

## REACTION OF TRIFLUOROETHYLENE WITH FLUOROCHLOROMETHANES IN THE PRESENCE OF ALUMINIUM CHLORIDE\*

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Reaction of trifluoroethylene with fluorotrichloromethane afforded a mixture of 2-hydryl-1,1,1-trichloro- (*Ia*) and 2-hydryl-1,1,3-trichlorotetrafluoropropane (*Ib*) in the ratio 70 : 30. An analogous reaction with fluorodichloromethane gave a mixture of 1,2-dihydryl-1,1-dichloro- (*II*) and 1,2-dihydryl-1,3-dichlorotetrafluoropropane (*III*) in the ratio 58 : 42. Compound *III* was separated by chromatography into the diastereoisomers *IIIa* and *IIIb* (ratio, 60 : 40). The high specificity of both the additions is discussed; the course of these reactions is in accordance with polarisation of the trifluoroethylene double bond.

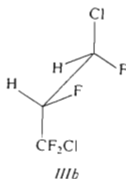
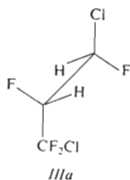
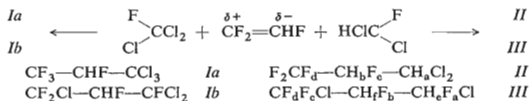
The ionic addition reactions of fluorochloromethanes with fluorinated olefins have been so far investigated<sup>1</sup> on a series of perhalogenated ethylenes. We have been now interested in the reaction course in the case of the partially fluorinated ethylene, namely, trifluoroethylene, the behaviour of which might be in this respect compared with that of trifluorochloroethylene<sup>2</sup>. Trifluoroethylene was prepared by dehalogenation of 1-bromo-1,1,2-trifluoro-2-chloroethane by the action of zinc in ethanol.

Reactions of trifluoroethylene with fluorotrichloromethane in the presence of aluminium chloride were effected under pressure to afford a fraction of tetrafluoro-trichloropropane (*I*) and a fraction of higher-chlorinated secondary products (Table I). The most favourable preparative yields of the product *I* were obtained at temperatures round 10°C. As inferred from the chromatographic analysis and <sup>19</sup>F NMR spectra, product *I* forms a mixture of 2-hydryl-1,1,1-trichlorotetrafluoropropane (*Ia*) and 2-hydryl-1,3,3-trichlorotetrafluoropropane (*Ib*) in the ratio 70 : 30. The higher-boiling fraction contains mainly trifluorotetrachloropropane (Table I) which consists from four (closely nonidentified) isomers, as indicated by mass spectra. The structure of compounds *Ia* and *Ib* was inferred from elemental and spectral analysis. The PMR spectrum of the isomer *Ia* contains a doublet of quartets and the <sup>19</sup>F NMR spectrum exhibits a doublet of doublets and a strong singlet while the analogous

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spectrum of the isomer *Ib* displays a double doublet of doublets and a quartet of sextets. Furthermore, the structure of isomers *Ia* and *Ib* was confirmed by occurrence of the main ionic species in mass spectra.

The reaction of trifluoroethylene with fluorodichloromethane at 0°C afforded a tetrafluorodichloropropane fraction (yield, 82.4%) which contained 1,2-dihydryl-1,1-dichlorotetrafluoropropane (*II*) and 1,2-dihydryl-1,3-dichlorotetrafluoropropane (*III*) in the ratio 58 : 42; the product *III* consisted of two diastereoisomers *IIIa* and *IIIb* in the ratio 60 : 40 (elution order on Carbowax 6000: *IIIa*, *II*, *IIIb*). The isomers *II*, *IIIa* and *IIIb* were identified by mass, PMR, and <sup>19</sup>F NMR spectra. The mass spectrum of compound *II* exhibits characteristic ionic species CF<sub>3</sub><sup>(+)</sup> and CHCl<sub>2</sub><sup>(+)</sup>. The mass spectra of the diastereoisomers *IIIa* and *IIIb* are identical and contain characteristic ionic species CHFCl<sup>(+)</sup> and CF<sub>2</sub>Cl<sup>(+)</sup>. The PMR as well as the <sup>19</sup>F NMR spectra display a doublet of doublets, a doublet of quintets, and a doublet of multiplets, resp.



The analysis of proton and fluorine magnetic resonance spectra of the diastereoisomers *IIIa* and *IIIb* combined with heterodecoupling made possible to obtain some values of coupling constants  $J_{\text{HH}}$  and  $J_{\text{HF}}$  and to use them for allotment of the relative configuration to compounds *IIIa* and *IIIb*. In this respect, the coupling constants of hydrogen and fluoro atoms at the two asymmetric carbons are most important. The isomer *IIIa* exhibits a fairly high coupling constant  $^3J_{\text{H}_e\text{H}_f}$  while the absolute value of  $^3J_{\text{H}_f\text{F}_a}$  and  $^3J_{\text{H}_e\text{F}_b}$  is low. On the other hand, the coupling constant  $^3J_{\text{H}_e\text{H}_f}$  of the diastereoisomer *IIIb* is low and the  $^3J_{\text{H}_f\text{F}_a}$  and  $^3J_{\text{H}_e\text{F}_b}$  values are high. When the antiperiplanar orientation of the chloro atom at C<sub>(1)</sub> and of the CF<sub>2</sub>Cl group at C<sub>(2)</sub> is taken as the predominant conformation of both the diastereoisomers, the constant values may be satisfactorily explained by allotment of the *erythro* configuration to the isomer *IIIa* and of the *threo* configuration to the isomer *IIIb*.

In the earlier investigated reactions of fluorotrichloromethane and fluorodichloromethane with asymmetrically substituted perhaloethylenes such as trifluorochloroethylene<sup>2,4</sup>, 1,1-difluorodichloroethylene<sup>5,6</sup>, and fluorotrichloroethylene<sup>7</sup>, the addition of the  $\text{CCl}_3^{(+)}$  and  $\text{CFCl}_2^{(+)}$ ,  $\text{CHCl}_2^{(+)}$  and  $\text{CHClF}^{(+)}$  particles took place unspecifically with respect to the polarisation of the double bond. It is of interest in this connection that additions of halomethanes to trifluoroethylene have not been observed to afford any product which would be formed by a nonspecific addition to the olefin. Table II presents a comparison of the specificity in additions of fluorotrichloromethane to some fluoroethylenes with  $\pi$  and  $\sigma$  charges on carbon atoms. In calculations of  $\pi$  charges, the simple Hückel method of molecular orbitals<sup>8</sup> (HMO) was used; the  $\sigma$  charges were calculated by the method of Del Re<sup>9</sup> based on bicentric molecular orbitals. Concerning the direction of the double bond polarisation in fluoroethylenes of Table II, an excess of  $\pi$  electrons and a relative excess of the  $\sigma$  charge occurs at those carbon atoms to which a lesser number of fluoro atoms is attached. There is no marked difference between trifluoroethylene and the other three haloethylenes in the magnitude of the  $\pi$  charge at  $\text{C}_{(2)}$ ; The difference of overall charges  $\Delta(\pi + \sigma)$  is almost identical with trifluoroethylene and 1,1-difluorodichloroethylene. On the other hand, the difference in the addition specificity to trifluoroethylene and the other olefins is of a qualitative nature. With the first three olefins of Table II, the addition of the bulky  $\text{CCl}_3^{(+)}$  and  $\text{CCl}_2\text{F}^{(+)}$  particles should occur at that carbon atom where the steric conditions are less favourable. With trifluoroethylene, the effect of the double bond polarisation and the steric preference operate in the same di-

TABLE I

Conditions and Results of the Reaction of Trifluoroethylene with Fluorotrichloromethane in the Presence of Anhydrous Aluminium Chloride (5.0 g; 37 mmol)

$\text{CF}_2=\text{CHF}$ g (mol)	$\text{CFCl}_3$ g (mol)	Time, h (temp., °C)	Yield <sup>a</sup>	
			$\text{C}_3\text{HCl}_3\text{F}_4$ g (%)	Fraction <sup>b</sup> 96–140°C g (%)
6.97 (0.085)	135 (0.98)	10 (0–14)	12.2 (65.3)	1.25 (5.2)
20.4 (0.25)	135 (0.98)	18 (10–20)	34.8 (62.4)	14.2 (20.2)
26.9 (0.33)	120 (0.875)	10 (0)	36.7 (59.1)	3.26 (4.8)

<sup>a</sup> Calculated from chromatograms; <sup>b</sup> mixture of four  $\text{C}_3\text{HCl}_4\text{F}_3$  isomers.

rection. An analogous conjunction of both the effects may be observed in additions of nucleophilic agents to fluorinated ethylenes<sup>10,11</sup>; in these reactions not a single case of an unspecific addition has been encountered. To our opinion, the main factor affecting the specificity in additions of fluorotrichloromethane to the fluoroethylenes of Table II consists in the steric effect of chloro atoms. A similar idea on the steric effect with respect to the specificity in electrophilic additions to trifluorochloroethylene has been proposed some time ago<sup>12</sup>.

## EXPERIMENTAL

Boiling points are uncorrected. Gas chromatography was performed on a Chrom III apparatus (Laboratory Equipment, Prague; indication by flame ionisation; Chromaton N-AW-DMCS as the stationary phase carrier; nitrogen as the carrier gas) and a Perkin-Elmer F-11 apparatus (5000 cm polyamide capillary; 100000 TP in the n-hexane test). The IR spectra were taken on a Perkin-Elmer 325 (Bodenseewerk) apparatus. The NMR spectra were measured on a BSS 477 (Tesla, Brno) apparatus and a Varian XL-100-15 (Palo Alto) apparatus (chemical shifts  $\delta$ , for <sup>1</sup>H with respect to tetramethylsilane, for <sup>19</sup>F referred to CFCl<sub>3</sub>; coupling constants *J* c/s; s, singlet; d, doublet; q, quartet; quin, quintet; sex, sextet; m, multiplet). Mass spectra were measured on a Gas Chromatograph-Mass Spectrometer LKB 9000 (Stockholm) apparatus.

*Materials.* Fluorotrichloromethane (Ledon 11) is produced by the Corporation for Chemical and Metallurgical Production, Ústí nad Labem, Czechoslovakia. Fluorodichloromethane (Frigen 21) is produced by Farbwerke Hoechst A. G. (West Germany). 1-Bromo-1,1,2-trifluoro-2-chloroethane was purchased from Lěčiva Works, Prague, Czechoslovakia.

TABLE II

Specificity of the Addition of Fluorotrichloromethane to Some Fluoroolefins and Electron Charges at Carbon Atoms

Olefin (ref.)	Carbon atom	Charge <sup>a</sup>			Specificity of the addition % rel.
		$\pi$	$\sigma$	$\Delta(\pi + \sigma)^b$	
1 2 F <sub>2</sub> C=CFCl (2)	1	-17	+394	144	44
	2	-74	+297		
1 2 F <sub>2</sub> C=CCl <sub>2</sub> (5)	1	+16	+408	317	48
	2	-98	+205		
1 2 FCIC=CCl <sub>2</sub> (7)	1	-6	+323	165	46
	2	-65	+217		
1 2 F <sub>2</sub> C=CHF	1	+11	+371	319	>99
	2	-89	+152		

<sup>a</sup> In thousandths; <sup>b</sup> difference of the sum of charges ( $\pi + \sigma$ ) at C<sub>(1)</sub> and C<sub>(2)</sub> carbon atoms.

*Calculations.* In the HMO model (cf.<sup>8</sup>) calculations, the earlier<sup>13</sup> parameters were used. The  $\sigma$ -electron charges were calculated by the method of Del Re and the parameters stated<sup>9</sup>.

### Trifluoroethylene

A solution of 1-bromo-1,1,2-trifluoro-2-chloroethane (780 g; 9.95 mol) in ethanol (250 ml) was added portionwise with stirring to a suspension of 20 g (0.306 gramatom) preactivated zinc dust (by the action of glacial acetic acid, 4 ml) and commercial zinc dust (370 g; 5.66 gramatom) in ethanol (550 ml). Rectification (temperature range, from  $-51^{\circ}\text{C}$  to  $-50^{\circ}\text{C}$ ; reported<sup>3</sup>,  $-51^{\circ}\text{C}$ ) afforded 250 g (78%) of trifluoroethylene, purity 99% (gas chromatography: 15% poly(propylene sebacate), 240 cm column,  $45^{\circ}\text{C}$ ). For the IR spectrum see ref.<sup>14</sup>

### Reaction of Trifluoroethylene with Fluorotrichloromethane

A steel pressure vessel was charged successively with anhydrous aluminium chloride, fluorotrichloromethane, and (*in vacuo*) liquid trifluoroethylene (Table I). When the reaction was completed, the gas phase (containing unreacted components and difluorodichloromethane) was collected in a gas reservoir. The liquid phase was diluted with trifluoropentachloropropane, decomposed with dilute aqueous hydrochloric acid, washed with aqueous sodium hydrogen carbonate and water, dried over anhydrous calcium chloride, and rectified. The fractions were taken at  $24-80^{\circ}\text{C}$  (fluorotrichloromethane and tetrachloromethane), at  $80-96^{\circ}\text{C}$  (the principal product *I*), and at  $96-140^{\circ}\text{C}$  (trifluorotetrachloropropane; gas chromatography: 15% Carbowax 6000, 520 cm column,  $100^{\circ}\text{C}$ ). The mixture of isomers *Ia* and *Ib* (ratio, 70 : 30; gas chromatography on a capillary column,  $50^{\circ}\text{C}$ ) was isolated by preparative gas chromatography on an analytical column. Mass spectra (ionic species, mass/relative intensity): Isomer *Ia*, 187/10; 185/58; (M-Cl), 183/90; 121/19; 119/53;  $\text{CCl}_3$ , 117/57; 114/12; 103/13; 101/21; 98/12; 87/32;  $\text{CF}_2\text{Cl}$ , 85/100; 82/13; 79/12;  $\text{CF}_3$ , 69/86;  $\text{CHClF}$ , 67/6;  $\text{CHF}_2$ , 51/12;  $\text{CCl}$ , 47/12; isomer *Ib*, (M-F), 199/5; 185/11; (M-Cl), 183/16; 165/14; 163/2; 103/29;  $\text{CFCl}_2$ , 101/47; 98/13; 87/32;  $\text{CF}_2\text{Cl}$ , 85/100;  $\text{CCl}_2$ , 82/8;  $\text{CF}_3$ , 69/26;  $\text{CHClF}$ , 67/10;  $\text{CHF}_2$ , 51/10. The PMR spectrum (deuteriochloroform) of compound *Ia*: dq 4.91,  $^2J_{\text{HF}} = 43$ ,  $^3J_{\text{HF}} = 5$ . The  $^{19}\text{F}$  NMR spectrum (tetrachloromethane): Isomer *Ia*, dd 180,  $^2J_{\text{FH}} = 45$  (-CHF-); s 71.5 ( $\text{CF}_3$ ); isomer *Ib*, dd 183,  $^2J_{\text{FH}} = 45$ ,  $^3J_{\text{FF}} = 25$  (-CHF-); dd 68.6,  $^3J_{\text{FF}} = 25$  (-CFCl-); q sex 61.6,  $^2J_{\text{FaFb}} = 475$ ,  $^3J_{\text{FF}} = 175$  (-CF<sub>2</sub>-). The signal integration of the mixture *Ia/Ib* is in the ratio 70 : 30. For the mixture of *Ia* and *Ib*,  $\text{C}_3\text{HCl}_3\text{F}_4$  (219.4) calculated: 16.37% C, 0.46% H, 34.58% F, 48.59% Cl; found: 16.48% C, 0.25% H, 34.63% F, 48.64% Cl.

### Reaction of Trifluoroethylene with Fluorodichloromethane

A mixture of anhydrous aluminium chloride (5 g; 37 mmol), fluorodichloromethane (23.8 g; 0.291 mol), and trifluoroethylene (12.8 g; 0.156 mol) was shaken at  $0^{\circ}\text{C}$  for 7 h (for the apparatus see the preceding paragraph) and then processed as above. Rectification afforded 29.7 g of a fraction ( $60-70^{\circ}\text{C}$ ) containing 23.85 g (82.7%) of a mixture of the constitutional isomers of tetrafluorodichloropropane (*II* and *III*; ratio, 58 : 42) and the diastereoisomers *IIIa* and *IIIb* (ratio, 60 : 40; gas chromatography: 15% Carbowax 6000, 360 cm column,  $160^{\circ}\text{C}$ ). For the analytical purpose, the isomers *II*, *IIIa*, and *IIIb* were isolated in the purity of about 99% by the preparative gas chromatography on an analytical column. The IR spectrum (carbon disulfide, tetrachloromethane;  $\text{cm}^{-1}$ ): Compound *II*, 682 m, 690 m, 782 m, 800 m, 1093 m, 1140 m, 1151 s, 1199 s, 1212 m, 1237 m, 1267 s, 1291 m, 1372 m, 1380 m, 2950 w, and 2985 w; compound *IIIa*, 631 m, 685 m, 780 m, 807 m, 981 m, 1048 s, 1066 m, 1099 m, 1127 m, 1139 s, 1155 s, 1186 m, 1209 m, 2940 vw, and 2980 vw; compound *IIIb*, 678 m, 700 s(sh), 705 s, 736 m, 757 m, 790 m, 804 m, 823 m,

836 m, 912 m, 960 m, 979 s, 1025 m, 1034 m, 1058 s, 1087 s, 1135 s, 1145 s, 1182 m, 1205 m, 1226 s, 1260 m, 2 958 vw, and 2985 vw. Mass spectra (ionic species, mass/relative intensity): Compound *II*: (M—Cl), 149/9; 87/15; CF<sub>2</sub>Cl, 85/78; CHCl<sub>2</sub>, 83/100; CF<sub>3</sub>, 69/33; CHClF, 67/10; CHF<sub>2</sub>, 51/14; the diastereoisomers *IIIa* and *IIIb*: 151/10; (M—Cl), 149/30; (M—HCl), 148/9; 113/10; 89/10; 87/16; CF<sub>2</sub>Cl, 85/49; CCl<sub>2</sub>, 82/86; CF<sub>3</sub>, 69/50; CHClF, 67/100; 64/19; 61/17; CHF<sub>2</sub>, 51/43. The PMR and <sup>19</sup>F NMR spectra (deuteriochloroform): Compound *II*, H<sub>a</sub> dd 5.83, H<sub>b</sub> dq 4.82; F<sub>c</sub> dm 195.9, F<sub>d</sub> dd 75.3; <sup>3</sup>J<sub>H<sub>a</sub>H<sub>b</sub> = 5.5, <sup>3</sup>J<sub>H<sub>a</sub>F<sub>c</sub> ≈ 11, <sup>2</sup>J<sub>H<sub>b</sub>F<sub>c</sub> = 45.2, <sup>3</sup>J<sub>H<sub>b</sub>F<sub>d</sub> = 5.5, <sup>3</sup>J<sub>F<sub>c</sub>F<sub>d</sub> ≈ 11; compound *IIIa*, H<sub>e</sub> dt 6.32, H<sub>f</sub> dm 4.78; F<sub>a</sub> dm 147.3, F<sub>b</sub> dm 195, F<sub>c</sub> + F<sub>d</sub> m 65.1 + m 62.5; <sup>2</sup>J<sub>H<sub>e</sub>F<sub>a</sub> = 48.5, <sup>3</sup>J<sub>H<sub>f</sub>F<sub>a</sub> = 5.5, <sup>2</sup>J<sub>H<sub>f</sub>F<sub>b</sub> = 44.5, <sup>3</sup>J<sub>H<sub>e</sub>H<sub>f</sub> = 6.2, <sup>3</sup>J<sub>H<sub>f</sub>F<sub>c</sub> ≈ 5.5, <sup>3</sup>J<sub>H<sub>f</sub>F<sub>d</sub> ≈ 7, <sup>3</sup>J<sub>H<sub>e</sub>F<sub>b</sub> ≈ 6, J<sub>F<sub>c</sub>F<sub>d</sub></sub> ≈ 178, <sup>4</sup>J<sub>H<sub>e</sub>F<sub>c</sub> ≈ <sup>4</sup>J<sub>H<sub>e</sub>F<sub>d</sub> ≈ 0; compound *IIIb*, H<sub>e</sub> ddd 6.36, H<sub>f</sub> dm 4.77; F<sub>a</sub> dm 152.1, F<sub>b</sub> dm 211, F<sub>d</sub> + F<sub>c</sub> m 63.3; <sup>2</sup>J<sub>H<sub>e</sub>F<sub>a</sub> = 48.5, <sup>2</sup>J<sub>H<sub>f</sub>F<sub>b</sub> = 44.5, <sup>3</sup>J<sub>H<sub>f</sub>F<sub>a</sub> = 14, <sup>3</sup>J<sub>H<sub>e</sub>H<sub>f</sub> = 3.5, <sup>3</sup>J<sub>H<sub>f</sub>F<sub>d</sub> ≈ <sup>3</sup>J<sub>H<sub>f</sub>F<sub>c</sub> = 6.7, <sup>3</sup>J<sub>H<sub>e</sub>F<sub>b</sub> = 12.5, <sup>4</sup>J<sub>H<sub>e</sub>F<sub>c</sub> ≈ <sup>4</sup>J<sub>H<sub>e</sub>F<sub>d</sub> ≈ 0. For the mixture of *II*, *IIIa*, and *IIIb*, C<sub>3</sub>H<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub> (185.0) calculated: 19.48% C, 1.29% H, 38.34% Cl, 41.09% F; found: 19.37% C, 1.24% H, 38.19% Cl, 41.12% F.</sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub>

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