

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

Fluorochloroethanes and Fluorochloroethylenes. II

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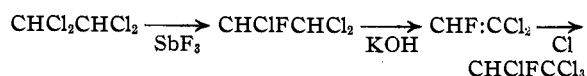
A preceding paper¹ has described organic fluorochlorides which were obtained by the progressive replacement of the chlorine atoms by fluorine in hexachloroethane and tetrachloroethylene. In general these compounds were characterized by an unusually high degree of stability and low degree of toxicity.

The investigation is now extended to fluorochloro derivatives of ethane and ethylene, containing one atom of hydrogen in their molecule. Its purpose is to ascertain whether the presence of the fluorine is capable of retarding or even completely preventing the shedding of two halogen atoms or one molecule of hydracid from the ethane molecule with resultant passage to an ethylenic or acetylenic compound. The compounds described hereunder can be visualized as derived from pentachloroethane and from trichloroethylene by gradual replacement of the chlorine atoms by fluorine atoms; however, in actual preparation it is necessary to proceed by roundabout ways in some of the cases, because the introduction of fluorine in these chlorides follows certain definite rules and tends to form asymmetrical compounds, in marked opposition to the cases reported in the first paper.

In every case fluorine has been introduced into the molecule by replacement of a chlorine atom. This scheme and its experimental details have been described in the preceding paper. Treated in the customary fashion with antimony fluoride, pentachloroethane gives, in the following order, $\text{CHCl}_2\text{CCl}_2\text{F}$, $\text{CHCl}_2\text{CClF}_2$ and very small quantities of $\text{CHClF}\cdot\text{CClF}_2$ and $\text{CHF}_2\text{CClF}_2$. No other derivative is formed, and consequently it can be said that the CCl_3 group is fluorinated first, in preference to the CHCl_2 group, and that only two of its chlorine atoms can be replaced by direct fluorination with antimony fluoride. The first point differs from the course of the fluorination of hexachloroethane, where the successive steps are as symmetrical as possible ($\text{CCl}_3\text{CCl}_3 \rightarrow \text{CCl}_2\text{FCCl}_3 \rightarrow \text{CCl}_2\text{FCCl}_2\text{F} \rightarrow \text{CClF}_2\text{CCl}_2\text{F} \rightarrow \text{CClF}_2\text{CClF}_2$) and where the three possible asymmetrical compounds ($\text{CCl}_3\text{CClF}_2$, CCl_3CF_3 and $\text{CF}_3\text{CCl}_2\text{F}$) fail to appear. The

second point, however, duplicates the results reported for hexachloroethane. In view of these points, it is evident that roundabout methods are needed to prepare some of the other possible derivatives, namely, CHClFCCl_3 , $\text{CHClFCCl}_2\text{F}$ and CHF_2CCl_3 .²

To prepare CHClFCCl_3 , the following scheme,³ is followed



The fluorination of CHClFCCl_3 takes place exclusively in the CCl_3 group, in perfect agreement with what has been said hereabove, and it is consequently easy to prepare $\text{CHFClCCl}_2\text{F}$.

The asymmetrical difluoride CHF_2CCl_3 is prepared by partial chlorination of $\text{CHF}_2\text{CHCl}_2$ ³ in sunlight. The chlorination affects the CHCl_2 group before it touches the CHF_2 group, and consequently an operation conducted in moderate sunlight with a deficiency of chlorine yields a large proportion of CHF_2CCl_3 , and a small quantity of higher boiling $\text{CClF}_2\text{CCl}_3$ ¹ which can be eliminated easily.

The ethylenic derivatives (and their dibromides) have all been prepared from the saturated compounds by removal of two halogen atoms with zinc in alcohol or by elimination of one molecule of hydracid with alcoholic potassium hydroxide.

The purification methods, the determination of the physical properties and the analysis procedure have been reported in the preceding paper. Because the fluorination was attended with a very pronounced splitting of hydrochloric acid, particularly when the reagents were not rigorously dried or when an excessive temperature prevailed, an additional step was inserted in the method of purification. The ethylenic derivatives thus formed have boiling points which are so close to those of some of the saturated products that their separation by fractional distillation is quite impractical. They are, however, conveniently removed by treatment with chlorine in the dark;

(2) Some of the more highly fluorinated derivatives, namely, CHCl_2CF_3 , $\text{CHF}_2\text{CCl}_2\text{F}$, $\text{CHClF}_2\text{CF}_3$ and CHF_2CF_3 have been prepared by chlorination of the corresponding fluorides and will be reported later.

(3) Swarts, *Mém. Cour. Roy. Acad. Belg.*, **61**, 44 (1901).

(1) Locke, Brode and Henne, *THIS JOURNAL*, **56**, 1726 (1934).

TABLE I

	M. p., °C.	B. p., °C.	T., °C.	d_4	n_D	n_D	n_B	Mol. wt.		Cl/F	
								Calcd.	Found	Calcd.	Found
(1) $\text{CHCl}_2\text{CCl}_2\text{F}$	- 82.6	116.6	20.0	1.62232	1.44634	1.44873	1.45873	185	189	4.0	4.0
(2) CHClFCCl_2	- 95.35	117.0	20.0	1.62525	1.45005	1.45253	1.45861	185	186	4.0	4.1
(3) $\text{CHCl}_2\text{CClF}_2$		71.9	25.0	1.5447			1.3889	169	165	1.5	1.5
(4) $\text{CHClFCCl}_2\text{F}$	Glass	72.5	20.0	1.55868	1.39216	1.39419	1.39873	169	169	1.5	1.6
(5) CHF_2CCl_2	Glass	73.0	20.0	1.56613	1.39590	1.39787	1.40278	169	167	1.5	1.6
(6) $\text{CHClFCF}_2\text{Cl}$		28.0	10.0	1.496				153	150	0.66	0.6
(7) $\text{CHF}_2\text{CF}_2\text{Cl}$		-12						136	130	0.25	0.2
(8) $\text{CHF}=\text{CCl}_2$	- 108.8	37.3	20.0	1.38327	1.40112	1.40364	1.41031	115	113	2.0	2.0
(9) $\text{CHCl}=\text{CClF}$		35.1	16.5	1.4032		1.372				2.0	2.0
(10) $\text{CHCl}=\text{CF}_2$		2.4								0.5	0.5
(11) CHClBrCClFBr		163.5	23	2.2833		1.5160		275	270		
(12) $\text{CHClBrCF}_2\text{Br}$		118.7	25	2.2319		1.4611		258	258		

this treatment is repeated until it no longer alters the physical properties (particularly the density and the melting point) of the distilled product.

The experimental results are reported in Table I. Determination of the configurations.

- (1) $\text{CHCl}_2\text{CCl}_2\text{F}$: Different from (2), whose structure is known; yields $\text{CHCl}=\text{CClF}$ by treatment with zinc, and $\text{CCl}_2=\text{CClF}$ with potassium hydroxide. Further fluorination yields $\text{CHCl}_2\text{CClF}_2$.
- (2) CHClFCCl_2 : Known; yields $\text{CHF}=\text{CCl}_2$ with zinc, and $\text{CClF}=\text{CCl}_2$ with potassium hydroxide. Its further fluorination yields $\text{CHClFCCl}_2\text{F}$.
- (3) $\text{CHCl}_2\text{CClF}_2$: Obtained from (1); its chlorination yields $\text{CCl}_2\text{CClF}_2$; zinc removes two chlorine atoms, yielding $\text{CHCl}=\text{CF}_2$; potassium hydroxide yields $\text{CCl}_2=\text{CF}_2$.
- (4) $\text{CHClFCCl}_2\text{F}$: Different from (3) and from (5); obtained from (2); chlorination gives $\text{CCl}_2\text{FCCl}_2\text{F}$; zinc removes two chlorines to yield $\text{CHF}=\text{CClF}$; potassium hydroxide yields $\text{CClF}=\text{CClF}$.
- (5) CHF_2CCl_2 : Obtained from $\text{CHCl}_2\text{CHF}_2$; chlorination gives $\text{CCl}_2\text{CClF}_2$; zinc removes one atom of chlorine and one atom of fluorine, yielding $\text{CHF}=\text{CCl}_2$; potassium hydroxide yields $\text{CF}_2=\text{CCl}_2$.
- (6) $\text{CHClFCF}_2\text{Cl}$: Obtained from (4) or (3).
- (7) $\text{CHF}_2\text{CF}_2\text{Cl}$: Obtained in very small amounts. Constitution established only by analogy.
- (8) $\text{CHF}=\text{CCl}_2$: Obtained from (2). Not separable into stereoisomers.
- (9) $\text{CHCl}=\text{CClF}$: Obtained from (1). Boiling range shows a range indicative of a mixture of stereoisomers.
- (10) $\text{CHCl}=\text{CF}_2$: Obtained from (3), no indication of isomer mixture.

Molecular Refraction.—The molecular refractions have been calculated by means of the Lorentz-Lorenz formula. The atomic refraction

of fluorine has been obtained by subtracting the "I. C. T." increments for C, H, Cl and Br from the experimental molecular refractions.

	Temp., °C.	MR. exptl.	At. refr., F
CHClFCCl_2	20.0	30.878	1.074
CHF_2CCl_2	20.0	26.100	1.136
$\text{CHClFCCl}_2\text{F}$	20.0	25.003	1.083
$\text{CHCl}_2\text{CCl}_2\text{F}$	20.0	30.711	0.907
$\text{CHF}=\text{CCl}_2$	20.0	20.300	0.697
$\text{CHCl}_2\text{CClF}_2$	25.0	25.92	1.06

So far as the physical properties go, it is thus apparent that it matters little where the fluorine substitution takes place, as the physical properties are about equally affected in the various isomers. It does not follow that fluorination occurs at random; in fact, fluorination preferably takes place in the group where no hydrogen is present, and tends to give asymmetrical compounds. The presence of the fluorine has a marked stabilizing effect on the whole molecule, and this stabilizing effect is particularly enhanced by the presence of two atoms of fluorine on the same carbon. The physiological effect of these compounds parallels their chemical behavior, and will be reported in a medical journal.

Summary

Derivatives of ethane and of ethylene, containing chlorine, fluorine and one atom of hydrogen are presented. Attention is directed to the preferential course of the fluorination during synthesis.

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