

## REACTION OF 1,2-DIFLUOROETHYLENE WITH FLUOROTRICHLOROMETHANE IN THE PRESENCE OF ALUMINUM CHLORIDE, AND RELATIVE REACTIVITY OF FLUORINATED HYDROETHYLENES\*

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Addition reaction of fluorotrichloromethane with 1,2-difluoroethylene in the presence of aluminum chloride afforded 1,2-dihydryl-1,1,2-trifluoro- (*Va*) and 1,2-dihydryl-1,2,3-trifluorotrichloropropane (*Vb*) in relative amounts of 75% and 25%. From parallel reactions with fluorotrichloromethane relative reactivity was calculated for 1,2-difluoroethylene, trifluoroethylene and tetrafluoroethylene to be 10 : 11.2 : 15.1. This sequence is in agreement with some quantum chemical criteria of reactivity (HMO method).

In a preceding paper<sup>1</sup> we investigated the reaction of trifluoroethylene with fluorochloromethanes and found that this reaction takes place specifically, in agreement with the double bond polarisation. In this paper we wished to compare the reactivity of 1,2-difluoroethylene and trifluoroethylene in the reaction with fluorotrichloromethane with respect to tetrafluoroethylene. A similar comparison of the reactivities was carried out earlier in the series of perhalogenated ethylenes<sup>2</sup>. The ionic addition reaction of 1,2-difluoroethylene with fluorotrichloromethane has not been studied so far.

When preparing 1,2-difluoroethylene we took 1,2-difluorotetrachloroethane as starting material which was first reduced to 1,2-difluoro-1,2-dichloroethane (*I*). In the literature<sup>3</sup> reduction with lithium aluminum hydride is described. In addition to this method we also carried out the reduction with 2-propanol and ultraviolet irradiation<sup>4</sup>. This method of reduction was used already<sup>5</sup> in a series of fluorinated halogenoalkanes. The advantage of the photochemical reduction consists in the easy working up of the reaction mixture and the possibility of continuous arrangement of the preparation. During the reduction a mixture of derivatives *I* and *II* is formed in various relative amounts, depending on reaction conditions (Table I). For the preparation of derivative *I* the ratio of halogenoalkane and 2-propanol 1 : 20 seems the best.

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Dehalogenation of compound *I* to 1,2-difluoroethylene (*III*) was carried out with magnesium in tetrahydrofuran. Olefin *III* was a mixture of *cis*- and *trans*-isomers in various ratios, depending on whether 1,2-difluoroethylene was prepared from compound *I* by photochemical reduction or complex hydride reduction (Table II). The addition of bromine to a mixture of *cis*- and *trans*-1,2-difluoroethylene (47 and 53% rel.) gave 1,2-dibromo-1,2-difluoroethane (*IV*) which we separated by gas chromatography to two fractions (*IVa*, *IVb*; 44 and 56% rel.). The mass spectra and the PMR spectra of compounds *IVa* and *IVb* are identical, in the IR spectra some differences could be observed. Therefore we consider the substances obtained as diastereoisomers.

The addition reaction of 1,2-difluoroethylene with fluorotrichloromethane in the presence of aluminum chloride was carried out under pressure. When compared with the analogous addition reaction of trifluoroethylene<sup>1</sup> the yields are distinctly lower. The addition afforded a trifluorotrichloropropane fraction (*V*) which contained two isomers in relative amounts 75 and 25%, i.e. 1,2-dihydryl-1,1,2-trifluorotrichloropropane (*Va*) and 1,2-dihydryl-1,2,3-trifluorotrichloropropane (*Vb*). The structure of both isomers was deduced from mass spectra. The PMR spectrum of the mixture of isomers is in agreement with the derived structures. Low yield of the addition product *V* may be explained by the deactivation of the catalyst, aluminum

TABLE I

Results of Photochemical Reduction of 1,2-Difluorotetrachloroethane (254.7 g; 1.25 mol; 2-propanol; 1500 g, 23 mol)

Time of irradiation, h	40.5	49.5	79
Yield of <i>I</i> , %w.	16.5	14.5	26
Yield of <i>II</i> , %w.	31	48	38

TABLE II

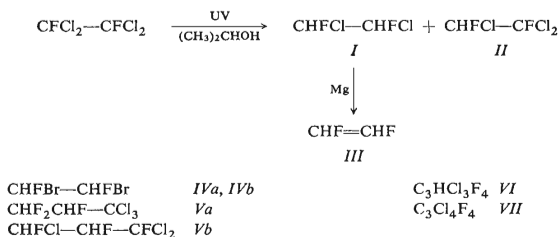
Conditions and the Results of Dehalogenation of 1,2-Difluoro-1,2-dichloroethane (*I*)

Compound <i>I</i> g/mol	Magnesium g/mol	Tetrahydrofuran ml	Olefin <i>III</i>	
			%	<i>cis/trans</i>
30.6 <sup>a</sup> /0.227	8.52/0.354	100	88	70/30
50.1 <sup>b</sup> /0.372	12.06/0.502	130	66	47/53

Compound *I* was prepared: <sup>a</sup> by reduction with lithium aluminum hydride; <sup>b</sup> by photoreduction.

chloride, caused by the chemical instability of 1,2-difluoroethylene. We base this explanation on the results of parallel addition of fluorotrichloromethane to 1,2-difluoroethylene together with other fluoroolefins during which the yields of addition to 1,2-difluoroethylene are substantially higher than during the independent addition.

From the literature it is known<sup>6-8</sup> that some chlorinated olefins, as well as those not halogenated, react by addition with chlorinated methanes in the presence of aluminum chloride and other Lewis acids. In this connection we were interested in whether the addition reaction of fluorotrichloromethane with 2-butene would take place in the presence of aluminum chloride. However, the result of this reaction was a high-boiling, organic chlorine containing fraction, in which we were unable to prove the presence of an individual product.



The reactivity of perhalogenated fluoroethylene in the reaction of fluorotrichloromethane was already investigated<sup>2</sup> in relation to the quantum chemical parameters and reactivity indexes which were computed on the basis of the simple Hückel's method of molecular orbitals<sup>9</sup> (HMO). The reactivity of halogenoethylenes was characterised by relative yields under standard conditions. We also used the same method in this paper. From parallel additions we determined relative yields of the pairs trifluoroethylene-trifluorochloroethylene and 1,2-difluoroethylene-trifluorochloroethylene (Table III). By calculation<sup>2</sup> we obtained the order of reactivity with respect to tetrafluoroethylene (Table IV). From Table IV it follows that the reactivity of fluoroethylenes decreases from tetrafluoroethylene to 1,2-difluoroethylene. The reactivity drop in this direction is also predicted by quantum chemical magnitudes, as the energy of the double bond  $\pi$ -electrons  $E_1$ , mean electron density on carbon atoms  $\bar{e}^2$  and mean electrophilic superdelocalisability  $\bar{S}_e$ . The mentioned magnitudes have a bearing on the electrophilic reaction and were applied for the evaluation of the reactivity of the mentioned series of halogenoethylenes<sup>2</sup>. The order of reactivity found is also in agreement with earlier<sup>2</sup> deductions which suggested

that the steric effect of the halogens in the ethylene molecule is not the decisive rate factor in the reaction of fluorochloromethanes in the presence of aluminum chloride.

### EXPERIMENTAL

Temperature data were not corrected. Gas chromatography was carried out on a CHROM 3 apparatus (Laboratorní přístroje, Prague; FID, column diameter 0.6 cm, stationary phase support Chromaton N-AW-DMCS), the infrared spectra were measured on a Perkin-Elmer 325 instrument (Bodenseewerk), PMR on a Varian XL-100-15 machine (Palo Alto; deuteriochloroform), and the mass spectra on a Gas Chromatograph-Mass Spectrometer LKB 9000 (Stockholm single focus, electron energy 70 eV, chromatographic inlet *via* a glass column 250 cm long, 0.23 cm diameter, support Chromaton N-AW, poly(ethylene glycol adipate)). 1,2-Difluorotetrachloroethane, fluorotrichloromethane and trifluorochloroethylene were supplied by Spolek pro chemickou a hutní výrobu, (Society for chemical and metallurgical production), Ústí n.L.

#### 1,2-Difluoro-1,2-dichloroethane (I)

A. *Photochemical reduction*<sup>4</sup>: A mixture of 1,2-difluorotetrachloroethane (255 g; 1.25 mol) and 2-propanol (1502.5 g; 25 mol) was irradiated by two high-pressure mercury lamps (RVK

TABLE III

Condition and Results of Parallel Addition of Fluorotrichloromethane to Trifluoroethylene and Trifluorochloroethylene

CF <sub>2</sub> =CHF/CF <sub>2</sub> =CFCI		°C	Time h	Addition products VI/VII	
g	mol			w.	mol : mol
21.0/29.8	0.256/0.256	0	7	21/16.4	1.28 : 1
16.8/24.5	0.199/0.21	20	2	48.8/37.5	1.30 : 1

TABLE IV

Relative Reactivity (*R*) of Fluorinated Hydroethylenes and Some Quantum Chemical Characteristics  $p_{12}$  C—C  $\pi$ -Bond Order;  $E_1$  Energy of the Last Occupied Orbital (HOMO;  $\beta$  units);  $\bar{c}^2$  Mean  $\pi$ -Electron Density on C-Atoms;  $\bar{S}_e$  mean Electrophilic Superdelocalisability (for calculation see<sup>2</sup>)

Olefin	R	$p_{1a}$	$E_1$	$\bar{c}^2$	$\bar{S}_e$
F <sub>2</sub> C=CF <sub>2</sub>	15.1	0.950	0.678	1.050	1.309
F <sub>2</sub> C=CHF	11.2	0.959	0.775	1.039	1.178
HFC=CHF	10	0.973	0.870	1.027	1.076

125 W; Tesla, Prague) in a quartz reactor at boiling point temperature. During the reaction a fraction was collected boiling in the 56–62°C range, and after the reaction the reactor content was submitted to fractional distillation and the fraction boiling at 56–79°C was collected. Both distillates were combined, washed three times with water and dried over anhydrous calcium chloride. During the rectification of this crude product which contained compounds *I* and *II*, diisopropyl ether and 2-chloropropane compound *I* distilled at 59–59.5°C (lit.<sup>3</sup> gives 59.5°C) and compound *II* at 72.5°C (lit.<sup>3</sup> 72.8°C). Both compounds were of 99% purity according to gas chromatography on 20% poly(ethylene glycol) 400, at 90 and 110°C. For the yields see Table I. The infrared spectra of compounds *I* and *II* are given in<sup>3</sup>. For C<sub>2</sub>HCl<sub>3</sub>F<sub>2</sub> (169.4) calculated: 14.19% C, 0.59% H, 62.81% Cl, 22.41% F; found: 14.78% C, 0.74% H, 62.72% Cl, 22.45% F. For C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>F<sub>2</sub> (134.9) calculated: 17.78% C, 1.48% H, 52.56% Cl, 28.18% F; found: 18.06% C, 1.55% H, 52.62% Cl, 28.39% F.

**B. Reduction with complex hydride<sup>3</sup>.** A suspension of lithium aluminum hydride (38 g; 1 mol) in dibutyl ether (400 ml) was added under stirring over 3 hours to a mixture of 1,2-difluoro-tetrachloroethane (204 g; 1 mol) and dibutyl ether (400 ml) at 20–22°C. After an additional 5 hour's stirring the reaction mixture was worked up and rectified. Fractions 40–71°C (63.1 g) and 71–123°C (68.8 g) were collected that contained 38.1 g (yield 28.2%) of compound *I* and 47.3 g (28%) of compound *II* (for gas chromatography see *A*).

### 1,2-Difluoroethylene (*III*)

Powdered magnesium was activated by heating with a small amount of iodine. A solution of compound *I* in tetrahydrofuran (1 : 1; 20 ml) was then added and the spontaneous reaction was kept going by addition of the mixture of the remaining amount of both components. The crude product was collected using a low-temperature rectification tube within the –50 to –17°C range. During the rectification olefin *III* distilled between –30 and –18°C (lit.<sup>10</sup> *cis*-isomer b.p. –26°C, *trans*-isomer –53.1°C). The weights and the yields are listed in Table II. The ratio of *cis*- and *trans*-isomer was determined gas chromatographically (silicone elastomer E 301, 360 cm, 30°C).

### 1,2-Difluoro-1,2-dibromoethane (*IV*)

1,2-Difluoroethylene (3.52 g; 0.055 mol; 47% *cis*-, 56% *trans*) was introduced into a solution of bromine (10 g; 0.06 mol) in 1,1,2-trifluorotrichloroethane (150 ml) under irradiation with an infrared lamp. The reaction mixture was shaken with a solution of sodium pyrosulfite and the organic layer was washed with a solution of sodium hydrogen carbonate and dried over calcium chloride. During rectification product *IV* was collected at 104–106°C (5.82 g; 47.2%) which was separated by gas chromatography to diastereoisomer *IVa*, *IVb* in relative amounts 56 and 44% (on poly(ethylene glycol) 400, 160°C, column 500 cm). Mass spectrum of diastereoisomers *IVa*, *IVb* (main ionic species; mass *m/e*, relative intensity): 31/19 (CF)<sup>+</sup>, 44/14 (C<sub>2</sub>HF)<sup>+</sup>, 45/19 (C<sub>2</sub>H<sub>2</sub>F)<sup>+</sup>, 64/48 (C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>)<sup>+</sup>, 111/12 (CHBrF)<sup>+</sup>, 113/12, 123/17 (C<sub>2</sub>HBrF)<sup>+</sup>, 125/16 (C<sub>2</sub>HBrF)<sup>+</sup>, 143/100 (C<sub>2</sub>H<sub>2</sub>BrF<sub>2</sub>)<sup>+</sup>, 145/97 (C<sub>2</sub>H<sub>2</sub>BrF<sub>2</sub>)<sup>+</sup>, 222/1.5 (C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub>F<sub>2</sub>)<sup>+</sup>. Infrared spectra (carbon disulfide, tetrachloromethane; cm<sup>-1</sup>): Compound *IVa*: 650 s, 720 m, 740 s, 892 m, 1022 s, 1082 m, 1053 s, 1103 m, 1132 m, 1145 m, 1165 m, 1199 m, 2950 w, 2980 w. Compound *IVb*: 658 s, 730 m, 752 m, 950 m, 1035 m, 1084 s, 1111 m, 1120 m, 1168 m, 1232 m, 1340 m, 2955 w, 2980 w. PMR spectrum of compounds *IVa* and *IVb* (deuteriochloroform): 6.50 δ (AA' part the AA'XX' spectrum: For C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub>F<sub>2</sub> (223.9) calculated: 10.38% C, 0.97% H, 71.70% Br, 16.95% F; found: 10.62% C, 1.06% H, 72.83 % Br, 16.77% F.

## Reaction of 1,2-Difluoroethylene with Fluorotrichloromethane

A mixture of fluorotrichloromethane (119 g; 0.876 mol), aluminum chloride (5 g; 0.0376 mol), and 1,2-difluoroethylene (12.7 g; 0.198 mol) was shaken in an autoclave at 15–17°C for 11 hours. The gaseous mixture after the reaction contained unreacted olefin, fluorotrichloromethane, and difluorodichloromethane (gas chromatography: silicone elastomer E 301, column 360 cm, 30°C). The reaction mixture was stirred with 50 ml of trifluoropentachloropropane, decomposed with dilute hydrochloric acid, washed with sodium hydrogen carbonate solution, and dried over magnesium sulfate. During rectification the fraction 85–145°C was collected from which a mixture of isomers *Va*, *Vb* was isolated by gas chromatography; the calculated yield was 0.22% (gas chromatography: poly(ethylene glycol) 400, column length 120 cm, 130°C, nitrogen). An analogous reaction carried out at 30–35°C for 32 hours gave product *V* in a 0.41% yield. Mass spectra (*m/e*, relative intensity): Compound *Va*: 199/8 ( $C_3HCl_3F_3$ )<sup>+</sup>, 165/53 ( $C_3H_2Cl_2F_3$ )<sup>+</sup>, 149/3 ( $M-CHF_2$ )<sup>+</sup>, 117/55 ( $CCl_3$ )<sup>+</sup>, 101/10 ( $C_2HF_4$ )<sup>+</sup>, 69/21 ( $CF_3$ )<sup>+</sup>, 51/100 ( $CHF_2$ )<sup>+</sup>, 67/34 ( $CHClF$ )<sup>+</sup>. Compound *Vb*: 199/10 ( $C_3HCl_3F_3$ )<sup>+</sup>, 129/17 ( $M-HCl_2$ )<sup>+</sup>, 103/47, 101/72 ( $CFCl_2$ )<sup>+</sup>, 100/10 ( $C_2F_4$ )<sup>+</sup>, 98/30 ( $C_2Cl_2H_4$ )<sup>+</sup>, 87/15, 85/50 ( $CClF_2$ )<sup>+</sup>, 83/20 ( $CHCl_2$ )<sup>+</sup>, 69/47 ( $CF_3$ )<sup>+</sup>, 67/100 ( $CHClF$ )<sup>+</sup>, 64/49 ( $C_2H_2F_2$ )<sup>+</sup>, 51/18 ( $CHF_2$ )<sup>+</sup>. The PMR spectrum of the mixture of isomers *Va*, *Vb* is in agreement with the proposed structures.

## Reaction of 2-Butene with Fluorotrichloromethane

A mixture of fluorotrichloromethane (127 g; 0.923 mol), aluminum chloride (5 g; 0.0376 mol), and 2-butene<sup>11</sup> (10.2 g; 0.182 mol) was shaken at 35°C for 21 hours. The liquid fraction was mixed with 80 ml of fluorotrichloromethane, washed with a sodium hydrogen carbonate solution, and dried over magnesium sulfate. During rectification the fraction boiling up to 80°C was collected (sec-butyl chloride), and the higher boiling part (5.92 g) was distilled *in vacuo* to give a fraction of b.p. 40–90°C/20 Torr (2.51 g) which contained 3.27% of elemental chlorine.

## Parallel Reactions of Fluoroethylenes and Fluorotrichloromethane

A. *Trifluoroethylene and trifluorochloroethylene* (Table III). The reaction mixture was shaken in a steel pressure bottle and worked up similarly as in the preceding examples. During rectification the fraction distilling up to 24°C was separated and the residue was analysed by gas chromatography (poly(ethylene glycol) 400, column 240 cm, 100°C, nitrogen). On the basis of this analysis the yields of products were calculated (Table III).

B. *1,2-Difluoroethylene and trifluorochloroethylene*. A mixture of fluorotrichloromethane (127 g; 0.923 mol), aluminum chloride (5 g; 0.0376 mol), 1,2-difluoroethylene (9.81 g; 0.153 mol), and trifluorochloroethylene (17.8 g; 0.153 mol) was shaken at 12°C for three hours. The reaction mixture was worked up as under A. From the chromatographic analysis (capillary column, 120°C, nitrogen) the yield of products *V* and *VII* were calculated (18.8% and 15.1% by weight; 1.25 : 1 mol).

*The spectra were measured in the department for infrared spectrometry (head Dr P. Adámek), mass spectrometry (head Dr V. Kubelka), and NMR spectra (head Dr P. Trška) of the Central Laboratories, Institute of Chemical Technology. Elemental analyses were carried out in the department of elemental analysis of the same Laboratories (head Dr L. Helešic) to which we express our gratitude.*

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