

## ADDITION REACTIONS OF HALOOLEFINS. XI.\*

REACTION OF TETRAFLUOROETHYLENE  
WITH MONOFLUOROMETHANES IN THE PRESENCE  
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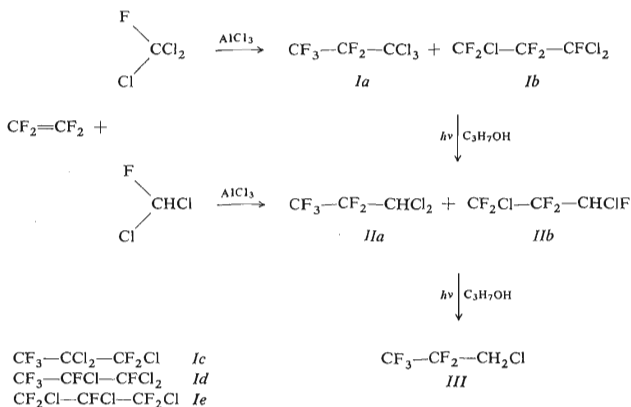
The reaction of tetrafluoroethylene with fluorotrichloromethane in the presence of aluminum chloride gave a mixture of 1,1,1-trichloro- (*Ia*) and 1,1,3-trichloropentafluoropropane (*Ib*) in 83 and 17% relative yields, respectively. Analogous reaction of tetrafluoroethylene with fluorodichloromethane gave a mixture of isomers, 1-hydryl-1,1-dichloro- (*IIa*) and 1-hydryl-1,3-dichloropentafluoropropane (*IIb*), in a relative ratio of 59% to 41%. Tetrafluoroethylene was found more reactive than ethylene during the competitive reaction with trifluorochloroethylene (1.9 times) as was already predicted on the basis of quantum chemical calculations. On photochemical reduction of a mixture of *Ia* and *Ib* in isopropyl alcohol substance *Ia* reacted more easily, giving rise to hydroderivative *IIa*, while on analogous photochemical reduction of a mixture of *IIa* and *IIb* the isomer *IIa* reacted exclusively under formation of 1-chloro-1,1-dihydryl-pentafluoropropane (*III*).

The reactions of tetrafluoroethylene with halomethanes in the presence of aluminum chloride were investigated earlier<sup>1-5</sup>. In particular the reactions of monofluorochloromethanes were mentioned in patent literature<sup>1,2</sup> and in an original paper<sup>3</sup>. At that time the easier splitting of the C—F bond when compared with that of C—Cl bonds in fluorochloromethanes was not known. As we have shown in this series of investigations<sup>6-8</sup> such splitting always takes place during the additions of monofluorochloromethanes in the presence of aluminum chloride. For this reason the conclusions given at that time<sup>3</sup> were not in agreement with the facts. In this paper we study the ionic addition of fluorotrichloromethane and fluorodichloromethane to tetrafluoroethylene with the aim of correcting earlier<sup>3</sup> incorrect conclusions and determining the reactivity of tetrafluoroethylene in relation to other tetrahaloethylenes.

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We carried out the addition of fluorotrichloromethane both at atmospheric pressure<sup>9</sup> and under increased pressure. In the first case<sup>9</sup> when tetrafluoroethylene was passed through a suspension of aluminum chloride in fluorotrichloromethane and carbon tetrachloride the conversion was 30.5%, and the yield of trichloropentafluoropropane (*I*) was almost 100%. When carried out under pressure (see also<sup>3</sup>) the preparative yields of product *I* were 55–60%. The reaction of fluorodichloromethane with tetrafluoroethylene<sup>3</sup> carried out in an analogous manner gave dichloropentafluoropropane (*II*) in a 60% yield. The composition of the addition products *I* and *II* is in agreement with the finding<sup>7,8</sup> that the C—F bond is split easier than the C—Cl bond in halomethane. The reaction of fluorotrichloromethane affords a mixture of 1,1,1-trichloropentafluoropropane (*Ia*) and 1,1,3-trichloropentafluoropropane (*Ib*) in relative amounts of 83% and 17%. Product *II* from the addition of fluorodichloromethane contained a mixture of 1-hydril-1,1-dichloropentafluoropropane (*IIa*) and 1-hydril-1,3-dichloropentafluoropropane (*IIb*) in a 59 : 41 ratio.

The structure of the products *Ia* and *Ib* was proved using gas chromatography, spectrographic, and chemical methods. Gas chromatography mainly helped us to check the structures of compounds *Ia* and *Ib*. For this purpose we prepared the isomers *Ib*–*Ie* (Tables I and II) by independent methods<sup>10</sup>. Under conditions<sup>11</sup> when chromatographic separation of isomers *Ia*–*Ie* took place we proved the identity of the isomer *Ib*, obtained on addition, with the standard. The chromatographic peak which did not coincide with any one of the standards *Ib*–*Ie* was attributed to the isomer *Ia* which represents 83% of the trichloropentafluoropropane (*I*) frac-



tion, the elemental composition of which was confirmed by analysis. The structure of compounds *Ib*–*Ie* followed from the structures of the starting compounds (Table I) which we submitted to fluorination with a mixture of antimony trifluoride and antimony pentachloride, and from the regularities characteristic of the mentioned fluorination<sup>12</sup>, as well as from their IR spectra (Table III). The isomers *Ib*–*Ie* were prepared earlier<sup>13–19</sup> by similar fluorination procedures.

On photochemical reduction of the trichloropentafluoropropane fraction (*I*) in isopropyl alcohol we obtained a mixture of hydro derivatives *Iia* and *Iib* in relative

TABLE I  
Conditions for the Preparation of Trichloropentafluoropropanes *Ib*–*Ie*

Starting material	g (mol)	Fluorination agent, g		Temperature °C Time, h	Product, g (%)	Fraction C <sub>3</sub> Cl <sub>4</sub> F <sub>4</sub> %
		SbF <sub>3</sub> (mol)	SbCl <sub>5</sub> (mol)			
CFCl <sub>2</sub> –CF <sub>2</sub> –CCl <sub>3</sub> <sup>a</sup>	43.3 (0.159)	121 (0.675)	70 (0.234)	80–110 24	<i>Ib</i> 11.5 (30.6)	32.8
CF <sub>3</sub> CCl <sub>2</sub> –CCl <sub>3</sub> <sup>b</sup>	63.2 (0.234)	184 (1.03)	120 (0.401)	80–130 32	<i>Ic</i> 25.2 (46.1)	25.3
CF <sub>3</sub> –CFCl–CCl <sub>3</sub> <sup>c</sup>	29.4 (0.116)	32 (0.179)	35 (0.117)	90–110 14	<i>Id</i> 17.2 (62.3)	—
CF <sub>2</sub> Cl–CFCl–CCl <sub>3</sub> <sup>d</sup>	230 (0.85)	224 (1.25)	220 (0.74)	80–120 21	<i>Ie</i> 57.8 (28.9)	49.4

<sup>a</sup> Ref. 6; <sup>b</sup> Ref. 7; <sup>c</sup> Ref. 10; <sup>d</sup> Ref. 8.

TABLE II  
Analyses, Purity and the Boiling Points of Isomers *Ib*–*Ie*

Substance	B.p., °C	Literature °C (ref.)	Purity <sup>a</sup> % rel.	Isomers <sup>b</sup> % rel.	Found <sup>c</sup>		
					% C	% Cl	% F
<i>Ib</i>	72.5–73.5	72–73 (2.12)	97	83.5 <i>Ib</i> ; 11.5 <i>Ic</i> ; 5 <i>Id</i>	15.32	44.81	40.26
<i>Ic</i>	71–73	71–72 (13.14)	98	100 <i>Ic</i>	14.94	44.83	40.16
<i>Id</i>	72–74	73.5 (15)	98	80 <i>Id</i> ; 20 <i>Ic</i>	14.93	45.08	40.04
<i>Ie</i>	73–74	73.7 (17.18)	99	93 <i>Ie</i> ; 7 <i>Id</i>	14.99	44.56	40.46

<sup>a</sup> Calculated for the mixture of C<sub>3</sub>Cl<sub>3</sub>F<sub>5</sub>; <sup>b</sup> ref. 11; <sup>c</sup> for C<sub>3</sub>Cl<sub>3</sub>F<sub>5</sub> (237.4) calculated: 15.18% C, 44.81% Cl, 40.01% F.

proportion 90% and 10%. The unreacted starting mixture was at the same time enriched by isomer *Ib* (from 17% to 94.5%). The result of the photoreduction showed that the isomer *Ia* with a terminal  $-\text{CCl}_3$  group reacted more rapidly than the isomer *Ib* with a  $-\text{CFCl}_3$  terminal group. On photochemical reduction of a mixture of *Ia* and *Ib* in isopropyl alcohol the  $\text{CHCl}_2$  group of compound *Ia* reacted exclusively, giving rise to 1,1-dihydryl-1-chloropentafluoropropane (*III*). These regularities of photochemical reduction in isopropyl alcohol were observed earlier<sup>20-22</sup> with similar structures.

The structure of compounds *Ia*, *Ib*, and *III* was demonstrated on the basis of PMR spectra, mass spectra, and IR spectra. In the mass spectra of these compounds molecular ions and characteristic fragments are present. The PMR spectrum of compounds *Ia* and *III* contains a triplet corresponding to  $-\text{CF}_2\text{CH}-$  and  $-\text{CF}_2\text{CH}_2-$  grouping, and the spectrum of compound *Ib* contains a doublet of a doublet of doublets characterising<sup>20</sup> the structure  $-\text{CF}_2-\text{CHFCl}$ . In the IR spectra of halopropanes *Ia-Ie*, *Ia*, *Ib* and *III* characteristic vibrations of the C—F bonds or also C—H bonds are visible (Table III). The assignment of the absorption bands to the vibrations of the C—F bonds in the CF,  $\text{CF}_2$ , and  $\text{CF}_3$  groups was carried out on the basis of published<sup>23-26</sup> spectra of fluorinated ethanes, and further on the basis of the

TABLE III

Absorption Maxima ( $\text{cm}^{-1}$ ) in the IR Spectra of Halopropanes *Ia-Ie*, *Ia*, *Ib*, and *III* (a solution in carbon tetrachloride)

Substance	Maximum
<i>Ia</i>	720 ms, 794 m, 842 ms, 859 m, 1 063 m; 1 180 s $\nu(\text{CF}_2)$ ; 1 228 s and 1 232 mw $\nu(\text{CF}_3)$
<i>Ib</i>	742 s, 806 m, 902 s, 973 m, 1 086 m; 1 120 m $\nu(\text{CF})$ ; 1 164 s, 1 176 s, 1 192 s and 1 213 m $\nu(\text{CF}_2)$
<i>Ic</i>	703 m, 815 m, 834 m, 903m, 932m, 1 028 m, 1 043 m; 1 147 m and 1 167 m $\nu(\text{CF}_2)$ ; 1223 vs and 1 238 $\nu(\text{CF}_3)$
<i>Id</i>	714 ms, 806 m, 840 m, 881 m, 902 m, 962 m, 1 026 w, 1 043 w; 1 108 m and 1 141 m $\nu(\text{CF})$ ; 1 220 vs and 1 270 m $\nu(\text{CF}_3)$
<i>Ie</i>	711 s, 797 ms, 822 s, 954 m, 1 015 m, 1 077 ms; 1 128 s $\nu(\text{CF})$ ; 1 172 s, 1 183 s, 1 197 s and 1 219 s $\nu(\text{CF}_2)$
<i>Ia</i>	709 ms, 794 m, 834 m, 1 034 s; 1 137 s and 1 201 vs $\nu(\text{CF}_2)$ ; 1 266 s and 1 345 m $\nu(\text{CF}_3)$ ; 2 994 w $\nu(\text{C-H})$
<i>Ib</i>	738 s, 813 m, 942 m, 955 s; 1 102 s $\nu(\text{CF})$ ; 1 170 s, 1 227 m and 1 254 m $\nu(\text{CF}_2)$ ; 2 992 w $\nu(\text{C-H})$
<i>III</i> <sup>a</sup>	709 m, 798 mw, 1 038 m, 1 061 m; 1 109 m, 1 132 m and 1 186 m $\nu(\text{CF}_2)$ ; 1 216 vs and 1 253 m $\nu(\text{CF}_3)$ ; 2 988 w $\nu(\text{C-H})$

<sup>a</sup> Measured in gaseous phase.

spectra of difluorohexachloropropanes<sup>6-8,27</sup> and trifluoropentachloropropanes<sup>6,7,10</sup> (Table IV) which was published earlier without interpretation. On the basis of the comparison of the spectra of the mentioned compounds it followed that for the CF group a strong absorption in the 1100–1130 cm<sup>-1</sup> region should be expected, for the CF<sub>2</sub> group a strong absorption between 1160–1180 cm<sup>-1</sup>, and for the CF<sub>3</sub> group a strong, or very strong, absorption in the 1210–1280 cm<sup>-1</sup> interval. In the IR spectra of pentafluoropropanes *Ia–Ie*, *IIa*, *IIb* and *III* (Table III) the vibrations of some C—F bonds are shifted to higher frequencies, as for example the vibrations of the CF group in *Id*, and in particular the vibrations of the C—F bonds in CF<sub>2</sub> groups of compounds *Ib*, *Ie*, *IIa*, *IIb*, and *III*.

In preceding papers<sup>6-8</sup> we demonstrated that the C—F bond in monofluorochloromethanes is cleaved more readily than the C—Cl bond during the additions to haloethylenes in the presence of aluminum chloride. As a consequence of this rule the additions also afford a mixture of isomers in the case of symmetrical haloethylenes<sup>8</sup>. The relative reactivity of the C—F and C—Cl bonds in fluorochloromethanes is dependent both on fluoromethane and haloethylene (Table V). In reactions with tetrafluoroethylene the relative reactivity of the C—F bond in fluorotrichloromethane is almost the greatest among the mentioned additions, and in fluorodichloromethane,

TABLE IV

Stretching Vibrations of C—F Bonds (cm<sup>-1</sup>) in Some Fluorinated Alkanes

Substance	$\nu(\text{CF})$	$\nu(\text{CF}_2)$	$\nu(\text{CF}_3)$	Ref.
CF <sub>3</sub> —CH <sub>3</sub>	—	—	1 233 s, 1 280 m	23
CF <sub>3</sub> —CH <sub>2</sub> Cl	—	—	1 159 s, 1 263 s, 1 277 s	24
CF <sub>3</sub> —CHCl <sub>2</sub>	—	—	1 139 s, 1 229 m, 1 272 s	24
CF <sub>3</sub> —CCl <sub>3</sub>	—	—	1 227 s, 1 255 m	25
CF <sub>3</sub> —CFCl <sub>2</sub>	1 103 s	—	1 217 s, 1 292 s	25
CF <sub>3</sub> —CF <sub>2</sub> Cl	—	1 120 m, 1 178 s	1 224 s, 1 240 s	25
CF <sub>2</sub> Cl—CCl <sub>3</sub>	—	1 163 s	—	26
CFCl <sub>2</sub> —CCl <sub>3</sub>	1 101 s	—	—	26
CFCl <sub>2</sub> —CCl <sub>2</sub> —CFCl <sub>2</sub>	1 108 s	—	—	7
CFCl <sub>2</sub> —CFCl—CCl <sub>3</sub>	1 109 s, 1 129 s	—	—	6
CF <sub>2</sub> Cl—CCl <sub>2</sub> —CCl <sub>3</sub>	—	1 160 s	—	27
CCl <sub>3</sub> —CF <sub>2</sub> —CCl <sub>3</sub>	—	1 107 m, 1 163 s	—	27
CF <sub>3</sub> —CCl <sub>2</sub> —CCl <sub>3</sub>	—	—	1 210 vs, 1 232 s	7
CF <sub>2</sub> Cl—CFCl—CCl <sub>3</sub>	1 120 s	1172 s	—	10
CF <sub>2</sub> Cl—CCl <sub>2</sub> —CFCl <sub>2</sub>	1 100 s	1 162 s	—	7
CFCl <sub>2</sub> —CF <sub>2</sub> —CCl <sub>3</sub>	1 098 s	1 143 m, 1 173 s	—	7
CFCl <sub>2</sub> —CFCl—CFCl <sub>2</sub>	1 128 s, 1 143 ms	—	—	6

on the contrary, it is the smallest (Table V). The differing course of single additions supports our supposition<sup>8</sup> that the reactions take place *via* a stage involving a transition complex composed of an ionised haloethane and fluoro-olefin, which is then decomposed giving rise to isomeric products.

The reactivity of haloethylenes with fluorotrichloromethane was correlated<sup>28</sup> with quantum chemical indices of reactivity, *i.e.* with the average medium electrophilic superdelocalizability  $S_e$ , average electronic density  $c^2$  on the carbon atoms, and with the energy of the last occupied orbital  $E_1$ . On the basis of correlations a larger reactivity was predicted for tetrafluoroethylene than for trifluorochloroethylene. In order to check the correctness of our prediction we carried out the concurrent reaction of both mentioned fluoroethylenes with fluorotrichloromethane. From the yields of the concurrent reaction we calculated a relative reactivity 1.89 : 1 in favour of tetrafluoroethylene. The value read from correlation dependencies<sup>28</sup> gives the 1.74 : 1 ratio. The good agreement of the experimental and the calculated reactivity of tetrafluoroethylene justifies the correlations<sup>28</sup> of reactivities with the given quantum chemical quantities which in a series of haloolefins may be considered as reactivity criteria<sup>28</sup>.

TABLE V

Relative Reactivities of C—F and C—Cl Bonds in Monofluoromethanes at Reactions with Haloethylenes

Halogenethylene	CCl <sub>3</sub> F		CHCl <sub>2</sub> F	
	C—F	C—Cl	C—F	C—Cl
CF <sub>2</sub> =CF <sub>2</sub>	83	17	59	41
CF <sub>2</sub> =CFCl <sup>d</sup>	89	11	76	24
CF <sub>2</sub> =CCl <sub>2</sub> <sup>b</sup>	86	14	90	10
CFCl=CFCl <sup>c</sup>	70	30	—	—

<sup>a</sup> See<sup>10</sup>; <sup>b</sup> see<sup>6,7</sup>; <sup>c</sup> see<sup>8</sup>.

## EXPERIMENTAL

Temperature data were not corrected. Gas chromatography was carried out on a Chrom 3 apparatus (Laboratorní přístroje, Prague; TC and FI detector, column diameter 0.6 cm, carrier of the stationary phase Celite 545). The separation of isomers of trichloropentafluoropropane (*I*) was carried out on a Perkin-Elmer F-11 apparatus (polyamide capillary column 5000 cm, diameter 0.028 cm, squalane, 23–26°C, efficiency 100000 theoretical plates — tested on *n*-hexane, dose 0.3–1 μl liquid at a 1 : 50 separation ratio. For quantitative evaluation the same response was supposed for all isomers. The areas were determined by multiplication of the height of the wave by its width at half the height). The IR spectra were measured on Zeiss UR 10 and Perkin-Elmer 325 (Bodensewerk) spectrographs, the PMR spectra on BSS 477 (Tesla, Brno) apparatus, and the mass spectra on a Gas Chromatograph-Mass Spectrometer LKB 9000 (LKB-Producter, AB Stockholm).

## Chemicals Used

Fluorotrichloromethane and trifluorochloroethylene (Spolek pro chemickou a hutní výrobu, Ústí n. Labem), fluorodichloromethane (Farbwerke Hoechst). Tetrafluoroethylene was prepared by dehalogenation of 1,2-dibromotetrafluoroethane with zinc in ethanol.

## Reaction of Fluorotrichloromethane with Tetrafluoroethylene

*A. Preparative reaction.* Tetrafluoroethylene (7.05 l; 29.2 g; 0.292 mol) was condensed into a mixture of fluorotrichloromethane (120 g; 0.873 mol) and aluminum chloride (5.0 g; 0.037 mol) in an autoclave and the mixture was shaken at 20–30°C for three hours. After reaction the gaseous components contained approx. 2 l of tetrafluoroethylene, *i.e.* the conversion was 70%. The reaction mixture was mixed with 50 ml of trifluoropentachloropropane<sup>8</sup> decomposed with dilute hydrochloric acid, and the oil was washed with a solution of sodium hydrogen carbonate and water and then dried over anhydrous calcium chloride. On rectification it gave fractions boiling at 70–72°C (53.1 g) and 72–75°C (7.4 g) containing in addition to trichloropentafluoropropane (*I*) also 25.5 and 54% of carbon tetrachloride, respectively (gas chromatography: 20% silicone elastomer E 301, column length 360 cm, 50°C, carrier gas hydrogen, thermal conductivity detection), *i.e.* the calculated yield of product *I* was 44.2% (totally 66% for total conversion 94%). The relative content of isomers *Ia* and *Ib* was the same in both fractions, *i.e.* 83% and 17% rel. The trichloropentafluoropropane fraction (40 g; content 25.5% of carbon tetrachloride), 20% oleum (20 ml), and mercuric oxide (0.3 g) were refluxed for 20 hours. The oily layer was washed with a sodium hydrogen carbonate solution and water, and then dried over phosphorus pentoxide. Distillation gave 23.2 g of trichloropentafluoropropane with the same content of isomers *Ia*, *Ib*. For  $C_3Cl_3F_5$  (237.4) calculated: 15.18% C, 44.81% Cl, 40.01% F; found: 14.91% C, 43.94% Cl, 40.62% F.

*B. Reaction at atmospheric pressure:* Gaseous tetrafluoroethylene (5.4 l; 22.8 g; 0.228 mol) was introduced under stirring into a mixture of carbon tetrachloride (100 ml), fluorotrichloromethane (110 g; 0.802 mol), and aluminum chloride (5 g; 0.037 mol) at a 15–20 ml/min rate and at 15°C. After working up (see *A*) and rectification the conversion was calculated at 30.5% (yield approx. 98%).

*C. Concurrent reaction with trifluorochloroethylene:* A mixture of tetrafluoroethylene and trifluorochloroethylene (6.04 l; 40% and 60% v/v; 0.109 and 0.161 mol), fluorotrichloromethane (131 g; 0.95 mol) and aluminum chloride (3.5 g; 0.026 mol) was agitated at 10–12°C for 5 hours. The unreacted gas (2.84 l) contained 6% of  $C_2F_4$ , 79%  $C_2F_3Cl$  and 15%  $CFCl_3$ . The reaction mixture after having been worked up as under *A* was rectified. From fractions 65–70, 70–75, 75–100 and 100–130°C the yields were calculated for substance *I* (89.8%) and for tetrafluoro-tetrachloropropane (76.5%). On the basis of the analysis of gases before and after the reaction the corresponding calculated yields were 91.8 and 28.5%. Relative reactivity  $C_2F_3 : C_2F_3Cl$  determined on the basis of the yields of the additions of the reagent was 1.89 : 1, and on the basis of the analysis of gases it was 4.8 : 1 (gas chromatography: see *A*, further on poly(ethylene glycol) 400, column length 360 cm, 25°C, nitrogen, thermal conductivity detection).

## Reaction of Fluorodichloromethane with Tetrafluoroethylene

A mixture of tetrafluoroethylene (5.4 l; 24.1 g; 0.241 mol), fluorodichloromethane (55 g; 0.534 mol), and aluminum chloride (4.0 g; 0.030 mol) was shaken in an autoclave at 15°C for 3.5 hours. After reaction the gaseous components contained approx. 1.9 l of tetrafluoroethylene, *i.e.* con-

version was 65%. After working up (see Reaction of fluorotrichloromethane) rectification was carried out and the following fractions collected: 45–50°C (7.3 g), 50–57°C (15.1 g); they contained 32% and 35% of chloroform. The calculated yield of pentafluorodichloropropane (*II*) was 14.1 g (58.2%), the content of isomers *Ila* and *Ilb* was 59% and 41% rel. (gas chromatography: 20% poly(ethylene glycol) 400, column length 360 cm, 50°C, hydrogen, thermal conductivity detection). For analytical purposes both isomers were purified on an analytical column. PMR spectra (carbon tetrachloride): compound *Ila*:  $t$  4.05 $\tau$ ,  $J_{\text{H-F}}^3$  8.6 c/s; compound *Ilb*: ddd 3.63  $\tau$ ,  $J_{\text{H-F}}^2$  58.2 c/s,  $J_{\text{H-F}}^3$  9.6 and 3.2 c/s. For  $\text{C}_3\text{HCl}_2\text{F}_5$  (202.9). Mass spectra: fragment, mass (relative intensity): compound *Ila*:  $\text{M}^+$  202 (0.8),  $(\text{M}-\text{CF}_3)^+$  133 (1.6),  $(\text{M}-\text{CHCl}_2)^+$  119 (1.7),  $(\text{CHCl}_2)^+$  83 (100),  $(\text{CF}_3)^+$  69 (55); compound *Ilb*:  $\text{M}^+$  202 (0.07),  $(\text{M}-\text{HCl})^+$  167 (21),  $(\text{M}-\text{CHClF})^+$  135 (1.6),  $(\text{M}-\text{CF}_2\text{Cl})^+$  117 (9),  $(\text{CF}_2\text{Cl})^+$  85 (52),  $(\text{CHClF})^+$  67 (100).

#### Photoreduction of Trichloropentafluoropropanes *Ia* and *Ib*

A solution of isomers *Ia* and *Ib* (4.32 g; 18.6 mmol; 80% and 20% rel.) in isopropyl alcohol (18.3 g; 301 mmol) was irradiated in closest proximity to an ultraviolet lamp (80 W, Tesla) at 25°C for 2.5 hours. After the reaction the mixture contained in addition to hydro derivatives *Ila* and *Ilb*, occurring in relative amounts 90% and 10%, also the unreacted starting material (approx. 12%) and dihydro derivative *III* (approx. 8%); gas chromatography: 20% Tridox, column length 360 cm, 65°C, hydrogen, thermal conductivity detection). During the rectification of the combined fractions from three reactions the fraction boiling at 40–70°C was collected and then freed from acetone and isopropyl alcohol by washing with water and concentrated calcium chloride solution and drying over phosphorus pentoxide. Using an analytical column substances *Ila*, *Ilb*, and *III* and the unreacted starting substance *I* were isolated in pure state. The IR spectra and PMR spectra of isomers *Ila* and *Ilb* were identical with those of substances prepared by addition reaction. The spectrum of substance *III* was also identical with the spectra of the substance prepared on subsequent reduction. The unreacted trichloropentafluoropropane contained isomers *Ia* and *Ib* in 5.5% and 94.5% yield (rel.).

#### 1,1-Dihydryl-1-chloropentafluoropropane (*III*)

A solution of isomers *Ila* and *Ilb* (4.62 g; 22.8 mmol; 59% and 41% rel.) in isopropyl alcohol (24.5 g; 402 mmol) was irradiated for 1.5 hours (see photoreduction). The isomer *Ila* reacted completely. On rectification of the products from two reactions the fraction boiling at 25–27°C (0.52 g; 23.2%) was collected which contained compound *III* of 94% purity (literature<sup>29</sup> b.p. 27.2°C); for gas chromatography see the preceding reduction. The subsequent fraction, boiling at 30–60°C was submitted to further separation on an analytical column. It yielded substances *Ilb* and *III*. For  $\text{C}_3\text{HClF}_5$  (168.5). Mass spectrum:  $\text{M}^+$  168 (32),  $(\text{M}-\text{CF}_3)^+$  99 (100),  $(\text{CF}_3)^+$  69 (78),  $(\text{CH}_2\text{Cl})^+$  49(46). PMR spectrum (carbon tetrachloride):  $t$  6.15 $\tau$ ,  $J_{\text{H-F}}^3$  13.8 c/s.

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