REACTION OF 3-CHLORONONAFLUORO-1,5-HEXADIENE WITH SODIUM CYANIDE*

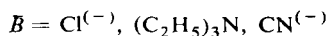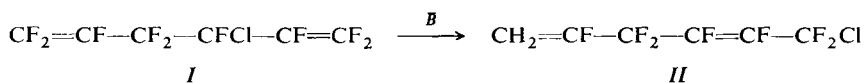Igor LINHART and Václav DĚDEK

Department of Organic Chemistry,
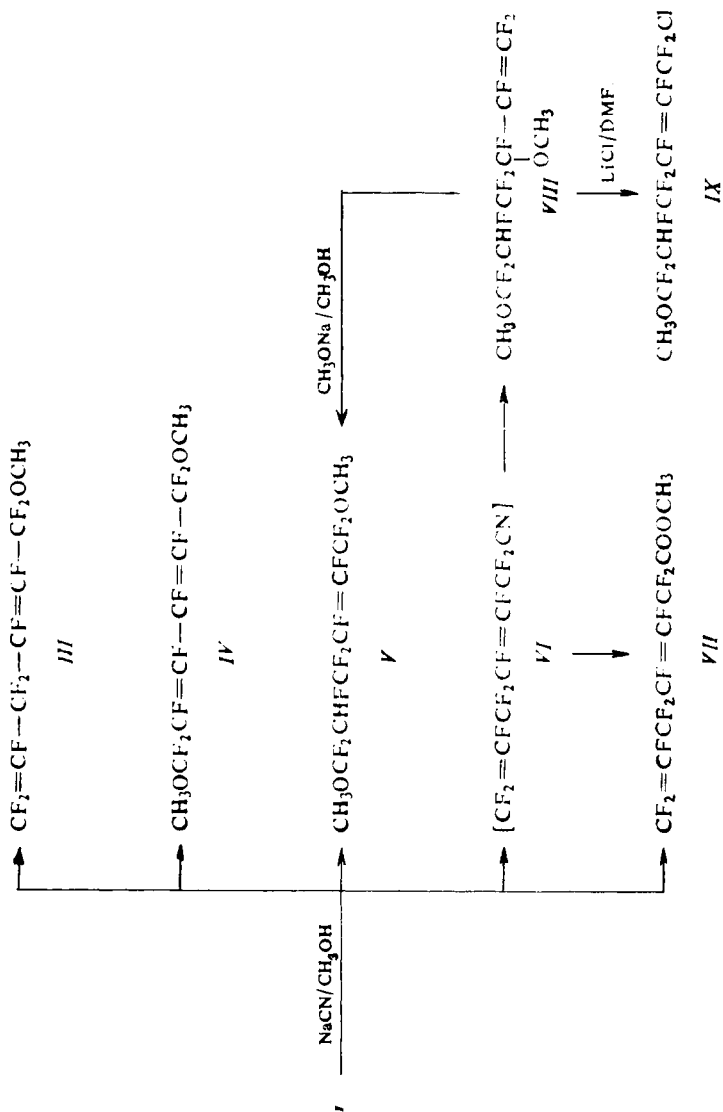*Prague Institute of Chemical Technology, 166 28 Prague*

3-Chlorononafluoro-1,5-hexadiene (*I*) is isomerized into 6-chlorononafluoro-1,4-hexadiene (*II*) by action of basic catalysts as sodium cyanide in anhydrous dimethylformamide, lithium chloride in dimethylformamide, and triethylamine in dioxane or dimethylformamide. Sodium cyanide also catalyzes addition of methanol to the chlorodiene *I*. The reaction course is more complex than in the alkoxide-catalyzed addition of primary alcohols to *I*. 6-Methoxynonafluoro-1,4-hexadiene (*III*), methyl perfluoro-3,6-heptadienoate (*VII*), and 3,6-dimethoxy-1,1,2,3,4,4,5,6,6-nonafluoro-1-hexene (*VIII*) have been isolated besides the known products 1,6-dimethoxy-1,1,2,3,4,5,6,6-octafluoro-2,4-hexadiene (*IV*) and 1,6-dimethoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene (*V*). The hexene *VIII* reacts with sodium methoxide in methanol to give the diether *V*, and with lithium chloride in dimethylformamide it gives 1-chloro-6-methoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene (*IX*). Stereospecificity and mechanism of the reaction are discussed.

Our previous papers dealt with reactions of 3-chlorononafluoro-1,5-hexadiene (*I*) with sodium alkoxides in the corresponding primary alcohols[1] and with diethylamine[2] which are characterized by preferred S_N2' substitution of chlorine in the perfluoroallyl grouping by the nucleophile. In contrast to these findings, the reaction of chlorodiene *I* with sodium cyanide in anhydrous dimethylformamide does not produce the corresponding nitrile, but it gives the product of the allyl rearrangement, 6-chlorononafluoro-1,4-hexadiene (*II*). This rearrangement to chlorodiene *II* is also accomplished by other basic catalysts as *e.g.* triethylamine in dioxane or dimethylformamide and lithium chloride in dimethylformamide.

$$CF_2{=}CF{-}CF_2{-}CFCl{-}CF{=}CF_2 \xrightarrow{B} CH_2{=}CF{-}CF_2{-}CF{=}CF{-}CF_2Cl$$

$$I \qquad\qquad\qquad II$$

$$B = Cl^{(-)}, (C_2H_5)_3N, CN^{(-)}$$

Conditions and results of the isomerizations are given in Table I. The reaction with triethylamine also gives minor amounts of perfluoro-2,4-hexadiene (X) besides the main product II. The reaction of diene I with sodium cyanide in methanol has a more complex course (Scheme 1). It involves both addition of methanol[3] (producing 6-methoxynonafluoro-1,4-hexadiene (III), 1,6-dimethoxy-1,1,2,3,4,5,6,6-octafluoro-2,4-hexadiene[1] (IV), and 1,6-dimethoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene[1] (V))

$$CF_2=CF-CF_2-CF=CF-CF_2OCH_3 \quad (III)$$

$$CH_3OCF_2CF=CF-CF=CF-CF_2OCH_3 \quad (IV)$$

$$CH_3OCF_2CHFCF_2CF=CFCF_2OCH_3 \quad (V)$$

$$[CF_2=CFCF_2CF=CFCF_2CN] \quad (VI)$$

$$CF_2=CFCF_2CF=CFCF_2COOCH_3 \quad (VII)$$

$$CH_3OCF_2CHFCF_2CF-CF=CF_2 \atop | \atop OCH_3 \quad (VIII)$$

$$CH_3OCF_2CHFCF_2CF=CFCF_2Cl \quad (IX)$$

NaCN/CH$_3$OH

CH$_3$ONa/CH$_3$OH

LiCl/DMF

SCHEME 1

and reaction of diene *I* with cyanide anion giving the transient perfluoro-3,6-hepta-dienenitrile *(VI)* which — at the reaction conditions — undergoes methanolysis to give methyl perfluoro-3,6-heptadienoate *(VII)*. Another isolated product was 3,6-dimethoxy-1,1,2,3,4,4,5,6,6-nonafluoro-1-hexene *(VIII)* which is not produced by methoxide-catalyzed addition of methanol[1]. Its formation is explained by attack of methoxide anion on the transition state of the allyl substitution of chlorine by cyanide and subsequent decomposition of the activated complex with releasing of chloride and cyanide ions. Direct S_N2 substitution of halogen in perfluoroalkyl halides is little likely, because it requires extreme conditions[4]. Conditions and results of the reaction are given in Table II.

Methoxyl group at 3 position of hexene *VIII* easily undergoes S_N2' substitution. With lithium chloride in dimethylformamide it gives 1-chloro-6-methoxy-1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene *(IX)*, and with sodium methoxide in methanol it is isomerized to diether *V* (Scheme 1). The intermediate nitrile *VI* could not be prepared at the conditions analogous to those of preparation of perfluoro-3-butenenitrile from per-fluoroallyl chloride[5], neither could it be prepared by addition of cyanide to the fluorinated olefinic double bond[6]. In both cases the starting diene underwent rapid carbonization.

According to ^{19}F NMR spectra, the products *II, III, V, VII*, and *IX* obtained by substitution reactions of the dienes *I* and *VIII* unambiguously possess *trans* configuration. Such stereospecific course of allyl substitutions was also observed in the reactions of chlorodiene *I* with other nucleophiles[1,2]. We presume that it cannot be explained by higher thermodynamic stability of the isomer formed, because *cis* isomers are usually more stable in the case of perfluoroallyl halides (the so-called *cis* effect of fluorine[7]), but by lower energy of the corresponding transition state. This presumption corresponds with planar transition states *XIa,b* involving simul-

TABLE I

Conditions and results of isomerization of chlorodiene *I*

Diene *I* g mmol^{-1}	Solvent ml	Reagent g	Temperature °C	Reaction time h	Conversion %	Yield^a %
1·5/5·4	DMF^b (10)	LiCl (0·5)	20	0·5	100	100
12/43·2	DMF (65)	NaCN (3)	4—5	3	100	100
2/1·08	dioxane (20)	$(C_2H_5)_3N$ (2)	20	6	91	71
4/14·4	DMF (30)	$(C_2H_5)_3N$ (1)	40	6	61	52

^{a} Determined by GLC analysis of the reaction mixture; ^{b} dimethylformamide.

TABLE II

Conditions and results of the reaction of chlorodiene I with sodium cyanide in methanol

Chlorodiene I g mmol^{-1}	Sodium cyanide g	Methanol ml	Reaction time h	Temperature °C	Conversion %	Yield g	Products, %				
							III	IV	V	VII	VIII
10/36	1·0	90	1·5	−35 to −40	20	1·1	20	36	7	17	20
10/36	1·2	100	1·5	−30 to −35	32	1·5	14	35	8	21	22
3/10·8	0·8	70	2	−15 to −20	55	0·6	14	34	8	21	23
3/10·8	0·8	70	2	−35 to −45	63	0·8	14	36	6	20	24
3/10·8	0·8	70	5	−30 to −45	66	1·0	16	36	9	15	24
3/10·8	0·8	70	1·5	− 3 to 0	70	0·9	13	26	6	30	24
5/18	1·0	80	1·5	− 3 to 0	70	4·0	14	27	7	28	24
6/22	1·0	90	2	−33 to −40	73	4·4	9	27	5	27	27

taneous existence of the partial bonds $Nu\cdots C_{(1)}$ and $Cl\cdots C_{(3)}$, *i.e.* synchronous or pseudosynchronous S_N2' mechanism.

XIa   *XIb*
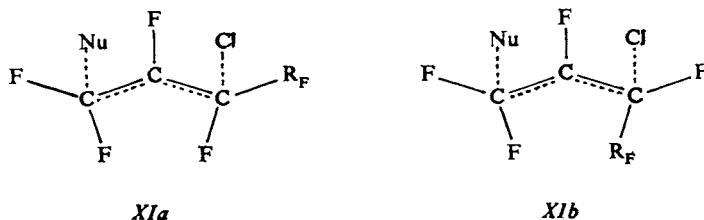
As the transition state *XIb* is more sterically hindered than *XIa*, the nucleophilic substitution in the perfluoroallyl system of diene *I* preferably gives *trans* isomers. The condition of planarity is also fulfilled by the carbocation formed by monomolecular splitting off of chloride anion from diene *I*. Such monomolecular splitting, however, would result in isomerization of chlorodiene *I* into diene *II*, which was not observed even after long-term standing of chlorodiene *I* in dipolar aprotic solvents (dioxane, dimethylformamide). Hence, the observed stereospecificity of substitution of chlorine in the perfluoroallyl grouping indicates synchronous or, more likely, pseudosynchronous S_N2' process with maintained planarity of the transition state, and it contrasts with the non-stereospecific course of nucleophilic addition to an isolated trifluorovinyl group *via* discrete intermediate carbanion[1,2,8].

EXPERIMENTAL

The temperature data are not corrected. The IR spectra were measured with a Perkin–Elmer 325 apparatus in tetrachloromethane; the NMR spectra were measured with a Varian XL 100 at 35°C in octadeuteriodioxane (if not stated otherwise) using tetramethylsilane (^{1}H NMR) and trichlorofluoromethane (^{19}F NMR) as internal standards. The mass spectra were measured with an LKB 9000 spectrometer. Both analytical and preparative GLC were carried out with a Chrom 3 apparatus using silicone elastomer SE 30 or E 301, and nitrogen as the carrier gas.

6-Chlorononafluoro-1,4-hexadiene (*II*)

A) *By reaction of* I *with sodium cyanide*: 12 g (43 mmol) chlorodiene *I* was added dropwise to a solution of 3 g (60 mmol) sodium cyanide in 65 ml anhydrous dimethylformamide with cooling below 10°C. Thereafter the mixture was stirred at 4–5°C 3 h. According to GLC the conversion of the starting diene was practically 100%. The single product — chlorodiene *II* — was distilled from the reaction mixture in vacuum and condensed in a cooling trap cooled with acetone–dry ice mixture. The product was redistilled at atmospheric pressure to give 9·5 g (80%) *II*, b.p. 74–76°C. For C_6ClF_9 (278·5) calculated: 25·87% C, 12·73% Cl, 61·40% F; found: 25·89% C, 12·34% Cl, 62·36% F. ^{19}F NMR spectrum (δ ppm): CF_2Cl: 58·0 (m, 2 F); CF=CF: 155·4 and 156·1 (dm, $^3J_{FF} = 135$ Hz, 2 F); CF_2: 107·1 (m, 2 F); CF_2=CF : 190·1 (dm, $^3J_{FF} = 115$ Hz, 1 F); CF_2=CF: 90·7 (ddm (tm), $J_{FF} = 50$ Hz, 1 F); and 106·0 (m, 1 F). IR spectrum

(cm^{-1}): 1 735 vw (ν(CF=CF)), 1 790 s (ν(CF$_2$=CF)). Mass spectrum (the main ionic species m/z/ relative intensity in %): M$^+$ 278/20 and 280/6·4, (M—F)$^+$ 259/6 and 261/2, (M—Cl)$^+$ 243/83, C$_5$ClF$_6^+$ 209/22 and 211/7, C$_4$ClF$_6^+$ 197/6 and 199/2, C$_5$F$_7^+$ 193/45, C$_5$F$_6^+$ 174/7, C$_4$F$_6^+$ 162/15, C$_5$F$_5^+$ 155/22, C$_3$Cl$^+$F$_4$ 147/30 and 149/10, C$_4$F$_5^+$ 143/75, C$_3$F$_5^+$ 131/73, C$_4$F$_4^+$ 124/21, C$_3$F$_4^+$ 112/10, C$_3$ClF$_2^+$ 109/9 and 111/3, C$_4$F$_3^+$ 105/7, C$_3$F$_3^+$ 93/61, C$_3$F$_2^+$ 74/16, CF$_3^+$ 69/100, C$_2$F$^+$ 43/8, CF$^+$ 31/56.

B) By reaction of I *with lithium chloride*: 1·5 g (5·4 mmol) diene *II* was added to a solution of 0·5 g (12 mmol) annealed lithium chloride in 10 ml anhydrous dimethylformamide, and the mixture was left to stand at room temperature 30 min. According to GLC the conversion of the starting diene was 100% after this time. The single product — chlorodiene *II* — was distilled from the reaction mixture in vacuum and condensed in a vessel cooled with acetone–dry ice mixture. The product was redistilled at atmospheric pressure to give 1·0 g (67%) *II*, b.p. 74—76°C.

C) By reaction of I *with triethylamine in dimethylformamide*: A mixture of 4 g (14 mmol) chlorodiene *I*, 1 g (10 mmol) triethylamine, and 30 ml anhydrous dimethylformamide was heated at 40°C. GLC analysis of the reaction mixture gave the following proportions of the products after 3 h: 57% *I*, 22% *II*, 9% perfluoro-2,4-hexadiene (*X*), and 12% non-identified products; after 6 h: 39% *I*, 32% *II*, 10% *X*, and 19% non-identified products. After 6 h, the mixture was neutralized with hydrochloric acid, volatile products were evaporated in vacuum and condensed in a vessel cooled with acetone–dry ice mixture. The yield of the raw product obtained was 3·1 g.

D) By reaction of I *triethylamine in dioxane*: A mixture of 3 g (11 mmol) chlorodiene *I*, 2 g (20 mmol) triethylamine, and 20 ml anhydrous dioxane was left to react at room temperature 6 h, neutralized with hydrochloric acid (diluted 1 : 3), and diluted with water up to a volume of 100 ml. The separated organic layer (3·1 g) was dried with magnesium sulphate and submitted to GLC analysis using authentic standards. The mixture contained 9% *I*, 65% *II*, and 10% *X*.

trans,trans-Perfluoro-2,4-hexadiene[9] (*X*)

The raw product obtained from diene *I* and triethylamine in dimethylformamide was dried with magnesium sulphate and separated by preparative GLC with the silicone elastomer SE 30 as the stationary phase at the column temperature 20°C. Compound *X* was identified by spectral methods. ^{19}F NMR spectrum (δ ppm): CF$_3$: 68·2 (m, 6 F); CF=CF: 154·5 and 157·2 (dm, $^3J_{FF}$ = 125 Hz, 4 F). IR spectrum (cm^{-1}): 1 712 w (ν(CF=CF)). Mass spectrum (the main ionic species m/z/ relative intesity in %): M$^+$ 262/13, C$_6$F$_9^+$ 243/18, C$_5$F$_8^+$ 212/15, C$_5$F$_7^+$ 193/26, C$_3$F$_5^+$ 131/31, C$_4$F$_4^+$ 124/11, C$_3$F$_4^+$ 112/7, C$_3$F$_3^+$ 93/26, CF$_3^+$ 69/100, CF$^+$ 31/24.

Reaction of Chlorodiene *I* with Sodium Cyanide in Methanol

A suspension of sodium cyanide in methanol was cooled at the temperature given in Table II, and methanolic solution of *I* was added thereto dropwise with constant stirring. The mixture was stirred 1·5 to 5 h (Table II), then it was cooled to −70°C, diluted with diethyl ether to a double volume, and finally treated with 200 ml water. The organic layer was separated, the aqueous layer was extracted with ether, the combined organic phases were washed with saturated solution of calcium chloride and dried with magnesium sulphate. Ether was distilled off through a 15 cm Vigreux column, and the residue was distilled in vacuum in a stream of nitrogen. Thus 5 g diene *I* gave 4 g distillate boiling within the limits from 52°C/4·4 kPa to 80°C/3 kPa and 0·8 g distillation residue. Table II gives relative amounts of products (determined by GLC analysis without calibration). The products were prepared from the distillate by preparative GLC.

6-*Methoxynonafluoro*-1,4-*hexadiene* (III). ^{1}H NMR spectrum (δ ppm): CH$_3$O: 3·69 (s). ^{19}F NMR spectrum (δ ppm): CF$_2$O: 76·3 (m, 2 F); CF=CF: 157·5 and 159·4 (dm, $^3J_{FF}$ = 135 Hz, 2 F); CF$_2$: 106·6 (m, 2 F); CF$_2$=CF: 190·8 (dm, $^3J_{FF}$ = 130 Hz, 1 F); CF$_2$=CF: 90·6 and 105·5 (m, 2 F). IR spectrum (cm^{-1}): 1 752 w (ν(CF=CF)). Mass spectrum (the main ionic species $m/z/$ relative intensity in %): M$^+$ 274/7, (M—F)$^+$ 255/7, (M—CH$_3$O)$^+$ 243/9, C$_6$F$_7$O$^+$ 221/4, C$_5$F$_7^+$ 193/27, C$_4$F$_5^+$ 143/27, C$_3$F$_5^+$ 131/39, C$_3$F$_3^+$ 93/24, CH$_3$OCF$_2^+$ 81/100, CF$_3^+$ 69/33, CH$_3$OH$^+$ 32/20, CHO$_3$$^+$ (CF$^+$) 31/22, CO$^+$ 28/83.

1,6-*Dimethoxy*-1,1,2,3,4,5,6,6-*octafluoro*-2,4-*hexadiene*[1] (IV) *and* 1,6-*dimethoxy*-1,1,2,3,4,4,5,6,6 -*nonafluoro*-2-*hexene*[1] (V) were identified by comparison of their ^{19}F NMR spectra with those of the authentic standards[1].

Methyl perfluoro-3,6-*heptadienoate* (VII). ^{1}H NMR spectrum (δ ppm): CH$_3$OOC: 3·94 (s). ^{19}F NMR spectrum (δ ppm): CF$_2$=CF: 90·1 (m, 1 F) and 105·5 (m, 1 F); CF$_2$=CF: 190·8 (dm, $^3J_{FF}$ = 115 Hz, 1 F); =CFCF$_2$CF=: 106·6 (m, 2 F); CF=CF: 157·6 and 159·1 (dm, $^3J_{FF}$ = 145 Hz, 2 F); CF$_2$COOCH$_3$: 109·9 (m, 2 F). IR spectrum (cm^{-1}): 1 750 s (ν(C=O)), 1 785 s (ν(CF$_2$=CF)). Mass spectrum (the main ionic species $m/z/$ relative intensity in %): (M—COOCH$_3$)$^+$ 243/2, C$_5$F$_7^+$ 193/5, C$_5$F$_5^+$ 155/5, C$_4$F$_5^+$ 143/34, C$_3$F$_5^+$ 131/11, C$_4$F$_4^+$ 124/5, C$_3$F$_3^+$ 93/20, C$_2$F$_3^+$ 81/18, CF$_3^+$ 69/32, (COOCH$_3$)$^+$ 59/100, CH$_3$O$^+$ (CF$^+$) 31/27.

3,6-*Dimethoxy*-1,1,2,3,4,4,5,6,6-*nonafluoro*-1-*hexene* (VIII) was isolated as a mixture of two diastereomeres. ^{1}H NMR spectrum (δ ppm): CH$_3$O: 3·65 (s, 6 H); CHF: 5·51 and 5·53 (dm, $^2J_{HF}$ = 42 Hz, 1 H). ^{19}F NMR spectrum (δ ppm): CF$_2$O: 80·9 and 83·6 (dm, with ^{1}H decoupling dtd (dq), $^2J_{FF}$ = 145 Hz, $^3J_{FF}$ = $^4J_{FF}$ = 12 Hz, 2 F); CHF: 209·1 and 210·0 (dm, with ^{1}H decoupling m, $^2J_{HF}$ = 42 Hz, 1 F); CHF—CF$_2$CF: AB systems 115·9, 123·5, and 114·9, 123·5 (dm, $^2J_{FF}$ = 175 Hz, 2 F); CF$_2$CF(OCH$_3$)—: 134·7 (m, 1 F); CF$_2$=CF: 178·2 (dm, $^3J_{FF}$ = 115 Hz, 1 F); CF$_2$=CF: 90·4 (m, 1 F) and 104·4 (dm, $^3J_{FF}$ = 115 Hz, 1 F). IR spectrum (cm^{-1}): 1 785 s (ν(CF$_2$=CF)). Mass spectrum (the main ionic species $m/z/$ relative intensity in %): (M—CH$_3$O)$^+$ 275/5, C$_5$F$_7^+$ 193/5, C$_4$H$_2$F$_3$O$^+$ 147/55, C$_3$H$_5^+$ 143/17, C$_3$F$_3$O$^+$ 109/10, C$_3$F$_3^+$ 93/22, 94/14, CH$_3$OCF$_2^+$ 81/100, CF$_3^+$ 69/24, C$_2$FO$^+$ 59/12, CHF$_2^+$ 51/10, CFO$^+$ 47/10, CH$_3$OH$^+$ 32/29, CH$_3$O$^+$ (CF$^+$) 31/17.

Verification of Structure of Dimethoxyhexene *VIII*

A) *By reaction with lithium chloride in dimethylformamide*: A solution of 0·5 g (12 mmol) annealed lithium chloride in 7 ml anhydrous dimethylformamide was treated with 150 mg (0·54 mmol) dimethoxyhexene *VIII*, and the mixture was left to stand at room temperature 2 h. According to GLC, conversion of the starting diether was practically 100%. Vacuum distillation gave 0·5 g distillate b.p. 48—55°C/1·9 kPa which, according to GLC, contained 15% of a single product in dimethylformamide. The product was identified as *trans*-1-chloro-6-methoxy-1- -1,1,2,3,4,4,5,6,6-nonafluoro-2-hexene (*IX*) by means of ^{19}F NMR spectrum and mass spectrum taken at the outlet of the GLC column. ^{19}F NMR spectrum (δ ppm): CF$_2$Cl: 58·0 (dd, $^3J_{FF}$ = 27 Hz, $^4J_{FF}$ = 10 Hz, 2 F); CF=CF: 153·8 and 156·4 (dm, $^3J_{FF}$ = 130 Hz, 2 F); =CFCF$_2$. .CHF: 114·0 (m, 2 F); CHF: 213·8 (dm, after dec. m, $^2J_{HF}$ = 44 Hz, 1 F); CF$_2$O: 81·3 and 85·3 (dm, $^2J_{FF}$ = 150 Hz, 2 F). Mass spectrum (the main ionic species $m/z/$ relative intensity in %): M$^+$ 310/4·5 and 312/1·5, (M—Cl)$^+$ 275/15, C$_3$ClF$_4^+$ 147/4·3 and 149/1·4, C$_4$F$_5^+$ 143/22, 144/3·3, C$_3$F$_4^+$ 112/3, 113/0·5, C$_3$F$_3^+$ 93/10, CH$_3$OCF$_2^+$ 81/100, 82/3, C$_2$F$_2$O$^+$ 78/3·3, CH$_3$O$^+$ (CF$^+$) 31/1.

B) *By reaction with sodium methoxide in methanol*: 0·05 g (2·2 mmol) sodium metal was dissolved in 2 ml methanol, and the obtained solution of sodium methoxide was cooled at —10°C

and treated with 100 mg (0·36 mmol) dimethoxyhexene *VIII*. After 10 min, the mixture was diluted with water, neutralized with hydrochloric acid, extracted with ether, and ether was evaporated in vacuum to give 70 mg compound identical with diether *V* (^{1}H and ^{19}F NMR spectra)[1].

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