The Action of Elementary Fluorine upon Organic Compounds. XVI. The Vapor Phase Fluorination of $CHCl=CCl—CHF_2$[1]

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The object of this work has been to study the vapor phase fluorination of the relatively highly deactivated halo-olefin, $CHCl=CCl—CHF_2$, under mild operating conditions. The reaction pattern involving certain preferred sequences has been shown to be quite similar to that observed in an earlier study of the fluorination of trichloroethylene; and it has to this extent been generalized. The structure of the olefin has now been proved unequivocally by a novel method involving direct fluorination followed by dechlorination. A number of new fluorochloro- and fluorobromopropanes and a tetrafluoropropene have been prepared and characterized.

This paper is the third[3] of a group dealing with the action of elementary fluorine on highly deactivated organic compounds, and reports an extension and generalization of the results obtained in our recent study of the fluorination of trichloroethylene. The compound $CHCl=CCl—CHF_2$ was chosen for study because it represents a fairly simple deactivated halo-olefin which was readily available commercially.[4] It was originally prepared by Whaley[5] by the dehydrohalogenation of $CHCl_2—CHCl—CHCl_2$ followed by indirect allylic fluorination, and assigned the isomeric structure $CCl_2=CH—CHF_2$ by Henne, Alderson and Newman.[5] However, Gerding, Prins and Rijnders[6] and also Whaley and Davis[7] have recently presented evidence which indicates that the correct structure of this halo-propene corresponds to the formula $CHCl=CCl—CHF_2$.

It soon became apparent that this structure could be proved unequivocally by direct fluorination followed by dechlorination. If the halo-olefin has the formula $CHCl=CCl—CHF_2$ rather than $CCl_2=CH—CHF_2$ then compounds I and III, in the chart below, will represent saturated halides with chlorine atoms attached to adjacent carbon atoms, and so should be easily dechlorinated, which would hardly be possible otherwise. These compounds have been prepared, dechlorinated and the resulting fluoro-olefins $CHF=CF—CHF_2$ and $CF_2=CF-CF_3$ have been isolated and adequately characterized. These results prove beyond reasonable doubt that our purified sample was to be represented by the formula $CHCl=CCl—CHF_2$, presumably in the *trans* configuration.

This material was fluorinated over a close metal packing essentially in the manner previously described, at the molar reaction ratios (F_2:sample:N_2) of $3:1:18$, $2.5:1:15$ and $2:1:12$, and reactor temperature of $112°$ in each case, which was high enough to discourage polymerization but low enough to avoid cracking. The crude products, which after washing and drying weighed roughly half again as much as the corresponding samples fed into the reactor, were carefully rectified in the usual manner. The chief products which were formed, with the preferred isomers not enclosed in parentheses, are illustrated in the following chart. Other more highly halogenated isomeric mixtures not shown were C_3F_7Cl and C_3HF_6Cl in appreciable amounts, while the presence of small quantities of C_3F_8, $C_3H_2F_5Cl$, $C_3F_4Cl_4$ and C_2F_5Cl among the products[8] was also indicated.
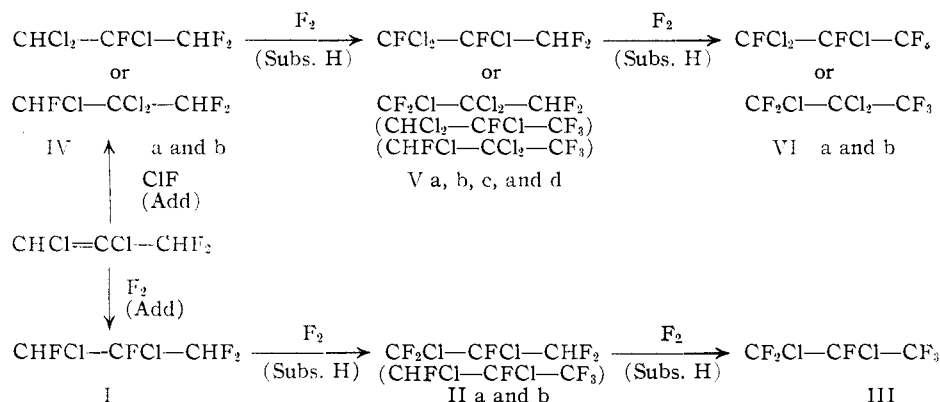
An examination of the above scheme will show that the reaction took place by two distinct preferred routes, the one involving the primary addition of fluorine and the other of chlorine fluoride, itself produced concurrently by displacement. Since I and IV were formed in nearly equal amounts under the mild conditions, whereas III and VI were produced in approximately the same proportions under the stronger conditions, VI must have been formed chiefly at the expense of IV, and III at the expense of I. In the fluorine sequence (below) the addition product I, b.p. $76°$ (presumably four stereoisomers), was isolated and fully characterized. On dechlorination with zinc, it yielded the expected mixture of *cis* and *trans* $CHF=CF—CHF_2$, b.p. $15-23°$ with a constant molecular weight throughout, and this in turn was

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(3) Preceding papers, This Journal, **72**, 3423, 2411 (1950).

(4) This material was furnished in quantity by the Columbia Organic Chemicals Co., Columbia, S. C.

(5) Henne, Alderson and Newman, This Journal, **67**, 918 (1945), (footnote).

(6) Gerding, Prins and Rijnders, *Rec. trav. chim.*, **65**, 165 (1946).

(7) Whaley and Davis, This Journal, **70**, 1026 (1948).

(8) In contrast to the trichloroethylene case, the fluorination of the propene yielded much less polymeric material, as would be expected, while no unsaturation could be detected in comparable fractions of the product.

easily brominated to form diastereomeric CHFBr—CFBr—CHF₂, b.p. 116.5°. The further fluorination of saturated I must take place by substitution to form either or both of the isomers II a and b, b.p. (observed) 56°, and IIa would be expected to boil the higher of the two. Now CHCl=CCl—CF₃[9] boils at 53.7°, and the addition of fluorine to this compound, which would be expected to lower the boiling point, would yield IIb. Also CHFCl—CF₂—CF₂Cl[10] boils at 51–53°, and IIb would be expected to boil somewhat lower than this. Since the actual sample boils at 56°, it is believed to consist chiefly if not entirely of IIa. Other available evidence, such as.that from exhaustive chlorination, supports this conclusion. The further fluorination of II removed the last hydrogen atom to form the known III[11] obtained in considerable yield under the stronger operating conditions. On dechlorination it yielded the known CF₂=CF—CF₃,[11] which on bromination gave the expected CF₂Br—CFBr—CF₃, b.p. 73°, which was perfectly stable on long standing. Simons and co-workers[12] have prepared C₃F₆Br₂ (b.p. 71–71.5°, structure not given), by substitution at high temperatures, and described it as unstable, even in a sealed glass ampoule. This product may have contained some of our dibromide, but the instability may have been due to the presence in it of the corresponding 1,1- or 1,3-isomers.

In the chlorine fluoride sequence the situation is much more complex, and on account of the extraordinary similarity in the physical properties of the various fluoro-chloropropanes involved, it has been possible to determine only in part the exact nature of the isomeric mixtures which were obtained. The addition of chlorine fluoride to the original halopropene can yield IV a and b, b.p. (observed) 110 to 111.5°. This fraction appeared to consist of a mixture of the chlorine fluoride adduct C₃H₂F₃Cl₃ with C₃F₄Cl₄, four known isomers[13] of which boil in the same range, in the ratio of about 6:1. Exhaustive chlorination of IV furnished C₃F₃Cl₅ and C₃F₄Cl₄ in this ratio, but yielded no information as to the orientation of the chlorine fluoride adduct. The further fluorination of IV by substitution can yield any or all of the isomers Va, b, c, and d, all of which are unreported, b.p. (observed) 96°, and Va and b would be expected to boil definitely higher than Vc and d. There are three known isomers of V[14] none of which contains either a —CHF₂ or a CF₃ group, and all of which boil below 92°. By inspection it appears that Vc and d should boil below 92° and certainly not higher than this, while V actually boils at 96°. Also the exhaustive chlorination of V yielded C₃F₄Cl₄, b.p. 113°, which crystallized slowly at −80°. The two known isomers of C₃F₄Cl₄[13] which

are derivable from Va and b melt below −40°, while the other two derivable from Vc and d melt near or above room temperature. Each of these observations indicates that V is best represented by a and/or b, but not c or d. The further fluorination of the isomers Va and b, or Vc and d, for that matter, would be expected to yield VI a and b, b.p. (observed) 73.8°, which froze to a glass. Both of these compounds are known[11,9] together with their dechlorination products CFCl=CF—CF₃[11,15] and CF₂=CCl—CF₃,[9] as well as a third isomer CF₂Cl—CFCl—CF₂Cl.[15] However, the physical properties of the isomers are so very nearly alike that no definite conclusion regarding the exact structure of VI can be drawn, especially when possible contamination by related compounds is considered. Variations in the freezing characteristics and the refractive indices do indicate, however, that the preferred isomer should be VIa.[16]

The conclusion to be drawn from these observations is that the reaction pattern in this fluorination is strikingly similar to that shown in the fluorination of trichloroethylene described previously,[3] and has thus been generalized to a certain extent. Also the theoretical considerations set forth earlier will presumably apply in this case as well.

Experimental

The Fluorination of CHCl=CCl—CHF₂.—The apparatus and general fluorination procedure have been referred to above. The commercial sample was repeatedly rectified, using a Podbielniak Hyper-Cal column, b.p. 89.7–90°, central cut b.p. 90°, f.p. −83.5 ± 1.5°, n^{20}D 1.4152, n^{30}D 1.4100; known[7] b.p. 89°, n^{20}D 1.4150. Measurements of the dielectric constants of successive fractions of this product by Hobbs and Cherry in this laboratory showed that the entire purified sample was essentially homogeneous.

Anal. Calcd. for C₃H₂Cl₂F₂: Cl, 48.3. Found: Cl, 48.2.

The detailed results from the three runs at reaction ratios of 3:1:18, 2.5:1:15 and 2:1:12, and reactor temperature of 112°, were quite similar, and consequently the exact figures corresponding to the last of these runs only will be presented here with appropriate comments further on regarding significant variations under the different conditions. In this case, nitrogen, at 8.4 l. per hour, was passed through the saturator at 60°, and carried 0.062 mole (9.1 g.) per hour of the sample into the reactor where it met and reacted with 0.124 mole of fluorine diluted with 9.9 l. per hour of nitrogen, at a reaction zone temperature maintained at 112°. Over a period of 22 hours the yield of crude product, which contained no free chlorine, was 276 g. after washing and drying. The results of the rectification in the Podbielniak Hyper-Cal column are collected in Table I.

Low-boiling Fraction.—At reaction ratio 3:1:18, 25 g. and at 2.5:1:15, 11 g. of this material were produced. The samples were mixed (43 g. in all) and rectified in a Booth–Podbielniak low temperature fractionating unit. More than a third of the product boiled from −6 to 0° (mostly −3°); mol. wt., 202, 203. Known CF₃—CFCl—CF₃,[11] b.p. −2°, mol. wt. 205, but the isomer CF₃—CF₂—CF₂Cl is unreported. About a quarter of the product boiled at 16–20°; mol. wt., 185, 187. Known CF₂Cl—CF₂—CHF₂,[18] b.p. 21°, mol. wt. 186.5, but the other isomers are unreported. There was also evidence that C₃F₈ and C₂F₅Cl were formed in small quantities, together with traces of CF₄.

(9) Henne, Whaley and Stevenson, THIS JOURNAL, **63**, 3478 (1941).

(10) Coffman, Cramer and Rigby, *ibid.*, **71**, 979 (1949).

(11) Henne and Waalkes, *ibid.*, **68**, 496 (1946).

(12) Brice, Pearlson and Simons, *ibid.*, **68**, 968 (1946).

(13) CFCl₂–CFCl–CF₂Cl, Henne and Haeckl, THIS JOURNAL, **63**, 3476 (1941); CF₂Cl–CCl₂–CF₂Cl, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 76; CCl₂–CFCl–CF₃[9]; and CFCl₂–CCl₂–CF₃.[11]

(14) CHCl₂–CF₂–CF₂Cl, McBee, Henne, Hass and Elmore, THIS JOURNAL, **62**, 3340 (1940); CHFCl–CF₂–CFCl₂[10]; CHFCl–CFCl–CF₂Cl.[13]

(15) Henne and Newby, THIS JOURNAL, **70**, 130 (1948).

(16) Since the submission of this paper for publication, Davis and Whaley[17] have reported the preparation of Vb together with further evidence indicating that our preferred isomers IIa, IVa, Va and VIa are probably correct.

(17) Davis and Whaley, *ibid.*, **72**, 4637 (1950).

(18) Park, Benning, Downing, Laucius and McHarness, *Ind. Eng. Chem.*, **39**, 354 (1947).

TABLE I

THE RECTIFICATION OF FLUORINATED $CHCl=CCl-CHF_2$
MOLAR REACTION RATIO 2:1:12 AT 112°

Compound	B.p., °C.	Weight, g.	Wt. % of crude product	Remarks
Low boiling	−78 to +22	7	2.5	Trace of CF_4 only
—	22–32	10.3	3.8	
$CF_2ClCFClCF_3$	32–33.5	21.3	7.7	Slightly impure
—	33.5–53	17.7	6.4	
$CF_2ClCFClCHF_2$	53–56	18.9	6.9	May contain $CHFClCFClCF_3$
—	56–70.5	11.6	4.2	
$C_3F_4Cl_3$	70.5–72.5	16.5	6.0	Slightly impure
—	72.5–76	8.9	3.2	
$CHFClCFClCHF_2$	76–76.5	13.5	4.9	
—	76.5–87.5	17.8	6.5	
$CHCl=CClCHF_2$	87.5–90	37.3	13.6	Recovered sample
—	90–95.5	6.6	2.4	
$C_3HF_4Cl_3$	95.5–96	3.6	1.3	
—	96–109.5	9.4	3.4	
$C_3H_2F_3Cl_3$	109.5–112	12.9	4.7	Contains $C_3F_4Cl_4$
—	112–140	11.7	4.3	
Low polymers	140–214	23.5	8.5	Probably mostly chlorofluoro-butanes and -pentanes
Residue	....	4.9	1.8	

$CF_2Cl—CFCl—CF_3$ Fraction.—Central cut, mol. wt. 211, 213; n^{20}D 1.3013. At 3:1:18, 14.5%, b.p. 34.5° (mostly), mol. wt. 220, 220; n^{20}D 1.3027. Known $CF_2Cl—CFCl—CF_3$,[11] b.p. 34.7°, mol. wt. 221, n^{20}D 1.3029. At 2.5:1:15, 8.5%, b.p. 32–35°.

$CF_2Cl—CFCl—CHF_2$ Fraction.—B.p. 55.5–56° (mostly), mol. wt. 203, 204; n^{20}D 1.3288. At 3:1:18, 5.3%; 2.5:1:15, 7.2%; anal. sample, b.p. 56.0°, n^{20}D 1.3288.

Anal. Calcd. for $C_3HF_5Cl_2$: Cl, 34.9; mol. wt., 203. Found: Cl, 35.2, 35.3; mol. wt., 203, 204.

$C_3F_5Cl_3$ Fraction.—Central cut, mol. wt. 219, 223; n^{20}D 1.3513. At 3:1:18, 14.4%, b.p. 71.5–74° (mostly 73.8°, f.p. glass), mol. wt., 235, 236; n^{20}D 1.3527. Known $CFCl_2—CFCl—CF_3$,[11] b.p. 73.5°, f.p. glass, n^{20}D 1.3529; $CF_2Cl—CCl_2—CF_3$,[9] b.p. 72°, f.p. −4.3°, n^{20}D 1.3519; $CF_2Cl—CFCl—CF_2Cl$,[15] b.p. 73.7°, f.p. −72 ± 3°, n^{20}D 1.3512, all mol. wts. 237. At 2.5:1:15, 7.7%, b.p. 71–72°, mol. wt. 235, n^{20}D 1.3523.

$CHFCl—CFCl—CHF_2$ Fraction.—Central cut, b.p. 76°, f.p. glass, n^{20}D 1.3551. This was pure $CHFCl—CFCl—CHF_2$.

Anal. Calcd. for $C_3H_2F_4Cl_2$: Cl, 38.3; mol. wt., 185. Found: Cl, 38.3, 38.3; mol. wt., 186, 187.

At 3:1:18, none; at 2.5:1:15, 5.6%, n^{20}D 1.3551.

$CHCl=CCl—CHF_2$ Fraction.—At 3:1:18, none; at 2.5:1:15, trace.

$C_3HF_4Cl_3$ Fraction.—Central cut, mol. wt. 223, 224; n^{20}D 1.3802. At 3:1:18, 6.4%, b.p. 93.5–96° (mostly 96°), mol.

wt. 220, 224, n^{20}D 1.3753. Central cut crystallized at dry ice–acetone temperature. At 2.5:1:15, 4.4%, b.p. 94–96.5°, mol. wt. 220, 221, n^{20}D 1.3771; anal. sample, b.p. 96°, n^{20}D 1.3771.

Anal. Calcd. for $C_3HF_4Cl_3$: C, 16.4; H, 0.46; mol. wt., 219. Found: C, 16.2; H, 0.52; mol. wt., 220, 221.

$C_3H_2F_3Cl_3$ Fraction.—Material b.p. 110.5°, mol. wt. 226, 227, n^{20}D 1.3940; b.p. 111°, n^{20}D 1.3960. At 3:1:18, 1.4%, b.p. 108.5–111°, mol. wt. 225, n^{20}D 1.3940. At 2.5:1:15, 7.3%, b.p. 108.5–112° (mostly 110.5–111.5°). Material b.p. 111.5°, mol. wt. 228, n^{20}D 1.3974; b.p. 110.5°, mol. wt. 219, n^{20}D 1.3941 (anal. sample).

Anal. Calcd. for $C_3H_2F_3Cl_3$: C, 17.9; H, 1.0; mol. wt., 201; and for $C_3F_4Cl_4$: C, 14.2; H, 0.0; mol. wt., 254. Found: C, 17.3, 17.6; H, 0.84, 0.86; mol. wt., 219.

Known $CH_2Cl—CF_2—CFCl_2$,[14] b.p. 108.3°, n^{20}D 1.3954; known four isomers[13] of $C_3F_4Cl_4$, b.p. 112–114°, n^{20}D 1.3958–1.4002.

Dechlorination of the $CF_2Cl—CFCl—CF_3$ Fraction, Table I.—The reaction was carried out in dioxane solution in the usual manner, and gave a practically quantitative yield of the corresponding perfluoropropene, which was then rectified, b.p. −29.5°, f.p. −153°, mol. wt. 149.5, 150; known $CF_2=CF—CF_3$,[11] b.p. −29.4°, f.p. −156.2° (cooling curve), mol. wt. 150. This olefin was brominated in strong light, while refluxing under a Dry-Ice condenser, by the addition of liquid bromine in small portions. In the initial stages, the bromine froze before reacting. The product was washed with sodium hydroxide–sodium bisulfite solution, dried over anhydrous magnesium sulfate, and on distillation through a 10-cm. Vigreux column gave a practically quantitative yield of colorless, stable $CF_2Br—CFBr—CF_3$, b.p. 71.5–75°, central cut, b.p. 73°, n^{20}D 1.3600.

Anal. Calcd. for $C_3F_6Br_2$: C, 11.6; mol. wt., 310. Found: C, 11.7; mol. wt., 307, 309.

Dechlorination of the $CHFCl—CFCl—CHF_2$ Fraction, Table I.—The reaction was carried out as described above, and gave an essentially quantitative yield of the corresponding propene, which was then carefully rectified, b.p. 15–23°, with a constant mol. wt. throughout of 113–114 (calcd. 114). This mixture of *cis–trans* isomers was brominated as before, and on distillation through the Vigreux column gave a nearly quantitative yield of colorless, stable $CHFBr—CFBr—CHF_2$, b.p. 116–117°, central cut, b.p. 116.5°, n^{20}D 1.4190.

Anal. Calcd. for $C_3H_2F_4Br_2$: Br, 58.4; mol. wt., 274. Found: Br, 58.2; mol. wt., 278.

Dechlorination of the $C_3F_5Cl_3$ Fraction, Table I.—This reaction was carried out in absolute ethanol, and gave a nearly quantitative yield of the corresponding olefins, which was then rectified, b.p. 3–6° (mostly 5–6°), central cut, mol. wt. 162. Known $CFCl=CF—CF_3$,[11,15] b.p. 7.9°, 8.4°; $CF_2=CCl—CF_3$,[9] b.p. 6.8°, mol. wt. 167.

Note.—Nearly all the analyses reported in this paper were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.