Chlorotrifluoroethylene was introduced into the reactor through a flow meter.

The radiation-induced addition of amine *IIIb* was carried out in a sealed 200 ml glass ampoule. After introduction of the amine, the ampoule was closed with a silicon rubber septum and flushed with nitrogen by means of two syringe needles. The ampoule was evacuated (final pressure 2.7 kPa) and cooled to −78 °C. Liquid chlorotrifluoroethylene was then introduced through a stainless steel capillary and the ampoule was sealed. The amount of the reactants was determined differentially from the weight of the empty ampoule, the evacuated ampoule containing the amine, and the full sealed ampoule. The reaction mixture was irradiated with a dose $3.45 \cdot 10^4$ Gy from ^{60}Co (mean energy of the emitted photons: 1.25 MeV) in a Gammacell apparatus (AEC Ltd., Canada) at the Institute for the Research, Production and Utilization of Radioisotopes, Prague.

The reaction mixtures were worked up by fractionation and the individual fractions were analyzed by GLC, the percentage being determined from the peak areas. The approximate absolute content of the individual products was determined from the GLC analyses and weight of the individual distillation fractions. The results are summarized in Table I.

Amines *IV* – *VII*

Amines *IV* and *V* were obtained by preparative GLC from the fraction boiling at 128 – 135 °C. Amine *VI*, containing 3% of amine *VII*, was obtained as the fraction of b.p. 100 – 101 °C/2.0 kPa.

6-Chloro-5,5,6-trifluoro-3-methyl-3-azahexane (*IV*)

^1H NMR spectrum: 1.06 t, 3 H, $^3J(H,H) = 7.5$ (CH_3); 2.37 s, 3 H (NCH_3); 2.58 qa, 2 H, $^3J(H,H) = 7.5$ (CH_2); 2.91 td, 2 H, $^3J(H,F) = 13$, $^4J(H,F) = 2$ (CH_2CF_2); 6.40 ddd, 1 H, $^2J(H,F) = 48$, $^3J(H,F) = 9$, $^3J(H,F) = 6.5$ (CHClF).

5-Chloro-4,4,5-trifluoro-2,3-dimethyl-2-azapentane (*V*)

^{1}H NMR spectrum: 1.15 dt, 3 H, ^3J(H,H) = 7.5, ^4J(H,F) = 2 (CH_3); 2.30 s, 6 H (NCH_3); 3.20 m, 1 H (CHN); 6.51 d, 1 H, ^2J(H,F) = 49 (CHClF).

1,7-Dichloro-1,2,2,6,6,7-hexafluoro-3,4-dimethyl-4-azaheptane (*VI*)

^{1}H NMR spectrum: 1.28 d, 3 H, ^3J(H,H) = 7.0 (CH_3); 2.53 s, 3 H (NCH_3); 3.25 m, 3 H (CH_2CF_2, $CHCF_2$); 6.33 dm, 2 H, ^2J(H,F) = 49 (CHClF).

1,7-Dichloro-4-ethyl-1,2,2,6,6,7-hexafluoro-4-azaheptane (*VII*)

About 3% of amine *VII* was present in amine *VI* as indicated by an ethyl signal in the spectrum of *VI*. ^{1}H NMR spectrum: 1.12 t, ^3J(H,H) = 7 (CH_3); 2.86 qa, ^3J(H,H) = 7 (CH_2).

Amines *VIII* and *IX*

Amine *VIII* was obtained as a fraction boiling at 67 – 70 °C/0.07 kPa, amine *IX* distilled at 105 – 106 °C/0.07 kPa.

5-Chloro-2-cyclohexyl-4,4,5-trifluoro-2-azapentane (*VIII*)

^{1}H NMR spectrum: 1.16 and 1.78 bs, 10 H ($(CH_2)_5$); 2.1 – 2.6 m (NCH); 2.34 s (NCH_3); 2.94 td, 2 H, ^3J(H,F) = 12, ^4J(H,F) = 2 (CH_2CF_2); 6.34 ddd, 1 H, ^2J(H,F) = 48, ^3J(H,F) = 10, ^3J(H,F) = 6 (CHClF).

1,7-Dichloro-1,2,2,6,6,7-hexafluoro-4-methyl-3,3-pentamethylen-4-azaheptane (*IX*)

^{1}H NMR spectrum: 1.5 – 2.1 m, 10 H ($(CH_2)_5$); 2.59 s (NCH_3); 3.39 t, 2 H, ^3J(H,F) = 16 (CH_2CF_2); 6.04 dt, 1 H, ^2J(H,F) = 47, ^3J(H,F) = 4 (CHClF); 6.11 dd, 1 H, ^2J(H,F) = 47, ^3J(H,F) = 16 (CHClF).

Amines *Xa* – *XIIa*, *XIVa* and *XVIa*

All the compounds (except amine *XIVa*) were isolated pure from the distillation fractions by preparative GLC. Amines *Xa* and *XIa* were obtained from fraction of b.p. 80 – 84 °C/4.7 kPa. In the case of amine *Xa*, both diastereoisomeric racemates Xa_1 and Xa_2 were isolated. Amine *XIIa* was obtained from fraction of b.p. 90 – 110 °C/2.1 kPa, amine *XVIa* from fraction boiling at 68 – 79 °C/4.7 kPa. Amine *XIVa* was not isolated pure and its structure was derived from the mass spectrum.

2-(2-Chloro-1,1,2-trifluoroethyl)-1-methylpyrrolidine (*X*)

Amine Xa_1: Mass spectrum, *m/z* (rel.%): 84 (100), 42 (36), 82 (8.4), 85 (6), 41 (6), 28 (5), 106 (4), 67 (4), 39 (4), 55 (4), 83 (3), 201 (0.7), 203 (0.3). ^{1}H NMR spectrum: 1.6 – 2.2 m, 4 H $(CH_2)_2$; 2.47 s (NCH_3); 2.2 – 2.7 m (CH_2N); 2.9 – 3.3 m ($CHCF_2$, CHN); 6.42 ddd, 1 H, ^2J(H,F) = 48, ^3J(H,F) = 11, ^3J(H,F) = 6 (CHClF).

Amine Xa_2: Mass spectrum, *m/z* (rel.%): identical with that of amine Xa_1. ^{1}H NMR spectrum: 1.6 – 2.2 m, 4 H ($(CH_2)_2$); 2.46 s (NCH_3); 2.2 – 2.7 m (CH_2N); 2.9 – 3.3 m ($CHCF_2$, CHN); 6.37 ddd, 1 H, ^2J(H,F) = 48, ^3J(H,F) = 12, ^3J(H,F) = 3 (CHClF).

1-(3-Chloro-2,2,3-trifluoropropyl)pyrrolidine (*XIa*)

Mass spectrum, *m*/*z* (rel.%): 84 (100), 42 (36), 55 (10), 41 (10), 28 (9), 85 (6), 67 (5), 56 (5), 39 (5), 51 (4), 43 (4), 30 (4), 29 (4), 201 (2), 203 (1). ^{1}H NMR spectrum: 1.5 – 2.2 m, 4 H ($(CH_2)_2$); 2.3 – 3.0 m, 4 H (CH_2NCH_2); 3.08 td, 2 H, ^3J(H,F) = 13.5, ^4J(H,F) = 2.5 (CH_2CF_2); 6.42 ddd, 1 H, ^2J(H,F) = 48, ^3J(H,F) = 8.5, ^3J(H,F) = 7 (CHClF).

2-(2-Chloro-1,1,2-trifluoroethyl)-1-(3-chloro-2,2,3-trifluoropropyl)pyrrolidine (*XIIa*)

Mass spectrum, *m*/*z* (rel.%): 200 (100), 45 (87), 202 (34), 28 (24), 89 (23), 42 (22), 73 (17), 43 (17), 83 (16), 44 (15), 31 (12), 29 (11), 87 (10), 82 (10), 41 (10), 201 (9), 84 (8), 67 (8), 58 (8), 55 (8), 316 (1.2), 318 (0.9), 317 (0.7), 319 (0.5). ^{1}H NMR spectrum: 1.6 – 2.2 m, 4 H ($(CH_2)_2$); 2.3 – 2.8 m, 2 H ($N(CH_2)_2$); 2.9 – 4.0 m, 3 H (CH_2CF_2, $CHCF_2$); 6.48 dm, 2 H, ^2J(H,F) = 46 (CHClF).

1-(3,5-Dichloro-2,2,3,4,4,5-hexafluoropentyl)pyrrolidine (*XIVa*)

Mass spectrum, *m*/*z* (rel.%): 84 (100), 45 (80), 42 (26), 89 (21), 73 (17), 44 (15), 43 (13), 86 (10), 31 (10), 29 (10), 59 (8), 58 (8), 85 (7), 82 (7), 88 (6), 41 (6), 133 (5), 103 (5), 55 (5), 83 (4), 75 (4), 67 (4), 102 (3), 30 (3), 316 (0.9), 318 (0.6), 317 (0.5), 319 (0.4).

1-Methyl-2-(1,1,2-trifluoroethyl)pyrrolidine (*XVIa*)

Mass spectrum, *m*/*z* (rel.%): 84 (100), 42 (39), 82 (10), 85 (6), 41 (6), 83 (5), 55 (5), 28 (5), 39 (4), 33 (3), 167 (1). ^{1}H NMR spectrum: 1.5 – 2.2 m, 4 H ($(CH_2)_2$); 2.46 s (NCH_3); 2.2 – 2.8 m (CH_2N); 2.8 – 3.3 m ($CHCF_2$); 4.58 ddd, 2 H, ^2J(H,F) = 47, ^3J(H,F) = 14, ^3J(H,F) = 11 (CH_2F).

Amines *Xb* – *XIIIb*

Pure amines *Xb* – *XIIIb* were isolated from distillation fractions by preparative GLC; amines *Xb* and *XIb* from fraction b.p. 90 – 92 °C/3.7 kPa, amines *XIIb* and *XIIIb* from fraction b.p. 89 – 92 °C/0.11 kPa.

2-(2-Chloro-1,1,2-trifluoroethyl)-1-methylpiperidine (*Xb*)

Amine *Xb* was a mixture of two diastereoisomeric racemates differing in chemical shift of the CHClF proton. Mass spectrum, *m*/*z* (rel.%): 98 (100), 42 (27), 70 (19), 99 (9), 55 (7), 43 (7), 41 (7), 180 (3), 96 (3), 82 (3), 67 (3), 97 (2), 69 (2), 68 (2), 57 (2), 56 (2), 54 (2), 51 (2), 196 (1). ^{1}H NMR spectrum: 1.3 – 1.9 m, 6 H ($(CH_2)_3$); 2.40 s (NCH_3); 2.3 – 3.1 m (CH_2NCH); 6.42 dt, ^2J(H,F) = 50, ^3J(H,F) = 8 (CHClF); 6.45 dt, 1 H, ^2J(H,F) = 45, ^3J(H,F) = 13 (CHClF).

1-(3-Chloro-2,2,3-trifluoropropyl)piperidine (*XIb*)

Mass spectrum, *m*/*z* (rel.%): 98 (100), 42 (25), 55 (13), 99 (9), 44 (6), 70 (5), 69 (5), 43 (5), 96 (4), 66 (4), 215 (3), 56 (3), 54 (3), 51 (3), 214 (2), 180 (2), 41 (2), 217 (1), 196 (1). ^{1}H NMR spectrum: 1.3 – 1.7 m, 6 H ($(CH_2)_3$); 2.57 t, 4 H, ^3J(H,H) = 5 (CH_2NCH_2); 2.87 td, 2 H, ^3J(H,F) = 13.5, ^4J(H,F) = 2 (CH_2CF_2); 6.42 ddd, 1 H, ^2J(H,F) = 48.5, ^3J(H,F) = 9, ^3J(H,F) = 6.5 (CHClF).

2-(2-Chloro-1,1,2-trifluoroethyl)-1-(3-chloro-2,2,3-trifluoropropyl)piperidine (*XIIb*)

Mass spectrum, *m*/*z* (rel.%): 214 (100), 216 (28), 55 (12), 215 (8), 186 (4), 67 (3), 42 (3), 160 (2), 158 (2), 131 (2), 43 (2), 296 (1.3), 298 (0.5), 330 (0.4), 313 (0.4), 332 (0.3), 315 (0.2). ^{1}H NMR

spectrum: 1.2 – 2.0 m, 6 H ($(CH_2)_3$); 2.3 – 3.5 m, 5 H ($CHN(CH_2)_2$); 6.27 dm, 2 H, ^2J(H,F) = 48 (CHClF).

2,6-Bis(2-chloro-1,1,2-trifluoroethyl)-1-methylpiperidine (*XIIIb*)

Mass spectrum, *m*/*z* (rel.%): 214 (100), 216 (36), 97 (13), 43 (11), 55 (8), 82 (3), 96 (5), 296 (2.3), 298 (1.0), 313 (0.7). ^{1}H NMR spectrum: 1.4 – 2.3 m, 6 H ($(CH_2)_3$); 2.32 s, 3 H (NCH_3); 3.0 – 3.6 m, 2 H (CHNCH); 6.30 dm, 2 H, ^2J(H,F) = 47 (CHClF).

Amines *Xc* – *XIIc*, *XIVc* and *XVIc*

Pure amines *Xc* – *XIIc* were isolated by preparative GLC from fraction boiling at 90 – 110 °C/2.0 kPa. Amines *XIVc* and *XVIc* were not isolated pure and their structure was derived from the mass spectra.

2-(2-Chloro-1,1,2-trifluoroethyl)-1-methylperhydroazepine (*Xc*)

Mass spectrum, *m*/*z* (rel.%): 112 (100), 42 (21), 41 (11), 113 (9), 55 (8), 44 (8), 58 (7), 28 (6), 84 (5), 70 (5), 43 (5), 39 (5), 106 (4), 29 (4), 229 (3.5), 56 (3.0), 231 (1.2). ^{1}H NMR spectrum: 1.1 – 2.2 m, 8 H ($(CH_2)_4$); 2.51 s (NCH_3); 2.6 – 3.6 m, 3 H (CH_2NCH); 6.49 dm, 1 H, ^2J(H,F) = 48 (CHClF).

1-(3-Chloro-2,2,3-trifluoropropyl)perhydroazepine (*XIc*)

Mass spectrum, *m*/*z* (rel.%): 112 (100), 42 (23), 41 (22), 69 (14), 55 (14), 28 (12), 58 (10), 113 (9), 44 (9), 110 (7), 84 (7), 43 (7), 39 (7), 229 (6), 200 (5), 67 (5), 29 (5), 70 (4), 56 (4), 30 (4), 82 (3), 57 (3), 51 (3), 231 (2). ^{1}H NMR spectrum: 1.57 bs, 8 H ($(CH_2)_4$); 2.5 – 3.0 m, 4 H (CH_2NCH_2); 3.09 td, 2 H, ^3J(H,F) = 13, ^4J(H,F) = 2 (CH_2CF_2); 6.43 ddd, 1 H, ^2J(H,F) = 48, ^3J(H,F) = 8, ^3J(H,F) = 7 (CHClF).

2-(2-Chloro-1,1,2-trifluoroethyl)-1-(3-chloro-2,2,3-trifluoropropyl)perhydroazepine (*XIIc*)

Mass spectrum, *m*/*z* (rel.%): 45 (100), 200 (96), 202 (33), 89 (26), 28 (24), 42 (22), 73 (19), 43 (19), 44 (17), 83 (16), 31 (12), 87 (11), 29 (11), 82 (10), 58 (10), 41 (10), 201 (9), 84 (8), 67 (8), 55 (8), 316 (1.2), 318 (0.8), 317 (0.6), 319 (0.4). ^{1}H NMR spectrum: 1.2 – 2.3 m, 8 H ($(CH_2)_4$); 2.7 – 3.7 m, 5 H ($CHN(CH_2)_2$); 6.48 dm, 2 H, ^2J(H,F) = 46 (CHClF).

1-(3,5-Dichloro-2,2,3,4,4,5-hexafluoropentyl)perhydroazepine (*XIVc*)

Mass spectrum, *m*/*z* (rel.%): 112 (100), 42 (18), 41 (15), 52 (12), 58 (9), 84 (6), 44 (6), 113 (4), 70 (4), 67 (4), 43 (4), 29 (4), 69 (3), 345 (2.2), 347 (1.5).

1-Methyl-2-(1,1,2-trifluoroethyl)perhydroazepine (*XVIc*)

Mass spectrum, *m*/*z* (rel.%): 112 (100), 42 (36), 41 (17), 58 (14), 70 (11), 55 (11), 44 (10), 113 (9), 39 (9), 28 (9), 84 (8), 43 (6), 83 (5), 29 (5), 195 (4), 106 (4), 82 (4), 56 (4), 98 (3).

Amines *Xd* – *XIVd*, *XV*, *XVId* and *XVII*

Pure amines *Xd* – *XIIId* were isolated from distillation fractions by preparative GLC; amines *Xd* and *XId* from fraction boiling at 110 – 117 °C/3.5 kPa, amines *XIId* and *XIIId* from fraction boiling at 117 – 140 °C/2.5 kPa. Amines *XIVd*, *XV*, *XVId* and *XVII* were not obtained in the pure state and their structure was derived from the mass spectra.

2-(2-Chloro-1,1,2-trifluoroethyl)-1-methylmorpholine (*Xd*)

Mass spectrum, *m*/*z* (rel.%): 100 (100), 42 (24), 43 (18), 28 (9), 44 (7), 101 (6), 72 (5), 41 (5), 56 (4), 182 (3), 217 (2), 219 (1). ^{1}H NMR spectrum: 2.1 – 2.7 m (NCH_2); 2.44 s (NCH_3); 2.7 – 3.3 m, 1 H (CF_2CHN); 3.4 – 4.1 m, 4 H (CH_2OCH_2); 6.41 dm, 1 H, ^2J(H,F) = 47 (CHClF).

1-(3-Chloro-2,2,3-trifluoropropyl)morpholine (*XId*)

Mass spectrum, *m*/*z* (rel.%): 100 (100), 28 (17), 56 (13), 42 (7), 41 (7), 101 (6), 29 (6), 43 (5), 217 (4), 70 (4), 67 (4), 51 (3), 219 (1). ^{1}H NMR spectrum: 2.2 – 2.7 m, 4 H (CH_2NCH_2); 2.90 td, 2 H, ^3J(H,F) = 14, ^4J(H,F) = 2 (CF_2CH_2); 3.64 t, 4 H, ^3J(H,H) = 5 (CH_2OCH_2); 6.40 ddd, 1 H, ^2J(H,F) = 48, ^3J(H,F) = 8, ^3J(H,F) = 7 (CHClF).

2-(2-Chloro-1,1,2-trifluoroethyl)-1-(3-chloro-2,2,3-trifluoropropyl)morpholine (*XIId*)

Mass spectrum, *m*/*z* (rel.%): 216 (100), 54 (81), 42 (47), 31 (45), 70 (40), 218 (34), 28 (25), 67 (17), 41 (14), 51 (13), 29 (11), 77 (10), 56 (10), 55 (10), 188 (9), 217 (8), 69 (8), 186 (7), 160 (7), 60 (7), 98 (6), 43 (6), 158 (5), 131 (5), 90 (5), 85 (4), 57 (4), 82 (3), 39 (3), 333 (1.7), 335 (1.2). ^{1}H NMR spectrum: 2.5 – 4.2 m, 9 H ($CHN(CH_2)_2$, CH_2OCH_2); 6.25 dm, 2 H, ^2J(H,F) = 48 (CHClF).

2,6-Bis(2-chloro-1,1,2-trifluoroethyl)-1-methylmorpholine (*XIIId*)

Mass spectrum, *m*/*z* (rel.%): 216 (100), 42 (83), 100 (11), 188 (9), 182 (9), 70 (9), 217 (8), 29 (8), 77 (8), 43 (7), 98 (6), 57 (6), 56 (6), 41 (6), 67 (5), 51 (5), 44 (5), 298 (4), 186 (4), 174 (4), 218 (3), 55 (3), 333 (1.4), 335 (0.9). ^{1}H NMR spectrum: 2.84 s, 3 H (NCH_3); 3.1 – 4.2 m, 6 H (CHNCH, CH_2OCH_2); 6.37 dm, 2 H, ^2J(H,F) = 49 (CHClF).

1-(3,5-Dichloro-2,2,3,4,4,5-hexafluoropentyl)morpholine (*XIVd*)

Mass spectrum, *m*/*z* (rel.%): 100 (100), 42 (84), 28 (16), 56 (14), 148 (11), 67 (9), 41 (9), 29 (8), 101 (6), 70 (6), 69 (6), 43 (5), 120 (4), 333 (3), 55 (3), 30 (3), 335 (2).

2-(2,4-Dichloro-1,1,2,3,3,4-hexafluorobutyl)-1-methylmorpholine (*XV*)

Mass spectrum, *m*/*z* (rel.%): 100 (100), 42 (51), 70 (18), 43 (15), 28 (8), 44 (7), 101 (6), 72 (6), 67 (5), 41 (5), 69 (3), 56 (3), 29 (3), 333 (0.3), 335 (0.2).

2-(1,1,2-Trifluoroethyl)-1-methylmorpholine (*XVId*)

Mass spectrum, *m*/*z* (rel.%): 100 (100), 42 (62), 43 (24), 28 (16), 70 (15), 44 (9), 72 (7), 101 (6), 41 (6), 29 (4), 58 (3), 56 (3), 183 (2).

1-(2,2,3-Trifluoropropyl)morpholine (*XVII*)

Mass spectrum, *m*/*z* (rel.%): 42 (100), 100 (98), 28 (31), 56 (18), 43 (10), 41 (8), 29 (8), 72 (7), 183 (6), 101 (6), 70 (6), 86 (5), 58 (5), 33 (5), 30 (4).

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