

refluxes to the reaction vessel. The heating is to be done in an oil-bath, and should be as high as 160° at the end of the operation to ensure yields better than 80%, usually about 90%. In this manner  $\text{CH}_2\text{BrCHBrF}$  and  $\text{CH}_2\text{BrCHF}_2$  have been prepared from  $\text{CH}_2\text{BrCHBr}_2$ ; similarly  $\text{CHBr}_2\text{CHBr}_2$  yields quantitatively  $\text{CHBr}_2\text{CHBrF}$  or  $\text{CHBr}_2\text{CHF}_2$ , according to the proportion of the reactants.

**Acyl Fluorides.**—The mode of operation is similar to that recommended for ethyl fluoride. Mercuric fluoride reacts vigorously with acetyl chloride, and the acetyl fluoride thus formed volatilizes through the reflux condenser. To gage the yields, acetyl fluoride was received in ethanol, with which it reacts at once. The quantity of ethyl acetate recovered corresponded to about a 50% yield of acetyl fluoride; it is felt that this yield could be considerably improved.

**Reaction with Ethanol.**—A small amount of gas is formed, and the reaction stops promptly. The gas is a mixture of ethylene and ethyl fluoride, the latter in about 2% yield.

**Cyclohexyl Derivatives.**—Cyclohexyl bromide treated with  $\text{HgF}_2$  in a solvent reacts at once, at room temperature. The reaction mass becomes purple, an indication that cyclohexylene is formed. Since it is impractical to separate the cyclohexyl fluoride from the reaction mass, settling is allowed to take place and the mercuric salts are filtered off. The clear filtrate is shaken with water, and examination of the water layer indicates the presence of hydrogen fluoride and cyclohexyl alcohol in quantities corresponding to about 10% yields of cyclohexyl fluoride. The same kind of results have been obtained from ortho- and from para-dibromocyclohexane.

### Summary

Mercuric fluoride is proposed as a new fluorinating agent. Its preparation, properties and uses are described.

THE MIDGLEY FOUNDATION  
COLUMBUS, OHIO

RECEIVED JANUARY 30, 1936

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

## Fluro Derivatives of Ethane and Ethylene. IV

BY ALBERT L. HENNE AND MARY W. RENOLL

Preceding papers<sup>1</sup> have described fluoro derivatives of ethane and ethylene containing no hydrogen, one hydrogen and two asymmetrically placed hydrogen atoms. The present paper presents fluoro derivatives containing two asymmetrically placed hydrogen atoms, and places emphasis on the different courses followed by the fluorination, when different fluorinating agents are used.

Swarts<sup>2</sup> has shown that the fluorination of acetylene tetrabromide by means of antimony fluoride yields successively  $\text{CHBr}_2\text{CHBrF}$  and  $\text{CHBr}_2\text{CHF}_2$ , where the fluorination stops completely and that acetylene tetrachloride yields  $\text{CHCl}_2\text{CHClF}$  and  $\text{CHCl}_2\text{CHF}_2$ , together with a very small amount of  $\text{CHClFCHF}_2$ . Swarts' observations and the physical constants reported by him have been verified, and there is no doubt that his determination of the molecular structure of the difluorides is correct. The only point which was never duplicated was the production of small quantities of  $\text{CHClFCHF}_2$ , and this may be due to the fact that Swarts operated in platinum equipment; it is known that platinum has a catalytic action on fluorination. The experiments carried out in this Laboratory were performed in steel, copper or nickel.

Since the fluorination of acetylene tetrabromide is considerably more rapid than that of acetylene tetrachloride, an effort was made to fluorinate  $\text{CHClBrCHClBr}$ , in the hope that this would yield  $\text{CHClFCHClF}$ , a compound which should undergo further fluorination without great difficulty.<sup>3</sup> However, the usual treatment with antimony fluoride gave rise to the following compounds:  $\text{CHCl}_2\text{CHClF}$ ,  $\text{CHCl}_2\text{CHF}_2$ ,  $\text{CHCl}_2\text{CCl}_2\text{F}$  and  $\text{CHCl}_2\text{CClF}_2$ , which were produced in small quantity, as by-products, and have been previously described, and two new compounds,  $\text{CHClBrCHClF}$ , and  $\text{CHClBrCHF}_2$ . The characteristics of these new compounds were measured and computed as in the preceding papers.<sup>1</sup>

### EXPERIMENTAL VALUES

Compound	$\text{CHClBrCHClF}$	$\text{CHClBrCHF}_2$
B. p., °C.	124.7–125.1	82.3–82.5
At mm.	736	743
$d_{20}^{20}$	1.932	1.879
$n_{20}^{20D}$	1.4776	1.4173
$M_{RD}$	28.48	24.04
Cl, %	36.1	19.7
Br, %	40.9	44.6
F, %	9.6	21.0
Mol. wt.	194.2	178.0

Neither substance freezes at solid carbon dioxide temperature. By subtracting from the observed

(1) THIS JOURNAL, 56, 1726 (1934); 58, 402, 404 (1936).

(2) Swarts, *Mem. Acad. Roy. Sci. Belg.*, 61, 1–94 (1901).

(3) See THIS JOURNAL, 58, 882 (1936).

MR<sub>D</sub> the increments given by "I. C. T." for C, H, Cl and Br, the atomic refraction of F is computed as 1.08 in the case of the difluoride, and 0.65 in the case of the monofluoride. The value 1.08 is excellent. The value 0.65 is low, but by no means out of line with observations on similar compounds. For instance, Swarts observes  $F = 0.83$  in  $\text{CHCl}_2\text{CHClF}$ , while in the case of  $\text{CHBr}_2\text{CHBrF}$ , the computed value of  $F$  becomes even negative.

As it was now evident that fluorination was invariably proceeding in an asymmetrical fashion, efforts were made to cause further fluorination by combining the following experimental conditions: (1) using either  $\text{CHCl}_2\text{CHF}_2$  or  $\text{CHBr}_2\text{CHF}_2$  as starting material; (2) adding increasing amounts of  $\text{SbF}_3\text{Cl}_2$  as catalyst; (3) operating under pressure; and (4) raising the temperature to 150–160°. In all cases considerable decomposition took place, but by operating in large quantities, it became possible to collect and isolate some reaction products: typical runs on 2 kilos of  $\text{C}_2\text{H}_2\text{Cl}_2\text{F}_2$  gave 350 g. boiling below 30°, while 1 kilo of  $\text{C}_2\text{H}_2\text{Br}_2\text{F}_2$  gave 200 g. boiling below 50°. Repeated refractionation gave, in addition to many compounds resulting from the replacement of one or both hydrogen atoms by chlorine or bromine, the following results. From the chlorides: a compound boiling at 6.1°, which proved to be  $\text{CH}_2\text{ClCF}_3$  and no indication of anything boiling about 17°, where  $\text{CHClFCHF}_2$  boils. From the bromides: some substance boiling at 23–25°, where  $\text{CH}_2\text{BrCF}_3$  should boil, and some substance boiling about 40°, where  $\text{CHBrFCHF}_2$  should boil; but in neither case, any indication of a compound at –23° or –35°, where  $\text{CHF}_2\text{CHF}_2$  and  $\text{CH}_2\text{FCF}_3$  would boil, respectively.

To demonstrate the course of the rearrangement, the compound boiling at 6° was prepared in larger quantity, and purified. Its characteristics were found to be: boiling point 6.1°;  $d_4^{20}$  1.389;  $n_D^{20}$  1.3090; MR<sub>D</sub> obsd. 16.4; Cl found 30.4%, calcd. 30.0%; F found 48.0%, calcd. 48.5%; mol. wt. found 118, calcd. 118.5. Computing the atomic refraction of fluorine as above gives  $F = 1.1$ , a good value. These properties indicate a gross formula  $\text{C}_2\text{H}_2\text{ClF}_3$ . Chlorination in sunlight gives exclusively  $\text{CCl}_3\text{CF}_3$ , a known compound, and thus demonstrates that the formula of the original compound is  $\text{CH}_2\text{ClCF}_3$ . As the corresponding bromide could not be obtained in a good state of purity without unjustified efforts,

its formula was accepted by analogy based on boiling points; in general fluorobromides boil about 20° higher than the corresponding fluorochlorides.

The resources of fluorination with antimony fluoride having thus been exhausted, another fluorinating agent was used, namely, mercuric fluoride, and its use made it possible to obtain the following sequence  $\text{CHBr}_2\text{CHBr}_2 \rightarrow \text{CHBr}_2\text{CHBrF} \rightarrow \text{CHBr}_2\text{CHF}_2 \rightarrow \text{CHBrFCHF}_2 \rightarrow \text{CHF}_2\text{CHF}_2$ . At all stages a single compound was made and the complete absence of isomerization made it a simple task to purify the products. The mono- and the difluoride have been adequately described by Swarts.<sup>2</sup> The tri- and the tetrafluoride are new substances, and their characteristics are as follows:  $\text{CHFBrCHF}_2$  boils at 40–41° under 735 mm., has a density  $d_4^{20}$  1.874, refractive index  $n_D^{20}$  1.36175, from which the molecular refraction (observed) is computed as 19.13. Subtracting from this observed MR<sub>D</sub> the sum of the increments for C, H and Br, an atomic refraction of 1.08 is found for fluorine, which is correct. It contains 49.0% Br and 34.8% F (calcd. 49.06 and 34.96) and its molecular weight is 161.5 (calcd. 163).

$\text{CHF}_2\text{CHF}_2$  boils at –23°, has an observed molecular weight of 102 (computed, 102) and contains 74.2% F (74.4% calcd.). The adoption of the proposed formula in preference to  $\text{CH}_2\text{FCF}_3$ , the only other possibility, is based on the facts that the treatment with  $\text{HgF}_2$  gave a single trifluoride, and a single tetrafluoride, and that the boiling points of their isomers, namely,  $\text{CH}_2\text{BrCF}_3$  and  $\text{CH}_2\text{FCF}_3$ , would have been about 25° and –36°, respectively, both sufficiently lower to eliminate any ambiguity.

### Experimental

**HgF<sub>2</sub> and CHBr<sub>2</sub>CHF<sub>2</sub>.**—One hundred cc. (1.03 mols) of  $\text{CHBr}_2\text{CHF}_2$  and 100 g. (0.42 mol) of  $\text{HgF}_2$  were heated electrically in a horizontal nickel tube connected to a vertical steel pipe acting as reflux condenser and dephlegmator, and closed by a needle valve; a pressure gage and thermocouple recorded the conditions of the system. The reaction products were led through a calcium carbonate suspension and a drying tube, into a receiver cooled with solid carbon dioxide. The pressure was kept between 120–150 pounds by purging and the temperature was held at 180–190°. Reaction continued for about nine hours. By slow purging it was possible to avoid removal of much trifluoride. After final purification 16 cc. of  $\text{CHF}_2\text{CHF}_2$  and 23 g. of  $\text{CHF}_2\text{CHBr}$  were obtained; the remainder was unreacted  $\text{CHBr}_2\text{CHF}_2$ .

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.

COLUMBUS, OHIO

RECEIVED MARCH 23, 1936

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

## 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>5</sub> and 10% SbF<sub>3</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).