

[CONTRIBUTION FROM THE KETTERING LABORATORY, MEDICAL COLLEGE, UNIVERSITY OF CINCINNATI]

## Fluorochloroethanes and Fluorochloroethylenes. III

BY ALBERT L. HENNE AND DONALD M. HUBBARD

The second paper of this series<sup>1</sup> has shown that the presence of one atom of hydrogen in the molecule influences markedly the course of the fluorination. The study of the fluorination of asymmetrical tetrachloroethane was undertaken, therefore, to find out whether the trends would be affected further by the presence of a second hydrogen atom, and such was found to be the case.

Asymmetrical tetrachloroethane,  $\text{CH}_2\text{ClCCl}_3$ , was prepared by sunlight chlorination of ethyl chloride, and all intermediate products were purified; since the physical properties were found to be significantly different from those reported in the literature, they were listed hereunder together with the properties of the newly synthesized fluorine derivatives. Moreover, their freezing curves were presented in order to make it possible for the reader to gauge the confidence to be placed in the present determinations.

together with a very considerable amount of ethylenic products. The importance of this side reaction (already reported in the preceding paper) was thus greatly magnified by the presence of a second hydrogen atom held in an asymmetrical position.

The fluorides were purified in the manner previously reported and they proved to be  $\text{CH}_2\text{ClCCl}_2\text{F}$  and  $\text{CH}_2\text{ClCClF}_2$ ; in  $\text{CH}_2\text{ClCCl}_3$  as in previously reported  $\text{CHCl}_2\text{CCl}_3$  the fluorination took place exclusively in the  $\text{CCl}_3$  group. However, in contrast to pentachloroethane (where the  $\text{CHCl}_2$  can be fluorinated) the  $\text{CH}_2\text{Cl}$  group remained perfectly inert toward further fluorination, even under the most severe conditions.

The determination of the configuration of  $\text{CH}_2\text{ClCClF}_2$  and of  $\text{CH}_2\text{ClCCl}_2\text{F}$  is quite simple. The chlorination of the difluoride in sunlight yields  $\text{CCl}_3\text{CClF}_2$ , a known compound; hence the two

TABLE I

No.	Formula	F. p., °C.	B. p., 760 mm. corr., °C.	Density and refractive indices at 1°				Mol. weight		Atomic Cl/F Ratio		
				$d_4^{20}$	$n_D^{20}$	$n_D^{20}$	$n_D^{20}$	Calcd.	Found	Calcd.	Found	
1	$\text{CH}_3\text{CHCl}_2$	-97.4	57.1	20	1.1755	1.41385	1.41638	1.42213	98.9	100.1		
2	$\text{CH}_2\text{CCl}_3$	-30.4	73.9	20	1.3492	1.43598	1.43838	1.44480	133.4	131.6		
3	$\text{CHCl}_2\text{CH}_2\text{Cl}$	-37.4	113.3	20	1.4411	1.46798	1.47064	1.47731	133.4	130.3		
4	$\text{CH}_2\text{ClCCl}_3$	-68.1	129.2	20	1.5532	1.47907	1.48211	1.48906	167.8	165.1		
5	$\text{CH}_2\text{ClCCl}_2\text{F}$	-104.7	88.0	20	1.4921	1.42269	1.42484	1.43055	151.4	150.5	3.00	3.10
6	$\text{CH}_2\text{ClCClF}_2$	-101.2	46.8	20	1.4163	1.36019	1.36193	1.36605	134.9	150.9	1.00	1.04

TABLE II

## MOLECULAR REFRACTION

	MR. $\alpha$		MR. $D$		MR. $\beta$		H $\beta$ - H $\alpha$	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
$\text{CH}_3\text{CHCl}_2$	21.04	21.06	21.17	21.19	21.40	21.42	0.36	0.36
$\text{CH}_2\text{CCl}_3$	25.85	25.90	25.97	26.04	26.30	26.35	0.45	0.45
$\text{CHCl}_2\text{CH}_2\text{Cl}$	25.73	25.90	25.86	26.04	26.17	26.35	0.44	0.45
$\text{CH}_2\text{ClCCl}_3$	30.64	30.74	30.81	30.90	31.19	31.28	0.55	0.54
$\text{CH}_2\text{ClCCl}_2\text{F}$	25.82		25.94		26.34			
$\text{CH}_2\text{ClCClF}_2$	21.04		21.13		21.34			

The fluorination of  $\text{CH}_2\text{ClCCl}_3$  was carried out under two different sets of conditions,<sup>2</sup> namely, (1) by means of antimony trifluoride with 10% of antimony pentachloride, (2) by means of anhydrous hydrofluoric acid, in the presence of antimony pentachloride.

From the reaction products, it became apparent that a monofluoride and a difluoride were formed,

(1) THIS JOURNAL, 58, 402 (1936).

(2) Locke, Brode and Henne, *ibid.*, 56, 1726 (1934).

TABLE III

## ATOMIC REFRACTION OF FLUORINE

	$F_\alpha$	$F_D$	$F_\beta$
$\text{CH}_2\text{ClCCl}_2\text{F}$	1.01	1.00	1.11
$\text{CH}_2\text{ClCClF}_2$	1.08	1.08	1.07

fluorine atoms must be located on the same carbon atom. Moreover, since the fluorination of the monofluoride gives only the one difluoride mentioned here, its constitution is thereby established.

The physical properties of the two new fluorinated compounds are listed together with those of several chlorides which did not agree with data of the literature.

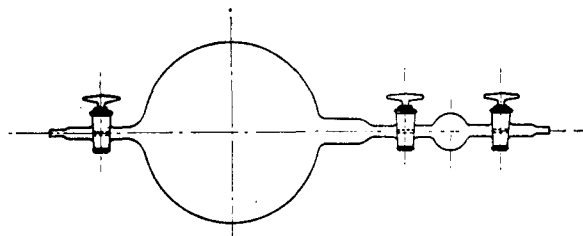


Fig. 1.

The values for the atomic refractions of fluorine as given by Swarts<sup>3</sup> vary with the type of com-

for a large variety of compounds, also the values given by Locke, Brode and Henne.<sup>2</sup>

### Experimental

**Preparation of Asymmetrical Tetrachloroethane.**—This compound was synthesized in two ways, namely: (1) ethyl chloride was chlorinated in sunlight; (2) methylchloroform<sup>4</sup> was chlorinated in sunlight. It was isolated by fractional distillation.

Method (2) is preferred; used in a closed system, it yields 45% of pure  $\text{CH}_2\text{ClCCl}_3$ . A large Pyrex two-bulbed chlorinating device was used (see Fig. 1). The capacities of the bulbs were approximately 22 liters and 250 cc. The large bulb was first evacuated, then filled with chlorine, and the methylchloroform was introduced. Approximately 200 cc. of water was placed in the small bulb. With the stopcock open between the two bulbs chlorination proceeded to completion in gentle sunlight,

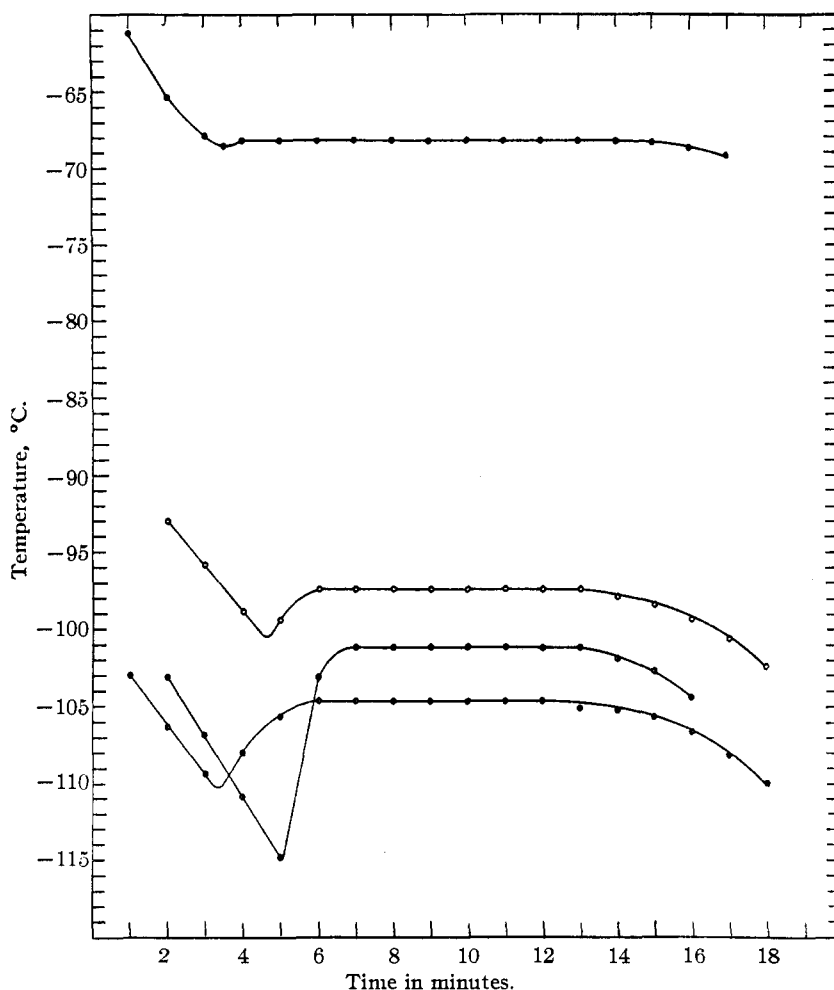


Fig. 2.—Freezing point curves: ●,  $\text{CH}_2\text{ClCCl}_3$ ; ○,  $\text{CH}_3\text{CHCl}_2$ ; ●,  $\text{CH}_2\text{ClCClF}_2$ ; ○,  $\text{CH}_2\text{ClCCl}_2\text{F}$ .

pound considered. The values found above agree very well with the values given by Swarts

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

the hydrochloric acid gas generated being absorbed by the water. The method was rapid and easily manipulated.

(4) Purchased from Dow Chemical Co., Midland, Michigan.

The best yields were obtained when the amount of chlorine used was approximately one-third of the theoretical amount needed to convert methylchloroform to asymmetrical tetrachloroethane; this reduced the amounts of pentachloroethane and hexachloroethane to a minimum.

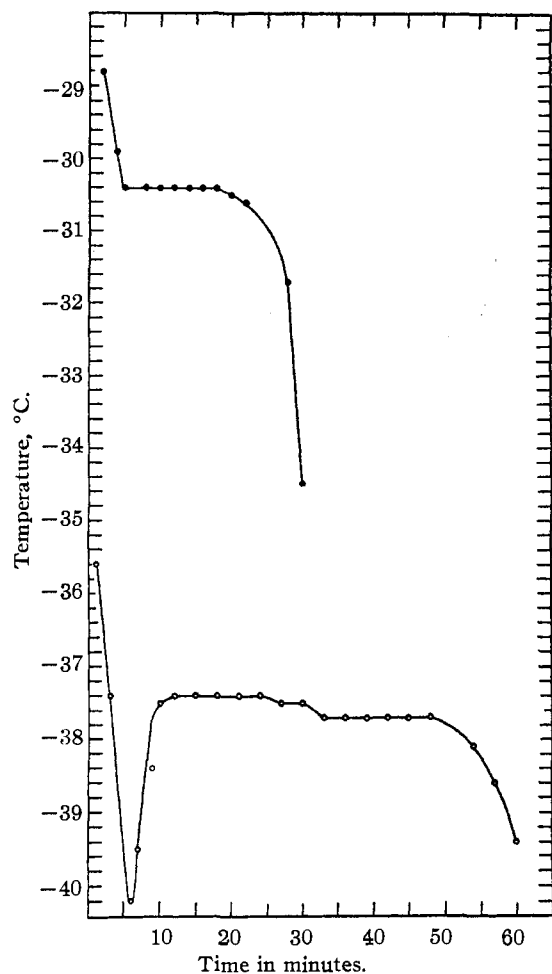


Fig. 3.—Freezing point curves: ●,  $\text{CH}_2\text{CCl}_3$ ; ○,  $\text{CH}_2\text{ClCHCl}_2$ .

**Analysis.**—Chlorine was determined by titration with silver nitrate and fluorine was titrated with cerium nitrate.

The method of Hubbard and Henne<sup>5</sup> was used with the following minor changes of technique.

(1) Approximately 4.25 m. of No. 30, B. and S. nichrome wire was wound directly on the combustion tube. The outside diameter of the combustion tube being 14 mm. permitted 100 turns, spaced approximately 1 mm. apart. The winding extended over 10 cm. of the entire length (30 cm.), and was centrally located. The voltage was 122 a. c. and a Wirtag voltage regulator maintained a heat of 900°, in the central zone of the furnace. The winding was coated with alundum cement and surrounded by the usual packing material of mixed magnesium oxide and asbestos; the whole furnace was encased in an aluminum cylinder with transite ends bearing the binding posts.

(2) A special evaporator was used for liquids, permitting removal for weighing without interrupting the gas flow through the furnace.

(3) Perchloric acid was used for neutralization of the absorption liquid, instead of nitric acid. The greater solubility of perchlorates prevented separation of salts upon evaporation. One neutralization sufficed for the determination of both the chlorine and fluorine ions. Aliquots were taken for analysis.

(4) The chlorine ion was determined by the method of Kolthoff, Lauer and Sunde.<sup>6</sup> The neutral solution (approximately 0.025 *N* with respect to chlorine) was titrated directly against 0.05 *N* silver nitrate solution using two drops of a 0.1% solution of dichlorofluorescein in 60% ethyl alcohol as an indicator. The titration was carried out at room temperature with constant shaking. The end-point coloration was salmon pink.

### Summary

The fluorination of asymmetrical tetrachloroethane with antimony fluoride gives 1-fluoro-1,1,2-trichloroethane and 1,1-fluoro-1,2-dichloroethane. Despite drastic conditions, the fluorination does not proceed further; it is attended with abundant loss of hydrochloric acid, but the fluorinated compounds themselves are stable.

CINCINNATI, OHIO

RECEIVED DECEMBER 30, 1935

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

(6) Kolthoff, Lauer and Sunde, *ibid.*, **51**, 3273 (1929).