

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

## Fluorinated Derivatives of Ethane and Ethylene. VII

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In the preparation of fluorinated derivatives of ethane and ethylene by conventional methods,<sup>1</sup> several hundred grams of various compounds have been available for purification. Physical measurements were thus made possible which are believed to be more precise than those in the literature and are claimed to be accurate to the extent shown by the significant decimals appearing in the table. Indications of high purity were: freezing ranges of about 0.1°; boiling points constancy of better than 0.1°; and atomic refractions for fluorine (*AR<sub>F</sub>*) very close to 1.0.

In general, the literature values hover closely around those reported here; data which diverge

rection for  $\text{CCl}_2\text{FCF}_3$ , previously reported<sup>3</sup> as "about -2°," and now found to be +3.6°; the former sample had been obtained from distillation heads of the industrial preparation of  $\text{CClF}_2\text{CClF}_2$  and was found contaminated by some  $\text{CF}_3\text{CClF}_2$ ; the present sample was synthesized from pure  $\text{CCl}_3\text{CF}_3$ .

Few freezing points appear in the literature. We are in contradiction with Booth<sup>4</sup> on the freezing point of  $\text{CClF}=\text{CCl}_2$ , which he gives as -82° while we observed -108.93°, with a total range of less than 0.1°. We agree fully with Booth's boiling point, and we note in his paper that his freezing point was not determined by himself.

TABLE OF PHYSICAL CONSTANTS

	F. p., °C.	B. p., °C.	<i>t</i> °	<i>dt/4</i>	<i>n<sub>D</sub></i>	<i>MR</i>	<i>AR<sub>F</sub></i>
$\text{CH}_2=\text{CFCI}$	-169	-24.0					
$\text{CH}_2=\text{CF}_2$		-84					
$\text{CHCl}=\text{CF}_2$	-138.5	-17.7					
$\text{CHBr}=\text{CF}_2$	-115.4	6.1	0.5	1.8175			
$\text{CClF}=\text{CF}_2$		-26.8					
$\text{CCl}_2=\text{CClF}$	-108.9	71.0	20.0	1.5460	1.4379	25.39	0.9
$\text{CH}_2\text{BrCF}_2\text{Br}$	-61.3	93.2	20.0	2.2238	1.4456	26.84	1.0
$\text{CClFBrCF}_2\text{Br}$	-72.9	93.1	20.0	2.2478	1.4278	31.63	1.0
$\text{CCl}_2\text{FCF}_3$	-56.6	3.6					
$\text{CH}_2\text{ClCF}_3$	-105.5	6.93	0	1.389			
$\text{CH}_2\text{BrCF}_3$	-93.9	26.3	20.0	1.7881	1.3331	18.75	1.0
$\text{CH}_2\text{BrCF}_2\text{Cl}$	-75.8	68.4	20.0	1.8300	1.4018	23.86	1.0

widely are as follows: The boiling point of  $\text{CHCl}=\text{CF}_2$  is -17.7°, and not "about +2.4°" as we erroneously reported<sup>2</sup> when we had only traces of this material. Next in importance is the cor-

## Summary

Improved physical constants are listed for twelve fluorinated derivatives of ethane and ethylene.

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(1) Henne in "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., p. 49.

(2) Henne and Ladd, *THIS JOURNAL*, **53**, 402 (1936).

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

(4) Booth, *ibid.*, **55**, 2231 (1933).