Reaction of 1,1,2-Trichloro-1,2,2-trifluoroethane and Other Fluorohalocarbons with Aluminum Halides in the Presence and Absence of Additives. Distinction in Carbonium Ion Character and Reaction Conditions between Substitution and Isomerization

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In the reaction of $CF_2ClCFCl_2$ with aluminum chloride, the addition of carbon disulfide, trichloroethylene, methylene chloride, *n*-hexane, cyclohexane, etc., was found to be effective in inhibiting the isomerization into CF_3CCl_3 without significantly retarding the substitution, which gives CF_2ClCCl_3. Cyclohexane was also used for similar purposes to obtain CF_3CClBr_2 from CF_3CFBr_2, CF_2BrCCl_2Br from $CF_2BrCFClBr$, $CF_2BrCClBr_2$ from $CF_2BrCFClBr$ (+ $AlBr_3$), and $CF_2ClCBrCl_2$ from $CF_2ClCFCl_2$ (+ $AlBr_3$). In each of these reactions cyclohexane–methylcyclopentane equilibration as well as formation of a small amount of a hydride-transfer product, such as $CF_2ClCHCl_2$, was noted. In the treatment of $CF_2ClCFCl_2$ with aluminum chloride, the isomerization was never complete as far as vigorous stirring was continued. Discontinuation of the stirring afforded aluminum fluoride precipitates effective for the isomerization of fluorohalocarbons. Reactions of $CF_2ClCFCl_2$ with aluminum halides in the presence of halomethanes and similar reactions of $CF_2BrCFClBr$ were also studied. For example, the reaction $CF_2ClCFCl_2 + CCl_4 + AlCl_3$ yielded CF_2ClCCl_3 and CF_2Cl_2 as the main products, but only a minor amount of CF_3CCl_3. The substitution reaction is considered to proceed in solution via the ion pair $CF_2ClC^+Cl_2{\cdot}AlFCl_3^-$ without rearrangement. The isomerization is considered predominantly a surface reaction, for which the following reactions are suggested to proceed when the carbonium ions are dissociated from the counteranions anchored on (or inside of) the solid surface: $CF_2ClCFCl_2 + {}^+CF_2CCl_3 \rightarrow CF_2ClC^+Cl_2 + CF_3CCl_3$; $CF_2ClC^+Cl_2 \rightleftarrows {}^+CF_2CCl_3$.

Substitution[1,2a] and isomerization[2b,3a] generally occur when chlorofluorocarbons are treated with aluminum chloride. However, the relationship between these two types of reactions, as well as the relationship between the isomerization and the disproportionation[3b] of chlorofluorocarbons, does not seem to be well understood. In repeated treatment of $CF_2ClCFCl_2$ with aluminum chloride for the preparation of CF_2ClCCl_3[4] (used as the precursor of $CF_2{=}CCl_2$),[5] we noted that the isomerization to CF_3CCl_3 sometimes did not occur when partially deteriorated aluminum chloride[6a] was used, while the substitution, which gives CF_2ClCCl_3, always occurred without failure. This appeared to give a clue for understanding the difference in nature between these two reactions. Hence, the reaction of $CF_2ClCFCl_2$ with aluminum chloride and related reactions have been studied in some detail in order to gain a mechanistic insight for these reactions as well as to find better ways for separate utilization of the two types of reactions.

Results

The reaction of $CF_2ClCFCl_2$ with aluminum chloride showed a marked stirring effect. Thus the isomerization was never complete as far as vigorous stirring[6b] was continued (for 2, 3, 5, and 7 h) with refluxing. When stirring and external heating were discontinued, refluxing ceased temporarily, but soon the reaction mixture began to reflux again, showing an active occurrence of the isomerization. Thirty minutes after the initial vigorous stirring had been stopped, unchanged $CF_2ClCFCl_2$ was practically absent from the reaction mixture. With less efficient stirring the isomerization was complete in a few hours even if the stirring was uninterrupted.

The resulting bulky precipitates of AlF_xCl_{3-x} had a catalytic activity for the isomerization and disproportionation of fluorohalocarbons. Use of such precipitates provides an efficient preparative method of CF_2ClCCl_3 by isomerization of $CFCl_2CFCl_2$ (a commercial sample containing CF_2ClCCl_3). The experimental procedure is described in a previous paper.[5] Direct treatment of $CFCl_2CFCl_2$ with aluminum chloride gives unsatisfactory results.[4,7,8]

Active mixtures of the reaction of $CF_2ClCFCl_2$ with aluminum chloride induced smooth isomerization of CF_2BrCF_2Br to CF_3CFBr_2[9] and subsequent reactions as shown in Figure 1. This smooth isomerization of CF_2BrCF_2Br is in marked contrast to the existence of long and variable induction periods (20–60 h, 14 h, 18 h, 33 h, >65 h: discontinued, 4 days)[10] in direct treatment of CF_2BrCF_2Br with aluminum chloride under refluxing conditions.[11] The isomerization of CF_2BrCF_2Br occurred without significant induction period and was even faster than the isomerization of $CF_2ClCFCl_2$, where a mixture of CF_2BrCF_2Br and $CF_2ClCFCl_2$ was treated with aluminum chloride.

Reactions of $CF_2ClCFCl_2$ (100 g) with aluminum chloride (10 g) in the presence of additives (30 mL) were also studied. In the presence of nitrobenzene, tetrahydrofuran, or triethylamine, neither the isomerization nor the substitution was observed, except that a small amount of CF_2ClCCl_3 was found in the case where triethylamine was used.[12] In the presence of benzene, chlorobenzene, trichloroethylene, cyclohexane, *n*-hexane, carbon disulfide,[13] and methylene chloride, only the substitution was observed. In the presence of tetrachloroethylene, bromine, carbon tetrachloride, and chloroform, both the isomerization and substitution were observed, though the proportion of the isomerization was greatly decreased in some cases (vide infra).

The reaction where cyclohexane was used as additive (Table I) is interesting because, although the isomerization of $CF_2ClCFCl_2$ was practically inhibited, the isomerization of cyclohexane was allowed to occur. The rate of approaching cyclohexane–methylcyclopentane equilibrium was, however, only moderate.[14] The formation of $CF_2ClCHCl_2$ was confirmed by the ^{19}F NMR spectrum of a $CF_2ClCHCl_2$-containing fraction obtained from this reaction and distilling at 53–76 °C, an authentic sample, and a mixture of the two. A further confirmation was obtained from the mass spectrum, which is identical with that of the authentic sample in GC–mass spectroscopy.

The reactions where carbon tetrachloride and chloroform were used as additives were characterized by the occurrence of exchange of chlorine and fluorine between molecules of the fluoroethane and halomethane at the expense of the isomerization of $CF_2ClCFCl_2$. In the reaction where chloroform was the additive, there was observed an induction period (1.5 h)

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Table I. Reaction of Fluorohalocarbons with Aluminum Chloride or Bromide in the Presence of Cyclohexane[a,b]

Substrate R*F*	$AlCl_3$, g	Time, h	Product distribution, %[c]				
			RF[d]	RCl	RBr	RH	R′F[e]
$\mathrm{CF_2ClC}F\mathrm{Cl_2}$	30	23	27	70		2	0.3
$\mathrm{CF_2ClC}F\mathrm{Cl_2}$	25 ($AlBr_3$)	5[f]	70	0.6	26	3[g]	0.3
$\mathrm{CF_2BrC}F\mathrm{ClBr}$	10	4	76	21		1[h]	2
$\mathrm{CF_2BrC}F\mathrm{ClBr}$	24 ($AlBr_3$)	2.5[i]	64		24[j]	1[h]	9
$\mathrm{CF_3C}F\mathrm{Br_2}$	20	20	43	49		8	
$\mathrm{C}F\mathrm{Cl_3}$	10	4[k]	72	28			
{$\mathrm{C}F\mathrm{Cl_3}$[l]	10	5[k]	70	30			
{$\mathrm{CF_2ClC}F\mathrm{Cl_2}$[l]			100				
{$\mathrm{CF_2ClC}F\mathrm{Cl_2}$[m]	10	3	98	2.5			
{$\mathrm{CF_2BrC}F\mathrm{ClBr}$[m]			67	32			1

[a] Aluminum chloride or bromide was added to a solution of 100 g of the substrate (or combined substrates) in 30 mL of cyclohexane, and unless otherwise stated the resulting mixture was refluxed for the indicated period of time with stirring. [b] The formation of methylcyclopentane was observed unless otherwise stated. [c] The product distribution was determined from ^{19}F NMR peak heights. The ratio $CCl_4/CFCl_3$ was determined by GC. [d] Unchanged substrate. [e] CF_3CCl_3 (from $CF_2ClCFCl_2$) or CF_3CClBr_2 (from $CF_2BrCFClBr$). [f] Initial heating induced a vigorous reaction. [g] The ratio $CF_2ClCHCl_2/CF_2ClCCl_2Br$ was determined from the ratio of ^{19}F NMR areas recorded on an expanded scale. [h] A small concentration of this compound ($CF_2BrCHClBr$) was practically undetectable by ^{19}F NMR because of signal multiplicity. See the footnote *m* of Table II. The ratio $CF_2BrCHClBr/CF_2BrCCl_2Br$ or $CF_2BrCHClBr/CF_2BrCClBr_2$ was determined from the GC area ratio assuming equal molar sensitivity. [i] Only for the last 20 min of this period the reaction mixture was heated (~60 °C). Each addition of aluminum bromide (in two portions in a 1-h interval) had induced a vigorous reaction. [j] In addition to this compound ($CF_2BrCClBr_2$), a compound (2%) which was suspected to be CF_2ClCBr_3 was formed. See footnote *g* of Table II. [k] Methylcyclopentane was not found in the resulting mixture. [l] Mixture of equal weights. [m] Equimolar mixture.

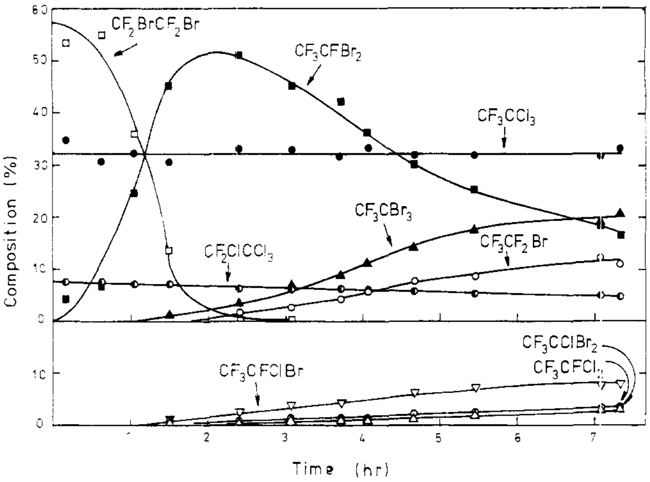

Figure 1. Reaction profile of room temperature treatment of CF_2BrCF_2Br with active precipitate obtained from $CF_2ClCFCl_2$ and aluminum chloride. (The active precipitate together with the accompanying liquid was placed in an NMR tube and the tube cooled with ice and sealed after addition of CF_2BrCF_2Br.)

for the formation of CF_3CCl_3 (and CHF_3) probably due to ethanol present as stabilizer in chloroform, while CF_2ClCCl_3 was formed from the beginning. After this period a brisk evolution of a gas (mostly CHF_3)[15] occurred over a short period (0.2 h), leaving a solidified mixture whose main component was hexachloroethane. On the other hand, when the reaction in which carbon tetrachloride was the additive was followed, there was observed a gradual and steady evolution of a gas (CF_2Cl_2 and small amounts of $CFCl_3$ and CF_3Cl).

In the reaction system $CF_2ClCFCl_2 + CFCl_3 + AlCl_3$, the initial reaction was the substitution reaction and disproportionation of $CFCl_3$. The formation of CF_2ClCCl_3 became appreciable (0.4%) only after 80% of the $CFCl_3$ had been converted into CCl_4 and CF_2Cl_2.

When aluminum bromide (10 g) was added to a solution of $CF_2BrCFClBr$ (100 g) in carbon tetrachloride (200 mL), an exothermic reaction occurred. The determined fluoroethane distributions of the resulting mixture after 4 min and 3.5 h (given in this order) were as follows: CF_3CClBr_2, 85, 86%; CF_2BrCCl_2Br, 8, 3%; $CF_2ClCClBr_2$, 7, 11%. Isomerization of CF_2BrCCl_2Br to $CF_2ClCClBr_2$, besides isomerization of $CF_2BrCFClBr$ to CF_3CClBr_2,[16] is apparent. It is also evident that the amount of CF_2BrCCl_2Br initially formed was equal to or greater than the amount of $CF_2ClCClBr_2$ initially formed.

Discussion

Substitution Reaction and Relative Carbonium Ion Stability. The rate of the substitution reaction is controlled by the solubilization of aluminum chloride as shown by the fact that, in spite of their considerable difference in reactivity under competitive conditions (Table I), $CF_2ClCFCl_2$ and $CFCl_3$ undergo the substitution reaction at comparable rates when individually treated. The first step of the substitution reaction, in the early stages, is considered the formation of ion pair $CF_2ClCCl_2^+ \cdot AlFCl_3^-$ from interaction with monomeric aluminum chloride, which exists in equilibrium with the dimer, the major soluble species. The decomposition of the ion pair into CF_2ClCCl_3 and $AlFCl_2$ does not seem to be spontaneous (in view of the formation of condensation products at the expense of CF_2ClCCl_3 in the presence of benzene).

The absence of rearrangement in the substitution reactions of this type is indicated by the formation of CF_2ClCCl_2Br and CF_2BrCCl_2Br as the exclusive substitution products of the following reactions:[17]

$$CF_2ClCFCl_2 \xrightarrow{AlBr_3\ \text{(cyclohexane)}} CF_2ClCCl_2Br$$

$$CF_2BrCFClBr \xrightarrow{AlCl_3\ \text{(cyclohexane)}} CF_2BrCCl_2Br$$

Since CF_2BrCCl_2Br is thermodynamically less stable than $CF_2ClCClBr_2$, as shown by the observation that the former was converted into the latter under isomerizing conditions, the generality of the absence of rearrangement in the substitution reactions of this type is little doubted.[17]

The relative stabilities of fluorohalocarbonium ions can be inferred from the reactivities of fluorohalocarbons with respect to the substitution with aluminum halides. For example, $CF_2ClC^+Cl_2$ is suspected to be more stable than $^+CF_2CCl_3$ from the much greater reactivity of $CF_2ClCFCl_2$ as compared with that of CF_3CCl_3. This view is supported by the much greater reactivity of the chlorine atoms of the CCl_3 group of CF_2ClCCl_3 than that of the chlorine atom of the CF_2Cl group of this compound with respect to the substitution of fluorine for chlorine with antimony fluorides.

From similar considerations, a carbonium ion having α-chlorine is generally inferred to be more stable than the corresponding carbonium ion having α-fluorine (at least for the ion pair state).[18] The reverse of this inference is often assumed.[19] However, the relative *overall* order of α-fluorine and α-chlorine in stabilizing the carbonium ion apparently has not been established, though greater "back-donating ability" [20] of α-fluorine is unequivocal.

Nature of Isomerization Catalyst and Effect of Stirring. The behavior of CF_2BrCF_2Br on treatment with aluminum chloride can be explained in terms of the view[21,22] that catalytically active aluminum fluoride is formed from aluminum chloride by the substitution reaction with $CF_2ClCFCl_2$ and other fluorohalocarbons. The catalytic activity of aluminum chloride as such for the isomerization of CF_2BrCF_2Br seems to be negligibly small. The substitution of chlorine for fluorine in CF_2BrCF_2Br also does not occur before the isomerization is induced. On the other hand, the isomerization product CF_3CFBr_2 undergoes smooth substitution with aluminum chloride to give CF_3CClBr_2 (Table I). Hence, once the isomerization is started somehow in the presence of aluminum chloride, the isomerization and substitution proceed rapidly.

The increase in catalytic activity with an increase in the extent of substitution of fluorine for chlorine of aluminum chloride is basically attributable to the increase in the stable coordination number around the aluminum atom (while the valence of aluminum is kept at three). The stable coordination number is six where the coordinating atoms are fluorine[23] and four where the coordinating atoms are chlorine. Hence, with aluminum fluoride even the solid surface has a coordinating ability,[24,25] whereas with aluminum chloride only the monomeric species is capable of coordination. Aluminum chloride fluorides may have intermediate properties.

The stirring effect on the isomerization is also explicable in terms of the catalytic activity of aluminum fluoride formed by the substitution reaction. The solubility of aluminum chloride in fluorohalocarbons is low in comparison with the rate of its consumption by the substitution reaction of $CF_2ClCFCl_2$, and the supply of aluminum chloride to the solution is greatly dependent on the efficiency of stirring (and particle size). When the stirring is stopped or its speed slowed down after vigorous stirring has been continued for some time, the supply of aluminum chloride is greatly reduced. Then the x value denoting the average composition AlF_xCl_{3-x} of the solid surface and soluble species will sharply rise as the substitution reaction proceeds and approach three (or possibly to a somewhat lower value), giving active aluminum fluoride.

Two conceivable modes of interaction of such a solid surface with RF is reversible (eq 1) and irreversible (eq 2) ionization of the latter:

$$RF + \mathit{AlF}_3 \rightleftarrows R^+ + \mathit{AlF}_4^- \qquad (1)$$

$$R\cdot{}^+\mathit{AlF}_4^- \rightleftarrows R^+ + \mathit{AlF}_4^- \qquad (2)$$

where AlF_3 represents an active point of the solid surface and AlF_4^- the corresponding fluoride-coordinated form. The mode (eq 2) action results in a catalytic activity if the carbonium ion abstracts a fluoride ion (and/or a chloride ion) from a neutral molecule. Irreversible ionization is also expected to occur by such processes as the occlusion of the fluoride ion inside of an aluminum fluoride cluster.

Isomerization and Related Reactions. The results of the reaction of $CF_2ClCFCl_2$ with aluminum chloride in the presence of additives indicate that the carbonium ion character is much greater in the isomerization than in the substitution reaction. More specifically, the necessity of a more reactive carbonium ion or related species and/or a longer existence of such an intermediate are suggested for the isomerization.

For the isomerization of $CF_2ClCFCl_2$ the following mechanism is suggested,[26] where the carbonium ions[27] apparently have to be dissociated from the counteranions for the reaction to proceed. This mechanism constitutes a chain process, though the chain nature of the reaction may be obscured by the interaction of carbonium ions[27] with counteranions.

$$CF_2ClCFCl_2 + {}^+CF_2CCl_3 \rightarrow CF_2ClC^+Cl_2 + CF_3CCl_3$$

$$CF_2ClC^+Cl_2 \rightleftarrows {}^+CF_2CCl_3$$

According to this mechanism the isomerization involves intermolecular transfer of fluoride[28] and intramolecular chloride shift (mechanistically, shift of chlorine having a partial positive charge), while related disproportionation reactions involve intermolecular transfer of fluoride[28] and chloride. It is implied that the fluoride transfer would be considerably easier than the chloride transfer.

The isomerization of CF_2BrCF_2Br is similarly represented by the following equations.

$$CF_2BrCF_2Br + {}^+CF_2CFBr_2 \rightarrow CF_2BrC^+FBr + CF_3CFBr_2$$

$$CF_2BrC^+FBr \rightleftarrows {}^+CF_2CFBr_2$$

The isomerization of CF_2BrCF_2Br, once appropriate isomerizing conditions are realized, is faster than that of $CF_2ClCFCl_2$ as confirmed by the reaction $CF_2ClCFCl_2$ + CF_2BrCF_2Br + $AlCl_3$.[29] This is attributable to easier intramolecular bromide shift, as compared with intramolecular chloride shift, coupled with the existence of fluoride acceptors sufficiently strong to abstract fluoride from CF_2BrCF_2Br as well as from $CF_2ClCFCl_2$.[30]

The retardation of isomerization of $CF_2ClCFCl_2$ by carbon tetrachloride is ascribed to chloride transfer from carbon tetrachloride in competition with fluoride transfer from $CF_2ClCFCl_2$. $CFCl_3$ is formed by fluoride transfer to $^+CCl_3$ from $CF_2ClCFCl_2$.

$$CCl_4 + CF_2ClC^+Cl_2 \rightarrow {}^+CCl_3 + CF_2ClCCl_3$$

$$CF_2ClCFCl_2 + {}^+CCl_3 \rightarrow CF_2ClC^+Cl_2 + CFCl_3$$

Likewise CF_2Cl_2 is considered as resulting from fluoride transfer to $^+CFCl_2$ from $CF_2ClCFCl_2$ and from $CFCl_3$. The importance of the latter process is evident from the results of the reaction $CF_2ClCFCl_2$ + $CFCl_3$ + $AlCl_3$, where the disproportionation, as well as the substitution reaction, of $CFCl_3$ occurred in preference to the formation of CF_2ClCCl_3.

$$CFCl_3 + {}^+CFCl_2 \rightarrow {}^+CCl_3 + CF_2Cl_2$$

$$CFCl_3 + {}^+CCl_3 \rightarrow {}^+CFCl_2 + CCl_4$$

A straightforward explanation for the inhibiting action of cyclohexane and n-hexane and for the formation of $CF_2ClCHCl_2$ is hydride transfer, a well-known mode of reac-

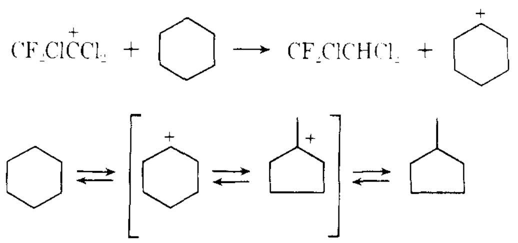

Table II. Physical Data and Method of Preparation of Fluorohalocarbons

Compd	Registry no.	Bp, °C	n^{20}_D or fp, °C	^{19}F NMR, ppm[a] CF_3	CF_2	CF	Starting compd and reagent[b]	Registry no.
CF_3CCl_3	354-58-5	45–47	1.3599	3.0			$CF_2ClCFCl_2$, i	
CF_3CCl_2Br	354-50-7	67	25	1.8			*c*	
CF_3CClBr_2	754-17-6	90–91	45	0.6			CF_3CFBr_2, ii	
CF_3CBr_3	354-48-3	115	69	−0.5			CF_2BrCF_2Br, iv	
CF_3CFBr_2	27366-23-8	46.5	1.3708	3.3[d]		−1.3[d]	CF_2BrCF_2Br, iv	
$CF_2ClCHCl_2$	354-21-2	71	1.3918		−16.0[e]		$CHCl_2CCl_3$, vi	76-01-7
CF_2ClCCl_3	76-11-9	92–93	40.5		−14.2		*f*	
CF_2ClCCl_2Br	50994-70-2	111–112.5	49		−16.0		$CF_2ClCFCl_2$, v	
$CF_2ClCClBr_2$	25856-30-8	137	72		−17.4		CFClBrCFClBr, iii	
CF_2BrCCl_2Br	558-57-6	136	45		−22.9		$CF_2{=}CCl_2$, vii	79-35-6
$CF_2BrCClBr_2$[g]	66270-59-5	85[h]	58		−24.4		$CF_2BrCFClBr$, v	
CF_2BrCF_2Br[i]	124-73-2		1.3704		−15.7			
$CF_2BrCFClBr$	354-51-8	92	1.4282		−18.5[j] −20.2[j]	−10.2	$CF_2{=}CFCl$, vii	79-38-9
$CF_2ClCFCl_2$[k]	76-13-1		1.3587		−11.1	−7.1		
$CFCl_2CFCl_2$	76-12-0	91.5–93	25			−11.5	CCl_3CCl_3, vi	67-72-1
$CFCl_2CCl_3$	354-56-3	139	98			−16.1	CCl_3CCl_3, vi	
CFClBrCFClBr		138–138.5	30			−14.7[l] −15.6[l]	CFCl=CFCl, vii	598-88-9

[a] 20% solution in carbon tetrachloride. Upfield relative to external CF_3CO_2H. Chemical shifts and coupling constants for compounds not isolated pure are given in footnote *m*. [b] (i) $AlCl_3$; (ii) $AlCl_3$ + cyclohexane; (iii) active mixture obtained from $CF_2ClCFCl_2 + AlCl_3$; (iv) $AlBr_3$; (v) $AlBr_3$ + cyclohexane; (vi) $SbF_3 + SbCl_5$; (vii) Br_2. [c] A mixture of 100 g of CF_3CFBr_2, 72 g of CF_3CCl_3, and 20 g of aluminum chloride was refluxed for a total of 70 h, and 8.6 g of CF_3CBrCl_2 was isolated. [d] J = 10 Hz. [e] J_{FH} = 6 Hz. [f] See the text. [g] Contaminated with ~7% of a compound showing a singlet at −18.4 ppm and thought to be CF_2ClCBr_3. [h] At 65 mm. [i] Daiflon 114B2, donated by Daikin Co. Ltd. [j] An AB pattern, J = 167 Hz; each peak further split into a doublet, J = 14 and 13 Hz. See J. J. Drysdale and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 319 (1957). [k] Daiflon S3, a commercial product. [l] The value −14.7 for the meso form and the value −15.6 for the *d,l* pair. See D. S. Thompson, R. A. Newmark, and C. H. Sederholm, *J. Chem. Phys.*, **37**, 411 (1962). [m] $CF_3CFClBr$ (the cold trap condensate of a reaction $CF_2ClCFCl_2 + CF_2BrCF_2Br + AlCl_3$, CCl_4 solution): 5.2 (doublet), −1.6 (quadruplet), J = 8 Hz. CF_3CFCl_2 (same as before): 6.2 (doublet), − 1.4 (quadruplet), J = 6 Hz. CF_3CF_2Br (same as before): 7.4 (triplet), −8.1 (quadruplet), J = 2.4 Hz. $CF_2BrCHClBr$ (a fraction boiling at 53–81 °C (65 mm), neat): an AB pattern, −26.3, −23.0, J = 161 Hz; each peak further split into a doublet, J_{FH} = 6 and 8 Hz; see the literature given in footnote *j*. CF_3CHBr_2 (a fraction boiling at 68–73 °C, neat): −3.4, J_{FH} = 6 Hz.

tion in the liquid phase[31] as well as in the gas phase.[32] This also explains why the isomerization of cyclohexane, which is not induced by aluminum chloride alone,[33] occurs in the reaction system.

Experimental Section

^{19}F NMR spectra were recorded on a JNM-C-60 during the early period of the study and on a Hitachi R-20BK during the later period. Unless otherwise stated, the relative amounts of fluorine compounds (including those for the figures) were determined from peak heights on charts recorded from full-range sweeps of 90 or 100 ppm, where signals of fluorohalocarbons were practically sharp lines. (The performance of the sliding resistor used in the scanning mechanism was critical for reproducibility in peak height on each of the instruments.) It was assumed that the ratios of peak heights are equal to the ratios of the numbers of the corresponding ^{19}F nucleus. That this method gives results reasonably accurate for the present purpose was confirmed in the following cases, where the ranges obtained from seven to ten sweeps each were compared with the theoretical values (given in parentheses). The CF_3CCl_3 percentages for neat mixtures of CF_3CCl_3 and $CF_2ClCFCl_2$ were 19.5–21.1 (19.8), 36.6–41.9 (39.6), 56.9–60.1 (59.4), and 76.3–78.2 (79.2). The CF_2ClCCl_3 percentages for solutions of CF_2ClCCl_3 and $CF_2ClCFCl_2$ in tetrachloroethylene were 11.4–13.4 (12.2) and 36.7–41.2 (40.7). The CF_2BrCF_2Br percentage of a neat mixture of CF_2BrCF_2Br and $CF_2ClCFCl_2$ was 40.5–43.4 (41.9).

GC works were performed using a 4-m column of Silicon-DC 550. The relative amount of two compounds (e.g., methylcyclopentane/cyclohexane) was determined from peak heights using reference solutions containing known amounts of the two compounds.

Temperatures are uncorrected. For withdrawal of aliquots of reaction mixtures which contained solids (aluminum chloride) and tended to solidify (due to the presence of CCl_3CCl_3), a special pipet was used, which has a relatively large bore on the bottom and contains a glass ball. For most of the experiments sublimed aluminum chloride powder (Merck 1081, as received) was used. The preparation and source of fluorohalocarbons are summarized in Table II.

Treatment of 1,1,2-Trichloro-1,2,2-trifluoroethane ($CF_2ClCFCl_2$) with Aluminum Chloride in Preparative Scale. (A) In the Presence of Carbon Tetrachloride. A mixture of $CF_2ClCFCl_2$ (1000 g, 5.34 mol), carbon tetrachloride (300 mL, 479 g, 3.11 mol), and aluminum chloride (100 g, 0.75 mol) was refluxed with stirring for 5.5 h, during which time the refluxing temperature increased from 55 to 74 °C. Volatile products were collected in a trap cooled with dry ice–acetone. Workup and fractional distillation afforded an isomeric mixture (124 g) of $CF_2ClCFCl_2$ (77%) and CF_3CCl_3 (23%), carbon tetrachloride (193 g), and CF_2ClCCl_3 (576 g, 53% based on charged $CF_2ClCFCl_2$). The cold trap condensate, whose main ingredient was CF_2Cl_2, steadily increased its weight (final weight 270 g).

(B) In the Presence of Carbon Disulfide. A mixture of $CF_2ClCFCl_2$ (1000 g, 5.34 mol), carbon disulfide (200 mL, 256 g), and aluminum chloride (200 g, 1.50 mol) was refluxed for 20.5 h with stirring. Workup and fractional distillation afforded CS_2–$CF_2ClCFCl_2$ azeotrope (bp 38 °C, 604 g), $CF_2ClCFCl_2$ (89 g, bp 47 °C), and CF_2ClCCl_3 (415 g, 38%). As the content of $CF_2ClCFCl_2$ in the azeotrope was determined as 63% by GC, the total amount of recovered $CF_2ClCFCl_2$ was calculated to be 470 g. Hence the yield of CF_2ClCCl_3 corresponds to 72% of unrecovered $CF_2ClCFCl_2$.

(C) In the Presence of *n*-Hexane. From a similar experiment where the additive was *n*-hexane (200 mL, 134 g) and the refluxing time was 24 h were obtained $CF_2ClCFCl_2$ (487 g), *n*-hexane (52 g), and CF_2ClCCl_3 (347 g, 32% and 62% yield based on charged and unrecovered $CF_2ClCFCl_2$, respectively).

Isomerization of 1,2-Dibromo-1,2-dichloro-1,2-difluoroethane (CFClBrCFClBr). A mixture of $CF_2ClCFCl_2$ (200 g) and aluminum chloride (20 g, 0.15 mol) was refluxed with efficient stirring for 2 h, after which time an exothermic isomerization of $CF_2ClCFCl_2$ into CF_3CCl_3 was induced by discontinuation of stirring and external heating. CFClBrCFClBr (218 g, 0.745 mol) was added, but the isomerization into $CF_2ClCClBr_2$ occurred only to a small extent in 18 min. (The failure of a smooth isomerization is suspected to be due to possible impurities, such as ethanol, in the substrate.) The resulting mixture was refluxed for 50 min and left standing overnight. The solidified mixture no longer contained CFClBrCFClBr. Hydrolysis, workup, and fractional distillation afforded $CF_2ClCClBr_2$ (93 g, 43%); bp 137 °C; fp 72 °C. The sample was found to contain ~3% CF_2BrCCl_2Br.

Registry No.—*meso*-CFClBrCFClBr, 42067-62-9; *dl*-CFClBrCFClBr, 42067-63-0; $CFCl_3$, 75-69-4; $AlCl_3$, 7446-70-0; $AlBr_3$, 7727-15-3.

Supplementary Material Available: Product yields of the reaction of $CF_2ClCFCl_2$ with aluminum chloride in the presence of additives (Table III); product distributions of the reactions of $CF_2ClCFCl_2$ and CF_2BrCF_2Br with aluminum halides in the presence of halomethanes (Table IV); and reaction profiles of the following reaction systems: (i) $CF_2ClCFCl_2 + CF_2BrCF_2Br + AlCl_3$; (ii) $CF_2ClCFCl_2 + AlCl_3$; (iii) $CF_2ClCFCl_2$ + a small proportion of $(C_2H_5)_3N + AlCl_3$; (iv) $CF_2ClCFCl_2 + CCl_4 + AlCl_3$ (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Reactions of the type $CF_2ClCFCl_2 + AlCl_3 \rightarrow CF_2ClCCl_3 + AlFCl_2$ are often referred to as halogen exchange. In this paper, however, the use of the term "halogen exchange" for such reactions is confusing because this term rather implies results such as the formation of CF_2ClCCl_3 and $CFCl_3$ from $CF_2ClCFCl_2$ and CCl_4 under aluminum fluoride catalysis, from which reactions of the above type have to be distinguished from the mechanistic point of view.

(2) (a) M. Hudlicky, "Chemistry of Organic Fluorine Compounds", 2nd ed, Ellis Horwood, Chichester, England, 1976, pp 234–236; (b) *ibid.*, pp 501–503.

(3) (a) E. Forche, *Methoden Org. Chem.*, **5**, part 3, 351–353 (1962); (b) *ibid.*, **5**, part 3, 354–357 (1962).

(4) W. T. Miller, Jr., E. W. Fager, and P. H. Griswald, *J. Am. Chem. Soc.*, **72**, 705 (1950).

(5) K. Okuhara, *J. Org. Chem.*, **41**, 1487 (1976).

(6) (a) A portion of the contents left unused in a reagent bottle whose seal was broken about 10 years before that time. (b) A 8 × 2 cm crescent polytetrafluoroethylene blade at ~600 rpm for a 500- or 1000-mL flask.

(7) M. Hudlicky and L. Lejhancova, *Collect. Czech. Chem. Commun.*, **30**, 2491 (1965).

(8) Treatment of $CFCl_2CFCl_2$ with aluminum bromide gives a higher yield of CF_2ClCCl_3: M. Hudlicky, Czechoslovakian Patent 113 114 (1969); *Chem. Abstr.*, **73**, 87406r (1970). See also ref 2, p 724.

(9) For the preparation of CF_3CFBr_2, CF_2BrCF_2Br was treated with aluminum bromide: P. Piccardi, M. Modena, and E. Santoro, *J. Chem. Soc., Perkin Trans. 1*, 1146 (1972).

(10) The isomerization was detected by a characteristic pattern in the recorded temperature curve. In each run a mixture of 100 g of CF_2BrCF_2Br and 10 g of aluminum chloride was refluxed with magnetic stirring.

(11) Long induction periods are implied in descriptions of previous experiments for this reaction system: (a) D. J. Burton, Ph. D. Thesis, Cornell University, 1961, p 101; (b) D. J. Burton and L. J. Kehoe, *J. Org. Chem.*, **35**, 1339 (1970).

(12) When a smaller portion of triethylamine was added (1 mL to 500 g of $CF_2ClCFCl_2$), the isomerization began to occur after an induction period (~3 h).

(13) The isomerization of $CF_2BrCFClBr$ was not inhibited by carbon disulfide, though a considerable retardation was apparent.

(14) When a mixture of $CF_2ClCFCl_2$ (100 g), cyclohexane (30 mL), and alumimum chloride (10 g) was refluxed, the percentage of methylcyclopentane determined by gas chromatography changed as follows: 8% (1 h), 14% (2 h), 16% (3 h), 17% (4 h), 17.5% (5 h), and 18% (21 h; 56 °C). When methylcyclopentane was used in place of cyclohexane, the percentage changed as follows: 68% (1 h), 40% (2 h), 27% (3 h), 22% (4 h), 20% (5 h), and 19% (21 h; 56 °C).

(15) The main portion of the gas did not condense in a dry ice–acetone cooled trap and was identified as CHF_3 (bp −84 °C) from its infrared spectrum, which is identical with the published one: J. H. Simons, *Fluorine Chem.*, **2**, 472 (1954).

(16) The isomerization of $CF_2BrCFClBr$ is described in ref 11a (p 107, 109) and 11b.

(17) The absence of $CF_2ClCClBr_2$ in the mixture obtained from the reaction of $CF_2BrCFClBr$ with aluminum chloride in the presence of cyclohexane was confirmed. In the corresponding reaction with aluminum bromide, however, there was evidence for the formation of CF_2ClCBr_3 besides $CF_2BrCClBr_2$ (see Table II, footnote *g*). A small portion of ion pair $CF_2BrC^+ClBr{\cdot}AlFBr_3^-$ probably dissociates. Bromide abstraction of the rearranged carbonium ion $CF_2ClC^+Br_2$ from $AlFBr_3^-$ gives CF_2ClCBr_3 together with $AlFBr_2$.

(18) Since in the tight ion pair the positive charge is expected to concentrate near the counteranion, that is, on the carbonium carbon to a greater extent than in the dissociated state, the importance of the electron-donating mesomeric effect relative to the electron-withdrawing inductive effect appears to be greater in the dissociated state than in the tight ion pair. Hence, although the overall positive charge stabilizing effect of α-chlorine is inferred to be greater than that of α-fluorine from reactivities in substitution reactions, this order could be reversed in the dissociated state because the electron-donating mesomeric effect of fluorine is greater than that of chlorine. The contribution from the halonium ion structure is also considered important only in the dissociated state.

(19) For example, the formation of CF_3CFClH from addition of HF to $CF_2{=}CFCl$ in $SbF_5–SO_2$ was explained in terms of the presumed greater stability of $^+CF_2CFClH$ as compared with that of HCF_2C^+FCl: G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **37**, 1028 (1972).

(20) G. A. Olah, Y. K. Mo, and Y. Halpern, *J. Am. Chem. Soc.*, **94**, 3551 (1972). G. A. Olah, G. Liang, and Y. K. Mo, *J. Org. Chem.*, **39**, 2394 (1974).

(21) D. J. Burton and G. C. Briney, *J. Org. Chem.*, **35**, 3036 (1970).

(22) Isomerization of $CF_2ClCFCl_2$ by a continuous process using aluminum chloride packed in a column and "activated" with $CF_2ClCFCl_2$ is described: K. H. Hellberg and J. Massonne, *Chem. Ztg.*, **93**, 209 (1969).

(23) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, pp 71–72.

(24) A number of patents use aluminum fluoride, particularly in the form of fine particles, as catalyst for fluorination and disproportionation reactions. For example, J. D. Calfee and C. B. Miller, U.S. Patent 2 767 227 (1956); *Chem. Abstr.*, **51**, 7398h (1957).

(25) Stereoregular polymerization of methyl vinyl ether using aluminum fluoride is also reported: R. J. Kern and J. D. Calfee, *J. Polym. Sci., Part A-1*, **4**, 1609 (1966).

(26) For previous mechanistic discussions, see ref 4, 11a (pp 52–60), and 21.

(27) For such polychlorofluorinated systems it is not certain whether the structure of the intermediate cation (or cations) in the dissociated state is equilibrating carbonium ions or a halonium ion. Further, even if the intermediate exists mainly as a halonium ion, the reaction may occur only via carbonium ions. Hence, the carbonium ion structure is tentatively adopted.

(28) The alternative of direct transfer of fluoride is indirect transfer via a series of reversible reactions ($RF + AlX_3 \rightleftarrows R^+ + AlFX_3^-$). Though an unequivocal choice between direct transfer and indirect transfer is difficult at present, the direct transfer is preferred by the present author. In the gas phase reaction easy transfer, necessarily direct, of fluoride has recently been recognized: (a) N. A. McAskill, *Aust. J. Chem.*, **23**, 2301 (1970); (b) T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **94**, 8934 (1972); (c) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *ibid.*, **96**, 1269 (1974).

(29) Under the competitive conditions participation of the following reactions is undoubted if the above mechanisms are correct.

$$CF_2BrCF_2Br + {}^+CF_2CCl_3 \rightarrow CF_2BrC^+FBr + CF_3CCl_3$$

$$CF_2ClCFCl_2 + {}^+CF_2CFBr_2 \rightarrow CF_2ClC^+Cl_2 + CF_3CFBr_2$$

(30) The existence of fluoride acceptors stronger than aluminum chloride under isomerizing conditions is also indicated by the fact that the yield of CCl_3CCl_3 obtained from the reaction of $CF_2ClCFCl_2$ with aluminum chloride under isomerizing conditions is much higher than that obtained under nonisomerizing conditions. The main route of the formation of CCl_3CCl_3 from $CF_2ClCFCl_2$ under isomerizing conditions is considered to involve the conversion of CF_2ClCCl_3 into $CFCl_2CCl_3$ by intermolecular fluoride and chloride transfer.

(31) C. D. Nenitzescu, *Carbonium Ions*, **2**, 463–520 (1970).

(32) F. H. Field in "Ion–Molecule Reactions", Vol. 1, J. L. Franklin, Ed., Plenum Press, New York, N.Y., 1972, pp 265, 271, 274–275.

(33) A. L. Glasebrook and W. G. Lovell, *J. Am. Chem. Soc.*, **61**, 1717 (1939).