PERFLUORO[α-AMINO CARBOXYLIC ACIDS] AND THEIR DERIVATIVES*

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Only isolated examples of perfluoro(amino carboxylic acids) are known. In [1] tetrafluoroglycyl fluoride and hexafluoroalanyl fluoride were prepared as a result of the following series of reactions:

$$SO_3 \xrightarrow{F_2} FSO_2O{-}OSO_2F \xrightarrow{N_2F_4} FSO_2ONF_2$$

$$CF_2{=}CF_2 + FSO_2ONF_2 \rightarrow F_2NCF_2CF_2OSO_2F \xrightarrow{KF} F_2NCF_2COF$$

$$CF_2{=}CFCF_3 + FSO_2ONF_2 \begin{cases} \rightarrow CF_3CF(NF_2)CF_2OSO_2F \xrightarrow{KF} CF_3CFCOF \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NF_2 \\ \rightarrow CF_3CF(OSO_2F)CF_2NF_2 \xrightarrow{KF} CF_3COCF_2NF_2 \end{cases}$$

We have shown recently [2] that heating of ethyl 3,3,3-trifluoro-2-nitroso-2-(trifluoromethyl)-propionate with dinitrogen tetrafluoride gives perfluoro(2-methylalanine) ethyl ester and ethyl 3,3,3-trifluoro-2-(fluoroazoxy)-2-(trifluoromethyl)propionate in 1 : 1 proportions:

$$\begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>\!C(N{=}O){-}COOC_2H_5 + N_2F_4 \begin{cases} \rightarrow (CF_3)_2C(NF_2){-}COOC_2H_5 \\ \rightarrow (CF_3)_2C(N(O){=}NF){-}COOC_2H_5 \end{cases}$$

However, the action of dinitrogen tetrafluoride on difluoronitrosoacetic and tetrafluoro-2-nitroso-propionic esters led almost exclusively to the corresponding fluoroazoxy compounds.

In the present investigation we have developed a new general method for the synthesis of perfluoro-[α-amino carboxylic acids] and their derivatives from readily accessible alkyl trifluorovinyl (and analogous alkenyl) ethers and dinitrogen tetrafluoride. Reaction between these substances with heating in an autoclave led in high yields to the corresponding adducts — alkyl perfluoro(1,2-diaminoalkyl) ethers:

$$R{-}CF{=}CF{-}OR' + N_2F_4 \rightarrow R{-}\underset{NF_2}{CF}{-}\underset{NF_2}{CF}{-}OR'$$

R=F, Cl, CF_3; R'=C_2H_5

The addition of dinitrogen tetrafluoride to olefins with formation of vicinal bisdifluoroamino compounds goes by a homolytic mechanism [3-6]. In our case this reaction is interesting in that it is an example of radical addition at the double bond of a perfluoro-1-alkenyl ether, whereas the addition of other reagents — halogens, hydrogen halides, nitrosyl fluoride and chloride, nitryl fluoride, and dinitrogen tetroxide — goes by an electrophilic mechanism [7]. To pass from the adducts obtained to derivatives of perfluoro[α-amino carboxylic acids] it was necessary to find a method of converting the group $-CF(NF_2)OR'$ into carboxyl or a potential carboxyl. Known methods of converting ethers of the type RCX_2OR' (X = halogen) into acids consist in the action of concentrated sulfuric acid or anhydrous aluminum chloride:

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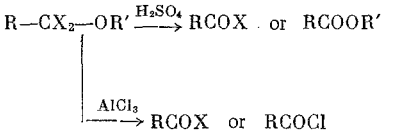
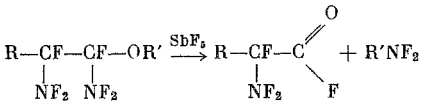


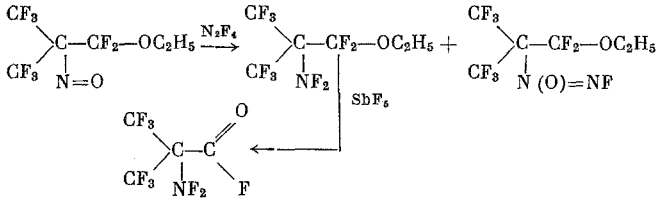
Both of these reagents proved to be unsuitable in the case of difluoroamino compounds. Sulfuric acid is practically inactive, and an attempt to use aluminum chloride led to an explosion, probably as a result of the replacement of N-fluorine atoms by chlorine. It was necessary to find a strong acid which would not affect the N—F bond. Antimony pentafluoride proved to be a suitable reagent. We succeeded in finding experimental conditions under which the reaction of adducts of alkyl perfluoroalkenyl ethers and dinitrogen tetrafluoride goes smoothly and leads in good yields to perfluoro(2-aminoalkanoyl) fluorides.



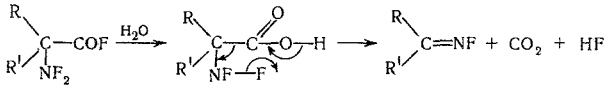
R=F, Cl, CF_3; R′=C_2H_5

The N,N-difluoroalkylamine eliminated is probably bound by the antimony pentafluoride [8].

We were unable to effect the synthesis of perfluoro(2-methylalanyl) fluoride by this scheme, and it was prepared in a different way:



Perfluoro(2-aminoalkanoyl) fluorides yield the corresponding esters smoothly under the action of alcohols. However, only in one case did the hydrolysis of the acid fluoride lead to the free acid: by the action of aqueous dioxane on F_2NCF_2COF we obtained tetrafluoroglycine, a liquid which fumes in air. The other perfluoro[α-amino carboxylic acids] were decarboxylated with simultaneous elimination of hydrogen fluoride and the formation of the corresponding perfluoro(alkylidenimines):



R=F, R′=Cl; R=F, R′=CF_3; R=R′=CF_3

Perfluoro(alkylidenimines) have scarcely been studied. In [9] a method is proposed for the synthesis of these compounds by the action of ferrocene on perfluoro(alkylamines):

$$RCF_2-NF_2 \xrightarrow{-2F} R-CF=NF$$

In this way $C_3F_7CF=NF$, $CFCl_2CF=NF$, $CF_2(CF=NF)_2$, and $\overline{CF_2CF_2CF_2CF_2-C}=NF$ were prepared. This reaction appears to provide a general method for the preparation of perfluoro(alkylidenimines), though it should be noted that there is at present no convenient preparative method for the synthesis of perfluoro(alkylamines). As regards earlier communications relating to members of this class of compounds, these are of a casual character. Thus, in the fluorination of tristrifluoromethyltriazine with elementary fluorine a yield of about 1.5% was obtained of a fraction boiling from −35 to −15°, and on the basis of the results of IR and mass spectroscopy it was concluded that this fraction contained $CF_3CF=NF$ [10]. In the investigation of the reaction of hexafluoropropene with nitrogen trifluoride and CsF at 320° a substance boiling from −13 to −11.7° was obtained; its elemental analysis and IR and mass spectra corresponded to the structure $(CF_3)_2C=NF$, but its F^{19} NMR spectrum contained five signals with an intensity ratio of 1:2:2:5:1 [11].

It is interesting to compare our results with these data. Pure $CF_3CF=NF$, prepared by us from $CF_3CF(NF_2)COF$, boils at −30°. The absorption frequency of the C=N bond in the IR spectrum of this

compound is at 1695 cm^{-1}, which agrees with the value given in [10]. It is probable that the fraction obtained in the investigation [10] did indeed contain $CF_3CF=NF$. Perfluoro(isopropylidenimine) $(CF_3)_2C=NF$, prepared by us from $(CF_3)_2C(NF_2)$—COF, boils at −6°, and its F^{19} NMR spectrum consists of three signals, two of which belong to nonequivalent (syn and anti) CF_3 groups and one (in the weak field) to the NF group, which is fully in accord with theory. The absorption frequency of the C=N bond was 1652 cm^{-1}, which agrees with the results of [11]. It is evident that in this case also the product was not the pure imine, but a mixture of it with other substances. Before we started the present work 1-chloro-N, 1-difluoromethylenimine had not been described (quite recently a communication appeared on its synthesis by another method [12]). We prepared $CFCl=NF$ by the hydrolysis of $CFCl(NF_2)COF$, and according to gas-liquid chromatography (GLC) and to its F^{19} NMR spectrum it is a mixture of syn and anti isomers in about 1 : 1 proportions.

EXPERIMENTAL

1-Ethoxynonafluoro-1,2-propanediamine $CF_3CF(NF_2)CF(NF_2)OC_2H_5$ (I). A mixture of 3.8 g of ethyl pentafluoropropenyl ether and 0.060 mole of dinitrogen tetrafluoride was heated up to 140-150° in a 100-ml stainless steel autoclave in the course of 4 h. Excess pressure was then released, the autoclave was cooled to −78°, and residual dinitrogen tetrafluoride was removed in a vacuum. The liquid reaction product was washed with water, dried with P_2O_5, and distilled. We obtained 4.81 g (80%) of (I), b.p. 62° (120 mm); n_D^{20} 1.3180; d_4^{20} 1.5145. Found %: C 21.72; H 1.84; F 61.20; N 9.84; MR 36.47. $C_5H_5F_9N_2O$. Calculated %: C 21.44; H 1.80; F 61.05; N 10.00; MR 36.53. IR spectrum: ν_{max} 940, 1020 cm^{-1} (CNF).

1-Chloro-2-ethoxyhexafluoroethylenediamine $CFCl(NF_2)CF(NF_2)OC_2H_5$ (II). In an analogous way a mixture of 6.4 g of 2-chlorodifluorovinyl ethyl ether and 0.060 mole of dinitrogen tetrafluoride was heated to 100-110° in the course of 4 h. We obtained 8.65 g (79%) of (II), b.p. 67° (95 mm); n_D^{20} 1.3545; d_4^{20} 1.4559. Found %: F 46.07; N 11.36; MR 36.85. $C_4H_5F_6ClN_2O$. Calculated %: F 46.24; N 11.36; MR 36.36. IR spectrum: ν_{max} 940, 1016 cm^{-1} (CNF).

1-Ethoxyheptafluoroethylenediamine $CF_2(NF_2)CF(NF_2)OC_2H_5$ (III). A mixture of 2.7 g of ethyl trifluorovinyl ether, 0.040 mole of dinitrogen tetrafluoride, and 3 ml of dichlorodifluoromethane was heated up to 100° in a 100-ml stainless steel autoclave in the course of 4 h. We obtained 4.15 g (80%) of (III), b.p. 50° (160 mm); n_D^{20} 1.3150; d_4^{20} 1.4231. Found %: C 20.87; H 2.36; F 57.63; N 12.21; MR 31.60. $C_4H_5F_7N_2O$. Calculated %: C 20.88; H 2.19; F 57.80; N 12.17; MR 31.63. IR spectrum: ν_{max} 940 (doublet), 1020 cm^{-1} (CNF).

2-Ethoxytetrafluoro-1,1-bistrifluoromethylethylamine (IV) and 1-Ethoxypentafluoro-2-(fluoroazoxy)-2-(trifluoromethyl)propane (V). A mixture of 6.15 g of 1-ethoxypentafluoro-2-nitroso-2-(trifluoromethyl)propane and 0.060 mole of dinitrogen tetrafluoride was heated up to 80° in a 100-ml stainless steel autoclave in the course of 3 h. We obtained 5.6 g of a mixture, which according to GLC contained 54% of (IV) (yield 48%) and 46% of (V) (yield 35%). The substance from three experiments was combined and fractionated. (IV), b.p. 55° (140 mm); n_D^{20} 1.3060; d_4^{20} 1.5217. Found %: C 24.70; H 1.76; F 63.94; N 4.81; MR 37.17. $C_6H_5F_{10}NO$. Calculated %: C 24.26; H 1.70; F 63.95; N 4.71; MR 37.12. (V), b.p. 71° (74 mm); n_D^{20} 1.3330; d_4^{20} 1.5661. Found %: C 23.40; H 1.35; F 55.83; N 9.18; MR 40.46. $C_6H_5F_9N_2O$. Calculated %: C 23.42; H 1.63; F 55.50; N 9.12; MR 40.83.

Hexafluoroalanyl Fluoride $CF_3CF(NF_2)COF$ (VI). A 10-ml distilling flask connected to a trap cooled to −78° was charged with 5 ml of antimony pentafluoride, and from a dropping funnel 7.7 g of (I) was added slowly. The condensed gas in the trap was distilled. We obtained 3.96 g (72%) of (VI) boiling from −5.5 to −5°. IR spectrum: ν_{max} 922, 965, 1030 (CNF), 1895 (CO) cm^{-1}. According to [1], IR spectrum: 925, 967, 1030, 1905 cm^{-1}. The F^{19} NMR spectrum also agreed with the published spectrum [1]. The mass spectrum contained a peak due to the molecular ion (M 199).

Hexafluoroalanine Ethyl Ester $CF_3CF(NF_2)COOC_2H_5$ (VII). With cooling to −78°, 3.35 g of (VI) and 2 ml of ethanol were mixed, the mixture was warmed slowly to room temperature and then poured into water, and the organic layer was separated, dried with P_2O_5, and distilled. We obtained 3.65 g (95%) of (VII), b.p. 48° (110 mm); n_D^{20} 1.3200; d_4^{20} 1.3801. Found %: C 26.66; H 2.38; F 51.08; N 6.17; MR 32.36. $C_5H_5F_6NO_2$. Calculated %: C 26.68; H 2.24; F 50.64; N 6.22; MR 31.95. IR spectrum: ν_{max} 910, 960, 1060 (CNF), 1795 (CO) cm^{-1}.

Hexafluoroalanine Methyl Ester $CF_3CF(NF_2)COOCH_3$ (VIII). This was prepared analogously in 95% yield; b.p. 47° (190 mm); n_D^{20} 1.3115; d_4^{20} 1.4728. Found %: C 23.15; H 1.60; F 54.07; N 6.81; MR 27.74. $C_4H_5F_6NO_2$. Calculated %: C 22.76; H 1.43; F 54.01; N 6.64; MR 27.34. IR spectrum: ν_{max} 910, 960, 1050 (CNF), 1790 (CO) cm^{-1}.

2-Chlorotrifluoroglycine Methyl Ester $F_2NCFClCOOCH_3$ (IX). A 10-ml distilling flask connected to a trap cooled to −78° was charged with 5 ml of antimony pentafluoride, and a little high-boiling perfluorocarbon oil was added so as to form a layer 1-1.5 mm in thickness above the antimony pentafluoride. 8.1 g of (II) was added slowly from a dropping funnel. At the end of the reaction with cooling to −78° 2 ml of methanol was added to the contents of the trap, and the mixture was treated as in the case of (VII). We obtained 3.52 g [61%, based on the (II) taken] of (IX), b.p. 45° (60 mm); n_D^{20} 1.3650; d_4^{20} 1.4485. Found %: C 20.52; H 1.79; F 32.16; N 7.92; MR 27.38. $C_3H_3F_3ClNO_2$. Calculated %: C 20.30; H 1.70; F 32.11; N 7.90; MR 27.16. IR spectrum: ν_{max} 893, 935, 1010 (CNF), 1790 (CO) cm^{-1}.

Tetrafluoroglycine Methyl Ester $F_2NCF_2COOCH_3$ (X). This was prepared like (IX) from 7.4 g of (III). Yield 3.01 g [58%, based on the (III) taken]; b.p. 59° (540 mm); n_D^{20} 1.3156; d_4^{20} 1.3957. Found %: C 22.37; H 1.96; F 47.46; N 8.76; MR 22.64. $C_3H_3F_4NO_2$. Calculated %: C 22.37; H 1.88; F 47.19; N 8.70; MR 22.34. IR spectrum: ν_{max} 930, 980, 998 (CNF), 1795 (CO) cm^{-1}.

Perfluoro(2-methylalanine) Ethyl Ester $(CF_3)_2C(NF_2)COOC_2H_5$ (XI). A 10-ml distilling flask connected to a trap cooled to −78° and to a water pump was charged with 5 ml of antimony pentafluoride, and with heating up to 70° under a residual pressure of 500 mm 3.04 g of (IV) was added gradually. At the end of the reaction 2 ml of ethanol was added to the contents of the trap with cooling. After the usual treatment we obtained 1.56 g [56%, based on the (IV) taken] of (XI), which was identified with a known sample [3] with the aid of GLC.

Pentafluoroethylidenimine $CF_3CF = NF$ (XII). With cooling to −78° 4.46 g of (VI) and 4 ml of 50% aqueous acetone were introduced into a 10-ml flask fitted with reflux condenser, also cooled to −78°. The cooling bath was then removed, and the mixture was kept at room temperature for about 30 min. The gaseous reaction product was driven off into a trap and then distilled. We obtained 2.07 g (70%) of (XII), b.p. −30°. Found %: C 17.75; F 72.30; mol. wt. 128. C_2F_5N. Calculated %: C 18.06; F 71.41; mol. wt. 133. IR spectrum: ν_{max} 880, 970 (NF), 1695 (C=N) cm^{-1}. F^{19} NMR spectrum: doublet of CF group, δ = 21.9 p.p.m.; triplet of CF_3 group, δ = 9.0 p.p.m.; broad peak of NF group, δ = −42.5 p.p.m.

Perfluoro(isopropylidenimine) $(CF_3)_2C = NF$ (XIII). Perfluoro(2-methylalanyl) fluoride was prepared as described in the experiment on the preparation of (XI) from 2.1 g of (IV) and treated with 2 ml of 50% aqueous dioxane as in the experiment on the synthesis of (XII). We obtained 0.42 g [32%, based on the (IV) taken] of (XIII), b.p. −6°. Found %: C 19.64; F 72.68; mol. wt. 182. C_3F_7N. Calculated %: C 19.69; F 72.66; mol. wt. 183. IR spectrum: ν_{max} 948, 1031 (NF), 1652 (C=N) cm^{-1}. F^{19} NMR spectrum: sextet of syn-CF_3 group, δ = 3.7 p.p.m.; doublet of quartets of anti-CF_3 group with center at δ = 0.06 p.p.m.; broad signal of NF group, δ = −108.6 p.p.m.

Tetrafluoroglycine F_2NCF_2COOH (XIV). At −78° in a flask fitted with reflux condenser, also cooled to −78°, tetrafluoroglycyl fluoride, prepared from 10.2 g of (III) as described in the experiment on the preparation of (IX), was mixed with 3 ml of 50% aqueous acetone, and then the cooling bath was removed and the flask was kept at room temperature for 5 min. The reaction mixture was extracted with ether, the extract was dried with $CaCl_2$, ether was driven off, 2 ml of concentrated H_2SO_4 was added to the residue, and the mixture was vacuum-distilled. We obtained 4.13 g [63.5%, based on the (III) taken] of (XIV), b.p. 61° (126 mm); n_D^{20} 1.3200; d_4^{20} 1.5220. Found %: C 16.87; H 0.77; F 51.83; N 9.57; neutralization equiv. 146.5. $C_2HF_4NO_2$. Calculated %: C 16.34; H 0.68; F 51.69; N 9.53; neutralization equiv. 147. IR spectrum: ν_{max} 931, 980 (CNF), 1780 (CO) cm^{-1}; broad absorption band in region of OH stretching vibrations.

1-Chloro-N,1-difluoromethylenimine $ClCF = NF$ (XV). 2-Chlorotrifluoroglycyl fluoride prepared from 8.2 g of (II) as described in the experiment on the synthesis of (IX) was treated with 4 ml of 50% aqueous acetone as in the preceding experiment. The yield of (XV) was 1.14 g [25%, based on the (II) taken]. For the preparation of an analytically pure substance, the product from four experiments was combined and distilled. Almost the whole of the substance distilled between −13 and −9°. Found %: C 12.17; F 37.94; mol. wt. 96. CF_2ClN. Calculated %: C 12.07; F 38.20; mol. wt. 99. IR spectrum: ν_{max} 950, 990 (NF), 1645 (C=N) cm^{-1}. F^{19} NMR spectrum: strongly split doublet with center at

δ = 6.17 p.p.m. due to CF group of anti isomer; weakly split doublet, δ = −22.9 p.p.m. due to CF group of syn isomer; strongly split doublet (two broad peaks) due to NF group of anti isomer with center at δ = −42.7 p.p.m.; and broad peak due to NF group of syn isomer, δ = −55.6 p.p.m. Ratio of amounts of isomers = about 1:1.

Mass spectrum (we give m/e, relative intensity in %, and assignment): 101 (33.4), 99 (80.5), M; 82 (31.9), 80 (100) M − F; 68 (4), 66 (13), CFCl; 63 (4.1), 61 (10.6), CClN; 52 (3.4), NF_2; 51 (30.3), 49 (8.9), 47 (30.2), CCl; 44 (8.8), CO_2; 37 (15), 35 (48), Cl; 33 (14.3), NF; 31 (46.6), CF; 26 (13.9), CN. The spectrum was determined by V. G. Sagitova with an MKh-13-03 instrument at 70 eV.

The F^{19} NMR spectra of the fluoroimines were determined with benzotrifluoride as internal standard on an NMR-100 JEOL instrument (working frequency 94 MHz) by Yu. S. Konstantinov, whom we thank.

CONCLUSIONS

1. A new method was developed for the synthesis of derivatives of perfluoro[α-amino carboxylic acids] from alkyl perfluoro-1-alkenyl ethers and dinitrogen tetrafluoride.

2. The decarboxylation of perfluoro[α-amino carboxylic acids] leads to perfluoro(alkylidenimines).

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