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

Chlorinated Derivatives of 2-Fluoropropane

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The purpose of this work is to show that the chlorination of 2-fluoropropane does not occur at random as that of propane itself, but follows a course almost as completely directed as that of 2,2-difluoropropane. This fact furnishes a good method of preparation of several new compounds.

It is known[1] that chlorination of $CH_3CF_2CH_3$ occurs in a completely asymmetrical manner, thus: $CH_3CF_2CH_2Cl \rightarrow CH_3CF_2CHCl_2 \rightarrow CH_3CF_2CCl_3 \rightarrow CH_2ClCF_2CCl_3 \rightarrow CHCl_2CF_2CCl_3 \rightarrow CCl_3CF_2CCl_3$. Chlorination tends to stop with the formation of $CH_3CF_2Cl_3$, which is a high melting solid, in contrast with the other compounds which are liquids. A study of the chlorination of $CH_3CH_2CF_3$[2] indicates that chlorination is also completely directed and yields $CH_2ClCH_2CF_3 \rightarrow CHCl_2CH_2CF_3 \rightarrow CCl_3CH_2CF_3$, where the reaction tends to stop, then $CCl_3CCl_2CF_3$.

Chlorination occurs in a contrasting fashion when there are no fluorine atoms in the molecule. Propane is affected at random, yields a complex mixture of chlorinated derivatives, does not favor the formation of any particular compound, and has not yet been completely chlorinated.[3] The chlorination of $CH_3CCl_2CH_2Cl$ produces two parts of $CH_3CCl_2CHCl_2$ to one part of $CH_2ClCCl_2CH_2Cl$, and it has proved impossible, so far, to chlorinate $CH_3CCl_2CCl_3$ further.[2]

In the present work, the starting point is $CH_3CClFCH_2Cl$ instead of CH_3CHFCH_3 or $CH_3CClFCH_3$. The main reasons are the general instability of monofluorides, and the difficulty of preparing $CH_3CClFCH_3$ on a large scale, because it tends to disproportionate to a mixture $CH_3CF_2CH_3$ and $CH_3CCl_2CH_3$ during its preparation. The chosen starting point is, of course, the only possible first step in the chlorination of $CH_3CClFCH_3$. As outlined below, chlorination gave successively $CH_3CClFCHCl_2$ (contaminated by traces of $CH_2ClCClFCH_2Cl$), then $CH_3CClFCCl_3$. The latter is a high-melting, crystalline compound, which tends to resist further chlorination. A small amount of its isomer, $CH_2ClCClFCHCl_2$ was also found and isolated. Subsequently the crystals of $CH_3CClFCCl_3$ were subjected to chlorination in strong sunlight, slowly to yield $CH_2ClCClFCCl_3$, $CHCl_2CClFCCl_3$, and $CCl_3CClFCCl_3$, all of which are liquids at room temperature. It is thus shown: (1) that a single atom of fluorine is capable of exerting a directing effect almost as strong as that of a CF_2 group or a CF_3 group; (2) that the tendency is to replace all the hydrogen atoms linked to a given carbon atom before affecting those attached to another carbon atom; (3) that compounds with all halogens linked to certain carbon atoms, and all hydrogens grouped together on other carbon atoms are high melting crystals; (4) that the presence of fluorine makes it practical to replace all the hydrogen atoms by chlorine, without decomposition of the molecule. The experimental results are summarized in Table I.

Experimental

1. Preparation of $CH_2{=}CClCH_2Cl$.—Hydrogen chloride was removed from 1,2,3-trichloropropane (b. p. 154–154.5°) obtained from the Shell Chemical Company. Two runs were made; one using a 40% ethanol solution of sodium hydroxide and the other using a 30% aqueous solution of sodium hydroxide. The alkali solution was added over a period of one hour and the mixture was refluxed for three hours more. The unsaturated compound was then slowly distilled, with continuous stirring, from the reaction flask by heating. When aqueous caustic solution was used the reaction required gentle heating to maintain a reflux, but no extraction with water was needed to remove alcohol before the final distillation for purification. After drying the unsaturated compound overnight, a single distillation gave yields of about 87% of $CH_2{=}CClCH_2Cl$ boiling at 92.5°.

2. Preparation of $CH_3CClFCH_2Cl$.—Two gram molecules of liquefied hydrogen fluoride was added to one mole of $CH_2{=}CClCH_2Cl$ in a steel container cooled with dry-ice. This was sealed and placed in a water-bath held at 50–60° for eight hours, and then allowed to stand overnight at room temperature. The contents were poured over a large amount of cracked ice, the mixture neutralized exactly and most of the water decanted. Steam distillation was used to remove the monofluoride from small amounts of tar and, after drying, the product was distilled. The distillation generally gave a small amount of difluoride, $CH_3CF_2CH_2Cl$, boiling at 55°[1] which is described in the table, then the desired monofluoride. Some unreacted olefin was recovered in the tailings and used in a subsequent operation. Typical operations on one mole of olefin gave 0.74 mole of monofluoride, 0.04 mole of difluoride, and 0.10 mole of recovered olefin.

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[1] Henne and Renoll, THIS JOURNAL, 59, 2434 (1937).

[2] A. M. Whaley, Dissertation, The Ohio State University, 1941, soon to be published.

[3] C. Ellis, "Chemistry of Petroleum Derivatives," Vol. I, The Chemical Catalog Co., Inc., New York, N. Y., 1934, p. 717.

TABLE I

PHYSICAL PROPERTIES OF COMPOUNDS

	Compound	F. p., °C.	B. p., °C.	d^{20}_4	n^{20}_D	MR_D	AR_F
1	$CH_3CClFCH_2Cl$	−92.5 to −92.7	88.5	1.2618	1.4121	25.83	1.14
2	$CH_3CClFCHCl_2$	Glass	116.7	1.4238	1.4360	30.38	0.83
3	$CH_3CClFCCl_3$	104–104.5	139.6				
4	$CH_2ClCClFCHCl_2$	Glass	50–51 (14 mm.)	1.5782	1.4694	35.3	.88
5	$CH_2ClCClFCCl_3$	−34.4	72 (14 mm.)	1.6867	1.4871	39.37	.68
6	$CHCl_2CClFCCl_3$	−31.6 to −33.5	87 (14 mm.)	1.7714	1.5012	44.89	.77
7	$CCl_3CClFCCl_3$	7.6–8.4	105 (14 mm.)	1.8515	1.5194	49.93	.91
8	$CH_3CF_2CH_2Cl$	−56.2	55–55.2	1.2001	1.3520	20.64	.96

3. Chlorination of $CH_3CClFCH_2Cl$.—A weighed amount of $CH_3CClFCH_2Cl$ was placed in a distilling flask and covered with a known amount of water. Chlorine was introduced by means of an inlet tube, reaching the bottom of the flask, at such a rate that it kept the organic layer colored, yet did not pass appreciably through the aqueous layer. The side arm of the flask was used to lead away accidental excesses of chlorine. The resulting hydrogen chloride dissolved in the water. The chlorination was performed in bright sunlight where its rate is easily gauged by the speed of bleaching. The progress of the chlorination was ascertained by weighing. After enough chlorine had been added to account for the formation of $CH_3CClFCCl_3$ the operation was interrupted, the organic layer separated, washed, dried and distilled. The distillation gave small quantities of unreacted material and of $CH_3CClFCHCl_2$, then mostly solid $CH_3CClFCCl_3$, after which came a liquid residue of the more highly chlorinated products. The components were rectified, and are described in Table I. After identification, the solid $CH_3CClFCCl_3$ was dissolved in a small quantity of carbon tetrachloride, and again subjected to chlorination. This treatment gave three more compounds, namely, $CH_2ClCClFCCl_3$, $CHCl_2CClFCCl_3$, and $CCl_3CClFCCl_3$, which were rectified under reduced pressure and are described in the table.

Identification.—Since fluorine was introduced only in the first reaction, it was deemed sufficient to analyze for fluorine only at the first and the last step. Chlorine, however, was determined at each step. The results are given in Table II.

TABLE II

ANALYSES

	Compound	% Cl, calcd.	% Cl, found	% F, calcd.	% F, found
1	$CH_3CClFCH_2Cl$	54.1	53.7	14.5	14.6
2	$CH_3CClFCHCl_2$	64.3	63.8		
3	$CH_3CClFCCl_3$	70.9	70.7		
4	$CH_2ClCClFCHCl_2$	70.9	70.2		
5	$CH\ ClCClFCCl_3$	75.7	75		
6	$CHCl_2CClFCCl_3$	79.2	78.9		
7	$CCl_3CClFCCl_3$	81.9	81.2	6.3	6.9

The first compound can only be $CH_3CClFCH_2Cl$ (A) or $CH_2FCHClCH_2Cl$ (B). Its method of synthesis, namely, the addition of hydrogen fluoride to $CH_2{=}CClCH_2Cl$ requires that A be preferred to B, if the rule of Markownikow is to be respected. Moreover, B is a monofluoride, from which hydrogen fluoride would split easily, which action was not observed. The boiling point observed, 88°, is that which is predictable from the fact that $CH_3CClFCH_3$ boils at 35–36°, and that the first replacement of hydrogen by chlorine raises the boiling point about 52°.

The second compound, made at the expense of the first, can be $CH_3CClFCHCl_2$ (C), or $CH_2ClCClFCH_2Cl$ (D). Its boiling point differs from that of A by only $116.7° - 88.5° = 28.2°$. This indicates that C, in which the chlorine substitution occurs on the same carbon atom, is more plausible than D, in which the substitution affects a new carbon atom. The boiling point of D should be considerably higher, and in the vicinity of 139°. It is probable that traces of D were formed because compound 2 could not be crystallized.

The third compound can only be $CH_3CClFCCl_3$ (E) or $CH_2ClCClFCHCl_2$ (F). The fact that it is a solid melting at 104° causes the preference of the asymmetrical formula, E, over F. This formula agrees well with the observed boiling point 139.6°. A prediction based on analogies would give about 140°.

The fourth compound is of necessity F, because it is isomeric with the third compound, and boils about 20–25° higher. Moreover, this fourth compound was isolated only as a by-product of the chlorination of $CH_3CClFCH_2Cl$, and did not appear in the chlorination of $CH_3CClFCCl_3$.

The fifth, the sixth and the seventh compounds were obtained by chlorination of the fourth compound and can have only the formula reported. No by-products were formed.

The eighth compound was described previously and is reported here because the larger amount available made it possible to improve the measurement of its physical constants.[1]

Freezing Points.—Freezing curves rather than freezing points were used as the criterion of purity whenever they could be obtained. They were taken with a platinum resistance thermometer reading to 0.01°, and the rate of cooling was made as slow as practicable. The plateaus observed were sharply defined and extended over periods ranging from five to thirty minutes. The second and fourth compounds became too viscous to stir and formed glasses, a behavior which is typical of symmetrical compounds bearing both hydrogen and halogen atoms on the same carbon. The first, third, fifth, and eighth compounds were quite pure, as the shape of their freezing curves showed. The sixth and seventh compounds caused a great deal of difficulty because they overcooled as much as 6 to 8°, even in the presence of several crystalline seeds. These two compounds were allowed to freeze, and as soon as they could no longer be easily stirred they were allowed to warm up slowly by substituting an empty, silvered

Dewar for the cooling bath. Stirring was continued, and the melting curve was determined. The freezing ranges were as indicated in the table.

The fact that $CH_2ClCClFCCl_3$ and $CHCl_2CClFCCl_3$ freeze almost at the same temperature is in good agreement with the close freezing points of $CH_2ClCCl_2CCl_3$ and $CHCl_2CCl_2CCl_3$.[2] These freeze at 30 and 29.5°, respectively.

Refraction.—The molecular refractions, MR_D, were calculated by means of the Lorentz–Lorenz formula. The atomic refraction for fluorine was obtained by subtracting from the molecular refraction the increments for carbon (2.418), hydrogen (1.100), and chlorine (5.967). This was done merely to obtain a confirmation of the gross formulas as the assumption cannot be made that the increments are absolutely constant.

Summary

$CH_3CClFCH_2Cl$ has been synthesized by addition of hydrogen fluoride to $CH_2{=}CClCH_2Cl$. The hydrofluorinated compound has been subjected to the action of chlorine in sunlight to yield $CH_3CClFCHCl_2$, $CH_3CClFCCl_3$, $CH_2ClCClFCCl_3$, $CHCl_2CClFCCl_3$ and $CCl_3CClFCCl_3$. As by-products, only a small amount of $CH_2ClCClFCHCl_2$ was isolated and traces of $CH_2ClCClFCH_2Cl$ were suspected. All the compounds have been tabulated and improved data for $CH_3CF_2CH_2Cl$ have been added.

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I. A Modified Heat Conduction Calorimeter[1,2]

BY WALDEMAR T. ZIEGLER AND CHARLES E. MESSER

The principle of the calibrated, heat-conduction calorimeter originally used by Andrews[3] has been the basis for a number of different calorimeters used by other investigators.[4] The simplicity and speed with which heat capacity data of adequate accuracy (1–3%) may be obtained, together with the fact that a continuous measurement of the change in heat content is simultaneously obtained, led the authors to choose this method as a means of determining the heat capacities of substances suspected of exhibiting anomalies of the type shown by ammonium chloride in the neighborhood of −30°. This paper presents a description of the construction, operation, and calibration of such a calorimeter, and an application of it to the study of the heat capacities of potassium chlorate, ammonium chloride and ammonium sulfate. These substances were chosen for study because their heat capacities had been determined by other investigators, and hence would permit an evaluation of the accuracy of the calorimeter. The experimental results for ammonium chloride would also permit the calculation of the entropy of this substance at 298.1°K. In later papers we shall present the results of similar studies of the thermal properties of cobaltous and cobaltic hexammine halides, and sodium and potassium cyanides.

The Heat Conduction Calorimeter

The determination of the heat capacity of a substance with a calibrated heat conduction calorimeter (see Fig. 1) is accomplished by comparing the time required to heat a known weight of the "unknown" substance through a definite interval of the temperature scale, with the time required to heat a known weight of a "standard" substance of known heat capcity through the same temperature interval under identical conditions (*i. e.*, the same temperature difference or "head" between mantle and calorimeter can, etc.) the time required to heat the empty can through the same interval having been determined previously. The mean molal heat capacity of the substance, C_{p_u}, in this interval may then be calculated from the expression

$$C_{p_u} = \frac{W_s M_u C_{p_s}}{W_u M_s} \times \frac{t_u - t_c}{t_s - t_c} \qquad (1)$$

In this expression t_u, t_s and t_c represent, respectively, the time (in seconds) required to heat W_u grams of the "unknown" substance (mol. wt., M_u), W_s grams of the "standard" substance (mol. wt., M_s), and the empty can through the *same* interval of the temperature scale. C_{p_s} is the mean molal heat capacity of the standard substance in this same temperature interval.

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(1) From a dissertation submitted to the Board of University Studies of The Johns Hopkins University by Waldemar T. Ziegler in conformity with the requirements for the degree of Doctor of Philosophy.

(2) Presented at the Symposium on Low-Temperature Research, Boston meeting of the American Chemical Society, September, 1939.

(3) Andrews, THIS JOURNAL, **48**, 1287 (1926).

(4) Andrews and Haworth, *ibid.*, **50**, 2998 (1928); Smith and Andrews, *ibid.*, **53**, 3644 (1931); Stull, *ibid.*, **59**, 2726 (1937).