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

Fluorochloroethanes and Fluorochloroethylenes

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During the last four years, a large number of fluorinated derivatives of ethane and of ethylene were prepared, but their complete presentation[1] was delayed. Some of these derivatives were reported recently by Booth and his students,[2] and, in general, both sets of data agree well. The results presented here are more detailed and complete; they embrace all the possible derivatives of ethane and of ethylene which have all the hydrogen atoms replaced by chlorine or fluorine.

Synthesis of the Saturated Derivatives.—The method of synthesis is based on the classical procedure of Swarts[3] which consists in heating together a mixture of hexachloroethane and antimony trifluoride, in the presence of about 10% of antimony pentachloride. However, in order to accelerate the operation, to be able to replace a larger number of chlorine atoms in the hexachloroethane molecule and to obtain better yields, three modifications of the process were adopted, namely: (1) the mixture of antimony trifluoride and antimony pentachloride was replaced by antimony fluorochloride, SbF_3Cl_2; (2) steel equipment was used; (3) the fluorination was performed under pressure and the desired fluorinated derivatives were removed from the reaction field as soon as formed. These improvements have been previously described in detail.[4] They make it possible to obtain from hexachloroethane almost quantitative yields of CCl_3CCl_2F, CCl_2FCClF_2, $CClF_2CCl_2F$, $CClF_2CClF_2$ or CF_3CClF_2.

The compounds CCl_3CClF_2 and CCl_3CF_3 which were needed for identification purposes were synthesized from $CHCl_2CHF_2$ and from CH_2ClCF_3, by chlorination in sunlight. Their properties are listed here, but their synthesis is the subject of another paper.

Purification.—The crude products were washed with water, then with a weak caustic solution, and dried by means of calcium chloride, or sulfuric acid. They were finally purified by fractional distillation, an operation which is extremely easy to perform because each replacement of a chlorine atom by a fluorine atom in C_2Cl_6 lowers the boiling point of the resulting chlorofluoride by about 45°.

Determination of the Physical Properties.—The methods used have been described before.[5]

Analysis.—The liquid compounds were burned in a Parr bomb, and after combustion the bomb content was dissolved in perchloric acid. The chlorine was titrated by means of silver nitrate, as usual, while the fluorine was titrated with cerium nitrate.[6] Gaseous compounds were analyzed by combustion over heated silica.[7] The molecular weight of liquids was computed from the observed freezing point depression in benzene, and the molecular weight of the gases was derived from the gravimetric analysis of a known volume, a procedure which gives correct results because gaseous chlorofluoro derivatives of ethane and ethylene are almost perfect gases.

Results

The physical properties and analyses appear in Table I.

Determination of the Configurations.—Only the compounds numbered from 1 to 6 (inclusive) are found in the fluorination of C_2Cl_6. After obtaining their formula by analysis and molecular weight determination, it remained to prove their spatial configuration, which was done as follows.

(1) **Monofluoropentachloroethane.**—Only one formula is possible, CCl_3CCl_2F. This compound, treated with zinc in alcohol, gives a quantitative yield of $CCl_2{=}CClF$ (described below) and zinc chloride. Only a trace of zinc fluoride was detected.

(2) **Difluorotetrachloroethane.**—Two formulas are possible, CCl_3CClF_2 (1) and CCl_2FCCl_2F (2). The first formula is improbable, because such a compound is reported to melt at 52°. Moreover, a treatment with zinc and alcohol gives a quantitative yield of dichlorodifluoroethylene, which is separable into two isomers. Since formula (1) would not permit the formation of geometrical isomerism in its ethylene derivative, it follows that formula (2) is correct and that the ethylenic compound is $CClF{=}CClF$.

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[1] Presented in part at the Buffalo meeting of the American Chemical Society, September, 1931.

[2] Booth and his collaborators, *Ind. Eng. Chem.*, **24**, 328–31 (1932); THIS JOURNAL, **55**, 223 (1933).

[3] Swarts, *Bull. Acad. Roy. Belg.*, [3] **24**, 474 (1892); and [3] **29**, 874 (1895).

[4] Midgley and Henne, *Ind. Eng. Chem.*, **22**, 542 (1930); also U. S. Patent 1,930,129, October 10, 1933.

[5] Shepard, Henne and Midgley, THIS JOURNAL, **53**, 1948 (1931).

[6] Batchelder and Meloche, *ibid.*, **53**, 2131 (1931).

[7] Hubbard and Henne, *ibid.*, **56**, 1078 (1934).

TABLE I

PROPERTIES AND CONSTANTS OF ETHANE DERIVATIVES

No.	Formula	M. p., °C.	B. p. 760 mm. corr., °C.	Density and refractive indices at t° $t°$	d_4	n_α	n_D	n_β	Mol. wt. Calcd.	Mol. wt. Found	Analyses, % Fluorine Calcd.	Analyses, % Fluorine Found	Analyses, % Chlorine Calcd.	Analyses, % Chlorine Found
1	CCl_3CCl_2F	101.3	137.9						220.3	217.9	8.62	8.82	80.48	79.96
2	CCl_2FCCl_2F	24.65	92.8	25.0	1.64470	1.41100	1.41297	1.41823	203.8	202.0	18.64	18.73	69.56	69.23
				35.0	1.62516	1.40656	1.40831	1.41368						
3	CCl_2FCClF_2	−36.4	47.7	0.0	1.6200				187.4	185.2	30.42	30.64	56.77	56.29
				25.0	1.56354	1.35413	1.35572	1.35981						
				35.0	1.53982	1.34933	1.35124	1.35488						
4	$CClF_2CClF_2$	Glass	3.8	0.0	1.5312	1.3073	1.3092		170.8	168	44.49	44.39	41.45	41.52
				25.0	1.455									
				35.0	1.422									
5	CCl_2FCF_3		−2 (about)											
6	$CClF_2CF_3$		−38											
7	CF_3CF_3		−78.3											
8	CCl_3CClF_2	40.6	91.5						203.8	198			69.6	70.1
9	$CCl_3.CF_3$	13.2	45.8	20.0	1.5702				187.4	184			56.8	57.1

Compounds 5 and 6 have been obtained only as by-products in the industrial preparation of compound 4.

Compound 7 has not been obtained by the present method. It can be made by electrolysis of CF_3CO_2H [Swarts, *Bull. soc. chim. Belg.*, **42**, 102 (1933)] or by passing CF_4 through a carbon arc [Ruff and Bretschneider, *Z. anorg. allgem. Chem.*, **210**, 173 (1933)].

Compounds 8 and 9 were obtained independently, by chlorination of $CHCl_2CHF_2$ and CH_2ClCF_3, respectively, as indicated in paragraph (2) of page 1726. The melting point of compound 8 is reported by Swarts, *Mémoires couronnés Acad. Roy. Belg.*, 61, 68 (1901), as 52°, but this could not be duplicated.

(3) **Trichlorotrifluoroethane.**—As this compound is prepared by the fluorination of CCl_2FCCl_2F, its formula is probably CCl_2FCClF_2. The configuration is proved by treatment with zinc and alcohol, which yields $CClF{=}CF_2$ and zinc chloride, but no zinc fluoride. This rules out the only other possible formula, CF_3CCl_3. Moreover, this latter compound was prepared by chlorination of CF_3-CH_2Cl in sunlight (to be reported later); it melts at 13° and boils at 45°.

(4) **Dichlorotetrafluoroethane.**—The formula, $CClF_2$-$CClF_2$, of this compound was proved by the formation of zinc chloride and $CF_2{=}CF_2$ in the treatment with zinc and alcohol. Had the formula been CCl_2FCF_3, the only other possibility, zinc would have removed one atom of chlorine and one atom of fluorine, to yield $CClF{=}CF_2$, zinc fluoride and zinc chloride. Moreover, in the industrial preparation, a limited amount of CCl_2FCF_3 was obtained; it has a boiling point of about −2°.

Ethylene Derivatives.—These compounds were all obtained from the corresponding saturated products by a treatment with zinc in absolute alcohol. As highly fluorinated materials have a low boiling point, it is impractical to carry the operation at atmospheric pressure, and the elimination of 2 chlorine atoms from $C_2Cl_3F_3$ and from $C_2Cl_2F_4$ was performed under pressure (10 atm.

TABLE II

DERIVATIVES OF ETHYLENE AND THEIR DIBROMIDES

No.	Formula	M. p., °C.	B. p., °C.	Density and refractive ind. d_4	n	t	Mol. wt. Calcd.	Mol. wt. Found	Analyses, % Chlorine Calcd.	Analyses, % Chlorine Found	Analyses, % Bromine Calcd.	Analyses, % Bromine Found	Analyses, % Fluorine Calcd.	Analyses, % Fluorine Found
11	$CCl_2{=}CClF$		72.1	1.5541	n_D 1.4360	20	149.4	148	71.2	71.2				
12	$CCl_2BrCClFBr$	122.5												
13	$CCl_2{=}CF_2$		15											
14	CCl_2BrCF_2Br	46	117.1				293	285	24.2	24.0	54.6	54.4		
15	$CClF{=}CF_2$	− 23												
16	$CClFBrCF_2Br$		92.9	2.2318	n_D 1.4272	20	276.5	268	12.87	12.5	57.85	57.9		
17	$CF_2{=}CF_2$		−78.4											
18	CF_2BrCF_2Br	−112	46.4	2.149		25	260	255			61.5	61.3		
19	$CClF{=}CClF$ *cis* isomer	−130.5	21.1	1.4950	n_α 1.3752 n_D 1.3777 n_β 1.3825	0			53.36	53.6			28.6	28.7
20	$CClF{=}CClF$ *trans* isomer	−110.3	22.0	1.4936	n_α 1.3764 n_D 1.3798 n_β 1.3850	0			53.36	53.4			28.6	28.6
21	$CClFBrCClFBr$	32.5	139.7				293	287	24.2	24.2	54.6	55.5	12.98	12.94

Compound 13 was also obtained from $CHCl_2CClF_2$ and alcoholic KOH. Compounds 19 and 20 were obtained as a mixture and were separated by fractional distillation.

and 60 atm., respectively) in a steel container. Under those circumstances, a considerable amount of ethylene appears, and the reaction stops short of completion. Table II gives the results.

Differences in the Boiling Points.—A tabulation of the boiling points makes apparent the regularity of the boiling point depression caused by replacing chlorine by fluorine.

	B. p., °C.	Depression
CCl_3CCl_3	186	
CCl_3CCl_2F	138	48
CCl_2FCCl_2F	92	46
or	or	or
CCl_3CClF_2	91	47
CCl_2FCClF_2	47	45
or	or	or
CCl_3CF_3	45	46
$CClF_2CClF_2$	3	46
or	or	or
CCl_2FCF_3	− 2	47
$CClF_2CF_3$	−38	41
CF_3CF_3	−78	40
$CCl_2{=}CCl_2$	120	
$CCl_2{=}CClF$	71	49
$CClF{=}CClF$	22	49
or	or	or
$CCl_2{=}CF_2$	15	56
$CClF{=}CF_2$	−23	45
$CF_2{=}CF_2$	−78.4	55
$CClFBrCClFBr$	139.6	
$CClFBrCF_2Br$	92.8	46.8
CF_2BrCF_2Br	46.4	46.8

Molecular Refractions.—The Lorentz-Lorenz formula has been used to calculate the molecular refractions, and from the experimental results the atomic refraction of fluorine has been computed by subtracting the sum of the atomic refractions of carbon, chlorine, double bonds and bromine ("International Critical Tables" values were used).

	t°	Molecular refraction			F. Atomic refraction		
			D	B		D	B
CCl_2FCCl_2F	25	30.768	30.896	31.242	1.105	1.096	1.097
	35	30.841	30.959	31.316	1.142	1.128	1.134
CCl_2FCClF_2	25	26.065	26.170	26.440	1.147	1.144	1.145
	35	26.142	26.273	26.516	1.173	1.179	1.170
$CClF_2CClF_2$	0	21.35	21.473	....	1.17	1.176	...
CCl_3CF_3	20	....	26.405	....	...	1.223	...
$CClFBrCF_2Br$	20	....	28.533	....	...	1.09	...
$CCl_2{=}CClF$	20	....	25.15	....	...	0.68	...
$CClF{=}CClF$	0	20.36	20.48	20.71	0.99	0.99	0.96
Cis and *trans*	0	20.44	20.60	20.85	1.03	1.05	1.03

The values found for the atomic refractions of fluorine agree well with the values given by Swarts[8] for a large variety of substances; they vary with the type of compound considered.

Summary

All the possible derivatives of ethane and of ethylene (together with their dibromides) which have all their hydrogen atoms replaced by chlorine or fluorine are described.

[8] Swarts, *J. Chim. Phys.*, **20**, 30 (1923).

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Correlation of Ultraviolet Absorption and Chemical Constitution in Various Pyrimidines and Purines

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It was shown previously that the ultraviolet irradiation[1] of dilute solutions of uracil and other pyrimidines and purines induces marked changes in their ultraviolet absorption spectra indicative of constitutional changes, and that, with sufficiently long continued irradiation, all selective absorption could be made to disappear. To afford a basis for the interpretation of these changes, information as to the absorption spectra of a series of related compounds was desirable. This paper presents the ultraviolet absorption spectra of eighteen such compounds, and permits comparisons to be made between their spectra and constitutions, so that conclusions may be drawn as to the manner in which various structural modifications are responsible for, or affect, the ultraviolet absorption of the compounds of this series.

Experimental

Method.—The technique used in determining the absorption spectra has been described previously. As there noted,[1,2] the measurements have not been corrected for certain deviations due to failure of the reciprocity law, but with the method employed these deviations are negligible, amounting to less than the experimental error at most wave lengths.

In all cases the solvent was redistilled water. The concentrations were chosen by trial so as to result in the greatest accuracy in the absorption determinations.

Values of P_H were determined by the quinhydrone elec-

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[1] Heyroth and Loofbourow, THIS JOURNAL, **53**, 3441 (1931).

[2] Loofbourow, *Bull. Bas. Sci. Res.*, in publication.