

**ADDITION OF PRIMARY ALCOHOLS  
TO 3-CHLORONONAFLUORO-1,5-HEXADIENE  
AND PERFLUORO-1,3,5-HEXATRIENE\***

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Sodium alkoxide-catalyzed addition of methanol, ethanol and propanol to 3-chlorononafluoro-1,5-hexadiene (*I*) proceeds at temperatures  $-35^{\circ}\text{C}$  to  $8^{\circ}\text{C}$  with allyl rearrangement, affording 1,6-dialkoxy-1,1,2,3,4,4,5,6,6-octafluoro-2,4-hexadiene (*V*) as the principal product, along with 1,6-dialkoxy-1,2,3,3,4,4,5,6,6-octafluoro-1,5-diene (*VI*) and *trans*-1,6-dialkoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene (*VII*). The ethers *Va*–*Vc* consist of the *cis,trans*- and *trans,trans*-isomers in about 3 : 1 ratio, whereas the ethers *VIa*–*VIc* have *trans,trans*-configuration. Ethers *Vc* and *VIc* react with concentrated sulfuric acid to give dipropyl 2,3,4,5-tetrafluoro-2,4-hexadienedioate (*IX*) and dipropyl 2,3,4,4,5-pentafluoro-2-hexenedioate (*X*), respectively, whereas the ether *VIIc* affords a mixture of propyl 6-propyloxy-2,3,4,4,5,6-heptafluoro-2-hexenoate (*XI*) and ester *X*. Addition of methanol to perfluoro-1,3,5-hexatriene (*II*) affords 1,1,2,3,4,5,6,6-octafluoro-1,6-dimethoxy-3-hexene (*XIII*) as the principal product.

In our preceding paper<sup>1</sup> we have proved that addition of primary alcohols to perfluoro-1,3-butadiene affords 1,4-dialkoxy-1,1,2,3,4,-pentafluoro-2-butene instead of 1,4-dialkoxy-1,2,3,4-tetrafluoro-2-butene as stated in an earlier paper<sup>2</sup>.

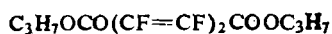
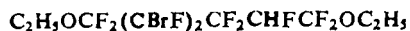
In the present communication we describe addition of primary alcohols to 3-chloro-1,1,2,3,4,4,5,6,6-nonafluoro-1,5-hexadiene (*I*) and perfluoro-1,3,5-hexatriene (*II*). The compounds *I* and *II* were prepared by dehalogenation of 1,6-dibromo-2,3,5-trichloro-1,1,2,3,4,4,5,6,6-nonafluorohexane (*III*), a side-product in our synthesis of perfluoro-1,3-butadiene<sup>3</sup>. Dehalogenation of the compound *III* with zinc in an alcoholic medium affords, besides chlorodiene *I* and triene *III*, also 6*H*-perfluoro-1,4-hexadiene (*IV*) which arises by subsequent reduction of the chlorodiene *I* with zinc. Best yields of *I* were obtained in dehalogenation of the triene *III* with zinc in boiling propanol under simultaneous removal of the products by distillation. Under these conditions the products *I*, *II* and *IV* were formed in the ratio 6.5 : 2.5 : 1, whereas in a higher-boiling solvent such as dioxane or butanol the formation of the triene *II* was preferred.

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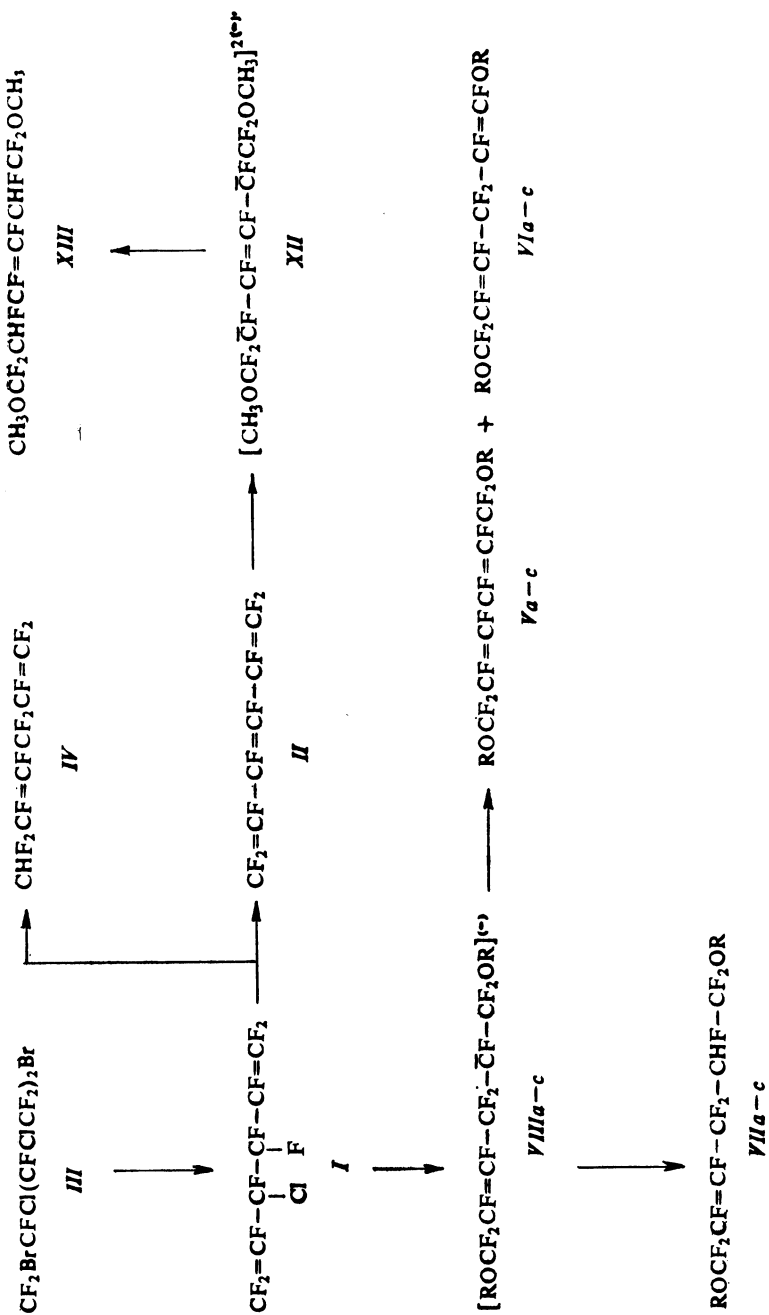
We performed the addition of methanol, ethanol, and propanol to the chlorodiene *I* in the presence of excess of the corresponding sodium alkoxide in temperature range  $-35^{\circ}\text{C}$  to  $20^{\circ}\text{C}$  (Table I). In the interval  $-35^{\circ}\text{C}$  to  $8^{\circ}\text{C}$  neither temperature nor reaction time had any marked effect on composition of the reaction mixture which afforded 1,6-dialkoxy-1,1,2,3,4,5,6,6-octafluoro-2,4-hexadienes (*Va–Vc*) as the principal products, along with 1,6-dialkoxy-1,2,3,3,4,5,6,6-octafluoro-1,4-hexadienes (*VIIa–VIIc*) and 1,6-dialkoxy-1,2,3,4,4,5,6,6-nonafluoro-2-hexenes (*Via–Vlc*). On the other hand, when the addition of ethanol to *I* was performed at  $20^{\circ}\text{C}$  for 12 h, decomposition occurred and only the diethoxyhexene *VIIb* was isolated.

The chlorodiene *I* represents a system with two perfluoroallyl groupings (Scheme 1). However, on the basis of our results we conclude that the allylic rearrangement takes place only by the  $\text{S}_{\text{N}}2'$  substitution of chlorine atom in the allylic grouping and not of the fluorine atom in position 4. The reaction intermediate is thus probably the carbanion *VIII* resulting from addition of the alkoxyl anion to the terminal trifluorovinyl group. The carbanion *VIII* loses fluoride anion to give the ethers *V* and *VI*, whereas its protonation leads to the dialkoxyhexene *VII*. This concept agrees also with the stability of compound *VIIb* in the reaction conducted at  $20^{\circ}\text{C}$  indicating that the formation of ethers *V* and *VI* by elimination of hydrogen fluoride from *VII* is less probable than formation of *VII* from the carbanion *VIII*.

The content of ethers *Via–Vlc* in the reaction mixture increases in the order  $\text{CH}_3\text{O} \ll \text{C}_2\text{H}_5\text{O} < \text{C}_3\text{H}_7\text{O}$ , reflecting apparently the increasing stability of the molecule due to increasing electron donor character of the ether oxygen.

*IX**X**XI**XIV**XV*

Unlike the adducts of primary alcohols to perfluoro-1,3-butadiene which are smoothly hydrolyzed at  $20^{\circ}\text{C}$  to the corresponding esters by silicon dioxide in water or 80% sulfuric acid in dichloromethane<sup>1</sup>, the diethers *V–VII* were stable toward hydrated silicon dioxide and underwent hydrolysis only on treatment with 90% sulfuric acid in boiling dichloromethane. Under such conditions, the diethers *V–VII* of the series *a* and *b* were hydrolyzed with simultaneous destruction of the molecule and no products could be isolated. On the contrary, hydrolysis of the dipropoxy derivatives *Vc–VIIc* gave well-isolable products: compound *Vc* afforded dipropyl 1,2,3,4-tetra-



In formulae V-III: a, R = CH<sub>3</sub>, b, R = C<sub>2</sub>H<sub>5</sub>, c, R = C<sub>3</sub>H<sub>7</sub>

SCHEME 1

TABLE I  
Addition of primary alcohols to 3-chlorononafluoro-1,5-hexadiene

Chlorodiene I g	Alcohol ml	Sodium g	Reaction time h	Temperature °C	Yield g	Products, %			
						V <sup>a</sup>	V <sup>b</sup>	VII	
7	CH <sub>3</sub> OH (50)	1.2	1	3-8	7.4	38	14.5	9.5	38
7	C <sub>2</sub> H <sub>5</sub> OH (50)	1.2	1	3-8	7.8	38.5	9.5	18	34
3.5	C <sub>2</sub> H <sub>5</sub> OH (25)	0.6	2	-12	3.9	36	10	22	32
2	C <sub>2</sub> H <sub>5</sub> OH (20)	0.35	4.5	3-6	1.7	34	9	23.5	33.5
3.5	C <sub>2</sub> H <sub>5</sub> OH (25)	0.6	12	20	3.6	—	—	—	100 <sup>c</sup>
2	C <sub>3</sub> H <sub>7</sub> OH (20)	0.35	1	3-6	1.9	33	10	22	35
2	C <sub>3</sub> H <sub>7</sub> OH (20)	0.35	2	-25	2.2	32	10	24	34
2	C <sub>2</sub> H <sub>7</sub> OH (20)	0.35	4.5	-25	2.1	33	8	24	35

<sup>a</sup> *cis,trans*-Isomer; <sup>b</sup> *trans,trans*-isomer; <sup>c</sup> several side-products (less than 5% based on VII).

fluoro-2,4-hexadienedioate (*IX*) with retention of configuration, the ether *VIc* gave dipropyl 2,3,4,4,5-pentafluoro-2-hexenedioate (*X*), and hydrolysis of dipropoxyhexene *VIIc* led to a mixture of propyl 2,3,4,4,5,6,6-heptafluoro-6-propyloxy-2-hexenoate (*XI*) and the diester *X*. These results are in accord with those obtained with analogous adducts to perfluoro-1,3-butadiene<sup>1</sup> for which the resistance of the alkoxydifluoromethylene groups toward hydrolysis decreases in the order  $-\text{CHF}\text{CF}_2\text{OR} > > -\text{CF}=\text{CF}\text{CF}_2\text{OR} > -\text{CH}=\text{CF}\text{CF}_2\text{OR} > -\text{CF}=\text{CH}\text{CF}_2\text{OR}$ .

Addition of methanol to perfluoro-1,3,5-hexatriene (*II*) in the presence of sodium methoxide at 0°C afforded a mixture of nine compounds (gas-liquid chromatography) with 1,1,2,3,4,5,6,6-octafluoro-1,6-dimethoxy-3-hexene (*XIII*) predominating (85%). This result corresponds to a double 1,2-addition of methoxide ion to the terminal trifluorovinyl groups of triene *II* under formation of the dianion *XII*, and agrees with the conjugation-hindering helical structure of perfluoro-1,3,5-triene<sup>4</sup>. At the same time, it also confirms the relative stability of ethers, containing the  $-\text{CHF}\text{CF}_2\text{OR}$  grouping, observed both in the addition of alcohols to chlorodiene *I* in this study and in the addition to perfluoro-1,3-butadiene<sup>1</sup>.

Configuration of the double bonds was determined from the coupling constants  $^3J_{\text{FF}}$ . Compounds *Va*–*Vc* are mixtures of *cis,trans*- and *trans,trans*-isomers with the former predominating. The *cis*-configuration at the  $-\text{CF}=\text{CF}-$  double bond in *cis,trans*-dialkoxyhexadienes *Va*–*Vc* is indicated by signals of the olefinic fluorine atoms which form multiplets at 140.2–140.6 ppm (width 60 Hz) and doublets of multiplets at 137.6–138 ppm with the coupling constant  $^3J_{\text{FF}} = 36$  Hz and 38 Hz. The multiplet widths are 30 Hz and thus the coupling constants  $^3J_{\text{FF}}$  are smaller than 30 Hz which corresponds to the *cis*-configuration. The *trans*-configuration at the second double bond  $-\text{CF}=\text{CF}-$  in the *cis,trans*-isomer of *V* follows directly from the coupling constant  $^3J_{\text{FF}} = 140$  Hz in the spectrum. The configuration of the second isomer of *V* is unequivocally *trans,trans*, according to the coupling constant  $^3J_{\text{FF}} = 120$  Hz.

For the compounds *Vla*–*Vlc* only configuration at the  $-\text{CF}=\text{CF}-\text{OR}$  double bond can be unequivocally determined: the coupling constant  $^3J_{\text{FF}} = 120$  Hz shows the *trans*-configuration. The signals of fluorine atoms at the second double bond,  $\text{RO}-\text{CF}_2-\text{CF}=\text{CF}$ , form a broad multiplet (50 Hz) and it is not possible to determine the coupling constant. No information in this respect was obtained from the IR spectrum since the region  $1\,710-1\,800\text{ cm}^{-1}$  is obscured by a broad absorption band due to the  $-\text{CF}=\text{CFOR}$  grouping. We assume, however, that in compounds *Vla*–*Vlc* the  $\text{ROCF}_2\text{CF}=\text{CF}-$  double bond has *trans*-configuration, analogously to compounds *Va*–*Vc* and *VIIa*–*VIIc*, since in all these types of compounds this grouping arises by  $\text{S}_{\text{N}}2'$  reaction of an alkoxide with the perfluoroallyl system.

The signals of the fluorine atoms at the double bond in the dialkoxyhexenes *VIIa* and *VIIc* form an AB system with chemical shifts 158.6 and 159.4 ppm and coupling

constant  $^3J_{\text{FF}} = 140$  Hz, the spectrum of *VIIb* exhibits signals at 158.2 and 159.0 ppm, the coupling constant being 145 Hz: these values correspond unequivocally to *trans*-configuration of the double bonds in these compounds.

The structure of the compounds *V* and *VII* has been proved also chemically: addition of bromine to *Vb* gave 2,3,4,5-tetrabromo-1,6-diethoxy-1,1,2,3,4,5,6,6-octafluorohexane (*XIV*) and the same reaction with *VIIb* afforded 2,3-dibromo-1,6-diethoxy-1,1,2,3,4,4,5,6,6-nonafluorohexane (*XV*).

## EXPERIMENTAL

NMR Spectra were measured on a Varian XL 100 instrument in deuteriochloroform or octa-deuteriodioxane using tetramethylsilane or trichlorofluoromethane as internal standards, IR spectra were recorded on a Perkin-Elmer 225 spectrometer in tetrachloromethane, and mass spectra were taken on an LKB 9000 instrument. Gas-liquid chromatographic analyses as well as preparations were done on a Chrom III chromatograph with flame-ionization detector. The temperature data are uncorrected.

### Dehalogenation of 1,6-Dibromo-2,3,5-trichlorononafluorohexane (*III*)

Compound *III* (ref.<sup>3</sup>; 50 g) in propanol (40 ml) was added during 20–25 min to a stirred boiling suspension of zinc powder (activated with glacial acetic acid) in 1-propanol (200 ml; dried over calcium oxide and fractionated) under simultaneous distillation of the product. After the end of the addition the distillate was collected for additional 5–10 min. The distillates from seven experiments were fractionated on a 1 m column filled with metal wire spirals:

*Perfluoro*-1,3,5-hexatriene (*II*); fraction boiling at 52–54.5°C (24 g; 15%), contained 95% of the triene *II*. For pertinent data on its structure see ref.<sup>4,5</sup>.

3-Chlorononafluoro-1,5-hexadiene (*I*): fraction boiling at 67–69°C; purity 97.5%, yield 79.6 g (50%).  $^{19}\text{F}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $=\text{CF}_2$  80.0 (m, 2 F) and 105.0 (m, 2 F);  $\text{CF}_2$  113.0 and 115.8 (dm,  $^2J_{\text{FF}} = 280$  Hz, 2 F);  $\text{CFCl}$  135.2 (m, 1 F);  $\text{CF}=\text{CF}_2$  179.0 (dm,  $^3J_{\text{FF}} = 115$  Hz, 2 F). IR Spectrum ( $\text{cm}^{-1}$ ): 618 vw, 685 w, 865 mw, 900 m, 985 mw, 1 012 m, 1 082 mw, 1 100 m, 1 168 ms, 1 187 ms, 1 290 m, 1 315 s, 1 350 s, 1 780 vs. Mass spectrum (principal ions  $m/z$  / rel. intensity):  $\text{M}^+$  278/0.7 and 280/0.2,  $\text{C}_6\text{F}_9^+$  174/4,  $\text{C}_4\text{F}_6^+$  162/8,  $\text{C}_5\text{F}_5^+$  155/12,  $\text{C}_3\text{ClF}_4^+$  147/87 and 149/30,  $\text{C}_3\text{F}_5^+$  131/100,  $\text{C}_4\text{F}_4^+$  124/13,  $\text{C}_5\text{F}_3^+$  117/7,  $\text{C}_3\text{F}_4^+$  112/9,  $\text{C}_4\text{F}_3^+$  105/6,  $\text{C}_3\text{F}_3^+$  93/51,  $\text{CClF}_2^+$  85/11 and 87/4,  $\text{C}_3\text{F}_3^+$  74/12,  $\text{CF}_3^+$  69/92,  $\text{C}_2\text{F}_2^+$  62/4,  $\text{C}_3\text{F}^+$  55/5,  $\text{CF}_2^+$  50/5,  $\text{C}_2\text{F}^+$  43/4,  $\text{CF}^+$  31/44.

6H-*Perfluoro*-1,4-hexadiene (*IV*) was isolated by preparative gas-liquid chromatography on trixylyl phosphate as stationary phase from 13.5 g of the intermediate fraction boiling in the range 54.5–67°C.  $^1\text{H}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{H}$  6.52 (tm,  $^2J_{\text{HF}} = 52$  Hz).  $^{19}\text{F}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $=\text{CF}_2$  106.5 (dm,  $^3J_{\text{FF}} = 110$  Hz, 1 F) and 90.7 (tm,  $J_{\text{FF}} = 47$  Hz, 1 F);  $\text{CF}=\text{CF}$  165.5 (m, 2 F);  $=\text{CF}_2$  108.6 (m, 2 F);  $\text{CF}=\text{CF}_2$  189.7 (dm,  $^3J_{\text{FF}} = 110$  Hz, 1 F);  $\text{CHF}_2$  127.7 (m, 2 F). IR Spectrum,  $\text{cm}^{-1}$ : 920 w, 950 w, 975 ms, 995 ms, 1 076 s, 1 110 s, 1 140 s, 1 167 ms, 1 188 ms, 1 237 s, 1 270 w, 1 303 s, 1 357 s, 1 390 m, 1 408 m, 1 732 w, 1 790 s. Mass spectrum (ions  $m/z$  / rel. intensity):  $\text{M}^+$  244/56, 245/4,  $(\text{M}-\text{F})^+$  225/13,  $\text{C}_6\text{HF}_7^+$  206/1.5,  $\text{C}_6\text{F}_7^+$  205/1.5,  $\text{C}_5\text{F}_7^+$  193/37, 194/26,  $\text{C}_5\text{F}_6^+$  174/19, 175/65,  $\text{C}_4\text{F}_6^+$  162.3, 163/11,  $\text{C}_5\text{F}_5^+$  155/15, 156/4,  $\text{C}_4\text{F}_5^+$  143/27, 144/27,  $\text{C}_3\text{F}_5^+$  131/78,  $\text{C}_4\text{F}_4^+$  124/16, 125/27,  $\text{C}_3\text{F}_4^+$  112/9, 113/67,  $\text{C}_3\text{F}_3^+$  105/4.5, 106/9,  $\text{C}_3\text{F}_2^+$  74/10, 75/33,  $\text{CF}_3^+$  69/89,  $\text{CHF}_2^+$  51/100,  $\text{C}_2\text{F}^+$  43/21,  $\text{CF}^+$  31/53.

## Addition of Primary Alcohols to Chlorodiene I

A solution of the diene I in the given alcohol was added dropwise to a stirred solution of sodium alkoxide in the corresponding alcohol (methanol, ethanol, 1-propanol) under cooling with a tetrachloromethane-ethanol-dry ice mixture. After end of the reaction, the mixture was neutralized with dilute hydrochloric acid and diluted with water. The organic layer was separated, dried over molecular sieve (Nalsit 4A) and analyzed by gas-liquid chromatography (15% Carbowax 20M on Chromatone N-AW). For reaction conditions see Table I. The products were isolated by preparative gas-liquid chromatography and their elemental analyses are given in Table II, mass spectra in Table III,  $^1\text{H}$  NMR spectra in Table IV and IR spectra in Table V.

1,6-Dimethoxy-1,1,2,3,4,5,6,6-octafluoro-2,4-hexadiene (Va): *cis,trans*-Isomer:  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  77.6 (dd,  $J_{\text{FF}} = 30$  and 18 Hz, 2 F) and 78.2 (m, 2 F); *cis*- $\text{CF}=\text{CF}$  138.0 (dm,  $J_{\text{FF}} = 36$  Hz, 1 F) and 140.4 (m, 1 F); *trans*- $\text{CF}=\text{CF}$  148.8 (ddtm,  $^3J_{\text{FF}} = 140$  Hz,  $J_{\text{FF}} = 36$  and 18 Hz, 1 F) and 152.3 (dm,  $^3J_{\text{FF}} = 140$  Hz, 1 F). *trans,trans*-Isomer:  $^{19}\text{F}$  NMR spectrum (octadeuteriodioxane),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  75.7 (m, 4 F);  $\text{CF}=\text{CF}$  151.1 (dm,  $^3J_{\text{FF}} = 120$  Hz, 2 F) and 157.8 (dm,  $^3J_{\text{FF}} = 120$  Hz, 2 F).

1,6-Diethoxy-1,1,2,3,4,5,6,6-octafluoro-2,4-hexadiene (Vb): *cis,trans*-Isomer:  $^{19}\text{F}$  NMR spectrum (octadeuteriodioxane),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  73.3 (m, 2 F) and 73.9 (m, 2 F); *cis*- $\text{CF}=\text{CF}$  137.6

TABLE II  
Elemental analyses

Compound	Formula (mol.wt.)	Calculated/Found		
		% C	% H	% F
Va	$\text{C}_8\text{H}_6\text{F}_8\text{O}_2$ (286.1)	33.58	2.11	53.12
		33.59	2.08	52.7
Vb	$\text{C}_{10}\text{H}_{10}\text{F}_8\text{O}_2$ (314.2)	38.23	3.21	48.28
		38.29	3.23	47.90
Vc	$\text{C}_{12}\text{H}_{14}\text{F}_8\text{O}_2$ (342.3)	42.11	4.12	44.41
		42.07	4.36	44.1
VIb	$\text{C}_{10}\text{H}_{10}\text{F}_8\text{O}_2$ (314.2)	38.23	3.21	48.28
		38.12	3.22	48.4
VIc	$\text{C}_{12}\text{H}_{14}\text{F}_8\text{O}_2$ (342.3)	42.11	4.12	44.41
		42.02	4.15	44.5
VIIa	$\text{C}_8\text{H}_7\text{F}_9\text{O}_2$ (306.2)	31.37	2.29	55.88
		31.21	2.43	56.40
VIIb	$\text{C}_{10}\text{H}_{11}\text{F}_9\text{O}_2$ (334.2)	35.94	3.32	51.20
		35.91	3.32	51.60
VIIc	$\text{C}_{12}\text{H}_{15}\text{F}_9\text{O}_2$ (362.3)	40.00	4.17	47.20
		40.16	4.20	47.50

(dm,  $J_{FF} = 36$  Hz, 1 F) and 140.2 (m, 1 F); *trans*-CF=CF 148.3 (ddtm,  $^3J_{FF} = 120$  Hz,  $J_{FF} = 36$  and 18 Hz, 1 F) and 151.2 (dm,  $^3J_{FF} = 120$  Hz, 1 F). *trans,trans*-Isomer:  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  73.9 (m, 4 F); CF=CF 150.9 and 157.7 (dm,  $^3J_{FF} = 125$  Hz, 4 F).

1,4-Dipropoxy-1,1,2,3,4,5,6,6-octafluoro-2,4-hexadiene (Vc): *cis,trans*-Isomer:  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ )  $\delta$  (ppm):  $\text{CF}_2\text{O}$  74.3 (m, 2 F) and 74.9 (m, 2 F); *cis*-CF=CF 137.7 (dm,  $J_{FF} = 38$  Hz, 1 F) and 140.6 (m, 1 F); *trans*-CF=CF 148.4 (ddtm,  $^3J_{FF} = 140$  Hz,  $J_{FF} = 38$  and 19 Hz, 1 F) and 152.1 (dm,  $^3J_{FF} = 140$  Hz, 1 F). *trans,trans*-isomer:  $^{19}\text{F}$  NMR spectrum (octa-deuteriodioxane),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  73.8 (m, 4 F); CF=CF 151.3 (dm,  $^3J_{FF} = 125$  Hz, 2 F) and 157.8 (dm,  $^3J_{FF} = 125$  Hz, 2 F).

1,6-Dimethoxy-1,2,3,3,4,5,6,6-octafluoro-1,4-hexadiene (VIa):  $^{19}\text{F}$  NMR spectrum (octa-deuteriodioxane),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  76.4 (m, 2 F); CF=CF 158.4 (m, 2 F);  $\text{CF}_2$  104.3 (m, 2 F); CF=CFO 111.3 (dtm,  $^3J_{FF} = 120$  Hz,  $^4J_{FF} = 20$  Hz, 1 F); CF=CFO 192.6 (dtm,  $^3J_{FF} = 120$  Hz,  $^3J_{FF} = 20$  Hz, 1 F).

1,6-Diethoxy-1,2,3,3,4,5,6,6-octafluoro-1,4-hexadiene (VIb):  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  75.1 (m, 2 F); CF=CF 158.8 (m, 2 F);  $\text{CF}_2$  105.2 (tm,  $^3J_{FF} = 4J_{FF} = 20$  Hz, 2 F); CF=CFO 190.0 (dtm,  $^3J_{FF} = 120$  and 20 Hz, 1 F); CF=CFO 109.6 (dtm,  $^3J_{FF} = 120$  Hz,  $^4J_{FF} = 20$  Hz, 1 F).

1,6-Dipropoxy-1,2,3,3,4,5,6,6-octafluoro-1,4-hexadiene (VIc):  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  74.2 (m, 2 F); CF=CF 158.7 (m, 2 F);  $\text{CF}_2$  105.5 (tm,  $^3J_{FF} = 4J_{FF} = 20$  Hz, 2 F); CF=CFO 190.5 (dtm,  $^3J_{FF} = 120$  Hz and 20 Hz, 1 F); CF=CFO 109.3 (dtm,  $^3J_{FF} = 120$  Hz,  $^4J_{FF} = 20$  Hz, 1 F).

1,6-Dimethoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene (VIIa):  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ):  $\text{CF}_2\text{O}$  77.4 (m, 2 F); CF=CF 158.6 and 159.4 (dm,  $^3J_{FF} = 140$  Hz, 2 F); =CFCF<sub>2</sub>CHF: 114.9 (m, 2 F); CHF 213.2 (dtm, after decoupling m,  $^2J_{HF} = 44$  Hz,  $^3J_{FF} = 13$  Hz, 1 F); CHF<sub>2</sub>CF<sub>2</sub>O 82.5 and 86.1 (dqm,  $^2J_{FF} = 145$  Hz,  $^3J_{FF} = 4J_{FF} = 12$  Hz, 1 F).

1,6-Diethoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene (VIIb):  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ):  $\text{CF}_2\text{O}$  74.1 (m, 2 F); CF=CF 158.2 and 159.0 (dm,  $^3J_{FF} = 145$  Hz, 1 F); =CFCF<sub>2</sub>CHF 111.8 and 118.6 (dm,  $^2J_{FF} = 295$  Hz, 1 F); CHF 213.8 (dtm, after decoupling tm,  $^2J_{HF} = 44$  Hz,  $^3J_{FF} = 13$  Hz, 1 F); CHF<sub>2</sub>CF<sub>2</sub>O 78.9 and 84.2 (dm,  $^2J_{FF} = 150$  Hz, 2 F).

1,6-Dipropoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene (VIIc):  $^{19}\text{F}$  NMR spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  74.3 (m, 2 F); CF=CF 158.6 and 159.4 (dm,  $^3J_{FF} = 140$  Hz, 1 F); =CFCF<sub>2</sub>CHF 114.7 (m, 2 F); CHF 213.4 (dtm,  $^2J_{HF} = 45$  Hz,  $^3J_{FF} = 12$  Hz, 1 F); CHF<sub>2</sub>CF<sub>2</sub>O 79.0 and 83.7 (dm,  $^2J_{FF} = 145$  Hz, 1 F).

#### Addition of Bromine to Diethers Vb–VIIb

Bromine (0.5 ml) was added to a mixture of Vb–VIIb (1 g; 48% Vb, 18% VIIb and 34% VIIc) in tetrachloromethane (15 ml). After irradiation with a 100 W tungstene lamp for 20 h, the unreacted bromine was removed by washing with sodium hydrogen carbonate solution, the organic layer was dried over magnesium sulfate, filtered and taken down *in vacuo*. According to gas-liquid chromatography, the residue contained two main products which were isolated by adsorption chromatography on a column of silica gel. Elution with light petroleum-chloroform (1–5% chloroform) gave products identified as 1,6-diethoxy-2,3,4,5-tetrabromo-1,1,2,3,4,5,6,6-octafluorohexane (XIV) and 2,3-dibromo-1,6-diethoxy-1,1,2,3,4,4,5,6,6-nonafluorohexane (XV).



TABLE III

Mass spectra of adducts of alcohols to 3-chlorononafluoro-1,5-hexadiene

Compound	Ion $m/z$ / relative intensity
<i>Va</i> <i>cis-trans</i>	$M^+$ 286/7, (M-OCH <sub>3</sub> ) <sup>+</sup> 255/6, C <sub>6</sub> F <sub>8</sub> <sup>+</sup> 229/1·6, C <sub>6</sub> F <sub>7</sub> <sup>+</sup> 205/33, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/11, C <sub>5</sub> F <sub>6</sub> <sup>+</sup> 174/5, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/4·6, C <sub>4</sub> F <sub>5</sub> O <sup>+</sup> 143/20, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 131/8, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/5, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/2, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/14, CH <sub>3</sub> OCF <sub>2</sub> <sup>+</sup> 81/100, CF <sub>3</sub> <sup>+</sup> 69/7, CFO <sup>+</sup> 47/5, C <sub>2</sub> F <sup>+</sup> 43/2, CF <sup>+</sup> 31/4, CHO <sup>+</sup> 29/5·5
<i>Va</i> <i>trans-trans</i>	$M^+$ 286/11, (M-OCH <sub>3</sub> ) <sup>+</sup> 255/6, C <sub>6</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 237/4, C <sub>6</sub> F <sub>7</sub> <sup>+</sup> 205/30, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/13, C <sub>5</sub> F <sub>6</sub> <sup>+</sup> 174/5·5, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/5·5, C <sub>4</sub> F <sub>5</sub> O <sup>+</sup> 159/8, C <sub>5</sub> F <sub>5</sub> <sup>+</sup> 155/7, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/28, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 131/9, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/7, 125/4·5, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/2·5, 113/9, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/18, CH <sub>3</sub> OCF <sub>2</sub> <sup>+</sup> 81/100, CF <sub>3</sub> <sup>+</sup> 69/10, CF <sup>+</sup> 31/5, CHO <sup>+</sup> 29/7
<i>Vb</i> <i>cis-trans</i>	(M-C <sub>2</sub> H <sub>5</sub> O) <sup>+</sup> 269/1·3, C <sub>8</sub> H <sub>6</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 266/2·5, C <sub>6</sub> HF <sub>7</sub> O <sub>2</sub> <sup>+</sup> 238/3, C <sub>6</sub> F <sub>8</sub> <sup>+</sup> 224/1, C <sub>6</sub> F <sub>7</sub> O <sup>+</sup> 221/3, C <sub>6</sub> F <sub>6</sub> O <sub>2</sub> <sup>+</sup> 218/5, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/2·5, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/4, C <sub>5</sub> F <sub>5</sub> <sup>+</sup> 155/2, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/3, C <sub>4</sub> HF <sub>5</sub> <sup>+</sup> 144/2, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/3, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 93/2·5, CF <sub>3</sub> <sup>+</sup> 69/2, C <sub>2</sub> H <sub>5</sub> O <sup>+</sup> 55/1, C <sub>2</sub> F <sup>+</sup> 43/2, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/100, C <sub>2</sub> H <sub>3</sub> <sup>+</sup> 27/10
<i>Vb</i> <i>trans-trans</i>	$M^+$ 314/3·5, (M-OC <sub>2</sub> H <sub>5</sub> ) <sup>+</sup> 269/7, C <sub>8</sub> H <sub>6</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 267/2, C <sub>8</sub> H <sub>5</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 266/2, C <sub>6</sub> HF <sub>7</sub> O <sub>2</sub> <sup>+</sup> 238/10, C <sub>6</sub> F <sub>6</sub> O <sub>2</sub> <sup>+</sup> 218/5, 219/3, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/4, C <sub>5</sub> F <sub>6</sub> O <sup>+</sup> 190/10, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 174/3, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/3, C <sub>5</sub> F <sub>5</sub> <sup>+</sup> 155/13, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/9, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/5, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 112/2·3, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/5, C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 81/7, CF <sub>3</sub> <sup>+</sup> 69/4, C <sub>2</sub> F <sup>+</sup> 43/5, CF <sup>+</sup> 31/2·3, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/100
<i>Vc</i> <i>cis-trans</i>	(M-OC <sub>3</sub> H <sub>7</sub> ) <sup>+</sup> 283/0·6, C <sub>6</sub> F <sub>8</sub> <sup>+</sup> 224/1·5, 225/0·3, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/0·7, C <sub>5</sub> F <sub>6</sub> <sup>+</sup> 174/1·2, 175/0·3, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/3·5, C <sub>5</sub> F <sub>5</sub> <sup>+</sup> 155/2·5, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/1·3, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/1·6, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 117/0·3, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/1·2, 113/1·3, C <sub>4</sub> F <sub>3</sub> <sup>+</sup> 105/0·3, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/1·2, CF <sub>3</sub> <sup>+</sup> 69/1·5, C <sub>3</sub> H <sub>7</sub> O <sup>+</sup> 59/0·6, 57/0·7, 55/0·2, C <sub>3</sub> H <sub>7</sub> <sup>+</sup> 43/100, 41/18, CF <sup>+</sup> 31/1, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/8
<i>Vc</i> <i>trans-trans</i>	$M^+$ 342/0·5, (M+1) <sup>+</sup> 343/0·1, (M-C <sub>3</sub> H <sub>7</sub> O) <sup>+</sup> 283/12, C <sub>6</sub> F <sub>8</sub> <sup>+</sup> 224/1, 225/0·2, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/0·4, C <sub>5</sub> F <sub>6</sub> <sup>+</sup> 174/0·8, C <sub>5</sub> HF <sub>6</sub> <sup>+</sup> 175/0·4, C <sub>5</sub> F <sub>5</sub> <sup>+</sup> 155/1·5, 156/0·2, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/0·8, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/0·8, C <sub>3</sub> HF <sub>4</sub> <sup>+</sup> 113/0·3, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/0·7, CF <sub>3</sub> <sup>+</sup> 69/1·2, C <sub>3</sub> H <sub>7</sub> O <sup>+</sup> 59/0·8, C <sub>3</sub> H <sub>7</sub> <sup>+</sup> 43/100, C <sub>3</sub> H <sub>5</sub> <sup>+</sup> 41/14, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/4
<i>Vla</i>	$M^+$ 286/6, (M-F) <sup>+</sup> 267/3, C <sub>7</sub> H <sub>4</sub> F <sub>8</sub> O <sup>+</sup> 256/3, (M-OCH <sub>3</sub> ) <sup>+</sup> 255/6, C <sub>7</sub> H <sub>3</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 252/3, C <sub>6</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 237/4, C <sub>7</sub> H <sub>3</sub> F <sub>6</sub> O <sup>+</sup> 233/2·5, C <sub>6</sub> F <sub>7</sub> O <sup>+</sup> 221/3, C <sub>6</sub> F <sub>7</sub> <sup>+</sup> 205/29, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/12, C <sub>5</sub> F <sub>6</sub> <sup>+</sup> 174/5, 175/4·7, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/5, C <sub>4</sub> F <sub>5</sub> O <sup>+</sup> 159/8, C <sub>5</sub> F <sub>5</sub> <sup>+</sup> 155/7, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/28, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 131/8, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/6, 125/4, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/2·5, 113/4, C <sub>3</sub> F <sub>3</sub> O <sup>+</sup> 109/8, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/17, 94/5, CH <sub>3</sub> OCF <sub>2</sub> <sup>+</sup> 81/100, CF <sub>3</sub> <sup>+</sup> 69/10, C <sub>2</sub> F <sup>+</sup> 43/6, CF <sup>+</sup> 31/5, CHO <sup>+</sup> 29/7

TABLE III  
(Continued)

Compound	Ion $m/z$ / relative intensity
<i>Vlb</i>	$M^+$ 314/1-3, (M-C <sub>2</sub> H <sub>4</sub> ) <sup>+</sup> 286/0-7, C <sub>8</sub> H <sub>5</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 266/5, 267/1-6, C <sub>6</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 237/1-3, 238/8, C <sub>6</sub> F <sub>7</sub> O <sup>+</sup> 221/3, C <sub>6</sub> F <sub>6</sub> O <sub>2</sub> <sup>+</sup> 218/6, 219/3, C <sub>6</sub> F <sub>5</sub> O <sub>2</sub> <sup>+</sup> 199/3, 200/1-2, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/5, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/11, 172/3, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 165/1-7, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/5, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 131/3, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/2-4, 125/1-4, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/2, 113/2, C <sub>3</sub> F <sub>3</sub> O <sup>+</sup> 109/3, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/5, C <sub>2</sub> F <sub>3</sub> <sup>+</sup> 81/1, CF <sub>3</sub> <sup>+</sup> 69/3, C <sub>2</sub> H <sub>5</sub> O <sup>+</sup> 45/3, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/100
<i>Vlc</i>	(M-C <sub>3</sub> H <sub>7</sub> ) <sup>+</sup> 283/0-4, C <sub>6</sub> F <sub>8</sub> <sup>+</sup> 224/0-4, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/0-5, C <sub>5</sub> F <sub>5</sub> <sup>+</sup> 155/0-7, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/0-8, C <sub>5</sub> F <sub>5</sub> O <sup>+</sup> 171/0-4, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 131/0-3, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/0-6, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/1, CF <sub>3</sub> <sup>+</sup> 69/0-8, C <sub>3</sub> H <sub>7</sub> O <sup>+</sup> 59/0-9, 57/0-7, 55/0-3, C <sub>3</sub> H <sub>7</sub> <sup>+</sup> 43/100, 41/19, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/4
<i>VIIa</i>	$M^+$ 306/2-3, (M-OCH <sub>3</sub> ) <sup>+</sup> 275/2, C <sub>7</sub> H <sub>4</sub> F <sub>9</sub> O <sup>+</sup> 273/3, C <sub>6</sub> F <sub>7</sub> O <sup>+</sup> 221/7, C <sub>6</sub> F <sub>6</sub> O <sub>2</sub> <sup>+</sup> 218/4, 219/0-7, C <sub>6</sub> F <sub>7</sub> <sup>+</sup> 205/2, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/5, C <sub>6</sub> HF <sub>6</sub> <sup>+</sup> 187/3, C <sub>5</sub> HF <sub>6</sub> <sup>+</sup> 175/2-5, C <sub>4</sub> F <sub>5</sub> O <sup>+</sup> 159/14, C <sub>4</sub> HF <sub>5</sub> <sup>+</sup> 144/5, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/68, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/2, 113/9, C <sub>3</sub> F <sub>3</sub> O <sup>+</sup> 109/8, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/10, 94/14, CH <sub>3</sub> OCF <sub>2</sub> <sup>+</sup> 81/100, 82/5, CF <sub>3</sub> <sup>+</sup> 69/7, C <sub>2</sub> FO <sup>+</sup> 59/2-3, 60/4-4, CFO <sup>+</sup> 47/5, C <sub>2</sub> F <sup>+</sup> 43/2-6, CF <sup>+</sup> 31/3-4 CHO <sup>+</sup> 29/5
<i>VIIb</i>	(M-C <sub>2</sub> H <sub>4</sub> ) <sup>+</sup> 287/1-4, 286/0-7, C <sub>6</sub> H <sub>2</sub> F <sub>8</sub> O <sub>2</sub> <sup>+</sup> 258/2, C <sub>6</sub> H <sub>2</sub> F <sub>7</sub> O <sub>2</sub> <sup>+</sup> 239/1-5, 238/6, C <sub>6</sub> HF <sub>6</sub> O <sub>2</sub> <sup>+</sup> 219/1-3, C <sub>5</sub> HF <sub>7</sub> O <sup>+</sup> 210/2, 209/1-5, C <sub>5</sub> HF <sub>5</sub> O <sup>+</sup> 172/1-3, C <sub>5</sub> HF <sub>4</sub> O <sub>2</sub> <sup>+</sup> 169/1-5, C <sub>4</sub> F <sub>5</sub> <sup>+</sup> 143/1, 144/1-1, C <sub>3</sub> F <sub>5</sub> <sup>+</sup> 131/1, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/1, 113/1-1, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/1-5, C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> 82/1, CF <sub>3</sub> <sup>+</sup> 69/1-4, C <sub>2</sub> H <sub>5</sub> O <sup>+</sup> 45/2-5, C <sub>2</sub> F <sup>+</sup> 43/2, CF <sup>+</sup> 31/1-6, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/100
<i>VIIc</i>	C <sub>6</sub> HF <sub>8</sub> O <sup>+</sup> 241/0-1, C <sub>5</sub> F <sub>7</sub> <sup>+</sup> 193/0-2, C <sub>5</sub> HF <sub>6</sub> <sup>+</sup> 175/0-4, C <sub>4</sub> F <sub>4</sub> <sup>+</sup> 124/0-9, 125/0-3, C <sub>3</sub> F <sub>4</sub> <sup>+</sup> 112/0-6, 113/0-8, C <sub>3</sub> F <sub>3</sub> <sup>+</sup> 93/1-3, C <sub>2</sub> HF <sub>3</sub> <sup>+</sup> 82/0-7, CF <sub>3</sub> <sup>+</sup> 69/1, C <sub>3</sub> H <sub>7</sub> O <sup>+</sup> 59/0-9, C <sub>3</sub> H <sub>7</sub> <sup>+</sup> 43/100, CF <sup>+</sup> 31/1, C <sub>2</sub> H <sub>5</sub> <sup>+</sup> 29/6

Compound *XIV* was prepared also by addition of bromine to pure diethoxyhexadiene *Vb*. The obtained product was identified by gas-liquid chromatography using an authentic standard.  $^1\text{H}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CH}_3$  1.34 (t,  $^3J_{\text{HH}} = 7$  Hz, 3 H);  $\text{CH}_2$  4.10 (q,  $^3J_{\text{HH}} = 7$  Hz, 2 H).  $^{19}\text{F}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  84.0 and 87.0 (dm,  $^2J_{\text{FF}} = 145$  Hz, 4 F);  $\text{CFBr}$  135.0 and 143.7 (m, 2 F). IR Spectrum ( $\text{cm}^{-1}$ ): 480 vw, 633 w, 857 m, 885 m, 915 m, 1027 s, 1085 s, 1108 vs, 1170 s, 1212 vs, 1235 vs, 1280 vs, 1378 ms, 1400 w, 1447 w, 1482 w, 2875 vw, 2920 w, 2940 w. Mass spectrum (ions  $m/z$  / relative intensity):  $\text{C}_6\text{BrF}_7\text{O}_2^+$  316/0.3 and 318/0.3,  $\text{C}_{10}\text{H}_{10}\text{F}_8\text{O}^+$  314/0.6,  $\text{C}_7\text{H}_5\text{BrF}_6\text{O}^+$  300/1 and 298/1,  $\text{C}_8\text{H}_5\text{F}_8\text{O}^+$  269/2,  $\text{C}_8\text{H}_5\text{F}_7\text{O}_2^+$  266/2,  $\text{C}_6\text{HF}_7\text{O}_2^+$  238/3.7,  $\text{C}_6\text{F}_7\text{O}^+$  221/2,  $\text{C}_6\text{F}_6\text{O}_2^+$  218/3.6,  $\text{C}_5\text{F}_7^+$  193/2.4,  $\text{C}_5\text{F}_6^+$  174/1.6,  $\text{C}_5\text{F}_5\text{O}^+$  171/4.3,  $\text{C}_5\text{F}_5^+$  155/2.7,  $\text{C}_4\text{HF}_5^+$  144/1, 143/3,  $\text{C}_3\text{F}_5^+$  131/1,  $\text{C}_3\text{F}_4^+$  124/3.4,  $\text{C}_2\text{H}_5\text{OCF}_2^+$  95/8,  $\text{C}_3\text{F}_3^+$  93/3.1,  $\text{CF}_3^+$  69/3,  $\text{CFO}^+$  47/1.6,  $\text{C}_2\text{H}_5\text{O}^+$  45/1.7,  $\text{C}_2\text{F}^+$  43/27,  $\text{C}_2\text{H}_3^+$  29/100,  $\text{C}_2\text{H}_3^+$  27/15.

Compound *XV* was prepared also by addition of bromine to pure diethoxyhexene *VIIIb*. The product was identified by gas-liquid chromatography using an authentic standard.  $^1\text{H}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CH}_3$  1.35 (t,  $^2J_{\text{HH}} = 7$  Hz, 3 H);  $\text{CH}_2$  4.06 and 4.10 (q,  $^3J_{\text{HH}} = 7$  Hz, 2 H).  $^{19}\text{F}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  73.4–82.5 (m, 4 F);  $\text{CF}_2\text{CHF}$  108–118 (m, 2 F);  $\text{CFBr}$  124.0 and 126.0 (m, 2 F);  $\text{CHF}$  206.0 (m, 1 F). IR Spectrum ( $\text{cm}^{-1}$ ): 540 w, 650 mw, 663 m, 670, 688 m, 840 m, 928 m, 1025 s, 1063 s, 1090 s, 1118 s, 1135 s, 1175 s, 1215 vs, 1270 vs, 1308 s, 1380 s, 1447 w, 1458 w, 1483 w, 2880 vw, 2920 w, 2940 w, 2995 m. Mass spectrum (principal ions  $m/z$  / relative intensity):  $\text{C}_6\text{BrF}_7\text{O}_2^+$  316/0.5, and 318/0.5,  $\text{C}_7\text{H}_5\text{BrF}_6\text{O}^+$  298/1.3 and 300/1.3,  $\text{C}_8\text{H}_6\text{F}_8\text{O}_2^+$  286/0.8,  $\text{C}_5\text{H}_5\text{BrF}_5\text{O}_2^+$  271/0.8 and 273.08,  $\text{C}_5\text{H}_5\text{BrF}_5\text{O}^+$  251/0.8 and 253/0.8,  $\text{C}_6\text{HF}_6\text{O}_2^+$  219/1.3,  $\text{C}_5\text{F}_7^+$  193/1.5,  $\text{C}_5\text{HF}_6\text{O}^+$  191/2.1,

TABLE IV

 $^1\text{H}$  NMR Spectra of adducts of alcohols to 3-chlorononafluoro-1,5-hexadiene

Proton <sup>a</sup>	$Va^b$	$Vb^b$	$Vc^b$	$Va^c$	$Vb^c$	$Vc^c$	$VIa$	$VIb$	$VIc$	$VIIa$	$VIIb$	$VIIc$
$\text{CH}_3$	3.65	1.26	1.00	3.70	1.35	0.98	3.66	1.32	1.00	3.69	1.26	1.00
	(s)	(t)	(m)	(s)	(t)	(t)	(s)	(m)	(m)	(s)	(m)	(m)
	3.69	1.32	—	—	—	—	3.70	—	—	3.93	—	—
	(s)	(t)	—	—	—	—	(s)	—	—	(s)	—	—
$\text{CH}_2$	—	—	1.72	—	—	1.74	—	—	1.70	—	—	1.75
	—	—	(m)	—	—	(m)	—	—	(m)	—	—	(m)
$\text{CH}_2\text{O}$	—	4.09	3.96	—	4.07	3.95	—	4.03	3.93	—	4.16	3.95
	—	(q)	(m)	—	(q)	(t)	—	(q)	(t)	—	(m)	(t)
	—	4.10	—	—	—	—	—	4.05	3.95	—	—	4.25
	—	(q)	—	—	—	—	—	(q)	(t)	—	—	(t)
$\text{CHF}$	—	—	—	—	—	—	4.84	4.82	4.84	—	—	—
	—	—	—	—	—	—	(dm)	(dm)	(dm)	—	—	—
$^2J_{\text{HF}}$	—	—	—	—	—	—	44	44	45	—	—	—
$^3J_{\text{HH}}$	—	7	—	—	7	7	—	7	7	—	—	—

<sup>a</sup> Chemical shifts in ppm, coupling constants in Hz; <sup>b</sup> *cis,trans*-isomer; <sup>c</sup> *trans,trans*-isomer.

$C_5HF_5O^+$  172/1.2,  $C_4F_6^+$  162/1.5, 163/0.7,  $C_4HF_5^+$  144/1,  $C_3F_5^+$  131/2,  $C_4F_4^+$  124/3.4,  $C_2H_5$ .  
 $.OCF_2^+$  95/11,  $C_3F_3^+$  93/2.5,  $CF_3^+$  69/3,  $CFO^+$  47/1.6,  $C_2H_5O^+$  45/3,  $C_2F^+$  43/2,  $C_2H_5^+$   
 29/100.

#### Hydrolysis of Mixture of Diethers *Vc*–*VIIc*

A mixture of the title diethers (3 g; 42% *Vc*, 24% *VIc*, and 34% *VIIc*), dichloromethane (10 ml) and 90% sulfuric acid (10 ml) was refluxed with stirring for 4 h. The organic layer was separated, washed with water, dried over magnesium sulfate, filtered, and the solvent was evaporated *in vacuo*. The obtained mixture (2.5 g) contained three principal products which were separated by preparative gas–liquid chromatography on poly(propylene sebacate):

*Propyl 2,3,4,4,5,6,6-heptafluoro-6-propyloxy-2-hexenoate* (XI) represented 63% of the product. Its formation from dipropyloxyhexene *VIIc* was confirmed by hydrolysis of pure *VIIc* (50 mg) with 90% sulfuric acid in boiling dichloromethane.  $^1H$  NMR Spectrum ( $C^2HCl_3$ ),  $\delta$  (ppm):  $CH_3$  0.96 (m, 6 H);  $CH_2$  1.68 (m, 4 H);  $CH_2O$  3.90 (t,  $^3J_{HH} = 7$  Hz, 2 H) and 4.20 (t,  $^3J_{HH} = 7$  Hz, 2 H).  $^{19}F$  NMR Spectrum ( $C^2HCl_3$ ),  $\delta$  (ppm):  $CF_2O$  77.7 and 82.1 (dm,  $^2J_{FF} = 145$  Hz, 2 F);  $CF_2$  113.6 (m, 2 F);  $CF=CF$  147.6 (dt,  $^3J_{FF} = 135$  Hz,  $J_{FF} = 10$  Hz, 1 F) and 155.0 (dtd,  $^3J_{FF} = 135$  Hz,  $J_{FF} = 25$  Hz and 6 Hz, 1 F);  $CHF$ . IR Spectrum ( $cm^{-1}$ ): 1 745 s ( $\nu(C=O)$ ), 1 733 mw( $\nu(CF=CF)$ ). Mass spectrum (principal ions  $m/z$  / relative intensity):  $(M-C_3H_6)^+$  298/0.4,  $(M-C_3H_7O)^+$  281/0.4,  $(M-C_6H_{14})^+$  256/6,  $C_6H_2F_6O_3^+$  236/9,  $C_5H_2F_4O_2^+$  170/0.4, 169/0.4,  $C_4HF_5^+$  144/0.5,  $C_4HF_4O^+$  140/1,  $C_4F_3O_2^+$  137/0.8,  $C_3F_4^+$  112/2, 113/1.6,  $C_3H_7OCF_2^+$  109/0.5,  $C_3F_3^+$  83/11,  $C_2HF_3^+$  82/0.7,  $C_3HF_2^+$  75/0.7,  $CF_3^+$  69/0.7,  $C_3H_7O^+$  59/1.2, 58/0.5, 57/1,  $C_2HF^+$  44/4,  $C_3H_7^+$  43/100, 42/10, 41/14,  $CF^+$  31/1.7.

*Dipropyl 2,3,4,5-tetrafluoro-2,4-hexadienedioate* (IX) (20% of the product) was formed by hydrolysis of pure *Vc*.  $^1H$  NMR Spectrum ( $C^2HCl_3$ ), (ppm):  $CH_3$  0.96 (m, 3 H);  $CH_2$  1.73 (m, 2 H);  $CH_2O$  4.22 (m, 2 H).  $^{19}F$  NMR Spectrum ( $C^2HCl_3$ ),  $\delta$  (ppm): *cis*- $CF=CF$  130.3 (ddd,  $J_{FF} = 41$  Hz, 9 Hz and 6 Hz, 1 F) and 135.3 (q,  $J_{FF} = 6$  Hz, 1 F); *trans*- $CF=CF$  139.0 (ddd,  $^3J_{FF} = 135$  Hz,  $J_{FF} = 41$  Hz and 6 Hz, 1 F) and 146.8 (ddd,  $^3J_{FF} = 135$  Hz,  $J_{FF} = 9$  Hz and 6 Hz, 1 F). IR

TABLE V

Characteristic absorption bands ( $cm^{-1}$ ) in the IR spectra of adducts *V*–*VII*

Compound	$Va^a$	$Vb^a$	$Va^b$	$Va^b$	$Vb^b$	$Vc^b$
$\nu(CF=CF)$	1 746 w 1 707 mw	1 743 w 1 705 w	1 746 w 1 705 w	1 750 w	1 735 w	1 748 w
Compound	<i>VIa</i>	<i>VIIb</i>	<i>VIIc</i>	<i>VIIa</i>	<i>VIIb</i>	<i>VIIc</i>
$\nu(CF=CF)$	1 755 ms	1 750 ms	1 750 ms	1 745 w	1 740 w	1 752 w

<sup>a</sup> *cis,trans*-isomer; <sup>b</sup> *trans,trans*-isomer.

Spectrum ( $\text{cm}^{-1}$ ): 1 750 vs ( $\nu(\text{C}=\text{O})$ ), 1 708 w ( $\nu(\text{CF}=\text{CF})$ ). Mass spectrum (principal ions  $m/z$  / relative intensity):  $(\text{M}-\text{C}_3\text{H}_6)^+$  256/0.5,  $(\text{M}-\text{C}_3\text{H}_7\text{O})^+$  239/0.8,  $\text{C}_9\text{H}_7\text{F}_3\text{O}_4^+$  236/1,  $\text{C}_6\text{H}_2\text{F}_4\text{O}_2^+$  214/12, 215/1.3,  $\text{C}_6\text{HF}_3\text{O}_2^+$  194/4.5,  $\text{C}_5\text{HF}_4\text{O}_2^+$  169/13,  $\text{C}_4\text{HF}_4\text{O}^+$  141/0.8,  $\text{C}_4\text{F}_4^+$  124/4, 125/0.6,  $\text{C}_4\text{F}_3\text{O}^+$  121/0.8,  $\text{C}_3\text{HF}_4^+$  113/0.7,  $\text{C}_4\text{F}_3^+$  105/1.4,  $\text{C}_3\text{F}_3^+$  93/3,  $\text{C}_3\text{F}_2^+$  74/1.75/1.5,  $\text{CF}_3^+$  69/0.6,  $\text{C}_3\text{H}_7\text{O}^+$  59/0.7, 57/0.5, 55/0.4,  $\text{C}_2\text{HF}^+$  44/4,  $\text{C}_3\text{H}_7^+$  43/100, 41/25, 39/5,  $\text{CF}^+$ , 31/2.

*Dipropyl 2,3,4,4,5-pentafluoro-2-hexenedioate* (X) (17% of the product) was formed both by hydrolysis of the compound *VIc* as a sole product and by hydrolysis of the diether *VIIc* together with the ester *XI*, as confirmed by hydrolysis of the pure compounds *VIc* and *VIIc* (50 mg).  $^1\text{H}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CH}_3$  1.01 (m, 6 H);  $\text{CH}_2$  1.77 (m, 4 H);  $\text{CH}_2\text{O}$  4.28 (m, 4 H); CHF 5.24 (dt,  $^2J_{\text{HF}} = 46$  Hz,  $^3J_{\text{HF}} = 11$  Hz, 1 H).  $^{19}\text{F}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}=\text{CFCO}$  145.7 (dt,  $^3J_{\text{FF}} = 135$  Hz,  $^4J_{\text{FF}} = 9$  Hz, 1 F);  $\text{CF}=\text{CFCO}$  154.4 (dtd,  $^3J_{\text{FF}} = 135$  Hz and 24 Hz,  $^4J_{\text{FF}} = 3.5$  Hz, 1);  $\text{CF}_2$  113.3 (m, 2 F); CHF 204.0 (dtm, after decoupling tm,  $^2J_{\text{HF}} = 46$  Hz,  $^3J_{\text{FF}} = 15$  Hz, 1 F). IR Spectrum ( $\text{cm}^{-1}$ ): 1 745 vs ( $\nu(\text{C}=\text{O})$ ). Mass spectrum (principal ions  $m/z$  / relative intensity):  $(\text{M}-\text{C}_3\text{H}_6)^+$  276/3,  $(\text{M}-\text{C}_3\text{H}_6-\text{HF})^+$  256/0.8,  $\text{C}_6\text{H}_2\text{F}_5\text{O}_4^+$  233/8, 234/5.5,  $\text{C}_6\text{HF}_5\text{O}_3^+$  216/2,  $\text{C}_6\text{HF}_4\text{O}_4^+$  213/7,  $\text{C}_5\text{H}_2\text{F}_5\text{O}_2^+$  189/2.5,  $\text{C}_5\text{H}_2\text{F}_4\text{O}_2^+$  170/0.7,  $\text{C}_5\text{HF}_3\text{O}_2^+$  150/0.7,  $\text{C}_4\text{HF}_5^+$  144/1.2,  $\text{C}_4\text{HF}_4\text{O}^+$  141/0.6,  $\text{C}_4\text{HF}_4^+$  125/1,  $\text{C}_4\text{H}_2\text{F}_2\text{O}_2^+$  104/5,  $\text{C}_3\text{F}_3^+$  93/2.4, 94/1.2,  $\text{C}_2\text{HF}_3^+$  82/1,  $\text{C}_3\text{HF}_2^+$  75/5.2,  $\text{CF}_3^+$  69/0.7,  $\text{C}_3\text{H}_7\text{O}^+$  59/1.4,  $\text{C}_2\text{HF}^+$  44/4.5,  $\text{C}_3\text{H}_7^+$  43/100, 41/10, 39/6,  $\text{CF}^+$  31/1.7.

#### 1,6-Dimethoxy-1,1,2,3,4,5,6,6-octafluoro-3-hexene (XIII)

The triene *II* (3 g; 13 mmol) was added dropwise into a solution of sodium (1 g; 44 mmol) in methanol (50 ml) at about  $0^\circ\text{C}$ . The reaction mixture was poured into dilute hydrochloric acid (100 ml), the separated oily layer was washed with water and dried over magnesium sulfate. The crude product (3.2 g) consisted of nine compounds of which the diether *XIII* (85%) was separated by preparative gas-liquid chromatography on poly(propylene sebacate).  $^1\text{H}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CH}_3$  3.65 (s, 6 H); CHF 5.19 (ddt,  $^2J_{\text{HF}} = 42$  Hz,  $^3J_{\text{HF}} = 20$  Hz and 5 Hz, 1 F).  $^{19}\text{F}$  NMR Spectrum ( $\text{C}^2\text{HCl}_3$ ),  $\delta$  (ppm):  $\text{CF}_2\text{O}$  86.5 (ddm,  $^2J_{\text{FF}} = 140$  Hz,  $^3J_{\text{FF}} = 90$  Hz, 4 F); CHF 200.5 (m, 2 F);  $\text{CF}=\text{CF}$  139.9 (m, 2 F). IR Spectrum ( $\text{cm}^{-1}$ ): 708 m, 839 m, 862 m, 875 w, 985 m, 1 035 s, 1 073 vs, 1 085 vs, 1 105 sh, 1 157 vs, 1 225 vs, 1 263 vs, 1 283 s, 1 301 vs, 1 342 s, 1 357 s, 1 455 s, 1 735 m, 2 870 w, 2 973 m, 3 010 w. Mass spectrum (principal ions  $m/z$  / relative intensity below 5%):  $(\text{M}-\text{HF}^+)$  268,  $\text{C}_8\text{H}_7\text{F}_6\text{O}_2^+$  249,  $\text{C}_5\text{F}_9^+$  231,  $\text{C}_6\text{H}_2\text{F}_7^+$  207,  $\text{C}_5\text{H}_5\text{F}_5\text{O}_2^+$  188,  $\text{C}_7\text{H}_4\text{F}_3\text{O}_2^+$  177,  $\text{C}_5\text{HF}_6^+$  175,  $\text{C}_6\text{H}_2\text{F}_5^+$  157,  $\text{C}_5\text{F}_5^+$  155,  $\text{C}_4\text{F}_5^+$  143,  $\text{C}_4\text{H}_2\text{F}_4^+$  126,  $\text{C}_3\text{HF}_4^+$  113,  $\text{C}_4\text{H}_2\text{F}_4^+$  107,  $\text{C}_3\text{F}_4^+$  93, 94,  $\text{CH}_3\text{OCF}_2^+$  81 (100%),  $\text{C}_2\text{HF}_2^+$  63,  $\text{C}_2\text{FO}^+$  59,  $\text{CHF}_2^+$  51,  $\text{CFO}^+$  47,  $\text{CH}_3\text{O}^+$  31.

#### REFERENCES

- Dědek V., Kováč M.: This Journal 44, 2660 (1979).
- Knunyanc I. L., Dyatkin B. L., German L. C.: Dokl. Akad. Nauk SSSR 124, 1065 (1959).
- Dědek V., Chvátal Z.: Czech. 200 953 (1980).
- Kováč M.: Thesis. Prague Institute of Chemical Technology, Prague 1980.
- Ruh R. P., Davis R. A., Allswede K. A.: U.S. 2 705 229 (1955).

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