chromatographed over a silica gel column (L 100/160) using hexane—alcohol 10:1 as the eluent. The solvent was evaporated and the residue was distilled under vacuum to yield 0.2 g (5%) of (IIIa) and 0.1 g (3.4%) of t-$BuS[CH_2C(CH_3)CO_2CH_3]_2H$ (IIIb), bp 132°C (1 mm), n_D^{20} 1.4700. Found %: C 56.90, H 8.81, S 11.36. $C_{14}H_{26}O_4S$. Calculated %: C 57.93, H 8.96, S 11.03.

CONCLUSIONS

1. In the telomerization of acrylic monomers with mercaptans, the change from initiation by peroxides to initiation by metal complexes leads to a significant change in the nature of the distribution of the homologs in favor of the adduct.

2. The distribution of the telomer homologs in reactions of n-butyl mercaptan with acrylonitrile, methyl acrylate, and methyl methacrylate with initiation by carbonyls of Mn, Mo, and Cr, in contrast to peroxide initiation, is practically insensitive to a change in the ratio of the reagents.

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SYNTHESIS OF N-SUBSTITUTED DIAMIDES OF DIFLUOROMALONIC AND TETRAFLUOROSUCCINIC ACIDS AND X-RAY STRUCTURE OF THE N,N'-BIS(2-CARBOXYETHYL)DIAMIDE OF TETRAFLUOROSUCCINIC ACID

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Recently α,ω-bis(fluorosulfonyloxy)perfluoroalkanes have been used for the synthesis of perfluoroalkanedicarboxylic acids and their derivatives [1-3]. In this work, 1,3-bis-fluorosulfonyloxy)hexafluoropropane (I) and 1,4-bis(fluorosulfonyloxy)octafluorobutane (II) were synthesized by a method developed by us [4, 5] in which an atom of chlorine (or bromine) is replaced in perfluorinated alkylchlorides (or bromides) by an FSO_2O group. Treatment of (I) and (II) with excess MeOH in the presence of KF produces the dimethyl esters of difluoromalonic (III) and tetrafluorosuccinic (IV) acids.

$$\mathrm{Br(CF_2)_{n+2}Br + 2ClOSO_2F \xrightarrow{HSO_3F/SbF_5} \underset{(I),\,(II)}{FSO_2O(CF_2)_{n+2}OSO_2F}}$$

$n = 1$ (I), 2 (II).

$$\mathrm{(I),\,(II) + MeOH\ (excess) \xrightarrow[-SO_2F_2]{KF} \underset{(III),\,(IV)}{MeOOC(CF_2)_n COOMe}}$$

$n = 1$ (III), 2 (IV).

N,N'-bis(ω-carboxyalkyl)diamides (V)-(VIII) and N,N'-bis(3-dimethylaminopropyl)diamide of tetrafluorosuccinic acid (IX) were obtained by acylation with the diesters (III) and (IV) of glycine, β-alanine, and γ-aminobutyric acid (GABA) and also N,N-dimethyl-1,3-propanediamine.

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$$(\mathrm{III}),(\mathrm{IV})\xrightarrow[2)\,\mathrm{H_2SO_4}]{1)\,\mathrm{H_2N(CH_2)}_m\mathrm{COONa}}(\mathrm{CF_2})_n[\mathrm{CONH(CH_2)}_m\mathrm{COOH}]_2$$

$$(\mathrm{V})\text{—}(\mathrm{VIII})$$

$$n = 1,\ m = 2\ (\mathrm{V});\ n = 2,\ m = 1\ (\mathrm{VI}),\ m = 2\ (\mathrm{VII}),\ m = 3\ (\mathrm{VIII}).$$

$$(\mathrm{IV})\xrightarrow{\mathrm{H_2N(CH_2)_3N(CH_3)_2}}(\mathrm{CF_2})_2[\mathrm{CONH(CH_2)_3N(CH_3)_2}]_2$$

$$(\mathrm{IX})$$

In order to unambiguously confirm the structures of the compounds obtained by us, the x-ray structural analysis (XSA) of the N,N'-bis(2-carboxyethyl)diamide of tetrafluorosuccinic acid (VI) was determined. The structure of (VI) from the XSA is shown in Fig. 1. The molecule (VI) is centrosymmetric with a crystallographic center of symmetry at (0, 0, 0), located in the middle of the C^2—C^2 bond. The bond lengths in (VI) are given in Fig. 1, the main bond angles are: C^1NC^4 = 120.63(8), O^1C^1N = 125.30(9), $O^1C^1C^2$ = 119.72(8), NC^1C^2 = 114.98(8), $F^1C^2F^2$ = 108.00(8), $F^1C^2C^1$ = 110.49(7), $F^1C^2C^2$ = 107.97(9), $F^2C^2C^1$ = 108.63(7), $F^2C^2C^2$ = 107.81 (9), $C^1C^2C^2$ = 113.77(9), $O^2C^3O^3$ = 125.4(1), $O^2C^3C^4$ = 111.0(1), $O^3C^3C^4$ = 123.5(1), NC^4C^3 = 112.66(9), H^1NC^1 = 122(1), H^1NC^4 = 117(1), $H^2O^2C^3$ = 104(2)°. The average C—F bond distance, 1.346(1) Å, coincides with that found in CH_2F_2 (1.344(4) Å [6]). The C^2—C^2 bond distance is slightly shorter than the average length of an ordinary $C(sp^3)$—$C(sp^3)$ bond, 1.541(3) Å [6]. The C^1—C^2 bond is lengthened, while the C^3—C^4 bond is shortened by comparison with the average length of an ordinary $(O)C(sp^2)$—$C(sp^3)$ bond, 1.516(5) Å [6]. The distribution of bond lengths in the peptide group $O^1{=}C^1$—N shows the important π-delocalization in the double bond: $O^1{=}C^1{=}N$ see, for example, [7]). The N—C^4 distance is similar to the analogous bond N^1—C^3, 1.45(1) Å, in the structure of $O_2NCF_2CONHCH_2Ph$ [7]. The distribution of bond lengths and angles in the —COOH group lie in the range of values known for carboxylic acids.

The conformation of (VI) is described by the torsion angles: $F^1C^2C^2F^1$ = 180, $F^2C^2C^2F^2$ = 180, $C^1C^2C^2C^1$ = 180, $F^1C^2C^2F^2$ = 63.6, $F^1C^2C^2C^1$ = −57.0, $F^2C^2C^2C^1$ = 59.5, $F^1C^2C^1N$ = −24.0, $F^2C^2C^1O^1$ = 38.6, $C^2C^2C^1O^1$ = −81.5, $C^2C^2C^1N$ = 97.7, $O^1C^1NC^4$ = −1.4, $C^2C^1NC^4$ = 179.6, $C^1NC^4C^3$ = −77.8, $NC^4C^3O^2$ = −179.3, and $NC^4C^3O^3$ = 0.8°. The position of substituents relative to the ordinary bond C^2—C^2 has a twisted conformation. Two planar fragments can be identified in the symmetrically independent half of (VI): 1) the plane of the peptide group, composed of atoms O^1, N, C^1, C^2, C^4, and H^1; and 2) the plane of the carboxyl group, which includes atoms O^2, O^3, C^3, C^4, N, and H^2. The angle between these planes is 78°.

Three-centered (forked or bifurcated) hydrogen bonds occur in (VI): C^2—$F^1...H^1...O^1{=}C^1$, in which atom H^1 on N simultaneously participates in intramolecular H bonds C^2—$F^1...H^1$—N and intermolecular H bonds N—$H^1...O^1{=}C^1$ (Fig. 1). Analogous three-centered H bonds were discussed and observed in the crystal structures of $O_2NCF_2CONHCH_2Ph$ and $O_2NCF_2CONHNHTol$ [7].

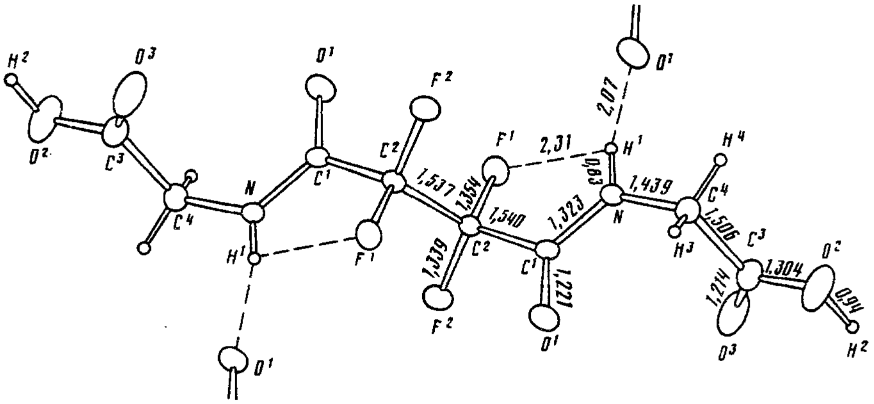


Fig. 1. X-ray structure of the N,N'-bis(2-carboxyethyl)diamide of tetrafluorosuccinic acid (VI). The molecule has a center of symmetry in the middle of the C^2—C^2 bond. Nonhydrogen atoms are shown by thermal probability ellipsoids (P = 30%). The bond lengths, d, are given in Å, for the nonhydrogen atoms σ(d) ≈ 0.001-0.002 Å. The hydrogen bonds to H^1 are shown by dotted lines.

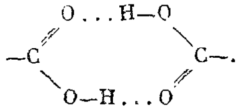
TABLE 1. Characteristics of Compounds (V)-(IX)

Compound	Yield, %	Mp, °C	Empirical formula	Found/calculated, %			
				C	H	F	N
(V)	31,5	174–175	$C_9H_{12}F_2N_2O_6$	38,35/38,29	4.11/4.25	13,42/13,47	9,90/9,92
(VI)	35,1	215 (decomp.)	$C_8H_8F_4N_2O_6$	31.65/31.59	2,89/2,63	25.33/25,00	9,10/9,21
(VII)	36,3	203–204	$C_{10}H_{12}F_4N_2O_6$	36.45/36,14	4,00/3,61	22.86/22,89	8,40/8,43
(VIII)	32,8	183–184	$C_{12}H_{16}F_4N_2O_6$	38,35/38.24	4,11/4,27	13,42/13,59	9,90/9,81
(IX)	72,6	59	$C_{14}H_{26}F_4N_4O_2$	47.46/46,93	7,24/7,26	21.26/21,23	15,25/15,64

TABLE 2. Coordinates (×10^4, ×10^3 for H) of the Independent Atoms in the Structure of (VI)

Atom	X	Y	Z
F^1	2085(2)	−1762(1)	502,4(5)
F^2	3065(2)	2850(2)	574,8(6)
O^1	−1557(2)	2176(2)	1778,4(7)
O^2	−3743(3)	−2043(4)	4489.6(8)
O^3	619(3)	−276(3)	3745,1(8)
N	−2056(2)	−2453(2)	1837,1(7)
C^1	−1052(3)	71(2)	1453,7(7)
C^2	860(2)	233(2)	513,5(7)
C^3	−2053(3)	−1581(3)	3704,9(9)
C^4	−3853(3)	−2888(3)	2720,7(8)
H^1	−170(4)	−385(4)	158(1)
H^2	−239(6)	−125(6)	505(2)
H^3	−520(4)	−206(5)	268(2)
H^4	−474(4)	−484(5)	279(2)

Intermolecular H bonds $N{-}H^1...O^1{=}C^1$ [X, Y − 1, Z] (distance $N...O^1$, 2.806(1) Å, angle $N{-}H^1...O^1$, 147(2)°) in the crystal structure of (VI) form infinite chains along the b axis. Intramolecular H bonds $C^2{-}F^1...H^1{-}N$ in (VI) are unusual, little studied H bonds, the existence of which in similar compounds was shown earlier by spectroscopic methods [8-10]. In the crystal of (VI), there are stable intermolecular H bonds of the $O^2{-}H^2...O^3$ type [−X, −Y, 1 − Z] (distance $O^2...O^3$, 2.678(1), $H^2...O^3$, 1.76(3) Å, angle $O^2{-}H^2...O^3$, 166(3)°), which join molecules of (VI) in infinite chains along the c axis in the following manner.



EXPERIMENTAL

1,3-Bis(fluorosulfonyloxy)hexafluoropropane (I). To a mixture of 290 g (2.15 moles) of $ClOSO_2F$, 50 g HSO_3F, and 16 g SbF_5 was added with stirring 221 g (1 mole) of 1,3-dibromohexafluoropropane. Stirring was continued for 6 h at 50-60°C. It was poured onto crushed ice, the organic layer was separated, washed with water (3 × 200 ml), and dried over $MgSO_4$. Fractionation gave 272 g (78%) of (I), bp 114-115°C, d_4^{20} 1.794, n_D^{20} 1.3000 (see [11]).

Under analogous conditions from 1,4-dibromooctafluorobutane was obtained (II) (yield 85%), bp 137-138°C, d_4^{20} 1.787, n_D^{20} 1.3105 (see [12]).

Dimethyl Ester of Difluoromalonic Acid (III). To a suspension of 90 g (1.55 moles) of dried KF in 500 ml absolute MeOH was added with stirring 229 g (0.66 mole) of (I), followed by refluxing for 10 h. The precipitate of KF was filtered, the filtrate was poured into 1 liter of 3% H_2SO_4, the organic layer was separated, and the aqueous layer was extracted with Freon-113. The combined extracts were washed with 10% soda solution, water, and dried over $MgSO_4$. Fractionation gave 81.2 g (73.2%) of (III), bp 167-169°C, d_4^{20} 1.310, n_D^{20} 1.3719 (see [13]).

Under analogous conditions from (II) was obtained (IV) (yield 76.6%), bp 172-174°C, d_4^{20} 1.463, n_D^{20} 1.3550 (see [13]).

N,N'-Bis(ω-carboxyalkyl)diamides of Perfluorodicarboxylic Acids (V)-(VIII). To a solution of 0.1 mole of the Na salt of glycine (β-alanine, GABA) in 40 ml water was added 0.05 mole of the ester (III) or (IV), followed by stirring at 40-60°C for 1 h until the disappearance of the ester layer. The reaction mixture was poured into 50 ml of 30% H_2SO_4 and cooled to −15°C. The precipitate which formed was quickly filtered, washed with ice water, Freon-113, and dried over P_2O_5. The precipitate was dissolved in absolute Et_2O to remove the Na_2SO_4 impurity. After removal of solvent, the residue was recrystallized from water. The characterisitcs of compounds (V)-(VIII) are given in Table 1.

N,N'-Bis(3-dimethylaminopropyl)diamide of Tetrafluorosuccinic Acid (IX). To 21.8 g (0.1 mole) of (IV) was added 26 g (0.26 mole) of N,N-dimethyl-1,3-propandiamine, followed by stirring for 2 h at 60°C. Fractionation gave 26 g (72.6%) of (IX), bp 180-185°C (1 mm) (see Table 1).

X-Ray Structure Analysis of (VI). XSA was carried out on an Enraf–Nonius CAD4-LSI11/02–PDP11/23 automatic diffractometer system (MoK_α radiation, graphite monochromator). Colorless, transparent crystals of (VI) are triclinic: $C_8H_8F_4N_2O_6$, M = 304.16; a = 4.891(2), b = 5.043(3), c = 13.126(3), α = 95.24(4), β = 90.20(2), γ = 112.71(5)°, V = 297.1(5) $Å^3$, Z = 1, d_{calc} = 1.700 g/cm³, $\mu(MoK_\alpha)$ = 1.72 cm^{-1}, and space group $P\bar{1}$. The intensities of 2373 reflections (ω/2θ scanning, $2\theta \leq 65°$) were measured in reciprocal space; 1588 independent observed reflections with $I \geq 3\sigma(I)$ were used in the final refinement. The crystal structure was solved by direct methods and refined by anisotropic (isotropic for H atoms) full matrix least squares methods (LSM) to R = 5.06 and R_w = 6.83%. The final atomic coordinates are given in Table 2. In the final difference Fourier synthesis, the majority of remaining electron density peaks ($\Delta\rho$ < 0.55 $eÅ^{-3}$) were located in the middle of covalent bonds. The weighting scheme for reflections in LSM (coefficient of the weighting scheme p = 0.085) was described in [7]. All x-ray structural calculations were done on minicomputer PDP 11/23 using the SDP-PLUS programs of Enraf–Nonius.

CONCLUSIONS

1. New N-substituted diamides of difluoromalonic and tetrafluorosuccinic acids were synthesized.

2. The molecular and crystal structure of the N,N'-bis(2-carboxyethyl)diamide of tetrafluorosuccinic acid was determined by x-ray structural analysis.

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