

ADDITION REACTIONS OF HALOOLEFINS. X.\*  
 THE REACTIVITY OF MONOFLUOROCHLOROMETHANES  
 AND INFLUENCE OF SOLVENTS  
 ON THE ADDITION RATE OF HALOGENOMETHANES

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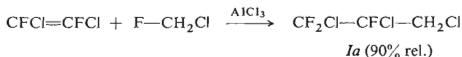
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In earlier papers of this Series relating to the reactivity of fluorotrichloromethane<sup>1</sup> and fluorodichloromethane<sup>2</sup>, the latter compound, *i.e.*, the derivative the chlorine content of which is lower than that of the former compound, was found to be more reactive. Consequently, it could be expected that fluorochloromethane with only one chloro atom in the molecule might be the most reactive of these compounds. This assumption seemed to be in accordance with the easy Friedel-Crafts alkylation of benzene with monofluoromonochloroalkanes under catalysis of Lewis acids weaker than aluminum chloride<sup>3</sup>. The experimental results, however, were opposite to these assumptions.

The required fluorochloromethane was prepared by the atmospheric fluorination (40 hours) of methylene chloride with a mixture of antimony trifluoride and antimony pentachloride in a relatively low yield (24%) along with a small amount of difluoromethane.

Addition of fluorochloromethane to 1,2-difluorochloroethylene, the most reactive representative of halogenoethylenes<sup>4</sup>, afforded a negligible yield of the addition product, namely, trifluorotrichloropropane (*I*) under conditions which lead to an almost quantitative reaction in the case of other monofluorochloromethanes<sup>5,6</sup>. On a capillary gas chromatographic column, the product *I* is separated into three components in the ratio 6.5 : 90.0 : 3.5. The principal component *Ia* was identified as 1,1,2-trifluoro-3,3-dihydriltrichloropropane. The remaining two compounds are probably isomers as usual in reactions of this type<sup>1,2,5</sup>. The PMR spectrum of compound *Ia* exhibits a doublet of protons of the grouping CH<sub>2</sub>—CF— ( $J_{\text{H-F}}^3 = 7.9$  c/s). The infrared spectrum contains vibrations of C—F bonds in groupings<sup>7-9</sup> CF<sub>2</sub>Cl (1147 cm<sup>-1</sup>), —CFCl— (1 073 cm<sup>-1</sup>), and vibrations of C—H bonds (2974 cm<sup>-1</sup>).



When compared with fluorodichloromethane<sup>2,6</sup> and fluorotrichloromethane<sup>1,5</sup>, the reactivity of fluorochloromethane is very low; in a separate reaction, the reactivity is hundred times lower. Under similar conditions, the following reactivity order was found: CHCl<sub>2</sub>F > CCl<sub>3</sub>F ≫ CH<sub>2</sub>ClF = 1.4 : 1 : 0.008; yields: 93% (ref.<sup>6,10</sup>), 68% (ref.<sup>5</sup>), and 0.55%. In a competitive reaction (Table I), the reactivity order of monofluorochloromethanes was considerably different: CHCl<sub>2</sub>F > CH<sub>2</sub>ClF > CCl<sub>3</sub>F; the difference in reactivities of halogenomethanes CHCl<sub>2</sub>F and CH<sub>2</sub>ClF was also considerable lower than in the preceding case. Furthermore, in contrast to the separate reaction, the yields of addition products of fluorodichloromethane and fluorotrichloromethane, namely, of the products C<sub>3</sub>HCl<sub>4</sub>F<sub>3</sub> (II) and C<sub>3</sub>Cl<sub>5</sub>F<sub>3</sub> (III), were considerably lower (Table II). The "competitive" reactivity order confirms the original idea in that

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TABLE I

Relative Reactivity of Monofluorochloromethanes in the Competitive Addition Reaction with 1,2-Difluorodichloroethylene

No	CCl <sub>3</sub> F	CHCl <sub>2</sub> F	CH <sub>2</sub> ClF
1	1.0	—	1.4
2	—	20.0	1.0
3	1.0	9.1	1.4

TABLE II

Competitive Reaction of Monofluorochloromethanes with 1,2-Difluorodichloroethylene (6 hours, 16°C, 3 g of aluminum chloride)

No	CH <sub>2</sub> ClF		CHCl <sub>2</sub> F		CCl <sub>3</sub> F		CFCl=CFCl		Yield, %		
	g	mol	g	mol	g	mol	g	mol	I	II	III
1	21.0	0.307	—	—	10	0.073	86.0	0.646 <sup>a</sup>	1.9	—	0.32
2	20.5	0.299	27.0	0.262	—	—	102	0.767 <sup>a</sup>	2.1	36.4	—
3	13.5	0.197	24.0	0.233	30	0.218	130.5	0.982 <sup>b</sup>	2.7	21.5	2.2

<sup>a</sup> 10 ml of carbon tetrachloride; <sup>b</sup> 30 ml of carbon tetrachloride.

TABLE III

Yields (%) of the Addition of Fluorotrichloromethane to 1,2-Difluorodichloroethylene in Dependence on the Solvent

Solvent	2.5 h	3.5 h
CCl <sub>4</sub>	17.2	21.6
CH <sub>2</sub> Cl <sub>2</sub>	18.9	19.7
CS <sub>2</sub>	16.0	19.4
CHCl <sub>3</sub>	0.75	0.9
Cyclohexane	<0.2	<0.2
CH <sub>2</sub> ClCH <sub>2</sub> Cl	<0.1	<0.1
CH <sub>3</sub> NO <sub>2</sub>	0	0

respect that fluorochloromethane is under similar conditions more reactive than fluorotrichloromethane. The low yields of products *II* and *III* in the competitive reaction and particularly the low yield of the fluorotrichloromethane addition suggest retardation of the addition reaction by the presence of fluorochloromethane. Related reactions<sup>1,2,4,5</sup> show that the retardation is due exclusively to deactivation of the catalyst. The probable deactivating effect of fluorochloromethane might be caused by the lowest chemical stability of this member of the monofluoromethane group as observed also in solvolysis<sup>11</sup>, nucleophilic substitution<sup>12</sup>, and formation of carbenes<sup>13</sup> from fluorochloromethane. On the other hand, the deactivation of aluminum chloride might be due to removal of hydrogen chloride from the addition product as observed in the group of chlorinated propanes<sup>14,15</sup> prepared by an analogous reaction<sup>16</sup>.

The role of solvents in the present addition is of great importance but of another type than in the somewhat related Friedel-Crafts reaction in the aliphatic series. Thus, alkylations of the benzene nucleus catalysed by aluminium chloride are known<sup>17</sup> to occur in carbon disulfide, sym-tetrachloroethane, 1,2-dichloroethane, aliphatic hydrocarbons, petroleum ether, and pentane. On the other hand, the alkylations proceed considerably slower<sup>17,19</sup> in nitro compounds, *e.g.*, nitromethane or nitrobenzene, in which solvents aluminum chloride passes into the solution forming a stable, isolable complex<sup>18</sup>.

As it may be seen from Table III, the reaction of fluorotrichloromethane with 1,2-difluorodichloroethylene in nitro compounds as solvents did not occur at all while negligible yields were obtained in chlorinated ethanes and cyclohexane. As suitable solvents were found methylene chloride, carbon disulfide, and especially carbon tetrachloride. In the latter solvent, the reaction was slow at the beginning, but then the rate increased and highest yields were obtained after 3,5 hours (Fig. 1). It is surprising in connection with other chlorinated methanes as solvents that chloroform exerted a great retarding effect on the reaction. The unsuccessful course of the addition in some solvents is mainly due to deactivation of the catalyst by conversion into a complex compound<sup>18,19</sup> (in nitro compounds) or by release of hydrogen chloride in the presence of aluminum chloride (in chlorinated ethanes and in chloroform). Moreover, aluminum chloride

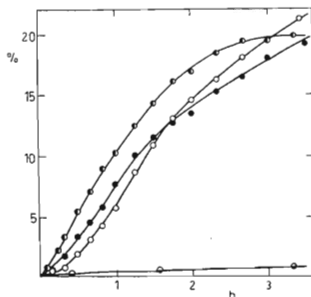


FIG. 1

Course of the Addition Reaction of Fluorotrichloromethane with 1,2-Difluorochloroethylene in Dependence on the Solvent

● CH<sub>2</sub>Cl<sub>2</sub>; ○ CCl<sub>4</sub>; ■ CS<sub>2</sub>; ◻ CHCl<sub>3</sub>.

is deactivated to some extent by the internal standard of the reaction, namely, sym-tetrachloroethane; for this reason the conversion of the present reaction was lower than of the reaction in carbon tetrachloride alone<sup>5</sup>. The failure of the addition in some solvents may be due to an insufficient solvation ability of the perhalogenated ionic intermediates<sup>4,5</sup> at the catalyst surface, e.g. in the case of the reaction in "inert" cyclohexane.

#### EXPERIMENTAL

Boiling points are uncorrected. Gas chromatography was performed on a Chrom 3 apparatus (Laboratorní přístroje, Prague; indication by thermal conductivity and flame ionisation, diameter of the stainless steel column 0.6 cm, Celite 545 as the carrier of the stationary phase, capillary column 5000 cm, diameter 0.02 cm, Apiezon L). The preparative gas chromatography was performed on an uncommercial apparatus. Infrared spectra were taken on a Zeiss UR 10 apparatus. PMR spectra were measured on a BSS 477 apparatus (Tesla Brno; 60 mc/s).

#### Materials

Fluorotrichloromethane (Ledon 11, Spolek pro chemickou a hutní výrobu, Ústí nad Labem, Czechoslovakia) and fluorodichloromethane (Farbwerke Hoechst, Germany) were commercial products. 1,2-Difluorodichloroethylene was prepared<sup>5</sup> by dehalogenation of 1,2-difluorotetrachloroethane (Ledon 112, for the manufacturer see above). Before the use, all reaction components and solvents were distilled over phosphorus pentoxide under nitrogen.

#### Fluorochloromethane

A mixture of methylene chloride (425 g; 5.03 mol), antimony trifluoride (616 g; 3.48 mol), and antimony pentachloride (129 g; 0.43 mol) was heated for 40 hours at 60–70°C under stirring. The gaseous products were condensed in a receiver cooled with Dry Ice. The condensate was washed with water, dried on a column of magnesium perchlorate and the acidity removed on a column of potassium fluoride. Rectification of the crude product (153.3 g; content: 81.5% of fluorochloromethane, 3.2% of difluoromethane, and 15.3% of methylene chloride) afforded 83.1 g (24.1%) of fluorochloromethane, b.p. –10 to –8.5°C (reported<sup>20,21</sup>, –9 to –8.5°C), of 99.5% purity (gas chromatography, silicone elastomer E 301, 120 cm column, 25°C, conductivity detection). For infrared spectrum see ref.<sup>22,23</sup>.

#### Reaction of Fluorochloromethane with 1,2-Difluorodichloroethylene

A mixture of fluorochloromethane (20.5 g; 0.300 mol), 1,2-difluorodichloroethylene (101 g; 0.761 mol), and aluminum chloride (4.0; 0.030 mol) was shaken for 7 hours in a glass ampoule at 14–17°C. The reaction mixture was decomposed with dilute hydrochloric acid, diluted with methylene chloride (10 ml), the oil washed with aqueous sodium hydrogen carbonate and water, dried over anhydrous calcium chloride, and the volatile substances removed by distillation. The residue (2.6 g) containing about 15% of trifluorotrichloropropane (*I*) was subjected to gas chromatography to afford the product which was identified as 1,1,2-trifluoro-1,2,3-trichloropropane (*Ia*) of 98.5% purity (silicone elastomer E 301, 60°C, 120 cm column, conductivity detection). Compound *I* affords on a capillary column (25°C) three waves in the relative quantity 6.5, 90 (*Ia*), and 3.5%. PMR spectrum of compound *Ia* in carbon tetrachloride: doublet 6.09 $\tau$ ,  $J_{\text{H-F}}^3 = 7.9$  c/s. Infrared spectrum (carbon disulfide, carbon tetrachloride;  $\text{cm}^{-1}$ ): 743 m, 769 m, 818 m, 922 m, 1010 s, 1049 m, 1073 s  $\nu(\text{C-F})$ , 1147 s  $\nu(\text{C-F})$ , 1208 m, 1234 m, 2974 w  $\nu(\text{C-H})$ .  $\text{C}_3\text{H}_2\text{Cl}_3\text{F}_3$  (201.4) calculated: 17.87% C, 1.01% H, 28.28% F; found: 17.79% C, 1.04% H, 28.31% F.

The competitive reactions of monofluorochloromethanes with 1,2-difluorodichloroethylene (Table II) were performed analogously to the reaction of fluorochloromethane alone. Yields of products I-III are based on analysis of the crude reaction product and fractions 76-110°C, above 110°C or 110-160°C.

#### Reaction of Fluorotrichloromethane with 1,2-Difluorodichloroethylene in Various Solvents

A mixture of fluorotrichloromethane (40.0 g; 0.281 mol), 1,2-difluorodichloroethylene (20.0g; 0.150 mol), aluminum chloride (3.0 g; 22.5 mmol), sym-tetrachloroethane (10.0 g), and the solvent (110 ml) was stirred at room temperature at 20°C. Samples of the reaction mixture were decomposed with water and their content of trifluoropentachloropropane determined in respect to sym-tetrachloroethane (internal standard) Gas chromatography: silicone elastomer E 301, 360 cm column, 150°C, conductivity detection.

*PMR spectra, infrared spectra, and elemental analyses were performed in Central Laboratories of this Institute.*

#### REFERENCES

1. Paleta O., Pošta A.: This Journal 31, 3584 (1966).
2. Paleta O., Pošta A., Bartl V., Balhar A.: This Journal 32, 3888 (1967).
3. Olah G. A., Kuhn S. J.: J. Org. Chem. 29, 2317 (1964).
4. Paleta O.: This Journal 34, 1766 (1969).
5. Paleta O., Pošta A.: This Journal 32, 1427 (1967).
6. Paleta O., Dědek V., Pošta A., Dvořák F., Martínek J.: Czechoslov. Pat. 110 199 (1962).
7. Nielsen J. R., Liang C. Y., Smith D. C., Alpert M.: J. Chem. Phys. 21, 1070 (1953).
8. Nielsen J. R., Liang C. Y., Smith D. C.: J. Phys. 21, 383 (1953).
9. Paleta O., Pošta A., Novotná Z.: This Journal 33, 2970 (1968).
10. Paleta O.: Unpublished results.
11. Boggs J. E., Mosher H. P.: J. Am. Chem. Soc. 82, 3517 (1960).
12. Paleta O.: Chem. listy 64, 31 (1970).
13. Hine J., Porter J. J.: J. Am. Chem. Soc. 79, 5493 (1957).
14. Prins H. J.: Rec. Trav. Chim. 65, 455 (1946).
15. Prins H. J.: Rec. Trav. Chim. 68, 898 (1949).
16. Barendrecht W.: Chem. Weekbl. 54, 404 (1958).
17. Novák J., Žemlička J.: *Preparative Reactions in Organic Chemistry* (in Czech), Vol. 7, p. 57. Published by Nakladatelství ČSAV, Prague 1962.
18. Gagnaux P., Susz B. P.: Helv. Chim. Acta 44, 1128, 1132 (1961).
19. Olah G. H., Chi-Hsiung Lin: J. Am. Chem. Soc. 90, 6468 (1968).
20. Henne A. L.: J. Am. Chem. Soc. 59, 1200 (1937).
21. Haszeldine R. N.: J. Chem. Soc. 1952, 4259.
22. Plyler E. K., Lamb M. A.: J. Res. Natl. Bur. Std. 45, 204 (1950).
23. Plyler E. K., Benedict W. S.: J. Res. Natl. Bur. Std. 47, 202 (1951).

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