

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

Fluorinated Derivatives of Propane. III

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Introduction.—In the preceding paper of this series,¹ the fluorination of C_3Cl_8 , of $\alpha-C_3HCl_7$, and of $\beta-C_3HCl_7$ was described. Formulas for the mono- and the difluorides were demonstrated and plausible formulas were presented for the trifluorides. The present paper proves the correctness of the trifluoride assumptions and describes newly prepared tetrafluorides, for which it offers plausible formulas.

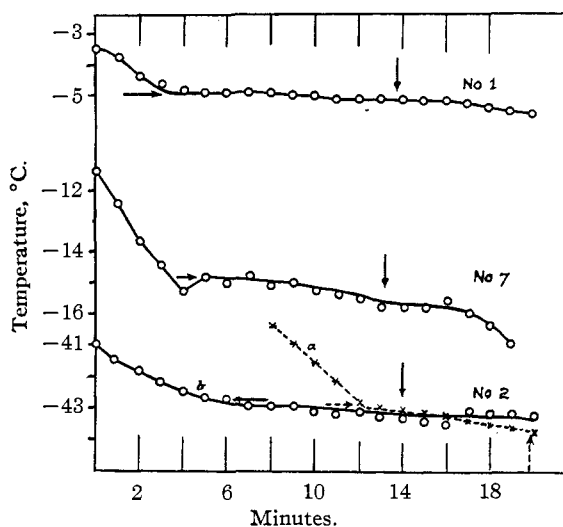


Fig. 1.—Horizontal arrows show the temperature at which crystals were unmistakably seen. Vertical arrows denote end of stirring. a, b and c denote different rates of cooling.

Procedure.—The methods of fluorination and chlorination were the ones used in the preceding papers. So also were the methods of purification and the physical measurements. The analyses for chlorine and fluorine were made after decomposing the organic fluorochlorides over red hot calcium oxide, in a small steel bomb. The freezing curves required a great deal of perseverance because the latent heat of fusion of polyfluorides is small, and because the mushy crystals create a viscous mass, difficult to stir adequately. The rate of cooling must be slow, and the best results were obtained with a cooling bath kept about 5° below the freezing point under measurement. These difficulties are illustrated graphically in Fig. 2.

(1) Henne and Ladd, *THIS JOURNAL*, **60**, 2491 (1938).

Results.—The actual experimental results appear in the table and diagrams. Figure 1 gives the freezing curve of $CCl_2FCCl_2CClF_2$ (no. 1), of $CCl_3CClFCClF_2$ (no. 7) and of $CClF_2CCl_2CClF_2$ (no. 2) taken at two different rates of cooling (a and b). Figure 2 refers to $CCl_3CClF_2CF_3$ (no. 8), taken at three different rates of cooling (a, b and c); it illustrates the difficulties prevailing when a small sample is used; on both curves b and c, the crystals were seen at -15.8° , and this was adopted as the freezing point, although it is quite probable that the true point may be as much as one degree higher.

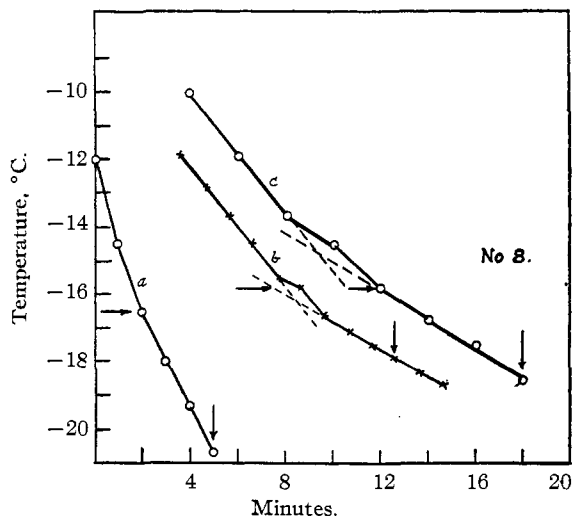


Fig. 2.—Horizontal arrows show the temperature at which crystals were unmistakably seen. Vertical arrows denote end of stirring. a, b and c denote different rates of cooling.

In the table, no comments are required except for no. 4. In this case the analysis result is explained by the presence of trichloroethylene.

Determination of the Formulas.—The procedure used follows that of the preceding paper. Specifically, the trifluorides were obtained from known difluorides, and since no reason exists to expect rearrangements of halogen atoms during fluorination, there are only a limited number of places available for the third fluorine atom. The same reasoning holds true for the fourth fluorine atom of the new tetrafluorides. Reactions with zinc in alcohol gave additional information as

TABLE I

No.	Name	F ₂ p., °C.	B ₂ p., °C.	<i>t</i>	<i>d</i> ₄	<i>n</i> _D	MR _D	AR _F	Cl/F	
									Found	Calcd.
1	CCl ₂ FCCl ₂ CClF ₂	-4.9	152.3	20	1.77023	1.43959	40.21	1.04	1.65	1.67
2	CClF ₂ CCl ₂ CClF ₂	-42.9	112.0	20	1.7199	1.39584	35.42	1.07	1.00	1.00
3	CCl ₂ FCHClCClF ₂	Glass	128.7	25	1.67471	1.41569	35.32	1.03	1.35	1.33
4	CClF ₂ CHClCClF ₂	Glass	88		See text				0.97	0.75
5	CHCl ₂ CClFCClF ₂	Glass	129.8	20	1.69124	1.41967	35.27	1.02	1.30	1.33
6	CHCl ₂ CClF ₂ CF ₃	Liquid	89.8	20	1.6368	1.37613	30.77	1.12	0.76	0.75
7	CCl ₃ CClFCClF ₂	-14.8	153.3	20	1.7702	1.43919	40.18	1.03	1.62	1.67
8	CCl ₃ CClF ₂ CF ₃	-15.8	112.3	20	1.7226	1.39797	35.57	1.10	1.02	1.00
9	CCl ₂ =CF ₂ CF ₃		43.5	10	1.555					
10	CCl ₂ BrCFBrCF ₃	35.5-37	154							

to the nature of the halogens attached to adjacent carbon atoms. Finally, the heptahalogenated derivatives (which form glasses at low temperature) were chlorinated in sunlight to crystallizable octahalogenated derivatives and the crystals were compared. The experimental evidence thus obtained was sufficient to establish definitely the formulas of the trifluorides. In the case of the tetrafluorides this did not suffice, as the experimental evidence could only reduce the choice to a limited number of possibilities, and establish a gradation as to their plausibility. The final choice was based on the agreement between predicted and observed melting points, a procedure which can be defended in this particular case on two counts: (a) there is a marked parallelism between the melting points on the one hand, and the number and place of the fluorine atoms on the other hand, which can be seen in the preceding papers on ethane and propane derivatives, and hence it is possible to predict melting points within 2 or 3°. (b) The final choices are to be made between alternates with widely separated melting points, that is, at least 40° apart. This is a consideration of paramount importance and in no case should a choice be made between melting points which can be considered as in the same range.

It should again be emphasized that in the following discussion, a clear cut distinction is always made between demonstrated formulas and plausible formulas, and in the latter case an effort is made to rate the degree of plausibility.

(1) CCl₂FCCl₂CClF₂, m. p. -4.9°.—This trifluoride was obtained from CCl₃CCl₂CClF₂ as well as from CCl₂FCCl₂CCl₂F, and in neither case was there another trifluoride formed. Consequently, the proposed formula is experimentally demonstrated.

(2) CClF₂CCl₂CClF₂, m. p. -42.9°.—This tetrafluoride was easily obtained from the preceding compound. Besides the proposed formulation, it can have only two alternates, namely, CCl₂FCClFCClF₂, or CCl₂FCCl₂CF₃. The choice results from the following reasons, based on general

analogies: (a) the fluorination course and the regularity of the freezing point depression recalls the case of CCl₃CCl₃, whose trifluoride CCl₂FCClF₂ (m. p. -36°) freezes 60° below the difluoride CCl₂FCCl₂F (m. p. 24°) and whose tetrafluoride CClF₂CClF₂ (m. p. -94°) freezes 58° lower than the trifluoride. (b) The alternate formulas call for widely different melting points, namely, about -80° for CCl₂FCClFCClF₂, and not lower than -5° for CCl₂FCCl₂CF₃. The formula adopted is therefore a plausible hypothesis.

(3) CCl₂FCHClCClF₂.—This compound was obtained from the established CCl₂FCHClCCl₂F, with much decomposition. To prove its structure, it was proposed to remove one molecule of hydrogen chloride by means of an alcoholic alkali, then to chlorinate the resulting olefin to obtain a fully halogenated trifluoride. The latter was expected to freeze at -4.9°, thereby proving identical with CCl₂FCCl₂CClF₂ (no. 1) and establishing the correctness of the proposed formula. However, the reaction did not follow the expected course, and hydrolysis occurred: the only reaction product that could be isolated boiled at 104-109° at 7 mm., had a density *d*₄²⁰ 1.1794, and a refractive index *n*_D²⁰ 1.4320. Its analysis indicated 5.62% H, 42.28% C, 18.87% Cl, and no fluorine. This information, and an experimental determination of the molecular magnitude as about 190, indicated that the compound was the diethyl ester of chloromalonic acid, and this was confirmed by the good agreement between the computed molecular refraction (42.54) and the experimental value (42.80) and by the literature. The chloromalonic ester proves that the central chlorine atom is still unreplaced by fluorine, and demonstrates therefore that the proposed formula of the trifluoride no. 3 is correct.

Efforts to replace the hydrogen atom by chlorine in sunlight, and directly to manufacture CCl₂FCCl₂CClF₂ (no. 1) failed completely on account of complete decomposition, an unpredicted behavior.

(4) CClF₂CHClCClF₂.—This compound, obtained with much decomposition from the preceding trifluoride, proved unstable and never was purified adequately. The best preparations were shown by analysis to be not better than 75% pure. Complete decomposition occurred during chlorination, or during a treatment with alkalis, and it was therefore impractical to link the formula with that of the tetrafluoride no. 2. The formula proposed rests merely on the assumption that fluorination takes place in a symmetrical fashion.

(5) CHCl₂CClFCClF₂.—This trifluoride was obtained with great ease from the known difluoride CHCl₂CCl₂-

CClF₂. By chlorination in sunlight it gives a compound C₃Cl₄F₃, melting at -15° and different from CCl₂FCCL₂-CClF₂ (no. 1), a fact which excludes CHClFCCl₂CClF₂ as its possible formulation. The choice is thus restricted to the proposed formula, or else to CHCl₂CCl₂CF₃. The alternate is not considered plausible, because its chlorination would yield CCl₃CCl₂CF₃, a compound which should melt at 20° or higher (CCl₃CF₃ melts at 13°, and a lengthening of the chain by a -CCl₂- group raises the melting point by more than 10°). To conclude, the proposed formula should be regarded as a very plausible hypothesis.

(6) CHCl₂CClF₂CF₃.—This compound was obtained from the preceding trifluoride (no. 5) at high temperature and with appreciable decomposition, in sharp contrast with the previous steps. Chlorination in sunlight gave a compound C₃Cl₄F₄, which melts at -15.5°, and which yields quantitatively an olefin C₃Cl₂F₄ and zinc chloride, when treated with zinc in alcohol. This proves that the central carbon atom still bears a chlorine atom. The choice is therefore restricted to CHClFCClFCClF₂ and CHCl₂CClF₂CF₃, if the formula of the parent trifluoride (no. 5) is accepted as proposed. The decision to select the second formula is based on the melting point of the compound obtained after chlorination, because the other formula would call for CCl₂FCCLFCClF₂ after sunlight chlorination, a compound which should freeze at about -70°.

For the sake of completeness, it might be added that by starting from the implausible formula of the parent compound, no. 5, *i. e.*, from CHCl₂CCl₂CF₃, the tetrafluoride no. 6 could only be CHClFCCl₂CF₃ or CHCl₂CClF₂CF₃, and the second formula (identical with that adopted in the preceding paragraph) could not be preferred to the first one because the compounds obtained after sunlight chlorination would have to be written CCl₂FCCL₂CF₃ or CCl₃-CClF₂CF₃, respectively, and both formulas would call for melting points in the vicinity of -15°.

The conclusion is therefore that the proposed formula is acceptable.

(7) CCl₃CClFCClF₂ was synthesized by chlorination of no. 5, and is discussed above, together with the formula of no. 5.

(8) CCl₃CClF₂CF₃ was obtained from no. 6 and is discussed together with it; its freezing curve was taken on a sample of a few grams only.

(9) CCl₂=CF₂CF₃ was obtained by the action of zinc on no. 8.

(10) CCl₂BrCF₂BrCF₃ resulted from the bromination of the preceding ethylenic compound. The freezing point was taken on 10 cc. of material obtained by three fractional crystallizations from a batch melting originally at 28°.

Discussion.—The experimental results show, in confirmation of the preceding paper, that -CCl₃ groups are by far the most sensitive to fluorination, that CHCl₂- groups are exceedingly resistant, and that -CHCl- groups undergo decomposition before being fluorinated. They show also that -CCl₂- groups are quite resistant to fluorination and require severe conditions to go from the -CClF- to the -CF₂- stage. This last observation applies only to -CCl₂- groups surrounded by halogenated groups and contrasts with the fact that -CCl₂- groups surrounded by hydrogen-bearing carbons are exceedingly easily fluorinated.²

The behavior of the compounds containing a -CHCl- group was novel on two counts, the breakage of the molecule at that point and the hydrolysis of the adjacent trihalogenated groups.

The synthesis of a -CF₃ group, despite the fact that it was adjacent to a halogen-bearing carbon atom, is a feature which has only one analogous but not identical precedent, namely, the fluorination of CHCl₂CHF₂ to CH₂ClCF₃.³ In other cases where -CF₃ groups were obtained, the adjacent group bore hydrogen exclusively.⁴ Besides showing the behavior of highly fluorinated compounds, the experimental results fortify the idea that (from the practical standpoint) high molecular polyfluorides should be synthesized by condensation of smaller highly fluorinated molecules, rather than by the fluorination of high molecular compounds obtained by condensation.

Summary

Ten new compounds listed in Table I have been synthesized, and their structural formulas have been discussed.

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(2) Henne and Renoll, *THIS JOURNAL*, **59**, 2434 (1937).

(3) Henne and Renoll, *ibid.*, **58**, 887 (1936).

(4) Henne and Renoll, *ibid.*, **58**, 889 (1936).