

HgF<sub>2</sub> and CHBr<sub>2</sub>CHBr<sub>2</sub>.—CHBr<sub>2</sub>CHBr<sub>2</sub> reacts with HgF<sub>2</sub> already at 100°, very easily at 150–160°, to form CHBr<sub>2</sub>CHF<sub>2</sub> quantitatively.

### Summary

The course of the fluorination of CHX<sub>2</sub>CHX<sub>2</sub>

compounds is presented. The following new compounds CHClBrCHClF, CHClBrCHF<sub>2</sub>, CH<sub>2</sub>-ClCF<sub>3</sub>, CHFBrCHF<sub>2</sub> and CHF<sub>2</sub>CHF<sub>2</sub> are described.

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## Fluoroethanes and Fluoroethylenes. V

BY ALBERT L. HENNE AND MARY W. RENOLL

The present paper presents the fluorination of halo derivatives of ethane containing three or four atoms of hydrogen in their molecule, and describes several new fluorinated compounds. Preceding papers<sup>1</sup> have shown the course of the fluorination in derivatives containing less hydrogen and have emphasized the tendency to lose hydrogen halides, to rearrange and to resist fluorination with antimony fluorides.

The main result of the present investigation is the finding that, when the halogen atoms are all located on the same carbon atom, fluorination proceeds rapidly to completion, without simultaneous chlorination or loss of hydrogen halides. In marked opposition, derivatives having both hydrogen and an halogen on each of their carbon atoms resist fluorination with antimony fluorides considerably, and when they are affected they undergo important decomposition and chlorination. The fluorinated compounds exhibit a marked difference in their stability, in favor of the asymmetrical compounds: CH<sub>3</sub>CHF<sub>2</sub> is perfectly stable, while CH<sub>2</sub>FCH<sub>2</sub>F decomposes spontaneously, and CH<sub>2</sub>FCHF<sub>2</sub> hydrolyzes slowly while CH<sub>3</sub>CF<sub>3</sub> is nearly inert physiologically as well as chemically.

Two methods of fluorination have been used, namely, (1) the interaction of an organic polychloride with antimony fluoride in the presence of SbCl<sub>5</sub> or Br, and (2) the interaction of a polybromide with mercuric fluoride. The first procedure gave excellent results with CH<sub>3</sub>CCl<sub>3</sub>, fair results with CH<sub>3</sub>CHCl<sub>2</sub>, mediocre results with CH<sub>2</sub>CHCl<sub>2</sub>, and no results with CH<sub>2</sub>ClCH<sub>2</sub>Cl and with CH<sub>3</sub>CH<sub>2</sub>Cl. The second method was used with success to fluorinate CH<sub>2</sub>BrCHClBr, CH<sub>2</sub>BrCHBr<sub>2</sub>, CH<sub>2</sub>ICHF<sub>2</sub>, CH<sub>2</sub>BrCH<sub>2</sub>Br, CH<sub>3</sub>CHBr<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>Br.

The properties of the new compounds only are listed in Table I. The known compounds produced had physical properties in good agreement with those published by Swarts (see Beilstein). The analyses of the new derivatives were successfully performed as previously described,<sup>2</sup> while the molecular weights were measured by freezing point depression in benzene for the liquids and by quantitative analysis of known volumes for the gases. All were close to the theoretical quantities, and appear in Table I.

The atomic refractions for fluorine listed in the seventh column of Table I were obtained by subtracting from the observed molecular refraction the sum of the increments for C, H, Cl and Br. Most values are in line with those obtained by Swarts<sup>3</sup> for similar compounds, but the very first one is entirely out of line, and this remains unexplained. This value was repeatedly verified, and no error was detected in the experimentation; it is true that CH<sub>3</sub>CCl<sub>2</sub>F is not extremely stable, but its decomposition is quite slow and does not explain the fact that the density is about 0.04 lower than could be expected by analogy. The chlorine analysis is also too high, an indication of impurity. The molecular weight is correct.

### Experimental Details

(1) **Fluorination of CH<sub>3</sub>CCl<sub>3</sub>.**—The fluorinating agent is a mixture of 90% SbF<sub>3</sub> and 10% SbF<sub>5</sub>Cl<sub>2</sub>. It is placed in a metal container, equipped with a metal dephlegmator bearing a pressure gage, thermometer and needle valve. The container is cooled in an ice-bath, with the needle valve closed. This creates a partial vacuum, and makes it possible to suck ice-cold CH<sub>3</sub>CCl<sub>3</sub> into the equipment. The relative quantities of reagents depend on whether the mono-, di- or trifluoride is the desired final product. The reaction vessel is allowed to come slowly to room temperature, as the reaction starts very vigorously. By control

(1) THIS JOURNAL, **58**, 402, 404, 887 (1936).

(2) Hubbard and Henne, THIS JOURNAL, **56**, 1078 (1934).

(3) Swarts, *J. chim. phys.*, **20**, 30 (1923).

TABLE I

	B. p., 760 mm., °C.	<i>t</i> <sup>o</sup>	<i>d</i> <sub>4</sub> <sup>20</sup>	<i>n</i> <sub>D</sub> <sup>20</sup>	MRD	A. R. F.	F, %	Cl, %	Br, %	Mol. wt.
CH <sub>3</sub> CCl <sub>2</sub> F	31.7-31.8	5	1.2673	1.38679	21.72	1.65	15.5	62.2	..	116.5
CH <sub>3</sub> CClF <sub>2</sub>	-9.6						35.1	38.2	..	100.0
CH <sub>3</sub> CF <sub>3</sub>	-46.7						67.8			84.0
CH <sub>2</sub> ClCHClF	73.7-73.9	20	1.3814	1.41132	21.03	0.96	16.2	60.4		116.0
CH <sub>2</sub> ClCHF <sub>2</sub>	35.1	15	1.312	1.3528	16.60	1.26	35.3	38.2		98.1
CH <sub>2</sub> FCHF <sub>2</sub>	5						67.6			83.7
CH <sub>2</sub> BrCHClF	96.6	20	1.82913	1.45463	23.93	0.96	11.8	21.8	49.5	161
CH <sub>2</sub> BrCH <sub>2</sub> F	71.5-71.8	25	1.7044	1.42261	18.96	0.86	15.2		63.9	125
CH <sub>2</sub> ICH <sub>2</sub> F	98-102									
CH <sub>3</sub> CHClF	16.1-16.2						22.9	42.8		80.9
CH <sub>3</sub> CHF <sub>2</sub>	-24.7						57.5			66.0
CH <sub>2</sub> FCH <sub>2</sub> F	10-11									

of the temperature and pressure, it is possible to distil from the dephlegmator the desired fluoride. CH<sub>3</sub>CCl<sub>2</sub>F and CH<sub>3</sub>CClF<sub>2</sub> have been obtained in yields of 85 to 90%, while CH<sub>3</sub>CF<sub>3</sub> has been obtained currently in 30% yield; this last yield could be considerably improved if one were to try to produce this compound exclusively. Rough indications are that a 60 to 70% yield would be obtained easily. If the reaction is allowed to start too suddenly, or if heating is applied too soon, a considerable amount of hydrogen chloride is evolved, and yields are greatly cut down. It was never found advisable to heat higher than 70° at the very end of the reaction. Runs have been made on several kilograms of material at a time, and the operation conducted substantially as it is in the production of CCl<sub>2</sub>F<sub>2</sub> from CCl<sub>4</sub>.<sup>4</sup>

(2) Fluorination of CH<sub>3</sub>CHCl<sub>2</sub>.—The operation is conducted substantially as it is in the preceding paragraph, but yields are not as favorable, and decomposition is more difficult to prevent. Hence this operation was abandoned in favor of the following one.

(3) Fluorination of CH<sub>3</sub>CHBr<sub>2</sub>.—Ethylidene bromide, made from paraldehyde, is placed in an ice-cold metal container equipped with an ice reflux condenser. Mercuric fluoride (theoretical quantity) is fed slowly into it through a wide rubber hose pinched by two screw clamps. The reaction proceeds rapidly, and CH<sub>3</sub>CHF<sub>2</sub> distills through the condenser, and is collected in a receiver cooled with solid carbon dioxide, while the CH<sub>3</sub>CHBrF and CH<sub>3</sub>CHBr<sub>2</sub> are returned by the condenser for further fluorination. The fluorine in the mercuric fluoride is completely utilized. The amount of intermediate CH<sub>3</sub>CHBrF is usually about 5%, when no effort is made to withdraw it from the reaction field as soon as it is formed.

(4) Fluorination of CH<sub>2</sub>BrCH<sub>2</sub>Br.—The equipment is the same as in the preceding case. The reaction is quite vigorous. The intermediate compound CH<sub>2</sub>BrCH<sub>2</sub>F is, however, more easy to isolate than its isomer CH<sub>3</sub>CHBrF. The reaction proceeds easily to complete utilization of the fluorine available in mercuric fluoride. However, due to the instability of CH<sub>2</sub>FCH<sub>2</sub>F very little of that compound is produced, and it is impossible to isolate it as a pure compound. Typical runs yielded about 50% CH<sub>2</sub>FCH<sub>2</sub>Br, about 10 to 15% of an unsaturated hydrocarbon which seemed to be a mixture of butadiene and butylene, about

10% of CH<sub>2</sub>FCH<sub>2</sub>F and from 25 to 30% of very pure butyl fluoride. Despite efforts to improve the operation, the results were consistently discouraging.

(5) Fluorination of CH<sub>2</sub>ICH<sub>2</sub>I.—The procedure is the same as above and the results were almost identical in every respect but one, namely, that only a very small quantity of intermediate CH<sub>2</sub>ICH<sub>2</sub>F was isolated.

(6) Fluorination of CH<sub>2</sub>ClCHCl<sub>2</sub>.—This compound, heated under pressure with HgF<sub>2</sub> at about 140° gives about 50% yields of CH<sub>2</sub>ClCHClF and only 8 to 10% of CH<sub>2</sub>ClCHF<sub>2</sub>. Fluorination with a mixture of SbF<sub>3</sub> and bromine (10%), at 160° does not have any effect, while with 10% of SbCl<sub>5</sub> instead of bromine, the reaction proceeds very slowly; with 20% of SbCl<sub>5</sub>, the reaction is considerably hastened, but side reactions make their appearance. With 20% of SbF<sub>3</sub>Cl<sub>2</sub> as catalyst the side reaction became predominant by far, and the final yields are not better than 30 to 35% of CH<sub>2</sub>ClCHClF and 8 to 10% of CH<sub>2</sub>ClCHF<sub>2</sub>. The purification is made considerably more difficult by the results of the side reactions.

(7) Synthesis of CH<sub>2</sub>FCHF<sub>2</sub>.—Mercuric fluoride is fed into CH<sub>2</sub>BrCHBr<sub>2</sub> (as in the third case) and the mixture is heated progressively to 140°; this causes the quantitative production of CH<sub>2</sub>BrCHBrF or CH<sub>2</sub>BrCHF<sub>2</sub>, according to the proportion of the reagents. Efforts to fluorinate the latter further failed repeatedly. It is better to obtain CH<sub>2</sub>ICH<sub>2</sub>Br by interaction of it with calcium iodide in alcohol, in sealed tube. (The yields were usually 60 to 65%, despite the fact that Swarts has obtained better than 85%.) This iodide is heated with HgF<sub>2</sub> in a nickel container in the manner described for the production of CHF<sub>2</sub>CHF<sub>2</sub><sup>5</sup> and yields about 60% of CH<sub>2</sub>FCHF<sub>2</sub>.

(8) Fluorination of CH<sub>2</sub>BrCHClBr.—Heating with mercuric fluoride gives a quantitative yield of CH<sub>2</sub>BrCHClF, but only traces of CH<sub>2</sub>BrCHF<sub>2</sub>.

### Summary

New fluorinated derivatives of ethane, containing three or four atoms of hydrogen in their molecule have been synthesized, and their physical properties are tabulated.

THE MIDGLEY FOUNDATION  
COLUMBUS, OHIO

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(4) Midgley and Henne, *Ind. Eng. Chem.*, **22**, 542 (1930).

(5) THIS JOURNAL, **58**, 884 (1936).