

REACTION OF 3-CHLORONONAFLUORO-1,5-HEXADIENE WITH DIETHYLAMINE*

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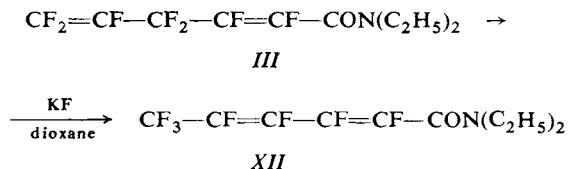
Reaction of diethylamine with 3-chlorononafluoro-1,5-hexadiene (*I*) in molar ratio of 1.5 : 1 to 2 : 1 at -30 to -17°C gives N,N-diethyl-1,1,2,3,4,4,5,6,6-nonafluoro-2,5-hexadienylamine (*II*) which is easily hydrolyzed to N,N-diethyl-2,3,4,4,5,6,6-heptafluoro-2,5-hexadienamide (*III*). The same reaction with the molar ratio 4 : 1 at 0 – 6°C and at 40°C produces a mixture of N,N,N',N'-tetraethyl-1,1,2,3,4,4,5,6,6-octafluoro-2,4-hexadiene-1,6-diamine (*IV*), N,N,N',N'-tetraethyl-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene-1,6-diamine (*V*), and N,N,N',N'-tetraethyl-1,2,3,3,4,4,5,6,6-octafluoro-1,4-hexadiene-1,6-diamine (*VI*), which on hydrolysis gives N,N,N',N'-tetraethyl-2,3,4,5-tetrafluoro-2,4-hexadienediamide (*VII*) and N,N,N',N'-tetraethyl-2,3,4,4,5-pentafluoro-2-hexenediamide (*VIII*). Reaction of the mixture of diamines *IV*–*VI* with methanol or 1-propanol gives dimethyl or dipropyl 2,3,4,5-tetrafluoro-2,4-hexadienedioate (*Xa,b*), respectively. Stereospecificity of the chlorine substitution in perfluoroallyl grouping and the reaction mechanism are discussed. Conformation of the butadiene skeleton of these compounds is also discussed on the basis of calculation of ^{19}F NMR spectra of *trans,trans*-2,3,4,5-tetrafluoro-2,4-hexadienedioic acid (*IX*) and its dimethyl ester *Xa*.

Our previous communication¹ describes the addition of primary alcohols to 3-chlorononafluoro-1,5-hexadiene² (*I*) which gives a mixture of dialkoxy derivatives with elimination of chloride anion. The present communication deals with the addition of diethylamine to the chlorodiene *I*, because additions of dialkylamines to fluoroolefins³ and to perfluoroallyl halides^{4–6} represent important synthetic procedures.

Molecules of 3-chlorononafluoro-1,5-hexadiene (*I*) contain both perfluoroallyl grouping and isolated trifluorovinyl group, and, in contrast to the addition of alcohols¹, it is possible to obtain addition products with either one or two diethylamine molecules depending on the reactant ratio and temperature. At the molar ratios $[(\text{C}_2\text{H}_5)_2\text{N}] : [\text{I}] \leq 2$ at temperatures -30 to -17°C allyl substitution of chlorine takes place giving N,N-diethyl-1,1,2,3,4,4,5,6,6-nonafluoro-2,5-hexadienylamine (*II*) which is easily hydrolyzed to N,N-diethyl-2,3,4,4,5,6,6-heptafluoro-2,5-hexadienamide (*III*). The reactions are stereospecific giving exclusively the *trans* isomers of *II* and *III*. At the molar ratio $[(\text{C}_2\text{H}_5)_2\text{N}] : [\text{I}] = 4$ at 0 – 6°C a mixture is ob-

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tained containing 55% N,N,N',N'-tetraethyl-1,1,2,3,4,5,6,6-octafluoro-2,4-hexadiene-1,6-diamine (IV), 30% N,N,N',N'-tetraethyl-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene-1,6-diamine (V), and 15% N,N,N',N'-tetraethyl-1,2,3,3,4,5,6,6-octafluoro-1,4-hexadiene-1,6-diamine (VI), which is easily hydrolyzed to a mixture of N,N,N',N'-tetraethyl-2,3,4,5-tetrafluoro-2,4-hexadienediamide (VII) and N,N,N',N'-tetraethyl-2,3,4,4,5-pentafluoro-2-hexenediamide (VIII) (Scheme 1). Tables I and II give conditions and results of the individual experiments. The diamides VII and VIII are formed as the main products also in the addition of diethylamine to the trifluorovinyl group of the amide III and subsequent hydrolysis. Structure of all the products isolated indicates stereospecific course of the primary. S_N2' substitution of chlorine and non-stereospecific course of the addition of diethylamine to the isolated trifluorovinyl group which proceeds *via* carbanion¹⁷. Also non-stereospecific is the reaction of fluoride anion with trifluorovinyl group of amide III. This reaction results in formation of two geometrical isomers: *cis,trans*- and *trans,trans*-N,N-diethyl-2,3,4,5,6,6,6-heptafluoro-2,4-hexadienamides (XII).



Structure of the diamines IV–VI and their proportions in the reaction mixture after the reaction in diethyl ether at 0–5°C could be determined from ¹⁹F NMR spectrum of the mixture. It was shown that the diamines IV–VI have analogous structures to that of the adducts of alcohols to the chlorodiene I (ref.¹). In accordance therewith is also the structure of the hydrolysis products – the diamides VII and VIII. According to ¹⁹F NMR spectrum the diamide VII represents a 1 : 1 mixture of *cis,trans* and *trans,trans* isomers. Its structure was confirmed by chemical correlation through the 2,3,4,5-tetrafluoro-2,4-hexadiene-1,6-dioic acid (IX) prepared by alkaline hydrolysis of its dimethyl ester Xa. The diamide VIII has *trans* configuration at the CF=CF double bond.

Fluorinated amines possessing —CF₂—NR₂ grouping^{3,7–9} or —CF=CF—NR₂ (R = alkyl) grouping^{10,11} are known to be efficient reagents for substitutions of hydroxyl group by fluorine. Their reaction with alcohols at 0°C produces unstable amino ethers which are hydrolyzed both to the respective ester and dialkylamine hydrofluorides and to alkylfluorides and dialkylamides^{9,11,12}. The mixture of diamines IV–VI was submitted to reactions with methanol and 1-propanol at 0°C and subsequent hydrolysis. From the complex reaction mixtures it was possible to isolate the corresponding alkyl fluorides and two geometrical isomers of dialkyl 2,3,4,5-tetrafluoro-2,4-hexadienedioate (X): *cis,trans* and *trans,trans*. GLC with authentic

TABLE I
Conditions and results of addition of diethylamine to 3-chlorononafluoro-1,5-hexadiene

Chlorodiene I g mmol ⁻¹	Diethylamine g mmol ⁻¹	Solvent ml	Temperature °C	Addition ^a	Reaction time min	Products, %		
						III	VII	VIII
5/18	10/137	(C ₂ H ₅) ₂ O (35)	2 to 6	A	30	—	36	64
5/18	10/137	CH ₂ Cl ₂ (35)	2 to 6	A	30	—	53	47
2/7.2	1.2/6	CH ₂ Cl ₂ (35)	40	B	20	—	75	25
6/21.6	2.4/32.8	(C ₂ H ₅) ₂ O (160)	-20 to -17	B	75	94	2	4
8/28.7	3.75/51.3	(C ₂ H ₅) ₂ O (200)	-30 to -27	B	45	80	6	14

^a A: the diene was added to the solution of amine; B: the amine was added to the solution of diene.

standards proved the presence of diethylamides *VII* and *VIII*. In accordance with the published data^{7,11,12} we presume the reaction to proceed *via* amino ether *IX* (Scheme 1). Analogous aminoethers could only be isolated, if they were stabilized by electro-negative substituents in alkoxy group, as *e.g.* in the case of reaction of N-(2-chloro-1,1,2-trifluoroethyl)diethylamine (the so-called Jarovenko's reagent⁸) with 1-fluoroalkylalkanols⁹.

The acid *X* as well as its esters *Xa,b*, diethylamide *VII*, and *XII* possess the structure of hexasubstituted 1,3-butadienes fulfilling the Braude condition¹³ of 1,1,3-substitution causing non-planarity of butadiene skeleton. This non-planarity of butadiene skeleton in fluorinated conjugated polyenes was proved experimentally for perfluoro-1,3-butadiene^{14,15} and perfluoro-1,3,5-hexatriene¹⁷⁻²¹. In some cases ¹⁹F NMR spectra give information on conformation of fluorinated 1,3-butadienes. Hirao and coworkers calculated an unambiguous dependence between the long-range coupling constants ⁵J_{FF} in ¹⁹F NMR spectra of fluorinated 1,3-butadienes and the dihedral angle¹⁶. This dependence agrees with the ⁵J_{FF} coupling constant values measured in rigid systems¹⁶. We carried out a calculation of the ¹⁹F NMR spectra of four-spin system for *trans,trans* isomers of the acid *X* and its dimethyl ester *Xa* with the aim of verification of non-planarity of their butadiene skeletons. The spectra of the two compounds were measured with the accuracy of 0.1 Hz in deuteriochloroform (acid *X*) or hexadeuteriodimethyl sulphoxide (ester *Xa*). The calculation was carried out by the iteration procedure using a program based on LAOCN3. The calculated values of chemical shifts and coupling constants are given in Table III. The obtained values of chemical shifts cannot be assigned unambiguously to the individual pairs of chemically equivalent fluorine atoms (—COCF=CF— and —COCF=CF—) in any of the cases. In spite of the way of assignment, however, the ⁵J_{FF} constants vary within the limits of 32.5 to 35.6 Hz for the two compounds studied. According to Hirao and coworkers¹⁶ these values correspond to a non-planar conformation deviated from the *s-cis* arrangement

TABLE II

Conditions and results of the isomerization of diethylamide *III* with potassium fluoride in boiling dioxane

Reaction time h	Conversion %	<i>XII</i> , %	
		<i>cis, trans</i>	<i>trans, trans</i>
2	37	75	25
12	99	73	27
15	100	73	27

by the dihedral angle of about 40° . This value agrees with those found for perfluoro-1,3-butadiene from photoelectronic spectrum¹⁴ (42°) and from electron diffraction¹⁵ ($47.4 \pm 2.4^\circ$). The conformation of 1,3-butadienes is not substantially affected by the *trans* substituent (with respect to the carbon skeleton; in our case carboxyl or methoxycarbonyl group), which agrees with the findings by Kováč²¹. The results given allow to consider the non-planar *cisoid* conformation of butadiene skeleton of acid *X* and its dimethyl ester *Xa* to be very likely.

EXPERIMENTAL

The temperature data are not corrected. The IR spectra were measured with a Perkin-Elmer 325 apparatus. The NMR spectra were obtained at 30°C on Tesla BS 567 apparatus in deuteriochloroform, if not otherwise stated; tetramethylsilane and trichlorofluoromethane were used as internal standards in the ^1H and ^{19}F NMR measurements, respectively. Upfield chemical shifts in the ^{19}F NMR spectra are denoted by positive values. The mass spectra were measured with an LKB 9000 spectrometer, the GLC analyses were carried out with a Chrom IV apparatus (stationary phase — the silicone elastomer SE 30 and OV 225; nitrogen as the carrier gas), the preparative chromatography was performed on a Chrom III apparatus.

Addition of Diethylamine to 3-Chlorononafluoro-1,5-hexadiene (*I*)

A) *Molar ratio of diethylamine: diene I* = 1.5. Solution of 3 g (10 mmol) diene *I* in 80 ml diethyl ether was stirred, and solution of 1.2 g (16 mmol) diethylamine in 5 ml ether was added thereto drop by drop within 45 min. The mixture was cooled at -20 to -17°C . After the addition was finished, the mixture was stirred at the same temperature for another 30 min.

N,N-Diethylnonafluoro-2,5-hexadienylamine (II): The above-given reaction mixture was filtered under nitrogen to remove diethylamine hydrochloride, and ether was evaporated to give a residue (2.5 g; 73%) which was identified as the amine *II* by means of ^1H and ^{19}F NMR and IR spectra. ^1H NMR spectrum (δ ppm, octadeuteriodioxane): CH_3 : 1.02 (t, $^3J_{\text{HH}} = 7$ Hz, 3 H); CH_2 : 2.88 (q, $^3J_{\text{HH}} = 7$ Hz, 2 H). ^{19}F NMR spectrum (δ ppm) octadeuteriodioxane): CF_2N : 76.9

TABLE III

Values of the chemical shifts (ppm) related to CFCl_3 as the internal standard and values of the J_{FF} coupling constants obtained by iterative calculation

Compound	$\delta_1 = \delta_4$	$\delta_2 = \delta_3$	$\Delta\delta$	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	RMS ^a
<i>X</i>	145.16	143.34	171.59	133.8	-16.8	-35.0	3.25	0.2516
<i>Xa</i>	147.79	145.96	175.30	132.7	-19.5	-35.6	32.7	0.0942

^a $\text{RMS} = [\sum A_i^2 / (N - \text{IP})]^{1/2}$, where RMS means standard deviation of the line, $\sum A_i^2$ is sum of squares of deviations of the calculated line from the measured line, *N* means number of the assigned lines, *IP* means number of sets of variable parameters (chemical shifts, coupling constants).

(m, 2 F); CF=CF: 149.9 and 158.4 (dm, $^3J_{FF} = 138$ Hz, 2 F); CF₂: 106.3 (m, 2 F); CF₂=CF—: 91.6 and 107.2 (m, 2 F); CF₂=CF—: 190.5 (dm, $^3J_{FF} = 130$ Hz, 1 F). IR spectrum (cm⁻¹): 1 740 w (ν(CF=CF)), 1 785 s (ν(CF=CF₂)).

N,N-Diethyl-2,3,4,4,5,6,6-heptafluoro-2,5-hexadieneamide (III): The mixture obtained from the reaction of diene *I* with diethylamine was hydrolyzed with 5% HCl at room temperature 20 min, whereupon it was neutralized with sodium hydrogen carbonate, the ethereal layer was separated, the aqueous layer was extracted with ether, the extract was dried with magnesium sulphate, filtered, ether was evaporated, and the raw product was vacuum distilled. Thus 6 g (20 mmol) of the starting diene *I* gave 3.9 g (81% with respect to diethylamine) amide *III* of 95% purity, b.p. 103–105°C/2 kPa, containing (according to GLC) 4% of the isomeric *N,N*-diethyl-2,3,4,4,5,6,6,6-heptafluoro-2,4-hexadieneamide (*XII*). For C₁₀H₁₀F₇NO (293.2) calculated: 40.90% C, 3.41% H, 45.36% F, 4.77% N; found: 40.68% C, 3.50% H, 45.66% F, 4.64% N. ¹H NMR spectrum (δ ppm): CH₃: 1.24 (m, 3 H); 3.45 (m, 2 H). ¹⁹F NMR spectrum (δ ppm): CF₂=CF: 92.3 (ddm, $^2J_{FF} = ^3J_{FF} = 40$ Hz, 1 F) and 106.9 (m, 1 F); CF₂=CF: 189.8 (ddm, $^3J_{FF} = 130$ Hz and 40 Hz, 1 F); CF₂: 106.9 (m, 2 F); CF=CFCO: 146.0 (dtm, $^3J_{FF} = 135$ Hz and 18 Hz, 1 F); CF=CFCO: 165.3 (dt, $^3J_{FF} = 135$ Hz, $^4J_{FF} = 16$ Hz, 1 F). IR spectrum (cm⁻¹): 1 663 vs (ν(C=O)) 1 750 w (ν(CF=CF)), 1 788 s (ν(CF₂=CF)). Mass spectrum (ionic species *m/z*/ relative intensity): M⁺ 293/7.5, (M+1)⁺ 294/5, (M-CH₃)⁺ 278/98, (M-CH₂)⁺ 277/11, (M-C₂H₅)⁺ 264/5, (M-C₃H₇)⁺ 250/14, C₅F₇CO⁺ 221/100, C₅F₆CO⁺ 202/9, C₅F₇⁺ 193/89, C₅F₆⁺ 174/8, 175/6, C₄F₆⁺ 162/36, C₄F₅⁺ 143/81, C₃F₅⁺ 131/28, C₄F₅⁺ 124/21, 125/6, C₃F₄⁺ 112/3, C₅H₁₀NO⁺ 100/7, C₃F₃⁺ 93/15, C₂H₅NCO⁺ 71/13, C₄H₁₀N⁺ 72/17, CF₃⁺ 69/20, C₂H₆N⁺ 56/38, C₂F⁺ 43/16, C₂H₄N⁺ 42/35, CF⁺ 31/11, C₂H₅ 29/53, metastable ion for 221→193.

B) *Molar ratio of diethylamine: diene I* = 4. To a solution of chlorodiene *I* in diethyl ether or dichloromethane a fourfold amount (mol/mol) of diethylamine in the same solvent was added drop by drop. Conditions and results of the individual experiments are given in Table I. The reaction mixture obtained from 3 g (10 mmol) diene *I* and 3g (40 mmol) diethylamine in ether at -17 to -20°C was filtered under nitrogen to remove diethylamine hydrohalides, and the solvent was evaporated from the filtrate in a stream of nitrogen. Yield: 2.5 g mixture of the diamines *IV*–*VI* whose ¹⁹F NMR spectrum agrees with the expected structure. Proportions of the individual diamines in the mixture (55% *IV*, 30% *V*, 15% *VI*) were determined from integral intensities of the ¹⁹F NMR signals. ¹⁹F NMR spectrum (octadeuteriodioxane, δ (ppm)/ relative integral intensity (mm)): NCF₂CF= (*IV* + *V* + *VI*): 76.4/185 (m, 4 F + 2 F + 2 F); NCF₂CHF (*V*): 92.9/19 and 86.7/19 (dm, $^2J_{FF} = 205$ Hz, 2 F); =CF—CF₂—CF= (*VI*): 100.0/18 (dddd, $^3J_{FF} = ^4J_{FF} = 18$ Hz, 2 F); CHF₂CF₂CF= (*V*): 110.3/19 and 113.9/19 (dm, $^2J_{FF} = 290$ Hz, 2 F); NCF=CF (*VI*): 117/10 (dt, $^3J_{FF} = 120$ Hz, $^4J_{FF} = 18$ Hz, 1 F); CF=CF (*IV* + *V* + *VI*): 132.4 and 143.8 and 151.1 and 157.3/186 (m, 4 F + 2 F + 2 F); NCF=CF (*VI*): 193.8/10 (dt, $^3J_{FF} = 120$ Hz and 18 Hz, 1 F); CHF (*V*): 207.8/20 (m, 1 F).

Hydrolysis of Diamines *IV*–*VI*

The reaction mixture obtained by addition of diethylamine to the chlorodiene *I* was hydrolyzed by stirring with diluted hydrochloric acid at room temperature; after 30 min it was neutralized with sodium hydrogen carbonate, the organic layer was separated, the aqueous layer was extracted with ether, the extract was dried with magnesium sulphate, and the solvent was evaporated in vacuum. Thus from 5 g (10 mmol) diene *I* we obtained 5 g evaporation residue whose GLC revealed two main products. Conditions and results of the individual experiments are given in Table I. The evaporation residue (650 mg) was submitted to gradient elution with toluene–ethyl acetate on silica gel to give 170 mg mixture of *cis,trans* and *trans,trans*-*N,N,N',N'*-tetraethyl-2,3,4,5-

-tetrafluoro-2,4-hexadienediamide (VII) (about 1 : 1) and 240 mg N,N,N',N'-tetraethyl-2,3,4,4,5-pentafluoro-2-hexenediamide (VIII) which were identified by spectral methods.

N,N,N',N'-Tetraethyl-2,3,4,5-tetrafluoro-2,4-hexadienediamide (VII): ^1H NMR spectrum (δ ppm): CH_3 : 0.99 (m, 3 H); CH_2 : 2.97 (m, 2 H); ^{19}F NMR spectrum (δ ppm): *trans,trans* isomer $\text{CF}=\text{CF}$: 140.1 (dm, $^3J_{\text{FF}} = 128$ Hz, 1 F) and 159.7 (dm, $^3J_{\text{FF}} = 128$ Hz, 1 F); *cis,trans* isomer: *cis*- $\text{CF}=\text{CF}$: 128.6 (m, 1 F) and 143.9 (m, 1 F); *trans*- $\text{CF}=\text{CF}$: 142.6 (ddd, $^3J_{\text{FF}} = 138$ Hz, $J_{\text{FF}} = 25$ Hz and 10 Hz, 1 F) and 158.6 (dd, $^3J_{\text{FF}} = 138$ Hz, $J_{\text{FF}} = 35$ Hz, 1 F). IR spectrum (cm^{-1}): 1 659 vs ($\nu(\text{C}=\text{O})$). Mass spectrum (ionic species m/z / relative intensity in %): M^+ 324/3, $(\text{M}-(\text{C}_2\text{H}_5)_2\text{N})^+$ 252/4, $(\text{M}-\text{CON}(\text{C}_2\text{H}_5)_2)^+$ 224/74, 225/12, $\text{C}_9\text{H}_{10}\text{F}_4\text{N}^+$ 206/22, $\text{C}_6\text{H}_2\text{F}_4\text{NO}_2^+$ 196/6, $\text{C}_7\text{H}_3\text{F}_3\text{NO}_2^+$ 190/4, $\text{C}_5\text{H}_2\text{F}_4\text{N}^+$ 168/15, $\text{C}_5\text{H}_4\text{O}^+$ 152/4, 153/6, C_4F_4^+ 124/5, 125/6, $(\text{CON}(\text{C}_2\text{H}_5)_2)^+$ 100/37, $\text{C}_4\text{H}_{11}\text{N}^+$ 72/62, $\text{C}_4\text{H}_{10}\text{N}^+$ 71/11, $\text{C}_4\text{H}_9\text{N}^+$ 70/10, $\text{C}_3\text{H}_6\text{N}^+$ 56/31, $\text{C}_2\text{H}_3\text{N}^+$ 42/23, $\text{C}_2\text{H}_5\text{N}^+$ 71/11, $\text{C}_4\text{H}_9\text{N}^+$ 70/10, $\text{C}_3\text{H}_6\text{N}^+$ 56/? , $\text{C}_2\text{H}_3\text{N}^+$ 42/23, $\text{C}_2\text{H}_5\text{N}^+$ 44/24, CH_4N^+ 30/5, C_2H_5^+ 29/100.

N,N,N',N'-Tetraethyl-2,3,4,4,5-pentafluoro-2-hexenediamide (VIII): ^1H NMR spectrum (δ ppm): CH_3 : 0.97 (m, 6 H); CH_2 : 1.76 (m, 4 H); CHF : 4.33 (ddd, $^2J_{\text{HF}} = 40$ Hz, $J_{\text{HF}} = 9$ Hz and 8 Hz, 1 H). ^{19}F NMR spectrum (δ ppm): $\text{CF}=\text{CF}$: 163.4 (dt, $^3J_{\text{FF}} = 135$ Hz, $^4J_{\text{FF}} = 12$ Hz, 1 F); $\text{CF}=\text{CF}$: 148.4 (dt, $^3J_{\text{FF}} = 135$ Hz, $^3J_{\text{FF}} = 22$ Hz, 1 F); CF_2 : 116.6 and 114.7 (dm, $^2J_{\text{FF}} = 290$ Hz, 2 F); CHF : 200.6 (dtm, with ^1H decoupling tm, $^2J_{\text{HF}} = 40$ Hz, $^3J_{\text{FF}} = 12$ Hz, 1 F). IR spectrum: 1 659 vs ($\nu(\text{C}=\text{O})$), 1 730 w ($\nu(\text{CF}=\text{CF})$). Mass spectrum (ionic species m/z / relative intensity in %): $(\text{M}-\text{N}(\text{C}_2\text{H}_5)_2)^+$ 272/18, 273/17, $(\text{M}-\text{CON}(\text{C}_2\text{H}_5)_2)^+$ 224/11, 225/6, $\text{C}_6\text{H}_2\text{F}_4\text{NO}_2^+$ 196/4, $\text{C}_8\text{H}_5\text{F}_3\text{NO}^+$ 188/4, $\text{C}_6\text{HF}_5\text{O}^+$ 185/4, $(\text{C}_2\text{H}_5)_2\text{NCOCF}=\text{CF}^+$ 162/15, $\text{C}_5\text{HF}_4\text{O}^+$ 153/5, C_4HF_4^+ 125/6, $(\text{CON}(\text{C}_2\text{H}_5)_2)^+$ 100/33, C_3F_3^+ 93/2, 94/2, $\text{C}_4\text{H}_{11}\text{N}^+$ 72/71, 71/22, 70/18, $\text{C}_3\text{H}_8\text{N}^+$ 58/27, 56/41, $\text{C}_2\text{H}_6\text{N}^+$ 44/28, 42/29, C_2H_5^+ 29/100.

Dimethyl 2,3,4,5-Tetrafluoro-2,4-hexadienedioate (Xa)

Mixture of amines IV–VI (5 g) was cooled and stirred (0°C), and 1.2 g (39 mmol) methanol was added thereto in a stream of nitrogen within 5 min. After further 10 min, the mixture was decomposed by addition of 10 ml water and heating at 30°C . The released methyl fluoride¹⁹ (0.2 g) was condensed in a vessel cooled with a mixture of dry ice and acetone. The mixture was diluted with water, extracted with ether, the extract was dried with magnesium sulphate, ether was distilled off, and the residue was distilled in vacuum. The distillate (2.1 g) b.p. $100-120^\circ\text{C}/2.4$ kPa contains (according to GLC) 64% *trans,trans*- and 27% *cis,trans*-isomer Xa, and the distillation residue (1.7 g) contains a greater number of substances (amides VII and VIII were found among them as minor products by GLC using internal standards).

trans,trans Isomer of diester Xa (ref.⁷) crystallized from the above-mentioned distillate. Recrystallization from methanol gave 1 g diester Xa, m.p. $74-75^\circ\text{C}$. Its spectra characteristics agree with the published data⁷.

cis,trans Isomer of diester Xa was obtained from the above-mentioned distillate by means of preparative GLC. ^1H NMR spectrum (δ ppm, octadeuteriodioxane): CH_3 : 3.85 (s, 1 H) and 3.88 (s, 1 H). ^{19}F NMR spectrum (δ ppm, octadeuteriodioxane): *cis*- $\text{CF}=\text{CF}$: 130.2 (ddd, $^3J_{\text{FF}} = 42$ Hz, $J_{\text{FF}} = 12$ Hz and 4 Hz, 1 F); *cis*- $\text{CF}=\text{CF}$: 136.3 (m, 1 F); *trans*- $\text{CF}=\text{CF}$: 140.4 (ddd, $^3J_{\text{FF}} = 138$ Hz and 42 Hz, $^4J_{\text{FF}} = 5$ Hz, 1 F); *trans*- $\text{CF}=\text{CF}$: 147.2 (dm, $^3J_{\text{FF}} = 138$ Hz, 1 F). IR spectrum (cm^{-1}): 1 755 s ($\nu(\text{C}=\text{O})$), 1 705 w ($\nu(\text{CF}=\text{CF})$). Mass spectrum (ionic species m/z / relative intensity in %): M^+ 242/3.5, $(\text{M}-\text{OCH}_3)^+$ 211/9, $(\text{M}-\text{COOCH}_3)^+$ 183/100, 184/7, $(\text{M}-\text{COOCH}_3-\text{CO})^+$ 155/6.5, $(\text{C}_2\text{F}_2\text{COOCH}_3)^+$ 121/7, C_3F_4^+ 112/8.5, C_4F_3^+ 105/6.5, $\text{C}_3\text{F}_4\text{CO}^+$ 140/5, C_4F_4^+ 124/7, 125/5.5, C_3F_3^+ 93/39, C_2F_3^+ 81/19, CF_3^+ 69/4.5,

$(\text{COOCH}_3)^+$ 59/58, CF^+ 31/10. For $\text{C}_8\text{H}_6\text{F}_4\text{O}_4$ (242.1) calculated: 39.68% C, 2.51% H, 31.4%; found: 39.24% C, 2.51% H, 31.4% F.

Dipropyl 2,3,4,5-Tetrafluoro-2,4-hexadienedioate (*Xb*)

The preparation was analogous to that of *Xa*: 5 g mixture of amines *IV*–*VI* reacted with 2.4 g (40 mmol) 1-propanol, and the product was hydrolyzed to give 0.3 g 1-fluoropropane²⁰, 1.6 g distillate boiling at 120–135°C/2 kPa, and 1.3 g distillation residue. Amides *VII* and *VIII* were detected as minor products (2% and 8% relatively to *Xb*) by GLC of the raw product with the use of authentic standards.

trans,trans Isomer of Xb represented 58% of the above-mentioned distillate which was submitted to preparative GLC. ¹H NMR spectrum (δ ppm): CH_3 : 0.97 (m, 3 H); CH_2 : 1.70 (m, 2 H); CH_2O : 4.24 (m, 2 H). ¹⁹F NMR spectrum (δ ppm): $\text{CF}=\text{CF}$: 146.3 (dm, ³ $J_{\text{FF}} = 145$ Hz, 1 F) and 148.0 (dm, ³ $J_{\text{FF}} = 145$ Hz, 1 F). IR spectrum (cm^{-1}): 1745 vs ($\nu(\text{C}=\text{O})$). Mass spectrum (ionic species m/z / relative intensity in %): M^+ 298/0.9, $(\text{M}-\text{C}_3\text{H}_6)^+$ 256/0.6, 255/0.3, $(\text{M}-\text{C}_3\text{H}_7\text{O})^+$ 239/7, $\text{C}_6\text{H}_7\text{F}_3\text{O}_3^+$ 236/1.1, $\text{C}_6\text{H}_2\text{F}_4\text{O}_2^+$ 214/18, $\text{C}_6\text{HF}_4\text{O}^+$ 197/1.7, $\text{C}_6\text{HF}_3\text{O}_2^+$ 194/7, 195/2, $\text{C}_5\text{HF}_4\text{O}_2^+$ 169/7, 170/2, C_3F_3^+ 93/6, $\text{C}_3\text{H}_7\text{O}^+$ 59/1.5, 58/1.3, 57/1.5, C_3H_7^+ 43/100, 41/35, CF^+ 31/4, C_2H_5^+ 29/14, 27/28.

cis,trans Isomer of Xb formed 32% of the above-mentioned distillate. It was also obtained by preparative GLC and was identified by comparison of its NMR spectra with those of the authentic standard¹.

Addition of Diethylamine to Amide *III*

Solution of 1 g (3.4 mmol) amide *III* in 50 ml dichloromethane was heated to boiling, and solution of 0.5 g (7 mmol) diethylamine in 5 ml dichloromethane was added thereto drop by drop. After 15 min, the mixture was hydrolyzed with 10 ml hydrochloric acid (diluted 1 : 2), neutralized with sodium hydrogen carbonate, the organic layer was separated and dried with calcium chloride. Two main products *VII* and *VIII* were identified by GLC on two stationary phases of different polarity with the use of authentic standards.

N,N-Diethyl-2,3,4,5,6,6-heptafluoro-2,4-hexadienamamide (*XII*)

0.7 g Amide *III* was boiled with suspension of 0.5 g anhydrous potassium fluoride in 15 ml dioxane 15 h. The reaction course was followed by GLC (Table II). The potassium fluoride was filtered off, and the solvent was distilled off, whereupon the product (0.4 g) was obtained by vacuum distillation, b.p. 85–100°C/2 kPa. It was separated by GLC into two isomers of amide *XII* (with *trans,trans* and *cis,trans* configurations).

cis,trans Isomer of XII: ¹H NMR spectrum (δ ppm): CH_3 : 1.23 (t, ³ $J_{\text{FF}} = 7$ Hz, 3 H); CH_2 : 3.40 (m, 2 H). ¹⁹F NMR spectrum (δ ppm): CF_3 : 70.1 (m, 3 F); $\text{CF}_3\text{CF}=\text{CF}$: 132.5 (dm, $J_{\text{FF}} = 40$ Hz, 1 F) and 143.5 (m, 1 F); $\text{CF}=\text{CFCO}$: 139.2 (dm, ³ $J_{\text{FF}} = 140$ Hz, 1 F); $\text{CF}=\text{CFCO}$: 155.0 (dd, ³ $J_{\text{FF}} = 140$ Hz, $J_{\text{FF}} = 40$ Hz, 1 F). IR spectrum (cm^{-1}): 1668 vs ($\nu(\text{C}=\text{O})$), 1735 w ($\nu(\text{CF}=\text{CF})$). Mass spectrum (ionic species m/z / relative intensity in %): M^+ 239/41, $(\text{M}-\text{CH}_3)^+$ 278/60, $(\text{M}-\text{HF})^+$ 273/11, $(\text{M}-\text{NC}_2\text{H}_5)^+$ 250/9, $\text{C}_5\text{F}_7\text{CO}^+$ 221/700, 222/6, C_5F_7^+ 193/98, 194/7, C_4F_5^+ 143/53, C_4F_4^+ 124/13, $(\text{C}_2\text{H}_5)_2\text{NCO}^+$ 100/4, C_3F_3^+ 93/18, $\text{C}_4\text{H}_{10}\text{N}^+$ 72/15, 71/6, 70/8, CF_3^+ 69/17, $\text{C}_3\text{H}_5\text{N}^+$ 56/29, $\text{C}_2\text{H}_4\text{N}^+$ 42/29, CF^+ 31/8, C_2H_5^+ 29/64.

trans,trans Isomer XII: ¹H NMR spectrum (δ ppm): CH_3 : 1.23 (m, ³ $J_{\text{FF}} = 7$ Hz, 3 H); CH_2 : 3.45 (m, 2 H). ¹⁹F NMR spectrum (δ ppm): CF_3 : 68.8 (m, 3 F); $\text{CF}=\text{CFCO}$: 137.7 (ddd, ³ $J_{\text{FF}} = 135$ Hz, $J_{\text{FF}} = 30$ Hz and 18 Hz, 1 F); $\text{CF}=\text{CFCO}$: 163.0 (ddd, ³ $J_{\text{FF}} = 135$ Hz, $J_{\text{FF}} = 27$

Hz and 9 Hz, 1 F); $\text{CF}_3\text{CF}=\text{CF}$: 154.8 and 157.0 (dm, $^3J_{\text{FF}} = 140$ Hz, 2 F). IR spectrum (cm^{-1}): 1 663 vs ($\nu(\text{C}=\text{O})$), 1 715 vw ($\nu(\text{CF}=\text{CF})$). Mass spectrum (ionic species as with the *cis,trans XII*, m/z / relative intensity in %): 293/30, 278/44, 273/12, 250/7, 221/85, 222/8, 193/100, 194/6.5, 143/22, 124/16, 100/5, 93/23, 72/16, 71/7, 70/9, 69/20, 56/42, 42/33, 31/9, 29/79.

trans,trans-2,3,4,5-Tetrafluoro-2,4-hexadienedioic Acid (*X*)

A mixture of 0.6 g dimethyl ester *Xa*, 10 ml dioxane, and 25 ml 2.5% aqueous sodium hydroxide was stirred at room temperature 1.5 h. The mixture was acidified with hydrochloric acid (Congo Red), saturated with sodium chloride, extracted with ether, the extract was dried with magnesium sulphate, filtered, and ether was distilled off in vacuum to give 0.35 g raw product. Its recrystallization from water gave 200 mg acid *X* which decomposes at 225°C. This acid was identified by comparison of its ^{19}F NMR and IR spectra with the published data².

Verification of Structure of Diamide *VII* by Chemical Correlation

A mixture of 150 mg acid *IX* and 0.4 g thionyl chloride was boiled 15 min, the unreacted thionyl chloride was evaporated in vacuum, and the residue was dissolved in 7 ml dioxane and treated with a solution of 0.3 g diethylamine in 3 ml dioxane. After 20 min, the mixture was poured in ice water, neutralized with hydrochloric acid, extracted with ether, the extract was dried with magnesium sulphate, filtered, and ether was evaporated to give 100 mg raw product identical with amide *VII* (comparison by GLC on two stationary phases of different polarity).

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